SIMPLE PREPARATION OF 4,5-DISUBSTITUTED 2-CYCLOPENTENONES

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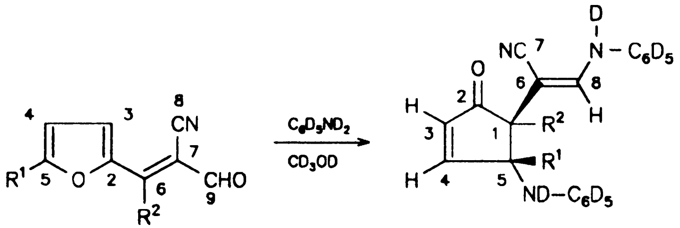
(*E*)-2-Formyl-3-(2-furyl)propenenitrile (*I*) reacts with primary aromatic amines under formation of 3-(arylamino)-2-[5-(arylamino)-2-oxo-3-cyclopenten-1-yl]propenenitriles (*IVa* – *IVi*). Condensation of *I* with salts of nitrogen bases in pyridine affords 2-(R-aminomethylidene)-3-(2-furyl)propenenitriles (*Va* – *Vm*).

Prostanoids represent an important group of natural compounds containing the cyclopentane skeleton[1]. Their practical utilization stimulated great interest in the synthesis of cyclopentenone derivatives. 2,4-Disubstituted cyclopentenones arise by reaction of 2-furancarbaldehyde with aromatic amines[2] via intermediate Stenhouse salts[3]. 3-(2-Furyl)propenal reacts analogously in an acid medium[4]. Also furan derivatives may be suitable precursors for the synthesis of 4,5-disubstituted cyclopentenones.

(*E*)-2-Formyl-3-(2-furyl)propenenitrile (*I*), whose reactions with aromatic amines are the subject of the present paper, is a polyfunctional derivative which may react with amines on the formyl group, on the activated double bond or in position 5 of the furan ring.

Treatment of the nitrile *I* with aniline in methanol afforded compound *IVa* whose ^{1}H NMR spectra showed the presence of two phenyl groups in the molecule. This was confirmed also by the mass spectrum of compound *VI* (M$^+$ 327), prepared by reaction of nitrile *I* with perdeuterated aniline (Scheme 1).

The ^{1}H NMR spectrum of compound *VI* showed two characteristic doublets of doublets at δ 6.44 (^3J = 6.0 Hz and ^4J = 1.5 Hz) and δ 7.87 (^3J = 6.0 Hz and ^4J = 2.1 Hz) which were assigned to the double bond protons[5]. The broad multiplet at δ 4.58 and doublet at δ 3.70 (^3J = 3.3) were ascribed to aliphatic protons. The presence of two different NH groups, one of which belongs to an enamine grouping, was proved by deuterium exchange in N–D on addition of water. In the ^{1}H NMR spectrum two new signals appeared: a doublet at δ 6.22 (^3J = 7.2 Hz) and a doublet at δ 9.11 (^3J = 13.5 Hz). At the same time, the original singlet at δ 7.87 changed into a doublet at δ 7.85 (^3J = 13.5 Hz). On the basis of comparison with the literature data[5 – 8] we assigned the compound *IVa* (or *VI*) the structure of 4,5-disubstituted cyclopentenone. A detailed assignment of the NMR signals and structural determination followed from the synthesis with deuterium-labeled starting compounds *II* and *III* (Scheme 1). Their reaction with perdeuterated aniline afforded the corresponding 4,5-disubstituted cyclopentenones *VII* and *VIII*. In accord with the literature data[6–8], the coupling constant ^3J(H-1,H-5) = 3.3 Hz corresponds to a trans-arrangement of the aliphatic protons H-1



I–III

VI–VIII

I, $R^1 = R^2 = H$

II, $R^1 = D$, $R^2 = H$

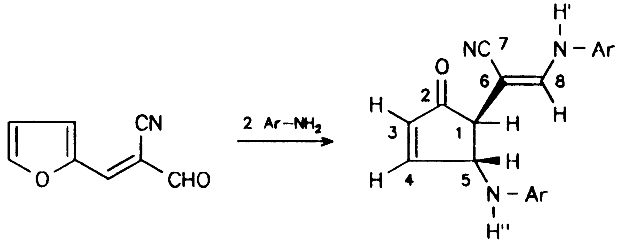
III, $R^1 = H$, $R^2 = D$

VI, $R^1 = R^2 = H$

VII, $R^1 = D$, $R^2 = H$

VIII, $R^1 = H$, $R^2 = D$

SCHEME 1



I

IVa–IVi

In formula *IV* :

