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Study of the stereoselectivity of the nucleophilic epoxidation of 3-hydroxy-2-methylene esters

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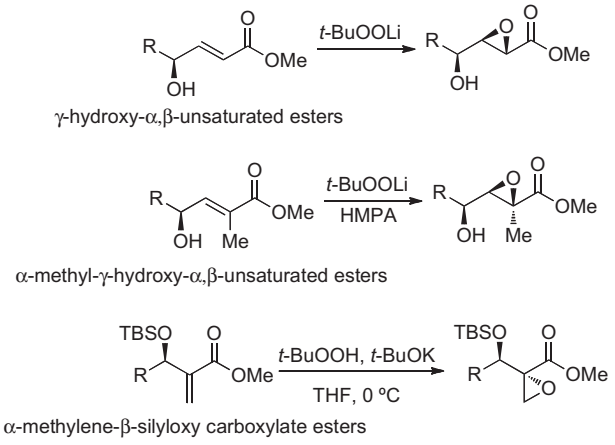
ABSTRACT

The diastereoselectivity of the nucleophilic epoxidation of 3-hydroxy-2-methylene esters has been studied. The 3-hydroxy-2-methylene esters were obtained through a Morita–Baylis–Hillman reaction. The resulting epoxyesters were treated with thiophenol for transformation into 2,3-dihydroxy-2-((phenylthio)methyl), which upon treatment with triphosgene afforded the corresponding cyclic carbonates.

1. Introduction

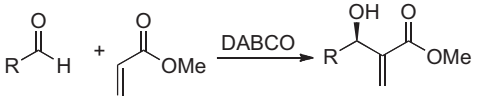
Stereoselective synthesis of α,β-epoxyesters is of considerable synthetic interest because a number of compounds can be obtained by the opening of the oxirane ring.[1–9] A convenient method for the preparation of α,β-epoxyesters is via nucleophilic epoxidation of chiral α,β-unsaturated esters.[2] We previously reported that the nucleophilic epoxidation of γ-hydroxy-α,β-unsaturated esters[8] (Scheme 1) is a diastereoselective reaction that favor the *syn* isomer. We have also reported that the stereoselectivity depends highly on the substitution of the double bond and that high *syn* stereoselectivity (dr >19:1) is observed for the α-methyl-substituted enoates[9] (Scheme 1). Free hydroxyl group resulted to be key for the control of the stereoselectivity. The nucleophilic epoxidation of methyl 2-methylene-3-*tert*-butyldimethylsilyloxycarboxylate esters has been recently reported by A. Myers to get the *anti* diastereomer with high selectivity[12] (Scheme 1). The epoxidation of Morita–Baylis–Hillman adducts is an interesting transformation because the resulting epoxides can be used in the total synthesis of interesting natural products.[10–12] We now report a study of the stereoselectivity of the nucleophilic epoxidation of β-hydroxy-α-methylene esters.



Scheme 1. Stereoselective nucleophilic epoxidations of unsaturated esters.

2. Results and discussion

We wanted to study the selectivity of epoxidation of 3-hydroxy-methylene carboxylate esters with a range of R alkyl and aryl groups (Scheme 2). For the preparation of the substrates, a comparison of different experimental procedures was performed as



1a, R = Me
1b, R = Et
1c, R = *n*-Pr
1d, R = *i*-Bu
1e, R = Chx
1f, R = CH_2CH_2Ph
1g, R = CH=CHPh
1h, R = Ph
1i, R = *p*-Tol
1j, R = *p*-MeOPh
1k, R = *p*-FPh
1l, R = *p*-ClPh
1m, R = *m*-ClPh
1n, R = *o*-ClPh
1o, R = *p*-BrPh
1p, R = *o*-NO_2Ph
1q, R = *m*-NO_2Ph
1r, R = *p*-NO_2Ph
1s, R = Furfuryl

Scheme 2. Preparation of substrates.

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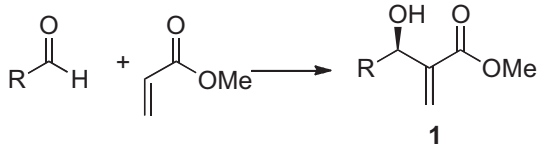
shown in Table 1. Most of the substrates were prepared in good yield using DABCO as a base and a (1:1) mixture of dioxane/water as reported.[13] We obtained higher yields when the reaction was performed at higher concentrations (10 M) than reported (see Experimental section). Compounds **1i** and **j** were obtained in best yields under solvent-free conditions and longer period of time, and compounds **1m** and **n** were prepared using dimethylsulfoxide as a solvent.

Table 1
Preparation of esters **1**

Entry	Substrate	Conditions	Yield
1	**1a**	DABCO, dioxane/H_2O (1:1), 10 M, 48 h, rt	99
2	**1b**	DABCO, dioxane/H_2O (1:1), 10 M, 48 h, rt	70
3	**1c**	DABCO, dioxane/H_2O (1:1), 10 M, 48 h, rt	99
4	**1d**	DABCO, dioxane/H_2O (1:1), 10 M, 48 h, rt	85
5	**1e**	DABCO, dioxane/H_2O (1:1), 10 M, 48 h, rt	81
6	**1f**	DABCO, dioxane/H_2O (1:1), 10 M, 48 h, rt	99
7	**1g**	DABCO, dioxane/H_2O (1:1), 10 M, 48 h, rt	99
8	**1h**	DABCO, dioxane/H_2O (1:1), 12 M, 48 h, rt	99
9	**1i**	DABCO, solvent-free 4 days, rt	82
10	**1j**	DABCO, solvent-free 5 weeks, rt	77
11	**1k**	DABCO, dioxane/H_2O (1:1), 10 M, 36 h, rt	99
12	**1l**	DABCO, solvent-free 5 days, rt	94
13	**1m**	DABCO, DMSO 7 M, 4 days, rt	99
14	**1n**	DABCO, DMSO 7 M, 4 days, rt	99
15	**1o**	DABCO, dioxane/H_2O (1:1), 10 M, 36 h, rt	89
16	**1p**	DABCO, dioxane/H_2O (1:1), 10 M, 16 h, rt	95
17	**1q**	DABCO, dioxane/H_2O (1:1), 10 M, 16 h, rt	87
18	**1r**	DABCO, dioxane/H_2O (1:1), 10 M, 3 h, rt	83
19	**1s**	DABCO, dioxane/H_2O (1:1), 10 M, 20 h, rt	85

