# Asymmetric 1,3-Dipolar Cycloadditions of 2-Diazocyclohexane-1,3-diones and Alkyl Diazopyruvates

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The 1,3-dipolar cycloaddition reactions of 2-diazocyclohexane-1,3-dione (**7a**; *Table 1*) and of alkyl diazopyruvates (**11a**–**e**; *Table 3*) to 2,3-dihydrofuran and other enol ethers have been investigated in the presence of chiral transition metal catalysts. With $Rh^{II}$ catalysts, the cycloadditions were not enantioselective, but those catalyzed by [$Ru^{II}Cl_2$(**1a**)] and [$Ru^{II}Cl_2$(**1b**)] proceeded with enantioselectivities of up to 58% and 74% ee, respectively, when diazopyruvates **11** were used as substrates. The phenyliodonium ylide **7c** yielded the adduct **8a** in lower yield and poorer selectivity than the corresponding diazo precursor **7a** (*Table 2*) upon decomposition with [Ru(pybox)] catalysts. This suggests that ylide decomposition by $Ru^{II}$ catalysts, contrary to that of the corresponding diazo precursors, does not lead to Ru-carbene complexes as reactive intermediates. Our method represents the first reproducible, enantioselective 1,3-cycloaddition of these types of substrates.

**Introduction.** – The transition-metal-catalyzed decomposition of diazo compounds carrying electron-accepting substituents differs significantly from that of simple diazo esters or diazo ketones. Thus, ethyl diazoacetoacetate (=ethyl 4-diazo-3-oxobutanoate) [1], ethyl diazopyruvate (=ethyl 3-diazo-2-oxopropanoate) [2][3] or 2-diazocyclohexane-1,3-diones [4] may react with olefins by formal 1,3-cycloadditions to afford dihydrofuran derivatives. The corresponding phenyliodonium ylides undergo the same 1,3-cycloadditions when exposed to transition metal catalysts [3][5]. Such cycloadditions occur typically with enol ethers, enol acetates, furans, and other polarizable olefins, but may also be observed with acetylenes [6][7], and even with styrene [8]. There is evidence that, in some cases, the cycloadditions are concerted [6][9]; however, a two-step mechanism involving an intermediate cyclopropane or cyclopropene, or a zwitterionic intermediate, is also conceivable.

The enantioselectivity of these reactions is controversial. The first examples of enantioselective cycloadditions of 2-diazodimedone (=2-diazo-5,5-dimethylcyclohexane-1,3-dione) to furan and dihydrofuran were reported in 1992 [10] and 1997 [11]. However, these initial results have not been confirmed.

Recently, we have re-investigated the cycloaddition of 2-diazocyclohexane-1,3-diones under the conditions described in the literature [10][11], but were unable to reproduce these results. In addition, only very modest enantioselectivities were observed with a large selection of structurally different, chiral $Rh^{II}$ catalysts [6][8]. This failure was tentatively attributed to the highly electrophilic nature of the intermediate metallocarbene, which is a consequence of the presence of the additional electron-withdrawing carbonyl substituent of the carbene. It is known that carbenoid reactions of diazoacetate esters carrying electron-donating substituents exhibit remarkably enhanced enantioselectivities in comparison to those of unsubstituted diazoacetates or

to diazoacetates with electron-accepting substituents. The *Hammett* reaction constant $\rho$ for the $[Rh_2^{II}\{(S)\text{-dosp}\}_4]$ catalyzed cyclopropanation of substituted styrenes with 4-methoxyphenyl diazoacetate is $-1.3$, while those for the corresponding phenyl and vinyl esters are $-1.0$[1]). In contrast, 2-diazomalonate and diazoacetate esters have $\rho$ constants of $-0.3$ and *ca.* 0. The carbenes having high negative $\rho$ values exhibit in general high enantioselectivities, while those with low negative $\rho$ values react with low enantioselectivity [12]. In application of the reactivity/selectivity principle [13], higher negative $\rho$ values of more-stabilized carbenes have been attributed to a later transition state for carbene transfer, and to a later transition state corresponds a higher selectivity. Unfortunately, these more-enantioselective carbenes do not, in general, undergo 1,3-dipolar cycloadditions.

In view of this, we turned our attention to Ru catalysts, which have been found to catalyze the cyclopropanation of certain olefins effectively, with high levels of asymmetric induction [14][15]. Actually, Ru has, besides Cu and Rh, emerged as the third important metal for carbenoid decomposition of diazo compounds [16]. In addition, Ru catalysts have recently been applied successfully to asymmetric nitrene transfer reactions [17]. We were particularly struck by the high $\rho$ value of $-2.5$ for the cyclopropanation of substituted styrenes with the catalyst $[Ru^{II}Cl\{pnnp\}]^+$ reported by *Bachmann* and *Mezzetti*[2]) [18]. This high negative reaction constant suggests that the Ru-carbene complexes might be more selective than their Rh analogues. In previous work, we had made the observation that the Ru-catalyzed diazo decomposition produced indeed metallocarbenes of rather low reactivity [19]. It, therefore, appeared plausible that the association of a highly reactive carbene with a Ru catalyst might produce a more-selective, yet sufficiently reactive, metallocarbene to effect the desired enantioselective cycloadditions of 2-diazocyclohexane-1,3-diones. On the other hand, we were aware that the reactivity/selectivity principle is controversial [20], and that extrapolations from Rh to Ru might be dangerous.

In this paper, we present our results concerning the asymmetric 1,3-dipolar cycloaddition of 2-diazocyclohexane-1,3-diones and diazopyruvate esters with olefins in the presence of various Ru catalysts containing the ligands **1**–**6** (*Figure*).

**Results and Discussion.** – 1. *Ruthenium-Catalyzed Cycloaddition of 2-Diazodimedone to 2,3-Dihydrofuran*. The diazo decomposition of 2-diazodimedone (**7a**) by 5 mol-% of the [Ru(pybox)] complex[3])of *Nishiyama et al.* [15], which was generated *in situ* from $[Ru(p\text{-cymene})Cl_2]_2$ and the chiral ligand **1b**, proceeded very sluggishly in toluene at room temperature. In the presence of 2,3-dihydrofuran, the cycloadduct **8a** was isolated after 3 d in 70 % yield (*Table 1*). No cyclopropane was detected in the mixture. The reaction time could be reduced to 16 h when 10 mol-% of catalyst was used. The enantioselectivity (in terms of enantiomeric excess; ee) varied from 55–57% ee at 25°. Increasing the temperature to 45° shortened the reaction time to 17 h (with 5 mol-% of catalyst), but slightly lowered the enantioselectivity (52% ee; *Table 1*). At

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[1]) dosp = (S)-[*N*-(4-Dodecylphenyl)sulfonyl]prolinate.

[2]) pnnp = *N*,*N*′-Bis[2-(diphenylphosphanyl)benzylidene]-1,2-diaminocyclohexane.

[3]) The term *pybox* stands for 2,6-bis(4,5-dihydro-1,3-oxazol-2-yl)pyridine.