a, Ar = C_6H_5

b, Ar = $4\text{-}CH_3C_6H_4$

c, Ar = $4\text{-}CH_3OC_6H_4$

d, Ar = $4\text{-}ClC_6H_4$

e, Ar = $4\text{-}BrC_6H_4$

f, Ar = $4\text{-}FC_6H_4$

g, Ar = $3\text{-}ClC_6H_4$

h, Ar = $3\text{-}BrC_6H_4$

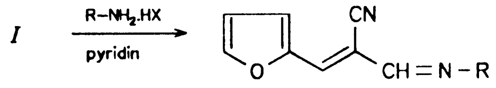
i, Ar = $4\text{-}CF_3OC_6H_4$

SCHEME 2

and H-5. The signal of proton H-5 is further split by interaction with proton H-3 (^4J = 1.8 Hz). No interaction with the H-4 proton was found in a COSY experiment. The stereochemistry of the double bond C(6)=C(8) was determined by comparison of the found ^3J(C-7,H-8) value (8.2 Hz) with the literature data[9 - 11].

The above reaction course was observed only with anilines possessing electron-donor substituents (Scheme 2). 4-Nitroaniline, even on prolonged reflux in methanol, did not afford any 4,5-disubstituted 2-cyclopentenone.

Change in the reaction conditions affects markedly the selectivity of the nucleophilic attack at the furan derivative *I*. Reaction of nitrile *I* with salts od nitrogen bases in pyridine gives the corresponding Schiff bases *Va* – *Vm* in high yields (Table I, Scheme 3). At higher temperatures and prolonged reaction time good yields were obtained even with 4-nitroaniline.



Va–Vm

In formula ***V*** :

a, R = C_6H_5
b, R = $4-CH_3C_6H_4$
c, R = $4-CH_3OC_6H_4$
d, R = $4-ClC_6H_4$
e, R = $4-BrC_6H_4$
f, R = $4-IC_6H_4$
g, R = 2-naphthyl
h, R = $4-CF_3C_6H_4$
i, R = OH
j, R = $NH_2.HCl$
k, R = C_6H_5NH
l, R = $NHCONH_2$
m, R = $4-NO_2C_6H_4$

SCHEME 3

EXPERIMENTAL

Melting points were determined on a Boetius block. Infrared spectra were recorded on an IR-75 (Zeiss, Jena) or on a Beckmann-Acculab (Beckmann) spectrophotometer (KBr technique, wavenumbers in cm^{-1}). Electronic absorption spectra were measured on an M-40 (Zeiss, Jena) spectrophotometer in methanol at concentration $1 . 10^{-4}$ (ε m^{-2} mol^{-1}). ^1H NMR (300 MHz) and ^{13}C NMR (75.05 MHz) spectra were taken on a Varian VXR-300 spectrometer at 25 °C in hexadeuteriodimethyl sulfoxide with tetramethylsilane as internal standard. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. Mass spectra were obtained with an AEI Manchester MS 902S instrument (direct inlet, ionizing electron energy 70 eV, electron current 100 μA, ionization chamber temperature 70 – 170 °C.

(*E*)-2-Formyl-3-(2-furyl)propenenitrile (*I*)

A) Sodium (2.3 g, 0.1 mol) was dissolved in anhydrous methanol (100 ml) and the solution was cooled to 10 °C. A solution of 2-furaldehyde (9.6 g, 0.1 mol) and β,β-dimethoxypropanenitrile[12] (11.5 g, 0.1 mol) in methanol (20 ml) was added dropwise during 1 h. After stirring for 72 h at room temperature, the mixture was adjusted to pH 6.5 with dilute (1 : 1) hydrochloric acid. The solid product was filtered and crystallized from methanol; yield 11 g (75%) of *I*, m.p. 156 – 157 °C.

