

Copper-Catalyzed Bis(methoxycarbonyl)carbene Reactions of α,β -Unsaturated Carboxamides

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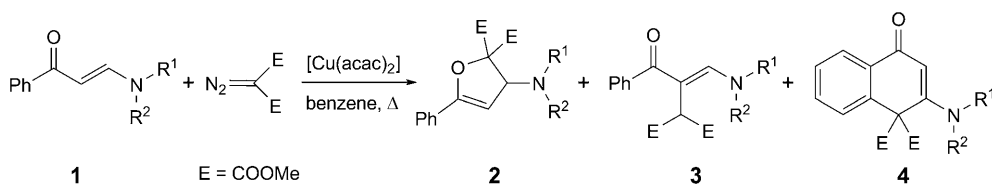
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The $[\text{Cu}(\text{acac})_2]$ -catalyzed reactions of α,β -unsaturated carboxamides with dimethyl diazomalonate yielded dihydrofuran derivatives by a 1,5-electrocyclic reaction at $\text{C}(\beta)$, and butadiene derivatives by carbene addition reaction at $\text{C}(\alpha)$ (Schemes 4 and 5; Table). Phenyl substituents at the N-atom of the amides seem to be effective on the reaction pathways (Table).

Introduction. – Carbene transfer to appropriate substrates is a highly versatile tool for the construction of carbon frameworks with increased functional and structural complexity. The formal $[2+1]$, $[4+1]$, and $[6+1]$ annulations [1][2] of $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl compounds have been widely applied in the enantioselective construction of rings such as oxiranes [3], cyclopropanes [4], dihydrofurans [5], dioxoles [6], dihydrobenzoxepines [7], and other possible derivatives of them. These ring-closure reactions lead to structures frequently occurring in biologically active compounds [8] and extremely useful synthetic intermediates [9] since they can be readily converted to highly functionalized derivatives.

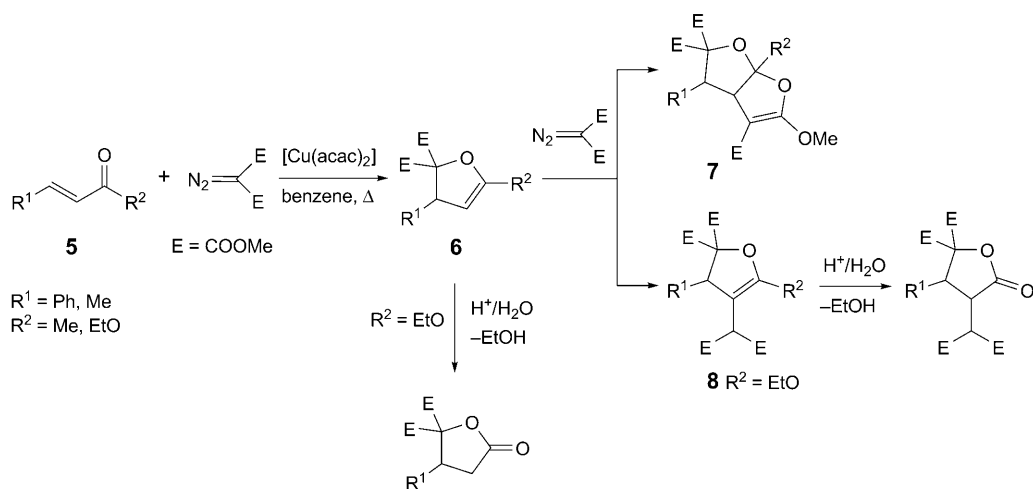
We previously reported on $[\text{Cu}(\text{acac})_2]$ -catalyzed reactions of dimethyl diazomalonate (= dimethyl 2-diazopropanedioate; $\text{E}_2\text{C}=\text{N}_2$) with aminoenones (acac = pentane-2,3-dionato). These reactions resulted in 1,5-cyclization and formal $\text{C}(\alpha)\text{--H}$ insertion products (see **2** and **3** in Scheme 1). In the case of anilino derivatives (R^1 or $\text{R}^2 = \text{Ph}$), products **4** dominated the reaction resulting from an unusual formal insertion to the benzoyl moiety [10]. A probable mechanism for the formation of this novel 3-anilino-naphthalen-1(4*H*)-one compounds **4** [10] might be realized by a ring-opening reaction of the present benzoyl-substituted push-pull cyclopropane and participation of the present phenyl ring by subsequent loss of two H-atoms. It was the first time that we obtained a product with the loss of two H-atoms. Its final structure **4** was revealed by a crystallographic analysis.

Scheme 1



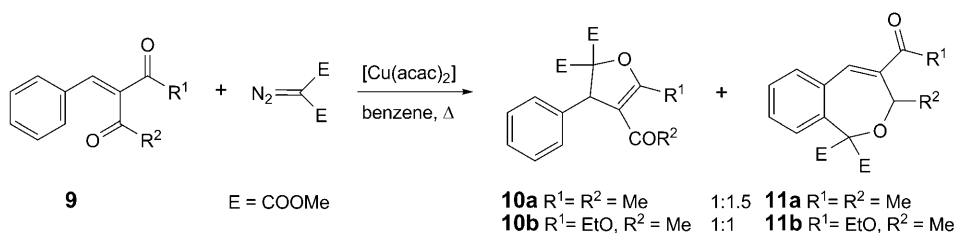
On the other hand, in a study with vinylidene- or benzylidene-containing ketones or esters **5** [11], we found furofuran **7** and β -bis[methoxycarbonyl)methyl] derivatives **8** as second-step products derived from dihydrofurans **6** (*Scheme 2*).

Scheme 2



In a recent investigation with 2-benzylidene-1,3-dicarbonyl compounds **9** [12], we obtained dihydrobenzoxepine derivatives **11** by 1,7-electrocyclization and dihydrofuran derivatives **10** by 1,5-electrocyclization in varying ratios (*Scheme 3*); other possible reaction products were not observed in these experiments.

