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A novel *N*-acetophenone cinchona ammonium salts as chiral phase transfer catalysts for the alkylation of Schiff base in water

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Abstract

Novel *N*-acetophenone cinchona ammonium salts have been successfully synthesized and used as chiral phase transfer catalysts for the asymmetric alkylation of *tert*-butyl benzophenone Schiff base derivatives in aqueous media at room temperature with the highest ee and yield up to 96 and 98%, respectively. We have also studied the influence of substituted acetophenone groups in quaternary ammonium salts derived from the cinchona alkaloids.

Keywords: Asymmetric alkylation; Cinchona alkaloid; Schiff base

1. Introduction

Chiral phase transfer catalysis (CPTC) is a very useful approach that typically involves simple experimental operations, mild reaction conditions, inexpensive and environmentally benign reagents and large-scale reaction [1–3]. The CPTC methodology has been applied to Michael addition [4,5], Darzen reaction [6–11], cyclopropanation [12], aldol condensation [13–15], fluorination [16–18], epoxidation [19–21], alkylation, etc.

Among these, asymmetric alkylation of *tert*-butyl benzophenone Schiff base derivatives **1** has received much attention and been successfully applied to the enantioselective synthesis of natural and unnatural amino acids (Scheme 1) [22–25]. In 1989, O'Donnell reported [26] that *N*-benzyl derivatives of the cinchona alkaloids could catalyze the process (Fig. 1). Later the same group [27] demonstrated that *N*-benzyl-*O*-alkyl cinchona alkaloids derivatives generated in the reactions could lead to remarkably higher enantiomeric excess [28–31]. Finally, the third generation of catalysts was reported in 1997 independently by Lygo et al. and Corey et al., who used the bulky *N*-methylanthracenyl group instead of the benzyl group, attaining substantially impoved ee. Recently, dimeric [32] and trimeric [33] cinchona alkaloid derivatives, guanidinium salts [34], C_2-symmetic ammonium salts derived from BINOL [35–37], phosphonium salts [38,39], TADDOL [40,41], tartaric derivatives [42], and other metal catalysts [43–47] have emerged as powerful variants.

Recently, polymer supported CPTCs have been widely used for asymmetric alkylation [48–54]. Our group was one of the pioneers of this research field. We anchored cinchona alkaloids to cross-linked polystyrene for the asymmetric alkylation of *tert*-butyl benzophenone Schiff base derivatives [55,56], although the enatioselectivity was not satisfactory. Subsequently, we successfully synthesized the dimeric cinchonine, which was *N*-anchored to a long linear PEG chain, and investigated asymmetric epoxidation of chalcones [57] and alkylation of *tert*-butyl benzophenone Schiff base derivatives catalyzed by this novel polymer supported-PTC in aqueous media.

Due to environmentally desirable media such as chlorinated solvents and moderate temperatures were often needed to achieve high reactivity and enantioselectivity, the asymmetric alkylation of *tert*-butyl benzophenone Schiff base derivatives could proceed in aqueous media catalyzed by the *N*-alkyl cinchonine prepared by the Corey's method was reported [58]. Unfortunately, the enantioselectivities were not satisfactorily catalyzed by the other CPTCs they used. It also indicated that the new methodology was not applicable to all kinds of CPTCs.

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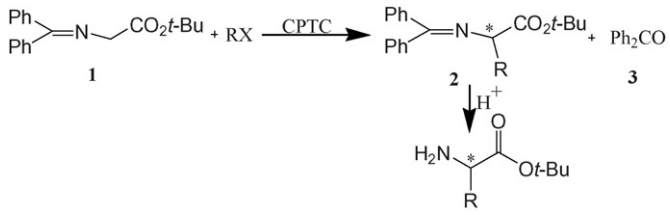
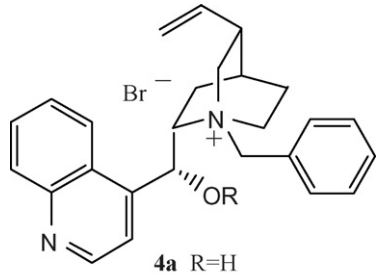
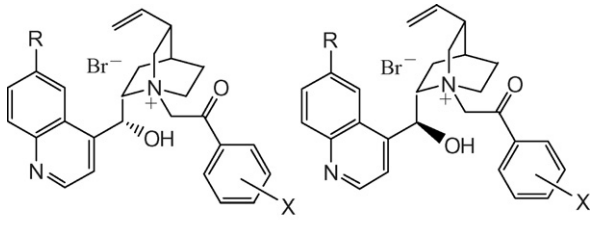


Scheme 1. Alkylation of *tert*-butyl benzophenone Schiff base derivative.



4a R=H
4b R=allyl

Fig. 1. Different types of CPTCs synthesized from cinchona alkaloids.



5 R=OCH_3, X=H;
6 R=OCH_3, X=4-Br;
7 R=OCH_3, X=4-Cl;
8 R=OCH_3, X=3-NO_2;
9 R=OCH_3, X=4-NO_2;
10 R=H, X=4-NO_2

11 R=H, X=4-NO_2

Fig. 2. Different CPTCs synthesized from cinchona alkaloids.

Since we have employed the new methodology where the alkylation could be carried out in water with PEG-supported cinchona alkaloids to afford high chemical yields and enatioselectivities, we desiderated a non-supported catalyst that can be used for the reaction in water with high catalytic efficiency. Moreover, the stringent basic reaction condition, which was reported for asymmetric alkylation previously, was not environmentally acceptable and could also affect the stability of the catalyst. Therefore, we laid a strong emphasis on the research of high efficient catalyst and mild reaction condition in the enantioselective synthesis of α-amino acid precursors. Finally, we successfully synthesized a novel *N*-acetophenone cinchona ammonium salt, which can be easily prepared by one step from cinchona alkaloids with the corresponding α-bromoacetophenone derivatives (Fig. 2). Further, we attempted the alkylation reaction catalyzed by our newly synthesized CPTCs in aqueous media.

