REVIEW

Compendium of Cycloaddition Reactions under High Pressure

by **Kiyoshi Matsumoto***, **Hiroshi Hamana**, and **Hirokazu Iida***

Faculty of Pharmaceutical Sciences, Chiba Institute of Science, Choshi, Chiba, 288-0025, Japan
(e-mail: kmatsumoto@cis.ac.jp; hiida@cis.ac.jp)

Dedicated to Professor Emeritus *Rolf Huisgen*, University of Munich, on the occasion of his 85th birthday and life-long career in organic chemistry[1])

High-pressure technology finds its major application in the field of organic synthesis, especially for cycloaddition reactions. The aim of this article is to review all examples of high-pressure strategies in cycloaddition and related reactions, to describe the scope and limitations of this technique, and to suggest some further possibilities.

1. Introduction. – Human beings with their exceptional capabilities grasp a global world that goes beyond the naturally delimited domain, and understand changes in the natural environment with time. The desire of man for a higher material standard of living has especially developed science and technology in the last half century. It has resulted in population explosion and a scale of industrialization that has placed great strains on the biosphere. The result of such an intractable situation is the exhaustion of natural resources. The devastation of a local resource leads eventually to the pollution of the environment on a global scale. Environmental pollution holds risks not only for life on this planet, but also for our species. Therefore, the relationships between the natural environment and modern science must be understood more exactly to solve these problems that arise by negative feedback. Mankind's technology must be on a substantial scale, so that we all benefit from a fully functioning natural environment. The natural environment can be divided into the categories water, air, and land, and the organisms in each category. High pressure, the phenomenon that is a feature of this study, is encountered, *e.g.*, in the deep sea, inside the Earth, and on other planets [2][3]; and it is likely to have been an agent in the geochemical conditions that formed coal and oil deposits (*Fig. 1*).

It is interesting to investigate the change of molecules at high pressure, because pressure affects the molecular environment. When covalent-bond formation takes place, it is simply assumed that one molecule collides with another molecule. But it has been clarified that solvent, concentration, temperature, and pressure strongly affect reactions.

The use of extreme conditions such as ultra-high pressure in material sciences and industry has led to the successful preparation of synthetic diamond, ruby, and borazone

[1]) For his biography and research history, see [1].

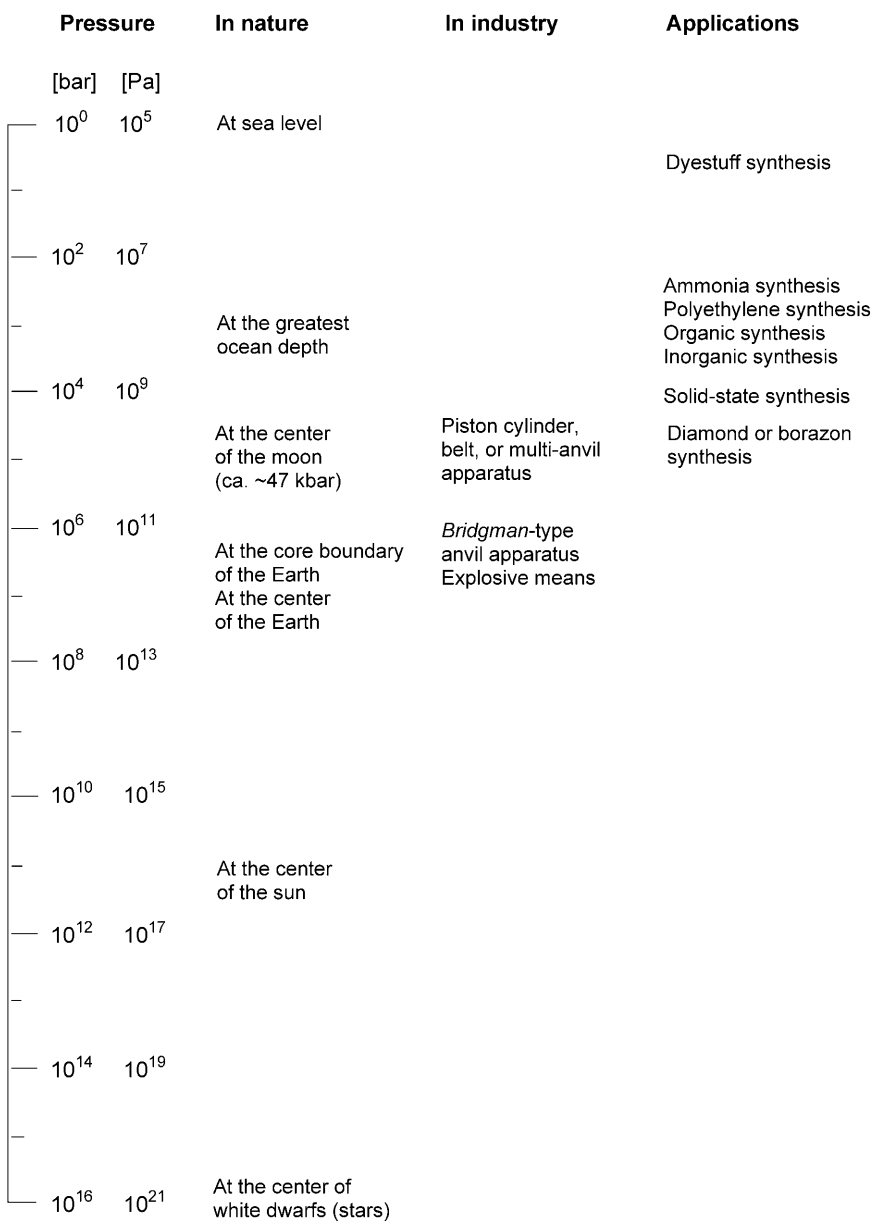


Fig. 1. *Pressure Scale and Technical Applications of High Pressure*

as early as in the 1950s [4][5]. Around 1980, high-pressure apparatus such as autoclaves became popular. But until then, the versatility of high pressure in organic synthesis has not been widely explored, in spite of its potential [2][6–13]. Of the many parameters that can be changed to improve the efficiency of synthetic transformations, most

attention has been paid to the study of electronic and steric effects by chemical modification of substrates and reagents, to thermal and photochemical effects, to the use of catalysts such as *Lewis* acids and bases, or phase-transfer reagents, to sonochemistry, microwave techniques [14][15], flash vacuum pyrolysis and other thermal processes, electro-organic transformations, reactions with solid-supported reagents and catalysts [16][17], as well as solvent-free organic synthesis [18]. Supercritical fluids have also been used, and this can often be an alternative to organic solvents under high pressure [19][20]. Much interest has been generated in high-pressure methodology, since it has been demonstrated that high pressure is not only useful in effecting cycloaddition reactions, but also several kinds of ionic reactions [21].

The aim of the present article is to review all examples of the use of high-pressure procedures in cycloaddition reactions and some related reactions, particularly focusing on synthetic applications, to describe the scope and limitations of this technique, and to suggest some further possibilities[2]). There are some monographs and reviews on chemical reactions at high pressure, especially covering the earlier literature of the past decade [22–34]. Furthermore, several kinds of monographs [6] and reviews [2][7–13] on high-pressure organic reactions have been published by *Matsumoto* and co-workers; and there is a recent review by *Klärner* and *Wurche* [25], and a monograph by *van Eldik* and *Klärner* [33], both of which cover recent progress in high-pressure organic synthesis up to the first half of 2000. Therefore, the present article covers only representative and the most-recent examples, more-detailed information up to *ca.* 2004 being summarized in the *Appendix*.

2. General Principles. – Present-day methods of organic synthesis are mostly based on chemical modification of reagents and catalysts. Nevertheless, frequent use has recently been made of 'distinctive' techniques such as ultrasound, flash-vacuum pyrolysis, electro-organic, microwave, supercritical, solvent-free (or solid-state), as well as even plasma conditions. The high-pressure technique is one of the most-developed unconventional tools for the preparation of both new and known compounds. Chemical reactions at high pressure require conditions characterized by high number densities of the reacting particles, so that very intense intermolecular interactions take place. In terms of the potential energy of interaction as a function of the distance between reacting molecules or atoms, the repulsive part of the relationship is mainly discussed. At lower number densities, interactions of this type take place only at higher temperature, but within a limited time interval determined by the impact parameters. At higher pressure, the duration of these strong interactions is much longer. This phenomenon may lead to a considerable increase in reaction rate (*Scheme 1*).

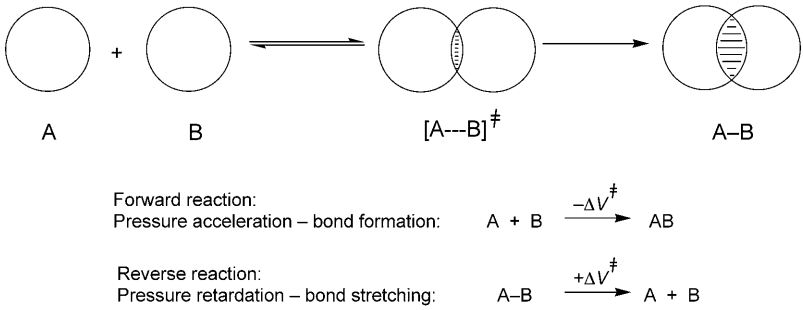
The fundamental equation (*Eqn. 1*) for the effect of (high) pressure on the rate constant of a reaction was deduced by *Evans* and *Polanyi* based on transition-state theory:

$$(\partial \ln k/\partial P)_T = -\Delta V^{\neq}/RT = -(V^{\neq} - V_r)/RT \quad (1)$$

---

[2]) For the sake of clarity, detailed literature data and examples are collected separately in the *Appendix*, whereas more-general aspects and selected examples are discussed in the main text.

Scheme 1. *High-Pressure Effects on Organic Reactions*



where $\Delta V^{\neq}$ is the so-called 'volume of activation', which corresponds to the difference between the volume of the activated complex ($V^{\neq}$), including the corresponding molecule(s) of its solvation shell, and the volume V_r of the reactant molecules (with their associated solvent molecule(s)), measured at constant pressure (P) and temperature (T) [35]. In *Fig. 2*, this principle is exemplified for a *Diels–Alder* reaction as one of the simplest cases.

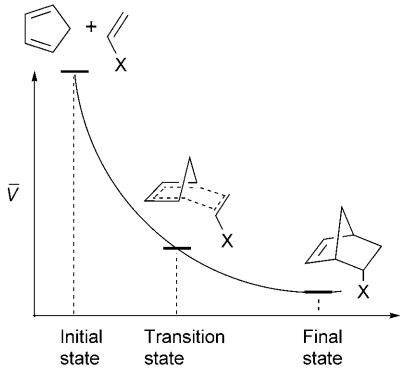


Fig. 2. *Mechanism and volume profile of the* Diels–Alder *reaction*

In general, bond formation, concentration of charge, and ionization during the transition state lead to a *negative* volume of activation, whereas bond cleavage, charge dispersal, neutralization in the transition state, and diffusion control lead to a positive activation volume. For reactions in which the polarity of the transition state changes, the influence of the solvent on $\Delta V^{\neq}$ is of importance. Thus, those types of organic reactions in which rate enhancement is expected on application of pressure may be summarized, as a preparative or synthetic guide, as follows [2a][36]:

- Reactions in which the molecularity decreases in the products (*e.g.*, cycloadditions or condensations)
- Reactions that proceed *via* cyclic transition states (*e.g.*, *Claisen* and *Cope* rearrangements)

- Reactions that take place through dipolar transition states (*e.g.*, *Menshutkin* reactions or electrophilic aromatic substitutions)
- Kinetically hindered reactions that either do not take place or give rise to low yields due to steric hindrance in the transition state.

As described above, the activation volume $\Delta V^{\neq}$ is the difference in partial molar volume between the transition state and the initial state. From a synthetic point of view, this can be often approximated by the difference in the molar volumes of the reactant(s) and product(s). Partial molar activation volumes, which can be divided into a structural and a solvent-dependent term, are of considerable value in speculating about the nature of the transition state. This thermodynamic property has led to many studies on the mechanisms of organic reactions. Thus, from *Eqn. 1*, the application of pressure accelerates reactions that have a negative volume of activation.

In *Table 1*, the effect of pressure on reaction rate is shown for different (negative) $\Delta V^{\neq}$ values. The system does not strictly obey the ideal rate equation for $P > 1$ GPa, since the activation volume itself is somewhat pressure-dependent. Thus, the values of $\Delta V^{\neq}$ generally decrease with increasing pressure. Innumerable data on $\Delta V^{\neq}$ values are now available [37][38]. And in case that $\Delta V^{\neq}$ is not available for a reaction type of interest, activation entropies ($\Delta S^{\neq}$) may serve as a guide, since a linear relationship between $\Delta V^{\neq}$ and $\Delta S^{\neq}$ has been reported for a variety of reactions [39][40].

Table 1. *Variation of Rate Constant with Pressure for Different Activation Volumes* ($\Delta V^{\neq}$) *and Temperatures* (T). The term k_P/k_0 corresponds to the ratio of the rate constant at pressure P *vs.* atmospheric pressure (k_0). In parentheses, $\Delta\Delta G^{\neq}$ [kJ/mol]

$\Delta V^{\neq}$ [cm³/mol]	T [°]	k_P/k_0					
		0.5 GPa	1.0 GPa	1.5 GPa	2.0 GPa	3.0 GPa	5.0 GPa
– 10	25	7.5	57	430	3200	1.8×10^5	7.5×10^8
	50	6.4	41	270	1700	7.1×10^5	1.5×10^8
	100	5.0	25	130	630	1.6×10^4	1.2×10^7
		(– 5)	(– 10)	(– 15)	(– 20)	(– 30)	(– 50)
– 20	25	57	3200	1.8×10^5	1.0×10^7	3.3×10^{10}	5.6×10^{17}
	50	41	1700	7.1×10^4	2.9×10^6	5.0×10^9	2.4×10^{16}
	100	25	630	1.6×10^4	4.0×10^5	2.5×10^8	1.5×10^{14}
		(– 10)	(– 20)	(– 30)	(– 40)	(– 50)	(– 60)
– 30	25	430	1.8×10^5	7.7×10^7	3.3×10^{10}	6.0×10^{15}	4.2×10^{26}
	50	270	7.1×10^4	1.9×10^7	5.0×10^9	3.6×10^{14}	3.7×10^{24}
	100	130	1.6×10^4	2.0×10^6	2.5×10^8	4.0×10^{12}	1.9×10^{21}
		(– 15)	(– 30)	(– 45)	(– 60)	(– 90)	(– 150)

The following pressure units are commonly being used: 1 kbar = 100 MPa = 1000 kg/cm² = 1000 atm = 7.5×10^5 mmHg (see *Table 2*). Note that the differences between these units can be ignored, as long as qualitative aspects are under discussion. This is mostly the case in high-pressure synthetic chemistry or preparations under pressure. In the *Système International d'Unités* (*SI* units) adopted by the *Conférence Générale des Poids et Mesures*, and endorsed by the *International Organization for Standardization*, the unit of force (F) is Newton [N = kg m s^{-1}]. The *SI* unit of pressure P is Newton per square meter (N m^{-2}), which is called Pascal [Pa], 10^5 Pa being 1 bar,

Table 2. *Common Pressure Units*

	kbar	MPa	kg/cm^2	atm	mmHg
1 kbar	1	100	1019.7	986.92	7.5006×10^5
1 MPa	0.01	1	10.197	9.8692	7.5006×10^3
1 kg/cm^2	9.8067×10^{-4}	9.8067×10^{-2}	1	0.9678	735.6
1 atm	1.0132×10^{-3}	1.0132×10^{-1}	1.0132	1	760.0
1 mmHg	1.333×10^{-6}	1.333×10^{-4}	1.3595×10^{-3}	1.3158×10^{-3}	1

which, in turn, corresponds to *ca*. 0.987 atm (*Table 2*). Thus, in this chapter, we will use Pa as pressure unit as an approximate to other units [21].

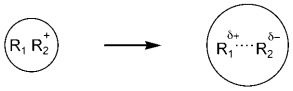
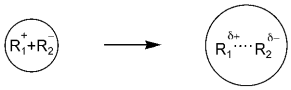
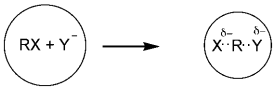
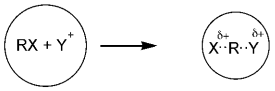
Before performing high-pressure experiments, it would be desirable to have knowledge of the effects of pressure on various physical properties of the solvent, such as freezing temperature, density, viscosity, solubility, compressibility, dielectric constant, and conductivity. Unfortunately, sufficient data on all these properties are often unavailable. The importance of the solvent in determining the effects of pressure on reaction rates has been recognized in general terms for a long time [41], but the first satisfactory discussion was given by *Buchanan* and *Hamann* only in 1953 [23]. A schematic compilation of pressure and solvent effects on reactions of different charge types, established by *Dack*, is given in *Table 3*, which also includes solvent-polarity effects on the activation volume.

Less-polar solvents have higher compressibilities and are, therefore, more constricted by ionic or dipolar solutes than more-polar solvents, which exhibit smaller compressibilities owing to stronger intermolecular interactions. An example of a conversion of *Type 2* (*Table 3*) is the *Diels–Alder* reaction (see also *Fig. 2* above). In agreement with an isopolar cyclic activated complex being intrinsically smaller than the reactants, $\Delta V^{\neq}$ is strongly negative. In reactions of *Type 3*, charge creation on the reacting species increases the intermolecular electrostatic forces between the solute and the permanent or induced dipoles in the solvating molecules. This leads to a volume reduction of the solvate complex, a process called 'electrostriction'. Corresponding to *Type 5*, increasing pressure leads to an increase in reaction rate, which is more pronounced in less-polar solvents, and clearly demonstrates that nonpolar solvents undergo more electrostriction than polar media. In general, effects of solvent polarity and high pressure can be used to draw conclusions about whether the activated complex is more dipolar (*i.e.*, interacts more strongly with the solvent) than the initial reactants. In this context, solvent-compressibility values [34] are of importance. A list of such values, taken from *Isaac*'s book [34], are given in *Table 4*.

Other important parameters are freezing point and viscosity of solvents. The freezing point of a liquid is known to increase with increasing pressure. This effect amounts to *ca*. 15–20° per 100 MPa. In *Tables 5* and *6*, the freezing temperatures [4] and the viscosities of common solvents are given at both ambient (0.1 MPa) and high pressure, respectively [34][42].

In the case of H_2O, an increase in pressure actually lowers the freezing point, because the volume of frozen water (ice) is larger than that of the liquid; thus, an increase in pressure lowers the freezing point according to the *Clausius–Claperon* equation.

Table 3. *Effects of High Pressure and Solvent Polarity on the Activation Volume and Rate of Reaction for Processes Involving Different Molecular-Charge Distributions*

Type	Transformation	$\Delta V^{\neq}$	$\Delta\Delta V^{\neq}$ [a])	Δk_P [b])
1		pos.	zero	neg.
2		neg.	zero	pos.
3		neg.	neg.	pos.
4		pos.	pos.	neg.
5		neg.	neg.	pos.
6		pos.	pos.	neg.
7		neg.	pos.	neg.
8		neg.	pos.	neg.

[a]) Effect of increased solvent polarity on activation volume. [b]) Effect of increased pressure on rate constant k.

Interestingly, it has been shown that some reactions take place only at pressures where the solvent employed is presumed to be frozen. This interesting phenomenon should be a subject of future work [18]. The solubility of solids in liquids often decreases as the pressure is raised, and the reagents often tend to crystallize out from the solvents. The viscosity of liquids increases approximately by a factor of two every 100 MPa; thus, diffusion control of the reaction is important [43]. The effects of viscosity on reaction rates have been extensively investigated by *Asano* and co-workers [44].

3. Mechanism and Stereochemistry. – The traditional electronic theory of organic reactions, based on *Ingold*'s work '*Structure and Mechanism in Organic Chemistry*' [45], did not fully address the mechanism and stereochemistry of cycloaddition reactions. Therefore, cycloadditions and related pericyclic reactions were called 'no-

Table 4. *Isothermal Compressibilities* (β_T) *of Common Liquids and Solvents.* The values refer to atmospheric pressure at 20° (unless indicated otherwise).

Compound	β_T [MPa^{-1}]	Compound	β_T [MPa^{-1}]
Hexane	15.40	Carbon disulfide	9.38
2,3-Dimethylbutane	17.97	Carbon tetrachloride	10.50
Heptane	13.4	Chloroform	9.96
Octane	11.3	Bromoethane	12.94
Cyclopentane	13.31	Iodoethane	9.82
Cyclohexane	11.30	1,1-Dichloroethane	7.97
Cyclooctane	9.22	Tetrachloroethylene (25°)	7.56
Dodecane (37.8°)	8.03	Trichloroethylene (25°)	8.57
Pentadecane (37.8°)	9.9	Methanol	12.14
Octadecane (60°)	9.1	Ethanol	11.19
Benzene	9.44	Propan-1-ol (0°)	8.43
Toluene	8.96	Butan-1-ol (0°)	8.10
m-Xylene	8.46	Pentan-1-ol (0°)	7.71
Chlorobenzene	7.45	Ethylene glycol	3.64
Bromobenzene	6.46	Octan-1-ol	6.82
Anisole	6.60	Acetic acid	9.08
Aniline	4.53	Ethyl acetate	11.32
Nitrobenzene	4.93	Acetone	12.62
Phenol (60°)	6.05	Diethyl ether	18.65
Water	4.58		

mechanism reactions' until 1965, when *Woodward* and *Hoffmann* published '*The Conservation of Orbital Symmetry*' [46]. *Fukui* and *Fleming* rationalized the mechanism of cycloaddition reactions with the Frontier Orbital Theory [47–49], by which the stereochemical aspects, especially of pericyclic reactions, can be predicted. With respect to stereochemistry, these aspects were particularly well predicted by this theory. More recently, computational calculations like MOPAC and *ab initio* methods have been popular to predict mechanisms and transition states, since a variety of software is now commercially available [50], and because ever more-powerful, yet inexpensive, hardware is on the market. Since *Klärner* and co-workers have already discussed the mechanistic aspects of [4 + 2] cycloaddition reactions [33], we will not repeat these discussions.

It is widely thought that cycloadditions and related reactions are not always concerted, and can often involve diradicals and/or polar intermediates [32][33][51]. Specifically, in 1989, it was speculated for pressure-accelerated *Diels–Alder* reactions [51] that the intrinsic contraction in bond-formation in the transition state is small (3–5% of $\Delta V^{\neq}$), and that most of the occurring volume contraction is due to loss of empty space surrounding the reactants, rather than being related to the reactants themselves. This is a very important conclusion, for it suggests that, in the cases investigated, the data for activation and reaction volumes should not be used for the deduction of reaction mechanism.

Neither the concerted nor the diradical mechanism for the *Diels–Alder* reaction can be established from high-pressure data. Thus, it is possible that the mechanism adopted by a particular cycloaddition may vary with pressure. Actually, the mechanism

Table 5. *Freezing Temperatures of Common Solvents at Ambient and High Pressure*

Compound	Freezing temperature [°]	
	at 0.1 MPa	at high pressure ([GPa])
Acetic acid	16.6	37.5 (0.1)
Acetone	– 94.8	20 (0.8)
Aniline	– 6.1	15.5 (0.1)
Benzene	5.5	33.4 (0.1)
Benzyl alcohol	– 10.0	0.2 (0.1)
Bromobenzene	– 30.6	– 10.7 (0.1)
Butanol	– 89.8	– 77.2 (0.1)
tert-Butyl alcohol	25.5	58.1 (0.1)
Carbon disulfide	– 111.6	– 98.0 (0.1)
Carbon tetrachloride	– 22.9	12.1 (0.1)
Chlorobenzene	– 45.5	– 28.1 (0.1)
Chloroform	– 61.0	– 45.2 (0.1)
Cyclohexane	6.5	58.9 (0.1)
Cyclohexanol	25.4	62.3 (0.1)
Diethylene glycol	– 10.5	0 (0.57)
Ethyl acetate	– 83.6	25 (1.21)
Ethanol	– 117.3	– 108.5 (0.1)
Diethyl ether	– 116.3	35 (1.2)
Ethylene glycol	– 17.4	0 (0.32)
Formic acid	8.5	20.6 (0.1)
Hexane	– 95.3	30 (1.02)
Methanol	– 97.7	25 (3.0)
Dichloromethane	– 96.7	– 85.8 (0.1)
Nitromethane	– 28.6	– 14.4 (0.1)
Phenol	40.7	53.9 (0.1)
Propanol	– 126.1	25 (5.0)
Isopropanol	– 89.5	25 (5.0)
Toluene	– 95.1	30 (0.96)
Water	0.0	– 9.0 (0.1)

of a particular alkylation reaction has been shown to be altered by increasing pressure [52]; and the discovery of other mechanistic changes caused by pressure must be expected [53]. We shall discuss selected stereochemical aspects of high-pressure cycloaddition reactions as they occur in the following sections.

3.1. *Scope and Limitations.* Of the wide variety of pericyclic reactions, cycloadditions have been most extensively studied both for mechanistic and synthetic aspects [54–57]. The reactions have been defined, classified, and reviewed in two fashions [46][58][59]. They can be facilitated under a variety of conditions such as addition of catalysts, application of high-temperature or high-pressure conditions, or use of microwave techniques, *etc.* As a result, the conditions of cycloaddition reactions can be usually selected in such a way as to accommodate sensitive functional groups in the substrate. An application of the high-pressure technique to this type of reaction is anticipated to be extremely fruitful both on kinetic ($\Delta V^{\neq} < 0$) and thermodynamic ($\Delta V < 0$) grounds. Indeed, activation volumes of cycloadditions range from -7 to -50 cm^3/mol [60][61]. It is noteworthy that high-pressure conditions often improve the yield of cycloadditions, and, in some cases, give rise to the opposite configuration of the cycloadducts compared with conventional methods [62–64].

Table 6. *Relative Increase in Solvent Viscosity as a Function of Pressure.* The term η_P/η_0 corresponds to the ratio of the viscosities at pressure P (0.1 or 0.4 GPa) *vs.* atmospheric pressure (1 atm). All values refer to a temperature of 30°.

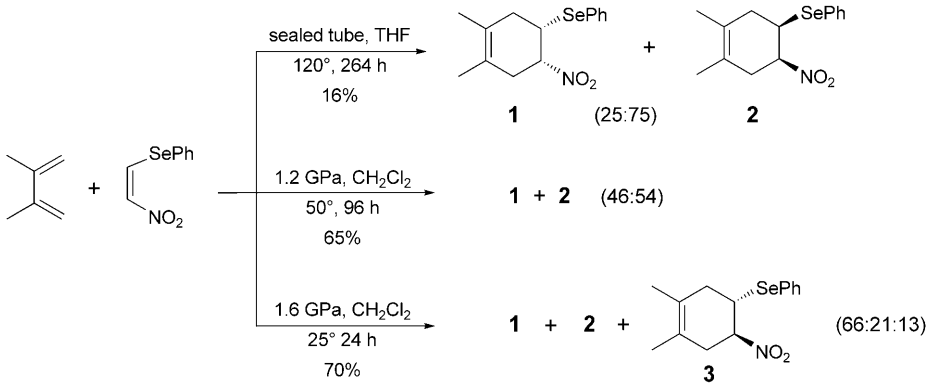
Compound	η_P/η_0	
	0.1 GPa	0.4 GPa
Acetone	1.68	4.03
Benzene	2.22	–
Bromobenzene	1.83	7.89
Butanol	2.09	8.60
Isobutanol	2.44	16.0
Carbon disulfide	1.44	3.23
Carbon tetrachloride	2.24	–
Chlorobenzene	1.79	7.36
Bromoethane	1.67	4.28
Chloroethane	1.75	4.46
Methylcyclohexane	2.44	–
Ethyl acetate	1.81	6.58
Ethanol	1.58	4.14
Diethyl ether	2.11	6.20
Hexane	2.15	8.2
Methanol	1.47	2.96
o-Xylene	2.05	–
m-Xylene	1.95	9.27
Propanol	1.92	6.86
Isopropanol	2.20	9.60
Toluene	1.95	7.89
Water	3.27	–

3.2. *Intermolecular [4+2] Cycloaddition Reactions.* Since *Diels* and *Alder* noticed nearly 75 years ago the formation of a 1:1 adduct in the reaction of cyclopentadiene with 1,4-benzoquinone, the *Diels–Alder* reaction, the prototype of [4+2] cycloadditions, has become indispensable to synthetic chemists. The [4+2] cycloaddition reaction has the advantages of excellent stereospecificity, predictable *endo*-stereoselectivity, and regioselectivity. Furthermore, it serves as an indirect and general method for the introduction and/or conversion of functional groups, especially through the *retro*-[4+2] cycloaddition of an initially formed adduct [65–67].

Intermolecular [4+2] cycloadditions exhibit a large negative volume of activation (*ca.* −25 to −45 cm^3/mol) [68][69], together with a large negative volume of reaction. Among high-pressure-mediated reactions, preparative intermolecular [4+2] cycloaddition reactions have been most-extensively explored.

3.3. *Reactions between Acyclic Dienes and Acyclic Dienophiles.* An intriguing example for the difference between low-pressure (sealed tube) and high-pressure conditions is the reaction between 2,3-dimethylbuta-1,4-diene and {[(*E*)-2-nitroethenyl]seleno}benzene (*Scheme 2*). Under low-pressure conditions, the adducts *endo*-**1** and *exo*-**2** were obtained in only 16% overall yield in a ratio of 25:75. In contrast, at high pressure (1.2 GPa), the yield increased to 65%, and the *endo*/*exo* ratio changed to 46:54. Under even higher pressure (1.6 GPa), 70% yield and an *endo*/*exo* 66:21 ratio were achieved. In the last case (1.6 GPa), the reaction, thus, mainly gave the *endo*-

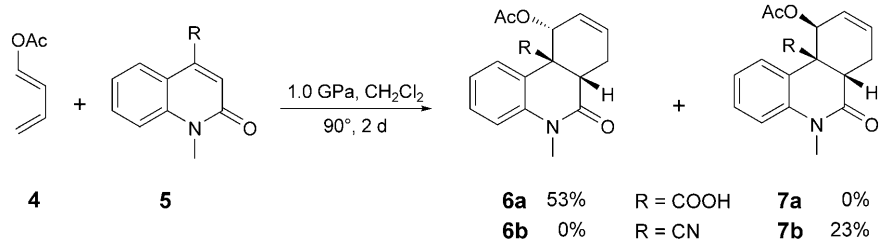
Scheme 2



adduct **1**, the smaller-activation-volume product, as well as the tautomerization product **3** (*Scheme 2*) [70].

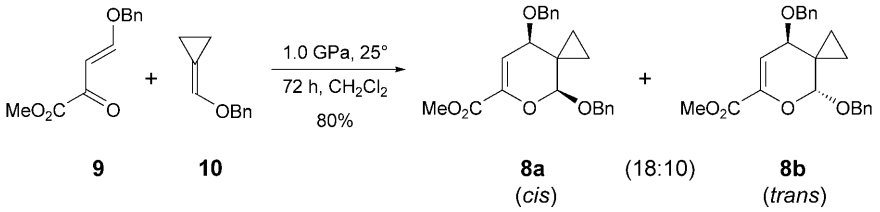
3.4. *Reactions between Acyclic Dienes and Cyclic Dienophiles.* In some cases, the functionality on the dienophile influences the stereochemistry of cycloaddition reactions under high-pressure conditions. For example, the reactions between (*E*)-buta-1,3-dienyl acetate (**4**) and the quinolin-2(1*H*)-ones **5** gave rise to different configurations in the products **6** and **7**, depending on the functional groups at 4-position of **5** (*Scheme 3*). These results reflect different activation energies (E_a) for the *trans*- and *cis*-adducts **6** and **7**, respectively. For R = COOH, the calculated E_a values for *endo*- *vs. exo*-addition to **6a** and **7a**, respectively, were reported as 33.5 *vs.* 34.2 kcal/mol. In the case of R = CN, the corresponding values for **6b** and **7b** were 36.9 *vs.* 35.9 kcal/mol, respectively. These results indicate that the pathway with the smaller activation volume was preferred under high-pressure conditions [71].

Scheme 3



3.5. *Reactions between Acyclic Heterodienes and Acyclic Dienophiles.* The desperate search for effective anticancer and anti-HIV therapeutic agents has greatly stimulated research on unnatural carbohydrates. Synthesis of the deoxysugars **8**, incorporating annelated 2-spirocyclopropane moieties, has been achieved by means of an inverse-demand hetero-*Diels–Alder* cycloaddition between the heterodiene **9** and the dienophile **10** as the key step (*Scheme 4*) [72].

Scheme 4



9 **10** **8a** (*cis*) (18:10) **8b** (*trans*)

The synthesis of diethyl 5-phosphono-3,4-dihydro-2*H*-thiopyrans **11** from ethyl 2-phosphono-3-aryl-prop-2-ene(dithioate)s **12** and enol ethers (and their thio congeners) **13** under high-pressure conditions gave rise to both improved yields and different configurations in the adducts, compared with the low-pressure (sealed tube) variant (*Scheme 5*). In the latter case (low pressure), the *cis*-adducts were formed predominantly, *via* kinetically controlled *syn*-transition states under thermal conditions. In contrast, at high pressure, the *trans*-adducts were favored, generated *via* the corresponding *anti*-transition states, associated with smaller activation volumes [73]. Interestingly, however, for X = O and R = *t*-Bu, the *syn*-approach was favored, probably owing to the steric hindrance of the *t*-Bu group.

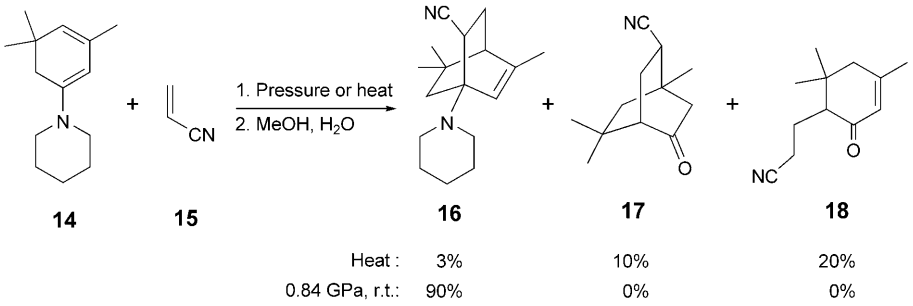
Scheme 5

12 **13** **11**

X	R	Ar	Conditions	Yield	*trans*/*cis*
O	*t*-Bu	4-MeO-C_6H_4	Sealed tube, toluene, 125°, 10 h	0%	–
O	*t*-Bu	4-MeO-C_6H_4	1.1 GPa, CH_2Cl_2, 20°, 192 h	76%	22:78
O	Et	C_6H_5	Sealed tube, toluene, 125°, 10 h	85%	15:85
O	Et	C_6H_5	1.1 GPa, CH_2Cl_2, 20°, 48 h	88%	68:32
S	Et	4-NO_2-C_6H_4	Sealed tube, toluene, 125°, 6 h	89%	7:93
S	Et	4-NO_2-C_6H_4	1.1 GPa, CH_2Cl_2, 20°, 48 h	83%	86:14

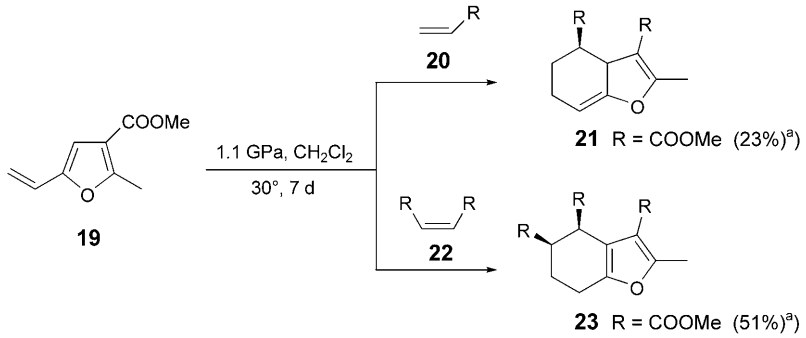
3.6. *Reactions between Cyclic Dienes and Acyclic Dienophiles.* From a vast amount of examples reported (see *Appendix*), a classical and highly intriguing reaction was selected because of its 'pioneering character': the *Diels–Alder* reaction between the isophorone derivative **14** and acrylonitrile (**15**; *Scheme 6*). When performed at 0.84 GPa, the adduct **16** was formed in high yield (90%) [74a], whereas, under thermal conditions [74b], a mixture of **16** and the two rearranged products **17** and **18** was found.

Scheme 6



Certain reactions that do not proceed under thermal conditions can be readily forced at high pressure. As shown in *Scheme 7*, this is the case for the reaction between methyl 5-ethenyl-2-methylfuran-3-carboxylate (**19**) and methyl acrylate (**20**), which gives rise to the adduct **21**, without concomitant aromatization, although only in moderate yield (23%) [75]. Note that, in the case of the similar reaction between **19** and dimethyl maleate (**22**), the resulting adduct **23** undergoes aromatization *via* C=C migration.

Scheme 7

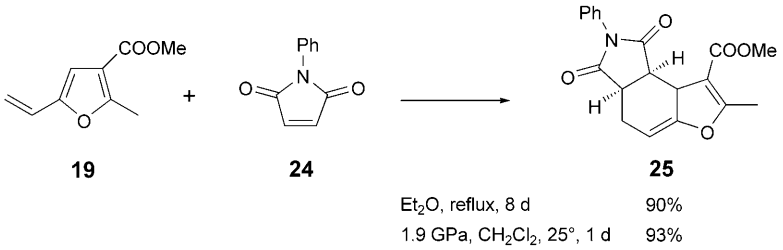


3.7. *Reactions between Cyclic Dienes and Cyclic Dienophiles.* High-pressure conditions are often effective to shorten reaction times. For example, the reaction between **19** and *N*-phenylmaleimide (**24**) in refluxing Et_2O for 8 d gave the adduct **25** in 90% yield (*Scheme 8*). When performed at 1.9 GPa at room temperature (25°), **25** was obtained in 93% yield after only 1 d [75].

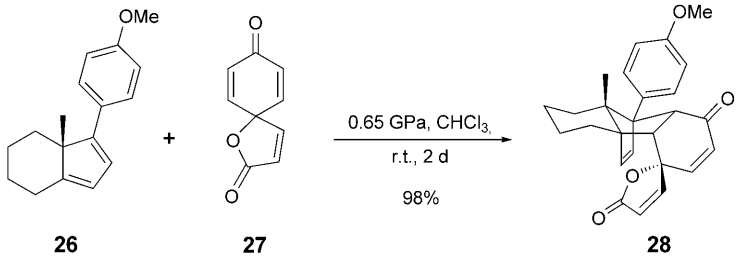
The cycloaddition between the indene derivative **26** and the (*S*)-configured spiro compound **27** at 0.65 GPa at ambient temperature led to the cycloadduct **28**, with perfect chemo-, regio-, and *endo*-selectivity (*Scheme 9*) [76]. Compound **28** seems to serve as a potential wistarin precursor.

Cantharidin (**29**) represents the simplest known inhibitor of the serine/threonine protein phosphatases 1 and 2A. The synthesis of **29** from furan and dimethylmaleic anhydride met with failure, even at pressures as high as 6.0 GPa, and at temperatures of

Scheme 8

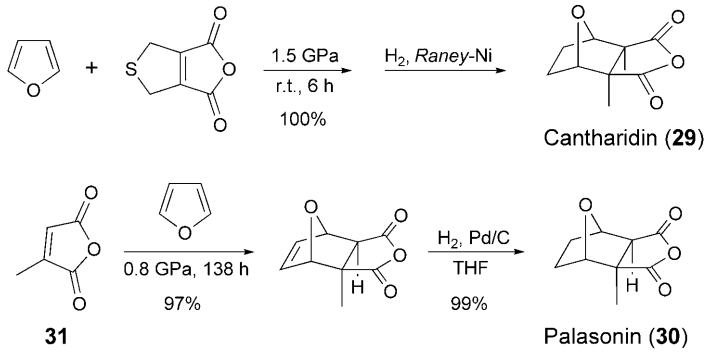


Scheme 9



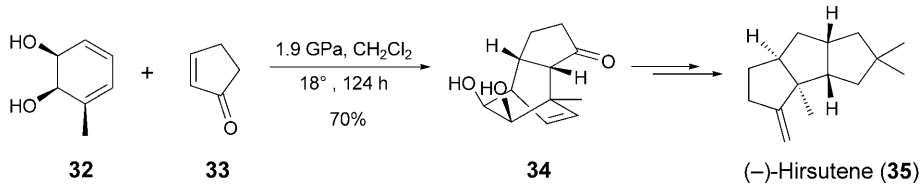
up to 350°, presumably due to the thermodynamic instability of the adduct at normal pressure, *e.g.*, when pressure is released [77a]. Nevertheless, high-pressure cycloaddition turned out to be very useful for the synthesis of cantharidin and its derivatives (*Scheme 10*) [77b][78]. For instance, (±)-palasonin (**30**) was synthesized from furan and citraconic anhydride (**31**) at 0.8 GPa for 138 h, followed by hydrogenation over Pd/C. Neither high temperatures nor *Grieco* conditions ($LiClO_4$, Et_2O, H_2O) could effect this transformation at atmospheric pressure.

Scheme 10



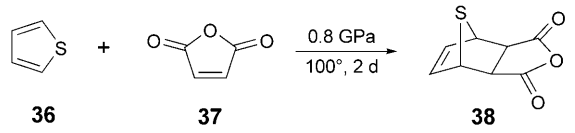
High-pressure cycloaddition of the *cis*-1,2-diol **32** with cyclopent-2-en-1-one (**33**), followed by 'oxa-di-π-methane' rearrangements of the adduct **34**, were used for the synthesis of (−)-hirsutene (**35**; *Scheme 11*), a sesquiterpene isolated from the fermented mycelium of *Coriolus consors* [79].

Scheme 11



It is known that thiophene (**36**), which is aromatic, does not undergo [4 + 2] cycloaddition reactions under conventional conditions. However, almost 25 years ago, the reaction with maleic anhydride (**37**) at 1.2 – 2.0 GPa and a temperature of 100° afforded the *exo*-adduct **38** in 40% yield. Recently, highly improved results have been reported under high pressure and under solvent-free conditions, as summarized in *Scheme 12* [18][80].

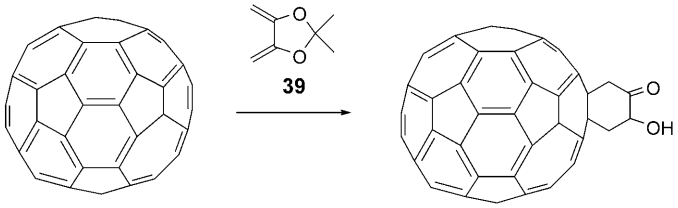
Scheme 12



36/37	Solvent	38
1:1	CH_2Cl_2	19%
4:1	CH_2Cl_2	21%
4:1	neat	93%
2:1	neat	87%

Buckmisterfullerene (C_{60}) reacts with electron-rich 2,3-bis(methylidene)-1,4-dioxanes under thermal conditions. However, with 2,2-dimethyl-4,5-bis(methylidene)-1,3-dioxolane (**39**) as the diene, high pressure was required to perform the [4 + 2] cycloaddition with C_{60}, which, after hydrolysis, afforded the acyloin derivative **40** (*Scheme 13*) [81].

Scheme 13



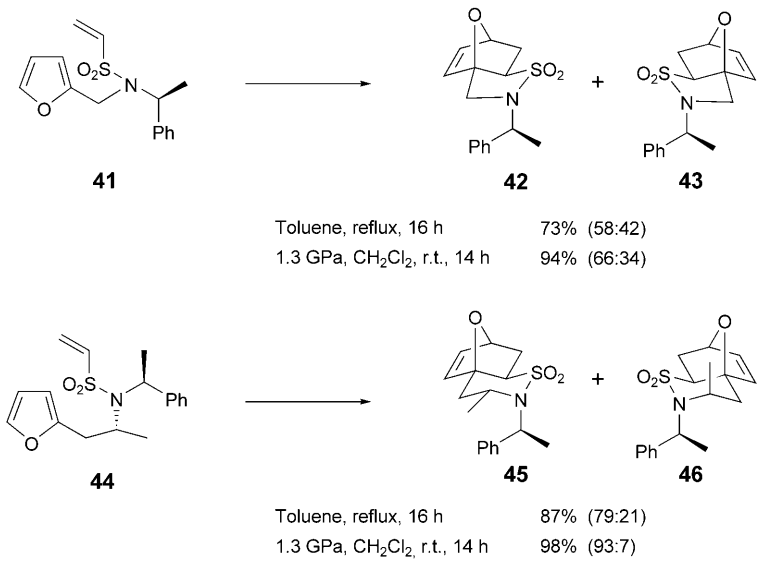
1,2-Dichlorobenzene, 25° 0%

1. 300 MPa, 1,2-dichlorobenzene, 24 h
2. CF_3COOH (TFA), 10 min 19%

3.8. *Intramolecular [4+2] Cycloaddition Reactions.* In recent years, there has been considerable interest in synthetic applications of intramolecular [4+2] cycloadditions, because the intramolecular process can offer some advantages over the intermolecular version, especially increased reaction rate and higher selectivity. Intramolecular [4+2] cycloaddition reactions allow the regioselective and stereospecific introduction of multiple stereogenic centers. Hence, these reactions have become a powerful method for the synthesis of polycyclic natural products. In one case, the activation volume has been determined as -25 cm^3/mol [82]. Thus, high pressure is anticipated to be useful in promoting this type of cycloaddition.

The preparation of enantiomerically pure δ- and γ-sultams was carried out by a high-pressure intramolecular [4+2] cycloaddition. In the case of the sulfone **41**, the reaction at 1.3 GPa gave both higher yield and better asymmetric induction than the corresponding thermal process in boiling toluene at ambient pressure (*Scheme 14*). The resulting *exo*-sultam **42** was favored over *endo*-**43** by the chiral (*S*)-1-phenylethyl substituent. In the case of **44**, where double stereodifferentiation was brought about by the presence of two stereogenic centers, the diastereoselectivity noted for the high-pressure cycloaddition was hardly affected by the chiral N-substituent. Here, equatorial disposition of the Me group on the δ-sultam **45** (and in the corresponding transition state) dominated the stereochemical outcome of the reaction, the diasteroisomer **46** being formed as the minor product (*Scheme 14*) [83].

Scheme 14



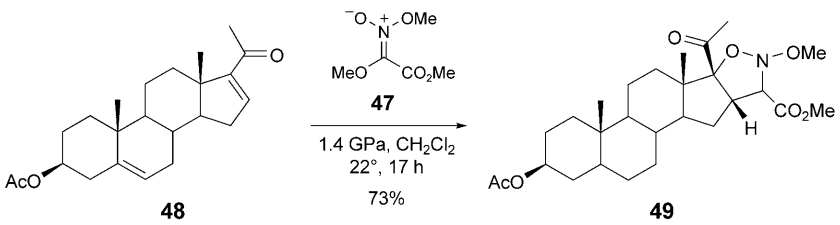
3.9. *[3+2] Cycloaddition Reactions.* The 1,3-dipolar ([3+2]) cycloaddition reaction, whether concerted or not, undoubtedly rivals *Diels–Alder* reactions in ubiquity as well as synthetic utility [32][65][84–90]; and its synthetic potential is still far from being exhausted. Both inter- and intramolecular 1,3-dipolar cycloadditions

represent an efficient method for the syntheses of a wide variety of carbo- and heterocyclic compounds, including natural products.

The activation volume for 1,3-dipolar cycloaddition reactions is typically highly negative (*ca.* -18 to -32 cm^3/mol) [91–94]. In spite of the broad applicability of 1,3-dipolar cycloadditions in organic synthesis, high-pressure data are still rare compared to [4+2] cycloadditions. Among other reasons, this is due to the fact that the formation of 1,3-dipoles often involves a bond-breaking process; also, in certain cases, 1,3-dipoles are prone to dimerization [60].

One of the classical and intriguing examples of such reactions is the 1,3-dipolar cycloaddition of the (*aci*-nitro)acetate **47** with the pregnadienone **48** as the dipolarophile to afford the pentacyclic steroid **49**, which has an additional isoxazolidine ring (*Scheme 15*). This reaction that takes place basically only at high pressure; under conventional conditions, **49** is formed in trace amounts ($\leq$2%) only. Note that *Lewis* acid catalyzed addition of **47** to **48** resulted in loss of MeOH from **49** [95].

Scheme 15

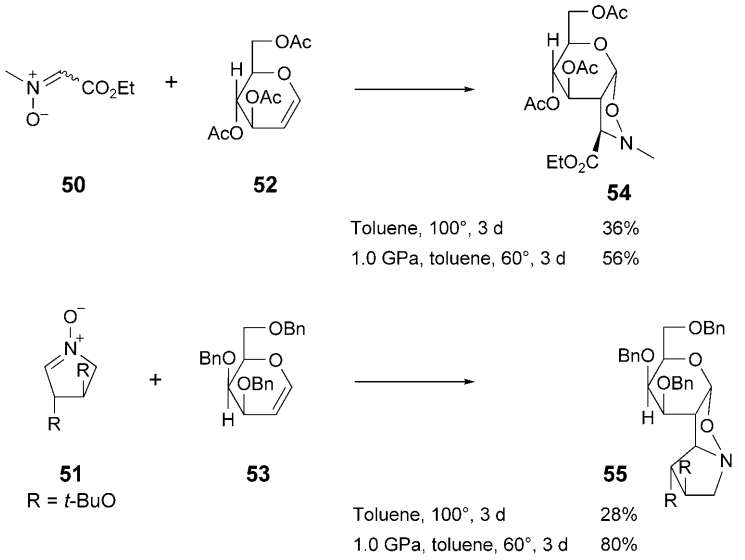


1,3-Dipolar cycloadditions of the enantiomerically pure, hydroxylated nitrones **50** and **51** to the glycols **52** and **53**, respectively, are strongly accelerated at high pressure, giving rise to the adducts **54** and **55**, respectively (*Scheme 16*). In the reaction leading to the cyclic glycoside derivative **55**, the D-tartaric acid derived nitrone **51** approaches **53** from the α-face (bottom). The stereoselectivity is controlled by the 3-BnO substituent of the glycal as well as by the *t*-BuO group next to the nitrone C=C bond. The process has been generalized, and allows direct access to stereodifferentiated tricyclic isoxazolidines [96].

3.10. *[2+2] Cycloaddition Reactions.* The formal [2+2] cycloaddition is a useful method for cyclobutane- as well as oxetane-ring formation. Thermal, concerted [2+2] cycloadditions are disallowed by orbital symmetry. Heteroallenes such as ketenes with two π-bonds are thought to undergo thermal concerted cycloaddition either *via* a $[_\pi2_s+_\pi2_s+_\pi2_s]$ or a $[_\pi2_s+_\pi2_a]$ process. Otherwise, [2+2] cycloadditions could take place stepwise, either *via* a biradical or a zwitterionic intermediate. [2+2] Cycloadditions have large negative activation volumes, with $\Delta V^{\neq}$ values in the range of -20 to -50 cm^3/mol for concerted [91][97][98], and -25 to -45 cm^3/mol for polar or stepwise reactions [91][99–101].

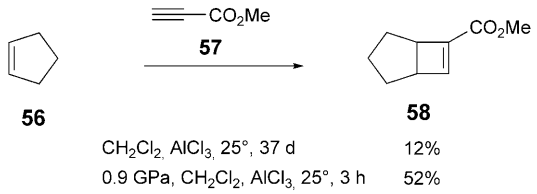
High-pressure conditions are, therefore, expected to be useful for [2+2]-type cycloadditions, though not many practical examples of pressured [2+2] cycloadditions have been reported. In the $AlCl_3$-catalyzed cycloaddition of cyclopentene (**56**) with methyl propynoate (**57**), the yield of the [2+2] cycloadduct **58** was improved under high pressure compared with atmospheric conditions (*Scheme 17*) [102]. A similar

Scheme 16



reaction of cyclohexene with **57** afforded an ene adduct, along with the [2 + 2] adduct, the chemoselectivity of the process not being affected by pressure (data not shown) [102].

Scheme 17

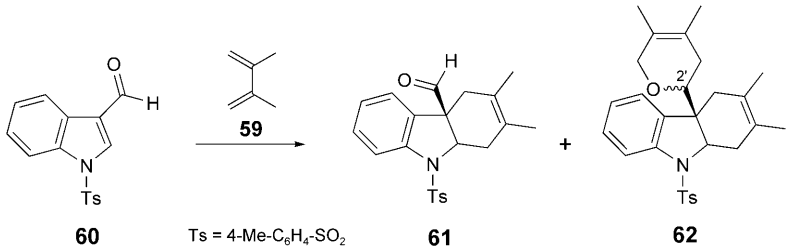


3.11. *Miscellaneous Cycloaddition Reactions.* 3.11.1. Lewis *Acid Catalyzed Reactions. Lewis* acid catalysts such as $SnCl_4$ and $ZnCl_2$ accelerate many cycloadditions, particularly [4 + 2]-type reactions [54]. Specifically, transition-metal catalysts in high-pressure cycloaddition reactions have been used by many groups.

A very recent example for the combination of *Lewis* acid catalyst and high pressure is the reaction between 2,3-dimethylbuta-1,3-diene (**59**) and the indole **60**. As shown in *Scheme 18*, quantitative yields of the adducts **61** and **62** were obtained under high-pressure conditions. Interestingly, combination of high pressure and $ZnCl_2$ as catalyst afforded mainly the opposite configuration in **62** [103]. It is passing note that all-carbon [4 + 2] cycloadditions are kinetically favored, which is in accord with the observed higher reactivity of the aromatic C=C bond relative to the (unaffected) formyl group in **60**, giving rise to **61** exclusively (in the absence of catalyst) under high pressure (*Scheme 18*).

Finally, it should be mentioned that, in the above reaction, both $SnCl_4$ and $ZnCl_2$ accelerate the second cycloaddition, in which the higher *trans*-cycloadduct was formed *via* an *anti*-type transition state under thermal conditions. In contrast, at high pressure, the corresponding *cis*-cycloadducts were formed *via* a *syn*-type transition state, which has a smaller activation volume (data not shown).

Scheme 18



60 Ts = 4-Me-C_6H_4-SO_2 **61** **62**

Sealed tube, toluene, 195°, 80 h	85%	100:0
Toluene, $ZnCl_2$, 110°, 48 h	77%	87:13 (**62**: (2'*R*))
1.6 GPa, CH_2Cl_2, 50°, 48 h	100%	100:0
1.2 GPa, CH_2Cl_2, $ZnCl_2$, 25°, 48 h	100%	2:98 (**62**: (2'*S*))

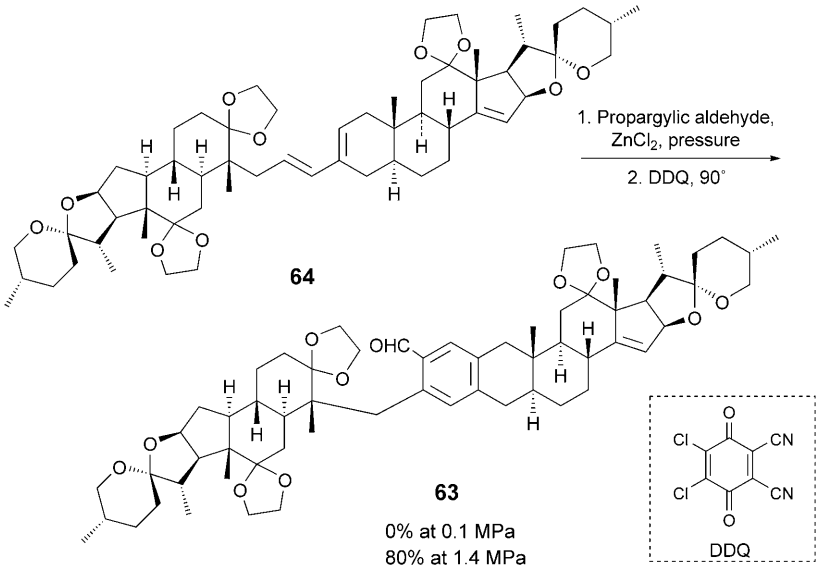
Another example of the combination of high pressure and a *Lewis* acid catalyst is the synthesis of the cephalostatin derivative **63** from the diene **64** and propargylic aldehyde (*Scheme 19*). This transformation could neither be effected under thermal conditions nor with the help of catalysts alone. However, the use of both high pressure and $ZnCl_2$ gave rise to a diastereoisomeric 3:1 mixture of the primary adduct, which was oxidized (aromatized) subsequently with DDQ to **63** as the single product in 80% yield [104].

3.11.2. *Reactions of Tropone and Its Derivatives* ([8 + 2] Cycloaddition). Cycloaddition reactions of tropones (=cyclohepta-2,4,6-trien-1-ones) with a variety of dienophiles have been investigated by *Takeshita* and co-workers [105]. Generally, these reactions afford mixtures of various products. For instance, the high-pressure cycloaddition of 2-chlorotropone (**65**) and ethyl vinyl ether (**66**) yielded a mixture of the [4 + 2] cycloadducts **67**–**69** and the corresponding [8 + 2] cycloadduct **70** (*Scheme 20*) [105].

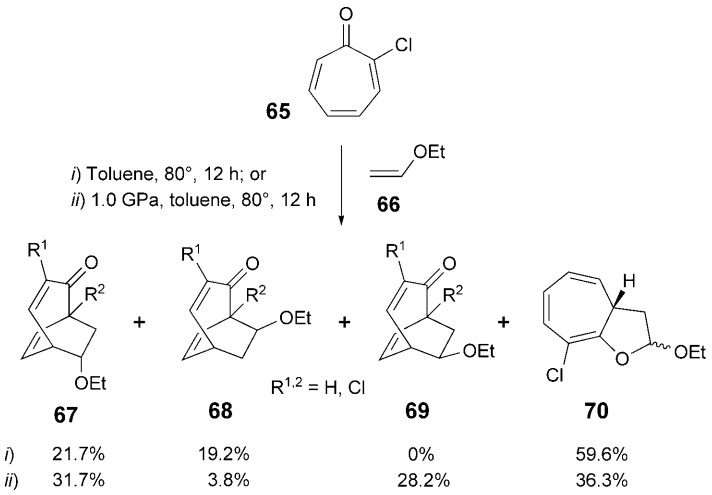
3.11.3. *Multicomponent Cycloaddition Reactions.* High-pressure conditions have proven useful for multicomponent reactions, and even for double-multicomponent reactions [106a]. For example, 3-[(*E*)-2-nitroethenyl]pyridine (**71**), the benzyl vinyl ether **72**, and methyl acrylate (**73**) underwent a three-component cycloaddition – *via* tandem [4 + 2]/[[3 + 2] reaction – to afford the bicyclic 'nitroso acetal' **74** as a mixture of three diastereoisomers (*Scheme 21*). When *N*-phenylmaleimide (**24**) was used instead of **73**, compound **75** was obtained as a single stereoisomer [106b].

Analogous three-component cycloadditions have been achieved under heterogeneous and high-pressure conditions, in which one reactant was immobilized, *e.g.*, the resin-bound nitroalkene **76** prepared by microwave-assisted *Knoevenagel* reaction (*Scheme 22*). Compound **76** was reacted at 1.5 GPa with ethyl vinyl ether (**66**) and

Scheme 19



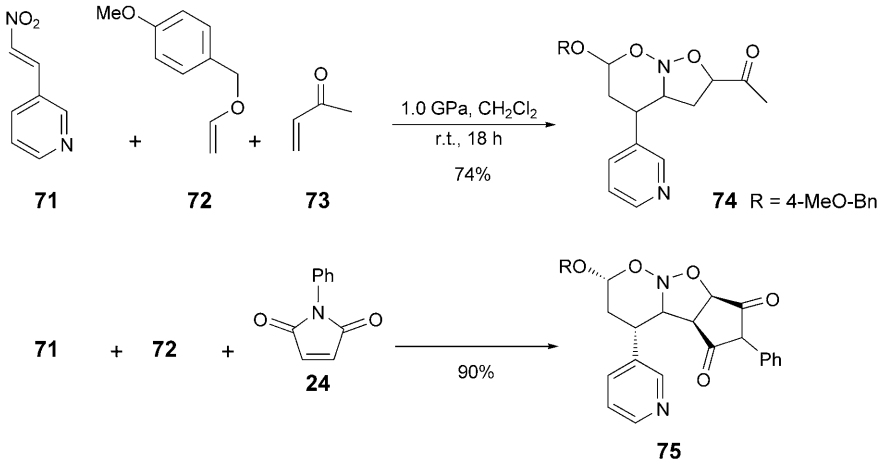
Scheme 20



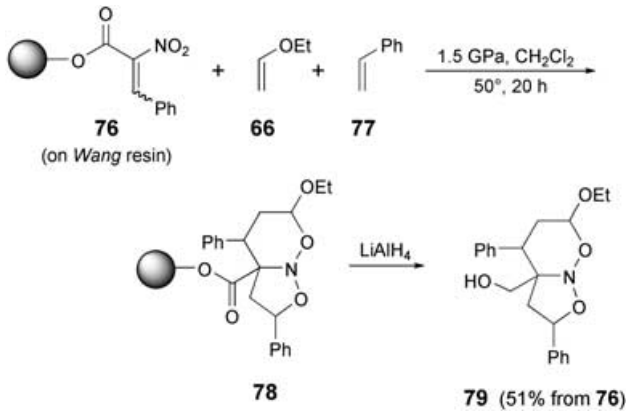
styrene (**77**) in a domino-[4 + 2]/[3 + 2] cycloaddition, affording the adduct **78**, which was reductively ($LiAlH_4$) cleaved from the support to provide the bicyclic compound **79** in an overall yield of 51% [107].

3.11.4. *Synthesis of Supramolecular Compounds* [2b] [7a]. Conjugate polymers with ribbon-type structures have been the subject of great synthetic and theoretical interest. These structures are predicted to form the structural basis for interesting electronic, optical, and magnetic properties. High-pressure-promoted repetitive *Diels–Alder*

Scheme 21



Scheme 22

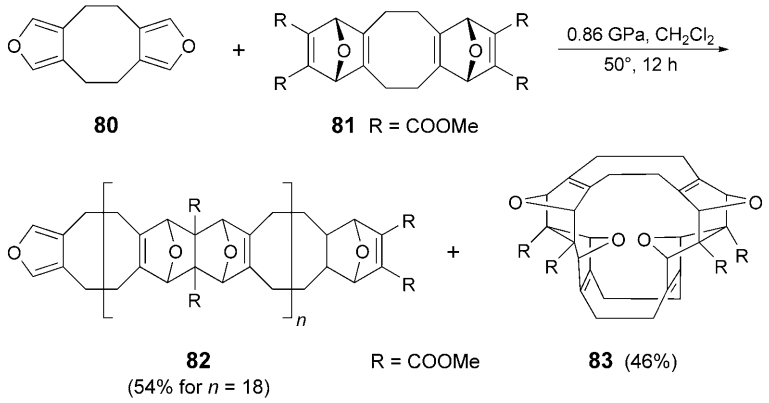


reactions have served as an effective method for the preparation of these kinds of compounds. Specifically, the reaction of cyclooctadiene derivatives such as '[2.2](3,4)furanophane' (=4,5,9,10-tetrahydrofuro[3′,4′:5,6]cycloocta[1,2-*c*]furan; **80**), with its acetylenedicarboxylate bisadduct **81** gave the ribbon-type polymers **82**, together with the cage-type compound **83** (*Scheme 23*) [108].

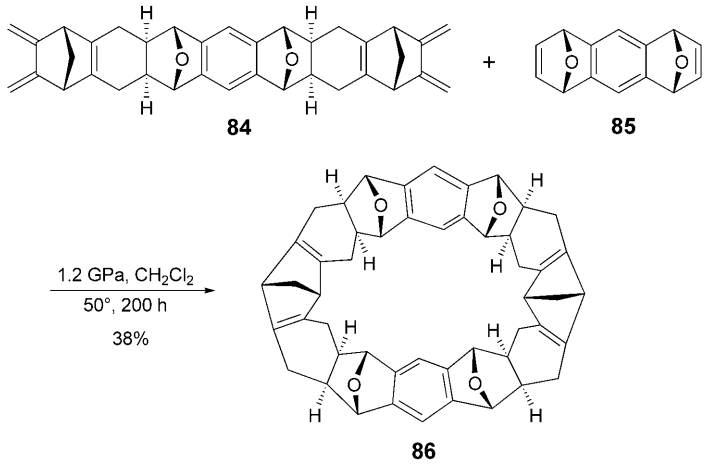
An analogous high-pressure process, based on the condensation of the double bis-diene **84** and the bis-dienophile **85**, gave smooth birth to the novel belt-type compound **86** (*Scheme 24*) [109]. However, the attempted dehydrogenation of **86** remained unsuccessful.

3.11.5. *Notable Unsuccessful High-Pressure Reactions.* There are several unrewarding examples that if these had met with success, would have had a great impact on the science community. In particular, the following spectacular high-pressure attempts are

Scheme 23



Scheme 24

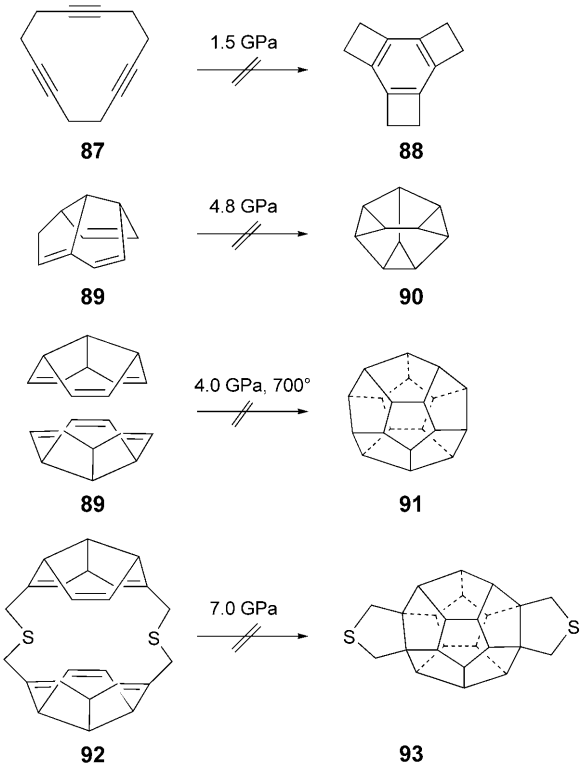


to be mentioned (*Scheme 25*): *1*) isomerization of cyclododeca-1,5,9-triyne (**87**) to 1,2:3,4:5,6-tricyclobutabenzene [110][111]; *2*) isomerization of triquinacene (**89**) to diademane (**90**) [112]; *3*) dimerization of triquinacene (**89**) to dodecahedron (**91**) [112]; and *4*) intramolecular dimerization of the bis(triquinacene)-type compound **92** to the dodecahedron derivative **93** [113].

All of the above attempted reactions were met with failure, even at ultra-high pressures of up to 7.0 GPa[3]). The reason for this are presumably inappropriate atom…atom distances and/or conformations of the starting molecules for the reactions to take place. In the future, sovent-free conditions, crystal-engineering strategies, and computer-based optimization and design of substrates and catalysts, as well as the

[3]) Roughly 70,000 times atmospheric pressure!

Scheme 25



optimization of other parameters such as light and shear, might give dramatic, yet smooth, birth of fascinating novel molecules.

4. High-Pressure Apparatus and Experimental Procedures. – This review includes only a brief account of the equipment used in high-pressure organic synthesis [2a][6][8][30][33][34][117]. The most general and convenient method for obtaining high pressure is disproportion, *i.e.*, application of *Pascal*'s principle. Particularly in organic synthesis, a piston-cylinder device may be most satisfactory. A maximum pressure of *ca*. 5.0 GPa is obtainable with such a device, when constructed of cemented tungsten carbide. Although miscellaneous types of piston and cylinder apparatus have been devised, depending on the purpose of experiments, they consist essentially of a high-pressure vessel, a pressure gauge (usually *Bourdon* or manganin gauges), a pump, and an intensifier. The source of high pressure is due to the intrusion of a piston into the cylinder (*Fig. 3*) [8].

There are basically four principles to produce high pressures (*Fig. 4*) by means of one of the following setups: simple piston cylinder (*A*), opposed-piston cylinder (*B*), anvil cylinder (*C*), and opposed/multiple anvils (*D*) [34]. For organic reactions to be performed on a semipreparative or preparative scale, anvils (*C*, *D*) are not suitable,

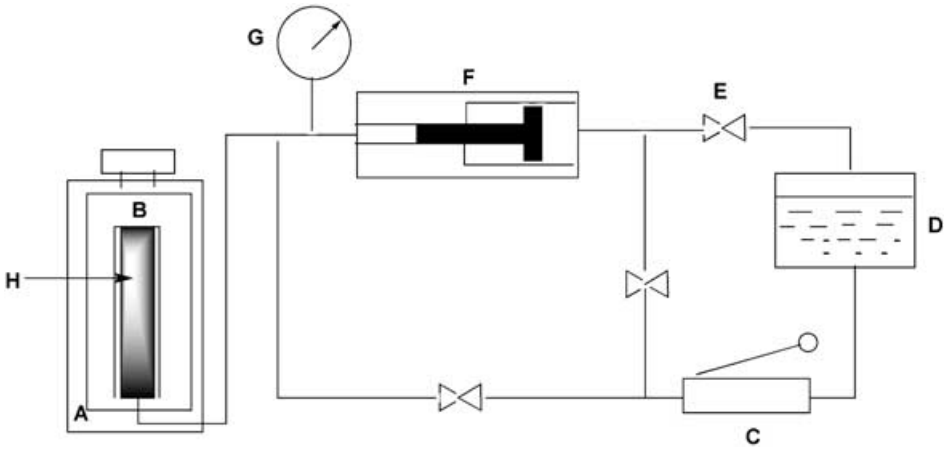


Fig. 3. *Schematic diagram of a high-pressure apparatus.* Legend: *A*, heater; *B*, double-wall pressure vessel; *C*, manual or electronic pump; *D*, oil reservoir; *E*, valve; *F*, intensifier; *G*, gauge; *H*, flexible sample container.

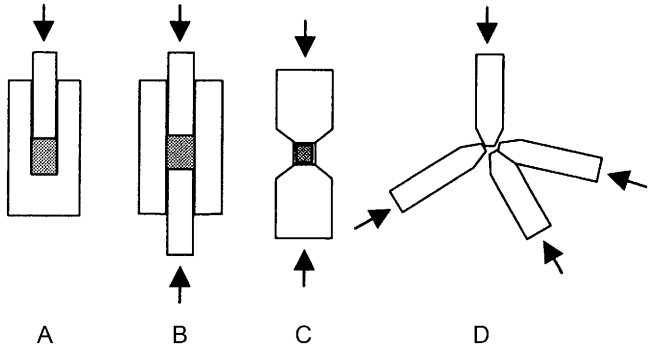


Fig. 4. *Arrangements for the generation of high pressures.* Legend: *A*, simple piston cylinder; *B*, cylinder with two opposed pistons; *C*, *Bridgman*-type anvil; *D*, tetrahedral multi-anvil device.

because their volume is too small. However, for micro-scale processes, they can be readily used.

Many kinds of flexible sample tubes have been devised [114]. Four different kinds of setups are shown in *Fig. 5*, *a*. In all cases, either polytetrafluoroethylene (PTFE) or metal bellows are used, and there is at least one threaded hole for withdrawal. For high-pressure reactions at temperatures of up to *ca.* 60°, several kinds of commercially available syringes and polyethylene tubes have also been used [8].

In *Fig. 5*, *b*, a high-pressure apparatus with a mechanical stirring unit is shown, as used at present in our laboratory. This device, however, can generate maximum pressures of up to 0.3 GPa 'only' [8].

