Thermal or Lewis acid-promoted electrocyclisation and hetero Diels–Alder cycloaddition of α,β-unsaturated (conjugated) carbodiimides: a facile synthesis of nitrogen-containing heterocycles

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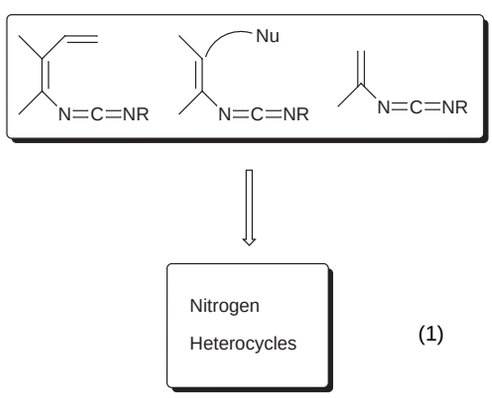
α,β-Diarylvinyl- and α-styryl-carbodiimides, prepared by the aza-Wittig reaction of iminophosphoranes with isocyanates, underwent either 6π-electrocyclisation upon heating or a Diels–Alder reaction under thermal or Lewis acid-promoted conditions with appropriate dienophiles such as tetracyanoethylene, dimethyl acetylenedicarboxylate, maleimide, ethyl propiolate and tosyl isocyanate, to give isoquinolines, pyridines, oxazines, pyrimidines and pyrrolopyridines. In contrast, β-styrylcarbodiimide was entirely unreactive toward either the electrocyclisation or the Diels–Alder reaction even under severe reaction conditions. 4-Coumarylcarbodiimide underwent an inverse electron-demand Diels–Alder reaction with an enamine either thermally or in the presence of a Lewis acid catalyst to afford chromenopyridines. Thus experimentally observed reactivity differences of the substituted vinylcarbodiimides toward the pericyclic reactions were rationalised by considering not only the heats of formation but also the probability of the existence of reactive conformers that were estimated by semi-empirical (AM1) and molecular mechanics calculations.

For many years carbodiimides have occupied a position as an important class of heterocumulene compounds in synthetic organic chemistry.[1] Of particular significance is their use as condensing agents in peptide and nucleotide synthesis and as oxidation agents combined with dimethyl sulfoxide (Pfitner–Moffatt oxidation). Other versatile uses of carbodiimides are as building blocks in heterocycle synthesis.[2] In this regard, the incorporation of unsaturated-conjugated units into reactive cumulenic systems is expected to provide useful and efficient systems as potent building blocks capable of taking part in ring-forming reactions such as electrocyclisation, cumulene-addition annulation and [4+2]cycloaddition reactions for heterocycle synthesis. In recent years powerful and useful synthetic routes to a wide range of heterocycles utilising functionalised carbodiimides have been developed.[3] The methods include, in particular, cycloaddition–heteroannulation of highly reactive carbodiimides containing one or more potentially available functionalities such as carbon–carbon double bond(s) in conjugation with the cumulene N=C bond or a remote nucleophilic centre (*e.g.* an OH or NH group) linked to the cumulene terminal nitrogen [eqn. (1)].[3] In earlier preliminary work we have reported the efficiency of these functionalised heterocumulenic species in the construction of a variety of nitrogen-heterocyclic systems such as pyridines, quinolines, isoquinolines, quinazolines, pyridoindoles, indoloquinolines, oxazines, pyridazines, pyrrolopyridines and chromenopyridines.[4–7] This paper gives a detailed account of this work.†



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Results and discussion

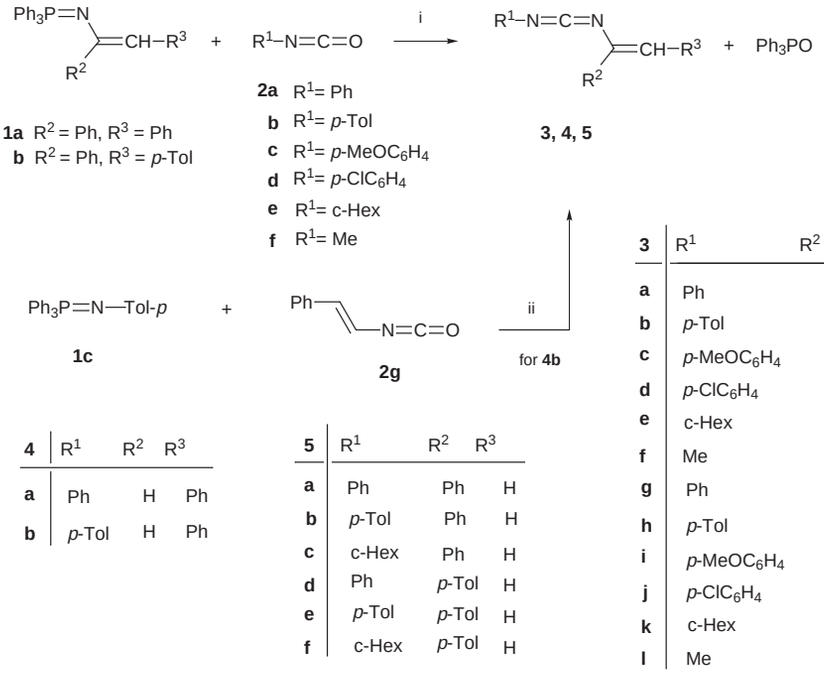
The synthesis of the carbodiimides **3**–**5** utilised an aza-Wittig reaction of iminophosphoranes **1** with isocyanates **2** consisting of two approaches as shown in Scheme 1. The carbodiimides **3**–**5** could be isolated in good yields as oils (except for **3d**, which is solid) by means of short-column chromatography, and used in the cycloaddition without further purification.‡

Cycloadditions of the carbodiimides 3–5

Upon heating at 140 °C in xylene the carbodiimides **3** readily underwent 6π-electrocyclisation involving the β-aryl ring, the olefinic bond and one of the cumulene N=C bonds to form the intermediates **6**, which rearomatised by way of H-migration to afford the 1-aminoisoquinolines **7** in fair to good yields (Scheme 2). The ^{1}H NMR spectra of **7** gave evidence for the exocyclic R^{1}NH group, particularly in the cases of **7e**,**f**,**k**,**l**; the NH signal for **7e**,**k** was observed as a doublet (J = 4 Hz),

† Part of this work has been reported as preliminary communications.[6,7]

‡ Prolonged column chromatography decreases the yields of carbodiimides probably due to their deterioration or polymerisation on silica gel. The carbodiimide **4a** was not prepared and was subjected only to the computational calculations (*vide infra*).

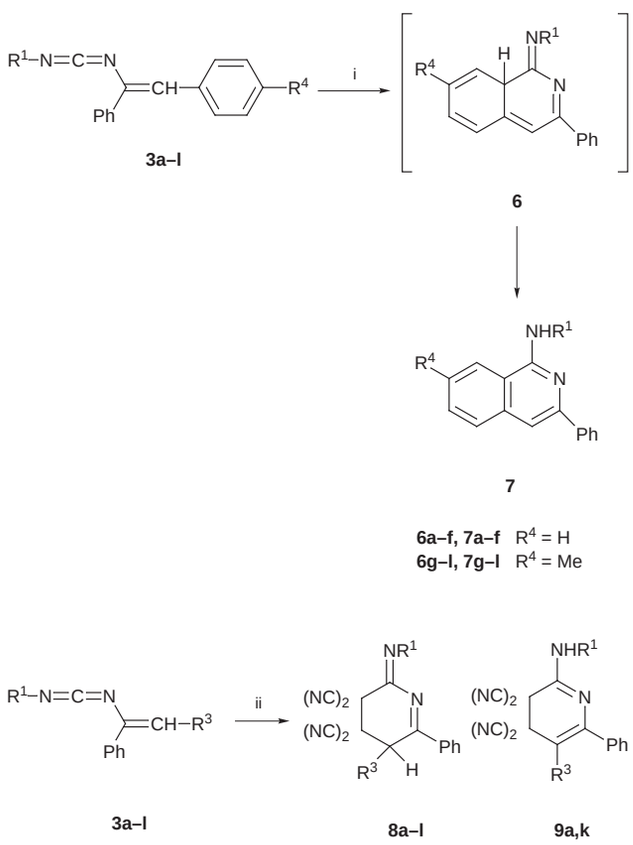


3	R^1	R^2	R^3
a	Ph	Ph	Ph
b	*p*-Tol	Ph	Ph
c	*p*-$MeOC_6H_4$	Ph	Ph
d	*p*-ClC_6H_4	Ph	Ph
e	c-Hex	Ph	Ph
f	Me	Ph	Ph
g	Ph	Ph	*p*-Tol
h	*p*-Tol	Ph	*p*-Tol
i	*p*-$MeOC_6H_4$	Ph	*p*-Tol
j	*p*-ClC_6H_4	Ph	*p*-Tol
k	c-Hex	Ph	*p*-Tol
l	Me	Ph	*p*-Tol

4	R^1	R^2	R^3
a	Ph	H	Ph
b	*p*-Tol	H	Ph

5	R^1	R^2	R^3
a	Ph	Ph	H
b	*p*-Tol	Ph	H
c	c-Hex	Ph	H
d	Ph	*p*-Tol	H
e	*p*-Tol	*p*-Tol	H
f	c-Hex	*p*-Tol	H

Scheme 1 *Conditions*: i, room temp., 1–2 h for **2a**–**d** (R^1 = aryl), 1–2 d for **2e,f** (R^1 = c-Hex or Me), in benzene; ii, room temp., 2 h, in benzene.



Scheme 2 *Reagents and conditions*: i, 140 °C, in xylene, 2 h for R^1 = aryl, 7–10 h for R^1 = alkyl; ii, TCNE, room temp., in MeCN, 1–11 d.

coupled with the cyclohexyl (R^1 = c-Hex) methine proton, and the methyl signal for **7f,l** appears as a doublet, being split due to coupling with the NH proton.

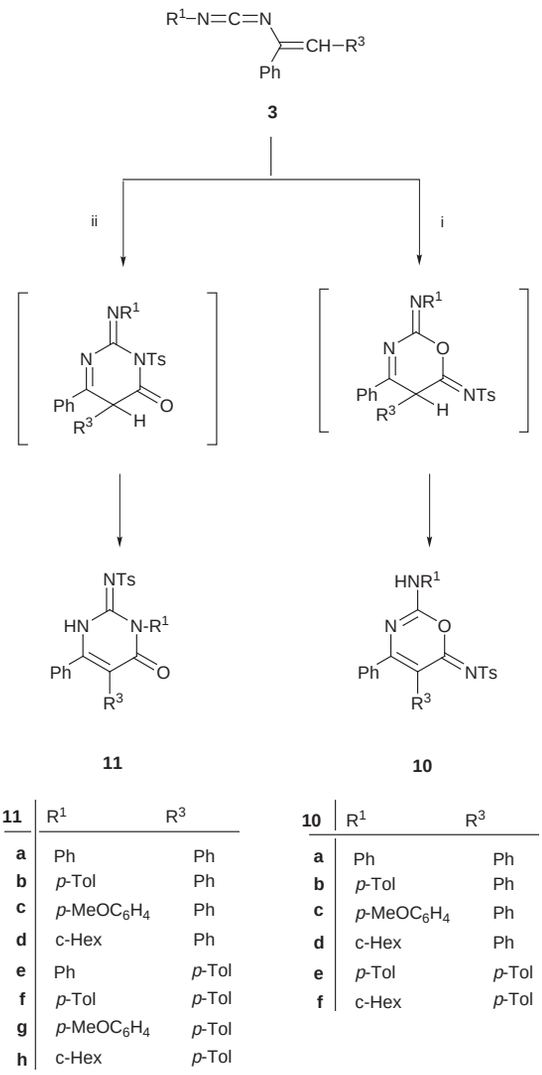
Since there are several possible sites for pericyclic reactions of such conjugated carbodiimides, we tried cycloaddition with some cycloaddends (dienophiles).[6]§ Unfortunately, the carbodiimides **3** did not react at all upon heating with the conventional dienophiles such as dimethyl acetylenedicarboxylate (DMAD), acrylonitrile, methyl acrylate, dimethyl fumarate and ethoxyethene. Instead, the electrocyclisation preferentially took place over the expected cycloaddition only to result in the exclusive formation of **7**. A strong dienophile, tetracyanoethylene (TCNE), was found to produce the [4+2]cycloadducts **8** when the reaction was performed at room temperature in acetonitrile. During the purification operation 1,5-H migrated isomers **9a**,**k** were incidentally formed from compounds **8a**,**k**.

The carbodiimides **3** also reacted as 2-azadienes (4π component) with *p*-tosyl isocyanate on the C=O bond (2π component) in refluxing benzene for 15–30 h to form the intermediary cycloadducts which, by way of H-migration, gave 2-amino-1,3-oxazin-6-imines **10**, while in acetonitrile at room temperature the reaction took place on the C=N bond to finally produce the 2-iminopyrimidin-4-ones **11** *via* the Dimroth-like rearrangement[12] of the initial cycloadducts (Scheme 3). Although the yields of products **10** and **11** were moderate, no other cycloadduct was found from the reaction mixture. The structures **10** and **11** were determined on the basis of spectroscopic studies (MS, IR, ^{1}H and ^{13}C NMR).¶

The reactions of β-styrylcarbodiimide **4b** were next attempted. Under similar reaction conditions the carbodiimide **4b** did not undergo either the electrocyclisation or the [4+2]-cycloaddition even with some strong dienophiles such as tetracyanoethylene (TCNE), dimethyl acetylenedicarboxylate

§ The intermolecular[8,9] and intramolecular[4,10] hetero Diels–Alder reactions of α,β-unsaturated (conjugated) carbodiimides have been reported. Also, the three-component reaction with the heterocycle-conjugated carbodiimides as the key intermediates has been documented.[11] These [4+2]cycloadditions can possibly involve ionic, stepwise mechanisms.

¶ The mass spectra of compounds **10** and **11** showed intense molecular ion peaks assigned as 1 : 1-cycloadducts. In the IR spectra of compounds **10**, a ν_{NH} absorption band was observed at 3380–3450 cm^{-1} and the peak observed at 1520–1560 cm^{-1} was reasonably assigned to that of $\nu_{C=NTs}$ rather than $\nu_{C=O}$. The ^{1}H NMR spectra of **10e,k** exhibited a characteristic NH resonance as a doublet coupled with the cyclohexyl (R^1) methine proton, the ^{13}C NMR spectra of **10** displaying resonances of C-2 at 168–169 ppm and of C-6 at 158–163 ppm or *vice versa*. The IR spectra of compounds **11** showed a ν_{NH} absorption at 3340–3400 cm^{-1}, a $\nu_{C=NTs}$ at 1530–1555 cm^{-1}, and a $\nu_{C=O}$ at 1670–1690 cm^{-1}. Resonances of C-2 and C-4 were observed at 158–159 and 161–163 ppm, respectively, in the ^{13}C NMR spectra.



11	R^1	R^3
a	Ph	Ph
b	*p*-Tol	Ph
c	*p*-$MeOC_6H_4$	Ph
d	c-Hex	Ph
e	Ph	*p*-Tol
f	*p*-Tol	*p*-Tol
g	*p*-$MeOC_6H_4$	*p*-Tol
h	c-Hex	*p*-Tol

10	R^1	R^3
a	Ph	Ph
b	*p*-Tol	Ph
c	*p*-$MeOC_6H_4$	Ph
d	c-Hex	Ph
e	*p*-Tol	*p*-Tol
f	c-Hex	*p*-Tol

Scheme 3 *Reagents and conditions*: i, TsNCO, reflux in benzene, 15–30 h; ii, TsNCO, room temp. in MeCN, 5 d for R^1 = c-Hex, 10–17 d for R^1 = aryl.

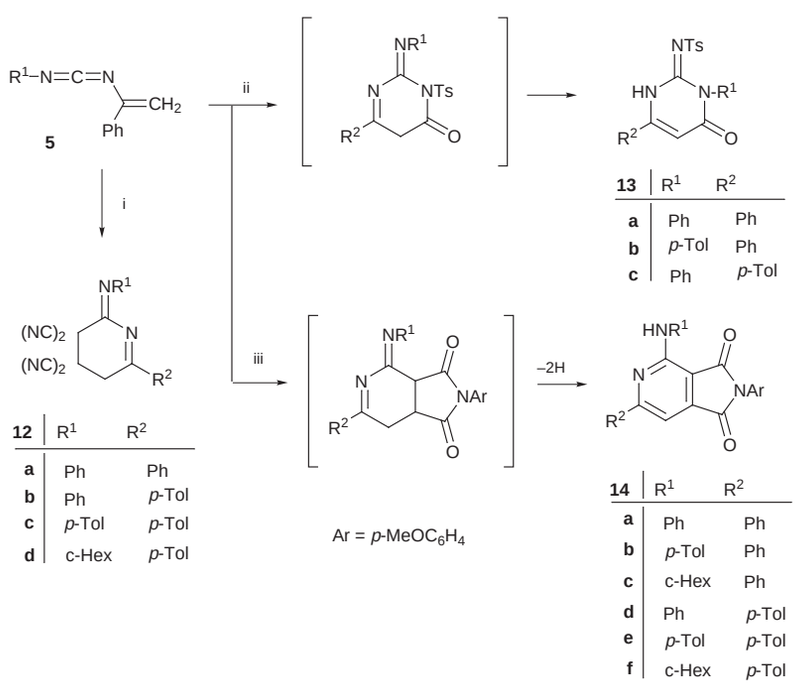
(DMAD), tosyl isocyanate and *N*-phenylmaleimide (NPMI) and gave none of the expected products.‖ At elevated temperatures no identifiable products were obtained.

The α-styrylcarbodiimides **5** smoothly underwent the [4+2]-cycloaddition with tetracyanoethylene, tosyl isocyanate and *N*-(*p*-methoxyphenyl)maleimide to produce compounds **12**–**14** as the sole cycloadducts, respectively (Scheme 4). Since it is structurally impossible for the carbodiimides **5** to undergo 6π-electrocyclisation, [4+2]cycloaddition with the maleimide could be effected by heating (Table 1). In all of these cases a trace amount of diarylcarbodiimide (R′ = aryl) was formed as a by-product which would arise from the disproportional dimerisation–fragmentation of **5** at a high temperature. The reaction in the presence of MnO_2 as a dehydrogenation agent gave a somewhat better yield of product **14a** than the other cases.

Dimethyl acetylenedicarboxylate (DMAD) reacted with the carbodiimides **5** in refluxing toluene to afford the 2-aminopyridines **15** in moderate yields (Scheme 5, Table 2). Nitta *et al.* also reported the thermal [4+2]cycloaddition reaction of **5a** with acetylenic dienophiles such as DMAD, methyl propiolate, phenyl acetylene and benzoylacetylene to give 2-aminopyridines in moderate yields.[8] In the presence of a Lewis acid catalyst ($AlCl_3$, 2 equiv.), the reaction proceeded smoothly at room temperature in dichloromethane to furnish good yields of the products **15**. The reaction of **5** with ethyl propiolate was also effected by the Lewis acid catalyst to afford the pyridine derivatives **16** in 43–51% yields (Scheme 5), whereas the thermal reaction gave only 9% yield of **16a** after heating a toluene solution of **5a** for 17 h. The reactions of **5a**,**b**,**d**,**e** with methyl fumarate and with methyl maleate under the same Lewis acid promoted conditions also gave **15** *via* dehydrogenation of the initially formed cycloadducts, albeit in poor (6–8%) yields.