Scheme 3

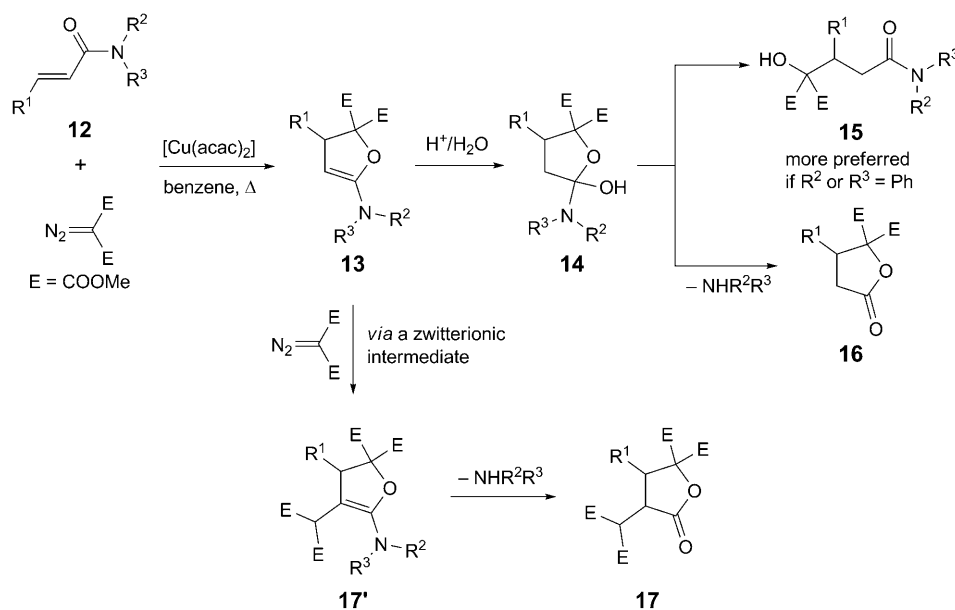


Results and Discussion. – In the present study, we explored the copper-catalyzed bis(methoxycarbonyl)carbene reaction of α,β -unsaturated carboxamides **12a–12i** with three reaction sites (N, $\text{C}(\alpha)$, and O) for the attack of electrophiles beside the carbene addition at the double bond. Due to the presence of various possible reaction pathways, the chemoselectivity of a carbene becomes an important issue that constitutes a recurrent theme over the last three decades, especially in transition-metal-catalyzed carbene-transfer reactions. The reaction of $\text{E}_2\text{C}=\text{N}_2$ with carboxamides **12a–12i**

permits to study the formation of new dihydrofurans and its expected derivatives by carbonyl ylide (= oxonium ylide) reaction, and also to investigate the possibility of the formation of products by a probable ammonium ylide or insertion reaction.

In the $[\text{Cu}(\text{acac})_2]$ -catalyzed reactions of **12a–12i** with $\text{E}_2\text{C}=\text{N}_2$, we observed the formation of a mixture of adducts with either 1 mol-equiv. or 2 mol-equiv. of carbene, *i.e.*, first- and second-step products (*Scheme 4*). Attempts to obtain only or predominantly the first- or the second-step products failed, and approximately the same product distributions were found in all attempts. No reaction by intervention of an ammonium ylide was observed. The yield of all identified first- and second-step products of carboxamides **12a–12i** with $\text{E}_2\text{C}=\text{N}_2$ are given as GC-determined values in the *Table*. Thus, from most of the carboxamides, mixtures of two to five products were obtained, some of which, *i.e.*, **15** and **16**, being certainly related to hydrolytic transformations of the postulated first formed dihydrofuran **13**. As expected, the electron-rich dihydrofuran **13**, which is a cyclic ketene O,N-acetal, is prone to hydrolysis and was not isolated or spectroscopically observed under our reaction conditions (*Scheme 4*). All the reactions, except for that of **12i**, yielded a compound **15** as a result of water addition to **13** and subsequent ring opening of **14**. The source of the γ -lactone derivative **16** was also the water addition product **14**, *via* protonation at the N-atom of **14** and H_2O elimination. It is remarkable that the percentage of **15** was noticeably high in the reactions of **12a–12d** with phenyl substituent(s) at the N-atom. This might be due to a positive-charge resonance stabilization by the phenyl

Scheme 4^{a)}



^{a)} See *Table* for R^1 , R^2 , and R^3 .

Table. Product Composition from the Reaction of Carboxamides **12a–12i** with Dimethyl Diazomalonate

	R ¹	R ²	R ³	Yield [%] ^{a)}				
				15	16	17	18	19
12a	Ph	Ph	Ph	75	8	–	–	–
12b	Me	Ph	Ph	77	–	–	–	–
12c	Ph	Ph	Me	43	21	4	–	19
12d	Me	Ph	Me	75	18	–	–	6
12e	Ph	Et	Et	6	19	–	24	47
12f	Ph	–(CH ₂) ₄ –		3	8	3	19	65
12g	Me	–(CH ₂) ₄ –		8	6	–	3	68
12h	Ph	–(CH ₂) ₅ –		6	9	–	24	61
12i	Me	–(CH ₂) ₅ –		–	7	–	6	75

^{a)} Percentages determined by GC/MS analyses; see *Schemes 4* and *5* for structures.

substituent(s) at the N-atom of the hydroxylated tetrahydrofuran derivatives **14a–14i**; the preferential protonation of the ring O-atom of **14a–14d** yields then **15a–15d**.

The ¹H-NMR spectrum of the major product **15a** from the reaction of **12a** shows three different *dd*, each counting for one H-atom at $\delta(\text{H})$ 4.31, 2.90, and 2.62 with coupling constants of 10.1 and 4.7, 15.0 and 10.1, and 15.1 and 4.7 Hz, respectively. These data represent the *ABX* spin system CH–CH₂. The *ca.* 15.0 Hz value for J_{gem} indicates an open-chain arrangement. The structure of **15a** was also determined by an X-ray crystal-structure analysis (*Fig. 1*)¹⁾.

In the reactions of **12c** and **12f**, the familiar [13] second-step products **17c** and **17f** were obtained *via* **17'** which were formed by addition of a second molequiv. of E₂C=N₂ to the initially formed dihydrofuran derivative **13** by a zwitterionic mechanism, albeit in minor amounts (*Scheme 4*).

On the other hand, in the reactions of carboxamides **12e**, **12f**, and **12h**, α -[bis(methoxycarbonyl)methyl] β -hydroxy-substituted amides **18** were obtained. These products might be formed by carbene addition to C(α) followed by water addition (*Scheme 5*). Another plausible mechanism for the formation of **18** may involve cyclopropane derivatives although cyclopropanation itself could not be observed under our conditions. Since the probable cyclopropanes of the studied carboxamides have acceptor groups, they might behave as homo-*Michael* systems, which readily undergo nucleophilic ring opening by H₂O [14].

Unexpected butadiene derivatives with four ester groups and an amide function, *i.e.*, compounds **19**, were also isolated (*Scheme 5*). The molecular masses of these derivatives showed the absence of two H-atoms per mol-equiv. of carboxamide by involvement of 2 mol-equiv. of carbene. Under our reaction conditions, we also obtained saturated carbene dimers [15], which might originate from compounds of type **19** with two missing H-atoms. It is also noteworthy that the percentages of **19e–19i**

¹⁾ CCDC-764748 (**15a**) and CCDC-764749 (**19e**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

