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Stereoselective electrochemical carboxylation: 2-phenylsuccinates from chiral cinnamic acid derivatives†

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Chiral 2-phenyl succinic ester derivatives have been obtained under mild conditions, in short times and with satisfactory yields by electrochemical reduction of chiral cinnamic acid derivatives under a CO_2 atmosphere. When 4*R*-(diphenylmethyl)-oxazolidin-2-one was used as a chiral auxiliary the two diastereoisomers could be easily separated by flash chromatography and the *R*-isomer was obtained as major product.

Introduction

Despite the efforts over previous decades to find efficient synthetic methodologies for the production of succinates, they remain target substances for many organic chemists. Succinates are useful compounds as synthetic intermediates, so it is important to study new approaches that enable them to be obtained in easy and suitable ways.

2-Arylsuccinates are key molecules in the synthesis of indan-1-carboxylic acids possessing anti-inflammatory activity,[2] they are precursors to anticonvulsant α-arylsuccinimides,[3] and, furthermore, 2-phenylsuccinic acids are antitumor agents.[4]

Several methods have been reported for the preparation of 2-arylsuccinates. They have been obtained by oxidative 1,2-aryl migration of 3-aroylpropionic acid,[5] by catalysed conjugated addition of aryl derivatives to α,β-unsaturated carbonyl compounds[6] and by palladium catalysed oxidative carbonylation of suitable olefins.[7] This latter methodology, which uses chiral palladium complexes, allows the enantioselective synthesis of chiral 2-arylsuccinates.[8]

Chiral 2-phenylsuccinates have also been obtained by asymmetric catalytic allylation and decarboxylation of malonates.[9]

Often these methodologies need hazardous or complex reagents, long reaction times and severe conditions.

The study of new methodologies for C–C, C–N and C–O bond formation lies at the heart of modern synthetic organic chemistry. In this context, particular attention has been dedicated to setting up ecocompatible processes, *i.e.*, synthetic processes carried out with high yields and selectivity, in short time, under mild and safe conditions and avoiding the use of toxic and dangerous chemicals as well as the formation of polluting by-products. Electrochemistry, which deals with a clean reagent, the electron, can fulfil these targets.

As regards the possible sources of carbon (such that these bonds can be formed) the employment of carbon dioxide, a cheap and abundant raw material, has been considered by several authors.[10] However, the thermodynamic stability and the relative kinetic inertness of CO_2 require its preliminary activation or, alternatively, the activation or modification of the substrates. The electrochemical activation of carbon dioxide, as well as the electrochemical modification of the substrates *via* simple procedures, has been proposed.

Carbon dioxide may be activated *via* monoelectronic cathodic reduction to $CO_2^{\bullet -}$.[11] Substrates containing a carbon–halogen bond or a double carbon–carbon bond may be activated *via* bielectronic cathodic cleavage of the carbon–halogen bond or *via* monoelectronic reduction of the double bond to the corresponding radical anion. The electrochemical reduction of the carbon–halogen bond[12] and of the activated double bond,[13] in the absence and in the presence of electrophilic substrates, have been extensively studied. Finally, molecules, containing a CH or NH group that is acidic enough, may be activated *vs.* electrophilic substrates by direct cathodic reduction or by deprotonation *via* electrogenerated bases.[14]

Recently, the diastereoselective electrochemical carboxylation of chiral α-bromocarboxylic acid derivatives was studied by us.[1] The cathodic cleavage of the carbon–halogen bond was achieved under galvanostatic control in CO_2-saturated aprotic solutions. At the end of the electrolysis, unsymmetrical alkylmalonic ester derivatives were isolated as main products.

Few electrochemical methods are reported for the synthesis of succinates. Mattiello *et al.*[15] obtained diethyl 2,3-bis-arylsuccinates by electrochemical reduction and subsequent dimerization of ethyl-α-bromoarylacetales (obtaining an excess of the racemic products *vs.* the meso ones).

2-Arylsuccinates have been prepared in good yields by electrochemical reduction of styrene in the presence of *N*-carboalkoxyimidazoles,[16] by electrochemical arylation of activated olefins[17] and by carboxylation of suitable substrates.

In the past, the cathodic reduction of some activated olefins (α,β-unsaturated esters, ketones, nitriles), carried out under potentiostatic control in CO_2-saturated DMF solutions, was studied by Savéant *et al.*[13b] The mechanism of the electrochemical carboxylation of the activated double bond was extensively discussed.

To our knowledge, however, no stereoselective electrochemical carboxylation of chiral cinnamic acid derivatives, to obtain chiral 2-phenyl succinates, has been reported. This prompted us to study the electrochemical behaviour of some chiral cinnamic acid derivatives in aprotic solvents in the absence and in the presence of carbon dioxide.

† Part 2 of a series; for part 1 see ref. 1.

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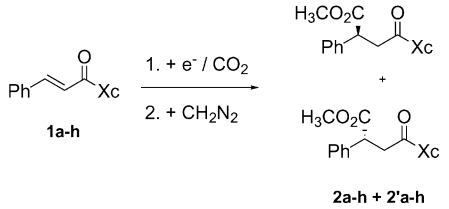
The aim of this study was the development of a possible electrochemical route to the stereoselective carboxylation of **1a**–**h** to chiral 2-phenylsuccinates **2a**–**h** (Scheme 1).