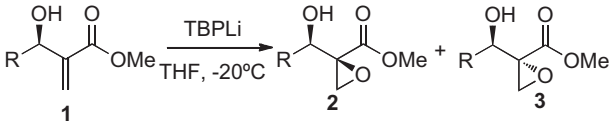


Esters **1** were epoxidized using lithium *tert*-butylperoxide (2 equiv) as the oxidizing reagent in THF as solvent at −20 °C.[2,8,9] Table 2 shows that the **2** *syn* isomer was the major product in all cases. For the aliphatic series (compounds **1a**–**f**), the higher steric volume of the R pendant alkyl group the higher stereoselectivity is observed (entries 1–6). When the R is an alkenyl group then the epoxidation reaction is not stereoselective (entry 7). Compounds **1h**–**s** having an aromatic group gave the corresponding *syn* isomer **2** in very good selectivity.

Table 2
Epoxidation of compounds **1**

Entry	Substrate	2/3	Yield[a]
1	Me	67/33	72
2	Et	76/24	70
3	*n*-Pr	81/19	79
4	*i*-Bu	81/19	71
5	Chx	92/8	85
6	$PhCH_2CH_2$	77/23	59
7	PhCH=CH	53/47	47
8	Ph	93/7	68
9	*p*-Tol	89/11	82
10	*p*-MeOPh	92/8	73
11	*p*-FPh	90/10	65
12	*p*-ClPh	84/16	52
13	*m*-ClPh	92/8	38
14	*o*-ClPh	92/8	52
15	*p*-BrPh	90/10	68
16	*o*-NO2Ph	83/17	43
17	*m*-NO2Ph	80/20	60
18	*p*-NO2Ph	91/9	65
19	Furfuryl	93/7	69

[a] Isolated yield of products corresponds to mixtures of *syn* and *anti* diastereomers.



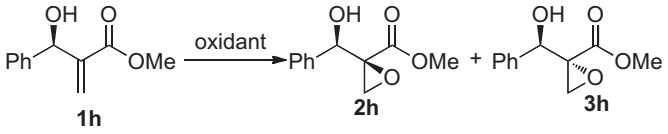
We also epoxidized compound **1h** by using oxidants other than lithium *tert*-butylperoxide (Table 3). If the reaction was carried out using *tert*-butyl hydrogenperoxide in the presence of substoichiometric amount of base (entry 1), then a slightly lower selectivity was observed compared to the reaction carried out using a stoichiometric amount of oxidant (entry 8, Table 2). Lithium cumylperoxide gave similar result to lithium *tert*-butylperoxide (entry 2). On the other hand, in the alkaline peroxides series, potassium gave poorer stereoselectivity than either lithium or sodium (entries 1 and 6–8). The yield of the epoxidation using *m*-CPBA (entry 3) was low at rt but it increased at higher temperature (entry 4), affording the *syn* isomer as the major one. When *m*-CPBA was used in the presence of potassium carbonate[14] (entry 5), only starting material was recovered.

Table 3
Epoxidation of compound **1h**

Entry	Conditions[a]	**2h**/**3h**	Yield (%)[b]
1	TBPLi	88/12	66
2	CMPLi	91/9	72
3	*m*-CPBA	90/10	28
4	*m*-CPBA	88/12	80
5	*m*-CPBA	—	NR
6	TBPNa	85/15	41
7	TBPNa	87/13	62
8	TBPK	83/17	61

[a] For entry 1: 1.5 equiv of TBHP, 0.8 equiv of MeLi, THF, −20 °C, 20 h. For entry 2: 1.5 equiv of CMHP, 1.1 equiv of MeLi, THF, −20 °C, 20 h. For entry 3: 2.1 equiv of *m*-CPBA, DCM, rt, 96 h. For entry 4: 2.1 equiv of *m*-CPBA, 70 °C (sealed tube), 96 h. For entry 5: 2.5 equiv of *m*-CPBA, 1.3 equiv of K_2CO_3, DCM, rt, 96 h. For entry 6: 2.0 equiv of TBHP, 1.0 equiv of *t*-BuONa, THF, 0 °C, 3 h. For entry 7: 2.0 equiv of TBHP, 0.25 equiv of *t*-BuONa, THF, 0 °C, 3 h. For entry 8: 2.0 equiv of TBHP, 0.25 equiv of *t*-BuOK, THF, 0 °C, 3 h.

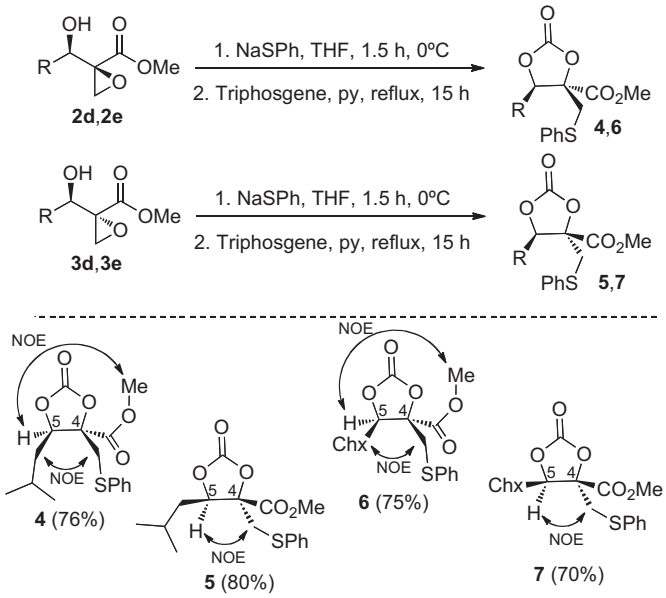
[b] Isolated yield of products corresponds to mixtures of *syn* and *anti* diastereomers.



