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PAPER

Regio- and stereoselective selenium dioxide allylic oxidation of (*E*)-dialkyl alkylidenesuccinates to (*Z*)-allylic alcohols: Synthesis of natural and unnatural butenolides†

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The first SeO_2 induced (*Z*)-selective allylic alcohol formation of dialkyl alkylidenesuccinates has been demonstrated to accomplish one-step syntheses of several essential butenolides and fused butenolides *via* an unusual *E*- to *Z*- carbon–carbon double bond isomerisation followed by the lactonization pathway. The observed regio- and stereoselective SeO_2 allylic oxidation protocol has also been extended to the diastereoselective total synthesis of bioactive natural product isomintlactone, its direct conversion to mintlactone and an example of the base-catalyzed intramolecular rearrangement of γ-lactone to δ-lactone.

Introduction

Natural and unnatural butenolides are an important class of compounds that find major applications in organic, medicinal and polymer chemistry.[1] A broad range of biological properties has been conferred on them and include strong antibiotic, antihelmintic, antifungal, antitumor, antiviral, anti-inflammatory, cytostatic, antiallergenic and anti-HIV activities.[1–4] Basically, a diverse range of butenolide skeletons have been elegantly designed by employing new C–O bond construction reactions and metal catalyzed C–C bond formations (Fig. 1).[5,6] The Guillemonat's selenium dioxide allylic oxidation of (*E*/*Z*)-alkenes to (*E*)-allylic alcohols *via* C–O bond formation is an imperative well established reaction in synthetic organic chemistry.[7,8] In continuation of our studies on the synthesis of bioactive natural products,[9] we herein report the regio- and stereoselective SeO_2 allylic oxidation of dialkyl alkylidenesuccinates to constitute a new one-step approach to several significant butenolides (Schemes 1–8 and Tables 1,2).

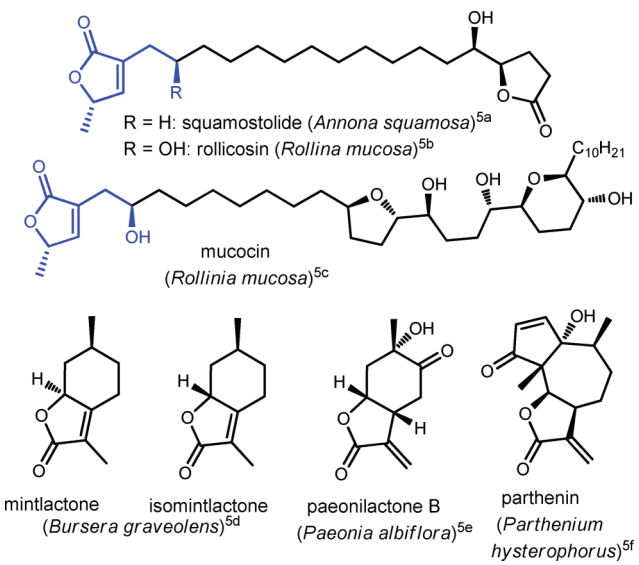
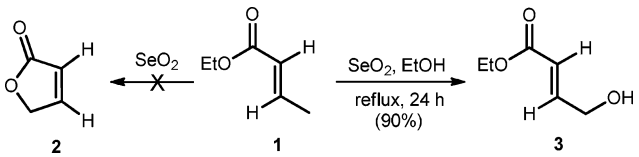


Fig. 1 Naturally occurring bioactive butenolides and fused butenolides.[5]

Results and discussion

We envisaged that selective SeO_2-induced allylic hydroxylation of dialkyl alkylidenesuccinates would constitute a new route to several pivotal furan/pyran frameworks *via* the intramolecular cyclization pathway. The SeO_2 oxidation of ethyl 3-methyl-2-butenoate (**1**) is known to exclusively furnish the corresponding product ethyl *trans*-3-(hydroxymethyl)-2-butenoate (**3**) in 90% yield (Scheme 1).[10a] On the basis of the above-mentioned reaction, a systematic study of the SeO_2 oxidation reactions of readily available starting materials (*E*)-dialkyl alkylidenesuccinates[11] was undertaken. As depicted in Scheme 2, the initial expectation was



Scheme 1 Stereoselective SeO_2 oxidation of ethyl 3-methyl-2-butenoate.

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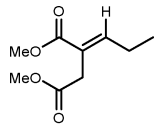
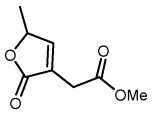
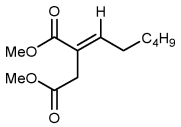
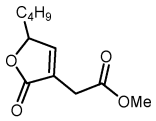
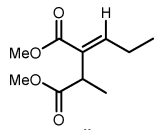
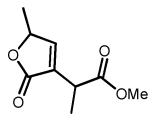
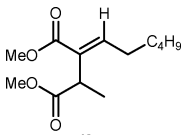
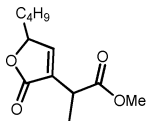
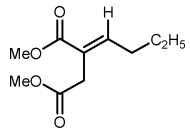
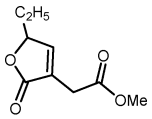
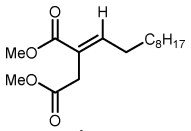
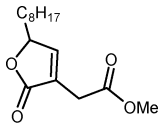
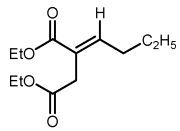
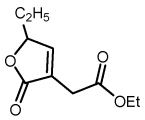
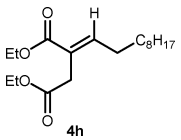
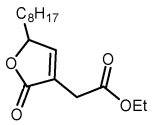
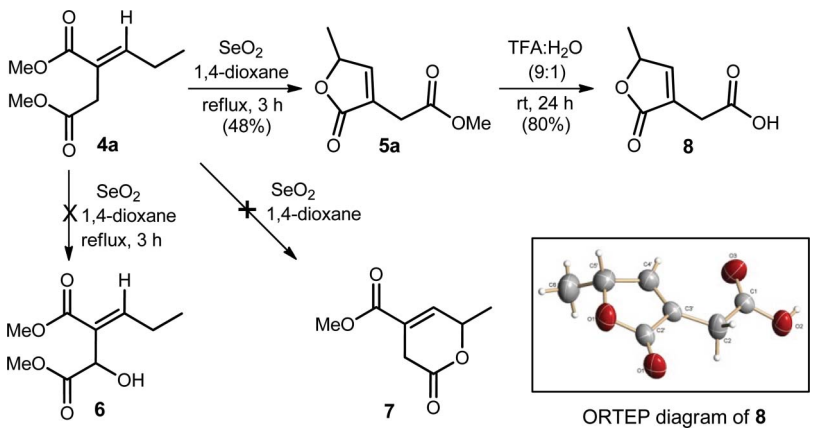
† Electronic supplementary information (ESI) available: Copies of ^1H NMR, ^{13}C NMR and DEPT spectra of compounds **4e**,**g**, **5a–h**, **8**, **13**, **15h**, **16a–h** and **19–27**. CCDC reference numbers 813260, 813261, 819769 and 819770 contain the supplementary crystallographic data for this paper. See DOI: 10.1039/c1ob05709j

Table 1 Trisubstituted (*E*)-dialkyl alkylidenesuccinates to butenolides[a]

Entry	SM[b] (**4**)	Product (**5**)	Entry	SM[b] (**4**)	Product (**5**)
1	 **4a**	 **5a** (48%)	5	 **4e**	 **5e** (44%)
2	 **4b**	 **5b/b'** (48%) (1:1 diastreomeric mixture)	6	 **4f**	 **5f/f'** (43%) (1:1 diastereomeric mixture)
3	 **4c**	 **5c** (45%)	7	 **4g**	 **5g** (45%)
4	 **4d**	 **5d** (43%)	8	 **4h**	 **5h** (42%)

[a] *Conditions*: SeO_2 (1.60 equiv), 1,4-dioxane, reflux, 3 h (42–48%). [b] SM = Starting material.

