Hetero Diels–Alder Reactions of Nitroso Alkenes with Alkoxyallene Derivatives Bearing Carbohydrate Auxiliaries: Asymmetric Synthesis of 6*H*-1,2-Oxazines and Subsequent Reductive Transformations

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Abstract: Alkoxyallene derivatives **1a**–**f** bearing carbohydrate auxiliaries at the oxygen were examined in asymmetric hetero Diels–Alder reactions with nitroso alkenes. Diacetoneglucose derived compound **1a** turned out to be the best precursor furnishing the primary cycloadducts **3a**–**c** with a diastereomeric ratio of approximately 90:10. Isomerization provided the thermodynamically more stable 6*H*-1,2-oxazines **4a**–**c**. Similarly, diacetonefructose derived allene **1f** gave compounds **4h**–**j** with good efficiency. Gratifyingly, it turned out that **1a** and **1f** were complementary with respect to the preferential absolute configuration at C-6 of 6*H*-1,2-oxazines **4a**–**c** and **4h**–**j**, respectively. Cycloadducts derived from **1a** have 6*S* configuration in excess whereas those derived from **1f** are predominantly 6*R* configured. Exhaustive hydrogenolysis of 6*H*-1,2-oxazines **4a** and **4h** in the presence of palladium on charcoal furnished the expected primary amine **5** in an enantioenriched form. If this reduction was performed under addition of hydrochloric acid, pyrrolidine derivative **6** together with secondary amine **7** as side product were isolated.

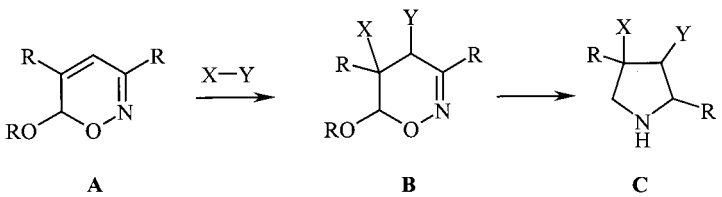
Key words: allenes, carbohydrates, asymmetric synthesis, hetero Diels–Alder reaction, 6*H*-1,2-oxazines, reduction, pyrrolidines

Introduction

6*H*-1,2-Oxazines **A** are heterocycles with promising potential for stereoselective synthesis of polyfunctionalized compounds. We already described their reductive conversions into γ-amino alcohols, pyrrolidine derivatives, amino acids and γ-lactams.[1,2] Even more important are the addition reactions to the 4,5-C,C double bond of 6*H*-1,2-oxazines. Additions of nucleophilic and electrophilic reagents,[3] cycloadditions[4] and dihydroxylations[5] furnish a great variety of highly substituted 5,6-dihydro-4*H*-1,2-oxazines **B**. These heterocycles serve subsequently as intermediates for stereoselective preparation of various interestingly functionalized compounds, for instance pyrrolidines **C**[6] (Scheme 1). So far these reactions have only been described with racemic 6*H*-1,2-oxazines as precursor compounds. However, we had reported preliminary examples on asymmetric hetero Diels–Alder reactions[7] demonstrating that enantiomerically highly enriched 6*H*-1,2-oxazines can be obtained when an alkoxyallene with a diacetoneglucose auxiliary was employed.[8] These promising results encouraged us to study the [4+2] cycloaddition in more detail using different carbohydrate based chiral auxiliaries.

Asymmetric Cycloadditions

The synthesis of the required enantiopure alkoxyallene derivatives **1** with the auxiliary group R^1 was published earlier.[9] Their reaction with in situ generated nitroso alkenes[10] is illustrated in Schemes 2– 4 and summarized in Table 1. Treatment of the corresponding α-halogen oxime **2** with freshly ground sodium carbonate delivers a low stationary concentration of the highly reactive nitroso alkenes which were trapped by the alkoxyallene **1** present (1–1.25 equiv). Thus, on trapping with the above-mentioned diacetoneglucose derived allene **1a**, these three nitroso alkenes gave excellent yields of the primary hetero Diels–Alder adducts **3a**–**c** with an exocyclic 5-methylene group (Scheme 2). The ratio of diastereomers (dr) was determined by NMR spectroscopy and is in the range of 90:10 for these three examples (Table 1, entries 1–3). Thus, the diacetoneglucose moiety has a surprisingly high inducing quality.



Scheme 1

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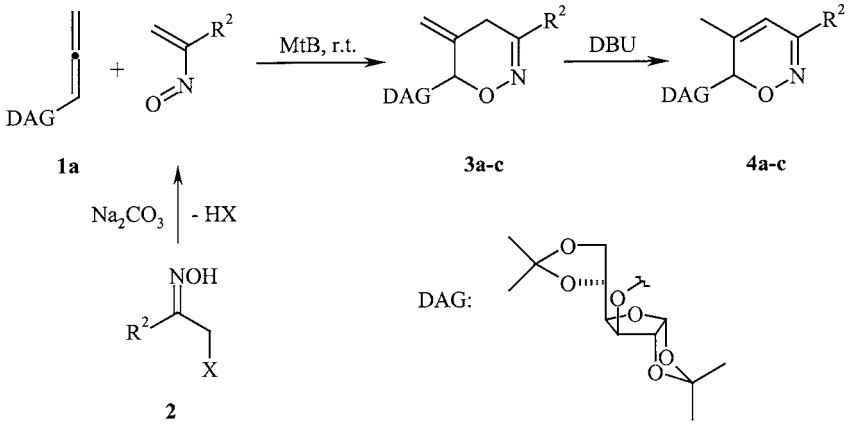


Scheme 2

The relatively labile primary adducts **3a**–**c** were converted into the thermodynamically more stable 5-methyl-6*H*-1,2-oxazines **4a**–**c** with a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[11] For **4a** and **4c** only one diastereomer could be detected by NMR whereas the dr for **4b** decreased slightly during isomerization (Table 1, entries 1–3). It is not clear whether differences at the stage of **3** and **4** are due to the inaccuracy of the NMR analysis or to enrichment of one diastereomer during the purification of **4**. It should also be mentioned that 1,2-oxazine-3-carboxylate **4b** (and also **4i**) is rather unstable and cannot be purified completely. The yields for the syntheses of **4a** and **4c** over the two steps are good. From **4a** suitable crystals could be obtained and an X-ray analysis showed that C-6 of the 1,2-oxazine ring has an *S* configuration.[12]