2. Experimental

2.1. Materials

Commercial reagents were used as received, unless otherwise stated. ^{1}H NMR and ^{13}C NMR were recorded on in $CDCl_3$ either a Bruker-DPX 300 or AV-400 spectrometer using TMS as internal standard. Mass spectra were obtained using an electrospray ionization (ESI) mass spectrometer. Melting points were determined using an electrothermal apparatus and uncorrected. Optical rotations were measured with a Perkin-Elmer 341 digital polarimeter at 20 °C. HPLC analysis was performed on a Shimadzu CTO-10AS chromatograph using Chiral OD-H purchased from Daicel Chemical Industries, Ltd.

2.2. Synthesis of quinium-N-acetophenone bromide (CPTC-*5*)

A mixture of quinine (1.62 g, 5 mmol) with 2-bromo-1-phenyl-ethanone (1.00 g, 5 mmol) in acetone (20 mL) was refluxed for 6 h. After cooling the reaction mixture to room temperature, the resulting supension was diluted with methanol (10 mL) and ether (30 mL) and stirred for 1 h. The solids were filtered, washed with ether. The crude solid was recrystallized from methanol-ether to afford 2.09 g (80% yield) of desired product as a light red solid. mp 176–178 °C; $[\alpha]_D^{20} = -103$ ($c = 0.1$, ethanol); IR (KBr): $\nu = 3445.1, 2953.3, 2983.2, 1620.4, 1559.3, 1450.4, 1024.1, 917.3, 832.6\ cm^{-1}$; ^{1}H NMR (300 MHz, DMSO-d_6): δ: 8.91 (d, $J = 4.5$ Hz, 1H), 8.04–8.00 (m, 2H), 7.89 (d, $J = 15.6$ Hz, 2H), 7.54–7.46 (m, 5H), 7.20 (s, 1H), 6.38 (d, $J = 7.5$ Hz, 1H), 5.91–5.80 (m, 1H), 5.35 (d, $J = 17.4$ Hz, 1H), 5.17 (d, $J = 10.5$ Hz, 1H), 4.60–4.58 (m, 1H), 4.43–4.38 (m, 1H), 4.27–4.23 (m, 1H), 3.98 (s, 3H), 3.83–3.71 (m, 2H), 2.86–2.79 (m, 2H), 2.01–1.99 (m, 2H), 1.80–1.78 (m, 1H), 1.59–1.56 (m, 1H), 1.21–0.96 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): 194.1, 158.5, 148.1, 144.4, 144.0, 139.0, 135.8, 134.8, 132.3, 129.7, 129.3, 126.0, 125.6, 121.1, 116.3, 101.5, 66.0, 63.6, 60.8, 57.8, 56.7, 37.3, 26.0, 25.5, 22.1. MS (ESI): Calc. 523.5, found 444.1 $[C_{28}H_{31}N_2O_3]^+$; $C_{28}H_{31}N_2O_3Br$: Calc. Value-C 64.25, H 5.97, N 5.35; found-C 64.17, H 5.85, N 5.46.

2.3. Synthesis of 4-Br-quinium-N-acetophenone bromide (CPTC-*6*)

A procedure similar to that for the synthesis of **5** was performed as described above. Yield: 70%; mp 180–182 °C; $[\alpha]_D^{20} = -85$ ($c = 0.1$, ethanol); IR (KBr) $\nu = 3414.2, 3147.5, 2939.3, 2360.4, 1687.4, 1619.1, 1586.2, 1507.1, 1469.6, 1397.4, 1239.3, 1024.7, 997.9, 860.5, 837.7\ cm^{-1}$; ^{1}H NMR (400 MHz, DMSO-d_6): δ: 8.76 (d, $J = 4$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 2H), 7.96–7.87 (m, 3H), 7.71 (d, $J = 4.0$ Hz, 1H), 7.42 (d, $J = 9.2$ Hz, 1H), 7.11 (s, 1H), 5.81–5.67 (m, 3H), 5.14–5.36 (dd, $J_1 = 17.6$, $J_2 = 10$ Hz, 1H), 5.50–5.41 (dd, $J_1 = 10.0$, $J_2 = 10.4$ Hz, 1H), 4.59 (d, $J = 10.0$ Hz, 2H), 4.21–4.18 (m, 1H), 4.07 (s, 3H), 3.85–3.72 (m, 2H), 3.32 (d, $J = 8.8$ Hz, 2H), 2.87 (s, 1H), 2.11–1.92 (m, 4H), 1.18–0.96 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ: 193.4, 158.4, 148.1, 144.3, 141.1, 139.0, 133.9, 132.8, 131.3, 130.1, 129.1, 126.0, 122.7, 121.1, 116.2, 101.6, 65.9, 63.5, 60.7, 57.6, 56.8, 37.3, 31.4, 26.0, 25.5, 22.1; MS (ESI): Calc. 602.4, found 521.5 $[C_{28}H_{30}N_2O_3Br]^+$; $C_{28}H_{30}N_2O_3Br_2$: Calc. Value-C 55.83, H 5.02, N 4.65; found-C 55.76, H 5.41, N 5.70.

