Highly Diastereoselective Hydrogenation of Furan-2-carboxylic Acid Derivatives on Heterogeneous Catalysts

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Abstract: The heterogeneously catalyzed diastereoselective hydrogenation of furan-2-carboxylic acid derivatives modified with chiral auxiliaries is described. Chiral auxiliaries, catalysts, solvents, and additives were optimized for the reaction. Finally, the hydrogenation of furan-2-yl-[(*S*)-2-(hydroxydiphenylmethyl)-pyrrolidin-1-yl]-methanone resulted in a high diastereoselectivity. Removal of the auxiliary gave the tetrahydrofuran-2-carboxylic acid in 95% ee.

Key words: heterogeneous catalysis, stereoselective hydrogenation, furans, heterocycle, chiral auxiliary

The stereoselective hydrogenation of heteroaromatic compounds is a promising method for the preparation of chiral heterocycles, which are important substructures of biologically active compounds.[1] Currently there are several homogeneous catalysts, which are used for the hydrogenation of substituted aromatic heterocycles such as quinolines,[2] pyridines,[3] and pyrroles.[4] In several cases the corresponding saturated chiral heterocycles can be obtained with good or even high enantioselectivity. However, most catalysts applied are not commercially available. Interestingly, only few heterogeneously catalyzed transformations have been published although the easy separation of catalyst and product is an important advantage of this methodology. Mostly, their performance is characterized by low stereoselectivities.[5] Recently, Glorius et al. developed an efficient method for the synthesis of chiral piperidines based on the heterogeneous palladium-catalyzed hydrogenation of 2-oxazoldinone-substituted pyridines.[6]

It is remarkable that asymmetric hydrogenations of furans were less studied, although enantiomerically pure tetrahydrofurans represent valuable building blocks for the synthesis of pharmaceutical products.[7] Pioneering investigations on the enantioselective hydrogenation of furan-2-carboxylic acid in the presence of a homogeneous rhodium–phosphine complex have been published by the Solvias group, but only ee values by up to 24% were obtained.[3a] Maris et al. hydrogenated furan and benzofurancarboxylic acid derivatives using a cinchonidine-modified heterogeneous palladium catalyst.[8] Under optimized conditions enantioselectivities with up to 50% were achieved. Furthermore, Albert and co-workers reduced 2,5-disubstituted furans with good enantioselectivities.[9] The best results in the asymmetric hydrogenation of several substituted furan derivatives were recently reported by the group of Pfaltz. Using a chiral iridium–phosphine complex as catalyst excellent enantioselectivities of 78–99% ee have been achieved.[10]

To the best of our knowledge there is no hydrogenation pathway for the synthesis of optically pure tetrahydrofuran-2-carboxylic acid. Herein, we will give evidence that this compound can be obtained based on a highly diastereoselective hydrogenation of chiral furan-2-carboxylic acid derivatives on heterogeneous catalysts.

The required chiral substrates **2a–f** for the hydrogenation were synthesized by treating furan-2-carboxylic acid (**1a**) and its acid chloride **1b**, respectively, with enantiomerically pure menthol, cyclohexanol, camphorsultam, and prolinol derivatives. Compounds **3a–f** were subsequently hydrogenated at 30 bar initial H_2 pressure. The nature of heterogeneous catalysts, auxiliaries, solvents, and additives on the diastereoselectivity was studied in detail, and the most efficient substrate **3f** was finally hydrolyzed to tetrahydrofuran-2-carboxylic acid (**4**, Scheme 1).

In order to identify the best reaction conditions several heterogeneous catalysts and solvents were used in the hydrogenation of furan-2-carboxylic acid menthyl ester (**2a**). The results are summarized in Table 1.

As shown in Table 1, no conversion of **2a** was observed using Raney nickel and platinum catalysts at a hydrogen pressure of 30 bar (entries 1–3). The hydrogenation on rhodium and ruthenium catalysts resulted in complete conversion, but only low de values of compound **3a** were observed (entries 4–6). Surprisingly, the hydrogenation with palladium on alumina failed (entries 7 and 8), whereas de values of up to 27% were achieved with $Pd(OH)_2$/C as the most effective catalyst (entries 9 and 10). The presence of acetic acid in isopropanol proved to be advantageous (33% de, entry 11). However, the pure acetic acid inhibited the reaction (entry 12).

