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Microwave assisted organic synthesis—a review

Pelle Lidström,[a,*] Jason Tierney,[b] Bernard Wathey[b,†] and Jacob Westman[a]

[a] *Personal Chemistry, Hamnesplanaden 5, SE-75319 Uppsala, Sweden*
[b] *Organon Laboratories Ltd, Research and Development, Newhouse, ML1 5SH, Scotland, UK*

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Contents

1. Introduction

In the electromagnetic spectrum, the microwave radiation region is located between infrared radiation and radio waves. Microwaves have wavelengths of 1 mm–1 m, corresponding to frequencies between 0.3 and 300 GHz. Telecommunication and microwave radar equipment occupy many of the band frequencies in this region. In general, in

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[*] Corresponding author. Tel.: +46-18-489-9000; fax: +46-18-489-9200; e-mail: pelle.lidstrom@personalchemistry.com

[†] Present address: BioFocus plc, Sittingbourne Research Centre, Sittingbourne, Kent, ME9 8AZ, UK

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order to avoid interference, the wavelength at which industrial and domestic microwave apparatus intended for heating operates is regulated to 12.2 cm, corresponding to a frequency of 2.450 (±0.050) GHz, but other frequency allocations do exist. It has been known for a long time that microwaves can be used to heat materials. In fact, the development of microwave ovens for the heating of food has more than a 50-year history.[2] In the 1970s, the construction of the microwave generator, the magnetron, was both improved and simplified. Consequently, the prices of domestic microwave ovens fell considerably, leading to them becoming a mass product. The design of the oven chamber or cavity, however, which is crucial for the heating characteristics, was not significantly improved until the end of the 1980s.

In inorganic chemistry, microwave technology has been used since the late 1970s, while it has only been implemented in organic chemistry since the mid-1980s. The development of the technology for organic chemistry has been rather slow compared, to for example, combinatorial chemistry and computational chemistry. This slow uptake of the technology has been principally attributed to its lack of controllability and reproducibility, safety aspects and a generally low degree of understanding of the basics of microwave dielectric heating. Since the mid-1990s, however, the number of publications has increased significantly (Fig. 1). The main reasons for this increase include the availability of commercial microwave equipment intended for organic chemistry and the development of the solvent-free technique, which has improved the safety aspects, but are mostly due to an increased interest in shorter reaction times.

The short reaction times and expanded reaction range that is offered by microwave assisted organic synthesis are suited to the increased demands in industry. In particular, there is a requirement in the pharmaceutical industry for a higher number of novel chemical entities to be produced, which requires chemists to employ a number of resources to reduce the time for the production of compounds. Chemistry databases, software for diversity selection, on-line chemical ordering systems, open-access and high throughput systems for analysis and high-speed, parallel and combinatorial synthesis equipment have all contributed in increasing the throughput. The common factors for these technical resources are automation and computer-aided control. They do not, however, speed up the chemistry itself. Developments in the chemistry have generally been concerned with novel highly reactive reagents in solution or on solid supports.

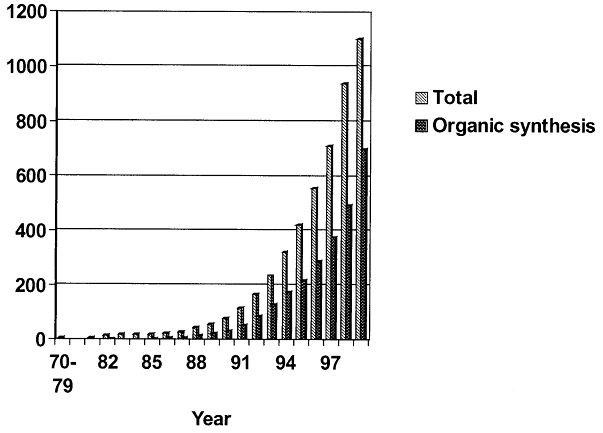


Figure 1. The accumulated number of published articles involving organic and inorganic microwave assisted synthesis 1970–1999.

In general, most organic reactions have been heated using traditional heat transfer equipment such as oil baths, sand baths and heating jackets. These heating techniques are, however, rather slow and a temperature gradient can develop within the sample. In addition, local overheating can lead to product, substrate and reagent decomposition.

In contrast, in microwave dielectric heating, the microwave energy is introduced into the chemical reactor remotely and direct access by the energy source to the reaction vessel is obtained. The microwave radiation passes through the walls of the vessel and heats only the reactants and solvent, not the reaction vessel itself. If the apparatus is properly designed, the temperature increase will be uniform throughout the sample, which can lead to less by-products and/or decomposition products. In pressurized systems, it is possible to rapidly increase the temperature far above the conventional boiling point of the solvent used.

Even though the total number of publications in this area is limited, the percentage of reviews is quite high and several articles are well worth reading. Mingos et al. have given a thorough explanation of the underlying theory of microwave dielectric heating.[3] Gedye[4] and Langa[5] have discussed the suggested 'specific microwave effect', Loupy et al.[6] have published a number of reviews on solvent-free reactions and Strauss has reported on organic synthesis in high temperature aqueous systems.[7] The last microwave organic chemistry review was published by Caddick[8] in 1995. Considering the developments in the field during previous years, we believe an update is now appropriate.

Apart from compiling an update on the chemistry performed, we hope to provide the chemist who is inexperienced in the field, a basic understanding of the theory behind microwave dielectric heating. An overview of the existing synthetic methodologies, as well as an outline of the benefits and limitations connected with microwave assisted organic synthesis, are additionally presented.

2. Background and theory

If two samples containing water and dioxane, respectively, are heated in a single-mode microwave cavity at a fixed radiation power and for a fixed time the final temperature will be higher in the water sample (Fig. 2).

In order to understand why this phenomenon occurs, it is necessary to comprehend the underlying mechanisms of microwave dielectric heating. As with all electromagnetic radiation, microwave radiation can be divided into an electric field component and a magnetic field component. The former component is responsible for the dielectric heating, which is effected via two major mechanisms.

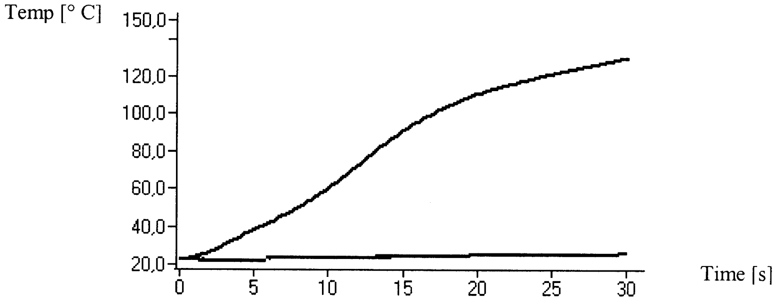


Figure 2. The temperature increases of water and dioxane, respectively, at 150 W microwave irradiation. The upper curve represents water and the lower plot represents dioxane.

2.1. Dipolar polarization mechanism

One of the interactions of the electric field component with the matrix is called the dipolar polarization mechanism. For a substance to generate heat when irradiated with microwaves it must possess a dipole moment, as has a water molecule. A dipole is sensitive to external electric fields and will attempt to align itself with the field by rotation, (Fig. 3).

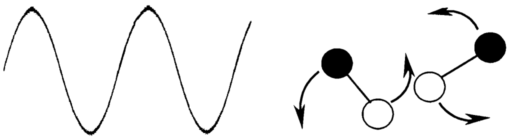


Figure 3. Dipolar molecules which try to align with an oscillating electric field.

The applied field provides the energy for this rotation. In gases, molecules are spaced far apart and their alignment with the applied field is, therefore, rapid, while in liquids instantaneous alignment is prohibited by the presence of other molecules. The ability of molecules in a liquid to align with the applied electric field will vary with different frequencies and with the viscosity of the liquid. Under low frequency irradiation, the molecule will rotate in phase with the oscillating electric field. The molecule gains some energy by this behaviour, but the overall heating effect by this full alignment is small. Alternatively, under the influence of a high frequency electric field the dipoles do not have sufficient time to respond to the oscillating field and do not rotate. Since no motion is induced in the molecules, no energy transfer takes place and therefore no heating occurs. If the applied field is in the microwave radiation region, however, a phenomenon occurs between these two extremes. In the microwave radiation region, the frequency of the applied irradiation is low enough so that the dipoles have time to respond to the alternating electric field and therefore rotate. The frequency is, however, not high enough for the rotation to precisely follow the field. Therefore, as the dipole re-orientates to align itself with the electric field, the field is already changing and generates a phase difference between the orientation of the field and that of the dipole. This phase difference causes energy to be lost from the dipole by molecular friction and collisions, giving rise to dielectric heating. Thus, in the earlier example, it becomes clear why dioxane, which lacks the dipole characteristics necessary for microwave dielectric heating, does not heat while water, which has a large dipole moment, heats readily. Similarly, this explains why gases could not be heated under microwave irradiation, since the distance between two rotating molecules is long enough for the molecules to be able to follow the electric field perfectly so that no phase difference will be generated.

2.2. Conduction mechanism

If two samples containing distilled water and tap water, respectively, are heated in a single mode microwave cavity at a fixed radiation power and for a fixed time, the final temperature will be higher in the tap water sample (Fig. 4).

This phenomenon is due to the second major interaction of the electric field component with the sample, the conduction mechanism. A solution containing ions, or even a single isolated ion with a hydrogen bonded cluster, in the sample the ions will move through the solution under the influence of an electric field, resulting in expenditure of energy due to

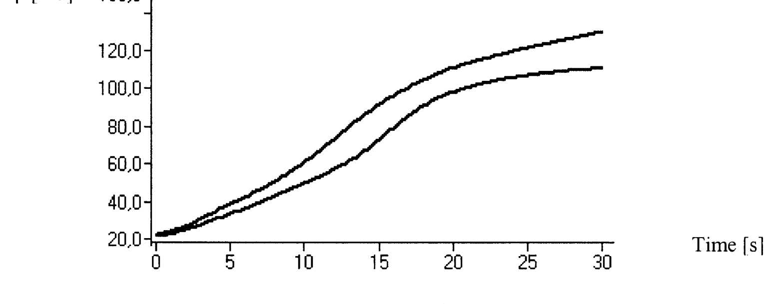


Figure 4. The temperature increases of distilled water and tap water, respectively, at 150 W microwave irradiation. The upper curve represents tap water and the lower plot represents distilled water sample.

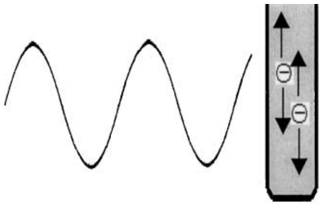


Figure 5. Charged particles in a solution will follow the applied electric field.

Table 1.
Dielectric constants and loss tangent values for some solvents relevant to organic synthesis

Solvent	Dielectric constant (ϵ_s)[a]	Loss tangent (tan δ)[b]
Hexane	1.9	
Benzene	2.3	
Carbon tetrachloride	2.2	
Chloroform	4.8	
Acetic acid	6.1	0.091
Ethyl acetate	6.2	0.174
THF	7.6	0.059
Methylene chloride	9.1	0.047
Acetone	20.6	0.042
Ethanol	24.6	0.054
Methanol	32.7	0.941
Acetonitrile	36	0.659
Dimethylformamide	36.7	0.062
DMSO	47	0.161
Formic acid	58	0.722
Water	80.4	0.123

[a] The dielectric constant, ϵ_s, equals the relative permittivity, ϵ', at room temperature and under the influence of a static electric field.

[b] Values determined at 2.45 GHz and room temperature.

an increased collision rate, converting the kinetic energy to heat (Fig. 5).

The conductivity mechanism is a much stronger interaction than the dipolar mechanism with regard to the heat-generating capacity. In the above example, the heat generated by the conduction mechanism due to the presence of ions adds to the heat produced through the dipolar mechanism, resulting in a higher final temperature in the tap water.

2.3. Loss angle

As mentioned above, polar solvents and/or ions are needed for microwave heating. How does the microwave heating effect differ for different solvents? The dielectric polarization depends primarily on the ability of the dipoles to reorientate in an applied electric field. It would seem reasonable to believe that the more polar the solvent, (i.e. the higher the dielectric constant it possesses), the more readily the microwave irradiation is absorbed and the higher the temperature obtained. This would appear to correspond well to what is observed in the case of water versus dioxane (Fig. 2). If, however, two solvents with comparable dielectric constants, ϵ_s, such as acetone and ethanol (Table 1), are heated at the same radiation power and for the same period of time as the water described above, the final temperature will be much higher in ethanol than in acetone (Fig. 6).

In order to be able to compare the abilities of different solvents to generate heat from microwave irradiation, their capabilities to absorb microwave energy and to convert the absorbed energy into heat must be taken into account. These factors may be considered using the loss angle, δ, which is usually expressed in the form of its tangent (Eq. (1)).

$$\tan\delta = \epsilon''/\epsilon' \qquad (1)$$

The dielectric constant, or relative permittivity, ϵ', represents the ability of a dielectric material to store electrical potential energy under the influence of an electric field. At room temperature and under the influence of a static electric field, ϵ', is equal to the dielectric constant, ϵ_s. The loss factor, ϵ'', quantifies the efficiency with which the absorbed energy is converted in-to heat. For solvents with comparable ϵ's and low values of tan δ, the loss factor provides a convenient parameter for comparing the abilities of different materials to convert microwave into thermal energy. The dielectric constants of acetone and ethanol are, indeed, in the same range (Table 1), but ethanol possesses a much higher loss tangent. For this reason, ethanol couples better with microwave irradiation, resulting in a more rapid temperature increase.

The re-orientation of dipoles and displacement of charge are equivalent to an electric current (Maxwell's displacement current). This displacement current will be 90° out of phase with the electric field when a dielectric precisely follows the field. As mentioned earlier, however, a dielectric that does not follow the oscillating electric field will have a phase difference between the orientation of the field and the dielectric. The resulting phase displacement, δ, produces a component, $I \sin\delta$, in phase with the electric field (Fig. 7A). This causes energy to be absorbed from the electric field, which is converted into heat and is described as the dielectric loss. The relationship between tan δ and ϵ' and ϵ'' is purely mathematical and can be described using simple trigonometric rules (Fig. 7B). The theory is quite complex

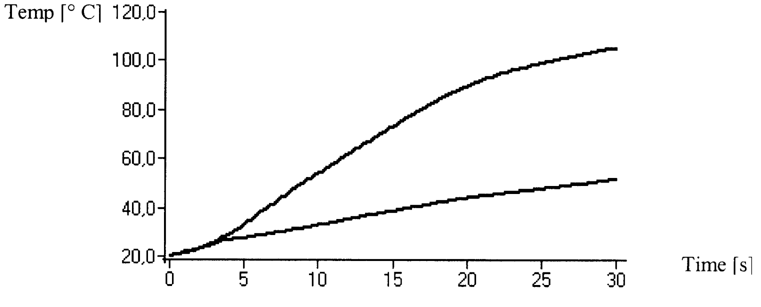


Figure 6. The temperature increase of ethanol and acetone, respectively, at 150 W microwave irradiation. The upper curve represents ethanol the lower plot represents acetone.

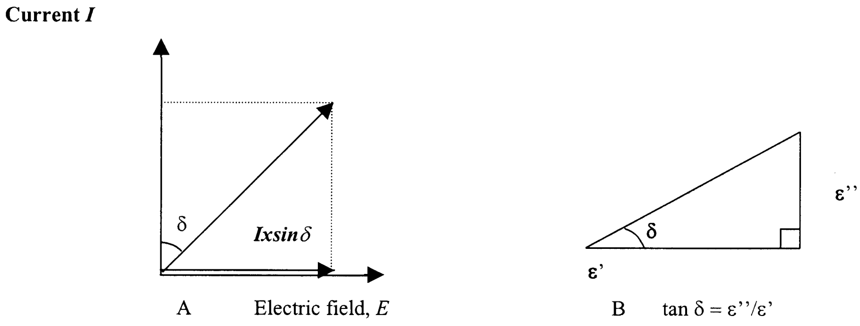


Figure 7. (A) A phase displacement which results when energy is converted to heat. (B) The relationship between ϵ' and ϵ'', $\tan \delta = \epsilon''/\epsilon'$.

and the review by Mingos et al.[3] is recommended for further details.

Besides the physical properties of the contents of the reaction vessel, both the volume of the contents and the geometry of the reaction vessel are crucial to provide uniform and reproducible heating.[9] The load volume (i.e. the volume of the load with respect to the oven cavity) is the more important of the two factors. Dramatic effects may occur when using volumes greater or smaller than those specified by the manufacturer of the microwave apparatus. In order to achieve the best possible reproducibility, reactions should be performed in carefully designed cavities and vessels, and, additionally, the use of a temperature control will help to overcome many of these problems.

2.4. Superheating effect

The relaxation time, τ, defines the time it takes for one molecule to return to 36.8% of its original situation when the electric field is switched off.[2] The relaxation time is temperature dependent and decreases as the temperature is increased. Since both ϵ' and ϵ'' are dependent on τ, the ability of a solvent to convert microwave energy into heat will be dependent not only on the frequency, but also on the temperature. Consequently, an organic solvent with a relaxation time >65 ps irradiated at 2.45 GHz will have a loss tangent that increases with temperature. The heating rate for these solvents will increase during microwave dielectric heating, most probably by limiting the formation of 'boiling nuclei'.[10] This phenomenon is described as superheating and may result in the boiling points of solvents being raised by up to 26°C above their conventional values.[3,10] In a pure solvent, the higher boiling point can be maintained as long as the microwave irradiation is applied. Substrates or ions present in the solvent will, however, aid the formation of 'boiling nucleuses' and the temperature will eventually return to that of the normal boiling point of the solvent. The superheating phenomenon is widely believed to be responsible for many of the rate increases which often accompany solution phase microwave assisted organic reactions at atmospheric pressure.[4]

2.5. Solvents in microwave assisted organic synthesis

Since the frequency for most types of microwave apparatus is set at 2.45 GHz, the dielectric constant can only change with temperature. When a solvent is heated, the dielectric

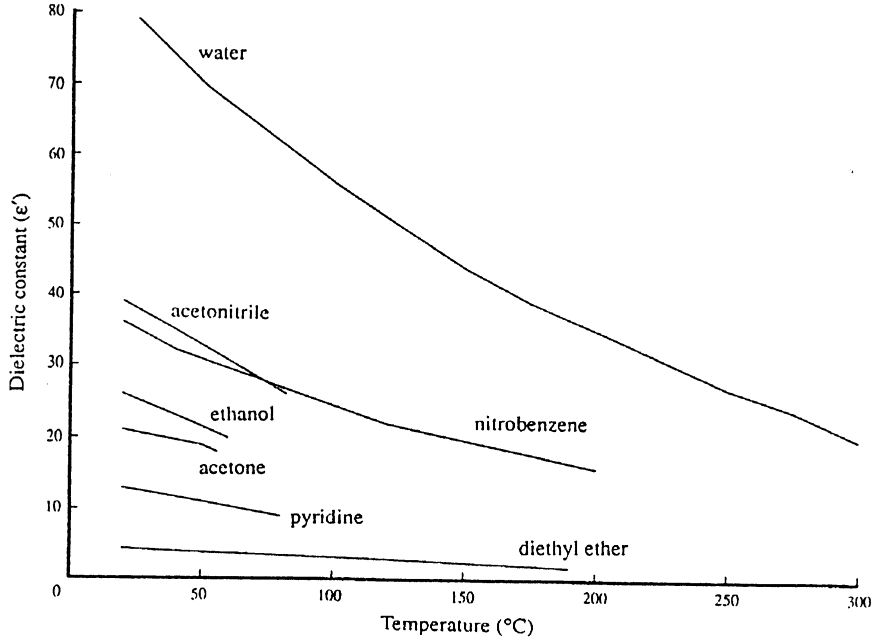


Figure 8. Plots of dielectric constants against temperature for various solvents [Dean, J. A. Ed.; *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985; p 99].

constant decreases as the temperature increases. Water has a dielectric constant which decreases from 78 at 25°C to 20 at 300°C (Fig. 8), the latter value being comparable to that of solvents such as acetone at ambient temperature.[11] Water can, therefore, behave as a pseudo-organic solvent at elevated temperatures, but this property is only valid in pressurized systems. It was mentioned earlier that non-polar solvents are not heated under microwave irradiation. The addition of small amounts of a polar solvent with a large loss tangent, however, usually leads to higher heating rates for the whole mixture. The energy transfer between the polar molecules that couple with the microwave radiation and the non-polar solvent bulk is rapid. This method provides an effective means of using non-polar solvents in microwave organic synthesis. Another way of increasing heating rates is the addition of salts to the solvent. Unfortunately, a solubility problem in many organic solvents results in heterogeneous mixtures. In microwave-assisted synthesis, a homogeneous mixture is preferred to obtain a uniform heating pattern. Ionic liquids have recently been reported as novel environmentally friendly and recyclable alternatives to dipolar aprotic solvents for organic synthesis.[12,13] The excellent dielectric properties of these ionic liquids offer large advantages when used as solvents in microwave assisted organic synthesis.

Ionic liquids absorb microwave irradiation in a very efficient manner and, additionally, they exhibit a very low vapour pressure, thereby enhancing their suitability even further for microwave heating. Despite ionic liquids being salts, they dissolve to an appreciable extent in a wide range of organic solvents as compared to water and alcohols.[12,13] Some ionic liquids are also soluble in many non-polar organic solvents and can therefore be used as microwave coupling agents when microwave transparent solvents are employed (Fig. 9).

2.6. Modes

When microwaves enter a cavity, they are reflected by the walls. The reflections of the waves eventually generate a three dimensional stationary pattern of standing waves within the cavity, called modes. The cavity in a domestic microwave oven is designed to have typically three to six different modes intended to provide a uniform heating pattern for general food items. Despite being a good solution for these purposes, the use of the multi-mode technique will provide a field pattern with areas of high and low field strength, commonly referred to as 'hot and cold spots'. The net result is that the heating efficiency can vary drastically between different positions of the load, when small loads are heated.

The cavity dimensions have to be fairly precise to obtain the best balance of modes. Typically, only a 2 mm deviation in a 300×300×200 mm cavity results in significant alterations of the field pattern in the cavity.[14] A small load situated at a fixed position in two cavities of the same type may, therefore, experience very different conditions, and two small samples in the same cavity will most probably experience different conditions. At present, the magnetrons for household ovens are usually optimized to provide high power for short heating periods. In order to withstand the stresses of empty operation, magnetrons are intentionally designed to decrease their power-output when they become hot. With a small load in a multi-mode cavity, the power-output is decreased by 15–25% after 3 min of use, thereby creating an additional source of variability. In addition, the magnetrons are optimized to give high efficiency for a 1000 g standard test load and consequently, they operate less reliably for small loads.

Ideally, to obtain a well-defined heating pattern for small loads, a microwave apparatus utilising a single mode cavity is preferred. As the name implies, this type of cavity allows only a single mode to be present. A properly designed cavity will prevent the formation of 'hot and cold spots' within the sample, resulting in a uniform heating pattern. This factor is very important when microwave technology is used in organic chemistry, since the actual heating pattern can also be controlled for small samples. This allows the achievement of a higher reproducibility and predictability of results. When used for synthetic purposes, yields can therefore be optimized, which are usually more difficult to optimize using a domestic microwave oven. Moreover, in single mode systems, much higher field strengths can be obtained, which will give rise to more rapid heating.

2.7. Why does microwave irradiation speed up chemical reactions?

Since the introduction of microwave assisted organic synthesis in 1986, the main debate has dealt with the question of what actually alters the outcome of the synthesis. Is it

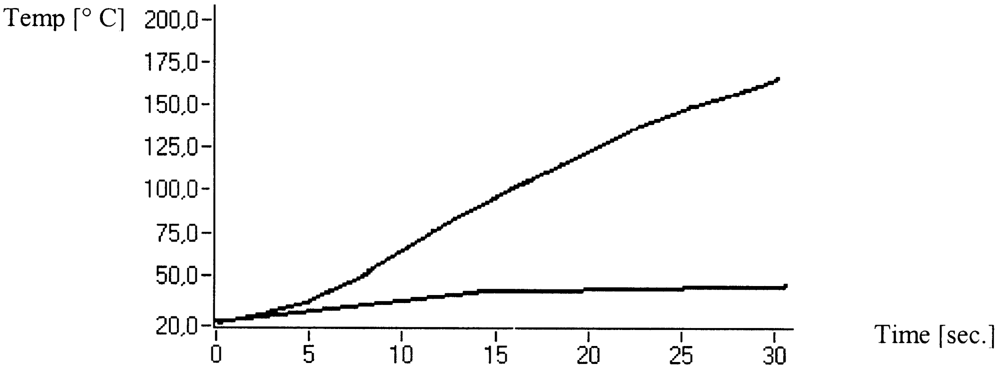


Figure 9. The impact of the addition of ionic liquids on the temperature increase of dioxane at 300 W microwave irradiation. The lower curve represents dioxane and the upper plot represents dioxane with the addition of 2 vol% 1-butyl-3-methyl-imidazolium hexafluorophosphate.

merely an effect of the thermal heat generated by the microwaves or is it an effect specific for microwave heating?

