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Efficient rearrangement of epoxides catalyzed by a mixed-valent iron trifluoroacetate [$Fe_3O(O_2CCF_3)_6(H_2O)_3$]

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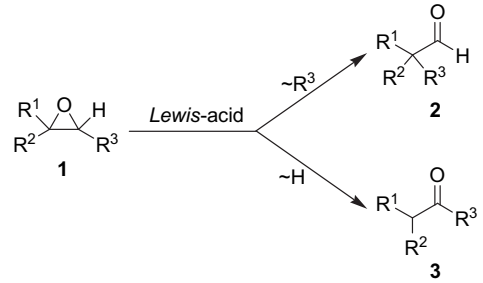
ABSTRACT

The mixed-valent oxo-centered triiron(III, III, II) trifluoroacetate complex [$Fe_2^{III}Fe^{II}O(O_2CCF_3)_6(H_2O)_3$] was prepared by reacting anhydrous iron(III) chloride with boiling trifluoroacetic acid under nitrogen. The non-hygroscopic and readily available mixed-valent triiron trifluoroacetate complex was found to be an efficient catalyst for the regioselective rearrangement of epoxides. A number of carbonyl compounds formed via the rearrangement of epoxides could be obtained by a simple filtration of the reaction mixture through a short plug of silica gel.

1. Introduction

Epoxides are one of the most important and versatile precursors in organic synthesis because they are readily available in racemic and enantiomerically enriched forms and can be converted into a variety of highly valuable products, usually in a stereoselective manner.[1] The rearrangement of epoxides (**1**) catalyzed by *Lewis*-acids affords aldehydes (**2**) via alkyl migration (~R) and/or ketones (**3**) via hydrogen migration (~H), easily and atom-economically (Scheme 1). The product distribution (aldehyde or ketone) of the rearrangement, in other words regioselectivity, is influenced by the migration aptitude of the substituents that are attached to the oxirane ring, catalyst, and solvent.



Scheme 1. *Lewis*-acid catalyzed epoxide rearrangement.

After the pioneering work on the epoxide rearrangement to carbonyl compounds from House,[2a] Filler and co-workers,[2b] Meinwald and co-workers,[2c] and Rickborn and Gerkin[2d,e] using stoichiometric amounts of *Lewis*- or *Brønsted*-acid catalysts, the development of catalytic systems for the epoxide rearrangement had been neglected for a long period of time until the 1990s. Then, a number of *Lewis*-acid catalysts and palladium(0) catalysts were identified for the rearrangement of epoxides with varying success in terms of regioselectivity and the amount of catalyst.[3–5] Indeed, although a number of methods have been developed for this rearrangement, only a few of them are regioselective and truly catalytic. In this respect, while Pd(0)/PR_3 (5 mol %),[4b,c] Bi(OTf)$_3\cdot x H_2O$ (0.1 mol %),[3k] $IrCl_3\cdot x H_2O$ (1 mol %),[3l] and Er(OTf)$_3$ (1 mol %)[3m] are noteworthy for the epoxide rearrangement via hydrogen migration, chromium(III) tetraphenylporphyrin triflate (CrTPP(OTf), 1 mol %)[4d] and chromium(III) phthalocyanine triflate (CrTBPC(OTf), 1 mol %)[4e] give the corresponding aldehydes from epoxides via alkyl migration in a stereoselective manner. The synthetic efficiency of the epoxide rearrangement has also been utilized many times in the literature.[6,1b] However, there remain drawbacks and limitations that need to be improved in the existing methods for the epoxide rearrangement, which include the use of toxic or expensive metal catalysts, high catalyst loading, narrow substrate scope, and moderate regioselectivity. Currently, the use of

