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# The Mg-Oppenauer Oxidation as a Mild Method for the Synthesis of Aryl and Metallocenyl Ketones

**Ralf J. Kloetzing,[b] Arkady Krasovskiy,[a] and Paul Knochel*[a]**

**Abstract:** Magnesium alkoxides undergo a hydride-transfer oxidation with benzaldehyde as the oxidant. This magnesium variant of the Oppenauer oxidation was used for the synthesis of polyfunctional biaryl ketones. LiCl was found to promote this reaction by enhancing the solubility of magnesium alkoxides. This mild oxidation method was especially useful for preparing ketones bearing a metallocenyl unit as well as various new ferrocenyl ketones and tricarbonylchromium complexes. This last class of ketones was reduced with the CBS catalyst (CBS = Corey–Bakshi–Shibata, diphenyl oxazaborolidine) to chiral benzhydrol complexes with high enantioselectivity enabling an asymmetric synthesis of electron-rich or -poor benzhydryl alcohols (up to 94% *ee*).

**Keywords:** asymmetric synthesis · Grignard reagents · ketones · metallocenes · oxidation

## Introduction

Several classes of organometallic intermediates readily undergo acylation reactions leading to polyfunctional ketones which are present in a great variety of pharmaceutical and material science related target molecules.[1] As a result of their high reactivity combined with a high tolerance towards functional groups, Grignard reagents are useful for the synthesis of polyfunctional ketones. Functionalized aryl- and heteroaryl-magnesium reagents have become readily available from the corresponding organic iodides or bromides through a halogen–magnesium exchange by the reaction with the mixed complex *i*PrMgCl·LiCl[2] or by deprotonation of aryls and heteroaryls with LiCl-solubilized magnesium amides.[3] Typical procedures for the preparation of the unsymmetrical diaryl ketones starting from arylmagnesium reagents involve the use of transition metals, such as $Cu^{I}$,[4] $Fe^{III}$,[5] $Ni^{II}$,[6] and $Pd^{II}$,[7] or expensive ligands[8] followed by the addition of corresponding acyl chlorides.

In 1937, Oppenauer[9,10] found that in the presence of aluminum *tert*-butoxide, acetone acts as a hydrogen acceptor for the oxidation of primary and secondary alcohols leading to the corresponding aldehydes or ketones.[11] The magnesium-Oppenauer oxidation reaction has been used for the synthesis of several aldehydes and symmetrical ketones,[12] but acceptable yields were obtained only in dibutyl ether or in diisopropyl ether. The use of THF leads to low yields.[13]

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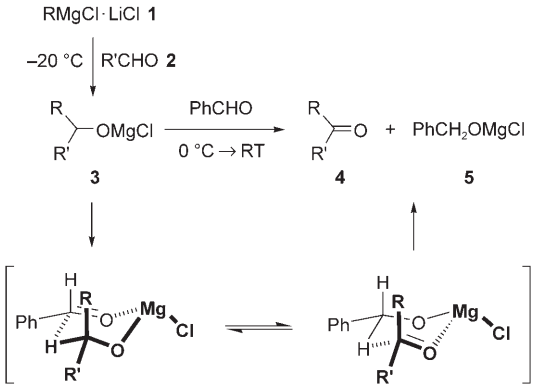
## Results and Discussion

Herein, we wish to report that the magnesium variant of the Oppenauer oxidation represents an efficient method for the synthesis of biaryl and metallocenyl ketones by using magnesium instead of aluminum alkoxides. The addition of Grignard reagents **1** to aldehydes **2** gives magnesium alkoxides **3** which are readily oxidized to the corresponding ketones **4** by using benzaldehyde as a hydride acceptor with the formation of benzyl alkoxide **5** as a byproduct (Scheme 1). In this sequence, the $Mg^{II}$ center promotes two consecutive reactions: the addition of the Grignard reagent **1** to the aldehyde **2** and the hydride-transfer oxidation of the alkoxide **3**.

Thus, benzophenone (**4a**) was obtained from phenylmagnesium chloride and benzaldehyde (2.2 equiv) in 98% yield (Table 1, entry 1). In this case, the magnesium-Oppenauer oxidation reaction proceeds at room temperature leading to the desired ketone with complete conversion after 1 h. Without LiCl, the reaction did not go to completion, even after 6 h, and several byproducts were formed. We found that the presence of LiCl in the reaction mixture dramatically accel-



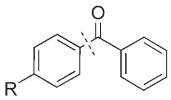
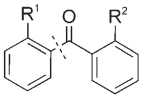
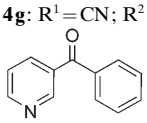
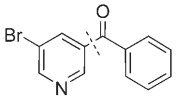
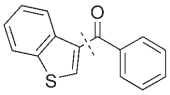
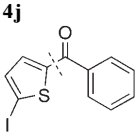
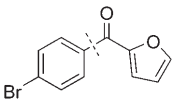
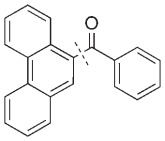

Scheme 1. Magnesium-Oppenauer oxidation with benzaldehyde.

erates the magnesium-Oppenauer oxidation reaction. We propose that the main role of LiCl is to solubilize the resulting alkoxide **3** in THF and additionally to activate the carbonyl function of benzaldehyde by playing the role of a Lewis acid. A wide range of functionalized unsymmetrical diaryl ketones can be prepared (Table 1) from the corresponding magnesium alkoxides. Neither electron-accepting nor -donating substituents appear to influence the reaction course (**4b**–**c**, entries 2 and 3). Although an *ortho*-substituent does not retard the reaction (**4d**–**f**, entries 4–6), the presence of two *ortho*-substituents inhibited the magnesium-Oppenauer reaction completely due to the high steric hindrance and no ketone was formed (entry 7). Various heterocyclic aryl ketones, such as pyridyl- (**4h** and **4i**), benzothiophenyl- (**4j**), thiophenyl- (**4k**), and furyl ketones (**4l**) are easily prepared. Importantly, the heterocyclic moiety can be introduced by the magnesium reagent as well or by the aldehyde. A polycyclic aromatic Grignard reagent, such as 9-phenanthrenylmagnesium chloride, leads, after the addition of benzaldehyde followed by the magnesium-Oppenauer oxidation, to the formation of the desired ketone **4m** in 94% yield.

As this oxidation reaction enables the synthesis of aromatic ketones under very mild conditions, it may be possible to prepare ketones bearing metallocene units which are not compatible with common oxidizing agents. First, we tested this method for the synthesis of ferrocenyl ketones from ferrocenyl alcohols. The ferrocenyl alcohols **7a**–**g** are readily available from the addition of ferrocenyllithium, generated by a tin–lithium exchange,[14] to various aldehydes (Table 2).

This method affords the benzofuryl and pyridyl alcohols **7a**–**e** in very good yields (entries 1–5). The yield for the indolyl alcohol **7f** is lower, as the electron-rich heterocyclic substituent facilitates the heterolytic cleavage of the C–O bond and the formation of the α-ferrocenyl cation (entries 6,

Table 1. One-pot synthesis of ketones **4a**–**m** starting from the corresponding Grignard reagents complexed with LiCl.

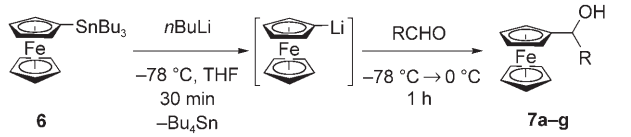
| Entry | Product of type **4**[a] | Yield [%][a] |
|---|---|---|
| |  | |
| 1 | **4a**: R = H | 98 |
| 2 | **4b**: R = CN | 90 |
| 3 | **4c**: R = OMe | 95 |
| |  | |
| 4 | **4d**: $R^1$ = OMe; $R^2$ = H | 95 |
| 5 | **4e**: $R^1$ = CN; $R^2$ = H | 92 |
| 6 | **4f**: $R^1$ = H; $R^2$ = Br | 91 |
| 7 | **4g**: $R^1$ = CN; $R^2$ = Br | 0 |
| |  | |
| 8 | **4h** | 89 |
| |  | |
| 9 | **4i** | 94 |
| |  | |
| 10 | **4j** | 85 |
| |  | |
| 11 | **4k** | 92 |
| |  | |
| 12 | **4l** | 95 |
| |  | |
| 13 | **4m** | 94 |

[a] Dotted lines indicate the C–C bond formed during the reaction of the Grignard reagent with the corresponding aldehyde. [b] Isolated yield of the analytical pure product.

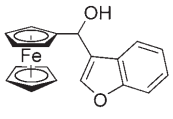
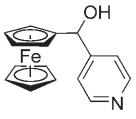
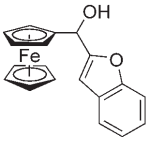
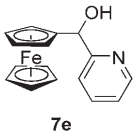
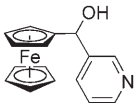
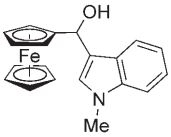
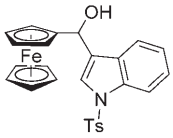
**Abstract in German:** *Magnesiumalkoholate gehen eine Oxidation durch Hydrid-Transfer mit Benzaldehyd als Oxidationsmittel ein. Diese Magnesium-Variante der Oppenauer-Oxidation wurde zur Synthese polyfunktioneller Biarylketone genutzt. Es wurde gefunden, dass LiCl die Reaktion begünstigt, indem es die Löslichkeit der Magnesiumalkoholate erhöht. Diese milde Oxidationsreaktion ist besonders nützlich, um Ketone mit einer Metalloceneinheit sowie verschiedene neue Ferrocenylketone und Tricarbonylchromkomplexe darzustellen. Letztere wurden mit dem CBS-Katalysator (CBS = Corey–Bakshi–Shibata, Diphenyloxazaborolidin) zu chiralen Benzhydrolkomplexen mit hoher Enantioselektivität reduziert, was eine asymmetrische Synthese elektronenreicher wie -armer Benzhydrylalkohole erlaubt (bis zu 94% ee).*

Table 2. Synthesis of ferrocenyl alcohols **7a–g** from monolithioferrocene and aldehydes.

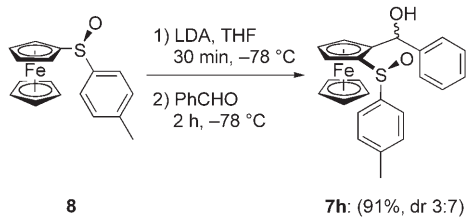



**6** **7a–g**

| Entry[a] | Product of type **7** | Yield [%][b] | Entry[a] | Product of type **7** | Yield [%][b] |
|---|---|---|---|---|---|
| 1 |  **7a** | 87 | 4 |  **7d** | 87 |
| 2 |  **7b** | 86 | 5 |  **7e** | 81 |
| 3 |  **7c** | 87 | 6 |  **7f** | 58 |
| 7 |  **7g** | 76 | | | |

[a] All reactions were performed on a 2 mmol scale with the following ratio: (tri-*n*-butylstannyl)ferrocene (1.0 equiv), *n*BuLi (1.0 equiv), and the aldehyde (1.1 equiv). [b] Isolated yield of analytical pure product.

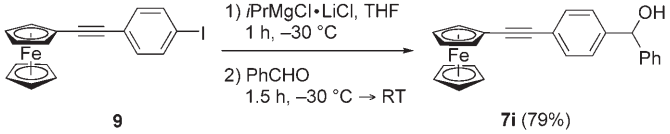
7). The ferrocenyl alcohol **7h** was prepared by *ortho*-lithiation of sulfoxide **8** and reaction with benzaldehyde. Alcohol **7h** was obtained as a mixture of diastereomers in a ratio of 3:7 with an overall yield of 91% (Scheme 2). The diastereomers could neither be separated by column chromatographical purification nor by recrystallization. The ratio of diastereomers was determined by integration of the $^1$H NMR spectrum.




**8** **7h**: (91%, dr 3:7)

Scheme 2. Synthesis of the ferrocenyl alcohol **7h**.

Ferrocenyl alcohol **7i** was prepared from the aryl iodide **9**[15] by an iodine–magnesium exchange and subsequent reaction with benzaldehyde (Scheme 3). The ferrocenyl alcohols **7a–i** were deprotonated with *i*PrMgCl·LiCl in 10 min at 0 °C and the resulting magnesium alcoholates were oxidized by hydride transfer to benzaldehyde (see Table 3).




**9** **7i** (79%)

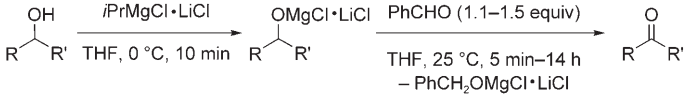
Scheme 3. Synthesis of the ferrocenyl alcohol **7i**.