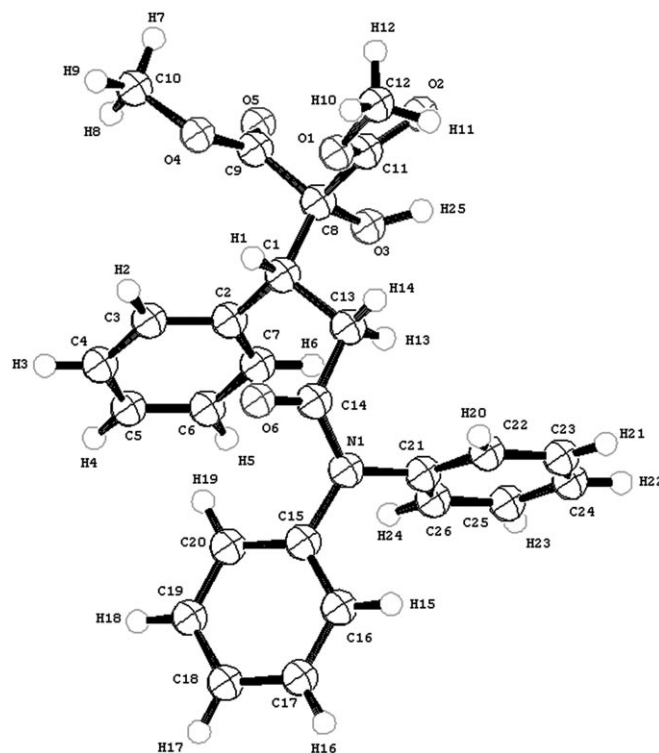
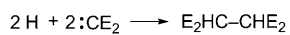
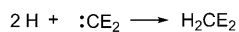
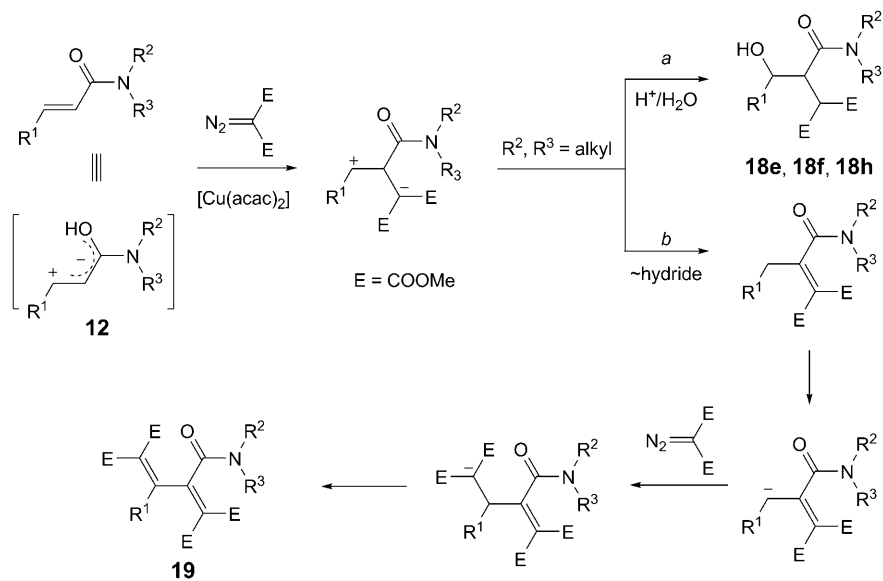


Fig. 1. X-Ray crystal structure of **15a** ($R^1 = R^2 = R^3 = \text{Ph}$). Arbitrary atom numbering.

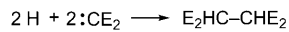
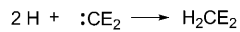
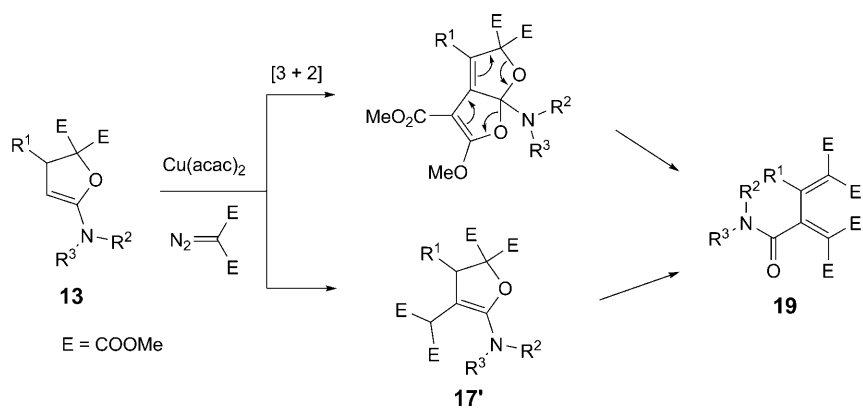
(with no Ph group at N) were apparently higher than those of **19c** and **19d** (with one Ph group at N) (see *Table*). However, compounds **19** were found in the reactions of **12a** and **12b** (with two Ph groups at N). Since compounds **18** were only formed in the reaction of carboxamides without Ph groups at the N-atom (see *Path a*), we suggest a mechanism for the formation of compounds **19** by carbene addition to C(α) as postulated in *Scheme 5* (*Path b*). The formation of some of the dihydrofuran derivative **15** in the reactions of **12e** – **12h** also allows to formulate alternative procedures for the formation of compounds **19** as shown in *Scheme 6*.

The ^1H -NMR spectrum of **19e** showed four different s at $\delta(\text{H})$ 3.81, 3.78, 3.73, and 3.44 for the methyl ester groups and also the signals for the H-atoms of the Et_2N and Ph group. Since no other H-signals were observable, we proposed a highly unsaturated structure for **19e**. The exact structure of **19e** was finally confirmed by an X-ray crystal-structure analysis (*Fig. 2*)¹.

Conclusions. – The reactions of α,β -unsaturated carboxamides and [bis(methoxycarbonyl)carbene]copper mainly led to the novel butadiene derivatives **19** if there is no Ph group at the N-atom of the carboxamides, in contrast to our previous results with α,β -conjugated ketones [13b,c], aminoenones [10], and esters [11]. This finding allows an efficient synthesis of methoxycarbonyl- and amido-substituted novel butadiene

Scheme 5^{a)}

^{a)} See *Table* for R^1 , R^2 , and R^3 .

Scheme 6^{a)}

^{a)} See *Table* for R^1 , R^2 , and R^3 .

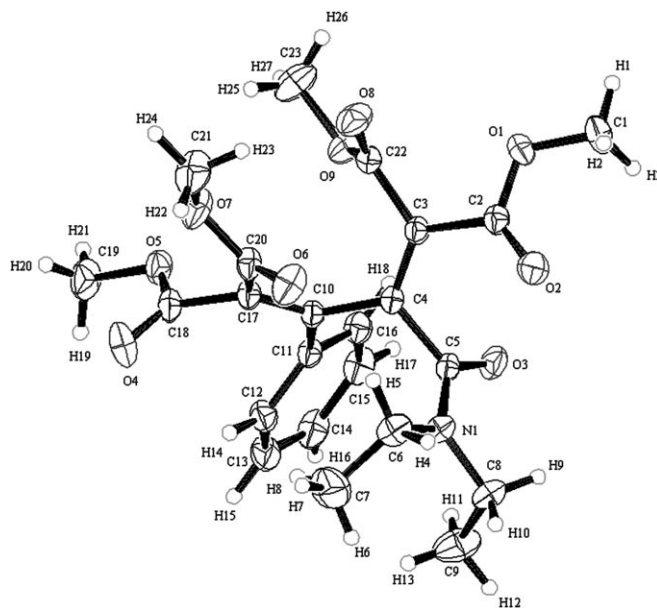


Fig. 2. X-Ray crystal structure of **19e** ($R^1 = \text{Ph}$, $R^2 = R^3 = \text{Et}$). Arbitrary atom numbering.

derivatives applying 2 mol-equiv. of bis(methoxycarbonyl)carbene to 1 mol-equiv. of *N,N*-dialkyl-substituted α,β -unsaturated carboxamide. The new compounds are promising derivatives due to their wide variety of functional groups at the butadiene moiety. In addition, as already previously observed, novel dihydrofuran derivatives are obtained in variable yields (maximum for *N*-phenylated amides).

