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TETRAHEDRON

A Highly Efficient Multicomponent Synthesis of Pyridones and Pyrimidones by a [2+2+2] Strategy

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To the memory of Professor Sir Derek Barton with admiration and affection

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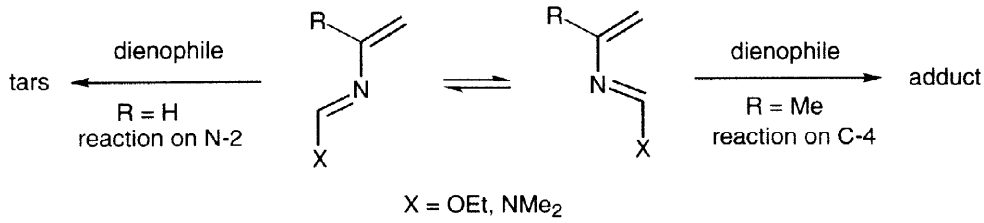
Abstract : The reaction of N-silylated iminoethers with 2-substituted acetyl chlorides yields activated 2-azadienes. These were shown to react with electron-deficient acetylenic dienophiles to yield pyridones. They also react with quinones to give the corresponding aromatized cycloadducts in good yields. The reaction of 2-azadienes with activated nitriles provided a very practical route towards polysubstituted pyrimidones. A multicomponent protocol is reported which combines a N-*t*-butyldimethylsilyl iminoether, an acetyl chloride derivative and a dienophile in the presence of triethylamine without isolation of any intermediate. This provides an extremely practical and versatile route to various mono- and polycyclic azaaromatics with a predictable substitution pattern. Yields ranged from 43 % to 94 % for the complete sequence.

Keywords : Diels-Alder reaction, 2-azadienes, pyridones, pyrimidones, isoquinolines, multicomponent reactions.

INTRODUCTION

The Diels-Alder reaction appears nowadays as the most powerful method of synthesis of six-membered rings.[1] The availability of highly functionalized dienes and the development of efficient catalysts have considerably widened the scope of the reaction.[1,2] In 1975, when we reported on the high reactivity of 1-amino-2-azadienes in Diels-Alder reaction with electron-poor dienophiles, we had noticed only very few representatives of enophiles incorporating a nitrogen atom in the conjugated system.[3] Times have changed and, nowadays, a wide variety of azadienes have been prepared and shown to react with dienophiles.[4]
In our earlier papers, we have underlined the importance of substitution of 2-azadienes at C-3 for the selection of a reaction site by the dienophile (Scheme 1).[5,6]



Scheme 1

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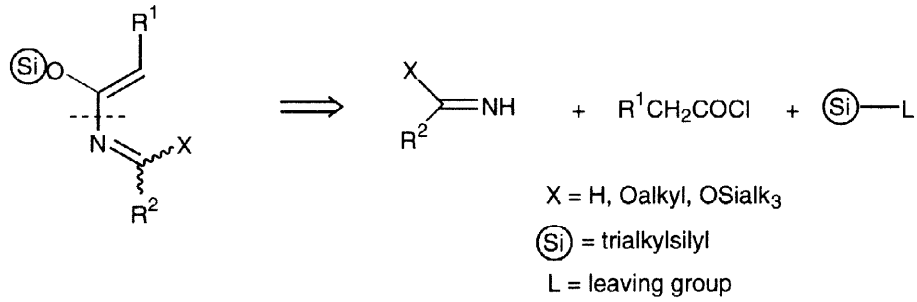
When R was a methyl group, the cycloaddition took place with great ease, probably as a result of an increased population of the cisoid conformation. When R=H, no cycloaddition was observed but both dienes and dienophiles quickly disappeared to give tars. This was ascribed to a reaction of the dienophile with the nucleophilic nitrogen atom of the most abundant transoid conformation of the azadiene.

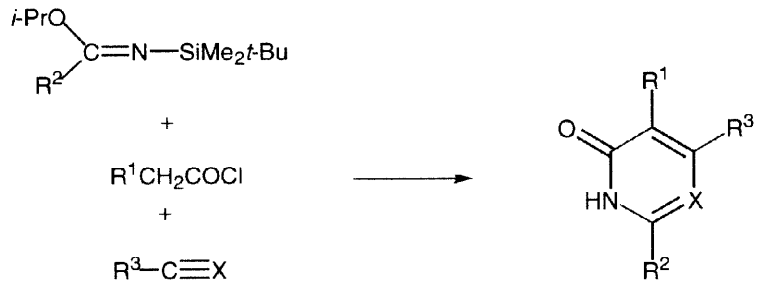
Bearing these observations in mind, we designed a new class of 2-azadienes which was expected to fit all structural requirements for a good enophile (Scheme 2). The important feature of this class of 2-azadienes is the presence of a trialkylsilyloxy group at C-3. This substituent should increase the nucleophilicity.



Scheme 2

of the diene at C-4 by raising the energy of the HOMO and increasing its coefficient at C-4. It should also decrease the energy barrier between the transoid and the cisoid conformation thus favouring the cycloaddition over reactions on the nitrogen atom. An additional advantage is that this class of 2-azadienes should be readily prepared by an appropriate assembly of an imine providing the C=N fragment and a substituted acetic acid derivative providing the C=C fragment.

A full account of the synthesis of a wide variety of azadienes according to the strategy of Scheme 2 has already appeared.[7] Also, in preliminary reports, we have demonstrated the high reactivity of these 2-azadienes in Diels-Alder cycloadditions.[5,8] Herein we report in detail on the reaction of 2-azadienes with activated acetylenes and nitriles and on a practical three-component synthesis of substituted pyridones and pyrimidones based on the [2+2+2] strategy outlined in Scheme 3.

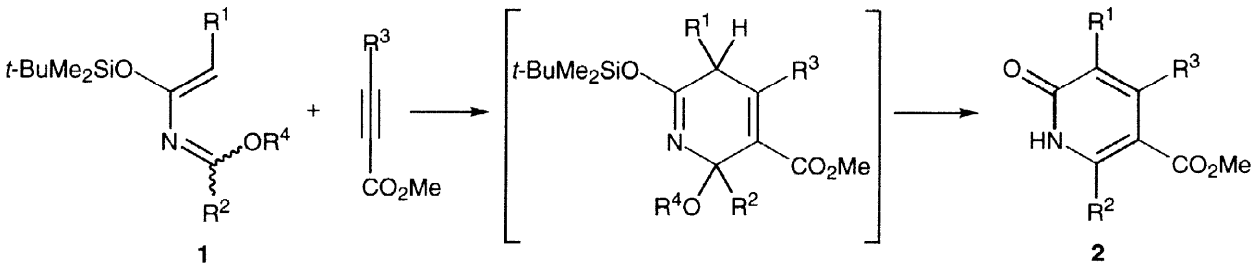


Scheme 3

CYCLOADDITIONS USING ISOLATED 2-AZADIENES

1. Acetylenic dienophiles

2-Azadienes **1** were prepared by the described procedures.[7] They readily reacted with dimethyl acetylenedicarboxylate (DMAD) and with methyl propiolate to give a primary adduct which spontaneously lost a molecule of alcohol or silanol. Hydrolysis or methanolysis gave good yields of substituted pyridones **2** (Scheme 4, Table 1).



1 **2**

1a, R^1=H, R^2=H, R^4=*t*-BuMe$_2$Si
1b, R^1=H, R^2=H, R^4=*i*-Pr
1c, R^1=Me, R^2=H, R^4=*i*-Pr
1d, R^1=Cl, R^2=H, R^4=*i*-Pr
1e, R^1=H, R^2=Me, R^4=*t*-BuMe$_2$Si
1f, R^1=H, R^2=Me, R^4=Et
1g, R^1=F, R^2=H, R^4=*i*-Pr
1h, R^1=Ph, R^2=H, R^4=*i*-Pr
1i, R^1=Bu, R^2=H, R^4=*i*-Pr

