Selected Transformations of 6-Cyclopropylidene-5-oxaspiro[2.3]hexan-4-one, a Highly Strained Tricyclic β-Lactone

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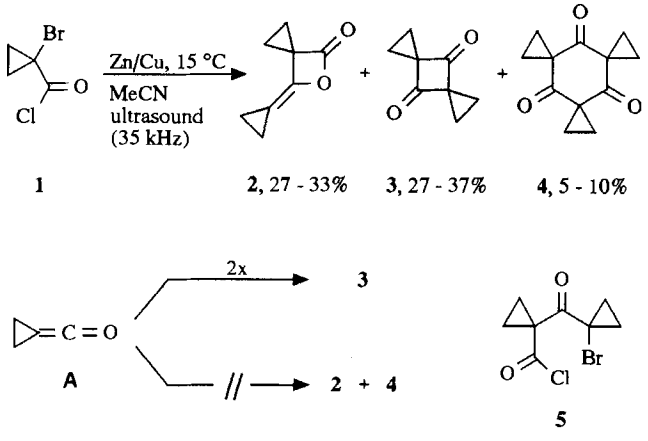
The title lactone **2** acylates a variety of amines including phenylalanine, sterically hindered alcohols, and phenols. With activated non-enolizable carbonyl compounds, bis-spiro 6-membered β-keto lactones are formed. Oxidative rearrangement of **2** affords bis-spiro lactones **12** and **13**.

Diketene is a versatile bulk chemical, which is of preparative, industrial, and general interest. For example, acetoacetylation of steroids, carbohydrates, and proteins is employed to increase lipophilicity and modify biological activities[1]. Diketene is also used for the production of intermediates in the synthesis of pharmaceuticals, pigments, and plant protecting agents[1b].

The title tricyclic lactone **2** is structurally related to diketene, and attempts to synthesize it go back to Staudinger more than 70 years ago[2]. We have prepared the lactone from 1-bromocyclopropanecarbonyl chloride[3] (**1**) under special conditions (ultrasound, organozinc chemistry, solvent acetonitrile, reaction temperature <20°C; see Scheme 1)[4,5].

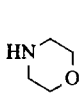
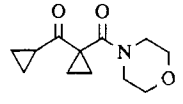
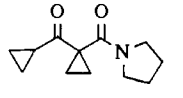
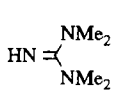
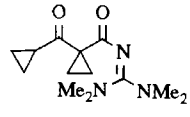
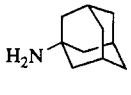
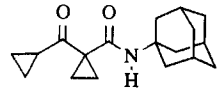
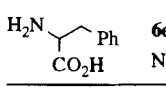
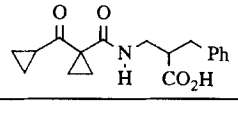
Scheme 1. Preparation of lactone **2** on a gram scale



Thus, lactone **2** is formally a dimer of dimethyleneketene (**A**), but is *not* formed by dimerization of *free* **A** which is known to yield dispiro[2.1.2.1]octane-4,8-dione (**3**) instead[6]. A key intermediate in the C–C coupling reactions summarized in Scheme 1 appears to be the acyl chloride **5**, which we have been able to isolate and identify. The concentration of **5** first rises and then falls en route from **1** to **2** (TLC control).

Tricyclic lactone **2** is highly strained and contains the shortest cyclopropylidene double bond (1.287 Å) on record[5]. It combines rapidly with amines (**6a–c**), giving β-keto amides **7a–c** at room temperature. In contrast, 1-adamantylamine (**6d**), which is poorly soluble in CH_2Cl_2, takes about 12 h to react. At the end of the reaction, the suspension of starting material has disappeared to furnish a solution of lipophilic **7d**. A common solvent for the acetoacetylation of amino acids with diketene is aqueous 2 N KOH[7]. These conditions are not compatible with reactive lactone **2**. Although phenylalanine (**6e**) is practically insoluble in CH_2Cl_2, it dissolves on stirring with **2** (NEt_3, catal), giving **7e** (Table 1).

Table 1. Reaction of **2** with amines and phenylalanine

Nucleophile		Reaction time r.t., CH_2Cl_2	Product (% Yield)	
	**6a**	< 1 min		**7a** (98)
	**6b**	< 1 min		**7b** (98)
	**6c**	ca. 5 min		**7c** (81)
	**6d**	ca. 12 h		**7d** (90)
	**6e**, NEt_3	ca. 12 h		**7e** (82)

Aliphatic alcohols including sterically hindered tertiary alcohols (**6f–i**) and phenols (**6j–n**) react more slowly with lactone **2**. The reaction is acid-catalyzed (H^+) and also cata-

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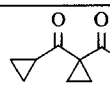
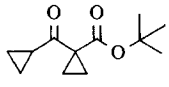
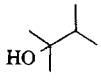
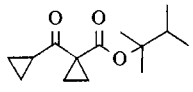
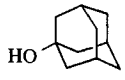
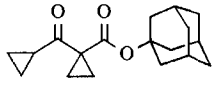
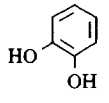
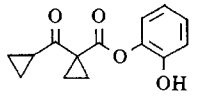
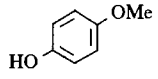
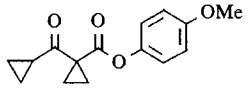
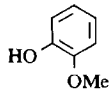
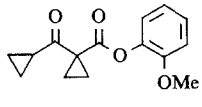
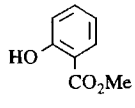
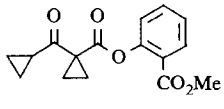
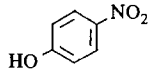
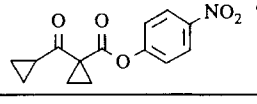
lyzed by NEt_3 (Table 2, **6m, n**). In the case of acidic phenols such as methyl salicylate (**6m**) and *p*-nitrophenol (**6n**) NEt_3 catalysis is more effective than acid catalysis. Catechol (**6j**) is selectively monoacylated in high yield. Since acetoacetylated products **7a–n** cannot enolize, their lipophilicity is increased further.

Table 2. Reaction of **2** with alcohols and phenols

Nucleophile		Reaction time, r.t., CH_2Cl_2	Product (% Yield)	
HOMe	**6f**, H^+	2h		**7f** (>95)
	**6g**, H^+	20 h		**7g** (78)
	**6h**, H^+	24 h		**7h** (74)
	**6i**, H^+	24 h		**7i** (84)
	**6j**, H^+	3 h		**7j** (83)
	**6k**, H^+	2 h		**7k** (83)
	**6l**, H^+	30 h		**7l** (72)
	**6m**, H^+	24 h[a]		**7m** (38)
	NEt_3	12 h		(69)
	**6n**, H^+	12 h		**7n** (45)
	NEt_3	12 h		(87)

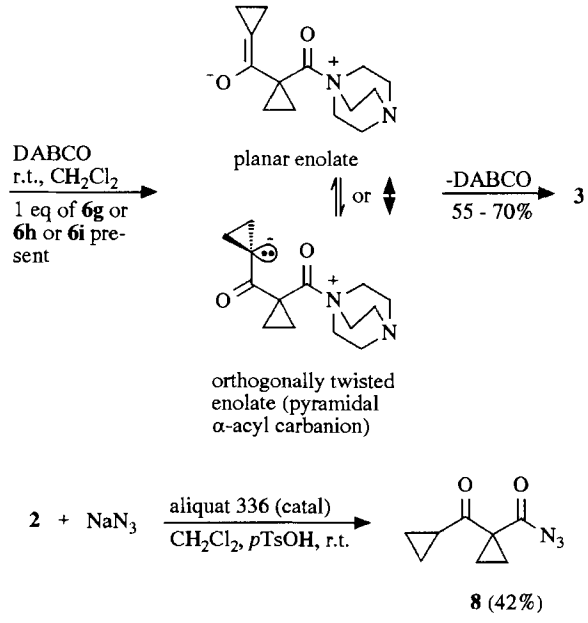
[a] Reaction at 40°C.

