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Chiral octahedral complexes of Co(III) as catalysts for asymmetric epoxidation of chalcones under phase transfer conditions.

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Stereochemically inert and positively charged chiral complexes of Co(III) were shown to catalyze the asymmetric epoxidation of chalcones with H_2O_2 under phase transfer conditions. The reaction products had enantiomeric purities of up to 55%. It was also shown that complex **1a** I^- catalyzed the coupling reaction of a resulting epoxide with CO_2 (conversion 72%).

Introduction

Enantiomerically enriched *α*,*β*-epoxy ketones are versatile chiral building blocks for access to natural compounds and drugs in medicinal chemistry.[1,2] They can be converted into many types of useful chiral compounds, such as *α*-hydroxy, *β*-hydroxy, *α*,*β*-dihydroxy carbonyl compounds, as well as epoxy alcohols.[3]
The basic method of producing the enantiomerically enriched epoxy ketones is the asymmetric oxidation of activated olefins.[4] By far the most attractive method for the preparation of epoxy ketones is asymmetric epoxidation of chalcones.[5]

A green and most cost effective approach is to use hydrogen peroxide as the oxidizing agent,[4e] because the only by-products of the reaction ~~is~~ are water and molecular oxygen. The catalytic protocols usually employ either chiral metal complexes of iron[6] and manganese[7] or chiral organocatalysts, in particular, those operating under phase transfer conditions.[8]

Recently we successfully elaborated chiral, positively charged, stereochemically inert complexes of Co(III) as chiral phase transfer catalysts for efficient asymmetric alkylation of a glycine Schiff base ester (O'Donnell substrate) with alkyl halides.[9a] In addition, the family of the complexes could be successfully applied for the asymmetric 1,4-addition of O'Donnell's substrate to activated olefins.[9b] The convincing evidence was put forward proving the complexes functioned in the reactions as "organic catalysts in disguise".[10] We believed further attempts at employing the catalysts in classical asymmetric reactions of C-C formation could be of interest.

Herein we describe the use of octahedral stereochemically inert and positively charged "chiral-at-metal" Co(III) complexes[9] (depicted on Fig. 1) of both Λ– and Δ-configurations. The complexes were used as catalysts for the asymmetric epoxidation of chalcones under phase-transfer conditions and some preliminary results on the CO_2 coupling with the forming epoxides, promoted by the same complexes.

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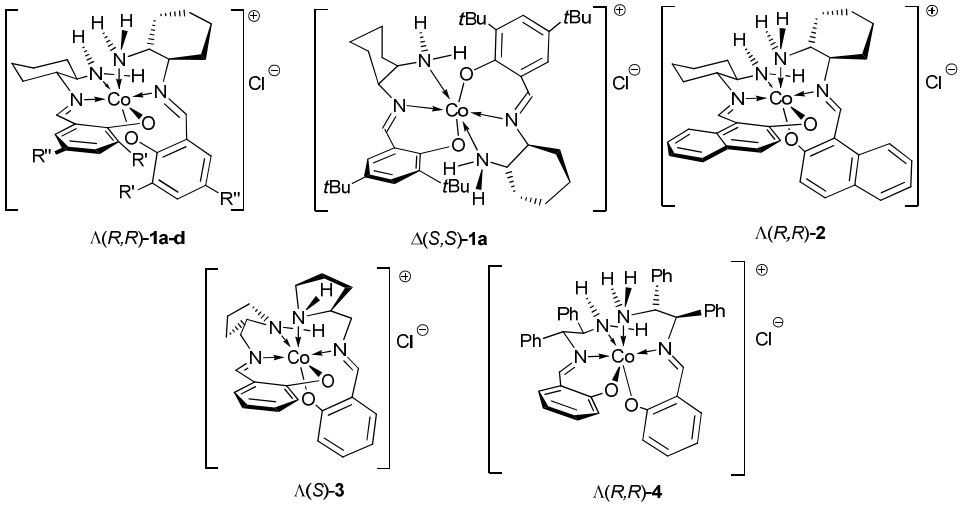
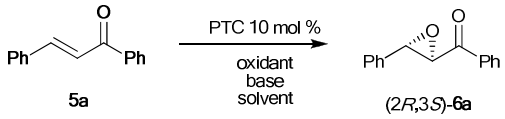


Fig. 1. The structures of catalysts **1–4** (a: R'=R"=*t*Bu; b: R'=*t*Bu, R"=H; c: R'=Ph, R"=H; d: R'=R"=H).

Results and discussion

The complexes **1-4** were prepared as described earlier.[9a] As the first substrate/catalyst couple to test the feasibility of the epoxidation reaction an unsubstituted trans-chalcone **5a** and Λ(*R*,*R*)-**1a** were chosen (Scheme 1). Initially, a 30% aqueous solution of hydrogen peroxide, as the oxidizing agent for this reaction, was selected. The first experiments conducted in ~~CH_2Cl_2~~-methyl *tert*-butyl ether (MTBE) and KOH as a base indicated the reaction was, indeed, successfully catalyzed by the Co(III) complex, furnishing enantiomerically enriched **6a** in a yield of ~~65~~81% and *ee* of ~~38~~50% (Table 1, entry 1). The absolute configuration (2*R*,3*S*) of the stereogenic centers in **6a** was assigned by the comparison with the literature data (optical rotation).[11] As expected, no reaction was observed without the base added (Table 1, entry 2), indicating HOO^- being the nucleophilic particle, attacking the chalcone substrate.[8]



Scheme 1. Asymmetric epoxidation of a chalcone **5a** under phase-transfer conditions promoted by the positively charged chiral complex Λ(*R*,*R*)-**1a**.

KOH as a base and 30% aq. H_2O_2 in different solvents, were then screened in the reaction (Table 1, entries 1-8). In each experiment formation of any side products wasn't observed and the conversion of the initial **5a** was equal to the chemical yield of the epoxide **6a**.

