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Hetero-*Diels-Alder* Reaction of 3-Aryl-2-benzoyl-2-propenenitriles with Enol Ethers. Synthesis of 2-Alkoxy-3,4-dihydro-2*H*-pyran-5-carbonitriles

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Summary. The hetero-*Diels-Alder* reaction of 3-aryl-2-benzoyl-2-propenenitriles **1a–d** with enol ethers **2a–c** yields *cis/trans* diastereoisomers of 2-alkoxy-4,6-diaryl-3,4-dihydro-2*H*-pyran-5-carbonitriles **3** and **4** in 79–98% yield. The similar reaction of **1a–c** with cyclic enol ether **5** affords diastereoisomeric cycloadducts **6** and **7** with *cis* annulated pyran rings. Reaction of **3** with sulfuric acid leads to 2-hydroxy-3,4-dihydro-2*H*-pyran-5-carbonitriles **8** and **9**.

Keywords. *Diels-Alder* reaction; α,β-Unsaturated carbonyl compounds; Enol ethers; 3,4-dihydro-2*H*-pyran-5-carbonitriles.

Hetero-*Diels-Alder*-Reaktion von 3-Aryl-2-benzoyl-2-propennitrilen mit Enolethern. Synthese von 2-Alkoxy-3,4-dihydro-2*H*-pyran-5-nitrilen

Zusammenfassung. Die Hetero-*Diels-Alder*-Reaktion der 3-Aryl-2-benzoyl-2-propennitrile **1a–d** mit den Enolethern **2a–c** ergibt die *cis/trans*-diastereomeren 2-Alkoxy-4,6-diaryl-3,4-dihydro-2*H*-pyran-5-nitrile **3** und **4** in einer Ausbeute von 79–98%. Dieselbe Reaktion von **1a–c** mit dem cyclischen Enolether **5** liefert die diastereomeren Cycloaddukte **6** und **7** mit *cis*-anellierten Pyranringen. Reaktion von **3** mit Schwefelsäure führt zu den 2-Hydroxy-3,4-dihydro-2*H*-pyran-5-nitrilen **8** und **9**.

Introduction

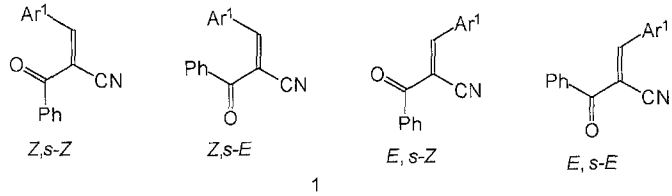
Hetero-*Diels-Alder* reactions of α,β-unsaturated carbonyl compounds containing an 1-oxa-1,3-butadiene system with enol ethers are an important method for the construction of the 3,4-dihydro-2*H*-pyran skeleton which is present in many natural products such as carbohydrates [1], alkaloides [2], and antibiotics [3]. These reactions belong to the class of $[4\pi + 2\pi]$ cycloadditions with inverse electron demand. Because of the low reactivity of α,β-unsaturated carbonyl compounds towards enol ethers, the reactions require severe experimental conditions, *e.g.* high temperature, and are characterized by low diastereoselectivity [4]. It was found that introducing an electron withdrawing group in the 1-oxadiene system

lowers the LUMO energy level which then can more easily overlap with the HOMO orbital of the dienophile. *Tietze et al.* have calculated the influence of various substituents on the energy and thus on the reactivity of LUMO orbitals in 4-*N*-acetylamino-1-oxa-1,3-butadienes using semiempirical methods [5]. It was found that the energy depends on the type and position of a substituent in the 1-oxadiene system. Among the electon withdrawing substituents, the cyano and trifluoromethyl groups were found to have the most pronounced influence on facilitating the reaction of 1-oxadienes with enol ethers. *Wyler et al.* have reported that α,β-unsaturated acyl cyanides exhibit an extraordinary reactivity towards enol ethers, yielding 3,4-dihydro-2*H*-pyran-6-carbonitriles at room temperature [6, 7]. Recently, we have reported on an efficient reaction of 2-cyano-enaminoketone with enol ethers leading to 4-amino-3,4-dihydro-2*H*-pyran derivatives that may be the versatile precursors in synthesis of 3-aminocarbohydrates.

Results and Discussion

The aim of the present work was to determine the influence of the type of aryl substituent at C-4 in α,β-unsaturated ketones containing a cyano group at C-3 on their reactivity in hetero-*Diels-Alder* reactions with enol ethers. In our experiments, we used the easily available *p*-substituted 2-benzoylcinnamonitriles **1a–c** and 2-benzoyl-3(4-pyridyl)-2-propenenitrile **1d** as starting materials. They were obtained according to *Kauffmann* [9] by condensation of benzoylacetonitrile with an appropriate aldehyde in the presence of piperidine as a catalyst. Compounds **1** can adopt four configurations/conformations (Fig. 1), and among those structures only two are suitable for cycloadditions. The ^{1}H and ^{13}C NMR spectra of **1** suggest that the *E* configuration is preferred. The chemical shift value of C(3)-H (δ = 8.06–8.13 ppm, [10]) and a steric interaction of benzoyl and aryl groups that would occur in the *Z* isomers suggest that compounds **1** exist as *E* isomers. Literature reports concerning the structure of α,β-unsaturated carbonyl compounds claims that the *s*-*Z* conformation is more stable than the *s*-*E* one [11]. Thus, **1** are supposed to exist in the *E*, *s*-*Z* form.

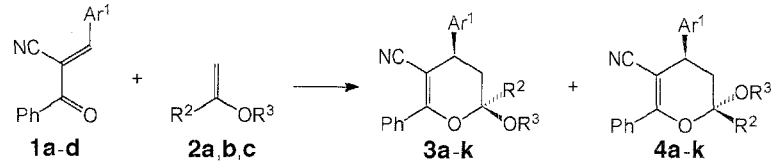
The reactions of dienes **1** with enol ethers **2** were performed in toluene solution at ambient temperature for 2 h to 48 h. The progress of the reactions was monitored by TLC. The yields of products **3** and **4** (Scheme 1) were excellent, ranging from



1

1a: $Ar^1 = C_6H_5$
1b: $Ar^1 = p\text{-}NO_2C_6H_4$
1c: $Ar^1 = p\text{-}CH_3OC_6H_4$
1d: Ar^1 = 4-pyridyl

Fig. 1. Configurations and conformations of dienes **1**



1	2	Products	Ar^1	R^2	R^3
a	**a**	**3a/4a**	C_6H_5	H	C_2H_5
a	**b**	**3b/4b**	C_6H_5	H	*i*-Bu
a	**c**	**3c/4c**	C_6H_5	CH_3	CH_3
b	**a**	**3d/4d**	*p*-$NO_2C_6H_4$	H	C_2H_5
b	**b**	**3e/4e**	*p*-$NO_2C_6H_4$	H	*i*-Bu
b	**c**	**3f/4f**	*p*-$NO_2C_6H_4$	CH_3	CH_3
c	**a**	**3g/4g**	*p*-$CH_3OC_6H_4$	H	C_2H_5
c	**b**	**3h/4h**	*p*-$CH_3OC_6H_4$	H	*i*-Bu
c	**c**	**3i/4i**	*p*-$CH_3OC_6H_4$	CH_3	CH_3
d	**a**	**3j/4j**	4-pyrydyl	H	C_2H_5
d	**c**	**3k/4k**	4-pyrydyl	CH_3	CH_3

Scheme 1

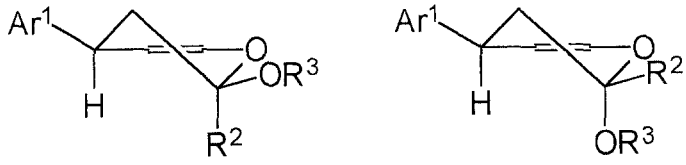
Table 1. Synthesis of dihydropyrans **3** and **4** (reaction conditions, yields, diastereoselectivity)

Products	Reaction time (h)	Yield (%)	Ratio of **3**:**4**[b)]
3a/4a	5[a)]	80	10:1[c)]
3b/4b	8	86.5	4.8:1
3c/4c	12	90.5	6.3:1
3d/4d	2	98	5.8:1
3e/4e	5	88	4.8:1
3f/4f	8	97	6.3:1
3g/4g	12	79	10:1
3h/4h	24	93	8.3:1
3i/4i	48	90	9.4:1
3j/4j	4	85	1.5:1
3k/4k	6	92	1.8:1

[a] Deine was dissolved in dienophile; [b]ratio of isomers (**3**:**4**) was determined from the ^{1}H NMR spectra of crude products; [c]ratio of diastereoisomers: **3a**:**4a** = 5.5 : 1 for reaction at 120–130°C

79–98% with the *cis* diastereoisomers **3** being always the main products (Table 1). Compounds **3** and **4** were separated by column chromatography. The ratio of diastereoisomers in the crude products was determined on the basis of ^{1}H NMR spectroscopy. The highest ratio of *cis*/*trans* diastereoisomers was observed for the reaction of dienes **1a** and **1c** with ethyl vinyl ether.

