Use of 2,2′-Dibenzothiazolyl Disulfide-Triphenylphosphine and Lawesson's Reagent in the Cyclization of *β*-Amino Acids

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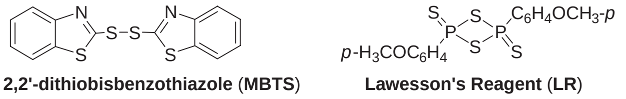
The disulfide reagents 2,2′-dithiobisbenzothiazole (MBTS) and 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (Lawesson's Reagent, LR) mediate the cyclization of *β*-amino acids with remarkable product yields. Compared to other cyclodehydrating agents, these have been found to be superior in terms of their cost, making them industrially viable. The advantageous properties of MBTS and LR make them useful and unique additions to the arsenal of cyclodehydrating agents.

In addition to the utility of monocyclic *β*-lactams as antibiotic agents, such as norcardicines, and monobactams,[1] their value in designing new enzyme inhibitors has caused a renewed interest in these compounds.[2] Moreover, azetidin-2-ones are important synthetic intermediates for the construction of highly functionalized natural and unnatural products. Considerable efforts have been focused on strategies for the de novo construction of the 4-membered ring system.[3–5] Although there are a variety of methods for the formation of *β*-lactam ring,[6–8] one of the most useful approaches is based on the dehydration of *β*-amino acids by means of condensing agents.[9–12] Several organophosphorus,[13,14] and triphenylphosphine-based reagents[15–18] have been used in *β*-lactam synthesis.

Recently, we demonstrated the utility of phosphoryl chloride[19] and (chloromethylene)dimethylammonium chloride[20] for the cyclodehydration of *β*-amino acids which proceeds via a mixed anhydride and active ester formation, respectively. In continuation of our work in this direction, we now wish to report the utility of two more efficient reagents. The first one, 2,2′-dithiobisbenzothiazole-triphenylphosphine (MBTS-TPP), is well-known as being useful for peptide synthesis[21] and amide synthesis[22] through oxidation–reduction condensation, introduced in 1970. More recently, we employed this reagent in the formation of azetidin-2-ones via a non concerted [2 + 2] cycloaddition.[23] Though dipyridyl disulfide has been used extensively for the cyclodehydration of *β*-amino acids,[24–28] to the best of our knowledge, there are no reports involving the use of 2,2′-dithiobisbenzothiazole to form *β*-lactam rings from a *β*-amino acid by intramolecular condensation, except for its use to prepare the carbapenem intermediate as mentioned in a Japanese patent.[29] The other reagent used in this study is Lawesson's reagent (LR), which is considered to be the most powerful reagent for the thionation of a wide variety of carbonyl compounds.[30] It is also useful as a racemization free coupling reagent in peptide synthesis.[31] Recently, this reagent has been used to prepare azetidin-2-ones via enolate–imine condensation reaction.[32] However, use of this reagent for cyclodehydration of *β*-amino acids to the corresponding azetidin-2-ones seems to be so far unexplored and is thus reported herein (Chart 1).



2,2′-dithiobisbenzothiazole (MBTS) **Lawesson's Reagent (LR)**

Chart 1.

Results and Discussion

Our success in using MBTS-TPP and LR for the synthesis of azetidin-2-ones via [2 + 2] cycloaddition reaction prompted us to explore the possibility of using them for the intramolecular cyclization of *β*-amino acids. In the MBTS-TPP mediated reaction, MBTS acts as oxidant and TPP as reductant. The proposed mechanism for the MBTS-TPP coupling reaction is shown in Scheme 1. The reaction proceeds with the formation of an addition adduct **1** of TPP and MBTS, which then reacts with the carboxylic acid functional group of the amino acid to generate the activated ester **3**. The nucleophilic character of the thiols makes them strong competitors for the amino group of acylating agents. Thus, attack of benzothiazole sulfide anion on the carbonyl carbon of **3** then leads to the formation of *β*-amino thioester **4** as shown. Thioester **4** was isolated and fully characterized by analytical and spectroscopic data. Finally, intramolecular attack of the amino nitrogen at the highly activated carbonyl carbon of thioester is facilitated by the tertiary base triethylamine (TEA) to afford the *β*-lactam **5** (pathway a). Alternatively, in the one-pot reaction, the formation of *β*-lactam can go directly through the active ester **3** itself, as shown in the pathway b.

