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Transition metal catalyzed cycloaddition reactions of chiral ketimines with alkenes and carbon monoxide: reaction conditions, substrate variations and stereoselectivity

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Abstract

The three component reaction of chiral *N*,*N*′-bis(aryl)tetrahydropyrrolo-[2,1-*c*][1,4]oxazine-3,4-diylidenediamines with carbon monoxide and terminal alkenes produces spiro lactams by a formal [2 + 2 + 1] cycloaddition reaction. The constitution of one of the tricyclic products is confirmed by X-ray analysis revealing the complete regioslectivity of the reaction since only the imine moiety next to the oxazine oxygen atom is transformed during the catalysis whereas the second imine function shows no reactivity at all. Terminal alkenes react quantitatively if $Ru_3(CO)_{12}$ is used as the catalyst precursor but the catalysis also works catalytically if $Fe_2(CO)_9$ is employed. The $Ru_3(CO)_{12}$ amount may be lowered to 0.5 mol%. Internal alkenes and acrylic acid methyl ester give the desired spiro lactams under analogous reaction conditions in very poor yields.

Keywords: Cycloaddition; Lactames; Iron; Ruthenium; X-ray diffraction

1. Introduction

Compared to classical methods for the synthesis of heterocyclic or carbocyclic compounds transition metal catalyzed cycloaddition reactions have repeatedly turned out to be advantageous in terms of selectivity and atom economy [1].

Recently, we were able to show that 1,4-diazabutadienes may be reacted with CO and ethylene catalyzed by $Ru_3(CO)_{12}$ to produce pyrrolidin-2-one derivatives selectively in a three component reaction [2]. This reaction formally corresponds to a [2 + 2 + 1] cycloaddition reaction. The most prominent example of this reaction type is the Pauson–Khand reaction, which is used for the formation of five-membered ring systems. Originally the Pauson–Khand reaction allowed the preparation of cyclopentenones in an intramolecular reaction from an alkyne, which is introduced to the reaction as an alkyne–$Co_2(CO)_6$ complex, an alkene and one of the CO ligands at cobalt [3]. In the past years catalytic variations of the Pauson–Khand reaction have been developed, although most of them still need stoichiometric amounts of additives like, e.g. phosphites in order to recover the catalytically active transition metal species [4]. In addition, there are some Hetero–Pauson–Khand reactions reported in the literature leading to the formation of unsaturated lactones or lactams from CO, an alkyne and an aldehyde or aldimine, respectively [5]. But it has to be pointed out, that most of these reactions still start from substrates,

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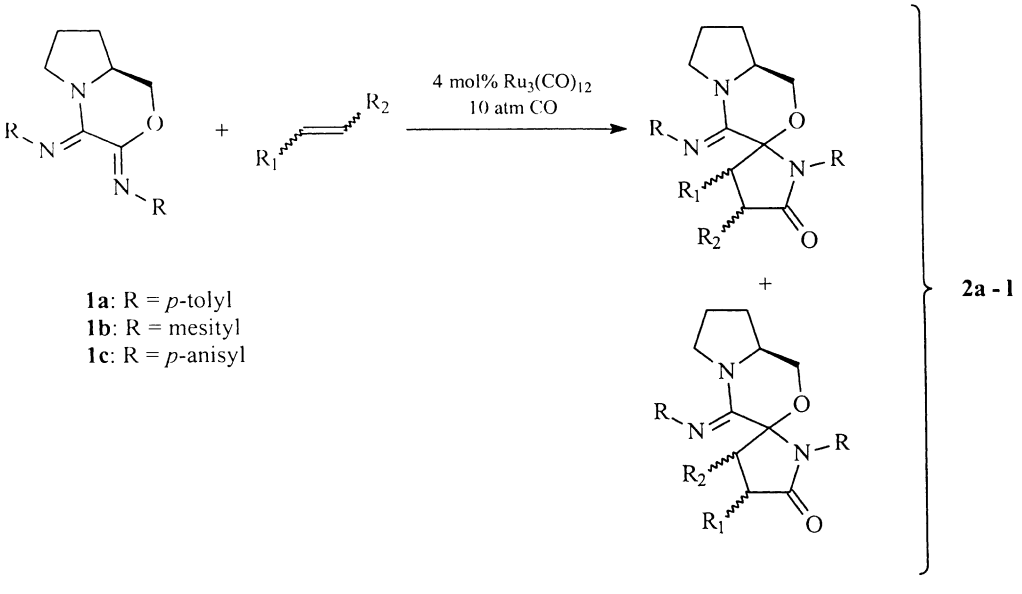
in which the alkyne and the aldehyde (or aldimine) moiety have to be present in one molecule. One exception is the synthesis of functionalized γ-butyrolactones from a ketone, ethylene and CO reported by Murai et al. [5(f)].

Since we used cyclic imines as the starting material we obtained spiro lactams from these reactions, in which regioselectively only one of the imine subunits of the starting material has been transformed. Spiro lactams have been reported as the key intermediates in a number of total synthesis procedures leading to natural products [6]. In addition, spiro[pyrrolidine-3,3′-oxindole] derivatives are known as natural products with high cytostatic potential [7].

So we wanted to explore the limits of the reaction that we described earlier in terms of a variation of reaction time, temperature, pressure, the precatalyst and it is concentration as well as for the use of a broader substrate spectrum in order to produce spiro lactams with other substitution patterns. The results of these investigations are described in the following.

2. Results and discussion

The cycloaddition reaction of a ketimine, an alkene and CO leads to spiro lactams and thus to the formation of a new stereogenic center at the spiro carbon atom. Thus, we decided to use ketimines with a defined stereochemistry. Scheme 1 shows the chiral *N*,*N*′-bis(aryl)tetrahydropyrrolo-[2, 1-*c*] [1, 4]oxazine-3,4-diylidenediamines **1a**–**1c**, which we used as the starting compounds. **1a**–**1c** may easily be obtained from the reaction of *S*-prolinol with the corresponding *N*,*N*′-bis(aryl)oxalimidoyl chlorides [8]. **1a**–**1c** formally represent 1,4-diazabutadiene derivatives, in which the two imine carbon atoms are differently substituted. We already had investigated the ligand properties of **1a**–**1c** and found that they form dinuclear iron carbonyl complexes in which regioselectively only the imine subunit next to the oxazine oxygen atom coordinates both iron centers whereas the other C–N double bond only shows an interaction with one of the $Fe(CO)_3$ moieties [8(c)]. So we thought that there might also be a discrimination between both the imine subunits in a catalytic reaction and that, in addition, the second imine moiety might act as a ligand towards the catalytically active transition metal fragment thus stabilizing the intermediates and transition states of the catalytic reaction. This should lead to an enhanced selectivity as well as to less decomposition reactions which again might enable us to lower the precatalyst concentrations.