The configurations and conformations of cycloadducts **3** and **4** have been established by ^{1}H NMR spectroscopy. The preferred conformation of **3** and **4** was



3 *(cis)* **4** *(trans)*

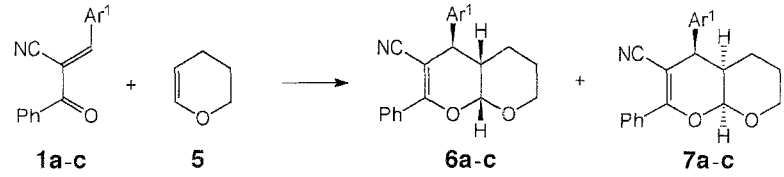
Fig. 2. Preferred conformations of cycloadducts **3** and **4**

deduced from chemical shift values and coupling constants of protons attached to C-2 and C-4 of the dihydropyran ring that exists in a half-chair conformation [12]. The ^{1}H NMR spectra of **3** (R^2 = H) reveal the signals of C(2)-H as a doublet of doublets at δ = 5.28–5.38 ppm with a large and a small coupling constant each (^3J = 6.1–8.6 Hz and ^3J = 1.55–2.35 Hz) due to coupling with two protons at C-3. Thus, the protons at C-2 in **3** obviously are axial. For diastereoisomers **4** (R^2 = H), the protons at C-2 resonate as a triplet at δ = 5.32–5.41 ppm with a small coupling constant (^3J = 2.55–3.05 Hz). Thus, the protons at C-2 in **4** are equatorial, and the alkoxy groups occupy the axial position. The configuration of substituents at C-4 was established similarly. In cycloadducts **3** and **4**, the protons at C-4 resonate as a doublet of doublets at δ = 3.77–4.09 ppm with two large coupling constants ^3J = 8.3–12.5 Hz (^3J = 6.1–7.3 Hz), also due to coupling with two protons at C-3. Thus, the protons at C-4 in both **3** and **4** occupy *pseudo*-axial positions, and the aryl groups are *pseudo*-equatorial. For diastereoisomers **3d-f** and **3j,k**, the signals for the C(4)-H protons appear as triplets at δ = 3.87–4.01 ppm (^3J = 6.35–7.55 Hz). The large values of coupling constants for these protons also indicate *pseudo*-axial positions of the C(4)-H protons.

The configuration of diastereoisomers **3c,f,i,k** and **4c,f,i,k**, containing methyl and methoxy substituents at C-2 were assigned by comparison of chemical shift values and coupling constants of the protons at C-4 with those of species of **3** and **4** with H and O*R* groups at C-2. Thus, in *cis* diastereoisomers of **3**, the alkoxy groups at C-2 are oriented equatorially and in the *trans* diastereoisomers of **4**, they occupy an axial position (Fig. 2). In both cycloadducts, the aryl substituents at C-4 adopts a *pseudo*-equatorial position.

A further confirmation of the structure of the cycloadducts was derived from IR and mass spectroscopy. The IR spectra reveal stretching vibration bands of the nitrile in the range of ν = 2194–2215 cm^{-1} and bands of double bonds at ν = 1574–1630 cm^{-1}. The mass spectra show a molecular ion of moderate intensity. The major peaks result from a *retro-Diels-Alder* fragmentation [13]. the base peaks are due to an enol ether fragment in most cases.

In the next series of experiments, dienes **1a–1c** were reacted with 3,4-dihydro-2*H*-pyran (**5**). The reactions of **1** with a ten-fold excess of **5** were conducted in toluene solution in a sealed tube at 120–130°C for 8–12 h and afforded products **6** and **7** (Scheme 2) in excellent yields (96–98%). The product ratios were derived from their ^{1}H NMR spectra, analyzing the signals of protons attached to C(4) and C(8a) in the crude products. The ratios varied from 1:1.5 (**6a/7a**) and 1:1.3 (**6b/7b**) to 1:2 (**6c/7c**). The products were separated by column chromatography, but only **6b**, **7b**, and **6c** could be isolated as analytically pure samples.



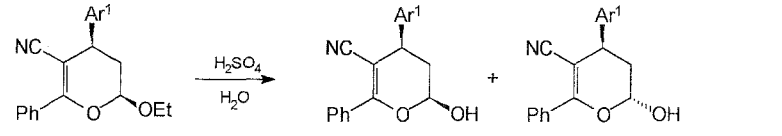
Scheme 2

The diastereoisomers **6** and **7** contain three chiral centres at C(4), C(4a), and C(8a). The configurations and conformations of cycloadducts **6** and **7** were deduced from an analysis of the signals of the protons attached to C(8a) and C(4). In the ^{1}H NMR spectra of **6a–c**, the signal of C(8a)-H is a singlet at $\delta = 5.67$–5.71 ppm. The spectra of **7a-c** reveal a doublet at $\delta = 5.3$–5.4 ppm ($^3J = 2.3$–2.4 Hz) for C(8a)-H. From these values of coupling constants it can be deduced that in **6** and **7** a *cis* annulation is present. The difference between diastereoisomers **6** and **7** concerns the configuration at C(4) and C(4a). In **6a–c**, the proton at C(4) resonates as a doublet at $\delta = 4.15$–4.35 ppm ($^3J = 6.3$–6.45 Hz) due to coupling with C(4a)-H, indicating a *trans* configuration. For compounds **7**, the protons at C(4) appear as a doublet at $\delta = 3.6$–3.75 ppm ($^3J = 2.3$–2.45 Hz), characteristic for a *cis* configuration.

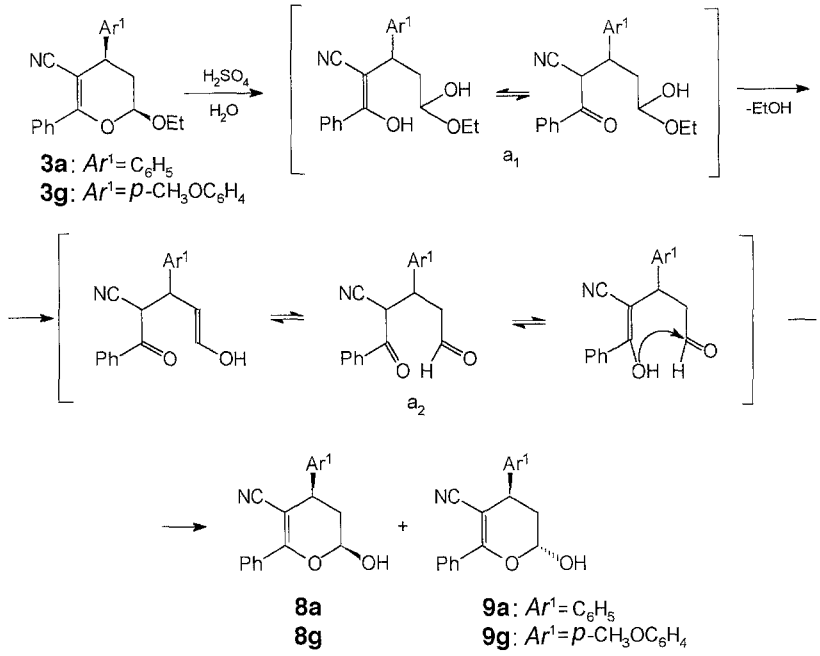
Reaction of pyrans **3** *with sulfuric acid*

Treatment of the cycloadducts **3a** and **3g** with 50% sulfuric acid at 100°C afforded 2-hydroxy-3,4-dihydro-2*H*-pyrans as a mixture of diastereoisomers **8a**, **9a** and **8g**, **9g**, respectively, in 65–68% yield (Scheme 3). Attempted separation of these diastereoisomers by column chromatography failed.

The structure of compounds **8** and **9** was established on the basis of the analysis of the signals of the protons attached to C(2) and C(4) in their ^{1}H NMR spectra. The conformation of **8** and **9** is governed by the equatorial orientation of the aryl group at C(4) as deduced from the chemical shifts and coupling constants of C(4)-H. In **8a**, **9a** the proton at C(4) resonates at $\delta = 3.89$ ppm (0.7 H) as a doublet of doublets with two large coupling constants ($^3J = 8.65/6.50$ Hz) and at $\delta = 3.99$ ppm (0.3 H) as a broad signal. The ^{1}H NMR spectra of compounds **8g**, **9g** revealed the signals of C(4)-H at $\delta = 3.91$ ppm (0.77 H) as a doublet with two large coupling constants ($^3J = 9.2/6.1$ Hz) and at $\delta = 3.86$ ppm (0.23 H, $^3J = 10.2/6.6$ Hz). These values clearly indicate an axial orientation of C(4)-H. The signals



Scheme 3



Scheme 4

for C(2)-H of **8a**, **9a** observed at $\delta = 5.59$ ppm are broad. For **8g**, **9g** the protons at C(2) resonate at $\delta = 5.56$ ppm (0.23 H) and at $\delta = 5.63$ ppm (0.77 H). The protons of the hydroxyl groups at C(2) are observed as broad signals at $\delta = 3.33$ ppm (**8a**, **9a**) and at $\delta = 3.65$ ppm (**8g**, **9g**). The diastereoisomeric ratios (**8a**:**9a** = 1 : 2.3, **8g**:**9g** = 1 : 3.4) were established on the basis of the intensity of the signals of the protons at C(4). Thus, the *trans* diastereoisomers **9a** and **9g** with an axial hydroxyl group are preferred due to stabilization by the anomeric effect [14]. The reaction of compounds **3** with sulfuric acid leading to **8** and **9** involves the transformation of one pyrane ring into another one and can be rationalized as depicted in Scheme 4.

In the first step, the reaction with sulfuric acid causes the opening of the pyrane ring to $\mathbf{a}_1$, followed by elimination of ethanol. In the next step, intramolecular cyclization of 1,5-dicarbonyl intermediate $\mathbf{a}_2$ results in hydroxy derivatives **8** and **9**.

Semiempirical calculations

In order to confirm the experimental results, frontier orbital (HOMO and LUMO) energies of dienes and dienophiles were calculated by semiempirical AM1 and PM3 methods using the MOPAC 7.0 suite of programs. As required by the concerted mechanism of *Diels-Alder* reactions, the *s-Z* conformation of 1-oxa-1,3-butadienes were submitted to refined geometry optimization. The calculated heats of formation and frontier orbital energies are listed in Table 2.