Coumarin-4-carbodiimides **18**, which were prepared in a similar way by the aza-Wittig reaction of **17**, were very moisture-sensitive and therefore the reaction with enamine was conducted in one-pot without isolation to result in the exclus-

‖ We found that the carbodiimide **4b** is sufficiently reactive to undergo an addition reaction with a carboxylic acid (acetic acid, benzoic acid in acetonitrile at room temperature) to afford both *N*- and *N*′-acylureas.[1a,b]



12	R^1	R^2
a	Ph	Ph
b	Ph	*p*-Tol
c	*p*-Tol	*p*-Tol
d	c-Hex	*p*-Tol

13	R^1	R^2
a	Ph	Ph
b	*p*-Tol	Ph
c	Ph	*p*-Tol

14	R^1	R^2
a	Ph	Ph
b	*p*-Tol	Ph
c	c-Hex	Ph
d	Ph	*p*-Tol
e	*p*-Tol	*p*-Tol
f	c-Hex	*p*-Tol

Scheme 4 *Reagents and conditions*: i, TCNE, room temp. in MeCN, 5–10 d; ii, TsNCO, room temp. in MeCN, 2–3 d; iii, *N*-(*p*-methoxyphenyl)maleimide, in refluxing solvent.

Table 1 Diels–Alder reaction of **5** with *N*-(*p*-methoxyphenyl)-maleimide

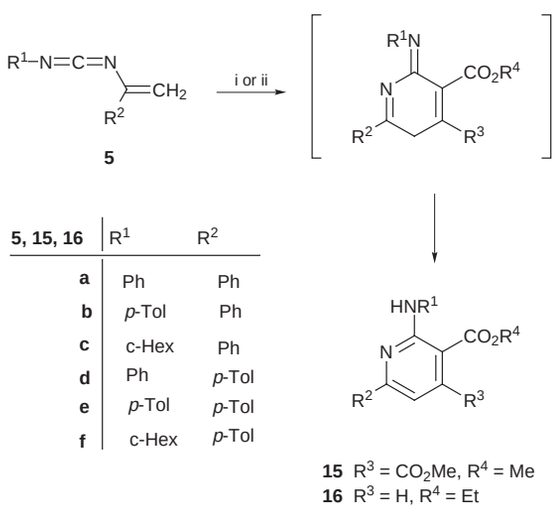
Carbodiimide	Solvent	Time/h	Additive	Product	Yield (%)[a]
5a	Benzene	50		**14a**	10
5a	Xylene	7		**14a**	41
5a	Mesitylene	10		**14a**	27
5a	Xylene	7	MnO_2	**14a**	51
5a	Xylene	6	S_8	**14a**	21
5a	Xylene	8	Nitrobenzene	**14a**	26
5a	Benzene	20	DDQ	**14a**	5
5b	Xylene	5		**14b**	32
5c	Xylene	2		**14c**	36
5d	Xylene	6		**14d**	32
5e	Xylene	7		**14e**	34
5f	Xylene	7		**14f**	30

[a] Isolated yield, not optimised.

Table 2 Diels–Alder reaction of **5** with DMAD

Carbodiimide	DMAD (equiv.)	Lewis acid (equiv.)	Time/h	Product	Yield (%)[a]
5a	1.1	$EtAlCl_2$ (1.1)	3	**15a**	14
5a	2.0	$EtAlCl_2$ (2.0)	25	**15a**	38
5a	1.1	$AlCl_3$ (1.1)	2	**15a**	26
5a	2.0	$AlCl_3$ (1.5)	2	**15a**	41
5a	2.0	$AlCl_3$ (2.0)	1	**15a**	77 (22)
5b	2.0	$AlCl_3$ (2.0)	0.5	**15b**	72 (22)
5c	2.0	$AlCl_3$ (2.0)	0.25	**15c**	70 (53)
5d	2.0	$AlCl_3$ (2.0)	1	**15d**	74 (28)
5e	2.0	$AlCl_3$ (2.0)	0.5	**15e**	70 (26)
5f	2.0	$AlCl_3$ (2.0)	0.25	**15f**	71 (45)

[a] Isolated yield, not optimised. The yield from the thermal reaction in refluxing toluene is given in parentheses.



Scheme 5 *Reagents and conditions*: i, DMAD, reflux in toluene, 3–9 h or ethyl propiolate, reflux in toluene, 17 h; ii, DMAD, Lewis acid, room temp. in CH_2Cl_2 or ethyl propiolate (2 equiv.), $AlCl_3$ (2 equiv.), −10 °C ⟶ room temp., 1 h, CH_2Cl_2.

ive formation of chromenopyridines **19**, albeit in moderate yields (Scheme 6, Table 3). The reaction probably involved a morpholine-elimination and an H-migration of the initially formed [4+2]cycloadducts.[8,9] Lewis acid also worked as a promoter in this inverse electron-demand [4+2]cycloaddition.

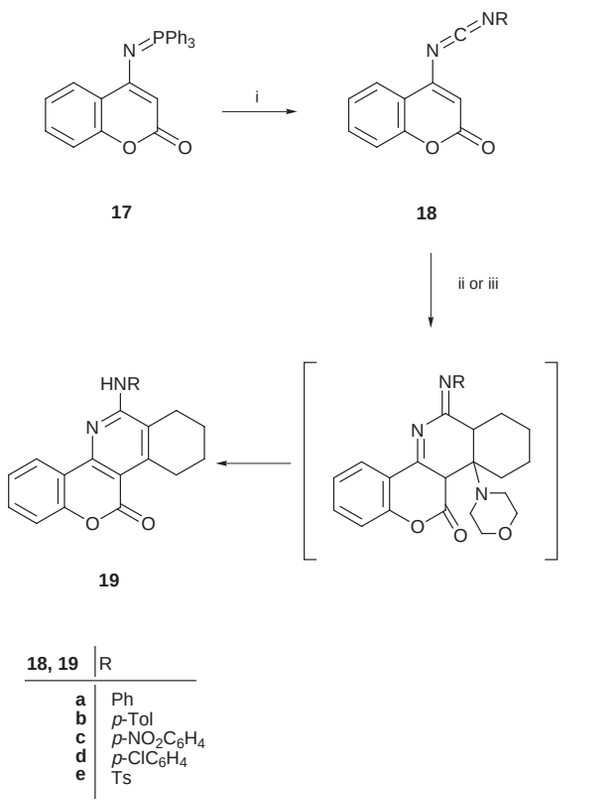
Comparisons of reactivities of carbodiimides 3–5

These Diels–Alder reactivity differences observed among carbodiimides **3**–**5** seemed to be somewhat unexpected at first sight since the β-styrylcarbodiimides **4** should react readily

Table 3 Diels–Alder reaction of **18** with enamine

Carbodiimide	$AlCl_3$ (equiv.)	Time/h **17→18**	Time/h **18→19**	Product	Yield (%)[a]
18a	*b*	0.5	4	**19a**	34
18a	0.2[c]	0.5	20	**19a**	20
18a	0.5[c]	0.5	20	**19a**	45
18a	1.0[c]	0.5	20	**19a**	31
18b	*b*	0.5	4	**19b**	30
18c	*b*	4	4	**19c**	23
18c	0.5[c]	0.5	20	**19c**	38
18d	*b*	4	4	**19d**	17
18e	*b*	2	5	**19e**	47
18e	1.0[c]	2	3	**19e**	57

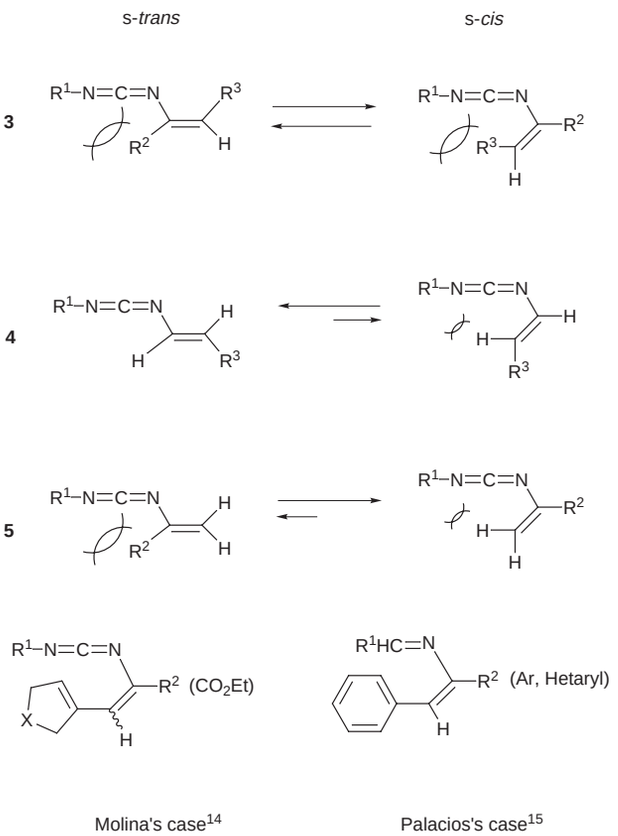
[a] Isolated yield, not optimised. [b] Thermal reaction under conditions i→ii. [c] Under conditions i→iii.



Scheme 6 *Reagents and conditions*: i, RNCO, 110 °C (room temp. for **e**, R = Ts), toluene or tetrachloroethylene, 0.5–5 h; ii, *N*-(cyclohex-1-enyl)morpholine, 110 °C, toluene, 4–5 h; iii, *N*-(cyclohex-1-enyl)-morpholine, Lewis acid, − 15 °C→room temp., tetrachloroethylene, 3–20 h.

owing to lower steric hindrance with a dienophile than with (1,2-diarylvinyl)carbodiimides **3** in the course of the cycloaddition. In fact, the carbodiimides **5** and **3** did undergo the Diels–Alder reaction but the carbodiimide **4b** did not, and the electrocyclisation occurred with **3** but did not with **4b**. If there are no significant differences in the electronic effects of the substituent(s) on their reactivity, their conformational populations can be envisaged as an important factor on the reactivity differences in these diene-s-*cis*-requiring Diels–Alder reactions as well as electrocyclisations to allow effective p-orbitals overlapping (Scheme 7).[13]

As for the carbodiimides **3** there is steric repulsion between the cumulene moiety and R^2, and R^3 in both s-*trans*- and s-*cis*-conformations, respectively, each being counter-balanced. Therefore, non-planar populations of **3** would increase, though the π-conjugation is lacking, giving intermediate reactivity of the three for the Diels–Alder reaction, and higher reactivity



Scheme 7

for the electrocyclisation than with **4** for which the geometrical isomerisation (*trans*→*cis*) of R^3 with respect to the C=C bond is necessary. The inert dienes **4** in cycloaddition reactions would most preferentially adopt an s-*trans* form in which there is no appreciable steric repulsion, although it exists in the s-*cis* form. According to the same argument, the azadienes **5** preferably adopt an s-*cis* conformation and hence readily undergo the [4+2]cycloaddition. Molina *et al.*[14] showed experimentally that certain carbodiimides of the type **3** which bear an R^2 substituent ($R^2 = CO_2Et$, R^1 = aryl or alkyl, R^3 = aryl or heteroaryl) readily underwent, on heating, electrocyclisation in a mechanism involving the conjugated system in R^3, although the *E*, *Z*-geometry was not specified, to give a variety of substituted nitrogen heterocycles. Palacios *et al.*[15] demonstrated that the 6π electrocyclisation of 4-phenyl-2-azadienes (R^3 = Ph), which were prepared by the aza-Wittig reaction of iminophosphoranes with aromatic (or heteroaromatic) aldehydes (R^1 = aryl or heteroaryl group), took place in refluxing xylene to afford 1,3-disubstituted isoquinolines. In these cases, all the cyclised 2-azadienes bore R^2 substituents of aryl or heteroaryl groups such as phenyl, furyl and thienyl groups, and they have *Z*-configuration with respect to the C=C bond, and *E*- or *Z*-geometry around the C=N bond, the latter geometry being varied by substituents. These results are consistent with the above argument.

Computational calculations

In order to support the above argument and precisely but qualitatively to understand the reactivity differences of these conjugated carbodiimides **3**–**5** for the pericyclic reactions, semi-empirical (AM1) and molecular mechanics calculations were performed. The frontier molecular orbital treatment clearly did not reflect the observed reactivities since it was difficult to specify their HOMO's and LUMO's which largely depended upon conformational rotations, whereas with a simple vinylcarbodiimide a FMO approach gave some information on the reactivity.[8]

Table 4 Heats of formation for Diels–Alder reaction and electrocyclisation of **3a**, **4a** (**4b**) and **5a**[a]

	ΔH_f/kcal mol^{-1}					
	S	TS	P	TS–S	TS–P	S–P
3a [DA]	303.3	342.0	287.4	38.7	54.6	15.9
3a [El]	150.5	181.9	152.3 (116.1)[b]	31.4	29.6	−1.8 (34.4)[b]
4a [DA][c]	270.4	307.4	253.4	37.0	54.6	17.0
5a [DA]	277.3	305.7	251.4	28.4	54.3	25.9

[a] Transition states were calculated by AM1 method. DA: Diels–Alder, El: Electrocyclisation, S: Starting reactant(s) system, TS: Transition state, P: Product system. [b] In parentheses, heat of formation for the final, re-aromatised H-migration product (**7a**). [c] For **4b** [DA] heat of formation: S, 263.4; TS, 299.4; P, 247.2; TS–S, 36.0; TS–P, 52.2 and S–P, 16.2 kcal mol^{-1}.

Table 5 Probability of existence of reactive conformers in Diels–Alder reaction and electrocyclisation of **3a**, **4a** (**4b**) and **5a** at 20 °C

	Probability (%)	
	Diels–Alder reaction	Electrocyclisation
3a	72 (62)[a]	8 (9)[a]
4a	29 (29)[b]	—
5a	36	—

[a] At 80 °C. [b] For **4b**.

It is known that conformational properties of reactant(s) are essential factors, as well as the activation energies, for evaluation of reactivities. It is true particularly in such a case that the former entropic factor is crucial for complete understanding of the real reactivities.[16] For example, rate acceleration induced by substituents in the connecting chain that influence the properly disposed conformer's population for cyclisation are often explained by the so-called geminal di-substituents effect or the Thorpe–Ingold effect.[17] Even for a bimolecular (intermolecular) reaction, rate enhancement, or reduction, is often observed when it is easy, or difficult, for a conjugated diene to adopt the s-*cis* conformation necessary to undergo a Diels–Alder reaction in a concerted mode. In this context, both the heats of formations and the probabilities of existence of the dienes in the demanding cisoid conformations necessary for reaction, were calculated for the Diels–Alder reactions of carbodiimides **3a**, **4a** and **5a** with TCNE, and for electrocyclisation of **3a**. The structures of the reactants and the products were evaluated using the intrinsic reaction coordinate (IRC) algorithm in connection with the transition states. The probabilities were assessed by applying steric energy values calculated by the MM2 force field,[18] to the Boltzmann distribution equation.[19] Sixteen, two and three conformers were generated for carbodiimides **3a**, **4a** and **5a**, respectively. Among them, the conformer(s) having dihedral angle(s) within 0 ± 90° was (were) taken into account for each Diels–Alder reaction. Fortunately, however, it was found that the conformers of $\theta = ca.\ \pm 90°$ having high energies, other than the cisoids ($50° \geqslant \theta \geqslant -50°$ for **3a**, $2° \geqslant \theta \geqslant -2°$ for **4a** and **5a**) make virtually no contribution to the DA reactivity because of their very small Boltzmann distribution. The results are shown in Tables 4 and 5 and Figs. 1–6.

Comparison of the reactivity of carbodiimide 3 in the electrocyclisation *versus* the Diels–Alder reaction

From the data in Tables 4 and 5 the following inferences can be made: (1) As far as the activation energies ($\Delta E_{TS\text{-}S}$) are concerned, the activation energy ($\Delta E^{El}_{TS\text{-}S} = 31.4$ kcal mol^{-1}) of the electrocyclisation is smaller than that ($\Delta E^{DA}_{TS\text{-}S} = 38.7$ kcal mol^{-1}) of the Diels–Alder reaction by 7.3 kcal mol^{-1}, suggesting that the electrocyclisation is likely to take place faster than the

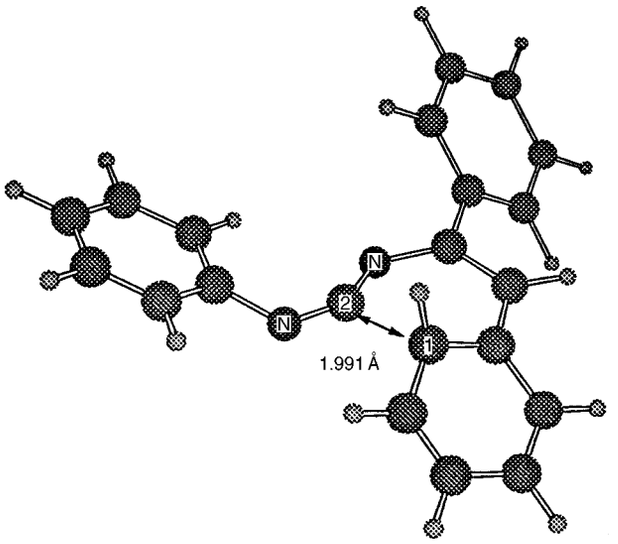


Fig. 1 Transition state of 1,6-electrocyclisation of **3a**.

Diels–Alder reaction (kinetic control). (2) In the Diels–Alder reaction the heat of formation of the product system ($\Delta E^{DA}_{TS\text{-}P}$ = 54.6 kcal mol^{-1}) is smaller than that ($\Delta E^{DA}_{TS\text{-}S}$ = 38.7 kcal mol^{-1}) of the starting reactants system by 15.9 kcal mol^{-1}, by which the product system is stabilised. On the contrary, the product system for the electrocyclisation is more destabilised than the reactant by 1.8 kcal mol^{-1} (thermodynamic control). (3) Furthermore, the Diels–Alder reaction has advantages over electrocyclisation because of the contribution of the probability of the existence of reactive conformers (72% for the former and 8–9% for the latter). (4) If the formation of the final, re-aromatised H-migration product (**7a**) stabilised by $\Delta E^{El}_{S\text{-}Pf}$ = 34.4 kcal mol^{-1} is taken into account, electrocyclisation can predominate. (5) Figs. 4–6 show that the C1–C2 bond distance becomes constant, immediately followed by the C3–C4 bond distance becoming constant just after the transition state. This suggests that the cycloaddition proceeds asynchronously.

In any event, the reaction in the presence of a sufficiently reactive dienophile at a low temperature (room temp.), such that the H-migration does not occur, would give the Diels–Alder product (kinetic control), while at a higher temperature the electrocyclisation product would be formed predominantly following H-migration (thermodynamic control). This rationalisation is qualitatively in agreement with the experimental observation.

