Chemoselective and Regiospecific Synthesis of Iminospiro-γ-lactones from Maleic Anhydride or Citraconic Anhydride and Alkyl Isocyanides with Dialkyl Acetylenedicarboxylates

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Isocyanides, dialkyl acetylenedicarboxylates (=dialkyl but-2-ynedioates), and anhydrides such as maleic anhydride (=furan-2,3-dione) or citraconic anhydride (=3-methylfuran-2,3-dione) react in one pot to afford novel iminospiro-γ-lactones in fairly good yields at room temperature (*Schemes 1* and *3*).

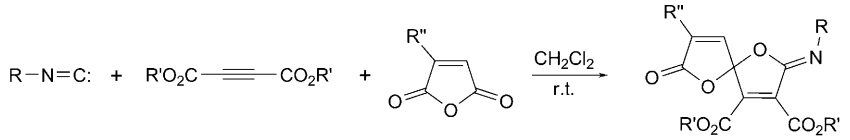
Introduction. – Multicomponent reactions (MCRs) have emerged as a highly valuable synthetic tool in the context of modern drug discovery [1][2]. The atom-economical and convergent character, the simplicity of a one-pot procedure, the possible structural variations, the attainable complexity of the molecules, as well as the huge number of accessible compounds are among the described advantages of MCRs [3–6]. Thus, they are perfectly amenable to automation for combinatorial synthesis [7]. Amongst the known multicomponent reactions, isocyanide-based MCRs such as the versatile *Ugi* and *Passerini* reactions are especially valuable [8–11].

Iminospiro-γ-lactones have been shown to be an important class of molecules owing to their interesting structures and biological activities [12]. The unique structural nature of these spirocyclic compounds has attracted the interest of many synthetic organic chemists [13][14]. The lactone moiety is also present in many natural products, especially insect pheromones, antifungal substances, and flavor components that occur in the essential oils of plants. Recently, spiro-γ-lactones attained great interest because of their effect as aldosterone inhibitors [15].

Although the trapping of the 1:1 intermediate formed between dialkyl acetylenedicarboxylates (=dialkyl but-2-ynedioates) and isocyanides with aldehydes [16], aromatic anhydrides [17], 1,3-diones [18], benzoyl chlorides [19], benzoyl cyanides [20], and carboxylic acids [21] has been studied in detail by a number of research groups [5], trapping of the initial 1:1 intermediate formed with citraconic anhydride (=3-methylfuran-2,5-dione) or maleic anhydride (=furan-2,5-dione) has not been reported. We report here on the MCR of alkyl isocyanides **1** and dialkyl acetylenedicarboxylates **2** in the presence of maleic anhydride (**3a**) or citraconic anhydride (**3b**) as trapping agents for the reactive zwitterionic intermediate. This three-component-condensation reaction produces highly functionalized iminospiro-γ-lactones **4** in fairly good yields (*Scheme 1*).

Results and Discussion. – The reaction of alkyl isocyanides **1** with electron-deficient acetylenic esters **2** in the presence of maleic anhydride (**3a**) or citraconic anhydride

Scheme 1



1a R = *t*-Bu
1b R = cHex

2a R' = Me
2b R' = Et
2c R' = *t*-Bu

3a R" = H
3b R" = Me

cHex = Cyclohexyl

	R	R'	R"	Yield [%]
4a	cHex	Me	H	98
4b	cHex	Et	H	70
4c	*t*-Bu	Et	H	75
4d	*t*-Bu	*t*-Bu	Me	61
4e	*t*-Bu	*t*-Bu	H	65
4f	cHex	Et	Me	69
4g	*t*-Bu	Et	Me	75
4h	cHex	*t*-Bu	Me	60
4i	cHex	Me	Me	95
4j	*t*-Bu	Me	Me	94
4k	*t*-Bu	Me	H	96
4l	cHex	*t*-Bu	H	50

(**3b**) proceeded spontaneously at room temperature in anhydrous CH_2Cl_2 and was completed after 1 d to afford corresponding dialkyl 2-(alkylimino)-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylates or dialkyl 8-methyl variants **4a**–**4l** in moderate to good yields (50–98%). ^{1}H- and ^{13}C-NMR spectra of the crude products clearly indicated the formation of the iminospiro-γ-lactones. The structures of the products were deduced from their IR and ^{1}H- and ^{13}C-NMR spectra, and elemental analyses. The mass spectra of compounds **4a**–**4l** displayed molecular-ion peaks at the calculated *m*/*z* values. Initial fragmentations involved cleavage of the side chains or their complete loss and scission of the spirolactone system.

