Hetero-*Diels-Alder* Cycloadditions of α,β-Unsaturated Acyl Cyanides

Part 4[1])

Substituent Effects in Reactions with *p*-Substituted Styrenes

by **Jin-Cong Zhuo** and **Hugo Wyler***

Institute of Organic Chemistry, University of Lausanne, BCH, CH-1015 Lausanne-Dorigny

Cycloadditions of α,β-unsaturated acyl cyanides (= 2-oxonitriles) **1**–**6** to styrene and its *p*-substituted derivatives **7a**–**f**,**h** are of inverse electron demand and provide, under mild conditions, regio- and stereoselectively 2-aryl-3,4-dihydro-2*H*-pyran-6-carbonitriles **8**–**13**, generally in good yield. Rates for the cycloaddition of acryloyl cyanide **1** to *p*-substituted styrenes, determined in competition reactions of substrate pairs relative to that of styrene, increase in the order of electron-donating ability $NO_2 < Cl < H < AcO < Me < AcNH < MeO$ of the *p*-substituent. Linear correlation of log (k_X/k_H), and σ_p^+ substituent constants (a *Hammett*-type plot), gives a reaction constant ρ_p^+ of -1.47 ± 0.17, supporting a concerted mechanism.

Introduction. – Reactions of '1-oxabuta-1,3-dienes' with electron-rich olefins lead to 3,4-dihydro-2*H*-pyrans and have been classed as heterodiene additions, or, more specifically, as *Diels-Alder* cycloadditions of inverse electron demand [2]. Structural variations make this type of synthesis particularly valuable as an access to carbohydrates and alkaloids [3]. Styrene, early known as dienophile component in the conventional *Diels-Alder* reaction [4], would be interesting noteably for the construction of a *C*-glycopyranoside, but has been used occasionally only[2]) since it reacts rather sluggishly with α,β-unsaturated carbonyl compounds [5]. Special conditions have been sought to overcome this drawback, such as high pressure [6] or *Lewis*-acid catalysis by ZnI_2 [7], $AlCl_3$ [8], $SnCl_4$ [9], and $[Eu(fod)_3]$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato) [10].

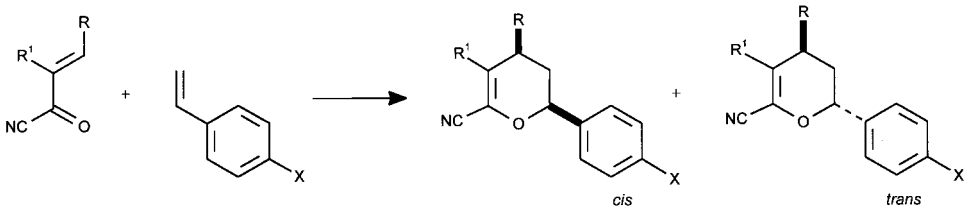
The diene reactivity of '1-heterobuta-1,3-dienes' is generally poor but becomes enhanced by electron-withdrawing substituents attached to it. We have been dealing in particular with α,β-unsaturated acyl cyanides, outstanding heterodienes, reacting under mild thermal conditions with various dienophiles, *e.g.*, ethoxyethene [11], methoxypropa-1,2-diene [12], 1-bromo-2-ethoxyethenes [1], and *N*-methylated uracils [13] which led to derivatives of 3,4-dihydro-2*H*-pyran-6-carbonitrile with high regio- and stereoselectivity, and in excellent yield.

The present investigation is intended to characterize the heterodiene ability of an α,β-unsaturated acyl cyanide (see **1**–**6**) by measuring reaction rates with a series of *p*-substituted styrenes **7**. This allows a comparison to kinetic studies on the *Diels-Alder* reaction with substituted 1,2,4,5-tetrazines, as versatile heterodienes, and styrenes,

---

[1]) Part 3, see [1]

[2]) Scattered examples have been reviewed by *Dujardin* and coworkers [10c].

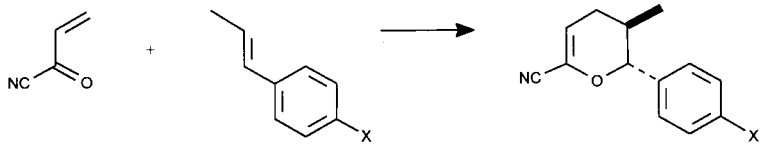


	R	R1
1	H	H
2	Me	H
3	COOEt	H
4	Ph	H
5	Me	Me
6	Me	Br

7

	X
a	H
b	Me
c	MeO
d	AcO
e	Cl
f	NO_2
g	NH_2
h	AcNH

	R	R1
8	H	H
9	Me	H
10	COOEt	H
11	Ph	H
12	Me	Me
13	Me	Br



1 **14** **15**

which led to the determination of *Hammett*'s ρ values as criteria of the dipolar character of the activated complex [14].

Results. – *Cycloadditions.* The 2-oxobut-3-enenitrile (acryloyl cyanide; **1**) in MeCN solution reacts gently with styrenes **7a**–**f**,**h** to produce 3,4-dihydro-2*H*-pyran-6-carbonitriles **8a**–**f**,**h**, respectively. It requires, at room temperature, rather long reaction times to arrive at good yields (*Table 1*). The fastest reaction, *p*-methoxystyrene (**7c**) providing 2*H*-pyran-6-carbonitrile **8c**, becomes quantitative within 1 d, whereas the most sluggish one, with *p*-nitrostyrene (**7f**), gives not more than 5% of **8f** in 4 d; reactions with other styrenes rank between 75 and 15%. At the temperature of boiling MeCN (81°), however, most of these reactions go to completion within 24 h.

Substituents on the diene modify the reactivity. The reaction becomes very sluggish, when a methyl group is attached to the β-position; *e.g.* 2-oxopent-3-enenitrile (**2**) needs to be heated to 60° for periods varying from 12 to 360 h to arrive at least at 70–80% of cycloadducts **9a**–**f**,**h**. Acyl cyanide **5**, with an additional Me group at C(3), reacts still slower; *e.g.*, with **7c**, it requires *ca.* 10-fold more time than diene **2** to reach the same yield. In contrast, diene **6,** having a bromo substituent instead of the Me group at C(3), reacts with **7c** comparably with great ease, producing, at room temperature within 8 h, **13c** in *ca.* 60% yield. Particularly reactive is an α,β-unsaturated acyl cyanide system with an alloxycarbonyl group at the β-position, as known: ethyl 4-cyano-4-oxobut-2-enoate (**3**) adds at room temperature more readily to styrenes than does **1**, giving 6-cyano-dihydro-2*H*-pyran-4-carboxylates **10a**–**f**,**h** with *ca.* 80% yield in remarkably short times; most efficient is its reaction with *p*-

Table 1. *Hetero*-Diels-Alder *Cycloadditions of α,β-Unsaturated Acyl Cyanides with Styrenes*

Styrene	Diene **1**		Diene **2**		Diene **3**	
	Conditions [a])	Product (yield)	Conditions [b])	Product (yield)	Conditions [b])	Product (yield)
7a (X = H)	r.t., 96 h	**8a** (50%)	60°, 240 h	**9a** (92%)	r.t., 36 h	**10a** (81%)
	81°, 24 h	**8a** (98%)		*cis*/*trans* 92 : 8		
7b (X = Me)	r.t., 96 h	**8b** (72%)	60°, 144 h	**9b** (75%)	r.t., 24 h	**10b** (74%)
	81°, 24 h	**8b** (99%)		*cis*/*trans* 95 : 5		
7c (X = MeO)	r.t., 22 h	**8c** (99%)	60°, 12 h	**9c** (69%)	r.t., 10 min	**10c** (89%)
	–			*cis*/*trans* 97 : 3		
7d (X = AcO)	r.t., 18 h	**8d** (15%)	60°, 180 h	**9d** (78%)	r.t., 24 h	**10d** (86%)
	81°, 24 h	**8d** (99%)		*cis*/*trans* 92 : 8		
7e (X = Cl)	r.t., 96 h	**8e** (34%)	60°, 360 h	**9e** (87%)	r.t., 48 h	**10e** (80%)
	81°, 24 h	**8a** (98%)		*cis*/*trans* 92 : 8		
7f (X = NO_2)	r.t., 96 h	**8f** (5%)	–		r.t., 86 h	**10f** (86%)
						cis/*trans* 84 : 16
	81°, 48 h	**8f** (83%)			90°, 16 h	**10f** (68%)
						cis/*trans* 50 : 50
7h (X = AcNH)	r.t., 22 h	**8h** (60%)	81°, 40 h	**9h** (65%)	r.t., 20 h	**10h** (88%)
	81°, 24 h	**8h** (98%)		*cis*/*trans* 94 : 6		
14a (X = H)	81°, 24 h	**15a** (34%)				
14c (X = MeO)	r.t., 168 h	**15c** (98%)				

Styrene	Diene **4**		Diene **5**		Diene **6**	
	Conditions [a])	Product (yield)	Conditions [a])	Product (yield)	Conditions [a])	Product (yield)
7c (MeO)	81°, 24 h	**11c** (82%)	60°, 120 h	**12c** (73%)	r.t., 8 h	**13c** (57%)
		cis/*trans* 95 : 5		*cis*/*trans* 96 : 4		*cis*/*trans* 98 : 2

[a]) *Conditions A:* 9 mmol of **1** in 30 ml of MeCN, and 5 mmol of styrene.
[b]) *Conditions B:* 5 mmol of **2**–**6**, and 5 mmol of styrene, neat.

methoxystyrene (**7c**), providing within 10 min adduct **10c** quantitatively. Acyl cyanide **4** with a Ph group at C(4) reacts comparably much slower.

A Me substituent on the dienophile part as in the styrene homologues (*E*)-prop-1-enylbenzenes **14a** and **14c** results again in a very slow cycloaddition compared to that of unsubstituted styrenes **7a** and **7c**, respectively. The reaction of **1** with **14a** at 81° produces within 1 d not more than 34% of cycloadduct **15a**, and even that of *p*-methoxy-activated **14c** takes at room temperature an entire week to be complete.

Cycloadducts of acyl cyanides **2** or **3** and styrenes have prevalent *cis*-configurations (> 92%), showing that the products result from the '*endo*' mode of addition. Also cyanodihydropyrancarboxylates **10a**–**f**,**h** are originally of *cis* configuration, but having a COOEt group at C(4), they undergo subsequent isomerization during chromatography or during storage. Chromatography of *cis*-**10f** on silica gel delivers a 1 : 2 *cis*/*trans* mixture. Originally pure *cis*-**10f** shows, after 3½ days at room temperature, a 84 : 16, and after 16 h at 90°, a 1 : 1 mixture of *cis*/*trans* diastereoisomers (see *Table 1*).

Product Structures. Cycloadducts **8**–**13**, purified by flash chromatography, were characterized by ^{1}H- and ^{13}C-NMR, IR, and mass spectra. The structures of the 2*H*-

dihydropyrans were assigned on the basis of NMR spectra. Their relative *cis*/*trans* configuration and preferred half-chair conformation were inferred from the coupling pattern of H–C(2), H–C(3), and H–C(4) (see *Fig. 1*).

