Radical Reactions Using Decacarbonyldimanganese under Biphasic Conditions

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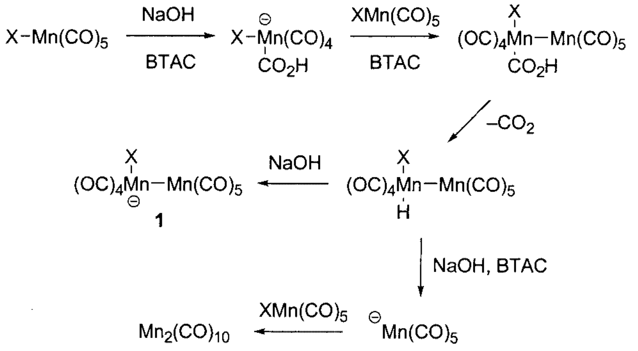
Radical reactions of alkyl halides, initiated by photolysis in the presence of decacarbonyldimanganese, can be performed in biphasic media. Reactions in the presence of aqueous sodium hydroxide together with a phase-transfer catalyst result in the efficient removal of manganese halide by-products and also lead to the regeneration of decacarbonyldimanganese. A range of efficient radical couplings, cyclisations and intermolecular addition reactions were performed under these conditions. This included the development of a new tandem radical addition–ionic cyclisation sequence that was employed in a short approach to (±)-coronamic acid.

Introduction

The reaction of alkyl halides with decacarbonyldimanganese, $Mn_2(CO)_{10}$, has proved to be a particularly mild and efficient method of forming carbon-centred radicals.[1] Homolytic cleavage of the weak Mn−Mn bond can be achieved by heating or irradiating $Mn_2(CO)_{10}$ with visible light to form the pentacarbonylmanganese radical, $^{\cdot}Mn(CO)_5$, which is able to abstract halogen atoms from a variety of organohalides bearing weak carbon−halogen bonds. Examples of radical coupling,[2] cyclisation,[3] intermolecular addition[4] and polymerisation reactions[5,6] have recently been reported by our group and others. These reactions produce pentacarbonylmanganese halides $[XMn(CO)_5]$ as by-products, which can be removed from the organic products either by reaction with DBU[2] or by aerial oxidation.[5] In both cases, polar manganese products are formed that can be removed from the organic products by filtration and/or column chromatography. However, separation of these polar manganese compounds can be problematic when working with polar organic products. Problems also arise when using organic compounds that can react with DBU, and the aerial oxidation method can be time-consuming. In order to develop a more general method for removing pentacarbonylmanganese halide by-products, our attention turned to the use of phase-transfer catalysed reactions.

Radical reactions in biphasic media are well-known[7] and we became interested in the use of these conditions in $Mn_2(CO)_{10}$-mediated radical reactions following the work of Gibson and co-workers.[8] This work showed that pentacarbonylmanganese halides, in benzene, react with aqueous sodium hydroxide in the presence of the phase-transfer catalyst benzyltriethylammonium chloride (BTAC) to produce a water-soluble binuclear anion **1** (Scheme 1). This method could therefore be used to remove organic-soluble pentacarbonylmanganese halide by-products (produced during halogen-atom abstraction reactions) from organic products by conversion into water-soluble salts. Furthermore, the formation of $Mn_2(CO)_{10}$ was observed under the phase-transfer reactions, which could be explained by the formation of the pentacarbonylmanganese anion, $^{-}Mn(CO)_5$, produced in the presence of the phase-transfer catalyst, as shown in Scheme 1.[9] Hence, rather than deprotonation of $(CO)_4MnH(X)-Mn(CO)_5$, nucleophilic attack by hydroxide ion could form $^{-}Mn(CO)_5$ and $(CO)_4MnH(X)-OH$. These results suggested that not only could the manganese halide by-products be removed from the organic layer but also that the radical initiator, namely $Mn_2(CO)_{10}$, could be regenerated.



Scheme 1. Reaction of pentacarbonylmanganese halides in biphasic media

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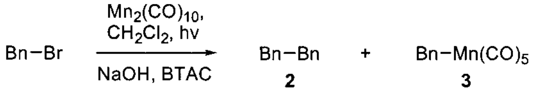
Results and Discussion