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Experimental Part

General. Flash chromatography (FC): silica gel. M.p.: *Gallenkamp* apparatus; uncorrected. IR Spectra (neat): *Perkin-Elmer Spectrum One*; in cm^{-1} . NMR Spectra: *Varian Unity Inova 500* and *Bruker AC 250*; if not otherwise stated, at 250 (^1H) and 60 MHz; (^{13}C); in CDCl_3 ; δ in ppm rel. to Me_4Si as internal standard, J in Hz. GC/MS: 6890 *Hewlett-Packard* GC instrument with *HP-1* capillary column (24 m) packed with cross-linked (phenylmethyl)siloxane; 5973 *HP* mass detector; column temp. program: isothermal at 100° for 5 min, heating to 290° with a rate of $20^\circ/\text{min}$, and staying isothermal for 10 min; t_{R} in min. EI-MS and MR-EI-MS: *HP5973* mass detector and *Micromass Autospec Ultima*, resp.; in m/z (rel. %).

Carboxamides 12a–12i: General Procedure. To a soln. of secondary amine (0.05 mol) in CH_2Cl_2 (25 ml) was added pyridine (0.05 mol) and the α,β -unsaturated acyl chloride (0.055 mol) at 0° . After stirring for 15 min at 0° , the mixture was allowed to warm to r.t. and was stirred for an additional 2 h. The resulting mixture was washed with H_2O , 5% HCl soln., 5% NaOH soln., and brine and dried (Na_2SO_4). After evaporation of the solvent, the residue was subjected to FC: carboxamide **12**.

N,N-Diphenylcinnamamide (= (2*E*)-*N,N*,3-Triphenylprop-2-enamide; **12a**): Yield 98%. Pale blue solid. M.p. 163° . IR: 3052, 1734, 1657, 1613, 1351, 1288. ^1H -NMR: 7.79 (*d*, $J = 15.6$, 1 H); 7.27–7.43 (*m*, 15 H); 6.51 (*d*, $J = 15.6$, 1 H). ^{13}C -NMR: 166.2; 142.8; 142.6; 135.2; 129.7; 129.2; 128.7; 128.0; 127.6; 126.8;

119.9. GC/MS: t_R 16.40. EI-MS: 299 (40, M^+), 222 (5), 169 (80), 131 (100), 103 (60), 77 (25). HR-EI-MS: 300.1391 (M^+ , $C_{21}H_{17}NO^+$; calc. 300.1388).

(2E)-N,N-Diphenylbut-2-enamide (**12b**): Yield 83%. Light orange solid. M.p. 112–113°. IR: 3060, 2350, 1664, 1488, 1343, 1287, 1250. 1H -NMR: 7.38–7.20 (m , 10 H); 7.02 (dq , J = 15.0, 7.0, 1 H); 5.86 (dq , J = 15.1, 1.7, 1 H); 1.77 (dd , J = 7.0, 1.7, 3 H). ^{13}C -NMR: 166.1; 142.9; 142.4; 129.2; 127.6; 126.7; 123.9; 18.0. GC/MS: t_R 12.06. EI-MS: 237 (65, M^+), 169 (100), 144 (5), 115 (5), 77 (10), 69 (70). HR-EI-MS: 238.1235 (M^+ , $C_{16}H_{15}NO^+$; calc. 238.1232).

N-Methyl-N-phenylcinnamamide (= (2E)-N-Methyl-N,3-diphenylprop-2-enamide; **12c**): Yield 96%. Yellow oil. IR: 3075, 3030, 2900, 2360, 1653, 1615, 1364 1239. 1H -NMR: 7.67 (d , J = 15.6, 1 H); 7.57–7.20 (m , 10 H); 6.36 (d , J = 15.6, 1 H); 3.40 (s , 3 H). ^{13}C -NMR: 166.1; 143.7; 141.7; 135.2; 129.6; 129.5; 128.7; 127.8; 127.6; 127.3; 118.8; 37.5. GC/MS: t_R 13.63. EI-MS: 237 (45, M^+), 160 (15), 131 (100), 107 (45), 103 (45), 77 (35). HR-EI-MS: 238.1236 (M^+ , $C_{16}H_{15}NO^+$; calc. 238.1232).

(2E)-N-Methyl-N-phenylbut-2-enamide (**12d**): Yield 75%. Yellow oil. IR: 3060, 2900, 2359, 1663, 1627, 1495, 1373, 1127. 1H -NMR: 7.36–7.21 (m , 3 H); 7.09 (dd , J = 7.7, 1.1, 2 H); 6.84 (dq , J = 15.0, 6.9, 1 H); 5.68 (d , J = 15.0, 1 H); 3.25 (s , 3 H); 1.64 (d , J = 6.9, 3 H). ^{13}C -NMR: 165.9; 143.7; 140.8; 129.4; 127.6; 122.7; 37.2; 17.8. GC/MS: t_R 9.85. EI-MS: 175 (60, M^+), 160 (7), 107 (100), 69 (65), 51 (8). HR-EI-MS: 176.1072 (M^+ , $C_{11}H_{13}NO^+$; calc. 176.1075).

N,N-Diethylcinnamamide (= (2E)-N,N-Diethyl-3-phenylprop-2-enamide; **12e**): Yield 81%. Pale yellow solid. M.p. 68°. IR: 2965, 2350, 1646, 1593, 1458, 1365, 1219, 1145. 1H -NMR: 7.70 (d , J = 15.5, 1 H); 7.54–7.21 (m , 2 H); 7.40–7.35 (m , 3 H); 6.82 (d , J = 15.5, 1 H); 3.53–3.43 (m , 4 H); 1.26 (t , J = 7.2, 3 H); 1.18 (t , J = 7.1, 3 H). ^{13}C -NMR: 165.7; 142.3; 135.6; 129.4; 128.7; 128.1; 127.7; 117.9; 42.3; 41.1; 15.0; 13.2. GC/MS: t_R 16.58. EI-MS: 203 (90, M^+), 188 (50), 174 (12), 131 (100), 126 (40), 103 (90), 77 (58). HR-EI-MS: 204.1391 (M^+ , $C_{13}H_{17}NO^+$; calc. 204.1388).

