Intramolecular Cycloadditions of Mesoionic Carbonyl Ylides with Alkynes. Synthesis of 5,6-Dihydro-4*H*-cyclopenta- and 4,5,6,7-Tetrahydrobenzo[*b*]furan Derivatives

Martin E. Maier* and Bärbel Schöffling

Fakultät für Chemie der Universität Konstanz,
Postfach 5560, D-7750 Konstanz, Germany

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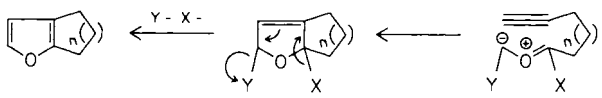
Intramolecular cycloaddition reactions of acetylenic isomünchnones, formed in situ by rhodium acetate catalyzed decomposition of *N*-(diazoacetyl)-*N*-methylalkynamide derivatives **16a–c**, **18c**, and **18d** have been studied. The intermediate cycloadducts fragmentate spontaneously under the reaction conditions (110°C) to afford the annulated furans **19a–c**, **20c**, and **20d**.

Intramolekulare Cycloadditionen von mesoionischen Carbonylyliden mit Alkinen. Synthese von 5,6-Dihydro-4*H*-cyclopenta- und 4,5,6,7-Tetrahydrobenzo[*b*]furan-Derivaten

Intramolekulare Cycloadditionen von acetylenischen Isomünchnonen, die in situ durch Rhodiumacetat-katalysierte Zersetzung von *N*-(Diazoacetyl)-*N*-methylalkinamid-Derivaten **16a–c**, **18c** und **18d** erzeugt wurden, sind untersucht worden. Die Primäraddukte fragmentieren unter den Reaktionsbedingungen (110°C) zu den anellierten Furanen **19a–c**, **20c** und **20d**.

Various types of sesqui- and diterpenes contain an annulated furan ring as a common structural feature[1]. Some prominent members of this class of compounds are the paniculides[2], the cytotoxic furanonaphthoquinones[3], as well as furodysin and furodysinin[4]. In most of the synthetic routes to annulated furans, the furan ring is assembled onto an existing ring[5]. Other methods start with a functionalized furan, to which subsequently another ring is being attached. This can be done, for example, by cationic cyclization reactions[6], where the furan ring acts as a nucleophilic trap for an electrophilic species, or by Diels-Alder reaction between a vinylfuran and a dienophil[7]. Another obvious approach to annulated furans would also be the intramolecular cycloaddition between an carbonyl ylide and an alkyne, followed by the elimination of the functional groups X and Y (Scheme 1). It is well known that mesoionic oxazolium ylides (isomünchnones), which represent cyclic equivalents of carbonyl ylides, are ideally suited for such a transformation. That is, isomünchnone/alkyne cycloadducts fragmentate through a retro Diels-Alder reaction into a furan and isocyanate[8]. It was also shown by Ibata that isomünchnones can easily be generated by transition-metal-catalyzed decomposition of *N*-(diazoacetyl)amide derivatives[8b]. However, intermolecular cycloaddition reactions of isomünchnones are restricted to highly activated dipolarophiles, thereby limiting the synthetic applications.

Scheme 1



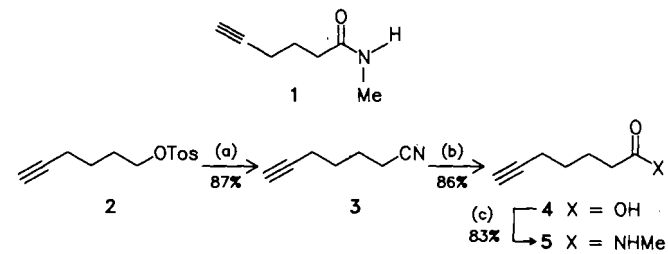
In a previous paper, we have shown that intramolecular cycloadditions of isomünchnones even occur with unactivated alkenes to afford cycloadducts in high yield[9]. Therefore, the question arose whether nonactivated alkynes would also react in a similar fashion to result eventually in annulated furan derivatives. In addition to the feasibility of the cycloaddition, it was also of interest what the influence of substituents at the connecting carbon chain would be. At this point we note that, at least in a formal sense, a transformation as depicted in Scheme 1 is realized in the intramolecular Diels-Alder reactions of acetylenic oxazoles[10].

In the following, we present our results of intramolecular isomünchnone/alkyne cycloadditions, leading to a new synthesis of annulated furans. The present work is restricted to isomünchnones bearing the alkyne side-chain in 2-position of the heterocycle.

A. Preparation of Diazo Compounds

The requisite acetylenic diazo compounds, which are the direct precursors for the reactive isomünchnones, were prepared from the corresponding amides **1**, **5**, **10**, and **14**. The *N*-methylamides were chosen over *N*-arylamides in order to prevent competing carbene insertion into an aryl C–H bond[11] during the generation of the isomünchnones. Amide **1** was prepared from the known 5-hexynoic acid[12] by treatment with thionyl chloride and by addition of the crude acid chloride to an etheral solution of methylamine. Alternatively, a commercially available ethanolic solution of methylamine can be used. The synthesis of amides **5**, **10**, and **14** is outlined in Scheme 2.

Scheme 2[a]



