113. Dehydroalanine-Containing Peptides by AcOH-Elimination from *O*-Acetylserine Residues with DBU/$LiClO_4$ in Tetrahydrofuran

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The elimination of H_2O from serine residues in peptides was found to be feasible by the following two steps: *O*-acylation with AcCl/pyridine in CH_2Cl_2 and treatment with an imidine base (DBU or DBN) in THF in the presence of large amounts of $LiClO_4$ (10 examples). Other Li salts such as LiBr and LiCl can also be used. No epimerization of the amino acid residues in the peptide could be detected under these conditions. Thus, a simple method for the preparation of peptides with dehydroalanine residues in high yield, directly from serine-containing precursors, is available.

From Li-Salt Effects to Dehydropeptides. – The effect of Li salts on the rate and stereochemical course of reactions in organic solvents has been known for many years. Prominent examples are the *Wittig* olefination [1], the *Diels-Alder* reaction [2] [3], the [3 + 4]-cycloaddition of cyclopropanones with furans [4], and conversions involving organolithium compounds [5]. In 1989, we discovered a dramatic effect of LiCl and other inorganic salts on the solubility of peptides in THF [6]. The changes of the peptide structure by LiCl were demonstrated for cyclosporin A in THF solution, using NMR-spectroscopic methods [7]. The effect was exploited for improvements in the solution [8] and solid-phase [9] peptide synthesis of certain amino-acid sequences. In the course of the latter work, we found that peptides can be detached from resins – without removing acid-labile protecting groups – by transesterification using the imidine base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in the presence of LiBr in alcohols [10]. When carrying out tests to learn, whether these conditions are compatible with the protecting groups commonly employed in peptide synthesis, we found that serine moieties are dehydrated by DBU/LiCl in the presence of 4-Å molecular sieve, albeit slowly and in poor yields [11]. This was the start of a project, the results of which are reported herein.

Peptides **A** containing dehydroamino acids have been studied for a long time (*Scheme 1*). They are normally made by incorporating a dehydroamino-acid residue into a peptide (**E**→**A**) [12] [13], and there are various methods of preparing suitable derivatives for this purpose (for reviews, see [14–17]), such as dehydration of serine and threonine (**E′**→**E**) [18–24], *N*-chlorination/dehydrochlorination of an amino-acid derivative (**E″**→**E**) [25–28], or *Wittig-Horner* olefination using α-phosphonylated glycine precursors (**F**→**E**) [29]. For further methods of preparing dehydroamino acids, we can only refer

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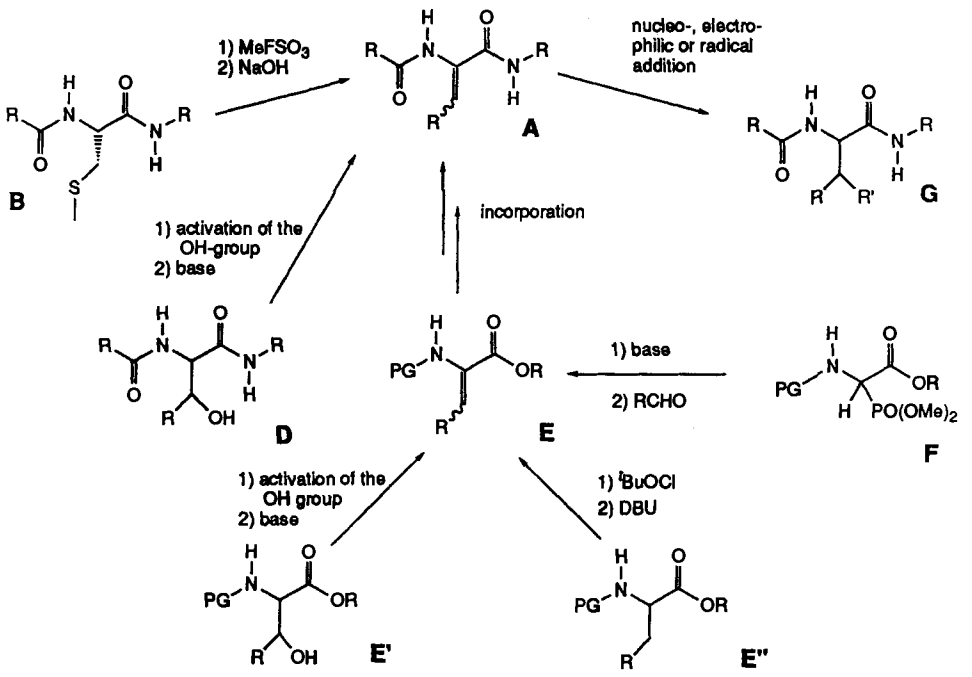
Scheme 1



to the literature [30–45]. There have also been reports about introducing a double bond into an amino-acid residue of a given peptide, for instance by *S*-methylation of a *S*-Me-cysteine unit and Me_2S elimination (**B**→**A**) [46] or by tosylation/dehydrotosylation of a serine moiety (**D**→**A**) [47] [48], *i.e.* the same methodology described herein with acetate.

The interest in dehydroamino-acid containing peptides is of course the fact that additions to the double bond – preferably stereoselectively – can furnish a host of peptide derivatives from a single intermediate (**A**→**G**). Examples are hydrogenations, additions of RMgX [49] or RHgX [50] [51] derivatives, most recently of glycosyl bromides using tin hydride methodology [52].

Results. – The serine-containing tri- and tetrapeptides for the present study were synthesized according to the standard procedure [53] of the mixed-anhydride method (using isobutyl chlorocarbonate). Since, as mentioned above, the direct dehydration was not very successful, a two-step procedure was developed for the conversion to dehydropeptides: Acetylation and elimination of AcOH (*Scheme 2* and *Table 1*).

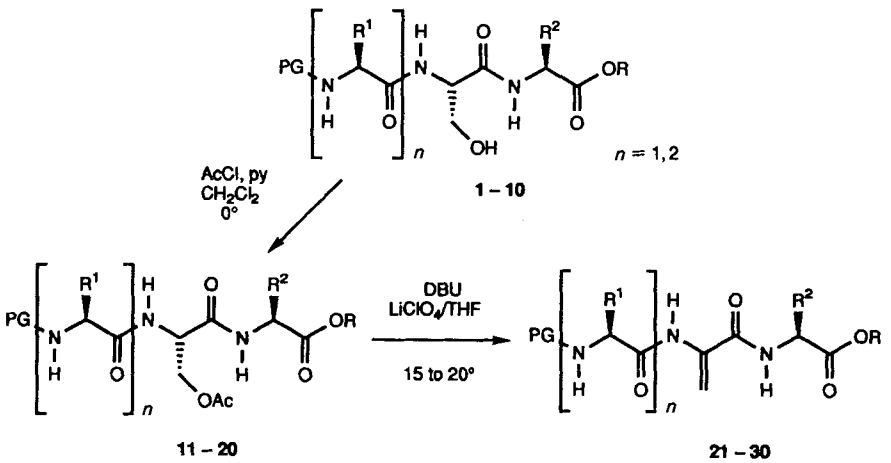
Elimination was effected preferably by DBU in $LiClO_4$-containing THF (ratio *O*-acetyl peptide/DBU/$LiClO_4$ 1:1.1:10). To keep the actual reaction temperature as low as possible (to prevent epimerizations of stereogenic centers [10]), the base was added at −15°; reaction ensued around 0°. Instead of DBU, we have employed with equal success DBN (1,5-diazabicyclo[4.3.0]non-5-ene); on the other hand, only traces of the desired product could be detected, even at elevated temperatures (> 50°), when tertiary amines

