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Asymmetric transfer hydrogenation of ferrocenyl ketones: a new simple route to chiral ferrocenyl alcohols

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Abstract—The asymmetric transfer hydrogenation (ATH) of ferrocenyl ketones, such as $FcC(O)CH_2Y$ [Fc = ferrocenyl, Y = H (**1a**), CH_3 (**1b**), Cl (**1c**) or N_3 (**1d**)] has been carried out using the Noyori/Ikariya catalysts [(−)-(1*R*,2*S*)-ephedrine] or *N*-tosyl-(1*R*,2*R*)-diphenylethylenediamine [(*R*,*R*)-TsDPEN] as chiral ligands combined with $[RuCl_2(\eta^6\text{-benzene})]_2$ and 2-PrOH or HCO_2H–Et_3N as the hydrogen sources, respectively. The best results were achieved with the [(*R*,*R*)-TsDPEN–$Ru^{II}HCO_2H$–Et_3N] catalytic system, which produced the ferrocenylalcohols (*R*)-**2a**, (*R*)-**2c**, and (*R*)-**2d** in good yields and excellent enantiomeric excesses (>98% ee).

1. Introduction

The ferrocenyl group has been widely explored in different areas, from polymers[1] to bioorganometallic chemistry.[2] Among several applications, the use of ferrocene-based chiral ligands in asymmetric synthesis is the most prominent.[3] A typical example is the production of the enantiomerically pure products (+)-biotin and dextromethorphan by Lonza Fine Chemicals, using ferrocenyl-type phosphine ligands developed by Ciba-Geigy, in catalytic asymmetric hydrogenations.[4] The synthesis of chiral ferrocenyl compounds frequently makes use of enantiopure 1-ferrocenyl alcohols as key intermediates,[5] and different procedures have been developed in order to obtain these compounds. Preparation methods described in the literature are either not simple or do not give satisfactory yields. Generally they use air-sensitive organometallic reagents. One method uses enantioselective reductions of prochiral ferrocenyl ketones with the Corey–Bakshi–Shibata (CBS) catalytic system to give the respective alcohols with a high yield and high ee in a few minutes.[5a,c,6] However, the chiral β-methylated oxazaborolidine catalyst is expensive and a large amount of catalyst is often required (typically 10–30 mol %). Another efficient method for the preparation of optically active alcohols is the catalytic alkylation of ferrocene carboxaldehydes with dialkylzincs in the presence of catalytic chiral aminoalcohols.[5d,7] Enantiomeric-rich ferrocene derivatives have also been obtained by resolution of the respective racemates with biocatalytic systems[5b,8] and by diastereoselective oxidation of ferrocenyl amino alcohol diastereoisomeric mixtures.[9]

Recently, we published the use of asymmetric transfer hydrogenation (ATH) to reduce and resolve some racemic arylketones–tricarbonylchromium complexes possessing planar chirality with Ru^{II}-aminoalcohol chiral catalyst in 2-PrOH as the solvent and hydrogen donor.[10] The tricarbonylchromium fragment, $Cr(CO)_3$, is an electron-withdrawing group attached to the six carbon atoms of the aryl ligand that reduces the electron density on the neighboring keto group.[11] However, the contrary effect occurs with electron-rich substrates,[12] such as ferrocenyl ketones, in this case due to the electron-rich η^5-cyclopentadienyl ligand.[13] These opposite eletronic effects and the possibility to obtain chiral 1-ferrocenyl alcohols with a simple and versatile catalytic system, motivated us to employ transfer hydrogenation for the asymmetric reduction of 1-ferrocenyl ketones.

2. Results and discussion

Ferrocenyl ketones **1a** and **1b** were synthesized from the reactions of ferrocene with the respective anhydride in the presence of phosphoric acid. Compound **1c** was synthesized from chloroacetyl chloride and ferrocene using