LR also works in a similar fashion, and the proposed mechanism is shown in Scheme 2. LR reacts with the carboxylate anion forming the mixed anhydride **7**, making the carboxylate carbonyl more electrophilic. This facilitates attack of the amino nitrogen in the presence of base to form the *β*-lactam.

While performing these reactions, we found that the order of addition of reagents was critical to the success of the reaction. If MBTS was added to a solution of *β*-amino acid in dichloromethane at 25–30 °C followed by TPP, a homogenous solution was obtained, but subsequent addition of triethylamine did not

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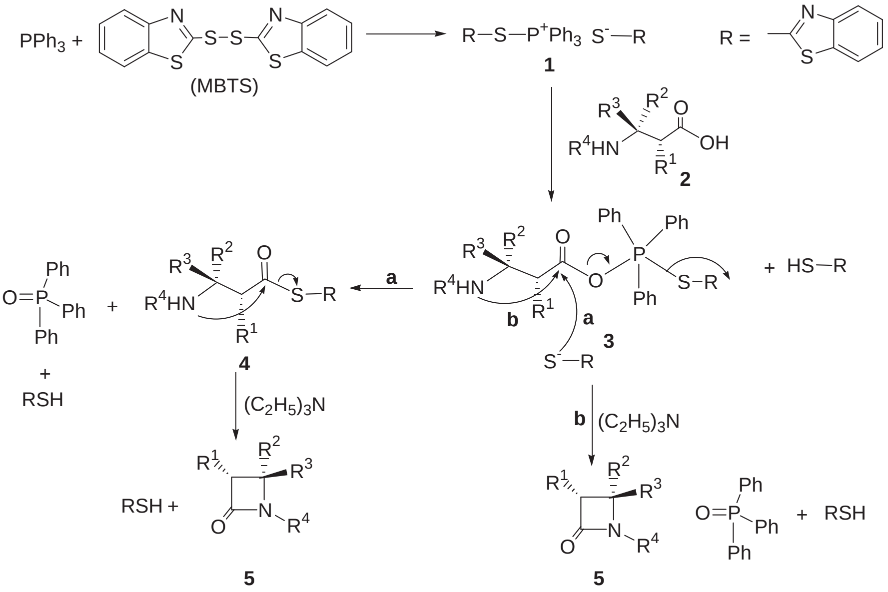
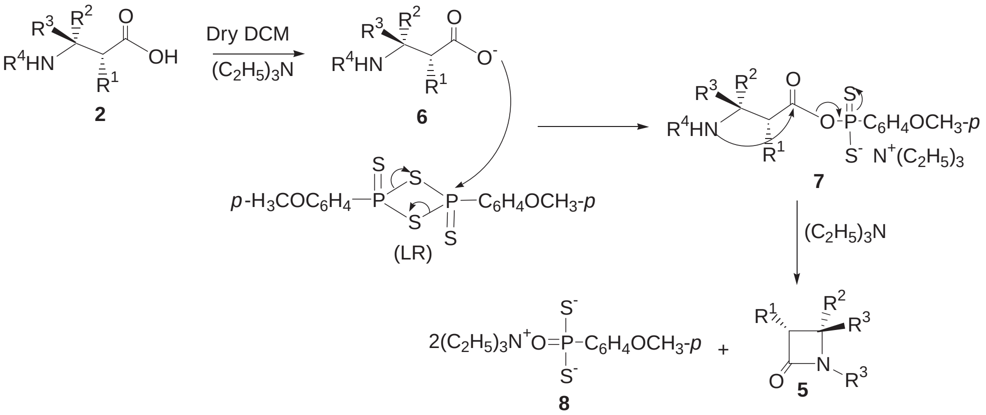


Scheme 1. Proposed mechanism for MBTS-TPP-mediated coupling.



