DOI: 10.1002/adsc.201200976

Enantioselective Phase-Transfer Catalytic α-Benzylation and α-Allylation of α-*tert*-Butoxycarbonyllactones

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Received: November 7, 2012; Revised: January 17, 2013; Published online: February 22, 2013

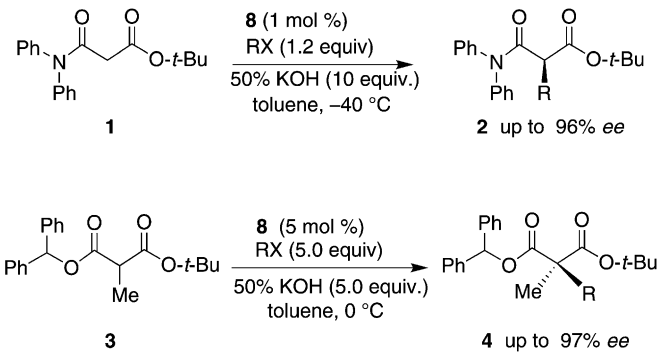
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201200976.

Abstract: A new enantioselective α-benzylation and α-allylation of α-*tert*-butoxycarbonyllactones was devloped. α-Benzylation and α-allylation of α-*tert*-butoxycarbonylbutyrolactone and α-*tert*-butoxycarbonylvalerolactone under phase-transfer catalytic conditions (50% cesium hydroxide, toluene, −60 °C) in the presence of (*S*,*S*)-3,4,5-trifluorophenyl-NAS bromide (1 mol%) afforded the corresponding α-substituted α-*tert*-butoxycarbonyllactones in very high chemical yields (up to 99%) and optical yields (up to 99% *ee*). The synthetic potential of this method has been successfully demonstrated by the asymmetric synthesis of unnatural α-quaternary homoserines, 3-alkyl-3-carboxypyrrolidine and 3-alkyl-3-carboxypiperidine.

Keywords: asymmetric allylation; asymmetric benzylation; enantioselectivity; phase-transfer catalysis

Malonate-type compounds are one of the most fundamental synthetic starting materials for C–C bond formation in organic synthesis.[1] In addition, chiral α-substituted malonates including α-carboxylactones and α-carboxylactams have been popularly employed for the construction of chiral quaternary carbon centers of biologically active natural products and pharmaceuticals.[2,3] The construction of chiral quaternary carbon centers by enantioselective α-alkylation of carbonyl systems[4] and β-keto ester systems,[5] and chiral induction of β-position to malonate by asymmetric conjugate addition or palladium-catalyzed allylation of malonates[6] have been widely developed to date. However, the enantioselective direct α-alkylation of malonate type compounds has not yet been extensively studied.[7]

Recently, we reported a new synthetic method for chiral α-mono-alkylmalonamide esters (**2**) by phase-transfer catalytic (PTC) mono-α-alkylation of *N*,*N*-diarylmalonamide esters (**1**) in the presence of (*S*,*S*)-3,4,5-trifluorophenyl-NAS bromide (**8**) and successfully proved its usefulness by applying to the synthesis of various chiral building blocks (Scheme 1).[8] As a continuing study, we successfully further expanded the PTC alkylation to the malonate system. The enantioselective α-alkylation of diphenylmethyl *tert*-butyl α-alkylmalonates (**3**) under phase-transfer catalysis condition afforded α,α-dialkylmalonates (**4**) in high chemical and optical yields which could be readily converted to versatile chiral intermediates for the construction of quaternary carbon centers.[9] With regard to lactones, a few cases were reported as part of studies, such as α-substitution of α-*tert*-butylcarboxybutyrolactone with cyclic sulfamidates,[10] α-fluorination of α-*tert*-butylcarboxy-lactones via chiral Pd(II)-bisphospine catalysis[11] and α-substitution of β-ketobutyrolactone,[12] However, there are no systematic studies on the asymmetric α-substitution of α-carboxy-lactones with high enantioselectivity. Based on



Scheme 1. Previous chiral phase-transfer catalysis of malonate type substrates.

