Diastereoselective Reaction of Buta-1,3-diene with Chiral Derivatives of Glyoxylic Acid: Effective Route to Optically Pure 2-Substituted 3,6-Dihydro-2*H*-pyrans

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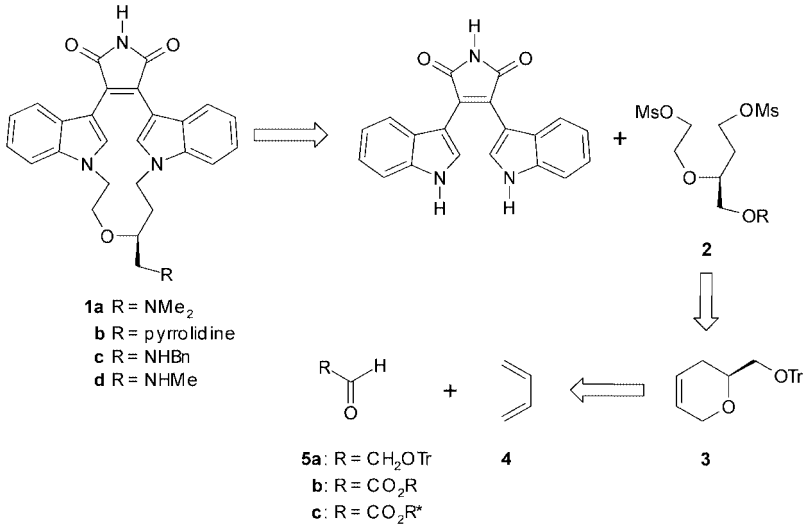
Abstract: The influence of Lewis acids on the diastereoselectivity of [4+2] cycloaddition of buta-1,3-diene (**4**) to *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam (**6a**) and (*R*)-8-phenylmenthyl glyoxylate (**6b**) was investigated and found to have high levels of asymmetric induction. The highest asymmetric induction (ca. 100% de) was obtained for the reaction of **4** with **6b** carried out in toluene and in the presence of chelating Lewis acids ($SnCl_4$, $TiCl_4$).

Key words: catalysis, chiral auxiliaries, Diels–Alder reactions, Lewis acids, stereoselectivity

The biologically active derivatives of natural alkaloids staurosporine and rebeccamycin – the macrocyclic bisindolylmaleimides of type **1** (Scheme 1) – are a group of reversible inhibitors of protein kinase C (PKC), the excessive activation of PKC being a cause of retinopathy and nephropathy in patients suffering from diabetes mellitus.[1,2] The high selectivity of these derivatives (discovered by Faul et al.[3]) with respect to PKC, as well as the very good therapeutic effect in the case of severe diabetic complications, prompted many researchers to search for an effective method of synthesis of these compounds.[3–7] The retrosynthetic analysis of compound **1** (Scheme 1) leads to the chiral precursor **2**; its preparation is a serious synthetic challenge. The retrosynthetic analysis (Scheme 1) indicates three independent pathways making use of the hetero-Diels–Alder reaction. The first pathway is based on the reaction between buta-1,3-diene (**4**) and glycolaldehyde-derived nonactivated heterodienophile **5a**, which fails to occur even under high pressure due to low activities of reactants. The second pathway makes use of the same 1,3-diene **4** and prochiral glyoxylates **5b**, leading to the product of desired stereochemistry only under chiral catalysis and high pressure,[8] although lower than in the former pathway. Finally, the third stereoselective pathway makes use of glyoxylic acid derivatives **5c** obtained from chiral alcohols or amines; due to the activated heterodienophile, this reaction proceeds in the presence of Lewis acid catalysts, under atmospheric pressure.[7]