B) Sodium (2.3 g, 0.1 mol) was dissolved in anhydrous methanol (50 ml). A solution of isoxazole[13] (6.9 g, 0.1 mol) in methanol (10 ml) was added dropwise at 0 °C and the mixture was stirred for 1 h. 2-Furaldehyde (9.6 g, 0.1 mol) was added in one portion. After standing for 24 h at 0 °C, the mixture was poured in water (150 ml) and adjusted to pH 6.5 with dilute (1 : 1) hydrochloric acid. The solid was filtered and purified by crystallization from methanol; yield 11.3 g, (77%), m.p. 156 – 157 °C. For $C_8H_5NO_2$ (147.1) calculated: 65.35% C, 3.42% H, 9.52% N; found: 65.12% C, 3.21% H, 9.13% N. ^1H NMR spectrum: 6.94 dd, 1 H (H-4, $^3J(4,3) = 3.4$; $^3J(4,5) = 1.7$); 7.55 d, 1 H (H-3, $^3J(3,4) = 3.4$); 8.27 s, 1 H (H-6); 7.85 d, 1 H (H-5, $^3J(5,4) = 1.7$); 9.55 s, 1 H (H-9). ^{13}C NMR spectrum: 106.9 s (C-7), 114.5 s (C-8, $^3J(H\text{-}6, C\text{-}8) = 12.2$), 114.5 d (C-4), 125.1 d (C-3), 144.1 d (C-6), 148.3 s (C-2), 150.9 d (C-5), 188.6 d (C-9). UV spectrum: λ_{max} 340 nm, log ε 3.00. IR spectrum: 2 316 (C≡N); 1 682 (CH=O; 1 620 (C=C).

(*E*)-2-Formyl-3-(5-[^2H]-2-furyl)propenenitrile (*II*)

The title compound was prepared according to the method *B*) (vide supra) from 5-[^2H]-2-furaldehyde[14] (0.97 g, 0.01 mol) and isoxazole (0.69 g, 0.01 mol): yield 1.13 g (76%), m.p. 157 – 158 °C. For $C_8H_4DNO_2$ (148.1) calculated: 64.92% C, 4.08% H + D, 9.45% N; found: 64.80% C, 3.82% H + D, 9.50% N. ^1H NMR spectrum: 6.89 d, 1 H (H-4, $^3J(4,3) = 3.4$); 7.54 d, 1 H (H-3, $^3J(3,4) = 3.4$); 8.25 s, 1 H (H-6); 9.49 s, 1 H (H-9).

(*E*)-2-Formyl-α-[^2H]-3-(2-furyl)propenenitrile (*III*)

The title compound was prepared by reaction of α-[^2H]-2-furaldehyde[15] (0.97 g, 0.01 mol) with isoxazole (0.69 g, 0.01 mol) according to method *B*) (vide supra); yield 1.11 g (75%), m.p. 157 – 158 °C. For $C_8H_4DNO_2$ (148.1) calculated: 64.92% C, 4.08% H + D, 9.45% N; found: 64.82% C, 3.91% H + D, 9.58% N. ^1H NMR spectrum: 6.89 dd, 1 H (H-4, $^3J(4,3) = 3.4$; $^3J(4,5) = 1.7$); 7.53 d, 1 H (H-3, $^3J(3,4) = 3.4$); 8.06 d, 1 H (H-5, $^3J(5,4) = 1.7$); 9.54 s, 1 H (H-9).

Preparation of Compounds *IVa* – *IVi*

Nitrile *I* (1.47 g, 0.01 mol) was suspended in methanol (10 ml) at 45 °C. After 15 min, a solution of the corresponding amine (0.02 mol) in methanol (5 ml) was added in one portion. The mixture was boiled for 1 – 2 min, cooled and stirred at room temperature for 45 min. After standing at 0 °C for 24 h, the solid was filtered and purified by crystallization from aqueous acetone. The physicochemical and spectral data for the obtained derivatives *IVa* – *IVi* are given in Tables I, III – V.

Preparation of Compounds *Va* – *VI*

Nitrile *I* (1.47 g, 0.01 mol) was dissolved in dry pyridine (10 ml) and the corresponding amine hydrobromide, hydroxylamine hydrochloride, hydrazine dihydrochloride, phenylhydrazine hydrochloride or semicarbazide hydrochloride (0.01 mol) was added in one portion under vigorous stirring. The mixture was stirred at room temperature for 15 min and poured in ice-cold water (300 ml). After vigorous stirring for 1 h, the solid material was filtered, washed thoroughly with water and ice-cold methanol and crystallized from

TABLE I
Yields, melting points and elemental analyses for compounds *IVa* – *IVl* and *Va* – *Vm*

