Cycloaddition Reaction of Schiff Bases with Ketenes Generated by Pyrolysis of 2-Aryl-substituted 1,5,7-Trioxaspiro[2.5]octane-4,8-diones

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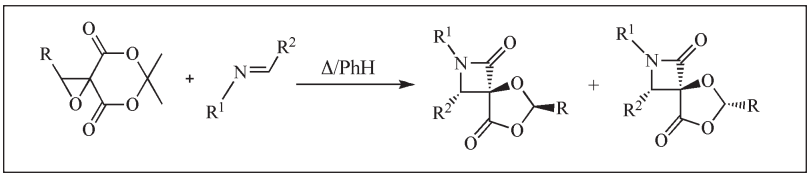

The α-oxo ketenes **6** which are generated by the pyrolysis of the 2-aryl-substituted 1,5,7-trioxaspiro[2.5]octane-4,8-diones **1**, were reacted with Schiff bases **2** to give spiro compounds constructed between the β-lactam and 1,3-dioxolan-4-one; *i.e.*, the 2,3,6-triaryl-2-aza-5,7-dioxaspiro[3.4]octane-1,8-diones **3** and **4**. Hydrogenation of the mixture of **3a** and **4a** in the presence of catalytic amount of Pd-C produced the *trans*-2-benzyloxy-1,4-diphenyl-β-lactam-3-carboxylic acid **9**.

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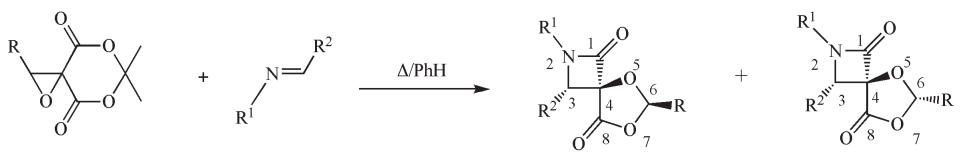
Meldrum's acids, 2,2-dimethyl-1,3-dioxane-4,6-dione, and its derivatives have been utilized as useful reagents for various organic syntheses [1,2]. Previously, we reported several reactions using methylene Meldrum's acids [3,4], and in our studies, the methylene Meldrum's acids were readily epoxidized with hydrogen peroxide without any catalyst and any base to give the 1,5,7-trioxaspiro[2.5]octane-4,8-diones **1** as good crystalline products [3]. These epoxides have two activated functional groups; *i.e.*, oxirane and Meldrum's acid rings. Hence, we expected that the epoxides can be used as new organic reagents and then noted the reaction with Schiff bases **2**. The pyrolysis of Meldrum's acid derivatives produced ketenes, which have been readily reacted with **2** to give heterocyclic compounds [5,6]. In addition, it is well known that carbonyl ylides generated from the pyrolysis of epoxides undergo a 1,3-dipolar cycloaddition with **2** to give 1,3-oxazolidines [7]. Thus, we expected that **1** possesses both the oxirane and Meldrum's acid rings as the activated functional groups, which undergoes any one of the above-mentioned reactions or a correlative reaction between both functional groups to give new heterocyclic compounds. In this paper, we report the reaction of **2** with **1**.

A solution of 6,6-dimethyl-2-phenyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**1a**) and benzylideneaniline (**2a**) in benzene was refluxed for 1 h. After evaporation of the solvent, the ^{1}H nmr spectrum of the residue showed the presence of two stereoisomers, whose ratio was **3a**:**4a** = 4:6. A similar reaction of several combinations between the epoxides **1a**-**e** and **2a**-**d** also gave two stereoisomers, whose ratios were in range of 1:1 to 4:6 of **3**:**4** based on their ^{1}H nmr analyses (Scheme 1). The isomers were readily separated by silica gel chromatography using hexane/EtOAc (8:2, *v/v*) as an eluent. In each reaction, **3a**-**m** were obtained from the first fraction by chromatography, while **4a**-**m** were in the next fraction (Table 1). The ir and ^{13}C nmr spectra of these isomers show two carbonyl groups in which one is the carbonyl of the β-lactam and the other is that of the 1,3-dioxolan-4-one [8]. Based on additional spectroscopic and elemental analytical data, we considered that these products, **3** and **4**, are 2,3,6-triaryl-substituted 2-aza-5,7-dioxaspiro[3.4]octane-1,8-diones which are spiro compounds constructed between the 5-position of the 1,3-dioxolan-4-one ring and 3-position of the β-lactam ring. Although these products have four possible stereoisomers between the 3- or 6-aryl-substituent and the substituents on the spiro-carbon, two stereoisomers were formed on the basis of the ^{1}H nmr analyses. The structures were clarified on the basis of the X-ray single crystallographic analysis of **3j** and **4j**. The ORTEP stereodrawings of **3j** and **4j** are shown in Figures 1 and 2 and their crystallographic data are summarized in Table 2

Scheme 1



1 **2** **3** **4**

Table 1
Preparation of 2,3,6-Triaryl-2-aza-5,7-dioxaspiro[3.4]octane-1,8-diones

Entry	R	R^1	R^2	*trans,trans*-Adduct	Yield (%)	*trans,cis*-Adduct	Yield (%)
1	Ph	Ph	Ph	**3a**	17	**4a**	24
2	4-BrC_6H_4	Ph	Ph	**3b**	16	**4b**	16
3	4-ClC_6H_4	Ph	Ph	**3c**	13	**4c**	21
4	3-MeC_6H_4	Ph	Ph	**3d**	22	**4d**	37
5	3-$MeOC_6H_4$	Ph	Ph	**3e**	31	**4e**	40
6	Ph	Ph	4-ClC_6H_4	**3f**	13	**4f**	12
7	4-BrC_6H_4	Ph	4-ClC_6H_4	**3g**	41	**4g**	37
8	3-MeC_6H_4	Ph	4-ClC_6H_4	**3h**	29	**4h**	36
9	3-$MeOC_6H_4$	Ph	4-ClC_6H_4	**3i**	32	**4i**	40
10	Ph	Ph	4-$MeOC_6H_4$	**3j**	17	**4j**	21
11	3-MeC_6H_4	Ph	4-$MeOC_6H_4$	**3k**	26	**4k**	32
12	4-BrC_6H_4	4-MeC_6H_4	4-MeC_6H_4	**3l**	20	**4l**	27
13	3-MeC_6H_4	4-MeC_6H_4	4-MeC_6H_4	**3m**	22	**4m**	32

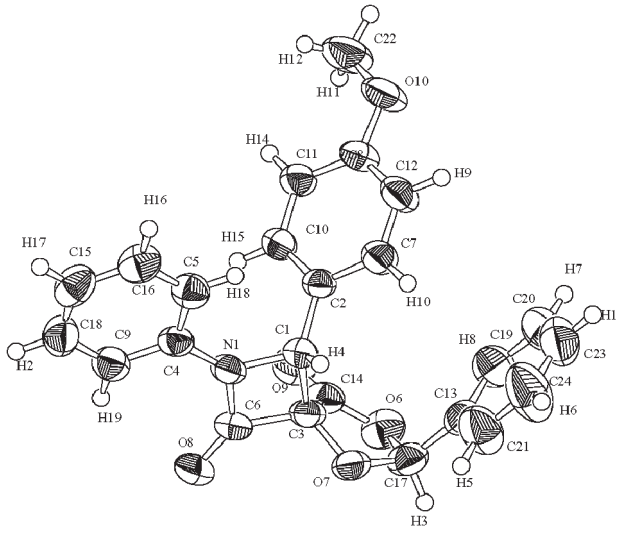


Figure 1. ORTEP drawing of **3j**.