The ^{1}H-NMR spectrum of **4a** consisted of a *m* for the cyclohexyl group (δ 1.15–1.91) and two single sharp lines for the MeO groups (δ 3.67 and 3.82). A *m* was observed for the CH–N group (δ 3.57), and two *d* (δ 6.38 and 7.19, $^3J = 5.5$ Hz) for two olefinic H-atoms, in agreement with the suggested structure. The ^{1}H-decoupled ^{13}C-NMR spectrum of **4a** showed 17 sharp signals in agreement with the proposed structure. The characteristic ^{13}C-NMR signal of the spiro atom C(5) was discernible (δ 111.40), as well as two signals for two olefinic CH groups (δ 123.92 and 149.98) and two signals for the other two olefinic C-atoms (δ 126.27 and 147.50) (see also *Exper. Part*). The structural assignment of **4a** made on the basis of the ^{1}H- and ^{13}C-NMR spectra, was supported by its IR spectrum which showed strong absorption at 1835, 1737, 1690, and 1632 cm^{-1} due to the C=O and C=N groups.

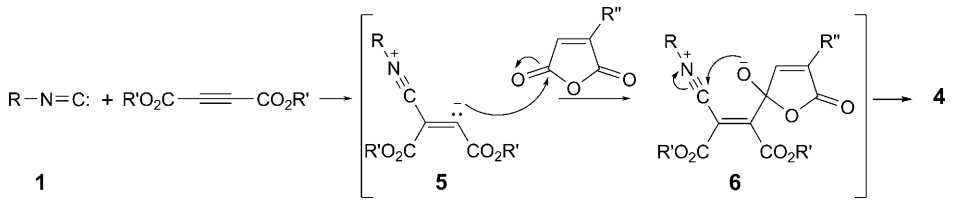
The ^{1}H- and ^{13}C-NMR spectra of **4b**–**4l** were similar to those of **4a**, except for the signals of the alkyl, ester, and alkyl isocyanide moieties (see also *Exper. Part*).

The regiospecificity observed in the reaction with citraconic anhydride is attributable to the higher electrophilicity of the C(5)=O *vs.* the C(2)=O group of this anhydride. The structure of the regioisomers **4d**–**4j** was confirmed by NOE experiments. For compound **4h**, irradiation of Me–C(8) (δ 1.93) led to a negative NOE effect for the Me_3C (δ 1.39), and its intensity was reduced by *ca.* 76%. Irradiation of Me–C(8) (δ 1.93) had no effect on Me_3C (δ 1.51). Irradiation of H–C(9) (δ 5.98) led

to an increase in the signal intensity by *ca.* 38% for Me–C(8) (δ 1.93), and by *ca.* 9% for Me_3C (δ 1.39).

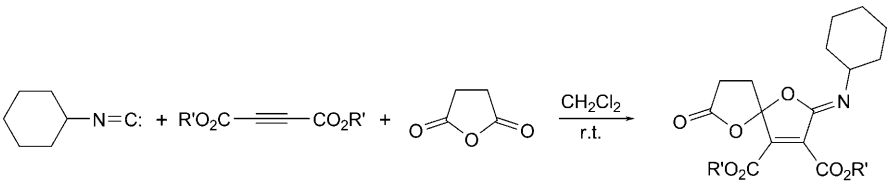
A plausible mechanism for the formation of spirolactones **4** is shown in *Scheme 2*. On the basis of the well-established chemistry of isocyanides [8][10][22–24], it is reasonable to assume that compounds **4** result from initial addition of alkyl isocyanides **1** to the acetylenic ester to form intermediate **5**, which adds to the C=O moiety of the anhydride in a [3+2] fashion or by a stepwise process involving nucleophilic addition of **5** to the reactive C=O group of the anhydrides to form nitrilium ions **6**, and cyclization to spirolactones **4**.