Compound	M. p., °C (yield, %)	Formula (M. w.)	Calculated/Found			
			% C	% H	% N	% Hal
IVa	150 – 152	$C_{20}H_{17}N_3O$	76.17	5.43	13.32	–
	(86)	(315.4)	75.50	5.58	13.06	–
IVb	158 – 160	$C_{22}H_{21}N_3O$	76.94	6.16	12.23	–
	(88)	(343.4)	77.09	6.27	12.46	–
IVc	155 – 157	$C_{22}H_{21}N_3O_3$	70.38	5.63	11.20	–
	(87)	(375.4)	70.12	5.46	11.01	–
IVd	154 – 156	$C_{20}H_{15}Cl_2N_3O$	62.51	3.93	10.93	18.45
	(76)	(384.3)	62.76	4.09	10.76	18.18
IVe	166 – 168	$C_{20}H_{15}Br_2N_3O$	50.76	3.19	8.88	33.77
	(79)	(473.2)	50.87	3.29	8.99	33.52
IVf	151 – 154	$C_{20}H_{15}F_2N_3O$	68.37	4.28	11.96	10.82
	(82)	(351.3)	68.74	4.39	12.34	10.44
IVg	144 – 148	$C_{20}H_{15}Cl_2N_3O$	62.51	3.93	10.93	18.45
	(76)	(384.3)	62.79	4.08	10.98	18.69
IVh	152 – 153	$C_{20}H_{15}Br_2N_3O$	50.76	3.19	8.88	33.77
	(78)	(473.2)	51.05	3.28	9.14	33.92
IVi	143 – 146	$C_{22}H_{15}F_6N_3O_3$	54.66	3.13	8.69	23.58
	(80)	(483.4)	54.30	3.13	8.85	23.72
Va	104 – 106	$C_{14}H_{10}N_2O$	75.64	4.53	12.60	–
	(75)	(222.3)	75.12	4.60	12.13	–
Vb	116 – 118	$C_{15}H_{12}N_2O$	76.25	5.12	11.85	–
	(92)	(236.3)	76.50	5.36	11.60	–
Vc	98 – 100	$C_{15}H_{12}N_2O_2$	71.42	4.79	11.10	–
	(80)	(252.3)	71.60	4.87	11.20	–
Vd	151 – 153	$C_{14}H_9ClN_2O$	65.51	3.53	10.91	13.81
	(86)	(256.7)	65.20	3.27	10.68	13.70
Ve	150 – 152	$C_{14}H_9BrN_2O$	55.83	3.01	9.30	26.53
	(87)	(301.2)	55.97	2.89	8.96	26.01
Vi	158 – 160	$C_8H_6N_2O_2$	59.29	3.72	17.27	–
	(86)	(162.2)	59.01	3.86	17.39	–
Vj	203 – 205	$C_8H_7N_3O$	59.62	4.37	26.07	–
	(91)	(161.2)	59.81	4.52	26.25	–
Vk	159 – 161	$C_{14}H_{11}N_3O$	70.87	4.67	17.71	–
	(83)	(237.3)	70.61	4.42	17.50	–
Vl	225 – 227	$C_9H_8N_4O_2$	52.94	3.94	27.43	–
	(100)	(204.2)	52.76	3.71	27.62	–
Vm	226 – 228	$C_{14}H_9N_3O_3$	62.92	3.39	15.72	–
	(84)	(267.3)	62.92	3.56	15.89	–

methanol. The physicochemical and spectral data of the obtained compounds *Va* – *Vl* are given in Tables I, II, IV and V.

Preparation of Compound *Vm*

A solution of nitrile *I* (1.47 g, 0.01 mol) and 4-nitroaniline (1.38 g, 0.01 mol) in methanol (10 ml) was refluxed for 5 h. After cooling to room temperature, the mixture was set aside for 24 h, the solid was filtered, washed with methanol and crystallized from dimethyl sulfoxide. The physicochemical data of *Vm* are given in Table I.