In order to be able to make this distinction, the term 'specific microwave effect' should be defined. Historically, 'specific microwave effects' have been claimed, when the outcome of a synthesis performed using microwave heating differs from its thermally heated counterpart. Some of the earlier reports have, in later experiments not been reproduced,[4] while some are definitely debatable and others are hard to explain.[15] The main advantage of using microwave assisted organic synthesis is the shorter reaction times. The rate of the reaction can be described by the Arrhenius Eq. (2).

$$K = A\,e^{-\Delta G/RT} \qquad (2)$$

Considering Eq. (2), there are basically two ways to increase the rate of a chemical reaction. First, the pre-exponential factor A, which describes the molecular mobility and depends on the frequency of vibrations of the molecules at the reaction interface. We have described previously how microwaves induce an increase in molecular vibrations and it has been proposed that this factor, A, can be affected.[5,16] Other authors, however, have proposed that microwave irradiation produces an alteration in the exponential factor by affecting the free energy of activation, ΔG.[17]

In most examples, the specific microwave effects claimed, can be attributed to thermal effects. Microwave heating can be very rapid, producing heat profiles not easy accessible by other heating techniques. Experiments performed using microwave assisted organic synthesis may therefore result in a different outcome when compared to conventionally heated reactions, even if the final temperature is the same. It has been shown, for example, that the heating profile can alter the regioselectivity in the sulfonation of naphthalene.[18] In poorly designed single mode systems, 'hot spots' may be encountered, which is frequently a problem in multi-mode systems. In these systems, the problem can give rise to local temperatures which are higher than the temperature measured in the bulk. Similarly, this superheating effect can also result in temperatures much higher than expected when performing reflux reactions in microwave ovens. These effects can sometimes give rise to unexpected results. Additionally, the accuracy of temperature measurements when performing microwave assisted organic synthesis can appear to be uncontrolled. These inaccuracies in temperature measurement often occur when performing the reactions in domestic ovens with microtitre plates or on solid supports, where there are inherent difficulties in measuring the temperature accurately.[3,5] Even if there is a 'specific microwave effect', the effect would appear to be less important than stated in earlier publications.

3. Microwave assisted synthesis techniques

3.1. Domestic household ovens—'solvent-free' open vessel reactions

Most of the published chemistry has been performed using domestic microwave ovens. The key reasons for using a device intended for heating food items to perform syntheses are that they are readily available and inexpensive. The use of domestic ovens might be one of the main reasons why microwave assisted organic synthesis has not increased greatly in popularity, due to factors outlined earlier (Section 2.6), and conducting syntheses in domestic microwave ovens is clearly not the intended application, as stipulated by the CE code for electrothermal appliances (IEC 335-2-25, IEC 335-2-220). These types of experiments are therefore conducted with an increased risk to the user,[19] and the use of domestic microwave ovens for microwave chemistry should be considered to be entirely at the risk of the operator, any equipment guarantees being invalidated.

The lack of control in domestic microwave ovens when performing microwave assisted synthesis has led to a vast number of incidents, including explosions, being reported. One method for avoiding this problem has been to omit the solvent from the reaction and perform the reactions on solid supports such as various clays, aluminum oxides and silica. A number of very interesting syntheses have been performed using this technique and a majority of the publications contain work conducted in this manner.[20,21] The solvent-free technique has been claimed to be particularly environmentally friendly, since it avoids the use of solvents and offers a simpler method of workup. The points regarding environmentally friendliness should be debated further, since solvents are often used to pre-absorb the substrates on to, and wash the products off the solid support. Presumably, an easier workup can only be claimed if the support has participated as a reagent in the reaction and can be removed from the reaction mixture simply by filtration, i.e. in the same manner as for solid-supported reagents. By altering the characteristics of the solid support, it is possible to strongly influence the outcome of the reaction. Various clays and other solid supports have been extensively employed in both solvent-free and solution phase techniques. As described in Section 2.7 it may be very difficult to obtain a good temperature control at the surface of the solids if the solvent-free technique is used. This would inevitably lead to problems regarding reaction predictability, reproducibility and controllability. There are, however, still benefits from using solvent-free approaches, which include improved safety by avoiding low-boiling solvents that would otherwise cause undesirable pressure increases during heating.

3.2. Reflux systems

A number of reflux systems have been developed in an effort to use solvents in microwave assisted organic synthesis without the risk of explosion. Some systems are modified domestic ovens, while others have been designed with single mode cavities. There is little risk of explosions with reflux systems, since the systems are at atmospheric pressure and flammable vapours cannot be released into the microwave cavity. The temperature, however, cannot be increased by more than 13–26°C above the normal boiling point of the solvent and only for a limited time (Section 2.4). Although this particular superheating effect will, of course, speed up the reactions to some extent, it will not result in the same effects that can be achieved at much higher temperatures.[7,22]

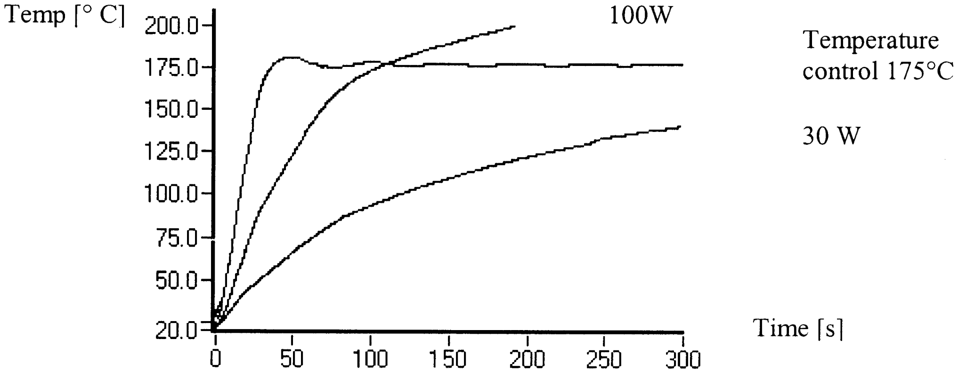


Figure 10. The different temperature profiles obtained when a sample of DMF is heated with temperature control or effect control, respectively.

3.3. Pressurized systems

Reactions performed under pressure in a microwave cavity also benefit from the rapid heating rates and remote heating of microwave dielectric heating. These types of experiments led to one of the very early developments using microwave assisted organic synthesis.[1] The lack of control, however, could make these reactions very unpredictable, often resulting in explosions. Nowadays, modern apparatus for running organic synthesis under pressure has overcome these problems. Most apparatus is now equipped with good temperature control and pressure measurement, which avoids a great deal of the failures due to thermal runaway reactions and poor heating (Fig. 10). The technique offers a simple method of performing rapid syntheses and is the most versatile of the approaches presented above, but has so far not been extensively explored.[7,22]

3.4. Continuous flow systems

If the outcome of a reaction is strongly dependent on the heating profile of the reaction mixture, it is crucial to maintain that heating profile when scaling up the reaction. If for example, 3 ml of a solvent is heated to 150°C in 20 s using microwave irradiation at 300 W, it will be necessary to use at least 15 kW power to heat 150 ml of the same solvent, in order to maintain the same heating profile. High power microwave equipment is widely used for non-synthetic process purposes, but is large and not easy to accommodate, often requiring water cooling When working with volumes >500 ml, single mode cavity microwaves are no longer the best choice and multi-mode cavity microwaves have to be used. An alternative approach is to use continuous flow systems[23] in which the reagents are pumped through the microwave cavity, allowing only a portion of the sample to be irradiated at a time. It is thus possible to maintain exactly the same heat profile, even for large-scale synthesis. The main drawback is that, for some reactions, not all substances will be in solution prior to, or after, microwave irradiation and this can cause the flow to stop, due to pipes becoming blocked.

4. Conclusions

Microwave heating is very convenient to use in organic synthesis. The heating is instantaneous, very specific and there is no contact required between the energy source and the reaction vessel.

Microwave assisted organic synthesis is a technique which can be used to rapidly explore 'chemistry space' and increase the diversity of the compounds produced. Nowadays, it could be considered that all of the previously conventionally heated reactions could be performed using this technique. The examples presented in Section 5 are impressive and provide a good insight into the field of microwave assisted organic synthesis. Within these examples, there are also some results that would appear to be unique for microwave assisted organic synthesis.

5. Literature survey

5.1. Introduction

This survey of microwave-assisted transformations is abstracted from the literature published from 1994 to June 2000. The reactions have been classified into sub-classes and the main reference in each class is represented by a graphical abstract format.

The vast majority of publications appears as a communication or letter. All synthesis techniques described earlier are represented in the material, with the solvent-free technique being the most popular. Most microwave assisted organic syntheses are unfortunately still performed in domestic household ovens. This causes the quality of the publications to vary greatly. The use of 70% of full power for 5 min in a domestic microwave oven will, for example, never be a quantitative measurement of the energy delivered to a reaction.

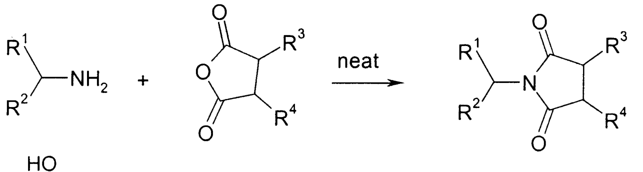
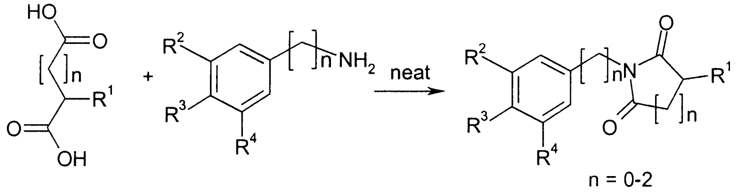
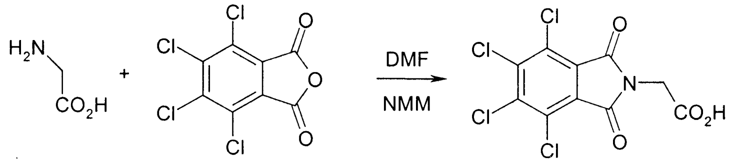
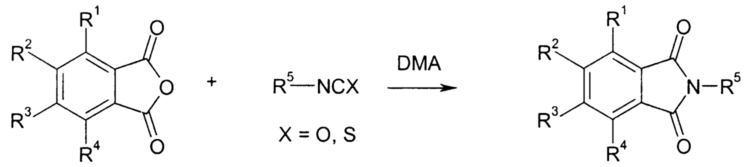
It is of interest to note that the country in which the technique seems to be most accepted, according to the number of publications, is India.

The benefits of microwave assisted organic synthesis are nevertheless, increasingly making the technique more established worldwide. In order to achieve further developments in this field, novel systems, which give rise to reproducible performance and which constitute a minimal hazard should be used rather than the domestic microwave oven.

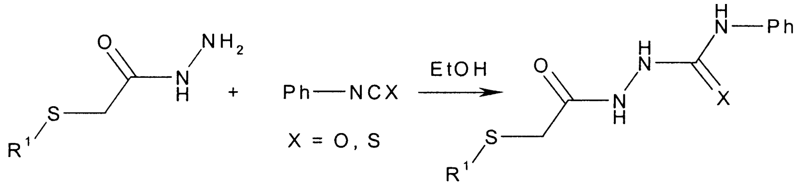
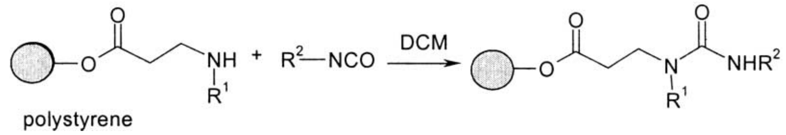
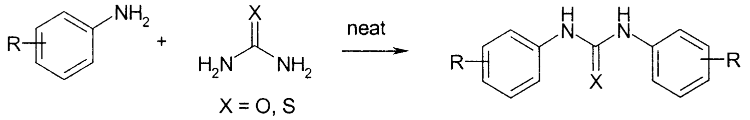
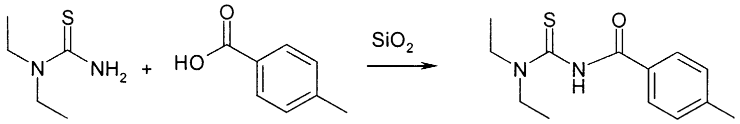
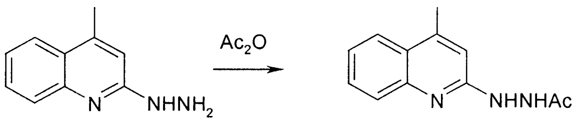
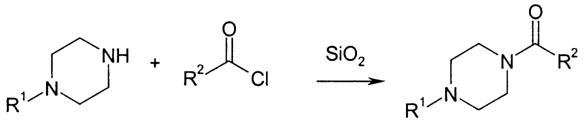
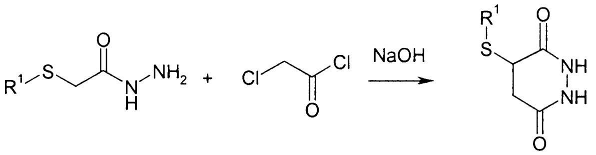
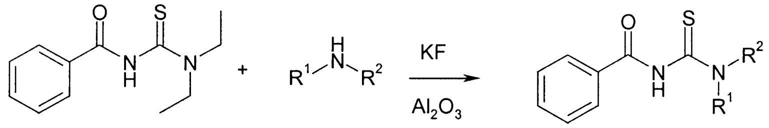
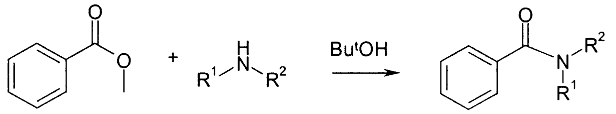
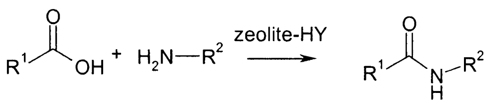
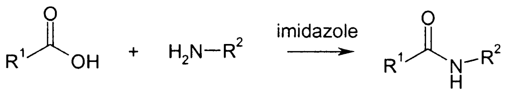
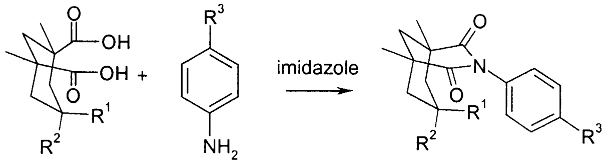
Abbreviations:

AIBN	azobisisobutyronitrile
bipy	2,2′-bipyridine
$[BMIm]^+BF_4^-$	1-butyl-3-methyl-imidazolium tetrafluoroborate
BSA	*N*,*O*-bis(trimethylsilyl) acetamide
BTF	benzotrifluoride
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	methylene chloride
DMF-DEA	dimethylformamide diethylacetal
DEAD	diethyl azodicarboxylate
DIAD	diisopropyl diazodicarboxylate
DMA	*N*,*N*-dimethylacetamide
DME	dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulphoxide
Dppe	1,2-bis(diphenylphosphino)ethane
Dppf	1,1′-bis(diphenylphosphino)ferrocene
Dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
EEDQ	2-ethoxy-*N*-ethoxycarbonyl-1,2-dihydroquinoline
EPIC	strong solid supported Brönsted acid
EPZ 10	solid supported Lewis acid
EPZG	solid supported Brönsted and Lewis acid
K10 clay	slightly acidic Montmorillonite clay
KSF clay	slightly acidic Montmorillonite clay
Ln	Lanthanoid
MOM	methoxymehtyl
MSA	*N*-methyl-*N*-(trimethylsilyl) acetamide
NCS	*N*-chlorosuccinimide
NMF	*N*-methylformamide
NMM	*N*-methylmorpholine
NMP	*N*-methyl-2-pyrrolidinone
o-DCB	*ortho*-dichlorobenzene
PCC	pyridinium chlorochromate
PPA	polyphosphoric acid
PPE	polyphosphate ester
PS-DMAP	polystyrene supported 4-dimethylaminopyridine
PTC	phase transfer catalyst
PTSA	toluene-*p*-sulfonic acid
TBAB	tetrabutylammonium bromide
TBACl	tetrabutylammonium chloride
TBAF	tetrabutylammonium fluoride
TBAOH	tetrabutylammonium hydroxide
TBAHS	tetrabutylammonium hydrogensulfate
TBDMS	*tert*-butyldimethylsilyl
TFA	trifluoroacetic acid
TFE	tetrafluoroethene
THF	tetrahydrofuran
Zeolite Hβ	acidic aluminosilicate
Zeolite-HY	acidic aluminosilicate

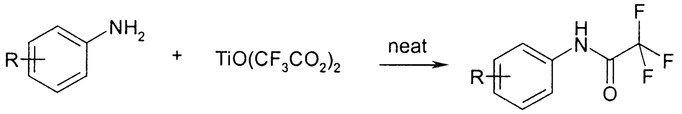
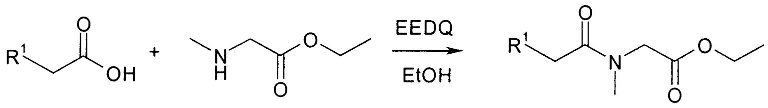
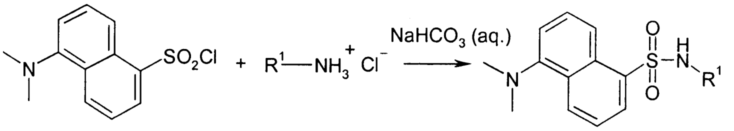
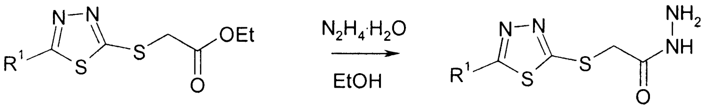
5.2. *N*-Acylation

Conditions	Type of reaction/yields/ number of examples	Reference	
		Described	Additional
	*N*-acylation-, maleimides, yields=82–96% (7 examples)	24	25
	*N*-acylation-, maleimides, yields=59–84% (12 examples)	26	
	*N*-acylation-, phthalimides, yield=94% (1 example)	27	28
	*N*-acylation, yields=85–96% (13 examples)	29	

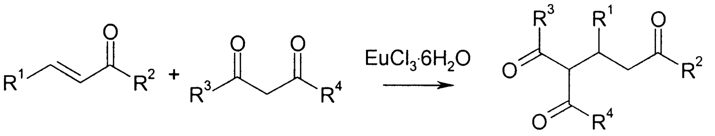
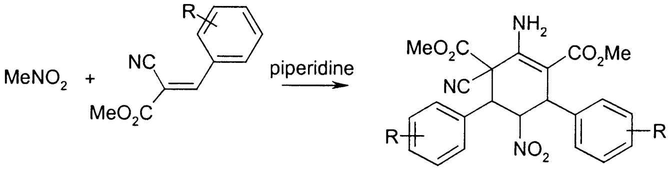
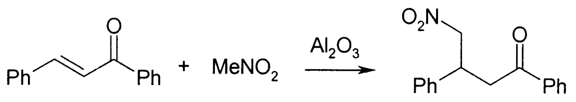
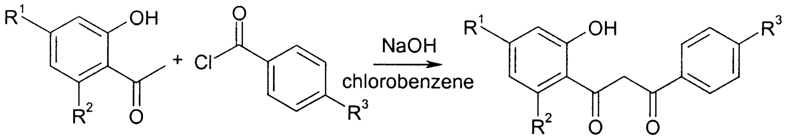
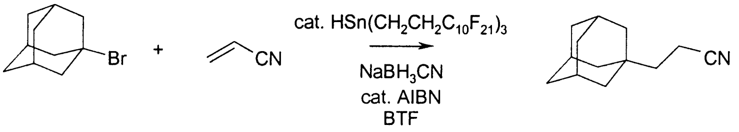
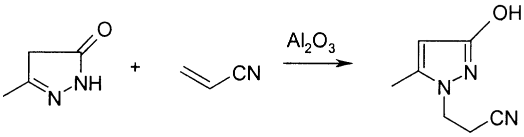
(*continued*)

Conditions	Type of reaction/yields/ number of examples	Reference	
		Described	Additional
	*N*-acylation, yields=86 and 88% (2 examples)	30	
	Urea formation, no yields quoted (5 examples)	31	
	Urea formation, yields= 40–90% (9 examples)	32	
	*N*-acylation, yield=85% (1 example)	33	
	*N*-acylation, yield=78% (1 example)	34	
	*N*-acylation, yields=72–97% (6 examples)	35	
	*N*-acylation, yield=84% (1 example)	30	
	Thiourea formation, transamidation, yields= 69–90% (6 examples)	36	
	*N*-acylation, yields=55–91% (7 examples)	37	
	*N*-acylation, yields=80–97% (12 examples)	38	
	*N*-acylation, yields=30–96% (5 examples)	39	
	*N*-acylation, yields=95 and 98% (2 examples)	39	

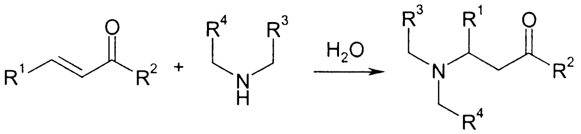
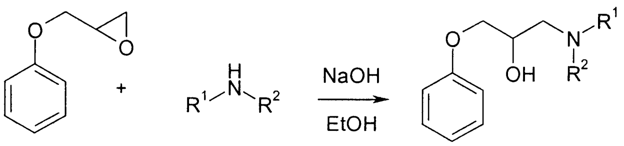
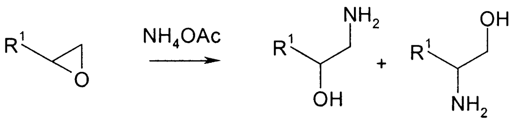
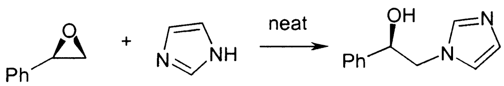
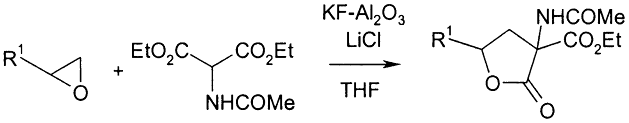
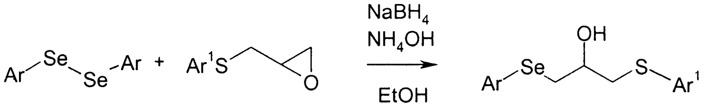
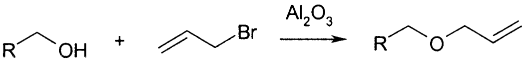
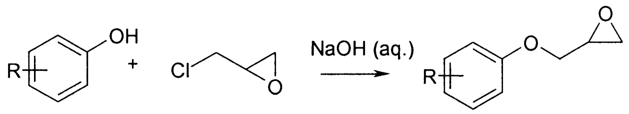
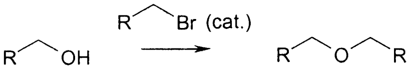
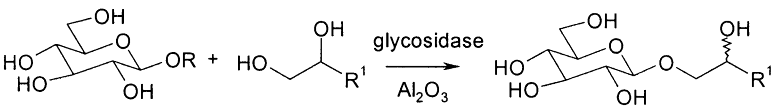
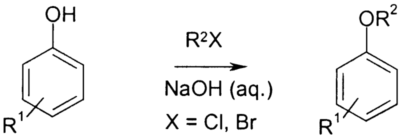
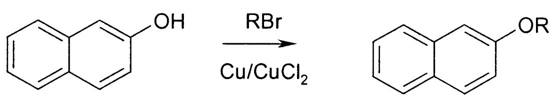
(*continued*)