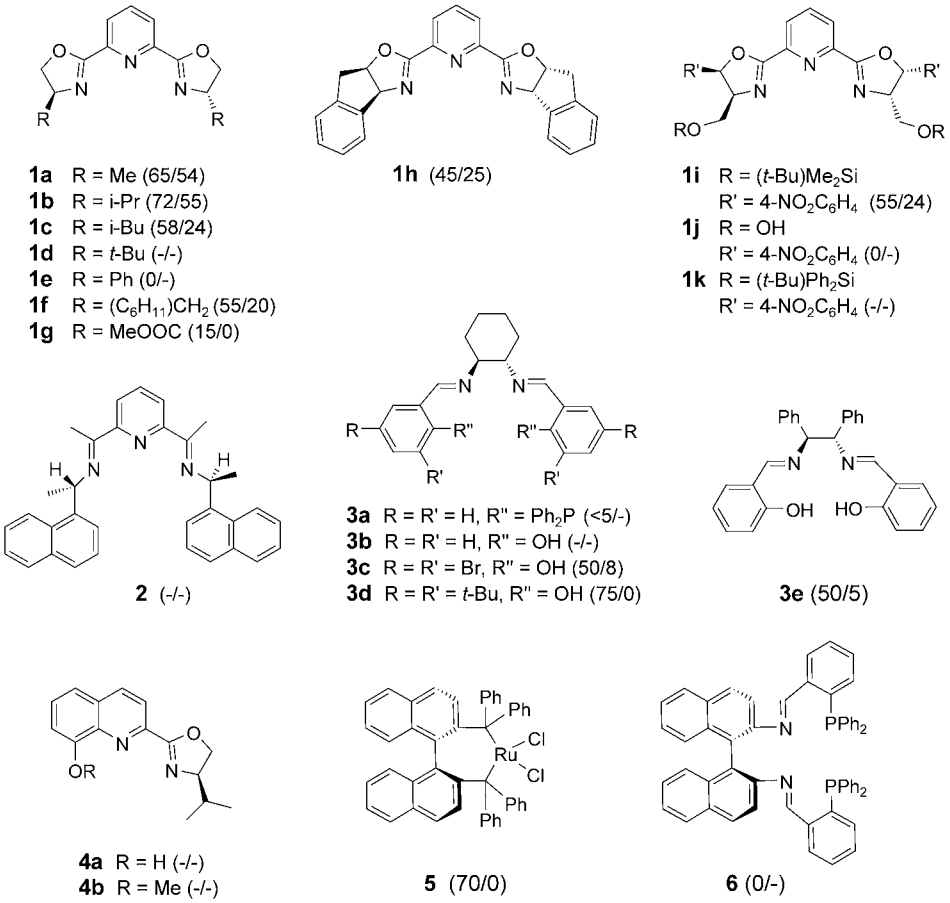


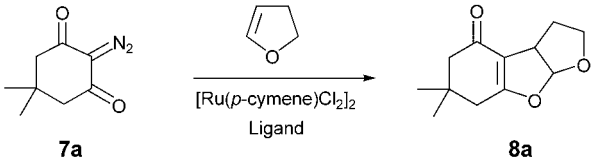

Figure. *Ligands* **1**–**6** *used in Ru catalyzed 1,3-dipolar cycloadditions.* The values in parentheses refer to yield/enantiomeric excess (%) of **8a** in the reaction between **7a** and 2,3-dihydrofuran (see *Table 1* below).

a temperature of 0°, basically no reaction took place, and the enantioselectivity was not increased.

Neither addition of silver salts ($AgPF_6$, $AgBF_4$) nor other solvents resulted in any improvement of the above transformation with ligand **1b**. With the pybox ligands **1a** and **1c**, similar results were obtained with respect to yield and selectivity as with **1b** (see *Figure*). The pnnp ligand [14] was also examined, but was found to be ineffective. Several other ligands were tested, but no significant enantioselectivities were achieved.

In contrast, the attempted cycloadditions of several structurally related 2-diazo-1,3-diones produced unsatisfactory results: methyl diazoacetoacetate, 2-diazocyclopentane-1,3-dione, and 3-diazo-2*H*-chromene-2,4-dione were unreactive towards the [Ru(pybox)] catalyst [$RuCl_2$(**1b**)] (data not shown). 2-Diazocyclohexane-1,3-dione (**7b**), in turn, reacted with 2,3-dihydrofuran with significantly lower yield and selectivity than **7a** (*Scheme 1*). The cycloaddition of the diazolactone **9** to **10** proceeded

Table 1. *Cycloaddition of Diazotized Dimedone* **7a** *to 2,3-Dihydrofuran in the Presence of the [Ru(pybox)] Catalyst [$RuCl_2$(***1b***)]*




**7a** **8a**

| Catalyst [mol-%] | Solvent | Time [h] | *T* [°] | Yield [%] | ee [%] |
|---|---|---|---|---|---|
| 5 | $CH_2Cl_2$ | 16 | 25 | 22 | 57 |
| 5 | $CH_2Cl_2$ | 18 | 25 | 40 | 57 |
| 10 | $CH_2Cl_2$ | 16 | 25 | 72 | 55 |
| 5 | $CH_2Cl_2$ | 72 | 25 | 70 | 56 |
| 5 | $CH_2Cl_2$ | 17 | 45 | 76 | 52 |
| 5 | $CH_2Cl_2$ | 72 | 0 | < 5 | 50 |
| 10[a]) | $CH_2Cl_2$ | 18 | 25 | 30 | 57 |
| 10[a]) | $CH_2Cl_2$ | 18 | 25 | 16 | 48 |
| 10 | $PhCH_3$ | 16 | 25 | 40 | 56 |
| 10 | HMI[b]) | 16 | 25 | 15 | 56 |
| 10 | THF | 16 | 25 | 25 | 55 |
| 10[c]) | $PhCH_3$ | 48 | 25 | 0 | – |

[a]) With $AgPF_6$ as additive. [b]) 1-Hexyl-3-methylimidazolium hexafluorophosphate. [c]) With [RuCl(**3a**)]($PF_6$).

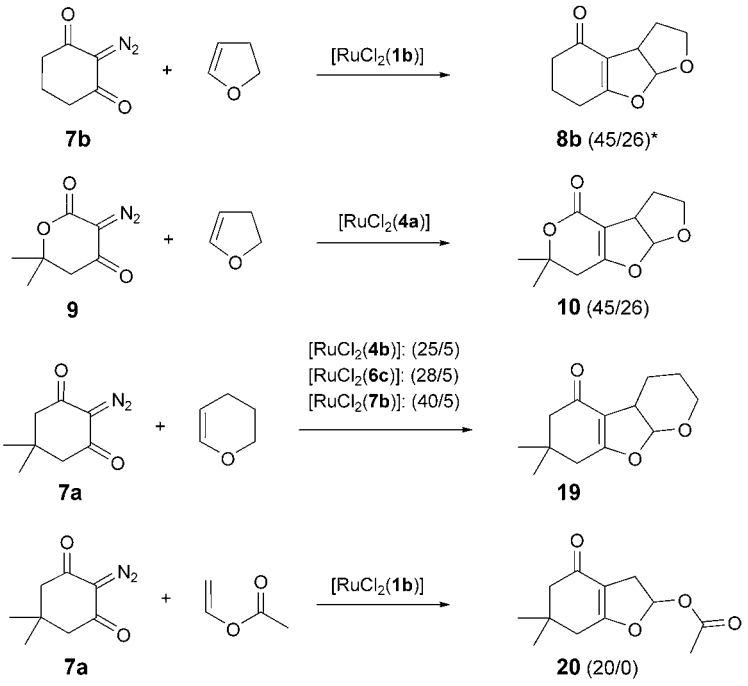
in both low yield and selectivity in the presence of ligand **4a**. No significant enantioselectivities resulted upon cycloaddition of **7a** to 3,4-dihydro-2*H*-pyran and vinyl acetate (*Scheme 1*), and no diazodecomposition of **7a** occurred in the presence of furan, ethyl vinyl ether, and *tert*-butyl vinyl ether.