As an acylation catalyst, NEt_3 is preferable to 1,4-diazabicyclo[2.2.2]octane (DABCO), which has been found to promote formation of dispiro[2.1.2.1]octane-4,8-dione (**3**) from **2**, also in the presence of alcohols **6g–i**, in a remarkably smooth rearrangement (Scheme 2). MMX calculations suggest that cyclic 1,3-diketone **3** is more stable than lactone **2** by at least 38 kcal/mol.

In a two-phase acylation procedure acyl azide **8** has been prepared in unoptimized 42% yield.

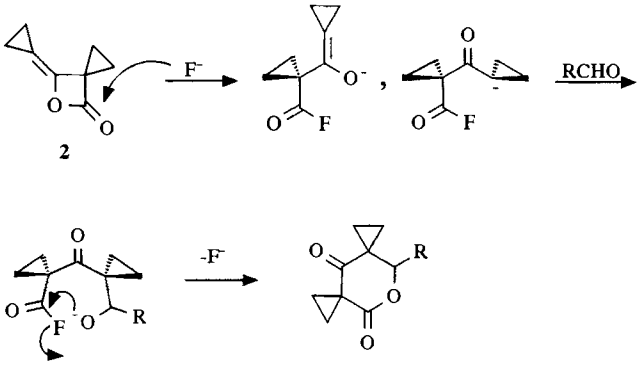
Fluoride Ion-Catalyzed Reactions of **2** *with Electrophiles:* Until now lactone **2** has been shown to react with nucleophiles, and the reaction was terminated by protonation of the resulting enolate and irreversible ketonization. Tricyclic **2** also combines with reactive electrophiles, provided that

Scheme 2. DABCO-catalyzed isomerization of lactone **2**



the reaction is initiated by catalytic amounts of KF in the presence of a crown ether (Scheme 3).

Scheme 3



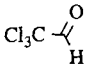
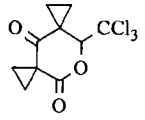
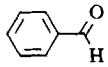
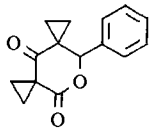
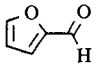
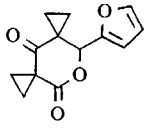
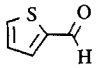
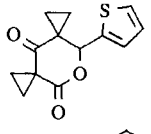
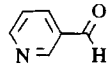
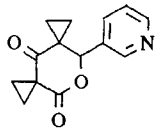
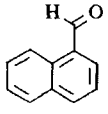
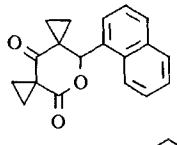
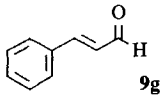
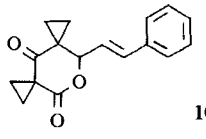
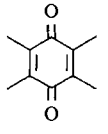
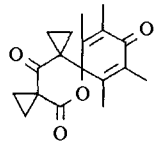
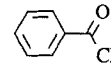
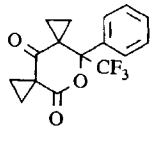
The resulting β-keto-δ-valerolactones **10a–i** (Table 3) are of potential interest in medicinal chemistry and as herbicides[1a,b] and cannot enolize. They are crystalline and can be handled readily.

Epoxidation of Lactone **2** *and Model Lactone* **14** *with 2-(p-Tolylsulfonyl)-3-phenyloxaziridine*[8]: Lactone **2** was epoxidized with Davis reagent[8] under aprotic conditions, giving an equimolar mixture of tetracycles **12** and **13**. Functionalized oxaspiropentane **11** is an obvious intermediate, ring expansion to cyclobutanone **12** being a well-known reaction type[9,11]. Another ring expansion mode of **11** affords ketolactone **13**, which is prepared more conveniently from dispiro[2.1.2.1]octene-4,8-dione (**3**) by Baeyer-Villiger rearrangement.

Under similar reaction conditions, the less reactive methylene lactone **14** was found to furnish ketolactone **15**, a non-enolizable tetronic acid derivative.

In summary, title lactone **2** is now readily accessible. It has an unusual tricyclic structure and undergoes a variety of reactions[3d,5]. As an acylating agent, the lactone is more

Table 3. KF/Crown ether-mediated preparation of bis-spiro-lactones **10a–i**

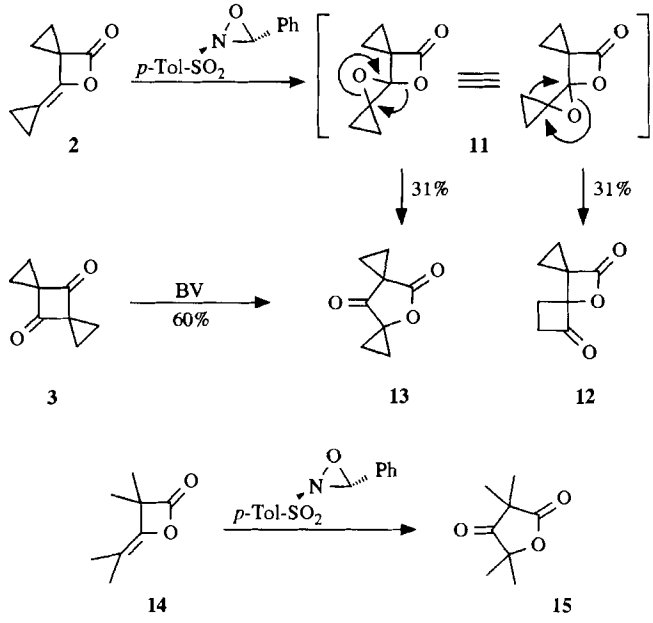
Carbonyl Component		Reaction time r.t., CH_2Cl_2	Product (% Yield)	
Cl_3C 	**9a**	24 h[a] 24 h[b]		**10a** (37) (14)
	**9b**	24 h[a] 36 h[b]		**10b** (37) (54)
	**9c**	24 h[a] 40 h[b]		**10c** (48) (10)
	**9d**	24 h[a] 43 h[b]		**10d** (40) (13)
	**9e**	48 h[b]		**10e** (11)
	**9f**	24 h[a]		**10f** (23)
	**9g**	24 h[a]		**10g** (17)
	**9h**	24 h[a]		**10h** (37)
	**9i**	24 h[a]		**10i** (45)

[a] KF (0.4 eq.), crown ether (0.05 eq.). – [b] DABCO (0.1 eq.). Yields are lower in this case, because the isomerization of **2** → **3** (Scheme 2) could not be suppressed.

reactive than conventional β-alkylidene lactones. Acylated derivatives show enhanced lipophilicity, while enolization of the β-keto ester grouping is blocked completely. The title lactone also enters into ring expansion reactions and combines with reactive carbonyl compounds to afford non-enolizable β-ketovalerolactones.

We thank *U. Eggert* for experimental contributions and the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for support of our work.

Scheme 4. Oxidative rearrangement of lactone **2**



Experimental

Melting points: Büchi apparatus. – IR: Perkin-Elmer 1710 spectrometer. – ^1H NMR: Bruker WP 200 SY. Chemical shifts are reported in δ values downfield from tetramethylsilane. – ^{13}C NMR: Bruker WP 200 SY. Chemical shifts are reported in δ values downfield from tetramethylsilane. – Low- and high-resolution EI MS: Finnigan MAT 312 spectrometer, 70 eV, room temperature, unless otherwise stated. – Microanalyses: Department of Organic Chemistry of the University of Hannover. – Preparative column chromatography: J. T. Baker silica gel (particle size 30–60 μm). – Analytical TLC: aluminium-backed 0.2-mm silica gel 60 F_{254} plates (E. Merck).