Scheme 2. Proposed mechanism for LR-mediated coupling.

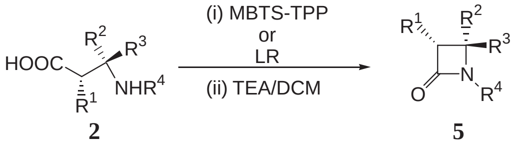
afford the expected β-lactam product. Instead, starting material was recovered unchanged. However, when MBTS was added to the stirred solution of TPP and β-amino acid in dichloromethane, adduct **1** was formed which then reacted with β-amino acid to form active ester **3**, which in the presence of triethylamine formed β-lactam **5**.

Similarly, in the case of LR-mediated cyclization, product formation was not observed if the β-amino acid was reacted as such with LR, without initial formation of carboxylate anion of β-amino acid. After formation of mixed anhydride **7** at 25–30 °C, triethylamine at 0 °C completes the intramolecular cyclization process. When the reaction was examined in different solvents, dichloromethane gave the best results in terms of chemical yields, although acetonitrile, tetrahydrofuran, and *N*,*N*-dimethylformamide were also effective. Furthermore, the reaction temperature was also studied from reflux to −10 °C. The optimum reaction conditions for MBTS-TPP-mediated cyclization are 25–30 °C and for LR, the best conditions for the formation of the mixed anhydride are 25–30 °C, 0 °C for nucleophilic attack at the carbonyl carbon of the mixed anhydride during the addition of triethylamine and finally stirring at 25–30 °C for approximately 10–12 h to complete the reaction.

Both MBTS-TPP and LR react with almost equal efficiency. To ascertain the reproducibility of these results, a variety of β-amino acids[33–36] were cyclized to the corresponding β-lactams as shown in Table 1. The reaction works well with both *erythro*- and *threo*-β-amino acids (**1s**–**1v**) to give the corresponding *cis* and *trans* β-lactams respectively, in excellent yields. The stereochemistry of the β-lactams was determined by ^{1}H NMR, based on the coupling constant values of the C_3–C_4 hydrogens ($J_{cis} > J_{trans}$). Normally *erythro*-β-amino acid ring closure occurs in low yield;[37–39] however, due to steric compression, the yield is higher with this method. The present methods are compatible with amino acids containing electron donating, aromatic groups, and aliphatic side chains at any position. Even the simplest β-amino acid, β-alanine cyclized to azetidin-2-one in good yield. Moreover, the workup is straightforward and involves just washing with sodium hydrogen carbonate and water.

Since the stereochemistry of the β-amino acids was preserved in the cyclization reaction, this procedure was used to determine unambiguously the isomers that were produced in

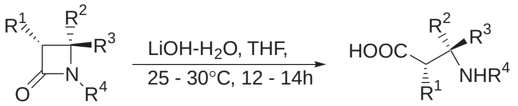
Table 1. β-Lactams Obtained in MBTS-TPP- and LR-Mediated Coupling