Comparison of the reactivity of carbodiimide 3, 4 and 5 in the Diels–Alder reaction

The activation energies of **3a**, **4a** (**4b**) and **5a** for the Diels–Alder reaction are 38.7, 37.0 (36.0) and 28.4 kcal mol^{-1}, respectively, suggesting increasing reactivity in the order of **5a** ⩾ **4a(b)** ⩾ **3a** if the reaction is kinetically controlled. On the other hand, the calculated probability of the carbodiimide dienes being in the s-*cis* conformations at 20 °C, are 72% for **3a**, 29% for **4a(b)**, and 36% for **5a** (Table 5). These data imply that the Diels–Alder reactivity should be observed in the order of **3a** ⩾ **5a** > **4a(b)** at the given temperature (20 °C). By taking both factors (probability and heat of formation) into account, it leads to the order of **5a** > **3a** > **4a(b)**. This prediction is in accord with the experimental observation.

In conclusion, we have demonstrated that the heteroannulation of conjugated carbodiimides offers a new entry to useful synthetic methods of a variety of nitrogen-containing heterocyclic systems and that a Lewis acid catalyst effects the Diels–Alder cycloaddition. The methodology can be applied to other suitable types of functionalised carbodiimides. Furthermore, the computational treatment rationalises the reactivity differences of conjugated carbodiimides in the cycloadditions.

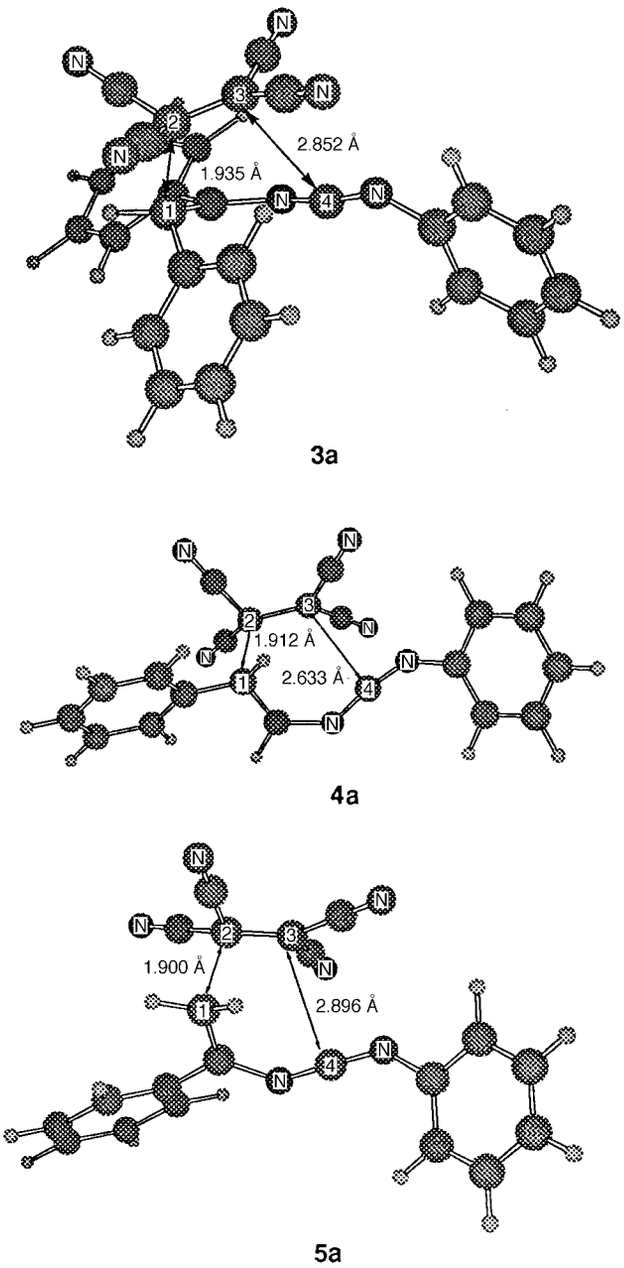


Fig. 2 Transition states of Diels–Alder reactions of **3a**, **4a** and **5a** with tetracyanoethylene.

Experimental

Melting points were determined on a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi Model 270-30 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on JEOL JNM-PMX60SI (60 MHz), JEOL JNM-FX-100 (100 MHz, 25 MHz) and/or JEOL JNM-EX 270 (270 MHz, 67.8 MHz) spectrometers in deuteriochloroform using tetramethylsilane as an internal standard unless otherwise specified. The same NMR instrument was used as stated initially, until a new citation appears. *J* Values are given in Hz. Mass spectra were obtained with a Hitachi Model RMU-7M double focusing mass spectrometer at an ionising potential of 70 eV and/or with a Hitachi Model M-80 spectrometer with a data processing system M-003. Elemental analyses were performed on a Yanaco MT-3 CHN recorder. Column chromatography and preparative and analytical TLC were performed on silica gel, Wakogel C-200, and B-5F and Merck Kieselgel 60 F_{254} plates, respectively. Solvents were purified by the usual method before use. Reactions were carried out under an argon atmosphere.

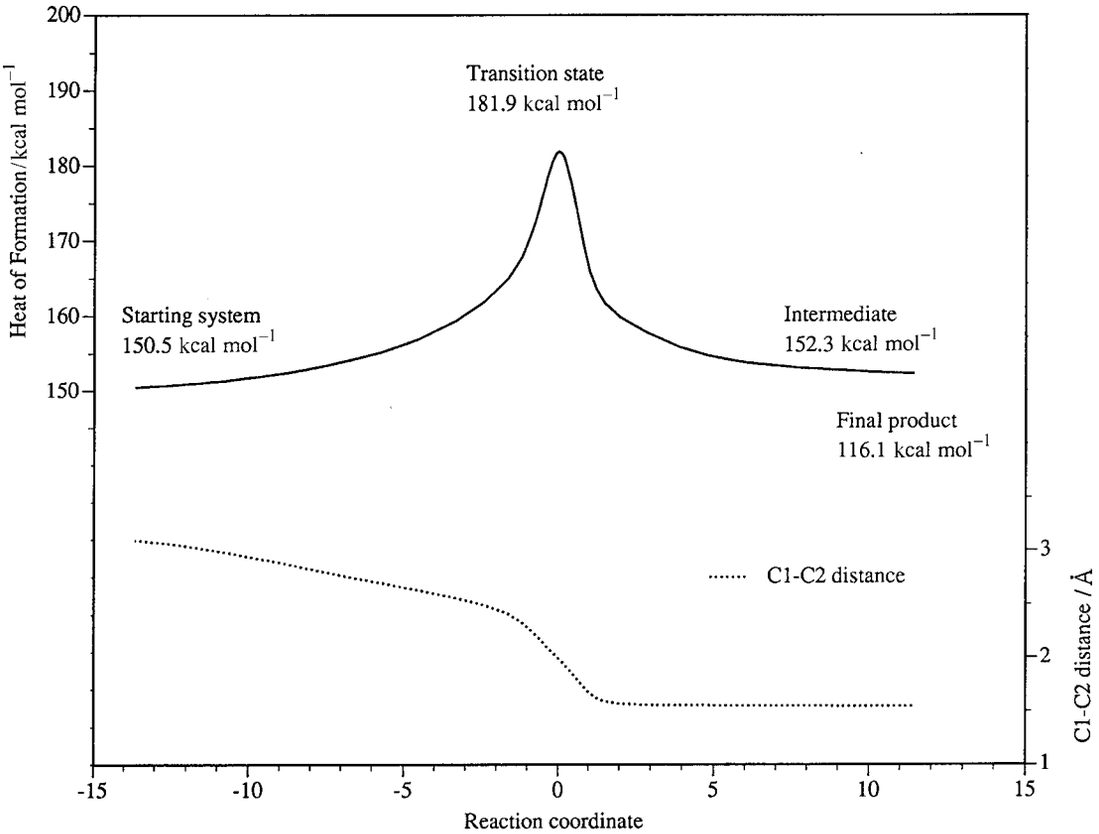


Fig. 3 Intrinsic reaction coordinate plots for the electrocyclisation of **3a**. The reaction proceeds from left to right with the transition state at zero. The solid line represents energy and the dotted line represents the C1–C2 distance (see Fig. 1).

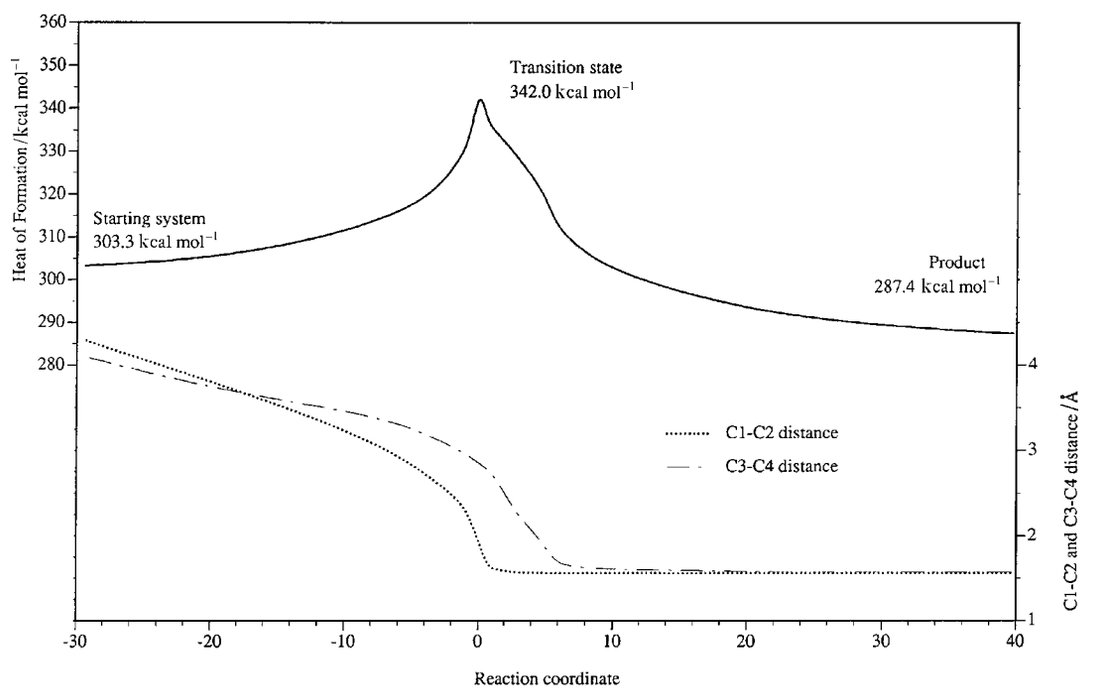


Fig. 4 Intrinsic reaction coordinate plots for the Diels–Alder reaction of **3a** with tetracyanoethylene. The reaction proceeds from left to right with the transition state at zero. The solid line represents energy, the dotted line represents the C1–C2 distance (see Fig. 2), and the dot-dashed line represents the C3–C4 distance.

Materials

The *N*-vinyliminophosphoranes **1a**,**b** were prepared by the Staudinger reaction[20] of vinyl azides with triphenylphosphine and/or by Ciganek's method[21] *via* the reaction of phosphonium methylides with aryl nitriles. The iminophosphorane **1c** was prepared by the Kirsanov method from *p*-toluidine and triphenylphosphine.[22]

Preparation of [*N*-(2-oxo-2*H*-chromen-4-yl)imino]triphenylphosphorane 17

4-*p*-Tolylsulfonyloxy-2*H*-chromen-2-one. To a solution containing 4-hydroxycoumarin (9.96 g, 61 mmol) and triethylamine (10.3 cm^3, 73 mmol) in dry tetrahydrofuran (THF) (100 cm^3) was added dropwise a THF solution (100 cm^3) of tosyl chloride (12.9 g, 67 mmol) with stirring at 0 °C for 1.5 h. After 0.5 h, the

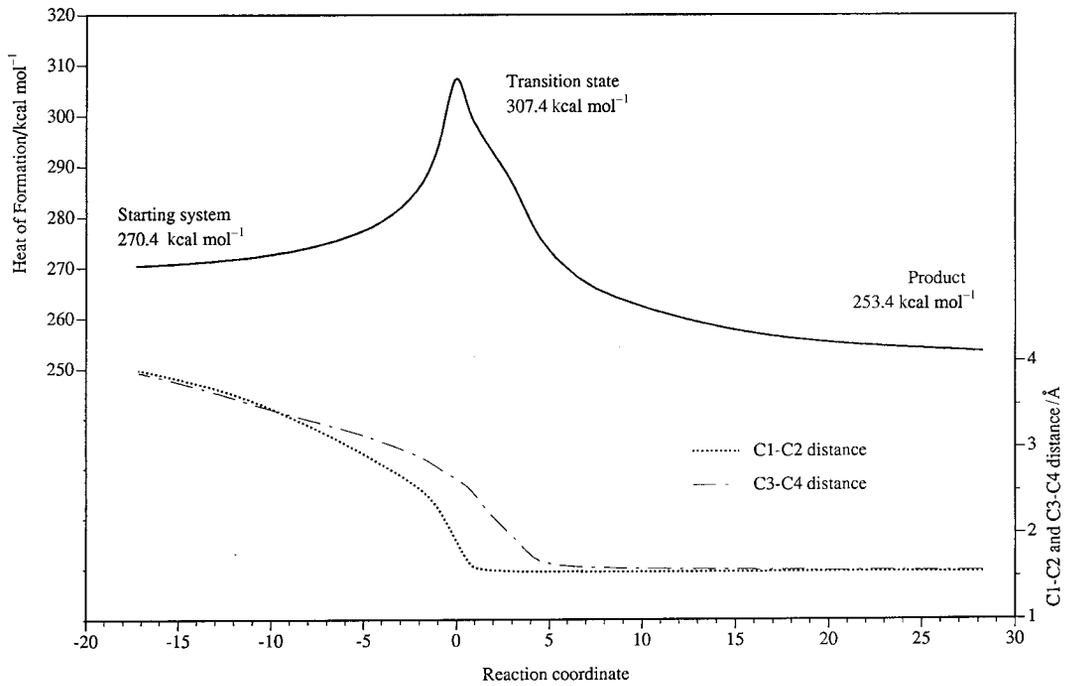


Fig. 5 Intrinsic reaction coordinate plots for the Diels–Alder reaction of **4a** with tetracyanoethylene. The reaction proceeds from left to right with the transition state at zero. The solid line represents energy, the dotted line represents the C1–C2 distance (see Fig. 2), and the dot-dashed line represents the C3–C4 distance.

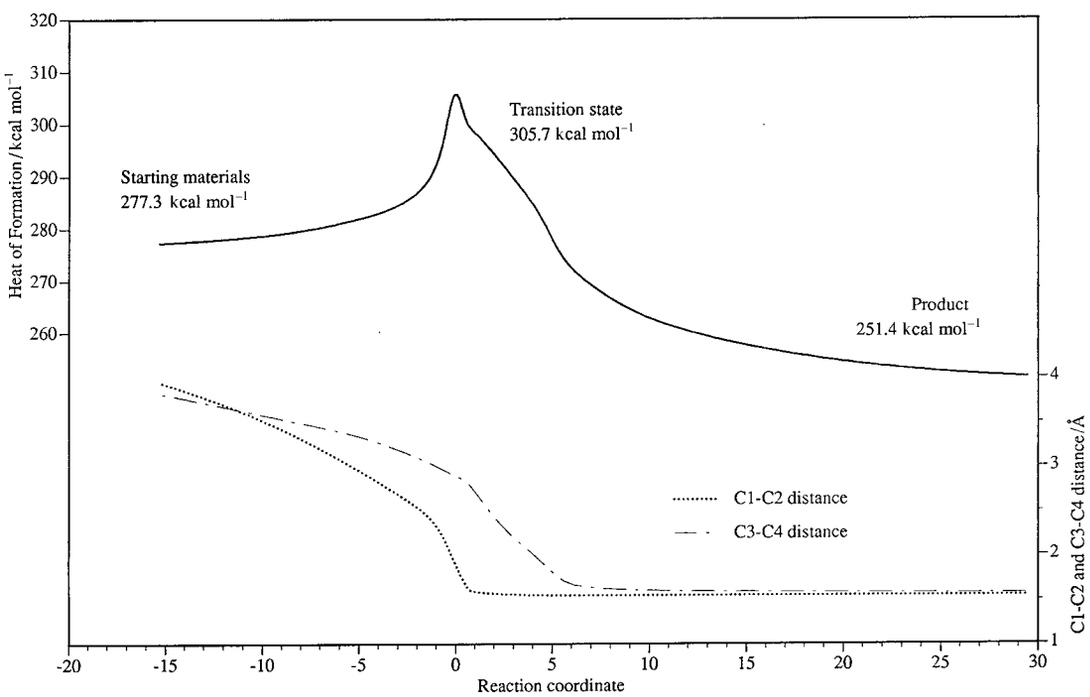


Fig. 6 Intrinsic reaction coordinate plots for the Diels–Alder reaction of **5a** with tetracyanoethylene. The reaction proceeds from left to right with the transition state at zero. The solid line represents energy, the dotted line represents the C1–C2 distance (see Fig. 2), and the dot-dashed line represents the C3–C4 distance.

reaction mixture was warmed to room temperature and then the precipitate was filtered and washed with ethyl acetate (EtOAc). Removal of the solvent from the filtrate and recrystallisation of the residue from diethyl ether afforded 18.7 g (97%) of the tosyl ester as colourless crystals, which was used without further purification (analytical) in the next reaction. δ_H (270 MHz) 2.47 (3H, s, Me), 6.32 (1H, s, 3-H), 7.26 (1H, d, *J* 7.26, 8-H), 7.31 (1H, dd, *J* 8.58, 7.92, 6-H), 7.40 (2H, d, *J* 8.58, Ts), 7.58 (1H, ddd, *J* 8.58, 7.26, 1.32, 7-H), 7.64 (1H, dd, *J* 7.92, 1.32, 5-H) and 7.90 (2H, d, *J* 8.58, Ts).

4-Azido-2*H*-chromen-2-one. To a methanol solution (75 cm^3) of the tosyl ester (15.4 g, 48.8 mmol) was added dropwise an aqueous solution (30 cm^3) of sodium azide (3.50 g, 53.7 mmol) with stirring at 0 °C. Being stirred at room temperature for 1.5 h, the reaction mixture was extracted with CH_2Cl_2 (50 cm^3 × 3), washed with brine, and dried ($MgSO_4$). The solvent was evaporated and the residue was column-chromatographed on silica gel using hexane–EtOAc (5 : 1–1 : 1) to give 8.77 g (96%) of the azide as a colourless solid, which was used without further purification (analytical) in the next reaction. ν_{max}(KBr)/cm^{-1} 2172 (N_3) and 1730 (C=O); δ_H (270 MHz) 6.13 (s, 3-H), 7.29 (1H, ddd, *J* 7.92, 7.26 and 0.99, 6-H), 7.35 (1H, dd, *J* 8.25 and

0.99, 8-H), 7.60 (1H, ddd, *J* 8.25, 7.26 and 1.65, 7-H) and 7.72 (1H, dd, *J* 7.92 and 1.65, 5-H).

