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A new class of bifunctional chiral phase transfer catalysts for highly enantioselective asymmetric epoxidation of α , β -unsaturated ketones at ambient temperature



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1. Introduction

Phase transfer catalysis has emerged as one of the most rapidly growing and promising areas in asymmetric synthesis [1]. The advantages of phase transfer catalysis consist of their operational simplicity, low cost, and low toxicity, which confers a massive unswerving benefit in the production of pharmaceutical intermediates [2]. The ready accessibility, user friendliness of phase transfer catalysts and the mild experimental conditions make asymmetric phase transfer reactions engaging both for academic research and for industrial applications [3]. Cinchona alkaloids were the first efficient phase transfer catalysts for asymmetric catalysis [3,4]. It was recognized early that the substituent's on both the oxygen and the nitrogen atom of the quinuclidine moiety of the cinchona alkaloids play a key role in the enantioselectivity [5,6]. Organocatalytic reactions are becoming powerful tools in the construction of complex molecular skeletons and chiral drug molecules [7]. The chiral drug industry has become a rapidly growing segment of the drug market [8]. The epoxide functional group is one of the most useful intermediates in organic synthesis and building blocks for

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ABSTRACT

A new type of bis-quaternary ammonium bromide as chiral multifunctional phase transfer catalysts derived from readily available inexpensive cinchona alkaloids has been developed and evaluated for the enantioselective asymmetric epoxidation of various chalcones in the presence of lower concentrations of various oxidants, bases, solvents and ambient temperature conditions. Under optimized reaction conditions, highest chemical yields of up to 98% along with the excellent enantioselectivities of about 99% were obtained by using the cinchona based chiral multifunctional phase transfer catalysts.

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the synthesis of biologically active compounds [9,10]. The fundamentals of enantioselective asymmetric epoxidation findings have largely expanded the scope of asymmetric synthesis and allowed a more targeted preparation of pharmaceutical products, such as antibiotics, anti-inflammatory drugs, and other medicines [11-14]. Asymmetric epoxidation reaction of electron deficient olefins, particularly α , β -unsaturated ketones such as chalcone have been investigated and reported lower to moderate yield and ee's under organocatalysts and phase transfer catalysts [15–30]. Jew et al., [31] have been reported the efficient enantioselective phase transfer epoxidation of trans-chalcone using cinchona based dimeric catalyst with higher concentration of oxidant (30 eq), strong base (KOH, 3 eq) and surfactants (Triton X-100). Further, Yoo et al. [32] have been reported the N-2,3,4-trifluorobenzyl-containing cinchona-PTCs 1b (Fig. 1) with sodium hypochlorite solution as an oxidant at RT and 0 °C for the effective epoxidation of chalcones with moderate yields (91%) and ee's (79%). Recently Zeng et al., [33] reported the enantioselective epoxidation of chalcones with excellent yields (99%) and ee's (99%) in the presence of prolinols based chiral catalyst 1a (Fig. 1) and TBHP as an oxidant at RT, but they were additionally used rare-earth metal amides such as Sm. Y. and Lu in the presence of phenoxy-functionalized chiral prolinols as a ligand. In this study, we used low concentration of oxidant (10 eq) and mild base (Cs₂CO₃, 1.5 eq) without adding any co-catalyst



Fig. 1. Previously reported cinchona and prolinol based chiral catalysts.



Scheme 1. Enantioselective synthesis of chiral epoxidation of chalcones under CMPTC conditions.



Scheme 2. Synthesis of bis quaternary ammonium ion as CMPTC for asymmetric epoxidation reaction.

(surfactants)/metal ligands achieved higher yields (up to 98%) and efficient ee's (up to 99%). Generally, the epoxidation reaction at low temperature 0 °C resulted in higher enantio selectivities than at room temperature. In this connection, we focused on the enantioselectivity and the chemical yield of asymmetric epoxidation reactions (Scheme 1) using new types of bis-quaternary ammonium bromides as chiral multifunctional phase transfer catalysts (CMPTCs **10**, Scheme 2).

Here, we report to synthesize a new series of multifunctional chiral phase transfer catalyst **10a** and **10b**. Further, the catalytic efficiencies were studied by the chiral epoxidation of chalcones with very good yields (up to 98%) and excellent ee's (99%) at ambient temperature conditions.

2. Experimental section

2.1. Materials and methods

All the chemicals and reagents used in this work were of analytical grade. Allylbromide, cinchonidine were obtained from Alfa Aesar, 4-methylbezaldehyde, N-bromosuccinimide, potassium tert-butoxide, cesium carbonate and potassium carbonate, 4-methylbenzene-1-sulfonyl chloride were obtained from Sigma-Aldrich, sodium hydroxide, pottassium hydroxide, were obtained from Merck and all the solvents were obtained from Laboratory Grade. The melting points were measured in open capillary tubes and are uncorrected. The ¹H, and ¹³C NMR spectra were recorded on a Bruker (Avance) 300 and 400 MHz NMR instrument using TMS as internal standard and CDCl₃ as a solvent. Standard Bruker software was used throughout. Chemical shifts were given in parts per million (δ -scale) and the coupling constants are given in Hertz. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of *n*-hexane and ethylacetate as an eluent. Column chromatography was carried out in silica gel (60–120 mesh) using *n*-hexane and ethylacetate as an eluent. Electrospray ionization mass spectrometry (ESI-MS) analyses were recorded in LCO Fleet, Thermo Fisher Instruments Limited, US. ESI-MS was performed in positive ion mode. The collision voltage and ionization voltage were -70 V and -4.5 kV, respectively, using nitrogen as atomization and desolvation gas. The desolvation temperature was set at 300 °C. The relative amount of each component was determined from the LC-MS chromatogram, using the area normalization method. The HPLC were recorded in SHIMADZU LC-6AD with Chiral column (Chiral cell OD-H), using HPLC grade *n*-hexane and isopropanol solvents.

