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Synthesis of Optically Active β-Amino-γ-butyrolactone Derivatives from Aspartic Acid†

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(3*S*, 4*R*)-3-Methoxycarbonylamino-4-phenyl-4-butanolide (**4a**) was prepared from L-aspartic acid by stereoselective reduction of ethyl (*S*)-3-methoxycarbonylamino-4-oxo-4-phenylbutyrate (**3a**).

α-Amino acids have recently been attracting much attention as versatile starting materials for the preparation of a variety of optically active compounds. For example, optically active β-amino alcohols and α-amino ketones have been synthesized by the conversion of α-carboxyl group with complete conservation of chirality on the α-carbon of amino acids.[1)]

In this respect, we have reported that aspartic acid can be used as the building block of a chiral molecule to produce optically active β-amino-γ-ketobutyrate.[1g)] In other examples, β-amino-γ-butyrolactone was obtained by selective reduction of the α-amino carboxyl group of the aspartic acid skeleton, which was shown to be a key intermediate for the synthesis of polyene macrolide amphotericin B.[2)] Ohno *et al.* employed the same aminolactone for the synthesis of *cis*-carbapenem, an antibiotic of current interest.[3)]

On the other hand, the synthesis of substituted β-amino-γ-butyrolactones has scarcely been undertaken: only reported have been the 4-alkyl derivatives[4)] such as 3-acetylamino-4-ethyl-4-butanolide, which is a degradation product of the β-lactam antibiotic PS-5.[4c)] Nonetheless, β-amino-γ-butyrolactones bearing an aryl group at the 4-position are generally considered to be useful starting materials for the preparation of various β-amino alcohols with significant pharmaceutical activity.[5)]

Therefore, it seemed of interest to synthesize optically active 4-aryl substituted β-amino-γ-butyrolactones. The synthetic strategy was similar to that of the non-substituted parent compound, starting from aspartic acid.[2,3)] Thus, reduction of the aforementioned optically active β-amino-γ-ketobutyrate[1g)] was carried out in the present study.

RESULTS AND DISCUSSION

Optically active β-amino-γ-ketobutyrate (**3a**) was prepared from L-aspartic acid *via* Friedel–Crafts acylation of benzene with *N*-methoxycarbonyl-α-L-aspartyl chloride β-ethyl ester (**2a**).[1g)]

Similarly, starting from the D-aspartic acid, the (3*R*)-isomer of **3a** was obtained with a reversed rotation of the product starting from L-aspartic acid. When toluene was used as a nucleophile instead of benzene, the corresponding toluoyl derivative (**3c**) was obtained. The enantiomeric excess (*e.e.*) of this product was determined by the use of (−)-PrDPPM[6)] as a shift reagent and was estimated to be 70.2% *e.e.*.

† Synthesis of Amino Acid and Related Compounds. Part XXXIII. For Part XXXII, see M. Seki, H. Kubota, T. Moriya, M. Yamagishi, S. Nishimoto and K. Matsumoto, *Chem. Pharm. Bull.*, **34**, 4516 (1986).

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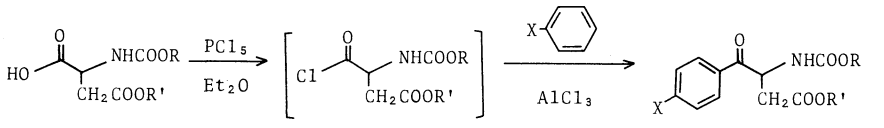


1a～c **2a～c** **3a～d**

1a, **2a**: (3*S*), R=Me, R′=Et
1b, **2b**: (3*R*), R=Me, R′=Et
1c, **2c**: (3*R*), R=Bzl, R′=Me

3a: (3*S*), R=Me, R′=Et, X=H
3b: (3*R*), R=Me, R′=Et, X=H
3c: (3*S*), R=Me, R′=Et, X=Me
3d: (3*R*), R=Bzl, R′=Me, X=H

SCHEME 1.

In general, *N*-benzyloxycarbonyl derivatives are more versatile and practical than the *N*-methoxycarbonyl derivatives. Regarding the synthesis of the *N*-benzyloxycarbonyl derivative, Buckley and Rapoport have already examined the Friedel–Crafts acylation using *N*-benzyloxycarbonyl-L-alanyl chloride and it's *N*-methyl derivative.[1a)] They demonstrated the process to be very sluggish, being accompanied by complete cleavage of the benzyloxycarbonyl group. Moreover, the integrity of the product was not established.