(2E)-3-Phenyl-1-(pyrrolidin-1-yl)prop-2-en-1-one (**12f**): Yield 83%. White solid. M.p. 123°. IR: 2969, 2873, 2360, 1650, 1592, 1429, 1196. 1H -NMR: 7.69 (d , J = 15.5, 1 H); 7.54–7.51 (m , 2 H); 7.35–7.34 (m , 3 H); 6.72 (d , J = 15.5, 1 H); 3.62 (t , J = 6.6, 2 H); 3.58 (t , J = 6.7, 2 H); 2.06–1.84 (m , 4 H). ^{13}C -NMR: 164.7; 141.7; 135.4; 129.5; 128.7; 127.8; 119.0; 46.6; 46.0; 26.1; 24.3. GC/MS: t_R 13.28. EI-MS: 201 (85, M^+), 131 (100), 103 (65), 77 (30), 70 (15). HR-EI-MS: 202.1238 (M^+ , $C_{13}H_{15}NO^+$; calc. 202.1232).

(2E)-1-(Pyrrolidin-1-yl)but-2-en-1-one (**12g**): Yield 79%. Yellow oil. IR: 2970, 2871, 2359, 1663, 1603, 1507, 1418, 1227. 1H -NMR: 6.72 (dq , J = 15.1, 6.8, 1 H); 5.96 (d , J = 15.1, 1 H); 3.34 (t , J = 5.8, 4 H); 1.86–1.66 (m , 4 H); 1.70 (d , J = 6.7, 3 H). ^{13}C -NMR: 164.5; 140.1; 123.1; 46.2; 45.4; 25.9; 24.1; 17.7. GC/MS: t_R 8.91. EI-MS: 139 (50, M^+), 124 (100), 98 (5), 69 (98). HR-EI-MS: 140.1080 (M^+ , $C_8H_{13}NO^+$; calc. 140.1075).

(2E)-3-Phenyl-1-(piperidin-1-yl)prop-2-en-1-one (**12h**): Yield 87%. White solid. M.p. 103°. IR: 2934, 1643, 1585, 1441, 1248, 1222, 1018. 1H -NMR: 7.63 (d , J = 15.5, 1 H); 7.52–7.50 (m , 2 H); 7.36–7.34 (m , 3 H); 6.89 (d , J = 15.5, 1 H); 3.65–3.58 (m , 4 H); 1.70–1.51 (m , 6 H). ^{13}C -NMR: 165.4; 142.1; 135.6; 129.3; 128.7; 127.6; 117.9; 47.0; 43.3; 26.7; 25.6; 24.6. GC/MS: t_R 13.40. EI-MS: 215 (100, M^+), 214 (55), 138 (40), 131 (90), 103 (50), 84 (22), 77 (25). HR-EI-MS: 216.1393 (M^+ , $C_{14}H_{17}NO^+$; calc. 216.1388).

(2E)-1-(Piperidin-1-yl)but-2-en-1-one (**12i**): Yield 65%. Yellow oil. IR: 2935, 2359, 1661, 1607, 1435, 1217. 1H -NMR: 6.18 (d , J = 15.1, 1 H); 6.72 (dq , J = 15.1, 6.8, 1 H); 3.64–3.38 (m , 4 H); 1.76 (d , J = 6.8, 3 H); 1.54–1.45 (m , 6 H). ^{13}C -NMR: 165.3; 140.4; 121.9; 46.6; 42.9; 26.5; 25.5; 24.5; 17.9. GC/MS: t_R 9.15. EI-MS: 153 (10, M^+), 138 (100), 110 (5), 84 (15), 69 (40). HR-EI-MS: 153.1158 (M^+ , $C_9H_{15}NO^+$; calc. 153.1154).

Catalytic Reactions of Carboxamides 12 with Dimethyl Diazomalonate ($E_2C=N_2$): General Procedure. To a soln. of one of the carboxamides **12a**–**12i** (6.6 mmol) in benzene (10 ml) was added $[Cu(acac)_2]$ (0.02 mmol), and the mixture was heated under reflux. A soln. of $E_2C=N_2$ (3.3 mmol) in benzene (5 ml) was added dropwise over 3 h. When the IR spectrum indicated total consumption of $E_2C=N_2$ (absence of the characteristic diazo band at 2130 cm^{-1}), the mixture was concentrated and the residue subjected to FC. The crude mixture contained varying amounts of unidentified compounds (max. 20% by GC/MS).

Dimethyl 2-[3-(Diphenylamino)-3-oxo-1-phenylpropyl]-2-hydroxypropanedioate (**15a**): Yield 68%. Colorless solid. M.p. 203°. IR: 3490, 3060, 2956, 1742, 1666, 1491, 1266, 1136. 1H -NMR: 7.26–6.82 (m , 15 H); 4.31 (dd , J = 10.1, 4.7, 1 H); 4.02 (s , 1 OH); 3.81 (s , 3 H); 3.52 (s , 3 H); 2.90 (dd , J = 15.0, 10.1, 1 H);

2.62 (*dd*, $J = 15.1, 4.7, 1$ H). ^{13}C -NMR: 171.0; 170.0; 142.7; 138.2; 129.6; 129.2; 128.1; 127.5; 126.9; 81.8; 53.5; 53.2; 47.1; 36.2. GC/MS: t_{R} 19.98. EI-MS: 447 (5, M^+), 388 (4), 279 (5), 169 (100), 121 (15), 77 (5). HR-EI-MS: 448.1766 (M^+ , $\text{C}_{26}\text{H}_{25}\text{NO}_6^+$; calc. 448.1760).

Dimethyl 2-[3-(Diphenylamino)-1-methyl-3-oxopropyl]-2-hydroxypropanedioate (15b): Yield 71%. Colorless oil. IR: 3483, 2956, 1742, 1665, 1592, 1493, 1243, 1156, 1083. ^1H -NMR: 7.52–6.80 (*m*, 10 H); 4.29 (*s*, OH); 3.77 (*s*, 3 H); 3.71 (*s*, 3 H); 3.14–3.04 (*m*, 1 H); 2.35 (*dd*, $J = 15.9, 4.9, 1$ H); 2.26 (*dd*, $J = 15.9, 8.0, 1$ H); 0.98 (*d*, $J = 6.8, 3$ H). ^{13}C -NMR: 171.8; 168.5; 166.8; 142.8 (2 C); 130.6–120.8 (10 C); 82.0; 53.8; 53.2; 36.8; 35.7; 14.6. GC/MS: t_{R} 14.97. EI-MS: 385 (3, M^+), 326 (5), 217 (3), 169 (100), 157 (8), 129 (12), 77 (5), 59 (10). HR-EI-MS: 386.1600 (M^+ , $\text{C}_{21}\text{H}_{23}\text{NO}_6^+$; calc. 386.1604).

Dimethyl 2-Hydroxy-2-[3-[methyl(phenyl)amino]-3-oxo-1-phenylpropyl]propanedioate (15c): Yield 41%. Yellow oil. IR: 3492, 2926, 1803, 1747, 1437, 1265, 1049. ^1H -NMR: 7.64–7.21 (*m*, 8 H); 6.96 (*d*, $J = 6.4, 2$ H); 4.25 (*dd*, $J = 9.4, 4.8, 1$ H); 4.7 (*br. s*, OH); 3.81 (*s*, 3 H); 3.50 (*s*, 3 H); 3.10 (*s*, 3 H); 2.69 (*dd*, $J = 15.3, 9.4, 1$ H); 2.43 (*dd*, $J = 15.9, 4.8, 1$ H). ^{13}C -NMR (100 MHz, CDCl_3): 169.7; 169.0; 168.9; 142.7; 137.5; 128.4; 128.3; 127.7; 127.6; 127.5; 127.1; 127.0; 126.9; 126.4; 126.3; 81.0; 52.5; 52.1; 45.7; 34.4; 28.7. GC/MS: t_{R} 15.65. EI-MS: 385 (2, M^+), 367 (5), 326 (15), 279 (3), 239 (15), 107 (100), 77 (15), 59 (6). HR-EI-MS: 386.1600 (M^+ , $\text{C}_{21}\text{H}_{23}\text{NO}_6^+$; calc. 386.1604).