6-Cyclopropylidene-5-oxaspiro[2.3]hexan-4-one[4,5] (**2**). A flame-dried Erlenmeyer flask was charged with zinc powder (50 g, 0.77 mol), CuCl (1 g, 0.01 mol), and anhydrous MeCN (80 ml) under N_2. The flask was placed in an ultrasonic bath (ELMA 480 H2, 35 kHz). 1-Bromocyclopropanecarbonyl chloride (**1**) (26.7 g, 0.146 mol) was added within 2.5 h (perfusor) at 10–20°C, and the mixture was allowed to react for further 15 min. After complete reaction (TLC control) the reaction mixture was filtered through silica gel (CH_2Cl_2). After removal of the solvent the crude product was purified by chromatography [silica gel, ether/light petroleum (b.p. 40–60°C), 1:2] as the eluent to yield lactone **2** (2.68 g, 27%), dione **3** (3.67 g, 37%), and trione **4** (0.5 g, 5%). The spectroscopic data corresponded with literature[4] [R_f values (silica gel, Merck 60F 254) lactone **2**, 0.59; triketone **4**, 0.37; diketone **3**, 0.30].

1-(1-Bromocyclopropylcarbonyl)cyclopropanecarbonyl Chloride (**5**): 1-Bromocyclopropanecarbonyl chloride (**1**) (10 g, 55 mmol) was allowed to react as described above. Finishing the reaction immediately after addition of the acyl chloride afforded **5** (308 mg, 4.5%), colorless liquid. – IR (film): $\tilde{\nu}$ = 2929 cm^{-1}, 1770, 1702, 1422, 1317, 1269, 1065, 968, 928, 891, 802, 757, 697, 642. – ^1H NMR ($CDCl_3$): δ = 1.48–1.68 (m, 4H), 1.77–1.89 (m, 4H). – ^{13}C NMR ($CDCl_3$, APT): δ = 19.75 (C-7,8), 23.80 (C-3,4), 34.10 (C-2), 43.54 (C-6), 171.33 (C-1), 198.02 (C-5). – MS, *m/z* (%): 254 (1) [M^+ + 4], 252 (3) [M^+ + 2], 250 (2) [M^+], 222 (13), 224 (17), 226 (5), 215 (3), 217 (30), 187 (8), 189 (7), 171 (100), 173 (33), 149 (49), 147 (52), 145 (23), 143 (75).

Procedures A–C for the Acetoacetylations. – A) *Without Catalyst:* A flame-dried two-necked flask was charged with amine (1 mmol) in anhydrous CH_2Cl_2 (2 ml). Lactone **2** (1 mmol) in anhydrous CH_2Cl_2 (1 ml) was added at room temp. under N_2. After complete reaction (TLC) the solvent was evaporated and the crude product purified by chromatography. – B) *Base-Catalyzed:* Amino acid or phenol (1.1 mmol), NEt_3 (0.1–0.15 mmol), and lactone **2** (1 mmol) were allowed to react as described for procedure A. – C) *Acid-Catalyzed:* Alcohol or phenol (1.1 mmol), *p*-TsOH (0.15 mmol) and lactone **2** (1 mmol) were allowed to react as described for procedure A.

1-(Cyclopropylcarbonyl)cyclopropanecarboxomorpholide (**7a**): Morpholine (0.1 g, 1.1 mmol) in anhydrous CH_2Cl_2 (3 ml) and lactone **2** (0.15 g, 1.1 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure A. Reaction time 1 min. Chromatography [ether/light petroleum (40–60°C), 3:1] and crystallization (ether) gave colorless crystals (0.235 g, 98%), m.p. 84°C. – IR ($CHCl_3$): $\tilde{\nu}$ = 3000 cm^{-1}, 2970, 1680, 1630, 1450, 1430, 1115, 1070, 1035, 960. – ^1H NMR ($CDCl_3$): δ = 0.89–1.05 (m, 2H, 7,8-H), 1.05–1.13 (m, 2H, 7,8-H), 1.3–1.42 (m, 2H, 2,3-H), 1.44–1.56 (m, 2H, 2,3-H), 2.01–2.15 (m, 1H, 6-H), 3.44–3.58 (m, 2H, 10,14-H), 3.60–3.77 (m, 6*H*, 10,14,11,13-H). – ^{13}C NMR ($CDCl_3$): δ = 12.05 (t, C-7,8), 16.50 (t, C-2,3), 17.97 (d, C-6), 37.17 (s, C-1), 42.66, 46.34 (t, C-10,14), 66.41, 66.68 (t, C-11,13), 168.50 (s, C-4), 205.95 (s, C-5). – MS, *m/z* (%): 223 (19) [M^+], 195 (16), 179 (12), 137 (16), 87 (76), 69 (100). – $C_{12}H_{12}NO_3$ (218.1): calcd. C 64.6, H 7.7, N 6.3; found C 64.5, H 7.6, N 6.3.

1-(Cyclopropylcarbonyl)cyclopropanecarboxopyrrolidide (**7b**): Freshly distilled pyrrolidine (0.10 g, 0.1 ml, 1.47 mmol) in anhydrous CH_2Cl_2 (3 ml) and lactone **2** (0.20 g, 1.47 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure A. Reaction time 1 min. Chromatography [ether/light petroleum (40–60°C), 4:1] gave colorless crystals (0.298 g, 98%), m.p. 80–82°C. – IR (KBr): $\tilde{\nu}$ = 3010 cm^{-1}, 2976, 1673, 1631, 1439, 1387, 1067. – ^1H NMR ($CDCl_3$): δ = 0.85–0.98 (m, 2H, 7,8-H), 0.98–1.1 (m, 2H, 7,8-H), 1.28–1.4 (m, 2H, 2,3-H), 1.4–1.5 (m, 2H, 2,3-H), 1.94 (m, 4H, 10,12-H), 2.11 (m, 1H, 6-H), 3.47 (t, 2H, ^3J = 6 Hz, 9-H), 3.52 (t, ^3J = 6 Hz, 2H, 12-H). – ^{13}C NMR ($CDCl_3$): δ = 11.5 (t, C-7,8), 16.3 (t, C-2,3), 17.8 (d, C-6), 24.3, 31.2 (t, C-10,11), 38.7 (s, C-1), 46.3, 46.7 (t, C-9,12), 168 (s, C-4), 206 (s, C-5). – MS; *m/z* (%): 208 (9) [M^+], 180 (9), 150 (6), 110 (8), 70 (100), 69 (54). – $C_{12}H_{17}NO_2$ (207.1): calcd. C 69.5, H 8.3; found C 69.6, H 8.1.

N-[Bis(dimethylamino)methylene]-1-(cyclopropylcarbonyl)-cyclopropanecarboxamide (**7c**): 1,1,3,3-Tetramethylguanidine (0.17 g, 0.18 ml, 1.47 mmol) in anhydrous CH_2Cl_2 (3 ml) and lactone **2** (0.20 g, 1.47 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure A. Reaction time 10 min. Column filtration and crystallization (ether) gave a colorless solid (0.30 g, 81%), m.p. 71–72°C. – IR (KBr): $\tilde{\nu}$ = 3006 cm^{-1}, 2930, 1697, 1610, 1593, 1558, 1520, 1405, 1065. – ^1H NMR ($CDCl_3$): δ = 0.81–0.94 (m, 2H, 7,8-H), 0.98–1.1 (m, 2H, 7,8-H), 1.2–1.31 (m, 2H, 2,3-H), 1.31–1.41 (m, 2H, 2,3-H), 2.49–2.65 (m, 1H, 6-H), 2.01 (s, 12H, Me). – ^{13}C NMR ($CDCl_3$): δ = 10.8 (t, C-7,8), 15.1 (t, C-2,3), 19.7 (d, C-6), 39.0 (s, C-1), 39.5 (s, 4 C, CH_3), 166.6 (s, C-2′), 176 (s, C-4), 207.6 (s, C-5). – MS (40°C), *m/z*: 251 (13) [M^+], 193 (23), 142 (100), 123 (20), 69 (66). – $C_{13}H_{21}N_3O_2$ (251.2): calcd. C 62.1, H 8.4, N 16.7; found C 61.5, H 8.2, N 15.8.

