DOI: 10.1002/adsc.200900331

Highly Stereoselective Halocyclopropanation of α,β-Unsaturated Amides

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Received: May 12, 2009; Revised: July 10, 2009; Published online: September 10, 2009

This paper is dedicated with best wishes to Professor José Font on the occasion of his 70th birthday.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200900331.

Abstract: A convenient highly stereoselective synthesis of chloro- and bromocyclopropanamides from di- tri- or tetrasubstituted (*E*)- or (*Z*)-α,β-unsaturated amides with total or high stereoselectivity promoted by chromium dichloride or dibromide is described. The transformation of chlorocyclopropanamides into the corresponding ketones or amines is also reported. A mechanism to explain these transformations is proposed.

Keywords: amides; chromium; cyclopropanation; stereoselectivity; synthetic methods

Introduction

The properties and reactivity of cyclopropanes are significantly different to those of other carbocycles.[1] The smallest cycloalkane is present in an important number of naturally occurring compounds[2] and compounds bearing this moiety are widely used to elucidate biological mechanisms.[3] In addition, an important number of applications of unnatural cyclopropane-containing compounds has been reported. Thus, many of these compounds have been prepared to verify theoretical calculations of the bonding features of these strained cycloalkanes[4] and to study enzyme mechanisms or inhibition.[5] From a synthetic viewpoint, cyclopropanes have been used as starting materials to obtain other cycloalkanes[6] and acyclic compounds.[7] Functionalized cyclopropanes are most interesting, especially when the functionality can be readily modified with total or high selectivity such as, for example, in halocyclopropanes. Thus, 1-chlorocyclopropanecarboxylic acids are precursors to a variety of aminocyclopropanecarboxylic acids known for their biological activity,[8] whereas 2-chlorocyclopropanecarboxylic acids are used to obtain agrochemical compounds,[9] and novel antitumour agents.[10]

The chlorocyclopropane motif can be mainly accessed through the addition of carbenoids (Simmons–Smith-like process)[11] or carbene[12] species to double bonds; from α,α-dichloroalkyl anions (conjugated nucleophilic addition followed by a ring closing reaction),[13] from *gem*-dichlorocyclopropanes,[14] and by utilizing other starting materials such as 2,2-dichlorobutanols (Favorskii rearrangement),[15] carboalkoxychlorodiazirines,[16] or pyrazolines.[17] However, the majority of these methods present some drawbacks such as: a) the use of explosive, flammable or harmful reagents[12b–c,16] or those which are not readily available;[13b,16,17] b) some methods proceed with low stereoselectivity,[11c–d,12c,13d,14b–c,16] or in poor yields;[11b–d,13a–b,d] and finally d) other methods have shown poor generality.[11c,d,12c–d,13,14b–d,15,16,17] In the case of bromocyclopropanation, to the best of our knowledge only one stereoselective synthesis of bromocyclopropanes has been reported *via* the bromination of cyclopropylindium reagents prepared from the allylindation of cyclopropenes which are not readily available.[18] The most employed method for the synthesis of bromocyclopropanes is based on the debromination of dibromocyclopropanes by using several reagents.[14a,d,19] In general terms, these methodologies took place with poor selectivity affording a mixture of both monobrominated

diastereoisomers and the corresponding fully debrominated cyclopropanes. Other methods are based on bromocyclopropanation through the addition of carbenoids to olefins, however these bromocyclopropane derivatives are generally obtained in low yields, low stereoselectivity and poor generality.[11b,d,12a,17,20]

The development of the synthetic applications of these compounds has been limited by the absence of a general method to obtain bromocyclopropanes in a selective manner. In spite of this important limitation, some synthetic applications such as the photochemical debromination,[21] dehydrobromination,[22] alkylation,[23] thermolysis[24] and the stereoselective radical addition of to electron-deficient olefins[25] have been described.

Taking into account these precedents a general, highly stereoselective chloro- and bromocyclopropanation of α,β-unsaturated acid derivatives with total stereoselectivity would be desirable.

Related to the $CrCl_2$-mediated cyclopropanation reaction, Takai has reported the iodo-[26,27] and the silylcyclopropanation[28] of terminal alkenes with high stereoselectivities in the iodocyclopropanation reaction or poor selectivity for the synthesis of silylcyclopropanes. Both methods were carried out in the presence of *N,N,N′,N′*-tetraethylethylenediamine (TEEDA). We have also reported the use of $CrCl_2$ to promote the highly stereoselective cyclopropanation,[29] or alkyl- and silylcyclopropanation[30] of α,β-unsaturated amides with total or high stereoselectivity. Herein we report the valuable, highly stereoselective chloro- and bromocyclopropanations of α,β-unsaturated amides mediated by $CrCl_2$,or $CrBr_2$ which take place in high yields and with total or high stereoselectivity.

Results and Discussion

Our first attempts to chlorocyclopropanate unsaturated amides were performed on (*E*)-*N,N*-diethylcinnamamide as a model substrate and chloroform as cyclopropanating reagent under similar conditions to those previously reported in the cyclopropanation of α,β-unsaturated amides.[29] Thus, treatment of (*E*)-*N,N*-diethylcinnamamide with 4 equivalents of $CrCl_2$ and 2 equivalents of $CHCl_3$ for 6 h at reflux, gave a 2/1 mixture of the chlorocyclopropanamide **I** and cyclopropanamide **II** (Scheme 1). To avoid this C–Cl bond reduction, we tested the reaction conditions shown in Scheme 1 without improving the initial results.

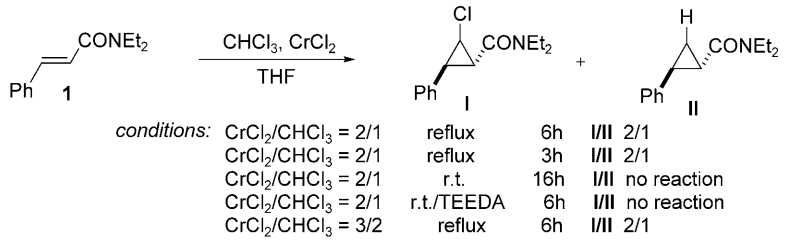
Therefore, we changed the chlorocyclopropanating agent, employing CCl_4 instead of $CHCl_3$. Hence treatment of cinnamamide **1** with 4 equivalents of $CrCl_2$ and 2 equivalents of CCl_4 in THF, at reflux afforded the corresponding chlorocyclopropanamide **I** in high yields, with an absence of the cyclopropanamide **II**.

After testing several conditions (varying equivalents of $CrCl_2$ or CCl_4, and reaction times), we found that the best reaction conditions utilized 1 equivalent of CCl_4, 3 equivalent of $CrCl_2$ in THF at reflux for 16 h. Thus, we performed the chlorocyclopropanation reaction with a range of α,β-unsaturated amides as is shown in Table 1.

Next efforts were directed towards the synthesis of bromocyclopropanecarboxamides by using a mixture of $CrCl_2/CBr_4$.

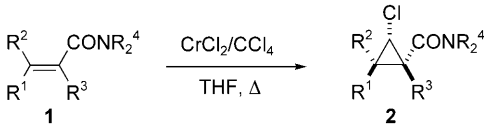
After trying different temperatures and conditions, using *N,N*-diethylcinnamamide **1** as the model substrate, we always observed the presence of both chlorocyclopropane and bromocyclopropane as a consequence of a halogen cross-over in the reaction medium. To overcome this problem, we performed the bromocyclopropanation reaction using $CrBr_2$ instead of $CrCl_2$. Since $CrBr_2$ was not commercially available, our next efforts were directed towards the synthesis of this salt. Several methods have previously been described to synthesise $CrBr_2$. Most of them employ the reaction of chromium metal. In those reports, chromium metal is treated with: (a) HBr-Br_2 mixture at 855 °C;[31] (b) bromine vapour at 700 °C;[32] and (c) HBr at high temperatures.[33] In another method $CrBr_2$ was obtained by the reduction of chromium(III) bromide with hydrogen at high temperatures (500–600 °C).[34]

We initially performed the *in situ* synthesis of chromium dibromide by treatment of $CrBr_3$ with $LiAlH_4$. Previously $CrBr_3$ was obtained by heating $CrBr_3 \cdot 6H_2O$ under vacuum.[35] Thus, we attempted the synthesis of bromocyclopropanes by using this $CrBr_2$, again employing (*E*)-*N,N*-diethylcinnamamide as a model substrate and $CrBr_2/CHBr_3$.



Scheme 1. Initial studies.

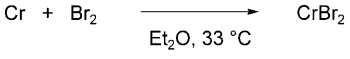
Table 1. Synthesis of chlorocyclopropanecarboxamides **2**.



Entry	**2**[a]	R^1	R^3	R^4	*dr*[b]	*dr*[c]	Yield [%][d]
1	**2a**	Me	H	Et	>98/2	>98/2	77
2	**2b**	*n*-C_5H_{11}	H	Me	78/22	76/24	78
3	**2c**	*n*-C_5H_{11}	H	Et	95/5	95/5	83
4	**2d**	*n*-C_5H_{11}	H	[e]	95/5	95/5	80
5	**2e**	*i*-Bu	H	Et	93/7	92/8	79
6	**2f**	Cy	H	Et	>98/2	96/4	56
7	**2g**	(*E*)-CH_3CH=CH	H	Et	90/10	88/18	75
8	**2h**	*n*-C_7H_{15}	Me	Et	>98/2	>98/2	87
9	**2i**	*i*-Bu	Me	Et	95/5	94/6	66
10	**2j**	(*E*)-CH_3CH=CH	Me	Et	95/5	95/5	87
11	**2k**	Ph	Me	Et	>98/2	>98/2	73
12	**2l**	*p*-ClC_6H_4	Me	*i*-Pr	80/20	80/20	74
13	**2m**	*p*$MeOC_6H_4$	Me	Et	95/5	95/5	81
14	**2n**	*p*-$MeOC_6H_4$	*n*-Bu	Et	97/3	96/4	66
15	**2o**[f]	Ph	H	Et	>98/2	>98/2	62

[a] Unless otherwise noted $R^2 = H$.
[b] Diastereoisomeric ratio of starting materials **1**.
[c] Diastereoisomeric ratio of compounds **2**, determined by GC-MS and/or ^1H NMR (300 MHz) analysis of the crude reaction products.
[d] Yields of the isolated major diastereoisomer (as depicted in table heading) after column chromatography based on compounds **1**.
[e] From morpholine.
[f] $R^2 = Et$.

When we performed this reaction, we obtained the corresponding bromocyclopropane in 91% yield although in an almost exactly 1/1 ratio of stereoisomers. From this result we inferred that this loss of stereoselectivity might be a consequence of the salts present of in the reaction after the *in situ* generation of $CrBr_2$. Next attempts were directed toward the synthesis of chromium dibromide in the absence of other salts. Masaguer and Bustelo[36] reported the halogenation of a number of elements in the presence of different electron-donating solvents. However these authors were not able to synthesise $CrBr_2$ under these conditions. We approached the synthesis of $CrBr_2$ by undertaking the reaction of chromium with bromine in the presence of ether as electron-donor solvent. After vigorous stirring of an equimolecular mixture of chromium and deoxygenated bromine at 33 °C for 3 days in deoxygenated and dry ether, $CrBr_2$ was formed as a white solid (Scheme 2).[37]



Scheme 2. Synthesis of chromium dibromide.

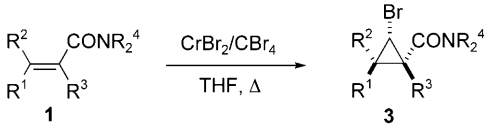
The white solid was thoroughly washed with distilled and deoxygenated ether, dried under vacuum and finally kept under nitrogen.

With the chromium(II) bromide in hand, we tested different conditions for the bromocyclopropanation process. The best results were obtained after treatment of cinnamamide **1** with 6 equivalents of $CrBr_2$ and 2 equivalents of CBr_4 in THF, at reflux. Thus, bromocyclopropanamide was obtained in high yield (76%), as a single stereoisomer, and in the absence of chlorocyclopropanamide (see Table 4).

The reaction of a range of (*E*)-α,β-unsaturated amides **1** with $CrBr_2/CBr_4$ at reflux for 16 h afforded the corresponding bromocyclopropanecarboxamides **3** in moderate to high yields (Table 2).