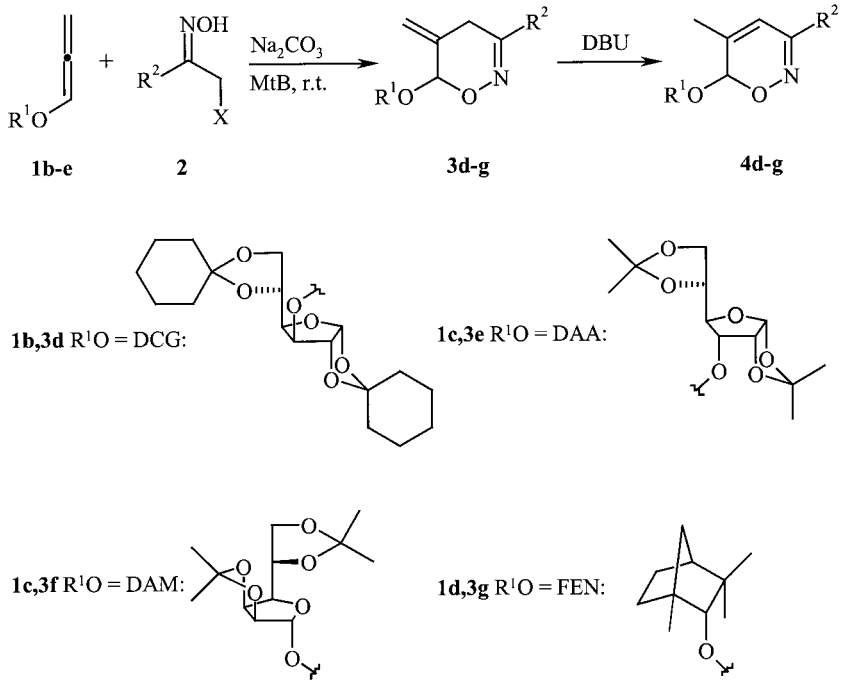
With α-nitrosostyrene as the standard heterodiene we investigated the influence of other carbohydrate auxiliaries in **1** on the diastereoselectivity of the Diels–Alder reaction (Scheme 3, Table 1). Exchange of the (dimethyl)methyl units in **1a** with cyclohexyl moieties in **1b** (dicyclohexanoneglucose as auxiliary) had no dramatic effect on the stereoselectivity of the cycloaddition. After base-catalyzed isomerization to 6*H*-1,2-oxazine **4d** an even slightly reduced dr of 90:10 was determined (entry 4). The configuration of the allenyloxy bearing carbon of the auxiliary was then inverted which led to diacetoneallose derivative **1c**. Rather surprisingly, its cycloaddition with α-nitrosostyrene was completely unselective furnishing a 50:50 mixture of the two possible diastereomers of **4e** (entry 5). The diastereoselectivity was again high when mannose derivative **1d** was used as dienophile which furnished 6*H*-1,2-oxazine **4f** as a 87:13 mixture (entry 6). We also studied fenchol derivative **1e** which provided the expected heterocycle **4g** in low yield and moderate diastereomeric ratio (entry 7).

With respect to carbohydrate auxiliaries we finally employed diacetonefructose modified allene **1f** (Table 1, entries 8–10, Scheme 4). Although the diastereoselectivities

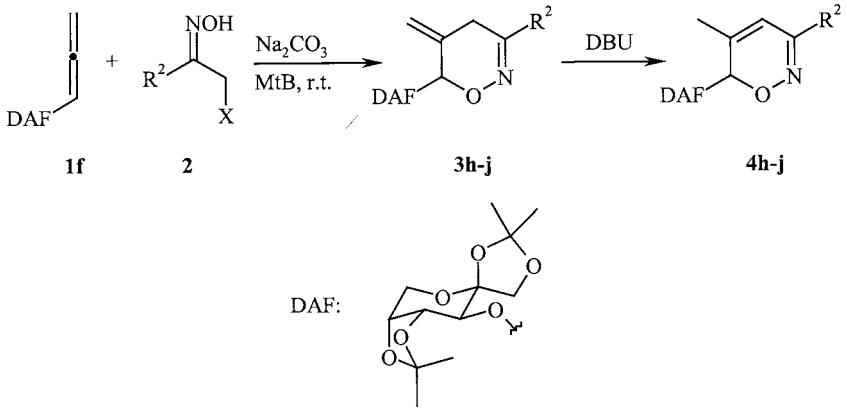
Table 1 Synthesis of **3** and Isomerization to **4**

Entry	**1**	R^1O	R^2	X	**3**	dr[a]	**4**	(6*S*):(6*R*)	Total Yield (%)
1	**1a**	DAG	Ph	Cl	**3a**	90:10	**4a**	>95:5	51
2	**1a**	DAG	CO_2Et	Br	**3b**	86:14	**4b**	79:21	82[b]
3	**1a**	DAG	CF_3	Br	**3c**	92:8	**4c**	>95:5	69
4	**1b**	DCG	Ph	Cl	**3d**	nd	**4d**	90:10	59
5	**1c**	DAA	Ph	Cl	**3e**	nd	**4e**	50:50	83
6	**1d**	DAM	Ph	Cl	**3f**	nd	**4f**	87:13	56
7	**1e**	FEN	Ph	Cl	**3g**	64:36	**4g**	68:32	29
8	**1f**	DAF	Ph	Cl	**3h**	23:77	**4h**	22:78	56
9	**1f**	DAF	CO_2Et	Br	**3i**	nd	**4i**	19:81	60[b]
10	**1f**	DAF	CF_3	Br	**3j**	18:82	**4j**	15:85	63

[a] nd = not determined.
[b] Crude product; purification by chromatography and distillation, respectively, was not possible.



Scheme 3



Scheme 4

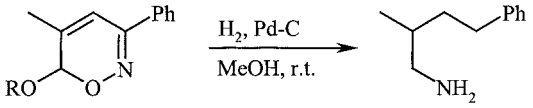
in its hetero Diels–Alder reactions with the three α-nitroso alkenes were in the range of 20:80 and not as high as those with diacetoneglucose, the results are particularly intriguing since with this auxiliary an inversion of the sense of diastereoselectivity could be observed. As shown by the subsequent reactions described below 1,2-oxazines **4h–j** have predominatly *R* configuration at C-6.

Reductions of 6*H*-1,2-oxazines

Catalytic reduction of 5,6-dihydro-4*H*-1,2-oxazines with hydrogen provides either pyrrolidine derivatives or – if the substituent at C-3 is an aryl group – it may also furnish acyclic amines which arise from reductive cleavage of the benzylic C–N bond of the intermediate pyrrolidines.[6] The mechanism of this multi-step reactions has been described and the behaviour of differently substituted 1,2-oxazines has been studied in many examples.[1,6b] Reduction of 6*H*-1,2-oxazines with hydrogen first saturates the 4,5-C,C double bond and therefore leads to identical product types. In this paper, we describe singular examples which allowed us to determine the predominating absolute configuration at C-6 of several 6*H*-1,2-oxazines **4** by comparison of the products with known compounds.

As depicted in Scheme 5, diacetoneglucose substituted 6*H*-1,2-oxazine **4a** (dr >95:5) was hydrogenated under standard conditions and furnished the expected 2-methyl-4-phenyl-1-butylamine (**5**) in 68% yield. This sample displayed a specific optical rotation of +12.4 ($CHCl_3$) and therefore it could be assigned to be a compound with *R* configuration (2*R*:2*S*, ca. 90:10).[13] This newly generated stereocentre is formed during the addition of hydrogen to **4a** under the influence of the rather bulky 6-alkoxy group. In many addition reactions we could observe very high or

exclusive *trans*-selectivity with respect to this substituent.[3–5] Since the configuration at C-6 of 6*H*-1,2-oxazine **4a** was unambiguously determined to be *S* the highly selective formation of *R*-**5** confirms this anticipated mechanistic scenario. Similar hydrogenation experiments performed with cycloadducts **4d**, **4e** and **4f** also gave *R*-**5** in excess; thus, all these precursor 1,2-oxazines should have predominantly *S* configuration at C-6.[14] Reduction of diacetonefructose substituted 6*H*-1,2-oxazine **4h** also provided primary amine **5** albeit in only 27% yield. Most interestingly, this sample has now a specific optical rotation of –8.9 ($CHCl_3$), thus the *S*-configured enantiomer is formed in excess (2*S*:2*R*, ca. 80:20). As mentioned above we can now conclude that the starting 6*H*-1,2-oxazine **4h** has predominantly *R*-configuration at C-6.