N-(1-Adamantyl)-1-(cyclopropylcarbonyl)cyclopropanecarboxamide (**7d**): 1-Adamantylamine (0.44 g, 2.94 mmol) in anhydrous CH_2Cl_2 (5 ml) and lactone **2** (0.20 g, 1.47 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to the procedure A. Reaction time 12 h. Chromatography [ether/light petroleum (40–60°C), 1:1] and crystallization (ether/light petroleum) gave colorless crystals (0.38 g, 90%), m.p. 113–115°C. – IR (KBr): $\tilde{\nu}$ = 3271 cm^{-1}, 3021, 2911, 2849, 1672, 1635, 1544, 1403, 1052, 1008. – ^1H NMR ($CDCl_3$): δ = 0.8–0.91 (m, 2H, 7,8-H), 0.98–1.08 (m, 2H, 7,8-H), 1.46–1.76 (m, 9H, 2,3,6,4′,6′,9′-H), 1.78–1.87 (m, 2H, 2,3-H), 1.97–2.13 (m, 9H, 2′,3′,5′,7′,8′,10′-H), 8.80 (br. s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 11.41 (t, C-7,8), 15.48 (d, C-6), 18.47 (t, C-2,3), 29.54 (d, C-3′,5′,7′), 34.42 (s, C-1), 36.53 (t, C-4′,6′,9′), 41.71 (t, C-2′,8′,10′), 51.59 (s, C-1′), 167.48 (s, C-4), 209.03 (s, C-5). – MS (50°C), *m/z* (%): 287 (38) [M^+], 259 (70), 230 (44), 135 (83), 69 (100). – $C_{18}H_{25}NO_2$ (287.2): calcd. C 75.2, H 8.8, N 4.9; found C 75.1, H 8.7, N 4.8.

N-[1-(Cyclopropylcarbonyl)cyclopropylcarbonyl]phenylalanine (**7e**): D,L-Phenylalanine (0.24 g, 1.47 mmol), NEt_3 (0.02 ml, 0.147 mmol) in anhydrous CH_2Cl_2 (5 ml), and lactone **2** (0.20 g, 1.47 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to the procedure B. Reaction time 20 h. Chromatography [ether/light petroleum (40–60°C), 5:1] and crystallization (ether/light petroleum) gave a colorless solid (0.36 g, 82%). – IR (KBr): $\tilde{\nu}$ = 3292 cm^{-1}, 1732, 1672, 1636, 1532, 1400, 1052, 1008, 972, 700. – ^1H NMR ($CDCl_3$): δ = 0.65–1.06 (m, 4H), 1.11–1.78 (m, 5H), 2.85–3.07 (m, 1H), 3.15–3.33 (m, 1H), 4.5–4.74 (m, 1H), 7.19 (s, 5H, aromatic H), 8.56 (m, 1H), 9.15–9.32 (m, 1H). – MS (80°C), *m/z* (%): 301 (0) [M^+], 119 (3), 86 (65), 84 (100).

Methyl 1-(Cyclopropylcarbonyl)cyclopropanecarboxylate (**7f**): Anhydrous MeOH (78 mg, 0.1 ml, 2.43 mmol), *p*-TsOH (57 mg, 0.33 mmol) in anhydrous CH_2Cl_2 (2 ml), and lactone **2** (0.30 g, 2.2 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to the procedure C. Reaction time 12 h. Chromatography [ether/light petroleum (40–60°C), 1:2] gave a colorless oil (0.35 g, 95%). – IR (film): $\tilde{\nu}$ = 3018 cm^{-1}, 2959, 1733, 1690, 1391, 1330, 1205, 1165, 1110, 1067. – ^1H NMR ($CDCl_3$): δ = 0.89–1.0 (m, 2H, 7,8-H), 1.01–1.12 (m, 2H, 7,8-H), 1.47 (m, 4H, 2,3-H), 2.48 (m, 1H, 6-H), 3.77 (s, 3H, OMe). – ^{13}C NMR ($CDCl_3$): δ = 12.0 (t, C-7,8), 18.1 (t, C-2,3), 20.1 (d, C-6), 35.2 (s, C-1), 52.3 (q, OCH_3), 171.9 (s, C-4), 205.0 (s, C-5). – MS, *m/z* (%): 168 (12) [M^+], 140 (62), 127 (56), 95 (16), 69 (100). – $C_9H_{12}O_3$: calcd. 168.0786, found 168.0786 (MS).

tert-Butyl 1-(Cyclopropylcarbonyl)cyclopropanecarboxylate (**7g**): Anhydrous *t*BuOH (0.18 g, 0.23 ml, 2.42 mmol), *p*-TsOH (57 mg, 0.33 mmol) in anhydrous CH_2Cl_2 (2 ml), and lactone **2** (0.30 g, 2.2 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure C. Reaction time 20 h. Chromatography [ether/light petroleum (40–60°C), 1:5] gave a colorless oil (0.36 g, 78%). – IR (film): $\tilde{\nu}$ = 3010 cm^{-1}, 2980, 2935, 1723, 1688, 1390, 1370, 1323, 1156, 1054. – ^1H NMR ($CDCl_3$): δ = 0.87–1.01 (m, 2H, 7,8-H), 1.02–1.13 (m, 2H, 7,8-H), 1.34–1.41 (m, 4H, 2,3-H), 1.50 (s, 9H, CMe_3), 2.33–2.49 (m, 1H, 7-H). – ^{13}C NMR ($CDCl_3$): δ = 11.8 (t, C-7,8), 17.2 (t, C-2,3), 20.5 (d, C-6), 28.1 (q, CMe_3), 36.4 (s, C-1), 81.7 (s, CMe_3), 170.5 (s, C-4), 205.4 (s, C-5). – MS (80°C), *m/z* (%): 210 (0) [M^+], 153 (37), 137 (27), 113 (56), 69 (78), 57 (100). – $C_8H_9O_3$: calcd. 153.0552, found 153.0552 (MS).

1,1,2-Trimethylpropyl 1-(Cyclopropylcarbonyl)cyclopropanecarboxylate (**7h**): Anhydrous 2,3-dimethyl-2-butanol (0.25 g, 0.3 ml, 2.42 mmol), *p*-TsOH (57 mg, 0.33 mmol) in anhydrous CH_2Cl_2 (2 ml), and lactone **2** (0.30 g, 2.2 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure C. Reaction time 24 h. Chromatography [ether/light petroleum (40–60°C), 1:10)] gave a colorless, viscous oil (0.39 g, 74%). – IR (film): $\tilde{\nu}$ = 3010 cm^{-1}, 2979, 1723, 1688, 1391, 1321, 1203, 1187, 1137, 1104, 1064, 1022. – ^1H NMR ($CDCl_3$): δ = 0.86–0.99 (m, 2H, 7,8-H), 0.92 (d, ^3J = 7

Hz, 6H, 4',6'-H), 1.01–1.10 (m, 2H, 7,8-H), 1.32–1.4 (m, 4H, 2,3-H), 1.46 (s, 6H, 1',5'-H), 2.22 (sept, ^3J=7 Hz, 1H, 3'-H), 2.44 (m, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ=11.9 (t, C-7,8), 17.0 (t, C-2,3), 17.3 (q, C-4',6'), 20.4 (d, C-6), 22.8 (q, C-1',5'), 36.4 (s, C-1), 36.6 (d, C-3'), 86.9 (s, C-2'), 170.3 (s, C-4), 205.1 (s, C-5). – MS (80°C), *m/z* (%): 238 (0) [M^+], 154 (25), 137 (100), 113 (23), 85 (80), 70 (68). – $C_8H_9O_3$: calcd. 153.0552, found 153.0551 (MS).

