One-Pot Three-Component Synthesis of 2-(Alkylimino)-7-oxo-1-oxa-6-azaspiro[4.4]nona-3,8-diene-3,4-dicarboxylates

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The reactive zwitterionic 1:1 intermediate **6** generated *in situ* from the reaction between an isocyanide **2** and a dialkyl acetylenedicarboxylate (=dialkyl but-2-ynedioate) **3** was trapped by an *N*-arylmaleimide or -phthalimide **4** to produce a highly functionalized 1-oxa-6-azaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate **5** in excellent yield (*Scheme* and *Table*).

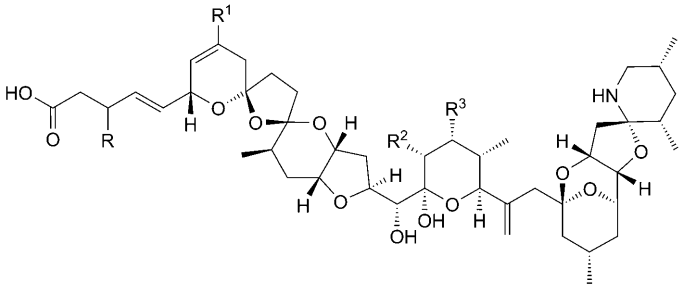
Introduction. – Multicomponent reactions (MCRs) have emerged as an efficient and powerful tool in modern synthetic organic chemistry due to their valued features such as atom economy, straightforward reaction design, and the opportunity to construct target compounds by the introduction of several diverse functions in a single chemical event. Typically, purification of products resulting from MCRs is also simple since all the organic reagents employed are consumed and are incorporated into the target compound [1]. MCRs leading to interesting heterocyclic scaffolds are particularly useful for the construction of diverse chemical libraries of 'drug-like' molecules. The isocyanide-based MCRs are especially important in this area [1g][1h].

Spiro compounds having cyclic structures connected at a C-atom are of interest due to their interesting conformational features and their structural implications on biological systems. The asymmetric character of a molecule due to the stereogenic spiro C-atom is one of the important criteria of the biological activities [2][3]. Spiroaminals represent an important class of naturally occurring spiro compounds characterized by their highly pronounced biological properties [4–7]. For example, azaspiracids **1** are the causative agents of a recently defined class of human poisoning resulting from consumption of tainted shellfish [8].

In the arena of photochromism, spiroaminals, due to their steric constraints, equilibrate with the corresponding non-spiro analogue and exhibit various photochemical phenomena [9]. Some more related applications based on this equilibrium are self-development photography, actinometry, displays, and filters and lenses of variable optical density [10].

The development of new methods for the synthesis of spiroaminals has thus attracted much attention in recent years [11].

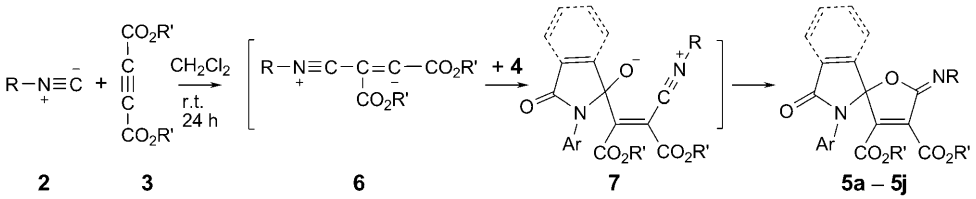
Results and Discussion. – As part of current studies of our group and others on the development of multicomponent reactions of isocyanides and electron-deficient



Azaspiracids **1**

acetylenic compounds for the preparation of biologically active heterocyclic compounds [12][13], we report herein a simple one-pot three-component synthesis of highly functionalized 1-oxa-6-azaspiro[4.4]nona-3,8-dienes using simple starting materials. Thus, a mixture of an isocyanide **2** and a dialkyl acetylenedicarboxylate (= dialkyl but-2-ynedioate) **3** in the presence of a cyclic conjugated imide **4** underwent a smooth 1:1:1 addition reaction in anhydrous CH_2Cl_2 at room temperature to produce. within 24 h, a 2-(alkylimino)-7-oxo-1-oxa-6-azaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate **5** in 85–97% yield (*Scheme* and *Table*).