Scheme 2



Similar results were obtained with other anhydrides yielding the iminospiro-γ-lactones **7a** and **7b**. Succinic anhydride (= 3,4-dihydrofuran-2,5-dione), on treatment with dimethyl or diethyl acetylenedicarboxylate and cyclohexyl isocyanide in CH_2Cl_2 at room temperature afforded the iminospiro-γ-lactones **7a** and **7b** in 70% yield (*Scheme 3*).

Scheme 3



2a R' = Me
2b R' = Et

7a R' = Me
7b R' = Et

In conclusion, the three-component reaction of alkyl isocyanides with electron-deficient acetylenic esters in the presence of maleic anhydride or citraconic anhydride provides a simple entry into the synthesis of polyfunctionalized iminospiro-γ-lactones of potential synthetic interest. The present procedure has the advantage that the reaction runs under neutral conditions and, moreover, the substances can be mixed without any further activation or modification.

Experimental Part

General. Dialkyl acetylenedicarboxylates, alkyl isocyanides, and other reagents and solvents used in this work were obtained from *Fluka* (Buchs, Switzerland) and used without further purification. M.p.: *Gallenkamp-electrothermal-9100* apparatus; not corrected. IR Spectra (KBr): *Bruker-Tensor-27* spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker-DRX-300-Avance* instrument, $CDCl_3$ solns.; δ in ppm

rel. to Me_4Si as internal standard, *J* in Hz. MS: *Shimadzu-QP-GC-100-EX* mass spectrometer; at 70 eV; in *m*/*z* (rel. %). Elemental analyses: *Heraeus-CHN-O-Rapid* analyzer. These results agreed favorably with the calculated values.

Compounds **4**: *General Procedure.* To a stirred soln. of maleic anhydride (0.098 g, 1 mmol) and dimethyl but-2-ynedioate (0.142 g, 1 mmol) in CH_2Cl_2 (10 ml) was added cyclohexyl isocyanide (0.109 g, 1 mmol) in CH_2Cl_2 (2 ml) at r.t. over 10 min *via* a syringe. The mixture was stirred at r.t. for 24 h. The solvent was evaporated and the residue purified by column chromatography (silica gel *60* (70–230 mesh; *Merck*), hexane/AcOEt 4:1): product **4**.

Dimethyl 2-(Cyclohexylimino)-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate (**4a**). Yield 0.342 g (98%). Yellow powder. M.p. 146–148°. IR: 1835, 1737, 1690 (C=O), 1632 (C=N). ^{1}H-NMR: 1.15–1.91 (*m*, 5 CH_2); 3.57 (*m*, CHN); 3.67, 3.82 (2*s*, 2 MeO); 6.38 (*d*, ^3J = 5.5, H–C(8)); 7.19 (*d*, ^3J = 5.5, H–C(9)). ^{13}C-NMR: 24.48, 25.67, 25.52, 32.63, 33.06 (5 CH_2); 53.42, 53.49 (2 MeO); 57.48 (CHN); 111.40 (C(5)); 123.92 (C(8)); 126.27 (C(3)); 147.50 (C(4)); 149.98 (C(9)); 150.48 (C(2)); 158.10, 159.21, 168.12 (3 C=O). EI-MS: 349 (13, M^+), 317 (19), 308 (77), 277 (20), 267 (100), 252 (85), 193 (19), 151 (13). Anal. calc. for $C_{17}H_{19}NO_7$ (349.33): C 58.45, H 5.48, N 4.01; found: C 58.6, H 5.6, N 4.1.