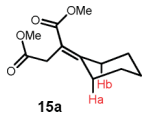
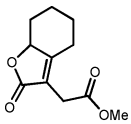
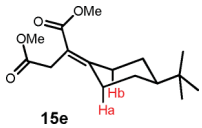
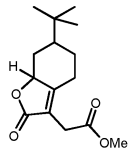
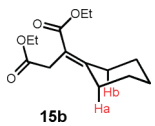
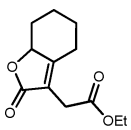
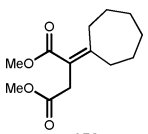
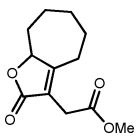
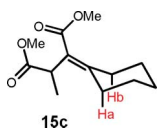
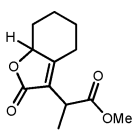
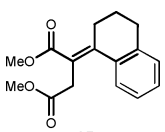
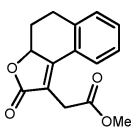
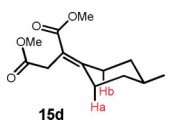
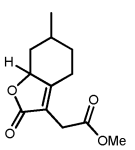
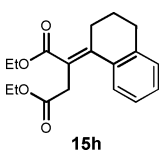
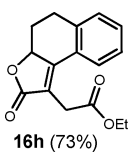


Scheme 2 Regio- and stereoselective SeO_2 oxidation of (*E*)-dimethyl 2-propylidenesuccinate.

that the regioselective SeO_2 allylic oxidation of (*E*)-dimethyl 2-propylidenesuccinate (**4a**) would provide pyran skeleton **7**. In our hands, the allylic oxidation of compound **4a** in the presence of a catalytic amount of SeO_2 and *tert*-butyl hydroperoxide in *tert*-butyl alcohol/1,4-dioxane at room temperature was not successful[12a] and the starting material remained unreacted even after 48 h. Fortunately, the reaction of compound **4a** with SeO_2 (1.60 equiv) in refluxing 1,4-dioxane was successful. To our surprise the above-specified SeO_2 allylic oxidation reaction was completely regioselective and exclusively provided the butenolide product **5a**, but only in 48% yield. We were conscious about the fact that the isomeric butenolide **5a** and the pyran **7** would display a very close resemblance in their NMR data. Hence the acid-catalyzed ester hydrolysis of our product **5a** was performed and the structure of the obtained acid **8** was unequivocally confirmed by using X-ray crystallographic data. The authentication of butenolide structure **5a** revealed that in the SeO_2-induced transformation of dimethyl (*E*)-2-propylidenesuccinate (**4a**) to product **5a**, apart from allylic hydroxylation, the course of reaction involves unexpected *E*- to *Z*- carbon–carbon double bond isomerization and an *in situ* intramolecular cyclization step.[12b,c]

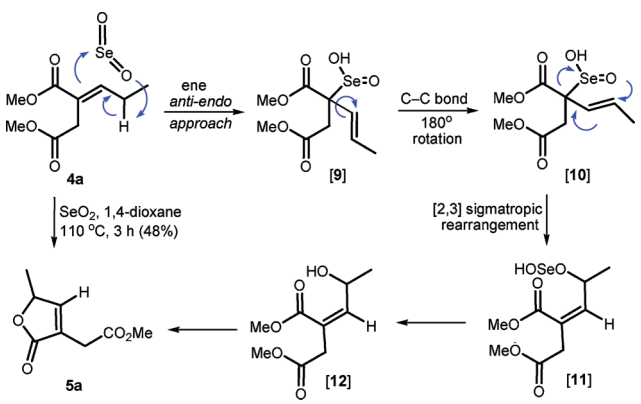
Rationalization of our present example indicated its usefulness in highlighting the mechanistic aspects involved in the SeO_2 allylic oxidation reactions. In the SeO_2-induced conversion of

Table 2 Tetrasubstituted (*E*)-dialkyl alkylidenesuccinates to fused butenolides[a]

Entry	SM[b] (**15**)	Product (**16**)	Entry	SM[b] (**15**)	Product (**16**)
1	 **15a**	 **16a** (74%)	5	 **15e**	 **16e/e'** (66%) (7:3 diastereomeric mixture)
2	 **15b**	 **16b** (72%)	6	 **15f**	 **16f** (68%)
3	 **15c**	 **16c/c'** (70%) (2:1 diastereomeric mixture)	7	 **15g**	 **16g** (76%)
4	 **15d**	 **16d/d'** (72%) (3:1 diastereomeric mixture)	8	 **15h**	 **16h** (73%)

[a] *Conditions*: SeO_2 (1.60 equiv), 1,4-dioxane, reflux, 3 h (66–76%). [b] SM = Starting material.

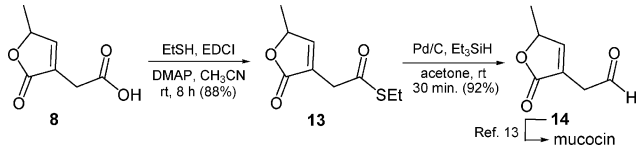
4a to **5a**, to the best of our knowledge, we witnessed the first example of a SeO_2 allylic oxidation reaction to selectively obtain (*Z*)-allylic alcohol *via* an *in situ* unforeseen *E*- to *Z*- carbon–carbon double bond isomerization step.[7,8,10] As reported earlier, in controlling the olefin geometry, the ene step is non selective[8d] and the subsequent [2,3] sigmatropic shift is governed by the release of 1,3-allylic strain. However, the strong preference for *E*- to *Z*- carbon–carbon bond isomerization in the conversion of compound **4a** to **5a** could be due to the unfavoured *pseudo*-axial orientation of comparatively bulkier $–CH_2CO_2Me$ group in the formation of a five membered cyclic transition state involved in a [2,3] sigmatropic rearrangement step which would lead to the corresponding (*E*)-alcohol. As depicted in Scheme 3, the energetically favored anti approach of selenium dioxide towards **4a** in an ene reaction to form the intermediate **9**, followed by an *in situ* 180° C_α–C_β bond rotation and then the [2,3] sigmatropic shift driven by the release of 1,3-allylic strain with the *pseudo*-equatorial orientation of the comparatively bulkier $–CH_2CO_2Me$ group and thermodynamically favored an *in situ* intramolecular cyclization to form butenolide **5a** could be the most promising pathway.[8d–f] Hence it also precludes the formation of the six membered compound **7** (Scheme 2). Herein, we reason that due to the lack of steric effect of the comparatively bulkier α-substituent, the SeO_2 oxidation of compound **1** does not result in the corresponding γ-lactone **2** (Scheme 1).



Scheme 3 Plausible mechanism for SeO_2 oxidation of **4a**.

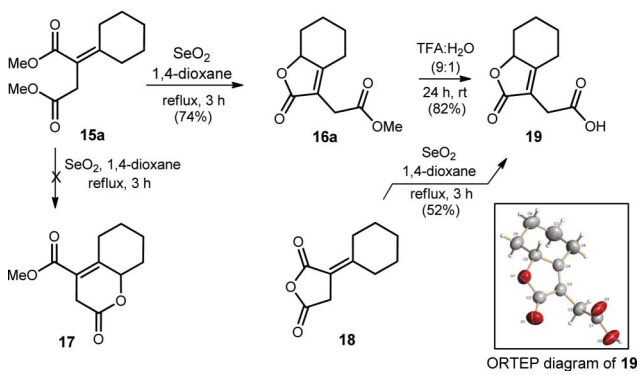
To generalize the above specified protocol as indicated in Table 1, the SeO_2 allylic oxidation reactions of (*E*)-dialkyl alkylidenesuccinates **4a–h** were performed to respectively deliver the corresponding desired products **5a–h** in one-step with 42–48% yields. As expected, the precursors **4b** and **4f** furnished the corresponding butenolides **5b/b′** and **5f/f′** as 1 : 1 diastereomeric mixtures. All our attempts to improve the yields by varying the reaction time, temperature, solvents (*t*-BuOH, C_2H_5OH, C_6H_6, CH_2Cl_2 and CH_3CO_2H) and molar amounts of SeO_2 were unsuccessful and always resulted in the formation of over-oxidized decomposed residues. The utility of our present approach was

illustrated by successfully transforming the butenolide **8** to the corresponding known mucocin precursor **14** in two steps *via* thioesterification followed by a chemoselective reduction sequence (Scheme 4).[13]



Scheme 4 Concise synthesis of mucocin precursor.