Scheme[a])

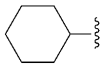
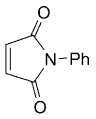
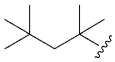
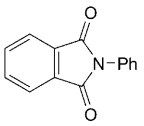
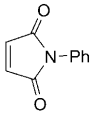
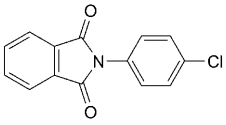
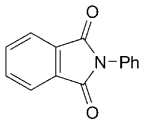
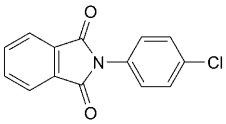
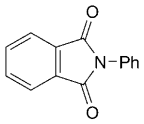
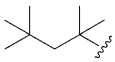
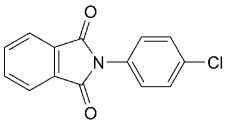
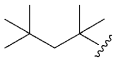
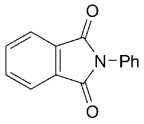
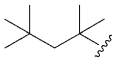
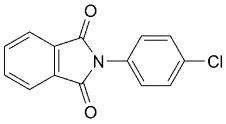


2 **3** **6** **7** **5a – 5j**

[a]) See *Table* for **4**, R and R′.

The structures of the isolated products **5a – 5j** were deduced from their elemental analyses and their IR, ^{1}H- and ^{13}C-NMR, and MS data. The MS of **5a** displayed the molecular-ion (M^+) peak at *m*/*z* 424, which was consistent with the 1:1:1 adduct of cyclohexyl isocyanide, dimethyl acetylenedicarboxylate, and *N*-phenylmaleimide. The ^{1}H-NMR spectrum of **5a** exhibited two sharp *s* for the two MeO groups (δ(H) 3.73 and 3.80), two *d* (δ(H) 6.47 and 6.91 (J = 5.8)) for the two H-atoms of the five-membered aza ring, and characteristic signals with appropriate chemical shifts and coupling constants for eleven cyclohexyl H-atoms and five aromatic H-atoms. The ^{1}H-decoupled ^{13}C-NMR spectrum of **5a** showed 21 distinct signals, in agreement with the proposed structure (see *Exper. Part*). The ^{1}H- and ^{13}C-NMR spectra of the products **5b – 5j** were similar to those of **5a**, except for the 2-(alkylimino) function, the ester groups, and the aza-ring moiety; they all exhibited characteristic signals with appropriate chemical shifts and coupling constants (see *Exper. Part*).

Table. *Reaction of Isocyanides* **2** *with Acetylenedicarboxylates* **3** *and Cyclic Conjugated Imides* **4**[1])

Product	R	R′	**4**	Yield [%]	Product	R	R′	**4**	Yield [%]
5a		Me		93	**5f**		Et		90
5b		Et		85	**5g**		Me		92
5c		Me		94	**5h**		Et		92
5d		Et		91	**5i**		Me		87
5e		Me		90	**5j**		Et		97

[a]) Reaction conditions: In anh. CH_2Cl_2 at r.t. for 24 h.

On the basis of the well-established chemistry of isocyanides [1g][1h][14–17], it is reasonable to assume that the 1-oxa-6-azaspiro[4.4]nona-3,8-diene-3,4-dicarboxylates **5** apparently result from the initial addition of the isocyanides to the acetylenedicarboxylates esters and subsequent nucleophilic attack of the zwitterionic 1:1 intermediates **6** on the C=O group of **4** and formation of the 1:1:1 adducts **7**. The intramolecular addition of the alkoxide to the nitrilium moiety within **7** yields the iminofuran derivatives **5** (*Scheme*).