Next we set out to investigate the influence of the auxiliary on the diastereoselectivity. Therefore, we hydrogenated furan-2-carboxylic acid derivatives **2b–f** on $Pd(OH)_2$/C. The results are given in Table 2 and show that all substrates (except **2e**) gave complete conversions into the

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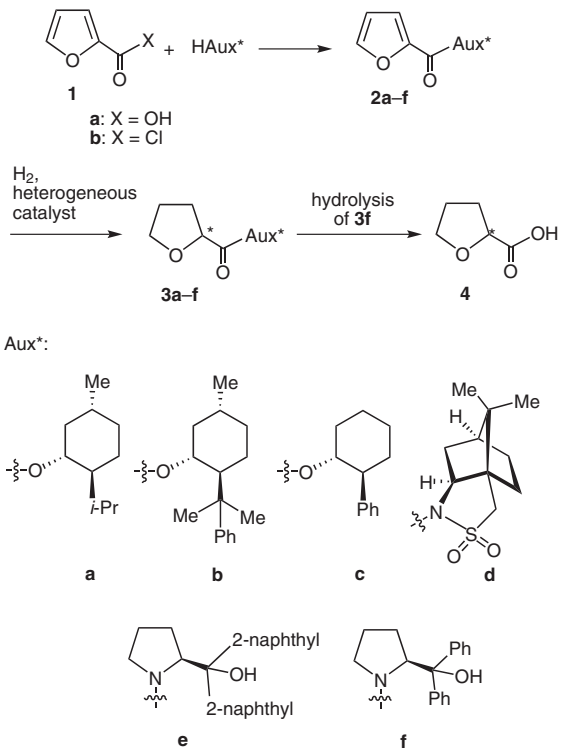
corresponding tetrahydrofuran derivatives **3b–d** and **3f** under mild conditions.



Scheme 1 Synthesis of furan-2-carboxylic acid esters and amides, diastereoselective hydrogenation, and removal of the chiral auxiliary

Table 1 Diastereoselective Hydrogenation of Furan-2-carboxylic Acid Menthyl Ester (**2a**) on Various Heterogeneous Catalysts[a]

Entry	Catalyst	Solvent	Time (h)	Temp (°C)	Conv. (%)[b]	de (%)[c]
1	Raney nickel	*i*-PrOH	20	25	0	0
2	PtO_2	*i*-PrOH	6	40	0	0
3	5% Pt/C	*i*-PrOH	6	25	0	0
4	5% Rh/Al_2O_3	*i*-PrOH	6	40	100	8
5	5% Rh/C	*i*-PrOH	6	40	100	9
6	5% Ru/C	*i*-PrOH	6	40	76	9
7	5% Pd/Al_2O_3	toluene	4	25	0	0
8	5% Pd/Al_2O_3	*i*-PrOH	6	40	0	0
9	$Pd(OH)_2/C$[d]	*i*-PrOH	6	40	98	27
10	$Pd(OH)_2/C$[d]	*i*-PrOH	6	25	100	27
11	$Pd(OH)_2/C$[d]	*i*-PrOH–AcOH	18	25	100	33
12	$Pd(OH)_2/C$[d]	AcOH	18	25	0	0

[a] Reaction conditions: **2a** (0.3 mmol), solvent (15 mL), catalyst (25 mg), H_2 (30 bar), 600 rpm.
[b] Determined by HPLC.
[c] Determined by ^{1}H NMR.
[d] 15–20% Pd.

Table 2 Diastereoselective Hydrogenation of **2b–f** on $Pd(OH)_2/C$ as Catalyst[a]

Entry	Substrate	Solvent	Time (h)	Conversion (%)[b]	de (%)[c]
1	**2b**	*i*-PrOH	17	99	58
2	**2c**	*i*-PrOH	20	100	17
3	**2d**	MeOH–EtOAc	21	100	47
4	**2e**	MeOH	21	43	19
5	**2f**	*i*-PrOH	21	99	72

[a] Reaction conditions: $Pd(OH)_2/C$ (25 mg; 15–20% Pd), solvent (15–20 mL), substrate **2** (0.3 mmol), 25 °C, H_2 (30 bar), 600 rpm.
[b] Determined by HPLC.
[c] Determined by ^{1}H NMR.