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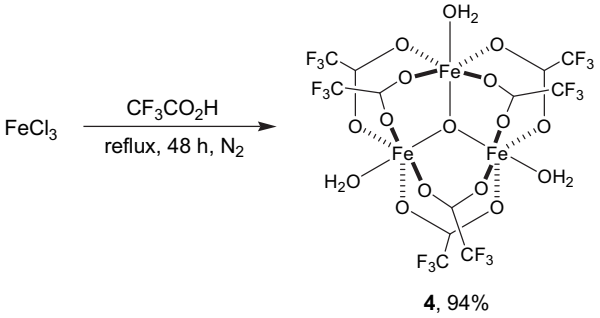
iron-based catalysts is attracting increasing attention, due to economic and environmental concerns, since iron salts and complexes are cost-effective and non-toxic compared to the other metal counterparts.[7] Because of the great abundance of iron in nature (second most abundant metal in the earth's crust, 4.7 wt %) and the environmental concerns, iron salts and iron complexes become the '*Rising Stars*' for the sustainable chemical industry.[7b] In the course of our recent investigations on the addition reactions to epoxides catalyzed by iron(III) trifluoroacetate [$Fe(O_2CCF_3)_3$],[8–10] we observed that epoxides underwent high yielding reactions to produce carbonyl products. Surprisingly, our brief literature survey revealed that only more complex iron(III) tetraphenylporphyrin complexes[3d,h,i] have been utilized as the iron based catalysts for the epoxide rearrangement so far. We would, therefore, like to report a readily available mixed-valent oxo-centered trinuclear iron trifluoroacetate complex, triiron(III, III, II) trifluoroacetate [$Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CCF_3)_6(H_2O)_3$] (**4**) that is a very efficient catalyst for the rearrangement of epoxides to carbonyl compounds.

2. Results and discussions

Triiron(III, III, II) trifluoroacetate complex **4** was easily prepared in 94% yield by reacting anhydrous iron(III) chloride with boiling trifluoroacetic acid under nitrogen (Scheme 2). The preparation of mixed-valent iron complex **4** by reacting different iron sources (e.g., metalic iron, Fe_2O_3, $Fe(NO_3)_3\cdot 9H_2O$) with trifluoroacetic acid was reported in the literature and its structure was well determined by X-ray analysis.[10,11] However, we easily prepared the iron complex **4** from readily available $FeCl_3$ and trifluoroacetic acid. The structure of **4** was elucidated by means of induced coupled plasma atomic emission spectroscopy (ICP-AES), elemental analysis (EA), and thermogravimetric analysis (TGA) and was proven to be [$Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CCF_3)_6(H_2O)_3$].[11] The existence of the iron(II) species was also empirically proven by titration against potassium dichromate. Compared to the other iron salts (e.g., $FeCl_3$), the iron trifluoroacetate complex **4** is remarkably non-hygroscopic and bench-stable for long periods (longer than 6 months during our studies) and has an enhanced *Lewis*-acid character.



Scheme 2. Preparation of triiron(III, III, II) trifluoroacetate complex [$Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CCF_3)_6(H_2O)_3$] (**4**).

Styrene oxide (**1a**) was first employed as the model substrate for the epoxide rearrangement. After the simple optimization of the rearrangement of styrene oxide (**1a**) in terms of the catalyst loading and the yield of the product, 2 mol % **4** in dichloromethane was found to be optimum. By stirring styrene oxide (**1a**) in the presence of 2 mol % **4** at room temperature for 3 h under nitrogen, phenylacetaldehyde (**2a**) was obtained in 92% yield (Table 1, entry 1). It could be speculated that trifluoroacetic acid is the actual catalyst formed by the partial hydrolysis of **4** with moisture present in the reaction mixture, if the rearrangement had not proceeded in the presence of dry K_2CO_3. Even in the presence of K_2CO_3, the rearrangement of styrene oxide (**1a**) using 2 mol % of **4** smoothly gave phenylacetaldehyde (**2a**) in the same yield indicating [$Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CCF_3)_6(H_2O)_3$] (**4**) is the *Lewis*-acid catalyst for the rearrangement of epoxides. In a similar manner to styrene oxide (**1a**), 2-(2-naphthyl)oxirane (**1b**) could be transformed into the corresponding aldehyde **2b** (2-(2-naphthyl)acetaldehyde) in 88% yield within 3 h at room temperature in the presence of 2 mol % **4** (entry 2). The rearrangement of 2,2-diphenyl oxirane (**1c**) furnished diphenylacetaldehyde (**2c**) in 82% yield (entry 3). The rearrangement of *trans*-stilbene oxide (**1d**) proceeded to give diphenylacetaldehyde (**2c**) in 86% yield under *full*-regioselectivity with exclusive aryl migration (entry 4). α-Methylstyrene oxide (**1e**) rearranged into 2-phenylpropanal (**2e**) in 78% yield (entry 5). The mixed-valent iron trifluoroacetate