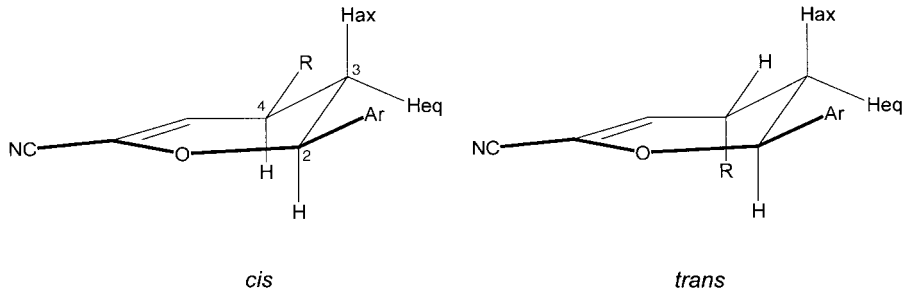


Fig. 1. *Configurations and prevailing conformations of cycloadducts* **8**–**13**

In the main product, *i.e.*, the *cis*-diastereoisomer, the ^3J coupling constants of H–C(2) (δ 4.78–5.12) are *ca.* 11 and 2 Hz; the large coupling constant refers to H_{ax}–C(3), and the small coupling constant to H_{eq}–C(3), hence H–C(2) must be pseudo-axial, and the aryl group at C(2) in this preferred conformation pseudo-equatorial. Another large ^3J coupling constant (*ca.* 11 Hz) for H_{ax}–C(3) with H–C(4) discloses pseudo-axial orientation of the latter; therefore, the substituent at C(4) must be pseudo-equatorial which establishes the overall *cis*-configuration in the prevailing '*endo*'-addition products **8**–**13**; other ^3J coupling constants, *ca.* 6 Hz for H–C(4) with H_{eq}–C(3), and *ca.* 2.5 Hz for H–C(4) with H–C(5), support this conclusion. The minor product is the *trans*-diastereoisomer, which also prefers the half-chair conformation with an equatorial aryl group, as inferred from one large and one small ^3J coupling constant for H–C(2) with its neighbors, *ca.* 10 Hz with H_{ax}–C(3) and *ca.* 2.5 Hz with H_{eq}–C(3). Pseudo-axial orientation of the substituent at C(4) in this isomer is indicated by smaller ^3J coupling constants for the pseudo-equatorial H–C(4) with the C(3) protons, *ca.* 2 Hz for H–C(4) with H_{eq}–C(3), and *ca.* 6 Hz for H–C(4) with H_{ax}–C(3).

Relative Reaction Rates. We have compared the reactivity of 2-oxobut-3-enenitrile towards styrene and some of its *p*-substituted derivatives in terms of relative reaction rates determined in competition experiments. Since all these reactions are virtually irreversible, a simplified experimental procedure is feasible for kinetics without the usually required periodic measurements [15]. Hence, the partial reactions of *Eqns. 1* and *2*, referring to the competing reaction of diene A with dienophile B and C, respectively, may be combined into *Eqn. 3* as a basis of calculation.

$$A + B \xrightarrow{k_B} AB \tag{1}$$

$$A + C \xrightarrow{k_C} AC \tag{2}$$

$$\frac{k_B}{k_C} = \frac{\log\ (1 + [AB]/[B])}{\log\ (1 + [AC]/[C])} \tag{3}$$

Reactions of diene A with equimolar amounts of a pair of dienophiles B and C have to be interrupted at a definite time before being complete. The parts of cycloadducts formed, [AB] and [AC], and unreacted styrenes, [B] and [C], are evaluated in the reaction mixture by ^{1}H-NMR integration (*Table 2*), and ratios of the rate constants k_B/k_C are calculated according to *Eqn. 3*. In most cases, the relative rate values k_X/k_H result directly from a competition with styrene. Only relative rates of **7c** or **7f** were calculated from rate quotients of two different substrate pairs. The relative reaction rates k_X/k_H

Table 2. *Competitive Reaction of a Pair of* (p-*Substituted) Styrenes B and C* (see **7a**–**f**) *with 2-Oxobut-3-enenitrile A* (acryloyl cyanide; **1**) *in MeCN at 20°, and Relative Reaction Rates*

p-Substituent X	Distribution of residual dienophiles B and C and cycloadducts AB and AC [%]				Calc. rel. rates	
	B	C	AB	AC	k_B/k_C[a])	k_X/k_H
H						1.00
Me	**7b** (39.7)	**7a** (47)	**8b** (10.3)	**8a** (3)	3.73	3.73
AcO	**7d** (44.5)	**7a** (45.1)	**8d** (5.5)	**8a** (4.9)	1.13	1.13
AcNH	**7h** (24.6)	**7a** (46.2)	**8h** (25.4)	**8a** (3.8)	8.97	8.97
Cl	**7e** (45.8)	**7a** (44.6)	**8e** (4.2)	**8a** (5.4)	0.77	0.77
MeO	**7c** (31)	**7b** (46.5)	**8c** (19)	**8b** (3.5)	6.59	24.58[b])
NO_2	**7f** (45.9)	**7e** (28)	**8f** (4.1)	**8e** (22)	0.15	0.11[c])

[a]) Calculated from the relative ratio of B, C, AB, and AC according to *Eqn. 3*. [b]) Calculated from **7c**/**7b** and **7b**/**7a**. [c]) Calculated from **7f**/**7e** and **7e**/**7a**.

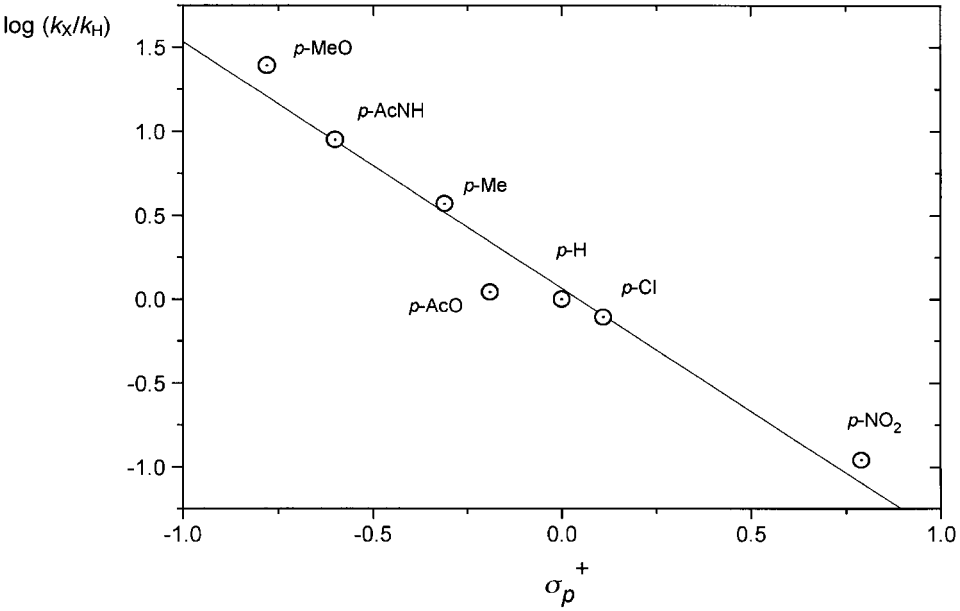


Fig. 2. Hammett *plot for cycloadditions of 2-oxobut-3-enenitrile* (**1**) *and* p-*substituted styrenes*

thus obtained decrease in the order: MeO (24.6) > AcNH (9.0) > Me (3.7) > AcO (1.1) ≈ H (1.00) > Cl (0.77) > NO_2 (0.11). A *Hammett* plot (*Fig. 2*) [16a] shows that log (k_X/k_H) correlates well with known σ_p^+ constants [16b]; linear regression gives a reaction constant ρ^+ of -1.47 ± 0.17 ($r = 0.98$).

Discussion. – Reactions of α,β-unsaturated acyl cyanides with styrene and some *p*-substituted styrenes have been shown to proceed in good yield, regio- and stereoselectively. A convincing example for the ease of these [2 + 4] cycloadditions is the quantitative reaction of acryloyl cyanide (**1**) and styrene at 81°, compared to that of

acrylaldehyde (= prop-2-enal) and styrene which provides, at 155°, not more than 15% of adduct [5].

It has been induced from frontier-molecular-orbital theory that the interaction between the LUMO of the heterodiene and the HOMO of the dienophile becomes rate-determining in the hetero-*Diels-Alder* cycloaddition of inverse electron demand [14]. Decreasing the energy gap between the two levels facilitates the reaction since it stabilizes the molecular complex in the transition state. The cycloaddition rate is enhanced by the presence of an electron-withdrawing substituent in the heterodiene system, lowering its LUMO and HOMO energy, as well as by an electron-donating substituent in the dienophile system raising its HOMO and LUMO energy. Recent MP2/6-31 + G* calculations confirm that the LUMO energy of 2-oxobut-3-enenitrile is much lower than that of acrylaldehyde [17]. Our findings are in agreement with these theoretical expectations.

Activation of the heterodiene system by a CN group at C(2) has also been found by *Fowler et al.* for the '1-azabuta-1,3-diene' system [18]. An enhancement of diene reactivity has been noted as well in a hetero-*Diels-Alder* variant with a 2-oxocarboxylic acid ester by *Boger et al.* [19]. Another electron-withdrawing alkoxycarbonyl group at C(4) of the 2-oxobut-3-ene system makes diene **3** still more reactive.

Increasing dienophile activity of styrenes towards heterodiene **1** reflects the order of electron-donating ability of a *p*-substituent. Log (k_X/k_H) fit well a *Hammett* plot against the σ_p^+ constants of the styrene moieties (*Fig. 2*). Kinetic measurements of additions of a series of *p*-substituted styrenes to various 3,6-disubstituted 1,2,4,5-tetrazines in apolar solvents, taken as model reactions for a *Diels-Alder* cycloaddition of inverse electron demand, gave correlations of σ_p^+ with log(rel. reaction constants) in the range of $\rho = -1$ to -0.5 [14][20]. Addition of styrenes to the acridizinium (= benzo[*b*]quinolizinium) ion gave a ρ_p^+ of -0.56 [21]. The rather low reaction constants were judged compatible with the view of only small partial charges in the transition state. The sensitivity of the reaction of α,β-unsaturated acyl cyanides with styrenes exhibiting a ρ_p^+ value of *ca.* -1.5 is notably higher than those mentioned above for *Diels-Alder* cycloadditions of inverse electron demand. In contrast, only electrophilic additions of *p*-substituted styrenes show higher values of reaction constants ($\varrho = -2.4$ to -5.4) [22], as well as [2 + 2] cycloadditions with tetracyanoethylene (= ethenetetracarbonitrile) *via* zwitterionic intermediates ($\rho = -7.1$) [23].

The higher ρ_p^+ value obtained with α,β-unsaturated acyl cyanides may be explained by the electron deficiency of the diene reducing the energy gap between $LUMO_{diene}$ and $HOMO_{dienophile}$ which corroborates the idea of enhanced partial positive charge in the transition state. Nevertheless, compared with cases of dipolar intermediates, this would still exclude a two-step mechanism *via* a zwitterionic intermediate, and be in agreement with a concerted, but nonsynchronous, mechanism.

We gratefully acknowledge financial support from the *Swiss National Science Foundation.*

Experimental Part

General. Column chromatography: silica gel *60* (200–400 mesh ASTM, *Merck 9385*); FC = flash chromatography. Melting points (m.p.): observed under the microscope with a *Mettler FP 52* apparatus ^{1}H- and ^{13}C-NMR Spectra: *Bruker WH 250*, *WH 360*, and *DPX-400* resp. δ in ppm rel. to $SiMe_4$ as internal

standard. IR Spectra (cm^{-1}): *Perkin-Elmer 1420*. Mass spectra (*m/z* (rel. int. [%])): *Nermag R 10-10C*; EI, electron impact; CI, chemical ionization in NH_3.

Starting Materials. The α,β-unsaturated acyl cyanides were prepared as reported previously: for **1**–**5**, see [11a], and for **6**, see [11b]. The 2-oxobut-3-enenitrile (**1**), *ca.* 0.3M in MeCN, was obtained from acryloyl chloride (18.1 g, 200 mmol), NaI (57.5 g, 375 mmol), CuCN (18 g, 200 mmol), and MeCN (400 ml), distilled with the solvent after 0.5 h, and stored at $-20°$ [1]. Styrenes **7a**–**c**,**e** and **14a**,**c** were purchased from *Fluka*, **7d** from *Aldrich*. The preparation of *p*-nitrostyrene (**7f**), *p*-aminostyrene (**7g**), and *p*-(acetylamino)styrene (**7h**) is described below.

Cycloaddition Conditions. Reactions between dienes and styrenes were performed under the conditions indicated in *Table 1*. *Conditions A:* The styrene (5 mmol) was added to a soln. of 2-oxobut-3-enenitrile (**1**; 9 mmol) in MeCN (30 ml). After the indicated reaction time, the solvent was evaporated and the product purified by FC (CH_2Cl_2). *Conditions B:* The styrene (5 mmol) and the unsaturated acyl cyanide (5 mmol) were mixed. The product was purified by FC (AcOEt/hexane).

