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Asymmetric synthesis of α,β-epoxysulfones via phase-transfer catalytic Darzens reaction

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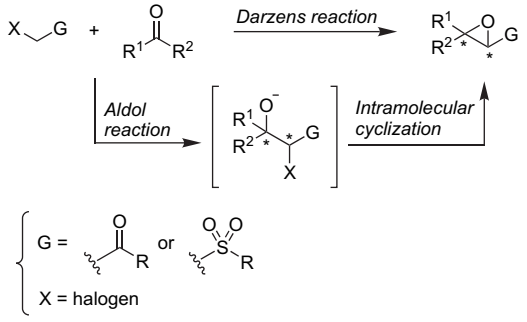
Abstract—Described is the asymmetric synthesis of α,β-epoxysulfones by the catalytic phase-transfer Darzens reaction of chloromethyl phenyl sulfone with various aromatic aldehydes in the presence of the *cinchona* alkaloid-derived chiral phase-transfer catalysts bearing *N*-2,3,4-trifluorobenzyl moiety. The *trans*-(α*R*,β*R*)-epoxysulfones were obtained in good chemical yields (81–95%) with high enantioselectivities (up to 97% ee) in the presence of *N*-(2,3,4-trifluorobenzyl)quinidinium bromide.

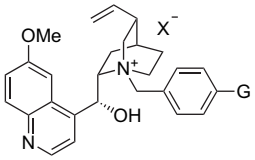
1. Introduction

Optically active α,β-epoxycarbonyl and α,β-epoxysulfonyl compounds can be easily converted to many types of useful chiral compounds such as chiral building blocks and synthetic intermediates for biologically active compounds.[1] The Darzens reaction, which consists of the sequential two reactions (i.e., the aldol reaction followed by the intramolecular cyclization), has been well known as one of the most potential methodologies for the construction of α,β-epoxycarbonyl, α,β-epoxysulfonyl compounds, and so forth (Scheme 1).[2]

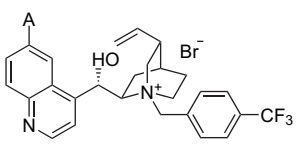


Scheme 1.

Since two stereogenic centers are newly formed from the Darzens reaction, a number of efforts have been made to develop an efficient asymmetric version of the Darzens reaction in the last decades. However, most of them require a stoichiometric amount of a chiral source[3] and only a few examples are known as catalytic methods.[4] Among the previous methods, we were interested in the catalytic asymmetric Darzens reaction promoted by phase-transfer catalysis.[4] Phase-transfer catalysis has been recognized as a practical methodology for organic synthesis due to its beneficial points such as a simple reaction procedure, mild conditions, inexpensive and safe reagents and solvents, and the ability to easily scale-up. Moreover, it is quite attractive that the use of chiral phase-transfer catalysts (chiral PTCs) can afford optically enriched products.[5] The chiral PTCs applied in the catalytic asymmetric Darzens condensation could be categorized basically into three types: ephedrinium salt,[4a] crown ether,[4b–e] and *cinchona*-derived salt.[4f–k] Since we have extensively studied on the development of the novel *cinchona*-derived PTCs and successfully applied them to various organic reactions, we especially focused on the last type of chiral PTC (i.e., *cinchona*-derived PTC).[6] The first application of the *cinchona*-derived PTC in Darzens reaction was disclosed in 1978 by Wynberg and Hummelen who used the *N*-benzylquininium chloride (**1**) as a chiral PTC.[4f] Two decades later, Arai et al. could significantly improve the enantioselectivity



1: G = H, X = Cl
2: G = CF_3, X = Br



3: A = OMe
4: A = H

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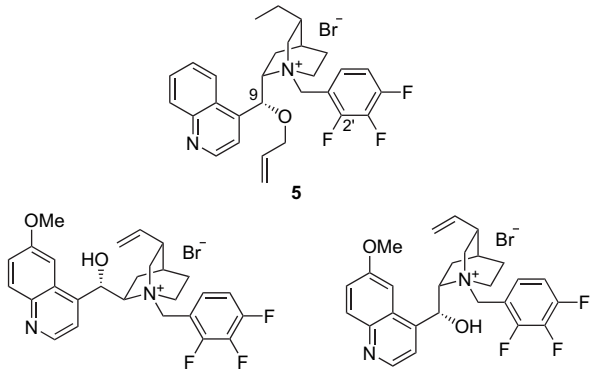
by using the new catalysts bearing *para*-trifluoromethyl on benzyl moiety (**2**–**4**).[4g–k]