Table 1. *Abbreviated Names, Numbers, Yields, and Specific Rotations of the Synthesized Oligopeptides Containing Serine, O-Acetylserine, and Dehydroalanine Residues.* For detailed general procedures, batch sizes, and NMR spectra, see *Exper. Part* and *Table 2.*

Ser-Containing Peptide	Acetylated Product	*Δ* Ala-Containing Peptide
Boc-Phe-Ser-Ala-O^{t}Bu **1** − 13.2 (c = 1.1, $CHCl_3$)	Boc-Phe-Ser(OAc)-Ala-O^{t}Bu **11** (99%) − 29.2 (c = 1.0, MeOH)	Boc-Phe-*Δ* Ala-Ala-O^{t}Bu **21** (87%) − 29.3 (c = 1.0, MeOH)
H_2N-Phe-Ser-Ala-O^{t}Bu **2** − 73.8 (c = 1.1, MeOH)	Ac-Phe-Ser(OAc)-Ala-O^{t}Bu **12** (90%) − 23.0 (c = 0.5, MeOH)	Ac-Phe-*Δ* Ala-Ala-O^{t}Bu **22** (87%) − 22.0 (c = 1.0, MeOH)
Boc-MeLeu-Ser-Ala-O^{t}Bu **3** − 44.6 (c = 1.1, MeOH)	Boc-MeLeu-Ser(OAc)-Ala-O^{t}Bu **13** (97%) − 63.6 (c = 1.0, MeOH)	Boc-MeLeu-*Δ* Ala-Ala-O^{t}Bu **23** (91%) − 84.3 (c = 1.0, MeOH)
Boc-D-Ala-Ser-Ala-O^{t}Bu **4** − 24.4 (c = 1.0, MeOH)	Boc-D-Ala-Ser(OAc)-Ala-O^{t}Bu **14** (95%) − 86.3 (c = 1.2, MeOH)	Boc-D-Ala-*Δ* Ala-Ala-O^{t}Bu **24** (85%) + 5.7 (c = 1.0, MeOH)[a]
Boc-Phe-Ser-Val-O^{t}Bu **5** − 12.7 (c = 1.0, $CHCl_3$)	Boc-Phe-Ser(OAc)-Val-O^{t}Bu **15** (99%) − 20.4 (c = 1.5, MeOH)	Boc-Phe-*Δ* Ala-Val-O^{t}Bu **25** (89%) + 4.5 (c = 1.0, $CHCl_3$)[b]
Ac-Leu-Ser-Val-O^{t}Bu **6** − 44.1 (c = 1.5, MeOH)	Ac-Leu-Ser(OAc)-Val-O^{t}Bu **16** (94%) − 49.4 (c = 0.9, MeOH)	Ac-Leu-*Δ* Ala-Val-O^{t}Bu **26** (85%) − 46.2 (c = 1.0, MeOH)[c]
Boc-Ala-Ser-Val-O^{t}Bu **7** − 49.6 (c = 1.0, MeOH)	Boc-Ala-Ser(OAc)-Val-O^{t}Bu **17** (97%) − 43.3 (c = 1.0, MeOH)	Boc-Ala-*Δ* Ala-Val-O^{t}Bu **27** (77%) − 37.6 (c = 1.0, MeOH)[d]
Boc-Val-Ser-Phe-O^{t}Bu **8** − 11.0 (c = 0.9, MeOH)	Boc-Val-Ser(OAc)-Phe-O^{t}Bu **18** (99%) − 23.2 (c = 1.2, MeOH)	Boc-Val-*Δ* Ala-Phe-O^{t}Bu **28** (87%) − 46.0 (c = 1.0, MeOH)[e]
Ac-Leu-Ser-Leu-OMe **9** − 39.3 (c = 0.9, $CHCl_3$)	Ac-Leu-Ser(OAc)-Leu-OMe **19** (75%) − 52.0 (c = 0.9, MeOH)	Ac-Leu-*Δ* Ala-Leu-OMe **29** (69%) − 56.7 (c = 1.0, MeOH)
Boc-Ala-Ala-Ser-Leu-OMe **10** − 61.7 (c = 1.1, MeOH)	Boc-Ala-Ala-Ser(OAc)-Leu-OMe **20** (96%) − 45.9 (c = 1.0, MeOH)	Boc-Ala-Ala-*Δ* Ala-Leu-OMe **30** (64%) − 67.0 (c = 1.0, MeOH)

[a]) Anal. calc. for $C_{18}H_{31}N_3O_6$: C 56.09, H 8.11, N 10.90, O 24.90; found: C 56.42, H 8.37, N 10.87.
[b]) Anal. calc. for $C_{26}H_{39}N_3O_6$: C 63.78, H 8.03, N 8.58, O 19.61; found: C 63.92, H 7.96, N 8.43.
[c]) Anal. calc. for $C_{20}H_{35}N_3O_6$: C 60.43, H 8.87, N 10.57, O 20.12; found: C 60.24, H 9.03, N 10.93.
[d]) Anal. calc. for $C_{20}H_{35}N_3O_6$: C 58.09, H 8.53, N 10.16, O 23.21; found: C 58.26, H 8.46, N 9.87.
[e]) Anal. calc. for $C_{26}H_{39}N_3O_6$: C 63.78, H 8.03, N 8.58, O 19.61; found: C 63.88, H 7.86, N 8.47.

Scheme 2



such as *Hünig*'s base ($EtN(i\text{-}Pr)_2$) or Et_3N were employed. Other Li salts, such as LiBr and LiCl have been tested as well, the former being as effective as the perchlorate, the latter somewhat less[2]). The reaction proceeds very slowly or not at all at room temperature in the absence of a Li salt or in an aprotic dipolar solvent such as DMF. *O*-Acyl groups in the precursor peptide other than *O*-acetyl have been tested as well. It turns out that benzoylation or pivaloylation/$PhCO_2H$ or *t*-$BuCO_2H$ elimination are also possible[3]), but much less efficient (lower yield of esterification and/or lower rate of elimination).

To check for epimerization of stereogenic centers in the two-step procedure, the dehydropeptides were hydrolyzed to the free amino acids[4]), the enantiomeric purity of which was determined by GC analysis of the *N*-(pentafluoropropionyl)-isopropyl-ester derivatives [54] on the chiral stationary phase *Chirasil-Val*® [55]. No racemization of the amino acids was discovered within the detection limits of this method[5]).

