Synthesis, Reactions, and Molecular Structures of Ethylzinc Enolates of Chiral *N*-Substituted *β*-Carbonyl Sulfoximines

Carsten Bolm,* Jürgen Müller, Margareta Zehnder, and Markus A. Neuburger

Abstract: The preparation, structural characterization, and reactivity of ethylzinc-containing enolates and organometallics derived from *β*-carbonyl sulfoximines are reported. X-ray crystal structures show significant differences between aggregated species obtained from *β*-keto and *β*-amido sulfoximines. Whereas the former gives an *O*-metalated ethylzinc enolate, the latter crystallizes as *C*-metalated carbonyl species. NMR investigations reveal the presence of chelated zinc enolates in solution. The relationship between structure and reactivity is demonstrated by the reaction profiles of the ethylzinc-containing compounds. A high diasteroselectivity (>90% *de*) was observed in the aldol reaction between the metalated *β*-amido sulfoximine and benzaldehyde in the presence of trimethylsilyl chloride.

Keywords
aggregates · asymmetric syntheses · stereochemistry · sulfoximines · zinc enolates

Introduction

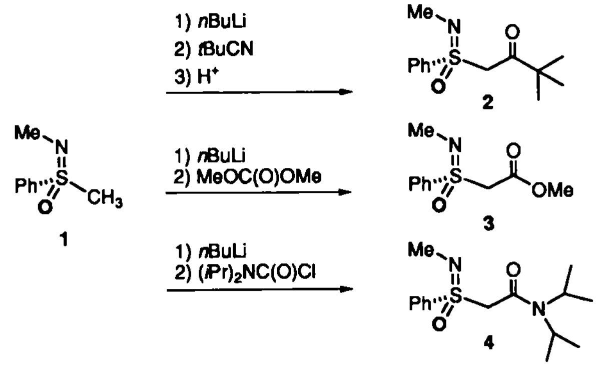
In 1983 Boersma and co-workers reported on the structural charcaterization of the Reformatsky reagent[1] prepared from *tert*-butyl bromoacetate and zinc metal in THF.[2] In the solid state a dimeric organozinc associate $[(BrZnCH_2COOC(CH_3)_3\cdot THF)_2]$ is formed in which the organic anion is bound to zinc through Zn–C and Zn–O bonds. Association measurements and IR and NMR spectroscopy showed that the reagent is dimeric in most solvents.[3] In the ^1H NMR spectra the chemical shift of the methylene resonances suggest the presence of *C*-metalated structures in solution.[4]

In addition to *halo*zinc organometallics,[4, 5] such as Reformatsky reagents, preparation and reactions of *alkyl*zinc enolates have been studied.[6–11] The main methods for their synthesis are deprotonation of carbonyl compounds with basic diorganozincs,[6–8] and addition reactions of dialkylzincs to α,*β*-unsaturated carbonyl and heterocarbonyl compounds.[9–11] Spectroscopic studies of resulting alkylzinc ketone enolates suggest the presence of oxygen- rather than carbon-bound metal species.[6, 10a] Oxygen-metalated compounds have also been found in *N*-protected α-amino-substituted zinc ester enolates.[5, 8, 9] There, the zinc atom is fixed through *N,O*-chelation, and intermolecular aggregates of various compositions are formed.

In connection with our studies of enantioselective catalysis with chiral sulfoximine/metal species,[11f, 12] we explored the synthesis of alkylzinc enolates derived from *β*-carbonyl sulfoximines, their molecular structures, and reactions with electrophiles.

Results and Discussion

Synthesis and Crystal Structures of Ethylzinc Enolates of *β*-Carbonyl Sulfoximines: The preparation of *β*-carbonyl sulfoximines **2**–**4** is depicted in Scheme 1. *N*-methylsulfoximine **1**, which is readily available in racemic and enantiomerically pure form,[13, 14] was deprotonated with *n*-butyllithium in THF, and the resulting anion was treated with 1.1–2 equiv of a suitable acylating reagent. Thus, addition of pivalonitrile to deprotonated **1** followed by acidic hydrolysis of the intermediate lithioketimine gave *β*-ketosulfoximine **2** in 63% yield. Ester **3** and amide **4** were obtained in low to moderate yields by reaction of the anion of **1** with dimethylcarbonate and *N,N*-diisopropylcar-



Scheme 1. Preparation of *β*-carbonyl sulfoximines **2**–**4**.

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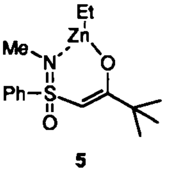
bamoyl chloride, respectively (**3**: 34%; **4**: 70%). All three compounds were prepared in racemic and optically active form. ^{1}H NMR spectroscopy of β-ketosulfoximine **2** in $CDCl_3$ revealed the presence of significant amounts of enol tautomer (keto:enol form = 63:37). In **3** and **4** no enol was detected.

Ethylzinc-containing compounds **5**–**7** were prepared by treatment of ether solutions of the corresponding β-carbonyl sulfoximines **2**–**4** with diethylzinc in hexane. Recrystallization of the resulting colorless precipitates from benzene afforded air- and moisture-sensitive crystals of **5**–**7** in 72–81% yield. Here, **5**–**7** are depicted in the *O*-metalated enolate form, which allows formation of a six-membered chelated ring. This arrangement is similar to that observed in an ethylzinc alkoxide prepared through the reaction of diethylzinc with a β-hydroxysulfoximine.[12a, b]



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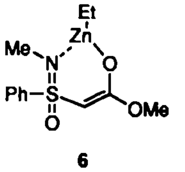

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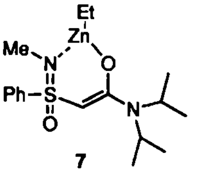

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Single crystals suitable for X-ray crystal structure determination were only obtained from *racemic* **5** and **7**. Neither **6** nor enolates prepared from optically active β-carbonyl sulfoximines gave suitable crystals. The molecular structure of **5** in the solid state is shown in Figure 1. Selected bond lengths and angles are summarized in Table 1.