In order to investigate the use of biphasic conditions, initial photolysis experiments concentrated on the dimerisation of benzyl bromide using different amounts of $Mn_2(CO)_{10}$, in the presence of aqueous sodium hydroxide and the phase-transfer catalyst BTAC, as shown in Scheme 2 and Table 1.[10] Disappointingly, when 0.5 equivalents of $Mn_2(CO)_{10}$ were used, this resulted in the desired dimer **2** in only 36% yield (compared to 99% yield in dichloromethane[2]) (Table 1, entry 1). Surprisingly, the major by-product was benzylpentacarbonylmanganese (**3**), which was only formed in the presence of the phase-transfer catalyst (Table 1, entry 2). This presumably arises from a nucleophilic substitution reaction of benzyl bromide with the pentacarbonylmanganese anion, which is conventionally prepared by reduction of $Mn_2(CO)_{10}$ using sodium/mercury amalgam.[11]



$$\text{Bn–Br} \xrightarrow[\text{NaOH, BTAC}]{Mn_2(CO)_{10},\ CH_2Cl_2,\ h\nu} \underset{\mathbf{2}}{\text{Bn–Bn}} + \underset{\mathbf{3}}{\text{Bn–Mn(CO)}_5}$$

Scheme 2. Radical coupling of benzyl bromide

Table 1. Reaction of benzyl bromide with $Mn_2(CO)_{10}$ in biphasic media

Entry	$Mn_2(CO)_{10}$ [eq.]	Time [h]	**2** [%]	**3** [%]
1	0.50	2	36	43
2[a]	0.50	2	80	0
3	0.25	2	40	9
4	0.25	4	80	0
5	0.20	6	75	0
6	0.10	16	53	0
7	0.05	96	25 (99)[b]	0

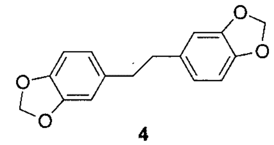
[a] No BTAC was used. [b] Yield based on recovered starting material.

On reducing the amount of $Mn_2(CO)_{10}$ to 0.25 or 0.20 equivalents, good yields of bibenzyl (**2**) were obtained after 4 and 6 h, respectively (Table 1, entries 3−5). Even the use of 0.1 or 0.05 equivalents of $Mn_2(CO)_{10}$ still allowed the formation of **2** in moderate yields of 53% and 25% respectively, after extended reaction times (Table 1, entries 6 and 7). Because 0.5 equivalents of $Mn_2(CO)_{10}$ are required for complete conversion of benzyl bromide to **2**, the reasonable-to-excellent yields obtained when using only 0.25−0.05 equivalents of $Mn_2(CO)_{10}$ provide good evidence for the regeneration of $Mn_2(CO)_{10}$ under the biphasic conditions. Interestingly, it should also be noted that benzylpentacarbonylmanganese (**3**) is only isolated after short reaction times, which suggests that by increasing the reaction time, **3** is converted into **2**. This may arise through homolysis of the weak Mn−C bond of **3** to give the benzyl radical,[12] although this could not be proved. In all cases, the use of biphasic conditions resulted in the efficient removal of the pentacarbonylmanganese bromide by-product from the organic product, as indicated by the ^1H NMR spectra of the crude products.

In order to prove that $Mn_2(CO)_{10}$ is regenerated from $BrMn(CO)_5$ under biphasic conditions, several dimerisation experiments were conducted starting with benzyl bromide and pentacarbonylmanganese bromide. On photolysis of benzyl bromide in the presence of 0.5−2 equivalents of $BrMn(CO)_5$ for 2−7 h, bibenzyl (**2**) was formed in 22−60% yield, together with benzylpentacarbonylmanganese (**3**) in 7−35% yield. In the absence of photolysis, only **3** was isolated (in 50% yield after 4 h), which again suggests that **2** is formed from **3** during photolysis. The formation of **2** is consistent with the conversion of $BrMn(CO)_5$ to $Mn_2(CO)_{10}$; TLC, IR and EIMS analysis of the crude products confirmed the presence of $Mn_2(CO)_{10}$. The use of pentacarbonylmanganese iodide or pentacarbonylmanganese chloride was also found to lead to the formation of **2**, although the yields were lower (typically around 23−28%) than when using pentacarbonylmanganese bromide, under the same conditions. To the best of our knowledge, this is the first time that pentacarbonylmanganese halides have been used to initiate radical reactions leading to the formation of a carbon−carbon bond.