[*N*-(2-Oxo-2*H*-chromen-4-yl)imino]triphenylphosphorane 17. To a CH_2Cl_2 solution (50 cm^3) of the azide (2.88 g, 15.4 mmol) was added dropwise a CH_2Cl_2 solution (40 cm^3) of triphenylphosphine (4.01 g, 15.4 mmol) at room temperature. The reaction mixture was stirred for 4 h at room temperature. Evaporation of the solvent and recrystallisation of the residue from CH_2Cl_2–hexane gave a quantitative yield of the iminophosphorane **17** (6.43 g, 99%) together with a crop from the mother liquor through chromatographic purification [silica gel, hexane–EtOAc–CH_2Cl_2 (4 : 2 : 1)]. Colourless solids; mp 239.2–240.5 °C (Found: M^+, 421.1226. $C_{27}H_{20}NO_2P$ requires *M*, 421.1229); ν_{max}(KBr)/cm^{-1} 1692 (C=O), 1532 and 1382; δ_H (270 MHz) 5.09 (1H, s, 3-H), 7.25 (1H, d, *J* 7.59, 8-H), 7.28 (1H, ddd, *J* 8.91, 7.59 and 1.32, 7-H), 7.43–7.85 (16H, m, Ph-H, 6-H) and 8.40 (1H, dd, *J* 7.91 and 1.32, 5-H); *m*/*z* 421 (M^+, 74%), 393 (10, $M^+ - CO$), 302 (16), 277 (10) and 185 (100, Ph_2P^+).

Preparation of *N*-vinylcarbodiimides 3–5. General procedure

To a dry benzene solution (50 cm^3) of iminophosphoranes **1** (5.27 mmol) was added dropwise a benzene solution (50 cm^3) of isocyanates **2** (5.83 mmol). The reaction mixture was stirred at room temperature for 1–2 h (R^1 = aryl, β-styryl) or for 1–2 d (R^1 = alkyl). Evaporation of the solvent and trituration of the residue with hexane afforded triphenylphosphine as colourless crystals. Removal of the solvent from the filtrate and short column chromatography of the residue [silica gel, benzene–hexane (1 : 5) as an eluent] gave the carbodiimides **3**–**5** as viscous oils or a solid (for **3d**) in good yields, which were immediately used in the next reaction. Further purification by distillation under reduced pressure failed.

***N*-Phenyl-*N′*-(1,2-diphenylvinyl)carbodiimide 3a.** Colourless oil (80% yield); ν_{max}(NaCl)/cm^{-1} 2130 (N=C=N); δ_H (60 MHz) 6.37 (1H, s, =CH) and 6.96–7.87 (15H, m, ArH); *m*/*z* 296 (M^+, 72%), 295 (88, $M^+ - 1$), 219 (8, $M^+ - Ph$) and 178 (100).

***N*-(1,2-Diphenylvinyl)-*N′*-(*p*-tolyl)carbodiimide 3b.** Colourless oil (97% yield); ν_{max}(NaCl)/cm^{-1} 2130 (N=C=N); δ_H 2.27 (3H, s, CH_3), 6.33 (1H, s, =CH) and 6.95–7.87 (14H, m, ArH); *m*/*z* 310 (M^+, 71%), 309 (75, $M^+ - 1$) and 178 (100).

***N*-(*p*-Methoxyphenyl)-*N′*-(1,2-diphenylvinyl)carbodiimide 3c.** Colourless oil (70% yield); ν_{max}(NaCl)/cm^{-1} 2130 (N=C=N); δ_H 3.76 (3H, s, OCH_3), 6.36 (1H, s, =CH) and 6.63–7.96 (14H, m, ArH).

***N*-(*p*-Chlorophenyl)-*N′*-(1,2-diphenylvinyl)carbodiimide 3d.** Colourless solid (75% yield), mp 103 °C; ν_{max}(NaCl)/cm^{-1} 2130 (N=C=N); δ_H 6.33 (1H, s, =CH) and 6.65–7.87 (14H, m, ArH).

***N*-Cyclohexyl-*N′*-(1,2-diphenylvinyl)carbodiimide 3e.** Colourless oil (86% yield); ν_{max}(NaCl)/cm^{-1} 2140 (N=C=N); δ_H 0.90–1.93 [10H, m, $(CH_2)_5$], 3.33 (1H, br s, CH), 6.12 (1H, s, =CH) and 7.10–7.83 (10H, m, ArH); *m*/*z* 302 (M^+, 30%), 220 (10, M^+ − c-Hex + 1) and 178 (100).

***N*-Methyl-*N′*-(1,2-diphenylvinyl)carbodiimide 3f.** Colourless oil (51% yield); ν_{max}(NaCl)/cm^{-1} 2130 (N=C=N); δ_H 2.68 (3H, s, NCH_3), 6.15 (1H, s, =CH) and 7.0–7.9 (10H, m, ArH).

***N*-Phenyl-*N′*-[1-phenyl-2-(*p*-tolyl)vinyl]carbodiimide 3g.** Colourless oil (90% yield); ν_{max}(NaCl)/cm^{-1} 2130 (N=C=N); δ_H 2.33 (3H, s, CH_3), 6.33 (1H, s, =CH) and 6.69–7.83 (14H, m, ArH).

***N*-[1-Phenyl-2-(*p*-tolyl)vinyl]-*N′*-(*p*-tolyl)carbodiimide 3h.** Colourless oil (94% yield); ν_{max}(NaCl)/cm^{-1} 2120 (N=C=N); δ_H 2.17 and 2.27 (3H, s, CH_3), 6.27 (1H, s, =CH) and 6.80–7.80 (13H, m, ArH).

***N*-(*p*-Methoxyphenyl)-*N′*-[1-phenyl-2-(*p*-tolyl)vinyl]carbodiimide 3i.** Colourless oil (75% yield); ν_{max}(NaCl)/cm^{-1} 2130 (N=C=N); δ_H 2.26 (3H, s, CH_3), 3.59 (3H, s, OCH_3), 6.25 (1H, s, =CH) and 6.46–7.86 (13H, m, ArH).

***N*-(*p*-Chlorophenyl)-*N′*-[1-phenyl-2-(*p*-tolyl)vinyl]carbodiimide 3j.** Colourless oil (70% yield); ν_{max}(NaCl)/cm^{-1} 2140 (N=C=N); δ_H 2.30 (3H, s, CH_3), 6.37 (1H, s, =CH) and 6.73–7.79 (13H, m, ArH).

***N*-Cyclohexyl-*N′*-[1-phenyl-2-(*p*-tolyl)vinyl]carbodiimide 3k.** Colourless oil (94% yield); ν_{max}(NaCl)/cm^{-1} 2130 (N=C=N); δ_H 0.9–2.0 [10H, m, $(CH_2)_5$], 2.35 (3H, s, CH_3), 3.30 (1H, br s, CH), 6.07 (1H, s, =CH) and 6.93–7.80 (9H, m, ArH).

***N*-Methyl-*N′*-[1-phenyl-2-(*p*-tolyl)vinyl]carbodiimide 3l.** Colourless oil (70% yield); ν_{max}(NaCl)/cm^{-1} 2130 (N=C=N); δ_H 2.27 (3H, s, CH_3), 2.91 (3H, s, NCH_3), 6.12 (1H, s, =CH) and 6.97–7.79 (9H, m, ArH).

***N*-(*p*-Tolyl)-*N′*-(2-phenylvinyl)carbodiimide 4b.** Colourless oil (65% yield); ν_{max}(NaCl)/cm^{-1} 2140 (N=C=N) and 1650 (C=C); δ_H 2.27 (3H, s, CH_3), 6.43 (1H, d, *J* 13.4, =CH), 6.92 (1H, d, *J* 13.4, =CH), 7.03 (4H, br s, TolH) and 7.20 (5H, br s, PhH); *m*/*z* 234 (M^+, 53%) and 233 ($M^+ - 1$, 100).

***N*-Phenyl-*N′*-(1-phenylvinyl)carbodiimide 5a.**[8] Colourless oil (87% yield); ν_{max}(NaCl)/cm^{-1} 2148 (N=C=N); δ_H 5.10 (1H, d, *J* 3.0, $=CH_2$), 5.27 (1H, d, *J* 3.0, $=CH_2$) and 6.95–7.65 (10H, m, PhH).

***N*-(1-Phenylvinyl)-*N′*-(*p*-tolyl)carbodiimide 5b.** Colourless oil (77% yield); ν_{max}(NaCl)/cm^{-1} 2140 (N=C=N); δ_H 2.40 (3H, s, Me), 5.10 (1H, d, *J* 2.2, $=CH_2$), 5.26 (1H, d, *J* 2.0, $=CH_2$) and 6.80–7.70 (9H, m, ArH).

***N*-Cyclohexyl-*N′*-(1-phenylvinyl)carbodiimide 5c.** Colourless oil (68% yield); ν_{max}(NaCl)/cm^{-1} 2936 (CH_2) and 2136 (N=C=N); δ_H 1.00–3.70 (11H, m, c-Hex-H), 5.00 (1H, br s, $=CH_2$), 5.20 (1H, br s, $=CH_2$) and 7.2–7.8 (5H, m, PhH).

***N*-Phenyl-*N′*-[1-(*p*-tolyl)vinyl]carbodiimide 5d.** Colourless oil (78% yield); ν_{max}(NaCl)/cm^{-1} 2140 (N=C=N); δ_H 2.3 (3H, s, Me), 5.1 (1H, d, *J* 2.0, $=CH_2$), 5.3 (1H, d, *J* 2.0, $=CH_2$) and 7.0–7.6 (9H, m, ArH).

***N*-*p*-Tolyl-*N′*-[1-(*p*-tolyl)vinyl]carbodiimide 5e.** Colourless oil (81% yield); ν_{max}(NaCl)/cm^{-1} 2140 (N=C=N); δ_H 2.3 (3H, s, Me), 2.4 (3H, s, Me), 5.1 (1H, d, *J* 2.0, $=CH_2$), 5.3 (1H, d, *J* 2.0, $=CH_2$) and 6.7–7.6 (8H, m, ArH).

***N*-Cyclohexyl-*N′*-(1-*p*-tolylvinyl)carbodiimide 5f.** Colourless oil (68% yield); ν_{max}(NaCl)/cm^{-1} 2936 (CH_2) and 2136 (N=C=N); δ_H 0.9–3.7 (11H, m, c-Hex-H), 2.3 (3H, s, Me), 5.0 (1H, br s, $=CH_2$), 5.2 (1H, br s, $=CH_2$) and 6.9–7.8 (4H, m, ArH).

Electrocyclisation of *N*-vinylcarbodiimides 3 leading to isoquinolines 7. General procedure

A solution of carbodiimide **3** (2.0 mmol) in xylene (20 cm^3) was heated under reflux for 2 h (for R^1 = aryl) or 7–10 h (for R^1 = alkyl) until **3** had been consumed (monitored by TLC). After being cooled, the solvent was evaporated and the residue was column-chromatographed on silica gel using benzene–hexane as an eluent to give isoquinoline **7**, which was recrystallised from benzene–hexane.

3-Phenyl-1-(phenylamino)isoquinoline 7a. Colourless crystals (81% yield); mp 104–105 °C (Found: C, 85.41; H, 5.59; N, 9.45%. $C_{21}H_{16}N_2$ requires C, 85.11; H, 5.44; N, 9.45%); ν_{max}(KBr)/cm^{-1} 3450 (NH) and 1630; δ_H (100 MHz) 6.92–7.92 (14H, m, ArH and NH) and 7.92–8.16 (2H, m, ArH); δ_C (25 MHz) 109.16, 117.83, 119.78, 121.14, 122.26, 126.21, 126.65, 127.92, 128.20, 128.50, 128.74, 129.87, 138.25, 139.66, 140.48, 148.73 and 151.40; *m*/*z* 296 (M^+, 69%), 295 (100, $M^+ - 1$) and 203 (79, $M^+ - PhNH_2$).

3-Phenyl-1-(*p*-tolylamino)isoquinoline 7b. Colourless needles (80% yield); mp 112–115 °C (Found: C, 84.93; H, 5.82; N, 9.01%. $C_{22}H_{18}N_2$ requires C, 85.13; H, 5.85; N, 9.02%); ν_{max}(KBr)/cm^{-1} 3460 (NH) and 1630; δ_H 2.29 (3H, s, CH_3), 6.94 (1H, s, NH), 6.98–7.68 (12H, m, ArH) and 7.95–8.12 (2H, m, ArH); δ_C 20.76 (CH_3), 108.72 (C-4), 117.68 (C-8a), 119.97 (C-2′), 121.09, 125.92, 126.60, 122.72, 128.06, 128.40, 129.18, 129.62, 131.58, 137.86, 138.10, 139.76 (C-1′), 148.58 (C-3) and 151.45 (C-1); *m*/*z* 310 (M^+, 100%), 233 (3, $M^+ - Ph$) and 204 (79, $M^+ - TolNH$).

3-Phenyl-1-(*p*-methoxyphenylamino)isoquinoline 7c. Colourless needles (75% yield); mp 152 °C (Found: C, 80.99; H, 5.50; N, 9.00%. $C_{22}H_{18}N_2O$ requires C, 80.95; H, 5.56; N, 8.58%); ν_{max}(KBr)/cm^{-1} 3420 (NH) and 1630; δ_H 3.81 (3H, s, OCH_3), 6.92 (2H, d, *J* 8.1, ArH), 7.00–7.91 (12H, m, ArH and NH) and 8.07 (1H, dd, *J* 8.1 and 1.0); δ_C 55.55 (OCH_3), 108.57 (C-4), 114.03 (C-2′), 117.64 (C-8a), 121.24 (C-5), 122.02 (C-2″), 126.06 (C-4″), 126.65 (C-7), 127.87 (C-8), 128.16 (C-3″), 128.45 (C-3′), 129.82 (C-6), 133.72 (C-4a), 138.29 (C-1″), 139.76 (C-1′), 148.77 (C-3), 151.89 (C-4′) and 155.30 (C-1); *m*/*z* 326 (M^+, 100%), 325 (47, $M^+ - 1$) and 311 (77, $M^+ - CH_3$).

3-Phenyl-1-(*p*-chlorophenylamino)isoquinoline 7d. Colourless needles (86% yield); mp 153 °C (Found: C, 76.13; H, 4.61; N, 8.55%. $C_{21}H_{15}N_2Cl$ requires C, 76.24; H, 4.57; N, 8.47%); ν_{max}(KBr)/cm^{-1} 3460 (NH) and 1630; δ_H 7.04 (1H, br s, NH), 7.15–7.76 (12H, m, ArH) and 7.86–8.16 (2H, m, ArH); δ_C 109.45 (C-4), 117.68 (C-8a), 121.00, 126.31, 126.60, 126.84, 127.92, 128.31, 128.55, 128.65, 129.96, 138.20 (C-1″), 139.03 (C-1′), 139.51 (C-4′), 148.53 (C-3) and 151.01 (C-1); *m*/*z* 330 (^{35}Cl) (M^+, 82%), 329 (100, $M^+ - 1$) and 294 (12).

3-Phenyl-1-(cyclohexylamino)isoquinoline 7e. Colourless needles (57% yield); mp 116–117 °C (Found: C, 83.23; H, 7.30; N, 9.22%. $C_{21}H_{22}N_2$ requires C, 83.40; H, 7.33; N, 9.26%); ν_{max}(KBr)/cm^{-1} 3470 (NH) and 1630; δ_H 1.00–2.20 [10H, m, $(CH_2)_5$], 4.28 (1H, br s, CH), 5.00 (1H, d, *J* 4.0, NH), 7.04–7.84 (8H, m, ArH) and 8.02–8.16 (2H, m, ArH); δ_C 25.14 (CH_2), 26.02 (CH_2), 33.19 (CH_2), 49.66 (CH), 106.08 (C-4), 117.20, 121.10, 125.24, 126.50, 127.53, 127.87, 128.31, 129.33, 137.95, 140.24, 148.87 (C-3) and 153.74 (C-1); *m*/*z* 302 (M^+, 21%), 220 (100, $M^+ - C_6H_{11} + 1$) and 204 (14, $M^+ - C_6H_{11}NH$).

3-Phenyl-1-(methylamino)isoquinoline 7f. Colourless crystals (40% yield); mp 105–106 °C (Found: C, 82.30; H, 6.15; N, 12.01%. $C_{16}H_{14}N_2$ requires C, 82.02; H, 6.02; N, 11.96%); ν_{max}(KBr)/cm^{-1} 3475 (NH) and 1625; δ_H 3.18 (3H, d, *J* 4.0, NCH_3), 5.12 (1H, br s, NH), 7.08–7.72 (8H, m, ArH) and 8.00–8.28 (2H, m, ArH); δ_C 28.65 (CH_3), 106.47 (C-4), 117.44 (C-8a), 121.24 (C-5), 125.38 (C-2′), 126.60 (C-4′), 127.53 (C-7), 127.96 (C-8), 128.35 (C-3′), 129.48 (C-6), 137.76 (C-3a), 140.20 (C-1′), 148.87 (C-3) and 155.21 (C-1); *m*/*z* 234 (M^+, 100%), 233 (58, $M^+ - 1$) and 204 (76, $M^+ - CH_3NH$).

7-Methyl-3-phenyl-1-(phenylamino)isoquinoline 7g. Colourless needles (73% yield); mp 118 °C (Found: C, 85.46; H, 5.77; N, 9.16%. $C_{22}H_{18}N_2$ requires C, 85.13; H, 5.85; N, 9.02%); ν_{max}(KBr)/cm^{-1} 3450 (NH) and 1630; δ_H 2.40 (3H, s, CH_3) and 6.90–8.20 (15H, m, ArH and NH); *m*/*z* 310 (M^+, 73%), 309 (100, $M^+ - 1$) and 295 (3, $M^+ - CH_3$).

7-Methyl-3-phenyl-1-(*p*-tolylamino)isoquinoline 7h. Colourless needles (70% yield); mp 112–114 °C (Found: C, 84.99; H, 6.25; N, 8.71%. $C_{23}H_{20}N_2$ requires C, 85.14; H, 6.21; N, 8.64%); ν_{max}(KBr)/cm^{-1} 3460 (NH) and 1640; δ_H 2.32 (3H, s, CH_3), 2.42 (3H, s, CH_3), 6.92 (1H, br s, NH) and 7.0–8.12 (13H, m, ArH); δ_C 20.76 (CH_3), 21.83 (CH_3), 108.57 (C-4), 117.73 (C-8a), 119.78, 120.22, 126.50, 127.58, 127.87, 128.35, 129.13, 131.32, 131.62, 135.86, 136.15, 138.01, 139.85 (C-1′), 147.60 (C-3) and 150.92 (C-1); *m*/*z* 324 (M^+, 81%), 323 (100, $M^+ - 1$) and 218 (5, $M^+ - TolNH$).

7-Methyl-3-phenyl-1-(*p*-methoxyphenylamino)isoquinoline 7i. Colourless needles (73% yield); mp 107 °C (Found: C, 81.40; H, 5.95; N, 8.33%. $C_{23}H_{20}N_2O$ requires C, 81.14; H, 5.92; N, 8.23%); ν_{max}(KBr)/cm^{-1} 3450 (NH) and 1635; δ_H 2.30 (3H, s, CH_3), 3.66 (3H, s, OCH_3), 6.70–7.76 (12H, m, ArH and NH) and 7.89–8.33 (2H, m, ArH); *m*/*z* 340 (M^+, 100%), 339 (47, $M^+ - 1$), 325 (70, $M^+ - CH_3$) and 218 (23, $M^+ - CH_3OPhNH$).