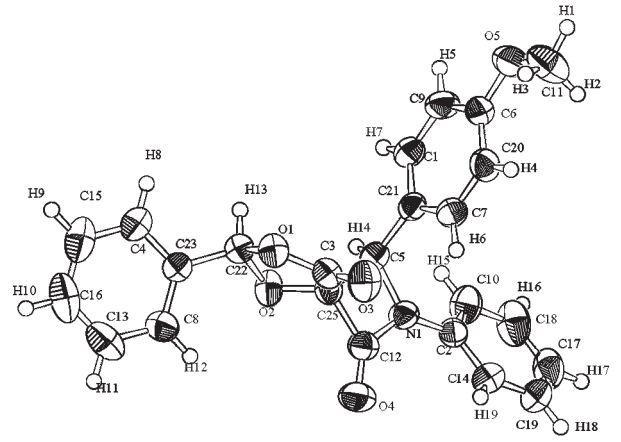


Figure 2. ORTEP drawing of **4j**.

[9]. For the conformations between the 3-(4-methoxyphenyl) group and 6-phenyl group and between the 5-oxa and 6-phenyl group, **3j** is the 4-r,3-*t*,6-*t*-form, while **4j** is the 4-r,3-*t*,6-*c*-one. Although the diaryl-substituted Schiff bases were good reagents in these reactions, in the case of the alkyl-substituted Schiff base, the expected spiro compounds were not obtained.

We have found that the pyrolysis of **1a** in aqueous benzene produced benzaldehyde and hydroxy Meldrum's acid [3]. We consider that **1a-e** undergo an intramolecular cyclization between the oxiran ring and carbonyl group to give 2,4,7,9-tetraoxabicyclo[3.4]nona-1^6-en-5-ones **5**. The compounds **5** have a 6-alkyloxy-1,3-dioxin-4-one structure. Because it is known that the 6-alkyloxy-1,3-dioxin-4-ones readily undergo ring opening [1,10], the hydrolysis of **5** produced the benzaldehyde and hydroxy Meldrum's acid. However, the compounds **5** under anhydrous conditions undergo a further intramolecular rearrangement with the loss of acetone to give α-oxo ketenes **6**. The Schiff bases **2** nucleophilically attack the center carbon of the α-oxo ketenes **6** from the a-side that is less bulky than the b-side

Scheme 2

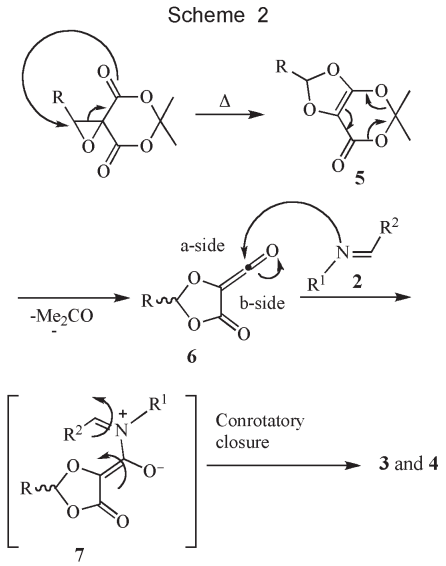


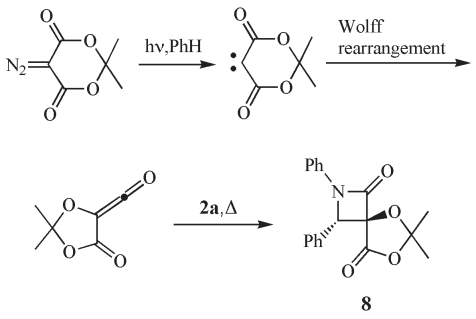
Table 2

Crystallographic Data for **3j** and **4j**

Compound	**3j**	**4j**
Formula (Weight)	$C_{24}H_{19}NO_5$ (401.42)	$C_{24}H_{19}NO_5$ (401.42)
Crystal Color, Habit	colorless, block	colorless, block
Crystal Dimensions (mm)	0.48 x 0.32 x 0.50	0.45 x 0.47 x 0.10
Crystal System	triclinic	monoclinic
Lattice Type	primitive	primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	2389 (9.5 –130.2°)	6686 (8.3 – 132.4°)
Camera Radius (mm)	127.40	127.40
a (Å)	9.8861(6)	11.2637(3)
b (Å)	11.9493(6)	9.9688(3)
c (Å)	9.0975(5)	18.6216(5)
α (°)	92.178 (2)	
β (°)	84.366(1)	104.858(1)
γ (°)	84.366(1)	
V (Å^3)	1010.52(10)	2021.02(9)
Space Group	P(#2)	$P2_1/c$ (#14)
Z value	2	6
D_{calc} (g cm^{-3})	1.319	1.199
F_{000}	420.0	768.00
μ (Cu*K*α) (cm^{-1})	7.66	8.50
λ (Å)	1.54178	1.54178
Temp. (K)	300.15	300.15
$2\theta_{max}$ (°)	136.4	136.4
No. of Reflections Measured		
Total	11332	20727
Unique (R_{int})	3418 (0.054)	3591 (0.052)
Structure Solution	Direct Method (SIR 92)	Direct Method (SIR 92)
R; R_w	0.068; 0.134	0.062; 0.116
R1	0.046	0.039

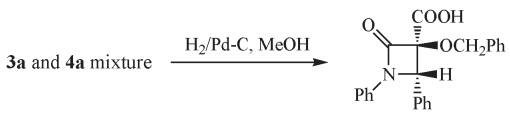
(Scheme 2), and the conrotatory ring-closure [11] of the generated zwitterions **7** affords the spiro compounds **3** and **4**. Because a similar intermediate **7** with the ketene **6** is prepared by the photolysis of diazo Meldrum's acid *via* Wolff rearrangement [12], we have examined the reaction of **2a** with diazo Meldrum's acid. From this result, the expected 2-aza-6,6-dimethyl-5,7-dioxa-2,3-diphenyl-spiro[3.4]octane-1,8-dione **8** was obtained in 45% yield (Scheme 3). This result strongly suggests that the α-oxo ketenes **6** were produced by the pyrolysis of **1**.

Scheme 3



8

Scheme 4



9

If the 1,3-dioxolane ring of the diastereomers **3** and **4** is able to open by some chemical method, it is expected that novel compounds that will maintain the stereochemistry of the β-lactam ring are obtained. We then investigated the hydrogenation of the **3a** and **4a** mixture in the presence of Pd/C. At room temperature in MeOH, the **3a** and **4a** mixtures readily underwent hydrogenation to produce the *trans*-2-benzyloxy-1,4-diphenyl-β-lactam-3-carboxylic acid **9** in 70% yield (Scheme 4).

As is well-known, the syntheses of the β-lactams are some of the most important methods in organic synthesis [13-15], and several efforts have been devoted to the synthesis of spiro-β-lactams [15]. Moreover, it is known that the 1,3-dioxolan-4-ones are useful precursors of α-oxo ketenes [16], which are also important intermediates in organic synthesis [17]. In conclusion, we found that the pyrolysis of **1** gave the α-oxo ketenes **6**, which underwent the cycloaddition reaction with Schiff bases **2** to yield the 2,3,6-triaryl-2-aza-5,7-dioxaspiro[3.4]octane-1,8-diones **3** and **4**.