Preparation of Compound *Vl*

Reaction of nitrile *I* (1.47 g, 0.01 mol) with perdeuterated aniline (2.0 g, 0.01 mol) under conditions described for preparation of *IVa* – *IVi* afforded 2.75 g (85%) of the product *Vl*, m.p. 155 – 157 °C. For $C_{20}H_5D_{12}N_3O$ (327.3) calculated: 73.40% C, 8.93% H + D, 12.84% N; found: 73.22% C, 8.19% H + D, 12.77% N. ^1H NMR spectrum: 3.70 d, 1 H (H-1, $^3J(1,5)$ = 3.3); 4.58 m, 1 H (H-5); 6.44 dd, 1 H (H-3, $^3J(3,4)$ = 6.0; $^4J(3,5)$ = 1.5); 7.85 s, 1 H (H-8); 7.87 dd, 1 H (H-4, $^3J(4,3)$ = 6.0; $^4J(4,1)$ = 2.1. ^1H NMR spectrum (CD_3SOCD_3 after addition of H_2O): 3.70 d, 1 H (H-1, $^3J(1,5)$ = 3.3); 4.58 m, 1 H (H-5), 6.22 d, 1 H (N-H', J(N-H', H-5 = 7.2); 6.44 dd, 1 H (H-3, $^3J(4,3)$ = 6.0; $^4J(3,5)$ = 1.8); 7.87 dd, 1 H (H-4, $^3J(4,3)$ = 6.0; $^4J(4,1)$ = 2.1); 7.85 d, 1 H (H-8, ^3J(H-8,N-H') = 13.5); 9.11 d, 1 H (N-H', ^3J(N-H', H-8) = 13.5). ^{13}C NMR spectrum: 50.9 d (C-1), 59.3 d, (C-5), 79.2 s (C-6), 120.9 s (C-7), 132.9 d (C-3), 143.5 d (C-8),

TABLE II
^1H NMR chemical shifts (δ, ppm) for compounds *Va* – *Vm*

Compound	Chemical shifts					
	H-3, d	H-4, q[a]	H-5, d[b]	H-6, s	H-9, s	Aromatic protons
Va	7.32	6.78	7.96	7.76	8.42	7.25 s, 5 H
Vb[c]	7.45	6.84	8.01	7.83	8.45	6.98 – 6.31 m, 4 H
Vc[d]	7.38	6.72	7.93	7.70	8.40	6.94 – 7.28 m, 4 H
Vd	7.35	6.81	7.98	7.83	8.43	7.25 – 7.43 m, 4 H
Ve	7.44	6.80	7.98	7.82	8.41	7.19 – 7.58 m, 4 H
Vf	7.43	6.80	8.00	7.85	8.40	7.08 – 7.77 m, 4 H
Vg	7.42	6.81	7.98	7.83	8.54	7.50 – 7.91 m, 7 H
Vh	7.39	6.86	7.99	7.86	8.59	7.26 – 7.49 m, 4 H
Vi[e]	7.24	6.73	7.86	7.42	8.00	–
Vj	7.28	6.76	7.82	8.07	8.46	–
Vk[f]	[g]	6.64	7.68	[g]	7.78	7.07 – 7.45 m, 7 H
Vl[h]	7.10	6.71	7.95	7.43	7.68	–
Vm	7.67	6.96	8.22	7.54	8.47	7.22 – 7.50 m, 4 H

[a] $^3J(4,3)$ = 3.4 – 3.5 Hz; $^3J(5,4)$ = 1.4 – 1.5 Hz; [b] $^3J(5,4)$ = 1.4 – 1.5 Hz; [c] other signals: 2.35 s, 3 H (CH_3); [d] other signals: 3.80 s, 3 H (CH_3O); [e] other signals: 10.88 m, 1 H (OH); [f] other signals: 9.83 m, 1 H (NH); [g] overlap with other proton signals; [h] other signals: 6.25 m, 2 H (NH_2).

163.4 d (C-3), 204.6 s (C-1). Mass spectrum, *m/z* (%): 227 (50), 186 (64), 138 (25), 109 (27), 98 (100), 82 (54), 71 (41).

Preparation of Compound *VII*

The title compound was prepared by reaction of nitrile *II* (1.48 g, 0.01 mol) with perdeuterated aniline (2.0 g, 0.02 mol) as described for compounds *Va* – *Vi*. Yield 2.88 g (88%), m.p. 159 – 160 °C. For $C_{20}H_4D_{13}N_3O$ (328.3) calculated: 73.20% C, 9.22% H + D, 12.80% N; found: 73.17% C, 8.79% H + D, 12.74% N. ^1H NMR spectrum: 3.61 s, 1 H (H-1), 6.37 d, 1 H (H-3, $^3J(3,4)$ = 6.0); 7.82 d, 1 H (H-4, $^3J(4,3)$ = 6.0); 7.80 s (H-8). ^{13}C NMR spectrum: 50.7 d (C-1), 79.1 s (C-6), 120.7 s (C-7), 143.2 (C-8), 133.2 d (C-3), 163.1 d (C-4), 204.3 s (C-2). Mass spectrum, *m/z* (%): 228 (56), 98 (100).