It is important to note that the relative configuration of the double bond of the starting amides was conserved in the cyclopropanation, as it was established by performing the reaction on the corresponding (*Z*)-unsaturated amides with $CrCl_2/CCl_4$ and $CrBr_2/CBr_4$ to afford compounds **4** and **5**, respectively (Table 3). In these cases the geometry of the alkene was also conserved and no differences were observed during the halocyclopropanation process of (*E*)- or (*Z*)-α,β-unsaturated amides, except for the different

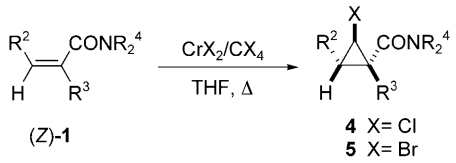
Table 2. Synthesis of bromocyclopropanecarboxamides **3**.



Entry	3	R^1	R^2	R^3	R^4	*dr*[a]	*dr*[b]	Yield [%][c]
1	**3a**	Me	H	H	Et	>98/2	>98/2	61
2	**3b**	*n*-C_5H_{11}	H	H	Et	95/5	95/5	66
3	**3c**	*i*-Bu	H	H	Et	93/7	92/8	69
4	**3d**	Cy	H	H	Et	96/4	96/4	66
5	**3e**	(*E*)-CH_3CH=CH	H	H	Et	90/10	84/16	67
6	**3f**	*n*-C_7H_{15}	H	Me	Et	>98/2	>98/2	62
7	**3g**	*i*-Bu	H	Me	*i*-Pr	90/10	91/9	60
8	**3h**	Cy	H	Me	Et	>98/2	>98/2	73
9	**3i**	Ph	H	Me	Et	>98/2	>98/2	63
10	**3j**	*p*-ClC_6H_4	H	Me	*i*-Pr	>98/2	97/3	65
11	**3k**	*p*-$MeOC_6H_4$	H	*n*-Bu	Et	>98/2	>98/2	61
12	**3l**	Et	Et	Me	Et	75/25	75/25	59
13	**3m**	*n*-Pr	Me	Me	Et	70/30	70/30	56
14	**3n**	Ph	Et	Me	Et	95/5	95/5	63

[a] *dr* of starting materials **1**.
[b] *dr* of compounds **3** determined by GC-MS and/or ^{1}H NMR (300 MHz) analysis of the crude reaction products.
[c] Yields of the isolated products (major diastereoisomer as depicted in table heading) after column chromatography based on compounds **1**.

Table 3. Halocylopropanation of (*Z*)-α,β-unsaturated amides.



Entry	4 or 5	R^2	R^3	R^4	X	*dr*[a]	Yield [%][b]
1	**4a**	*n*-C_5H_{11}	H	Me	Cl	76/24[c]	81
2	**4b**	Ph	H	Et	Cl	>98/2	72
3	**4c**	*p*-ClC_6H_4	Me	*i*-Pr	Cl	>98/2	61
4	**5a**	*n*-C_5H_{11}	H	Me	Br	78/22[c]	82
5	**5b**	*p*-ClC_6H_4	Me	*i*-Pr	Br	>98/2	59

[a] Determined by GC-MS and/or ^{1}H NMR (300 MHz) analysis of the crude reaction products.
[b] Yields of the isolated major stereoisomer (as depicted in table heading) after column chromatography based on compounds (*Z*)-**1**.
[c] *dr* of the starting amide 78/22.

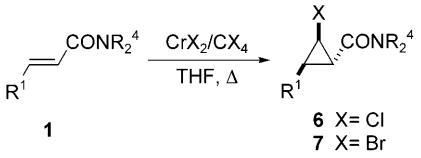
relative position of the halogen atom in compounds **2** or **3** (*cis*), and **4** or **5** (*trans*) with respect to the amide group.[38] This fact will be explained in the mechanistic proposal.

Several points relating to chloro- and bromocyclopropanation processes are worth noting: (1) this halocyclopropanation reaction seems to be general and can be carried out on aliphatic (linear, cyclic, branched and unsaturated), and aromatic (with electron-donating or electron-withdrawing substituents) α,β-unsaturated amides **1**. (2) The cyclopropanation took place with total chemoselectivity since the polyunsaturated amides (Table 1, entries 7 and 10/Table 2, entry 5) were monocyclopropanated on the α,β-double bond. (3) The stereoselectivity or yield of the halocyclopropanation process was not affected by the groups attached to the amide nitrogen in the starting compounds (R^4=Me, Et, *i*-Pr and morpholine[39]). (4) This halocyclopropanation process took place with α,β-unsaturated amides **1** in which C=C bond is di-, tri-, or tetrasubstituted.

According to the silylcyclopropanation model,[30] the relative position of the halogen atom in the cyclopropanes obtained from disubstituted (*E*)-cinnamamides was opposite with respect to that obtained from the other unsaturated amides, (*trans* with respect to the carboxamide group). As can be observed in Table 4, the reaction from disubstituted cinnamamides also took place with total stereoselectivity and in high yields. Substituents on the aromatic ring and the amine on cinnamamides (R^4=Me, Et, *i*-Pr or morpholine) did not affect the yield and the stereoselectivity, except for *p*-nitrocinnamamide (Table 4, entry 6), with which no reaction took place.

The different relative positions of substituents on halocyclopropanes **2–7** were established by analysis of the ^{1}H NMR coupling constants of the cyclopropane protons and from the NOESY experiments of cyclo-

Table 4. Halocyclopropanation of disubstituted cinnamamides.



1

6 X= Cl
7 X= Br

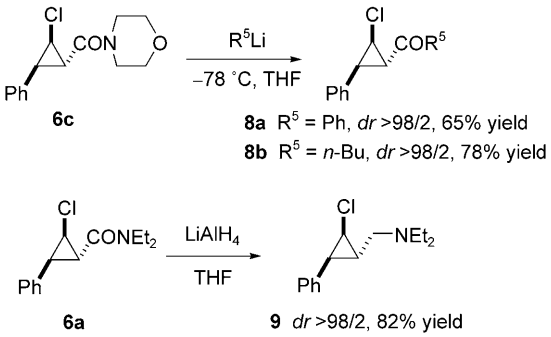
Entry	**6** or **7**	R^1	R^4	X	*dr*[a]	Yield [%][b]
1	**6a**	Ph	Et	Cl	>98/2	91
2	**6b**	Ph	*i*-Pr	Cl	>98/2	92
3	**6c**	Ph	[c]	Cl	>98/2	78
4	**6d**	*p*-FC_6H_4	Et	Cl	91/9[d]	74
5	**6e**	*p*-$MeOC_6H_4$	Et	Cl	>98/2	85
6	**6f**	*p*-$NO_2C_6H_4$	Et	Cl	–	*No reaction*
7	**7a**	Ph	Et	Br	>98/2	76
8	**7b**	Ph	*i*-Pr	Br	>98/2	76
9	**7c**	Ph	[c]	Br	90/10	69
10	**7d**	*p*-FC_6H_4	Et	Br	92/8	70
11	**7e**	*p*-$MeOC_6H_4$	Et	Br	96/4	69

[a] Determined by GC-MS and/or ^{1}H NMR (300 MHz) analysis of the crude reaction products.
[b] Yields of the isolated major diastereoisomer (as depicted in table heading) after column chromatography based on compounds **1**.
[c] From morpholine.
[d] *dr* of the starting amide 93/7.

propylamides **2b**, **2f**, **2i**, **2k**, **2o**, **3e**, **4a–c**, **5b**, **6a**, and **7e**. The relative configurations of **4c**, **5b**, **7e**, and **6c** were unambiguously assigned based on the studies of single-crystal X-ray diffraction of **4c**, **5b**, **7e** and ketone **8a** derived from **6c** (see below) since in our hands, no recrystallization of compounds **6** has been possible. The X-ray determinations confirmed the structural NOESY assignments of products **4c**, **5b**, **7e** and **8a** and the assignments of the other compounds were made by analogy.[40]

We also attempted the synthesis of iodocyclopropanes employing $CrCl_2/CHI_3$, $CrBr_2/CHI_3$, and $CrCl_2/CI_4$ under several conditions but no iodocyclopropanes were obtained except when a $CrCl_2/CHI_3$ mixture was used. In this latter case, a mixture of iodocyclopropane/cyclopropane in a 1/3 ratio was obtained.

To illustrate some synthetic possibilities of this method, the amide derived from morpholine[41] **6c** was transformed into the corresponding phenyl **8a** or butyl ketone **8b**, by reaction with phenyllithium and *n*-butyllithium, respectively at −78 °C for one hour. As was previously indicated, the X-ray analysis of compound **8a** was utilized to confirm the structure for **6**. In addition, cyclopropylamine **9** was also accessed by treatment of **6a** with $LiAlH_4$ at reflux (Scheme 3). Chlorocyclopropyl ketones **8a** and **8b**, and chlorocyclopropylamine **9** were isolated without any loss of diastereoisomeric purity and in high yields (Scheme 3).

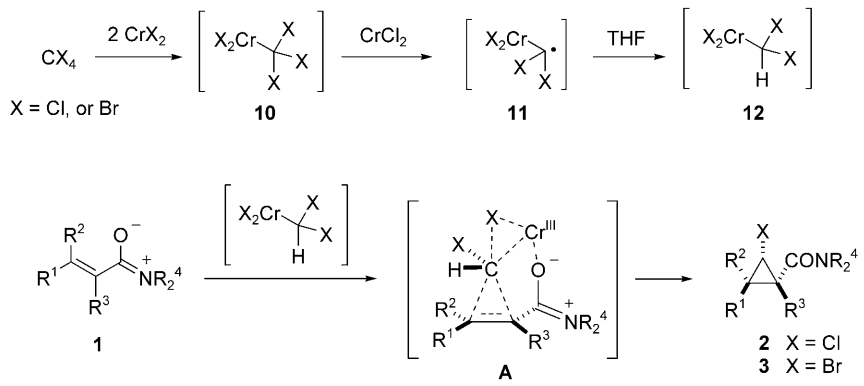


Scheme 3. Transformations of chlorocyclopropanamides **6a** and **6c**.

In most of the reactions reported in Table 1, Table 2, Table 3, and Table 4, only one diastereoisomer of compounds **2–7** was obtained. When a mixture of diastereoisomers was observed in the crude materials, the diastereoisomeric ratio was the same as that shown by the starting unsaturated amides. Thus, the new stereogenic centre was generated with total or very high stereoselectivity.

Mechanism

This halocyclopropanation process could be explained by assuming the initial formation of a chromium(III) carbenoid intermediate **10**, after the reaction of 2 equivalents of CrX_2 with 1 equivalent of CX_4 (X = Cl, or Br). This carbenoid could undergo a single electron transfer from another equivalent of CrX_2 to afford a radical intermediate **11**, which subsequently could abstract a hydrogen atom from the THF to afford the cyclopropanating carbenoid **12**.[42] After generating the carbenoid **12**, this intermediate could react with α,β-unsaturated amides **1** to give the corresponding halocyclopropanes, through a similar mechanism to that proposed by Houk for the addition of carbenoids to olefins.[43] Tentatively, we propose transition state model **A** depicted in Scheme 4, in which the coordination of the Cr(III) centre with the oxygen atom of the amide group provides the obtained cyclopropylamides **2–7**, while maintaining the C=C bond geometry, explaining the different relative configurations of the products obtained from *Z*- or *E*-unsaturated amides.[44] The generation of the new stereogenic centre with total or high stereoselectivity could be explained based on the steric hindrance between the halogen atom and R^1 and/or R^2. Thus, to minimise the steric hindrances, the halogen atom could occupy a *cis* relative position with respect to the H (R^2 = H, *E*-amides) or (R^1 = H, *Z*-amides). Similarly, this steric hindrance could explain the absence of halocyclopropanation in the tetrasubstituted amides due to R^1 and $R^2 \neq H$.



Scheme 4. Proposed mechanism.

