Synthesis of β-Hydroxy α-Sulfanyl Esters by Using Nanocrystalline Magnesium Oxide

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Aldol-type reaction between electron deficient aldehydes and sulfonium salts to afford the corresponding β-hydroxy α-sulfanyl esters in moderate-to-good yields by using nanocrystalline MgO is described. The sulfanyl group is a useful group for further transformations in organic synthesis. Low R_f-value isomer is *anti*-configured as revealed by X-ray diffraction study and consistent with the assignment of ^{1}H-NMR spectrum.

Introduction. – β-Hydroxy α-sulfanyl esters have found widespread use in organic synthesis, particularly for the synthesis of natural products and pharmaceuticals [1]. The sulfanyl functionality is expected to act as a useful group for further transformations in the synthesis of a large number of target molecules [2].

Consequently, numerous methods have been reported for the synthesis of β-hydroxy α-sulfanyl esters. Aldol condensation of α-alkylsulfanylacetates with aldehydes catalyzed by LDA, diazaborolidine, $TiCl_4/Et_3N$ have been presented [3]. Ketene silyl acetals derived from 2-(alkylsulfanyl)propanoates were reacted with aldehydes in the presence of $Sn(OTf)_2$, $MgBr_2$, oxazaborolidinone, to afford β-hydroxy α-methyl α-(methylsulfanyl) esters in good yields [4]. The nucleophilic ring opening of the cyclic carbonates of *threo*-2,3-dihydroxy esters with thiols [5] and reduction of β-keto α-sulfenyl esters using $Ca(BH_4)_2$ or *Baker*'s yeast as catalyst [6] produce also β-hydroxy α-sulfanyl esters. Alternatively, stereoselective conjugate addition of lithium or sodium thiolate to the *Baylis–Hillman* adducts [7], and a combination of α,β-unsaturated ester, aldehyde, lithium or magnesium thiolate leads, in a one-pot *Michael*/aldol tandem reaction [8], to α-[(1-alkylsulfanyl)alkyl] β-hydroxy esters in good yields. However, to the best of our knowledge, there is no report on synthesis of β-hydroxy α-sulfanyl esters by using heterogeneous catalysts.

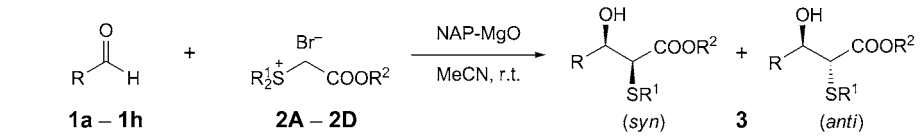
Nanocrystalline metal oxides found excellent applications as active adsorbents for gases, for destruction of hazardous chemicals [9], and as catalysts for various organic transformations [10]. These high reactivities are due to high surface areas combined with unusually reactive morphologies. In continuation of our work on the application of nanomaterials in synthetic methodologies, here, we report an effective aldol-type

reaction between electron-deficient aldehydes and various sulfonium salts to afford β-hydroxy α-sulfanyl esters in moderate-to-good yields by using nanocrystalline magnesium oxide (NAP-MgO).

Results and Discussion. – Electron-deficient aldehydes **1** react with sulfonium salts **2** in an aldol-type reaction in the presence of NAP-MgO catalyst to afford β-hydroxy α-sulfanyl esters (*Scheme 1*). The results obtained are in contrast to many reports in which epoxides are the final products [3a][11]. Earlier, a similar difference was observed, when the reaction was performed between *N*-tosyl aldimine and (2-ethoxy-2-oxoethyl)(dimethyl)sulfonium bromide (**2A**) by using NAP-MgO, since β-amino α-sulfanyl ester [10d] was obtained instead of the predicted aziridine [12].

To understand the relationship between structure and reactivity, various forms of

Scheme 1. *NAP-MgO-Catalyzed Aldol-Type Reaction between Aldehydes* **1** *and Sulfonium Salts* **2**



MgO crystals (CM-MgO (commercial MgO, SSA: 30 m^2/g), NA-MgO (NanoActive MgO, conventionally prepared MgO, SSA: 250 m^2/g), NAP-MgO (NanoActive Plus MgO, aerogel prepared MgO, SSA: 590 m^2/g), and silylated MgO, Sil-NAP-MgO) were initially evaluated in the reaction between 4-nitrobenzaldehyde (**1a**) and **2A** (*Scheme 1*). It was found that all forms of MgO catalyze the reaction in good yields, however, the high surface area NAP-MgO was found to be superior to that of NA-MgO and CM-MgO (*Table 1*).

Table 1. *Aldol-Type Reaction between 4-Nitrobenzaldehyde* (**1a**) *and (2-Ethoxy-2-oxoethyl)(dimethyl)-sulfonium Bromide* (**2A**) *with Various Catalysts*[a])

Entry	Catalyst	Time [d]	Yield [%][b])	*syn*:*anti*[c])
1	NAP-MgO	1.5, 2	79, 74[d])	53:47
2	NA-MgO	2.5	72	52:48
3	CM-MgO	4	67	50:50
4	Sil-NAP-MgO	3	65	50:50
5	None	4	n.r.[e])	–

[a]) Reaction conditions: aldehyde **1a** (2 mmol), sulfonium salt **2A** (4 mmol), catalyst (0.25 g), MeCN (8 ml) at r.t. [b]) Yield of both diastereoisomers. [c]) The *syn*/*anti* ratio of the isomers was determined by ^{1}H-NMR spectroscopy of the crude reaction mixture. [d]) Third cycle. [e]) n.r. = No Reaction.

Various solvents were examined for optimization of the aldol-type reaction of **1a** and **2A** by using NAP-MgO at room temperature. The nature of the solvent had a striking effect on the yield of the reaction product **3aA**. The use of a non-coordinating

solvent like toluene led to lower yields, when compared to polar solvents. In polar solvents (THF, CH_2Cl_2, DMF, and $CHCl_3$), the product was obtained in moderate yields. However, in MeCN a good yield was achieved, which was, therefore, selected as solvent for further reactions (*Table 2*).