We then also examined the Friedel–Crafts reaction using the *N*-benzyloxycarbonyl-α-D-aspartyl chloride β-methyl ester. The acid chloride was generated by a similar procedure to that for the *N*-methoxycarbonyl derivative and subjected to Friedel–Crafts reaction using aluminum chloride and benzene. In this case, the *N*-benzyloxycarbonyl group was also completely cleaved, the deblocked product bearing the free amino group being monitored by TLC. It was then treated with benzyloxycarbonyl chloride and sodium bicarbonate to afford the target (**3d**) in a 20% yield. The optical purity of **3d** was estimated to be 62% *e.e.* by ^{1}H-NMR, using (−)-PrDPPM as a shift reagent. This low yield of the product was due to decarbonylation, considerable foaming being observed during the reaction.

The reduction of the optically active ketone compound (**3a**) was investigated using four different reducing agents, the results being summarized in Table II. Using phenyldimethylsilane in trifluoroacetic acid[7)] as a reducing agent, *trans*-β-methoxycarbonylamino-γ-butyrolactone (**4a**) was directly obtained with high stereoselectivity from **3a** (*trans*/*cis*=92/8) in an 87% yield; the intermediate γ-hydroxy-β-amino ester corresponding to **4a** was spontaneously cyclized. The diastereomer ratio was clearly determined by ^{1}H-NMR spectra, in which the benzylic proton of the *trans* isomer appeared at 5.42 ppm as a doublet with a coupling constant of 3.6 Hz, while the signal of the *cis* isomer appeared at 5.64 ppm as a doublet with a coupling constant of 6.0 Hz.

TABLE I. SYNTHESIS OF OPTICALLY ACTIVE β-AMINO γ-KETOBUTYRATE (**3**)

Compd.	Yield (%)[a]	$[\alpha]_D^{25}$/°(*c*, MeOH)	*e.e.* (%)
3b	52	+88.9(2.0)	>95[c]
3c	30	−82.2(2.0)	70[d]
3d	20[b]	+51.8(0.5)	62[d]

[a] Based on **1**.
[b] Reprotection step was included.
[c] Refer to ref. 1 g.
[d] Estimated by ^{1}H-NMR using (−)-PrDPPM as a shift reagent.

On the other hand, reduction with phenyldimethylsilane in hexamethylphosphorus triamide (HMPA) and tetra-*n*-butylammoniumfluoride[7)] did not show such high selectivity. In the case of sodium borohydride or catalytic hydrogenation, selectivity was hardly observed as shown in Table II.

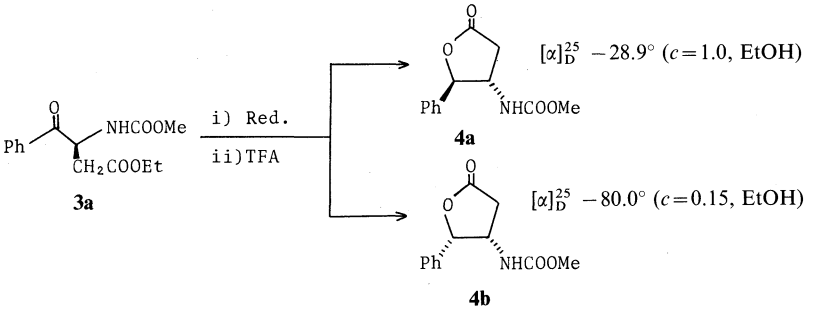
Estimation of the *e.e.* of the aminolactone (**4a**) was carried out by conversion to (+)-α-methoxy-α-(trifluoromethyl)phenylacetamide (MTPA amide). The methoxycarbonyl group was deblocked to an aminolactone (**9**) by

refluxing in 6 N-hydrochloric acid for 1 hr in a 46.2% yield. Subsequently, this was converted to an MTPA amide (**10**) by the reported method.[8] The standard racemic *trans* derivative (**8**) was prepared *via* highly stereoselective hydrogenation of racemic β-benzyloxycarbonylamino-γ-ketobutyrate (**6**). In the case of the ^{1}H-NMR spectrum of the MTPA amide of the racemic standard (**8**), two pairs of signals of benzylic methine and methylene protons were clearly observed. On the other hand, the MTPA amide (**10**) showed only one pair of signals. Thus, the aminolactone (**9**) was shown to be >95% enantiomerically pure.