Dimethyl 2-Hydroxy-2-[1-methyl-3-[methyl(phenyl)amino]-3-oxopropyl]propanedioate (15d): Yield 70%. Dark red oil. IR: 3490, 2958, 1800, 1743, 1437, 1211, 1193, 1081. ^1H -NMR: 7.62–7.31 (*m*, 3 H); 7.13 (*d*, $J = 7.04, 2$ H); 4.65 (*br. s*, OH); 3.75 (*s*, 3 H); 3.71 (*s*, 3 H); 3.23 (*s*, 3 H); 3.00 (*dd*, $J = 12.5, 6.5, 1$ H); 2.14–2.07 (*m*, 2 H); 0.88 (*d*, $J = 6.7, 3$ H). ^{13}C -NMR (100 MHz, CDCl_3): 172.4; 170.7; 169.7; 142.8; 128.9 (2 C); 128.2; 127.0; 126.3; 86.6; 52.5; 52.2; 35.3; 34.7; 34.1; 14.3. GC/MS: t_{R} 13.85. EI-MS: 323 (7, M^+), 264 (12), 217 (3), 204 (11), 157 (11), 129 (15), 107 (100), 77 (10), 59 (12). HR-EI-MS: 324.1442 (M^+ , $\text{C}_{16}\text{H}_{21}\text{NO}_6^+$; calc. 324.1447).

Dimethyl 2-[3-(Diethylamino)-3-oxo-1-phenylpropyl]-2-hydroxypropanedioate (15e): Yield 3%. Orange oil. IR: 3492, 2955, 1741, 1634, 1435, 1221, 1134. ^1H -NMR: 7.37–7.16 (*m*, 5 H); 4.42 (*s*, OH); 4.27 (*dd*, $J = 9.1, 4.8, 1$ H); 3.86 (*s*, 3 H); 3.51 (*s*, 3 H); 3.26–3.14 (*m*, 4 H); 2.92 (*dd*, $J = 15.3, 9.2, 1$ H); 2.64 (*dd*, $J = 15.3, 4.8, 1$ H); 1.05 (*t*, $J = 7.2, 3$ H); 0.91 (*t*, $J = 7.1, 3$ H). ^{13}C -NMR: 170.11 (2 C); 169.8; 138.8; 129.2; 128.5; 128.0; 127.3; 82.2; 53.5; 53.1; 46.6; 42.0; 42.3; 34.4; 14.3; 12.8. GC/MS: t_{R} 13.25. EI-MS: 351 (7, M^+), 333 (20), 292 (60), 274 (55), 205 (30), 131 (25), 100 (100), 72 (40), 59 (10). HR-EI-MS: 352.1757 (M^+ , $\text{C}_{18}\text{H}_{25}\text{NO}_6^+$; calc. 352.1760).

Dimethyl 2-Hydroxy-2-[3-oxo-1-phenyl-3-(pyrrolidin-1-yl)propyl]propanedioate (15f): Yield 2%. Orange oil. IR: 3397, 2973, 1798, 1741, 1624, 1436, 1231, 1048. ^1H -NMR: 7.37–7.18 (*m*, 5 H); 4.26 (*dd*, $J = 8.9, 4.9, 1$ H); 3.80 (*s*, 3 H); 3.84 (*s*, OH); 3.49 (*s*, 3 H); 3.38–3.17 (*m*, 4 H); 2.85 (*dd*, $J = 15.4, 9.1, 1$ H); 2.64 (*dd*, $J = 15.4, 4.7, 1$ H); 1.86–1.65 (*m*, 4 H). ^{13}C -NMR (125 MHz, CDCl_3): 170.0; 169.2 (2 C); 139.0; 129.2 (2 C); 128.1 (2 C); 127.3; 82.2; 53.5; 53.1; 46.7; 46.2; 45.6; 36.4; 26.0; 24.3. GC/MS: t_{R} 15.22. EI-MS: 349 (5, M^+), 331 (12), 290 (90), 272 (50), 230 (25), 203 (35), 131 (15), 98 (100), 70 (25), 59 (7). HR-EI-MS: 350.1659 (M^+ , $\text{C}_{18}\text{H}_{23}\text{NO}_6^+$; calc. 350.1604).

Dimethyl 2-Hydroxy-2-[1-methyl-3-oxo-3-(pyrrolidin-1-yl)propyl]propanedioate (15g): Yield 6%. Dark red oil. IR: 3492, 2956, 1801, 1739, 1621, 1435, 1226, 1042. ^1H -NMR: 3.82 (*s*, OH); 3.79 (*s*, 3 H); 3.76 (*s*, 3 H); 3.45 (*t*, $J = 6.8, 2$ H); 3.38 (*t*, $J = 6.8, 2$ H); 3.11–2.98 (*m*, 1 H); 2.42–2.24 (*m*, 2 H); 1.95–1.79 (*m*, 4 H); 0.97 (*d*, $J = 6.7, 3$ H). ^{13}C -NMR: 170.8; 170.6; 170.1; 82.2; 53.3; 53.2; 46.9; 45.8; 36.4; 35.1; 26.0; 24.3; 14.5. GC/MS: t_{R} 13.41. EI-MS: 287 (10, M^+), 228 (70), 168 (68), 140 (100), 98 (45), 59 (15). HR-EI-MS: 288.1442 (M^+ , $\text{C}_{13}\text{H}_{21}\text{NO}_6^+$; calc. 288.1447).

Dimethyl 2-Hydroxy-2-[3-oxo-1-phenyl-3-(piperidin-1-yl)propyl]propanedioate (15h): Yield 5%. Dark yellow oil. IR: 3472, 2952, 1782, 1735, 1634, 1436, 1259, 1142, 1023. ^1H -NMR: 7.37–7.20 (*m*, 5 H); 4.24 (*dd*, $J = 9.2, 4.5, 1$ H); 3.84 (*s*, OH); 3.81 (*s*, 3 H); 3.51 (*s*, 3 H); 3.42–3.32 (*m*, 4 H); 2.97 (*dd*, $J = 15.1, 9.2, 1$ H); 2.64 (*dd*, $J = 15.3, 4.4, 1$ H); 1.54–1.30 (*m*, 6 H). ^{13}C -NMR (125 MHz, CDCl_3): 172.4; 169.1; 169.0; 137.7; 128.2; 127.7; 127.1; 127.0; 126.4; 81.2; 52.5; 52.2; 45.8; 45.5; 41.8; 33.3; 25.3; 24.4; 23.5. GC/MS: t_{R} 15.47. EI-MS: 363 (10, M^+), 345 (25), 304 (100), 286 (75), 244 (30), 217 (35), 126 (30), 112 (95), 84 (30), 59 (10). HR-EI-MS: 364.1756 (M^+ , $\text{C}_{19}\text{H}_{25}\text{NO}_6^+$; calc. 364.1760).

