Stereoselective 1,3-Dipolar Cycloaddition of a Maleate Derivative with Azomethine Ylides Derived from α-Amino Esters: Synthesis of 3-Pyrrolines

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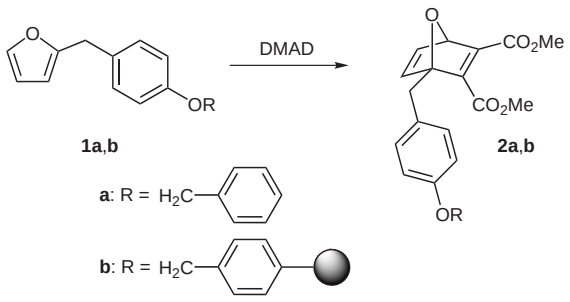
Abstract: A new preparation of 3-pyrrolines is described by [3+2] cycloadditions of N-metalated azomethine ylides derived from α-amino esters with a dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate derivative, followed by retro-Diels–Alder reactions. This two-step sequence appears superior to the direct reaction of ylides with dimethyl acetylenedicarboxylate and should be applicable to solid-phase synthesis.

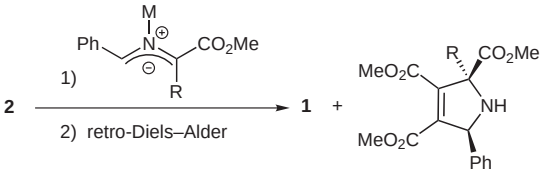
Key words: cycloadditions, amino esters, ylides, diastereoselectivity, retro reactions

We recently reported that some N-lithiated azomethine ylides generated from *N*-arylidene-α-amino esters react unusually with dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate **2a** (Scheme 1) to give β-amino diesters (structural type **8**, Scheme 3) instead of the expected [3+2] cycloadducts.[1] The choice of the substrate **2a**, prepared by reaction of dimethyl acetylenedicarboxylate (DMAD) with the furanic compound **1a**, was justified by the aim of a subsequent application of these reactions in heterogeneous conditions using the polymer-supported diester **2b** (Scheme 1), as previously related in a similar strategy.[2]



Scheme 1

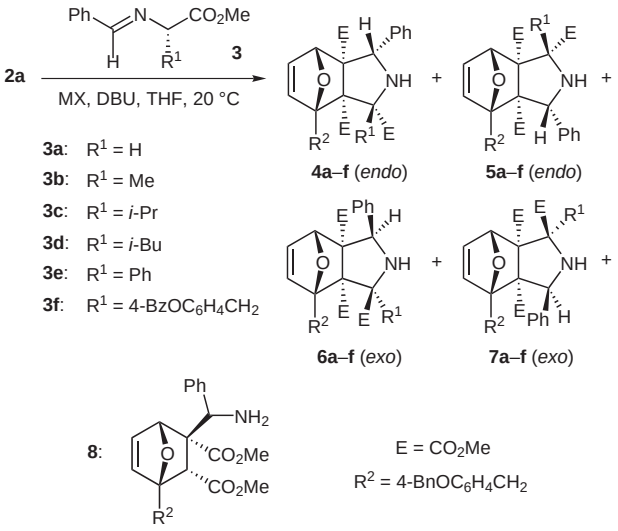
We describe, in this communication, a two-step pathway for the preparation of 3-pyrrolines involving [3+2] cycloaddition reactions of the maleate derivative **2a** with azomethine ylides. The 3-pyrrolines were thereafter obtained by retro-Diels–Alder reactions from the 1,3-dipolar products (Scheme 2). This strategy is expected to be more efficient than the direct reaction of azomethine ylides with dialkyl acetylenedicarboxylates which often gives moderate yields, due to subsequent reactions of the pyrrolines with the dienophiles.[3,4]



Scheme 2

1,3-Dipolar cycloaddition reactions of azomethine ylides derived from imines of α-amino esters with olefins have been extensively studied.[5] Utilization of LiBr/DBU and AgOAc/DBU are recognized to be useful conditions in metal-catalyzed cycloadditions that can allow different stereochemical pathways.[6] Under these conditions, the dissymmetric olefin **2a** should lead, *a priori*, to the four stereoisomers **4**–**7** by cycloaddition with the N-metalated *E*,*E*-ylides since addition generally occurs on the *exo*-face of such 7-oxabicycloheptadienic substrates (Scheme 3).