2.2. Catalyst preparation

2.2.1. Synthesis of cinchonidine (contains free C_9 -OH) based CMPTC (10a)

A mixture of 4,4'-sulfonylbis (bromomethyl) (benzene) **7** (0.1 g, 10 mmol), cinchonidine **8** (0.21 g, 30 mmol) was dissolved in 5 mL of EtOH:DMF:ACN (30:50:20 ratio) and the whole mixture was refluxed for overnight, the white solid was filtered off, washed with diethylether and dried it, to get pure di-site chiral PTC (**10a**). The yield is 95%. FT-IR (KBr) cm⁻¹: 3068.12, 1735.72, 1590.70, 1509.04, 1460.72, 1418.97, 1309.15, 1206.95, 1156.73, 1106.79, 1049.13, 994.74, 936.02, 904.15, 886.67, 831.81, 801.48; ¹H NMR (400 MHz, CDCl₃): δ_{ppm} 8.84 (d, *J* = 3.9 Hz, 2H), 8.07 (d, *J* = 8.6 Hz, 4H), 7.95 (d, *J* = 8.1 Hz, 4H), 7.79 (d, *J* = 8.4 Hz, 4H), 7.62 (s, 4H), 7.38 (m, 2H), 6.01 (m, 2H), 5.88 (s, 2H), 5.08 (s, 4H), 3.45 (d, *J* = 8.5 Hz, 2H), 3.11 (s, 2H), 2.96 (d, *J* = 13.2 Hz, 4H), 2.82 (m, 4H), 2.28 (d, *J* = 7.9 Hz, 6H), 2.08 (m, 2H), 1.79 (s, 2H), 1.54 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ_{ppm} 150.14, 149.47, 148.09,147.86, 139.15, 134.70, 130.28, 129.83, 129.03, 126.80, 125.37, 122.86, 119.61, 118.43, 115.62, 70.08, 60.22,

49.90, 49.26, 39.22, 28.02, 25.48, 21.99, 20.32. ESI–MS Calculated (*m*/*z*) = 990.2389, Found (*m*/*z*) = 990.2395.

2.2.2. Synthesis of allylated cinchonidine based CMPTC (10b)

A mixture of 4,4'-sulfonylbis (bromomethyl) (benzene) 7 (0.1 g, 10 mmol), allylated cinchonidine 9 (0.24 g, 30 mmol) was dissolved in 5 mL of THF:ACN (1:1 ratio) and heated to reflux for about overnight, the off white solid was filtered, washed with diethylether and dried it, to get pure di-site chiral PTC (10b) with 96% yield. FT-IR (KBr) cm⁻¹: 3373.83, 2944.49, 2869.75, 2519.30, 1956.93, 1684.44, 1638.23, 1590.27, 1530.68, 1507.23, 1460.17, 1412.72, 1308.17, 1412.72, 1308.17, 1234.81, 1211.68, 1154.52, 1104.27, 1070.12, 992.03, 925.83, 852.43, 828.03, 800.19; ¹H NMR (400 MHz, CDCl₃): δ_{ppm} 8.83 (d, J=4.0 Hz, 2H), 8.07 (d, J=9.1 Hz, 4H), 7.94 (d, J=8.1 Hz, 4H), 7.79 (d, J=7.4 Hz, 4H), 7.63 (s, 4H), 7.38 (m, 2H), 5.92 (m, 2H), 5.70 (dd, *J* = 9.7, 7.5 Hz, 2H), 5.22 (dd, *J* = 17.2, 10.5 Hz, 10H), 4.92 (d, /=17.1 Hz, 2H), 4.87 (d, /=10.3 Hz, 2H), 3.93 (m, 2H), 3.88 (m, 2H), 3.41 (s, 2H), 3.07 (dd, J = 10.0, 2.8 Hz, 4H), 2.64 (m, 2H), 2.25 (s, 1H), 1.83 (s, 2H), 1.53 (d, J=11.2 Hz, 6H), 1.26 (s, 2H), 0.81 (m, 2H); 13 C NMR (75 MHz, CDCl₃) δ_{ppm} 149.83, 148.49, 142.43, 139.46, 135.92, 135.08, 133.28, 132.40, 130.36, 129.93, 128.22, 125.45, 123.41, 119.98, 118.29, 117.99, 74.35, 70.59, 60.00, 49.39, 48.38, 36.98, 27.44, 23.14, 22.16, 18.51. ESI-MS: Calculated (m/z) = 1070.3016, Found (m/z) = 1070.3022.

2.3. General method for a synthesis of chalcones (3a–j) [35–40]

Acetophenone (1eq) and aromatic aldehyde (1eq) were dissolved in 2 mL of ethanol and 10% sodium hydroxide was added, the mixture was stirred for 5–15 min. After completion of the reaction, the mixture was poured into ice the precipitate was filtered and recrystallized with ethanol, to get pure chalcone.

2.4. General procedures for enantioselective catalytic epoxidation of α , β -unsaturated compounds in the presence of CMPTCs. (10)

To a mixture of chalcone **3a–h** (1eq), oxidant (H_2O_2 , NaOCl, PMS, APS 10eq) and CMPTC catalyst **10 (10a/10b)** (5 mol%) was dissolved in 1 mL of toluene and 0.5 mL of 10% base (like NaOH, KOH, K^tOBu, K₂CO₃, Cs₂CO₃, 1.5eq) was added. Then the reaction mixture was stirred at room temperature, until chalcone was disappeared (detected by TLC), after that the reaction mixture was extracted with ethylacetate, washed with water (3 × 2 mL), brine (5 mL) and dried over sodium sulphate and concentrated it. The crude material was purified by column chromatography (*n*-hexane/ethyl acetate as an eluent).

2.5. Characterization of epoxidation compounds (4a-j)

2.5.1. Trans-(2R,

3S)-epoxy-3-(4-methoxyphenyl)-1-phenylproan-1-one (4a)

Light yellow solid, m.p: $81-82 \circ C$. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 8.11 (d, *J*=4.0 Hz, 2H), 7.71 (m, 3H), 7.61 (d, *J*=7.0 Hz, 2H), 7.05 (d, *J*=8.5 Hz, 2H), 4.42 (d, *J*=8.2 Hz, 1H), 4.32 (d, *J*=8.1 Hz, 1H), 3.87 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ_{ppm} 197.64, 161.54, 144.58, 132.36, 130.15, 128.39, 128.23, 119.57, 114.27, 65.10, 58.30, 55.25. The enantiomeric excess was determined by HPLC, chiral column (chiral cell OD-H), 254 nm, hexane: IPA=99:01, flow rate = 1 mL/min, retention time: 4.99 min (minor), 15.40 min (major).