EXPERIMENTAL

The epoxides **1a**-**e** were prepared according to our published procedure [3]. The melting points were determined on a micro hot-stage (Yazawa) and are uncorrected. The ir spectra were recorded using a BIO-RAD FTS-60A spectrophotometer as KBr disks. The ms spectra were measured with a JEOL JMS-600H spectrometer. The nmr spectra were recorded in a $CDCl_3$ or DMSO-d_6 solution on a Bruker Avance-400 or a JEOL JNM-EX90 spectrometer; and all chemical shifts were reported in ppm using tetramethylsilane as the internal standard. Column chromatography was carried out using silica gel (Merck: Art 9385).

General Procedure for the Reaction of Schiff Bases (**2**) with 1,5,7-Trioxaspiro[2.5]octane-4,8-diones (**1**).

A solution of **1a**-**e** (1.5 mmol) and **2a**-**d** (1.5 mmol) in benzene (20 ml) was refluxed for 1 h under an Ar atmosphere. The reaction was monitored by the disappearance of **1** or **2** on TLC (EtOAc/hexane, 2:8, *v/v*). After evaporation of the solvent, the residue was chromatographed on silica gel using EtOAc/hexane (2:8, *v/v*) as the eluent. The first fraction produced the 4-r,3-*t*,6-*t*-2,3,6-triaryl-2-aza-5,7-dioxaspiro[3.4]octane-1,8-diones (**3a**-**m**), and its 4-r,3-*t*,6-*c*-isomers (**4a**-**m**) were obtained from the next fraction (Table 1). The physical and analytical data are as follows.

4-r,3-*t*,6-*t*-2-Aza-5,7-dioxa-2,3,6-triphenylspiro[3.4]octane-1,8-dione (**3a**).

This compound was obtained as colorless crystals (acetonitrile), mp 162 - 163°; ir: CO 1806, CON 1768 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$): δ 5.25 (s, 1H, 3-H), 6.75 (s, 1H, 6-H), 6.98 - 7.55 (m, 15H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 67.8 (3-C), 88.4 (4-C), 103.5 (6-C), 118.1, 125.3, 126.1, 127.5, 128.5, 129.0, 129.3, 129.9, 130.7, 135.4, 136.2, 159.6 (CON), 164.5 (COO); ms: m/z 371 (M^+, 4), 253 (4), 252 (24), 181 (42), 180 (20), 119 (11), 118 (100), 105 (6), 90 (15), 89 (5), 77 (15), 51 (4).

Anal. Calcd. for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.70; H, 4.57; N, 3.82.

4-r,3-*t*,6-*c*-2-Aza-5,7-dioxa-2,3,6-triphenylspiro[3.4]octane-1,8-dione (**4a**).

This compound was obtained as colorless crystals (acetonitrile), mp 195 - 196°; ir: CO 1804, CON 1761 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$): δ 5.48 (s, 1H, 3-H), 6.59 (s, 1H, 6-H), 7.12 - 7.18 (m, phenyl proton, 1H), 7.27 - 7.53 (m, phenyl proton, 12H), 7.60 - 7.61 (m, phenyl proton, 2H); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 68.1 (3-C), 89.6 (4-C), 104.2 (6-C), 118.1, 126.7, 127.3, 128.9, 129.3, 129.5, 130.7, 131.1, 133.9, 136.3, 159.2 (CON), 164.4 (COO); ms: m/z 371 (M^+, 4), 253 (5), 252 (27), 182 (8), 181 (45), 180 (24), 121 (7), 119 (12), 118 (100), 105 (8), 90 (15), 88 (15), 77 (21), 51 (5).

Anal. Calcd. for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.57; H, 4.49; N, 3.81.

4-r,3-*t*,6-*t*-2-Aza-6-(4-bromophenyl)-5,7-dioxa-2,3-diphenylspiro-[3.4]octane-1,8-dione (**3b**).

This compound was obtained as colorless crystals (chloroform-hexane), mp 178 - 179°; ir: CO 1801, CON 1748 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 5.25 (s, 1H, 3-H), 6.72 (s, 1H, 6-H), 7.08 (d, 2H, phenyl proton, J = 6.8 Hz), 7.11 - 7.16 (m, phenyl proton, 1H), 7.27 - 7.37 (m, phenyl proton, 9H), 7.63 (d, 2H, phenyl proton, J = 8.4 Hz); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 67.7 (3-C), 86.6 (4-C), 102.7 (6-C), 118.1, 125.1, 125.3, 127.5, 127.7, 128.6, 129.3, 129.6, 129.8, 132.2, 134.4, 136.2, 159.4 (CON), 164.3 (COO); ms: m/z 451 (2), 449 (M^+, 2), 332 (9), 330 (9), 182 (6), 181 (43), 180 (22), 152 (4), 119 (13), 118 (100), 90 (15), 89 (7), 77 (14), 51 (4).

Anal. Calcd. for $C_{23}H_{16}BrNO_4$: C, 61.35; H, 3.58; N, 3.11. Found: C, 61.10; H, 3.66; N, 3.08.

4-r,3-*t*,6-*c*-2-Aza-6-(4-bromophenyl)-5,7-dioxa-2,3-diphenylspiro[3.4]octane-1,8-dione (**4b**).

This compound was obtained as colorless crystals (ether), mp 162 - 163°; ir: CO 1808, CON 1769 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 5.48 (s, 1H, 3-H), 6.56 (s, 1H, 6-H), 7.13 - 7.18 (m, 1H, phenyl proton), 7.28 - 7.43 (m, 9H, phenyl proton), 7.48 (d, 2H, phenyl proton, J = 8.4 Hz), 7.61 (d, 2H, phenyl proton, J = 8.4 Hz); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 68.0 (3-C), 89.4 (4-C), 103.3 (6-C), 118.1, 125.3, 125.5, 127.3, 128.3, 129.0, 129.3, 129.6, 130.5, 132.1, 133.0, 136.2, 159.1 (CON), 164.1 (COO); ms: m/z 451 (2), 449 (M^+, 2), 332 (9), 330 (9), 182 (5), 181 (39), 180 (18), 119 (11), 118 (100), 90 (12), 89 (5), 77 (11).

Anal. Calcd. for $C_{23}H_{16}BrNO_4$: C, 61.35; H, 3.58; N, 3.11. Found: C, 61.00; H, 3.65; N, 3.07.

4-r,3-*t*,6-*t*-2-Aza-6-(4-chlorophenyl)-5,7-dioxa-2,3-diphenylspiro[3.4]octane-1,8-dione (**3c**).

This compound was obtained as colorless crystals (ether), mp 185 - 186°; ir: CO 1802, CON 1748 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$): δ 5.25 (s, 1H, 3-H), 6.72 (s, 1H, 6-H), 7.03 - 7.54 (m, 14H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 67.7 (3-C), 88.3 (4-C), 102.7 (6-C), 118.1, 125.3, 127.4, 127.5, 128.6, 129.3, 129.5, 129.8, 133.9, 136.2, 136.8, 159.4 (CON), 164.3 (COO); ms: m/z 407 (1), 405 (M^+, 3), 288 (4), 286 (12), 237 (3), 211 (7), 182 (7), 181 (52), 180 (27), 152 (3), 140 (3), 139 (6), 119 (11), 118 (100), 111 (3), 104 (5), 91 (4), 90 (19), 89 (8), 78 (4), 77 (22), 51 (7).