Investigations to quantify the amount of $Mn_2(CO)_{10}$ produced from pentacarbonylmanganese halides (in the presence of aqueous sodium hydroxide and BTAC) were also carried out. After photolysis for 2 h, pentacarbonylmanganese bromide and iodide produced $Mn_2(CO)_{10}$ in 16−17% yield, whereas a higher yield of 35% (after 2 h) or 46% (after 1 h) was obtained when using pentacarbonylmanganese chloride. This work also showed that BTAC is not required for the formation of $Mn_2(CO)_{10}$, since photolysis of a solution of $ClMn(CO)_5$ in dichloromethane, together with aqueous sodium hydroxide, produced $Mn_2(CO)_{10}$ in 43% yield after 2 h. Interestingly, when benzyl bromide was treated with 0.5 equivalents of $ClMn(CO)_5$ (for 4 h) in the absence of BTAC, bibenzyl (**2**) was isolated in 83% yield but benzylpentacarbonylmanganese (**3**) was formed in only 2% yield (cf. Table 1, entry 1). These results suggest that whereas $ClMn(CO)_5$ can react with the aqueous layer to form $Mn_2(CO)_{10}$ in the absence of BTAC, BTAC is required to transfer the pentacarbonylmanganese anion into the organic layer, where it can form $BnMn(CO)_5$ (**3**). At present, the mechanism by which $ClMn(CO)_5$ is converted into $Mn_2(CO)_{10}$ in the absence of BTAC is unclear.

Application of the biphasic system to a variety of alternative coupling reactions was then investigated. Hence photolysis of 5-(bromomethyl)-1,3-benzodioxole or 5-(bromomethyl)-1,2,3-trimethoxybenzene in dichloromethane with $Mn_2(CO)_{10}$ (0.5 equivalents) in the presence of aqueous sodium hydroxide and BTAC formed the naturally occurring dimers[13] **4** and **5** in 47% and 36% yield, respectively. Although similar reactions, carried out solely in dichloromethane, were higher-yielding (70% and 48% for **4** and **5**, respectively), addition of DBU was required in order to remove the $BrMn(CO)_5$ by-product.



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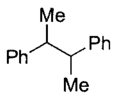

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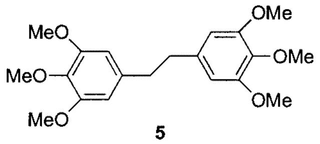

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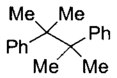

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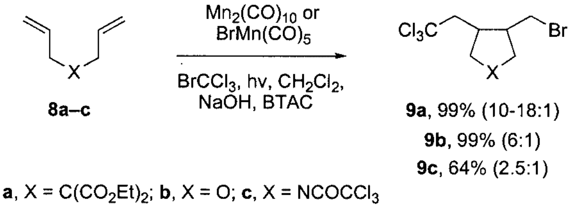
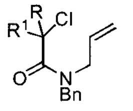
An interesting contrast in reactivity between $Mn_2(CO)_{10}$-mediated couplings carried out in biphasic media, as opposed to dichloromethane, was observed on reaction with 1-bromoethylbenzene. Whereas photolysis of 1-bromoethylbenzene with $Mn_2(CO)_{10}$ (0.5 equivalents) in dichloromethane afforded only starting material, the same reaction using 0.5 equivalents of $Mn_2(CO)_{10}$ in biphasic media afforded 2,3-diphenylbutane (**6**) (as a 1:1 mixture of diastereomers) in 70% yield. A similar reaction using one equivalent of $BrMn(CO)_5$ in biphasic conditions also afforded **6** in a slightly improved yield of 79%. Also, whereas attempted coupling of (1-bromo-1-methylethyl)benzene using $Mn_2(CO)_{10}$ was unsuccessful in dichloromethane, in biphasic media, 2,3-dimethyl-2,3-diphenylbutane (**7**) was isolated in 25% yield. The use of biphasic media therefore extends the scope of precursors that can be employed in manganese carbonyl-mediated radical reactions to secondary and tertiary (as well as primary) benzylic halides. These contrasting results also provide further evidence to support the fact that the reaction mechanism in biphasic media is different to that in dichloromethane.

In order to expand the synthetic applications of the biphasic system, halogen-atom transfer cyclisations of the 1,6-dienes **8a−c** were investigated by reaction with bromotrichloromethane in the presence of $Mn_2(CO)_{10}$ or $BrMn(CO)_5$ (Scheme 3). Photolysis of the malonate **8a** with $BrCCl_3$ (3 equivalents) and 0.1 equivalents of $Mn_2(CO)_{10}$ or 0.2 equivalents of $BrMn(CO)_5$ both gave the cyclopentane **9a** in quantitative yield (in a *cis*:*trans* ratio of 10−18:1). Similarly, reaction of diallyl ether (**8b**) with either $Mn_2(CO)_{10}$ or $BrMn(CO)_5$, under the same conditions as for **8a**, gave the tetrahydrofuran **9b** in quantitative yield (as a 6:1 mixture of separable *cis*:*trans* diastereomers). (It should be noted that control reactions in the absence of $Mn_2(CO)_{10}$ gave unchanged starting material[3a]).