As expected, hydrogenation of furan derivatives with sterically demanding auxiliaries such as **2b** and **2d** resulted in higher de values (Table 2, entries 1 and 3, 58% and 47%) compared to those obtained with the compounds **2a** and **2c** (Table 1, entry 10, 27% and Table 2, entry 2, 17%). However, the highest de value of 72% was achieved in the hydrogenation of substrate **2f** with (*S*)-α,α-diphenyl-2-pyrrolidinemethanol as ester auxiliary (entry 5). An attempt to increase the diastereoselectivity with the more bulky substrate **2e** was not successful (entry 4).

Table 3 illustrates the influence of solvents on the hydrogenation of the most promising furan-2-carboxylic acid derivative **2f**. Only moderate de values of 51% and 54% were obtained in dichloromethane and trifluoroethanol (entries 1 and 2), respectively. The hydrogenation in alco-

Table 3 Effect of Solvents on the Diastereoselective Hydrogenation of **2f**[a]

Entry	Solvent	Conversion (%)[b]	de (%)[c]
1	CH_2Cl_2	72	51
2	CF_3CH_2OH	100	54
3	toluene	99	68
4	EtOAc	99	69
5	EtOH	100	71
6	*i*-PrOH	100	72
7	MeOH	100	72
8	acetone	100	73
9	DMF	99	79
10	THF	98	80
11	NMP	99	83

[a] Reaction conditions: substrate **2f** (0.3 mmol), 25 °C, 21 h, solvent (15–20 mL), $Pd(OH)_2/C$ (25 mg; 15–20% Pd), H_2 (30 bar), 600 rpm.
[b] Determined by HPLC.
[c] Determined by ^{1}H NMR.

hols such as ethanol, isopropanol, and methanol similarly resulted an enhanced diastereoselectivity (71–72%, entries 5–7). The highest de values of 80% and 83% were observed in THF and NMP (*N*-methyl-pyrrolidin-2-one) as solvents (entries 10 and 11).

Complexation of the furan oxygen and the amide group in **2f** by a metal ion (e.g., Zn^{2+} and Ti^{4+}) can lead to a more rigid molecule conformation.[11] Thus, the binding interaction of the substrate at the catalyst surface can be influenced. To study the effect on the diastereoselectivity we used several additives in the hydrogenation of **2f**. Table 4 shows that the presence of triethylborate had no significant effect on the diastereoselectivity and on the conversion of **2f** (entry 1), respectively. The addition of ethyldicyclohexylamine as basic reagent enhanced the de value slightly up to 77% but the reaction proceeded with lower conversion (entry 2). Additives such as zinc acetate or diethylzinc inhibited the hydrogenation (entries 3–5). The use of zirconium(IV) or aluminium(III) alkoxides resulted in increased diastereoselectivities of 81% (entry 6) and 78% (entry 7). For comparison, the hydrogenation without an additive in ethyl acetate afforded 69% de (Table 3, entry 4). Titanium(IV) alkoxides were applied for further experiments, whereby the use of titanium ethoxide gave a de of 83% (entry 10).

Table 4 Effect of Additives on the Diastereoselective Hydrogenation of **2f**[a]

Entry	Additive (equiv)	Solvent	Conv. (%)[b]	de (%)[c]
1	$B(OEt)_3$ (4)	EtOAc	99	70
2	$(C_6H_{11})_2NC_2H_5$ (1.3)	MeOH	73	77
3	$Zn(OAc)\cdot 2H_2O$ (1.3)	MeOH	0	0
4	$Zn(acac)_2$ (1.3)	MeOH	0	0
5	$Zn(Et)_2$[d] (2)	EtOAc	4	59
6	$Zr(OPr)_4$ (2)	EtOAc	100	81
7	Al(O-*sec*-Bu)$_3$ (2)	EtOAc	98	78
8	$Ti(acac)_2$ (1.3)	MeOH	99	77
9	$Ti[NMe_2]_4$ (2)	DMF	19	80
10	$Ti(OEt)_4$ (4)	EtOAc	99	83

[a] Reaction conditions: substrate **2f** (0.3 mmol), 25 °C, 21 h, solvent (15–20 mL), $Pd(OH)_2/C$ (25 mg; 15–20% Pd), H_2 (30 bar), 600 rpm.
[b] Determined by HPLC.
[c] Determined by ^{1}H NMR.
[d] 1.5 M in toluene.