Anal. Calcd. for $C_{23}H_{16}ClNO_4$: C, 68.07; H, 3.97; N, 3.45. Found: C, 67.70; H, 3.92; N, 3.36.

4-r,3-*t*,6-*c*-2-Aza-6-(4-chlorophenyl)-5,7-dioxa-2,3-diphenylspiro[3.4]octane-1,8-dione (**4c**).

This compound was obtained as colorless crystals (chloroform-hexane), mp 195 - 196°; ir: CO 1807, CON 1769 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$): δ 5.47 (s, 1H, 3-H), 6.57 (s, 1H, 6-H), 7.12 - 7.63 (m, 14H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 68.0 (3-C), 89.5 (4-C), 103.3 (6-C), 118.1, 125.4, 127.3, 128.2, 129.0, 129.2, 129.3, 129.6, 130.5, 132.6, 136.2, 137.2, 159.1 (CON), 164.6 (COO); ms: m/z 407 (4), 405 (M^+, 8), 288 (11), 287 (6), 286 (29), 237 (8), 215 (3), 211 (5), 182 (13), 181 (88), 180 (43), 152 (6), 141 (3), 140 (4), 139 (9), 119 (20), 118 (10), 111 (4), 104 (7), 91 (5), 90 (34), 89 (11), 78 (6), 77 (31), 75 (3), 63 (3), 51 (7).

Anal. Calcd. for $C_{23}H_{16}ClNO_4$: C, 68.07; H, 3.97; N, 3.45. Found: C, 67.79; H, 3.90; N, 3.33.

4-r,3-*t*,6-*t*-2-Aza-6-(3-methylphenyl)-5,7-dioxa-2,3-diphenylspiro[3.4]octane-1,8-dione (**3d**).

This compound was obtained as colorless crystals (acetonitrile), mp 155 - 156°; ir: CO 1806, CON 1771 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, Me), 5.23 (s, 1H, 3-H), 6.73 (s, 1H, 6-H), 7.04 - 7.40 (m, 12H, phenyl proton); ^{13}C nmr (100 MHz, $CDCl_3$): δ 21.4 (Me), 67.8 (3-C), 88.3 (4-C), 103.5 (6-C), 118.1, 123.2, 125.2, 127.5, 128.5, 128.9, 129.2, 129.4, 131.4, 135.4, 136.2, 138.9, 159.6 (CON), 164.6 (COO); ms: m/z 385 (M^+, 4), 267 (3), 266 (19), 182 (5), 181 (39), 180 (21), 119 (18), 118 (100), 104 (4), 91 (9), 90 (17), 89 (5), 78 (3), 77 (14) 51 (4).

Anal. Calcd. for $C_{24}H_{19}NO_4$: C, 74.79; H, 4.97; N, 3.63. Found: C, 74.45; H, 5.05; N, 3.67.

4-r,3-*t*,6-*c*-2-Aza-6-(3-methylphenyl)-5,7-dioxa-2,3-diphenylspiro[3.4]octane-1,8-dione (**4d**).

This compound was obtained as colorless crystals (acetonitrile), mp 170 - 171°; ir: CO 1801, CON 1764 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, Me), 5.47 (s, 1H, 3-H), 6.55 (s, 1H, 6-H), 7.11 - 7.20 (m, 1H, phenyl proton), 7.30 - 7.43 (m, 13H, phenyl proton); ^{13}C nmr (100 MHz, $CDCl_3$): δ 21.6 (Me), 68.2 (3-C), 89.8 (4-C), 104.5 (6-C), 118.3, 124.1, 125.4, 127.4, 127.5, 128.9, 129.5, 129.7, 130.8, 132.1, 133.9, 136.5, 139.0, 159.4 (CON), 164.6 (COO); ms: m/z 385 (M^+, 5), 267 (5), 266 (24), 182 (7), 181 (47), 180 (25), 119 (19), 118 (100), 91 (10), 90 (15), 89 (5), 78 (4), 77 (14).

Anal. Calcd. for $C_{24}H_{19}NO_4$: C, 74.79; H, 4.97; N, 3.63. Found: C, 74.74; H, 5.06; N, 3.58.

4-r,3-*t*,6-*t*-2-Aza-6-(3-methoxyphenyl)-5,7-dioxa-2,3-diphenylspiro[3.4]octane-1,8-dione (**3e**).

This compound was obtained as colorless crystals (ether-hexane), mp 100 - 102°; ir: CO 1812, CON 1771 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 3.83 (s, 3H, Me), 5.24 (s, 1H, 3-H), 6.74 (s, 1H, 6-H), 6.91(t, 1H, phenyl proton, J = 2.1 Hz), 7.04 (dt, 2H, phenyl proton, J = 1.8, 7.1 Hz), 7.11 - 7.16 (m, 1H, phenyl proton), 7.27 - 7.39 (m, 9H, phenyl proton), 7.40 (t, 1H, phenyl proton, J = 7.9 Hz); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 55.4 (Me), 67.8 (3-C), 88.3 (4-C), 103.2 (6-C), 111.3, 116.4, 118.2, 125.3, 127.5, 128.5, 129.3, 129.4, 129.9, 130.2, 136.2, 137.0, 160.6, 159.5 (CON), 164.5 (COO); ms: m/z 401 (M^+, 8), 283 (4), 282 (20), 212 (4), 211 (26), 182 (6), 181 (43), 180 (20), 148 (6), 136 (4), 135 (6), 120 (4), 119 (14), 118 (100), 107 (3), 91 (5), 90 (15), 89 (4), 78 (3), 77 (16), 51 (3).

Anal. Calcd. for $C_{24}H_{19}NO_5$: C, 71.81; H, 4.77; N, 3.49. Found: C, 71.61; H, 4.68; N, 3.48.

4-r,3-*t*,6-*c*-2-Aza-6-(3-methoxyphenyl)-5,7-dioxa-2,3-diphenylspiro[3.4]octane-1,8-dione (**4e**).

This compound was obtained as colorless crystals (acetonitrile), mp 160 - 161°; ir: CO 1799, CON 1771 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 3.86 (s, 3H, Me), 5.48 (s, 1H, 3-H), 6.57 (s, 1H, 6-H), 7.01 (ddd, 1H, phenyl proton, J = 0.5, 2.5, 8.4 Hz), 7.12 - 7.17 (m, 2H, phenyl proton), 7.19 (t, 1H, phenyl proton, 2.2 Hz), 7.27 - 7.46 (m, 10H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 55.4 (Me), 68.0 (3-C), 89.5 (4-C), 104.0 (6-C), 111.3, 117.3, 118.1, 119.0, 125.2, 127.3, 127.5, 128.9, 129.2, 129.5, 129.9, 130.6, 135.4, 136.2, 160.0, 159.3 (CON), 164.3 (COO); ms: m/z (M^+, 4), 283 (4), 278 (21), 211 (3), 182 (6), 181 (39), 180 (18), 136 (4), 135 (6), 119 (11), 118 (100), 104 (3), 91 (3), 90 (11), 89 (3), 78 (3), 77 (12), 51 (3).

Anal. Calcd. for $C_{24}H_{19}NO_5$: C, 71.81; H, 4.77; N, 3.49. Found: C, 71.61; H, 4.68; N, 3.48.