In summary, we have demonstrated that the one-pot three-component reaction between isocyanides, dialkyl acetylenedicarboxylates, and cyclic conjugated imides provides a simple method for the preparation of 2-(alkylimino)-7-oxo-1-oxa-6-azaspiro[4.4]nona-3,8-diene-3,4-dicarboxylates of potential synthetic and pharmacological interest. Excellent yields of the products, the ready availability of the starting materials, as well as mild reaction conditions and simplicity of the reaction are the main advantages of this method. The present transformation has the additional advantage of being performed under neutral conditions and requiring no activation or modification of the starting materials.

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Experimental Part

General. Dimethyl and diethyl acetylenedicarboxylates, cyclohexyl and 1,1,3,3-tetramethylbutyl isocyanides, as well as imides **4** were obtained from *Merck* (Germany), and were used without further purification. Column chromatography (CC): silica gel *60* (SiO_2; *Merck*). Melting points (M.p.): *Electrothermal-9100* apparatus; uncorrected. IR Spectra: *Shimadzu-IR-460* spectrometer; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-DRX-500-Avance* (at 500.1 and 125.8 MHz, resp.) and *Bruker-DPX-250* (at 250.1 and 62.9 MHz, resp.) instruments; in $CDCl_3$; δ in ppm rel. to Me_4Si (= 0 ppm), *J* in Hz. EI-MS (20 eV): *Agilent-Technologies-(HP)-5973* mass spectrometer; in *m*/*z* (rel. %). Elemental analyses: *Heraeus-CHN-O-Rapid* analyzer.

Preparation of Compounds **5**: *General Procedure.* To a magnetically stirred soln. of **3** (1 mmol) and **4** (1 mmol) in anh. CH_2Cl_2 (6 ml), was added dropwise a soln. of **2** (1 mmol) in anh. CH_2Cl_2 (2 ml) at 25° over 10 min. The mixture was stirred for 24 h. The solvent was evaporated and the residue purified by CC (SiO_2, hexane/AcOEt 3:1) and recrystallization (hexane/AcOEt 1:1).

Dimethyl 2-(Cyclohexylimino)-7-oxo-6-phenyl-1-oxa-6-azaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate (**5a**). Yield 93%. Colorless crystals. M.p. 187–188°. IR (KBr): 1788, 1753, 1732, 1701, 1659 (C=O), 1466, 1420, 1373, 1344, 1317, 1275, 1215, 1090, 1011, 945, 918, 878, 752. ^1H-NMR (500.1 MHz, $CDCl_3$): 1.20–1.74 (*m*, 10 H); 3.65–3.71 (*m*, 1 H); 3.73 (*s*, 3 H); 3.80 (*s*, 3 H); 6.47 (*d*, *J* = 5.8, 1 H); 6.91 (*d*, *J* = 5.8, 1 H); 7.15 (*d*, *J* = 8.0, 2 H); 7.30 (*t*, *J* = 7.0, 1 H); 7.33–7.37 (*m*, 2 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 24.5; 24.6; 25.6; 33.3; 33.4; 52.8; 53.1; 57.1; 101.2; 126.8; 128.1; 129.3; 129.7; 133.8; 137.0; 140.6; 142.7; 151.0; 159.7; 161.2; 168.7. EI-MS: 424 (5, M^+), 373 (100), 289 (45), 169 (75), 92 (24), 77 (20). Anal. calc. for $C_{23}H_{24}N_2O_6$ (424.45): C 65.08, H 5.70, N 6.60; found: C 64.89, H 5.79, N 6.51.