Scheme 1.

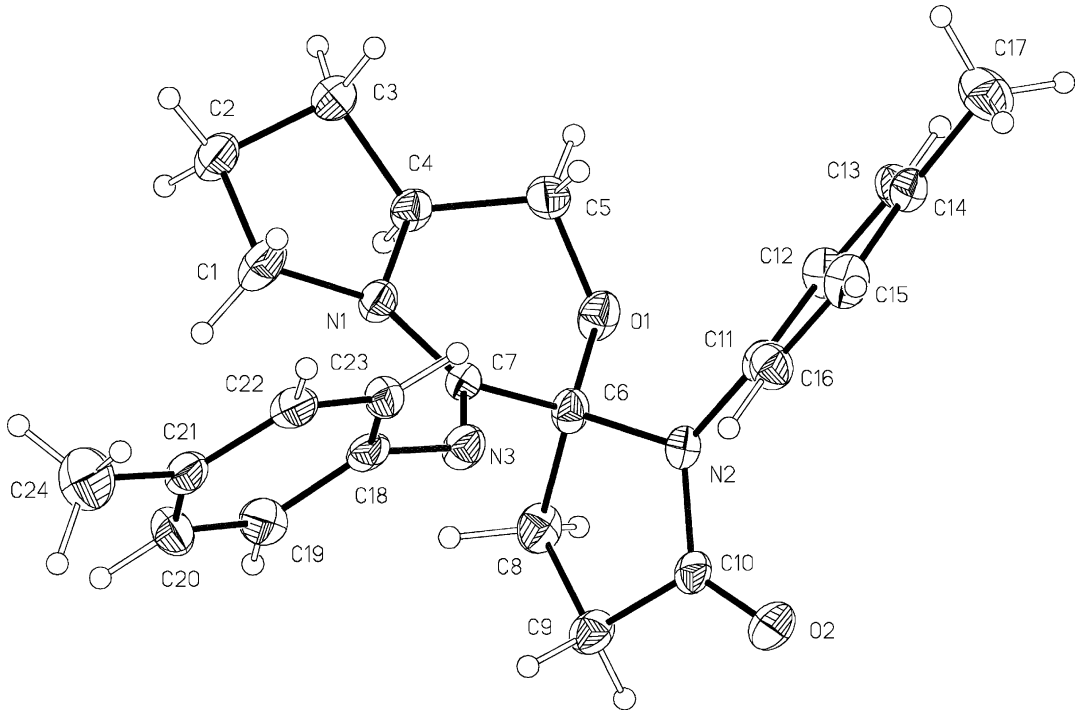


Fig. 1. Molecular structure of **2a**: N1–C4 150.0(4), C4–C5 150.2(5), C5–O1 143.9(4), O1–C6 141.7(4), C6–C7 154.9(5), C7–N1 136.2(4), C6–N2 148.0(4), N2–C10 137.2(4), C10–O2 122.1(4), C10–C9 150.7(5), C9–C8 153.0(5), C8–C6 154.0(5), C7–N3 128.4(4); O1–C6–C7 114.9(3), O1–C6–N2 109.4(3), O1–C6–C8 108.8(3), N2–C6–C8 102.1(3), N2–C6–C7 111.7(3), C7–C6–C8 109.2(3), C6–N2–C10 112.5(3), C6–N2–C11 122.8(3), N2–C10–O2 125.6(3), C6–C8–C9 104.1(3), C8–C9–C10 104.6(3), C9–C10–N2 108.3(3), C9–C10–O2 126.1(3), C7–N3–C18 125.8(3).

If **1a**–**1c** are treated with 12 atm of carbon monoxide together with 8 atm of ethylene in the presence of 4 mol% $Ru_3(CO)_{12}$ for 16 h the spiro lactams **2a** and **2c** are formed quantitatively, whereas **2b** is only produced in a 54% yield presumably due to the higher steric demands of the mesityl groups. The reaction proceeds with perfect regioselectivity meaning that only one of the imine moieties is engaged in the formal [2 + 2 + 1] cycloaddition reaction. Again the C–N bond next to the oxazine oxygen atom is the more reactive one compared to the imine subunit next to the nitrogen atom of the oxazine system, which remains unreacted. **2a**–**2c** are produced as a mixture of diastereomers since they exhibit two stereogenic centers. The *S*-configuration originally introduced from the use of enantiomerically pure *S*-prolinol still is preserved and the new stereogenic center at the spiro carbon atom is observed in both *R*- and *S*-configuration. The diastereoselectivity of the cycloaddition reaction is quite poor and lies in the range of 1:1 up to 2:1. Crystallization from toluene afforded single crystals of **2a** suitable for X-ray diffraction. The result of the structure analysis proved the regio- and stereochemistry of the catalytic formation of **2a** and is shown in Fig. 1 [2].[1]

In order to explore the limitations of the catalytic cycloaddition reaction, we performed the reaction of **1a** with CO and ethylene under different reaction conditions. First of all, we had a look at the influence of the reaction time. The result is depicted in Fig. 2 and

[1] Crystal and intensity data for **2a**: 183 K, yellow crystal, crystal size 0.3 mm × 0.1 mm × 0.02 mm, orthorhombic, $a = 8.2350(4)$ Å, $b = 11.1009(6)$ Å, $c = 23.009(2)$ Å, $V = 2103.4(2)$ Å^3, $Z = 4$, $F(000) = 832$, $\rho_{calc} = 1.230\,g\,cm^{-3}$, spacegroup $P2_12_12_1$, absolute coefficient $0.079\,mm^{-1}$, θ-limit 3.55–27.51°, ϕ- and ω-scan, 11462 reflection measured, 4734 independent reflection, 3079 observed reflection $F_o^2 > 2\sigma(F_o^2)$, 268 parameters, GOOF = 0.987, $R_1 = 0.0830$, $wR_2 = 0.1507$, final difference map electron density [e Å^{-3}] 0.214.