*3,4-Dihydro-2-phenyl-2*H*-pyran-6-carbonitrile* (**8a**). Oil. IR (neat): 3060*m*, 3030*m*, 2226*s*, 1640v*s*, 1605*w*, 1495*s*, 1305v*s*, 1290v*s*, 1235v*s*, 1145v*s*, 1035v*s*, 952*s*, 935*m*, 910*s*, 755v*s*, 700v*s*. ^{1}H-NMR ($CDCl_3$): 7.43–7.28 (*m*, C_6H_5); 5.77 (*ddd*, *J* = 5.0, 3.1, 1.0, H–C(5)); 4.91 (*dd*, *J* = 10.3, 2.5, H_α–C(2)); 2.38 (*dddd*, *J* = 19.0, 10.3, 6.3, 3.1, H_α–C(4)); 2.23 (*dddd*, *J* = 19.0, 5.8, 5.0, 2.5, H_β–C(4)); 2.13 (*ddtd*, *J* = 14.2, 6.3, 2.5, 1.0, H_α–C(3)); 1.98 (*dtd*, *J* = 14.2, 10.3, 5.8, H_β–C(3)). ^{13}C-NMR ($CDCl_3$): 139.5 (C (Ph)); 129.6 (C(6)); 128.4 (2 CH (Ph)); 128.1 (CH (Ph)); 125.7 (2 CH, (Ph)); 116.9 (C(5)); 114.7 (CN); 78.4 (C(2)); 28.4 (C(3)); 21.2 (C(4)). EI-MS: 131 (19), 129 (14), 105 (11), 104 (100), 103 (18), 91 (5), 78 (19), 77 (11). CI-MS: 185 (4, M^+), 131 (13), 129 (12), 116 (3), 105 (12), 104 (100), 103 (12), 91 (8), 77 (15).

*3,4-Dihydro-4-methyl-2-phenyl-2*H*-pyran-6-carbonitrile* (**9a**). Oil, *cis*/*trans* 92 : 8. IR (neat): 3065*m*, 3035*m*, 2230*s*, 1638v*s*, 1605*w*, 1497*s*, 1453*s*, 1380*m*, 1285v*s*, 1227v*s*, 1152v*s*, 1058v*s*, 1037v*s*, 986*s*, 908*s*, 878*s*, 758*s*, 700*s*. ^{1}H-NMR ($CDCl_3$): *c*-**9a**: 7.36 (*m*, C_6H_5); 5.60 (*dd*, *J* = 2.4, 1.6, H–C(5)); 4.93 (*dd*, *J* = 11.5, 1.9, H_α–C(2)); 2.68 (*m*, *J* = 11.0, 7.1, 6.3, 2.4, H_α–C(4)); 2.18 (*dddd*, *J* = 14.0, 6.3, 1.9, 1.6, H_α–C(3)); 1.62 (*ddd*, *J* = 14.0, 11.5, 11.0, H_β–C(3)); 1.12 (*d*, *J* = 7.1, Me–C(4)); *t*-**9a**: 5.73 (*dd*, *J* = 4.6, 1.4, H–C(5)); 1.19 (*d*, *J* = 7.1, *Me*–C(4)). ^{13}C-NMR ($CDCl_3$): *c*-**9a**: 139.2 (C (Ph)); 128.6 (C(6)); 128.2 (2 CH (Ph)); 128.0 (CH (Ph)); 125.6 (2 CH (Ph)); 122.4 (C(5)); 114.5 (CN); 78.9 (C(2)); 37.7 (C(3)); 28.0 (C(4)); 19.5 (*Me*–C(4)); *t*-**9a**: 122.1 (C(5)); 74.8 (C(2)); 35.3 (C(3)); 25.3 (C(4)); 21.0 (*Me*–C(4)). EI-MS: 199 (2, M^+), 143 (6), 128 (3), 105 (12), 104 (100), 103 (13), 102 (2), 91 (7), 78 (8), 65 (3), 51 (5).

*Ethyl 6-Cyano-3,4-dihydro-2-phenyl-2*H*-pyran-4-carboxylate* (**10a**). Crude product: *c*-**10a**/*t*-**10a** > 98 : < 2; after FC (AcOEt/hexane 1 : 6), *c*-**10a**/*t*-**10a** 75 : 25 (1.03 g, 81%). Crystallization of a mixture from Et_2O/hexane 1 : 1 gave pure *t*-**10a**. *c*-**10a**/*t*-**10a** > 98 : < 2: IR (neat): 3070*m*, 3040*m*, 2232*s*, 1735v*s*, 1645v*s*, 1498*m*, 1453*s*, 1370*s*, 1295v*s*, 1253v*s*, 1185v*s*, 1150v*s*, 1052v*s*, 1025v*s*, 968*s*, 950*s*, 903*s*, 758v*s*, 700v*s*. EI-MS: 258 (4, $[M+H]^+$), 257 (6, M^+), 185 (14), 184 (18), 129 (11), 128 (9), 115 (5), 104 (100), 91 (17), 78 (12), 77 (16), 65 (4), 51 (11).

Data of c-**10a** (from *c*/*t*-**10a** > 98 : < 2): ^{1}H-NMR ($CDCl_3$): 7.38 (*m*, C_6H_5); 5.90 (*dd*, *J* = 2.5, 1.9, H–C(5)); 4.99 (*dd*, *J* = 11.3, 2.0, H_α–C(2)); 4.18 (*q*, *J* = 7.1, MeCH_2O); 3.56 (*ddd*, *J* = 11.3, 6.3, 2.5, H_α–C(4)); 2.46 (*dddd*, *J* = 14.1, 6.3, 2.0, 1.9, H_α–C(3)); 2.17 (*dt*, *J* = 14.1, 11.3, H_β–C(3)); 1.28 (*t*, *J* = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 170.1 (*C*=O); 138.3 (C (Ph)); 130.2 (C(6)); 128.4 (2 CH (Ph)); 128.2 (CH (Ph)); 125.7 (2 CH (Ph)); 113.9 (CN); 113.7 (C(5)); 78.4 (C(2)); 61.3 (Me*C*H_2O); 38.5 (C(4)); 31.4 (C(3)); 13.8 (*Me*CH_2O).

Data of Pure t-**10a**: M.p. 61.8–61.9°. ^{1}H-NMR ($CDCl_3$): 7.38 (*m*, C_6H_5); 5.90 (*dd*, *J* = 5.3, 1.3, H–C(5)); 4.99 (*dd*, *J* = 11.0, 2.2, H_β–C(2)); 4.23 (*q*, *J* = 7.1, MeCH_2O); 3.26 (*ddd*, *J* = 5.9, 5.3, 2.0, H_α–C(4)); 2.50 (*dddd*, *J* = 14.1, 2.2, 2.0, 1.3, H_α–C(3)); 1.97 (*ddd*, *J* = 14.1, 11.0, 5.9, H_β–C(3)); 1.32 (*t*, *J* = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 170.7 (C=O); 138.6 (C (Ph)); 130.4 (C(6)); 128.4 (2 CH (Ph)); 128.2 (CH (Ph)); 125.6 (2 CH (Ph)); 114.0 (CN); 112.8 (C(5)); 76.6 (C(2)); 61.4 (Me*C*H_2O); 36.5 (C(4)); 29.9 (C(3)); 13.8 (*Me*CH_2O).

*3,4-Dihydro-2-(4-methylphenyl)-2*H*-pyran-6-carbonitrile* (**8b**). Oil. IR (neat): 3060*m*, 3025*m*, 2228*s*, 1640v*s*, 1615*m*, 1517*s*, 1440*s*, 1370*s*, 1304v*s*, 1290v*s*, 1235v*s*, 1145v*s*, 1035v*s*, 955*s*, 930*s*, 873*s*, 812v*s*, 785*s*, 760*s*. ^{1}H-NMR ($CDCl_3$): 7.25–7.16 (*m*, C_6H_4); 5.76 (*ddd*, *J* = 5.0, 3.1, 1.1, H–C(5)); 4.89 (*dd*, *J* = 10.3, 2.5, H_α–C(2)); 2.39 (*dddd*, *J* = 19.0, 10.3, 6.5, 3.1, H_α–C(4)); 2.38 (*s*, Me–C(4′)); 2.23 (*dddd*, *J* = 19.0, 5.7, 5.0, 2.5, H_β–C(4)); 2.12 (*dddd*, *J* = 14.0, 6.5, 2.5, 1.1, H_α–C(3)); 1.98 (*dtd*, *J* = 14.0, 10.3, 5.7, H_β–C(3)). ^{13}C-NMR ($CDCl_3$): 137.6 (C (Ph)); 136.4 (C (Ph)); 129.4 (C(6)); 128.8 (2 CH (Ph)); 125.5 (2 CH (Ph)); 116.7 (C(5)); 114.6 (CN); 78.2 (C(2)); 28.1 (C(3)); 21.1 (C(4)); 20.7 (*Me*–C(4′)). EI-MS: 199 (1, M^+), 146 (2), 145 (15), 144 (2), 143 (9), 129 (2), 119 (15), 118 (100), 117 (53), 115 (14), 105 (6), 103 (5), 91 (16), 89 (3), 78 (3), 77 (5), 65 (5), 51 (4). CI-MS: 199 (3, M^+), 146 (1), 145 (9), 144 (1), 143 (4), 129 (1), 128 (2), 119 (16), 118 (100), 117 (35), 115 (13), 105 (6), 103 (5), 91 (24), 89 (4), 78 (4), 77 (8).

*3,4-Dihydro-4-methyl-2-(4-methylphenyl)-2*H*-pyran-6-carbonitrile* (**9b**). Crude product: *cis*/*trans* 95:5. M.p. 83.8–85.8°. IR (KBr): 3070*m*, 3035*m*, 2228*s*, 1638v*s*, 1613*m*, 1518*s*, 1455*s*, 1440*s*, 1380*s*, 1327v*s*, 1284v*s*, 1152v*s*, 1058v*s*, 1042v*s*, 985*s*, 908*s*, 880*s*, 808v*s*, 765*m*. ^{1}H-NMR ($CDCl_3$): *c*-**9b**: 7.26–7.16 (*m*, C_6H_4); 5.58 (*dd*, *J* = 2.2, 1.8, H–C(5)); 4.89 (*dd*, *J* = 11.3, 1.7, H_α–C(2)); 2.67 (*m*, *J* = 11.3, 7.0, 6.2, 2.2, H_α–C(4)); 2.37 (*s*, *Me*–C(4′)); 2.14 (*dddd*, *J* = 14.0, 6.2, 1.8, 1.7, H_α–C(3)); 1.62 (*dt*, *J* = 14.0, 11.3, H_β–C(3)); 1.12 (*d*, *J* = 7.0, Me–C(4)); *t*-**9b**: 1.18 (Me–C(4)). ^{13}C-NMR ($CDCl_3$): 138.2 (C (Ar)); 136.6 (C (Ar)); 129.2 (2 CH (Ar)); 129.2 (C(6)); 125.9 (2 CH (Ar)); 122.4 (C(5)); 114.8 (CN); 79.3 (C(2)); 38.1 (C(3)); 28.5 (C(4)); 21.1 (*Me*–C(4′)); 19.9 (*Me*–C(4)). CI-MS: 213 (18, M^+), 159(3), 157(3), 129(2), 128(2), 119(13), 118(100), 117(55), 115(11), 105(5), 103(3), 102(2), 96(8), 91(27), 83(13), 78(5), 75(6).

*Ethyl 6-Cyano-3,4-dihydro-2-(4-methylphenyl)-2*H*-pyran-4-carboxylate* (**10b**). The product was crystallized from hexane/Et_2O 1:1: pure *c*-**10b** (1.00 g, 74%). FC (AcOEt/hexane 1:6) of the product gave *cis*/*trans* 75:25.