4a (dr ≥ 95:5)
4h (dr = 22:78)

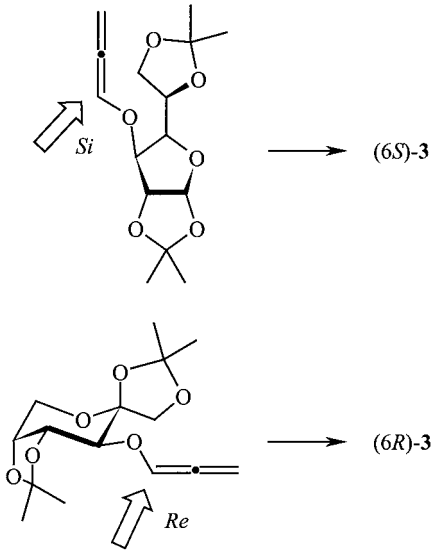
5 68 % (*R*, ee ca 80 %)
27 % (*S*, ee ca 60 %)

Scheme 5

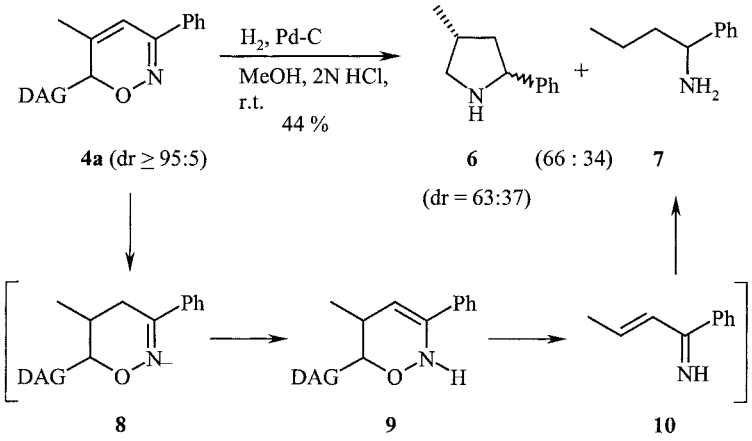
Finally, diacetoneglucose substituted 6*H*-1,2-oxazine **4a** was hydrogenated in the presence of 2 N HCl (Scheme 6). Here the multi-step reduction process stops at the stage of disubstituted pyrrolidine derivative **6**, which is formed as a 63:37 mixture of *cis-trans* isomers. In addition, the product mixture contains the unexpected compound **7**. This amine is probably formed by isomerization of the primary reduction product **8** to 5,6-dihydro-2*H*-1,2-oxazine **9** which undergoes a retro Diels–Alder reaction to α,β-unsaturated imine **10** and a formyl ester. Imine **10** is then rapidly reduced to furnish the isolated amine **7**. Although speculative this mechanism for formation of **7** seems rather plausible. Similar cleavage products, which have lost C-6 of the precursor 1,2-oxazine were occasionally observed in low yields when acid was present during hydrogenolysis. Protons may catalyze the isomerization at the 1,2-oxazine stage (e.g. **8** to **9**) and particularly the retro Diels–Alder reaction. [6c,15]

Discussion

The diastereotopic faces of the allenyloxy moieties of compounds **1** presented in this report are apparently shielded in different manner. Whereas the differentiation is already satisfying for mannose derivative **1d**, which bears the allenyloxy substitutent at the anomeric centre, it is clearly surpassed by the diacetoneglucose unit of **1a**. A sound interpretation of these results is complicated by the conformational flexibility of these carbohydrate allene derivatives, however, we assume that an approach of the nitroso compounds to the *Si* face of the allene double bond of **1a** occurs as illustrated in Scheme 7. It is also the *Si* face which is attacked when simple enol ethers with the diacetoneglucose auxiliary react with nitroso alkenes.[7,16,17] In contrast, the *Re* face of diacetonefructose derivative **1f** is preferentially approached by the nitroso compounds giving cycloadducts with 6*R* configuration mainly.



Scheme 7



Scheme 6

Conclusion

We could establish that two easily available carbohydrate auxiliaries[18,19] are well suited for syntheses of 6*H*-1,2-oxazines with differing absolute configuration at C-6. Whereas diacetoneglucose derived alkoxyallene **1a** provided heterocycles **4a–c** with excellent diastereoselectivity and predominant 6*S* configuration, the diacetonefructose compound **1f** afforded the corresponding 6*H*-1,2-oxazines **4h–j** with slightly decreased stereoselection, but the major diastereomer has 6*R* configuration. Other auxiliaries studied resulted in lower asymmetric induction. The complementary 6*H*-1,2-oxazines **4a** and **4h** were transformed by catalytic hydrogenation into enantiomerically enriched primary amines **5**. In the presence of acid **4a** provided pyrrolidine derivative **6** together with the fragmentation product **7**.

All reactions were performed under argon in flame-dried flasks, and the components were added by means of syringes. All solvents were dried by standard methods. IR spectra were measured with Beckman IR Acculab 4, Beckman IR 5A, Perkin-Elmer IR 1420 or Perkin Elmer FT-IR spectrometer Nicolet 5 SXC. ^{1}H and ^{13}C NMR spectra were recorded on Bruker instruments (AC 500, WM 300, WH 270, AC 250) in $CDCl_3$ solution. The chemical shifts are given in relative to the TMS or to the $CDCl_3$ signal (δ_H = 7.27, δ_C = 77.0). Higher order NMR spectra were approximately interpreted as first-order spectra if possible. Missing signals of minor isomers are hidden by signals of major isomers, or they could not be unambiguously identified due to low intensity. Neutral alumina (activity III, Merck) was used for column chromatography. Melting points (uncorrected) were measured with an apparatus from Büchi (SMP-20). Optical rotations were determined in a 1 mL cell with a pathlength of 10 cm using a Perkin-Elmer 241 polarimeter (Na_D line). The $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1} and the concentrations are given in g/100 cm^3.

Starting materials **1a–f**,[9] **2a**,[20] **2b**,[21] and **2c**[22] were prepared by literature procedure. All other chemicals are commercially available and were used as received.

5-Methylene-4*H*-1,2-oxazines 3; General Procedure 1

To a solution of the corresponding α-halogen oxime **2** in anhyd *tert*-butyl methyl ether (MtB; 20–25 mL/mmol of **2**) was added the allene derivative **1** (1–1.25 equiv). To this solution was added freshly ground Na_2CO_3 (3.2–9.5 mmol/mmol of **2**) and the suspension was mechanically stirred at r.t. for the time indicated in Table 2. The progress of the reaction was controlled by TLC. After consumption of the oxime, the mixture was filtered through a sintered glass plug which contained a pad of Celite. The filtrate was concentrated in vacuo (30–35 °C/100 mbar); the crude 1,2-oxazine **3** was purified by column chromatography on neutral alumina (activity III) or the crude product was used as obtained in the next reaction. The analytical and spectroscopic data of **3** are given in Tables 2 and Tables 4–6.

Isomerization to 6*H*-1,2-Oxazines 4; General Procedure 2

The primary cycloadduct **3** was dissolved in CH_2Cl_2 (approximately 10 mL/mmol) and stirred with the amount of DBU as indicated in Table 3. The crude product **4** was purified by column chromatography. For spectroscopic and analytical data see Tables 3, 4 and 7–8.

Catalytic Hydrogenation of 6*H*-1,2-Oxazines 4; General Procedure 3

Anhyd MeOH (10–20 mL/mmol of **4**) and 10% Pd/C (0.100 g/mmol of **4**) were saturated with H_2 for 1 h at r.t. Then, the corresponding 6*H*-1,2-oxazine **4** was added, and the mixture was stirred under H_2 atmosphere at normal pressure for 24–60 h at r.t. The suspension was filtered through a sintered glass plug, which contained a pad of Celite eluting with MeOH. The filtrate was concentrated in vacuo and the crude product was purified by Kugelrohr distillation.