Diethyl 2-(Cyclohexylimino)-7-oxo-6-phenyl-1-oxa-6-azaspiro[4.4]nona-3,8-diene-3,4-dicarboxylate (**5b**). Yield 85%. Colorless crystals. M.p. 96–97°. IR (KBr): 1747, 1718, 1688 (C=O), 1495, 1448, 1377, 1361, 1339, 1271, 1246, 1097, 1026, 951, 829, 762, 716. ^1H-NMR (250.1 MHz, $CDCl_3$): 1.20–1.75 (*m*, 10 H); 1.23, 1.27 (2*t*, *J* = 7.3, 6 H); 3.65–3.76 (*m*, 1 H); 4.19 (*q*, *J* = 7.3, 2 H); 4.28 (*q*, *J* = 7.3, 2 H); 6.47 (*d*, *J* = 6.0, 1 H); 6.93 (*d*, *J* = 6.0, 1 H); 7.15–7.19 (*m*, 2 H); 7.25–7.39 (*m*, 3 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 13.8; 13.9; 24.5; 24.6; 25.7; 33.3; 33.4; 56.9; 62.1; 62.4; 101.3; 126.8; 128.1; 129.3; 129.6; 133.8; 136.9; 140.6; 142.9; 151.2; 159.3; 160.8; 168.8. EI-MS: 452 (7, M^+), 401 (100), 317 (60), 254 (27), 197 (81), 120 (19), 77 (17). Anal. calc. for $C_{25}H_{28}N_2O_6$ (452.51): C 66.36, H 6.24, N 6.19; found: C 66.22, H 6.30, N 6.03.

*Dimethyl 5-(Cyclohexylimino)-2′,3′-dihydro-3′-oxo-2′-phenylspiro[furan-2(5*H*),1′-[1*H*]isoindole]-3,4-dicarboxylate* (**5c**). Yield. 94%. Colorless crystals. M.p. 155–156°. IR (KBr): 1755, 1728, 1690, 1655 (C=O), 1492, 1436, 1350, 1284, 1261, 1174, 1039, 970, 883, 746, 702. ^1H-NMR (250.1 MHz, $CDCl_3$): 1.24–1.75 (*m*, 10 H); 3.60 (*s*, 3 H); 3.61–3.65 (*m*, 1 H); 3.84 (*s*, 3 H); 7.25 (*dd*, *J* = 7.9, 1.4, 2 H); 7.35–7.44 (*m*, 4 H); 7.62–7.67 (*m*, 2 H); 7.96–8.02 (*m*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 24.5; 24.6; 25.6; 33.2; 33.4; 52.8; 53.2; 57.1; 100.1; 122.0; 124.4; 127.4; 128.5; 129.4; 131.0; 131.2; 133.3; 134.0; 137.7; 140.0; 140.5; 151.5; 159.7; 161.3; 166.9. EI-MS: 474 (29, M^+), 442 (38), 392 (67), 377 (65), 317 (81), 301 (100), 290 (54), 231 (83), 202 (70), 163 (48), 69 (48), 55 (74). Anal. calc. for $C_{27}H_{26}N_2O_6$ (474.51): C 68.34, H 5.52, N 5.90; found: C 68.19, H 5.61, N 5.82.

*Diethyl 5-(Cyclohexylimino)-2′,3′-dihydro-3′-oxo-2′-phenylspiro[furan-2(5*H*),1′-[1*H*]isoindole]-3,4-dicarboxylate* (**5d**). Yield 91%. Colorless crystals. M.p. 124°. IR (KBr): 1794, 1736, 1728, 1688, 1663 (C=O), 1495, 1466, 1356, 1277, 1215, 1178, 1115, 1039, 999, 758, 702. ^1H-NMR (250.1 MHz, $CDCl_3$): 1.02 (*t*, *J* = 7.0, 3 H); 1.22–1.75 (*t*, *J* = 7.0, 3 H, and *m*, 10 H); 3.67–3.69 (*m*, 1 H); 3.95–4.15 (2*dq*, ^2J = 11.0, ^3J = 7.0, 2 H); 4.30 (*q*, *J* = 7.0, 2 H); 7.25 (*dd*, *J* = 7.9, 1.5, 2 H); 7.34–7.45 (*m*, 4 H); 7.55–7.77 (*m*, 2 H); 7.96–8.00 (*m*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 13.6; 13.9; 24.5; 24.5; 25.6; 33.2; 33.4; 57.0; 61.8; 62.4; 100.0; 122.0; 124.3; 127.4; 128.4; 129.4; 130.9; 131.3; 133.2; 134.1; 137.8; 140.5; 141.1; 151.6; 159.2; 160.9; 166.9. EI-MS: 502 (15, M^+), 456 (22), 421 (30), 405 (34), 376 (15), 331 (35), 302 (100), 276 (18), 231 (35), 202 (49), 149 (24), 55 (18). Anal. calc. for $C_{29}H_{30}N_2O_6$ (502.57): C 69.31, H 6.02, N 5.57; found: C 69.17, H 6.16, N 5.44.