A variety of experimental results indirectly support this mechanism. Thus, an alternative synthesis of compounds **2** and **4** from the corresponding *gem*-dichlorocyclopropane (through a metallation process) should be discarded since the treatment of 2,2-dichloro-*N,N*-diethyl-1-methylcyclopropanecarboxamide with 2 equivalents of $CrCl_2$ afforded the unchanged starting dichlorocyclopropane. In addition, when the chlorocyclopropanation reaction of *N,N*-diethylcinnamamide **1** was quenched with a DCl solution in D_2O, no deuterated chlorocyclopropane was obtained. The stoichiometry of this reaction (CCl_4/$CrCl_2$ 1/3) is also in accordance with the proposed $CrCl_2$-metallation of two C–Cl bonds, which would give an anionic and a radical intermediate. For this reason, generation of *gem*-dichromium species from CCl_4 should be also discarded.[45] In addition, when lower amounts of $CrCl_2$ were used the cyclopropanation was incomplete. The generation of a radical intermediate could be also supported by the presence of 40% of the starting cinnamamide when the cyclopropanation was carried out in the presence of AIBN.

The essential coordination between the Cr(III) centre and the oxygen atom of the α,β-unsaturated amides would be consistent with the absence of cyclopropanation of α,β-unsaturated esters (weaker electron-donating character of the oxygen of esters than nitrogen of amides). All experimental results were in accordance with this proposed mechanism except the relative configuration of the CH–X (X = Cl, or Br) bond obtained from *E*-cinnamamides. In this case, stereoelectronic effects could control the cyclopropanation, since the presence of an electron-withdrawing group in the phenyl ring returned the starting material unaltered (Table 4, entry 6).

Conclusions

In conclusion, we have described a general chromium(II)-promoted halocyclopropanation of α,β-unsaturated amides, which takes place with total or high stereoselectivity and in high yields. A simple and new synthesis of chromium(II) bromide, to promote the bromocyclopropanation reaction, is also described. Cyclopropanamides could be transformed into other synthetically valuable compounds such as chlorocyclopropyl ketones or amines, without any loss of diastereoisomeric purity. To explain the halocyclopropanation reaction, a mechanism is proposed. Studies aimed towards fully delineating the factors involved in this transformation, including explanation of the relative configuration of halocyclopropanamides from cinnamamides, and the synthesis of enantiopure halocyclopropylamides are currently under investigation in our laboratory.

Experimental Section

General

All reactions involving organometallic or other moisture-sensitive reagents were carried out under a nitrogen or argon atmosphere using standard vacuum-line techniques and glassware that was flame-dried and cooled under nitrogen before use. THF was distilled from sodium/benzophenone ketyl immediately prior to use. All other solvents were used as supplied (analytical or HPLC grade) without prior purification. All reagents were purchased in the highest quality available and were used without further purification. Organic layers were dried over Na_2SO_4. Thin layer chromatography was performed on aluminium plates coated with 60 F_{254} silica. Plates were visualised using UV light (254 nm), iodine, 1% aqueous $KMnO_4$, or 10% ethanolic phosphomolybdic acid. Flash column chromatography was performed on Kieselgel 60 silica. NMR spectra were recorded in the deuterated solvent stated and the field was locked by external referencing to the relevant deuteron resonance. ^{1}H NMR spectra were recorded on spectrometers at 300 or 400 MHz. ^{13}C NMR spectra and DEPT experiments were determined at 75 or 100 MHz. Unless otherwise stated NMR spectra were recorded at room temperature. Chemical shifts are given in ppm relative to tetramethylsilane (TMS),

which is used as an internal standard. GC-MS and HR-MS were measured at 70 eV. Only the most important IR absorptions (in cm^{-1}) and the molecular ions and/or base peaks in MS are given.

Synthesis of Chlorocyclopropanes 2, 4, and 6

To a suspension of anhydrous $CrCl_2$ (1.5 mmol, 3.0 equiv.) in THF (5 mL) was added the corresponding α,β-unsaturated amide **1** (0.5 mmol, 1.0 equiv.) in THF (2 mL) and CCl_4 (0.5 mmol, 1 equiv.) at room temperature and under an inert atmosphere. After stirring for 16 h at reflux the reaction mixture was quenched by the addition of 1.0 M aqueous HCl (5 mL) and extracted with diethyl ether (3×10 mL). The combined extracts were washed with saturated NH_4Cl solution and water, dried over Na_2SO_4, concentrated under vacuum and filtered through a pad of Celite®. Purification by column chromatography on silica gel (hexane/EtOAc, 10:1) afforded pure compounds **2**, **4**, and **6**.

(1*S,2*S**,3*R**)-2-Chloro-*N*,*N*-diethyl-3-methylcyclopropanecarboxamide (2a):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.52 (dd, J = 7.6, 3.2 Hz, 1H, C*H*Cl), 3.47–3.32 (m, 4H, N(CH_2CH$_3$)$_2$), 1.77–1.65 (m, 1H, C*H*CO), 1.60 (dd, J = 5.7, 3.2 Hz, 1H, C*H*CH$_3$), 1.28 (d, J = 6.3 Hz, 3H, CHCH_3), 1.23 (t, J = 7.0 Hz, 3H, NCH$_2$CH_3), 1.10 (t, J = 7.0 Hz, 3H, NCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.3 (C), 42.2 (CH_2), 40.9 (CH_2), 40.3 (CH), 29.6 (CH), 21.4 (CH), 14.9 (CH_3), 13.1 (CH_3), 12.3 (CH_3); MS (70 eV, EI): *m/z* (%) = 189 [M^+] (16), 154 (97), 119 (68), 72 (97), 58 (100); IR (neat): ν = 2976, 1632, 1485, 1150 cm^{-1}; HR-MS (70 eV): *m/z* = 189.0882, calcd. for $C_9H_{16}ClNO$: 189.0920; R_f = 0.63 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*R**)-2-Chloro-*N*,*N*-dimethyl-3-pentylcyclopropanecarboxamide (2b):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.56 (dd, J = 6.9, 3.2 Hz, 1H, C*H*Cl), 3.16 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 1.78–1.71 (m, 1H, C*H*CO), 1.68–1.56 [m, 4H, CH(CH_2)$_2$], 1.53–1.43 [m, 1H, C*H*-(CH$_2$)$_4$], 1.40–1.26 [m, 4H, (CH_2)$_2$CH$_3$], 0.91 [t, J = 7.0 Hz, 3H, (CH$_2$)$_4$CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3 (C), 40.0 (CH), 37.2 (CH_3), 35.7 (CH_3), 31.4 (CH_2), 28.5 (CH_2), 28.4 (CH), 27.6 (CH_2), 27.3 (CH), 22.4 (CH_2), 13.9 (CH_3); MS (70 eV, EI): *m/z* (%) = 217 [M^+] (11), 182 (100), 146 (11), 102 (10), 68 (47); IR (neat): ν = 3054, 2987, 1634, 1265 cm^{-1}; HR-MS (70 eV); *m/z* = 217.1185, calcd. for $C_{11}H_{20}ClNO$: 217.1233; R_f = 0.55 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*R**)-2-Chloro-*N*,*N*-diethyl-3-pentylcyclopropanecarboxamide (2c):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.54 (dd, J = 6.4, 3.8 Hz, 1H, C*H*Cl), 3.48–3.31 [m, 4H, N(CH_2CH$_3$)$_2$], 1.67–1.56 [m, 5H, C*H*CO, CH-(CH_2)$_2$], 1.50–1.40 [m, 1H, C*H*(CH$_2$)$_4$], 1.36–1.30 [m, 4H, (CH_2)$_2$CH$_3$], 1.24 (t, J = 7.0 Hz, 3H, NCH$_2$CH_3), 1.10 (t, J = 7.0 Hz, 3H, NCH$_2$CH_3), 0.88 [t, J = 7.0 Hz, 3H, (CH$_2$)$_4$CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.4 (C), 42.1 (CH_2), 40.8 (CH_2), 40.1 (CH), 31.4 (CH_2), 28.6 (CH), 28.4 (CH_2), 27.6 (CH_2), 27.0 (CH), 22.4 (CH_2), 15.0 (CH_3), 13.9 (CH_3), 13.1 (CH_3); MS (70 eV, EI): *m/z* (%) = 210 [M^+−Cl] (100), 169 (8), 152 (5), 137 (6), 68 (10); IR (neat): 3054, 2934, 1627, 1265 cm^{-1}; HR-MS (70 eV): *m/z* = 210.1860, calcd. for [$C_{13}H_{24}ClNO$−Cl]: 210.1857; R_f = 0.50 (hexane/EtOAc, 1:1).

4-[(1*S,2*S**,3*R**)-2-Chloro-3-pentylcyclopropylcarbon-1-yl]morpholine (2d):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74–3.56 (m, 9H, C*H*Cl,*H* from morpholine), 1.71–1.26 [m, 10H, C*H*(CH_2)$_4$CH$_3$, C*H*CO], 0.90 (apparent t, 3H, CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.9 (C), 66.6 (2 x CH_2), 45.9 (CH_2), 42.4 (CH_2), 39.8 (CH), 31.3 (CH_2), 28.4 (CH_2), 28.1 (CH), 27.5 (CH_2), 27.3 (CH), 22.4 (CH_2), 13.9 (CH_3); MS (70 eV, EI): *m/z* (%) = 259 [M^+] (3), 224 (100), 181 (28), 118 (27), 69 (45); IR (neat): ν = 2927, 1634, 1463, 1236 cm^{-1}; HR-MS (70 eV): *m/z* = 259.1317, calcd. for $C_{13}H_{22}ClNO_2$: 259.1339; R_f = 0.50 (hexane/EtOAc, 1:1)

(1*S,2*S**,3*R**)-2-Chloro-*N*,*N*-diethyl-3-isobutylcyclopropanecarboxamide (2e):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55 (dd, J = 7.3, 3.5 Hz, 1H, C*H*Cl), 3.48–3.35 (m, 4H, N(CH_2CH$_3$)$_2$), 1.84–1.64 (m, 2H, C*H*CO, C*H*CH$_2$), 1.63–1.42 [m, 3H, (CH$_3$)$_2$C*H*CH_2], 1.25 (t, J = 7.0 Hz, 3H, NCH$_2$CH_3), 1.21 (t, J = 7.0 Hz, 3H, NCH$_2$CH_3), 0.97 [d, J = 7.6 Hz, 6H, CH(CH_3)$_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.2 (C), 42.0 (CH_2), 40.7 (CH_2), 40.0 (CH), 36.3 (CH_2), 28.5 (CH), 27.8 (CH), 25.4 (CH), 22.3 (CH_3), 22.1 (CH_3), 14.8 (CH_3), 13.0 (CH_3); MS (70 eV, EI): *m/z* (%) = 196 [M^+−Cl] (100), 188 (21), 174 (20), 119 (56), 72 (53); IR (neat): ν = 3055, 2985, 1628, 1265 cm^{-1}; HR-MS (70 eV): *m/z* = 196.1732, calcd. for [$C_{12}H_{22}ClNO$−Cl]: 196.1701; R_f = 0.73 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*R**)-2-Chloro-3-cyclohexyl-*N*,*N*-diethylcyclopropanecarboxamide (2f):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.57 (dd, J = 7.5, 3.2 Hz, 1H, C*H*Cl), 3.52–3.28 [m, 4H, N(CH_2CH$_3$)$_2$], 1.80–1.65 (m, 1H, C*H*CO), 1.72 (dd, J = 6.3, 3.2 Hz, 1H, C*H*Cy), 1.56–1.47 [m, 1H, C*H*(CH$_2$)$_5$], 1.35–1.17 [m, 10H, CH(CH_2)$_5$], 1.27 (t, J = 7.1 Hz, 3H, NCH$_2$CH_3), 1.12 (t, J = 7.1 Hz, 3H, NCH$_2$CH_3);^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5 (C), 42.1 (CH_2), 40.8 (CH_2), 39.9 (CH), 37.1 (CH), 33.2 (CH), 32.6 (CH_2), 32.3 (CH_2), 27.5 (CH), 26.2 (CH_2), 26.1 (CH_2), 25.7 (CH_2), 15.0 (CH_3), 13.1 (CH_3); MS (70 eV, EI): *m/z* (%) = 257 [M^+] (2), 222 (100), 174 (19), 100 (41), 72 (53); IR (neat): 2926, 2851, 1633, 1483 cm^{-1}; HR-MS (70 eV): *m/z* = 257.1560, calcd. for $C_{14}H_{24}ClNO$: 257.1546; R_f = 0.73 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*R**)-2-Chloro-*N*,*N*-diethyl-3-(propen-1-yl)cyclopropanecarboxamide (2g):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.75–5.61 (m, 1H, CH$_3$C*H*=CH), 5.25 (dd, J = 15.2, 8.8 Hz, 1H, CH$_3$CH=C*H*), 3.54 (dd, J = 7.6, 3.8 Hz, 1H, C*H*Cl), 3.40–3.23 [m, 4H, N(CH_2CH$_3$)$_2$], 2.20 (dd, J = 13.9, 7.6 Hz, 1H, C*H*CO), 1.83 (apparent t, J = 3.8 Hz, 1H, CH$_3$CH=CHC*H*), 1.62 (dd, J = 6.9, 1.3 Hz, 3H, CH_3CH=CH), 1.14 (t, J = 6.9 Hz, 3H, NCH$_2$CH_3), 1.01 (t, J = 6.9 Hz, 3H, NCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.6 (C), 129.7 (CH), 125.4 (CH), 42.2 (CH_2), 40.9 (CH_2), 39.3 (CH), 29.8 (CH), 29.6 (CH), 18.1 (CH_3), 14.9 (CH_3), 13.1 (CH_3); MS (70 eV, EI) *m/z* (%) = 215 [M^+] (2), 180 (100), 100 (37), 79 (22), 72 (38); IR (neat): ν = 3054, 2985, 1629, 1265 cm^{-1}; HR-MS (70 eV): *m/z* = 215.1087, calcd. for $C_{11}H_{18}ClNO$: 215.1077; R_f = 0.78 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*R**)-2-Chloro-*N*,*N*-diethyl-3-heptyl-1-methylcyclopropanecarboxamide (2h):** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48–3.21 [m, 4H, N(CH_2CH$_3$)$_2$], 3.36 (d, J = 7.0 Hz, 1H, C*H*Cl), 1.52–1.04 [m, 19H, C*H*-(CH_2)$_6$CH$_3$, N(CH$_2$CH_3)$_2$], 1.23 (s, 3H, CCH_3), 0.87 [apparent t, J = 6.6 Hz, 3H, (CH$_2$)$_6$CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.5 (C), 41.7 (CH), 40.9 (CH_2), 38.8 (CH_2), 31.7 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 28.5 (CH_2), 28.0 (C), 25.3 (CH), 23.2 (CH_2), 22.5 (CH_2), 13.9 (CH_3), 13.6 (CH_3), 12.3 (CH_3), 11.5 (CH_3); MS (70 eV, EI): *m/z* (%) = 287 [M^+] (1), 252 (100), 188 (45), 100 (37), 72 (39); IR (neat): ν =