4-r,3-*t*,6-*t*-2-Aza-3-(4-chlorophenyl)-5,7-dioxa-2,6-diphenylspiro[3.4]octane-1,8-dione (**3f**).

This compound was obtained as colorless crystals (acetonitrile), mp 166 - 169°; ir: CO 1809, CON 1771 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 5.25 (s, 1H, 3-H), 6.73 (s, 1H, 6-H), 7.08 (d, 2H, phenyl proton, J = 6.8 Hz), 7.11 - 7.16 (m, 1H, phenyl proton), 7.23-7.38 (m, 9H, phenyl proton), 7.47 (d, 2H, phenyl proton, J = 8.4 Hz); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 67.0 (3-C), 88.2 (4-C), 103.4 (6-C), 118.0, 125.4, 126.0, 128.4, 128.8, 128.9, 129.0, 129.3, 130.7, 135.3, 135.4, 135.9, 159.2 (CON), 164.5 (COO); ms: m/z 407 (1), 405 (M^+, 3), 288 (3), 286 (12), 182 (5), 181 (36), 180 (18), 152 (3), 139 (4), 119 (10), 118 (100), 104 (3), 90 (15), 89 (5), 77 (13), 51 (3).

Anal. Calcd. for $C_{23}H_{16}ClNO_4$: C, 68.07; H, 3.97; N, 3.45. Found: C, 68.06; H, 4.01; N, 3.42.

4-r,3-*t*,6-*c*-2-Aza-3-(4-chlorophenyl)-5,7-dioxa-2,6-diphenylspiro-[3.4]octane-1,8-dione (**4f**).

This compound was obtained as colorless crystals (acetonitrile), mp 159 - 160°; ir: CO 1793, CON 1776 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 5.44 (s, 1H, 3-H), 6.59 (s, 1H, 6-H), 7.14 - 7.18 (m, 1H, phenyl proton), 7.28 - 7.49 (m, 11H, phenyl proton), 7.58 - 7.68 (m, 1H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 67.2 (3-C), 89.5 (4-C), 104.3 (6-C), 118.0, 125.4, 126.7, 128.8, 128.9, 129.1, 129.3, 131.1, 133.7, 135.4, 135.9, 159.0 (CON), 164.0 (COO); ms: m/z 407 (3), 405 (M^+, 8), 288 (9), 287 (5), 286 (23), 271 (3), 252 (7), 237 (3), 217 (16), 216 (13), 215 (52), 214 (18), 182 (6), 181 (40), 180 (19), 155 (3), 154 (28), 153 (8), 152 (83), 139 (4), 124 (9), 119 (12), 118 (100), 111 (3), 105 (8), 104 (6), 91 (4), 90 (15), 89 (14), 86 (5), 84 (3), 78 (5), 77 (32), 63 (3), 51 (7).

Anal. Calcd. for $C_{23}H_{16}ClNO_4$: C, 68.07; H, 3.97; N, 3.45. Found: C, 68.11; H, 3.91; N, 3.47.

4-r,3-*t*,6-*t*-2-Aza-6-(bromophenyl)-3-(4-chlorophenyl)-5,7-dioxa-2-phenylspiro[3.4]octane-1,8-dione (**3g**).

This compound was obtained as colorless crystals (acetonitrile), mp 202 - 205°; ir: CO 1803, CON 1751 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 5.20 (s, 1H, 3-H), 6.73 (s, 1H, 6-H), 7.15 (t, 1H, phenyl proton, J = 8.0 Hz), 7.22 - 7.31 (m, 8H, phenyl proton), 7.63 (d, 2H, phenyl proton, J = 6.6 Hz); ^{13}C nmr (100 MHz, $CDCl_3$): δ 67.0 (3-C), 88.1 (4-C), 102.7 (6-C), 118.0, 125.1, 125.5, 127.6, 128.2, 128.8, 128.9, 129.1, 129.4, 132.3, 134.3, 135.6, 135.8, 159.0 (CON), 164.3 (COO); ms: m/z 485 (4), 483 (M^+, 3), 368 (3), 366 (9), 364 (7), 271 (4), 218 (3), 217 (18), 216 (14), 215 (60), 214 (19), 198 (3), 196 (4), 185 (5), 183 (5), 183 (5), 155 (5), 154 (35), 153 (10), 152 (100), 126 (4), 124 (11), 119 (4), 104 (4), 89 (11), 77 (18), 76 (3), 51 (4).

Anal. Calcd. for $C_{23}H_{15}BrClNO_4$: C, 56.98; H, 3.12; N, 2.89. Found: C, 56.64; H, 3.16; N, 2.88.

4-r,3-*t*,6-*c*-2-Aza-6-(bromophenyl)-3-(4-chlorophenyl)-5,7-dioxa-2-phenylspiro[3.4]octane-1,8-dione (**4g**).

This compound was obtained as colorless crystals (acetonitrile), mp 157 - 158°; ir: CO 1805, CON 1773 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 5.49 (s, 1H, 3-H), 6.56 (s, 1H, 6-H), 7.16 (t, 1H, phenyl proton, J = 8.4 Hz), 7.27-7.38 (m, 8H, phenyl proton), 7.46 (d, 2H, phenyl proton, J = 8.5 Hz), 7.61 (dd, 2H, phenyl proton, J = 1.7, 6.7 Hz); ^{13}C nmr (100 MHz, $CDCl_3$): δ 67.2 (3-C), 89.2 (4-C), 103.5 (6-C), 118.0, 125.5, 125.6, 128.3, 128.8, 128.9, 129.0, 129.3, 129.4, 132.2, 135.7, 135.9, 158.9 (CON), 164.1 (COO); ms: m/z 485 (3), 483 (M^+, 2), 368 (3), 366 (11), 364 (9), 271 (4), 218 (3), 217 (18), 216 (15), 215 (60), 214 (19), 198 (3), 196 (4), 185 (5), 183 (5), 154 (35), 153 (9), 152 (100), 126 (4), 124 (10), 119 (3), 104 (4), 89 (12), 77 (18), 51 (4).

Anal. Calcd. for $C_{23}H_{15}BrClNO_4$: C, 56.98; H, 3.12; N, 2.89. Found: C, 56.65; H, 3.06; N, 2.87.

4-r,3-*t*,6-*t*-2-Aza-3-(4-chlorophenyl)-5,7-dioxa-6-(3-methylphenyl)-2-phenylspiro[3.4]octane-1,8-dione (**3h**).

This compound was obtained as colorless crystals (acetonitrile), mp 118 - 119°; ir: CO 1804, CON 1770 cm^{-1}; ^1H nmr (400

MHz, $CDCl_3$): δ 2.41 (s, 3H, Me), 5.18 (s, 1H, 3-H), 6.73 (s, 1H, 6-H), 6.95 (d, 2H, phenyl proton, J = 8.4 Hz), 7.14 (ddt, 1H, phenyl proton, J = 1.3, 1.3, 7.2 Hz), 7.18 - 7.40 (m, 10H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 21.4 (Me), 67.2 (3-C), 88.2 (4-C), 103.5 (6-C), 118.0, 123.1, 125.4, 126.5, 128.5, 128.8, 129.0, 129.3, 131.4, 135.4, 135.9, 138.9, 159.3 (CON), 164.6 (COO); ms: m/z 421 (1), 419 (5 M^+,), 302 (4), 301 (3), 300 (12), 218 (3), 217 (18), 216 (14), 215 (55), 214 (19), 195 (3), 155 (3), 154 (31), 153 (9), 152 (100), 132 (6), 126 (4), 124 (12), 119 (8), 104 (5), 91 (8), 89 (10), 78 (3), 77 (18), 65 (3), 51 (3).