Data of Pure c-**10b**: M.p. 72.5–73.5°. IR (KBr): 3078*m*, 2232*s*, 1732v*s*, 1642v*s*, 1518*s*, 1455*s*, 1390*s*, 1368*s*, 1337v*s*, 1257v*s*, 1173v*s*, 1160v*s*, 1050v*s*, 1020v*s*, 970*m*, 877*m*, 820v*s*, 762*s*. ^{1}H-NMR ($CDCl_3$): 7.23 (*m*, C_6H_4); 5.88 (*dd*, *J* = 2.2, 1.6, H–C(5)); 4.95 (*dd*, *J* = 11.5, 2.0, H_α–C(2)); 4.18 (*q*, *J* = 7.1, MeCH_2O); 3.53 (*ddd*, *J* = 11.3, 6.5, 2.2, H_α–C(4)); 2.42 (*dddd*, *J* = 14.2, 6.5, 2.0, 1.6, H_α–C(3)); 2.37 (*s*, Me–C(4′)); 2.17 (*ddd*, *J* = 14.2, 11.5, 11.3, H_β–C(2)); 1.27 (*t*, *J* = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 170.5 (C=O); 138.7 (C (Ar)); 135.6 (C (Ar)); 130.8 (C(6)); 129.3 (2 CH (Ar)); 126.0 (2 CH, (Ar)); 114.1 (CN); 113.6 (C(5)); 78.7 (C(2)); 61.6 (Me*C*H_2O); 39.0 (C(4)); 31.7 (C(3)); 21.1 (*Me*–C(4′)); 14.1 (*Me*CH_2O). EI-MS: 272 (4, $[M+H]^+$), 271 (6, M^+), 226(3), 225(3), 199(16), 198(25), 197(12), 128(10), 119(16), 118(100), 105(7), 91(15), 77(8), 65(7), 51(5).

Data of t-**10b** (from *c*/*t*-**10b** 75:25): ^{1}H-NMR ($CDCl_3$): 7.29–7.18 (*m*, C_6H_4); 5.89 (*dd*, *J* = 5.4, 1.4, H–C(5)); 4.96 (*dd*, *J* = 11.0, 2.0, H_β–C(2)); 4.24 (*q*, *J* = 7.1, MeCH_2O); 3.26 (*ddd*, *J* = 6.0, 5.4, 2.2, H_α–C(4)); 2.52 (*dddd*, *J* = 14.2, 2.2, 2.0, 1.4, H_β–C(3)); 2.39 (*s*, Me–C(4′)); 1.98 (*ddd*, *J* = 14.1, 11.0, 6.0, H_α–C(3)); 1.33 (*t*, *J* = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 170.9 (C=O); 138.1 (C (Ar)); 135.8 (C (Ar)); 130.7 (C(6)); 129.1 (2 CH (Ar)); 125.7 (2 CH (Ar)); 114.1 (CN); 112.7 (C(5)); 76.7 (C(2)); 61.4 (Me*C*H_2O); 36.7 (C(4)); 30.0 (C(3)); 20.9 (*Me*–C(4′)); 13.9 (*Me*CH_2O).

*3,4-Dihydro-2-(4-methoxyphenyl)-2*H*-pyran-6-carbonitrile* (**8c**). Oil. IR (neat): 3065*m*, 2225*s*, 1640v*s*, 1610v*s*, 1583*s*, 1514*s*, 1460*s*, 1370*m*, 1293v*s*, 1245v*s*, 1175v*s*, 1142v*s*, 1078v*s*, 1028v*s*, 955*s*, 925*m*, 870*m*, 825v*s*, 785*s*, 760*s*. ^{1}H-NMR ($CDCl_3$): 7.28 (*m*, 2 H (Ar)); 6.93 (*m*, 2 H (Ar)); 5.76 (*dddd*, *J* = 5.2, 3.0, 1.0, 1.4, H–C(5)); 4.85 (*dd*, *J* = 10.3, 2.4, H_α–C(2)); 3.82 (*s*, MeO); 2.38 (*dddd*, *J* = 19.3, 10.7, 6.6, 3.0, H_α–C(4)); 2.24 (*dddd*, *J* = 19.3, 5.8, 5.2, 2.4, H_β–C(4)); 2.13 (*ddtd*, *J* = 14.0, 6.6, 2.4, 1.0, H_α–C(4)); 1.98 (*dddd*, *J* = 14.0, 10.7, 10.3, 5.8, H_β–C(4)). ^{13}C-NMR ($CDCl_3$): 158.9 (C(4′)); 131.2 (C(1′)); 129.0 (C(6)); 126.8 (CH(3′), CH(5′)); 116.7 (C(5)); 114.4 (CN); 113.2 (CH(2′), CH(6′)); 77.8 (C(2)); 54.4 (MeO); 27.6 (C(3)); 20.9 (C(4)). EI-MS: 216 (17, $[M+H]^+$), 215 (15, M^+), 187(1), 161(2), 159(3), 135(14), 134(100), 119(22), 115(4), 103(3), 102(2), 92(6), 91(28), 89(6), 78(6), 77(16), 65(17), 64(5), 63(10), 55(5), 51(11).

*3,4-Dihydro-2-(4-methoxyphenyl)-4-methyl-2*H*-pyran-6-carbonitrile* (**9c**). FC (AcOEt/hexane 1:10) gave **9c** (0.79 g, 69%); *cis*/*trans* 97:3. M.p. 47.6–49.1°. IR (neat): 3060*m*, 2228*s*, 1637v*s*, 1612v*s*, 1585*m*, 1515v*s*, 1457*s*, 1285v*s*, 1248v*s*, 1178v*s*, 1150v*s*, 1058v*s*, 1035v*s*, 983*s*, 870*m*, 827v*s*, 810*s*, 765*m*. ^{1}H-NMR ($CDCl_3$): 7.28 (*m*, 2 H (Ar)); 6.91 (*m*, 2 H (Ar)); 5.59 (*dd*, *J* = 2.2, 1.6, H–C(5)); 4.87 (*dd*, *J* = 11.5, 1.9, H_α–C(2)); 3.83 (*s*, MeO); 2.67 (*m*, *J* = 11.0, 7.0, 6.1, 2.2, H_α–C(4)); 2.13 (*dddd*, *J* = 14.0, 6.1, 1.9, 1.6, H_α–C(3)); 1.64 (*ddd*, *J* = 14.0, 11.5, 11.0, H_β–C(3)); 1.12 (*d*, *J* = 7.0, *Me*–C(4)). ^{13}C-NMR ($CDCl_3$): *c*-**9c**: 159.6 (C(4′)); 131.5 (C(1′)); 129.1 (C(6)); 127.4 (CH(3′), CH(5′)); 122.4 (C(5)); 114.7 (CN); 113.8 (CH(2′), CH(6′)); 79.1 (C(2)); 55.2 (MeO); 37.9 (C(3)); 28.5 (C(4)); 19.9 (*Me*–C(4)); *t*-**9c**: 74.9 (C(2)); 35.3 (C(3)); 25.8 (C(4)); 21.3 (*Me*–C(4)). EI-MS: 230 (5, $[M+H]^+$), 229 (5, M^+), 134(100), 119(16), 103(3), 91(21), 89(4), 77(21), 65(12), 51(6).

*Ethyl 6-Cyano-3,4-dihydro-2-(4-methoxyphenyl)-2*H*-pyran-4-carboxylate* (**10c**). Crude product: *cis*/*trans* >98: <2; after FC (AcOEt/hexane 1:8) and crystallization: 1.28 g (89%), *cis*/*trans* 39:61. *c*/*t*-**10c** >98: <2: M.p. 41.3–43.2°. IR (KBr): 3075*m*, 2230*s*, 1730v*s*, 1640v*s*, 1610v*s*, 1585*m*, 1460*s*, 1365*s*, 1295v*s*, 1250v*s*, 1175v*s*, 1145v*s*, 1030v*s*, 965*s*, 830v*s*, 760*s*. ^{1}H-NMR ($CDCl_3$): *c*-**10c**: 7.29 (*m*, 2 H (Ar)); 6.92 (*m*, 2 H (Ar)); 5.89 (*dd*, *J* = 2.3, 1.5, H–C(5)); 4.94 (*dd*, *J* = 11.5, 2.0, H_α–C(2)); 4.20 (*q*, *J* = 7.1, MeCH_2O); 3.83 (*s*, MeO); 3.54 (*ddd*, *J* = 11.5, 6.4, 2.3, H_α–C(4)); 2.41 (*dddd*, *J* = 14.2, 6.2, 2.0, 1.5, H_α–C(3)); 2.19 (*dt*, *J* = 14.2, 11.5, H_β–C(3)); 1.29 (*t*, *J* = 7.1, *Me*CH_2O); *t*-**10c**: 7.29 (*m*, 2 H (Ar)); 6.92 (*m*, 2 H (Ar)); 5.89 (*dd*, *J* = 5.5, 1.5, H–C(5)); 4.93 (*dd*, *J* = 11.0, 2.2, H_β–C(2)); 4.23 (*q*, *J* = 7.1, Me*C*H_2O); 3.83 (*s*, MeO); 3.27 (*ddd*, *J* = 6.0, 5.5, 2.0, H_α–C(4)); 2.47 (*dddd*, *J* = 14.2, 2.2, 2.0, 1.5, H_β–C(3)); 1.99 (*ddd*, *J* = 14.2, 11.0, 6.0, H_α–C(3)); 1.32 (*t*, *J* = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): *c*-**10c**: 170.1 (C=O); 159.4 (C(4′)); 130.3 (C(1′)); 130.0 (C(6)); 127.1 (CH(3′), CH(5′)); 113.8 (CN); 113.5 (CH(2′), CH(6′)); 113.45 (C(5)); 78.1 (C(2)); 61.0 (Me*C*H_2O); 54.7 (MeO); 38.4 (C(4)); 31.0 (C(3)); 13.6 (*Me*CH_2O). *t*-**10c**: 171.0 (C=O); 159.8 (C(4′)); 130.8 (C(1′)); 130.5 (C(6)); 127.3 (C(3′),

C(5′)); 114.1 (CN); 113.9 (C(2′), C(6′)); 112.6 (C(5)); 76.6 (C(2)); 61.5 (Me*C*H$_2$O); 55.2 (MeO); 36.9 (C(4)); 29.9 (C(3)); 14.0 (*Me*CH$_2$O). EI-MS: 288 (2, $[M+H]^+$), 287 (3, M^+), 242(3), 241(4), 215(8), 213(6), 134(100), 119(9), 103(2), 91(14), 77(9), 65(7), 51(5).

*3,4-Dihydro-2-(4-methoxyphenyl)-4-phenyl-2*H*-pyran-6-carbonitrile* (**11c**). FC (AcOEt/hexane 1:6) gave an oil (1.20 g, 82%); *cis*/*trans* 95:5. IR (neat): 3060*s*, 3030*s*, 2840*s*, 2230*s*, 1637v*s*, 1610v*s*, 1585*s*, 1513v*s*, 1492*s*, 1450*s*, 1350*s*, 1300v*s*, 1260*s*, 1250v*s*, 1175v*s*, 1140v*s*, 1030v*s*, 935*s*, 830v*s*, 760v*s*, 700v*s*. ^{1}H-NMR ($CDCl_3$): *c*-**11c**: 7.39–7.17 (*m*, 7 H (Ph, Ar)); 6.92–6.85 (*m*, 2 H (Ar)); 5.80 (*dd*, *J* = 2.4, 1.6, H–C(5)); 5.06 (*dd*, *J* = 11.4, 1.8, H$_\alpha$–C(2)); 3.82 (*ddd*, *J* = 11.4, 6.3, 2.4, H$_\alpha$–C(4)); 3.80 (*s*, MeO); 2.36 (*dddd*, *J* = 14.0, 6.3, 1.8, 1.6, H$_\alpha$–C(3)); 2.01 (*dt*, *J* = 14.0, 11.4, H$_\beta$–C(3)); *t*-**11c**: 5.85 (*dd*, *J* = 5.0, 1.7, H–C(5)); 4.84 (*dd*, *J* = 11.0, 2.0, H–C(2)). ^{13}C-NMR ($CDCl_3$): *c*-**11c**: 159.3 (C (Ar)); 141.5 (C (Ph)); 130.7 (C (Ar)); 129.9 (C(6)); 128.5 (2 CH (Ph)); 127.2 (2 CH (Ar)); 126.8 (CH (Ph)); 126.6 (2 CH (Ph)); 119.7 (C(5)); 114.4 (CN); 113.5 (2 CH (Ar)); 78.9 (C(2)); 54.7 (MeO); 39.2 (C(4)); 38.2 (C(3)); *t*-**11c**: 74.3 (C(2)). CI-MS: 291 (3, M^+), 135 (16), 134 (100), 119(11), 105(2), 104(4), 103(6), 102(6), 101(3), 91(26), 77(14).