2.4. Synthesis of 4-Cl-quinium-N-acetophenone bromide (CPTC-7)

A procedure similar to that for the synthesis of **5** was performed as described above. Yield: 72%; mp 174–176 °C; $[\alpha]_D^{20} = 82$ ($c = 0.1$, ethanol); IR (KBr) $\nu = 3414.0$, 3125.8, 2360.1, 1638.9, 1400.1, 1262.1, 1084.3, 871.9, 800.2 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ: 8.76 (d, $J = 4.4$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 2H), 7.95 (d, $J = 9.2$ Hz, 1H), 7.75–7.71 (m, 3H), 7.44–7.41 (m, 1H), 7.12 (s, 1H), 5.81–5.64 (m, 3H), 5.21 (d, $J = 17.2$ Hz, 1H), 5.01 (d, $J = 10.4$ Hz, 1H), 4.63–4.58 (m, 2H), 4.22–4.19 (m, 1H), 4.07 (s, 3H), 3.85–3.74 (m, 2H), 3.11 (s, 2H), 2.87 (s, 1H), 2.12–2.05 (m, 4H), 1.08–1.06 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ: 193.2, 158.4, 148.1, 144.4, 144.1, 140.8, 139.0, 133.6, 131.3, 129.8, 126.0, 122.7, 121.1, 116.2, 101.6, 65.9, 63.5, 60.7, 57.8, 56.8, 37.3, 31.4, 26.0, 26.5, 22.1; MS (ESI): Calc. 557.9, found: 477.5 $[C_{28}H_{30}ClN_2O_3]^+$; $C_{28}H_{30}N_2O_3BrCl$: Calc. Value-C 60.28, H 5.42, N 5.02; found-C 60.41, H 5.41, N 5.50.

2.5. Synthesis of 3-NO_2-quinium-N-acetophenone bromide (CPTC-8)

A procedure similar to that for the synthesis of **5** was performed as described above. Yield: 70%; mp 225–227 °C; $[\alpha]_D^{20} = -83$ ($c = 0.1$, ethanol); IR (KBr): 3447.8, 3373.6, 2970.6, 2360.5, 1642.8, 1589.6, 1508.9, 1487.7, 1437.2, 1243.2, 1094.4, 936.5, 893.4, 840.7 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ: 8.94 (d, $J = 4.5$ Hz, 1H), 8.90–8.79 (m, 1H), 8.58–8.65 (t, $J = 8.4$ Hz, 1H), 8.41–8.32 (dd, 1H, $J_1 = 7.8$, $J_2 = 8.7$ Hz), 8.05–7.97 (m, 1H), 7.88–7.74 (m, 2H), 7.50–7.47 (m, 1H), 7.24–7.16 (m, 1H), 6.43 (d, $J = 7.5$ Hz, 1H), 5.95–5.58 (m, 2H), 5.40–5.04 (m, 3H), 4.60–4.01 (m, 2H), 4.12 (s, 1H), 4.00 (s, 3H), 3.35 (m, 2H), 2.88–2.82 (m, 2H), 2.16–2.14 (m, 1H), 2.01–2.02 (m, 1H), 1.47–1.24 (m, 1H), 1.00–1.25 (m, 1H), 0.96–0.98 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ: 192.7, 159.6, 148.6, 145.5, 144.1, 140.9, 138.9, 136.2, 135.5, 133.4, 132.3, 131.5, 130.9, 129.6, 126.3, 124.3, 119.7, 116.8, 101.4, 65.7, 62.8, 61.0, 57.4, 56.6, 53.8, 37.6, 26.2, 24.9, 22.4; MS (ESI): Calc. 568.5, found: 488.4 $[C_{28}H_{30}N_3O_5]^+$; $C_{28}H_{30}N_3O_5Br$: Calc. Value-C 59.16, H 5.32, N 7.39; found-C 58.90, H 5.74, N 7.54.

2.6. Synthesis of 4-NO_2-quinium-N-acetophenone bromide (CPTC-9)

A procedure similar to that for the synthesis of **5** was performed as described above. Yield 87%; mp 199–201 °C; $[\alpha]_D^{20} = -69$ ($c = 0.1$, DMSO). IR (KBr): 3345, 3171, 2953, 2883, 1705, 1620, 1509, 1451, 1042, 1228, 1085, 1024, 917, 832 cm^{-1}. ^1H H NMR (300 MHz, DMSO-d_6): δ: 8.93 (d, $J = 4.8$ Hz, 1H), 8.37 (d, $J = 8.7$ Hz, 2H), 8.19 (d, $J = 8.7$ Hz, 2H), 8.06–8.02 (m, 2H), 7.51–7.47 (dd, $J_1 = 2.4$, $J_2 = 1.2$ Hz, 1H), 7.23 (d, $J = 2.1$ Hz, 1H), 6.42 (d, $J = 7.5$ Hz, 1H), 5.93–5.57 (m, 1H), 5.18 (d, $J = 10.8$ Hz, 1H), 4.69–4.65 (m, 1H), 4.56 (d, $J = 13.5$ Hz, 1H), 4.36 (d, $J = 13.5$ Hz, 1H), 4.00 (s, 3H), 3.84–3.81 (m, 2H), 3.35 (s, 4H), 2.88–2.82 (m, 2H), 1.83 (br, 1H), 1.60–1.57 (m, 1H), 1.23–1.19 (m, 1H), 1.00–0.97 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ: 192.7, 159.0, 150.2, 148.4, 144.1, 140.9, 138.8, 132.3, 128.5, 126.3, 124.2, 123.0, 119.9, 116.8, 101.4, 65.7, 62.8, 61.0, 57.3, 37.5, 26.1, 24.9, 22.3; MS (ESI): Calc. 568.5, found: 488.5 $[C_{28}H_{30}N_3O_5]^+$; $C_{28}H_{30}N_3O_5Br$: Calc. Value-C 59.16, H 5.32, N 7.39; found-C 58.79, H 5.69, N 7.48. Calc. 568.5, found: 488.5 $[C_{28}H_{30}N_3O_5]^+$; $C_{28}H_{30}N_3O_5Br$: Calc. Value-C 59.16, H 5.32, N 7.39; found-C 58.79, H 5.69, N 7.48.