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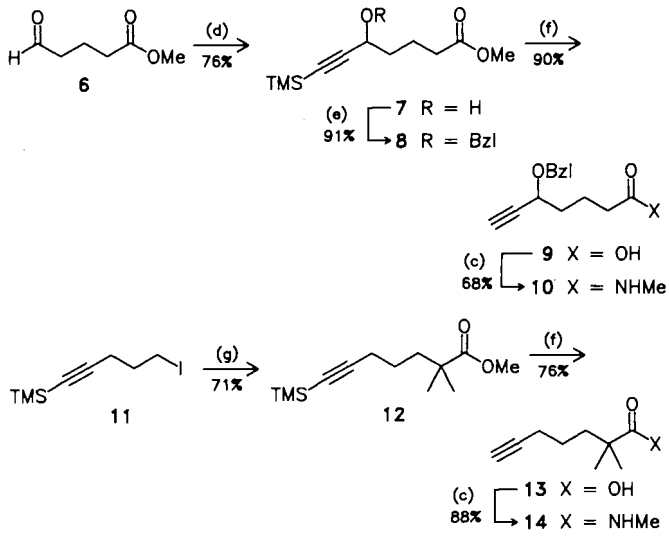
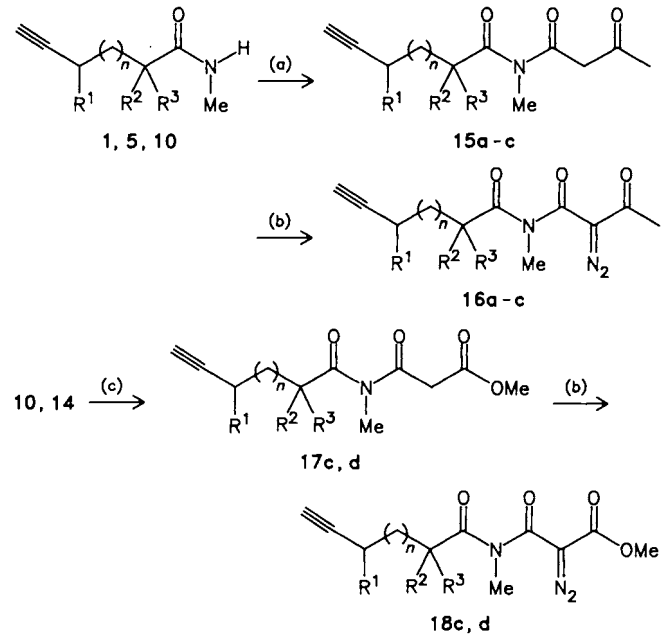


[a] Reagents and conditions: (a) NaCN, DMSO, 90°C; (b) NaOH, $EtOH/H_2O$, reflux; (c) $SOCl_2$, benzene, then $MeNH_2$; (d) $TMSC{\equiv}CLi$, THF, −78°C; (e) benzyl trichloroacetimidate, CF_3SO_3H, pentane/CH_2Cl_2, 25°C; (f) KOH, $EtOH/H_2O$, reflux; (g) methyl isobutyrate, LDA, THF, −78°C, then **11**.

Tosylation[13] of 5-hexyn-1-ol[14], introduction of cyanide, and base hydrolysis afforded 6-heptynoic acid (**4**)[15], which then was converted by the above procedure to the *N*-methylamide **5**. Amide **10** was obtained by reaction of lithio(trimethylsilyl)acetylene with aldehyde **6**[16] at −78°C, followed by protection of the hydroxyl group with benzyl 2,2,2-trichloroacetimidate[17], subsequent hydrolysis of the ester and the trimethylsilyl group, and finally conversion to **10**. The preparation of amide **14** involved alkylation of methyl isobutyrate with iodoalkyne **11**[18]. Base hydrolysis, treatment with thionyl chloride, and the reaction of the acid chloride with methylamine completed the synthesis. With the amides in hand, the preparation of the diazo compounds could next be examined (Scheme 3).

Deprotonation[19] of the amides **1**, **5**, and **10** with one equivalent of *n*-butyllithium at −78°C, followed by the addition of diketene, afforded the *N*-(acetoacetyl)-*N*-methylalkynamides **15a–c** in about 50–60% yield. For the diazo transfer reaction, yielding compounds **16a–c**, we found the use of *p*-acetamidobenzenesulfonyl azide[20] superior over tosyl azide[21] regarding yields and ease of workup. Since the sulfonamide byproduct could be removed by simple filtration, a base wash during workup, which would otherwise have been detrimental to the base-sensitive diacylamine function[19], was unnecessary. Coupling of the *N*-methylalkynamides **10** and **14** with methyl malonyl chloride was achieved first by silylation[22] of the amides and then by treatment with malonyl chloride. In the case of the malonic ester derivative **17d**, attempted chromatographic purification resulted in extensive hydrolysis of the diacylamine function. Therefore, crude **17d** was carried onto the next step without further purification. On the other hand, the α-unsubstituted amide **10** could be acylated to **17c** by this procedure in good yield. Again, diazo transfer was carried out as described above to give the desired diazo compounds **18c** and **18d** in 66% and 42% yield, respectively.

Scheme 3[a]



			R^1	R^2	R^3	n		
1	15a	16a	H	H	H	1		
5	15b	16b	H	H	H	2		
10	15c	16c	OBzl	H	H	2	17c	18c
14			H	Me	Me	2	17d	18d

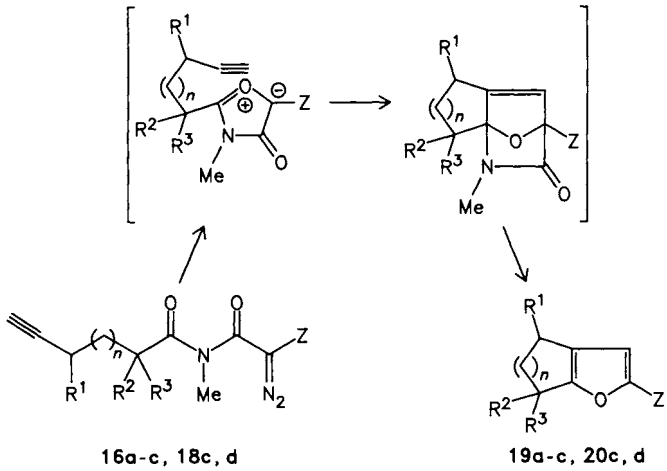
[a] Reagents and conditions: (a) *n*-BuLi, diketene, THF, −78°C to 25°C; (b) NEt_3, *p*-ABSA, CH_3CN, 0°C to 25°C; (c) NEt_3, TMSCl, benzene, reflux, then methyl malonyl chloride, benzene, 25°C.

B. Intramolecular Cycloadditions of Acetylenic Isomünchnones

For the "cyclization/cycloaddition/fragmentation reaction", a 0.3 M solution of the diazo compound in toluene was added dropwise to the same amount of refluxing toluene, which contained about 1 mol% of rhodium(II) acetate. Following the addition, the reaction mixture was refluxed for another 15 min. The subsequent evaporation of the solvent, followed by chromatography, resulted in the pure products. The results are summarized in Scheme 4.