2. Results and discussion

We recently found that the introduction of *N*-2′,3′,4′-trifluorobenzyl moiety such as **5** instead of *N*-benzyl group dramatically improves the catalytic efficiency in the enantioselective alkylation of the benzophenone imine of glycine *tert*-butyl ester and the β-naphthyl-aldimine of alanine *tert*-butyl ester affording the optically active α-amino acid derivatives.[6d,e] We proposed that this improvement can be possible by the electronic interaction involving water between C(9)–O and 2′-F in catalyst such as hydrogen bonding or induced dipole–dipole interaction, which can provide more rigid beneficial conformation of the catalyst leading to high enantioselectivity of the alkylation.[6d,g]

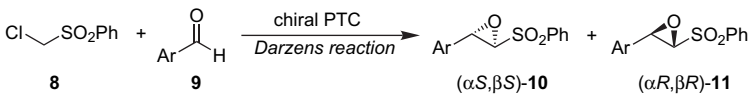


These findings prompted us to examine the asymmetric phase-transfer catalytic Darzens condensation with the 2,3,4-trifluorobenzyl-incorporated *cinchona* PTCs (**5**–**7**). α,β-Epoxysulfones have been regarded as very versatile synthetic intermediates or chiral building blocks for the synthesis of biologically active natural products.[7] Moreover, it has been well known that α-halomethyl sulfone could generate the corresponding carbanion rather than the enolate form under quite mild basic conditions so that chiral quaternary ammonium cation can directly form ionic complex with the anion of α-halomethyl sulfone, which might proceed via phase-transfer catalytic reaction during the aldol reaction step.[4k] In this article, we report an enantioselective synthetic method for *trans*-(α*R*,β*R*)-epoxysulfones via phase-transfer catalytic Darzens reaction of the chloromethyl phenyl sulfone (**8**) as a pro-α-halo-α-carbanion substrate in the presence of 2,3,4-trifluorobenzyl-incorporated *cinchona*-derived PTCs (**5**–**7**).

Arai et al. group first reported the asymmetric synthesis of α,β-epoxysulfones by asymmetric phase-transfer catalysis (Scheme 2).[4j,k] They obtained optically enriched *trans*-(α*S*,β*S*)-epoxysulfones (**10**) with moderate to good enantioselectivities (64–81% ee) utilizing *N*-(4-trifluoromethylbenzyl)quininium bromide (**2**) as the chiral PTC catalyst in the Darzens reaction of chloromethyl phenyl sulfone with various aromatic aldehydes. But the pseudoenantiomeric catalysts of **2**, *N*-(4-trifluoromethylbenzyl)quinidinium bromide (**3**) and *N*-(4-trifluoromethylbenzyl)cinchoninium bromide (**4**), could give *trans*-(α*R*,β*R*)-epoxysulfones (**11**) in poor enantioselectivities (49 and 27% ee, respectively) under the same reaction conditions.[4j] Since the quinidine/quinine-derived PTCs showed better enantioselectivities in Darzens reactions than cinchonine/cinchonidine-derived ones in Arai et al. results, our research was commenced with the preparation of 2,3,4-trifluorobenzyl-incorporated quinidine and quinine derivatives (**6** and **7**) by the reported method.[4j] With these chiral PTCs (**6** and **7**) prepared, we evaluated their catalytic efficiency using the known PTC-mediated Darzens reaction conditions established by Arai et al.[4j,k] The Darzens reaction was performed with chloromethyl phenyl sulfone (**8**), benzaldehyde (**9a**), and solid KOH in the presence of **6** at room temperature in toluene solvent (entry 1 in Table 1).