7-Methyl-3-phenyl-1-(*p*-chlorophenylamino)isoquinoline 7j. Colourless crystals (42% yield); mp 150 °C (Found: C, 76.74; H, 4.98; N, 8.16%. $C_{22}H_{17}N_2Cl$ requires C, 76.62; H, 4.97; N, 8.13%); ν_{max}(KBr)/cm^{-1} 3460 (NH) and 1630; δ_H 2.50 (3H, s, CH_3), 7.00 (1H, br s, NH), 7.16–7.80 (11H, m, ArH) and 7.90–8.08 (2H, m, ArH); *m*/*z* 344 (^{35}Cl) (M^+, 90%), 343 (100, $M^+ - 1$) and 307 (12).

7-Methyl-3-phenyl-1-(cyclohexylamino)isoquinoline 7k. Colourless needles (67% yield); mp 120–123 °C (Found: C, 83.55; H, 7.71; N, 8.88%. $C_{22}H_{24}N_2$ requires C, 83.50; H, 7.65; N, 8.85%); ν_{max}(KBr)/cm^{-1} 3460 (NH) and 1630; δ_H 1.00–2.40 [10H, m, $(CH_2)_5$], 2.44 (3H, s, CH_3), 4.30 (1H, br s, CH), 4.98 (1H, d, *J* 4.0, NH), 7.16–7.55 (7H, m, ArH) and 8.00–8.20 (2H, m, ArH); δ_C 21.78 (CH_3), 25.19 (CH_2), 26.12 (CH_2), 33.33 (CH_2), 49.70 (CH), 106.08, 117.34, 120.41, 126.41, 127.43, 127.67, 128.31, 131.28, 135.02 (C-7), 136.00 (C-4a), 140.39 (C-1″), 147.99 (C-3) and 153.35 (C-1); *m*/*z* 316 (M^+, 23%), 234 (100, $M^+ - C_6H_{11}$) and 218 (10, $M^+ - C_6H_{11}NH$).

7-Methyl-3-phenyl-1-(methylamino)isoquinoline 7l. Colourless crystals (64% yield); mp 70–71 °C (Found: C, 82.28; H, 6.45; N, 11.21%. $C_{17}H_{16}N_2$ requires C, 82.22; H, 6.49; N, 11.28%); ν_{max}(KBr)/cm^{-1} 3430 (NH) and 1625; δ_H 2.36 (3H, s, CH_3), 3.14 (3H, d, *J* 4.0, NCH_3), 5.04 (1H, br s, NH), 7.15–7.55 (7H, m, ArH) and 8.04–8.20 (2H, m, ArH); δ_C 21.64 (CH_3), 28.60 (NCH_3), 106.33 (C-4), 117.49 (C-8a), 120.51, 126.45, 127.23, 127.72, 128.26, 131.32, 135.13 (C-7), 135.67 (C-4a), 140.24 (C-1″), 147.80 (C-3) and 154.71 (C-1); *m*/*z* 248 (M^+, 100%), 247 (62, $M^+ - 1$) and 218 (32, $M^+ - CH_3NH$).

Cycloaddition of carbodiimide 3 with tetracyanoethylene (TCNE). General procedure

A solution of carbodiimide **3** (2.0 mmol) and TCNE (2.2 mmol) in acetonitrile (10 cm^3) was stirred at room temperature for 1–11 h. Removal of the solvent *in vacuo* and column chromatography of the residue on silica gel using CH_2Cl_2–hexane as an eluent afforded the cycloadduct **8** and/or its isomer **9** as yellow needles or fine crystals after recrystallization from CH_2Cl_2–Et_2O–hexane. In the case of carbodiimide **3j**, neither compound **8j** nor compound **9j** was obtained due to the low reactivity of **3j** under the conditions.

3,3,4,4-Tetracyano-5,6-diphenyl-2-(phenylimino)-2,3,4,5-tetrahydropyridine 8a. (25% yield) mp 162 °C (decomp.) (Found: C, 76.34; H, 3.91; N, 19.95%. $C_{27}H_{16}N_6$ requires C, 76.40; H, 3.80; N, 19.80%); ν_{max}(KBr)/cm^{-1} 2240 (CN) and 1585 (C=N); δ_H (100 MHz) 4.84 (1H, s, CH) and 7.12–7.88 (15H, m, PhH); δ_C (25 MHz) 28.47 (C-5), 84.36, 108.55 (CN), 108.73, 111.49, 114.19, 117.36, 126.70, 129.28, 129.40, 129.69, 130.04, 130.16, 130.51, 130.69, 131.39, 131.92, 132.04, 135.74, 170.03 (C-6) and 180.83 (C-2); *m*/*z* 424 (M^+, 2%), 397 (67, $M^+ - HCN$) and 77 (100, Ph^+).

3,3,4,4-Tetracyano-5,6-diphenyl-2-(phenylamino)-3,4-dihydropyridine 9a. (41% yield) mp 183 °C (decomp.) ν_{max}(KBr)/cm^{-1} 3430 (NH), 2240 (CN) and 1670 (C=N); δ_H 6.65–7.55 (16H, m, PhH, NH); δ_C 88.12, 92.82, 109.55, 113.13, 115.25, 116.48, 122.06, 123.58, 124.11, 127.22, 128.34, 129.16, 129.52, 129.92, 130.69, 132.33, 133.63, 135.39, 137.27, 144.60, 152.41 and 164.50; *m*/*z* 424 (M^+, 1%), 396 (76, $M^+ - HCN - 1$) and 77 (100, Ph^+).

3,3,4,4-Tetracyano-5,6-diphenyl-2-(*p*-tolylimino)-2,3,4,5-tetrahydropyridine 8b. (71% yield) mp 198 °C (decomp.) (Found: C, 76.43; H, 4.18; N, 19.54%. $C_{28}H_{18}N_6$ requires C, 76.69; H, 4.14; N, 19.17%); ν_{max}(KBr)/cm^{-1} 2235 (CN) and 1585; δ_H 2.36 (3H, s, CH_3), 4.76 (1H, s, CH) and 7.12–7.88 (14H, m, PhH); δ_C 21.44 (CH_3), 28.41 (C-5), 84.25, 108.52 (CN), 108.77 (CN), 126.67, 127.33, 127.87, 129.23, 130.15, 130.45, 130.84, 130.93, 131.42, 131.81, 135.61, 142.63, 170.08 (C-6) and 180.69 (C-2); *m*/*z* 438 (M^+, vw), 411 (50%, $M^+ - HCN$) and 77 (100, Ph^+).

3,3,4,4-Tetracyano-5,6-diphenyl-2-(*p*-methoxyphenylimino)-2,3,4,5-tetrahydropyridine 8c. (63% yield) mp 202 °C (decomp.) (Found: C, 74.03; H, 4.00; N, 18.55%. $C_{28}H_{18}N_6O$ requires C, 73.99; H, 3.99; N, 18.49%); ν_{max}(KBr)/cm^{-1} 2230 (CN) and 1590 (C=N); δ_H 3.78 (3H, s, OCH_3), 4.87 (1H, s, 5-H) and 6.88–7.92 (14H, m, ArH); δ_C 28.41 (C-5), 55.60 (OCH_3), 84.30, 108.67, 108.86, 111.74, 114.42 (CN), 115.10, 115.64, 122.70, 126.70, 127.38, 129.23, 130.06, 130.45, 130.69, 130.89, 131.38, 131.81, 135.67, 161.98, 170.46 (C-6) and 180.93 (C-2); *m*/*z* 454 (M^+, vw) and 427 (100%, $M^+ - HCN$).

3,3,4,4-Tetracyano-5,6-diphenyl-2-(*p*-chlorophenylimino)-2,3,4,5-tetrahydropyridine 8d. (60% yield) mp 190 °C (decomp.) (Found: C, 70.55; H, 3.41; N, 18.44%. $C_{27}H_{15}N_6Cl$ requires C, 70.65; H, 3.30; N, 18.32%); ν_{max}(KBr)/cm^{-1} 2230 (CN) and 1580 (C=N); δ_H 4.96 (1H, s, 5-H) and 7.00–7.88 (14H, m, ArH); δ_C 28.60 (C-5), 84.40, 108.57, 108.67, 111.59, 114.08, 126.65, 127.04, 129.18, 129.33, 129.76, 130.45, 130.60, 131.08, 131.38, 132.06, 135.86, 138.29, 170.07 (C-6) and 181.03 (C-2); *m*/*z* 458 (^{35}Cl) (M^+, vw), 431 (97%, $M^+ - HCN$) and 430 (100, $M^+ - HCN - 1$).

3,3,4,4-Tetracyano-5,6-diphenyl-2-(cyclohexylimino)-2,3,4,5-tetrahydropyridine 8e. (60% yield) mp 200 °C (decomp.) (Found: C, 75.30; H, 5.22; N, 19.61%. $C_{27}H_{22}N_6$ requires C, 75.33; H, 5.15; N, 19.52%); ν_{max}(KBr)/cm^{-1} 2230 (CN) and 1580 (C=N); δ_H 0.88–2.00 [10H, m, $(CH_2)_5$], 3.36 (1H, br s, CH), 5.18 (1H, s, 5-H) and 7.24–7.60 (10H, m, ArH); δ_C 23.20, 25.49, 28.99, 31.09, 56.58, 85.10, 108.42, 109.20, 115.73, 117.44, 168.61 and 179.86 (C-2); *m*/*z* 430 (M^+, 2%), 403 (33, $M^+ -$ HCN) and 321 (100, $M^+ - CN - C_6H_{11}$).

3,3,4,4-Tetracyano-5,6-diphenyl-2-(methylimino)-2,3,4,5-tetrahydropyridine 8f. (69% yield) mp 187 °C (decomp.) (Found: C, 72.50; H, 3.98; N, 23.55%. $C_{22}H_{14}N_6$ requires C, 72.91; H, 3.89; N, 23.19%); ν_{max}(KBr)/cm^{-1} 2225 (CN) and 1600 (C=N); δ_H (DMSO-d_6–$CDCl_3$) 3.24 (3H, s, NCH_3), 4.54 (1H, s, 5-H) and 7.28–7.84 10H, m, PhH); δ_C (DMSO-d_6–$CDCl_3$) 30.53 (NCH_3, C-5), 84.07, 126.70, 127.17, 128.81, 129.05, 130.39, 130.69, 130.92, 131.33, 135.15 and 182.06 (C-2); *m*/*z* 362 (M^+, 1%), 335 (73, $M^+ - HCN$) and 334 (100, $M^+ - HCN - 1$).

3,3,4,4-Tetracyano-6-phenyl-5-(*p*-tolyl)-2-(phenylimino)-2,3,4,5-tetrahydropyridine 8g. (62% yield) mp 135 °C (decomp.) (Found: C, 76.86; H, 3.92; N, 19.22%. $C_{28}H_{18}N_6$ requires C, 76.69; H, 4.14; N, 19.17%); ν_{max}(KBr)/cm^{-1} 2220 (CN) and 1580 (C=N); δ_H 2.36 (3H, s, CH_3), 5.18 (1H, s, 5-H) and 6.92–7.96 (14H, m, ArH); δ_C 21.34 (CH_3), 28.60 (C-5), 84.45, 108.72, 108.86, 111.64, 114.42 (CN), 126.60, 126.70, 129.18, 129.43, 129.67, 131.08, 131.38, 133.86, 135.67, 141.02, 142.53, 144.83, 170.07 (C-6) and 181.22 (C-2); *m*/*z* 438 (M^+, vw), 411 (97%, $M^+ - HCN$) and 410 (100, $M^+ - HCN - 1$).

3,3,4,4-Tetracyano-6-phenyl-5-(*p*-tolyl)-2-(*p*-tolylimino)-2,3,4,5-tetrahydropyridine 8h. (60% yield) mp 163–166 °C (decomp.) (Found: C, 76.96; H, 4.59; N, 18.88%. $C_{29}H_{20}N_6$ requires C, 76.97; H, 4.46; N, 18.57%); ν_{max}(KBr)/cm^{-1} 2230 (CN) and 1590 (C=N); δ_H 2.36 (3H, s, CH_3), 2.46 (3H, s, CH_3), 4.78 (1H, s, 5-H) and 6.86–7.88 (13H, m, ArH); δ_C 21.39 (CH_3), 28.49 (C-5), 84.30, 108.67, 108.86, 111.69, 114.42, 126.60, 126.89, 127.43, 127.96, 128.31, 129.18, 130.84, 131.03, 131.38, 135.56, 142.53, 170.07 (C-6) and 180.98 (C-2); *m*/*z* 452 (M^+, vw) and 425 (100%, $M^+ - HCN$).

3,3,4,4-Tetracyano-6-phenyl-5-(*p*-tolyl)-2-(*p*-methoxyphenylimino)-2,3,4,5-tetrahydropyridine 8i. (60% yield) mp 163 °C (decomp.) (Found: C, 73.92; H, 4.21; N, 18.35%. $C_{29}H_{20}N_6O$ requires C, 74.34; H, 4.30; N, 17.94%); ν_{max}(KBr)/cm^{-1} 2220 (CN) and 1590 (C=N); δ_H 2.46 (3H, s, CH_3), 3.78 (3H, s, OCH_3), 4.82 (1H, s, 5-H), 6.88–7.92 (13H, m, ArH); δ_C 21.34 (CH_3), 28.41 (C-5), 55.56 (OCH_3), 84.21, 108.72, 108.87, 111.79, 114.47, 114.95 (C-3′), 122.75, 126.55, 126.84, 129.13, 130.69, 130.84, 130.99, 131.32, 135.52, 142.39, 161.88, 170.36 (C-6) and 180.98 (C-2); *m*/*z* 468 (M^+, vw), 441 (100%, $M^+ - HCN$) and (90, $M^+ - HCN - 1$).

3,3,4,4-Tetracyano-6-phenyl-5-(*p*-tolyl)-2-(cyclohexylimino)-2,3,4,5-tetrahydropyridine 9k. (67% yield) mp 97–99 °C (decomp.) (Found: C, 75.25; H, 5.40; N, 19.05%. $C_{28}H_{24}N_6$ requires C, 75.65; H, 5.44; N, 18.91%); ν_{max}(KBr)/cm^{-1} 3250 (NH), 2220 (CN) and 1580; δ_H 1.0–2.0 [10H, $(CH_2)_5$], 2.44 (3H, s, CH_3), 3.38 (1H, br s, CH), 6.14 (1H, br s, NH) and 7.16–7.76 (9H, m, ArH); δ_C 21.83 (CH_3), 24.46 (CH_2), 24.75 (CH_2), 32.94 (CH_2), 53.90 (CH), 111.93, 115.00, 115.20, 128.35, 128.98, 129.33, 129.76, 130.45, 132.45, 134.44, 145.70, 167.77, 168.02 (C-6) and 168.94 (C-2); *m*/*z* 444 (M^+, 16), 417 (16, $M^+ - HCN$), 335 (47) and 55 (100).

3,3,4,4-Tetracyano-6-phenyl-5-(*p*-tolyl)-2-(methylimino)-2,3,4,5-tetrahydropyridine 8l. (67% yield) mp 174–176 °C (decomp.) (Found: C, 72.98; H, 4.31; N, 22.51%. $C_{23}H_{16}N_6$ requires C, 73.39; H, 4.28; N, 22.33%); ν_{max}(KBr)/cm^{-1} 2240 (CN) and 1590 (C=N); δ_H 2.37 (3H, s, CH_3), 3.16 (3H, s, NCH_3), 4.38 (1H, s, 5-H) and 7.2–7.85 (9H, m, ArH); δ_C 20.71 (CH_3), 29.73 (NCH_3, C-5), 84.99, 95.41, 115.00, 115.44, 126.55, 127.04, 127.23, 129.09, 130.06, 130.54, 135.03, 140.87, 169.53 (C-6) and 183.45 (C-2); *m*/*z* 376 (M^+, 3%), 349 (76, $M^+ - HCN$) and 348 (100, $M^+ - HCN - 1$).

Cycloaddition of carbodiimides 3 with tosyl isocyanate. General procedure

Method A. A benzene solution (20 cm^3) of **3** (2.0 mmol) and tosyl isocyanate (3.0 mmol) was heated under reflux for 15–30 h. Evaporation of the solvent and column chromatography of the residue on silica gel using benzene–CH_2Cl_2 (10 : 1–2 : 1) as an eluent, followed by recrystallization from benzene–hexane gave oxazine **10**.

Method B. A mixture of **3** (2.0 mmol) and tosyl isocyanate (3.0 mmol) in dry acetonitrile (20 cm^3) was stirred at room temperature for 5 d (for R^1 = cyclohexyl) or 10–17 d (for R^1 = aryl). The solvent was removed *in vacuo* and the residue was column-chromatographed [silica gel, benzene–CH_2Cl_2 as eluent] gave crude pyrimidine **11**, which was recrystallised from benzene–hexane.

4,5-Diphenyl-2-(phenylamino)-6-(tosylimino)-6*H*-1,3-oxazine 10a. Colourless crystals (12% yield); mp 204–206 °C (Found: C, 70.65; H, 4.72; N, 8.51%. $C_{29}H_{23}N_3O_3S$ requires C, 70.58; H, 4.70; N, 8.52%); ν_{max}(KBr)/cm^{-1} 3380 (NH) 1600 and 1520 (C=N); δ_H (100 MHz) 2.37 (3H, s, CH_3), 7.66 (2H, d, *J* 8.5) and 6.95–7.57 (18H, m, ArH and NH); δ_C (25 MHz) 21.69 (CH_3), 114.39, 119.55, 123.00, 127.50, 127.84, 128.18, 128.42, 128.91, 129.25, 129.50, 129.69, 130.91, 132.57, 134.08, 137.54, 138.80, 145.04, 157.81, 162.44 (C=N) and 168.63 (C=N); *m*/*z* 493 (M^+, 100%), 428 (43, $M^+ - SO_2H$) and 338 (79, $M^+ -$ Ts).

4,5-Diphenyl-2-(*p*-tolylamino)-6-(tosylimino)-6*H*-1,3-oxazine 10b. Colourless crystals (18% yield); mp 240–242 °C (Found: C, 71.11; H, 5.01; N, 8.22%. $C_{30}H_{25}N_3O_3S$ requires C, 70.99; H, 4.97; N, 8.28%); ν_{max}(KBr)/cm^{-1} 3400 (NH) 1600 and 1520 (C=N); δ_H 2.34 (3H, s, CH_3), 2.41 (3H, s, CH_3) and 6.99–7.81 (19H, m, ArH and NH); δ_C 20.90 (CH_3), 21.70 (CH_3), 119.80, 125.94, 126.47, 127.45, 127.84, 128.18, 128.42, 129.25, 129.45, 129.64, 129.93, 130.91, 131.20, 132.62, 134.13, 136.22, 137.64, 145.00, 158.00 (C=N) and 168.44 (C=N); *m*/*z* 507 (M^+, 100%), 442 (28, $M^+ - SO_2H$) and 352 (92, $M^+ -$ Ts).