Conditions	Type of reaction/yields/ number of examples	Reference	
		Described	Additional
	*N*-acylation, yields=60–98% (11 examples)	40	
	*N*-acylation, yields=92–97% (3 examples)	41	
	*N*-sulfonylation, no yields quoted (4 examples)	42	
	Hydrazide formation, yields=77–85% (4 examples)	43	

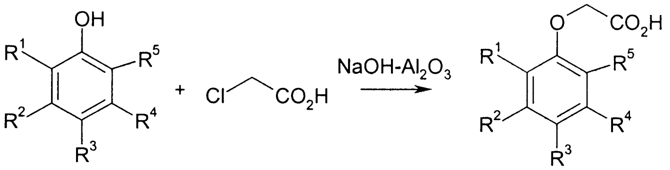
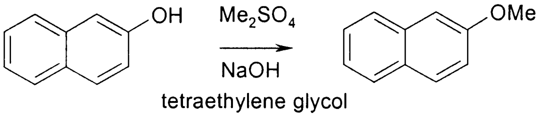
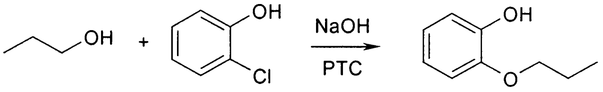
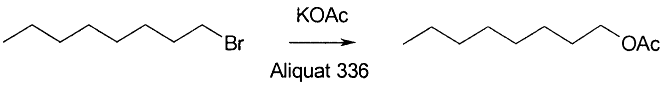
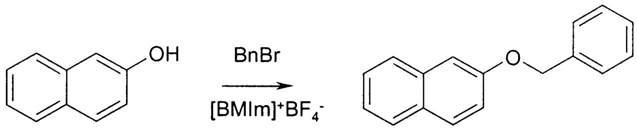
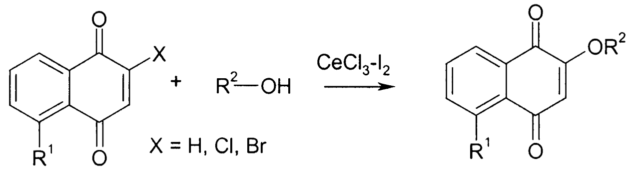
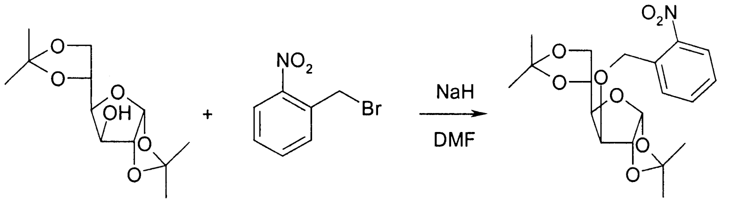
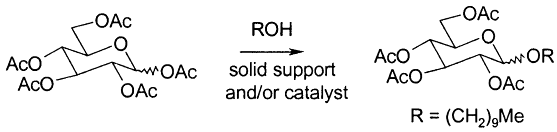
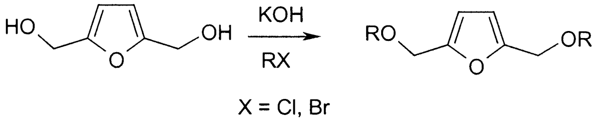
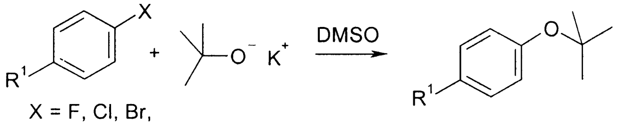
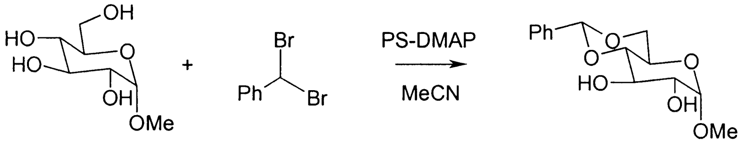
5.3. Alkylation

Conditions	Type of reaction/yields/ number of examples	Reference	
		Described	Additional
	*C*-alkylation-, Michael addition, yields=54–95% (8 examples)	44	45–47
	*C*-alkylation-, double Michael addition, yields=70–75% (13 examples)	48	49
	*C*-alkylation-, Michael addition, yields=60–90% (8 examples)	50	
	*C*-alkylation, yields=90–96% (6 examples)	51	
	Radical Michael addition reaction, yield=77% (1 example)	52	
	*N*-alkylation-, Michael addition, yield=59% (1 example)	53	

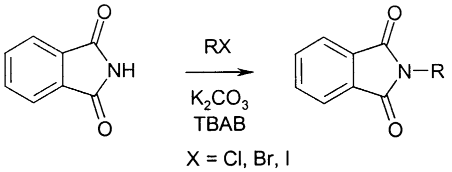
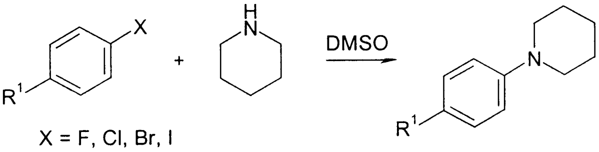
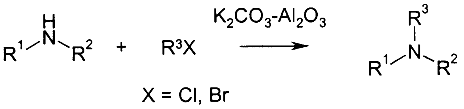
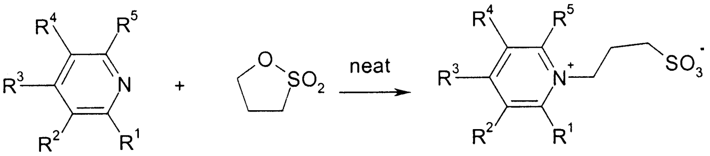
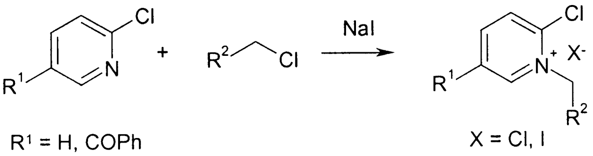
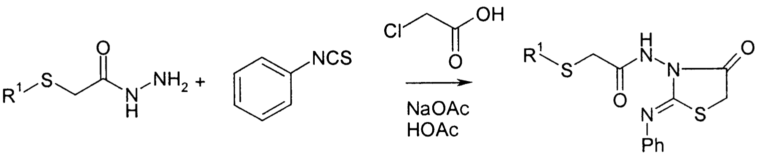
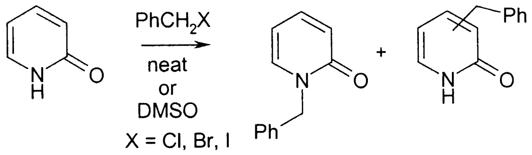
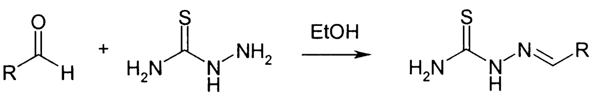
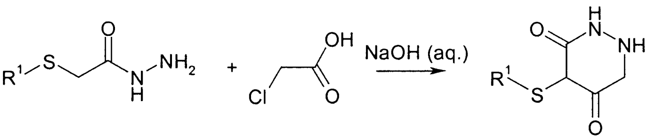
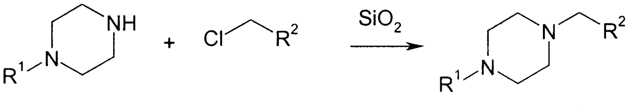
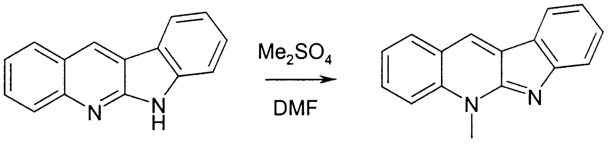
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	*N*-alkylation-, Michael addition, yields=25–100% (11 examples)	54	55,56
	*N*-alkylation-, ring opening of epoxides, yields=83–95% (15 examples)	57	58
	*N*-alkylation-, ring opening of epoxides, yields=70–85% (15 examples)	59	60
	*N*-alkylation-, ring opening of epoxides, yields=90 and >90% (2 examples)	61	
	Ring formation via ring opening of epoxides, yield=82% (1 example)	62	
	Selenide ethers-, ring opening of epoxides, yields=73–87% (13 examples)	63	64
	*O*-alkylation-, allylation, yields=52–71% (3 examples)	65	
	*O*-alkylation, yields=63–88% (8 examples)	66	67,68
	*O*-alkylation-, catalytic etherification, yields=8–76% (7 examples)	69	
	*O*-glycosidation, yields=3–77% (3 examples)	70	
	*O*-alkylation-, Williamson reaction, yields=48–100% (13 examples)	71	72–76
	*O*-alkylation, yields=61–99% (9 examples)	77	78

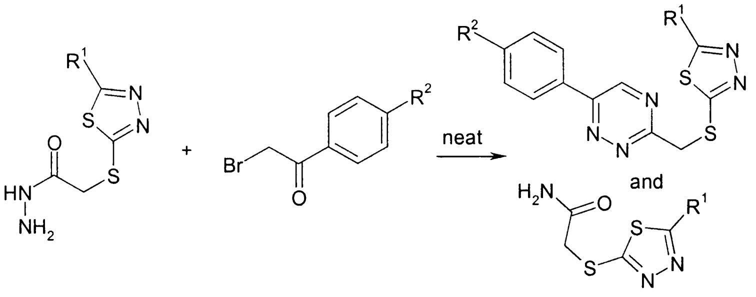
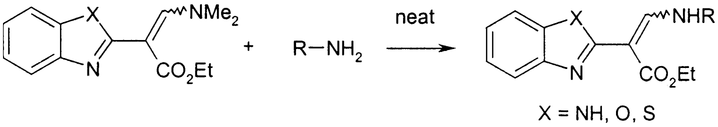
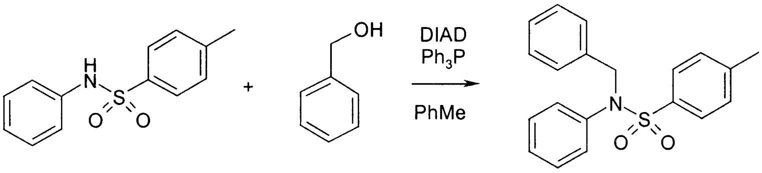
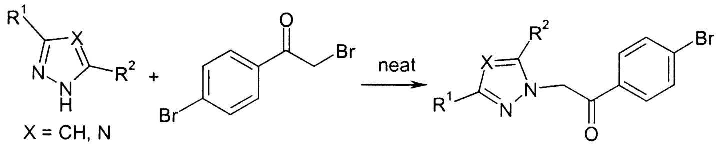
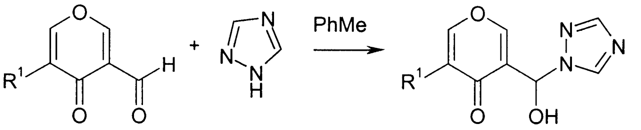
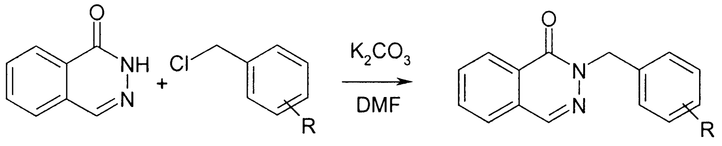
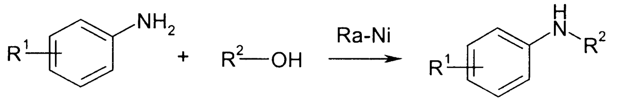
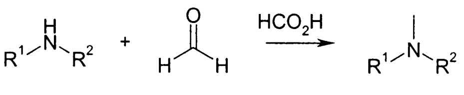
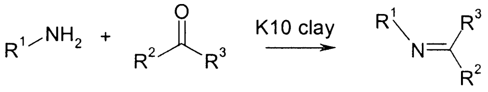
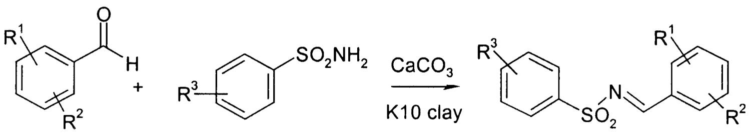
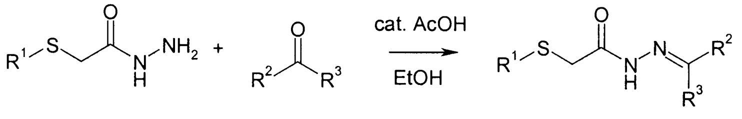
(*continued*)

Conditions	Type of reaction/yields/ number of examples	Reference	
		Described	Additional
	*O*-alkylation, yields=55–76% (9 examples)	79	80,81
	*O*-alkylation, yield=50–70% (1 example)	82	83
	*O*-alkylation, yields=63–82% (8 examples)	84	
	*O*-alkylation, yield=80% (1 example)	82	
	*O*-alkylation, yields=75–90% (10 examples) alkylation with ionic liquids as the solvent	85	
	*O*-alkylation, yields=57–90% (8 examples)	86	87
	*O*-alkylation, yields=68–96% (7 examples)	88	
	*O*-glycosidation, yields=7–77% (14 examples)	89	
	*O*-alkylation, yields=74–94% (7 examples)	90	
	*O*-alkylation, yields=31–81% (4 examples)	91	
	Benzylidene formation, yields=76 and 83% (2 examples)	88	261

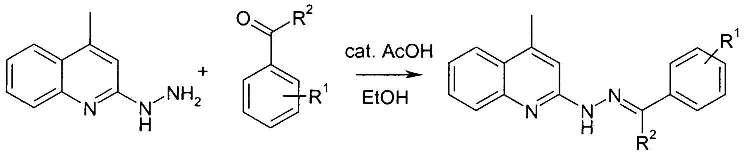
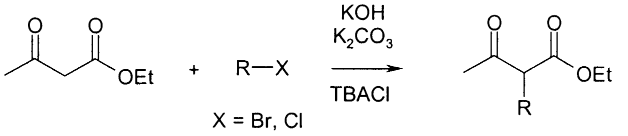
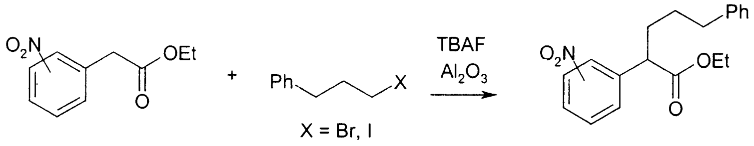
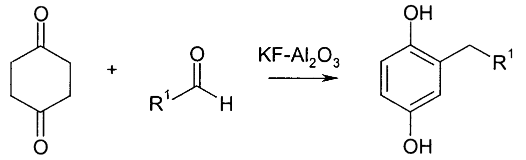
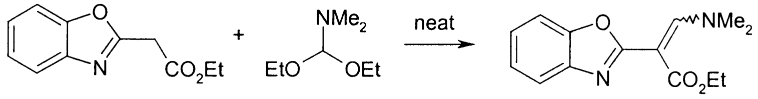
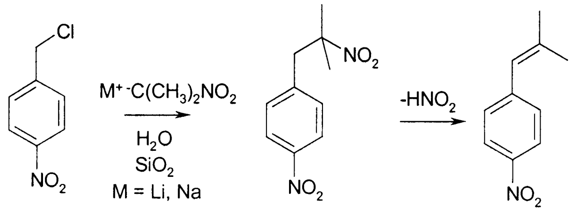
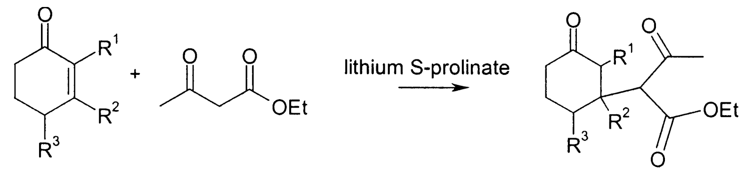
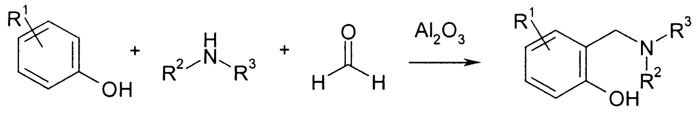
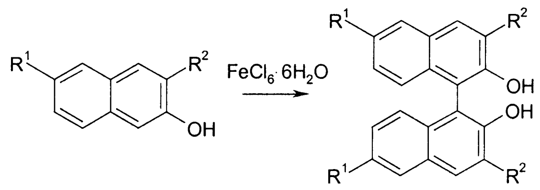
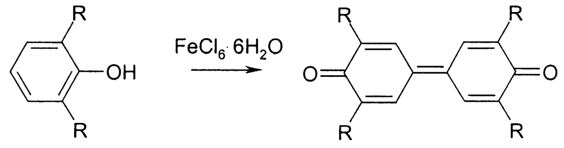
(*continued*)

Conditions	Type of reaction/yields/ number of examples	Reference	
		Described	Additional
	*N*-alkylation, yields=49–95% (9 examples)	93	
	*N*-alkylation, yields=9–93% (9 examples)	91	94
	*N*-alkylation, yields=43–98% (8 examples)	95	96–98
	*N*-alkylation-, sulfopropylation, yields=68–95% (8 examples)	99	
	*N*-alkylation-, quaternisation, yields=0–91% (10 examples)	100	
	*N*-alkylation, yields=71–79% (3 examples)	30	
	*N*-alkylation, no yields quoted (12 examples)	101	
	*N*-alkylation thiosemicarbazones, yields=79–91% (7 examples)	102	
	*N*-alkylation, yields=77 and 81% (2 examples)	30	
	*N*-alkylation, yields=75–99% (3 examples)	35	
	*N*-methylation, yield=75% (1 example)	103	

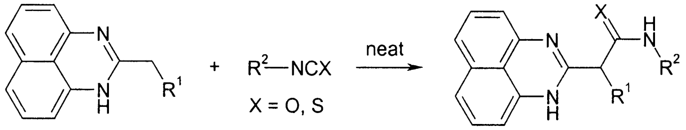
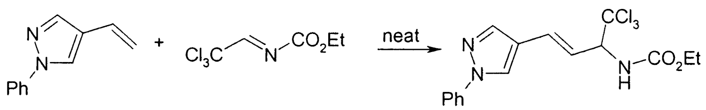
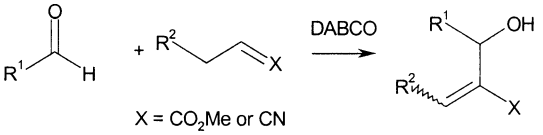
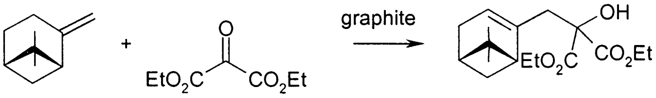
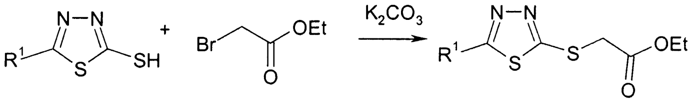
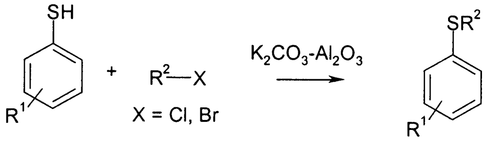
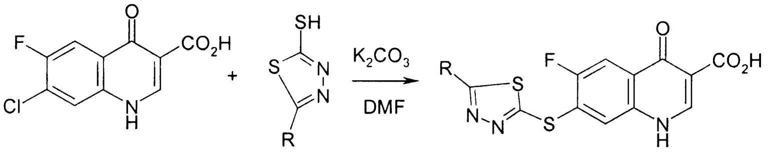
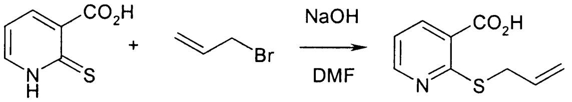
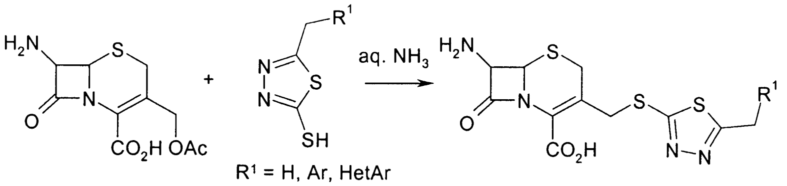
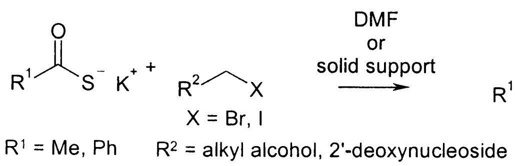
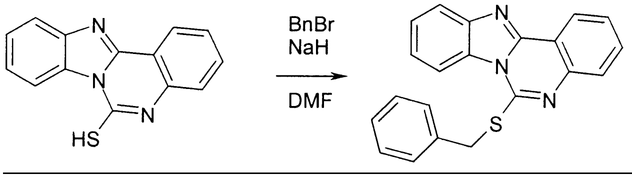
(*continued*)

Conditions	Type of reaction/yields/ number of examples	Reference	
		Described	Additional
	*N*-alkylation, yields=74–86% (8 examples) one molecule of the phenacyl bromide, undergoes N-alkylation and condensation with two molecules of the acetylhydrazone	104	
	Transamination, yields= 90–98% (11 examples) *E*/*Z*=90:10–100:0.	105	
	*N*-alkylation-, Mitsunobu reaction, yields=83–93% (4 examples)	106	
	*N*-alkylation of heterocycles, yields=80–98% (5 examples)	107	108–111
	*N*-alkylation of heterocycles, yields=78–90% (6 examples)	112	
	*N*-alkylation of heterocycles, yields=52–75% (8 examples)	113	114
	*N*-alkylation of anilines, yields=19–91% (12 examples)	115	
	*N*-methylation, yields=43–76% (5 examples)	116	117
	Imine and enamine formation, yields=75–97% (10 examples)	118	119,120
	Sulfonylimine formation, yields=52–91% (11 examples)	121	
	*N*-alkylation-, condensation to form hydrazone, yields= 92–95% (10 examples)	30	

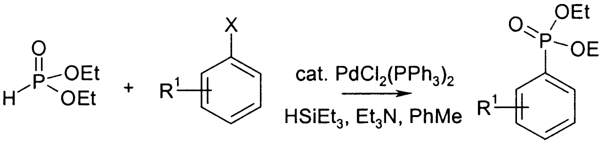
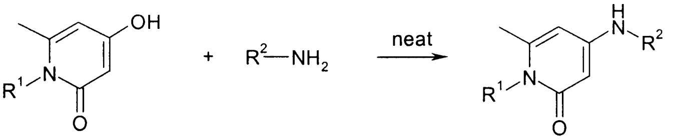
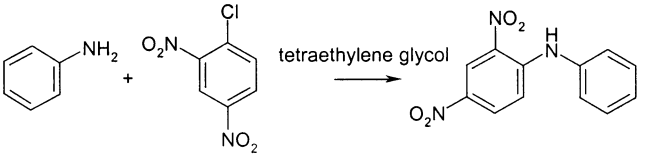
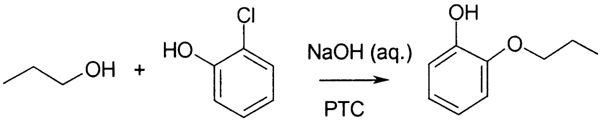
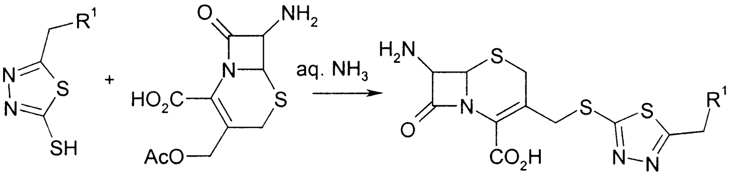
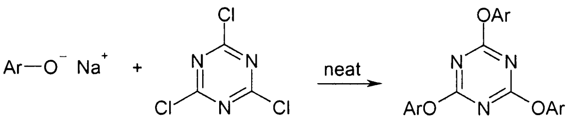
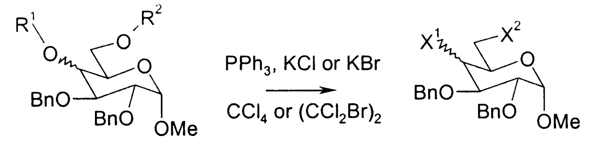
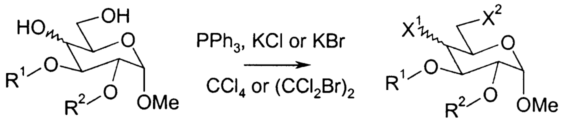
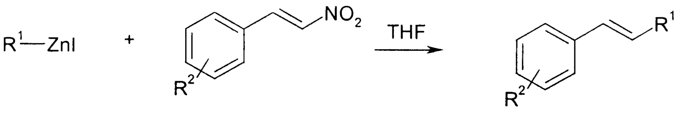
(*continued*)