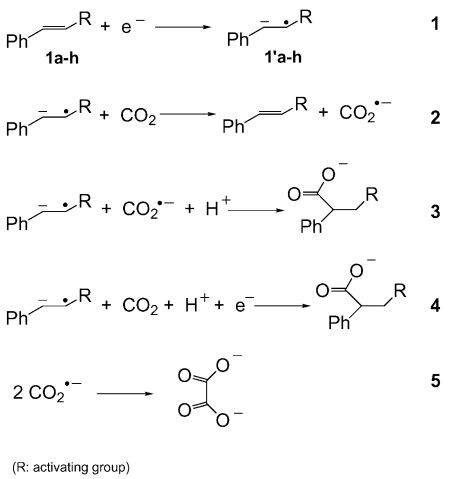


Scheme 1

Results and discussion

The voltammetric analysis of DMF solutions, containing the chiral cinnamic acid derivatives **1a**–**h** in the presence and in the absence of carbon dioxide, allows us to compare the electrochemical behaviour of **1a**–**h** with the one of the previously studied activated olefins.

The voltammetric curves of **1a**–**h** (DMF–(0.1 mol dm^{-3} Bu_4NBF_4), Pt cathode, $v = 0.2$ V s^{-1}) show a single irreversible and diffusion controlled reduction peak (in the range of −1.35 to −1.60 V *vs.* SCE), which is related to the monoelectronic reduction of the activated double bond and to the formation of the corresponding radical anions **1a**′–**h**′ (Scheme 2, reaction 1). In the presence of carbon dioxide, *i.e.*, in CO_2-saturated DMF–(0.1 mol dm^{-3} Bu_4NBF_4) solutions, the peak currents increase depending on the nature of the activating groups (Table 1). According to the Savéant model,[13b] the increases can be related to hypothesis (a), a solution electron transfer between radical anions **1a**′–**h**′ and CO_2, followed by a coupling reaction between radical anions **1a**′–**h**′ and CO_2 (Scheme 2, reactions 2 and 3) or hypothesis (b), to a coupling reaction between CO_2, as electrophilic agent, and radical anions **1a**′–**h**′ (Scheme 2, reaction 4).



Scheme 2

The *Ep* values of chiral cinnamic acid derivatives **1a**–**h** (Table 1) show that the monoelectronic reduction of the activated double bonds takes place at a potential strongly more positive with respect to the reduction potential of CO_2 to $CO_2^{\bullet-}$ ($\Delta E >$ 400 mV). Therefore, as regards substrates **1a**–**h**, according to the Savéant model, the mechanism *via* electron transfer [hypothesis (a)] is not competitive enough *vs.* the coupling CO_2-radical anions [(hypothesis (b)]. In addition, in the voltammetric curves of **1a**–**h**. as regards the peak currents in the presence of CO_2 (i_1) and in the absence of CO_2 (i_0), both the conditions are verified: $i_1 > i_0$ and $i_1 < 2i_0$. Therefore, the formation of oxalate *via* the catalytic reduction of CO_2 to $CO_2^{\bullet-}$ at the reduction potential of substrates **1a**–**h** by the electron transfer (Scheme 2, reactions 1, 2 and 5) may be rejected. In fact, no oxalates were isolated at the end of the electrolyses (see Experimental).

A carbon dioxide-saturated DMF–(0.1 mol dm^{-3} Bu_4NBF_4) solution, containing **1a** taken as a model compound, was electrolysed (undivided cell, Pt cathode, Al sacrificial anode) under potentiostatic control ($E = -1.6$ V *vs.* SCE). The reduction of the double bond and the dissolution of the Al metal (to Al^{3+} anion) take place at the Pt cathode and at the sacrificial anode, respectively, yielding (after the coupling of the radical anion with carbon dioxide) a stable aluminium carboxylate. Recently, the use of a sacrificial anode (Mg, Al) and the effect of the electrogenerated ions (Mg^{2+}, Al^{3+}) on the overall synthetic process have been reported and discussed by several authors.[18] At the end of the electrolysis, after treatment with diazomethane, **2a** + **2a**′[19] were isolated in 46% yield and with a good diastereoisomeric ratio (75 : 25) (Table 2, entry 1). Along with these two desired products, the hydrogenated product **3a** and 4*R*-phenyloxazolidin-2-one **4a** were obtained as by-products (Fig. 1). The formation of the free chiral auxiliary **4a** can be ascribed to the decomposition of the enolate of **1a**, probably *via* a ketene pathway.[20]

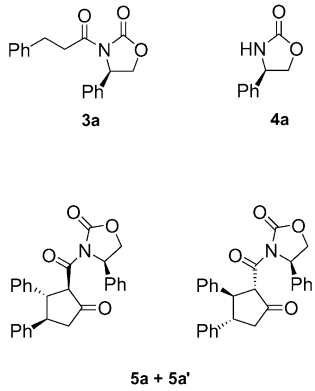


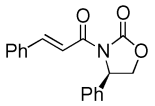
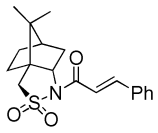
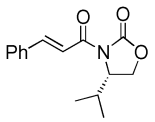
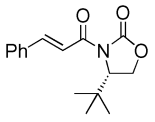
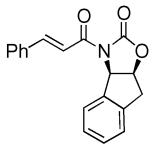
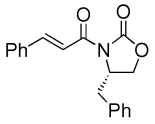
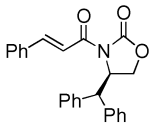
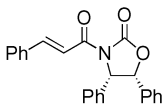
Fig. 1 By-products of the electrochemical reduction of **1a** in the presence of CO_2.