The stereochemistry of epoxides **2b** and **h** was confirmed by comparison with already reported data.[12,15] The epoxyesters **2d**, **3d**, **2e**, and **3e** were transformed into cyclic carbonates through a one-pot sequence: treatment with thiophenol in the presence of a base, which resulted in the opening of the oxirane ring and then addition of triphosgene to give carbonates **4**, **5**, **6**, and **7**, respectively (Scheme 3). The stereochemical assignment of the carbonates was performed by NOE experiments (Scheme 3). Carbonates **4** and **6** gave NOE between H-5 and methyl ester whilst **5** and **7** gave NOE between H-5 and methylene from the (phenylthio)methyl group.

3. Conclusions

In summary, the diastereoselectivity of the nucleophilic epoxidation of 3-hydroxy-2-methylene esters has been studied. The *syn* isomer was the major one in all cases. The resulting 3-hydroxy 2-epoxyesters were treated with thiophenol for transformation into 2,3-dihydroxy-2-((phenylthio)methyl), which upon treatment with triphosgene afforded the corresponding cyclic carbonates.



Scheme 3. Cyclic carbonates **4**–**7**.

4. Experimental section

4.1. General experimental methods

All solvents used in reactions were freshly distilled from appropriate drying agents before use. ^{1}H NMR spectra and ^{13}C NMR spectra were measured in $CDCl_3$ (^{1}H, 7.24 ppm; ^{13}C 77.0 ppm) solution at 30 °C on a 300 MHz or a 500 MHz NMR spectrometer. IR spectra were recorded as oil films or KBr discs or NaCl pellets on a FT-IR spectrometer. EM Science Silica Gel 60 was used for column chromatography while TLC was performed with precoated plates (Kieselgel 60, F_{254}, 0.25 mm). Unless otherwise specified, all reactions were carried out under argon atmosphere with magnetic stirring.

4.2. General experimental procedure for the preparation of compounds 1a–s

To a solution of aldehyde (1 mmol) in dioxane/water (1:1) (0.1 mL) was added methyl acrylate (3 mmol) and DABCO (1 mmol). The reaction was monitored by TLC. Upon completion, water (70 mL) was added and poured onto a separatory funnel and extracted with ethyl ether or dichloromethane (3×30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude was purified through chromatography (silicagel, hexanes/ethyl acetate (8:2), (6:4)) to afford the desired compound.

4.2.1. Methyl 3-hydroxy-2-methylenebutanoate ***1a***.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.19 (1H, s), 5.81 (1H, s), 4.59 (1H, q, J=6.5 Hz), 3.76 (3H, s), 2.61 (1H, br s), 1.36 (3H, d, J=6.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 143.6, 124.0, 67.2, 51.8, 22.1 ppm.

4.2.2. Methyl 3-hydroxy-2-methylenepentanoate ***1b***.[17] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.22 (1H, s), 5.78 (s, 1H), 4.31 (1H, t, J=7.0 Hz), 3.76 (3H, s), 2.43 (1H, br s), 1.73–1.61 (2H, m), 0.93 (3H, t, J=7.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 142.3, 124.7, 72.0, 51.5, 29.0, 10.0 ppm.

4.2.3. Methyl 3-hydroxy-2-methylenehexanoate ***1c***.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.20 (1H, s), 5.78 (1H, s), 4.38 (1H, t, J=6.5 Hz), 3.76 (3H, s), 2.41 (1H, br s), 1.63–1.58 (2H, m), 1.49–1.45 (1H, m), 1.31–1.38 (1H, m), 0.90 (3H, t, J=6.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 142.5, 124.7, 71.3, 52.0, 38.5, 19.0, 14.0 ppm.

4.2.4. Methyl 3-hydroxy-5-methyl-2-methylenehexanoate ***1d***.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.18 (1H, s), 5.78 (1H, s), 4.45 (1H, dd, J=8.5, 4.3 Hz), 3.76 (3H, s), 2.40 (1H, br s), 1.80–1.75 (1H, m), 1.58–1.51 (1H, m), 1.44–1.38 (1H, m), 0.92 (6H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 142.8, 124.6, 71.3, 69.9, 51.9, 45.5, 24.8, 23.3, 21.8 ppm.

4.2.5. Methyl 2-(cyclohexyl(hydroxy)methyl)acrylate ***1e***.[19] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (1H, s), 5.71 (1H, s), 4.06 (1H, d, J=7.2 Hz), 3.76 (3H, s), 2.44 (1H, br s), 1.94 (1H, m), 1.50–1.76 (5H, m), 1.24–0.92 (5H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 141.2, 126.0, 53.4, 52.0, 42.4, 29.8, 28.1, 26.3, 26.1, 25.9 ppm.

4.2.6. Methyl 3-hydroxy-2-methylene-5-phenylpentanoate ***1f***.[20] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.17 (5H, m), 6.24 (1H, s), 5.81 (1H, s), 4.42 (1H, dd, J=7.5, 5.7 Hz), 3.77 (3H, s), 2.85–2.79 (1H, m), 2.73–2.69 (1H, m), 2.42 (1H, br s), 2.00–1.95 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 141.8, 128.5, 125.9, 125.0, 70.1, 51.8, 38.0, 32.0 ppm.

4.2.7. (E)-Methyl 3-hydroxy-2-methylene-5-phenylpent-4-enoate ***1g***.[19] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.22 (5H, m), 6.67 (1H, d, J=16.0 Hz), 6.29 (2H, m), 5.91 (1H, s), 5.13 (1H, m), 3.78 (3H, s), 2.97 (1H, br s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 141.3, 136.5, 131.5, 129.2, 128.5, 127.8, 126.6, 125.8, 72.1, 52.0 ppm.