Scheme 1

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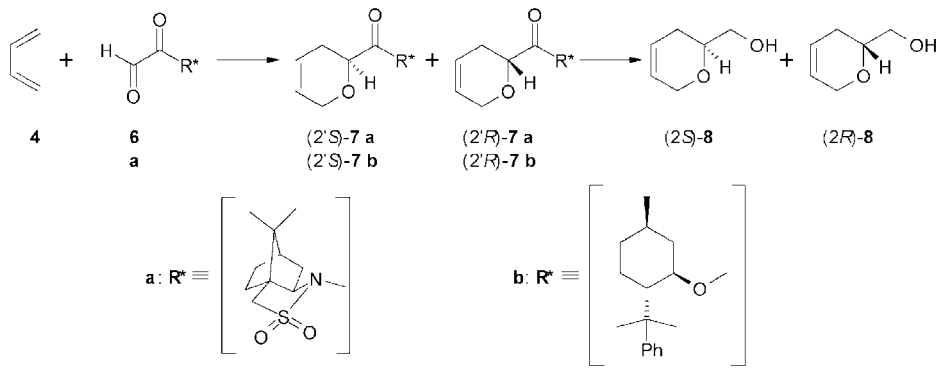
Our recently published[7] efficient synthesis of the optically pure precursor **2** was based on this synthetic pathway. The first step in the synthesis of the derivative **2** was the highly diastereoselective hetero-Diels–Alder reaction of buta-1,3-diene (**4**) with the chiral heterodienophile **6a** (Scheme 2), which afforded a mixture of diastereoisomers (2′*S*)-**7a** and (2′*R*)-**7a**. This, after separation, gave the desired pure isomer having the *S*-configuration at the newly formed stereogenic centre, in very good yield. The next stage of the synthesis was reduction of the diastereoisomer (2′*S*)-**7a** to the corresponding enantiomerically pure alcohol (2*S*)-**8**, whose optical purity was confirmed by GC. Following protection of the hydroxy group of alcohol (2*S*)-**8** using trityl chloride, we obtained the derivative **3** (Scheme 1). Its absolute configuration was confirmed by X-ray structural analysis.[7] The derivative **3** was subjected to ozonolysis followed by reduction to the corresponding diol, and then protected using mesyl chloride. The synthesis gave the enantiomerically pure (>99% ee) precursor of biologically active macrocyclic bisindolylmaleimides **2** in 15% chemical yield. This interesting method for the preparation of the chiral precursor **2** employing the diastereoselective version of hetero-Diels–Alder reaction between the chiral derivative of glyoxylic acid, i.e. *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam (**6a**) and the 1,3-diene of low activity, i.e., buta-1,3-diene (**4**) seriously competes with the other methods, among others, due to economical reasons.

This prompted us to perform further studies in this area, which included investigation of the course of this reaction under various conditions (the effects of solvent and temperature), as well as detailed analysis of the mixtures of the resulting diastereoisomers, and also a comparison of the performance of two chiral auxiliaries used as inducing systems in the above-mentioned reaction.

In order to perform a thorough analysis of the composition of diastereoisomeric mixtures of the products of hetero-[4+2] cycloaddition, we used gas chromatography on a chiral column. This method of determining diastereoisomeric excess is more precise than ^{1}H NMR spectroscopy of reaction mixtures after chromatographic purification. However, it requires an additional transformation of the diastereoisomeric mixture into the pair of the enantiomeric alcohols **8** (Scheme 2), which are separated on the gas chromatograph equipped with a chiral column. We have developed conditions for the separation of the alcohols **8** on a chiral column and assigned their absolute configurations due to separate reduction of the chromatographically separated pure diastereoisomers (2′*S*)-**7a** and (2′*R*)-**7a**. Their absolute configuration was confirmed by X-ray structural analysis[7] of the monocrystal of the diastereoisomer (2′*S*)-**7a** being the major reaction product. Having devised a very precise analysis of the diastereoisomeric composition of cycloadducts, we started the detailed study on the effect of solvents and temperature on the reaction course and asymmetric induction in order to obtain the best (from the synthetic point of view) diastereoisomeric excess accompanied by good chemical yield.

The first investigated reaction was the [4+2] cycloaddition of diene **4** to *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam (**6a**) as a heterodienophile (Scheme 2). In all the investigated cases of Lewis acids (Table 1, entries 1, 3, 5, 9), the reaction proceeded in dichloromethane at room temperature and gave the major product having the *S*-configuration at the newly generated stereogenic centre. The best diastereoisomeric excess was obtained for the reaction carried out in the presence of $BF_3{\cdot}Et_2O$ (entry 1) as a catalyst, in a moderate chemical yield of 31%. Good asymmetric induction and good yield (75%) were obtained in the same solvent using $ZnBr_2$ (entry 3) as a catalyst.