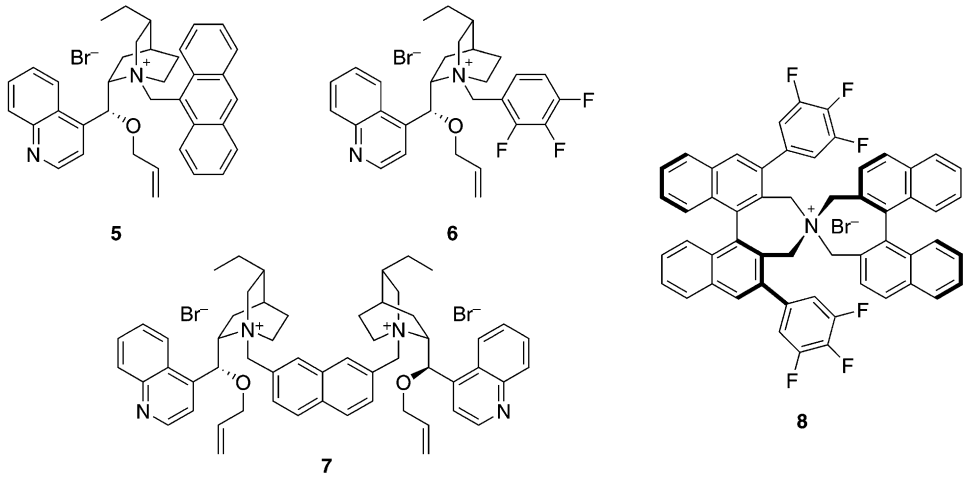


Figure 1. Chiral phase-transfer catalysts.

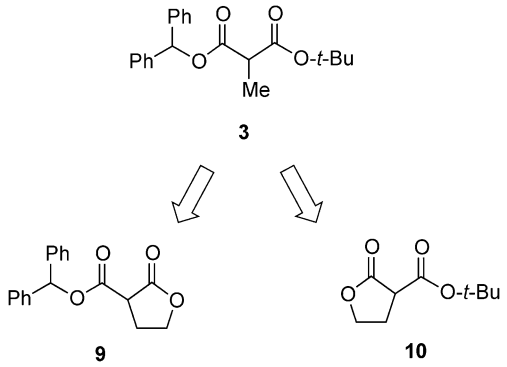
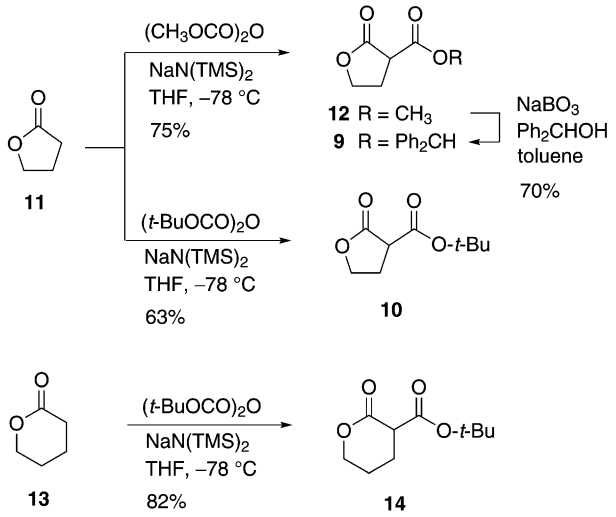


Figure 2. Design of α-carboxylactones as substrates.



Scheme 2. Preparation of α-carboxylactones.

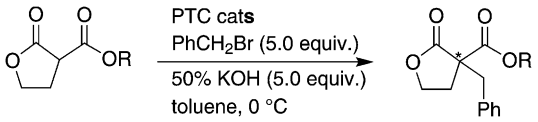
a series of our previous studies, we attempted to develop a new asymmetric synthetic method for α-quaternary lactone system. Here we reported a new and highly efficient enantioselective α- benzylation and α-allylation of α-carboxy-lactones under phase-transfer catalytic conditions.[13]

First, we needed to design an α-carboxy-lactone as a substrate for the initial study. Since the *tert*-butyl ester group and diphenylmethyl ester group are quite essential for high enantioselectivity in enantioselective PTC α-alkylations of the malonate system (**3**)[9] in the presence of a catalyst **8**, both ester groups were employed to α-carboxy-lactone substrates. For the preliminary study, α-diphenylmethoxycarbonylbutyrolactone (**9**) and α-*tert*-butoxycarbonylbutyrolactone (**10**) were prepared (Figure 2, Scheme 2).