4.2.8. Methyl 2-(hydroxy(phenyl)methyl)acrylate ***1h***.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.26 (5H, m), 6.33 (1H, s), 5.83 (1H, s), 5.56 (1H, s), 3.72 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 142.3, 141.6, 128.3, 127.7, 126.8, 125.6, 72.7, 51.8 ppm.

4.2.9. Methyl 2-(hydroxy(p-tolyl)methyl)acrylate ***1i***.[18] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (2H, d, J=8.0 Hz), 7.15 (2H, d, J=8.0 Hz), 6.32 (1H, s), 5.85 (1H, s), 5.53 (1H, s), 3.71 (3H, s), 2.34 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 142.1, 138.4, 137.5, 129.1, 126.5, 125.8, 73.1, 51.9, 21.1 ppm.

4.2.10. Methyl 2-(hydroxy(4-methoxyphenyl)methyl)acrylate ***1j***.[20] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (2H, d, J=8.8 Hz), 6.86 (2H, d, J=8.7 Hz), 6.31 (1H, s), 5.84 (1H, s), 5.52 (1H, s), 3.79 (3H, s), 3.71 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 159.2, 142.2, 133.5, 127.9, 125.5, 113.8, 72.7, 55.2, 51.9 ppm.

4.2.11. Methyl 2-((4-fluorophenyl)(hydroxy)methyl)acrylate ***1k***.[20] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (2H, dd, J=8.5, 5.5 Hz), 7.01 (2H, t, J=8.7 Hz), 6.32 (1H, s), 5.82 (1H, s), 5.53 (1H, s), 3.73 (3H, s), 3.02 (1H, br s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 162.3 (d, J=245 Hz), 141.9, 137.0, 128.3 (dd, J=7.2, 21.3 Hz), 126.0 (dd, J=15.0, 21.3 Hz), 115.2 (dd, J=12.5, 22.5 Hz), 72.6, 52.2 ppm.

4.2.12. Methyl 2-((4-chlorophenyl)(hydroxy)methyl)acrylate ***1l***.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (1H, m), 7.34 (1H, m), 7.21–7.30 (2H, m), 6.32 (1H, s), 5.97 (1H, s), 5.58 (1H, m), 3.76 (3H, s), 3.26 (1H, br s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 141.6, 139.8, 133.6, 128.6, 127.9, 126.3, 72.7, 52.0 ppm.

4.2.13. Methyl 2-((3-chlorophenyl)(hydroxy)methyl)acrylate ***1m***.[20] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (1H, s), 7.26 (3H, m), 6.34 (1H, s), 5.83 (s, 1H), 5.51 (1H, s), 3.72 (s, 3H), 3.03 (1H, br s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 143.4, 141.4, 134.4, 129.7, 127.9, 126.7, 126.6, 124.7, 72.7, 52.0 ppm.

4.2.14. Methyl 2-((2-chlorophenyl)(hydroxy)methyl)acrylate ***1n***.[20] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (1H, m), 7.34 (1H, m), 7.21–7.30

(2H, m), 6.32 (1H, s), 5.97 (1H, s), 5.58 (1H, m), 3.76 (3H, s), 3.25 (1H, br s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 140.9, 134.5, 132.8, 128.9, 128.1, 127.0, 126.8, 68.9, 52.0 ppm.

4.2.15. Methyl 2-((4-bromophenyl)(hydroxy)methyl)acrylate ***1o***.[20] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (2H, m), 7.25 (2H, m), 6.33 (1H, s), 5.82 (1H, s), 5.51 (1H, m), 3.73 (3H, s), 3.04 (1H, br s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 141.9, 140.6, 131.4, 128.6, 125.9, 121.6, 71.9, 51.9 ppm.

4.2.16. Methyl 2-((2-nitrophenyl)(hydroxy)methyl)acrylate ***1p***.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (1H, dd, J=8.2, 1.3 Hz), 7.75 (1H, dd, J=7.9, 1.3 Hz), 7.64 (1H, td, J=7.7, 1.3 Hz), 7.46 (1H, td, J=8.5, 1.4 Hz), 6.37 (1H, s), 6.20 (1H, s), 5.73 (1H, s), 3.73 (3H, s), 3.35 (1H, br s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 145.6, 138.5, 133.7, 130.8, 126.3, 126.0, 123.7, 121.9, 64.7, 49.5 ppm.

4.2.17. Methyl 2-((3-nitrophenyl)(hydroxy)methyl)acrylate ***1q***.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (1H, m), 8.14 (1H, ddd, J=8.2, 2.3, 1.2 Hz), 7.75 (1H, m), 7.52 (1H, t, J=7.92 Hz), 6.41 (1H, s), 5.89 (1H, s), 5.63 (1H, s), 3.75 (3H, s), 3.25 (1H, br s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 148.3, 143.7, 141.0, 132.8, 129.5, 126.9, 122.8, 121.7, 72.4, 52.3 ppm.

4.2.18. Methyl 2-((4-nitrophenyl)(hydroxy)methyl)acrylate ***1r***.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (2H, d, J=10.9 Hz), 7.56 (2H, d, J=10.9 Hz), 6.38 (1H, s), 5.86 (1H, s), 5.62 (1H, m), 3.73 (3H, s), 3.32 (1H, br s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 148.6, 143.7, 141.0, 127.3, 127.2, 123.6, 72.7, 52.2 ppm.

4.2.19. Methyl 2-(furan-2-yl(hydroxy)methyl)acrylate ***1s***.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (1H, s), 6.37 (1H, s), 6.31 (1H, m), 6.24 (1H, m), 5.93 (1H, s), 5.57 (1H, s), 3.74 (3H, s), 3.21 (1H, br s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 154.1, 142.3, 143.7, 139.5, 126.7, 110.4, 107.1, 67.2, 52.0 ppm.