Entry	R^1	R^2	R^3	R^4	Yield/%[a)]	
					MBTS-TPP	LR
a.[36]	H	H	H	H	54	76
b.[20]	H	H	H	$CH_2C_6H_5$	80	80
c.[36]	H	CH_3	H	$CH_2C_6H_5$	83	79
d.[20]	H	CH_3	H	$CH_2CH_2C_6H_5$	85	82
e.[19]	H	CH_3	H	$(CH_2)_3CH_3$	75	81
f.[19]	H	CH_3	H	$CH_2CH(CH_3)_2$	82	78
g.[19]	H	CH_3	H	CH_2CH_2OH	83	79
h.[19]	H	CH_3	H	$CH_2CH(OH)CH_3$	79	82
i.[41]	CH_3	H	H	$CH_2C_6H_5$	85	85
j.[20]	CH_3	H	H	$CH_2CH_2C_6H_5$	86	81
k.[20]	CH_3	H	H	$(CH_2)_3CH_3$	73	82
l.[19]	CH_3	H	H	$CH_2CH(CH_3)_2$	81	80
m.[19]	CH_3	H	H	CH_2CH_2OH	82	83
n.[20]	CH_3	H	H	$CH_2CH(OH)CH_3$	84	84
o.[19]	H	C_6H_5	H	$CH_2C_6H_5$	80	81
p.[42]	H	C_6H_5	H	H	54	82
q.[20]	H	Piperonyl	H	H	50	80
r.[20]	H	$C_6H_4OCH_3$(p)	H	H	51	79
s.	CH_3	H	$C_6H_4CH_3$(p)	$C_6H_4CH_3$(p)	79	75
t.	C_2H_5	CH_3	H	$CH_2C_6H_5$	75	70
u.	$CH_2C_6H_5$	CH_3	H	$CH_2C_6H_5$	73	69
v.	$C_6H_5CH_2O$	C_6H_5	H	$CH_2C_6H_5$	70	77

a) Yields based on the weight of isolated product; all β-lactams prepared were racemic mixtures; fully characterized by their physical and spectroscopic data.

Table 2. β-Lactam Ring-Opening Reaction



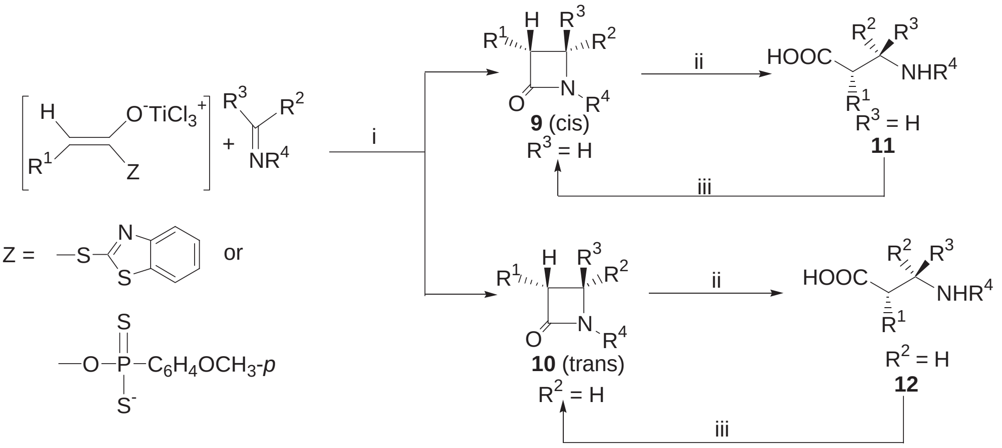
Entry	R^1	R^2	R^3	R^4	Yield/%
11a.	OC_6H_5	Piperonal	H	$C_6H_4OCH_3$	80
11b.	OC_6H_5	$CH{=}CHC_6H_5$	H	$C_6H_4OCH_3$	75
12a.	SC_6H_5	H	Piperonal	H	82
12b.	Phth	H	C_6H_5	$C_6H_4OCH_3$	78

a synthetic plan leading to β-amino acids. In connection with the studies directed towards the synthesis of non proteinogenic amino acids, a class of compounds that represents an important group of natural products,[40] we found that the treatment of 1,3,4-trisubstituted β-lactams with lithium hydroxide afforded the desired β-amino acids without epimerization at any of the two chiral centers. For this purpose, the starting β-lactams **9** and **10** were prepared by our recently developed titanium enolate–imine condensation.[23,32] Pure cis and trans isomers were subjected to treatment with lithium hydroxide in a tetrahydrofuran–water mixture and after usual workup, the corresponding β-amino acids were obtained in quantitative yields, Table 2. When β-amino acid **11** was allowed to react with the MBTS-TPP or LR in the presence of triethylamine, the corresponding β-lactam **9** was formed as the sole reaction product. Similarly, **12** afforded β-lactam **10**, thus confirming the absence of epimerization during β-lactam ring opening (Scheme 3).