1-Adamantyl 1-(Cyclopropylcarbonyl)cyclopropanecarboxylate (**7i**): 1-Adamantanol (0.37 g, 2.42 mmol), *p*-TsOH (57 mg, 0.33 mmol) in anhydrous CH_2Cl_2 (2 ml), and lactone **2** (0.30 g, 2.2 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure C. Reaction time 24 h. Chromatography [ether/light petroleum (40–60°C), 1:10] gave colorless crystals (0.53 g, 84%), m.p. 46°C. – IR (film): $\tilde{\nu}$=3010 cm^{-1}, 2913, 2854, 1720, 1687, 1388, 1329, 1299, 1201, 1176, 1062. – ^{1}H NMR ($CDCl_3$): δ=0.83–0.97 (m, 2H, 7,8-H), 0.94–1.1 (m, 2H, 7,8-H), 1.35 (m, 4H, 2,3-H), 1.68 (m, 6H, 4',6',10'-H), 2.16 (m, 9H, 2',3',5',7',8',9'-H), 2.44 (m, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ=11.8 (t, C-7,8), 17.3 (t, C-2,3), 20.4 (d, C-6), 31.0 (d, C-3',5',7'), 36.2 (s, C-1), 36.3 (t, C-4',6',10'), 41.4 (t, C-2',8',9'), 81.5 (s, C-1'), 170.1 (s, C-4), 205.0 (s, C-5). – MS (100°C), *m/z* (%): 289 (0) [M^+], 155 (9), 135 (100), 119 (7), 92 (20), 69 (20). – $C_{18}H_{24}O_3$ (288.2): calcd. C 75.0, H 8.4; found C 75.0, H 8.3.

2-Hydroxyphenyl 1-(Cyclopropylcarbonyl)cyclopropanecarboxylate (**7j**): Catechol (0.27 g, 2.42 mmol), *p*-TsOH (57 mg, 0.33 mmol) in anhydrous CH_2Cl_2 (2 ml), and lactone **2** (0.30 g, 2.2 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure C. Reaction time 3 h. Chromatography [ether/light petroleum (40–60°C), 1:3] gave a colorless, viscous oil (0.45 g, 83%). – IR (film): $\tilde{\nu}$ = 3359 cm^{-1} (OH), 3013, 2959, 1752, 1664, 1511, 1496, 1462, 1397, 1322, 1175, 1061, 747. – ^{1}H NMR ($CDCl_3$): δ = 0.87–1.02 (m, 2H, 7,8-H), 1.09–1.25 (m, 2H, 7,8-H), 1.66–1.82 (m, 4H, 2,3-H), 2.01–2.16 (m, 1H, 6-H), 6.69–7.15 (m, 4H, aromatic H), 7.72 (br. s, 1H, OH). – ^{13}C NMR ($CDCl_3$): δ=12.40 (t, C-7,8), 17.35 (t, C-2,3), 17.41 (d, C-6), 36.28 (s, C-1), 117.35 (d, C-3'), 120.82 (d, C-6'), 122.57 (d, C-5'), 127.32 (d, C-4'), 138.28 (s, C-1'), 147.96 (s, C-2'), 169.26 (s, C-4), 206.4 (s, C-5). – MS, *m/z* (%): 246 (2) [M^+], 245 (7), 194 (11), 136 (46), 110 (22), 69 (100). – $C_{14}H_{14}O_4$: calcd. 246.0892, found 246.0893 (MS).

4-Methoxyphenyl 1-(Cyclopropylcarbonyl)cyclopropanecarboxylate (**7k**): 4-Methoxyphenol (0.30 g, 0.27 ml, 2.42 mmol), *p*-TsOH (57 mg, 0.33 mmol) in anhydrous CH_2Cl_2 (2 ml), and lactone **2** (0.30 g, 2.2 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure C. Reaction time 2 h. Chromatography [ether/light petroleum (40–60°C), 1:2] gave a colorless oil (0.47 g, 83%). – IR (film): $\tilde{\nu}$=3010 cm^{-1}, 2956, 1744, 1687, 1507, 1389, 1310, 1251, 1195, 1141, 1061. – ^{1}H NMR ($CDCl_3$): δ=0.89–1.01 (m, 2H, 7,8-H), 1.05–1.16 (m, 2H, 7,8-H), 1.53–1.61 (m, 2H, 2,3-H), 1.61–1.69 (m, 2H, 2,3-H), 2.58 (m, 1H, 6-H), 3.74 (s, 3H, OMe), 6.81–6.92 (m, 2H, aromatic H), 6.96–7.07 (m, 2H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ=12.1 (t, C-7,8), 18.4 (t, C-2,3), 20.3 (d, C-6), 35.3 (s, C-1), 55.5 (q, OMe), 114.5, 122.1 (d, 4 aromatic C), 144.1, 157.5 (s, 2 aromatic C), 170.3 (s, C-4), 204.3 (s, C-5). – MS, *m/z* (%): 260 (18) [M^+], 219 (1), 137 (76), 124 (12), 109 (7), 69 (100). – $C_{15}H_{16}O_4$: calcd. 260.1049, found 260.1047 (MS).

2-Methoxyphenyl 1-(Cyclopropylcarbonyl)cyclopropanecarboxylate (**7l**): Guajacol (0.30 g, 0.27 ml, 2.42 mmol), *p*-TsOH (57 mg, 0.33 mmol) in anhydrous CH_2Cl_2 (2 ml), and lactone **2** (0.30 g, 2.2 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure C. Reaction time 30 h. Chromatography [ether/light petroleum (40–60°C), 1:3] gave a colorless oil (0.41 g, 72%). – IR (film): $\tilde{\nu}$=3011 cm^{-1}, 2841, 1751, 1685, 1607, 1504, 1392, 1310, 1260, 1199, 1174, 1143, 1110, 1060, 749. – ^{1}H NMR ($CDCl_3$): δ = 0.89–1.01 (m, 2H, 7,8-H), 1.04–1.16 (m, 2H, 7,8-H), 1.55–1.66 (m, 2H, 2,3-H), 1.66–1.78 (m, 2H, 2,3-H), 2.78 (m, 1H, 6-H), 3.76 (s, 3H, OMe), 6.89–6.99, 7.0–7.08, 7.1–7.24 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ=12.3 (t, C-7,8), 19.1 (t, C-2,3), 20.2 (d, C-6), 35.1 (s, C-1), 55.8 (q, OMe), 112.4, 114.6, 120.8, 127.1 (d, 4 aromatic C), 139.5, 151.1 (s, 2 aromatic C), 169.7 (s, C-4), 204.8 (s, C-5). – MS, *m/z* (%): 260 (8) [M^+], 154 (2), 137 (73), 124 (64), 109 (65), 81 (35), 69 (100). – $C_{15}H_{16}O_4$: calcd. 260.1049, found 260.1047 (MS).

Methyl O-[1-(Cyclopropylcarbonyl)cyclopropylcarbonyl]salicylate (**7m**): Anhydrous methyl salicylate (0.37 g, 0.31 ml, 2.42 mmol), *p*-TsOH (57 mg, 0.33 mmol) in anhydrous CH_2Cl_2 (2 ml), and lactone **2** (0.30 g, 2.2 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure C. Reaction time 24 h at 40°C. Chromatography [ether/light petroleum (40–60°C), 1:2] gave 0.24 g (38%) of **7m**. – Method B: yield 0.44 g (69%); colorless crystals, m.p. 48–50°C. – IR ($CHCl_3$): $\tilde{\nu}$=3005 cm^{-1}, 2960, 1745, 1722, 1605, 1430, 1390, 1300, 1275, 1265, 1105, 1060. – ^{1}H NMR ($CDCl_3$): δ=0.92–1.05 (m, 2H, 7,8-H), 1.05–1.17 (m, 2H, 7,8-H), 1.62–1.75 (m, 2H, 2,3-H), 1.75–1.88 (m, 2H, 2,3-H), 2.72–2.86 (m, 1H, 6-H), 3.87 (s, 3H, OMe), 7.12 (dd, ^3J=8, ^4J=2 Hz, 1H, 6'-H), 7.33 (m, ^3J=8, ^4J = 2 Hz, 1H, 4'-H), 7.58 (m, ^3J=8, ^4J=2 Hz, 1H, 5'-H), 8.03 (dd, ^3J = 8, ^4J = 2 Hz, 1H, 3'-H). – ^{13}C NMR ($CDCl_3$): δ=12.35 (t, C-7,8), 19.15 (t, C-2,3), 21.29 (d, C-6), 35.31 (s, C-1), 52.21 (q, OMe), 123.43 (s, C-2'), 123.59 (d, C-6'), 126.26 (d, C-4'), 131.83 (d, C-3'), 133.90 (d, C-5'), 150.13 (s, C-1'), 164.77 (s, CO_2Me), 170.07 (s, C-4), 204.88 (s, C-5). – MS, *m/z* (%): 288 (8) [M^+], 260 (4), 151 (4), 137 (58), 69 (100).