In most preparative experiments under high pressure, the procedure is as follows: pressure is applied at room temperature to a sample tube containing the reagents and, if

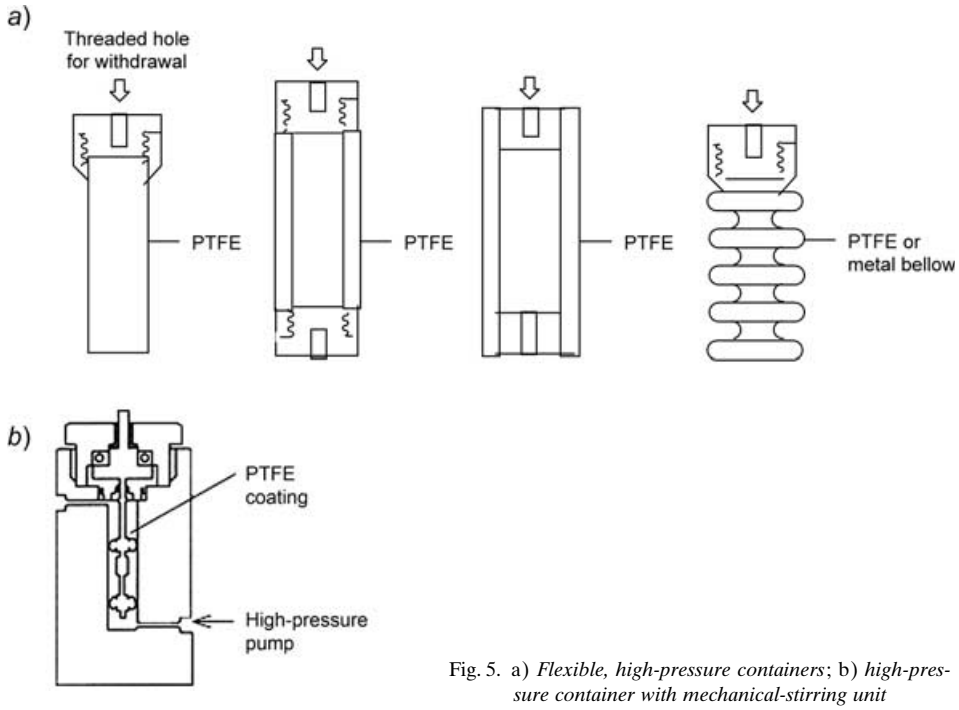


Fig. 5. a) *Flexible, high-pressure containers*; b) *high-pressure container with mechanical-stirring unit*

necessary, catalysts and solvent, before the temperature is raised, if required. After a suitable time, the heater is switched off, followed by releasing the pressure, and the sample is removed from the vessel. When the reaction at high pressure does not take place at ambient temperature, according to GC, TLC, NMR or other analytical techniques, an increase of pressure and/or temperature might be effective in certain cases, or a catalyst may be added additionally.

The apparatus and procedure described above are based upon the recovery method. However, non-recovery methods like the flow method are often more satisfactory, particularly for preparative or industrial applications. A very high-pressure flow apparatus that may enable operation at pressures of up to 1.5 GPa has, indeed, been designed [115]. More specifically, a high pressure/high temperature apparatus made up of HPLC equipment and a GC furnace has been operated for a variety of reactions at pressures of up to 50 MPa and temperatures of up to 600° [116].

High-pressure equipments [117] are available from the following major companies (in alphabetical order):

- *Autoclave Engineers, Inc.*, Erie, PA-16509, USA
- *BuTech Pressure Systems*, Costa Mesa, CA-92626, USA
- *Dresser Industries, Inc.*, Dallas, TX-75201, USA
- *Drukker International B. V.*, NL-5431 SH Cuijk, The Netherlands
- *Harwood Engineering Co., Inc.*, Walpole, MA-02081, USA

- *Haskel International, Inc.*, Burbank, CA-91502, USA
- *High Pressure Equipment Co.*, Erie, PA-16505, USA
- *Hikari Koatsu Kiki Co., Ltd*, Hiroshima, 733-0012, Japan
- *Hydro-Pac, Inc.*, Fairview, PA-16415, USA
- *Leco Corporation*, Bellefonte, PA-16823, USA
- *Nova Swiss*, CH-8307, Effretikon, Switzerland

An ingenious method for the generation of high pressure consists of water-freezing [118–122]. The volume of H_2O increases by *ca.* 10% on freezing. For example, when H_2O is frozen in an autoclave at $-20°$, a pressure of up to *ca.* 200 MPa can be obtained. For this purpose, only an appropriate autoclave and a household electric refrigerator are required. Scale-up with this method may be easier compared to the usual high-pressure technology. The detailed procedure has been described by *Hayakawa et al.* [120].

H. I. would like to thank Prof. *Katsuhiko Yoshimoto*, Tokushima University School of Dentistry, Japan, for kind suggestions and encouragement. This work was supported, in part, by a Grant-in-Aid for Scientific Research from the *Ministry of Education, Culture, Sports, Science, and Technology*, Japan (to *K. M.*) for purchasing high-pressure instruments, and by a Grant-in-Aid for Encouragement of Young Scientists (B, No. 16710157) from the *Japan Society for the Promotion of Science* (to *H. I.*). *H. I.* extends his gratitude to Sasakawa Scientific Research Grants (No. 6-182 and 7-199K) and to Sasakawa Grants for Science Fellows (No. F 02-109) from the *Japan Science Society* for research support. Generous and encouraging support from the Chiba Institute of Science (CIS) are greatly acknowledged. Finally, many thanks are extended to the editors of *Verlag Helvetica Chimica Acta* for the great effort of editing such a big article.

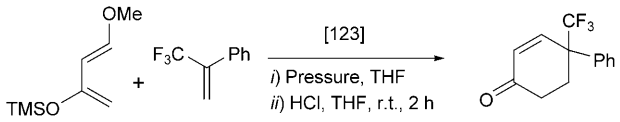
Appendix

A compilation of the high-presssure literature data up to nearly the end of 2004 is given in the form of schemes and tables. In *App. 1–371* and *372–407*, inter- and intramolecular $4+2$ cycloadditions are summarized, respectively. In *App. 408–480*, intermolecular $3+2$ cycloadditions are treated, and in *App. 481–526* and *527–533*, respectively, $2+2$ cycloadditions as well as miscellaneous high-pressure additions are to be found.

App. 1

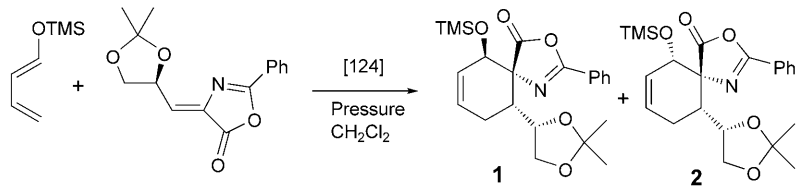
R^1	R^2	R^3	R^4	R^5	R^6	*P*	*T*	*t*	Yield
MeOOC	H	H	pyrrolidino	H	Me	0.1 MPa	80°	12 h	80%
MeOOC	H	H	pyrrolidino	H	Me	1.0 GPa	r.t.	18 h	88%
pyrrolidino	H	H	MeOOC	H	H	0.1 MPa	20°	24 h	94%
pyrrolidino	H	H	MeOOC	H	H	1.36 GPa	r.t.	30 m	95%

App. 2



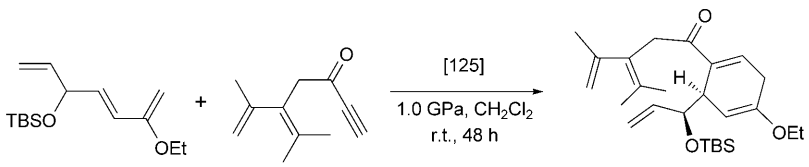
Condition	*T*	*t*	Yield
Sealed tube	140°	140 h	75%
1.5 GPa	50°	66 h	80%

App. 3



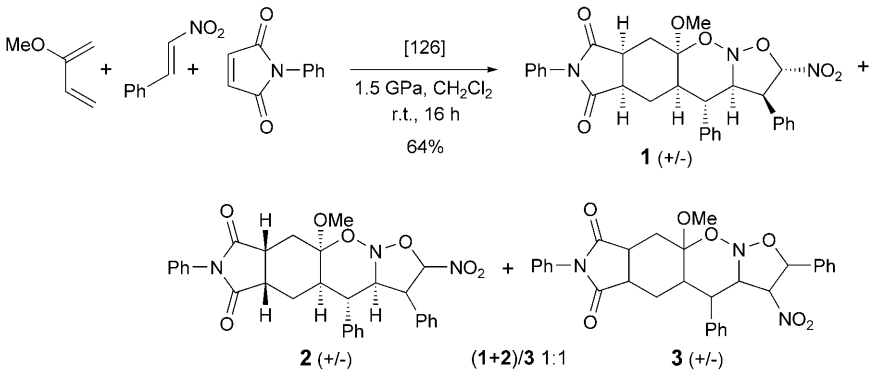
P	*T*	*t*	Products	Yield
1.25 GPa	60°	120 h	**1**	90%
0.1 MPa	r.t.	24 h	**1**/**2** 1:2	70%

App. 4

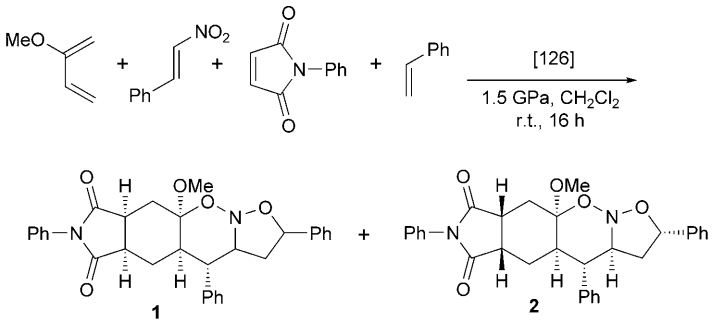


55% (dr 29:10)

App. 5

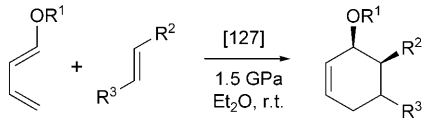


App. 6



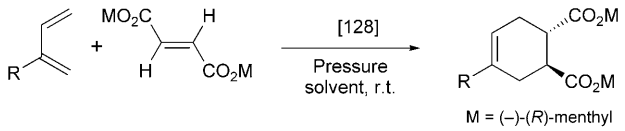
Total yield: 83% (**1**/**2** 65:35)

App. 7



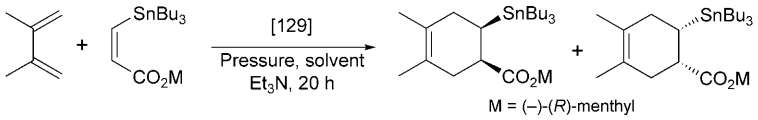
R^1	R^2	R^3	*t*	Yield
MeCO	H	CHO	4 h	81%
MeCO	Me	CHO	11 h	5%
MeCO	H	COMe	4 h	45%
Me	H	CHO	4 h	47%
Me	Me	CHO	4 h	30%
Me	Me	CO_2Me	12 h	–

App. 8



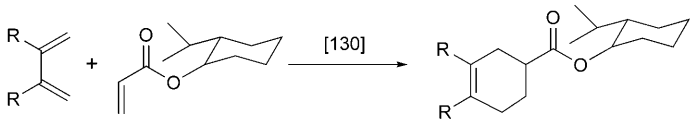
R	*P*	Solvent	*t*	Yield	Optical yield
H	0.1 MPa	PhMe	300 h	70%	not reported
H	0.69 GPa	PhMe	20 h	quant.	12.8%
Me	0.78 GPa	CH_2Cl_2	20 h	quant.	11.2%

App. 9



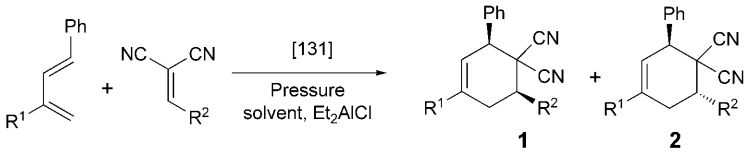
P	Solvent	*T*	*t*	Yield	de
0.1 MPa	Et_2O	140°	65 h	quant.	8%
1.2 GPa	CH_2Cl_2	7°	65 h	65%	13%
2.5 GPa	CH_2Cl_2	45°	56 h	quant.	2.6%

App. 10



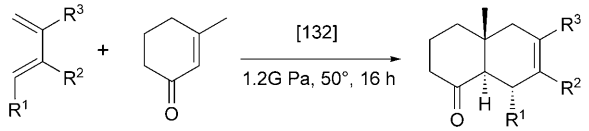
R	*P*	Solvent	Yield	ee	Config.
H	0.5 GPa	PhMe/PhH 7:3	39%	2.0%	(+)-(*R*)
H	0.71 GPa	PhMe/PhH 7:3	47%	2.7%	(+)-(*R*)
H	0.9 GPa	PhMe/PhH 7:3	55%	3.2%	(+)-(*R*)
H	1.12 GPa	PhMe/PhH 7:3	64%	4.1%	(+)-(*R*)
Me	0.79 GPa	CH_2Cl_2	77%	0.9%	(+)-(*R*)

App. 11



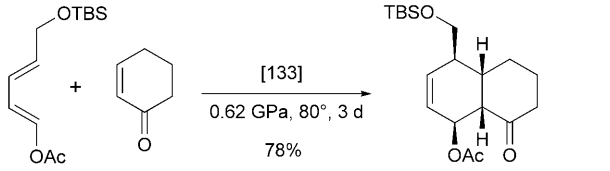
R^1	R^2	*P*	Solvent	*T*	*t*	Yield	**1/2**
Et	i-Pr	0.1 MPa	PhMe	120°	48 h	69%	1:1.56
Et	*t*-Bu	1.0 GPa	CH_2Cl_2	55°	12 h	96%	1:5.88
i-Pr	i-Pr	1.0 GPa	CH_2Cl_2	55°	36 h	31%	1:3.33
i-Pr	*t*-Bu	1.0 GPa	CH_2Cl_2	55°	24 h	70%	< 1:99

App. 12



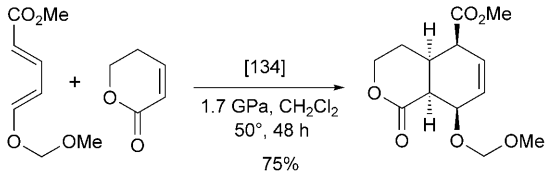
R^1	R^2	R^3	Solvent	$EtAlCl_2$	Yield
Me	H	H	CH_2Cl_2	0.25 equiv.	60%.
H	H	Me	CH_2Cl_2	0.50 equiv.	25%
H	H	Me	$CHCl_3$	0.50 equiv.	44%

App. 13

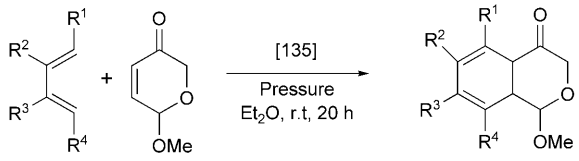


endo/exo/regioisomers 18:1:1

App. 14

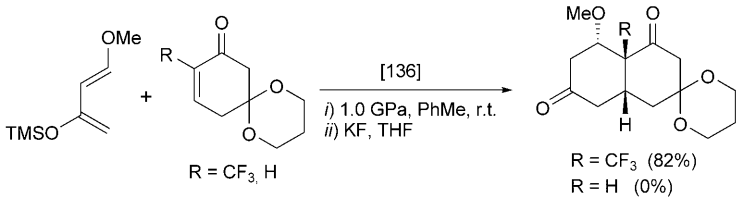


App. 15

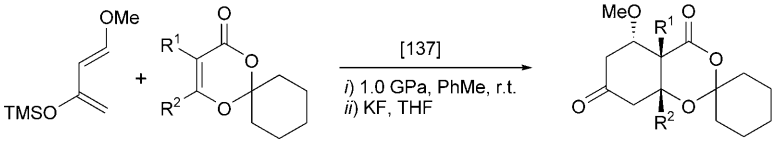


R^1	R^2	R^3	R^4	*P*	Yield	dr
H	H	H	H	1.09 GPa	73%	98:2
H	Me	Me	H	1.10 GPa	91%	98:2
Me	H	H	Me	1.05 GPa	51%	99:1
Me	H	H	H	1.08 GPa	66%	99:1
H	Me	H	H	1.07 GPa	79%	98:2

App. 16

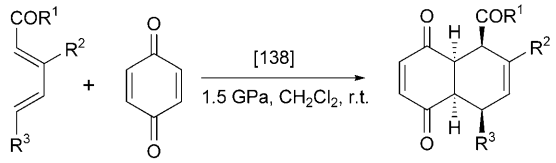


App. 17



R^1	R^2	*T*	*t*	Yield
CF_3	H	20°	40 h	82%
F	H	75°	40 h	72%
F	Me	75°	40 h	–

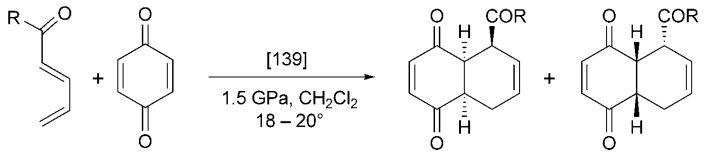
App. 18



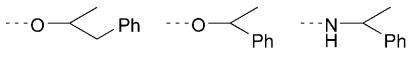
R^1	R^2	R^3	*t*	Yield
MeO	H	H	18 h	64%
MeO	Et	H	3 h	60%
H	H	Me	18 h	90%
(–)-menthyl	H	H	18 h	51%[a])

[a]) Diastereoisomers.

App. 19

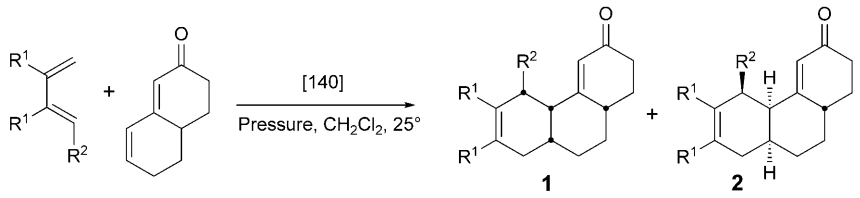


R	*t*	Yield	ee
A	23 h	98%	2%
B	21 h	98%	6%
C	19 h	94%	14%



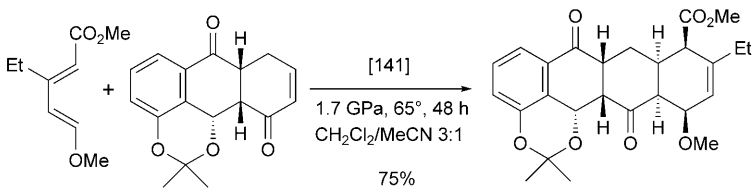
(+)-**A** (–)-**B** (+)-**C**

App. 20

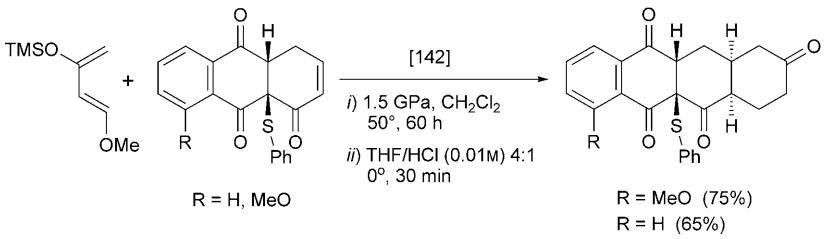


R^1	R^2	*P*	*t*	Yield	**1/3**
H	H	0.7 GPa	22 h	70%	9:1
H	H	0.1 MPa	240 h	55%	1:9
H	Me	0.7 GPa	65 h	80%	19:1

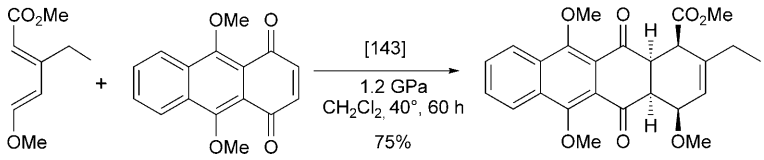
App. 21



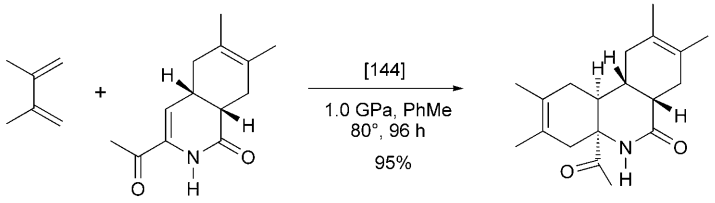
App. 22



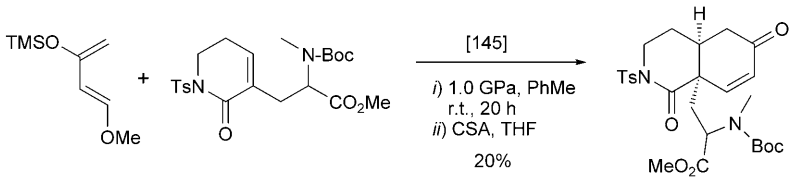
App. 23



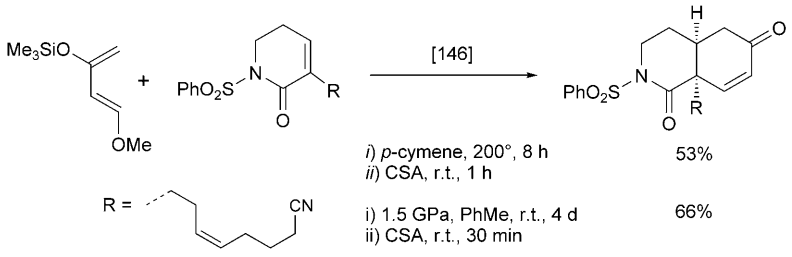
App. 24



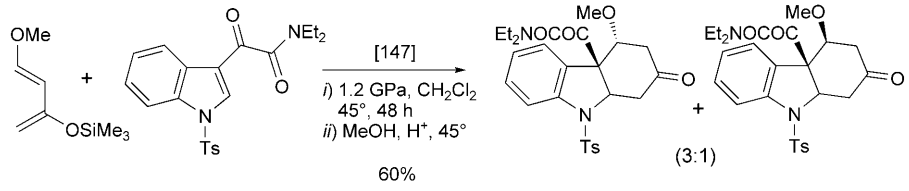
App. 25



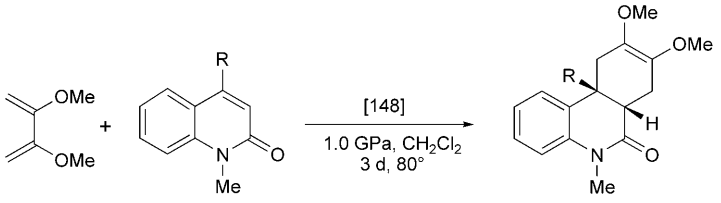
App. 26



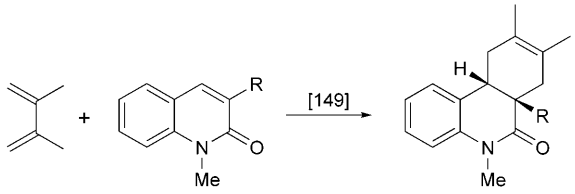
App. 27



App. 28

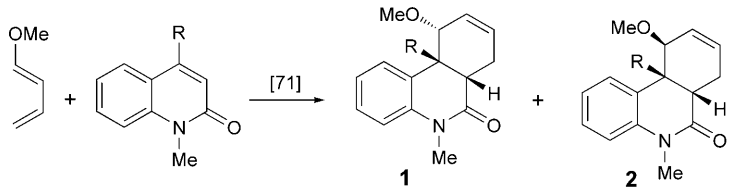


App. 29



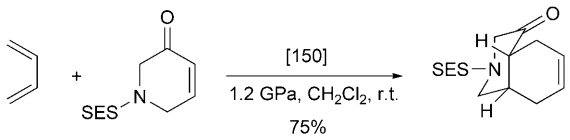
R	*P*	Solvent	*T*	*t*	Yield
MeOOC	0.1 MPa	*o*-xylene	180°	3 d	40%
MeOOC	1.0 GPa	CH_2Cl_2	120°	2 d	51%
CN	0.1 MPa	*o*-xylene	180°	3 d	46%
CN	1.0 GPa	CH_2Cl_2	120°	2 d	7%

App. 30

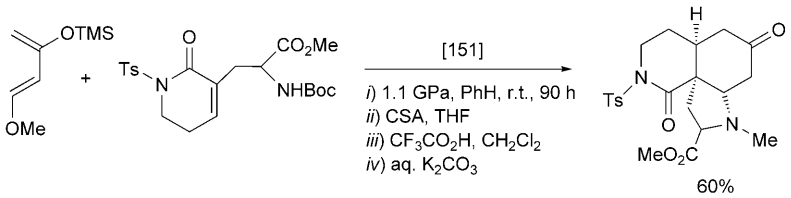


R	Condition	Solvent	*T*	*t*	**1**	**2**
MeOOC	sealed tube	*o*-xylene	180°	6 d	67%	21%
MeOOC	sealed tube	*o*-xylene	160°	4 d	14%	59%
MeOOC	1.0 GPa	CH_2Cl_2	90°	2 d	14%	20%
CN	sealed tube	*o*-xylene	180°	6 d	27%	30%
CN	sealed tube	*o*-xylene	180°	6 d	32%	24%
CN	1.0 GPa	CH_2Cl_2	90°	2 d	29%	31%

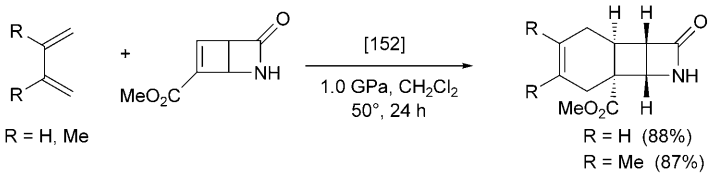
App. 31



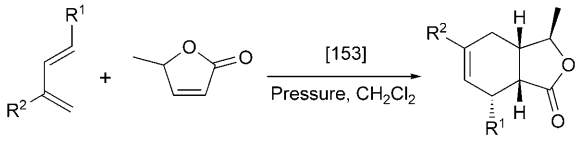
App. 32



App. 33

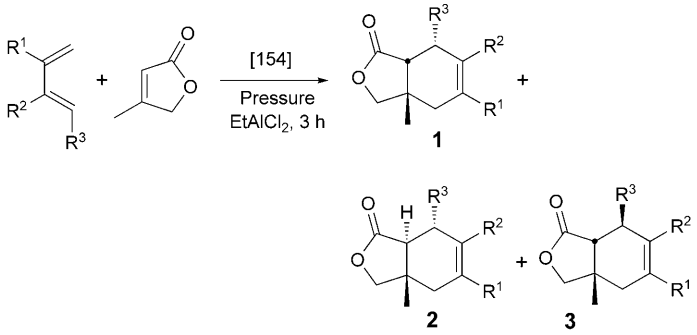


App. 34



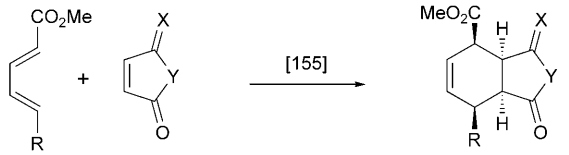
R^1	R^2	*P*	*T*	*t*	Yield
MeO	Me_3SiO	1.0 GPa	40°	48 h	90%
Me_3SiO	H	1.2 GPa	50°	65 h	85%

App. 35



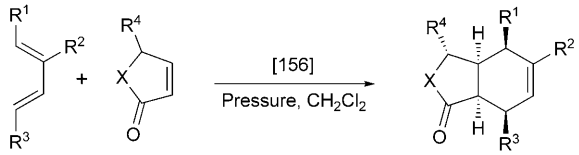
R^1	R^2	R^3	*P*	Solvent	*T*	*t*	Products	Yield
Me	H	H	1.2 GPa	$CH_2Cl_2/CHCl_3$ 2:1	65°	16 h	**1**	40%
H	H	Me	1.2 GPa	CH_2Cl_2	65°	3.5 h	**1/2** 10:27	65%
Me	Me	H	1.2 GPa	$CH_2Cl_2/CHCl_3$ 2:1	65°	16 h	**1**	34%
Me	H	Me	1.5 GPa	$CH_2Cl_2/CHCl_3$ 2:5	50°	16 h	**2/3** 27:10	30%

App. 36



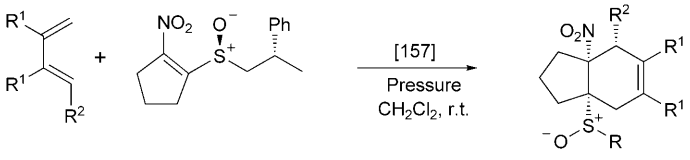
R	X	Y	*P*	Solvent	*T*	*t*	Yield
$MeOCH_2O$	O	O	0.1 MPa	CH_2Cl_2	20°	48 h	35%
$MeOCH_2O$	O	O	1.0 GPa	CH_2Cl_2	r.t.	24 h	80%
$MeOCH_2O$	H_2	CH_2	1.5 GPa	CH_2Cl_2	r.t.	4 d	85%
MeO	H_2	CH_2	1.7 GPa	CH_2Cl_2	r.t.	9 d	40%

App. 37

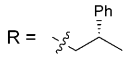


R^1	R^2	R^3	R^4	X	*P*	*T*	*t*	Yield
H	H	Me_3SiO	Me	O	1.2GPa	50°	65 h	85%
H	H	Me_3SiO	H	CH_2	1.2GPa	50°	65 h	70%
MeOOC	Et	MeO	Me	O	1.5GPa	50°	66 h	65%
MeOOC	H	MEM-O	H	CH_2	1.5GPa	75°	48 h	85%

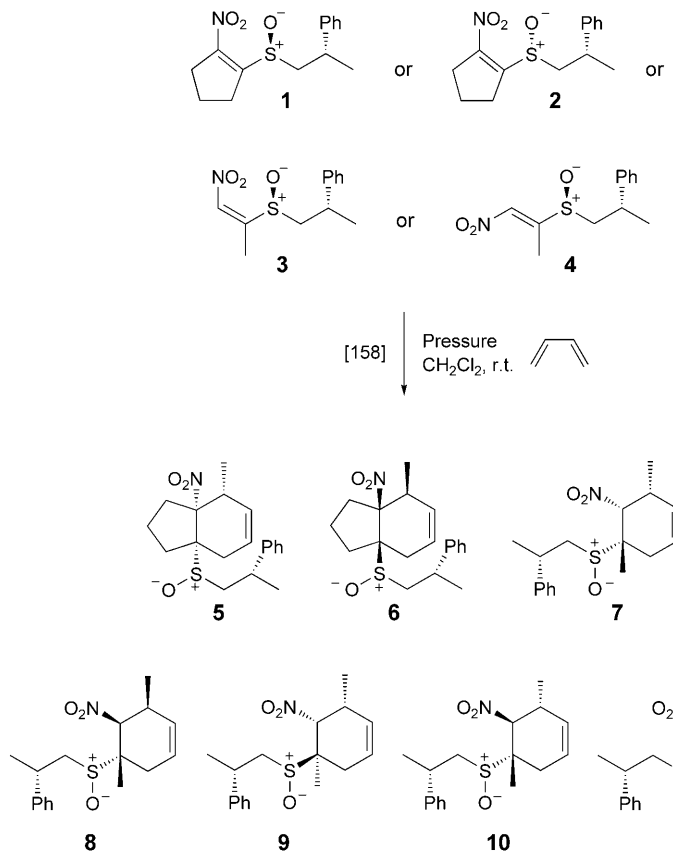
App. 38



R^1	R^2	*P*	*t*	Yield
H	Me	0.8 GPa	5 d	80%
H	Me	0.1 MPa	11 d	–
Me	H	0.8 GPa	5 d	77%

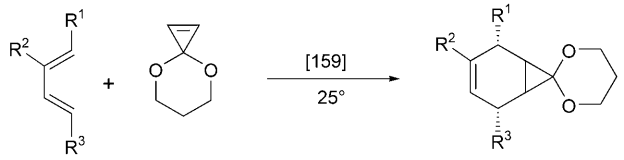


App. 39



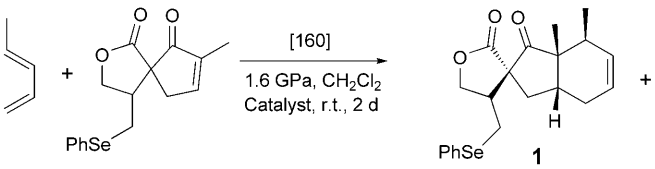
Dienophile	*P*	*t*	Products	Yield
1	0.8 GPa	5 d	**5**	80%
1	0.1 MPa	11 d	–	–
2	0.8 GPa	5 d	**6**	88%
3	0.8 GPa	5 d	**7**	81%
4	0.8 GPa	5 d	**8**/**9**/**10**/**11** 3:1:2:1	72%

App. 40

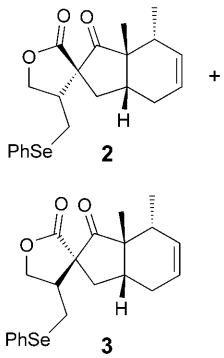


R^1	R^2	R^3	Pressure	Solvent	*t*	Yield
EtOOC	H	Me	0.1 MPa	neat	120 h	46%
EtOOC	H	Me	0.62 GPa	CH_2Cl_2	24 h	45%
H	Me	H	0.1 MPa	neat	113 h	57%
H	Me	H	0.62 GPa	neat	40 h	96%

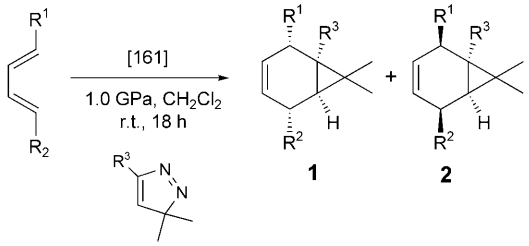
App. 41



Catalyst (equiv.)	Yield	**1/2/3**
none	34%	40:0:60
ZnI_2 (1.41)	76%	40:0:60
$AlCl_3$ (0.49)	83%	61:6:33
$MeAlCl_2$ (0.13)	49%	61:8:31
$BF_3{\cdot}OEt_2$ (0.55)	90%	51:10:39
$Eu(fod)_3$ (0.20)	76%	33:15:52
$SnCl_4$ (0.55)	48%	44:22:34
$TiCl_4$ (0.62)	82%	46:28:26
$TiCl_2(Oi\text{-}Pr)_2$ (0.61)	78%	45:25:30
TADDOL (87)	87%	31:35:34

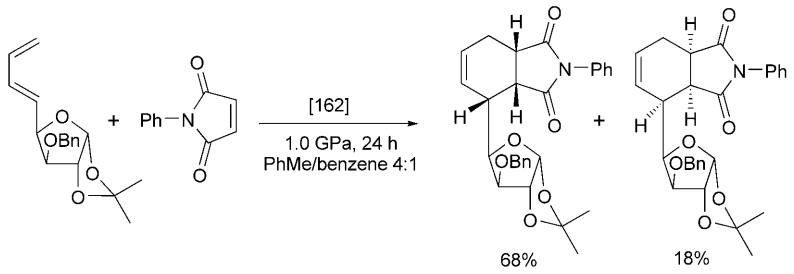


App. 42

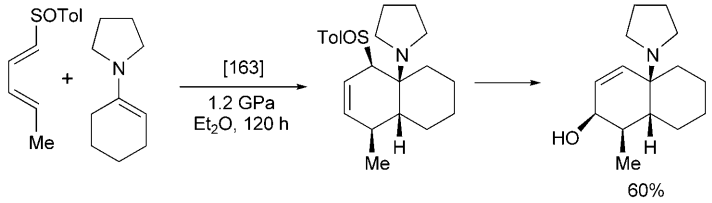


R^1	R^2	R^3	Yield	**1/2**
MeO	H	MeOOC	92%	1:22
Me_3SiO	H	MeOOC	89%	1:5
MeO	H	Ac	98%	1:19
$-CH_2CH_2-$		Ac	92%	1:50

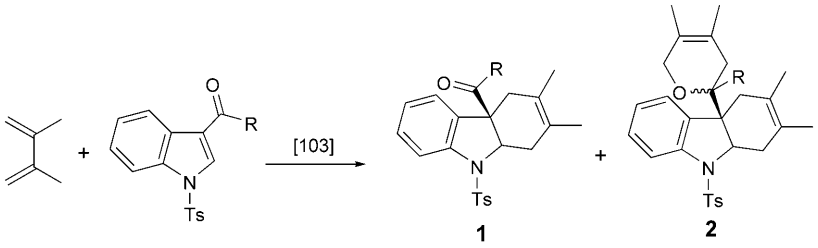
App. 43



App. 44

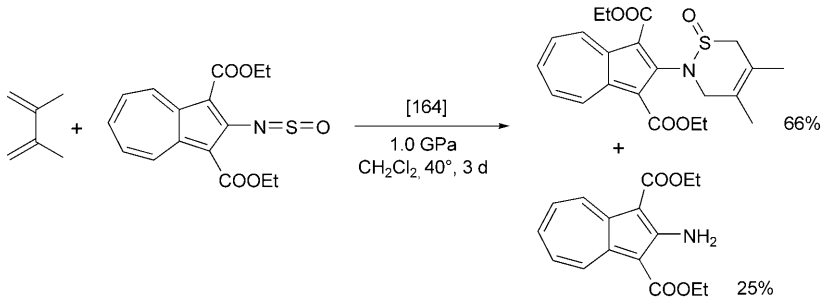


App. 45

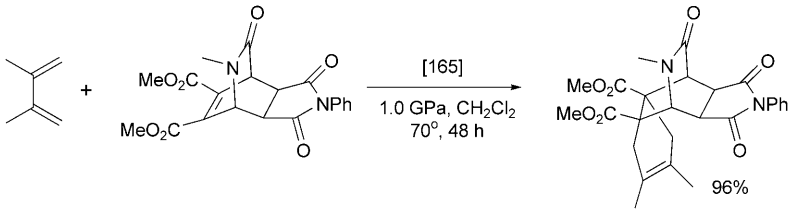


Equiv.	R	Condition	Solvent	Catalyst	*T*	*t*	Products	Conv.
12	H	sealed tube	PhMe	none	195°	80 h	**1**	85%
12	H	0.1 MPa	PhMe	$ZnCl_2$	110°	48 h	**1**/**2** 87:13	77%
12	H	1.2 GPa	CH_2Cl_2	$ZnCl_2$	25°	48 h	**1**/**2** 97:3	67%
6	MeOOC	1.6 GPa	CH_2Cl_2	$ZnCl_2$	25°	24 h	**2**	95%
12	MeOOC	1.6 GPa	CH_2Cl_2	none	50°	48 h	**1**	100%

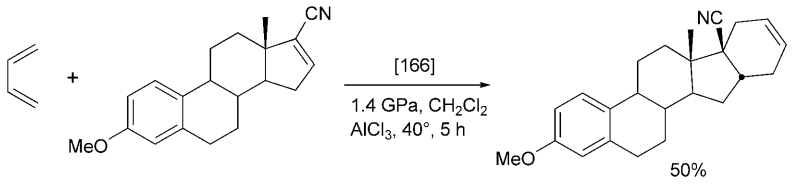
App. 46



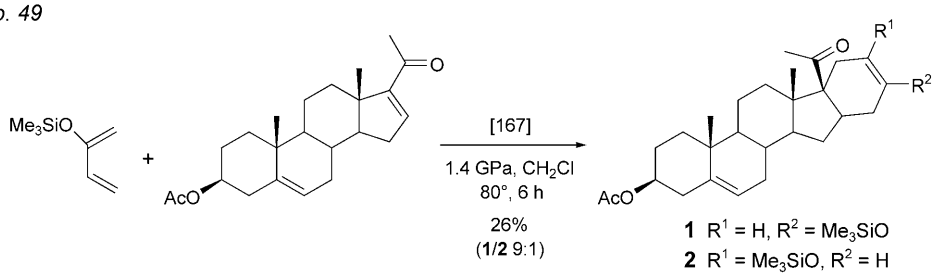
App. 47



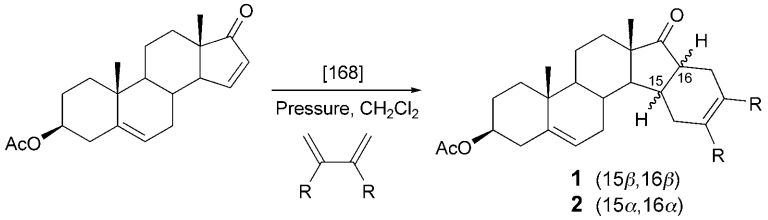
App. 48



App. 49

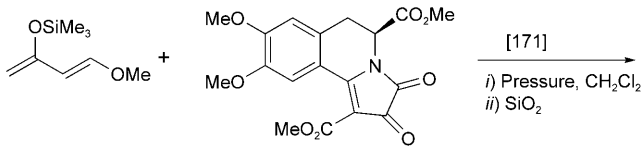


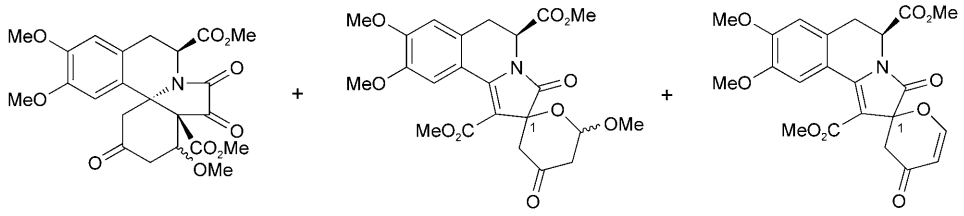
App. 50



R	Catalyst	*P*	*T*	*t*	**1**	**2**
H	-	1.4 GPa	80°	12 h	37%	7%
Me	-	1.4 GPa	80°	6 h	49%	26%
Me	$AlCl_3$	0.1 MPa	20°	24 h	–	28%

App. 51

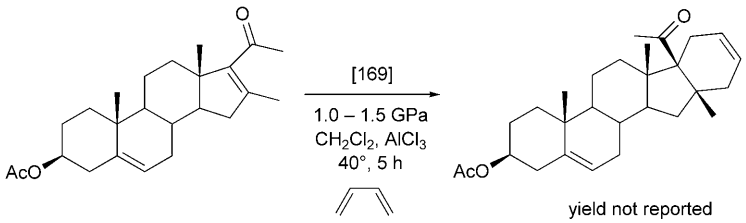




1 **2** (1*R*) **3** (1*S*) **4** (1*R*) **5** (1*S*)

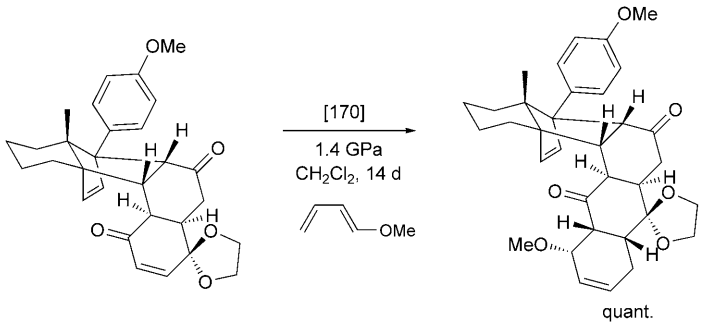
P	**1**	**2**	**3**	**4**	**5**
0.1 MPa	–	13%	–	45%	14%
1.0 GPa	40 – 50%	*ca.* 20%	trace	–	–

App. 52



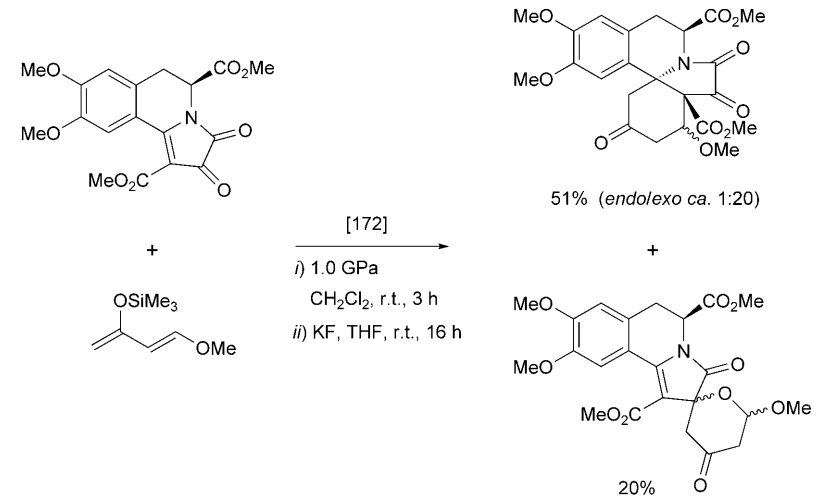
yield not reported

App. 53

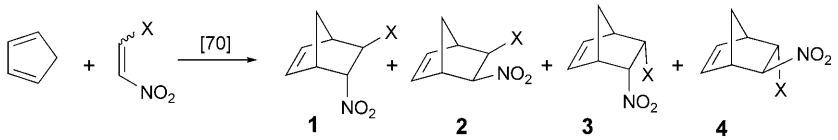


quant.

App. 54

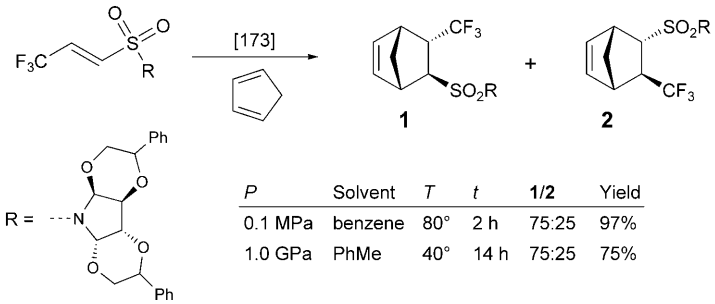


App. 55



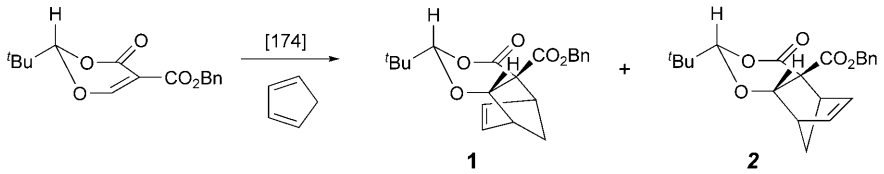
X	Conditions	Solvent	*T*	*t*	Yield	Products
PhS (*E*)	sealed tube	THF	110°	4 h	95%	**1/2** 88:12
PhSe (*Z*)	sealed tube	THF	110°	24 h	35%	**1/2/3/4** 31:26:34:9
PhS (*E*)	1.2 GPa	CH_2Cl_2	25°	72 h	82%	**1/2** 95:5
PhSe (*Z*)	1.6 GPa	CH_2Cl_2	50°	96 h	33%	**1/2/3** 25:12:63

App. 56



P	Solvent	*T*	*t*	**1/2**	Yield
0.1 MPa	benzene	80°	2 h	75:25	97%
1.0 GPa	PhMe	40°	14 h	75:25	75%

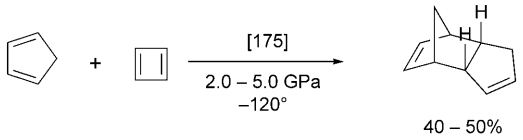
App. 57



1 **2**

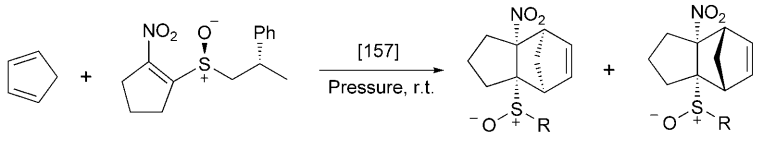
P	Solvent	Catalyst	*T*	*t*	**1**	**2**
0.1 MPa	PhMe	none	r.t.	10 d	–	20%
0.1 MPa	PhMe	Et_2AlCl	0°	2 h	–	31%
1.1 GPa	CH_2Cl_2	none	r.t.	2 d	6%	64%

App. 58



40 – 50%

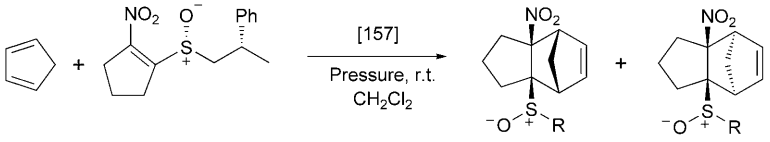
App. 59



1 **2**

P	Solvent	*t*	**1**	**2**
0.8 GPa	THF	5 d	39%	61%
0.1 MPa	CH_2Cl_2	11 d	14%	32%

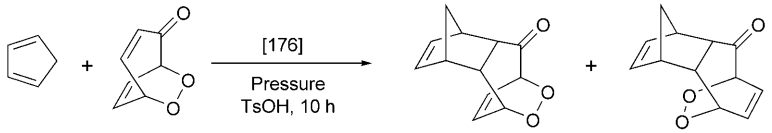
App. 60



1 **2**

P	*t*	**1**	**2**
0.8 GPa	5 d	41%	59%
0.1 MPa	7 d	19%	32%

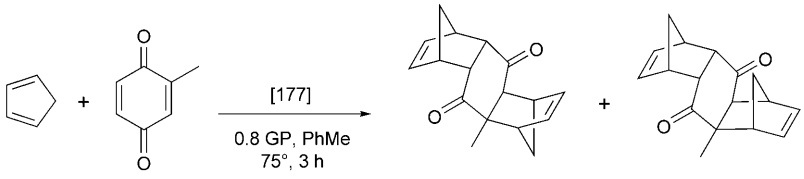
App. 61



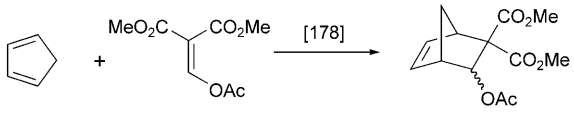
1 **2**

P	Solvent	*T*	**1**	**2**
0.1 MPa	benzene	80°	2%	3%
0.25 GPa	cumene	40°	36%	28%

App. 62

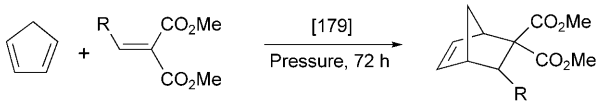


App. 63



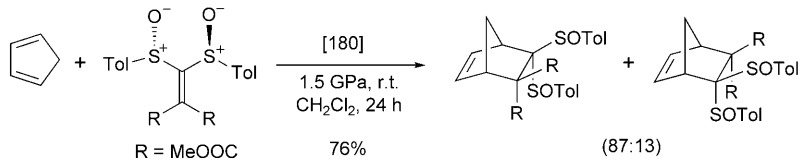
P	Solvent	Catalyst	*T*	*t*	Yield	*endo*/*exo*
0.1 MPa	benzene	none	80 – 90°	72 h	80%	0.33
0.1 MPa	PhMe	$TiCl_4$	15°	4 h	74%	1.50
1.3 GPa	PhMe	none	15°	60 h	95%	0.39

App. 64

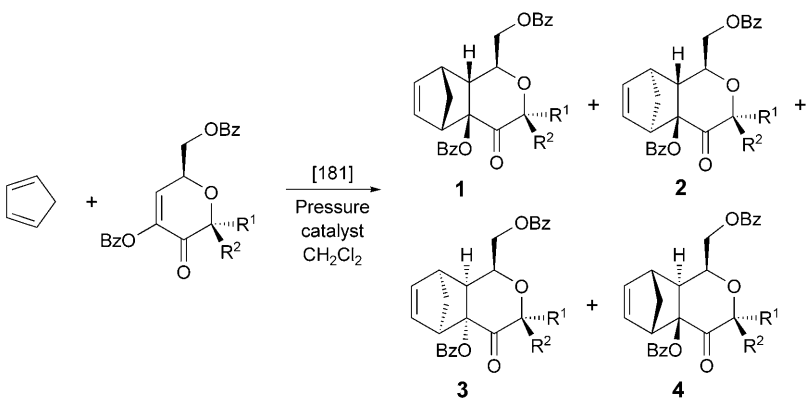


R	*P*	Solvent, catalyst	*T*	Yield	*endo*/*exo*
AcNH	0.1 MPa	Et_2O, $LiClO_4$	r.t.	21%	3.07
AcNH	1.1 GPa	PhMe	r.t.	22%	0.29
AcNH	1.1 GPa	PhMe	60°	38%	0.36
AcNH	1.1 GPa	CH_2Cl_2, $ZnCl_2$	r.t.	57%	0.33
MeO	0.1 MPa	Et_2O, $LiClO_4$	r.t.	40%	2.00
MeO	1.1 GPa	PhMe	r.t.	–	–

App. 65

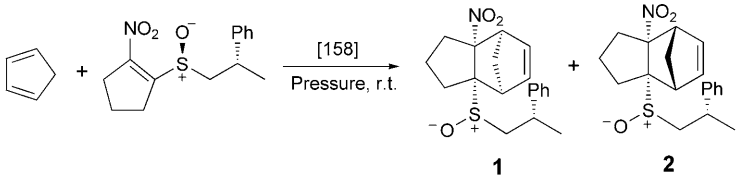


App. 66



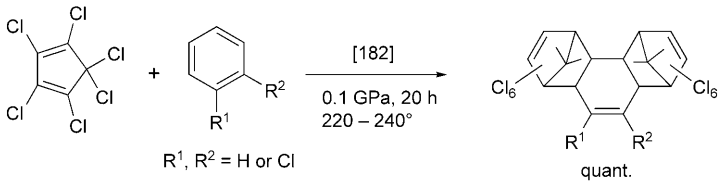
R^1	R^2	*P*	Catalyst	*T*	*t*	Yield [%]			
						1	**2**	**3**	**4**
H	MeO	0.1 MPa	$AlCl_3$	–78°	1 h	41	trace	–	–
H	MeO	0.1 MPa	$AlCl_3$	–25°	18 h	42	8	trace	3
H	MeO	0.1 MPa	$TiCl_4$	–78°	40 min	81	1	–	–
H	MeO	0.1 MPa	$SnCl_4$	–78°	20 min	45	1	1	4
H	H	1.5 GPa	none	25°	2 d	53	11	17	4
MeO	H	1.5 GPa	none	25°	2 d	3	3	33	5
BzO	H	1.5 GPa	none	25°	2 d	11	3	69	11
H	MeO	1.5 GPa	none	25°	2 d	84	11	1	1

App. 67

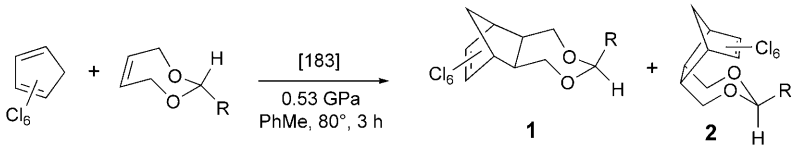


P	Solvent	*t*	**1**	**2**
0.8 GPa	THF	5 d	39%	61%
0.1 MPa	CH_2Cl_2	11 d	14%	32%

App. 68

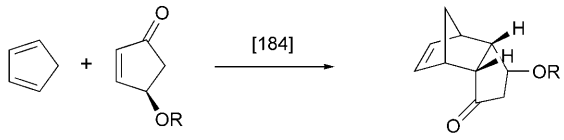


App. 69



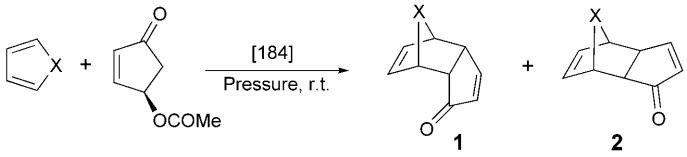
R = Me (**1**/**2** 65:35)
R = Et (**1**/**2** 70:30)

App. 70



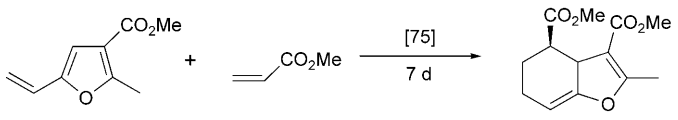
R	Conditions	Catalyst	*T*	*t*	Yield (ee)
Ac	0.1 MPa, MeCN	$ZnCl_2$	r.t.	90 h	86% (46)
Ac	1.5 GPa, benzene	$ZnCl_2$	r.t.	19 h	90% (47)
Ac	1.5 GPa, MeCN	$ZnCl_2$	r.t.	18 h	64% (41)
H	1.5 GPa, benzene	none	r.t.	16 h	54% (59)
Ac	1.5 GPa, benzene	none	r.t.	16 h	77% (63)
H	ultrasound, H_2O	none	45°	22 h	82% (82)
Ac	*Baker*'s yeast, buffer	none	37°	24 h	72% (64)

App. 71



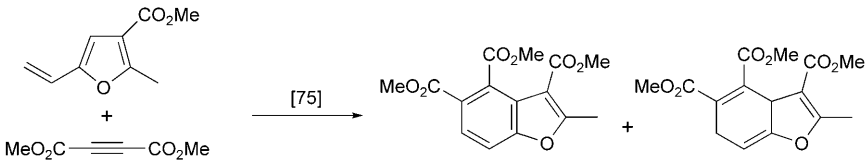
X	*P*	Solvent	Catalyst	*t*	Yield	ee
CH_2	0.1 MPa	benzene	$ZnCl_2$	19 h	95%	48% (**1**)
$(CH_2)_2$	1.2 GPa	MeCN	$ZnCl_2$	18 h	68%	63% (**1**)
$(CH_2)_2$	1.5 GPa	benzene	none	18 h	51%	59% (**1**)
$(CH_2)_3$	1.5 GPa	MeCN	$ZnCl_2$	17 h	–	–
O	1.2 GPa	MeCN	$ZnCl_2$	3 d	35%	53% (**2**)

App. 72



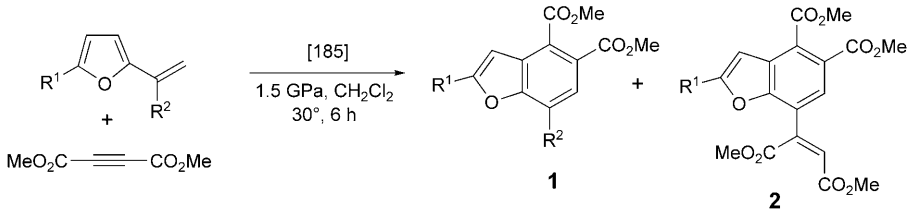
0.1 MPa, Et_2O, reflux	0%
1.1 GPa, CH_2Cl_2, 30°	23%

App. 73



0.1 MPa, Et_2O, reflux, 19 d	61%	0%
1.9 GPa, CH_2Cl_2, 25°, 1 d	49%	24%

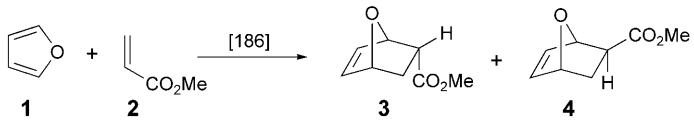
App. 74



1 **2**

R^1	R^2	Molar ratio	**1**	**2**
H	H	1:1	33%	–
Me	H	1:1	28%	–
H	OAc	1:1	20%	25%
H	OAc	1:2	16%	36%

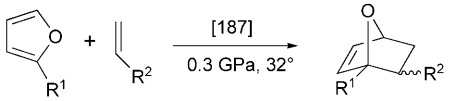
App. 75



1 **2** **3** **4**

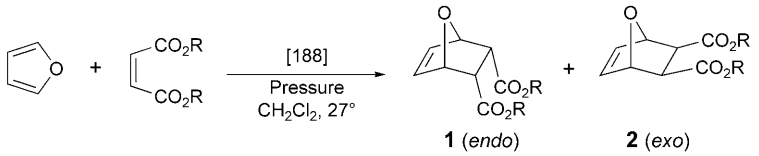
1/2	*P*	*T*	*t*	Yield	**3/4**
2:1	0.21 GPa	25°	24 h	2%	1.3:1
2:1	0.21 GPa	25°	72 h	16%	1.2:1
2:1	0.21 GPa	25°	168 h	33%	1.2:1
1:2	0.6 GPa	25°	168 h	10%	1.2:1
1:2	0.21 GPa	70°	24 h	55%	1:1.5
2:1	0.21 GPa	70°	24 h	21%	1:1.4
1:1	0.21 GPa	70°	24 h	38%	1:2.0

App. 76



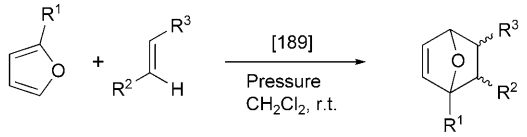
R^1	R^2	Solvent	*endo*
H	Ac	Et_2O	80%
H	CN	Et_2O	66%
Me	MeOOC	Et_2O	60%
H	Ac	CH_2Cl_2	74%

App. 77



R	*P*	*t*	Yield	**1/2**
Me	2.0 GPa	8 h	94%	81:19
Bu	1.5 GPa	6h	37%	83:17

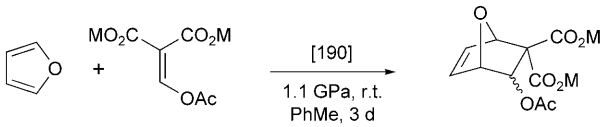
App. 78



R^1	R^2	R^3	*P*	*t*	Yield	*endo*/*exo*
MeS	MeOOC	H	1.5 GPa	8 h	64%	2:1
AcO	ClOC	H	0.1 MPa [a])	96 h	>90%	1:1
AcO	MeOOC	MeOOC	1.5 GPa	8 h	54%	1:0

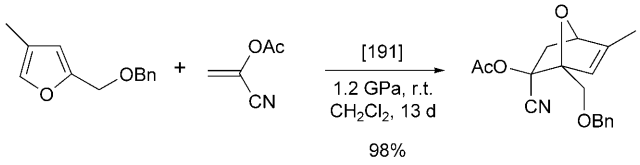
[a]) In the presence of a few drops of proxylene oxide

App. 79

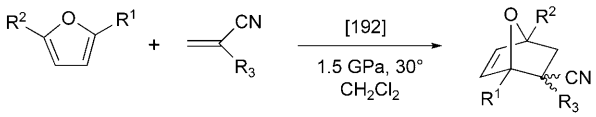


40% *endo* (54% de)
20% *exo* (61% de)

App. 80

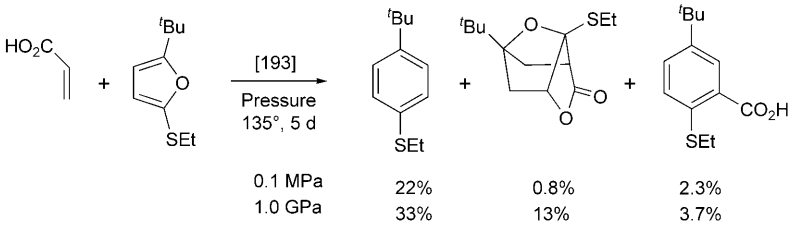


App. 81

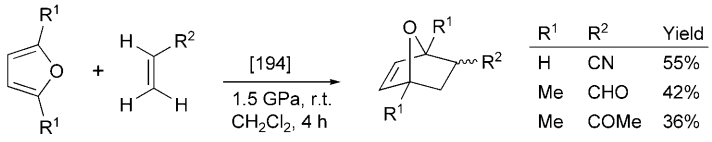


R^1	R^2	R^3	*t*	Yield
H	H	Cl	8 h	83%
Me	H	Cl	8 h	85%
Me	Me	Cl	8 h	85%
	H	OAc	15 h	65%

App. 82

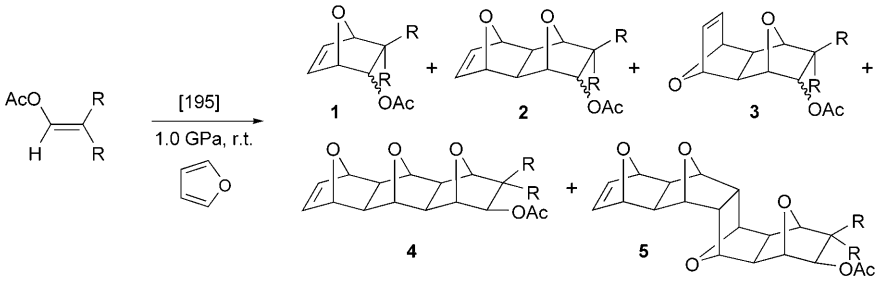


App. 83



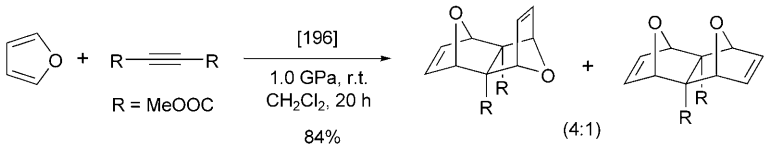
R^1	R^2	Yield
H	CN	55%
Me	CHO	42%
Me	COMe	36%

App. 84

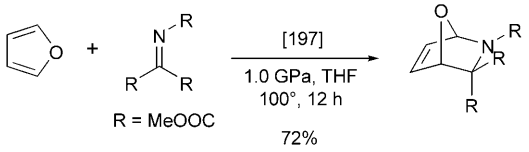


R	*t*	*endo*-**1**	*exo*-**1**	*endo*-**2**	*exo*-**2**	*endo*-**3**	*exo*-**3**	**4**	**5**
MeOOC	10 d	mixture	mixture	–	–	–	–	–	–
EtOOC	9 d	36.4%	4.1%	mixture	5.1%	6.8%	mixture	0.5%	0.4%

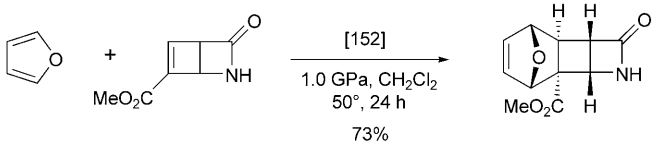
App. 85



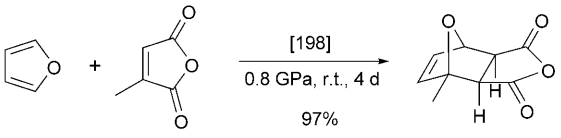
App. 86



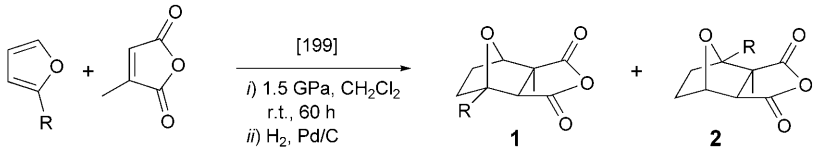
App. 87



App. 88

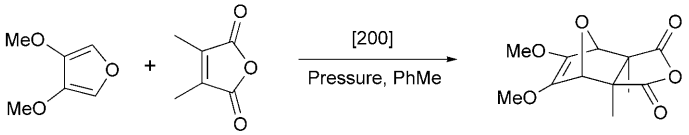


App. 89



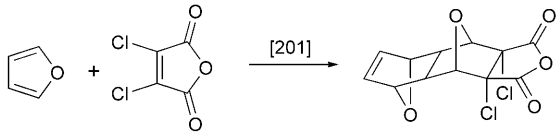
R	Yield	**1/2**
EtO_2C	0%	–
$^tBuO_2CCH_2$	54%	1:1
MeO_2CCH_2	59%	5:6
$BnOCH_2$	31%	7:5

App. 90



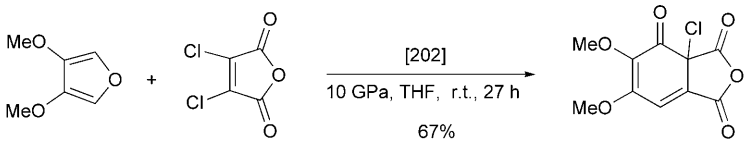
P	*T*	*t*	Yield
1.0 GPa	r.t.	6 h	–
1.0 GPa	60°	16 h	–
2.2 GPa	60°	16 h	50%

App. 91

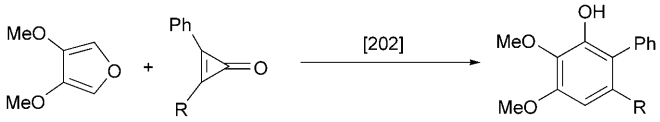


P	Solvent	*T*	*t*	Yield
sealed tube	neat	r.t.	14 d	complex mixture
sealed tube	neat	80 – 90°	3 d	complex mixture
0.5 GPa	THF	50°	15 h	22%

App. 92

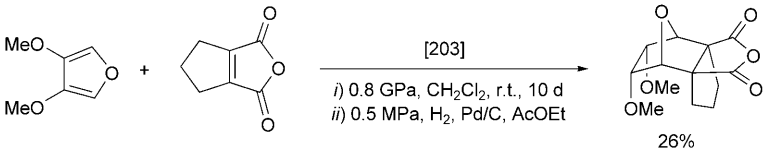


App. 93

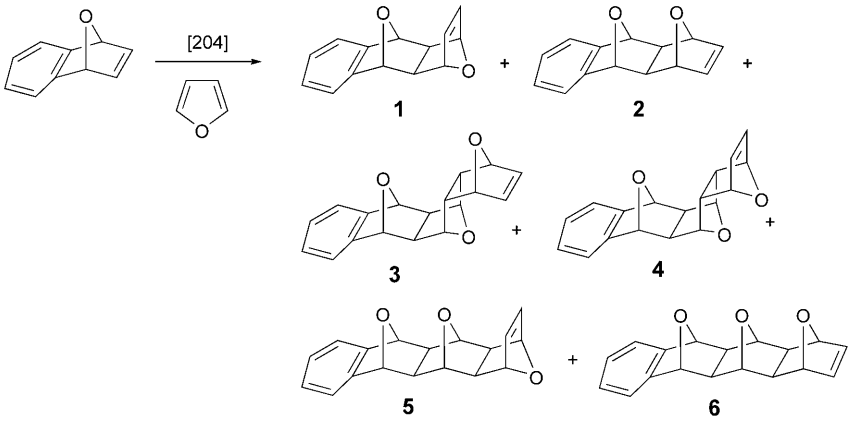


R	*P*	Solvent	*T*	*t*	Yield
Ph	0.1 MPa	toluene	reflux	44 h	24%
Ph	0.8 GPa	CH_2Cl_2	55°	48 h	51%
Me	0.1 MPa	toluene	reflux	46 h	9%
Me	0.8 GPa	CH_2Cl_2	55°	48 h	68%

App. 94

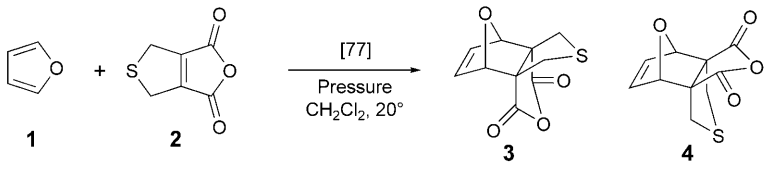


App. 95



Condition	Solvent	*T*	*t*	**1/2/3/4/5/6**
sealed tube	$CHCl_3$	150°	12 h	2:2:1:tr:tr:tr (tr = trace)
1.4 GPa	CH_2Cl_2	r.t.	3 d	0:17:6:8:3:tr
0.8 GPa	CH_2Cl_2	r.t.	3 d	90:3:7:0:0:0
0.8 GPa	CH_2Cl_2	r.t.	12 h	90:2:8:0:0:0
microwave	$CHCl_3$	r.t.	30 min	100:tr:tr:0:0:0

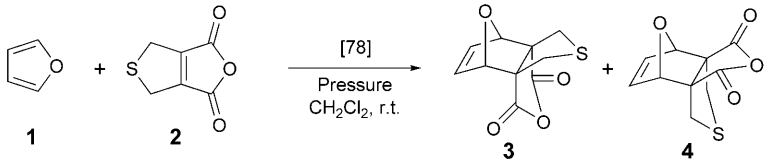
App. 96



1 **2** **3** **4**

1/2	*P*	*t*	Conversion	**3/4**
26	0.7 GPa	24 h	95%	20:80
34	0.7 GPa	29 h	100%	20:80
62	0.1 MPa	144 h	95%	20:80

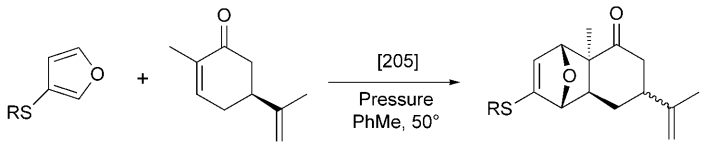
App. 97



1 **2** **3** **4**

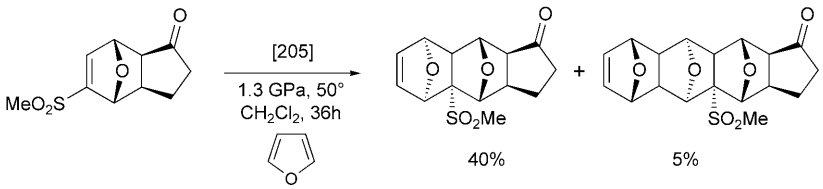
1/2	*P*	*t*	Yield	**3/4**
1.2	1.5 GPa	6 h	quant.	15:85
1.2	0.8 GPa	42 h	79%	15:85
3.4	0.4 GPa	88 h	57%	15:85

App. 98



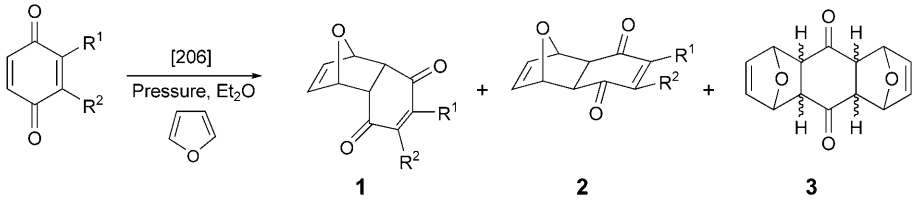
R	*P*	*t*	Yield
Me	1.5 GPa	48 h	23%
Ph	1.5 GPa	72 h	–