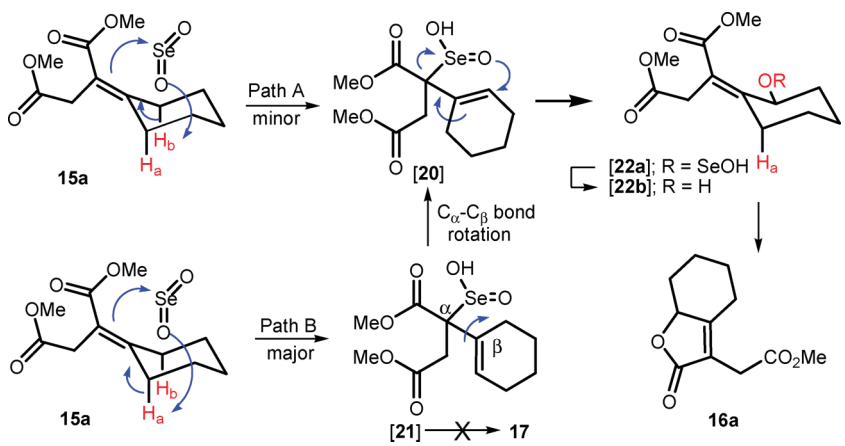
In the second segment of studies, the SeO_2 oxidation protocol was extended to symmetrically and unsymmetrically tetrasubstituted dialkyl alkylidenesuccinates (Scheme 5, Table 2). As expected, the regio- and stereoselective SeO_2 (1.60 equiv) oxidation of dimethyl 2-cyclohexylidenesuccinate (**15a**) in refluxing 1,4-dioxane also furnished the desired fused butenolide **16a** in one-step in 74% yield. The SeO_2 oxidation of cyclohexylidenesuccinic anhydride (**18**)[14] and an acid catalyzed hydrolysis of ester **16a** furnished the same desired product, the acid **19**, in very good yields. The structure of the acid **19** was also unambiguously established on the basis of X-ray crystallographic data. Similarly, the reactions of substrates **15b–h** with SeO_2 provided the desired fused butenolides **16b–h** in 66–76% yields. Herein the formed products **16a–h** could



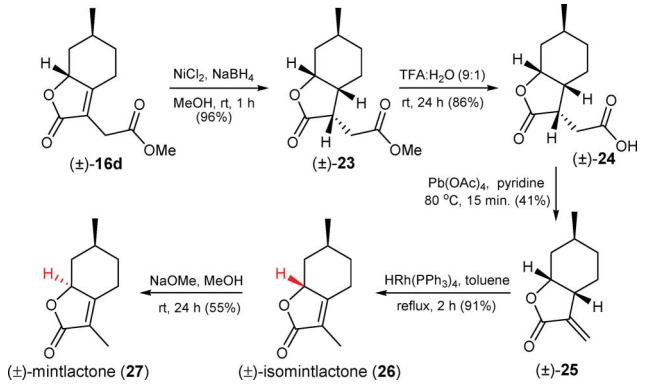
Scheme 5 Regio- and stereoselective SeO_2 oxidation of dimethyl 2-cyclohexylidenesuccinates.

be more stable under our set of reaction conditions and hence were obtained in higher yields. As expected the products **16c/c′** were obtained as the corresponding diastereomeric mixture with 2 : 1 ratio. Similarly, stereoselective conversion of **15d/e** respectively furnished the diastereomeric mixtures of **16d/d′** and **16e/e′** with 3 : 1 and 7 : 3 ratio. The present stereoselective conversion can be clearly explained by ene reaction followed by [2,3] sigmatropic shift mechanistic pathway as proposed by Sharpless *et al.*[8b,c] In the conversion of **15a–f** to **16a–f** plausibly two independent stereoselective pathways might be operational (Scheme 6). In the conversion of **15d/e** to the respective diastereomeric mixtures of **16d/d′** and **16e/e′**, the involvement of more acidic (*E*)-allylic axial proton-H_a in the ene reaction followed by C_α–C_β bond rotation, [2,3] sigmatropic shift and lactonization could be resulting in the diastereoselective formation of the kinetically controlled major product **16d** (Path B). The involvement of the relatively less acidic (*Z*)-allylic axial proton-Hb in the ene reaction followed by [2,3] sigmatropic shift and lactonization should be directly resulting in the diastereoselective formation of thermodynamically controlled minor product **16d′** (Path A), which supports the proposed mechanism.

As an extension of the present approach to fused butenolides, the total synthesis of bioactive natural products isomintlactone and mintlactone (*Bursera graveolens*)[7d] were planned. One recrystallization of a mixture of diastereomers **16d/d′** with petroleum ether provided the diastereomerically pure (±)-**16d** in 66% yield (Scheme 7). The tentative stereochemical assignment of **16d** was made by comparison of the reported ^{1}H NMR data of mintlactone and isomintlactone.[15,16] The chemo- and diastereoselective reduction of **16d** with $NaBH_4$ in the presence of $NiCl_2$ exclusively furnished product **23** in 96% yield with the generation of two new asymmetric centres. In the reduction process of **16d**, the addition of hydride at β-carbon of α,β-unsaturated lactone from the less hindered side with the conversion of twist boat to chair form followed by the pick-up of proton by the thus formed stable axial carbanion from the same face, stereosectively results in product **23**. Acid catalyzed hydrolysis of ester **23** provided the corresponding carboxylic acid **24** in 86% yield. The stereochemical assignments of both (±)-**23**/**24** were finally established on the basis of X-ray crystallographic analysis data of the acid (±)-**24** (Fig. 2). Oxidative decarboxylation[17] of primary acid **24** with



Scheme 6 Plausible mechanism for SeO_2 oxidation of **15a**.



Scheme 7 Synthesis of (±)-mintlactone and (±)-isomintlactone.

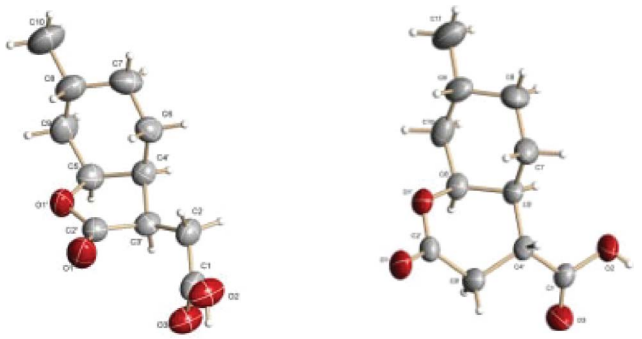


Fig. 2 X-ray crystallographic data of γ/δ-lactones (±)-**24** and (±)-**28**.