*3,4-Dihydro-2-(4-methoxyphenyl)-4,5-dimethyl-2*H*-pyran-6-carbonitrile* (**12c**). FC (AcOEt/hexane 1:6) gave a crystalline product (0.89 g, 73%); *cis*/*trans* 96:4. M.p. 94.9–96.8°. IR (KBr): 3070*m*, 2220*s*, 1633v*s*, 1612v*s*, 1583*m*, 1510v*s*, 1453*s*, 1440*s*, 1380*m*, 1365*m*, 1248v*s*, 1173v*s*, 1110v*s*, 1030v*s*, 975*m*, 885*m*, 828v*s*. ^{1}H-NMR ($CDCl_3$): *c*-**12c**: 7.28 (*m*, 2 H (Ar)); 6.90 (*m*, 2 H (Ar)); 4.78 (*dd*, *J* = 11.5, 1.8, H$_\alpha$–C(2)); 3.83 (*s*, MeO); 2.53 (*m*, *J* = 11.0, 7.0, 6.3, 1.3, H$_\alpha$–C(4)); 2.16 (*ddd*, *J* = 14.0, 6.3, 1.8, H$_\alpha$–C(3)); 1.92 (*d*, *J* = 1.3, Me–C(5)); 1.72 (*ddd*, *J* = 14.0, 11.5, 11.0, H$_\beta$–C(3)); 1.12 (*d*, *J* = 7.0, Me–C(4)); *t*-**12c**: 4.87 (*dd*, *J* = 11.5, 1.8, H–C(2)); 1.23 (*d*, *J* = 7.0, Me–C(4)). ^{13}C-NMR ($CDCl_3$): *c*-**12c**: 159.5 (C (Ar)); 131.9 (C (Ar)); 130.1 (C(6)); 127.3 (2 CH (Ar)); 125.6 (C(5)); 114.4 (CN); 113.8 (2 CH (Ar)); 78.2 (C(2)); 55.2 (MeO); 39.2 (C(3)); 32.3 (C(4)); 18.0 (*Me*–C(4)); 16.2 (*Me*–C(5)); *t*-**12c**: 73.8 (C(2)). EI-MS: 244 (2, $[M+H]^+$), 243 (2, M^+), 134(100), 119(13), 103(3), 91(17), 77(9), 65(10), 51(4).

*5-Bromo-3,4-dihydro-2-(4-methoxyphenyl)-4-methyl-2*H*-pyran-6-carbonitrile* (**13c**). FC (AcOEt/hexane 1:6) gave an oil (0.88 g, 57%); *cis*/*trans* 98:2. IR (neat): 3070*m*, 2228*s*, 1610v*s*, 1585*m*, 1513v*s*, 1453*s*, 1370*m*, 1300*s*, 1240v*s*, 1172v*s*, 1035v*s*, 1000v*s*, 930*s*, 870*s*, 827v*s*, 770*m*. ^{1}H-NMR ($CDCl_3$): *c*-**13c**: 7.27 (*m*, 2 H (Ar)); 6.91 (*m*, 2 H (Ar)); 4.94 (*dd*, *J* = 11.7, 1.7, H$_\alpha$–C(2)); 3.83 (*s*, MeO); 2.85 (*m*, *J* = 11.0, 7.0, 6.4, H$_\alpha$–C(4)); 2.33 (*ddd*, *J* = 14.2, 6.4, 1.7, H$_\alpha$–C(3)); 1.94 (*ddd*, *J* = 14.2, 11.7, 11.0, H$_\beta$–C(3)); 1.27 (*d*, *J* = 7.0, Me–C(4)); *t*-**13c**: 1.37 (*d*, *J* = 7.0, Me–C(4)). ^{13}C-NMR ($CDCl_3$): *c*-**13c**: 159.5 (C (Ar)); 130.1 (C (Ar)); 129.2 (C(6)); 127.3 (2 CH (Ar)); 121.3 (C(5)); 113.6 (2 CH (Ar)); 113.5 (CN), 79.1 (C(2)); 54.9 (MeO); 39.1 (C(3)); 34.8 (C(4)); 19.6 (*Me*–C(4)); *t*-**13c**: 74.6 (C(2)). EI-MS: 310/308 (0.5/0.5, $[M+H]^+$), 309/307 (1/1, M^+), 134(100), 119(15), 91(16), 77(9), 65(10), 51(5).

*2-[4-(Acetyloxy)phenyl]-3,4-dihydro-2*H*-pyran-6-carbonitrile* (**8d**). M.p. 119.1–119.7°. IR (KBr): 2220*s*, 1740v*s*, 1630*s*, 1505*s*, 1360*s*, 1285*s*, 1218v*s*, 1190v*s*, 1140v*s*, 1015v*s*, 964*s*, 910v*s*, 852*s*, 790*s*. ^{1}H-NMR ($CDCl_3$): 7.36 (*m*, 2 H (Ar)); 7.12 (*m*, 2 H (Ar)); 5.78 (*ddd*, *J* = 5.2, 3.2, 1.1, H–C(5)); 4.92 (*dd*, *J* = 10.3, 2.3, H$_\alpha$–C(2)); 2.40 (*dddd*, *J* = 19.0, 10.3, 6.4, 3.2, H$_\alpha$–C(4)); 2.31 (*s*, MeCO); 2.26 (*dddd*, *J* = 19.0, 6.0, 5.2, 2.7, H$_\beta$–C(4)); 2.14 (*ddddd*, *J* = 14.0, 6.4, 2.7, 2.3, 1.1, H$_\alpha$–C(3)); 1.96 (*dtd*, *J* = 14.0, 10.3, 6.0, H$_\beta$–C(3)). ^{13}C-NMR ($CDCl_3$): 169.2 (Me*C*O); 150.3 (C (Ar)); 137.1 (C (Ar)); 129.5 (C(6)); 126.8 (2 CH (Ar)); 121.6 (2 CH (Ar)); 116.9 (C(5)); 114.6 (CN); 77.9 (C(2)); 28.4 (C(3)); 21.2 (C(4)); 20.9 (*Me*CO). CI-MS: 261 (100, $[M+NH_4]^+$), 244 (1, $[M+H]^+$), 243 (3, M^+), 201(4), 188(7), 162(4), 121(5), 120(53), 91(7).

*2-[(4-Acetyloxy)phenyl]-3,4-dihydro-4-methyl-2*H*-pyran-6-carbonitrile* (**9d**). FC (AcOEt/hexane 1:4; R_f 0.33) gave an oil (0.95 g, 78%); *cis*/*trans* 92:8. IR (neat): 3060*m*, 2225*s*, 1750v*s*, 1630v*s*, 1605*s*, 1500v*s*, 1445*s*, 1365v*s*, 1325*s*, 1280v*s*, 1215v*s*, 1190v*s*, 1160v*s*, 1055*s*, 1010*s*, 980*s*, 905v*s*, 843*s*. ^{1}H-NMR ($CDCl_3$): *c*-**9d**: 7.36 (*m*, 2 H (Ar)); 7.11 (*m*, 2 H (Ar)); 5.61 (*dd*, *J* = 2.2, 1.8, H–C(5)); 4.93 (*dd*, *J* = 11.3, 1.8, H$_\alpha$–C(2)); 2.69 (*m*, *J* = 11.3, 7.0, 6.2, 2.2, H$_\alpha$–C(4)); 2.33 (*s*, MeCO); 2.17 (*ddt*, *J* = 14.0, 6.2, 1.8, H$_\alpha$–C(3)); 1.60 (*dt*, *J* = 14.0, 11.3, H$_\beta$–C(3)); 1.12 (*d*, *J* = 7.0, Me–C(4)); t-**9d**: 7.36 (*m*, 2 H (Ar)); 7.11 (*m*, 2 H (Ar)); 5.74 (*dd*, *J* = 4.5, 1.3, H–C(5)); 4.93 (*dd*, *J* = 10.0, 2.5, H$_\beta$–C(2)); 2.44 (*m*, *J* = 7.0, 6.0, 4.5, 3.0, H$_\alpha$–C(2)); 2.37 (*s*, MeCO); 2.08 (*ddd*, *J* = 14.1, 10.0, 6.0, H$_\alpha$–C(3)); 1.81 (*dddd*, *J* = 14.1, 3.0, 2.5, 1.3, H$_\beta$–C(3)); 1.19 (*d*, *J* = 7.0, Me–C(4)). ^{13}C-NMR ($CDCl_3$): *c*-**9d**: 169.3 (Me*C*O); 150.3 (C (Ar)); 137.0 (C (Ar)); 128.8 (C(6)); 126.9 (2 CH (Ar)); 122.6 (C(5)); 121.6 (2 CH (Ar)); 114.5 (CN); 78.6 (C(2)); 39.0 (C(3)); 28.2 (C(4)); 20.9 (*Me*CO); 19.7 (*Me*–C(4)); *t*-**9d**: 169.4 (Me*C*O); 150.4 (C (Ar)); 137.2 (C (Ar)); 128.9 (C(6)); 126.9 (2 CH (Ar)); 122.3 (C(5)); 121.7 (2 CH (Ar)); 114.7 (CN); 74.4 (C(2)); 35.8 (C(3)); 25.7 (C(4)); 21.4 (*Me*CO); 19.9 (*Me*–C(4)). CI-MS: 257 (15, M^+), 231(31), 213(17), 207(27), 202(18), 187(4), 162(1), 161(13), 155(9), 149(21), 136(5), 126(10), 122(32), 120(100), 113(7), 111(5), 107(9), 104(14), 102(7), 88(11), 84(14), 81(28), 79(14), 70(16).

*Ethyl 2-[4-(Acetyloxy)phenyl]-6-cyano-3,4-dihydro-2*H*-pyran-4-carboxylate* (**10d**). Residual starting materials were distilled off (100°/0.02 Torr) to leave pure *c*-**10d** (1.35 g, 86%). IR (neat): 3060*m*, 2228*s*, 1755*vs*, 1725*vs*, 1635*s*, 1500*s*, 1363*vs*, 1290*vs*, 1245*vs*, 1215*vs*, 1185*vs*, 1160*vs*, 1145*vs*, 1040*vs*, 1015*vs*, 970*s*, 940*s*, 905*vs*, 853*s*, 760*s*. ^{1}H-NMR ($CDCl_3$): 7.38 (*m*, 2 H (Ar)); 7.12 (*m*, 2 H (Ar)); 5.91 (*dd*, *J* = 2.5, 1.7, H–C(5)); 4.99 (*dd*, *J* = 11.4, 2.0, H_α–C(2)); 4.19 (*q*, *J* = 7.1, MeCH_2O); 3.55 (*ddd*, *J* = 11.4, 6.3, 2.5, H_α–C(4)); 2.44 (*dddd*, *J* = 14.1, 6.3, 2.0, 1.7, H_α–C(3)); 2.32 (*s*, MeCO); 2.15 (*dt*, *J* = 14.1, 11.4, H_β–C(3)); 1.28 (*t*, *J* = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 170.1 (*C*OOEt); 169.0 (Me*C*O); 150.4 (C (Ar)); 135.8 (C (Ar)); 130.0 (C(6)); 126.8 (2 CH (Ar)); 121.5 (2 CH (Ar)); 113.8 (CN); 113.8 (C(5)); 77.7 (C(2)); 61.3 (Me*C*H_2O); 38.4 (C(4)); 31.3 (C(4)); 20.7 (*Me*CO); 13.7 (*Me*CH_2O). CI-MS: 333 (100, $[M+NH_4]^+$), 316 (3, $[M+H]^+$), 315 (19, M^+), 273 (10), 227 (4), 200 (4), 162 (2), 120 (59), 91 (5).

