# Alkoxycarbonylcarbene Transfer to Semicyclic Enaminones – A Route to Cyclopenta[*b*]pyrrole and Indole Ring Systems

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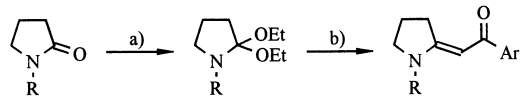
Copper-catalyzed decomposition of alkyl diazoacetates in the presence of semicyclic enaminones **1a**–**o** leads primarily to enamino esters **2** which constitute formal products of C–C insertion of the carbene unit. In the case of *N*-methyl (**1a**–**e**) and *N*-benzyl (**1f**–**i**) enaminones, **2a**–**i** are accompanied by 2,3,5,6-tetrahydroindoles **3a**–**i**, in which two carbene moieties are incorporated. At 250 °C, compounds **2b**–**e**, which could not be isolated in pure form, undergo cyclocondensation to form 1,2,3,5-tetrahydrocyclopenta-[*b*]pyrroles **4b**–**e**. In contrast, **2f**–**i** can be isolated as *Z*,*E* mixtures and are transformed thermally into **4f**–**i** only in the presence of silica gel. Carbene transfer to *N*-phenyl enaminones **1j**–**m** and *N*-methyl enamino esters **1n**,**o** leads only to the 1:1 adducts, enamino esters **2j**–**o**, which do not undergo the cyclocondensation reaction under the previous conditions. Dehydrogenation of tetrahydroindoles **3c**–**e** with tetrachloro-*p*-benzoquinone can be controlled to give either 1,2-dihydroindole-6,7-dicarboxylates **5** or indole-6,7-dicarboxylates **6**.

In the hands of synthetic organic chemists, reactions of in situ generated carbenes and carbenoids with a great variety of substrates are versatile tools for the construction of acyclic and cyclic target molecules with increased functional and structural complexity[1]. Metal-catalyzed intermolecular acylcarbene transfer is a particularly important strategy in this area[2]. Considering the fact, that easily accessible enaminones have several centres of enhanced electron density, it is rather astonishing to note that they have not found particular attention as reaction partners of electrophilic carbenes or carbenoids. Only recently, Kascheres and coworkers have studied the copper-catalyzed decomposition of diazocarbonyl compounds in the presence of primary and secondary enaminones[3][4]. Depending on the structure and substitution pattern of the enaminone, insertion of the carbene unit in the N−H or the olefinic C−H bond are the initial events. In contrast to these observations, we have found that alkoxycarbonylcarbene transfer to acyclic *tertiary* enamino ketones and enamino esters leads to 2-acyl-3-aminocyclopropane-1-carboxylates which are extremely sensitive to ring-opening[5]. In this communication, we show that an analogous reaction sequence applies when semicyclic rather than acyclic tertiary enaminones are used and that the initial reaction products can be transformed further into derivatives of cyclopenta[*b*]pyrroles and indoles.

## Results

Semicyclic enamino ketones of type **1** are usually prepared from the corresponding lactam acetals and methyl ketones[6][7]. The so far unknown enamino ketones **1f**−**m** were prepared analogously (Scheme 1). It should be mentioned that for the preparation of 2,2-diethoxy-1-phenylpyrrolidine, the initial *O*-alkylation of 1-phenylpyrrolidin-2-one had to be performed with a trialkyloxonium salt, while the more nucleophilic oxygen atom of 1-benzyl-2,2-diethoxypyrrolidine could be alkylated with dimethyl sulfate[8]. Only one diastereomer of **1f**−**m** was detected by NMR; since a ROESY experiment did not show a through-space effect between the double-bond substituents [irradiation at δ(=CH) did not cause an intensity enhancement of the signal for the *ortho*-protons of *N*-Ph or the 3′-$CH_2$ protons of the pyrrolidine ring], the *E* configuration (with the phenyl ring perpendicular to the pyrrolidine ring) is assumed.

Scheme 1. Conditions: R = $CH_2Ph$: a) $(MeO)_2SO_2$, then NaOEt (2 equiv.); b) $H_3CCOAr$, 80°C. − R = Ph: a) $Et_3OBF_4$, then NaOEt; b) $H_3CCOAr$, 80°C




**1**

The catalytic decomposition of methyl diazoacetate in the presence of enamino ketones **1a**−**e** was investigated first (Scheme 2). With respect to product yields, copper(I) triflate as the catalyst was found to be superior to copper(II) acetylacetonate, and $Rh_2(OAc)_4$ was nearly useless. In all cases, formation of considerable amounts of the formal carbene dimers, dimethyl fumarate and maleate, was a problem; in the case of copper(I) triflate as a catalyst, it was necessary to keep the stationary concentration of the diazo ester extremely low, but even then, the carbene dimers were formed in considerable yield. From the product mixtures obtained from the reaction between the respective enami-

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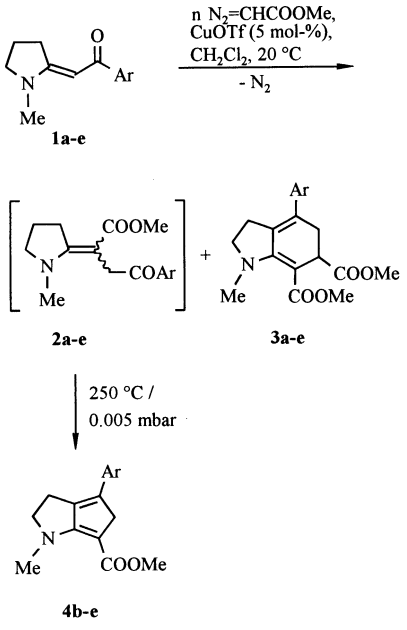
none and two equivalents of diazo ester, tetrahydroindoles **3a**−**e** could be isolated after chromatography and fractional crystallization. The crude product mixtures also contained enamino esters **2** which withstood, however, all attempts to isolate them. Therefore, the material left after the separation of the tetrahydroindoles was heated at 250°C, under which conditions a cyclocondensation of **2** leading to the novel tetrahydrocyclopenta[*b*]pyrroles **4** occurred. These products could be isolated and their structure was clarified by NMR spectra and X-ray diffraction (see below). It is obvious that enamino esters **2** represent 1:1 adducts of enamino ketones **1** and methoxycarbonylcarbene, while the tetrahydroindoles correspond to a 1:2 stoichiometry. We observed that mixtures of **2** and **3** were formed already when a 1:1 stoichiometry of the reactants was used, and that better yields of **3** were obtained when two equivalents of diazo ester were applied. In the case of a 1:3 ratio of the reactants, the yield of tetrahydroindoles **3** increased again, and **4** (resulting from **2**) could no longer be isolated.

Scheme 2



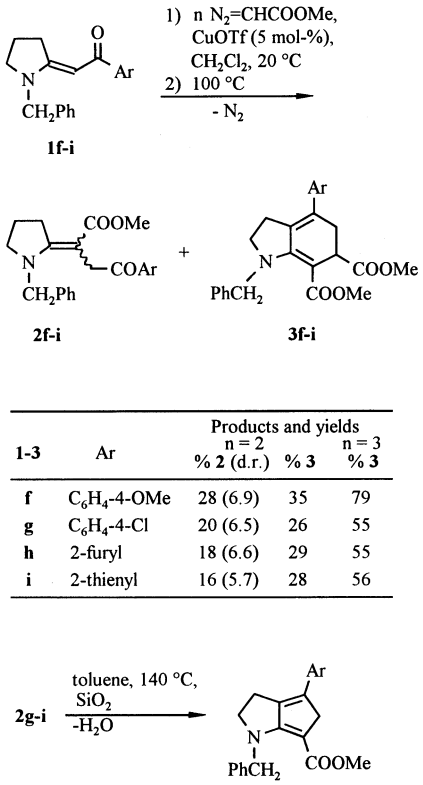

| 1-4 | Ar | Products (yields, %) n[a] = 2 | n[a] = 3 |
|---|---|---|---|
| **a** | Ph | **3** (35) | **3** (47) |
| **b** | $C_6H_4$-4-OMe | **3** (26), **4** (15) | **3** (47) |
| **c** | $C_6H_4$-4-Cl | **3** (31), **4** (12) | **3** (51) |
| **d** | 2-furyl | **3** (33), **4** (8) | **3** (47) |
| **e** | 2-thienyl | **3** (28), **4** (6) | **3** (42) |

[a] Equivalents of methyl diazoacetate.

Methoxycarbonylcarbene transfer to *N*-benzyl enamino ketones **1f**−**i** resulted in the same product pattern as described above for the *N*-methyl enamino ketones (Scheme 3). However, enamino esters **2f**−**i** could be isolated by column chromatography without problems, and tetrahydroindoles **3f**−**i** were formed much more slowly than their *N*-methyl-substituted relatives. We observed by NMR that the amount of **3** increased when the crude product mixture (obtained after separation from the catalyst by fast chromatography on silica gel) was kept at ambient temperature for several days. Obviously, the tetrahydroindoles are not the initial products of the carbene reaction and their immediate precursor (see mechanistic discussion) is still present at the end of the diazo decomposition reaction. In order to speed up the formation of the tetrahydroindoles, the reaction mixtures were heated at 100°C for a brief period before work-up.

In contrast to their relatives **2a**−**e**, enamino esters **2f**−**i**, which were isolated as mixtures of *Z*,*E* diastereomers, underwent the thermal cyclocondensation reaction to afford tetrahydrocyclopenta[*b*]pyrroles **4f**−**i** quantitatively only in the presence of a small amount of silica gel.

Scheme 3

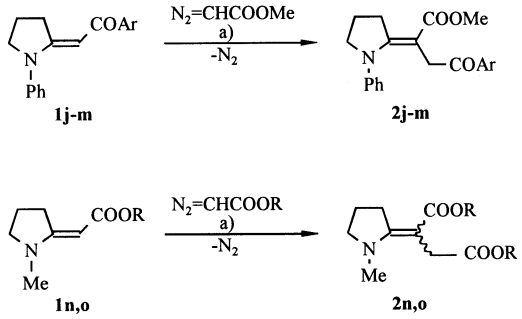



| 1-3 | Ar | Products and yields n = 2 % **2** (d.r.) | % **3** | n = 3 % **3** |
|---|---|---|---|---|
| **f** | $C_6H_4$-4-OMe | 28 (6.9) | 35 | 79 |
| **g** | $C_6H_4$-4-Cl | 20 (6.5) | 26 | 55 |
| **h** | 2-furyl | 18 (6.6) | 29 | 55 |
| **i** | 2-thienyl | 16 (5.7) | 28 | 56 |

For carbene transfer from methyl or *tert*-butyl diazoacetate to *N*-phenyl enaminones **1j**−**m** and to *N*-methyl enamino esters **1n**,**o**, copper(II) acetylacetonate turned out to be a better catalyst than copper(I) triflate and $Rh_2(OAc)_4$. Enamino esters **2j**−**o** were the only products found besides the carbene dimers. Optimum yields were obtained when two equivalents of diazo ester were applied (yield of **2m** for the three catalysts mentioned: 68, 34, and 7%). With a 1:3 ratio of the reactants, the yield could be increased only marginally, and even under these conditions, no tetrahydroindoles of type **3** were obtained. Enamino esters **2j**−**o** could not be transformed into tetrahydrocyclopenta[*b*]pyrroles under the conditions that worked for **2a**−**i** nor in the pres-

ence of catalytic amounts of toluenesulfonic acid, of $P_4O_{10}$ or in the presence of $Et_2AlCl$.

Scheme 4

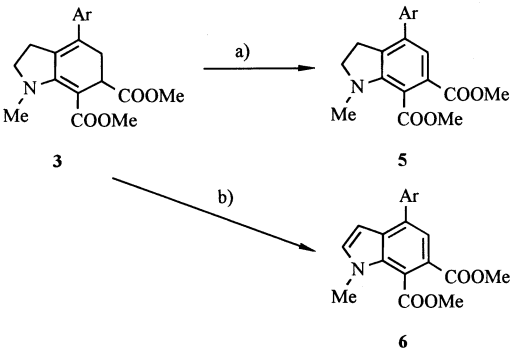



a) diazoester (2 equiv.), $Cu(acac)_2$ (5 mol-%), ethyl acetate, reflux

| 1,2 | Ar | Yield (%) | 1,2 | R | Yield (%) |
|---|---|---|---|---|---|
| **j** | $C_6H_4$-4-OMe | 53 | **n** | Me | 55 (d.r. = 2.0) |
| **k** | $C_6H_4$-4-Cl | 50 | **o** | *t*-Bu | 54 (d.r. = 2.4) |
| **l** | 2-furyl | 54 | | | |
| **m** | 2-thienyl | 68 | | | |

Indoles with a wide range of substitution patterns constitute an important class of heterocycles with various biological and pharmaceutical activities[9]. Therefore, we were interested to convert tetrahydroindoles **3** by dehydrogenation into dihydroindoles **5** and indoles **6**. In fact, with tetrachloro-*p*-benzoquinone (chloranil) as the oxidant, both goals could be achieved depending on the stoichiometry and the reaction temperature, as has been demonstrated for **3c**−**e** (Scheme 5).