The change of solvent to the less polar toluene was accompanied by dramatic decrease in asymmetric induction (entries 2, 6, 10). In the case of strongly chelating Lewis acids, $SnCl_4$ and $TiCl_4$, this change reversed the direction of induction (entries 6, 10). Because of reduced reaction rate, the experiments at low temperature were carried out only in the presence of $SnCl_4$ and $TiCl_4$ (entries 7, 8, 11, 12). In these cases, lowering of temperature caused a similar reversal of direction of the asymmetric induction, compared to the experiments performed at room temperature in dichloromethane as a solvent (entries 7, 11). By changing the solvent from dichloromethane to toluene and decreasing the temperature, we achieved an increase in the asymmetric induction value at –20 °C. Unfortunately, the direction of the induction *R* was undesired from the



Scheme 2

Table 1 The Results of the Reaction of Heterodienophile **6a** with Diene **4** under Atmospheric Pressure

Entry	Catalyst	Solvent	Temp (°C)	Yield (%)[a]	Diastereoisomeric Ratio[b] (2′*S*)-**7a**:(2′*R*)-**7a**
1	$BF_3{\cdot}Et_2O$	CH_2Cl_2	28	31	81:19
2	$BF_3{\cdot}Et_2O$	toluene	25	ca. 100	63:37
3	$ZnBr_2$	CH_2Cl_2	28	75	80:20
4	$ZnBr_2$	toluene	25	38	84:16
5	$SnCl_4$	CH_2Cl_2	28	62	58:42
6	$SnCl_4$	toluene	25	94	46:54
7	$SnCl_4$	CH_2Cl_2	–20	86	45:55
8	$SnCl_4$	toluene	–20	92	38:62
9	$TiCl_4$	CH_2Cl_2	28	98	60:40
10	$TiCl_4$	toluene	25	89	47:53
11	$TiCl_4$	CH_2Cl_2	–20	46	48:52
12	$TiCl_4$	toluene	–20	44	42:58

[a] Isolated yields.
[b] Determined by GC.

point of view of the planned synthesis of chiral precursor **2**.

The unsatisfactory results obtained using (2*R*)-bornane-10,2-sultam as a chiral auxiliary prompted us to search for a more effective inducing system. Our attention was directed to (*R*)-8-phenylmenthol which, in the form of the corresponding derivative of glyoxylic acid, turned out to be a better reactant for diastereoselective hetero-[4+2] cycloaddition with buta-1,3-diene (**4**).

The hetero-Diels–Alder reaction of the diene **4** with (*R*)-8-phenylmenthyl glyoxylate (**6b**) carried out both in dichloromethane and in toluene, gave the major product having *S*-configuration at the newly created stereogenic centre (Table 2). In the case of the non-chelating Lewis acids, toluene clearly decreased the asymmetric induction (Table 2, entries 2, 5). In the cases of both chelating Lewis acids, $SnCl_4$ and $TiCl_4$, which gave ca. 100% diastereoisomeric excess (entries 6, 7, 9), the change of the solvent from dichloromethane to toluene caused only an increase in the chemical yield to quantitative. Concluding this stage of study, we solved the problem of the key transformation of the planned synthesis of the chiral precursor **2**, since we obtained, in quantitative yield and at ca. 100% asymmetric induction, the product (2′*S*)-**7b**, having the absolute *S*-configuration at the newly created stereogenic centre.

Table 2 The Results of the Reaction of Heterodienophile **6b** with Diene **4** at Room Temperature under Atmospheric Pressure

Entry	Catalyst	Solvent	Yield (%)[a]	Diastereoisomeric Ratio[b] (2′*S*)-**7b**:(2′*R*)-**7b**
1	$BF_3{\cdot}Et_2O$	CH_2Cl_2	45	80:20
2	$BF_3{\cdot}Et_2O$	toluene	72	73:27
3	$AlCl_3$	CH_2Cl_2	65	87:13
4	$ZnBr_2$	CH_2Cl_2	43	91:9
5	$ZnBr_2$	toluene	17	84:16
6	$SnCl_4$	CH_2Cl_2	88	ca. 100:0
7	$SnCl_4$	toluene	ca. 100	ca. 100:0
8	$TiCl_4$	CH_2Cl_2	65	95:5
9	$TiCl_4$	toluene	ca. 100	ca. 100:0

[a] Isolated yields.
[b] Determined by GC.