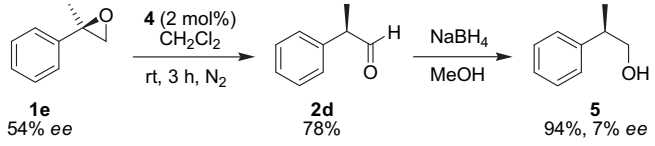
Table 1
[$Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CCF_3)_6(H_2O)_3$] (**4**) catalyzed rearrangement of epoxides[a]

Entry	Epoxide	Time (h)	Product	Yield (%)
1	**1a**	3	**2a**	92
2	**1b**	3	**2b**	88
3	**1c**	3	**2c**	82
4	**1d**	3	**2c**	86
5	**1e**	3	**2d**	78
6[b]	**1f**	1	**2d** + **2e**	74 (**2d**/**2e**=27/73)
7	**1g**	3	**2f**	88
8[b]	**1h**	1	**2g**	72
9	**1i**	1	Polymerization	
10[b]	**1j**	24	No reaction	

[a] The reactions were carried out by employing 1.0 mmol of epoxide in the presence of 2 mol % **4** in dichloromethane at room temperature under nitrogen.
[b] The reactions were carried out in 1,2-dichloroethane in an oil bath at 80 °C under nitrogen.

complex **4** could not effect the rearrangement of *trans*-β-methylstyrene oxide (**1f**) at room temperature. By heating the reaction mixture at 80 °C for 1 h in 1,2-dichloroethane, the rearrangement of *trans*-β-methylstyrene oxide (**1f**) proceeded to give 2-phenylpropanal (**2d**) and phenylacetone (**2e**) in 74% total yield and under low regioselectivity (**2d**/**2e**=27:73) in favor of phenylacetone (**2e**) via the preferential hydrogen migration (entry 6). The rearrangement of 1-phenyl-1,2-epoxycyclohexane (**1g**) led to the ring contracted product **2f** (1-phenyl-1-cyclopentane carboxaldehyde) in 88% yield via alkyl migration (entry 7). α-Pinene oxide (**1h**), as a representative for the trisubstituted aliphatic epoxides, had to be heated at 80 °C for 1 h in 1,2-dichloroethane in the presence of 2 mol % **4** to give the rearranged product **2g** (campholenic aldehyde) in 72% yield (entry 8). Cyclohexene oxide (**1i**) underwent rapid polymerization in the presence of 2 mol % **4** to give poly(-cyclohexene oxide) (entry 9). However, 1,2-epoxyhexane (**1j**) was found to be unreactive toward rearrangement in the presence of 2 mol % **4**, even by heating at 80 °C in 1,2-dichloroethane (entry 10). The purity of the products was determined by ^{1}H NMR spectroscopy. The products **2a**, **2c**, **2d**, and **2f** were isolated in satisfactory NMR purities by simple filtration of the reaction mixtures through a short plug of silica gel using ca. 100 mL dichloromethane as the eluent.

The chiral version of the epoxide rearrangement that was catalyzed by the triiron trifluoroacetate complex **4** was tested by employing enantiomerically enriched (*R*)-(−)-α-methylstyrene oxide (**1e**, 54% ee), which was prepared from α-methylstyrene by enantioselective epoxidation with a Jacobsen catalyst ((*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride). The enantiomeric excess of **1e** was determined by HPLC (Chiralpak OD; *n*-hexane/^{i}PrOH (99:1); 0.5 mL/min; t_R=12.3 min (*ent*-**1e**), t_R=13.5 (**1e**)). The primary product of the rearrangement (2-phenylpropanal, **2d**) was then transformed into the corresponding alcohol **5** by sodium borohydride reduction since a better enantiomeric separation for **5** and *ent*-**5** could be performed by HPLC. However, the enantiopurity of **1e** was predominantly lost after the rearrangement and the subsequent sodium borohydride reduction (**5**, 7% ee, Scheme 3). During the rearrangement of **1e**, we are expecting the preferential migration of the hydride *syn* to the less hindered site of the epoxide ring (Me vs Ph) resulting in the selective formation of **2d** accompanied by the partial inversion of the starting epoxide **1e**. The favored migration of hydride *syn* to the less hindered site of the epoxide ring has been already observed in the MABR catalyzed rearrangement of α,α-disubstituted epoxides by Yamamoto et al.[12]



Scheme 3. Rearrangement of chiral α-methylstyrene oxide (**1e**).