4.3. General experimental procedure for the epoxidation of esters 1a–s

To a −78 °C cold THF (3.5 mL) was added TBHP (3.3 M in toluene) (2 mmol) and then methyllithium (1.6 M in hexanes) (1.7 mmol). The resulting mixture was stirred at −78 °C for 15 min and then a solution of compound **1** (1 mmol) in THF (2 mL) was added drop wise and then the mixture was left at −20 °C (fridge) for 20 h. Then solid Na_2SO_3 (120 mg) was added in one portion and stirred for 15 min, then diluted with water and extracted with Et_2O (3×30 mL), the organic layers were washed (brine), dried (Na_2SO_4), and concentrated. The crude oil was purified through chromatography (silica-gel, hexanes/EtOAc (7:3) and (1:1)).

4.3.1. Methyl 2-(1-hydroxyethyl)oxirane-2-carboxylate ***2a***/***3a***. (Yield=167 mg, 99%) (ratio of diastereomers 67/33). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (1H, q, J=6.6 Hz) (minor), 4.16 (1H, q, J=6.4 Hz) (major), 3.71 (3H, s), 3.10 (1H, d, J=5.9 Hz) (major), 4.64 (1H, d, J=6.1 Hz) (minor), 2.99 (1H, d, J=6.0 Hz) (minor), 2.96 (1H, d, J=5.8 Hz) (major), 2.08 (1H, br s), 1.31 (3H, d, J=6.4 Hz) (major), 1.29 (3H, d, J=6.6 Hz) (minor). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0 (minor), 169.9 (major), 65.1 (major), 64.9 (minor), 59.6 (minor), 59.0 (major), 52.5 (major), 52.4 (minor), 49.3 (minor), 49.2 (major), 18.6 (minor), 18.2 (major) ppm. IR (KBr) δ 3932, 3839, 2984, 2363, 1738, 1519, 1382, 1285, 1173, 1095, 971, 913, 853 cm^{-1}. HRMS m/z calcd for $C_6H_{10}O_4Na$ [M+Na$^+$]: 169.0477, found: 169.0478.

4.3.2. Methyl 2-(1-hydroxypropyl)oxirane-2-carboxylate ***2b***/***3b***. (Yield=128 mg, 70%) (ratio of diastereomers 76/24). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (1H, m), 3.71 (3H, s), 3.12 (1H, d, J=6.0 Hz), 2.98 (1H, d, J=6.0 Hz), 2.55 (1H, br s), 1.72 (1H, m), 1.48 (1H, m), 0.98 (3H, t, J=6.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 71.0, 50.1, 52.5, 49.6, 26.0, 9.9 ppm. IR (KBr) δ 3770, 3457, 2939, 2360, 1869, 1637, 1541, 1440, 1348, 1197, 1139, 1055, 950, 758 cm^{-1}. HRMS m/z calcd for $C_7H_{12}O_4Na$ [M+Na$^+$]: 183.0633, found: 183.0636 (Yield **2c**/**3c**=99%).

4.3.3. syn-Methyl 2-(1-hydroxybutyl)oxirane-2-carboxylate ***2c***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84–3.87 (1H, m), 3.78 (3H, s), 3.12 (1H, d, J=5.9 Hz), 2.98 (1H, d, J=5.9 Hz), 1.69–1.40 (4H, m), 0.94 (3H, t, J=7.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 69.3, 58.3, 52.4, 49.6, 35.0, 18.7, 13.8 ppm. IR (KBr) δ 3649, 2960, 2361, 1740, 1560, 1457, 1382, 1197, 1139, 1077, 983, 760 cm^{-1}. HRMS m/z calcd for $C_8H_{14}O_4Na$ [M+Na$^+$]: 197.0790, found: 197.0786.

4.3.4. anti-Methyl 2-(1-hydroxybutyl)oxirane-2-carboxylate ***3c***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12–4.10 (1H, m), 3.78 (3H, s), 3.08 (1H, d, J=6.0 Hz), 2.98 (1H, d, J=6.0 Hz), 1.77 (1H, br s), 1.61–1.37 (4H, m), 0.94 (3H, t, J=7.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 69.0, 59.4, 52.5, 49.3, 35.1, 18.9, 13.7 ppm. IR (KBr) δ 3466, 2960, 1739, 1639, 1567, 1441, 1356, 1287, 1212, 1197, 1138, 1129, 1036, 982, 957 cm^{-1} (Yield **2d**/**3d**=71%).

4.3.5. syn-Methyl 2-(1-hydroxy-3-methylbutyl)oxirane-2-carboxylate ***2d***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (1H, dd, J=3.8, 9.2 Hz), 3.78 (3H, s), 3.12 (1H, d, J=5.9 Hz), 2.98 (1H, d, J=5.9 Hz), 1.93–1.86 (1H, m), 1.41–1.51 (2H, m), 0.95 (6H, t, J=6.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 68.0, 58.5, 52.5, 49.6, 41.8, 24.4, 23.5, 21.4 ppm. IR (KBr) δ 3743, 2956, 2361, 1738, 1438, 1368, 1171, 1116, 1078, 994, 919, 864, 758 cm^{-1}. HRMS m/z calcd for $C_9H_{16}O_4Na$ [M+Na$^+$]: 211.0946, found: 211.0942.

4.3.6. anti-Methyl 2-(1-hydroxy-3-methylbutyl)oxirane-2-carboxylate ***3d***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20 (1H, dd, J=3.8, 9.2 Hz), 3.77 (3H, s), 3.09 (1H, d, J=5.9 Hz), 2.98 (1H, d, J=5.9 Hz), 2.06–1.96 (1H, br s), 1.76–1.82 (1H, m), 1.48–1.51 (1H, m), 1.27–1.35 (1H, m), 0.95 (6H, t, J=6.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 67.5, 59.6, 52.5, 49.3, 42.0, 24.4, 23.5, 21.3 ppm. IR (KBr) δ 3491, 2957, 2393, 1738, 1440, 1368, 1184, 1115, 1094, 993, 919, 879 cm^{-1}.