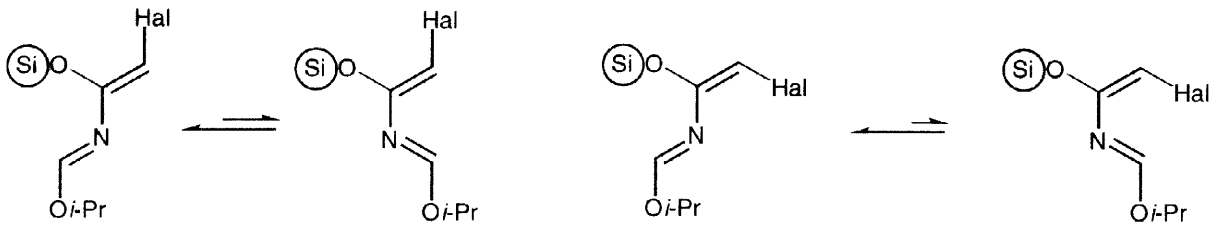
Scheme 4

Table 1 : Cycloadditions of 2-azadienes to acetylenic esters

Entry	R^1	R^2	R^3	R^4	Conditions	Yields % of **2**
a	H	H	CO_2Me	*t*-BuMe$_2$Si	benzene, 1 h 30, reflux	**2a**, 64[a]
b	H	H	CO_2Me	*i*-Pr	$CHCl_3$, 3 h, reflux	**2a**, 60[a]
c	Me	H	CO_2Me	*i*-Pr	benzene, 3 h, reflux	**2b**, 40
d	Cl	H	CO_2Me	*i*-Pr	benzene, 3 h, reflux	**2c**, 28
e	H	Me	CO_2Me	*t*-BuMe$_2$Si	benzene, 2 h, reflux	**2d**, 63
f	H	Me	CO_2Me	Et	benzene, 3 h, reflux	**2d**, 61
g	H	H	H	*t*-BuMe$_2$Si	benzene, 18 h, reflux	**2e**, 64
h	H	Me	H	*t*-BuMe$_2$Si	benzene, 8 h, reflux	**2f**, 52
i	Me	H	H	*i*-Pr	$CHCl_3$, 7 h, reflux	**2g**, 50
j	F	H	H	*i*-Pr	benzene, 18 h, reflux	**2h**, 24
k	Me	H	Me	*i*-Pr	benzene, reflux	0

a : 8 % of compound **3a** were also produced (see Scheme 6).

Lower yields were obtained when R^1 = Cl, F (entry d and j). This is probably due to the use of a mixture of diastereoisomeric azadienes.[7] Only those bearing the halogen atom cis to the trialkylsilyloxy group would allow the azadiene to adopt the cisoid conformation required for a successful cycloaddition (Scheme 5).

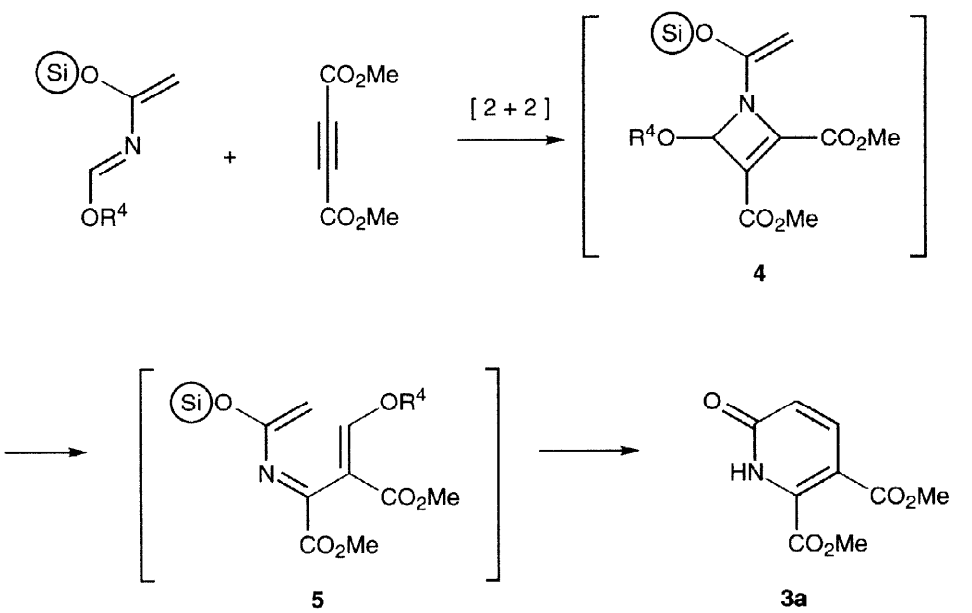


Scheme 5

In most cases, non-polar solvents such as benzene, toluene or chloroform gave the best results. Acetonitrile usually gave lower yields. No cycloadduct could be obtained when R^3 = Me (entry k). However no attempts were made to use high pressure or Lewis acid catalysis to increase the rate of this reaction.

The structures of pyridones **2** followed from the examination of their spectral properties or by comparison with authentic samples. The regioselectivity of the reactions with methyl propiolate is in full agreement with that predicted by FMO theory.

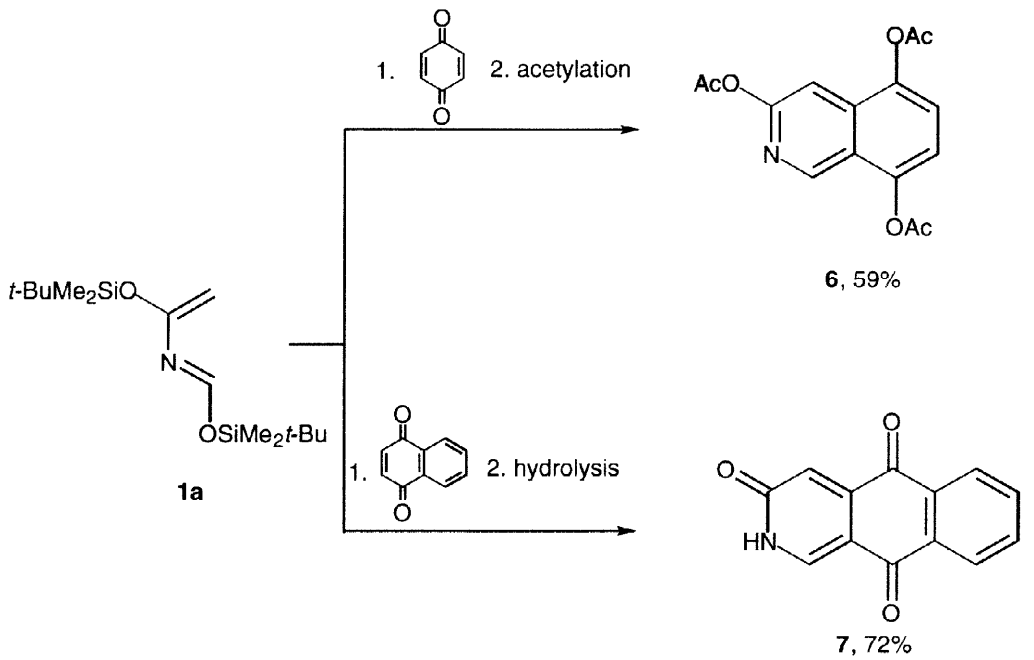
In the reactions corresponding to entries a and b of Table 1, we were able to isolate ± 8 % of an isomer **3a** of the main product **2a**. The structure of **3a** was confirmed by comparison with an authentic sample. This minor product could result from a [2+2] cycloaddition of DMAD to the C=N bond of the azadiene followed by a fast electrocyclisation of the resulting push-pull azetine **4** to give the isomeric azadiene **5**. A second electrocyclisation followed by aromatization would give the observed pyridone **3a** (Scheme 6).



Scheme 6

2. *Quinones*

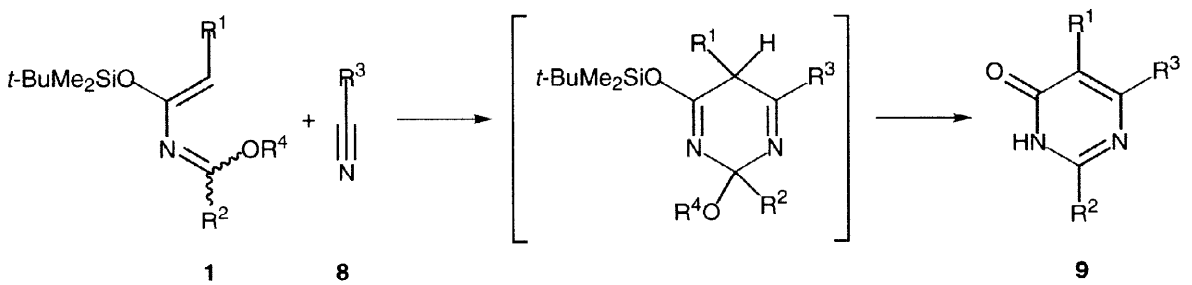
The reaction of benzoquinone with azadiene **1a** gave an adduct which was directly acetylated to yield the isoquinoline derivative **6** (Scheme 7). Similarly, 2-azadiene **1a** reacted with 1,4-naphtoquinone to give a good yield of azaanthraquinone **7**.