Experimental Part

1. *General.* Inorg. salts were dried at 100° under high vacuum (h.v.) and stored in a desiccator over P_2O_5. THF was freshly distilled from K under Ar. Other solvents were purchased from *Fluka AG* (*puriss*). DBU was distilled from CaH_2 and stored under Ar. Medium-pressure column chromatography (FC): *Merck*, silica gel *60* (40–63 mm). TLC: silica gel *60 F254* (*Merck*), detection with Cl_2/TDM (*N,N,N',N'*-tetramethyl-4,4'-methylenebis-[aniline]) reagent [56]. GC (amino acids): *Chirasil-Val*® column (*Macherey-Nagel*, 25 m, 0.4 mm), *Carlo-Erba-Fractovap-4160-HR* GC; injector temp. 220°, detector temp. 220° (FID); carrier gas, 0.5 bar H_2; temp. program: 3 min at 85°, 4°/min till 180°. IR Spectra: *Perkin-Elmer-241* spectrophotometer. ^1H- and ^{13}C-NMR spectra:

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[2]) Higher concentrations of Li salts (30 equiv., up to saturated solutions) lead to slightly faster formation of the dehydropeptides in one examined case, but analysis by TLC showed the appearance of side products.

[3]) The eliminations of AcOH, PivOH, and PhCOOH may all occur through E_2 or E_{1cB} mechanisms. Alternatively, AcOH can also be eliminated through an acetate-ester enolate in a *retro*-ene-type reaction. We have not spent any efforts towards determining the mechanism of the elimination step.

[4]) A procedure, which of course destroys the dehydroalanine residues (→pyruvate)!

[5]) Since **24** contains a D- and an L-alanine residue, the configurational purity of this peptide could, of course, not be determined by this method.

Bruker-WM-300 (300 and 75 MHz, resp.), *Varian-Gem-200* (200 and 50 MHz, resp.); $CDCl_3$ solns., δ in ppm rel. to internal TMS, J in Hz and integrals (I) relative to each other. FAB-MS: *VG-ZAB2-SEQ* in a 3-nitrobenzyl alcohol matrix; in m/z (% of basis peak). Peptide numbering according to [57]. All intermediates not described herein have been isolated and fully characterized ($[\alpha]_D^{r.t.}$, R_f, ^{1}H-NMR, ^{13}C-NMR, and IR). The corresponding data can be obtained from the authors upon request.

2. *General Procedure for the Coupling of Amino Acids and Peptides (Mixed-Anhydride Method).* Under Ar, the C-protected amino acid or dipeptide is dissolved in DMF. If the hydrochloride of this coupling component is used, 1 equiv. of *N*-methylmorpholine (NMM) is added. In a second flask, an ice-cooled soln. of a *C*-protected amino acid or oligopeptide in THF is neutralized with 1 equiv. NMM. 1 equiv. of isobutyl chlorocarbonate is added. After 2 min, the former soln. with the first compound is transferred to the second flask. The first flask is rinsed with a small amount of DMF. The reaction mixture is allowed to warm up to r.t. As soon as no more starting material can be detected by TLC analysis, AcOEt is added, and the soln. is washed twice with a soln. of 5% citric acid in H_2O, then once with 1N $NaHCO_3$ and 1N NaCl. After a short period, drying ($MgSO_4$), filtering, and removing the solvents, the coupling products are normally isolated in pure enough form to be subjected to the following reaction.

3. *General Procedure for the Coupling of Amino Acids and Peptides (Active-Ester Method).* Under Ar, the *C*-protected amino acid or dipeptide is dissolved in DMF and the soln. cooled with ice. The solid *N*-protected amino-acid *p*-nitrophenylester is added. The cooling bath is removed, and the soln. is allowed to warm to r.t. After 12 h as a maximum, most of the solvent is removed, AcOEt is added and twice washed with cold 2N aq. NaOH. The org. phase is washed with a sat. NaCl soln. and the solvent removed to dryness. Thus, a high yield of the desired tripeptide in pure form is obtained. For data of the ten peptides **1**–**10** thus prepared, see *Tables 1* and *2*.

Table 2. *NMR-Spectroscopic*

	^{1}H-NMR			^{13}C-NMR		^{1}H-NMR		
	δ [ppm]	Position	J [Hz]	δ [ppm] (mult.)		δ [ppm]	Position	J [Hz]
1	7.35–7.10	1H–N(2.2), 1H–N(2,3), 5 arom. H	*m*	172.0 (*s*); 171.9 (*s*); 169.9 (*s*);	**11**	7.33–7.11	5 arom. H, 1NH	*m*
	5.27	1H–N(2.1)	br. *s*	155.5 (*s*);		7.01	1NH	*d* (7)
	4.56	1H–C(3.2)	*m*	136.4 (*s*);		5.26	1H–N(2.1)	*d* (7)
	4.44	1H–C(2.2)	*m*	129.3 (*d*);		4.80	1H–C(2.2)	*q* (8)
	4.41	1H–C(2.3)	*m*	128.7 (*d*);		4.50–4.25	1H–C(2.1)	*m*
	3.96	1H–C(3.2)	*m*	127.0 (*d*);		4.18	1H–C(3.2)	*dd* (11; 6)
	3.78	1H–C(3.2)	br. *s*	82.2 (*s*); 80.3 (*s*);		3.04	2H–C(3.1)	*m*
	3.62	1H–C(3.2)	*m*	62.9 (*t*); 55.9 (*d*);		2.01	CH_3COO(3.2)	*s*
	3.06	2H–C(3.1)	*m*	54.4 (*d*); 49.1 (*d*);		1.44	^{t}BuOCON(2.1)	*s*
	1.46	^{t}BuOCON(2.1)	*s*	38.3 (*t*); 28.2 (*q*);		1.36	^{t}BuOC(1.3)	*s*
	1.38	^{t}BuOC(1.3)	*s*	28.0 (*q*); 17.9 (*q*)		1.33	3H–C(3.3)	*d* (8)
	1.37	3H–C(3.3)	*d* (7)					
2	8.14	1NH	*d* (8)		**12**	7.33–7.15	5arom. H	*m*
	7.37	1NH	*d* (8)			7.10	1NH	*d* (7)
	7.40–7.15	5 arom. H	*m*			6.97	1NH	*d* (8)
	4.56	1H–C(2.2)	*m*			6.42	1H–N(2.1)	*d* (9)
	4.39	1H–C(2.2)	*m* (7)			4.86–4.72	1H–C(2.1), 1H–C(2.2)	*m*
	3.93	1H–C(d.s)	*dd* (12, 5)			4.40	1H–C(2.3)	*m* (7)
	3.69	1H–C(2.1)	*m*			4.33	1H–C(3.2)	*dd* (11; 5)
	3.65	1H–C(3.2)	*dd* (12, 6)			4.20	1H–C(3.2)	*dd* (11; 6)
	3.22	1H–C(3.1)	*dd* (14, 5)			3.07	2H–C(3.1)	*d* (7)
	2.74	1H–C(3.1)	*dd* (14, 9)			2.03	CH_3COO(3.2)	*s*
	2.62	1OH, 2NH	br. *s*			1.99	CH_3CON(2.1)	*s*
	1.42	^{t}BuOC(1.3)	*s*			1.47	^{t}BuOC(1.3)	*s*
	1.34	3H–C(3.3)	*d* (7)			1.36	2H–C(3.3)	*d* (7)

4. *General Procedure for the Acetylation of Peptides Containing Serine Residues.* To an ice-cooled soln. of the serine-containing oligopeptides in CH_2Cl_2, pyridine and AcCl are added. After disappearance of the peptide as checked by TLC, the mixture is washed with 5% citric acid in H_2O, 1N $NaHCO_3$ in H_2O, and sat. NaCl soln., and dried ($MgSO_4$). ^{1}H-NMR spectroscopically pure product is obtained after removal of the solvent. For data of the ten AcO-serine-containing peptides **11**–**20** thus prepared, see *Tables 1* and *2*.