App. 99



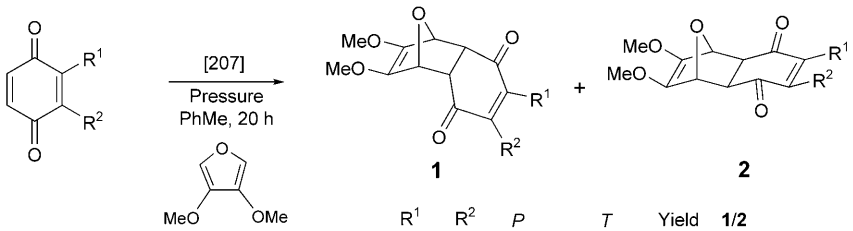
40% 5%

App. 100



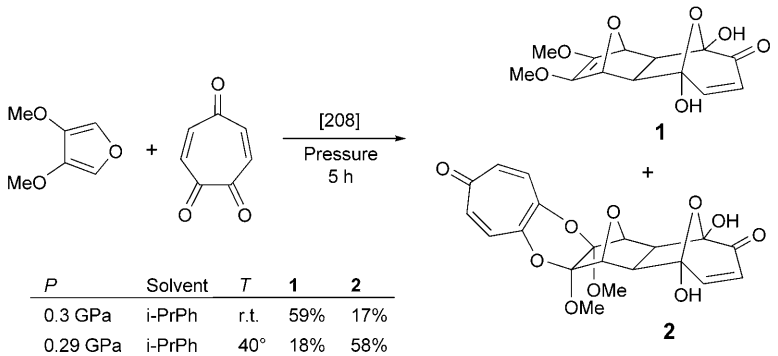
R^1	R^2	*P*	*T*	*t*	**1**	**2**	**3**
H	H	2.0 GPa	r.t.	68 h	14%	15%	–
H	Me	2.0 GPa	r.t.	68 h	10%	28%	–
Me	MeO	2.0 GPa	r.t.	68 h	10%	18%	–
H	H	2.2 GPa	60°	8 h	–	–	*ca.* 50%

App. 101



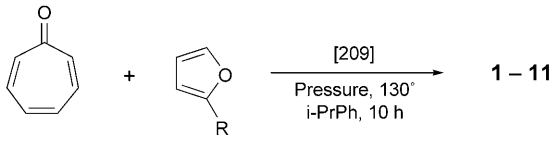
R^1	R^2	*P*	*T*	Yield	**1/2**
H	H	0.7 GPa	25°	90%	89:11
MeO	MeO	1.9 GPa	50°	92%	70:30

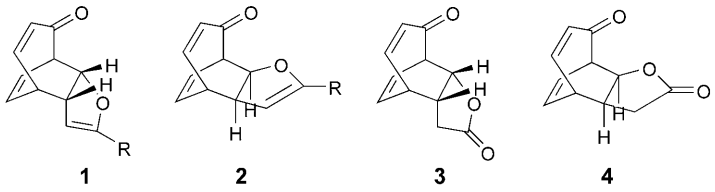
App. 102

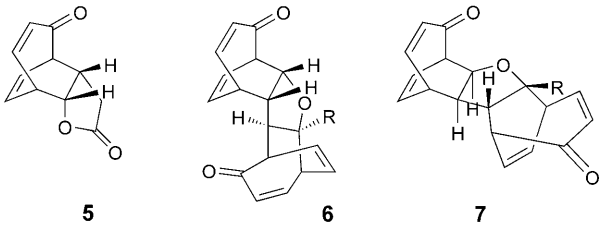


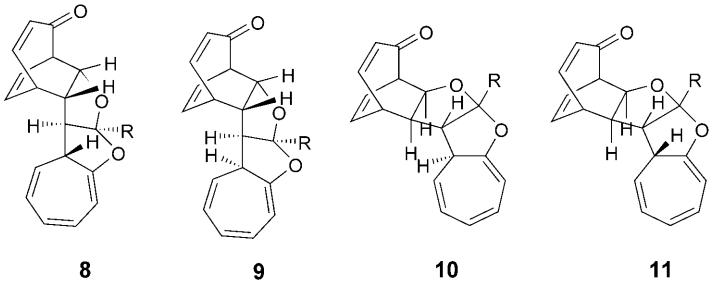
P	Solvent	*T*	**1**	**2**
0.3 GPa	i-PrPh	r.t.	59%	17%
0.29 GPa	i-PrPh	40°	18%	58%
0.1 MPa	Benzene	r.t.	49%	–

App. 103



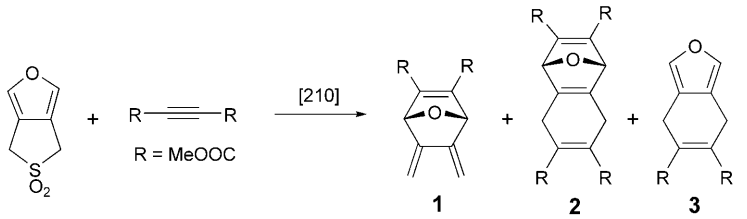






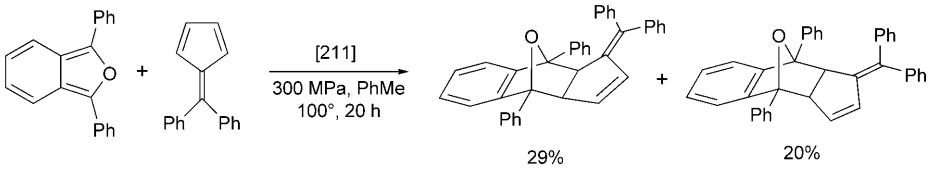
R	Condition	1	2	3	4	5	6	7	8	9	10	11
H	sealed tube	–	–	–	–	–	–	–	–	–	–	–
H	0.3 GPa	6%	5%	–	–	–	–	–	–	–	–	–
MeO	sealed tube	–	–	13%	3%	–	–	–	–	–	–	–
MeO	0.3 GPa	–	–	35%	13%	1%	6%	0.5%	4%	3%	3%	2%

App. 104

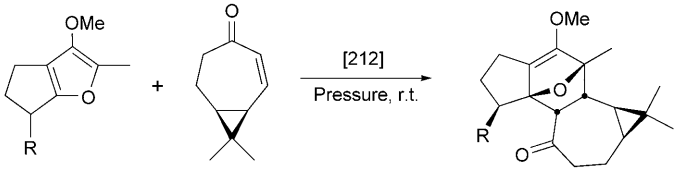


Equiv.	Condition	Solvent	*T*	*t*	**1**	**2**	**3**
3	sealed tube	benzene	150°	1 h	45%	47%	–
3	0.1 MPa	CH_2Cl_2	0°	90 d	quant.	–	–
3	0.4 GPa	CH_2Cl_2	28°	24 h	97%	–	3%

App. 105

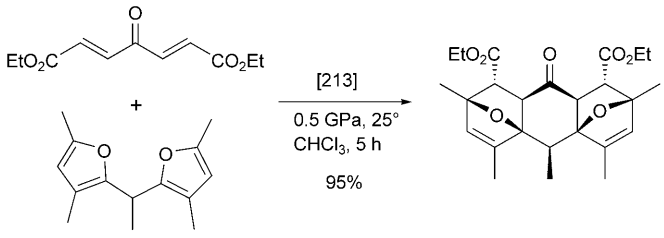


App. 106

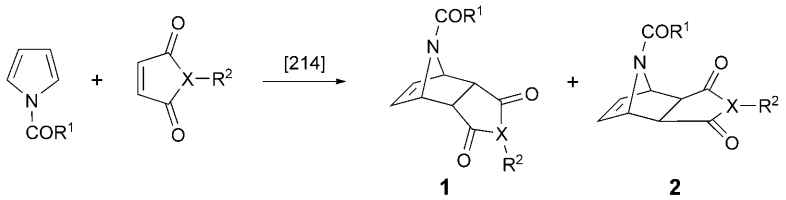


R	*P*	*t*	Yield
H	0.5 GPa	72 h	80%
BnO	0.5 GPa	4 d	2.4%
BnO	0.7 GPa	14 d	19%

App. 107

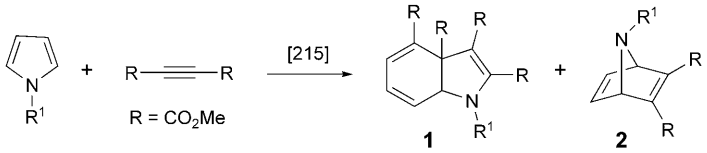


App. 108



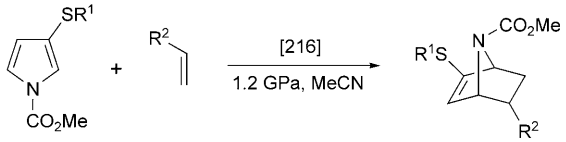
R^1	X	R^2	*P*	Solvent	*T*	*t*	**1**	**2**
Ph	N	Ph	1.4 GPa	AcOEt	34°	90 h	45%	46%
Ph	N	Ph	1.1 GPa	CH_2Cl_2	40°	18 h	–	–
EtO	O	–	1.2 GPa	CH_2Cl_2	24°	160 h	–	26%
BnO	N	Ph	1.4 GPa	CH_2Cl_2	30°	48 h	90%	–
4-Cl-C_6H_4	N	Ph	1.2 GPa	CH_2Cl_2	30°	24 h	90%	–

App. 109



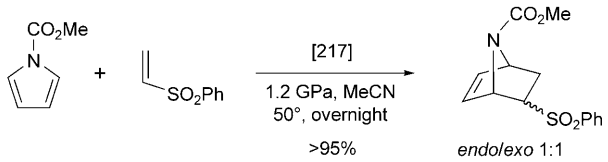
R^1	*P*	Solvent	*T*	*t*	Yield
H	0.1 MPa	neat	r.t.	90 h	–
H	1.5 GPa	CH_2Cl_2	40°	15 h	–
Me	0.1 MPa	neat	r.t.	48 h	70% (**1**)
Me	0.1 MPa	Et_2O	reflux	96 h	>80% (**1**)
Me	1.5 GPa	CH_2Cl_2	40°	17 h	50% (**1**)
Me	1.5 GPa	CH_2Cl_2	40°	6 h	quant. (**1**)
Ac	0.1 MPa	neat	125°	7 h	45 (**2**)
Ac	1.5 GPa	CH_2Cl_2	40°	4 h	57% (**2**)
Ac	1.5 GPa	CH_2Cl_2	40°	24 h	83% (**2**)

App. 110

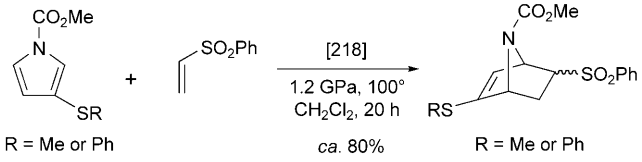


R^1	R^2	*T*	*t*	Yield	*endo*/*exo*
Me	PhO_2S	r.t.	6 h	9%	not reported
Ph	PhO_2S	r.t.	6 h	58%	not reported
Ph	PhO_2S	50°	16 h	*ca.* 80%	1:1

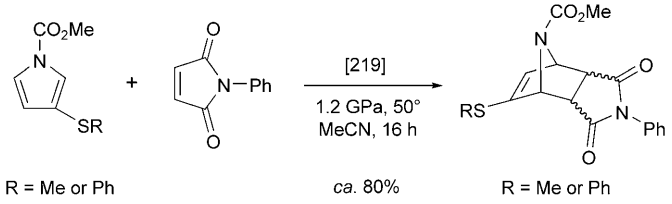
App. 111



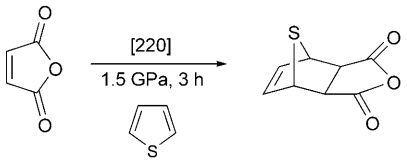
App. 112



App. 113

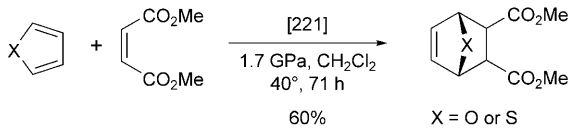


App. 114

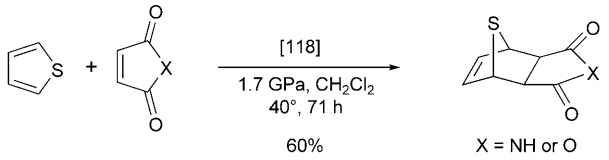


Solvent	*T*	Yield
CH_2Cl_2	r.t.	–
CH_2Cl_2	40°	–
CH_2Cl_2	80°	8%
CH_2Cl_2	100°	37 – 47%
acetone	100°	–

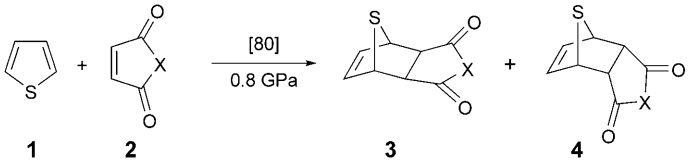
App. 115



App. 116

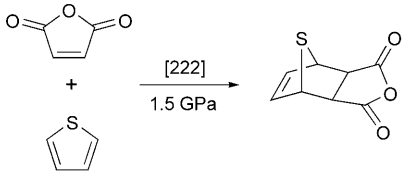


App. 117



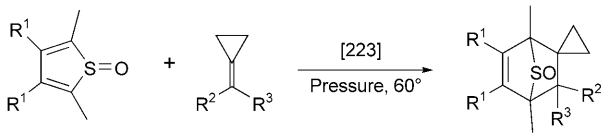
X	**1/2**	Solvent	*T*	*t*	**3**	**4**
O	1:1	CH_2Cl_2	100°	2 d	19%	–
O	4:1	CH_2Cl_2	100°	2 d	21%	–
O	4:1	$Cl_2CHCHCl_2$	100°	2 d	23%	–
O	4:1	C_6F_{14}	100°	2 d	77%	–
O	4:1	neat	100°	2 d	93%	–
O	2:1	neat	100°	2d	87%	–
PhN	4:1	neat	100°	2 d	48%	51%
MeN	4:1	neat	80°	7 d	34%	47%
MeON	4:1	neat	80°	7 d	35%	58%

App. 118



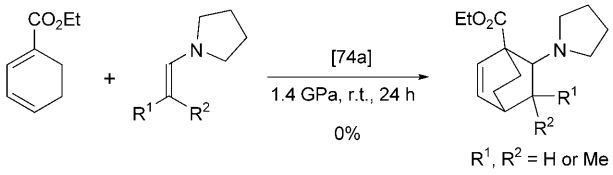
Solvent	*T*	*t*	Yield
CH_2Cl_2	r.t.	3 d	–
CH_2Cl_2	40°	3 h	–
CH_2Cl_2	80°	3 h	8%
CH_2Cl_2	100°	3 h	37 – 47%
CH_2Cl_2	120°	3 h	18%
CH_2Cl_2	150°	3 h	–
$CHCl_2CHCl_2$	100°	3 h	47%
benzene	100°	3 h	6 – 7%
AcOEt	100°	3 h	15 – 19%

App. 119

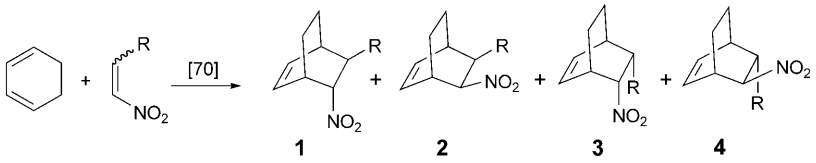


R^1	R^2	R^3	*P*	Solvent	*t*	Yield
Bn	MeOOC	Cl	0.1 MPa	$CHCl_3$	24 h	60%
Bn	MeOOC	Cl	1.0 GPa	MeCN	24 h	92%
4-^{t}Bu-C_6H_4-CH_2	$-CH_2CH_2-$		1.0 GPa	MeCN	5 d	48%
Bn	$-CH_2CH_2-$		1.0 GPa	MeCN	5 d	43%
4-^{t}Bu-C_6H_4-CH_2	$-CH_2CH_2-$		1.0 GPa	MeCN	24 h	31%
Bn	$-CH_2CH_2-$		1.0 GPa	MeCN	24 h	39%
Bn	MeOOC	Me	1.0 GPa	MeCN	24 h	–
Bn	MeOOC	H	1.0 GPa	MeCN	24 h	–
Bn	MeOOC	Br	1.0 GPa	MeCN	24 h	slow reaction

App. 120

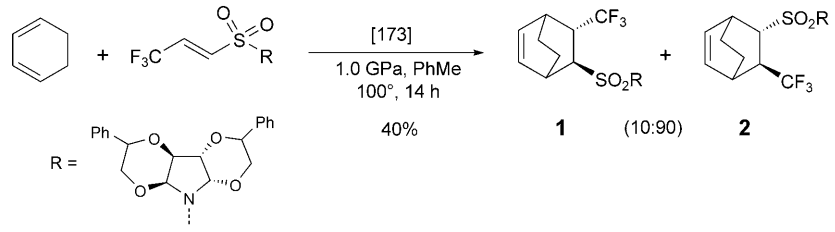


App. 121

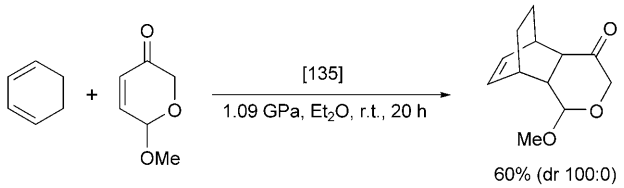


R	Condition	Solvent	*T*	*t*	Yield	Products
PhS (*E*)	sealed tube	THF	130°	72 h	75%	**1/2** 80:20
PhSe (*Z*)	sealed tube	THF	120°	264 h	16%	**3/4** 25:75
PhS (*E*)	1.2 GPa	CH_2Cl_2	25°	48 h	33%	**1/2** 84:16
PhS (*E*)	1.6 GPa	CH_2Cl_2	50°	24 h	49%	**1/2** 99:1
PhSe (*Z*)	1.2 GPa	CH_2Cl_2	50°	96 h	65%	**3/4** 46:54
PhSe (*Z*)	1.6 GPa	CH_2Cl_2	25°	24 h	70%	**2/3/4** 13:66:21

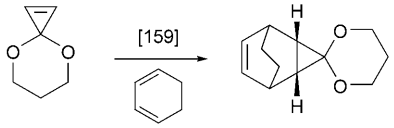
App. 122



App. 123

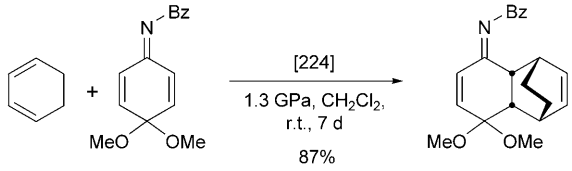


App. 124

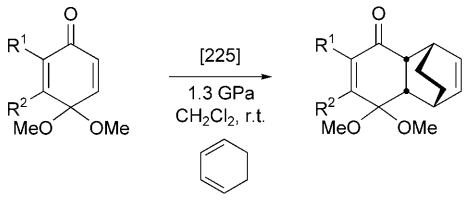


P	Solvent	*T*	*t*	Yield
0.1 MPa	neat	25°	14 d	–
0.1 MPa	benzene	80°	22 h	–
0.62 GPa	neat	25°	7 d	25%

App. 125

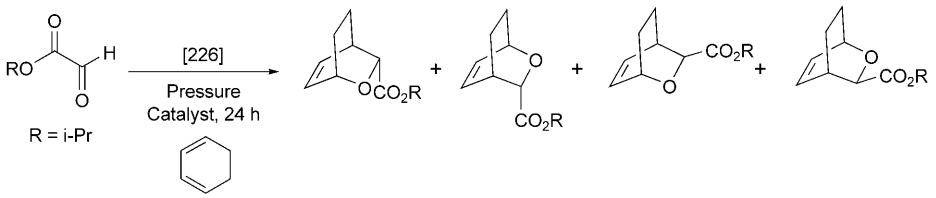


App. 126

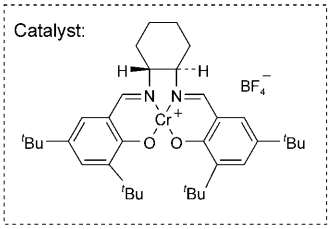


R^1	R^2	*t*	Yield
Et	H	2 d	86%
H	Me	3.5 d	63%

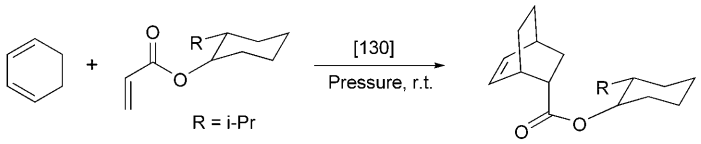
App. 127



P	Solvent	*T*	Yield	*endo*/*exo*	ee (*endo*)	ee (*exo*)
0.1 MPa	PhMe	25°	84%	70:30	80%	10%
0.1 MPa	PhMe	–15°	53%	75:25	84%	12%
0.1 MPa	PhMe	–15°	47%	80:20	90%	10%
0.1 MPa	CH_2Cl_2	25°	90%	45:55	52%	5%
0.1 MPa	anisol	25°	65%	62:38	69%	13%
0.1 MPa	*t*-BuOMe	25°	68%	60:40	65%	14%
1.0 GPa	PhMe	25°	83%	45:55	58%	31%

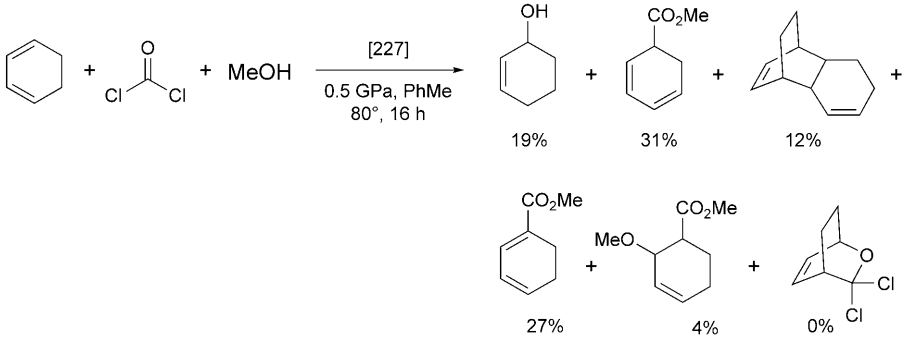


App. 128

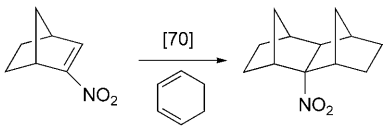


P	Solvent	Yield	ee
0.82 GPa	PhMe/benzene 7:3	65%	3.9%
0.91 GPa	PhMe/benzene 7:3	67%	4.7%
1.00 GPa	PhMe/benzene 7:3	74%	5.4%
1.25 GPa	PhMe/benzene 7:3	79%	7.5%
0.79 GPa	hexane	55%	1.7%
1.04 GPa	hexane	59%	3.5%
1.20 GPa	hexane	70%	4.3%
0.77 GPa	CH_2Cl_2	75%	1.5%

App. 129

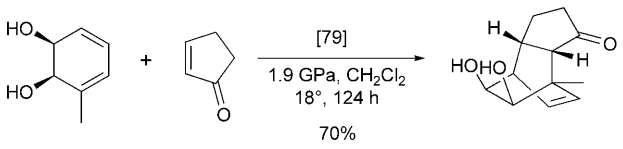


App. 130

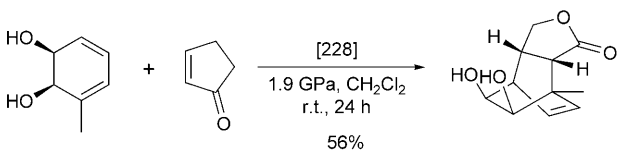


P	Solvent	*T*	*t*	Yield
0.1 MPa	neat	130°	3 h	81%
1.2 GPa	CH_2Cl_2	25°	96 h	70%
1.6 GPa	CH_2Cl_2	25°	96 h	71%

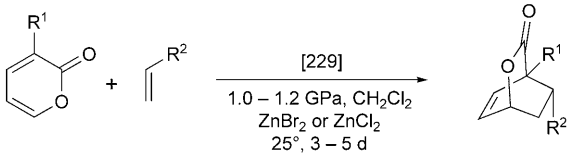
App. 131



App. 132

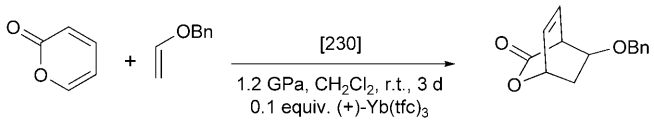


App. 133

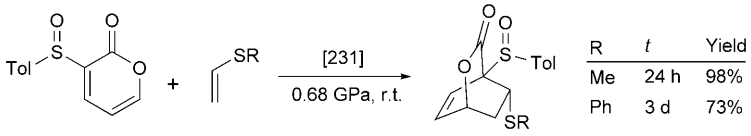


R^1	R^2	Yield	*endo*/*exo* (*syn*)	*endo*/*exo* (*anti*)
Br	C_3H_7	99%	3:1	–
Br	$(EtO)_3SiCH_2$	80%	>20:1	>20:1
Br	^{t}Bu(Me)$_2$SiO(CH$_2$)$_2$	60%	>20:1	4:1
Br	BnO(CH$_2$)$_2$	–	–	–
MeOOC	^{t}Bu(Me)$_2$SiO(CH$_2$)$_2$	77%	25:1	8:1
MeOOC	$(EtO)_3SiCH_2$	76% *endo*, 9% *exo*	–	–
MeOOC	Bn	64% *endo*, 13% *exo*	–	–

App. 134

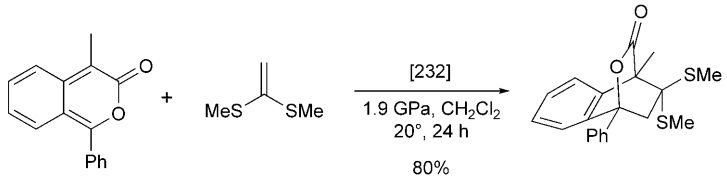


App. 135

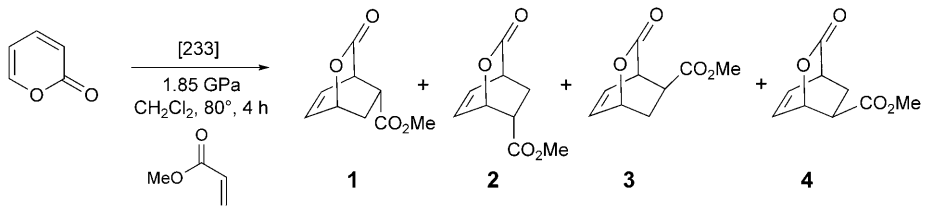


R	*t*	Yield
Me	24 h	98%
Ph	3 d	73%

App. 136

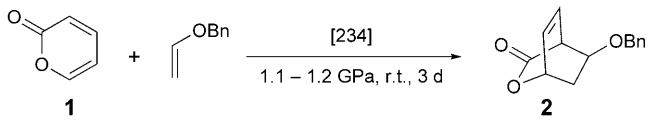


App. 137



(**1**/**2**/**3**/**4** 85:35:15:7)

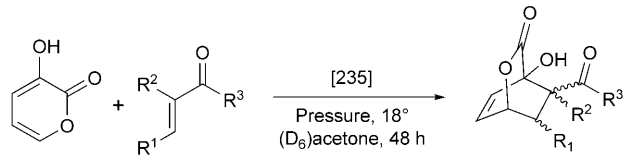
App. 138



1 **2**

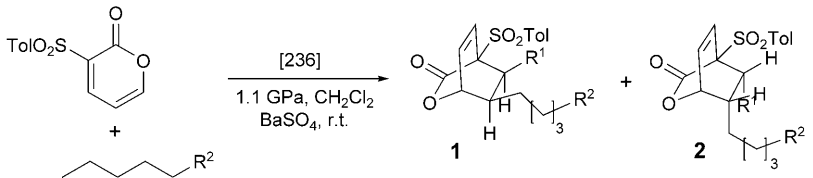
Equiv (**1**)	Solvent	Catalyst	**2**
2	neat	(+)-Yb(tfc)$_3$	91%
2	neat	Yb(fod)$_3$	72%
5	neat	Yb(fod)$_3$	94%
2	neat	Yb(NO$_3$)$_3$·5 H$_2$O	31%
5	neat	Yb(NO$_3$)$_3$·5 H$_2$O	90%
2	neat	ZnCl$_2$	24%
5	neat	ZnCl$_2$	73%
5	CH_2Cl_2	ZnCl$_2$	92%

App. 139



R^1	R^2	R^3	*P*	*endo*/*exo*
H	H	Me	1.7 GPa	>10:1a
H	Me	MeO	3.2 GPa	3:1
Me	H	MeO	4.0 GPa	3:2

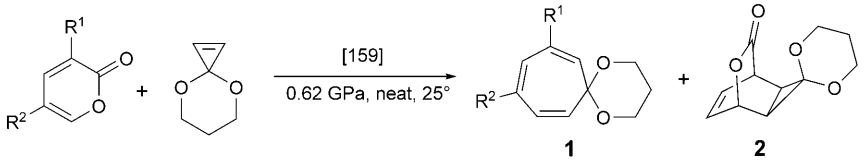
App. 140



1 **2**

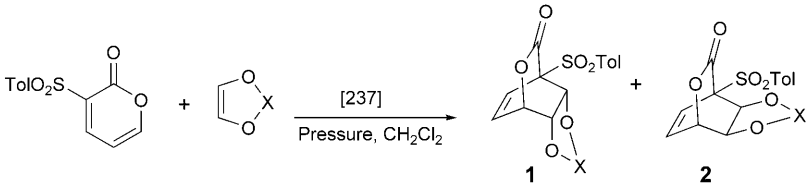
R^1	R^2	*t*	**1**	2
MeO	^{t}Bu(Me)$_2$Si	5 d	19%	3%
^{t}Bu(Me)$_2$Si	^{t}Bu(Ph)$_2$Si	4 d	60%	–

App. 141



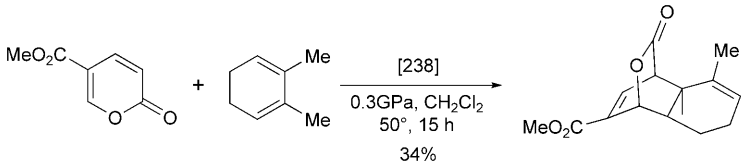
R^1	R^2	*t*	Products	Yield
H	H	14 d	**1/2** 1:1	50%
MeOOC	H	7 d	**1**	47%
H	MeOOC	48 h	**1**	59%

App. 142

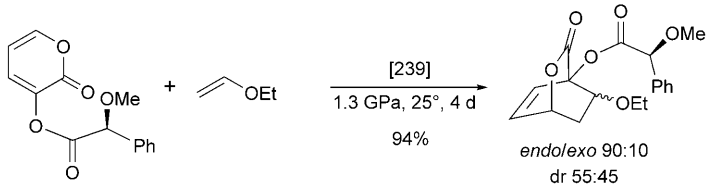


X	*P*	*T*	*t*	**1**	**2**
CH_2	0.1 MPa	80°	36 h	78%	5%
CH_2	1.1 – 1.25 GPa	25°	4 d	86%	14%
Me_2C	0.1 MPa	60°	64 h	63%	14%
Me_2C	0.1 MPa	80°	69 h	77%	23%
$(i\text{-}Pr)_2C$	1.25 GPa	25°	4 d	20%	–

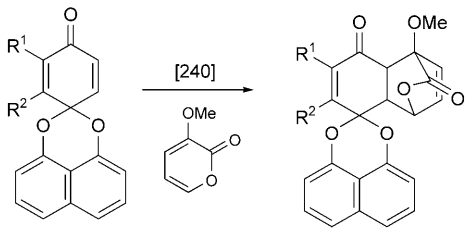
App. 143



App. 144

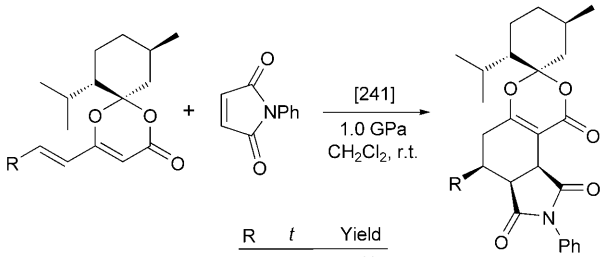


App. 145



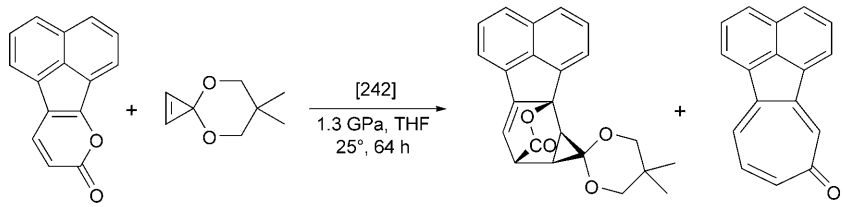
R^1	R^2	Conditions	Yield
H	H	1.2 – 1.5 GPa	quant.
H	H	0.1 MPa, PhH, reflux	55%
H	Me	1.2 – 1.5 GPa	quant.
MeO	H	1.2 – 1.5 GPa	quant.

App. 146

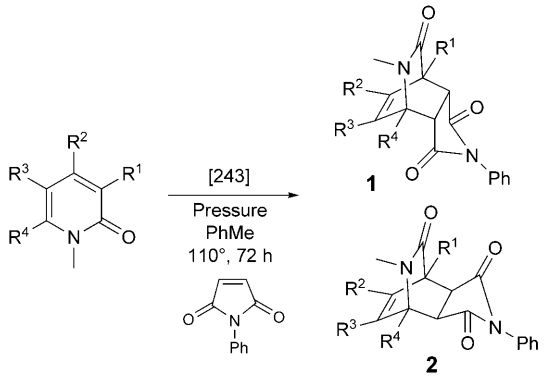


R	*t*	Yield
Me	1 d	30%
Et	4 d	96%

App. 147

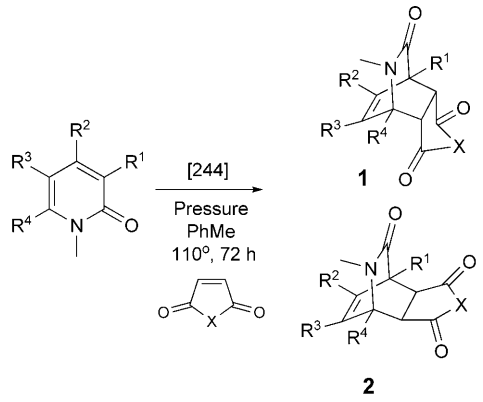


App. 148



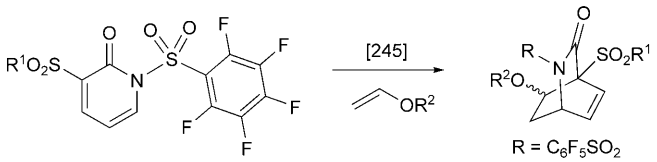
R^1	R^2	R^3	R^4	*P*	**1**	**2**
Ph	H	H	H	0.1 MPa	–	–
Ph	H	H	H	1.0 GPa	26%	50%
H	Ph	H	H	0.1 MPa	50%	–
H	Ph	H	H	1.0 GPa	11%	2%
H	H	Ph	H	0.1 MPa	90%	–
H	H	Ph	H	1.0 GPa	78%	18%
H	H	H	Ph	0.1 MPa	–	–
H	H	H	Ph	1.0 GPa	76%	8%

App. 149



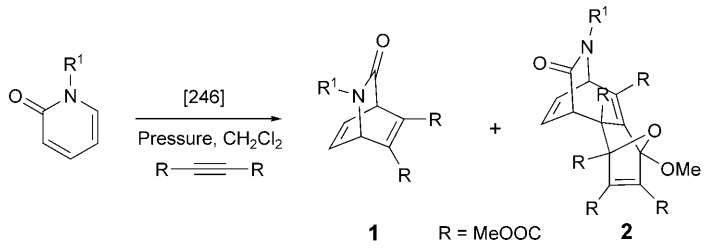
R^1	R^2	R^3	R^4	X	*P*	**1**	**2**
Ph	H	H	H	O	0.1 MPa	–	–
H	Ph	H	H	O	0.1 MPa	55%	–
H	H	Ph	H	O	0.1 MPa	44%	–
H	H	H	Ph	O	0.1 MPa	–	–
Ph	H	H	H	PhN	0.1 MPa	–	–
H	Ph	H	H	PhN	0.1 MPa	50%	–
H	H	Ph	H	PhN	0.1 MPa	90%	–
H	H	H	Ph	PhN	0.1 MPa	–	–
Ph	H	H	H	PhN	1.0 GPa	26%	50%
H	Ph	H	H	PhN	1.0 GPa	11%	2%
H	H	Ph	H	PhN	1.0 GPa	8%	18%
H	H	H	Ph	PhN	1.0 GPa	76%	8%

App. 150



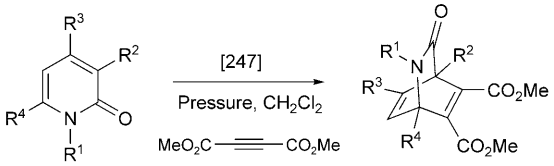
R^1	R^2	*P*	Solvent	*T*	*t*	Yield
Tol	Et	0.1 MPa	CH_2Cl_2	100°	40 h	56%
Tol	Et	0.5 GPa	CH_2Cl_2	50°	56 h	78% (*endo*/*exo* 68:10)
4-Br-C_6H_4	Et	0.1 MPa	CH_2Cl_2	100°	60 h	76%
4-F-C_6H_4	Bu	0.1 MPa	PhMe	90°	34 h	40%
4-NO_2-C_6H_4	Et	0.1 MPa	CH_2Cl_2	100°	42 h	67%
4-NO_2-C_6H_4	Bu	0.1 MPa	PhMe	90°	40 h	78%
C_6F_5	Et	0.1 MPa	CH_2Cl_2	25°	21 h	trace
C_6F_5	Et	0.1 MPa	CH_2Cl_2	40°	96 h	85%
C_6F_5	Et	0.7 GPa	CH_2Cl_2	25°	6 h	89% (*endo*/*exo* 54:10)

App. 151



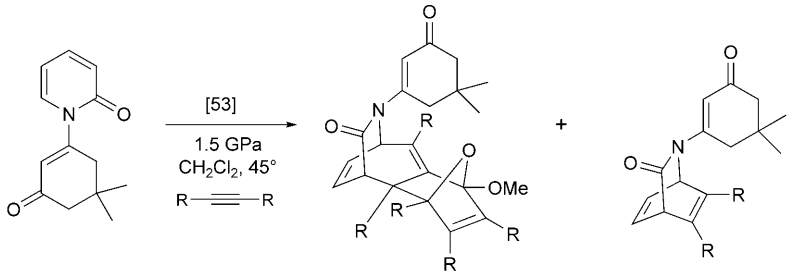
R^1	*P*	*T*	*t*	**1**	**2**
Dimedonyl	1.5 GPa	46°	72 h	36%	36%
i-Pr	1.0 GPa	35°	106 h	4%	3%
Ph	1.0 GPa	40°	72 h	10%	20%
Me	1.0 GPa	70°	12 h	14%	4%
Bn	1.0 GPa	35°	120 h	6%	4%

App. 152



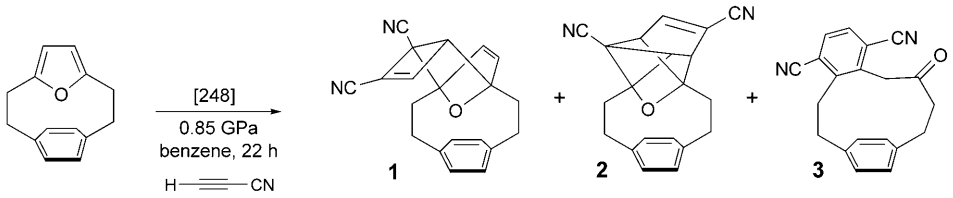
R^1	R^2	R^3	R^4	*P*	*T*	*t*	Yield
Me	H	H	H	1.0 GPa	70°	12 h	16%
Me	H	H	H	1.5 GPa	60°	16 h	22%
Me	Me	H	H	1.5 GPa	60°	15 h	40%
MeO	H	Me	Me	1.5 GPa	60°	48 h	15%

App. 153



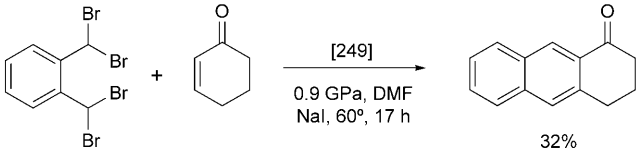
36% R = MeOOC 36%

App. 154



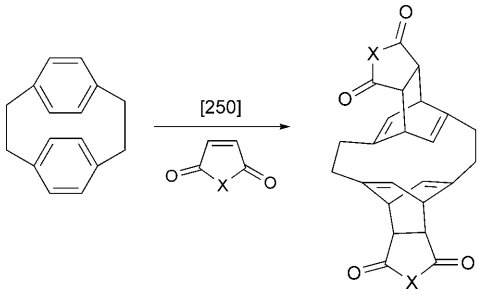
T	1	2	3
60°	39%	58%	3%
80°	36%	54%	11%

App. 155



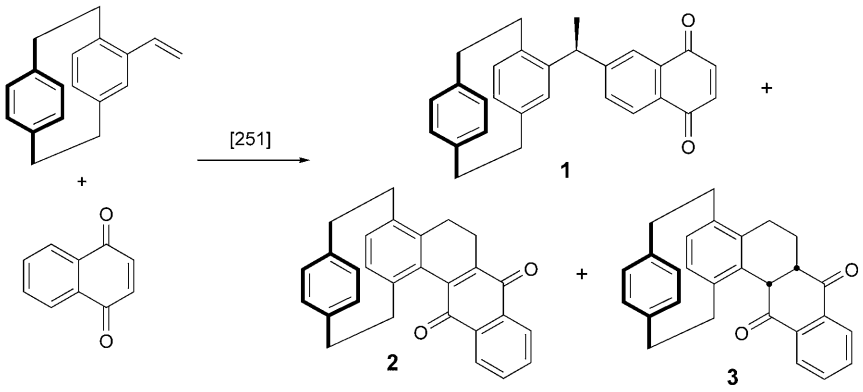
32%

App. 156



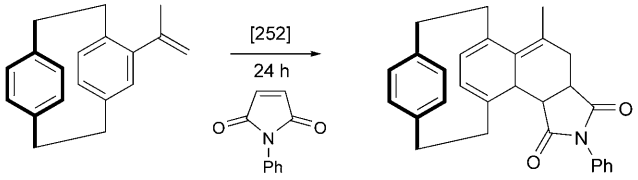
X	*P*	*T*	*t*	Yield
O	0.6 GPa	70°	21 h	53%
NH	0.8 GPa	80°	14 h	35%
MeN	0.8 GPa	70°	14 h	28%
EtN	0.8 GPa	70°	14 h	22%
PhN	0.6 GPa	70°	21 h	26%

App. 157



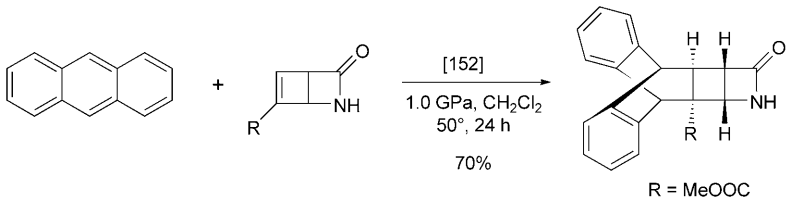
P	Solvent	Catalyst	*T*	*t*	Yield
0.8 GPa	PhMe	CCl_3CO_2H	r.t.	18 h	68% (**3**/**2** 76:10)
0.8 GPa	CH_2Cl_2	$BF_3{\cdot}OEt_2$	50°	16 h	–
0.1 MPa	PhMe	CCl_3CO_2H	reflux	18 h	57% (**1**/**2** 17:10)

App. 158

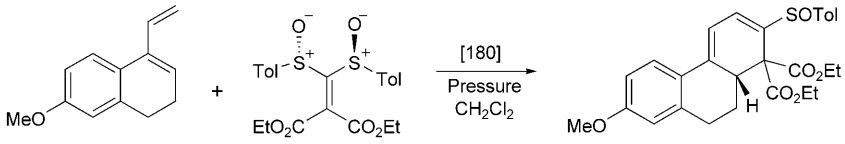


P	Solvent	*T*	Yield
0.1 MPa	PhMe	reflux	–
1.7 GPa	CH_2Cl_2	r.t.	80%

App. 159

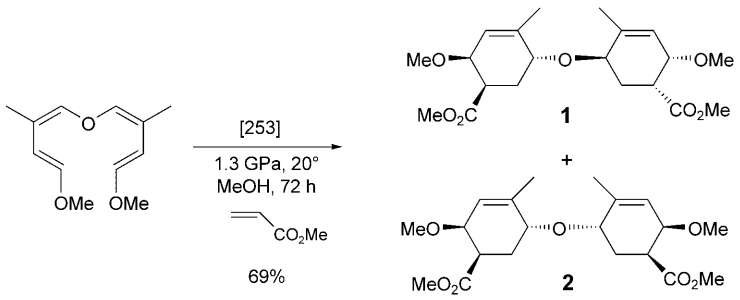


App. 160



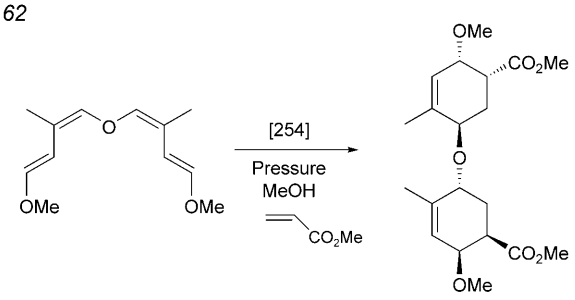
P	Catalyst	*t*	Yield
1.3 GPa	none	68 h	56%
1.3 GPa	$ZnBr_2$	46 h	74%

App. 161



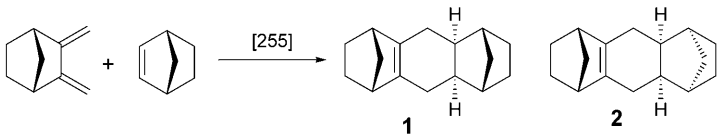
1/2 78:22

App. 162



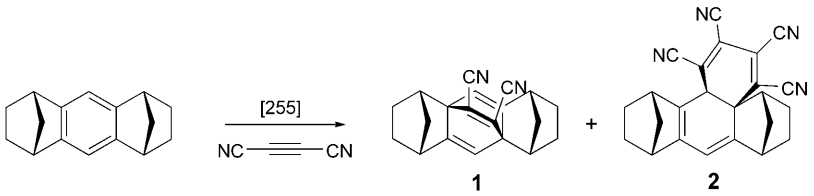
Condition	*T*	*t*	Yield
sealed tube	80°	240 h	29%
1.3 GPa	r.t.	24 h	75%

App. 163



P	*T*	*t*	Yield	**1/2**
0.1 MPa	160°	22 h	50%	88:12
0.79 GPa	75°	6 h	30%	96:4

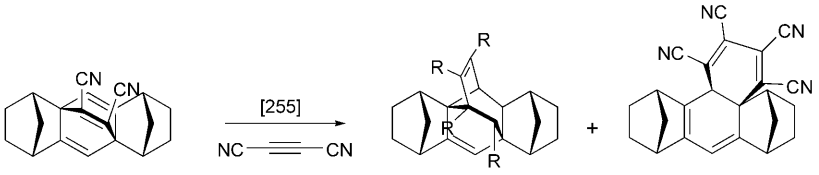
App. 164



1 **2**

Condition	Solvent	*T*	*t*	**1**	**2**	**1/2**
sealed tube	benzene	127°	17 h	49%	11%	4:1
0.9 GPa	PhMe	83°	17 h	8%	28%	1:2

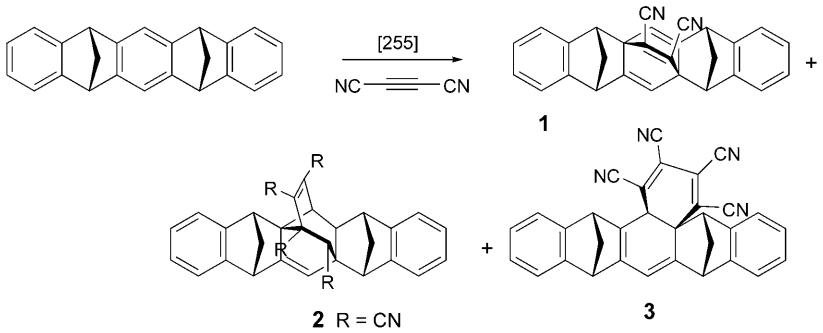
App. 165



1 R = CN **2**

Condition	Solvent	*T*	*t*	**1**	**2**
sealed tube	benzene	127°	17 h	45%	–
1.2 GPa	PhMe	20°	90 h	35%	9%

App. 166

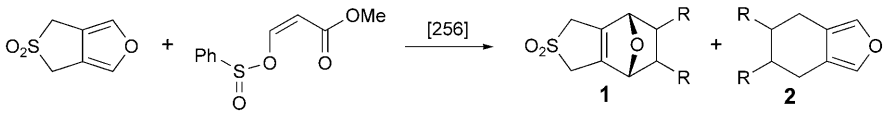


1

2 R = CN **3**

Condition	Solvent	*T*	*t*	**1**	**2**	**3**
sealed tube	PhMe	130°	41 h	22%	–	–
1.2 GPa	PhMe	50°	44 h	32%	1.5%	3%

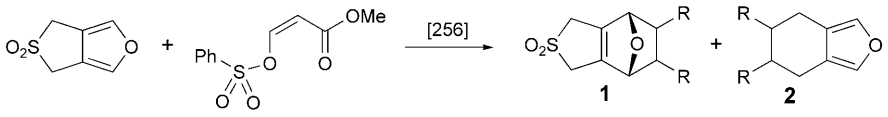
App. 167



1 **2**

Condition	Solvent	*T*	*t*	**1**	**2**
sealed tube	benzene	90°	20 h	82%	–
1.2 GPa	CH_2Cl_2	28°	48 h	5%	79%

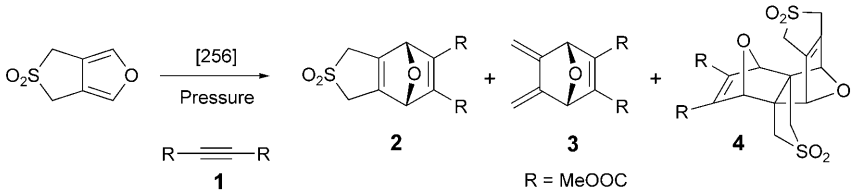
App. 168



1 **2**

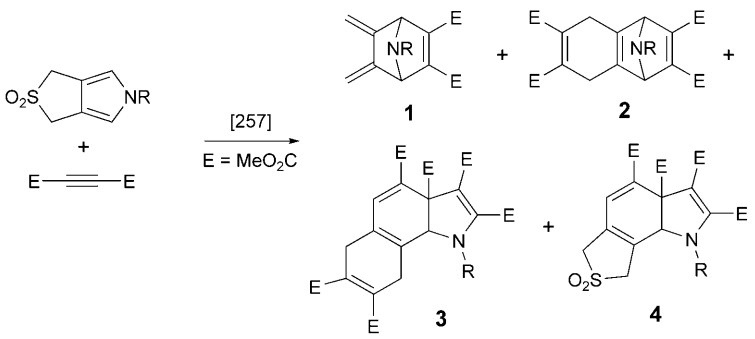
Condition	Solvent	*T*	*t*	**1**	**2**
sealed tube	benzene	120°	20 h	50%	–
1.2 GPa	CH_2Cl_2	28°	48 h	7%	80%

App. 169



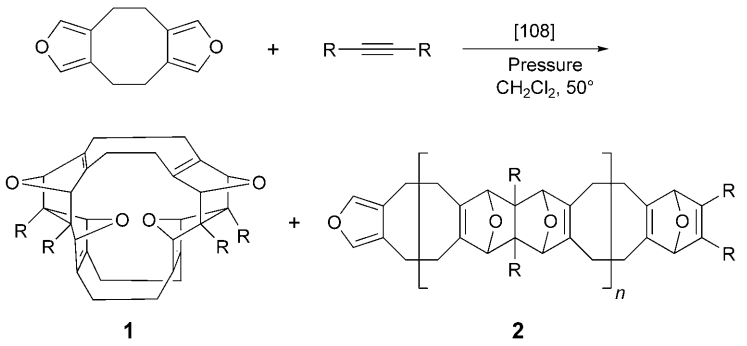
1 (equiv.)	Condition	Solvent	*T*	*t*	**2**	**3**	**4**
3	0.1 MPa	CH_2Cl_2	28°	7 d	54%	39%	–
1	0.1 MPa	CH_2Cl_2	28°	7 d	35%	–	–
3	sealed tube	benzene	120°	1 h	62%	29%	–
1	sealed tube	benzene	120°	1 h	40%	3%	–
3	0.4 GPa	CH_2Cl_2	28°	24 h	97%	3%	–
3	1.2 GPa	CH_2Cl_2	28°	48 h	–	–	53%
3	0.6 GPa	CH_2Cl_2	28°	24 h	–	26%	23%

App. 170



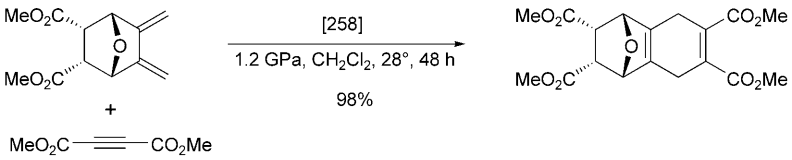
R	*P*	Solvent	*T*	*t*	**1**	**2**	**3**	**4**
Bn	0.1 MPa	benzene	100°	4 d	28%	0.1%	47%	–
Bn	0.1 MPa	benzene	140°	16 d	–	–	97%	–
Bn	0.4 GPa	CH_2Cl_2	rt	48 d	–	–	62%	–
Bn	1.2 GPa	CH_2Cl_2	rt	48 d	–	–	–	38%
Me	0.1 MPa	benzene	150°	2 d	–	–	73%	–
BnOOC	0.1 MPa	benzene	150°	13 d	–	85%	–	–
BnOOC	1.2 GPa	CH_2Cl_2	rt	48 d	–	52%	–	–
Ts	0.1 MPa	benzene	170°	14 d	–	97%	–	–
Bz	0.7 GPa	benzene	170°	7 d	–	99%	–	–

App. 171

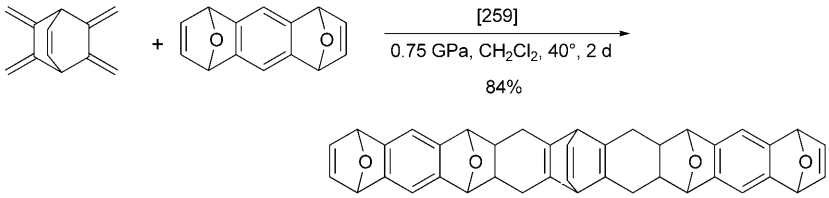


R	*P*	*t*	**1**	**2**
$C_8H_{17}O_2C$	0.86 GPa	5 d	54%	46% (*n* = 27)
CO_2Me	0.7 GPa	12 h	46%	54% (*n* = 18)

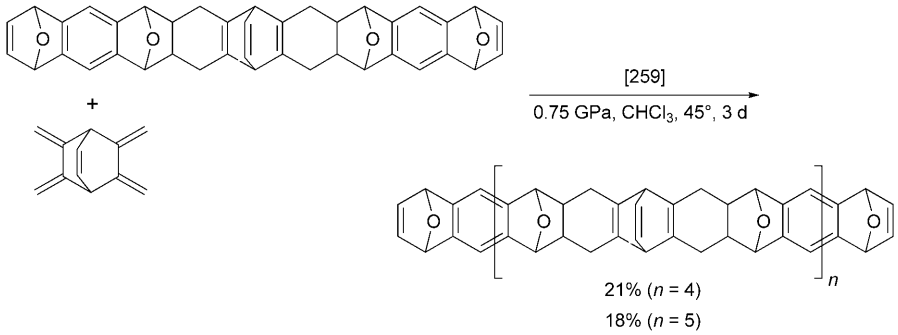
App. 172



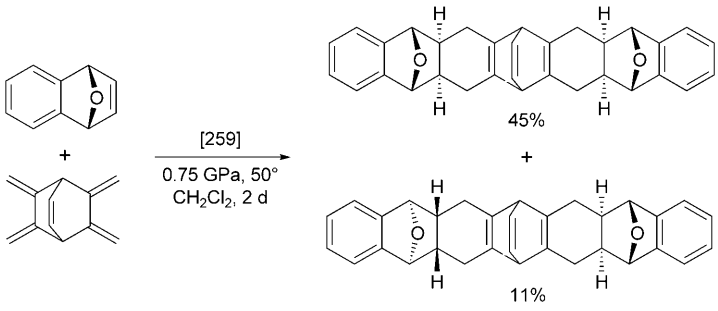
App. 173



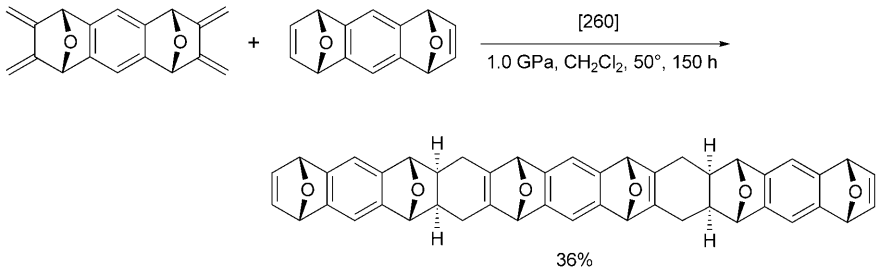
App. 174



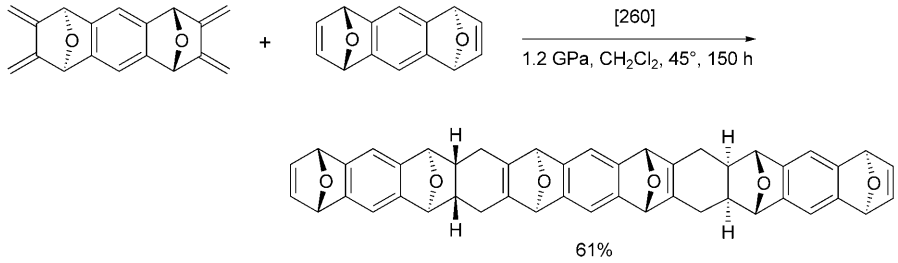
App. 175



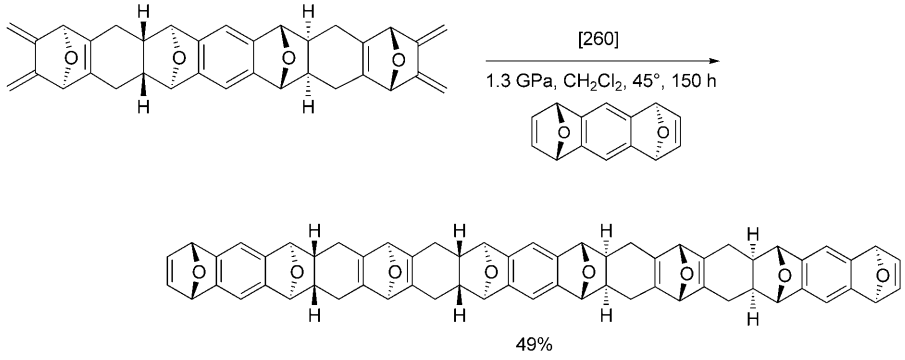
App. 176



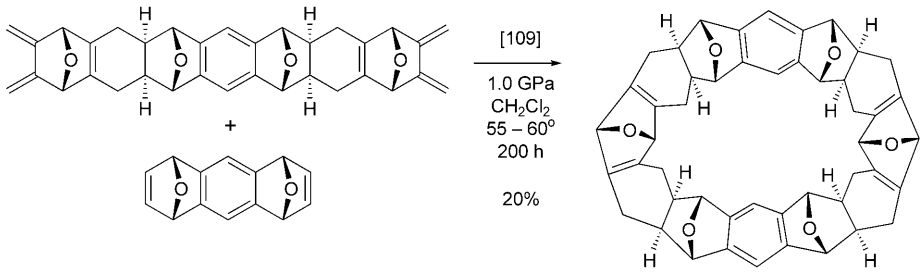
App. 177



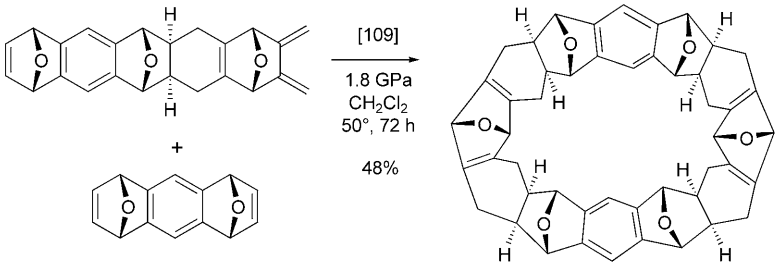
App. 178



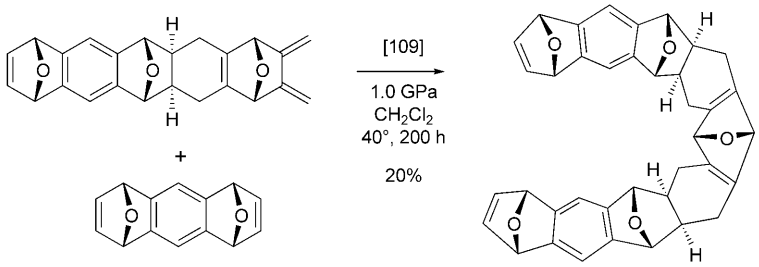
App. 179



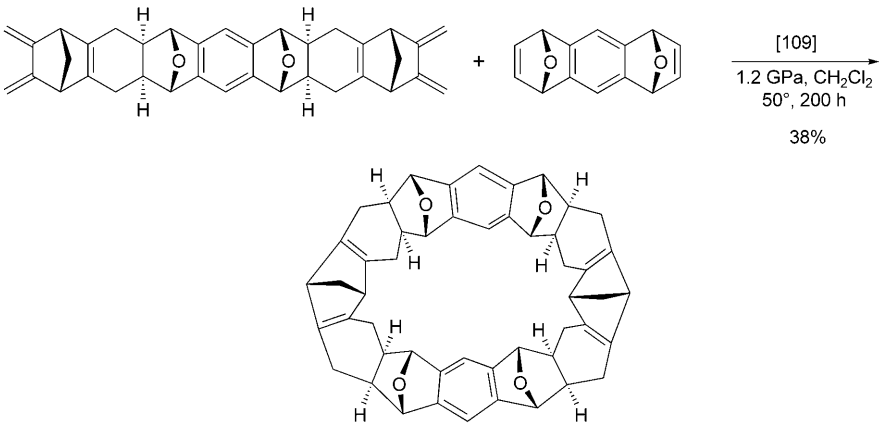
App. 180



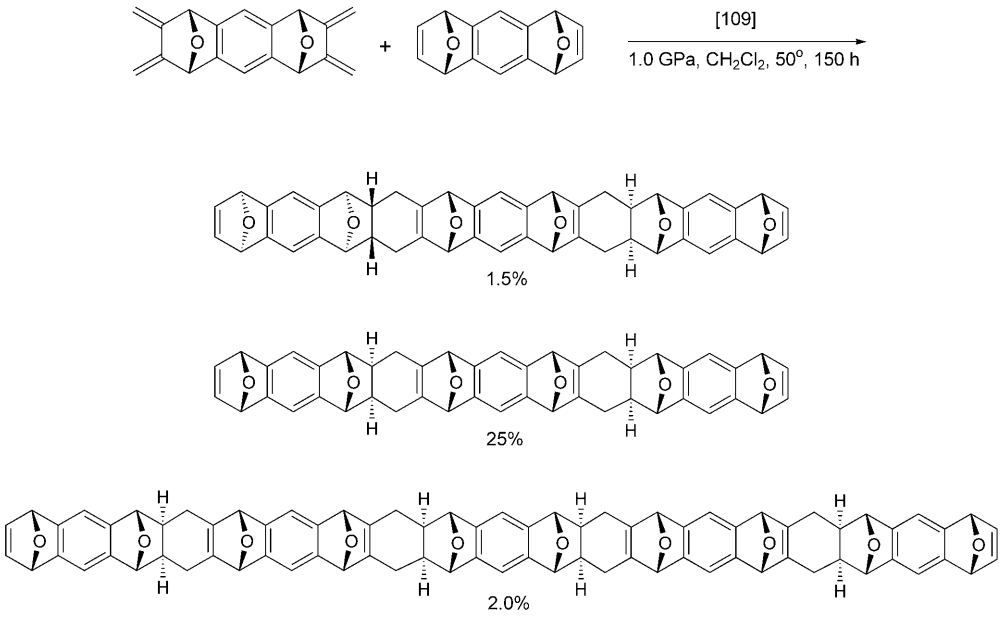
App. 181



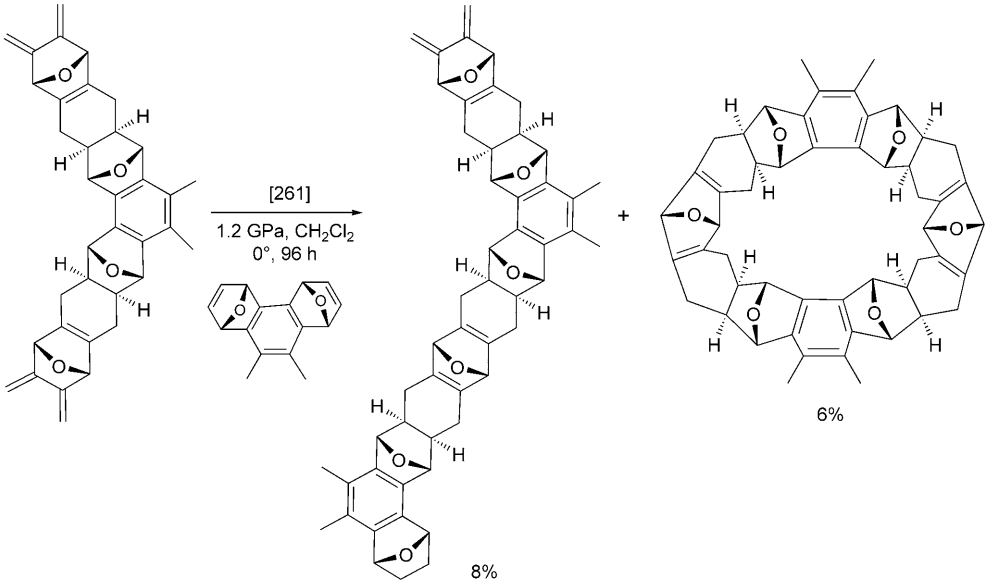
App. 182



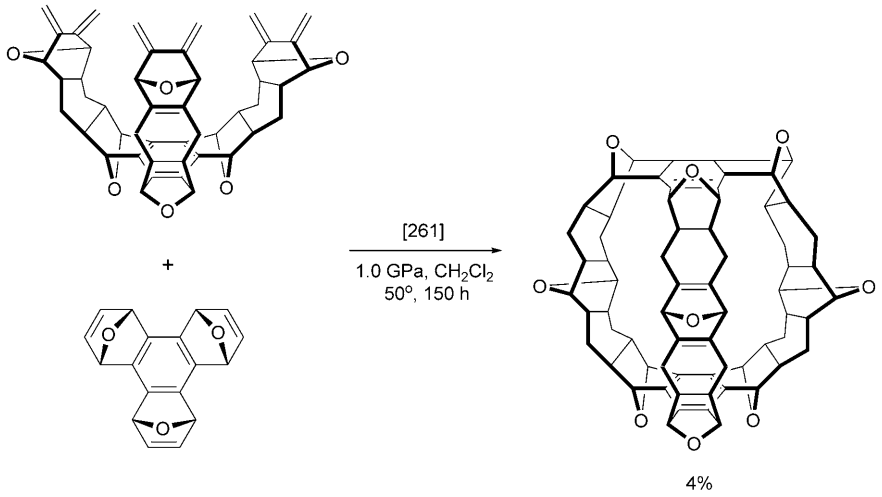
App. 183



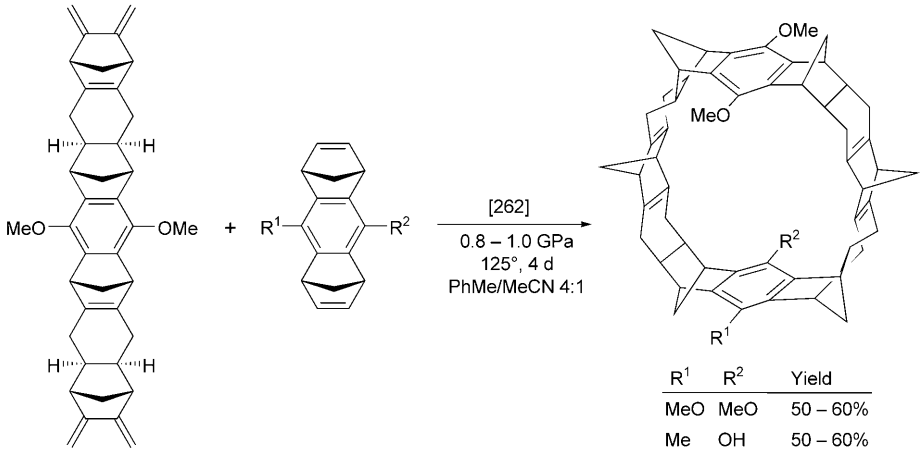
App. 184



App. 185

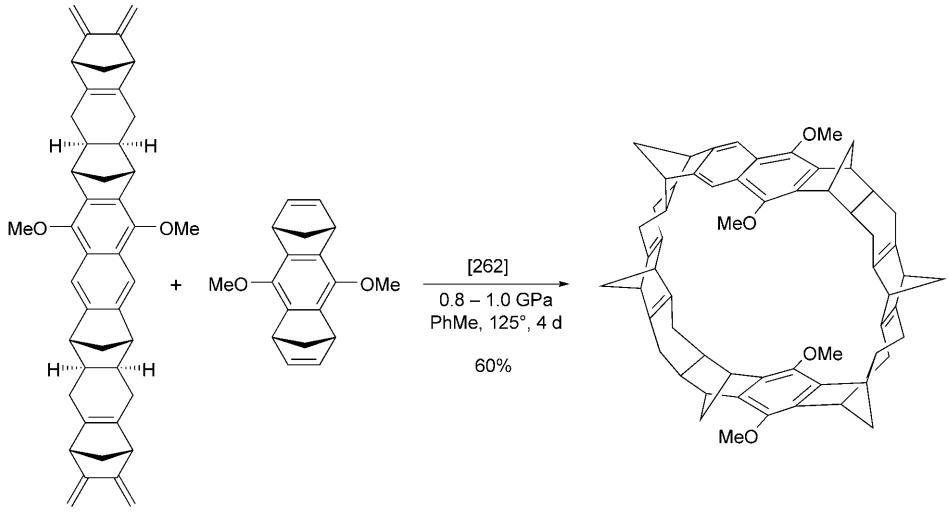


App. 186

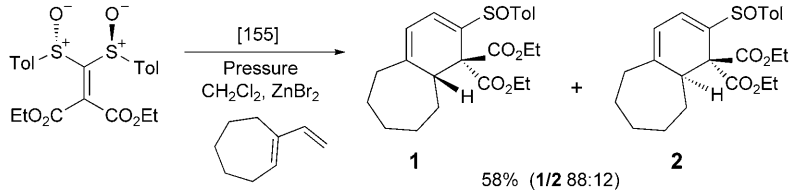


R^1	R^2	Yield
MeO	MeO	50 – 60%
Me	OH	50 – 60%

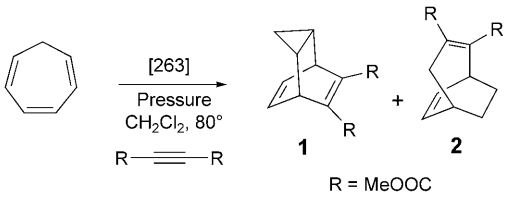
App. 187



App. 188

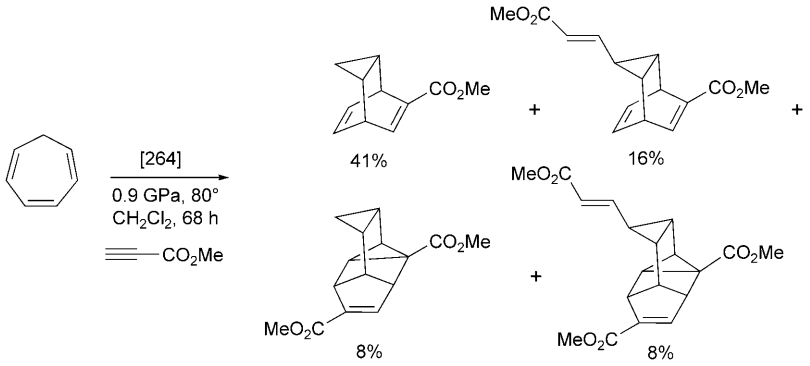


App. 189

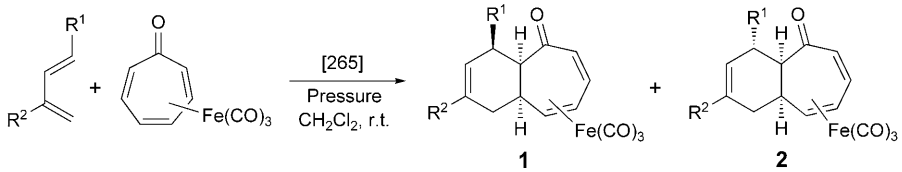


P	*t*	1/2
0.1 MPa	8 – 48 h	68:32
0.1 GPa	6 – 20 h	73:27
0.2 GPa	15 h	78:22
0.4 GPa	1 h	82:18
0.4 GPa	5 h	90:10
0.4 GPa	16 h	90:10
0.6 GPa	5.5 h	95:5
0.8 GPa	3 h	97:3
0.8 GPa	15 h	99:1
0.9 GPa	1 h	100:0