A comparison of the heats of formation shows that the *E,s-z* configurations/conformations are more stable than the *Z,s-Z* ones. Both methods (AM1 and PM3) gave similar values of energy differences between the LUMO of the diene and the

Table 2. Heats of formation and energies of HOMO and LUMO orbitals of dienes **1a-d** and ethyl vinyl ether (**2a**)

	Method	Heat of formation (kcal/mol)	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{LUMO}(\mathbf{1})-E_{HOMO}(\mathbf{2a})$
1a (*E*)	AM1		−8.965	−1.117	8.240
	PM3	70.621	−9.607	−1.030	8.429
1a (*Z*)	AM1		−9.617	−0.750	8.607
	PM3	72.251	−9.628	−1.040	8.419
1b (*E*)	AM1		−9.983	−1.575	7.782
	PM3	87.103	−9.905	−1.416	8.043
1b (*Z*)	AM1		−10.246	−1.823	7.534
	PM3	92.868	−10.370	−1.820	7.639
1c (*E*)	AM1		−9.144	−1.015	8.342
	AM3	32.079	−9.247	−0.988	8.471
1c (*Z*)	AM1		−9.096	−0.811	8.546
	PM3	33.546	−9.143	−0.985	8.474
1d (*E*)	AM1		−10.056	−1.281	8.076
	PM3	78.969	−10.226	−1.177	8.282
1d (*Z*)	AM1		−10.067	−1.156	8.201
	PM3	80.135	−10.177	−1.263	8.196
2a	AM1		−9.000	0.945	–
	PM3		−8.988	0.562	–

HOMO of the enol ethers molecules. These differences are smaller for dienes **1b** and **1d** than for **1a** and **1c**. The obtained results are in agreement with the observations concerning the influences of electron withdrawing and electron releasing substituents on the LUMO energy in 1-oxa-1,3-dienes. On the basis of energy difference $\Delta E = E_{LUMO}(\mathbf{1}) - E_{HOMO}(\mathbf{2a})$, one can conclude that the reactivity of dienes **1** towards enol ether **2a** increases in the sequence **1c**, **1a**, **1d**, **1b**. This is in accordance with experimental findings concerning the yields of products and the required reaction times.

Experimental

Melting points were determined on a Boetius hot stage apparatus. IR spectra: Bruker IFS 48, KBr pellets; ^1H and ^{13}C NMR spectra: Bruker AMX 500 (500.14 MHz for ^1H, 125.77 MHz for ^{13}C) in $CDCl_3$ solutions with *TMS* as an internal standard; ^{13}C signal assignments were confirmed by the DEPT technique; MS spectra: Finnigan Mat 95 (70 eV); microanalyses: Perkin Elmer Analyser 240.

Synthesis of 2-benzoyl-3-aryl-2-propenenitriles **1a–d**

Compounds **1a-d** were synthesized according to the procedure reported in Ref. [9a, b] by condensation of benzoyloacetonitrile with appropriate aldehydes in anhydrous ethanol in the presence of piperidine. Yield: 89–92%; colourless prisms from ethanol (86–92%).

2-Benzoyl-3-phenyl-2-propenenitrile (**1a**)

^{1}H NMR ($CDCl_3$): δ = 7.51–8.04 (m, 10H, Ph-H), 8.06 (s, 1H, 3-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 110.19 (C-2), 116.84 (CN), 128.67, 129.31, 129.33, 131.09, 131.81, 133.37, 133.41, 135.79 (*o,m,p,i*-Ph), 155.50 (C-3), 188.91 (C=O) ppm.

2-Benzoyl-3-(4-nitrophenyl)-2-propenenitrile (**1b**)

^{1}H NMR ($CDCl_3$): δ = 7.55–8.38 (m, 9H, Ph-H), 8.10 (s, 1H, 3-H)ppm.

2-Benzoyl-3-(4-methoxyphenyl)-2-propenenitrile (**1c**)

^{1}H NMR ($CDCl_3$, δ [ppm]): 3.91 (s, 3H, OCH_3), 7.01–8.05 (m, 9H, Ph-H), 8.07 (s, 1H, 3-H) ^{13}C NMR ($CDCl_3$, δ [ppm]: 55.65 (OCH_3), 106.71 (C-2), 114.86 (CN), 117.68, 124.69, 128.56, 129.16, 133.04, 133.84, 136.33 (*o,m,p,i*-Ph, *o,m,i*-$CH_3OC_6H_4$), 155.25 (C-3), 163.99 (*p*-$CH_3OC_6H_4$), 189.33 (C=O) ppm.

2-Benzoyl-3-pyridyl-2-propenenitrile (**1d**)

^{1}H NMR ($CDCl_3$): δ = 7.0–8.48 (m, 9H, Ph-H), 8.13 (s, 1H, 3-H) ppm.

Reaction of dienes **1** *with enol ethers* **4***; synthesis of dihydropirans* **3a–k** *and* **4a–k**

To a solution of **1** (5 mmol) in anhydrous toluene the appropriate vinyl ether **2** (50 mmol, 10 equivalents) was added. The mixture was kept at room temp. for 2–48 h. The progress of the reaction was monitored by TLC. Toluene was evaporated, and the residue was separated and purified by column chromatography on silica gel using petrol ether and *t*-butyl methyl ether: **3a/4a**, **3b/4b**, **3f/4f** (1:1); **3g/4g**, **3i/4i** (1:2), **3c/4c**, **3h/4h** (1:3); **3d/4d**, **3e/4e**, **3j/4j** (1.5:1); **3k/4k** (2:1). Recrystallization from petrol ether/*t*-butyl methyl ether (5:1) afforded crystalline colourless products. **4b** was not separated and purified.

(2R,4S*)-(±)-2-Ethoxy-4,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**3a**)

Colourless prisms; m.p.: 95°C; yield: 73%; IR (KBr): ν = 3029, 2989, 2945 (CH), 2215 (C≡N), 1609 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.28 (*t*, J = 7.1 Hz, 3H, OCH_2CH_3), 2.11 (ddd, J_{gem} = 13.75 Hz, J(2-H, 3-H_{ax}) = 8.7 Hz, J(4-H, 3-H_{ax}) = 10.3 Hz, 1H, 3-H_{ax}), 2.42 (ddd, J_{gem} = 13.75 Hz, J(2-H, 3-H_{eq}) = 1.95 Hz, J(4-H, 3-H_{eq}) = 6.85 Hz, 1H, 3-H_{eq}), 3.73 (dq, J_{gem} = 9.4 Hz, J(CH_3, OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 3.88 (dd, J(3-H_{eq}, 4-H) = 6.85 Hz, J(3-H_{ax}, 4-H) = 10.3 Hz, 1H, 4-H), 4.09 (dq, J_{gem} = 9.4 Hz, J(CH_3, OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 5.32 (dd, J(3-H_{ax}, 2-H) = 8.6 Hz, J(3-H_{eq}, 2-H) = 1.95 Hz, 1H, 2-H), 7.25–7.81 (m, 10H, Ph-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 15.05 (OCH_2CH_3), 36.45 (C-3), 40.51 (C-4), 65.25 (OCH_2CH_3), 88.10 (C-5), 101.22 (C-2), 119.36 (CN), 127.53, 127.71, 128.14, 128.36, 128.85, 130.88 (*o,m,p*-Ph), 132.94, 140.86 (*i*-Ph), 163.96 (C-6) ppm; MS: *m/z* (%) = 305.4 (20) $M^{+\cdot}$, 259.3 (10) [M-C_2H_5OH]$^{+\cdot}$, 233.3 (10) [M-$C_2H_3OC_2H_5$]$^{+\cdot}$, 105.1 (52) [COPh]$^+$, 77.1 (31) [Ph]$^+$, 72.1 (100) [$C_2H_3OC_2H_5$]$^{+\cdot}$; $C_{20}H_{19}NO_2$ (305:38); calcd: C 78.66, H 6.27, N 4.59; found: C 78.66, N 6.64, N 4.62.

(2R,4R*)-(±)-2-Ethoxy-4,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**4a**)

Colourless prisms; m.p.: 110°C; yield: 7.3%; IR (KBr): ν = 3029, 2079, 2920 (CH), 2205 (C≡N), 1613 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.3 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.04 (sept,

J_{gem} = 13.6 Hz, J(2-H,3-H_{ax}) = 2.9 Hz, J(4-H, 3-H_{ax}) = 10.5 Hz, 1H, 3-H_{ax}), 2.29 (ddd, J_{gem} = 13.6 Hz, J(2-H,3-H_{eq}) = 3.1 Hz, J(4-H,3-H_{eq}) = 6.2 Hz, 1H, 3-H_{eq}), 3.74 (dq, J_{gem} = 9.5 Hz, J(CH_3,OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 3.93 (dd, J(3-H_{eq},4-H) = 6.2 Hz, J(3-H_{ax},4-H) = 10.3 Hz, 1H, 4-H), 4.04 (dq, J_{gem} = 9.5 Hz, J(CH_3,OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 5.36 (t, J(3-H,2-H) = 3.05 Hz, 1H, 2-H), 7.26–7.81 (m, 10 H, Ph-H) ppm, ^{13}C NMR ($CDCl_3$): δ = 15.11 (OCH_2CH_3), 35.18 (C-3), 36.85 (C-4), 64.96 (OCH_2CH_3), 88.37 (C-5), 97.92 (C-2), 119.44 (CN), 127.48, 127.91, 128.10, 128.35, 128.94, 130.70 (*o,m,p*-Ph), 133.36, 141.35 (*i*-Ph), 162.90 (C-6) ppm; Ms: *m/z* (%) = 305.1 (54) $M^{+\cdot}$, 259.1 (17) $[M\text{-}C_2H_5OH]^{+\cdot}$, 233.1 (18) $[M\text{-}C_2H_3OC_2H_5]^{+\cdot}$, 105.0 (70) $[COPh]^{+\cdot}$, 77.0 (54) $[Ph]^{+\cdot}$, 72.0 (100) $[C_2H_3OC_2H_5]^{+\cdot}$; $C_{20}H_{19}NO_2$ (305.38); calcd.: C 78.66, H 6.27, N 4.59; found: C 78.56, H 6.88, N 4.77.