5. *General Procedure for the Elimination of AcOH from Peptides Containing Acetylated Serine Residues.* In a two-necked reaction flask, the oligopeptide and $LiClO_4$ are dissolved in dry THF under Ar and the resulting soln. cooled to −15° in a mixture of ice with NaCl. DBU is added *via* a syringe, and the soln. is allowed to warm up to r.t. in the cooling bath. When no more starting material can be detected by TLC, AcOEt is added and the mixture worked up with 1N NH_4Cl, 1N $NaHCO_3$, and sat. aq. NaCl soln. After short drying of the org. phase ($MgSO_4$) and removal of the solvent, the dehydropeptide is obtained in high yield. This procedure was usually carried out on a scale of 0.4 up to 4.0 mmol. For data of the ten dehydropeptides **21**–**30** thus prepared, see *Tables 1* and *2*.

6. *General Procedure for Peptide Hydrolysis and Preparation of Amino-Acid Derivatives for GC Analysis.* In a screw-capped vial, 10 mg of peptide were hydrolyzed with conc. HCl soln. at 110° for 12 h. Then, H_2O was removed in an airflow, 1 ml of a soln. of AcCl (5.7 ml) and Me_2CHOH (10 ml, prepared at 0°) were added, and the vial was tightly closed. Heating at 110° for 1 h, removing of excess reagent in an airflow, and further reaction with $(CF_3CF_2CO)_2O$ (80 µl) in CH_2Cl_2 (200 µl) for 20 min gave, after removal of excess reagent in an airflow, the derivatives of the individual amino acids. This crude mixture was dissolved in Et_2O and injected directly into the *Chirasil-Val®* column.

Data of the Synthesized Peptides

^{13}C-NMR		^{1}H-NMR			^{13}C-NMR
δ [ppm] (mult.)		δ [ppm]	Position	J [Hz]	δ [ppm] (mult.)
171.3 (*s*); 171.2 (*s*);	**21**	7.33–7.11	5 arom. H, 1 NH	*m*	171.3 (*s*); 171.2 (*s*);
170.5 (*s*); 167.5 (*s*);		7.01	1 NH	*d* (7)	170.5 (*s*); 167.5 (*s*);
155.2 (*s*); 136.1 (*s*);		5.26	1 H–N(2.1)	*d* (7)	155.2 (*s*); 136.1 (*s*);
128.9 (*d*); 128.4 (*d*);		4.80	1 H–C(2.2)	*q* (8)	128.9 (*d*); 128.4 (*d*);
126.7 (*d*); 81.7 (*s*);		4.50–4.25	1 H–C(2.1),	*m*	126.7 (*d*); 81.7 (*s*);
80.0 (*s*); 63.6 (*t*);			1 H–C(2.3),		80.0 (*s*); 63.6 (*t*);
55.6 (*d*); 51.7 (*s*);			1 H–C(3.2)		55.6 (*d*); 51.7 (*s*);
48.6 (*d*); 38.0 (*t*);		4.18	1 H–C(3.2)	*dd* (11; 6)	48.6 (*d*); 38.0 (*t*);
28.0 (*q*); 27.6 (*q*);		3.04	2 H–C(3.1)	*m*	28.0 (*q*); 27.6 (*q*);
20.4 (*q*); 18.1 (*q*)		2.01	CH_3COO(3.2)	*s*	20.4 (*q*); 18.1 (*q*)
		1.44	*t*-BuOCON(2.1)	*s*	
		1.36	*t*-BuOC(1.3)	*s*	
		1.33	3 H–C(3.3)	*d* (8)	
171.7 (*s*); 171.2 (*s*);	**22**	8.44	1 H–N(2.2)	*s*	172.8 (*s*); 169.9 (*s*);
170.8 (*s*); 170.2 (*s*);		7.35–7.10	5 arom. H	*m*	169.7 (*s*); 162.5 (*s*);
167.6 (*s*); 136.2 (*s*);		6.93	1 H–N(2.3)	*d* (6)	135.8 (*s*); 133.4 (*s*);
129.2 (*d*); 128.7 (*d*);		6.38	1 H–C(3.2)	*d* (2)	128.9 (*d*); 128.4 (*d*);
127.1 (*d*); 82.2 (*s*);			(*trans* to C=O)		126.8 (*d*); 102.5 (*t*);
63.7 (*t*); 54.4 (*d*);		6.31	1 H–N(2.1)	*d* (8)	82.3 (*t*); 54.8 (*d*); 48.9 (*d*);
52.1 (*d*); 48.9 (*d*);		5.34	1 H–C(3.1)	*d* (2)	37.8 (*t*); 27.7 (*q*); 22.8 (*q*);
38.3 (*t*); 27.9 (*q*);			(*cis* to C=O)		18.1 (*q*)
23.1 (*q*); 20.7 (*q*);		4.80	1 H–C(2.1)	*t* (8)	
18.5 (*q*)		4.44	1 H–C(2.2)	*m* (7)	
		3.10	2 H–C(3.1)	*m*	
		1.97	CH_3CON(2.1)	*s*	
		1.45	*t*-BuOC(1.3)	*s*	
		1.40	3 H–C(3.3)	*d* (8)	

Table 2 (cont.)