If the electrolysis was carried out under galvanostatic control ($I = 1.6$ mA cm^{-2}), a good chemoselectivity was obtained (Table 2, entry 2); the only products obtained were **2a** + **2a**′ in 44% yield, but the diastereoisomeric ratio was lower (60 : 40).

To verify a possible effect of the nature of the solvent on the yield and on the diastereometric ratio of the carboxylated products **2a** + **2a**′, the reduction of **1a** was carried out in CO_2-saturated THF–(0.1 mol dm^{-3} Bu_4NBF_4) solutions and in CO_2-saturated CH_3CN–(0.1 mol dm^{-3} Bu_4NBF_4) solutions (Table 2, entries 3–6). Good yields in carboxylated products were obtained in THF at −20 °C, with an increase of the dr (68 : 32, entry 3). An increase of the temperature (rt, entry 5) yielded a very good dr (9 : 91), but a poor chemoselectivity. Moreover, a new couple of products, **5a** + **5a**′, could be isolated (Fig. 1). The formation of all-*trans* cyclic hydrodimers **5a** + **5a**′ is described by Kise,[21] where the reduction is carried out in the absence of carbon dioxide and derives from the dimerization of the radical anion relative to **1a** (formed by addition of only one electron per molecule) with subsequent cyclization and elimination of one molecule of oxazolidinone **4a**. The formation of **4a** can be therefore due also to the formation of **5a** + **5a**′. The same results of entry 5 were obtained when MeCN was used as solvent (entry 6). The chemical shifts of hydrogen atoms of the methoxycarbonyl group of **2a** + **2a**′ showed that, in CH_3CN and in THF at rt, the diastereoisomeric ratio was the opposite of the one obtained in DMF (Table 2, entries 5 and 6).

During the electrolyses of **1a** in THF, the current density often dropped to zero. To reset the initial conditions, a careful cleaning of the electrode surfaces was necessary. The same drawback occurred also during the reduction of substrates other than **1a**. As regards substrates **1b** and **1c**, no detectable flow of current

Table 1 Voltammetric data for solutions of **1a**–**h**[a] in DMF (Ep_0 and i_0) and in carbon dioxide saturated DMF (Ep_1 and i_1)[b]

Entry	Substrate	$-Ep_0$/V	i_0/μA	$-Ep_1$/V	i_1/μA	Δi (%)[c]
1	 **1a**	1.54	9.05	1.66	15.16	67.4
2	 **1b**	1.59	8.75	1.58	11.45	30.8
3	 **1c**	1.56	8.95	1.57	10.60	18.4
4	 **1d**	1.40	8.95	1.51	8.95	—
5	 **1e**	1.40	8.90	1.41	10.30	15.7
6	 **1f**	1.39	6.30	1.45	8.50	36.0
7	 **1g**	1.42	8.10	1.40	14.30	76.5
8	 **1h**	1.38	6.7	1.41	9.20	37.3

[a] $c = 5.0 \times 10^{-3}$ mol dm^{-3}. [b] Pt cathode and anode; $v = 0.2$ V s^{-1}; Bu_4NBF_4 as supporting electrolyte. [c] $\Delta i(\%) = (i_1 - i_0)100/i_0$

could be recorded. Replacing the platinum cathode with other solid electrodes did not produce significant improvements.

DMF and galvanostatic conditions seemed the best choice for the carboxylation of chiral cinnamic acid derivatives (Table 2, entry 2), because there was no problem of passivation at the electrodes (the current was constant during the electrolysis) and all the reduced substrate **1a** reacted with CO_2 to give the carboxylated products **2a** + **2a**′. Furthermore, the constant current method offers many advantages over the controlled-potential method, that requires a references electrode and hence a more complex cell.

DMF was therefore chosen as solvent, and electrolyses were carried out with the aim of consuming all the starting material, increasing the amount of electricity and the current density (reducing in this way the reaction time to 1 h) (Table 2, entries 7–9), but with only a little improvement.

Using the experimental conditions of entry 8 (Table 2) (the best compromise between yields, current efficiency and reaction time), we tried to improve the diastereomeric ratio, varying the chiral auxiliary. These results are reported in Table 3.

In all cases the desired products were obtained, but the best yields were with the substrates **1a** and **1c** (Table 3, entries 1 and 3); as regards the diastereoisomeric ratio, satisfactory results were achieved with substrate **1b** and **1g** (Table 3, entries 2 and 7). In fact, in these two cases, when Oppolzer's camphor sultam and 4*R*-(diphenylmethyl)-oxazolidin-2-one have been used as chiral auxiliaries, the two carboxylated diasteomers **2** + **2**′ were very easy to isolate in pure form by simple flash chromatography.

Table 2 Distribution and yields of the products (Scheme 1 and Fig. 1) from the electrochemical reduction of **1a** in carbon dioxide saturated solutions[a]

						Products (% yield)[d]			
Entry	Solvent	T/°C	*E* or *I*[b]	*Q*[c]	Recovered **1a**	**3a**	**5a** + **5a′**	**4a**	**2a** + **2a′** (dr)[e]
1	DMF	−20	*E*	1.3	13	10	—	15	46 (75 : 25)
2	DMF	−20	I_1	2.0	46	—	—	—	44 (60 : 40)
3	THF	−20	I_1	2.0	24	—	—	5	66 (68 : 32)
4	THF	0	I_1	2.0	24	—	—	25	47 (62 : 38)
5	THF	Rt	I_1	2.0	27	—	35	21	28 (9 : 91)
6	MeCN	−20	I_1	2.0	—	Trace	46	26	18 (47 : 53)
7	DMF	−20	I_1	6.0	24	—	—	—	57 (64 : 36)
8	DMF	−20	I_2	6.0	30	—	—	—	59 (59 : 41)
9	DMF	−20	I_2	8.0	28	—	—	—	60 (59 : 41)