Scheme 5




a) chloranil (1 equiv.), toluene, 120 °C, 3 h

b) chloranil (2 equiv.), toluene, 160 °C, 3 h

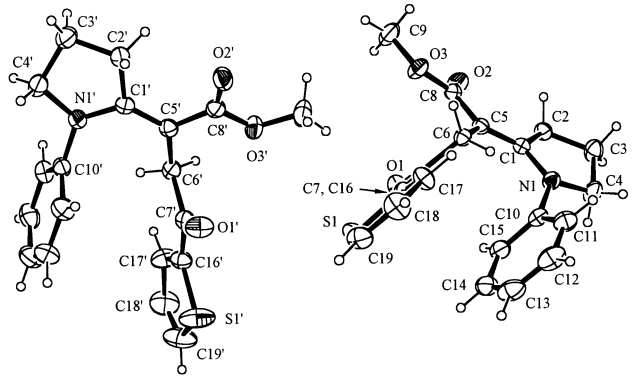
| 3,5,6 | Ar | Yield (%) 3→5 | 3→6 |
|---|---|---|---|
| **c** | $C_6H_4$-4-Cl | n.i. | 90 |
| **d** | 2-furyl | 92 | 94 |
| **e** | 2-thienyl | 91 | 89 |

It should be mentioned that indole-6,7-dicarboxylic acid derivatives or their dihydro or tetrahydro forms can also be prepared by other methods, such as [4+2] cycloaddition reactions with 3-vinylpyrroles[10], $\eta^2$-osmium complexes thereof[11], and (2-pyrrolyl)maleates[12], furthermore by reaction of enaminones of type **1** with dimethyl acetylenedicarboxylate[13].

**Structural and NMR Characterization of 2, 3, and 4**

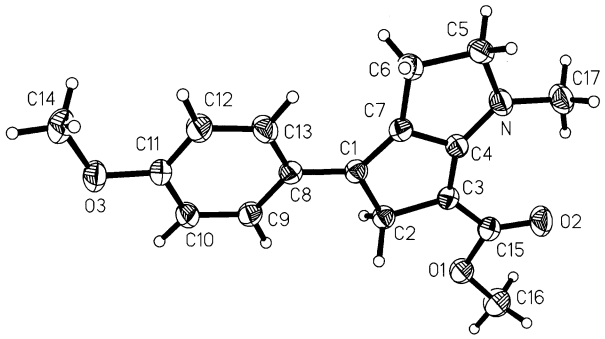
Enamino esters **2a**−**i**,**n**,**o** were obtained as *Z*,*E* mixtures of diastereomers. The *E* configuration could be assigned to the major isomer by $^1$H-NMR (ROESY) experiments. In contrast, analogous experiments gave no positive evidence for the configuration of **2j**−**m** for which only one diastereomer was isolated [irradiation at δ($CH_2$-allyl, chain) did not cause an intensity enhancement either of the C$H_2$Ph or the NCC$H_2$ signal]. An X-ray crystal-structure analysis of **2m** revealed the *E* configuration, however (Figure 1).

Figure 1. Structure of compound (*E*)-**2m** in the crystal; the two independent molecules in the unit cell are shown in the correct orientation[a]




[a] Selected bond lengths [Å], bond angles [°], and torsion angles [°]; values for the second, symmetry-independent molecule are given in brackets: N1−C1 1.370(4) [1.369(4)], C1−C5 1.371(4) [1.372(4)], C8−O2 1.216(4) [1.210(4)], C5−C8 1.453(4) [1.455(5)]; C1−N1−C4 113.6(3) [112.9(3)], C4−N1−C10 116.3(3) [116.1(3)], C1−N1−C10 126.3(3) [127.4(3)]; C6−C7−C16−C17 0.2(5) [−5.9(5)], C1−C5−C6−C7 −103.4(3) [−109.2(3)].

Figure 2. Structure of compound **4b** in the crystal; ellipsoids of thermal vibration are shown at the 30% level[a]




[a] Selected bond lengths [Å], bond angles [°], and torsion angles [°]: N−C4 1.336(3), C3−C4 1.360(4), C3−C15 1.417(4), C4−C7 1.426(3), C1−C7 1.335(3); C4−N−C5 111.8(2), C4−N−C17 128.9(2), C5−N−C17 119.2(2); C15−C3−C4−N 5.0(6), C4−C3−C15−O2 8.1(5), C7−C1−C8−C9 173.3(3).

The structure of cyclopenta[*b*]pyrrole **4b** was also established by single-crystal X-ray diffraction (Figure 2). The expected π conjugation in the enamino ester moiety is reflected in the bond-length deviations from typical single- or double-bond values. In line with this, one finds the $^{13}C$ resonance for the enaminic β-C atom at rather high field [δ(NC=*C*) = 86.0]. $^{13}C$-NMR-chemical shifts of **4b**−**i** could be assigned based on C,H correlation and gradient-selected HMBC spectra (Table 1). The same techniques allowed also to establish the constitution of tetrahydroindoles **3**. The $^{13}C$-NMR data for these compounds are also given in Table 1.

primarily formed and sometimes isolable push-pull-substituted cyclopropanes. Analogously, we propose that enamino esters **2** are formed via intermediary 3-acyl-2-aminocyclopropane-1-carboxylates **7** which open regioselectively the more polarized ring C−C bond (Scheme 6)[14]. A repetition of this homologation sequence (**2** → **8** → **11**) prepares the stage for the formation of tetrahydroindoles **3** in which obviously two carbon equivalents have been incorporated. Although we did not succeed to isolate or identify unequivocally a compound **11** from any of the product mixtures, an FD mass spectrum of the corresponding product fraction obtained from **1i** showed peaks at *m*/*z* = 427, 409, and 355

Table 1. $^{13}C$-NMR-chemical shifts of compounds **3** and **4** (δ values, $CDCl_3$, TMS)[a]

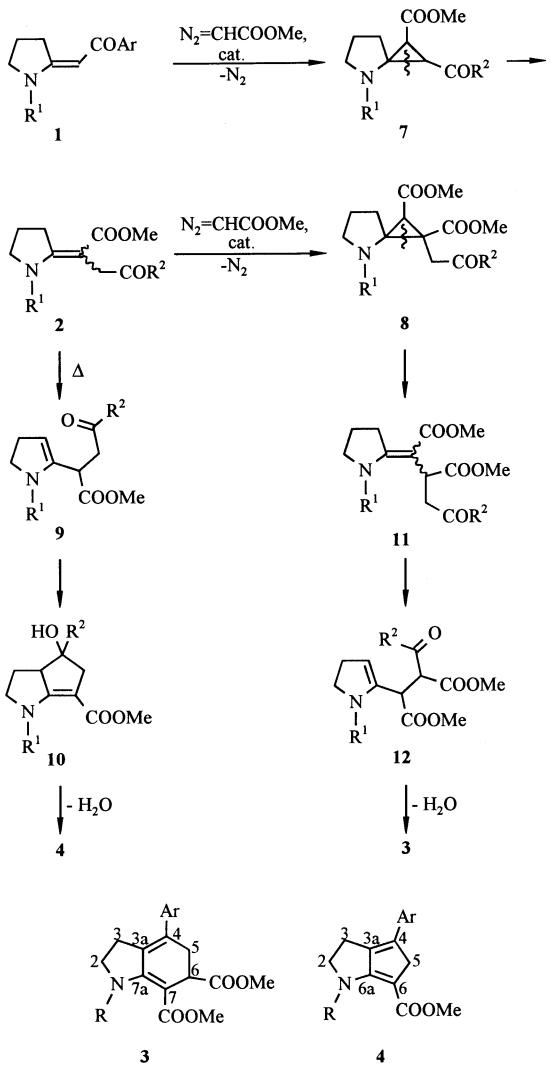
| Compound | $NCH_3$ or $NCH_2Ph$ C-2 | C-3 | C-3a | C-4 | C-5 | C-6 | C-7 | C-6a or C-7a | Other signals |
|---|---|---|---|---|---|---|---|---|---|
| **3a** | 39.84 | 55.60 | 26.38 | [b] | [b] | 32.51 | 40.73 | 83.33 | 156.36 | 50.55, 51.85, 126.89, 127.41, 128.17, 133.22, 134.41, 140.17, 167.28, 175.29 |
| **3b** | 39.80 | 55.56 | 26.48 | 131.94 | 133.93 | 32.44 | 40.68 | 82.97 | 156.67 | 50.43, 51.73, 55.10, 113.49, 128.17, 132.44, 158.79, 167.19, 175.79 |
| **3c** | 39.83 | 55.54 | 26.38 | 133.77 | 138.97 | 32.36 | 40.64 | 83.57 | 155.97 | 50.61, 51.92, 128.27 (2 ×), 128.41, 133.22, 167.27, 175.66 |
| **3d** | 40.32 | 55.86 | 26.87 | 130.86 | 122.86 | 28.43 | 40.02 | 82.83 | 156.81 | 50.57, 51.97, 109.98, 111.64, 142.86, 153.55, 167.26, 175.98 |
| **3e** | 40.12 | 55.61 | 27.47 | 131.43 | 127.56 | 31.70 | 40.65 | 82.90 | 156.74 | 50.63, 52.03, 126.02, 126.27, 127.28, 142.82, 167.21, 175.91 |
| **3f** | 55.08 | 52.33 | 26.70 | 132.56 | 134.91 | 32.59 | 41.01 | 84.36 | 158.95 | 50.67, 51.89, 55.27, 113.65, 127.05, 127.78, 128.33, 128.41, 132.69, 137.91, 167.60, 175.90 |
| **3g** | 54.98 | 52.27 | 26.54 | [b] | [b] | 32.34 | 40.82 | 84.78 | 155.90 | 50.78, 52.00, 127.12, 127.50, 127.75, 128.31, 128.44, 133.24, 134.02, 134.26, 137.67, 138.65, 167.90, 175.64 |
| **3h** | 54.99 | 52.34 | 26.87 | 131.23 | 123.61 | 28.34 | 40.39 | 83.95 | 156.33 | 50.64, 51.93 or 52.34, 110.26, 111.67, 127.06, 127.70, 128.42, 137.83, 142.93, 153.44, 167.49, 175.87 |
| **3i** | 55.15 | 52.11 | 27.51 | 131.89 | 127.14 | 31.72 | 40.81 | 84.23 | 156.23 | 50.73, 52.02, 126.21, 126.39, 127.31, 127.78, 128.36, 128.47, 137.75, 142.84, 167.50, 175.81 |
| **4b** | 35.72 | 61.04 | 23.92 | 140.35 | 137.28 | 45.33 | 86.04 | | 164.62 | 50.05, 55.26, 114.06, 126.67, 127.68, 158.99, 165.42 |
| **4c** | 35.75 | 60.98 | 24.05 | 143.13 | 136.08 | 45.33 | 86.87 | | 164.00 | 50.17, 127.50, 128.80, 133.05, 133.80, 165.50 |
| **4d** | 35.69 | 61.07 | 23.16 | 141.68 | 127.56 | 43.92 | 85.79 | | 164.20 | 50.08, 107.56, 111.53, 142.32, 151.55, 165.49 |
| **4e** | 35.39 | 61.03 | 23.38 | 141.51 | 131.94 | 45.78 | 91.16 | | 163.86 | 50.10, 124.42, 125.47, 127.64, 139.38, 165.36 |
| **4g** | 52.18 | 57.45 | 23.86 | 143.10 | 136.44 | 45.48 | 87.03 | | 163.52 | 50.30, 127.24, 127.54, 128.11, 128.55, 128.85, 133.14, 133.79, 138.17, 165.40 |
| **4h** | 52.24 | 57.58 | 23.02 | 141.48 | 127.98 | 44.15 | 86.23 | | 157.42 | 50.18, 107.71, 111.58, 127.18, 128.11, 128.52, 138.34, 142.40, 151.63, 165.43, 142.40, 151.63, 165.43 |
| **4i** | 52.07 | 57.44 | 23.07 | 139.23 | 132.22 | 45.79 | 85.70 | | 163.39 | 50.19, 124.44, 125.55, 127.13, 127.63, 128.02, 128.46, 138.08, 141.20, 165.27 |

[a] Spectra were recorded at 125.77 MHz (**3b**,**d**−**f**,**h**,**i**; **4b**,**g**,**h**,**i**) or 50.32 MHz; assigments are based on C,H correlation and HMBC spectra for **3b**,**d**,**e**,**h**,**i** and **4e**,**g**,**h**. − [b] Signal not assigned.