Table 2. *Solvent Screening in Aldol-Type Reaction of 4-Nitrobenzaldehyde* (**1a**) *with (2-Ethoxy-2-oxoethyl)(dimethyl)sulfonium Bromide* (**2A**) *Catalyzed by NAP-MgO*[a])

Entry	Solvent	Time [d]	Yield [%][b])	*syn*/*anti*[c])
1	Toluene	3	36	50 : 50
2	THF	2	64	48 : 52
3	CH_2Cl_2	2.5	65	56 : 44
4	DMF	3	56	55 : 45
5	$CHCl_3$	3	61	46 : 54
6	MeCN	1.5	79	53 : 47

[a]) Reaction conditions: aldehyde **1a** (2 mmol), sulfonium salt **2A** (4 mmol), catalyst (0.25 g), MeCN (8 ml) at r.t. [b]) Yield of both diastereoisomers. [c]) The *syn*/*anti* ratio of the isomers was determined by ^{1}H-NMR spectroscopy of the crude reaction mixture.

Initially, benzaldehyde was reacted with sulfonium salt **2A** using NAP-MgO under the optimized conditions. After stirring for 3 d at room temperature, the desired product was isolated in trace amounts. Interestingly, when electron-deficient **1a** was used under these conditions for 36 h, a smooth reaction was observed to yield 79% of isolated product with a *syn*/*anti* ratio of 53 : 47. When the reaction was performed with electron rich *p*-anisaldehyde, no desired product was obtained, even after prolonged reaction times. These observations suggested that electron-deficient aldehydes were suitable candidates for the applied reaction conditions. Next, to determine the generality of this reaction, a variety of structurally different electron-deficient aldehydes with various ester sulfonium salts **2A**–**2D** were employed under the optimized conditions (*Table 3*). The reaction of 4-nitro- or 4-cyanobenzaldehyde (**1a** or **1c**, resp.) and sulfonium salts **2A**–**2C** in the presence of NAP-MgO afforded the corresponding products, **3aA**, **3cA**, **3aB**, and **3aC**, in good yields, whereas 4-chloro- or 4-(trifluoromethyl)benzaldehyde (**1f** or **1e**, resp.) with **2A**–**2C** gave the corresponding products, **3eA**, **3fA**, **3eB**, and **3eC**, in moderate yields. Not only mono-substituted benzaldehydes, also 4-chloro-3-nitrobenzaldehyde (**1g**) was reacted with sulfonium salt **2A** and afforded the product **3gA** in good yield. Also furfural gave with **2A** the aldol adduct **3hA** in good yield. On the other hand, sulfonium salt **2D** and aldehyde **1a** and **1g** led to the desired products **3aD** and **3gD** in moderate yields. The diastereoselectivity of the reactions was low as compared with *Mannich*-type reaction of sulfonyl imines with sulfonium salts [10d]. This may be due to the steric hinderance of the bulky sulfonyl groups of imines in *Mannich* type reactions, whereas there is no steric hindrance in the present aldol type reactions with aldehydes.

To establish the relative configurations of the obtained *syn*- and *anti*-isomers, the diastereoisomers of **3cA** (*Table 3*, *Entry 3*) were reduced ($LiAlH_4$, THF, 0°, 1 h) to the corresponding 1,3-diols, which were converted into *syn*- and *anti*-acetonides **4a** and **4b** (2,2-dimethoxypropane, cat. TsOH, dry acetone, r.t.), respectively, as depicted in

Table 3. *Aldol-Type Reaction of Various Aldehydes* **1a**–**1h** *with Various Sulfonium Salts* **2A**–**2D** *Catalyzed by NAP-MgO*[a])

Entry	Aldimine **1**		Sulfonium salt **2**			Time [d]	Products **3**		
		R		R^1	R^2			Yield [%][b])	*syn*/*anti*[c])
1	**1a**	4-NO_2–C_6H_4	**2A**	Me	Et	1.5	**3aA**	79	53 : 47
2	**1b**	3-NO_2–C_6H_4	**2A**	Me	Et	3	**3bA**	75	54 : 46
3	**1c**	4-CN–C_6H_4	**2A**	Me	Et	2	**3cA**	81	55 : 45
4	**1d**	3-CN–C_6H_4	**2A**	Me	Et	2.5	**3dA**	76	52 : 48
5	**1e**	4-CF_3–C_6H_4	**2A**	Me	Et	2	**3eA**	62	42 : 58
6	**1f**	4-Cl–C_6H_4	**2A**	Me	Et	3	**3fA**	56	48 : 52
7	**1g**	4-Cl,3-NO_2–C_6H_3	**2A**	Me	Et	2.5	**3gA**	76	43 : 57
8	**1h**	Furan-2-yl	**2A**	Me	Et	2	**3hA**	72	50 : 50
9	**1a**	4-NO_2–C_6H_4	**2B**	Me	^{t}Bu	1.5	**3aB**	80	58 : 42
10	**1e**	4-CF_3–C_6H_4	**2B**	Me	^{t}Bu	2	**3eB**	64	54 : 46
11	**1a**	4-NO_2–C_6H_4	**2C**	Me	Me	1.5	**3aC**	77	45 : 55
12	**1e**	4-CF_3–C_6H_4	**2C**	Me	Me	2	**3eC**	58	43 : 57
13	**1a**	4-NO_2–C_6H_4	**2D**	Et	Et	2	**3aD**	65	58 : 42
14	**1g**	4-Cl,3-NO_2–C_6H_3	**2D**	Et	Et	2.5	**3gD**	61	55 : 45

[a]) Reaction conditions: aldehyde **1** (2 mmol), sulfonium salt **2** (4 mmol), catalyst (0.25 g), MeCN (8 ml) at r.t.

Scheme 2. The relative configuration at C(4) and C(5) was deduced from the coupling constants of **4a** (^3J = 3.0 Hz, *cis*-coupling) and **4b** (^3J = 10.8 Hz, *trans*-coupling) in the ^{1}H-NMR spectra. The ^3J coupling was typically larger for the *anti*-diastereoisomer compared to its *syn*-analog [3c].

In **4a**, the small coupling (*ca.* 3 Hz) between H–C(4) and H–C(5), as well as those of H_{ax}–C(6) and H_{eq}–C(6) with H–C(5) confirms that H–C(5) is in equatorial position. The NOE between H–C(4) and one H–C(6) at δ(H) 4.43 confirms that H–C(4) is in axial position. In **4b**, the large coupling (*ca.* 11 Hz) between H–C(4) and H–C(5), as well as that of H–C(5) with one of the H–C(6) at δ(H) 3.8 confirms that H–C(4) and H–C(5) are in axial positions. This observation is supported by the absence of NOE between H–C(4) and H–C(5). Furthermore, the NOE between H–C(4) and H_{ax}–C(6) at δ(H) 3.8 confirms that H–C(4) is in axial position.