In summary, we have optimised the first stage of the synthesis of (*S*)-3-[2-{methylsulfonyl)oxy}ethoxy]-4-(triphenylmethoxy)butan-1-ol methanesulfonate (**2**) which is the key intermediate for biologically important alkaloids **1**. Our method, characterised by ca. 100% chemical yield and ca. 100% asymmetric induction, improves significantly the overall yield of the synthesis of precursor **2**, from 15 up to 75%, and is highly competitive to other methods of preparation of this compound.

Melting points were determined on a Kofler hot-stage apparatus with a microscope, and are uncorrected. All reported NMR spectra were recorded with a Varian Unity plus spectrometer at 500 (^{1}H NMR) and 125 (^{13}C NMR) MHz. Chemical shifts are reported as δ values relative to TMS peak defined at δ = 0.00 (^{1}H NMR) or δ = 0.0 (^{13}C NMR). IR spectra were obtained on a Perkin-Elmer 1640 FTIR spectrometer. Mass spectra were obtained on an AMD 604 Intectra instrument using the EI technique, or on a Mariner BioSystem unit using the ESI technique. Optical rotations were recorded using a Perkin-Elmer 241 polarimeter with a thermally jacketed 10 cm cell. Analytical TLC was carried out on commercially prepared plates coated with 0.25 mm of Merck Kieselgel 60. Preparative flash silica gel chromatography was performed using Merck Kieselgel 60 (230–400 mesh). Enantiomeric excesses of products were determined by GC performed using a Hewlett-Packard 5890 unit equipped with a FID detector and a capillary chiral column β-dex 225 (30 m × 0.25 mm I.D., Supelco, Bellefonte, USA). Chromatographic conditions: carrier gas: argon, 100 kPa; injection temp.: 200 °C; detector temp: 250 °C. Chromatographic parameters of enantioseparation of investigated compounds are as follows, compound (*S*)-**8**: t_R 15.13 min (temp 95 °C); compound (*R*)-**8**; t_R 16.16 min (temp 95 °C).

All commercially available chemicals were used as received unless otherwise noted. Reagents grade solvents were dried and distilled prior use. *N*-Glyoxyloyl-(*2R*)-bornane-10,2-sultam (**6a**)[9] and (*R*)-8-phenylmenthyl glyoxylate (**6b**)[10] were prepared according to the literature procedures.

[4+2] Cycloaddition of Buta-1,3-diene to Heterodienophile 6a; Lewis Acid Catalyzed Reaction; Diastereoisomers (2′*S*)-7a and (2′*R*-7a); Typical Procedure

To a solution of heterodienophile **6a** (0.5 mmol) in anhyd CH_2Cl_2 or toluene (10 mL) was added the Lewis acid (0.5 mmol) and the mixture was stirred for 20 min at r.t. Then the mixture was cooled to –78 °C and buta-1,3-diene (**4**, 2.5 mmol) was added dropwise, and the mixture was stirred for additional 24 h at r.t. or –20 °C. The progress of the reaction was monitored by TLC. When the reaction was complete, after usual work-up, the residue was chromatographed on a silica gel column using a mixture of hexane–acetone–EtOAc (2.5:3:1) to give two diastereoisomerically pure products (2′*S*)-**7a** and (2′*R*)-**7a**, which were subjected to chemical correlation.

Diastereoisomer (2′*S*)-7a

Mp 189–191°C; $[\alpha]_D^{20}$ –193.3 (*c* = 1, $CHCl_3$).