$Pb(OAc)_4$ in the presence of $Cu(OAc)_2$ furnished the anticipated exocyclic α-methylene-γ-lactone product **25** with 41% yield. From a bioactivity point of view, among all types of butenolides, the α-methylene-γ-butyrolactones are of contemporary special interest as an alkylating agents *via* Michael-type acceptor of biological cellular nucleophiles or cysteine residues of functional proteins.[6,18] They possess a wide range of important biological activities and the provision of new synthetic routes to such class of compounds is a challenging task of current interest.[18] Our present protocol also provides a concise and efficient new access to these exotic α-methylene-γ-butyrolactones. Finally, the rhodium catalyzed[19] disubstituted exocylic to tetrasubstituted endocyclic carbon–carbon double bond isomerization in **25** provided the desired natural product (±)-isomintlactone (**26**) in 91% yield. A number of independent syntheses of mintlactone and isomintlactone have been well known in the literature, but the conversion of isomintlactone to the isomeric natural product mintlactone is not known to date.[15,16] On the basis of stereochemical features, we contemplated that the isomintlactone could be a kinetically controlled product (twist boat form).[16] Hence we stirred (±)-isomintlactone (**26**) with NaOMe (1.20 equiv) in MeOH at room temperature and indeed obtained the thermodynamically more stable yet another natural product, the (±)-mintlactone (**27**) (chair form) in 55% yield *via* the inversion of configuration at an allylic centre. Starting from dimethyl 2-(4-methylcyclohexylidene)succinate (**15d**) the (±)-isomintlactone (**26**) and (±)-mintlactone (**27**) were respectively obtained in five/six steps with 14/8% overall yields, and the obtained analytical and spectral data for both the natural products were in complete agreement with the reported data.[15,16] One step conversion of mintlactone/isomintlactone to yet another natural product, (±)-menthofuran is well known in the literature.[20]

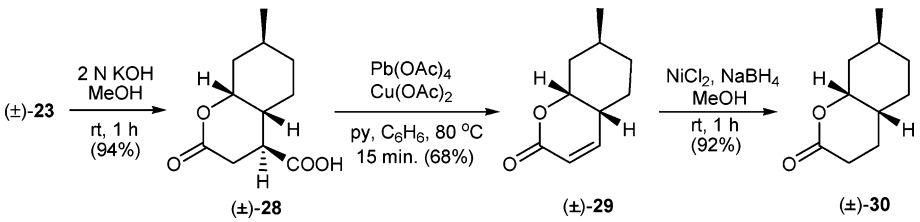
Finally, the regioselectivity in our lactone **16d** was altered to device a new approach to essential chromenones (Scheme 8).[21] It was rewarding that the base-catalyzed hydrolysis of the reduced γ-lactone (±)-**23** followed by an acidification exclusively furnished the desired δ-lactone carboxylic acid (±)-**28** in 94% yield *via* ring opening followed by 180° carbon–carbon bond rotation and ring closing pathway. The structure of acid (±)-**28** was also explicitly established using X-ray crystallographic analysis data (Fig. 2). Oxidative decarboxylation of the secondary acid (±)-**28** with $Pb(OAc)_4$ in the presence of $Cu(OAc)_2$ furnished the anticipated oxidized hexahydrochromenone product (±)-**29** in 68% yield. Similarly, the nickel-catalyzed $NaBH_4$ reduction of α,β-unsaturated carbon–carbon double bond provided the octahydrochromenone (±)-**30** in 92% yield.

Conclusion

In summary, we have demonstrated the first example of (*Z*)-selective allylic alcohol formation in the SeO_2 oxidation of dialkyl alkylidenesuccinates to design a new general one-step approach to the diverse range of natural and unnatural butenolides and fused butenolides *via* an exceptional *E*- to *Z*- carbon–carbon double bond isomerization. The present protocol has been successfully extended for the synthesis of a mucocin precursor and the diastereoselective total synthesis of the natural product (±)-isomintlactone and its first time conversion to (±)-mintlactone. Our present protocol would also be useful for the synthesis of desired natural and unnatural α-methylene-γ-butyrolactones. We have also successfully altered the regioselectivity in lactonization with the ring expansion of γ-lactone to δ-lactone and provided a new approach to chromenone skeletons.

Experimental section

The ^{1}H NMR spectra were recorded on 200 MHz NMR spectrometer, 400 MHz NMR and 500 MHz NMR spectrometers using TMS as an internal standard. The ^{13}C NMR spectra were recorded on 200 NMR spectrometer (50 MHz), 400 NMR



Scheme 8 Ring expansion of γ-lactone to δ-lactone: Synthesis of chromenone.

spectrometer (100 MHz) and 500 NMR spectrometers (125 MHz). Mass spectra were taken on a MS-TOF mass spectrometer. The IR spectra were recorded on an FT-IR spectrometer. HRMS were taken on an ESI mass spectrometer. Column chromatographic separations were carried out on silica gel (60–120 mesh). Commercially available dimethyl succinate, diethyl succinate, dimethyl methylsuccinate, propanal, butanal, hexanal, decanal, cyclohexanone, 4-methylcyclohexanone, *tert*-butylcyclohexanone, cycloheptanone, α-tetralone, selenium dioxide, sodium methoxide, trifloroacetic acid, ethanethiol, *N*-ethyl *N′*-(3-dimethylpropyl)carbodiimide (EDCI), triethylsilane, lead tetraacetate, cupric acetate, DMAP, 10% Pd/C, $NiCl_2 \cdot 6H_2O$ and potassium *tert*-butoxide were used. $HRh(PPh_3)_4$ was prepared using a known procedure (J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, **1970**, 2947). Starting materials **4a**, **4c–e**, **4g**,**h**, **15a–c**, **15e–h** were prepared using the known procedures.[14,22–26]

(*E*)-Dimethyl 2-methyl-3-propylidenesuccinate (4b)

To a stirred solution of dimethyl citraconate (3.16 g, 20.00 mmol) and tributylphosphine (4.44 g, 22.00 mmol) in THF (30 mL) at room temperature was drop wise added a solution of propionaldehyde (1.74 g, 30.00 mmol) in THF (10 mL) and the reaction mixture was stirred for 4 h. The reaction mixture was concentrated *in vacuo* and the obtained residue was dissolved in ethyl acetate (50 mL). The organic layer was washed with water, brine and dried over Na_2SO_4. The concentration of organic layer *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 10% ethyl acetate/petroleum ether as an eluent afforded pure product **4b** as a colorless oil (3.36 g, 84%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.07 (t, J = 8 Hz, 3H), 1.32 (d, J = 8 Hz, 3H), 2.20 (doublet of quintet, J = 8 and 4 Hz, 2H), 3.59 (q, J = 8 Hz, 1H), 3.65 (s, 3H), 3.71 (s, 3H), 6.83 (t, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.0, 15.8, 21.8, 37.5, 51.7, 51.9, 131.5, 145.5, 166.9, 174.1; ESIMS (*m*/*z*) 223 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1746, 1715, 1643 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.37; H, 7.69.

(*E*)-Dimethyl 2-decylidenesuccinate (4g)

It was obtained from dimethyl maleate (2.88 g, 20.00 mmol), tributylphosphine (4.44 g, 22.00 mmol) and decanal (4.68 g, 30.00 mmol) using the same procedure described above for **4b**, as a thick oil (4.60 g, 81%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.88 (t, J = 8 Hz, 3H), 1.26 (br s, 12H), 1.45 (quintet, J = 8 Hz, 2H), 2.18 (q, J = 8 Hz, 2H), 3.36 (s, 2H), 3.68 (s, 3H), 3.75 (s, 3H), 6.98 (t, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.0, 22.6, 28.4, 28.9, 29.22, 29.25, 29.34, 29.41, 31.8, 32.0, 51.87, 51.91, 125.2, 146.2, 167.4, 171.3; ESIMS (*m*/*z*) 307 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1736, 1716, 1652 cm^{-1}. Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.34; H, 9.78.

Methyl 2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)acetate (5a)

To a stirred solution of alkylidenesuccinate **4a** (1.86 g, 10.00 mmol) in 1,4-dioxane (20 mL) was added SeO_2 (1.78 g, 16.00 mmol) and the reaction mixture was refluxed for 3 h. The reaction mixture was allowed to attain room temperature. The deposited selenium metal was filtered off and the residue was washed with 1,4-dioxane (5 mL). The filtrate was concentrated *in vacuo* and the obtained residue was dissolved in ethyl acetate (30 mL). The organic layer was washed with saturated $NaHCO_3$ solution, water, brine and dried over Na_2SO_4. The concentration of organic layer *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 40% ethyl acetate/petroleum ether as an eluent afforded pure product **5a** as a colorless oil (816 mg, 48%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.44 (d, J = 6 Hz, 3H), 3.33 (t, J = 2 Hz, 2H), 3.72 (s, 3H), 5.08 (qq, J = 6 and 2 Hz, 1H), 7.40 (q, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.8, 30.1, 52.2, 78.0, 126.5, 152.6, 169.8, 172.9; ESIMS (*m*/*z*) 193 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1756, 1748, 1662 cm^{-1}. Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.39; H, 6.00.