Dimethyl Dihydro-5-oxo-3-phenylfuran-2,2(3H)-dicarboxylate (16a = 16c = 16e = 16f = 16h): Yield 4% (for **16a**), 20% (for **16c**), 15% (for **16e**), 4% (for **16f**), and 5% (for **16h**). Yellow oil. IR: 2956, 2359, 1801, 1741, 1435, 1240, 1157, 1071. ^1H -NMR: 7.30–7.25 (*m*, 5 H); 4.45 (*t*, $J = 8.7, 1$ H); 3.84 (*s*, 3 H); 3.82

(s, 3 H); 3.07 (dd, $J = 17.5, 8.7, 1$ H); 2.98 (dd, $J = 17.5, 8.7, 1$ H). ^{13}C -NMR (125 MHz, CDCl_3): 172.4; 165.5; 164.7; 134.3; 127.7 (2 C); 127.5; 127.0 (2 C); 87.6; 52.7; 51.7; 44.9; 33.0. GC/MS: t_{R} 12.67. EI-MS: 278 (50, M^+), 246 (5), 218 (70), 191 (80), 131 (55), 104 (100), 77 (20), 59 (20). HR-EI-MS: 279.0865 (M^+ , $\text{C}_{14}\text{H}_{14}\text{NO}_3^+$; calc. 279.0869).

Dimethyl Dihydro-3-methyl-5-oxofuran-2,2(3H)-dicarboxylate (16d = 16g = 16i): Not isolated in pure form. GC/MS: t_{R} 9.80. EI-MS: 216 (2, M^+), 173 (2), 157 (75), 129 (77), 101 (25), 69 (19), 59 (100).

Dimethyl Dihydro-4-[2-methoxy-1-(methoxycarbonyl)-2-oxoethyl]-5-oxo-3-phenylfuran-2,2(3H)-dicarboxylate (17c = 17f): Yield 2% (for **17c**) and 1% (for **17f**): Dark red oil. IR: 2957, 1798, 1743, 1435, 1259, 1233, 1102, 1025. ^1H -NMR: 7.35–7.25 (m, 5 H); 4.78 (d, $J = 12.0, 1$ H); 3.94 (d, $J = 5.0, 1$ H); 3.86 (s, 3 H); 3.82 (dd, $J = 12.0, 5.0, 1$ H); 3.64 (s, 3 H); 3.34 (s, 3 H); 3.20 (s, 3 H). ^{13}C -NMR (125 MHz, CDCl_3): 171.9; 166.2; 165.7; 165.2; 165.0; 132.1; 128.8; 128.1; 127.7; 127.6 (2 C); 86.0; 52.6; 52.0; 51.9; 51.4; 48.7; 42.0; 28.7. GC/MS: t_{R} 14.98. EI-MS: 408 (2, M^+), 345 (7), 317 (8), 277 (100), 257 (10), 229 (23), 201 (6), 171 (7), 115 (25), 59 (8). HR-EI-MS: 409.1141 (M^+ , $\text{C}_{19}\text{H}_{20}\text{NO}_6^+$; calc. 409.1135).

Dimethyl 2-[2-(Diethylamino)-1-[hydroxy(phenyl)methyl]-oxoethyl]propanedioate (18e): Yield 18%. Yellow oil. ^1H -NMR (500 MHz, CDCl_3): 7.21–7.16 (m, 5 H); 3.79 (s, OH); 3.76–3.73 (m, 1 H); 3.70 (s, 5 H); 3.49 (q, $J = 7.1, 2$ H); 3.43–3.36 (m, 1 H); 3.42 (s, 3 H); 3.24 (d, $J = 7.7, 1$ H); 3.18 (q, $J = 7.0, 2$ H); 1.23 (t, $J = 7.1, 3$ H); 1.04 (t, $J = 7.1, 3$ H). ^{13}C -NMR (125 MHz, CDCl_3): 168.2; 165.8; 165.4; 132.7; 129.3; 127.5; 127.4; 127.3; 126.5; 87.5; 51.9; 51.8; 47.5; 43.1; 41.3; 39.8; 13.6; 11.9. GC/MS: t_{R} 13.84. EI-MS: 333 (5, $[M - \text{H}_2\text{O}]^+$), 302 (15), 274 (100), 258 (5), 233 (90), 212 (65), 173 (50), 145 (10), 113 (35), 100 (45), 72 (25), 59 (5). HR-EI-MS: 352.1764 (M^+ , $\text{C}_{18}\text{H}_{25}\text{NO}_6^+$; calc. 352.1760).

Dimethyl 2-[2-Hydroxy-2-phenyl-1-(pyrrolidin-1-ylcarbonyl)ethyl]propanedioate (18f): Yield 15%. Colorless oil. IR: 3467, 2954, 2925, 1743, 1790, 1646, 1436, 1258, 1012. ^1H -NMR (500 MHz, CDCl_3): 7.36–7.17 (m, 5 H); 3.80 (s, OH); 3.74 (s, 3 H); 3.69–3.61 (m, 2 H); 3.68 (t, $J = 7.7, 2$ H); 3.65 (d, $J = 9.5, 1$ H); 3.45–3.39 (m, 1 H); 3.42 (s, 3 H); 3.21 (d, $J = 7.7, 1$ H); 1.98–1.92 (m, 2 H); 1.87–1.80 (m, 2 H). ^{13}C -NMR (125 MHz, CDCl_3): 166.0; 165.4; 164.5; 132.7; 127.5; 127.4; 127.3 (2 C); 126.5; 86.3; 52.0; 51.7; 45.9; 45.2; 42.9; 34.5; 25.0; 23.4. GC/MS: t_{R} 14.85. EI-MS: 331 (7, $[M - \text{H}_2\text{O}]^+$), 300 (12), 272 (100), 233 (90), 210 (50), 173 (40), 145 (10), 115 (27), 98 (55), 70 (6), 59 (3). HR-EI-MS: 350.1609 (M^+ , $\text{C}_{18}\text{H}_{23}\text{NO}_6^+$; calc. 350.1604).

Dimethyl 2-[2-Hydroxy-2-phenyl-1-(piperidin-1-ylcarbonyl)ethyl]propanedioate (18h): Yield 21%. Dark yellow oil. IR: 3467, 3060, 2955, 1792, 1742, 1666, 1491, 1266, 1229, 1136. ^1H -NMR (500 MHz, CDCl_3): 7.40–7.15 (m, 5 H); 3.81 (s, OH); 3.77–3.69 (m, 5 H); 3.60–3.55 (m, 1 H); 3.72 (s, 3 H); 3.60–3.55 (m, 1 H); 3.42 (s, 3 H); 3.29 (d, $J = 7.8, 1$ H); 1.63–1.41 (m, 6 H). ^{13}C -NMR (125 MHz, CDCl_3): 168.2; 165.4; 163.9; 132.7; 129.3; 127.5; 127.4; 127.3; 126.5; 87.5; 51.9; 51.8; 47.5; 45.8; 42.7; 42.4; 25.4; 24.5; 23.5. GC/MS: t_{R} 15.07. EI-MS: 345 (7, $[M - \text{H}_2\text{O}]^+$), 314 (15), 286 (100), 233 (90), 224 (65), 173 (50), 145 (14), 114 (30), 112 (35), 84 (15), 69 (18), 59 (5). HR-EI-MS: 364.1765 (M^+ , $\text{C}_{19}\text{H}_{25}\text{NO}_6^+$; calc. 364.1760).