(2R,4S*)-(±)-2-iso-Butoxy-4,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**3b**)

Colourless prisms; m.p.: 112°C; yield: 72%; IR (KBr): ν = 3029, 2968, 2923 (CH), 2215 (C≡N), 1617 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.91 (d, J(CH, CH_3) = 6.7 Hz, 3H, $OCH_2CH(CH_3)_2$), 0.92 (d, J(CH,CH_3) = 6.7 Hz, 3H, $OCH_2CH(CH_3)_2$), 1.89 (m, J = 6.7 Hz, 1H, $OCH_2CH(CH_3)_2$), 2.14 (ddd, J_{gem} = 13.8 Hz, J(2-H,3-H_{eq}) = 2.1 Hz, J(4-H,3-H_{eq}) = 6.9 Hz, 1H, 3-H_{eq}), 2.43 (ddd, J_{gem} = 13.8 Hz, J(2-H,3-H_{ax}) = 8.3 Hz, J(4-H,3-H_{ax}) = 9.9 Hz, 1H, 3-H_{ax}), 3.39 (dd, J_{gem} = 9.1 Hz, J(CH,OCH_2 = 6.75 Hz, 1H, $OCH_2CH(CH_3)_2$), 3.81 (dd, J_{gem} = 9.1 Hz, J(CH,OCH_2) = 6.5 Hz, 1H, $OCH_2CH(CH_3)_2$), 3.89 (dd, J(3-H_{eq},4-H) = 6.9 Hz, J(3-H_{ax},4-H) = 9.9 Hz, 1H, 4-H), 5.29 (dd, J(3-H_{ax},2-H) = 8.2 Hz, J(3-H_{eq},2-H) = 2.1 Hz, 1H, 2-H), 7.03–7.99 (m, 10 H, Ph-H) ppm; MS: *m/z* (%) = 333.4 (100) $M^{+\cdot}$, 259.2 (48) $[M\text{-}C_4H_9OH]^{+\cdot}$, 234.2 (57) $[M\text{-}C_2H_2OC_4H_9]^{+\cdot}$, 105.1 (83) $[COPh]^{+\cdot}$, 100.1 (56) $[C_2H_3OC_4H_9]^{+\cdot}$, 77.1 (33) $[Ph]^{+\cdot}$; $C_{22}H_{23}NO_2$ (333.43); calcd: C 79.25, H 6.95, N 4.20; found: C 78.88, H 7.03, N 4.22.

(2R,4S*)-(±)-2-Methoxy-2-methyl-4,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**3c**)

Colourless prisms; m.p.: 108°C; yield: 78%; IR (KBr): ν = 3029, 3000, 2896 (CH), 2205 (C≡N), 1616 (C=C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.61 (s, 3H, CH_3), 2.19 (dd, J_{gem} = 13.7 Hz, J(4-H, 3-H_{eq}) = 7.2 Hz, 1H, 3-H_{eq}), 2.24 (dd, J_{gem} = 13.7 Hz, J(4-H,3-H_{ax}) = 8.3 Hz, 1H, 3-H_{ax}), 3.39 (s, 3H, OCH_3), 3.82 (dd, J(3-H_{eq},4-H) = 8.3 Hz, J(3-H_{ax},4-H) = 7.3 Hz, 1H, 4-H), 7.26–7.83 (m, 10 H, Ph-H) ppm; Ms: *m/z* (%) = 305.3 (15) $M^{+\cdot}$, 273.3 (7) $[M\text{-}CH_3OH]^{+\cdot}$, 234.2 (4) $[M\text{-}C_2H(CH_3)OCH_3]^{+\cdot}$, 105.1 (13) $[COPh]^{+\cdot}$, 77.1 (11) $[Pb]^{+\cdot}$, 72.1 (100) $[C_2H_2(CH_3)OCH_3]^{+\cdot}$; $C_{20}H_{19}NO_2$ (305.38); calcd.: C 78.66, H 6.27, N 4.59; found: 78.59, 6.66, 4.52.

(2R,4R*)-(±)-2-Methoxy-2-methyl-4,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**4c**)

Colourless prisms; m.p.: 90–92°C; yield: 12.4%; IR (KBr): ν = 3029, 3000, 2896 (CH), 2205 (C≡N), 1616 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.61 (s, 3H, CH_3), 1.88 (dd, J_{gem} = 13.7 Hz, J(4-H,3-H_{ax}) = 12.5 Hz, 1H, 3-H_{ax}), 2.32 (dd, J_{gem} = 13.7 Hz, J(4-H,3-H_{eq}) = 6.3 Hz, 1H, 3-H_{eq}), 3.48 (s, 3H, OCH_3), 3.92 (dd, J(3-H_{eq}, 4-H) = 6.3 Hz, J(3-H_{ax}, 4-H) = 12.5 Hz, 1H, 4-H), 7.26–7.83 (m, 10 H, Ph-H) ppm; MS: *m/z* (%) = 305.3 (19) $M^{+\cdot}$; $C_{20}H_{19}NO_2$ (305.38); calcd.: C 78.66, H 6.27, N 4.59; found: 78.59, 6.66, 4.52.

(2R,4S*)-(±)-2-Ethoxy-6-phenyl-4-(4-nitrophenyl)-3,4-dihydro-2H-pyran-5-carbonitrile* (**3d**)

Colourless prisms; m.p.: 121°C; yield: 84%; IR (KBr): ν = 3073, 3045, 2884 (CH), 2194 (C≡N), 1601 (C=C), 1522, 1350 (NO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.21 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.16 (quint, J_{gem} = 14.0 Hz, J(2-H,3-H_{ax} = 7.0 Hz, J(4-H,3-H_{ax}) = 7.4 Hz, 1H, 3-H_{ax}), 2.46 (ddd, J_{gem} = 14.0 Hz, J(2-H,3-H_{eq}) = 2.0 Hz, J(4-H,3-H_{eq}) = 7.3 Hz, 1H, 3-H_{eq}), 3.69 (dq, J_{gem} = 9.2 Hz, J(CH_3,OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 4.01 (t, J(3-H,4-H) = 7.4 Hz, 1H, 4-H), 4.04 (dq,

J_{gem} = 9.2 Hz, $J(CH_3,OCH_2)$ = 7.1 Hz, 1H, OCH_2CH_3), 5.38 (dd, J(3-H_{ax},2-H) = 6.45 Hz, J(3-H_{eq},2-H) = 2.0 Hz, 1H, 2-H), 7.46–8.24 (m, 9H, Ph-H) ppm; MS: *m/z* (%) 350.3 (39) $M^{+\cdot}$, 304.3 (10) $[M\text{-}C_2H_5OH]^{+\cdot}$, 262.2 (4) $[M\text{-}C_2H_3OC_2H_5,OH]^{+\cdot}$, 105.1 (100) $[COPh]^{+\cdot}$, 77.1 (16) $[Ph]^{+\cdot}$, 72.1 (28) $[C_2H_3OC_2H_5]^{+\cdot}$; $C_{20}H_{18}N_2O_4$ (350.37); calcd.: C 68.56, H 5.18, N 7.99; found: C 69.00, H 5.25, N 8.15.

(2R,4R*)-(±)-2-Ethoxy-4-(4-nitrophenyl)-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**4d**)

Colourless prisms; m.p.: 121°C; yield: 14%; IR (KBr): ν = 3087, 2979, 2929 (CH), 2205 (C≡N), 1613 (C=C), 1521, 1355 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.32 (t, $J(OCH_2,CH_3)$ = 7.1 Hz, 3H, OCH_2CH_3), 1.99 (sept, J_{gem} = 13.6 Hz, J(2-H,3-H_{ax}) = 2.2 Hz, J(4-H,3-H_{ax}) = 11.4 Hz, 1H, 3-H_{ax}), 2.32 (ddd, J_{gem} = 13.6 Hz, J(2-H,3-H_{eq}) = 2.9 Hz, J(4-H,3-H_{eq}) = 6.0 Hz, 1H, 3-H_{eq}), 3.78 (dq, J_{gem} = 9.3 Hz, $J(CH_3,OCH_2)$ = 7.1 Hz, 1H, OCH_2CH_3), 4.04 (dq, J_{gem} = 9.3 Hz, $J(CH_3,OCH_2)$ = 7.1 Hz, 1H, OCH_2CH_3), 4.08 (dd, J(3-H_{ax},4-H) = 11.7 Hz, J(3-H_{eq},4-H) = 6.1 Hz, 1H, 4-H), 5.41 (t, J(3-H,2-H) = 2.5 Hz, 1H, 2-H), 7.45–8.28 (m, 9 H, Ph-H) ppm; MS: *m/z* (%) = 350.1 (16) $M^{+\cdot}$, 304.1 (4) $[M\text{-}C_2H_5OH]^{+\cdot}$, 262.1 (1) $[M\text{-}C_2H_3OC_2H_5,OH]^{+\cdot}$, 105.0 (20) $[COPh]^{+\cdot}$, 77.0 (13) $[Ph]^{+\cdot}$, 72.0 (100) $[C_2H_3OC_2H_5]^{+\cdot}$; $C_{20}H_{18}N_2O_4$ (350.37); calcd.: C 68.56, H 5.18, N 7.99: found: C 68.89, H 5.24, N 8.16.