**Mechanistic Considerations**

Alkoxycarbene transfer to enaminones **1a**−**o** leads to enamino esters **2** which can be considered as products of carbene insertion into the carbon chain of the precursor. This transformation is completely analogous to that of acyclic tertiary enaminones[5] for which we have shown that the insertion products result from a ring-opening reaction of which can be attributed to the 2:1 insertion product **11i**, tetrahydroindole **3i**, and 1:1 insertion product **2i**, respectively. Since enamino esters **2** were the only carbene transfer products formed from enamino ketones **1j**−**m** and enamino esters **1n**,**o**, it is to be assumed that in these cases, the olefinic C−C bond is no longer sufficiently electron-rich to react with the electrophilic carbene or (more likely) the (carbene)copper complex.

Scheme 6



The cyclization of carbene-insertion products **9** and **11** to form tetrahydrocyclopenta[*b*]pyrroles **4** and tetrahydroindoles **3** rests on enamine reactivity. In both cases, we postulate a tautomerization which converts the exocyclic into the endocyclic enamine (**2** → **9** and **11** → **12**), followed by an enamine-to-carbonyl cyclization[15] (**9** → **10** and **11** → **3**). The interconversion semicyclic/cyclic enamine is a known fact, although it must be added that the five-membered enamine largely prefers the exocyclic form[16]. The feasability of the cyclization reaction **9** → → **4** decreases in the sequence NMe > $NCH_2Ph$ > NPh, which reflects the decreasing nucleophilicity of the enamine function. Similarly, the cyclization **11** → **3** occurs more readily for NMe than for $NCH_2Ph$. In the case of the *N*-phenyl systems **2j**−**m**, the cyclization did not even occur under conditions which were supposed to activate the carbonyl group by proton or Lewis acid catalysis.

## Conclusion

Alkoxycarbonylcarbene transfer to semicyclic tertiary enaminones **1** leads in acceptable yields to enamino esters **2** which formally represent products of carbene insertion into the carbon chain of the enaminone. If the enaminic C=C bond of **2** is still sufficiently electron-rich, this homologation sequence can be repeated. The accumulation of functional groups makes these 1:1 and 1:2 carbene-insertion products interesting building blocks for further transformations. This has been demonstrated here for the cyclocondensation reactions leading to cyclopenta[*b*]pyrrole and indole ring systems (**4** and **3**, respectively). Since the tetrahydroindoles **3** can be dehydrogenated effectively, alkoxycarbonylcarbene transfer to semicyclic enaminones **1** opens a short, convenient route to indole-6,7-dicarboxylates.

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## Experimental Section

All reactions were carried out in oven-dried glassware and under argon. Solvents were dried by standard procedures. The petroleum ether used had a boiling range of 30−65°C. Column chromatography was performed under hydrostatic conditions (silica gel Si 60, Macherey-Nagel, 0.063−0.2 mm) and under medium-pressure conditions (Merck LiChroprep columns, Si 60, particle size 40−63 μm; two columns (240 × 10 mm and 310 × 25 mm) connected; gradient pump Merck-Hitachi L6200). − NMR: Bruker AMX 500 ($^1H$: 500.14 MHz; $^{13}C$: 125.77 MHz) and Bruker AC 200 ($^1H$: 200.13 MHz; $^{13}C$: 50.32 MHz); $CDCl_3$ was used as solvent. As the internal reference, $Me_4Si$ was used for the proton spectra, and the solvent signal for the $^{13}C$-NMR spectra [$\delta(CDCl_3)$ = 77.0]. − IR: Perkin-Elmer IR 883 spectrometer. − MS: Varian MAT 711. − Microanalyses: Perkin-Elmer EA 240 and EA 2400.

*Synthesis of Enamino Ketones:* Enamino ketones **1a**−**e**[6] were prepared by published methods.

*2-(1-Benzyltetrahydro-1H-pyrrol-2-ylidene)-1-(4−chlorophenyl)-1-ethanone* (**1g**) − *Typical Procedure:* A two-phase mixture of 1-benzylpyrrolidin-2-one (34.95 g, 0.20 mol) and dimethyl sulfate (25.29 g, 0.20 mol) was heated at 80°C for 12 h. After cooling, the homogeneous liquid was washed with ether (50 ml) and residual solvent was removed in vacuo. The liquid residue was slowly added to a solution of NaOEt prepared from sodium (9.19 g, 0.40 mmol) in ethanol (300 ml). After 4 h, the precipitate (sodium methyl sulfate) was filtered off with suction in argon, the solvent was evaporated, and the residue was distilled at 100−105°C/0.01 mbar to give 1-benzyl-2,2-diethoxypyrrolidine (43.6 g; ref.[8]: b.p. 102−104°C/6 mbar) which was used immediately. A mixture of this acetal (43.6 g, 0.18 mol) and of 4-chloroacetophenone (27.06 g, 0.18 mol) was heated at 80°C for 8 h. The ethanol formed was removed in vacuo, and **1g** was precipitated from the remaining liquid by addition of ether and stirring at 0°C; yield: 30.01 g (55.0%); m.p. 114−115 °C, yellow needles. − IR (KBr): $\tilde{\nu}$ = 1620, 1586, 1570, 1530, 1476, 1450, 1354, 1305, 1219, 1192, 1177, 1082, 1009 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.02 (quint, 2 H, 4′-$CH_2$), 3.41−3.50 (2 t, 4 H, 3′-$CH_2$, 5′-$CH_2$), 4.49 (s, 2 H, C$H_2$Ph), 5.80 (s, 1 H, NC=CH), 7.19−7.38 (m, 5 H, $C_6H_5$), 7.29/7.73 (AA′BB′ system, 4 H, $C_6H_4$). − $^{13}C$ NMR (125.77 MHz): δ = 20.84 (C-4′), 33.84 (C-3′), 50.30 (*C*$H_2$Ph), 52.71 (C-5′), 86.44 (NC=*C*), 127.09, 127.73, 128.08, 128.58, 128.85, 135.31, 136.20, 140.28 (C−Cl), 167.75 (C-2′), 186.30 (C=O). − $C_{19}H_{18}ClNO$ (311.8): calcd. C 73.19, H 5.82, N 4.49; found C 72.93, H 5.74, N 4.27.

*2-(1-Benzyltetrahydro-1H-pyrrol-2-ylidene)-1-(4-methoxyphenyl)-1-ethanone* (**1f**): From 1-benzyl-2,2-diethoxypyrrolidine

and 4-methoxyacetophenone; yield: 72%; m.p. 143°C. − IR (KBr): $\tilde{\nu}$ = 1732, 1619, 1599, 1574, 1528, 1495, 1478, 1302, 1243, 1225, 1158, 1023 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.03 ($m_c$, 2 H, 4′-$CH_2$), 3.42 ($m_c$, 2 H), 3.47 ($m_c$, 2 H), 3.80 (s, 3 H, OMe), 4.51 (s, 2 H, C*H*$_2$Ph), 5.88 (s, 1 H, =CH), 6.85/7.81 (AA′BB′ system, 4 H, $C_6H_4$), 7.22−7.37 (m, 5 H, $C_6H_5$). − $^{13}C$ NMR (125.77 MHz): δ = 21.52 (4′-$CH_2$), 33.62, 54.75, 55.24, 88.81 (NC=*C*), 113.17, 124.77, 126.41, 129.15, 129.56, 134.26, 141.37, 161.61, 165.47, 187.52 (C=O). − $C_{20}H_{21}NO_2$ (307.4): calcd. C 78.15, H 6.89, N 4.56; found C 77.97, H 6.87, N 4.52.

*2-(1-Benzyltetrahydro-1H-pyrrol-2-ylidene)-1-(2-furyl)-1-ethanone* (**1h**): From 1-benzyl-2,2-diethoxypyrrolidine and 2-acetylfuran; yield: 25.29 g (83%); m.p. 144 °C. − IR (KBr): $\tilde{\nu}$ = 1610, 1562, 1535, 1477, 1449, 1305, 1244, 1148, 1098, 1012, 1004 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.00 (quint, 2 H, 4′-$CH_2$), 3.38 (t, 2 H, 5′-$CH_2$), 3.44 (t, 2 H, 3′-$CH_2$), 4.51 (s, 2 H, C*H*$_2$Ph), 5.91 (s, 1 H, NC=CH), 6.41 (dd, *J* = 3.3, 1.8 Hz, 4-$H_{furyl}$), 6.96 (dd, *J* = 3.3, 0.8 Hz, 3-$H_{furyl}$), 7.23 (d, 2 H, *o*-Ph), 7.30 (t, 1 H, *p*-Ph), 7.34 (t, 2 H, *m*-Ph), 7.39 (dd, *J* = 1.8, 0.8 Hz, 1 H, 5-$H_{furyl}$). − $^{13}C$ NMR (125.77 MHz): δ = 20.74 (C-4′), 33.68 (C-3′), 50.13 (*C*H$_2$Ph), 52.26 (C-5′), 85.72 (NC=*C*), 111.48, 111.97, 127.22, 127.61, 128.72, 135.41, 143.21, 155.82, 167.20 (C-2), 176.92 (C=O). − $C_{17}H_{17}NO$ (267.3): calcd. C 76.38, H 6.41, N 5.24; found C 76.14, H 6.28, N 5.00.

*2-(1-Benzyltetrahydro-1H-pyrrol-2-ylidene)-1-(2-thienyl)-1-ethanone* (**1i**): From 1-benzyl-2,2-diethoxypyrrolidine and 2-acetylthiophene; yield: 42.11 g (77%); m.p. 110−112 °C. − IR (KBr): $\tilde{\nu}$ = 1590, 1535, 1470, 1442, 1408, 1335, 1297, 1215, 1186, 1079, 1022 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 1.99 (quint, 2 H, 4′-$CH_2$), 3.39−3.48 (2 t, 4 H, 3′-, 5′-$CH_2$), 4.48 (s, 2 H, C*H*$_2$Ph), 5.79 (s, 1 H, NC=CH), 6.99 (dd, 1 H, *J* = 5.0, 3.7 Hz, 4-$H_{thienyl}$), 7.20−7.36 (m, 6 H, $C_6H_5$ + 5-$H_{thienyl}$), 7.46 (dd, *J* = 3.7, 1.2 Hz, 3-$H_{thienyl}$). − $^{13}C$ NMR (125.77 MHz): δ = 20.79 (C-4′), 33.64 (C-3′), 50.22 (*C*H$_2$Ph), 52.56 (C-5′), 86.26 (NC=*C*), 127.12, 127.18, 127.30, 127.62, 128.75, 129.31, 135.40, 149.06, 166.96 (C-2), 180.13 (C=O). − $C_{17}H_{17}NOS$ (283.4): calcd. C 72.05, H 6.05, N 4.94; found C 72.07, H 6.18, N 4.93.