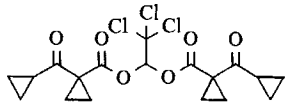
4-Nitrophenyl 1-(Cyclopropylcarbonyl)cyclopropanecarboxylate (**7n**): *p*-Nitrophenol (0.34 g, 2.42 mmol), *p*-TsOH (57 mg, 0.33 mmol) in anhydrous CH_2Cl_2 (2 ml), and lactone **2** (0.30 g, 2.2 mmol) in anhydrous CH_2Cl_2 (1 ml) were allowed to react according to procedure C. Reaction time 12 h. Chromatography [ether/light petroleum (40–60°C), 1:2] gave 0.27 g (45%) of **7n**. – Method B: yield 0.53 g (87%); colorless crystals, m.p. 75–76°C. – IR (KBr): $\tilde{\nu}$=3116 cm^{-1}, 3088, 3012, 1760, 1680, 1624, 1348, 1308, 1208, 1128, 1104, 1052, 860, 741. – ^{1}H NMR ($CDCl_3$): δ=0.96–1.08 (m, 2H, 7,8-H), 1.11–1.21 (m, 2H, 7,8-H), 1.63–1.79 (m, 4H, 2,3-H), 2.55 (m, 1H, 6-H), 7.28–7.39 (m, 2H, aromatic H), 8.23–8.34 (m, 2H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ=12.41 (t, C-7,8), 19.03 (t, C-2,3), 20.21 (d, C-6), 122.30, 125.29 (d, 4 aromatic C), 145.48, 155.09 (s, 2 aromatic C), 169.23 (s, C-4), 203.67 (s, C-5). – MS (90°C), *m/z* (%): 275 (1) [M^+], 247 (1), 137 (87), 109 (3), 79 (2), 69 (100). – $C_{14}H_{13}NO_5$ (275.1): calcd. C 61.10, H 4.8, N 5.1; found C 61.15, H 4.8, N 5.3.

1-(Cyclopropylcarbonyl)cyclopropanecarbonyl Azide (**8**): To a suspension of sodium azide (0.21 g, 3.2 mmol), *p*-TsOH (0.25 g, 1.47 mmol), and aliquat 300 (0.06 g, 0.15 mmol) in anhydrous CH_2Cl_2 (5 ml) was added lactone **2** (0.40 g, 2.94 mmol) in anhydrous CH_2Cl_2 (2 ml). After 8 h CH_2Cl_2 (5 ml) was added, the organic phase was extracted with water (10 ml) and dried ($MgSO_4$). The solvent was removed and the residue purified by chromatography [ether/light petroleum (40–60°C), 1:2] to afford the azide as a colorless oil (0.22 g, 42%). – IR (film): $\tilde{\nu}$=3013 cm^{-1}, 2235, 2146, 1698, 1685, 1391, 1318, 1181, 1012. – ^{1}H NMR ($CDCl_3$): δ=0.92–1.05 (m, 2H, 7,8-H), 1.05–1.16 (m, 2H, 7,8-H), 1.57 (m, 4H, 2,3-H), 2.50 (m, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ=12.60 (t, C-7,8), 19.4 (t, C-2,3), 20.3 (d, C-6), 37.6 (s, C-1), 178.4 (s, C-4), 204 (s, C-5). – MS (100°C), *m/z* (%): 179 (0) [M^+], 151 (3), 137 (5), 95 (8), 82 (13), 69 (75), 41 (100).

General Procedure for the Preparation of Spiro β-Keto-δ-valerolactones (**10a–h**). – *Method A:* An oven-dried flask was charged

with lactone **2** (1 eq.), aldehyde (5–10 eq.), 18-crown-6 (0.05 eq.), KF (0.4 eq.), and CH_2Cl_2 (5 ml). The mixture was stirred for 24 h at room temp. under N_2. The solvent was removed and the crude product purified by chromatography [ether/light petroleum (40–60°C), 1:2] to afford the β-ketovalerolactone. – *Method B:* A solution of lactone **2** (1 eq.), aldehyde (10–20 eq.), and DABCO (0.1 eq.) in CH_2Cl_2 (3 ml) was stirred for 36–48 h at room temp. under N_2. The mixture was worked up as described above.

10-(Trichloromethyl)-9-oxadispiro[2.1.2.3]decane-4,8-dione (**10a**): Lactone **2** (400 mg, 2.94 mmol), chloral (4.32 g, 29.4 mmol), KF (68 mg, 1.18 mmol), and 18-crown-6 (40 mg, 0.147 mmol) were allowed to react according to procedure A to give **10a** (305 mg, 37%). – Method B (10 eq. of chloral): yield 109 mg (14%); colorless solid, m.p. 121°C. – IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2968, 1751, 1708, 1367, 1295, 1148, 1063, 835, 774, 745, 732, 723, 621. – ^1H NMR ($CDCl_3$): δ = 0.94–1.09 (m, 1H), 1.26–1.41 (m, 1H), 1.72–1.99 (m, 4H), 2.02–2.14 (m, 1H), 2.19–2.34 (m, 1 H), 4.55 (s, 1H). – ^{13}C NMR ($CDCl_3$): δ = 12.0, 20.9 (t, C-1,2), 26.6, 28.9 (t, C-5,6), 28.6 (s, C-3), 33.4 (s, C-7), 90.2 (d, C-10), 100.0 (s, C-11), 169.5 (s, C-8), 199.1 (s, C-4). – MS (60°C), *m/z* (%): 282 (0) [M^+], 165 (100), 137 (4), 109 (3), 97 (37), 81 (2), 69 (9), 50 (5), 40 (12).

B 

Product **B** was isolated as a byproduct (11–25%) in the presence of chloral hydrate (without previous removal of water). – IR (film): $\tilde{\nu}$ = 3013 cm^{-1}, 2986, 2929, 1768, 1688, 1391, 1348, 1300, 1154, 1099, 1062, 1010, 916, 846, 790. – ^1H NMR ($CDCl_3$): δ = 0.92–1.06 (m, 4H, 7,8,7′,8′-H), 1.06–1.18 (m, 4H, 7,8,7′,8′-H), 1.52–1.73 (m, 8H, 2,3,2′,3′-H), 2.54 (m, 2H, 6,6′-H), 7.36 (s, 1H, 9-H). – ^{13}C NMR ($CDCl_3$): δ = 12.7, 12.8 (t, C-7,8,7′,8′), 19.4, 19.6 (t, C-2,3,2′,3′), 20.4 (d, C-6,6′), 34.7 (s, C-1,1′), 90.3 (d, C-9), 95.7 (s, C-10), 168.5 (s, C-4,4′), 203.4 (s, C-5,5′). – MS (90°C), *m/z* (%): 437 (0) [M^+], 262 (1), 152 (2), 137 (87), 108 (3), 91 (1), 69 (100).

10-Phenyl-9-oxadispiro[2.1.2.1]decane-4,8-dione (**10b**): Lactone **2** (400 mg, 2.94 mmol), benzaldehyde (3.12 g, 3 ml, 29.4 mmol), KF (68 mg, 1.18 mmol), and 18-crown-6 (40 mg, 0.147 mmol) were allowed to react according to procedure A to give **10b** (266 mg, 37%). – Method B (20 eq. of benzaldehyde): yield 387 mg (54%); colorless solid, m.p. 138°C. – IR (KBr): $\tilde{\nu}$ = 3013 cm^{-1}, 1730, 1699, 1387, 1358, 1303, 1178, 1064, 1014, 762, 729, 702. – ^1H NMR ($CDCl_3$): δ = 0.93–1.10 (m, 2H), 1.30–1.44 (m, 1H), 1.46–1.69 (m, 3H), 1.76–1.95 (m, 2H), 5.52 (s, 1H, 10-H), 7.31–7.44 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 13.1, 16.0 (t, C-1,2), 24.5, 24.6 (t, C-5,6), 31.2 (s, C-3), 32.9 (s, C-7), 80.7 (d, C-10), 127.2, 128.6, 128.9 (d, C, aromatic C), 136.1 (s, aromatic C), 171.7 (s, C-8), 202.7 (s, C-4). – MS (60°C), *m/z* (%): 242 (78) [M^+], 228 (2), 214 (94), 199 (33), 186 (39), 174 (40), 165 (21), 146 (33), 129 (63), 118 (52), 105 (72), 91 (53), 77 (71), 68 (78), 51 (38), 41 (100).