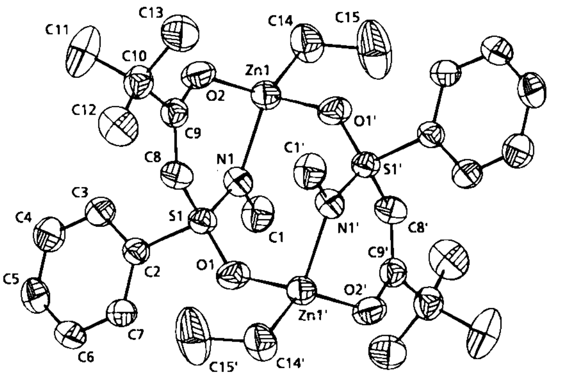


Fig. 1. Crystal structure of **5** [15].

Table 1. Selected bond distances [Å] and angles [°] for **5** and **7**; standard deviation in parentheses [15].

	5	7
C(8)-C(9)	1.370(4)	1.477(3)
C(9)-O(2)	1.283(4)	1.252(3)
S(1)-C(8)	1.693(3)	1.730(2)
Zn(1)-O(2)	1.950(2)	2.032(1)
Zn(1)-O(1')	2.211(2)	–
Zn(1)-N(1)	2.020(3)	2.069(2)
Zn(1)-C(8)	–	2.159(2)
S(1)-C(8)-C(9)	129.5(2)	116.9(1)
C(8)-C(9)-O(2)	126.7(3)	121.4(2)
Zn(1)-O(2)-C(9)	124.3(2)	126.1(1)
S(1)-O(1)-Zn(1')	134.3(1)	–
Zn(1)-N(1)-S(1)	125.0(2)	123.1(1)
O(2)-Zn(1)-O(1')	95.4(1)	–
N(1)-Zn(1)-O(1')	100.0(1)	–
N(1)-Zn(1)-O(2)	94.3(1)	91.82(7)
O(2)-Zn(1)-C(8)	–	109.85(7)
N(1)-Zn(1)-C(8)	–	105.61(8)
S(1)-C(8)-Zn(1)	–	112.9(1)

The crystal structure of **5** shows a dimeric associate that is linked through dative $Zn-O_{sulfoximine}$ bonds.[16] Two enolates of opposite chirality are connected, forming an eight-membered $(Zn\text{-}O\text{-}S\text{-}N)_2$-ring in a centrosymmetric tricyclic 6/8/6-associate with heterochiral enolate units. The C(8)–C(9) bond length is 1.37 Å; this indicates the presence of a C=C double bond. This value is slightly larger than the ones determined for chelated zinc enolates derived from a *N,N*-disubstituted β-amino ketone (1.27 Å in a dimeric associate)[9a] or a *N,N*-disubstituted glycine ester (1.33 Å in a tetramer).[8] The C–C bond length in the Reformatsky reagent discussed in the introduction is 1.41 Å.[2] The magnitude of the dihedral angle S(1)-C(8)-C(9)-O(2) of −8.8° in **5** is in agreement with sp^2 hybridization of C(8) and C(9). A similar value (−7°) was found by van Koten and coworkers in the crystal structure of a related zinc enolate.[9a] The C(8)-C(9)-O(2) and S(1)-C(8)-C(9) angles in **5** are 126.7(3)° and 129.5(2)°, respectively; this indicates a slight distortion of the enolate double bond in the flattened six-membered heterocycle. Compared to those in other chelated zinc enolates[8, 9a] the C(9)–O(2) bond of 1.28 Å and the normal Zn(1)–O(2) bond of 1.95 Å are relatively short. This is also the case for the dative Zn(1)–N(1) bond length, which has a value of 2.02 Å.

The four-coordination at the zinc atom in **5** is completed by a dative oxygen/zinc bond; the bonding geometry at zinc is thus approximately tetrahedral. This dative bond between the sulfoximine oxygen and the zinc atom is unusual in that it has not been found in other sulfoximine zinc complexes.[12a, f, 17, 18] It is significantly longer (2.21 Å) than the *intra*enolate Zn–O bond (1.95 Å) or the dative bonds in other intermolecularly bridged zinc enolates.[8, 9a]

The molecular structure of **7** is shown in Figure 2. Apparently, a dimeric associate of two heterochiral zinc species is formed in this case too. *However, the two halves of the molecule are not bridged through dative Zn–O bonds, but through Zn–C bonds!* The central eight-membered ring formed by the $(Zn\text{-}C\text{-}C\text{-}O)_2$ atom sequence is reminiscent of the structure of the Reformatsky reagent studied by Boersma and co-workers.[2]

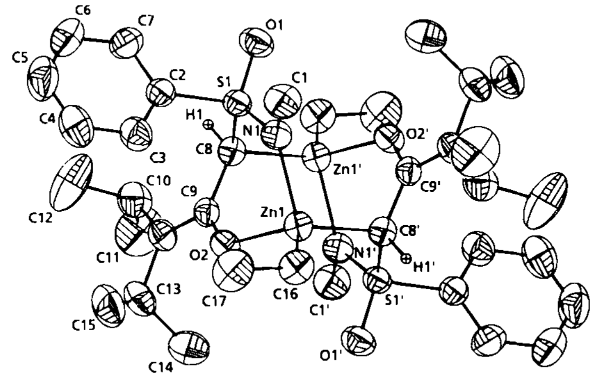
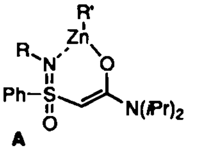


Fig. 2. Crystal structure of **7** [15].

In contrast to C(8) in **5**, the α-sulfur carbon in **7** is sp^3-hybridized with a tetrahedral bonding geometry. Considering the additional Zn–C interaction, **7** can be regarded as *C*-metalated carbonyl species **B**, rather than *O*-metalated enolate **A**.