*1-(4-Methoxyphenyl)-2-(1-phenyltetrahydro-1H-pyrrol-2-ylidene)-1-ethanone* (**1j**). − *Typical Procedure:* Triethyloxonium tetrafluoroborate (35.24 g, 0.18 mol) was added at 20°C to a stirred solution of 1-phenylpyrrolidin-2-one (29.89 g, 0.18 mol) in toluene (40 ml). After 1 h, two layers had formed, and the upper one was pipetted off. The remaining solution was cooled (0°C), and a solution of NaOEt, prepared from sodium metal (5.11 g, 0.22 mol) and ethanol (130 ml), was added. After 10 h, the precipitate ($NaBF_4$) was filtered off with suction in argon, the solvent was evaporated, and the residue was distilled at 130°C/0.004 mbar to give 2,2-diethoxy-1-phenylpyrrolidine as a colorless oil (28.5 g, 65%). To the lactam acetal (7.00 g, 29.7 mmol) was added 4-methoxyacetophenone (4.40 g, 29.7 mmol) and after heating the mixture in an oil bath (100°C) for 6 h, **1j** was precipitated by addition of petroleum ether at room temperature; yield: 5.40 g (62%); m.p. 125°C. − IR (KBr): $\tilde{\nu}$ = 1677, 1599, 1572, 1526, 1526, 1474, 1390, 1303, 1243, 1207, 1177, 1155, 1112, 1049, 1020 $cm^{-1}$. − $^1H$ NMR (200.13 MHz): δ = 2.15 (quint, 2 H, 4′-$CH_2$), 3.55 (dt, *J* = 7.8, 1.0 Hz, 2 H, $CH_2$), 3.80 (t, *J* = 7.1 Hz, 2 H, 5′-$CH_2$), 3.80 (s, 3 H, $OCH_3$), 6.09 (s, 1 H, NC=CH), 6.83/7.54 (AA′BB′ system, 4 H, $C_6H_4$), 7.25−7.49 (m, 5 H, $C_6H_5$). − $^{13}C$ NMR (50.32 MHz): δ = 21.54 (C-4′), 33.65 (C-3′), 54.78 ($NCH_2$), 55.27 ($OCH_3$), 88.81 (NC=*C*), 113.17, 124.78, 126.42, 129.17, 129.57, 134.24, 141.34 (N*C*$_{Ph}$), 161.61 (*C*OMe), 165.50 (N*C*=C), 187.53 (C=O). − $C_{19}H_{19}NO_2$ (293.4): calcd. C 77.79, H 6.53, N 4.77; found C 77.84, H 6.56, N 4.81.

*1-(4-Chlorophenyl)-2-(1-phenyltetrahydro-1H-pyrrol-2-ylidene)-1-ethanone* (**1k**): From 2,2-diethoxy-1-phenylpyrrolidine and 4-chloroacetophenone; yield: 6.73 g (76%), colorless crystals; m.p. 140−141°C. − IR (KBr): $\tilde{\nu}$ = 1618, 1587, 1569, 1530, 1494, 1470, 1410, 1300, 1249, 1209, 1172, 1110, 1089, 1049, 1009 $cm^{-1}$. − $^1H$ NMR (200.13 MHz): δ = 2.16 (quint, 2 H, 4′-$CH_2$), 3.56 (t, *J* = 7.7 Hz, 2 H, 3′-$CH_2$), 3.82 (t, *J* = 7.4 Hz, 2 H, 5′-$CH_2$), 6.00 (s, 1 H, NC=CH), 7.26−7.70 (m, 9 H, H-aryl). − $^{13}C$ NMR (50.32 MHz): δ = 21.40 (C-4′), 33.83 (C-3′), 55.07 (C-5′), 88.59 (NC=*C*), 124.83, 126.81, 128.14, 128.65, 129.66, 136.46, 139.87, 140.94, 166.64 (N*C*=C), 186.92 (C=O). − $C_{18}H_{16}ClNO$ (297.8): calcd. C 72.60, H 5.42, N 4.70; found C 72.59; H 5.50, N 4.66.

*1-(2-Furyl)-2-(1-phenyltetrahydro-1H-pyrrol-2-ylidene)-1-ethanone* (**1l**): From 2,2-diethoxy-1-phenylpyrrolidine and 2-acetylfuran; yield: 6.09 g (63%), pale-yellow crystals; m.p. 167−168°C. − IR (KBr): $\tilde{\nu}$ = 1618, 1544, 1495, 1467, 1407, 1301, 1232, 1162, 1021 $cm^{-1}$. − $^1H$ NMR (200.13 MHz): δ = 2.16 (quint, 2 H, 4′-$CH_2$), 3.55 (dt, *J* = 7.8, 1.1 Hz, 2 H, 3′-$CH_2$), 3.81 (t, *J* = 7.2 Hz, 2 H, 5′-$CH_2$), 6.03 (s, 1 H, NC=CH), 6.39 (dd, *J* = 3.4, 1.7 Hz, 1 H, 4-$H_{furyl}$), 6.90 (d, *J* = 2.7 Hz, 1 H, 4-$H_{furyl}$), 7.25−7.50 (m, 6 H, $C_6H_5$ + 5-$H_{furyl}$). − $^{13}C$ NMR (50.32 MHz): δ = 21.44 (C-4′), 33.76 (C-3′), 54.93 (C-5′), 88.26 (NC=*C*), 111.56, 112.51, 124.73, 126.58, 129.57, 143.64, 155.64, 161.27, 165.80 (N*C*=C), 177.69 (C=O). − $C_{16}H_{13}NO_2$ (251.3): calcd. C 75.87, H 5.97, N 5.53; found C 75.92, H 6.03, N 5.50.

*2-(1-Phenyltetrahydro-1H-pyrrol-2-ylidene)-1-(2-thienyl)-1-ethanone* (**1m**): From 2,2-diethoxy-1-phenylpyrrolidine and 2-acetylthiophene; yield: 2.51 g (67%), yellow crystals; m.p. 149°C. − IR (KBr): $\tilde{\nu}$ = 1732, 1680, 1601, 1575, 1541, 1509, 1491, 1453, 1439, 1421, 1266, 1222, 1169, 1106, 1031 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.14 (quint, 2 H, 4′-$CH_2$), 3.52 (dt, *J* = 7.3, 1.2 Hz, 2 H, 3′-$CH_2$), 3.79 (t, *J* = 7.2 Hz, 2 H, 5′-$CH_2$), 5.96 (s, 1 H, NC=CH), 6.95 (dd, *J* = 5.0, 3.7 Hz, 1 H, 4-$H_{thienyl}$), 7.29 ($m_c$, 3 H, $H_{Ph}$), 7.33 (dd, $^3J$ = 3.7, 1.2 Hz, 1 H, 3-$H_{thienyl}$), 7.35 (dd, *J* = 4.9, 1.2 Hz, 1 H, 5-$H_{thienyl}$), 7.44 ($m_c$, 2 H, *o*-$H_{Ph}$). − $^{13}C$ NMR (125.77 MHz): δ = 21.43 (C-4′), 33.69 (C-3′), 54.93 (C-5′), 88.63 (NC=*C*), 124.57, 126.67, 127.39, 127.66, 129.57, 129.89, 141.02 ($NC_{Ph}$), 148.95 (C-$2_{thienyl}$), 165.75 (N*C*=C), 181.00 (C=O). − MS (EI, 70 eV); *m/z* (%): 269 (92) [$M^+$], 252 (49), 236 (12), 186 (23), 158 (100) [$M^+ - COC_4H_3S$], 111 (37) [$COC_4H_3S$]. − $C_{16}H_{15}NOS$ (269.4): calcd. C 71.34, H 5.61, N 5.20; found C 71.49, H 5.63, N 5.14.

*Catalytic Decomposition of Diazoacetates in the Presence of Enaminones* **1a−o**

*General Procedure.* − a) *Reactions with Enaminones* **1a−i**: To a solution of the enaminone (2.5 mmol) and of copper(I) trifluoromethanesulfonate benzene complex [$CuO_3SCF_3 \cdot 0.5\ H_2O$, 63 mg, 0.25 mmol) in dichloromethane was added a solution of methyl diazoacetate[17] (MDA, 500 mg, 5.0 mmol) during 26 h via a syringe pump (Bioblock Scientific, model A-99, flow rate about 0.25 ml/h). The solvent was evaporated (20°C/0.005 mbar), and the residue was separated by column chromatography on silica gel (40 g, ethyl acetate as eluant). A fraction containing the "carbene dimers" dimethyl fumarate and dimethyl maleate was eluated first [combined yield determined after additional purification by Lobar-column chromatography, diethyl ether/petroleum ether (3:7)]. The following product fractions were combined and processed further as follows:

a$_1$) *Reactions with Compounds* **1a−e**: The solvent was replaced by ethyl acetate (5 ml). Fractional crystallization of **3a−e** could be achieved by slowly reducing the volume of the solution during several days. The crystals obtained were washed with cold ethyl acetate, the mother liquor and the filtrate were combined, and the crys-

tallization was repeated until **3** was no longer present in solution (NMR control). Then, the residual mother liquor was concentrated, and the residue was subjected to bulb-to-bulb distillation at 250°C/0.009 mbar to produce cyclopenta[*b*]pyrrole derivatives **4b**−**e** which were crystallized from ethyl acetate (−78°C). When the reactions were carried out with 3 equivalents of methyl diazoacetate (751 mg, 7.5 mmol), products **4** were not formed in significant quantities, and only **3a**−**e** had to be isolated.

a$_2$) *Reactions with Enaminones* **1f**−**i**: The product fractions were collected, the solvent was stripped off, and the residue was heated at 100°C for 10 min in a Kugelrohr apparatus. Lobar-column chromatography [eluant diethyl ether/petroleum ether (8:2)] yielded first enamino esters **2f**−**i**, then tetrahydroindoles **3f**−**i**.

b) *Reactions with Enaminones* **1j**−**o**: A solution of enaminone **1** (2.5 mmol) and of copper(II) acetylacetonate (65 mg, 0.25 mmol) in ethyl acetate (10 ml) was heated at reflux, and a solution of the diazo compound − methyl diazoacetate[17] (MDA, 500 mg, 5.0 mmol) or *tert*-butyl diazoacetate[18] (BDA, 710 mg, 5.0 mmol) − was added dropwise during 1 h. For the isolation of **2j**−**m**, the solvent was evaporated (20°C/0.005 mbar), and the residue was separated by column chromatography on silica gel (40 g, ethyl acetate as eluant). A fraction containing the "carbene dimers" dimethyl fumarate and dimethyl maleate was eluated first [combined yield determined after additional purification by Lobar-column chromatography, diethyl ether/petroleum ether (3:7)]. The subsequent product fraction was purified by Lobar-column chromatography (diethyl ether as eluant) and furnished **2j**−**m** after crystallization from diethyl ether at −20°C.

For the isolation of **2n**,**o**, the solvent was evaporated and the residue was directly subjected to Lobar-column chromatography (eluant: diethyl ether) to furnish the products.

*Dimethyl 1-Methyl-4-phenyl-2,3,5,6-tetrahydro-1H-indole-6,7-dicarboxylate* (**3a**): From **1a** and MDA; yield: 35% (47% when 3 equivalents of MDA were applied); yellow crystals, m.p. 140°C. − IR (KBr): $\tilde{\nu}$ = 1732, 1680, 1582, 1440, 1261, 1231, 1205, 1196, 1175, 1124, 1084 cm$^{-1}$. − $^1$H NMR (200.13 MHz): δ = 2.65−2.90 (m, 2 H, 3-CH$_2$), 2.97 (m$_c$, 2 H, 5-CH$_2$), 3.14 (s, 3 H, NCH$_3$), 3.48 (m$_c$, 2 H, 2-CH$_2$), 3.62 (s, 3 H, OCH$_3$), 3.71 (s, 3 H, OCH$_3$), 3.92 (X part of ABX system, 1 H, 6-H), 7.20−7.40 (m, 5 H, C$_6$H$_5$). − $C_{19}H_{21}NO_4$ (327.3): calcd. C 69.72, H 6.47, N 4.28; found C 69.5, H 6.4, N 4.2.

*Dimethyl 4-(4-Methoxyphenyl)-1-methyl-2,3,5,6-tetrahydro-1H-indole-6,7-dicarboxylate* (**3b**) *and Methyl 4-(4-Methoxyphenyl)-1-methyl-1,2,3,5-tetrahydrocyclopenta[b]pyrrole-6-carboxylate* (**4b**): From **1b** and MDA; yield of **3b**: 26% (47% when 3 equivalents of MDA were applied); yield of **4b**: 15%.

**3b**: Yellow crystals, m.p. 107°C. − IR (KBr): $\tilde{\nu}$ = 1670, 1603, 1512, 1444, 1421, 1216, cm$^{-1}$. − $^1$H NMR (500.14 MHz): δ = 2.65−2.98 (m, 4 H, 3-CH$_2$, 5-CH$_2$), 3.14 (s, 3 H, NCH$_3$), 3.44−3.57 (m, 2 H, 2-CH$_2$), 3.62 (OCH$_3$), 3.71 (OCH$_3$), 3.82 (s, 3 H, OCH$_3$), 3.90 (dd, *J* = 6.6, 6.5 Hz, 1 H, 6-H), 6.90/7.26 (AA′BB′ system, 4 H, C$_6$H$_4$). − $C_{20}H_{23}NO_5$ (357.4): calcd. C 67.22, H 6.49, N 3.92; found C 67.20, H 6.71, N 3.94.