The diazo compounds **16a** and **16b** afforded the furans **19a** and **19b** in 44% and 52% yield, respectively. The low yield of isolated furans must be due to substantial decomposition during chromatographic workup, since TLC analysis did indicate clean reactions. While furan **19b** was fairly stable, **19a** gradually decomposed on standing at room temperature. Ring strain in **19a** might be responsible for the instability. In contrast to the above results, the next higher homologue of **16b** gave neither a cycloadduct nor a furan derivative[23]. When the diazo compounds **16c** and **18c** were subjected to the same reaction conditions, the 4,5,6,7-te-

Scheme 4. Intramolecular cycloadditions of 2-alkinyl isomünchnones



16a-c, 18c, d 19a-c, 20c, d

compd.	R^1	R^2	R^3	Z	*n*	product	yield (%)
16a	H	H	H	COMe	1	**19a**	44
16b	H	H	H	COMe	2	**19b**	52
16c	OBzl	H	H	COMe	2	**19c**	63
18c	OBzl	H	H	CO_2Me	2	**20c**	60
18d	H	Me	Me	CO_2Me	2	**20d**	49

trahydrobenzo[*b*]furans **19c** and **20c** were formed in 63% and 60% yield, respectively. With a possible synthesis of the sesquiterpene furodysin[4] in mind, the reaction of compound **18d** was examined. In this case, a 49% yield of benzofuran **20d** could be obtained. The structures of all furan derivatives are supported by elemental analysis, ^{1}H-, and ^{13}C-NMR data, as well as mass spectrometry. The signal for the furan proton in **19a, 19b,** and **20d** appears at $\delta \approx 7$, whereas the 4-benzyloxy group in benzofurans **19c** and **20c** causes the signal to shift downfield to $\delta \approx 7.11$ and 7.16, respectively. The similar yields for furan **19c** and **20c** show the acyl and carbomethoxy group to be equal in activating the intermediate isomünchnone towards cycloaddition. While these electron-withdrawing groups Z (see Scheme 4) are necessary for the diazo transfer and cycloaddition reaction, they are not present in natural furanosesquiterpenes. Therefore, for future applications, the carbomethoxy group is certainly more advantageous than the acyl group, since it can be removed far more easily.

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Experimental

Merck silica gel 60 (230–400 mesh) was used for flash chromatography. – Thin-layer chromatography was carried out on Merck precoated TLC plates (silica gel 60 F_{254}). – IR spectra were recorded with a Mattson Polaris FT-IR spectrometer using CH_2Cl_2 as solvent. – ^{1}H-NMR spectra were obtained with either a Bruker WP 80 CW (80 MHz), a Bruker WM 250 (250 MHz), or a Jeol JNM GX 400 (400 MHz) instrument. – ^{13}C-NMR spectra were obtained using a Jeol JNM GX 400 (100 MHz) instrument. All spectra were recorded in $CDCl_3$ as solvent with TMS as internal standard. – Mass spectra were recorded at 70 eV on a Finnigan MAT S Instrument. – All reactions involving organometallic and air-sensitive reagents were carried out in oven-dried glassware under nitrogen. Solvents and reagents were purified by standard methods[24]. Petroleum ether with a boiling range of 35–80°C was used. THF was distilled from sodium benzophenone ketyl immediately before use.

N-Methyl-5-hexynamide (**1**): To a solution of 5.0 g (44 mmol) of 5-hexynoic acid[12] in 5 ml of benzene was added dropwise 6.5 ml (10.6 g, 89 mmol) of thionyl chloride. The solution was stirred at room temp. for 24 h and then at 40°C for 1 h. Solvent and excess thionyl chloride were evaporated and the crude acid chloride, dissolved in 25 ml of ether, was added to a solution of 3.0 g (96 mmol) of methylamine in 15 ml of ether at 0°C. Alternatively, 12 ml (96 mmol) of 8 M ethanolic methylamine solution (Fluka) may be used. The mixture was stirred for 3 h at room temp. and then poured into water (100 ml). The layers were separated, and the aqueous layer was extracted with ether (5 × 80 ml). The organic extracts were washed with 2 N HCl and with saturated $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated. The residue was purified by flash chromatography [petroleum ether/methyl acetate (2:1)]; yield 2.6 g (59%). – IR: ν = 3457 cm^{-1}, 3307, 2990, 2944, 2118, 1663 (C=O), 1528. – ^{1}H NMR (250 MHz): δ = 1.83–1.91 (m, 2H, CH_2), 1.98 (s, 1H, alkyne H), 2.26–2.63 (m, 4H, CH_2), 2.80 (d, *J* = 4.5 Hz, 3H, NCH_3), 6.30 (s, 1H, NH). – MS: *m/z* (%) = 125 (13) [M^+], 110 (8), 95 (5), 58 (56), 40 (26).

$C_7H_{11}NO$ (125.2) Calcd. C 67.17 H 8.86 N 11.19
Found C 67.06 H 8.92 N 11.00

5-Hexyne-1-yl p-toluenesulfonate (**2**): To a solution of 14.0 g (143 mmol) of 5-hexyne-1-ol[14] in 50 ml of CH_2Cl_2 were added 15 ml (22.5 g, 285 mmol) of pyridine and 40.8 g (214 mmol) of tosyl chloride. The mixture was allowed to warm to room temp., then, after 24 h, poured into water (250 ml), and extracted with CH_2Cl_2 (5 × 100 ml). The combined extracts were washed with 2 N HCl and saturated $NaHCO_3$, dried ($MgSO_4$), and evaporated. The crude tosylate was purified by flash chromatography [petroleum ether/methyl acetate (7:1)]; yield 35.2 g (98%). – TLC [petroleum ether/methyl acetate (7:1)]: R_f = 0.5. – ^{1}H NMR (80 MHz): δ = 1.25–2.25 (m, 7H, CH_2 and alkyne H), 2.50 (s, 3H, aromatic H), 4.02 (t, *J* = 4.8 Hz, 2H, CH_2O), 7.60 (m, 4H, aromatic H).