*Dimethyl 2′,3′-Dihydro-3′-oxo-2′-phenyl-5-[(1,1,3,3-tetramethylbutyl)imino]spiro[furan-2(5*H*),1′-[1*H*]isoindole]-3,4-dicarboxylate* (**5e**). Yield 90%. Colorless crystals. M.p. 146–147°. IR (KBr): 1749, 1730, 1724, 1684 (C=O), 1497, 1437, 1354, 1279, 1257, 1173, 1034, 974, 914, 773, 690. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 0.96 (*s*, 9 H); 1.30 (*s*, 3 H); 1.35 (*s*, 3 H); 1.52 (*d*, ^2J = 14.5, 1 H); 1.63 (*d*, ^2J = 14.5, 1 H); 3.60 (*s*, 3 H); 3.81 (*s*, 3 H); 7.28 (*dd*, *J* = 7.9, 1.5, 2 H); 7.35–7.45 (*m*, 4 H); 7.59–7.68 (*m*, 2 H); 7.96–8.02 (*m*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 29.6; 29.8; 31.6; 31.9; 52.7; 52.9; 55.5; 58.9; 100.6; 121.7; 124.4; 127.5; 128.4; 129.4; 130.9; 131.1; 133.2; 134.1; 135.9; 141.2; 142.2; 148.1; 159.7; 161.6; 167.0. EI-MS: 504 (7, M^+), 433 (21), 401 (32), 377 (61), 342 (42), 317 (37), 281 (36), 149 (35), 97 (37), 57 (100). Anal. calc. for $C_{29}H_{32}N_2O_6$ (504.58): C 69.03, H 6.39, N 5.55; found: C 68.83, H 6.47, N 5.40.

*Diethyl 2′,3′-Dihydro-3′-oxo-2′-phenyl-5-[(1,1,3,3-tetramethylbutyl)imino]spiro[furan-2(5*H*),1′-[1*H*]isoindole]-3,4-dicarboxylate* (**5f**). Yield 90%. Colorless crystals. M.p. 116–117°. IR (KBr): 1743, 1736, 1685 (C=O), 1497, 1466, 1355, 1335, 1273, 1213, 1174, 1036, 928, 903, 773, 702. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 0.96 (*s*, 9 H); 1.02 (*t*, *J* = 7.3, 3 H); 1.28 (*t*, *J* = 7.3, 3 H); 1.31 (*s*, 3 H); 1.35 (*s*, 3 H); 1.53 (*d*, ^2J = 14.5, 1 H); 1.64 (*d*, ^2J = 14.5, 1 H); 4.03 (*q*, *J* = 7.3, 2 H); 4.28 (*q*, *J* = 7.3, 2 H); 7.28 (*dd*, *J* = 8.0, 1.5, 2 H); 7.33–7.42 (*m*, 4 H); 7.56–7.69 (*m*, 2 H); 7.96–8.00 (*m*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 12.6; 12.9; 28.7; 28.8; 30.5; 30.9; 54.5; 57.8; 60.7; 61.1; 99.5; 120.8; 123.2; 126.5; 127.3; 128.3; 129.8; 130.2; 132.1; 133.1; 135.0; 140.4; 141.3; 147.2; 158.2; 160.2; 165.9. EI-MS: 532 (9, M^+), 517 (9), 461 (32), 405 (100), 342 (89), 304 (58), 276 (51), 231 (46), 202 (70), 149 (33), 57 (58). Anal. calc. for $C_{31}H_{36}N_2O_6$ (532.64): C 69.91, H 6.81, N 5.26; found: C 69.73, H 6.85, N 5.11.