3. Conclusions

In conclusion, we have shown that 2 mol % of the readily available mixed-valent iron trifluoroacetate complex **4** [$Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CCF_3)_6(H_2O)_3$] can catalyze the regioselective rearrangement of a wide variety epoxides to carbonyl compounds. In general, the products were able to be isolated in high yields by the simple filtration of the reaction mixtures through a short plug of silica gel. The non-toxicity, ready availability of the iron trifluoroacetate complex **4** along with the great abundance of iron in nature make this catalytic system rather attractive for large scale applications.

4. Experimental

4.1. General

All reactions were carried out in oven-dried Schlenk tubes with magnetic stirring under a positive pressure of nitrogen. Dichloromethane and 1,2-dichloroethane were freshly distilled from calcium hydride prior to use under a nitrogen atmosphere. Epoxides **1a**, **1h**, **1i**, **1j**, anhydrous iron(III) chloride, and trifluoroacetic acid were purchased from Aldrich and used as received. Epoxides **1b**, **1d**, **1f**, **1g** were prepared by the epoxidation of the corresponding olefins with *m*-chloroperbenzoic acid.[13] Epoxides **1c** and **1e** were synthesized by the Corey–Chaykovsky epoxidation of corresponding ketones with trimethylsulfoxonium iodide. Thin layer chromatography (TLC) was conducted on aluminum sheets that were pre-coated with silica gel *SIL G/UV$_{254}$* from MN GmbH & Co., in which the spots were visualized in UV-light (λ=254 nm) and/or by staining with phosphomolybdic acid. Chromatographic separations were performed using silica gel (MN-silicagel 60, 230–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX400 NMR spectrometer. Chemical shifts δ are reported in parts per million (ppm) relative to the residual protons in the NMR solvent ($CHCl_3$: δ 7.24) and carbon resonance of the solvent ($CDCl_3$: δ 77.0). NMR peak multiplicities were given as follows: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. Elemental analyses (EA) were performed using a ThermoFinnigan FLASH 1112 SERIES EA instrument. ICP-AES was recorded on a Thermo Jarrel Ash AtomScan 25 instrument.

*4.1.1. Preparation of the iron trifluoroacetate complex [$Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CCF_3)_6(H_2O)_3$] (**4**).* Anhydrous iron(III) chloride (1.62 g, 10.0 mmol) and 16 mL of trifluoroacetic acid were added into a 100 mL one-necked round bottomed flask. The mixture was then refluxed under a nitrogen atmosphere for 48 h. After the removal of the excessive trifluoroacetic acid by rotary evaporation under reduced pressure, the residue was filtered off using a sintered glass funnel and washed with a plenty of *n*-hexane. The light orange solid was dried under vacuum (approx. 10^{-3} mbar) at 80 °C for 12 h. The iron trifluoroacetate complex **4** was obtained as a light orange powder (2.87 g, 3.13 mmol, 94%). Mp: 151–173 °C (decomposition). EA: Anal. Calcd for $C_{12}H_6F_{18}Fe_3O_{16}$: C, 15.74; H, 0.66. Found: C, 16.12; H, 0.95. ICP-AES: Anal. Calcd for $C_{12}H_6F_{18}Fe_3O_{16}$: Fe, 18.30. Found: Fe, 18.20.