10-(2-Furyl)-9-oxadispiro[2.1.2.3]decane-4,8-dione (**10c**): Lactone **2** (400 mg, 2.94 mmol), furfural (1.42 g, 1.23 ml, 14.7 mmol), KF (68 mg, 1.18 mmol), and 18-crown-6 (40 mg, 0.147 mmol) were allowed to react according to procedure A to give **10c** (328 mg, 48%). – Method B (5 eq. of furfural): yield 68 mg (10%); colorless solid, m.p. 71°C. – IR (KBr): $\tilde{\nu}$ = 3002 cm^{-1}, 1734, 1701, 1389, 1358, 1291, 1236, 1142, 1058, 1047, 1011, 872, 840. – ^1H NMR ($CDCl_3$): δ = 0.97–1.10 (m, 1H), 1.20–1.36 (m, 2H), 1.63–2.08 (m, 5H), 5.51 (s, 1H), 6.30–6.42 (m, 2H, aromatic H), 7.37–7.47 (m, 1H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 11.79, 20.30 (t, C-1,2), 24.08, 27.05 (t, C-5,6), 29.97 (s, C-3), 32.87 (s, C-7), 76.01 (d, C-10), 109.61, 110.48, 143.67 (d, aromatic C), 150.41 (s, aromatic C), 171.49 (s, C-8), 202.05 (s, C-4). – MS (80°C), *m/z* (%): 232 (100) [M^+], 204 (54), 187 (92), 173 (29), 160 (92), 136 (37), 120 (42), 108 (23), 95 (38), 91 (97), 79 (33), 68 (48). – $C_{13}H_{12}O_4$ (232.1): calcd. C 67.23, H 5.21; found C 67.14, H 5.15.

10-(2-Thienyl)-9-oxadispiro[2.1.2.3]decane-4,8-dione (**10d**): Lactone **2** (400 mg, 2.94 mmol), 2-thiophenecarbaldehyde (1.65 g, 1.4 ml, 14.7 mmol), KF (68 mg, 1.18 mmol), and 18-crown-6 (40 mg, 0.147 mmol) were allowed to react according to procedure A to give **10d** (294 mg, 40%). – Method B (5 eq. of 2-thiophenecarbaldehyde): yield 95 mg (13%); colorless solid, m.p. 79°C. – IR (KBr): $\tilde{\nu}$ = 3003 cm^{-1}, 1738, 1695, 1397, 1358, 1323, 1308, 1200, 1167, 1062, 1006, 729. – ^1H NMR ($CDCl_3$): δ = 1.10–1.41 (m, 4H), 1.41–1.58 (m, 2H), 1.81–2.03 (m, 2H), 5.38 (s, 1H), 6.94–7.11 (m, 2H, aromatic H), 7.30–7.39 (m, 1H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 12.23, 19.46 (t, C-1,2), 23.41, 26.91 (t, C-5,6), 31.90 (s, C-3), 33.08 (s, C-7), 78.40 (d, C-10), 126.46, 126.62, 126.94 (d, aromatic C), 140.92 (s, aromatic C), 171.41 (s, C-8), 201.97 (s, C-4). – MS (80°C), *m/z* (%): 248 (100) [M^+], 220 (30), 189 (29), 176 (42), 152 (20), 135 (48), 91 (27), 68 (27). – $C_{13}H_{12}O_3S$ (248.1): calcd. C 62.88, H 4.87; found C 62.88, H 5.85.

10-(3-Pyridyl)-9-oxadispiro[2.1.2.3]decane-4,8-dione (**10e**): Lactone **2** (300 mg, 2.2 mmol), 3-pyridinecarbaldehyde (2.36 g, 2.1 ml, 22 mmol), and DABCO (25 mg, 0.22 mmol) were allowed to react according to procedure B to give **10e** (60 mg, 11%). – IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 1732, 1699, 1579, 1388, 1356, 1324, 1307, 1175, 1064, 1013. – ^1H NMR ($CDCl_3$): δ = 0.94–1.08 (m, 2H), 1.39–1.51 (m, 1H), 1.51–1.64 (m, 1H), 1.64–1.78 (m, 2H), 1.81–2.00 (m, 2H), 5.59 (s, 1H), 7.78, 8.59–8.70 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 13.0, 15.9 (t, C-1,2), 24.9, 25.0 (t, C-5,6), 30.9 (s, C-3), 32.9 (s, C-7), 78.8 (d, C-10), 123.5 (d, aromatic C), 131.9 (s, aromatic C), 134.8, 148.6, 150.5 (d, aromatic C), 171.2 (s, C-8), 201.8 (s, C-4). – MS (90°C), *m/z* (%): 243 (100) [M^+], 215 (37), 198 (30), 175 (19), 130 (47), 105 (22), 97 (20), 78 (23), 68 (30). – $C_{14}H_{13}NO_3$ (243.1): calcd. C 69.13, H 5.39, N 5.80; found C 68.92, H 5.60, N 6.33.

10-(1-Naphthyl)-9-oxadispiro[2.1.2.3]decane-4,8-dione (**10f**): Lactone **2** (400 mg, 2.94 mmol), 2-naphthaldehyde (2.3 g, 2 ml, 14.7 mmol), KF (68 mg, 1.18 mmol), and 18-crown-6 (40 mg, 0.147 mmol) were allowed to react according to procedure A to give **10f** (193 mg, 23%); colorless solid, m.p. 135°C. – IR (KBr): $\tilde{\nu}$ = 2927 cm^{-1}, 1734, 1696, 1375, 1321, 1184, 1064, 1048, 1005, 800, 755. – ^1H NMR ($CDCl_3$): δ = 0.87–1.09 (m, 2H), 1.34–1.49 (m, 1H), 1.51–1.81 (m, 3H), 1.81–1.98 (m, 2H), 6.15 (s, 1H), 7.35–7.61 (m, 4H, aromatic H), 7.75–7.91 (m, 2H, aromatic H), 8.06–8.16 (m, 1H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 13.47, 18.09 (t, C-1,2), 24.54, 25.41 (t, C-5,6), 30.75 (s, C-3), 32.67 (s, C-7), 78.33 (d, C-10), 123.69, 124.62, 125.41, 126.13, 126.97, 128.85, 130.03 (d, aromatic C), 131.14, 131.22, 133.74 (s, aromatic C), 171.41 (s, C-8), 203.40 (s, C-4). – MS (100°C), *m/z* (%): 292 (100) [M^+], 233 (11), 179 (21), 165 (23), 141 (23), 127 (21), 97 (7), 79 (8), 68 (11). – $C_{19}H_{16}O_3$ (292.1): calcd. C 78.06, H 5.52; found C 76.63, H 5.48.

10-(trans-Styryl)-9-oxadispiro[2.1.2.3]decane-4,8-dione (**10g**): Lactone **2** (400 mg, 2.94 mmol), *trans*-cinnamaldehyde (1.94 g, 1.9 ml, 14.7 mmol), KF (68 mg, 1.18 mmol), and 18-crown-6 (40 mg, 0.147 mmol) were allowed to react according to procedure A to give **10g** (137 mg, 17%); colorless solid, m.p. 111°C. – IR (KBr): $\tilde{\nu}$ = 3015 cm^{-1}, 1729, 1693, 1391, 1357, 1302, 1183, 1063, 1042, 1027, 1009, 979, 746, 695. – ^1H NMR ($CDCl_3$): δ = 1.04–1.23 (m, 2H), 1.23–1.39 (m, 1H), 1.49–1.61 (m, 1H), 1.71–2.00 (m, 4H), 4.91–5.00 (dd, ^4J = 2, ^3J = 8 Hz, 1H), 6.13–6.28 (dd, ^3J = 8, ^3J = 16

Hz, 1H), 6.63–6.77 (dd, ^4J=2, ^3J = 16 Hz, 1H), 7.25–7.44 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ=12.31, 17.12 (t, C-1,2), 24.24, 25.15 (t, C-5,6), 30.67 (s, C-3), 32.64 (s, C-7), 80.12 (d, C-10), 123.41 (d, C-1'), 126.77, 128.67, 128.73 (d, aromatic C), 134.66 (d, C-2'), 135.28 (s, aromatic C), 171.65 (s, C-8), 202.44 (s, C-4). – MS (80°C), *m/z* (%): 268 (68) [M^+], 253 (20), 240 (33), 225 (19), 191 (20), 177 (35), 155 (17), 141 (20), 131 (41), 115 (55), 104 (100), 91 (67), 77 (39), 68 (32). – $C_{17}H_{16}O_3$ (268.1): calcd. C 76.10, H 6.01; found C 74.88, H 6.00.