2. *Ruthenium-Catalyzed Cycloaddition with a Phenyliodonium Ylide Derived from Dimedone.* In the case of $Rh^{II}$ and $Cu^{I}$ catalysts, the enantioselectivity for carbene transfer with diazo compounds is identical to that observed with the corresponding phenyliodonium ylides, although there are exceptions owing to occurrence of secondary reaction pathways [21]. This suggests that the reactions proceed *via* the same reactive intermediate, *i.e.*, the Rh- or Cu-complexed carbene. Since phenyliodonium ylides usually decompose under milder conditions than the corresponding diazo compounds, we have examined the suitability of the ylide **7c** as reagent for the Ru-catalyzed cycloadditions, in the hope of being able to carry out the reaction at lower temperature, thereby increasing the selectivity.

A series of cycloadditions to 2,3-dihydrofuran were carried out with **7c** and catalyst [$RuCl_2$(**1b**)] (*Table 2*). However, the yield of **8a** was disappointing and, in addition, the enantioselectivity was significantly below that obtained with the diazo precursor **7a** (see *Table 1*). Again, some other ligands were tested, but the resulting enantioselectivities were insignificant in all cases.

The poor yields indicate that the Ru catalysts were not sufficiently reactive to decompose the ylide efficiently to afford a Ru-carbene complex. Since the enantio-

*Scheme 1*

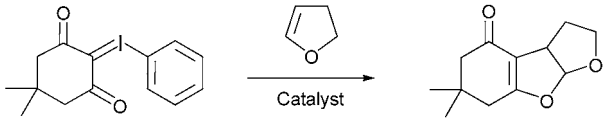



* Yield [%] / enantiomeric excess [%]

selectivity with ylide **7c** is different from that of the diazo precursor **7a** for a given ligand, its reaction may not proceed through the same reactive intermediate. While for the Ru-catalyzed diazo decomposition a metallocarbene intermediate is plausible [14–16], the intermediate resulting from decomposition of **7c** with the [Ru(pybox)] catalysts must be a different species, presumably **7c** associated to the Ru complex. Apparently, this intermediate is less sensitive to the presence of the chiral ligands than the (hypothetical) metallocarbene that results from decomposition of the diazo precursor **7a**. This contrasts with the situation observed in $Rh^{II}$ and $Cu^{I}$ catalyzed reactions, where decomposition of the ylide and the corresponding diazo precursor proceeds *via* the same intermediary metal-carbene complex.

3. *Enantioselective Cycloadditions of Alkyl Diazopyruvates.* In view of the low reactivity of 2-diazodimedone (**7a**) in Ru-catalyzed carbene transfer, and in view of the inability of Ru catalysts to decompose phenyliodonium ylides such as **7c** efficiently, we turned our attention to alkyl diazopyruvates of type **11** as substrates. It is well-known that the diazo decomposition of precursors having a single substituent on the diazo C-atom occurs under milder conditions than that of their disubstituted analogues [22]. Although diazopyruvates react with nonpolar olefins *via* cyclopropanation, they are known to undergo formal 1,3-dipolar cycloadditions to polarizable olefins such as 2,3-dihydrofuran [1][2].

Table 2. *Ru Catalyzed Cycloaddition of Phenyliodonium Ylide* **7c** *to 2,3-Dihydrofuran*. Conditions: catalyst, 10 mol-equiv.; 2,3-dihydropyran, 30-fold excess; ligand, three-fold excess rel. to Ru; in toluene at 20°.




**7c** **8a**

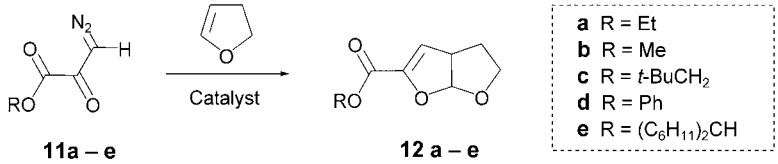
| Catalyst | Time [h] | Yield [%] | ee [%] |
|---|---|---|---|
| [Ru(*p*-cymene)$Cl_2$]$_2$ | 24 | 54 | – |
| [$RuCl_2$(**1b**)] | 24 | 35 | 15 |
| [$RuCl_2$(**1b**)] | 72 | 75 | 17 |
| [$RuCl_2$(**1b**)][a]) | 16 | 70 | 5 |
| [$RuCl_2$(**1b**)] | 48 | 55 | 0 |
| [$RuCl_2$(**1b**)][b]) | 48 | 40 | 0 |
| [$RuCl_2$(**1b**)][c]) | 48 | 55 | 11 |
| [$RuCl_2$(**1b**)][c]) | 48 | 52 | 12 |
| [$RuCl_2$(**1f**)] | 72 | 35 | 0 |
| [$RuCl_2$(**1g**)] | 72 | 26 | 0 |
| [$RuCl_2$(**1e**)] | 72 | 10 | 0 |
| [$RuCl_2$(**1k**)] | 72 | 35 | 0 |
| [$RuCl_2$(**2**)] | 72 | 34 | 0 |
| [$RuCl_2$(**3a**)] | 72 | 30 | 0 |
| [$RuCl_2$(**3b**)] | 72 | 25 | 0 |
| [$RuCl_2$(**6**)] | 72 | 28 | 12 |

[a]) Reaction conducted at 50°. [b]) In fluorobenzene. [c]) With $Ag^+PF_6^-$ as an additive (1.5-fold excess rel. to catalyst).

Ethyl diazopyruvate (**11a**) was prepared according to a literature procedure (see *Exper. Part*) [23]. The cycloaddition of **11a** to 2,3-dihydropyran was first examined with $Rh^{II}$ catalysts known to be efficient for diazo decomposition (*Table 3*). This reaction gave rise to the cycloadduct **12a** in acceptable yields (70–85%), but without significant enantioselectivity. No cyclopropane was detected in the reaction mixture. The same result was obtained with several $Cu^I$-based catalysts [24]. However, the diazo decomposition of **11a** proceeded smoothly at room temperature with different $Ru^{II}$ catalysts, giving rise to **12a–e** in medium-to-good yields within 15 h (*Table 3*), as described earlier in a preliminary communication [25].