Scheme 7

3. *Activated nitriles*

The scope of this Diels-Alder methodology for the preparation of six membered azaaromatic compounds was further extended by the observation that 2-azadienes **1** smoothly reacted with activated nitriles **8** (Scheme 8, Table 2). Here again the primary adduct could not be identified : it spontaneously aromatized to give the pyrimidone derivatives **9** after methanolysis. Table 2 shows that these hetero Diels-Alder reactions allowed the preparation of a wide variety of polyfunctionalised pyrimidones.



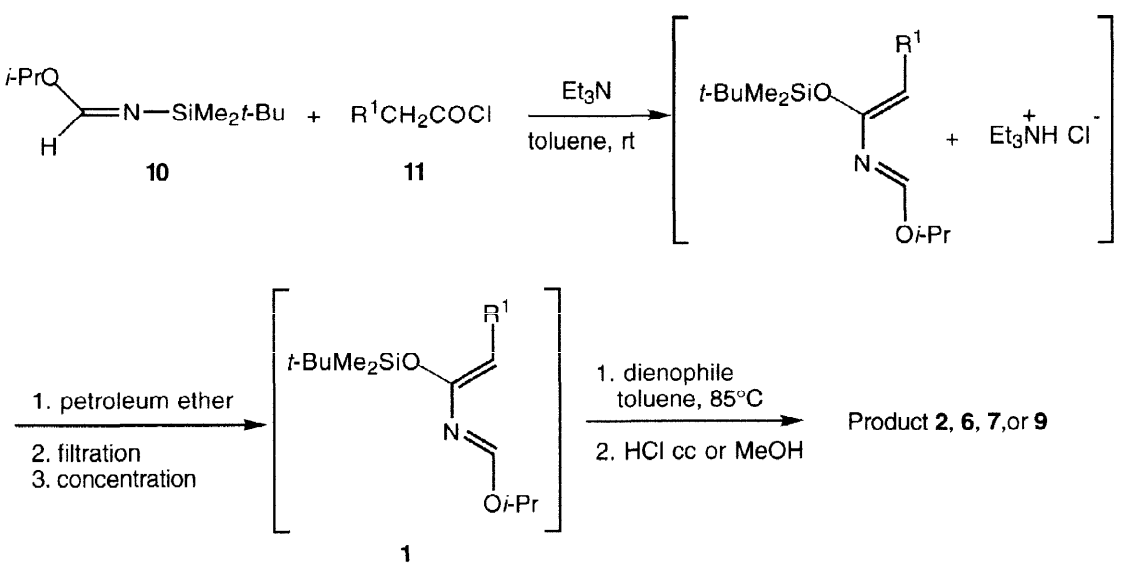
Scheme 8

Table 2 : Cycloaddition of 2-azadienes 1 with activated nitriles

Entry	R^1	R^2	R^3	R^4	Conditions	Yields % of **9**
a	H	H	*p*-Tos	*i*-Pr	benzene, 30 min., 25° C	**9a**, 93
b	Me	H	*p*-Tos	*i*-Pr	benzene, 30 min., 50° C	**9b**, 76
c	F	H	*p*-Tos	*i*-Pr	benzene, 1 h, 50° C	**9c**, 59
d	Cl	H	*p*-Tos	*i*-Pr	benzene, 1 h, 50° C	**9d**, 51
e	Bu	H	*p*-Tos	*i*-Pr	benzene, 1 h, 50° C	**9e**, 60
f	H	H	Cl_3C	*i*-Pr	neat, 15 min., reflux	**9f**, 94
g	Me	H	Cl_3C	*i*-Pr	neat, 3 h., reflux	**9g**, 73
h	Bu	H	Cl_3C	*i*-Pr	neat, 10 h, reflux	**9h**, 49
i	H	Me	Cl_3C	*i*-Pr	neat, 3 h, reflux	**9i**, 84
j	H	H	CO_2Et	*i*-Pr	$CHCl_3$, 1 h, reflux	**9j**, 82
k	Me	H	CO_2Et	*i*-Pr	benzene, 12 h, reflux	**9k**, 63
j	H	Me	CO_2Et	Et	neat, reflux	0

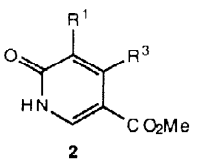
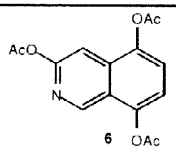
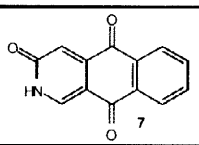
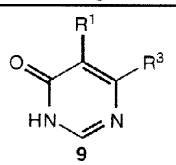
THREE-COMPONENT SYNTHESIS OF PYRIDONE AND PYRIMIDONE DERIVATIVES

The broad scope of the cycloaddition reactions of 2-azadienes led us to examine whether the synthesis of the 2-azadienes and the cycloaddition reactions followed by aromatization could not be effected in a single operation. These studies led to an optimised protocol which allows the transformation of an iminoether **10**, an acid chloride **11** and a dienophile into the corresponding heterocycles **2**, **6**, **7** or **9** in a one-pot process (Scheme 9, Table 3).



Scheme 9

Table 3 : Synthesis of azaaromatics 2, 6, 7 and 9 from iminoether 10, acid chlorides 11 and dienophiles in toluene at 85° C.

Product	R^1	R^3	Diene (equiv.)	Time	Yield (%) one-pot process	Yield (%) stepwise process
 2	H	CO_2Me	2	1 h 30	81	44
	Me	CO_2Me	1.5	3 h 30	65	31
	Ph	CO_2Me	1.5	16 h 30	76	-
	Cl	CO_2Me	2	18 h	63	20
	H	H	2	3 h 10	78	56
	Me	H	1.5	3 h 25	85	39
	Ph	H	1.5	16 h	60	-
	Cl	H	2	23 h	43	42
	F	H	2	20 h	43	13
 6	-	-	1.5	6 h[a]	47	52[b]
 7	-	-	2	3 h	52	63[b]
 9	H	*p*-Tos	1.5	35 min.[a]	94	69
	Me	*p*-Tos	1.5	1 h	66	59

a : the cycloaddition step was done at 25° C.
b : from 2-azadiene **1a**.

The optimised protocol first involves the addition of the acid chloride **11** to a solution of the iminoether **10** and triethylamine in toluene. We found that both triethylamine hydrochloride and excess triethylamine had to be eliminated before addition of the dienophile. Heating the azadiene in the presence of triethylamine hydrochloride led to extensive decomposition. Also, some highly electrophilic dienophiles (e.g. DMAD) can react with excess triethylamine. The cycloaddition was effected by heating the solution of the diene and the dienophile in toluene at 85° C. The reaction mixture was worked-up with concentrated HCl and then neutralised with sodium bicarbonate. Table 3 clearly shows that this protocol gave in general much better yields than the two-step process involving the synthesis and isolation of 2-azadienes.

CONCLUSIONS

In summary, we have developed a concise and highly convergent approach towards polysubstituted pyridones and pyrimidones from simple and readily accessible starting materials. The method should provide access to a wide range of substitution patterns which are defined by an appropriate choice of the starting materials. The three-component protocol is the most practical and gives the best yields. The stepwise procedure involving the isolation of the 2-azadiene will only be used in special cases. These findings are now being extended to the synthesis of piperidine derivatives.

EXPERIMENTAL PART

Melting points were taken using a Leitz-Wetzlar HM-Lux microscope equipped with a hot plate. IR spectra were recorded on Perkin-Elmer 297 or 681 spectrometers. ^{1}H NMR spectra were obtained on Varian T-60, XL-100, XL-200, VXR-200 or Gemini-300BB spectrometers [δ=0 (TMS), $CDCl_3$, J in Hertz]. ^{13}C NMR spectra were recorded at 20 MHz on Varian CFT-20, at 50 MHz on Varian XL-200 or VXR-200, at 75 MHz on Gemini-300BB (δ in ppm, relative to internal TMS, J in Hertz). Mass spectral data were measured on Varian MAT-44 or FINNIGAN MAT-TSQ-70 spectrometers (electronic impact 70 eV or chemical ionisation 100 eV with 200 μbar isobutane as ionising gas). Benzene, toluene and diethylether were distilled from sodium-benzophenone ketyl. Petroleum ether and triethylamine were distilled from calcium hydride. Acid chlorides were distilled immediately before use. All azadienes were prepared and purified according to the published procedures.[7]

General procedures:

Method A refers to the cycloaddition using a purified diene and the dienophile (neat or in $CHCl_3$, benzene, toluene). Work-up protocols 1 or 2 were applied except in specified cases.