Table 2 Synthesis of 5-Methylen-4*H*-1,2-oxazines **3a–j** (General Procedure 1)

1 [g (mmol)]	**2** [g (mmol)]	Na_2CO_3 [g (mmol)]	Time (d)	Yield of **3** [g (%)][a]	dr[b]
1a 0.715 (2.40)	**2a** 0.322 (1.90)	0.636 (6.00)	6	**3a** 0.442 (54)	90:10
1a 0.597 (2.00)	**2b** 0.420 (2.00)	2.00 (18.9)	7	**3b** 0.705 (82)	86:14
1a 0.597 (2.00)	**2c** 0.412 (2.00)	2.00 (18.9)	7	–[c]	92:8
1b 1.56 (4.12)	**2a** 0.582 (3.43)	1.09 (10.3)	7	**3d** 1.60 (91)[d]	nd
1c 0.197 (0.52)	**2a** 0.074 (0.43)	0.176 (1.66)	7	**3e** 0.183 (124)[d]	nd
1d 0.662 (2.22)	**2a** 0.314 (1.85)	0.59 (5.57)	7	**3f** 0.50 (63)[d]	nd
1e 1.00 (5.20)	**2a** 0.882 (5.20)	5.20 (49.1)	10	**3g** 0.658 (39)[e]	64:36
1f 0.597 (2.00)	**2a** 0.339 (2.00)	0.636 (6.00)	10	**3h** 0.925 (107)[d]	23:77
1f 0.655 (2.23)	**2b** 0.468 (2.23)	1.91 (18.0)	7	**3i** 0.929 (98)[d]	nd
1f 0.597 (2.00)	**2c** 0.412 (2.00)	1.91 (18.0)	7	**3j** 0.874 (103)[d,f]	18:82

[a] Yield of the crude product.
[b] Not determined.
[c] Chromatography (hexane–MtB, 3:2) of the crude product **3c** yielded the isomerized compound **4c** (0.586 g, 69%, dr >95:5).
[d] The crude product contains the corresponding allene **1**.
[e] After purification by chromatography (hexane–MtB, 3:2).
[f] Chromatography (hexane–MtB, 3:2) of the crude product **3j** yielded the isomerized compound **4j** (0.531 g, 63%, dr 85:15).

Table 3 Isomerization of 5-Methylen-4*H*-1,2-oxazines **3** to 6*H*-1,2-Oxazines **4** (General Procedure 2)

3[a] (g)	DBU	Time, Temp.	Yield of **4** [g (%)][b,c]	6*S*:6*R*
3a 0.344[d]	152 mg	20 h, r.t.	**4a** 0.334 (91)	>95:5
3b 0.200[e]	200 mg	2 d, r.t.	**4b** 0.241[f]	79:21
3d 1.60	5 drops	1 d, r.t.	**4d** 1.04 (59)	90:10
3e 0.183	5 drops	1 d, r.t.	**4e** 0.156 (83)	50:50
3f 0.500	10 drops	1 d, r.t.	**4f** 0.448 (56)	87:13
3g 0.200[g]	200 mg	4 h, 40 °C	**4g** 0.148 (74)	68:32
3h 0.925	10 drops	2 d, r.t.	**4h** 0.484 (56)	22:78
3i 0.929	10 drops	3 d, r.t.	**4i** 0.542 (57)[f]	19:81

[a] Crude product, see Table 2.
[b] Satisfactory microanalysis obtained: C ±0.33, H ±0.27, N ±0.36; exceptions: **4e** (C +0.64), **4j** (C –1.09).
[c] Total yield concerning the corresponding oxime **2**.
[d] 0.797 mmol scale.
[e] 0.468 mmol scale.
[f] Purification of the crude product by chromatography was not possible.
[g] 0.615 mmol scale.

Table 4 Analytical Data for 5-Methylen-4*H*-1,2-oxazines **3** and 6*H*-1,2-Oxazines **4**

Product	$[\alpha]_D$ (*c*, g/100 mL)[a]	mp (°C)	IR (cm^{-1})[b]
3a	nd	oil	3140–2780 (C–H, =CH), 1670 (C=C), 1590 (C=N)
3g	nd	134	–
4a	+62 (*c* = 2)	136	3150–2790 (C–H, =CH), 1670 (C=C), 1580 (C=N)
4c	+111 (*c* = 1.05)	131	3000–2780 (C–H, =CH), 1670 (C=C), 1590 (C=N), 1205, 1185, 1145 (CF_3)
4d	+61 (*c* = 1.2)	73–75	3060–2860 (C–H, =CH), 1660 (C=C), 1540 (C=N)
4e	+78 (*c* = 1.2)	112–114	3100–2860 (C–H, =CH), 1660 (C=C), 1580 (C=N)
4f	+41 (*c* = 1.1)	132–134	3060–2860 (C–H, =CH), 1660 (C=C), 1540 (C=N)
4g	nd	132–135	3130–2820 (C–H, =CH), 1665 (C=C), 1585 (C=N)
4h	nd	51–53	3100–2800 (C–H, =CH), 1660 (C=C), 1530 (C=N)
4j	nd	oil	3020–2820 (C–H, =CH), 1660 (C=C), 1570 (C=N), 1210, 1180, 1140 (CF_3)

[a] Specific optical rotation determined in $CHCl_3$; nd = not determined.
[b] Oils and resins as film or in CCl_4, foams as KBr pellets.

(*R*)-(+)-2-Methyl-4-phenyl-1-butylamine [(*R*)-(+)-5]
According to the general procedure 3, a mixture of **4a** (0.820 g, 1.90 mmol, dr ≥ 95:5) and 10% Pd/C (0.250 g) in MeOH (20 mL) was stirred for 24 h at r.t. The resulting residue was purified by Kugelrohr distillation (100 °C/0.08 mbar) to give the amine **5** (0.162 g, 68%) as a colourless oil; $[\alpha]_D^{20}$ +12.4 (*c* = 2.0, $CHCl_3$); ee ca 80%.[13]

(*S*)-(–)-2-Methyl-4-phenyl-1-butylamine [(*S*)-(–)-5]
According to the general procedure 3, a mixture of **4h** (0.393 g, 0.91 mmol, dr 78:22) and 10% Pd/C (0.100 g) in MeOH (10 mL) was stirred for 24 h at r.t. The resulting residue was purified by Kugelrohr distillation (100 °C/0.09 mbar) to give the amine **5** (0.040 g, 27%) as a colourless oil; $[\alpha]_D^{20}$ –8.9 (*c* = 1.4, $CHCl_3$); ee ca 60%.[13]

Hydrogenation of 4a to Pyrrolidine 6 and Amine 7
According to the general procedure 3, a mixture of **4a** (0.431 g, 1.00 mmol, dr ≥ 95:5) and 10% Pd/C (0.100 g) in MeOH (10 mL) and 2 N HCl solution (1 mL) was stirred for 24 h at r.t. The resulting residue was purified by Kugelrohr distillation (50 °C/0.09 mbar) to give an oily 66:34-mixture of pyrrolidine **6** and amine **7** (0.068 g, 44%; **6** as a mixture of 2 diastereomers, 63:37). Pyrrolidine **6** slowly crystallized out from this mixture and a few pure crystals could be isolated; mp 80–82 °C.