2-(*p*-Methoxyphenylamino)-4,5-diphenyl-6-(tosylimino)-6*H*-1,3-oxazine 10c. Pale yellow crystals (20% yield); mp 220–222 °C (Found: C, 68.85; H, 4.82; N, 8.12%. $C_{30}H_{25}N_3O_4S$ requires C, 68.82; H, 4.81; N, 8.03%); ν_{max}(KBr)/cm^{-1} 3400 (NH) 1600 and 1510 (C=N); δ_H 2.36 (3H, s, CH_3), 3.80 (3H, s, OCH_3), 6.83 (2H, d, *J* 8.1), 6.92–7.45 (15H, m, ArH and NH) and 7.62 (2H, d, *J* 8.1); δ_C 21.68 (CH_3), 55.56 (CH_3), 114.19, 121.84, 127.84, 128.18, 128.47, 128.76, 129.20, 129.45, 129.64, 131.00, 131.93, 132.71, 134.13, 137.68, 144.95, 155.91, 158.20, 162.54 (C=N) and 168.63 (C=N); *m*/*z* 523 (M^+, 22%), 458 (4, $M^+ - SO_2H$) and 91 (100, Ph^+).

2-(Cyclohexylamino)-4,5-diphenyl-6-(tosylimino)-6*H*-1,3-oxazine 10d. Slightly yellowish crystals (40% yield); mp 176–178 °C (Found: C, 69.47; H, 5.78; N, 8.40%. $C_{29}H_{29}N_3O_3S$ requires C, 69.72; H, 5.85; N, 8.41%); ν_{max}(KBr)/cm^{-1} 3400 (NH) 1605 and 1550 (C=N); δ_H 1.0–2.2 [10H, m, $(CH_2)_5$], 2.44 (3H, s, CH_3), 3.62 (1H, br s, CH), 5.20 (1H, d, *J* 8.0, NH), 6.8–7.4 12H, m, ArH) and 7.80 (2H, d, *J* 8.0, ArH); δ_C 21.64 (CH_3), 24.76 (CH_2), 25.64 (CH_2), 32.95 (CH_2), 49.66 (CH), 111.90, 127.11, 127.74, 128.03, 128.23, 128.91, 129.45, 131.06, 131.35, 133.05, 138.03, 144.75, 159.91, 162.78 and 168.58; *m*/*z* 499 (M^+, 20), 416 (16, M^+ − c-Hex) and 344 (100, $M^+ -$ Ts).

4-Phenyl-5-(*p*-tolyl)-2-(*p*-tolylamino)-6-(tosylimino)-6*H*-1,3-oxazine 10e. Colourless crystals (18% yield); mp 202–205 °C (Found: C, 71.45; H, 5.20; N, 8.15%. $C_{31}H_{27}N_3O_3S$ requires C, 71.39; H, 5.22; N, 8.06%) ν_{max}(KBr)/cm^{-1} 3400 (NH) 1595 and 1530 (C=N); δ_H 2.30 (3H, s, CH_3), 2.33 (3H, s, CH_3), 2.39 (3H, s, CH_3) and 6.86–7.78 (18H, m, ArH and NH); δ_C 20.81 (CH_3), 21.25 (CH_3), 21.64 (CH_3), 114.05, 119.80, 126.38, 127.84, 128.42, 128.91, 129.40, 129.59, 130.67, 132.47, 134.08, 136.22, 137.10, 137.59, 143.39, 144.95, 157.81, 162.54 (C=N) and 168.53 (C=N); *m*/*z* 521 (M^+, 4%), 388 (85, $M^+ - TolNCO$) and 323 (100).

2-(Cyclohexylamino)-4-phenyl-5-(*p*-tolyl)-6-(tosylimino)-6*H*-1,3-oxazine 10f. Colourless crystals (48% yield); mp 215–216 °C (Found: C, 70.25; H, 6.09; N, 8.22%. $C_{30}H_{31}N_3O_3S$ requires C, 70.16; H, 6.08; N, 8.18%); ν_{max}(KBr)/cm^{-1} 3450 (NH) and 1525 (C=N); δ_H 1.0–2.2 [10H, m, $(CH_2)_5$], 2.23 (3H, s, CH_3), 2.46 (3H, s, CH_3), 3.64 (br s, CH), 5.22 (1H, d, *J* 8.0, NH), 6.90–7.40 (11H, m, ArH) and 7.83 (2H, d, *J* 8.0); δ_C 21.20 (CH_3), 21.64 (CH_3), 24.76 (CH_2), 25.64 (CH_2), 32.95 (CH_2), 49.66 (CH), 111.90, 126.33, 127.69, 128.23, 128.81, 129.40, 129.50, 129.84, 130.81, 135.10, 136.71, 138.12, 144.65, 159.81, 162.88 (C=N) and 168.58 (C=N); *m*/*z* 513 (M^+, 100%).

3,5,6-Triphenyl-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 11a. Colourless crystals (33% yield); mp 202–204 °C (Found: C, 70.60; H, 4.71; N, 8.55%. $C_{29}H_{23}N_3O_3S$ requires C, 70.58; H, 4.70; N, 8.52%); ν_{max}(KBr)/cm^{-1} 3340 (NH) 1680 (CO) and 1550 (C=N); δ_H (100 MHz) 2.40 (3H, s, CH_3), 6.96–7.78 (16H, m, ArH), 8.00 (2H, d, *J* 8.0) and 9.87 (1H, s, NH); δ_C (25 MHz) 21.82 (CH_3), 116.13, 122.33, 124.85, 127.19, 127.59, 128.06, 128.88, 129.06, 129.53, 129.93, 131.16, 133.68, 136.08, 137.42, 137.54, 146.14, 146.37, 158.48 (C=N) and 161.58 (CO); *m*/*z* 493 (M^+, 100%), 428 (37, $M^+ - SO_2H$) and 338 (43, $M^+ - Ts$).

5,6-Diphenyl-3-(*p*-tolyl)-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 11b. Colourless crystals (37% yield); mp 241–242 °C (Found: C, 71.05; H, 5.00; N, 8.33%. $C_{30}H_{25}N_3O_3S$ requires C, 70.99; H, 4.97; N, 8.28%); ν_{max}(KBr)/cm^{-1} 3350 (NH) 1670 (CO) and 1540 (C=N); δ_H 2.35 (3H, s, CH_3), 2.41 (3H, s, CH_3), 6.90–7.60 (16H, m, ArH) 7.95 (2H, d, *J* 8.0) and 9.86 (1H, s, NH); δ_C 20.94 (CH_3), 21.96 (CH_3), 115.78, 122.39, 127.13, 127.59, 128.00, 129.06, 129.41, 129.53, 129.99, 131.22, 134.56, 134.79, 136.14, 137.60, 146.08, 146.61, 158.66 (C=N) and 161.64 (CO); *m*/*z* 507 (M^+, 83%), 442 (29, $M^+ - SO_2H$) and 91 (100, Tol^+).

3-(*p*-Methoxyphenyl)-5,6-diphenyl-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 11c. Pale yellow crystals (52% yield); mp 217–219 °C (Found: C, 68.90; H, 4.88; N, 8.13%. $C_{30}H_{25}N_3O_4S$ requires C, 68.82; H, 4.81; N, 8.03%); ν_{max}(KBr)/cm^{-1} 3350 (NH) 1680 (CO) and 1540 (C=N); δ_H 2.40 (3H, s, CH_3), 3.78 (3H, s, OCH_3), 6.87 (2H, d, *J* 8.01), 6.85–7.36 (13H, m, ArH), 7.54 (2H, d, *J* 8.01), 8.01 (2H, d, *J* 8.01) and 9.78 (1H, s, NH); δ_C 21.74 (CH_3), 55.46 (CH_3), 114.05, 124.23, 127.06, 127.55, 127.99, 129.01, 129.50, 129.93, 130.28, 131.20, 133.78, 136.08, 137.59, 146.07, 146.94, 156.94, 158.69 (C=N) and 161.61 (CO); *m*/*z* 523 (M^+, 100%), 458 (10, $M^+ - SO_2H$) and 368 (77, $M^+ - Ts$).

3-Cyclohexyl-5,6-diphenyl-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 11d. Colourless crystals (45% yield); mp 183–185 °C (Found: C, 70.23; H, 6.20; N, 8.15%. $C_{30}H_{31}N_3O_3S$ requires C, 70.16; H, 6.08; N, 8.18%); ν_{max}(KBr)/cm^{-1} 3400 (NH) 1690 (CO) and 1555 (C=N); δ_H 1.2–2.3 [10H, m, $(CH_2)_5$], 2.24 (3H, s, CH_3), 2.42 (3H, s, CH_3), 4.12 (br s, CH), 6.78–7.78 (11H, m, ArH) and 7.94 (2H, d, *J* 8.1); δ_C 21.20 (CH_3), 21.73 (CH_3), 24.46 (CH_2), 25.73 (CH_2), 32.36 (CH_2), 50.53 (CH), 113.39, 127.43, 128.26, 128.65, 128.79, 129.33, 129.82, 131.08, 136.34, 136.45, 138.25, 145.61, 148.48, 159.00 (C=N) and 161.83 (C=N); *m*/*z* 499 (M^+, 17%), 416 (M^+ − c-Hex) and 344 (100, $M^+ - Ts$).

3,6-Diphenyl-5-(*p*-tolyl)-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 11e. Colourless crystals (42% yield); mp 163–164 °C (Found: C, 71.15; H, 5.05; N, 8.15%. $C_{30}H_{25}N_3O_3S$ requires C, 70.99; H, 4.97; N, 8.28%); ν_{max}(KBr)/cm^{-1} 3350 (NH) 1680 (CO) and 1540 (C=N); δ_H 2.25 (3H, s, CH_3), 2.43 (3H, s, CH_3), 6.90–7.70 (16H, m, ArH), 8.05 (2H, d, *J* 8.0) and 9.95 (1H, s, NH); δ_C 21.20 (CH_3), 21.74 (CH_3), 116.14, 122.28, 124.77, 127.60, 128.86, 129.11, 129.50, 129.93, 130.57, 130.96, 136.08, 136.86, 137.49, 137.64, 146.12, 146.26, 158.15 (C=N) and 161.76 (CO); *m*/*z* 507 (M^+, 10%), 442 (3, $M^+ - SO_2H$) and 104 (100).

6-Phenyl-3,5-di-*p*-tolyl-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 11f. Colourless crystals (36% yield); mp 182–183 °C (Found: C, 71.44; H, 5.25; N, 8.12%. $C_{31}H_{27}N_3O_3S$ requires C, 71.39; H, 5.22; N, 8.06%) ν_{max}(KBr)/cm^{-1} 3350 (NH) 1680 (CO) and 1540 (C=N); δ_H 2.23 (3H, s, CH_3), 2.35 (3H, s, CH_3), 2.43 (3H, s, CH_3), 6.95–7.67 (15H, m, ArH), 8.05 (2H, d, *J* 8.0) and 9.84 (1H, s, NH); δ_C 20.89 (CH_3), 21.18 (CH_3), 21.70 (CH_3), 119.93, 122.45, 127.59, 128.82, 129.12, 129.47, 130.05, 130.29, 130.46, 131.10, 134.56, 135.14, 136.55, 136.78, 137.95, 146.00, 146.61, 158.31 (C=N) and 161.81 (CO); *m*/*z* 521 (M^+, 100%), 456 (24, $M^+ - SO_2H$) and 366 (83, $M^+ - Ts$).

3-(*p*-Methoxyphenyl)-6-phenyl-5-(*p*-tolyl)-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 11g. Colourless crystals (35% yield); mp 175–176 °C (Found: C, 69.25; H, 5.10; N, 7.85%. $C_{31}H_{27}N_3O_4S$ requires C, 69.26; H, 5.06; N, 7.82%) ν_{max}(KBr)/cm^{-1} 3350 (NH) 1680 (CO) and 1550 (C=N); δ_H 2.24 (3H, s, CH_3), 2.42 (3H, s, CH_3), 3.80 (3H, s, OCH_3), 6.85–7.36 (11H, m, ArH), 6.86 (2H, d, *J* 8.0), 7.54 (2H, d, *J* 8.0), 8.01 (2H, d, *J* 8.0) and 9.76 (1H, s, NH); δ_C 21.23 (CH_3), 21.77 (CH_3), 55.49 (CH_3), 114.02, 124.21, 127.56, 128.85, 129.06, 129.47, 129.94, 130.35, 130.69, 130.97, 136.08, 136.77, 137.72, 146.05, 146.80, 146.00, 156.90, 158.34 (C=N) and 161.75 (CO); *m*/*z* 537 (M^+, 100%), 472 (7, $M^+ - SO_2H$) and 382 (62, $M^+ - Ts$).

3-Cyclohexyl-6-phenyl-5-(*p*-tolyl)-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 11h. Colourless crystals (35% yield); mp 190–192 °C (Found: C, 70.23; H, 6.15; N, 8.25%. $C_{30}H_{31}N_3O_3S$ requires C, 70.16; H, 6.08; N, 8.18%) ν_{max}(KBr)/cm^{-1} 3400 (NH) 1690 (CO) and 1555 (C=N); δ_H 1.2–2.3 [10H, m, $(CH_2)_5$], 2.24 (3H, s, CH_3), 2.42 (3H, s, CH_3), 4.12 (1H, br s, CH), 6.78–7.78 (11H, m, ArH), 7.94 (2H, d, *J* 8.1, ArH) and 7.90 (1H, s, NH); δ_C 21.20 (CH_3), 21.73 (CH_3), 24.46 (CH_2), 25.73 (CH_2), 32.36 (CH_2), 50.53 (CH), 113.39, 127.43, 128.26, 128.65, 128.79, 129.33, 129.82, 131.08, 136.34, 136.45, 138.25, 145.61, 148.48, 159.00 (C=N) and 161.83 (CO); *m*/*z* 513 (M^+, 31) and 358 (100, $M^+ - Ts$).

Cycloaddition of carbodiimide 5 with tetracyanoethylene (TCNE). General procedure

A solution of carbodiimide **5** (2.0 mmol) and TCNE (2.2 mmol) in acetonitrile (20 cm^3) was stirred at room temperature for 5–10 d until **5** had been consumed (monitored by TLC). Removal of the solvent *in vacuo* and column chromatography of the residue on silica gel using EtOAc–CH_2Cl_2–benzene as an eluent, followed by recrystallization from EtOAc–CH_2Cl_2–benzene afforded pyridine **12**. Compounds **12** are rather labile and gradually deteriorate in a hot solution.

3,3,4,4-Tetracyano-6-phenyl-2-(phenylimino)-2,3,4,5-tetrahydropyridine 12a. Reddish crystals (45% yield); mp 260 °C (decomp.) (Found: M^+, 348.1124. $C_{21}H_{12}N_6$ requires *M* 348.1123; FAB-HRMS Found: M^++1, 349.1220. $C_{21}H_{13}N_6$ requires *M* + 1 349.1166); ν_{max}(KBr)/cm^{-1} 2230 and 1570; δ_H (270 MHz, $CDCl_3$+DMSO-d_6) [NH-isomer] 7.50–7.81 (10H, m, ArH), 8.28 (1H, s, =CH) and 11.37 (1H, s, NH); δ_C (67.8 MHz, DEPT) 91.32 (C-5) , 109.81 (CN), 111.52 (CN), 126.90 (CH), 128.63 (CH), 130.05 (CH), 130.10 (CH), 131.33 (CH), 133.27 (CH), 136.48 (C), 159.89 (C) and 170.71 (C); *m*/*z* 348 (M^+, 5%), 346 (96, $M^+ - 2$) and 320 (100, $M^+ - 2 - CN$).

3,3,4,4-Tetracyano-2-(phenylimino)-6-(*p*-tolyl)-2,3,4,5-tetrahydropyridine 12b. Reddish crystals (33% yield); mp 264 °C (decomp.) (Found: C, 72.78; H, 3.81; N, 23.46%. M^+, 362.1278.

$C_{22}H_{14}N_6$ requires C, 72.91; H, 3.89; N, 23.19%. *M*, 362.1282); ν_{max}(KBr)/cm^{-1} 2220 and 1570; δ_H (100 MHz) 1.58 (2H, s, CH_2), 2.49 (3H, s, CH_3) and 7.05–7.85 (9H, m, ArH); *m*/*z* 362 (M^+, 6%), 360 (100, $M^+ - 2$) and 334 (56, $M^+ - 2 - CN$).

3,3,4,4-Tetracyano-6-(*p*-tolyl)-2-(*p*-tolylimino)-2,3,4,5-tetrahydropyridine 12c. Reddish crystals (31% yield); mp 270 °C (decomp.) (Found: C, 73.20; H, 4.22; N, 23.51%. M^+, 376.1446. $C_{23}H_{16}N_6$ requires C, 73.39; H, 4.28; N, 22.33%. *M*, 376.1422); ν_{max}(KBr)/cm^{-1} 2240 and 1570; δ_H 1.56 (2H, s, CH_2), 2.48 (3H, s, CH_3), 2.51 (3H, s, CH_3), 7.12–7.50 (6H, m, ArH) and 7.76–7.78 (2H, m, ArH); *m*/*z* 376 (M^+, 8%), 374 (100, $M^+ - 2$) and 348 (58, $M^+ - 2 - CN$).

3,3,4,4-Tetracyano-2-(cyclohexylimino)-6-(*p*-tolyl)-2,3,4,5-tetrahydropyridine 12d. Reddish crystals (20% yield); mp 195 °C (decomp.) (Found: C, 71.68; H, 5.44; N, 22.95%. M^+, 368.1734. $C_{22}H_{20}N_6$ requires C, 71.72; H, 5.47; N, 22.81%. *M*, 368.1777); ν_{max}(KBr)/cm^{-1} 2220 and 1560; δ_H 1.05–2.8 [12H, m, CH_2, $(CH_2)_5$], 2.46 (3H, s, CH_3), 4.62 (1H, br s, CH), 7.12–7.65 (4H, m, ArH); *m*/*z* 368 (M^+, 1%), 366 (6, $M^+ - 2$) and 83 (100, c-Hex$^+$).

Cycloaddition of carbodiimide 5 with tosyl isocyanate. General procedure

A solution of carbodiimide **5** (2.0 mmol) and tosyl isocyanate (3.0 mmol) in acetonitrile (20 cm^3) was stirred at room temperature for 2–3 d until **5** had been consumed. Removal of the solvent *in vacuo*, column chromatography of the residue (silica gel, CH_2Cl_2–benzene as an eluent) and recrystallization (CH_2Cl_2–benzene) afforded **13**.

3,6-Diphenyl-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 13a. Colourless crystals (45% yield), mp 161–163 °C (Found: C, 66.29; H, 4.61; N, 10.01%. $C_{23}H_{19}N_3O_3S$ requires C, 66.18; H, 4.59; N, 10.07%); ν_{max}(KBr)/cm^{-1} 3350 (NH) 1700 (C=O) and 1540 (C=N); *m*/*z* 417 (M^+, 72%), 352 (44, $M^+ - SO_2H$), 262 (100, $M^+ - Ts$) and 155 (9, Ts^+).