*Dimethyl 2′-(4-Chlorophenyl)-5-(cyclohexylimino)-2′,3′-dihydro-3′-oxospiro[furan-2(5*H*),1′-[1*H*]isoindole]-3,4-dicarboxylate* (**5g**). Yield 92%. Colorless crystals. M.p. 209–210°. IR (KBr): 1753, 1730, 1683, 1655 (C=O), 1497, 1437, 1362, 1280, 1039, 972, 746. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 1.22–1.74 (*m*, 10 H); 3.60 (*s*, 3 H); 3.62–3.69 (*m*, 1 H); 3.86 (*s*, 3 H); 7.21 (*d*, *J* = 8.8, 2 H); 7.39 (*d*, *J* = 8.8, 2 H); 7.35–7.43 (*m*, 1 H); 7.60–7.70 (*m*, 2 H); 7.95–8.01 (*m*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 24.5; 24.6; 25.6; 33.2; 33.5; 52.9; 53.2; 57.2; 100.0; 122.0; 124.5; 128.5; 129.7; 130.8; 131.1; 132.7; 133.5; 134.2; 137.4; 140.5; 140.8; 151.2; 159.6; 161.2; 166.8. EI-MS: 510 (13, M^+ (^{37}Cl)), 508 (39, M^+ (^{35}Cl)), 476 (20), 426 (62), 411 (82), 351 (65), 335 (100), 324 (40), 302 (68), 265 (43), 236 (54), 163 (80), 55 (40). Anal. calc. for $C_{27}H_{25}ClN_2O_6$ (508.96): C 63.72, H 4.95, N 5.50; found: C 63.66, H 5.03, N 5.37.

*Diethyl 2′-(4-Chlorophenyl)-5-(cyclohexylimino)-2′,3′-dihydro-3′-oxospiro[furan-2(5*H*),1′-[1*H*]isoindole]-3,4-dicarboxylate* (**5h**). Yield 92%. Colorless crystals. M.p. 170°. IR (KBr): 1747, 1736, 1724, 1688 (C=O), 1493, 1466, 1356, 1296, 1273, 1178, 1078, 1039, 968, 904, 854, 721. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 1.03 (*t*, *J* = 7.3, 3 H); 1.18–1.76 (*t*, *J* = 7.3, 3 H, and *m*, 10 H); 3.60–3.74 (*m*, 1 H); 3.94–4.10 (2*dq*, ^2J = 11.0, ^3J = 7.3, 2 H); 4.32 (*q*, *J* = 7.3, 2 H); 7.22 (*d*, *J* = 8.8, 2 H); 7.38 (*d*, *J* = 8.8, 2 H); 7.41–7.45 (*m*, 1 H); 7.59–7.71 (*m*, 2 H); 7.93–7.99 (*m*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 13.6; 14.0; 24.4; 24.5; 25.6; 33.2; 33.5; 57.0; 62.0; 62.5; 100.0; 122.1; 124.3; 128.6; 129.6; 131.0; 131.0; 132.8; 133.4; 134.1; 137.5; 140.6; 140.9; 151.3; 159.1; 160.7; 166.8. EI-MS: 539 (3, M^+ (^{37}Cl)), 537 (9, M^+ (^{35}Cl)), 454 (44), 439 (78), 365 (46), 335 (100), 236 (47), 202 (32), 149 (32). Anal. calc. for $C_{29}H_{29}ClN_2O_6$ (537.01): C 64.86, H 5.44, N 5.22; found: C 64.78, H 5.36, N 5.19.

