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Asymmetric synthesis of chiral α-keto esters via Grignard addition to oxalates

David I. MaGee,* Tammy C. Mallais and Marijanna Eic

Department of Chemistry, PO Box 45222, University of New Brunswick, Fredericton, N.B., E3B 6E2, Canada

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Abstract—While enroute to an asymmetric synthesis of the chlorine containing metabolite (−)-cryptosporiopsin an efficient and reliable asymmetric synthesis of chiral α-keto esters was required. These compounds can be conveniently generated in 51–84% yields via Grignard addition to either symmetrical or mixed oxalates at −40°C in tetrahydrofuran. The reaction works equally well with aliphatic or aromatic Grignard reagents.

1. Introduction

While involved in a synthetic program targeted at the chlorine fungal metabolite (−)-cryptosporiopsin[1] **1** we required a short and efficient synthesis of a variety of chiral α-keto-esters derivatives such as **2**, Fig. 1. There are numerous literature reports that describe the synthesis of α-keto esters.[2] These compounds have attracted attention as synthetic targets due to the fact that their functionality is present in many natural products and that they play an important role in biological processes.[3] Common methods of synthesis include oxidation of α-hydroxy esters with either PCC or Dess–Martin periodinane,[4] hydrolysis and esterification of acyl cyanides,[5] oxidative cleavage of cyano ketophosphoranes,[6] the reaction of organometallic species with oxalic ester derivatives,[7] and acylation or alkylation of mono-substituted 1,3-dithianes.[8] Surprisingly most of these procedures have only been used to construct simple α-keto-esters, for instance methyl or ethyl esters. In fact, we could only find a single report where an α-keto-ester bearing a chiral ester functionality was generated.[9]

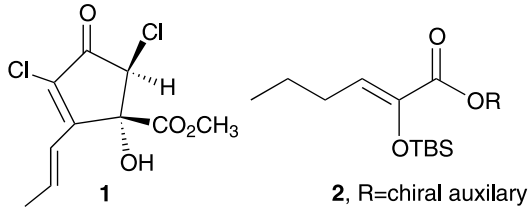

Figure 1. (−)-Cryptosporiopsin **1** and the requisite chiral enol-ester required for its synthesis.

Unsure which route would prove most useful for our purposes we pursued several different avenues. The oxidation of a variety of caproic acid ester enolates with camphorsulfonyl oxaziridine or dimethyl dioxirane proved capricious since the yields of product ranged from 29–73% depending upon which ester was used. Using the Corey procedure proved equally frustrating. Starting with 2-butyl-1,3-dithiane and acylating the anion with CO_2 proceeded uneventfully, however, attempts to generate the ester under a variety of conditions met with little success, yields in the order of 25–38% being normal. Reversing the steps, namely acylating first and then alkylating the anion proved equally unsuccessful. Granted moderate success was realized in some instances, however, to carry out the research we planned it was necessary to have a short and general synthesis since we were going to have to screen a number of α-keto-esters possessing a chiral alcohol auxiliary. Consequently it was decided to explore the utility of the most direct route, namely Grignard addition to an oxalate.

* Corresponding author. Tel.: 506-453-4870; fax: 506-453-4981; e-mail: dmagee@unb.ca

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2. Results and discussion

The initial foray into this line of research began with menthol as the chiral auxiliary. To this end, menthol, **3**, was reacted with oxalyl chloride, **4**, in the presence of pyridine to give dimenthyl oxalate **5** in 43% yield, Scheme 1. Following a literature protocol,[10] one equivalent of Grignard reagent was added slowly over one hour to oxalate **5** while the temperature was kept at 0°C. This resulted in the isolation of the desired α-keto ester **6** in 15% yield. The yield was improved to 56% by increasing the amount of Grignard reagent to 1.5 equivalents and using a faster addition time of 45 min. Although yields as high of 56% could be obtained the results were inconsistent and in many runs extremely low yields were obtained. There was precedent for encountering difficulties using this route.[11]

The need therefore became to improve the Grignard reaction between chiral oxalates and alkyl Grignard reagents. Recently, Rambaud[7] and Singh[12] independently demonstrated that alkyl Grignard reagents could be efficiently added to diethyl oxalate when the temperature was maintained at −80°C and one equivalent of Grignard reagent was used. They found that control of the stoichiometry (1:1) of the reactants along with low temperatures were the key to success in this reaction. With this in mind, subjecting symmetrical dimenthyl oxalate **5** with commercial *n*-butyl magnesium chloride under these conditions for several hours led to no reaction! Given the previous results at 0°C it became evident that temperature was having a profound effect on the outcome of this reaction. Consequently a study was initiated to delineate what temperature would give rise to the highest yields. The results of this study are shown in Table 1 and it is easily seen that this Grignard reaction is very sensitive to the reaction conditions. However, with appropriate attention to detail an excellent and reproducible yield could be achieved if the reaction was run at −40°C, external bath temperature, in the presence of 1.5 equivalents of Grignard reagent.