6-Phenyl-3-(*p*-tolyl)-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 13b. Colourless crystals (40% yield); mp 157–159 °C (Found: C, 66.85; H, 4.99; N, 9.80%. $C_{24}H_{21}N_3O_3S$ requires C, 66.81; H, 4.91; N, 9.74%) ν_{max}(KBr)/cm^{-1} 3350 (NH) 1695 (C=O) and 1550 (C=N); δ_H (100 MHz) 2.37 (3H, s, CH_3), 2.42 (3H, s, CH_3), 6.15 (1H, s, 5-H), 7.1–8.0 (11H, m, ArH), 8.07 (2H, d, *J* 8.0) and 9.86 (1H, s, NH); δ_C (25 MHz) 20.94 (CH_3), 21.76 (CH_3), 99.86 (C-5), 122.86, 126.42, 127.19, 128.59, 128.82, 129.06, 129.41, 130.93 and 134.67, 134.91, 135.79, 136.02, 146.26, 148.71, 160.53 (C=N) and 161.70 (CO); *m*/*z* 431(M^+, 67%), 366 (44, $M^+ - SO_2H$), 276 (99, $M^+ - Ts$) and 155 (12, Ts^+).

3-Phenyl-6-(*p*-tolyl)-2-(tosylimino)-2,3-dihydropyrimidin-4(1*H*)-one 13c. Colourless crystals (40% yield); mp 157–159 °C (Found: C, 66.95; H, 5.01; N, 9.70%. $C_{24}H_{21}N_3O_3S$ requires C, 66.81; H, 4.91; N, 9.74%); ν_{max}(KBr)/cm^{-1} 3350 (NH) 1700 (C=O) and 1550 (C=N); δ_H 2.35 (3H, s, CH_3), 2.43 (3H, s, CH_3), 6.17 (1H, s, 5-H), 7.03–8.23 (13H, m, ArH) and 9.96 (1H, s, NH); δ_C 21.41 (CH_3), 21.76 (CH_3), 99.57 (C-5), 122.80, 125.08, 127.19, 128.88, 129.06, 129.41, 132.98, 136.02 and 137.36, 141.52, 146.26, 148.36, 160.41 (C=N) and 161.64 (CO); *m*/*z* 431(M^+, 88%), 367 (44, $M^+ - SO_2$), 366 (52, $M^+ - SO_2H$) and 276 (100, $M^+ - Ts$).

Cycloaddition of carbodiimide 5 with *N*-(*p*-methoxyphenyl)-maleimide (NPMI). General procedure

A solution of carbodiimide **5** (1.0 mmol) and NPMI (2.0 mmol) in the appropriate solvent (benzene, xylene and mesitylene; see Table 1) (20 cm^3) was heated under reflux for 2–50 h in the absence or presence of an additive [MnO_2 (200 mg), S_8 (50 mg) or nitrobenzene (2 cm^3); with DDQ, the reaction mixture was treated after the reaction]. Product **14** partially precipitated on cooling. Evaporation of the solvent *in vacuo* and column chromatography of the residue on silica gel using CH_2Cl_2–benzene as an eluent, followed by recrystallization from CH_2Cl_2–benzene afforded diazaindanedione **14** (yield in Table 1). Compound **14** is sparingly soluble in $CDCl_3$ for ^{13}C NMR measurement.

2-(*p*-Methoxyphenyl)-6-phenyl-4-(phenylamino)-2,5-diazaindane-1,3-dione 14a. Orange solid; mp 245.3–246.5 °C (decomp.) (Found: C, 74.29; H, 4.56; N, 9.90%. $C_{26}H_{19}N_3O_3$ requires C, 74.09; H, 4.54; N, 9.97%); ν_{max}(KBr)/cm^{-1} 3380 (NH) and 1710 (C=O); δ_H (270 MHz) 3.87 (3H, s, OMe), 7.0–8.2 (14H, m, ArH), 7.70 (1H, s, 7-H) and 8.48 (1H, s, NH); *m*/*z* 421 (M^+, 100%), 299 (4, $M^+ - MeOC_6H_4N - H$), 270 (4, $M^+ - MeOC_6H_4NCO - 2H$) and 243 (12, $M^+ - MeOC_6H_4NCOCO - H$).

2-(*p*-Methoxyphenyl)-6-phenyl-4-(*p*-tolylamino)-2,5-diazaindane-1,3-dione 14b. Orange solid; mp 197.9–199.8 °C (decomp.) (Found: C, 74.44; H, 4.98; N, 9.60%. $C_{27}H_{21}N_3O_3$ requires C, 74.47; H, 4.86; N, 9.65%); ν_{max}(KBr)/cm^{-1} 3388 (NH) and 1698 (C=O); δ_H 2.36 (3H, s, Me), 3.85 (3H, s, OMe), 7.00–8.11 (13H, m, ArH), 7.63 (1H, s, 7-H) and 8.37 (1H, s, NH); *m*/*z* 435 (M^+, 100%), 313 (5, $M^+ - MeOC_6H_4N - H$), 284 (5, $M^+ - MeOC_6H_4NCO - 2H$) and 257 (14, $M^+ - MeO - C_6H_4 - NCOCO - H$).

4-(Cyclohexylamino)-2-(*p*-methoxyphenyl)-6-phenyl-2,5-diazaindane-1,3-dione 14c. Yellow needles; mp 199.5–200.2 °C (decomp.) (Found: C, 73.33; H, 5.98; N, 9.80%. $C_{26}H_{25}N_3O_3$ requires C, 73.05; H, 5.90; N, 9.83%); ν_{max}(KBr)/cm^{-1} 3416 (NH), 2936 (CH) and 1708 (C=O); δ_H 1.2–2.2 (10H, m, c-HexH), 3.84 (3H, s, OMe), 4.29 (1H, m, c-HexH), 6.35 (1H, d, *J* 7.92, NH), 7.01–8.12 (9H, m, ArH) and 7.48 (1H, s, 7-H); δ_C (67.8 MHz, DEPT) 24.75 (C-3″), 25.70 (C-4″), 32.99 (C-2″), 49.26 (C-1″), 55.47 (MeO), 102.34 (C-7), 103.25 (C-3a), 114.43 (C-3′), 124.24 (C-1′), 127.49 (C-2″), 127.76 (C-2′), 128.77 (C-3‴), 130.40 (C-4‴), 138.47 (C-1‴), 142.35 (C-7a), 153.55 (C-4′), 159.16 (C-4), 163.83 (C-6), 167.15 (C=O) and 169.15 (C=O); *m*/*z* 427 (M^+, 84%), 398 (6, $M^+ - CO - H$), 384 (17, $M^+ - CO - Me$), 370 (27, $M^+ - 2CO - H$), 345 (100, $M^+ - c\text{-}Hex + H$) and 257 (14, $M^+ - MeOC_6H_4$).

2-(*p*-Methoxyphenyl)-4-(phenylamino)-6-(*p*-tolyl)-2,5-diazaindane-1,3-dione 14d. Orange solid; mp 288.6–289.7 °C (decomp.) (Found: C, 74.62; H, 4.88; N, 9.65%. $C_{27}H_{21}N_3O_3$ requires C, 74.47; H, 4.86; N, 9.65%). ν_{max}(KBr)/cm^{-1} 3384 (NH) and 1710 (C=O); δ_H 2.45 (3H, s, Me), 3.87 (3H, s, OMe), 7.02–8.06 (13H, m, ArH), 7.68 (1H, s, 7-H) and 8.47 (1H, br s, NH); *m*/*z* 435 (M^+, 100%), 313 (5, $M^+ - MeOC_6H_4N - H$), 284 (5, $M^+ - MeOC_6H_4NCO - 2H$) and 257 (14, $M^+ - MeOC_6H_4NCOCO - H$).

2-(*p*-Methoxyphenyl)-6-(*p*-tolyl)-4-(*p*-tolylamino)-2,5-diazaindane-1,3-dione 14e. Orange solid; mp 226.4–227.2 °C (decomp.) (Found: C, 74.90; H, 5.21; N, 9.40%. $C_{28}H_{23}N_3O_3$ requires C, 74.81; H, 5.16; N, 9.35%). ν_{max}(KBr)/cm^{-1} 3384 (NH) and 1704 (C=O); δ_H 2.37 (3H, s, Me), 2.44 (3H, s, Me), 3.86 (3H, s, OMe), 7.03–8.02 (12H, m, ArH), 7.63 (1H, s, 7-H) and 8.37 (1H, br s, NH); *m*/*z* 449 (M^+, 100%), 327 (5, $M^+ - MeOC_6H_4N - H$), 298 (5, $M^+ - MeOC_6H_4NCO - 2H$) and 271(14, $M^+ - MeOC_6H_4NCOCO - H$).

4-(Cyclohexylamino)-2-(*p*-methoxyphenyl)-6-(*p*-tolyl)-2,5-diazaindane-1,3-dione 14f. Yellow needles; mp 214.6–215.8 °C (decomp.) (Found: C, 73.56; H, 6.21; N, 9.48%. $C_{27}H_{27}N_3O_3$ requires C, 73.45; H, 6.16; N, 9.52%). ν_{max}(KBr)/cm^{-1} 3420 (NH), 2932 (CH) and 1710 (C=O); δ_H 1.20–2.14 (10H, m, c-HexH), 2.43 (3H, s, Me), 3.85 (3H, s, OMe), 4.29 (1H, m, c-HexH), 6.33 (1H, d, *J* 7.92, NH), 7.01–8.01 (8H, m, ArH) and 7.46 (1H, s, 7-H); *m*/*z* 441 (M^+, 86%), 398 (6, $M^+ - CO - H$), 398(17, $M^+ - CO - Me$), 384 (22, $M^+ - 2CO - H$), 359 (100, $M^+ - c\text{-}Hex + H$) and 334 (10, $M^+ - MeOC_6H_4$).

Cycloaddition of carbodiimide 5 with dimethyl acetylenedicarboxylate (DMAD). General procedure

Thermal reaction. A mixture of carbodiimide **5** (1.50 mmol)

and DMAD (277 μl, 2.25 mmol) in toluene (25 cm^3) was heated under reflux for 3–9 h until **5** had been consumed. Removal of the solvent *in vacuo*, column chromatography of the residue [silica gel, EtOAc–hexane (20 : 1) as an eluent] and recrystallization (CH_2Cl_2–hexane) afforded pyridine **15** as needles (yields in Table 2).

Lewis acid-promoted reaction. To a CH_2Cl_2 solution (15 cm^3) of DMAD (135–246 μl, 1.10–2.00 mmol) was successively added a Lewis acid solution ($AlCl_3$, $EtAlCl_2$) (1.10–2.20 mmol) and a CH_2Cl_2 solution (15 cm^3) of carbodiimide **5** (1.00 mmol) with stirring at room temperature for 0.25–3 h. The reaction was quenched with cold saturated aq. NH_4Cl (20 cm^3) and the mixture was extracted with CH_2Cl_2 (20 cm_3 × 3), washed with aq. $NaHCO_3$ and brine, and dried ($MgSO_4$). Work-up for the purification to give pyridine **15** was the same as described above (yields in Table 2).

3,4-Bis(methoxycarbonyl)-6-phenyl-2-(phenylamino)pyridine 15a. Yellow needles; mp 109.2–110.3 °C (Found: C, 69.82; H, 4.85; N, 7.53%, $C_{21}H_{18}N_2O_4$ requires C, 69.60; H, 5.00; N, 7.73%) ν_{max}(KBr)/cm^{-1} 3284 (NH) and 1744 (C=O); δ_H (270 MHz) 3.89 (3H, s, OMe), 3.93 (3H, s, OMe), 7.08–8.03 (10H, m, ArH), 7.21 (1H, s, 5-H) and 9.89 (1H, br s, NH); δ_C (67.8 MHz, DEPT) 52.60 (OMe), 52.76 (OMe), 102.61 (C-3), 108.70 (C-5), 120.99 (C-2′), 123.02 (C-4′), 127.39 (C-2″), 128.73 (C-3′, C-3″), 130.28 (C-4″), 137.68 (C-1″), 139.50 (C-1′), 145.53 (C-4), 155.13 (C-2) 159.80 (C-6), 167.06 (C=O) and 168.71 (C=O); *m*/*z* 362 (M^+, 100%), 329 (11, M^+ − OMe-2H), 301 (8, M^+ − CO_2Me − 2H) and 244 (97, M^+ − $2CO_2Me$).

3,4-Bis(methoxycarbonyl)-6-phenyl-2-(*p*-tolylamino)pyridine 15b. Yellow needles; mp 125.7–128.5 °C (Found: C, 70.27; H, 5.28; N, 7.37%. $C_{22}H_{20}N_2O_4$ requires C, 70.20; H, 5.36; N, 7.44%) ν_{max}(KBr)/cm^{-1} 3288 (NH) and 1738 (C=O); δ_H 2.34 (3H, s, Me), 3.88 (3H, s, OMe), 3.92 (3H, s, OMe), 7.17–8.03 (9H, m, ArH), 7.18 (1H, s, 5-H) and 9.83 (1H, br s, NH); δ_C 20.88 (Me), 52.60 (OMe), 52.79 (OMe), 102.23 (C-3), 108.35 (C-5), 121.15 (C-2′), 127.40 (C-2″), 128.75 (C-3″), 129.25 (C-3′), 130.28 (C-4″), 132.59 (C-4′), 136.87 (C-1′), 137.73 (C-1″), 145.57 (C-4), 155.27 (C-2), 159.82 (C-6), 167.08 (C=O) and 168.86 (C=O); *m*/*z* 376 (M^+, 100%), 344 (9, M^+ − OMe − H) and 258 (75, M^+ − $2CO_2Me$).

2-(Cyclohexylamino)-3,4-bis(methoxycarbonyl)-6-phenylpyridine 15c. Yellow needles; mp 111.3–112.4 °C (Found: C, 68.56; H, 6.62; N, 7.71%. $C_{21}H_{24}N_2O_4$ requires C, 68.46; H, 6.57; N, 7.60%). ν_{max}(KBr)/cm^{-1} 3364 (NH), 2932 (CH) and 1740 (C=O); δ_H 1.25–2.10 (10H, m, c-HexH), 3.83 (3H, s, OMe), 3.90 (3H, s, OMe), 4.24 (1H, m, c-HexH), 6.97 (1H, s, 5-H), 7.40–8.03 (5H, m, PhH) and 7.81 (1H, d, *J* 7.26, NH); δ_C 24.82 (C-3′), 25.98 (C-4′), 32.88 (C-2′), 49.40 C-1′), 52.13 (MeO), 52.60 (MeO), 100.48 (C-3), 105.91 (C-5), 127.24 (C-2″), 128.64 (C-3″), 130.04 (C-4″), 138.24 (C-1″), 145.64 (C-4), 157.32 (C-2), 159.93 (C-6), 167.08 (C=O) and 169.36 (C=O); *m*/*z* 368 (M^+, 30%), 336 (26, M^+ − OMe − H), 286 (100, M^+ − c-Hex +H), 279 (33) and 250 (10, M^+ − $2CO_2Me$).

3,4-Bis(methoxycarbonyl)-2-phenylamino-6-(*p*-tolyl)pyridine 15d. Yellow needles; mp 123.3–124.8 °C (Found: C, 70.35; H, 5.41; N, 7.45%. $C_{22}H_{20}N_2O_4$ requires C, 70.20; H, 5.36; N, 7.44%) ν_{max}(KBr)/cm^{-1} 3268 (NH) and 1742 (C=O); δ_H 2.41(3H, s, Me), 3.90 (3H, s, OMe), 3.94 (3H, s, OMe), 7.0–8.0 (9H, m, ArH), 7.20 (1H, s, 5-H) and 9.93 (1H, br s, NH); δ_C 21.37 (Me), 52.58 (OMe), 52.78 (OMe), 102.08 (C-3), 108.37 (C-5), 120.91 (C-2′), 122.93 (C-4′), 127.33 (C-2″), 128.70 (C-3′), 129.50 (C-3″), 134.89 (C-1″), 139.57 (C-1′), 140.66 (C-4″), 145.48 (C-4), 155.11 (C-2), 159.84 (C-6), 167.08 (C=O) and 168.87 (C=O); *m*/*z* 376 (M^+, 100%), 343 (12, M^+ − OMe − 2H), 315 (9, M^+ − CO_2Me − 2H) and 258 (100, M^+ − $2CO_2Me$).

3,4-Bis(methoxycarbonyl)-6-(*p*-tolyl)-2-(*p*-tolylamino)-pyridine 15e. Yellow needles; mp 123.7–125.0 °C (Found: C, 70.76; H, 5.50; N, 7.14%. $C_{23}H_{22}N_2O_4$ requires C, 70.75; H, 5.68; N, 7.18%); ν_{max}(KBr)/cm^{-1} 3276 (NH) and 1744 (C=O); δ_H 2.34 (3H, s, Me), 2.38 (3H, s, Me), 3.88 (3H, s, OMe), 3.92 (3H, s, OMe), 7.15 (1H, s, 5-H), 7.16 (2H, d, *J* 8.25, ArH), 7.24 (2H, d, *J* 8.25, ArH), 7.61 (2H, d, *J* 8.25, ArH), 7.93 (2H, d, *J* 8.25, ArH) and 9.84 (1H, br s, NH); δ_C 20.86 (Me), 21.38 (Me), 52.54 (OMe), 52.76 (OMe), 101.78 (C-3), 108.05 (C-5), 121.11 (C-2′), 127.35 (C-2″), 129.22 (C-3″), 129.49 (C-3″), 132.50 (C-4′), 134.98 (C-1″), 136.94 (C-1′), 140.61 (C-4″), 145.50 (C-4), 155.27 (C-2), 159.85 (C-6), 167.10 (C=O) and 168.98 (C=O); *m*/*z* 390 (M^+, 100%), 358 (9, M^+ − OMe − H) and 272 (75, M^+ − $2CO_2Me$).

2-(Cyclohexylamino)-3,4-bis(methoxycarbonyl)-6-(*p*-tolyl)-pyridine 15f. Yellow needles; mp 114.6–116.2 °C (Found: C, 68.96; H, 7.07; N, 7.12%. $C_{22}H_{26}N_2O_4$ requires C, 69.09; H, 6.85; N, 7.33%); ν_{max}(KBr)/cm^{-1} 3368 (NH), 2928 (CH) and 1744 (C=O); δ_H 1.23–2.16 (10H, m, c-HexH), 2.40 (3H, s, Me), 3.83 (3H, s, OMe), 3.90 (3H, s, OMe), 4.23 (1H, m, c-HexH), 6.94 (1H, s, 5-H), 7.26 (2H, d, *J* 8.25, *p*-TolH), 7.83 (1H, d, *J* 7.25, NH) and 7.94 (2H, d, *J* 8.25, *p*-TolH); δ_C 21.38 (Me), 24.82 (C-3′), 25.95 (C-4′), 32.83 (C-2′), 49.33 (C-1′), 52.15 (OMe), 52.63 (OMe), 99.84 (C-3), 105.52 (C-5), 127.15 (C-2″), 129.38 (C-3″), 135.40 (C-1″), 140.32 (C-4″), 145.51 (C-4), 157.27 (C-2), 159.94 (C-6), 167.06 (C=O) and 169.52 (C=O); *m*/*z* 382 (M^+, 30%), 350 (26, M^+ − OMe − H), 300 (100, M^+ − c-Hex + H), 293 (26) and 264 (10, M^+ − $2CO_2Me$).