The cycloaddition reactions were run with equimolar amounts of diester **2a** and imine **3** in the presence of 1.5 equivalents of metal salt and 1.2 equivalents of DBU in



Scheme 3

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tetrahydrofuran at room temperature. The structure of the products **4**–**8** has been established from their NMR spectra.

We report, in Figure 1, the selected effects in the NOESY experiments carried out with compounds **4a**,[7] **5a**, **7d**[1] and **7f**[8] which secured their stereochemistries. The structure of adducts **4b**, **5b**, **7a** and **7b**[9] were determined by analogy of the chemical shifts of their characteristic protons with those of compounds **4a**, **5a**, **7d** and **7f** (see Table 2). The characteristic protons of the minor cycloadduct **6b** were distinct from those of stereoisomers **4b**, **5b** and **7b** and were closer to those of isomer **7b**. An *exo*-type structure was thus attributed to this compound.

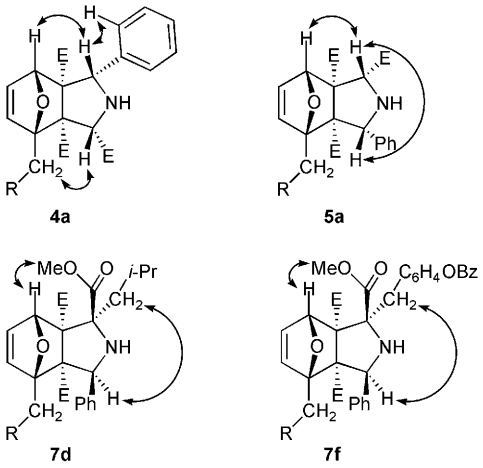


Figure 1 NOESY experiments for the structural determination of *exo* and *endo* stereochemistries of the adducts.

The results, reported in Table 1, show that 1,3-dipolar cycloadditions have generally occurred. In some cases, the desired cycloadducts could not be obtained either by an absence of reactivity in the presence of silver acetate (entries 6, 10), or by an unusual reactivity of the intermediate N-lithiated ylides previously observed[1] (entries 7, 9). Amine **8** was also present in the reaction mixture of the LiBr-catalyzed reaction of **3b** (entry 3). With the imine **3c**, formed from valine, reaction in the presence of LiBr (entry 5) led to an intractable mixture of unidentified products.

The Ag(I)-catalyzed reactions led, mainly or exclusively, to the cycloadducts **6** and **7** resulting from *exo* transition states (entries 2, 4, 8, 12). In contrast, use of LiBr allowed the products **4** and **5** to be obtained via *endo* transition states (entries 1, 3). Such different behaviors with the 7-oxabicycloheptadienedicarboxylate **2a** could result from different chelation sites of the lithium or the silver cation. Pyrroline **9f**, isolated after LiBr-catalyzed reaction of **3f** (entry 11), should proceed from unstable *endo* cycloadduct isomer(s).

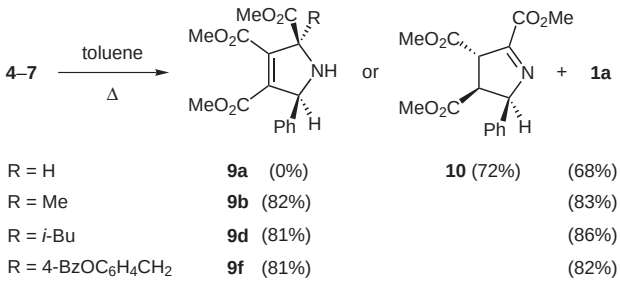
Retro-Diels–Alder reactions of cycloadducts **4**–**7** were generally run under argon in toluene at 75 °C for 16 hours. Results, reported in Scheme 4, show the formation of pyrrolines **9b**,[10] **9d**,[1] **9f**[11] or **10**[12] in excellent yields and the starting furanic compound **1a** was recovered. Structures of pyrrolines were established from their NMR spectra. In the case of R = H, the isolated 1-pyrroline **10** was probably formed by 1,3-hydrogen shifts from the related 3-pyrroline. This isomerization was highly stereoselective. Its structure was unambiguously determined using HSQC, NOESY, HMBC and INADEQUAT NMR programs. Relative stereochemistry of 1-pyrroline **10** was confirmed by analogy of its ^{1}H NMR spectrum with those of similar reported compounds.[13]