2.5.2. Trans-(2R,

3S)-epoxy-3-(4-methylphenyl)-1-phenylproan-1-one (4b)

White solid, m.p: 69–71 °C. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 7.82 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 6.3 Hz, 1H), 7.34 (t, *J* = 6.7 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.96 (d, *J* = 7.7 Hz, 2H), 4.42 (d, *J* = 8.2 Hz,

Optimization of catalysts for enantioselective epoxidation reaction.

Ar ¹	PTCs of Ar ² Toluene	(2a,2b / 10a,10b) H ₂ O ₂		, Ar ²			
3		RT	4				
Entry	Enone	Ar ¹	Ar ²	Catalyst	Product	Yield (%) ^a	% of ee ^b (Abs.Conf.) ^c
1	3c	Ph	4-Cl- C ₆ H ₄	2a	4c	72	75 (2R,3S)
2	3c	Ph	4-Cl- C ₆ H ₄	2b	4c	72	80 (2R,3S)
3	3c	Ph	4-Cl- C ₆ H ₄	10a	4c	98	98 (2R,3S)
4	3c	Ph	4-Cl- C ₆ H ₄	10b	4c	98	99 (2R,3S)
5	3i	CH ₃	Ph	2a	4i	70	71 (2R,3S)
6	3i	CH ₃	Ph	2b	4i	70	73 (2R,3S)
7	3i	CH ₃	Ph	10a	4i	90	87 (2R,3S)
8	3i	CH ₃	Ph	10b	4i	90	91 (2R,3S)

^a Isolated yield of purified materials.

^b Enantiomeric excess of 4 was determined by HPLC analysis using a chiral column (chiral cell OD-H) with hexane:IPA as an eluent.

^c The absolute configuration of 4 was determined to be (2R,3S) by comparison with the HPLC retention time using known literature data [21].

1H), 4.32 (d, J = 8.1 Hz, 1H), 2.40 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) $\delta_{\rm ppm}$ 197.59, 137.35, 136.87, 136.65, 133.01, 129.05, 128.12, 128.02, 65.14, 58.21, 21.07. The enantiomeric excess was determined by HPLC, chiral column (chiral cell OD-H), 254 nm, hexane: IPA = 99:01, flow rate = 1 mL/min, retention time: 4.71 min (minor), 16.58 min (major).

2.5.3. Trans-(2R,

3S)-epoxy-3-(4-chlorophenyl)-1-phenylproan-1-one (4c)

Yellow solid, m.p: 68-71 °C. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 8.03 (d, *J* = 7.8 Hz, 2H), 7.60 (m, 3H), 7.54 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.33 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ_{ppm} 197.62, 138.21, 137.92, 133.29, 132.87, 129.53, 129.19, 128.55, 128.44, 65.17, 58.21. The enantiomeric excess was determined by HPLC, chiral column (chiral cell OD-H), 254 nm, hexane: IPA = 99:01, flow rate = 1 mL/min, retention time: 4.91 min (minor), 10.56 min (major).

2.5.4. Trans-(2R,

3S)-epoxy-3-(4-nitrophenyl)-1-phenylproan-1-one (4d)

Yellow solid m.p: 140–142 °C. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 8.29 (d, *J*=8.5 Hz, 2H), 7.80 (dd, *J*=15.0, 10.5 Hz, 3H), 7.61 (dd, *J*=14.0, 5.0 Hz, 2H), 7.53 (m, 2H), 4.42 (d, *J*=8.6 Hz, 1H), 4.33 (d, *J*=8.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ_{ppm} 197.69, 148.58, 141.07, 137.56, 133.36, 128.91, 128.82, 128.60, 124.24, 65.16, 58.21. The enantiomeric excess was determined by HPLC, chiral column (chiral cell OD-H), 254 nm, hexane: IPA=99:01, flow rate = 1 mL/min, retention time: 5.23 min (minor), 49.49 min (major).

2.5.5. Trans-(2R, 3S)-epoxy-1-(4-bromophenyl)-3-(4-methoxylphenyl) proan-1-one (4e)

Light yellow solid, m.p: 81-82 °C. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 7.87 (d, J=6.8 Hz, 2H), 7.64 (d, J=8.6 Hz, 2H), 7.53 (d, J=6.5 Hz, 2H), 7.23 (d, J=6.6 Hz, 2H), 4.42 (d, J=8.6 Hz, 1H), 4.33 (d, J=8.7 Hz, 1H), 2.39 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ_{ppm} 197.79, 145.34, 137.13, 131.94, 129.99, 129.72, 128.55, 127.66, 65.15, 58.25, 21.25. The enantiomeric excess was determined by HPLC, chiral column (chiral cell OD-H), 254 nm, hexane: IPA=99:01, flow rate = 1 mL/min, retention time: 4.97 min (minor), 18.08 min (major).

2.5.6. Trans-(2R,

3S)-epoxy-1-(4-bromophenyl)-3-(4-methylphenyl) proan-1-one (4f)

White solid, m.p: 100–101 °C. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 7.87 (d, *J* = 8.7 Hz, 2H), 7.62 (m, 4H), 6.94 (d, *J* = 9.0 Hz, 2H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.32 (d, *J* = 8.1 Hz, 1H), 2.40 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ_{ppm} 197.78, 161.81, 137.22, 131.87, 130.37, 129.95, 127.43, 118.99, 114.36, 65.50, 58.21, 21.04. The enantiomeric excess was determined by HPLC, chiral column (chiral cell OD-H), 254 nm, hexane: IPA = 99:01, flow rate = 1 mL/min, retention time: 4.92 min (minor), 9.92 min (major).

2.5.7. Trans-(2R,

3S)-epoxy-1-(4-bromophenyl)-3-(4-chlorophenyl) proan-1-one (4g)

White solid, m.p: $65-66 \circ C.^{1}$ H NMR (300 MHz, CDCl₃): δ_{ppm} 7.87 (d, J = 6.8 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 6.0 Hz, 2H), 7.39 (d, J = 9.0 Hz, 2H), 4.42 (d, J = 8.2 Hz, 1H), 4.33 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, CDCl₃) δ_{ppm} 197.64, 136.59, 133.07, 131.88, 129.92, 129.56, 129.22, 128.07, 65.15, 58.20. The enantiomeric excess was determined by HPLC, chiral column (chiral cell OD-H), 254 nm, hexane: IPA = 99:01, flow rate = 1 mL/min, retention time: 4.97 min (minor), 11.36 min (major).