	^{1}H-NMR			^{13}C-NMR		^{1}H-NMR		
	δ [ppm]	Position	J [Hz]	δ [ppm] (mult.)		δ [ppm]	Position	J [Hz]
3	7.11	1H–N(2.3)	*d* (7)	172.0 (*s*); 170.2 (*s*);	**13**	6.99, 6.83	1H–N(2.2) (rotamers)	2*s*
	7.07, 6.89	1H–N(2.2) (rotamers)	2*s*	155.3 (*s*); 82.3 (*s*); 80.7 (*s*);		6.89	1H–N(2.3)	*d* (7)
	4.70, 4.57	1H–C(2.1) (rotamers)	2*s*	62.9 (*t*); 56.7 (*d*); 54.1 (*d*); 49.0 (*d*);		4.71	1H–C(2.2), 1H–C(2.1)	*m*
	4.50	1H–C(2.2)	*q* (6)	36.7 (*t*); 28.3 (*q*);		4.42	1H–C(2.3)	*m* (7)
	4.43	1H–C(2.3)	*m* (7)	28.0 (*q*); 24.9 (*d*);		4.28	2H–C(3.2)	*m*
	3.97	1H–C(3.2)	*m*	23.2 (*q*); 21.8 (*q*);		2.75	CH_3N(2.1)	*s*
	3.68	1OH	br. *s*	17.9 (*q*)		2.07	CH_3COO(3.1)	*s*
	3.63	1H–C(3.2)	br. *s*			1.67	2H–C(3.1), 1H–C(4.1)	*m*
	2.77	CH_3N(2.1)	*s*			1.49	*t*-BuOCON(2.1)	*s*
	2.10	1H–C(4.1)	*s*			1.38	*t*-BuOC(1.3)	*s*
	1.67	2H–C(3.1)	*m*			0.96	3H–C(5.1)	*d* (7)
	1.48	*t*-BuOCON(2.1)	*s*			0.92	3H–C(5′.1)	*d* (7)
	1.46	*t*-BuOC(1.3)	*s*					
	1.38	3H–C(3.3)	*d* (7)					
	0.95	3H–C(5.1)	*d* (7)					
	0.92	3H–C(5′.1)	*d* (7)					
4	7.37	1NH	*d* (7)	173.6 (*s*);	**14**	7.12	1H–N(2.3)	*d* (8)
	7.28	1NH	*d* (7)	172.0 (*s*); 170.3 (*s*);		7.14, 6.98	1H–N(2.2) (rotamers)	2*s*
	5.37	1H–N(2.1)	br. *s*	155.6 (*s*);		5.25	1H–N(2.1)	*d* (7)
	4.56	1H–N(2.2)	*m*	82.2 (*s*); 80.3 (*s*);		4.80	1H–C(2.2)	*m*
	4.39	1H–C(2.3)	*m* (7)	62.8 (*t*); 54.3 (*d*); 50.6 (*d*); 49.1 (*d*);		4.41	1H–C(3.2), 1H–C(2.3)	*m*
	4.19	1H–C(2.1)	*m*	28.4 (*q*); 28.0 (*q*);		4.28	1H–C(3.2)	*dd* (11; 5)
	3.97	1H–C(3.2)	*m*	17.9 (*q*); 17.8 (*q*)		4.19	1H–C(2.1)	*m* (7)
	3.86	1OH	br. *s*			2.07	CH_3COO(3.2)	*s*
	3.67	1H–C(3.2)	*m*			1.46	*t*-BuOCON(2.1)	*s*
	1.43	*t*-BuOCON(2.1)	*s*			1.44	*t*-BuOC(1.3)	*s*
	1.41	*t*-BuOC(1.3)	*s*			1.38	3CH	*d* (7)
	1.36	3CH	*d* (7)			1.37	3CH	*d* (7)
	1.35	3CH	*d* (8)					
5	7.33–7.10	5 arom. H, 1H–N(2.2), 1H–N(2.3)	*m*	171.9 (*s*); 170.5 (*s*); 170.1 (*s*);	**15**	7.37–7.14	5 arom. H	*m*
	5.32	1H–N(2.1)	br. *d* (7)	155.2 (*s*);		6.86	1NH	*d* (7)
	4.61	1H–C(2.1)	*m*	136.2 (*s*);		6.69	1NH	*d* (9)
	4.45	1H–C(2.2)	*m*	129.0 (*d*);		4.92	1H–N(2.1)	br. *s*
	4.37	1H–C(2.3)	*dd* (9, 5)	128.3 (*d*);		4.65	1H–C(2.1)	*q* (6)
	4.00–3.70	1H–O, 1H–C(3.2)	*m*	126.6 (*d*); 81.9 (*q*); 80.0 (*q*); 62.5 (*t*); 57.7 (*d*);		4.45–4.25	1H–C(2.2), 1H–C(2.3), 1H–C(3.2)	*m*
	3.70–3.52	1H–C(3.2)	*m*	55.5 (*d*); 54.0 (*d*);		4.15	1H–C(3.2)	*dd* (11; 6)
	3.05	2H–C(3.1)	*m*	38.1 (*t*); 30.6 (*d*);		3.09	2H–C(3.1)	*d* (7)
	2.17	1H–C(3.3)	*m*	27.9 (*q*); 27.7 (*q*);		2.15	1H–C(3.3)	*m*
	1.45	*t*-BuOCON(2.1)	*s*	18.8 (*q*); 17.4 (*q*)		2.04	CH_3COO(3.2)	*s*
	1.34	*t*-BuOC(1.2)	*s*			1.46	*t*-BuOCON(2.1)	*s*
	0.93	3H–C(4.3)	*d* (7)			1.44	*t*-BuOC(1.3)	*s*
	0.90	3H–C(4′.3)	*d* (7)			0.92	3H–C(4.3)	*d* (5)
						0.89	3H–C(4′.3)	*d* (5)

Table 2 (cont.)

^{13}C-NMR		^{1}H-NMR			^{13}C-NMR
δ [ppm] (mult.)		δ [ppm]	Position	J [Hz]	δ [ppm] (mult.)
171.6 (*s*); 170.6 (*s*);	**23**	8.63, 8.51	1 H–N(2.2)	2*s*	171.9 (*s*); 170.6 (*s*);
167.8 (*s*); 155.3 (*s*);			(rotamers)		163.0 (*s*); 101.5 (*t*);
82.2 (*s*); 80.7 (*s*);		6.74	1 H–N(2.3)	*d* (6)	82.5 (*s*); 80.4 (*s*); 58.2 (*d*);
63.8 (*t*); 56.6 (*d*);		6.46	1 H–C(3.2)	*s*	57.3 (*d*); 49.2 (*d*); 36.5 (*t*);
52.1 (*d*); 48.9 (*d*);			(*trans* to C=O)		29.9 (*q*); 28.3 (*q*); 28.0 (*s*);
36.5 (*t*); 30.1 (*q*);		5.29	1 H–C(3.2)	*d* (3)	24.7 (*d*); 23.2 (*q*); 21.6 (*q*);
28.4 (*q*); 28.0 (*q*);			(*cis* to C=O)		18.5 (*q*)
24.8 (*d*); 23.2 (*q*);		4.85, 4.62	1 H–C(3.1)	2 br. *s*	
21.8 (*q*); 20.7 (*q*);			(rotamers)		
18.5 (*q*)		4.48	1 H–C(2.3)	*m* (7)	
		2.77	CH_3N(2.1)	*s*	
		1.69	2 H–C(3.1),	*m*	
			1 H–C(4.1)		
		1.50	*t*-BuOCON(2.1)	*s*	
		1.48	*t*-BuOC(1.3)	*s*	
		1.42	3 H–C(3.3)	*d* (7)	
		0.96	3 H–C(5.1)	*d* (7)	
		0.93	3 H–C(5′.1)	*d* (7)	
173.1 (*s*); 171.6 (*s*);	**24**	8.59	1 H–N(2.2)	*s*	171.7 (*s*); 163.1 (*s*);
170.8 (*s*); 168.0 (*s*);		6.81	1 H–N(2.3)	*d* (7)	155.3 (*s*); 133.9 (*s*);
155.6 (*s*); 82.0 (*s*);		6.47	1 H–C(3.2)	*d* (2)	102.1 (*t*); 82.6 (*s*);
80.3 (*s*); 63.7 (*t*);			(*trans* to C=O)		80.3 (*s*); 51.2 (*d*); 49.2 (*d*);
52.0 (*d*); 50.4 (*d*);		5.33	1 H–C(3.2)	*d* (3)	28.3 (*q*); 28.0 (*q*); 18.5 (*q*)
49.0 (*d*); 28.3 (*q*);			(*cis* to C=O)		
27.9 (*q*); 20.7 (*q*);		5.07	1 H–N(2.1)	br. *s*	
18.2 (*q*)		4.48	1 H–C(2.3)	*m* (7)	
		4.25	1 H–C(2.1)	br. *s*	
		1.48	*t*-BuOCON(2.1)	*s*	
		1.45	*t*-BuOC(1.3)	*s*	
		1.42	3 CH	*d* (7)	
		1.40	3 CH	*d* (7)	
172.0 (*s*); 171.0 (s);	**25**	8.46	1 H–N(2.2)	*s*	170.7 (*s*); 170.4 (*s*);
170.7 (*s*); 168.6 (*s*);		7.35–7.15	5 arom. H	*m*	163.3 (*s*); 155.3 (*s*);
154.8 (*s*); 136.5 (*s*);		6.66	1 H–N(2.3)	*d* (9)	136.3 (*s*); 133.8 (*s*);
129.6 (*d*); 128.9 (*d*);		6.49	1 H–C(3.2)	*d* (2)	129.2 (*d*); 128.7 (*d*);
52.6 (*d*); 38.1 (*t*);			(*trans* to C=O)		127.0 (*d*); 102.1 (*t*);
31.7 (*d*); 28.2 (*q*);		5.35	1 H–C(3.2)	*s*	82.5 (*s*); 80.4 (*s*); 57.9 (*d*);
28.0 (*q*); 20.8 (*q*);			(*cis* to C=O)		38.4 (*t*); 31.6 (*d*); 28.2 (*q*);
19.1 (*q*); 17.9 (*q*)		5.02	1 H–N(2.1)	*d* (8)	28.0 (*q*); 18.8 (*q*); 17.7 (*q*)
		4.52–4.35	1 H–C(2.1),	*m*	
			1 H–C(2.3)		
		3.20–3.00	2 H–C(3.1)	*m*	
		2.19	3 H–C(4.3)	*m*	
		0.90	3 H–C(4′.3)	*d* (7)	