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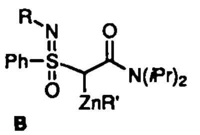
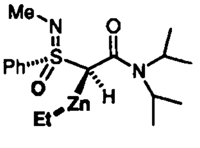


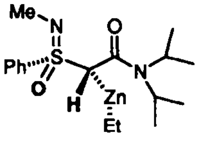
B

Selected bond lengths and angles are included in Table 1. The C(8)-C(9) bond in **7** of 1.48 Å is considerably longer than the corresponding one in **5** (1.37 Å); this indicates its single-bond character. The same is true for the S(1)-C(8) bond length, which has a value of 1.73 Å in **7** compared to 1.69 Å in **5**. The sp^3 hybridization of C(8) in **7** is further verified by the dihedral angle S(1)-C(8)-C(9)-O(2) of $-48.8°$, and the angles S(1)-C(8)-Zn(1) (112.9°) and S(1)-C(8)-C(9) (116.9°). In comparison to **5** and other compounds of this type,[2,8,9a] the C(9)-O(2) bond in **7** of 1.25 Å is short; this indicates a relatively high double-bond character. The Zn(1)-O(2) and Zn(1)-N(1) bonds in **7** are longer than the ones in **5**. The two carbon atoms bound to zinc, C(8') and C(16), have different bond distances to the zinc atom. The $Zn(1)-C(16)_{ethyl}$ bond (1.99 Å) is significantly shorter than the bridging Zn(1)-C(8') bond (2.16 Å). The $Zn-C_{ethyl}$ bond length is in good agreement with those of other ethylzinc-containing compounds.[7b,8,9,19a]

As first pointed out by Seebach,[20,21] aggregation of organometallics can influence reactivity and selectivity in their reactions with other substrates. Mutual recognition of chiral organometallics is the basis of "nonlinear effects" in asymmetric synthesis.[22] The main features of **7** relevant to this discussion are 1) the formation of a *hetero*chiral associate, and 2) the stereochemical control of the new stereogenic center at C(8). The latter aspect is of particular interest since only one diastereomer [(R^*,R^*)-**7**] is found in the crystal. Presumably, its formation is preferred for steric reasons due to Zn-ethyl/phenyl interactions in diastereomer (R^*,S^*)-**7**.



(R^*,R^*)-7



(R^*,S^*)-7

NMR Investigation of Ethylzinc Enolates of β-Carbonyl Sulfoximines: Solution structures of enolates **5**–**7** were investigated by ^{1}H and ^{13}C NMR spectroscopy. For these studies crystals of **5** and **7** or the recrystallized precipitate of **6** were dissolved in various deuterated solvents and the chemical shifts and coupling constants were recorded. Spectra of **6** and **7** indicated the formation of single species in solution. ^{1}H NMR spectra of **5** in [D$_8$]toluene revealed the presence of two different species, presumably aggregates, in a 3:1 ratio. NOE experiments showed interactions between the *N*-methyl and the Zn-ethyl group in **5**; this is consistent with the presence of a chelated structure containing a dative Zn-N bond. Further NOEs were measured between *N*-methyl/*tert*-butyl and Zn-ethyl/vinyl-H. These enhancements may be explained by *inter*molecular interactions and thus confirm the formation of aggregated species in toluene solution at room temperature.

Upon metalation of the β-carbonyl sulfoximines, the resonances of the hydrogens at the carbon α to the sulfoximine group were shifted downfield. A comparison of ^{1}H NMR chemical shift data of enolates **5**–**7** reveals that the vinyl-CH proton of **7** resonates most upfield; this indicates that the electron density is highest at this proton [**5** (in [D$_8$]toluene): $\delta = 4.82$ (major)/4.94 (minor); **6** (in [D$_6$]benzene): $\delta = 4.40$; **7** (in [D$_8$]toluene): $\delta = 4.01$]. This distribution of negative charge is also manifested in the structural features in the solid state (vide supra).

^{13}C NMR spectra were recorded and selected chemical shift data are summarized in Table 2. Due to problems of line broadening and solubility in [D$_8$]toluene, the ^{13}C resonances of zinc enolates **6** and **7** were measured in [D$_8$]THF and [D$_6$]DMSO, respectively.

Table 2. Selected ^{13}C chemical shifts of β-carbonyl sulfoximines and their corresponding ethylzinc enolates at ambient temperature.

Compound	*C*-O	*C*H-CO	N*C*H$_3$	Solvent
2	181.1	59.9	29.1	[D$_8$]toluene [a]
5	172.3	83.2	30.7	[D$_8$]toluene
3	163.3	52.8	29.6	CDCl$_3$
6	171.3	65.1	30.4	[D$_8$]THF
4	160.3	62.1	29.7	[D$_8$]toluene
7	168.7	62.9	30.1	[D$_6$]DMSO

[a] Measured at 253 K.

Even taking into account the shifts of the ^{13}C signals due to solvent effects, significant differences in the ^{13}C resonances ($\Delta\delta$) were observed between the nonmetalated and the corresponding zinc-containing compounds. Thus, upon metalation of β-keto sulfoximine **2** to give **5** an upfield shift of 8.8 ppm for the carbonyl carbon resonance occurred. In contrast, ethylzinc enolates **6** and **7** gave spectra in which these ^{13}C signals were shifted downfield by 8.0 and 8.5 ppm, respectively, compared to the resonances of **3** and **4**. The largest shift of a ^{13}C signal ($\Delta\delta$) was observed when **2** was metalated. The resonance of the carbon atom α to sulfur shifted from $\delta = 59.9$ in **2** to 83.2 in **5**; this indicates a significant decrease of electron density at this position. Metalation of **3** and **4** also resulted in downfield shifts for the α-sulfur carbons; however, the magnitude of $\Delta\delta$ was much smaller (+12.3 and +0.8 ppm, respectively). A comparison of the relative positions of the ^{13}C signals reveals an increase of partial negative charge at the α-sulfur carbon in the order of $\mathbf{5} \ll \mathbf{6} < \mathbf{7}$. Although this statement is in accord with evidence from solid state molecular structures and reactivity (vide infra) it should be regarded with caution, owing to the potential formation of differently aggregated zinc species in the various solvents used in this NMR study.