^1H and ^{13}C NMR data of pyrrolidine **6** are identical with those reported earlier.[1]

Table 5 ^{1}H NMR Data for 5-Methylen-4*H*-1,2-oxazines **3** (300 MHz, $CDCl_3$/TMS); δ, *J* (Hz)

Product	Oxazine Part	Auxiliary Part
3a (major)	7.74–7.69, 7.43–7.38 (2 m, 2 H and 3 H, C_6H_5), 5.56 (s, 1 H, 6-H), 5.24, 5.14 (2 d, *J* = 2.5, 2 H, $=CH_2$), 3.49, 3.20 (dt, d, *J* = 2.5, J_{AB} = 18, 2 H, 4-H)	5.76 (d, *J* = 3.5, 1 H, 1-H), 4.64–3.96 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H), 1.49, 1.44, 1.36, 1.27 (4 s, 3 H each, 4 CH_3)
3a (minor)[a]	5.55 (s, 1 H, 6-H), 5.24, 5.16 (2 d, *J* = 2.5, 2 H, $=CH_2$), 3.45, 3.25 (dt, d, *J* = 2.5, J_{AB} = 20, 2 H, 4-H)	–
3b (major)	5.60 (s, 1 H, 6-H), 5.24, 5.14 (2 d, *J* = 2.5, 2 H, $=CH_2$), 3.22 (m_c, 2 H, 4-H), 1.40 (t, *J* = 7, 3 H, OCH_2CH_3)[b]	5.81 (d, *J* = 3.5, 1 H, 1-H), 4.60–3.90 (m, 8 H, 2-H, 3-H, 4-H, 5-H, 6-H), 1.48, 1.42, 1.34, 1.27 (4 s, 3 H each, 4 CH_3)
3b (minor)[a]	5.58 (s, 1 H, 6-H), 5.27, 5.17 (2 d, *J* = 2.5, 2 H, $=CH_2$), 3.22 (m_c, 2 H, 4-H)	5.74 (d, *J* = 3.5, 1 H, 1-H)
3c (major)	5.60 (s, 1 H, 6-H), 5.31, 5.21 (2 d, *J* = 2.5, 2 H, $=CH_2$), 3.24, 2.98 (dt, d, *J* = 2.5, J_{AB} = 18, 2 H, 4-H)	5.82 (d, *J* = 3.6, 1 H, 1-H), 4.60–3.94 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H), 1.49, 1.44, 1.36, 1.27 (4 s, 3 H each, 4 CH_3)
3c (minor)[a]	5.51 (s, 1 H, 6-H), 5.34, 5.24 (2 d, *J* = 2.5, 2 H, $=CH_2$)	–
3g (major)	7.71–7.41 (m, 5 H, C_6H_5), 5.18, 5.05 (2 d, *J* = 2.5, 2 H, $=CH_2$), 5.17 (s, 1 H, 6-H), 3.48, 3.28 (dt, d, *J* = 2.5, J_{AB} = 19, 2 H, 4-H)	3.32 (m_c, 1 H, 2-H), 1.30–0.81 (m, 7 H, 4-H, 5-H, 6-H, 7-H), 1.07, 1.04, 0.88 (3 s, 3 H each, 3 CH_3)
3g (minor)[a]	5.26 (s, 1 H, 6-H), 3.49, 3.21 (dt, d, *J* = 2.5, J_{AB} = 19, 2 H, 4-H)	3.34 (m_c, 1 H, 2-H), 1.63–0.81 (m, 7 H, 4-H, 5-H, 6-H, 7-H), 1.09, 1.02, 0.81 (3 s, 3 H each, 3 CH_3)
3h (major)	7.69–7.65, 7.41–7.34 (2 m, 2 H and 3 H, C_6H_5), 5.91 (s, 1 H, 6-H), 5.31, 5.14 (2 d, *J* = 2.5, 2 H, $=CH_2$), 3.48, 3.23 (dt, d, *J* = 2.5, J_{AB} = 19.6, 2 H, 4-H)	4.42–3.84 (m, 7 H, 1-H, 3-H, 4-H, 5-H, 6-H), 1.65, 1.41, 1.39, 1.22 (4 s, 3 H each, 4 CH_3)
3h (minor)[a]	5.63 (s, 1 H, 6-H), 5.24 (d, *J* = 2.5, 1 H, $=CH_2$), 3.24 (d, J_{AB} = 19.6, 1 H, 4-H)	–
3i (major)	5.93 (s, 1 H, 6-H), 5.32, 5.16 (2 d, *J* = 2.5, 2 H, $=CH_2$), 4.35 (t, *J* = 7, 2 H, OCH_2CH_3), 3.24, 3.18 (dt, d, *J* = 2.5, J_{AB} = 18.5, 2 H, 4-H), 1.36 (t, *J* = 7, 3 H, OCH_2CH_3)	4.25–3.84 (m, 7 H, 1-H, 3-H, 4-H, 5-H, 6-H), 1.62, 1.44, 1.38, 1.30 (4 s, 3 H each, 4 CH_3)
3j (major)	5.93 (s, 1 H, 6-H), 5.39, 5.21 (2 d, *J* = 2.5, 2 H, $=CH_2$), 3.25, 2.98 (dt, d, *J* = 2.5, J_{AB} = 20.5, 2 H, 4-H)	4.39–3.85 (m, 7 H, 1-H, 3-H, 4-H, 5-H, 6-H), 1.62, 1.46, 1.39, 1.32 (4 s, 3 H each, 4 CH_3)
3j (minor)[a]	5.63 (s, 1 H, 6-H), 5.30, 5.19 (2 d, *J* = 2.5, 2 H, $=CH_2$)	–

[a] Missing signals are hidden by signals of the major isomer.
[b] For OCH_2 signal see column 'auxiliary part' (multiplet at 4.60–3.90).

1-Phenyl-1-butylamine (7)[23]
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.25–7.16 (m, 5 H, C_6H_5), 3.87 (t, *J* = 6.9 Hz, 1 H, 1-H), 2.10 (s, 2 H, NH_2), 1.67–1.57 (m, 2 H, 2-H), 1.40–1.20 (m, 2 H, 3-H), 0.90 (t, *J* = 7.3 Hz, 3 H, 4-H).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 146.7, 126.7, 126.4, 126.2 (s, 3 d, Ph), 55.9 (d, C-1), 41.7 (t, C-2), 19.6 (t, C-3), 13.9 (q, C-4).

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Table 6 ^{13}C NMR Data for 5-Methylen-4*H*-1,2-oxazines **3** (75.5 MHz, $CDCl_3$); δ, *J* (Hz)