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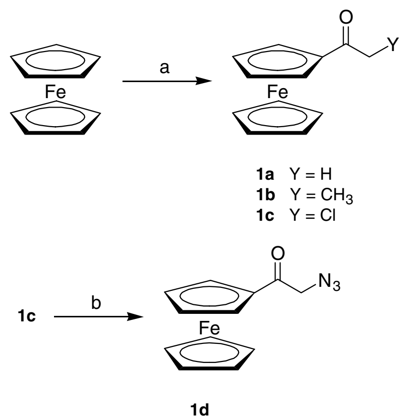
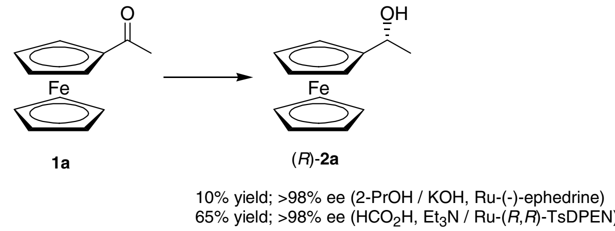
aluminum chloride[14] and it was the starting material to obtain α-azidoacetylferrocene **1d** by halogen-azido substitution (Scheme 1). Compound **1d** was isolated as orange crystals (mp 63–64 °C) and characterized by NMR and elemental analysis.



Scheme 1. Syntheses of ferrocenyl ketones **1a**–**d**. Reagents: (a) Acetic anhydride for **1a** or propionic anhydride for **1b**, H_3PO_4; (b) NaN_3, CH_2Cl_2/DMF.

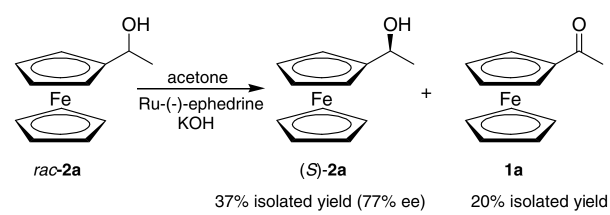
Initial experiments with ATH were carried out using either **1a** (Scheme 2) or **1b** having 2-PrOH as the hydrogen donor and the combination $[RuCl_2(\eta^6\text{-benzene})]$/(−)-(1*R*,2*S*)-ephedrine as the catalyst precursor. The conversions to their respective alcohols (*R*)-**2a** (>98% ee) and **2b** (1-ferrocenylpropanol) were relatively low at room temperature: 22% for the hydrogenation of **1a** and only 6% for **1b**. A small increment of **1b** conversion to **2b** (13%) was observed by increasing the reaction temperature to 60 °C. Alcohol **2b** was isolated, but it had decomposed somewhat. Reductions of the corresponding arylketones, acetophenone, and propiophenone, under the same reaction conditions at room temperature, resulted in high conversions (93–97%) to their respective alcohols (*R*)-1-phenylethanol (62% ee) and (*R*)-1-phenylpropanol (41% ee). The organochromium complexes (η^6-acetophenone)$Cr(CO)_3$ and (η^6-propiophenone)-$Cr(CO)_3$ also demonstrated high conversions to the respective alcohols (95% and 96%).[10] The lower conversion of the ferrocenyl ketones in comparison to the respective arylketones and arylketone–$Cr(CO)_3$ complexes can be explained by electronic effects. The $Cr(CO)_3$ fragment is an electron-withdrawing group,[15] while the cyclopentadienyl ring at the ferrocene moiety is rich in electrons,[13] reducing the positive character of the carbonyl carbon. The acetophenone and propiophenone are in an intermediate situation. In opposition to the low yield, the ee determined for (*R*)-**2a** (>98%) demonstrated a highly enantioselective process when compared with ATH of the compound (η^6-acetophenone)$Cr(CO)_3$ to (*R*)-(η^6-phenylethanol)$Cr(CO)_3$ (33% ee). The enantioselectivity of ATH catalyzed with Ru^{II}-arene complexes is attributed to the CH/π attraction between the η^6-arene–Ru and the aryl substituent in the ketone.[16] With the ferrocenyl ketones, the π electrons of the cyclopentadienyl ring are responsible for this attraction, which must be more effective than for aryl rings.



Scheme 2. Catalytic transfer hydrogenation of **1a**.

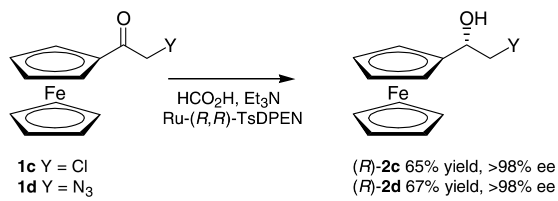
The good ee obtained for the initial reductions of ferrocenyl-ketones motivated us to keep employing the benzene derivative of the arene–Ru catalyst instead of the more commonly used *p*-cymene derivative for the asymmetric reduction of 1-ferrocenyl ketones.