These results indicated the *syn*-configuration for the high-R_f-value isomers (**4a**) and *anti*-configuration for the low-R_f-value isomers (**4b**) on the basis of chemical shifts and coupling constants.

Additional confirmation for the assignments was obtained by a single-crystal X-ray-analysis of the low-R_f-value isomer of **3aC** (*Table 3*, *Entry 11*). A crystal was grown from $CHCl_3$, and the determined structure showed *anti*-configuration (*Fig.*), consistent with the NMR spectroscopic assignments[1]).

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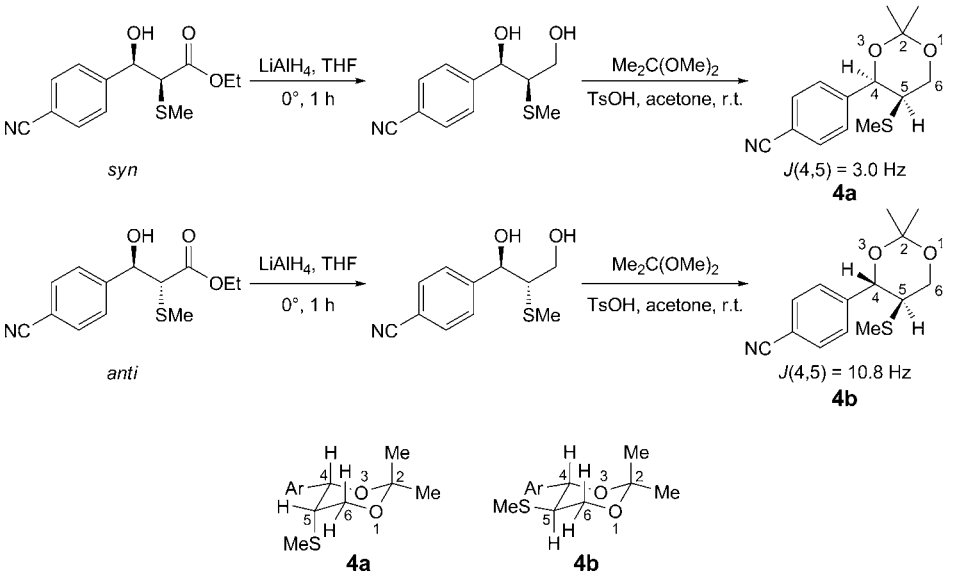
[1]) Crystal structure and refinement data for methyl 3-hydroxy-(2-methylsulfanyl)-3-(4-(nitrophenyl)-propanoate (low-R_f-value isomer, **3aC**; *Table 3*, *Entry 11*) are available as the Supporting Information (available from the authors). The crystal structure has been deposited with the *Cambridge Crystallographic Data Centre* under the deposition No. CCDC-805988.

Scheme 2. *Synthesis of Acetonides* **4a** *and* **4b**



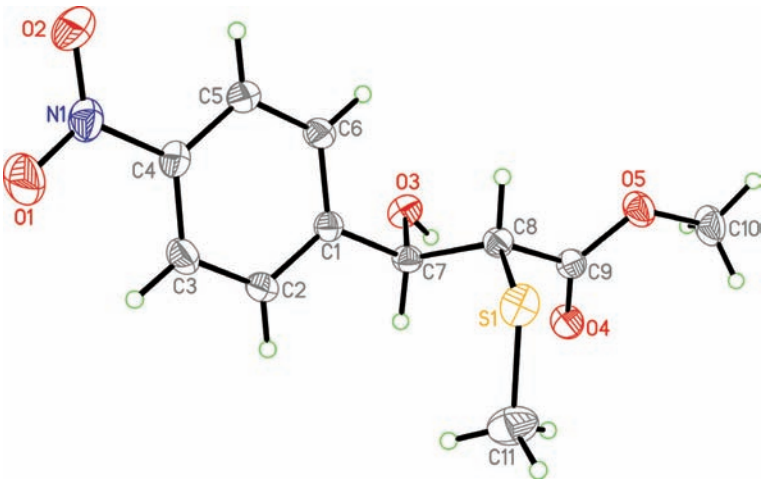


Figure. *Thermal ellipsoidal plot of compound* **3aC** (low-R_f-value isomer; *Table 3*, *Entry 11*). Displacement ellipsoids are drawn at the 30% probability level except for the H-atoms, which are shown as circles of arbitrary radius.

To disclose the relationship between structure and reactivity of the catalyst in the aldol-type reaction, it is prerequisite to have information on the structure and nature of the reactive sites of NAP-MgO. NAP-MgO has single-crystallites with three-dimensional polyhedral structure, which possess high surface concentrations of edge/corner arrangement and various exposed crystal planes (such as 002, 001, 111), leading to

inherently high surface reactivity per unit area. Thus, NAP-MgO indeed displayed the highest activity compared to that of NA-MgO and CM-MgO. Besides, the NAP-MgO has *Lewis* acidic sites Mg^{2+}, *Lewis* basic sites O^{2-} and O^{-}, lattice-bound and isolated *Brønsted* hydroxy, and anionic and cationic vacancies [13]. Generally, aldol-type reactions are known to be driven by base catalysts [3a–3c], and, accordingly, the surface OH, O^{2-} sites of these oxide crystals are expected to trigger these reactions. To examine the role of OH, the Sil-NAP-MgO [14] devoid of free OH, was tested in this aldol-type reaction. It is found that the rate of the reaction was slow, and a longer reaction time was required in this aldol-type reaction (*Table 1*, *Entry 4*). Although both NAP-MgO and NA-MgO possess defined shapes and the same average concentrations of surface OH groups, a possible rationale for the display of higher reactivity to β-hydroxy α-sulfanyl esters by the NAP-MgO is the presence of more surface *Lewis* acidic site Mg^{2+} ions (20%) and OH groups present on the edge and corner sites of the NAP-MgO, which are stretched in three-dimensional space, and are more isolated and accessible for the reactants. Thus, NAP-MgO indeed displayed the highest activity compared to NA-MgO and CM-MgO. In the aldol-type reaction, O^{2-}/O^{-} (*Lewis* base) of NAP-MgO activates the sulfonium salt **2**, which forms the sulfur ylide, coordinated to unsaturated Mg^{2+}/Mg^{+} (*Lewis* acid type) of the NAP-MgO. The aldol-type reaction proceeds *via* dual activation of both substrates (electrophiles and nucleophiles) by NAP-MgO. Thus, the *Lewis* base moiety (O^{2-}/O^{-}) of the catalyst activates the sulfonium salt and the *Lewis* acid moiety (Mg^{2+}/Mg^{+}) activates the aldehyde [15].