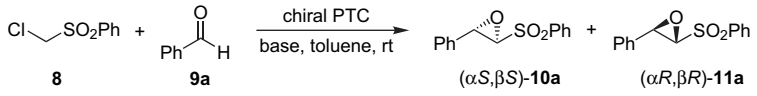
As shown in Table 1, catalyst **6** afforded the corresponding *trans*-α,β-epoxysulfone in 95% yield with an enantiomeric mixture of (α*S*,β*S*)-**10a** and (α*R*,β*R*)-**11a** in the ratio of 20:80 (60% ee). The coupling constant between H(α) and H(β) observed in the NMR spectral data could confirm that only *trans*-isomer was formed and the absolute configuration of the major enantiomer could be assigned as α*R*,β*R* by the chiral HPLC analysis (entry 1). Notably, the enantioselectivity is higher than that of the previous report (47% ee with **3**) under the same reaction conditions.[4j] We next optimized the basic conditions. A significant increase of enantioselectivity was achieved with 50% aqueous KOH base with slower reaction rate and slightly lower chemical yield (entry 2). Further optimization with various aqueous inorganic bases revealed that 50% aqueous RbOH base in the presence of the chiral PTC **6** showed the best result (entry 3; 91%, 90% ee). Furthermore, the opposite enantiomeric isomer, (α*S*,β*S*)-**10a**, could be obtained by employing the pseudoenantiomeric catalyst (**7**) derived from quinine with 87% ee (entry 5), which has higher enantioselectivity than that of the previous result (69% ee).[4j]

With these optimal reaction conditions, we explored the scope of this reaction system by using various aromatic aldehydes and the results are summarized in Table 2. As shown in Table 2, all the reactions smoothly proceeded to afford the corresponding *trans*-(α*R*,β*R*)-epoxysulfones (**11a**–**11k**) in good chemical yields (80–95%) with high enantioselectivities (up to 97% ee) and *N*-(2,3,4-trifluorobenzyl)quinidinium bromide (**6**) showed very high catalytic efficiency in the asymmetric phase-transfer catalytic Darzens reaction



Scheme 2. Asymmetric phase-transfer catalytic Darzens reaction.

Table 1. Effect of chiral PTC and base in asymmetric Darzens reaction[a]

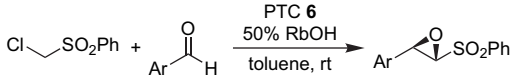


8 **9a** (αS,βS)-**10a** (αR,βR)-**11a**

Entry	PTC	Base	Time (h)	Yield[b] (%)	ee[c] (%)	config.[d]
1	**6**	Solid KOH	2	95	60	*trans*-(αR,βR)
2	**6**	50% KOH	20	82	77	*trans*-(αR,βR)
3	**6**	50% RbOH	8	91	90	*trans*-(αR,βR)
4	**6**	50% CsOH	8	75	79	*trans*-(αR,βR)
5	**7**	50% RbOH	10	84	87	*trans*-(αS,βS)

[a] The reaction was carried out with 1.2 equiv of benzaldehyde (**9a**) and 4 equiv of each base in the presence of 10 mol % of catalyst **6** or **7** in toluene under the given conditions.
[b] Isolated yields.
[c] Enantiopurity was determined by HPLC analysis of α,β-epoxysulfones using a chiral column (Chiralcel OD) with hexanes/2-propanol (volume ratio=9:1) as the eluant; in this case it was established by analysis of the racemate, in which the enantioisomers were fully resolved.
[d] Absolute configuration was determined by comparison of the HPLC retention time with the authentic sample independently synthesized by the reported procedure.[4j,k]

Table 2. Asymmetric phase-transfer catalytic Darzens reaction[a]