Product	Oxazine Part	Auxiliary Part
3a (major)	156.7 (s, C-3), 137.1, 133.7, 129.6, 128.4, 125.9 (2 s, 3 d, C_6H_5, C-5), 112.7 (t, $=CH_2$), 98.7 (d, C-6), 26.2 (t, C-4)	111.9, 109.1 [2 s, 2 *C*$(CH_3)_2$], 105.4 (d, C-1), 83.5, 80.1, 80.0 (3 d, C-2, C-3, C-4), 72.6 (d, C-5), 67.9 (t, C-6), 26.6, 26.5, 26.0, 25.9 (4 q, 4 CH_3)
3a (minor)	134.4, 129.1, 127.9 (s, 2 d, C_6H_5, C-5), 112.5 (t, $=CH_2$)	105.0 (d, C-1), 80.0, 79.5 (2 d, C-2, C-3, C-4), 65.5 (t, C-6), 27.1, 24.1 (2 q, 2 CH_3)
3b (major)	162.3, 62.1, 13.9 (s, t, q, $CO_2CH_2CH_3$), 150.5 (s, C-3), 132.1 (s, C-5), 113.7 (t, $=CH_2$), 99.1 (d, C-6), 25.4 (t, C-4)	109.1, 108.9 [2 s, 2 *C*$(CH_3)_2$], 105.4 (d, C-1), 83.5, 80.1, 80.0 (3 d, C-2, C-3, C-4), 72.6 (d, C-5), 67.9 (t, C-6), 26.6, 26.5, 26.0, 25.9 (4 q, 4 CH_3)
3b (minor)	162.4, 61.6 (s, t, $CO_2CH_2CH_3$), 150.2 (s, C-3), 117.0 (t, $=CH_2$), 96.1 (d, C-6), 25.7 (t, C-4)	109.2, 108.7 [2 s, 2 *C*$(CH_3)_2$], 83.0, 79.8 (2 d, 2 CH), 72.8 (d, C-5), 67.3 (t, C-6)
3c (major)	148.7 (q, $^2J_{CF}$ = 34, C-3), 130.4 (s, C-5), 120.1 (q, $^1J_{CF}$ = 275, CF_3), 114.7 (t, $=CH_2$), 99.1 (d, C-6), 23.4 (t, C-4)	112.1, 109.3 [2 s, 2 *C*$(CH_3)_2$], 105.1 (d, C-1), 83.3, 81.2, 81.0 (3 d, C-2, C-3, C-4), 72.3 (d, C-5), 67.9 (t, C-6), 26.7, 26.6, 26.0, 25.1 (4 q, 4 CH_3)
3c (minor)	117.0 (t, $=CH_2$), 97.5 (d, C-6)	83.1, 81.8, 81.2 (3 d, C-2, C-3, C-4), 67.3 (t, C-6)
3g (major)	155.7 (s, C-3), 135.6, 135.3, 129.7, 128.5, 125.6 (2 s, 3 d, C_6H_5, C-5), 111.1 (t, $=CH_2$), 100.2 (d, C-6), 26.1 (t, C-4)	91.1 (d, C-2), 49.4, 39.6 (2 s, C-1, C-3), 48.6 (d, C-4), 41.4, 27.6, 26.2 (3 t, C-5, C-6, C-7), 30.0, 21.2, 19.9 (3 q, 3 CH_3)
3g (minor)	155.4 (s, C-3), 135.2, 129.6 (s, d, C_6H_5), 110.9 (t, $=CH_2$), 98.3 (d, C-6)	88.2 (d, C-2), 41.1, 27.4, 25.9 (3 t, C-5, C-6, C-7), 31.8, 20.6, 19.4 (3 q, 3 CH_3)
3h (major)	156.8 (s, C-3), 134.6, 134.4, 129.9, 128.5, 125.5 (2 s, 3 d, C_6H_5, C-5), 112.6 (t, $=CH_2$), 97.2 (d, C-6), 27.0 (t, C-4)	111.8, 109.3 [2 s, 2 *C*$(CH_3)_2$], 104.1 (s, C-2), 77.8 (d, C-4), 73.8, 72.4 (2 d, C-3, C-5), 71.6 (t, C-1), 59.9 (t, C-6), 27.3, 26.3, 26.1, 25.1 (4 q, 4 CH_3)
3h (minor)	155.9 (s, C-3), 134.7, 134.5 (2 s, C_6H_5, C-5), 112.4 (t, $=CH_2$), 98.4 (d, C-6)	–
3i (major)	162.3, 62.1, 13.9 (s, t, q, $CO_2CH_2CH_3$), 151.0 (s, C-3), 132.4 (s, C-5), 113.6 (t, $=CH_2$), 97.6 (d, C-6), 25.8 (t, C-4)	111.9, 109.3 [2 s, 2 *C*$(CH_3)_2$], 103.8 (s, C-2), 77.5 (d, C-4), 73.7, 72.9 (2 d, C-3, C-5), 71.7 (t, C-1), 59.9 (t, C-6), 28.0, 26.3, 26.2, 26.0 (4 q, 4 CH_3)
3j (major)	148.7 (q, $^2J_{CF}$ = 35, C-3), 130.4 (s, C-5), 119.9 (q, $^1J_{CF}$ = 276, CF_3), 114.5 (t, $=CH_2$), 97.7 (d, C-6), 23.4 (t, C-4)	111.8, 109.3 [2 s, 2 *C*$(CH_3)_2$], 103.5 (s, C-2), 77.3 (d, C-4), 73.6, 73.2 (2 d, C-3, C-5), 71.4 (t, C-1), 59.8 (t, C-6), 27.8, 26.6, 26.0, 25.6 (4 q, 4 CH_3)
3j (minor)	130.6 (s, C-5), 114.1 (t, $=CH_2$), 98.5 (d, C-6), 23.3 (t, C-4)	111.4, 108.9 [2 s, 2 *C*$(CH_3)_2$], 103.3 (s, C-2), 75.6 (d, C-4), 74.9, 72.9 (2 d, C-3, C-5), 72.6 (t, C-1), 61.0 (t, C-6)

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Table 7 ^{1}H NMR Data for 6*H*-1,2-Oxazines **4** (300 MHz, $CDCl_3$/TMS); δ, *J* (Hz)