Method B refers to the three-component strategy from N-*t*-butyldimethylsilyl iminoether **10**, the appropriate acid chloride **11** and the dienophile :

A solution of acid chloride (3.26 to 4.97 mmol) in 1 ml of dry toluene was added dropwise to a solution of N-*t*-butyldimethylsilyl iminoether **10** (3.26 to 4.97 mmol) and triethylamine in 2.5 ml of dry toluene. The resulting mixture was stirred for 2 hours at room temperature. Then 3 ml of petroleum ether (bp: 40-60° C) were added in one portion. The precipitate of triethylamine hydrochloride was filtered off under dry argon, washed with 3 portions of 1 ml of petroleum ether. Removal of the solvents at reduced pressure (oil pump) and addition of 3.5 ml of dry toluene gave a solution of the azadiene to which 1 equivalent of the dienophile was added. The mixture was heated at 85° C.

Two different work-ups have been used :

Work-up 1 : Addition of 4 ml of methanol to the reaction mixture at room temperature followed by removal of the solvents (rotavapor). Addition of small amount of diethylether to the residue gaves a crystalline material.

Work-up 2 : The reaction mixture was quenched with 0.5 ml of concentrated hydrochloric acid at room temperature. The mixture was concentrated *in vacuo* and the residue was taken up in chloroform to give a solution which was washed with 5 % $NaHCO_3$ in water. The organic layer was dried over $MgSO_4$. Removal of the solvent and addition of diethylether gave crystalline material. In all cases, the crystals were of satisfactory purity. Analytical samples were obtained after recrystallization or chromatography on silica gel.

4,5-bis(methoxycarbonyl)-2-pyridone* 2a *(RN: 80658-29-3)

Method A: 1.03 gr (3.27 mmol) of azadiene **1a**, 0.8 ml (6.5 mmol) of DMAD, 3 ml of benzene, 1 h 30 at reflux. *Work-up 2*. Chromatography on silica gel (AcOEt). Yield **2a**: 0.445 gr (64 %). R_f: 0.3 (AcOEt). mp: 151-152° C. ^{1}H NMR ($CDCl_3$, TMS, 60 MHz, ppm): 3.82 (s, 3H); 3.92 (s, 3H); 6.53 (s, 1H); 8.1 (s, 1H); 12.5-13.3 (s, 1H). IR ($CHCl_3$, PSt, cm^{-1}) 3400; 1745; 1730; 1670; 1620; 1420; 1300; 1120; 1080. MS (EI) m/e=211 ($M^{+\cdot}$, 4 %); 180 ($M^{+\cdot}$-$CH_3O^{\cdot}$, 10 %); 159 ($M^{+\cdot}$-C_2H_2O, 6 %); 128 (159-$CH_3O^{\cdot}$, 7 %); 100 (159-$CO_2CH_3^{\cdot}$, 31 %). Exact mass calcd for $C_9H_9NO_5$ requires m/e 211.0480; found m/e 211.0472. Minor isomer: ***4,5-bis(methoxycarbonyl)-2-pyridone* 3a *(RN: 32383-11-2)***: Yield **3a**: 0.053 gr (8 %). R_f: 0.26 (AcOEt). ^{1}H NMR ($CDCl_3$, TMS, 60 MHz, ppm): 3.99 (s, 3H);

4.02 (s, 3H); 6.71 (d, 1H, ^{3}J=6.4 Hz); 7.56 (d, 1H, ^{3}J= 6.4 Hz); 8.5-11.0 (s, 1H). ^{13}C NMR (CD_3OD, TMS, 20 MHz, ppm): 53.49; 54.01; 106.22; 127.54; 138.53; 142.42; 162.40; 166.14; 167.70. IR (KBr, PSt, cm^{-1}) 3640; 3300; 1740 (broad); 1660 (broad); 1640; 1555; 1495; 1465; 1440; 1280; 1250; 1150; 1130; 1070; 1025; 850; 760. MS (EI) m/e = 211 ($M^{+\cdot}$, 27 %); 180 ($M^{+\cdot}$-$CH_3O^{\cdot}$, 43 %); 179 ($M^{+\cdot}$-CH_3OH, 44 %); 149 (180-$CH_3O^{\cdot}$, 19 %); 148 (180-CH_3OH, 18 %); 121 (180-$CO_2CH_3^{\cdot}$, 32 %); 120 (179-$CO_2CH_3^{\cdot}$, 28 %); 92 (100 %).

Method A (from azadiene **1b**): 0.60 gr (2.47 mmol) of azadiene **1b**, 0.610 ml (4.96 mmol) of DMAD, 5 ml of $CHCl_3$, 3 h at reflux. *Work-up 2*. Chromatography on silica gel (AcOEt). Yield **2a**: 0.315 gr (60 %). Minor isomer: ***4,5-bis(methoxycarbonyl)-2-pyridone*** **3a**: Yield **3a**: 0.042 gr (8 %).

Method B : 0.7 gr (3.48 mmol, 2 eq.) of iminoether **10**, 0.48 ml (3.48 mmol, 2 eq.) of Et_3N, 0.25 ml (3.48 mmol, 2 eq.) of acetyl chloride, 0.21 ml (1.74 mmol, 1 eq.) of DMAD, 1 h 30 at 85° C. *Work-up 2*. Yield **2a**: 0.298 gr (81 %).

4,5-bis(methoxycarbonyl)-3-methyl-2-pyridone **2b**

Method A : 0.359 gr (1.4 mmol) of azadiene **1c**, 0.340 ml (2.8 mmol) of DMAD, 5 ml of benzene, 3 h at reflux. *Work-up 2*. Recrystallization from CH_3CN. Yield **2b**: 40 %. mp: 193° C. ^{1}H NMR ($CDCl_3$, TMS, 200 MHz, ppm): 1.96 (d, 3H, ^{6}J=0.59Hz); 3.76 (s, 3H); 3.86 (s, 3H); 7.98 (d, 1H, ^{6}J=0.59Hz); 10.4 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz, ppm): 167.07; 165.18; 163.57; 142.83; 137.86; 126.09; 107.89; 52.75; 52.26; 13.05. IR (KBr, PSt, cm^{-1}) 1750; 1725; 1645; 1620; 1445; 1420; 1380; 1310; 1260; 1200; 1160; 1065. MS (EI) m/e= 225 ($M^{+\cdot}$, 34 %); 210 ($M^{+\cdot}$-$CH_3^{\cdot}$, 11 %); 193 ($M^{+\cdot}$-CH_3OH, 91 %); 178 (210-CH_3OH, 12 %); 166 ($M^{+\cdot}$-$CO_2Me^{\cdot}$, 3 %); 149 (193-CO_2, 8 %); 135 (166-$CH_3O^{\cdot}$, 29 %); 123 (166-CONH, 2 %); 107 (135-CO, 15 %); 73 (18 %). Exact mass calcd for $C_{10}H_{11}NO_5$ requires m/e 225.0637; found m/e 225.0643.

Method B : 0.654 gr (3.26 mmol, 1.5 eq.) of iminoether **10**, 2.26 ml (16.3 mmol, 7.5 eq.) of Et_3N, 0.28 ml (3.26 mmol, 1.5 eq.) of propionyl chloride, 0.27 ml (2.17 mmol, 1 eq.) of DMAD, 3 h 30 at 85° C. *Work-up 2*. Yield **2b**: 0.319 gr (65 %).

3-chloro-4,5-bis(methoxycarbonyl)-2-pyridone **2c**

Method A : 0.388 gr (1.4 mmol) of azadiene **1d**, 0.340 ml (2.8 mmol) of DMAD, 5 ml of benzene, 3h at reflux. *Work-up 2*. Recrystallization from CH_3CN. Yield **2c**: 28 %. mp: 219° C. ^{1}H NMR ($CDCl_3$, TMS, 200 MHz, ppm): 3.78 (s, 3H); 3.89 (s, 3H); 8.07 (s, 1H); 10.4 (s, 1H). ^{13}C NMR (CD_3SOCD_3, 75 MHz, ppm): 164.33; 162.79; 157.94; 142.15; 140.70; 121.43; 105.48; 53.12; 52.57. IR (KBr, PSt, cm^{-1}) 1750; 1730; 1650; 1450; 1425; 1305; 1250; 1235; 1150; 1100. MS (EI) m/e= 245 ($M^{+\cdot}$, 69 %); 214 ($M^{+\cdot}$-$CH_3O^{\cdot}$, 100 %); 186 ($M^{+\cdot}$-$CO_2Me^{\cdot}$, 4 %); 182 (214-CH_3OH, 4 %); 171 (182-HNCO, 6 %); 127 (186-$CO_2Me^{\cdot}$, 3 %); 43 ($HNCO^{+\cdot}$, 20 %). Elemental analysis: % calculated C : 44.01 %, H : 3.28 %, Cl : 14.43 %, N : 5.70 %; % found C : 43.97 %, H : 3.12 %, Cl : 14.57 %, N : 5.56 %.

