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Short and efficient synthesis of 2*H*-pyrroles from 7-oxanorbornadiene derivatives

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ABSTRACT

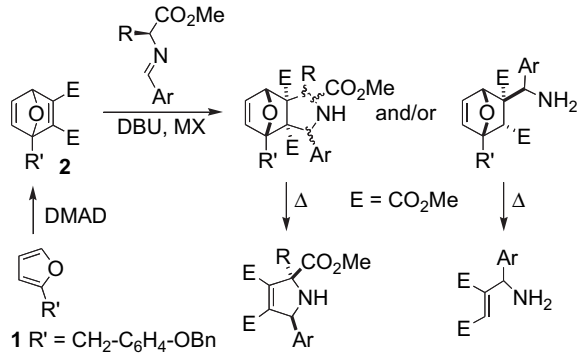
A microwave-assisted tandem [3+2] cycloaddition/retro-Diels–Alder reaction of azomethine ylides derived from imines of α-amino esters to dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate derivatives is described. The procedure delivers, in a short reaction time, pyrrolines in high yields. In a such sequence, the oxanorbornadiene derivatives behave as masked forms of dimethyl acetylenedicarboxylate. Subsequent oxidation of the synthesized 3-pyrrolines with DDQ affords 2*H*-pyrroles with yields in the 76–88% range. If this three-step sequence is run on the non-substituted 7-oxabicycloheptadienedicarboxylate, purification of the intermediate 3-pyrrolines is avoided to afford 2*H*-pyrroles in less than 2 h.

1. Introduction

2*H*-Pyrroles are interesting intermediates to prepare various types of heterocyclic compounds.[1,2] For example, the Battersby's group has reported a very intensive work where 2*H*-pyrroles were used to access to porphyrins in order to sustain a proposed biogenetic synthetic way.[3,4] Even if the first synthesis of a 2*H*-pyrrole (the pentachloro derivative) was reported in 1897,[5–7] few methods allow an efficient preparation of these compounds. The alkylation of magnesium derivatives of 2,5-disubstituted pyrroles,[8,9] the addition of nitrile ylides with vinylphosphonium derivatives,[9] vinylsulfones[10] or acetylenic compounds,[11] the base-induced addition of ketones to 2*H*-azirines,[12,13] and the cyclization of 1,4-diones in the presence of ammonium acetate and acetic acid[14] were found among the methods that should be generalized. When an hydrogen atom is present on the carbon 2, tautomerization occurs and a 1*H*-pyrrole is isolated, but recently was described the isolation of a boron complex of the parent unsubstituted 2*H*-pyrrole.[15,16] 2*H*-Pyrroles were also easily obtained by reaction of acetylenic compounds with 3-aza-1-metalla-1,3-dienes,[17,18] or by cyclization of 5-aza-1-metalla-1,3,5-trienes.[19]

Among the class of 2*H*-pyrroles, compounds with ester groups on the 3 and 4 positions[20] could be prepared by reactions of dimethyl acetylenedicarboxylate with nitrile ylides[11a,c,d,21] or from 3-aza-1-metalla-1,3-dienes.[18a,b] Recently, formation of some 2*H*-pyrroles unsubstituted in the 5 position was reported from 5-[2-(*N*,*N*-dimethylamino)-4-oxo-4*H*-pyrido[1,2-*a*]pyrimidin-3-yl]-3-pyrrolines. Cleavage of the C–C bond between the pyrroline core and the heterocyclic substituent occurred easily by heating with elimination of the pyrrolinic nitrogen proton.[22] Our strategy is based on oxidation of 3-pyrrolines.

Recently, we have reported the preparation of some 3-pyrrolines by metal salt/base-catalyzed cycloadditions of azomethine ylides generated from *N*-arylidene-α-amino esters with a dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate derivative **2** and a subsequent thermal retro-Diels–Alder reaction. The oxabicycloheptadienic dicarboxylate **2**, prepared by reaction of dimethyl acetylenedicarboxylate (DMAD) with a furanic compound **1**, appears like a masked form of the acetylenic reagent (Scheme 1).[23]



Scheme 1. From Refs. 23 and 24.

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Whatever the salt used to catalyze the cycloaddition (silver acetate or lithium bromide), the scope of the reaction was limited. The expected cycloadducts or the resulting 3-pyrrolines were not detected in the reactions with the valine or the phenylglycine derivatives. Moreover, in the presence of lithium bromide, the cycloaddition of phenylglycinate or leucinate derivatives yielded, exclusively or as a secondary product, primary benzylamines resulting from an unusual Michael addition of the Cγ-atom of the lithiated azomethine ylides.[24]

Until now, some 7-oxabicyclo[2.2.1]hepta-2,5-diene derivatives have been used with various nucleophiles,[25] organic azides, and nitrile oxides[26] to allow the preparation of ethylenic and heterocyclic compounds. We emphasize the usefulness of such 7-oxanorbornadienes derivatives as masked forms of acetylenic partners.

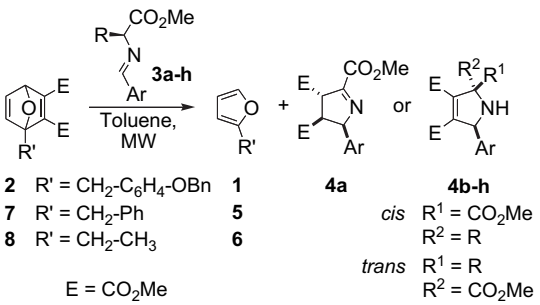
We herein report a more general and efficient method to prepare 3-pyrrolines by a microwave-assisted tandem [3+2] cycloaddition/retro-Diels–Alder reaction based on oxanorbornadiene derivatives type **2** and iminoesters. Facile oxidation of these heterocycles into 2*H*-pyrroles is also described.

2. Results and discussion

2.1. Preparation of 3-pyrrolines

Microwave(MW)-assisted [3+2] cycloadditions of azomethine ylides were already reported.[27,28] By comparison with the thermal conditions (oil bath), the MW-assisted reactions show generally a large decrease of the reaction time and frequently an increase of the yields.

The [3+2] cycloadditions of the maleate-like dipolarophile **2** with the azomethine ylides obtained by 1,2-prototropy in the *N*-benzylidene amino esters **3a**–**h** were run in closed vessels with a monomode microwave oven. Generally, toluenic solutions of equimolar amounts of the maleate **2** and the iminoester **3a**–**h** were irradiated (maximum power 300 W) in order to reach 180 °C. Under these conditions, the target was hit after 2 min and the internal pressure reached 4–4.5 bar. After 16 min, excepted for the valine derivative **3d**, quasi-complete conversions were noticed. Interestingly, ^{1}H NMR spectra of the reaction mixtures showed mainly the presence of the furan derivative **1** and a pyrroline **4** (Scheme 2). The reaction conditions brought about the retro-Diels–Alder reaction of the [3+2] cycloadducts. In the case of the valinate derivative **3d** under the previous conditions, incomplete reaction was observed. An increase of both the temperature (210 °C, xylene was used at the place of toluene) and of the reaction time (20 min) allowed the complete conversion but various unidentified products were obtained in addition to furan **1** and pyrroline **4d**. Table 1 reports the yields of the easily separated products and, for comparison, yields noted by Grigg et al. for the synthesis of pyrrolines from DMAD and azomethine ylides.[29] In this direct method, various by-products arose from the intermediates formed by the Michael addition of the 3-pyrroline to the acetylenic partner.[29] Generally, our tandem [3+2] cycloaddition/retro-Diels–Alder reaction sequence delivers, in a short time, 3-pyrrolines with yields in the 76–89% range. It is noteworthy that, in few cases, a decrease of the reaction rates was noticed mainly with new reactor vessels or freshly distilled imines. These could be restored by introduction of some additives[30] (tributylammonium chloride, water) or by previous washing of the vessel with successively a 1 M NaOH aqueous solution and water.