2.5.8. Trans-(2R, 3S)-epoxy-1-(4-bromo

phenyl)-3-(4-nitrophenyl) proan-1-one (4h)

White solid, m.p: 130–132 °C. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 8.29 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 11.4 Hz, 2H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.33 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ_{ppm} 197.69, 148.55, 141.07, 137.56, 133.38, 128.91, 128.82, 128.62, 124.23, 65.15, 58.25. The enantiomeric excess was determined by HPLC, chiral column (chiral cell OD-H), 254 nm, hexane: IPA = 99:01, flow rate = 1 mL/min, retention time: 5.04 min (minor), 10.23 min (major).

2.5.9. Trans-(2R, 3S)-1-(3-phenyloxiran-2-yl) ethanone (4i)

Light yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 7.77 (m, 3H), 7.63 (m, 2H), 4.08 (d, *J* = 3.9 Hz, 1H), 3.61 (d, *J* = 3.9 Hz, 1H), 2.19 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ_{ppm} 196.21, 135.12, 128.89, 127.41, 126.74, 126.65, 125.55, 74.59, 58.92, 25.11. The enantiomeric excess was determined by HPLC, chiral column (chiral cell OD-H), 254 nm, hexane: IPA = 99:01, flow rate = 1 mL/min, retention time: 3.41 min (minor), 10.34 min (major).

2.5.10. Trans-(2R, 3S)-(3-ethyloxiran-2-yl)(phenyl) methanone (4j)

Yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 7.97 (d, *J* = 7.0 Hz, 2H), 7.47 (m, 3H), 4.04 (d, *J* = 3.2 Hz, 1H), 3.02 (d, *J* = 3.5 Hz, 1H), 1.31 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ_{ppm} 196.21, 134.84, 133.04, 128.86, 127.33, 126.75, 125.56, 60.52, 59.32, 22.95, 12.11. The enantiomeric excess was determined by HPLC, chiral column (chiral cell OD-H), 254 nm, hexane: IPA = 99:01, flow rate = 1 mL/min, retention time: 3.49 min (minor), 9.51 min (major).

3. Results and discussion

The synthetic routes for the synthesis of compound **7** [34], chiral precursors **8** and **9** [35,36] were synthesized by previously reported procedure (Scheme 2). Compound 4,4'-sulfonylbis(methylbenzene) **6** was prepared by a Friedel–Crafts acylation from 4-methylbenzene-1-sulfonyl chloride **5** and toluene with a yield of 68%. The bromination of compound **6** by employing *N*-bromosuccinimide (NBS) in benzene successfully afforded the desired compound **7**. Catalytic asymmetric epoxidation is an extremely important reaction owing to its role in producing the lifesaving drugs. Based on their track record, cinchona alkaloids have continued to play a pivotal role in this area (asymmetric synthesis) exclusively for the synthesis of various epoxide products from α , β -unsaturated compounds. Hence, we focused to optimize the reaction conditions.

First, we carried out the reactivity of the monomeric and dimeric catalysts for the enantioselective epoxidation of chalcones. In this connection, we performed the enantioselective epoxidation of trans-chalcones by using 3 mol% of the monomeric (2a/2b) and dimeric catalysts **10a/10b** along with H_2O_2 and 10 mol% of Cs_2CO_3 in toluene at room temperature. From the Table 1, dimeric catalysts mediated **10a** and **10b** showed higher yields and ee's when compared with the corresponding monomeric catalysts **2a/2b** (Table 1, entries 1,2 and 5,6). This is due to the **10a** and **10b** having multiactive site present in the molecules.

Further we carried out our attention on finding optimal basic and oxidant conditions for the enantioselective epoxidation of chalcone in the presence of different bases under room temperature condition. From the observed results (Table 2, entries 1–24) among the bases, the Cs₂CO₃ used epoxidation reaction was observed higher chemical yield and ee's than the other bases such as K₂CO₃, K^tOBu, KOH and NaOH. The enantioselective epoxidation of chalcone at higher concentration of base irrespective of CMPTCs/oxidants gave disparate results, which can be explained by invoking a catalyst degradation mechanism [41] (Fig. 2).

Further, we observed the moderate chemical yield and ee's in presence of NaOH, KOH and K^tOBu due to the formation of secondary product (i.e. cleavage of epoxide to diol formation) for the enantioselective epoxidation reaction. In this cleavage is not applicable when we are using carbonate containing bases. In addition to that the size of the cations is also important to the formation of epoxidation product, the chemical yield of epoxide increases with the size of the cation and in the close relation to the cohesion energy of the carbonates [42].

Furthermore, we carried out the optimization of oxidant for the enantioselective epoxidation of chalcone **3** by using 3 mol% of the dimeric catalysts **10a** and **10b** along with different oxidant and 10% aqueous Cs_2CO_3 in toluene at room temperature. As shown in (Table 2) even though the reaction time was somewhat very short (4.5–5.5 h), the dimeric catalyst **10a** and **10b** provided very good yield (95-98%) and enantiomeric excess (92–99%) in the presence of H_2O_2 and NaOCl as an oxidant (Table 2, enties 1–4).

At high concentrations of base, initially, the deprotonation of the catalyst **10a** (C_9 free –OH) occurs leading to the formation of zwitterionic alkoxide **11**, this in turn undergoes a slow fragmentation to epoxide **12**. In the case of C_9 (O) allylated CPTC **10b**, at high concentration of base, Hofmann elimination occurred and giving compound of **13** viz., olefinic compound. Hence we observed the lower chemical yield and ee's presence of NaOH and KOH.

Further, the epoxidation reaction is carried out in the presence of PMS and APS as oxidants, we got moderate yield and ee's obtained from more than 12 hrs. This may be due to the longer the reaction time should affect the epoxidation reaction rate (i.e., epoxide ring is cleaved and to form diol) and which can be reduced the chemical yield as well as enantiomeric excess. (Table 2, enties 5–8).