$C_{13}H_{16}O_3S$ (252.3) Calcd. C 61.88 H 6.39
Found C 61.78 H 6.39

6-Heptynenitrile (**3**): To a solution of 18 g (71 mmol) of tosylate **2** in 90 ml of DMSO was added 4.8 g (98 mmol) of NaCN, and the mixture was stirred for 4 h at 90°C. The mixture was poured into water (150 ml) and then extracted with ether (4 × 100 ml). The organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography [petroleum ether/methyl acetate (8:1)]; yield 6.6 g (87%). – TLC [petroleum ether/methyl acetate (8:1)]: R_f = 0.3. – IR: ν = 3300 cm^{-1}, 2250, 2120. – ^{1}H NMR (80 MHz): δ = 1.75–2.00 (m, 4H, CH_2), 2.10 (t, *J* = 2.4 Hz, 1H, alkyne H), 2.20–2.60 (m, 4H, CH_2).

6-Heptynoic acid (**4**)[15]: To 6.6 g (62 mmol) of nitrile **3** were added 10 ml of ethanol and a solution of 4.8 g (122 mmol) of NaOH in 20 ml of water. The mixture was refluxed for 20 h, cooled to room temp., and most of the ethanol was removed in vacuo. The residue was diluted with water (40 ml), acidified (6 N HCl) at 0°C, and extracted with ether (8 × 80 ml). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated; yield 6.6 g

(86%). – TLC [petroleum ether/methyl acetate (1:1)]: R_f = 0.6. – ^{1}H NMR (80 MHz): δ = 1.50–1.80 (m, 4H, CH_2), 2.00 (t, J = 2.4 Hz, 1H, alkyne H), 2.15–2.50 (m, 4H, CH_2), 11.47 (s, 1H, CO_2H).

N-Methyl-6-heptynamide (**5**): Acid **4** (4.00 g, 31.7 mmol) was converted to the amide **5** with 4.62 ml (7.55 g, 64 mmol) of thionyl chloride and 2.07 g (66 mmol) of methylamine as described for the preparation of amide **1**. Purification was done by flash chromatography [petroleum ether/methyl acetate (1:1)]; yield 3.60 g (83%). – TLC [petroleum ether/methyl acetate (1:1)]: R_f = 0.2. – IR: ν = 3470 cm^{-1}, 3300, 3025, 2980, 2120, 1670 (C=O), 1530. – ^{1}H NMR (80 MHz): δ = 1.52–1.60 (m, 2H, CH_2), 1.72–1.79 (m, 2H, CH_2), 1.96 (t, J = 2.4 Hz, 1H, alkyne H), 2.18–2.24 (m, 4H, CH_2), 2.79 (d, J = 4.8 Hz, 3H, NCH_3), 6.26 (s, 1H, NH). – MS: *m/z* (%) = 139 (2) [M^+], 125 (7), 110 (4), 100 (5), 81 (11), 79 (16), 73 (100), 58 (67), 53 (13), 41 (17), 39 (14).

$C_8H_{13}NO$ (139.2) Calcd. C 69.03 H 9.41 N 10.06
Found C 68.87 H 9.42 N 9.50

Methyl 5-Hydroxy-7-trimethylsilyl-6-heptynoate (**7**): To a solution of 5.0 g (51 mmol) of trimethylsilylacetylene (Janssen) in 50 ml of THF at –78 °C was added 36.5 ml (51 mmol) of 1.4 M *n*-BuLi in hexane. After 1 h at –78 °C, the solution of lithio(trimethylsilyl)-acetylene was added by cannula to a cooled (–78 °C) solution of 6.6 g (51 mmol) of aldehyde **6**[16] in 50 ml of THF. The reaction mixture was stirred for 2 h at –78 °C, treated with 20 ml of half-saturated NH_4Cl, and partly evaporated to remove most of the THF. The aqueous residue was extracted with ether (7 × 100 ml). The organic extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The product was purified by flash chromatography [petroleum ether/methyl acetate (3:1)]; yield 8.8 g (76%). – TLC [petroleum ether/methyl acetate (3:1)]: R_f = 0.43. – IR: ν = 3600 cm^{-1}, 3550, 2940, 2120, 1730, 1600. – ^{1}H NMR (400 MHz): δ = 0.12 [s, 9H, $Si(CH_3)_3$], 1.51 (d, J = 5.9 Hz, 1H, OH), 1.66–1.78 (m, 4H, CH_2), 2.34 (t, J = 6.8 Hz, 2H, CH_2), 3.64 (s, 3H, CO_2Me), 4.33 (dd, J = 5.9 and 11.5 Hz, 1H, *CH*OH). – MS: *m/z* (%) = 213 (19) [$M^+ - CH_3$], 127 (23), 99 (31), 89 (40), 74 (100), 59 (38), 43 (24).

$C_{11}H_{20}O_3Si$ (228.4) Calcd. C 57.86 H 8.83
Found C 57.13 H 8.81

Methyl 5-Benzyloxy-7-trimethylsilyl-6-heptynoate (**8**): To a solution of 0.40 g (1.75 mmol) of alcohol **7** in 5 ml of pentane/CH_2Cl_2 (2:1) were added 0.53 g (2.10 mmol) of benzyl trichloroacetimidate and 23 µl of trifluoromethansulfonic acid[17]. After the mixture was stirred for 2 h at room temp., it was filtered and the precipitate was washed with pentane. The filtrate was washed with saturated $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. Purification was achieved by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 0.51 g (91%). – TLC [petroleum ether/methyl acetate (3:1)]: R_f = 0.65. – IR: ν = 2950 cm^{-1}, 2200, 1730, 1600. – ^{1}H NMR (250 MHz): δ = 0.00 [s, 9H, $Si(CH_3)_3$], 1.54–1.62 (m, 4H, CH_2), 2.14 (t, J = 7.3 Hz, 2H, CH_2), 3.46 (s, 3H, CO_2Me), 3.86 (t, J = 6.4 Hz, 1H, CHOBzl), 4.29, 4.59 (2 d, J = 11.5 Hz, CH_2Ph), 7.06–7.16 (m, 5H, aromatic H). – MS: *m/z* (%) = 304 (0.2), 196 (23), 92 (100), 73 (7).