Diethyl 2-(Cyclohexylimino)-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate (**4b**). Yield 0.263 g (70%). Brown oil. IR: 1808, 1737, 1684 (C=O), 1631 (C=N). ^{1}H-NMR: 1.37, 1.43 (2*t*, ^3J = 6.9, 2 Me); 1.20–1.91 (*m*, 5 CH_2); 3.65 (*m*, CHN); 4.21, 4.40 (2*q*, ^3J = 6.9, 2 CH_2O); 6.38 (*d*, ^3J = 5.5, H–C(8)); 7.19 (*d*, ^3J = 5.5, H–C(9)). ^{13}C-NMR: 13.96, 14.30 (2 *Me*CH_2O); 24.45, 25.16, 25.52, 33.66, 33.09 (5 CH_2); 62.34, 62.76 (2 CH_2O); 57.25 (CHN); 111.14 (C(5)); 123.90 (C(8)); 126.19 (C(3)); 147.70 (C(4)); 150.08 (C(9)); 150.43 (C(2)); 158.97, 160.77, 168.44 (3 C=O). EI-MS: 185 (14), 184 (90), 157 (27), 86 (100), 84 (60), 50 (29), 47 (90). Anal. calc. for $C_{19}H_{23}NO_7$ (377.40): C 60.47, H 6.14, N 3.71; found: C 60.6, H 5.9, N 3.6.

*Diethyl 2-[(*tert*-Butyl)imino]-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate* (**4c**). Yield 0.263 g (75%). Brown oil. IR: 1818, 1714, 1685 (C=O), 1620 (C=N). ^{1}H-NMR ($CDCl_3$): 1.28, 1.33 (2*t*, ^3J = 7.2, 2 Me); 1.29 (*s*, *t*-Bu); 4.21, 4.40 (2*q*, ^3J = 7.2, 2 CH_2O); 6.38 (*d*, ^3J = 5.6, H–C(8)); 7.19 (*d*, ^3J = 5.6, H–C(9)). ^{13}C-NMR: 12.36, 13.57 (2 *Me*CH_2O); 29.96 (*Me*$_3$C); 56.04 (Me_3C); 61.55, 61.61 (2 CH_2O); 111.10 (C(5)); 123.93 (C(8)); 126.22 (C(3)); 147.66 (C(4)); 148.68 (C(2)); 150.01 (C(9)); 159.54, 161.42, 168.25 (3 C=O). EI-MS: 351 (34, M^+), 296 (97), 250 (43), 240 (37), 194 (100), 158 (19), 98 (25). Anal. calc. for $C_{17}H_{21}NO_7$ (351.35): C 58.11, H 6.02, N 3.99; found: C 58.3, H 6.1, N 4.1.

*Di(*tert*-butyl) 2-[(*tert*-Butyl)imino]-8-methyl-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate* (**4d**). Yield 0.257 g (61%). Pale brown powder. M.p. 132–134°. IR: 1812, 1715, 1685 (C=O), 1618 (C=N). ^{1}H-NMR: 1.24, 1.40, 1.52 (3*s*, 3 *t*-Bu); 1.93 (*d*, ^4J = 1.5, Me–C(8)); 6.01 (*q*, ^4J = 1.5, H–C(9)). ^{13}C-NMR: 13.71 (Me); 27.73, 28.10, 29.56 (3 *Me*$_3$C); 55.94 (Me_3CN); 84.17, 84.38 (2 Me_3CO); 111.46 (C(5)); 119.32, 162.18 (C(8), C(9)); 134.65 (C(3)); 141.48 (C(4)); 148.62 (C(2)); 158.21, 160.05, 168.71 (3 C=O). EI-MS: 421 (1, M^+), 406 (37), 295 (32), 294 (100), 273 (26), 264 (28), 208 (20), 58 (75), 41 (23). Anal. calc. for $C_{22}H_{31}NO_7$ (421.48): C 62.69, H 7.41, N 3.32; found: C 62.6, H 7.5, N 3.2.