The cycloaddition of **11a** to 2,3-dihydrofuran was optimized with the i-Pr substituted pybox ligand **1b**, giving rise to the catalyst [$RuCl_2$(**1b**)]. The best results were obtained in toluene, with 68% ee at room temperature. Upon lowering the temperature to 0°, **12a** was obtained in 74% ee. Variation of the ligand substituents R at the oxazolidine rings had a significant effect on the yield and ee value of the adduct. All ligands, except **1d** and **1e**, were efficient in diazo decomposition, and afforded **12a** in yields of 40–67%. When ligand **1e**, with its bulky Ph groups, was added to [$RuCl_2$(*p*-cymene)]$_2$, a color change was observed indicating formation of the corresponding Ru catalyst. However, no reaction occurred, even after prolonged reaction times or raising

Table 3. *Optimization of the Cycloaddition of Diazopyruvates* **11** *to 2,3-Dihydrofuran*. Conditions: catalyst, 10 mol-equiv.; 2,3-dihydropyran, 30-fold excess; ligand, threefold excess rel. to Ru; temperature, 25°.




**11a – e** **12 a – e**

| Product | Catalyst | Solvent | Yield [%] | ee [%] |
|---|---|---|---|---|
| **12a** | $[Rh_2(OAc)_4]$ | $PhCH_3$ | 85 | 0 |
| | $[Rh_2\{(S)\text{-tbsp}\}_4]$ | $PhCH_3$ | 70 | 0 |
| | $[Rh_2\{(S)\text{-ntv}\}_4]$ | $PhCH_3$ | 80 | 12 |
| | $[RuCl_2(\mathbf{1a})]$ | $PhCF_3$ | 50 | 58 |
| | $[RuCl_2(\mathbf{1b})]$ | Neat | 65 | 62 |
| | $[RuCl_2(\mathbf{1b})]$ | $PhCH_3$ | 65 | 68 |
| | $[RuCl_2(\mathbf{1b})]$[a]) | $PhCH_3$ | 68 | 74 |
| | $[RuCl_2(\mathbf{1b})]$ | $CH_2Cl_2$ | 55 | 56 |
| | $[RuCl_2(\mathbf{1b})]$ | $C_6H_{14}$ | 20 | 66 |
| | $[RuCl_2(\mathbf{1b})]$ | $PhCH_3$ | 36 | 26 |
| | $[RuCl_2(\mathbf{1d})]$ | $PhCH_3$ | 40 | < 5 |
| | $[RuCl_2(\mathbf{1e})]$ | $PhCH_3$ | 0 | – |
| | $[RuCl_2(\mathbf{1f})]$ | $PhCH_3$ | 50 | 22 |
| | $[RuCl_2(\mathbf{1g})]$ | $PhCH_3$ | 63 | 36 |
| | $[RuCl_2(\mathbf{1h})]$ | $PhCH_3$ | 67 | 47 |
| | $[RuCl_2(\mathbf{1i})]$ | $PhCH_3$ | 60 | 46 |
| | $[RuCl_2(\mathbf{1j})]$ | $PhCH_3$ | 50 | 11 |
| | $[RuCl(\mathbf{3a})](PF_6)$ | $PhCH_3$ | 0 | – |
| **12b** | $[RuCl_2(\mathbf{1b})]$ | $PhCH_3$ | 55 | 70 |
| **12c** | $[RuCl_2(\mathbf{1b})]$ | $PhCH_3$ | 50 | 65 |
| **12d** | $[RuCl_2(\mathbf{1b})]$ | $PhCH_3$ | 40 | 65 |
| **12e** | $[RuCl_2(\mathbf{1b})]$ | $PhCH_3$ | 80 | 59 |

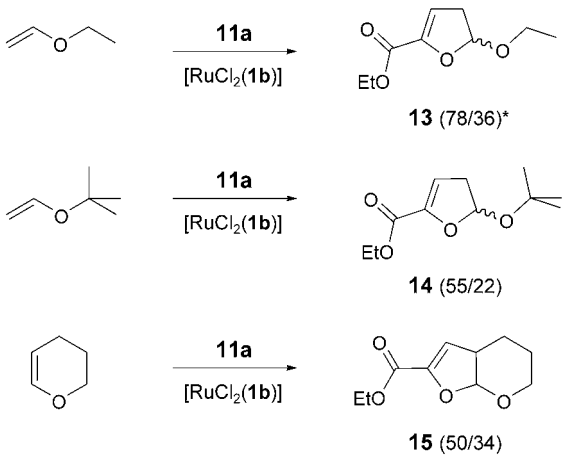
[a]) Reaction conducted at 0°.

the temperature. This is most likely due to steric hindrance. In the case of the *t*-Bu-substituted **1d**, no color change was observed at all when the ligand was added to $[RuCl_2(p\text{-cymene})]_2$; apparently, the complex did not form. The negligible ee value of $< 5\%$ indicated that diazo decomposition occurred with unreacted achiral $[RuCl_2(p\text{-cymene})]_2$.

The enantioselectivity of the above cycloaddition varied from 11 to 74% ee within the series of Ru catalysts tested, the highest ee value (74%) occurring with ligand **1b** (R = i-Pr). Sterically less-demanding ligands such as **1a** (R = Me) or **1f** (R = $C_6H_{11}CH_2$) afforded lower enantioselectivities (26 and 22% ee, resp.), while the bulkier ligands resulted in a less-reactive (for **1c**) or completely unreactive catalyst (for **1d**). The larger, disubstituted pybox ligands **1h** – **1j**, in turn, were found to be less effective than **1b** with respect to enantioselectivity. No cycloadduct was obtained with the $[RuCl_2\{pnnp\}]^+$ catalyst of *Bachmann* and *Mezzetti* [18]. The use of other alkyl pyruvates **11b** – **11e** had no significant effect on both the yield and enantioselectivity of the reaction.

The cycloaddition of **11a** to ethyl vinyl ether in the presence of [$RuCl_2$(**1b**)] proceeded, by analogy, to compound **13** in 78% yield (*Scheme 2*), but with lower enantioselectivity. Both yield and enantioselectivity dropped further with the more-hindered *tert*-butyl vinyl ether, which gave rise to adduct **14**. Finally, cycloaddition to 3,4-dihydro-2*H*-pyran afforded **15** [26] in lower yield and selectivity than in the case of 2,3-dihydrofuran (*Scheme 2*). However, no diazo decomposition of **11a** occurred in the presence of furan or vinyl acetate as substrates.