App. 190

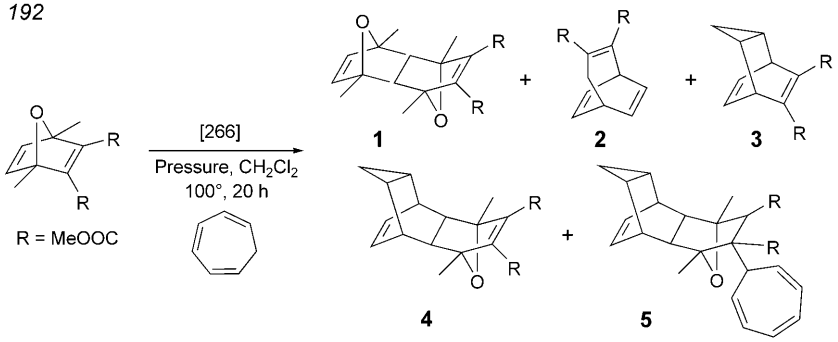


App. 191



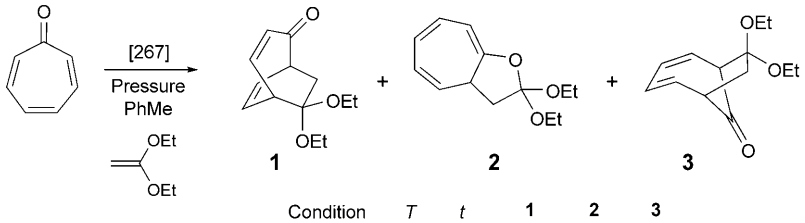
R^1	R^2	*P*	Products	Yield
Me_3SiO	H	1.0 GPa	**1/2** 3:1	96%
3,5-$(NO_2)_2$-C_6H_3	H	1.2 GPa	**1/2** 4:3	74%
H	Me_3SiO	0.8 GPa	**1**	47%
AcO	H	1.2 GPa	**1/2** 1:1	75%

App. 192



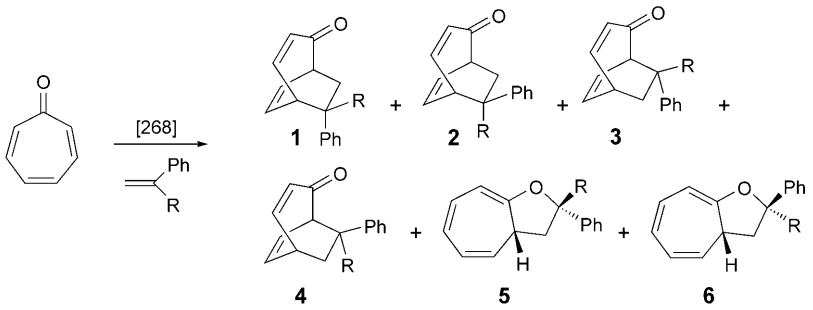
P	1	2	3	4	5
0.3 GPa	10.7%	10.0%	–	–	–
0.5 GPa	22.4%	34.0%	3.2%	5.2%	–
1.0 GPa	11.1%	12.3%	14.9%	19.4%	1.8%

App. 193



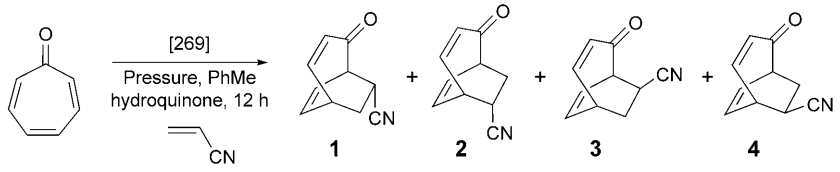
Condition	*T*	*t*	1	2	3
sealed tube	90°	48 h	9.2%	0.7%	1.9%
0.1 MPa	110°	17 h	47%	5.2%	15%
0.1 MPa	120°	10 h	9.1%	3.1%	1.1%
0.3 GPa	120°	10 h	17%	–	13%

App. 194



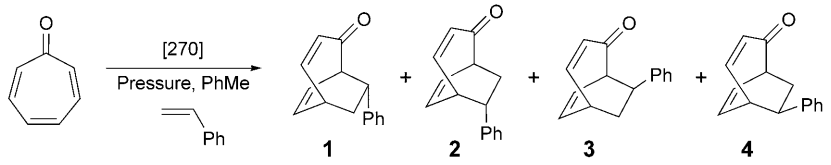
R	*P*	*T*	*t*	Yield	Product ratio
H	15 MPa	140°	10 h	37%	(**1**+**3**)/(**2**+**4**) 54:46
H	1.0 GPa	140°	10 h	78%	(**1**+**3**)/(**2**+**4**) 67:33
H	1.0 GPa	20°	124 h	13%	(**1**+**3**)/(**2**+**4**) 78:22
Me	0.8 GPa	100°	10 h	58%	**1**/**2**/**3**/**5**/**6** 21:21:5:43:10

App. 195



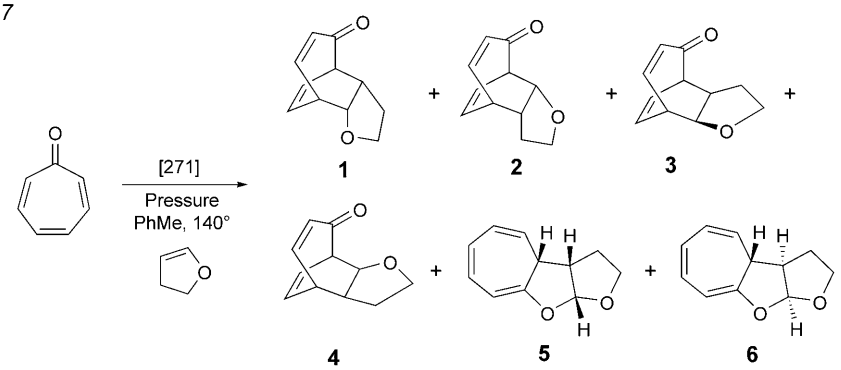
P	*T*	Yield	**1/2/3/4**
0.1 MPa	140°	91%	12:70:9:9
0.6 GPa	80°	31%	8:67:5:20
0.8 GPa	80°	52%	9:66:6:19
1.0 GPa	80°	90%	8:66:7:19
1.0 GPa	20°	16%	8:68:0:24
1.0 GPa	140°	100%	6:74:7:13

App. 196



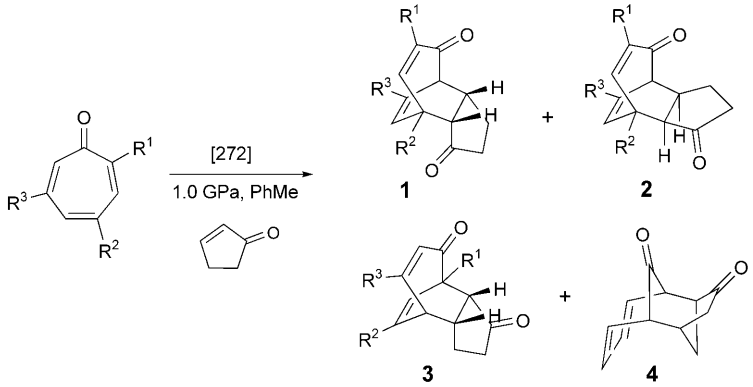
P	*T*	t	Yield	**1/2/3/4**
15 MPa	100°	24 h	37%	4:50:trace:46
60 MPa	100°	24 h	56%	7:57:4:32
0.1 GPa	100°	24 h	66%	6:60:3:31
0.5 GPa	100°	24 h	87%	8:57:7:28
1.0 GPa	100°	24 h	78%	9:58:8:26
1.0 GPa	20°	124 h	13%	6:72:3:19

App. 197



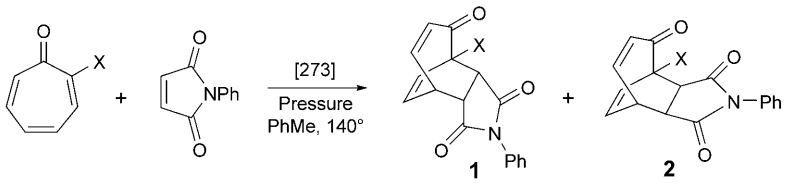
P	*t*	Yield	**1/2/3/4/5/6**
0.1 MPa	70 h	10%	18:3:24:2:43:12
0.2 GPa	8 h	24%	32:6:24:4:24:12
0.5 GPa	7 h	37%	34:4:26:3:19:14

App. 198



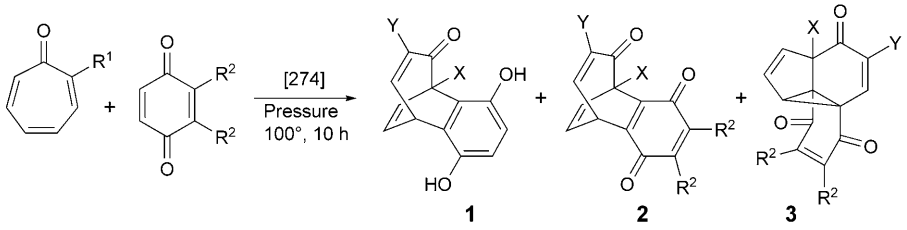
R^1	R^2	R^3	*T*	*t*	**1**	**2**	**3**	**4**
H	H	H	100°	10 h	7%	2%	4%	7%
MeO	H	H	100°	10 h	8%	2%	34%	–
OH	H	H	100°	10 h	–	–	–	–
Cl	H	H	100°	10 h	–	–	–	–
MeO	i-Pr	H	150°	30 h	15%	–	46%	–
MeO	H	i-Pr	150°	30 h	4%	5%	58%	–

App. 199



X	*P*	*T*	*t*	Products	Yield
H	0.1 MPa	110°	10 h	**1**/**2** 93:7	quant.
H	1.0 GPa	20°	70 h	**1**	95%
H	1.0 GPa	100°	10 h	**1**	quant.
OH	0.1 MPa	110°	3 h	–	–
OH	0.1 MPa	135°	50 h	**1**/**2** 35:65	68%
OH	1.0 GPa	25°	100 h	**1**/**2** 20:80	quant.
OH	1.0 GPa	120°	20 h	**2**	quant.

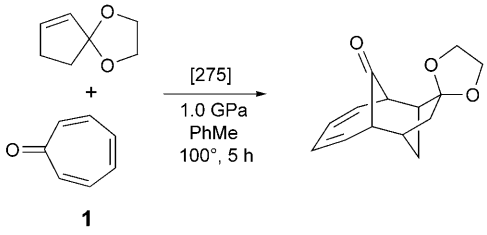
App. 200



1 **2** **3**

R^1	R^2	*P*	**1**	**2**	**3**
H	H	0.3 GPa	66% (X = Y = H)	7% (X = Y = H)	1%
H	H	0.3 GPa	63% (X = Y = H)	5% (X = Y = H)	1%
H	H	1.0 GPa	60% (X = Y = H)	25% (X = Y = H)	–
H	H	1.0 GPa	–	–	–
Cl	H	0.3 GPa	16% (X = Cl, Y = H); 23% (X = H, Y = Cl)	11% (X = H, Y = Cl)	–
Cl	H	1.0 GPa	16% (X = Cl, Y = H); 36% (X = H, Y = Cl)	26% (X = H, Y = Cl)	–
MeO	H	0.3 GPa	46% (X = MeO, Y = H); 7% (X = H, Y = MeO)	–	–
MeO	H	1.0 GPa	51% (X = MeO, Y = H); 13% (X = H, Y = MeO)	–	–
H	$(CH=CH)_2$	0.3 GPa	46% (X = Y = H)	–	8%
H	$(CH=CH)_2$	1.0 GPa	42% (X = Y = H)	–	–
Cl	$(CH=CH)_2$	0.3 GPa	16% (X = H, Y = Cl)	–	–
Cl	$(CH=CH)_2$	1.0 GPa	29% (X = H, Y = Cl)	–	–
MeO	$(CH=CH)_2$	0.3 GPa	27% (X = H, Y = MeO)	–	–
MeO	$(CH=CH)_2$	1.0 GPa	25% (X = H, Y = MeO)	–	–

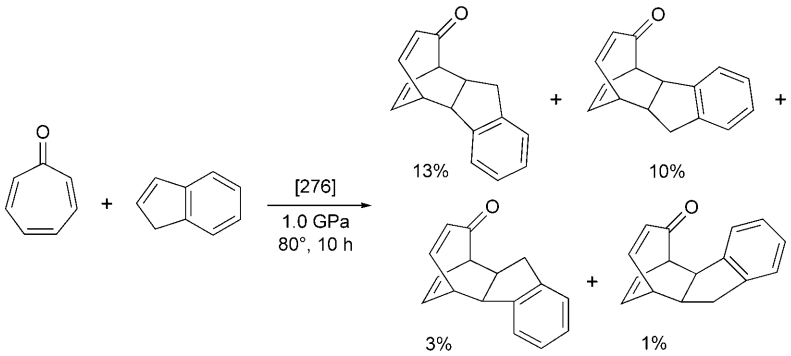
App. 201



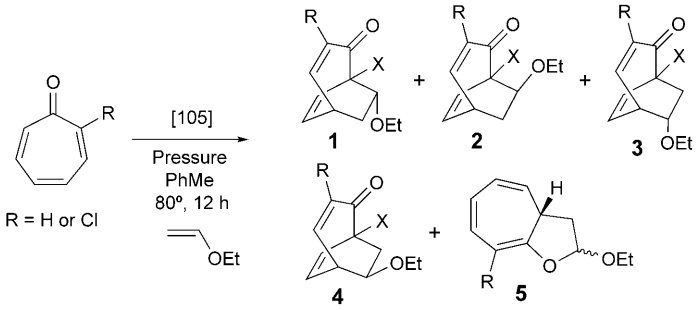
1

Solvent	Consumption of **1**
PhMe	54%
MeCN	46%
PhMe/pyridine 95:5	52%
MeCN/pyridine 95:5	45%
pyridine	7.5%

App. 202



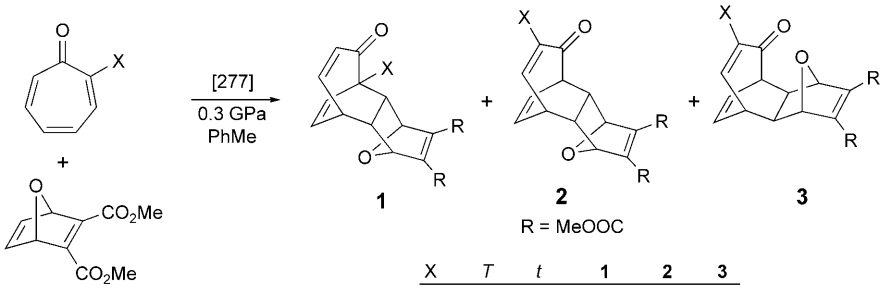
App. 203



R	*P*	**1**	**2**	**3**	**4**	**5**
H	0.1 MPa	2.1%	4.1%	35%	26.3%	32.5%
H	1.0 GPa	2.3%	4.5%	44.2%	32.8%	16.2%
Cl	0.1 MPa	19.2%[a])	–	–	21.7%[a])	59.6%
Cl	1.0 GPa	3.8%[a])	–	28.2%[a])	31.7%[a])	36.3%

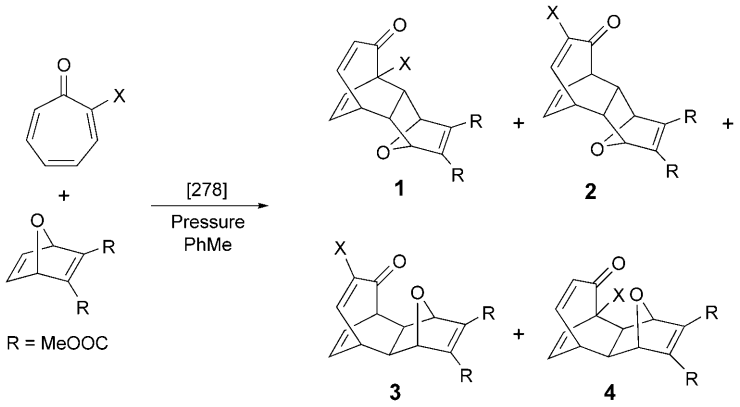
[a]) R = H, X = Cl

App. 204



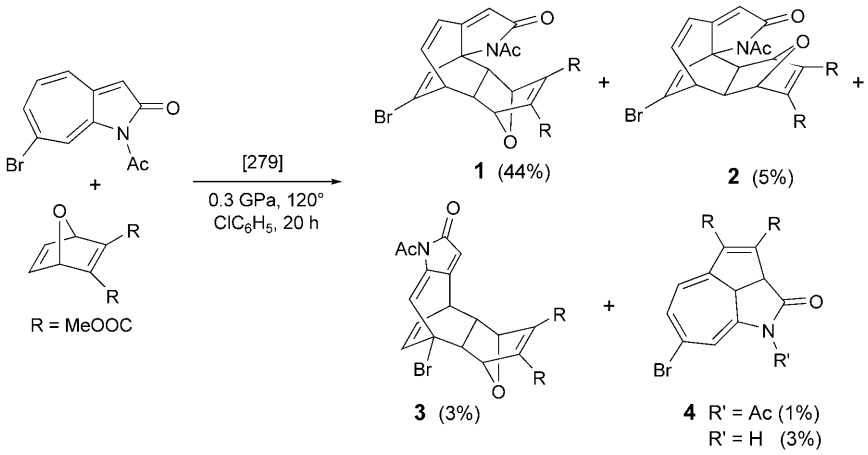
X	*T*	*t*	**1**	**2**	**3**
H	100°	11 h	88%	–	–
OH	120°	12 h	66%	–	–
MeO	120°	12 h	34%	12%	4%
Cl	120°	12 h	44%	20%	7%

App. 205

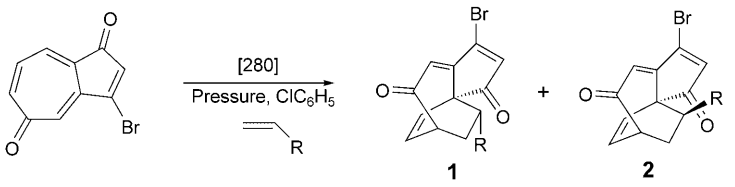


X	*P*	*T*	*t*	**1**	**2**	**3**	**4**
H	0.3 GPa	100°	11 h	88%	–	–	–
H	0.1 MPa	130°	12 h	64%	–	–	–
OH	0.3 GPa	120°	12 h	67%	–	–	–
OH	0.1 MPa	130°	12 h	50%	–	–	–
MeO	0.3 GPa	120°	12 h	34%	12%	4%	–
MeO	0.1 MPa	130°	12 h	24%	11%	3.4%	2.6%
MeO	0.1 MPa	130°	20 h	25%	–	–	–
Cl	0.3 GPa	120°	12 h	44%	20%	7%	–
Cl	0.1 MPa	130°	20 h	28%	13%	5%	6%

App. 206

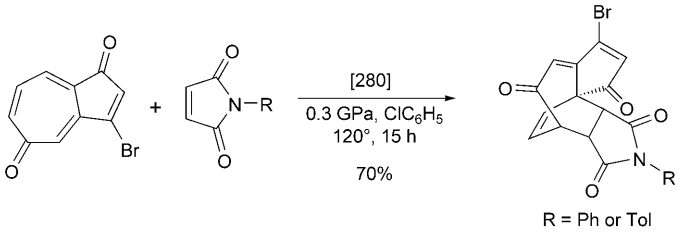


App. 207

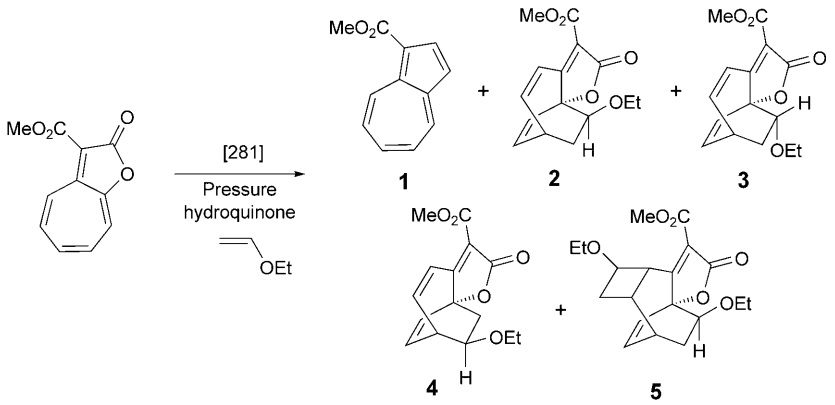


R	*P*	*T*	*t*	**1**	**2**
H	4 MPa	130°	5 h	55%	–
CN	0.3 GPa	130°	15 h	17%	31%
Ph	0.3 GPa	130°	15 h	24%	53%

App. 208



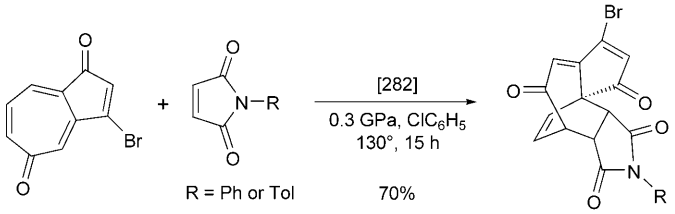
App. 209



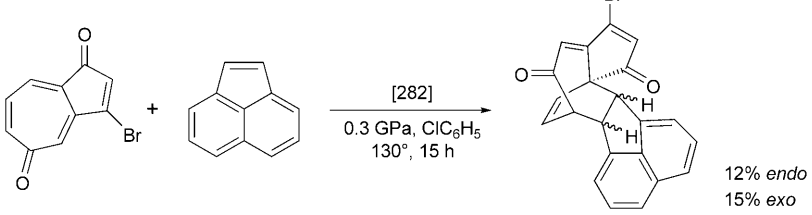
P	Solvent	Catalyst[a])	*T*	*t*	**1**	**2 – 4**	**5**
0.1 MPa	PhMe	no	160°	40 h	74%	21%	–
0.3 GPa	ClC_6H_5	yes	150°	10 h	39%	28%	1.1%
0.5 GPa	ClC_6H_5	no	150°	10 h	28%	28%	3.2%
0.5 GPa	ClC_6H_5	yes	150°	10 h	33%	31%	5.0%
1.0 GPa	ClC_6H_5	yes	150°	10 h	25%	26%	4.0%
1.0 GPa	ClC_6H_5	yes	150°	1 h	33%	24%	5.8%

[a]) Hydroquinone.

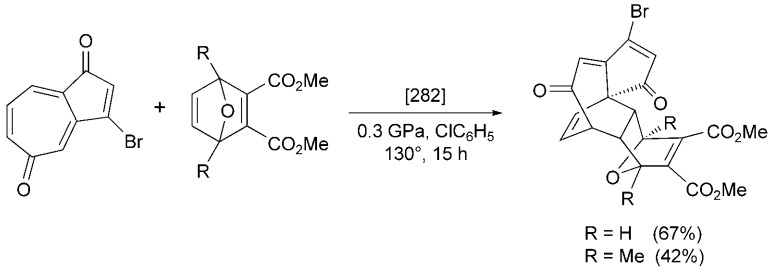
App. 210



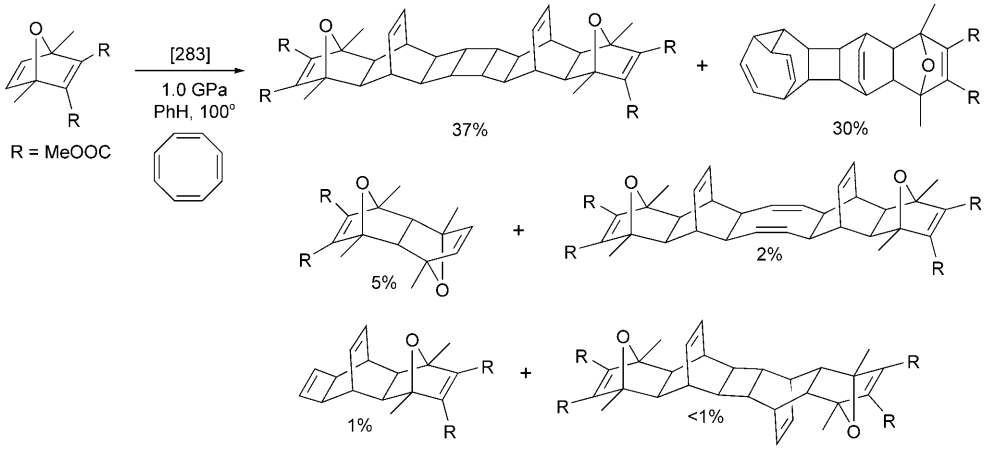
App. 211



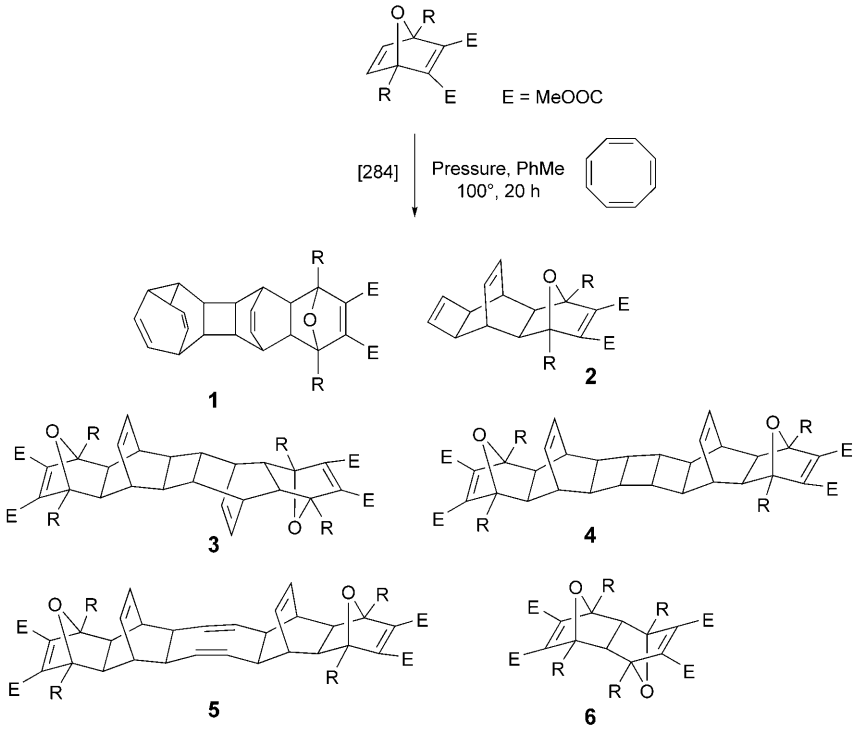
App. 212



App. 213

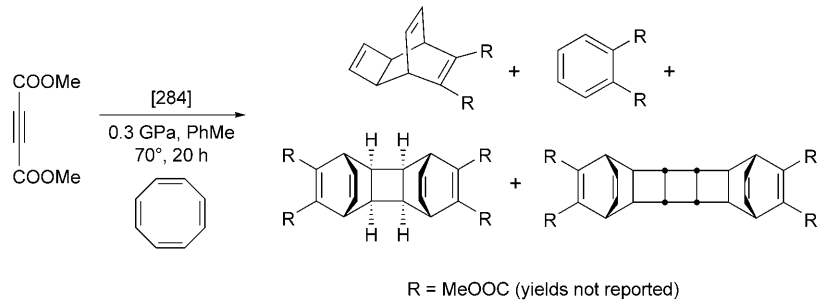


App. 214



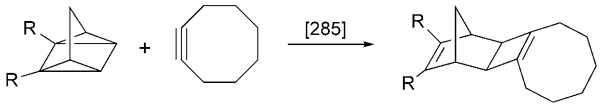
R	*P*	1	2	3	4	5	6
Me	1.0 GPa	30%	1%	<1%	37%	2%	5%
Me	0.3 GPa	25%	10%	6%	37%	2%	9%
H	0.3 GPa	15%	–	–	1%	–	2%

App. 215



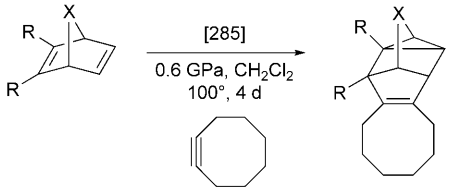
R = MeOOC (yields not reported)

App. 216



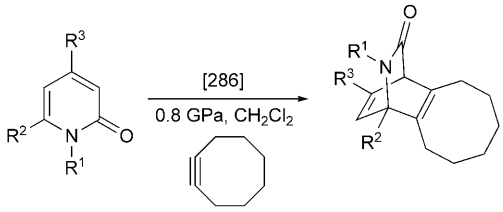
R	*P*	Solvent	*T*	*t*	Yield
MeOOC	0.1 MPa	PhMe	reflux	13 h	89%
H	0.6 GPa	CH_2Cl_2	100°	4 d	30%

App. 217



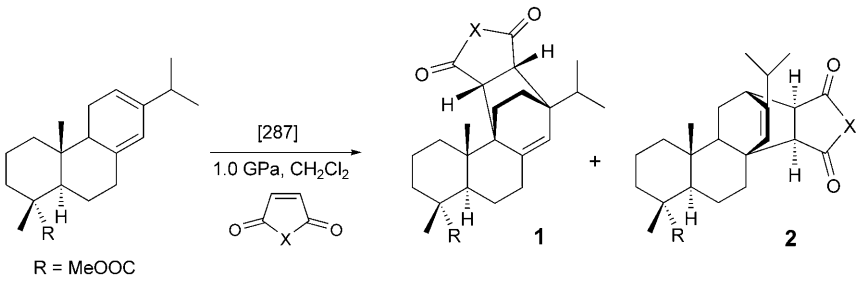
X	R	Yield
O	MeO_2C	31%
MeO_2CN	MeO_2C	22%
CH_2	H	11%
CH_2	MeO_2C	11%

App. 218



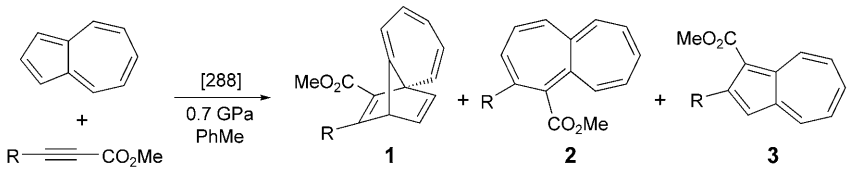
R^1	R^2	*T*	R^3	*t*	Yield
Me	H	90°	H	10 d	77%
Bn	H	90°	H	10 d	80%
i-Pr	H	90°	H	10 d	62%
Me	H	90°	Me	10 d	70%
Me	Me	90°	H	10 d	16%
Me	MeO	60°	H	5 d	4%
Me	MeO	90°	H	10 d	24%

App. 219



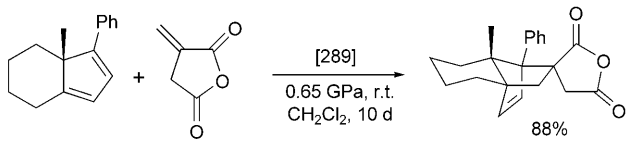
X	*T*	*t*	**1**	**2**
O	85°	70 h	19%	8%
PhN	80°	48 h	68%	–

App. 220

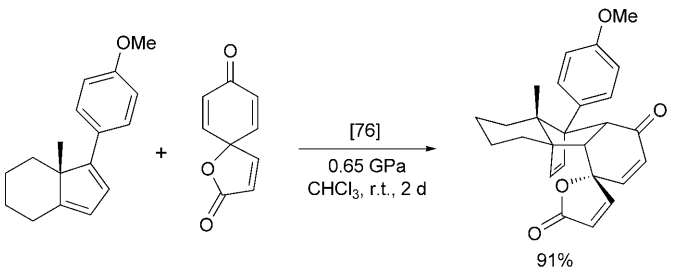


R	*T*	*t*	**1**	**2**	**3**
H	50°	66 h	39.4%	11.7%	*ca.* 1%
MeOOC	70°	67 h	*ca.* 1%	–	–

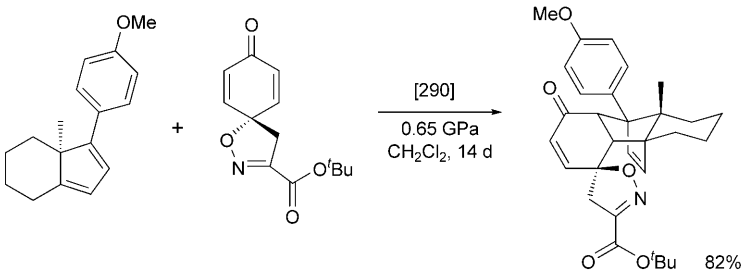
App. 221



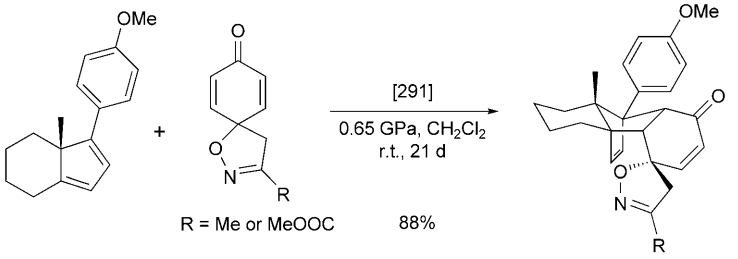
App. 222



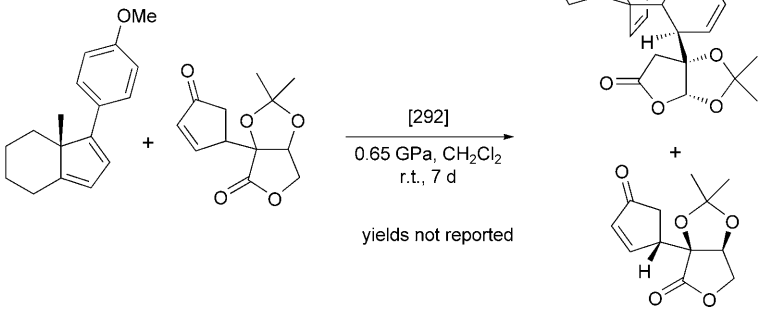
App. 223



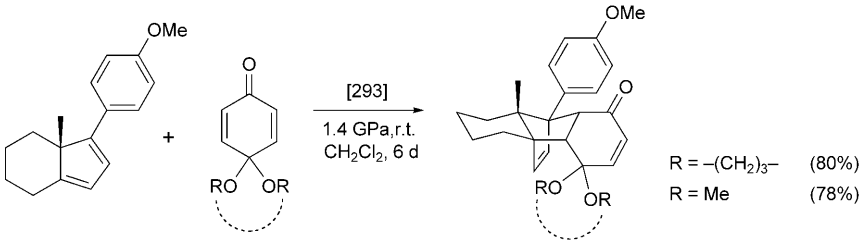
App. 224



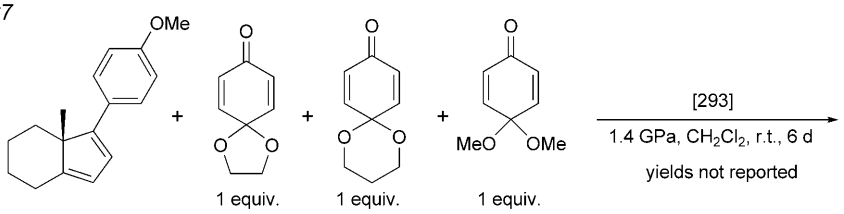
App. 225

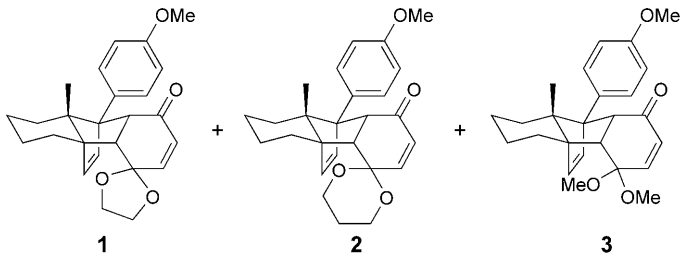


App. 226



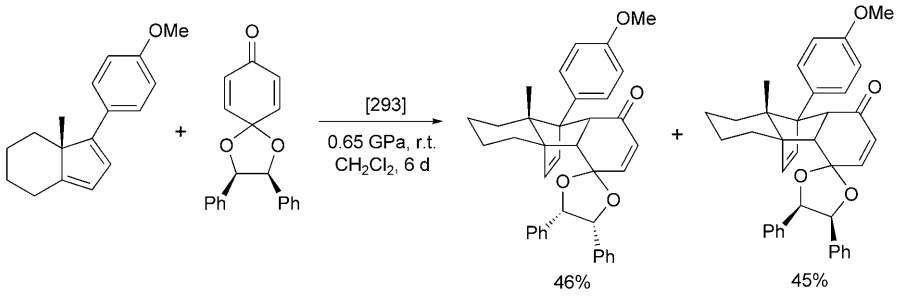
App. 227



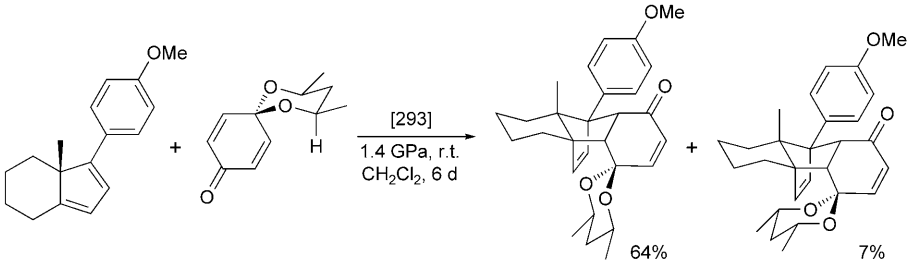


1/**2**/**3** 10:5:0

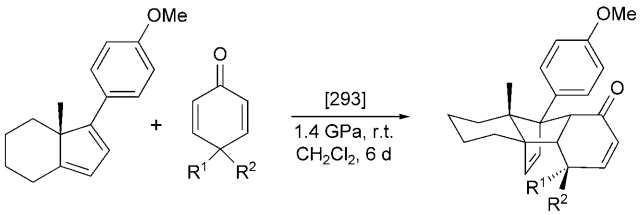
App. 228



App. 229



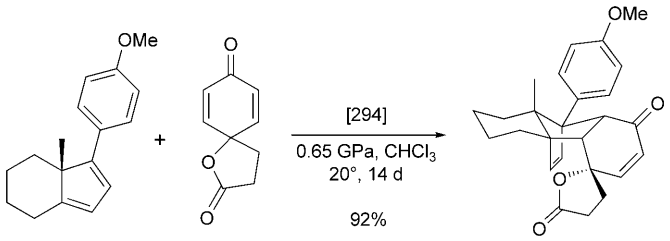
App. 230



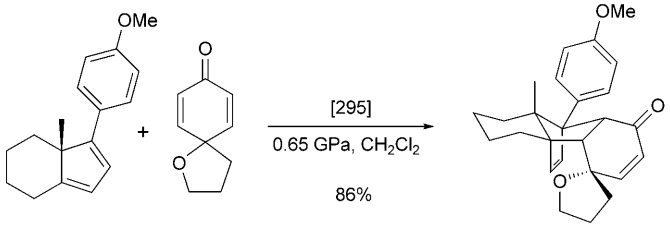
R^1	R^2	Solvent	*t*	Yield
–$OCH_2C(O)CH_2$–		CH_2Cl_2	6 d	85%
–OCH_2CH=C(OMe)–		CH_2Cl_2	6 d	89%
–OCH=$CHCH_2$–		CH_2Cl_2	6 d	74%
–OCH(O)CH_2CH_2–		CH_2Cl_2	13 d	78%
–OCH(OEt)CH_2CH_2–		CH_2Cl_2	13 d	34%[a])
OH	CH_2CN	MeCN	6 d	89%
OH	Me	CH_2Cl_2	13 d	79%
OH	$CH_2CH_2CH(OCH_2)_2$	CH_2Cl_2	20 d	87%
AcO	$CH_2CH_2CH(OCH_2)_2$	CH_2Cl_2	20 d	61%
OH	CH=CHCH$(OEt)_2$ (*trans*)	CH_2Cl_2	6 d	77%
AcO	CH=CHCH$(OEt)_2$ (*trans*)	CH_2Cl_2	20 d	51%

[a]) Plus 29% of diastereoisomer.

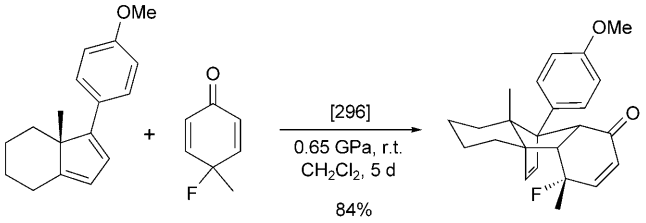
App. 231



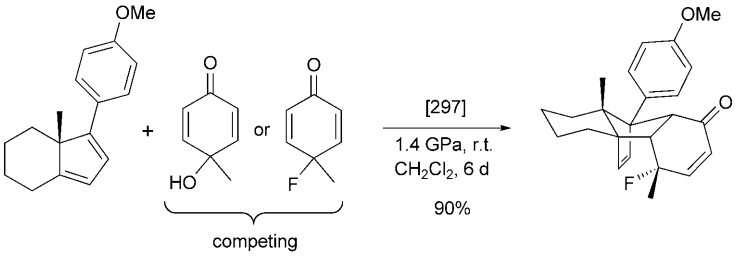
App. 232



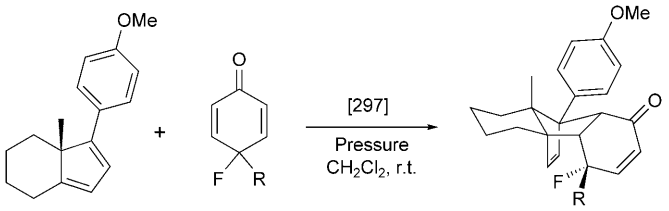
App. 233



App. 234

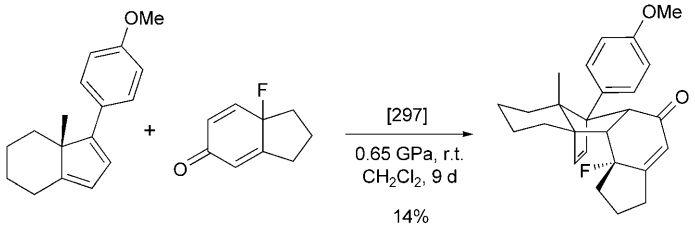


App. 235

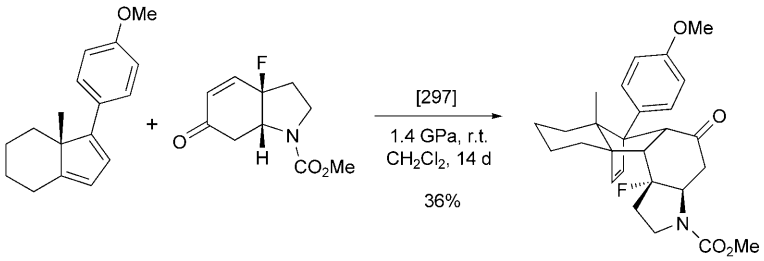


R	*P*	*t*	Yield
allyl	1.4 GPa	7 d	quant.
$MeO_2C(CH_2)_2$	0.65 GPa	10 d	76%
MeO_2C	0.65 GPa	7 d	81%
$MeO_2CNH(CH_2)_2$	0.65 GPa	14 d	75%
t-Bu	0.65 GPa	14 d	72%

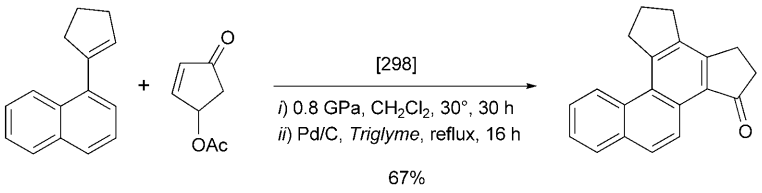
App. 236



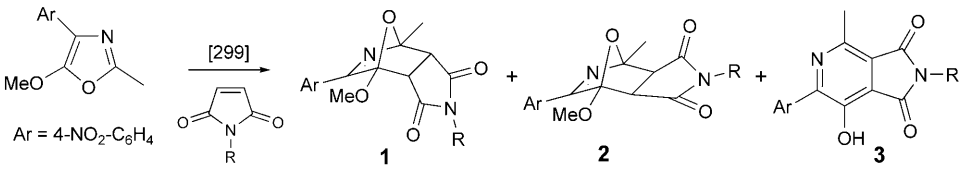
App. 237



App. 238

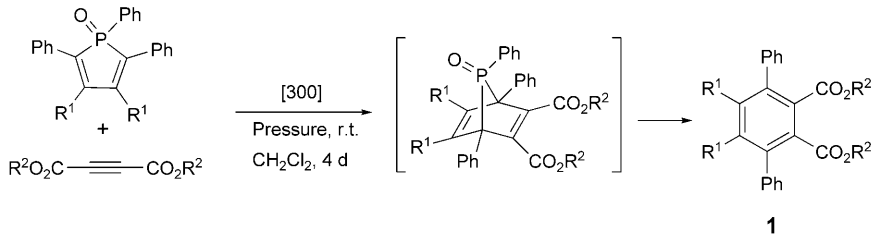


App. 239



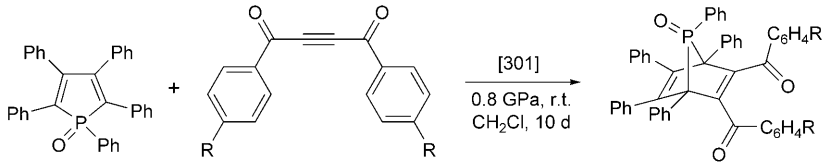
R	*P*	Solvent	*T*	*t*	**1**	**2**	**3**
Ph	0.1 MPa	benzene	40°	240 h	43%	17%	–
Ph	0.1 MPa	benzene	60°	25 h	41%	18%	–
Ph	0.1 MPa	benzene	80°	50 h	13%	21%	–
Ph	1.0 GPa	benzene	60°	25 h	65%	35%	–
Ph	1.0 GPa	benzene	60°	100 h	45%	54%	–
Ph	1.0 GPa	CH_2Cl_2	60°	50 h	24%	56%	19%
Ph	1.0 GPa	CH_2Cl_2	60°	100 h	0.2%	0.5%	98%
Ph	1.0 GPa	CH_3CN	60°	100 h	5%	–	86%
Me	0.1 MPa	benzene	60°	25 h	52%	14%	–
Me	1.0 GPa	benzene	60°	50 h	55%	31%	12%
Me	1.0 GPa	benzene	60°	100 h	47%	10%	43%
Me	1.0 GPa	CH_2Cl_2	60°	100 h	–	–	quant.

App. 240



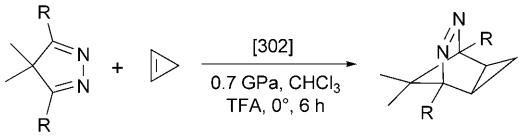
R^1	R^2	*P*	Yield (**1**)
Ph	Me	1.0 GPa	16%
Ph	*t*-Bu	1.0 GPa	10%
H	Me	0.9 GPa	68%
H	*t*-Bu	0.9 GPa	60%

App. 241



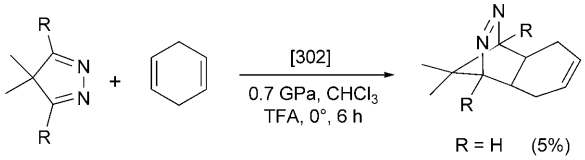
R = H (50%)
R = Me (48%)
R = Cl (38%)

App. 242



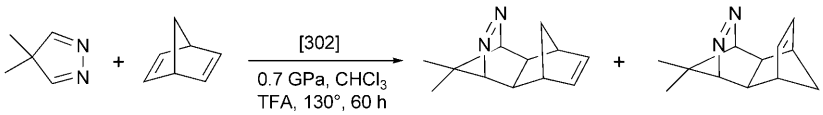
R = H (10%)
R = Me (7%)

App. 243



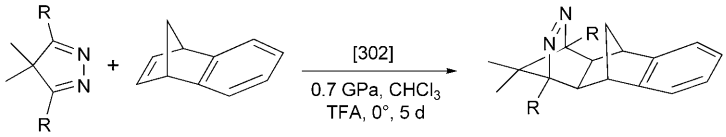
R = H (5%)
R = Me (30%)

App. 244



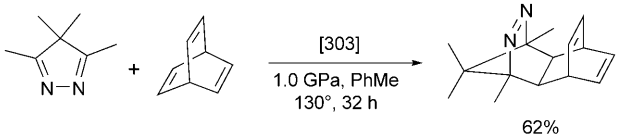
30% *exo* 10% *endo*

App. 245



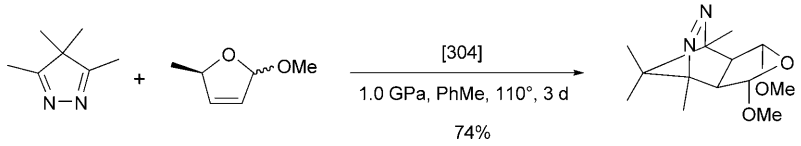
R = H (63%)
R = Me (75%)

App. 246

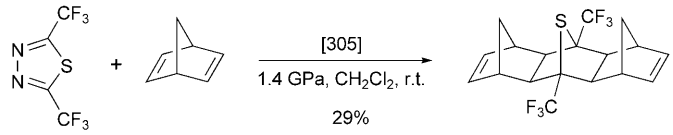


62%

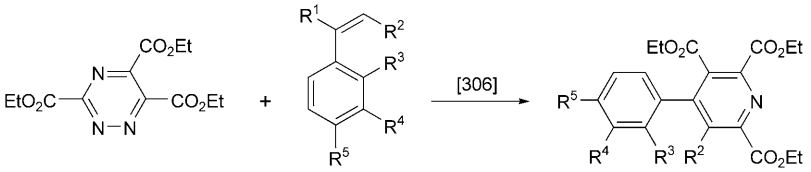
App. 247



App. 248



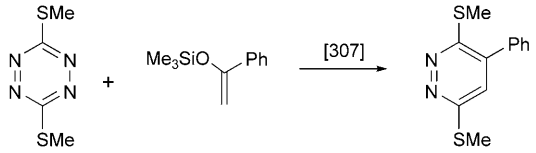
App. 249



R^1	R^2	R^3	R^4	R^5	*P*	Solvent	*T*	*t*	Yield[a])
Me_3SiO	H	H	H	H	0.1 MPa	$CHCl_3$	60°	22 h	72% (71:10)
Me_3SiO	H	H	H	H	0.62 GPa	CH_2Cl_2	25°	24 h	54% (>95:5)
Me_3SiO	Me	H	H	H	0.1 MPa	$CHCl_3$	60°	16 h	–
Me_3SiO	Me	H	H	H	0.62 GPa	CH_2Cl_2	25°	24 h	–
EtS	Me	H	H	H	0.1 MPa	$CHCl_3$	80 – 160°	10 – 20 h	–
Me_3SiO	Me	BnO	MeO	MeO	0.1 MPa	$CHCl_3$	65°	24 h	–
Me_3SiO	Me	BnO	MeO	MeO	0.62 GPa	CH_2Cl_2	25°	24 h	–

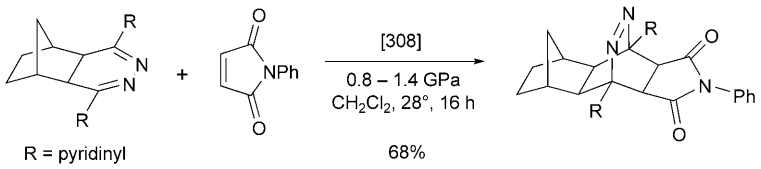
[a]) In parentheses, regioisomer ratio

App. 250



P	Solvent	*T*	*t*	Yield
1.3 GPa	CH_2Cl_2	25°	48 h	88%
0.1 MPa	xylene	140°	26 h	78%
0.1 MPa	dioxane	100°	24 – 30 h	trace

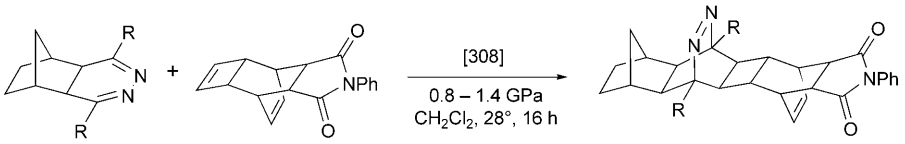
App. 251



R = pyridinyl

68%

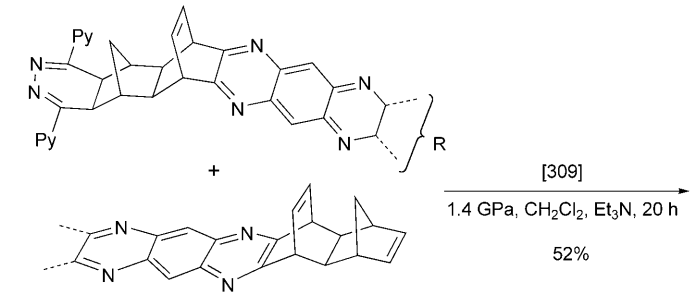
App. 252



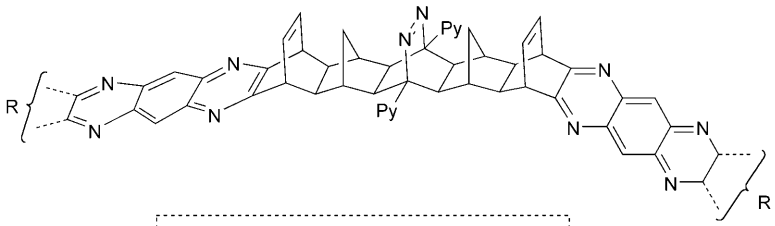
R = pyridinyl

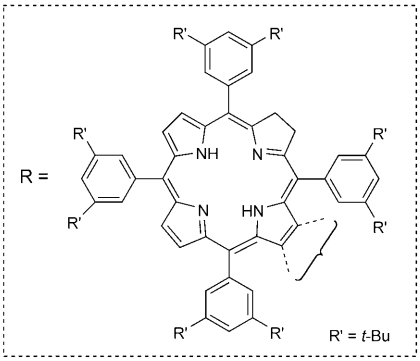
60%

App. 253

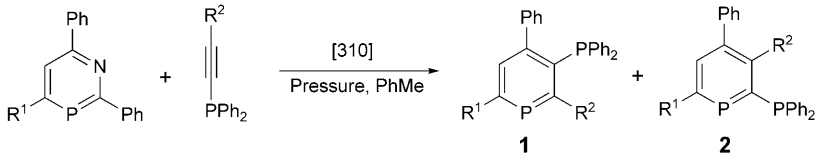


52%



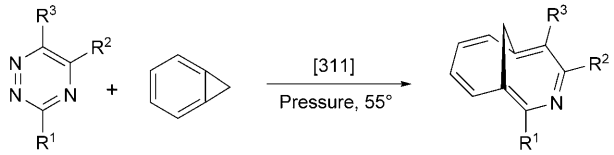


App. 254



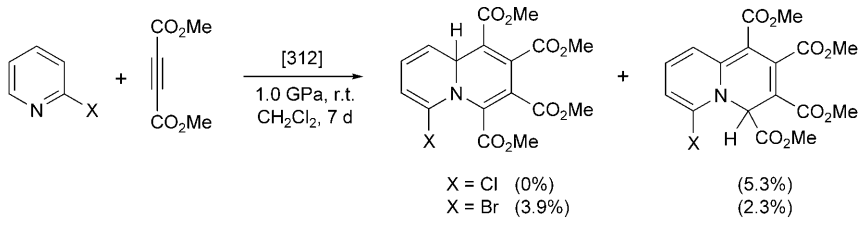
R^1	R^2	*P*	*T*	*t*	**1**	**2**
Ph	H	0.93 GPa	120°	22 h	8%	–
Tol	H	0.80 GPa	100°	20 h	25%	–
Ph	Ph_2P	0.82 GPa	140°	70 h	27%	–
Tol	Ph_2P	0.85 GPa	140°	72 h	34%	–
Ph	Me	0.82 GPa	130°	23 h	–	36%
Tol	Me	0.90 GPa	130°	46 h	–	35%
Ph	Ph	0.86 GPa	100°	21 h	–	60%
Tol	Ph	0.89 GPa	100°	24 h	–	33%

App. 255

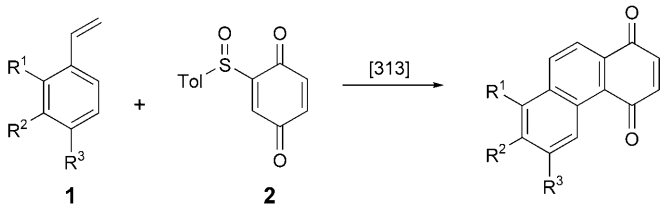


R^1	R^2	R^3	*P*	Solvent	*t*	Yield
EtOOC	EtOOC	EtOOC	0.1 MPa	AcOEt/hexane 2:1	26 h	67%
CN	EtOOC	EtOOC	0.1 MPa	AcOEt/hexane 2:1	17 h	70%
H	EtOOC	EtOOC	1.5 GPa	CH_2Cl_2/hexane 2:1	27 h	41%
EtOOC	H	H	1.5 GPa	CH_2Cl_2/hexane 2:1	27 h	33%

App. 256



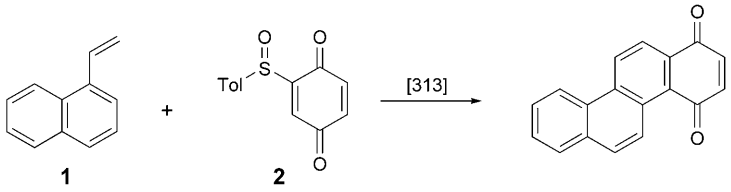
App. 257



1 **2**

R^1	R^2	R^3	**1/2**	*P*	Solvent	*T*	*t*	Yield
H	H	H	6:1	0.1 MPa	PhMe	110°	24 h	34%
H	H	H	1:6	1.25 GPa	CH_2Cl_2	20°	96 h	55%
H	H	Br	6:1	0.1 MPa	MeCN	80°	96 h	24%
H	H	Br	1:6	1.3 GPa	MeOH	20°	48 h	53%
H	H	$(Et_2O)CH$	1:6	1.35 GPa	PhMe	20°	72 h	33%
H	H	AcO	6:1	0.1 MPa	MeCN	80°	96 h	19%
H	H	AcO	1:6	1.3 GPa	CH_2Cl_2	20°	24 h	49%
MeO	MeO	H	1:6	0.1 MPa	PhMe	110°	24 h	30%
MeO	MeO	H	1:6	1.0 GPa	PhMe	20°	60 h	65%
H	MeO	MeO	1:6	0.1 MPa	PhMe	110°	24 h	60%
H	MeO	MeO	1:6	1.3 GPa	PhMe	20°	48 h	25%
H	MeO	AcO	1:6	1.3 GPa	MeCN	20°	48 h	65%

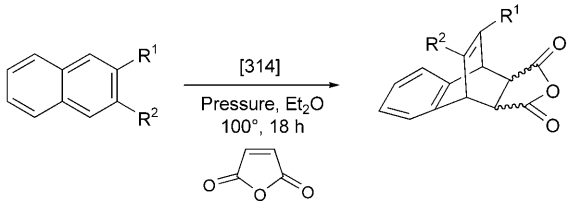
App. 258



1 **2**

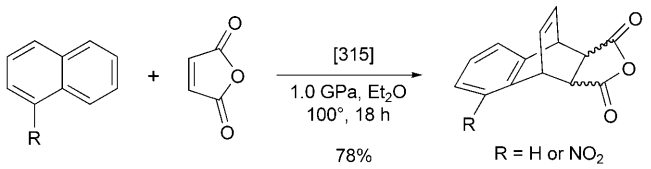
P	Solvent	*T*	*t*	**1/2**	Yield
0.1 MPa	AcOH	120°	4 h	1:6	75%
0.1 MPa	MeCN	80°	96 h	1:3	50%
1.2 GPa	CH_2Cl_2	20°	18 h	1:3	80%

App. 259

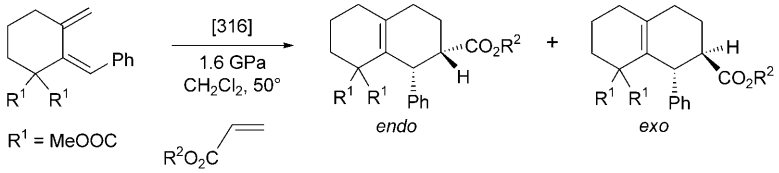


R^1	R^2	*P*	Yield
Me	H	0.93 GPa	12%
Et	Et	0.90 GPa	61%

App. 260

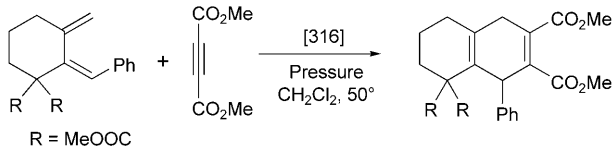


App. 261



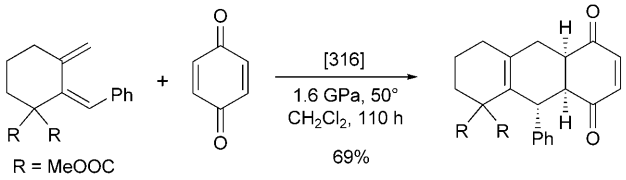
R^2	*t*	Yield	*endo*/*exo*
Ph	90 h	70%	40:60
Me	110 h	82%	20:80

App. 262

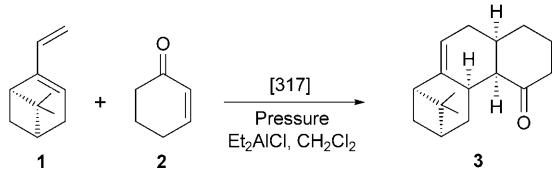


P	Solvent	*T*	*t*	Yield
0.1 MPa	PhMe	reflux	48 h	–
1.6 GPa	CH_2Cl_2	50°	70 h	53%

App. 263



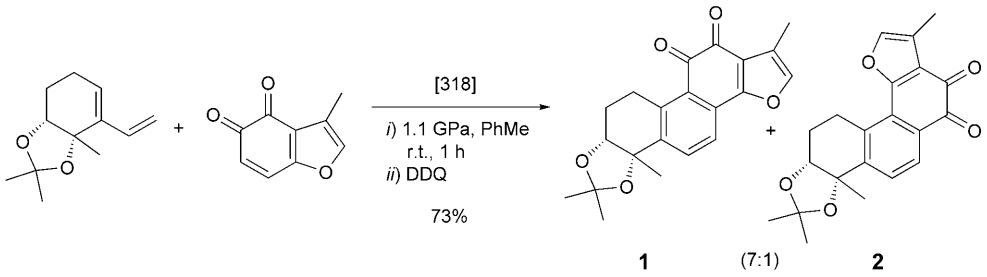
App. 264



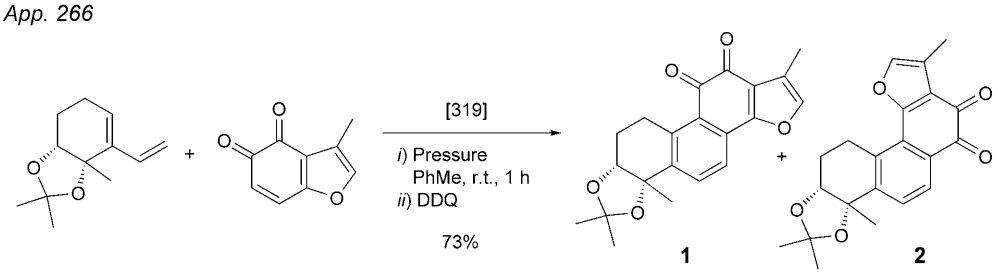
1 **2** **3**

1/**2**	Et_2AlCl/**2**	*P*	Solvent	*T*	*t*	**3**
3:2	1	0.1 MPa	PhMe	25°	7 h	47%
1:2	0.15	0.5 GPa	CH_2Cl_2	35°	18 h	55%

App. 265

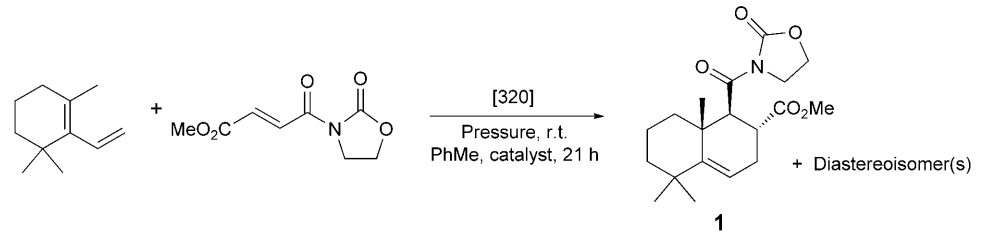


App. 266

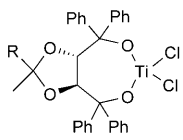


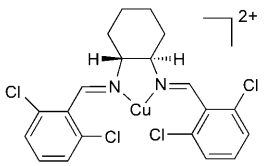
P	Solvent	*T*	*t*	Yield	**1/2**
0.1 MPa	benzene	reflux	8 h	15%	1:1
1.1 GPa	PhMe	r.t.	1 h	73%	7:1
0.1 MPa	neat	45°	2 h	76%	5:1

App. 267

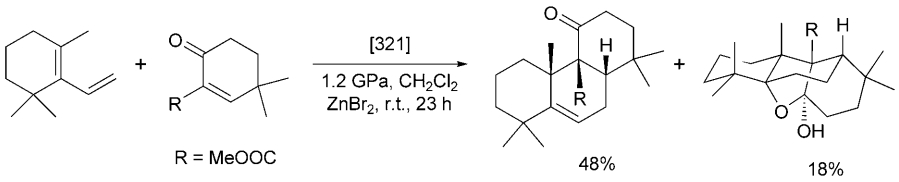


Catalyst	*P*	Yield	Product distribution
2	1.5 GPa	30%	6% ee
3	1.5 GPa	66%	0% ee
4	1.5 GPa	55%	dr 89:11, 43% ee
4	1.2 GPa	65%	dr 91:9, 60% ee
$TiCl_2(O^iPr)_2$	1.5 GPa	80%	dr 88:12

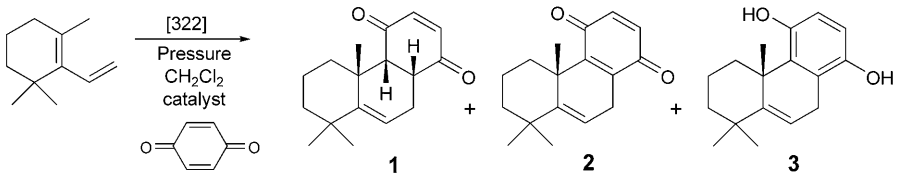




App. 268

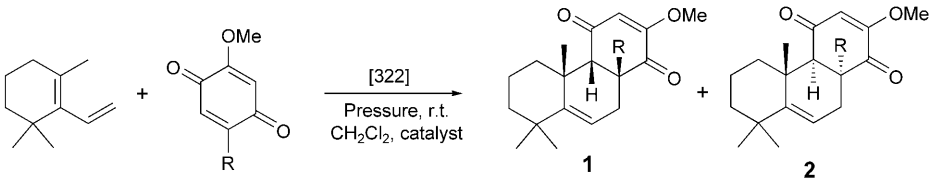


App. 269



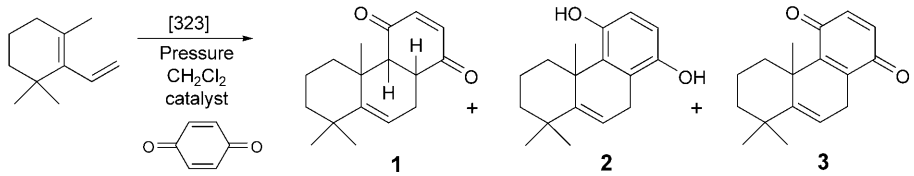
P	Catalyst	*T*	*t*	**1**	**2**	**3**
0.6 GPa	none	r.t.	14 d	32%	14%	16%
0.1 MPa	$SnCl_4$	–40°	3 h	69%	–	–
0.1 MPa	$BF_3{\cdot}OEt_2$	0°	5 h	55%	14%	–
1.2 GPa	none	r.t.	1 h	19%	8%	–
1.2 GPa	$ZnBr_2$	r.t.	1 h	67%	8%	–

App. 270



R	*P*	Catalyst	*t*	**1**	**2**
H	0.7 GPa	none	14 d	80%	–
H	1.2 GPa	none	5 d	71%	3%
H	1.2 GPa	none	14 d	86%	10%
H	1.1 GPa	$ZnBr_2$	15 h	52%	–
Me	1.2 GPa	$ZnBr_2$	14 d	92%	–

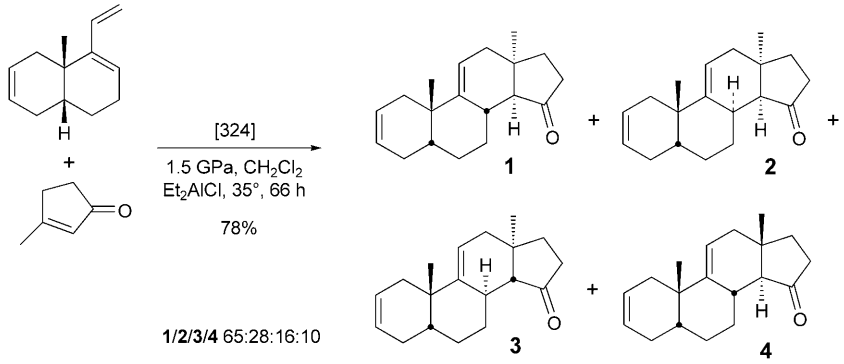
App. 271



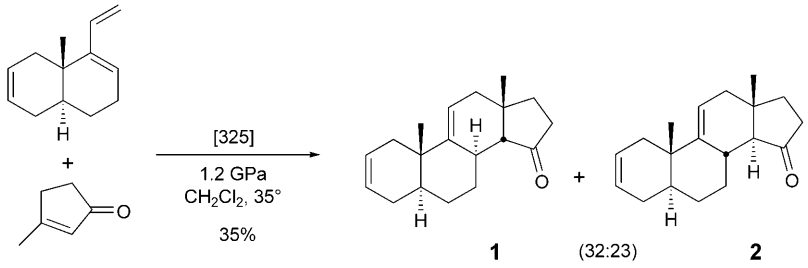
P	Cat.	*T*	*t*	**1**	**2**	**3**
0.7 GPa	none	r.t.	14 d	32%	16%	14%
0.1 MPa	none	0°	3 h	69%[a]) (**1**/**3** 4:1)		
0.1 MP	$SnCl_4$	–40°	3 h	69%	–	–

[a]) **1** + **2** + **3**.