To complete our investigations we studied the effect of several Ti(IV) alkoxides in NMP as the best solvent. Table 5 shows that in all reactions excellent de values were obtained. Thus, tetrahydrofuran-2-carboxylic acid amide **3f** was obtained with a de value of 95% at 99% conversion (entry 4) when performing the reaction at 30 bar initial hydrogen pressure using $Pd(OH)_2/C$ as heterogeneous catalyst in the presence of $Ti(OEt)_4$ in NMP as solvent.

Table 5 Influence of Ti(IV) Additives in the Hydrogenation of **2f**[a]

Entry	Additive	Conversion (%)[b]	de (%)[c]
1	Ti(O*t*-Bu)$_4$	91	92
2	Ti(O*i*-Pr)$_4$	94	93
3	Ti(O*n*-Pr)$_4$	98	94
4	$Ti(OEt)_4$	99	95

[a] Reaction conditions: substrate **2f** (0.3 mmol), 25 °C, 21 h, H_2 (30 bar), 600 rpm, $Pd(OH)_2/C$ (25 mg; 15–20% Pd), NMP (15 mL), additive (4 equiv).
[b] Determined by HPLC.
[c] Determined by ^{1}H NMR.

In order to show that the auxiliary can principally be cleaved we treated (*R*)-tetrahydrofuran-2-carboxylic amide **3f** obtained from a scaled-up trial in accordance to entry 4 of Table 5 with hydrochloric acid at elevated temperature. (*R*)-Tetrahydrofuran-2-carboxylic acid **4** was isolated in 86% yield and with an enantiomeric excess of 95% (determined by HPLC).

In summary, based on the heterogeneously catalyzed hydrogenation of chiral furan-2-carboxylic acid esters or amides tetrahydrofuran-2-carboxylic acid can be produced with high yield and excellent enantioselectivity.

All chemicals and solvents were provided from commercial suppliers and used without further purification. All possible reaction products were synthesized or purchased for analytic comparison. The ^{1}H NMR spectra were recorded at 298 K with a Varian Unityplus-500 (500 MHz) using TMS as internal standard.^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer (100 MHz). Optical rotations were measured on a Gyromat-HP instrument (Dr. Kernchen). Elemental analyses were performed on a CE instruments EA-1110 CHN. High resolution mass spectra were recorded on a Agilent 6200 Time-of-Flight LC/MS System. Column chromatography separations were carried out on a Daicel Chiralcel OD-H (150 × 4.6 mm) using a Merck L-4500 diode array detector and a Merck Hitachi L-6200 intelligent pump. The procedures for the synthesis of chiral furan-2-carboxylic acid derivatives **2a–e** can be obtained from the authors on request.

Furan-2-yl-[(*S*)-2-(hydroxydiphenylmethyl)pyrrolidin-1-yl]-methanone (2f)

Under argon atmosphere Cs_2CO_3 (5.54 g, 17 mmol) was added to a solution of (*S*)-α,α-diphenyl-2-pyrrolidine-methanol (3.04 g, 12 mmol) in MeCN (200 mL). After stirring for 30 min at ambient temperature, 2-furoyl chloride (1.57 g, 12 mmol) was added and the mixture was stirred for 4 h. The suspension was filtered, and the residue was extracted with EtOAc (150 mL). The organic phase was evaporated and the resulting solid dried at 50 °C to give **2f** as a colorless powder (4.11 g, 99%).

R_f = 0.58 (CH_2Cl_2–MeOH, 28:1). ^{1}H NMR ($CDCl_3$): δ = 1.08 (1 H, m, CH_2), 1.62 (1 H, m, CH_2), 2.00 (1 H, m, CH_2), 2.11 (1 H, m, CH_2), 3.29 (1 H, m, CH_2), 3.80 (1 H, m, CH_2), 5.49 (1 H, m, CH), 6.36 (1 H, br s, OH), 6.47 (1 H, m, CH), 6.97 (1 H, m, CH), 7.24–7.36 (6 H, m, arom. H), 7.42–7.47 (4 H, m, arom. H), 7.51 (1 H, m, CH). ^{13}C NMR ($CDCl_3$): δ = 23.7 (CH_2), 28.7 (CH_2), 49.6 (CH_2N), 67.1 (CH), 82.0 (C), 111.4 (CH), 117.0 (CH), 127.1, 127.2, 127.4,