Methyl 2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)propanoate (5b/b′, diastereomeric mixture, 1 : 1)

It was obtained from alkylidenesuccinate **4b** (2.00 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil (846 mg, 46%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.45 (d, J = 6 Hz, 6H), 3.55 (tq, J = 8 and 2 Hz, 1H), 3.73 (s, 3H), 5.08 (qq, J = 8 and 2 Hz, 1H), 7.26 (q, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 16.6, 19.0, 36.2, 52.3, 77.76, 77.80, 133.1, 133.2, 150.4, 150.5, 172.33, 172.34, 173.2; ESIMS (*m*/*z*) 207 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1758, 1746, 1667 cm^{-1}. Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.64; H, 6.43.

Methyl 2-(5-ethyl-2-oxo-2,5-dihydrofuran-3-yl)acetate (5c)

It was obtained from alkylidenesuccinate **4c** (2.00 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil[27] (828 mg, 45%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.01 (t, J = 8 Hz, 3H), 1.60–1.95 (m, 2H), 3.36 (t, J = 2 Hz, 2H), 3.73 (s, 3H), 4.90–5.02 (m, 1H), 7.41 (q, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 9.0, 26.3, 30.2, 52.2, 82.7, 127.0, 151.3, 169.9, 173.0; ESIMS (*m*/*z*) 207 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1756, 1747, 1668 cm^{-1}. Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.52; H, 6.25.

Ethyl 2-(5-ethyl-2-oxo-2,5-dihydrofuran-3-yl)acetate (5d)

It was obtained from alkylidenesuccinate **4d** (2.28 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil (851 mg, 43%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.98 (t, J = 8 Hz, 3H), 1.25 (t, J = 8 Hz, 3H), 1.55–1.93 (m, 2H), 3.32 (t, J = 2 Hz, 2H), 4.16 (q, J = 8 Hz, 2H), 4.87–5.00 (m, 1H), 7.38 (q, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 8.9, 14.0 26.3, 30.4, 61.2, 82.6, 127.0, 151.2, 169.4, 173.0; ESIMS (*m*/*z*) 221 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1756, 1748, 1667 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.87; H, 7.19.

Methyl 2-(5-butyl-2-oxo-2,5-dihydrofuran-3-yl)acetate (5e)

It was obtained from alkylidenesuccinate **4e** (2.28 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil[28] (933 mg, 44%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.91 (t, J = 8 Hz, 3H), 1.20–1.55 (m, 4H), 1.55–1.85 (m, 2H), 3.36 (t, J = 2 Hz, 2H), 3.74 (s, 3H), 4.93–5.05 (m, 1H), 7.41 (q, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.8, 22.4, 27.0, 30.2, 32.9, 52.2, 81.8, 126.8, 151.6, 169.9, 173.0; ESIMS (*m*/*z*) 235 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1756, 1748, 1666 cm^{-1}.

Methyl 2-(5-butyl-2-oxo-2,5-dihydrofuran-3-yl)propanoate (5f/f′, diastereomeric mixture, 1 : 1)

It was obtained from alkylidenesuccinate **4f** (2.42 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil (972 mg, 43%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90 (t, J = 8 Hz, 3H), 1.25–1.50 (m, 4H), 1.43 (d, J = 8 Hz, 3H), 1.55–1.85 (m, 2H), 3.54 (tq, J = 8 and 2 Hz, 1H), 3.71 (s, 3H), 4.96 (t, J = 8 Hz, 1H), 7.25 (q, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.8, 16.5, 16.6, 22.4, 26.86, 26.91, 32.9, 36.19, 36.21, 52.3, 81.5, 81.6, 133.2, 133.3, 149.5, 172.41, 172.44, 173.2; ESIMS (m/z) 227 $[M+H]^+$, 249 $[M+Na]^+$, 265 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 1757, 1747, 1668 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.80; H, 7.77.

Methyl 2-(5-octyl-2-oxo-2,5-dihydrofuran-3-yl)acetate (5g)

It was obtained from alkylidenesuccinate **4g** (2.84 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil (1.21 g, 45%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.88 (t, J = 6 Hz, 3H), 1.27 (br s, 10H), 1.35–1.55 (m, 2H), 1.55–1.85 (m, 2H), 3.36 (t, J = 2 Hz, 2H), 3.74 (s, 3H), 4.93–5.05 (m, 1H), 7.42 (q, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.1, 22.6, 24.9, 29.1, 29.26, 29.31, 30.2, 31.8, 33.3, 52.3, 81.9, 126.7, 151.7, 169.9, 173.0; ESIMS (m/z) 269 $[M+H]^+$, 291 $[M+Na]^+$, 307 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 1759, 1748, 1667 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 66.79; H, 8.80.

Ethyl 2-(5-octyl-2-oxo-2,5-dihydrofuran-3-yl)acetate (5h)

It was obtained from alkylidenesuccinate **4h** (3.12 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil (1.18 g, 42%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.87 (t, J = 6 Hz, 3H), 1.28 (br s, 10H), 1.31 (t, J = 6 Hz, 3H), 1.35–1.55 (m, 2H), 1.55–1.85 (m, 2H), 3.33 (t, J = 2 Hz, 2H), 4.19 (q, J = 6 Hz, 2H), 4.92–5.05 (m, 1H), 7.40 (q, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.05, 14.07, 22.6, 24.9, 29.1, 29.26, 29.29, 30.4, 31.8, 33.3, 61.2, 81.8, 126.8, 151.6, 169.5, 173.1; ESIMS (m/z) 283 $[M+H]^+$, 305 $[M+Na]^+$, 321 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 1759, 1740, 1665 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found: C, 68.16; H, 9.53.

2-(5-Methyl-2-oxo-2,5-dihydrofuran-3-yl)acetic acid (8)

A solution of compound **5a** (680 mg, 4.00 mmol) in aqueous TFA (90%, 10 mL) was stirred for 24 h at room temperature. The concentration of reaction mixture *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 50% ethyl acetate/petroleum ether as an eluent furnished pure product **8** as a white solid (499 mg, 80%). Mp 130–132 °C; ^{1}H NMR (acetone-d_6, 200 MHz) δ 1.41 (d, J = 6 Hz, 3H), 3.34 (t, J = 2 Hz, 2H), 5.14 (qq, J = 8 and 2 Hz, 1H), 7.57 (q, J = 2 Hz, 1H); ^{13}C NMR (acetone-d_6, 50 MHz) δ 19.1, 30.6, 78.6, 127.5, 154.0, 170.9, 173.4; ESIMS (m/z) 179 $[M+Na]^+$; HRMS (ESI) calcd for $C_7H_8O_4Na$ 179.0320, found 179.0322; IR ($CHCl_3$) ν_{max} 2934, 2857, 1745, 1739, 1657 cm^{-1}.

***S*-Ethyl 2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)ethanethioate (13)**

To a stirred solution of acid **8** (400 mg, 2.56 mmol), ethanethiol (239 mg, 3.85 mmol) and DMAP (31 mg, 0.26 mmol) in CH_3CN (15 mL) at room temperature was drop wise added a solution of EDCI (995 mg, 5.13 mmol) in CH_3CN (5 mL). The reaction mixture was further stirred for 8 h and then quenched with water (10 mL). The reaction mixture was concentrated *in vacuo* and the obtained residue was dissolved in ethyl acetate (30 mL). The organic layer was washed with water, brine and dried over Na_2SO_4. The concentration of organic layer *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 40% ethyl acetate/petroleum ether as an eluent afforded pure product **13** as a colorless oil (451 mg, 88%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.27 (t, J = 8 Hz, 3H), 1.46 (d, J = 6 Hz, 3H), 2.92 (q, J = 8 Hz, 2H), 3.55 (t, J = 2 Hz, 2H), 5.10 (qq, J = 8 and 2 Hz, 1H), 7.39 (q, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.5, 18.8, 23.7, 39.1, 78.1, 126.4, 153.0, 172.7, 194.9; ESIMS (m/z) 223 $[M+Na]^+$; HRMS (ESI) calcd for $C_9H_{12}O_3NaS$ 223.0404, found 223.0396; IR ($CHCl_3$) ν_{max} 1747, 1728, 1649 cm^{-1}.