One-bond carbon-proton coupling constants (J_{CH}) were determined for enolates **5**–**7**. The largest J_{CH} value for the carbon α to the sulfur atom was found for compound **5** (172.3 Hz). The coupling constants of this carbon in **6** and **7** are 168.7 and 164.0 Hz, respectively. These values are indicative for sp^2 hybridization with a more flattened C-atom, that is, for oxygen metalation.[23]

Reactions of Ethylzinc Enolates 5–7 with Electrophiles: NMR spectroscopy and investigations of solid state molecular structures of enolates **5**–**7** indicated the highest electron density at the α-sulfur carbon in ethylzinc enolate **7**. Evidence from reactivity studies is in accord with these observations. Ethylzinc enolate **5**, obtained from β-ketosulfoximine **2** and diethylzinc, did not react with electrophiles such as methyl iodide or benzaldehyde. Even at elevated temperatures (+50 °C) no alkylation or aldol addition occurred. In contrast, treatment of ester

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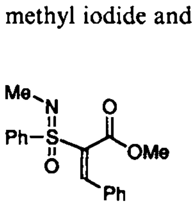
enolate **6** with benzaldehyde gave **8** as a single diastereomer in 70% yield. The (*E*) configuration of the double bond was verified by NOE experiments. Attempts to silylate the intermediate zinc alkoxide by performing the reaction in the presence of trimethylsilyl chloride were unsuccessful, and **8** was obtained as the only product. Methyl iodide did not react with **6**. Having a relatively high electron density at C(8), **7** reacted with both methyl iodide and benzaldehyde to give **9** and **10**, respectively.



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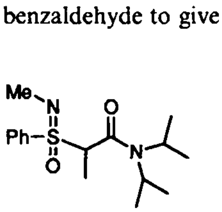

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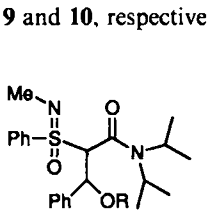

10a: R = H,
10b: R = $SiMe_3$

Alkylated product **9** was obtained as a 2.5:1 mixture of diastereomers in 69% yield.[26] Aldol reaction of **7** with benzaldehyde followed by aqueous workup gave a product (presumably **10a**), which decomposed in the attempt to purify it by column chromatography. In the presence of trimethylsilyl chloride, aldol addition of **7** with benzaldehyde afforded **10b** with >90% diastereoselectivity as determined by NMR spectroscopy of the crude product. After chromatography a single diastereomer of **10b** was obtained in 62% yield.[26] Apparently, the presence of the silyl group in **10b** is essential for the stability of the aldol addition product.

Conclusions

Aggregated ethylzinc reagents **5**–**7** were obtained by reaction of β-carbonyl sulfoximines with diethylzinc. NMR spectroscopy gave evidence for the formation of chelated enolate associates in solution. X-ray crystallographic studies revealed significant structural differences between **5** and **7**, obtained from β-ketosulfoximine **2** and β-amidosulfoximine **4**, respectively. Whereas in **5** the two halves of the molecule are linked through dative Zn–O bonds, they are connected through Zn–C interactions in **7**. In this respect, the latter compound is similar to a Reformatsky reagent for which Boersma and co-workers suggested the presence of both zinc–carbon and zinc–oxygen bonds.

The reactivity of the zinc-containing compounds **5**–**7** differs substantially. As expected from the result of structural investigations in solution and in the solid state, **7** reacts readily with electrophiles such as methyl iodide or benzaldehyde, whereas **5** is inert. Enolate **6** gives the aldol product from reaction with benzaldehyde, but is not alkylated. High stereocontrol was achieved in the aldol reactions of **6** and **7**.

Experimental Section

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques. Solvents were dried and purified according to published methods [27]. NMR spectra were measured on a Varian Gemini 300 or Bruker AT 200 at ambient temperature unless noted otherwise; ^1H NMR spectra at 300 and 200 MHz referenced to tetramethylsilane ($\delta = 0.00$), $C_6D_5CD_2H$ ($\delta = 2.09$) in $[D_8]$toluene, $[D_5]$DMSO ($\delta = 2.49$) in $[D_6]$DMSO, $[D_5]$benzene ($\delta = 7.15$) in $[D_6]$benzene, and $[D_7]$THF ($\delta = 1.73$) in $[D_8]$THF. ^{13}C NMR spectra at 75 and 50 MHz referenced to the central line of $CDCl_3$ ($\delta = 77.0$), $[D_8]$toluene ($\delta = 20.4$), $[D_6]$DMSO ($\delta = 39.5$) or $[D_8]$THF ($\delta = 25.3$). Mass spectra were measured on a VG 70–250. Elemental analyses were performed on a Leco CHN-900 or a CHN-Rapid (Heraeus). Thin-layer chromatography (TLC) was performed on Macherey & Nagel silica gel 60 (Alugram SIL G/UV_{254}) TLC plates. For column chromatography silica gel C 560 (35–70 µm, Chemische Fabrik Uetikon) was used. Products were detected by UV or revealed by coloration with phosphomolybdic acid (PMA) followed by heating. *N,S*-Dimethyl-*S*-phenylsulfoximine (**1**) was synthesized according to published methods [13]. All other reagents were purchased from Fluka and used without further purification.