Confident that optimum conditions were now defined, a series of α-keto-esters was synthesized (Scheme 1). These are shown in Table 2. Most notable from the results is the generality of the reaction and the consistent yields obtained, both with aliphatic and aromatic Grignard reagents. In some instances it was difficult to achieve complete separation of the product from starting oxalate; in such cases treatment of the crude reaction mixture with TMSCl or TBSCl and DBU in refluxing THF provided the silyl-enol ether esters which could be conveniently separated from other by-products. Simple hydrolysis (TBAF, HF/Py or 1 M HCl) then regenerated the requisite α-keto esters.

Given the success of this approach, it seemed appropriate to investigate whether this reaction could be conducted without releasing one equivalent of the chiral alcohol along with the desired α-keto ester product. Although this is not a concern when using commercially available alcohols as auxiliaries it becomes problematic when more precious alcohols have to be retrieved. Recently Flynn and Beight[9] reported the addition of phenylethyl magnesium bromide to a mixed oxalate, therefore there was optimism that this would prove equally viable in our study.

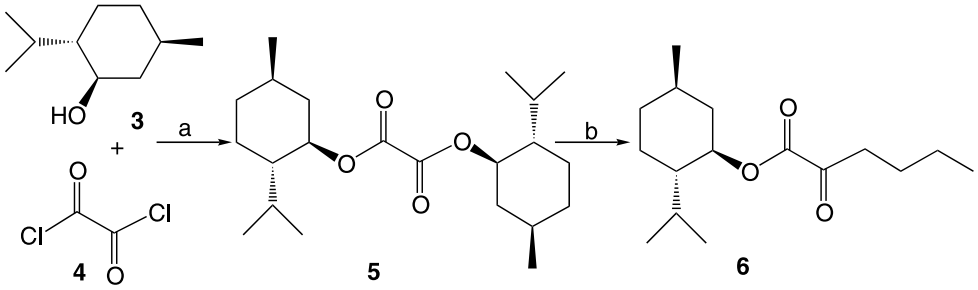
To initiate this, the requisite mixed oxalates were synthesized following Flynn and Bleight's protocol.[9] Subjection of each mixed oxalate to our standard conditions generated the expected α-keto-esters in moderate to good yields, Table 2. It is evident from comparison of the two routes that use of unsymmetrical oxalates generally produces α-keto esters with slightly inferior yields. This is primarily due to the fact that Grignard addition is not completely regioselective and that some methyl 2-oxo-hexanoate is produced. Attempts to completely suppress this side reaction by varying the conditions, including temperature, failed.

3. Conclusion

We have shown that Grignard addition to symmetrical and mixed oxalates bearing chiral alcohol auxiliaries is a quick and efficient method to synthesize α-keto esters in good to excellent yields. It is crucial that the temper-