2.7. Synthesis of 4-NO_2-cinchonidium-N-acetophenone bromide (CPTC-10)

A mixture of cinchonidine (1.47 g, 5 mmol) with 2-bromo-4′-NO_2-1-phenyl-ethanone (1.21 g, 5 mmol) in ethanol (20 mL) was refluxed for 6 h. After cooling the reaction mixture to room temperature, the resulting supension was diluted with methanol (10 mL) and ether (30 mL) and stirred for 1 h. The solids were filtered, and washed with ether. The crude solid was recrystallized from methanol-ether to afford 2.09 g (80% yield) of desired product as a light yellow solid. mp 186–188 °C; $[\alpha]_D^{20} = -36$ ($c = 0.1$, ethanol). IR (KBr): 3442.0, 3148.6, 2360.4, 1703.8, 1600.8, 1523.8, 1463.7, 1348.9, 1219.4, 1037.3, 930.3, 856.1, 775.9, 759.4 cm^{-1}; ^1H NMR (300 MHz, DMSO): δ: 8.97 (d, $J = 4.5$ Hz, 1H), 8.38 (d, $J = 8.7$ Hz, 2H), 8.20 (d, $J = 8.7$ Hz, 2H), 8.14–8.12 (m, 2H), 7.73 (d, $J = 4.5$ Hz, 1H), 7.42 (d, $J = 4.4$ Hz, 1H), 7.23–7.20 (m, 1H), 6.56 (d, $J = 7.2$ Hz, 1H), 6.02–5.91 (m, 1H), 5.28 (d, $J = 7.5$ Hz, 1H), 4.61–4.58 (m, 2H), 4.60–4.47 (m, 3H), 3.77–3.55 (m, 2H), 3.46–3.41 (m, 1H), 2.21–2.17 (m, 2H), 2.12–1.86 (m, 3H), 1.16–1.04 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ: 192.7, 151.1, 150.1, 148.2, 145.7, 142.0, 138.8, 130.9, 130.7, 130.5, 128.5, 124.2, 123.7, 119.8, 117.2, 95.1, 65.6, 63.2, 61.2, 56.9, 53.7, 37.9, 26.4, 25.0, 22.3, 19.2; MS (ESI): Calc. 538.4, found: 458.5 $[C_{27}H_{28}N_3O_4]^+$; $C_{27}H_{28}N_3O_4Br$: Calc. Value-C 60.23, H 5.24, N 7.80; found-C 59.89, H 5.39, N 7.68.

2.8. Synthesis of 4-NO_2-cinchoninium-N-acetophenone bromide (CPTC-11)

A procedure similar to that for the synthesis of **11** was performed to synthesize compound **10** from cinchonine (1.47 g, 5 mmol). Yield 71%; mp 210–212 °C(dec.); $[\alpha]_D^{20} = +63$ ($c = 0.1$, ethanol); IR (KBr): 3441.8, 3349.3, 2360.7, 1653.1, 1600.7, 1530.7, 1496.7, 1455.6, 1027.8, 759.4 cm^{-1}; ^1H NMR (300 MHz, DMSO): δ: 8.95 (d, $J = 4.5$ Hz, 1H), 8.38 (d, $J = 8.4$ Hz, 2H), 8.22 (d, $J = 8.4$ Hz, 2H), 7.82–7.56 (m, 3H), 7.29 (d, $J = 7.2$ Hz, 2H), 6.54 (d, $J = 7.2$ Hz, 1H), 6.02–5.91 (m, 1H), 5.28 (d, $J = 7.5$ Hz, 1H), 5.27–5.21 (dd, $J_1 = 17$ Hz, $J_2 = 10$ Hz, 2H), 4.81–4.72 (m, 2H), 4.60–4.43 (m, 3H), 3.77–3.51 (m, 2H), 3.46–3.41 (m, 1H), 2.82–2.80 (m, 1H), 2.12–1.86 (m, 3H), 1.07–1.05 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ: 191.9, 150.4, 147.6, 141.2, 138.9, 136.1, 130.0, 129.8, 126.7, 124.5, 124.0, 123.6, 123.2, 118.7, 116.7, 94.3, 64.9, 62.9, 61.0, 58.5, 56.8, 36.5, 26.6, 22.6, 20.8; MS (ESI): Calc. 538.4, found: 458.4 $[C_{27}H_{28}N_3O_4]^+$; $C_{27}H_{28}N_3O_4Br$: Calc. Value-C 60.23, H 5.24, N 7.80; found-C 60.68, H 5.17, N 7.61.

2.9. General procedure for asymmetric alkylation of tert-butyl benzophenone Schiff base derivative **1** under CPTC conditions

N-acetophenone cinchona ammonium salt (0.01 mmol) and *N*-(diphenylmethylene)glycine *tert*-butyl ester (59 mg, 0.2 mmol) dissolved in two milliliter 1 M aqueous potassium hydroxide solution at room temperature. After the dropwise addition of benzyl bromide (1.0 mmol), the reaction mixture was further stirred for 6 h at room temperature (determined by TLC). Then 10 mL water was added, and the resulting mixture was extracted by CH_2Cl_2 (10 mL × 3 mL). The combined organic phase was washed with water (10 mL × 2 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the crude product **2**. Further purification by column chromatography on silica gel (petroleum/ethyl acetate 30:1 as the eluent, neutralized with 1% Et_3N) afforded **2** as a colorless oil.