Conditions	Type of reaction/yields/ number of examples	Reference	
		Described	Additional
	*N*-alkylation condensation to form hydrazone, yields=94–98% (12 examples)	34	122
	*C*-alkylation of ethyl acetoacetate, yields=59–82% (5 examples)	123	
	*C*-alkylation of activated methylenes, yields=48–79% (5 examples)	124	
	*C*-alkylation-, synthesis of 2-hydroxyquinones, yields=75–95% (14 examples)	125	
	*C*-alkylation, yields=90–98% (11 examples)	105	126–128
	*C*-alkylation, yields=72–95% (3 examples)	129	
	*C*-alkylation-, Michael addition, yields=55–75% (4 examples)	130	
	*C*-alkylation, yields=46–100% (16 examples)	131	
	*C*-alkylation, yields=40–96% (6 examples)	132	
	*C*-alkylation, yields=85–95% (3 examples)	132	

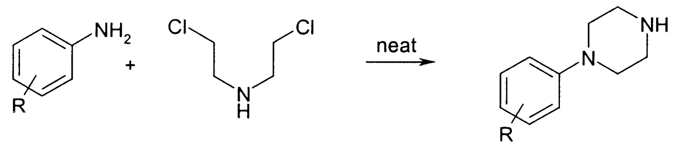
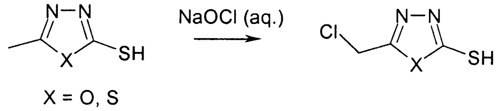
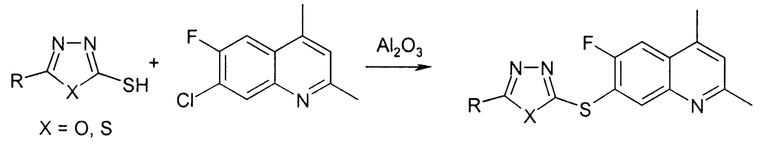
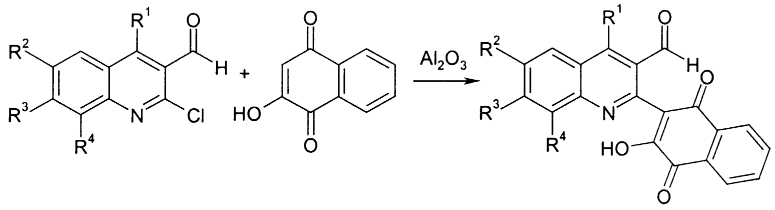
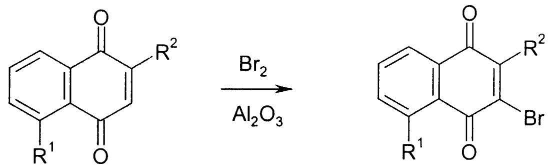
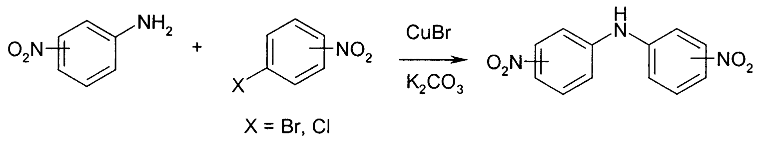
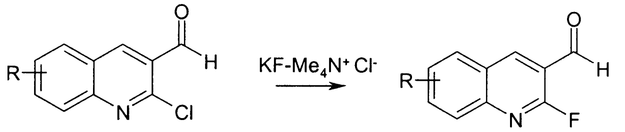
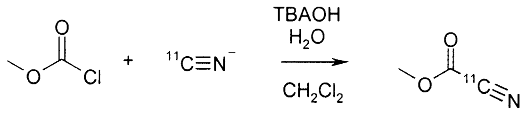
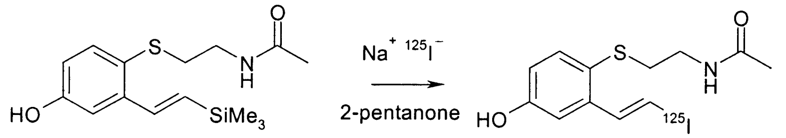
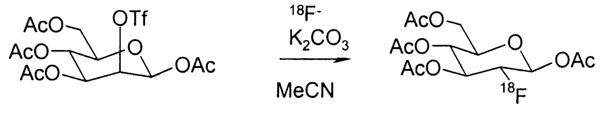
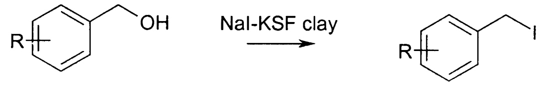
(*continued*)

Conditions	Type of reaction/yields/ number of examples	Reference	
		Described	Additional
	*C*-alkylation-, addition to isocyanates, yields=75–80% (4 examples)	133	
	*C*-alkylation, yields=22–70% (5 examples)	134	
	*C*-alkylation, yields=10–95% (12 examples)	135	
	*C*-alkylation carbonyl-ene reaction, yields=50–80% (3 examples)	136	
	*S*-alkylation, yields=82–86% (4 examples)	104	
	*S*-alkylation, yields=70–98% (3 examples)	95	
	*S*-arylation, yields=50–72% (6 examples)	137	138
	*S*-alkylation, yields=57–81% (7 examples)	106	
	*S*-alkylation, yields=80–85% (5 examples)	139	
	*S*-alkylation, yields=40–100% (17 examples)	140	
	*S*-alkylation, yields=85–95% (3 examples)	141	

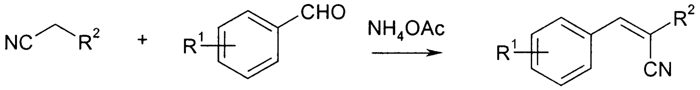
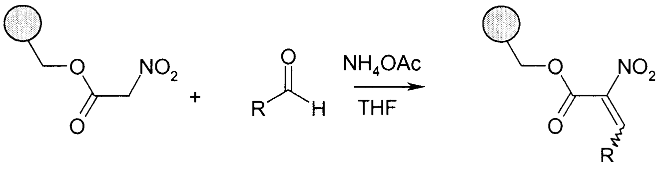
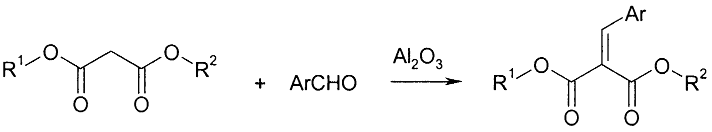
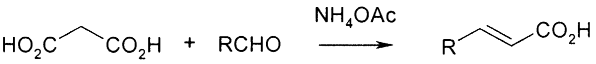
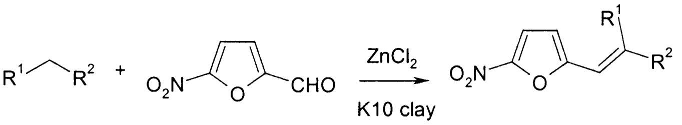
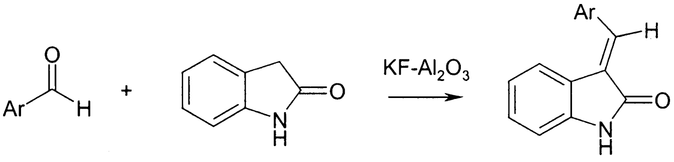
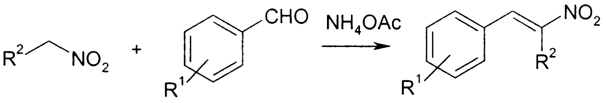
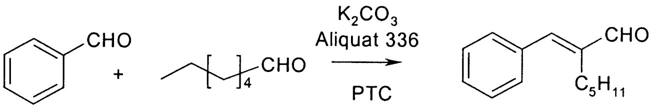
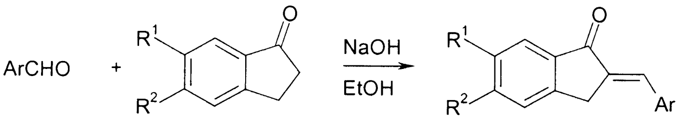
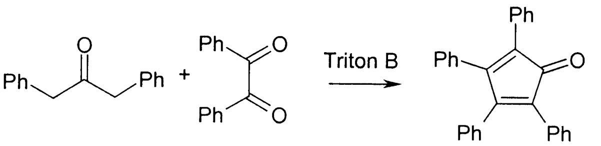
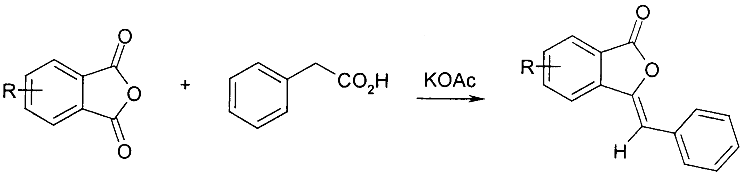
5.4. Aromatic and nucleophilic substitution

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
 X = Cl, Br, I, OTf	Phosphonation of aryl halides, yields=0–87% (18 examples)	142	
	Aromatic nucleophilic substitution, yields=60–91% (11 examples)	143	
	Aromatic nucleophilic substitution, yields=70–85% (1 example)	82	144
	Aromatic nucleophilic substitution, yields=63–82% (8 examples)	145	
 R^1 = H, Ar, HetAr	Nucleophilic substitution, yields=80–85% (5 examples)	139	146
	Aromatic nucleophilic substitution, yields=85–90% (12 examples)	147	148
 R^1 and R^2 = H, Bn or Ac X^1 and X^2 = Cl, Br, OR^1 or OR^2	Halogenation of carbohydrates, yields=40–91% (7 examples)	149	
 R^1 and R^2 = H, Bn X^1 and X^2 = Cl, Br, OH	Halogenation of carbohydrates, yields=25–95% (16 examples)	149	
	Substitution of NO_2 group, yields=76–83% (9 examples)	150	

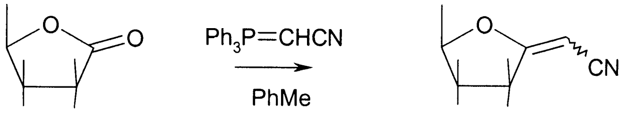
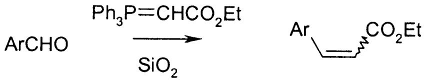
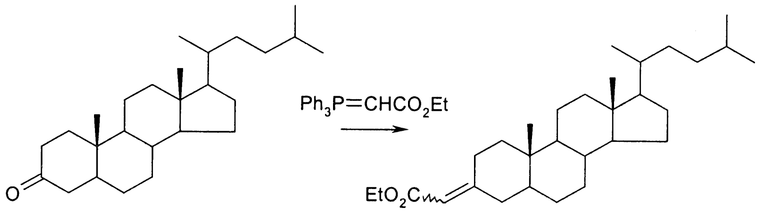
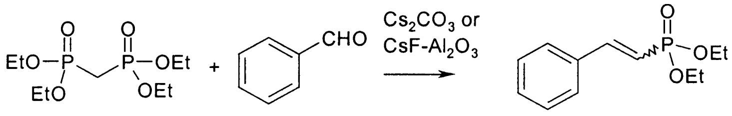
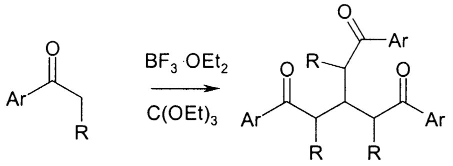
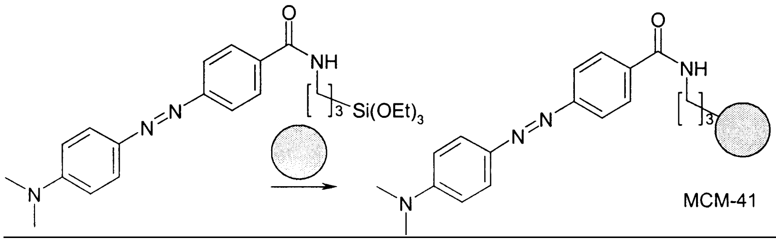
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Arylpiperazine formation, yields=47–73% (7 examples)	151	
	Chlorination of heterocycles, yields=89–95% (6 examples)	152	
	Aromatic nucleophilic substitution, yields=75–80% (6 examples)	153	
	Aromatic nucleophilic substitution, yields=70–82% (5 examples)	153	
	Bromination of quinones, yields=80–96% (17 examples)	154	
	Synthesis of dinitrophenylamines, yields=17–68% (4 examples)	155	
	Halogenation, yields=66–96% (5 examples)	156	157,158
	Nucleophilic substitution, no yield quoted. (1 example)	159	
	Halogenation, yield=48% (1 example)	160	
	Halogenation, yield=90% (1 example)	161	162
	Halogenation, yields=55–90% (4 examples)	163	164

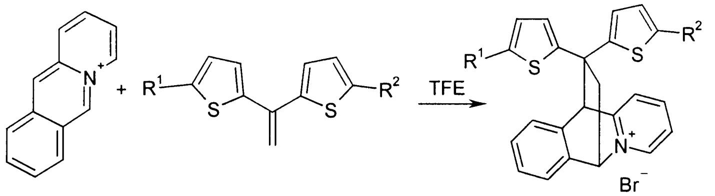
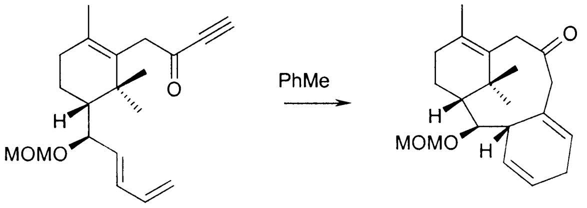
5.5. Condensation

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Knoevenagel condensation, yields=89–97% (15 examples)	165	166–170
	Knoevenagel condensation, no yields quoted. (5 examples)	171	
	Knoevenagel condensation, yields=70–96% (7 examples)	172	173–175
	Knoevenagel condensation, yields=95–98% (10 examples)	176	177,178
	Knoevenagel condensation, yields=62–98% (8 examples)	179	
	Knoevenagel condensation, yields=69–94% (8 examples)	180	181–183
	Knoevenagel condensation-, Henry reaction, yields= 80–92% (11 examples)	184	185
	Aldol condensation, yield=82% (1 example)	186	187
	Aldol condensation, yields=85–100% (22 examples)	188	187–193
	Aldol condensation, yield=75% (1 example)	194	
	Gabriel synthesis of phthalides, yields=20–89% (11 examples)	195	

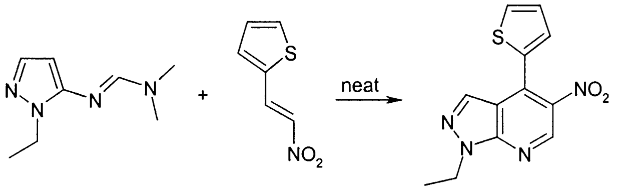
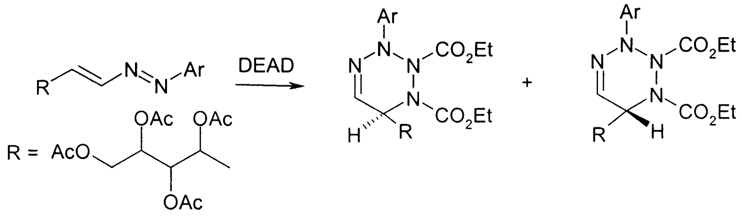
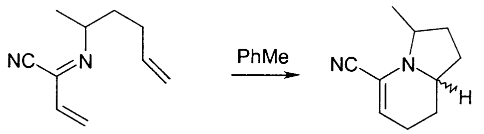
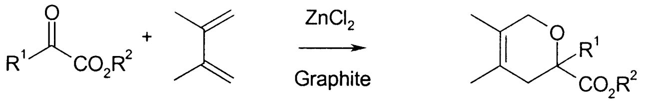
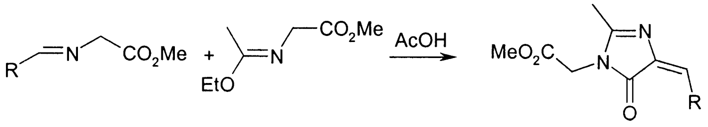
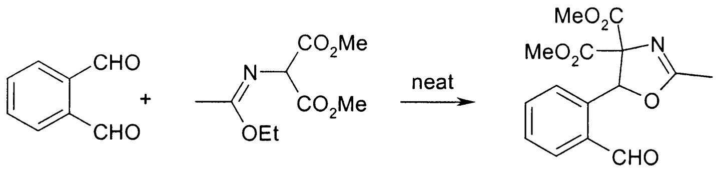
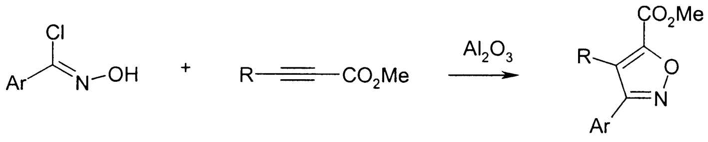
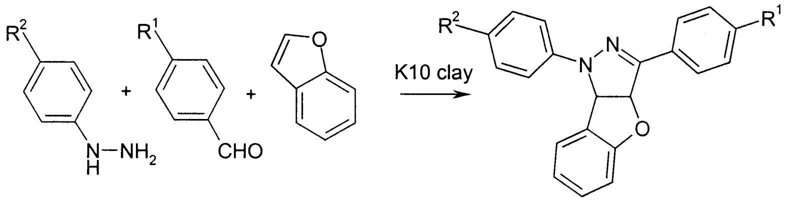
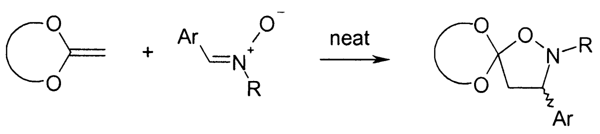
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Wittig olefination, yields=85–98% (8 examples)	196	197
	Wittig olefination, yields=82–96% (7 examples)	198	199
	Wittig olefination, yields=76–86% (4 examples)	200	
	Horner olefination, yields=72 and 74% (2 examples)	201	
	Condensation with triethyl orthoformate, yields=55–85% (10 examples)	202	
	Hydrothermal co-condensation, no yields quoted (2 examples)	203	

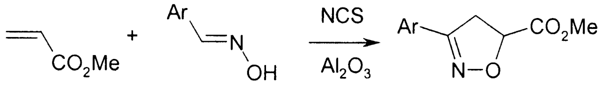
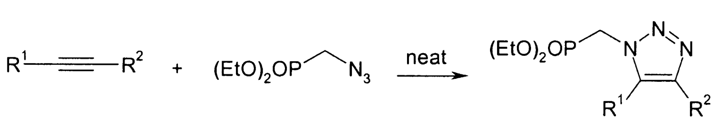
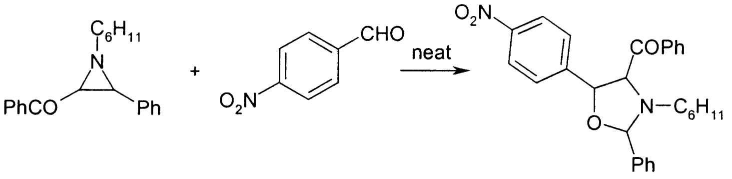
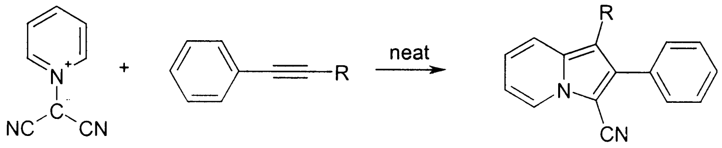
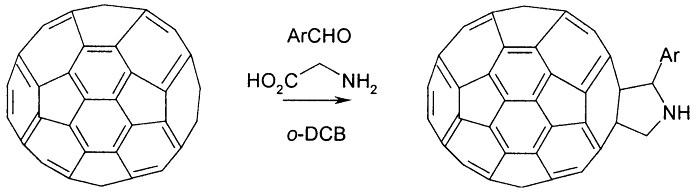
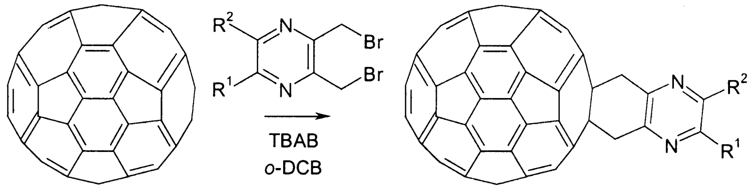
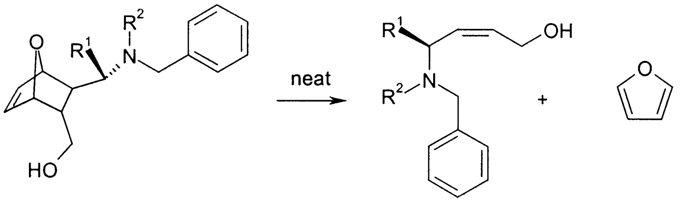
5.6. Cycloaddition

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Diels–Alder reaction, yields=58–78% (6 examples)	204	136,194, 205, 206–210
	Intramolecular Diels–Alder reaction, yield=30–40% (1 examples) stereoselective cycloaddition approach to Taxoid skeleton	211	212

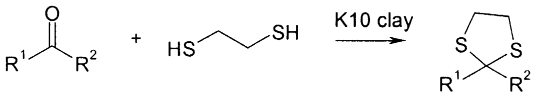
(*continued*)

Conditions	Type of reaction/yields/ number of examples	Reference	
		Described	Additional
	Hetero Diels–Alder reaction, yields=32–84% (7 examples)	213	214–216
	Hetero Diels–Alder reaction, yields=80–96% diastereomeric ratio= 85:15–35:65 (6 examples)	217	
	Intramolecular hetero Diels–Alder reaction, yield=70% (1 example)	218	
	Hetero Diels–Alder reaction, yields=54–87% (3 examples)	136	
	1,3-Dipolar cycloaddition using imidates, yields=71–98% (6 examples)	219	220
	Hetero 1,3-dipolar cycloaddition, yield=83% (1 example)	221	
	1,3-Dipolar cycloaddition using nitrile imines or nitrile oxides, yields=0–85% (20 examples)	222	223,224
	1,3-Dipolar cycloaddition-, multicomponent reaction, yields=60–75% (14 examples)	225	226,227
	1,3-Dipolar cycloaddition using nitrones, yields=70–95% (10 examples)	228	229–234