Table 2 (cont.)

	^{1}H-NMR			^{13}C-NMR		^{1}H-NMR		
	δ [ppm]	Position	J [Hz]	δ [ppm] (mult.)		δ [ppm]	Position	J [Hz]
6	7.97	1 NH	*d* (7)	173.0 (*s*); 170.7 (*s*);	**16**	7.57	1 NH	*d* (8)
	7.88	1 NH	*d* (9)	170.4 (*s*); 170.3 (*s*);		7.50	1 NH	*d* (8)
	7.49	1 NH	*d* (9)	81.6 (*s*); 62.8 (*t*);		6.90	1 NH	*d* (8)
	4.92	1 H–C(2.2)	*q* (6)	57.5 (*d*); 54.3 (*d*);		5.08	1 H–C(2.2)	*q* (8)
	4.72	1 H–C(2.1)	*q* (7)	51.3 (*d*); 41.9 (*d*);		4.69	1 H–C(2.1)	*q* (6)
	4.39	1 H–C(2.3)	*q* (7)	30.9 (*t*); 27.7 (*q*);		4.44	1 H–C(2.3)	*dd* (9; 5)
	3.90–3.60	2 H–C(3.2)	*m*	24.4 (*d*); 22.6 (*q*);		4.37	1 H–C(3.2)	*dd* (11; 6)
	3.39	1 H–O(3.2)	br. *s*	22.5 (*q*); 22.0 (*q*);		4.24	1 H–C(3.2)	*dd* (11; 6)
	2.14	1 H–C(3.3)	*m*	18.6 (*q*); 17.4 (*q*)		2.17	1 H–C(3.3)	*m*
	1.97	CH_3CON(2.1)	*s*			2.04	CH_3COO	*s*
	1.80–1.35	2 H–C(3.1), 1 H–C(4.1)	*m*			2.03	CH_3CON(2.1)	*s*
						1.74–1.50	2 H–C(3.1), 1 H–C(4.1)	*m*
	1.00–0.75	3 H–C(5.1), 3 H–C(5′.1), 3 H–C(4.3), 3 H–C(4′3)	*m*			1.47	*t*-BuOC(1.3)	*s*
						1.05–0.85	3 H–C(5.1), 3 H–C(5′.1), 3 H–C(4.3), 3 H–C(4′.3)	*m*
7	7.30	1 NH	*d* (7)	173.6 (*s*);	**17**	7.11	1 NH	*d* (7)
	7.20	1 NH	*d* (9)	170.7 (*s*);		6.91	1 NH	*d* (7)
	5.35	1 H–N(2.1)	*d* (7)	155.5 (*s*);		5.12	1 H–N(2.1)	*d* (7)
	4.58	1 H–C(2.2)	*m*	82.2 (*s*); 80.2 (*s*);		4.76	1 H–C(2.2)	*q* (8)
	4.39	1 H–C(2.3)	*dd* (9; 5)	62.7 (*t*); 58.0 (*d*);		4.45–4.35	1 H–C(2.1)	*m*
	4.25	1 H–C(2.1)	*m*	54.2 (*d*); 50.3 (*d*);		4.40	1 H–C(2.3)	*dd* (9; 5)
	4.05–4.00	1 H–C(2.2)	*m*	30.9 (*d*); 28.3 (*q*);		4.25	1 H–C(3.2)	*dd* (11; 6)
	3.87	1 H–O(3.2)	br. *s*	28.0 (*q*); 19.0 (*q*);		4.20	1 H–C(3.2)	*m*
	3.75–3.65	1 H–C(3.2)	*m*	18.6 (*q*); 17.5 (*q*)		2.16	1 H–C(3.3)	*m*
	2.15	1 H–C(3.3)	*m*			2.08	CH_3COO(3.2)	*s*
	1.47	*t*-BuOCON(2.1)	*s*			1.47	*t*-BuOCON(2.1)	*s*
	1.43	*t*-BuOC(1.3)	*s*			1.44	*t*-BuOC(1.3)	*s*
	1.37	3 H–C(3.1)	*d*			1.38	3 H–C(3.1)	*d* (7)
	0.94	3 H–C(4.3)	*d* (7)					
	0.91	3 H–C(4′.3)	*d* (7)					
8	7.35–7.20	5 arom. H	*m*	172.6;	**18**	7.33–7.10	5 arom. H	*m*
	7.15	1 NH	*d* (7)	170.8;		6.78	1 NH	*d* (8)
	6.93	1 NH	*d* (8)	170.5;		6.72	1 NH	*d* (8)
	5.10	1 H–N(2.1)	*d* (8)	143.3;		5.02	1 H–N(2.1)	*d* (7)
	4.71	1 H–C(2.3)	*q* (8)	136.3; 129,7;		4.70	1 H–C(2.2), 1 H–C(2.3)	*m*
	4.49	1 H–C(2.2)	*m*	128.9;		4.36	1 H–C(3.2)	*dd* (11; 5)
	4.05–3.90	1 H–C(3.2), 1 H–C(2.3)	*m*	127.4; 83.0; 63.1;		4.18	1 H–C(3.2)	*dd* (11; 6)
	3.70–3.54	1 H–C(3.2)	*m*	60.4; 54.4;		3.95	1 H–C(2.1)	*dd* (8; 6)
	3.30	1 H–C(3.2)	*t* (6)	54.3; 38.0;		3.09	2 H–C(3.3)	*d* (6)
	3.08	2 H–C(3.2)	*d* (6)	31,0; 28.5;		2.13	1 H–C(3.1)	*m*
	2.10	1 H–C(3.1)	*m*	28.1; 19.5;		2.10	CH_3COO	*s*
	1.44	*t*-BuOCON(2.1)	*s*	17.8		1.43	*t*-BuOCON(2.1)	*s*
	1.41	*t*-BuOC(1.3)	*s*			1.38	*t*-BuOC(1.3)	*s*
	0.93	3 H–C(4.1)	*d* (7)			0.95	3 H–C(4.1)	*d* (7)
	0.89	3 H–C(4′.1)	*d* (7)			0.88	3 H–C(4′.1)	*d* (7)