The NAP-MgO was reused for three cycles with consistent activity (*Table 1*, *Entry 1*). After completion of the reaction, the catalyst was centrifuged and washed with AcOEt for several times. The recovered catalyst was activated at 250° for 1 h under N_2 before reuse.

Conclusions. – In conclusion, nanocrystalline MgO has been demonstrated to be an effective catalyst for the aldol-type reaction of various electron-deficient aldehydes with a variety of sulfonium salts to afford the corresponding β-hydroxy α-sulfanyl esters in moderate-to-good yields under mild conditions. NMR Spectroscopic data suggest the *syn*-configuration to the high-R_f-value isomer, **4a**, and *anti*-configuration to the low-R_f-value isomer, **4b**, and is consistent with the outcome of a single-crystal X-ray diffraction study on one example of the low-R_f-value isomer, which showed *anti*-configuration.

K. M. thanks the *CSIR*, India for the award of senior research fellowship.

Experimental Part

1. *General.* Nanocrystalline MgO samples were obtained from *NanoScale Materials Inc.* (formally *Nanotek, Inc.*) Manhattan, Kansas, USA. All catalysts were calcined at 400° for 4 h before use. Other chemicals and solvents were purchased from *Aldrich Chemicals* and *S.D Fine Chemicals Pvt. Ltd. India* and used as received. Column chromatography (CC): *ACME* silica gel (SiO_2; 100–200 mesh). TLC: *Merck* precoated silica-gel *60-F_{254}* aluminium sheets. M.p.: in open glass capillaries; uncorrected. IR Spectra: *NEXUS 670* FT-IR spectrometer (*Necolet Corporation Ltd.*, USA) as KBr discs; in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Varian Gemini 200* MHz or *Bruker Avance 300* MHz spectrometer; chemical shifts (δ) in ppm rel. to TMS ($\delta = 0$) as an internal standard, in $CDCl_3$, coupling constants (J) in Hz. MS: *QSTAR XL* high-resolution mass spectrometer (*Applied Biosystems*, Foster City, USA).

2. *General Procedure.* To a stirred soln. of sulfonium salt **2A** – **2D** (4 mmol) in MeCN (8 ml) was added NAP-MgO (0.25 g) at ambient temp. After 5 – 10 min, the aldehyde **1** (2 mmol) was added, and the mixture was stirred at r.t. After completion of the reaction (monitored by TLC), the catalyst was centrifuged and washed with AcOEt (3 × 5 ml). The combined org. solvent was removed under reduced pressure. The crude product was purified by CC (SiO_2 (100 – 200 mesh); AcOEt/hexane in varying proportions) to afford the pure products. All the products were characterized by IR, ^{1}H- and ^{13}C-NMR, and HR-MS analyses.

*Ethyl (2*R**,3*S**)- and (2*R**,3*R**)-3-Hydroxy-2-(methylsulfanyl)-3-(4-nitrophenyl)propanoate* (**3aA**). *Data of* syn-**3aA**. R_f (hexane/AcOEt 6 : 4) 0.49. Viscous oil. IR: 3486, 2983, 2926, 1724, 1348, 1156. ^{1}H-NMR (300 MHz): 1.2 (*t*, *J* = 6.8, 3 H); 2.19 (*s*, 3 H); 3.24 (*d*, *J* = 7.6, 1 H); 3.51 (br. *s*, 1 H); 4.02 – 4.2 (*m*, 2 H); 5.05 (*d*, *J* = 7.6, 1 H); 7.58 (*d*, *J* = 9.1, 2 H); 8.2 (*d*, *J* = 9.1, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.8; 14.0; 55.1; 61.5; 70.5; 123.4; 127.7; 147.3; 147.6; 170.2. ESI-MS: 284 ($[M-H]^+$). HR-ESI-MS: 284.0594 ($C_{12}H_{14}NO_5S^+$; calc. 284.0592).

Data of anti-**3aA**. R_f (hexane/AcOEt 6 : 4) 0.44. Pale yellow solid. M.p. 73 – 75°. IR: 3440, 2985, 2928, 1704, 1346, 1180. ^{1}H-NMR (300 MHz): 1.29 (*t*, *J* = 7.6, 3 H); 2.08 (*s*, 3 H); 3.33 (*d*, *J* = 8.3, 1 H); 3.42 (*d*, *J* = 5.3, 1 H); 4.15 – 4.28 (*m*, 2 H); 5.02 (*dd*, *J* = 5.3, 8.3, 1 H); 7.58 (*d*, *J* = 9.1, 2 H); 8.22 (*d*, *J* = 9.1, 2 H). ESI-MS: 284 ($[M-H]^+$). HR-ESI-MS: 284.0598 ($C_{12}H_{14}NO_5S^+$; calc. 284.0592).

*Ethyl (2*R**,3*S**)- and (2*R**,3*R**)-3-Hydroxy-2-(methylsulfanyl)-3-(3-nitrophenyl)propanoate* (**3bA**). *Data of* syn-**3bA**. R_f (hexane/AcOEt 6 : 4) 0.48. Viscous oil. IR: 3475, 2979, 2922, 1711, 1348, 1152. ^{1}H-NMR (200 MHz): 1.21 (*t*, *J* = 6.8, 3 H); 2.21 (*s*, 3 H); 3.29 (*d*, *J* = 7.8, 1 H); 3.6 (br. *s*, 1 H); 4.05 – 4.2 (*m*, 2 H); 5.07 (*d*, *J* = 7.8, 1 H); 7.52 (*t*, *J* = 7.8, 1 H); 7.74 (*d*, *J* = 7.8, 1 H); 8.16 (*d*, *J* = 8.7, 1 H); 8.27 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.7; 13.8; 55.2; 61.5; 70.5; 121.8; 122.9; 129.1; 133.0; 142.2; 148.0; 170.2. ESI-MS: 308 ($[M+Na]^+$). HR-ESI-MS: 308.0564 ($C_{12}H_{15}NNaO_5S^+$; calc. 308.0568).