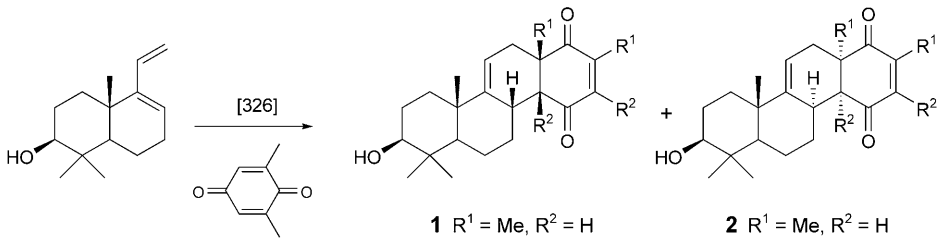
App. 272



App. 273



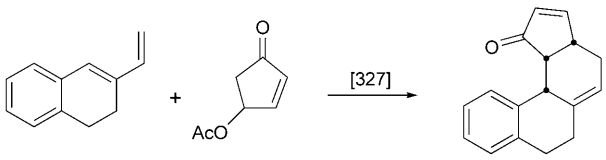
App. 274



1 R^1 = Me, R^2 = H **2** R^1 = Me, R^2 = H
3 R^1 = H, R^2 = Me **4** R^1 = H, R^2 = Me

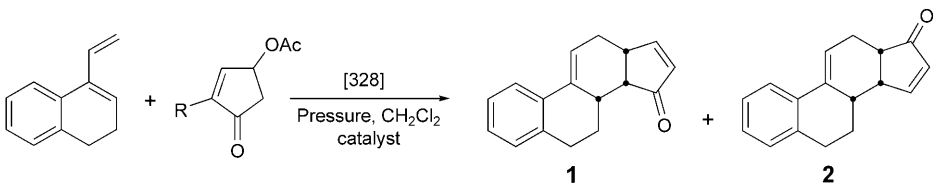
P	Catalyst	Solvent	*T*	*t*	Yield	Distribution
0.1 MPa	$Sc(OTf)_3$	MeCN	–40°	6 h	96%	**1/2/3** 56:30:14
0.1 MPa	$Sc(OTf)_3$	CH_2Cl_2	–78°	8 h	92%	**1/2/3** 77:15:8
0.1 MPa	$Sc(OTf)_3$	CH_2Cl_2	4°	17 h	72%	**1/2/3** 67:22:11
0.1 MPa	$Sc(OTf)_3$	THF/H_2O	25°	21 h	18%	**3/4** 75:25
0.1 MPa	$Sc(OTf)_3$	CH_2Cl_2/H_2O	25°	20 h	96%	**1/3/4** 2:77:21
0.1 MPa	LiCl	H_2O	25°	7 h	79%	**3/4** 76:24
1.0 GPa	LiCl	CH_2Cl_2	50°	24 h	96%	**3/4** 75:25
0.1 MPa	none	PhMe/H_2O	25°	24 h	67%	**3/4** 75:25
0.1 MPa	$AlCl_3$	CH_2Cl_2	–70°	2 h	80%	**1/2** 58:42
0.1 MPa	$TiCl_4$	CH_2Cl_2	–78°	3 h	70%	**1/2** 89:11
0.1 MPa	$Eu(fod)_3$	CH_2Cl_2	25°	24 h	?	**3/4** 42:58
0.1 MPa	none	benzene	reflux	20 h	96%	**3**

App. 275

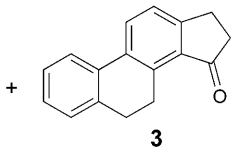


P	Solvent	*T*	*t*	Yield
0.1 MPa	CH_2Cl_2	20°	2 h	15%
1.0 GPa	CCl_4	35°	66 h	70%

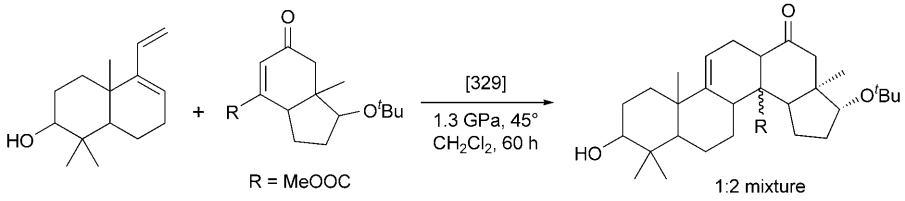
App. 276



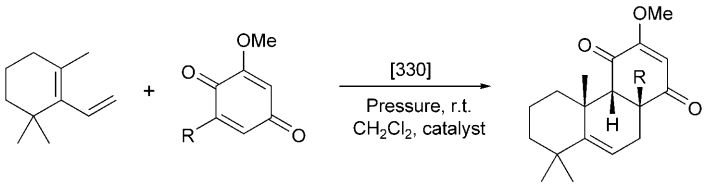
R	*P*	Catalyst	*T*	*t*	Yield
H	0.1 MPa	$EtAlCl_2$	0°	30 min	75% (**1** + **2**)
H	1.0 GPa	none	35°	16 h	68% (**1** + **2**)
Br	1.0 GPa	none	30°	15 h	60% (**3**)



App. 277

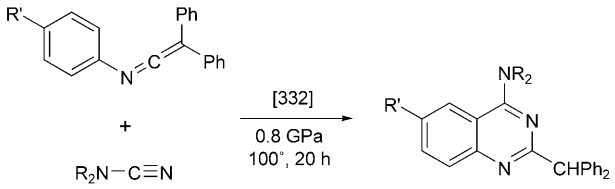


App. 278



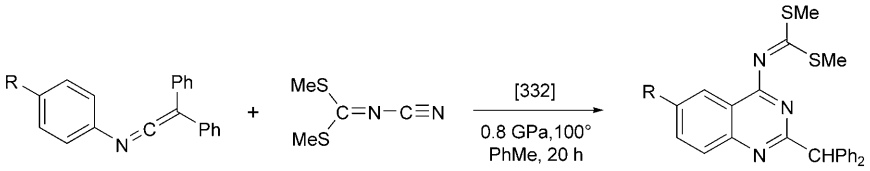
R	*P*	Catalyst	*t*	Yield
H	0.7 GPa	none	14 d	80%
H	1.2 GPa	$ZnBr_2$	15 h	52%
H	1.2 GPa	none	15 h	–
Me	1.2 GPa	$ZnBr_2$	14 d	>90%

App. 279



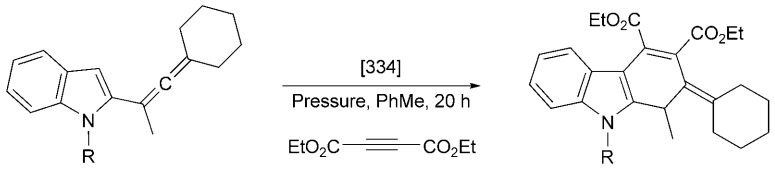
R'	R_2N	Yield
H	Me_2N	71%
Me	Me_2N	66%
MeO	Me_2N	47%
Me	Et_2N	65%
Me	$(i\text{-}Pr)_2N$	44%
Me	pyrrolidino	60%
Me	piperidino	67%
Me	morpholino	43%

App. 280



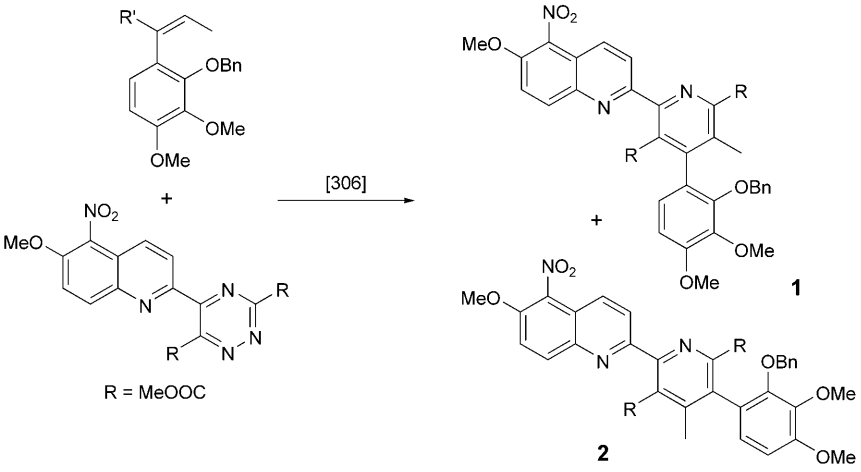
R = H (55%)
R = Me (37%)

App. 281



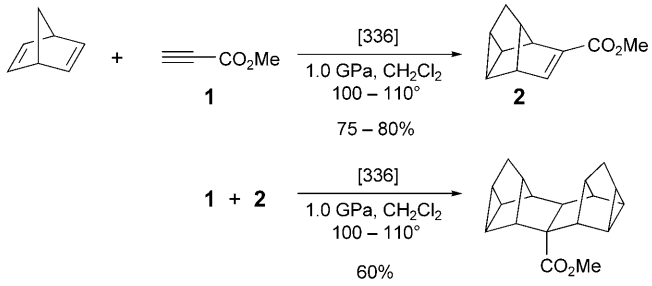
R	Condition	*T*	Yield
Me	sealed tube	150°	14% (R' = Me)
Me	0.98 GPa	r.t.	30% (R' = Me)
MeO	sealed tube	150°	64% (R' = H)
Meo	0.98 GPa	r.t.	50% (R' = H) + 36% (R' = $HOCH_2$)

App. 282

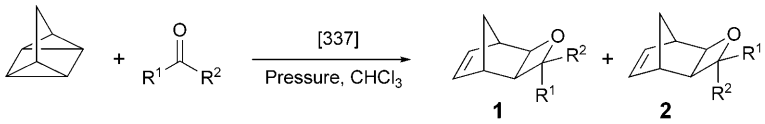


R'	*P*	Solvent	*T*	*t*	Yield	**1/2**
morpholino	0.1 MPa	MeCN	80°	12 – 24 h	15 – 26%	4:1
	0.1 MPa	MeCN	120°	16 h	30%	1:1
	0.1 MPa	$CHCl_3$	45 – 80°	12 – 48 h	–	–
	0.1 MPa	$CHCl_3$	120°	16 h	30%	1:1
	0.1 MPa	$CHCl_3$	120°	42 h	68%	1:1
	0.62 GPa	CH_2Cl_2	25°	120 h	58%	1.4:1
	0.62 GPa	MeCN	25°	96 h	–	–
pyrrolidino	0.1 MPa	$CHCl_3$	60 – 120°	12 – 48 h	–	–
	0.1 MPa	MeCN	60 – 120°	12 – 48 h	–	–
	0.62 GPa	CH_2Cl_2	25°	120 h	37%	2.8:1
	0.62 GPa	CH_2Cl_2	25°	120 h	65%	2.8:1

App. 283

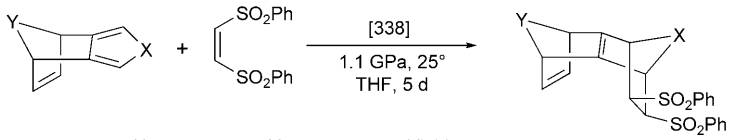


App. 284



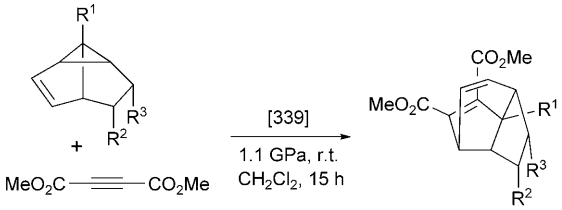
R^1	R^2	*P*	*T*	Yield	**1/2**
MeOOC	MeOOC	0.1 MPa	100°	95%	
MeOOC	Ph	0.1 MPa	100°	13%	62:38
MeOOC	Ph	0.8 GPa	75°	60%	56:44
EtOOC	Me	0.8 GPa	80°	90%	50:50
Bz	Cl	0.85 GPa	80°	59%	0:100
$CHCl_2$	Ph	0.85 GPa	80°	20%	40:60
Me	MeO	0.9 GPa	80°	–	–
MeO	MeO	0.8 GPa	80°	–	–
$-(CH_2)_4-$		0.85 GPa	80°	–	–

App. 285



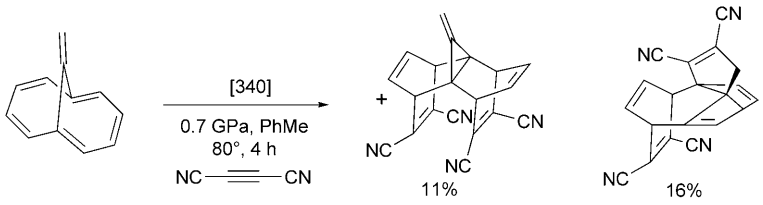
X	Y	Yield
$Me_2C=C$	CH_2	98%
cyclopropyl	CH2	87% (1:1 mixture)
CH_2	$Me_2C=C$	quant.
CH_2	cyclopropyl	98%
cyclopropyl	cyclopropyl	quant.

App. 286

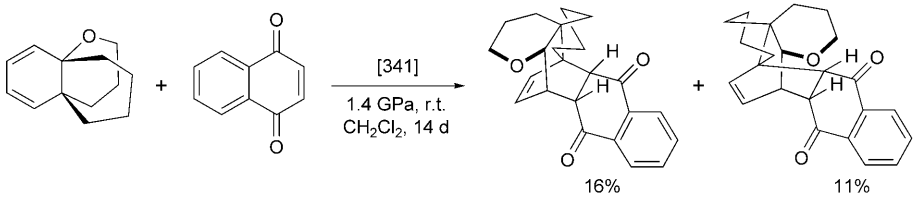


R^1	R^2	R^3	Yield
H	alkyl or alkoxy		–
Me	alkyl or alkoxy		–
MeO	alkyl or alkoxy		–
MeO	$-(CH_2)_6-$		95%
Me	$-(CH_2)_6-$		not reported

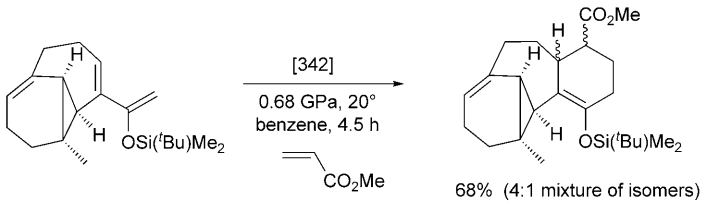
App. 287



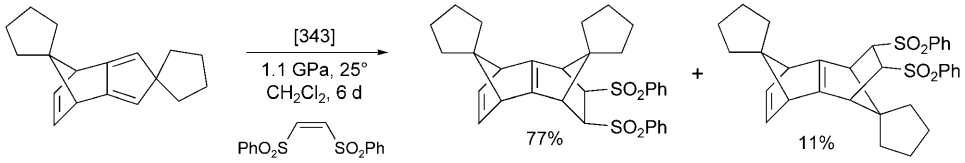
App. 288



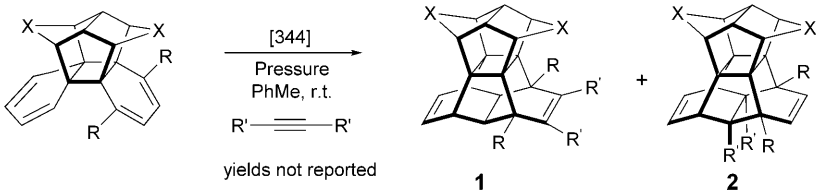
App. 289



App. 290

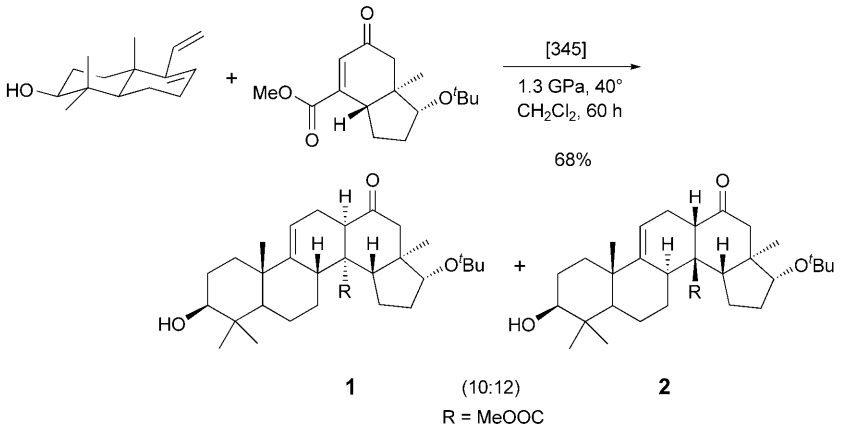


App. 291

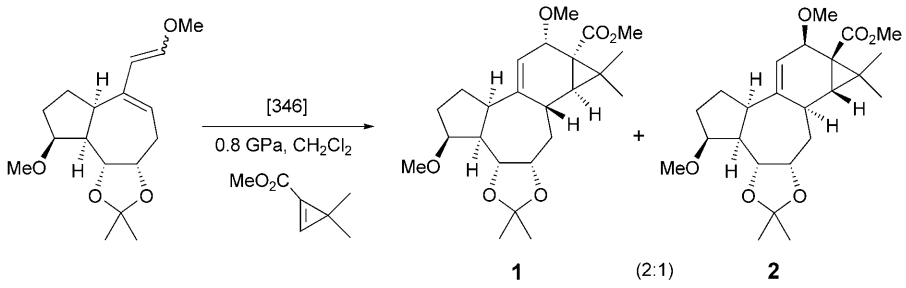


X	R	R'	*P*	**1/2**
CH_2	H	MeOOC	1.4 GPa	97:3
CH_2	H	CN	1.2 GPa	15:85
$MeOCH_2$	H	MeOOC	1.4 GPa	100:0
$MeOCH_2$	H	CN	1.4 GPa	13:87
$MeOCH_2$	H	CN	0.1 MPa	19:81
2-Ph	MeO	CN	1.2 GPa	63:37
CH_2	H	CN	1.4 GPa	100:0
CH_2	H	CN	0.1 MPa	100:0

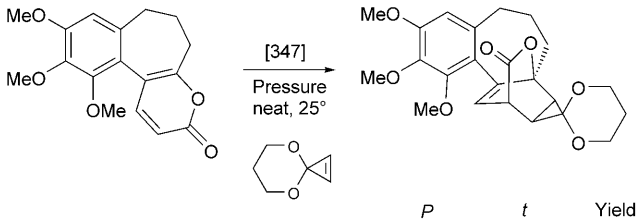
App. 292



App. 293

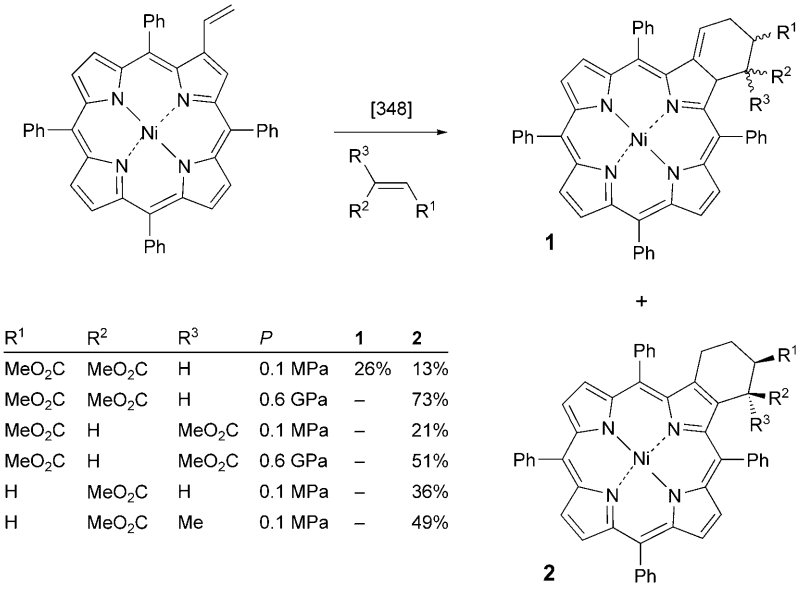


App. 294



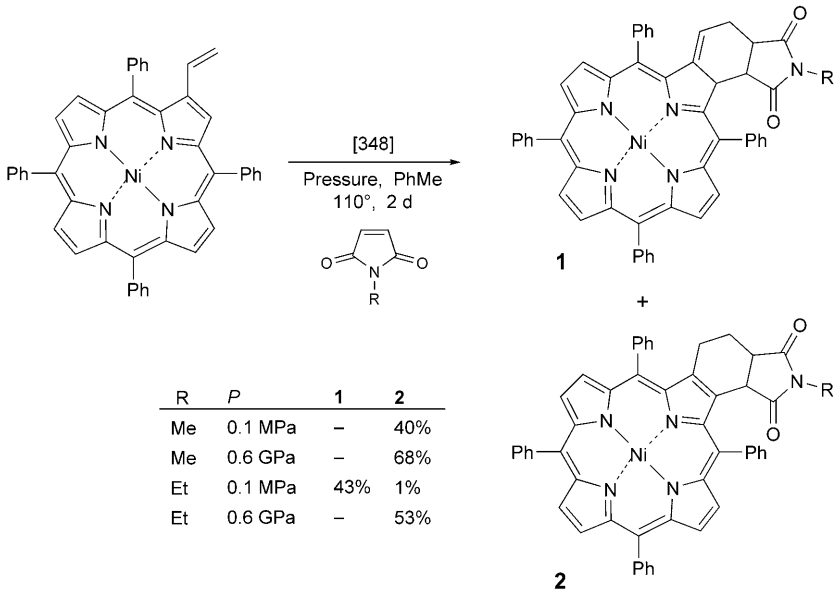
P	*t*	Yield
0.1 MPa	96 h	–
0.1 MPa	240 h	5%
0.62 GPa	24 h	33%
0.62 GPa	65 h	56%
0.62 GPa	108 h	88%

App. 295



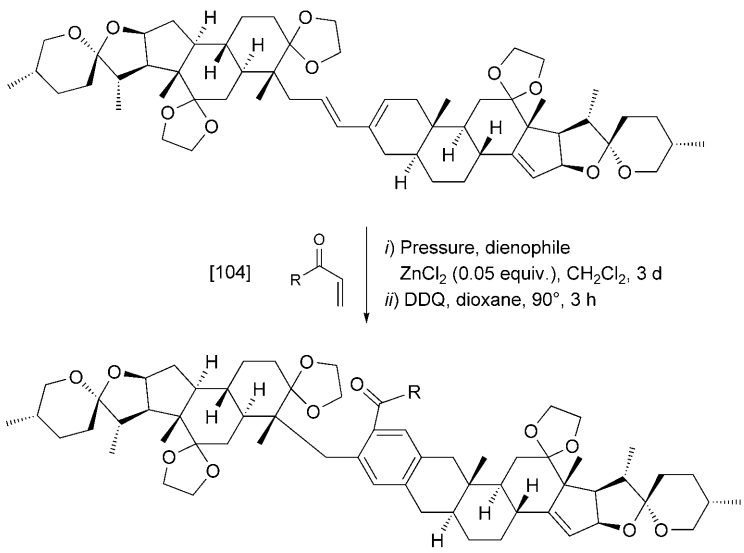
R^1	R^2	R^3	*P*	**1**	**2**
MeO_2C	MeO_2C	H	0.1 MPa	26%	13%
MeO_2C	MeO_2C	H	0.6 GPa	–	73%
MeO_2C	H	MeO_2C	0.1 MPa	–	21%
MeO_2C	H	MeO_2C	0.6 GPa	–	51%
H	MeO_2C	H	0.1 MPa	–	36%
H	MeO_2C	Me	0.1 MPa	–	49%

App. 296



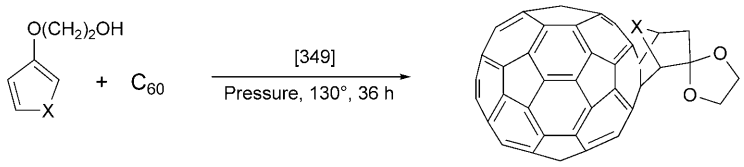
R	*P*	**1**	**2**
Me	0.1 MPa	–	40%
Me	0.6 GPa	–	68%
Et	0.1 MPa	43%	1%
Et	0.6 GPa	–	53%

App. 297



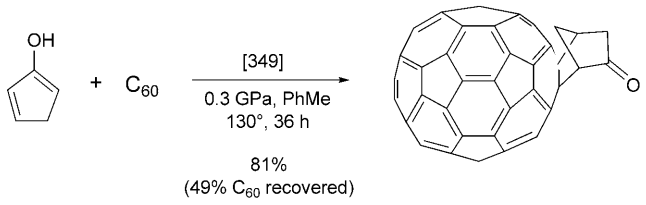
Dienophile	R	*P*	Yield
methyl propiolate	MeO	0.1 MPa	–
methyl propiolate	MeO	1.4 GPa	67%
but-3-yn-2-one	Me	1.4 GPa	96%
propynal	H	1.4 GPa	80%

App. 298

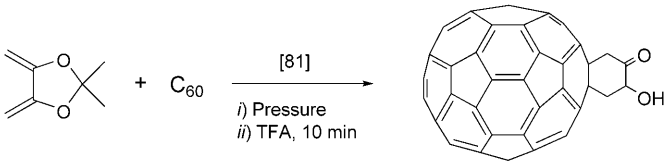


X	*P*	Solvent	Yield	C_{60} recovered
CH_2	0.3 GPa	PhMe	85%	20%
CH_2	0.1 MPa	xylene	82%	48%
$(CH_2)_2$	0.3 GPa	PhMe	82%	50%
$(CH_2)_2$	0.1 MPa	xylene	71%	80%

App. 299

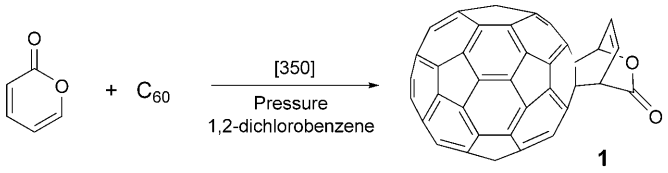


App. 300



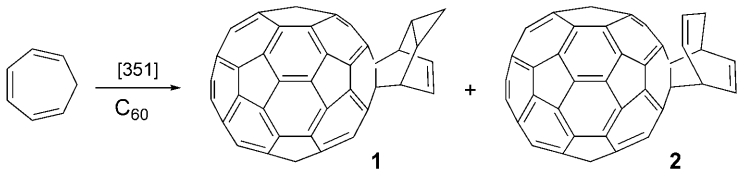
0.1 MPa, 1,2-dichlorobenzene, 25°	0%
300 MPa, 24 h, 1,2-dichlorobenzene	19%

App. 301



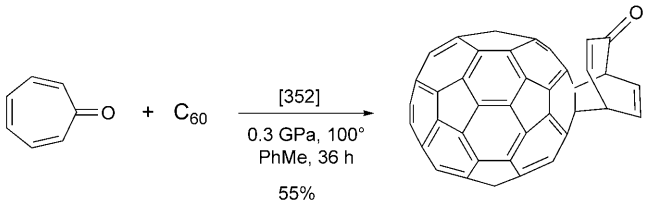
P	*T*	*t*	**1**	Bisadduct
0.3 GPa	90°	38 h	47.8%	25.1%
0.5 GPa	90°	18 h	45.4%	42.8%
0.3 GPa	100°	30 h	50.7%	16.3%
0.5 GPa	120°	5 h	50.4%	13.5%
0.1 MPa	120°	24 h	7.4%	–

App. 302

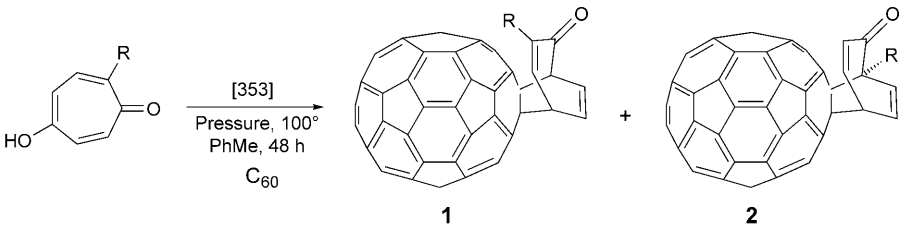


P	Solvent	*T*	*t*	**1**	**2**
0.3 GPa	PhMe	100°	36 h	52%	–
0.1 MPa	neat	120°	24 h	20%	3%
0.1 MPa	PhMe	reflux	2 min	1%	0.2%

App. 303



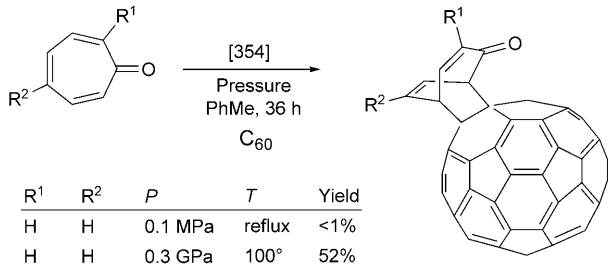
App. 304



1 **2**

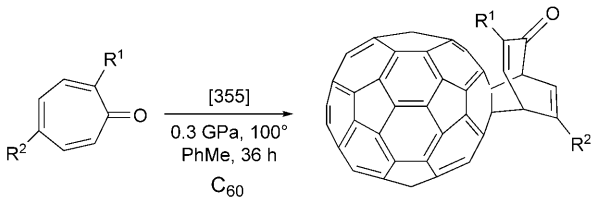
R	*P*	**1**	**2**
H	0.3 GPa	30%	–
H	0.1 MPa	16%	–
MeO	0.3 GPa	38%	31%
MeO	0.1 MPa	28%	16%
Cl	0.3 GPa	13%	12%
Cl	0.1 MPa	15%	–

App. 305



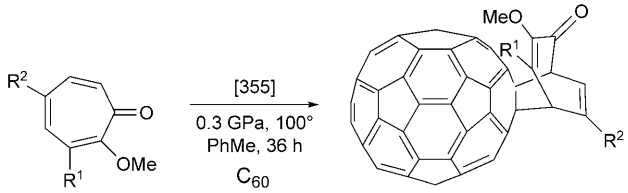
R^1	R^2	*P*	*T*	Yield
H	H	0.1 MPa	reflux	<1%
H	H	0.3 GPa	100°	52%
MeO	H	0.1 MPa	reflux	<1%
MeO	H	0.3 GPa	100°	68%
Br	H	0.3 GPa	100°	65%
H	AcO	0.3 GPa	100°	63%
H	AcO	0.3 GPa	100°	54%

App. 306



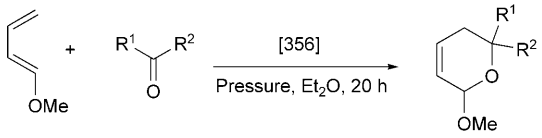
R^1	R^2	Yield
H	H	55%
MeO	H	68%
Br	H	65%
H	AcO	73%
H	MeO	54%
MeO	MeO	69%
MeO	Br	75%
MeO	Cl	68%
MeO	i-Pr	72%
MeO	BuOOC	74%
Cl	Cl	73%

App. 307



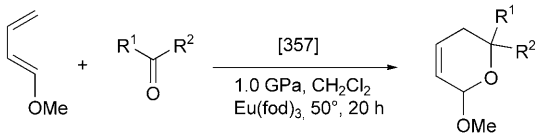
R^1 = H, R^2 = i-Pr (72%)
R^1 = i-Pr, R^2 = H (65%)

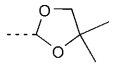
App. 308



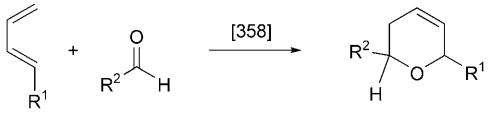
R^1	R^2	*P*	*T*	Yield	*cis*/*trans*
Me	$C_{10}H_{19}O_2C$	1.5 GPa	20°	53%	73:27
Me	$C_{10}H_{19}O_2C$	2.0 GPa	20°	65%	75:25
Me	$C_{10}H_{19}O_2C$	2.5 GPa	20°	79%	79:21
Me	MeOOC	2.0 GPa	50°	85%	70:30
CF_3	Ph	1.95 GPa	20°	81%	64:36
H	Ph	1.95 GPa	50°	80%	75:25
H	2-furyl	1.95 GPa	50°	73%	73:27
H	Me	2.0 GPa	65°	62%	70:30
H	pentyl	2.35 GPa	20°	16%	78:22
H	pentyl	2.0 GPa	65°	28%	71:29

App. 309



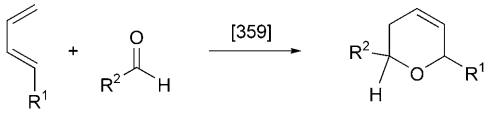
R^1	R^2	Yield	*cis*/*trans*
Me	MeOOC	81%	1:1
H	BnO_2CNHCH_2	50%	1:1
H	$Me_3SiO(Me)CH$	35%	6:4
H	Me	53%	1:1
H	Ph	15%	3:7
H	furyl	12%	1:1
H		17%	4:6

App. 310



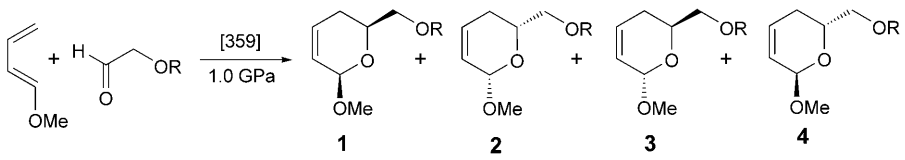
R^1	R^2	Condition	*T*	Yield	*cis*/*trans*
Me	Me	sealed tube	160 – 180°	2%	31:69
Me	Me	1.4 GPa	80°	50%	70:30
Me	Et	sealed tube	160 – 180°	–	–
Me	Et	1.4 GPa	80°	40%	65:35

App. 311

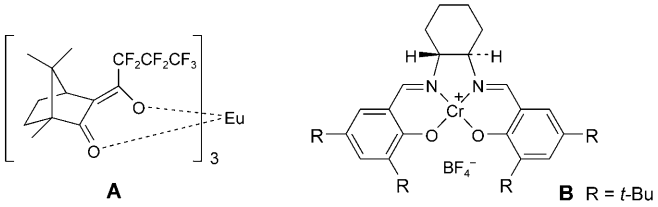


R^1	R^2	Condition	*T*	Yield	*cis*/*trans*
Me	Me	sealed tube	160 – 180°	2%	31:69
Me	Me	1.4 GPa	80°	50%	70:30
Et	Me	sealed tube	160 – 180°	2%	34:66
Et	Me	1.4 GPa	80°	50%	70:30

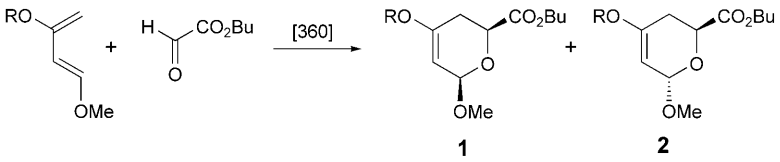
App. 312



R	Solvent	Catalyst	*T*	Yield	**1/2/3/4**
t-Bu(Me)$_2$Si	CH_2Cl_2	**A** (2%)	50°	40%	32:27:20:21
t-Bu(Me)$_2$Si	PhMe	**A** (2%)	50°	45%	29:24:22:25
Ac	CH_2Cl_2	**B** (5%)	25°	40%	6:6:43:45
Ac	PhMe	**B** (5%)	25°	46%	3:3:45:49

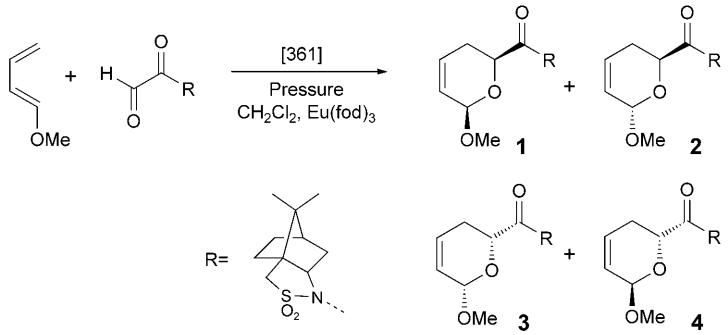


App. 313



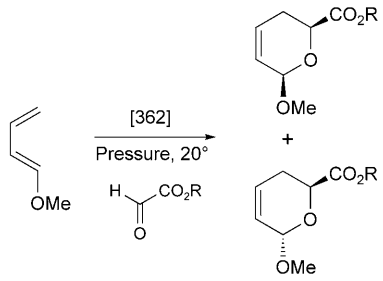
R	*P*	Solvent	Catalyst	*T*	*t*	Yield	**1/2**
Me_3Si	0.1 MPa	benzene	none	reflux	20 h	40%	1:1
Me_3Si	1.0 GPa	Et_2O	none	r.t.	24 h	80%	5:1
^{t}Bu(Me)$_2$Si	0.1 MPa	benzene	none	reflux	15 h	30%	4:1
^{t}Bu(Me)$_2$Si	1.0 GPa	Et_2O	none	r.t.	24 h	85%	10:1
^{t}Bu(Me)$_2$Si	0.1 MPa	Et_2O	Eu(fod)$_3$	r.t.	48 h	75%	7:3

App. 314



P	Eu(fod)$_3$	*T*	*t*	Yield	**1**/**2**/**3**/**4**
0.1 MPa	none	20°	20 h	73%	73:27
1.0 GPa	none	20°	20 h	76%	71:29
1.0 GPa	2%	20°	20 h	80%	75:25
0.1 MPa	2%	20°	20 h	81%	89:11
0.1 MPa	2%	20°	1 h	81%	94:6
0.1 MPa	2%	–15°	16 h	47%	96:4
0.1 MPa	2%	–20°	16 h	35%	>96:4
0.1 MPa	2%	–78°	75 h	36%	>96:4

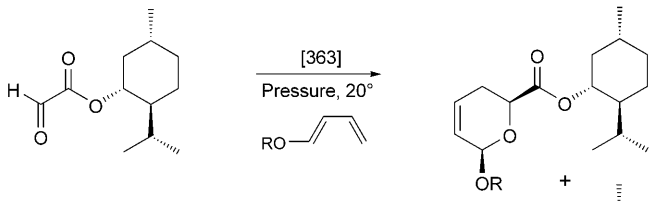
App. 315



R = (–)-(*R*)-Menthyl glyoxylate

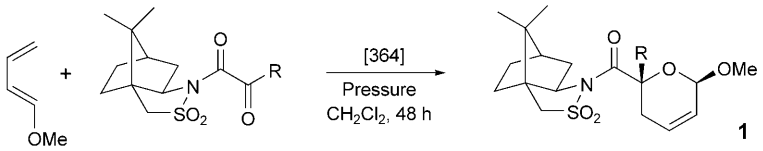
P	Solvent	Yield	*cis*/*trans*
0.27 GPa	PhMe	85%	64:36
0.44 GPa	PhMe	90%	66:34
0.56 GPa	PhMe	quant.	67:33
0.71 GPa	PhMe	quant.	68:32
0.84 GPa	PhMe	quant.	69:31
0.87 GPa	PhMe	quant.	69:31
0.85 GPa	Et_2O	quant.	67:33
1.11 GPa	Et_2O	quant.	70:30
1.55 GPa	Et_2O	quant.	72:28
0.25 GPa	CH_2Cl_2	88%	65:35
0.40 GPa	CH_2Cl_2	92%	67:33
0.61 GPa	CH_2Cl_2	quant.	69:31
0.79 GPa	CH_2Cl_2	quant.	70:30

App. 316



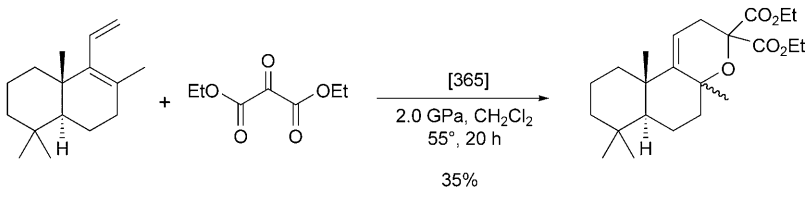
P	Solvent	*t*	Yield	*cis*/*trans*
0.1 MPa	PhMe	140 h	90%	60:40
0.85 GPa	PhMe	19 h	95%	70:30
0.79 GPa	PhMe	19 h	95%	68:32
0.1 MPa	CH_2Cl_2	140 h	90%	61:39
0.80 GPa	CH_2Cl_2	19 h	96%	70:30
0.77 GPa	CH_2Cl_2	19 h	95%	69:31

App. 317

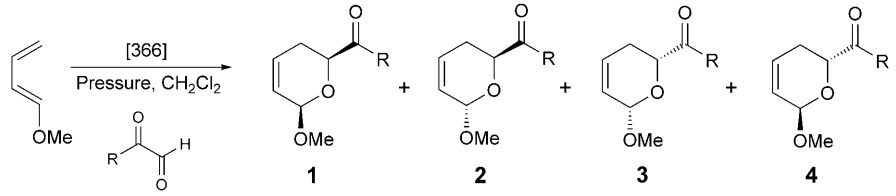


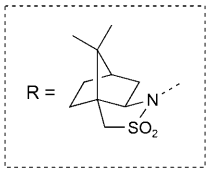
R	*P*	*T*	Yield	**1/2**
H	1.2 GPa	20°	80%	28:72
Me	1.4 GPa	50°	86%	66:34
Ph	1.4 GPa	50°	86%	63:37

App. 318



App. 319

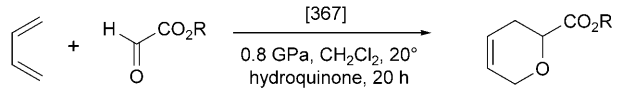




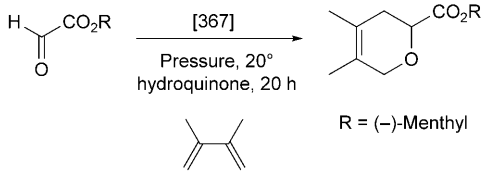
P	Catalyst	*T*	*t*	Yield	**1/2/3/4**
0.1 MPa	none	20°	20 h	73%	44:29:14:13
0.8 GPa	none	20°	20 h	75%	42:27:16:15
1.2 GPa	$Eu(fod)_3$ (2%)	20°	20 h	83%	30:47:6:17
0.1 MPa	$Eu(fod)_3$ (2%)	20°	20 h	81%	8:81:2:9
0.1 MPa	$Eu(fod)_3$ (2%)	20°	3 h	81%	5:89:1:5
0.1 MPa	$Eu(fod)_3$ (2%)	–78°	75 h	36%	*ca.* 3:92:4[a])

[a]) **1/2/(3+4)**

App. 320

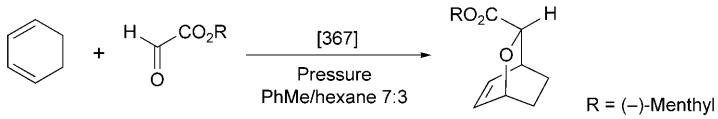


App. 321



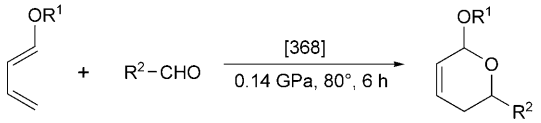
P	Solvent	Yield	$[\alpha]_{578}^{20}$
0.89 GPa	PhMe	32%	–56.2 (*c* = 1.04)
0.95 GPa	hexane	29%	–55.9 (*c* =1.05)
1.02 GPa	hexane	30%	–55.6 (*c* = 1.01)
0.79 GPa	CH_2Cl_2	42%	–65.0 (*c* = 1.08)
0.83 GPa	CH_2Cl_2	46%	–64.5 (*c* = 1.01)

App. 322



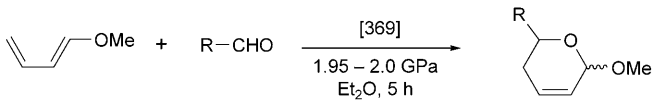
P	Yield	$[\alpha]_{578}^{20}$	Optical yield
1.08 GPa	31%	–15.7 (*c* = 2.70)	14.6%
1.24 GPa	37%	–18.9 (*c* = 2.26)	17.5%

App. 323



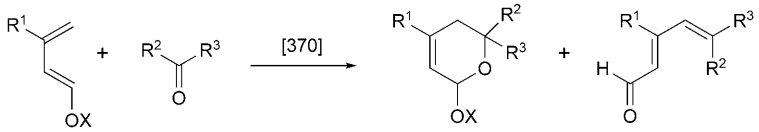
R^1	R^2	Yield
Me	Me	50%
Et	Me	50%
Me	Et	40%
Me	Ph	60%
Et	Ph	65%

App. 324



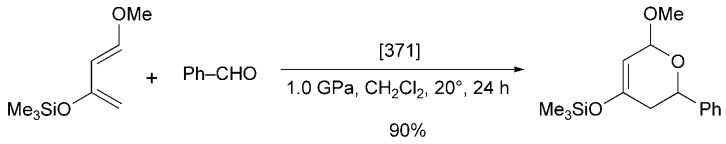
$R = C_5H_{11}$	$T = 65°$	28%
R = Ph	$T = 50°$	80%

App. 325

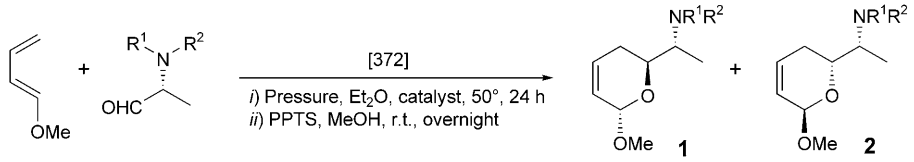


X	R^1	R^2	R^3	P	Solvent	T	t	**1**	**2**
Ac	Me	H	$^iPrO_2C$	0.1 MPa	toluene	110°	3 h	–	48%
Me_3Si	Me	H	$^iPrO_2C$	0.1 MPa	toluene	110°	3 h	65%	–
Me_3Si	Me	H	$^iPrO_2C$	1.0 GPa	pentane	r.t.	20 – 24 h	58%	–
Ac	Me	MeO_2C	MeO_2C	0.1 MPa	toluene	110°	3 h	–	42%
Ac	Me	MeO_2C	MeO_2C	1.0 GPa	pentane	r.t.	20 – 24 h	54%	–
Me_3Si	Me	MeO_2C	MeO_2C	0.1 MPa	toluene	110°	3 h	85%	–
Ac	H	H	$^iPrO_2C$	0.1 MPa	toluene	r.t.	3 h	50%	–
Ac	H	H	$^iPrO_2C$	1.0 GPa	pentane	r.t.	20 – 24 h	22%	–
Me_3Si	H	H	$^iPrO_2C$	0.1 MPa	toluene	110°	3 h	71%	–
Me_3Si	H	H	$^iPrO_2C$	1.0 GPa	pentane	110°	20 – 24 h	60%	–

App. 326

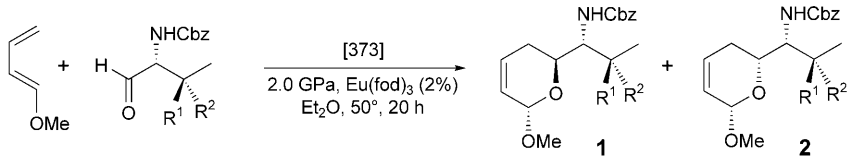


App. 327



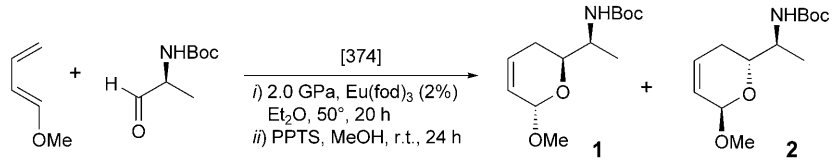
R^1	R^2	*P*	Catalyst	Yield	**1/2**
H	Cbz	1.5 GPa	$Eu(fod)_3$ (2%)	50%	33:67
H	Cbz	2.5 GPa	none	35%	33:67
H	Boc	1.5 GPa	$Eu(fod)_3$ (2%)	55%	25:75
H	Boc	2.5 GPa	none	12%	25:75
Bn	Bn	1.5 GPa	$Eu(fod)_3$ (2%)	58%	92:8
Bn	Ts	1.5 GPa	$Eu(fod)_3$ (2%)	79%	94:6
Bn	Boc	1.5 GPa	$Eu(fod)_3$ (2%)	80%	94:6
–phthaloyl–		1.5 GPa	$Eu(fod)_3$ (2%)	75%	83:17

App. 328



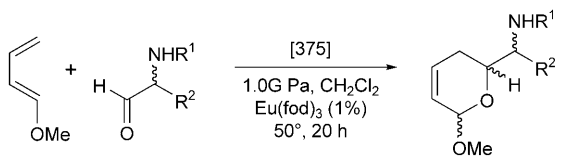
R^1	R^2	Yield	**1/2**
$BnOCH_2$	H	70 – 80%	1:2
$^t Bu(Ph)_2SiO$	H	70 – 80%	1:4
H	$BnOCH_2$	70 – 80%	1:2
H	$^t Bu(Ph)_2SiO$	70 – 80%	1:8

App. 329



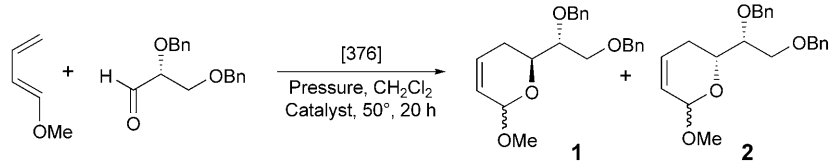
70% (**1/2** 2:1)

App. 330



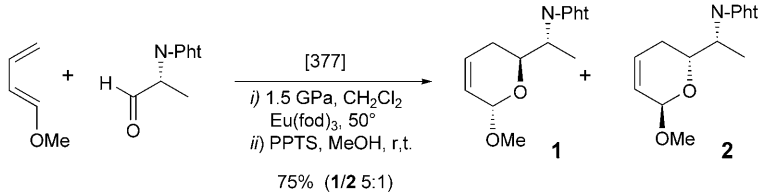
R^1	R^2	Yield
Cbz	H	50%
Cbz	Me	41%
Ts	Me	35%
Cbz	i-Bu	40%
Boc	i-Bu	20%
Cbz	Bn	65%
Ts	Bn	67%

App. 331

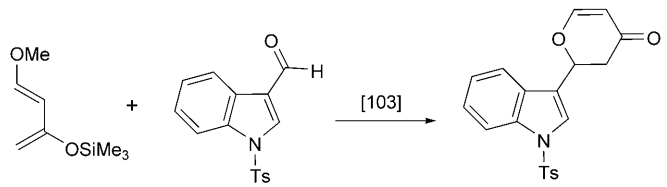


P	Catalyst	Yield	**1/2**
2.0 GPa	none	36%	74:26
2.0 GPa	$Eu(fod)_3$	60%	31:69
1.5 GPa	$Eu(fod)_3$	48%	25:75
0.7 GPa	$Eu(fod)_3$	24%	51:49

App. 332

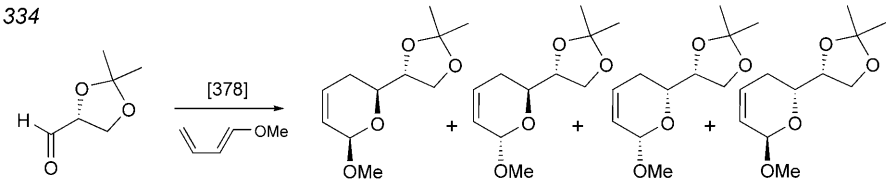


App. 333



Condition	Solvent	Catalyst	*T*	*t*	Yield
sealed tube	PhMe	none	170°	24 h	82%
0.1M Pa	PhMe	$ZnCl_2$	110°	24 h	56%
1.2 GPa	CH_2Cl_2	none	45°	96 h	99%

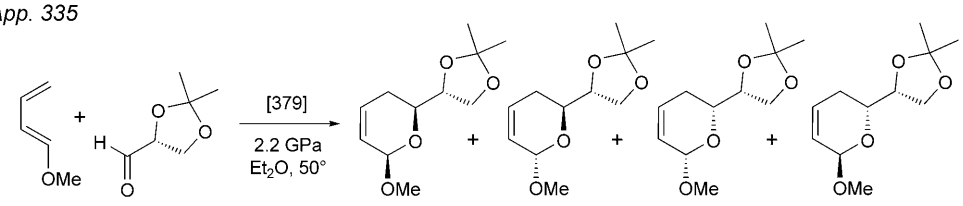
App. 334



P	Solvent	*T*	Yield	**1**/**2**/**3**/**4**	de (*endo*)[a])	de (*exo*)[b])
1.45 GPa	Et_2O	50°	42%	63:15:15:6.5	61.5	40.9
1.8 GPa	Et_2O	50°	74%	65:15:14:6	64.6	42.9
2.0 GPa	Et_2O	25°	15%	69:15:12:4	70.4	57.9
2.0 GPa	Et_2O	50°	75%	65.5:14.5:14.5:5.5	63.8	45.0
2.2 GPa	Et_2O	25°	18%	71.5:14.5:10.5:3.5	74.4	61.1
2.2 GPa	Et_2O	50°	80%	66:16:13:5	67.1	52.4
1.45 GPa	PhMe/PhH 7:3	50°	40%	61.5:16:15.5:7.0	59.1	39.1
2.0 GPa	PhMe/PhH 7:3	25°	11%	74:13:10:3	76.2	62.5
2.0 GPa	PhMe/PhH 7:3	50°	71%	66:14.5:14:5.5	65.0	45.0
2.2 GPa	PhMe/PhH 7:3	50°	73%	67.5:14:13.5:5	66.7	47.7
1.45 GPa	CH_2Cl_2	50°	58%	55:18:18:9	50.7	33.3
2.0 GPa	CH_2Cl_2	25°	20%	64:16:14:6	64.1	45.5
2.0 GPa	CH_2Cl_2	50°	79%	59.5:16.5:16.5:7.5	56.6	37.5
2.2 GPa	CH_2Cl_2	25°	21%	68.5:13.5:13.5:4.5	67.1	50.0
2.2 GPa	CH_2Cl_2	50°	86%	64:15:15:6	62.0	42.9

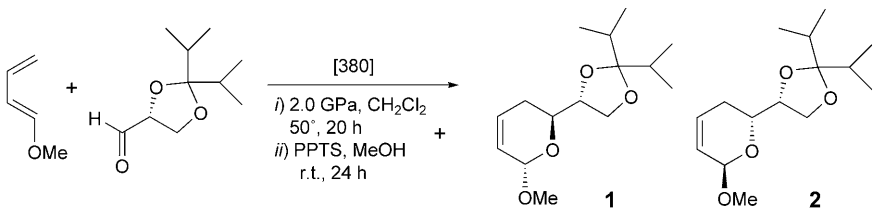
[a]) (**1** – **3**)/(**1** + **3**). [b]) (**2** – **4**)/(**2** + **4**).

App. 335



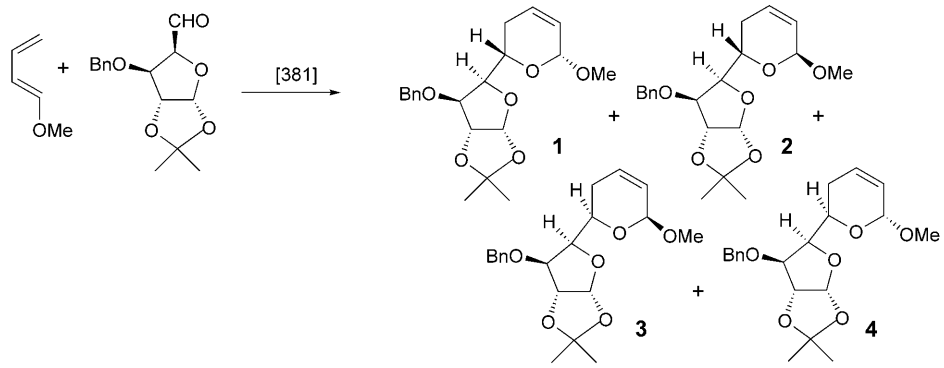
80% (**1**/**2**/**3**/**4** 66:16:13:5)

App. 336



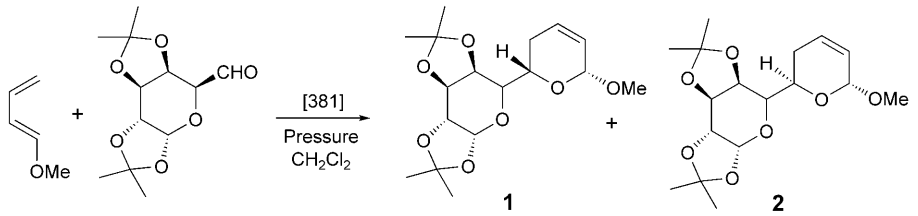
$Eu(fod)_3$ as catalyst	64% (**1** + **2**)
without catalyst	57% (**1** + **2**)

App. 337



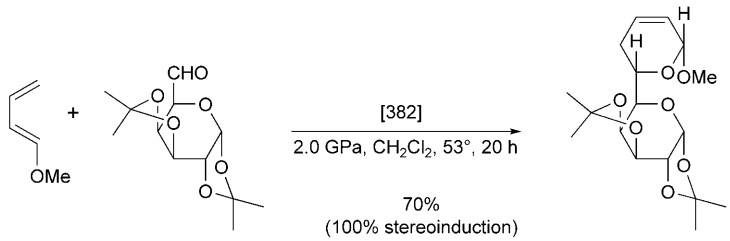
P	Catalyst	*T*	Yield	**1/2/3/4**
2.0 GPa	none	53°	55%	65.3:26.7:5.5:2.5
1.1 GPa	$Eu(fod)_3$	50°	33%	54.1:26.2:12.7:7.0

App. 338

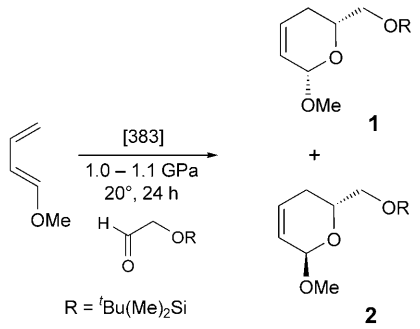


P	Catalyst	*T*	Yield	**1/2**
2.0 GPa	none	53°	72%	100:0
1.1 GPa	$Eu(fod)_3$	50°	56%	98:2

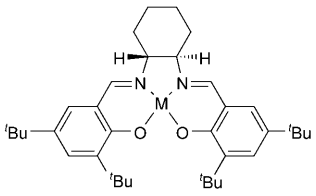
App. 339



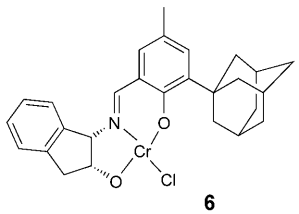
App. 340



Catalyst	Solvent	Yield	**1**/**2**	ee (**1**)	ee (**2**)
3 (5%)	CH_2Cl_2	61%	93:7	93	73
3 (2%)	CH_2Cl_2	52%	93:7	92	70
3 (0.5%)	CH_2Cl_2	30%	90:10	81	43
3 (2%)	PhMe	33%	88:12	75	48
3 (5%)	CH_2Cl_2	52%	95:5	94	74
3 (2%)	CH_2Cl_2	47%	95:5	94	79
4 (2%)	CH_2Cl_2	32%	81:19	75	32
5 (5%)	CH_2Cl_2	80%	91:9	84	66
5 (2%)	CH_2Cl_2	70%	95:5	85	65
5 (2%)	PhMe	84%	96:4	87	78
5 (2%)	CH_2Cl_2	88%	93:7	83	69
5 (0.5%)	CH_2Cl_2	60%	96:4	85	65
3 (2%)	neat, mol. sieves	5%	95:5	80	?
5 (2%)	neat, mol. sieves	45%	92:8	64	?
6 (2%)	CH_2Cl_2	80%	98:2	65	?

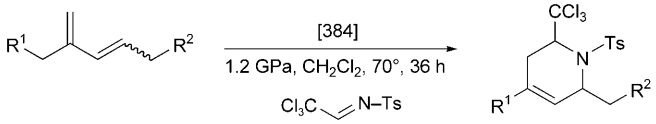


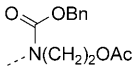
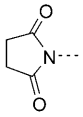
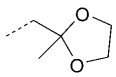
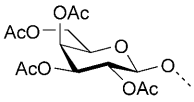
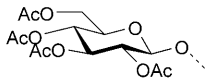
3 M = Co
4 M = CoCl
5 M = CrCl



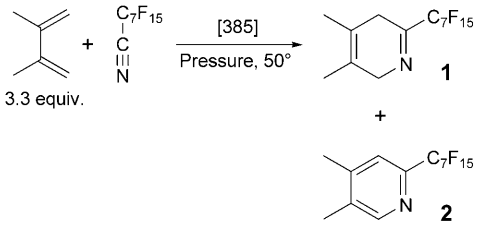
6

App. 341



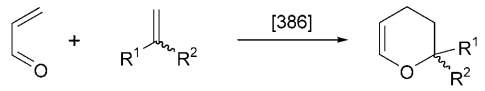
R^1	R^2	Yield
AcO	BnO_2CCH_2	89%
AcO	$BnO(CH_2)_2$	91%
BnO	^{t}Bu(Me)$_2$SiO	62%
^{t}Bu(Me)$_2$SiO	$BnO(CH_2)_2$	60%
trityloxy		72%
	EtO	77%
C_5H_{11}		67%
		61%

App. 342



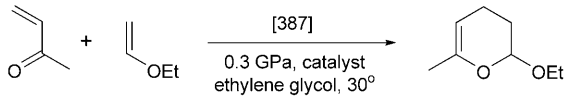
P	*t*	**1**	**2**
0.1 MPa	2 h	1.6%	–
0.1 MPa	67 h	23.7%	4.4%
0.1 MPa	98 h	27.0%	10.2%
0.15 GPa	2 h	5.6%	–
0.15 GPa	4 h	8.0%	–
0.15 GPa	5.5 h	12.0%	0.5%
0.15 GPa	29 h	29.1%	7.8%
0.15 GPa	44 h	28.6%	8.5%
0.15 GPa	67 h	31.3%	13.3%
0.15 GPa	98 h	26.4%	20.8%

App. 343



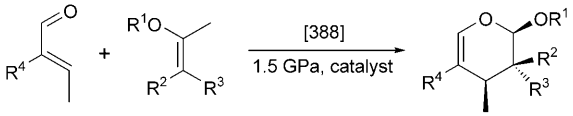
Condition	Solvent	*T*	*t*	Yield
sealed tube	neat	230°	5 h	1%
sealed tube	neat	230°	5 h	8%
sealed tube	neat	230°	5 h	4%
1.4 GPa	acetone	80°	15 h	21%
1.4 GPa	acetone	80°	5 h	7%
1.4 GPa	neat	80°	5 h	35%
1.4 GPa	neat	80°	5 h	12%
1.0 GPa	PhMe	80°	5 h	25%
1.0 GPa	neat	80°	5 h	55%
0.8 GPa	hexane	80°	5 h	20%
1.0 GPa	neat	80°	5 h	15%

App. 344



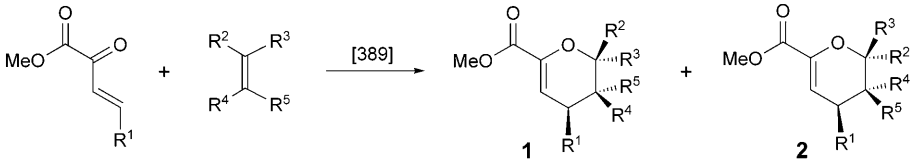
with $Yb(OTf)_3$ catalyst	100%
without catalyst	28%

App. 345



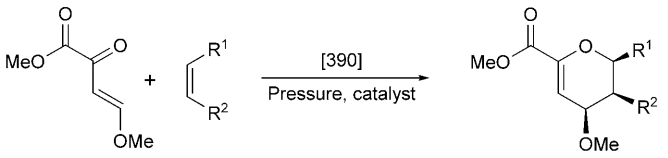
R^1	R^2	R^3	R^4	Catalyst	*T*	*t*	Yield
i-Pr	Me	H	H	$Eu(fod)_3$	r.t.	16 h	85%
i-Pr	Me	H	H	$Eu(tfc)_3$	r.t.	16 h	75%
Et	Me	Me	H	$Eu(fod)_3$	r.t.	16 h	65%
Et	Me	Me	H	$Eu(fod)_3$	r.t.	2 d	85%
Et	Me	Me	H	$Eu(tfc)_3$	r.t.	3 d	71%
i-Pr	Me	H	Me	$Eu(fod)_3$	50°	3 d	37%
Et	Me	Me	Me	$Eu(fod)_3$	50°	3 d	36%
$-(CH_2)_3-$		H	H	$Eu(fod)_3$	50°	3 d	23%

App. 346



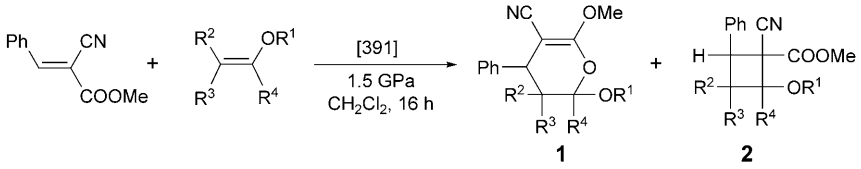
R^1	R^2	R^3	R^4	R^5	Pressure	Solvent	Catalyst	*T*	*t*	Yield	**1/2**
MeO	H	EtO	H	H	0.1M Pa	PhMe	none	110°	29 h	48%	1.8:1.0
MeO	H	EtO	H	H	1.3 GPa	neat	none	24°	65 h	82%	5.7:1.0
MeO	H	EtO	H	H	0.62 GPa	CH_2Cl_2	none	24°	108 h	75%	5.7:1.0
MeO	H	EtO	H	H	0.1 MPa	CH_2Cl_2	$EtAlCl_2$	–78°	5 min	75%	0.8:1.0
MeO	H	EtO	H	H	0.1 MPa	CH_2Cl_2	$TiCl_4$	–78°	5 min	61%	1.0:3.0
MeO	MeO	MeO	H	H	0.1 MPa	CH_2Cl_2	none	40°	6 h	63%	–
MeO	MeO	MeO	H	H	1.3 GPa	CH_2Cl_2	none	24°	48 h	41%	–
MeO	H	BnO	H	Me	0.95 GPa	CH_2Cl_2	none	24°	48 h	50%	19:1
MeO	H	BnO	H	Me	0.1 MPa	benzene	none	80°	20 h	11%	3:1
MeO	H	BnO	H	Me	0.1 MPa	CH_2Cl_2	$TiCl_4$	–78°	5 min	46%	6:1
MeO	MeO	MeO	H	MeO	0.95 GPa	CH_2Cl_2	none	24°	108 h	41%	1:2
MeO	H	MeO	=C(H)OMe	–	0.95 GPa	CH_2Cl_2	none	24°	108 h	51%	1:1
MeO	MeO	MeO	H	Ac	1.2 GPa	CH_2Cl_2	none	24°	96 h	31%	2.3:1
MeO	MeO	H	H	Ac	1.3 GPa	CH_2Cl_2	none	24°	98 h	39%	2:1
MeO	MeO	H	H	MeO_2CCO	1.3 GPa	CH_2Cl_2	none	24°	84 h	15%	35:1
Ph	H	EtO	H	H	0.1 MPa	benzene	none	80°	16 h	73%	4:1
Ph	H	EtO	H	H	0.62 GPa	neat	none	24°	124 h	86%	9:1

App. 347



R^1	R^2	Pressure	Solvent	Catalyst	*T*	*t*	Yield	*endo*/*exo*
EtO	H	1.3 GPa	neat	none	24°	65 h	82%	5.7:1.0
EtO	H	0.62 GPa	CH_2Cl_2	none	24°	108 h	75%	5.7:1.0
EtO	H	0.1 MPa	PhMe	none	110°	29 h	48%	1.8:1.0
EtO	H	0.1 MPa	PhMe	none	25°	36 h	–	–
EtO	H	0.1 MPa	CH_2Cl_2	$EtAlCl_2$	–78°	5 min	75%	0.8:1.0
EtO	H	0.1 MPa	CH_2Cl_2	$TiCl_4$	–78°	5 min	61%	1.0:3.0
BnO	AcO	1.3 GPa	CH_2Cl_2	none	24°	80 h	49%	>45:1

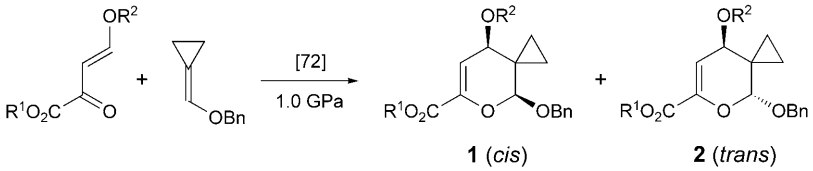
App. 348



R^1	R^2	R^3	R^4	*T*	**1**	**2**
Et	H	H	H	r.t.	not reported	–
t-Bu	H	H	H	r.t.	53%	30%
t-Bu	H	H	H	50°	–	70%
PhCH(Me)	H	H	H	r.t.	65% (4:1)[a]	–
4-MeO-C_6H_4-CH(Me)	H	H	H	r.t.	45% (4:1)[a]	–
i-Pr	Me	H	H	r.t.	45%	–
i-Pr	H	Me	H	r.t.	40%	–
Me	H	H	Me	r.t.	quant.[b]	–
–(CH_2)–		H	H	r.t.	70%	–

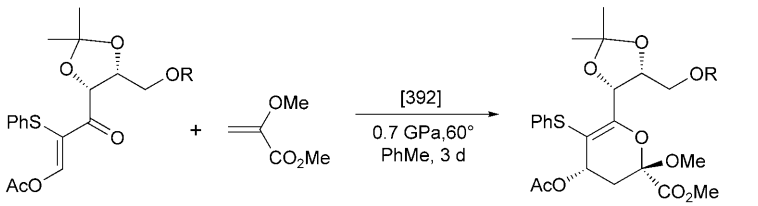
[a]) Ratio *endo*/diastereoisomer. [b]) By NMR.

App. 349



R^1	R^2	Solvent	*T*	*t*	Yield	**1/2**
Et	Et	CH_2Cl_2	25°	20 h	53%	3.0
Et	Et	CH_2Cl_2	32°	44 h	57%	2.8
Et	Et	CH_2Cl_2	40°	70 h	62%	2.1
Et	Et	MeCN	40°	70 h	60%	2.1
Et	Et	MeCN	50°	30 h	64%	2.2
Me	Bn	CH_2Cl_2	25°	72 h	80%	1.8

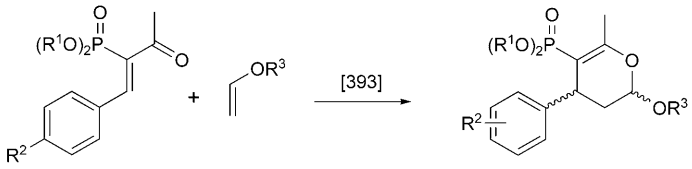
App. 350



R = ^{t}Bu(Me)$_2$Si

73%
(diastereoisomeric 9:1 mixture)

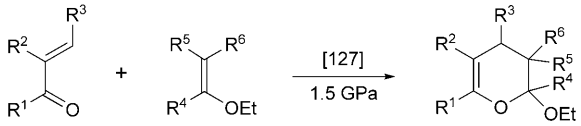
App. 351



R^1	R^2	R^3	Condition	Catalyst	*T*	*t*	Yield	*trans*/*cis*
Me	NO_2	Et	sealed tube	none	130°	2 h	94%	56:44
Me	NO_2	Et	1.0 GPa	none	20°	24 h	95%	75:25
Me	NO_2	Et	1.0 GPa	*t*-BuOH[a])	20°	24 h	95%	92:8
Me	NO_2	*t*-Bu	sealed tube	none	130°	1.5 h	96%	25:75
Me	NO_2	*t*-Bu	1.0 GPa	*t*-BuOH[a])	20°	24 h	95%	50:50
Et	NO_2	Et	sealed tube	none	130°	5 h	95%	55:45
Et	NO_2	*t*-Bu	sealed tube	none	130°	4 h	93%	27:73
i-Pr	NO_2	Et	sealed tube	none	130°	24 h	94%	61:39
i-Pr	NO_2	Et	1.0 GPa	none	20°	24 h	95%	84:16
Me	H	Et	sealed tube	none	130°	12 h	87%	54:46
Me	H	Et	1.0GPa	none	45°	48 h	92%	60:40
Me	H	Et	1.0GPa	*t*-BuOH[a])	45°	48 h	91%	85:15

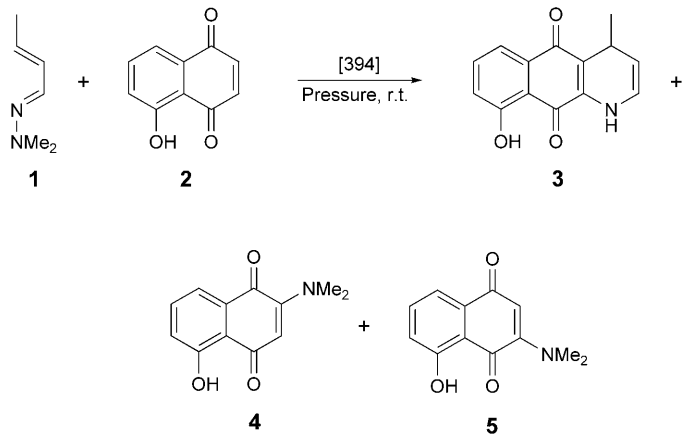
[a]) 1 Equiv.