**4b**: Yellow needles, m.p. 156−158°C. − IR (KBr): $\tilde{\nu}$ = 1665, 1625, 1580, 1495, 1430, 1340, 1292, 1277, 1240, 1170, 1102, 1070, 1024 cm$^{-1}$. − $^1$H NMR (500.14 MHz): δ = 2.87 (m, 2 H, 3-CH$_2$), 3.47 (s, 3 H, NMe), 3.69 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 3.87 (m$_c$, 2 H, 2-CH$_2$), 3.91 (s, 2 H, 5-CH$_2$), 6.87/7.39 (AA′BB′ system, 4 H, C$_6$H$_4$). − $C_{17}H_{19}NO_3$ (285.3): calcd. C 71.55, H 6.71, N 4.91; found C 71.6, H 6.7, N 4.8.

*Dimethyl 4-(4-Chlorophenyl)-1-methyl-2,3,5,6-tetrahydro-1H-indole-6,7-dicarboxylate* (**3c**) *and Methyl 4-(4-Chlorophenyl)-1-methyl-1,2,3,5-tetrahydrocyclopenta[b]pyrrole-6-carboxylate* (**4c**): From **1c** and MDA; yield of **3c**: 31% (51% when 3 equivalents of MDA were applied); yield of **4c**: 12%.

**3c**: Yellow crystals, m.p. 166°C. − IR (KBr): $\tilde{\nu}$ = 1737, 1680, 1580, 1492, 1479, 1438, 1400, 1313, 1290, 1262, 1251, 1228, 1207, 1193, 1171, 1123, 1096, 1075, 1023, 1011 cm$^{-1}$. − $^1$H NMR (200.13 MHz): δ = 2.55−3.00 (m, 4 H, 3-CH$_2$, 5-CH$_2$), 3.14 (s, 3 H, NCH$_3$), 3.50 (m$_c$, 2 H, NCH$_2$), 3.62 (s, 3 H, OCH$_3$), 3.71 (s, 3 H, OCH$_3$), 3.92 (dd, *J* = 5.1, 4.9 Hz, 1 H, 6-H), 7.22/7.33 (AA′BB′ system, 4 H, C$_6$H$_4$). − $C_{19}H_{20}ClNO_4$ (361.8): calcd. C 63.07, H 5.57, N 3.87; found C 62.8, H 5.5, N 3.8.

**4c**: Yellow crystals, m.p. 129°C. − IR (KBr): $\tilde{\nu}$ = 1737, 1680, 1580, 1438, 1251, 1229, 1207, 1194, 1172, 1123, 1097 cm$^{-1}$. − $^1$H NMR (200.13 MHz): δ = 2.93 (m$_c$, 2 H, 3-CH$_2$), 3.48 (s, 3 H, NCH$_3$), 3.69 (s, 3 H, OCH$_3$), 3.90 (s + pseudo-t, 4 H, 2-CH$_2$ + 5-CH$_2$), 7.31−7.35 (AA′BB′ system, 4 H, C$_6$H$_4$). − $C_{16}H_{16}ClNO_2$ (289.7): calcd. C 66.33, H 5.56, N 4.83; found C 66.5, H 5.6, N 4.7.

*Dimethyl 4-(2-Furyl)-1-methyl-2,3,5,6-tetrahydro-1H-indole-6,7-dicarboxylate* (**3d**) *and Methyl 4-(2-Furyl)-1-methyl-1,2,3,5-tetrahydrocyclopenta[b]pyrrole-6-carboxylate* (**4d**): From **1d** and MDA; yield of **3d**: 33% (47% when 3 equivalents of MDA were applied); yield of **4d**: 8%.

**3d**: Yellow crystals, m.p. 128−129°C. − IR (KBr): $\tilde{\nu}$ = 1718, 1664, 1571, 1478, 1461, 1442, 1274, 1233; 1186, 1116, 1083 cm$^{-1}$. − $^1$H NMR (500.14 MHz): δ = 2.75−2.79 and 2.95−2.99 (2 m, 2 H, 3-CH$_2$, 3.04 (m$_c$, 2 H, 5-CH$_2$), 3.15 (s, 3 H, NCH$_3$), 3.58 (s, 1 H, OCH$_3$), 3.61 (partly covered m, 2 H, NCH$_2$), 3.66 (s, 3 H, OCH$_3$), 3.91 (X part of ABX system, 1 H, 6-H), 6.47 (pseudo-d, 2 H, 3-H- and 4-H$_{furyl}$), 7.47 (br. s, 1 H, 5-H$_{furyl}$). − $C_{17}H_{19}NO_5$ (317.3): calcd. C 64.35, H 6.04, N 4.41; found C 63.90, H 6.07, N 4.36.

**4d**: Yellow microcrystals, m.p. 151° C. − IR (KBr): $\tilde{\nu}$ = 1729, 1666, 1643, 1603, 1473, 1445, 1427, 1412, 1344, 1312, 1288, 1252, 1216, 1187, 1121, 1081, 1059, 1040, 981, 908 cm$^{-1}$. − $^1$H NMR (200.13 MHz): δ = 2.87 (m$_c$, 2 H, 3-CH$_2$), 3.67 (s, 3 H, OCH$_3$), 3.80−3.90 (m, 2 H, 2-CH$_2$), 3.86 (br. s, 2 H, 5-CH$_2$), 6.35 (d, *J* = 3.3 Hz, 1 H, 3-H$_{furyl}$), 6.41 (dd, *J* = 3.3, 1.7 Hz, 1 H, 4-H$_{furyl}$), 7.39 (d, *J* = 1.7 Hz, 1 H, 5-H$_{furyl}$). − $C_{14}H_{15}NO_3$ (245.3): calcd. C 68.56, H 6.16, N 5.70; found C 68.7, H 6.1, N 5.6.

*Dimethyl 1-Methyl-4-(2-thienyl)-2,3,5,6-tetrahydro-1H-indole-6,7-dicarboxylate* (**3e**) *and Methyl 1-Methyl-4-(2-thienyl)-1,2,3,5-tetrahydrocyclopenta[b]pyrrole-6-carboxylate* (**4e**): From **1e** and MDA; yield of **3e**: 28% (42% when 3 equivalents of MDA were applied); yield of **4e**: 6%.

**3e**: Yellow crystals, m.p. 106−107°C. − IR (KBr): $\tilde{\nu}$ = 1717, 1664, 1568, 1441, 1268, 1227, 1184, 1116 cm$^{-1}$. − $^1$H NMR (500.14 MHz): δ = 2.95 (m$_c$, 2 H, 3-CH$_2$), 3.14 (s, 3 H, NCH$_3$), 3.23 (m$_c$, 2 H, 5-CH$_2$), 3.62 (s, 3 H, OCH$_3$), ca. 3.65 (partly covered m, 2 H, 2-CH$_2$), 3.70 (s, 3 H, OCH$_3$), 3.93 (dd, *J* = 7.5, 7.0 Hz, 1 H, 6-H), 7.10 (dd, *J* = 5.1, 3.8 Hz, 1 H, 4-H$_{thienyl}$), 7.22 (d, *J* = 3.8 Hz, 1 H, 3-H$_{thienyl}$), 7.38 (d, *J* = 5.1 Hz, 1 H, 5-H$_{thienyl}$). − MS (EI, 70 eV); *m/z* (%): 333 (21) [M$^+$], 302 (3), 274 (100), 215 (48). − $C_{17}H_{19}NO_4S$ (333.4): calcd. C 61.24, H 5.74, N 4.02; found C 60.88, H 5.60, N 4.09.

**4e**: Yellow oil. − IR (film): $\tilde{\nu}$ = 1668, 1608, 1260, 1222, 1205, 1183, 1121, 1080 cm$^{-1}$. − $^1$H NMR (200.13 MHz): δ = 2.81 (m$_c$, 2 H, 3-CH$_2$), 3.47 (NCH$_3$), 3.69 (OCH$_3$), 3.90 (pseudo-t, 2 H, 2-CH$_2$), 3.93 (br. s, 2 H, 5-CH$_2$), 7.03 (dd, *J* = 3.6, 1.1 Hz, 1 H, 3-

$H_{thienyl}$), 7.08 (dd, $J$ = 4.3, 3.6 Hz, 1 H, 4-$H_{thienyl}$), 7.24 (dd, $J$ = 4.3, 1.1 Hz, 1 H, 5-$H_{thienyl}$). − $C_{14}H_{15}NO_2S$ (261.3): calcd. C 64.35, H 5.79, N 5.36; found C 64.6, H 5.6, N 5.4.

*Methyl 2-(1-Benzyltetrahydro-1H-pyrrol-2-ylidene)-4-(4-methoxyphenyl)-4-oxobutanoate* (**2f**) *and Dimethyl 1-Benzyl-4-(4-methoxyphenyl)-2,3,5,6-tetrahydro-1H-indole-6,7-dicarboxylate* (**3f**): From **1f** and MDA; yield of **2f**: 28%; yield of **3f**: 35% (79% when 3 equivalents of MDA were applied).

**2f**: Yellow crystals, mixture of two diastereomers (6.9:1 by NMR), m.p. 108°C. − IR (KBr): $\tilde{\nu}$ = 1686, 1595, 1510, 1493, 1451, 1439, 1419, 1404, 1360, 1344, 1324, 1304, 1291, 1263, 1217, 1201, 1190, 1171, 1111, 1065, 1030, 1012 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 1.99 [minor isomer: 1.88] (quint, 2 H, $NCH_2CH_2$), 3.29 [2.60] (t, $J$ = 7.7[7.6] Hz, 2 H, $CH_2$), 3.39 [?] (t, $J$ = 6.9 Hz, 2 H, $CH_2$), 3.56 [3.47] (s, 3 H, $OCH_3$), 3.81 [3.79] (s, 3 H, $OCH_3$), 3.86 [3.92] (s, 2 H, $CH_2CO$), 4.42 [4.61] (s, 2 H, $CH_2Ph$), 6.79 [6.93]/7.69 [8.03] (AA′BB′ system, 4 H, $C_6H_4$), 7.06 ($m_c$, 2 H, Ph), 7.21−7.39 (m, 3 H, Ph). − $^{13}C$ NMR signals of major isomer (125.77 MHz): δ = 22.00 ($NCH_2CH_2$), 35.47 ($NCH_2CH_2CH_2$), 37.97 (C-3), 50.59 ($OCH_3$), 53.91 ($CH_2Ph$), 55.36 ($OCH_3$), 55.65 ($NCH_2$), 87.93 (NC=*C*), 113.56, 125.72, 127.06, 128.74, 138.38, 130.43, 163.09 (*C*OMe), 165.20 (NC=), 170.63 (*C*OOMe), 198.95 (C=O). − $C_{23}H_{25}NO_4$ (379.4): calcd. C 72.81, H 6.64, N 3.69; found C 72.05, H 6.31, N 3.61.

**3f**: Pale-yellow crystals, m.p. 109−110°C. − IR (KBr): $\tilde{\nu}$ = 1731, 1679, 1604, 1561, 1509, 1464, 1439, 1428, 1271, 1255, 1225, 1205, 1179, 1166, 1110 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.70−2.75 (m, 2 H, 3-$CH_2$), 2.95−2.98 (m, 2 H, 5-$CH_2$), 3.35−3.39 (m, 2 H, 2-$CH_2$), 3.59 (s, 3 H, $OCH_3$), 3.63 (s, 3 H, $OCH_3$), 3.82 (s, 3 H, $OCH_3$), 3.93 (X part of ABX system, 1 H, 6-H), 4.75/5.02 (AB system, $^2J$ = 15.8 Hz, 2 H, $CH_2Ph$), 6.88 (part of AA′BB′ system, 2 H, $C_6H_4$), 7.23−7.34 (m, 7 H, $H_{Ar}$). − $C_{26}H_{27}NO_5$ (433.5): calcd. C 72.04, H 6.28, N 3.23; found C 71.35, H 6.21, N 3.19.

*Methyl 2-(1-Benzyltetrahydro-1H-pyrrol-2-ylidene)-4-(4-chlorophenyl)-4-oxobutanoate* (**2g**) *and Dimethyl 1-Benzyl-4-(4-chlorophenyl)-2,3,5,6-tetrahydro-1H-indole-6,7-dicarboxylate* (**3g**): From **1g** and MDA; yield of **2g**: 20%; yield of **3g**: 26% (55% when 3 equivalents of MDA were applied).