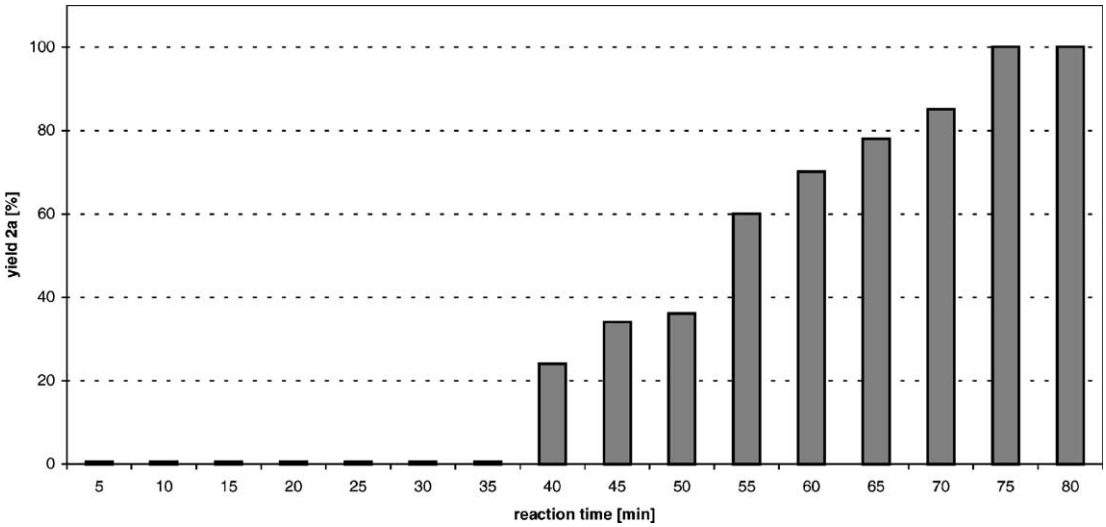


Fig. 2. The influence of reaction time on the formation of **2a**.

shows that the reaction is finished after 75 min. The time was measured from the point when the reactants had been placed in the autoclave and the heating began. During our first investigations we recognized, that there is no reaction at all if the temperature remains below 120 °C. So if the reaction temperature of 130 °C is reached after 50 min, the conversion of **1a**–**2a** is quantitatively performed during the next 25 min.

Fig. 3 shows the dependency of the reaction towards the pressure of the gaseous reactants CO and ethylene. The two components always were used in a 1:1.5 ratio with a higher partial pressure of carbon monoxide. The reaction of **1a**–**2a** still is quantitative with a pressure of 1 bar ethylene together with 1.5 bar CO. Further reduction towards atmospheric pressure leads to a decrease of the yield of **2a** to 54%, leaving 46% of the starting compound **1a** unreacted. So the regio- and chemoselectivity of the reaction still works perfectly although turnover frequencies are somewhat smaller.

In Fig. 4 the dependency of the yield of **2a** on the amount of the corresponding precatalyst is depicted. We used $Ru_3(CO)_{12}$, $Fe_2(CO)_9$ and an 1:1 mixture

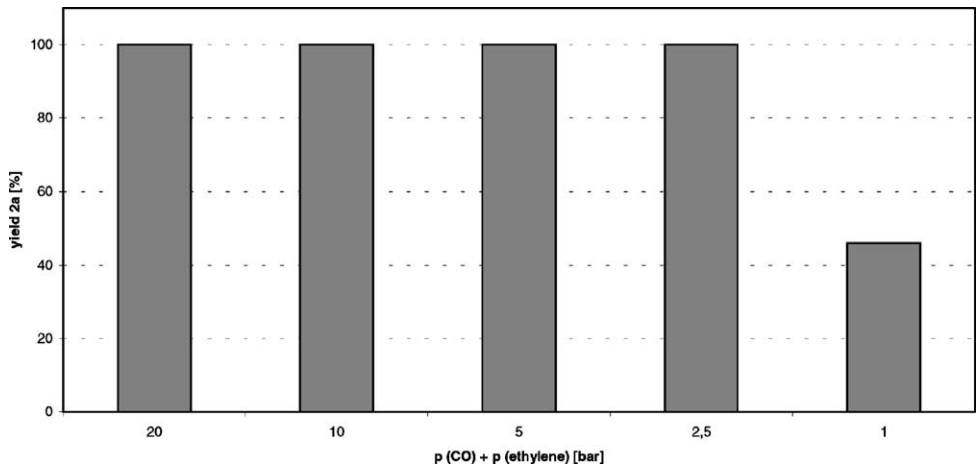


Fig. 3. The influence of CO and C_2H_4 pressure on the formation of **2a**.

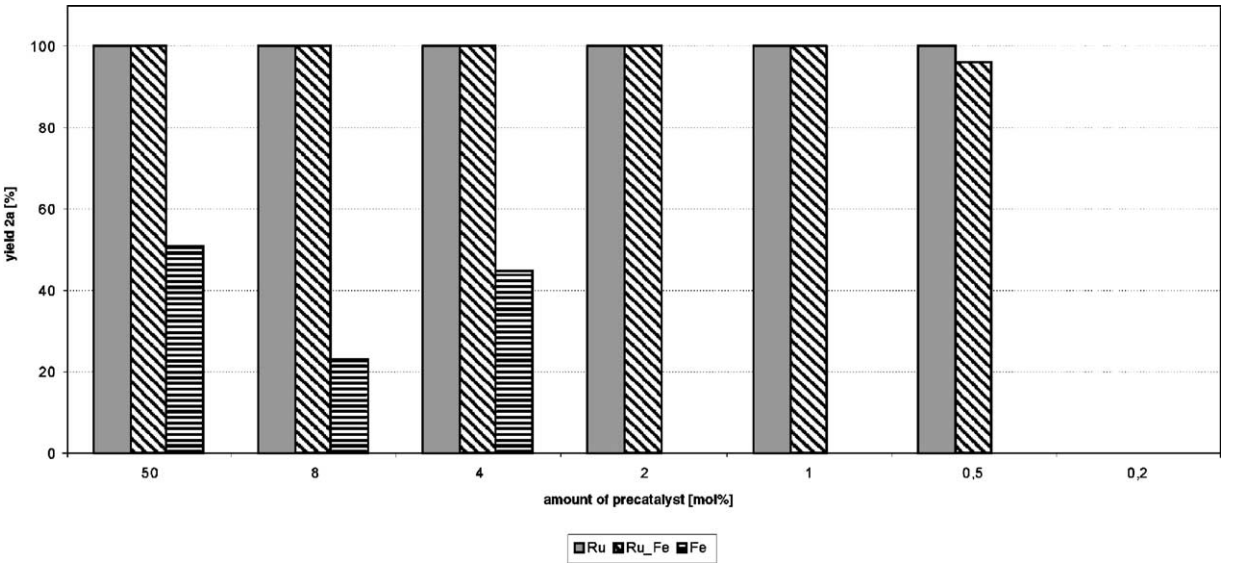


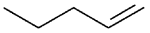
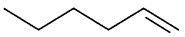
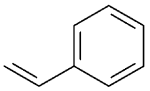
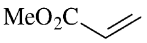
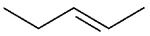
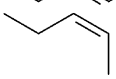
Fig. 4. The influence of the amount of precatalyst on the formation of **2a**.

of both as the catalyst precursors. $Fe_3(CO)_{12}$ or $RuCl_3{\cdot}H_2O$ gave no reaction even at higher concentrations. From Fig. 4 it can be shown that $Ru_3(CO)_{12}$ works perfectly down to an amount of 0.5 mol%. $Fe_2(CO)_9$ may act as a catalyst for the described reaction although turnover numbers are much lower. If 4 mol% $Fe_2(CO)_9$ are employed in the reaction **2a** is formed with a 45% yield. If the amount of $Fe_2(CO)_9$ is raised, there is not only no proportional increase of the formation of **2a** but even a decrease in reactivity first. This is followed by a slight increase of the yields of **2a** if the precatalyst amount is raised further (Fig. 4). This finding obviously is due to the formation of stable dinuclear iron carbonyl complexes of **1a** which we described earlier from stoichiometric reactions [8(c)].