Anal. Calcd. for $C_{24}H_{18}ClNO_4$: C, 68.66; H, 4.32; N, 3.34. Found: C, 68.64; H, 4.51; N, 3.27.

4-r,3-*t*,6-*c*-2-Aza-3-(4-chlorophenyl)-5,7-dioxa-6-(3-methylphenyl)-2-phenylspiro[3.4]octane-1,8-dione (**4h**).

This compound was obtained as colorless crystals (acetonitrile), mp 183 - 185°; ir: CO 1794, CON 1778 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, Me), 5.44 (s, 1H, 3-H), 6.55 (s, 1H, 6-H), 7.14 - 7.42 (m, 13H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 21.4 (Me), 67.2 (3-C), 88.2 (4-C), 103.5 (6-C), 118.0, 123.1, 125.4, 126.4, 128.5, 128.8, 128.9, 129.2, 129.3, 131.4, 135.4, 135.9, 138.9, 159.3 (CON), 164.6 (COO); ms: m/z 421 (1), 419 (M^+, 4), 302 (5), 301 (3), 300 (15), 218 (3), 217 (19), 216 (15), 215 (58), 214 (21), 155 (3), 154 (32), 153 (9), 152 (100), 132 (3), 126 (4), 124 (11), 119 (8), 104 (5), 91 (8), 89 (9), 78 (3), 77 (17), 51 (3).

Anal. Calcd. for $C_{24}H_{18}ClNO_4$: C, 68.66; H, 4.32; N, 3.34. Found: C, 68.63; H, 4.44; N, 3.33.

4-r,3-*t*,6-*t*-2-Aza-3-(4-chlorophenyl)-5,7-dioxa-6-(3-methoxyphenyl)-2-phenylspiro[3.4]octane-1,8-dione (**3i**).

This compound was obtained as colorless crystals (acetonitrile), mp 125 - 127°; ir: CO 1797, CON 1755 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 3.83 (s, 3H, Me), 5.18 (s, 1H, 3-H), 6.74 (s, 1H, 6-H), 6.99 (t, 1H, phenyl proton, J = 2.0 Hz), 6.93 (d, 2H, phenyl proton, J = 8.4 Hz), 7.01 (d, 1H, phenyl proton, J = 7.6 Hz), 7.05 (dd, 1H, phenyl proton, J = 2.2, 8.1 Hz), 7.14 (ddt, 1H, phenyl proton, J = 1.1, 1.1, 7.2 Hz), 7.22 - 7.31 (m, 6H, phenyl proton), 7.41 (t, 1H, phenyl proton, J = 8.0 Hz); ^{13}C nmr (22.5 MHz, DMSO-d_6): δ 55.4 (Me), 67.2 (3-C), 88.2 (4-C), 103.2 (6-C), 111.3, 116.3, 118.0, 125.5, 128.4, 128.8, 128.9, 129.3, 130.2, 135.4, 135.9, 137.0, 159.2 (CON), 160.1, 164.5 (COO); ms: m/z 437 (3), 435 (9), 318 (4), 316 (11), 271 (3), 218 (3), 217 (20), 216 (16), 215 (61), 214 (22), 209 (6), 154 (32), 153 (9), 152 (100), 136 (7), 135 (10), 132 (6), 126 (4), 124 (13), 119 (7), 107 (4), 104 (5), 91 (5), 89 (10), 78 (3), 77 (21), 65 (3), 53 (3), 51 (4).

Anal. Calcd. for $C_{24}H_{18}ClNO_5$: C, 66.14; H, 4.16; N, 3.21. Found: C, 66.05; H, 4.29; N, 3.24.

4-r,3-*t*,6-*c*-2-Aza-3-(4-chlorophenyl)-5,7-dioxa-6-(3-methoxyphenyl)-2-phenylspiro[3.4]octane-1,8-dione (**4i**).

This compound was obtained as colorless crystals (acetonitrile), mp 150 - 152°; ir: CO 1794, CON 1778 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 3.86 (s, 3H, Me), 5.44 (s, 1H, 3-H), 6.57 (s, 1H, 6-H), 7.02 (dd, 1H, phenyl proton, J = 1.9, 8.2 Hz), 7.13 - 7.38 (m, 12H, phenyl proton); ^{13}C nmr (22.5 MHz, DMSO-d_6): δ 55.5 (Me), 67.3 (3-C), 89.4 (4-C), 104.2 (6-C), 111.2, 117.4, 118.1, 118.9, 125.5, 128.8, 129.1, 129.2, 129.4, 130.0, 135.4, 135.6, 136.0, 159.2 (CON), 160.1, 164.3 (COO); ms: m/z 435 (M^+, 6), 318 (7), 317 (4) 316 (17), 271 (3), 218 (3), 217 (21), 216 (17), 215 (63), 214 (25), 211 (4), 155 (3), 154 (33), 153 (9), 152 (100), 136 (8), 135 (12), 126 (4), 124 (13), 119 (6), 118 (3), 107 (4), 104 (4), 91 (4), 89 (10), 78 (3), 77 (19), 51 (4).

Anal. Calcd. for $C_{24}H_{18}ClNO_5$: C, 66.14; H, 4.16; N, 3.21. Found: C, 66.18; H, 4.29; N, 3.22.

4-r,3-*t*,6-*t*-2-Aza-5,7-dioxa-3-(4-methoxyphenyl)-2,6-diphenylspiro[3.4]octane-1,8-dione (**3j**).

This compound was obtained as colorless crystals (acetonitrile), mp 194 - 195°; ir: CO 1798, CON 1777 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$): δ 3.77 (s, 3H, Me), 5.19 (s, 1H, 3-H), 6.75 (s, 1H, 6-H), 6.78 (ddd, 2H, phenyl proton, J = 2.2, 2.2, 8.9 Hz), 6.99 (ddd, 2H, phenyl proton, J = 2.2, 2.2, 8.9 Hz), 7.10 - 7.55 (m, 10H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 55.2 (Me), 67.6 (3-C), 88.4 (4-C), 103.4 (6-C), 113.9, 118.1, 121.6, 125.2, 126.0, 128.9, 129.2, 130.6, 135.5, 136.2, 159.6 (CON), 160.4, 164.7 (COO); ms: m/z 401 (M^+, 10), 267 (3), 239 (7), 212 (21), 211 (100), 210 (3), 167 (5), 149 (5), 148 (44), 133 (3), 120 (16), 119 (4), 118 (7), 106 (4), 105 (8), 104 (3), 92 (3), 91 (9), 90 (5), 89 (5), 78 (5), 77 (33), 65 (4), 51 (9).

Anal. Calcd. for $C_{24}H_{19}NO_5$: C, 71.81; H, 4.77; N, 3.49. Found: C, 71.44; H, 4.96; N, 3.44.

4-r,3-*t*,6-*c*-2-Aza-5,7-dioxa-3-(4-methoxyphenyl)-2,6-diphenylspiro[3.4]octane-1,8-dione (**4j**).