*Scheme 2*




* Yield [%] / enantiomeric excess [%]

4. *Enantioselective Cycloaddition of Ethyl 3-Diazo-3-(2-nitrophenyl)pyruvate and 2,3-Dihydrofuran*. Preliminary results have shown that ethyl 3-diazo-3-(2-nitrophenyl)pyruvate (**16**), which can be readily prepared from **17**, undergoes cycloaddition to 2,3-dihydrofuran upon diazo decomposition with $Rh^{II}$ and $Ru^{II}$ catalysts to **18** (*Scheme 3*). The regioselectivity of the reaction was derived from the $^1$H-NMR chemical shift of the single acetal H-atom of **18**, which resonates at $\delta$(H) 5.59, comparable to the corresponding H-atom in **12a** ($\delta$(H) 5.84). Whereas **18** obtained with the chiral $Rh^{II}$ catalyst [$Rh_2${(*S*)-nttl}$_4$][4]) was racemic, a low degree of chiral induction (5%) was obtained with [$RuCl_2$(**1b**)].

**Conclusions.** – To our knowledge, our findings represent the first reproducible, enantioselective 1,3-dipolar cycloadditions of 2-diazocyclohexane-1,3-diones and alkyl diazopyruvates to enol ethers. The enantioselectivity of the reactions are not yet satisfactory, but with the introduction of novel $Ru^{II}$-based catalysts, this problem might eventually be overcome. It was not possible, in the context of this project, to determine the absolute configurations of the adducts. However, we think that this project is sufficiently advanced and promising to be further elaborated in the future.

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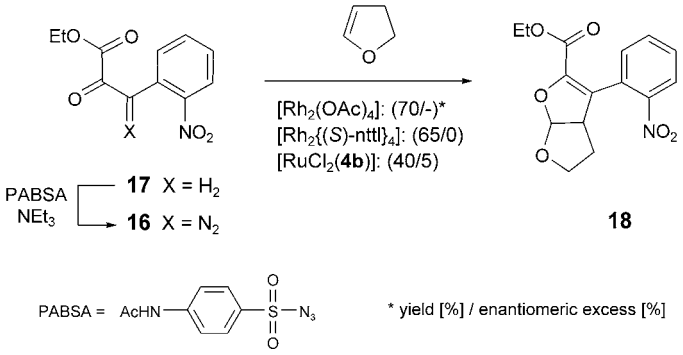
[4]) (*S*)-nttl = (*S*)-*N*-1,8-naphthoyl-*t*-leucinate.

*Scheme 3*

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## Experimental Part

1. *General:* see [27]. The following chiral ligands and catalysts were synthesized according to published procedures: **1a** [28]; **1b**, **1d**, **1e** [29]; **1c** [30]; **1i**–**k** and **1f** [31]; **1g** [32]; **1h** [33]; **2** [34]; **3a** and **6** [35]; **3b**–**d** [36]; **3e** [37]; **4a**,**b** [38]; $[Rh_2\{(S)\text{-nttl}\}_4]$ [39]; $[Rh_2\{(S)\text{-ntv}\}_4]$ [40]; $[Rh_2\{(S)\text{-tbsp}\}_4]$ [41]. Ligand **5** is commercially available. All reactions were carried out under inert Ar atmosphere. Toluene, $CH_2Cl_2$, and hexane were dried by passage through solvent-purification columns. 2,3-Dihydrofuran and (trifluoromethyl)benzene were distilled before use. Flash chromatography (FC): silica gel 0.32–0.636 μm (*Merck*). The enantiomeric excess (ee) was determined by chiral GC on a *Supelco β-dex* column under isothermal conditions, or by chiral HPLC; retention or elution times $\tau$ in min. NMR Spectra were recorded on a *Bruker AMX-300* spectrometer; $\delta$ in ppm, $J$ in Hz. EI- and ESI-MS: *Varian CH4* or *SM1* spectrometers; HR-MS: *VG-7070* analytical spectrometer; in $m/z$ (rel. %).

2. *Cycloadditions of Compounds* **7a**, **7b**, *and* **9**. 2.1. *Cycloaddition of* **7a** *to 2,3-Dihydrofuran* (see *Table 1*). The ligand 2,6-bis[(*S*)-4,5-dihydro-4-isopropyloxazol-2-yl]pyridine (**1b**; 72 mg, 0.24 mmol) in $CH_2Cl_2$ (1.0 ml) was added to a soln. of $[RuCl_2(p\text{-cymene})]_2$ (36 mg, 0.06 mmol) in $CH_2Cl_2$ (1.0 ml). The dark red mixture was stirred at r.t. for 1 h under Ar. The solvent was removed under reduced pressure, and the solid residue was taken up in 2,3-dihydrofuran (1.8 ml). Compound **7a** (100 mg, 0.6 mmol) [6] and toluene (3.0 ml) were added. After 16 h, the mixture was concentrated, and the residue was purified by FC ($SiO_2$; AcOEt/pentane 60:40) to afford *2,3,3a,4,5,6,7,8a-Octahydro-6,6-dimethylfuro[2,3-*b*][1]benzofuran-4-one* (**8a**; 90 mg, 72%). Pale yellow solid. M.p. 98°. GC ($T = 140°$): $\tau_1 = 40.2$, $\tau_2 = 41.8$. $[\alpha]_{20}^{D} = -124$ for 57% ee ($c = 1.0$, $CHCl_3$). For spectroscopic data, see [6].

2.2. *2,3,3a,4,5,6,7,8a-Octahydrofuro[2,3-*b*][1]benzofuran-4-one* (**8b**) [6]. As described in *Sect. 2.1*, but from **7b** and 2,3-dihydrofuran. Purification by FC ($SiO_2$, AcOEt/pentane 60:40) afforded **8b** in 45% yield. Yellow solid. $[\alpha]_{20}^{D} = -24$ for 26% ee ($c = 1.1$, $CHCl_3$). GC ($T = 150°$): $\tau_1 = 26.0$, $\tau_2 = 27.6$. For spectroscopic data, see [6].

2.3. *2,3,3a,6,7,8a-Hexahydro-6,6-dimethylfuro[3′,2′:4,5]furo[3,2-*c*]pyran-4(4*H*)-one* (**10**) [8]. As described in *Sect. 2.1*, but from **9** and 2,3-dihydrofuran. Purification by FC ($SiO_2$; AcOEt/pentane 60:40) afforded **10** in 45% yield. Yellow solid. M.p. 125°. GC ($T = 145°$): $\tau_1 = 67.1$, $\tau_2 = 69.4$. $[\alpha]_{20}^{D} = -50$ for 26% ee ($c = 1.2$, $CHCl_3$). For spectroscopic data, see [8].

2.4. *3,4,4a,5,6,7,8,9a-Octahydro-7,7-dimethylpyrano[2,3-*b*][1]benzofuran-5(2*H*)-one* (**19**) [5]. As described in *Sect. 2.1*, but from **7a** and 3,4-dihydro-2*H*-pyran. Purification by FC ($SiO_2$, AcOEt/pentane 60:40) afforded **19** in 25% yield. Yellow solid. M.p. 95°. GC ($T = 140°$): $\tau_1 = 63.9$, $\tau_2 = 65.7$. IR: 2960, 1640, 1220. $^1$H-NMR

(300 MHz, $CDCl_3$): 6.05 (*d*, *J* = 7.5, 1 H); 3.80 (*m*, 1 H); 3.15 (*m*, 1 H); 2.40 (*m*, 2 H); 2.20 (*m*, 2 H); 1.95 (*m*, 2 H); 1.55 (*m*, 2 H); 1.17 (*s*, 6 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 189.4 (*s*); 169.0 (*s*); 110.8 (*s*); 94.4 (*d*); 79.5 (*s*); 65.3 (*t*); 51.5 (*t*); 44.1 (*t*); 40.3 (*d*); 29.9 (*s*); 27.5 (*q*); 27.2 (*q*); 22.5 (*t*); 19.5 (*t*). MS: 222 (100, $M^+$).