~~Methyl *tert*-butyl ether (~~MTBE~~)~~ was the solvent of choice (Table 1, entry 1~~) as **6a** was obtained in the solvent in a good yield (81%) and a reasonable enantiomeric purity (*ee* 50%)~~. The next good solvent was CH_2Cl_2 which gave sizable chemical yield (65%) and reasonable enantioselectivity (*ee* 38%) (Table 1, entry 3). Expectedly, MeCN was a too polar reaction media with low chemical yields (10%) and enantioselectivity (21%) (Table 1, entry 4). In 1,4-dioxane the enantioselectivity of the reaction was better (*ee* 54%), but the conversion was low (38%) (Table 1,

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entry 6). The conversion was good in none polar hexane (67%), but the enantioselectivity of the reaction was low (8%) with the opposite enantiomer formed in excess (Table 1, entry 7). Both THF and *tert*-butyl alcohol (Table 1, entries 8, 9) were bad solvents with no product formed in the reaction medias.

Table 1. Epoxidation of chalcone **5a** catalyzed by cationic complex Λ(*R*,*R*)-**1a**[a]

Entry	Solvent	Base	Oxidant	Conversion, %[b]	*ee*, %[c]
1	MTBE	KOH	30% aq. H_2O_2	81	50
2	MTBE	-	30% aq. H_2O_2	-	-
3	CH_2Cl_2	KOH	30% aq. H_2O_2	65	38
4	MeCN	KOH	30% aq. H_2O_2	10	21
5	toluene	KOH	30% aq. H_2O_2	32	48
6	1,4-dioxane	KOH	30% aq. H_2O_2	38	54
7	hexane	KOH	30% aq. H_2O_2	67	-8[d]
8	THF	KOH	30% aq. H_2O_2	traces	n.d.
9	^{t}BuOH	KOH	30% aq. H_2O_2	traces	n.d.
10	MTBE	KOH	oxone[e]	traces	n.d.
11	MTBE	KOH	3-chloroperbenzoic acid[e]	traces	n.d.
12	MTBE	KOH	^{t}BuOOH[e]	100	8
13	MTBE	KOH	CumOOH[e,f]	100	0
14	MTBE	NaOH	30% aq. H_2O_2	50	49
15	MTBE	CsOH×H_2O	30% aq. H_2O_2	73	55
16	MTBE	K_3PO_4	30% aq. H_2O_2	15	47
17	MTBE	Cs_2CO_3	30% aq. H_2O_2	18	48
18	MTBE	CsF	30% aq. H_2O_2	5	50
19	MTBE	^{t}BuOK	30% aq. H_2O_2	85	55
20[g]	MTBE+ ^{t}BuOH	KOH	30% aq. H_2O_2	79	42
21	MTBE	^{t}BuOK	$(NH_2)_2CO$×H_2O_2[h]	50	52

[a] Reaction conditions: 0.13 mmol chalcone **5a**, 0.013 mmol Λ(*R*,*R*)-**1a**, 1mL solvent, 1 eq. base (0.13 mmol) and 5 eq. 30% aq. of H_2O_2 (0.65 mmol) for 48 h at room temperature.

[b] Conversion determined by NMR.

[c] Enantiomeric purity was established by chiral HPLC (The absolute configuration of the stereogenic centers were (2*R*,3*S*)).

[d] The absolute configuration of the stereogenic centers were (2*S*,3*R*).

[e] 3 eq.

[f] CumOOH = cumene hydroperoxide.

[g] The ratio of ^{t}BuOH/KOH was 1:1.

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[h] 2 eq.

The nature of the oxidant was very important, affecting both the yield and the enantioselectivity of the reaction. For example, oxone or 3-chloroperbenzoic acid were not efficient oxidants (Table 1, entries 10, 11), whereas both *tert*-butyl hydroperoxide and cumene hydroperoxide gave the reaction product in good chemical yields but with very low enantioselectivity (*ee*s 8% and 0% correspondingly) (Table 1, entries 12, 13). Thus, the optimum oxidizer was found to be hydrogen peroxide.

As could be expected, the nature of the base affected the chemical yield of the reaction and had little if any influence on its enantioselectivity (Table 1, entries 14-19). The best result (conversion 85% and *ee* 55%, Table 1, entry 19) was obtained using potassium *tert*-butylate. Surprisingly, the mixture of *tert*-butyl alcohol and KOH, which should have been formed in the experiment, gave worse chemical yield and *ee* (Table 1, entry 20). An attempt at using the complex of urea with hydrogen peroxide to avoid water involvement in the oxidation led to a decreased chemical yield without any significant changes in the reaction stereoselectivity (Table 1, compare entries 19 and ~~19~~21).

After optimizing the reaction conditions, other catalysts were tested in the same reaction under the optimum settings (Table 2).

Table 2. Catalyst screening[a]

Entry	Catalyst	Conversion, %[b]	*ee*, %[c]
1	Λ(*R*,*R*)-**1a**	50-85[d]	55
2	Λ(*R*,*R*)-**1a**[e]	31	52
3	Δ(*S*,*S*)-**1a**	84	-55[f]
4	Λ(*R*,*R*)-**1b**	61	55
5	Λ(*R*,*R*)-**1c**	63	46
6	Λ(*R*,*R*)-**1d**	58	50
7	Λ(*R*,*R*)-**2**	94	45
8	Λ(*S*)-**3**	16	10
9	Λ(*R*,*R*)-**4**	100	9
10[g]	Λ(*R*,*R*)-**1a**	84	43
11[h]	Δ(*S*,*S*)-**1a**	54	-49[f]

[a] Reaction conditions: 0.13 mmol chalcone **5a**, 0.013 mmol catalyst, 1mL MTBE, 1 eq. ^{t}BuOK (0.13 mmol) and 5 eq. 30% aq. H_2O_2 (0.65 mmol) for 4 h at room temperature.

[b] Conversion determined by NMR.

[c] Enantiomeric purity was established by chiral HPLC analysis of the product (The absolute configuration of the stereogenic centers were (2*R*,3*S*)).

[d] When playing the experiment conversion varied in the range of 50-85 %.

[e] The counteranion of Λ(*R*,*R*)-**1a** was I^-.

[f] The absolute configuration of the stereogenic centers were (2*S*,3*R*).

[g] Conducted at 0°C.