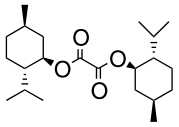
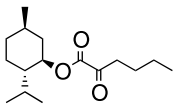
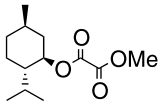
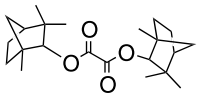
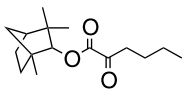
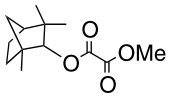
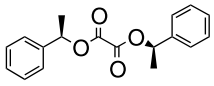
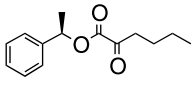
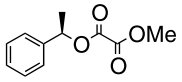
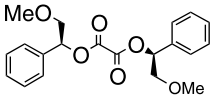
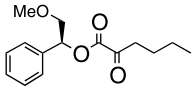
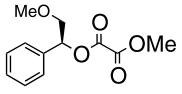
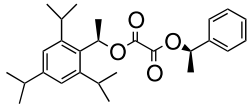
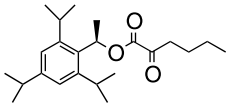
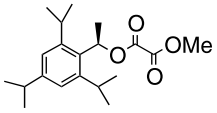
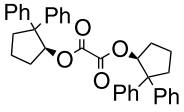
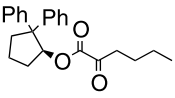
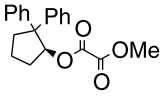
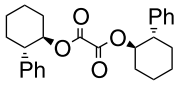
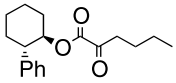
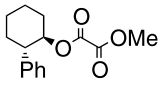
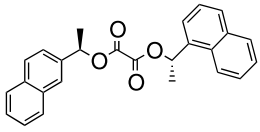
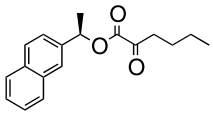
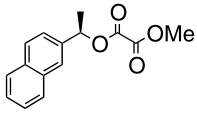
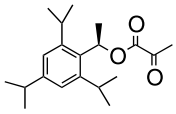
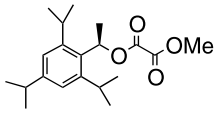
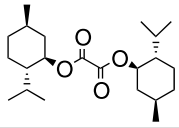
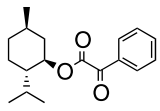
Table 1. Temperature studies on *n*-butyl Grignard addition to dimenthyl oxalate

Temp (°C)	Yield (%) of **6** or ratio **6**:**5**
0	2.1:1
−20	2.4:1
−40	73
−60	NR



Scheme 1. *Reagents and conditions*: (a) CH_2Cl_2, pyridine, DMAP, rt; (b) THF, *n*-BuMgCl, −40°C.

Table 2. Synthesis of chiral α-keto esters via Grignard addition to symmetrical and mixed oxalates, (a) isolated as the TBS-enol ether ester

Entry	Symmetrical Oxalate	α-Keto ester	Yield symm. mixed	Mixed Oxalate
1			83 72	
2			71 62	
3			62[a] 55[a]	
4			63 51	
5			84 79	
6			78 70	
7			78 72	
8			83 75	
9			-- 76	
10			85 --	

ature be controlled or else spurious results will be obtained. The use of this chemistry for the synthesis of the fungal metabolite (−)-cryptosporiopsin **1** is currently being pursued and will be communicated in due course.

4. General experimental procedures

All reactions except those stated otherwise were performed under inert atmospheres of either argon or nitrogen in flame dried glassware (pyrex). Solvents, such as ether, tetrahydrofuran, xylenes, benzene and toluene, were distilled over sodium, using benzophenone as an indicator, prior to use. Other solvents such as dichloromethane, triethylamine and acetonitrile were used freshly distilled from calcium hydride. Standard techniques were used in handling air sensitive reagents. All commercially available reagents and solvents were purchased either from Aldrich, Fluka or Fisher and used without further purification. 2-methoxy-1-phenylethanol,[13] 1-(2,4,6-triisopropylphenyl)ethanol,[14] 2,2-diphenylcyclopentanol[15] and *trans*-2-phenyl-1-cyclohexanol[16] were synthesized according to literature procedures. All preparative SiO_2 (flash) chromatography was done using Silicycle Ultra Pure Silica Gel for

chromatography. All ^{1}H and ^{13}C NMR spectra were recorded on a Varian UNITY 400 MHz spectrometer. Optical rotations were performed on a Perkin–Elmer 241 Polarimeter using the Na lamp. All IR spectra were done on a Bruker IFS 25 instrument and mass spectra were run on a Kratos MS50 instrument.

4.1. General procedure for the preparation of symmetrical oxalates

A solution of alcohol (20 mmol), pyridine (1.62 mL, 20 mmol) and DMAP (24 mg, 2 mmol) in dichloromethane (100 mL) was allowed to stir at rt for 5 min then cooled in an ice bath. Oxalyl chloride (0.88 g, 10 mmol) was then added dropwise over 5 min, the ice bath was removed and the mixture was stirred at rt overnight. It was then diluted with ether (200 mL), washed with aq. HCl (10%, 2×), H_2O (1×), brine (1×), dried over $MgSO_4$ and the solvent removed in vacuo. The residue was purified by SiO_2 chromatography (hexanes:ethyl acetate) to provide the pure oxalates.