4.3.7. syn-Methyl 2-(cyclohexyl(hydroxy)methyl)oxirane-2-carboxylate ***2e***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (3H, s), 3.39 (1H, d, J=6.7 Hz), 3.11 (1H, d, J=5.9 Hz), 2.96 (1H, d, J=5.9 Hz), 2.12 (1H, br s), 1.88 (1H, m), 1.75–1.63 (5H, m), 1.26–1.03 (5H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 75.1, 57.3, 52.4, 49.7, 41.2, 29.3, 28.2, 26.2, 26.0, 25.8 ppm. IR (KBr) δ 3799, 2930, 2669, 2342, 1741, 1377, 1306, 1200, 1124, 1087, 1030, 932, 761 cm^{-1}. HRMS m/z calcd for $C_{11}H_{18}O_4Na$ [M+Na$^+$]: 237.1103, found: 237.1105.

4.3.8. anti-Methyl 2-(cyclohexyl(hydroxy)methyl)oxirane-2-carboxylate ***3e***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.77 (3H, s), 3.69 (1H, d, J=6.5 Hz), 3.02 (1H, d, J=5.9 Hz), 2.97 (1H, d, J=5.9 Hz), 1.94 (1H, m), 1.78–1.64 (5H, m), 1.30–0.94 (5H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 74.5, 65.7, 58.7, 52.5, 49.6, 41.5, 29.6, 28.2, 26.1, 25.8, 15.1 ppm. IR (KBr) δ 3752, 2936, 2668, 2341, 1740, 1422, 1232, 1153, 1104, 1069, 1052, 974, 957 cm^{-1}.

4.3.9. syn-Methyl 2-(1-hydroxy-3-phenylpropyl)oxirane-2-carboxylate ***2f***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.20 (5H, m), 3.95 (1H, m), 3.77 (3H, s), 3.12 (1H, d, J=6.0 Hz), 2.95 (1H, d, J=6.0 Hz), 2.93–2.88 (1H, m), 2.77–2.65 (1H, m), 2.20–2.01 (1H, m), 1.82–1.93 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 141.5, 128.4, 126.1, 68.9, 58.3, 52.6, 49.3, 34.8, 31.7 ppm. IR (KBr) δ 3873, 3063, 3003, 2924, 2364, 1748, 1290, 1240, 1132, 1075, 754, 701 cm^{-1}.

4.3.10. anti-Methyl 2-(1-hydroxy-3-phenylpropyl)oxirane-2-carboxylate ***3f***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.17 (5H, m),

4.11 (1H, d, J=9.3 Hz), 3.76 (3H, s), 3.05 (1H, d, J=6.0 Hz), 3.00 (1H, d, J=6.0 Hz), 2.93–2.87 (1H, m), 2.75–2.69 (1H, m), 1.99–1.93 (1H, m), 1.89–1.82 (1H, m), 1.54 (1H, br s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 141.3, 128.4, 126.0, 68.9, 59.1, 52.3, 49.3, 34.5, 31.8 ppm.

4.3.11. (E)-Methyl 2-(1-hydroxy-3-phenylallyl)oxirane-2-carboxylate ***2g/3g***. (Yield=103 mg, 47%) (ratio of diastereomers 53/47). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.24 (m, 5H), 6.74 (1H, d, J=16.0 Hz) (major and minor), 6.27 (1H, dd, J=6.3, 12.0 Hz) (major), 6.23 (1H, dd, J=5.8, 13.2 Hz) (minor), 4.85 (1H, dd, J=6.3, 1.3 Hz) (minor), 4.71 (1H, dd, J=6.5, 1.2 Hz) (major), 3.80 (3H, s) (major), 3.79 (3H, s) (minor), 3.15 (1H, d, J=5.9 Hz) (major), 3.13 (1H, d, J=6.1 Hz) (minor), 3.06 (1H, d, J=6.1 Hz) (minor), 3.00 (1H, d, J=5.9 Hz) (major). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8 (minor), 169.7 (major), 136.2 (minor), 136.1 (major), 133.5 (major), 133.1 (minor), 128.6, 128.1, 128.0, 126.7 (major and minor), 125.9 (minor), 125.6 (major), 70.7 (major), 70.0 (minor), 59.0 (minor), 58.5 (major), 52.7, 52.6 (major and minor), 49.9 (major), 49.2 (minor) ppm. HRMS m/z calcd for $C_{13}H_{14}O_4Na$ [M+Na$^+$]: 257.0790, found: 257.0792.

4.3.12. syn-Methyl 2-(hydroxy(phenyl)methyl)oxirane-2-carboxylate ***2h***.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.30 (5H, m), 5.18 (1H, s), 3.73 (3H, s), 3.12 (1H, d, J=5.9 Hz), 2.86 (1H, d, J=5.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 138.4, 128.4, 127.0, 71.7, 59.0, 52.6, 49.7 ppm. IR (KBr) δ 3487, 3064, 2910, 2359, 1739, 1269, 1160, 1082, 1027, 947, 757 cm^{-1}. HRMS m/z calcd for $C_{11}H_{12}O_4Na$ [M+Na$^+$]: 231.0633, found: 231.0632.

4.3.13. syn-Methyl 2-(hydroxy(p-tolyl)methyl)oxirane-2-carboxylate ***2i***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (2H, d, J=8.0 Hz), 7.26 (2H, d, J=8.0 Hz), 5.15 (1H, s), 3.72 (3H, s), 3.11 (1H, d, J=5.9 Hz), 2.86 (1H, d, J=5.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 137.9, 135.5, 128.9, 127.0, 71.4, 59.1, 52.6, 49.6, 21.1 ppm. IR (KBr) δ 3502, 3005, 2923, 1743, 1197, 1125, 1020, 943, 837, 765, 686 cm^{-1}. HRMS m/z calcd for $C_{12}H_{14}O_4Na$ [M+Na$^+$]: 245.0790, found: 245.0787.