127.6, 127.8, 128.0 (arom. CH), 143.2 (arom. C), 144.6 (CH), 146.0 (arom. C), 147.6 (arom. C), 161.1 (C=O). Anal. Calcd for $C_{22}H_{21}NO_3$: C, 76.06; H, 6.09; N, 4.03. Found: C, 76.15; H, 6.02; N, 4.25. HRMS: *m/z* calcd for $C_{22}H_{21}NO_3Na$ $[M + Na]^+$: 370.1414; found: 370.1410.

Tetrahydrofuran-2-yl-[(*S*)-2(hydroxydiphenylmethyl)pyrrolidin-1-yl]-methanone (3f)

For HPLC analysis the diastereomerically pure reference substrates (*R*,*S*)-**3f** and (*S*,*S*)-**3f** were prepared. To a solution of racemic tetrahydrofuran-2-carboxylic acid (0.49 g, 4.13 mmol) in THF (60 mL) was added 1,1′-carbonyldiimidazole (0.746 g, 4.60 mmol). After stirring at ambient temperature for 45 min, (*S*)-α,α-diphenyl-2-pyrrolidinemethanol (1.046 g, 4.13 mmol) was added, and stirring was continued for 24 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (50 mL). The organic phase was washed with 0.5 M HCl (3 × 15 mL), sat. aq $NaHCO_3$ (3 × 15 mL), dried (Na_2SO_4), and concentrated under reduced pressure. Purification by column chromatography on SiO_2 (hexane–EtOAc, 1:2) gave 27% (*R*,*S*)-**3f** (0.39 g) and 28% (*S*,*S*)-**3f** (0.40 g).

Compound (*R*,*S*)-**3f**: R_f = 0.35 (hexane–EtOAc, 1:2); $[\alpha]_D^{23}$ –147 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ = 1.09 (1 H, m, CH_2), 1.47 (1 H, m, CH_2), 1.70–2.17 (6 H, m, CH_2), 2.98 (1 H, m, CH_2), 3.47 (1 H, m, CH_2), 3.68 (2 H, m, CH_2), 4.41 (1 H, m, CH), 5.05 (1 H, m, CH), 6.80 (1 H, s, OH), 7.14–7.27 (6 H, m, arom. H), 7.27–7.42 (4 H, m, arom. H). ^{13}C NMR ($CDCl_3$): δ = 23.6, 25.4, 28.4, 29.4 (CH_2), 48.3 (CH_2N), 67.9 (CH), 68.9 (CH_2O), 77.4 (CH), 81.7 (C), 127.1, 127.2, 127.4, 127.7, 127.9, 128.0 (arom. CH), 143.0, 146.0 (arom. C), 174.3 (C=O). Anal. Calcd for $C_{22}H_{25}NO_3$: C, 75.15; H, 7.17; N, 3.99. Found: C, 75.00; H, 7.10; N, 4.17. HRMS: *m/z* calcd for $C_{22}H_{25}NO_3Na$ $[M + Na]^+$: 374.1727; found: 374.1725.

Compound (*S*,*S*)-**3f**: R_f = 0.25 (hexane–EtOAc, 1:2); $[\alpha]_D^{23}$ –128 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.16 (1 H, m, CH_2), 1.52 (2 H, m, CH_2), 1.68–2.05 (5 H, m, CH_2), 2.79 (1 H, m, CH_2), 3.48 (1 H, m, CH_2), 3.76 (1 H, m, CH_2), 3.92 (1 H, m, CH_2),4.41 (1 H, m, CH), 5.05 (1 H, m, CH), 6.96 (1 H, s, OH), 7.13–7.28 (6 H, m, arom. H), 7.28–7.43 (4 H, m, arom. H). ^{13}C NMR ($CDCl_3$): δ = 23.7, 25.3, 29.0, 29.6 (CH_2), 47.9 (CH_2N), 68.2 (CH), 69.2 (CH_2O), 76.3 (CH), 81.7 (C), 127.1, 127.2, 127.3, 127.7, 127.8, 127.9 (arom. CH), 143.0, 145.7 (arom. C), 174.2 (C=O). Anal. Calcd for $C_{22}H_{25}NO_3$: C, 75.15; H, 7.17; N, 3.99. Found: C, 74.97; H, 7.12; N, 4.14. HRMS: *m/z* calcd for $C_{22}H_{25}NO_3Na$ $[M + Na]^+$: 374.1727; found: 374.1721.