However, the low conversions obtained for the reductions of **1a** and **1b** by ATH in 2-PrOH, led us to try the reverse reaction in the resolution of *rac*-**2a** (Scheme 3). The reaction procedure was practically identical to that used for ATH reductions of ferrocenyl ketones with the Ru(η^6-benzene)/(−)-ephedrine catalytic system. The only modification was the change of solvent after the generation of the pre-catalyst: 2-PrOH was evaporated and acetone was added. The reaction was carried out after the addition of the substrate and KOH solution in 2-PrOH. After 20 h, the reaction was interrupted and ^1H NMR analysis of the products mixture showed 41% of acetylferrocene and 59% of unreacted alcohol, isolated in 36% yield of (*S*)-**2a** (77% ee). A similar experiment was described with a chiral diamine–Ru^{II} catalyst: [Ru(η^6-mesitylene)(1*S*,2*S*)-TsDPEN]. 51% of unreacted (*R*)-**2a** in 98% ee was recovered after 36 h of reaction.[17]



Scheme 3. Resolution of *rac*-**2a** by catalytic transfer hydrogenation using acetone as the hydrogen acceptor.

In an attempt to increase the yields of 1-ferrocenyl alcohols (*R*)-**2a** and (*R*)-**2b** we carried out the reductions of **1a** and **1b** with formic acid/triethylamine azeotrope as the hydrogen donor. The chiral modifier used as the ruthenium catalyst was the diamine (1*R*,2*R*)-TsDPEN. The reduction of **1a** for 4 days showed a conversion of 89% to (*R*)-**2a** in 98% ee (Scheme 2). The gain in conversion was significant in comparison to ATH in 2-PrOH with the Ru^{II}-(−)-ephedrine catalytic system, representing an improvement in the yield achieved by Patti and Pedotti (35% yield, 92% ee).[18] The reduction of **1b** showed a conversion of 23% to **2b**, approximately four times the conversion observed for the reduction using 2-PrOH/Ru^{II}-(−)-ephedrine system at room temperature, but the crude product did show some decomposition before being purified.



Scheme 4. Catalytic transfer hydrogenation of **1c** and **1d** using formic acid–triethylamine azeotrope as hydrogen donor.

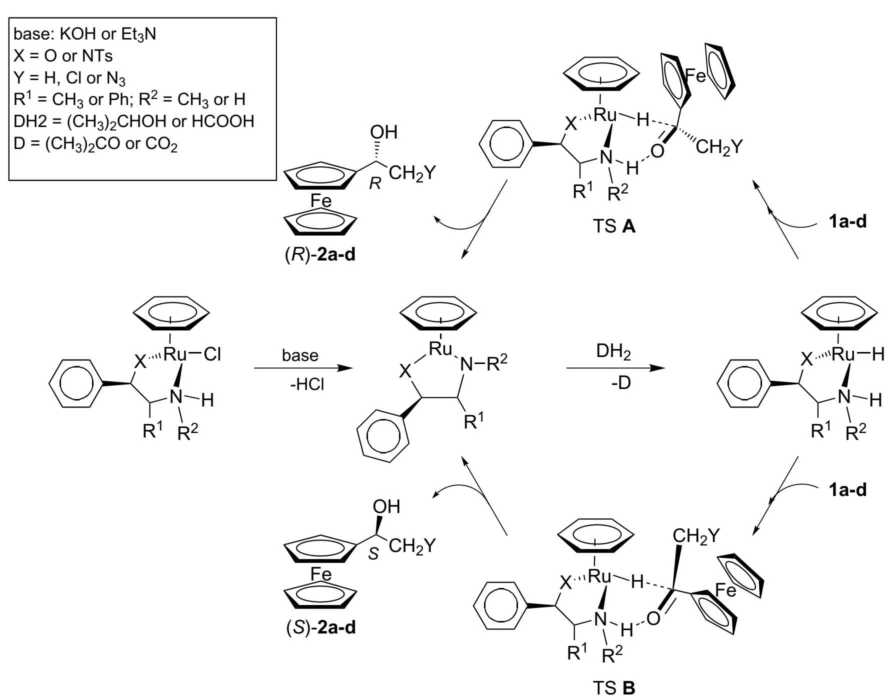
The efficiency gain using formic acid as the hydrogen donor in comparison with 2-PrOH is probably due to irreversibility of the reaction. This hydrogen donor produces carbon dioxide, which is eliminated from the reaction mixture preventing the reverse reaction. In the case of ATH using 2-PrOH as hydrogen donor, the acetone produced remains in the reaction medium and can act as a hydrogen acceptor, allowing reversibility of the reaction.[19] This effect may be responsible for the low conversion observed for the ATH of **1a** with 2-PrOH.