Scheme 2. Microwave-assisted synthesis of pyrrolines **4**.

Table 1
Reaction of maleate adducts **2**, **7** or **8** with imines **3a**–**h** under microwave irradiation[a]

Imine			Maleate adduct	Furan	Pyrroline **4**[b]	
	R	Ar		Yield[c] [%]	Yield[c] [%]	lit.[d] Yield [%]
3a	H	Ph	**2**	**1** 73	71[e]	—
3b	Me	Ph	**2**	**1** 85	85	[g]
3c	Ph	Ph	**2**	**1** 88	82	53
3d[f]	i-Pr	Ph	**2**	**1** 63	39	34
3e	i-Bu	Ph	**2**	**1** 90	89	—
3e	i-Bu	Ph	**7**	**5** —	84	—
3e	i-Bu	Ph	**8**	**6** —	80	—
3f	4-BzO–C_6H_4–CH_2	Ph	**2**	**1** 87	86	—
3g	Ph	4-MeO–C_6H_4	**2**	**1** 83	81	16
3h	Ph	4-Br–C_6H_4	**2**	**1** 80	76	—

[a] Reactions were carried out in toluene during 16 min (maximum power: 300 W, maximum temperature: 180 °C).
[b] Generally, a 3-pyrroline was obtained.
[c] Isolated yields after silica gel column chromatography.
[d] See Ref. 29.
[e] A 1-pyrroline was isolated.
[f] Reaction was carried out in xylene during 20 min (maximum power: 300 W, maximum temperature: 210 °C).
[g] Contrary to the claim, compound **4b** was not obtained (see Ref. 23).

With the glycinate derivative **3a**, 1-pyrroline **4a** resulting from a double bond migration in the initially formed 3-pyrroline was obtained. This 1-pyrroline **4a** showed the two methoxycarbonyl groups and the phenyl in successively *trans* and *cis* relationships.[23] Reaction of the valinate derivative **3d** gave the pyrroline **4d** in a lower yield because degradation does occur at the high temperature required to increase the rate of the [3+2] cycloaddition. The microwave-assisted reaction with the imine **3c**, delivered a 70/30 mixture of the *cis*-pyrroline **4c** and another product. The pure solid *cis*-**4c**[29] was easily isolated after trituration in diethyl ether of this separated mixture. A pure sample of the unexpected product was also obtained by preparative silica gel thin layer chromatography, and its spectroscopic data were in agreement with a *trans*-3-pyrroline. In particular, ^{1}H NMR spectrum of the *trans*-**4c** shows a singlet attributed to the proton linked to the carbon 5 of the pyrrolinic core at a lower field (5.49 ppm) than that of the major *cis*-isomer (5.37 ppm). Colorless single crystals of *trans*-**4c** suitable for X-ray analysis were obtained. An X-ray diffraction study of this crystalline compound supports unambiguously our proposed structure (Fig. 1).[31]

From imine **3g** and **3h**, similar 65/35 and 70/30 mixtures, respectively, of the *cis*- and *trans*-stereoisomers **4g** and **4h** were obtained. These stereoisomers were separated in order to confirm their structures. From imines **3b** and **3d**–**f**, ^{1}H NMR spectra of the reaction mixtures obtained after irradiation show, in addition to the signal of the *cis*-3-pyrroline **4**,[23,24] a minor signal (≤10%) at a lower field, which could be attributed to the *trans*-stereoisomer. The formation of *trans*-stereoisomers was probably due to a partial stereomutation of the azomethine ylides.[32] The isolated *cis*-3-pyrroline **4c** remained unchanged after microwave-assisted heating at 180 °C in the same reaction conditions than previously, in the

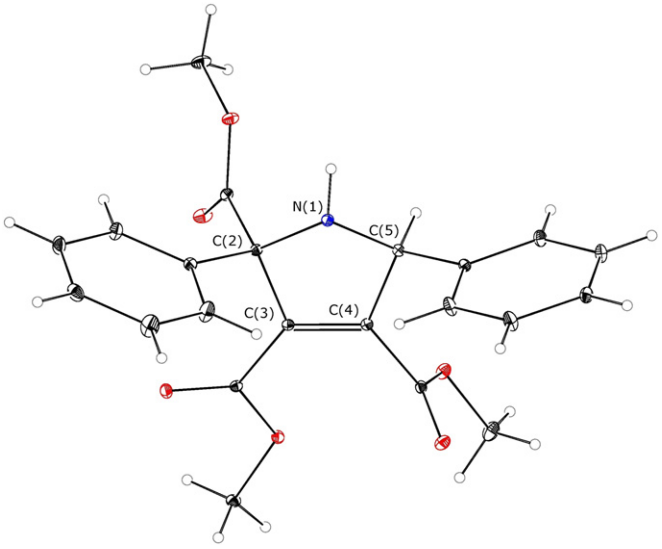


Fig. 1. ORTEP[31] drawing of *trans*-pyrroline **4c** with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level.

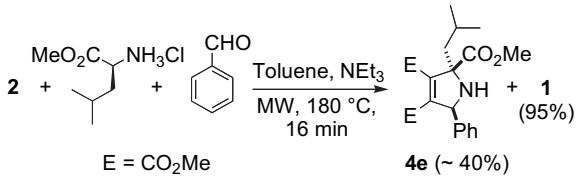
absence or presence of 0.2 equiv of imine **3c**. Substantial dipole stereomutation was reported in the case of phenylglycinate derivatives.[33]

Results of these MW-assisted reactions were better than those obtained with classical heating. For example, heating during 16 min a toluenic solution of phenylglycinate derivative **3c** and maleate **2**, with an oil bath at 180 °C, in the same reaction vessel than that used in the microwave oven gave the pyrroline **4c** (*cis*/*trans*=71/29) and the furan **1** in, respectively, 53 and 55% yield. Similar yields (55%) were obtained when this reaction was run with an oil bath at 150 °C during 1.5 h. Complete conversion of the reactants was observed after 15 h at 150 °C (in a vacuum-sealed bulb), but thin layer chromatography and ^{1}H NMR spectrum of the reaction mixture showed the presence the furan **1** (isolated in 95% yield) and various unidentified products. Clearly the pyrroline **4c** was degradated under these reaction conditions. Some attempts were also made to prepare the pyrroline **4d** by heating mixtures of the valinate derivative **3d** and maleate **2** with an oil bath. The furan **1** could be isolated from the reaction mixtures (yields were, respectively, 20 and 70% after 63 h at 100 °C or 15 h at 150 °C) but pyrroline **4d** was completely degradated.

Microwave-assisted reactions of the leucinate derivative **3e** in toluene (180 °C, 16 min) with 7-oxanorbornadiene derivatives **7** and **8**,[34] easily accessible from 2-benzylfuran **5**[35] or commercially available 2-ethylfuran **6**, delivered also the pyrroline **4e** in 84 and 80% yield, respectively (Scheme 2, Table 1).

A three-component reaction was also attempted since formation of azomethine ylides by heating a mixture of an aminoester and an aromatic aldehyde is well-established in the literature.[27d,36] ^{1}H NMR spectrum of the crude mixture obtained after reaction, under our standard MW-assisted conditions, of an equimolar mixture of benzaldehyde, methyl leucinate hydrochloride, triethylamine and the maleate derivative **2** showed the complete conversion of the Diels–Alder adduct **2** and the presence of furan **1** and pyrroline **4e** in the ratio 1/0.35. Thin layer chromatography of the reaction mixture showed various unidentified products with R_f values close to that of the pyrroline **4e**. So, impure pyrroline **4e** (~40% yield, Scheme 3) was isolated.