*Di(*tert*-butyl) 2-[(*tert*-Butyl)imino]-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate* (**4e**). Yield 0.264 g (65%). Pale yellow oil. IR: 1806, 1731, 1694 (C=O), 1643 (C=N). ^{1}H-NMR: 1.35, 1.42, 1.47 (3*s*, 3 *t*-Bu); 6.38 (*d*, ^3J = 5.5, H–C(8)); 7.20 (*d*, ^3J = 5.5, H–C(9)). ^{13}C-NMR: 27.95, 28.02, 28.65 (3 *Me*$_3$C); 56.74 (Me_3CN); 84.05, 85.92 (2 Me_3CO); 111.41 (C(5)); 123.21 (C(8)); 125.82 (C(3)); 148.17 (C(4)); 149.28 (C(2)); 150.62 (C(9)); 159.12, 160.81, 167.67 (3 C=O). EI-MS: 407 (2, M^+), 240 (8), 198 (27), 166 (23), 155 (16), 135 (52), 109 (12), 86 (21), 84 (100), 58 (98), 41 (83). Anal. calc. for $C_{21}H_{29}NO_7$ (407.46): C 61.90, H 7.17, N 3.44; found: C 61.8, H 7.3, N 3.3.

Diethyl 2-[(Cyclohexyl)imino]-8-methyl-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate (**4f**). Yield 0.270 g (69%). Yellow powder. M.p. 146–148°. IR: 1792, 1752, 1731 (C=O), 1625 (C=N). ^{1}H-NMR: 1.25, 1.35 (2*t*, ^3J = 7.2, 2 Me); 1.30–1.81 (*m*, 5 CH_2); 1.98 (*d*, ^4J = 1.5, Me–C(8)); 3.67 (*m*, CHN); 4.26, 4.39 (2*q*, ^3J = 7.2, 2 CH_2O); 6.06 (*q*, ^4J = 1.5, H–C(9)). ^{13}C-NMR: 12.21 (Me); 17.09, 17.50 (2 *Me*CH_2); 25.61, 26.20, 26.72, 32.33, 34.10 (5 CH_2); 57.25 (CHN); 62.19, 62.36 (2 CH_2O); 110.49 (C(5)); 119.78, 161.50 (C(8), C(9)); 135.77 (C(3)); 140.80 (C(4)); 150.76 (C(2)); 158.99, 160.58, 168.60 (3 C=O). EI-MS: 391 (19, M^+), 345 (30), 295 (37), 290 (15), 266 (26), 219 (100), 192 (15), 162 (12), 148 (15). Anal. calc. for $C_{20}H_{25}NO_7$ (391.41): C 61.37, H 6.44, N 3.58; found: C 61.2, H 6.5, N 3.7.

*Diethyl 2-[(*tert*-Butyl)imino]-8-methyl-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate* (**4g**). Yield 0.274 g (75%). Pale brown oil. IR: 1814, 1731, 1689 (C=O), 1637 (C=N). ^{1}H-NMR: 1.27 (*s*, *t*-Bu); 1.22, 1.34 (2*t*, ^3J = 6.6, 2 *Me*CH_2); 1.95 (*d*, ^4J = 1.5, Me–C(8)); 4.20, 4.37 (2*q*, ^3J = 6.6, 2 CH_2O); 6.04 (*q*, ^4J = 1.5, H–C(9)). ^{13}C-NMR: 14.01, 14.07 (2 *Me*CH_2); 12.96 (Me); 29.55 (*Me*$_3$C); 55.84 (Me$_3$*C*N); 62.07, 62.54 (2 CH_2O); 111.13 (C(5)); 119.67, 161.59 (C(8), C(9)); 134.56 (C(3)); 141.60 (C(4)); 148.30 (C(2)); 159.01, 160.84, 168.37 (3 C=O). EI-MS: 365 (5, M^+), 352 (35), 350 (100), 304 (38), 27 (18), 258 (19), 208 (57), 163 (33), 149 (37), 113 (40), 96 (47), 68 (70). Anal. calc. for $C_{18}H_{23}NO_7$ (365.38): C 59.17, H 6.34, N 3.83; found: C 59.3, H 6.2, N 3.7.