[a] Undivided cell; Al anode and Pt cathode; CO_2 atmosphere; Bu_4NBF_4 as supporting electrolyte. [b] Electrolysis carried out under potentiostatic control ($E = -1.6$ V *vs* SCE) or galvanostatic control ($I_1 = 1.6$ μA cm^{-2}, $I_2 = 8.0$ μA cm^{-2}). [c] Faradays mol^{-1} of **1a**. [d] Yields of isolated products calculated with respect to starting **1a**. [e] The diastereomeric ratio was determined by ^{1}H-NMR.

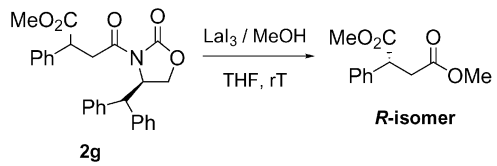
Table 3 Electrochemical carboxylation of **1a**–**h**[a]

		Products (% yield)[b]		
Entry	Substrate	Recovered **1**	**2** + **2′**(dr)[c]	δ(Me)[d]
1	**1a**	30	59 (59 : 41)	3.50–3.63
2	**1b**	43	20 (74 : 26)	3.64–3.66
3	**1c**	31	61 (68 : 32)[e]	3.66–3.66
4	**1d**	35	56 (69 : 31)	3.65–3.63
5	**1e**	47	53 (67 : 33)	3.68–3.70
6	**1f**	46	54 (64 : 36)[e]	3.69–3.69
7	**1g**	41	48 (70 : 30)	3.70–3.64
8	**1h**	32	30 (51 : 49)	3.64–3.52

[a] Solutions of **1** in DMF–Bu_4NBF_4, undivided cells, Pt cathode and Al anode, CO_2 atmosphere, $T = -20$ °C, galvanostatic conditions: $I = 8$ mA cm^{-2}, 6 F mol^{-1} of **1**. [b] Yields of isolated products, calculated with respect to starting **1**. [c] The diastereoisomeric ratio was determined by ^{1}H-NMR. The reported ratio is the one between the more abundant isomer and the less abundant one. [d] Chemical shifts (ppm) of the hydrogen atoms of the methoxycarbonyl group. [e] The diastereoisomeric ratio was determined by ^{13}C-NMR.

In order to establish the identity of major and minor diastereoisomers **2g** and **2g′**, the deprotection of the more abundant **2g** was carried out following the method of Fukuzawa[22] (using mild conditions to avoid racemization), transforming compound **2g** into the corresponding methyl ester (a known compound).

This reaction has permitted us to establish the absolute configuration of the new chiral center of the more abundant isomer **2g** as the *R*-isomer (Scheme 3).



Scheme 3

Conclusions

Chiral 2-phenyl succinic ester derivatives have been obtained under mild conditions, short time (1 h) and in satisfactory yields (30–61%) by electrochemical reduction of chiral acid cinnamic derivatives under a CO_2 atmosphere.

The influence of electrolysis conditions and of the various chiral auxiliaries on the yields and the diastereoisomeric ratio has been studied.

When Oppolzer's camphor sultam and 4*R*-(diphenylmethyl)-oxazolidin-2-one have been used as chiral auxiliaries the two diastereoisomers can be easy separated by flash chromatography. In particular, using 4*R*-(diphenylmethyl)-oxazolidin-2-one, the *R*-isomer has been obtained as major product.

Experimental

Tetrahydrofuran was distilled from Na–benzophenone and acetonitrile was distilled twice from P_2O_5 and CaH_2. DMF was anhydrous grade and used as received. All other reagents were used as received.

Flash column chromatography was carried out using Merck 60 Kieselgel (230–400 mesh) under pressure. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter. GC-MS measurements were carried out on a SE 54 capillary column using a Fisons 8000 gas chromatograph coupled with a Fisons MD 800 quadrupole mass selective detector. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature using a Bruker AC 200 spectrometer using $CDCl_3$ as internal standard.

Where a compound has been characterised as an inseparable mixture of diastereoisomers, the NMR data for the major and minor isomer have been reported as far as was discernable from the spectrum of the mixture.

Electrochemistry

Voltammetric measurements were performed with an Amel 552 potentiostat equipped with an Amel 566 function generator and an Amel 563 multipurpose unit in a three-electrode cell; the curves were dispayed on an Amel 863 recorder assisted by Nicolet 3091 digital oscilloscope. A 492/Pt/1 Amel microelectrode was employed. The reference electrode was a modified saturated calomel electrode. Its potential was −0.07 V *vs.* SCE. All the potentials are referred to modified SCE.

Electrolyses under galvanostatic control were carried out with an Amel 552 potentiostat equipped with an Amel 721 integrator. A one-compartment cell was used and the cathode was a Pt spiral (apparent area 6.25 cm^2) and the counter electrode was an Al foil (apparent area 21.00 cm^2).