Treatment of methoxycarbonyl anhydride with butyrolactone (**11**) under basic conditions with sodium trimethylsilylamide, followed by transesterification using sodium perborate as a catalyst, afforded **9** (53% in two steps). Compound **10** could be obtained by *tert*-butoxycarbonylation of butyrolactone (**11**) using Boc_2O under basic conditions with sodium trimethylsilylamide (63%). Their substrate efficiency was examined by α-benzylation under typical PTC conditions. The enantioselective PTC benzylation of **9** and **10** was performed in the presence of representative chiral PTC catalysts (**5**–**8**)[14] (Figure 1), along with benzyl bromide (5.0 equiv.) and 50% aqueous KOH (5.0 equiv.) at 0 °C in toluene (Table 1).

As shown in Table 1, α-*tert*-butoxycarbonylbutyrolactone (**10**, 90% *ee*) afforded quite high enantioselectivity with lower chemical yield than that of α-diphenylmethoxycarbonylbutyrolactone (**9**, 62% *ee*) in the presence of **8**, suggesting that the *tert*-butyl ester group is more efficient for enantioselectivity than the diphenylmethyl ester group. All of the *Cinchona*-derived catalysts (**5**–**7**) afforded quite low enantioselectivities compared to that of catalyst **8**, which was in accord with previous results.[8,9] We chose α-*tert*-butoxycarbonylbutyrolactone (**10**) as an optimal lactone substrate for further study. Optimization of base and

Table 1. Optimization of substrates and catalysts.



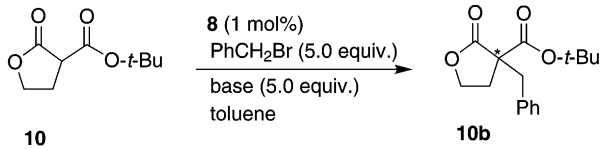
Entry	R	Cat.	Time [h]	Yield [%][a]	*ee* [%][b]
1	Ph_2CH (**9**)	**8** (1 mol%)	2	94	62
2	*t*-Bu (**10**)	**8** (1 mol%)	1.5	66	90
3	*t*-Bu (**10**)	**5** (10 mol%)	0.2	80	19
4	*t*-Bu (**10**)	**6** (10 mol%)	0.2	87	25
5	*t*-Bu (**10**)	**7** (10 mol%)	90	85	18

[a] Isolated yields.
[b] The enantiopurity was determined by HPLC analysis of α-benzylated product using a chiral column (Chiralcel OD-H or Chiralpak AD-H) with hexanes/2-propanol as eluents.

temperature conditions using substrate **10** was performed.

As shown in Table 2, PTC benzylation under various base conditions revealed that aqueous alkali base generally gave both higher chemical yield and enantioselectivity than did the corresponding solid alkali bases (entry 1–6), and lower temperatures afforded higher enantioselectivity with higher chemical yields (entry 6–10). We speculated that the lower chemical yield of solid bases might be due to hydrolysis of the lactone ring by their stronger basicity. Best enantioselectivity was observed in the case of 50% CsOH base conditions at −60 °C (entry 9, 94%, 99% *ee*), but the

Table 2. Optimization of bases and temperatures.



10 **10b**

Entry	Base	Temp. [°C]	Time [h]	Yield [%][a]	*ee* [%][b]
1	NaOH	0	2	31	27
2	KOH	0	1.5	30	37
3	CsOH	0	0.2	25	45
4	50% NaOH	0	1.5	61	75
5	50% KOH	0	0.2	66	90
6	50% CsOH	0	0.2	62	94
7		−20	0.5	70	96
8		−40	1.5	75	97
9		−60	3	94	99
10		−78	90	72	97

[a] Isolated yields.[b] The enantiopurity was determined by HPLC analysis of **10b** using a chiral column (Chiralcel OD-H or Chiralpak AD-H) with hexanes/2-propanol as eluents.

lower reaction temperature gave slightly lower enantioselectivity and chemical yield (entry 10, 72%, 97% *ee*) with quite longer reaction time (90 h).