4.2. General procedure for mixed oxalate formation

Methyl chlorooxoacetate (0.20 mL, 2.2 mmol) and dichloromethane (15 mL) were cooled in an ice bath and then the alcohol (1.9 mmol) in dichloromethane (5 mL) was added followed immediately by pyridine (0.24 mL, 3.0 mmol). The reaction mixture was allowed to warm to rt and stir for 1 h. When complete, the solution was diluted with ether, washed with 10% HCl (2×), H_2O (1×), brine (1×), dried over $MgSO_4$ and solvent evaporated. The crude product was purified by SiO_2 chromatography (hexanes: ethyl acetate) to yield the mixed oxalate.

4.3. General procedure for the preparation of α-keto ester via Grignard reaction

Oxalate (0.15 mmol) in THF was cooled to −40°C, then *n*-butyl magnesium chloride (0.11 mL, 0.22 mmol) was added dropwise over 1 h 20 min [in two examples phenyl magnesium bromide and methyl magnesium bromide were used in place of the butyl Grignard reagent]. After complete addition the reaction mixture was stirred for 2 h at the same temperature and then diluted with ether, washed with cold HCl (5%, 2×), brine (1×), dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by SiO_2 chromatography (hexane:ethyl acetate) to provide the α-keto esters.

4.4. (*R*)-1-Phenylethyl Z-*tert*.butyldimethylsilyloxy-2-hexenoate

Colourless liquid. ^{1}H NMR ($CDCl_3$): δ 0.09 (s, 3H), 0.13 (s, 3H), 0.95 (t, $J=7.5$ Hz, 3H), 0.95 (s, 9H), 1.43 (sextet, $J=7.5$ Hz, 2H), 1.58 (d, $J=5.0$ Hz, 3H), 2.17 (dq, $J=0.9$, 7.2 Hz, 2H), 5.94 (q, $J=6.3$ Hz, 1H), 6.08 (t, $J=7.5$ Hz, 1H), 7.25–7.4 (m, 5H). ^{13}C NMR ($CDCl_3$): δ −3.98, −3.93, 14.3, 18.9, 22.4, 22.5, 26.2, 28.2, 73.2, 123.5, 126.5, 128.2, 128.8, 141.2, 141.9, 164.6. IR (NaCl plates, cm^{-1}): 2946, 2855, 1720, 1640, 1456, 1368, 1258, 1142, 834. MS: $m^=/z$-$C_{12}H_{18}$= 186.07171 (calculated = 186.07123), C_8H_9 (105.07053, calculated = 105.070425). $[\alpha]_D$ = +2.2 ($c=1.08$, CH_2Cl_2).

4.5. (1*R*,2*S*,5*R*)-Menthyl 2-oxo-hexanoate

Colourless liquid. ^{1}H NMR ($CDCl_3$): δ 0.77 (d, $J=7.0$ Hz, 3H), 0.87 (t+2d, 9H), 1.06 (septet, $J=12.1$ Hz, 3H), 1.36 (m, 2H), 1.50 (m, 2H), 1.66 (m, 1H), 1.73 (d of d, $J=3.25$, 6.15 Hz, 2H), 1.86 (m, 1H), 2.04 (d of pentet, $J=3.42$, 10.25 Hz, 1H), 2.81 (t of d, $J=1.54$, 7.18 Hz, 2H), 4.82 (t of d, $J=4.44$, 10.94 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 13.8, 16.2, 20.6, 21.9, 22.1, 23.3, 25.1, 26.2, 31.4, 34.0, 39.1, 40.4, 46.7, 76.7, 161.1, 195.2. IR (NaCl plates, cm^{-1}): 2932, 1750, 1726, 1455, 1250, 1125, 1054. MS: $m^=/z$ = 268.20382 (calculated = 268.203845). $[\alpha]_D$ = −64.6 ($c=2.34$, EtOH).

4.6. (1*R*)-Fenchyl 2-oxo-hexanoate

Colourless liquid. ^{1}H NMR ($CDCl_3$): δ 0.81 (s, 3H), 0.93 (t, $J=7.35$ Hz, 3H), 1.07 (s, 3H), 1.25 (dd, $J=1.54$, 10.43 Hz, 1H), 1.37 (m, 2H), 1.48 (m, 1H), 1.65 (m, 3H), 1.76 (m, 3H), 2.81 (td, $J=2.39$, 7.18 Hz, 2H), 4.48 ppm (d, $J=1.88$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 13.7, 19.3, 20.1, 22.1, 25.1, 25.7, 26.5, 29.6, 39.3, 39.7, 41.3, 48.2, 48.5, 88.5, 161.9, 194.8. IR (NaCl plates, cm^{-1}): 2936, 1750, 1728, 1464, 1280, 1244, 1120, 1054. MS: $m^=/z$ = 252.17249 (calculated = 252.172545). $[\alpha]_D$ = +33.8 ($c=0.34$, EtOH).