(2R,4S*)-(±)-2-iso-Butoxy-4-(4-nitrophenyl)-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**3e**)

Colourless prisms; m.p.: 115°C; yield: 73%; IR (KBr): ν = 3073, 2968, 2874 (CH), 2194 (C≡N), 1597 (C=C), 1522, 1355 (NO_2) cm^{-1} ^1H NMR ($CDCl_3$): δ = 0.83 (d, $J(CH,CH_3)$ = 6.7 Hz, 3H, $OCH_2CH(CH_3)_2$), 0.86 (d, $J(CH,CH_3)$ = 6.7 Hz, 3H, $OCH_2CH(CH_3)_2$), 1.79 (m, J = 6.7 Hz, 1H, $OCH_2CH(CH_3)_2$), 2.21 (ddd, J_{gem} = 13.95 Hz, J(2-H,3-H_{ax}) = 6.2 Hz, J(4-H,3-H_{ax}) = 7.3 Hz, 1H, 3-H_{ax}), 2.47 (ddd, J_{gem} = 13.95 Hz, J(2-H,3-H_{eq}) = 2.4 Hz, J(4-H,3-H_{eq}) = 7.3 Hz, 1H, 3-H_{eq}), 3.35 (dd, J_{gem} = 9.1 Hz, $J(CH,OCH_2)$ = 6.7 Hz, 1H, $OCH_2CH(CH_3)_2$), 3.76 (dd, J_{gem} = 9.1 Hz, $J(CH,OCH_2)$ = 6.4 Hz, 1H, $OCH_2CH(CH_3)_2$), 4.01 (t, J(3-H,4-H) = 7.25 Hz, 1H, 4-H), 5.36 (dd, J(3-H_{ax}, 2-H) = 6.1 Hz, J(3-H_{eq},2-H) = 2.35 Hz, 1H, 2-H), 7.48–8.23 (m, 9 H, Ph-H) ppm; MS: *m/z* (%) = 378.4 (40) $M^{+\cdot}$, 305.3 (18) $[M\text{-}OC_4H_9]^{+\cdot}$, 279.3 (18) $[M\text{-}C_2H_2OC_4H_9]^{+\cdot}$, 105.1 (77) $[COPh]^{+\cdot}$, 100.1 (75) $[C_2H_3OC_4H_9]^{+\cdot}$, 77.1 (27) $[Ph]^{+\cdot}$, 571 (100) $[C_4H_9]^{+\cdot}$; $C_{22}H_{22}N_2O_4$(378.43); calcd.: C 69.83, H 5.86, N 7.40; found: C 69.28, H 5.87, N 7.30.

(2R,4R*)-(±)-2-iso-Butoxy-4-(4-nitrophenyl)-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**4e**)

Colourless prisms; m.p.: 162°C; yield: 15%; IR (KBr): ν = 3053, 2962, 2917, 2875 (CH), 2202 (C≡N), 1616 (C=C), 1521, 1348 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.96 (d,$J(CH,CH_3)$ = 6.7 Hz, 6H, $OCH_2CH(CH_3)_2$), 1.95 (m, J = 6.65 Hz, 1H, $OCH_2CH(CH_3)_2$), 1.99 (sept, J_{gem} = 13.7 Hz, J (2-H,3-H_{ax}) = 2.5 Hz, J(4-H,3-H_{ax}) = 11.4 Hz, 1H, 3-H_{ax}), 2.33 (ddd, J_{gem} = 13.65 Hz, J(2-H,3-H_{eq}) = 2.6 Hz, J(4-H,3-H_{eq}) = 6.15 Hz, 1H, 3-H_{eq}), 3.495 (dd, J_{gem} = 9.1 Hz, $J(CH,OCH_2)$ = 6.6 Hz, 1H, $OCH_2CH(CH_3)_2$), 3.73 (dd, J_{gem} = 9.1 Hz, $J(CH,OCH_2)$ = 6.6 Hz, 1H, $OCH_2CH(CH_3)_2$), 4.08 (dd, J(3-H_{ax},4-H) = 11.4 Hz, J(3-H_{eq},4-H) = 6.1 Hz, 1H, 4-H), 5.39 (t, J(3-H,2-H) = 2.55 Hz, 1H, 2-H), 7.46–8.28 (m, 9 H, Ph-H) ppm; MS: *m/z* (%) = 378.4 (40) $M^{+\cdot}$; $C_{22}H_{22}N_2O_4$ (378.43); calcd.: C 69.83, H 5.86, N 7.40; found: C 69.30, H 5.58, N 7.30.

(2R,4S*)-(±)-2-Methoxy-2-methyl-4-(4-nitrophenyl)-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**3f**)

Colourless prisms; m.p.: 180°C; yield: 84%; IR (KBr): ν = 3062, 3012, 2947, 2847, 2836 (CH), 2205 (C≡N), 1626 (C=C), 1522, 1338 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.60 (s, 3H, CH_3), 2.31

(d, J(4-H,3-H) = 6.4 Hz, 2H, 3-H), 3.32 (s, 3H, OCH_3), 3.96 (t, J(3-H,4-H) = 6.35 Hz, 1H, 4-H), 7.46–8.23 (m, 9 H, Ph-H) ppm; MS: m/z (%) = 350.3 (10) $M^{+\cdot}$, 318.3 (3) $[M\text{-}CH_3OH]^{+\cdot}$, 279.3 (2) $[M\text{-}C_2H(CH_3)OCH_3]^{+\cdot}$, 105.1 (8) $[COPh]^+$ 77.1 (8) $[Ph]^{+\cdot}$, 72.1 (100) $[C_2H_2(CH_3)OCH_3]^{+\cdot}$; $C_{20}H_{18}N_2O_4$ (350.37); calcd.: C 68.56, H 5.18, N 7.99; found: C 68.87, H 5.15, N 7.79.

(2R,4R*)-(±)-2-Methoxy-2-methyl-4-(4-nitrophenyl)-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**4f**)

Colourless prisms; m.p.: 157°C; yield: 13%; IR (KBr): ν = 3067, 2990, 2941, 2896 (CH), 2202 (C≡N), 1611 (C=C), 1524, 1346 (NO_2) cm^{-1} ^1H NMR ($CDCl_3$): δ = 1.64 (s, 3H, CH_3), 1.86 (dd, J_{gem} = 13.55 Hz, J(4-H,3-H_{ax}) = 12.45 Hz, 1H, 3-H_{ax}), 2.34 (dd, J_{gem} = 13.6 Hz, J(4-H,3-H_{eq})= 6.15 Hz, 1H, 3-H_{eq}), 3.49 (s, 3H, OCH_3), 4.08 (dd, J(3-H_{eq}, 4-H) = 6.15 Hz, J(3-H_{ax}, 4-H) = 12.45 Hz, 1H, 4-H), 7.46–8.27 (m, 9H, Ph-H) ppm; MS: m/z (%) = 350.3 (10) $M^{+\cdot}$; $C_{20}H_{18}N_2O_4$ (350.37); calcd.: C 68.56, H 5.18, N 7.99; found: C 68.74, H 5.33, N 7.86.

(2R,4S*)-(±)-2-Ethoxy-4-(4-methoxyphenyl)-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**3g**)

Colourless prisms; m.p.: 105°C; yield: 72%; IR (KBr): ν = 3046, 2979, 2926 (CH), 2205 (C≡N), 1605 (C=C) cm^{-1} ^1H NMR ($CDCl_3$): δ = 1.29 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.08 (ddd, J_{gem} = 13.65 Hz, J(2-H,3-H_{ax})= 8.7 Hz, J(4-H,3-H_{ax}) = 10.5 Hz, 1H, 3-H_{ax}), 2.39 (ddd, J_{gem} = 13.65 Hz, J(2-H,3-H_{eq}) = 1.75 Hz, J(4-H, 3-H_{eq})= 6.9 Hz, 1H, 3-H_{eq}), 3.73 (dq, J_{gem} = 9.3 Hz, J(CH_3,OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 3.81 (s, 81 (s, 3H, OCH_3), 3.84 (dd, J(3-H_{ax},4-H) = 10.5 Hz, J(3-H_{eq},4-H) = 7.0 Hz, 1H, 4-H), 4.09 (dq, J_{gem} = 9.3 Hz, J(CH_3,OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 5.31 (dd, J(3-H_{ax},2-H) = 8.6 Hz, J(3-H_{eq},2-H) = 1.75 Hz, 1H, 2-H), 6.89–7.81 (m, 9 H, Ph-H) ppm; MS: m/z (%) = 335.4 (21) $M^{+\cdot}$, 289.3 (20) $[M\text{-}C_2H_5OH]^{+\cdot}$, 263.3 (100) $[M\text{-}C_2H_2OC_2H_5]^{+\cdot}$, 105.1 (83) $[COPh]^{+\cdot}$, 77.1 (23) $[Ph]^{+\cdot}$; $C_{21}H_{21}NO_3$ (335.40); calcd.: C 75.20. H 6.31, N 4.18; found: C 75.22, H 6.57, N 3.73.