**2g**: Yellow crystals, mixture of diastereomers (6.5:1 by NMR), m.p. 86°C. − IR (KBr): $\tilde{\nu}$ = 1691, 1578, 1493, 1484, 1452, 1428, 1420, 1399, 1361, 1341, 1325, 1286, 1208, 1188, 1171, 1107, 1092, 1066, 1028, 1011. 985 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.00 [minor isomer: 1.89] (m, 2 H, $NCH_2CH_2$), 3.28 [2.62] (t, $J$ = 7.7 [7.8] Hz, 2 H, $NCH_2CH_2CH_2$), 3.41 [3.33] (t, $J$ = 6.9 Hz [7.1 Hz], 2 H, $NCH_2$), 3.56 [3.47] (s, 3 H, $OCH_3$), 3.85 [3.92] (s, 2 H, $CH_2C$=O), 4.41 [4.60] (s, 2 H, $CH_2Ph$), 7.06 (br. d, 2 H, $H_{Ph}$), 7.21−7.32 (m, 3 H, $H_{Ph}$), 7.29 [7.40]/7.62 [7.97] (AA′BB′ system, 4 H, $C_6H_4$). − $^{13}C$ NMR (125.77 MHz): δ = 22.00 [minor isomer: 26.55] ($NCH_2CH_2$), 35.47 [32.42] ($NCH_2CH_2CH_2$), 38.48 [40.88] (C-3), 50.65 [52.00] ($OCH_3$), 54.05 [55.02] ($CH_2Ph$), 55.76 [52.30] ($NCH_2CH_2$), 87.62 (NC=*C*) 125.61, 127.19, 127.86, 128.40, 128.52, 128.71, 128.85, 129.37, 129.68, 134.29, 135.38, 138.23, 138.92, 165.64 (NC=), 169.90 (*C*OOMe), 199.41 (C=O). − MS (FD, 8 kV): *m/z* (%) = 383 [M+] (100). − $C_{22}H_{22}ClNO_3$ (383.8): calcd. C 68.84, H 5.78, N 3.65; found C 69.10, H 6.01, N 3.88.

**3g**: Yellow oil which could not be separated from polymeric impurities by distillation or chromatography. − $^1H$ NMR (200.13 MHz): δ = 2.60−2.80 (m, 2 H, 3-H, 5-H), 2.89−2.93 (m, 2 H, 3-H, 5-H), 3.35−3.45 (m, 2 H, 2-$CH_2$), 3.60 and 3.63 (each s, 3 H, $OCH_3$), 3.92 (X part of ABX system, 1 H, 6-H), 4.75/5.03 (AB system, $^2J$ = 15.5 Hz, 2 H, $CH_2Ph$), 7.25−7.35 (m, 9 H, $H_{Ar}$). − No correct elemental analysis was obtained.

*Methyl 2-(1-Benzyltetrahydro-1H-pyrrol-2-ylidene)-4-(2-furyl)-4-oxobutanoate* (**2h**) *and Dimethyl 1-Benzyl-4-(2-furyl)-2,3,5,6-tetrahydro-1H-indole-6,7-dicarboxylate* (**3h**): From **1h** and MDA; yield of **2h**: 18%; yield of **3h**: 29% (55% when 3 equivalents of MDA were applied).

**2h**: Yellow crystals, mixture of diastereomers (6.6:1 by NMR), m.p. 88°C. − IR (KBr): $\tilde{\nu}$ = 1678, 1579, 1468, 1451, 1439, 1431, 1417, 1396, 1324, 1288, 1242, 1226, 1202, 1190, 1161, 1108, 1084, 1069, 1024 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 1.98 [minor isomer: 1.92] (quint, 2 H, 4′-$CH_2$), 3.29 [2.69] (t, $J$ = 7.5 Hz, 2 H, 3′-$CH_2$), 3.39 [3.34] (t, $J$ = 7.0 Hz, 2 H, 5′-$CH_2$), 3.56 [3.47] (s, 3 H, $OCH_3$), 3.81 [3.86] (s, 2 H, $CH_2CO$), 4.51 [4.63] (s, 2 H, $CH_2Ph$), 6.41 [6.46] (dd, $J$ = 3.5, 1.5 Hz, 1 H, 4-$H_{furyl}$), 6.96 [?] (d, $J$ = 3.5 Hz, 1 H, 3-$H_{furyl}$), 7.22−7.30 (m, 5 H, $C_6H_5$), 7.45 [7.59] (d, $J$ = 1.5 Hz, 5-$H_{furyl}$). − $^{13}C$ NMR of major isomer (125.77 MHz): δ = 21.92 (C-4′), 35.55 ($CH_2CO$), 37.87 (C-3′), 50.85 ($OCH_3$), 54.03 (C-5′), 55.64 ($CH_2$), 86.96 (NC=*C*), 111.76, 116.81, 125.77, 127.10, 128.40, 138.26, 145.94 (C-5$_{furyl}$), 152.52 (C-2$_{furyl}$), 165.69 (N*C*=C), 169.86 (*C*OOCH$_3$), 189.54 (C=O). − $C_{20}H_{21}NO_4$ (339.4): calcd. C 70.79, H 6.24, N 4.13; found C 69.89, H 6.01, N 4.12.

**3h**: Yellow oil. − IR (film): $\tilde{\nu}$ = 1712, 1649, 1573, 1442, 1430, 1418, 1342, 1261, 1220, 1206, 1127 $cm^{-1}$. − $^1H$ NMR ($CDCl_3$, 500.14 MHz): δ = 2.77−2.83 (m, 1 H. 5-H), 2.87−2.90 (m, 1 H, 3-H), 3.07−3.12 (m, 1 H, 3-H), 3.14 (dd, $^2J$ = 16.8 Hz, $^3J$ = 1.6 Hz, 1 H, 5-H), 3.42−3.55 (m, 2 H, 2-$CH_2$), 3.56 ($OCH_3$), 3.62 ($OCH_3$), 3.96 (X part of ABX, 1 H, 6-H), 4.77/5.04 (AB system, $^2J$ = 16.0 Hz, 2 H, $CH_2Ph$), 6.47 (dd, $J$ = 3.4, 1.3 Hz, 1 H, 4-$H_{furyl}$), 6.51 (d, $J$ = 3.4 Hz, 1 H, 3-$H_{furyl}$), 7.20−7.40 (m, 5 H, $C_6H_5$), 7.48 (d, $J$ = 1.3 Hz, 1 H, 5-$H_{furyl}$). − MS (FD, 8 kV); *m/z* (%): 393 [$M^+$] (100). − $C_{23}H_{23}NO_5$ (393.4): calcd. C 70.22, H 5.89, N 3.56; found C 69.50, H 6.02, N 3.45.

*Methyl 2-(1-Benzyltetrahydro-1H-pyrrol-2-ylidene)-4-oxo-4-(2-thienyl)butanoate* (**2i**) *and Dimethyl 1-Benzyl-4-(2-thienyl)-2,3,5,6-tetrahydro-1H-indole-6,7-dicarboxylate* (**3i**): From **1i** and MDA; yield of **2i**: 16%; yield of **3i**: 28% (56% when 3 equivalents of MDA were applied).

**2i**: Yellow crystals, mixture of diastereomers (5.7:1 by NMR); m.p. 95°C − IR (KBr): $\tilde{\nu}$ = 1685, 1664, 1587, 1573, 1415, 1289, 1268, 1236, 1192, 1181, 1108, 1074, 1059 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 1.99 [minor isomer: 1.90] (quint, 2 H, 4′-$CH_2$), 3.30 [2.79] (t, $J$ = 8.0 [8.0] Hz, 2 H, 3′-$CH_2$), 3.46 [3.43] (t, $J$ = 7.0 [7.0] Hz, 2 H, 5′-$CH_2$), 3.50 [3.42] (s, 3 H, $OCH_3$), 3.84 [3.90] (s, 2 H, $CH_2CO$), 4.51 [4.63] (s, 2 H, $CH_2Ph$), 7.07−7.29 (m, 5 H, $C_6H_5$), 6.98 (dd, $J$ = 4.5, 3.5 Hz, 1 H, 4-$H_{thienyl}$), 7.40 [7.57] (dd, $J$ = 4.5, 1.0 Hz, 1 H, 3-$H_{thienyl}$), 7.53 [7.82] (dd, $J$ = 3.5, 1.0 Hz, 1 H, 5-$H_{thienyl}$). − $^{13}C$ NMR (125.77 MHz): δ = 21.90 [minor isomer: 20.65] (C-4′), 35.54 [34.92] (C-3′), 38.84 [41.83] ($CH_2CO$), 50.65 [50.56] ($OCH_3$), 54.02 [55.39] ($CH_2Ph$), 55.59 [54.55] ($NCH_2$), 87.28 [85.36] (NC=*C*), 125.69, 127.11, 127.68, 127.73, 128.68, 128.79, 131.65 [131.50], 132.96, 138.20, 143.73, 165.48 (N*C*=C), 169.86 (*C*OOMe), 193.32 [192.30] (C=O). − MS (EI, 70 eV): *m/z* (%) = 355 (9) [$M^+$], 324 (4), 244 (100). − $C_{20}H_{21}NO_3S$ (355.4): calcd. C 67.58, H 5.96, N 3.94; found C 67.61, H 5.96, N 3.98.

**3i**: Yellow microcrystals, m.p. 112°C − IR (KBr): $\tilde{\nu}$ = 1712, 1649, 1573, 1442, 1430, 1417, 1342, 1262, 1220, 1206, 1192, 1127 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.83−2.86 (m, 1 H, 3-H), 2.92−2.96 (m, 2 H, 3-H, 5-H), 3.25 (dd, $^2J$ = 17.0 Hz, $^3J$ = 2.5 Hz, 1 H, 5-H), 3.51 ($m_c$, 2 H, 2-$CH_2$), 3.59 (s, 3 H, $OCH_3$), 3.62 (s, 3 H, $OCH_3$), 3.97 (dd, $J$ = 7.5, 2.5 Hz, 1 H, 6-H), 4.77/5.02 (AB system, $^2J$ = 15.6 Hz, 2 H, $CH_2Ph$), 7.10 (dd, $J$ = 5.1, 3.8 Hz, 4-$H_{thienyl}$), 7.23−7.34 (m, 6 H, $C_6H_5$ and 3-$H_{thienyl}$), 7.39 (dd, $J$ =

5.1, 0.9 Hz, 5-$H_{thienyl}$). − $C_{23}H_{23}NO_4S$ (409.5): calcd. C 67.47, H 5.66, N 3.42; found C 67.46, H 5.66, N 3.42.

*Methyl 4-(4-Methoxyphenyl)-4-oxo-2-(1-phenyltetrahydro-1H-pyrrol-2-ylidene)butanoate* (**2j**): From **1j** and MDA; yield: 53%; yellow crystals, m.p. 108°C. − IR (KBr): $\tilde{\nu}$ = 1678, 1601, 1575, 1509, 1453, 1437, 1421, 1330, 1287, 1262, 1219, 1170, 1107, 1066, 1030 $cm^{-1}$. − $^1H$ NMR (200.13 MHz): δ = 2.06 (quint, 2 H, 4′-$CH_2$), 3.34 (t 2 , 3′-$CH_2$), 3.54 (s, 2 H, $CH_2CO$), 3.60 (s, 3 H, 3.69 (t, 2 H, 5′-$CH_2$), 3.81 (s, 3 H, $OCH_3$), 6.76/7.54 (AA′BB′ system, 4 H, $C_6H_4$), 6.86 ($m_c$, 1 $H_{Ph}$), 7.14−6.98 (m, 4 H, $H_{Ph}$). − $^{13}C$ NMR (50.32 MHz): δ = 21.87 (C-4′), 34.76 (C-3′), 38.51 (*C*$H_2$CO), 50.74 ($OCH_3$), 55.26 ($OCH_3$), 57.20 (C-5′), 92.58 (NC=*C*), 113.02, 124.58, 124.99, 129.11, 129.66, 130.25, 144.60, 160.63, 162.69 (N*C*=C), 170.05 (*C*OOMe), 196.46 (C=O). − $C_{22}H_{23}NO_4$ (365.4): calcd. C 72.31, H 6.34, N 3.83; found C 72.33, H 6.24, N 3.65.