General procedure

A solution of 3-*trans*-cinnamoyl-(*4R*)-phenyl-2-oxazolidinone (**1a**, 0.5 mmol) in 25 cm^3 of DMF–(0.1 mol dm^{-3} Bu_4NBF_4) was electrolyzed (undivided cells, Pt cathode, Al anode, at −20 °C) under galvanostatic conditions ($I = 8.0$ mA cm^{-2}) in presence of carbon dioxide ($p = 1$ atm). After the consumption of 6 F mol^{-1} of **1a**, the current flow was stopped and the mixture of electrolysis was poured into 150 cm^3 of water. The resulting aqueous phase was extracted with diethyl ether (3 × 30 cm^3). The combined organic extracts were washed with water and brine. After they were cooled at 0 °C and treated with ethereal CH_2N_2.[23] (Caution: diazomethane is toxic and prone to cause

development of specific sensitivity; in addition, it is potentially explosive.) The usual workup gave the mixture of **2a**, **2a′** and **1a**. The diastereomeric ratio of **2a** and **2a′** was calculated by ^{1}H NMR of the crude. The mixture of two isomers was obtained after flash column chromatography (*n*-hexane–ethyl acetate 8 : 2 as eluent). In no case was the presence of dimethyl oxalate evidenced.

Starting materials and electrolysis products. Spectral data of known compounds have been compared with those reported in the literature:

3-*trans*-Cinnamoyl-(4*R*)-phenyl-2-oxazolidinone (**1a**).[21]

3-(3-Phenylpropanoyl)-(4*R*)-phenyl-2-oxazolidinone (**3a**).[24]

(4*R*)-Phenyl-2-oxazolidinone (**4a**): commercial.

3-(5-Oxo-2,3-diphenyl-cyclopentancarbonyl)-4*R*-phenyl-2-oxazolidinone (mixture of two diastereomers, **5a** + **5a′**).[21]

N-[(5*R*)-10,10-Dimethyl-3,3-dioxo-3-thia-4-azatricyclo[5.2.1.0^{1,5}]dec-4-yl]-(*E*)-3-phenylpropenoylamide (**1b**).[25]

3-*trans*-Cinnamoyl-(4*S*)-isopropyl-2-oxazolidinone (**1c**).[21]

3-*trans*-Cinnamoyl-(4*S*)-*tert*-butyl-2-oxazolidinone (**1d**).[25]

3-*trans*-Cinnamoyl-(4*R*,5*S*)-indano[1,2-*d*]-2-oxazolidinone (**1e**).[25]

3-*trans*-Cinnamoyl-(4*S*)-benzyl-2-oxazolidinone (**1f**).[21]

3-*trans*-Cinnamoyl-(4*R*)-diphenylmethyl-2-oxazolidinone (**1g**).[26]

3-*trans*-Cinnamoyl-(4*S*,5*R*)-diphenyl-2-oxazolidinone (**1h**).[27]

(*R*)-(−)-Dimethyl phenyl succinate.[28]

3-(3-Methoxycarbonyl-3-phenylpropionyl)-(4*R*)-phenyl-2-oxazolidinone (2a + 2a′, mixture of two isomers). More abundant isomer: δ_H(200 MHz; $CDCl_3$) 3.28 (1 H, dd, *J* 18.1 and 4.7, COC*H*H), 3.50 (3 H, s, OCH_3), 3.31–3.97 (1 H, m, COC*H*H), 4.02–4.14 (1 H, m, COC*H*), 4.20–4.30 (1 H, m, OC*H*H), 4.60–4.74 (1 H, m, NC*H*), 7.25–7.43 (10 H, m, ar); δ_C(50 Mhz; $CDCl_3$) 39.4, 46.5, 52.1 57.5, 70.1, 125.7, 127.6, 127.9, 128.6, 128.8, 129.1, 137.5, 138.5, 153.6, 170.7, 173.0; GC-MS *m*/*z* ($M^{\bullet+}$ absent) 322 ($M^{\bullet+}$ − OCH_3, 2%), 162 (16), 132 (6), 104 (100).

Less abundant isomer: δ_H(200 MHz; $CDCl_3$) 3.15 (1 H, dd, *J* 18.0 and 2.7, COC*H*H), 3.63 (3 H, s, OCH_3), 3.31–3.97 (1 H, m, COC*H*H), 4.02–4.14 (1 H, m, COC*H*), 4.20–4.30 (1 H, m, OC*H*H), 4.60–4.74 (1 H, m, NC*H*), 7.25–7.43 (10 H, m, ar); δ_C(50 Mhz; $CDCl_3$) 39.5, 46.3, 52.3, 57.5, 70.2, 125.9, 127.8, 127.9, 128.7, 128.8, 129.1, 137.3, 138.5, 153.6, 170.7, 173.7; GC-MS *m*/*z* ($M^{\bullet+}$ absent) 322 ($M^{\bullet+}$ − OCH_3, 2%), 162 (16), 132 (6), 104 (100).