*Di(*tert*-butyl) 2-(Cyclohexylimino)-8-methyl-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate* (**4h**). Yield 0.268 g (60%). Yellow powder. M.p. 158–160°. IR: 1820, 1736, 1697 (C=O), 1640 (C=N). ^{1}H-NMR 1.39, 1.51 (2*s*, 2 *t*-Bu); 1.46–1.81 (*m*, 5 CH_2); 1.93 (*d*, ^4J = 1.8, Me–C(8)); 3.35 (*m*, CHN); 5.98 (*q*, ^4J = 1.8, H–C(9)). ^{13}C-NMR: 13.32 (Me); 27.30, 27.82 (2 *Me*$_3$C); 27.72, 27.79, 28.01, 32.75, 32.84 (5 CH_2); 56.42 (CHN); 83.76, 84.02 (2 Me$_3$*C*O); 111.07 (C(5)); 119.41, 162.12 (C(8), C(9)); 135.85 (C(3)); 140.20 (C(4)); 150.61 (C(2)); 158.22, 159.78, 168.61 (3 C=O). EI-MS: 336 (45), 335 (100), 318 (60), 290 (37), 237 (24), 148 (26), 98 (21), 58 (76). Anal. calc. for $C_{24}H_{33}NO_7$ (447.52): C 64.41, H 7.43, N 3.13; found: C 64.3, H 7.3, N 3.1.

Dimethyl 2-(Cyclohexylimino)-8-methyl-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate (**4i**). Yield 0.344 g (95%). Pale yellow oil. IR: 1828, 1741, 1687 (C=O), 1645 (C=N). ^{1}H-NMR: 1.36–1.81 (*m*, 5 CH_2); 1.97 (*d*, ^4J = 1.5, Me–C(8)); 3.66 (*m*, NCH); 3.74, 3.92 (2*s*, 2 MeO); 6.06 (*q*, ^4J = 1.5, H–C(9)). ^{13}C-NMR: 13.10 (Me); 25.01, 25.17, 25.21, 32.41, 32.74 (5 CH_2); 57.42 (*C*HN); 50.61, 50.86 (2 MeO); 110.91 (C(5)); 119.82, 161.35 (C(8), C(9)); 135.93 (C(3)); 140.24 (C(4)); 150.65 (C(2)); 159.44, 160.97, 168.17 (3 C=O). EI-MS: 349 (8), 268 (12), 250 (15), 224 (34), 208 (14), 193 (18), 120 (57), 113 (100), 96, (83), 86, (98). Anal calc. for $C_{18}H_{21}NO_7$ (363.36): C 59.50, H 5.83, N 3.85; found: C 59.6, H 5.7, N 3.7.

*Dimethyl 2-(*tert*-Butylimino)-8-methyl-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate* (**4j**). Yield 0.317 g (94%). Yellow powder. M.p. 135–137°. IR: 1805, 1755, 1687 (C=O), 1648 (C=N). ^{1}H-NMR: 1.28 (*s*, *t*-Bu); 1.97 (*d*, ^4J = 1.6, Me–C(8)); 3.77, 3.92 (2*s*, 2 MeO); 6.06 (*d*, ^4J = 1.6, H–C(9)). ^{13}C-NMR: 12.28 (Me); 29.91 (*Me*$_3$C); 53.36, 53.44 (2 MeO); 56.03 (Me$_3$*C*N); 111.30 (C(5)); 119.75, 161.39 (C(8), C(9)); 134.76 (C(3)); 142.01 (C(4)); 148.39 (C(2)); 159.47, 161.21, 168.34 (3 C=O). EI-MS: 365 (5, M^+), 322 (100), 296 (11), 258 (12), 208 (23), 179 (23). Anal. calc. for $C_{16}H_{19}NO_7$ (337.33): C 59.97, H 5.68, N 4.15; found: C 60.1, H 5.8, N 4.1.

*Dimethyl 2-[(*tert*-Butyl)imino]-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate* (**4k**). Yield 0.310 g (96%). Dark brown oil. IR: 1828, 1720, 1695 (C=O), 1620 (C=N). ^{1}H-NMR: 1.27 (*s*, *t*-Bu); 3.82, 3.92 (2*s*, 2 MeO); 6.38 (*d*, ^3J = 5.5, H–C(8)); 7.18 (*d*, ^3J = 5.5, H–C(9)). ^{13}C-NMR: 30.06 (*Me*$_3$C); 53.47, 53.77 (2 MeO); 56.03 (Me$_3$*C*N); 110.45 (C(5)); 123.94 (C(8)); 126.21 (C(3)); 147.67 (C(4)); 148.07 (C(2)); 149.95 (C(9)); 159.51, 161.47, 168.12 (3 C=O). EI-MS: 365 (5, M^+), 322 (100), 296 (11), 258 (12), 208 (23), 179 (23). Anal. calc. for $C_{15}H_{17}NO_7$ (323.30): C 55.73, H 5.30, N 4.33; found: C 55.6, H 5.4, N 4.2.