In addition, we introduced a number of different alkenes to the reaction in order to look at the influence of functional groups and of steric properties on the reaction products (Scheme 1). Table 1 shows the alkenes we used as well as the numbering scheme of the products, their yield and the number of stereoisomers observed by ^{13}C NMR spectroscopy. **1a** was used as the starting compound in all cases except the reactions leading to **2b** and **2c**.

It can be seen that terminal alkenes work very well giving a quantitative yield of the corresponding spiro lactams. On the other hand, one has to keep in mind that the use of substituted alkenes instead of ethylene leads to the formation of additional stereogenic centers in the product molecules. So terminal alkenes produce spiro lactams with three stereogenic centers namely the chiral carbon atom which already was introduced from *S*-prolinol, the spiro carbon atom and the carbon atom of the former alkene bearing the substituent. In addition, the reaction of terminal alkenes leads to a problem of regioselectivity. So if we propose that the stereogenic center corresponding to *S*-prolinol is retained in it's stereochemistry, there are eight different regio- and diastereomers possible from the reaction of **1a** with terminal alkenes. The crude product mixtures were investigated by NMR spectroscopy showing that **1a** had been consumed quantitatively during the reaction time. In addition, it can be concluded from the NMR spectra that regio- and stereoselectivity in some cases is quite low. If propene is introduced to the reaction leading to **2d** five different diastereomers can be identified by the characteristic resonance of the spiro carbon atom at about 90 ppm (see Section 4). In the catalysis starting from 1-pentene (**2e**) four and for the reaction of 1-hexene (**2f**) six stereoisomers can be detected this way. Since the different stereoisomers are detected by ^{13}C NMR spectroscopy it is not possible to give an exact ratio, but it is obvious

Table 1
Alkenes used in catalytic cycloaddition reactions, yields of spiro lactam derivatives **2a**–**2l**

Entry	R	Alkene	R_1	R_2	Product	Yield (%)	No. of isomers
1	*p*-Tolyl		H	H	**2a**	>98	2
2	Mesityl		H	H	**2b**	54	2
3	*p*-Anisyl		H	H	**2c**	>98	2
4	*p*-Tolyl		CH_3	H	**2d**	>98	5
5	*p*-Tolyl		*n*-C_3H_7	H	**2e**	>98	4
6	*p*-Tolyl		*n*-C_4H_9	H	**2f**	>98	6
7	*p*-Tolyl		Ph	H	**2g**	>98	1
8	*p*-Tolyl		CO_2Me	H	**2h**	<5	[a]
9	*p*-Tolyl		C_2H_5	CH_3	**2i**	<5	[a]
10	*p*-Tolyl		C_2H_5	CH_3	**2k**	<5	[a]
11	*p*-Tolyl		$(CH_2)_4$	$(CH_2)_4$	**2l**	<5	[a]

[a] Not determined.

from the spectra that four of them are produced in a significantly higher amount than the others. These are probably due to the formation of the less sterically crowded regioisomers with R_1 situated next to the carbonyl group of the lactam ring (Scheme 1).

A special case is the reaction of styrene. We observed the formation of polystyrene from the excess styrene being present in the reaction mixture. If the solvent is evaporated from the crude reaction mixture and the remaining precipitate consisting of polystyrene and molecular reaction products is extracted with ethanol the NMR spectra still show traces of styrene oligomers as well as the formation of only one diastereomer of the expected spiro lactam **2g**. Again, the starting compound **1a** was consumed quantitatively. So obviously the catalytic cycloaddition reaction producing **2g** works very fast leaving the excess substrate as well as organo ruthenium species which in subsequent catalytic reactions form styrene oligomers and polymers. On the other hand, we never observed any formation of polyethylene or polypropylene in the reactions producing **2a** or **2d**, respectively. Unfortunately it was not possible to separate the cycloaddition product **2g** from the styrene oligomers either by chromatography or fractionate crystallization and thus we were not able to determinate absolute configuration of the spiro carbon atom in **2g**.

The reaction of acrylic acid methyl ester leads to the formation of **2h** in very poor yields, although it is still undoubtedly detectable by IR spectroscopy and mass spectrometry. So obviously carboxy groups are not tolerated in this catalytic system and lead to alternative reaction pathways. The reactions of internal alkenes like *E*-2-pentene, *Z*-2-pentene or cyclohexene all produced the desired spiro lactams, but also in very poor yields. In addition, these results clearly indicate, that the products obtained from the reactions of terminal alkenes (vide supra) do not correspond to a reaction sequence in which first the terminal alkenes are isomerized into internal alkenes and then a subsequent cycloaddition reaction is performed. So these results still are important since the isomerization of double bonds catalyzed by transition metal compounds (e.g. ruthenium compounds) is a commonly known and industrially used process [9].

We also tried to perform the catalytic cycloaddition reaction with alkynes instead of alkenes. Only in the case of phenylacetylene the formation of a corresponding cyclic lactam is observed in very poor yields. In

all other cases as acetylene itself, silylated acetylenes or acetylene carboxylic acid derivatives, respectively, the formation of the desired spiro lactams was not observed at all. Bis-trimethylsilyl-acetylene and acetylene bis-carboxylic acid dimethyl ester showed no catalytic reaction whatsoever. Trimetylsilyl-acetylene did not react with **1a**, but the formation of cyclodimers and cyclotrimers of the acetylene itself were observed. The reaction of acetylene carboxylic acid methyl ester also resulted in the formation of the corresponding benzene derivatives by cyclotrimerization of the acetylene. Since there have been numerous reports in the literature about cyclooligomerization of alkynes catalyzed by transition metal compounds [10], we did not investigate these reactions in detail.

3. Conclusions

We were able to show that the catalytic reaction of ketimines, carbon monoxide and ethylene leads to the quantitative formation of spiro lactams by a formal [2 + 2 + 1] cycloaddition reaction as long as the organic substituent at the imine nitrogen atom is not too bulky. The synthesis works perfectly in the presence of 0.5 mol% $Ru_3(CO)_{12}$ as the catalyst precursor and is also catalytic if $Fe_2(CO)_9$ is used instead, although in this case the reaction is not quantitative anymore. The reaction is finished approximately 30 min after the minimum reaction temperature of 120 °C is reached. The pressure of carbon monoxide and ethylene may be lowered nearly to atmospheric pressure.