The α-chloro- and α-azidoacetylferrocene, **1c** and **1d**, respectively, were submitted to reduction with formic acid/triethylamine azeotrope in the presence of the Ru^{II}(benzene)-(1*R*,2*R*)-TsDPEN catalytic system. After 24 h, **1c** was completely consumed and the respective alcohol (*R*)-**2c** was isolated in a 64% yield with an excellent enantiomeric excess (>98% ee) (Scheme 4). This compound was obtained in a 92% yield with the same ee via the (*S*)-CBS catalyst (30 mol %) and $BH_3{\cdot}SMe_2$ as the hydride source.[6a] We attempted to reduce **1c** with 2-PrOH using the Ru^{II}-(−)-ephedrine system, but the conversion to **2c** was low (≈15%) and the reaction was not further explored. The azido compound **1d** was completely consumed after 4 days at room temperature and the respective alcohol (*R*)-**2d** was isolated in 67% yield with high ee (>98%) (Scheme 4). The ATH of **1d** with the 2-PrOH/Ru^{II}-(−)-ephedrine system consumed the substrate without the formation of the expected alcohol **2d**, probably due to the basic medium and side reactions at the sensitive α-halogenated center.[20] Therefore, the Ru^{II}–arene–TsDPEN complex remains as one of the best catalysts for the enantioselective reduction of a carbonyl group.[12]

Considering the ATH of **1a**, **1c**, and **1d**, producing (*R*)-**2a**, (*R*)-**2c**, and (*R*)-**2d** in good yields and excellent ee, it is possible to explain the high stereoselectivity using the mechanism for ATH proposed by Noyori[21] for metal ligand bifunctional catalysts, adapted here for our case (Scheme 5), via a concerted six-membered transition state, which is supported by computational studies.[22] The chiral auxiliaries (−)-ephedrine and (*R*,*R*)-TsDPEN probably lead to hydride intermediates with an (*S*)-configuration at the Ru atom based on NMR and X-ray diffraction studies.[23] According to Scheme 5, the resultant TS **A** must be favored in comparison to TS **B** due to the CH/π attraction between the η^6-benzene–Ru and the electron-rich cyclopentadienyl ring of the ferrocenyl ketone.[16] The TS **A** is responsible for the (*R*)-configuration for the 1-ferrocenyl alcohols produced, while TS **B** is the responsible for their (*S*)-enantiomers. These results have recently been proven by Wills et al. in their studies on the enantiocontrol of Noyori/Ikariya catalysts in the ATH of ketones.[24]

3. Conclusions

In conclusion, we have demonstrated a new possibility for the enantioselective synthesis of 1-ferrocenylethanol,



Scheme 5. Catalytic cycles for transfer hydrogenation with Ru–benzene adapted from the catalytic cycle as proposed by Noyori.[21]

2-chloro-1-ferrocenylethanol, and 2-azido-1-ferrocenylethanol from the respective ferrocenyl ketones using the simple ATH catalyzed Ru^{II}(benzene)-diamine system, with $HCO_2H–Et_3N$ as the hydrogen transfer agent. The compounds produced in a high ee (⩾98%) are important precursors of chiral ferrocene derivatives, including the ligands for asymmetric catalysis.