Data of anti-**3bA**. R_f (hexane/AcOEt 6 : 4) 0.41. Viscous oil. IR: 3466, 2984, 2927, 1725, 1351, 1158. ^{1}H-NMR (300 MHz): 1.3 (*t*, *J* = 7.6, 3 H); 2.07 (*s*, 3 H); 3.37 (*d*, *J* = 8.3, 1 H); 3.57 (br. *s*, 1 H); 4.18 – 4.28 (*m*, 2 H); 5.03 (*d*, *J* = 8.3, 1 H); 7.53 (*t*, *J* = 7.6, 1 H); 7.73 (*d*, *J* = 7.6, 1 H); 8.17 (*d*, *J* = 8.3, 1 H); 8.26 (*s*, 1 H). ESI-MS: 308 ($[M+Na]^+$). HR-ESI-MS: 308.0569 ($C_{12}H_{15}NNaO_5S^+$; calc. 308.0568).

*Ethyl (2*R**,3S*)- and (2*R**,3*R**)-3-(4-Cyanophenyl)-3-hydroxy-2-(methylsulfanyl)propanoate* (**3cA**). *Data of* syn-**3cA**. R_f (hexane/AcOEt 6 : 4) 0.44. White solid. M.p. 75 – 77°. IR: 3532, 2982, 2922, 2226, 1708, 1325, 1193. ^{1}H-NMR (300 MHz): 1.19 (*t*, *J* = 6.8, 3 H); 2.19 (*s*, 3 H); 3.22 (*d*, *J* = 7.6, 1 H); 3.5 (br. *s*, 1 H); 4.04 – 4.16 (*m*, 2 H); 4.99 (*d*, *J* = 7.6, 1 H); 7.52 (*d*, *J* = 8.3, 2 H); 7.63 (*d*, *J* = 8.3, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.8; 13.9; 55.2; 61.4; 70.7; 111.9; 118.5; 127.5; 132.0; 145.3; 170.2. ESI-MS: 264 ($[M-H]^+$). HR-ESI-MS: 264.0691 ($C_{13}H_{14}NO_3S^+$; calc. 264.0694).

Data of anti-**3cA**. R_f (hexane/AcOEt 6 : 4) 0.38. White solid. M.p. 70 – 72°. IR: 3469, 2990, 2925, 2232, 1735, 1292, 1160. ^{1}H-NMR (300 MHz): 1.29 (*t*, *J* = 6.8, 3 H); 2.06 (*s*, 3 H); 3.31 (*d*, *J* = 8.3, 1 H); 3.37 (*d*, *J* = 6.1, 1 H); 4.16 – 4.27 (*m*, 2 H); 4.96 (*dd*, *J* = 6.1, 8.3, 1 H); 7.51 (*d*, *J* = 8.3, 2 H); 7.65 (*d*, *J* = 8.3, 2 H). ESI-MS: 264 ($[M-H]^+$). HR-ESI-MS: 264.0696 ($C_{13}H_{14}NO_3S^+$; calc. 264.0694).

*Ethyl (2*R**,3S*)- and (2*R**,3*R**)-3-(3-Cyanophenyl)-3-hydroxy-2-(methylsulfanyl)propanoate* (**3dA**). *Data of* syn-**3dA**. R_f (hexane/AcOEt 6 : 4) 0.44. Viscous oil. IR: 3467, 2983, 2928, 2232, 1724, 1298, 1153. ^{1}H-NMR (300 MHz): 1.19 (*t*, *J* = 7.6, 3 H); 2.19 (*s*, 3 H); 3.25 (*d*, *J* = 7.6, 1 H); 3.58 (br. *s*, 1 H); 4.06 – 4.16 (*m*, 2 H); 4.97 (*d*, *J* = 7.6, 1 H); 7.44 (*t*, *J* = 7.6, 1 H); 7.57 (*d*, *J* = 7.6, 1 H); 7.62 (*d*, *J* = 7.6, 1 H); 7.7 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.8; 13.9; 55.2; 61.4; 70.4; 112.3; 118.5; 129.0; 130.5; 131.2; 131.7; 141.5; 170.2. ESI-MS: 288 ($[M+Na]^+$). HR-ESI-MS: 288.0680 ($C_{13}H_{15}NNaO_3S^+$; calc. 288.0670).

Data of anti-**3dA**. R_f (hexane/AcOEt 6 : 4) 0.4. Viscous oil. IR: 3465, 2982, 2926, 2231, 1725, 1305, 1152. ^{1}H-NMR (300 MHz): 1.3 (*t*, *J* = 7.6, 3 H); 2.04 (*s*, 3 H); 3.31 (*d*, *J* = 8.3, 1 H); 3.59 (br. *s*, 1 H); 4.17 – 4.28 (*m*, 2 H); 4.94 (*d*, *J* = 8.3, 1 H); 7.46 (*t*, *J* = 7.6, 1 H); 7.59 (*d*, *J* = 7.6, 1 H); 7.63 (*d*, *J* = 7.6, 1 H); 7.7 (*s*, 1 H). ESI-MS: 288 ($[M+Na]^+$). HR-ESI-MS: 288.0677 ($C_{13}H_{15}NNaO_3S^+$; calc. 288.0670).

*Ethyl (2*R**,3S*)- and (2*R**,3*R**)-3-Hydroxy-2-(methylsulfanyl)-3-[4-(trifluoromethyl)phenyl]propanoate* (**3eA**). *Data of* syn-**3eA**. R_f (hexane/AcOEt 7 : 3) 0.41. Viscous oil. IR: 3474, 2985, 2928, 1726, 1326, 1164. ^{1}H-NMR (200 MHz): 1.11 (*t*, *J* = 7.3, 3 H); 2.15 (*s*, 3 H); 3.21 (*d*, *J* = 8.1, 1 H); 3.65 (br. *s*, 1 H); 3.96 – 4.11 (*m*, 2 H); 4.93 (*d*, *J* = 8.1, 1 H); 7.46 (*d*, *J* = 8.4, 2 H); 7.55 (*d*, *J* = 8.4, 1 H). ^{13}C-NMR ($CDCl_3$,

75 MHz): 13.7; 13.9; 55.4; 61.4; 70.7; 125.3 (*q*; *J* = 3.7); 127.2; 143.9; 170.3. ESI-MS: 307 ($[M-H]^+$). HR-ESI-MS: 307.0624 ($C_{13}H_{14}F_3O_3S^+$; calc. 307.0615).