The noteworthy features of the present methodology can be summarized as: (1) A variety of β-amino acids can be used with the system, i.e., Ph_3P-MBTS-TEA-DCM and LR-TEA-DCM, under mild conditions. Hence, there is no need for the protection of sensitive functional group like hydroxy substitutents; (2) very "high dilutions" and high temperatures (reflux) are not required and instead the reaction proceeds well in low dilutions and at room temperature;[28] (3) both *N*-substituted and *N*-unsubstituted β-amino acids can be cyclized; (4) the order of addition and also quantities of reactants play an important role; (5) the efficiency of these condensing systems is indeed remarkable, since the DCC method afforded β-lactams in 10–30% yield in most cases and, the Ph_3P-$(PyS)_2$ method, though yields are good, requires "high dilution" and reflux temperatures; and (6) the stereochemistry of the β-amino acid was preserved in the cyclization. As well the commercial availability and lower cost of the reagents, make these processes industrially viable.

Conclusion

In conclusion, the present methods offer several advantages over previously known methods in terms of simplicity, applicability, mildness, high yields, and availability of the reagents,



Scheme 3. Reagents and conditions: (i) NEt_3, DCM, −78 to 0 °C, 6 h; (ii) $LiOH{\cdot}H_2O$, THF–water, 25–30 °C, 12–14 h; (iii) TPP, MBTS, TEA, DCM, 25–30 °C, 14–16 h, or TEA, LR, DCM, 0–25 °C, 12–14 h.

therefore, the present methods as useful additions to the known methods.

Experimental

Melting points (Mp, °C) were determined on a Buchi SMP-20 Instrument and are uncorrected. The FT-IR spectra were recorded on a Perkin-Elmer Model 1430 spectrophotometer and were calibrated against polystyrene. Only the principal peaks of interest are reported and expressed in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded on a 300 MHz Bruker AC 300F spectrometer. Chemical shifts are expressed as δ values (ppm) downfield from tetramethylsilane (TMS). Elemental analysis (C, H, N) was performed using a Perkin-Elmer 2400 (C, H, N) elemental analyzer. Thin layer chromatography was performed using TLC grade Silica gel (G) and was developed in an atmosphere of iodine vapors. Acetonitrile was dried and purified by distillation over calcium hydride. Tetrahydrofuran was distilled over sodium and benzophenone. Dichloromethane was shaken with concentrated sulfuric acid, dried over potassium carbonate and distilled.

General Procedure for the Preparation of *S*-Benzothiazol-2-yl Thiocarboxylate. To a stirred solution of amino acid (0.1 mmol) and triphenylphosphine (31.5 mg, 0.12 mmol) in dichloromethane (1.0 mL) was added di(benzothiazol-2-yl) disulfide (36.6 mg, 0.1 mmol), and the mixture was stirred for 24 h at 25–30 °C. The reaction was quenched by the addition of water (1.0 mL), and the organic layer separated, washed with water (1.0 mL) and dried over anhydrous sodium sulfate. The excess solvent was removed under vacuum, and the remaining residue chromatographed over silica gel to provide the *S*-benzothiazol-2-yl thiocarboxylate.