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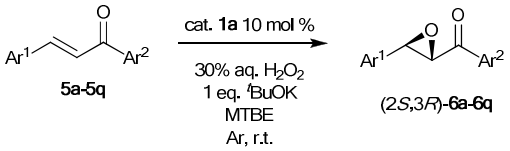
[h] The recovered catalyst Δ(*S*,*S*)-**1a** was used.

The exchange of the counteranion in **1a** (chlorine by iodide) did not change the enantioselectivity of the reaction but decreased the conversion of the chalcone to 31% (Table 2, compare entries 1 and 2). Changing the structure of the salicylic moiety of the catalysts had almost no influence on the enantioselectivity of the reaction, and only affected the yields of the product (Table 2, entries 1, 4-7). But in the case of catalysts based on (*S*)-aminomethylpirrolidine and (*R*,*R*)-diphenylethylenediamine the enantioselectivity of the reaction dramatically decreased (Table 2, entries 8, 9). Catalyst **1a** having Λ(*R*,*R*)-configuration furnished the product of (2*R*,3*S*)-configuration whereas **1a** with Δ(*S*,*S*)-configuration afforded the (2*S*,3*R*)-enantiomer (Table 2, entries 1 and 3). It was also shown that lowering the reaction temperature negatively affected the enantioselectivity of the reaction. Thus at 0°C *ee* of the product was 43% at a conversion of 84% (Table 2, compare entries 1 and 10). The catalyst 1a could be regenerated and reused. The results were slightly worse than the initial runs (conversion 54%, *ee* 49%) (Table 2, compare entries 3 and 11).

We next investigated the scope of the epoxidation of different chalcone derivatives promoted with catalyst Δ(*S*,*S*)-**1a**. The data is summarized in Table 3.

Table 3. Chalcone substrate scope of epoxidation catalyzed by cationic complex of Co(III) Δ(*S*,*S*)-**1a**[a]



Entry	Substrate	Ar^1	Ar^2	Conversion, %[b]	*ee*, %[c]
1	**5a**	Ph	Ph	85	55
2	**5b**	4-$NO_2C_6H_4$	Ph	98	48
3	**5c**	4-ClC_6H_4	Ph	85	49
4	**5d**	2-ClC_6H_4	Ph	50	50
5	**5e**	4-FC_6H_4	Ph	89	50
6	**5f**	3-FC_6H_4	Ph	100	49
7	**5g**	2-FC_6H_4	Ph	96	44
8	**5h**	4-MeC_6H_4	Ph	78	47
9	**5i**	4-$MeOC_6H_4$	Ph	62	48
10	**5j**	3-$PhOC_6H_4$	Ph	90	42
11	**5k**	1-naphthalenyl	Ph	96	35
12	**5l**	2-naphthalenyl	Ph	47	48
13	**5m**	9-anthracenyl	Ph	99	52 (98)[d]
14	**5n**	2-pyridinyl	Ph	100	8
15	**5o**	2-furanyl	Ph	50	n.d.
16	**5p**	Ph	2-pyridinyl	100	42
17	**5q**	Ph	C_6F_5	traces	-

[a] Reaction conditions: 0.13 mmol chalcone, 10 mg (0.013 mmol) catalyst, 1mL MTBE, 1 eq. ^{t}BuOK (0.13 mmol) and 5 eq. 30% aq. H_2O_2 (0.65 mmol) for 4 h at room temperature.

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[b] Conversion determined by NMR.

[c] Enantiomeric purity was established by chiral HPLC analysis of the product (The absolute configuration of the stereogenic centers were (2*S*,3*R*)).

[d] Enantiomeric purity after recrystallization.

Basically, the nature of the substituents on the phenyl ring of **5** only affected the conversion of the chalcones, whereas the enantiomeric purity of the products was mostly insignificantly influenced (the range of *ee* lied mostly within the range of 42-55%, Table3, entries 1-10). The cases of chalcone derivatives **5k** and **5n** were an exception as the enantiomeric purity of epoxide **6k** was low (35%) and that of **6n** was only 8%. In case of perfluorinated chalcone **5q** only trace amounts of **6q** were detected in the reaction mixture.

The enantiomeric purities of the epoxides could be further increased. For example, the enantiomeric purity of **6m** was amplified to 98% after its recrystallization and its absolute configuration (2*S*,3*R*)-**6m** was established by a single crystal X-ray structure analysis (Fig. 2) and found to be similarly to that of other epoxides.

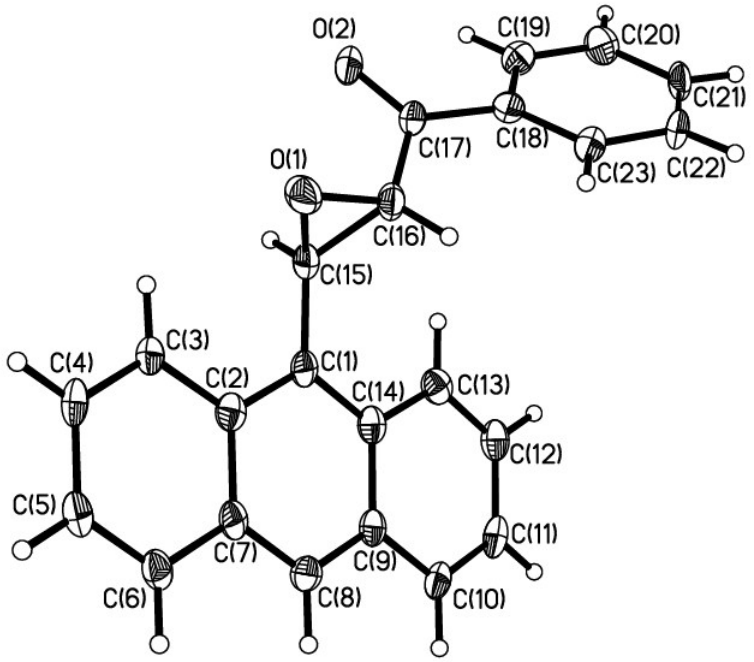
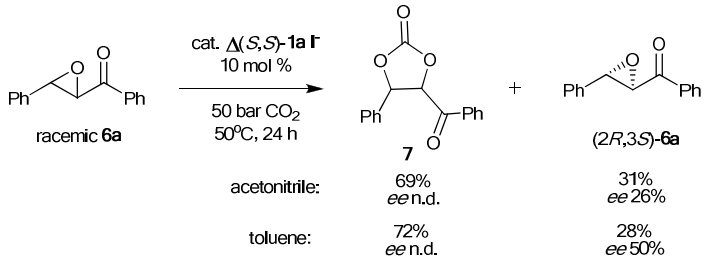


Fig. 2. ORTEP drawing of the X-ray structure of **6m** with thermal ellipsoids at the 50% probability level.