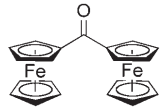
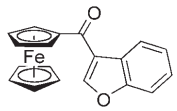
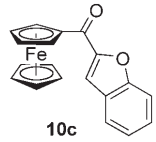
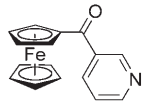
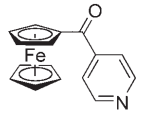
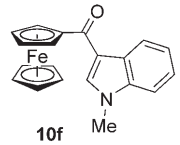
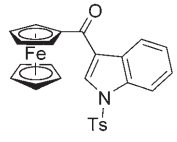
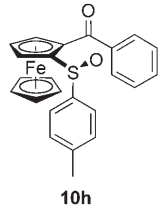
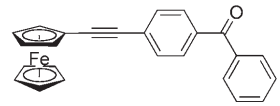
The first experiment for the synthesis of metallocenyl ketones from the corresponding alcohols was carried out with diferrocenylmethanol. Only 5 min after the addition of benzaldehyde, diferrocenyl ketone (**10a**) precipitated from the reaction mixture and was isolated by filtration in 85% yield (Table 3, entry 1). Under the conditions for the Oppenauer oxidation with aluminum tri-*tert*-butoxide (1.65 equiv) and acetone (70 equiv), this ketone was not formed even after 12 h at 60 °C. The previously unknown benzofuran derivatives **10b**,**c**[16] are obtained after 3 h reaction time (81–91% yield; entries 2 and 3). It has been reported that attempts to synthesize the pyridyl ferrocenyl ketones **10d** and **10e** failed.[17] However, the magnesium-Oppenauer oxidation enables the preparation of these ketones **10d**,**e** in 66 and 68% yields after a reaction time of 12 h (entries 4 and 5). The addition of DMPU as a cosolvent ensured, additionally, the solubility of the magnesium alcoholates. The use of LiCl proved to be essential especially for the less soluble alcoholates derived from the pyridine derivatives **7c**,**d**. Without LiCl, no oxidation was observed. The hydride-transfer oxidation did not proceed with the 2-pydridyl ferrocenyl alcohol **7e**. After a reaction time of 6 h, N-methylindole derivative **10f** was isolated in 89% yield (entry 6).[18] The N-tosylindolyl ketone **10g** was unexpectedly unstable and was isolated in 52% yield after 6 h reaction time (entry 7). The diastereomeric mixture of alcohol **7h** was oxidized by hydride transfer. Both diastereomers underwent the hydride transfer and ketone **10h** was isolated in 65% yield after a reaction time of 14 h. It should be noted, that the preparation of the ketone **10h** by *ortho*-lithiation of sulfoxide **8**, transmetallation to copper, and reaction with benzoyl chloride was not possible.[19] Thus, the hydride transfer oxidation is the only access to ketone **10h** (entry 8). Finally, the alkyne **10i** was prepared with a reaction time of 16 h and was isolated in 88% yield (entry 9).

The synthesis of the ferrocenyl ketones **10a–i** was performed in two steps. As monolithioferrocene is readily available[14] and as it adds smoothly to aldehydes, the alcohols **7a–i** could be easily prepared. The magnesium alcoholates were then formed by deprotonation of the alcohols with *i*PrMgCl·LiCl. However, the addition of Grignard reagents to metallocenyl aldehydes enables the direct preparation of magnesium alcoholates. Grignard reagents **1**, which were prepared either by insertion of magnesium into aromatic

Table 3. Synthesis of ferrocenyl ketones **10a–i** from ferrocenyl alcohols.




| Entry[a] | Product | Yield [%][b] | Reaction time [h] |
|---|---|---|---|
| 1 |  **10a** | 85 | 0.1 |
| 2 |  **10b** | 91 | 3 |
| 3 |  **10c** | 81 | 3 |
| 4 |  **10d** | 68[c] | 12 |
| 5 |  **10e** | 66[c] | 12 |
| 6 |  **10f** | 89 | 6 |
| 7 |  **10g** | 52 | 6 |
| 8 |  **10h** | 65 | 14 |
| 9 |  **10i** | 88 | 16 |

[a] All reactions were performed on a 1 mmol scale with the following ratio: alcohol (1.0 equiv), *i*PrMgCl·LiCl (1.05 equiv), and benzaldehyde (1.5 equiv). [b] Isolated yield of analytically pure product. [c] DMPU (DMPU = 1,3-dimethyltetrahydropyrimidin-2-one) was used as a cosolvent.

bromides in the presence of LiCl or by an iodine–magnesium exchange with *i*PrMgCl·LiCl, were added to ferrocene aldehyde **11**, cymantrene aldehyde **12**, and tricarbonylchromium benzaldehyde **13** (see Table 4). The resulting magnesium alcoholates were oxidized directly to the corresponding ketones **14** with benzyldehyde by hydride transfer (Table 4).

3-Benzofuryl ferrocenyl ketone (**10b**) which was also prepared by the two-step sequence described above (Table 3, entry 2) was now prepared in a one-pot synthesis starting from 3-bromobenzofuran. The bromine–magnesium exchange, addition to ferrocene alydehyde, and hydride transfer oxidation gave the ketone **10b** in 79% yield on a 5 gram scale.

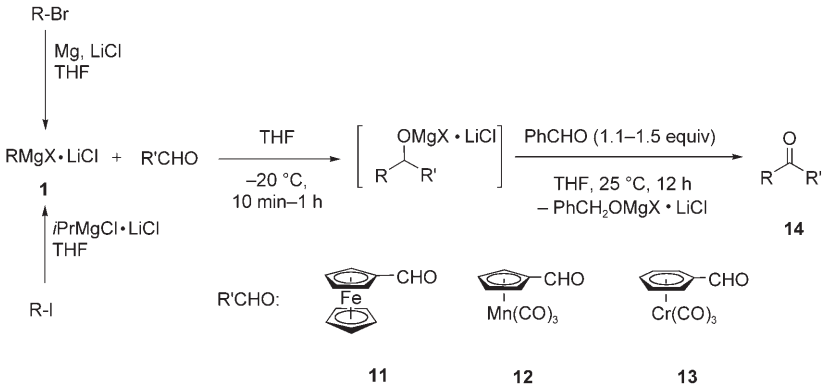
The addition of PhMgCl·LiCl to cymantrene aldehyde and oxidation with benzaldehyde afforded the ketone **14a** in 80% yield.[20] Various aromatic Grignard reagents were also readily added to tricarbonylchromium benzaldehyde **11** within 10 min at −20 °C.[21] A stepwise synthesis of the ketones **14c**,**e**,**f** is not possible as the tricarbonyl chromium complexes of benzhydrols with electron-donating substituents are easily decomposed upon isolation. However, the direct oxidation with benzaldehyde within 12 h at room temperature gave the ketones **14b–l**, which were purified by crystallization.[22,23] With nonfunctionalized or electron-rich ketones, 65–92% yields were obtained. With halogenated arylmagnesium reagents, 28–59% yields were observed. The best results gave the *p*-bromo derivative **14i** (entry 10) which was isolated in 59% yield. In general, lower yields are obtained in reactions for which the Grignard reagent was prepared by the halogen–magnesium exchange instead of the direct insertion of magnesium turnings. The oxidation leading to the ketones **14c**,**e**,**f** (entries 4, 6, and 7) shows that the Mg-Oppenauer oxidation enables a selective synthesis of tricarbonylchromium complexes of benzophenones with complexation of the less electron-rich ring. In contrast, the direct formation of tricarbonylchromium complexes of substituted benzophenones by using chromium hexacarbonyl gives a mixture of products.[24] The complex with the most electron-rich aromatic ring is formed preferentially with a low selectivity.

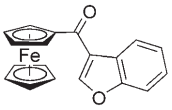
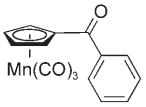
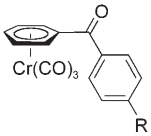
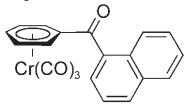
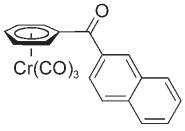
The enantioselectivity of the asymmetric reduction of *p*-subsituted benzophenones depends on the interaction with the *p*-subsituent and the catalyst. As a result of the remote positions, these reductions usually proceed with low enantioselectivity.[25] However, in the case of complexation with a tricarbonylchromium unit the CBS reduction[26,27] gives chiral benzhydrol derivatives[28] with high enantioselectivity (see Table 5).

The asymmetric reduction was first examined with the tricarbonylchromium complex **14c** leading to the benzhydrol **15a** (Table 5, entry 1). The best results were obtained when the ketone was reduced with borane–dimethyl sulfide complex and with 20 mol% of the CBS catalyst (*S*)-CBS within 30 min in THF. After complete conversion of the ketone, water was added and the reaction mixture was filtered through silica gel. The filtrate was treated with iodine for decomplexation. The benzhydrol **15a** was isolated in 90%

Table 4. Synthesis of metallocenyl ketones **14a–l** from metallocenyl aldehydes.




| Entry | Product | Yield [%][a] |
|---|---|---|
| |  | |
| 1[b] | **10b** | 79 |
| |  | |
| 2[c] | **14a** | 80 |
| |  | |
| 3[c] | **14b**: R = H | 85 |
| 4[d] | **14c**: R = OMe | 73 |
| 5[d] | **14d**: R = Ph | 69 |
| 6[d] | **14e**: R = Me | 65 |
| 7[d] | **14f**: R = $NMe_2$ | 92 |
| 8[b] | **14g**: R = D | 72 |
| 9[e] | **14h**: R = Cl | 40 |
| 10[e] | **14i**: R = Br | 59 |
| 11[e] | **14j**: R = I | 28 |
| |  | |
| 12[d] | **14k** | 78 |
| |  | |
| 13[d] | **14l** | 82 |

[a] Isolated yield of analytically pure product. [b] Preparation of the Grignard reagent **1** by a bromine–magnesium exchange from the corresponding aryl bromide and *i*PrMgCl•LiCl in 5 h at −40 °C. [c] The Grignard reagent **1** was obtained from Chemetall (Frankfurt). [d] Preparation of the Grignard reagent **1** by insertion of magnesium turnings into the corresponding aryl bromide. [e] Preparation of the Grignard reagent **1** by an iodine–magnesium exchange from the corresponding aryl iodide and *i*PrMgCl•LiCl.

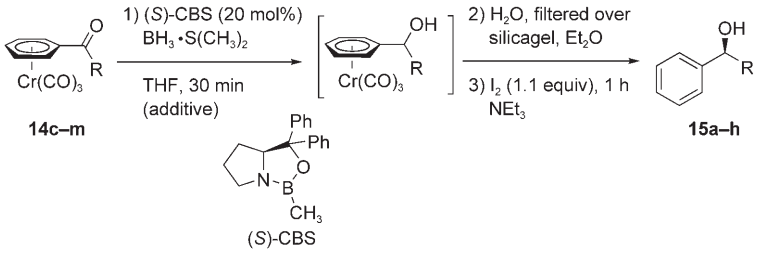
yield and with 93% *ee*. This direct decomplexation enables a formal CBS reduction of the ketone **14c**. Attempts to isolate the tricarbonylchromium complex of the alcohol failed as a result of its low stability. The enantioselectivity of the reaction leading to the biphenyl derivative **15b** (entries 2–4) could be improved when one equivalent of *N*,*N*-diethylaniline[29] was added as an additive to the borane–dimethyl sulfide complex. When the reaction was performed at room temperature the benzhydrol **15b** was obtained with 89% *ee*. All reductions proceed in almost quantitative yields. In the case of the *p*-methylphenyl ketone **15c** the enantioselectivity was improved from 90 (entry 5) to 93% *ee* (entry 6). The 2-naphthyl ketone **15d** was reduced with an enantioselectivity of only 81% *ee* without additive (entry 7) and with 94% *ee* with *N*,*N*-diethylaniline. The most substantial improvement was observed for the *p*-bromo ketone **15e**, which was reduced without additive with 55% *ee* (entry 9). In presence of *N*,*N*-diethylaniline, 88% *ee* was obtained (entry 10). Good enantioselectivities were also observed for the *p*-chlorobenzhydrol (**15f**; 89% *ee;* entry 11) and for the *p*-iodobenzhydrol (**15g**, 86% *ee*, entry 12). The *p*-dimethylaminoketone **14f** was reduced without additive and lead to the *p*-dimethylaminobenzhydrol **15h** in 96% yield with 84% *ee* (entry 13).

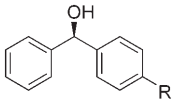
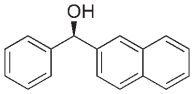
## Conclusion

We have developed an efficient method for the synthesis of unsymmetrical aryl and heteroaryl ketones starting from easily accessible Grignard reagents and aldehydes. The mild reaction conditions enable the preparation of various ketones bearing a metallocene unit, of which most were previously unavailable. The resulting tricarbonylchromium complexes of unsymmetrical ketones could be efficiently reduced by CBS reduction to give chiral benzhydrol derivatives with high enantioselectivity.