The high molar amount of furan **1** compared to pyrroline **4e** could be explained by the instability of the Diels–Alder adduct **2** in the reaction conditions. Indeed, microwave-assisted heating at 180 °C of a toluenic solution of adduct **2** gave, after 16 min, a 33/67 mixture of adduct **2** and furan **1**. For the reactions reported in Table 1, with the benzylidene derivatives **3** previously prepared and



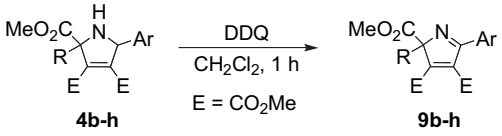
Scheme 3. Domino synthesis of pyrroline **4e**: imine formation, [3+2] cycloaddition and retro-Diels–Alder reaction.

isolated, this side-reaction seemed to be less important (generally, close to equimolar amounts of furan **1** and of pyrroline **4** were present in the crude reaction mixtures). Moreover, treatment of an equimolar mixture of imine **3e** and DMAD in our standard MW-assisted conditions afforded a 10/90 mixture of pyrroline **4e** and **3e**. So, from the maleate derivative **2** and the iminoesters **3**, formation of pyrroline **4** via the DMAD[29] obtained by retro-Diels–Alder reaction should be of little importance.

2.2. Synthesis of 2*H*-pyrroles

Various groups have reported the formation of 1*H*-pyrroles by oxidation of 3-pyrrolines bearing hydrogen atoms at carbons 2 and 5 with, for example, MnO_2,[37] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[38] or *o*-iodoxybenzoic acid (IBX).[39] Oxidation of 2,2-disubstituted 3-pyrrolines with tetrapropylammonium perruthenate (TPAP) in the presence of *N*-methylmorpholine *N*-oxide (NMO) gave 2*H*-pyrroles.[40] In some cases, 2,2,4,5-tetrasubstituted pyrrolines obtained from methyl propiolate and azomethine ylides proved to be difficult to purify and these were characterized after oxidation with DDQ. Formation of 2*H*-pyrroles was suspected but the isolated 1*H*-pyrroles should result from migration of an ester group from the carbon 2 to the carbon 3.[29]

Treatment of the mixtures of *cis*- and *trans*-3-pyrrolines **4b–h** with DDQ (1.2 equiv) in dichloromethane at room temperature allowed the facile formation of the unknown 2*H*-pyrroles **9b–h** with yields in the 76–88% range after separation from the by-products by silica gel chromatography (Scheme 4, Table 2).



Scheme 4. Preparation of 2*H*-pyrroles **9** by oxidation of 3-pyrrolines **4**.

Table 2
Synthesis of 2*H*-pyrroles **9** from purified or unpurified pyrrolines **4**[a]

	R	Ar	From purified pyrroline **4**		From adduct **10**[b]
			Yield [%][c]	Overall yield [%][d]	Overall yield [%][e]
9b	Me	Ph	83	71	—
9c	Ph	Ph	87	71	—
9d[f]	i-Pr	Ph	76	30	—
9e	i-Bu	Ph	86	77	75
9f	4-BzO–C_6H_4–CH_2	Ph	88	76	80
9g	Ph	4-MeO–C_6H_4	88	71	—
9h	Ph	4-Br–C_6H_4	81	61	81
9i	Ph	4-CN–C_6H_4	—	—	61

[a] Unless otherwise noted, oxidations were carried out in dichloromethane during 1 h with 1.2 equiv of DDQ at room temperature.
[b] Crude pyrrolines **4** were obtained by reaction of Diels–Alder adduct **10** with imines **3** under microwaves (see text and Table 1 for the conditions).
[c] Isolated yields after silica gel column chromatography from purified pyrrolines **4**.
[d] Overall yields calculated from Diels–Alder adduct **2**.
[e] Overall yields after silica gel column chromatography from Diels–Alder adduct **10**.
[f] Oxidation was carried out in dichloromethane during 3 h with 2 equiv of DDQ.

The presence of a tetrasubstituted carbon signal between 85 and 92 ppm in the ^{13}C NMR spectra of 2*H*-pyrroles **9** was in agreement with the attributed structure. An X-ray diffraction study of the crystalline compound **9c** supports unambiguously our proposed structure (Fig. 2).[41] Comparison of the structures of compounds *trans*-**4c** and **9c** shows in the former a N(1)–C(5) bond length of 1.4699 Å, which is 1.2945 Å in the oxidized product.

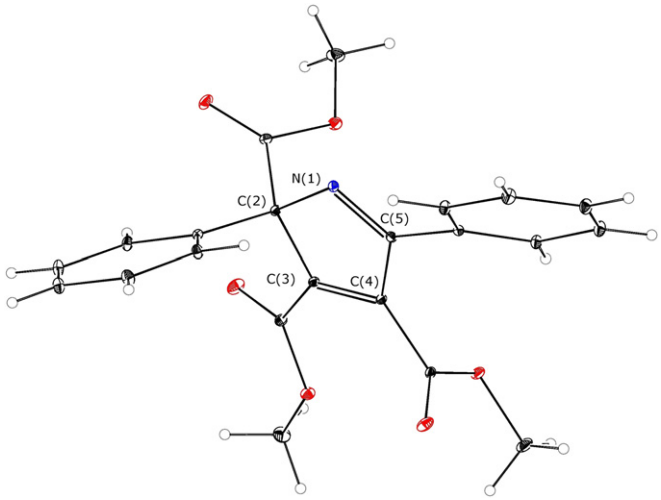
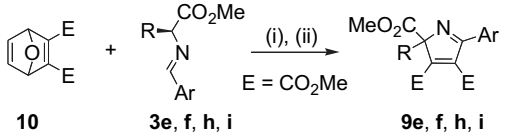


Fig. 2. ORTEP[41] drawing of 2*H*-pyrrole **9c** with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level.

Various attempts to transform the pyrroline **4b** into the 2*H*-pyrrole **9b** by action of MnO_2 were completely unsuccessful whatever the solvent (toluene or dichloromethane), the temperature (20 °C or reflux) and the amount of oxidant.

In order to obtain a more efficient method to prepare 2*H*-pyrroles **9**, we decided to avoid the purification step of the intermediate pyrrolines **4**. We choose the unsubstituted dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate **10**[42] with the purpose to liberate the volatile furan in the retro-Diels–Alder reaction of the intermediate [2+3] cycloadducts (Scheme 5).



Scheme 5. Preparation of 2*H*-pyrroles **9** without purification of the intermediates. Reagents and conditions: (i) Toluene, MW, 300 W, 180 °C, 16 min; (ii) DDQ, CH_2Cl_2, rt, 1 h.

After microwave-assisted reactions of the oxanorbornadiene **10** with the imines **3e**, **3f** and the bromo- and cyano-phenyl derivatives **3h** and **3i** in our standard MW-assisted conditions, oxidation with DDQ was run in dichloromethane (1 h) after evaporation of toluene and the extruded furan. After the first part of the procedure with the cyanophenyl derivative **3i**, ^1H NMR spectrum of the crude reaction mixture showed signals at 5.46 and 5.54 ppm in the ratio 62/38, attributed, respectively, to the *cis*- and the *trans*-pyrrolines **4i** (for the brominated pyrrolines **4h**, the corresponding signals appear at 5.35 and 5.45 ppm with a 64/36 ratio). The unusual higher internal pressure (6.5 bar) noticed in the reaction vessel with this cyanophenyl imine **3i** is an indication of intensive decomposition. After oxidation and column chromatography, the 2*H*-pyrroles **9e**, **f**, **h** and **i** were isolated with overall yields in the 61–81% range for this three-step sequence with a single purification process (Scheme 5, Table 2).

Oxidation of the intermediate pyrroline **4i** in toluene appeared much slower than the reaction in dichloromethane and the entire sequence was less time-consuming with a change of solvent.