The asymmetric epoxidation reaction was carried out in different solvents using CMPTCs 10a and 10b under room temperature, the other parameters are kept as constant. The obtained results (Table 3) shows that, the change of solvent is found to be an important decisive factor in the epoxidation reaction due to their polarity, degree of solvation and dielectric constant of the solvents. The product yield and ee's have been found to decrease gradually, using non polar to polar solvents (Table 3, enties 1–14). Further, we concluded that most probably the high polar solvents should reduce the ionic pair interaction between the catalyst and oxidants and hence reducing the chemical yield and ee's (Table 3, enties 9-14). The polarity of the solvents as follows, cyclohexane > toluene > benzene > THF > 1,4-dioxane > ACN > DMF. In the case of toluene, cyclohexane and benzene they are nonpolar solvents, the degree of solvation of CMPTC's is considerably less. Hence, the degree of decay due to solvation of CMPTC's of the catalyst is almost minimized/ignored. Otherwise, the interaction between R_4N^+ of the catalyst and oxidant is more than the more polar solvents [42]. This is in turn improves the potential of the catalyst as well as effective attraction of the substrate and catalyst and hence the reaction yield and ee's are found to be higher in presence of toluene, cyclohexane, benzene medium (Table 3, enties 1 - 8)

A good correlation was observed when enantioselectivity was plotted as a function of solvent polarity, E_T30 , (Table 3 and Fig. 3). The enantioselectivity directly depends on the solvent polarity with the less polar solvents giving superior enantioselectivity compare to high polar solvents (Table 3, entries 1–14). A similar trend was observed for using both C_9 free –OH containing CMPTC **10a** (Fig. 3a) and C_9 (O) protected CMPTC **10b**. (Fig. 3b).

The optimization of the epoxidation reaction was carried out in the presence of different reaction temperature conditions. From the observed results, higher chemical yield and ee's are obtained at room temperature when compared with other temperature conditions (i.e., -10 °C, ultrasonic and 55 °C) (Table 4, entries 1–8). The low yield of the epoxide at high temperature is probably due to the decomposition of the oxidizing agents. The most suitable temperature for this reaction is room temperature [43]. Through extensive screening, the optimized reaction conditions are found to be 3 mol% of catalyst **10**, CS₂CO₃ as base, toluene as solvent and H₂O₂ as oxidant at room temperature.

In general, all homogeneous catalysis reaction rates are directly proportional to the catalyst loading amount. From the observed results, the catalysts amounts are increased from 1 mol% to 15 mol% the epoxidation reaction yield as well as the ee's reduced. That means the catalysts poison taking place in this reaction irrespective of the catalysts **10a** and **10b** (Table 5, entries 1–10). This may be due to the lower the catalyst concentration of sulfonyldibenze spacer between the two cinchona units influences the binding of the catalyst with chalcone **3** and peroxide than the higher concentration of the catalysts.

The obtained results indicated that the stereochemical course of the epoxidation mainly depends on the stereochemistry/molecular





Entry	Base	Oxidant	Catalyst	Time (h)	Yield (%) ^a	% of ee ^b (Abs.Conf.) ^c
1	CS ₂ CO ₃	H_2O_2	10a	4.5	98	98 (2R,3S)
2	CS_2CO_3	H_2O_2	10b	4.5	98	99 (2R,3S)
3	CS_2CO_3	NaOCl	10a	5.5	95	91 (2R,3S)
4	CS_2CO_3	NaOCl	10b	5.5	95	94 (2R,3S)
5	CS_2CO_3	PMS ^d	10a	12.5	85	84 (2R,3S)
6	CS_2CO_3	PMS ^d	10b	12.5	85	86 (2R,3S)
7	CS_2CO_3	APS ^d	10a	14.5	80	83 (2R,3S)
8	CS_2CO_3	APS ^d	10b	14.5	80	87 (2R,3S)
9	K ₂ CO ₃	H_2O_2	10a	5.0	93	95 (2R,3S)
10	K ₂ CO ₃	H_2O_2	10b	5.0	93	97 (2R,3S)
11	K ₂ CO ₃	NaOCl	10a	7.0	90	90 (2R,3S)
12	K ₂ CO ₃	NaOCl	10b	7.0	90	93 (2R,3S)
13	K ^t OBu	H_2O_2	10a	6.0	86	83 (2R,3S)
14	K ^t OBu	H_2O_2	10b	6.0	86	86 (2R,3S)
15	K ^t OBu	NaOCl	10a	9.0	82	82 (2R,3S)
16	K ^t OBu	NaOCl	10b	9.0	82	85 (2R,3S)
17	КОН	H_2O_2	10a	7.0	70	73 (2R,3S)
18	КОН	H_2O_2	10b	7.0	70	78 (2R,3S)
19	КОН	NaOCl	10a	9.5	65	73 (2R,3S)
20	КОН	NaOCl	10b	9.5	65	75 (2R,3S)
21	NaOH	H_2O_2	10a	10.0	62	71 (2R,3S)
22	NaOH	H_2O_2	10b	10.0	62	73 (2R,3S)
23	NaOH	NaOCl	10a	11.5	60	36 (2R,3S)
24	NaOH	NaOCl	10b	11.5	60	36 (2R,3S)

^a Isolated yield of purified materials.

^b Enantiomeric excess of 4 was determined by HPLC analysis using a chiral column (chiral cell OD-H) with hexane: IPA as an eluent.

^c The absolute configuration of 4 was determined to be (2R,3S) by comparison with the HPLC retention time using known literature data [21].

^d PMS – potassium peroxy monosulphate, APS – ammonium peroxysulphate.



Fig. 2. A schematic representation for the catalyst decomposition studies.

assembly between the substrates such as chalcone **3** and CMPTC's. The formation of higher epoxidation yield (Table 2, entries 1–24, Table 3, entries 1–14 and Table 5, entries 1–10) and its ee's of each reaction catalyzed by C_9 (O) protected CMPTCs would be mainly attributed to an effective contact of ion-pair formed between the positive quaternary onium ions (R_4N^+) of the respective CMPTC's

with enolate anion of the chalcones due to electrostatic attraction (Fig. 4c). The results also suggested that apart from the ionic interaction between the catalyst and substrates, there is also a π - π stacking interaction between the benzyl group of the respective C₉ (O) protected CMPTCs with aryl group of the chalcone derivatives which would further facilitate the binding of the two species

Effect of various solvents on asymmetric epoxidation reaction.