*Di(*tert*-butyl) 2-(Cyclohexylimino)-7-oxo-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate* (**4l**). Yield 0.216 g (50%). Dark brown powder. M.p. 144–146°. IR: 1792, 1752, 1731 (C=O), 1649 (C=N). ^{1}H-NMR: 1.40, 1.48 (2*s*, 2 *t*-Bu); 1.69–1.89 (*m*, 5 CH_2); 3.73 (*m*, CHN); 6.38 (*d*, ^3J = 5.5, H–C(8)); 7.18 (*d*, ^3J = 5.5, H–C(9)). ^{13}C-NMR: 27.95, 28.65 (2 *Me*$_3$CO); 25.16, 25.22, 25.72, 32.75, 32.49 (5 CH_2); 57.11 (CHN); 82.57, 84.12 (2 Me$_3$*C*O); 111.14 (C(5)); 123.94 (C(8)); 127.19 (C(3)); 148.70 (C(4)); 150.08 (C(9)); 150.59 (C(2)); 158.59, 160.77, 168.44 (3 C=O). EI-MS: 296 (27), 251 (15), 240 (12), 194 (28), 166 (19), 125 (24), 111 (40), 97 (41), 71 (45), 58 (100). Anal. calc. for $C_{21}H_{31}NO_7$ (433.50): C 63.73, H 7.21, N 3.23; found: C 63.8, H 6.9, N 3.1.

Dimethyl 2-(Cyclohexylimino)-7-oxo-1,6-dioxaspiro[4.4]non-3-ene-3,4-dicarboxylate (**7a**). Yield 0.245 g (70%). Yellow solid. M.p. 115–117°. IR: 1825, 1735, 1687 (C=O), 1630 (C=N).^{1}H-NMR: 1.20–1.91 (*m*, 5 CH_2); 2.56–2.67 (*m*, CH_2(8)); 2.81–2.90 (*m*, CH_2(9)); 3.65 (*m*, CHN); 3.87, 3.89 (2*s*, 2 MeO). ^{13}C-NMR: 24.50, 25.51, 25.54, 32.59, 33.24 (5 CH_2); 33.63, 38.70 (2 CH_2); 50.51, 53.71 (2 MeO); 68.17 (CHN); 109.10 (C(5)); 128.77, 130.90, 132.40 (C(3), C(4), C(2)); 167.77, 170.89, 173.84 (3 C=O). Anal. calc. for $C_{17}H_{21}NO_7$ (351.34): C 58.11, H 6.02, N 3.99; found: C 58.2, H 5.9, N 3.9.

Diethyl 2-(Cyclohexylimino)-7-oxo-1,6-dioxaspiro[4.4]non-3-ene-3,4-dicarboxylate (**7b**). Yield 0.269 g (71%). Dark yellow oil. IR: 1830, 1737, 1685 (C=O), 1634 (C=N). ^{1}H-NMR: 0.98, 1.03 (2*t*, ^3J = 6.9, 2 Me); 1.16–1.85 (*m*, 5 CH_2); 2.41–2.52 (*m*, CH_2(8)); 2.82–2.96 (*m*, CH_2(9)); 3.62 (*m*, CHN); 4.15–4.40 (2*q*, ^3J = 7.0, 2 MeCH_2O). ^{13}C-NMR: 11.16, 14.10 (2 Me); 24.16, 24.28, 25.17, 32.28, 33.39 (5 CH_2); 61.94, 62.68 (2 CH_2O); 59.46 (CHN); 110.06 (C(5)); 124.12, 128.80, 135.94 (C(3), C(4), C(2)); 157.98, 165.18, 170.48 (3 C=O). Anal. calc. for $C_{19}H_{25}NO_7$ (379.40): C 60.15, H 6.64, N 3.69; found: C 60.3, H 6.5, N 3.6.

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