Procedure for the Cyclization of *S*-Benzothiazol-2-yl Thiocarboxylate. To the thiocarboxylate (0.1 mmol) in dichloromethane (1.5 mL), triethylamine (0.2 mmol) in dichloromethane (1.0 mL) was added dropwise. The reaction mixture was stirred overnight, and the progress was monitored by TLC. The reaction was quenched with a saturated solution of sodium hydrogen carbonate (0.5 mL) and washed with water (0.5 mL), and the organic phase was separated and dried. The solvent evaporated under reduced pressure. Chromatography of the residue on silica gel using ethyl acetate:hexane (2:8) as an eluent afforded pure azetidin-2-one.

Cyclization of *β*-Amino Acid Using MBTS-TPP General Procedure. TPP (31.5 mg, 0.12 mmol), followed by MBTS (36.6 mg, 0.11 mmol), were added to a 0.07 M suspension of β-amino acid (0.1 mmol) in dry dichloromethane (1.5 mL) at 25–30 °C while stirring. After 5 min, the reaction mixture became homogenous. At this stage, triethylamine (19.7 mg, 0.195 mmol) in dry dichloromethane (1.0 mL) was added dropwise. The reaction mixture was stirred overnight and then quenched with a saturated solution of sodium hydrogen carbonate (0.5 mL). The solution was washed with water (0.5 mL), and the organic phase was separated and dried. The solvent was evaporated under reduced pressure. Chromatography of the residue on silica gel using ethyl acetate:hexane (2:8) as an eluent afforded pure azetidin-2-one.

Cyclization of *β*-Amino Acid Using LR General Procedure. To a suspension of a β-amino acid (0.1 mmol) in dry dichloromethane (10 mL, 0.01 M) was added triethylamine (0.2 g, 1.77 mmol) and the mixture was stirred at 25–30 °C for 30 min. LR (20.2 mg, 0.050 mmol) was added to this mixture, and the mixture was again stirred till it became homogenous (≈30 min). Then, the reaction mixture was cooled to 0 °C, and triethylamine (0.4 g, 3.55 mmol) in dry dichloromethane (1.0 mL) was added dropwise under stirring. The reaction mixture was stirred overnight at 25–30 °C and then quenched with water (5 mL). The organic phase was separated and dried over anhydrous sodium sulphate, and the solvent was evaporated under reduced pressure. Chromatography of the residue on silica gel using ethyl acetate:hexane (1:9) as the eluent afforded pure azetidin-2-one.

General Procedure for *β*-Lactam Ring Opening. To a solution of β-lactam (2 mmol) in tetrahydrofuran (7 mL) and water (3 mL), $LiOH–H_2O$ (0.14 g, 3.5 mmol) was added, and the resulting mixture was stirred overnight at rt. The solution was extracted with diisopropyl ether (2 × 20 mL), and after phase separation, the aqueous layer was acidified to pH ≈ 2 with saturated NaH_2PO_4 and then extracted with diisopropyl ether (20 mL) to yield after crystallization (DIPE/hexane) the β-amino acid (80%).

***erythro*-3-*p*-Anisidino-3-(1,3-benzodioxol-5-yl)-2-phenoxypropanoic Acid (11a):** FT-IR: 1600 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.55–6.86 (m, 3H, ArH), 7.37–6.86 (m, 5H, ArH), 6.90 (br s, 2H, NH and –COOH), 6.67–6.61 (m, 4H, ArH), 5.98 (d, $J = 2.78$ Hz, 1H, OCH_2O), 5.96 (d, $J = 2.78$ Hz, 1H, OCH_2O), 5.15 (d, $J = 4.15$ Hz, 1H, CHCO), 5.06 (d, $J = 4.15$ Hz, 1H, CHNH), 3.65 (s, 3H, OCH_3). ^{13}C NMR: δ 174.81, 157.54, 152.38, 149.46, 148.76, 141.72, 128.91 (2C), 127.24, 122.56, 122.37, 118.59 (2C), 117.12 (2C), 115.68 (2C), 111.36, 107.76, 101.30, 80.48, 55.57, 55.08. Anal. Found: C, 67.69; H, 5.30; N, 3.59%. Calcd for $C_{23}H_{21}NO_6$: C, 67.80; H, 5.20; N, 3.44%.