Data of anti-**3eA**. R_f (hexane/AcOEt 7:3) 0.35. Pale yellow solid. M.p. 48–50°. IR: 3453, 2986, 2927, 1724, 1326, 1125. ^{1}H-NMR (300 MHz): 1.27 (*t*, *J* = 7.6, 3 H); 2.01 (*s*, 3 H); 3.33 (*d*, *J* = 9.1, 1 H); 3.62 (*d*, *J* = 4.5, 1 H); 4.14–4.25 (*m*, 2 H); 4.94 (*dd*, *J* = 4.5, 9.1, 1 H); 7.49 (*d*, *J* = 8.3, 1 H); 7.6 (*d*, *J* = 8.3, 1 H). ESI-MS: 307 ($[M-H]^+$). HR-ESI-MS: 307.0619 ($C_{13}H_{14}F_3O_3S^+$; calc. 307.0615).

Ethyl (2R,3S*)- and (2R*,3R*)-3-(4-Chlorophenyl)-3-hydroxy-2-(methylsulfanyl)propanoate* (**3fA**). *Data of* syn-**3fA**. R_f (hexane/AcOEt 7:3) 0.39. Viscous oil. IR: 3490, 2981, 2922, 1719, 1349, 1161. ^{1}H-NMR (300 MHz): 1.15 (*t*, *J* = 8.1, 3 H); 2.18 (*s*, 3 H); 3.24 (*d*, *J* = 8.3, 1 H); 3.3 (br. *s*, 1 H); 4.01–4.11 (*m*, 2 H); 4.86 (*d*, *J* = 8.3, 1 H); 7.26–7.32 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.6; 13.9; 55.5; 61.3; 70.6; 128.2; 128.4; 133.9; 138.4; 170.2. ESI-MS: 297 ($[M+Na]^+$). HR-ESI-MS: 297.0331 ($C_{12}H_{15}ClNaO_3S^+$; calc. 297.0328).

Data of anti-**3fA**. R_f (hexane/AcOEt 7:3) 0.33. Viscous oil. IR: 3481, 2978, 2925, 1729, 1345, 1151. ^{1}H-NMR (300 MHz): 1.28 (*t*, *J* = 7.6, 3 H); 2.0 (*s*, 3 H); 3.3 (*d*, *J* = 8.5, 1 H); 3.39 (br. *s*, 1 H); 4.15–4.25 (*m*, 2 H); 4.86 (*d*, *J* = 8.5, 1 H); 7.28–7.33 (*m*, 4 H). ESI-MS: 297 ($[M+Na]^+$). HR-ESI-MS: 297.0334 ($C_{12}H_{15}ClNaO_3S^+$; calc. 297.0328).

Ethyl (2R,3S*)- and (2R*,3R*)-3-(4-Chloro-3-nitrophenyl)-3-hydroxy-2-(methylsulfanyl)propanoate* (**3gA**). *Data of* syn-**3gA**. R_f (hexane/AcOEt 6:4) 0.5. Viscous oil. IR: 3486, 2984, 2927, 1723, 1352, 1155. ^{1}H-NMR (300 MHz): 1.23 (*t*, *J* = 7.2, 3 H); 2.19 (*s*, 3 H); 2.23 (*d*, *J* = 7.4, 1 H); 3.62 (br. *s*, 1 H); 4.09–4.21 (*m*, 2 H); 5.01 (*d*, *J* = 7.4, 1 H); 7.5 (*d*, *J* = 8.3, 1 H); 7.57 (*d*, *J* = 8.3, 1 H); 7.91 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.7; 13.9; 55.0; 61.7; 69.9; 123.9; 126.3; 131.5; 131.6; 140.6; 147.6; 170.3. ESI-MS: 318 ($[M-H]^+$). HR-ESI-MS: 318.0193 ($C_{12}H_{13}ClNO_5S^+$; calc. 318.0202).

Data of anti-**3gA**. R_f (hexane/AcOEt 6:4) 0.46. Viscous oil. IR: 3467, 2987, 2926, 1724, 1350, 1155. ^{1}H-NMR (300 MHz): 1.31 (*t*, *J* = 7.6, 3 H); 2.08 (*s*, 3 H); 3.3 (*d*, *J* = 8.3, 1 H); 3.66 (br. *s*, 1 H); 4.17–4.28 (*m*, 2 H); 4.96 (*d*, *J* = 8.3, 1 H); 7.5–7.57 (*m*, 2 H); 7.93 (*s*, 1 H). ESI-MS: 318 ($[M-H]^+$). HR-ESI-MS: 318.0199 ($C_{12}ClH_{13}NO_5S^+$; calc. 318.0202).

Ethyl (2R,3S*)- and (2R*,3R*)-3-(Furan-2-yl)-3-hydroxy-2-(methylsulfanyl)propanoate* (**3hA**). *Data of* syn-**3hA**. R_f (hexane/AcOEt 6:4) 0.48. Brown viscous liquid. IR: 3465, 2982, 2926, 1727, 1352, 1153. ^{1}H-NMR (300 MHz): 1.21 (*t*, *J* = 7.7, 3 H); 2.17 (*s*, 3 H); 3.18 (br. *s*, 1 H); 3.59 (*d*, *J* = 8.3, 1 H); 4.13 (*q*, *J* = 7.7, 2 H); 4.95 (*d*, *J* = 8.3, 1 H); 6.3–6.33 (*m*, 2 H); 7.34–7.36 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.6; 14.0; 52.7; 61.3; 65.6; 108.0; 110.3; 142.4; 152.4; 169.9. ESI-MS: 253 ($[M+Na]^+$). HR-ESI-MS: 253.0515 ($C_{10}H_{14}NaO_4S^+$; calc. 253.0510).