$C_{18}H_{26}O_3Si$ (318.5) Calcd. C 67.88 H 8.23
Found C 67.59 H 8.26

5-Benzyloxy-6-heptynoic acid (**9**): To a solution of 0.51 g (1.64 mmol) of ester **8** in 2.5 ml of ethanol was added 0.89 g (16 mmol) of potassium hydroxide, dissolved in 2.5 ml of water, and the mixture was refluxed for 24 h. The solution was acidified (6 N HCl) and extracted with ether (4 × 20 ml). The organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. The crude acid was purified by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 0.33 g (90%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.2. – ^{1}H NMR (250 MHz): δ = 1.82–1.85 (m, 4H, CH_2), 2.36–2.41 (m, 2H, CH_2CO_2H), 2.49 (d, J = 2.1 Hz, 1H, alkyne H), 4.09–4.14 (m, 1H, CHOBzl), 4.47, 4.81 (2 d, J = 11.7 Hz, 2H, CH_2Ph), 7.28–7.38 (m, 5H, aromatic H).

N-Methyl-5-benzyloxy-6-heptynamide (**10**): As described for amide **1**, 210 mg (0.94 mmol) of acid **9** was converted with 134 µl (220 mg, 1.87 mmol) of thionyl chloride and 61 mg (2.00 mmol) ethanolic methylamine to the amide **10**. Purification was done by flash chromatography [petroleum ether/methyl acetate (1:1)]; yield 156 mg (68%). – TLC [petroleum ether/methyl acetate (1:1)]: R_f = 0.2. – IR: ν = 3680 cm^{-1}, 3450, 3280, 1675, 1550. – ^{1}H NMR (400 MHz): δ = 1.79–1.87 (m, 4H, CH_2), 2.18 (t, J = 7.3 Hz, 2H, $CH_2CONHMe$), 2.49 (d, J = 1.9 Hz, 1H, alkyne H), 2.75 (d, J = 4.9 Hz, 3H, NCH_3), 4.09–4.13 (m, 1H, CHOBzl), 4.48, 4.81 (2 d, J = 11.5 Hz, 2H, CH_2Ph), 5.53 (s, 1H, NH), 7.28–7.35 (m, 5H, aromatic H). – MS: *m/z* (%) = 213 (1) [$M^+ - 32$], 139 (25), 92 (100), 82 (28), 73 (24), 58 (50).

$C_{15}H_{19}NO_2$ (245.3) Calcd. C 73.44 H 7.81 N 5.71
Found C 73.08 H 7.89 N 5.50

Methyl 2,2-Dimethyl-7-trimethylsilyl-6-heptynoate (**12**): To a solution of 0.57 ml (0.41 g, 4.07 mmol) of i-Pr_2NH in 5 ml of THF at –5 °C was added 2.54 ml (4.07 mmol) of 1.6 M *n*-BuLi in hexane. After 15 min, the solution was cooled to –78 °C, and 0.46 ml (0.42 g, 4.07 mmol) of methyl isobutyrate (Fluka) was added. After 40 min at –78 °C, a solution of 1.30 g (4.88 mmol) of iodide **11**[18] in 0.71 ml (0.73 g, 4.07 mmol) of hexamethylphosphoric triamide was added, and the resulting mixture was stirred for 30 min at –78 °C. The mixture was poured into saturated NH_4Cl (20 ml) and then extracted with ether (4 × 25 ml). The organic extracts were washed with brine, dried ($MgSO_4$), and evaporated to give the crude ester **12**, which was purified by flash chromatography [petroleum ether/methyl acetate (10:1)]; yield 0.73 g (71%). – TLC (petroleum ether/methyl acetate (10:1)]: R_f = 0.5. – ^{1}H NMR (250 MHz): δ = 0.00 [s, 9H, $Si(CH_3)_3$], 1.03 (s, 6H, CH_3), 1.22–1.33 (m, 2H, CH_2), 1.42–1.44 (m, 2H, CH_2), 2.04 (t, J = 7.0 Hz, 2H, CH_2), 3.51 (s, 3H, CO_2Me).

$C_{13}H_{24}O_2Si$ (240.4) Calcd. C 64.95 H 10.06
Found C 64.71 H 10.32

2,2-Dimethyl-6-heptynoic acid (**13**): To a solution of 1.00 g (4.14 mmol) of ester **12** in 6 ml of ethanol was added 2.32 g (41.6 mmol) of potassium hydroxide, dissolved in 6 ml of water, and the mixture was refluxed for 24 h. The solution was acidified (6 N HCl) and extracted with ether (5 × 20 ml). The organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to give the acid **13**, which was used without further purification; yield 0.48 g (76%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.3. – ^{1}H NMR (80 MHz): δ = 1.12 (s, 6H, CH_3), 1.45–1.60 (m, 4H, CH_2), 1.87 (t, J = 2.7 Hz, alkyne H), 2.02–2.25 (m, 2H, CH_2), 11.50 (s, 1H, CO_2H).

N,2,2-trimethyl-6-heptynamide (**14**): As described for amide **1**, 390 mg (2.56 mmol) of acid **13** was converted to the amide **14** with 38 µl (61 mg, 5.12 mmol) of thionyl chloride and 170 mg (5.38 mmol) of ethanolic methylamine. Purification was done by flash chromatography [petroleum ether/methyl acetate (1:1)]; yield 377 mg (88%). – TLC [petroleum ether/methyl acetate (1:1)]: R_f = 0.4. – IR: ν = 3500 cm^{-1}, 3300, 2950, 1750, 1660, 1520, 1220. – ^{1}H NMR (250 MHz): δ = 1.18 (s, 6H, CH_3), 1.42–1.56 (m, 2H, CH_2), 1.57 to 1.65 (m, 2H, CH_2), 1.96 (t, J = 2.7 Hz, 1H, alkyne H), 2.17 (dt, J = 2.4 and 6.9 Hz, 2H, $CH_2C{\equiv}CH$), 2.80 (d, J = 4.6 Hz, 3H,

NCH_3), 5.98 (s, 1H, NH). – MS: *m/z* (%) = 167 (0.4) [M^+], 152 (3), 101 (100), 67 (43), 58 (35), 41 (38).