This compound was obtained as colorless crystals (acetonitrile), mp 188 - 189°; ir: CO 1806, CON 1769 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$): δ 3.80 (s, 3H, Me), 5.42 (s, 1H, 3-H), 6.57 (s, 1H, 6-H), 6.92 (ddd, 2H, phenyl proton, J = 2.4, 2.4, 8.8 Hz), 7.01 - 7.64 (m, 12H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 55.3 (Me), 67.8 (3-C), 89.7 (4-C), 104.1 (6-C), 114.4, 118.1, 122.4, 125.2, 126.8, 128.8, 129.2, 131.0, 134.0, 136.3, 159.3 (CON), 160.5, 164.6 (COO); ms: m/z 401 (M^+, 21), 267 (6), 239 (14), 213 (4), 212 (46), 211 (100), 210 (79), 196 (4), 195 (4), 168 (3), 167 (10), 149 (7), 148 (71), 133 (4), 121 (3), 120 (24), 119 (5), 106 (5), 105 (12), 104 (4), 92 (4), 91 (12), 90 (5), 89 (7), 78 (6), 77 (39), 55 (5), 53 (3), 51 (10).

Anal. Calcd. for $C_{24}H_{19}NO_5$: C, 71.81; H, 4.77; N, 3.49. Found: C, 71.74; H, 5.02; N, 3.40.

4-r,3-*t*,6-*t*-2-Aza-5,7-dioxa-3-(4-methoxyphenyl)-6-(3-methylphenyl)-2-phenylspiro[3.4]octane-1,8-dione (**3k**).

This compound was obtained as colorless crystals (acetonitrile), mp 150 - 151°; ir: CO 1804, CON 1767 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, Me), 3.77 (s, 3H, OMe), 5.17 (s, 1H, 3-H), 6.71 (s, 1H, 6-H), 6.79 (d, 2H, phenyl proton, J = 8.7 Hz), 6.98 (d, 2H, phenyl proton, J = 8.7 Hz), 7.07 - 7.39 (m, 9H, phenyl proton); ^{13}C nmr (100 MHz, $CDCl_3$): δ 21.6 (Me), 55.4 (OMe), 67.9 (3-C), 88.5 (4-C), 103.6 (6-C), 114.0, 118.3, 121.3, 125.3, 126.7, 129.0, 129.2, 129.4, 131.5, 135.6, 136.4, 139.0, 159.8 (CON), 165.0 (COO); ms: m/z 415 (M^+, 10), 267 (3), 239 (4), 210 (24), 211 (100), 167 (3), 149 (4), 148 (23), 120 (12), 119 (9), 118 (3), 91 (9), 77 (11), 65 (3), 51 (3).

Anal. Calcd. for $C_{25}H_{21}NO_5$: C, 72.28; H, 5.10; N, 3.37. Found: C, 72.01; H, 5.12; N, 3.31.

4-r,3-*t*,6-*c*-2-Aza-5,7-dioxa-3-(4-methoxyphenyl)-6-(3-methylphenyl)-2-phenylspiro[3.4]octane-1,8-dione (**4k**).

This compound was obtained as colorless crystals (acetonitrile), mp 77 - 78°; ir: CO 1797, CON 1767 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, Me), 3.80 (s, 3H, Me), 5.42 (s, 1H, 3-H), 6.53 (s, 1H, 6-H), 6.91 (ddd, 2H, phenyl proton, J = 2.9, 2.9, 8.7 Hz), 7.13 (ddt, 1H, phenyl proton, J = 1.9, 1.9, 6.8 Hz),

7.27 - 7.41 (m, 10H, phenyl proton); ^{13}C nmr (100 MHz, $CDCl_3$): δ 21.6 (Me), 55.5 (Me), 68.1 (3-C), 89.9 (4-C), 104.4 (6-C), 114.5, 118.3, 122.5, 124.2, 125.4, 127.4, 128.9, 129.0, 129.4, 132.0, 133.9, 136.5, 139.0, 159.4 (CON), 160.6, 164.8 (COO); ms: m/z 415 (M^+, 10), 267 (3), 212 (17), 211 (100), 210 (23), 167 (3), 149 (3), 148 (25), 120 (11), 119 (8), 91 (8), 84 (6), 77 (10).

Anal. Calcd. for $C_{25}H_{21}NO_5$: C, 72.28; H, 5.10; N, 3.37. Found: C, 72.09; H, 5.17; N, 3.40.

4-r,3-*t*,6-*t*-2-Aza-6-(4-bromophenyl)-5,7-dioxa-2,3-bis(4-methylphenyl)spiro[3.4]octane-1,8-dione (**3l**).

This compound was obtained as colorless crystals (acetonitrile), mp 184 - 185°; ir: CO 1803, CON 1744 cm^{-1}; ^{1}H nmr (400 MHz, $CDCl_3$): δ 2.28 (s, 3H, Me), 2.32 (s, 3H, Me), 5.17 (s, 1H, 3-H), 6.70 (s, 1H, 6-H), 6.95 (d, 2H, phenyl proton, J = 8.0 Hz), 7.07 (d, 2H, phenyl proton, J = 8.5 Hz), 7.09 (d, 2H, phenyl proton, J = 8.2 Hz), 7.10 (d, 2H, phenyl proton, J = 8.2 Hz), 7.15 (d, 2H, phenyl proton, J = 8.5 Hz), 7.30 (d, 2H, phenyl proton, J = 8.5 Hz), 7.62 (d, 2H, phenyl proton, J = 8.5 Hz); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 21.0 (Me), 21.3 (Me), 67.6 (3-C), 88.3 (4-C), 102.7 (6-C), 118.1, 125.0, 126.8, 127.4, 127.8, 129.3, 129.8, 131.2, 133.7, 134.4, 135.1, 139.6, 159.1 (CON), 164.4 (COO); ms: m/z 479 (M^+, 6), 477 (6), 346 (4), 344 (5), 265 (4), 211 (3), 210 (15), 209 (87), 208 (24), 185 (4), 183 (5), 181 (3), 133 (13), 132 (100), 104 (14), 103 (4), 91 (13), 89 (3), 78 (4), 77 (5), 65 (4).

Anal. Calcd. for $C_{25}H_{20}BrNO_4$: C, 62.77; H, 4.21; N, 2.93. Found: C, 62.41; H, 4.21; N, 2.97.

4-r,3-*t*,6-*c*-2-Aza-6-(4-bromophenyl)-5,7-dioxa-2,3-bis(4-methylphenyl)spiro[3.4]octane-1,8-dione (**4l**).

This compound was obtained as colorless crystals (acetonitrile), mp 138 - 140°; ir: CO 1805, CON 1765 cm^{-1}; ^{1}H nmr (400 MHz, $CDCl_3$): δ 2.30 (s, 3H, Me), 2.35 (s, 3H, Me), 5.41 (s, 1H, 3-H), 6.54 (s, 1H, 6-H), 7.09 (d, 2H, phenyl proton, J = 8.3 Hz), 7.19 (d, 2H, phenyl proton, J = 8.0 Hz), 7.21 (d, 2H, phenyl proton, J = 8.3 Hz), 7.29 (d, 2H, phenyl proton, J = 8.0 Hz), 7.47 (d, 2H, phenyl proton, J = 8.4 Hz), 7.60 (d, 2H, phenyl proton, J = 8.4 Hz); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 21.0 (Me), 21.3 (Me), 67.9 (3-C), 89.5 (4-C), 103.4 (6-C), 118.1, 125.5, 127.3, 127.5, 128.4, 129.6, 129.8, 132.1, 133.1, 133.8, 135.1, 139.6, 158.8 (CON), 164.3 (COO); ms: m/z 479 (M^+, 6), 477 (5), 346 (7), 344 (7), 275 (3), 265 (5), 256 (5), 225 (5), 211 (3), 210 (17), 209 (100), 208 (31), 194 (3), 186 (5), 185 (10), 184 (5), 183 (10), 149 (6), 133 (14), 132 (91), 119 (11), 118 (8), 104 (17), 91 (22), 86 (47), 84 (69), 77 (9), 65 (7), 57 (7).