3054, 2929, 1630, 1265 cm^{-1}; HR-MS (70 eV): m/z = 287.2045, calcd. for $C_{16}H_{30}ClNO$: 287.2016; R_f = 0.40 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Chloro-*N*,*N*-diethyl-3-isobutyl-1-methylcyclopropanecarboxamide (2i):** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.53–3.22 [m, 4H, $N(CH_2CH_3)_2$], 3.38 (d, J = 8.2 Hz, 1H, C*H*Cl), 1.81–1.68 (m, 1H, C*H*CH_2), 1.46–1.04 [m, 9H, $N(CH_2CH_3)_2$, $CH_2CH(CH_3)_2$], 1.23 (s, 3H, CCH_3), 0.98 [d, J = 7.0 Hz, 6H, $CH(CH_3)_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6 (C), 41.9 (CH), 41.0 (CH_2), 38.8 (CH_2), 31.8 (CH_2), 27.9 (C), 27.8 (CH), 23.8 (CH), 22.4 (CH_3), 22.3 (CH_3), 13.6 (CH_3), 12.4 (CH_3), 11.7 (CH_3); MS (70 eV, EI): m/z (%) = 245 [M^+] (2), 210 (100), 154 (18), 100 (23), 72 (24); IR (neat): ν = 2960, 1636, 1458, 1266 cm^{-1}; HR-MS (70 eV): m/z = 245.1567, calcd. for $C_{13}H_{24}ClNO$: 245.1546; R_f = 0.30 (hexane/EtOAc, 5:1).

(1*S,2*S**,3*R**)-2-Chloro-*N*,*N*-diethyl-1-methyl-3-(propen-1-yl)cyclopropanecarboxamide (2j):** White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.84 (dq, J = 6.4 Hz, 1H, CH_3CH= CH), 5.31–5.19 (m, 1H, CH_3CH=C*H*), 3.55 (d, J = 8.3 Hz, 1H, C*H*Cl), 3.48–3.29 [m, 4H, $N(CH_2CH_3)_2$], 2.03 (apparent t, J = 8.3 Hz, 1H, CH_3CH=CHC*H*), 1.77 (d, J = 6.4 Hz, 3H, CH_3CH=CH), 1.30 (s, 3H, CCH_3), 1.27–1.06 [m, 6H, $N(CH_2CH_3)_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.9 (C), 130.9 (CH), 122.4 (CH), 42.2 (CH), 40.9 (CH_2), 38.8 (CH_2), 30.2 (C), 28.6 (CH), 18.4 (CH_3), 13.7 (CH_3), 12.4 (CH_3), 12.1 (CH_3); MS (70 eV, EI): m/z (%) = 229 [M^+] (12), 228 (100), 181 (9), 100 (10), 72 (11); IR (neat): ν = 3055, 2987, 1634, 1266 cm^{-1}; HR-MS (70 eV): m/z = 229.1197, calcd. for $C_{12}H_{20}ClNO$: 229.1233; R_f = 0.65 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*R**)-2-Chloro-*N*,*N*-diethyl-1-methyl-3-phenylcyclopropanecarboxamide (2k):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.21 (m, 5H, *Ph*), 3.69 (d, J = 8.2 Hz, 1H, C*H*Cl), 3.60–3.32 [m, 4H, $N(CH_2CH_3)_2$], 2.73 (d, J = 8.2 Hz, 1H, C*H*Ph), 1.25 (s, 3H, CCH_3), 1.31–1.10 [m, 6H, $N(CH_2CH_3)_2$]; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.7 (C), 133.2 (C), 130.4 (2×CH), 128.0 (2×CH), 126.6 (CH), 41.6 (CH), 41.0 (CH_2), 39.0 (CH_2), 30.6 (C), 29.0 (CH), 13.6 (CH_3), 13.5 (CH_3), 12.3 (CH_3); MS (70 eV, EI): m/z (%) = 265 [M^+] (<1), 230 (100), 129 (34), 115 (16), 72 (20); IR (neat): ν = 2974, 1637, 1428, 1282 cm^{-1}; HR-MS (70 eV): m/z = 265.1260, calcd. for $C_{15}H_{20}ClNO$: 265.1233; R_f = 0.57 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*R**)-2-Chloro-3-(4-chlorophenyl)-1-methyl-*N*,*N*-diisopropylcyclopropanecarboxamide (2l):** Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.3 Hz, 2H, *p*-ClC_6H_4), 6.96 (d, J = 8.3 Hz, 2H, *p*-ClC_6H_4), 4.36–4.21 [m, 1H, $NCH(CH_3)_2$], 3.64 (d, J = 7.9 Hz, 1H, C*H*Cl), 3.44–3.24 [m, 1H, $NCH(CH_3)_2$], 2.65 (d, J = 7.9 Hz, 1H, C*H*Ph), 1.47–1.11 {m, 12H, $N[CH(CH_3)_2]_2$}, 1.17 (s, 3H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0 (C), 135.3 (C), 132.0 (C), 131.8 (2×CH), 128.3 (2×CH), 48.7 (CH), 45.7 (CH), 41.5 (CH), 32.1 (C), 31.4 (CH), 28.6 (CH_3), 20.4 (CH_3), 20.0 (CH_3), 13.9 (CH_3), 13.4 (CH_3); MS (70 eV, EI): m/z (%) = 327 [M^+] (< 1), 291 (6), 192 (100), 163 (37), 128 (94); IR (neat): ν = 3054, 2972, 1634, 1265 cm^{-1}; HR-MS (FAB$^+$): m/z = 328.1222, calcd. for $C_{17}H_{24}Cl_2NO^+$ [M^++H]$^+$: 328.1229; R_f = 0.70 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*R**)-2-Chloro-*N*,*N*-diethyl-3-(4-methoxyphenyl)-1-methylcyclopropanecarboxamide (2m):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.8 Hz, 2H, *p*-$MeOC_6H_4$), 6.89 (d, J = 8.8 Hz, 2H, *p*-$MeOC_6H_4$), 3.81 (s, 3H, OCH_3), 3.66 (d, J = 8.2 Hz, 1H, C*H*Cl), 3.60–3.27 [m, 4H, $N(CH_2CH_3)_2$], 2.66 (d, J = 8.2 Hz, 1H, C*H*Ph), 1.33–1.11 [m, 9H, $N(CH_2CH_3)_2$, CCH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0 (C), 158.4 (C), 131.6 (2×CH), 125.3 (C), 113.6 (2×CH), 55.1 (CH_3), 41.9 (CH), 41.2 (CH_2), 39.1 (CH_2), 30.7 (C), 28.5 (CH), 13.6 (CH_3), 13.5 (CH_3), 12.5 (CH_3); MS (70 eV, EI): m/z (%) = 260 [M^+−Cl] (18), 259 (100), 230 (83), 202 (26), 131 (50); IR (neat): ν = 3055, 2984, 1630, 1266 cm^{-1}; HR-MS (70 eV): m/z = 260.1623, calcd. for [$C_{16}H_{22}ClNO_2$−Cl]: 260.1650; R_f = 0.60 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*R**)-1-Butyl-2-chloro-*N*,*N*-diethyl-3-(4-methoxyphenyl)cyclopropanecarboxamide (2n):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.5 Hz, 2H, *p*-$MeOC_6H_4$), 6.88 (d, J = 8.5 Hz, 2H, *p*-$MeOC_6H_4$), 3.81 (s, 3H, OCH_3), 3.77 (d, J = 7.9 Hz, 1H, C*H*Cl), 3.66–3.32 [m, 4H, $N(CH_2CH_3)_2$], 2.61 (d, J = 7.9 Hz, 1H, C*H*Ph), 1.62–1.33 [m, 4H, $C(CH_2)_2$], 1.30–1.09 [m, 8H, $N(CH_2CH_3)_2$, $C(CH_2)_2CH_2$], 0.83 [t, J = 7.3 Hz, 3H, $C(CH_2)_3CH_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.6 (C), 158.5 (C), 131.3 (2×CH), 125.5 (C), 113.6 (2×CH), 55.0 (CH_3), 41.9 (CH), 41.1 (CH_2), 39.2 (CH_2), 34.8 (C), 29.3 (CH), 28.1 (CH_2), 27.4 (CH_2), 22.7 (CH_2), 13.8 (CH_3) 13.7 (CH_3), 12.4 (CH_3); MS (70 eV, EI): m/z (%) = 302 [M^+−Cl] (20), 301 (100), 230 (61), 199 (24), 187 (23); IR (neat): ν = 3054, 2961, 1634, 1266 cm^{-1}; HR-MS (70 eV): m/z = 302.2120, calcd. for [$C_{19}H_{28}ClNO_2$−Cl]: 302.212; R_f = 0.68 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*S**)-2-Chloro-*N*,*N*-diethyl-3-ethyl-3-phenylcyclopropanecarboxamide (2o):** Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.09 (m, 5H, *Ph*), 4.28 (d, J = 3.8 Hz, 1H, C*H*Cl), 3.81–3.27 (m, 3H, NCH_2CH_3, $NCHHCH_3$), 3.01–2.85 (m, 1H, $NCHHCH_3$), 2.24–2.13 (m, 1H, $CHHCH_3$), 2.12 (d, J = 3.8 Hz, 1H, C*H*CO), 1.95–1.81 (m, 1H, $CHHCH_3$), 1.32 (t, J = 7.3 Hz, 3H, CH_2CH_3), 0.91 [t, J = 7.3 Hz, 3H, NCH_2CH_3], 0.90 (t, J = 7.3 Hz, 3H, NCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0 (C), 137.8 (C), 128.8 (2×CH), 127.9 (2×CH), 126.8 (CH), 42.7 (CH), 41.7 (C), 41.6 (CH_2), 40.0 (CH_2), 35.9 (CH), 30.0 (CH_2), 14.5 (CH_3), 12.4 (CH_3), 10.7 (CH_3); MS (70 eV, EI): m/z (%) = 244 [M^+−Cl] (40), 171 (60), 143 (45), 128 (57), 68 (100); IR (neat): ν = 3055, 2986, 1636, 1265 cm^{-1}; HR-MS (70 eV): m/z = 244.1668, calcd. for [$C_{16}H_{22}ClNO$−Cl]: 244.1701; R_f = 0.67 (hexane/EtOAc, 1:1).