App. 352



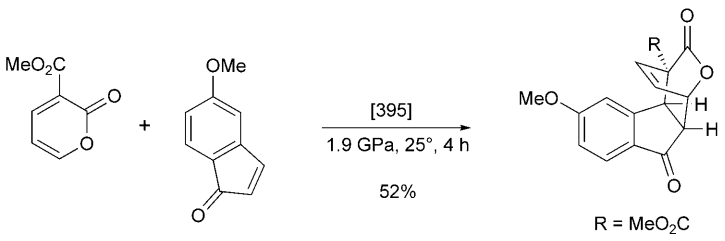
R^1	R^2	R^3	R^4	R^5	R^6	*T*	*t*	Yield
H	H	H	H	H	H	r.t.	20 h	69%
H	H	H	H	H	Me	r.t.	23 h	53%
H	H	H	H	Me	Me	r.t.	20 h	44%
H	H	H	Me	H	H	r.t.	19 h	23%
H	Me	H	H	H	H	r.t.	20 h	–
H	H	Me	H	H	H	75°	24 h	89%
H	H	Me	H	H	Me	100°	20 h	35%
H	H	Me	H	Me	Me	100°	20 h	–
H	H	Ph	H	H	H	75°	24 h	95%
Me	H	H	H	H	H	r.t.	20 h	62%

App. 353

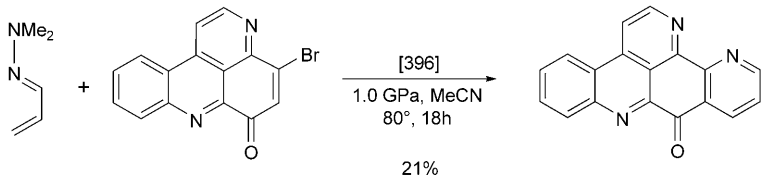


1/2	Condition	Solvent	*t*	3	4	5
3:2	ultrasound	PhMe	6 h	32%	10%	10%
3:2	0.1 MPa	PhMe	24 h	26%	trace	trace
3:2	1.0 GPa	PhMe	6 h	48%	trace	trace
3:2	1.0 GPa	PhMe	24 h	24%	15%	15%
3:2	ultrasound	MeOH	6 h	14%	trace	trace
3:2	0.1 MPa	MeOH	6 h	15%	trace	trace
3:1	ultrasound	neat	6 h	15%	trace	trace
3:1	0.1 MPa	neat	6 h	14%	trace	trace

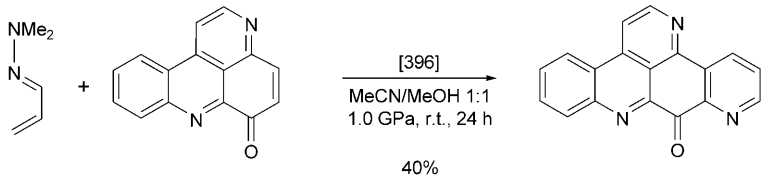
App. 354



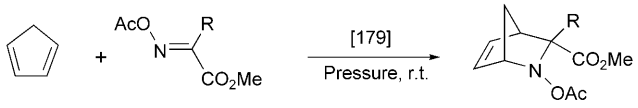
App. 355



App. 356

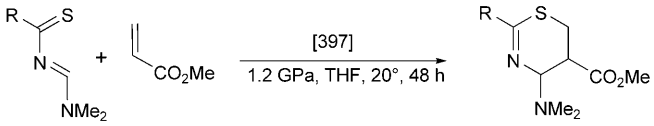


App. 357



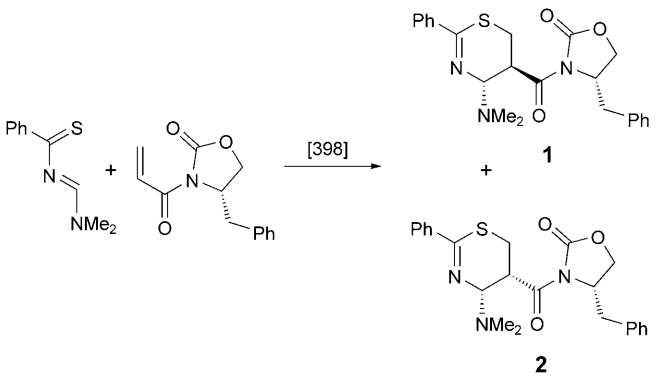
R	P	Condition	*t*	Yield	*endo*/*exo*
CN	0.1 MPa	neat	18 h	25%	6.5
CN	0.1 MPa	Et_2O	18 h	12%	6.4
CN	0.1 MPa	Et_2O/aq. 5M $LiClO_4$	5 h	51%	9.0
CN	1.0 GPa	PhMe	40 h	99%	7.6
MeOOC	0.1 MPa	Et_2O, 1M $LiClO_4$	24 h	32%	–
MeOOC	0.1 MPa	Et_2O, 3M $LiClO_4$	24 h	41%	–
MeOOC	0.1 MPa	Et_2O, 5M $LiClO_4$	24 h	49%	–
MeOOC	1.0 GPa	PhMe	48 h	17%	–

App. 358



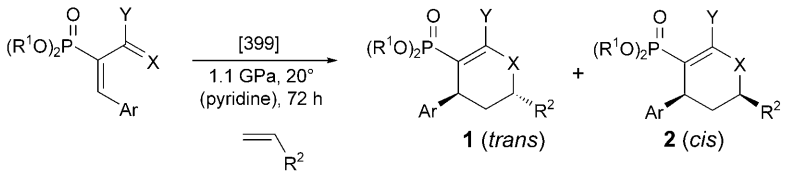
R = EtO (49%)
R = BnS (60%)

App. 359



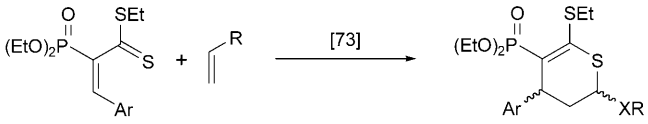
P	Solvent	Catalyst	*T*	*t*	Yield	**1/2**
0.1 MPa	CH_2Cl_2	none	110°	20 h	75%	20:80
1.0 GPa	THF	none	20°	40 h	95%	16:84
0.1 MPa	CH_2Cl_2	$MgCl_2$	0°	3 h	95%	100:0

App. 360



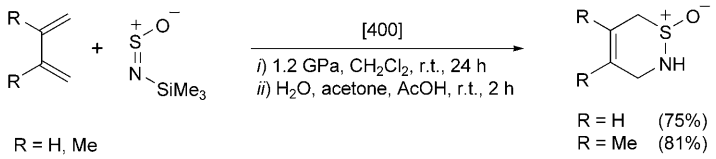
R^1	X	Y	Ar	R^2	Pyridine	Yield	**1/2**
Et	S	EtO	Ph	EtS	none	84%	66:34
Et	S	EtO	Ph	EtS	1 equiv.	88%	1.5:98.5
Et	S	EtO	4-NO_2-C_6H_4	EtS	none	83%	86:14
Et	S	EtO	4-NO_2-C_6H_4	EtS	1 eq	86%	6.5:93.5
Me	O	Me	4-NO_2-C_6H_4	EtO	none	95%	75:25
Me	O	Me	4-NO_2-C_6H_4	EtO	1 equiv.	93%	30:70
Me	O	Me	4-NO_2-C_6H_4	EtS	none	89%	93:7
Me	O	Me	4-NO_2-C_6H_4	EtS	1 equiv.	91%	18:82

App. 361

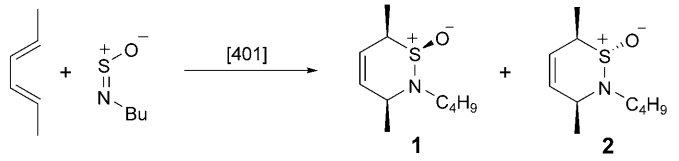


R	Ar	*P*	*T*	*t*	Yield	*trans*/*cis*
EtO	Ph	sealed tube	125°	10 h	85%	15:85
EtO	Ph	1.1 GPa	20°	48 h	88%	68:32
EtO	4-NO_2-C_6H_4	sealed tube	125°	2 h	86%	15:85
EtO	4-NO_2-C_6H_4	1.1 GPa	20°	24 h	90%	64:36
EtO	4-CF_3-C_6H_4	sealed tube	125°	3 h	87%	16:84
EtO	4-CF_3-C_6H_4	1.1 GPa	20°	60 h	87%	75:25
EtO	4-MeO-C_6H_4	sealed tube	125°	12 h	79%	16:84
EtO	4-MeO-C_6H_4	1.1 GPa	20°	96 h	85%	60:40
EtO	3-pyridyl	sealed tube	125°	6 h	87%	19:81
EtO	3-pyridyl	1.1 GPa	20°	18 h	89%	15:85
EtO	4-pyridyl	sealed tube	125°	2.5 h	82%	81:19
EtO	4-pyridyl	1.1 GPa	20°	52 h	84%	15:85
t-BuO	Ph	sealed tube	125°	24 h	79%	22:78
t-BuO	Ph	1.1 GPa	20°	72 h	84%	25:75
t-BuO	4-NO_2-C_6H_4	sealed tube	125°	11 h	85%	21:79
t-BuO	4-NO_2-C_6H_4	1.1 GPa	20°	48 h	88%	24:76
t-BuO	4-CF_3-C_6H_4	sealed tube	125°	12 h	82%	32:68
t-BuO	4-CF_3-C_6H_4	1.1 GPa	20°	72 h	85%	39:61
t-BuO	4-MeO-C_6H_4	sealed tube	125°	10 h	–	–
t-BuO	4-MeO-C_6H_4	1.1 GPa	20°	192 h	76%	22:78
t-BuO	3-pyridyl	sealed tube	125°	6 h	90%	31:69
t-BuO	3-pyridyl	1.1 GPa	20°	48 h	82%	16:84
t-BuO	4-pyridyl	sealed tube	125°	4 h	88%	80:20
t-BuO	4-pyridyl	1.1 GPa	20°	4 h	88%	15:85
EtS	4-NO_2-C_6H_4	sealed tube	125°	6 h	89%	7:93
EtS	4-NO_2-C_6H_4	1.1 GPa	20°	48 h	83%	86:14

App. 362

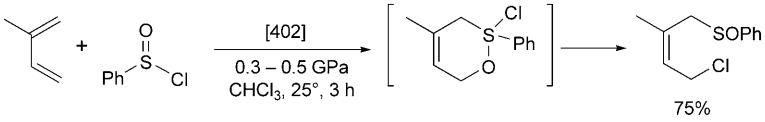


App. 363

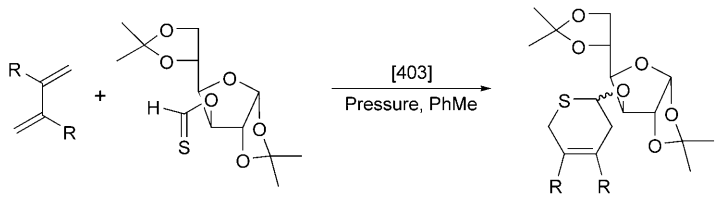


P	Solvent	Catalyst	*T*	Yield	**1/2**
0.1 MPa	CH_2Cl_2	$TiCl_4$	–78°	27%	100:0
0.1 MPa	CH_2Cl_2	$SnCl_4$	–78°	47%	40:60
0.1 MPa	CH_2Cl_2	$BF_3{\cdot}OEt_2$	–78°	54%	100:0
1.2 GPa	Et_2O	none	r.t.	56%	11:89
1.2 GPa	hexane	none	r.t.	66%	12:88
1.2 GPa	CH_2Cl_2	none	r.t.	80%	18:82
0.6 GPa	CH_2Cl_2	none	r.t.	22%	15:85

App. 364

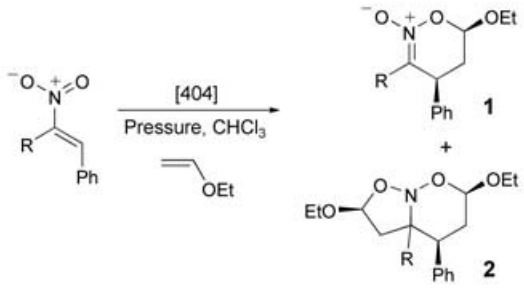


App. 365



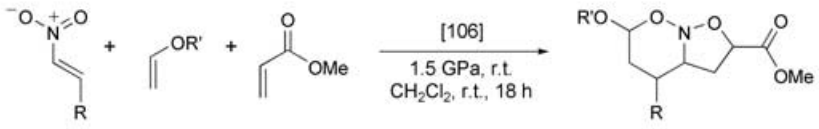
R	Condition	*T*	*t*	dr
H	sealed tube	150°	10 – 16h	1:1
H	0.25 GPa	r.t.	6 d	8:6
Me	sealed tube	150°	10 –16h	1:1
Me	0.25 GPa	r.t.	6 d	5:2

App. 366



P	*t*	Yield	**1/2**
0.5 GPa	5 d	35%	0.2
0.8 GPa	5 d	85%	0.16
1.0 GPa	5 d	quant.	0.17
1.2 GPa	5 d	quant.	0.19
1.0 GPa	2 h	90%	2.6
1.0 GPa	23 h	quant.	0.25
1.0 GPa	40 h	quant.	0.05
1.5 GPa	2 h	quant.	0.05

App. 367

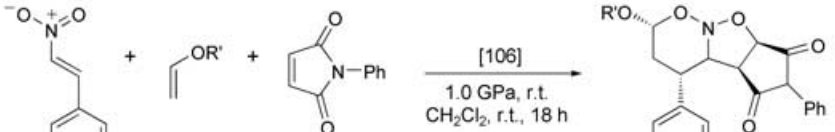


R' = 4-MeO-C_6H_4-CH_2

R = 3-pyridyl (74%)
R = pyrrol-2-yl (53%)
R = indol-3-yl (59%)

Diastereoisomeric mixtures

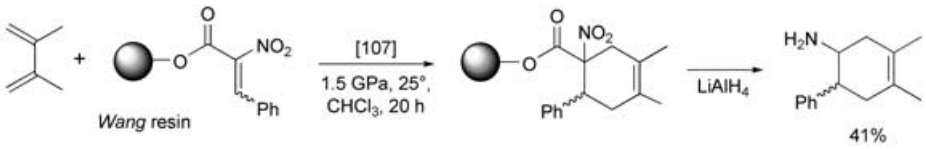
App. 368



R' = 4-MeO-C_6H_4-CH_2

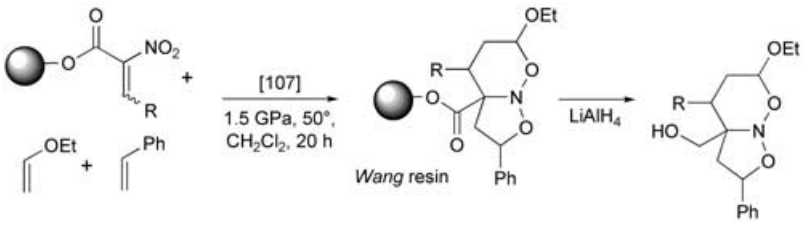
90%

App. 369



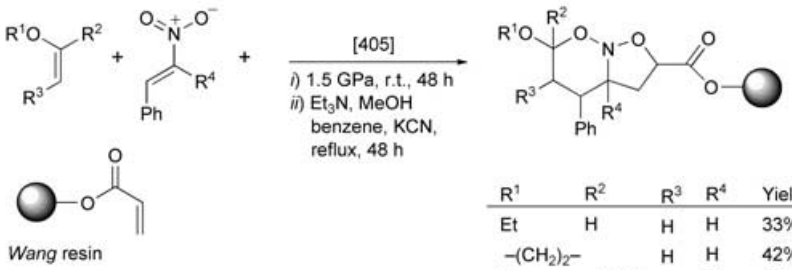
41%

App. 370



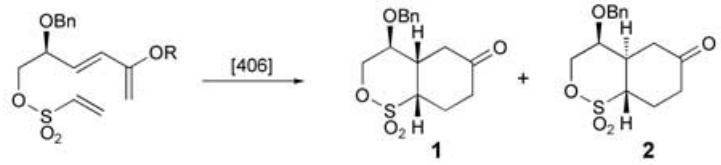
R = Ph	51%
R = 3-pyridyl	56%
R = pyrrol-2-yl	29%
R = 2-furyl	34%
R = i-Pr	51%

App. 371



R^1	R^2	R^3	R^4	Yield
Et	H	H	H	33%
$-(CH_2)_2-$		H	H	42%
Me	$-(CH_2)_2-$		H	52%
Et	H	H	Me	44%
$-(CH_2)_2-$		H	Me	38%
Me	$-(CH_2)_2-$		Me	37%

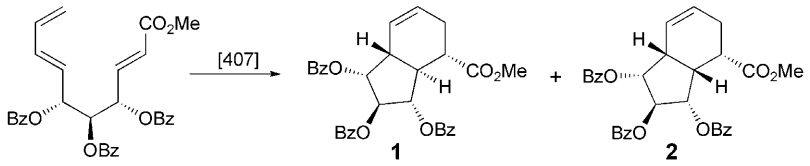
App. 372



R	*P*	*T*	*t*	Yield	**1/2**
Me_3Si	1.0 GPa	r.t.	18 h	64%	74:17[a])
Me_3Si	1.0 GPa	r.t.	18 h	72%	78:22
$^tBu(Me)_2Si$	1.2 GPa	130°	4 h	67%	82:18

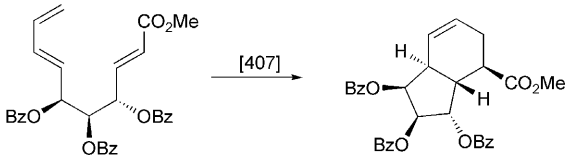
[a]) Plus 9% of other isomer.

App. 373



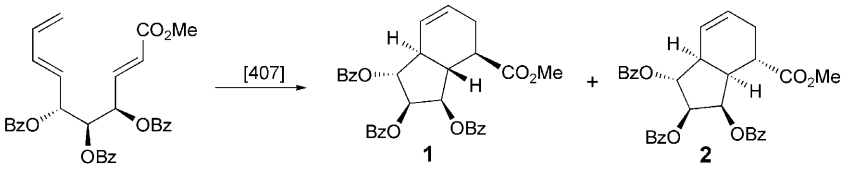
P	Solvent	Catalyst	*T*	*t*	Yield	**1/2**
0.1 MPa	PhMe/Et_2O	$AlCl_3$	r.t.	1 h	85%	5:2
1.5 GPa	PhMe	none	50°	24 h	78%	1:0

App. 374



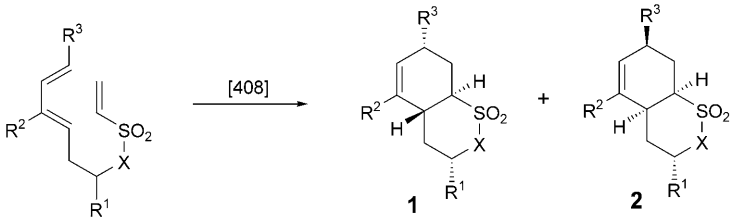
P	Solvent	Catalyst	*T*	*t*	Yield
0.1 MPa	PhMe/Et_2O	$AlCl_3$	r.t.	1 h	80%
1.5 GPa	PhMe	none	50°	24 h	70%

App. 375



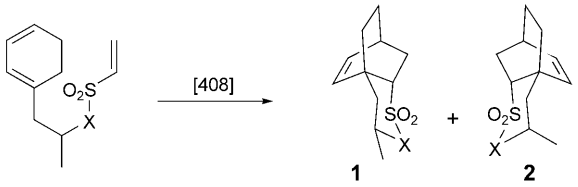
P	Solvent	Catalyst	*T*	*t*	Yield	**1/2**
0.1 MPa	PhMe/Et_2O	$AlCl_3$	r.t.	1 h	78%	2:1
1.5 GPa	PhMe	none	50°	24 h	80%	1:0

App. 376



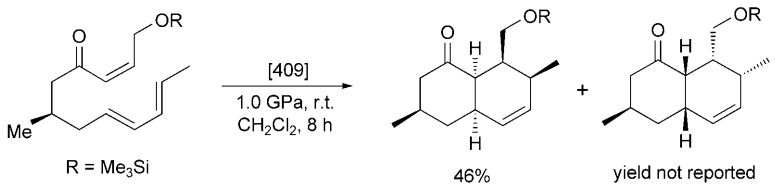
X	R^1	R^2	R^3	*P*	Solvent	*T*	*t*	Yield	**1/2**
O	H	H	H	0.1 MPa	PhMe/BHT	reflux	12 h	76%	1.0:1.0
O	H	H	H	1.3 GPa	CH_2Cl_2	r.t.	24 h	88%	1.0:2.3
O	Me	H	Me	0.1 MPa	PhMe/BHT	reflux	12 h	64%	1.4:1.0
O	Me	H	Me	1.3 GPa	CH_2Cl_2	r.t.	24 h	78%	1.0:2.0
O	^{t}Bu	Me	H	0.1 MPa	PhMe/BHT	reflux	12 h	76%	4.7:1.0
O	^{t}Bu	Me	H	1.3 GPa	CH_2Cl_2	r.t.	24 h	79%	3.6:1.0
BnN	H	H	H	0.1 MPa	PhMe/BHT	reflux	12 h	76%	1.0:1.0
BnN	H	H	H	1.3 GPa	CH_2Cl_2	r.t.	24 h	79%	1.0:1.6
BnN	Me	H	Me	0.1 MPa	PhMe/BHT	reflux	12 h	61%	1.6:1.0
BnN	Me	H	Me	1.3 GPa	CH_2Cl_2	r.t.	24 h	81%	1.0:1.9

App. 377

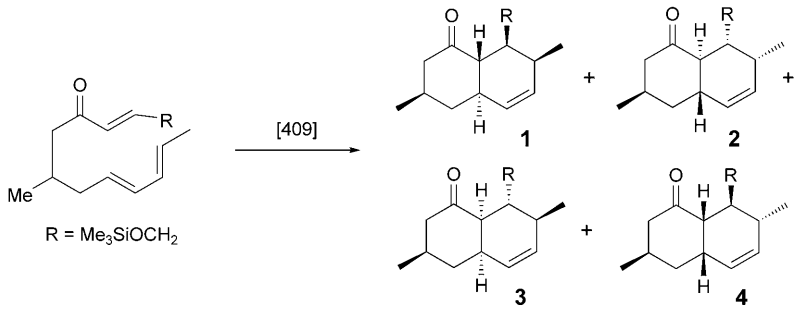


X	*P*	Solvent	*T*	*t*	Yield	**1/2**
O	0.1 MPa	PhMe/BHT	reflux	3 h	58%	10.2:1
O	1.3 GPa	CH_2Cl_2	r.t.	12 h	92%	54.6:1
BnN	0.1 MPa	PhMe/BHT	reflux	3 h	77%	9.3:1
BnN	1.3 GPa	CH_2Cl_2	r.t.	12 h	93%	30.3:1

App. 378

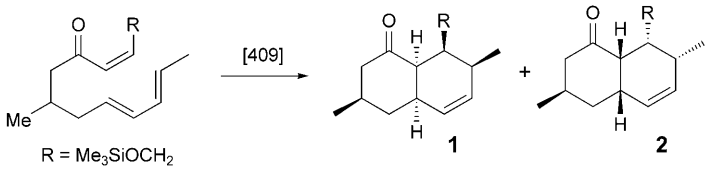


App. 379



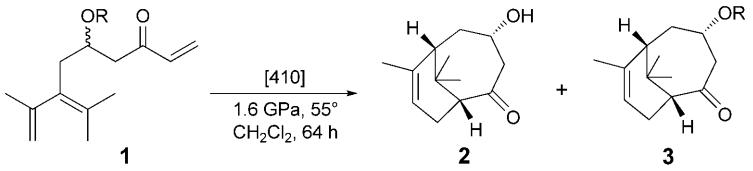
Pressure	Solvent	Catalyst	*T*	*t*	**1**	**2**	**3**	**4**
1.0 GPa	CH_2Cl_2	none	r.t.	8 h	7%	2%	47%	22%
0.1 MPa	CH_2Cl_2	Et_2AlCl	0°	12 h	13%	trace	27%	11%
0.1 MPa	PhCl	none	reflux	12 h	17%	3%	29%	22%

App. 380



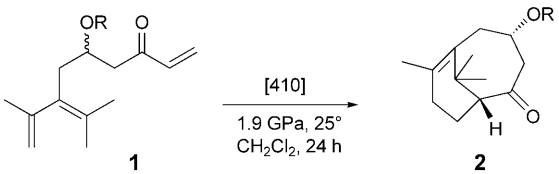
Pressure	Solvent	Catalyst	*T*	*t*	**1**	**2**
1.0 GPa	CH_2Cl_2	none	r.t.	8 h	53%	8%
0.1 MPa	CH_2Cl_2	Et_2AlCl	0°	12 h	42%	16%
0.1 MPa	PhCl	none	reflux	12 h	20%	5%

App. 381



1/2/3 1:2:2 (by ^{1}H-NMR)
yield not reported

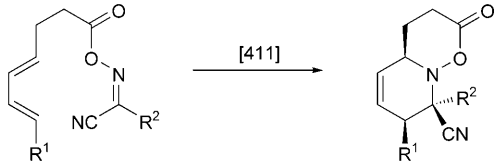
App. 382



1 R = ^{t}Bu(Me)$_2$Si

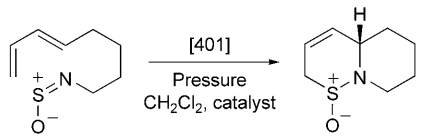
2 **1/2** 4:1 (by ^{1}H-NMR)

App. 383



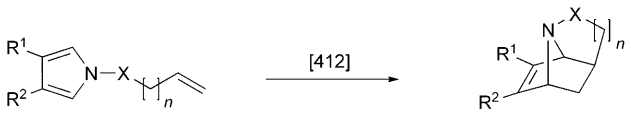
R^1	R^2	*P*	Solvent	*T*	*t*	Yield
H	CN	0.1 MPa	toluene	reflux	24 h	68%
H	EtOOC	0.1 MPa	toluene	reflux	24 h	70%
H	CN	1.0 GPa	CH_2Cl_2	r.t.	overnight	65%
H	EtOOC	1.0 GPa	CH_2Cl_2	r.t.	overnight	76%
Ph	CN	0.1 MPa	toluene	reflux	24 h	52%
Ph	EtOOC	0.1 MPa	toluene	reflux	24 h	74%
Ph	EtOOC	1.0 GPa	CH_2Cl_2	r.t.	overnight	63%

App. 384



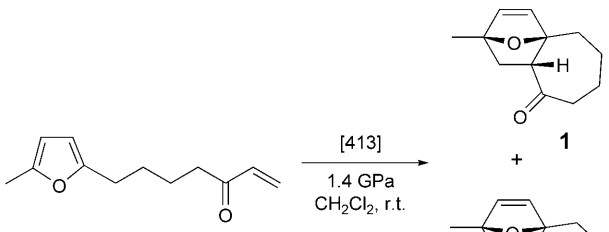
P	Catalyst	*T*	Yield
0.1 MPa	BF_3·OEt_2	–78°	40%
1.0 GPa	none	r.t.	82%

App. 385



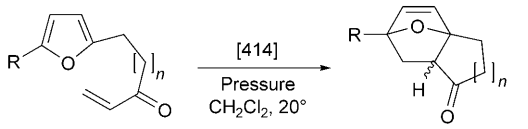
R^1	R^2	X	*n*	Condition	Solvent	*T*	*t*	Yield
$-CH_2SO_2CH_2-$		C(O)O	1	sealed tube	benzene	150°	24 h	46%
$-CH_2SO_2CH_2-$		C(O)O	1	1.2 GPa	CH_2Cl_2	28°	72 h	66%
$-CH_2SO_2CH_2-$		CO	2	sealed tube	benzene	150°	24 h	45%
$-CH_2SO_2CH_2-$		CO	2	0.4 GPa	CH_2Cl_2	28°	72 h	–
$-CH_2SO_2CH_2-$		CO	2	0.8 GPa	CH_2Cl_2	28°	24 h	16%
$-CH_2SO_2CH_2-$		CO	2	1.2 GPa	CH_2Cl_2	28°	72 h	69%
H	H	CO	1	sealed tube	benzene	150°	24 h	–
H	H	CO	1	1.2 GPa	CH_2Cl_2	28°	72 h	–
$-CH_2SO_2CH_2-$		CO	1	sealed tube	benzene	150°	24 h	48%
$-CH_2SO_2CH_2-$		CO	1	1.2 GPa	CH_2Cl_2	28°	72 h	54%
H	H	CO	0	sealed tube	benzene	150°	24 h	–
H	H	CO	0	1.2 GPa	CH_2Cl_2	28°	72 h	–
$-CH_2SO_2CH_2-$		SO_2	2	sealed tube	benzene	150°	24 h	49%
$-CH_2SO_2CH_2-$		SO_2	2	1.2 GPa	CH_2Cl_2	28°	72 h	54%
H	H	SO_2	1	sealed tube	benzene	150°	24 h	–
H	H	SO_2	1	1.2 GPa	CH_2Cl_2	28°	72 h	–
$-CH_2SO_2CH_2-$		SO_2	1	sealed tube	benzene	150°	24 h	43%
$-CH_2SO_2CH_2-$		SO_2	1	1.2 GPa	CH_2Cl_2	28°	72 h	53%
H	H	SO_2	0	sealed tube	benzene	150°	24 h	–
H	H	SO_2	0	1.2 GPa	CH_2Cl_2	28°	72 h	–

App. 386



t	**1**	**2**
24 h	55%	39%
50 h	69%	28%

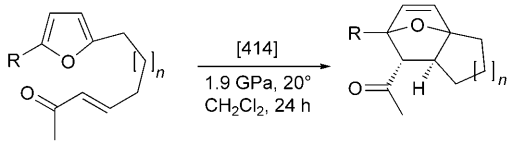
App. 387



Yields not reported

R	*n*	*P*	*t*	*exo*/*endo*
H	1	1.9 GPa	24 h	–
Me	1	1.9 GPa	24 h	–
H	2	1.0 GPa	10 min	95:5
Me	2	1.0 GPa	10 min	100:0
H	3	1.2 GPa	24 h	50:50
Me	3	1.2 GPa	24 h	40:50

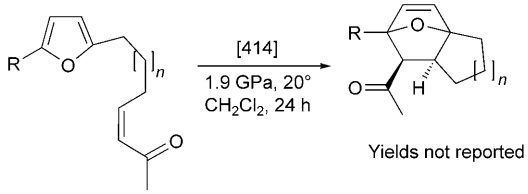
App. 388



Yields not reported

R	*n*	*exo*/*endo*
H	2	70:15
Me	2	95:5
H	3	30:20
Me	3	–

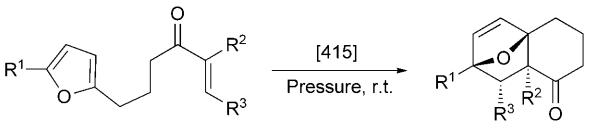
App. 389



Yields not reported

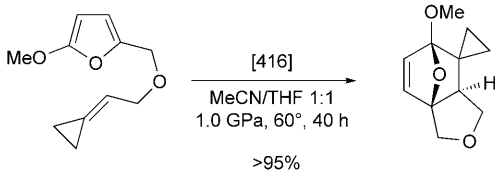
R	*n*	*exo*/*endo*
H	2	15:85
Me	2	–
H	3	–
Me	3	–

App. 390

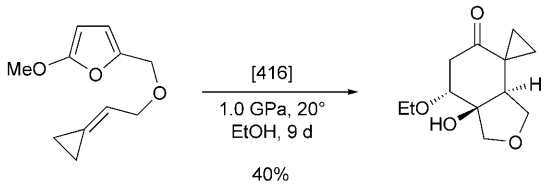


R^1	R^2	R^3	*P*	Solvent	*t*	Yield
H	H	H	0.1 MPa	CH_2Cl_2/*Florisil*	6 d	71%
H	H	H	0.1 MPa	2M $CaCl_2$	4 d	66%
H	H	H	1.25 GPa	CH_2Cl_2	1 d	51%
H	H	H	0.52 GPa	CH_2Cl_2	12 h	65%
H	Me	H	0.1 MPa	CH_2Cl_2/*Florisil*	14 d	65%
H	Me	H	0.1 MPa	2M $CaCl_2$	4 d	68%
H	Me	H	1.25 GPa	CH_2Cl_2	1 d	55%
H	Me	H	0.52 GPa	CH_2Cl_2	12 h	–
H	H	Me	0.1 MPa	CH_2Cl_2/*Florisil*	14 d	–
H	H	Me	0.1 MPa	2M $CaCl_2$	4 d	73%
H	H	Me	1.25 GPa	CH_2Cl_2	1 d	52%
Me	H	H	0.1 MPa	CH_2Cl_2/*Florisil*	14 d	–
Me	H	H	0.1 MPa	2M $CaCl_2$	4 d	78%
Me	H	H	1.25 GPa	CH_2Cl_2	1 d	56%
Me	Me	H	0.1 MPa	CH_2Cl_2/*Florisil*	14 d	–
Me	Me	H	0.1 MPa	2M $CaCl_2$	4 d	69%
Me	Me	H	1.25 GPa	CH_2Cl_2	1 d	50%
Me	H	Me	0.1 MPa	CH_2Cl_2/*Florisil*	14 d	–
Me	H	Me	0.1 MPa	2M $CaCl_2$	4 d	61%
Me	H	Me	1.25 GPa	CH_2Cl_2	1 d	43%

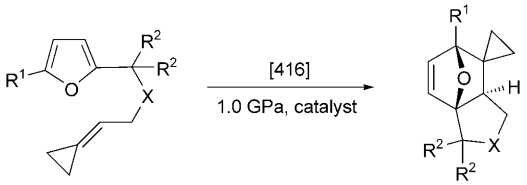
App. 391



App. 392

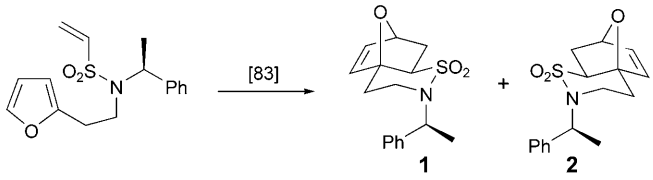


App. 393



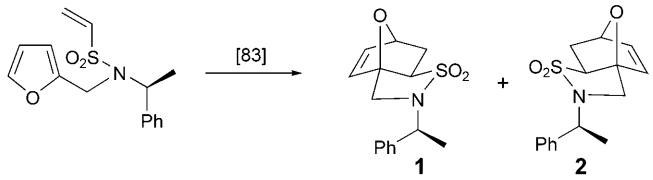
R^1	R^2	X	Solvent	Catalyst	*T*	*t*	Yield
H	H	O	EtOH	none	70°	24 h	>95%
H	Me	O	EtOH	none	70°	24 h	>95%
Me	H	O	EtOH	none	70°	24 h	74%
MeO	H	O	NMP	$Pd(dba)_2$/dppb	70°	24 h	>95%
H	H	MeN	MeCN/THF 1:1	$Pd(dba)_2$/dppb	70°	42 h	50%
H	=O	MeN	MeCN/THF 1:1	$Pd(dba)_2$/dppb	60°	42 h	55%

App. 394



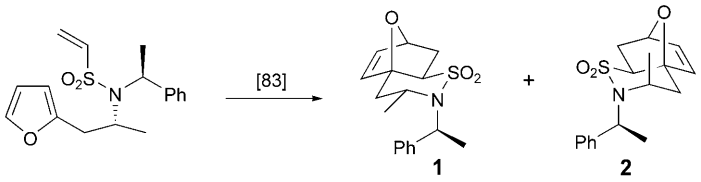
P	Solvent	*T*	*t*	Yield	**1/2**
0.1 MPa	PhMe	reflux	10 h	80%	62:38
1.3 GPa	CH_2Cl_2	r.t.	12 h	98%	50:50

App. 395



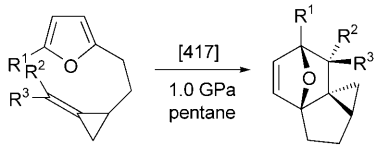
P	Solvent	*T*	*t*	Yield	**1/2**
0.1 MPa	PhMe	reflux	16 h	73%	58:42
1.3 GPa	CH_2Cl_2	r.t.	14 h	94%	66:34

App. 396



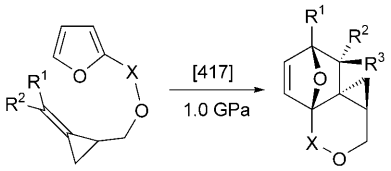
P	Solvent	*T*	*t*	Yield	**1/2**
0.1 MPa	PhMe	reflux	16 h	87%	79:21
1.3 GPa	CH_2Cl_2	r.t.	14 h	98%	93:7

App. 397



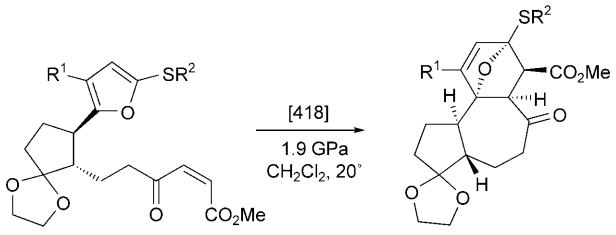
R^1	R^2	R^3	*T*	*t*	Yield
H	$-(CH_2)_2-$		90°	43 h	32%
MeO	$-(CH_2)_2-$		85°	20 h	>95%
H	H	H	100°	17 h	82%

App. 398



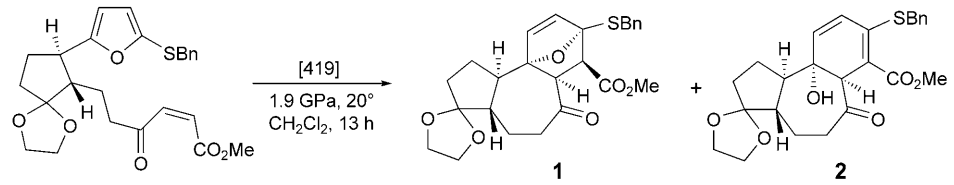
R^1	R^2	X	Solvent	*T*	*t*	Yield
$-(CH_2)_2-$		CH_2	MeCN/THF 1:1	70°	48 h	46%
$-(CH_2)_2-$		CH_2	MeCN/THF 1:1	75°	70 h	42%
$-(CH_2)_2-$		Me_2Si	Et_2O	130°	20 h	83%
H	H	CH_2	MeCN/THF 1:1	85°	45 h	47%
H	H	CH_2	MeCN/THF 1:1	100°	20 h	50%
H	H	Me_2Si	Et_2O	125°	30 h	25%

App. 399



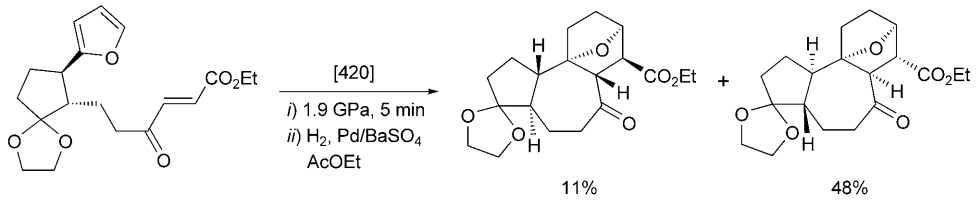
R^1	R^2	*t*	Yield
H	Bn	15 h	66%
Me	Ph	15 h	–
Me	Bn	19 h	45%

App. 400

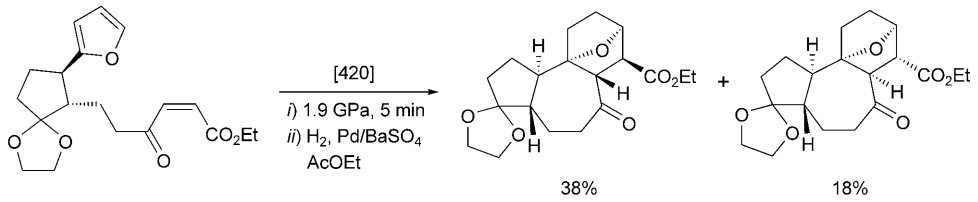


Conc.	Yield	**1/2**
ca. 0.1M	68%	1:0
ca. 0.02M	?	1:2

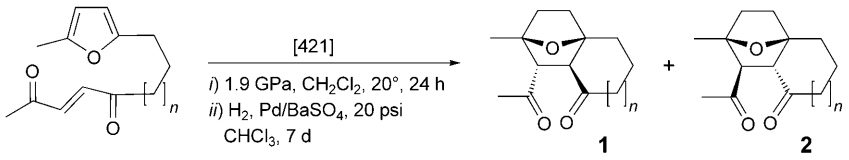
App. 401



App. 402

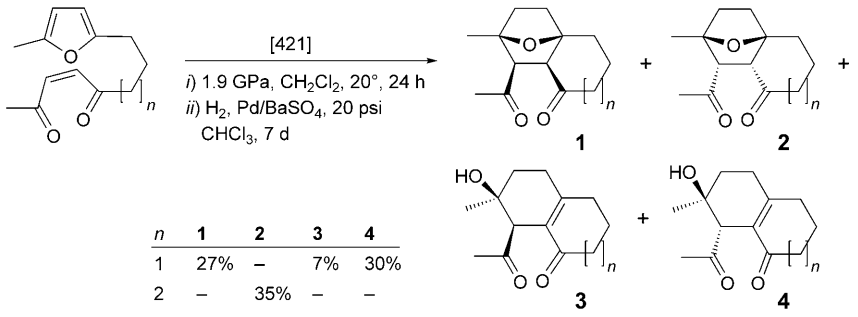


App. 403



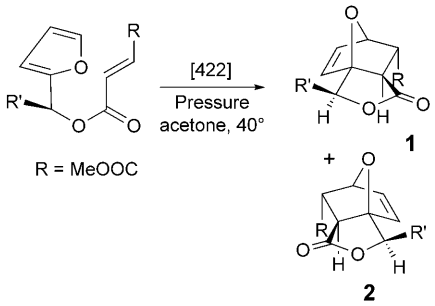
n	**1**	**2**
1	54%	–
2	5%	25%

App. 404



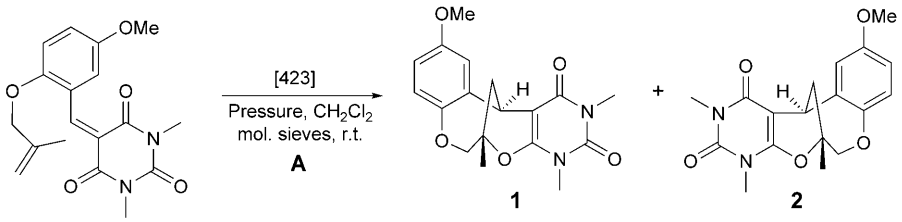
n	**1**	**2**	**3**	**4**
1	27%	–	7%	30%
2	–	35%	–	–

App. 405

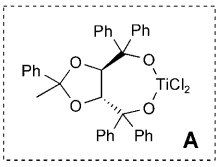


R'	*P*	*t*	Yield	**1/2**	de
Me	0.7 GPa	18 h	96%	55:45	10%
Me	0.1 MPa	5 d	41%	55:45	10%
Et	0.7 GPa	18 h	36%	68:32	36%
i-Pr	0.7 GPa	18 h	90%	90:10	80%
i-Pr	0.1 MPa	5 d	31%	78:22	56%
t-Bu	0.7 GPa	18 h	92%	93:7	86%
t-Bu	0.1 MPa	5 d	44%	92:8	84%
t-BuCH$_2$	0.7 GPa	18 h	93%	69:31	38%

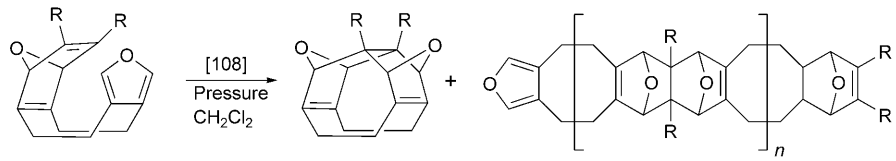
App. 406



P	*t*	Yield	ln (**1**/**2**)	ee
0.1 MPa	31 h	50%	0.089	4.5%
0.1 GPa	26 h	85%	0.131	6.6%
0.2 GPa	26 h	81%	0.203	10.1%
0.28 GPa	24 h	89%	0.216	10.7%
0.36 GPa	24 h	95%	0.341	16.9%
0.5 GPa	7 h	89%	0.414	20.4%



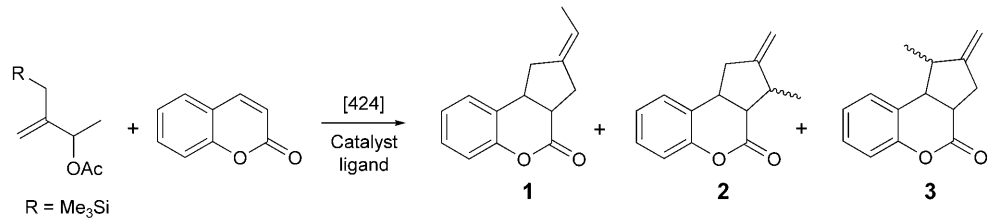
App. 407



R = MeOOC **1** **2**

R	*P*	*T*	*t*	**1**	**2**
$MeO(CH_2)_2O_2C$	0.65 GPa	100°	3 d	60%	40% (*n* = 25)
$(H_{17}C_8)O_2C$	0.8 GPa	50°	1 d	20%	80% (*n* = 17)

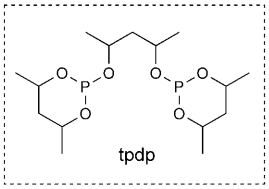
App. 408



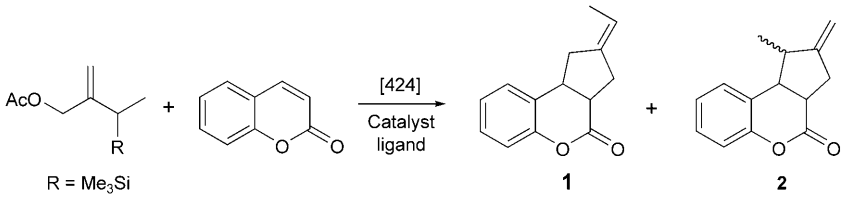
R = Me_3Si **1** **2** **3**

P	Solvent	Catalyst	Ligand	*T*	Yield	Products
0.1 MPa	THF	$Pd(PPh_3)_4$	–	65°	63%	**1**/**3** 10:89
1.5 GPa	PhMe/PhH 7:3	$[\eta^3\text{-}C_3H_5PdCl]_2$	PPh_3	70°	38%	(**1**+**2**)/**3** 32:10[a]
0.98 GPa	toluene	$Pd(OAc)_2$	$(i\text{-}PrO)_3P$	25°	12%	**1**/**3** 37:10
0.98 GPa	toluene	$Pd(OAc)_2$	$(i\text{-}PrO)_3P$	25°	30%	**1**/**3** 14:10
0.98 GPa	PhMe/PhH 7:3	$[\eta^3\text{-}C_3H_5PdCl]_2$	$(i\text{-}PrO)_3P$	25°	71%	**1**/**3** 14:10
1.5 GPa	PhMe/PhH 7:3	$[\eta^3\text{-}C_3H_5PdCl]_2$	$(i\text{-}PrO)_3P$	25°	64%	(**1**+**2**)/**3** 33:10[b]
1.5 GPa	PhMe/PhH 7:3	$[\eta^3\text{-}C_3H_5PdCl]_2$	tpdp	70°	77%	(**1**+**2**)/**3** 33:10[c]

[a]) **1**/**2** 22:10. [b]) **1**/**2** 29:10. [c]) **1**/**2** 31:10.

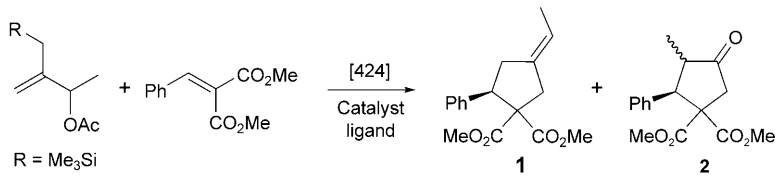


App. 409



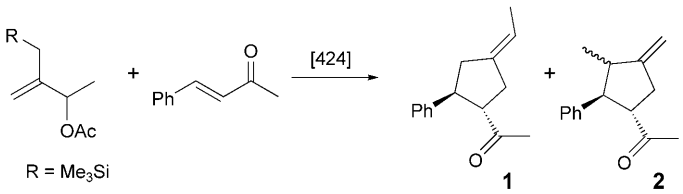
P	Solvent	Catalyst	Ligand	*T*	Yield	**1/2**
0.1 MPa	THF	$Pd(PPh_3)_4$	–	65°	63%	10:101
1.5 GPa	PhMe/PhH 7:3	$[\eta^3\text{-}C_3H_5PdCl]_2$	$(i\text{-}PrO)_3P$	25°	67%	10:140

App. 410

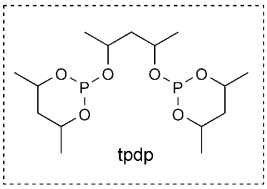


P	Solvent	Catalyst	Ligand	Yield	**1/2**
0.1 MPa	THF	$Pd(PPh_3)_4$	–	82%	1.3:1
1.0 GPa	PhMe	$Pd(OAc)_2$	$(i\text{-}PrO)_3P$	72%	1:0

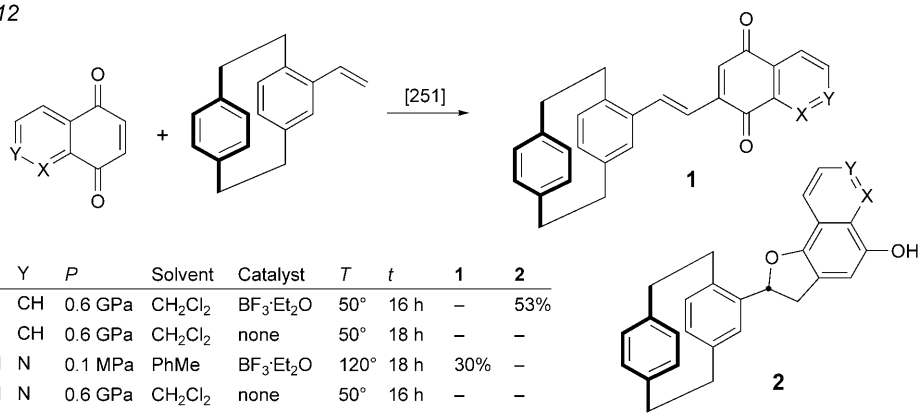
App. 411



P	Solvent	Catalyst	Ligand	Yield	**1/2**
0.1 MPa	PhMe	$Pd(OAc)_2$	–	38%	10:30
1.5 GPa	PhMe/PhH 7:3	$[\eta^3\text{-}C_3H_5PdCl]_2$	tpdp	90%	36:10

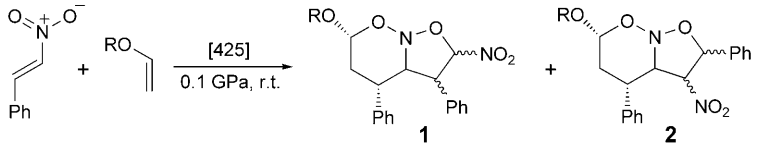


App. 412



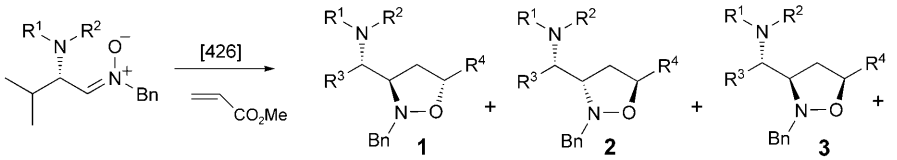
X	Y	*P*	Solvent	Catalyst	*T*	*t*	**1**	**2**
N	CH	0.6 GPa	CH_2Cl_2	$BF_3{\cdot}Et_2O$	50°	16 h	–	53%
N	CH	0.6 GPa	CH_2Cl_2	none	50°	18 h	–	–
CH	N	0.1 MPa	PhMe	$BF_3{\cdot}Et_2O$	120°	18 h	30%	–
CH	N	0.6 GPa	CH_2Cl_2	none	50°	16 h	–	–

App. 413

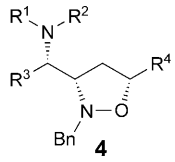


R	*t*	Yield	**1/2**
Et	2 h	63%	6:4
4-MeO-C_6H_4-CH_2	4 h	87%	7:3
Me	15 h	90%	7:3
H	1.5 h	68%	3:7

App. 414

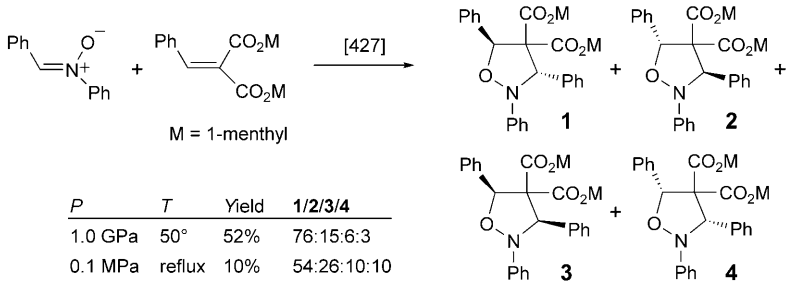


R^1	R^2	*P*	Solvent	*T*	*t*	Yield	**1/2/3/4**
Bn	Bn	0.1 MPa	PhMe	110°	3 d	82%	59:22:12:7
Bn	Bn	0.1 MPa	PhMe	r.t.	3 d	–	–
Bn	Bn	1.3 GPa	PhMe	r.t.	2 d	84%	54:19:14:13
Bn	Bn	1.3 GPa	PhMe	60°	2 d	80%	52:20:15:13
Cbz	H	0.1 MPa	PhMe	110°	1 h	89%	51:44:5:0
Cbz	H	0.1 MPa	CH_2Cl_2	40°	12 h	91%	62:34:5:0
Cbz	H	0.1 MPa	CH_2Cl_2	r.t.	4 d	84%	64:36:0:0
Cbz	H	1.3 GPa	CH_2Cl_2	r.t.	2 d	85%	54:36:6:0
Cbz	H	1.3 GPa	CH_2Cl_2	60°	2 d	87%	54:41:5:0
Boc	H	0.1 MPa	PhMe	110°	3 d	92%	45:50:5:0
Boc	H	0.1 MPa	CH_2Cl_2	40°	12 h	90%	58:37:5:0
Boc	H	0.1 MPa	CH_2Cl_2	r.t.	4 d	85%	64:36:0:0



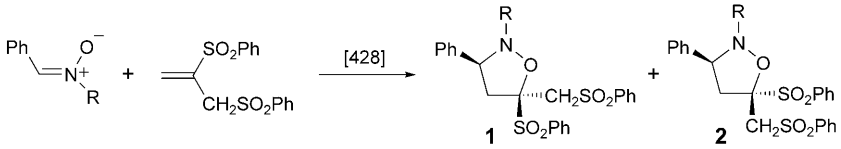
R^3 = i-Pr
R^4 = MeOOC

App. 415



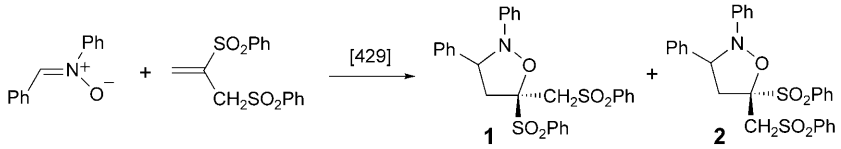
P	*T*	Yield	**1/2/3/4**
1.0 GPa	50°	52%	76:15:6:3
0.1 MPa	reflux	10%	54:26:10:10

App. 416



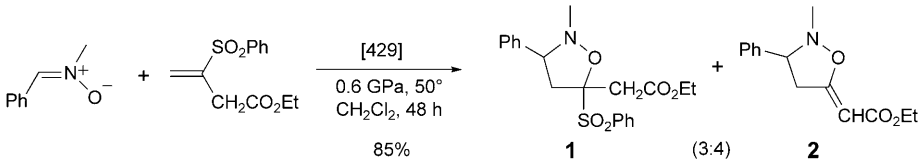
R	*P*	*T*	*t*	Yield
Me	0.1 MPa	80°	4 d	79% (**1**)
Ph	0.1 MPa	80°	4 d	85% (**1**)
Ph	0.3 GPa	r.t.	36 h	92% (**2**)

App. 417

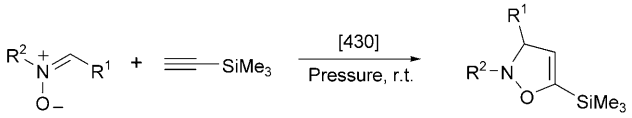


P	Solvent	*T*	*t*	**1**	**2**
0.1 MPa	benzene	80°	96 h	85%	–
0.5 GPa	CH_2Cl_2	r.t.	36 h	–	92%

App. 418

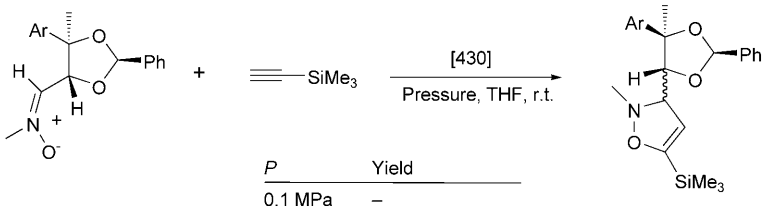


App. 419



R^1	R^2	*P*	Solvent	*t*	Yield
Ph	Bn	0.1 MPa	THF	48 h	–
Ph	Bn	0.9 GPa	THF	48 h	91%
cyclohexyl	Me	0.1 MPa	THF	48 h	trace
cyclohexyl	Me	0.9 GPa	THF	48 h	90%
Ph	Bn	0.1 MPa	THF	48 h	–
Ph	Bn	0.9 GPa	THF	48 h	65%
Ph	Bn	0.9 GPa	CH_2Cl_2	240 h	98%
Ph	Bn	0.9 GPa	MeCN	48 h	67%

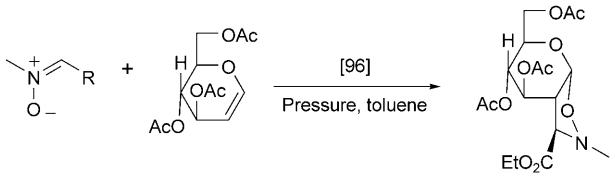
App. 420



P	Yield
0.1 MPa	–
0.9 GPa	96%[a])

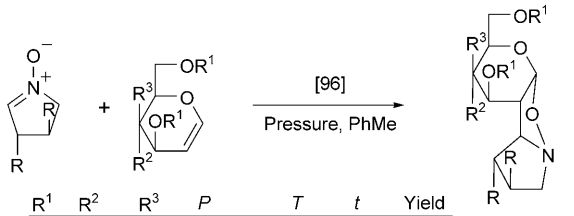
[a]) 6:1 Mixture of diastereoisomers.

App. 421



R	*P*	*T*	*t*	Yield
Ph	0.1 MPa	100°	?	–
Ph	1.0 GPa	60°	3 d	–
EtO_2C (*E*/*Z*)	0.1 MPa	100°	?	36%
EtO_2C (*E*/*Z*)	1.0 GPa	60°	3 d	56%

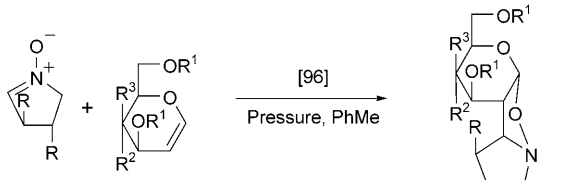
App. 422



R^1	R^2	R^3	*P*	*T*	*t*	Yield
Ac	AcO	H	0.1 MPa	100°	?	61%
Ac	AcO	H	1.0 GPa	60°	3 d	100%
Bn	BnO	H	0.1 MPa	100°	?	53%
Bn	BnO	H	1.0 GPa	60°	3 d	96%
Ac	H	AcO	0.1 MPa	100°	?	28%
Ac	H	AcO	1.0 GPa	60°	3 d	81%
Bn	H	BnO	0.1 MPa	100°	?	28%
Bn	H	BnO	1.0 GPa	60°	3 d	80%

R = ^{t}BuO

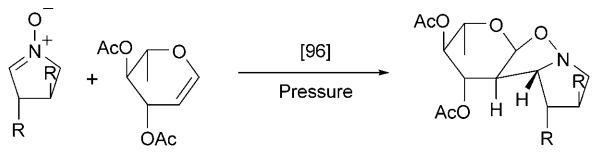
App. 423



R^1	R^2	R^3	*P*	*T*	*t*	Yield
Ac	AcO	H	0.1 MPa	100°	?	33%
Ac	AcO	H	1.0 GPa	60°	3 d	63%

R = ^{t}BuO

App. 424



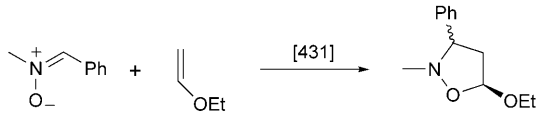
P	*T*	*t*	Yield
0.1 MPa	100°	?	22%
1.0 GPa	60°	3 d	98%

R = ^{t}BuO

App. 425

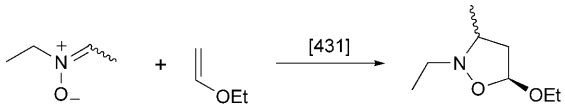
P	Solvent	*T*	*t*	Yield (ratio)
0.1 MPa	PhMe	115°	72 h	51% (50:50)
2.0 GPa	CH_2Cl_2	25°	48 h	50% (33:67)

App. 426



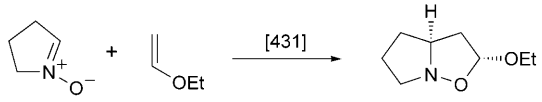
P	Solvent	*T*	*t*	Yield	Isomer ratio
0.1 MPa	PhMe	80°	72 h	78%	50:50
0.1 GPa	CH_2Cl_2	25°	72 h	–	–
0.2 GPa	CH_2Cl_2	25°	72 h	25%	50:50
0.4 GPa	CH_2Cl_2	25°	96 h	10%	57:43
0.2 GPa	CH_2Cl_2	50°	6 h	83%	?

App. 427



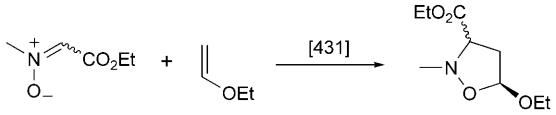
P	Solvent	*T*	*t*	Yield	Isomer ratio
0.1 MPa	PhMe	120°	96 h	42%	67:33
2.0 GPa	CH_2Cl_2	25°	90 h	17%	58:42

App. 428



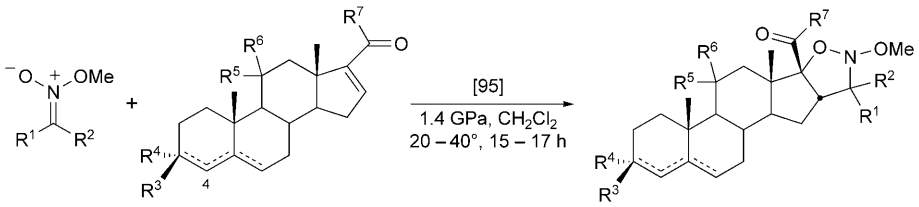
P	Solvent	*T*	*t*	Yield
0.1 MPa	PhMe	80°	24 h	–
2.0 GPa	CH_2Cl_2	50°	24 h	83%

App. 429



P	Solvent	*T*	*t*	Yield
0.1 MPa	PhMe	80°	6 h	92%
0.4 GPa	CH_2Cl_2	50°	6 h	92%

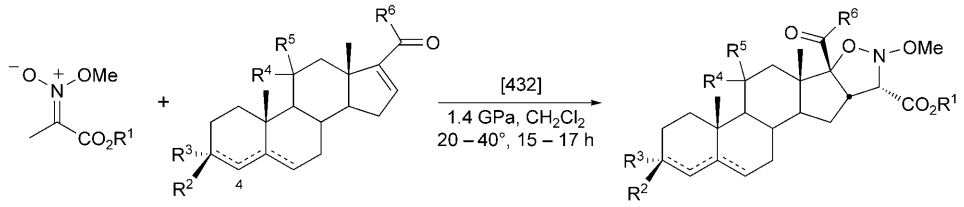
App. 430



R^1	R^2	R^3	R^4	R^5	R^6	R^7	C=C	*T*	*t*	Yield
H, MeO_2C		OH	H	H	H	Me	Δ^5	30°	18 h	80%
H, MeO_2C		AcO	H	H	H	Me	Δ^5	22°	17 h	73%
H, MeO_2C		=O	–	H	H	Me	Δ^4	22°	17 h	32%
H	MeO_2C	$-O(CH_2)_2O-$		H	H	Me	Δ^5	22°	20 h	17%
H, MeO_2C		AcO	–	=O		Me	$\Delta^{3,5}$	22°	19 h	27%
MeO_2C	H	AcO	H	H	H	Me	Δ^5	22°	40 h	26%
EtO_2C	H	=O	–	H	H	$AcOCH_2$	Δ^4	22°	40 h	26%[a])

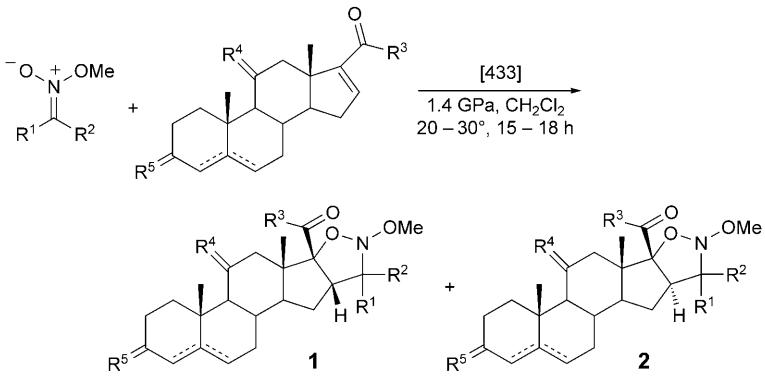
[a]) Plus 10% of isomer.

App. 431



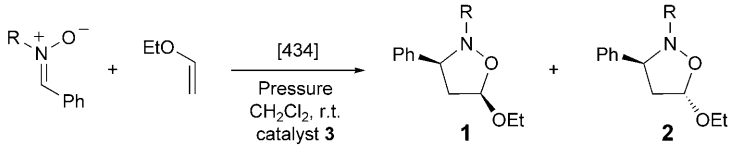
R^1	R^2	R^3	R^4	R^5	R^6	C=C	Yield
Me	OH	H	H	H	Me	Δ^5	65 – 80%
Me	OAc	H	H	H	Me	Δ^5	65 – 80%
Et	OAc	H	H	H	Me	Δ^5	65 – 80%
Me	=O		H	H	Me	Δ^4	65 – 80%
Me	OAc	–	=O		$AcOCH_2$	$\Delta^{3,5}$	65 – 80%

App. 432



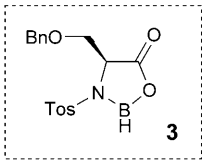
R^1	R^2	R^3	R^4	R^5	**1**	**2**
H	MeO_2C	Me	H, H	H, β-OH	80%	–
H	MeO_2C	Me	H, H	H, β-OAc	73%	–
H	H	$AcOCH_2$	O	AcO, $\Delta^{3,5}$	50%	27%
H	H	Me	H, H	O, Δ^4	41%	32%
H	H	Me	H, H	$-O(CH_2)_2O-$	32%	17%
MeO_2C	H	Me	H, H	H, β-OAc	?	?
MeO_2C	H	Me	H, H	O, Δ^4	12%	26%

App. 433

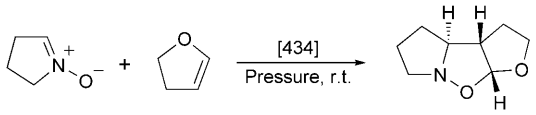


0 – 38% ee

R	*P*	**3**	*t*	Yield	**1/2**
Me	0.1 MPa	20 mol-%	18 h	64%	40:60
Me	0.2 GPa	none	18 h	–	–
Me	0.2 GPa	20 mol-%	18 h	84%	42:58
Ph	0.1 MPa	20 mol-%	21 h	56%	37:63
Ph	0.2 GPa	none	18 h	14%	100:0
Ph	0.2 GPa	20 mol-%	19 h	60%	38:62
Bn	0.1 MPa	20 mol-%	21 h	80%	40:60
Bn	0.2 GPa	none	18 h	–	–
Bn	0.2 GPa	20 mol-%	19 h	65%	40:60

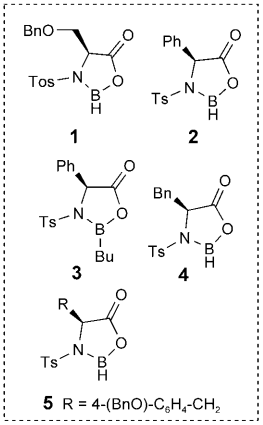


App. 434

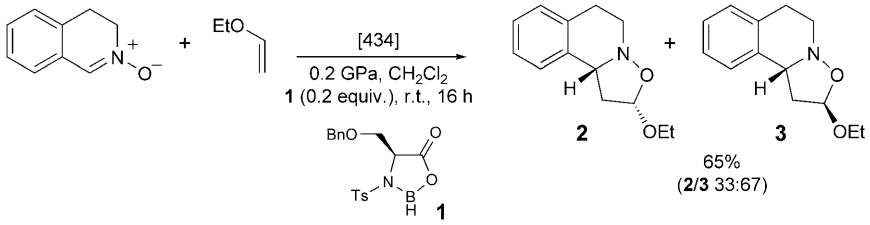


P	Catalyst[a])	Solvent	*t*	Yield	ee
0.1 MPa	**1**	neat	20 h	65%	–
0.1 MPa	**2**	neat	20 h	56%	38%
0.1 MPa	**3**	neat	20 h	74%	34%
0.1 MPa	**4**	neat	20 h	58%	18%
0.1 MPa	**5**	neat	20 h	54%	–
0.2 GPa	none	CH_2Cl_2	18 h	65%	–
0.2 GPa	**1**	CH_2Cl_2	18 h	69%	–
0.2 GPa	**2**	CH_2Cl_2	18 h	61%	–

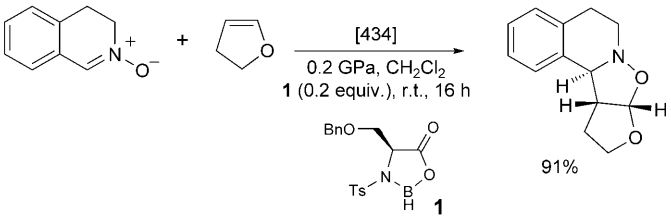
[a]) 20 mol-%.