2.9.1. tert-Butyl 3-phenyl-2-(diphenylmethyleneamino)propanoate (2a, S)

Synthesized according to the reaction conditions listed in Table 1, entry 3. Yield 99%. $[\alpha]_D^{20} = -12.9$ ($c = 0.2$, $CHCl_3$). ee = 83%. ^{1}H NMR (300 MHz, $CDCl_3$): 7.56–7.58 (m, 2H, Ph-H), 7.26–7.38 (m, 6H, Ph-H), 7.13–7.21 (m, 3H, Ph-H), 7.04–7.06 (m, 2H, Ph-H), 6.60 (br, d, 2H, $J = 6.0$ Hz, Ph-H), 4.10 (dd, 1H, $J = 4.4$, 9.6 Hz, CHC = O), 3.23 (dd, 1H, $J = 4.4$, 13.6 Hz, $PhCH_2$), 3.15 (dd, 1H, $J = 9.6$, 13.6 Hz, $PhCH_2$), 1.44 (s, 9H, *t*-Bu) ppm. IR (KBr): 2978, 1732, 1624, 1576, 1495, 1447, 1367, 1286, 1150, 1082, 1030, 849, 756, 696 cm^{-1}. HPLC analysis: DAICEL Chiralcel OD-H, hexane/isopropyl alcohol = 99.5:0.5, flow rate = 0.5 mL/min, retention time: 16.9 min (R) and 24.1 min (S).

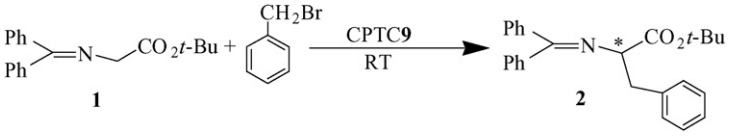
2.9.2. tert-Butyl 3-(2-methylphenyl)-2-(diphenylmethyleneamino)propanoate (2b, S)

Synthesized according to the reaction conditions listed in Table 1, entry 3. Yield 90%. $[\alpha]_D^{20} = -14.6$ ($c = 0.2$, $CHCl_3$). ee = 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.69–7.71 (m, 3H, Ph-H), 7.50–7.59 (m, 3H, Ph-H), 7.29–7.32 (m, 4H, Ph-H), 6.63–7.08 (m, 4H, Ph-H), 3.19–4.08 (dd, 1H, $J = 9.2$, 4.4 Hz, CHC=O), 3.17 (dd, 2H, $J = 13.6$, 9.2 Hz, $PhCH_2$), 2.26 (s, 3H, CH_3), 1.44 (s, 9H, *t*-Bu) ppm. IR (neat) 2972, 2927, 1732, 1621, 1511, 1444, 1367, 1286, 1151, 894, 840, 762 cm^{-1}. HPLC analysis: DAICEL Chiralcel OD-H, hexane/isopropyl alcohol = 99.5:0.5, flow rate = 0.5 mL/min, retention time: 20.7 min (R) and 29.6 min (S).

2.9.3. tert-Butyl 3-(3-methylphenyl)-2-(diphenylmethyleneamino)propanoate (2c, S)

Synthesized according to the reaction conditions listed in Table 1, entry 3. Yield 87%. $[\alpha]_D^{20} = -13.8$ ($c = 0.2$, $CHCl_3$). ee = 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.68−7.73 (m, 3H, Ph-H), 7.50–7.58 (m, 5H, Ph-H), 7.26–7.30 (m, 2H, Ph-H),

Table 1
Asymmetric alkylation of **1** with catalyst **9** in aqueous media



Entry	Base (aq. M)	Solvent (mL)	Catalyst **9** (equiv.)	BnBr (equiv.)	Yield (%)[a]	ee (%)[b] (Configuration)[c]
1	1 M KOH	2	0.05	1.2	43	63(S)
2	1 M KOH	2	0.05	2.5	72	79(S)
3	1 M KOH	2	0.05	5.0	99	86(S)
4	1 M KOH	2	0.05	10.0	98	85(S)
5	1 M KOH	5	0.05	5.0	90	79(S)
6	1 M KOH	5	0.05	10.0	91	83(S)
7	1 M KOH	5	0.1	10.0	93	81(S)
8	1 M KOH	1	0.05	10.0	88	78(S)
9	1 M KOH	1	0.05	5.0	86	76(S)
10	0.5 M KOH	2	0.05	5.0	76	76(S)
11	10 M KOH	2	0.05	5.0	97	79(S)
12	1 M KOH	2	0.01	5.0	94	82(S)
13	1 M KOH	2	0.1	5.0	96	81(S)
14[d]	1 M KOH	2	0.05	5.0	65	74(S)
15[e]	1 M KOH	2	0.05	5.0	48	68(S)
16	1 M NaOH	2	0.05	5.0	89	78(S)
17	1 M LiOH	2	0.05	5.0	81	68(S)
18	1 M K_2CO_3	2	0.05	5.0	88	65(S)

[a] The isolated yield.
[b] Enantiomeric excess was determined by HPLC analysis using a chiral column (DAICEL Chiralcel OD-H) with hexane-isopropanol (99.5:0.5) as an eluent.
[c] The absolute configuration was confirmed by comparison of the HPLC retention time of an authentic sample, which was synthesized independently by reported procedures [29].
[d] The reaction was performed at 10 °C.
[e] The reaction was perfomed at 0 °C.

7.03–7.06 (m, 2H, Ph-H), 6.56–6.61 (m, 2H, Ph-H), 4.09–4.24 (dd, 1H, J = 9.2, 4.4 Hz, CHC=O), 3.13–3.18 (dd, 2H, J = 13.6, 9.2 Hz, $PhCH_2$), 2.28 (s, 3H, CH_3), 1.44 (s, 9H, *t*-Bu) ppm; IR (neat) 2972, 2927, 1732, 1621, 1511, 1444, 1367, 1286, 1151, 894, 840, 762 cm^{-1}; HPLC analysis: DAICEL Chiralcel OD-H, hexane/isopropyl alcohol = 99.5:0.5, flow rate = 0.5 mL/min, retention time: 20.6 min (R) and 24.5 min (S).