IR (KBr): 1054, 1135, 1337, 1713, cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$–TMS, 27 °C): δ = 0.97 (s, 3 H), 1.13 (s, 3 H), 1.34–1.47 (m, 2 H), 1.85–1.96 (m, 3 H), 1.99–2.04 (m, 1 H), 2.10–2.14 (dd, 1 H, J_1 = 8, J_2 = 14 Hz), 2.27–2.35 (m, 1 H), 2.41–2.47 (m, 1 H, J_1 = 1.5, J_2 = 3.5, J_3 = 15 Hz), 3.47 (AB, 2 H, J_1 = 13.5 Hz), 3.96 (dd, 1 H, J_1 = 4.75, J_2 = 7.75 Hz), 4.27–4.39 (m, 2 H), 4.71 (dd, 1 H, J_1 = 3, J_2 = 10.25 Hz), 5.74–5.77 (m, 1 H, J_1 = 1.5, J_2 = 10.5 Hz), 5.81–5.85 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$–TMS, 27 °C): δ = 19.9, 20.7, 26.4, 28.6, 32.7, 38.1, 44.5, 47.9, 48.7, 53.1, 65.0, 65.8, 72.8, 122.7, 126.1, 170.6.

MS (EI-LR): *m*/*z* (%) = 325 (M^+, 1.6), 244 (10.9), 177 (15.0), 135 (23.4), 93 (15.5), 83 (100), 82 (32.8), 75 (48.1), 55 (51.6), 41 (10.8).

Anal. Calcd for $C_{16}H_{23}NSO_4$: C, 59.05; H, 7.12; N, 4.30; S, 9.85. Found: C, 58.79; H, 7.25; N, 4.14; S, 9.65%.

Diastereoisomer (2′*R*)-7a

Mp 144–145 °C; $[\alpha]_D^{20}$ –32 (*c* = 1, $CHCl_3$).

IR (KBr): 1080, 1138, 1332, 1691 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$–TMS, 27 °C): δ = 0.99 (s, 3 H), 1.21 (s, 3 H), 1.32–1.43 (m, 2 H), 1.85–1.97 (m, 3 H), 2.09 (dd, 1 H, J_1 = 8, J_2 = 13.5 Hz), 2.14–2.19 (m, 1 H), 2.24–2.31 (m, 1 H), 2.47–2.55 (m, 1 H), 3.47 (AB, 2 H, J_1 = 13.5 Hz), 3.95 (dd, 1 H, J_1 = 5, J_2 = 7.75 Hz), 4.23–4.33 (m, 2 H), 4.60 (dd, 1 H, J_1 = 3.25, J_2 = 10.5 Hz), 5.71–5.75 (m, 1 H, J_1 = 10 Hz), 5.83–5.88 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$–TMS, 27 °C): δ = 19.9, 21.3, 26.3, 26.4, 33.3, 38.6, 45.0, 47.8, 48.6, 53.3, 65.8, 66.1, 72,7, 123.2, 125.7, 170.2.

MS (EI-LR): *m*/*z* (%) = 325 (M^+, 2.0), 244 (10.3), 177 (10.6), 135 (21.9), 93 (15.3), 83 (100), 82 (31.3), 55 (51.6), 41 (13.6).

Anal. Calcd for $C_{16}H_{23}NSO_4$: C, 59.05; H, 7.12; N, 4.30; S, 9.85. Found: C, 59.02; H, 7.16; N, 4.27; S, 9.70%.

[4+2] Cycloaddition of Buta-1,3-diene (4) to Heterodienophile 6b

The reaction was performed as in the former case, and after usual work-up, the residue was chromatographed on a silica gel column using a hexane–EtOAc (20:1) system to give two diastereoisomerically pure products (2′*S*)-**7b** and (2′*R*)-**7b**, which were subjected to chemical correlation.

Diastereoisomer (2′*S*)-7b

$[\alpha]_D^{24}$ –23.0 (*c* = 1, $CHCl_3$).

IR (film): 701, 765, 977, 1031, 1050, 1100, 1182, 1212, 1242, 1289, 1370, 1389, 1444, 1457, 1495, 1600, 1725, 2869, 2923, 2955, 3021, 3518 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$–TMS, 25 °C): δ = 0.87 (d, 3 H, J_1 = 6.6 Hz), 1.20, 1.31 (2 s, 2 × 3 H), 0.89–2.12 (m, 10 H), 3.22 (dd, 1 H, J_1 = 9.2, J_2 = 4.4 Hz), 4.04–4.35 (m, 2 H), 4.91 (td, 1 H, J_1 = 10.8, J_2 = 4.4 Hz), 5.66 (s, 2 H), 7.07–7.29 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$–TMS, 25 °C): δ = 22.0, 23.7, 26.5, 27.7, 29.2, 31.4, 34.7, 39.7, 41.7, 50.5, 65.5, 71,5, 74.6, 123.1, 125.1, 125.6, 126.2, 128.1, 152.1, 170.76.