*Methyl 4-(4-Chlorophenyl)-4-oxo-2-(1-phenyltetrahydro-1H-pyrrol-2-ylidene)butanoate* (**2k**): From **1k** and MDA; yield: 462 mg (50%); yellow crystals, m.p. 132°C. − IR (KBr): $\tilde{\nu}$ = 1728, 1675, 1590, 1575, 1519, 1496, 1453, 1438, 1417, 1355, 1266, 1236, 1106, 1067 $cm^{-1}$. − $^1H$ NMR (200.13 MHz): δ = 2.09 ($m_c$, 2 H, 4′-$CH_2$), 3.34 (t, *J* = 7.7 Hz, 2 H, 3′-$CH_2$), 3.54 (s, 2 H, C*H*$_2$CO), 3.65 (t, *J* = 7.7 Hz, 2 H, 5′-$CH_2$), 6.80−7.16 (m, 5 H, $C_6H_5$), 7.27/7.49 (AA′BB′ system, 4 H, $C_6H_4$). − $^{13}C$ NMR (50.32 MHz): δ = 21.81 (C-4′), 34.83 (C-3′), 38.82 (*C*$H_2$C=O), 50.78 ($OCH_3$), 57.31 (C-5′), 91.83 (NC=*C*), 124.74, 125.21, 128.17, 128.90, 129.19, 135.38, 138.39, 144.45, 160.92 (N*C*=C), 169.85 (*C*$OOCH_3$), 196.74 (C=O). − $C_{21}H_{21}ClNO_3$ (369.8): calcd. C 68.21, H 5.45, N 3.79; found C 68.17, H 5.48, N 3.85.

*Methyl 4-(2-Furyl)-4-oxo-2-(1-phenyltetrahydro-1H-pyrrol-2-ylidene)butanoate* (**2l**): From **1l** and MDA; yield: 439 mg (54%), viscous yellow oil. − IR (film): $\tilde{\nu}$ = 1683, 1597, 1490, 1415, 1397, 1322, 1310, 1297, 1228, 1214, 1195, 1103, 1066, 1055, 1027 $cm^{-1}$. − $^1H$ NMR (200.13 MHz): δ = 2.06 (quint, 2 H, 4′-$CH_2$), 3.34 (t, *J* = 7.7 Hz, 2 H, 3′-$CH_2$), 3.45 (s, 2 H, $CH_2CO$), 3.61 (s, 3 H, $OCH_3$), 3.69 (t, *J* = 7.0 Hz, 2 H, 5′-$CH_2$), 6.36 (dd, *J* = 3.5, 1.7 Hz, 1 H, 4-$H_{furyl}$), 6.76 (d, *J* = 3.6 Hz, 1 H, 3-$H_{furyl}$), 6.85−7.26 (m, 5 H, $C_6H_5$), 7.36 (d, *J* = 1.7 Hz, 1 H, 5-$H_{furyl}$). − $^{13}C$ NMR (125.77 MHz): δ = 21.79 (C-4′), 34.87 (C-3′), 38.35 (*C*$H_2$CO), 50.75 ($OCH_3$), 57.31 (C-5′), 91.07 (NC=*C*), 111.41 (C-$3_{furyl}$), 115.51 (C-$4_{furyl}$), 124.80, 125.13, 129.03, 144.32 (N*C*$_{Ph}$), 145.17 (C-$5_{furyl}$), 152.37 (C-$2_{furyl}$), 161.17 (N*C*=C), 169.92 (*C*OOMe), 186.98 (C=O). − $C_{19}H_{19}NO_4$ (325.3): calcd. C 70.15, H 5.89, N 4.31; found C 69.73, H 5.72, N 4.27.

*Methyl 4-Oxo-2-(1-phenyltetrahydro-1H-pyrrol-2-ylidene)-4-(2-thienyl)butanoate* (**2m**): From **1m** and MDA; yield: 119 mg (68%); yellow crystals, m.p. 124°C. − IR (KBr): $\tilde{\nu}$ = 1671, 1570, 1492, 1418, 1398, 1325, 1294, 1279, 1235, 1213, 1177, 1164, 1101, 1077, 1054, 1029 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.07 (quint, 2 H, 4′-$CH_2$), 3.35 (t, *J* = 7.7 Hz, 2 H, 3′-$CH_2$), 3.55 (s, 2 H, $CH_2CO$), 3.62 (s, 3 H, $OCH_3$), 3.70 (t, *J* = 3.7 Hz, 2 H, 5′-$CH_2$), 6.91 (dd, *J* = 4.9, 3.8 Hz, 1 H, 4-$H_{thienyl}$), 7.10−7.30 (m, 5 H, $C_6H_5$), 7.20 (dd, *J* = 3.8, 1.1 Hz, 1 H, 3-$H_{thienyl}$), 7.44 (dd, *J* = 5.0, 1.1 Hz, 1 H, 5-$H_{thienyl}$). − $^{13}C$ NMR (125.77 MHz): δ = 21.83 (C-4′), 34.89 (C-3′), 39.45 (*C*$H_2$CO), 50.81 ($OCH_3$), 57.38 (C-5′), 91.68 (NC=*C*), 124.80, 125.19, 127.29, 129.14, 130.57 (C-$4_{thienyl}$), 132.00 (C-$5_{thienyl}$), 143.87 (C-$2_{thienyl}$), 144.38, 161.14 (NC=), 169.92 (*C*OOMe), 190.69 (C=O). − MS (EI, 70 eV); *m/z* (%): 341 (8) [$M^+$], 230 (100) [$M^+$ − O=$CC_4H_4S$]. − $C_{19}H_{19}NO_3S$ (341.4): calcd. C 66.85, H 5.60, N 4.10 found C 66.74, H 5.40 N 4.10.

*Dimethyl 2-(1-Methyltetrahydro-1H-pyrrol-2-ylidene)-1,4-butanedioate* (**2n**): From **1n**[19] and MDA; yield: 312 mg (55%), mixture of diastereomers (2:1 by NMR); colorless powder, m.p. 135°C. − IR (KBr): $\tilde{\nu}$ = 1737, 1682, 1578, 1434, 1344, 1323, 1290, 1224, 1170, 1112, 1088, 1061 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 1.88 [minor isomer: 1.94] (quint, 2 H, 4′-$CH_2$), 3.05 [2.94] (s, 3 H, $NCH_3$], 3.12 [2.64] (t, *J* = 7.8 Hz, 2 H, 3′-$CH_2$), 3.35 [3.52] (t, *J* = 7.4 Hz, 2 H, 5′-$CH_2$), 3.47 [3.33] ($CH_2$C=O), 3.62 [3.64] (s, 3 H, $OCH_3$), 3.70 [3.68] (s, 3 H, $OCH_3$). − $^{13}C$ NMR (125.77 MHz): δ = 21.59 [20.56] (4′-C), 33.60 [36.18] (*C*$H_2$CO), 35.46 [33.96] (3′-C), 38.16 [39.98] ($NCH_3$), 50.58 ($OCH_3$), 51.79 [51.68] ($OCH_3$), 57.22 [57.97] (5′-C), 86.07 [85.99] (NC=*C*), 165.44 (N*C*=C), 170.06 (C=O), 174.54 [174.30] (C=O). − $C_{11}H_{17}NO_4$ (227.2): calcd. C 58.14, H 7.54, N 6.16; found C 57.98, H 7.26, N 6.16.

*Di-tert-butyl 2-(1-Methyltetrahydro-1H-pyrrol-2-ylidene)-1,4-butanedioate* (**2o**): From **1o**[20] and BDA; yield: 420 mg (54%), mixture of diastereomers (2.4:1 by NMR); colorless oil. − IR (film): $\tilde{\nu}$ = 1733, 1674, 1582, 1478, 1454, 1392, 1364, 1343, 1325, 1289, 1240, 1223, 1148, 1120, 1092, 1052, 1011 cm $^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 1.43−1.46 (4 s, 18 H, *t*Bu of both isomers), 1.84 [minor isomer: 1.93] (quint, 2 H, 4′-$CH_2$), 3.01 [2.90] (s, 3 H, $NCH_3$), 3.06 [2.60] (t, *J* = 7.7 [7.8] Hz, 2 H, 3′-$CH_2$), 3.27 [3.46] (t, *J* = 6.9 [6.9] Hz, 2 H, 5′-$CH_2$), 3.32 (s, 2 H, $CH_2CO$). − $^{13}C$ NMR (125.77 MHz): δ = 21.91 [20.10] (C-4′), 28.17 [28.17], 28.57 [28.52], 33.75 (*C*$H_2$C=O), 35.31 [35.36] ($CH_2$), 38.32 [38.04] ($NCH_3$), 56.99 [57.82] (C-5′), 79.75 and 78.05 th *C*$(CH_3)_3$], 89.08 (NC=*C*), 164.20 (N*C*=C), 169.0 (C=O), 173.41 (C=O). − $C_{17}H_{29}NO_4$ (311.4): C 65.57, H 9.39, N 4.50; found C 64.86, H 9.10, N 4.72.

*Tetrahydrocyclopenta[b]pyrroles* **4g**−**i**

*General Procedure:* A solution of enamino esters **2g**−**i** (100 mg) in toluene (2 ml), to which ca. 30 mg of silica gel had been added, was kept in a Schlenk pressure tube at 140°C during 1 h. After cooling, the silica gel was filtered off, and the solvent was evaporated. The oily residue crystallized after addition of diethyl ether.

*Methyl 1-Benzyl-4-(4-chlorophenyl)-1,2,3,5-tetrahydrocyclopenta[b]pyrrole-6-carboxylate* (**4g**): Obtained from **2g**; yield: 93%; yellow microcrystals, m.p. 73°C. − IR (KBr): $\tilde{\nu}$ = 1672, 1634, 1593, 1581, 1444, 1261, 1250, 1212, 1172, 1102 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.88 ($m_c$, 2 H, 3-$CH_2$), 3.69 (s, 3 H, $OCH_3$), 3.82 (t, *J* = 7.5 Hz, 2 H, 2-$CH_2$), 3.97 (s, 2 H, 5-$CH_2$), 5.26 (s, 2 H, C*H*$_2$Ph), 7.27−7.38 (m, 9 H, $H_{Ar}$). − $C_{22}H_{20}ClNO_2$ (365.8): calcd. C 72.23, H 5.51, N 3.83; found C 72.39, H 5.41, N 3.76.

*Methyl 1-Benzyl-4-(2-furyl)-1,2,3,5-tetrahydrocyclopenta[b]pyrrole-6-carboxylate* (**4h**): Obtained from **2k**; yield: 94%; yellow needles, m.p. 124°C. − IR (KBr): $\tilde{\nu}$ = 1675, 1646, 1590, 1486, 1462, 1442, 1409, 1262, 1224, 1202, 1169, 1147, 1094, 1065, 1028 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.85 ($m_c$, 2 H, 3-$CH_2$), 3.67 (s, 3 H, $OCH_3$), 3.79 (t, *J* = 7.5 Hz, 2 H, 2-$CH_2$), 3.90 (s, 2 H, 5-$CH_2$), 5.24 (s, 2 H, C*H*$_2$Ph), 6.38 (d, *J* = 3.5 Hz, 1 H, 3-$H_{furyl}$), 6.41 (dd, *J* = 3.5, 1.0 Hz, 1 H, 4-$H_{furyl}$), 7.22−7.31 (m, 5 H, $C_6H_5$), 7.40 (d, *J* = 1.0 Hz, 1 H, 5-$H_{furyl}$). − $C_{20}H_{19}NO_3$ (321.4): calcd. C 74.75, H 5.96, N 4.36; found C 74.77, H 6.10, N 4.54.

*Methyl 1-Benzyl-4-(2-thienyl)-1,2,3,5-tetrahydrocyclopenta[b]-pyrrole-6-carboxylate* (**4i**): Obtained from **2j**; yield: 95%; yellow crystals, m.p. 111°C. − IR (KBr): $\tilde{\nu}$ = 1672, 1599, 1579, 1347, 1254, 1202, 1177, 1154, 1104, 1041 $cm^{-1}$. − $^1H$ NMR (200.13 MHz): δ = 2.79 ($m_c$, 2 H, 3-$CH_2$), 3.68 (s, 3 H, $OCH_3$), 3.80 (t, *J* = 7.2 Hz, 2 H, 2-$CH_2$), 3.99 (5-$CH_2$), 5.24 (s, 2 H, C*H*$_2$Ph), 6.90−7.33 (m, 8 H, $C_6H_5$ and $C_4H_3S$). − $C_{20}H_{19}NO_2S$ (337.4): calcd. C 71.19, H 5.68, N 4.15; found C 70.81, H 5.71, N 4.31.