2.5. *2-Acetoxy-2,3,4,5,6,7-hexahydro-6,6-dimethylbenzofuran-4-one* (**20**) [42]. As described in *Sect. 2.1*, but from **7a** and vinyl acetate. Purification by FC ($SiO_2$; AcOEt/pentane 60 : 40) afforded **20** in 20% yield. Yellow solid. M.p. 90°. GC (*T* = 140°): $\tau_1$ = 50.3, $\tau_2$ = 50.9. IR: 2960, 1750, 1640, 1220. $^1$H-NMR (300 MHz, $CDCl_3$): 6.58 (*dd*, *J* = 5.5, 1 H); 3.08 (*m*, 1 H); 2.81 (*m*, 1 H); 2.41 (*m*, 1 H); 2.35 (*m*, 1 H); 2.29 (*m*, 2 H); 2.15 (*s*, 3 H); 1.27 (*s*, 6 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 190.4 (*s*); 175.3 (*s*); 170.8 (*s*); 111.4 (*s*), 99.4 (*d*); 51.5 (*t*); 37.3 (*t*); 34.5 (*t*); 32.1 (*s*); 29.5 (*q*); 28.4 (*q*); 21.2 (*q*). MS: 255.22 (100, $M^+$).

3. *Syntheses of Alkyl 3-Diazopyruvates* **11**. 3.1. *Ethyl 3-Diazo-2-oxopropanoate* (**11a**) [23]. To a mixture of ethyl chloro(oxo)acetate (1.35 g, 9.9 mmol) in THF (20 ml) at 0° was added dropwise (trimethylsilyl)diazomethane (15 ml; 2M soln. in hexane). The mixture was stirred at r.t. for 3 h, the solvent was removed, and the product was purified by FC ($SiO_2$; AcOEt/pentane 30 : 70 → 50 : 50) to afford **11a** (900 mg, 70%). Pale yellow solid. M.p. 75°. IR: 3050, 2960, 2140, 1727, 1625. $^1$H-NMR (300 MHz, $CDCl_3$): 6.20 (*s*, 1 H); 4.35 (*q*, *J* = 7.1, 2 H); 1.40 (*t*, *J* = 7.1, 3 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 176.9 (*s*); 160.4 (*s*); 62.9 (*t*); 56.9 (*d*); 14.0 (*q*). HR-MS: 143.0857 ($[M+1]^+$, $C_5H_7N_2O_3^+$; calc. 143.0457).

3.2. *General Procedure for the Preparation of* **11b**–**11d**. To oxalyl chloride (= ethanedioyl dichloride) was added the appropriate alcohol (1 equiv.) in $CH_2Cl_2$ at 0° over 30 min. The mixture was stirred at r.t. for 1.5 h. The solvent and residual oxalylchloride were removed. The resulting oil was dissolved in THF (20 ml), and (trimethylsilyl)diazomethane (3 equiv; 2M soln. in hexane) was added dropwise. After stirring for 3 h at r.t., the mixture was concentrated, and the residue was purified by FC ($SiO_2$; AcOEt/pentane 70 : 30).

*Methyl 3-Diazo-2-oxopropanoate* (**11b**) [43]. Yield 75%. M.p. 95°. IR: 3050, 2965, 2142, 1720, 1621. $^1$H-NMR (300 MHz, $CDCl_3$): 6.18 (*s*, 1 H); 3.57 (*s*, 1 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 175.9 (*s*); 160.4 (*s*); 56.9 (*d*); 50.9 (*q*). HR-MS: 128.0230 ($C_4H_4N_2O_3^+$; calc. 128.0222).

*2,2-Dimethylpropyl 3-Diazo-2-oxopropanoate* (**11c**). Yield: 65%. IR: 3047, 2955, 2150, 1720, 1625. $^1$H-NMR (300 MHz, $CDCl_3$): 5.98 (*s*, 1 H); 3.81 (*s*, 1 H); 0.84 (*s*, 9 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 176.8 (*s*); 160.3 (*s*); 75.85 (*t*); 57.0 (*d*); 26.5 (*q*); 26.4 (*q*); 26.3 (*q*).

*Phenyl 3-Diazo-2-oxopropanoate* (**11d**) [44]. Yield 40%. M.p. 93°. IR: 3320, 3047, 2955, 2130, 1705, 1625. $^1$H-NMR (300 MHz, $CDCl_3$): 7.35 (*m*, 2 H); 7.25 (*m*, 1 H); 7.10 (*m*, 2 H); 6.15 (*s*, 1 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 176.2 (*s*); 159.3 (*s*); 150.1 (*s*); 129.2 (*d*); 126.5 (*d*); 121.2 (*d*); 56.8 (*d*).

*Dicyclohexylmethyl 3-Diazo-2-oxopropanoate* (**11e**). Yield 80%. M.p. 95°. IR: 3120, 2945, 2130, 1715, 1615. $^1$H-NMR (300 MHz, $CDCl_3$): 6.17 (*s*, 1 H); 3.85 (*t*, *J* = 6, 1 H); 2.07 (*m*, 2 H); 1.77–1.1 (*m*, 20 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 176.2 (*s*); 160.3 (*s*); 82.1 (*d*); 56.8 (*d*); 41.2 (*d*); 40.9 (*d*); 28.7 (*t*); 28.5 (*t*); 27.6 (*t*); 26.5 (*t*); 26.4 (*t*); 26.2 (*t*); 26.1 (*t*); 25.9 (*t*). HR-MS: 293.1813 ($[M+1]^+$, $C_{16}H_{25}N_2O_3^+$; calc. 293.1865).