This reaction principle may be extended to substituted alkenes instead of ethylene. Terminal alkenes also react quantitatively to produce mixtures of regio- and diastereomers. A promising result is the reaction with styrene leading to only one stereoisomer.

Acrylic acid methyl ester, internal alkenes as well as alkynes mostly do not give the desired spiro lactams but end up either in the degradation of the bicyclic system of the starting compounds or the observation of cyclodimers and cyclotrimers of the acetylenes, respectively.

Attempts in order to improve the stereoselectivity of the reaction of terminal alkenes, e.g. by the use of precatalysts with chiral ligands are ongoing.

4. Experimental

4.1. General

All procedures were carried out under an argon atmosphere in anhydrous, freshly distilled solvents. The preparation of **1a**–**1c** was done following the procedures published in [8]. Infrared spectra were recorded on a Perkin-Elmer FT-IR System 2000 using 0.2 mm KBr cuvettes. NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H: 200 MHz, ^{13}C: 50.32 MHz, $CDCl_3$ as internal standard) and on a Bruker DRX 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100.62 MHz with $CDCl_3$ as internal standard). Mass spectra and GC–MS spectra were recorded on a Finnigan MAT SSQ 710 instrument. High resolution mass spectra were recorded on a Finnigan MAT 95 XL using ESI techniques and methanol as the solvent. Elemental analyses were carried out at the Institute of Organic and Macromolecular Chemistry of the Friedrich-Schiller-University, Jena.

4.2. X-ray crystallographic study

The structure determination of **2a** was carried out on an Enraf Nonius Kappa CCD diffractometer, crystal detector distance 25 mm, 180 frames, using graphite monochromated Mo Kα radiation. The crystal was mounted in a stream of cold nitrogen. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined by full-matrix least squares techniques against F^2 using the programs SHELXS-86 and SHELXL-93 [11]. Computation of the structure was done with the program XPMA [12] and the molecular illustration was drawn using the program XP [13]. The crystal and intensity data are given in footnote 1. Additional material on the structure analysis is available from the Cambridge Crystallographic Data Centre by mentioning the deposition number CCDC-151894.

4.3. Synthesis of *2a–2l*

One millimol of the corresponding *N*,*N*′-bis-aryl-tetrahydropyrrolo-[2, 1-c] [1,4]oxazine-3, 4-diylidene-diamine (**1a**: R = *p*-tolyl, 333 mg; **1b**: R = *p*-anisyl, 365 mg; **1c**: R = Mes, 390 mg) is transferred together with 0.04 mmol $Ru_3(CO)_{12}$ (26 mg) into a 75 ml

stainless steel autoclave. Then the autoclave is evaporated and 3 ml of toluene are added. Afterwards the autoclave is pressurized with 12 atm CO and 8 atm ethylene or propene, respectively. If liquid alkenes are used in the reaction, 33 mmol of the alkene are transferred into the autoclave together with toluene. The reaction mixture is heated to 140 °C for 16 h. After the autoclave is cooled down to room temperature the pressure is released and the solution is transferred into a Schlenk tube. After the toluene is evaporated a brown oily residue is obtained. This residue was used to determine the yield of **2a**–**2g** by inverse gated decoupling experiments. **2h**–**2l** were not detectable by NMR techniques but were unequivocally proven by GC–MS measurements. In the case of **2a** the residue is recrystallized from toluene to produce crystals of one of the diastereomers of **2a**, in which C6 is *R*-configurated and which by NMR spectroscopy is the major component of the crude reaction mixture.

4.4. Analytical data of ***2a***

1-(*p*-Tolyl) - 10-(*p*- tolyl)imino - hexahydropyrrolo-[2,1-h]-6-oxa-1,9-diaza-spiro[4.5]decan-2-one; yield: >98%; elemental analysis [%] found (calculated): C 74.02 (74.01), H 7.05 (6.99), N 10.47 (10.79); MS (CI, H_2O) [*m*/*z*] (fragment, %): 390 (MH^+, 100), 334 ($C_{21}H_{24}N_3O^+$, 1), 269 ($C_{16}H_{19}N_3O^+$, 14), 244 ($C_{14}H_{18}N_3O^+$, 1), 201 ($C_{13}H_{17}N_2^+$, 6), 131 ($C_7H_5N_3^+$, 21), 93 ($C_7H_9^+$, 53); IR (Nujol, 293 K) [cm^{-1}]: 1702 (C=O), 1635 (C=N); NMR-spectra (*R*-configuration at C6): ^{1}H NMR ($CDCl_3$, 293 K) [ppm]: 0.98–1.01 (m, 1H), 1.54–1.73 (m, 3H), 2.20–2.23 (m, 1H), 2.25 (s, 3H), 2.34 (s, 3H), 2.51–3.12 (m, 6H), 3.53–3.58 (m, 1H), 3.78–3.83 (m, 1H), 6.62 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 6.97 (d, $^3J_{HH}$ = 7.9 Hz, 2H), 7.19 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.37 (d, $^3J_{HH}$ = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 293 K) [ppm]: 20.7, 21.1, 23.5, 27.4, 29.6, 35.6, 49.8, 57.9, 67.3, 94.3, 120.8, 128.5, 129.2, 129.5, 130.2, 134.4, 137.6, 147.4, 149.2, 175.2; *S*-configuration at C6: ^{1}H NMR ($CDCl_3$, 293 K) [ppm]: 0.94–1.32 (m, 2H), 1.35–2.04 (m, 4H), 2.25 (s, 3H), 2.36 (s, 3H), 2.55–3.15 (m, 4H), 3.52–3.74 (m, 2H), 4.05–4.18 (m, 1H) 6.74–7.28 (m, 8H); ^{13}C NMR ($CDCl_3$, 293 K) [ppm]: 20.5, 20.9, 23.0, 27.6, 29.6, 32.9, 50.2, 57.3, 66.4, 95.6, 120.8, 127.9, 128.3, 129.1, 129.9, 134.1, 136.7, 147.5, 149.5, 175.1.