(1*R,2*S**,3*R**)-2-Chloro-*N*,*N*-dimethyl-3-pentylcyclopropanecarboxamide (4a):** Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.45 (apparent t, J = 3.9 Hz, 1H, C*H*Cl), 3.10 (s, 3H, NCH_3), 2.93 (s, 3H, NCH_3), 2.11 (dd, J = 10.7, 3.9 Hz, 1H, C*H*CO), 1.68–1.56 [m, 1H, $CH(CH_2)_4$], 1.45–1.21 [m, 8H, $CH(CH_2)_4$], 0.85 [apparent t, J = 6.9 Hz, 3H, $(CH_2)_4CH_3$]; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1 (C), 37.1 (CH_3), 36.8 (CH), 35.3 (CH_3), 31.4 (CH), 31.1 (CH_2), 28.6 (CH), 28.3 (CH_2), 25.7 (CH_2), 22.3 (CH_2), 13.8 (CH_3); MS (70 eV, EI): m/z (%) = 217 [M^+] (13), 182 (100), 146 (9), 110 (13), 68 (46); IR (neat): ν = 2930, 1640, 1421, 1265 cm^{-1}; HR-MS (70 eV): m/z = 217.1185, calcd. for $C_{11}H_{20}ClNO$: 217.1233; R_f = 0.70 (hexane/EtOAc, 1:1).

(1*R,2*S**,3*R**)-2-Chloro-*N*,*N*-diethyl-3-phenylcyclopropanecarboxamide (4b):** Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.12 (m, 5H, *Ph*), 4.22 (apparent t, J = 4.4 Hz, 1H, C*H*Cl), 3.62–3.40 (m, 2H, NCH_2CH_3), 3.20–3.07 (m, 1H, $NCHHCH_3$), 3.03–2.91 (m, 1H, $NCHHCH_3$), 2.87 (dd, J = 10.7, 5.1 Hz, 1H, C*H*CO), 2.53 (dd, J = 10.7, 4.4 Hz, 1H, C*H*Ph), 1.14 (t, J = 7.0 Hz, 3H, NCH_2CH_3), 0.78 (t, J =

7.0 Hz, 3H, NCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9 (C), 134.2 (C), 128.0 (2×CH), 127.7 (2×CH), 126.8 (CH), 41.3 (CH_2), 39.9 (CH_2), 36.2 (CH), 34.9 (CH), 33.3 (CH), 14.1 (CH_3), 12.3 (CH_3); MS (70 eV, EI): *m/z* (%) = 216 [M^+−Cl] (100), 144 (11), 115 (21), 100 (20), 72 (27); IR (neat): ν = 2975, 1634, 1481, 1141 cm^{-1}; HR-MS (70 eV): *m/z* = 216.1385, calcd. for [$C_{14}H_{18}ClNO$−Cl]: 216.1388; R_f = 0.63 (hexane/EtOAc, 1:1).

(1*R,2*S**,3*R**)-2-Chloro-3-(4-chlorophenyl)-1-methyl-*N*,*N*-diisopropylcyclopropanecarboxamide (4c):** Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.3 Hz, 2H, *p*-ClC_6H_4), 6.95 (d, *J* = 8.3 Hz, 2H, *p*-ClC_6H_4), 4.07 (d, *J* = 5.0 Hz, 1H, C*H*Cl), 3.93–3.84 [m, 1H, NC*H*(CH_3)$_2$], 3.17–3.08 [m, 1H, NC*H*(CH_3)$_2$], 2.21 (d, *J* = 5.0 Hz, 1H, C*H*Ph), 1.59 (s, 3H, CCH_3), 1.34 [d, *J* = 6.6 Hz, 3H, NCH(CH_3)$_2$], 1.22 [d, *J* = 6.6 Hz, 3H, NCH(CH_3)$_2$], 1.13 [d, *J* = 6.6 Hz, 3H, NCH(CH_3)$_2$], 0.17 [d, *J* = 6.6 Hz, 3H, NCH(CH_3)$_2$]; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7 (C), 135.3 (C), 132.6 (C), 128.4 (2×CH), 127.9 (2×CH), 48.4 (CH), 45.9 (CH), 44.6 (CH), 40.3 (CH), 38.8 (C), 20.8 (CH_3), 19.9 (CH_3), 19.8 (2×CH_3), 18.1 (CH_3); MS (70 eV, EI): *m/z* (%) = 327 [M^+] (20), 312 (100), 192 (42), 157 (44), 118 (72); IR (neat): ν = 2975, 1625, 1496, 1265 cm^{-1}; HR-MS (70 eV): *m/z* = 327.1217, calcd. for $C_{17}H_{23}Cl_2NO$: 327.1157; R_f = 0.83 (hexane/EtOAc, 1:1).

(1*S,2*R**,3*S**)-2-Chloro-*N*,*N*-diethyl-3-phenylcyclopropanecarboxamide (6a):** Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.27 (m, 5H, *Ph*), 3.80 (dd, *J* = 7.2, 3.8 Hz, 1H, C*H*Cl), 3.54 (q, *J* = 7.1 Hz, 2H, NCH_2CH$_3$), 3.45 (q, *J* = 7.1 Hz, 2H, NCH_2CH$_3$), 3.01 (apparent t, *J* = 7.2 Hz, 1H, C*H*CO), 2.45 (dd, *J* = 6.3, 3.8 Hz, 1H, C*H*Ph), 1.31 (t, *J* = 7.1 Hz, 3H, NCH$_2$CH_3), 1.16 (t, *J* = 7.1 Hz, 3H, NCH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5 (C), 134.2 (C), 128.8 (2×CH), 128.0 (2×CH), 127.0 (CH), 42.3 (CH_2), 41.0 (CH_2), 39.8 (CH), 31.3 (CH), 28.0 (CH), 15.0 (CH_3), 13.0 (CH_3); MS (70 eV, EI): *m/z* (%) = 251 [M^+] (3), 216 (100), 144 (14), 115 (73), 100 (45), 72 (56); IR (neat): ν = 2975, 1633, 1462, 1270 cm^{-1}; HR-MS (70 eV): *m/z* = 251.1100, calcd. for $C_{14}H_{18}ClNO$: 251.1077; R_f = 0.63 (hexane/EtOAc, 1:1).

(1*S,2*R**,3*S**)-2-Chloro-3-phenyl-*N*,*N*-diisopropylcyclopropanecarboxamide (6b):** Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 5H, *Ph*), 4.30–4.10 [m, 1H, NC*H*(CH_3)$_2$], 4.06–3.87 [m, 1H, NC*H*(CH_3)$_2$], 3.79 (dd, *J* = 7.6, 3.5 Hz, 1H, C*H*Cl), 3.01 (apparent t, *J* = 7.3 Hz, 1H, C*H*CO), 2.49 (dd, *J* = 6.9, 3.5 Hz, 1 H ,C*H*Ph), 1.40–1.30 {m, 12H, N[CH(CH_3)$_2$]$_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1 (C), 134.4 (C), 128.8 (2×CH), 128.0 (2×CH), 127.0 (CH), 47.3 (CH), 45.8 (CH), 39.5 (CH), 30.8 (CH), 30.1 (CH), 21.7 (CH_3), 21.6 (CH_3), 20.4 (CH_3), 20.3 (CH_3); MS (70 eV, EI): *m/z* (%) = 279 [M^+] (3), 244 (100), 130 (28), 115 (89), 86 (76); IR (neat): ν = 2974, 1631, 1449, 1265 cm^{-1}; HR-MS (70 eV): *m/z* = 279.1408, calcd. for $C_{16}H_{22}ClNO$: 279.1390; R_f = 0.77 (hexane/EtOAc, 1:1).

4-**[(1*S**,2*R**,3*S**)-(2-Chloro-3-phenylcyclopropyl)carbonyl]morpholine (6c):** Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.24 (m, 5H, *Ph*), 3.83 (dd, *J* = 7.9, 3.4 Hz, 1H, C*H*Cl), 3.79–3.64 (m, 8H, *H* from morpholine), 3.01 (apparent t, *J* = 7.2 Hz, 1H, C*H*CO), 2.47 (dd, *J* = 6.6, 3.4 Hz, 1H, C*H*Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.2 (C), 133.9 (C), 128.8 (2×CH), 128.1 (2×CH), 127.2 (CH), 66.5 (2×CH_2), 45.9 (CH_2), 42.5 (CH_2), 39.6 (CH), 31.5 (CH), 27.6 (CH); MS (70 eV, EI): *m/z* (%) = 265 [M^+] (3), 230 (100), 144 (12), 124 (8), 115 (73); IR (neat): ν = 3055, 1636, 1443, 1265 cm^{-1}; HR-MS (70 eV): *m/z* = 265.0864, calcd. for $C_{14}H_{16}ClNO_2$: 265.0870; R_f = 0.45 (hexane/EtOAc, 1:1).

(1*S,2*R**,3*S**)-2-Chloro-*N*,*N*-diethyl-3-(4-fluorophenyl)-cyclopropanecarboxamide (6d):** Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.22 (m, 2H, *p*-FC_6H_4), 7.07–7.01 (m, 2H, *p*-FC_6H_4), 3.75 (dd, *J* = 7.8, 3.9 Hz, 1H, C*H*Cl), 3.53 (q, *J* = 7.0 Hz, 2H, NCH_2CH$_3$), 3.44 (q, *J*- = 7.0 Hz, 2H, NCH_2CH$_3$), 2.98 (apparent t, *J* = 7.5 Hz, 1 H C*H*CO), 2.38 (dd, *J* = 6.9, 3.9 Hz, 1H, C*H*Ph), 1.30 (t, *J* = 7.0 Hz, 3H, NCH$_2$CH_3), 1.16 (t, *J* = 7.0 Hz, 3H, NCH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2 (C), 161.7 (d, $^1J_{CF}$ = 245.1 Hz, C), 130.4 (d, $^3J_{CF}$ = 7.1 Hz, 2×CH), 129.9 (C), 114.9 (d, $^2J_{CF}$ = 21.4 Hz, 2×CH), 42.2 (CH_2), 41.0 (CH_2), 39.6 (CH), 30.4 (CH), 28.2 (CH), 14.9 (CH_3), 12.9 (CH_3); MS (70 eV, EI): *m/z* (%) = 234 [M^+−Cl] (100), 162 (14), 133 (36), 100 (12), 72 (28); IR (neat): ν = 2983, 1636, 1464, 1266 cm^{-1}; HR-MS (70 eV): *m/z* = 234.1301, calcd. for [$C_{14}H_{17}ClFNO$−Cl]: 234.1294; R_f = 0.70 (hexane/EtOAc, 1:1).

(1*S,2*R**,3*S**)-2-Chloro-*N*,*N*-diethyl-3-(4-methoxyphenyl)-cyclopropanecarboxamide (6e):** Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.5 Hz, 2H, *p*-$MeOC_6H_4$), 6.89 (d, *J* = 8.5 Hz, 2H, *p*-$MeOC_6H_4$), 3.81 (s, 3H, OCH_3), 3.75 (dd, *J* = 7.6, 3.5 Hz, 1H, C*H*Cl), 3.51 (q, *J* = 7.1 Hz, 2H, NCH_2CH$_3$), 3.42 (q, *J* = 7.1 Hz, 2H, NCH_2CH$_3$), 2.93 (apparent t, *J* = 7.0 Hz, 1H, C*H*CO), 2.35 (dd, *J* = 6.4, 3.5 Hz, 1H, C*H*Ph), 1.29 (t, *J* = 7.1 Hz, 3H, NCH$_2$CH_3), 1.14 (t, *J* = 7.1 Hz, 3H, NCH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5 (C), 158.4 (C), 129.7 (2×CH), 126.0 (C), 113.3 (2×CH), 54.9 (CH_3), 42.1 (CH_2), 40.8 (CH_2), 39.8 (CH), 30.5 (CH), 28.0 (CH), 14.8 (CH_3), 12.9 (CH_3); MS (70 eV, EI): *m/z* (%) = 246 [M^+−Cl] (100), 230 (28), 216 (17), 188 (17), 100 (9); IR (neat): ν = 2983, 1631, 1463, 1265 cm^{-1}; HR-MS (70 eV): *m/z* = 246.1535, calcd. for [$C_{15}H_{20}ClNO_2$−Cl]: 246.1494; R_f = 0.60 (hexane/EtOAc, 1:1).