TABLE III
^1H NMR spectral parameters for compounds *IVa* – *IVi*. Chemical shifts in ppm (δ-scale), coupling constants (*J*) in Hz

Compound	H-3, dd (*J*(3,4); *J*(3,5))	H-4, d (*J*(4,3); *J*(4,1))	H-5, m	H-1, d (*J*(1,5))	H-8, d (*J*(8,N-H'))	N-H', d (*J*(N-H',8))	Aromatic protons
IVa	6.45 (6.0; 1.5)	7.88 (6.0; 2.1)	4.58	3.69 (3.3)	7.84 (13.5)	8.54 (13.5)	6.5 – 7.70 m, 10 H
IVb[a]	6.31 (5.7; 1.5)	7.73 (5.7; 2.1)	4.42	3.50 (3.3)	7.64 (13.5)	8.92 (13.5)	6.5 – 6.9 m, 8 H
IVc[b]	6.30 (5.8; 1.7)	7.72 (5.8; 2.1)	4.38	3.46 (3.0)	7.56 (13.2)	8.87 (13.2)	6.6 – 7.0 m, 8 H
IVd	6.35 (6.0; 1.5)	7.78 (6.0; 2.1)	4.47	3.61 (3.3)	7.68 (13.2)	9.03 (13.2)	6.5 – 7.3 m, 8 H
IVe	6.36 (6.0; 1.5)	7.79 (6.0; 2.1)	4.51	3.66 (3.3)	7.74 (13.4)	9.18 (13.4)	6.9 – 7.5 m, 8 H
IVf	6.51 (6.0; 1.5)	7.91 (6.0; 2.1)	4.62	3.68 (3.3)	7.92 (12.8)	9.02 (12.8)	6.6 – 7.3 m, 8 H
IVg	6.43 (5.9; 1.9)	7.84 (5.9; 2.3)	4.53	3.61 (3.3)	7.86 (13.0)	8.99 (13.0)	6.5 – 7.4 m, 8 H
IVh[c]	6.48 (5.8; 2.1)	7.89 (5.8; 2.1)	4.59	3.66 (3.0)	7.79 (13.3)	9.17 (13.3)	6.7 – 7.2 m, 8 H
IVi	6.44 (5.8 ; 1.7)	7.85 (5.8; 2.1)	4.58	3.64 (3.3)	7.77 (13.4)	9.21 (13.4)	6.7 – 7.3 m, 8 H

[a] Other signals: 2.01 s, 2.11 s, 2 × 3 H (2 × CH_3); [b] other signals: 3.48 s, 3.58 s, 2 × 3 H (2 × CH_3); [c] other signals: 6.12 d, 1 H (N-H''); *J*(N-H'',5) = 7.2.

TABLE IV
^{13}C NMR chemical shifts (δ, ppm) for compounds *IVa* – *IVi*

Compound	C-2, s	C-3, d	C-4, d	C-5, d	C-1, d	C-6, s	C-7, s	C-8, s	Other signals
IVa	204.6	134.2	163.4	59.3	51.0	80.2	120.8	143.5	112.3, 114.8, 117.3, 128.5, 128.8, 131.2, 140.8, 147.1
IVb	205.6	133.7	164.3	60.4	51.5	78.8	121.9	144.3	113.7, 115.9, 126.4, 130.2, 130.5, 131.6, 139.1, 145.5, 25.7, 25.9,
IVc	205.3	133.3	163.9	60.8	51.3	77.7	121.6	144.4	55.5, 55.6, 114.7, 114.9, 117.1, 134.7, 134.8, 141.4, 151.9, 154.9
IVd	204.8	133.6	163.5	59.8	51.2	80.4	120.9	144.0	112.1, 112.6, 114.3, 116.8, 120.7, 131.2, 143.2, 146.2
IVe	204.9	133.5	163.6	60.1	51.4	80.2	120.9	144.1	112.4, 112.9, 117.6, 120.8, 121.6, 136.3, 143.9, 148.4
IVf	205.1	133.5	163.8	60.3	51.3	79.2	121.3	144.3	114.2, 115.8, 116.3, 117.2, 137.6, 137.7, 154.8, 157.6
IVg	204.8	133.6	163.5	59.3	51.1	80.7	120.7	143.3	112.0, 114.4, 115.1, 118.1, 119.5, 122.6, 122.7, 124.7, 131.1, 131.5, 142.7, 148.9
IVh	204.7	133.6	163.5	59.3	51.2	80.7	120.7	143.3	111.7, 112.2, 114.1, 115.2, 116.7, 121.7, 130.8, 131.2, 134.1, 143.2, 142.6, 148.8
IVi	204.8	133.6	163.6	59.8	51.3	80.5	120.9	143.8	113.6, 116.7, 118.7, 118.8, 122.2, 122.4, 122.6, 139.6, 140.1, 140.4 143.1, 143.3, 146.6