4. *Cycloadditions of Diazopyruvates* **11** (see *Table 3*). 4.1. *Reaction of* **11a** *with 2,3-Dihydrofuran*. Ligand **1b** (86 mg, 0.294 mmol) in $CH_2Cl_2$ (1.0 ml) was added to a soln. of $[RuCl_2(p\text{-cymene})]_2$ (58 mg, 0.095 mmol) in $CH_2Cl_2$ (1.0 ml). The dark-red mixture was stirred at r.t. for 1 h under Ar. The solvent was removed under reduced pressure. Then, 2,3-dihydrofuran (1.4 ml) and **11a** (100 mg, 0.95 mmol) dissolved in toluene (3.0 ml) were added. The resulting suspension was stirred until the starting material disappeared (TLC). The mixture was concentrated, and the residue was purified by FC ($SiO_2$; AcOEt/pentane 60 : 40) to afford *ethyl 3a,4,5,6a-tetrahydrofuro[2,3-*b*]furan-2-carboxylate* (**12a**). Yield: 104 mg (68%). Pale yellow oil. GC (*T* = 140°): $\tau_1$ = 43.9, $\tau_2$ = 45.7. $[\alpha]_{20}^{D}$ = +17 for 74% ee (*c* = 1.12, $CHCl_3$). IR: 2983, 2281, 1737, 1633. $^1$H-NMR (300 MHz, $CDCl_3$): 6.25 (*d*, *J* = 8.0, 1 H); 5.84 (*d*, *J* = 3.5, 1 H); 4.32 (*q*, *J* = 9.3, 2 H); 4.11 (*m*, 1 H); 3.78 (*m*, 2 H); 2.13 (*m*, 1 H); 1.96 (*m*, 3 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 159.7 (*s*); 148.8 (*s*); 111.7 (*d*); 110.5 (*d*); 67.1 (*t*); 61.4 (*t*); 47.6 (*d*); 31.2 (*t*); 14.2 (*q*). HR-MS: 184.0718 ($M^+$, $C_9H_{12}O_4^+$; calc. 184.0736).

4.2. *Methyl 3a,4,5,6a-Tetrahydrofuro[2,3-*b*]furan-2-carboxylate* (**12b**). As described in *Sect. 4.1*, but with **11b**. Purification by FC ($SiO_2$, AcOEt/pentane 60 : 40) afforded **12b** in 55% yield. Yellow oil. GC (*T* = 140°): $\tau_1$ = 31.1, $\tau_2$ = 32.2. $[\alpha]_{20}^{D}$ = +17.0 for 70% ee (*c* = 1.12, $CHCl_3$). IR: 2958, 2880, 1753, 1633. $^1$H-NMR (300 MHz, $CDCl_3$): 6.17 (*d*, *J* = 8.3, 1 H); 5.83 (*d*, *J* = 2.9, 1 H); 4.50 (*q*, *J* = 8.5, 2 H); 3.97 (*m*, 1 H); 3.80 (*s*, 3 H); 2.04 (*m*, 1 H); 1.79 (*m*, 1 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 158.9 (*s*); 149.5 (*s*); 111.7 (*d*); 110.5 (*d*); 67.0 (*t*); 52.6 (*d*); 42.5 (*q*); 34.3 (*t*). HR-MS: 170.0622 ($M^+$, $C_8H_{10}O_4^+$; calc. 170.0579).

4.3. *2,2-Dimethylpropyl 3a,4,5,6a-Tetrahydrofuro[2,3-*b*]furan-2-carboxylate* (**12c**). As described in *Sect. 4.1*, but with **11c**. Purification by FC ($SiO_2$; AcOEt/pentane 60 : 40) afforded **12c** in 50% yield. Yellow oil. GC (*T* = 140°): $\tau_1$ = 53.2, $\tau_2$ = 54.8. $[\alpha]_{20}^{D}$ = +16.8 for 65% ee (*c* = 1.2, $CHCl_3$). IR: 2940, 2870, 2180, 1734, 1615. $^1$H-NMR (300 MHz, $CDCl_3$): 6.24 (*d*, *J* = 8.3, 1 H); 5.78 (*d*, *J* = 3.5, 1 H); 4.09 (*t*, *J* = 10.8, 1 H); 3.93 (*s*, 1 H);

3.92 (*s*, 1 H); 3.75 (*m*, 2 H); 2.12 (*m*, 1 H); 1.96 (*m*, 1 H); 0.98 (*s*, 9 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 159.8 (*s*), 148.8 (*s*), 111.3 (*d*), 110.3 (*d*), 74.3 (*t*), 67.2 (*t*), 47.5 (*d*), 31.8 (*s*), 31.2 (*t*), 26.4 (*q*).

4.4. *Phenyl 3a,4,5,6a-Tetrahydrofuro[2,3-*b*]furan-2-carboxylate* (**12d**). As described in *Sect. 4.1*, but with **11d**. Purification by FC ($SiO_2$; AcOEt/pentane 60:40) afforded **12d** in 40% yield. Yellow oil. HPLC (*OD-H* column; i-PrOH/hexane 95:5): $\tau_1 = 21.8$, $\tau_2 = 29.9$. $[\alpha]_{20}^{D} = +16.4$ for 65% ee ($c = 1.2$, $CHCl_3$). IR: 2920, 2840, 1705, 1598, 870. $^1$H-NMR (300 MHz, $CDCl_3$): 7.43 (*m*, 3 H); 7.18 (*d*, $J = 11.8$, 2 H); 6.32 (*d*, $J = 8.3$, 1 H); 6.06 (*d*, $J = 3.6$, 1 H); 4.14 (*m*, 1 H); 3.86 (*m*, 2 H); 2.18 (*m*, 1 H); 2.04 (*m*, 1 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 157.9 (*s*); 150.1 (*s*); 148.1 (*s*); 113.6 (*d*); 110.6 (*d*); 129.5 (*s*); 126.1 (*s*); 121.4 (*s*); 67.2 (*t*); 47.8 (*d*); 31.2 (*t*).

4.5. *Dicyclohexylmethyl 3a,4,5,6a-Tetrahydrofuro[2,3-*b*]furan-2-carboxylate* (**12e**). As described in *Sect. 4.1*, but with **11e**. Purification by FC ($SiO_2$; AcOEt/pentane 60:40) afforded **12e** in 87% yield. Yellow solid. M.p. 63–65°. HPLC (*OD-H* column; i-PrOH/hexane 5:95): $\tau_1 = 17.9$, $\tau_2 = 26.6$). $[\alpha]_{20}^{D} = +13.6$ for 59% ee ($c = 0.70$, $CHCl_3$). IR: 2890, 2830, 2150, 1759, 16120. $^1$H-NMR (300 MHz, $CDCl_3$): 6.26 (*d*, $J = 6.1$, 1 H); 5.79 (*d*, $J = 2.8$, 1 H); 4.78 (*m*, 1 H); 4.12 (*m*, 1 H); 4.10–3.72 (*m*, 2 H); 2.12 (*m*, 1 H); 1.96 (*m*, 1 H); 2.12–1.55 (*m*, 22 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 158.8 (*s*); 147.9 (*s*); 110.0 (d); 109.3 (*d*); 82.6 (*d*); 67.1 (*t*); 47.6 (*d*); 37.3 (*d*); 37.2 (*d*); 31.2 (*t*); 29.9 (*t*); 29.8 (*t*); 29.6 (*t*); 27.6 (*t*); 27.4 (*t*); 26.4 (*t*); 26.23 (*t*); 26.21 (*t*); 26.1 (*t*); 26.0 (*t*). HR-MS: 334.2148 ($M^+$, $C_{20}H_{30}O_4^+$; calc. 334.2144).