The catalyst **1a** could also catalyze the coupling of racemic epoxide **6a** with CO_2 (Scheme 2).



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Scheme 2. Synthesis of organic carbonate **7** promoted by a chiral complex of Co(III) Δ(*S*,*S*)-**1a** I^-.

Using the catalyst Δ(*S*,*S*)-**1a** with chlorine counteranion we observed only the formation of the polyether and not the cyclic carbonate **7**. The use of Δ(*S*,*S*)-**1a** with a more nucleophilic iodide counteranion was successful as the conversion of the chalcone **6a** to the corresponding cyclic carbonate **7** was 69%. The remaining epoxide was partially enantiomerically enriched (*ee* of (2*R*,3*S*)-enantiomer 26% in acetonitrile and 50% in toluene). The hydrolysis of the carbonate would lead to the corresponding chiral diols.[12] To the best of our knowledge, it was the first example of the preparation of the cyclic carbonate **7** using such approach.

Experimental

General

Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 and Bruker Avance III-400 (operating at 300/75 for ^{1}H, ^{13}C and 400/100/282 MHz for ^{1}H, ^{13}C and ^{19}F NMR respectively) NMR spectrometers. Chemical shifts (on the δ scale) are reported in ppm relative to the residual solvent peak ($CHCl_3$: δ = 7.26 ppm for ^{1}H NMR, δ = 77.16 for ^{13}C NMR) and relative to $CFCl_3$ (δ = 0.0 ppm for ^{19}F NMR). NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t= triplet, m = multiplet), coupling constant, integration, nucleus. Melting points were taken using Electrothermal MELTING POINT APPARATUS (England). Optical rotations were measured on a Perkin–Elmer 341 polarimeter in a thermostated at 25°C 5-cm cell. Enantiomeric excesses were determined by HPLC analysis using a Shimadzu LC-10 ADVP equipped with a Shimadzu SPD-M10AVP diode array detector, eluent and chiral column are indicated to any determination, flow rate: 1 mL/min. Racemic products for reference purposes were synthesized using achiral catalysts (quaternary ammonia salts). X-ray crystallography diffraction data was collected on a Bruker SMART APEX II diffractometer, λ(CuKα) = 1.54190 Å, ω-scan technique, T = 120(2) K. Commercial reagents were used as received unless stated otherwise. Column chromatography was performed using Silica Gel Kieselgel 60 (Merck).

General procedure for the preparation of *α,β*-unsaturated ketones

Corresponding substituted benzaldehyde (4.2 mmol) was dissolved in methanol (10 mL) and the resulting solution was cooled down to 0 °C. Then aqueous NaOH solution (10% wt., 2.2 mL) was added dropwise, followed by slow addition of the corresponding ketone (4.2 mmol). The reaction mixture was stirred allowing to slowly warm up to room temperature (2-24 h). After the addition was complete the product precipitated as a powder. The pure chalcone derivatives were filtered and the solid recrystallized from ethanol in high yields.[13a] Most products obtained were known compounds.

(*E*)-chalcone 5a. Yellow powder; mp 56–58 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J*=7.1 Hz, 2H), 7.75 (d, *J*=15.7 Hz, 1H), 7.59-7.56 (m, 2H), 7.53-7.41 (m, 4H), 7.37-7.34 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6 (C=O), 144.9 (-CH=), 138.2, 134.9, 132.8, 130.5, 129.0, 128.9, 128.6, 128.4, 122.1 (-CH=).

(*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one 5b. Yellow powder; mp 152–154 °C (lit.[13a] 158–159 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J*=8.5 Hz, 2H), 8.04 (d, *J*=8.2 Hz, 2H), 7.86-7.76 (m, 3H), 7.68-7.60 (m, 2H), 7.54 (t, *J*=7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7 (C=O), 148.5, 141.5 (-CH=), 141.0, 137.5, 133.4, 129.0, 128.8, 128.6, 125.7, 124.2 (-CH=).

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(*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one 5c. White flaky solid; mp 105–107 °C (lit.[13b] 105–107 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J*=7.5 Hz, 2H), 7.76 (d, *J*=15.7 Hz, 1H), 7.65–7.47 (m, 6H), 7.41-7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2 (C=O), 143.3 (-CH=), 138.0, 136.4, 133.4, 132.9, 129.6, 129.3, 128.7, 128.5, 122.5 (-CH=).

(*E*)-3-(2-chlorophenyl)-1-phenylprop-2-en-1-one 5d. White flaky solid; mp 47–49 °C (lit.[13c] 48 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J*=15.8 Hz, 1H), 8.06–7.99 (m, 2H), 7.78-7.72 (m, 1H), 7.63-7.56 (m, 1H), 7.55–7.41 (m, 4H), 7.37–7.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5 (C=O), 140.7 (-CH=), 138.0, 135.5, 133.3, 133.0, 131.2, 130.3, 128.7, 128.6, 127.8, 127.1, 124.9 (-CH=).

(*E*)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one 5e. White flaky powder; mp 79–81 °C (lit.[13b] 75–78 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.98 (m, 2H), 7.78 (d, *J*=15.7 Hz, 1H), 7.68–7.56 (m, 3H), 7.55–7.43 (m, 3H), 7.12 (t, *J*=8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3 (C=O), ~~165.5, 162.8~~ 164.2 (d, $^{1}J_{C\text{-}F}$=252.2 Hz, Ar), 143.5 (br.s., -CH=), 138.1, 132.9, 131.1 (d, $^{4}J_{C\text{-}F}$=2.8 Hz, Ar), 130.4 (d, $^{3}J_{C\text{-}F}$=8.5 Hz, Ar), 128.7, 128.5, 121.8 (d, $^{5}J_{C\text{-}F}$=2.0 Hz,-CH=), 116.1 (d, $^{2}J_{C\text{-}F}$=22.0 Hz, Ar). ^{19}F NMR (377 MHz, $CDCl_3$) δ -31.35 (s, 1F).