Product	Oxazine Part	Auxiliary Part
4a (major)	7.72–7.65, 7.42–7.34 (2 m, 2 H, 3 H, C_6H_5), 6.34 (q, *J* = 1, 1 H, 4-H), 5.61 (s, 1 H, 6-H), 2.09 (d, *J* = 1, 3 H, 5-CH_3)	5.75 (d, *J* = 3.5, 1 H, 1-H), 4.63 (d, *J* = 3.5, 1 H, 2-H), 4.44–3.96 (m, 5 H, 3-H, 4-H, 5-H, 6-H), 1.49, 1.44, 1.36, 1.27 (4 s, 3 H each, 4 CH_3)
4a (minor)[a]	2.13 (d, *J* = 1.5, 3 H, 5-CH_3)	–
4b (major)	6.29 (q, *J* = 2, 1 H, 4-H), 5.68 (s, 1 H, 6-H), 4.61–3.94 (m, 2 H, OC$H_2$$CH_3$), 2.06 (d, *J* = 2, 3 H, 5-CH_3), 1.40 (t, *J* = 7, 3 H, $OCH_2C$$H_3$)[b]	5.94 (d, *J* = 3.5, 1 H, 1-H), 4.61–3.96 (m, 8 H, 2-H, 3-H, 4-H, 5-H, 6-H), 1.50, 1.39, 1.35, 1.32 (4 s, 3 H each, 4 CH_3)
4b (minor)[a]	6.49 (q, *J* = 2, 1 H, 4-H), 5.61 (s, 1 H, 6-H), 2.03 (d, *J* = 2, 3 H, 5-CH_3)	5.78 (d, *J* = 3.5, 1 H, 1-H)
4c (major)	6.10 (q, *J* = 2, 1 H, 4-H), 5.69 (s, 1 H, 6-H), 2.10 (d, *J* = 2, 3 H, 5-CH_3)	5.79 (d, *J* = 3.5, 1 H, 1-H), 4.53–3.96 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H), 1.50, 1.44, 1.35, 1.31 (4 s, 3 H each, 4 CH_3)
4d (major)	7.66–7.61, 7.38–7.31 (2 m, 2 H, 3 H, C_6H_5), 6.27 (q, *J* = 1.5, 1 H, 4-H), 5.58 (s, 1 H, 6-H), 2.03 (d, *J* = 1.5, 3 H, 5-CH_3)	5.68 (d, *J* = 3.5, 1 H, 1-H), 4.52 (d, *J* = 3.5, 1 H, 2-H), 4.39 (d, *J* = 3, 1 H, 3-H), 4.17–3.99, 3.90 (m, dd, *J* = 4.9, 8.5, 3 H, 1 H, 4-H, 5-H, 6-H), 1.60–1.10 (m, 20 H, 10 CH_2)
4d (minor)[a]	5.55 (s, 1 H, 6-H)	5.78 (d, *J* = 3.5, 1 H, 1-H), 4.54 (d, *J* = 3, 1 H, 2-H)
4e	7.72–7.66, 7.41–7.36 (2 m, 2 H, 3 H, C_6H_5), 6.38–6.36 (m, 1 H, 4-H), 5.70, 5.61 (2 s, 0.5 H each, 6-H), 2.10, 2.09 (2 d, *J* = 1.5 each, 1.5 H each, 5-CH_3)	5.89 (d, *J* = 4, 0.5 H, 1-H), 5.71 (d, *J* = 4, 0.5 H, 1-H), 4.86–4.81 (m, 1 H, 2-H), 4.47, 4.35–4.28, 4.20–3.92, 3.88, 3.74 (d, *J* = 8.6, 2 m, dd, *J* = 6.4, 8.2, t, *J* = 8.2, 0.5 H, 1.5 H, 2 H, 0.5 H, 0.5 H, 3-H, 4-H, 5-H, 6-H), 1.62–1.21 (m, 12 H, 4 CH_3)
4f (major)	7.74–7.68, 7.44–7.39 (2 m, 2 H, 3 H, C_6H_5), 6.37 (q, *J* = 1.5, 1 H, 4-H), 5.71 (s, 1 H, 6-H), 2.05 (d, *J* = 1.5, 3 H, 5-CH_3)	5.58 (s, 1 H, 1-H), 4.74 (dd, *J* = 3.7, 5.9, 1 H, 3-H), 4.56 (d, *J* = 5.9, 1 H, 2-H), X part of ABX-system (δ_X = 4.43, *J* = 7.1, 1 H, 5-H), AB part of ABX-system (δ_A = 4.14, δ_B = 4.06, J_{AB} = 8.7, J_{AX} = 6.3, J_{BX} = 4.6, 1 H, 6-H), 3.97 (dd, *J* = 3.6, 7.3, 1 H, 4-H), 1.46, 1.39, 1.28 (3 s, 6 H, 3 H, 3 H, 4 CH_3)
4f (minor)[a]	5.30 (s, 1 H, 6-H), 2.07 (d, *J* = 1.5, 3 H, 5-CH_3)	5.65 (s, 1 H, 1-H), 4.58 (d, *J* = 5.8, 1 H, 2-H), 4.40–4.36 (m, 1 H, 5-H), 1.37, 1.31, 1.26 (3 s, 6 H, 3 H, 3 H, 4 CH_3)
4g (major)	7.71–7.41 (m, 5 H, C_6H_5), 6.29 (d, *J* = 1.5, 1 H, 4-H), 5.32 (s, 1 H, 6-H), 2.07 (d, *J* = 1.5, 3 H, 5-CH-$_3$)	3.32 (m_c, 1 H, 2-H), 1.60–0.84 (m, 7 H, 4-H, 5-H, 6-H, 7-H), 1.07, 1.04, 0.88 (3 s, 3 H each, 3 CH_3)
4g (minor)[a]	5.37 (s, 1 H, 6-H)	3.40 (m_c, 1 H, 2-H), 1.40–0.89 (m, 7 H, 4-H, 5-H, 6-H, 7-H), 1.11, 1.01, 0.95 (3 s, 3 H each, 3 CH_3)
4h (major)	7.67–7.64, 7.44–7.38 (2 m, 2 H, 3 H, C_6H_5), 6.32 (q, *J* = 1.5, 1 H, 4-H), 5.90 (s, 1 H, 6-H), 2.13 (d, *J* = 1.5, 3 H, 5-CH_3)	4.29 (dd, *J* = 5.4, 7.5, 1 H, 4-H), 4.21–4.00 (m, 5 H, 1-H, 5-H, 6-H), 3.94 (d, *J* = 8.9, 1 H, 3-H), 1.64, 1.43, 1.39, 1.12 (4 s, 3 H each, 4 CH_3)
4h (minor)[a]	7.73–7.70 (m, 2 H, C_6H_5), 6.33 (q, *J* = 1.5, 1 H, 4-H), 5.73 (s, 1 H, 6-H), 2.12 (d, *J* = 1.5, 3 H, 5-CH_3)	4.44 (dd, *J* = 4.8, 6.8, 1 H, 4-H), 3.76 (d, *J* = 12.5, 1 H, 6-H), 1.50, 1.42, 1.32 (3 s, 6 H, 3 H, 3 H, 4 CH_3)
4i (major)	6.44 (q, *J* = 1.7, 1 H, 4-H), 5.99 (s, 1 H, 6-H), 4.37 (t, *J* = 7, 2 H, OC$H_2$$CH_3$), 2.08 (d, *J* = 1.7, 3 H, 5-CH_3), 1.37 (t, *J* = 7, 3 H, $OCH_2C$$H_3$)	4.33–3.90 (m, 7 H, 1-H, 3-H, 4-H, 5-H, 6-H), 1.61, 1.44, 1.38, 1.36 (4 s, 3 H each, 4 CH_3)
4i (minor)[a]	5.80 (s, 1 H, 6-H)	–
4j (major)	6.07 (q, *J* = 1.5, 1 H, 4-H), 5.96 (s, 1 H, 6-H), 2.12 (d, *J* = 1.5, 3 H, 5-CH_3)	4.26 (dd, *J* = 5.4, 7.7, 1 H, 4-H), 4.20–4.07 (m, 5 H, 1-H, 5-H, 6-H), 4.02 (d, *J* = 7.7, 1 H, 3-H), 1.62, 1.45, 1.38, 1.20 (4 s, 3 H each, 4 CH_3)
4j (minor)[a]	5.79 (s, 1 H, 6-H), 2.11 (d, *J* = 1.5, 3 H, 5-CH_3)	1.51, 1.49, 1.40, 1.35 (4 s, 3 H each, 4 CH_3)

[a] Missing signals are hidden by signals of the major isomer.
[b] For OCH_2 signal see column 'auxiliary part' (multiplet at 4.61–3.96).