9,10,12,13-Tetramethyl-14-oxatrispiro[2.1.2.0.5.2]pentadeca-9,12-diene-4,11,15-trione (**10h**): Lactone **2** (200 mg, 1.47 mmol), tetramethyl-*p*-benzoquinone (241 mg, 1.47 mmol), KF (25.6 mg, 0.44 mmol), and 18-crown-6 (4 mg, 0.0147 mmol) were allowed to react according to procedure A to give **10h** (165 mg, 37%); colorless solid, m.p. 85°C. – IR (KBr): ν̃ = 2929 cm^{-1}, 1740, 1681, 1641, 1349, 1263, 1175, 1075, 1034, 1005, 905, 764. – ^{1}H NMR ($CDCl_3$): δ=0.67–0.82 (q, *J*=4 Hz, 2H), 1.41–1.57 (q, *J*=4 Hz, 2H), 1.74, 2.04 (m, 16H). – ^{13}C NMR ($CDCl_3$): δ=11.25, 16.16 (q, C-16,17,18,19), 22.55, 27.51 (t, C-1,2,6,7), 29.94 (s, C-5), 31.64 (s, C-3), 84.19 (s, C-8), 131.79 (s, C-9,13), 147.71 (s, C-10,12), 170.50 (s, C-15), 184.10 (s, C-11), 210.56 (s, C-4). – MS, *m/z* (%): 300 (19) [M^+], 299 (100), 285 (34), 257 (16), 244 (15), 217 (19), 204 (11), 189 (18), 176 (19), 161 (11), 136 (34), 118 (17), 91 (19), 79 (18), 68 (16).

10-Phenyl-10-(trifluoromethyl)-9-oxadispiro[2.1.2.3]decane-4,8-dione (**10i**): Lactone **2** (136 mg, 1 mmol), phenyl trifluoromethyl ketone (348 mg, 2 mmol), KF (17 mg, 0.3 mmol), and 18-crown-6 (2.6 mg, 0.01 mmol) in CH_2Cl_2 (5 ml) were allowed to react according to procedure A to give **10i** (138 mg, 45%). – IR ($CHCl_3$): ν̃=2924 cm^{-1}, 1760, 1704, 1448, 1348, 1292, 1188, 1168, 1144, 1068, 720. – ^{1}H NMR ($CDCl_3$): δ=0.99–1.11 (m, 1H), 1.38–1.75 (m, 5H), 1.84–2.02 (m, 2H), 7.38–7.49 (m, 3H, aromatic H), 7.54–7.69 (m, 2H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ=12.25, 15.74 (t, C-1,2), 25.16, 27.58 (t, C-5,6), 32.07 (s, C-7), 32.52 (s, C-3), 83.64 (s, C-10), 121.14 (s, C-11), 127.08 (d, C-2',6'), 128.75 (d, C-3',5'), 130.01 (d, C-4'), 133.17 (s, C-1'), 169.77 (s, C-8), 199.79 (s, C-4). – MS, *m/z* (%): 310 (1) [M^+], 309 (5), 282 (2), 242 (17), 241 (91), 213 (6), 173 (18), 146 (6), 129 (11), 128 (11), 105 (100), 91 (22), 86 (22), 84 (33), 77 (40), 69 (21), 68 (10).

8-Oxadispiro[2.0.3.2]nonane-7,9-dione (**12**) *and 8-Oxadispiro[2.1.2.2]nonane-4,9-dione* (**13**): A flame-dried 10-ml two-necked flask was charged with lactone **2** (136 mg, 1 mmol) and 3-phenyl-2-(*p*-tolylsulfonyl)oxaziridine (275 mg, 1 mmol) in anhydrous $CHCl_3$ (2 ml). The reaction mixture was stirred for 8 h at 60°C under N_2. Evaporation of the solvent and chromatography [silica gel, ether/light petroleum (40–60°C), 1:1] afforded **12** (60 mg, 39%) and **13** (60 mg, 39%).

12: m.p. 74–76°C. – IR (KBr): ν̃=3014 cm^{-1}, 1844, 1799, 1151, 1088, 1053, 1006, 979, 809. – ^{1}H NMR ($CDCl_3$): δ=1.05–1.32 (m, 2H), 1.36–1.67 (m, 2H), 2.27–3.22 (m, 4H). – ^{13}C NMR ($CDCl_3$): δ=9.76–11.01 (t, C-1,2), 23.03 (t, C-5), 38.42 (s, C-3), 41.90 (t, C-6), 91.5 (s, C-4), 171.47 (s, C-9), 204.26 (s, C-7). – MS, *m/z* (%): 152 (0) [M^+], 123 (61), 109 (16), 96 (26), 81 (14), 68 (100), 56 (49). – $C_8H_8O_3$ (152.1): calcd. C 63.15, H 5.3; found C 61.90, H 5.3.

13: m.p. 69–71°C. – IR ($CHCl_3$): ν̃=3010 cm^{-1}, 1790, 1740, 1360, 1330, 1200, 1140, 975. – ^{1}H NMR ($CDCl_3$): δ=1.49–1.6 (m, 2H, 6,7-H), 1.5–1.72 (m, 2H, 6,7-H), 1.82–1.92 (m, 2H, 1,2-H), 1.92–2.03 (m, 2H, 1,2-H). – ^{13}C NMR ($CDCl_3$): δ=15.54 (t, C-6,7), 23.56 (t, C-1,2), 29.26 (s, C-3), 70.26 (s, C-5), 173.84 (s, C-9), 206.68 (s, C-4). – MS, *m/z* (%): 152 (100) [M^+], 135 (19), 124 (96), 96 (47), 68 (65). – $C_8H_8O_3$ (152.1): calcd. C 63.15, H 5.3; found C 62.85, H 5.3.

Baeyer-Villiger Route to **13**: A flame-dried 10-ml two-necked flask was charged with dione **3** (500 mg, 3.67 mmol) and $Na_2HPO_4 \cdot 12\ H_2O$ (7.88 g, 22 mmol) in CH_2Cl_2 (5 ml). The mixture was heated to 50°C and peroxyacetic acid (2.3 ml, 11 mmol, 32% solution) was added dropwise. After 1 h CH_2Cl_2 (10 ml) was added, and the mixture was washed with H_2O (20 ml). The organic phase was dried ($MgSO_4$) and the solvent evaporated. Chromatography [silica gel, ether/light petroleum (40–60°C), 1:3] gave **13** (370 mg, 66%). For spectroscopic data see above.

3,3,5,5-Tetramethyl-2,4(3H,5H)-furandione (**15**): The reaction conditions were not optimized. The Davis reagent decomposed at the reaction temperature, and lactone **14** was reisolated (64%). Lactone **14** (560 mg, 4.0 mmol) and 3-phenyl-2-(*p*-tolylsulfonyl)oxaziridine (1.1 g, 4.0 mmol) were allowed to react for 6 h as described for compounds **12/13**. Kugelrohr distillation (125°C/12 Torr) gave a mixture of product and **14**. Yield: 75 mg (12%, GC analysis). – ^{1}H NMR ($CDCl_3$): δ=1.36 (s, 6H), 1.52 (s, 6H).

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