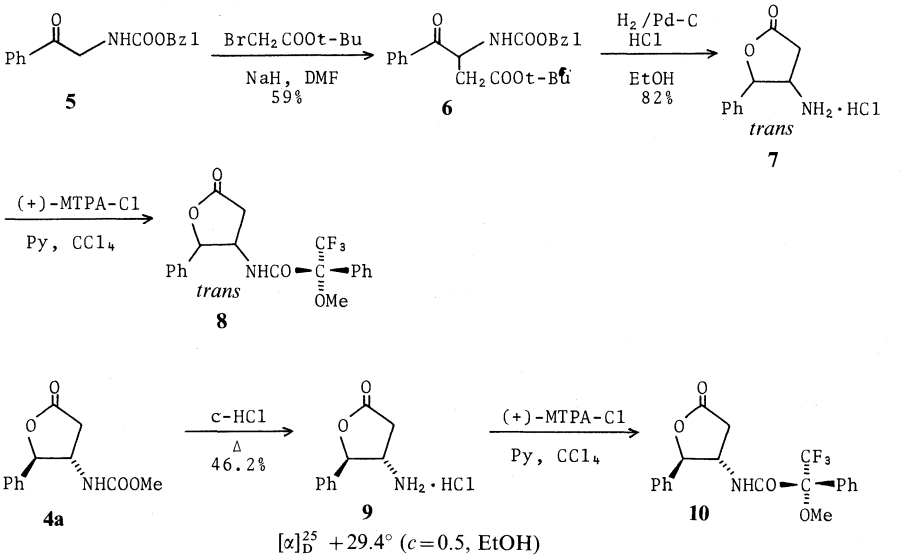
Thus, aspartic acid was recognized as one of the most efficient materials for the synthesis of optically active 4-phenyl substituted β-amino-γ-butyrolactone *via* β-amino-γ-ketobutyrate with high stereoselectively.

TABLE II. SYNTHESIS OF OPTICALLY ACTIVE β-AMINO-γ-BUTYROLACTONE (**4**)

Reducing agent	Temp. (°C)	Period (hr)	**4a**/**4b**	Yield (%)
$PhMe_2SiH$/TFA	0	16	92/8	87
$PhMe_2SiH$/*n*-Bu_4NF, HMPA	0	16	74/26	24
$NaBH_4$	5	1	64/36	77
H_2/Pd–C	20	11	47/53	93



SCHEME 2.



SCHEME 3.

EXPERIMENTAL

Melting points (mp) were measured on a Yamato melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-27G infrared spectrophotometer. NMR spectra were obtained using Hitachi R-40 and JEOL FX-100S NMR spectrometers with Me_4Si as the internal standard. Mass spectra were taken on a Hitachi RMU-6M spectrometer at an ionizing potential of 30 eV. Optical rotations were taken on a Perkin-Elmer 241 polarimeter, and column chromatography was accomplished using Kieselgel 60 (230～400 mesh, Merck).

Ethyl (S)-3-methoxycarbonylamino-4-oxo-4-phenylbutyrate (**3a**). This was prepared from **1a** in a 40% yield by following the reported procedure.[1g] mp 57～58°C (lit.[1g] mp 57～59°C). $[\alpha]_D^{25}$ −88.5° (c=2, MeOH) (lit.[1g] $[\alpha]_D^{25}$ −88.3° (c=2, MeOH)).

Ethyl (R)-3-methoxycarbonylamino-4-oxo-4-phenylbutyrate (**3b**). According to the procedure described for the preparation of **3a**, **3b** was obtained from **1b** in a 52% yield. mp 57～58°C. The IR, NMR and mass spectra were the same as those of **3a**. $[\alpha]_D^{25}$ +88.9° (c=2, MeOH). *Anal.* Found: C, 60.29; H, 6.13; N, 5.04. Calcd. for $C_{14}H_{17}NO_5$: C, 60.21; H, 6.13; N, 5.02%.