*4.1.2. Phenylacetaldehyde[3o] (**2a**, typical procedure for the rearrangement of the epoxides).* The iron trifluoroacetae complex **4** (18 mg, 20 μmol, 2 mol %) was placed in an oven-dried Schlenk tube and then the tube was capped with a glass stopper. The tube was evacuated for 15 min and back-filled with nitrogen. The glass stopper was replaced with a rubber septum under positive pressure of nitrogen. After addition of dry dichloromethane (5 mL) as the solvent, styrene oxide (**1a**, 120 mg, 1.0 mmol) was dropwise added to the suspension at room temperature. Upon addition of the epoxide, a homogenous solution formed instantaneously. The reaction progress was monitored by TLC. After completion of the reaction (room temperature, 3 h), the reaction mixture was filtered through a short plug of silica gel using dichloromethane (100 mL) as the eluent. After removing the solvent by rotary evaporation under reduced pressure, phenylacetaldehyde (**2a**, 110 mg, 0.92 mmol, 92%) was obtained as a colorless oil. R_f=0.23 (silica gel, *n*-hexane/EtOAc 10:0.4). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.61 (d, $^3J_{H-H}$=2.0 Hz, 2H, CH_2), 7.14–7.16 (m, 2H, H_{aryl}), 7.24–7.32 (m, 3H, H_{aryl}), 9.67 (t, $^3J_{H-H}$=2.0 Hz, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ=50.5, 127.3, 128.9, 129.5, 131.8, 199.2.

*4.1.3. 2-(2-Naphthyl)acetaldehyde[3c] (**2b**).* After stirring 2-(2-naphthyl)oxirane (**1b**, 170 mg, 1.0 mmol) in the presence of 2 mol % **4** in dichloromethane (5 mL) at room temperature for 3 h under

nitrogen, the rearranged product **2b** was obtained as a colorless oil (150 mg, 0.88 mmol, 88%) via column chromatographic purification. R_f=0.21 (silica gel, *n*-hexane/EtOAc 10:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.69 (d, $^3J_{H-H}$=2.4 Hz, 2H, CH_2), 7.18 (dd, $^3J_{H-H}$=8.4 Hz, $^4J_{H-H}$=1.6 Hz, 1H, H_{aryl}), 7.35–7.38 (m, 2H, H_{aryl}), 7.54 (s, 1H, H_{aryl}), 7.67–7.73 (m, 3H, H_{aryl}), 9.67 (t, $^3J_{H-H}$=2.4 Hz, 1H, C*H*O). ^{13}C NMR (100 MHz, $CDCl_3$): δ=50.6, 126.0, 126.4, 127.4, 127.5, 127.7, 128.4, 128.7, 129.4, 132.5, 133.5, 199.2.

4.1.4. Diphenylacetaldehyde[3c] (***2c***). After stirring 2,2-diphenyl oxirane (**1c**, 196 mg, 1.0 mmol) in the presence of 2 mol % **4** in dichloromethane (5 mL) at room temperature for 3 h under nitrogen, the rearranged product **2c** was obtained as a colorless oil (161 mg, 0.82 mmol, 82%) via simple filtration through a short plug of silica gel using dichloromethane (100 mL) as the eluent. R_f=0.20 (silica gel, *n*-hexane/EtOAc 10:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.81 (d, $^3J_{H-H}$=2.4 Hz, 1H, C*H*), 7.14–7.32 (m, 10H, H_{aryl}), 9.87 (d, $^3J_{H-H}$=2.4 Hz, 1H, C*H*O).

4.1.5. 2-Phenylpropanal[3n] (***2d***). After stirring α-methylstyrene oxide (**1e**, 134 mg, 1.0 mmol) in the presence of 2 mol % **4** in dichloromethane (5 mL) at room temperature for 3 h under nitrogen, the rearranged product **2d** was obtained as a colorless oil (105 mg, 0.78 mmol, 78%) via simple filtration through a short plug of silica gel using dichloromethane (100 mL) as the eluent. R_f=0.32 (silica gel, *n*-hexane/EtOAc 10:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.37 (d, $^3J_{H-H}$=4.0 Hz, 3H, CH_3), 3.54 (dq, $^3J_{H-H}$=1.2 Hz, $^3J_{H-H}$=7.6 Hz, 1H, C*H*), 7.06–7.31 (m, 5H, H_{aryl}), 9.60 (d, $^3J_{H-H}$=1.4 Hz, 1H, C*H*O).