Comparison of these three-step sequences with or without purification of the intermediate pyrrolines **4** shows the uselessness of such purification since any by-product of the one-pot two-step tandem reaction was prejudicial to the final chromatography and similar overall yields were obtained.

3. Conclusion

In conclusion, we described a new sequence to prepare 3-pyrrolines in good yields by [3+2] cycloaddition of dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate derivatives with azomethine ylides obtained by 1,2-prototropy in *N*-arylidene-α-amino esters followed by a retro-Diels–Alder reaction. Under microwave activation, these two steps occur simultaneously and transformations were over in less than 20 min. Efficiency of this two-step sequence underlined the synthetic interest of the masked forms of the acetylenic partner. Moreover, oxidation of the 3-pyrrolines with DDQ allowed generally the preparation of 2*H*-pyrroles in good yields in 1 h.

Molecular diversity in 3-pyrrolines and 2*H*-pyrroles should be theoretically increased by the use of acetylenic compounds bearing two different electron-withdrawing groups. Diels–Alder reactions between furan and/or mono-substituted furans with such acetylenic dienophiles is poorly described in the literature. Study of the regioselectivity in the [4+2] and/or [3+2] cycloadditions is under current investigation.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were recorded on Bruker AC250 (250 and 62.9 MHz, respectively), Bruker DRX300 (300 and 75.5 MHz, respectively), Bruker AM360 (360 and 90.6 MHz, respectively) or Bruker DRX400 (400 and 100.6 MHz, respectively) spectrometers. Chemical shifts (δ) are given in parts per million using solvent ($CDCl_3$) signals as internal standards ($CHCl_3$ δ=7.27 ppm; $CDCl_3$ δ=77.14 ppm). Assignments were aided by JMOD pulse sequences and heteronuclear two-dimensional experiments (HSQC, HMBC). Positive electrospray (ES^+) mass spectra (MS) and high resolution mass spectra (HRMS) were recorded with a Finnigan MAT 95S spectrometer or a Waters-Micromass spectrometer (Gif-sur-Yvette, France). Positive chemical ionization (CI^+) mass spectrum was recorded with a Thermo Scientific DSQ spectrometer. Infrared (IR) spectra were recorded using an FT-IR Perkin–Elmer spectrophotometer (Spectrum One). Elemental analyses were performed by the Microanalysis Service of the I.C.S.N. (Gif-sur-Yvette, France). Melting points were determined with a Büchi B-545 apparatus. Microwave irradiation experiments were carried out with a monomode CEM-Discover apparatus, operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W. All experiments were performed in MW process vials (10 mL) with control of the temperature by infrared detection and measure of the pressure. After completion of the reaction, the vial was cooled to 50 °C with air jet. X-ray diffraction data were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo*Kα* radiation (λ=0.71073 Å). The temperature of the crystal was maintained at 100 K by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. Data were corrected for Lorentz polarization and absorption effects. The structures were solved by direct methods using SHELXS-97[43] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[44] with anisotropic displacement parameters for all

non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[45]

Microwave-assisted reactions were conduced with toluene of technical purity, which was spent on a basic alumine column and kept under argon on molecular sieves. Imines **3a**–**i**,[46] furan derivatives **1**[25c] and **5**,[35b] and Diels–Alder cycloadducts **2**,[25c] **8**[34] (**6** and 3 equiv of DMAD, toluene, 110 °C, 4 h, 96% yield), **10**[26,42c] (1.4 equiv of furan, DMAD, toluene, sealed-tube, 80 °C, 14 h, 63% yield after distillation) were prepared according to the literature, and their spectroscopic data are comparable to those described.

4.2. Preparation of Diels–Alder cycloadduct 7

*4.2.1. Dimethyl 1-benzyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**7**).* A solution of 2-benzylfuran **5** (1.57 g, 9.9 mmol) and distilled dimethyl acetylenedicarboxylate (3.7 mL, 29.8 mmol) in toluene (11 mL) was heated at reflux, under argon, for 4 h. After cooling to room temperature and concentration in vacuo, the crude product was purified by silica gel column chromatography (petroleum ether/Et_2O, 2:1) to afford cycloadduct **7** (2.62 g, 88%) as a pale yellow oil. ^{1}H NMR (360 MHz, $CDCl_3$): δ=3.52 (s, 2H, CH_2–Ph), 3.76 (s, 3H, CO_2CH_3), 3.78 (s, 3H, CO_2CH_3), 5.67 (d, J=2.2 Hz, 1H, 4-H), 7.05 (d, J=5.0 Hz, 1H, 6-H), 7.15 (dd, J=5.0, 2.2 Hz, 1H, 5-H), 7.20–7.30 (m, 5H, CH_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=34.9 (CH_2–Ph), 52.00 (CO_2CH_3), 52.01 (CO_2CH_3), 83.2 (C-4), 97.3 (C-1), 126.6 (CH_{Ar}), 128.1 (CH_{Ar}), 129.8 (CH_{Ar}), 135.8 (C_{Ar}), 144.2 (C-5), 144.9 (C-6), 151.2 and 155.5 (C-2, C-3), 162.4 (CO_2CH_3), 165.0 (CO_2CH_3) ppm. IR (neat): ν=3031, 2953, 1717, 1640, 1455, 1436, 1319, 1268, 1230, 1214, 1202, 1115, 1081, 703 cm^{-1}. MS (ES$^+$): m/z (%)=165 (42) [DMAD+Na]$^+$, 181 (11) [**5**+Na]$^+$, 297 (13), 323 (100) [M+Na]$^+$. HRMS (ES$^+$): calcd for $C_{17}H_{16}O_5Na$ [M+Na]$^+$ 323.0890; found 323.0897.

4.3. Typical procedure for the preparation of pyrrolines 4 under microwave irradiation

A mixture of the given Diels–Alder adduct **2**, **7**, **8** or **10** (0.26 mmol), imine **3a**–**h** (0.26 mmol) and toluene (1 mL) was irradiated in a closed vessel to 180 °C for 16 min at 300 W maximum power. After cooling, the reaction mixture was concentrated under vacuum and the crude residue was purified by silica gel column chromatography to give the expected pyrrolines **4a**–**h**. In the reactions from Diels–Alder adducts **2** and **7**, furan **1** and **5** were also isolated.

*4.3.1. Trimethyl (cis,trans)-2-phenyl-3,4-dihydro-2H-pyrrole-3,4,5-tricarboxylate (**4a**)*[23]. Eluent: petroleum ether/AcOEt (9/1). Yield: 71% (furan **1** was isolated in 73% yield).

*4.3.2. Trimethyl (cis)-2-methyl-5-phenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (**4b**)*[23]. Eluent: petroleum ether/Et_2O (1/1). Yield: 85% (furan **1** was isolated in 85% yield).

*4.3.3. Trimethyl (cis and trans)-2,5-diphenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (**4c**).* Eluent: petroleum ether/Et_2O (1/1). Chromatography afforded furan **1** in 88% yield and a 70/30 mixture of *cis*-**4c** and *trans*-**4c** in an 82% overall yield. Further preparative silica gel TLC (petroleum ether/Et_2O: 2/1, five elutions) gave pure samples of each isomer.