Ethyl (S)-3-methoxycarbonylamino-4-oxo-4-tolylbutyrate (**3c**). The acid chloride (**2a**) prepared from **1a** (7.44 g, 0.034 mol) and PCl_5 (7.07 g, 0.034 mol) in Et_2O (100 ml) by the same procedure as that mentioned for **3a** was dissolved in toluene (80 ml), and then $AlCl_3$ (12.5 g, 0.102 mol) was added with ice-cooling. The mixture was stirred overnight at room temperature and subjected to a similar work-up to that for **3a** to afford **3c** (2.99 g, 30%). mp 78～79°C. IR ν_{max} (Nujol) cm^{-1}: 3310, 1730, 1696, 1675; NMR δ ($CDCl_3$): 1.21 (3H, t, J=7.0 Hz), 2.41 (3H, s), 2.60～3.05 (2H, m), 3.69 (3H, s), 4.10 (2H, q, J=7.0 Hz), 5.18～5.62 (1H, m), 5.62～6.00 (1H, br.), 7.24 (2H, d, J=8.1 Hz), 7.84 (2H, d, J=8.1 Hz); MS m/z: 293 (M^+). $[\alpha]_D^{25}$ −82.2° (c=2, MeOH). *Anal.* Found: C, 61.24; H, 6.48; N, 4.83. Calcd. for $C_{15}H_{19}NO_5$: C, 61.42; H, 6.53; N, 4.78%.

Methyl (R)-3-benzyloxycarbonylamino-4-oxo-4-phenylbutyrate (**3d**). The acid chloride (**2c**) was generated from **1c** (11.2 g, 0.04 mol), PCl_5 (8.33 g, 0.04 mol) and Et_2O (120 ml) by a similar procedure to that for **3a**. Then, **2c** was dissolved in abs. benzene, and $AlCl_3$ (10.7 g, 0.08 mol) was added with ice-cooling. The mixture was stirred overnight at room temperature. The reaction was quenched with dil. HCl (the product bearing a free amino group, TLC *Rf*: 0.4 ($CHCl_3$: MeOH : AcOH = 85 : 15 : 3)). The aqueous layer was separated, washed with EtOAc and neutralized by adding 2 N-NaOH with ice-cooling. Into the aqueous solution, $NaHCO_3$ (10 g, 0.12 mol) and benzyloxycarbonyl chloride (6.82 g, 0.04 mol) were added with ice-cooling, and the mixture was vigorously stirred for 1 hr. After acidifying the reaction mixture to pH 4.0 with dil. HCl, the product was extracted with EtOAc. The crude product was chromatographed on SiO_2-gel (n-hex : EtOAc = 1 : 1) to afford **3d** (2.73 g, 20%). mp 51～52°C. IR ν_{max} (Nujol) cm^{-1}: 3320, 1730, 1690; NMR δ ($CDCl_3$): 2.60～3.40 (2H, m), 3.62 (3H, s), 5.06 (2H, s), 5.41～5.64 (1H, m), 5.70～6.02 (1H, br.), 7.20～7.64 (3H, m), 7.84～8.02 (m, 2H); MS m/z: 341 (M^+). $[\alpha]_D^{25}$ +51.8° (c=0.5, MeOH). *Anal.* Found: C, 66.68; H, 5.50; N, 4.09. Calcd. for $C_{19}H_{19}NO_5$: C, 66.85; H, 5.61; N, 4.10%.

(3S,4R) or (3S,4S)-3-Methoxycarbonylamino-4-phenyl-4-butanolide (**4a**, **4b**). The α-amino ketone (**3a**) was subjected to react under four types of reducing conditions subsequently described to produce **4a** and **4b**.