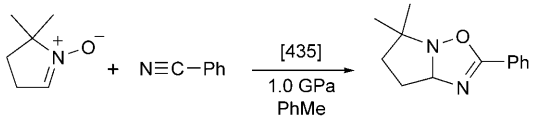
App. 435



App. 436

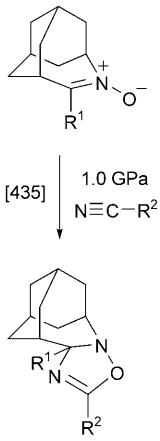


App. 437



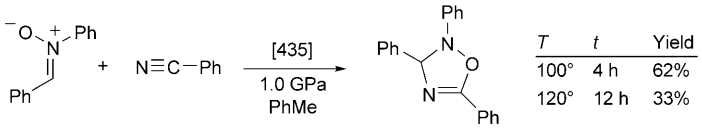
T	*t*	Yield
60°	24 h	88%
100°	1 h	90%
120°	12 h	54%

App. 438



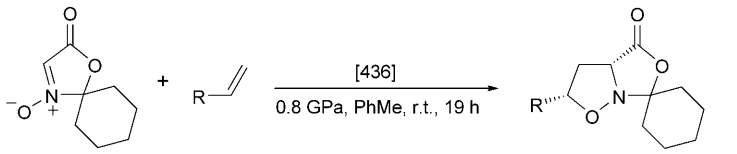
R^1	R^2	Solvent	*T*	*t*	Yield
H	Me	MeCN	100°	1 h	42%
H	Me	MeCN	150°	15 d	53%
H	Ph	PhMe	100°	1 h	71%
H	Ph	PhMe	60°	12 h	56%
H	Ph	PhMe	150°	15 h	51%
H	2-NO_2-C_6H_4	PhMe	100°	1 h	84%
H	2-NO_2-C_6H_4	PhMe	100°	24 h	trace
H	3-NO_2-C_6H_4	PhMe	100°	1 h	90%
H	3-NO_2-C_6H_4	PhMe	100°	18 h	64%
H	4-NO_2-C_6H_4	PhMe	100°	1 h	90%
H	4-NO_2-C_6H_4	PhMe	100°	12 h	58%
H	2-MeO-C_6H_4	PhMe	100°	1 h	54%
H	2-MeO-C_6H_4	PhMe	120°	48 h	trace
H	3-MeO-C_6H_4	PhMe	100°	1 h	86%
H	3-MeO-C_6H_4	PhMe	120°	8 h	50%
H	4-MeO-C_6H_4	PhMe	100°	1 h	70%
H	4-MeO-C_6H_4	PhMe	100°	18 h	58%
Me	Me	MeCN	100°	1 h	32%
Me	Me	MeCN	150°	15 d	–

App. 439



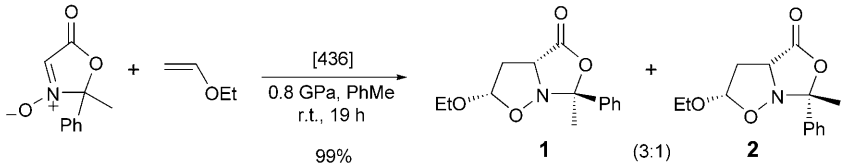
T	*t*	Yield
100°	4 h	62%
120°	12 h	33%

App. 440

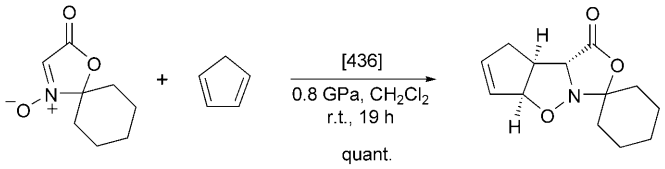


R = EtO (99%)
R = Me_3SiCH_2 (quant.)

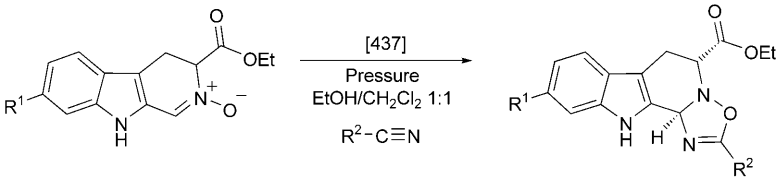
App. 441



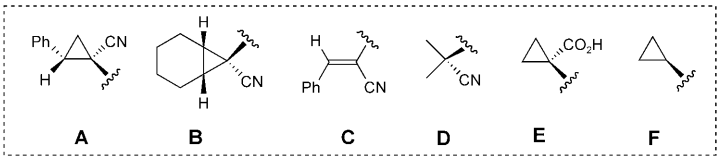
App. 442



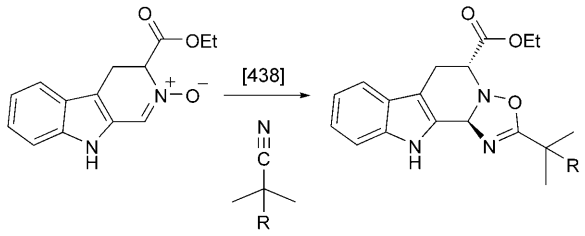
App. 443



R^1	R^2	*P*	*T*	*t*	Yield
H	**A**	0.1 MPa	100°	2 d	74% (1:1)
H	**A**	1.2 GPa	r.t.	2 d	90% (1:1)
H	**B**	1.2 GPa	r.t.	5 d	92%
H	**C**	0.1 MPa	80°	3 d	78%
H	**D**	0.1 MPa	80°	1 h	quant.
H	**E, F**	1.2 GPa	r.t.	7 d	–
MeO	**C**	0.1 MPa	60°	7 h	95%

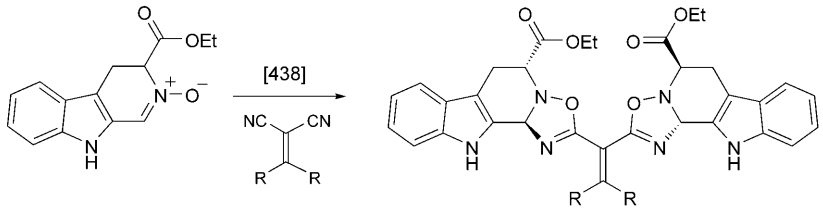


App. 444



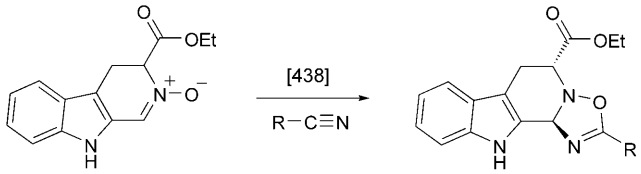
R	*P*	Solvent	*T*	*t*	Yield
EtOOC	0.1 MPa	PhMe	80°	7 d	26%
EtOOC	1.2 GPa	DMF	50°	28 h	75%
Ph	0.1 MPa	PhMe	80°	7 d	11%
Ph	1.2 GPa	DMF	50°	2 d	56%
Me	0.1 MPa	PhMe	80°	6 d	12%
Me	1.2 GPa	DMF	50°	3 d	87%

App. 445



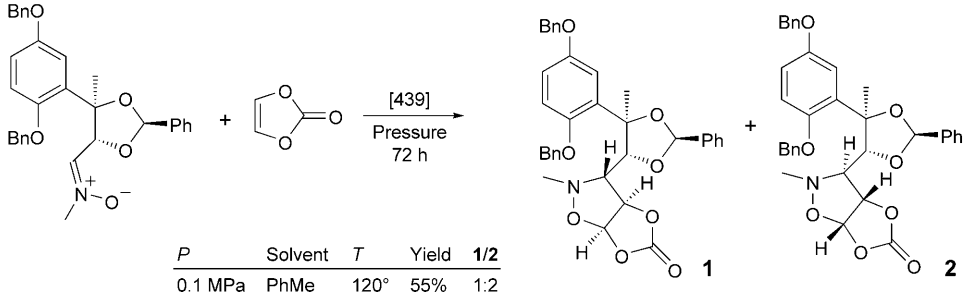
R	*P*	Solvent	*T*	*t*	Yield
Ph	0.1 MPa	PhMe	80°	1 d	11%
Ph	1.2 GPa	DMF	r.t.	1 d	84%
MeS	1.2 GPa	DMF	r.t.	1 d	78%

App. 446



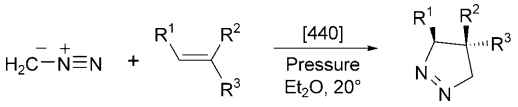
R	*P*	Solvent	*T*	*t*	Yield
Ph	0.1 MPa	PhMe	80°	2 d	87%
Me	0.1 GPa	neat	reflux	1 d	–
Me	1.2 GPa	DMF	r.t.	3 d	–

App. 447



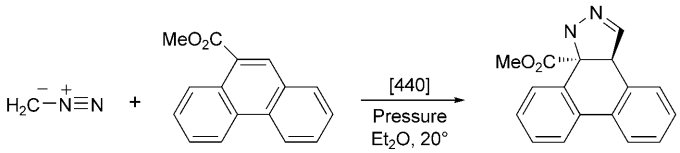
P	Solvent	*T*	Yield	**1/2**
0.1 MPa	PhMe	120°	55%	1:2
1.2 GPa	Et_2O	r.t.	60%	1:4

App. 448



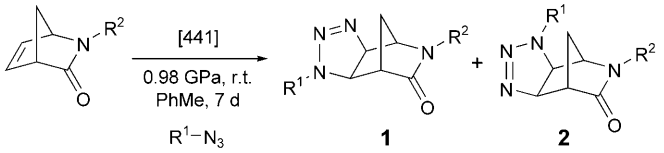
R^1	R^2	R^3	*P*	*t*	Yield
Ph	H	Ph	0.1 MPa	72 h	–
Ph	H	Ph	0.5 GPa	170 h	quant.
Ph	Ph	H	0.1 MPa	72 h	–
Ph	Ph	H	0.5 GPa	792 h	40%
4-NO_2-C_6H_4	H	4-NO_2-C_6H_4	0.1 MPa	144 h	5%
4-NO_2-C_6H_4	H	4-NO_2-C_6H_4	0.5 GPa	144 h	70%

App. 449



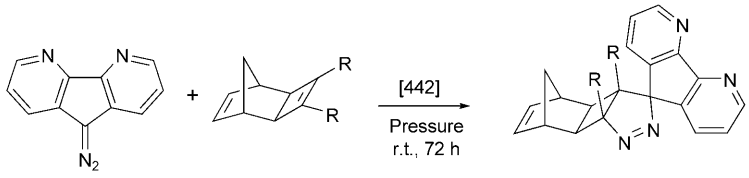
Pressure	*t*	Yield
0.1 MPa	49 h	7%
0.5 GPa	49 h	45%h

App. 450



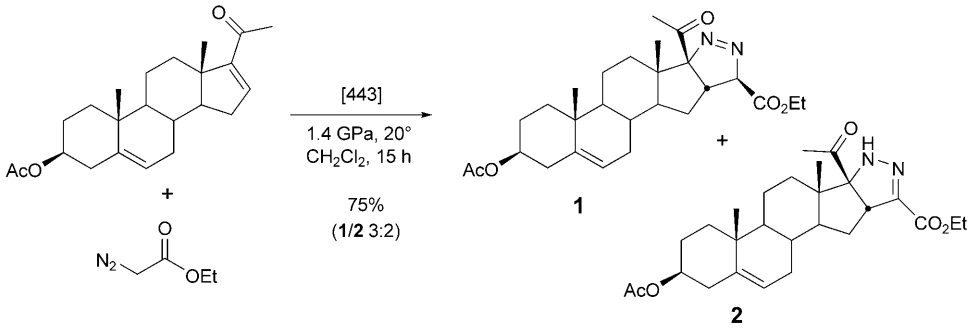
R^1	R^2	**1**	**2**
EtOOC	Boc	52%	21%
$(PhO)_2P(O)$	Boc	56%	14%
Ph	Boc	60%	16%
$(PhO)_2P(O)$	Cbz	–	–

App. 451

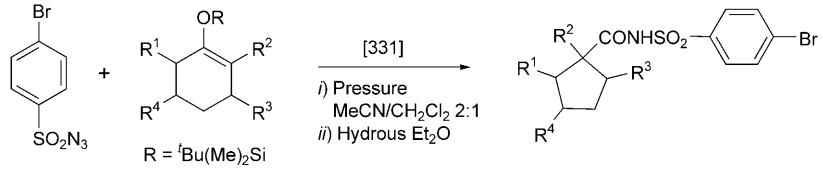


P	Solvent	Yield
0.1 MPa	benzene	–
1.4 GPa	CH_2Cl_2/benzene 3:1	>90%

App. 452

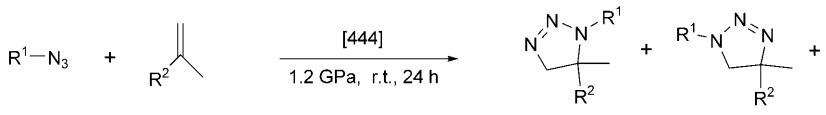


App. 453



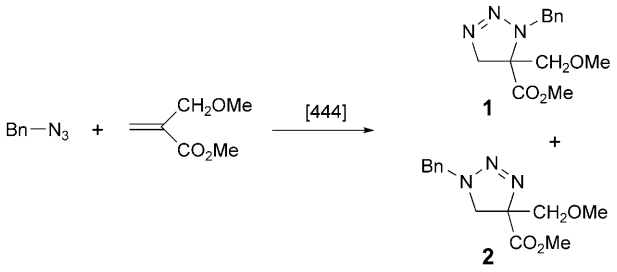
R^1	R^2	R^3	R^4	Condition	*T*	*t*	Yield
H	H	H	H	1.5 GPa	18°	36 h	87%
H	H	H	H	sealed tube	75°	96 h	66%
Me	H	H	H	1.5 GPa	18°	36 h	84%

App. 454



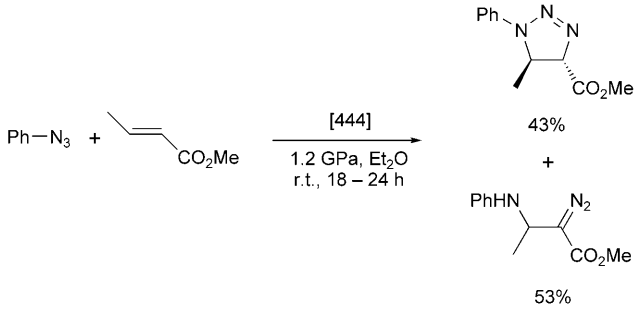
R^1	R^2	Solvent	Yield	(**1**+**2**)/**3**
Ph	CN	CH_2Cl_2	79%	86:14
Ph	MeOOC	Et_2O	89%	68:32
Ph	Ac	Et_2O	93%	55:45
Ph	$NH_2C(O)$	MeOH	55%	>99:1
Bu	CN	CH_2Cl_2	72%	>99:1
Bu	MeOOC	CH_2Cl_2	86%	>99:1
Bu	Ac	Et_2O	95%	82:18
Bu	$NH_2C(O)$	MeOH	64%	99:1
Bn	CN	AcOEt	63%	>99:1
Bn	MeOOC	Et_2O	95%	92:8
Bn	Ac	AcOEt	96%	80:20
Bn	$NH_2C(O)$	MeOH	67%	>99:1

App. 455

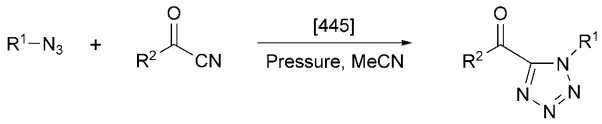


P	Solvent	*T*	*t*	**1**	**2**
0.1 MPa	benzene	80°	24 h	50%	50%
1.2 GPa	CH_2Cl_2	r.t.	18 h	<5%	>95%

App. 456

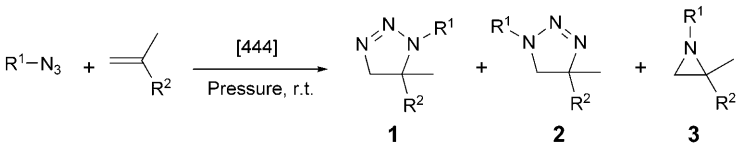


App. 457



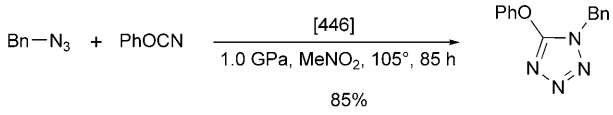
R^1	R^2	*P*	*T*	*t*	Yield
H	Me	1.0 GPa	40°	6 h	70%
H	Ph	0.5 GPa	70°	6 h	81%
EtO_2CCH_2	Ph	1.0 GPa	80°	12 h	90%
EtO_2CCH_2	Me	1.0 GPa	80°	12 h	98%
Bn	Ph	1.0 GPa	100°	25 h	90%
Bn	Me	1.0 GPa	80°	10 h	92%
$EtOCOCH_2$	Me	1.0 GPa	80°	10 h	35%
C_5H_{11}	Me	1.0 GPa	80°	8 h	92%

App. 458

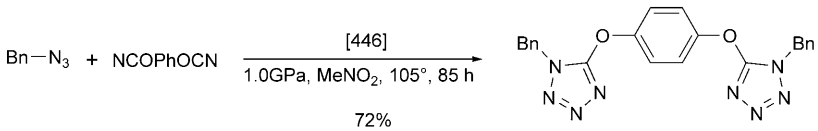


R^1	R^2	Pressure	Solvent	*t*	Yield	**2/1 or 3/1**
Ph	CN	1.2 GPa	CH_2Cl_2	24 h	79%	86:14
Ph	CN	0.1 MPa	CH_2Cl_2	30 d	10%	86:14
Ph	MeOOC	1.2 GPa	Et_2O	24 h	89%	68:32
Ph	MeOOC	0.1 MPa	Et_2O	69 d	?	75:25
Ph	Ac	1.2 GPa	Et_2O	24 h	93%	55:45
Ph	Ac	0.1 MPa	Et_2O	20 d	65%	70:30
Ph	$NH_2C(O)$	1.2 GPa	MeOH	24 h	55%	>99:1
Ph	$NH_2C(O)$	0.1 MPa	MeOH	150 d	35%	90:10
Bu	CN	1.2 GPa	CH_2Cl_2	24 h	72%	>99:1
Bu	CN	0.1 MPa	CH_2Cl_2	30 d	25%	94:6
Bu	MeOOC	1.2 GPa	CH_2Cl_2	24 h	86%	>99:1
Bu	MeOOC	0.1 MPa	CH_2Cl_2	15 d	65%	94:6
Bu	Ac	1.2 GPa	Et_2O	24 h	95%	82:18
Bu	Ac	0.1 MPa	Et_2O	20 d	70%	92:8
Bu	$NH_2C(O)$	1.2 GPa	MeOH	24 h	64%	99:1
Bu	$NH_2C(O)$	0.1 MPa	MeOH	150 d	55%	100:0
Bn	CN	1.2 GPa	AcOEt	24 h	63%	>99:1
Bn	MeOOC	1.2 GPa	Et_2O	24 h	95%	92:8
Bn	Ac	1.2 GPa	AcOEt	24 h	96%	80:20
Bn	$NH_2C(O)$	1.2 GPa	MeOH	24 h	67%	>99:1

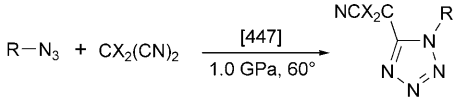
App. 459



App. 460

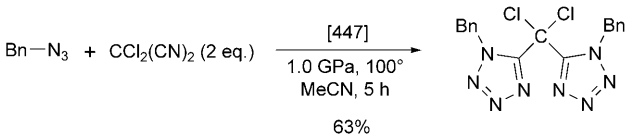


App. 461

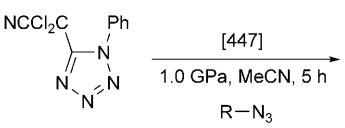


R	X	Solvent	*t*	*T*	Yield
Bn	Cl	MeCN	5 h	60°	72%
Bn	Br	CCl_4	1 d	60°	70%
Ph	Cl	MeCN	5 h	100°	61%
$HO(CH_2)_2$	Cl	MeCN	5 h	60°	47%

App. 462

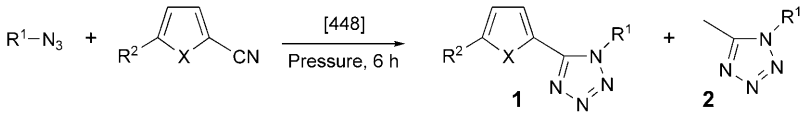


App. 463



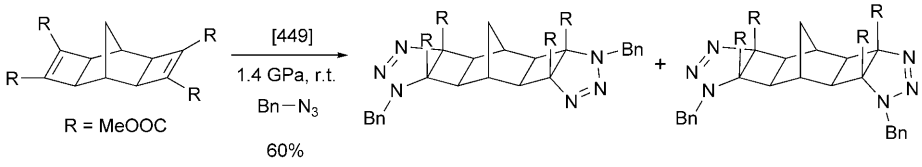
R	*T*	Yield
Ph	120°	–
Bn	110°	52%

App. 464

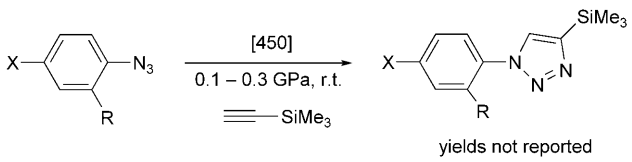


R^1	R^2	X	*P*	Solvent	*T*	**1**	**2**
Me	NO_2	O	1.0 GPa	MeCN	90°	57%	–
Bn	NO_2	O	1.0 GPa	MeCN	100°	78%	–
EtO_2CCH_2	NO_2	O	1.0 GPa	MeCN	100°	85%	–
C_5H_{11}	NO_2	O	1.0 GPa	MeCN	100°	42%	–
Bn	H	O	1.0 GPa	MeCN	110°	7%	–
EtO_2CCH_2	H	O	1.0 GPa	MeCN	110°	11%	–
Bn	NO_2	S	1.0 GPa	CH_2Cl_2	140°	58%	–
EtO_2CCH_2	NO_2	S	1.0 GPa	CH_2Cl_2	140°	64%	–
Bn	NO_2	S	1.0 GPa	MeCN	120°	15%	15%
Bn	NO_2	S	1.4 GPa	MeCN	120°	30%	26%

App. 465

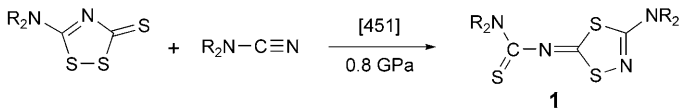


App. 466



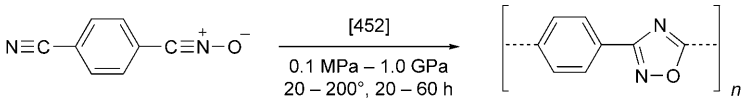
X	R	*t*
NO_2	H	2 h
Cl	H	4 h
H	Ph	<15 h
MeO	H	1.5 h

App. 467

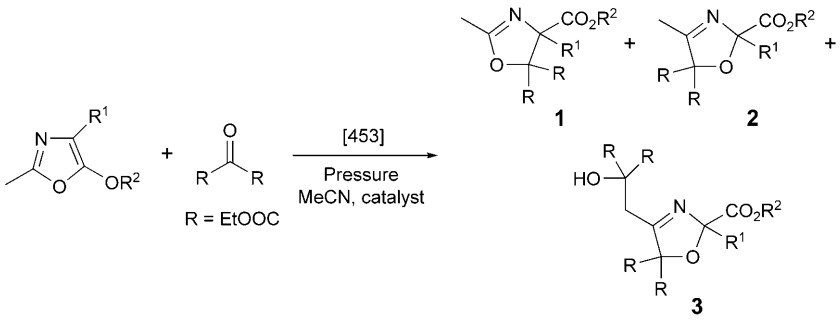


R_2N	*T*	**1**	**2**
Me_2N	70°	40%	–
Et_2N	160°	–	37%
pyrrolidinyl	70°	77%	–
pyrrolidinyl	160°	–	64%
morpholinyl	70°	–	–
morpholinyl	160°	–	4.5%

App. 468

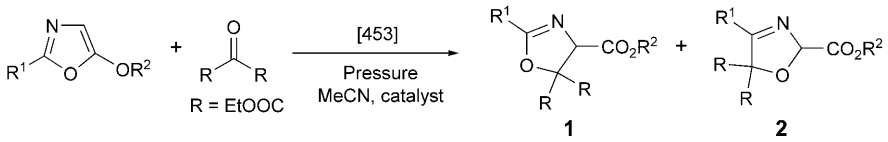


App. 469



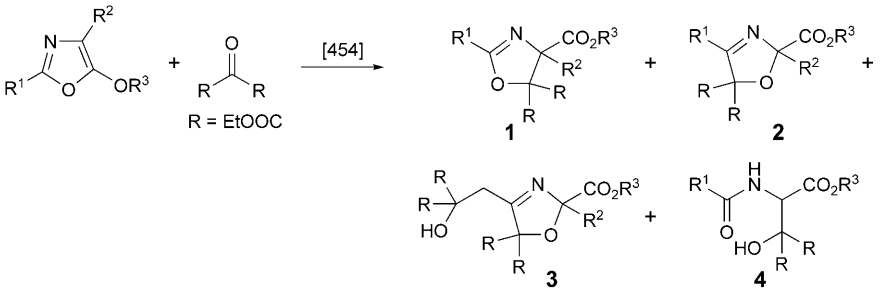
R^1	R^2	Pressure	Catalyst	*T*	*t*	Yield	**1/2/3**
H	Et	0.1 MPa	$SnCl_4$	r.t.	72 h	16%	100:0:0
H	Et	0.85 GPa	$ZnCl_4$	60°	69 h	73%	96:4:0
H	Et	0.1 MPa	none	reflux	24 h	10%	0:100:0
4-NO_2-C_6H_4	Me	0.1 MPa	$SnCl_4$	r.t.	33 h	56%	94:6:0
4-NO_2-C_6H_4	Me	0.1 MPa	MATBr	r.t.	62 h	40%	30:70:0
4-NO_2-C_6H_4	Me	0.85 GPa	none	40°	120 h	47%	0:0:100
4-NO_2-C_6H_4	Me	0.85 GPa	none	40°	120 h	45%	0:0:100
Me	Me	0.1 MPa	$SnCl_4$	r.t.	46 h	89%	34:66:0
Me	Me	0.85 GPa	none	40°	74 h	68%	0:0:100
i-Pr	Me	0.1 MPa	$SnCl_4$	r.t.	96 h	78%	0:100:0
H	Me	0.85 GPa	$ZnCl_4$	40°	90 h	55%	100:0:0

App. 470



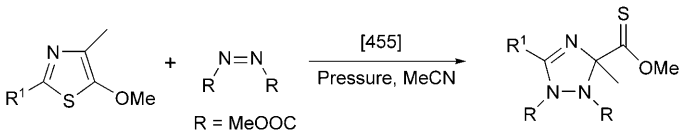
R^1	R^2	*P*	Catalyst	*T*	*t*	Yield	**1/2**
Ph	Et	0.1 MPa	$SnCl_4$	r.t.	19 h	79%	100:0
Ph	Et	0.1 MPa	none	60°	44 h	96%	55:45
4-MeO-C_6H_4	Me	0.1 MPa	$SnCl_4$	60°	111 h	79%	100:0
4-MeO-C_6H_4	Me	0.85 GPa	none	60°	44 h	12%	100:0
4-MeO-C_6H_4	Me	0.85 GPa	$ZnCl_4$	60 °	111 h	67%	100:0

App. 471



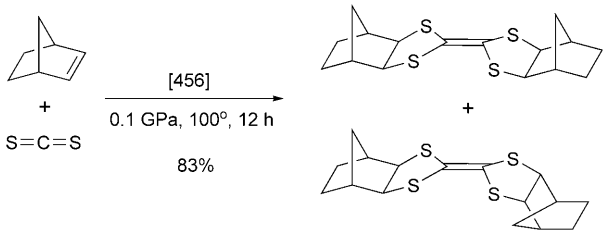
R^1	R^2	R^3	*P*	Catalyst	Solvent	*T*	*t*	Yield
4-MeO-C_6H_4	H	Me	0.1 MPa	$SnCl_4$	MeCN	r.t.	19 h	79% (**1**)
4-MeO-C_6H_4	H	Me	0.85 GPa	none	MeCN	40°	44 h	(12% (**1**), 13% (**4**)
Ph	H	Et	0.1 MPa	$SnCl_4$	MeCN	r.t.	19 h	79% (**1**)
Ph	H	Et	0.1 MPa	none	xylene	reflux	46 h	96% (**1/2** 55:45)
4-MeO-C_6H_4	Ph	Me	0.1 MPa	$SnCl_4$	MeCN	r.t.	20 h	95% (**1**)
4-MeO-C_6H_4	Ph	Me	0.1 MPa	none	xylene	reflux	69 h	23% (**1/2** 1:99)
4-MeO-C_6H_4	4-MeO-C_6H_4	Me	0.1 MPa	$SnCl_4$	MeCN	r.t.	72 h	60% (**1**)
4-MeO-C_6H_4	Me	Me	0.1 MPa	$SnCl_4$	MeCN	r.t.	2 h	97% (**1**)
4-MeO-C_6H_4	i-Pr	Me	0.1 MPa	$SnCl_4$	MeCN	r.t.	120 h	40% (**1/2** 78:22)
Me	H	Et	0.1 MPa	$SnCl_4$	MeCN	r.t.	72 h	16% (**1**), 31% (**4**)
Me	H	Et	0.85 GPa	$ZnCl_4$	MeCN	40°	68.5 h	73% (**1/2** 96:4), 9% (**4**)
Me	H	Et	0.1 MPa	none	xylene	reflux	24 h	(10% (**2**)
Me	4-MeO-C_6H_4	Me	0.1 MPa	$SnCl_4$	MeCN	r.t.	33 h	56% (**1/2** 94:6)
Me	4-MeO-C_6H_4	Me	0.1 MPa	$SnCl_4$	MeCN	r.t.	62 h	40% (**1/2** 30:70)
Me	4-MeO-C_6H_4	Me	0.85 GPa	none	MeCN	40°	120 h	47% (**2/3** 21:26)
Me	4-MeO-C_6H_4	Me	0.85 GPa	none	MeCN	40°	120 h	45% (**3**)

App. 472

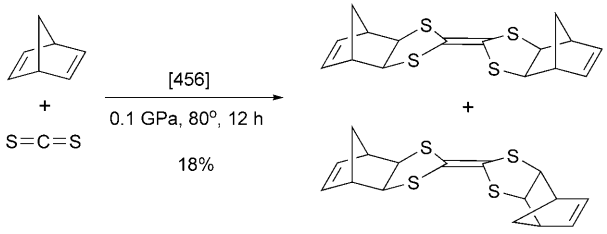


R^1	Ratio	*P*	*T*	*t*	Yield
4-MeO-C_6H_4	1:2	0.1 MPa	reflux	500 h	31%
4-MeO-C_6H_4	1:2	0.85 GPa	60°	100 h	33%
4-MeO-C_6H_4	1:1	0.85 GPa	50°	70 h	31%
4-MeO-C_6H_4	1:2	0.85 GPa	50°	215 h	45%
Me	1:2	0.8 GPa	50°	70 h	66%

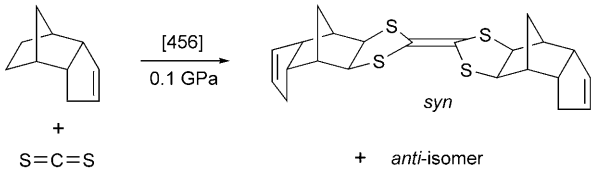
App. 473



App. 474

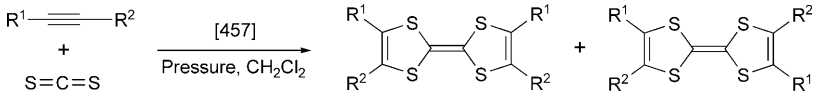


App. 475



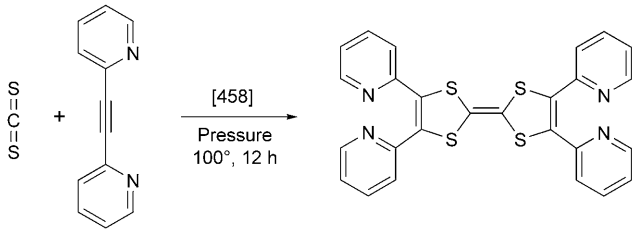
T	*t*	Yield
110°	12 h	48%
100°	16 h	26%

App. 476



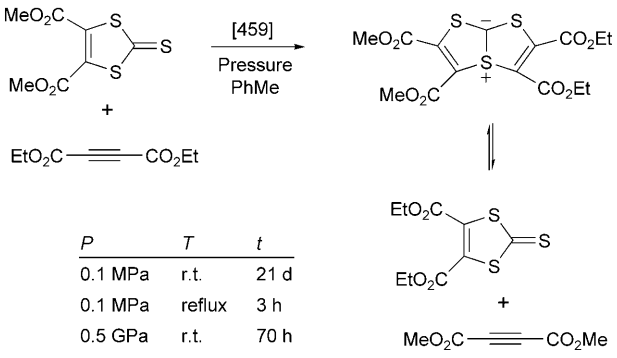
R^1	R^2	*P*	*T*	*t*	Yield (**1**+**2**)
MeOOC	MeOOC	0.5 GPa	100°	24 h	87%
MeOOC	MeOOC	0.45 GPa	20°	70 h	–
MeOOC	H	0.55 GPa	100°	26 h	96%
MeOOC	H	0.4 GPa	80°	24 h	88%
MeOOC	H	10 MPa	100°	24 h	12%
MeOOC	H	1 MPa	100°	24 h	3%
HOOC	H	0.55 GPa	80°	19 h	69%
HOOC	H	0.55 GPa	95°	25 h	20%
HOOC	H	10 MPa	100°	23 h	12%
HOOC	H	1 MPa	100°	22 h	5%

App. 477



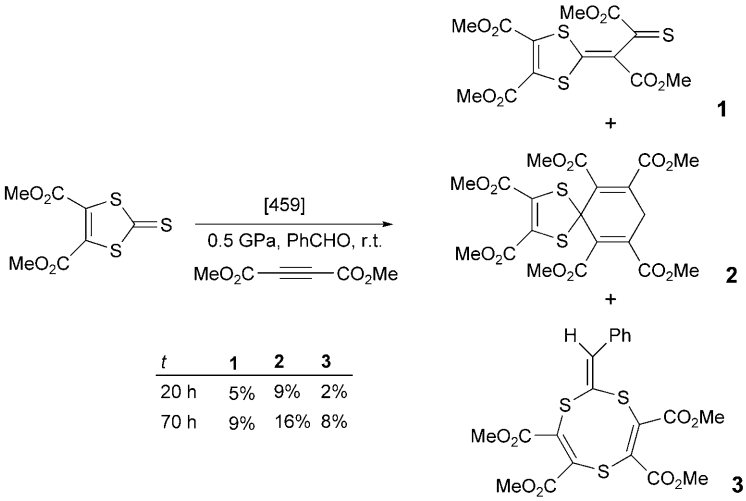
P	Catalyst	Yield
0.45 GPa	none	56%
0.5 GPa	AcOH	–
0.5 GPa	TFA	–

App. 478



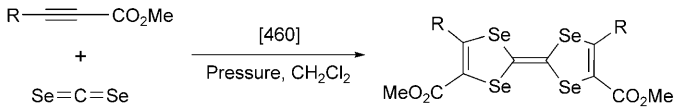
P	*T*	*t*
0.1 MPa	r.t.	21 d
0.1 MPa	reflux	3 h
0.5 GPa	r.t.	70 h

App. 479



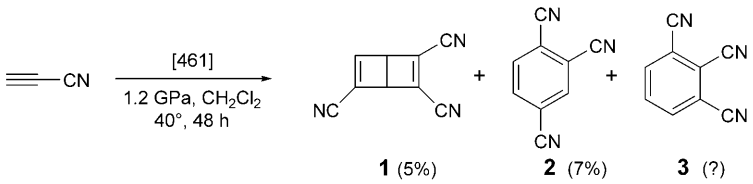
t	**1**	**2**	**3**
20 h	5%	9%	2%
70 h	9%	16%	8%

App. 480



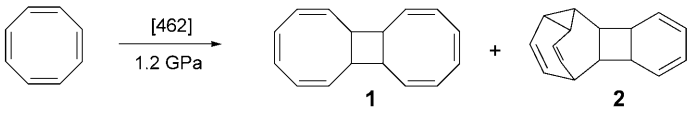
R^1	Condition	*T*	*t*	Yield
MeOOC	0.5GPa	60°	13 h	90%
MeOOC	sealed tube	70 – 80°	72 h	10%
H	0.5GPa	60°	13 h	85%
H	sealed tube	70 – 80°	72 h	72%

App. 481



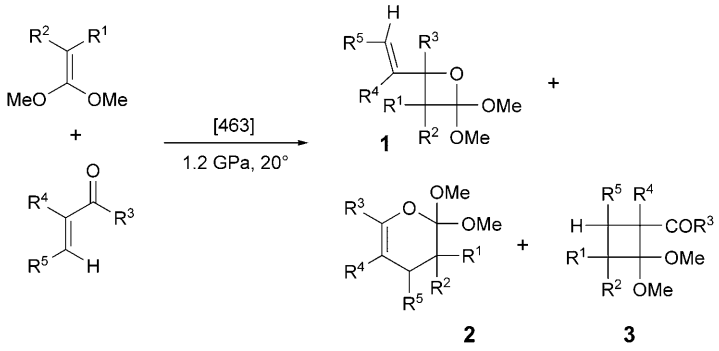
1/2/3 16:6:1 (by ^{1}H-NMR)

App. 482



Solvent	*T*	*t*	Yield	**1/2**
hexane	20°	12 h	30%	3:1
hexane	70°	12 h	85%	0:1
benzene/DMSO	120°	14 h	quant.	0:1

App. 483

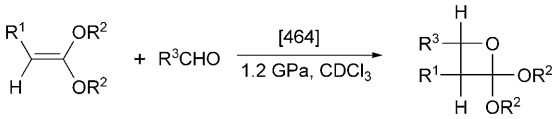


R^1	R^2	R^3	R^4	R^5	Solvent	*t*	**1**	**2**	**3**
H	Me	H	H	H	MeCN	0.5 h	–	35%	65%
H	Me	H	H	H	hexane	0.5 h	–	80%	20%
MeO	MeO	H	H	H	MeCN	24 h	–	30%	70%
H	Me	H	Me	H	MeCN	0.5 h	10%	10%	80%
H	Me	H	Me	H	hexane	0.5 h	30%	30%	40%
MeO	MeO	H	Me	H	MeCN	48 h	–	–	>95%
H	Me	H	H	Me	MeCN	0.5 h	20%	60%	20%
MeO	MeO	H	H	Me	hexane	0.5 h	30%	70%	–
H	Me	Me	H	H	MeCN	12 h	–	>90%	–
MeO	MeO	Me	H	H	MeCN	24 h	–	–	–
H	Me	H	H	Ph	MeCN	12 h	50%	50%	–
MeO	MeO	H	H	Ph	MeCN	24 h	–	–	–

App. 484

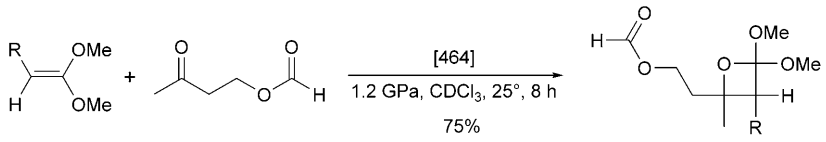
R^1	R^2	*P*	Yield	*cis*/*trans*
H	Me	1.2 GPa	38%	–
H	Me	1.0 GPa	25%	–
H	Me	0.8 GPa	<5%	–
Me	Me	1.2 GPa	94%	20:80
Me	Me	1.0 GPa	66%	25:75
Me	Me	0.8 GPa	38%	25:75
Me	Et	1.2 GPa	92%	30:70
Me	Et	1.0 GPa	76%	30:70
Me	Et	0.8 GPa	52%	30:70
Cl	Me	1.2 GPa	18%	20:80
Cl	Me	1.0 GPa	<5%	–
Cl	Et	1.2 GPa	31%	35:65
Cl	Et	1.0 GPa	25%	35:65
Cl	Et	0.8 GPa	<5%	–
MeO	Me	1.2 GPa	35%	35:65
MeO	Me	1.0 GPa	30%	35:65
MeO	Me	0.8 GPa	*ca.* 10%	–

App. 485

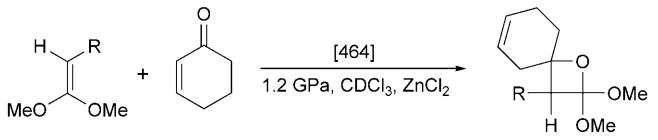


R^1	R^2	R^3	*T*	*t*	Yield	*cis*/*trans*
H	Me	Ph	25°	3 h	70%	–
Me	Me	Ph	25°	1 h	90%	20:80
Cl	Et	Ph	25°	8 h	60%	<5:95
Me	Me	cyclohexyl	25°	8 h	80%	–
Me	Me	*t*-Bu	50°	8 h	30%	<5:95

App. 486

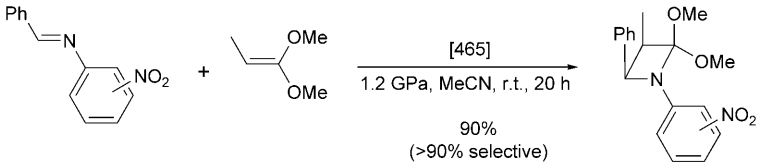


App. 487

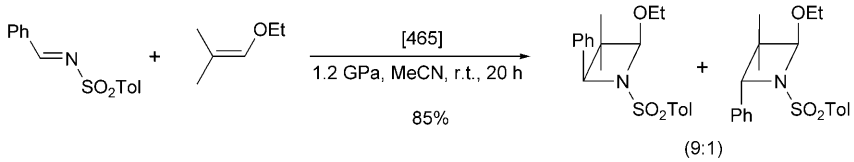


R	*T*	*t*	Yield
Me	25°	5 h	80%
MeO	50°	15 h	70%

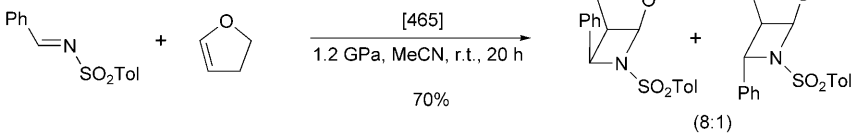
App. 488



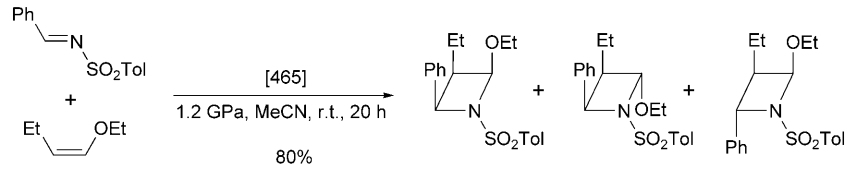
App. 489



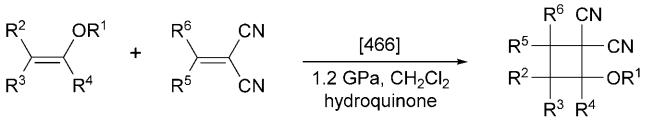
App. 490



App. 491

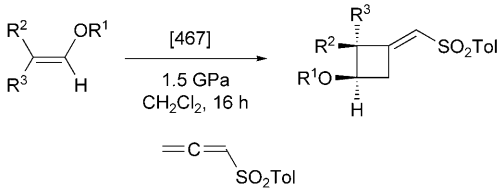


App. 492



R^1	R^2	R^3	R^4	R^5	R^6	*T*	*t*	Yield	*cis*/*trans*
Et	H	H	H	–$(CH_2)_5$–		50°	20 h	65%	–
Et	H	H	H	H	Ph	50°	20 h	85%	15:4
Et	H	H	H	H	2-furyl	50°	20 h	70%	3:2
Et	H	H	H	H	2-naphthyl	50°	20 h	80%	3:1
t-Bu	H	H	H	H	Ph	50°	20 h	85%	15:4
i-Pr	Me	H	H	H	Ph	50°	20 h	82%	3:2
i-Pr	H	Me	H	H	Ph	50°	20 h	85%	>9:1
Me	Me	Me	H	H	Ph	50°	48 h	83%	2:1
Et	Me	Me	H	H	Ph	50°	48 h	80%	2:1
–$(CH_2)_2$–		H	H	H	Ph	25°	6 h	88%	*ca.* 1:1
Me	H	–$(CH_2)_4$–		H	Ph	25°	6 h	81%	>95:5
Me_3Si	H	Me	H	H	Ph	50°	48 h	80%	9:1
Me_3Si	H	H	Me	H	Ph	25°	20 h	50%	4:1
Me_3Si	Me	H	Et	H	Ph	25°	20 h	35%	7:3
Me_3Si	H	–$(CH_2)_4$–		H	Ph	25°	20 h	78%	>95:5

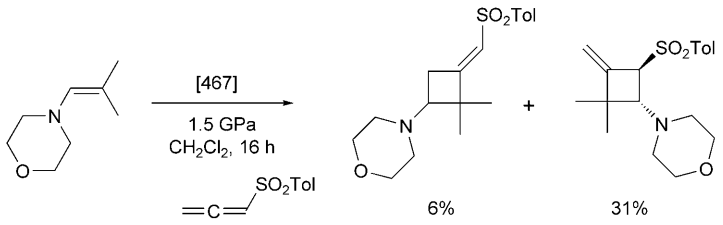
App. 493



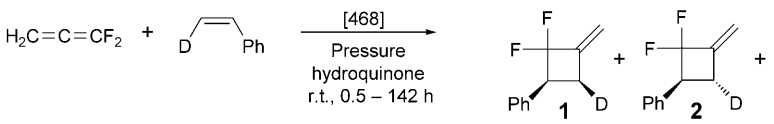
R^1	R^1	R^3	*T*	Yield
Et	H	H	50°	74%
t-Bu	H	H	r.t.	71%
C_6H_5-CH(Me)	H	H	50°	44%[a])
i-Pr	H	Me	50°	75%
i-Pr	Me	H	50°	62%
Me	Me	Me	50°	65%
–CH_2CH_2–		H	r.t.	55%

[a]) Plus 23% of diastereoisomer.

App. 494

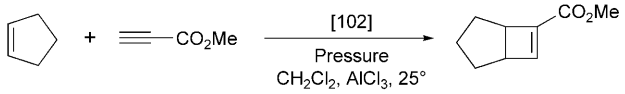


App. 495



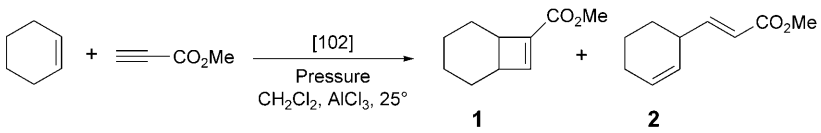
P	**1+2**	**1/2**	**3+4**	**3/4**
0.1 8GPa	86.1%	66.3:33.7	13.9%	88.0:12.0
0.41 GPa	84.1%	71.6:28.4	15.9%	89.9:10.1
0.59 GPa	82.1%	73.2:26.8	17.9%	91.2:8.8
0.8 GPa	77.7%	74.5:25.5	22.3%	92.3:7.7
1.1 GPa	70.6%	83.2:16.8	29.4%	94.6:5.4
1.3 GPa	69.6%	85.5:14.5	30.4%	95.2:4.8

App. 496



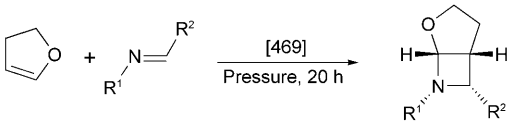
P	*t*	Yield
0.1 MPa	37 d	12%
0.9 GPa	3 h	52%

App. 497



P	*t*	Yield	**1/2**
0.1 MPa	37 d	12%	71:29
0.3 GPa	3 h	42%	72:28
0.9 GPa	3 h	93%	70:30

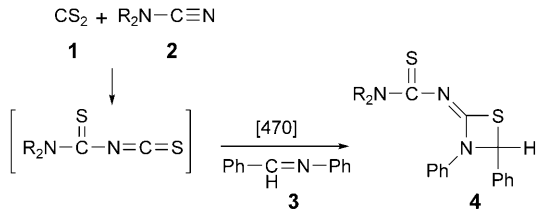
App. 498



R^1	R^2	*P*	Solvent	*T*	Yield
p-tolyl	Ph	0.1 MPa	neat	160°	–
p-tolyl	Ph	0.8 GPa	neat	160°	66%
p-tolyl	Ph	1.3 GPa	neat	100°	31%
p-tolyl	Ph	0.8 GPa	hexane	160°	32%
p-tolyl	Ph	0.8 GPa	PhMe	160°	40%
p-tolyl	Ph	0.8 GPa	AcOEt	160°	37%
p-tolyl	Ph	0.8 GPa	THF	160°	37%
p-tolyl	Ph	0.8 GPa	DHF[a])	160°	54%
Ph	4-Cl-C_6H_4	0.8 GPa	neat	160°	32%
Ph	4-MeO-C_6H_4	0.8 GPa	neat	160°	32%

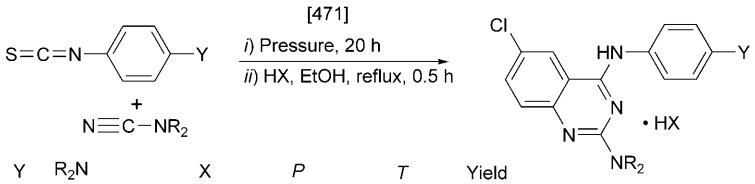
[a]) 2,3-Dihydrofuran.

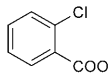
App. 499



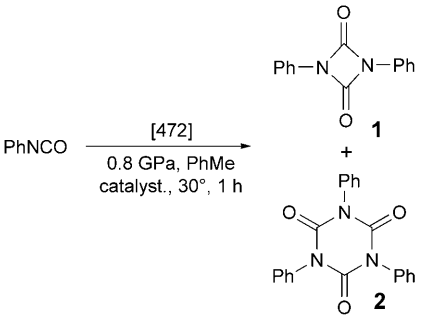
1 (equiv.)	**2** (equiv.)	R_2N	**3** (equiv.)	*P*	*T*	**4**
0.5	0.5	Me_2N	0.5	0.8 GPa	100°	30%
0.5	1.0	Me_2N	0.5	0.8 GPa	100°	46%
1.0	0.5	Me_2N	0.5	0.8 GPa	100°	58%
0.5	0.5	Me_2N	1.0	0.8 GPa	100°	30%
1.0	1.0	Me_2N	0.5	0.8 GPa	100°	68%
2.0	1.0	Me_2N	0.5	0.8 GPa	100°	84%
1.0	0.5	Me_2N	0.5	0.8 GPa	70°	7%
1.0	0.5	Me_2N	0.5	0.6 GPa	100°	53%
1.0	0.5	Me_2N	0.5	0.4 GPa	100°	18%
1.0	0.5	Me_2N	0.5	0.2 GPa	100°	3%
2.0	1.0	Et_2N	0.5	0.8 GPa	100°	23%
2.0	1.0	1-pyrrolidinyl	0.5	0.8 GPa	100°	56%
2.0	1.0	1-piperidinyl	0.5	0.8 GPa	100°	52%
2.0	1.0	1-morpholinyl	0.5	0.8 GPa	100°	61%

App. 500



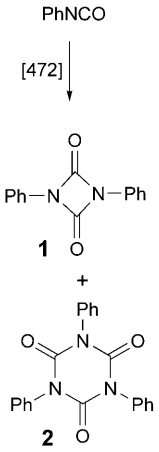
Y	R_2N	X	*P*	*T*	Yield
H	Me_2N	Cl	0.8 GPa	100°	86%
H	1-pyrrolidinyl	Cl	0.8 GPa	130°	78%
H	1-piperidinyl	Cl	0.8 GPa	130°	62%
H	1-morpholinyl	Cl	0.8 GPa	130°	51%
H	1-morpholinyl	Cl	0.1 MPa	100°	–
H	1-morpholinyl	Cl	0.2 GPa	100°	16%
H	1-morpholinyl	Cl	0.4 GPa	100°	37%
H	1-morpholinyl	Cl	0.8 GPa	100°	67%
H	1-morpholinyl	Cl	0.8 GPa	40°	0.7%
H	1-morpholinyl	Cl	0.8 GPa	70°	8.5%
H	1-morpholinyl	Cl	0.8 GPa	130°	79%
Cl	Me_2N		0.8 GPa	100°	74%

App. 501



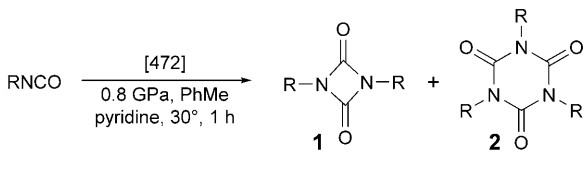
Catalyst	**1**	**2**
none	–	–
pyridine	33%	2%
2-methylpyridine	4%	–
3-methylpyridine	63%	5%
4-methylpyridine	81%	–
2,6-dimethylpyridine	1%	–
N-methylmorpholine	9%	47%
Et_3N	7%	67%
$(i\text{-}Pr)_2NEt$	–	16%

App. 502



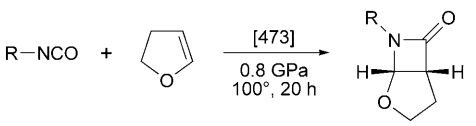
P	Solvent	*T*	*t*	**1**	**2**
0.1 MPa	hexane	40°	20 h	–	–
0.61 GPa	hexane	40°	20 h	50%	21%
0.8 GPa	hexane	40°	20 h	59%	19%
0.8 GPa	hexane	30°	1 h	17%	7%
0.8 GPa	hexane	30°	20 h	45%	6%
0.8 GPa	hexane	70°	20 h	61%	32%
0.4 GPa	PhMe	30°	1 h	2%	3%
0.8 GPa	PhMe	30°	1 h	33%	2%
0.8 GPa	PhMe	30°	20 h	89%	5%
0.8 GPa	PhMe	100°	20 h	71%	5%
0.8 GPa	neat	30°	1 h	35%	4%
0.8 GPa	hexane	30°	1 h	17%	7%
0.8 GPa	PhMe	30°	1 h	33%	2%
0.8 GPa	CH_2Cl_2	30°	1 h	39%	2%
0.8 GPa	$i\text{-}Pr_2O$	30°	1 h	29%	4%
0.8 GPa	THF	30°	1 h	42%	13%
0.8 GPa	AcOEt	30°	1 h	45%	9%
0.8 GPa	MeCN	30°	1 h	17%	82%
0.8 GPa	DMF	30°	1 h	35%	44%

App. 503



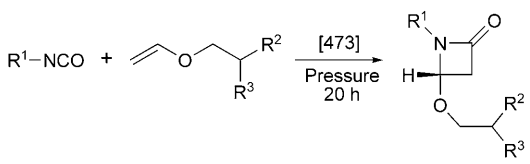
R	**1**	**2**
C_6H_5	89%	5%
2-Cl-C_6H_4	–	–
3-Cl-C_6H_4	80%	–
4-Cl-C_6H_4	93%	–
3-Me-C_6H_4	65%	–

App. 504



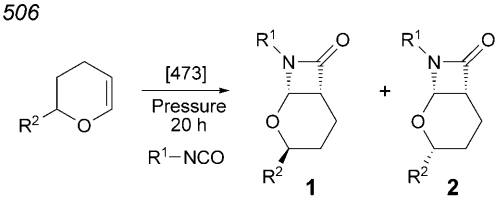
R	Yield
Me	71%
Et	92%
Bu	77%
C_6H_{11}	68%
t-Bu	23%
Bn	quant.

App. 505



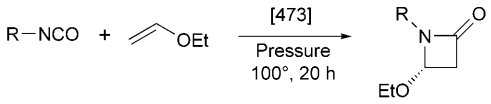
R^1	R^2	R^3	*P*	*T*	Yield
Ph	H	H	0.8 GPa	70°	93%
Ph	Et	Bu	0.8 GPa	100°	97%
Me	H	H	0.8 GPa	100°	21%
Me	Et	Bu	0.8 GPa	100°	20%
Me	Et	Bu	1.2 GPa	100°	31%
Me	Et	Bu	1.2 GPa	100°	12%

App. 506



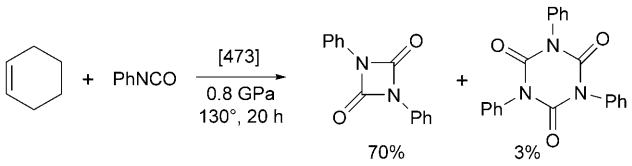
R^1	R^2	*P*	*T*	**1**	**2**
Ph	H	0.8 GPa	70°	82%	–
Ph	MeO	0.8 GPa	100°	5%	2%
Ph	MeO	0.8 GPa	100°	59%	30%
Me	H	0.8 GPa	100°	12%	–
Me	H	1.2 GPa	100°	33%	–

App. 507

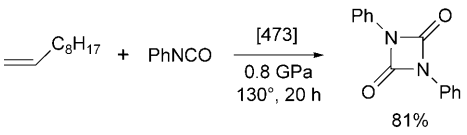


R	*P*	Yield
Bu	0.8 GPa	8%
Bu	1.2 GPa	14%
C_6H_{11}	1.2 GPa	4%
t-Bu	1.2 GPa	–
Bn	0.8 GPa	42%

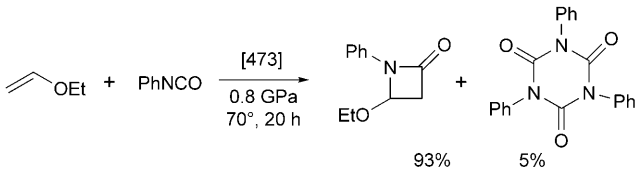
App. 508



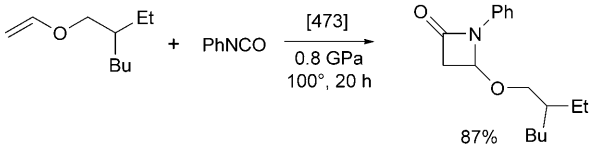
App. 509



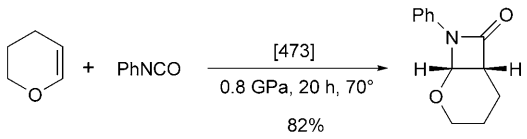
App. 510



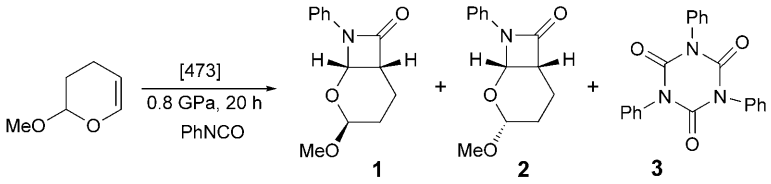
App. 511



App. 512

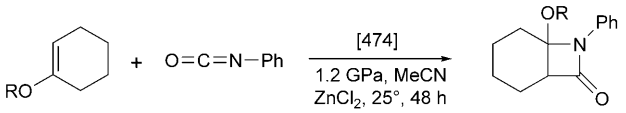


App. 513



T	**1**	**2**	**3**
100°	5%	2%	26%
130°	59%	30%	–

App. 514

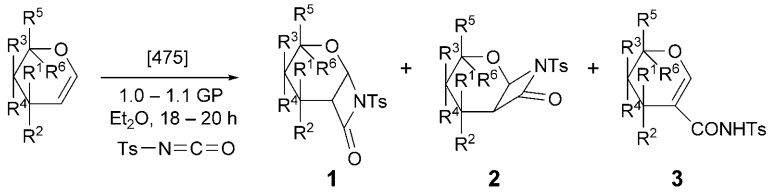


R = Me (70%)
R = Et (80%)

App. 515

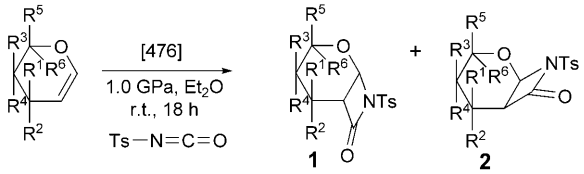
R^1	R^2	R^3	R^4	*t*	Yield	dr
–$(CH_2)_4$–		EtO	H	16 h	35%	–
–$(CH_2)_4$–		EtO	Me	16 h	60%	–
–$(CH_2)_4$–		EtO	i-Pr	48 h	56%	–
–$O(CH_2)_3$–		H	H	16 h	47%	–
–$O(CH_2)_3$–		H	Me	16 h	78%	50:50
–$O(CH_2)_3$–		H	i-Pr	48 h	62%	37:49
–$O(CH_2)_3$–		H	$MeOCH_2$	16 h	50%	50:50
i-PrO	Me	H	Me	48 h	50%	44:47
i-PrO	Me	H	i-Pr	48 h	20%	40:48

App. 516



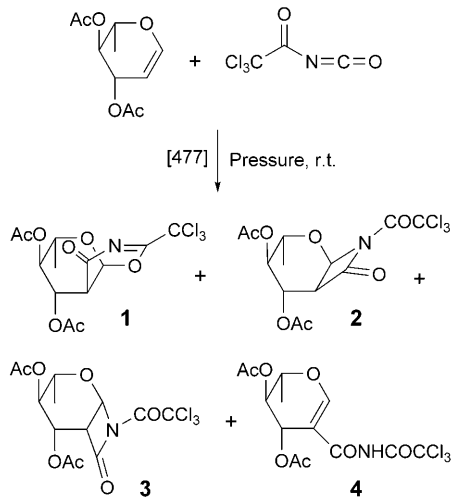
R^1	R^2	R^3	R^4	R^5	R^6	*T*	Yield
AcO	H	H	AcO	$AcOCH_2$	H	r.t.	43% (**1**)
AcO	H	H	AcO	$AcOCH_2$	H	50°	59% (**1**), 5% (**3**)
AcO	H	AcO	H	$AcOCH_2$	H	r.t.	–
H	AcO	AcO	H	H	H	r.t.	75% (**1**)
H	AcO	AcO	H	H	H	50°	25% (**3**)
H	AcO	AcO	H	H	Me	r.t.	77% (**1**/**2** 5:95)
H	H	H	AcO	$AcOCH_2$	H	r.t.	65% (**1**/**2** 75:25)
H	H	H	H	$AcOCH_2$	H	r.t.	81% (**1**/**2** 65:35)
^{t}Bu$(Me)_2$SiO	H	H	^{t}Bu$(Me)_2$SiO	^{t}Bu$(Me)_2$SiOCH_2	H	r.t.	?

App. 517



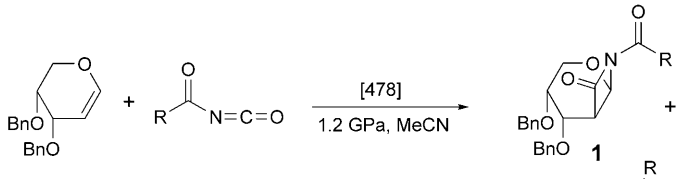
R^1	R^2	R^3	R^4	R^5	R^6	Yield
AcO	H	H	AcO	$AcOCH_2O$	H	60 – 77% (**1**)
AcO	H	AcO	H	$AcOCH_2O$	H	60 – 77% (**1**)
H	AcO	H	AcO	H	H	60 – 77% (**2**)
H	AcO	AcO	H	H	Me	60 – 77% (**2**)

App. 518



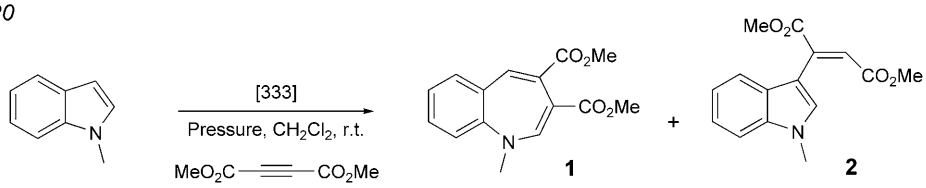
P	Solvent	*t*	**1**	**2**	**3**	**4**
0.6 GPa	CD_3CN	0.5 h	29%	18%	9%	4%
0.6 GPa	CD_3CN	1 h	40%	20%	11%	5%
0.6 GPa	CD_3CN	3 h	44%	25%	13%	5%
0.6 GPa	CD_3CN	6 h	50%	28%	14%	5%
0.6 GPa	$CDCl_3$	5 h	29%	13%	6%	–
0.6 GPa	$CDCl_3$	20 h	42%	22%	13%	6%
0.6 GPa	$CDCl_3$	24 h	45%	22%	11%	5%
0.6 GPa	$CDCl_3$	36 h	52%	22%	10%	5%
0.6 GPa	$CDCl_3$	140 h	52%	23%	10%	5%
0.6 GPa	Et_2O	1 h	40%	24%	14%	3%
1.0 GPa	Et_2O	1 h	56%	24%	16%	4%
1.5 GPa	Et_2O	1 h	55%	25%	14%	7%

App. 519



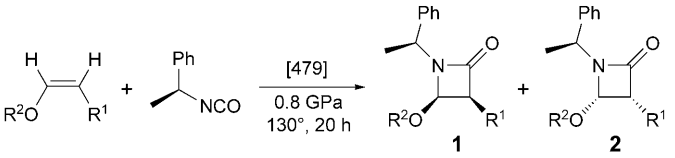
R	*T*	*t*	**1**	**2**	**3**
EtO	r.t.	24 h	65%	–	–
EtO	50°	3 h	80%	–	20%
EtO	50°	4 h	75%	–	25%
BnO	50°	3 h	71%	–	–
BnO	50°	6 h	90%	–	<10%
Ph	50°	3 h	60%	–	40%
Ph	r.t.	24 h	28%	28%	6%
$(NO_2)_2C_6H_3$	r.t.	6 h	28%	28%	19%
$(NO_2)_2C_6H_3$	50°	2 h	58%	–	42%

App. 520



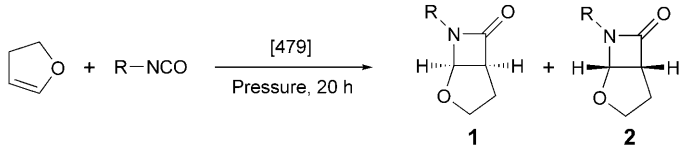
P	*t*	**1**	**2**
0.1 MPa	112 d	14.5%	4.4%
1.0 GPa	7 d	20%	–

App. 521



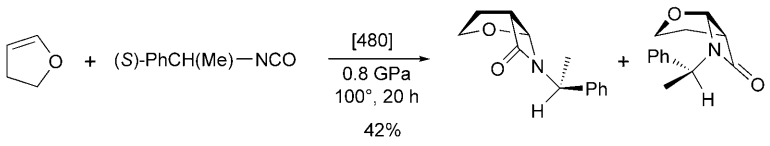
R^1	R^2	Yield	**1/2**
H	Et	86%	49:51
H	Bu	45%	45:55
H	i-Bu	68%	47:53
H	Bu(Et)$CHCH_2$	55%	56:44
–$(CH_2)_3$–		46%	48:52

App. 522

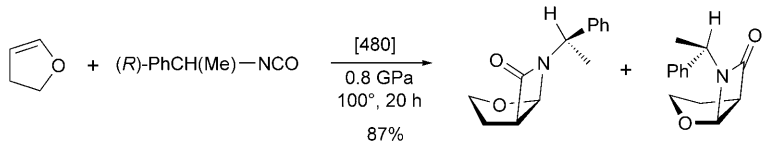


R	*P*	Solvent	*T*	Yield	**1/2**
(–)-(*S*)-C_6H_4-CH(Me)	0.5 MPa	neat	100°	–	–
(–)-(*S*)-C_6H_4-CH(Me)	0.2 GPa	neat	100°	21%	51:49
(–)-(*S*)-C_6H_4-CH(Me)	0.4 GPa	neat	100°	68%	51:49
(–)-(*S*)-C_6H_4-CH(Me)	0.8 GPa	neat	100°	80%	53:47
(–)-(*S*)-C_6H_4-CH(Me)	1.0 MPa	neat	130°	9%	51:49
(–)-(*S*)-C_6H_4-CH(Me)	0.4 GPa	neat	130°	90%	51:49
(–)-(*S*)-C_6H_4-CH(Me)	0.8 GPa	neat	130°	92%	52:48
(–)-(*S*)-C_6H_4-CH(Me)	0.8 GPa	PhMe	100°	48%	51:49
(–)-(*S*)-C_6H_4-CH(Me)	0.8 GPa	CH_2Cl_2	100°	58%	50:50
(–)-(*S*)-C_6H_4-CH(Me)	0.8 GPa	MeCN	100°	16%	49:51
(–)-(*S*)-C_6H_4-CH(Me)	0.8 GPa	THF	100°	37%	50:50
(–)-(*S*)-C_6H_4-CH(Me)	0.8 GPa	DMF	100°	37%	50:50
(–)-(*S*)-C_6H_4-CH(Me)	0.8 GPa	$(i\text{-}Pr)_2O$	100°	28%	50:50
(+)-(*R*)-C_6H_4-CH(Me)	0.8 GPa	neat	40°	87%	48:52
(+)-(*R*)-C_6H_4-CH(Me)	1.2 GPa	neat	70°	26%	48:52
(+)-(*R*)-C_6H_4-CH(Me)	1.2 GPa	neat	100°	75%	48:52
(+)-(*S*)-Naph-CH(Me)	0.2 GPa	neat	100°	26%	52:48
(+)-(*S*)-Naph-CH(Me)	0.8 GPa	neat	100°	94%	52:48
(+)-(*S*)-Naph-CH(Me)	0.8 GPa	neat	130°	81%	50:50
(+)-(*S*)-Naph-CH(Me)	1.2 GPa	neat	40°	32%	51:49
(+)-(*S*)-Naph-CH(Me)	1.2 GPa	neat	70°	71%	49:51

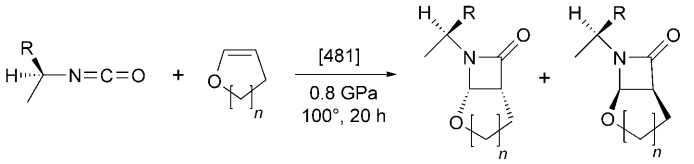
App. 523



App. 524

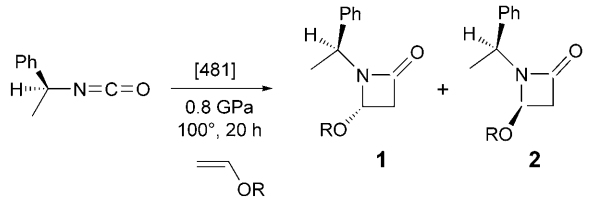


App. 525



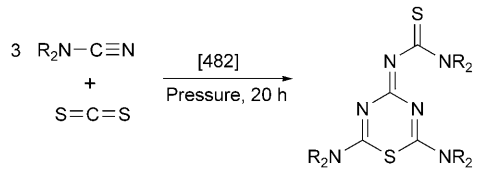
R	*n*	Yield	**1/2**
Ph	1	80%	53:47
1-naphthyl	1	94%	52:48
Ph	2	46%	52:48

App. 526



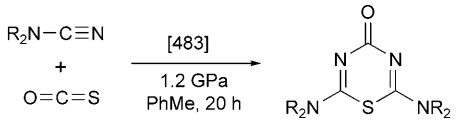
R	Yield	**1/2**
Et	86%	49:51
i-Bu	68%	47:53
Bu	45%	45:55

App. 527



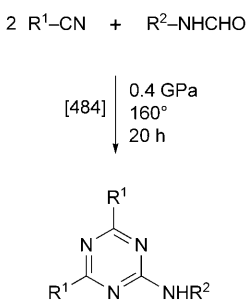
R_2N	*P*	*T*	Yield
Me_2N	0.8 GPa	50°	4.7%
Me_2N	0.8 GPa	100°	72%
Me_2N	0.5 GPa	100°	84%
Me_2N	0.2 GPa	100°	16%
1-pyrrolidino	0.8 GPa	50°	71%
1-piperidino	0.8 GPa	70°	55%

App. 528



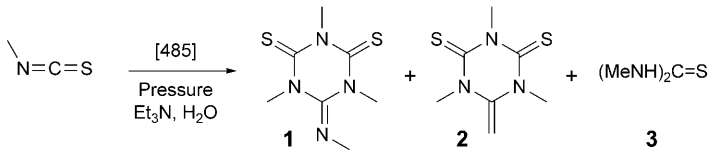
R_2N	*P*	*T*	Yield
Me_2N	0.8 GPa	130°	92%
Me_2N	0.4 GPa	130°	33%
Me_2N	0.2 GPa	130°	7%
Me_2N	3.0 MPa	130°	–
Me_2N	1.25 GPa	100°	29%
Me_2N	0.8 GPa	100°	14%
Me_2N	0.53 GPa	100°	7%
1-pyrrolidino	0.8 GPa	130°	74%
piperidino	0.8 GPa	160°	94%
piperidino	0.8 GPa	130°	67%
piperidino	0.8 GPa	100°	13%
mopholino	0.8 GPa	130°	77%

App. 529



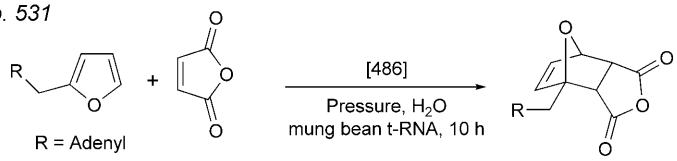
R^1	R^2	Yield
piperidino	H	60%
piperidino	Me	50%
piperidino	Ph	37%
morpholino	H	52%
morpholino	Me	66%
morpholino	Ph	58%
pyrrolidino	H	72%
pyrrolidino	Me	64%
pyrrolidino	Ph	66%
Me_2N	H	65%
Me_2N	Me	35%
Me_2N	Ph	61%

App. 530



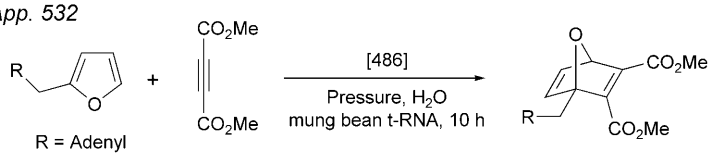
P	Solvent	Et_3N (equiv.)	H_2O (equiv.)	*T*	*t*	**1**	**2**	**3**
0.1 MPa	DMF	0.1	2	40°	20 h	–	–	–
0.4 GPa	DMF	0.1	2	40°	20 h	17%	21%	14%
0.61 GPa	DMF	0.1	2	40°	20 h	48%	16%	15%
0.8 GPa	DMF	0.1	2	40°	20 h	52%	10%	15%
0.8 GPa	DMF	0.1	2	100°	20 h	6%	41%	13%
0.8 GPa	DMF	0.1	2	40°	1 h	33%	6%	4%
0.8 GPa	DMF	0.1	–	40°	20 h	4%	28%	–
0.8 GPa	DMF	–	2	40°	20 h	–	–	–
0.8 GPa	MeCN	0.1	2	40°	20 h	31%	15%	14%
0.8 GPa	i-Pr_2NEt	0.1	2	40°	20 h	2%	17%	21%
0.8 GPa	benzene	0.1	2	40°	20 h	12%	68%	4%
1.2 GPa	DMF	0.02	0.4	30°	3 h	80%	2%	trace

App. 531



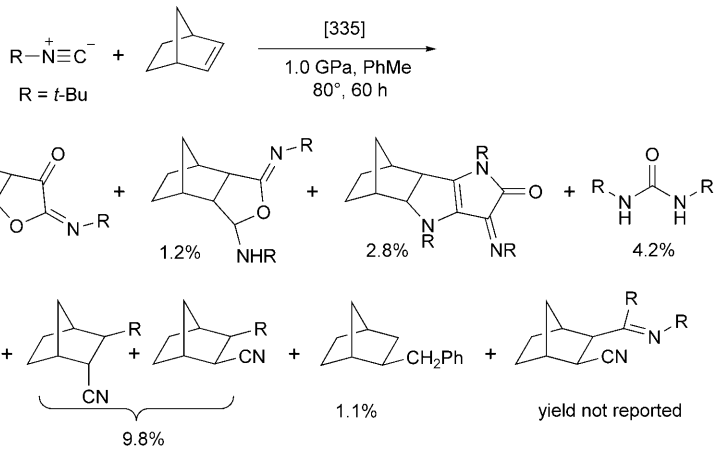
P	Analysis
1.0 GPa	formed (by MS)
0.1 MPa	not formed

App. 532



P	Analysis
1.0 GPa	formed (by MS)
0.1 MPa	not formed

App. 533



REFERENCES

[1] R. Huisgen, '*The Adventure Playground of Mechanisms and Novel Reactions*', in 'Profiles, Pathways, and Dreams: Autobiographies of Eminent Chemists', Ed. J. I. Seeman, American Chemical Society, Washington, DC, 1994.
[2] a) K. Matsumoto, A. Sera, T. Uchida, *Synthesis* **1985**, 1; b) K. Matsumoto, M. Toda, *Kagaku* **1995**, *50*, 90.
[3] A. Sharma, J. H. Scott, G. D. Cody, M. L. Fogel, R. M. Hazen, R. J. Hemley, W. T. Huntress, *Science* **2002**, *295*, 1514.
[4] S. D. Hammann, 'Physico-Chemical Effects of Pressure', Butterworth, London, 1957.
[5] P. W. Bridgman, 'The Physics of High Pressure', G. Bell & Sons, London, 1952.
[6] 'Organic Synthesis at High Pressure', Eds. K. Matsumoto, R. M. Acheson, John Wiley & Sons, New York, 1991.
[7] a) M. Toda, K. Matsumoto, *Koatsuryoku no Kagaku to Gijutsu* **1994**, *3*, 360; b) N. Hayashi, K. Matsumoto, *Kagakukougyou* **1996**, *47*, 833; c) Y. Misumi, J. C. Kim, K. Matsumoto, *Koatsuryoku no Kagaku to Gijutsu* **2001**, *11*, 304.
[8] K. Matsumoto, T. Ibata, 'Organic Synthesis under Ultra High Pressure' ['Chokoatsu Yuki Gosei'], Nakanishiya Shuppan Co., Ltd., Kyoto, 1999.
[9] K. Matsumoto, M. Kaneko, H. Katsura, N. Hayashi, T. Uchida, R. M. Acheson, *Heterocycles* **1998**, *47*, 1135.
[10] M. Ciobanu, K. Matsumoto, *Liebigs Ann./Recueil* **1997**, 623.
[11] H. Iida, T. Uchida, K. Matsumoto, *Koatsuryoku no Kagaku to Gijutsu* **1993**, *2*, 103.
[12] K. Matsumoto, A. Sera, *Synthesis* **1985**, 999.
[13] K. Matsumoto, T. Uchida, R. M. Acheson, *Heterocycles* **1981**, *16*, 1367.
[14] L. Perreux, A. Loupy, *Tetrahedron* **2001**, *57*, 9199.
[15] A. Lew, P. O. Krutzik, M. E. Hart, A. R. Chamberlin, *J. Comb. Chem.* **2002**, *4*, 95.
[16] G. Jenner, *Tetrahedron* **2002**, *58*, 5185.
[17] T.-L. Ho, 'Distinctive Techniques for Organic Synthesis', World Scientific, Toh Tuck Link, Singapore, 1981.
[18] K. Tanaka, F. Toda, *Chem. Rev.* **2000**, *100*, 1025.
[19] Y. Arai, T. Sako, Y. Takebayashi, 'Supercritical Fluids – Molecular Interactions, Physical Properties and New Applications', Springer-Verlag, Berlin, 2002.
[20] P. E. Savage, *Chem. Rev.* **1999**, *99*, 603.
[21] R. M. Acheson, in 'Organic Synthesis at High Pressure', Eds. K. Matsumoto, R. M. Acheson, John Wiley & Sons, New York, 1991, p. 3.
[22] G. Jenner, *Tetrahedron* **1997**, *53*, 2669.
[23] J. Buchanan, S. D. Hamann, *Trans. Faraday Soc.* **1953**, *49*, 1425.
[24] L. W. A. van Berkom, G. J. T. Kuster, H. W. Scheeren, *Mol. Diversity* **2003**, *6*, 271.
[25] F. G. Klärner, F. Wurche, *J. Prakt. Chem.* **2000**, *342*, 609.
[26] L. Minuti, A. Taticchi, L. Costantini, *Recent Res. Dev. Org. Chem.* **1999**, *3*, 105.
[27] C. O. Kappe, S. S. Murphree, A. Padwa, *Tetrahedron* **1997**, *53*, 14179.
[28] G. H. Posner, in 'Stereocontrolled Organic Synthesis', Ed. B. M. Trost, Blackwell Science, Oxford, 1994, p. 177.
[29] C. Borm, D. Meibom, E. Winterfeldt, *Chem. Commun.* **1996**, 887.
[30] B. Baranowski, J. Jurczak, 'High Pressure Chemical Synthesis', Elsevier, New York, 1989.
[31] P. DeShong, C. M. Dicken, J. J. Perez, R. M. Shoff, *Org. Prep. Proc. Int.* **1982**, *14*, 369.
[32] R. Huisgen, in 'Chemistry and Biological Activity of Oxygen and Sulfur-Containing Heterocycles', 2nd International Conference, Moscow, October 14 – 17, 2003 , p. 83.
[33] 'High Pressure Chemistry', Eds. R. van Eldik, F.-G. Klärner, Wiley-VCH, Weinheim, 2002.
[34] N. S. Isaacs, 'Liquid Phase High Pressure Chemistry', John Wiley & Sons, New York, 1981.
[35] A. Sera, *Kagaku* **1977**, *32*, 510.
[36] G. Jenner, *Nouv. J. Chim.* **1979**, *3*, 329.
[37] T. Asano, W. J. le Noble, *Chem. Rev.* **1978**, *78*, 407.
[38] R. van Eldik, T. Asano, W. J. le Noble, *Chem. Rev.* **1989**, *89*, 549.
[39] D. Chen, K. J. Laidler, *Trans. Faraday Soc.* **1958**, *54*, 1026.
[40] K. J. Laidler, D. Chen, *Can. J. Chem.* **1959**, *37*, 599.
[41] C. Reichardt, 'Solvents and Solvent Effects in Organic Chemistry', 2nd edn., Wiley-VCH, New York, 1988.
[42] R. A. Firestone, M. A. Vitale, *J. Org. Chem.* **1981**, *46*, 2160.
[43] C. McKee, M. Mortimer, in 'Chemical Kinetics and Mechanism: The Molecular World', Ed. M. Mortimer, P. G. Taylor, Royal Society of Chemistry, Cambridge, 2002, p. 86.