Cycloaddition of carbodiimides 5 with ethyl propiolate (EP). General procedure

Thermal reaction. A solution of carbodiimide **5a** (0.59 mmol) and EP (120 μl, 1.17 mmol) in toluene (10 cm^3) was refluxed for 17 h. The solvent was evaporated *in vacuo* and the residue was column-chromatographed on silica gel using EtOAc–hexane (1 : 100) as an eluent to give pyridine **16a**, which was recrystallised from CH_2Cl_2–hexane (9% yield).

Lewis acid-promoted reaction. To a CH_2Cl_2 solution (10 cm^3) of EP (238 μl, 2.32 mmol) was successively added $AlCl_3$ (2.32 mmol) and carbodiimide **5** (1.16 mmol) in CH_2Cl_2 (10 cm^3) with stirring at − 10 °C. The reaction mixture was warmed up to room temperature and stirred for 1 h. The reaction was quenched with cold saturated aq. NH_4Cl (20 cm^3) and the mixture was extracted with CH_2Cl_2 (20 cm^3 × 3), washed with aq. $NaHCO_3$ and brine, and dried ($MgSO_4$). Work-up for the purification to give pyridine **16** was the same as described above.

3-Ethoxycarbonyl-6-phenyl-2-(phenylamino)pyridine 16a. Yellowish crystals (47% yield); mp 94.8–95.6 °C (Found: C, 75.61; H, 5.72; N, 8.95%. $C_{20}H_{18}N_2O_2$ requires C, 75.45; H, 5.70; N, 8.80%); ν_{max}(KBr)/cm^{-1} 3272 (NH) and 1686 (C=O); δ_H (270 MHz) 1.41 (3H, t, *J* 7.26, CH_3), 4.37 (2H, q, *J* 7.26, CH_2), 7.05 (1H, t, *J* 7.25, ArH), 7.18 (1H, d, *J* 8.25, 5-H), 7.37 (2H, dd, *J* 7.58 and 7.25, ArH), 7.42–7.50 (3H, m, ArH), 7.84 (2H, d, *J* 7.58, ArH), 8.06 (2H, dd, *J* 7.92 and 1.98, ArH), 8.28 (1H, d, *J* 8.25, 4-H) and 10.32 (1H, br s, NH); δ_C (67.8 MHz, DEPT) 14.29 (CH_3), 61.11 (CH_2), 105.64 (C-3), 109.70 (C-5), 120.54 (C-2′), 122.39 (C-4′), 127.38 (C-2′), 128.70 (C-3′, C-3″), 129.79 (C-4″), 138.60 (C-1″), 140.02 (C-1′), 140.91 (C-4), 155.63 (C-2), 160.00 (C-6) and 167.51 (C=O); *m*/*z* 318 (M^+, 100%), 289 (3, M^+ − Et), 271 (22, M^+ − OEt − 2H), 244 (47, M^+ − CO_2Et − H) and 167 (3, M^+ − CO_2Et − Ph − H).

3-Ethoxycarbonyl-6-phenyl-2-(*p*-tolylamino)pyridine 16b. Yellowish crystals (43% yield); mp 108.9–109.8 °C (Found: C, 75.93; H, 6.13; N, 8.45%. $C_{21}H_{20}N_2O_2$ requires C, 75.88; H, 6.07; N, 8.43%); ν_{max}(KBr)/cm^{-1} 3272 (NH) and 1678 (C=O); δ_H 1.41 (3H, t, *J* 7.26, CH_3), 2.34 (3H, s, CH_3), 4.37 (2H, q, *J* 7.26, CH_2), 7.16 (1H, d, *J* 8.25, 5-H), 7.17 (2H, d, *J* 8.25, ArH), 7.38–7.49 (3H, m, ArH), 7.71 (2H, d, *J* 8.25, ArH), 8.07 (2H, dd, *J* 8.25 and 1.98, ArH), 8.26 (1H, d, *J* 8.25, 4-H) and 10.23 (1H, br s, NH); δ_C 14.30 (CH_3, Et), 20.84 (Me), 61.04 (CH_2, Et), 105.41 (C-3), 109.36 (C-5), 120.70 (C-2′), 127.38 (C-2″), 128.66 (C-3″), 129.20 (C-3′), 129.76 (C-4″), 131.88 (C-4′),

137.41 (C-1″), 138.67 (C-1′), 140.90 (C-4), 155.74 (C-2), 160.00 (C-6) and 167.54 (C=O); *m*/*z* 332 (M^+, 100%), 286 (33, $M^+ - OEt - H$), 258 (30, $M^+ - CO_2Et - H$) and 242 (8, $M^+ - p$-Tol + H).

2-(Cyclohexylamino)-3-ethoxycarbonyl-6-phenylpyridine 16c. Pale yellow oil (51% yield); (Found: M^+, 324.1833. $C_{20}H_{24}N_2O_2$ requires *M*, 324.1839). ν_{max}(NaCl)/cm^{-1} 3368 (NH), 2932 (CH) and 1688 (C=O); δ_H 1.25–2.13 (10H, m, CH_2, c-Hex), 1.38 (3H, t, *J* 7.26, Et), 4.21–4.26 (1H, m, CH, c-Hex), 4.32 (2H, q, *J* 7.26, Et), 6.97 (1H, d, *J* 7.92, 5-H), 7.41–7.49 (3H, m, PhH), 8.00 (1H, br d, *J* 6.92, NH), 8.06 (2H, dd, *J* 7.92 and 1.98, Ph-H) and 8.16 (1H, d, *J* 8.24, 4-H); δ_C 14.38 (CH-3, Et), 24.89 (C-3′), 26.04 (C-4′), 33.03 (C-2′), 48.93 (C-1′), 60.48 (CH_2, Et), 104.06 (C-3), 106.88 (C-5), 127.19 (C-2″), 128.53 (C-3″), 129.52 (C-4″), 139.06 (C-1″), 140.73 (C-4), 157.70 (C-2), 160.02 (C-6) and 167.67 (C=O); *m*/*z* 324 (M^+, 29%), 295 (15, $M^+ - Et$), 267 [25, $M^+ - (CH_2)_4 - H$], 242 (100, M^+ - c-Hex + H) and 170 (32).

3-Ethoxycarbonyl-2-(phenylamino)-6-(*p*-tolyl)pyridine 16d. Yellowish crystals (46% yield); mp 93.1–94.1 °C (Found: C, 75.93; H, 6.11; N, 8.45%. $C_{21}H_{20}N_2O_2$ requires C, 75.88; H, 6.07; N, 8.43%); ν_{max}(KBr)/cm^{-1} 3272 (NH) and 1686 (C=O); δ_H 1.40 (3H, t, *J* 7.26, CH_3, Et), 2.40 (3H, s, CH_3), 4.37 (2H, q, *J* 7.26, CH_2), 7.04 (1H, t, *J* 7.59, PhH), 7.15 (1H, d, *J* 8.25, 5-H), 7.26 (2H, d, *J* 8.58, *p*-TolH), 7.36 (2H, dd, *J* 7.91 and 7.59, Ph-H), 7.84 (2H, d, *J* 7.91, PhH), 7.97 (2H, d, *J* 8.58, *p*-TolH), 8.25 (1H, d, *J* 8.25, 4-H) and 10.31 (1H, br s, NH); δ_C 14.29 (CH_3, Et), 21.35 (Me), 61.04 (CH_2, Et), 105.32 (C-3), 109.40 (C-5), 120.48 (C-2′), 122.30 (C-4′), 127.31 (C-2′), 128.66 (C-3′), 129.41 (C-3′), 135.85 (C-1′), 140.02 (C-1′), 140.11 (C-4′), 140.82 (C-4), 155.63 (C-2), 160.05 (C-6) and 167.54 (C=O); *m*/*z* 332 (M^+, 100%), 285 (21, $M^+ - OEt - 2H$), 258 (51, $M^+ - O_2Et - H$) and 242 (9, $M^+ - p$-Tol + H).

3-Ethoxycarbonyl-6-(*p*-tolyl)-2-(*p*-tolylamino)pyridine 16e. Yellowish crystals (46% yield); mp 67.9–68.5 °C (Found: C, 76.31; H, 6.51; N, 8.23%. $C_{22}H_{22}N_2O_2$ requires C, 76.27; H, 6.40; N, 8.09%); ν_{max}(KBr)/cm^{-1} 3276 (NH) and 1682 (C=O); δ_H 1.41 (3H, t, *J* 7.26, CH_3, Et), 2.35 (3H, s, CH_3), 2.40 (3H, s, CH_3), 4.37 (2H, q, *J* 7.26, CH_2), 7.13 (1H, d, *J* 8.25, 5-H), 7.17 (2H, d, *J* 8.25, ArH), 7.27 (2H, d, *J* 8.25, ArH), 7.71 (2H, d, *J* 8.25, ArH), 7.97 (2H, d, *J* 8.25, ArH), 8.25 (1H, d, *J* 8.25, 4-H) and 10.22 (1H, br s, NH); δ_C 14.32 (CH_3, Et), 20.84 (CH_3), 21.37 (CH_3), 60.99 (CH_2, Et), 105.08 (C-3), 109.07 (C-5), 120.66 (C-2′), 127.31 (C-2″), 129.16 (C-3′), 129.40 (C-3″), 131.79 (C-4′), 135.92 (C-1″), 137.46 (C-1′), 139.96 (C-4″), 140.81 (C-4), 155.74 (C-2), 160.05 (C-6) and 167.58 (C=O); *m*/*z* 346 (M^+, 100%), 317 (3, $M^+ - Et$), 300 (32, $M^+ - OEt - H$), 272 (44, $M^+ - CO_2Et - H$), 256 (9, M^+ *p*-Tol + H) and 181 (4, $M^+ - CO_2Et$-*p*-Tol − H).

2-(Cyclohexylamino)-3-ethoxycarbonyl-6-(*p*-tolyl)pyridine 16f. Pale yellow oil (49% yield) (Found: M^+, 338.1993. $C_{20}H_{24}N_2O_2$ requires *M*, 338.1996); ν_{max}(NaCl)/cm^{-1} 3368 (NH), 2932 (CH) and 1684 (C=O); δ_H 1.25–2.12 (10H, m, CH_2, c-Hex), 1.37 (3H, t, *J* 6.93, CH_3), 2.39 (3H, s), 4.23–4.30 (1H, m, CH, c-Hex), 4.31 (2H, q, *J* 6.93, CH_2), 6.94 (1H, d, *J* 8.24, 5-H), 7.25 (2H, d, *J* 8.25, *p*-TolH), 7.96 (2H, d, *J* 8.25, *p*-TolH) 7.98 (1H, br d, *J* 6.26, NH) and 8.13 (1H, d, *J* 8.24, 4-H); δ_C 14.38 (CH_3, Et), 21.35 (CH_3, *p*-Tol), 24.89 (C-3′), 26.04 (C-4′), 33.01 (C-2′), 48.91 (C-1′), 60.39 (CH_2, Et), 103.70 (C-3), 106.59 (C-5), 127.10 (C-2″), 129.27 (C-3″), 136.31 (C-1″), 139.64 (C-4″), 140.63 (C-4), 157.68 (C-2), 160.05 (C-6) and 167.69 (C=O); *m*/*z* 338 (M^+, 26%), 309 (15, $M^+ - Et$), 281 [25, $M^+ - (CH_2)_4 - H$], 256 (100, M^+ - c-Hex + H) and 184 (32).

Aza-Wittig reaction of iminophosphoranes 17 with isocyanates and cycloaddition of carbodiimides 18 with *N*-(cyclohexen-1-yl)-morpholine. General procedure

Thermal reaction. A mixture containing iminophosphorane **17** (421 mg, 1.00 mmol) and isocyanate (1.00 mmol) in toluene (30 cm^3) was heated under reflux for 0.5–5 h. After the enamine (335 mg, 2.00 mmol) was added, heating was continued for 4–5 h. Evaporation of the solvent, column chromatography of the residue [silica gel, EtOAc–hexane (1:4)] and recrystallization (CH_2Cl_2–hexane) gave pure chromenoisoquinolinone **19** (yields in Table 3).

Lewis acid-promoted reaction. A mixture containing iminophosphorane **17** (421 mg, 1.00 mmol) and isocyanate (1.00 mmol) in tetracyanoethylene (30 cm^3) was heated at 110 °C for 0.5–2 h. The reaction mixture was cooled to − 15 °C and then $AlCl_3$ (0.2–1.0 mmol) and the enamine (2.0 mmol) in tetrachloroethylene (40 cm^3) were successively added to the mixture. The reaction mixture was warmed up to room temperature with stirring for 3–20 h, quenched with cold saturated aq. NH_4Cl (20 cm^3), extracted with CH_2Cl_2 (30 cm^3 × 3), washed with aq. $NaHCO_3$ and brine, and dried ($MgSO_4$). Work-up for the purification to give chromenoisoquinolinone **19** was the same as described in Method A (yields in Table 3).

6-(Phenylamino)-7,8,9,10-tetrahydro-11*H*-chromeno[4,3-*c*]-isoquinolin-11-one 19a. Colourless plates, mp 230.8–231.9 °C (Found: C, 76.89; H, 5.33; N, 7.96%. $C_{22}H_{18}N_2O_2$ requires C, 77.17; H, 5.30; N, 8.18%); ν_{max}(KBr)/cm^{-1} 3340 (NH) and 1696 (C=O); δ_H (270 MHz) 1.76–2.00 (4H, m, 8-H, 9-H), 2.56 (2H, m, 7-H), 3.33 (2H, m, 10-H), 6.70 (1H, br s, NH), 7.16 (1H, t, *J* 7.92, 4′-H), 7.24–7.50 (5H, m, 3′-H, 1-H, 2-H, 3-H), 7.74 (2H, d, *J* 7.92, 2′-H) and 8.35 (1H, dd, *J* 8.25 and 1.65, 4-H); δ_C (67.8 MHz, DEPT) 21.42 (8-C or 9-C), 21.90 (9-C or 8-C), 24.33 (10-C), 29.18 (7-C), 108.21 (4a-C), 116.30 (1-C), 118.20 (10b-C), 120.00 (6a-C), 121.13 (2′-C), 123.63 (4′-C), 123.93 (3-C), 125.05 (4-C), 128.88 (3′-C), 131.07 (2-C), 139.14 (1′-C), 150.78 (10a-C), 150.85 (4b-C), 152.61 (12a-C), 155.92 (6-C) and 160.75 (11-C); *m*/*z* 342 (M^+, 100%), 327 (M^+, 20%), 313 (11), 265 ($M^+ - Ph$, 5) and 251 (15).

6-(*p*-Tolylamino)-7,8,9,10-tetrahydro-11*H*-chromeno[4,3-*c*]-isoquinolin-11-one 19b. Colourless plates, mp 230.0–231.1 °C; (Found: C, 77.59; H, 5.76; N, 7.85%. $C_{23}H_{20}N_2O_2$ requires C, 77.50; H, 5.66; N, 7.86%); ν_{max}(KBr)/cm^{-1} 3360 (NH) and 1698 (C=O); δ_H 1.80–1.92 (4H, m, 8-H, 9-H), 2.39 (3H, s, CH_3), 2.55 (2H, m, 7-H), 3.33 (2H, m, 10-H), 6.65 (1H, br s, NH), 7.21–7.30 (4H, m, 3′-H, 1-H, 3-H), 7.46 (1H, ddd, *J* 7.92, 7.43 and 1.65, 2-H), 7.61 (2H, d, *J* 8.58, 2′-H) and 8.35 (1H, dd, *J* 8.09 and 1.65, 4-H); *m*/*z* 356 (M^+, 100%), 341 ($M^+ - NH$, 18), 327 (9), 265 ($M^+ - Tol$, 4), 251 (15), 178 (5) and 91 (4).

6-(*p*-Nitrophenylamino)-7,8,9,10-tetrahydro-11*H*-chromeno-[4,3-*c*]isoquinolin-11-one 19c. Yellow needles, mp 333.5–334.8 °C (Found: M^+, 387.1214. $C_{22}H_{17}N_3O_4$ requires *M*, 387.1220); ν_{max}(KBr)/cm^{-1} 3456 (NH) and 1724 (C=O); δ_H 1.84–2.02 (4H, m, 8-H, 9-H), 2.69 (2H, m, 7-H), 3.42 (2H, m, 10-H), 7.04 (1H, br s, NH), 7.33–7.41 (2H, m, 1-H, 3-H), 7.55 (1H, ddd, *J* 7.92, 7.92 and 1.32, 2-H), 7.97 (2H, d, *J* 9.24, 2′-H), 8.34 (2H, d, *J* 9.24, 3′-H) and 8.39 (1H, dd, *J* 7.92 and 1.32, 4-H); *m*/*z* 387 (M^+, 100%), 372 ($M^+ - NH$, 12), 340 ($M^+ - NO_2H$, 8), 312 (6), 265 ($M^+ - NO_2Ph$, 5) and 251 (19).

6-(*p*-Chlorophenylamino)-7,8,9,10-tetrahydro-11*H*-chromeno-[4,3-*c*]isoquinolin-11-one 19d. Colourless plates, mp 282.5–283.9 °C (Found: C, 70.17; H, 4.63; N, 7.56%. $C_{22}H_{17}N_2O_2Cl$ requires C, 70.14; H, 4.55; N, 7.43%); ν_{max}(KBr)/cm^{-1} 3456 (NH) and 1724 (C=O); δ_H 1.81–1.99 (4H, m, 8-H, 9-H), 2.61 (2H, m, 7-H), 3.38 (2H, m, 10-H), 6.69 (1H, br s, NH), 7.30 (1H, dd, *J* 6.93 and 1.32, 1-H), 7.34 (1H, ddd, *J* 7.92, 7.10 and 1.32, 3-H), 7.40 (2H, d, *J* 8.91, 2′-H), 7.50 (1H, ddd, *J* 7.10, 6.93 and 1.65, 4-H), 7.70 (2H, d, *J* 8.91, 3′-H) and 8.34 (1H, dd, *J* 7.92 and 1.65, 4-H); *m*/*z* 376 (M^+, 100%), 361 ($M^+ - NH$, 15), 325 (5), 312 (4), 265 ($M^+ - ClPh$, 5) and 251 (22).

6-(Tosylamino)-7,8,9,10-tetrahydro-11*H*-chromeno[4,3-*c*]-isoquinolin-11-one 19e. Colourless needles, mp 239.7–240.9 °C (Found: C, 65.75; H, 4.88; N, 6.71%. $C_{23}H_{20}N_2O_4S$ requires C, 65.70; H, 4.80; N, 6.66%); ν_{max}(KBr)/cm^{-1} 3348 (NH), 1732 (C=O), 1338 and 1164; δ_H 1.7–1.9 (4H, m, 8-H and 9-H), 2.37

(3H, s, Me), 2.60 (2H, br s, 1-H), 3.20–3.35 (2H, m, 4-H), 7.2–8.0 (7H, m, ArH and NH) and 8.10 (2H, d, *J* 7.82, TsH); *m*/*z* 420 (M^+, 9%), 265 (100, $M^+ - Ts$), 250 (3, $M^+ - TsNH$) and 91(22).

Computational calculations

Semiempirical calculations were carried out using the AM1 Hamiltonian implemented MOPAC93.[23] Transition states were optimized with TS and NLLSQ algorithms. The force constant matrix of the transition state revealed the single negative eigenvalue. The IRC (intrinsic reaction coordinate) algorithm was applied connecting the transition state with reactant and product by following the transition vector in both directions.

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