Synthesis of Anhydrous $CrBr_2$

To a suspension of anhydrous chromium powder (3.0 mmol) in diethyl ether (30 mL) was added dropwise bromine (3.0 mmol) at room temperature and under an inert atmosphere. After stirring for 72 h at 30 °C a white solid was formed. The solvent was removed by decantation, the solid was washed with anhydrous diethyl ether (3×15 mL) and used without further purification.

Synthesis of Bromocyclopropanes 3, 5, and 7

To a suspension of anhydrous $CrBr_2$ (1.5 mmol, 3.0 equiv.) in THF (5 mL) was added the corresponding α,β-unsaturated amide **1** (0.5 mmol, 1.0 equiv.) in THF (2 mL) and CBr_4 (0.5 mmol, 1 equiv.) at room temperature and under an inert atmosphere. After stirring for 16 h at reflux the reaction mixture was quenched by the addition of 1.0 M aqueous HCl (5 mL) and extracted with diethyl ether (3×10 mL). The combined extracts were washed with saturated NH_4Cl solution and water, dried over Na_2SO_4, concentrated under vacuum and filtered through a pad of Celite®. Purification by column chromatography on silica gel (hexane/EtOAc, 10:1) afforded pure compounds **3**, **5**, and **7.**

(1*S,2*S**,3*R**)-2-Bromo-*N*,*N*-diethyl-3-methylcyclopropanecarboxamide (3a):** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.47–3.30 [m, 5H, N(CH_2CH_3)$_2$, C*H*Br], 1.72–1.56 (m, 2H, C*H*CO, C*H*CH_3), 1.29 (d, J = 6.0 Hz, 3H, CHCH_3), 1.24 (t, J = 7.1 Hz, 3H, NCH_2CH_3), 1.17–1.03 (m, 3H, NCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.5 (C), 42.2 (CH_2), 40.9 (CH_2), 29.9 (CH), 29.8 (CH), 20.8 (CH), 14.9 (CH_3), 14.6 (CH_3), 13.1 (CH_3); MS (70 eV, EI): *m/z* (%) = 233 [M$^+$] (2), 154 (100), 133 (11), 126 (9), 83 (30); IR (neat): ν = 2984, 1629, 739 cm^{-1}; HR-MS (ESI$^+$): *m/z* = 234.0488, calcd. for [C_9H_{17}BrNO]$^+$ [M$^+$ + H]$^+$: 234.0494; R_f = 0.43 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-*N*,*N*-dimethyl-3-pentylcyclopropanecarboxamide (3b):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48–3.31 [m, 5H, N(CH_2CH_3)$_2$, C*H*Br], 1.71 (apparent dd, J = 5.1, 3.8 Hz, 1H, C*H*CO), 1.62–1.28 [m, 9H, C*H*(CH_2)$_4$$CH_3$], 1.24 (t, J = 7.0 Hz, 3H, NCH_2CH_3), 1.10 (t, J = 7.0 Hz, 3H, NCH_2CH_3), 0.88 [t, J = 7.0 Hz, 3H, (CH_2)$_4$$CH_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.5 (C), 42.1 (CH_2), 40.9 (CH_2), 31.4 (CH_2), 29.9 (CH_2), 29.3 (CH), 28.8 (CH), 28.3 (CH_2), 26.3 (CH), 22.4 (CH_2), 15.0 (CH_3), 13.9 (CH_3), 13.1 (CH_3); MS (70 eV, EI): *m/z* (%) = 210 [M$^+$−Br] (100), 181 (38), 131 (51), 100 (27), 69 (26); IR (neat): ν = 2933, 1629, 1461, 740 cm^{-1}; HR-MS (70 eV): *m/z* = 210.1853, calcd. for [$C_{13}H_{24}$BrNO−Br]: 210.1858; R_f = 0.53 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-*N*,*N*-diethyl-3-isobutylcyclopropanecarboxamide (3c):** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.51–3.32 [m, 5H, N(CH_2CH_3)$_2$, C*H*Br], 1.84–1.68 (m, 2H, C*H*CO, C*H*CH_2), 1.64–1.50 [m, 2H, (CH_3)$_2$$CHCH_2$], 1.49–1.38 [m, 1H, ($CH_3$)$_2$$CHCH_2$], 1.24 (t, J = 7.0 Hz, 3H, NCH_2CH_3), 1.11 (t, J = 7.0 Hz, 3H, NCH_2CH_3), 0.96 [d, J = 6.9 Hz, 6H, CH(CH_3)$_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.5 (C), 42.1 (CH_2), 40.9 (CH_2), 38.6 (CH_2), 29.4 (CH), 28.9 (CH), 27.8 (CH), 24.8 (CH), 22.6 (CH_3), 22.1 (CH_3), 15.80 (CH_3), 13.1 (CH_3); MS (70 eV, EI): *m/z* (%) = 196 [M$^+$−Br] (100), 181 (22), 169 (36), 131 (31), 119 (51); IR (neat): ν = 2961, 1628, 1463, 739 cm^{-1}; HR-MS (70 eV): *m/z* = 196.1658, calcd. for [$C_{12}H_{22}$BrNO−Br]: 196.1702; R_f = 0.55 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-3-cyclohexyl-*N*,*N*-diethylcyclopropanecarboxamide (3d):** Orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.49–3.25 [m, 5H, N(CH_2CH_3)$_2$, C*H*Br], 1.98–1.89 (m, 1H, C*H*CO), 1.80–1.59 [m, 2H, C*HCH*(CH_2)$_5$], 1.39–1.04 [m, 10H, CH(CH_2)$_5$], 1.24 (t, J = 7.1 Hz, 3H, NCH_2CH_3), 1.09 (t, J = 7.1 Hz, 3H, NCH_2CH_3);^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.6 (C), 42.1 (CH_2), 40.8 (CH_2), 39.1 (CH), 32.5 (CH_2), 32.3 (CH), 32.0 (CH_2), 28.8 (CH), 27.7 (CH), 26.1 (CH_2), 26.0 (CH_2), 25.6 (CH_2), 15.0 (CH_3), 13.1 (CH_3); MS (70 eV, EI): *m/z* (%) = 301 [M$^+$] (2), 222 (100), 208 (4), 100 (9), 72 (7); IR (neat): ν = 2928, 1626, 1462, 739 cm^{-1}; HR-MS (70 eV): *m/z* = 301.1043, calcd. for $C_{14}H_{24}$BrNO: 301.1041; R_f = 0.50 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-*N*,*N*-diethyl-3-(propen-1-yl)cyclopropanecarboxamide (3e):** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.80–5.67 (m, 1H, CH_3C*H*=CH), 5.35–5.22 (m, 1H, CH_3CH=C*H*), 3.51 (dd, J = 7.6, 3.8 Hz, 1H, C*H*Br), 3.44–3.30 [m, 4H, N(CH_2CH_3)$_2$], 2.21–2.11 (m, 1H, C*H*CO), 1.94 (dd, J = 5.7, 3.8 Hz, 1H, CH_3CH=CHC*H*), 1.70 (dd, J = 6.3, 1.9 Hz, 3H, C*H*$_3$CH=CH), 1.20 (t, J = 7.0 Hz, 3H, NCH_2CH_3), 1.08 (t, J = 7.0 Hz, 3H, NCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.6 (C), 129.5 (CH), 127.2 (CH), 42.2 (CH_2), 40.9 (CH_2), 29.8 (CH), 28.9 (CH), 27.6 (CH), 17.9 (CH_3), 14.9 (CH_3), 13.1 (CH_3); MS (70 eV, EI): *m/z* (%) = 180 [M$^+$−Br] (100), 169 (45), 131 (13), 100 (27), 69 (39); IR (neat): ν = 2981, 1629, 1265, 739 cm^{-1}; HR-MS (70 eV): *m/z* = 180.1375, calcd. for [$C_{11}H_{18}$BrNO−Br]: 180.1389; R_f = 0.50 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-*N*,*N*-diethyl-3-heptyl-1-methylcyclopropanecarboxamide (3f):** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.49–3.22 [m, 4H, N(CH_2CH_3)$_2$], 3.35 (d, J = 7.6 Hz, 1H, C*H*Br), 1.52–1.04 [m, 19H, N-(CH_2C*H*$_3$)$_2$,C*H*(CH_2)$_6$$CH_3$], 1.26 (s, 3H, CC*H*$_3$), 0.89 [apparent t, J = 5.3 Hz, 3H, (CH_2)$_6$C*H*$_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.5 (C), 40.9 (CH_2), 38.8 (CH_2), 34.4 (CH), 31.7 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 28.3 (CH_2), 27.6 (C), 25.4 (CH_2), 24.8 (CH), 22.5 (CH_2), 14.0 (CH_3), 13.7 (CH_3), 13.6 (CH_3), 12.4 (CH_3); MS (70 eV, EI): *m/z* (%) = 252 [M$^+$−Br] (100), 232 (2), 180 (2), 166 (2), 109 (2); IR (neat): ν = 2928, 1630, 1428, 741 cm^{-1}; HR-MS (70 eV): *m/z* = 252.2312, calcd. for [$C_{16}H_{30}$BrNO−Br]: 252.2328; R_f = 0.61 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-3-isobutyl-1-methyl-*N*,*N*-diisopropylcyclopropanecarboxamide (3g):** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.25–4.08 [m, 1H, NC*H*(CH_3)$_2$], 3.39–3.20 [m, 1H, NC*H*(CH_3)$_2$], 3.33 (d, J = 8.2 Hz, 1H, C*H*Br), 1.82–1.66 [m, 2H, C*H*$_2$CH(CH_3)$_2$], 1.45–1.09 {m, 14H, N[CH(C*H*$_3$)$_2$]$_2$, C*H*CH$_2$C*H*(CH_3)$_2$}, 1.21 (s, 3H, CC*H*$_3$), 0.97 [dd, J = 6.3, 2.5 Hz, 6H, CH(C*H*$_3$)$_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0 (C), 48.4 (CH), 45.5 (CH), 34.8 (CH), 34.0 (CH_2), 28.6 (C), 27.7 (CH), 23.3 (CH), 22.4 (2 × CH_3), 22.3 (2 × CH_3), 20.3 (2 × CH_3), 13.7 (CH_3); MS (70 eV, EI): *m/z* (%) = 240 [M$^+$−Br] (100), 198 (9), 101 (14), 96 (11), 68 (11); IR (neat): ν = 2967, 1629, 1439, 740 cm^{-1}; HR-MS (ESI$^+$): *m/z* = 318.1427, calcd. for [$C_{15}H_{29}$BrNO]$^+$ [M$^+$ + H]$^+$: 318.1432; R_f = 0.83 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-3-cyclohexyl-*N*,*N*-diethyl-1-methylcyclopropanecarboxamide (3h):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48–3.16 [m, 4H, N(CH_2CH_3)$_2$], 3.25 (d, J = 7.4 Hz, 1H, C*H*Br), 1.88–1.56 [m, 2H, C*HCH*-(CH_2)$_5$], 1.27 (s, 3H, CC*H*$_3$), 1.25–0.98 [m, 16H, CH(CH_2)$_5$, N(CH_2C*H*$_3$)$_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3 (C), 40.9 (CH_2), 39.0 (CH_2), 35.1 (CH), 33.3 (CH), 31.5 (CH_2), 31.3 (CH_2), 30.2 (CH), 27.8 (C), 26.1 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 14.0 (CH_3), 13.8 (CH_3), 12.4 (CH_3); MS (70 eV, EI): *m/z* (%) = 236 [M$^+$−Br] (100), 163 (7), 153 (5), 121 (5), 72 (6); IR (neat): ν = 2930, 1629, 1429, 739 cm^{-1}; HR-MS (70 eV): *m/z* = 236.2017, calcd. for [$C_{15}H_{26}$BrNO−Br]: 236.2015; R_f = 0.53 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-*N*,*N*-diethyl-1-methyl-3-phenylcyclopropanecarboxamide (3i):** Orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.22 (m, 5H, *Ph*), 3.62 (d, J = 8.0 Hz, 1H, C*H*Br), 3.58–3.23 [m, 4H, N(CH_2CH_3)$_2$], 2.72 (d, J = 8.0 Hz, 1H, C*H*Ph), 1.23 (s, 3H, CC*H*$_3$), 1.31–1.05 [m, 6H, N(CH_2C*H*$_3$)$_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.8 (C), 134.0 (C), 130.5 (2 × CH), 128.0 (2 × CH), 126.7 (CH), 41.1 (CH_2), 39.2 (CH_2), 33.1 (CH), 30.2 (C), 28.6 (CH), 16.0 (CH_3), 13.8 (CH_3), 12.4 (CH_3); MS (70 eV, EI): *m/z* (%) = 230 [M$^+$−Br] (12), 229 (100), 214 (14), 200 (31), 172 (26); IR (neat): ν = 2979, 1630, 1430, 739 cm^{-1}; HR-MS (70 eV): *m/z* = 230.1483, calcd. for [$C_{15}H_{20}$BrNO−Br]: 230.1545; R_f = 0.70 (hexane/EtOAc, 1:1).