*4.3.3.1. Trimethyl (cis)-2,5-diphenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (cis-**4c**).* White solid: mp 136 °C (lit.[29] mp 135–137 °C). ^{1}H NMR (360 MHz, $CDCl_3$): δ=3.22 (br s, 1H, NH), 3.61 (s, 3H, CO_2CH_3), 3.79 (s, 3H, CO_2CH_3), 3.84 (s, 3H, CO_2CH_3), 5.37 (s, 1H, 5-H), 7.32–7.41 (m, 8H, CH_{Ar}), 7.49–7.52 (m, 2H, CH_{Ar}) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ=51.9 (CO_2CH_3), 52.2 (CO_2CH_3), 52.9 (CO_2CH_3), 68.9 (C-5), 79.3 (C-2), 126.6 (CH_{Ar}), 127.5 (CH_{Ar}), 127.9 (CH_{Ar}), 128.20 (CH_{Ar}), 128.22 (CH_{Ar}), 128.6 (CH_{Ar}), 139.9 (C-2–C_{Ar}), 140.3 (C-5–C_{Ar}), 140.7 (C-3), 141.7 (C-4), 163.1 (CO_2CH_3), 163.7 (CO_2CH_3), 171.8 (C-2–CO_2CH_3) ppm. IR (KBr): ν=3361, 3027, 2950, 1739, 1732, 1714, 1664, 1439, 1357, 1328, 1286, 1198, 1035, 1026, 699 cm^{-1}. MS (ES$^+$): m/z (%)=418 (100) [M+Na]$^+$, 419 (23). HRMS (ES$^+$): calcd for $C_{22}H_{21}O_6NNa$ [M+Na]$^+$ 418.1261; found 418.1269. $C_{22}H_{21}O_6N$ (395.41): calcd C 66.83, H 5.35, N 3.54; found C 66.23, H 5.42, N 3.48.

*4.3.3.2. Trimethyl (trans)-2,5-diphenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (trans-**4c**).* Colorless crystals: mp 100 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ=3.50 (br s, 1H, NH), 3.61 (s, 3H, CO_2CH_3), 3.69 (s, 3H, CO_2CH_3), 3.88 (s, 3H, CO_2CH_3), 5.49 (s, 1H, 5-H), 7.28–7.47 (m, 8H, CH_{Ar}), 7.53–7.58 (br d, J=7.4 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=52.3 (CO_2CH_3), 52.4 (CO_2CH_3), 53.2 (CO_2CH_3), 67.9 (C-5), 79.5 (C-2), 127.3 (CH_{Ar}), 128.0 (CH_{Ar}), 128.3 (CH_{Ar}), 128.6 (CH_{Ar}), 138.4, 140.0, 140.4 and 143.6 (C-3, C-4, 2C_{Ar}), 163.5 (CO_2CH_3), 163.8 (CO_2CH_3), 172.8 (C-2–CO_2CH_3) ppm. IR (KBr): ν=3375, 3063, 3034, 2998, 2949, 2848, 1737, 1727, 1644, 1490, 1458, 1436, 1385, 1328, 1282, 1255, 1227, 1207, 1153, 1114, 1023 cm^{-1}. MS (ES$^+$): m/z (%)=304 (17), 336 (22), 358 (20), 396 (26) [M+H]$^+$, 418 (100) [M+Na]$^+$, 419 (27). HRMS (ES$^+$): calcd for $C_{22}H_{21}O_6NNa$ [M+Na]$^+$ 418.1267; found 418.1254.

*4.3.4. Trimethyl (cis)-2-isopropyl-5-phenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (**4d**).* Following the general procedure, the reaction mixture was irradiated to 210 °C in xylene for 20 min at 300 W maximum power. Eluent: pentane/Et_2O (2/1). Yield: 39% (furan **1** was isolated in 63% yield). Pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.82 (d, J=6.6 Hz, 3H, CH–CH_3), 1.03 (d, J=6.6 Hz, 3H, CH–CH_3), 2.50 (sept, J=6.6 Hz, 1H, CH–CH_3), 2.84 (br s, 1H, NH), 3.57 (s, 3H, CO_2CH_3), 3.81 (s, 3H, CO_2CH_3), 3.87 (s, 3H, CO_2CH_3), 5.12 (s, 1H, 5-H), 7.29–7.37 (m, 5H, CH_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=16.1 (CH–CH_3), 17.2 (CH–CH_3), 34.7 (CH–CH_3), 52.0 (CO_2CH_3), 52.4 (CO_2CH_3), 52.8 (CO_2CH_3), 70.0 (C-5), 82.0 (C-2), 127.8 (CH_{Ar}), 128.1 (CH_{Ar}), 128.6 (CH_{Ar}), 137.0 (C-4), 141.4 (C_{Ar}), 143.9 (C-3), 162.3 (CO_2CH_3), 165.2 (CO_2CH_3), 172.8 (C-2–CO_2CH_3) ppm. IR (neat): ν=3354, 3031, 2955, 2875, 1737, 1729, 1658, 1456, 1435, 1322, 1281, 1246, 1201, 1148, 1028, 914, 733, 699 cm^{-1}. MS (CI$^+$): m/z (%)=360 (11), 362 (100) [M+H]$^+$, 363 (20). HRMS (ES$^+$): calcd for $C_{19}H_{24}O_6N$ [M+H]$^+$ 362.1598; found 362.1607.

*4.3.5. Trimethyl (cis)-2-isobutyl-5-phenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (**4e**)*[24]. Eluent: petroleum ether/Et_2O (2/1). Yield: 89% (furan **1** was isolated in 90% yield). Pale yellow crystals: mp 42–43 °C.

*4.3.6. Trimethyl (cis)-2-[4-(benzoyloxy)phenylmethyl]-5-phenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (**4f**)*[23]. Eluent: petroleum ether/Et_2O (3/1). Yield: 86% (furan **1** was isolated in 87% yield).

*4.3.7. Trimethyl (cis and trans)-5-(4-methoxyphenyl)-2-phenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (**4g**).* Eluent: petroleum ether/Et_2O (1/1). Chromatography afforded furan **1** in 83% yield and a 65/35 mixture of *cis*-**4g** and *trans*-**4g** in 81% overall yield. Further preparative silica gel TLC (petroleum ether/Et_2O: 1/1, three elutions) gave pure samples of each isomer.

*4.3.7.1. Trimethyl (cis)-5-(4-methoxyphenyl)-2-phenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (cis-**4g**).* Colorless crystals: mp 143 °C (lit.[29] mp 141–143 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.17 (br s, 1H, NH), 3.61 (s, 3H, $C_{Ar}OCH_3$), 3.77 (s, 3H, CO_2CH_3), 3.80 (s, 3H, CO_2CH_3), 3.83 (s, 3H, CO_2CH_3), 5.31 (s, 1H, 5-H), 6.88 (br d, J=8.8 Hz,

2H, CH_{Ar}), 7.26–7.39 (m, 5H, CH_{Ar}), 7.48 (br d, J=8.8 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ=52.3 (CO_2CH_3), 52.5 (CO_2CH_3), 53.2 (CO_2CH_3), 55.4 ($C_{Ar}OCH_3$), 68.7 (C-5), 79.4 (C-2), 114.3 (CH_{Ar}), 126.9 (CH_{Ar}), 128.2 (CH_{Ar}), 128.5 (CH_{Ar}), 129.0 (CH_{Ar}), 132.2 (C_{Ar}–C-5), 140.6, 140.7 and 142.4 (C-3, C-4, C_{Ar}–C-2), 159.8 (OC_{Ar}), 163.6 (CO_2CH_3), 164.0 (CO_2CH_3), 172.2 (C-2–CO_2CH_3) ppm. IR (KBr): ν=3390, 2997, 2954, 2840, 1740, 1714, 1659, 1609, 1510, 1440, 1345, 1304, 1249, 1198, 1121, 1109, 1031, 1006 cm^{-1}. MS (ES$^+$): m/z (%)=448 (100) [M+Na]$^+$, 449 (25). HRMS (ES$^+$): calcd for $C_{23}H_{23}O_7NNa$ [M+Na]$^+$ 448.1367; found 448.1375.