4.5. Analytical data of ***2b***

1-(Mesityl) - 10-(mesityl)imino-hexahydropyrrolo-[2,1-h]-6-oxa-1,9-diaza-spiro[4.5]decan-2-one; yield: 54%; HRMS $C_{28}H_{35}N_3O_2$ (445.60): 446.28283, $C_{28}H_{36}N_3O_2$ (MH^+), Δ = −2.0777 mmu; MS (CI, H_2O) [*m*/*z*] (fragment, %): 446 (MH^+, 2), 390 ($C_{24}H_{27}N_3O_2^+$, 100), 374 ($C_{23}H_{23}N_3O_2^+$, 10), 136 ($C_7H_{10}N_3^+$, 15), 93 ($C_7H_9^+$, 85); IR (Nujol, 293 K) [cm^{-1}]: 1693 (C=O), 1634 (C=N); NMR-spectra (mixture of diastereomers): ^{1}H NMR ($CDCl_3$, 293 K) [ppm]: 0.92–1.22 (m, 2H), 1.28–1.65 (m, 4H), 1.82–2.45 (m, 18H), 2.52–2.78 (m, 2H), 2.85–3.52 (m, 4H), 3.89–4.02 (m, 1H), 6.80–6.96 (m, 2H), 7.23–7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 293 K) [ppm]: 18.7, 18.8, 18.9, 19.2, 19.4, 19.5, 19.6, 20.6, 20.9, 23.3, 23.9, 27.4, 28.3, 31.3, 31.7, 36.2, 38.4, 47.7, 48.1, 55.8, 56.8, 66.8, 69.3, 92.7, 97.2, 126.7, 127.0, 127.4, 127.5, 127.7, 128.4, 128.7, 128.9, 129.1, 129.5, 129.6, 130.2, 130.3, 132.0, 133.0, 137.9, 138.0, 138.3, 138.4, 138.7, 144.3, 144.8, 148.2, 152.0, 174.7, 175.8.

4.6. Analytical data of ***2c***

1-(*p*-Anisyl)-10-(*p*-anisyl)imino-hexahydropyrrolo-[2,1-h]-6-oxa-1,9-diaza-spiro[4.5]decan-2-one; yield >98%; HRMS $C_{24}H_{27}N_3O_4$ (421.50): 422.20851, $C_{24}H_{28}N_3O_4$ (MH^+), Δ = −0.52876 mmu; MS (CI, H_2O) [*m*/*z*] (fragment, %): 422 (MH^+, 98), 344 ($C_{21}H_{18}N_3O_2^+$, 9), 307 ($C_{18}H_{17}N_3O_2^+$, 8), 301 ($C_{17}H_{21}N_2O_3^+$, 21), 279 ($C_{16}H_{13}N_3O_2^+$, 19), 261 ($C_{16}H_{11}N_3O^+$, 24), 235 ($C_{14}H_9N_3O^+$, 50), 180 ($C_{11}H_4N_2O^+$, 13), 158 ($C_9H_6N_2O^+$, 48), 124 ($C_7H_{10}NO^+$, 100), 108 ($C_7H_{10}N^+$, 19), 84 ($C_5H_{10}N^+$, 14); IR (Nujol, 293 K) [cm^{-1}]: 1705 (C=O), 1631 (C=N); NMR-spectra (mixture of diastereomers): ^{1}H NMR ($CDCl_3$, 293 K) [ppm]: 0.75–1.40 (m, 2H), 1.43–2.52 (m, 4H), 2.65–3.28 (m, 4H), 3.36–3.72 (m, 2H), 3.72 (s, 3H), 3.79 (s, 3H), 4.08–4.21 (m, 1H), 6.39–6.52 (m, 1H), 6.65–7.09 (m, 4H), 7.17–7.68 (m, 3H); ^{13}C NMR ($CDCl_3$, 293 K) [ppm]: 23.2, 23.5, 27.5, 29.5, 32.8, 35.4, 49.8, 50.3, 55.3, 55.4, 57.3, 57.9, 66.2, 67.2, 94.3, 95.6, 113.2, 113.4, 113.7, 113.8, 114.0, 121.7, 121.8, 128.1, 128.9, 129.4, 129.6, 129.7, 130.5, 143.4, 149.9, 154.2, 154.3, 158.6, 159.0, 175.3.

4.7. Analytical data of **2d**

1-(*p*-Tolyl)-3-methyl-10-(*p*-tolyl)imino-hexahydro-pyrrolo- [2, 1-h]-6- oxa-1, 9-diaza- spiro[4.5] decan-2-one and 1-(*p*-tolyl)-4-methyl-10-(*p*-tolyl)imino-hexa-hydro-pyrrolo-[2,1-h]-6 - oxa-1,9-diaza - spiro[4.5]decan-2-one; yield >98%; HRMS $C_{25}H_{29}N_3O_2$ (403.52): 404.23366, $C_{25}H_{30}N_3O_2$ (MH^+), Δ=0.142100 mmu; MS (CI, H_2O) [*m*/*z*] (fragment, %): 404 (MH^+, 100), 334 ($C_{21}H_{24}N_3O^+$, 4), 269 ($C_{16}H_{19}N_3O^+$, 10), 245 ($C_{14}H_{19}N_3O^+$, 8), 156 ($C_7H_{14}N_3O^+$, 5), 136 ($C_8H_{10}NO^+$, 42), 108 ($C_7H_{10}N^+$, 56), 93 ($C_7H_9^+$, 94), 84 ($C_5H_{10}N^+$, 32); IR (Nujol, 298 K) [cm^{-1}]: 1731–1614 (several poorly resolved bands); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.75–1.09 (m), 1.09–1.42 (m), 1.42–1.61 (m), 1.61–1.84 (m), 2.07–2.51 (m), 2.51–2.59 (m), 2.59–3.01 (m), 3.02–3.22 (m,), 3.22–3.35 (m), 3.38–3.74 (m), 3.74–3.97 (m), 3.97–4.19 (m), 6.40–6.56 (m), 6.56–6.72 (m), 6.76–7.05 (m), 7.05–7.71 (m); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 13.2, 13.6, 13.6, 14.1, 14.5, 15.5, 17.5, 17.6, 20.6, 21.1, 21.1, 21.3, 23.1, 23.3, 23.5, 23.6, 26.1, 26.4, 26.9, 27.1, 27.2, 27.5, 29.2, 29.6, 34.6, 35.4, 36.1, 37.5, 37.6, 37.8, 38.6, 39.4, 40.2, 41.7, 42.1, 49.4, 49.8, 50.2, 50.3, 56.6, 56.8, 57.1, 57.3, 57.5, 58.0, 58.7, 66.1, 66.4, 67.3, 67.8, 67.9, 94.1, 95.6, 96.4, 96.6, 97.0, 118.7, 119.2, 119.5, 119.6, 119.7, 120.8, 120.9, 121.0, 122.5, 125.2, 127.2, 127.8, 128.1, 128.2, 128.3, 128.4, 128.4, 128.9, 128.9, 129.0, 129.1, 129.2, 129.3, 129.4, 129.4, 129.5, 129.6, 129.7, 129.8, 129.9, 130.0, 130.0, 130.1, 130.7, 133.7, 133.7, 134.0, 134.1, 134.4, 134.5, 134.9, 135.1, 136.3, 136.6, 136.9, 137.2, 137.4, 137.5, 137.5, 137.6, 137.7, 145.5, 147.1, 147.4, 147.5, 147.6, 147.6, 148.1, 148.3, 174.4, 174.6, 175.2, 175.5, 177.3, 178.0. The NMR spectra show that the crude reaction mixture at least consists of five stereoisomers (cf. signals for spiro carbon atoms 94.1–97.0 ppm). Resonances of low intensity thus may not be detectable, ^{1}H NMR spectra cannot be fully analyzed.