Data of anti-**3hA**. R_f (hexane/AcOEt 6:4) 0.42. Brown viscous liquid. IR: 3442, 2981, 2926, 1726, 1258, 1157. ^{1}H-NMR (300 MHz): 1.31 (*t*, *J* = 7.6, 3 H); 2.09 (*s*, 3 H); 3.24 (br. *s*, 1 H); 3.61 (*d*, *J* = 8.3, 1 H); 4.23 (*q*, *J* = 7.6, 2 H); 4.97 (*d*, *J* = 8.3, 1 H); 6.33 (*s*, 2 H); 7.36 (*s*, 1 H). ESI-MS: 253 ($[M+Na]^+$). HR-ESI-MS: 253.0519 ($C_{10}H_{14}NaO_4S^+$; calc. 253.0510).

tert-*Butyl (2R*,3S*)- and (2R*,3R*)-3-Hydroxy-2-(methylsulfanyl)-3-(4-nitrophenyl)propanoate* (**3aB**). *Data of* syn-**3aB**. R_f (hexane/AcOEt 7:3) 0.5. Yellow solid. M.p. 46–48°. IR: 3430, 2980, 2924, 1709, 1347, 1149. ^{1}H-NMR (300 MHz): 1.38 (*s*, 9 H); 2.18 (*s*, 3 H); 3.17 (*d*, *J* = 7.6, 1 H); 3.78 (br. *s*, 1 H); 5.04 (*d*, *J* = 7.6, 1 H); 7.59 (*d*, *J* = 9.1, 2 H); 8.18 (*d*, *J* = 9.1, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.8; 27.8; 56.0; 70.6; 82.6; 123.3; 127.8; 147.4; 147.6; 169.5. ESI-MS: 336 ($[M+Na]^+$). HR-ESI-MS: 336.0889 ($C_{14}H_{19}NNaO_5S^+$; calc. 336.0881).

Data of anti-**3aB**. R_f (hexane/AcOEt 7:3) 0.46. Yellow solid. M.p. 78–80°. IR: 3420, 2979, 2924, 1696, 1345, 1147. ^{1}H-NMR (300 MHz): 1.45 (*s*, 9 H); 2.1 (*s*, 3 H); 3.25 (*d*, *J* = 7.6, 1 H); 3.55 (br. *s*, 1 H); 4.97 (*d*, *J* = 7.6, 1 H); 7.57 (*d*, *J* = 9.1, 2 H); 8.21 (*d*, *J* = 9.1, 2 H). ESI-MS: 336 ($[M+Na]^+$). HR-ESI-MS: 336.0885 ($C_{14}H_{19}NNaO_5S^+$; calc. 336.0881).

tert-*Butyl (2R*,3S*)- and (2R*,3R*)-3-Hydroxy-2-(methylsulfanyl)-3-[4-(trifluoromethyl)phenyl]-propanoate* (**3eB**). *Data of* syn-**3eB**. R_f (hexane/AcOEt 8:2) 0.46. White solid. M.p. 62–64°. IR: 3506, 2982, 2929, 1708, 1334, 1156. ^{1}H-NMR (200 MHz): 1.35 (*s*, 9 H); 2.19 (*s*, 3 H); 3.17 (*d*, *J* = 7.8, 1 H); 3.51 (br. *s*, 1 H); 4.94 (*d*, *J* = 7.8, 1 H); 7.51 (*d*, *J* = 8.7, 2 H); 7.59 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.7; 27.7; 56.3; 71.0; 82.4; 125.2 (*q*, *J* = 3.6); 125.8; 127.3; 130.1; 144.0; 169.5. ESI-MS: 359 ($[M+Na]^+$). HR-ESI-MS: 359.0914 ($C_{15}H_{19}F_3NaO_3S^+$; calc. 359.0904).

Data of anti-**3eB**. R_f (hexane/AcOEt 8:2) 0.41. White solid. M.p. 94–96°. IR: 3432, 2985, 2930, 1721, 1328, 1122. ^{1}H-NMR (200 MHz): 1.45 (*s*, 9 H); 2.09 (*s*, 3 H); 3.27 (*d*, *J* = 7.8, 1 H); 3.32 (*d*, *J* = 6.1, 1 H); 4.93 (*t*, *J* = 7.8, 1 H); 7.5 (*d*, *J* = 8.3, 2 H); 7.62 (*d*, *J* = 8.3, 2 H). ESI-MS: 359 ([*M* + Na]$^+$). HR-ESI-MS: 359.0911 ($C_{15}H_{19}F_3NaO_3S^+$; calc. 359.0904).

*Methyl (2*R**,3*S**)- and (2*R**,3*R**)-3-Hydroxy-2-(methylsulfanyl)-3-(4-nitrophenyl)propanoate* (**3aC**). *Data of* syn-**3aC**. R_f (hexane/AcOEt 6:4) 0.47. Yellow solid. M.p. 85–88°. IR: 3472, 2925, 2853, 1723, 1350, 1163. ^{1}H-NMR (300 MHz): 2.19 (*s*, 3 H); 3.27 (*d*, *J* = 7.6, 1 H); 3.49 (br. *s*, 1 H); 3.66 (*s*, 3 H); 5.05 (*d*, *J* = 7.6, 1 H); 7.57 (*d*, *J* = 9.1, 2 H); 8.2 (*d*, *J* = 9.1, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.9; 52.4; 55.1; 70.5; 123.4; 127.6; 147.2; 147.7; 170.6. ESI-MS: 294 ([*M* + Na]$^+$). HR-ESI-MS: 294.0413 ($C_{11}H_{13}NNaO_5S^+$; calc. 294.0412).

Data of anti-**3aC**. R_f (hexane/AcOEt 6:4) 0.44. Yellow solid. M.p. 101–104°. IR: 3467, 2924, 2852, 1699, 1346, 1169. ^{1}H-NMR (300 MHz): 2.08 (*s*, 3 H); 3.26 (*d*, *J* = 5.3, 1 H); 3.35 (*d*, *J* = 8.3, 1 H); 3.79 (*s*, 3 H); 5.03 (*dd*, *J* = 8.3, 8.3, 1 H); 7.57 (*d*, *J* = 8.3, 2 H); 8.23 (*d*, *J* = 8.3, 2 H). ESI-MS: 294 ([*M* + Na]$^+$). HR-ESI-MS: 294.0417 ($C_{11}H_{13}NNaO_5S^+$; calc. 294.0412).

*Methyl (2*R**,3*S**)- and (2*R**,3*R**)-3-Hydroxy-2-(methylsulfanyl)-3-[4-(trifluoromethyl)phenyl]propanoate* (**3eC**). *Data of* syn-**3eC**. R_f (hexane/AcOEt 7:3) 0.37. Colorless solid. M.p. 59–60°. IR: 3514, 2951, 2924, 1713, 1326, 1169. ^{1}H-NMR (300 MHz): 2.19 (*s*, 3 H); 3.29 (*d*, *J* = 7.6, 1 H); 3.45 (br. *s*, 1 H); 3.63 (*s*, 3 H); 4.98 (*d*, *J* = 7.6, 1 H); 7.5 (*d*, *J* = 8.3, 2 H); 7.59 (*d*, *J* = 8.3, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.7; 52.3; 55.3; 70.6; 125.3 (*q*, *J* = 3.6); 127.1; 143.9; 170.7. ESI-MS: 317 ([*M* + Na]$^+$). HR-ESI-MS: 317.0436 ($C_{12}H_{13}F_3NaO_3S^+$; 317.0435).