Anal. Calcd. for $C_{25}H_{20}BrNO_4$: C, 62.77; H, 4.21; N, 2.93. Found: C, 62.56; H, 4.28; N, 2.89.

4-r,3-*t*,6-*t*-2-Aza-5,7-dioxa-6-(3-methylphenyl)-2,3-bis(4-methylphenyl)spiro[3.4]octane-1,8-dione (**3m**).

This compound was obtained as colorless crystals (acetonitrile), mp 136 - 138°; ir: CO 1805, CON 1762 cm^{-1}; ^{1}H nmr (400 MHz, $CDCl_3$): δ 2.28 (s, 3H, Me), 2.32 (s, 3H, Me), 2.41 (s, 3H, Me), 5.18 (s, 1H, 3-H), 6.72 (s, 1H, 6-H), 6.94 (d, 2H, phenyl proton, J = 8.0 Hz), 7.06 - 7.39 (m, 10H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 20.09 (Me), 21.2 (Me), 21.4 (Me), 67.8 (3-C), 88.3 (4-C), 103.4 (6-C), 118.0, 123.2, 126.5, 126.9, 127.5, 128.8, 129.1, 129.6, 131.3, 133.8, 134.9, 135.4, 138.8, 139.2, 159.3 (CON), 164.7 (COO); ms: m/z 413 (M^+, 11), 281 (3), 280 (10), 265 (4), 210 (14), 209 (85), 208 (28), 152 (4), 133 (12), 132 (100), 120 (4), 119 (9), 118 (3), 105 (3), 104 (16), 103 (5), 92 (3), 91 (20), 78 (5), 77 (4), 65 (6).

Anal. Calcd. for $C_{26}H_{23}NO_4$: C, 75.53; H, 5.61; N, 3.39. Found: C, 75.23; H, 5.69; N, 3.36.

4-r,3-*t*,6-*c*-2-Aza-5,7-dioxa-6-(3-methylphenyl)-2,3-bis(4-methylphenyl)spiro[3.4]octane-1,8-dione (**4m**).

This compound was obtained as colorless crystals (acetonitrile), mp 172 - 173°; ir: CO 1805, CON 1759 cm^{-1}; ^{1}H nmr (400 MHz, $CDCl_3$): δ 2.29 (s, 3H, Me), 2.35 (s, 3H, Me), 2.40 (s, 3H, Me), 5.41 (s, 1H, 3-H), 6.53 (s, 1H, 6-H), 7.09 (d, 2H, phenyl proton, J = 8.3 Hz), 7.19 - 7.41 (m, 10H, phenyl proton); ^{13}C nmr (22.5 MHz, $CDCl_3$): δ 21.0 (Me), 21.4 (Me), 68.1 (3-C), 89.9 (4-C), 104.3 (6-C), 118.1, 123.9, 124.5, 127.2, 127.8, 128.7, 129.6, 129.7, 131.8, 133.9, 135.0, 137.7, 138.8, 139.5, 159.3 (CON), 164.7 (COO); ms: m/z 413 (M^+, 10), 281 (3), 280 (14), 265 (3), 217 (3), 215 (7), 210 (15), 209 (92), 208 (24), 154 (3), 152 (13), 133 (12), 132 (100), 120 (3), 119 (8), 118 (3), 104 (14), 103 (5), 91 (16), 89 (3), 78 (4), 88 (5), 65 (5).

Anal. Calcd. for $C_{26}H_{23}NO_4$: C, 75.53; H, 5.61; N, 3.39. Found: C, 75.36; H, 5.60; N, 3.40.

trans-2-Aza-5,7-dioxa-6,6-dimethyl-2,3-diphenylspiro[3.4]-octane-1,8-dione (**8**).

A Pyrex photochemical glass vessel was connected with a condenser and an introducing glass filter of dry nitrogen gas. A benzene solution (200 ml) of diazo Meldrum's acid (54 mg, 0.32 mmol) and **2a** (54 mg, 0.32 mmol) was added to the Pyrex vessel and then fully degassed with dry nitrogen. The solution was heated under reflux and then irradiated for 3 h with a 100-W high pressure-mercury lamp with a quartz jacket. The reaction mixture was evaporated *in vacuo* and recrystallization of the residue from dichloromethane/hexane gave **8** in 43% (44 mg) yield, mp 205 - 209°; ir: CO 1797, CON 1761 cm^{-1}; ^{1}H nmr (400 MHz, $CDCl_3$): δ 1.64 (s, 3H, Me), 1.74 (s, 3H, Me), 5.30 (s, 1H, 3-H), 7.10 - 7.15 (m, 1H, phenyl proton), 7.28 - 7.42 (m, 9H, phenyl proton); ^{13}C nmr (100 MHz, $CDCl_3$): δ 27.9 (Me), 28.1 (Me), 68.5 (3-C), 90.0 (4-C), 104.3 (6-C), 112.0, 118.5, 125.5, 127.9, 129.1, 129.6, 129.8, 130.8, 136.7, 160.8 (CON), 165.1 (COO).

Anal. Calcd. for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.62; H, 5.35; N, 4.21.

trans-2-Benzyloxy-1,4-diphenyl-β-lactam-3-carboxylic acid (**9**).

A mixture of **3a** and **4a** (206 mg, 1.11 mmol, ratio of 4:6) was added to a methanol (200 ml) in the presence of catalytic amount of Pd-C. The mixture was vigorously stirred under hydrogen atmosphere for 3 h and then filtrated. The mother liquor was evaporated *in vacuo*. Recrystallization of the residue from dichloromethane/hexane gave **9** in 70% (290 mg) yield, mp 187 - 189°; ir: OH 3300-2700, CON 1756, COO 1730, 1712 cm^{-1}; ^{1}H nmr (400 MHz, $CDCl_3$): δ 4.77 (d, 1H, d, J = 10.4 Hz), 5.06 (d, 1H, J = 10.4 Hz), 5.22 (s, 1H, 4-H), 7.05 - 7.18 (m, 1H, phenyl proton), 7.20 - 7.53 (m, 14H, phenyl proton), 12.50 (br s, 1H, COOH); ^{13}C nmr (100 MHz, $CDCl_3$): δ 66.9, 71.2, 94.0, 118.2, 125.3, 127.6, 128.8, 128.9, 129.0, 129.5, 139.6, 131.7, 136.8, 137.0, 161.4 (CON), 170.2 (COO); ms: m/z 373 (M^+, 0.3), 282 (20), 254 (3), 182 (12), 181 (12), 180 (12), 107 (8), 104 (11), 92 (8), 91 (100), 78 (3), 77 (21), 65 (7), 51 (4), 44 (4).

Anal. Calcd. for $C_{23}H_{19}NO_4$: C, 73.98; H, 5.13; N, 3.75. Found: C, 73.69; H, 5.25; N, 3.65.

X-Ray crystallographic analyses of **3j** and **4j** [9].

All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphitic monochromated Cu-$K\alpha$ radiation. The crystallographic data for **3j** and **4j** are described in Table 2.

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