2-(5-Methyl-2-oxo-2,5-dihydrofuran-3-yl)acetaldehyde (14)

To a stirred suspension of thioester **13** (300 mg, 1.50 mmol) and 10% Pd/C (30 mg) in acetone (15 mL) at room temperature was drop wise added triethylsilane (Et_3SiH, 348 mg, 3.00 mmol) and the reaction mixture was stirred for 30 min. The reaction mixture was filtered through Celite and washed with acetone (5 mL). The concentration of the filtrate *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 5% ethyl acetate/petroleum ether as an eluent afforded product **14** as a colorless oil (193 mg, 92%).

Dimethyl 2-(4-methylcyclohexylidene)succinate (15d)

To a stirred solution of *t*-BuOK (2.24 g, 20.00 mmol) in *t*-BuOH (20 mL) at room temperature was added a solution of dimethyl succinate (2.92 g, 20.00 mmol) in *t*-BuOH (10 mL) in a drop wise fashion under argon atmosphere with constant stirring. After stirring the reaction mixture for 10 min, a solution of 4-methyl cyclohexanone (2.69 g, 24.00 mmol) in *t*-BuOH (10 mL) was added drop wise under argon atmosphere and the reaction mixture was stirred for 45 min at room temperature. The reaction mixture was concentrated in vacuo. The obtained residue was dissolved in water (60 mL) and the aqueous layer was washed with ethyl acetate (30 mL × 2). The aqueous layer was acidified to pH 2 using 2 N HCl (30 mL). The acidified aqueous layer was extracted with ethyl acetate (20 mL × 3), washed with water, brine and dried over Na_2SO_4. The organic layer was concentrated *in vacuo* and the dried residue was dissolved in MeOH (40 mL). To the above solution was added concentrated H_2SO_4 (2 mL) and it was refluxed for 2 h with constant stirring. The reaction mixture was allowed to attain room temperature and concentrated in vacuo. The obtained residue was dissolved in ethyl acetate (60 mL) and the organic layer was washed with saturated $NaHCO_3$ solution, brine and dried over Na_2SO_4. The concentration of organic layer *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 10% ethyl acetate/petroleum ether as an eluent afforded pure product **15d** as a thick oil (3.26 g, 68%). ^{1}H

NMR ($CDCl_3$, 200 MHz) δ 0.91 (d, J = 6 Hz, 3H), 0.95–1.30 (m, 2H), 1.50–1.75 (m, 1H), 1.75–2.10 (m, 4H), 2.45–2.65 (m, 1H), 3.22–3.38 (m, 1H), 3.39 (s, 2H), 3.68 (s, 3H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.5, 31.6, 31.8, 32.3, 34.7, 35.9, 36.2, 51.5, 51.9, 117.4, 155.0, 168.9, 171.9; ESIMS (m/z) 263 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1746, 1717, 1635 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.64; H, 8.70.

Methyl 2-(2-oxo-2,4,5,6,7,7a-hexahydrobenzofuran-3-yl)acetate (16a)

It was obtained from alkylidenesuccinate **15a** (2.26 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil[29] (1.55 g, 74%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20–1.62 (m, 3H), 1.84–2.10 (m, 2H), 2.21 (dt, J = 14 and 6 Hz, 1H), 2.45–2.61 (m, 1H), 2.74–2.88 (m, 1H), 3.31 (s, 2H), 3.70 (s, 3H), 4.67 (dd, J = 10 and 6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.6, 26.2, 26.7, 28.4, 34.3, 52.3, 80.4, 117.0, 166.5, 170.0, 173.4; ESIMS (m/z) 211 $[M+H]^+$, 233 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1759, 1747, 1690 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.47; H, 6.85.

Ethyl 2-(2-oxo-2,4,5,6,7,7a-hexahydrobenzofuran-3-yl)acetate (16b)

It was obtained from alkylidenesuccinate **15b** (2.54 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil (1.61 g, 72%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.24 (dt, J = 8 and 2 Hz, 3H), 1.20–1.60 (m, 3H), 1.80–2.07 (m, 2H), 2.19 (dt, J = 14 and 6 Hz, 1H), 2.40–2.60 (m, 1H), 2.79 (dd, J = 14 and 2 Hz, 1H), 3.27 (s, 2H), 4.13 (dq, J = 8 and 2 Hz, 2H), 4.65 (dd, J = 12 and 6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.0, 22.5, 26.1, 26.7, 28.5, 34.2, 61.1, 80.3, 117.0, 166.4, 169.5, 173.4; ESIMS (m/z) 225 $[M+H]^+$, 247 $[M+Na]^+$, 263 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 1752, 1734, 1687 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.38; H, 7.50.

Methyl 2-(2-oxo-2,4,5,6,7,7a-hexahydrobenzofuran-3-yl)-propanoate (16c/c′, diastereomeric mixture, 2 : 1)

It was obtained from alkylidenesuccinate **15c** (2.40 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil (1.57 g, 70%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.10–1.60 (m, 3H), 1.40 (d, J = 8 Hz, 1H), 1.41 (d, J = 8 Hz, 2H), 1.83–2.25 (m, 3H), 2.45–2.60 (m, 1H), 2.80–2.95 (m, 1H), 3.60 (q, J = 6 Hz, 1H), 3.69 (s, 3H), 4.60 (dd, J = 10 and 6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.7, 16.1, 22.5, 26.2, 26.3, 26.4, 26.5, 34.3, 34.4, 34.6, 34.8, 52.19, 52.24, 80.0, 122.8, 164.5, 172.9, 173.2; ESIMS (m/z) 225 $[M+H]^+$, 247 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1759, 1747, 1681 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.17; H, 6.83.

Methyl 2-((±)-6-methyl-2-oxo-2,4,5,6,7,7a-hexahydrobenzofuran-3-yl)acetate (16d/d′, diastereomeric mixture, 3 : 1)

It was obtained from alkylidenesuccinate **15d** (2.40 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a white solid (1.61 g, 72%). Recrystalization of **16d/d′** with petroleum ether provided analytically pure **16d** as a white solid. Mp 86–88 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.15 (d, J = 6 Hz, 3H), 1.43 (dt, J = 12 and 4 Hz, 1H), 1.52–1.72 (m, 1H), 1.75–1.90 (m, 1H), 2.18–2.55 (m, 3H), 2.61–2.75 (m, 1H), 3.31 (s, 2H), 3.70 (s, 3H), 4.90 (dd, J = 12 and 6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.1, 22.2, 27.1, 28.3, 31.6, 39.6, 52.2, 77.7, 116.7, 167.0, 170.0, 173.5; ESIMS (m/z) 247 $[M+Na]^+$, 263 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 1754, 1737, 1691 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.13; H, 6.84.

Methyl 2-(6-(*tert*-butyl)-2-oxo-2,4,5,6,7,7a-hexahydrobenzofuran-3-yl)acetate (16e/e′, diastereomeric mixture, 7 : 3)

It was obtained from alkylidenesuccinate **15e** (2.82 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a white solid (1.76 g, 66%). Mp 70–73 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.87 (s, 9H), 0.90–2.35 (m, 5H), 2.45–2.87 (m, 2H), 3.25 (s, 0.60H), 3.27 (s, 1.40H), 3.67 (s, 3H), 4.67 (dd, J = 12 and 6 Hz, 0.30H), 4.97 (t, J = 8 Hz, 0.70H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.2, 24.3, 25.9, 27.2, 27.4, 27.5, 28.2, 28.6, 30.6, 32.3, 32.8, 35.3, 43.0, 44.6, 52.0, 78.5, 80.9, 116.5, 117.9, 166.6, 167.2, 169.7, 169.9, 173.3, 173.8; ESIMS (m/z) 267 $[M+H]^+$, 289 $[M+Na]^+$, 305 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 1759, 1755, 1748, 1732, 1688 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33. Found: C, 67.71; H, 8.60.