Method B : 0.874 gr (4.34 mmol, 2 eq.) of iminoether **10**, 0.6 ml (4.34 mmol, 2 eq.) of Et_3N, 0.345 ml (4.34 mmol, 2 eq.) of chloroacetyl chloride, 0.266 ml (2.17 mmol, 1 eq.) of DMAD, 18 h at 85° C. *Work-up 2*. Yield **2c**: 0.333 gr (63 %).

4,5-bis(methoxycarbonyl)-6-methyl-2-pyridone **2d**

Method A (from azadiene **1e**) : 0.854 gr (2.6 mmol) of azadiene **1e**, 0.32 ml (2.6 mmol) of DMAD, 2 ml of benzene, 2 h at reflux. *Work-up 2*. Chromatography on silica gel (AcOEt). Yield **2d**: 0.368 gr (63 %). R_f: 0.30 (AcOEt). mp: 157-158° C. ^{1}H NMR ($CDCl_3$, TMS, 60 MHz, ppm): 2.53 (s, 3H); 3.79 (s, 3H); 3.85 (s, 3H); 6.55 (s, 1H); 12.7-13.7 (s, 1H). IR (KBr, PSt, cm^{-1}) 3430; 3320; 1730; 1715; 1665; 1620; 1440; 1420; 1325; 1270; 1250; 1200; 1160; 1120; 955; 885; 790; 780; 640. MS (CI) m/e= 226(M+1)$^+$. Elemental analysis : % calculated C : 53.33 %, H : 4.92 %, N : 6.22 %; % found C : 53.25 %, H 4.97 %, N : 6.21 %.

Method A (from azadiene **1f**) : 0.418 gr (1.7 mmol) of azadiene **1f**, 0.42 ml (3.4 mmol) of DMAD, 6 ml of benzene, 3 h at reflux. *Work-up 2*. Yield **2d**: 0.236 gr (61 %).

5-(methoxycarbonyl)-2-pyridone **2e** ***(RN: 66171-50-4)***

Method A : 0.500 gr (1.58 mmol) of azadiene **1a**, 0.282 ml (3.18 mmol) of methyl propiolate, 5 ml of benzene, 18 h at reflux. *Work-up 2*. Chromatography on silica gel (CH_2Cl_2/*i*PrOH: 9/1). Yield **2e**: 0.155 gr (64 %). R_f: 0.30 (CH_2Cl_2/*i*PrOH: 9/1). mp: 163-164° C. ^{1}H NMR ($CDCl_3$, TMS, 200 MHz, ppm): 3.87 (s, 3H); 6.5 (d, 1H, ^{3}J=9 Hz); 7.87 (dd, 1H, ^{3}J=9Hz, ^{4}J=2Hz); 8.1 (d, 1H, ^{4}J=2Hz); 10.3-12 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 50 MHz, ppm): 165.58; 164.52; 140.99; 139.85; 119.49;

111.03; 52.07. IR ($CHCl_3$, PSt, cm^{-1}) 3650; 3400; 1720; 1660; 1620; 1440; 1300; 1120. Exact mass calcd for $C_7H_7NO_3$ requires m/e 153.0426; found m/e 153.0427.
Method B : 0.7 gr (3.48 mmol, 2 eq.) of iminoether **10**, 0.48 ml (3.48 mmol, 2 eq.) of Et_3N, 0.25 ml (3.48 mmol, 2 eq.) of acetyl chloride, 0.156 ml (1.74 mmol, 1 eq.) of methyl propiolate, 3 h 10 at 85° C. *Work-up 2.* Yield **2e**: 0.207 gr (78 %).

***5-(methoxycarbonyl)-6-methyl-2-pyridone* 2f**
Method A : 1.178 gr (3.58 mmol) of azadiene **1e**, 0.636 ml (7.16 mmol) of methyl propiolate, 7 ml of benzene, 8 h at reflux. *Work-up 2.* Chromatography on silica gel (CH_2Cl_2/*i*PrOH: 9/1). Yield **2f**: 0.311 gr (52 %). R_f: 0.36 (CH_2Cl_2/*i*PrOH: 9/1). mp: 220-221° C. ^1H NMR ($CDCl_3$, TMS, 100 MHz, ppm): 2.78 (s, 3H); 3.9 (s, 3H); 6.48 (d, 1H, ^3J=9.4 Hz); 8.1 (d, 1H, ^3J=9.4 Hz); 13.0-13.5 (s, 1H). IR ($CHCl_3$, PSt, cm^{-1}) 3350; 1705; 1645; 1600; 1430; 1270. MS (EI) m/e = 167 ($M^{+\cdot}$, 73 %); 149 ($M^{+\cdot}$-$H_2O^{\cdot}$, 7 %); 136 ($M^{+\cdot}$-$OCH_3^{\cdot}$, 100 %); 135 ($M^{+\cdot}$-CH_3OH; 30 %); 108 ($M^{+\cdot}$-$CO_2CH_3^{\cdot}$; 22 %); 43 ($HNCO^{+\cdot}$; 20%). Elemental analysis % calculated C : 57.48 %, H : 5.43 %, N : 8.38 %; % found C : 57.30 %, H : 5.45 %, O : 8.25 %.

5-(methoxycarbonyl)-3-methyl-2-pyridone* 2g *(RN: 66909-31-7)
Method A : 0.468 gr (1.8 mmol) of azadiene **1c**, 0.30 ml (3.6 mmol) of methyl propiolate, 3 ml of $CHCl_3$, 7 h at reflux. *Work-up 2.* Recrystallization from CH_3CN. Yield **2g**: 0.152 gr (50 %). mp: 216° C. ^1H NMR ($CDCl_3$, TMS, 200 MHz, ppm): 2.18 (s, 3H); 3.86 (s, 3H); 7.86 (d, 1H, ^4J=2.4 Hz); 8.14 (d, 1H, ^4J=2.4 Hz); 13.0 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 50 MHz, ppm): 164.66; 164.32; 137.07; 136.59; 128.43; 109.41; 51.44; 16.09. IR (KBr, PSt, cm^{-1}) 1725; 1675; 1595; 1575; 1445; 1350; 1310; 1240; 1200; 1150. MS (EI) m/e = 167 ($M^{+\cdot}$, 100 %); 136 ($M^{+\cdot}$-$CH_3O^{\cdot}$, 77 %); 108 ($M^{+\cdot}$-$CO_2Me^{\cdot}$, 16 %); 53 (35 %); 43 ($HNCO^{+\cdot}$, 31 %). Elemental analysis % calculated C : 57.48 %, H : 5.43 %, O : 28.71 %; % found C : 57.38 %, H : 5.40 %, O : 28.86 %.
Method B : 0.654 gr (3.26 mmol, 1.5 eq.) of iminoether **10**, 2.26 ml (16.3 mmol, 7.5 eq.) of Et_3N, 0.28 ml (3.26 mmol, 1.5 eq.) of propionyl chloride, 0.195 ml (2.17 mmol, 1 eq.) of methyl propiolate, 3 h 25 at 85° C. *Work-up 2.* Yield **2g**: 0.31 gr (85 %).

***3-fluoro-5-(methoxycarbonyl)-2-pyridone* 2h**
Method A: 0.860 gr (3.3 mmol) of azadiene **1g**, 0.547 ml (6.6 mmol) of methyl propiolate, 3 ml of benzene, 18 h at reflux. *Work-up 2.* Chromatography on silica gel (CH_2Cl_2/*i*PrOH: 96/4). Yield **2h**: 0.158 gr (28 %). R_f: 0.29 (CH_2Cl_2/*i*PrOH: 96/4). mp: 206-207° C. ^1H NMR ($CDCl_3$, TMS, 200 MHz, ppm): 3.80 (s, 3H); 7.61 (dd, 1H, $^4J_{HH}$=2.2Hz, $^3J_{HF}$=11.1Hz); 7.88 (dd, 1H, $^4J_{HH}$=2.2Hz, $^5J_{HF}$=0.9Hz); 11.0 (s, 1H). ^{13}C NMR (CD_3SOCD_3, 75 MHz, ppm): 163.96; 156.09; 150.95; 136.10; 119.89; 107.37; 52.24. IR (KBr, PSt, cm^{-1}) 1710; 1670; 1630; 1485; 1445; 1430; 1310; 1260; 1230; 1160; 1095. MS (EI) m/e= 171 ($M^{+\cdot}$, 4 %); 140 ($M^{+\cdot}$-$CH_3O^{\cdot}$, 5 %); 131 (17 %); 103 (29 %); 51 (37 %); 43 ($HNCO^{+\cdot}$, 7 %). Elemental analysis : % calculated C : 49.1 %, H : 3.5 %, N : 8.2 %; % found C : 48.81 %, H : 3.27 %, N : 7.97 %.
Method B : 1 gr (4.97 mmol, 2 eq.) of iminoether **10**, 6.9 ml (4.97 mmol, 20 eq.) of Et_3N, 0.479 gr (4.97 mmol, 2 eq.) of fluoroacetyl chloride, 0.222 ml (2.5 mmol, 1 eq.) of methyl propiolate, 20 h at 85° C. *Work-up 1.* Yield **2h**: 0.183 gr (43 %).