$C_{10}H_{17}NO$ (167.3) Calcd. C 71.81 H 10.25 N 8.37
Found C 71.29 H 10.24 N 8.00

N-(Acetoacetyl)-N-methyl-5-hexynamide (**15a**): To a solution of 4.0 g (28.7 mmol) of amide **1** in 90 ml of THF at −78°C was added 18 ml (28.8 mmol) of 1.6 M *n*-BuLi in hexane. After 1 h at −78°C, a solution of 2.7 ml (2.9 g, 34.5 mmol) of freshly distilled diketene in 30 ml of THF was added dropwise[19]. With the cooling bath still attached, the mixture was allowed to reach room temp. Stirring was continued for another 12 h and then 14 ml (28.4 mmol) of 2 N HCl was added before most of the THF was evaporated in vacuo. The aqueous red residue was diluted with water (20 ml) and extracted with ether (4 × 100). The organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification was done by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 3.4 g (54%), yellow oil. Since **15a** decomposes upon prolonged standing, it was used directly for the next step. – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.18. – ^{1}H NMR (400 MHz): δ = 1.81–1.88 (m, 2H, CH_2), 1.97–2.06 (m, 2H, CH_2), 1.99 (t, *J* = 2.4 Hz, 1H, alkyne H), 2.26 (s, 3H, CH_3CO), 2.70 (t, *J* = 7.5 Hz, 2H, CH_2CH_2CONMe), 3.27 (s, 3H, NCH_3), 3.97 (s, 2H, $COCH_2COCH_3$).

N-(Acetoacetyl)-N-methyl-6-heptynamide (**15b**): The amide **5** (2.00 g, 14.3 mmol) was converted with 9.00 ml (14.4 mmol) of 1.6 M *n*-BuLi in hexane and 1.33 ml (1.45 g, 17.2 mmol) of diketene to amide **15b** by the procedure described for **15a**. Purification was accomplished by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 1.60 g (54%). This material was used directly for the next step. – ^{1}H NMR (400 MHz): δ = 1.54–1.61 (m, 2H, CH_2), 1.72–1.79 (m, 2H, CH_2), 1.96 (t, *J* = 2.4 Hz, 1H, alkyne H), 2.21–2.25 (m, 2H, CH_2), 2.26 (s, 3H, CH_3CO), 2.58 (t, *J* = 7.1 Hz, 2H, CH_2CH_2CONMe), 3.25 (s, 3H, NCH_3), 3.97 (s, 2H, $COCH_2COCH_3$).

N-(Acetoacetyl)-5-benzyloxy-N-methyl-6-heptynamide (**15c**): The amide **10** (0.70 g, 2.85 mmol) was converted with 2.10 ml (2.95 mmol) of 1.4 M *n*-BuLi in hexane and 0.27 ml (0.29 g, 3.40 mmol) of diketene to **15c** by the procedure described for **15a**. The crude product was used without further purification for the next step; yield 1.03 g, yellow oil. – ^{1}H NMR (80 MHz): δ = 1.76–1.98 (m, 4H, CH_2), 2.02 (s, 3H, CH_3CO), 2.51–2.62 (m, 3H, alkyne H and CH_2), 3.25 (s, 3H, NCH_3), 4.03 (s, 2H, $COCH_2COCH_3$), 4.08–4.31 (m, 1H, CHOBzl), 4.54, 4.89 (2 d, *J* = 11.9 Hz, 2H, CH_2Ph), 7.27–7.36 (m, 5H, aromatic H).

N-(Diazoacetoacetyl)-N-methyl-5-hexynamide (**16a**): To a solution of 2.40 g (11.8 mmol) of diacylamine **15a** in 20 ml of acetonitrile at 0°C were added 4.93 ml (3.58 g, 35.4 mmol) of triethylamine and 2.90 g (12.0 mmol) of *p*-acetamidobenzenesulfonyl azide (*p*-ABSA)[20]. The resulting mixture was stirred for 24 h in the dark at room temp., evaporated, and the residue was stirred with 20 ml of petroleum ether/ether (1:1) for 10 min. The slurry was filtered and the precipitate washed with 10 ml of petroleum ether/ether (1:1). The filtrate was concentrated and purified by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 1.40 g (55%), yellow oil. – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.19. – IR: ν = 2300 cm^{-1}, 2120 (CN_2), 1670 (C=O), 1310, 1225. – ^{1}H NMR (400 MHz): δ = 1.86–1.89 (m, 2H, CH_2), 1.99 (t, *J* = 2.7 Hz, 1H, alkyne H), 2.30 (dt, *J* = 2.7 and 6.7 Hz, 2H, $CH_2C{\equiv}CH$), 2.46 (s, 3H, CH_3CO), 2.70 (t, *J* = 7.0 Hz, 2H, CH_2), 3.23 (s, 3H, NCH_3).

$C_{11}H_{13}N_3O_3$ (235.2) Calcd. C 56.16 H 5.57 N 17.86
Found C 56.14 H 5.56 N 17.50

N-(Diazoacetoacetyl)-N-methyl-6-heptynamide (**16b**): The diacylamine **15b** (3.4 g, 15.3 mmol) was converted to **16b** with 6.3 ml (4.6 g, 45.9 mmol) of triethylamine and 3.7 g (15.6 mmol) of *p*-ABSA by the procedure described for **16a**. Purification was done by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 2.6 g (70%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.2. – IR: ν = 2130 cm^{-1} (CN_2), 1670 (C=O), 1325. – ^{1}H NMR (400 MHz): δ = 1.55–1.62 (m, 2H, CH_2), 1.76–1.84 (m, 2H, CH_2), 1.96 (t, *J* = 2.4 Hz, 1H, alkyne H), 2.24 (dt, *J* = 2.7 and 6.8 Hz, 2H, $CH_2C{\equiv}CH$), 2.46 (s, 3H, CH_3CO), 2.58 (t, *J* = 7.6 Hz, 2H, CH_2), 3.21 (s, 3H, NCH_3).

$C_{12}H_{15}N_3O_3$ (249.3) Calcd. C 57.82 H 6.07 N 16.86
Found C 57.76 H 6.17 N 16.50

N-(Diazoacetoacetyl)-5-benzyloxy-N-methyl-6-heptynamide (**16c**): The diacylamine **15c** (400 mg, 1.21 mmol) was converted to **16c** with 0.51 ml (367 mg, 3.63 mmol) of triethylamine and 300 mg (1.25 mmol) of *p*-ABSA by the procedure described for **16a**. Purification was done by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 203 mg (47%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.2. – IR: ν = 3200 cm^{-1}, 2120 (CN_2), 1660 (C=O), 1320. – ^{1}H NMR (80 MHz): δ = 1.76–1.98 (m, 5H, CH_2 and alkyne H), 2.45–2.68 (m, 2H, CH_2), 2.50 (s, 3H, CH_3CO), 3.20 (s, 3H, NCH_3), 4.10–4.32 (m, 1H, CHOBzl), 4.51, 4.92 (2 d, *J* = 11.9 Hz, 2H, CH_2Ph), 7.27–7.36 (m, 5H, aromatic H).