Methyl 2-(2-oxo-4,5,6,7,8,8a-hexahydro-2*H*-cyclohepta[*b*]furan-3-yl)acetate (16f)

It was obtained from alkylidenesuccinate **15f** (2.40 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil (1.52 g, 68%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.15–1.70 (m, 4H), 1.70–2.05 (m, 3H), 2.25–2.45 (m, 1H), 2.45–2.83 (m, 2H), 3.27 (s, 2H), 3.70 (s, 3H), 4.88–5.00 (m, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 25.4, 26.1, 27.6, 28.7, 29.7, 33.6, 52.2, 83.8, 119.9, 169.3, 169.7, 173.3; ESIMS (m/z) 225 $[M+H]^+$, 247 $[M+Na]^+$, 263 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 1756, 1747, 1669 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.07; H, 7.27.

Methyl 2-(2-oxo-2,3a,4,5-tetrahydronaptho[2,1-*b*]furan-1-yl) acetate (16g)

It was obtained from alkylidenesuccinate **15g** (2.74 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil (1.96 g, 76%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.70–1.95 (m, 1H), 2.62–2.76 (m, 1H), 3.06–3.17 (m, 2H), 3.53 (dd, J = 16 and 2 Hz, 1H), 3.73 (d, J = 16 Hz, 1H), 3.75 (s, 3H), 5.10 (dd, J = 14 and 6 Hz, 1H), 7.29–7.46 (m, 3H), 7.63 (dd, J = 6 and 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 27.6, 30.1 (2 carbons), 52.5, 79.0, 116.1, 127.1, 127.67, 127.73, 129.4, 131.1, 138.1, 159.5, 170.0, 173.9; ESIMS (m/z) 259 $[M+H]^+$, 281 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1749, 1659 cm^{-1}. Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.68; H, 5.72.

Ethyl 2-(2-oxo-2,3a,4,5-tetrahydronaptho[2,1-*b*]furan-1-yl)acetate (16h)

It was obtained from alkylidenesuccinate **15h** (3.02 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a thick oil (1.99 g, 73%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.25 (t, J = 8 Hz, 3H), 1.70–1.95 (m, 1H), 2.60–2.75 (m, 1H), 3.05–3.20 (m, 2H), 3.52 (dd, J = 16 and 2 Hz, 1H), 3.70 (d, J

= 16 Hz, 1H), 4.19 (q, J = 8 Hz, 2H), 5.09 (dd, J = 12 and 6 Hz, 1H), 7.25–7.45 (m, 3H), 7.63 (dd, J = 6 and 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.1, 27.6, 30.2, 30.3, 61.4, 79.0, 116.3, 127.0, 127.6, 127.8, 129.3, 131.0, 138.1, 159.4, 169.5, 173.9; ESIMS (m/z) 295 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1754, 1731, 1657 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.84; H, 5.77.

2-(2-Oxo-2,4,5,6,7,7a-hexahydrobenzofuran-3-yl)acetic acid (19)

It was obtained from butenolide **16a** (1.05 g, 5.00 mmol) and TFA (90%, 15 mL) using the same procedure described above for **8**, as a white solid (804 mg, 82%). It was also obtained from cyclohexylidenesuccinic anhydride (**18**) (1.80 g, 10.00 mmol) and SeO_2 (1.78 g, 16.00 mmol) using the same procedure described above for **5a**, as a white solid[30] (1.02 g, 52%). Mp 122–124 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.15–1.63 (m, 3H), 1.85–2.11 (m, 2H), 2.23 (dt, J = 12 and 6 Hz, 1H), 2.45–2.64 (m, 1H), 2.75–2.90 (m, 1H), 3.36 (s, 2H), 4.69 (dd, J = 12 and 8 Hz, 1H), 8.28 (br s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.6, 26.2, 26.7, 28.5, 34.2, 80.7, 116.5, 167.1, 173.7, 174.7; ESIMS (m/z) 197 $[M+H]^+$, 219 $[M+Na]^+$, 235 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 2929, 2852, 1748, 1712, 1674 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16. Found: C, 60.92; H, 6.59.

Methyl 2-((±)-6-methyl-2-oxo-octahydrobenzofuran-3-yl)acetate (23)

To a stirred solution of butenolide **16d** (1.00 g, 4.50 mmol) and $NiCl_2{\cdot}6H_2O$ (213 mg, 0.89 mmol) in MeOH (20 mL) at room temperature was portion wise added $NaBH_4$ (848 mg, 22.30 mmol) and the reaction mixture was stirred for 1 h. The reaction mixture was concentrated *in vacuo* and the obtained residue was dissolved in ethyl acetate (30 mL). The organic layer was washed with water, brine and dried over Na_2SO_4. The concentration of organic layer *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 30% ethyl acetate/petroleum ether as an eluent afforded pure product **23** as a colorless oil (969 mg, 96%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.82–1.31 (m, 3H), 0.92 (d, J = 8 Hz, 3H), 1.43–1.74 (m, 3H), 2.24 (qd, J = 15 and 4 Hz, 1H), 2.36–2.56 (m, 1H), 2.45 (dd, J = 18 and 10 Hz, 1H), 2.85 (dd, J = 18 and 4 Hz, 1H), 3.21 (ddd, J = 10, 6 and 6 Hz, 1H), 3.72 (s, 3H), 4.53 (dd, J = 6 and 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.8, 23.0, 26.1, 29.3, 31.7, 35.9, 37.6, 44.2, 52.0, 78.6, 172.1, 177.6; ESIMS (m/z) 249 $[M+Na]^+$, 265 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 1775, 1740 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.91; H, 7.93.

2-((±)-6-Methyl-2-oxo-octahydrobenzofuran-3-yl)acetic acid (24)

It was obtained from butenolide **23** (900 mg, 10.00 mmol) and aqueous TFA (90%, 10 mL) using the same procedure described above for **8**, as a white solid (726 mg, 86%). Mp 128–130 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.80–1.32 (m, 3H), 0.93 (d, J = 6 Hz, 3H), 1.42–1.75 (m, 3H), 2.24 (qd, J = 15 and 4 Hz, 1H), 2.35–2.55 (m, 1H), 2.50 (dd, J = 18 and 10 Hz, 1H), 2.89 (dd, J = 18 and 4 Hz, 1H), 3.21 (ddd, J = 10, 5 and 5 Hz, 1H), 4.54 (dd, J = 6 and 2 Hz, 1H), 8.50 (br s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.8, 23.0, 26.0, 29.4, 31.6, 35.8, 37.5, 44.0, 78.8, 177.3, 177.8; ESIMS (m/z) 235 $[M+Na]^+$, 263 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 1766, 1727, 1638 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.38; H, 7.46.

(±)-6-Methyl-3-methylene-hexahydrobenzofuran-2(3*H*)-one (25)

To a stirred suspension of acid **24** (700 mg, 3.30 mmol), $Pb(OAc)_4$ (1.90 g, 4.29 mmol) and $Cu(OAc)_2$ (60 mg, 0.33 mmol) in dry benzene (20 mL) at 80 °C was drop wise added pyridine (783 mg, 9.91 mmol) and the reaction mixture was further refluxed for 15 min. until the reaction mixture became blue in color. The reaction mixture was allowed to attain room temperature. The reaction mixture was concentrated *in vacuo* and the obtained residue was dissolved in ethyl acetate (30 mL). The organic layer was washed with saturated $NaHCO_3$ solution, saturated $CuSO_4$ solution, water, brine and dried over Na_2SO_4. The concentration of organic layer *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 40% ethyl acetate/petroleum ether as an eluent afforded pure product **25** as a colorless oil[31] (225 mg, 41%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.80–1.05 (m, 1H), 0.94 (d, J = 6 Hz, 3H), 1.20–1.45 (m, 2H), 1.55–1.75 (m, 2H), 1.75–1.90 (m, 1H), 2.20 (qd, J = 15 and 4 Hz, 1H), 2.84 (ddd, J = 11, 6 and 4 Hz, 1H), 4.52 (dd, J = 6 and 4 Hz, 1H), 5.53 (d, J = 1 Hz, 1H), 6.10 (d, J = 1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 25.6, 28.3, 31.2, 35.7, 39.4, 77.2, 119.6, 142.2, 171.0; ESIMS (m/z) 167 $[M+H]^+$, 189 $[M+Na]^+$, 205 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 1771, 1668, 1641 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.44; H, 8.16.