2.9.4. tert-Butyl 3-(4-methylphenyl)-2-(diphenylmethyleneamino)propanoate (2d, S)

Synthesized according to the reaction conditions listed in Table 1, entry 3. Yield 92%. $[\alpha]_D^{20} = -15.3$ (c = 0.2, $CHCl_3$). ee = 87%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.69–7.72 (m, 1H, Ph-H), 7.50–7.60 (m, 3H, Ph-H), 7.29–7.32 (m, 4H, Ph-H), 7.03–7.05 (m, 4H, Ph-H), 6.62–6.64 (m, 2H, Ph-H), 4.07–4.13 (m, 1H, CHC=O), 3.18–3.19 (m, 2H, $PhCH_2$), 2.26 (s, 3H, CH_3),1.44 (s, 9H, *t*-Bu) ppm; IR (neat) 2978, 2928, 1735, 1624, 1516, 1447, 1367, 1286, 1151, 910, 845, 779, 696 cm^{-1}; HPLC analysis: DAICEL Chiralcel OD-H, hexane/isopropyl alcohol = 99.5:0.5, flow rate = 0.5 mL/min, retention time: 12.8 min (S) and 21.2 min (R).

2.9.5. tert-Butyl 3-(2-chlorophenyl)-2-(diphenylmethyleneamino)propanoate (2f, S)

Synthesized according to the reaction conditions listed in Table 1, entry 3. Yield 93%. $[\alpha]_D^{20} = -15.9$ (c = 0.2, $CHCl_3$). ee = 91%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.61–7.62 (m, 2H, Ph-H), 7.39–7.41 (m, 2H, Ph-H), 7.27–7.38 (m, 6H, Ph-H), 7.12–7.17 (t, 1H, J = 7.2 Hz, Ph-H), 7.04–7.06 (m, 3H, Ph-H), 4.38–4.39 (m, 1H, CHC=O), 3.47–3.48 (m, 2H, $PhCH_2$), 1.47 (s, 9H, *t*-Bu) ppm; IR (neat) 2978, 2928, 1728, 1626, 1508, 1447, 1369, 1285, 1221, 1148, 841, 781, 698 cm^{-1}; HPLC analysis: DAICEL Chiralcel OD-H, hexane/isopropyl alcohol = 99.5:0.5, flow rate = 0.5 mL/min, retention time: 15.6 min (R) and 17.8 min (S).

2.9.6. (S)-tert-Butyl 3-(3-chlorophenyl)-2-(diphenylmethyleneamino)propanoate (2g, S)

Synthesized according to the reaction conditions listed in Table 1, entry 3. Yield 89%. $[\alpha]_D^{20} = -16.3$ (c = 0.2, $CHCl_3$). ee = 91%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57–7.60 (m, 2H, Ph-H), 7.36–7.56 (m, 6H, Ph-H), 7.12–7.14 (m, 2H, Ph-H), 6.91–7.07 (m, 2H, Ph-H), 6.66–6.68 (m, 2H, Ph-H), 4.11–4.13 (m, 1H, CHC=O), 3.19–3.21 (m, 2H, $PhCH_2$), 1.46 (s, 9H, *t*-Bu) ppm; IR (neat) 2974, 2921, 1726, 1624, 1506, 1447, 1369, 1286, 1148, 865, 787, 742 cm^{-1}; HPLC analysis: DAICEL Chiralcel OD-H, hexane/isopropyl alcohol = 99.5:0.5, flow rate = 0.5 mL/min, retention time: 14.8 min (S) and 21.8 min (R).

2.9.7. tert-Butyl 3-(4-chlorophenyl)-2-(diphenylmethyleneamino)propanoate (2h, S)

Synthesized according to the reaction conditions listed in Table 1, entry 3. Yield 98%. $[\alpha]_D^{20} = -16.2$ (c = 0.2, $CHCl_3$). ee = 96%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.60–7.62 (m, 2H, Ph-H), 7.25–7.36 (m, 6H, Ph-H), 7.16 (d, 2H, J = 8.0 Hz, Ph-H), 7.04 (d, 1H, J = 8.0 Hz, Ph-H), 6.63 (m, 3H, Ph-H), 4.48 (m, 1H, CHC=O), 3.48–3.69 (m, 2H, $PhCH_2$), 1.45 (s, 9H, *t*-Bu) ppm; IR (neat) 2978, 1732, 1661, 1622, 1560, 1437, 1369, 1286, 1148, 841, 787, 698 cm^{-1}; HPLC analysis: DAICEL Chiralcel OD-H, hexane/isopropyl alcohol = 99.5:0.5, flow rate = 0.5 mL/min, retention time: 12.1 min (S) and 21.1 min (R).

2.9.8. tert-Butyl 3-(2-allyl)-2-diphenylmethyleneamino)propanoate (2j, S)

Synthesized as Section 2.9 according to the reaction conditions listed in Table 1, entry 3. Yield 79%. $[\alpha]_D^{20} = -11.3$ (c = 0.2, $CHCl_3$). ee = 83%. ^{1}H NMR (300 MHz, CDCl3) δ: 7.62–7.65 (2H, m, Ph-H), 7.29–7.47 (6H, m, Ph-H), 7.16–7.20 (2H, m, Ph-H), 5.60–5.62 (m, 1H, $CH{=}CH_2$), 5.03 (dd, 1H, J = 17.2, 1.5 Hz, $CH{=}CH_2$), 5.01 (dd, 1H, J = 10.2, 1.5 Hz, $CH{=}CH_2$), 4.00 (dd, 1H, J = 7.6, 5.6 Hz, CHC=O), 2.57–2.69 (m, 2H, CH_2–$CH{=}CH_2$), 1.44 (s, 9H, *t*-Bu) ppm. IR (neat) 2978, 1735, 1624, 1447, 1367, 1286, 1151, 916, 847, 781, 696 cm^{-1}; HPLC analysis: DAICEL Chiralcel OD-H, hexane/isopropyl alcohol = 99.5:0.5, flow rate = 0.5 mL/min, retention time: 9.3 min (S) and 10.9 min (R).