Interestingly the 3-pyrrolinic urea **11**[14] was obtained in high yield, by reaction of the 60:40 mixture of **4a** and **5a** with phenylisocyanate at room temperature. In these con-

Table 1 Reactions of Diester **2a** with Imines **3a**–**f**

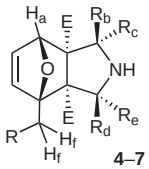
Entry	Imine	Reaction conditions[a]	Products (ratio)	Yield (%)[b]
1	**3a**	LiBr, DBU, 1.5 h	**4a** + **5a** (60:40)	82
2	**3a**	AgOAc, DBU, 1.5 h	**4a** + **5a** + **7a** (33:18:48)	86
3	**3b**	LiBr, DBU, 1.5 h	**4b** + **5b** + **8**[c] (60:14:26)	93
4	**3b**	AgOAc, DBU, 1.5 h	**7b** + **6b** (85:15)	74
5	**3c**	LiBr, DBU, 1.5 h	mixture of products	–
6	**3c**	AgOAc, DBU, 72 h[d]	no reaction	–
7	**3d**	LiBr, DBU, 2 h	**8**[c]	66
8	**3d**	AgOAc, DBU, 2 h	**7d**	96
9	**3e**	LiBr, DBU, 1.5 h	**8**[c]	79
10	**3e**	AgOAc, DBU, 72 h	no reaction	–
11	**3f**	LiBr, DBU, 1.5 h	**9f**[e]	66
12	**3f**	AgOAc, DBU, 2 h	**7f**	68

[a] Reactions were carried out in THF at r.t.
[b] Isolated yields after silica gel column chromatography.
[c] This compound was formed after hydrolysis of the reaction mixture. See ref. 1.
[d] Reaction was also carried out in MeCN up to 72 h.
[e] The pyrroline **9f** (Scheme 4) was obtained after a subsequent retro-Diels–Alder reaction.



Scheme 4

Table 2 Selected Chemical Shifts (ppm) of Characteristic Protons of 1,3-Dipolar Cycloadducts



4–7

E = CO_2Me

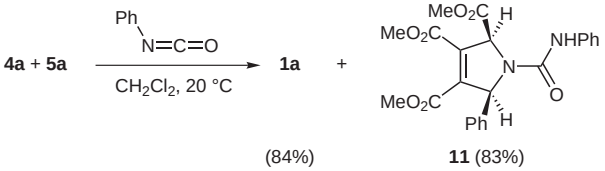
R = 4-$BnOC_6H_4$

Related Amino acid	Assignments	**4** *endo*	**5** *endo*	**6** *exo*	**7** *exo*
Glycine **a**	H_a	4.95	5.02		4.86
	H_f	3.25, 3.48[a]	3.47, 3.58[a]		2.40, 2.50[a]
	PhC*H*	4.41 (H_b)	4.28 (H_d)		5.28 (H_e)
	MeO_2CCH	4.45 (H_d)	4.72 (H_b)		n.d.[b]
Alanine **b**	H_a	4.88	4.99	4.63	4.84
	H_f	3.00–4.00[a]	n.d.[b]	n.d.[b]	1.96, 2.37[a]
	PhC*H*	4.73 (H_b)	4.55 (H_d)	5.32 (H_c)	5.71 (H_e)
Leucine **d**	H_a				4.69
	H_f				1.95, 2.37[a]
	PhC*H*				5.53 (H_e)
Tyrosine **f**	H_a				4.77
	H_f				1.95, 2.40[a]
	PhC*H*				5.97 (H_e)

[a] AB system.
[b] Not determined.

ditions, urea formation from the 1,3-dipolar adducts induced the retro-Diels–Alder reaction at a lower temperature (Scheme 5).

Preparation of pyrroline **9b**[10] requires special comments. The high reported yield was achieved when the cycloreversion was run in a vacuum-sealed tube for two hours to prevent further degradation. The spectroscopic data of this 3-pyrroline are different from those of the compound prepared by reaction of DMAD with imine **3b** under thermal conditions.[3c] The X-ray diffraction study of crystalline compound **9b** supports unambiguously our proposed structure (Figure 2).[15] In addition, we were not able to observe either the reported compound or pyrroline **9b** on reproducing the reported reaction. This result strengthens the advantage of our two-step preparation of 3-pyrrolines.