Table 5. Preparation of the benzhydrol derivatives **15a–h**.




| Entry[a] | Product **15** | Additive | $T$ [°C] | Yield [%][b] | Enantioselectivity [% *ee*][c] |
|---|---|---|---|---|---|
| |  | | | | |
| 1 | **15a**: R = OMe | – | 0 | 90 | 93 |
| 2 | | – | 0 | quant. | 67 |
| 3 | **15b**: R = Ph | $PhNEt_2$[d] | −5 | quant. | 86 |
| 4 | | $PhNEt_2$[d] | 22 | 97 | 89 |
| 5 | | – | 0 | 93 | 90 |
| 6 | **15c**: R = Me | $PhNEt_2$[d] | 22 | 95 | 9 |
| |  | | | | |
| 7 | | – | 0 | 89 | 81 |
| | **15d** | | | | |
| 8 | | $PhNEt_2$[d] | 22 | 95 | 94 |
| 9 | | – | 0 | quant. | 55 |
| 10 | **15e**: R = Br | $PhNEt_2$[d] | 22 | 96 | 88 |
| 11 | **15f**: R = Cl | $PhNEt_2$[d] | 22 | quant. | 90 |
| 12 | **15g**: R = I | $PhNEt_2$[d] | 22 | 94 | 86 |
| 13 | **15h**: R = $NMe_2$ | – | 0 | 96 | 84 |

[a] All reactions were performed on an 0.5 mmol scale with the CBS catalyst (20 mol%). The borane–dimethyl sulfide complex (1.3 equiv) was added dropwise (30 min). [b] Isolated yield obtained after purification by column chromatography. [c] The enantiomeric excess was determinded by chiral HPLC (Chiralcel OD-H, OJ, OB, AD). [d] Borane–dimethyl sulfide complex and *N*,*N*-diethylaniline were premixed in a 1:1 ratio.

## Experimental Section

**General**: All reactions were carried out under argon by using standard Schlenk techniques. Melting points are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AMX 300, AMX 600 or Varian VXR 400 S instrument. Chemical shifts ($\delta$) are given as ppm relative to the residual solvent peak ([$D_1$]chloroform 7.25/77.0 ppm; [$D_6$]benzene 7.16/128.0 ppm; [$D_6$]acetone 2.04/206.7 ppm). IR spectra were recorded on a Perkin–Elmer 1420 infrared spectrometer. Mass spectra were recorded on a Finnnigan MAT 95 Q spectrometer. Optical rotations were measured on a Perkin–Elmer 241 polarimeter (temperature: 20°C). Column chromatography was performed on Merck silica gel 60 (230–400 mesh ASTM). Enantiomeric excesses were determined by HPLC (Chiralcel, Daicel Chemical Industries, column was run with *n*-heptane/isopropanol as mobile phase and detection was carried out by a diode array UV/Vis detector at the given wavelength). THF was dried with sodium/benzophenone and distilled. Elemental analyses were performed on an Elementar vario EL and with a Metrohm Titroprocessor 686.

**Synthesis of the ketones 4a–m**

*Procedure A*: The titrated[30] Grignard reagent[2] (2 mmol) was cooled to −20°C and the corresponding aldehyde (2.0 mmol) was added dropwise neat or as a solution in THF. After 10 min benzaldehyde (2.4 mmol) was added and reaction mixture was warmed to RT. The mixture was stirred at RT. (appropriate time was checked by GC analysis of reaction aliquots, the conversion was more than 98%), then a saturated $NH_4Cl$ solution (20 mL) was added and the mixture was extracted with ethyl acetate (40 mL). The combined organic layers were dried ($Na_2SO_4$). The crude material was purified by column chromatography. Analytical data was found to match literature data: **4a**,[31] **4b**,[5] **4c**,[32] **4d**,[33] **4e**,[34] **4f**,[35] **4h**,[36] **4i**,[37] **4j**,[38] **4l**,[39] and **4m**,[40].

Compound **4k**: White crystals; m.p. 132–133°C); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ = 7.84 (m, 2H), 7.62 (m, 1H), 7.51 (m, 1H), 7.35 (d, $J$ = 4.0 Hz, 1H), 7.28 ppm (d, $J$ = 4.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 187.0, 149.8, 138.4, 137.9, 136.0, 132.9, 129.4, 128.9, 86.3 ppm; MS (EI, 70 eV): $m/z$ (%): 313 (100) $[M]^+$, 237 (57), 187 (12), 105 (35), 82 (11), 77 (24), 51 (8); HR-EIMS: $m/z$: calcd for $^{12}C_{11}{}^1H_7{}^{127}I^{16}O^{32}S$: 313.9262; found: 313.9262.

**Synthesis of the ferrocenyl alcohols 7a–i**

*Procedure B*: *n*BuLi (16% solution in *n*-hexane, 1.0 equiv) was added to a solution of (tri-*n*-butylstannyl)ferrocene (**18**) in THF (3.3 mL mmol$^{-1}$ (tri-*n*-butylstannyl)ferrocene) at −78°C. The mixture was then warmed to RT and stirred for 30 min. After this time, the mixture was cooled to −78°C and the aldehyde (1.05 equiv) was added. Liquid aldehydes were added without additional solvent, solid aldehydes as concentrated solutions in a small amount of THF. The mixture was stirred for 1 h at RT and then a saturated $NH_4Cl$ solution was added and the mixture was extracted with diethyl ether (30 mL mmol$^{-1}$). The combined organic layers were washed with brine and dried ($MgSO_4$). The crude material was purified by column chromatography.

**(α-Hydroxy(3-benzofuryl)methyl) ferrocene (7a)**: According to procedure B (tri-*n*-butylstannyl)ferrocene (575 mg, 1.21 mmol) was treated with *n*BuLi (0.73 mL, 1.65 M, 1.21 mmol) and benzo[*b*]furan-3-carbaldehyde (169 mg, 1.16 mmol). The alcohol **7a** was purified by column chromatography (silica gel, *n*-pentane/diethyl ether 15:1 to 3:1) and obtained as yellow crystals (336 mg, 1.01 mmol, 87%). M.p. 113°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.94–7.89 (m, 1H), 7.86–7.81 (m, 1H), 7.40–7.30 (m, 2H), 7.27 (d, $^4J$ = 0.9 Hz, 1H), 5.83 (br d, $^3J$ = 2.5 Hz, 1H), 4.34–4.31 (m, 1H), 4.29–4–25 (m, 1H), 4.27 (s, 5H), 4.24–4.21 (m, 1H), 4.21–4.18 (m, 1H), 2.56 ppm (d, $^3J$ = 3.6 Hz, 1H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 154.9, 145.4, 139.4, 123.5 (CH), 119.2 (CH), 111.1 (CH), 106.7 (CH), 95.1 (CH), 72.3, 68.8 (CH), 68.2 (CH), 68.1 (CH), 67.7 (CH), 66.4 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3083 (m), 1561 (w), 1524 (w), 1459 (m), 1427 (s), 1402 (m), 1388 (m), 1257 (m), 1243 (m), 1225 (m), 1174 (m), 1105 (s), 1077 (m), 1049 (s), 1035 (m), 1019 (m), 1001 (s), 918 (m), 859 (m), 819 (s), 781 (m), 763 (s), 734 (s), 499 (s), 484 (s), 450 (m), 421 cm$^{-1}$ (m); EIMS (70 eV):

*m/z* (%): 348 (43) $[M]^+$, 346 (16), 332 (100), 265 (17), 209 (74); HR-EIMS: *m/z*: calcd for $^{12}C_{19}{}^{1}H_{16}{}^{56}Fe^{16}O^{32}S$: 348.0271; found: 348.0250.

**(α-Hydroxy(2-benzofuryl)methyl) ferrocene (7b)**: According to procedure B, (tri-*n*-butylstannyl)ferrocene (295 mg, 0.622 mmol) was treated with *n*BuLi (0.37 mL, 1.62 M, 0.60 mmol) and benzo[b]furan-2-carbaldehyde (79 mg, 0.54 mmol). The alcohol **7b** was purified by column chromatography (silica gel, *n*-pentane/diethyl ether 20:1 to 3:1) and obtained as yellow crystals (155 mg, 0.467 mmol, 86%). M.p. 97 °C; $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 7.44–7.29 (m, 2H), 7.12–7.02 (m, 2H), 6.45 (s, 1H), 5.45 (d, $^3J$ = 5.2 Hz, 1H), 4.21–4.18 (m, 1H), 4.15–4.11 (m, 1H), 4.00 (s, 5H), 3.95–3.91 (m, 2H), 2.10 ppm (d, $^3J$ = 5.3 Hz, 1H); $^{13}$C NMR (150 MHz, $C_6D_6$): $\delta$ = 159.6, 155.3, 128.7, 124.3 (CH), 123.1 (CH), 121.3 (CH), 111.4 (CH), 103.1 (CH), 70.4, 69.0 (CH), 68.4 (CH), 68.3 (CH), 67.6 (CH), 67.1 (CH), 66.8 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3536 (s), 3098 (m), 2920 (w), 1453 (s), 1251 (m), 1172 (m), 1044 (m), 998 (m), 818 (m), 740 cm$^{-1}$ (s); EIMS (70 eV): *m/z* (%): 332 (26) $[M]^+$, 330 (33) $[M-2H]^+$, 315 (100) $[M-OH]^+$, 249 (15), 194 (29), 165 (21), 121 (12); HR-EIMS: *m/z*: calcd for $^{12}C_{19}{}^{1}H_{16}{}^{56}Fe^{16}O_2$: 332.0494; found: 332.0475.

**(α-Hydroxy(3-pyridyl)methyl) ferrocene (7c)**: According to procedure B, (tri-*n*-butylstannyl)ferrocene (997 mg, 2.10 mmol) was treated with *n*BuLi (1.27 mL, 1.65 M, 2.10 mmol) and pyridine-3-carbaldehyde (237 mg, 2.21 mmol). The alcohol **7c** was purified by column chromatography (silica gel, *n*-pentane/diethyl ether 1:2 to diethyl ether/ethyl acetate 5:1) and obtained as yellow crystals (533 mg, 1.82 mmol, 87%). M.p. 101 °C; $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 8.84 (d, $^4J$ = 2.2 Hz, 1H), 8.45 (dd, $^3J$ = 4.9, $^4J$ = 2.2 Hz, 1H), 7.52 (ddd, $^3J$ = 7.7, $^4J$ = 2.2 Hz, 1H), 6.74 (dd, $^3J$ = 7.7, $^3J$ = 4.9 Hz, 1H), 5.25 (d, $^3J$ = 3.1 Hz, 1H), 4.08–4.04 (m, 1H), 3.96 (s, 5H), 3.90–3.86 (m, 3H), 2.63 ppm (d, $^3J$ = 3.1 Hz, 1H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 149.0 (CH), 148.8 (CH), 139.6, 133.5 (CH), 123.1 (CH), 93.9, 70.1 (CH), 68.8 (CH), 68.4 (CH), 67.5 (CH), 66.1 ppm (CH); IR (KBr): $\tilde{\nu}$ = 2836 (w), 1421 (m), 1013 (s), 1106 (m), 820 (s), 760 (m), 717 (m), 516 (m), 500 (m), 486 cm$^{-1}$ (s); EIMS (70 eV): *m/z* (%): 293 (100) $[M]^+$, 228 (73), 154 (27), 138 (22); HR-EIMS: *m/z*: calcd for $^{12}C_{16}{}^{1}H_{15}{}^{56}Fe^{14}N^{16}O_2$: 293.0498; found: 293.0493.

**(α-Hydroxy(4-pyridyl)methyl) ferrocene (7d)**: According to procedure B, (tri-*n*-butylstannyl)ferrocene (1.08 g, 2.27 mmol) was treated with *n*BuLi (1.38 mL, 1.65 M, 2.27 mmol) and pyridine-4-carbaldehyde (259 mg, 2.42 mmol). The alcohol **7d** was purified by column chromatography (silica gel, *n*-pentane/diethyl ether 1:2 to diethyl ether/ethyl acetate 5:1) and obtained as yellow crystals (580 mg, 1.98 mmol, 87%). M.p. 128 °C; $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 8.57–8.53 (m, 2H), 7.12–7.08 (m, 2H), 5.12 (d, $^3J$ = 3.5 Hz, 1H), 3.98–3.95 (m, 1H), 3.95 (s, 5H), 3.92–3.88 (m, 2H), 3.87–3.84 (m, 1H), 2.46 ppm (d, $^3J$ = 3.5 Hz, 1H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 152.3, 150.1 (CH), 121.2 (CH), 93.6, 70.7 (CH), 68.8 (CH), 68.5 (CH), 68.3 (CH), 67.6 (CH), 66.1 ppm (CH); IR (KBr): $\tilde{\nu}$ = 1599 (s), 1410 (s), 1178 (m), 1107 (m), 1061 (m), 999 (m), 1019 (s), 818 (s), 505 (m), 483 cm$^{-1}$ (s); EIMS (70 eV): *m/z* (%): 293 (100) $[M]^+$, 277 (13), 228 (89), 154 (13), 138 (16); HR-EIMS: *m/z*: calcd for $^{12}C_{16}{}^{1}H_{15}{}^{56}Fe^{14}N^{16}O_2$: 293.0498; found: 293.0495.