*2-[4-(Acetylamino)phenyl]-3,4-dihydro-2*H*-pyran-6-carbonitrile* (= N-*[4-(6-Cyano-3,4-dihydro-2*H*-pyran-2-yl)phenyl]acetamide*; **8h**). M.p. 163.5–164.0°. R_f 0.56 (AcOEt). IR (KBr): 3300*s*, 3250*s*, 3190*s*, 3060*s*, 2215*s*, 1665*vs*, 1638*s*, 1600*vs*, 1545*vs*, 1530*vs*, 1510*vs*, 1410*vs*, 1365*s*, 1315*vs*, 1290*s*, 1260*s*, 1230*s*, 1140*vs*, 1025*vs*, 960*s*, 830*vs*, 775*s*. ^{1}H-NMR ($CDCl_3$): 7.52 (*m*, 2 H (Ar)); 7.41 (br., NH); 7.29 (*m*, 2 H (Ar)); 5.77 (*ddd*, *J* = 5.0, 3.2, 1.0, H–C(5)); 4.88 (*dd*, *J* = 10.3, 2.4, H_α–C(2)); 2.38 (*dddd*, *J* = 19.0, 10.3, 6.4, 3.2, H_α–C(4)); 2.23 (*dddd*, *J* = 19.0, 5.8, 5.0, 2.8, H_β–C(4)); 2.19 (*s*, *Me*CONH); 2.11 (*ddddd*, *J* = 14.0, 6.4, 2.8, 2.4, 1.0, H_β–C(3)); 1.95 (*dtd*, *J* = 14.0, 10.3, 5.8, H_α–C(3)). ^{13}C-NMR ($CDCl_3$): 169.0 (Me*C*ONH); 138.0 (C (Ar)); 135.2 (C (Ar)); 129.6 (C(6)); 126.4 (2 CH (Ar)); 120.0 (2 CH (Ar)); 117.1 (C(5)); 114.8 (CN); 78.2 (C(2)); 28.3 (C(3)); 24.3 (*Me*CONH); 21.3 (C(4)). CI-MS: 260 (1, $[M+NH_4]^+$), 243 (50, $[M+H]^+$), 242 (17, M^+), 214 (4), 187 (11), 162 (9), 161 (44), 144 (1), 120 (14), 119 (100), 118 (14), 117 (4), 106 (2), 104 (3), 91 (21), 78 (4).

*2-[4-(Acetylamino)phenyl]-3,4-dihydro-4-methyl-2*H*-pyran-6-carbonitrile* (= N-*[4-(6-Cyano-3,4-dihydro-4-methyl-2*H*-pyran-2-yl)phenyl]acetamide;* **9h**). FC (AcOEt/hexane 1:4) gave a crystalline product (0.83 g, 65%); *cis*/*trans* 94:6. M.p. 122.4–123.8°. R_f 0.41 (AcOEt/hexane 1:2). IR (KBr): 3230*vs*, 3170*s*, 3100*s*, 3070*m*, 2220*s*, 1655*vs*, 1630*vs*, 1590*s*, 1525*vs*, 1510*vs*, 1405*vs*, 1367*vs*, 1305*vs*, 1263*s*, 1150*s*, 1060*vs*, 1035*s*, 985*s*, 965*s*, 905*s*, 880*s*, 820*vs*, 740*s*. ^{1}H-NMR ($CDCl_3$): c-**9h**: 7.52 (*m*, 2 H (Ar)); 7.32 (br., NH); 7.30 (*m*, Ar); 5.60 (*dd*, *J* = 2.3, 1.7, H–C(5)); 4.90 (*dd*, *J* = 11.3, 2.0, H_α–C(2)); 2.68 (*m*, *J* = 11.3, 7.0, 6.0, 2.3, H_α–C(4)); 2.19 (*s*, *Me*CONH); 2.14 (*dddd*, *J* = 14.0, 6.0, 2.0, 1.7, H_α–C(3)); 1.60 (*dt*, *J* = 14.0, 11.3, H_β–C(3)); 1.12 (*d*, *J* = 7.0, Me–C(4)); *t*-**9h**: 5.73 (*dd*, *J* = 4.8, 1.2, H–C(5)); 1.18 (*d*, *J* = 7.0, Me–C(4)). ^{13}C-NMR ($CDCl_3$): *c*-**9h**: 169.0 (Me*C*ONH); 138.1 (C (Ar)); 135.1 (C (Ar)); 128.8 (C(6)); 126.5 (2 CH (Ar)); 122.8 (C(5)); 120.0 (2 CH (Ar)); 114.8 (CN); 78.9 (C(2)); 37.9 (C(3)); 24.2 (*Me*CONH); 28.4 (C(4)); 19.8 (*Me*–C(4)); *t*-**9h**: 74.8 (C(2)); 35.5 (C(3)); 25.7 (C(4)); 21.3 (NHCO*Me*); 17.9 (*Me*–C(4)). CI-MS: 274 (3, $[M+NH_4]^+$), 257 (49, $[M+H]^+$), 256 (19, M^+), 235 (1), 201 (5), 162 (16), 161 (100), 136 (2), 120 (19), 119 (100), 118 (17), 106 (8), 91 (15), 87 (3).

*Ethyl 2-[4-(Acetylamino)phenyl]-6-cyano-3,4-dihydro-2*H*-pyran-4-carboxylate* (**10h**). FC (AcOEt/hexane 1:2) gave a product with *cis*/*trans* 2:1. IR (KBr): 3280*s*, 3240*s*, 3180*s*, 3110*s*, 3060*s*, 2225*s*, 1725*vs*, 1660*vs*, 1640*s*, 1600*vs*, 1545*vs*, 1530*vs*, 1510*vs*, 1410*s*, 1365*s*, 1315*s*, 1265*s*, 1245*s*, 1180*vs*, 1145*s*, 1045*s*, 1015*vs*, 833*vs*, 760*s*. CI-MS: 332 (12, $[M+NH_4]^+$), 315 (49, $[M+H]^+$), 314 (21, M^+), 288 (6), 287 (7), 286 (6), 260 (7), 259 (28), 241 (4), 214 (13), 198 (5), 186 (3), 162 (17), 161 (67), 144 (3), 120 (20), 119 (100), 118 (10), 106 (8), 91 (19), 89 (5), 80 (12), 79 (15), 77 (6).

Data of Pure c-**10h**: Crystalline *c*-**10h** was obtained on treatment of the crude product with hexane/Et_2O. M.p. 122.8–124.0°. ^{1}H-NMR ($CDCl_3$): 7.54 (*m*, 2 H (Ar)); 7.52 (br., NH); 7.30 (*m*, 2 H (Ar)); 5.90 (*dd*, *J* = 2.4, 2.0, H–C(5)); 4.96 (*dd*, *J* = 11.3, 1.7, H_α–C(2)); 4.19 (*q*, *J* = 7.1, MeCH_2O); 3.55 (*ddd*, *J* = 11.3, 6.4, 2.4, H_α–C(4)); 2.42 (*dddd*, *J* = 14.0, 6.4, 2.0, 1.7, H_α–C(3)); 2.19 (*s*, *Me*CONH); 2.15 (*dt*, *J* = 14.0, 11.3, H_β–C(3)); 1.29 (*t*, *J* = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 170.4 (*C*OOEt); 169.1 (Me*C*ONH); 138.5 (C (Ar)); 133.8 (C (Ar)); 130.2 (C(6)); 126.5 (2 CH (Ar)); 119.9 (2 CH (Ar)); 114.0 (CN); 113.8 (C(5)); 78.2 (C(2)); 61.4 (Me*C*H_2O); 38.6 (C(4)); 31.3 (C(4)); 24.0 (*Me*CONH); 13.8 (*Me*CH_2O).

Data of t-**10h** (from *c*/*t*-**10** 2:1): ^{1}H-NMR ($CDCl_3$): 7.58 (br., HN); 7.53 (*m*, 2H (Ar)); 7.29 (*m*, 2 H (Ar)); 5.90 (*dd*, *J* = 5.5, 1.6, H–C(5)); 4.94 (*dd*, *J* = 11.0, 2.3, H_β–C(2)); 4.23 (*q*, *J* = 7.1, MeCH_2O); 3.26 (*ddd*, *J* = 6.0, 5.5, 1.6, H_α–C(4)); 2.46 (*dddd*, *J* = 14.1, 2.3, 2.0, 1.6, H_β–C(3)); 2.19 (*s*, *Me*CONH); 1.95 (*ddd*, *J* = 14.1, 11.0, 6.0, H_α–C(3)); 1.32 (*t*, *J* = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 170.9 (*C*OOEt); 169.1 (Me*C*ONH); 138.3 (C (Ar)); 134.1 (C (Ar)); 130.4 (C(6)); 126.3 (2 CH (Ar)); 119.9 (2 CH (Ar)); 114.1 (CN); 113.0 (C(5)); 76.4 (C(2)); 61.5 (Me*C*H_2O); 36.6 (C(4)); 29.7 (C(4)); 24.0 (*Me*CONH); 13.8 (*Me*CH_2O).

*2-(4-Chlorophenyl)-3,4-dihydro-2*H*-pyran-6-carbonitrile* (**8e**). Oil. IR (neat): 3070*m*, 2230*s*, 1643*vs*, 1598*m*, 1493*vs*, 1442*m*, 1295*vs*, 1288*vs*, 1236*vs*, 1145*vs*, 1090*vs*, 1040*vs*, 955*s*, 932*m*, 875*m*, 820*s*, 778*s*. ^{1}H-NMR ($CDCl_3$): 7.36 (*m*, 2 H (Ar)); 7.28 (*m*, 2 H (Ar)); 5.77 (*ddd*, *J* = 5.1, 3.2, 1.1, H–C(5)); 4.89 (*dd*, *J* = 10.3, 2.5, H_α–C(2)); 2.38 (*dddd*, *J* = 19.1, 10.3, 6.5, 3.2, H_α–C(4)); 2.23 (*dddd*, *J* = 19.1, 5.9, 5.1, 2.5, H_β–C(4)); 2.12 (*ddtd*, *J* = 14.0, 6.5, 2.5, 1.1, H_α–C(3)); 1.93 (*dtd*, *J* = 14.0, 10.3, 5.9, H_β–C(3)). ^{13}C-NMR ($CDCl_3$): 138.1 (C (Ar)); 133.8 (C

(Ar)); 129.4 (C(6)); 128.5 (2 CH (Ar)); 127.1 (2 CH (Ar)); 117.0 (C(5)); 114.5 (CN); 77.7 (C(2)); 28.4 (C(3)); 21.1 (C(4)). EI-MS: 221/219 (2/5, M^+), 140/138 (34/100), 103 (37), 102 (9), 77 (18).

*2-(4-Chlorophenyl)-3,4-dihydro-4-methyl-2*H*-pyran-6-carbonitrile* (**9e**). FC (AcOEt/hexane 1:8) gave a crystalline product (1.02 g, 87%); *cis*/*trans* 92:8. M.p. 90.7–91.2°. IR (KBr): 3060*m*, 2230*s*, 1638v*s*, 1598*m*, 1492*s*, 1453*s*, 1380*s*, 1286v*s*, 1152v*s*, 1088v*s*, 1060v*s*, 986*s*, 910*s*, 878*s*, 820v*s*. ^{1}H-NMR ($CDCl_3$): *c*-**9e**: 7.37 (*m*, 2 H (Ar)); 7.28 (*m*, 2 H (Ar)); 5.61 (*dd*, J = 2.5, 1.6, H–C(5)); 4.90 (*dd*, J = 11.5, 1.8, H_α–C(2)); 2.68 (*m*, J = 11.0, 7.0, 6.3, 2.5, H_α–C(4)); 2.16 (*dddd*, J = 14.0, 6.3, 1.8, 1.6, H_α–C(3)); 1.58 (*ddd*, J = 14.0, 11.5, 11.0, H_β–C(3)); 1.12 (*d*, J = 7.0, Me–C(4)); *t*-**9e**: 5.74 (*dd*, J = 4.7, 1.3, H–C(5)); 1.19 (*d*, J = 7.0, Me–C(4)). ^{13}C-NMR ($CDCl_3$): *c*-**9e**: 137.9 (C (Ar)); 133.6 (C (Ar)); 128.5 (C(6)); 128.3 (2 CH (Ar)); 127.1 (2 CH (Ar)); 122.6 (C(5)); 114.4 (CN); 78.2 (C(2)); 37.7 (C(3)); 28.0 (C(4)); 19.5 (*Me*–C(4)); *t*-**9e**: 74.2 (C(2)); 35.4 (C(3)); 25.4 (C(4)); 21.0 (*Me*–C(4)). EI-MS: 235/233 (1/4, M^+), 197 (3), 140/138 (32/100), 128 (5), 125 (6), 119 (13), 103 (27), 102 (7), 77 (12), 51 (7).