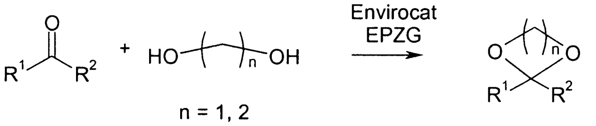
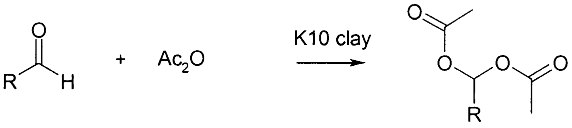
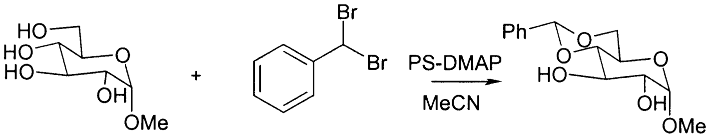
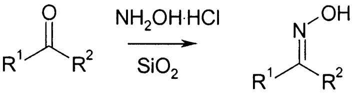
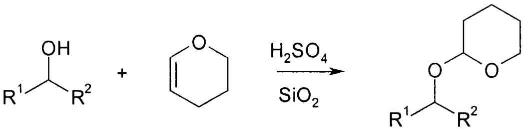
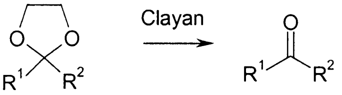
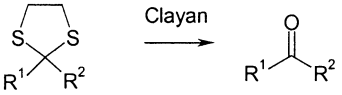
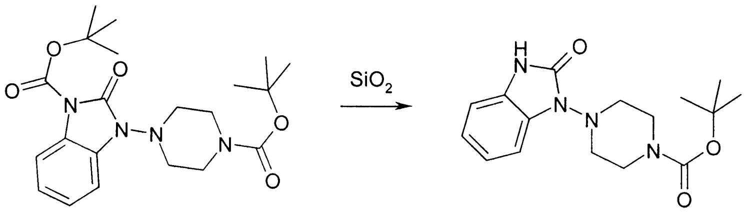
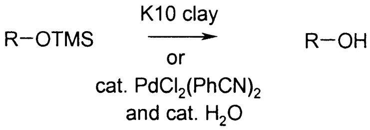
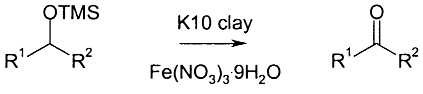
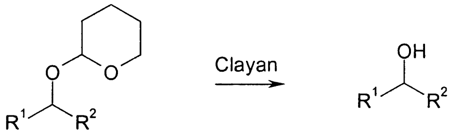
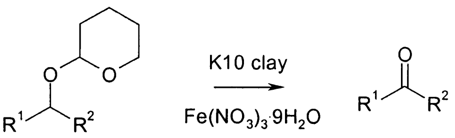
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	1,3-Dipolar cycloaddition using nitrile oxides, yields=55–77% (8 examples)	235	236–240
	Hetero 1,3-dipolar cycloaddition using azidomethyl phosphonates, yields=40–99% (5 examples)	241	
	Carbonyl 1,3-dipolar cycloaddition using azidomethine ylide, yields=35–80% (6 examples)	242	243
	1,3-Dipolar cycloaddition using azidomethine ylide, yields=46 and 87% (2 examples)	244	
	1,3-Dipolar cycloaddition to C$_{60}$-fullerene, yields=15–37% (3 examples)	245	246
	Cycloaddition to C$_{60}$-fullerene, yields=9–26% (5 examples)	247	248
	Retro Diels–Alder, yields=50–84% (5 examples)	249	

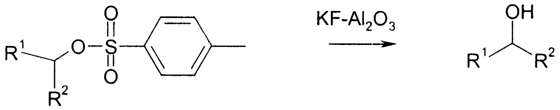
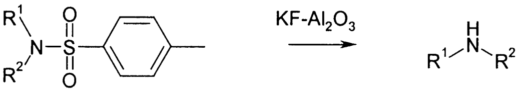
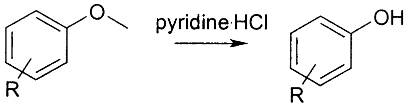
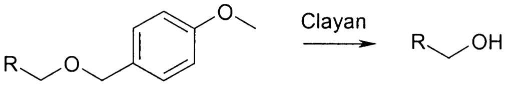
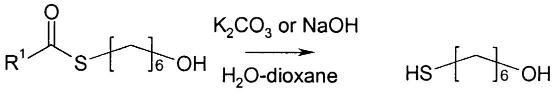
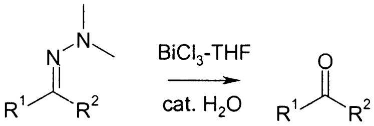
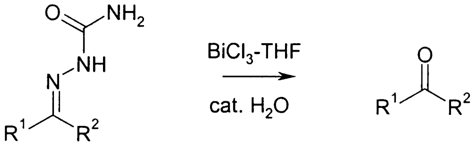
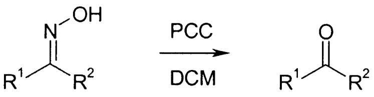
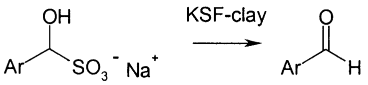
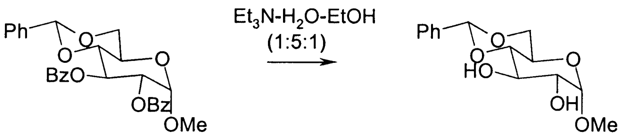
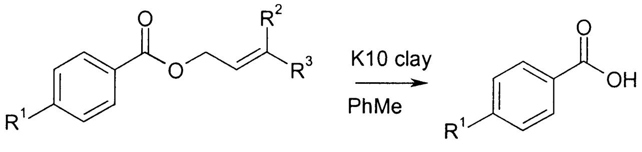
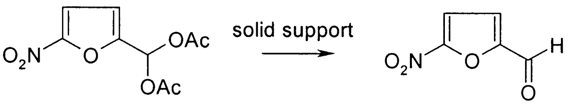
5.7. Deprotection and protection

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	1,3-Dithiolanes from carbonyl compounds, yields=70–90% (7 examples)	250	

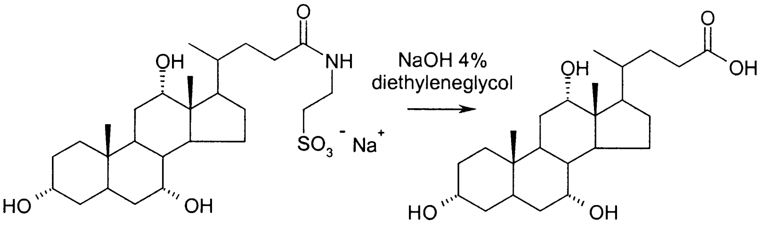
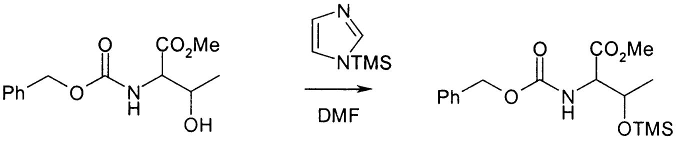
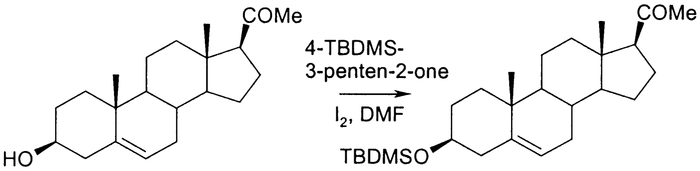
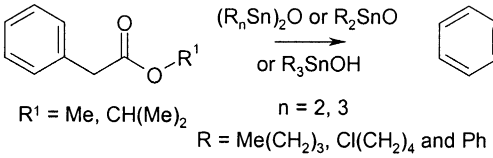
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Acetalization and ketalization of carbonyls, yields=40–97% (11 examples)	251	252–259
	Acylal formation, yields=75–98% (12 examples)	260	
	Benzylidene formation, yields=76 and 83% (2 examples) solid supported reagent	88	261
	Oximes from carbonyl compounds, yields=0–94% (18 examples)	262	263
	Protection of alcohols as tetrahydropyranyl ethers, yields=80–92% (11 examples)	264	
	Acetal deprotection, yields=70–90% (7 examples)	265	266
	Thioacetal deprotection, yields=80–89% (13 examples)	267	
	*N*-Boc deprotection, yields=56–98% (12 examples) example of chemoselective deprotection.	268	269
	Trimethylsilyl ether deprotection, yields=88–100% (22 examples)	270	
	Oxidative deprotection of silyl ethers, yields=70–95% (8 examples)	271	272
	Deprotection of tetrahydropyranyl ethers, yields=76–90% (9 examples)	265	264
	Deprotection of tetrahydropyranyl ethers, yields=80–90% (9 examples)	272	273,274

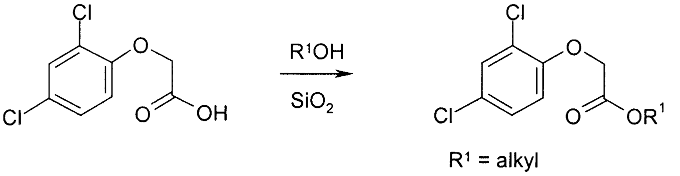
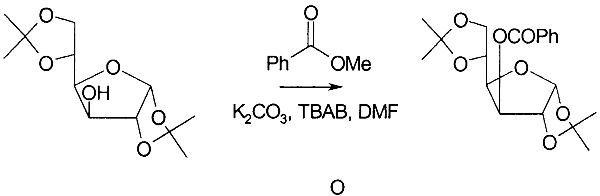
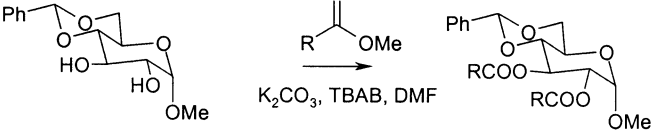
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Cleavage of sulfonates, yields=83–90% (14 examples)	275	
	Cleavage of sulfonamides, yields=76–85% (11 examples)	275	276
	Cleavage of alkyl ethers, yields=74–95% (11 examples)	277	278
	Cleavage of benzyl ethers, yields=70–88% (13 examples)	279	
 R^1 = Me, Ph	*S*-acyl deprotection, yields=100% (4 examples)	140	
	Regeneration of carbonyls from hydrazones, yields=75–98% (11 examples)	280	281,282
	Regeneration of carbonyls from semicarbazones, yields= 55–90% (14 examples)	283	282,284,285
	Regeneration of carbonyls from oximes, yields=90–97% (14 examples)	286	285,287–291
	Regeneration of aldehydes from bisulfites, yields=85–98% (12 examples)	292	
	Deprotection of benzyl groups, yields=71–78% (3 examples)	88	89,293–296
	Ester hydrolysis, yields= 0–97% (20 examples)	297	
	Deacylation, yields=5–99% (4 examples)	298	178

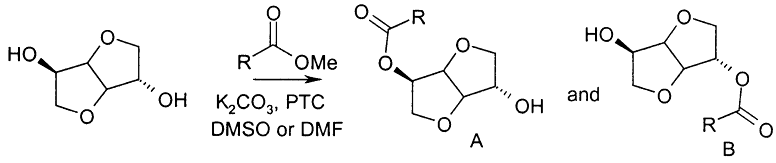
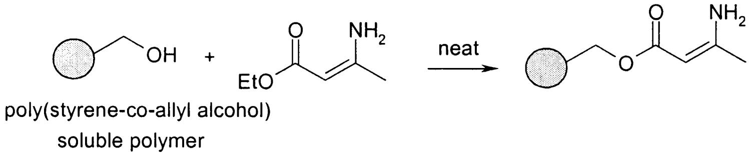
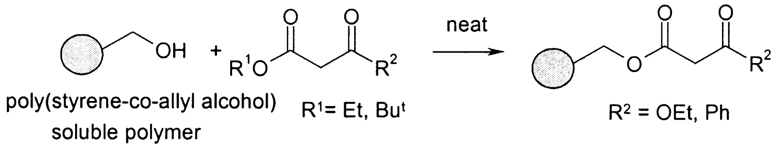
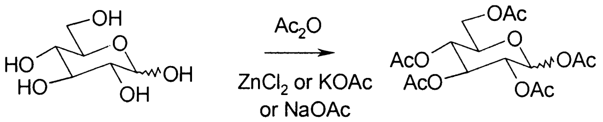
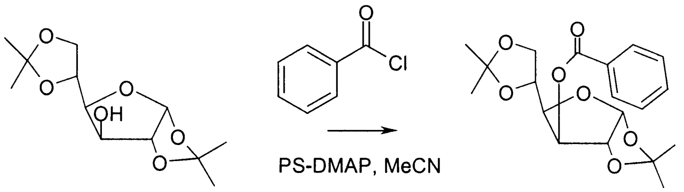
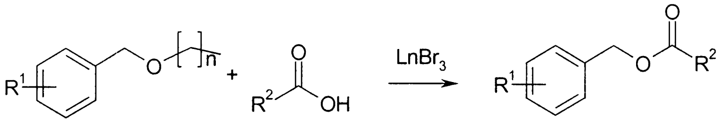
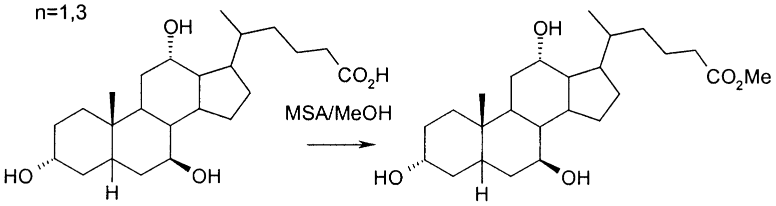
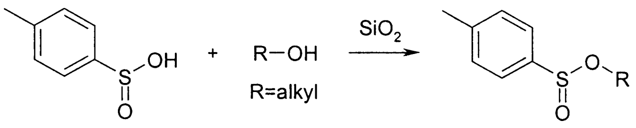
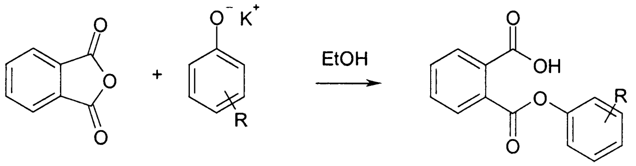
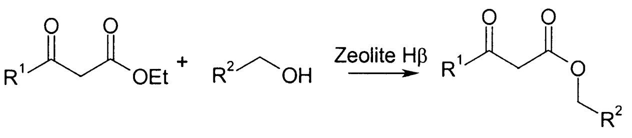
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Basic amide hydrolysis Yield=86% (1 example)	299	
	Silylation, yields=63–99% (8 examples)	106	
	Silylation, yields=56–82% (8 examples)	106	
	Saponification, yields= 0–100% (12 examples)	300	

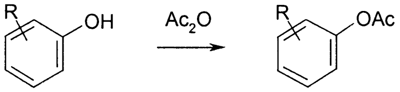
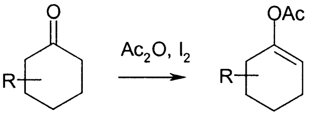
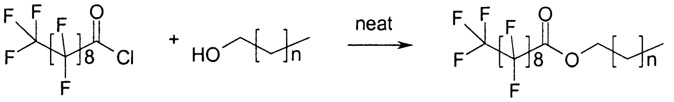
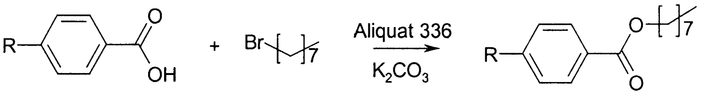
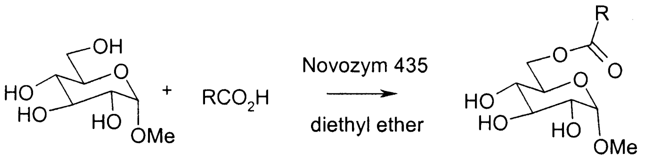
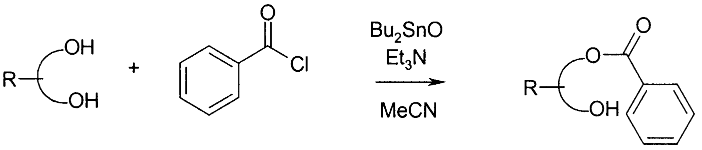
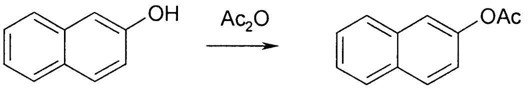
5.8. Esterification and transesterification

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Esterification of 2,4-dichlorophenoxy-acetic acid, yields=95–99% (9 examples)	301	302,303
	Transesterification-, benzoylation, yields=60–96% (7 examples)	304	
	Transesterification-, mixture of monoestericication and diesterification, yields= 15–100% (9 examples)	304	

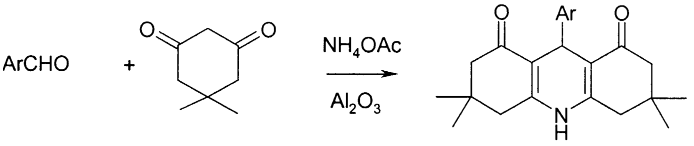
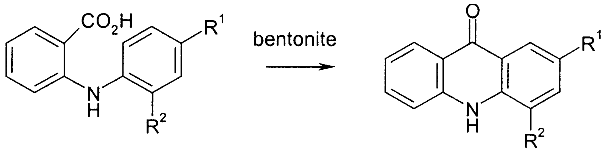
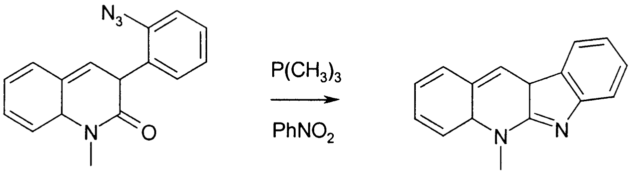
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Transesterification-, mixture of products, yields=44–63% (5 examples)	304	
	Transesterification-, polymer-bound product was further elaborated, no yield quoted (1 example)	305	
	Transesterification-, polymer-bound product was further elaborated, no yields quoted (3 examples)	305	
	Peracetylation, yields= 80–98% (6 examples)	89	
	Esterification-, solid supported reagent, yields=68–96% (9 examples)	88	
	Esterification LnBr$_3$ catalysed, yields=41–84% (17 examples)	306	
	Esterification, yield=97% (1 example)	307	300–302
	Sulfinate esters, yields= 65–95% (10 examples)	92	
	Synthesis of orthophthalic acid monoesters, yields=28–90% (8 examples)	308	
	Transesterification, yields= 60–95% (6 examples)	309	310

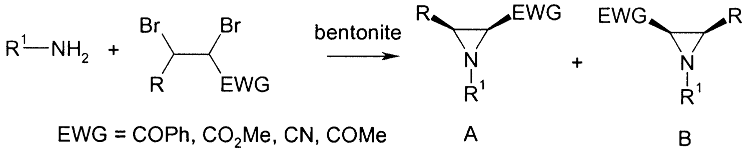
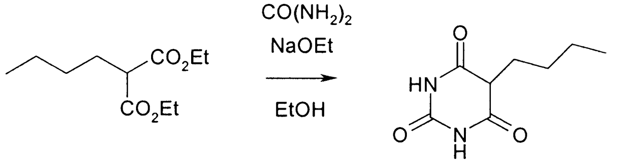
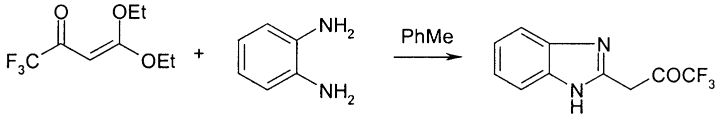
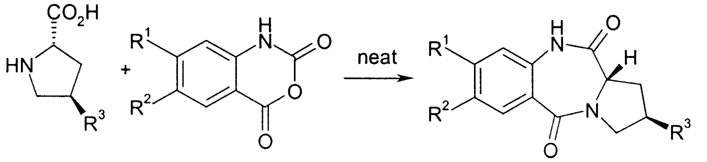
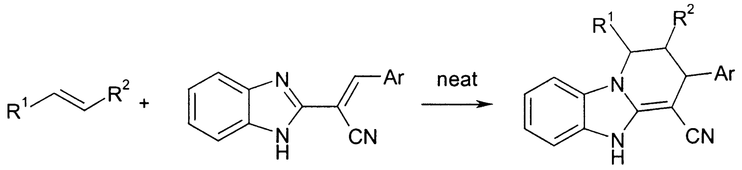
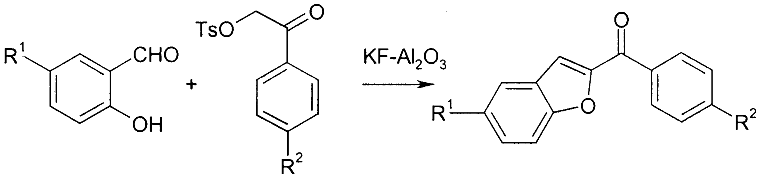
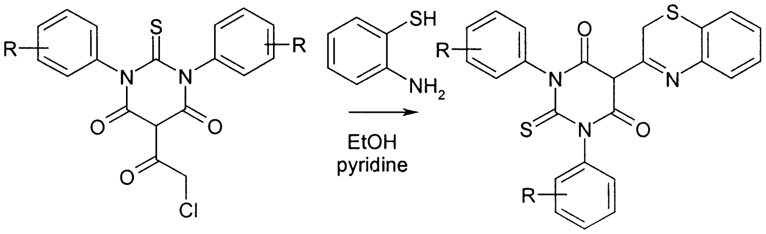
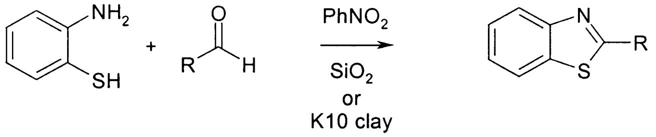
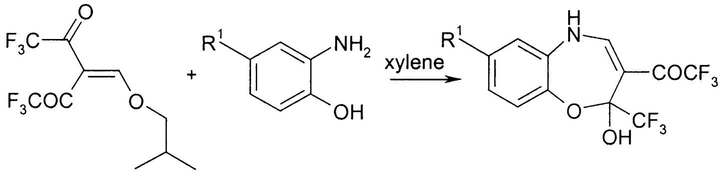
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Esterification, yields=92–98% (4 examples)	311	
	Esterification of enols, yields=0–90% (10 examples)	312	
	Esterification-, derivatization, no yields quoted (6 examples)	313	
 R = H, NMe_2, OMe, CN, NO_2	Esterification, yields= 95–100% (5 examples)	314	
	Esterification-, enzymatic, yields=92 and 97% (2 examples)	315	
	Selective esterification, yields=0–92% (4 examples)	316	317,318
	*O*-acylation, yield=60–80% (1 example)	82	77,311

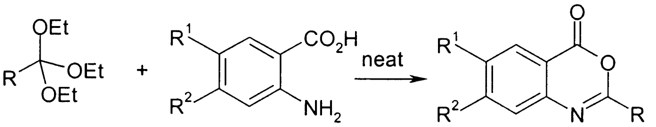
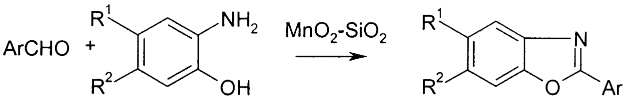
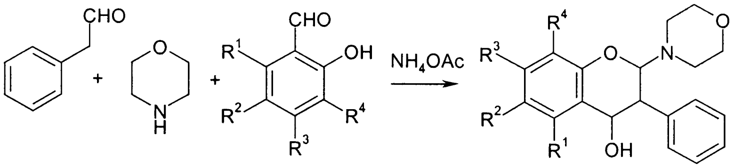
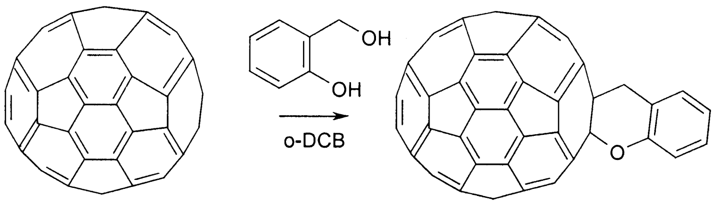
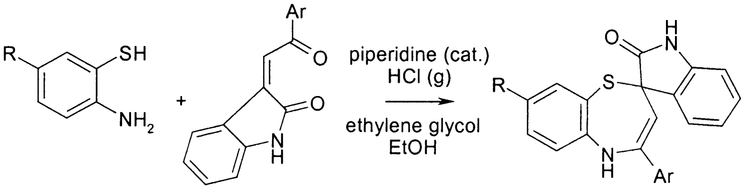
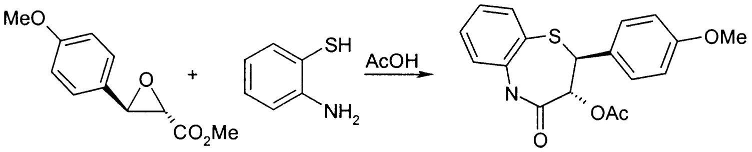
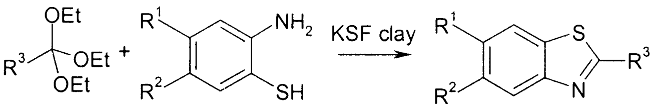
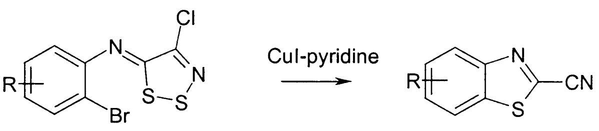
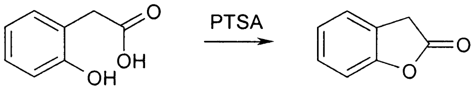
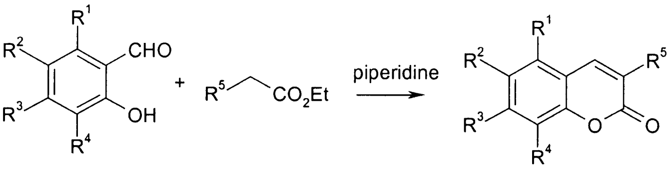
5.9. Heterocycles