Optimized Procedure for the Asymmetric Hydrogenation of Substrate 2f to Product 3f

The hydrogenation was performed in a 250 mL autoclave (Parr Instrument) equipped with a stirring unit. Substrate **2f** (3.12 g, 9 mmol) was dissolved in NMP (100 mL) and $Ti(OEt)_4$ (8.22 g, 36 mmol) and $Pd(OH)_2$/C (0.75 g, 15–20% Pd, 50% wet, Fluka, No. 76063) were added. The reaction mixture was hydrogenated at 30 bar H_2 pressure for 22 h at ambient temperature. To the suspension H_2O (10 mL) was added, and the yielded precipitate was removed by filtration. The filter cake was washed several times with MeOH (4 × 50 mL) and the organic phase was concentrated under reduced pressure. Chiral amide **3f** (95% de for *R*,*S*-diastereomer) was obtained with 94% yield. HPLC analysis of the reaction mixture: Daicel Chiralcel OD-H (150 × 4.6 mm), hexane–2-PrOH (85:15), 1.5 mL/min, t_R = 5.7 min for (*R*,*S*)-**3f** and t_R = 15.7 min for (*S*,*S*)-**3f**.

Removal of the Chiral Auxiliary in 3f

A solution of diastereomerically pure (*R*,*S*)-**3f** (1.70 g, 4.84 mmol) in 1 M HCl (30 mL) was stirred for 20 h at 90 °C and filtered after cooling. The residue was washed with cooled H_2O (3 × 10 mL), and the solution was slowly adjusted to pH 5 by addition of 2 M NaOH. The solvent was evaporated and the residue was treated with Et_2O (4 × 25 mL). After filtration the combined organic phases were dried over Na_2SO_4. Evaporation of ether yielded the (*R*)-tetrahydrofuran-2-carboxylic acid (0.48 g, 86%).

Analytical Data of Compound (*R*)-4

$[\alpha]_D^{23}$ +30.2 (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ = 1.75–1.90 (2 H, m, CH_2), 1.97 (1 H, m, CH_2), 2.19 (1 H, m, CH_2), 3.85 (2 H, m, CH_2O), 4.39 (1 H, dd, *J* = 5.3, 8.5 Hz, CH), 11.08 (1 H, br s, OH). ^{13}C NMR ($CDCl_3$): δ = 24.9 (CH_2), 29.9 (CH_2), 69.2 (OCH_2), 75.9 (OCH), 177.5 (C=O).

To determine the optical purity of the (*R*)-tetrahydrofuran-2-carboxylic acid, 50 mg of crude mixture was dissolved in MeOH (2 mL) and treated with $SOCl_2$ (60 mg). After 2 h stirring, the solvent was carefully evaporated, and (*R*)-tetrahydrofuran-2-carboxylic acid methyl ester was obtained with 95% ee (analyzed by HPLC).

Analytical Data of (*R*)- and (*S*)-4-Methyl ester

^{1}H NMR ($CDCl_3$): δ = 1.76–2.05 (3 H, m, CH_2), 2.17 (1 H, m, CH_2), 3.68 (3 H, s, OCH_3), 3.85 (1 H, m, H_a of OCH_2), 3.95 (1 H, m, H_b of OCH_2), 4.40 (1 H, dd, *J* = 5.2, 8.3 Hz, CH). ^{13}C NMR ($CDCl_3$): δ = 25.2 (CH_2), 30.1 (CH_2), 52.0 (OCH_3), 69.1 (OCH_2), 76.6 (OCH), 173.7 (C=O). HPLC analysis: Chiralcel OD-H (150 × 4.6 mm), hexane–2-PrOH (98:2), 1.2 mL/min, t_R = 4.2 min for (*S*)-tetrahydrofuran-2-carboxylic acid methyl ester and t_R = 6.2 min for (*R*)-tetrahydrofuran-2-carboxylic acid methyl ester.

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