**(α-Hydroxy(2-pyridyl)methyl) ferrocene (7e)**: According to procedure B, (tri-*n*-butylstannyl)ferrocene (1.15 g, 2.42 mmol) was treated with *n*BuLi (1.47 mL, 1.65 M, 2.42 mmol) and pyridine-2-carbaldehyde (269 mg, 2.51 mmol). The alcohol **7e** was purified by column chromatography (silica gel, *n*-pentane/diethyl ether 3:1 to 1:3) and obtained as yellow crystals (575 mg, 1.96 mmol, 81%). M.p. 104 °C; $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 8.27 (ddd, $^3J$ = 4.8, $^4J$ = 1.9, $^5J$ = 1.3 Hz, 1H), 7.04–6.93 (m, 2H), 6.55 (ddd, $^3J$ = 6.8, $^3J$ = 4.8, $^4J$ = 2.1 Hz, 1H), 5.52 (d, $^3J$ = 3.3 Hz, 1H), 4.65 (d, $^3J$ = 3.3 Hz, 1H), 4.25–4.22 (m, 1H), 4.21–4.18 (m, 1H), 4.15 (s, 5H), 4.00–3.97 (m, 1H), 3.97–3.94 ppm (m, 1H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 162.2, 148.0 (CH), 136.1 (CH), 122.1 (CH), 120.9 (CH), 93.0, 71.5 (CH), 69.1 (CH), 68.3 (CH), 68.0 (CH), 67.8 (CH), 66.2 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3013 (w), 2914 (w), 2690 (w), 1594 (s), 1568 (m), 1476 (m), 1434 (s), 1104 (s), 1075 (m), 1046 (m), 1020 (m), 1003 (s), 811 (s), 754 (s), 502 (m), 484 cm$^{-1}$ (s); EIMS (70 eV): *m/z* (%): 293 (100) $[M]^+$, 291 (11) $[M-2H]^+$, 228 (61), 210 (42), 154 (22); HR-EIMS: *m/z*: calcd for $^{12}C_{16}{}^{1}H_{15}{}^{56}Fe^{14}N^{16}O_2$: 293.0498; found: 293.0490.

**α-Hydroxy(1-methyl-3-indolyl)methyl ferrocene (7f)**: According to procedure B, (tri-*n*-butylstannyl)ferrocene (913 mg, 1.92 mmol) was treated with *n*BuLi (1.40 mL, 1.58 M, 2.21 mmol) and *N*-methylindole-3-carbaldehyde (350 mg, 2.20 mmol). The crude product was recrystallized (*n*-hexane/ethyl acetate 15:4). α-Hydroxy(1-methyl-3-indolyl)methylferrocene (**7f**) was obtained as red/brown crystals (315 mg, 0.912 mmol, 48%). The mother liquor was purified by column chromatography (silica gel, *n*-pentane/diethyl ether 9:1 to 1:2 with 5 to 0% triethylamine) to obtain further product (63 mg, 0.18 mmol, 10%). M.p. 127–129 °C (red); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 8.02–7.97 (m, 1H), 7.27–7.19 (m, 3H), 7.03–6.97 (m, 1H), 6.59 (s, 1H), 5.92 (d, $J$ = 3.6 Hz, 1H), 4.47–4.45 (m, 1H), 4.18–4.15 (m, 1H), 4.10 (s, 5H), 4.01–3.99 (m, 1H), 3.98–3.96 (m, 1H), 2.86 ppm (s, 3H); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 137.7, 127.3, 126.7 (CH), 122.2, 122.0 (CH), 120.5 (CH), 119.6 (CH), 109.5 (CH), 94.0, 68.9 (CH), 67.9 (CH), 67.8 (CH), 67.8 (CH), 66.5 (CH), 66.4 (CH), 31.8 ppm ($CH_3$); IR (KBr): $\tilde{\nu}$ = 3539 (s), 3081 (w), 2894 (w), 1540 (w), 1474 (s), 1330 (m), 1251 (m), 1040 (m), 998 (m), 938 (w), 824 (s), 774 (m), 748 (s), 499 (s), 487 cm$^{-1}$ (s); EIMS (70 eV): *m/z* (%): 345 (76) $[M]^+$, 329 (30), 280 (21), 262 (40), 206 (100), 186 (13); HR-EIMS: *m/z*: calcd for $^{12}C_{20}{}^{1}H_{19}{}^{56}Fe^{14}N^{16}O$: 345.0816; found: 345.0833.

**α-Hydroxy(1-tosyl-3-indolyl)methyl ferrocene (7g)**: According to procedure B, (tri-*n*-butylstannyl)ferrocene (927 mg, 1.95 mmol) was treated with *n*BuLi (1.40 mL, 1.58 M, 2.21 mmol) and *N*-methylindole-3-carbaldehyde (659 mg, 2.20 mmol). The alcohol **7g** was purified by column chromatography (silica gel, *n*-pentane/diethyl ether 5:1 to 0:1 with 12.5 to 0% triethylamine) and obtained as yellow crystals (721 mg, 1.49 mmol, 76%). M.p. 76–78 °C (brown); $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 8.28 (d, $J$ = 8.0 Hz, 1H), 7.75 (d, $J$ = 1.0 Hz, 1H), 7.70–7.62 (m, 3H), 7.19–7.13 (m, 1H), 7.08–7.02 (m, 1H), 6.46 (d, $J$ = 8.0 Hz, 2H), 5.52 (br s, 1H), 4.14–4.11 (m, 1H), 4.05–4.02 (m, 1H), 3.98 (s, 5H), 3.92–3.86 (m, 2H), 2.03 (br s, 1H), 1.63 ppm (s, 3H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 144.4, 136.2, 136.1, 129.9, 129.8, 126.9 (CH), 126.7 (CH), 125.0 (CH), 123.7 (CH), 123.4 (CH), 121.4 (CH), 112.8 (CH), 89.1, 68.8 (CH), 68.2 (CH), 67.7 (CH), 66.8 (CH), 66.0 (CH), 20.9 ppm ($CH_3$); IR (KBr): $\tilde{\nu}$ = 3092 (w), 1597 (w), 1446 (m), 1369 (s), 1274 (w), 1188 (m), 1174 (s), 1120 (s), 1097 (m), 973 (w), 814 (w), 747 (m), 683 (s), 578 (s), 486 cm$^{-1}$ (w); EIMS (70 eV): *m/z* (%): 485 (100) $[M]^+$, 469 (16), 338.1 (18), 313 (55), 247 (20), 192 (73); HR-EIMS: *m/z*: calcd for $^{12}C_{26}{}^{1}H_{23}{}^{56}Fe^{14}N^{16}O_3{}^{32}S$: 485.0748; found: 485.0723.

**($S_{Fc}$)-(2-(α-Hydroxy(phenyl)methyl)ferrocene-1-yl)-*p*-(*S*)-tolyl sulfoxide (7h)**: A solution of (*S*)-*p*-tolylferrocenyl sulfoxide (**8**, 648 mg, 2.00 mmol) in THF (25 mL) was cooled to −78 °C and LDA (2.20 mmol, ca. 0.5 M in THF, *n*-hexane) was added dropwise over 10 min. The mixture was stirred for 30 min and benzaldehyde (0.29 mL, 0.30 g, 2.9 mmol) was added. The mixture was then stirred for 90 min at −78 °C. After this time, NaOH (2 N, 20 mL) was added and the mixture was warmed to RT. Water was added, the organic layer was separated and the aqueous phase was extracted with diethyl ether (180 mL). The combined organic layers were washed with water and brine, and then dried ($MgSO_4$). The crude product was purified by column chromatography (silica gel; *n*-pentane/diethyl ether 8:1 to 1:1). The product **7h** (781 mg, 1.81 mmol, 91%) was obtained as a yellow solid and as a mixture of diastereomers. The ratio was determined by integration of the $^1$H NMR spectrum to be 32:68 (A/B). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ = 7.48 (d, $^3J$ = 8.2 Hz, 2H; B), 7.38–7.28 (m, 2H, 1H; A and B, respectively), 7.25–7.18 (m, 1H; B), 7.15–7.01 (m, 2H, 3H; A and B, respectively), 6.91–6.83 (m, 3H; A), 6.75 (d, $^3J$ = 8.2 Hz, 2H; B), 6.67 (s, 1H; B), 6.52 (d, $^3J$ = 8.4 Hz, 2H; A), 6.47 (d, $^3J$ = 9.0 Hz, 1H; A), 5.49 (d, $^3J$ = 9.0 Hz, 1H; A), 5.40 (s, 1H; B), 4.45 (s, 5H; B), 4.36 (s, 5H; A), 4.30–4.24 (m, 1H; B), 4.09–4.05 (m, 1H; A), 3.97–3.92 (m, 1H; A), 3.81 (dd, $^3J$ = 2.5 Hz, 1H; A), 3.67 (dd, $^3J$ = 2.6 Hz, 1H; B), 3.43–3.37 (m, 1H; B), 1.86 (s, 3H; B), 1.85 ppm (s, 3H; A).

**2-[4-(α-Hydroxy(phenyl)methyl)phenyl]ethinyl ferrocene (7i)**: A solution of 2-(4-iodophenyl)ethinyl ferrocene (99, 206 mg, 0.500 mmol) in THF (4 mL) was cooled to −30 °C and *i*PrMgCl·LiCl (0.42 mL, 1.31 M, 0.55 mmol, 1.1 equiv) was added. The mixture was stirred 1 h and then benzaldehyde (0.070 mL, 73 mg, 0.69 mmol) was added. The resulting mixture was stirred for 1.5 h at RT and a saturated $NH_4Cl$ solution was added. The mixture was extracted with diethyl ether (40 mL). The combined organic layers were washed with brine and dried ($MgSO_4$). Before the solvent evaporation, silica gel (5 g) was added. A yellow powder was

obtained which was used directly in the purification by column chromatography (silica gel; *n*-pentane/diethyl ether 8:1 to 3:1). The alcohol **7i** was obtained as yellow oil (155 mg, 0.395 mmol, 79%). $^1$H NMR (600 MHz, $C_6D_6$): $\delta$ = 7.50 (d, $^3J$ = 8.6 Hz, 2H), 7.22 (d, $^3J$ = 7.6 Hz, 2H), 7.18–7.09 (m, 4H), 7.06–7.02 (m, 1H), 5.38 (d, $^3J$ = 3.1 Hz, 1H), 4.47 (dd, $J$ = 1.7 Hz, 1H), 4.08 (s, 5H), 3.93 (dd, $J$ = 1.7 Hz, 1H), 1.49 ppm (d, $^3J$ = 3.1 Hz, 1H); $^{13}$C NMR (151 MHz, $C_6D_6$): $\delta$ = 144.4, 144.3, 131.7 (CH), 128.5 (CH), 127.6 (CH), 127.0 (CH), 126.9 (CH), 123.5, 89.1, 86.5, 75.9 (CH), 71.8 (CH), 70.3 (CH), 69.2 (CH), 66.0 ppm; IR (KBr): $\tilde{\nu}$ = 3086 (w), 3029 (w), 2904 (w), 2206 (m), 1512 (m), 1453 (m); 1410 (m), 1190 (m), 1107 (m), 1034 (s), 1024 (s), 1014 (s), 1002 (s), 817 (s), 810 (s), 746 (m), 699 (s), 596 (m), 566 (m), 496 cm$^{-1}$ (s); EIMS (70 eV): *m*/*z* (%): 392 (100) $[M]^+$, 390 (35) $[M-2H]^+$, 376 (13), 254 (39), 252 (27); HR-EIMS: *m*/*z*: calcd for $^{12}C_{25}{}^1H_{20}{}^{56}Fe^{16}O$: 392.0858; found: 392.0877.

**Hydride-transfer oxidation of ferrocenyl alcohols**

*Procedure C*: A solution of the ferrocenyl alcohol **7** in THF (3 mL mmol$^{-1}$) was cooled to 0°C and *i*PrMgCl·LiCl (1.05 equiv) was added. The mixture was stirred for 10 min, then benzaldehyde (1.50 equiv) was added and the mixture was stirred at RT for the indicated time. Two types of workup procedures were used. Type 1: The mixture was diluted with diethyl ether (40 mL mmol$^{-1}$ alcohol) and silica gel (10 g mmol$^{-1}$ alcohol) was added. The solvent was removed under reduced pressure and the resulting powder was used directly for purification by column chromatography. Type 2: A saturated $NH_4Cl$ solution was added and the mixture was extracted with diethyl ether (60 mL mmol$^{-1}$ alcohol). The combined organic layer was washed with brine and dried ($MgSO_4$). The crude product was purified by column chromatography.

**Diferrocenyl ketone (10a)**:[41] According to procedure C, diferrocenylmethanol (80 mg, 0.20 mmol) was treated with *i*PrMgCl·LiCl (0.17 mL, 1.30 M, 0.22 mmol) and benzaldehyde (0.040 mL, 42 mg, 0.40 mmol). After 5 min, the red product was isolated by filtration, and then washed with water and a small amount of diethyl ether. Ketone **11j** (67 mg, 0.17 mmol, 85%) was obtained as a red solid. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 4.99 (dd, $J$ = 2.0 Hz, 2H), 4.52 (dd, $J$ = 2.0 Hz, 2H), 4.20 ppm (s, 5H).