4.8. Analytical data of **2e**

1-(*p*- Tolyl)-3-(*n*-propyl)-10-(*p*-tolyl)imino-hexahydropyrrolo-[2,1-h]-6-oxa-1,9-diaza-spiro[4.5]decan-2-one and 1-(*p*-tolyl)-4-(*n*-propyl)-10-(*p*-tolyl)imino-hexa-hydropyrrolo-[2,1-h]-6-oxa-1,9-diaza-spiro[4.5] decan-2-one; yield: >98%; HRMS $C_{27}H_{33}N_3O_2$ (431.58): 432.26495, $C_{27}H_{34}N_3O_2$ (MH^+), Δ = 0.152220 mmu; MS (CI, H_2O) [*m*/*z*] (fragment, %): 432 (MH^+, 100), 334 ($C_{21}H_{24}N_3O^+$, 12), 245 ($C_{14}H_{19}N_3O^+$, 26), 219 ($C_{13}H_{19}N_2O^+$, 13), 201 ($C_{13}H_{17}N_2^+$, 6), 134 ($C_8H_{10}N_2^+$/$C_8H_8NO^+$, 22), 108 ($C_7H_{10}N^+$, 61), 84 ($C_5H_{10}N^+$, 17), 70 ($C_4H_8N^+$, 10); IR (in Nujol, 298 K) [cm^{-1}]: 1706 (vs, br) (C=O), 1634 (vs, br) (C=N); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.51–1.08 (m), 1.09–1.53 (m), 1.53–1.83 (m), 1.84–2.06 (m), 2.06–2.45 (m), 2.45–2.64 (m), 2.64–3.00 (m), 3.01–3.28 (m), 3.28–3.37 (m), 3.37–3.73 (m), 3.73–3,91 (m), 3.96–4.23 (m), 6.28–6.54 (m), 6.54–6.75 (m), 6.75–7.05 (m), 7.06–7.61 (m); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 13.9, 14.0, 14.3, 14.4, 20.3, 20.6, 20.7, 20.7, 20.8, 21.0, 21.1, 21.1, 21.4, 23.1, 23.2, 23.2, 23.4, 23.6, 27.0, 27.2, 27.3, 29.6, 30.8, 31.0, 31.6, 34.3, 35.4, 35.7, 36.2, 36.7, 39.7, 39.8, 43.9, 44.8, 47.5, 50.0, 50.4, 50.4, 56.7, 57.1, 57.6, 58.5, 66.1, 66.5, 66.8, 67.9, 67.9, 84.8, 95.3, 96.4, 96.5, 120.8, 120.9, 120.9, 125.2, 128.1, 128.3, 128.4, 128.5, 128.9, 129.0, 129.0, 129.1, 129.3, 129.3, 129.4, 129.5, 129.5, 129.7, 129.8, 130.0, 130.2, 130.3, 133.7, 134.1, 134.4, 135.2, 136.3, 136.6, 137.6, 137.7, 146.1, 147.4, 147.6, 147.9, 148.5, 174.5, 175.3, 175.7. The NMR spectra show that the crude reaction mixture at least consists of four stereoisomers (cf. signals for spiro carbon atoms 84.8–96.5 ppm). Resonances of low intensity thus may not be detectable, ^{1}H NMR spectra cannot be fully analyzed.

4.9. Analytical data of **2f**

1-(*p*-Tolyl)-3-(*n*-butyl)-10-(*p*-tolyl)imino-hexahydropyrrolo-[2, 1-h] - 6-oxa- 1,9-diaza-spiro[4.5]decan-2-one and 1-(*p*-tolyl)-4-(*n*-butyl)-10-(*p*-tolyl)imino-hexahydro-pyrrolo-[2,1-h]-6-oxa-1,9-diaza-spiro[4.5] decan-2-one; yield: >98%; HRMS $C_{28}H_{35}N_3O_2$ (445.60): 446.28113, $C_{28}H_{36}N_3O_2$ (MH^+), Δ = −0.37772 mmu; MS (CI, H_2O) [*m*/*z*] (fragment, %): 446 (MH^+, 100), 334 ($C_{21}H_{24}N_3O^+$, 9), 223 ($C_{15}H_{15}N_2^+$, 10), 201 ($C_{13}H_{17}N_2^+$, 6), 145 ($C_9H_9N_2^+$, 5), 134 ($C_8H_{10}N_2^+$/$C_8H_8NO^+$, 69), 108 ($C_7H_{10}N^+$, 38), 85 ($C_6H_{13}^+$, 69); IR (in Nujol, 298 K) [cm^{-1}]: 1715–1694 (vs, C=O), 1651–1622 (vs, C=N), several poorly resolved bands; ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.67–1.10 (m), 1.10–1.61 (m), 1.61–1.86 (m), 1.87–2.13 (m), 2.14–2.52 (m),