4.7. (*R*)-2-Methoxy-1-phenylethyl 2-oxohexanoate

Colourless liquid. ^{1}H NMR ($CDCl_3$): δ 0.91 (t, $J=7.2$ Hz, 3H), 1.35 (m, 2H), 1.61 (m, 2H), 2.83 (dt, $J=1.1$, 7.4 Hz, 2H), 3.40 (s, 3H), 3.62 (dt, $J=3.6$, 11.1 Hz, 1H), 3.83 (m, 1H), 6.06 (dd, $J=3.6$, 8.5 Hz, 1H), 7.33 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 13.8, 22.1, 25.0, 39.1, 59.2, 75.0, 76.5, 126.8, 128.7, 128.8, 136.1, 160.5, 194.3. IR (NaCl plates, cm^{-1}): 2936, 2874, 1750, 1726, 1456, 1120, 702. MS: $m^=/z$ = 264.136152 (calculated = 264.13617). $[\alpha]_D$ = −55.4 ($c=1.3$, EtOH).

4.8. (*S*)-1-(2-Naphthyl)ethyl 2-oxohexanoate

Colourless liquid. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, $J=7.3$ Hz, 3H), 1.32 (p, $J=7.5$ Hz, 2H), 1.59 (p, $J=7.9$ Hz, 2H), 1.72 (d, $J=6.5$ Hz, 3H), 2.80 (t, $J=7.4$ Hz, 2H), 6.14 (q, $J=6.6$ Hz, 1H), 7.47 (m, 3H), 7.83 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 13.8, 22.1, 25.1, 39.1, 60.5, 75.0, 123.9, 125.5, 126.4, 126.5, 127.8, 128.2, 128.7, 133.2, 133.3, 137.7, 160.8, 194.75. IR (NaCl plates, cm^{-1}): 3054, 2948, 2928, 2864, 1714, 1601, 1454, 1264, 1050, 814. MS: $m^=/z$ = 284.14124 (calculated = 284.141245). $[\alpha]_D$ = −39.3 ($c=1.37$, CH_2Cl_2).

4.9. (*S*)-2,2-Diphenyl-1-cyclopentyl 2-oxohexanoate

Colourless liquid. ^{1}H ($CDCl_3$): δ 0.81 (t, $J=7.4$ Hz, 3H), 1.16 (m, 2H), 1.34 (m, 2H), 1.58 (m, 1H), 1.89 (m, 3H), 2.26 (m, 3H), 2.52 (m, 3H), 2.66 (m, 1H), 6.22 (d, $J=5.5$ Hz, 1H), 7.20 (m, 10H). ^{13}C ($CDCl_3$): δ 13.6, 20.6, 22.0, 24.7, 30.7, 38.9, 59.8, 82.0, 126.1, 126.4,

126.5, 127.8, 128.1, 128.5, 144.4, 144.7, 160.5, 194.8. IR (NaCl plates, cm^{-1}): 2958, 1750, 1728, 1442, 1280, 1156, 696. MS: $m^+/z = 350.18813$ (calcd = 350.18820). $[\alpha]_D = +117.9$ ($c = 1.1$, EtOH).

4.10. (1*R*,2*S*)-*trans*-Phenylcyclohexyl 2-oxohexanoate

Colourless liquid. ^1H NMR ($CDCl_3$): δ 0.81 (t, $J = 7.2$ Hz, 3H), 1.18 (m, 2H), 1.34 (m, 3H), 1.57 (m, 3H), 1.81 (dd, $J = 2.6$, 12.6 Hz, 1H), 1.94 (m, 2H), 2.15 (dd, $J = 5.5$, 8.7 Hz, 1H), 2.43 (td, $J = 2.7$, 7.3 Hz, 2H), 2.77 (m, 1H), 5.08 (m, 1H), 7.19 (m, 3H), and 7.26 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.6, 22.0, 24.7, 24.8, 25.6, 31.9, 33.4, 39.0, 49.7, 78.6, 126.7, 127.6, 128.4, 142.3, 160.6, 195.1. IR (NaCl plates, cm^{-1}): 2936, 2854, 1750, 1728, 1450, 1274, 1046, 696. MS: $[m^+/z^- C_9H_9O_3] = 159.1187$ (calculated = 159.11737). $[\alpha]_D = -41.8$ ($c = 1.41$, EtOH).