***4,5-(bismethoxycarbonyl)-3-phenyl-2-pyridone* 2j**
Method B : 0.654 gr (3.26 mmol, 1.5 eq.) of iminoether **10**, 0.45 ml (3.26 mmol, 1.5 eq.) of Et_3N, 0.43 ml (3.26 mmol, 1.5 eq.) of phenylacetyl chloride, 0.27 ml (2.17 mmol, 1 eq.) of DMAD. 16 h 30 at 85° C. *Work-up 2.* Recrystallization from CH_3CN. Yield **2j**: 0.476 gr (76 %). mp: 237-238° C. ^1H NMR (CD_3SOCD_3, 200 MHz, ppm): 3.51 (s, 3H); 3.74 (s, 3H); 7.19-7.4 (m, 5H); 8.14 (s, 1H); 12.60 (s, 1H). ^{13}C NMR (CD_3SOCD_3, 50 MHz, ppm): 166.19; 163.66; 161.46; 142.07; 141.27; 133.63; 129.65; 128.89; 128.29; 128.00; 105.39; 52.35; 52.23. IR (KBr, PSt, cm^{-1}) 3025; 1750; 1715; 1636; 1430; 1325. MS (CI) m/e= 288 $(M+1)^+$. Elemental analysis : % calculated C : 62.71 %, H : 4.56 %, N : 4.87 %; % found C : 62.63 %, H : 4.52 %, N : 4.85 %.

***5-(methoxycarbonyl)-3-phenyl-2-pyridone* 2k**
Method B : 0.654 gr (3.26 mmol, 1.5 eq.) of iminoether **10**, 0.45 ml (3.26 mmol, 1.5 eq.) of Et_3N, 0.43 ml (3.26 mmol, 1.5 eq.) of phenylacetyl chloride, 0.193 ml (2.17 mmol, 1 eq.) of methyl propiolate, 16 h at 85° C. *Work-up 2.* Recrystallization from CH_3CN. Yield **2k**: 0.296 gr (60 %). mp: 183-184° C. ^1H NMR (CD_3SOCD_3, 300 MHz, ppm): 3.77(s, 3H); 7.30-7.72 (m, 5H); 7.89 (d, 1H, ^4J=2.4 Hz); 8.03 (d,

1H, ^{4}J=2.4 Hz); 13.54 (s, 1H). ^{13}C NMR (CD_3SOCD_3, 75 MHz, ppm): 164.58; 161.50; 139.60; 136.60; 135.91; 129.72; 128.34; 128.22; 128.00; 108.67; 52.03. IR (KBr, PSt, cm^{-1}) 3050; 1720; 1655; 1619; 1440; 1244. MS (CI) m/e= 230(M+1)$^+$. Exact mass calcd for $C_{13}H_{11}NO_3$ requires m/e 229.0738; found m/e 2229.0733.

3,5,8-triacetoxyisoquinoline* 6 *(RN: 80662-18-6)

Method A : 1.548 gr (4.9 mmol) of azadiene **1a**, 0.356 gr (3.3 mmol) of *p*-benzoquinone, 7 ml of $CHCl_3$, 6 h at 25° C. *Work-up*: 10 ml of acetic anhydride and 1 drop of pyridine were added. The reaction mixture was then heated at reflux for 16 h. After removing the solvents, the residue was purified by chromatography on silica gel (AcOEt/hexane: 4/6). Yield **6** (oil): 0.56 gr (59 %). R_f: 0.35(AcOEt/hexane: 4/6). ^{1}H NMR ($CDCl_3$, TMS, 200 MHz, ppm): 2.40 (s, 3H); 2.44 (s, 3H); 2.46 (s, 3H); 7.20 (d, 1H, ^{3}J=8.4Hz); 7.32 (d, 1H, ^{5}J=1.2Hz); 7.34 (d, 1H, ^{3}J=8.4Hz); 9.02 (d, 1H, ^{5}J=1.2Hz). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): 168.90; 168.66; 168.58; 154.59; 146.65; 144.56; 142.73; 132.89; 122.74; 121.30; 118.42; 105.04; 20.86; 20.65; 20.51. IR (CH_2Cl_2, PSt, cm^{-1}) 1760; 1630; 1595; 1360; 1185 (broad); 1135; 1050; 1000. MS (EI) m/e= 303 ($M^{+\cdot}$,2 %); 261 ($M^{+\cdot}$-C_2H_2O; 4 %); 219 (261-C_2H_2O; 8 %); 177 (219- C_2H_2O, 23 %); 43 ($HNCO^{+\cdot}$, 100 %). Exact mass calcd for $C_{15}H_{13}NO_6$ requires m/e 303.0743; found m/e 303.0743.

Method B : 0.654 gr (3.26 mmol, 1.5 eq.) of iminoether **10**, 0.45 ml (3.26 mmol, 1.5 eq.) of Et_3N, 0.23 ml (3.26 mmol, 1.5 eq.) of acetyl chloride, 0.234 gr (2.17 mmol, 1 eq.) of *p*-benzoquinone, 6 h at 25° C. *Work-up*: 6.5 ml of acetic anhydride and 1 drop of pyridine were added. The reaction mixture was then heated at reflux for 16 h. After removing the solvents, the residue was purified by chromatography on silica gel (AcOEt/hexane: 4/6). Yield **6**: 0.31 gr (47 %).

benzo[g]isoquinoline-3,5,10(2H)-trione* 7 *(RN: 80658-30-6)

Method A : 1.106 gr (3.5 mmol) of azadiene **1a**, 0.369 gr (2.34 mmol) of 1,4-naphtoquinone, 7 ml of $CHCl_3$, 3 h at reflux. *Work-up*: 130 µl of concentrated HCl were added and the mixture was stirred for 16 h at room temperature. After removing the solvents *in vacuo*, the residue was treated at reflux in a mixture of ethanol and ether (6/4) and the solid was filtered off. Yield **7**: 0.378 gr (72 %). mp: 280-285° C. ^{1}H NMR (CF_3COOD, TMS, 200 MHz, ppm): 7.99 (s, 1H); 8.17 (m, 2H); 8.60 (m, 2H); 9.18 (s, 1H). ^{13}C NMR (CF_3COOD, 75 MHz, ppm): 183.30; 183.16; 167.54; 145.37; 141.96; 137.76; 137.30; 134.69; 134.59; 129.71; 129.32; 118.89; 117.97. IR (KBr, PSt, cm^{-1}) 3200-2500; 1690; 1670; 1655; 1590; 1550; 1445; 1345; 1295; 1250; 970; 920; 800; 770; 750; 720; 690; 610. MS (EI) m/e= 225 ($M^{+\cdot}$,100 %); 197 ($M^{+\cdot}$-CO; 30 %); 169 (197-CO; 19 %); 141 (169-CO, 11 %); 43 ($HNCO^{+\cdot}$, 70 %). Exact mass calcd for $C_{13}H_7NO_3$ requires m/e 225.0426; found m/e 225.0424.

Method B : 0.654 gr (3.26 mmol, 2 eq.) of iminoether **10**, 0.45 ml (3.26 mmol, 2 eq.) of Et_3N, 0.23 ml (3.26 mmol, 2 eq.) of acetyl chloride, 0.257 gr (1.63 mmol, 1 eq.) of 1,4-naphtoquinone, 3 h at reflux. *Work-up*: 90 µl of concentrated HCl were added and the mixture was stirred for 16 h at room temperature. After removing the solvents *in vacuo*, the residue was treated at reflux in a mixture of ethanol and ether (6/4) and the solid was filtered off. Yield **7**: 0.19 gr (52 %).