***erythro*-3-*p*-Anisidino-2-phenoxy-5-phenyl-4-pentenoic Acid**

(11b): FT-IR: 1603 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.40–6.86 (m, 5H, ArH), 7.35–7.19 (m, 5H, ArH), 6.90 (br s, 2H, NH and –COOH), 6.75 (d, $J = 15.50$ Hz, 1H, =CHPh), 6.65–6.57 (m, 4H, ArH), 5.98 (dd, $J = 15.50$, 8.22 Hz, 1H, –CCH=), 4.70 (dd, $J = 8.22$, 4.16 Hz, 1H, CHNH), 4.57 (d, $J = 4.16$ Hz, 1H, CHOPh), 3.63 (s, 3H, OCH_3). ^{13}C NMR: δ 173.07, 156.99, 152.47, 144.02, 137.16, 133.00, 129.25 (2C), 129.15 (2C), 128.07 (2C), 127.28, 126.49, 122.37, 116.95 (2C), 116.86 (2C), 115.50 (2C), 81.12, 55.56, 52.95. Anal. Found: C, 74.29; H, 5.49; N, 3.48%. Calcd for $C_{24}H_{23}NO_4$: C, 74.02; H, 5.95; N, 3.60%.

***threo*-3-*p*-Anisidino-3-(1,3-benzodioxol-5-yl)-2-phenylthiopropanoic Acid (12a):** FT-IR: 1610 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.01 (br s, 2H, NH and –COOH), 7.50–7.17 (m, 5H, ArH), 7.37–7.07 (m, 3H, ArH), 6.84–6.80 (m, 5H, ArH), 5.99 (d, $J = 2.79$ Hz, 1H, OCH_2O), 5.97 (d, $J = 2.79$ Hz, 1H, OCH_2O), 4.85 (d, $J = 7.42$ Hz, 1H, NHCH), 4.00 (d, $J = 7.42$ Hz, 1H, CHSPh), 3.49 (s, 3H, OCH_3). ^{13}C NMR: δ 179.19, 152.26, 149.25, 148.12, 140.87, 133.90, 131.08 (2C), 129.36 (2C), 127.72, 126.68, 121.75, 117.09 (2C), 116.78 (2C), 110.73, 106.43, 101.30, 63.03, 55.50, 51.69. Anal. Found: C, 65.03; H, 5.21; N, 3.18%. Calcd for $C_{23}H_{21}NO_5S$: C, 65.23; H, 5.00; N, 3.31%.

***threo*-3-*p*-Anisidino-2-(1,3-dihydro-1,3-dioxo-2*H*-isoindol-2-yl)-3-phenylpropanoic Acid (12b):** FT-IR: 1605 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.77–7.71 (m, 4H, ArH), 7.56–7.09 (m, 5H, ArH), 6.92 (br s, 2H, NH and –COOH), 6.64–6.43 (m, 4H, ArH), 4.79 (d, $J = 3.66$ Hz, 1H, CHNH), 4.17 (d, $J = 3.66$ Hz, 1H, CHCOOH), 3.49 (s, 3H, OCH_3). ^{13}C NMR: δ 173.46, 167.72 (2C), 152.26, 142.83, 134.43, 134.00 (2C), 131.61 (2C), 128.88 (2C), 128.26 (2C), 127.43, 124.09 (2C), 116.88 (2C), 116.56 (2C), 55.50, 52.86, 41.32, 40.40. Anal. Found: C, 69.61; H, 5.01; N, 6.40%. Calcd for $C_{24}H_{20}N_2O_5$: C, 69.23; H, 4.84; N, 6.73%.

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Supporting Information

The compounds that were prepared were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis, and details are provided in the Supporting Information. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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