(±)-3,6-Dimethyl-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (Isomintlactone, 26)

To a stirred solution of butenolide **25** (200 mg, 1.21 mmol) in dry toluene (10 mL) was added catalyst $[RhH(Ph_3P)_4]$ (139 mg, 0.12 mmol) and the reaction mixture was refluxed for 2 h until all **25** was consumed (monitored by GC). The reaction mixture was allowed to attain room temperature. The reaction mixture was filtered off and the residue was washed with toluene (5 mL). The filtrate was concentrated *in vacuo* and the silica gel column chromatographic purification of the resulting residue using 20% ethyl acetate/petroleum ether as an eluent afforded pure product **26** as a white solid[31] (182 mg, 91%). Mp 78–80 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.15 (d, J = 4 Hz, 3H), 1.37 (dt, J = 12 and 4 Hz, 1H), 1.50–1.62 (m, 1H), 1.73–1.85 (m, 1H), 1.81 (s, 3H), 2.22–2.31 (m, 1H), 2.31–2.43 (m, 2H), 2.69 (dd, J = 14 and 4 Hz, 1H), 4.82 (dd, J = 10 and 4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 8.2, 17.2, 21.7, 27.3, 31.6, 39.5, 77.5, 119.3, 163.0, 175.0; ESIMS (m/z) 167 $[M+H]^+$ 189 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1756, 1641 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.15; H, 8.12.

(±)-3,6-Dimethyl-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (Mintlactone, 27)

To a stirred solution of isomintlactone, (**26**) (200 mg, 1.21 mmol) in dry MeOH (10 mL) was added NaOMe (78 mg, 1.45 mmol) and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was then concentrated in vacuo. The obtained residue was dissolved in ethyl acetate (15 mL) and acidified to pH 2 using 2 N HCl (5 mL). The organic layer was separated and the aqueous layer was further extracted with ethyl acetate (10 mL

× 2). The combined organic layer was washed with water, brine and dried over Na_2SO_4. Concentration of the organic layer *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 20% ethyl acetate/petroleum ether as an eluent furnished pure product **27** as a colorless oil[31] (110 mg, 55%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90–1.20 (m, 2H), 1.01 (d, J = 8 Hz, 3H), 1.60–1.80 (m, 1H), 1.81 (t, J = 2 Hz, 3H), 1.87–2.02 (m, 1H), 2.19 (dt, J = 14 and 4 Hz, 1H), 2.36–2.49 (m, 1H), 2.80 (ddd, J = 14, 6 and 2 Hz, 1H), 4.63 (dd, J = 11 and 6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 8.2, 21.2, 25.4, 29.8, 34.5, 42.0, 79.9, 119.6, 162.3, 174.9; ESIMS (m/z) 167 $[M+H]^+$, 189 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1756, 1645, 1715, 1688 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.16; H, 8.07.

(±)-7-Methyl-2-oxo-octahydro-2*H*-chromene-4-carboxylic acid (28)

An aqueous solution of 2 N KOH (5 mL) was added to a stirring solution of **23** (678 mg, 3.00 mmol) in MeOH (20 mL) at room temperature and the reaction mixture was stirred for 1 h. The reaction mixture was then concentrated in vacuo. The obtained residue was dissolved in ethyl acetate (15 mL) and acidified to pH 2 using 2 N HCl (5 mL). The organic layer was separated and the aqueous layer was further extracted with ethyl acetate (10 mL × 2). The combined organic layer was washed with water, brine and dried over Na_2SO_4. Concentration of the organic layer *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 50% ethyl acetate/petroleum ether as an eluent furnished pure product **28** as a white solid (598 mg, 94%). Mp 141–143 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.92 (d, J = 6 Hz, 3H), 0.98–1.32 (m, 2H), 1.51 (dq, J = 14 and 4 Hz, 1H), 1.64–1.92 (m, 3H), 2.02–2.24 (m, 2H), 2.58–2.96 (m, 3H), 4.55 (d, J = 4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.8, 25.6, 27.9, 29.0, 33.7, 36.4, 38.2, 41.9, 75.5, 171.2, 178.6; ESIMS (m/z) 213 $[M+H]^+$, 230 $[M+NH_3]^+$, 235 $[M+Na]^+$, 251 $[M+K]^+$; IR ($CHCl_3$) ν_{max} 2923, 1732, 1602 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.11; H, 7.19.

(±)-7-Methyl-4a,5,6,7,8,8a-hexahydrochromen-2-one (29)

To a stirred suspension of acid **28** (530 mg, 2.50 mmol), $Pb(OAc)_4$ (1.44 g, 3.25 mmol) and $Cu(OAc)_2$ (46 mg, 0.25 mmol) in dry benzene (20 mL) at 80 °C was drop wise added pyridine (593 mg, 7.50 mmol). The reaction mixture was further refluxed for 15 min. until the reaction mixture became blue in color. The reaction mixture was allowed to attain room temperature. The reaction mixture was concentrated *in vacuo* and the obtained residue was dissolved in ethyl acetate (30 mL). The organic layer was washed with saturated $NaHCO_3$ solution, saturated $CuSO_4$ solution, water, brine and dried over Na_2SO_4. The concentration of organic layer *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 20% ethyl acetate/petroleum ether as an eluent afforded pure product **29** as a colorless oil (282 mg, 68%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.83–1.10 (m, 1H), 0.93 (d, J = 8 Hz, 3H), 1.13–1.43 (m, 2H), 1.62–1.93 (m, 3H), 2.04–2.22 (m, 2H), 4.56 (dd, J = 6 and 2 Hz, 1H), 5.97 (dd, J = 10 and 2 Hz, 1H), 6.97 (dd, J = 10 and 6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.8, 25.9, 26.8, 32.9, 35.2, 38.2, 76.4, 120.1, 150.8, 165.1; ESIMS (m/z) 167 $[M+H]^+$, 189 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1729 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.66; H, 8.36.

(±)-7-Methyl-octahydrochromen-2-one (30)

To a stirred solution of lactone **29** (200 mg, 1.21 mmol) and $NiCl_2{\cdot}6H_2O$ (57 mg, 0.24 mmol) in MeOH (20 mL) at room temperature was portion wise added $NaBH_4$ (229 mg, 6.02 mmol) and the reaction mixture was stirred for 1 h. The reaction mixture was concentrated *in vacuo* and the obtained residue was dissolved in ethyl acetate (30 mL). The organic layer was washed with water, brine and dried over Na_2SO_4. The concentration of organic layer *in vacuo* followed by silica gel column chromatographic purification of the resulting residue using 20% ethyl acetate/petroleum ether as an eluent afforded pure product **30** as a colorless oil (186 mg, 92%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90 (d, J = 6 Hz, 3H), 0.90–1.30 (m, 2H), 1.40–1.90 (m, 6H), 1.95–2.20 (m, 2H), 2.48 (d, J = 8 Hz, 1H), 2.52 (d, J = 8 Hz, 1H), 4.51 (dd, J = 6 and 4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.8, 24.6, 25.6, 26.1, 26.4, 32.2, 33.7, 38.9, 78.4, 172.7; ESIMS (m/z) 169 $[M+H]^+$, 191 $[M+Na]^+$; IR ($CHCl_3$) ν_{max} 1732 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.47; H, 9.06.

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