***N*-[(5*R*)-10,10-Dimethyl-3,3-dioxo-3-thia-4-azatricyclo-[5.2.1.0^{1,5}]dec-4-yl]-(*E*)-3-methoxycarbonyl-3-phenylpropionamide (2b or the more abundant, less polar isomer 2b′).** δ_H(200 MHz; $CDCl_3$) 0.95 (3 H, s, CCH_3), 1.20 (3 H, s, CCH_3), 1.23–1.43 (2 H, m, C*H*H and C*H*H), 1.86–1.90 (3 H, m, C*H*H, C*H*H and C*H*), 2.02–2.15 (2 H, m, C*H*H and C*H*H), 2.99 (1 H, dd, *J* 17.2 and 4.2, COC*H*H), 3.39 (1 H, d, AB, *J* 14.0, Δ*v* 17.3, C*H*HSO_2), 3.48 (1 H, d, AB, *J* 14.0, Δ*v* 17.3, C*H*HSO_2), 3.60 (1 H, dd, *J* 17.3 and 10.8, COC*H*H), 3.64 (3 H, s, OCH_3), 3.82 (1 H, dd, *J* 7.5 and 5.0, NC*H*), 4.17 (1 H, dd, *J* 10.8 and 4.2, COC*H*) and 7.23–7.33 (5 H, m, ar); δ_C(50 Mhz; $CDCl_3$) 19.8, 20.8, 26.5, 32.8, 38.3, 38.9, 44.7, 46.6, 47.8, 48.7, 52.3, 52.9, 65.1, 127.6, 127.9, 128.8, 137.5, 169.7, 173.2; GC-MS *m*/*z* ($M^{\bullet+}$ absent) 373 (2%), 191 (9), 132 (11); $[a]_D^{29}$ −144.8 (*c* 0.58 in $CHCl_3$). Found: C, 62.19; H, 6.73; N, 3.44; O, 19.72. $C_{21}H_{27}NO_5S$ requires C, 62.20; H, 6.71; N, 3.45; O, 19.73%.

***N*-[(5*R*)-10,10-Dimethyl-3,3-dioxo-3-thia-4-azatricyclo-[5.2.1.0^{1,5}]dec-4-yl]-(*E*)-3-methoxycarbonyl-3-phenylpropionamide (2b or the less abundant, more polar isomer 2b′).** δ_H(200 MHz; $CDCl_3$) 0.92 (3 H, s, CCH_3), 0.99 (3 H, s, CCH_3), 1.23–1.41 (2 H, m, C*H*H and C*H*H), 1.81–1.88 (3 H, m, C*H*H, C*H*H and C*H*), 1.98–2.01 (2 H, m, C*H*H and C*H*H), 3.11 (1 H, dd, *J* 17.1 and 5.0, COC*H*H), 3.44 (2 H, s, CH_2SO_2), 3.59 (1 H, dd, *J* 17.6 and 9.8, COC*H*H), 3.66 (3 H, s, OCH_3), 3.85 (1 H, t, *J* 6.2, NC*H*), 4.11 (1 H, dd, *J* 9.8 and 4.9, COC*H*) and 7.24–7.27 (5 H, m, ar); δ_C(50 Mhz; $CDCl_3$) 19.8, 20.7, 26.4, 32.9, 38.4, 38.9, 44.8, 46.9, 47.7, 48.6, 52.3, 52.9, 65.2, 127.6, 128.0, 128.8, 137.3, 169.6, 173.0; GC-MS *m*/*z* ($M^{\bullet+}$ absent) 373 (2%), 191 (9), 132 (11); $[a]_D^{29}$ +122.2 (*c* 0.63 in $CHCl_3$).). Found: C, 62.21; H, 6.70; N, 3.46; O, 19.74. $C_{21}H_{27}NO_5S$ requires C, 62.20; H, 6.71; N, 3.45; O, 19.73%.

3-(3-Methoxycarbonyl-3-phenylpropionyl)-(4*S*)-isopropyl-2-oxazolidinone (2c + 2c′, mixture of two isomers). More abundant isomer: δ_H(200 MHz; $CDCl_3$) 0.87 (3 H, d, *J* 6.9, CH_3), 0.89 (3 H, d, *J* 6.9, CH_3), 2.29–2.34 (1 H, m, C*H*$(CH_3)_2$), 3.25 (1 H, dd, *J* 18.4 and 3.6, COC*H*H), 3.66 (3 H, s, OCH_3), 3.73–3.94 (1 H, m, COC*H*H), 4.09–4.28 (3 H, m, OCH_2 and COC*H*), 4.33–4.43 (1 H, m, NC*H*) and 7.24–7.29 (5 H, m, ar); δ_C(50 Mhz; $CDCl_3$) 14.6, 17.9, 28.4, 39.4, 46.5, 52.3, 58.5, 63.6, 127.6, 127.8, 127.9, 128.8, 137.4, 153.9, 171.3, 173.7; GC-MS *m*/*z* ($M^{\bullet+}$ absent) 288 ($M^{\bullet+}$ − OCH_3, 3%), 260 (4), 132 (10), 104 (28).

Less abundant isomer: δ_H(200 MHz; $CDCl_3$) 0.80 (3 H, d, *J* 6.8, CH_3), 0.87 (3 H, d, *J* 6.8, CH_3), 2.29–2.34 (1 H, m, C*H*$(CH_3)_2$), 3.19 (1 H, dd, *J* 20.3 and 4.2, COC*H*H), 3.66 (3 H, s, OCH_3), 3.73–3.94 (1 H, m, COC*H*H), 4.09–4.28 (3 H, m, OCH_2 and COC*H*), 4.33–4.43 (1 H, m, NC*H*) and 7.24–7.29 (5 H, m, ar); δ_C(50 Mhz; $CDCl_3$) 14.7, 17.8, 28.4, 39.5, 46.6, 52.3, 58.4, 63.6, 127.6, 127.8, 127.9, 128.8, 137.6, 153.9, 171.3, 173.4; GC-MS *m*/*z* ($M^{\bullet+}$ absent) 288 ($M^{\bullet+}$ − OCH_3, 3%), 260 (4), 132 (10), 104 (28).