8 **9** (αR,βR)-**11**

Entry	Aromatic aldehyde **9**	Time (h)	Yield[b] (%)	ee[c] (%)
a	**9a**: Ar=C_6H_5–	8	**11a**: 91	90
b	**9b**: Ar=4-Me–C_6H_4–	8	**11b**: 90	87
c	**9c**: Ar=4-*i*-Pr–C_6H_4–	10	**11c**: 93	93
d	**9d**: Ar=4-*i*-Bu–C_6H_4–	10	**11d**: 83	86
e	**9e**: Ar=4-*t*-Bu–C_6H_4–	8	**11e**: 81	97
f	**9f**: Ar=4-Ph–C_6H_4–	3	**11f**: 93	77
g	**9g**: Ar=3-Me–C_6H_4–	6	**11g**: 95	80
h	**9h**: Ar=4-Cl–C_6H_4–	8	**11h**: 91	71
i	**9i**: Ar=4-Br–C_6H_4–	4	**11i**: 91	72
j	**9j**: Ar=3,5-*t*-Bu_2–C_6H_3–	10	**11j**: 80	82
k	**9k**: Ar=2-naphthyl–	3	**11k**: 92	74

[a] The reaction was carried out with 1.2 equiv of aromatic benzaldehyde **9** and 4 equiv of 50% RbOH in the presence of 10 mol % of catalyst **6** in toluene at room temperature under the given conditions.
[b] Isolated yields.
[c] Enantiopurity was determined by HPLC analysis of the α,β-epoxysulfones **11** using a chiral column (Chiralcel OD) with hexanes/2-propanol as the eluant; in each case it was established by analysis of the racemate, in which the enantioisomers were fully resolved.

for the synthesis of optically enriched *trans*-(αR,βR)-epoxysulfones.

3. Conclusion

We have developed the highly enantioselective phase-transfer catalytic Darzens reaction from chloromethyl phenyl sulfone (**8**) and aromatic aldehydes (**9**) affording the corresponding optically enriched α,β-epoxysulfones (**10** and **11**). *N*-(2,3,4-Trifluorobenzyl)quinidinium bromide (**6**) is found to be an effective chiral PTC for the synthesis of *trans*-(αR,βR)-epoxysulfones **11** and *N*-(2,3,4-trifluorobenzyl)quininium bromide (**7**) is for the opposite enantiomeric isomer, *trans*-(αS,βS)-epoxysulfones **10**. Rubidium hydroxide base of 50% provides both good chemical yields and high enantioselectivities. Further studies on the optimal Darzens reaction conditions of aliphatic aldehydes or ketones with chloromethyl phenyl sulfone are under investigation.

4. Experimental

4.1. General

Infrared (IR) spectra were recorded on a JASCO FT/IR-300E and Perkin–Elmer 1710 FT spectrometers. Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were measured on a JEOL JNM-LA 300 [300 MHz (^{1}H)] spectrometer and JEOL JNM-GSX 400 [100 MHz (^{13}C)] spectrometer, using DMSO-d_6 or $CHCl_3$-*d* as a solvent, and were reported in parts per million relative to DMSO (δ 2.50) or $CHCl_3$ (δ 7.26) for ^{1}H NMR and relative to the central DMSO-d_6 (δ 39.51) or $CHCl_3$-*d* (δ 77.23) resonance for ^{13}C NMR. Coupling constants (*J*) in ^{1}H NMR are given in hertz. High performance liquid chromatography (HPLC) was performed on Hitachi L-7100 instruments using 4.6 mm×25 cm Chiralcel OD chiral column. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. Mass spectra (MS) were recorded on a VG Trio-2 GC–MS spectrometer. Melting points were measured on a Buchi B-540 melting point apparatus and were not corrected. For thin-layer chromatographic (TLC) analysis, Merck precoated TLC plate (silica gel 60 GF_{254}, 0.25 mm) was used. For flash column chromatography, E. Merck Kieselgel 60 (70–230 mesh) was used. All solvents and commercially available chemicals were used without additional purification.

4.2. Preparation of *N*-(2,3,4-trifluorobenzyl)quinidinium bromide (6)

A mixture of (+)-quinidine (3.0 g, 9.2 mmol) with 2,3,4-trifluorobenzyl bromide (2.5 g, 10.2 mmol) in a mixture of ethanol (7.5 mL), DMF (9 mL), and chloroform (3 mL) was stirred at 100 °C for 4 h. After cooling the reaction mixture to room temperature, the reaction mixture was diluted with methanol (50 mL) and then added to ether (400 mL) dropwise with stirring. The solid that precipitated was filtered and washed with ether (600 mL). The crude solid was recrystallized from methanol/ether to afford 4.7 g (93% yield) of **6** as a light yellow solid. IR (KBr) ν 3431, 1622, 1514, 1311, 1241, 1030, 828, 586 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (d, *J*=4.5 Hz, 1H), 8.03 (d, *J*=9.2 Hz, 1H), 7.80–7.73 (m, 2H), 7.63–7.57 (m, 1H), 7.51 (dd, *J*=9.2, 2.6 Hz, 1H), 7.44 (d, *J*=8.3 Hz, 1H), 6.88 (d,