(*SS*)-*S*-(3,3-Dimethylbutan-2-onyl)-*S*-phenyl-*N*-methylsulfoximine (**2**) [28]: To a stirred solution of (*SS*)-**1** (500 mg, 2.96 mmol) in THF (20 mL) was slowly added a 1.58 M solution of *n*-butyllithium in *n*-hexane (2.06 mL, 2.96 mmol) at −78 °C. After 0.5 h at 0 °C the yellow solution was treated with 2 equiv of pivalonitrile (450 µL, 5.92 mmol). Stirring was continued for 12 h at that temperature to afford a yellow precipitate. After the addition of 2 N H_2SO_4 (ca. 20 mL) the mixture was concentrated under reduced pressure to about a half its volume. The resulting aqueous solution was refluxed for 3 h and then cooled to ambient temperature. After neutralization with a saturated aqueous solution of $NaHCO_3$ (ca. 20 mL), the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with $MgSO_4$, and the solvent was removed by rotary evaporation. The dark yellow oily crude product was purified by flash column chromatography (SiO_2, hexane/ethyl acetate, 1:1). Yield: 470 mg (63%) of **2** as a slightly yellowish oil in a 63:37 ratio of ketone and enol as determined by 300 MHz ^1HNMR spectroscopy. TLC: $R_f = 0.25$ (hexane/ethyl acetate, 1:1); ^1HNMR (300 MHz, $CDCl_3$) ketone: $\delta = 7.90$ (m, 2H, Ar-*H*), 7.64–7.53 (m, 3H, Ar-*H*), 4.48 (d, 1H, $J = 18$ Hz, CH_2CO), 4.43 (d, 1H, $J = 18$ Hz, CH_2CO), 2.74 (s, 3H, NCH_3), 1.12 (s, 9H, $C(CH_3)$; enol: $\delta = 7.84$ (m, 2H, Ar-*H*), 7.64–7.53 (m, 3H, Ar-*H*), 4.78 (s, 1H, CHCO), 2.60 (s, 3H, NCH_3), 1.15 (s, 9H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 243 K): $\delta = 181.1$, 138.7, 132.3, 124.4, 124.3, 59.9, 38.5, 27.9, 28.0–24.5 (broad); EI MS (70 eV) *m/e* (%): 254 (3) $[M^+ + 1]$, 196 (47), 154 (38), 125 (48), 106 (44), 77 (100); CI MS (NH_3) *m/e* (%) 254 (100) $[M^+ + 1]$, 170 (10); $C_{13}H_{19}NO_2S$ (253.4): calcd C 61.62, H 7.56, N 5.53; found C 61.52, H 7.60, N 5.43.

(*SS*)-Methyoxycarbonylmethyl-*S*-phenyl-*N*-methyl-sulfoximine (**3**) [29]: To a stirred solution of (*SS*)-**1** (1.00 g, 5.92 mmol) in THF (25 mL) was slowly added a 1.45 M solution of *n*-butyllithium in *n*-hexane (4.1 mL, 5.92 mmol) at −78 °C. After 0.5 h at 0 °C the yellow solution was treated with 1.1 equiv of dimethyl carbonate (0.6 mL, 6.5 mmol). Stirring was continued to afford a colorless precipitate. After warming to ambient temperature, a saturated aqueous solution of $NaHCO_3$ (20 mL) was added. The mixture was extracted with ethyl acetate (3 × 30 mL), and the combined organic layers were dried with $MgSO_4$. The solvent was removed by rotary evaporation to give a yellow oily crude product, which was purified by column chromatography (SiO_2, ethyl acetate). Yield: 450 mg (34%) of **3** as a colorless oil. TLC: $R_f = 0.5$ (ethyl acetate); ^1HNMR (300 MHz, $CDCl_3$): $\delta = 7.98$–7.92 (m, 2H, Ar-*H*), 7.69–7.54 (m, 3H, Ar-*H*), 4.17 (s, 2H, SCH_2), 3.69 (s, 3H, OCH_3, 2.83 (s, 3H, NCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 163.3$, 137.9, 133.4, 129.2, 60.1, 52.8, 29.6; EI MS (70 eV) *m/e* (%): 227 (2) $[M^+]$, 154 (100), 125 (37), 106 (44), 77 (63); CI MS (NH_3) *m/e* (%) 228 (100) $[M^+ + 1]$, 154 (11); $C_{10}H_{13}NO_3S$ (227.3): calcd C 52.84, H 5.76, N 6.16; found: C 52.98, H 5.58, N 6.43.

(*SS*)-*S*-(*N,N*-Diisopropylaminocarbonylmethyl)-*S*-phenyl-*N*-methyl-sulfoximine (**4**) was prepared as described for **3**, with (*SS*)-**1** (1.0 g, 5.9 mmol), THF (25 mL), a 1.45 M solution of *n*-butyllithium in *n*-hexane (4.1 mL, 5.9 mmol), and a solution of 1.1 equiv of *N,N*-diisopropylcarbamoyl chloride (1.5 g, 6.5 mmol) in 5 mL of THF. The yellowish oily crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate, 1:1). Yield: 1.2 g (70%) of **4** as colorless crystals: M.p. 98 °C; TLC: $R_f = 0.16$ (hexane/ethyl acetate, 1:1); ^1HNMR (300 MHz, $CDCl_3$): $\delta = 7.89$–7.86 (m, 2H, Ar-*H*), 7.64–7.51 (m, 3H, Ar-*H*), 4.36 (d, $J = 14$ Hz, 1H, CH_2), 4.25 (sept, $J = 7$ Hz, 1H, $CH(CH_3)_2$), 4.13 (d, $J = 14$ Hz, 1H, CH_2), 3.43 (sept, $J = 7$ Hz, 1H, $CH(CH_3)_2$, 1.38–1.19 (m, 12H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 160.2$, 137.2, 133.1, 129.6, 129.1, 61.5, 50.8, 46.4, 29.6, 20.8, 20.6, 20.1, 20.0; EI MS (70 eV) *m/e* (%): 297 (39) $[M^+ + 1]$, 267 (9), 154 (20), 100 (100), 84 (61), 77 (51), 58 (58); CI MS (NH_3) *m/e* (%): 297 (100) $[M^+ + 1]$; $C_{15}H_{24}N_2O_2S$ (296.4): calcd C 60.77, H 8.16, N 9.45; found: C 60.46, H 8.25, N 9.60.