	$\begin{array}{c} \text{CMPTCs (10, 3 mol\%)} \\ \text{H}_2\text{O}_2 \\ \text{Solvents, 10\% Cs}_2\text{CO}_3 \\ \text{RT} \end{array}$		1		
Entry	Solvents	Catalyst	Time (h)	Yield (%) ^a	% of ee ^b (Abs.Conf.) ^c
1	Toluene	10a	4.5	98	98 (2R,3S)
2	Toluene	10b	4.5	98	99 (2R,3S)
3	Cyclohexane	10a	5.0	95	96 (2R,3S)
4	Cyclohexane	10b	5.0	95	97 (2R,3S)
5	Benzene	10a	5.5	93	92 (2R,3S)
6	Benzene	10b	5.5	93	95 (2R,3S)
7	1,4-dioxane	10a	6.5	85	90 (2R,3S)
8	1,4-dioxane	10b	6.5	85	94 (2R,3S)
9	THF	10a	8.0	80	82 (2R,3S)
10	THF	10b	8.0	80	85 (2R,3S)
11	DMF	10a	9.0	78	73 (2R,3S)
12	DMF	10b	9.0	78	78 (2R,3S)
13	Acetonitrile	10a	8.5	75	71 (2R,3S)
14	Acetonitrile	10b	8.5	75	75 (2R,3S)

^a Isolated yield of purified materials.

^b Enantiomeric excess of 4 was determined by HPLC analysis using a chiral column (chiral cell OD-H) with hexane: IPA as a solvent.

^c The absolute configuration of 4 was determined to be (2R,3S) by comparison with the HPLC retention time using known literature data [21].



Fig. 3. Plot of enantiomeric excess (ee) against polarity (E_T30) for solvent variations. (a) Using C₉ free –OH containing CMPTC 10a. (b) Using C₉ (O) protected CMPTC 10b.

Table 4

Optimization of asymmetric epoxidation reaction in various conditions.

	$\begin{array}{c} CMPTCs (10, 3 \text{ m} \\ H_2O_2 \\ \hline Toluene, 10\% \text{ Cs} \\ Temperature \end{array}$	$2^{2}CO_{3}$ 4	J_CI		
Entry	Catalyst	Condition	Time (h)	Yield (%) ^a	% of ee ^b (Abs.Conf.) ^c
1	10a	US ^d	3.5	93	82 (2R,3S)
2	10b	US ^d	3.5	93	84 (2R,3S)
3	10a	55 °C	8.0	90	71 (2R,3S)
4	10b	55 °C	8.0	90	75 (2R,3S)
5	10a	−10 °C	10.0	92	85 (2R,3S)
6	10b	−10 °C	10.0	92	89 (2R,3S)
7	10a	RT	4.5	98	98 (2R,3S)
8	10b	RT	4.5	98	99 (2R,3S)

^a Isolated yield of purified materials.

^b Enantiomer excess of 4 was determined by HPLC analysis using a chiral column (chiral cell OD-H) with hexane: IPA as a solvent.

^c The absolute configuration of 4 was determined to be (2R,3S) by comparison with the HPLC retention time using known literature data [21].

^d Ultrasonication.

	$\begin{array}{c} CMPTCs (\\ H_2O_2 \\ \hline \\ Cl \end{array} \\ \hline \\ \hline \\ Tolune, 10\% 0 \\ RT \end{array}$	$(10) \qquad 0 \qquad * \qquad \\ (2s_2CO_3) \qquad (10) $.ci		
Entry	Catalyst	Mol% of Catalyst	Time (h)	Yield (%) ^a	% of ee ^b (Abs.Conf.) ^c
1	10a	1	7.0	92	90 (2R,3S)
2	10a	3	4.5	98	98 (2R,3S)
3	10a	5	4.0	97	96 (2R,3S)
4	10a	10	6.0	85	87 (2R,3S)
5	10a	15	6.0	82	84 (2R,3S)
6	10b	1	7.0	92	92 (2R,3S)
7	10b	3	4.5	98	99 (2R,3S)
8	10b	5	4.5	97	97 (2R,3S)
9	10b	10	6.0	85	89 (2R,3S)
10	10b	15	6.0	82	85 (2R,3S)

The asymmetric epoxidation of chalcone 3 under various concentration of CMPTCs 10 (10a/10b).

^a Isolated yield of purified materials.

^b Enantiomeric excess of 4 was determined by HPLC analysis using a chiral column (chiral cell OD-H) with hexane:IPA as a solvent.

^c The absolute configuration of 4 was determined to be (2R,3S) by comparison with the HPLC retention time using known literature data [21].



Fig. 4. Formation of various intermediates/molecular assemblies during enantioselective epoxidation reaction using C₉ free –OH and C₉ (O) protected CMPTCs.

(Fig. 5a). This in turn shows to facilitate effective ion-pair interaction and thus effect for parallel increasing of yield and ee than their corresponding CMPTCs containing C_9 free –OH in H_2O_2 as an oxidant. While the decreased epoxidation product yield and ee's noticed in C_9 free –OH of cinchonidine CMPTCs (Table 2, entries 1–24, Table 3, entries 1–14 and Table 5, entries 1–10) are due to the formation of the hydrogen bond between the reactant **3** and the free hydroxyl group present at C_9 free –OH position of the CMPTCs (Fig. 4a).

The asymmetric epoxidation reaction was carried from the different chalcone derivatives under identical reaction conditions. There is no influence on the chemical yield as well as the ee's in presence of electron releasing or electron withdrawing groups present on the phenyl ring of the chalcone (Table 6). Aromatic group substituted chalcone derivatives have better yields and ee's than the aliphatic group containing chalcones [(Ar¹ or Ar²), (Table 6, entries 17–20)], this may be due to the π - π interaction is more between the quinoline part of the catalysts and aryl group of the chalcones (Ar^1 and Ar^2 = Aryl) and hence, increase the ion pair interaction between the enolate anion and R_4N^+ of the catalysts (Table 6, entries 1–20)

Additional, from the observed results, allyl protected catalyst **10b** has more efficient than the free C_9 –OH containing catalyst **10a** (Table 6, entries 1–16) due to the allyl protected catalyst has more binding with the chalcone and oxidants. In the case of **10a** as a CMPTC, hydrogen bonding between the enolate anion of the chalcone with the C_9 -OH of the catalyst which can prevent the perfect ion pair interaction between the catalyst and anion of the chalcones, hence we got moderate yield as well as the ee's (Fig. 4b).