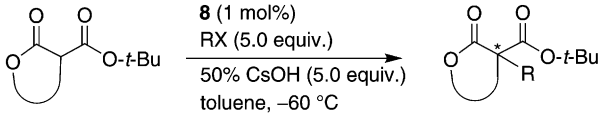
The promising results with 5-membered lactone **10** encouraged us to expand the ring size to a 6-membered lactone. α-*tert*-Butoxycarbonylvalerolactone (**14**) was prepared by the same method (82%) as α-*tert*-butoxycarbonylbutyrolactone (**10**) and substrate efficiency was examined by benzylation in the presence of **8** (1 mol%) under the optimized PTC conditions (Table 2, entry 9). High enantioselectivity was observed along with a 5-membered lactone substrate (Table 3, entry 7; 93%, 96% *ee*).

The lactone substrates **10** and **14** were chosen for further investigation into the scope and limitations of our enantioselective PTC alkylation with various electrophiles (Table 3). Both lactone systems gave very high enantioselectivities with allylic and benzylic bromides, and generally butyrolactone gave slightly higher enantioselectivity compared to that of valerolactone. However, unactivated alkyl halide such as methyl iodide provided poor chemical yields (CH_3I, 40%, 89% *ee*). These very high enantioselectivities (up to 99% *ee*) indicate that this method is a very efficient enantioselective synthetic method for α-alkyl-α-carboxylactones.

α-Benzylated lactones **10b** (99% *ee*) and **14b** (96% *ee*) were converted to the corresponding amides by ammonolysis using saturated ammonia in methanol at room temperature (Scheme 3). The Hofmann rearrangement of amides **15** and **16** using lead tetraacetate in *tert*-butyl alcohol, followed by hydrolysis with 6N HCl provided unnatural amino acids **21** and **22**. The absolute configuration of **21** {$[\alpha]_D^{23} = -24$ (*c* 1.0, H_2O)} was confirmed as *S* by comparison of the specific optical rotation value with reported value {(*R*)-**21**, $[\alpha]_D^{23}$: +25 (*c* 0.5, H_2O)}.[15] α-Benzylated butyrolactone **10b** (99% *ee*) and valerolactone **14b** (96% *ee*) were also converted to pyrrolidine **27** and piperidine **28**, respectively (Scheme 4). The selective reduction of **10b** and **14b** with $NaBH_4$ in the presence of $CeCl_3$ afforded diols **23** and **24**.[16] The dimesylation of diols, **23** and **24**, followed by double *N*-alkylation with methylamine successfully provided pyrrolidine **27** and piperidine **28**, respectively.

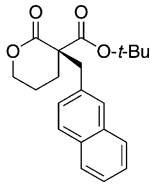
In conclusion, enantioselective synthetic methods of α-benzyl- and allyllactones were developed. The asymmetric PTC α-benzylation and allylation of α-*tert*-butoxycarbonylbutyrolactone and α-*tert*-butoxycarbonylvalerolactone afforded the corresponding α-substituted α-*tert*-butoxycarbonyllactones in high chemical (up to 99%) and optical yields (up to 99% *ee*). The synthetic potential of this method was successively demonstrated by the synthesis of unnatural α-quaternary homoserines, pyrrolidine and piperidine derivatives. Our new catalytic systems provide attractive synthetic methods for lactone-based chiral inter-

Table 3. Enantioselective phase-transfer α-benzylation and α-allylation of **10** and **14** with various benzyl and allyl halides.