3-(3-Methoxycarbonyl-3-phenylpropionyl)-(4*S*)-*tert*-butyl-2-oxazolidinone (2d + 2d′, mixture of two isomers). More abundant isomer: 0.90 (3 H, s, 3 × CH_3), 3.20 (1 H, dd, *J* 18.2 and 4.2, COC*H*H), 3.63 (3 H, s, OCH_3), 3.85 (1 H, t, *J* 18.2, COC*H*H), 4.09–4.28 (3 H, m, OCH_2 and COC*H*), 4.35–4.40 (1 H, m, NC*H*) and 7.18–7.27 (5 H, m, ar); δ_C(50 Mhz; $CDCl_3$) 25.5, 35.8, 39.6, 46.7, 52.2, 60.8, 65.4, 127.5, 127.9, 128.8, 137.5, 154.5, 171.3, 173.3; GC-MS *m*/*z* ($M^{\bullet+}$ absent) 302 ($M^{\bullet+}$ − OCH_3, 5%), 132 (7), 104 (33), 59 (12).

Less abundant isomer: δ_H(200 MHz; $CDCl_3$) 0.86 (3 H, s, 3 × CH_3), 3.23 (1 H, dd, *J* 18.2 and 4.0, COC*H*H), 3.65 (3 H, s, OCH_3), 3.84 (1 H, dd, *J* 18.2 and 2.6, COC*H*H), 4.09–4.28 (3 H, m, OCH_2 and COC*H*), 4.35–4.40 (1 H, m, NC*H*) and 7.18–7.27 (5 H, m, ar); δ_C(50 Mhz; $CDCl_3$) 25.6, 35.6, 39.6, 46.8, 52.2, 61.1, 65.5, 127.6, 127.9, 128.8, 137.5, 154.6, 171.3, 173.6; GC-MS *m*/*z* ($M^{\bullet+}$ absent) 302 ($M^{\bullet+}$ − OCH_3, 5%), 132 (7), 104 (33), 59 (12).

3-(3-Methoxycarbonyl-3-phenylpropionyl)-(4*R*,5*S*)-indano-[1,2-*d*]-2-oxazolidinone (2e + 2e′, mixture of two isomers). More abundant isomer: δ_H(200 MHz; $CDCl_3$) 3.27 (1 H, dd, *J* 18.4 and 4.5, COC*H*H), 3.36 (2 H, d, *J* 3.2, CH_2), 3.68 (3 H, s, OCH_3), 3.80 (1 H, dd, *J* 18.4 and 10.3, COC*H*H), 4.19 (1 H, dd, *J* 10.3 and *J* 4.5, COC*H*), 5.21–5.32 (1 H, m, OC*H*), 5.89 (1 H, d, *J* 6.8, NC*H*) and 7.19–7.59 (9 H, m, ar); δ_C(50 Mhz; $CDCl_3$) 37.9, 39.4, 46.8, 52.3, 62.8, 78.4, 125.1, 127.2, 127.9, 128.8, 129.9, 137.6, 139.3, 152.9, 171.6, 173.2.

Less abundant isomer: δ_H(200 MHz; $CDCl_3$) 3.17 (1 H, dd, *J* 19.0 and 3.3, COC*H*H), 3.36 (2 H, d, *J* 3.2, CH_2), 3.70 (3 H, s, OCH_3), 3.85 (1 H, dd, *J* 19.0 and 9.2, COC*H*H), 4.19 (1 H, dd, *J* 10.3 and *J* 4.5, COC*H*), 5.21–5.32 (1 H, m, OC*H*), 5.89 (1 H, d, *J* 6.8, NC*H*) and 7.19–7.59 (9 H, m, ar); δ_C(50 Mhz; $CDCl_3$) 37.9, 39.5, 46.5, 52.3, 63.1, 78.4, 125.2, 127.2, 127.6, 128.8, 129.9, 137.4, 139.5, 152.9, 171.6, 173.7.

3-(3-Methoxycarbonyl-3-phenylpropionyl)-(4*S*)-benzyl-2-oxazolidinone (2f + 2f′, mixture of two isomers). More abundant isomer: δ_H(200 MHz; $CDCl_3$) 2.81 (1 H, dd, *J* 13.4 and 9.2, COC*H*H), 3.24–3.31 (2 H, m, CH_2Ph), 3.69 (3 H, s, OCH_3), 3.75–3.97 (1 H, m, COC*H*H), 4.13–4.25 (3 H, m, COC*H* and OCH_2), 4.58–4.70 (1 H, m, NC*H*) and 7.13–7.41 (10 H, m, ar); δ_C (50 MHz; $CDCl_3$) 37.6, 39.6, 46.5, 52.3, 54.9, 66.2, 127.3,

127.9, 128.6, 128.8, 129.1, 129.3, 135.0, 137.5, 153.3, 171.3, 173.4; GC-MS m/z ($M^{\bullet+}$ absent) 336 ($M^{\bullet+} - OCH_3$, 14%), 191 (16), 176 (5), 91 (41).

More abundant isomer: δ_H(200 MHz; $CDCl_3$) 2.71 (1 H, dd, J 13.3 and 9.6, COC*H*H), 3.15–3.22 (2 H, m, CH_2Ph), 3.69 (3 H, s, OCH_3), 3.75–3.97 (1 H, m, COC*H*H), 4.13–4.25 (3 H, m, COC*H* and OCH_2), 4.58–4.70 (1 H, m, NC*H*) and 7.13–7.41 (10 H, m, ar); δ_C (50 MHz; $CDCl_3$) 37.7, 39.6, 46.5, 52.3, 55.1, 66.3, 127.3, 127.6, 128.6, 128.9, 129.3, 129.4, 135.1, 137.4, 153.3, 171.3, 173.6; GC-MS m/z ($M^{\bullet+}$ absent) 336 ($M^{\bullet+} - OCH_3$, 14%), 191 (16), 176 (5), 91 (41).