Table 2 (cont.)

^{13}C-NMR		^{1}H-NMR			^{13}C-NMR
δ [ppm] (mult.)		δ [ppm]	Position	J [Hz]	δ [ppm] (mult.)
172.7 (*s*); 170.7 (*s*);	**26**	7.57	1 NH	*d* (8)	172.7 (*s*); 170.7 (*s*);
170.6 (*s*); 170.2 (*s*);		7.50	1 NH	*d* (8)	170.6 (*s*); 170.2 (*s*);
168.8 (*s*); 82.0 (*s*);		6.90	1 NH	*d* (8)	168.8 (*s*); 82.0 (*s*);
63.8 (*t*); 57.8 (*d*);		5.08	1 H–C(2.2)	*q* (8)	63.8 (*t*); 57.8 (*d*);
52.0 (*d*); 51.6 (*d*);		4.69	1 H–C(2.1)	*q* (6)	52.0 (*d*); 51.6 (*d*);
41.8 (*t*); 31.5 (*d*);		4.44	1 H–C(2.3)	*dd* (9; 5)	41.8 (*t*); 31.5 (*d*);
28.0 (*q*); 24.8 (*d*);		4.37	1 H–C(3.2)	*dd* (11; 6)	28.0 (*q*); 24.8 (*d*);
23.0 (*q*); 22.8 (*q*);		4.24	1 H–C(3.2)	*dd* (11; 6)	23.0 (*q*); 22.8 (*q*);
22.7 (*q*); 22.3 (*q*);		2.17	1 H–C(3.3)	*m*	22.7 (*q*); 22.3 (*q*);
20.7 (*q*); 18.8 (*q*);		2.04	CH_3COO(3.2)	*s*	20.7 (*q*); 18.8 (*q*);
17.7 (*q*)		2.03	CH_3CON(2.1)	*s*	17.7 (*q*)
		1.74–1.50	2 H–C(3.1), 1 H–C(4.1)	*m*	
		1.47	*t*-BuOC(1.3)	*s*	
		1.05–0.85	3 H–C(5.1), 3 H–C(5′.1), 3 H–C(4.3), 3 H–C(4′.3)	*m*	
172.9 (*s*); 170.9 (*s*);	**27**	8.60	1 H–N(2.2)	br. *s*	172.3 (*s*); 171.3 (*s*);
170.4 (*s*); 168.4 (*s*);		6.83	1 H–N(2.3)	*d* (8)	164.0 (*s*); 155.7 (*s*);
155.5 (*s*); 82.1 (*s*);		6.38	1 H–C(3.2) (*trans* to C=O)	*s*	134.4 (*t*); 102.6 (*s*);
80.3 (*s*); 63.8 (*t*);					82.7 (*s*); 78.0 (*s*); 58.3 (*d*);
57.8 (*d*); 52.4 (*d*);		5.33	1 H–C(3.2) (*cis* to C=O), 1 H–N(2.1)	br. *s*	51.4 (*d*); 31.6 (*d*); 28.4 (*q*);
50.4 (*d*); 31.4 (*d*);					28.2 (*q*); 19.0 (*q*); 18.4 (*q*);
28.3 (*q*); 28.0 (*q*);					18.0 (*q*)
20.7 (*q*); 18.9 (*q*);		4.38	1 H–C(2.3)	*dd* (9; 5)	
18.2 (*q*); 17.7 (*q*)		4.05	1 H–C(2.1)	*m*	
		2.12	1 H–C(3.3)	*m* (5)	
		1.41	*t*-BuOCON(2.1)	*s*	
		1.36	*t*-BuOC(1.3)	*s*	
		1.31	3 H–C(2.1)	*d* (6)	
		0.87	3 H–C(4.3), 3 H–C(4′.3)	*d* (7)	
171.5 (*s*); 170.4 (*s*);	**28**	8.52	1 H–N(2.2)	*s*	170.6 (*s*); 170.2 (*s*);
169.6 (*s*); 167.6 (*s*);		7.30–7.10	5 arom. H	*m*	163.0 (*s*); 155.7 (*s*);
155.6 (*s*); 135.6 (*s*);		6.99	1 H–N(2.3)	*d* (6)	135.8 (*d*); 133.4 (*t*);
129.1 (*d*); 128.1 (*d*);		6.42	1 H–C(3.2) (*trans* to C=O)	*s*	129.1 (*d*); 128.1 (*d*);
126.7 (*d*); 82.2 (*s*);					126.7 (*d*); 101.9 (*s*);
79.8 (*s*); 63.3 (*t*);		5.22	1 H–N(2.1)	*d* (6)	82.4 (*s*); 79.6 (*s*); 59.9 (*d*);
59.8 (*d*); 53.6 (*d*);		5.20	1 H–C(3.2) (*cis* to C=O)	*s*	54.0 (*d*); 37.3 (*t*); 30.9 (*d*);
51.7 (*d*); 37.6 (*t*);					28.0 (*q*); 27.7 (*q*); 19.0 (*q*);
30.4 (*d*); 28.0 (*q*);		4.71	1 H–C(2.3)	*q* (7)	17.2 (*q*)
27.6 (*q*); 20.4 (*q*);		4.18	1 H–C(2.1)	*m*	
19.0 (*q*); 17.2 (*q*)		3.11	2 H–C(3.3)	*d* (6)	
		2.13	1 H–C(3.1)	*m*	
		1.42	*t*-BuOCON(2.1)	*s*	
		1.41	*t*-BuOC(1.3)	*s*	
		0.95	3 H–C(4.1)	*d* (7)	
		0.88	3 H–C(4′.1)	*d* (7)	

Table 2 (cont.)