Preparation of Zinc Enolate 5: To a stirred solution of *rac*-**2** (100 mg, 0.39 mmol) in diethyl ether (2 mL) was slowly added a 1 M solution of diethylzinc in *n*-hexane (0.44 mL, 0.44 mmol) at 0 °C. After sedimentation of the colorless precipitate, the supernatant solution was decanted. Benzene (1 mL) was added to the crystalline residue, and warming to 60 °C afforded a clear solution. Slow cooling in the heating bath to ambient temperature gave colorless prisms. The solvent was decanted and, after brief drying of the remaining crystals under reduced pressure, 102 mg (76%) of **5** was obtained. A colorless, air- and moisture-sensitive crystal was sealed under argon in a Mark capillary and used for the X-ray data collection. For NMR spectroscopy, 50 mg (0.14 mmol) of **5** was placed into a carefully flame-dried Schlenk flask under argon. Predried $[D_8]$toluene (1 mL) was added and the resulting clear solution was transferred under argon into a dry NMR tube equipped with a rubber cap. After cooling of the solution to −95 °C, the NMR tube was sealed under vacuum. All spectra were recorded at room temperature. Two species (**5α** and **5β**) in a 3:1 ratio were identified by ^1HNMR spectroscopy:

5α (major): ^1HNMR (300 MHz, $[D_8]$toluene): $\delta = 7.85$–7.74 (m, 2H, Ar-*H*), 7.1–6.9 (m, 3H, Ar-*H*), 4.82 (s, 1H, *H*C=C), 2.62 (s, 3H, NCH_3), 1.5 (t, $J = 7.5$ Hz,

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3H, $\mathrm{ZnCH_2\text{-}C}H_3$), 1.09 (s, 9H, $\mathrm{C(C}H_3)_3$), 0.55 (q, $J = 7.5$ Hz, 2H, $\mathrm{ZnC}H_2$); ^{13}C NMR (75 MHz, [D$_8$]toluene): $\delta = 172.3$ (s), 141.4 (s), 131.9 (d, $^1J_{CH} = 165$ Hz), 129.2 (d, $^1J_{CH} = 165$ Hz), 127.9 (d, $^1J_{CH} = 165$ Hz), 83.2 (d, $^1J_{CH} = 172$ Hz), 41.1 (s), 31.0 (q, $^1J_{CH} = 137$ Hz), 28.3 (q, $^1J_{CH} = 126$ Hz), 12.7 (q, $^1J_{CH} = 125$ Hz), 0.4 (t, $^1J_{CH} = 125$ Hz).

5β (minor): ^{1}H NMR (300 MHz, [D$_8$]toluene): $\delta = 8.05$ (m, 2H, Ar-H), 4.94 (s, 1H, $H\mathrm{C{=}C}$), 2.64 (s, 3H, $\mathrm{NC}H_3$), 1.03 (s, 9H, $\mathrm{C(C}H_3)_3$), other signals overlapping with those of **5α**.

Zinc Enolate 6 was prepared as described for zinc enolate **5** with *rac*-**3** (100 mg, 0.44 mmol), diethyl ether (2 mL), and diethylzinc (1 M solution in *n*-hexane, 0.44 mL, 0.44 mmol). Enolate **6** was obtained by crystallization from benzene as described for **5**. Yield: 114 mg (81 %) of **6** as colorless, air- and moisture-sensitive crystals, unsuitable for X-ray analysis. For NMR spectroscopy 50 mg (0.15 mmol) of recrystallized **6** was used. The samples were prepared as described for **5** with [D$_6$]benzene and [D$_8$]THF as solvents (1 mL each). ^{1}H NMR (300 MHz, [D$_6$]benzene): $\delta = 7.95-7.70$ (m, 2H, Ar-H), 6.98–6.85 (m, 3H, Ar-H), 4.40 (s, 1H, $H\mathrm{C{=}C}$), 3.34 (s, 3H, $\mathrm{OC}H_3$), 2.65 (s, 3H, $\mathrm{NC}H_3$), 1.86 (t, $J = 8.4$ Hz, 3H, $\mathrm{ZnCH_2C}H_3$), 0.92 (q, $J = 8.4$ Hz, 2H, $\mathrm{ZnC}H_2$); ^{1}H NMR (300 MHz, [D$_8$]THF): $\delta = 7.76-7.73$ (m, 2H, Ar-H), 7.47–7.45 (m, 3H, Ar-H), 3.81 (s, 1H, $H\mathrm{C{=}C}$), 3.55 (s, 3H, $\mathrm{OCH_3}$), 2.56 (s, 3H, $\mathrm{NC}H_3$), 1.23 (t, $J = 8.4$ Hz, 3H, $\mathrm{ZnCH_2\text{-}C}H_3$) 0.21 (q, $J = 8.4$ Hz, 2H, $\mathrm{ZnC}H_2$); ^{13}C NMR ([D$_8$]THF, 75 MHz): $\delta = 171.3$ (s), 145.2 (s), 131.9 (d, $^1J_{CH} = 163$ Hz), 129.6 (d, $^1J_{CH} = 163$ Hz), 127.8 (d, $^1J_{CH} = 163$ Hz), 65.1 (d, $^1J_{CH} = 169$ Hz), 51.1 (q, $^1J_{CH} = 144$ Hz), 30.4 (q, $^1J_{CH} = 133$ Hz), 13.2 (q, $^1J_{CH} = 122$ Hz), −3.7 (t, $^1J_{CH} = 122$ Hz).

Zinc Enolate 7 was prepared as described for zinc enolate **5** with *rac*-**4** (100 mg, 0.33 mmol), diethyl ether (2 mL), and diethylzinc (1 M solution in *n*-hexane, 0.37 mL, 0.37 mmol). Enolate **7** was obtained by crystallization from benzene as described for **5**. Yield: 92 mg (72%) of **7** as colorless, air- and moisture-sensitive crystals. X-ray data collection was performed on a crystal that was sealed under argon in a Mark capillary. For NMR spectroscopy, 40 mg (0.1 mmol) of **7** was used. The samples were prepared as described for **5** with [D$_8$]toluene and [D$_6$]DMSO as solvents (1 mL each). ^{1}H NMR (300 MHz, [D$_8$]toluene): $\delta = 8.20-7.70$ (bm, 2H, Ar-H), 7.18–6.90 (bm, 3H, Ar-H), 4.01 (bs, 1H, $H\mathrm{C{=}C}$), 3.48–3.3 (bm, 2H, $\mathrm{N[C}H\mathrm{(CH_3)_2]}$), 2.82 (bs, 3H, $\mathrm{NC}H_3$), 1.32–0.76 {bm, 15H, $\mathrm{N[CH(C}H_3)_2]$, $\mathrm{ZnCH_2\text{-}C}H_3$}, 0.75–0.65 (m, 2H, $\mathrm{ZnC}H_2$); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 7.73-7.67$ (m, 2H, Ar-H), 7.55–7.43 (m, 3H, Ar-H), 3.68 {sept, $J = 6.9$ Hz, 2H, $\mathrm{N[C}H\mathrm{(CH_3)_2]_2}$}, 3.56 (s, 1H, $H\mathrm{C{=}C}$), 2.38 (s, 3H, $\mathrm{NC}H_3$), 1.21–1.07 {m, 15H, $\mathrm{N[CH(CH_3)_2]_2}$, $\mathrm{ZnCH_2\text{-}C}H_3$}, −0.91 (q, $J = 8.1$ Hz, 2H, $\mathrm{ZnC}H_2$); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 168.7$ (s), 145.7 (s), 130.4 (d, $^1J_{CH} = 161$ Hz), 128.7 (d, $^1J_{CH} = 164$ Hz), 125.8 (d, $^1J_{CH} = 164$ Hz), 62.9 (d, $^1J_{CH} = 164$ Hz), 45.7 (d, $^1J_{CH} = 136$ Hz), 30.1 (q, $^1J_{CH} = 136$ Hz), 21.7 (q, $^1J_{CH} = 126$ Hz), 20.6 (q, $^1J_{CH} = 126$ Hz), 13.2 (q, $^1J_{CH} = 126$ Hz), −2.3 (t, $^1J_{CH} = 114$ Hz).