2.9.9. tert-Butyl 3-ethyl-2-(diphenylmethyleneamino)propanoate (2k, S)

Synthesized as Section 2.9 according to the reaction conditions listed in Table 1, entry 3. Yield 81%. $[\alpha]_D^{20} = -11.9$ (c = 0.2, $CHCl_3$). ee = 82%. ^{1}H NMR (300 MHz, CDCl3) δ: 7.62–7.65 (m, 2H, Ph-H), 7.30–7.50 (m, 6H, Ph-H), 7.17–7.20 (m, 2H, Ph-H), 3.85 (dd, 1H, J = 5.7, 3.9 Hz, CHC=O), 1.86–1.95 (m, 2H, CH_2CH_3), 1.44 (s, 9H, *t*-Bu), 0.87 (t, 3H, J = 5.4 Hz, CH_3) ppm. IR (neat) 2978, 1735, 1624, 1447, 1367, 1279, 1153, 696 cm^{-1}. HPLC analysis: DAICEL Chiralcel OD-H, hexane/isopropyl alcohol = 99.5:0.5, flow rate = 0.5 mL/min, retention time: 11.6 min (S) and 13.3 min (R).

2.9.10. tert-Butyl 3-methyl-2-(diphenylmethyleneamino)propanoate (2l, S)

Synthesized as Section 2.9 according to the reaction conditions listed in Table 1, entry 3. Yield 82%. $[\alpha]_D^{20} = -10.6$ (c = 0.2, $CHCl_3$). ee = 80%. ^{1}H NMR (300 MHz, CDCl3) δ: 7.62–7.65 (m, 2H, Ph-H), 7.30–7.51 (m, 6H, Ph-H), 7.17–7.20 (m, 2H, Ph-H), 4.03 (q, 1H, J = 6.8 Hz, CHC=O), 1.46 (d, 3H, J = 6.8 Hz, CH_3), 1.44 (s, 9H, *t*-Bu) ppm. IR (neat) 2978, 1735, 1624, 1447, 1367, 1286, 1153, 1030, 849, 781, 696 cm^{-1}; HPLC analysis: DAICEL Chiralcel OD-H, hexane/isopropyl alcohol = 99.5:0.5, flow rate = 0.5 mL/min, retention time: 10.7 min (S) and 12.0 min (R).

3. Results and discussion

The catalytic efficiency of the CPTCs was evaluated by enantioselective phase transfer alkylation of *tert*-butyl benzophenone Schiff base derivative **1** (Scheme 1) with different electrophiles. Various factors affecting the reaction were examined, such as temperature, solvent, the species and concentration of the inorganic bases, the amounts of the benzyl bromide and the type of CPTC.

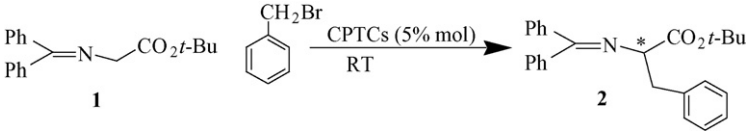
Firstly, we attempted to study the influence of various inorganic bases, reaction temperature and amounts of benzyl

bromide and catalyst in the presence of catalyst **9**. Eventually, the best reaction condition was obtained when the reaction proceeded with benzyl bromide (5.0 equiv.), and CPTC (5 mol%) in 1 M aqueous solution of KOH (10 equiv., 2 mL) at room temperature. The highest ee and yield were 86% and 99%, respectively (Table 1, entry 3) with benzyl bromide as the electrophiles. We also performed the reaction at lower temperature (Table 1, entries 14 and 5). But the results were unsatisfactory, as the solubility of the substrate and catalyst was low when the temperature is low. The optimum temperature for alkylation is room temperature, implying that higher temperature was beneficial to the solubility of the reactant so that good chemical yield as well as enantioselective could be achieved. The good solubility of the substrate is the precondition of the asymmetric alkylation. As shown in Table 1, the moderate concentration of KOH aqueous solution afforded the best result. It implied neither a decrease nor an increase in the concentration of base is beneficial to the chemical yield and enantioselectivity. Further, the high concentration of CPTC showed little influence on the result owing to its lower solubility in the aqueous solution. The excess CPTC could not dissolve in the reaction system to participate in the phase transfer catalytic procedure. After optimizing the reaction condition, we considered whether the catalyst could be decomposed or not during the reaction procedure. So we reclaimed the catalyst and investigated its structure. The catalyst could be separated from the reaction mixture when we added diethyl ether to the reaction residue, because of the reaction product could dissolve in diethyl ether and the catalyst was insoluble in it. We found that the catalyst was not decomposed under the present condition examined by ^{1}H NMR. It indicated that the catalyst is stable under the reaction condition.

Secondly, we completed the optimization of the reaction conditions with CPTC **9**. In Table 2, we found the chemical yield was higher when the solvent was water than when classical organic solvents were used. Unfortunately, the lower ee was obtained than the conventional reaction condition. The similar observation was notified by Li et al. [59]. We speculate it should be due to the less solubility of the electrophiles in water. The amount of benzophenone **3** is also decreased in aqueous media. It indicated that it was the best way to prevent the decomposition of **2** when water is used as the solvent and the new methodology was suitable for alkylation.