*Dimethyl 2′-(4-Chlorophenyl)-2′,3′-dihydro-3′-oxo-5-[(1,1,3,3-tetramethylbutyl)imino]spiro[furan-2(5*H*),1′-[1*H*]isoindole]-3,4-dicarboxylate* (**5i**). Yield 87%. Colorless crystals. M.p. 164°. IR (KBr): 1732, 1691 (C=O), 1495, 1468, 1439, 1354, 1259, 1215, 1092, 1036, 974, 816, 791. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 0.97 (*s*, 9 H); 1.31 (*s*, 3 H); 1.36 (*s*, 3 H); 1.52 (*d*, ^2J = 14.5, 1 H); 1.64 (*d*, ^2J = 14.5, 1 H); 3.60 (*s*, 3 H); 3.84 (*s*, 3 H); 7.23 (*d*, *J* = 8.8, 2 H); 7.38 (*d*, *J* = 8.8, 2 H); 7.38–7.41 (*m*, 1 H); 7.60–7.68 (*m*, 2 H); 7.95–7.99 (*m*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 29.6; 29.8; 31.6; 31.9; 52.8; 53.0; 55.5; 59.0; 100.5; 121.8; 124.5; 128.6; 129.6; 130.8; 131.0; 132.8; 133.4; 134.1; 135.5; 141.1; 142.3; 147.8; 159.6; 161.2; 167.0. EI-MS: 541 (< 1, M^+ (^{37}Cl)), 539 (4, M^+ (^{35}Cl)), 435 (11), 411 (16), 281 (49), 84 (37), 57 (100), 43 (53). Anal. calc. for $C_{29}H_{31}ClN_2O_6$ (539.03): C 64.62, H 5.80, N 5.20; found: C 64.57, H 5.76, N 5.09.

*Diethyl 2′-(4-Chlorophenyl)-2′,3′-dihydro-3′-oxo-5-[(1,1,3,3-tetramethylbutyl)imino]spiro[furan-2(5*H*),1′-[1*H*]isoindole]-3,4-dicarboxylate* (**5j**). Yield 97%. Colorless crystals. M.p. 118–119°. IR (KBr): 1733, 1682, 1657 (C=O), 1607, 1493, 1466, 1396, 1362, 1336, 1257, 1213, 1178, 1086, 1036, 903, 854, 820, 746, 688. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 0.96 (*s*, 9 H); 1.03 (*t*, *J* = 7.3, 3 H); 1.30 (*t*, *J* = 7.3, 3 H); 1.31 (*s*, 3 H); 1.35 (*s*, 3 H); 1.52 (*d*, ^2J = 14.5, 1 H); 1.65 (*d*, ^2J = 14.5, 1 H); 3.94–4.13 (2 *dq*, ^2J = 11.0, ^3J = 7.3, 2 H); 4.30 (*q*, *J* = 7.3, 2 H); 7.24 (*d*, *J* = 8.8, 2 H); 7.38 (*d*, *J* = 8.8, 2 H); 7.38–7.42 (*m*, 1 H); 7.58–7.70 (*m*,

2 H); 7.95 – 7.99 (*m*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 13.6; 14.0; 29.8; 29.9; 31.7; 31.9; 55.5; 58.9; 61.9; 62.3; 100.5; 121.8; 124.3; 128.7; 129.6; 130.9; 130.9; 132.9; 133.4; 134.0; 135.8; 141.4; 142.4; 148.0; 159.2; 161.1; 166.9. EI-MS: 569 (< 1, M^+ (^{37}Cl)), 567 (2, M^+ (^{35}Cl)), 495 (32), 439 (72), 376 (57), 338 (36), 296 (38), 194 (53), 57 (100). Anal. calc. for $C_{31}H_{35}ClN_2O_6$ (567.08): C 65.66, H 6.22, N 4.94; found: C 65.48, H 6.36, N 4.88.

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