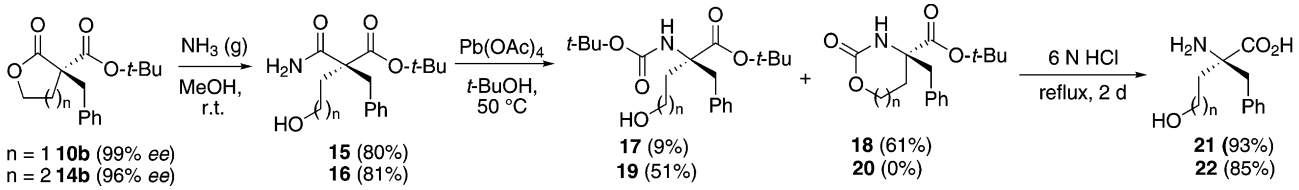


Entry	Substrate	RX	Product	Time [h]	Yield [%][a]	*ee* [%][b]
1	**10**	allyl bromide (**a**)	**10a**	8	85	98 (+)
2		BnBr (**b**)	**10b**	3	94	99 (*R*)[c] (+)
3		4-$MeC_6H_4CH_2Br$ (**c**)	**10c**	6	98	98 (+)
4		4-$FC_6H_4CH_2Br$ (**d**)	**10d**	5	98	99 (+)
5		2-bromomethylnaphthalene (**e**)	**10e**	24	99	96 (+)
6[d]	**14**	allyl bromide (**a**)	**14a**	24	88	86 (+)
7		BnBr (**b**)	**14b**	24	93	96 (+)
8		4-$MeC_6H_4CH_2Br$ (**c**)	**14c**	24	94	95 (–)
9		4-$FC_6H_4CH_2Br$ (**d**)	**14d**	24	99	92 (+)

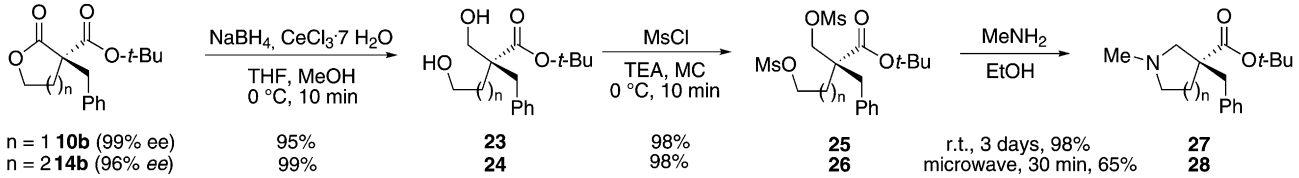
Table 3. (Continued)

Entry	Substrate	RX	Product		Time [h]	Yield [%][a]	*ee* [%][b]
10		2-bromomethylnaphthalene (**e**)		**14e**	24	89	93 (+)

[a] Isolated yields.
[b] The enantiopurity was determined by HPLC analysis of α-alkylated products (**10a–e** to **14a–e**) using a chiral column (Chiralcel OD-H or Chiralpak AD-H) with hexanes/2-propanol as eluents.
[c] The absolute configuration was confirmed as *R* by comparison of the specific optical rotation value of the derivatized compound **21** from **10d** with reported value.
[d] The reaction temperature was −40 °C.



Scheme 3. Conversion of **10b** and **14b** to amino acids **21** and **22**.



Scheme 4. Conversion of **10b** and **14b** to pyrrolidine **27** and piperidine **28**.

mediates including quaternary carbon centers. Further applications are now under investigation.

Experimental Section

For details on the synthesis of **10b**, see the Supporting Information.

Typical Procedure for the Enantioselective Phase-Transfer Catalytic α-Benzylation and α-Allylation of *tert*-Butoxycarbonyl-γ-butyrolactone (10) under Phase-Transfer Conditions (Benzylation)

To a toluene solution (0.9 mL) of *tert*-butoxycarbonyl-γ-butyrolactone (**10**) (50 mg, 0.27 mmol), (*S*,*S*)-3,4,5-trifluorophenyl-NAS bromide (2.46 mg, 0.0027 mmol) and 50% CsOH (117 μL, 1.34 mmol), benzyl bromide (160 μL, 1.34 mmol) was added at −60 °C. The reaction mixture was stirred vigorously for 3 h. After completion of the reaction, the reaction mixture was diluted with ethyl acetate (10 mL), washed with water (5 mL × 2), dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (silica gel, hexane : EtOAc = 30:1) to afford **10b** as a white solid; yield: 69.8 mg (94%); $[\alpha]_D^{23}$: +34.22 (*c* 1.0, $CHCl_3$). The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel AD-H, hexane : 2-propanol = 98.0:2.0, flow rate = 1.0 mL min^{-1}, 23 °C, λ = 217 nm): retention time; *S* isomer (major) 10.7 min, *R* isomer (minor) 12.7 min, 99.0% *ee*.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MEST) (2012-002956) and the National Research Foundation (NRF) grant funded by the Korean government (MEST) (No. 201000017).

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