J=3.2 Hz, 1H), 6.51 (s, 1H), 6.09–6.00 (m, 1H), 5.27–5.21 (m, 2H), 5.12 (d, J=13.3 Hz, 1H), 4.84 (d, J=13.2 Hz, 1H), 4.25–4.18 (m, 1H), 4.07 (s, 3H), 4.01–3.88 (m, 2H), 3.51 (t, J=11.1 Hz, 1H), 3.19–3.11 (m, 1H), 2.66–2.60 (m, 1H), 2.38 (t, J=11.1 Hz, 1H), 1.92 (s, 1H), 1.87–1.77 (m, 2H), 1.13–1.06 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.9, 147.8, 144.1, 143.6, 137.5, 131.8, 130.7, 125.8, 121.8, 120.7, 117.5, 114.0, 102.8, 67.9, 65.2, 56.6, 54.7, 37.4, 26.5, 23.6, 21.0 ppm; mp 156 °C; $[\alpha]_D^{23}$ +193.3 (c 1.00, CH_3OH); MS (FAB): 470 $[M+1]^+$.

4.3. Preparation of *N*-(2,3,4-trifluorobenzyl)quininium bromide (7)

A mixture of (−)-quinine (3.0 g, 9.2 mmol) with 2,3,4-trifluorobenzyl bromide (2.5 g, 10.2 mmol) in a mixture of ethanol (7.5 mL), DMF (9 mL), and chloroform (3 mL) was stirred at 100 °C for 4 h. After cooling the reaction mixture to room temperature, the reaction mixture was diluted with methanol (50 mL) and then added to ether (400 mL) dropwise with stirring. The solid that precipitated was filtered and washed with ether (600 mL). The crude solid was recrystallized from methanol/ether to afford 4.6 g (92% yield) of **7** as a light yellow solid. IR (KBr) ν 3433, 1621, 1515, 1493, 1311, 1241, 1029, 827, 587 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.80 (d, J=4.4 Hz, 1H), 8.01 (d, J=9.2 Hz, 1H), 7.75–7.72 (m, 2H), 7.61–7.56 (m, 1H), 7.49 (dd, J=9.1, 2.3 Hz, 1H), 7.38 (d, J=2.4 Hz, 1H), 6.75 (d, J=3.7 Hz, 1H), 6.55 (s, 1H), 5.80–5.69 (m, 1H), 5.51 (d, J=12.7 Hz, 1H), 5.14–4.99 (m, 2H), 4.75 (d, J=12.9 Hz, 1H), 4.24–4.21(m, 1H), 4.00 (s, 3H), 3.98–3.96 (m, 1H), 3.76–3.67 (m, 1H), 3.50–3.36 (m, 1H), 2.70–2.65 (m, 1H), 2.20–2.15 (m, 2H), 2.00 (s, 1H), 1.81–1.77 (m, 1H), 1.46–1.38 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.4, 147.4, 143.7, 137.9, 131.4, 131.3, 125.4, 121.5, 120.3, 116.7, 113.7, 102.2, 68.3, 63.8, 59.1, 56.4, 55.6, 50.9, 37.3, 25.8, 24.4, 20.4 ppm; mp 158 °C; $[\alpha]_D^{23}$ −199.0 (c 1.00, CH_3OH); MS (FAB): 470 $[M+1]^+$.