Tetramethyl 2-[[Methyl(phenyl)amino]carbonyl]-3-phenylbuta-1,3-diene-1,1,4,4-tetracarboxylate (19c): Yield 16%. Yellow oil. IR: 2956, 1731, 1651, 1434, 1222, 1160, 1003. ^1H -NMR (500 MHz, CDCl_3): 7.39–7.11 (m, 10 H); 3.83 (s, 3 H); 3.79 (s, 6 H); 3.72 (s, 6 H). ^{13}C -NMR (125 MHz, CDCl_3): 167.7; 167.5 (2 C); 165.8 (2 C); 164.5; 163.5; 146.4; 133.8; 128.7–126.6 (12 C); 55.4; 53.0; 52.9; 52.1; 37.5. GC/MS: t_{R} 18.09. EI-MS: 495 (10, M^+), 464 (12), 436 (20), 404 (30), 380 (27), 361 (12), 329 (100), 301 (6), 106 (13), 77 (15), 59 (10). HR-EI-MS: 496.1611 (M^+ , $\text{C}_{26}\text{H}_{25}\text{NO}_8^+$; calc. 496.1608).

Tetramethyl 2-Methyl-3-[[methyl(phenyl)amino]carbonyl]buta-1,3-diene-1,1,4,4-tetracarboxylate (19d): Not isolated in pure form. GC/MS: t_{R} 15.35. EI-MS: 433 (1, M^+), 402 (18), 374 (35), 342 (20), 327 (55), 295 (60), 263 (100), 235 (12), 207 (10), 134 (8), 106 (16), 77 (20), 59 (12).

Tetramethyl 2-[(Diethylamino)carbonyl]-3-phenylbuta-1,3-diene-1,1,4,4-tetracarboxylate (19e): Yield 46%. Colorless solid. M.p. 187°. IR: 2923, 2390, 1731, 1639, 1444, 1218, 1085. ^1H -NMR: 7.41–7.25 (m, 5 H); 3.78 (s, 3 H); 3.77 (s, 3 H); 3.73 (s, 3 H); 3.44 (s, 3 H); 3.41 (q, $J = 7.06, 2$ H); 3.17 (q, $J = 7.05, 2$ H); 0.97 (t, $J = 7.01, 3$ H); 0.86 (t, $J = 7.06, 3$ H). ^{13}C -NMR: 165.4; 164.6; 163.5 (2 C); 163.3; 148.7; 147.7; 134.5; 129.7; 128.7; 128.5; 128.1; 52.7 (2 C); 52.3 (2 C); 42.0; 39.0; 13.3; 11.8. GC/MS: t_{R} 15.72. EI-MS: 461 (10, M^+), 430 (30), 402 (100), 358 (65), 329 (28), 298 (33), 271 (15), 100 (30), 72 (100), 59 (7). HR-EI-MS: 462.1769 (M^+ , $\text{C}_{23}\text{H}_{27}\text{NO}_8^+$; calc. 462.1764).

Tetramethyl 2-Phenyl-3-(pyrrolidin-1-ylcarbonyl)buta-1,3-diene-1,1,4,4-tetracarboxylate (19f): Yield 63%. Yellow oil. IR: 2954, 2990, 1732, 1638, 1434, 1226, 1089. ^1H -NMR: 7.35–7.25 (m, 5 H); 3.76 (s, 6 H);

3.74 (s, 3 H); 3.45 (s, 3 H); 3.28 (t, $J = 6.1$, 2 H); 3.23 (t, $J = 5.9$, 2 H); 1.25–1.19 (m, 4 H). ^{13}C -NMR (125 MHz, CDCl_3): 164.3; 163.4; 162.7; 162.3; 161.5; 147.2; 146.4; 133.8; 128.7; 127.8; 127.4; 127.3; 126.8; 52.0; 51.8; 51.7; 51.4; 46.1; 45.0; 24.9; 22.9. GC/MS: t_{R} 16.85. EI-MS: 459 (7, M^+), 428 (20), 358 (40), 329 (15), 298 (30), 272 (10), 203 (6), 153 (7), 129 (7), 98 (15), 55 (12). HR-EI-MS: 460.1612 (M^+ , $\text{C}_{23}\text{H}_{25}\text{NO}^+$; calc. 460.1608).

Tetramethyl 2-Methyl-3-(pyrrolidin-1-ylcarbonyl)buta-1,3-diene-1,1,4,4-tetracarboxylate (19g): Not isolated in pure form. GC/MS: t_{R} 14.79. EI-MS: 397 (3, M^+), 366 (65), 338 (100), 299 (70), 164 (65), 232 (60), 205 (25), 98 (70), 70 (60), 59 (20).

Tetramethyl 2-Phenyl-3-(piperidin-1-ylcarbonyl)buta-1,3-diene-1,1,4,4-tetracarboxylate (19h): Yield 60%. Yellow oil. IR: 2951, 2360, 1731, 1712, 1633, 1429, 1221, 1091. ^1H -NMR: 7.42–7.32 (m, 5 H); 3.80 (s, 3 H); 3.79 (s, 3 H); 3.77 (s, 3 H); 3.46 (s, 3 H); 3.36 (t, $J = 4.8$, 2 H); 3.25 (t, $J = 4.9$, 2 H); 1.48–1.37 (m, 4 H); 1.18–1.08 (m, 2 H). ^{13}C -NMR: 165.1; 164.3; 163.5; 163.3; 162.6; 148.5; 146.6; 134.7; 130.3; 129.5; 128.7; 128.6; 128.3; 127.8; 127.2; 53.8; 52.8; 52.7; 52.3; 47.0; 42.8; 25.3; 25.2; 24.2. GC/MS: t_{R} 17.29. EI-MS: 473 (3, M^+), 442 (15), 414 (100), 358 (65), 298 (35), 271 (10), 112 (10), 64 (15), 59 (6). HR-EI-MS: 474.1761 (M^+ , $\text{C}_{24}\text{H}_{27}\text{NO}^+$; calc. 474.1764).

Tetramethyl 2-Methyl-3-(piperidin-1-ylcarbonyl)buta-1,3-diene-1,1,4,4-tetracarboxylate (19i): Not isolated in pure form. GC/MS: t_{R} 14.99. EI-MS: 411 (3, M^+), 380 (50), 352 (100), 299 (50), 264 (55), 232 (47), 205 (20), 177 (10), 112 (50), 84 (52), 59 (14).

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