(*E*)-3-(3-fluorophenyl)-1-phenylprop-2-en-1-one 5f[13d]. White flaky powder; mp 43–45 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.99 (m, 2H), 7.76 (d, *J*=15.7 Hz, 1H), 7.63-7.47 (m, 4H), 7.44–7.31 (m, 3H), 7.14-7.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2 (C=O), ~~164.3, 161.9~~ 163.1 (d, $^{1}J_{C\text{-}F}$=246.9 Hz, Ar), 143.3 (d, *J*=2.6 Hz, -CH=), 138.0, 137.2 (d, $^{3}J_{C\text{-}F}$=7.6 Hz, Ar), 133.0, 130.5 (d, $^{3}J_{C\text{-}F}$=8.2 Hz, Ar), 128.7, 128.5, 124.5 (d, $^{4}J_{C\text{-}F}$=2.7 Hz, Ar), 123.2 (-CH=), 117.3 (d, $^{2}J_{C\text{-}F}$=22.0 Hz, Ar), 114.4 (d, $^{2}J_{C\text{-}F}$=22.0 Hz, Ar). ^{19}F NMR (377 MHz, $CDCl_3$) δ -34.74 (s, 1F).

(*E*)-3-(2-fluorophenyl)-1-phenylprop-2-en-1-one 5g. White flaky powder; mp 35–37 °C (lit.[13e] 36 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.98 (m, 2H), 7.91 (d, *J*=15.9 Hz, 1H), 7.73–7.56 (m, 3H), 7.51 (t, *J*=7.5 Hz, 2H), 7.42–7.33 (m, 1H), 7.19 (t, *J*=7.5 Hz, 1H), 7.16–7.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5 (C=O), ~~163.3, 160.5~~ 161.7 (d, $^{1}J_{C\text{-}F}$=253.2 Hz, Ar), 138.0, 137.5 (-CH=), 132.9, 131.9 (d, $^{3}J_{C\text{-}F}$=8.9 Hz, Ar), 129.8 (d, $^{3}J_{C\text{-}F}$=2.8 Hz, Ar), 128.7, 128.6, 124.7 (d, $^{4}J_{C\text{-}F}$=7.0 Hz, Ar), 124.5 (d, *J*=4.0 Hz, -CH=), 123.0 (d, $^{2}J_{C\text{-}F}$=11.4 Hz, Ar), 116.2 (d, $^{2}J_{C\text{-}F}$=22.0 Hz, Ar). ^{19}F NMR (377 MHz, $CDCl_3$) δ -35.66 (s, 1F).

(*E*)-1-phenyl-3-p-tolylprop-2-en-1-one 5h. White flaky powder; mp 88–90 °C (lit.[13c] 90-92 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.96 (m, 2H), 7.80 (d, *J*=15.7 Hz, 1H), 7.63–7.44 (m, 6H), 7.23 (d, *J*=7.8 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7 (C=O), 145.0 (-CH=), 141.1, 138.4, 132.7, 132.2, 129.7, 128.6, 128.5, 121.1 (-CH=), 21.6 (-CH_3).

(*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one 5i. White flaky powder; mp 63–65 °C (lit.[13f] 63-65 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J*=7.5 Hz, 2H), 7.79 (d, *J*=15.6 Hz, 1H), 7.69–7.46 (m, 5H), 7.42 (d, *J*=15.6 Hz, 1H), 6.93 (d, *J*=8.3 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6 (C=O), 161.7 ($Ar_{C\text{-}OMe}$), 144.7 (-CH=), 138.5, 132.6, 130.3, 128.6, 128.4, 127.6, 119.8 (-CH=), 114.4 ($Ar_{o\text{-}C\text{-}COMe}$), 55.4 (-$OCH_3$).

(*E*)-3-(3-phenoxyphenyl)-1-phenylprop-2-en-1-one 5j. White flaky powder; mp 59–61 °C (lit.[13g] 62-64 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.98 (m, 2H), 7.75 (d, *J*=15.7 Hz, 1H), 7.61–7.56 (m, 1H), 7.54–7.45 (m, 3H), 7.41–7.34 (m, 4H), 7.29 (s, 1H), 7.15 (t, *J*=7.4 Hz, 1H), 7.09-7.02 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4 (C=O), 157.9 ($Ar_{C\text{-}OPh}$), 156.8 ($Ar_{C\text{-}OPh}$), 144.1 (-CH=), 138.1, 136.8, 132.9, 130.3, 130.0, 128.7, 128.5, 123.7, 123.5, 122.8 (-CH=), 120.8, 119.1, 118.2.

(*E*)-3-(naphthalen-1-yl)-1-phenylprop-2-en-1-one 5k. Yellow powder; mp 78–80 °C (lit.[13h] 78-79 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J*=15.4 Hz, 1H), 8.27 (d, *J*=8.3 Hz, 1H), 8.10 (d, *J*=7.3 Hz, 2H), 7.96-7.87 (m, 3H), 7.68-7.49 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3 (C=O), 141.8 (-CH=), 138.2, 133.8, 132.9, 132.4, 131.8, 130.8, 128.8, 128.7, 128.6, 127.0, 126.3, 125.5, 125.1, 124.7, 123.5 (-CH=).

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(*E*)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one 5l. White flaky powder; mp 159–161 °C (lit.[13i] 158-160 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.03 (m, 3H), 7.99 (d, *J*=15.7 Hz, 1H), 7.93–7.83 (m, 3H), 7.83–7.78 (m, 1H), 7.66 (d, *J*=15.7 Hz, 1H), 7.63–7.58 (m, 1H), 7.57-7.50 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6 (C=O), 145.0 (-CH=), 138.3, 134.4, 133.4, 132.8, 132.4, 130.7, 128.8, 128.7, 128.5, 127.8, 127.4, 126.8, 123.7 (-CH=), 122.2.