*4.3.7.2. Trimethyl (trans)-5-(4-methoxyphenyl)-2-phenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (trans-**4g**).* Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.63 (s, 3H, CO_2CH_3), 3.69 (s, 3H, CO_2CH_3), 3.80 (s, 3H, $C_{Ar}OCH_3$), 3.84 (br s, 1H, NH), 3.87 (s, 3H, CO_2CH_3), 5.44 (s, 1H, 5-H), 6.86 (br d, J=8.7 Hz, 2H, CH_{Ar}), 7.28–7.44 (m, 5H, CH_{Ar}), 7.48 (br d, J=8.1 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=52.3 (CO_2CH_3), 52.4 (CO_2CH_3), 53.2 (CO_2CH_3), 55.4 ($C_{Ar}OCH_3$), 67.5 (C-5), 79.4 (C-2), 114.1 (CH_{Ar}), 127.3 (CH_{Ar}), 128.3 (2CH_{Ar}), 129.2 (CH_{Ar}), 132.1 (C_{Ar}–C-5), 138.1, 140.5 and 144.1 (C-3, C-4, C_{Ar}–C-2), 159.6 (OC_{Ar}), 163.6 (CO_2CH_3), 164.0 (CO_2CH_3), 172.9 (C-2–CO_2CH_3) ppm. IR (neat): ν=3355, 3062, 3003, 2954, 2841, 1738, 1732, 1716, 1652, 1610, 1514, 1435, 1318, 1243, 1176, 1114, 1032, 912 cm^{-1}. MS (ES$^+$): m/z (%)=334 (24), 366 (18), 426 (53) [M+H]$^+$, 427 (13), 446 (11), 448 (100) [M+Na]$^+$, 449 (27). HRMS (ES$^+$): calcd for $C_{23}H_{23}O_7NNa$ [M+Na]$^+$ 448.1367; found 448.1369.

*4.3.8. Trimethyl (cis and trans)-5-(4-bromophenyl)-2-phenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (**4h**).* Eluent: petroleum ether/Et_2O (2/1 then 1/1). Chromatography afforded furan **1** in 80% yield and a 70/30 mixture of *cis*-**4h** and *trans*-**4h** in 76% overall yield. Further preparative silica gel TLC (petroleum ether/Et_2O: 2/1) gave pure samples of each isomer.

*4.3.8.1. Trimethyl (cis)-5-(4-bromophenyl)-2-phenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (cis-**4h**).* Colorless crystals: mp 159 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.17 (br s, 1H, NH), 3.63 (s, 3H, CO_2CH_3), 3.78 (s, 3H, CO_2CH_3), 3.85 (s, 3H, CO_2CH_3), 5.35 (s, 1H, 5-H), 7.25 (br d, J=8.5 Hz, 2H, CH_{Ar}), 7.33–7.42 (m, 3H, CH_{Ar}), 7.45–7.51 (m, 4H, CH_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=52.4 (CO_2CH_3), 52.6 (CO_2CH_3), 53.3 (CO_2CH_3), 68.4 (C-5), 79.6 (C-2), 122.5 (BrC_{Ar}), 126.7 (CH_{Ar}), 128.4 (CH_{Ar}), 128.6 (CH_{Ar}), 129.5 (CH_{Ar}), 132.0 (CH_{Ar}), 139.3, 140.4, 141.0 and 141.4 (C-3, C-4, 2C_{Ar}), 163.1 (CO_2CH_3), 163.9 (CO_2CH_3), 172.0 (C-2–CO_2CH_3) ppm. IR (KBr): ν=3358, 3060, 3026, 3007, 2952, 2844, 1741, 1731, 1713, 1667, 1483, 1436, 1404, 1341, 1325, 1286, 1209, 1171, 1123, 1077, 1035, 1009, 934 cm^{-1}. MS (ES$^+$): m/z (%)=382 (26) and 384 (24), 414 (18) and 416 (18), 474 (36) and 476 (36) [M+H]$^+$, 496 (98) and 498 (100) [M+Na]$^+$, 512 (8) and 514 (8) [M+K]$^+$. HRMS (ES$^+$): calcd for $C_{22}H_{21}BrO_6N$ [M+H]$^+$ 474.0547; found 474.0542. $C_{22}H_{20}BrO_6N$ (474.30): calcd C 55.71, H 4.25, N 2.95; found C 55.44, H 4.32, N 2.88.

*4.3.8.2. Trimethyl (trans)-5-(4-bromophenyl)-2-phenyl-2,5-dihydro-1H-pyrrole-2,3,4-tricarboxylate (trans-**4h**).* Pale yellow oil. ^{1}H NMR (360 MHz, $CDCl_3$): δ=3.42 (br s, 1H, NH), 3.63 (s, 3H, CO_2CH_3), 3.69 (s, 3H, CO_2CH_3), 3.87 (s, 3H, CO_2CH_3), 5.45 (s, 1H, 5-H), 7.28 (br d, J=8.6 Hz, 2H, CH_{Ar}), 7.34–7.41 (m, 3H, CH_{Ar}), 7.44–7.51 (m, 4H, CH_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=52.42 (CO_2CH_3), 52.46 (CO_2CH_3), 53.3 (CO_2CH_3), 67.0 (C-5), 79.5 (C-2), 122.3 (BrC_{Ar}), 127.2 (CH_{Ar}), 128.4 (CH_{Ar}), 128.5 (CH_{Ar}), 129.7 (CH_{Ar}), 131.8 (CH_{Ar}), 138.9, 139.3, 140.3 and 142.6 (C-3, C-4, 2C_{Ar}), 163.49 (CO_2CH_3), 163.50 (CO_2CH_3), 172.6 (C-2–CO_2CH_3) ppm. IR (neat): ν=3355, 3059, 3022, 2953, 2844, 1739, 1731, 1714, 1652, 1589, 1486, 1434, 1316, 1276, 1258, 1239, 1156, 1114, 1071, 1011 cm^{-1}. MS (ES$^+$): m/z (%)=382 (19) and 384 (18), 414 (13) and 416 (12), 474 (25) and 476 (25) [M+H]$^+$, 496 (100) and 498 (99) [M+Na]$^+$, 512 (10) and 514 (10) [M+K]$^+$. HRMS (ES$^+$): calcd for $C_{22}H_{20}BrO_6NNa$ [M+Na]$^+$ 496.0366; found 496.0352.

4.4. Typical procedure for the oxidation of 3-pyrrolines 4 into 2*H*-pyrroles 9

To a solution of pyrrolines **4b**–**h** (0.30 mmol) in dichloromethane (1 mL) was introduced DDQ (0.36 mmol). After stirring for 1 h at room temperature, the reaction mixture was hydrolyzed with a saturated aqueous NH_4Cl (or $NaHCO_3$) solution. The organic layer was then separated and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic fractions were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to afford 2*H*-pyrroles **9b**–**h**.

*4.4.1. Trimethyl 2-methyl-5-phenyl-2H-pyrrole-2,3,4-tricarboxylate (**9b**).* Eluent: petroleum ether/Et_2O (1/1). Yield: 83%. White solid: mp 90–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.82 (s, 3H, C–CH_3), 3.69 (s, 3H, CO_2CH_3), 3.86 (s, 3H, CO_2CH_3), 3.92 (s, 3H, CO_2CH_3), 7.40–7.52 (m, 3H, CH_{Ar}), 7.76 (br d, J=7.5 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=19.8 (C–CH_3), 52.8 (CO_2CH_3), 53.1 (CO_2CH_3), 53.3 (CO_2CH_3), 85.0 (C-2), 128.0 (CH_{Ar}), 128.9 (CH_{Ar}), 131.4 (CH_{Ar}), 132.5 (C_{Ar}), 140.5 (C-4), 156.2 (C-3), 161.1 (CO_2CH_3), 165.0 (CO_2CH_3), 167.9 (C-2–CO_2CH_3), 170.1 (C-5) ppm. IR (KBr): ν=3035, 3004, 2955, 2925, 2851, 1758, 1742, 1720, 1625, 1540, 1493, 1449, 1437, 1371, 1349, 1327, 1312, 1286, 1231, 1123, 1111, 1064, 1014 cm^{-1}. MS (ES$^+$): m/z (%)=288 (13), 354 (100) [M+Na]$^+$, 355 (19). HRMS (ES$^+$): calcd for $C_{17}H_{17}O_6NNa$ [M+Na]$^+$ 354.0948; found 354.0961.