(2R,4R*)-(±)-2-Ethoxy-4-(4-methoxyphenyl)-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**4g**)

Colourless prisms; m.p.: 116°C; yield: 7%; IR (KBr): ν = 3023, 2973, 2929 (CH), 2201 (C≡N), 1599 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.29 (t, J = 7.05 Hz, 3H, OCH_2CH_3), 2.01 (ddd, J_{gem} = 13.2 Hz, J(2-H,3-H_{ax}) = 2.25 Hz, J(4-H,3-H_{ax}) = 10.3 Hz, 1H, 3-H_{ax}), 2.25 (ddd, J_{gem} = 13.6 Hz, J(2-H,3-H_{eq}) = 3.7 Hz, J(4-H,3-H_{eq}) = 6.1 Hz, 1H, 3-H_{eq}), 3.73 (dq, J_{gem} = 9.4 Hz, J(CH_3,OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 3.81 (s, 3H, OCH_3), 3.88 (dd, J(3-H_{ax},4-H) = 10.25 Hz, J(3-H_{eq},4-H) = 6.15 Hz, 1H, 4-H), 4.03 (dq, J_{gem} = 9.4 Hz, J(CH_3,OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 5.33 (br, 1H, 2-H), 6.90–7.79 (m; 9 H, Ph-H) ppm; MS: m/z (%) = 335.1 (34) $M^{+\cdot}$; $C_{21}H_{21}NO_3$ (335.40); calcd.: C 75.20, H 6.31, N 4.18; found: C 74.82, H 6.24, N 4.01.

(2R,4S*)-(±)-2-iso-Butoxy-4-(4-methoxyphenyl)-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**3h**)

Colourless prisms; m.p.: 98°C; yield: 83%; IR (KBr): ν = 2958, 2905, 2879 (CH), 2205 (C≡N), 1609 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.92 (d, J(CH,CH_3) = 6.6 Hz, 3H, $OCH_2CH(CH_3)_2$), 0.93 (d, J(CH,CH_3) = 6.6 Hz, 3H, $OCH_2CH(CH_3)_2$), 1.90 (m, J = 6.6 Hz, 1H, $OCH_2CH(CH_3)_2$), 2.1 (ddd, J_{gem} = 13.7 Hz, J(2-H,3-H_{ax}) = 8.3 Hz, J(4-H,3-H_{ax}) = 6.3 Hz, 1H, 3-H_{ax}), 2.4 (ddd, J_{gem} = 13.65 Hz, J(2-H,3-H_{eq}) = 1.6 Hz, J(4-H,3-H_{eq}) 6.75 = Hz, 1H, 3-H_{eq}), 3.39 (dd, J_{gem} = 9.0 Hz, J(CH,OCH_2) = 6.85 Hz, 1H, $OCH_2CH(CH_3)_2$), 3.80 (s, 3H, OCH_3), 3.83 (dd, J(3-H_{ax},4-H) = 10.2 Hz, J(3-H_{eq},4-H) = 7.1 Hz, 1H, 4-H), 3.83 (dd, J_{gem} = 9.0 Hz, J(CH,OCH_2) = 6.85 Hz, 1H,

$OCH_2CH(CH_3)_2$), 5.28 (dd, J(3-H_{ax},2-H) = 8.25 Hz, J(3-H_{eq},2-H) = 1.55 Hz, 1H, 2-H), 6.89–7.80 (m, 9 H, Ph-H) ppm; MS: m/z (%) = 363.4 (20) $M^{+\cdot}$, 289.3 (23) $[M\text{-}C_4H_9OH]^{+\cdot}$, 263.3 (100) $[M\text{-}C_2H_3OC_4H_9]^{+\cdot}$, 105.1 (33) $[COPh]^{+\cdot}$, 77.1 (9) $[Ph]^{+\cdot}$; $C_{23}H_{25}NO_3$ (363.46); calcd.: C 76.01, H 6.93, N 3.85; found: C 75.72, H 6.95, N 3.50.

(2R,4R*)-(±)-*)-(±)-2-iso-Butoxy-4-(4-methoxyphenyl)-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**4h**)

Colourless prisms; m.p.: 77°C; yield: 10%; IR (KBr): ν = 2958, 2912, 2874 (CH), 2194 (C≡N), 1605 (C=C) cm^{1-}; ^1H NMR ($CDCl_3$): δ = 0.95 (d, J(CH,CH_3) = 6.6 Hz, 6H, $OCH_2CH(CH_3)_2$), 1.93 (m, J = 6.6 Hz, 1H, $OCH_2CH(CH_3)_2$), 2.0 (sept, 1H, 3-H_{ax}), 2.27 (ddd, J_{gem} = 13.5 Hz, J(2-H,3-H_{eq}) = 3.5 Hz, J(4-H,3-H_{eq}) = 6.1 Hz, 1H, 3-H_{eq}), 3.45 (dd, J_{gem} = 8.7 Hz, J(CH,OCH_2) = 6.9 Hz, 1H, $OCH_2CH(CH_3)_2$), 3.72 (dd, J_{gem} = 8.7 Hz, J(CH, OCH_2) = 7.0 Hz, 1H, $OCH_2CH(CH_3)_2$), 3.82 (s, 3H, OCH_3), 3.88 (dd, J(3-H_{ax},4-H) = 10.4 Hz, J(3-H_{eq},4-H) = 6.2 Hz, 1H, 4-H), 5.32 (br, 1H, 2-H), 6.91–7.79 (m, 9 H, Ph-H) ppm; MS: m/z (%) = 363.4 (22) $M^{+\cdot}$; $C_{23}H_{25}NO_3$ (363.46); calcd. C 76.01, H 6.93, N 3.85; found: C 75.98, H 6.72, N 3.62.

(2R,4S*)-(±)-2-Methoxy-4-(4-methoxyphenyl)-2-methyl-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**3i**)

Colourless prisms; m.p.: 97°C; yield: 81%; IR (KBr): ν = 3004, 2958, 2832 (CH), 2205 (C≡N), 1605 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$); δ = 1.57 (s, 3H, CH_3), 2.18 (m, 2H, 3-H), 3.40 (s, 3H, 2-OCH_3), 3.77 (br, 1H, 4-H), 3.81 (s, 3H, p-OCH_3), 6.89–7.81 (m, 9 H, Ph-H), ppm; MS: m/z (%) = 335.1 (10) $M^{+\cdot}$, 303.1 (9) $[M\text{-}CH_3OH]^{+\cdot}$, 263.1 (100) $[M\text{-}C_2H_2(CH_3)OCH_3]^{+\cdot}$, 105.0 (51) $[COPh]^{+\cdot}$, 77.0 (10) $[Ph]^{+\cdot}$, 72.0 (9) $[C_2H_2(CH_3)OCH_3]^{+\cdot}$; $C_{21}H_{21}NO_3$ (335.40); calcd.: C 75.20, H 6.31, N 4.18; found: C 74.73, H 6.37, N 3.78.

(2R,4R*)-(±)-2-Methoxy-4-(4-methoxyphenyl)-2-methyl-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile* (**4i**)

Colourless prisms; m.p.: 127°C; yield: 9%; IR (KBr): ν = 2998, 2935, 2835 (CH), 2201 (C≡N), 1630 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.60 (s, 3H, CH_3), 1.85 (dd, J_{gem} = 13.65 Hz, J(4-H,3-H_{ax}) = 12.45 Hz, 1H, 3-H_{ax}), 2.29 (dd, J_{gem} = 13.7 Hz, J(4-H,3-H_{eq}) = 6.25 Hz, 1H, 3-H_{eq}), 3.47 (s, 3H, 2-OCH_3), 3.81 (s, 3H, p-OCH_3), 3.87 (dd, J(3-H_{ax},4-H) = 12.45 Hz, J(3-H_{eq},4-H) = 6.2 Hz, 1H, 4-H), 6.90–7.79 (m, 9 H,Ph-H) ppm; MS: m/z (%) = 335.1 (9) $M^{+\cdot}$, $C_{21}H_{21}NO_3$ (335.40); calcd: C 75.20, H 6.31, N 4.18; found C 75.06, H 6.32, N 4.01.

(2R,4R*)-(±)-2-Ethoxy-6-phenyl-4-(4-pyridyl)-3,4-dihydro-2H-pyran-5-carbonitrile* (**3j**)

Colourless prisms; m.p.: 113–115°C; yield: 51%; IR (KBr): ν = 3061, 2973, 2885 (CH), 2201 (C≡N), 1613 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.21 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.14 (ddd, J_{gem} = 13.4 Hz, J(2-H,3-H_{ax}) = 6.7 Hz, J(4-H,3-H_{ax}) = 7.5 Hz, 1H, 3-H_{ax}), 2.42 (ddd, J_{gem} = 13.4 Hz, J(2-H,3-H_{eq}) = 2.2 Hz, J(4-H,3-H_{eq}) = 7.5 Hz, 1H, 3-H_{eq}), 3.67 (dq, J_{gem} = 9.35 Hz, J(CH_3,OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 3.87 (t, J(3-H,4-H) = 7.55 Hz, 1H, 4-H), 4.04 (dq, J_{gem} = 9.4 Hz, J(CH_3,OCH_2) = 7.1 Hz, 1H, OCH_2CH_3), 5.35 (dd, J(3-H_{eq},2-H) = 2.2 Hz, J(3-H_{ax},2-H) = 6.7 Hz, 1H, 2-H), 7.28–8.64 (m, 9 H, Ph-H, C_5H_4N) ppm; ^{13}C NMR ($CDCl_3$): δ = 14.97 (OCH_2CH_3), 34.84 (C-3), 38.89 (C-4), 65.28 (OCH_2CH_3), 85.80 (C-5), 100.07 (C-2), 119.13 (CN), 123.05 (p-Ph), 128.13 (o-Ph), 128.49 (m-Ph), 131.21 (i-Ph), 132.70 (i-C_5H_4N), 150.15 (m-C_5H_4N), 150.43 (o-C_5H_4N), 164.72 (C-6) ppm; MS: m/z (%) = 306.1 (74) $M^{+\cdot}$; $C_{19}H_{18}N_2O_2$ (306.36); calcd.: C 74.49, H 5.92, N 9.14; found: C 74.25, H 5.80, N 9.04.