4.3.14. syn-Methyl 2-(hydroxy(4-methoxyphenyl)methyl)oxirane-2-carboxylate ***2j***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (2H, d, J=8.8 Hz), 6.87 (2H, d, J=8.8 Hz), 5.16 (1H, s), 3.79 (3H, s), 3.67 (3H, s), 3.12 (1H, d, J=6.0 Hz), 2.85 (1H, d, J=6.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 159.5, 130.4, 128.5, 113.8, 71.2, 59.1, 55.2, 52.6, 49.5 ppm. IR (KBr) δ 3493, 3003, 2910, 1742, 1197, 1124, 1031, 978, 917, 836, 756 cm^{-1}. HRMS m/z calcd for $C_{12}H_{14}O_5Na$ [M+Na$^+$]: 261.0739, found: 261.0738.

4.3.15. syn-Methyl 2-((4-fluorophenyl)(hydroxy)methyl)oxirane-2-carboxylate ***2k***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (2H, dd, J=8.5, 5.5 Hz), 7.03 (2H, t, J=8.7 Hz), 5.15 (1H, s), 3.73 (3H, s), 3.13 (1H, d, J=6.0 Hz), 2.85 (1H, d, J=6.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 162.2 (d, J=245 Hz), 134.2, 129.0 (dd, J=7.2, 21.3 Hz), 115.2 (dd, J=12.5, 22.5 Hz), 71.1, 65.8, 52.7, 49.6 ppm. IR (KBr) δ 3477, 3070, 2958, 2342, 1737, 1509, 1398, 1271, 1197, 1128, 1045, 980, 842, 756 cm^{-1}. HRMS m/z calcd for $C_{11}H_{11}FO_4Na$ [M+Na$^+$]: 249.0539, found: 249.0535.

4.3.16. syn-Methyl 2-((4-chlorophenyl)(hydroxy)methyl)oxirane-2-carboxylate ***2l***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (2H, d, J=8.0 Hz), 7.32 (2H, d, J=8.0 Hz), 5.29 (1H, s), 3.73 (3H, s), 3.14 (1H, d, J=6.0 Hz), 2.88 (1H, d, J=6.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 137.0, 134.1, 128.6, 128.5, 71.2, 58.7, 52.7, 49.7 ppm. IR (KBr) δ 3518, 3001, 2929, 1723, 1411, 1287, 1160, 1107, 1049, 982, 920, 756 cm^{-1}. HRMS m/z calcd for $C_{11}H_{11}ClO_4Na$ [M+Na$^+$]: 265.0244, found: 265.0245.

4.3.17. syn-Methyl 2-((3-chlorophenyl)(hydroxy)methyl)oxirane-2-carboxylate ***2m***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (1H, s), 7.32 (3H, m), 5.10 (1H, s), 3.73 (3H, s), 3.16 (1H, d, J=6.0 Hz), 2.90 (1H, d, J=6.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 140.6, 134.3, 129.6, 128.4, 127.1, 125.3, 71.3, 58.7, 52.8, 49.8 ppm. IR (KBr) δ 3466, 3020, 2964, 1736, 1463, 1264, 1154, 1170, 1083, 962, 918, 877 cm^{-1}.

4.3.18. syn-Methyl 2-((2-chlorophenyl)(hydroxy)methyl)oxirane-2-carboxylate ***2n***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (1H, m), 7.33 (1H, m), 7.24–7.29 (2H, m), 6.04 (1H, s), 3.82 (3H, s), 3.06 (1H, d, J=6.0 Hz), 2.35 (1H, d, J=6.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 135.0, 132.9, 129.5, 127.9, 126.9, 67.9, 58.6, 52.9, 50.5 ppm. IR (KBr) δ 3741, 3019, 2938, 1734, 1472, 1390, 1297, 1195, 1064, 1028, 1028, 758, 741 cm^{-1}.

4.3.19. syn-Methyl 2-((4-bromophenyl)(hydroxy)methyl)oxirane-2-carboxylate ***2o***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (2H, d, J=8.0 Hz), 7.32 (2H, d, J=8.0 Hz), 5.29 (1H, s), 3.73 (3H, s), 3.14 (1H, d, J=6.0 Hz), 2.88 (1H, d, J=6.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 137.5, 131.5, 129.0, 122.2, 71.2, 58.7, 52.7, 48.9 ppm. IR (KBr) δ 3711, 3077, 2957, 2360, 1923, 1592, 1728, 1460, 1333, 1286, 1196, 1127, 1049, 935, 755 cm^{-1}. HRMS m/z calcd for $C_{11}H_{11}BrO_4Na$ [M+Na$^+$]: 308.9738, found: 308.9735.

4.3.20. syn-Methyl 2-((2-nitrophenyl)(hydroxy)methyl)oxirane-2-carboxylate ***2p***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (1H, dd, J=8.2, 1.3 Hz), 7.79 (1H, dd, J=7.9, 1.3 Hz), 7.65 (1H, td, J=7.7, 1.3 Hz), 7.48 (1H, td, J=8.5, 1.4 Hz), 6.17 (1H, s), 3.82 (3H, s), 3.13 (1H, d, J=6.0 Hz), 2.37 (1H, d, J=6.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 148.3, 133.3, 129.8, 129.1, 124.6, 66.8, 58.1, 53.1, 51.0 ppm. IR (KBr) δ 3648, 3093, 2957, 1725, 1440, 1357, 1267, 1200, 1156, 1053, 947, 747 cm^{-1}.

4.3.21. syn-Methyl 2-((3-nitrophenyl)(hydroxy)methyl)oxirane-2-carboxylate ***2q***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (1H, m), 8.17 (1H, ddd, J=8.2, 2.3, 1.2 Hz), 7.81 (1H, m), 7.52 (1H, t, J=7.92 Hz), 5.19 (1H, s), 3.74 (3H, s), 3.22 (1H, d, J=6.0 Hz), 2.95 (1H, d, J=6.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 148.2, 133.3, 129.2, 123.2, 122.1, 71.0, 65.7, 52.8, 49.7 ppm. IR (KBr) δ 3712, 3092, 3006, 2957, 2876, 1735, 1441, 1353, 1289, 1163, 1096, 976, 935, 866, 758 cm^{-1}.