Preparation of Compound *VIII*

The title compound was prepared by reaction of nitrile *III* (1.48 g, 0.01 mol) with perdeuterated aniline (2.0 g, 0.02 mol) as described for derivatives *Va* – *Vi*. Yield 2.88 g (86%), m.p. 160 – 161 °C. For $C_{20}H_4D_{13}N_3O$ (328.3) calculated: 73.20% C, 9.22% H + D, 12.80% N; found: 73.17% C, 8.79% H + D, 12.74% N. ^{1}H NMR spectrum (CD_3SOCD_3): 4.43 m, 1 H (H-5); 6.30 d, 1 H (H-3, $^3J(3,4)$ = 6.0); 7.64 d, 1 H (H-4, $^3J(4,3)$ = 6.0); 7.71 s, 1 H (H-8). ^{13}C NMR spectrum (CD_3SOCD_3): 59.2 d (C-5), 79.2 s (C-6), 120.8 s (C-7), 133.4 d (C-3), 143.4 d (C-8), 163.2 d (C-4), 204.4 s (C-2). Mass spectrum, *m/z* (%): 228 (42), 98 (100).

TABLE V
Infrared and UV data for compounds *IVa* – *IVi* and *Va* – *Vm*

Compound	UV spectra		IR spectra		
	λ_{max} (log ε) nm (m^2 mol^{-1})	λ_{max} (log ε) nm (m^2 mol^{-1})	ν(C≡N) cm^{-1}	ν(C=X) cm^{-1}	ν(N–H) cm^{-1}
IVa	333 (2.76)	287 (2.49)	2 200	1 705[a]	3 390
IVb	334 (2.69)	306 (2.52)	2 199	1 714[a]	3 395
IVc	333 (2.73)	301 (2.49)	2 198	1 715[a]	3 392
IVd	349 (2.76)	291 (2.53)	2 201	1 708[a]	3 308
IVe	342 (2.70)	298 (2.46)	2 234	1 709[a]	3 270
IVf	341 (2.76)	302 (2.50)	2 228	1 700[a]	3 308
IVg	331 (2.70)	286 (2.49)	2 197	1 718[a]	3 394
IVh	340 (2.68)	296 (2.45)	2 198	1 714[a]	3 381
IVi	345 (2.78)	302 (2.55)	2 195	1 714[a]	3 310
Va	340 (2.68)	248 (2.39)	2 230	1 607[b]	–
Vb	344 (2.72)	248 (2.34)	2 232	1 602[b]	–
Vc	341 (2.58)	249 (2.41)	2 230	1 608[b]	–
Vd	350 (2.72)	248 (2.34)	2 238	1 600[b]	–
Ve	349 (2.71)	248 (2.35)	2 236	1 602[b]	–
Vf	349 (2.70)	251 (2.41)	2 238	1 600[b]	–
Vg	347 (2.73)	242 (2.61)	2 230	1 617[b]	–
Vh	346 (2.71)	248 (2.50)	2 234	1 607[b]	–
Vi	333 (2.64)	226 (2.40)	2 231	1 630[b]	3 320
Vj	405 (2.72)	311 (2.38)	2 230	1 618[b]	3 248
Vk	393 (2.61)	237 (2.26)	2 230	1 605[b]	3 282
Vl	348 (2.86)	244 (2.42)	2 232	1 606[b]	3 400
Vm	385 (2.74)	250 (2.50)	2 238	1 619[b]	–

[a] Values for ν(C=O); [b] values for ν(C=C).

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