*Ethyl 2-(4-Chlorophenyl)-6-cyano-3,4-dihydro-2*H*-pyran-4-carboxylate* (**10e**). The crude product was pure *c*-**10e**. FC (AcOEt/hexane 1:8) gave a mixture (1.17 g, 80%); *cis*/*trans* 1:1. IR (KBr): 3080*m*, 2232*s*, 1733v*s*, 1642v*s*, 1600*m*, 1492v*s*, 1445*m*, 1370*s*, 1300v*s*, 1250v*s*, 1185v*s*, 1150v*s*, 1090v*s*, 1055v*s*, 1015v*s*, 965*s*, 950*s*, 825v*s*, 770*m*.

Data of Pure c-**10e**. ^{1}H-NMR ($CDCl_3$): 7.41–7.28 (*m*, 4 H (Ar)); 5.92 (*dd*, J = 2.5, 1.5, H–C(5)); 4.97 (*dd*, J = 11.3, 2.1 H_α–C(2)); 4.19 (*q*, J = 7.1, MeCH_2O); 3.55 (*ddd*, J = 11.3, 6.3, 2.5, H_α–C(4)); 2.42 (*dddd*, J = 14.1, 6.3, 2.1, 1.5, H_α–C(3)); 2.13 (*dt*, J = 14.1, 11.3, H_β–C(3)); 1.28 (*t*, J = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 169.9 (*C*OO); 136.9 (C (Ar)); 133.8 (C (Ar)); 130.0 (C(6)); 128.4 (2 CH (Ar)); 127.0 (2 CH (Ar)); 112.9 (C(5)); 113.7 (CN); 77.6 (C(2)); 61.2 (Me*C*H_2O); 38.4 (C(4)); 31.3 (C(3)); 13.7 (*Me*CH_2O). EI-MS: 294/292 (4.7/13.2, $[M+H]^+$), 293/291 (10/25, M^+), 221/219 (11/34), 220/218 (20/47), 140/138 (35/100), 128 (12), 127 (12), 125 (11), 113 (2), 111 (5), 103 (15), 89 (7), 77 (16).

Data of t-**10e** (from *c*/*t*-**10e** 1:1): 7.41–7.28 (*m*, 4 H (Ar)); 5.91 (*dd*, J = 5.5, 1.4, H–C(5)); 4.96 (*dd*, J = 11.0, 2.1, H_β–C(2)); 4.24 (*q*, J = 7.1, MeCH_2O); 3.26 (*ddd*, J = 6.0, 5.5, 2.0, H_α–C(4)); 2.48 (*dddd*, J = 14.3, 2.1, 2.0, 1.4, H_β–C(3)); 1.91 (*ddd*, J = 14.3, 11.0, 6.0, H_α–C(3)); 1.33 (*t*, J = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 170.5 (*C*OOEt); 137.2 (C (Ar)); 134.0 (C (Ar)); 130.2 (C(6)); 128.4 (2 CH (Ar)); 127.1 (2 CH (Ar)); 113.8 (C(5)); 113.7 (CN); 75.8 (C(2)); 61.4 (Me*C*H_2O); 36.4 (C(4)); 29.8 (C(3)); 13.7 (*Me*CH_2O).

1-Ethenyl-4-nitrobenzene (= p-*Nitrostyrene*; **7f**). To a soln. of 2-(4-nitrophenyl)ethanol (10 g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 43.6 g) in THF (125 ml) at 0°, methanesulfonyl chloride (14.1 g) was added within 30 min (as noted in [24] for *o*-nitrostyrene). The mixture was stirred for 16 h and then filtered, the solid washed with Et_2O (400 ml), and the combined filtrate washed with 5% HCl soln. (2 × 100 ml), H_2O, and brine, dried (Na_2SO_4) and evaporated to give an oil which solidified upon cooling (8.6 g, 96% yield). ^{1}H-NMR ($CDCl_3$): 8.20 (*dt*, (A_2X_2) J = 9, H–C(3), H–C(5)); 7.54 (A_2X_2, H–C(2), H–C(6)); 6.79 (*dd*, J = 18, 11, H–C(1′)); 5.94 (*d*, J = 18, H–C(2′) *trans* to H–C(1′)); 5.51 (*d*, J = 11, H–C(2′) *cis* to H–C(1′)). ^{13}C-NMR ($CDCl_3$): 143.5 (C(1)); 126.5 (C(2), C(6)); 123.5 (C(3), C(5)); 146.7 (C(4)); 134.6 (C(1′)); 118.3 (C(2′)).

4-Ethenylbenzeneamine (= *4-Aminostyrene*; **7g**). A soln. of NH_4Cl (5 g) in H_2O (20 ml) was added to a soln. of **7f** (7.5 g, 0.05 mol) in acetone (75 ml) [25]. The mixture was heated to boiling temp., and Zn powder (10 g) was added in small portions to maintain a moderate reaction. More Zn (5 g) was added and the mixture heated on a water bath under reflux for another 30 min. The soln. was filtered hot and the residue washed twice with acetone. The combined solns. were concentrated to *ca*. 30 ml and extracted with CH_2Cl_2 (2 × 100 ml). The extract was washed with H_2O, dried (Na_2SO_4), and evaporated: **7g** (6.0 g). ^{1}H-NMR ($CDCl_3$): 7.24 (*dt*(A_2X_2), J = 8.5, H–C(2), H–C(6)); 6.65 (A_2X_2, H–C(3), H–C(5)); 6.63 (*dd*, J = 18, 11, H–C(1′)); 5.56 (*dd*, J = 18, 1, H–C(2′) *trans* to H–C(1′)); 5.05 (*dd*, J = 11, 1, H–C(2′) *cis* to H–C(1′)). ^{13}C-NMR ($CDCl_3$): 126.9 (C(4)); 127.0 (C(3), C(5)); 114.6 (C(2), C(6)); 146.2 (C(1)); 136.3 (C(1′)); 109.5 (C(2′)).

N-*(4-Ethenylphenyl)acetamide* (= *4-(Acetylamino)styrene*, **7h**). *p*-Aminostyrene (**7g**; 6 g) in CH_2Cl_2 (40 ml) was added to Ac_2O (6 g) and pyridine (6 g) and left overnight. The soln. was evaporated and the residue treated with Et_2O. The solid was filtered and washed with Et_2O to give **7h** (3 g, 37%). The filtrate was evaporated and the residue purified by FC (hexane/AcOEt 1:1): **7h** (3.9 g, 48%). ^{1}H-NMR ($CDCl_3$): 7.48 (*dt*(A_2X_2), J = 8.5, H–C(2), H–C(6)); 7.37 (*dt*(A_2X_2), H–C(3), H–C(5)); 6.68 (*dd*, J = 18, 11, H–C(1′)); 5.69 (*d*, J = 18, H–C(2′) *trans* to H–C(1′)); 5.20 (*d*, J = 11; H–C(2′) *cis* to H–C(1′)). ^{13}C-NMR ($CDCl_3$): 24.2, 169.0 (AcNH); 133.5 (C(4)); 126.6 (C(3), C(5)); 120.1 (C(2), C(6)); 137.6 (C(1)); 136.0 (C(1′)); 112.9 (C(2′)).

*3,4-Dihydro-2-(4-nitrophenyl)-*2H*-pyran-6-carbonitrile* (**8f**). Oil (0.76 g, 83%). IR (neat): 3110*m*, 3080*m*, 2228*s*, 1640v*s*, 1600v*s*, 1515v*s*, 1345v*s*, 1290v*s*, 1247v*s*, 1145v*s*, 1050v*s*, 1037v*s*, 950*s*, 850v*s*, 820*s*, 780*s*, 747*s*, 697*s*. ^{1}H-NMR ($CDCl_3$): 8.25 (*m*, 2 H (Ar)); 7.53 (*m*, 2 H (Ar)); 5.83 (*ddd*, J = 5.0, 3.2, 1.2, H–C(5)); 5.03 (*dd*, J = 10.5, 2.4, H_α–C(2)); 2.44 (*dddd*, J = 19.3, 10.5, 6.5, 3.2, H_α–C(4)); 2.27 (*dddd*, J = 19.3, 6.0, 5.0, 2.6, H_β–C(4));

2.20 (*ddddd*, J = 14.0, 6.5, 2.6, 2.4, 1.2, H_α–C(3)); 1.93 (*dtd*, J = 14.0, 10.5, 6.0, H_β–C(3)). ^{13}C-NMR ($CDCl_3$): 147.3 (C (Ar)); 146.7 (C(Ar)); 129.0 (C(6)); 126.4 (2 CH (Ar)); 123.5 (2 CH (Ar)); 117.4 (C(5)); 114.3 (CN); 77.1 (C(2)); 28.4 (C(3)); 20.9 (C(4)). CI-MS: 231 (9, $[M+H]^+$), 230 (11, M^+), 213 (2), 204 (6), 203 (56), 176 (9), 174 (5), 149 (21), 129 (10), 128 (13), 119 (53), 116 (9), 115 (14), 104 (9), 103 (48), 102 (24), 92 (8), 91 (62), 90 (10), 89 (17), 78 (19), 77 (100), 76 (19), 74 (13).

*Ethyl 6-Cyano-3,4-dihydro-2-(4-nitrophenyl)-2*H*-pyran-4-carboxylate* (**10f**). The residual starting materials were distilled off (100°/0.02 Torr) to leave pure *c*-**10f** (1.30 g, 86%). FC (AcOEt/hexane 1:8) gave a mixture; *cis*/*trans* 1:2. IR (neat): 3010*m*, 3080*m*, 2230*s*, 1730v*s*, 1640v*s*, 1604v*s*, 1520v*s*, 1347v*s*, 1295v*s*, 1252v*s*, 1220v*s*, 1205v*s*, 1185v*s*, 1150v*s*, 1110v*s*, 1060v*s*, 1030v*s*, 970*s*, 950*s*, 850v*s*, 750*s*, 697*s*. CI-MS: 303 (49, $[M+H^+]$), 302 (100, M^+), 273 (19), 256 (7), 245 (18), 230 (14), 229 (69), 228 (20), 202 (35), 158 (7), 156 (7), 149 (19), 128 (34), 127 (21), 119 (33), 116 (11), 115 (20), 103 (47), 102 (17), 92 (11), 91 (44), 90 (18), 78 (32), 77 (58), 76 (29).

Data of Pure c-**10f**: ^{1}H-NMR ($CDCl_3$): 8.28 (*m*, 2 H (Ar)); 7.57 (*m*, 2 H (Ar)); 5.98 (*dd*, J = 2.5, 1.7, H–C(5)); 5.12 (*dd*, J = 11.3, 2.0, H_α–C(2)); 4.20 (*q*, J = 7.1, MeCH_2O); 3.60 (*ddd*, J = 11.3, 6.3, 2.5, H_α–C(4)); 2.50 (*dddd*, J = 14.2, 6.3, 2.0, 1.7, H_α–C(3)); 2.13 (*dt*, J = 14.2, 11.3, H_β–C(4)); 1.29 (*t*, J = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 169.8 (*C*OOEt); 147.5 (C (Ar)); 145.8 (C (Ar)); 129.8 (C(6)); 126.6 (2 CH (Ar)); 123.7 (2 CH (Ar)); 114.3 (C(5)); 113.6 (CN); 77.2 (C(2)); 61.6 (Me*C*H_2O); 38.4 (C(4)); 31.5 (C(3)); 13.9 (*Me*CH_2O).