Scheme 5

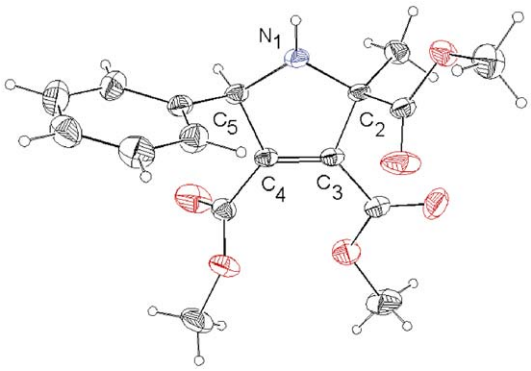


Figure 2 ORTEP[16] structure of compound **9b**. Ellipsoids are drawn at the 30% probability level.

In conclusion, we describe a new sequence to prepare 3-pyrrolines by reaction of ylides derived from α-amino esters with dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, followed by a thermal retro-Diels–Alder reaction. This methodology could be applicable to solid-phase employing ester-type **2b**, since the thermal stability of the [3+2] cycloadducts allows the reactants to be removed before the thermal cycloreversion.

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References and Notes

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(7) **Trimethyl (1*S**,3*S**,3a*R**,4*R**,7*S**,7a*S**)-7-[4-(Benzyloxy)phenylmethyl]-3-phenyl-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-epoxyisoindole-1,3a,7a-tricarboxylate (4a)**
White solid; mp 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.93 (s, 3 H), 3.25 (d, *J* = 15.2 Hz, 1 H), 3.48 (d, *J* = 15.2 Hz, 1 H), 3.81 (s, 3 H), 3.86 (s, 3 H), 4.41 (s, 1 H), 4.45 (s, 1 H), 4.95 (s, 1 H), 5.07 (s, 2 H), 6.15 (d, *J* = 6.0 Hz, 1 H), 6.66 (d, *J* = 6.0 Hz, 1 H), 6.96 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 7.29–7.92 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.0, 51.5, 52.0, 52.4, 66.6, 70.0, 70.1, 73.5, 82.6, 83.9, 94.5, 114.5, 127.2, 127.6, 128.1, 128.4, 128.5, 128.6, 129.3, 131.4, 133.4, 137.2, 137.8, 141.3, 157.6, 169.8, 170.9, 171.2. IR (KBr): 3307, 1744, 1731, 1609, 1581, 1511, 1452, 1431, 1245, 1222, 1106 cm^{-1}. MS (ES$^+$): *m/z* (%) = 320 (100) [pyrroline **10** + H]$^+$, 342 (16) [pyrroline **10** + Na]$^+$. Anal. Calcd for $C_{34}H_{33}NO_8$: C, 69.97; H, 5.70; N, 2.40. Found: C, 69.81; H, 5.67; N, 2.27.
(8) **Trimethyl (1*S**,3*S**,3a*R**,4*S**,7*R**,7a*S**)-1-[4-(Benzoyloxy)phenylmethyl]-4-[4-(benzyloxy)phenylmethyl]-3-phenyl-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-epoxyisoindole-1,3a,7a-tricarboxylate (7f)**
Oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.95 (d, *J* = 15.0 Hz, 1 H), 2.40 (d, *J* = 15.0 Hz, 1 H), 3.09 (d, *J* = 14.0 Hz, 1 H), 3.49 (d, *J* = 14.0 Hz, 1 H), 3.73 (s, 3 H), 3.84 (s, 3 H), 3.99 (s, 3 H), 4.77 (d, *J* = 1.8 Hz, 1 H), 4.94 (s, 2 H), 5.97 (br s, 1 H), 6.00 (dd, *J* = 5.5, 1.8 Hz, 1 H), 6.49 (d, *J* = 5.5 Hz, 1 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 7.04 (d, *J* = 8.5 Hz, 2 H), 7.31–7.60 (m, 15 H), 8.15 (d, *J* = 7.0 Hz, 2 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 35.1, 37.1, 52.1, 52.5, 52.8, 65.2, 69.8, 70.8, 74.4, 81.7, 83.6, 96.9, 114.1, 120.9, 127.4, 127.7, 127.8, 127.9, 128.1, 128.5, 130.1, 130.4, 131.0, 131.6, 131.8, 132.5, 133.2, 133.3, 133.4, 137.1, 137.4, 145.6, 149.6, 157.1, 165.0, 169.5, 170.6, 172.9. IR (neat): 3327, 3060, 3028, 3005, 2951, 2851, 1738, 1729, 1713, 1604, 1584, 1506, 1469, 1451, 1433, 1245, 1198, 1169, 1080, 1060 cm^{-1}. MS (ES$^+$): *m/z* (%) = 522 (100) [pyrroline **9f** + Na]$^+$.
(9) **Trimethyl (1*S**,3*S**,3a*R**,4*S**,7*R**,7a*S**)-4-[4-(Benzyloxy)phenylmethyl]-1-methyl-3-phenyl-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-epoxyisoindole-1,3a,7a-tri-carboxylate (7b)**
Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.62 (s, 3 H), 1.96 (d, *J* = 14.8 Hz, 1 H), 2.37 (d, *J* = 14.8 Hz, 1 H), 3.63 (s, 3 H), 3.91 (s, 3 H), 3.94 (s, 3 H), 4.21 (br s, 1 H), 4.84 (br s, 1 H), 4.94 (s, 2 H), 5.71 (s, 1 H), 5.94 (d, *J* = 5.2 Hz, 1 H), 6.45 (d, *J* = 5.2 Hz, 1 H), 6.74 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 7.24–7.60 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 34.9, 51.7, 52.4, 52.6, 65.7, 69.2, 69.7, 69.9, 80.9, 83.0, 96.7, 113.9, 127.2, 127.6, 127.7, 128.2, 128.3, 130.3, 130.4, 130.8, 132.0, 136.9, 137.3, 145.4, 156.9, 169.3, 171.7, 171.9. IR (neat): 3450, 3062, 3032, 3003, 2951, 1744, 1726, 1654, 1611, 1511, 1454, 1434, 1249, 1225, 1079 cm^{-1}. MS (ES$^+$): *m/z* (%) = 274 (33), 334 (100), 598 (15) [M + H]$^+$. HRMS (ES$^+$): *m/z* calcd for $C_{35}H_{36}O_8N$: 598.2435; found: 598.2453.
(10) **Trimethyl (2*S**,5*S**)-2-Methyl-5-phenyl-2,5-dihydro-1*H*-pyrrole-2,3,4-tricarboxylate (9b)**
White solid; mp 62–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66 (s, 3 H), 2.74 (br s, 1 H), 3.60 (s, 3 H), 3.80 (s, 3 H), 3.83 (s, 3 H), 5.35 (s, 1 H), 7.20–7.35 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 52.2, 52.4, 52.9, 69.0, 73.0, 127.4, 128.3, 128.4, 140.1, 140.9, 141.2, 163.5, 163.7, 172.9. IR (KBr): 3359, 2992, 2950, 2832, 1733, 1715, 1656, 1449, 1433, 1334, 1244, 1204 cm^{-1}. MS (ES$^+$): *m/z* (%) = 274 (74), 334 (77) [M + H]$^+$, 356 (100) [M + Na]$^+$. HRMS (ES$^+$): *m/z* calcd for $C_{17}H_{19}O_6NNa$: 356.1105; found: 356.1119.
(11) **Trimethyl (2*S**,5*S**)-2-[4-(Benzoyloxy)phenylmethyl]-5-phenyl-2,5-dihydro-1*H*-pyrrole-2,3,4-tricarboxylate (9f)**
Oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.83 (br s, 1 H), 3.32 (s, 2 H), 3.54 (s, 3 H), 3.80 (s, 3 H), 3.90 (s, 3 H), 4.68 (br s, 1 H), 7.14 (d, *J* = 8.5 Hz, 2 H), 7.26–7.30 (m, 5 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 7.46–7.52 (m, 2 H), 7.57–7.67 (m, 1 H), 8.20 (d, *J* = 7.0 Hz, 2 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 42.5, 52.0, 52.5, 52.8, 69.1, 77.5, 121.1, 127.7, 128.1, 128.5, 128.6, 129.5, 130.0, 131.8, 133.1, 133.5, 140.4, 140.7, 141.1, 150.0, 162.7, 164.5, 165.0, 171.9. IR (neat): 3367, 3063, 3032, 3005, 2953, 2847, 1739, 1731, 1713, 1659, 1601, 1507, 1452, 1434, 1250, 1200, 1168, 1082, 1063, 1024 cm^{-1}. MS (ES$^+$): *m/z* (%) = 552 (100) [M + Na]$^+$. HRMS (ES$^+$): *m/z* calcd for $C_{30}H_{27}O_8NNa$: 552.1629; found: 552.1628.
(12) **Trimethyl (3*S**,4*S**,5*R**)-5-Phenyl-4,5-dihydro-3*H*-pyrrole-2,3,4-tricarboxylate (10)**
Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.15 (s, 3 H), 3.76 (s, 3 H), 3.87 (dd, *J* = 9.2, 6.0 Hz, 1 H), 3.93 (s, 3 H), 4.72 (dd, *J* = 6.0, 2.4 Hz, 1 H), 5.86 (dd, *J* = 9.2, 2.4 Hz, 1 H), 7.05–7.08 (m, 2 H), 7.22–7.32 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.8, 52.7, 52.9, 56.5, 56.6, 78.9, 127.4, 128.2, 128.3, 135.6, 161.9, 164.0, 170.0, 170.1. IR (neat): 3059, 3033, 3007, 2956, 2919, 2847, 1726, 1648, 1452, 1437, 1369, 1312, 1258, 1217, 1101 cm^{-1}. MS (ES$^+$): *m/z* (%) = 260 (100), 342 (82) [M + Na]$^+$. HRMS (ES$^+$): *m/z* calcd for $C_{16}H_{17}O_6NNa$: 342.0948; found: 342.0955.
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(14) **Trimethyl (2*S**,5*S**)-1-(Phenylcarbamoyl)-5-phenyl-2,5-dihydro-1*H*-pyrrole-2,3,4-tricarboxylate (11)**
White solid; mp 156–157 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.69 (s, 3 H), 3.86 (s, 3 H), 3.93 (s, 3 H), 5.60 (d, *J* = 3.0 Hz, 1 H), 5.96 (d, *J* = 3.0 Hz, 1 H), 6.76 (br s, 1 H), 6.99 (t,