(*E*)-*S*-(1-Methoxycarbonyl-2-phenylethenyl)-*S*-phenyl-*N*-methyl-sulfoximine (8): To a stirred solution of *rac*-**3** (200 mg, 0.88 mmol) in THF (10 mL) was slowly added a 1 M solution of diethylzinc in *n*-hexane (0.9 mL, 0.9 mmol) at 0 °C. After 5 h at 0 °C, benzaldehyde (93 mg, 0.88 mmol) was added to the clear solution, followed by trimethylsilyl chloride (0.11 mL, 0.88 mmol). Stirring was then continued for 12 h at ambient temperature. After the addition of a saturated aqueous solution of $\mathrm{NaHCO_3}$ (15 mL), the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with $\mathrm{MgSO_4}$, and the solvent was removed by rotary evaporation. The remaining oily crude product was purified by flash column chromatography ($\mathrm{SiO_2}$, hexane/ethyl acetate, 3:1). Yield: 192 mg (70%) of **8** as a colorless oil. NOE experiments determined the (*E*) configuration of the double bond. TLC: $R_f = 0.23$ (hexane/ethyl acetate, 3:1); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 8.03-7.99$ (m, 2H, Ar-H), 7.69 (s, 1H, $\mathrm{C}H$–Ph), 7.58–7.49 (m, 3H, Ar-H), 7.38–7.35 (m, 5H, Ar-H), 3.75 (s 3H, $\mathrm{OC}H_3$), 2.92 (s, 3H, $\mathrm{NC}H_3$); ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 164.7$, 142.1, 139.0, 134.1, 132.9, 131.8, 130.9, 129.3, 128.9, 128.8, 52.9, 29.5; EI MS (70 eV) *m/e* (%): 316 (0.2) [$M^+ + 1$], 190 (17), 158 (39), 131 (57), 125 (47), 121 (62), 107 (100), 77 (62); CI MS ($\mathrm{NH_3}$) *m/e* (%): 316 (65) [$M^+ + 1$], 156 (100); $\mathrm{C_{17}H_{17}NO_3S}$ (315.4): calcd C 64.73, H 5.43, N 4.44; found: C 64.59, H 5.52, N 4.48.

***S*-(1-Diisopropylaminocarbonylethyl)-*S*-phenyl-*N*-methylsulfoximine (9)**: To a stirred solution of *rac*-**4** (150 mg, 0.51 mmol) in THF (10 mL) was slowly added a 1 M solution of diethylzinc in *n*-hexane (0.51 mL, 0.51 mmol) at 0 °C. The cooling bath was then removed, and the mixture stirred for 0.5 h at ambient temperature. To the resulting colorless solution was added 1.1 equiv of methyl iodide (0.1 mL, 0.56 mmol). After 12 h at ambient temperature the solution was treated with a saturated aqueous solution of $\mathrm{NaHCO_3}$ (10 mL), and the resulting mixture extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with $\mathrm{MgSO_4}$, and the solvent was removed by rotary evaporation. The remaining yellow oily crude product was purified by column chromatography ($\mathrm{SiO_2}$, hexane/ethyl acetate, 1:1). Yield: 111 mg (69%) of **9** as a slightly yellowish oil in a 2.5:1 ratio of diastereomers (**9a** and **9b**).

9a (major isomer): TLC: $R_f = 0.18$ (hexane/ethyl acetate, 1:1); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.86-7.75$ (m, 2H, Ar-H), 7.67–7.48 (m, 3H, Ar-H), 4.51 (q, $J = 6.5$ Hz, 1H, $\mathrm{C}H\mathrm{CH_3}$), 4.45–4.30 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.62–3.47 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 2.80 (s, 3H, $\mathrm{NC}H_3$), 1.51–1.13 (m, 15H, $\mathrm{CHC}H_3$, $\mathrm{CH(C}H_3)_2$); ^{13}C {^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 164.0$, 134.4, 132.8, 130.6, 128.4, 61.4, 49.4, 46.4, 29.4, 21.3, 20.6, 20.3, 20.0, 15.1.

9b (minor isomer): TLC: $R_f = 0.25$ (hexane/ethyl acetate, 1:1); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.86-7.75$ (m, 2H, Ar-H), 7.67–7.48 (m, 3H, Ar-H), 4.42 (q, $J = 6.5$ Hz, 1H, $\mathrm{C}H\mathrm{CH_3}$), 4.45–4.30 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.51–3.41 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 2.72 (s, 3H, $\mathrm{NC}H_3$), 1.51–1.13 (m, 15H, $\mathrm{CHC}H_3$, $\mathrm{CH(C}H_3)_2$); ^{13}C {^{1}H} NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 164.2$, 134.9, 132.7, 130.8, 128.4, 61.9, 49.6, 46.3, 29.7, 21.2, 20.6, 20.2, 20.0, 13.3.