[44] K. Sugita, Y. Goto, M. Ono, K. Yamashita, K. Hayase, T. Takahashi, Y. Ohga, T. Asano, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1803.
[45] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry', Cornell University Press, New York, 1934.
[46] R. B. Woodward, R. Hoffmann, 'The Conservation of Orbital Symmetry', Academic Press, San Diego, 1970.
[47] I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions', John Wiley & Sons, London, 1976.
[48] K. Fukui, T. Yonezawa, H. Shingu, *J. Chem. Phys.* **1952**, *20*, 722.
[49] K. Fukui, *Acc. Chem. Res.* **1971**, *4*, 57.
[50] W. J. Hehre, 'A Guide to Molecular Mechanics and Quantum Chemical Calculations', Wavefunction, Inc., Irvine, 2003.
[51] R. A. Firestone, G. A. Smith, *Chem. Ber.* **1989**, *122*, 1089.
[52] A. Katritzky, K. Sakizadeh, B. Gabrielson, W. J. le Noble, *J. Am. Chem Soc.* **1984**, *106*, 1879.
[53] K. Matsumoto, K. Hamada, T. Uchida, H. Yoshida, *Heterocycles* **1989**, *29*, 21.
[54] W. Carruthers, 'Cycloaddition Reactions in Organic Synthesis', Pergamon Press, Oxford, 1990.
[55] W. Carruthers, 'Some Modern Methods of Organic Synthesis', 3rd edn., Cambridge University Press, Cambridge, 1987.
[56] T. Wagner-Jauregg, *Synthesis* **1980**, 165.
[57] T. Wagner-Jauregg, *Synthesis* **1980**, 769.
[58] R. Huisgen, R. Grashey, J. Sauer, in 'The Chemistry of Alkenes', Ed. S. Patai, John Wiley & Sons, New York, 1964, Chapt. 11.
[59] R. Huisgen, *Angew. Chem., Int. Ed.* **1968**, *7*, 321.
[60] W. J. le Noble, B. A. Ojosipe, *J. Am. Chem. Soc.* **1975**, *97*, 5939.
[61] R. A. Grieger, C. A. Eckert, *Ind. Eng. Chem. Fundam.* **1971**, *10*, 369.
[62] L. F. Tietze, P. L. Steck, in 'High Pressure Chemistry', Eds. R. van Eldik, F.-G. Klärner, Wiley-VCH, Weinheim, 2002, p. 239.
[63] M. Chmielewski, J. Jurczak, *J. Carbohydr. Chem.* **1987**, *6*, 1.
[64] L. F. Tietze, G. Kettschau, J. A. Gewert, A. Schuffenhauer, *Curr. Org. Chem.* **1998**, *2*, 19.
[65] 'Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry toward Heterocycles and Natural Products', Eds. A. Padwa, W. H. Pearson, John Wiley & Sons, New York, 2003.
[66] F. Fringuelli, A. Taticchi, 'The Diels–Alder Reaction: Selected Practical Methods', John Wiley & Sons, New York, 2002.
[67] S. Kobayashi, K. A. Jorgensen, 'Cycloaddition Reactions in Organic Synthesis', John Wiley & Sons, New York, 2001.
[68] D. von der Brück, R. Bühler, C.-C. Heuk, H. Plieninger, K. E. Weale, J. Westphal, D. Wild, *Chem.-Ztg.* **1970**, *94*, 183.
[69] J. R. McCabe, C. A. Eckert, *Acc. Chem. Res.* **1974**, *7*, 251.
[70] R. Deléens, A. Gautier, S. R. Piettre, *Tetrahedron Lett.* **2002**, *43*, 4963.
[71] R. Fujita, K. Oikawa, T. Yoshisuji, Y. Okuyama, H. Nakano, H. Matsuzaki, *Chem. Pharm. Bull.* **2003**, *51*, 295.
[72] A. de Meijere, A. Leonov, T. Heiner, M. Noltemeyer, M. T. Bes, *Eur. J. Org. Chem.* **2003**, 472.
[73] H. Al-Badri, N. Collignon, J. Maddaluno, S. Masson, *Tetrahedron* **2000**, *56*, 3909.
[74] a) W. G. Dauben, A. P. Kozikowski, *J. Am. Chem. Soc.* **1974**, *96*, 3664; b) H. Nozaki, T. Yamaguti, S. Ueda, K. Kondo, *Tetrahedron* **1968**, *24*, 1445.
[75] M. G. B. Drew, A. Jahans, L. M. Harwood, S. A. B. H. Apoux, *Eur. J. Org. Chem.* **2002**, 3589.
[76] C. Knappwost-Gieseke, F. Nerenz, R. Wartchow, E. Winterfeldt, *Chem. – Eur. J.* **2003**, *9*, 3849.
[77] a) K. Matsumoto, S. Hashimoto, Y. Ikemi, S. Otani, T. Uchida, *Heterocycles* **1986**, *24*, 1835; b) W. G. Dauben, J. M. Gerdeo, D. B. Smith, *J. Org. Chem.* **1985**, *50*, 2576.
[78] W. G. Dauben, C. R. Kessel, K. H. Takemura, *J. Am. Chem. Soc.* **1980**, *102*, 6893.
[79] M. G. Banwell, A. J. Edwards, G. J. Harfoot, K. A. Jolliffe, *J. Chem. Soc., Perkin Trans. 1* **2002**, 2439.
[80] K. Kumamoto, I. Fukada, H. Kotsuki, *Angew. Chem., Int. Ed.* **2004**, *43*, 2015.
[81] G. Torres-García, J. Mattay, *Tetrahedron* **1996**, *52*, 5421.
[82] N. S. Isaacs, P. van der Beeke, *Tetrahedron Lett.* **1982**, *23*, 2147.
[83] V. O. Rogatchov, H. Bernsmann, P. Schwab, R. Frohlich, B. Wibbeling, P. Metz, *Tetrahedron Lett.* **2002**, *23*, 4753.
[84] R. Huisgen, *J. Org. Chem.* **1968**, *33*, 2291.
[85] R. Huisgen, *J. Org. Chem.* **1976**, *41*, 403.
[86] R. A. Firestone, *J. Org. Chem.* **1968**, *33*, 2285.

[87] R. A. Firestone, *J. Chem. Soc. A* **1970**, 1570.
[88] R. A. Firestone, *J. Org. Chem.* **1972**, *37*, 2181.
[89] R. A. Firestone, *Tetrahedron* **1976**, *33*, 3009.
[90] A. Padwa, '1, 3-Dipolar Cycloaddition Chemistry', John Wiley & Sons., New York, 1984.
[91] N. S. Isaacs, E. Rannala, *J. Chem. Soc., Perkin Trans. 2* **1975**, 1555.
[92] G. Swieton, J. von Jouanne, H. Kelm, *J. Org. Chem.* **1983**, *48*, 1035.
[93] Y. Yoshimura, J. Osugi, M. Nakahara, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 680.
[94] Y. Yoshimura, J. Osugi, M. Nakahara, *J. Am. Chem. Soc.* **1983**, *105*, 5414.
[95] A. V. Kamernitzky, I. S. Levina, E. I. Mortikova, V. M. Shitkin, B. S. El'yanov, *Tetrahedron* **1977**, *33*, 2135.
[96] F. Cardona, P. Salanski, M. Chmielewski, S. Valenza, A. Goti, A. Brandi, *Synlett* **1998**, 1444.
[97] G. Swieton, J. von Jouanne, H. Kelm, R. Huisgen, *J. Chem. Soc., Perkin Trans. 2* **1983**, 37.
[98] P. G. Wiering, H. Steinberg, *Recl. Trav. Chim. Pay-Bas* **1981**, *100*, 13.
[99] J. von Jouanne, H. Kelm, R. Huisgen, *J. Am. Chem. Soc.* **1979**, *101*, 151.
[100] M. Sasaki, H. Tsuzuki, M. Okamoto, *J. Org. Chem.* **1979**, *44*, 652.
[101] M. Sasaki, H. Tsuzuki, J. Osugi, *J. Chem. Soc., Perkin Trans. 2* **1980**, 1596.
[102] G. Jenner, M. Papadopoulos, *Tetrahedron Lett.* **1996**, *37*, 1417.
[103] A. Chrétien, I. Chataigner, N. L'Hélias, S. R. Piettre, *J. Org. Chem.* **2003**, *68*, 7990.
[104] T. Flessner, V. Ludwig, H. Siebeneicher, E. Winterfeldt, *Synthesis* **2002**, 1373.
[105] A. Mori, Z.-H. Li, H. Takeshita, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2257.
[106] a) K. Matsumoto, J.-C.Kim, H. Iida, H. Hamana, K. Kumamoto, H. Kotsuki, G. Jenner, *Helv. Chim. Acta* **2005**, *88*, 1734; b) G. J. T. Kuster, R. H. J. Steeghs, H. W. Scheeren, *Eur. J. Org. Chem.* **2001**, 553.
[107] G. J. Kuster, J. W. Scheeren, *Tetrahedron Lett.* **2000**, *41*, 515.
[108] M. Pollmann, K. Müllen, *J. Am. Chem. Soc*. **1994**, *116*, 2318.
[109] P. R. Ashton, G. R. Brown, N. S. Isaacs, D. Giuffrida, F. H. Kohnke, J. P. Matheias, A. M. Z. Slawin, D. R. Smith, J. F. Stoddart, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 6330.
[110] A. J. Barkovich, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1976**, *98*, 2667.
[111] A. J. Barkovich, E. S. Strauss, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1977**, *99*, 8321.
[112] J. A. Gladysz, *CHEMTECH* **1979**, *9*, 372.
[113] W. J. le Noble, *Chem. unserer Zeit* **1983**, *17*, 152.
[114] M. Kurabayashi, *Koatsu Gasu* **1974**, *11*, 695.
[115] M. Kurabayashi, *Kagaku Kogyo Shiryo, Tokoshi Nyusu* **1978**, *13*, 93.
[116] P. Köll, J. Metzger, *Angew. Chem., Int. Ed.* **1978**, *17*, 754.
[117] W. B. Holzapfel, N. S. Isaacs, 'High-Pressure Techniques in Chemistry and Physics', Oxford University Press, Oxford, 1997.
[118] Y. Hayashi, W. Tsuboi, M. Shoji, N. Suzuki, *J. Am. Chem. Soc.* **2003**, *125*, 11208.
[119] Y. Hayashi, W. Tsuboi, M. Shoji, N. Suzuki, *Tetrahedron Lett.* **2004**, *45*, 4353.
[120] K. Hayakawa, Y. Ueno, S. Kawamura, T. Kato, R. Hayashi, *Appl. Microbiol. Biotechnol.* **1988**, *50*, 415.
[121] Y. Hayashi, K. Nishimura, *Chem. Lett.* **2002**, 296.
[122] Y. Hayashi, K. Okado, I. Ashimine, M. Shoji, *Tetrahedron Lett.* **2002**, *43*, 8683.
[123] J.-P. Bégué, D. Bonnet-Delpon, T. Lequeux, J. d'Angelo, A. Guingant, *Synlett* **1992**, 146.
[124] R. M. Ortuño, J. Ibarzo, J. d'Angelo, F. Dumas, A. Alvarez-Larena, J. F. Piniella, *Tetrahedron: Asymmetry* **1996**, *7*, 127.
[125] J. D. Winkler, J. M. Holland, D. A. Peters, *J. Org. Chem.* **1996**, *61*, 9074.
[126] L. W. A. van Berkom, G. J. T. Kuster, F. Kalmoua, R. de Gelder, H. W. Scheeren, *Tetrahedron Lett.* **2003**, *44*, 5091.
[127] W. G. Dauben, H. O. Krabbenhoft, *J. Org. Chem*. **1977**, *42*, 282.
[128] J. Jurczak, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3438.
[129] A. Rahm, F. Ferkous, M. Degueil-Castaing, J. Jurczak, A. Golebiowski, *Synth. React. Inorg. Met.-Org. Chem.* **1987**, *17*, 937.
[130] J. Jurczak, M. Tkacz, *Bull. Polish Acad. Sci., Chem.* **1984**, *32*, 59.
[131] L. F. Tietze, M. Henrich, A. Niklaus, M. Buback, *Chem. – Eur. J.* **1999**, *5*, 297.
[132] R. W. M. Aben, L. Minuti, H. W. Scheeren, A. Taticchi, *Tetrahedron Lett.* **1991**, *32*, 6445.
[133] R. Hirsenkorn, B. Haag-Zeino, R. R. Schmidt, *Tetrahedron Lett.* **1990**, *31*, 4433.
[134] C. Ferroud, G. Revial, J. d'Angelo, *Tetrahedron Lett.* **1985**, *26*, 3981.
[135] J. Jurczak, M. Tkacz, *Synthesis* **1979**, 42.
[136] T. Iwaoka, T. Murohashi, N. Katagiri, M. Sato, C. Kaneko, *J. Chem. Soc., Perkin Trans. 1* **1992**, 1393.

[137] T. Iwaoka, N. Katagiri, M. Sato, C. Kaneko, *Chem. Pharm. Bull.* **1992**, *40*, 2319.
[138] W. G. Dauben, W. R. Baker, *Tetrahedron Lett.* **1982**, *23*, 2611.
[139] W. G. Dauben, R. A. Bunce, *Tetrahedron Lett.* **1982**, *23*, 4875.
[140] L. Minuti, A. Taticchi, E. Gacs-Baitz, E. Wenkert, *Tetrahedron* **1995**, *51*, 10033.
[141] A. Guingant, J. d'Angelo, *Tetrahedron Lett.* **1986**, *27*, 3729.
[142] a) S. Laugraud, A. Guingant, J. d'Angelo, *High Pressure Res.* **1992**, *11*, 153; b) S. Laugraud, A. Guingant, J. d'Angelo, *High Pressure Biotechnol.* **1992**, *224*, 387.
[143] S. Laugraud, A. Guingant, J. d'Angelo, *Tetrahedron Lett.* **1992**, *33*, 1289.
[144] H. Nakano, T. Date, K. Okamura, H. Tomisawa, H. Hongo, *Chem. Pharm. Bull* **1991**, *39*, 2471.
[145] Y. Torisawa, M. Nakagawa, H. Arai, Z. Lai, T. Hino, T. Nakata, T. Oishi, *Tetrahedron Lett.* **1990**, *31*, 3195; Y. Torisawa, M. A. Ali, F. Tavet, A. Kageyama, M. Aikawa, N. Fukui, T. Hino, M. Nakagawa, *Heterocycles* **1996**, *42*, 677; Y. Torisawa, M. Nakagawa, T. Hosaka, K. Tanabe, Z. Lai, K. Ogata, T. Nakata, T. Oishi, T. Hino, *J. Org. Chem.* **1992**, *57*, 5741.
[146] I. Chataigner, E. Hess, L. Toupet, S. R. Piettre, *Org. Lett.* **2001**, *3*, 515.
[147] R. Fujita, T. Yoshisuji, K. Watanabe, H. Hongo, H. Matsuzaki, *Yakugaku Zasshi* **2002**, *122*, 177.
[148] R. Fujita, K. Watanabe, T. Yoshisuji, C. Kabuto, H. Matsuzaki, H. Hongo, *Chem. Pharm. Bull.* **2001**, *49*, 893.
[149] L. Minuti, A. Taticchi, E. Gacs-Baitz, A. Marrocchi, *Tetrahedron* **1998**, *54*, 10891.
[150] N. Matzanke, R. J. Gregg, S. M. Weinreb, *J. Org. Chem.* **1997**, *62*, 1920.
[151] Y. Torisawa, M. Nakagawa, H. Arai, Z. Lai, T. Hno, T. Nakata, T. Oishi, *Tetrahedron Lett.* **1990**, *31*, 4433.
[152] H. Nakano, H. Hongo, *Chem. Pharm. Bull.* **1993**, *41*, 1885.
[153] R. M. Ortuño, A. Guingant, J. d'Angelo, *Tetrahedron Lett.* **1988**, *29*, 6989.
[154] L. Minuti, A. Taticchi, E. Gacs-Baitz, E. Wenkert, *Synth. Commun* **1992**, *22*, 2965.
[155] G. Revial, M. Blanchard, J. d'Angelo, *Tetrahedron Lett*. **1983**, *24*, 899.
[156] V. Branchadell, M. Sodupe, R. M. Ortuno, A. Oliva, D. Gomez-Pardo, A. Guingant, J. d'Angelo, *J. Org. Chem.* **1991**, *56*, 4135.
[157] K. Fuji, K. Tanaka, H. Abe, K. Matsumoto, T. Taga, Y. Miwa, *Tetrahedron: Asymmetry* **1992**, *3*, 609.
[158] K. Fuji, K. Tanaka, H. Abe, K. Matsumoto, T. Harayama, A. Ikeda, T. Taga, Y. Miwa, M. Node, *J. Org. Chem.* **1994**, *59*, 2211.
[159] D. L. Boger, C. E. Brotherton, *Tetrahedron* **1986**, *42*, 2777; D. L. Boger, C. E. Brotherton, *J. Am. Chem. Soc.* **1986**, *108*, 6695.
[160] T. G. Back, P. L. Gladstone, M. Parvez, *J. Org. Chem.* **1996**, *61*, 3806.
[161] J. H. Rigby, P. C. Kierkus, D. Head, *J. Am. Chem. Soc.* **1989**, *111*, 4125.
[162] S. Jarosz, K. Szewczyk, S. Skóra, Z. Ciunik, A. Pietrzak, *Tetrahedron: Asymmetry* **2002**, *13*, 2223.
[163] M. C. Carreño, M. B. Cid, J. L. G. Ruano, M. Santos, *Tetrahedron: Asymmetry* **1997**, *8*, 2093.
[164] S. Ito, T. Okujima, C. Kabuto, N. Morita, *Tetrahedron* **2003**, *59*, 4651.
[165] I. S. Levina, L. E. Kulikova, A. V. Kamernitskii, B. S. El'yanov, E. M. Gonikberg, *Izvestiya Akademi Nauk, Seriya Khimicheskaya* **1992**, 1622.
[166] H. Nakano, H. Hongo, *Heterocycles* **1993**, *35*, 37.
[167] I. S. Levina, L. E. Kulikova, B. S. El'yanov, *Seriya Khimicheskaya* **1982**, 1399.
[168] A. V. Kamernitskii, T. N. Galakhova, I. S. Levina, V. A. Pavlov, B. S. El'yanov, *Seriya Khimicheskaya* **1982**, 2147.
[169] B. S. El'yanov, I. S. Levina, L. E. Kulikova, A. V. Kamernitskii, E. M. Gonikberg, *Seriya Khimicheskaya* **1989**, 743.
[170] M. Wolter, C. Borm, E. Merten, R. Wartchow, E. Winterfeldt, *Eur. J. Org. Chem.* **2001**, 4051.
[171] Y. Tsuda, S. Hosoi, N. Katagiri, C. Kaneko, T. Sano, *Heterocycles* **1992**, *33*, 497.
[172] Y. Tsuda, S. Hosoi, N. Katagiri, C. Kaneko, T. Sano, *Chem. Pharm. Bull.* **1993**, *41*, 2087.
[173] H. Tsuge, T. Nagai, T. Okano, S. Eguchi, H. Kimoto, *Synlett* **1996**, 1106.
[174] M. Sato, Y. Abe, C. Kaneko, *J. Chem. Soc., Perkin Trans. 1* **1990**, 1779.
[175] V. S. Abramov, A. A. Zharov, V. M. Zhulin, *Seriya Khimicheskaya* **1977**, 965.
[176] H. Takeshita, A. Mori, S. Sugiyama, T. Tsuda, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3988.
[177] S. Srivastava, A. P. Marchand, V. Vidyasagar, J. L. Flippen-Anderson, R. G. Gilardi, C. Z. Zachwieja, W. J. Le Noble, *J. Org. Chem.* **1989**, *54*, 247.
[178] N. Katagiri, N. Watanabe, C. Kaneko, *Chem. Pharm. Bull.* **1990**, *38*, 69.
[179] N. Katagiri, A. Kurimoto, C. Kaneko, *Chem. Pharm. Bull.* **1992**, *40*, 1737.
[180] C. Carretero, J. L. Garciá Ruano, L. M. Martín Cabrejas, *Tetrahedron: Asymmetry* **1997**, *3*, 409.
[181] W. G. Dauben, B. A. Kowalczyk, F. W. Lichtenthaler, *J. Org. Chem.* **1990**, *55*, 2391.

[182] W. Jarre, D. Bieniek, F. Korte, *Angew. Chem., Int. Ed.* **1975**, *14*, 181.
[183] Y. G. Shtyrlin, V. Y. Fedorenko, E. N. Klimovitskii, *Russ. J. Gen. Chem.* **2001**, *71*, 819.
[184] P. P. M. A. Dols, A. J. H. Klunder, B. Zwanenburg, *Tetrahedron* **1994**, *50*, 8515.
[185] H. Kotsuki, A. Kondo, H. Nishizawa, M. Ochi, K. Matsuoka, *J. Org. Chem.* **1981**, *46*, 5454.
[186] P. DeShong, N. E. Lowmaster, *Synth. Commun.* **1983**, *13*, 537.
[187] G. Jenner, *Tetrahedron Lett.* **1994**, *35*, 1189.
[188] H. Kotsuki, H. Nishizawa, M. Ochi, K. Matsuoka, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 496.
[189] H. Kotsuki, Y. Mori, T. Ohtsuka, H. Nishigawa, M. Ochi, K. Matsuoka, *Heterocycles* **1987**, *26*, 2347.
[190] N. Katagiri, H. Akatsuka, C. Kaneko, A. Sera, *Tetrahedron Lett.* **1988**, *29*, 5397.
[191] D. S. Brown, L. A. Paquette, *J. Org. Chem.* **1992**, *57*, 4512.
[192] H. Kotsuki, H. Nishizawa, *Heterocycles* **1981**, *16*, 1287.
[193] Y. L. Gol'dfarb, B. S. El'yanov, Y. L. Danyushevskii, M. A. Marakatkina, G. M. Parfenova, *Zhurnal Organicheskoi Khimii* **1971**, *7*, 1915.
[194] W. G. Dauben, H. O. Krabbenhoft, *J. Am. Chem. Soc.* **1976**, *98*, 1992.
[195] A. Sera, M. Ohara, T. Kubo, K. Itoh, H. Yamada, Y. Mikata, C. Kaneko, N. Katagiri, *J. Org. Chem.* **1988**, *53*, 5460.
[196] J. Jurczak, S. Belniak, T. Kozluk, S. Pikul, P. Salanski, *Bull. Polish Acad. Sci., Chem.* **1984**, *32*, 135.
[197] D. von der Brück, R. Bühler, H. Plieninger, *Tetrahedron* **1972**, *28*, 791.
[198] W. G. Dauben, J. Y. L. Lam, Z. R. Guo, *J. Org. Chem.* **1996**, *61*, 4816.
[199] P. H. Beusker, R. W. M. Aben, J.-P. G. Seerden, J. M. M. Smits, H. W. Scheeren, *Eur. J. Org. Chem.* **1998**, 2483.
[200] J. Jurczak, T. Kozluk, S. Filipek, C. H. Eugster, *Helv. Chim. Acta* **1982**, *65*, 1021.
[201] Y. Okamoto, S. Giandinoto, M. C. Bochnik, *J. Org. Chem.* **1983**, *48*, 3830.
[202] K. Matsumoto, Y. Ikemi, S. Hashimoto, H. S. Lee, Y. Okamoto, *J. Org. Chem.* **1986**, *51*, 3729.
[203] K. Matsumoto, S. Hashimoto, Y. Ikemi, S. Otani, T. Uchida, *Heterocycles* **1986**, *24*, 1835.
[204] D. Margetic, D. N. Butler, R. N. Warrener, *ECSOC-6* **2002**, 205.
[205] H. S. P. Rao, R. Murali, A. Taticchi, H. W. Scheeren, *Eur. J. Org. Chem.* **2001**, 2869.
[206] J. Jurczak, T. Kozluk, S. Filipek, C. H. Eugster, *Helv. Chim. Acta* **1983**, *66*, 222.
[207] J. Jurczak, T. Kozluk, M. Tkacz, C. H. Eugster, *Helv. Chim. Acta* **1983**, *66*, 218.
[208] T. Tsuda, S. Sugiyama, A. Mori, H. Takashita, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2695.
[209] S. Sugiyama, T. Tsuda, A. Mori, H. Takeshita, M. Kodama, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3633; S. Sugiyama, T. Tsuda, A. Mori, H. Takeshita, M. Kodama, *Chem. Lett.* **1986**, 1315.
[210] T. Suzuki, K. Kuboyama, H. Takayama, *J. Chem. Soc., Perkin Trans. 1* **1997**, 251.
[211] K. Kubo, K. Hirowatari, N. Kato, A. Mori, *Heterocycles* **2003**, *59*, 47.
[212] A. B. Smith III, N. J. Liverton, N. J. Hrib, H. Sivaramakrishnan, K. Winzenberg, *J. Am. Chem. Soc.* **1986**, *108*, 3040.
[213] C. Marchionni, P. Vogel, P. Roversi, *Tetrahedron Lett.* **1996**, *37*, 4149.
[214] M. G. B. Draw, A. V. George, N. S. Isaacs, H. S. Rzepa, *J. Chem Soc., Perkin Trans. 1* **1985**, 1277.
[215] H. Kotsuki, Y. Mori, H. Nishizawa, M. Ochi, K. Matsuoka, *Heterocycles* **1982**, *19*, 1915.
[216] J. Keijsers, B. Hams, C. Kruse, H. W. Scheeren, *Heterocycles* **1989**, *29*, 79.
[217] J.-P. G. Seerden, M. T. M. Tulp, H. W. Scheeren, C. G. Kruse, *Bioorg. Med. Chem.* **1998**, *6*, 2103.
[218] R. W. M. Aben, J. Keijsers, B. Hams, C. G. Kruse, H. W. Scheeren, *Tetrahedron Lett.* **1994**, *35*, 1299.
[219] J. Keijsers, B. Hams, C. G. Kruse, H. W. Scheeren, *Heterocycles* **1988**, *29*, 79.
[220] H. Kotsuki, F. Nishizawa, S. Kitagawa, M. Ochi, N. Yamasaki, K. Matsuoka, T. Tokoroyama, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 544.
[221] A. McCluskey, M. A. Keane, C. C. Walkom, M. C. Bowyer, A. T. R. Sim, D. J. Young, J. A. Sakoff, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 391.
[222] H. Kotsuki, S. Kitagawa, H. Nishizawa, T. Tokoroyama, *J. Org. Chem.* **1978**, *43*, 1471.
[223] T. Thiemann, D. Ohira, Y. Li, T. Sawada, S. Mataka, K. Rauch, M. Noltemeyer, A. de Meijere, *J. Chem. Soc., Perkin Trans. 1* **2000**, 2968.
[224] M. A. Kerr, *Synlett* **1995**, 1165.
[225] E. R. Jarvo, S. R. Boothroyd, M. A. Kerr, *Synlett* **1996**, 897.
[226] P. Kwiatkowski, M. Asztemborska, J.-C. Caille, J. Jurczak, *Adv. Synth. Catal.* **2003**, *345*, 506.
[227] K. Kurz, H. Plieninger, *Chem. Ber.* **1980**, *113*, 3666.
[228] M. G. Banwell, A. J. Edwards, M. D. McLeod, S. G. Stewart, *Aust. J. Chem.* **2004**, *57*, 641.
[229] G. H. Posner, R. H. Hutchings, B. T. Woodward, *Synlett* **1997**, 432.

[230] G. H. Posner, H. Dai, D. S. Bull, J.-K. Lee, F. Eydoux, Y. Ishihara, W. Welsh, N. Pryor, S. Petr Jr., *J. Org. Chem*. **1996**, *61*, 671.
[231] G. H. Posner, A. Haces, W. Harrison, C. M. Kinter, *J. Org. Chem.* **1987**, *52*, 4836.
[232] R. W. Bates, A. J. Pratt, P. M. Rendle, W. T. Robinson, *Aust. J. Chem.* **1998**, *51*, 383.
[233] I. E. Markó, P. Seres, T. M. Swarbrick, I. Staton, H. Adam, *Tetrahedron Lett.* **1992**, *33*, 5649.
[234] G. H. Posner, Y. Ishihara, *Tehtrahedron Lett.* **1994**, *35*, 7545.
[235] J. A. Gladysz, S. J. Lee, J. A. V. Tomasello, Y. S. Yu, *J. Org. Chem.* **1977**, *42*, 4170.
[236] G. H. Posner, N. Johnson, *J. Org. Chem.* **1994**, *59*, 7855.
[237] G. H. Posner, T. D. Nelson, *Tetrahedron* **1990**, *46*, 4573.
[238] T. Hatsui, T. Hashiguchi, H. Takeshita, *Chem. Lett.* **1994**, 1415.
[239] V. Prapansiri, E. R. Thornton, *Tetrahedron Lett.* **1991**, *32*, 3147.
[240] I. G. C. Coutts, R. W. Allcock, H. W. Scheeren, *Tetrahedron Lett.* **2000**, *41*, 9105.
[241] R. Hoffmann, J. Mattay, *Liebigs Ann./Recueil* **1995**, 1455.
[242] D. L. Boger, K. Takahashi, *J. Am. Chem. Soc.* **1995**, *117*, 12452.
[243] H. Tomisawa, H. Nakano, H. Hongo, *Heterocycles* **1990**, *30*, 359.
[244] H. Nakano, T. Kato, H. Tomisawa, H. Hongo, *Heterocycles* **1994**, *39*, 723.
[245] G. H. Posner, C. Switzer, *J. Org. Chem.* **1987**, *52*, 1642.
[246] K. Matsumoto, Y. Ikemi, S. Nakamura, T. Uchida, R. M. Acheson, *Heterocycles* **1982**, *19*, 499.
[247] K. Matsumoto, Y. Ikemi-Kono, T. Uchida, R. M. Acheson, *J. Chem. Soc., Chem. Commun.* **1979**, 1091.
[248] V. Breitkopf, P. Bubenitschek, H. Hopf, P. G. Jones, F.-G. Klärner, D. Schomburg, B. Witulski, B. Zimny, *Liebigs Ann. Recl.* **1997**, 127.
[249] L. Minuti, A. Taticchi, E. Gacs-Baitz, A. Marrocchi, *Tetrahedron* **1998**, *54*, 10891.
[250] K. Matsumoto, *Chem. Lett.* **1985**, 1681.
[251] L. Minuti, A. Taticchi, D. Lanari, A. Marrocchi, E. Gacs-Baitz, *Tetrahedron: Asymmetry* **2003**, *14*, 2387.
[252] L. Minuti, A. Taticchi, D. Lanari, A. Marrocchi, E. Gacs-Baitz, *Tetrahedron: Asymmetry* **2003**, *14*, 2775.
[253] A. Guillam, L. Toupet, J. Maddaluno, *J. Org. Chem.* **1999**, *64*, 9348.
[254] S. Aime, H. Oulyadi, J. Maddaluno, P. Venturello, *Org. Lett.* **1999**, *1*, 1631.
[255] F.-G. Klärner, R. Ehrhardt, H. Bandmann, R. Boese, D. Bläser, B. R. Beno, *Chem. – Eur. J.* **1999**, *5*, 2119.
[256] T. Suzuki, K. Kubomura, H. Takayama, *Heterocycles* **1994**, *38*, 961.
[257] K. Ando, M. Kankake, T. Suzuki, H. Takayama, *J. Chem. Soc., Chem. Commun.* **1992**, 1100.
[258] T. Suzuki, K. Kubomura, H. Fuchii, H. Takayama, *J. Chem. Soc., Chem. Commun.* **1990**, 1687.
[259] S. Wegener, K. Müllen, *Chem. Ber.* **1991**, *124*, 2101.
[260] U. Girreser, D. Giuffrida, F. H. Kohnke, J. P. Matheias, D. Philp, J. F. Stoddart, *Pure Appl. Chem.* **1993**, *65*, 119; P. R. Ashton, J. P. Mathias, J. F. Stoddart, *Synthesis* **1993**, 221.
[261] P. R. Ashton, U. Girreser, D. Giuffrida, F. H. Kohnke, J. P. Matheias, F. M. Raymo, A. M. Z. Slawin, D. R. Smith, J. F. Stoddart, D. J. Williams, *J. Am. Chem Soc.* **1993**, *115*, 5422.
[262] J. Benkhoff, R. Boese, F. G. Klärner, A. E. Wigger, *Tetrahedron Lett.* **1994**, *35*, 73.
[263] G. Jenner, M. Papadopoulos, *J. Org. Chem.* **1986**, *51*, 585.
[264] M. Papadopoulos, G. Jenner, *Tetrahedron Lett.* **1985**, *26*, 3335.
[265] J. H. Rigby, C. O. Ogbu, *Tetrahedron Lett.* **1990**, *31*, 3385.
[266] H. Takeshita, A. Mori, Y. Kurahashi, Y. Nagano, *Chem. Express* **1993**, *8*, 109.
[267] H. Takeshita, H. Nakashima, S. Sugiyama, A. Mori, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 573.
[268] Z. H. Li, S. Hirayama, N. Kato, A. Mori, H. Takeshita, *Chem. Express* **1991**, *6*, 331.
[269] Z. H. Li, A. Mori, H. Takeshita, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3713.
[270] Z. H. Li, A. Mori, H. Takeshita, *Rep. Inst. Adv. Mater.* **1991**, *5*, 1.
[271] Z. H. Li, A. Mori, H. Takeshita, Y. Nagano, *Chem. Express* **1992**, *7*, 213.
[272] Z.-H. Li, A. Mori, N. Kato, H. Takeshita, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2778.
[273] Z. H. Li, A. Mori, H. Takeshita, *Chem. Express* **1991**, *6*, 29.
[274] A. Mori, Z.-H. Li, H. Nakashima, H. Takeshita, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1636.
[275] S. Hirayama, A. Mori, H. Takeshita, *Chem. Express* **1991**, *6*, 861.
[276] S. Hirayama, Z. H. Li, N. Kato, A. Mori, H. Takeshita, *Chem. Express* **1991**, *6*, 591.
[277] G. R. Tian, S. Sugiyama, A. Mori, H. Takeshita, *Chem. Lett.* **1987**, 1557.
[278] G. R. Tian, S. Sugiyama, A. Mori, H. Takeshita, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2393.
[279] G. R. Tian, A. Mori, H. Takeshita, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3727.
[280] T. Nozoe, H. Takeshita, Y. Z. Yan, A. Mori, *Synlett* **1995**, 375.
[281] A. Mori, Y. Nukii, H. Takeshita, T. Nozoe, *Heterocycles* **1994**, *35*, 863.

[282] A. Mori, Y. Z. Yan, H. Takesita, T. Nozoe, *J. Chem. Soc., Perkin Trans. 1* **1998**, 3219.
[283] A. Mori, N. Kato, H. Takeshita, Y. Kurahashi, T. Nozoe, *J. Chem. Soc., Chem. Commun.* **1994**, 869.
[284] H. Takeshita, A. Mori, N. Kato, Y. Kurahashi, M. Ito, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2669.
[285] K. Matsumoto, H. Taketsuna, Y. Ikemi, A. Kakehi, T. Uchida, S. Otani, *Heterocycles* **1998**, *49*, 79.
[286] K. Matsumoto, M. Ciobanu, M. Yoshida, T. Uchida, *Heterocycles* **1997**, *45*, 15.
[287] H. Kotsuki, M. Kataoka, K. Matsuo, S. Suetomo, M. Shino, H. Nishizawa, *J. Chem. Soc., Perkin Trans. 1* **1993**, 2773.
[288] F. G. Klärner, B. Dogan, W. R. Roth, K. Hafner, *Angew. Chem., Int. Ed.* **1982**, *21*, 708.
[289] E. Winterfeldt, V. Wray, *Chem. Ber.* **1992**, *125*, 2159.
[290] K. Goldenstein, T. Fendert, P. Proksch, E. Winterfeldt, *Tetrahedron* **2000**, *56*, 4173.
[291] W. Beil, P. G. Jones, F. Nerenz, E. Winterfeldt, *Tetrahedron* **1998**, *54*, 7273.
[292] K. Goldenstein, F. Nerenz, E. Winterfeldt, *Polish J. Chem.* **1999**, *73*, 3.
[293] M.-E. Trân-Huu-Dâu, R. Wartchow, E. Winterfeldt, Y.-S. Wong, *Chem. – Eur. J.* **2002**, *7*, 2349.
[294] P. G. Jines, H. Weinmann, E. Winterfeldt, *Angew. Chem., Int. Ed.* **1995**, *34*, 448.
[295] B. Wegener, M. Hansen, E. Winterfeldt, *Tetrahedron: Asymmetry* **1993**, *4*, 345.
[296] H. Weinmann, E. Winterfeldt, *Synthesis* **1996**, *3*, 357.
[297] D. Meibom, H. Weinmann, E. Winterfeldt, *ARKIVOC* **2004**, 4.
[298] A. Marrocchi, L. Minuti, G. Morozzi, L. Pampanella, A. Taticchi, *Carcinogenesis* **1996**, *17*, 2009.
[299] T. Ibata, H. Nakawa, Y. Isogami, K. Matsumoto, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3197.
[300] K. Matsumoto, S. Hashimoto, S. Otani, T. Uchida, *Heterocycles* **1984**, *22*, 2713.
[301] K. Matsumoto, S. Hashimoto, T. Uchida, *Heterocycles* **1990**, *30*, 201.
[302] K. Beck, S. Hünig, F.-G. Klärner, P. Kraft, U. Artschwagen-Perl, *Chem. Ber.* **1987**, *120*, 2041.
[303] S. Hünig, P. Kraft, F.-G. Klärner, U. Artsschwanger-Perl, K. Peters, H.-G. von Schnering, *Liebigs Ann./ Recueil.* **1995**, 351.
[304] K. Exner, D. Hochstrate, M. Keller, F.-G. Klärner, H. Prinzbach, *Angew. Chem., Int. Ed.* **1996**, *35*, 2256.
[305] R. N. Warrener, D. Margetic, E. R. T. Tiekink, R. A. Russell, *Synlett* **1997**, 196.
[306] D. L. Boger, J. S. Panek, *J. Am. Chem. Soc.* **1985**, *107*, 5745.
[307] D. L. Boger, S. Sakya, M., *J. Org. Chem.* **1988**, *53*, 1415.
[308] R. N. Warrener, D. Margetic, R. A. Russell, *Synlett* **1998**, 585.
[309] R. N. Warrener, M. R. Johnston, M. J. Gunter, *Synlett* **1998**, 593.
[310] G. Märkl, C. Doerges, T. Riedl, F.-G. Klärner, C. Lodwig, *Tetrahedron Lett.* **1990**, *31*, 4589.
[311] M. L. Maddox, J. C. Martin, J. M. Muchowski, *Tetrahedron Lett.* **1980**, *21*, 7.
[312] K. Matsumoto, Y. Ikemi-Kono, T. Uchida, *J. Chem. Soc., Chem. Commun.* **1978**, 543.
[313] M. C. Carreño, J. Mahugo, A. Urbano, *Tetrahedron Lett.* **1997**, *38*, 3047.
[314] H. Plieninger, D. Wild, J. Westphal, *Tetrahedron* **1969**, *25*, 5561.
[315] W. H. Jones, D. Marrgold, H. Plieninger, *Tetrahedron* **1962**, *18*, 267.
[316] T. Lomberget, I. Chataigner, D. Bouyssi, J. Maddaluno, G. Balme, *Tetrahedron Lett.* **2004**, *45*, 3437.
[317] L. Minuti, A. Taticchi, A. Marrocchi, A. Broggi, E. Gacs-Baitz, *Tetrahedron: Asymmetry* **2004**, *7*, 1187.
[318] M. Haiza, J. Lee, J. K. Snyder, *J. Org. Chem.* **1990**, *55*, 5008.
[319] J. Lee, J. K. Snyder, *J. Am. Chem. Soc.* **1989**, *111*, 1522.
[320] J. Knol, A. Meetsma, B. L. Feringa, *Tetrahedron: Asymmetry* **1995**, *6*, 1069.
[321] T. A. Engler, U. Sampath, D. V. Velde, F. Takusagawa, *Tetrahedron* **1992**, *48*, 9399.
[322] T. A. Engler, U. Sampath, S. Naganathan, D. V. Velde, F. Takusagawa, D. Yohannes, *J. Org. Chem.* **1989**, *54*, 5712.
[323] T. A. Engler, S. Naganathan, *Tetrahedron Lett.* **1986**, *27*, 1015.
[324] E. Gacs-Baitz, L. Minuti, H. W. Scheeren, R. Selvaggi, A. Taticchi, *Nat. Prod. Lett.* **1993**, *2*, 91.
[325] E. Gacs-Baitz, A. Marrocchi, L. Minuti, H. W. Scheeren, A. Taticchi, *Nat. Prod. Lett.* **1994**, *5*, 165.
[326] S. Arseniyadis, R. Rodriguez, D. V. Yashunsky, J. Camara, G. Ourisson, *Tetrahedron Lett.* **1994**, *35*, 4843.
[327] L. Minuti, A. Taticchi, E. Gacs-Baitz, A. Marrocchi, *Tetrahedron* **1995**, *51*, 8953.
[328] E. Gacs-Baitz, L. Minuti, A. Taticchi, *Tetrahedron* **1994**, *50*, 10359.
[329] S. Arseniyadis, R. Rodriguez, J. Camara, E. Guittet, L. Toupet, *Tetrahedron Lett.* **1993**, *34*, 1141.
[330] T. A. Engler, S. Naganathan, F. Takusagawa, D. Yohannes, *Tetrahedron Lett.* **1987**, *28*, 5267.
[331] W. G. Dauben, R. A. Bunce, *J. Org. Chem.* **1982**, *47*, 5042.
[332] M. Shimizu, A. Ohishi, Y. Taguchi, Y. Gama, I. Shibuya, *Chem. Pharm. Bull.* **2002**, *51*, 426.
[333] K. Matsumoto, S. k. Nakamura, T. Uchida, R. M. Acheson, *Heterocycles* **1980**, *14*, 1959.
[334] M. Ishikura, H. Uchiyama, A. Hino, N. Katagiri, *J. Heterocycl. Chem.* **2001**, *38*, 675.

[335] A. Nonnenmacher, H. Plieninger, M. L. Ziegler, *Chem. Ber.* **1985**, *118*, 3275.
[336] G. Jenner, *Tetrahedron Lett.* **1987**, *28*, 3927.
[337] M. Papadopoulos, R. Jost, G. Jenner, *J. Chem. Soc., Chem. Commun.* **1983**, 221.
[338] G. A. O'Doherty, R. D. Rogers, L. A. Paquette, *J. Am. Chem. Soc.* **1994**, *116*, 10883.
[339] G. A. Fenton, N. S. Isaacs, A. Gilbert, *Tetrahedron Lett.* **1985**, *26*, 1597.
[340] F. G. Klärner, B. M. J. Dogan, R. Weider, D. Ginsburg, E. Vogel, *Angew. Chem., Int. Ed.* **1986**, *25*, 346.
[341] L. A. Paquette, B. M. Branan, R. D. Rogers, *J. Org. Chem.* **1995**, *60*, 1852.
[342] L. A. Paquette, M. A. Poupart, *J. Org. Chem.* **1993**, *58*, 4245.
[343] L. A. Paquette, C.-C. Shen, *J. Am. Chem. Soc.* **1990**, *112*, 1159.
[344] F. G. Klärner, D. Schroer, *Chem. Ber.* **1989**, *122*, 179.
[345] S. Arseniyadis, R. Rodriguez, J. Camara, J. F. Gallard, E. Guittet, L. Toupet, G. Ourisson, *Tetrahedron* **1995**, *51*, 9947.
[346] J. H. Rigby, P. C. Kierkus, D. Head, *Tetrahedron Lett.* **1989**, *30*, 5073.
[347] D. L. Boger, C. E. Brothrton, *J. Am. Chem. Soc.* **1986**, *108*, 6713.
[348] K. Matsumoto, S. Kimura, T. Morishita, Y. Misumi, N. Hayashi, *Synlett* **2000**, 233.
[349] H. Takeshita, J.-F. Liu, N. Kato, A. Mori, R. Isobe, *Chem. Lett.* **1995**, 377.
[350] S. Mori, T. Karita, K. Komatsu, N. Sugita, T. S. M. Wan, *Synth. Commun.* **1997**, *27*, 1475.
[351] J.-F. Liu, N. Kato, A. Mori, H. Takeshita, R. Isobe, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1507.
[352] H. Takeshita, J.-F. Liu, N. Kato, A. Mori, *Chem. Lett.* **1993**, 1697.
[353] A. Mori, Y. Takamori, H. Takeshita, *Chem. Lett.* **1997**, 395.
[354] H. Takeshita, J.-F. Liu, A. Mori, R. Isobe, *J. Chem. Soc., Perkin Trans. 1* **1994**, 1433.
[355] J.-F. Liu, A. Mori, N. Kato, H. Takeshita, *Fullerene Sci. Technol.* **1995**, *3*, 45.
[356] J. Jurczak, M. Chmielewski, S. Filipek, *Synthesis* **1979**, 41.
[357] J. Jurczak, A. Golebiowski, T. Bauer, *Synthesis* **1985**, 928.
[358] S. M. Makin, Y. E. Raifel'd, B. S. El'yanov, *Seriya Khimicheskaya* **1976**, 831.
[359] M. Malinowska, P. Salanski, J.-C. Caille, J. Jurczak, *Synthesis* **2002**, 2702.
[360] J. Jurczak, A. Golebiowski, A. Rahm, *Tetrahedron Lett.* **1986**, *27*, 853.
[361] T. Bauer, C. Chapuis, J. Kozak, J. Jurczak, *Helv. Chim. Acta* **1989**, *72*, 482.
[362] J. Jurczak, *Polish J. Chem.* **1979**, *53*, 2539.
[363] J. Jurczak, B. Baranowski, *Polish J. Chem.* **1978**, *52*, 1857.
[364] J. Kiegiel, C. Chapuis, Z. Urbanczyk-Lipkowska, J. Jurczak, *Helv. Chim. Acta* **1998**, *81*, 1672.
[365] T. Bauer, C. Chapuis, A. Jezewski, J. Kozak, J. Jurczak, *Tetrahedron: Asymmetry* **1996**, *7*, 1391.
[366] W. M. Daniewski, E. Kubak, J. Jurczak, *J. Org. Chem.* **1985**, *50*, 3963.
[367] J. Jurczak, M. Tkacz, *J. Org. Chem.* **1979**, *44*, 3347.
[368] S. M. Makin, B. S. El'yanov, Y. E. Raifel'd, *Seriya Khimicheskaya* **1974**, 2654.
[369] M. Chmielewski, J. Jurczak, *J. Org. Chem.* **1981**, *46*, 2230.
[370] O. Achmatowicz Jr., E. Blalecka-Florjanczyk, *Tetrahedron* **1990**, *46*, 5317.
[371] Y. Yamamoto, *Chem. Lett.* **1987**, 945.
[372] A. Golebiowski, J. Raczko, U. Jacobsson, J. Jurczak, *Tetrahedron* **1991**, *47*, 1053.
[373] A. Golebiowski, J. Jurczak, *Tetrahedron* **1991**, *47*, 1037.
[374] A. Golebiowski, U. Jacobsson, J. Jurczak, *Tetrahedron* **1987**, *43*, 3063.
[375] A. Golebiowski, J. Izdebski, U. Jacobsson, J. Jurczak, *Heterocycles* **1986**, *24*, 1205.
[376] J. Jurczak, T. Bauer, *Carbohydr. Res.* **1987**, *160*, C1.
[377] J. Jurczak, A. Golebiowski, J. Raczko, *Tetrahedron Lett.* **1988**, *29*, 5975.
[378] J. Jurczak, T. Bauer, *Tetrahedron* **1986**, *42*, 5045.
[379] J. Jurczak, T. Bauer, S. Filipek, M. Tkacz, K. Zygo, *J. Chem. Soc., Chem. Commun.* **1983**, 540; J. Jurczak, T. Bauer, J. Kihlberg, *J. Carbohydr. Chem.* **1985**, *4*, 447; J. Jurczak, T. Bauer, J. Kihlberg, *Bull. Polish Acad. Sci., Chem.* **1986**, *34*, 321
[380] T. Bauer, J. Jurczak, *Polish J. Chem.* **1992**, *66*, 1999.
[381] J. Jurczak, T. Bauer, S. Jarosz, *Tetrahedron* **1986**, *42*, 6477.
[382] J. Jurczak, T. Bauer, S. Jarosz, *Tetrahedron Lett.* **1984**, *25*, 4809.
[383] M. Malinowska, P. Kwiatkowski, J. Jurczak, *Tetrahedron Lett.* **2004**, *45*, 7693.
[384] S. C. Schürer, S. Blechert, *Tetrahedron Lett.* **1999**, *40*, 1877.
[385] H. Junge, G. Oehme, *Tetrahedron* **1998**, *54*, 11027.
[386] S. M. Makin, Y. E. Raifel'd, B. S. El'yanov, *Seriya Khimicheskaya* **1976**, 1094.
[387] G. Jenner, R. Ben Salem, *New J. Chem.* **2000**, *24*, 203.

[388] D. A. L. Vandenput, H. W. Scheeren, *Tetrahedron* **1995**, *51*, 8383.
[389] D. L. Boger, K. D. Robarge, *J. Org. Chem.* **1988**, *53*, 3373.
[390] D. L. Boger, K. D. Robarge, *J. Org. Chem.* **1988**, *53*, 5793.
[391] R. W. M. Aben, R. de Gelder, H. W. Scheeren, *Eur. J. Org. Chem.* **2002**, 3126.
[392] B. Haag-Zeino, R. R. Schmidt, *Liebigs Ann./Recueil* **1990**, 1197.
[393] H. Al-Badri, J. Maddalun, S. Masson, N. Collignon, *J. Chem. Soc., Perkin Trans. 1* **1999**, 2255.
[394] Z. Bouaziz, P. Nebois, H. Fillion, J.-L. Luche, G. Jenner, *Tetrahedron* **1995**, *51*, 4057.
[395] H. Zhang, D. C. Appels, D. C. R. Hockless, L. N. Mander, *Tetrahedron Lett.* **1998**, *39*, 6577.
[396] M. Álvarez, L. Feliu, W. Ajana, J. A. Joule, J. L. Fernández-Puentes, *Eur. J. Org. Chem.* **2000**, 849.
[397] C. Cellerin, C. G. Tea, J. P. Pradere, A. Guingant, P. Guenot, *Sulfur Lett.* **1988**, *8*, 205.
[398] A. Marchand, D. Mauger, A. Guingant, J.-P. Predére, *Tetrahedron: Asymmetry* **1995**, *6*, 853.
[399] H. Al-Badri, N. Collignon, J. Maddaluno, S. Masson, *Chem. Commun.* **2000**, 1191.
[400] S. I. Bell, M. Parvez, S. M. Weinreb, *J. Org. Chem.* **1991**, *56*, 373.
[401] S. I. Bell, S. M. Weinreb, *Tetrahedron Lett.* **1988**, *29*, 4233.
[402] A. M. Moiseenkov, V. V. Veselovskii, Z. G. Makarova, V. M. Zhulin, V. A. Smit, *Tetrahedron Lett.* **1984**, *25*, 5929.
[403] P. Herczegh, M. Zsely, R. Bognar, S. Laszlo, *Tetrahedron Lett.* **1986**, *27*, 1509.
[404] R. M. Uittenboogaard, J.-P. G. Seerden, H. W. Scheeren, *Tetrahedron* **1997**, *53*, 11929.
[405] G. J. Kuster, H. W. Scheeren, *Tetrahedron Lett.* **1998**, *39*, 3613.
[406] G. Galley, M. Pätzel, *J. Chem. Soc., Perkin Trans. 1* **1996**, 2297.
[407] S. Jarosz, E. Kozloeska, A. Jezewski, *Tetrahedron* **1997**, *53*, 10775.
[408] B. Plietker, D. Seng, R. Frohlich, P. Metz, *Tetrahedron* **2000**, *56*, 873.
[409] Y. Araki, T. Konoike, *J. Org. Chem.* **1997**, *62*, 5299.
[410] A. J. Phillips, J. C. Morris, A. D. Abell, *Tetrahedron Lett.* **2000**, *41*, 2723.
[411] D. C. Bland, B. C. Rausdenbush, S. M. Weinreb, *Org. Lett.* **2000**, *2*, 4007.
[412] T. Suzuki, H. Takayama, *J. Chem. Soc., Chem. Commun.* **1995**, 807.
[413] S. J. Burrell, A. E. Derome, M. S. Edenborough, L. M. Harwood, S. A. Leeming, N. S. Isaacs, *Tetrahedron Lett.* **1985**, *26*, 2229.
[414] L. M. Harwood, S. A. Leeming, N. S. Isaacs, G. Jones, J. Pickard, R. M. Thomas, D. Watkin, *Tetrahedron Lett.* **1988**, *29*, 5017.
[415] B. A. Keay, P. W. Dibble, *Tetrahedron Lett.* **1989**, *30*, 1045.
[416] T. Heiner, S. Michalski, K. Gerke, G. Kuchta, M. Buback, A. de Meijere, *Synlett* **1995**, 355.
[417] T. Heiner, S. I. Kozhushkov, M. Noltemeyer, T. Haumann, R. Boese, A. de Meijere, *Tetrahedron* **1996**, *52*, 12185.
[418] A. C. Brickwood, M. G. B. Drew, L. M. Harwood, T. Ishikawa, P. Marais, V. Morisson, *J. Chem. Soc., Perkin Trans. 1* **1999**, 913.
[419] L. M. Harwood, T. Ishikawa, H. Phillips, D. Watkin, *J. Chem. Soc., Chem. Commun.* **1991**, 527.
[420] L. M. Harwood, B. Jackson, G. Jones, K. Prout, R. M. Thomas, F. J. Witt, *J. Chem. Soc., Chem. Commun.* **1990**, 608.
[421] L. M. Harwood, G. Jones, J. Pickard, R. M. Thomas, D. Watkin, *Tetrahedron Lett.* **1988**, *29*, 5825.
[422] T. Butz, J. Sauer, *Tetrahedron: Asymmetry* **1997**, *8*, 703.
[423] L. F. Tietze, C. Ott, K. Gerke, M. Buback, *Angewandte Chem., Int. Ed.* **1993**, *32*, 1485.
[424] B. M. Trost, J. R. Parquette, A. L. Marquart, *J. Am. Chem. Soc.* **1995**, *117*, 3284.
[425] G. J. Kuster, F. Kalmoua, R. de Gelder, H. W. Scheeren, *Chem. Commun.* **1999**, 855.
[426] I. Blanarikova-Hlobilova, Z. Kubanova, L. Fisera, M. K. Cyranski, P. Salanski, J. Jurczak, N. Pronayova, *Tetrahedron* **2003**, *59*, 3333.
[427] N. Katagiri, N. Watanabe, J. Sakaki, T. Kawai, C. Kaneko, *Tetrahedron Lett.* **1990**, *31*, 4633.
[428] A. Padwa, D. N. Kline, B. H. Norman, *Tetrahedron Lett.* **1988**, *29*, 265.
[429] A. Padwa, D. N. Kline, B. H. Norman, *J. Org. Chem.* **1989**, *54*, 810.
[430] J. W. Kennington Jr., W. Li, P. DeShong, *High Pressure Res.* **1992**, *11*, 163.
[431] C. M. Dicken, P. DeShong, *J. Org. Chem.* **1982**, *47*, 2047.
[432] A. V. Kamernitzkii, I. S. Levina, E. I. Mortikova, B. S. El'yanov, *Tetrahedron Lett.* **1975**, 3235.
[433] A. V. Kamernitskii, T. N. Galakhova, I. S. Levina, B. S. El'yanov, V. S. Bogdanov, E. G. Cherepanova, *Seriya Khimicheskaya* **1985**, 1893.
[434] J.-P. G. Seerden, M. M. M. Boeren, H. W. Scheeren, *Tetrahedron* **1997**, *53*, 11843.
[435] Y. Yu, H. Fujita, M. Ohno, S. Eguchi, *Synthesis* **1995**, 498.

[436] N. Katagiri, H. Sato, A. Kurimoto, M. Okada, A. Yamada, C. Kaneko, *J. Org. Chem.* **1994**, *59*, 8101.
[437] R. Plate, P. H. Hemkens, J. M. Smits, R. J. Nivard, H. C. Ottenheijm, *J. Org. Chem.* **1987**, *52*, 1047.
[438] P. H. H. Hermkens, J. H. v. Maarseveen, C. G. Kruse, H. W. Scheeren, *Tetrahedron* **1988**, *44*, 6491.
[439] P. DeShong, W. Li, J. W. Kennington Jr, H. L. Ammon, J. M. Leginus, *J. Org. Chem.* **1991**, *56*, 1364.
[440] H. de Suray, G. Leroy, J. Weiler, *Tetrahedron Lett.* **1974**, 2209.
[441] M. Ishikura, S. Kudo, A. Hino, N. Ohnuki, N. Katagiri, *Heterocycles* **2000**, *53*, 1499.
[442] R. N. Warrener, A. B. B. Ferrira, E. R. T. Tieknik, *Tetrahedron Lett.* **1996**, *37*, 2161.
[443] A. V. Kamernitskii, T. N. Galakhova, I. S. Levina, B. S. El'yanov, *Seriya Khimicheskay* **1977**, 2374.
[444] G. T. Anderson, J. R. Henry, S. M. Weinreb, *J. Org. Chem.* **1991**, *56*, 6946.
[445] I. V. Zavarzin, V. M. Zhulin, V. N. Yarovenko, M. M. Krayushkin, *Seriya Khimicheskaya* **1988**, 1168.
[446] M. M. Krayushkin, A. M. Beskopyl'nyi, S. G. Zlotin, O. A. Luk'yanov, V. M. Zhulin, *Seriya Khimicheskaya* **1980**, 2668.
[447] M. M. Krayushkin, V. N. Yarovenko, O. A. Luk'yanov, V. M. Zhulin, *Seriya Khimicheskaya* **1981**, 2764.
[448] M. M. Krayushkin, A. M. Beskopyl'nyi, E. B. Zhuravleva, V. M. Zhulin, *Seriya Khimicheskaya* **1985**, 461.
[449] D. N. Butler, J. R. Malpass, D. Margetic, R. A. Russell, G. Sun, R. N. Warrener, *Synlett* **1998**, 588.
[450] V. Melai, A. Brillante, P. Zanirato, *J. Chem. Soc., Perkin Trans. 2* **1998**, 2447.
[451] T. Tsuchiya, M. Yasumoto, I. Shibuya, *Chem. Lett.* **1989**, 1357.
[452] K. Itoya, M. Kakimoto, Y. Imai, O. Fukunaga, *Polym. J.* **1992**, *24*, 979.
[453] H. Suga, X. Shi, T. Ibata, *Chem. Lett.* **1994**, 1673.
[454] H. Suga, X. Shi, T. Ibata, A. Kakehi, *Heterocycles* **2001**, *55*, 1711.
[455] X. Shi, T. Ibata, H. Suga, K. Matsumoto, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3315.
[456] H. Plieninger, C. C. Heuck, R. Bühler, *Tetrahedron* **1972**, *28*, 73.
[457] J. E. Rice, Y. Okamoto, *J. Org. Chem.* **1981**, *46*, 446.
[458] T. Nagawa, Y. Zama, Y. Okamoto, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2035.
[459] J. Nakayama, A. Kaneko, Y. Sugihara, A. Ishii, A. Oishi, I. Shibuya, *Heteroat. Chem.* **2000**, *11*, 434.
[460] Y. Okamato, P. S. Wojciechowski, *J. Chem. Soc., Chem. Commun.* **1981**, 669.
[461] V. Breitkopf, H. Hopf, F. G. Klärner, B. Witulski, B. Zimny, *Liebigs Ann./Recueil* **1995**, 613.
[462] J. Roemer-Mähler, D. Bieniek, F. Korte, *Z. Naturforsch. B* **1975**, *30*, 290.
[463] R. W. M. Aben, H. W. Scheeren, *Tetrahedron Lett.* **1985**, *26*, 1889.
[464] R. W. M. Aben, H. W. Scheeren, *Tetrahedron Lett.* **1983**, *24*, 4613.
[465] R. W. M. Aben, R. Smit, J. W. Sheeren, *J. Org. Chem.* **1987**, *52*, 365.
[466] R. W. M. Aben, J. Goudriaan, J. M. M. Smits, H. W. Scheeren, *Synthesis* **1993**, 37.
[467] R. W. M. Aben, S. Braverman, H. W. Scheeren, *Eur. J. Org. Chem.* **2003**, 894.
[468] W. R. Dolbier Jr, S. L. Weaver, *J. Org. Chem.* **1990**, *55*, 711.
[469] A. Oishi, Y. Taguchi, T. Tsuchiya, I. Shibuya, *Rev. High Pressure Sci. Technol.* **1998**, *7*, 1253.
[470] T. Tsuchiya, M. Yasumoto, I. Shibuya, Y. Taguchi, K. Yamamoto, M. Goto, *Chem. Lett.* **1990**, 1423.
[471] A. Oishi, M. Yasumoto, M. Goto, T. Tsuchiya, Y. Taguchi, *Heterocycles* **1994**, *38*, 2073.
[472] Y. Taguchi, A. Oishi, T. Tsuchiya, I. Shibuya, *Nippon Kagakukaishi* **1994**, 146.
[473] Y. Taguchi, T. Tsuchiya, A. Oishi, I. Shibuya, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1667.
[474] R. W. M. Aben, E. P. Limburg, H. W. Scheeren, *High Pressure Res.* **1992**, *11*, 167.
[475] M. Chmielewski, Z. Kaluza, C. Belzecki, P. Salanski, J. Jurczak, H. Adamowicz, *Tetrahedron* **1985**, *41*, 2441.
[476] M. Chmielewski, Z. Kaluza, C. Belzecki, P. Salanski, J. Jurczak, *Tetrahedron Lett.* **1984**, *25*, 4797.
[477] M. Chmielewski, Z. Kaluza, D. Mostowicz, C. Belzecki, E. Baranowska, J. P. Jacobsen, P. Salanski, J. Jurczak, *Tetrahedron* **1987**, *43*, 4555.
[478] M. Chmielewski, Z. Kaluza, P. Salanski, J. Jurczak, *High Pressure Res.* **1992**, *11*, 171.
[479] Y. Taguchi, A. Oishi, *Rev. High Pressure Sci. Technol.* **1998**, *7*, 1271.
[480] C. García-Martínez, Y. Taguchi, A. Oishi, K. Hayamizu, *Magn. Reson. Chem.* **1998**, *36*, 429.
[481] C. García-Martínez, Y. Taguchi, A. Oishi, K. Hayamizu, *Tetrahedron: Asymmetry* **1988**, *9*, 955.
[482] T. Tsuchiya, M. Yasumoto, I. Shibuya, M. Goto, *J. Chem. Soc., Perkin Trans. 1* **1990**, 1218.
[483] M. Yasumoto, T. Tsuchiya, Y. Taguchi, I. Shibuya, K. Yonemoto, M. Goto, *Chem. Lett.* **1991**, 1229.
[484] I. Shibuya, A. Oishi, M. Yasumoto, *Heterocycles* **1998**, *48*, 1659.
[485] Y. Taguchi, M. Yasumoto, T. Tsuchiya, A. Oishi, I. Shibuya, *Chem. Lett.* **1993**, 1097.
[486] M. Mielcarek, M. Z. Barciszewska, P. Salanski, M. Stobiecki, J. Jurczak, J. Barciszewski, *Biochem. Biophys. Res. Commun.* **2002**, *294*, 145.

Received February 26, 2005