*4.4.2. Trimethyl 2,5-diphenyl-2H-pyrrole-2,3,4-tricarboxylate (**9c**).* Eluent: petroleum ether/Et_2O (1/1). Yield: 87%. White solid: mp 127 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ=3.80 (s, 3H, CO_2CH_3), 3.81 (s, 3H, CO_2CH_3), 3.92 (s, 3H, CO_2CH_3), 7.29–7.58 (m, 8H, CH_{Ar}), 7.86 (br d, J=7.5 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=52.7 (CO_2CH_3), 53.0 (CO_2CH_3), 53.6 (CO_2CH_3), 90.6 (C-2), 127.9 (CH_{Ar}), 128.1 (CH_{Ar}), 128.3 (CH_{Ar}), 128.6 (CH_{Ar}), 128.8 (CH_{Ar}), 131.6 (CH_{Ar}), 132.1 (C_{Ar}), 133.4 (C_{Ar}), 140.1 (C-4), 156.6 (C-3), 161.2 (CO_2CH_3), 164.6 (CO_2CH_3), 167.2 (C-2–CO_2CH_3), 171.3 (C-5) ppm. IR (KBr): ν=3076, 3032, 3007, 2953, 2848, 1759, 1732, 1716, 1627, 1603, 1545, 1492, 1447, 1437, 1428, 1323, 1290, 1232, 1200, 1147, 1118, 1062, 1020, 990 cm^{-1}. MS (ES$^+$): m/z (%)=287 (5), 350 (4), 416 (100) [M+Na]$^+$, 417 (24), 432 (4) [M+K]$^+$. HRMS (ES$^+$): calcd for $C_{22}H_{19}O_6NNa$ [M+Na]$^+$ 416.1105; found 416.1112. $C_{22}H_{19}O_6N$ (393.39): calcd C 67.17, H 4.87, N 3.56; found C 66.82, H 4.98, N 3.50.

*4.4.3. Trimethyl 2-isopropyl-5-phenyl-2H-pyrrole-2,3,4-tricarboxylate (**9d**).* Following the general procedure, pyrroline **4d** was oxidized with 2 equiv of DDQ at room temperature for 3 h. Eluent: petroleum ether/Et_2O (1/1). Yield: 76%. Pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.67 (d, J=6.8 Hz, 3H, CH–CH_3), 1.32 (d, J=6.8 Hz, 3H, CH–CH_3), 3.17 (sept, J=6.8 Hz, 1H, CH–CH_3), 3.69 (s, 3H, CO_2CH_3), 3.85 (s, 3H, CO_2CH_3), 3.86 (s, 3H, CO_2CH_3), 7.39–7.55 (m, 3H, CH_{Ar}), 7.76 (br d, J=7.8 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=16.1 (CH–CH_3), 19.9 (CH–CH_3), 34.6 (CH–CH_3), 52.8 (CO_2CH_3), 52.9 (CO_2CH_3), 53.1 (CO_2CH_3), 91.9 (C-2), 128.1 (CH_{Ar}), 128.7 (CH_{Ar}), 131.0 (CH_{Ar}), 132.7 (C_{Ar}), 138.8 (C-4), 156.8 (C-3), 162.0 (CO_2CH_3), 164.3 (CO_2CH_3), 167.7 (C-2–CO_2CH_3), 171.3 (C-5) ppm. IR (neat): ν=3027, 2957, 2872, 1741, 1731, 1630, 1539, 1490, 1447, 1434, 1300, 1262, 1231, 1128, 1011 cm^{-1}. MS (ES$^+$): m/z (%)=286 (8), 308 (9), 318 (17), 340 (10), 382 (100) [M+Na]$^+$, 383 (22). HRMS (ES$^+$): calcd for $C_{19}H_{21}O_6NNa$ [M+Na]$^+$ 382.1267; found 382.1265.

*4.4.4. Trimethyl 2-isobutyl-5-phenyl-2H-pyrrole-2,3,4-tricarboxylate (**9e**).* Eluent: petroleum ether/Et_2O (1/1). Yield: 86%. Pale yellow

solid: mp 78 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ=0.81 (d, J=6.8 Hz, 3H, CH–CH_3), 0.86 (d, J=6.8 Hz, 3H, CH–CH_3), 1.25–1.40 (m, 1H, CH–CH_3), 2.33 (dd, J=14.0, 6.5 Hz, 1H) and 2.72 (dd, J=14.0, 5.8 Hz, 1H) (AB system, CH_2), 3.67 (s, 3H, CO_2CH_3), 3.86 (s, 3H, CO_2CH_3), 3.91 (s, 3H, CO_2CH_3), 7.39–7.53 (m, 3H, CH_{Ar}), 7.76 (br d, J=7.5 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=24.1 (CH–CH_3), 24.5 (CH–CH_3), 42.4 (CH_2), 52.7 (CO_2CH_3), 53.0 (CO_2CH_3), 53.3 (CO_2CH_3), 88.5 (C-2), 127.9 (CH_{Ar}), 128.8 (CH_{Ar}), 131.2 (CH_{Ar}), 132.4 (C_{Ar}), 141.1 (C-4), 155.4 (C-3), 161.3 (CO_2CH_3), 164.9 (CO_2CH_3), 167.7 (C-2–CO_2CH_3), 170.4 (C-5) ppm. IR (KBr): ν=3008, 2958, 2869, 1755, 1742, 1722, 1627, 1541, 1492, 1450, 1436, 1346, 1322, 1310, 1292, 1219, 1168, 1129, 1040, 1017, 1002 cm^{-1}. MS (ES$^+$): m/z (%)=217 (4), 330 (5), 396 (100) [M+Na]$^+$, 397 (23). HRMS (ES$^+$): calcd for $C_{20}H_{23}O_6NNa$ [M+Na]$^+$ 396.1418; found 396.1423.

*4.4.5. Trimethyl 2-[4-(benzoyloxy)phenylmethyl]-5-phenyl-2H-pyrrole-2,3,4-tricarboxylate (**9f**).* Eluent: petroleum ether/Et_2O (1/2). Yield: 88%. Pale yellow oil. ^{1}H NMR (360 MHz, $CDCl_3$): δ=3.76 (s, 3H, CO_2CH_3), 3.79 (s, 3H, CO_2CH_3), 3.86 (d, J=13.3 Hz, 1H) and 4.01 (d, J=13.3 Hz, 1H) (AB system, CH_2), 3.92 (s, 3H, CO_2CH_3), 6.99 (d, J=8.5 Hz, 2H, m-CH_{Ar} of Bn), 7.08 (d, J=8.5 Hz, 2H, o-CH_{Ar} of Bn), 7.36–7.54 (m, 5H, CH_{Ar} of Ph), 7.57–7.67 (m, 3H, p-CH_{Ar} and m-CH_{Ar} of Bz), 8.16 (br d, J=7.5 Hz, 2H, o-CH_{Ar} of Bz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=39.4 (CH_2), 52.8 (CO_2CH_3), 52.9 (CO_2CH_3), 53.4 (CO_2CH_3), 88.0 (C-2), 120.9 (m-CH_{Ar} of Bn), 127.8 (CH_{Ar}), 128.6 (CH_{Ar}), 128.7 (CH_{Ar}), 129.7 (C_{Ar}), 130.1 (o-CH_{Ar} of Bz), 131.2 (p-CH_{Ar} of Ph, o-CH_{Ar} of Bn), 131.5 (C_{Ar}), 132.3 (C_{Ar}), 133.5 (p-CH_{Ar} of Bz), 142.2 (C-4), 150.1 (OC_{Ar}), 153.9 (C-3), 161.3 (CO_2CH_3), 164.3 (CO_2CH_3), 165.0 (CO_2C_{Ar}), 167.5 (C-2–CO_2CH_3), 171.2 (C-5) ppm. IR (neat): ν=3066, 3034, 3003, 2955, 2848, 1744, 1739, 1732, 1634, 1602, 1539, 1508, 1493, 1447, 1435, 1330, 1267, 1200, 1167, 1122, 1082, 1063, 1025, 1006 cm^{-1}. MS (ES$^+$): m/z (%)=550 (100) [M+Na]$^+$, 551 (32), 552 (7), 566 (5) [M+K]$^+$. HRMS (ES$^+$): calcd for $C_{30}H_{25}O_8NNa$ [M+Na]$^+$ 550.1472; found 550.1472.