(*E*)-3-(anthracen-9-yl)-1-phenylprop-2-en-1-one 5m. Yellow powder; mp 115–117 °C (lit.[13j] 122-123 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J*=15.9 Hz, 1H), 8.49 (s, 1H), 8.31 (d, *J*=9.0 Hz, 2H), 8.12-8.02 (m, 4H), 7.66–7.47 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7 (C=O), 141.9, 137.9, 133.1 (-CH=), 131.3, 131.1, 130.2, 129.7, 128.9, 128.8, 128.7, 128.4 (-CH=), 126.5, 125.4, 125.3.

(*E*)-1-phenyl-3-(pyridin-2-yl)prop-2-en-1-one 5n. Yellow powder; mp 56–58 °C (lit.[13k] 60-61 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J*=4.0 Hz, 1H), 8.18 (d, *J*=15.3 Hz, 1H), 8.14–8.06 (m, 2H), 7.83–7.71 (m, 2H), 7.64–7.55 (m, 1H), 7.54–7.45 (m, 3H), 7.32 (dd, *J*=7.0, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3 (C=O), 152.9 ($Ar_{C\text{-}CH=}$), 149.7 ($Ar_{o\text{-}C\text{-}N}$), 142.1 (-CH=), 137.7, 137.5, 133.2, 128.8, 128.7, 126.2 (-CH=), 125.6, 124.5.

(*E*)-3-(furan-2-yl)-1-phenylprop-2-en-1-one 5o[13l]. Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.07 (m, 2H), 7.65–7.45 (m, 6H), 6.73 (d, *J*=3.3 Hz, 1H), 6.52 (dd, *J*=3.3, 1.8 Hz, 1 H). 13C NMR (CDCl3, 75 MHz): δ 189.8 (C=O), 151.7, 145.0, 138.1, 132.8, 130.7, 128.6, 128.5, 119.3 (-CH=), 116.3 (-CH=), 112.7.

(*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one 5p. White powder; mp 68–71 °C (lit.[13k] 71-72 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, *J*=4.5 Hz, 1H), 8.32 (d, *J*=16.0 Hz, 1H), 8.20 (d, *J*=7.8 Hz, 1H), 7.95 (d, *J*=16.0 Hz, 1H), 7.86 (td, *J*=7.7, 1.7 Hz, 1H), 7.77–7.70 (m, 2H), 7.57–7.34 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.2 (C=O), 154.3 ($Ar_{C\text{-}C=O}$), 148.7 (-CH=), 145.0 ($Ar_{o\text{-}C\text{-}N}$), 137.4, 135.0, 130.7, 128.9, 127.0, 123.1 (-CH=), 120.8.

(*E*)-1-(perfluorophenyl)-3-phenylprop-2-en-1-one 5q. White powder; mp 97–99 °C (lit.[13m] 98-100 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.56 (m, 2 H), 7.53 (d, *J*=15.9 Hz, 1H), 7.49-7.38 (m, 3H), 7.03 (d, *J*=16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8 (C=O), 148.3 (-CH=), 144.3 (dm, $^2J_{C\text{-}F}$=252.4 Hz, Ar), 142.8 (dm, $^1J_{C\text{-}F}$=257.5 Hz, Ar), 137.90 (dm, $^3J_{C\text{-}F}$=256.7 Hz, Ar), 133.6, 131.8, 129.2, 128.9, 126.1 (-CH=), 115.2-114.5 (m, Ar). ^{19}F NMR (282 MHz, $CDCl_3$) δ -140.46 (d, *J*=16.3 Hz, 2F), -150.17 (t, *J*=20.3 Hz, 1F), -159.88 (t, *J*=17.5 Hz, 2F).

General procedure for the epoxidation of α,β-unsaturated ketones

The flasks were evacuated while being heated with a heat gun. The flasks were then cooled to room temperature under an argon flow. To a mixture of catalyst ~~**1a** (10 mg~~10 mol%, 0.013 mmol), chalcone (0.13 mmol) and ~~^{t}BuOK~~ base (~~14,6 mg~~1 eq, 0.13 mmol) in ~~methyl *tert*-butyl ether (1 mL)~~ 1 mL solvent was added ~~hydrogen peroxide~~ oxidizing agent (~~0.053 mL, 0.65 mmol~~2, 3 or 5 eq; 0.26, 0.39 or 0.65 mmol) at ~~a~~ room temperature. The resulting reaction mixture was stirred vigorously for 4 h at ~~the~~room temperature. Purification of the reaction mixture by flash chromatography on silica (diethyl ether) afforded the desired product as a powder. The enantioselectivity was determined by chiral HPLC analysis of the epoxide. The absolute configuration was determined by comparison with the literature data (optical rotation).[11]

(2*S*,3*R*)-Phenyl-3-phenyloxiran-2-yl)methanone 6a. White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J*=7.5 Hz, 2H), 7.62 (t, *J*=7.4 Hz, 1H), 7.49 (t, *J*=7.7 Hz, 2H), 7.46–7.31 (m, 5H), 4.31 (d, *J*=1.8 Hz, 1H), 4.08 (d, *J*=1.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0 (C=O), 134.4, 133.0, 128.2, 127.6, 127.3, 124.8, 60.0 (C_{epox}), 58.4 (C_{epox}). HPLC (Kromasil 3-AmyCoat column; 25°C, hexane/isopropanol 95:5, λ = 254 nm; t_R = 10.1 (major), 10.9 min.

((2*S*,3*R*)-3-(4-nitrophenyl)oxiran-2-yl)(phenyl)methanone 6b. White yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J*=8.7 Hz, 2H), 8.01 (d, *J*=7.6 Hz, 2H), 7.65 (t, *J*=7.4 Hz, 1H), 7.60–7.47 (m, 4H), 4.28 (d, *J*=1.6 Hz,

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1H), 4.21 (d, *J*=1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1 (C=O), 148.4, 142.8, 135.2, 134.4, 129.0, 128.4, 126.7, 124.1, 60.9 (C_{epox}), 58.0 (C_{epox}). HPLC (Kromasil 3-AmyCoat column; 25°C, hexane/isopropanol 95:5, λ = 254 nm; t_R = 36.2 (major), 50.1 min.