$PhMe_2SiH$/TFA. Into the α-amino ketone (**3a**, 1.5 g, 5.38 mmol) in CF_3CO_2H (9 ml) was added $PhMe_2SiH$ (890 mg, 6.53 mmol) at 0°C, and the mixture was stirred at 0°C for 16 hr. After evaporating the solvent, the product was extracted with EtOAc. The combined EtOAc solution was successively washed with H_2O, sat. aq. $NaHCO_3$ and H_2O, dried over $MgSO_4$, and evaporated to afford a mixture of **4a** and **4b** (1.1 g, 87%, **4a**/**4b** = 92/8). The mixture was separated by SiO_2-column chromatography (n-hex : EtOAc = 1 : 1). **4a**. mp 107～109°C. IR ν_{max} (Nujol) cm^{-1}: 3320, 1790, 1690; NMR δ ($CDCl_3$): 2.54 (1H, dd, J=4.5 and 18 Hz), 2.90 (1H, dd, J=7.5 and 18 Hz), 3.65 (3H, s), 4.10～4.50 (1H, m), 5.42 (1H, d, J=3.6 Hz), 5.68 (1H, d, J=6.0 Hz), 7.28 (5H, s); MS m/z: 235 (M^+). $[\alpha]_D^{25}$ −28.9° (c=1, EtOH). *Anal.* Found: C, 61.19; H, 5.47; N, 5.85. Calcd. for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95%. **4b**. mp 143～144°C. IR ν_{max} (Nujol) cm^{-1}: 3380, 1770, 1730; NMR δ ($CDCl_3$): 2.60 (1H, dd, J=4.5 and 18 Hz), 2.97 (1H, dd, J=7.5 and 18 Hz), 3.42 (3H, s), 4.55～5.10 (2H, m), 5.64 (1H, d, J=6.0 Hz), 7.00～7.50 (5H, m); MS m/z: 235 (M^+). $[\alpha]_D^{25}$ −80.0° (c=0.15, EtOH). *Anal.* Found: C, 61.18; H, 5.48; N, 5.93. Calcd. for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95%.

$PhMe_2SiH$/n-Bu_4NF, HMPA. To a solution of **3a** (700 mg, 2.51 mmol) in HMPA (5 ml) were added n-Bu_4NF (1 M in hexane, 0.126 ml, 0.126 mmol) and $PhMe_2SiH$ (411 mg, 3.01 mmol). The mixture was stirred at 0°C for 16 hr, before the reaction was quenched with H_2O and the product was extracted with Et_2O. The combined Et_2O solution was washed with H_2O, dried over $MgSO_4$ and evaporated. The residue was dissolved in CF_3CO_2H (5 ml) and evaporated. The crude product was chromatographed on SiO_2-gel (n-hex : EtOAc = 1 : 1) to afford a mixture of **4a** and **4b** (140 mg, 24%) (**4a**/**4b** = 74 : 26).

$NaBH_4$. Into a solution of **3a** (1.5 g, 5.38 mmol) in MeOH (20 ml) was added portionwise $NaBH_4$ (305 mg, 8.07 mmol) with ice-cooling. After stirring at 5°C for 1 hr,

AcOH was added and the mixture was evaporated. The product was extracted with EtOAc, before the combined EtOAc solution was washed with H_2O, dried over $MgSO_4$ and evaporated. The residue was treated with CF_3CO_2H (5 ml) and evaporated. The crude product was chromatographed on SiO_2-gel (*n*-hex : EtOAc = 1 : 1) to afford a mixture of **4a** and **4b** (970 mg, 77%, **4a**/**4b** = 64/36).

H_2/Pd–C. A mixture of **3a** (1 g, 3.58 mmol) and 10% Pd–C (200 mg) in EtOH (10 ml) was shaken under 3.5 kg/cm^2 of H_2 at 20°C for 11 hr. The mixture was then filtered and the filtrate was evaporated. The residue was treated with CF_3CO_2H (5 ml) and evaporated. The crude product was chromatographed on SiO_2-gel (*n*-hex : EtOAc = 1 : 1) to afford **4a** and **4b** (780 mg, 93%, **4a**/**4b** = 47/53).

t-Butyl 3-benzyloxycarbonylamino-4-oxo-4-phenylbutyrate (**6**). Into a suspension of 61.4% NaH (17.2 g, 0.456 mol) in DMF (300 ml) was added dropwise a solution of **5** (81 g, 0.423 mol) and *t*-butyl bromoacetate (86.8 g, 0.445 mol) in DMF (610 ml) at −40 to −50°C. After stirring for 1 hr at 10°C, the mixture was poured into ice-cooled water. The product was extracted with Et_2O. The combined ether solution was washed with H_2O, dried over $MgSO_4$ and evaporated. The crude product was chromatographed on SiO_2-gel (*n*-hex : $CHCl_3$: EtOAc = 5 : 5 : 1) to afford **6** (96 g, 59.2%). mp 69 ~ 70°C. IR ν_{max} (Nujol) cm^{-1}: 3250, 1715, 1680; NMR δ ($CDCl_3$): 1.38 (9H, s), 2.65 (1H, dd, J = 6.0 and 15 Hz), 2.92 (1H, dd, J = 6.0 and 15 Hz), 5.12 (2H, s), 5.40 ~ 5.70 (1H, m), 5.70 ~ 6.10 (1H, br.), 7.80 ~ 8.15 and 7.20 ~ 7.70 (10H, m); MS *m/z*: 384 (M^+). *Anal.* Found: C, 68.75; H, 6.52; N, 3.68. Calcd. for $C_{22}H_{25}NO_5$: C, 68.91; H, 6.57; N, 3.65%.