***6-(p-toluenesulphonyl)pyrimidin-4(3H)-one* 9a**

Method A : 1.3 gr (5.35 mmol) of azadiene **1b**, 0.968 gr (5.35 mmol) of tosyl cyanide, 10 ml of benzene, 30 minutes at 25° C. *Work-up 1*. Recrystallization from CH_3CN. Yield **9a**: 1.23 gr (93 %). mp: 280° C. ^{1}H NMR (CD_3SOCD_3, 200 MHz, TMS, ppm): 13.1 (s, 1H); 8.31 (d, 1H, ^{5}J=0.9 Hz); 7.88 and 7.50 (AB system, 4H, ^{3}J=8.3Hz); 7.04 (d, 1H, ^{5}J=0.9Hz); 2.44 (s, 3H). ^{13}C NMR (CF_3COOD, TMS, 20 MHz, ppm): 163.84; 162.75; 152.20; 149.06; 131.25; 130.66; 129.10; 116.00; 20.14. IR (KBr, PSt, cm^{-1}) 3600-3300; 3150-2700; 1670; 1600; 1550; 1410; 1330; 1300; 1210; 1160; 1060; 980; 940; 900; 880; 805; 750; 745; 680; 630. MS (CI) m/e =251 (M+1)$^+$; 501 (2M+1)$^+$. Elemental analysis : % calculated C : 52.80 %, H : 4.00 %, N : 11.20 %, O : 19.20 %, S : 12.80 %; % found C : 52.74 %, H : 3.97 %, N : 11.18 %, O : 19.13 %, S : 12.98 %.

Method B : 0.654 gr (3.26 mmol, 1.5 eq.) of iminoether **10**, 0.45 ml (3.26 mmol, 1.5 eq.) of Et_3N, 0.23 ml (3.26 mmol, 1.5 eq.) of acetyl chloride, 0.41 gr (2.17 mmol, 1 eq.) of tosyl cyanide (95 %), 35 minutes at 25° C. *Work-up 1*. Yield **9a**: 0.511 gr (94 %).

***5-methyl-6-(p-toluenesulphonyl)pyrimidin-4(3H)-one* 9b**

Method A : 1.197 gr (4.65 mmol) of azadiene **1c**, 0.842 gr (4.65 mmol) of tosyl cyanide (95 %), 10 ml of benzene, 30 minutes at 50° C. *Work-up 1*. Recrystallization from CH_3CN. Yield **9b**: 0.932 gr (76 %). mp: 212° C. ^{1}H NMR (CD_3SOCD_3, TMS, 200 MHz, ppm): 13.0 (s, 1H); 8.13 (s, 1H); 7.87 and 7.51

(AB system, 4H, ^{3}J=8.4Hz); 2.48 (s, 3H); 2.43 (s, 3H). ^{13}C NMR (CF_3COOD, TMS, 20 MHz, ppm): 161.50; 149.62; 149.07; 148.87; 131.94; 131.06; 130.61; 128.34; 19.87; 9.86. IR (KBr, PSt, cm^{-1}) 3600-3400; 3100-2700; 1680; 1660; 1590; 1380; 1330; 1300; 1170; 1140; 1090; 1040; 920; 800; 690. MS (CI) m/e =265 $(M+1)^+$; 529 $(2M+1)^+$. % calculated C : 54.55 %, H :4.55 %, N : 10.61 %, O : 18.18 %, S : 12.12 %; % found C : 54.64 %, H : 4.62 %, N : 10.80 %, O : 18.05 %, S : 11.89 %.
Method B : 0.654 gr (3.26 mmol, 1.5 eq.) of iminoether **10**, 2.26 ml (16.3 mmol, 7.5 eq.) of Et_3N, 0.28 ml (3.26 mmol, 1.5 eq.) of propionyl chloride, 0.41 gr (2.17 mmol, 1 eq.) of tosyl cyanide (95 %), 1 h at 85° C. *Work-up 1.* Yield **9b**: 0.377 gr (66 %).

***5-fluoro-6-(p-toluenesulphonyl)pyrimidin-4(3H)-one* 9c**
Method A : 1.719 gr (6.58 mmol) of azadiene **1g**, 1.192 gr (6.58 mmol) of tosyl cyanide (95 %), 10 ml of benzene, 1 h at 50° C. *Work-up 1.* Recrystallization from CH_3CN. Yield **9c**: 1.05 gr (59 %). mp: 266° C. ^{1}H NMR (CD_3SOCD_3, TMS, 200 MHz, ppm): 13.5 (s, 1H); 8.11 (d, 1H, $^5J_{HF}$=1.4Hz); 7.87 and 7.52 (AB system, 4H, ^{3}J=8.0Hz); 2.45 (s, 3H). IR (KBr, PSt, cm^{-1}) 3400; 3060; 2900; 1700; 1600; 1340; 1310; 1250; 1230; 1185; 1170; 1150; 1085; 830; 815; 690. MS (CI) m/e = 269 $(M+1)^+$. Elemental analysis : % calculated C : 49.25 %, H : 3.38 %, N : 10.44 %, S : 11.95 %; % found C : 49.19 %, H : 3.41 %, N : 10.36 %, S : 12.05 %.

***5-chloro-6-(p-toluenesulphonyl)pyrimidin-4(3H)-one* 9d**
Method A : 1.608 gr (5.79 mmol) of azadiene **1d**, 1.050 gr (5.79 mmol) of tosyl cyanide (95 %), 10 ml of benzene, 1 h at 50° C. *Work-up 1.* Recrystallization from CH_3CN. Yield **9d**: 0.841 gr (51 %). mp: 257° C. ^{1}H NMR (CD_3SOCD_3, 200 MHz, TMS, ppm): 13.5-13.0 (s, 1H); 8.25 (s, 1H); 7.86 and 7.51 (AB system, 4H, ^{3}J=8.6Hz); 2.46 (s, 3H). IR (KBr, PSt, cm^{-1}) 3400; 3100-2900; 1690; 1580; 1330; 1280; 1160; 1130; 1085; 1050; 890; 780; 680. MS (CI) m/e =285 $(M+1)^+$, 569 $(2M+1)^+$. Elemental analysis : % calculated C : 46.40 %, H: 3.19 %, N: 9.84 %, Cl: 12.45 %, S: 11.25 %; % found C: 46.37 %, H: 2.99 % N: 9.94 % Cl: 12.30 % S: 11.26 %.

***5-butyl-6-(p-toluenesulphonyl)pyrimidin-4(3H)-one* 9e**
Method A : 1.198 gr (4 mmol) of azadiene **1i**, 0.725 gr (4 mmol) of tosyl cyanide (95 %), 10 ml of benzene, 1 h at 50° C. *Work-up 1.* Recrystallization from CH_3CN. Yield **9e**: 0.740 gr (60 %). mp: 225° C. ^{1}H NMR (CD_3SOCD_3, TMS, 200 MHz, ppm): 13.0 (s, 1H); 8.13 (s, 1H); 7.86 and 7.51 (AB system, 4H, ^{3}J=8.2Hz); 2.97 (m, 2H); 2.46 (s, 3H); 1.15 (m, 4H); 1.00 (t, 3H, ^{3}J= 6.8 Hz). ^{13}C NMR (CF_3COOD, TMS, 20 MHz, ppm): 160.62; 149.54; 149.00; 147.72; 132.41; 130.63; 128.28; 28.66; 25.66; 22.31; 19.86; 11.69. IR (KBr, PSt, cm^{-1}) 3400; 3000-2300; 1660 (broad); 1590; 1390; 1310; 1300; 1290; 1240; 1140; 1120; 1070; 820; 720; 680; 650. MS (EI) m/e=306 (M^+, 1 %); 277 (M^+-CHO, 12 %); 241 (5 %); 213 (10 %); 200 (100 %); 151 (M^+-Tos, 30%); 139 (10 %); 97 ($C_7H_7^+$, 16 %). Elemental analysis : % calculated C : 58.80 %, H: 5.92 %, N: 9.14 %, O: 15.67 %, S: 10.46 %; % found C: 58.90 %, H: 6.01 %, N: 8.83 %, O: 15.75 %, S: 10.51 %.