3-(3-Methoxycarbonyl-3-phenylpropionyl)-(4*R*)-diphenylmethyl-2-oxazolidinone (2g or the more abundant, less polar isomer 2g′). δ_H(200 MHz; $CDCl_3$) 3.21 (1 H, dd, J 18.6 and 4.1, COC*H*H), 3.70 (3 H, s, OCH_3), 3.79 (1 H, dd, J 18.6 and 10.6, COC*H*H), 4.13 (1 H, dd, J 10.6 and 4.1, COC*H*), 4.44 (2 H, d, J 5.2, OCH_2), 4.76 (1 H, d, J 4.4, C*H*$(Ph)_2$), 5.23–5.31 (1 H, m, NC*H*), 7.05–7.17 (5 H, m, ar) and 7.24–7.41 (10 H, m, ar); δ_C (50 MHz; $CDCl_3$) 39.6, 46.4, 49.9, 52.3, 56.1, 64.7, 127.0, 127.6, 127.9, 128.2, 128.6, 128.7, 128.8, 128.9, 129.5, 137.6, 137.8, 139.6, 153.2, 171.1, 173.4; GC-MS m/z 443 ($M^{\bullet+}$, 3%), 412 (2), 276 (2), 191 (100), 167 (50); $[a]_D^{27}$ −138.6 (c 0.70 in $CHCl_3$). Found: C, 73.11; H, 5.69; N, 3.17. $C_{27}H_{25}NO_5$ requires C, 73.12; H, 5.68; N, 3.16%.

3-(3-Methoxycarbonyl-3-phenylpropionyl)-(4*R*)-diphenylmethyl-2-oxazolidinone (2g or the less abundant, more polar isomer 2g′). δ_H(200 MHz; $CDCl_3$) 3.04 (1 H, dd, J 18.4 and 3.6, COC*H*H), 3.64 (3 H, s, OCH_3), 3.68–3.81 (1 H, m, COC*H*H), 4.02 (1 H, dd, J 10.8 and 3.6, COC*H*), 4.34–4.49 (2 H, m, OCH_2), 4.65 (1 H, d, J 5.7, C*H*$(Ph)_2$), 5.25–5.32 (1 H, m, NC*H*), 7.01–7.08 (5 H, m, ar) and 7.24–7.37 (10 H, m, ar); δ_C (50 MHz; $CDCl_3$) 39.4, 46.4, 50.9, 52.3, 56.4, 65.3, 127.1, 127.7, 127.9, 128.4, 128.6, 128.7, 128.8, 128.9, 129.2, 137.5, 137.9, 139.5, 153.3, 170.9, 173.6; GC-MS m/z 443 ($M^{\bullet+}$, 3%), 412 (2), 276 (2), 191 (100), 167 (50); $[a]_D^{29}$ +68.1 (c 0.71 in $CHCl_3$). Found: C, 73.13; H, 5.67; N, 3.15. $C_{27}H_{25}NO_5$ requires C, 73.12; H, 5.68; N, 3.16%.

3-(3-Methoxycarbonyl-3-phenylpropionyl)-(4*S*,5*R*)-diphenyl-2-oxazolidinone (2h + 2h′, mixture of two isomers). More abundant isomer: δ_H(200 MHz; $CDCl_3$) 3.30 (1 H, dd, J 17.7 and 2.9, COC*H*H), 3.64 (3 H, s, OCH_3), 3.87–4.04 (1 H, m, COC*H*H), 4.07–4.18 (1 H, m, COC*H*), 5.64 (1 H, d, AB, J 7.2, $\Delta\nu$ 58.3, NC*H*), 5.93 (1H, d, AB, J 7.2, $\Delta\nu$ 58.3, OC*H*), 6.78–7.31 (15 H, m, ar); δ_C (50 MHz; $CDCl_3$) 39.7, 46.4, 52.2, 62.8, 80.5, 126.2, 126.6, 127.9, 128.1, 128.3, 128.5, 128.9, 132.7, 134.3, 137.4, 153.6, 170.6, 173.6; GC-MS m/z ($M^{\bullet+}$ absent) 398 ($M^{\bullet+} - OCH_3$, 11%), 180 (77), 132(24).

Less abundant isomer: δ_H(200 MHz; $CDCl_3$) 3.36 (1 H, dd, J 17.2 and 3.9, COC*H*H), 3.52 (3 H, s, OCH_3), 3.87–4.04 (1 H, m, COC*H*H), 4.07–4.18 (1 H, m, COC*H*), 5.60 (1 H, d, AB, J 7.5, $\Delta\nu$ 45.0, NC*H*), 5.83 (1H, d, AB, J 7.5, $\Delta\nu$ 45, OC*H*), 6.78–7.31 (15 H, m, ar); δ_C (50 MHz; $CDCl_3$) 39.5, 46.6, 52.2, 62.7, 80.6, 126.1, 126.6, 127.6, 128.0, 128.2, 128.4, 128.8, 132.7, 134.0, 137.7, 153.6, 170.5, 173.0; GC-MS m/z ($M^{\bullet+}$ absent) 398 ($M^{\bullet+} - OCH_3$, 11%), 180 (77), 132(24).

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