4.1.6. 2-Phenylpropanal[3n] (***2d***) *and phenylacetone*[14] (***2e***). After stirring *trans*-β-methylstyrene oxide (**1f**, 134 mg, 1.0 mmol) in the presence of 2 mol % **4** in 1,2-dichloroethane (5 mL) in an oil bath at 80 °C for 1 h under nitrogen, 2-phenylpropanal (**2d**) and phenylacetone (**2e**) were obtained in 74% total yield (99 mg, 0.74 mmol) via simple filtration through a short plug of silica gel using dichloromethane (100 mL) as the eluent. The regioisomeric ratio was found to be **2d**/**2e**=27:73 by means of ^{1}H NMR. Compound **2e**: R_f=0.20 (silica gel, *n*-hexane/EtOAc 10:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.08 (s, 3H, CH_3), 3.63 (s, 2H, CH_2), 7.13–7.31 (m, 5H, H_{aryl}).

4.1.7. 1-Phenyl-1-cyclopentane carboxaldehyde[4d] (***2f***). After stirring 1-phenyl-1,2-epoxycyclohexane (**1g**, 174 mg, 1.0 mmol) in the presence of 2 mol % **4** in dichloromethane (5 mL) at room temperature for 3 h under nitrogen, the ring-contracted product **2f** was isolated as a colorless oil (153 mg, 0.88 mmol, 88%) via simple filtration through a short plug of silica gel using dichloromethane (100 mL) as the eluent. R_f=0.46 (silica gel, *n*-hexane/EtOAc 10:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.54–1.60 (m, 2H), 1.64–1.68 (m, 2H), 1.76–1.83 (m, 2H), 2.41–2.47 (m, 2H), 7.15–7.19 (m, 3H, H_{aryl}), 7.24–7.28 (m, 2H, H_{aryl}), 9.31 (s, 1H, C*H*O). ^{13}C NMR (100 MHz, $CDCl_3$): δ=24.2, 32.3, 63.6, 127.1, 127.6, 128.7, 140.3, 200.6.

4.1.8. Campholenic aldehyde[15] (***2g***). After stirring α-pinene oxide (**1g**, 152 mg, 1.0 mmol) in the presence of 2 mol % **4** in 1,2-dichloroethane (5 mL) in an oil bath at 80 °C for 1 h under nitrogen, campholenic aldehyde (2 g) was obtained as a colorless oil (109 mg, 0.72 mmol, 72%) via column chromatographic purification. R_f=0.37 (silica gel, *n*-hexane/EtOAc 10:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.79 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.61–1.62 (m, 3H, CH_3), 1.85–1.93 (m, 1H), 2.25–2.31 (m, 1H), 2.34–2.42 (m, 2H), 2.52 (ddd, $^3J_{H-H}$=2.0 Hz, $^3J_{H-H}$=4.4 Hz, $^3J_{H-H}$=15.6 Hz, 1H), 5.23 (m, 1H), 9.80 (t, $^3J_{H-H}$=2.4 Hz, 1H, C*H*O). ^{13}C NMR (100 MHz, $CDCl_3$): δ=12.5, 20.0, 25.6, 35.5, 44.2, 45.0, 46.9, 121.5, 147.9, 202.8.

4.1.9. 2-Phenyl-1-propanol[16] (***5***). 2-Phenylpropanal (**2d**) prepared by the rearrangement of enantiomerically enriched (*R*)-(−)-α-methylstyene oxide (**1e**, 54% ee) in the presence of 2 mol % **4** was reduced to 2-phenyl-1-propanol (**5**) with sodium borohydride in methanol. The alcohol product **5** (94%) was purified by flash chromatography. R_f=0.42 (silica gel, *n*-hexane/EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.28 (d, $^3J_{H-H}$=8.0 Hz, 3H, CH_3), 2.94 (q, $^3J_{H-H}$=8.0 Hz, 1H, C*H*), 3.69 (d, $^3J_{H-H}$=8.0 Hz, 2H,CH_2OH), 7.22–7.25 (m, 3H, H_{aryl}), 7.30–7.34 (m, 2H, H_{aryl}). HPLC: Chiralpak AD-H; *n*-hexane/^{i}PrOH (99.5:0.5); 1 mL/min; t_R=86.5 min (**5**), t_R=107.8 min (*ent*-**5**).

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