**3-Benzofuryl ferrocenyl ketone (10b)**: According to procedure C, alcohol **7a** (239 mg, 0.719 mmol) was treated with *i*PrMgCl·LiCl (0.58 mL, 1.30 M, 0.76 mmol) and benzaldehyde (0.11 mL, 0.11 g, 1.1 mmol). After 2 h, workup procedure 2 (see above) was used. Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 15:1 to 4:1) gave ketone **10b** (215 mg, 0.651 mmol, 91%) as a red solid. M.p. 172–173°C; $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 8.65 (d, $J$ = 8.0 Hz, 1H), 7.97 (s, 1H), 7.36 (d, $J$ = 8.0 Hz, 1H), 7.21–7.14 (m, 1H), 7.12–7.04 (m, 1H), 4.75 (dd, $J$ = 2 Hz, 2H), 4.10 (dd, $J$ = 2 Hz, 2H), 3.86 ppm (s, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 193.7 (CO), 156.7, 146.2 (CH), 135.1, 127.1 (CH), 125.0 (CH), 121.9 (CH), 111.1 (CH), 107.2, 78.6, 72.4 (CH), 71.7 (CH), 70.2 ppm (CH); IR (KBr): $\tilde{\nu}$ = 1618 (s), 1552 (m), 1480 (m), 1447 (s), 1382 (m), 1292 (s), 1184 (w), 1120 (s), 1088 (m), 1024 (w), 818 (s), 779 (w), 754 (s), 582 (w), 502 cm$^{-1}$ (m); EIMS (70 eV): *m*/*z* (%): 330 (100) $[M]^+$, 265 (9) $[M-C_5H_5]^+$, 181 (5), 173 (17), 152 (10), 121 (6), 89 (7); HR-EIMS: *m*/*z*: calcd for $^{12}C_{19}{}^1H_{14}{}^{56}Fe^{16}O_2$: 330.0343; found: 330.0319.

**2-Benzofuryl ferrocenyl ketone (10c)**: According to procedure C, alcohol **7b** (121 mg, 0.364 mmol) was treated with *i*PrMgCl·LiCl (0.31 mL, 1.23 M, 0.38 mmol) and benzaldehyde (0.060 mL, 63 mg, 0.59 mmol). After 11 h, workup procedure 1 was used. Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 20:1 to 2:1) gave the ketone **10c** (97 mg, 0.294 mmol, 81%) as a red solid. M.p. 147°C; $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 7.52 (d, $J$ = 0.9 Hz, 1H), 7.36–7.31 (m 2H), 7.15–7.09 (m 1H), 7.05–6.99 (m, 1H), 5.30 (dd, $J$ = 2.0 Hz, 1H), 4.25 (dd, $J$ = 2.0 Hz, 1H), 3.93 ppm (s, 5H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 185.3, 155.6, 155.1, 127.4 (CH), 123.9 (CH), 123.2 (CH), 112.2 (CH), 112.0 (CH), 78.7, 72.8 (CH), 71.4 (CH), 70.4 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3100 (w), 1624 (s), 1612 (s), 1551 (s), 1476 (m), 1446 (s), 1378 (m), 1300 (s), 1136 (m), 1056 (m), 744 cm$^{-1}$ (s); EIMS (70 eV): *m*/*z* (%): 330 (100) $[M]^+$, 173 (11); HR-EIMS: *m*/*z*: calcd for $^{12}C_{19}{}^1H_{14}{}^{56}Fe^{16}O_2$: 330.0338; found: 330.0353.

**3-Pyridyl ferrocenyl ketone (10d)**: According to procedure C, alcohol **7c** (297 mg, 1.01 mmol) was treated with *i*PrMgCl·LiCl (0.82 mL, 1.30 M, 1.1 mmol) and benzaldehyde (0.15 mL, 0.16 g, 1.5 mmol). DMPU (2 mL) as a cosolvent was added. After 12 h at RT and 5 h at 45°C, workup procedure 2 was used. Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 2:1 to 0:1) gave the ketone **10d** (201 mg, 0.690 mmol, 68%) as a red solid. M.p. 91°C; $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 9.41 (d, $^4J$ = 1.3 Hz, 1H), 8.56 (dd, $^3J$ = 4.5, $^4J$ = 1.3 Hz, 1H), 7.91 (dd, $^3J$ = 8.0, $^4J$ = 1.8 Hz, 1H), 6.73 (dd, $^3J$ = 8.0, $^3J$ = 4.5 Hz, 1H), 4.63 (dd, $J$ = 1.8 Hz, 2H), 4.12 (dd, $J$ = 1.8 Hz, 2H), 3.86 ppm (s, 5H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 195.9, 152.4 (CH), 149.8 (CH), 135.5, 135.4 (CH), 123.3 (CH), 78.7, 72.8 (CH), 71.6 (CH), 70.4 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3115 (w), 1624 (vs), 1581 (m), 1448 (s), 1377 (m), 1295 (s), 1023 (m), 828 (m), 823 (m), 752 (m), 712 (m), 497 cm$^{-1}$ (m); EIMS (70 eV): *m*/*z* (%): 291 (100) $[M]^+$, 198 (8), 121 (7); HR-EIMS: *m*/*z*: calcd for $^{12}C_{16}{}^1H_{13}{}^{56}Fe^{14}N^{16}O$: 291.0341; found: 291.0342.

**4-Pyridyl ferrocenyl ketone (10e)**: According to procedure C, alcohol **7d** (299 mg, 1.02 mmol) was treated with *i*PrMgCl·LiCl (0.82 mL, 1.30 M, 1.1 mmol) and benzaldehyde (0.16 mL, 0.17 g, 1.6 mmol). DMPU (0.5 mL) was added as a cosolvent. After 12 h at RT and 2 h at 45°C, workup procedure 2 was used. Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 2:1 to 0:1) gave the ketone **10e** (196 mg, 0.673 mmol, 66%) as a red solid. M.p. 145–146°C; $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 8.61 (d, $^3J$ = 6.2 Hz, 2H), 7.39 (d, $^3J$ = 6.2 Hz, 2H), 4.67 (dd, $J$ = 2.0 Hz, 2H), 4.14 (dd, $J$ = 2.0 Hz, 2H), 3.85 ppm (s, 5H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 196.6, 150.7 (CH), 146.3, 121.6 (CH), 77.9, 73.0 (CH), 71.5 (CH), 70.4 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3100 (w), 3066 (m), 1640 (vs), 1598 (m), 1548 (m), 1453 (s), 1407 (m), 1377 (s), 1295 (s), 1056 (m), 834 (m), 817 (s), 764 (m), 670 (s), 514 (s), 497 (m), 483 cm$^{-1}$ (m); EIMS (70 eV): *m*/*z* (%): 291 (100) $[M]^+$, 185 (4), 121 (5); HR-EIMS: *m*/*z*: calcd for $^{12}C_{16}{}^1H_{13}{}^{56}Fe^{14}N^{16}O$: 291.0341; found: 291.0359.

**1-Methyl-3-indolyl ferrocenyl ketone (10f)**: According to procedure C, alcohol **7f** (207 mg, 0.600 mmol) was treated with *i*PrMgCl·LiCl (0.55 mL, 1.19 M, 0.66 mmol) and benzaldehyde (0.090 mL, 94 mg, 0.89 mmol). After 6 h, workup procedure 1 was used. Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 10:1 to 1:1) gave the ketone **10f** (179 mg, 0.533 mmol, 89%) as a red oil. $^1$H NMR (600 MHz, $C_6D_6$): $\delta$ = 9.07 (d, $J$ = 8.2 Hz, 1H), 7.36 (s, 1H), 7.31 (dd, $^3J$ = 8.2, $^4J$ = 1.2 Hz, 1H), 7.22 (dd, $^3J$ = 8.2, $^4J$ = 1.2 Hz, 1H), 6.92 (d, $J$ = 8.2 Hz, 1H), 6.92 (d, $J$ = 8.2 Hz, 1H), 4.99 (dd, $J$ = 1.9 Hz, 2H), 4.19 (dd, $J$ = 1.9 Hz, 2H), 4.05 (s, 5H), 2.81 ppm (s, 3H); $^{13}$C NMR (150 MHz, $C_6D_6$): $\delta$ = 190.2 (CO), 137.4, 134.0 (CH), 123.8 (CH), 123.7, 123.4 (CH), 122.6 (CH), 117.3, 109.5 (CH), 83.1, 70.9 (CH), 70.8 (CH), 70.3 (CH), 32.3 ppm ($CH_3$); IR (KBr): $\tilde{\nu}$ = 2927 (m), 1606 (m), 1525 (m), 1467 (m), 1374 (w), 1269 (w), 1241 (m), 1166 (w), 1125 (w), 1080 (w), 960 (w), 818 (w), 778 (w), 750 (m), 498 cm$^{-1}$ (m, br); EIMS (70 eV): *m*/*z* (%): 343.2 (100) $[M]^+$, 278.1 (6), 249.1 (6), 194.2 (8), 186.1 (4); HR-EIMS: *m*/*z*: calcd for $^{12}C_{20}{}^1H_{17}{}^{56}Fe^{14}N^{16}O$: 343.0660; found: 343.0649.

**1-Tosyl-3-indolyl ferrocenyl ketone (10g)**: According to procedure C, alcohol **7g** (486 mg, 1.00 mmol) was treated with *i*PrMgCl·LiCl (0.80 mL, 1.38 M, 1.10 mmol) and benzaldehyde (0.15 mL, 0.16 g, 1.5 mmol). After 6 h, workup procedure 1 was used. Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 10:1 to 2:1) gave the ketone **10g** (254 mg, 0.524 mmol, 52%) as a red solid. M.p. 47–48°C; $^1$H NMR (600 MHz, $C_6D_6$): $\delta$ = 8.69 (d, $J$ = 8 Hz, 1H), 8.67 (s, 1H), 8.19 (d, $J$ = 8 Hz, 1H), 7.65 (d, $J$ = 8.4 Hz, 2H), 7.18–7.10 (m, 2H), 6.44 (d, $J$ = 8.4 Hz, 2H), 4.89 (dd, $J$ = 1.9 Hz, 2H), 4.13 (dd, $J$ = 1.9 Hz, 2H), 3.97 (s, 5H), 1.64 ppm (s, 3H); $^{13}$C NMR (150 MHz, $C_6D_6$): $\delta$ = 191.1 (CO), 145.2, 135.4, 130.1 (CH), 129.7 (CH), 126.9 (CH), 125.9 (CH), 125.0 (CH), 123.9 (CH), 122.1, 113.5 (CH), 81.0, 72.1 (CH), 71.1 (CH), 70.0 (CH), 21.0 ppm ($CH_3$); IR (KBr): $\tilde{\nu}$ = 1624 (s), 1537 (m), 1446 (s), 1380 (s), 1298 (w), 1217 (m), 1176 (s), 1126 (s), 1086 (m), 1041 (w), 979 (s), 816 (s), 751 (m), 664 (s), 574 cm$^{-1}$ (s); EIMS (70 eV): *m*/*z* (%): 483.1 (100) $[M]^+$, 328.1 (35) $[M-Ts]^+$, 300.1 (60), 262.1 (17), 121 (30); HR-EIMS: *m*/*z*: calcd for $^{12}C_{26}{}^1H_{21}{}^{56}Fe^{14}N^{16}O_3{}^{32}S$: 483.0592; found: 483.0573.

**($S_{Fc}$)-(2-Benzoylferrocen-1-yl)-*p*-(*S*)-tolyl sulfoxide (10h)**: According to procedure C, alcohol **7h** (mixture of diastereomers, 694 mg, 1.61 mmol) was treated with *i*PrMgCl·LiCl (1.30 mL, 1.30 M, 1.69 mmol) and benzaldehyde (0.25 mL, 0.26 g, 2.5 mmol). After 14 h at 0°C to RT, workup procedure 2 was used. Purification by column chromatography (silica gel, *n*-

pentane/diethyl ether 1:1 to diethyl ether/ethyl acetate 9:1) gave the ketone **10h** (458 mg, 1.07 mmol, 66%) as a red solid. M.p. 69°C (decomp); $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ = 8.02 (d, $^3J$ = 8.0 Hz, 2H), 7.71 (d, $^3J$ = 6.8 Hz, 2H), 7.19–7.02 (m, 3H), 6.94 (d, $^3J$ = 8.0 Hz, 2H), 4.35–4.30 (m, 2H), 3.99–3.94 (m, 1H), 3.73 (s, 5H), 2.00 ppm (s, 3H); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 197.0, 144.6, 140.8, 139.7, 131.0 (CH), 130.1 (CH), 129.6 (CH), 129.2 (CH), 125.7 (CH), 101.9, 78.9, 74.7 (CH), 73.4 (CH), 72.7 (CH), 72.1 (CH), 71.7 (CH), 70.8 (CH), 21.7 ppm ($CH_3$); IR (KBr): $\tilde{\nu}$ = 3083 (w), 2922 (w), 1734 (w), 1640 (vs), 1597 (m), 1576 (m), 1447 (m), 1424 (s), 1375 (m), 1326 (s), 1260 (s), 1166 (m), 1081 (m), 1040 (s), 1005 (m), 872 (m), 814 (m), 729 (m), 700 (m), 501 (m), 477 (m), 461 cm$^{-1}$ (m); EIMS (70 eV): *m*/*z* (%): 428 (51) $[M]^+$, 412 (100) $[M-O]^+$, 305 (26), 289 (26), 260 (15), 256 (12), 105 (20), 77 (10); HR-EIMS: *m*/*z*: calcd for $^{12}C_{24}{}^1H_{20}{}^{56}Fe^{32}N^{16}O_2$: 428.052; found: 428.0563.