4. Experimental

All reagents and solvents were obtained from commercial sources. Ethyl acetate, hexanes, and chloroform were distilled under argon before use. The solvents dichloromethane and methanol were distilled under argon from suspensions over calcium hydride and calcium oxide, respectively. Hexanes and diethyl ether were distilled under argon from a mixture containing sodium. Dimethylformamide (DMF) was dried over barium oxide, filtered and distilled at reduced pressure. Thin layer chromatography (TLC) analyses were performed with precoated aluminium sheets (silica gel 60 Merck) and glass plates coated with aluminium oxide GF_{254} (type E) Merck. Flash column chromatography was carried out on silica (200–400 mesh, Merck). Preparative thin layer chromatography separations were performed with glass plates coated with aluminum oxide GF_{254} (type E) Merck.[25] ^{1}H NMR spectra were determined at 300 (Varian Gemini 300) or 500 MHz (INOVA-500), and ^{13}C NMR spectra were determined at 75.5 MHz (Varian Gemini 300) or 125.7 MHz (INOVA 500). Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) in $CDCl_3$. Optical rotations were measured with a Perkin Elmer Polarimeter 341. Melting points were measured on a Microquimica MQ APF-301. Enantiomeric excesses were measured by HPLC using Daicel ChiralCel OJ-H [cellulose tris-(4-methylbenzoate) coated on 5 μm silica-gel substrate; column size: 0.46 cm ID × 25 cm] at room temperature—flow rate: 1 mL/min, hexane:2-PrOH: 97:3, λ: 254 nm. Elemental analysis was performed on a Perkin Elmer 2400 CHN.

4.1. Synthesis of 1-ferrocenylketones

Complexes **1a** and **1b** were prepared as described in the literature.[26] Complex **1c** was synthesized as described by Fang et al.[14]

4.1.1. Preparation of α-azidoacetylferrocene 1d. α-Chlorocetylferrocene **1c** (0.300 g, 1.14 mmol) and sodium azide (0.300 g, 4.58 mmol) were suspended in CH_2Cl_2 (4 mL) at 0–5 °C. DMF (4 mL) was added in small portions and the CH_2Cl_2 was evaporated. The reaction temperature was allowed to rise to 25 °C. After 4 h, CH_2Cl_2 (10 mL) was added to the brown suspension. The mixture was washed with water (3 × 10 mL), dried with anhydrous sodium sulfate and evaporated to give a brown oil. Purification on a short column of silica using hexane:CH_2Cl_2 (2:1) as the eluent and crystallization overnight at −20 °C gave orange crystals of the desired product in 65% yield, mp 63–64 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.81 (t, $J = 2.0$ Hz, 2H, C_5H_4), 4.60 (t, $J = 1.8$ Hz, 2H, C_5H_4), 4.26 and 4.25 (s, s, 7H, C_5H_5 and CH_2). ^{13}C {^{1}H} NMR ($CDCl_3$, 125.7 MHz): δ 197.5; 75.7; 73.0; 70.1; 69.1; 55.0. The ^{1}H and ^{13}C NMR analyses were in good agreement with the literature.[5a] Anal. Calcd for $C_{12}H_{11}FeN_3$ (269.09 g mol^{-1}): C, 53.56; H, 4.12; N, 15.62. Found: C, 53.93; H, 4.56; N, 15.21.

4.2. General procedure for the ATH of the ferrocenyl ketones 1a–d using 2-PrOH as the hydrogen donor

A solution of [$RuCl_2(\eta^6$-benzene)]$_2$ (6 μmol) and (−)-(1*R*,2*S*)-ephedrine hemi-sulfate (24 μmol) in dry 2-propanol (3 mL) was heated at 80 °C for 30 min under argon. It was cooled to room temperature and transferred to a flask containing a solution of the 1-ferrocenyl ketone (0.6 mmol) and KOH (60 μmol) in 2-propanol (3 mL). The resulting mixture was then stirred under argon at room temperature (or other indicated temperature) until stabilization of conversion (aluminum oxide TLC analyses). After evaporation of volatiles under vacuum, the products were purified by flash column chromatography on silica gel and by preparative TLC on aluminum oxide.

4.2.1. ATH of acetylferrocene 1a. ^{1}H NMR analysis of the product mixture indicated 22% conversion to (*R*)-**2a**, which was isolated as a yellow solid in 10% yield: (*R*)-1-ferrocenylethanol, (*R*)-**2a**: $[\alpha]_D^{21} = -29$ (c 0.65, benzene), 98% ee. Lit.[5c] $[\alpha]_D = -31$ (c3.4, benzene), >95% ee. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.56 (dq, $J = 6.1$ Hz, $J = 4.3$ Hz, 1H, CH); 4.24–4.16 (m, 9H, C_5H_4 and C_5H_5); 1.85 (d, $J = 4.5$ Hz, 1H, OH); 1.45 (d, $J = 6.4$ Hz, 3H, CH_3).

4.2.2. ATH of propionylferrocene 1b (60 °C). ^{1}H NMR analysis of the product mixture indicated 13% conversion to **2b**.