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Acridine, yields=50–70% (5 examples)	319	
	Acridone, yields=70–85% (5 examples)	320	
	Azaindole Aza–Wittig reaction, yield=40% (1 example)	321	

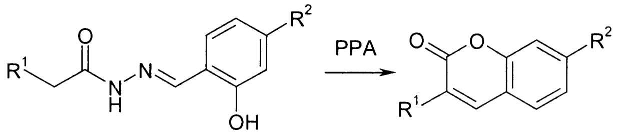
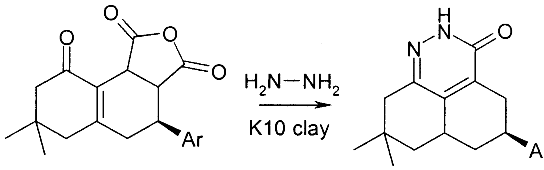
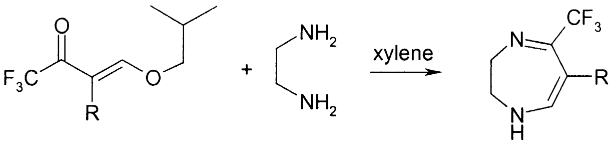
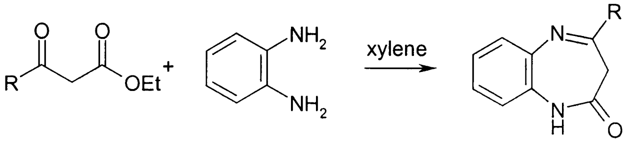
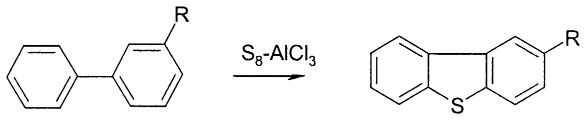
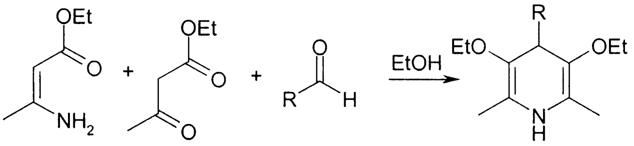
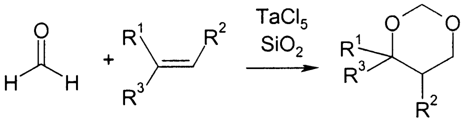
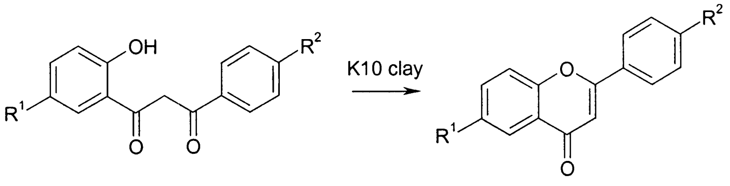
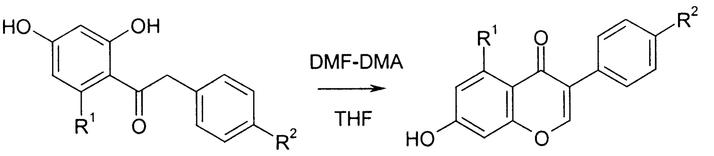
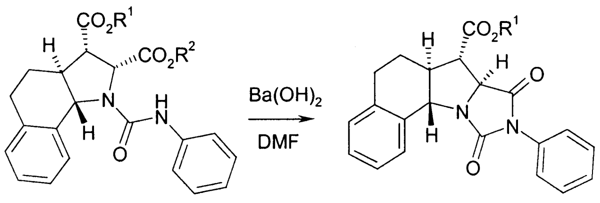
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Aziridine, yields A and/or B=0–100% (14 examples)	322	
	Barbituric acid, yield=80% (1 example)	323	
	Benzimidazole, yields=86–92% (3 examples)	339	325–331
	Benzodiazepine, yields= 80–92% (8 examples)	332	324,326,333
	Benzo[*g*]imidazo [1,2-*a*]pyridine Diels–Alder reaction, yields=80–90% (6 examples)	334	
	Benzofuran, yields=89–96% (8 examples)	335	337
	Benzothiazine, yields=63–68% (6 examples)	336	
	Benzothiazole, yields=61–98% (10 examples)	338	
	Benzoxazepine, yields= 76–89% (4 examples)	339	324

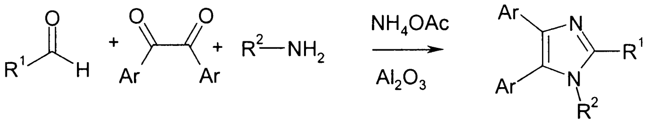
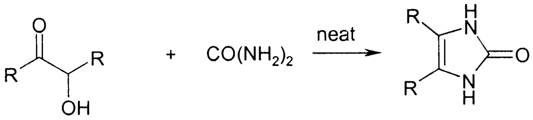
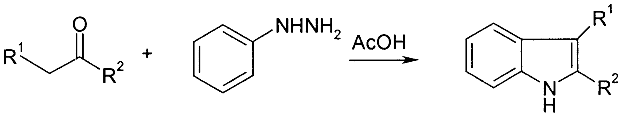
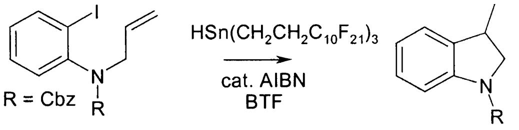
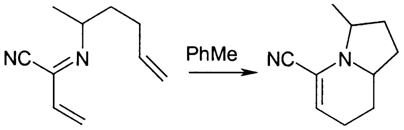
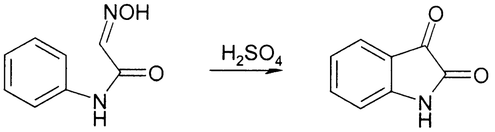
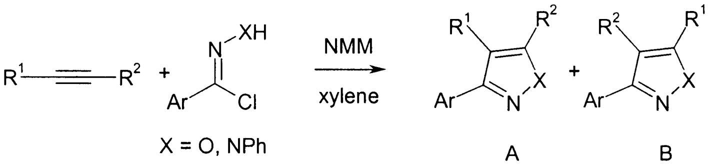
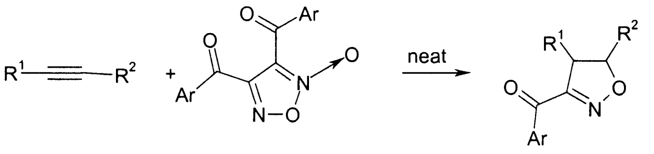
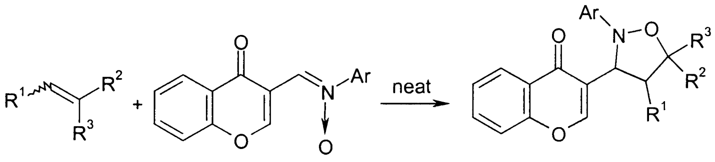
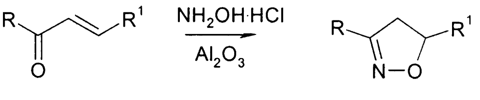
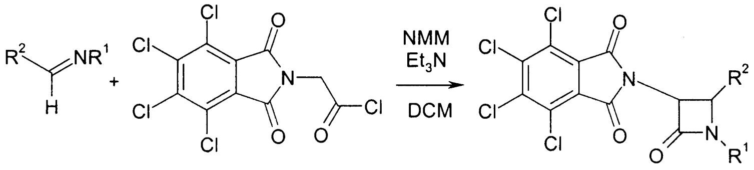
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Benzoxazinone, yields=76–94% (6 examples)	340	
	Benzoxazole, yields=84–97% (17 examples)	331	325,339
	Benzopyran, yields=71–88% (11 examples)	341	323,342
	Benzopyran, yields=21 and 27% (2 examples)	245	246
	Benzothiazepine, yields=53–65% (5 examples)	343	339,344,345
	Benzothiazepinone-, reversible diastereoselectivity, yields=75 and 84% (2 examples)	346	
	Benzothiazole, yields=70 and 74% (2 examples)	325	338,339
	Benzothiazole, yields=70 and 74% (2 examples)	347	348–350
	Coumaran-2-one, yield=85% (1 example)	351	
	Coumarin, yields=55–94% (16 examples)	352	353–355

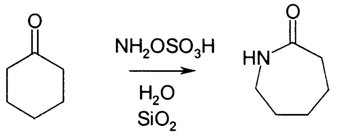
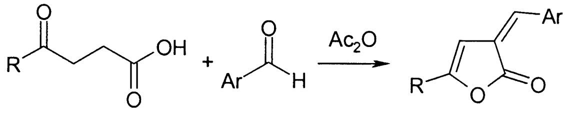
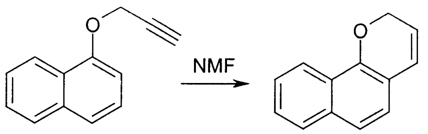
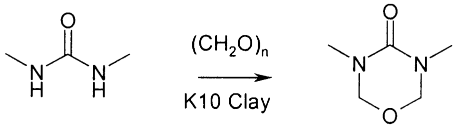
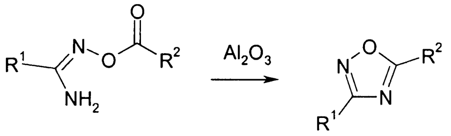
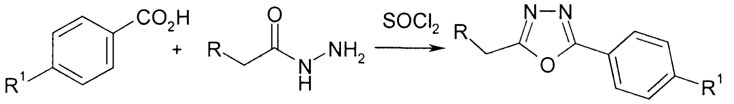
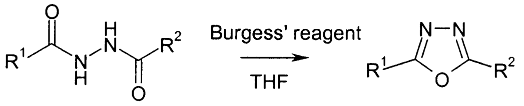
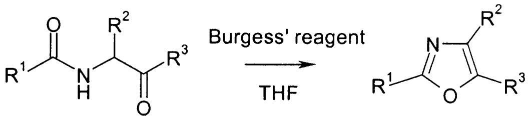
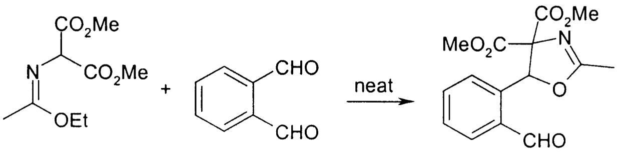
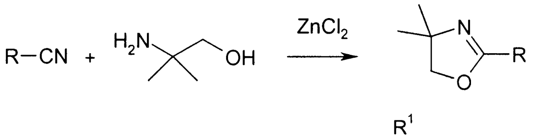
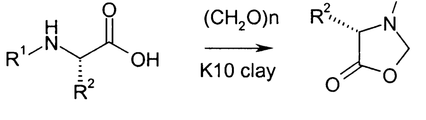
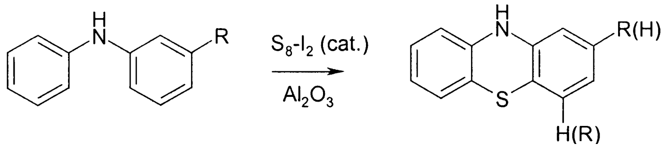
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Coumarin, yields=55–68% (4 examples)	122	356,357
	Diazaphenalene, yields=54–81% (3 examples)	358	
	Diazepine, yields=73 and 77% (2 examples)	324	
	Diazepinone, yields=82–98% (11 examples)	359	
	Dibenzothiophene, yield=55% (1 example)	360	
	Dihydropyridine, yields=81–96% (8 examples)	361	362–365
	Dioxane, yields=78–90% (9 examples)	366	
	Flavone, yields=72–80% (7 examples)	367	
	Isoflavone, yields=71–91% (4 examples)	368	369
	Hydantoin, yields=81–94% (6 examples)	370	371

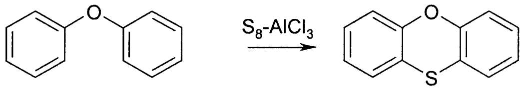
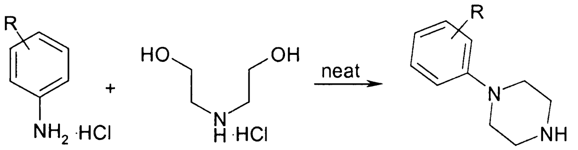
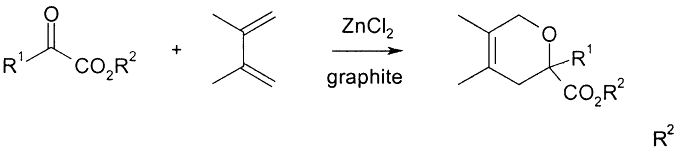
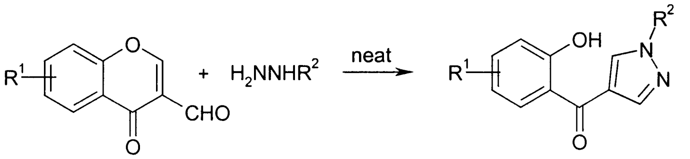
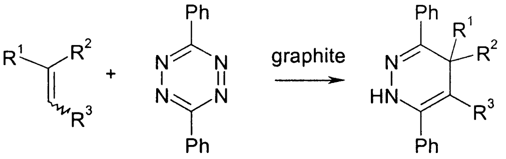
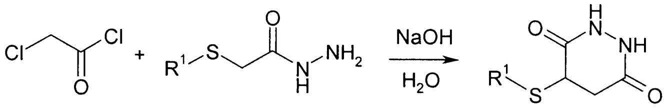
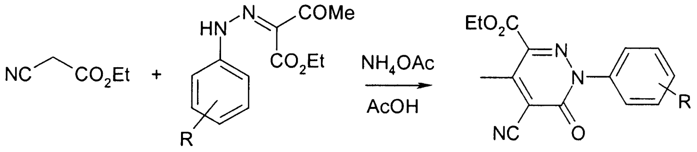
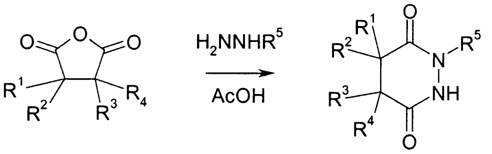
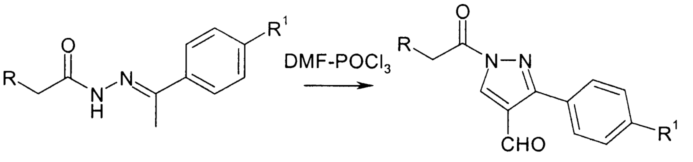
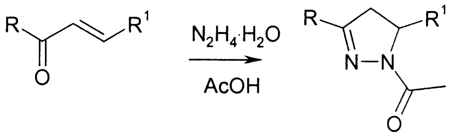
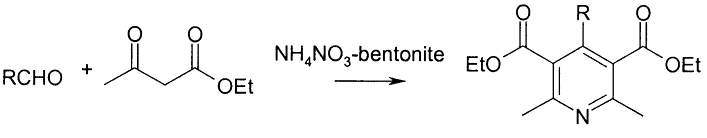
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Imidazole, yields=68–82% (8 examples)	372	
	Imidazolinone, yields=68–82% (8 examples)	373	219,220
	Indole, yield=100% (1 example)	323	374,375
	Indoline, yield=93% (1 example)	52	
	Indolizidine, yields=32–84% (7 examples)	218	244
	Isatin, yields=61–85% (5 examples)	376	
	Isoxazole, yields (A)=25–73%, yields (B)=0–22% (8 examples)	222	
	Isoxazole-, capture by dipolarophiles, yields=55–65% (8 examples)	377	
	Isoxazoline, yields=50–90% (11 examples)	378	222,229–234,239
	Isoxazoline, yields=63 and 67% (2 examples)	379	
	β-Lactam, yields=83–99% (5 examples)	27	380–386

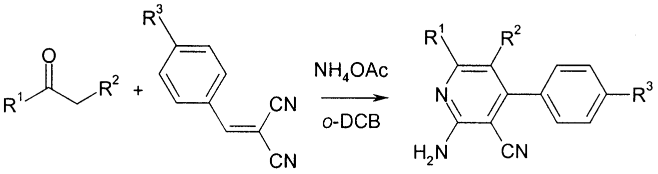
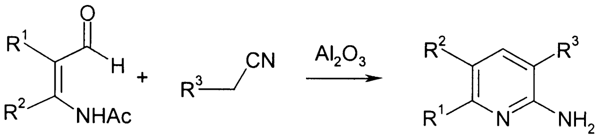
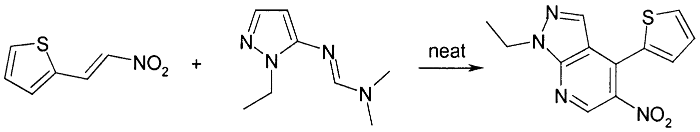
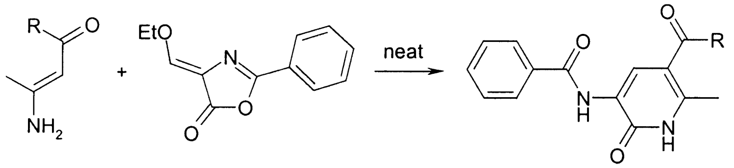
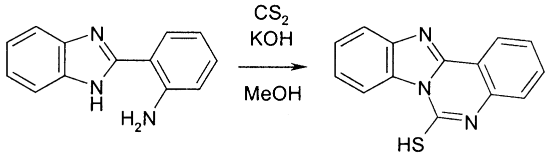
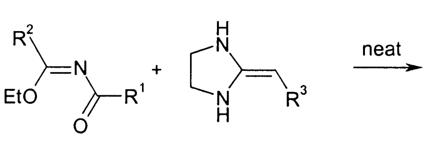
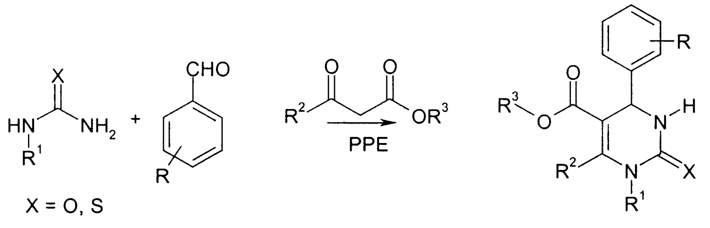
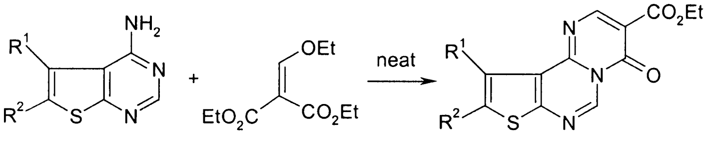
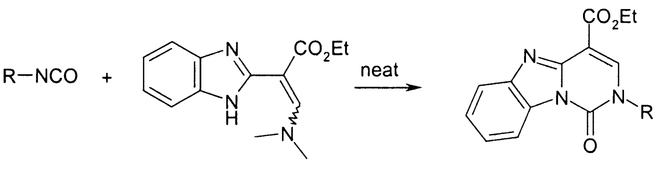
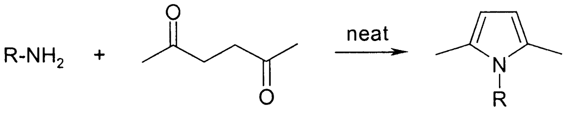
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Lactam, yields=60–86% (6 examples)	387	
	Lactone, yields=60–86% (6 examples)	388	389,390
	Naphthopyran, yields=75–96% (6 examples)	391	392
	Oxadiazinone, yield=67% (1 example)	388	
	1,2,4-Oxadiazole, yields=50–95% (9 examples)	393	
	1,3,4-Oxadiazole, yields=68–80% (4 examples)	122	393
	1,3,4-Oxadiazole, yields=70–98% (16 examples)	394	
	1,3-Oxazole, yields=72–100% (11 examples)	395	396
	Oxazoline, yield=83% (1 example)	221	397
	Oxazoline, yields=43–94% (15 examples)	398	399
	Oxazolidinone, yields=90–96% (14 examples)	400	
	Phenothiazine, yields=48–94% (4 examples)	401	402

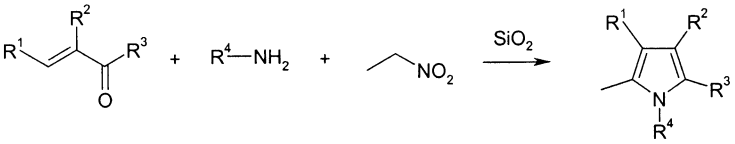
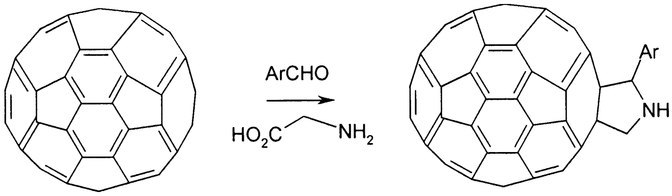
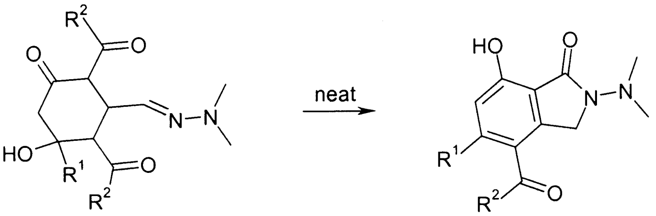
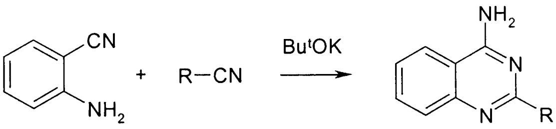
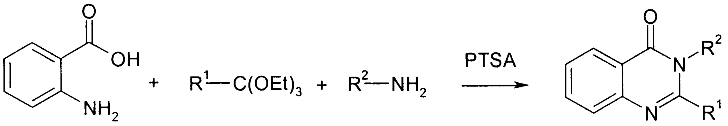
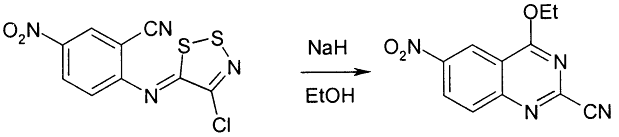
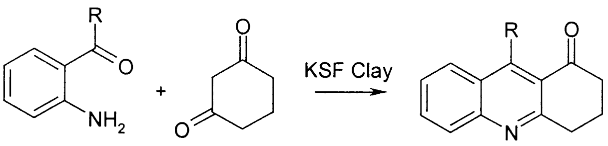
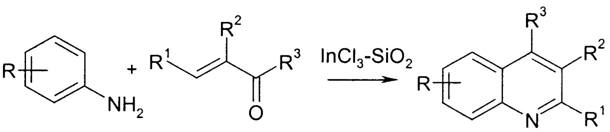
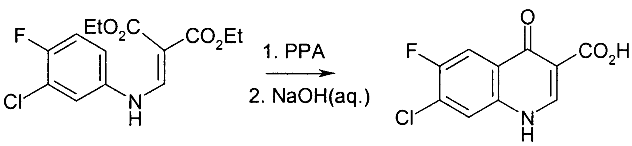
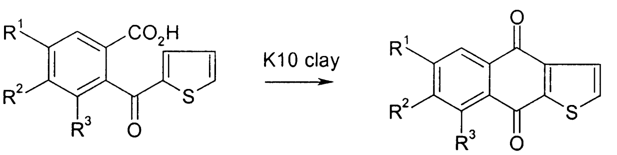
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Phenoxathiin, yield=85% (1 example)	360	
	Piperazine, yields=18–51% (7 examples)	403	
	Pyran, yields=54–87% (3 examples)	136	404
	Pyrazole, yields=67–89% (10 examples)	405	222,225–227,330,329
	Pyridazine, yields=60- 93% (4 examples)	216	406
	Pyridazinedione, yield=84% (1 example)	30	
	Pyridazinone, yields=97–98% (4 examples)	407	408
	Pyridazinedione, yields= 40–87% (9 examples)	409	
	Pyrazole, yields=75–83% (4 examples)	122	35,410
	Pyrazoline, yields=73–88% (11 examples)	411	379
	Pyridine, yields=70% (96 examples)	20	412