**2-(4-Benzoylphenyl)ethinyl ferrocene (10i)**: According to procedure C, alcohol **7i** (83.4 mg, 0.213 mmol) was treated with *i*PrMgCl·LiCl (0.17 mL, 1.30 M, 0.22 mmol) and benzaldehyde (0.030 mL, 31 mg, 0.30 mmol). After 16 h at RT, workup procedure 2 was used. Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 100:1 to 10:1) gave the ketone **10i** (73 mg, 0.19 mmol, 88%) as a red solid. M.p. 153°C; $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 7.68–7.64 (m, 2H), 7.61 (d, $^3J$ = 8.6 Hz, 2H), 7.44 (d, $^3J$ = 8.6 Hz, 2H), 7.15–7.09 (m, 1H), 7.07–7.00 (m, 2H), 4.48 (dd, $J$ = 1.9 Hz, 2H), 4.08 (s, 5H), 3.96 ppm (dd, $J$ = 1.9 Hz, 2H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 194.8, 138.2, 136.8, 132.0 (CH), 131.3 (CH), 130.4 (CH), 130.1 (CH), 92.6, 86.1, 72.0 (CH), 70.4 (CH), 69.5 (CH), 65.1 ppm; IR (KBr): $\tilde{\nu}$ = 3100 (w), 2206 (m), 1654 (vs), 1599 (vs), 1448 (m), 1404 (m), 1309 (s), 925 (m), 742 (m), 702 (s), 499 cm$^{-1}$ (m); EIMS (70 eV): *m*/*z* (%): 390 (100) $[M]^+$, 121 (4); HR-EIMS: *m*/*z*: calcd for $^{12}C_{25}{}^1H_{18}{}^{56}Fe^{16}O$: 390.0702; found: 390.0714.

**One-pot synthesis of metallocene ketones**

*Procedure D:* The Grignard reagent was prepared first. Type 1 (direct insertion of magnesium): In a two-necked Schlenk flask with reflux condenser and tap-funnel, LiCl (1.0 equiv) was dried in vacuo by using a heat gun for 10 min and then Mg turnings (1.1 equiv) and THF (0.5 mL mmol$^{-1}$ LiCl) were added. A solution of the aryl bromide (1.0 equiv) in THF (0.5 mL mmol$^{-1}$) was added within 20 min. The mixture started to boil and no cooling bath was used. The mixture was allowed to settle and the concentration of the Grignard reagent in the supernatant liquid was determined by titration with iodine (ca. 0.5 mmol) in THF (1 mL) at 0°C. Type 2 (iodine–magnesium exchange): The aryl iodide was dissolved in THF (1 mL mmol$^{-1}$) and *i*PrMgCl·LiCl (1.0 equiv) was added dropwise at −30°C. The mixture was stirred for 30 min. Addition and oxidation: A solution of the metallocene aldehyde in THF (0.5 mL mmol$^{-1}$) was cooled to −20°C and the Grignard reagent (1.05 to 1.10 equiv) was added. The mixture was stirred for 10 min and it turned from orange to yellow. The conversion of the aldehyde was checked for completion by TLC or by GC (in case of the cymantrene aldehyde). Benzaldehyde (1.5 equiv) was added and the mixture was then warmed to RT and stirred for 12 h. The yellow solution turned orange again. The conversion was checked for completion and the mixture was diluted with diethyl ether (10 mL mmol$^{-1}$) and silica gel (5 g mmol$^{-1}$) was added. The solvent was removed and the remaining powder was used directly for purification by column chromatography. The tricarbonylchromium arenes were crystallized from *n*-pentane/diethyl ether at 30°C.

**3-Benzofurylferrocenyl ketone (10b)**: According to procedure D, the Grignard reagent was generated (Type 2) from 3-bromobenzofuran[42] (4.93 g, 25.0 mmol) and *i*PrMgCl·LiCl (31.6 mL, 0.79 M, 25.0 mmol). Variational to procedure D, the ketone was dissolved in only 5 mL THF. Furthermore, the exchange was performed at −40°C over 6 h. Ferrocene aldehyde (4.45 g, 20.8 mmol) was dissolved in THF (5 mL) and the Grignard reagent was added at 0°C and stirred for 1 h before benzaldehyde (4.06 mL, 4.24 g, 40.0 mmol) was added. Purification was carried out according to procedure D by column chromatography (silica gel, *n*-pentane/diethyl ether 40:1 to 2:1; large amounts of solvent are necessary) and crystallization from ethyl acetate/diethyl ether (1st fraction: 300 mL, 1:2; 2nd fraction from diethyl ether). The ketone **10b** was obtained as red crystals (5.44 g, 16.5 mmol, 79%). For the analytical data, see above.

**Benzoylcymantrene (14a)**:[19] The Grignard reagent was obtained from Chemetall (Frankfurt). Benzoylcymantrene (**14a**) was prepared according to procedure D from cymantrene aldehyde (204 mg, 0.879 mmol), PhMgCl·LiCl (0.64 mL, 1.44 M, 0.92 mmol), and benzaldehyde (0.13 mL, 0.14 g, 1.3 mmol). The compound was purified by column chromatography (silica gel, *n*-pentane/diethyl ether 6:1 to 1:1) and crystallization, giving the product as red crystals (271 mg, 0.851 mmol, 85%). M.p. 70–71°C; $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta$ = 7.90–7.77 (m, 2H), 7.69–7.46 (m, 3H), 5.70 (s, 2H), 5.21 ppm (s, 2H); $^{13}$C NMR (75 MHz, [D$_6$]acetone): $\delta$ = 195.1, 192.8, 139.4, 133.9 (CH), 130.0 (CH), 129.5 (CH), 93.8, 90.1 (CH), 86.2 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3268 (w), 3111 (m), 3070 (w), 2018 (m), 1948 (m), 1926 (s), 1913 (vs), 1639 (s), 1597 (m), 1453 (m), 1443 (m), 1375 (m), 1286 (m), 1170 (w), 1066 (w), 1038 (w), 855 (w), 842 (w), 721 cm$^{-1}$ (w); EIMS (70 eV): *m*/*z* (%): 308 (7) $[M]^+$, 252 (16) $[M-2CO]^+$, 224 (100) $[M-3CO]^+$, 132 (20), 55 (10); HR-EIMS: *m*/*z*: calcd for $^{12}C_{15}{}^1H_9{}^{55}Mn^{16}O_4$: 307.9881; found: 307.9895; elemental analysis calcd (%) for $C_{15}H_9MnO_4$ (308.2): C 58.46, H 2.94; found: C 58.28, H 3.33.

**Benzoyl tricarbonylchromium benzene (14b)**: The Grignard reagent was obtained from Chemetall (Frankfurt). Benzoyl tricarbonylchromium benzene (**14b**) was prepared according to procedure D from tricarbonylchromium benzaldehyde (242 mg, 1.00 mmol), PhMgCl·LiCl (0.73 mL, 1.44 M, 1.05 mmol) and benzaldehyde (0.15 mL, 0.16 g, 1.5 mmol). This compound was purified by column chromatography (silica gel, *n*-pentane/diethyl ether 6:1 to 1:1) and crystallization, giving the product as red crystals (271 mg, 0.851 mmol, 85%). M.p. 90–91°C; $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta$ = 7.86–7.78 (m, 2H), 7.71–7.63 (m, 1H), 7.61–7.52 (m, 2H), 6.21 (d, $^3J$ = 6.3 Hz 2H), 6.00 (t, $^3J$ = 6.3 Hz, 1H), 5.67 ppm (dd, $^3J$ = 6.3 Hz, 2H); $^{13}$C NMR (75 MHz, [D$_6$]acetone): $\delta$ = 233.3, 194.5, 138.2, 133.8 (CH), 130.1 (CH), 130.0 (CH), 99.0, 98.3 (CH), 98.1 (CH), 92.9 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3100 (m), 3074 (w), 1968 (s), 1917 (s), 1885 (vs), 1654 (s), 1596 (m), 1512 (m), 1295 (m), 1267 cm$^{-1}$ (m); elemental analysis calcd (%) for $C_{16}H_{10}CrO_4$ (318.2): C 60.38, H 3.17; found: C 60.31, H 3.20.

**4-Methoxybenzoyl tricarbonylchromium benzene (14c)**:[20] According to procedure D, the Grignard reagent was generated (Type 1) from *p*-bromoanisol (3.74 g, 20.0 mmol), magnesium (535 mg, 22.0 mmol), and LiCl (848 mg, 20.0 mmol). 4-Methoxybenzoyl tricarbonylchromium benzene (**14c**) was prepared from tricarbonylchromium benzaldehyde (832 mg, 3.44 mmol), Grignard reagent (4.40 mL, 0.82 M, 3.61 mmol), and benzaldehyde (0.52 mL, 0.54 g, 5.2 mmol). Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 8:1 to 1:1) gave the product as red crystals (875 mg, 2.51 mmol, 73%). M.p. 126–127°C; $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta$ = 7.88 (d, $^3J$ = 9.1 Hz 2H), 7.09 (d, $^3J$ = 9.1 Hz, 2H), 6.19 (d, $^3J$ = 6.3 Hz 2H), 5.95 (t, $^3J$ = 6.3 Hz, 1H), 5.71 (dd, $^3J$ = 6.3 Hz, 2H), 3.91 ppm (s, 3H); $^{13}$C NMR (75 MHz, [D$_6$]acetone): $\delta$ = 233.3, 204.2, 165.0, 132.8 (CH), 130.4, 115.3 (CH), 101.0, 98.2 (CH), 97.8 (CH), 92.9 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3104 (w), 3021 (w), 1955 (vs), 1874 (vs), 1655 (s), 1591 (s), 1570 (m), 1509 (m), 1422 (m), 1258 (s), 1176 (m), 1142 cm$^{-1}$ (m); elemental analysis calcd (%) for $C_{17}H_{12}CrO_5$ (348.3): C 58.63, H 3.47; found: C 58.57, H 3.35.

**4-Phenylbenzoyl tricarbonylchromium benzene (14d)**: According to procedure D, the Grignard reagent was generated (Type 1) from 4-bromobiphenyl (4.66 g, 20.0 mmol), magnesium (535 mg, 22.0 mmol), and LiCl (848 mg, 20.0 mmol). As a result of the low solubility, a maximum concentration of 0.48 M was reached. 4-Phenylbenzoyl tricarbonylchromium benzene (**14d**) was prepared from tricarbonylchromium benzaldehyde (484 mg, 2.00 mmol), Grignard reagent (4.58 mL, 0.48 M, 2.20 mmol), and benzaldehyde (0.31 mL, 0.32 g, 3.0 mmol). Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 9:1 to 1:1) and crystallization gave the product as red crystals (549 mg, 1.39 mmol, 70%). M.p. 156–158°C; $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta$ = 7.94 (d, $^3J$ = 8.0 Hz, 2H), 7.85 (d, $^3J$ = 8.0 Hz, 2H), 6.26 (d, $^3J$ = 6.1 Hz, 2H), 6.00 (t, $^3J$ = 6.1 Hz, 1H), 5.73 ppm (dd, $^3J$ = 6.1 Hz, 2H); $^{13}$C NMR (75 MHz, [D$_6$]acetone): $\delta$ = 233.0, 194.0, 146.2, 140.9, 136.8, 130.8 (CH), 130.4 (CH), 129.7 (CH), 128.5 (CH), 128.3 (CH), 99.3, 98.2 (CH), 98.0 (CH), 92.8 ppm (CH); IR (KBr): $\tilde{\nu}$ = 3090 (m), 3032 (w), 1958 (s), 1908 (m), 1893 (m), 1873 (vs), 1654 (s), 1603 (m), 1297 (m), 1261 (m), 747 (m),

696 $cm^{-1}$ (m); elemental analysis calcd (%) for $C_{22}H_{14}CrO_4$ (394.3): C 67.01, H 3.47; found: C 66.85, H 3.62.

**4-Methylbenzoyl tricarbonylchromium benzene (14e)**:[21] According to procedure D, the Grignard reagent was generated (Type 1) from 4-bromotoluene (17.1 g, ca. 12.3 mL, 100 mmol), magnesium (2.67 g, 110 mmol), and LiCl (4.24 g, 100 mmol). 4-Methylbenzoyl tricarbonylchromium benzene (**14e**) was prepared from tricarbonylchromium benzaldehyde (709 mg, 2.93 mmol), Grignard reagent (4.52 mL, 0.81 M, 3.66 mmol), and benzaldehyde (0.56 mL, 0.58 g, 5.5 mmol). Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 8:1 to 2:1) and crystallization gave the product as red crystals (634 mg, 1.91 mmol, 65%). M.p. 112–114 °C; $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta = 7.77$ (d, $^3J = 7.5$ Hz, 2H), 7.40 (d, $^3J = 7.5$ Hz, 2H), 6.22 (d, $^3J = 6.3$ Hz, 2H), 6.00 (t, $^3J = 6.3$ Hz, 1H), 5.72 (dd, $^3J = 6.3$ Hz, 2H), 2.45 ppm (s, 3H); $^{13}$C NMR (75 MHz, [D$_6$]acetone): $\delta = 233.1$, 194.0, 144.6, 135.3, 130.5 (CH), 130.3 (CH), 99.7, 98.2 (CH), 97.9 (CH), 92.8 (CH), 22.0 ppm ($CH_3$); IR (KBr): $\tilde{\nu} = 3098$ (m), 1964 (s), 1891 (vs), 1645 (s), 1604 (s), 1522 (w), 1403 (w), 1294 (m), 1265 (m), 917 (m), 832 (m), 752 $cm^{-1}$ (m); elemental analysis calcd (%) for $C_{17}H_{12}CrO_4$ (332.3): C 61.45, H 3.64; found: C 61.26, H 3.56.