Data of t-**10f** (from *c*/*t*-**10f** 1:2): ^{1}H-NMR ($CDCl_3$): 8.28 (*m*, 2 H (Ar)); 7.58 (*m*, 2 H (Ar)); 5.98 (*dd*, J = 5.5, 1.8, H–C(5)); 5.10 (*dd*, J = 11.2, 2.2, H_β–C(2)); 4.26 (*q*, J = 7.1, MeCH_2O); 3.31 (*ddd*, J = 6.0, 5.5, 1.8, H_α–C(4)); 2.55 (*ddt*, J = 14.2, 2.2, 1.8, H_β–C(2)); 1.89 (*ddd*, J = 14.2, 11.2, 6.0, H_α–C(3)); 1.34 (*t*, J = 7.1, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$): 170.6 (*C*OOEt); 145.8 (C (Ar)); 145.5 (C (Ar)); 130.1 (C(6)); 126.5 (2 CH (Ar)); 123.7 (2 CH (Ar)); 113.7 (CN); 113.3 (C(5)); 75.6 (C(2)); 61.7 (Me*C*H_2O); 36.4 (C(4)); 30.1 (C(4)); 13.9 (*Me*CH_2O).

trans-3,4-*Dihydro-3-methyl-2-phenyl-2*H-*pyran-6-carbonitrile* (**15a**; from *trans*-1-phenylprop-1-ene (**14a**; 0.59 g, 5 mmol) and **1** (9 mmol). FC (AcOEt/hexane 1:5) gave **15a**. Colorless oil (0.34 g, 34%). IR (neat): 3070*w*, 3035*w*, 2232*m*, 1645*s*, 1495*m*, 1455*s*, 1380*m*, 1348*m*, 1328*m*, 1288*m*, 1170*s*, 1092*s*, 1035*s*, 1000*s*, 945*m*, 760*s*, 700*s*. ^{1}H-NMR ($CDCl_3$): 7.43–7.28 (*m*, Ph); 5.76 (*dd*, J = 5.3, 2.9, H–C(5)); 4.46 (*d*, J = 9.3, H_α–C(2)); 2.32 (*ddd*, J = 18.1, 5.3, 4.7, H_β–C(4)); 2.05 (*ddqd*, J = 9.9, 9.3, 6.3, 4.7, H_β–C(3)); 1.98 (*ddd*, J = 18.1, 9.9, 2.9, H_α–C(4)); 0.78 (*d*, J = 6.3, *Me*–C(3)). ^{13}C-NMR ($CDCl_3$): 137.9 (C (Ph)); 129.3 (C(6)); 128.3 (2 CH (Ph)); 128.2 (2 CH (Ph)); 126.9 (CH (Ph)); 116.6 (C(5)); 114.5 (CN); 84.6 (C(2)); 31.8 (C(3)); 29.5 (C(4)); 17.1 (*Me*–C(3)). EI-MS: 199 (1, M^+), 145 (3), 143 (8), 129 (2), 128 (5), 127 (2), 119 (11), 118 (100), 117 (67), 115 (19), 105 (7), 103 (6), 91 (17), 77 (9), 65 (4), 51 (7).

trans-*3,4-Dihydro-2-(4-methoxyphenyl)-3-methyl-2*H-*pyran-6-carbonitrile* (**15c**; from *trans*-1-(4-methoxyphenyl)prop-1-ene (**14c**; 0.74 g, 5 mmol) and **1** (9 mmol). FC (AcOEt/hexane 1:4; R_f 0.50) gave **15c** (1.12 g, 98%). M.p. 72.0–72.5°. IR (neat): 3070*w*, 3035*w*, 2230*s*, 1640v*s*, 1610v*s*, 1585*s*, 1515v*s*, 1455*s*, 1380*s*, 1348*s*, 1320v*s*, 1245v*s*, 1170v*s*, 1138v*s*, 1090*s*, 1030v*s*, 1000*s*, 987v*s*, 830v*s*, 790*s*, 760*m*. ^{1}H-NMR ($CDCl_3$): 7.23 (*m*, 2 H (Ar)); 6.92 (*m*, 2 H (Ar)); 5.75 (*dd*, J = 5.4, 2.9, H–C(5)); 4.42 (*d*, J = 9.4, H_α–C(2)); 3.83 (*s*, MeO); 2.33 (*ddd*, J = 18.0, 5.4, 4.5, H_β–C(4)); 2.06 (*ddqd*, J = 10.0, 9.4, 6.5, 4.5, H_β–C(3)); 1.98 (*ddd*, J = 18.1, 10.0, 2.9, H_α–C(4)); 0.77 (*d*, J = 6.5, Me–C(3)). ^{13}C-NMR ($CDCl_3$): 159.5 (C (Ar)); 130.1 (C (Ar)); 129.5 (C(6)); 128.3 (2 CH (Ar)); 116.6 (C(5)); 114.6 (CN); 113.7 (2 CH (Ar)); 84.4 (C(2)); 55.0 (MeO); 31.8 (C(3)); 29.7 (C(4)); 17.2 (*Me*–C(3)). EI-MS: 230 (6, $[M+H]^+$), 229 (12, M^+), 203 (1), 187 (3), 149 (14), 148 (100), 147 (26), 135 (5), 133 (10), 121 (15), 117 (18), 116 (7), 115 (16), 105 (10), 104 (4), 103 (12), 92 (9), 91 (21), 79 (10), 78 (13), 77 (29).

Competition Experiment. Diene A (**1**; *ca*. 0.9 mmol in 3 ml of MeCN) and an equimolar mixture of styrenes B and C (1 mmol each) were left for 24 h at r.t. (20°). In case of styrenes **7e** and **7f**, the mixture was left for 7 d. The solvent was removed *in vacuo* (*ca*. 100 Torr) at 0°, and the residual mixture was analyzed by ^{1}H-NMR integration. Calculated rate quotients and relative rates are compiled in *Table 2*. A plot of log (k_X/k_H) values *vs.* σ_p^+ constants for *p*-substituents (*Fig. 2*) exhibits a linear relationship with a slope ρ of – 1.47 (r = 0.980, s.d. = 0.17).

REFERENCES

[1] J.-C. Zhuo, H. Wyler, K. Schenk, *Helv. Chim. Acta* **1995**, *78*, 151.

[2] L. F. Tietze, G. Kettschau, 'Hetero-*Diels-Alder* Reactions in Organic Chemistry', *Top. Curr. Chem*. **1997**, *189*, 1; D. L. Boger, 'Heterodiene Additions', Chapt. 4.3 in 'Comprehensive Organic Synthesis', Eds. B. M. Trost and Ian Fleming, Pergamon Press, Oxford-New York-Seoul-Tokyo, 1991, Vol. 5, Ed. L. A. Paquette, p. 451; D. L. Boger, S. M. Weinreb, 'Oxabutadienes', Chapt. 7 in 'Hetero-*Diels-Alder* Methodology in

Organic Synthesis', Academic Press, San Diego-New York-Berkely-Boston-London-Sydney-Tokyo-Toronto, 1987, p. 167–213; G. Desimoni, G. Tacconi, *Chem. Rev.* **1975**, *75*, 651.
[3] D. J. Ager, M. B. East, *Tetrahedron* **1993**, *49*, 5683; L. F. Tietze, *J. Heterocycl. Chem.* **1990**, *27*, 45; T. Kametani, S. Hibino, The Synthesis of Natural Heterocyclic Products by Hetero-*Diels-Alder* Cycloaddition Reaction, 'Advances in Heterocyclic Chemistry', Ed. A. R. Katritzky, Academic Press, Orlando-San Diego-New York-Austin-Boston-London-Sydney-Tokyo-Toronto, 1987, Vol. 42, p. 245–333; R. R. Schmidt, *Pure Appl. Chem.* **1987**, *59*, 415; S. J. Danishefsky, M. P. DeNinno, *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 15.
[4] K. Alder and H. T. Rickert, *Chem. Ber.* **1938**, *71*, 379.
[5] C. W. Smith, D. G. Norton, S. A. Ballard, *J. Am. Chem. Soc.* **1951**, *73*, 5273.
[6] M. Buback, W. Tost, T. Hübeck, E. Voss, L. F. Tietze, *Chem. Ber.* **1989**, *122*, 1179; K. Matsumoto, A. Sera, T. Uchida, *Synthesis* **1985**, 1; K. Matsumoto, A. Sera, *ibid*. **1985**, 999; T. Asano, W. J. Le Noble, *Chem. Rev.* **1978**, *78*, 407.
[7] D. Dvorak, Z. Arnold, *Tetrahedron Lett*. **1982**, *23*, 4401.
[8] Z. M. Ismail, H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 859.
[9] A. Sera, M. Ohara, H. Yamada, E. Egashira, N. Ueda, J. Setsune, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1912.
[10] a) G. Dujardin, M. Maudet, E. Brown, *Tetrahedron Lett*. **1997**, *38*, 1555; b) P. Hayes, G. Dujardin, C. Maignan, *ibid*. **1996**, *37*, 3687; c) G. Dujardin, M. Maudet, E. Brown, *ibid*. **1994**, *35*, 8619; d) G. Dujardin, S. Rossignol, S. Molato, E. Brown, *Tetrahedron* **1994**, *50*, 9037.
[11] a) R. A. John, V. Schmid, H. Wyler, *Helv. Chim. Acta* **1987**, *70*, 600; b) M. A. Hashem, T. Hossain, *Indian J. Chem., Sect. B* **1995**, *34*, 768.
[12] M. Conrads, J. Mattay, *Chem. Ber.* **1991**, *124*, 1425.
[13] J.-C. Zhuo, H. Wyler, *Helv. Chim. Acta* **1993**, *76*, 1916.
[14] J. Sauer, R. Sustmann, *Angew. Chem., Int. Ed. Engl*. **1980**, *19*, 779.
[15] R. M. Noyes, 'Kinetics and Mechanisms of Complex Reactions', 'Investigation of Rates and Mechanisms of Reactions, Part I', 4th edn., Ed. C. F. Bernasconi, in 'Techniques of Chemistry', Vol VI, Ed. A. Weissberger, J. Wiley & Sons, New York-Chichester-Brisbane-Toronto-Singapore, 1986, p. 373 (see p. 403–406).
[16] a) O. Exner, 'Correlation Analysis of Chemical Data', Plenum Press, New York-London, 1988; b) C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165.
[17] L. F. Tietze, G. Kettschau, J. A. Gewert, A. Schuffenhauer, *Curr. Org. Chem.* **1998**, *2*, 19.
[18] N. J. Sisti, E. Zeller, D. S. Grierson, F. W. Fowler, *J. Org. Chem.* **1997**, *62*, 2093; C. Trione, L. M. Toledo, S. D. Kuduk, F. W. Fowler, D. S. Grierson, *ibid*. **1993**, *58*, 2075; M. Teng, F. W. Fowler, *ibid*. **1990**, *55*, 5646; *Tetrahedron Lett*. **1989**, *30*, 2481.
[19] D. L. Boger, K. D. Robarge, *J. Org. Chem.* **1988**, *53*, 5793.
[20] J. W. Wijnen, S. Zavarise, Jan B. F. N. Engberts, *J. Org. Chem.* **1996**, *61*, 2001.
[21] I. J. Westerman, C. K. Bradsher, *J. Org. Chem.* **1971**, *36*, 969.
[22] A. Lewis, *J. Org. Chem.* **1987**, *52*, 3099; J. B. Levy, D. M. Sterling, *ibid*. **1985**, *50*, 5615 and ref. cit. therein; A. D. Allen, M. Rosenbaum, N. O. L. Seto, T. T. Tidwell, *ibid*. **1982**, *47*, 4234.
[23] P. D. Bartlett, *Quart. Rev. Chem. Soc.* **1970**, *24*, 473.
[24] C. Subramanyam, M. Noguchi, S. M. Weinreb, *J. Org. Chem.* **1989**, *54*, 5580.
[25] J. H. Boyer, H. Alul, *J. Am. Chem. Soc.* **1959**, *81*, 2136.

Received March 13, 1999