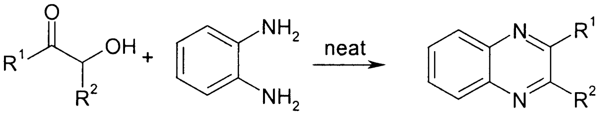
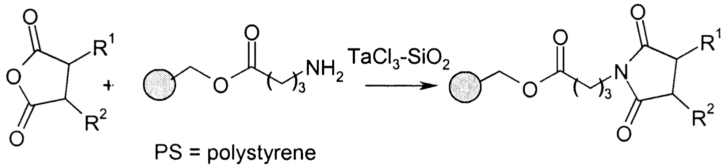
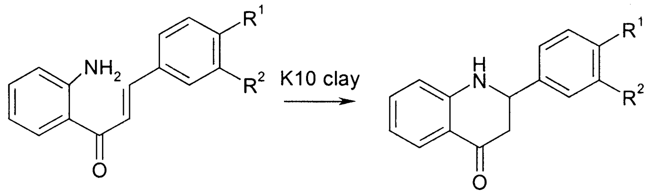
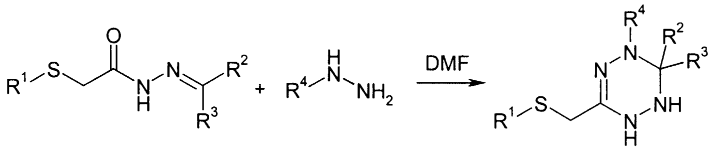
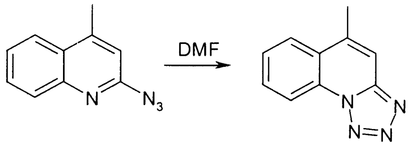
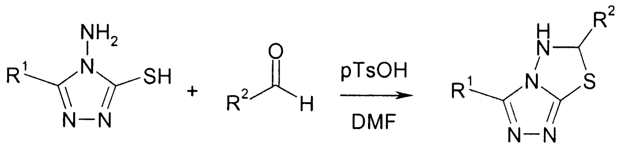
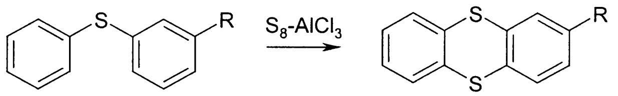
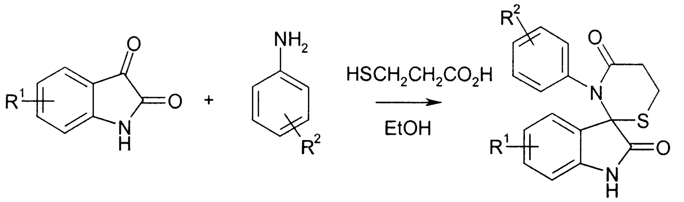
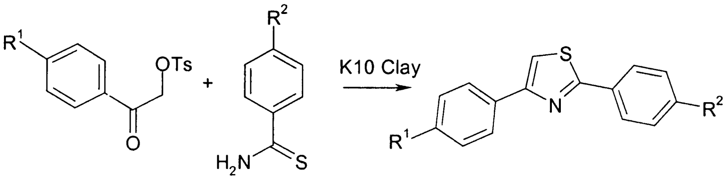
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Pyridines, yields=69–78% (8 examples)	413	
	Pyridine, yields=81–88% (12 examples)	414	
	Pyridine, yields=32–84% (7 examples)	213	214–216
	Pyridinone, yields=quantitative (3 examples)	415	
	Pyrimidine, yield=95% (1 example)	141	
	Pyrimidine, yields=60–92% (5 examples)	416	361,410,417
	Pyrimidinone, yields=65–95% (15 examples)	418	379,419–423
	Pyrimidinone, yields=80–83% (6 examples)	424	425
	Pyrimidinone, yields=52–82% (6 examples)	426	
	Pyrrole, yields=75–90% (8 examples)	427	

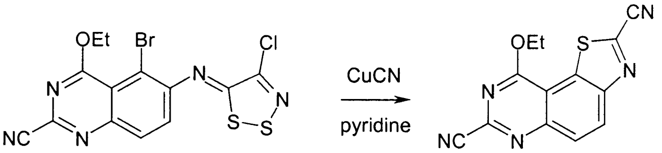
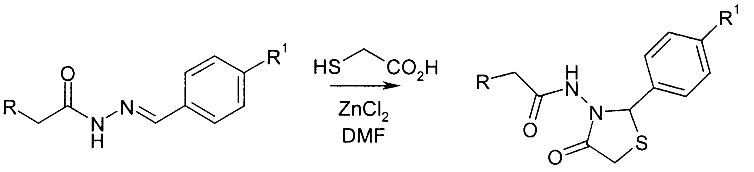
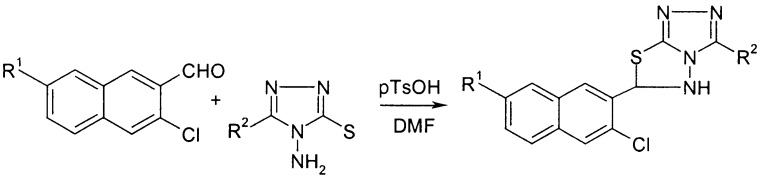
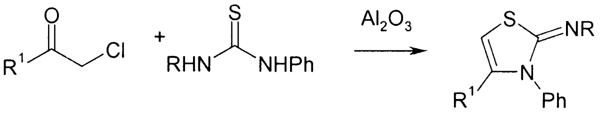
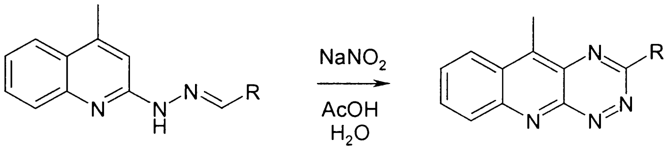
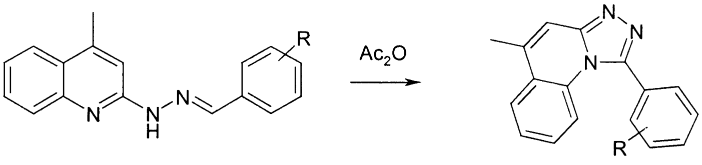
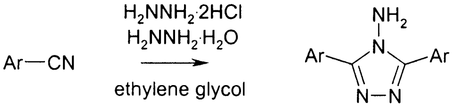
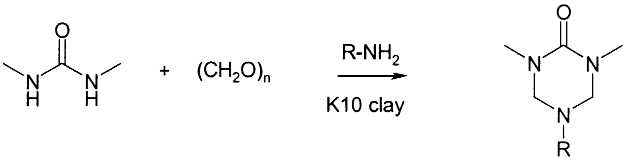
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Pyrrole, yields=60–72% (16 examples)	428	410
	Pyrrolidine, yields=15–37% (3 examples)	245	242,246
	Pyrrolidinone, yields=60–87% (3 examples)	429	
	Quinazoline, yields=73–93% (10 examples)	430	
	Quinazolinone, yields=72–89% (9 examples)	431	432
	Quinazoline, yield=61% (1 example)	433	434,435
	Quinoline, yields=45–72% (10 examples)	436	437
	Quinoline, yields=55–87% (15 examples)	438	
	Quinolone, yield=78% (1 example)	137	321,439
	Quinone, yields=21–92% (5 examples)	440	

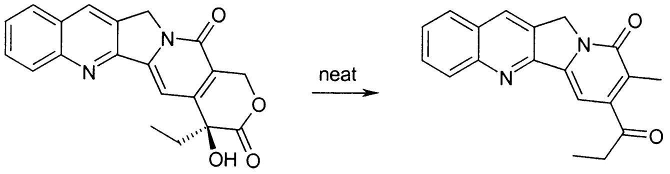
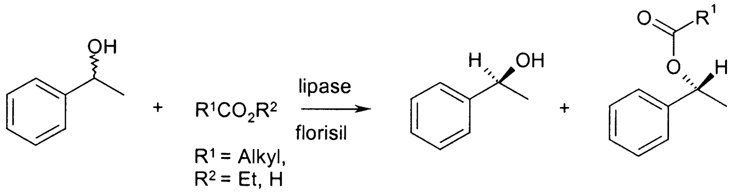
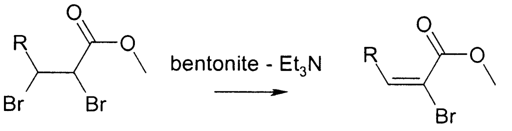
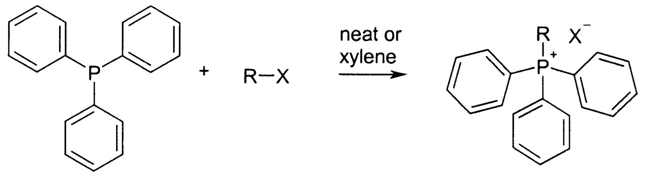
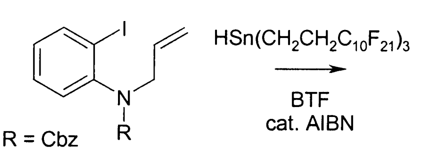
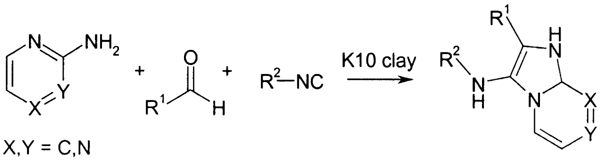
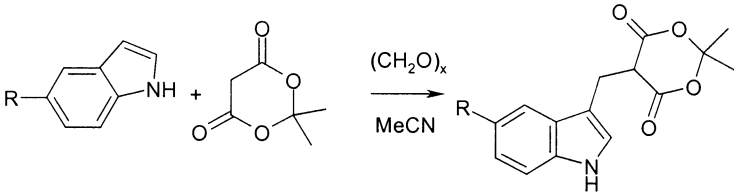
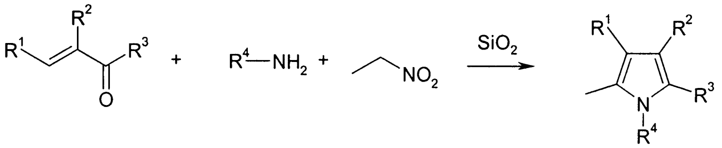
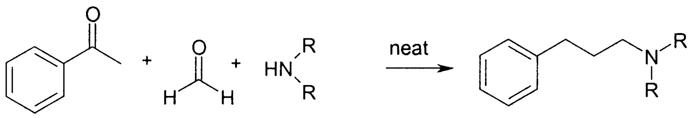
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Quinoxaline, yields=20–93% (8 examples)	441	442,443
	Succinimide, overall yields=60–65%, after cleavage of acid from resin. (3 examples)	444	
	Tetrahydro-, quinolone, yields=70–80% (7 examples)	445	
	Tetrazine, yields=51–65% (10 examples)	30	217
	Tetrazole, yield=73% (1 example)	34	
	1,3,4-Thiadiazole, yields=70–100% (31 examples)	446	447–449
	Thianthrene, yield=95% (1 example)	360	
	Thiazinone, yields=62–84% (5 examples)	450	451
	Thiazole, yields=85–96% (14 examples)	336	452

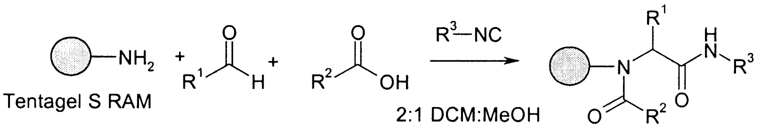
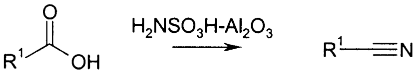
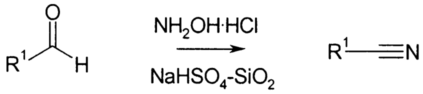
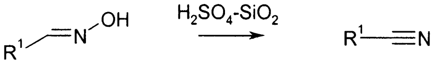
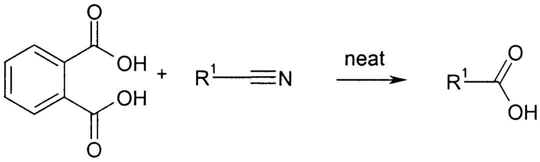
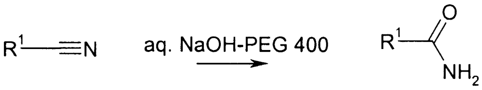
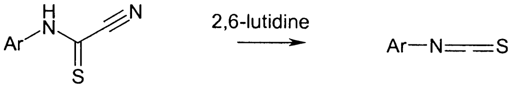
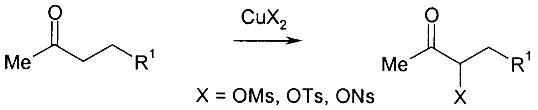
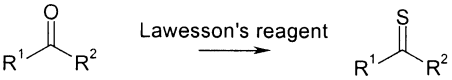
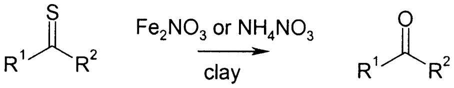
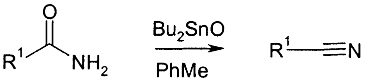
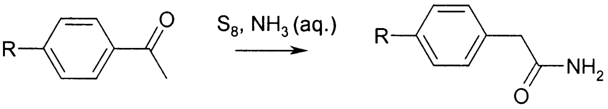
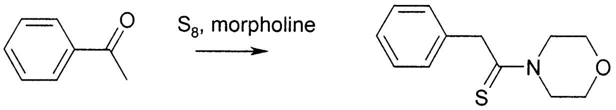
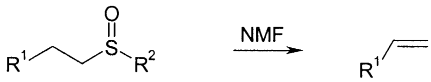
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Thiazole, yield=53% (1 example)	433	
	Thiazolidinone, yields=59–70% (4 examples)	122	453
	Thiazolidinone, yields=59–70% (4 examples)	444	
	Iminothiazoline, yields=77–98% (12 examples)	454	30
	1,2,4-Triazine, yields=68–88% (6 examples)	455	104,122,456
	1,2,4-Triazole, yields=84–92% (8 examples)	34	241
	1,2,4-Triazole, yields=61–97% (4 examples)	457	
	Triazone, yields=71–84% (6 examples)	458	

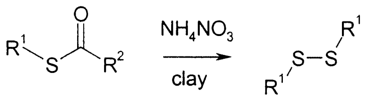
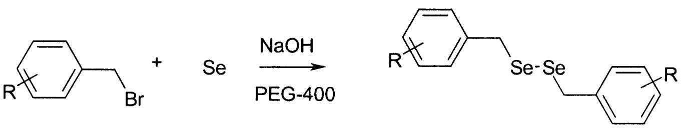
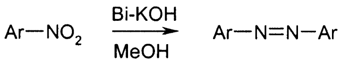
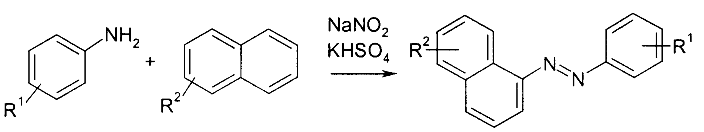
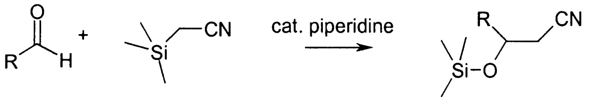
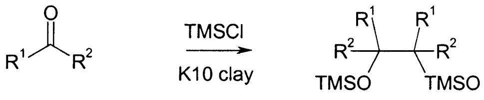
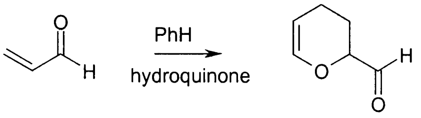
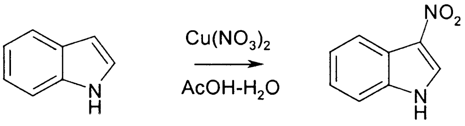
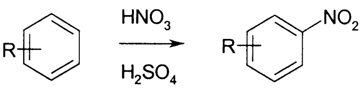
5.10. Miscellaneous

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Decarboxylation, yield=96% (1 example)	459	460
	Enzymatic resolution, yields=36–52% ee=32–100% (5 examples)	461	462
	Elimination of HBr, yields=100% *E*/*Z*=55/45 (4 examples)	463	464
	Phosphonium salt formation, yields=83–99% (7 examples)	465	
	Radical intramolecular cyclization reaction, yield=93% (1 example)	52	
	Three-component reaction, yields=56–88% (14 examples)	466	
	Three-component reaction, yields=15–63% (5 examples)	467	
	Pyrrole three-component reaction, yields=60–72% (16 examples)	428	
	Mannich three-component reaction, yields=60–83% (12 examples)	468	

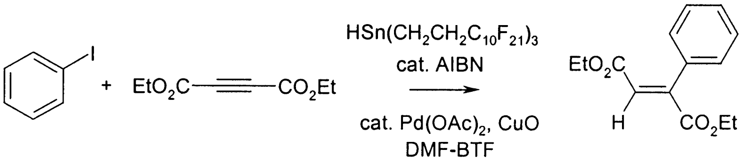
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Ugi four-component condensation, yields=24–96% (18 examples)	469	
	Conversion of carboxylic acids to nitriles, yields=20–93% (20 examples)	470	
	Conversion of aldehydes to nitriles, yields=80–97% (11 examples)	471	472–474
	Conversion of aldoximes to nitriles, yields=64–91% (12 examples)	475	476
	Conversion of nitriles to carboxylic acids, yields=64–91% (8 examples)	477	478
	Conversion of nitriles to amides, yields=21–91% (14 examples)	479	
	Conversion of thioanilides to isothiocyanates, yields=54 and 57% (2 examples)	480	
	Sulfonyloxylation, yields=55–80% (18 examples)	481	
	Conversion of carbonyls to thiocarbonyls, yields=76–97% (27 examples)	482	
	Conversion of thiocarbonyls to carbonyls, yields=88–95% (8 examples)	483	
	Conversion of amides to nitriles, yields=80–95% (12 examples)	484	
	Willgerodt reaction, yields=61–72% (4 examples)	485	
	Willgerodt–Kindler reaction, yields=40–81% (8 examples)	486	
	Dehydro-, sulfenylation, yields=80–99% (12 examples)	487	

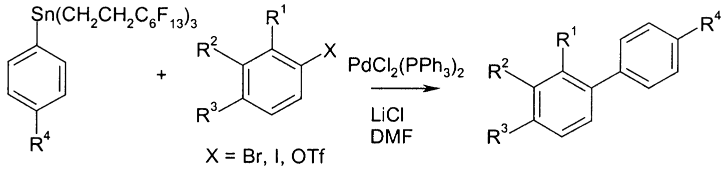
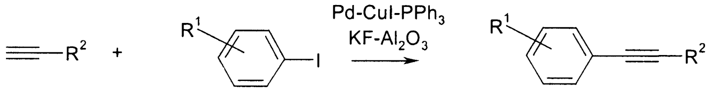
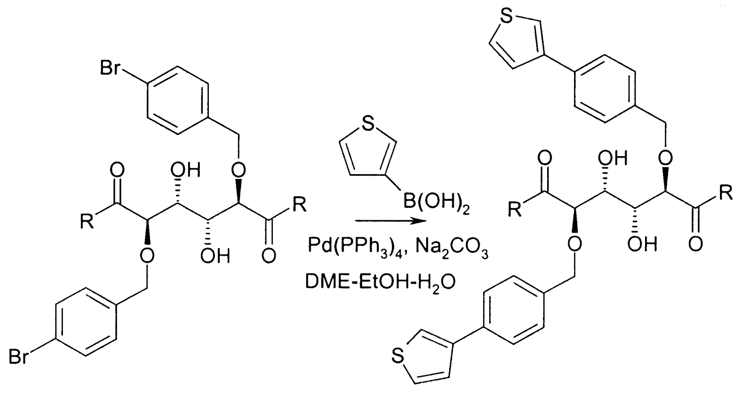
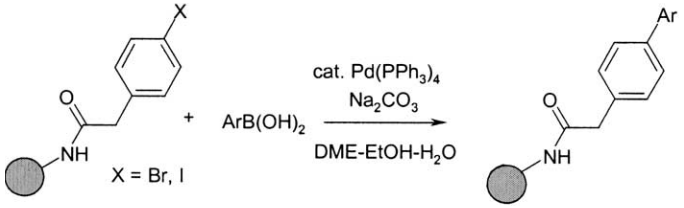
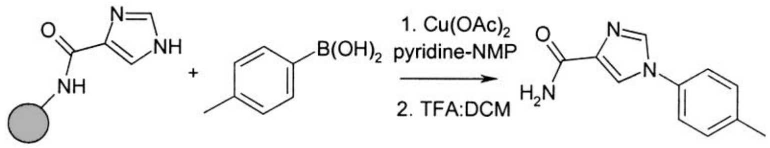
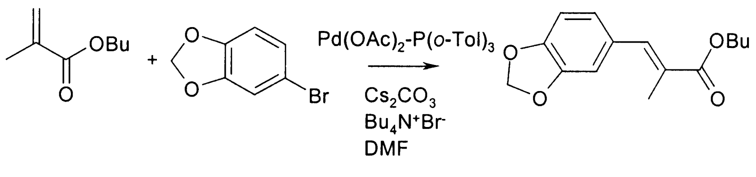
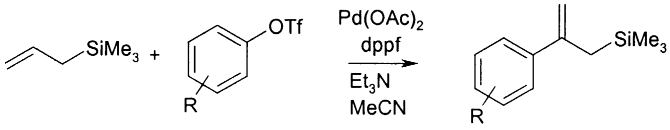
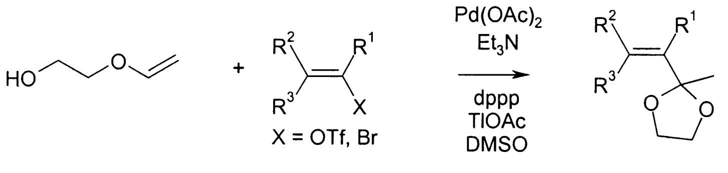
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Disulfide formation, yields=57–98% (13 examples)	488	489
	Diselenide formation, yields=72–91% (8 examples)	490	491
	Azo formation, yields=60–85% (12 examples)	492	
	Azo formation, yields=60–100% (6 examples)	493	
	β-Trimethylsiloxy nitriles, yields=38–67% (5 examples)	494	
	Bis-(trimethylsilyl) pinacols, yields=56–90% (8 examples)	495	
	Dimerization, yield=91% (1 example)	496	
	Nitration, yields=50–92% (6 examples)	497	
	Nitration, yields=57–89% (6 examples)	311	