$C_{19}H_{21}N_3O_4$ (355.4) Calcd. C 64.21 H 5.96 N 11.82
Found C 64.43 H 6.03 N 11.78

Methyl 9-Benzyloxy-4-methyl-3,5-dioxo-4-aza-10-undecynoate (**17c**): To a solution of 156 mg (0.63 mmol) of amide **10** in 1 ml of benzene were added 138 µl (100 mg, 1.00 mmol) of triethylamine and 92 µl (100 mg, 0.95 mmol) of trimethylsilyl chloride. The solution was refluxed for 7 h and then stirred for 12 h at room temp. The mixture was filtered under nitrogen, and the filtrate was evaporated in vacuo. The residue was redissolved in 2 ml of benzene, treated with 68 µl (87 mg, 0.63 mmol) of methyl malonyl chloride (Fluka), and stirred for 24 h at room temp. The solution was evaporated, and the residue was purified by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 128 mg (60%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.2. – ^{1}H NMR (250 MHz): δ = 1.81–1.83 (m, 4H, CH_2), 2.51 (d, *J* = 2.2 Hz, 1H, alkyne H), 2.60 (t, *J* = 6.7 Hz, 2H, CH_2), 3.18 (s, 3H, NCH_3), 3.71 (s, 3H, CO_2Me), 3.83 (s, 2H, $COCH_2CO_2Me$), 4.11–4.12 (m, 1H, CHOBzl), 4.48, 4.80 (2 d, *J* = 11.6 Hz, 2H, CH_2Ph), 7.29–7.35 (m, 5H, aromatic H).

Methyl 4,6,6-Trimethyl-3,5-dioxo-4-aza-10-undecynoate (**17d**): The amide **14** (1.00 g, 5.9 mmol) was converted to **17d** with 1.35 ml (0.98 g, 9.7 mmol) of triethylamine, 1.14 ml (0.97 g, 8.9 mmol) of trimethylsilyl chloride, and 0.64 ml (0.80 g, 5.9 mmol) of methyl malonyl chloride in 2 ml of benzene as described for **17c**. Since **17d** decomposes on silica gel, it is used without further purification for the next step; yield 1.40 g (88%). – ^{1}H NMR (80 MHz): δ = 1.20 (s, 6H, CH_3), 1.49–1.53 (m, 2H, CH_2), 1.57–1.63 (m, 2H, CH_2), 1.96 (t, *J* = 2.7 Hz, 1H, alkyne H), 2.00–2.20 (m, 2H, CH_2), 2.82 (s, 3H, NCH_3), 3.81 (s, 3H, CO_2Me), 3.90 (s, 2H, $COCH_2CO_2Me$).

Methyl 9-Benzyloxy-2-diazo-4-methyl-3,5-dioxo-4-aza-10-undecynoate (**18c**): The ester **17c** (128 mg, 0.73 mmol) was converted to **18c** with 156 µl (113 mg, 1.11 mmol) of triethylamine and 91 mg (0.38 mmol) of *p*-ABSA by the procedure described for **16a**. Purification was done by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 85 mg (66%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.2. – IR: ν = 3300 cm^{-1}, 2120 (CN_2), 1725 (C=O), 1650. – ^{1}H NMR (400 MHz): δ = 1.79–1.87 (m,

4H, CH_2), 2.48 (d, J = 1.9 Hz, 1H, alkyne H), 2.59 (t, J = 6.6 Hz, 2H, CH_2), 3.14 (s, 3H, NCH_3), 3.79 (s, 3H, CO_2Me), 4.10–4.12 (m, 1H, CHOBzl), 4.49, 4.79 (2 d, J = 11.7 Hz, CH_2Ph), 7.28–7.35 (m, 5H, aromatic H).

$C_{19}H_{21}N_3O_5$ (371.4) Calcd. C 61.45 H 5.70 N 11.31
Found C 61.66 H 5.82 N 11.00

Methyl 2-Diazo-4,6,6-trimethyl-3,5-dioxo-4-aza-10-undecynoate (**18d**): The ester **17d** (300 mg, 1.12 mmol) was converted to **18d** with 482 µl (350 mg, 3.42 mmol) of triethylamine and 270 mg (1.14 mmol) of *p*-ABSA by the procedure described for **16a**. Purification was done by flash chromatography [petroleum ether/methyl acetate (5:1)]; yield 138 mg (42%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.4. – IR: ν = 2150 cm^{-1} (CN_2), 1730 (C=O), 1330. – ^1H NMR (400 MHz): δ = 1.30 (s, 6H, CH_3), 1.49–1.53 (m, 2H, CH_2), 1.62–1.78 (m, 2H, CH_2), 1.80 (dt, J = 2.4 and 7.0 Hz, 2H, CH_2), 1.95 (t, J = 2.7 Hz, 1H, alkyne H), 3.15 (s, 3H, NCH_3), 3.81 (s, 3H, CO_2Me).

$C_{14}H_{19}N_3O_4$ (293.3) Calcd. C 57.33 H 6.53 N 14.33
Found C 57.47 H 6.44 N 14.00

2-Acetyl-5,6-dihydro-4H-cyclopenta[b]furan (**19a**): A solution of 153 mg (0.651 mmol) of diazo compound **16a** in 2.5 ml of toluene (ca. 0.3 M) was added dropwise to a refluxing mixture of 2.8 mg (1 mol%) of rhodium(II) acetate in 2.5 ml of toluene. After complete addition, the mixture was stirred for another 15 min, cooled, and evaporated in vacuo (0.1 Torr). The crude furan was purified by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 43 mg (43%), slightly yellow oil. – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.55. – IR: ν = 2955 cm^{-1}, 1663 (C=O), 1501. – ^1H NMR (400 MHz): δ = 2.41 (s, 3H, CH_3CO), 2.45–2.52 (m, 2H, 5-H), 2.58–2.61 (m, 2H, CH_2), 2.74–2.77 (m, 2H, CH_2), 7.02 (s, 1H, furan H). – ^{13}C NMR (100 MHz): δ = 22.84, 24.63, 25.25, 27.43, 115.66, 128.47, 156.87, 165.96, 185.87. – MS: m/z (%) = 150 (31) [M^+], 135 (100), 77 (23), 42 (28).