((2*S*,3*R*)-3-(4-chlorophenyl)oxiran-2-yl)(phenyl)methanone 6c. Yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J*=7.5 Hz, 2H), 7.63 (t, *J*=7.4 Hz, 1H), 7.49 (t, *J*=7.7 Hz, 2H), 7.37 (d, *J*=8.4 Hz, 2H), 7.30 (d, *J*=8.4 Hz, 2H), 4.25 (d, *J*=1.3 Hz, 1H), 4.06 (d, *J*=1.3 Hz, 1H). HPLC (Chiralpak AD column; 25°C, heptane/isopropanol 90:10, λ = 254 nm; t_R = 12.5 (major), 14.2 min.

((2*S*,3*R*)-3-(2-chlorophenyl)oxiran-2-yl)(phenyl)methanone 6d. White yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (dd, *J*=8.4, 1.2 Hz, 2H), 7.66-7.62 (t, *J*=10.0 Hz, 1H), 7.53-7.49 (t, *J*=7.2Hz, 2H), 7.42-7.40 (m, 2H), 7.34-7.32 (m, 2H), 4.43 (d, *J*=1.8 Hz, 1H), 4.20 (d, *J*=1.8 Hz, 1H). HPLC (Chiralpak AD column; 25°C, heptane/isopropanol 90:10, λ = 254 nm; t_R = 8.3, 8.7 (major) min.

((2*S*,3*R*)-3-(4-fluorophenyl)oxiran-2-yl)(phenyl)methanone 6e. Yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.00 (m, 2H), 7.69-7.61 (m, 1H), 7.56-7.48 (m, 2H), 7.41-7.34 (m, 2H), 7.16-7.07 (m, 2H), 4.29 (d, *J*=0.7 Hz, 1H), 4.09 (d, *J*=0.4 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.15 (s, 1F). HPLC (Kromasil 3-AmyCoat column; 25°C, hexane/isopropanol 95:5, λ = 254 nm; t_R = 11.2 (major), 11.8 min.

((2*S*,3*R*)-3-(3-fluorophenyl)oxiran-2-yl)(phenyl)methanone 6f. Yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.98 (m, 2H), 7.65-7.60 (m, 1H), 7.53-7.46 (m, 2H), 7.41-7.33 (m, 1H), 7.17 (d, *J*=7.6 Hz, 1H), 7.10-7.03 (m, 2H), 4.26 (d, *J*=1.4 Hz, 1H), 4.08 (d, *J*=1.4 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -34.34 (s, 1F). HPLC (Kromasil 3-AmyCoat column; 25°C, hexane/isopropanol 95:5, λ = 254 nm; t_R = 9.9, 11.9 (major) min.

((2*S*,3*R*)-3-(2-fluorophenyl)oxiran-2-yl)(phenyl)methanone 6g. Yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.00 (m, 2H), 7.65-7.58 (m, 1H), 7.55-7.47 (m, 2H), 7.40-7.32 (m, 2H), 7.24-7.16 (m, 1H), 7.14-7.06 (m, 1H), 4.35 (d, *J*=1.7 Hz, 1H), 4.30 (d, *J*=1.7 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -42.36 (s, 1F). HPLC (Chiralpak AS-H column; 25°C, heptane/isopropanol 90:10, λ = 254 nm; t_R = 10.3 (major), 23.0 min.

(2*S*,3*R*)-phenyl(3-p-tolyloxiran-2-yl)methanone 6h. White flaky powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J*=7.2 Hz, 2H), 7.62 (t, *J*=7.2 Hz, 1H), 7.48 (t, *J*=7.2 Hz, 2H), 7.28-7.21 (m, 4H), 4.30 (d, *J*=1.6 Hz, 1H), 4.05 (d, *J*=1.6 Hz, 1H), 2.38 (s,3H). HPLC (Kromasil 3-AmyCoat column; 25°C, heptane/isopropanol 90:10, λ = 254 nm; t_R = 6.2 (major), 6.5 min.

((2*S*,3*R*)-3-(4-methoxyphenyl)oxiran-2-yl)(phenyl)methanone 6i. White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J*=7.2 Hz, 2H), 7.62-7.59 (m, 1H), 7.49-7.46 (m, 2H), 7.29 (d, *J*=8.8 Hz, 2H), 6.93 (d, *J*=8.8 Hz, 2H), 4.29 (d, *J*=1.7 Hz, 1H), 4.02 (d, *J*=1.2 Hz, 1H), 3.82 (s, 3H). HPLC (Chiralpak AD column; 25°C, hexane/isopropanol 90:10, λ = 254 nm; t_R = 14.0 (major), 17.9 min.

((2*S*,3*R*)-3-(3-phenoxyphenyl)oxiran-2-yl)(phenyl)methanone 6j. White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.99 (m, 2H), 7.65-7.60 (m, 1H), 7.53-7.47 (m, 2H), 7.39-7.33 (m, 3H), 7.14-7.09 (m, 2H), 7.06-6.98 (m, 4H), 4.26 (d, *J*=1.6 Hz, 2H), 4.05 (1H, d, *J*=1.6 Hz, 2H). HPLC (Chiralpak IA column; 25°C, hexane/isopropanol 98:2, λ = 254 nm; t_R = 22.4, 30.3 (major) min.

((2*S*,3*R*)-3-(naphthalen-1-yl)oxiran-2-yl)(phenyl)methanone 6k. White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.08 (m, 2H), 8.05-8.00 (m, 1H), 7.97-7.88 (m, 2H), 7.68-7.63 (m, 1H), 7.59-7.49 (m, 6H), 4.76 (d, *J*=1.9 Hz, 1H), 4.34 (d, *J*=1.9 Hz, 1H). HPLC (Kromasil 3-AmyCoat column; 25°C, hexane/isopropanol 90:10, λ = 254 nm; t_R = 5.9 (major), 6.4 min.