Mixture of **9a** and **9b**: EI MS (70 eV) *m/e* (%): 311 (0.3) [$M^+ + 1$], 154 (46), 114 (65), 100 (100), 84 (50), 77 (49), 58 (62); CI MS ($\mathrm{NH_3}$) *m/e* (%): 311 (100) [$M^+ + 1$], 156 (39); $\mathrm{C_{16}H_{26}N_2O_2S}$ (310.5): calcd C 61.89, H 8.44, N 9.03; found: C 62.07, H 9.01, N 9.58.

***S*-(1-Methoxycarbonyl-2-phenyl-2-trimethylsilyloxyethyl)-*S*-phenyl-*N*-methylsulfoximine (10b)**: To a stirred solution of *rac*-**4** (150 mg, 0.51 mmol) in THF (10 mL) was slowly added a 1 M solution of diethylzinc in *n*-hexane (0.51 mL, 0.51 mmol) at 0 °C. The cooling bath was the removed, and the mixture stirred for 0.5 h at ambient temperature. To the resulting colorless solution was added 1.1 equiv of benzaldehyde (50 µL, 0.56 mmol) followed by 1.1 equiv of trimethylsilyl chloride (50 µL, 0.56 mmol). After 1 h at ambient temperature **4** could no longer be detected by TLC. A saturated aqueous solution of $\mathrm{NaHCO_3}$ (10 mL) was added and the resulting mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with $\mathrm{MgSO_4}$, and the solvent was removed by rotary evaporation. ^{1}H NMR spectroscopy of the crude oily product revealed the predominant formation of one diastereomer (ca. 97%). After column chromatography ($\mathrm{SiO_2}$, hexane/ethyl acetate, 5:1) **10b** was obtained in diastereomerically pure form as determined by 300 MHz ^{1}H NMR. Yield: 150 mg (62%) of **10b** as colorless crystals: M.p. 96–97 °C; TLC: $R_f = 0.18$ (hexane/ethyl acetate, 5:1); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.55-7.53$ (m, 2H, Ar-H), 7.46–7.19 (m, 8H, Ar-H), 5.50 (d, $J = 8.5$ Hz, 1H, $\mathrm{C}H\mathrm{Ph}$), 4.71 (d, $J = 8.5$ Hz, 1H, $\mathrm{SC}H$), 4.06 (sept, $J = 6.4$ Hz, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.45–3.29 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 2.55 (s, 3H, $\mathrm{NC}H_3$), 1.41 (d, $J = 6.4$ Hz, 3H, $\mathrm{CHC}H_3$), 1.31 (d, $J = 6.4$ Hz, 3H, $\mathrm{CHC}H_3$), 1.20 (d, $J = 6.4$ Hz, 3H, $\mathrm{CHC}H_3$), 0.99 (d, $J = 6.4$ Hz, 3H, $\mathrm{CHC}H_3$), −0.13 (s, 9H, $\mathrm{Si(C}H_3)_3$); ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 163.2$, 140.5, 138.2, 131.8, 129.6, 129.1, 128.5, 128.4, 127.5, 74.3, 72.2, 49.7, 46.6, 29.1, 20.6, 20.2, 0.0; EI MS (70 eV) *m/e* (%): 475 (0.2) [$M^+ + 1$], 368 (17), 231 (30), 219 (29), 131 (28), 106 (79), 86 (63), 73 (70); CI MS ($\mathrm{NH_3}$) *m/e* (%): 476 (33), 475 (100) [$M^+ + 1$], 320 (37), 297 (44), 156 (25); $\mathrm{C_{25}H_{38}N_2O_3SSi}$ (474.7): calcd C 63.25, H 8.07, N 5.90; found: C 63.09, H 8.04, N 5.87.

Crystallography [15]: Colorless crystals of **5** and **7** suitable for X-ray diffraction were obtained as described above. Unit cell parameters were determined by centering 25 strong, independent reflections. The data were collected on a 4-circle diffractometer CAD4 (Enraf-Nonius). The usual corrections were applied. The absorption correction was determined by psi-scans. The structures were solved by direct methods with the program SIR92 (C. Giacovazzo, University of Bari, 1992). Anisotropic least-

Table 3. Experimental data for the X-ray diffraction studies of compounds **5** and **7**.

	5	**7**
crystal dimensions [mm]	0.30 × 0.32 × 0.50	0.20 × 0.30 × 0.40
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
Z	2	2
a [Å]	9.483(3)	10.100(2)
b [Å]	17.950(4)	14.669(3)
c [Å]	10.670(6)	13.651(2)
α	90	90
β	108.583(35)	101.645(16)
γ	90	90
volume [Å^3]	1721.55(1.23)	1980.80(0.69)
ρ_{calcd} [gcm^{-3}]	1.338	1.307
θ_{max}	30.44	28.0
radiation (wavelength [Å^3])	$\mathrm{Mo_{K\alpha}}$ (0.71069)	$\mathrm{Mo_{K\alpha}}$ (0.71069)
scan mode	$\omega/2\theta$	$\omega/2\theta$
temperature of measurement [K]	298	298
no. of measured reflections	5643	5221
no. of independent reflections	5200	4762
no. of reflections included in refinement	3176	3575
σ limit	$F_0 > 3\sigma(F_0)$	$F_0 > 3\sigma(F_0)$
absorption correction	psi-scans	psi-scans
μ [cm^{-1}]	15.77	13.79
min/max transmission	0.69/1.00	0.75/1.00
no. of parameters	181	212
R	5.31	3.35
R_w	5.44	3.76
$\Delta\rho$	0.83/−0.88	0.38/−0.30

sqares refinement was carried out on all non-H atoms by using the program CRYSTALS (D. Watkin, University of Oxford, 1990). Hydrogen atoms are in calculated positions with exception of H(1) in structure **7**, which was refined isotropically while restraining the distance C(8)–H(1) to 1.0 Å. Scattering factors were taken from the International Tables for Crystallography, Vol. IV, Table 2.2B. Crystal data and other numerical details of the structure determination are listed in Table 3.

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