**4-*N*,*N*-Dimethylaminobenzoyl tricarbonylchromium benzene (14f)**:[22] According to procedure D, the Grignard reagent was generated (Type 1) from 4-bromo-*N*,*N*-dimethylaniline (20.0 g, 100 mmol), magnesium (2.67 g, 110 mmol), and LiCl (4.24 g, 100 mmol). 4-*N*,*N*-Dimethylaminobenzoyl tricarbonylchromium benzene (**14f**) was prepared from tricarbonylchromium benzaldehyde (484 mg, 2.00 mmol), Grignard reagent (2.63 mL, 0.80 M, 2.10 mmol), and benzaldehyde (0.31 mL, 0.32 g, 3.0 mmol). Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 4:1 to 1:3) gave the product as red crystals (667 mg, 1.85 mmol, 92%). While the crude material was dried with silica gel the color turned from red to green and then to blue. However, no effect on the purity or yield was observed. M.p. 138–139 °C (brown); $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta = 7.85$ (d, $^3J = 9.1$ Hz, 2H), 6.80 (d, $^3J = 9.1$ Hz, 2H), 6.15 (d, $^3J = 6.3$ Hz, 2H), 5.89 (t, $^3J = 6.3$ Hz, 1H), 5.70 (dd, $^3J = 6.3$ Hz, 2H), 3.10 ppm (s, 6H); $^{13}$C NMR (75 MHz, [D$_6$]acetone): $\delta$ 233.7, 191.1, 155.2, 133.1 (CH), 124.7, 112.2 (CH), 103.8, 98.1 (CH), 97.4 (CH), 92.9 (CH), 40.7 ($CH_3$); IR (KBr): $\tilde{\nu} = 3092$ (m), 2911 (m), 1949 (s), 1866 (vs), 1636 (m), 1596 (s, br), 1375 (m), 1233 (m), 818 (m), 765 $cm^{-1}$ (m); elemental analysis calcd (%) for $C_{18}H_{15}CrNO_4$ (361.3): C 59.84, H 4.18, N 3.88; found: C 59.86, H 4.13, N 3.93.

**4-D-Benzoyl tricarbonylchromium benzene (14g)**: According to procedure D, the Grignard reagent was generated (Type 1) from 4-D-1-bromobenzene[43] (332 mg, 2.10 mmol) and *i*PrMgCl·LiCl (2.7 mL, 0.79 M, 2.1 mmol). Variational to procedure D, the exchange was carried out at RT. 4-D-Benzoyl tricarbonylchromium benzene (**14g**) was prepared from tricarbonylchromium benzaldehyde (484 mg, 2.00 mmol), Grignard reagent, and benzaldehyde (0.31 mL, 0.32 g, 3.0 mmol). Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 8:1 to 2:1) and crystallization gave the product as red crystals (462 mg, 1.45 mmol, 72%). M.p. 87–90 °C; $^1$H NMR (400 MHz, [D$_6$]acetone): $\delta = 7.82$ (d, $^3J = 8.0$ Hz, 2H), 7.56 (d, $^3J = 8.0$ Hz, 2H), 6.21 (d, $^3J = 6.4$ Hz, 2H), 6.00 (t, $^3J = 6.4$ Hz, 1H), 5.71 ppm (dd, $^3J = 6.4$ Hz, 2H); $^{13}$C NMR (100 MHz, [D$_6$]acetone): $\delta = 233.0$, 194.6, 138.2, 133.5 (t, $^2J$(C,D) = 24.3 Hz), 130.1 (CH), 129.9 (CH), 99.1, 98.3 (CH), 98.2 (CH), 92.9 ppm (CH); IR (KBr): $\tilde{\nu} = 3100$ (m), 1968 (s), 1916 (s), 1890 (vs), 1656 (s), 1512 (m), 1295 (m), 1265 (m), 1145 (w), 921 (w), 863 $cm^{-1}$ (w); elemental analysis calcd (%) for $C_{16}H_9CrDO_4$ (319.2): C 60.19, H 3.47; found: C 59.94, H 3.24.

**4-Chlorobenzoyl tricarbonylchromium benzene (14h)**:[24] According to procedure D, the Grignard reagent was generated (Type 1) from 4-chloro-1-bromobenzene (3.83 g, 20.0 mmol), magnesium (535 mg, 22.0 mmol), and LiCl (848 mg, 20.0 mmol). 4-Chlorobenzoyl tricarbonylchromium benzene (**14h**) was prepared from tricarbonylchromium benzaldehyde (484 mg, 2.00 mmol), Grignard reagent (2.62 mL, 0.84 M, 2.20 mmol), and benzaldehyde (0.30 mL, 0.31 g, 2.9 mmol). Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 20:1 to 2:1) and crystallization gave the product as red crystals (279 mg, 0.791 mmol, 40%). M.p. 103–105 °C; $^1$H NMR (400 MHz, [D$_6$]acetone): $\delta = 7.84$ (d, $^3J = 8.5$ Hz, 2H), 7.61 (d, $^3J = 8.5$ Hz, 2H), 6.23 (d, $^3J = 6.4$ Hz, 2H), 6.01 (t, $^3J = 6.4$ Hz, 1H), 5.71 ppm (dd, $^3J = 6.4$ Hz, 2H); $^{13}$C NMR (100 MHz, [D$_6$]acetone): $\delta = 233.0$, 193.6, 139.4, 136.8, 131.9 (CH), 130.3 (CH), 98.6, 98.3 (CH), 98.2 (CH), 92.8 ppm (CH); IR (KBr): $\tilde{\nu} = 3100$ (m), 1970 (s), 1876 (vs), 1651 (s), 1584 (m), 1510 (m), 1296 (m), 1264 (m), 1088 (w), 918 (w), 844 (w), 760 $cm^{-1}$ (w); elemental analysis calcd (%) for $C_{16}H_9ClCrO_4$ (352.7): C 54.49, H 2.57; found: C 54.38, H 2.82.

**4-Bromobenzoyl tricarbonylchromium benzene (14i)**:[24c] According to procedure D, the Grignard reagent was generated (Type 2) from 4-bromo-1-iodobenzene (622 mg, 2.20 mmol) and *i*PrMgCl·LiCl (1.68 mL, 1.25 M, 2.10 mmol). 4-Bromobenzoyl tricarbonylchromium benzene (**14i**) was prepared from tricarbonylchromium benzaldehyde (484 mg, 2.00 mmol), Grignard reagent (2.10 mmol), and benzaldehyde (0.31 mL, 0.32 g, 3.0 mmol). Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 10:1 to 1:1) and crystallization gave the product as red crystals (467 mg, 1.18 mmol, 59%). M.p. 136–137 °C; $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta = 7.90$–$7.69$ (m, 4H), 6.22 (d, $^3J = 6.6$ Hz, 2H), 6.01 (t, $^3J = 6.6$ Hz, 1H), 5.71 ppm (dd, $^3J = 6.6$ Hz, 2H); $^{13}$C NMR (75 MHz, [D$_6$]acetone): $\delta = 232.8$, 193.6, 137.1, 133.2 (CH), 132.1 (CH), 127. 8, 98.4, 98.2 (CH). 98.1 (CH), 92.7 ppm (CH); IR (KBr): $\tilde{\nu} = 3098$ (m), 1961 (s), 1868 (vs), 1651 (s), 1584 (m), 1510 (m), 1296 (m), 1263 (m), 1009 (w), 839 (w), 759 $cm^{-1}$ (w); elemental analysis calcd (%) for $C_{16}H_9BrCrO_4$ (397.1): C 48.39, H 2.28; found: C 48.37, H 2.37.

**4-Iodobenzoyl tricarbonylchromium benzene (14j)**: According to procedure D, the Grignard reagent was generated (Type 2) from 1,4-diiodobenzene (726 mg, 2.20 mmol) and *i*PrMgCl·LiCl (1.68 mL, 1.25 M, 2.10 mmol). 4-Iodobenzoyl tricarbonylchromium benzene (**14j**) was prepared from tricarbonylchromium benzaldehyde (484 mg, 2.00 mmol), Grignard reagent (2.10 mmol), and benzaldehyde (0.31 mL, 0.32 g, 3.0 mmol). Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 8:1 to 2:1) and crystallization gave the product as red crystals (248 mg, 0.558 mmol, 28%). M.p. 160–161 °C; $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta = 7.98$ (d, $^3J = 8.4$ Hz, 2H), 7.60 (d, $^3J = 8.4$ Hz, 2H), 6.22 (d, $^3J = 6.5$ Hz, 2H), 6.01 (t, $^3J = 6.5$ Hz, 1H), 5.70 ppm (dd, $^3J = 6.5$ Hz, 2H); $^{13}$C NMR (75 MHz, [D$_6$]acetone): $\delta = 233.0$, 194.0, 139.3 (CH), 137.7, 131.7 (CH), 100.6, 98.5, 98.3 (CH), 98.2 (CH), 92.8 ppm (CH); IR (KBr): $\tilde{\nu} = 3099$ (m), 1968 (m), 1893 (vs), 1650 (s), 1579 (m), 1510 (m), 1296 (m), 1262 (m), 1142 (w), 1006 (w), 863 (w), 757 $cm^{-1}$ (w); elemental analysis calcd (%) for $C_{16}H_9CrIO_4$ (444.1): C 43.27, H 2.04; found: C 43.25, H 2.32.

**1-Naphthyl tricarbonylchromiumphenyl ketone (14k)**: According to procedure D, the Grignard reagent was generated (Type 1) from 1-bromonaphthalene (4.14 g, 2.78 mL, 20.0 mmol), magnesium (535 mg, 22.0 mmol), and LiCl (848 mg, 20.0 mmol). 1-Naphthyl tricarbonylchromiumphenyl ketone (**14k**) was prepared from tricarbonylchromium benzaldehyde (242 mg, 1.00 mmol), Grignard reagent (2.14 mL, 0.49 M, 1.05 mmol), and benzaldehyde (0.15 mL, 0.16 g, 1.5 mmol). Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 8:1 to 1:1) and crystallization gave the product as red crystals (287 mg, 0.779 mmol, 78%). M.p. 145–147 °C; $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta = 8.13$ (d, $^3J = 8.0$ Hz 1H), 8.07–7.97 (m, 2H), 7.75 (dd, $^3J = 7.1$, $^4J = 1.3$ Hz, 1H), 7.67–7.55 (m, 3H), 6.21 (dd, $^3J = 6.5$, $^4J = 1.1$ Hz, 2H), 6.07 (t, $^3J = 6.5$ Hz, 1H), 5.64 ppm (dd, $^3J = 6.5$ Hz, 2H); $^{13}$C NMR (75 MHz, [D$_6$]acetone): $\delta = 232.8$, 195.7, 136.2, 135.2, 132.5 (CH), 131.9, 130.0 (CH), 128.7 (CH), 128.1 (CH), 127.6 (CH), 126.6 (CH), 126.0 (CH), 99.0 (CH), 98.8 (CH), 98.3, 92.2 ppm (CH); IR (KBr): $\tilde{\nu} = 3090$ (m), 1966 (s), 1894 (vs), 1880 (vs), 1653 (s), 1508 (m), 1295 (m), 1250 (m), 1201 (w), 777 $cm^{-1}$ (m); elemental analysis calcd (%) for $C_{20}H_{12}CrO_4$ (369.2): C 65.22, H 3.28; found: C 64.95, H 3.30.

**2-Naphthyl tricarbonylchromiumphenyl ketone (14l)**: According to procedure D, the Grignard reagent was generated (Type 1) from 2-bromonaphthalene (4.15 g, 20.0 mmol), magnesium (535 mg, 22.0 mmol) and LiCl (848 mg, 20.0 mmol). As a result of the low solubility, a maximum concentration of 0.67 M was reached. 2-Naphthyl tricarbonylchromiumphenyl ketone (**14l**) was prepared from tricarbonylchromiumbenzaldehyde (484 mg, 2.00 mmol), Grignard reagent (3.28 mL, 0.67 M, 2.20 mmol), and benzaldehyde (0.31 mL, 0.32 g, 3.0 mmol). Purification by column chromatography (silica gel, *n*-pentane/diethyl ether 9:1 to 1:1) and crystallization gave the product as red crystals (605 mg, 1.64 mmol,

82%). M.p. 97–99°C; $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta$=8.49 (s, 1H), 8.11–7.99 (m, 3H), 7.86 (dd, $^3J$=8.6, $^4J$=1.5 Hz, 1H), 7.72–7.60 (m, 2H), 6.32 (d, $^3J$=6.5 Hz, 2H), 6.03 (t, $^3J$=6.5 Hz, 1H), 5.73 ppm (dd, $^3J$=6.5 Hz, 2H); $^{13}$C NMR (75 MHz, [D$_6$]acetone): $\delta$=233.1, 194.4, 136.6, 135.3, 133.7, 131.4 (CH), 130.7 (CH), 130.0 (CH), 129.8 (CH), 129.2 (CH), 128.5 (CH), 126.3 (CH), 99.4, 98.6 (CH), 98.1 (CH), 92.8 ppm (CH); IR (KBr): $\tilde{\nu}$=3094 (w), 1962 (s), 1871 (vs), 1650 (s), 1518 (w), 1501 (w), 1300 (m), 1275 (m), 1234 cm$^{-1}$ (m); elemental analysis calcd (%) for $C_{20}H_{12}CrO_4$ (369.2): C 65.22, H 3.28; found: C 65.12, H 3.20.