4.3.22. syn-Methyl 2-((4-nitrophenyl)(hydroxy)methyl)oxirane-2-carboxylate ***2r***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (2H, d, J=8.0 Hz), 7.65 (2H, d, J=8.0 Hz), 5.13 (1H, s), 3.73 (3H, s), 3.48 (1H, d, J=6.0 Hz), 2.94 (1H, d, J=6.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 146.0, 128.1, 127.8, 123.4, 71.4, 58.4, 53.0, 49.9 ppm. IR (KBr) δ 3902, 3087, 2958, 2342, 1925, 1715, 1517, 1442, 1221, 1096, 1053, 946, 777 cm^{-1}. HRMS m/z calcd for $C_{11}H_{11}NO_6Na$ [M+Na$^+$]: 276.0484, found: 276.0482.

4.3.23. syn-Methyl 2-(furan-2-yl(hydroxy)methyl)oxirane-2-carboxylate ***2s***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (1H, s), 7.26 (1H, s), 6.39 (1H, m), 6.33 (1H, m), 5.29 (1H, s), 3.75 (3H, s), 3.23 (1H, d, J=6.0 Hz), 3.05 (1H, d, J=6.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 125.6, 142.5, 110.4, 107.7, 64.5, 52.6, 49.0 ppm. IR (KBr) δ 3932, 3153, 3004, 2957, 1734, 1633, 1359, 1231, 1048, 975, 753 cm^{-1}.

4.4. General experimental procedure for the preparation of cyclic carbonates

An ice-bath cold suspension of sodium hydride (60% in mineral oil) (1.12 mmol) in THF (1 mL) was treated with thiophenol (2.25 mmol). The mixture was stirred at rt for 15 min and then a solution of the epoxyester 2 (0.75 mmol) in THF (1 mL) was added drop wise and the mixture was stirred at rt for 1.5 h. Then was treated with pyridine (0.22 mmol) and triphosgene (0.48 mmol). The mixture was refluxed for 15 h. Then brine was added and extracted with Et_2O (3×20 mL), the organic layers were washed

(brine), dried (Na_2SO_4), and concentrated. The crude oil was purified through chromatography (silica-gel, hexanes/EtOAc (8:2) and (7:3)).

4.4.1. syn-Methyl 5-isobutyl-2-oxo-4-((phenylthio)methyl)-1,3-dioxolane-4-carboxylate ***4***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (2H, m), 7.25–7.33 (3H, m), 4.73 (1H, m), 3.81 (3H, s), 3.58 (1H, d, J=15.0 Hz), 3.47 (1H, d, J=15.0 Hz), 1.77 (1H, m), 1.44 (1H, m), 1.35 (1H, m), 0.92 (3H, d, J=6.5 Hz), 0.84 (3H, d, J=6.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 152.7, 134.7, 131.3, 129.3, 127.7, 86.6, 80.4, 53.2, 39.6, 38.6, 25.1, 23.0, 21.2 ppm. IR (KBr) δ 3059, 2959, 1811, 1743, 1626, 1540, 1470, 1387, 1306, 1200, 1116, 1025, 968, 746 cm^{-1}. HRMS m/z calcd for $C_{16}H_{20}O_5SNa$ [M+Na$^+$]: 347.0929, found: 347.0929.

4.4.2. anti-Methyl 5-isobutyl-2-oxo-4-((phenylthio)methyl)-1,3-dioxolane-4-carboxylate ***5***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (2H, m), 7.25–7.33 (3H, m), 4.76 (1H, m), 3.70 (3H, s), 3.42 (2H, s), 1.71 (1H, m), 1.49 (1H, m), 1.47 (1H, m), 0.98 (3H, d, J=6.5 Hz), 0.95 (3H, d, J=6.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 152.2, 134.4, 131.9, 129.2, 127.8, 85.6, 80.4, 53.4, 37.9, 37.5, 24.9, 23.2, 21.2 ppm. IR (KBr) δ 3059, 2959, 1806, 1749, 1582, 1439, 1360, 1257, 1132, 1048, 963, 744 cm^{-1}.

4.4.3. syn-Methyl 5-cyclohexyl-2-oxo-4-((phenylthio)methyl)-1,3-dioxolane-4-carboxylate ***6***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (2H, m), 7.25–7.17 (3H, m), 4.37 (1H, m), 3.73 (3H, s), 3.57 (1H, d, J=15.0 Hz), 3.35 (1H, d, J=15.0 Hz), 1.80 (1H, m), 1.40–1.77 (5H, m), 1.24–0.79 (5H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 152.4, 134.8, 131.9, 129.2, 127.8, 86.0, 85.7, 53.5, 37.7, 37.3, 29.5, 28.1, 25.7, 25.4, 25.1 ppm. IR (KBr) δ 3060, 2929, 2857, 1741, 1582, 1402, 1195, 1024, 927, 845, 713, 629 cm^{-1}. HRMS m/z calcd for $C_{18}H_{22}O_5SNa$ [M+Na$^+$]: 373.1086, found: 373.1089.

4.4.4. anti-Methyl 5-cyclohexyl-2-oxo-4-((phenylthio)methyl)-1,3-dioxolane-4-carboxylate ***7***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (2H, m), 7.24–7.33 (3H, m), 4.43 (1H, m), 3.76 (3H, s), 3.56 (1H, d, J=15.0 Hz), 3.48 (1H, d, J=15.0 Hz), 1.77 (1H, m), 1.68–1.76 (5H, m), 1.10–1.25 (5H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 152.6, 134.7, 131.7, 129.2, 127.7, 86.6, 85.8, 53.3, 40.8, 38.6, 28.6, 28.5, 25.7, 25.2, 25.0 ppm. IR (KBr) δ 2934, 2854, 1747, 1584, 1584, 1440, 1178, 1052, 930, 634 cm^{-1}.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.11.014.

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