(2R,4R*)-(±)-2-Ethoxy-6-phenyl-4-(4-pyridyl)-3,4-dihydro-2H-pyran-5-carbonitrile* (**4j**)

Colourless prisms; m.p.: 132°C; yield: 34%; IR (KBr): ν = 3061, 2973, 2885 (CH), 2201 (C≡N), 1613 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.31 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.99 (ddd, J_{gem} = 13.55 Hz, J(2-H,3-H_{ax}) = 2.7 Hz, J(4-H,3-H_{ax}) = 10.8 Hz, 1H, 3-H_{ax}), 2.29 (ddd, J_{gem} = 13.55 Hz, J(2-H,3-H_{eq}) = 3.0 Hz, J(4-H,3-H_{eq}) = 6.2 Hz, 1H, 3-H_{eq}), 3.76 (dq, J_{gem} = 9.5 Hz, $J(CH_3,OCH_2)$ = 7.1 Hz, 1H, OCH_2CH_3), 3.93 (dd, J(3-H_{eq},4-H) = 6.2 Hz, J(3-H_{ax},4-H) = 10.75 Hz, 1H, 4-H), 4.03 (dq, J_{gem} = 9.5 Hz, $J(CH_3,OCH_2)$ = 7.1 Hz, 1H, OCH_2CH_3), 5.37 (t, J(3-H,2-H) = 2.8 Hz, 1H, 2-H), 7.28–8.64 (m, 9 H, Ph-H, C_5H_4N) ppm; ^{13}C NMR ($CDCl_3$): δ = 15.09 (OCH_2CH_3), 34.54 (C-3), 36.27 (C-4), 65.13 (OCH_2CH_3), 86.67 (C-5), 97.58 (C-2), 118.97 (CN), 123.13 (*p*-Ph), 128.11 (*o*-Ph), 128.47 (*m*-Ph), 131.06 (*i*-Ph), 132.99 (*i*-C_5H_4N), 150.31 (*m*-C_5H_4N), 150.44 (*o*-C_5H_4N), 163.77 (C-6) ppm; MS: *m/z* (%) = 306.1 (74) $M^{+\cdot}$, 277.1 (23) $[M\text{-}C_2H_5]^{+\cdot}$, 260.1 (9) $[M\text{-}C_2H_5OH]^{+\cdot}$, 235.1 (15) $[M\text{-}C_2H_2OC_2H_5]^{+\cdot}$, 72.0 (100) $[C_2H_3OC_2H_5]^{+\cdot}$; $C_{19}H_{18}N_2O_2$ (306.36); calcd.: C 74.49, H 5.92, N 9.14; found: C 74.33, H 5.90, N 8.88.

(2R,4S*)-(±)-2-Methoxy-2-methyl-6-phenyl-4-(4-pyridyl)-3,4-dihydro-2H-pyran-5-carbonintrile* (**3k**)

Colourless prisms; m.p.: 160°C; yield: 59%; IR (KBr): ν = 3029, 2986, 2945 (CH), 2195 (C≡N), 1598 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.50 (s, 3H, CH_3), 2.27 (m, 2H, 3-H), 3.30 (s, 3H, 2-OCH_3), 3.82 (t, J(3-H,4-H) = 6.1 Hz, 1H, 4-H), 7.26–8.59 (m, 9H, Ph-H, C_5H_4N) ppm; MS: *m/z* (%) = 306.0 (56) $M^{+\cdot}$, 275.0 (10) $[M\text{-}OCH_3]^{+\cdot}$, 235.0 (80) $[M\text{-}C_2H(CH_3)OCH_3]^{+\cdot}$, 105.0 (21) $[COPh]^{+\cdot}$, 77.0 (21) $[Ph]^{+\cdot}$, 72.0 (100) $[C_2H_2(CH_3)OCH_3]^{+\cdot}$; $C_{19}H_{18}N_2O_2$ (306.36); calcd.: C 74.49, H 5.92, N 9.14; found: C 74.74, H 6.16, N 9.07.

(2R,4R*)-(±)-2-Methoxy-2-methyl-6-phenyl-4-(4-pyridyl)-3,4-dihydro-2H-pyran-5-carbonintrile* (**4k**)

Colourless prisms; m.p.: 164°C; yield: 33%; IR (KBr): ν = 3073, 2998, 2945 (CH), 2214 (C≡N), 1615 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.63 (s, 3H, CH_3), 1.83 (t, J_{gem} = 13.0 Hz, J(4-H,3-H_{ax}) = 13.0 Hz, 1H, 3-H_{ax}), 2.31 (dd, J_{gem} = 13.65 Hz, J(4-H,3-H_{eq}) = 6.2 Hz, 1H, 3-H_{eq}), 3.48 (s, 3H, 2-OCH_3), 3.93 (dd, J(3-H_{eq},4-H) = 6.2 Hz, J(3-H_{ax},4-H) = 12.4 Hz, 1H, 4-H), 7.28–8.63 (m, 9H, Ph-H, C_5H_4N) ppm; MS: *m/z* (%) = 306.1 (63) $M^{+\cdot}$, 275.1 (25) $[M\text{-}OCH_3]^{+\cdot}$, 235.0 (100) $[M\text{-}C_2H(CH_3)OCH_3]^{+\cdot}$, 217.0 (13) $[M\text{-}C_2H_2(CH_3)OCH_3,OH]^{+\cdot}$, 105.0 (5) $[COPh]^{+\cdot}$, 77.0 (3) $[Ph]^{+\cdot}$; $C_{19}H_{18}N_2O_2$ (306.36); calcd.: C 74.49, H 5.92, N 9.14; found: C74.65, H 6.12, N 9.07.

Reaction of **1a–c** *with 3,4-dihydro-2H-pyrane* **5**

To a solution of **1** (5 mmol) in anhydrous toluene (10 ml), hydropyrane (**5**, 50 mmol) and some crystals of hydroquinone were added. The mixture was heated at 130°C in a pressure flask for 5–12 h (TLC control). After removal of toluene and excess of **5**, the mixture was separated and purified by column chromatography on silica gel using petrol ether/*t*-butyl-methyl ether 1:4 or 1:1.

(4R,4aS*,8aR*)-(±)-2,4-Diphenyl-1,4,4a,5,6,7,8,8a-octahydro-1,8-dioxa-naphtho-3-carbonitrile* (**6a**)

Colourless prisms; m.p.: 145–150°C; mixture of **6a** (38%) and **7a** (58%); IR (KBr): ν = 3061, 2954, 2879 (CH), 2201 (C≡N), 1608 (C=C) cm^{-1}; = ^1H NMR ($CDCl_3$): δ = 1.1–2.25 (m, 5H, 4a-H, 5-H, 6-H) 3.75 (m, 1H, 7-H), 3.93 (m, 1H, 7-H), 4.2 (d, J(4a-H,4-H) = 6.35 Hz, 1H, 4-H), 5.69 (s, 1H, 8a-H), 7.25–7.90 (m, 10H, Ph-H) ppm; MS: *m/z* (%) = 317.1 (18) $M^{+\cdot}$, 234.1 (19) $[M\text{-}C_5H_7O]^{+\cdot}$, 105.0 (19) $[COPh]^{+\cdot}$, 84.0 (100) $[C_5H_8O]^{+\cdot}$, 77.0 (16) $[Ph]^{+\cdot}$; $C_{21}H_{19}NO_2$ (317.39); calcd.: C 79.47, H 6.03, N 4.41; found: C 78.96, H 6.05, N 4.37.

(4R,4aR*,8aR*)-(±)-2,4-Diphenyl-1,4,4a,5,6,7,8,8a-octahydro-1,8-dioxa-naphtho-3-carbonitrile* (**7a**)

^{1}H NMR ($CDCl_3$); δ = 1.1–2.15 (m, 5H, 4a-H, 5-H, 6-H), 3.61 (d, J(4a-H, 4-H) = 2.3 Hz, 1H, 4-H), 3.75 (m, 1H, 7-H), 3.93 (m, 1H, 7-H), 5.34 (d, J(4a-H,8a-H) = 2.3 Hz, 1H, 8a-H), 7.24–7.93 (m, 10H, Ph-H) ppm.

(4R,4aS*,8aR*)-(±)-2-Phenyl-4-(4-nitrophenyl)-1,4,4a,5,6,7,8,8a-octahydro-1,8-dioxa-naphtho-3-carbonitrile* (**6b**)

Colourless prisms; m.p.: 256°C; yield: 43%; IR (KBr): ν = 3065, 2954, 3000 (CH), 2208 (C≡N), 1611 (C=C), 1518, 1347 (NO_2) cm^{-1} ^{1}H NMR ($CDCl_3$): δ = 1.0–2.3 (m, 5H, 4a-H, 5-H, 6-H), 3.75 (m, 1H, 7-H), 3.95 (m, 1H, 7-H), 4.35 (d, J(4a-H,4-H) = 6.4 Hz, 1H, 4-H), 5.71 (s, 1H, 8a-H), 7.45–8.3 (m, 9H, Ph-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 18.98 (C-6), 24.19 (C-5), 37.46 (C-4a), 44.59 (C-4), 61.69) (C-7), 83.64 (C-3), 98.85 (C-8a), 119.16 (CN), 123.89, 128.31, 128.55, 129.58, 131.49 (*o,m,p*-Ph), 145.01, 147.47 (*i*-Ph), 166.21 (C-2) ppm; MS: *m/z* (%) = 362.1 (5) $M^{+\cdot}$, 202.1 (6) $[M\text{-}C_5H_8O,C_6H_4]^{+\cdot}$, 105.0 (7) $[COPh]^{+\cdot}$, 84.0 (100) $[C_5H_8O]^{+\cdot}$, 77.0 (3) $[Ph]^{+\cdot}$; $C_{21}H_{18}N_2O_4$ (362.39); calcd: C 68.60, H 5.01, N 7.73; found: C 68.61, H 4.75, N 7.39.