4.11. (*R*)-1-(2,4,6-Triisopropylphenyl)ethyl 2-oxohexanoate

Colourless liquid. ^1H NMR ($CDCl_3$): δ 0.84 (t, $J = 7.2$ Hz, 3H), 1.18 (d, $J = 6.7$ Hz, 6H), 1.19 (d, $J = 6.8$ Hz, 6H), 1.25 (d, $J = 6.8$ Hz, 6H), 1.30 (p, $J = 7.7$ Hz, 2H), 1.51 (p, $J = 7.5$ Hz, 2H), 1.65 (d, $J = 6.8$ Hz, 3H), 2.79 (t, $J = 7.2$ Hz, 2H), 2.84 (heptet, $J = 7.0$ Hz, 1H), 3.49 (heptet, $J = 6.7$ Hz, 2H), 6.5 (q, $J = 6.8$ Hz, 1H), 7.02 (s, 2H). ^{13}C NMR (DMS0-d_6, 80°C): δ 13.8, 21.8, 22.2, 24.0, 24.1, 24.4, 24.9, 25.1, 29.2, 33.8, 38.6, 122.1, 131.6, 147.2, 148.5, 160.9, 194.8. IR (NaCl plates, cm^{-1}): 2950, 2905, 2876, 1726, 1608, 1466, 1382, 1276, 1240, 1050, 1002. MS: $m^+/z = 360.26645$ (calculated = 360.266495). $[\alpha]_D = -25.6$ ($c = 1.7$, CH_2Cl_2).

4.12. (*S*)-1-(2,4,6-Triisopropylphenyl)ethyl 2-oxoproanoate

White solid. Mp = 55–56.5°C. ^1H NMR ($CDCl_3$): δ 1.22 (d, $J = 6.9$ Hz, 6H), 1.24 (d, $J = 6.9$ Hz, 6H), 1.30 (d, $J = 6.9$ Hz, 6 H), 1.72 (d, $J = 7.2$ Hz, 3H), 2.43 (s, 3H), 2.86 (septet, $J = 6.9$ Hz, 1H), 2.52 (br, 2H), 6.60 (q, $J = 6.9$ Hz, 1H), 7.02 (bs, 2H). ^{13}C NMR (DMS0-d_6, 80°C): δ 21.3, 23.2, 23.23, 23.6, 24.1, 25.9, 28.0, 28.4, 32.9, 69.9, 121.3, 130.8, 146.3, 147.6, 159.5, 191.2. IR (NaCl plates, cm^{-1}): 2936, 2854, 1750, 1728, 1450, 1274, 1046, 696. MS: $m^+/z = 318.21948$ (calculated = 318.219495). $[\alpha]_D = +20.6$ ($c = 2.7$, CH_2Cl_2).

4.13. (1*R*,2*S*,5*R*)-Menthyl oxophenylacetate

Colourless oil. ^1H NMR ($CDCl_3$): δ 0.84 (d, $J = 7.0$ Hz, 3H), 0.90, (d, $J = 7.0$ Hz, 3H), 0.96 (d, $J = 6.5$ Hz, 3H), 1.03–1.27 (m, 5H), 1.46–1.62 (m, 3H), 1.64–1.80 (m, 3H), 1.83–2.01 (m, 1H), 2.19 (dt, $J =$ Hz, 1H), 5.01 (dt, $J = 4.5$, 10.9 Hz, 1H), 7.51 (t, $J = 8.2$ Hz, 2H), 7.66 (dt, $J = 1.2$, 7.5 Hz, 1H), 7.98 (dd, $J = 1.4$, 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 16.3, 20.8, 22.1, 23.4, 26.3, 31.7, 34.2, 40.7, 46.9, 77.1, 129.0, 130.0, 132.7, 134.9, 164.0, 186.9. IR (NaCl plates, cm^{-1}): 2958, 2912, 2664, 1738, 1678, 1596, 1454, 1300, 1204, 1170, 754. MS: $m^+/z^- C_{10}H_{19} = 149.02369$ (calculated = 149.023870), $C_{10}H_{19}$ (139.14824, calculated = 139.14868). $[\alpha]_D = -54.9$ ($c = 1.38$, CH_2Cl_2).

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