$C_9H_{10}O_2$ (150.2) Calcd. C 71.98 H 6.71
Found C 71.92 H 6.69

2-Acetyl-4,5,6,7-tetrahydrobenzo[b]furan (**19b**): Diazo compound **16b** (300 mg, 1.2 mmol) was converted to furan **19b** in the presence of 5.3 mg (1 mol%) of rhodium(II) acetate by the procedure described for **19a**. Purification was done by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 101 mg (52%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.5. – IR: ν = 1670 cm^{-1} (C=O), 1600. – ^1H NMR (400 MHz): δ = 1.73–1.78 (m, 2H, CH_2), 1.83–1.89 (m, 2H, CH_2), 2.41 (s, 3H, CH_3CO), 2.45–2.48 (m, 2H, CH_2), 2.64–2.67 (m, 2H, CH_2), 7.00 (s, 1H, furan H). – ^{13}C NMR (100 MHz): δ = 21.77, 22.53, 22.73, 23.53, 25.49, 118.83, 120.17, 150.85, 156.97, 186.15. – MS: m/z (%) = 164 (5) [M^+], 149 (76), 136 (29), 121 (31), 84 (80), 42 (100).

$C_{10}H_{12}O_2$ (164.2) Calcd. C 73.15 H 7.37
Found C 72.73 H 7.37

2-Acetyl-4-benzyloxy-4,5,6,7-tetrahydrobenzo[b]furan (**19c**): Diazo compound **16c** (174 mg, 0.492 mmol) was converted to furan **19c** in the presence of 2 mg (1 mol%) of rhodium(II) acetate by the procedure described for **19a**. Purification was done by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 82 mg (63%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.2. – IR: ν = 1670 cm^{-1} (C=O), 1300. – ^1H NMR (400 MHz): δ = 1.84–1.99 (m, 2H, CH_2), 2.01–2.26 (m, 2H, CH_2), 2.42 (s, 3H, CH_3CO), 2.57–2.78 (m, 2H, CH_2), 4.48 (t, J = 4.4 Hz, 1H, CHOBzl), 4.60, 4.65 (2 d, J = 11.9 Hz, 2H, CH_2Ph), 7.11 (s, 1H, furan H), 7.29–7.37 (m, 5H, aromatic H). – ^{13}C NMR (100 MHz): δ = 18.60, 23.48, 25.67, 28.65, 69.88, 70.58, 118.02, 121.39, 127.63, 127.66, 128.45, 138.52, 151.32, 158.52, 186.23. – MS: m/z (%) = 270 (6) [M^+], 179 (44), 163 (44), 121 (20), 91 (100), 43 (62).

$C_{17}H_{18}O_3$ (270.3) Calcd. C 75.53 H 6.71
Found C 75.58 H 6.69

Methyl 4-Benzyloxy-4,5,6,7-tetrahydrobenzo[b]furan-2-carboxylate (**20c**): Diazo ester **18c** (300 mg, 0.8 mmol) was converted to furan **20c** in the presence of 3.5 mg (1 mol%) of rhodium(II) acetate by the procedure described for **19a**. Purification was done by flash chromatography [petroleum ether/methyl acetate (4:1)]; yield 135 mg (60%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.4. – IR: ν = 3070 cm^{-1}, 2980, 1720 (C=O). – ^1H NMR (400 MHz): δ = 1.80–2.02 (m, 2H, CH_2), 2.07–2.10 (m, 2H, CH_2), 2.57–2.74 (m, 2H, CH_2), 3.38 (s, 3H, CO_2Me), 4.46 (t, J = 4.4 Hz, CHOBzl), 4.49, 4.46 (2 d, J = 11.9 Hz, CH_2Ph), 7.16 (s, 1H, furan H), 7.27–7.36 (m, 5H, aromatic H). – ^{13}C NMR (100 MHz): δ = 18.60, 23.41, 28.67, 51.67, 69.75, 70.45, 118.43, 120.85, 127.56, 127.58, 128.40, 138.55, 142.78, 157.93, 159.31. – MS: m/z (%) = 286 (4) [M^+], 255 (46), 195 (5), 179 (37), 91 (100).

$C_{17}H_{18}O_4$ (286.3) Calcd. C 71.31 H 6.34
Found C 71.38 H 6.32

Methyl 7,7-Dimethyl-4,5,6,7-tetrahydrobenzo[b]furan-2-carboxylate (**20d**): Diazo ester **18d** (32 mg, 0.11 mmol) was converted to furan **20d** in the presence of 0.5 mg (1 mol%) of rhodium(II) acetate by the procedure described for **19a**. Purification was done by flash chromatography [petroleum ether/methyl acetate (8:1)]; yield 11 mg (49%). – TLC [petroleum ether/methyl acetate (4:1)]: R_f = 0.6. – IR: ν = 1720 cm^{-1} (C=O), 1670, 1600. – ^1H NMR (400 MHz): δ = 1.26 (s, 6H, CH_3), 1.56–1.64 (m, 2H, CH_2), 1.71–1.77 (m, 2H, CH_2), 2.39 (t, J = 6.1 Hz, 2H, CH_2), 3.83 (s, 3H, CO_2Me), 6.92 (s, 1H, furan H). – ^{13}C NMR (100 MHz): δ = 20.12, 22.50, 27.54, 32.72, 39.17, 51.49, 118.04, 118.91, 142.23, 159.59, 162.73. – MS: m/z (%) = 208 (10) [M^+], 193 (100), 177 (5), 149 (6), 133 (15), 105 (9).

$C_{12}H_{16}O_3$ (208.3) Calcd. C 69.21 H 7.74
Found C 69.19 H 7.71

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[1] In the context of this paper the term "annulated furan" implies that the annulated ring is attached at positions 2 and 3 of the furan ring.

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