As we know, most of the cinchona alkaloids derivatives were reported with the excellent enantioselectivities since the steric effect plays an important role in the asymmetric alkylation of *tert*-butyl benzophenone Schiff base derivatives [28,29]. But we cannot ignore that electronic effect may be another significant factor [31,60,61]. Hence, we synthesized a series of *N*-acetophenone cinchona ammonium salts and catalyzed the asymmetric alkylation in water. The different catalytic efficiencies were found due to the acetophenones substituted at the *ortho*-, *meta*- or *para*-position with various functional groups such as nitro and halides. In Table 2, we show the catalytic efficiencies of CPTCs such as **4a**, **4b** prepared by O'Donnell (Fig. 1) and other *N*-acetophenone cinchona ammonium salts we synthesized. Other variable parameters such as base, temperature and solvent were kept constant. It is clear that the CPTC 4-NO_2-quinium-*N*-acetophenone bromide **9** afforded the best result. It indicated the electron-withdrawing *N*-acetophenone quinine group caused by the overall electron deficiency of the positive charge helped to enhance the degree of the ion pairing with enolate. The more tight ion pairing was formed the better

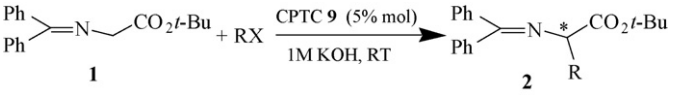
Table 2
Asymmetric alkylation of **1** with different catalysts



Entry	PTC	Solvent	Yield (%)[a]	ee (%)[b] (Configuration)[c]
1	**4a**	1 M KOH	81	61(S)
2	**4b**	1 M KOH	85	68(S)
3[d]	**9**	Toluene/$CHCl_3$ 7:3	83	96(S)
4	**9**	1 M KOH	99	86(S)
5	**5**	1 M KOH	89	73(S)
6	**6**	1 M KOH	96	80(S)
7	**7**	1 M KOH	92	84(S)
8[d]	**7**	Toluene/$CHCl_3$ 7:3	77	88(S)
9	**8**	1 M KOH	92	79(S)
10	**10**	1 M KOH	89	78(S)
11[d]	**10**	Toluene/$CHCl_3$ 7:3	75	91(S)
12	**11**	1 M KOH	91	76(R)
13[d]	**11**	Toluene/$CHCl_3$ 7:3	79	94(R)

[a] Isolated yield.
[b] Enantiomeric excess was determined by HPLC analysis using a chiral column (DAICEL Chiralcel OD-H) with hexane-isopropanol (99.5:0.5) as an eluent.
[c] The absolute configuration was confirmed by comparison of the HPLC retention time of an authentic sample, which was synthesized independently by reported procedures [29].
[d] The reaction was performed with Toluene/$CHCl_3$ 7:3 (2 mL), 10M KOH (0.25 mL, 12.5 equiv.), benzyl bromide (5.0 equiv.) and CPTC (5 mol%) at room temperature.

Table 3
Asymmetric alkylation with various electrophiles using catalyst **9** in aqueous media



1 2

Entry	R'X	Yield (%)[a]	ee.(%)[b] (Configuration)[c]
2a	$PhCH_2Br$	99	86(S)
2b	*o*-CH_3 $PhCH_2Br$	90	85(S)
2c	*m*-CH_3 $PhCH_2Br$	87	90(S)
2d[d]	*p*-CH_3 $PhCH_2Br$	92	87(S)
2e	*p*-CH_3 $PhCH_2Br$	51	63(S)
2f	*o*-Cl $PhCH_2Br$	93	91(S)
2g	*m*-Cl $PhCH_2Br$	89	91(S)
2h[d]	*p*-Cl $PhCH_2Br$	98	96(S)
2i	*p*-Cl $PhCH_2Br$	48	58(S)
2j	CH_2=$CHCH_2Br$	79	83(S)
2k	C_2H_5I	81	82(S)
2l	CH_3I	82	80(S)

[a] Isolated yield.
[b] Enantiomeric excess was determined by HPLC analysis using a chiral column (DAICEL Chiralcel OD-H) with hexane-isopropanol (99.5:0.5) as an eluent.
[c] The absolute configuration was confirmed by comparison of the HPLC retention time of an authentic sample, which was synthesized independently by reported procedures [22,28,29,32,35].
[d] 1% mol $PhCH_3$ was added.

enantioselective was obtained [29]. Moreover, we found the solubility of catalyst **9** in the reaction mixture was better than other catalysts like **4a** and **4b**. The arylcarbonylmethylene moiety of catalyst **9** could improve the solubility in the reaction mixture. We speculated that the solubility is a factor in improving the enantioselectivity.

Encouraged by these preliminary results, different benzyl bromides were employed as electrophiles (Table 3). The equally satisfactory ee and yields were obtained under the above alkylation condition with substituted benzyl bromide, allylic bromide and alkyl iodide. The best result (ee up to 96%) was obtained with *p*-Cl benzyl bromide. We can see from the Table 3 (entries 2d, 2e, 8, 9), the solid state of *p*-CH_3 benzyl bromide and *p*-Cl benzyl bromide affect the yields and ee. It suggests that the solid or liquid state and the amounts of the electrophiles showed significant influence on the enantioselectivity and yield, which agrees with what has been reported [58,59]. As the solid halides dissolved into the added 1% toluene and the replaced liquid halide as the organic phase, the organic phase came into being, and the phase transfer process well proceeded. Since the liquid halides acted as the organic phase in the reaction system, the moderate excess of liquid halides was helpful to the chemical yield and enantioselectivity.

4. Conclusion

In summary, we have successfully synthesized the novel CPTC, and completed the asymmetric alkylation of *tert*-butyl benzophenone Schiff base derivatives with high chemical yields and enantioselectivities in aqueous media. It demonstrated that the new methodology may be widely used. We also studied the influence of substituted *N*-acetophenone cinchona ammonium group on the enantioselectivity of the reaction. The electron-withdrawing group was shown to enhance the catalytic efficiency. In addition, further research on the application of the novel CPTCs is under investigation in our lab.

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