**Asymmetric synthesis of benzhydrols from tricarbonylchromium complexes**

*Procedure E:* First, a borane solution was prepared at RT. Type 1 (without additive): THF was added to borane–dimethyl sulfide complex (0.95 mL, 0.76 g, 10 mmol) until a total volume of 10 mL was reached. Type 2 (with *N*,*N*-diethylaniline as additive): Borane-dimetyl sulfide complex (0.95 mL, 0.76 g, 10 mmol) was dissolved in THF (5 mL) and then *N*,*N*-diethylaniline (1.59 mL, 1.49 g, 10.0 mmol) and THF were added until a total volume of 10 mL was reached. CBS reduction: The tricarbonylchromium ketone **14** (ca. 0.5 mmol) was dissolved in THF (2 mL). In a Schlenk flask the oxazaborolidine (*S*)-CBS (CBS catalyst, 20 mol%) was dissolved in THF (0.5 mL). Then the solution of the tricarbonylchromium ketone **14** and the borane solution (1M, 1.4 equiv) were added simultaneously at 0°C (Type 1, without additive) or at RT (Type 2, with *N*,*N*-diethylaniline as additive) within 30 min. The color changed from orange to yellow, showing the disappearance of the ketone. After the addition had been completed, the mixture was stirred for 10 min and then water (0.1 mL) was added (CAUTION: gas evolution). The mixture was filtered over a silica pad (40 mL; *n*-pentane/diethyl ether 1:3). THF (10 mL), triethylamine (0.1 mL), and iodine (1.1 equiv) were added to the eluate and the mixture was stirred for 1 h at RT. After this time, a saturated $Na_2S_2O_3$ solution was added, the organic layer was separated and the aqueous phase was extracted twice with diethyl ether (10 mL). The combined organic layers were washed with brine and dried ($Na_2SO_4$). The crude products were purified by column chromatography (silica gel, *n*-pentane/diethyl ether 20:1, 6:1, 2:1).

**(4-Methoxyphenyl)phenylmethanol (15a)**:[44] According to procedure E (Type 1), the tricarbonylchromium phenyl ketone **14c** (106 mg, 0.304 mmol) was reduced with the CBS catalyst (28 mg, 0.10 mmol, 33 mol%) and borane solution (0.45 mL, 0.45 mmol, 1.5 equiv). The decomplexation was performed with iodine (85 mg, 0.33 mmol). The benzhydrol **15a** was isolated as a white crystalline solid (59 mg, 0.28 mmol, 91%, 93% *ee* (*R*)). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$=7.34–7.27 (m, 2H), 7.20–7.10 (m, 3H), 7.09–7.01 (m, 2H), 6.71 (d, $^3J$=8.6 Hz, 2H), 5.50 (s, 1H), 3.26 (s, 3H), 1.79 ppm (br s, 1H); $^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta$=159.5, 145.1, 137.1, 128.5 (CH), 128.3 (CH), 127.3 (CH), 126.9 (CH), 114.0 (CH), 75.8 (CH), 54.7 ppm (CH$_3$); HPLC analysis (OJ, *n*-heptane/isopropanol 80:20, 0.8 mL min$^{-1}$, 229 nm): $t_R$ (min): 20.3 (*R*), 22.5 (*S*).

**(*p*-Biphenyl)phenylmethanol (15b)**:[45] According to procedure E (Type 2), the tricarbonylchromium phenyl ketone **14d** (193 mg, 0.484 mmol) was reduced with the CBS catalyst (1M in toluene, 0.10 mL, 0.10 mmol, 20 mol%) and borane solution (0.59 mL, 0.59 mmol, 1.2 equiv). The decomplexation was performed with iodine (137 mg, 0.538 mmol). The benzhydrol **15b** was isolated as a white crystalline solid (124 mg, 0.475 mmol, 97%, 89% *ee* (*R*)). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$=7.30–7.22 (m, 4H), 7.18–7.13 (m, 3H), 7.06–7.00 (m, 2H), 7.00–6.92 (m, 4H), 6.91–6.86 (m, 1H), 5.50 (s, 1H), 5.37 (s, 1H), 1.62 ppm (s, 1H); $^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta$=144.7, 143.8, 141.3, 140.6, 129.0 (CH), 128.6 (CH), 127.6 (CH), 127.4 (CH), 127.4 (CH), 127.3 (CH), 127.0 (CH), 76.0 ppm (CH); HPLC analysis (AD, *n*-heptane/isopropanol 95:5, 0.8 mL min$^{-1}$, 254 nm): $t_R$ (min): 25.0 (*S*), 27.4 (*R*).

**(4-Methylphenyl)phenylmethanol (15c)**:[41] According to procedure E (Type 2), the tricarbonylchromium phenyl ketone **14e** (154 mg, 0.478 mmol) was reduced with the CBS catalyst (1M in toluene, 0.10 mL, 0.10 mmol, 20 mol%) and borane solution (0.52 mL, 0.52 mmol, 1.2 equiv). The decomplexation was performed with iodine (133 mg, 0.526 mmol). The benzhydrol **15c** was isolated as a white crystalline solid (90 mg, 0.46 mmol, 95%, 93% *ee* (*R*)). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$=7.41–7.22 (m, 7H), 7.15 (d, $^3J$=7.8 Hz, 2H), 5.80 (s, 1H), 2.34 (s, 3H), 2.25 (br s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$=143.0, 140.9, 137.2, 129.1, 128.4, 127.4, 126.5, 126.4, 76.1, 21.1 ppm; HPLC analysis (OD, *n*-heptane/isopropanol 94:6, 0.7 mL min$^{-1}$, 222 nm): $t_R$ (min): 17.9 (*S*), 20.1 (*R*).

**(2-Naphthyl)phenylmethanol (15d)**:[46] According to procedure E (Type 2), the tricarbonylchromium phenyl ketone **14l** (175 mg, 0.475 mmol) was reduced with the CBS catalyst (1M in toluene, 0.10 mL, 0.10 mmol, 20 mol%) and borane solution (0.71 mL, 0.71 mmol, 1.5 equiv). The decomplexation was performed with iodine (133 mg, 0.526 mmol). The benzhydrol **15d** was isolated as a white crystalline solid (105 mg, 0.450 mmol, 95%, 94% *ee* (*R*)). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$=7.60 (s, 1H), 7.48–7.34 (m, 3H), 7.20–7.13 (m, 2H), 7.12–7.04 (m, 2H), 7.01–6.92 (m, 3H), 6.91–6.85 (m, 1H), 5.46 (d, $^3J$=2.1 Hz, 1H), 1.76 ppm (d, $^3J$=2.1 Hz, 1H); $^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta$=144.5, 142.1, 133.8, 133.4, 128.6 (CH), 128.5 (CH), 128.4 (CH), 127.9 (CH), 127.6 (CH), 127.1 (CH), 126.3 (CH), 126.0 (CH), 125.5 (CH), 125.4 (CH), 76.3 ppm (CH); HPLC analysis (OD, *n*-heptane/isopropanol 90:10, 1.0 mL min$^{-1}$, 228 nm): $t_R$ (min): 14.7 (*S*), 18.0 (*R*).

**(4-Bromophenyl)phenylmethanol (15e)**:[43] According to procedure E (Type 2), the tricarbonylchromium phenyl ketone **14i** (202 mg, 0.509 mmol) was reduced with the CBS catalyst (1M in toluene, 0.10 mL, 0.10 mmol, 20 mol%) and borane solution (0.61 mL, 0.61 mmol, 1.2 equiv). The decomplexation was performed with iodine (142 mg, 0.560 mmol). The benzhydrol **15e** was isolated as a white crystalline solid (128 mg, 0.486 mmol, 96%, 88% *ee* (*R*)). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$=7.36 (d, $^3J$=8.5 Hz, 2H), 7.27–7–09 (m, 7H), 5.68 (s, 1H), 2.05 ppm (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$=143.3, 142.7, 131.5, 128.6, 128.2, 127.8, 126.5, 121.4, 75.6 ppm; HPLC analysis (AD, *n*-heptane/isopropanol 90:10, 0.75 mL min$^{-1}$, 225 nm): $t_R$ (min): 16.7 (*R*), 18.2 (*S*).

**(4-Chlorophenyl)phenylmethanol (15f)**:[41] According to procedure E (Type 2), the tricarbonylchromium phenyl ketone **14h** (182 mg, 0.516 mmol) was reduced with the CBS catalyst (1M in toluene, 0.10 mL, 0.10 mmol, 20 mol%) and borane solution (0.62 mL, 0.62 mmol, 1.2 equiv). The decomplexation was performed with iodine (144 mg, 0.568 mmol). The benzhydrol **15f** was isolated as a white crystalline solid (95 mg, 0.52 mmol, quant., 90% *ee* (*R*)). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$=7.29–7.15 (m, 9H), 5.70 (s, 1H), 2.21 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$=143.4, 142.2, 133.2, 128.6, 128.5, 127.9, 127.8, 126.5, 75.6 ppm; HPLC analysis (AD, *n*-heptane/isopropanol 95:5, 1.0 mL min$^{-1}$, 225 nm) $t_R$ (min): 12.6 (*R*), 13.7 (*S*).

**(4-Iodophenyl)phenylmethanol (15g)**: According to procedure E (Type 2), the tricarbonylchromium phenyl ketone **14j** (135 mg, 0.304 mmol) was reduced with the CBS catalyst (1M in toluene, 0.060 mL, 0.060 mmol, 20 mol%) and borane solution (0.36 mL, 0.36 mmol, 1.2 equiv). The decomplexation was performed with iodine (85 mg, 0.33 mmol). The benzhydrol **15g** was isolated as a white crystalline solid (89 mg, 0.29 mmol, 94%, 86% *ee* (*R*)). M.p. 70–72°C; $[\alpha]_D^{20}$=−4.8 (*c*=0.46 in ethanol); IR (KBr): $\tilde{\nu}$=3303 (s, br), 3060 (m), 3026 (m), 2881 (w), 1481 (m), 1451 (m), 1394 (m), 1188 (w), 1002 (s), 788 (s), 749 (s), 695 cm$^{-1}$ (s); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$=7.66 (d, $^3J$=8.1 Hz, 2H), 7.38–7.22 (m, 5H), 7.12 (d, $^3J$=8.1 Hz, 2H), 5.76 (s, 1H), 2.19 ppm (s, br, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$=143.4, 143.3, 137.5, 128.6, 128.4, 127.9, 126.5, 93.0, 75.7 ppm; EIMS (70 eV): *m*/*z* (%): 310 (24) [*M*]$^+$, 231 (29), 165 (12), 105 (100), 77 (21); HR-EIMS: *m*/*z*: calcd for $^{12}C_{13}{}^1H_{11}{}^{127}I^{16}O$: 309.9855; found: 309.9831; HPLC analysis (AD, *n*-heptane/isopropanol 90:10, 0.7 mL min$^{-1}$, 235 nm): $t_R$ (min): 12.8 (*R*), 14.4 (*S*).

**(4-*N*,*N*-Dimethylaminophenyl)phenylmethanol (15h)**: According to procedure E (Type 1), the tricarbonylchromium phenyl ketone **11r** (170 mg, 0.470 mmol) was reduced with the CBS catalyst (1M in toluene, 0.090 mL, 0.090 mmol, 20 mol%) and borane solution (0.57 mL, 0.57 mmol, 1.2 equiv). The decomplexation was performed with iodine (346 mg, 1.36 mmol). The benzhydrol **15h** was isolated as a white crystalline solid (103 mg, 0.453 mmol, 96%, 84% *ee*). Purification by column chromatography was carried out with *n*-pentane/diethyl ether 8:1 to 1:1 (addition of 5 vol% triethylamine). M.p. 68°C (turned green); $[\alpha]_D^{20}$=+33.3 (*c*=0.51 in ethanol); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.42–7.16 (m, 7H), 6.69 (d, $^3J$=8.8 Hz, 2H), 5.77 (d, $^3J$=3.4 Hz, 1H), 2.92 (s, 6H), 2.13 ppm (d, $^3J$=3.4 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$=150.2, 144.3, 132.0, 128.3, 127.7, 127.1, 126.3, 112.5, 76.0, 40.6 ppm; IR (KBr):

$\tilde{\nu}$ = 3273 (s, br), 3027 (w), 2880 (m), 2799 (m), 1613 (s), 1520 (s), 1444 (m), 1342 (s), 1164 (m), 1012 (s), 793 (s), 695 $cm^{-1}$ (m); EIMS (70 eV): *m*/*z* (%): 227 (100) $[M]^+$, 210 (100), 150 (61), 122 (37), 105 (21), 77 (20); HR-EIMS: *m*/*z*: calcd for $^{12}C_{15}{}^{1}H_{17}{}^{14}N^{16}O$: 309.1305; found: 227.1297; HPLC analysis (OD-H, *n*-heptane/isopropanol 80:20; 0.6 mL $min^{-1}$; 261 nm): $t_R$ (min): 25.8, 27.6.

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