2.52–2.64 (m), 2.64–3.03 (m), 3.04–3.31 (m), 3.31–3.40 (m), 3.43–3.73 (m), 3.73–3.97 (m), 3.97–4.18 (m), 6.32–6.56 (m), 6.57–6.78 (m), 6.78–7.07 (m), 7.07–7.66 (m); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 12.6, 13.5, 13.6, 13.8, 13.9, 17.8, 20.6, 20.6, 21.0, 21.1, 21.3, 22.0, 22.5, 22.6, 22.7, 22.7, 23.1, 23.2, 23.3, 23.5, 23.8, 25.4, 26.2, 26.4, 26.9, 27.1, 27.3, 27.5, 27.7, 28.3, 28.8, 28.9, 29.3, 29.5, 29.6, 29.7, 29.8, 30.1, 30.4, 30.7, 31.0, 31.0, 31.5, 31.9, 32.2, 32.6, 33.0, 33.3, 34.6, 35.5, 35.7, 36.3, 37.6, 37.8, 38.9, 39.9, 40.6, 41.3, 42.5, 44.0, 45.0, 47.5, 47.7, 49.5, 50.0, 50.3, 50.4, 51.0, 52.8, 54.6, 56.7, 57.0, 57.3, 57.6, 58.0, 58.5, 66.1, 66.4, 66.8, 67.6, 67.8, 67.9, 92.7, 94.0, 94.3, 95.3, 96.4, 96.5, 96.8, 110.0, 114.0, 118.8, 119.5, 119.8, 120.4, 120.7, 120.8, 120.9, 121.8, 122.5, 123.7, 124.6, 125.2, 127.1, 127.3, 127.5, 127.6, 128.1, 128.2, 128.2, 128.2, 128.4, 128.5, 128.9, 128.9, 129.0, 129.1, 129.3, 129.4, 129.5, 129.6, 129.8, 129.9, 130.1, 130.2, 130.5, 130.8, 131.3, 132.0, 132.3, 133.8, 134.1, 134.4, 134.5, 135.1, 135.2, 136.2, 136.5, 136.9, 137.2, 137.3, 137.5, 137.6, 137.7, 139.0, 146.2, 147.4, 147.6, 147.6, 148.0, 148.6, 149.0, 149.3, 149.8, 149.9, 174.3, 174.5, 175.2, 175.6, 176.8, 176.9, 177.3. The NMR spectra show that the crude reaction mixture at least consists of six stereoisomers (cf. signals for spiro carbon atoms 92.7–96.8 ppm). Resonances of low intensity thus may not be detectable, ^{1}H NMR spectra cannot be fully analyzed.

4.10. Analytical data of **2g**

Polystyrene as well as oligomers of styrene, which are produced from excess styrene, were removed by extraction with anhydrous ethanol. Evaporation of the solvent led to **2g** with traces of styrene oligomers. 1-(*p*-tolyl)-3-(phenyl)-10-(*p*-tolyl)imino-hexahydropyrrolo-[2,1-h]-6-oxa-1,9-diaza-spiro[4.5]decan-2-one or 1-(*p*-tolyl)-4-(phenyl)-10-(*p*-tolyl)imino-hexa-hydropyrrolo-[2, 1-h]-6-oxa-1, 9-diaza-spiro[4.5]decan-2-one; yield: >98%; HRMS $C_{30}H_{31}N_3O_2$ (465.60): 465.24166, $C_{30}H_{31}N_3O_2$ (M^+), $\Delta = -0.03287$ mmu; MS (CI, H_2O) [*m*/*z*] (fragment, %): 466 (MH^+, 10), 334 ($C_{21}H_{24}N_3O^+$, 1), 313 ($C_{24}H_{25}^+$, 15), 245 ($C_{14}H_{19}N_3O^+$, 2), 235 ($C_{18}H_{19}^+$, 58), 219 ($C_{13}H_{19}N_2O^+$, 4), 207 ($C_{16}H_{15}^+$, 27), 136 ($C_8H_{10}NO^+$, 22), 134 ($C_8H_{10}N_2^+/C_8H_8NO^+$, 6), 131 ($C_{10}H_{11}^+$, 54), 108 ($C_7H_{10}N^+$, 26), 105 ($C_8H_9^+$, 100), 91 ($C_7H_7^+$, 34), 84 ($C_5H_{10}N^+$, 8), 78 ($C_6H_6^+$, 7); IR (Nujol, 298 K) [cm^{-1}]: 1721–1615 (C=O, C=N), several poorly resolved bands; ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.68–0.93 (m), 0.94–1.16 (m), 1.29–1.46 (m), 1.46–1.93 (m), 2.08–2.42 (m), 2.42–2.63 (m), 2.64–3.07 (m), 3.33–3.49 (m), 3.77–3.93 (m), 6.41–6.54 (m), 6.55–6.80 (m), 6.80–7.06 (m), 7.06–7.60 (m); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 20.7, 21.3, 23.3, 26.9, 35.0, 49.1, 53.0, 57.9, 68.2, 97.6, 120.8, 121.0, 121.1, 125.2, 125.5, 125.8, 126.0, 126.1, 126.2, 126.6, 126.8, 127.0, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.5, 128.6, 128.6, 128.8, 128.8, 129.2, 129.5, 129.5, 129.7, 130.1, 130.3, 130.6, 133.8, 134.6, 135.6, 136.9, 145.6, 147.4, 173.9, 174.8. The NMR spectra show that the crude reaction mixture at least consists of two stereoisomers (cf. signals for carbonyl carbon atoms 173.9 and 174.8 ppm). Resonances of low intensity thus may not be detectable, ^{1}H NMR spectra cannot be fully analyzed, carbon resonances of aromatic carbon atoms partly may be due to styrene oligomers.

4.11. Analytical data of **2h**

Yield: <5%; the desired product is only detectable by GC–MS or GC-IR methods but not by NMR; HRMS $C_{26}H_{29}N_3O_4$ (447.53): 448.22559, $C_{26}H_{30}N_3O_4$ (MH^+), $\Delta = -1.9587$ mmu; MS (CI, H_2O) [*m*/*z* (fragment)]: 448 (MH^+); IR (Nujol, 298 K) [cm^{-1}]: 1754–1694 (vs, C=O), 1634–1617 (vs, C=N), several poorly resolved bands.

4.12. Analytical data of **2i**

Yield: <5%; the desired product is only detectable by GC–MS or GC-IR methods but not by NMR; HRMS $C_{27}H_{33}N_3O_2$ (431.58): 431.25675, $C_{27}H_{33}N_3O_2$ (M^+), $\Delta = 0.527190$ mmu; MS (CI, H_2O) [*m*/*z* (fragment)]: 432 (MH^+); IR (Nujol, 298 K) [cm^{-1}]: 1738–1615 (vs, C=O, C=N), several poorly resolved bands.

4.13. Analytical data of **2k**

Yield: <5%; the desired product is only detectable by GC–MS or GC-IR methods but not by NMR; HRMS $C_{27}H_{33}N_3O_2$ (431.58): 431.25696, $C_{27}H_{33}N_3O_2$ (M^+), $\Delta = 0.287190$ mmu; MS (CI, H_2O) [*m*/*z* (fragment)]: 432 (MH^+); IR (Nujol, 298 K) [cm^{-1}]:

1738–1615 (vs, C=O, C=N), several poorly resolved bands.

4.14. Analytical data of **2l**

Yield: <5%; the desired product is only detectable by GC–MS or GC-IR methods but not by NMR; HRMS $C_{28}H_{33}N_3O_2$ (443.59): 444.26503, $C_{28}H_{34}N_3O_2$ (MH^+), $\Delta = 0.072220$ mmu; MS (CI, H_2O) [*m*/*z* (fragment)]: 444 (MH^+); IR (Nujol, 298 K) [cm^{-1}]: 1738–1615 (vs, C=O, C=N), several poorly resolved bands.

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