(1*S,2*S**,3*R**)-2-Bromo-3-(4-chlorophenyl)-1-methyl-*N*,*N*-diisopropylcyclopropanecarboxamide (3j):** Orange solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.27 (m, 4H, *p*-ClC_6H_4), 4.36–4.20 [m, 1H, NC*H*$(CH_3)_2$], 3.61 (d, J = 8.2 Hz, 1H, C*H*Br), 3.44–3.28 [m, 1H, NC*H*$(CH_3)_2$], 2.67 (d, J = 8.2 Hz, 1H, C*H*Ph), 1.48–1.16 {m, 12H, N[CH(CH_3)$_2$]$_2$}, 1.19 (s, 3H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0 (C), 132.6 (2×C), 131.7 (2×CH), 128.2 (2×CH), 48.6 (CH), 45.8 (CH), 32.7 (CH), 31.5 (C), 28.2 (CH), 20.3 (2×CH_3), 20.0 (CH_3), 15.7 (2×CH_3); MS (ESI$^+$-TOF): *m/z* (%) = 372 [M$^+$+H]$^+$ (75), 332 (2), 314 (10), 292 (40); IR (neat): ν = 2972, 1630, 1439, 739 cm^{-1}; HR-MS (ESI$^+$): *m/z* = 372.0724, calcd. for [$C_{17}H_{24}$ClBrNO]$^+$ [M$^+$+H]$^+$: 372.0730; R_f = 0.65 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-1-butyl-*N*,*N*-diethyl-3-(4-methoxyphenyl)cyclopropanecarboxamide (3k):** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.4 Hz, 2H, *p*-$MeOC_6H_4$), 6.87 (d, J = 8.4 Hz, 2H, *p*-$MeOC_6H_4$), 3.80 (s, 3H, OCH_3), 3.66 (d, J = 8.2 Hz, 1H, C*H*Br), 3.62–3.36 [m, 4H, N(CH_2CH_3)$_2$], 2.62 (d, J = 8.2 Hz, 1H, C*H*Ph), 1.56–1.33 [m, 4H, C(CH_2)$_2$], 1.28–1.09 [m, 8H, N(CH_2CH_3)$_2$, C-(CH_2)$_2$CH_2], 0.82 [t, J = 7.2 Hz, 3H, C(CH_2)$_3$CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.6 (C), 158.3 (C), 131.1 (2×CH), 126.1 (C), 113.5 (2×CH), 55.0 (CH_3), 41.1 (CH_2), 39.3 (CH_2), 34.1 (C), 33.2 (CH), 29.6 (CH_2), 28.9 (CH), 28.1 (CH_2), 22.7 (CH_2), 13.7 (2×CH_3), 12.4 (CH_3); MS (70 eV, EI): *m/z* (%) = 302 [M$^+$−Br] (100), 201 (16), 187 (12), 159 (12), 121 (10); IR (neat): ν = 2961, 1629, 1515, 739 cm^{-1}; HR-MS (ESI$^+$): *m/z* = 382.1376, calcd. for [$C_{19}H_{29}BrNO_2$]$^+$ [M$^+$+H]$^+$: 382.1382; R_f = 0.40 (hexane/EtOAc, 3:1).

(1*S,2*S**)-2-Bromo-3,3-diethyl-*N*,*N*-diethyl-1-methylcyclopropanecarboxamide (3l):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.54–3.38 (m, 3H, NCH_2CH$_3$, C*H*Br), 3.29–3.08 (m, 2H, NCH_2CH$_3$), 1.62–1.18 [m, 4H, C(CH_2CH_3)$_2$], 1.28 (s, 3H, CCH_3), 1.21 (t, J = 7.1 Hz, 3H, NCH$_2$CH_3), 1.12–1.01 (m, 6H, NCH$_2$CH_3, CCH$_2$CH_3), 0.85 (t, J = 7.1 Hz, 3 H CCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.5 (C), 41.1 (CH_2), 40.3 (CH), 38.6 (CH_2), 33.0 (C), 29.1 (C), 19.4 (2×CH_2), 15.5 (CH_3), 14.6 (CH_3), 13.9 (2×CH_3), 12.2 (CH_3); MS (70 eV, EI): *m/z* (%) = 210 [M$^+$−Br] (100), 110 (15), 101 (7), 73 (7), 67 (8); IR (neat): ν = 2964, 1627, 1459, 740 cm^{-1}; HR-MS (ESI$^+$): *m/z* = 290.1114, calcd. for [$C_{13}H_{25}BrNO$]$^+$ [M$^+$+H]$^+$: 290.1119; R_f = 0.50 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-3-ethyl-*N*,*N*-diethyl-1-methyl-3-propylcyclopropanecarboxamide (3m):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.58–3.39 (m, 3H, NCH_2CH$_3$, C*H*Br), 3.30–3.11 (m, 2H, NCH_2CH$_3$), 1.67–0.72 [m, 4H, C-(CH_2)$_2$CH$_3$], 1.28 (s, 3H, CCH_3),1.21 (t, J = 7.0 Hz, 3H, NCH$_2$CH_3), 1.09 (s, 3H, CCH_3), 1.11–1.04 (m, 3H, NCH$_2$CH_3), 0.85 [t, J = 7.0 Hz, 3H, C(CH_2)$_2$CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.5 (C), 41.1 (CH_2), 40.3 (CH), 38.6 (CH_2), 33.8 (C), 33.0 (C), 19.4 (CH_2), 18.7 (CH_2), 15.5 (CH_3), 14.6 (CH_3), 13.9 (2×CH_3), 12.2 (CH_3); MS (70 eV, EI): *m/z* (%) = 210 [M$^+$−Br] (100), 110 (14), 96 (6), 73 (7), 70 (8); IR (neat): ν = 2965, 1626, 1459, 745 cm^{-1}; HR-MS (ESI$^+$): *m/z* = 290.1114, calcd. for [$C_{13}H_{25}BrNO$]$^+$ [M$^+$+H]$^+$: 290.1119; R_f = 0.55 (hexane/EtOAc, 3:1).

(1*S,2*S**,3*R**)-2-Bromo-3-ethyl-*N*,*N*-diethyl-1-methyl-3-phenylcyclopropanecarboxamide (3n):** White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.14 (m, 5H, *Ph*), 3.60–3.47 (m, 1H, C*H*Br), 3.38–3.26 (m, 1H, NC*H*HCH$_3$), 2.88–2.62 (m, 2H, NCH_2CH$_3$), 2.25–2.12 (m, 1H, NC*H*HCH$_3$), 1.80–1.67 (m, 2H, CCH_2CH$_3$),1.52 (s, 3H, CCH_3), 1.13 (t, J = 7.2 Hz, 3H, NCH$_2$CH_3), 0.80 (t, J = 7.2 Hz, 3H, NCH$_2$CH_3), 0.43 (t, J = 7.2 Hz, 3H, CCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.8 (C), 137.4 (C), 128.1 (2×CH), 127.9 (2×CH), 126.6 (CH), 41.2 (CH_2), 38.4 (CH_2), 38.3 (C), 38.2 (CH), 36.0 (C), 24.1 (CH_2), 15.4 (CH_3), 13.5 (CH_3), 11.06 (CH_3), 10.0 (CH_3); MS (ESI$^+$-TOF): *m/z* (%) = 338 [M$^+$+H]$^+$ (88), 280 (58), 277 (10), 258 (100), 245 (9); IR (neat): ν = 2984, 1625, 1430, 740 cm^{-1}; HR-MS (ESI$^+$): *m/z* = 338.1114, calcd. for [$C_{17}H_{25}BrNO$]$^+$ [M$^+$+H]$^+$: 338.1119; R_f = 0.58 (hexane/EtOAc, 3:1).

(1*R,2*S**,3*R**)-2-Bromo-*N*,*N*-dimethyl-3-pentylcyclopropanecarboxamide (5a):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.31 (apparent t, J = 4.0 Hz, 1H, C*H*Br), 3.09 (s, 3H, NCH_3), 2.92 (s, 3H, NCH_3), 2.15 (dd, J = 10.3, 4.0 Hz, 1H, C*H*CO), 1.71–1.62 [m, 1H, C*H*(CH_2)$_4$], 1.44–1.19 [m, 8H, CH(CH_2)$_4$], 0.84 [apparent t, J = 6.3 Hz, 3H, (CH_2)$_4$CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.2 (C), 37.1 (CH_3), 35.4 (CH_3), 31.6 (CH), 31.1 (CH_2), 28.7 (CH), 28.3 (CH_2), 26.1 (CH_2), 23.4 (CH), 22.3 (CH_2), 13.8 (CH_3); MS (70 eV, EI): *m/z* (%) = 182 [M$^+$−Br] (70), 148 (5), 124 (2), 72 (100), 41 (11); IR (neat): ν = 2929, 1638, 1420, 739 cm^{-1}; HR-MS (ESI$^+$): *m/z* = 262.0801, calcd. for [$C_{11}H_{21}BrNO$]$^+$ [M$^+$+H]$^+$: 262.0806; R_f = 0.50 (hexane/EtOAc, 3:1).

(1*R,2*S**,3*R**)-2-Bromo-3-(4-chlorophenyl)-1-methyl-*N*,*N*-diisopropylcyclopropanecarboxamide (5b):** White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, J = 8.5 Hz, 2H, *p*-ClC_6H_4), 6.95 (d, J = 8.5 Hz, 2H, *p*-ClC_6H_4), 4.04 (d, J = 5.4 Hz, 1H, C*H*Br), 3.90–3.811 [m, 1H, NC*H*$(CH_3)_2$], 3.17–3.04 [m, 1H, NC*H*$(CH_3)_2$], 2.29 (d, J = 5.4 Hz, 1H, C*H*Ph), 1.61 (s, 3H, CCH_3), 1.33 [d, J = 6.8 Hz, 3H, NCH(CH_3)$_2$], 1.21 [d, J = 6.8 Hz, 3H, NCH(CH_3)$_2$], 1.12 [d, J = 6.8 Hz, 3H, NCH(CH_3)$_2$], 0.18 [d, J = 6.8 Hz, 3H, NCH(CH_3)$_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.5 (C), 135.5 (C), 132.7 (C), 128.4 (2×CH), 127.9 (2×CH), 48.5 (CH), 46.0 (CH), 40.8 (CH), 38.1 (C), 34.1 (CH), 20.8 (CH_3), 20.7 (CH_3), 20.0 (CH_3), 19.9 (CH_3), 19.8 (CH_3); MS (ESI$^+$-TOF): *m/z* (%) = 372 [M$^+$+H]$^+$ (74), 314 (18), 292 (60), 258 (3); IR (neat): ν = 2971, 1625, 1265, 739 cm^{-1}; HR-MS (ESI$^+$): *m/z* = 372.0724, calcd. for [$C_{17}H_{24}$BrClNO]$^+$ [M$^+$+H]$^+$: 372.0730; R_f = 0.68 (hexane/EtOAc, 3:1).