J = 8.6 Hz, 1 H), 7.14 (d, *J* = 7.6 Hz, 2 H), 7.19–7.22 (m, 2 H), 7.41–7.48 (m, 3 H), 7.72 (d, *J* = 7.2 Hz, 2 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 52.3, 52.6, 52.9, 67.0, 69.3, 119.2, 123.2, 127.9, 128.6, 129.1, 129.2, 131.2, 136.5, 137.8, 140.6, 152.9, 161.8, 161.9, 169.5. IR (neat): 3365, 3033, 3007, 2956, 2919, 2847, 1749, 1726, 1646, 1541, 1447, 1434, 1363, 1333, 1279, 1247 cm^{-1}. MS (ES^+): *m/z* (%) = 461 (100) $[M + Na]^+$. HRMS (ES^+): *m/z* calcd for $C_{23}H_{22}O_7N_2Na$: 461.1319; found: 461.1328.

(15) **X-ray Crystal Data of 9b**
$C_{17}H_{19}NO_6$, *M* = 333.33, triclinic, space group *P*-1, *Z* = 2, *a* = 6.0095 (8) Å, *b* = 8.1268 (13) Å, *c* = 18.151 (3) Å, *α* = 78.363 (3)°, *β* = 89.035 (2)°, *γ* = 77.285 (3)°, *V* = 846.6 (2) $Å^3$, *d* = 1.308 g/cm^3, 3217 independent reflections were collected with MoKα radiation on Kappa X8 APEX II system. Data analysis was carried out with Bruker program SMART and SAINT,[17] the structure was solved and refined by direct methods using SHELXTL program[18] to *R*1 = 0.0572, *wR*2 = 0.1505. The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif. Please quote reference number CDDC 630085.

(16) Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.

(17) Bruker SMART and SAINT, Bruker AXS Inc., Madison, Wisconsin, USA, **1997**.

(18) Bruker SHELXTL, Version 6.3.1, Bruker AXS Inc., Madison, Wisconsin, USA, **2004**.