Data of anti-**3eC**. R_f (hexane/AcOEt 7:3) 0.32. Colorless solid. M.p. 60–62°. IR: 3455, 2926, 2921, 1728, 1326, 1163. ^{1}H-NMR (300 MHz): 2.1 (*s*, 3 H); 3.35 (*d*, *J* = 8.3, 1 H); 3.54 (br. *s*, 1 H); 3.76 (*s*, 3 H); 4.95 (*d*, *J* = 9.1, 1 H); 7.49 (*d*, *J* = 8.3, 2 H); 7.61 (*d*, *J* = 8.3, 2 H). ESI-MS: 317 ([*M* + Na]$^+$). HR-ESI-MS: 317.0439 ($C_{12}H_{13}F_3NaO_3S^+$; calc. 317.0435).

*Ethyl (2*R**,3*S**)- and (2*R**,3*R**)-2-(Ethylsulfanyl)-3-hydroxy-3-(4-nitrophenyl)propanoate* (**3aD**). *Data of* syn-**3aD**. R_f (hexane/AcOEt 7:3) 0.44. Viscous oil. IR: 3442, 2969, 2926, 1631, 1384, 1153. ^{1}H-NMR (200 MHz): 1.18–1.27 (*m*, 6 H); 2.57–2.75 (*m*, 2 H); 3.28 (*d*, *J* = 7.0, 1 H); 3.63 (br. *s*, 1 H); 4.01–4.24 (*m*, 2 H); 5.05 (*d*, *J* = 7.0, 1 H); 7.58 (*d*, *J* = 8.9, 2 H); 8.19 (*d*, *J* = 8.9, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.9; 14.4; 25.9; 54.8; 61.6; 71.2; 123.3; 127.7; 147.3; 147.6; 171.1. ESI-MS: 298 ([*M* + Na]$^+$). HR-ESI-MS: 298.0755 ($C_{13}H_{16}NO_5S^+$; calc. 298.0749).

Data of anti-**3aD**. R_f 0.39 (hexane/AcOEt 7:3). Viscous oil. IR: 3448, 2969, 2926, 1632, 1385, 1151. ^{1}H-NMR (300 MHz): 1.14 (*t*, *J* = 7.6, 3 H); 1.29 (*t*, *J* = 7.6, 3 H); 2.47 (*q*, *J* = 7.6, 2 H); 3.39 (*d*, *J* = 8.3, 1 H); 4.16–4.27 (*m*, 2 H); 4.99 (*d*, *J* = 9.1, 1 H); 7.58 (*d*, *J* = 8.9, 2 H); 8.21 (*d*, *J* = 8.9, 2 H). ESI-MS: 298 ([*M* + Na]$^+$). HR-ESI-MS: 298.0752 ($C_{13}H_{16}NO_5S^+$; calc. 298.0749).

*Ethyl (2*R**,3*S**)- and (2*R**,3*R**)-3-(4-Chloro-3-nitrophenyl)-2-(ethylsulfanyl)-3-hydroxypropanoate* (**3gD**). *Data of* syn-**3gD**. R_f (hexane/AcOEt 7:3) 0.46. Viscous oil. IR: 3487, 2982, 1725, 1352, 1150. ^{1}H-NMR (300 MHz): 1.24 (*t*, *J* = 7.6, 6 H); 2.57–2.75 (*m*, 2 H); 3.26 (*d*, *J* = 7.6, 1 H); 3.68 (br. *s*, 1 H); 4.07–4.24 (*m*, 2 H); 5.01 (*d*, *J* = 7.6, 1 H); 7.5 (*d*, *J* = 8.3, 1 H); 7.57 (*d*, *J* = 8.3, 1 H); 7.91 (*s*, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): 13.8; 14.3; 25.9; 54.5; 61.7; 70.5; 123.8; 126.3; 131.5; 140.6; 147.5; 171.1. ESI-MS: 332 ([*M* − H]$^+$). HR-ESI-MS: 332.0349 ($C_{13}H_{15}ClNO_5S^+$; calc. 332.0359).

Data of anti-**3gD**. R_f (hexane/AcOEt 7:3) 0.41. Viscous oil. IR: 3465, 2986, 1725, 1350, 1154. ^{1}H-NMR (300 MHz): 1.15 (*t*, *J* = 7.6, 3 H); 1.3 (*t*, *J* = 7.6, 3 H); 2.5 (*q*, *J* = 7.6, 2 H); 3.35 (*d*, *J* = 8.6, 1 H); 3.64 (br. *s*, 1 H); 4.17–4.27 (*m*, 2 H); 4.93 (*d*, *J* = 8.6, 1 H); 7.51 (*d*, *J* = 8.3, 1 H); 7.57 (*d*, *J* = 8.3, 1 H); 7.93 (*s*, 1 H). ESI-MS: 332 ([*M* − H]$^+$). HR-ESI-MS: 332.0351 ($C_{13}H_{15}ClNO_5S^+$; calc. 332.0359).

*(4*R**,5*S**)- and (4*R**,5*R**)-4-[2,2-Dimethyl-5-(methylsulfanyl)-1,3-dioxan-4-yl]benzonitrile* (**4**). *Data of* syn-*Acetonide* **4a**. ^{1}H-NMR (300 MHz): 1.52 (*s*, 6 H); 1.69 (*s*, 3 H); 2.68 (*m*, 1 H); 4.05 (*dd*, *J* = 2.3, 12.1, 1 H); 4.4 (*dd*, *J* = 3.0, 12.1, 1 H); 5.29 (*d*, *J* = 3.0, 1 H); 7.47 (*d*, *J* = 8.3, 2 H); 7.64 (*d*, *J* = 8.3, 2 H).

Data of anti-*Acetonide* **4b**. ^{1}H-NMR (200 MHz): 1.45 (*s*, 3 H); 1.54 (*s*, 3 H); 1.69 (*s*, 3 H); 2.58 (*sext.*, *J* = 10.8, 5.3, 11.2, 1 H); 3.78 (*t*, *J* = 11.2, 1 H); 4.01 (*dd*, *J* = 11.2, 5.3, 1 H); 4.63 (*d*, *J* = 10.8, 1 H); 7.57 (*d*, *J* = 8.3, 2 H); 7.65 (*d*, *J* = 8.3, 2 H).

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