(1*S,2*R**,3*S**)-2-Bromo-*N*,*N*-diethyl-3-phenylcyclopropanecarboxamide (7a):** Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.26 (m, 5H, *Ph*), 3.72 (dd, J = 8.2, 3.8 Hz, 1H, C*H*Br), 3.54 (q, J = 7.3 Hz, 2H, NCH_2CH$_3$), 3.45 (q, J = 7.3 Hz, 2H, NCH_2CH$_3$), 2.96 (apparent t, J = 7.0 Hz, 1H, C*H*CO), 2.51 (dd, J = 6.4, 3.8 Hz, 1H, C*H*Ph), 1.32 (t, J = 7.3 Hz, 3H, NCH$_2$CH_3), 1.17 (t, J = 7.3 Hz, 3H, NCH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6 (C), 135.2 (C), 128.8 (2×CH), 127.9 (2×CH), 127.0 (CH), 42.2 (CH_2), 41.0 (CH_2), 30.5 (CH), 28.7 (CH), 27.9 (CH), 14.9 (CH_3), 13.0 (CH_3); MS (70 eV, EI): *m/z* (%) = 295 [M$^+$] (2), 216 (100), 200 (18), 158 (11), 115 (25); IR (neat): ν = 2986, 1632, 1447, 739 cm^{-1}; HR-MS (70 eV): *m/z* = 295.0564, calcd. for $C_{14}H_{18}BrNO$: 295.0572; R_f = 0.65 (hexane/EtOAc, 1:1).

(1*S,2*R**,3*S**)-2-Bromo-3-phenyl-*N*,*N*-diisopropylcyclopropanecarboxamide (7b):** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.23 (m, 5H, *Ph*), 4.26–4.15 [m, 1H, NC*H*-(CH_3)$_2$], 4.00–3.83 [m, 1H, NC*H*$(CH_3)_2$], 3.67 (dd, J = 8.0, 4.0 Hz, 1H, C*H*Br), 2.93 (apparent t, J = 7.3 Hz, 1H, C*H*CO), 2.50 (dd, J = 6.5, 4.0 Hz, 1H, C*H*Ph), 1.43–1.26 {m, 12H, N[CH(CH_3)$_2$]$_2$}; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.3 (C), 135.4 (C), 128.8 (2×CH), 128.0 (2×CH), 127.0 (CH), 47.4 (CH), 45.8 (CH), 30.1 (CH), 30.0 (CH), 28.7 (CH), 21.8

(2×CH_3), 20.3 (2×CH_3); MS (70 eV, EI): *m/z* (%) = 323 [M^+] (7), 244 (97), 160 (53), 144 (45), 115 (100); IR (neat): ν = 2972, 1630, 1448, 738 cm^{-1}; HR-MS (70 eV): *m/z* = 323.0885, calcd. for $C_{16}H_{22}BrNO$: 323.0885; R_f = 0.65 (hexane/EtOAc, 3:1).

4-[(1*S,2*R**,3*S**)-(2-Bromo-3-phenylcyclopropyl)carbonyl]morpholine (7c):** Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.21 (m, 5H, *Ph*), 3.81–3.63 (m, 9H, *H* from morpholine, C*H*Br), 2.95 (apparent t, *J* = 7.3 Hz, 1H, C*H*CO), 2.51 (dd, *J* = 6.4, 3.8 Hz, 1H, C*H*Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.4 (C), 135.0 (C), 128.8 (2×CH), 128.1 (2×CH), 127.3 (CH), 66.6 (2×CH_2), 46.0 (CH_2), 42.6 (CH_2), 30.7 (CH), 28.4 (CH), 27.7 (CH); MS (70 eV, EI): *m/z* (%) = 309 [M^+] (3), 230 (100), 202 (7), 115 (53), 70 (18); IR (neat): ν = 2987, 1638, 1442, 739 cm^{-1}; HR-MS (70 eV): *m/z* = 309.0361, calcd. for $C_{14}H_{16}BrNO_2$: 309.0364; R_f = 0.20 (hexane/EtOAc, 3:1).

(1*S,2*R**,3*S**)-2-Bromo-*N*,*N*-diethyl-3-(4-fluorophenyl)-cyclopropanecarboxamide (7d):** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.17 (m, 2H, *p*-FC_6H_4), 7.07–6.97 (m, 2H, *p*-FC_6H_4), 3.64 (dd, *J* = 7.7, 4.0 Hz, 1H, C*H*Br), 3.64 (q, *J* = 7.1 Hz, 2H, NCH_2CH_3), 3.51 (q, *J* = 7.1 Hz, 2H, NCH_2CH_3), 2.90 (apparent t, *J* = 7.1 Hz, 1H, C*H*CO), 2.41 (dd, *J* = 6.2, 4.0 Hz, 1H, C*H*Ph), 1.28 (t, *J* = 7.1 Hz, 3H, NCH_2CH_3), 1.14 (t, *J* = 7.0 Hz, 3H, NCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5 (C), 161.9 (d, $^1J_{C,F}$ = 244.2 Hz, C), 131.1 (C), 130.4 (d, $^3J_{C,F}$ = 8.1 Hz, 2×CH), 115.0 (d, $^2J_{C,F}$ = 21.4 Hz, 2×CH), 42.3 (CH_2), 41.1 (CH_2), 29.7 (CH), 28.6 (CH), 28.3 (CH), 15.1 (CH_3), 13.1 (CH_3); MS (70 eV, EI): *m/z* (%) = 313 [M^+] (3), 234 (100), 218 (18), 133 (20), 69 (17); IR (neat): ν = 2982, 1633, 1514, 739 cm^{-1}; HR-MS (70 eV): *m/z* = 313.0509, calcd. for $C_{14}H_{17}BrFNO$: 213.0478; R_f = 0.70 (hexane/EtOAc, 1:1).

(1*S,2*R**,3*S**)-2-Bromo-*N*,*N*-diethyl-3-(4-methoxyphenyl)-cyclopropanecarboxamide (7e):** Brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8.5 Hz, 2H, *p*-$MeOC_6H_4$), 6.87 (d, *J* = 8.5 Hz, 2H, *p*-$MeOC_6H_4$), 3.79 (s, 3H, OCH_3), 3.66 (dd, *J* = 7.0, 4.0 Hz, 1H, C*H*Br), 3.51 (q, *J* = 7.2 Hz, 2H, NCH_2CH_3), 3.42 (q, *J* = 7.2 Hz, 2H, NCH_2CH_3), 2.85 (apparent t, *J* = 7.0 Hz, 1H, C*H*CO), 2.41 (dd, *J* = 6.2, 4.0 Hz, 1H, C*H*Ph), 1.28 (t, *J* = 7.2 Hz, 3H, NCH_2CH_3), 1.14 (t, *J* = 7.2 Hz, 3H, NCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8 (C), 158.6 (C), 129.8 (2×CH), 127.3 (C), 113.5 (2×CH), 55.1 (CH_3), 42.3 (CH_2), 41.0 (CH_2), 29.9 (CH), 29.1 (CH), 28.2 (CH), 15.0 (CH_3), 13.1 (CH_3); MS (70 eV, EI): *m/z* (%) = 246 [M^+−Br] (17), 245 (100), 230 (32), 202 (3), 188 (20); IR (neat): ν = 2976, 1631, 1517, 1251 cm^{-1}; HR-MS (70 eV): *m/z* = 246.1462, calcd. for [$C_{15}H_{20}BrNO_2$−Br]: 246.1494; R_f = 0.75 (hexane/EtOAc, 1:1).

Synthesis of Cyclopropyl Ketones 8

The corresponding organolithium compound (1.2 mmol, 3.0 equiv.) was added dropwise to a solution of the amide **6c** (0.4 mmol, 1.0 equiv.) in anhydrous THF (2 mL) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 1 h. The reaction was then quenched with an saturated aqueous solution of ammonium chloride (5 mL) and extracted with dichloromethane (3×10 mL). The organic layers were washed with water, dried over Na_2SO_4, and concentrated under vacuum. Purification by column chromatography on silica gel (hexane/EtOAc, 5:1) yielded the ketones **8**.

(1*S,2*R**,3*S**)-[2-Chloro-3-phenylcycloprop-1-yl] phenyl ketone (8a):** Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10–7.35 (m, 10H, *Ph*), 3.90 (dd, *J* = 7.7, 3.5 Hz, 1H, C*H*Cl), 3.30 (dd, *J* = 6.2, 3.5 Hz, 1H, C*H*CO), 3.10 (apparent t, *J* = 7.7 Hz, 1H, C*H*Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.4 (C), 136.9 (C), 133.9 (C), 133.5 (CH), 129.1 (2×CH), 128.8 (2×CH), 128.3 (2×CH), 128.2 (2×CH), 127.5 (CH), 42.0 (CH), 34.8 (CH), 33.4 (CH); MS (70 eV, EI): *m/z* (%) = 256 [M^+] (<1), 221 (100), 181 (11), 169 (12), 115 (12); IR (neat): ν = 3063, 1667, 1216, 793 cm^{-1}; HR-MS (70 eV): *m/z* = 256.0627, calcd. for $C_{16}H_{13}ClO$: 256.0655; R_f = 0.80 (hexane/EtOAc, 1:1).

(1*S,2*R**,3*S**)-Butyl [2-chloro-3-phenylcycloprop-1-yl] ketone (8b):** Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.10 (m, 5H, *Ph*), 3.65 (dd, *J* = 7.8, 3.5 Hz, 1H, C*H*Cl), 2.87 (apparent t, *J* = 7.8 Hz, 1H, C*H*CO), 2.62–2.54 [m, 3H, C*H*Ph, $CH_2(CH_2)_2CH_3$], 1.58 (m, *J* = 7.2 Hz, 2H, $CH_2CH_2CH_3$), 1.30 (m, *J* = 7.2 Hz, 2H, $CH_2CH_2CH_3$), 0.86 [t, *J* = 7.2, 3H, $(CH_2)_3CH_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.1 (C), 133.7 (C), 128.9 (2×CH), 128.2 (2×CH), 127.4 (CH), 44.1 (CH_2), 41.3 (CH), 36.0 (CH), 34.3 (CH), 25.8 (CH_2), 22.2 (CH_2), 13.7 (CH_3); MS (70 eV, EI): *m/z* (%) = 201 [M^+−Cl] (18), 131 (13), 115 (45), 85 (100), 57 (41); IR (neat): ν = 3062, 1701, 1402, 765 cm^{-1}; HR-MS (70 eV): *m/z* = 201.1296, calcd. for [$C_{14}H_{17}ClO$−Cl]: 201.1279; R_f = 0.83 (hexane/EtOAc, 1:1).

Synthesis of (1*S**,2*R**,3*S**)-2-Chloro-1-(*N*,*N*-diethylaminomethyl)-3-phenylcyclopropane (9)

To a suspension of $LiAlH_4$ (2 mmol, 5 equiv.) in THF (2 mL) was added dropwise a solution of **6a** (0.4 mmol, 1 equiv.) in anhydrous THF (4 mL) at 0 °C. The mixture was stirred for 15 h at reflux, then cooled at 0 °C and the reaction quenched by the addition of a mixture of ice/water. The mixture was then filtered through a pad of Celite and extracted with diethyl ether (3×10 mL). The organic layers were washed with water, dried over Na_2SO_4, and concentrated under vacuum. Purification by chromatography on silica gel (hexane/EtOAc, 5:1) afforded the pure compound **9** as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.00 (m, 5H, *Ph*), 3.10 (dd, *J* = 7.5, 3.9 Hz, 1H, C*H*Cl), 2.80–2.40 [m, 6H, $CH_2N(CH_2CH_3)_2$], 2.09 (apparent t, *J* = 7.5 Hz, 1H, C*H*Ph), 1.67–1.59 (m, 1H, $CHCH_2N$), 1.07 [t, *J* = 7.3 Hz, 6H, $N(CH_2CH_3)_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.7 (C), 129.0 (2×CH), 127.9 (2×CH), 126.6 (CH), 54.8 (CH_2), 46.7 (2 x CH_2), 39.4 (CH), 28.6 (CH), 25.6 (CH), 11.6 (2×CH_3); MS (70 eV, EI): *m/z* (%) = 237 [M^+] (4), 222 (40), 202 (82), 129 (45), 86 (100); IR (neat): ν = 3031, 1455, 1373, 780 cm^{-1}; HR-MS (70 eV): *m/z* = 237.1255, calcd. for $C_{14}H_{20}ClN$: 237.1284; R_f = 0.35 (hexane/EtOAc, 3:1).

Acknowledgements

We acknowledge MICINN (CTQ2007-61132 and MAT2006-01997), Principado de Asturias (FICYT IB08-028) and European Union (Fondo Europeo de Desarrollo Regional) for financial support. J.M.C. thanks his wife Carmen Fernández-

Flórez for her time. H.R.S. and E.G.B thank MICINN for a Ramón y Cajal Contract and Principado the Asturias for a predoctoral fellowship, respectively. Our thanks to Dr Euan C. Goddard (CRL, University of Oxford) for his revision of the English.

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