MS (ESI-HR): *m*/*z* calcd for $C_{22}H_{30}O_3Na^+$: 365.2087, found: 365.2083.

Anal. Calcd for $C_{22}H_{30}O_3$: C, 77.16; H, 8.83; O, 14.02. Found C, 77.22; H, 8.68.

Diastereoisomer (2′*R*)-7b

$[\alpha]_D^{24}$ +41.6 (*c* = 1.08, $CHCl_3$).

^1H NMR (200 MHz, $CDCl_3$–TMS, 25 °C): δ = 0.86 (d, 3 H, J_1 = 6.4 Hz), 1.24, 1.34 (2 s, 2 × 3 H), 1.56 (s, 4 H), 1.89–2.20 (m, 4 H), 3.75 (dd, 1 H, J_1 = 8.8, J_2 = 4.8 Hz), 4.05–4.30 (m, 2 H), 4.95 (td, 1 H, J_1 = 10.8, J_2 = 4.4 Hz), 5.65–5.81 (m, 2 H), 7.14–7.30 (m, 5 H).

MS (ESI-HR): *m*/*z* calcd for $C_{22}H_{30}O_3Na^+$: 365.2093; found: 365.2099.

Anal. Calcd for $C_{22}H_{30}O_3$: C, 77.16; H, 8.83; O, 14.02. Found C, 76.81; H, 9.19.

Chemical Correlation of Cycloadducts 7 to Alcohol 8

To a solution of $LiAlH_4$ (0.5 equivalent) in distilled anhyd Et_2O, cooled to 0 °C was added a mixture of diastereoisomers (1 equiv) dissolved in anhyd Et_2O (or in the case of **7a** in anhyd CH_2Cl_2) dropwise, and the reaction mixture was stirred for 2 h in r.t. After the usual work-up, the crude product was analysed by GC to determine the diastereoisomeric excess.

(2*S*)-3,6-Dihydro-2*H*-pyran-2ylmethanol [(2*S*)-8]

$[\alpha]_D^{20}$ –154.5 (*c* = 0.95, $CHCl_3$); $[\alpha]_D^{20}$ –147.4 (*c* = 1.02, $CDCl_3$); >99% ee (determined by GC on chiral column β-dex 225).

IR (film): 463, 655, 792, 825, 954, 1025, 1057, 1087, 1183, 1247, 1388, 1429, 1641, 2836, 2889, 2928, 3037, 3393 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$–TMS, 27 °C): δ = 1.87–1.93 (m, 1 H), 2.06–2.14 (m, 1 H), 2.18–2.53 (m, 1 H, OH), 3.56–3.60 (m, 1 H), 3.65–3.69 (m, 1 H), 3.67–3.70 (m, 1 H), 4.22–4.24 (m, 2 H), 5.67–5.76 (m, 1 H), 5.80–5.85 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$–TMS, 27 °C): δ = 26.5, 65.6, 65.7, 74.1, 123.7, 126.2.

MS (ESI-HR): *m*/*z* calcd for $C_6H_{10}O_2Na^+$: 137.0573; found: 137.0579.

(2*R*)-3,6-Dihydro-2*H*-pyran-2ylmethanol [(2*R*)-8]

$[\alpha]_D^{15}$ +140.7 (*c* = 1, $CDCl_3$); >99% ee (determined by GC on chiral column β-dex 225).

^1H NMR (500 MHz, $CDCl_3$–TMS, 27 °C): δ = 1.83–1.87 (m, 1 H), 1.92–1.97 (m, 1 H), 2.01–2.17 (m, 1 H, OH), 3.61–3.74 (m, 3 H), 4.20–4.26 (m, 2 H), 5.70–5.88 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$–TMS, 25 °C): δ = 27.18, 66.4, 74.7, 124.4, 126.9.

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