4.4. The representative procedure for the asymmetric Darzens reaction under catalytic phase-transfer conditions: synthesis of (2*R*,3*R*)-2-phenyl-3-(phenylsulfonyl)-oxirane (11a)

A mixture of chloromethyl phenyl sulfone **8** (80 mg, 0.42 mmol), *N*-(2,3,4-trifluorobenzyl)quinidinium bromide (**6**) (23.1 mg, 0.042 mmol), and 50% aqueous RbOH (0.34 mL, 1.68 mmol) in toluene (2.5 mL) was stirred for 15 min and then benzaldehyde **9a** (0.05 mL, 0.5 mmol) was added. The resulting solution was stirred at room temperature for 10 h. The reaction was quenched with 1 N HCl, and the mixture was extracted with ethyl acetate, washed with brine, and dried over $MgSO_4$. Removal of the solvent followed by flash column chromatography (silica gel, hexanes/ethyl acetate=10:1) gave the desired product **11a** (100 mg, 91%, 90% ee). White solid; mp 135 °C; IR (Nujol) ν 1325, 1152 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.02–7.98 (m, 2H), 7.76–7.71 (m, 1H), 7.65–7.60 (m, 2H), 7.38–7.32 (m, 3H), 7.28–7.24 (m, 2H), 4.59 (d, J=1.5 Hz, 1H), 4.19 (d, J=1.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.4, 71.0, 128.8, 129.2, 129.5, 132.6, 134.5, 138.6 ppm; MS (EI): 260 $[M^+]$; HPLC: Chiralcel OD, flow rate 1.0 mL/min, hexanes/2-PrOH=90:10, retention time 12.4, 17.5 min.

4.4.1. (2*R*,3*R*)-2-(4-Isopropylphenyl)-3-(phenylsulfonyl)-oxirane (11c). Colorless solid; mp 110 °C; IR (neat) ν 1447, 1308, 1186, 1147 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.06–8.02 (m, 2H), 7.81–7.75 (m, 1H), 7.69–7.64 (m, 2H), 7.30–7.21 (m, 4H), 4.61 (d, J=1.4 Hz, 1H), 4.24 (d, J=1.7 Hz, 1H), 3.01–2.88 (m, 1H), 1.29 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6, 34.3, 57.5, 72.3, 126.5, 128.7, 129.4, 130.4, 131.6, 133.6, 136.6, 142.9 ppm; MS (EI): 302 $[M^+]$; HPLC: Chiralcel OD, flow rate 1.0 mL/min, hexanes/2-PrOH=500:4, retention time 27.0, 30.7 min.

4.4.2. (2*R*,3*R*)-2-(4-Isobutylphenyl)-3-(phenylsulfonyl)-oxirane (11d). Colorless solid; mp 103 °C; IR (neat) ν 1426, 1293, 1183 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.00–7.97 (m, 2H), 7.76–7.70 (m, 1H), 7.65–7.60 (m, 2H), 7.18–7.11 (m, 4H), 4.56 (d, J=1.4 Hz, 1H), 4.19 (d, J=1.4 Hz, 1H), 2.46 (d, J=7.3 Hz, 2H), 0.89 (s, 3H), 0.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 30.1, 45.1, 57.3, 71.9, 126.8, 128.7, 129.2, 129.4, 130.2, 134.4, 143.7, 148.3 ppm; MS (EI): 316 $[M^+]$; HPLC: Chiralcel OD, flow rate 1.0 mL/min, hexanes/2-PrOH=500:10, retention time 18.3, 20.8 min.

4.4.3. (2*R*,3*R*)-2-(3,5-Di-*tert*-butylphenyl)-3-(phenylsulfonyl)oxirane (11j). Colorless solid; mp 113 °C; IR (neat) ν 1447, 1363, 1327, 1154 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.02–8.00 (m, 2H), 7.77–7.72 (m, 1H), 7.66–7.61 (m, 2H), 7.43 (t, J=1.8 Hz, 1H), 7.08 (d, J=1.7 Hz, 1H), 4.60 (d, J=1.4 Hz, 1H), 4.19 (d, J=1.7 Hz, 1H), 1.30 (s, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 34.9, 58.2, 71.1, 124.8, 125.8, 128.9, 129.1, 129.5, 134.1, 136.6, 151.6 ppm; MS (FAB): 373 $[M^+$+1]; HPLC: Chiralcel OD, flow rate 1.0 mL/min, hexanes/2-PrOH=500:2.5, retention time 11.5, 13.7 min.

Acknowledgements

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