4.2.3. ATH of α-chlorocetylferrocene 1c. ^{1}H NMR analysis of the product mixture indicated 15% conversion to **2c**.

4.3. Resolution of *rac*-2a using acetone as the hydrogen acceptor

A solution of [$RuCl_2(\eta^6$-benzene)]$_2$ (2.9 μmol) and (−)-(1*R*,2*S*)-ephedrine hemi-sulfate (11 μmol) in dry 2-propanol (3 mL) was heated at 80 °C for 30 min under argon. It was cooled to room temperature and evaporated to dryness. Acetone (2.0 mL), *rac*-1-ferrocenylethanol *rac*-**2a** (128 mg, 0.56 mmol) and a solution of KOH in 2-PrOH (65 μmol in 0.80 mL) were added. The resulting mixture was then stirred under argon at room temperature for 20 h. After evaporation of the volatiles under vacuum, the products were purified by flash column chromatography on silica gel and by preparative TLC on aluminum oxide. 48 mg (37%) of (*S*)-**2a** was isolated as a yellow solid: (*S*)-1-ferrocenylethanol, (*S*)-**2a**: $[\alpha]_D^{21} = +21$ (c 1.08, benzene), 77% ee, HPLC t_R: 18.3 min. Lit.:[5d] $[\alpha]_D = +30.3$ (c 1.04, benzene), 96.6% ee.

4.4. General procedure for the ATH of the ferrocenyl ketones 1a–d using formic acid–triethylamine azeotrope as a hydrogen donor

A mixture of $[RuCl_2(\eta^6\text{-arene})]_2$ (2.0 μmol), (1*R*,2*R*)-TsDPEN (4.5 μmol) and triethylamine (1.4 μL) in dry 2-propanol (2 mL) was heated at 80 °C for 60 min under argon. It was cooled to room temperature and evaporated under reduced pressure. To the residue were added dichloromethane (2 mL), the ferrocenyl ketone (0.4 mmol) and the formic acid–triethylamine azeotrope (0.40 mL). The mixture was stirred at room temperature (or at the indicated temperature) until stabilization of conversion (aluminum oxide TLC analyses). The volatiles were removed under reduced pressure and the residue was purified by flash column on silica and/or preparative TLC coated with aluminum oxide GF_{254}.

4.4.1. ATH of acetylferrocene 1a with formic acid. ^1H NMR analysis of the product mixture indicated 89% conversion to (*R*)-**2a**, which was isolated as a yellow solid in 65% yield: (*R*)-1-ferrocenylethanol, (*R*)-**2a**: $[\alpha]_D^{21} = -29.4$ (*c* 1.43, benzene), >98% ee, HPLC t_R: 16.4 min.

4.4.2. ATH of propionylferrocene 1b with formic acid. ^1H NMR analysis of the product mixture indicated 23% conversion to **2b**, but it had shown decomposition before being purified.

4.4.3. ATH of α-chlorocetylferrocene 1c with formic acid. ^1H NMR analysis of the product mixture indicated complete conversion to (*R*)-**2c**; which was isolated as a yellow solid in 65% yield: 2-chloro-1-ferrocenylethanol, (*R*)-**2c**: $[\alpha]_D = -18$ (*c* 0.93, benzene); >98% ee, HPLC t_R: 24.2 min. Lit.:[6c] $[\alpha]_D = -19.6$ (*c* 0.73, $CHCl_3$); >98% ee. ^1H NMR analysis was in good agreement with the literature.

4.4.4. ATH of α-azidoacetylferrocene 1d with formic acid. ^1H NMR analysis of products mixture indicated complete conversion to (*R*)-**2d**; which was isolated as a yellow solid in 67% yield: 2-azido-1-ferrocenylethanol, (*R*)-**2d**: $[\alpha]_D = -80$ (*c* 0.79, benzene). >98% ee, HPLC t_R: 27.8 min. Lit.:[5a] $[\alpha]_D = -77$ (*c* 0.73, $CHCl_3$); >98% ee. ^1H NMR analysis was in good agreement with the literature.

4.5. Preparation of the racemic ferrocenyl alcohols *rac*-2a–2d

rac-**2a** and *rac*-**2b** were synthesized by the reductions of **1a** and **1b** with lithium aluminum hydride,[27] while *rac*-**2c** and *rac*-**2d** were synthesized by the reductions of **1c** and **1d** with sodium borohydride.[28]

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