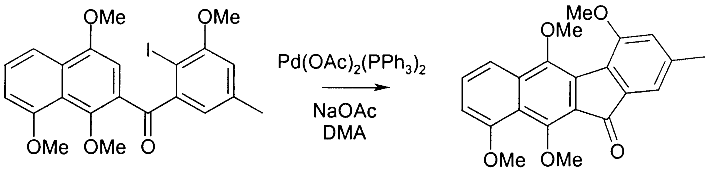
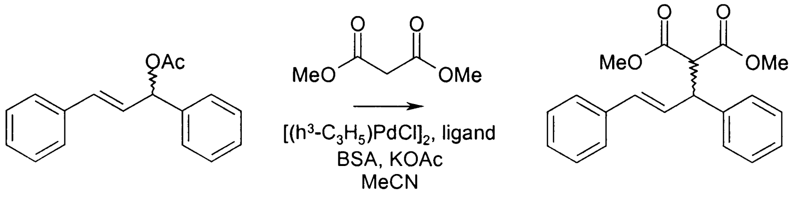
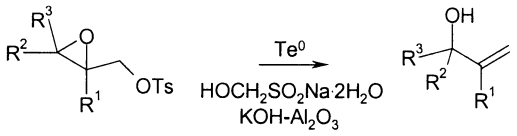
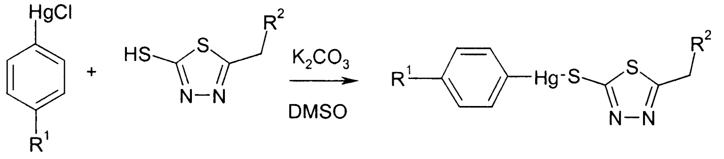
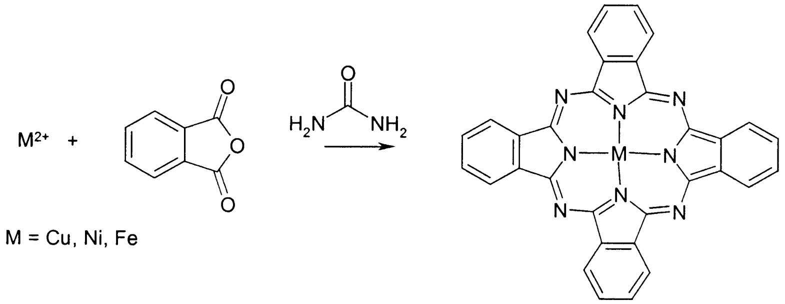
5.11. Organometallic reactions

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Hydrostannylation and vinylic Stille coupling *E*/*Z*=5:1, yield=77% (1 example)	52	

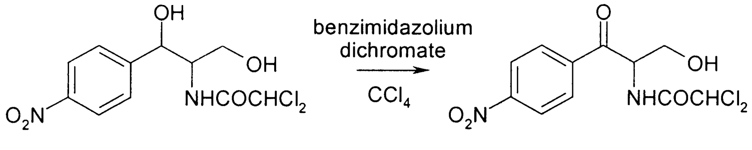
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Stille coupling, yields=49–96% (16 examples)	498	52,501
	Sonogashira coupling, yields=67–97% (12 examples)	499	
	Suzuki coupling, yields= 38–96% (9 examples)	500	106,501,502
	Suzuki coupling, yields=84–99%, after cleavage of amide from resin (14 examples)	503	504
	Copper-mediated C–N cross coupling, yields=55–64% (4 examples)	505	
	Heck reaction, yields=25–89% (6 examples)	106	501,506,507
	Internal Heck reaction, yields=28–69% (8 examples)	508	
	Heck vinylation, yields= 45–89% (8 examples)	509	

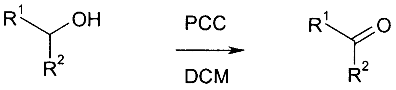
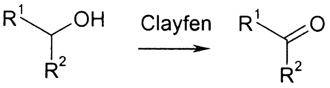
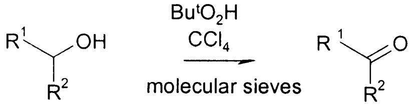
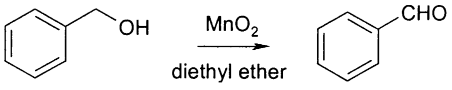
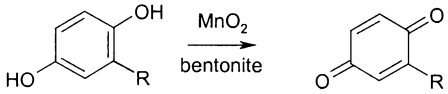
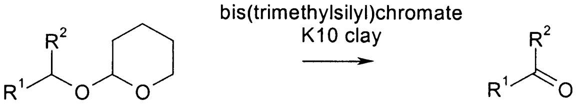
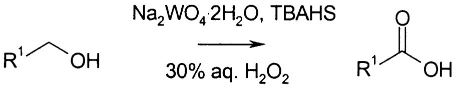
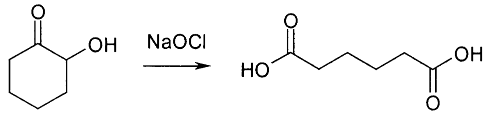
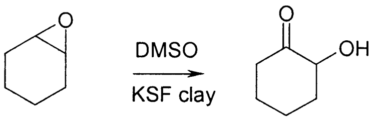
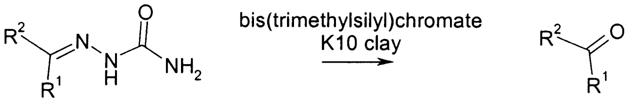
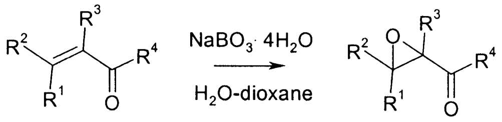
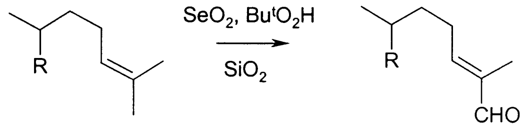
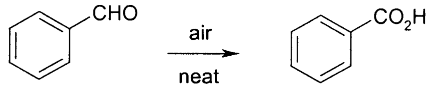
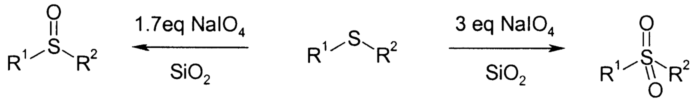
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Intramolecular Heck reaction, yield=53% (1 example)	510	
	Asymmetric alkylation, yields=96 and 99% ee=65–85% (2 examples)	511	512,513
	Nucleophilic reduction, yields=50 and 83% (2 examples)	514	
$M(CO)_6 \xrightarrow[\text{diglyme}]{L} ML(CO)_4$ L = bipy, en, dppm or dppe	Cyclometallation, yields=55–99% (12 examples)	515	516
	Organomercurials, yields=68–88% (12 examples)	517	518–520
	Metallophthalo-cyanines, yields=86–91% (4 examples)	521	522

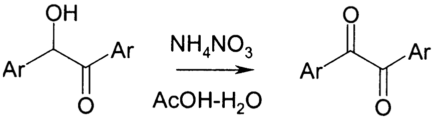
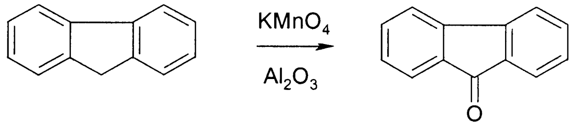
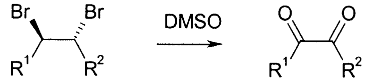
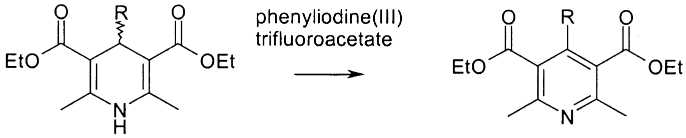
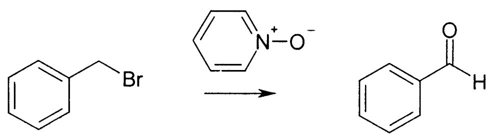
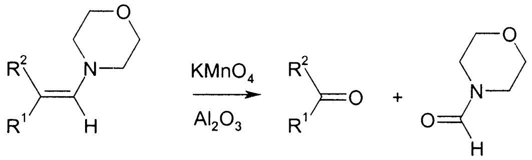
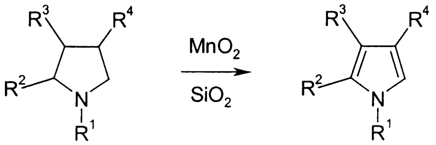
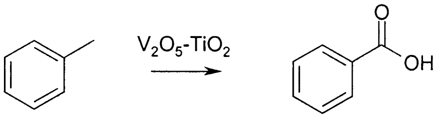
5.12. Oxidation

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Oxidation of benzylic and allylic alcohols, yields=73–97% (12 examples)	523	524,525

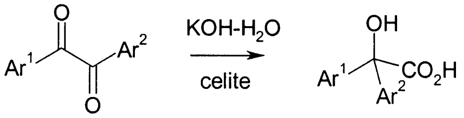
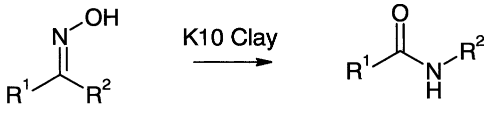
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Oxidation of primary and secondary alcohols, yields=70–99% (14 examples)	526	527–529
	Oxidation of primary and secondary alcohols, yields=87–96% (8 examples)	530	531–534
	Oxidation of secondary and benzylic alcohols, yields=18–97% (7 examples)	535	
	Oxidation, yields=52–82% (3 examples)	323	536–538
	Oxidation, yields=30–100% (5 examples)	539	
	Oxidative deprotection, yields=75–92% (10 examples)	527	
	Oxidation of primary alcohols, yield=60–84% (4 examples)	540	
	Oxidation of α-substituted carbonyl groups, yields=65–92% (9 examples)	541	
	Oxidation of epoxides, yields=55–90% (6 examples)	542	
	Oxidative deprotection, yields=62–96% (11 examples)	543	
	Epoxidation, yields=73–93% (6 examples)	544	545
	Oxidation of allylic methyl groups, yields=68–85% (6 examples)	546	547
	Oxidation of aromatic aldehydes, yields=58–81% (12 examples)	548	
	Oxidation of sulfides, yields=72–93% (16 examples)	549	550,551

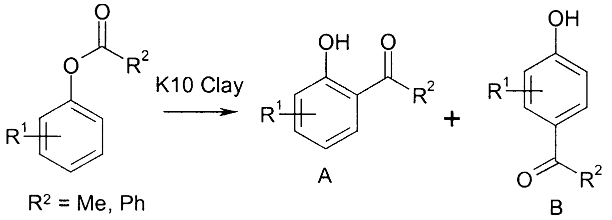
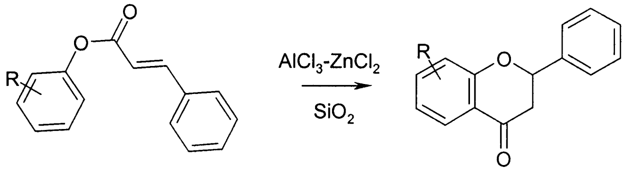
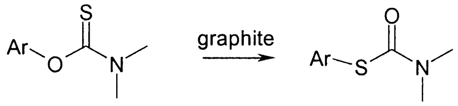
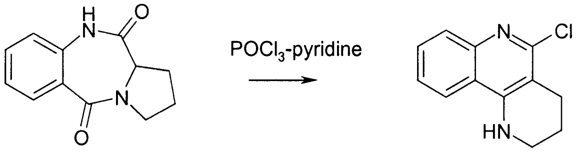
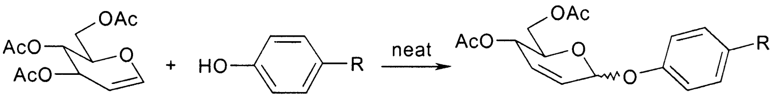
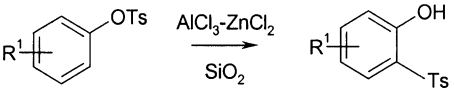
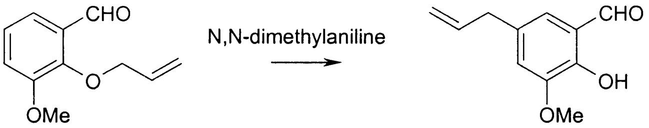
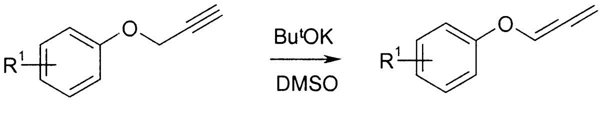
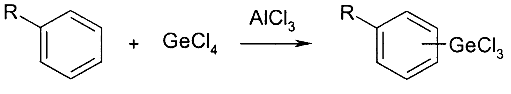
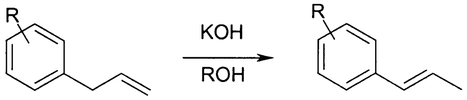
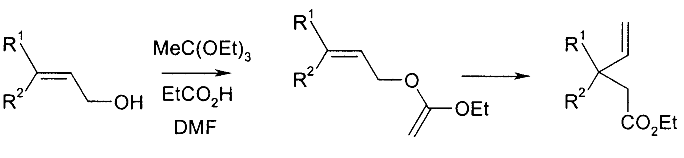
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Oxidation of hydroxyketones, yields=78–94% (15 examples)	552	553
	Oxidation of arenes, yields=70–100% (5 examples)	554	
	Oxidation of 1,2-dibromides, yields=51–75% (8 examples)	555	
	Oxidation of 1,4-dihydropyridines, yields=68–90% (9 examples)	556	
	Oxidation of benzylic bromides to aldehydes, yields=15–92% (6 examples)	557	
	Oxidative cleavage of substituted enamines, yields=11–83% (3 examples)	558	
	Dehydrogenation of pyrrolidines, yields=58–96% (10 examples)	559	
	Oxidation of toluene, yield=51% (1 example)	560	

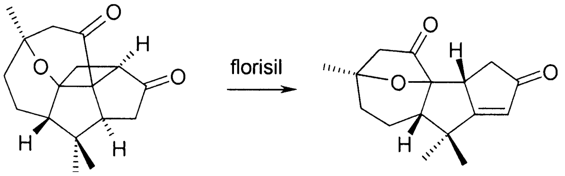
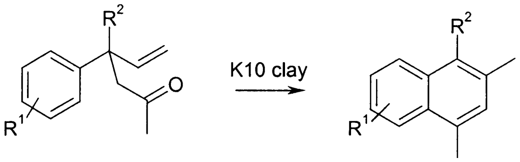
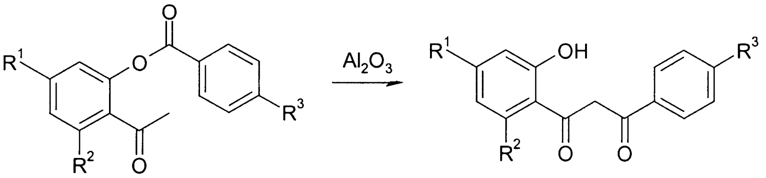
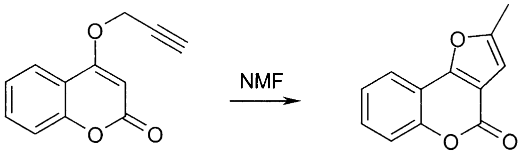
5.13. Rearrangement

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Benzil-benzilic acid rearrangement, yields=56–98% (5 examples)	561	
 R^1 = Me, Ph, Cycloalkyl R^2 = Ar, Cycloalkyl	Beckmann rearrangement, yields=21–96% (6 examples)	562	563

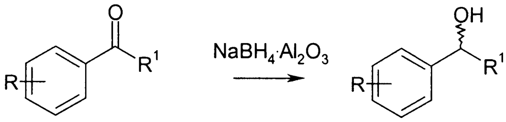
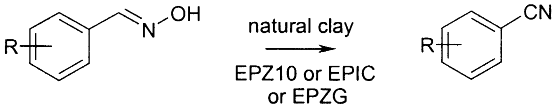
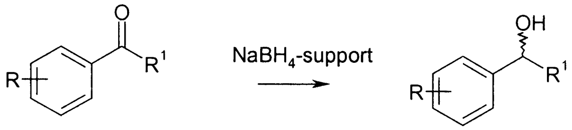
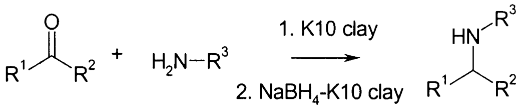
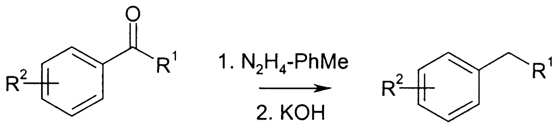
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Fries rearrangement Mixture of *ortho*-(A) and *para*-(B) products. A usually major product, yields=50–97% (13 examples)	564	565–567
	Fries rearrangement, yields=73–87% (4 examples)	566	
	Rearrangement of *O*-aryl *N*,*N*-dimethyl-thiocarbamates, yields=30–90% (5 examples)	568	
	Rearrangement of benzodiazepine-diones, yields=28–53% (6 examples)	569	570,571
	Ferrier rearrangement, yields=72–83% (7 examples)	572	
	Thia-Fries rearrangement of arylsulfonates, yields=67–92% (8 examples)	573	
	Rearrangement, yield=65% (1 example)	574	
	Isomerisation of propargyl ethers into allenyl ethers, yields=74–92% (10 examples)	575	
	Syntheses of alkyl- or aryl-halogermanes, yields=80–95% (5 examples)	576	
	Isomerization of safrole and eugenol, yields=98 and 99% (2 examples)	577	
	Ortho ester Claisen rearrangement, yields=60–92% (11 examples)	578	391,392,579

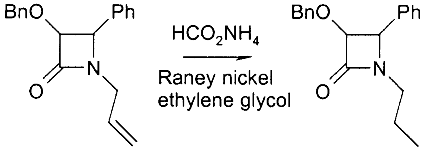
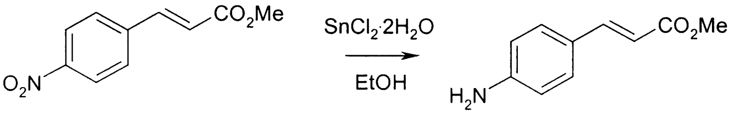
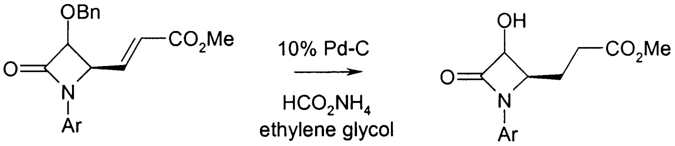
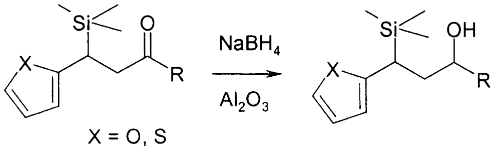
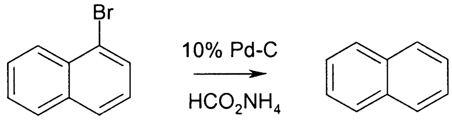
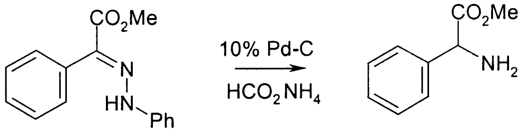
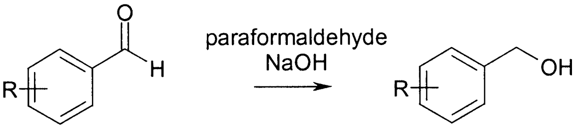
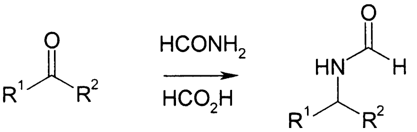
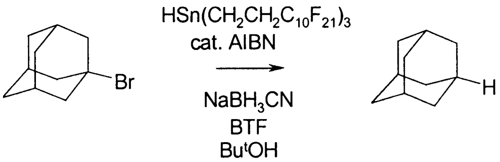
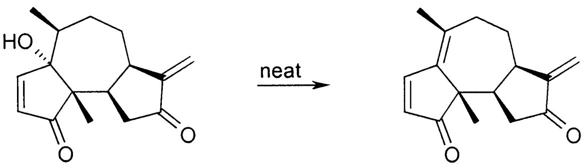
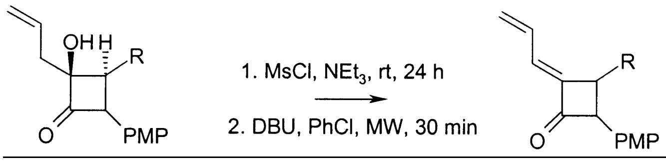
(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Thermal rearrangment with the use of florisil, yield=93% (1 example)	580	
	Thermal rearrangement, yields=45–69% (9 examples)	581	
	Rearrangement of *o*-aryloxyaceto-phenones, yields=50–66% (4 examples)	51	
	Rearrangement of hydroxy coumarin propargyl ethers, yields=62–82% (8 examples)	582	

5.14. Reduction

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Reduction of aldehydes and ketones, yields=62–93% (9 examples)	583	584,585
	Reduction of aldoximes to nitriles, yields=52–95% (21 examples)	586	
	Reduction of ketones, yields=81–98% (10 examples)	587	588
	Reductive amination, yields=78–97% (24 examples)	589	
	Wolff–Kishner reduction, yields=75–97% (12 examples)	590	591

(*continued*)

Conditions	Type of reaction/yields/number of examples	Reference	
		Described	Additional
	Allyl reduction, yields∼80% (5 examples)	592	553,593
	Reduction of nitrogroups, yields=55–99% (8 examples)	106	
	Reduction of unsaturated esters, yields=80 and 90% (2 examples)	594	
	Reduction of β-trimethylsilyl carbonyls, yields=60–100% (6 examples)	595	
	Dehalogenation, no yields quoted (10 examples)	594	
	Imine reduction, yield=90% (1 example)	594	
	Cross-Cannizzaro reaction, yields=85–95% (11 examples)	596	597,598
	Leuckart reductive amination, yields=91–99% (5 examples)	599	600
	Radical reduction reaction, yield=81% (1 example)	52	
	Dehydration, yield=68% (1 example)	601	602
	Dehydration, yields=79–96% (4 examples)	603	

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Biographical sketch

Pelle Lidström, received his PhD in radiopharmaceutical organic chemistry from Uppsala University in 1997 where he worked with the synthesis of positron emitting radiotracers for applications in positron emission tomography together with Professor Bengt Långström. He then joined Pharmacia and Upjohn where he worked both with radiopharmaceutical and medicinal chemistry. Since 1999 he has been working at Personal Chemistry as a research scientist.

Jason Tierney, Between November 1995 and June 1997, Jason Tierney studied with Professor Alex Alexakis at the Universite Pierre et Marie Curie as a CNRS research associate in the area of asymmetric synthesis. Prior to this, he studied with Professor Donald Craig for a PhD at Imperial College, London on the synthesis of C-glycosides. He also graduated from Imperial College, London in 1992. Jason joined Organon Research (pharmaceutical division of Akzo Nobel) in July 1997, as a medicinal chemist synthesizing focussed libraries for in-house CNS targeted projects. In September 1998, he became a Senior Scientist within the Combinatorial Chemistry (CC) team of the Lead Discovery Unit at Newhouse synthesizing larger lead finding libraries. He became responsible for CC automation and the implementation of associated technologies within the CC team. Currently, he is the Senior Chemist of a Hit Optimisation (HO) project within Lead Discovery. In Lead Discovery, Jason implements parallel synthesis, automation and associated technologies including microwave assisted synthesis for the generation of Lead candidates.

Bernard Wathey, was born in Leeds and read Industrial Chemistry at the University of Wales, Cardiff. After studying for a PhD in Medicinal Chemistry he undertook a post doctoral research project at the University of Bath. He has several years experience in Medicinal and Combinatorial Chemistry with both Novartis and Organon. He is presently Head of High-Throughput Chemistry at BioFocus.

Jacob Westman, was born 1966 in Stockholm, Sweden. He received his MSc in Mathematics and Chemistry from the Stockholm University in 1990. He then joined Kabi AB (later Pharmacia and Upjohn) as an industrial PhD student and he received his PhD degree in 1995 in the area of oligosaccharide synthesis of Heparin analogous in an angiogenes modulation project. After his PhD degree he took part of the build-up of the combinatorial chemistry department at Pharmacia and Upjohn and later took a position as a group leader in the Department of Medicinal Chemistry. In early 1999 he took a position as senior scientist at Personal Chemistry AB.