*4.4.6. Trimethyl 5-(4-methoxyphenyl)-2-phenyl-2H-pyrrole-2,3,4-tricarboxylate (**9g**).* Eluent: petroleum ether/Et_2O (1/1). Yield: 88%. Pale yellow solid: mp 154–155 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.79 (s, 3H, CO_2CH_3), 3.80 (s, 3H, CO_2CH_3), 3.86 (s, 3H, $C_{Ar}OCH_3$), 3.93 (s, 3H, CO_2CH_3), 6.96 (br d, J=9.0 Hz, 2H, CH_{Ar}), 7.27–7.42 (m, 5H, CH_{Ar}), 7.83 (br d, J=9.0 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=52.5 (CO_2CH_3), 52.9 (CO_2CH_3), 53.4 (CO_2CH_3), 55.3 (C_{Ar}-OCH_3), 90.1 (C-2), 114.1 (m-CH_{Ar} of $MeOC_6H_4$), 124.5 (C_{Ar}–C-5), 127.7 (CH_{Ar}), 128.1 (CH_{Ar}), 128.4 (CH_{Ar}), 129.8 (o-CH_{Ar} of $MeOC_6H_4$), 133.5 (C_{Ar}), 140.1 (C-4), 155.9 (C-3), 161.1 (CO_2CH_3), 162.2 (OC_{Ar}), 164.9 (CO_2CH_3), 167.3 (C-2–CO_2CH_3), 170.2 (C-5) ppm. IR (KBr): ν=3106, 3065, 3039, 3010, 2951, 2847, 1756, 1735, 1721, 1633, 1609, 1507, 1491, 1447, 1428, 1282, 1258, 1232, 1207, 1179, 1118, 1061, 1021 cm^{-1}. MS (ES$^+$): m/z (%)=380 (14), 446 (100) [M+Na]$^+$, 447 (25), 448 (6), 462 (3) [M+K]$^+$. HRMS (ES$^+$): calcd for $C_{23}H_{21}O_7NNa$ [M+Na]$^+$ 446.1210; found 446.1195.

*4.4.7. Trimethyl 5-(4-bromophenyl)-2-phenyl-2H-pyrrole-2,3,4-tricarboxylate (**9h**).* Eluent: petroleum ether/Et_2O (1/1 then 1/2). Yield: 81%. Yellow solid: mp 129 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.807 (s) and 3.812 (s) (6H, $2CO_2CH_3$), 3.92 (s, 3H, CO_2CH_3), 7.30–7.44 (m, 5H, CH_{Ar}), 7.61 (br d, J=6.8 Hz, 2H, CH_{Ar}), 7.73 (br d, J=6.8 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ=52.8 (CO_2CH_3), 53.1 (CO_2CH_3), 53.7 (CO_2CH_3), 90.9 (C-2), 126.4 (C_{Ar}–C-5), 127.9 (CH_{Ar}), 128.4 (CH_{Ar}), 128.8 (CH_{Ar}), 129.7 (o-CH_{Ar} of BrC_6H_4), 131.1 (BrC_{Ar}), 132.1 (m-CH_{Ar} of BrC_6H_4), 133.2 (C_{Ar}), 139.6 (C-4), 157.1 (C-3), 161.2 (CO_2CH_3), 164.4 (CO_2CH_3), 166.9 (C-2–CO_2CH_3), 170.3 (C-5) ppm. IR (KBr): ν=3091, 3063, 3003, 2952, 2844, 1760, 1723, 1628, 1593, 1489, 1439, 1428, 1400, 1317, 1284, 1230, 1203, 1117, 1063, 1016, 989 cm^{-1}. MS (ES$^+$): m/z (%)=396 (5) and 398 (5), 428 (35) and 430 (36), 472 (6) and 474 (6) [M+H]$^+$, 494 (100) and 496 (100) [M+Na]$^+$, 495 (24) and 497 (24), 510 (8) and 512 (9) [M+K]$^+$. HRMS (ES$^+$): calcd for $C_{22}H_{18}BrO_6NNa$ [M+Na]$^+$ 494.0210; found 494.0206. $C_{22}H_{18}BrO_6N$ (472.29): calcd C 55.95, H 3.84, N 2.97; found C 56.31, H 4.15, N 2.69.

4.5. Typical procedure for the direct preparation of 2*H*-pyrroles from cycloadduct 10

A mixture of the Diels–Alder adduct **10** (0.26 mmol), imine **3e**, **f**, **h** or **i** (0.26 mmol) and toluene (1 mL) was irradiated in a closed vessel to 180 °C for 16 min at 300 W maximum power. After cooling, the reaction mixture was concentrated under vacuum and diluted with dichloromethane (1 mL). After introduction of DDQ (0.31 mmol) and stirring for 1 h at room temperature, the reaction mixture was hydrolyzed with a saturated aqueous NH_4Cl (or $NaHCO_3$) solution. The organic layer was then separated and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic fractions were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to afford, respectively, 2*H*-pyrroles **9e**, **f**, **h** or **i**.

*4.5.1. Trimethyl 5-(4-cyanophenyl)-2-phenyl-2H-pyrrole-2,3,4-tricarboxylate (**9i**).* Eluent: petroleum ether/Et_2O (2/3). Yield: 61%. White solid: mp 128 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.81 (s, 3H, CO_2CH_3), 3.83 (s, 3H, CO_2CH_3), 3.92 (s, 3H, CO_2CH_3), 7.31–7.44 (m, 5H, CH_{Ar}), 7.76 (br d, J=8.2 Hz, 2H, CH_{Ar}), 7.96 (br d, J=8.2 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ=52.9 (CO_2CH_3), 53.2 (CO_2CH_3), 53.8 (CO_2CH_3), 91.4 (C-2), 115.1 (NCC_{Ar}), 118.1 (CN), 127.9 (CH_{Ar}), 128.6 (CH_{Ar}), 129.0 ($2CH_{Ar}$), 132.5 (m-CH_{Ar} of NCC_6H_4), 133.0 (C_{Ar}), 136.3 (C_{Ar}–C-5), 139.0 (C-4), 158.2 (C-3), 161.3 (CO_2CH_3), 164.0 (CO_2CH_3), 166.6 (C-2–CO_2CH_3), 169.9 (C-5) ppm. IR (KBr): ν=3066, 3010, 2955, 2844, 2229, 1741, 1732, 1631, 1535, 1492, 1433, 1405, 1340, 1317, 1282, 1251, 1152, 1116, 1062, 1023, 1001 cm^{-1}. MS (ES$^+$): m/z (%)=329 (9), 375 (61), 419 (6) [M+H]$^+$, 441 (100) [M+Na]$^+$, 442 (28), 457 (8) [M+K]$^+$. HRMS (ES$^+$): calcd for $C_{23}H_{18}O_6N_2Na$ [M+Na]$^+$ 441.1057; found 441.1060.

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