Based on this results, we proposed plausible transition state of the catalytic asymmetric epoxidation (Fig. 5a). The chalcone is located between the two cinchona units in **10a** and **10b**. The β -phenyl group of chalcone has a π - π stacking interaction with one of the quinoline moieties. The carbonyl oxygen atom is placed as close to the N⁺ center as permitted by van der Waals forces. The other R₄N⁺ center is ion paired with the hydrogen peroxide



Fig. 5. (a) Formation of π - π interaction between the spacer chain (aromatic) of all the CMPTCs with aromatic ring of the chalcones. (b) C_2 -symmetric *trans*-cinchona bis catalysts strong binding with the enolate anion of the chalcone and peroxides due to electrostatic attraction.

Table 6
Catalytic asymmetric epoxidation of chalcone derivatives under CMPTCs conditions.

	12	CMPTCs (10a,10b) H ₂ O ₂	\rightarrow Ar ¹	Ar ²			
Ar-	AI ⁻ Tolue	ene, 10% aq. Cs ₂ CO ₃					
3		RT (4.5 h)	4				
Entry	Enone	Ar ¹	Ar ²	Catalyst	Product ^a	Yield (%) ^b	% of ee ^c (Abs.Conf.) ^d
1	3a	Ph	4-OMe-C ₆ H ₄	10a	4a	95	97 (2R,3S)
2	3a	Ph	4-OMe-C ₆ H ₄	10b	4a	95	98 (2R,3S)
3	3b	Ph	4-CH3-C6H4	10a	4b	94	92 (2R,3S)
4	3b	Ph	4-CH3-C6H4	10b	4b	94	94 (2R,3S)
5	3c	Ph	4-Cl- C ₆ H ₄	10a	4c	98	98 (2R,3S)
6	3c	Ph	4-Cl- C ₆ H ₄	10b	4c	98	99 (2R,3S)
7	3d	Ph	4-NO2- C6H4	10a	4d	92	95 (2R,3S)
8	3d	Ph	4-NO2- C6H4	10b	4d	92	96 (2R,3S)
9	3e	$4-Br-C_6H_4$	4-OMe-C ₆ H ₄	10a	4e	93	94 (2R,3S)
10	3e	$4-Br-C_6H_4$	4-OMe-C ₆ H ₄	10b	4e	93	96 (2R,3S)
11	3f	$4-Br-C_6H_4$	4-CH3-C6H4	10a	4f	90	95 (2R,3S)
12	3f	$4-Br-C_6H_4$	4-CH3-C6H4	10b	4f	90	97 (2R,3S)
13	3g	$4-Br-C_6H_4$	4-Cl- C ₆ H ₄	10a	4g	97	92 (2R,3S)
14	3g	$4-Br-C_6H_4$	4-Cl- C ₆ H ₄	10b	4g	97	93 (2R,3S)
15	3h	$4-Br-C_6H_4$	4-NO2- C6H4	10a	4h	95	94 (2R,3S)
16	3h	$4-Br-C_6H_4$	4-NO2- C6H4	10b	4h	95	95 (2R,3S)
17	3i	CH ₃	Ph	10a	4i	90	87 (2R,3S)
18	3i	CH₃	Ph	10b	4i	90	91 (2R,3S)
19	Зј	Ph	C_2H_5	10a	4j	86	89 (2R,3S)
20	3ј	Ph	C ₂ H ₅	10b	4j	86	92 (2R,3S)

^a The asymmetric epoxidation of chalcones 3 (1eq), NaOCI (10 eq), CMPTCs 10 (10a/10b 3 mol%), with 1 mL toluene and 0.5 mL of 10 mol% KtoBu in ultrasonic conditions. ^b Isolated yield of purified materials.

^c Enantiopurity of 4 was determined by HPLC analysis using a chiral column (chiral cell OD-H) with hexane:IPA as a solvent.

^d The absolute configuration of 4 was determined to be (2R,3S) by comparison of the HPLC retention time with known literature data [21].

ion through hydrogen bonding with the oxygen of C_9 free –OH containing ammonium salt. As a consequence, hydrogen peroxide can only approach the β carbon atom of chalcone from the upside in the 1, 4-addition to afford the α S and β R isomer of **10**, which is in very good agreement with the observed results. Cinchona alkaloid catalysts **10a** and **10b** have C₂-symmetric type of catalysts. Hence, the two cinchona units should present at the end of the 4,4'-sulfonylbis(methyl) benzene due to steric hindrance of the guinoline mojety of the cinchona alkaloids. Hence the 4.4'sulfonylbis(methyl) benzene catalysts (10a and 10b) can strongly binding with the two equivalence of the enolate anion of the chalcones (Fig. 5b) simultaneously and hence we found higher yield and ee's at lower concentration of catalysts, oxidant, base and lesser time (Table 1-6).

4. Conclusion

In summary, we reported a highly enantioselective asymmetric epoxidation for α,β - unsaturated ketones using easily obtained cinchona based chiral phase transfer catalyst 10 (10a and 10b) as a catalyst and H₂O₂ as an oxidant. High yields (up to 98%) and excellent enatioselectivity (up to 99%) have been obtained for a number of substrates with different electron donating and withdrawing groups are present. The asymmetric epoxidation reactions were performed with a simple and mild protocol without any protection and additional treatment, so an impressive breakthrough was achieved for asymmetric epoxidation for α , β -unsaturated ketones.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2015.08. 016.

References

- [1] T. Ooi, K. Maruoka, Angew, Chem. Int. Ed. 46 (2007) 4222–4266.
- [2] S. Shirakawa, K. Maruoka, Angew. Chem. Int. Ed. 52 (2013) 4312-4348.
- [3] T. Hashimoto, K. Maruoka, Chem. Rev. 107 (2007) 5657–5682.