4.6. *Ethyl 5-Ethoxy-4,5-dihydrofuran-2-carboxylate* (**13**). As described in *Sect. 4.1*, but with **11a** and ethyl vinyl ether. Purification by FC ($SiO_2$; AcOEt/pentane 60:40) afforded **13** in 78% yield. Yellow oil. GC ($T = 130°$): $\tau_1 = 56.4$, $\tau_2 = 57.4$. $[\alpha]_{20}^{D} = +11.5$ for 36% ee ($c = 1.1$, $CDCl_3$). IR: 2944, 2275, 1732, 1630. $^1$H-NMR (300 MHz, $CDCl_3$): 5.88 (*dd*, $J = 2.7$, 2.9, 1 H); 5.59 (*dd*, $J = 7.0$, 2.5, 1 H); 4.21 (*qq*, $J = 7.0$, 1.8, 2 H); 3.86 (*qtqt*, $J = 7.0$, 1 H); 3.53 (*qt*, $J = 7.0$, 1 H); 2.90 (*dddd*, $J = 7.0$, 18, 2.5 Hz, 1 H); 2.6 (*dddd*, $J = 18$, 2.9, 2.9, 1 H); 1.3 (*t*, $J = 7$, 3 H); 1.2 (*t*, $J = 7$, 3 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 160.2 (*s*); 146.6 (*s*); 110.0 (*d*); 105.5 (*d*); 64.2 (*t*); 61.1 (*t*); 37.4 (*t*); 15.0 (*q*); 14.2 (*q*).

4.7. *Ethyl 5-(*tert*-Butoxy)-4,5-dihydrofuran-2-carboxylate* (**14**). As described in *Sect. 4.1*, but with **11a** and *tert*-butyl vinyl ether. Purification by FC ($SiO_2$; AcOEt/pentane 60:40) afforded **14** in 55% yield. Yellow oil. GC ($T = 140°$): $\tau_1 = 27.5$, $\tau_2 = 28.2$. $[\alpha]_{20}^{D} = +12.9$ for 22% ee ($c = 1.9$, $CDCl_3$). IR: 2954, 2235, 1742, 1610. $^1$H-NMR (300 MHz, $CDCl_3$): 5.94 (*m*, 2 H); 4.30 (*q*, $J = 9.3$, 2 H); 3.01 (*dddd*, $J = 3.5$, 9.8, 24, 1 H); 2.61 (*dddd*, $J = 4$, 8, 24, 1 H); 1.34 (*m*, 12 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 159.5 (*s*); 147.8 (*s*); 109.7 (*d*); 100.6 (*d*); 60.5 (*t*); 38.1 (*t*); 28.8 (*q*); 14.2 (*q*). HR-MS: 214.1223 ($M^+$, $C_{11}H_{18}O_4^+$; calc. 214.1205).

4.8. *Ethyl 3a,5,6,7a-Tetrahydro-4*H*-furo[2,3-*b*]pyran-2-carboxylate* (**15**) [25]. As described in *Sect. 4.1*, but with **11a** and 3,4-dihydro-2*H*-pyran. Purification by FC ($SiO_2$; AcOEt/pentane 60:40) afforded **15** in 50% yield. Yellow oil. GC ($T = 140°$): $\tau_1 = 41.8$, $\tau_2 = 43.5$. $[\alpha]_{20}^{D} = +12.3$ for 34% ee ($c = 1.3$, $CDCl_3$). IR: 2920, 2854, 2180, 1732, 1632. $^1$H-NMR (300 MHz, $CDCl_3$): 6.00 (*d*, $J = 3.8$, 1 H); 5.88 (*d*, $J = 10.0$, 1 H); 4.35 (*m*, 3 H); 3.90 (*m*, 2 H); 1.95 (*m*, 2 H); 1.61 (*m*, 2 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 158.3 (*s*); 148.6 (*s*); 112.7 (*d*); 101.5 (*d*); 67.1 (*t*); 62.4 (*t*); 47.5 (*d*); 31.2 (*t*); 28.6 (*d*); 14.1 (*q*).

5. *Cycloaddition of* **16** *to 2,3-Dihydrofuran.* 5.1. *Ethyl 3-Diazo-3-(2-nitrophenyl)-2-oxopropanoate* (**16**). To 4-methylbenzenesulfonic acid (TsOH; 545 mg, 2.8 mmol) in EtOH (100 ml) was added dropwise '*o*-nitrophenylpyruvic acid' (= 3-(2-nitrophenyl)-2-oxopropanoic acid; 3.00 g, 14 mmol) in EtOH (50 ml). The mixture was heated at reflux for 12 h. The solvent was removed, and the resulting residue was distilled at $120°/10^{-2}$ mm Hg to afford ethyl 3-(2-nitrophenyl)-2-oxopropanoate. The latter (1.0 g, 4.2 mmol) was dissolved in MeCN (60 ml) at 0°, and 4-(acetylamino)benzenesulfonyl azide (1.00 g, 4.2 mmol) and $Et_3N$ (430 mg, 4.25 mmol) were added. The mixture was stirred for 15 h. The solvent was evaporated, and the residue was purified by FC ($SiO_2$; AcOEt/pentane 70:30) to afford **16** (330 mg, 45%). Colorless oil. IR: 3340, 2980, 2854, 1732, 1702, 1598, 1542. $^1$H-NMR (300 MHz, $CDCl_3$): 8.19 (*d*, $J = 8.2$, 1 H); 7.75 (*m*, 1 H); 7.60 (*m*, 21 H); 4.40 (*m*, 2 H); 1.35 (*m*, 3 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 189.4 (*s*); 171.2 (*s*); 160.6 (*s*); 133.9 (*d*); 133.7 (*d*); 132.6 (*d*); 125.6 (*d*); 103.6 (*s*); 63.4 (*t*);14.2 (*q*).

5.2. *Ethyl 3a,4,5,6a-Tetrahydro-3-(2-nitrophenyl)furo[2,3-*b*]furan-2-carboxylate* (**18**). Prepared as described in *Sect. 4.1*, but with **16** and 2,3-dihydrofuran. Purification by FC ($SiO_2$; AcOEt/pentane 60:40) afforded **18** in 50% yield. Yellowish solid. M.p. 110°. HPLC (*OJ* column, EtOH/hexane 10:90): $\tau_1 = 40.6$, $\tau_2 = 49.6$. IR: 2980, 2854, 1732, 1620, 1542. $^1$H-NMR (300 MHz, $CDCl_3$): 7.99 (*dd*, $J = 1.5$, 7.8, 1 H); 7.62 (*tt*, $J = 1.5$, 7.3, 1 H); 7.30 (*tt*, $J = 1.0$, 7.6, 1 H); 7.10 (*d*, $J = 8.1$, 1 H); 5.59 (*d*, $J = 5.1$, 1 H); 4.36 (*m*, 3 H); 4.04 (*m*, 1 H); 3.96 (*m*, 1 H); 2.69 (*m*, 1 H); 2.41 (*m*, 1 H); 1.35 (*t*, $J = 7.1$, 3 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 183.8 (*s*); 163.7 (*s*); 152.0 (*s*); 135.8 (*d*); 127.8 (*d*); 125.8 (*d*); 120.1 (*s*); 119.8 (*d*); 94.4 (*d*); 93.1 (*s*); 67.9 (*d*); 67.3 (*t*); 62.9 (*t*); 28.8 (*t*); 14.1 (*q*).

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