(4R,4aR*,8aR*)-(±)-2-Phenyl-4-(4-nitrophenyl)-1,4,4a,5,6,7,8,8a-octahydro-1,8-dioxa-naphtho-3-carbonitrile* (**7b**)

Colourless prisms; m.p.: 203°C; yield: 58%; IR (KBr): ν = 3067, 2950, 2870 (CH), 2200 (C≡N), 1620 (C=C), 1513, 1349 (NO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.85–2.15 (m, 5H, 4a-H, 5-H, 6-H), 3.74 (d, J(4a-H,4-H) = 2.45 Hz, 1H, 4-H), 3.75 (m, 1H, 7-H), 3.95 (m, 1H, 7-H), 5.3 (d, J(4a-H,8a-H) = 2.4 Hz, 1H, 8a-H), 7.45–8.3 (m, 9H, Ph-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 23.85 (C-6), 24.08 (C-5), 39.09 (C-4a), 45.88 (C-4), 62.39 (C-7), 82.0 (C-8a), 95.29 (C-3), 119.46 (CN), 124.33, 128.08, 128.57, 128.77, 131.39 (*o,m,p*-Ph), 147.46, 148.60 (*i*-Ph), 164.75 (C-2) ppm; MS: *m/z* (%) = 362.1 (28) $M^{+\cdot}$, 84.0 (100) $[C_5H_8O]^{+\cdot}$; $C_{21}H_{18}N_2O_4$ (362.39); calcd.: C 68.60, H 5.01, N 7.73; found: 68.09, H 5.11, N 7.29.

(4R,4aS*,8aR*)-(±)-2-Phenyl-4-(4-methoxyphenyl)-1,4,4a,5,6,7,8,8a-octahydro-1,8-dioxa-naphtho-3-carbonitrile* (**6c**)

Colourless prisms; m.p.: 146°C; yield: 32%; IR (KBr): ν = 3030, 2954, 2835 (CH), 2208 (C≡N), 1620 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.17–2.18 (m, 5H, 4a-H, 5-H, 6-H), 3.77 (m, 1H, 7-H), 3.82 (s, 3H, OCH_3), 3.91 (m, 1H, 7-H), 4.15 (d, J(4a-H,4-H) = 6.3 Hz, 1H, 4-H), 5.67 (s, 1H, 8a-H), 6.9–7.9) (m, 9H, Ph-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 18.95 (C-6), 24.43 (C-5), 37.94 (C- 4a), 43.87 (C-4), 55.26) (OCH_3), 61.73 (C-7), 85.62 (C-8a), 99.14 (C-3), 119.67 (CN), 128.29, 128.38, 128.18, 129.68, 130.99 (*o,m,p*-Ph), 132.68, 158.57 (*i*-Ph), 165.15 (C-2) ppm; MS: *m/z* (%) = 347.1 (33) $M^{+\cdot}$, 263.1 (100) $[M\text{-}C_5H_8O]^{+\cdot}$, 105.0 (25) $[COPh]^{+\cdot}$, 84.0 (12) $[C_5H_8O]^{+\cdot}$; $C_{22}H_{21}NO_3$ (347.41); calcd.: C 76.06, H 6.09, N 4.03; found: C 75.89, H 6.23, N 3.78.

(4R,4aR*,8aR*)-(±)-2-Phenyl-4-(4-methoxypenyl)-1,4,4a,5,6,7,8,8a-octahydro-1,8-dioxa-naphtho-3-carbonitrile* (**7c**)

Colourless prisms; m.p.: 115°C; yield: 65%; IR (KBr): ν = 3030, 2954, 2835, (CH), 2208 (C≡N), 1620 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.14–2.18 (m, 5H, 4a-H, 5-H, 6-H), 3.77 (m, 1H, 7-H), 3.80 (s, 3H, OCH_3), 3.91 (m, 1H, 7-H), 3.56 (d, J(4a-H,4-H) = 2.4 Hz, 1H, 4-H), 5.33 (d, J(4a-H,8a-H) = 2.35 Hz, 1H, 8a-H), 6.9–8.0 (m, 9H, Ph-H) ppm; $C_{22}H_{21}NO_3$ (347.41); calcd.: C 76.06, H 6.09, N 4.03; found: C 75.97 H 6.23, N 3.98.

Reaction of compounds **3a** *and* **3g** *with sulfuric acid*

3a: (0.45 g, 15 mmol) was suspended in sulfuric acid (10 ml, 50%) and heated under reflux at 70–80°C for 6 h. The mixture was poured onto crushed ice (10 g), extracted with chloroform (3 times each 15 ml), and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated, and the residue was chromatographed on silica gel using petrol ether/*t*-butyl methyl ether (1:1) as eluent. The reaction with compound **3g** was performed similarly.

4,6-Diphenyl-2-hydroxy-3,4-dihydro-2H-pyrane-5-carbonitrile (**8a**, **9a**)

Colourless prisms from petrol ether/*t*-buty-methyl ether (5:2); m.p.: 170–175°C; yield: 68%; IR (KBr): ν = 3375 (OH), 3029, 2961 (CH), 2214 (C≡N), 1608 (C=C) cm^{-1}; ^1H NMR (*DMSO*-d_6): δ = 1.81 (m, 0.3H, 3-H), 1.92 (m, 0.7H, 3-H), 2.14 (m, 0.7H, 3-H), 2.32 (m, 0.3H, 3-H), 3.33 (br, 1H, 2-OH), 3.89 (dd, J(3-H_{ax},4-H) = 8.65 Hz, J(3-H_{eq},4-H) = 6.5 Hz, 0.7H, 4-H), 3.99 (br, 0.3H, 4-H), 5.59 (br, 1H, 2-H), 7.3–7.8 (m, 10 H, Ph-H) ppm; MS: *m/z* (%) = 277.0 (100) $M^{+\cdot}$, 248.0 (35) $[M\text{-}CHO]^{+\cdot}$, 234.0 (73) $[M\text{-}CHO,CH_2]^{+\cdot}$, 172.0 (11) $[M\text{-}PhCO]^{+\cdot}$, 133.0 (9) $[C_6H_5C_2H_3CHO]^{+\cdot}$, 105.0 (18) $[COPh]^{+\cdot}$, 77.0 (26) $[Ph]^{+\cdot}$; $C_{18}H_{15}NO_2$ (277.32); calcd.: C 77.96, H 5.45, N 5.05; found: C 77.67, H 5 5.66, N 4.69.

6-Phenyl-2-hydroxy-4-(4-methoxyphenyl)-3,4-dihydro-2H-pyran-5-carbonitrile (**8g**, **9g**)

Colourless prisms from petrol ether/*t*-butyl-methyl ether (2:1); m.p.: 135–140; yield: 65%; IR (KBr): ν = 3356 (OH), 3036, 2961, 2885 (CH), 2214 (C≡N) cm^{-1} 1611 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.05 (m, 1H, 3-H), 2.25 (ddd, J(4-h,3-H_{eq}) = 6.0 Hz, J(2-H,3-H_{eq}) = 4.55 Hz, J_{gem} = 13.6 Hz, 0.77H, 3-H), 2.46 (ddd, J(4-H,3-H_{eq}) = 6.5 Hz, J(2-H,3-H_{eq}) = 2.0 Hz, J_{gem} = 13.6 Hz, 0.23H, 3-H), 3.65 (br, 1H, 2-OH), 3.81 (s, 3H, OCH_3), 3.86 (dd, J(3-H_{ax},4-H) = 10.2 Hz, J(3-H_{eq},4-H) = 6.6 Hz, 0.23H, 4-H), 3.91 (dd, J(3-H_{ax},4-H) = 9.2 Hz, J(3-H_{eq},4-H) = 6.1 Hz, 0.77H, 4-H), 5.56 (br, 0.23H, 2-H), 5.63 (br, 0.77H, 2-H), 6.9–7.8 (m, 9H, Ph-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 35.57, 35.94 (C-3), 37.67, 39.49 (C-4), 55.29 (OCH_3), 88.15, 88.29 (C-5), 92.55, 95.90 (C-2), 114.41, 119.36 (CN), 128.11, 128.21, 128.39, 128.60, 128.92, 130.77, 130.96, 132.47, 132.69, 133.08, 133.14, 132.67, 133.12 (*i,o,m,p*-Ph,*i,o,m*-$C_6H_4OCH_3$), 158.98, 159.09 (*p*-$C_6H_4OCH_3$), 162.85, 164.0 (C-6) ppm; MS: *m/z* (%) = 307.1 (42) $M^{+\cdot}$, 278.1 (5) $[M\text{-}CHO]^{+\cdot}$, 264.1 (20) $[M\text{-}CHO,CH_2]^{+\cdot}$, 202.1 (8) $[M\text{-}PhCO]^{+\cdot}$, 163.0 (100) $[p\text{-}OCH_3C_6H_4C_2H_3CHO]^{+\cdot}$, 135 (68) $[p\text{-}OCH_3C_6H_4C_2H_4]^{+\cdot}$, 105.0 (83) $[COPh]^{+\cdot}$, 77.0 (47) $[Ph]^{+\cdot}$; $C_{19}H_{17}NO_3$ (307.35); calcd.: C 74.25, H 5.58, N 4.56; found: C 74.48, H 5.59, N 4.49.

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