***6-(trichloromethyl)pyrimidin-4(3H)-one* 9f**
Method A : 0.241 gr (9.91 mmol) of azadiene **1b**, 3 ml (30 mmol) of trichloroacetonitrile, 15 minutes at reflux. *Work-up 1.* Recrystallization from EtOH. Yield **9f**: 0.199 gr (94 %). mp: 253° C. ^{1}H NMR (CD_3SOCD_3, TMS, 200 MHz, ppm): 13.0 (s, 1H); 8.42 (s, 1H); 6.95 (d, 1H, ^{5}J=0.9Hz). ^{13}C NMR (CF_3COOD, TMS, 20 MHz, ppm): 162.94; 157.94; 151.41; 111.48; 90.01. IR (KBr, PSt, cm^{-1}) 3600-3400; 3200-2700; 1650 (broad); 1610; 1420; 1350; 1200; 1150; 980; 960; 920; 855; 800; 760; 660. MS (CI) m/e = 213 $(M+1)^+$. Elemental analysis : % calculated C : 28.10 %, H : 1.41 %, N : 13.11 %, O : 7.49 %, Cl : 49.88 %; % found C : 28.23 %, H : 1.44 %, N : 13.02 %, O : 7.40 %, Cl : 49.91 %.

***5-methyl-6-(trichloromethyl)pyrimidin-4(3H)-one* 9g**
Method A: 0.262 gr (1.02 mmol) of azadiene **1c**, 3.0 ml (30 mmol) of trichloroacetonitrile, 3 h at reflux. *Work-up 1.* Recrystallization from $AcOEt/C_6H_{12}$. Yield **9g**: 0.169 gr (73 %). mp: 200° C. ^{1}H NMR (CD_3SOCD_3, TMS, 200 MHz, ppm): 13.0 (s, 1H); 8.26 (s, 1H); 2.35 (s, 3H). ^{13}C NMR (CF_3COOD,TMS,20 Mhz,ppm): 161.28; 148.46; 146.57; 129.67; 88.30; 12.85. IR (KBr, PSt, cm^{-1}) 3600-3300; 3200-2700; 1650; 1600; 1540; 1400; 1380; 1230; 1210; 1120; 930; 880; 810-800; 770; 650. MS (CI) m/e =227 $(M+1)^+$. Elemental analysis : % calculated C : 31.65 %, H : 2.18 %, N : 12.31 %, Cl : 46.81 %; % found C : 31.76 %, H : 2.20 %, N : 12.38 %, Cl : 47.08 %.

***5-butyl-6-(trichloromethyl)pyrimidin-4(3H)-one* 9h**
Method A : 1.631 gr (5.75 mmol) of azadiene **1i**, 11.5 ml (0.11 mole) of trichloroacetonitrile, 10 h at reflux. *Work-up 1.* Recrystallization from CH_3CN. Yield **9h**: 0.763 gr (49 %). mp: 192-193° C. ^{1}H NMR (CD_3SOCD_3, TMS, 200 MHz, ppm): 13.1 (s, 1H); 8.28 (s, 1H); 2.80 (m, 2H); 1.55 (m, 4H); 1.0 (t, 3H, ^{3}J=6.2Hz). ^{13}C NMR (CF_3COOD, TMS, 50 MHz, ppm): 159.64; 157.21; 144.86; 99.08; 38.65; 38.24; 32.83; 22.28. IR (KBr, PSt, cm^{-1}) 3600-3300; 3000-2800; 1660; 1595; 1380; 1240; 1120; 1080; 870; 805-795; 765. MS (EI) m/e=268 ($M^{+\cdot}$, 8 %); 233 ($M^{+\cdot}$-Cl$^{\cdot}$, 30 %); 226 ($M^{+\cdot}$-NCO$^{\cdot}$, 35 %); 197 (233-HCl, 20 %); 191 (233-NCO$^{\cdot}$, 100 %); 190 (226-HCl, 90 %); 163 (191-CO, 8 %); 155 (191-HCl, 20 %); 151 ($M^{+\cdot}$-$CCl_3^{\cdot}$, 100 %); 133 (151-H_2O, 10 %). Elemental analysis : % calculated C : 40,01 %, H : 4.11 %, N : 10.39 %, O : 5.94 %, Cl : 39.46 %; % found C : 40.25 %, H : 4.10 %, N : 10.40 %, O : 6.04 %, Cl: 39.21 %.

***2-methyl-6-(trichloromethyl)pyrimidin-4(3H)-one* 9i**
Method A: 0.282 gr (1.16 mmol) of azadiene **1f**, 3.5 ml (35 mmol) of trichloroacetonitrile, 3 h at reflux. *Work-up 1.* Recrystallization from AcOEt/C_6H_{12}. Yield **9i**: 0.221 gr (84 %). mp: 203° C. ^{1}H NMR (CD_3SOCD_3, TMS, 200 MHz, ppm): 12.9 (s, 1H); 6.80 (s, 1H); 2.41 (s, 3H). ^{13}C NMR (CF_3COOD, TMS, 20 MHz, ppm): 165.87; 159.77; 152.83; 110.55; 87.02; 17.5. IR (KBr, PSt, cm^{-1}) 3600-3200; 3100-2700; 1655; 1605; 1560; 1470; 1365; 1300; 1230; 1160; 1020; 970; 950; 820-790; 730; 660. MS (CI) m/e=227 $(M+1)^+$. Elemental analysis : % calculated C : 31.65 %, H : 2.20 %, N : 12.31 %, Cl : 46.81 %; % found C : 31.77 %, H : 2.25 %, N : 12.25 %, Cl : 47.12 %.

***6-(ethoxycarbonyl)pyrimidin-4(3H)-one* 9j**
Method A : 0.229 gr (0.43 mmol) of azadiene **1b**, 0.93 ml (9.43 mmol) of ethyl cyanoformate, 2 ml of $CHCl_3$, 1 h at reflux. *Work-up*: 3 ml of EtOH was added and the reaction mixture was heated further for 30 minutes. The solvent was removed *in vacuo* and the resulting brown residue was purified on silica gel chromatography (CH_2Cl_2/*i*PrOH: 9/1). An analytical sample could be obtained by recrystallization from AcOEt/C_6H_{12}. Yield **9j**: 82 %. R_f: 0.30 (CH_2Cl_2/*i*PrOH: 9/1). mp: 211° C. ^{1}H NMR (CD_3CN, TMS, 200 MHz, ppm): 10.2 (s, 1H); 8.18 (s, 1H); 7.05 (d, 1H, ^{5}J=1.0Hz); 4.39 (q, 2H, ^{3}J=7.1Hz); 1.39 (t, 3H, ^{3}J=7.1Hz). ^{13}C NMR (CD_3SOCD_3, TMS, 20 MHz, ppm): 163.78; 161.42; 152.41; 150.91; 117.48; 61.77; 13.99. IR (KBr, PSt, cm^{-1}) 3400; 3050; 3000; 2850; 1740; 1690 (broad); 1600; 1550; 1365; 1250; 1100; 1000; 880; 800. MS (CI) m/e =169 $(M+1)^+$; 337 $(2M+1)^+$. Elemental analysis : % calculated C : 50.00 %, H : 4.80 %, N : 16.66 %, O : 28.54 %; % found C : 50.05 %, H : 4.93 %, N : 16.40 %, O : 28.62 %.

***6-(ethoxycarbonyl)-5-methylpyrimidin-4(3H)-one* 9k**
Method A : 0.180 gr (7 mmol) of azadiene **1c**, 0.7 ml (0.7 mmol) of ethyl cyanoformate, 2 ml of benzene, 12 h at reflux. *Work-up*: 3 ml of EtOH was added and the reaction mixture was heated further for 30 minutes. The solvent was removed *in vacuo* and the resulting brown residue was purified on silica gel chromatography (CH_2Cl_2/*i*PrOH: 9/1). An analytical sample could be obtained by recrystallization from AcOEt/C_6H_{12}. Yield **9k**: 0.080 gr (63 %). R_f: 0.30 (CH_2Cl_2/*i*PrOH: 9/1). mp: 168° C. ^{1}H NMR (CD_3OD, TMS, 200 MHz, ppm): 10.3 (s, 1H); 8.17 (s, 1H); 4.48 (q, 2H, ^{3}J=7.2 Hz); 2.28 (s, 3H); 1.47 (t, 3H, ^{3}J=7.2 Hz). ^{13}C NMR (CD_3SOCD_3, TMS, 20 MHz, ppm): 165.41; 162.04; 149.99; 147.53; 124.44; 61.42; 14.02; 11.32. IR (KBr, PSt, cm^{-1}) 3400; 3100-2700; 1720; 1670; 1610; 1550; 1370; 1340; 1240; 1120; 1060; 940; 880; 860; 760. MS (CI) m/e =183 $(M+1)^+$; 365 $(2M+1)^+$. Elemental analysis : % calculated C : 52.75 %, H : 5.49 %, N : 15.38 %, O : 26.37 %; % found C : 52.76 %, H : 5.63 %, N : 15.42 %, O : 26.19 %.

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