	^{1}H-NMR			^{13}C-NMR		^{1}H-NMR		
	δ [ppm]	Position	J [Hz]	δ [ppm] (mult.)		δ [ppm]	Position	J [Hz]
9	4.55–4.35	1H–C(2.1), 1H–C(2.2), 1H–C(2.3)	*m*	175.0 (*s*); 174.5 (*s*); 173.6 (*s*);	**19**	7.46	1NH	br. *s*
	3.78	2H–C(3.2)	*d* (6)	172.3 (*s*);		7.41	1NH	br. *s*
	3.70	3H–C(1.3)	*s*	63.0 (*t*); 56.5 (*d*);		6.67	1NH	br. *s*
	1.98	CH_3CON(2.1)	*s*	53.6 (*d*); 52.7 (*q*);		4.91	1H–C(2.2)	*q* (7)
	1.80–1.50	2H–C(3.1), 1H–C(4.1), 2H–C(3.3), 1H–C(4.3)	*m*	52.3 (*d*); 41.8 (*t*); 41.6 (*t*); 26.0 (*d*); 25.9 (*d*); 23.4 (*q*); 23.3 (*q*); 22.5 (*q*);		4.65–4.55	1H–C(2.1), 1H–C2.3)	*m*
	0.96	3H–C(5)	*d* (6)	22.0 (*q*); 21.9 (*q*)		4.38	1H–C(3.2)	*dd* (10; 6)
	0.94	3H–C(5)	*d* (5)			4.27	1H–C(3.2)	*dd* (10; 6)
	0.93	3H–C(5)	*d* (6)			3.73	3H–C(3.1), 1H–C(4.1), 2H–C(3.3), 1H–C(4.3)	*s*
	0.91	3H–C(5)	*d* (6)			1.00–0.85	3H–C(5.1), 3H–C(5′.1), 3H–C(5.3), 3H–C(5′.3)	*m*
10	7.62	1NH	*d* (8)	173.0;	**20**	7.43	1NH	*d* (8)
	7.57	1NH	*d* (8)	172.6;		7.17	1NH	*d* (8)
	7.42	1NH	*d* (8)	172.5;		7.02	1NH	*d* (6)
	5.55	1H–N(2.1)	*d* (8)	170.4;		5.24	1H–N(2.1)	*d* (6)
	4.75–4.00	1H–C(2.1), 1H–C(2.2), 1H–C(2.3), 1H–C2.4), 1H–O(3.3)	*m*	155.4; 80.0; 62.4; 54.0; 52.1; 50.8; 49.9; 48.7; 40.5;		4.84	1H–C(2.3)	*m*
	3.96	1H–C(3.3)	*dd* (11; 3)	28.0; 24.5;		4.61	1H–C(2.4)	*m*
	3.71	CH_3OC(1.4)	*s*	22.5; 21.4;		4.48	1H–C(2.2)	*m* (7)
	3.69	1H–C(3.3)	buried	18.6		4.40	1H–C(3.3)	*dd* (11; 6)
	1.74–1.55	2H–C(3.4), 1H–C(4.4)	*m*			4.33	1H–C(3.3)	*dd* (11; 6)
	1.40	*t*-BuOCON(2.1)	*s*			4.18	1H–C(2.1)	*m* (7)
	1.38	3H–C(3.1)	*d* (7)			3.72	3H–COC(1.4)	*s*
	1.30	3H–C(3.2)	*d* (7)			2.04	CH_3COO(3.2)	*s*
	0.90	3H–C(5.4), 3H–C(5′.4)	*m*			1.85	1H–C(4.4)	*m*
						1.66	2H–C(3.4)	*m*
						1.44	*t*-BuOCON(2.1)	*s*
						1.42	3H–C(3.2)	*d* (7)
						1.38	3H–C(3.1)	*d* (7)
						0.93	3H–C(5.4), 3H–C(5′.4)	*t*

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Table 2 (cont.)

^{13}C-NMR		^{1}H-NMR			^{13}C-NMR
δ [ppm] (mult.)		δ [ppm]	Position	J [Hz]	δ [ppm] (mult.)
173.0 (*s*); 172.6 (*s*);	**29**	8.65	1 H–N(2.2)	*s*	173.5 (*s*); 171.4 (*s*);
171.0 (*s*); 170.4 (*s*);		7.32	1 NH	*d* (8)	170.2 (*s*); 163.3 (*s*);
168.6 (*s*); 63.7 (*t*);		6.56	1 NH	*d* (8)	133.4 (*t*); 103.0 (*s*);
52.3 (*q*); 52.2 (*d*);		6.35	1 H–C(3.2)	*s*	52.2 (*q*); 52.2 (*d*); 51.2 (*d*);
51.9 (*d*); 51.0 (*d*);			(*trans* to C=O)		40.8 (*t*); 40.5 (*t*); 24.6;
41.5 (*t*); 41.3 (*t*);		5.37	1 H–C(3.2)	*s*	24.6; 22.7; 22.5; 21.4
24.9 (*q*); 23.0 (*q*);			(*cis* to C=O)		
22.8 (*q*); 22.2 (*q*);		4.70–4.50	1 H–C(2.1).	*m*	
21.9 (*q*); 20.7 (*q*)			1 H–C(2.3)		
		3.75	3 H–COC(1.3)	*s*	
		1.99	CH_3CON(2.1)	*s*	
		1.75–1.50	2 H–C(3.1),	*m*	
			1 H–C(4.1),		
			2 H–C(3.3),		
			1 H–C(4.3)		
		1.00–0.80	3 H–C(5.1),	*m*	
			3 H–C(5′.1),		
			3 H–C(5.3),		
			3 H–C(5′.3)		
173.2 (*s*); 172.8 (*s*);	**30**	8.58	1 H–N(2.3)	*s*	173.2 (*s*); 172.8 (*s*);
172.2 (*s*); 170.8 (*s*);		6.93	1 NH	br. *s*	171.0 (*s*); 163.6 (*s*);
168.0 (*s*); 155.9 (*s*);		6.78	1 NH	*d* (8)	155.6 (*s*); 133.9 (*t*);
80.7 (*s*); 63.9 (*t*);		6.41	1 H–C(3.3)	*d* (2)	103.4 (*s*); 80.3 (*s*);
52.5 (*d*); 52.3 (*q*);			(*trans* to C=O)		52.5 (*q*); 51.4 (*d*); 49.8 (*d*);
51.0 (*d*); 50.8 (*d*);		5.39	1 H–C(3.3)	*d* (2)	41.4 (*t*); 28.3 (*q*); 24.9 (*d*);
49.6 (*d*); 41.0 (*t*);			(*cis* to C=O)		22.8 (*q*); 21.9 (*q*); 18.3 (*q*);
28.3 (*q*); 24.8 (*d*);		5.18	1 H–N(2.1)	*d* (8)	18.0 (*q*)
22.9 (*q*); 21.7 (*q*);		4.66	1 H–C(2.4)	*m*	
20.7 (*q*); 18.0 (*q*)		4.56	1 H–C(3.2)	*m* (7)	
		4.21	1 H–C(3.4),	*m*	
			1 H–C(4.4)		
		1.44	*t*-BuOCON(2.1)	*s*	
		1.41	3 H–C(2.2)	*d* (7)	
		1.36	3 H–C(2.1)	*d* (7)	
		1.02–0.85	3 H–C(5.4),	*m*	
			3 H–C(5′.4)		

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