- [4] C. Hofstetter, P.S. Wilkinson, T.C. Pochapsky, J. Org. Chem. 64 (1999) 8794-8800
- S.S. Jew, M.S. Yoo, B.S. Jeong, I.Y. Park, H.G. Park, Org. Lett. 4 (2002) 4245-4248.
- B. Lygo, B.I. Andrews, J. Crosby, J.A. Peterson, Tetrahedron Lett. 43 (2002) [6] 8015-8018
- P.I. Dalko, L. Moisan, Angew. Chem. Int. Ed. 43 (2004) 5138-5175.
- [8] P.I. Dalko, L. Moisan, Angew. Chem. Int. Ed. 40 (2001) 3726-3748.
- [9] L. Jiang, Y.C. Chen, Catal. Sci. Technol. 1 (2011) 354-365.
- [10] O.A. Wong, Y. Shi, Chem. Rev. 108 (2008) 3958-3987.
- Q.H. Xia, H.Q. Ge, C.P. Ye, Z.M. Liu, K.X. Su, Chem. Rev. 105 (2005) 1603-1662. [11]
- [12] P.J. Walsh, H. Li, C.A.D. Parrodi, Chem. Rev. 107 (2007) 2503-2545
- [13] O. Lifchits, C.M. Reisinger, B. List, J. Am. Chem. Soc. 132 (2010) 10227–10229.
- [14] Y. Nishikawa, H. Yamamoto, J. Am. Chem. Soc. 133 (2011) 8432-8435. [15] A. Mako, Z. Rapi, G. Keglevich, A. Szollosy, L. Drahos, L. Heged, P. Bako,
- Tetrahedron Asymmetry 21 (2010) 919-925.
- [16] K. Hori, M. Tamura, K. Tani, N. Nishiwaki, M. Ariga, Y. Tohda, Tetrahedron Lett. 47 (2006) 3115-3118
- [17] J. Ye, Y. Wang, R. Liu, G. Zhang, Q. Zhang, J. Chen, X. Liang, Chem. Commun. (2003) 2714-2715.
- [18] K.J. Bartelson, L. Deng, Chem. Sci. 2 (2011) 1301-1304.
- [19] S.S. Jew, J.H. Lee, B.S. Jeong, M.S. Yoo, M.J. Kim, Y.J. Lee, J. Lee, S.H. Choi, K. Lee, M.S. Lah, H.G. Park, Angew. Chem. Int. Ed. 44 (2005) 1383-1385.
- [20] S.S. Jew, H.G. Park, Chem. Commun. (2009) 7090-7103.
- [21] J. Lu, Y.H. Xu, F. Liu, T.P. Loh, Tetrahedron Lett. 49 (2008) 6007-6008.
- [22] J.W. Feast, W.P. Lovenich, H. Pushmann, C. Taliani, Chem. Commun. (2001) 505-506
- [23] S.A. Soomro, R. Benmouna, R. Berger, H. Meier, Eur. J. Org. Chem. (2005) 3586. [24] T. Ooi, D. Ohara, M. Tamura, K. Maruoka, J. Am. Chem. Soc. 126 (2004)
- 6844-6845. [25] V.K. Aggarwal, J.P.H. Charmant, D. Fuentes, J.N. Harvey, G. Hynd, D. Ohara, W. Picoul, R. Robiette, C. Smith, J.L. Vasse, C.L. Winn, J. Am. Chem. Soc. 128 (2006) 2105-2114.
- [26] N. Kumaraswamy, M.N.V. Jena, G. Sastry, K. Venkata Rao, J. Mol. Catal. A Chem. 230 (2005) 59-67
- [27] J. Lv, X. Wang, J. Liu, L. Zhang, Y. Wang, Tetrahedron Asymmetry 17 (2006) 330-335.
- [28] H. Jin, H. Zhao, F. Zhao, S. Li, W. Liu, G. Zhou, K. Tao, T. Hou, Ultrason. Sonochem. 16 (2009) 304-307.
- [29] Y. Zhu, Q. Wang, R.G. Cornwall, Y. Shi, Chem. Rev. 114 (2014) 8199-8256. [30] R.L. Davis, J. Stiller, T. Naicker, H. Jiang, K.A. Jørgensen, Angew. Chem. Int. Ed.
- 53 (2014) 7406-7426. [31] S.S. Jew, J.H. Lee, B.S. Jeong, M.S. Yoo, M.J. Kim, Y.J. Lee, J. Lee, S.H. Choi, K. Lee, M.S. Lah, H. Park, Angew. Chem. Int. Ed. 44 (2005) 1383-1385.
- [32] M.S. Yoo, D.G. Kim, M.W. Ha, S.S. Jew, H.G. Park, B.S. Jeong, Tetrahedron Lett. 51 (2010) 5601-5603.
- [33] C. Zeng, D. Yuan, B. Zhao, Y. Yao, Org. Lett. 17 (2015) 2242-2245.
- [34] K. Li, J. Qu, B. Xu, Y. Zhou, L. Liu, P. Peng, W. Tian, New J. Chem. 33 (2009) 2120-2127.
- [35] A. Jesin Beneto, J. Sivamani, V. Ashokkumar, R. Balasaravanan, K. Duraimurugan, A. Siva, New J. Chem. 39 (2015) 3098-3104.
- [36] J. Sivamani, K. Duraimurugan, A. Jesin Beneto, P. Subha, R. Balasaravanan, A. Siva. Svnlett. 25 (2014) 1685-1691.
- O. McConville, J. Saidi, J. Blacker, J. Org. Chem. 74 (2009) 2692-2698. [37]
- [38] X. Zhou, X. Li, W. Zhang, J. Chen, Tetrahedron Lett. 55 (2014) 5137–5140.
 [39] A. Lattanzi, Org. Lett. 7 (2005) 2579–2582.
- [40] H. Wang, Z. Wang, K. Ding, Tetrahedron Lett. 50 (2009) 2200–2203.
 [41] M.J. O'Donnell, S. Wu, J.C. Huffman, Tetrahedron 50 (1994) 4507–4518.
- [42] Y. Moussaoui, K. Said, R.B. Salem, ARKIVOC 12 (2006) 1–22.
- [43] K. Gupta, S. Naithani, Curr. Sci. 58 (1989) 1016-1018.