trans-3-Amino-4-phenyl-4-butanolide hydrochloride (**7**). To a solution of **6** (1.7 g, 4.4 mmol) in EtOH (30 ml) were added conc. HCl (1.1 ml) and 10% Pd–C (500 mg), the whole being shaken under 3.5 kg/cm^2 of H_2 for 1 hr. The mixture was filtered and the filtrate was evaporated. The resulting solid was recrystallized from MeOH–Et_2O to afford **7** (780 mg, 82%). mp 231 ~ 232°C (dec.). IR ν_{max} (Nujol) cm^{-1}: 1780; NMR δ (DMSO-d_6): 2.72 (1H, dd, J = 4.5 and 18 Hz), 3.18 (1H, dd, J = 4.5 and 18 Hz), 3.82 ~ 4.10 (1H, m), 5.66 (1H, d, J = 3.0 Hz), 7.15 ~ 7.50 (5H, m), 8.60 ~ 9.25 (3H, br.). MS *m/z*: 177 (M^+ − HCl). *Anal.* Found: C, 56.29; H, 5.54; N, 6.55; Cl, 16.49. Calcd. for $C_{10}H_{12}NO_2Cl$: C, 56.21; H, 5.66; N, 6.56; Cl, 16.59%.

(3S,4R)-3-Amino-4-phenyl-4-butanolide hydrochloride (**9**). A mixture of **4a** (0.6 g, 2.55 mmol) and 6 N-HCl (10 ml) was refluxed for 2 hr. After evaporating the mixture, the product was crystallized by adding Et_2O to afford **9** (250 mg, 46%). mp 245 ~ 248°C (dec). IR ν_{max} (Nujol) cm^{-1}: 1775. The NMR and mass spectra were identical with **7**. $[\alpha]_D^{25}$ +29.4° (*c* = 0.5, EtOH). *Anal.* Found: C, 56.17; H, 5.57; N, 6.53; Cl, 16.43. Calcd. for $C_{10}H_{12}NO_2Cl$: C, 56.21; H, 5.66; N, 6.56; Cl, 16.59%.

General procedure for the preparation and analysis of (+)-α-methoxy-α-(trifluoromethyl)phenylacetamides (**8**, **10**). Into a suspension of aminolactone (**7** or **9**, 31.6 mg, 0.148 mmol) in CCl_4 (0.45 ml) were added (+)-MTPA–chloride (37.9 mg, 0.15 mmol) and pyridine (0.3 ml). After standing at room temperature overnight, H_2O (1 ml) and Et_2O (20 ml) were added, and the Et_2O solution was successively washed with dil. HCl, sat. aq. $NaHCO_3$ and H_2O, dried over $MgSO_4$ and finally evaporated. The residue was dissolved in $CDCl_3$ (0.3 ml) and subjected to ^{1}H-NMR measurement.

8. δ ($CDCl_3$): 2.47 and 2.55 (dd, J = 4.5 and 18 Hz, 1H), 2.83 and 2.93 (dd, J = 7.5 and 18 Hz, 1H), 3.30 ~ 3.55 (m, 3H), 4.39 ~ 4.84 (m, 1H), 5.35 and 5.44 (d, J = 3.6 Hz, 1H), 7.15 ~ 7.70 (m, 11H).

10. δ ($CDCl_3$): 2.55 (dd, J = 4.5 and 18 Hz, 1H), 2.93 (dd, J = 7.5 and 18 Hz, 1H), 3.20 ~ 3.50 (m, 3H), 4.40 ~ 4.70 (m, 1H), 5.35 (d, J = 3.6 Hz, 1H), 7.15 ~ 7.67 (m, 11H).

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