*Dehydrogenation of Tetrahydroindoles* **3c**−**e**

*General Procedure.* − a) For the synthesis of dihydroindoles **5d**,**e**, a mixture of tetrahydroindoles **3d**,**e** (0.60 mmol) and tetrachloro-*p*-

benzoquinone (162 mg, 0.66 mmol) in toluene (5 ml) was heated at reflux for 3 h. After cooling, the solvent was evaporated, and the residue was separated by Lobar-column chromatography [eluant: ethyl acetate/petroleum ether (9:1)].

b) For the synthesis of indoles **6c−e**, a mixture of tetrahydroindoles **3c−e** (0.60 mmol) and tetrachloro-*p*-benzoquinone (1.32 mmol) in toluene (5 ml) was kept in a Schlenk pressure tube at 160°C for 3 h. After cooling, the solvent was evaporated, and the residue was separated by Lobar-column chromatography (eluant: ethyl acetate).

*Dimethyl 4-(2-Furyl)-1-methyl-2,3-dihydro-1H-indole-6,7-dicarboxylate* (**5d**): Obtained from **3d**; yield: 92%; colorless powder, m.p. 135°C (dec.; ref.[13]: 137°C). − IR (KBr): $\tilde{\nu}$ = 1727, 1555, 1501, 1469, 1454, 1432, 1416, 1304, 1285, 1262, 1240, 1208, 1188, 1173, 1152, 1140, 1097, 1033, 1000 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.81 (s, 3 H, $NCH_3$), 3.20 (t, *J* = 8.5 Hz, 2 H, 3-$CH_2$), 3.56 (t, *J* = 8.5 Hz, 2 H, 2-$CH_2$), 3.82 (s, 3 H, $OCH_3$), 3.87 (s, 3 H, $OCH_3$), 6.50 (dd, *J* = 3.5, 1.0 Hz, 1 H, 4-$H_{furyl}$), 6.59 (d, *J* = 3.5 Hz, 3-$H_{furyl}$), 7.50 (d, *J* = 1.0 Hz, 1 H, 5-$H_{furyl}$), 7.63 (s, 1 H, 5-H). − $^{13}C$ NMR (125.77 MHz): δ = 28.85 (C-3), 36.48 ($NCH_3$), 52.31 (2 $OCH_3$), 56.60 (C-2), 108.44 (C-$4_{furyl}$), 111.62 (C-$2_{furyl}$), 112.40, 116.79, 126.6, 128.2, 132.2, 142.4, 150.1, 152.1, 167.1 (C=O), 169.5 (C=O). − MS (EI, 70 eV); *m/z* (%): 315 (100) [$M^+$], 284 (25), 268 (41), 256 (7), 198 (12), 197 (62), 168 (10). − $C_{17}H_{17}NO_5$ (315.3): calcd. C 64.76, H 5.43, N 4.44; found C 64.15, H 5.07, N 4.50.

*Dimethyl 1-Methyl-4-(2-thienyl)-2,3-dihydro-1H-indole-6,7-dicarboxylate* (**5e**): Obtained from **3e**; yield: 91%; colorless powder, m.p. 115°C (dec.) − IR (KBr): $\tilde{\nu}$ = 1720, 1605, 1582, 1555, 1501, 1468, 1453, 1433, 1416, 1305, 1264, 1243, 1205, 1187, 1172, 1140, 1096, 1031, 1000 $cm^{-1}$. − $^1H$ NMR (500.14 MHz): δ = 2.85 (s, 3 H, $NCH_3$), 3.17 (t, *J* = 7.1 Hz, 2 H, 3-$CH_2$), 3.53 (t, *J* = 7.1 Hz, 2 H, 2-$CH_2$), 3.87 (s, 3 H, $OCH_3$), 3.89 (s, 3 H, $OCH_3$), 7.09 (dd, *J* = 3.6, 1.1 Hz, 1 H, 3-$H_{thienyl}$), 7.23 (dd, *J* = 5.0, 3.6 Hz, 1 H, 4-$H_{thienyl}$), 7.35 (dd, *J* = 5.0, 1.1 Hz, 1 H, 5-$H_{thienyl}$), 7.48 (s, 1 H, 5-H). − $^{13}C$ NMR (125.77 MHz): δ = 28.89 (C-3), 36.59 ($NCH_3$), 52.29 (2 $OCH_3$), 56.68 (C-2), 112.80 (C-7), 119.84 (C-5), 125.78 (C-$5_{thienyl}$), 125.95 (C-$2_{thienyl}$), 127.50 (C-$4_{thienyl}$), 128.80, 131.10, 133.65, 141.39 (C-$2_{thienyl}$), 150.19 (C-7a), 169.38 (C=O), 166.79 (C=O). − $C_{17}H_{17}NO_4S$ (331.4): calcd. C 61.62, H 5.17, N 4.22; found C 61.44, H 5.15, N 4.21.

*Dimethyl 4-(4-Chlorophenyl)-1-methyl-1H-indole-6,7-dicarboxylate* (**6c**): Obtained from **3c**; yield: 90%; colorless powder, m.p. 167°C. − IR (KBr): $\tilde{\nu}$ = 1729, 1715, 1504, 1488, 1431, 1389, 1339, 1308, 1299, 1276, 1248, 1224, 1204, 1154, 1017 $cm^{-1}$. − $^1H$ NMR (200.13 MHz): δ = 3.84 (s, 3 H, $NCH_3$), 3.93 (s, 3 H, $OCH_3$), 4.06 (s, 3 H, $OCH_3$), 6.58 (d, *J* = 3.0 Hz, 1 H, 3-H), 7.17 (d, *J* = 3.0 Hz, 1 H, 2-H), 7.44/7.56 (AA′BB′ system, 4 H, $C_6H_4$), 7.78 (s, 1 H, 5-H). − $^{13}C$ NMR (50.32 MHz): δ = 34.86 ($NCH_3$), 52.31 ($OCH_3$), 52.74 ($OCH_3$), 100.75 (C-3), 119.43, 120.30 (C-5), 120.95, 128.75, 130.01, 131.74, 131.93, 133.58, 133.80, 134.66, 138.22 (C-2), 166.93 (C=O), 169.50 (C=O). − $C_{19}H_{16}ClNO_4$ (357.8): calcd. C 63.79, H 4.51, N 3.92; found C 63.71, H 4.41, N 3.71.

*Dimethyl 4-(2-Furyl)-1-methyl-1H-indole-6,7-dicarboxylate* (**6d**): Obtained from **3d**; yield: 94%; nearly colorless oil. − IR (film): $\tilde{\nu}$ = 1715, 1664, 1571, 1479, 1462, 1443, 1408, 1326, 1275, 1229, 1202, 1185, 1157, 1118, 1088, 1078, 1018 $cm^{-1}$. − $^1H$ NMR (200.13 MHz): δ = 3.82 (s, 3 H, $NCH_3$), 3.94 (s, 3 H, $OCH_3$), 4.04 (s, 3 H, $OCH_3$), 6.55 (dd, *J* = 3.4, 1.7 Hz, 1 H, 4-$H_{furyl}$), 6.87 (d, *J* = 3.4 Hz, 1 H, 3-$H_{furyl}$), 6.99 (d, *J* = 3.2 Hz, 1 H, 3-H), 7.22 (d, *J* = 3.2 Hz, 1 H, 2-H), 7.58 (d, *J* = 1.7 Hz, 1 H, 5-$H_{furyl}$), 8.12 (s, 1 H, 5-H). − $^{13}C$ NMR (125.77 MHz): δ = 34.90 ($NCH_3$), 52.37 ($OCH_3$), 52.77 ($OCH_3$), 101.69 (C-3), 107.88 ($CH_{furyl}$), 111.69 ($CH_{furyl}$), 117.28, 118.91, 120.93, 123.63, 132.58, 134.71 (C-$5_{furyl}$), 143.25, 142.38 (C-2), 153.05, 166.97 (C=O), 169.62 (C=O). − $C_{17}H_{15}NO_5$ (313.3): calcd. C 65.18, H 4.83, N 4.47; found C 64.41, H 4.71, N 4.44.

*Dimethyl 1-Methyl-4-(2-thienyl)-1H-indole-6,7-dicarboxylate* (**6e**): Obtained from **3e**; yield: 89%; colorless powder, m.p. 150°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1726, 1708, 1589, 1565, 1495, 1428, 1400, 1363, 1339, 1302, 1273, 1252, 1195, 1155, 1098, 1079, 1035 $cm^{-1}$. − $^1H$ NMR (200.13 MHz): δ = 3.84 (s, 3 H, $NCH_3$), 3.94 (s, 3 H, $OCH_3$), 4.05 (s, 3 H, $OCH_3$), 6.93 (d, *J* = 3.2 Hz, 1 H, 3-H), 7.22 (d, *J* = 3.2 Hz, 1 H, 2-H), 7.17 (dd, *J* = 4.1, 3.6 Hz, 1 H, 4-$H_{thienyl}$), 7.40 (d, *J* = 4.1 Hz, 1 H, 3-$H_{thienyl}$), 7.47 (d, *J* = 3.6 Hz, 1 H, 5-$H_{thienyl}$), 7.97 (s, 1 H, 5-H). − $^{13}C$ NMR (50.32 MHz): δ = 35.01 ($NCH_3$), 52.43 ($OCH_3$), 52.82 ($OCH_3$), 101.44 (C-3), 118.59, 120.14, 121.04, 125.63 (C-$5_{thienyl}$), 125.82 (C-$3_{thienyl}$), 127.69 (C-$4_{thienyl}$), 127.86, 131.09, 134.7 (C-2), 141.99 (C-$2_{thienyl}$), 166.96 (C=O), 169.56 (C=O). − $C_{17}H_{15}NO_4S$ (329.3): calcd C 62.00, H 4.59, N 4.25; found C 61.22, H 4.59, N 4.19.

*X-ray Crystal-Structure Determination of* (*E*)-**2m**[21]. − *Crystal Data:* $C_{19}H_{19}NO_3S$; *M* = 341.4 g/mol; triclinic space group $P\bar{1}$, *a* = 10.299(1), *b* = 11.005(1), *c* = 15.418(1) Å, α = 89.13(1), β = 87.82, γ = 87.10(1)°; *V* = 1443.8(3) $Å^3$; *Z* = 4; $d_{calcd.}$ = 1.300 Mg/$m^3$; μ(Mo-$K_\alpha$) = 0.202 $mm^{-1}$. − *Data Collection:* *T* = 293 K, crystal size 0.6 × 0.4 × 0.2 mm, diffractometer Siemens P4; radiation Mo-$K_\alpha$; Θ range 1.32−22.50°; 5459 reflections collected, 4543 independent reflections ($R_{int}$ = 0.0205). − *Structure Solution and Refinement:* Structure solution by direct methods (program SHELXS-86), full-matrix least-squares refinement on $F^2$ (program SHELXL-93) with 4542 data and 435 variables. Hydrogen atoms are in calculated positions and were treated as riding atoms. *R* = 0.0750 for all reflections [0.0483 for 3303 reflections with $I > 2\sigma(I)$], $R_w$ = 0.1377 (0.1152), residual electron density between 0.17 and −0.33 e $Å^{-3}$.

*X-ray Crystal-Structure Determination of* **4b**[21]. − *Crystal Data:* $C_{17}H_{19}NO_3$; *M* = 285.3 g/mol; monoclinic space group $P2_1/c$, *a* = 7.991(2), *b* = 20.581(5), *c* = 8.575(2) Å, β = 97.85(1)°; *V* = 1397.1(6) $Å^3$; *Z* = 4; $d_{calcd.}$ = 1.357 Mg/$m^3$; μ(Mo-$K_\alpha$) = 0.093 $mm^{-1}$. − *Data Collection:* *T* = 295 K, crystal size 0.7 × 0.25 × 0.2 mm, diffractometer Siemens P4; radiation Mo-$K_\alpha$; Θ range 1.98−23.51°; 2686 reflections collected, 2043 independent reflections ($R_{int}$ = 0.0382). − *Structure Solution and Refinement*: Structure solution by direct methods (program SHELXS-86), full-matrix least-squares refinement on $F^2$ (program SHELXL-93) with 2042 data and 235 variables. Methyl-hydrogen atoms are in calculated positions and were treated as riding atoms, all other H atom positions were taken from a Δ*F* map and refined with isotropic temperature factors. *R* = 0.0811 for all reflections [0.0485 for 1410 reflections with $I > 2\sigma(I)$], $R_w$ = 0.1150 (0.1419), residual electron density between 0.15 and −0.16 e $Å^{-3}$.

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