Table 8 ^{13}C NMR Data for 6*H*-1,2-Oxazines **4** (75.5 MHz, $CDCl_3$); δ, *J* (Hz)

Product	Oxazine Part	Auxiliary Part
4a (major)	154.1 (s, C-3), 137.1, 133.7, 129.6, 128.4, 125.9 (2 s, 3 d, C_6H_5, C-5), 112.5 (d, C-4), 96.7 (d, C-6), 18.7 (q, 5-CH_3)	112.0, 109.4 [2 s, 2 *C*$(CH_3)_2$], 105.2 (d, C-1), 83.2, 81.1, 80.5 (3 d, C-2, C-3, C-4), 72.6 (d, C-5), 67.7 (t, C-6), 26.6, 26.5, 26.0, 25.9 (4 q, 4 CH_3)
4b (major)	162.1, 62.2, 14.0 (s, t, q, $CO_2CH_2CH_3$), 148.2 (s, C-3), 139.8 (s, C-5), 110.8 (d, C-4), 97.6 (d, C-6), 18.6 (q, 5-CH_3)	112.0, 109.1 [2 s, 2 *C*$(CH_3)_2$], 105.4 (d, C-1), 83.5, 80.1, 80.0 (3 d, C-2, C-3, C-4), 72.6 (d, C-5), 67.9 (t, C-6), 26.6, 26.5, 26.0, 25.9 (4 q, 4 CH_3)
4b (minor)	134.0 (s, C-5), 111.0 (d, C-4), 94.6 (d, C-6), 18.5 (q, 5-CH_3)	–
4c (major)	147.8 (q, $^2J_{CF}$ = 34, C-3), 138.8 (s, C-5), 120.3 (q, $^1J_{CF}$ = 275, CF_3), 108.1 (d, C-4), 97.5 (d, C-6), 18.9 (q, 5-CH_3)	112.0, 109.4 [2 s, 2 *C*$(CH_3)_2$], 105.5 (d, C-1), 83.4, 81.5, 81.3 (3 d, C-2, C-3, C-4), 72.5 (d, C-5), 68.1 (t, C-6), 26.9, 26.7, 26.3, 25.3 (4 q, 4 CH_3)
4d (major)	154.4 (s, C-3), 134.4, 133.9, 130.0, 128.6, 126.2 (2 s, 3 d, C_6H_5, C-5), 112.4 (d, C-4), 96.9 (d, C-6), 19.1 (q, 5-CH_3)	112.6, 109.7 [2 s, 2 *C*$(CH_2)_5$], 105.2 (d, C-1), 83.0, 81.4, 80.9, 72.2 (4 d, C-2, C-3, C-4, C-5), 67.6 (t, C-6), 36.5, 36.4, 35.6, 35.0, 26.9, 25.1, 24.8, 24.1, 23.9, 23.5 (10 t, 10 CH_2)
4d (minor)	154.0 (s, C-3), 134.0, 133.7, 125.9 (2 s, d, C_6H_5, C-5), 112.3 (d, C-4), 19.0 (q, 5-CH_3)	68.2 (t, C-6)
4e	154.3 (s, C-3), 137.6, 137.0, 134.1, 133.9, 129.8, 129.7, 128.7, 128.5, 126.3, 126.1 (4 s, 6 d, C_6H_5, C-5), 112.8, 111.8 (2 d, C-4), 96.1, 93.6 (2 d, C-6), 19.1, 19.0 (2 q, 5-CH_3)	113.0, 112.9, 109.9, 109.7 [4 s, 2 *C*$(CH_3)_2$], 104.7, 103.2 (2 d, C-1), 79.8, 77.9, 77.8, 77.0, 76.7, 75.3, 74.7, 72.8 (8 d, C-2, C-3, C-4, C-5), 66.2, 64.6 (2 t, C-6), 27.1, 27.0, 26.7, 26.5, 26.4, 26.1, 25.9, 24.8 (8 q, 4 CH_3)
4f (major)	154.0 (s, C-3), 137.0, 133.9, 129.8, 128.6, 126.1 (2 s, 3 d, C_6H_5, C-5), 112.2 (d, C-4), 91.5 (d, C-6), 19.0 (q, 5-CH_3)	112.8, 109.2 [2 s, 2 *C*$(CH_3)_2$], 102.7 (d, C-1), 84.8, 81.0, 79.3, 73.0 (4 d, C-2, C-3, C-4, C-5), 66.8 (t, C-6), 26.9, 25.8, 25.2, 24.5 (4 q, 4 CH_3)
4f (minor)	136.9, 129.9 (s, d, C_6H_5, C-5), 112.0 (d, C-4), 95.1 (d, C-6), 18.8 (q, 5-CH_3)	106.2 (d, C-1), 85.5, 81.3, 79.6, 72.8 (4 d, C-2, C-3, C-4, C-5), 67.3 (t, C-6), 26.7, 26.0, 25.5, 24.8 (4 q, 4 CH_3)
4g (major)	153.5 (s, C-3), 137.3, 134.5, 129.4, 128.6, 126.1 (2 s, 3 d, C_6H_5, C-5), 111.7 (d, C-4), 98.0 (d, C-6), 19.5 (q, 5-CH_3)	92.0 (d, C-2), 50.0, 39.9 (2 s, C-1, C-3), 48.9 (d, C-4), 41.0, 26.0, 25.9 (3 t, C-5, C-6, C-7), 30.1, 20.2, 19.8 (3 q, 3 CH_3)
4g (minor)	154.0 (s, C-3), 137.7 (s, C-5), 111.6 (d, C-4), 95.9 (d, C-6)	87.9 (d, C-2), 49.2 (d, C-4), 41.4 (t, CH_2), 21.5 (q, CH_3)
4h (major)	159.9 (s, C-3), 138.1, 134.0, 129.7, 128.7, 126.1 (2 s, 3 d, C_6H_5, C-5), 111.6 (d, C-4), 95.5 (d, C-6), 19.0 (q, 5-CH_3)	112.0, 109.4 [2 s, 2 *C*$(CH_3)_2$], 104.3 (s, C-2), 77.8 (d, C-4), 73.9, 72.8 (2 d, C-3, C-5), 71.2 (t, C-1), 59.7 (t, C-6), 28.3, 27.1, 26.5, 25.3 (4 q, 4 CH_3)
4h (minor)	154.0 (s, C-3), 137.6 (s, C-5), 111.9 (d, C-4), 96.6 (d, C-6), 19.1 (q, 5-CH_3)	110.4, 109.5 [2 s, 2 *C*$(CH_3)_2$], 103.6 (s, C-2), 74.4 (d, C-4), 73.6, 72.4 (2 d, C-3, C-5), 74.3 (t, C-1), 62.8 (t, C-6), 26.9, 26.6, 25.9, 25.2 (4 q, 4 CH_3)
4i (major)	163.1, 61.9, 13.8 (s, t, q, $CO_2CH_2CH_3$), 148.3 (s, C-3), 137.0 (s, C-5), 109.9 (d, C-4), 95.4 (d, C-6), 18.4 (q, 5-CH_3)	111.8, 109.1 [2 s, 2 *C*$(CH_3)_2$], 103.8 (s, C-2), 77.3 (d, C-4), 73.4, 73.0 (2 d, C-3, C-5), 71.0 (t, C-1), 59.6 (t, C-6), 28.0, 26.7, 26.1, 25.2 (4 q, 4 CH_3)
4i (minor)	147.7 (s, C-3), 109.1 (d, C-4), 96.7 (d, C-6)	–
4j (major)	148.5 (q, $^2J_{CF}$ = 34, C-3), 139.6 (s, C-5), 120.4 (q, $^1J_{CF}$ = 275, CF_3), 107.3 (d, C-4), 96.0 (d, C-6), 18.9 (q, 5-CH_3)	112.3, 109.5 [2 s, 2 *C*$(CH_3)_2$], 103.5 (s, C-2), 75.5 (d, C-4), 73.9, 73.7 (2 d, C-3, C-5), 71.1 (t, C-1), 59.8 (t, C-6), 28.3, 27.0, 26.4, 25.2 (4 q, 4 CH_3)
4j (minor)	147.3 (q, $^2J_{CF}$ = 34, C-3), 138.7 (s, C-5), 107.6 (d, C-4), 96.9 (d, C-6), 19.0 (q, 5-CH_3)	110.9, 109.7 [2 s, *C*$(CH_3)_2$], 75.4 (d, C-4), 73.8, 72.5 (2 d, C-3, C-5), 73.9 (t, C-1), 62.4 (t, C-6), 26.9, 26.4, 25.9, 25.3 (4 q, 4 CH_3)

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