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((2*S*,3*R*)-3-(naphthalen-2-yl)oxiran-2-yl)(phenyl)methanone 6l. White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J*=8.0 Hz, 1H), 7.91–7.84 (m, 3H), 7.63–7.50 (m, 8H), 4.41 (d, *J*=1.8 Hz, 1H), 4.25 (d, *J*=1.6 Hz, 1H). HPLC (Kromasil 3-AmyCoat column; 25°C, hexane/isopropanol 95:5, λ = 254 nm; t_R = 10.4, 11.2 (major) min.

((2*S*,3*R*)-3-(anthracen-9-yl)oxiran-2-yl)(phenyl)methanone 6m. Yellow powder; $[\alpha]_D^{27}$ = -115.9 (c 0.073, $CDCl_3$) at 98% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.46 (d, *J*=8.3 Hz, 2H), 8.25 (d, *J*=7.5 Hz, 2H), 8.04 (d, *J*=7.8 Hz, 2H), 7.71 (t, *J*=7.4 Hz, 1H), 7.58 (t, *J*=7.6 Hz, 2H), 7.55–7.46 (m, 4H), 5.01 (d, *J*=1.6 Hz, 1H), 4.49 (d, *J*=1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5 (C=O), 135.6, 134.3, 131.1, 130.1, 129.14–128.83 (m, 3C), 128.6, 126.6, 126.5, 125.3, 124.5, 58.5 (C_{epox}), 58.0 (C_{epox}). HPLC (Kromasil 3-AmyCoat column; 25°C, hexane/isopropanol 95:5, λ = 254 nm; t_R = 9.6, 12.5 (major) min.

(2*S*,3*R*)-phenyl(3-(pyridin-2-yl)oxiran-2-yl)methanone 6n. Yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J*=4.2 Hz, 1H), 8.04-8.00 (m, 2H), 7.73 (td, *J*=7.7, 0.9 Hz, 1H), 7.62-7.56 (m, 1H), 7.51-7.44 (m, 2H), 7.39 (d, *J*=8.0 Hz, 1H), 7.32-7.27 (m, 1H), 4.57 (d, *J*=0.9 Hz, 1H), 4.20 (d, *J*=1.1 Hz, 1H). HPLC (Kromasil 3-AmyCoat column; 25°C, hexane/isopropanol 90:10, λ = 254 nm; t_R = 13.1, 14.5 (major)min.

((2*S*,3*R*)-(3-(furan-2-yl)oxiran-2-yl)(phenyl)methanone 6o. Yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.01 (m, 2H), 7.65-7.43 (m, 4H), 6.59 (d, *J*=3.3 Hz, 1H), 6.41 (dd, *J*=3.2, 1.8 Hz, 1H), 4.79 (d, *J*=2.0 Hz, 1H), 4.10 (d, *J*=1.9 Hz, 1H). The absolute configuration was not determined.

((2*S*,3*R*)-3-phenyloxiran-2-yl)(pyridin-2-yl)methanone 6p. Yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68-8.65 (m, 1H), 8.12-8.08 (m, 1H), 7.88 (td, *J*=7.7, 1.7 Hz, 1H), 7.54–7.49 (m, 1H), 7.41–7.35 (m, 5H), 5.12 (d, *J*=1.7 Hz, 1H), 4.09 (d, *J*=1.7 Hz, 1H). HPLC (Chiralcel OJ column; 25°C, hexane/isopropanol 80:20, λ = 220 nm; t_R = 15.1, 16.0 (major) min.

Coupling reaction of CO_2 and epoxide 6a

Typically, the autoclave was charged with 0.1 equiv. of catalyst Δ(*S,S*)-**1a I**$^-$, 1.0 equiv. of epoxide **6a** and were dissolved in acetonitrile or in toluene (0.1 mL). The reactor was purged twice with CO_2, pressurized with CO_2 to 50 bars, heated to 50°C and stirred for 24 h. Subsequently, the reactor was cooled to ambient temperature and CO_2 was released slowly. The reaction mixture was filtered over SiO_2 (CH_2Cl_2), and the volatiles were removed under reduced pressure.

4-benzoyl-5-phenyl-1,3-dioxolan-2-one 7[14]. White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J*=7.5 Hz, 2H), 7.66 (t, *J*=7.5 Hz, 1H), 7.55–7.43 (m, 7H), 5.98 (d, *J*=6.2 Hz, 1H), 5.60 (d, *J*=6.2 Hz, 1H).

X-ray diffraction study of 6m

Crystals of **6m** ($C_{23}H_{16}O_2$, *M* = 324.36) are orthorhombic, space group $P2_12_12_1$, at 120K *a* = 5.0152(7), *b* = 15.450(2), *c* = 20.528(3) Å, *V* = 1590.6(4) Å^3, *Z* = 4, $d_{calc.}$ = 1.354 g/cm^3, μ = 0.676 mm^{-1}. Data collection was carried out with a Bruker SMART APEX II diffractometer, λ(CuKα) = 1.54190 Å, ω-scan technique, *T* = 120(2) K, 2580 independent reflections (R_{int} = 0.0528) with 2.0° < 2θ < 130.0° collected and used in refinement. The APEX II software[15] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction, and SHELXTL[16] for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full matrix least-squares technique against F^2 with the anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and included in the structure factors

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calculation in the riding motion approximation. The refinement converged to wR_2 = 0.2060 and GOF = 1.001 for all independent reflections (R_1 = 0.0672 was calculated against *F* for 2508 observed reflections with I > 2σ(I)). CCDC 1407467 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Recovering of the catalyst Δ(*S,S*)-1a. After flash chromatography the remaining SiO_2 with the adsorbed catalyst was separated and stirred in a biphasic mixture of saturated aqueous solution of NaCl and CH_2Cl_2. Then the solution was filtered, the solid washed with methanol and the combined organic solutions were evaporated. The resulting mixture was purified on SiO_2 and the recovered catalyst was isolated.[9a]

Conclusions

In this study, it was shown that ~~chiral stereochemically inert~~ octahedral stereochemically inert and positively charged "chiral-at-metal" Co(III) complexes efficiently and stereoselectively catalyzed the epoxidation reaction of various chalcones. Also, using the same type of complexes of Co(III) as the catalyst, we were able to couple the resulting epoxide **6a** with CO_2. At present, work on CO_2 fixation and study of the mechanism of this reaction are ongoing.

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Notes and references

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