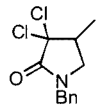


Scheme 3. Radical cyclisation of 1,6-dienes using bromotrichloromethane

The mild conditions and chemoselective nature of this method of radical generation was further exemplified by the formation of the pyrrolidine **9c** (as a 2.5:1 mixture of diastereomers) on cyclisation of the trichloroamide **8c** with $BrCCl_3$ (3 equivalents) in the presence of $BrMn(CO)_5$ (0.65 equivalents). It should be noted, however, that trichloroamides can be reduced under these conditions in the absence of $BrCCl_3$. This is illustrated by the reaction of the benzamide **10** with $BrMn(CO)_5$, which produced the reduced products **11** and **12** in 46% and 26% yield, respectively, together with a 3% yield of the pyrrolidinone **13**. These reduced products may be derived from hydrogen-atom abstraction reactions, or alternatively, the intermediate radicals could be reduced to carbanions that are subsequently protonated.



10; R = R^1 = Cl
11; R = Cl, R^1 = H
12; R = R^1 = H



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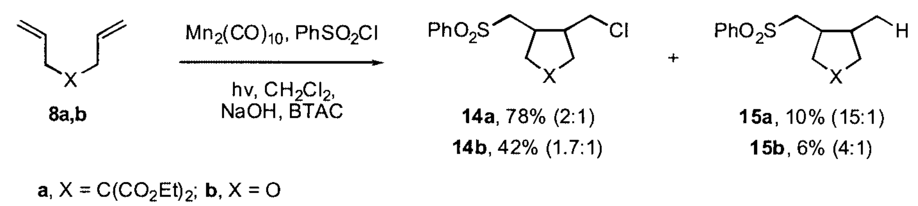
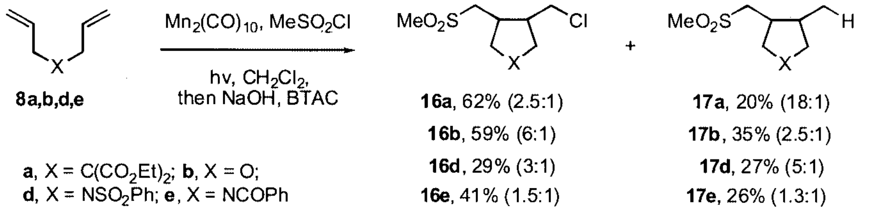
Related halogen-atom transfer cyclisations were observed on reaction of the dienes **8a−e** with sulfonyl chlorides (Schemes 4 and 5). Addition of benzenesulfonyl chloride (3 equivalents) to the malonate **8a** (1 equivalent) in the presence of $Mn_2(CO)_{10}$ (0.3 equivalents), under biphasic conditions, afforded the expected chlorine-atom transfer product **14a** in 78% yield (as a 2:1 mixture of *cis*:*trans* isomers). In addition, the 3-methylcyclopentane **15a** was isolated in 10% yield. The formation of **15a** may be explained by abstraction of a hydrogen atom from dichloromethane by the primary radical, formed by 5-*exo*-trig cyclisation.[3a] A similar reaction, to give the tetrahydrofurans **14b** and **15b**, was observed when diallyl ether (**8b**) was treated with $Mn_2(CO)_{10}$ under the same conditions.

Attempts to react **8a**,**b** (1 equivalent) with methanesulfonyl chloride (3 equivalents) and $Mn_2(CO)_{10}$ under biphasic conditions were disappointing, presumably due to the instability of methanesulfonyl chloride in the presence of water. However, these cyclisations can be carried out in dichloromethane, and the $ClMn(CO)_5$ by-product removed (from the cyclic products) at the end of the reaction by adding aqueous sodium hydroxide solution and BTAC — this has the added advantage of hydrolysing unchanged $MeSO_2Cl$ (which is used in threefold excess) (Scheme 5). Under these conditions, the malonate **8a** is converted into the cyclopentanes **16a** and **17a** in a combined yield of 82%, whereas diallyl ether (**8b**) gives rise to the methyl sulfones **16b** and **17b** in 59% and 35% yield, respectively. The synthesis of pyrrolidines is also possible, as illustrated by the reaction of methanesulfonyl chloride and $Mn_2(CO)_{10}$ with the benzenesulfonamide **8d** and benzamide **8e**. As well as the expected chlorides **16d** and **16e**, good yields of methyl pyrrolidines **17d** and **17e** were isolated from competitive hydrogen-atom abstraction reactions.



Scheme 4. Radical cyclisation of 1,6-dienes using benzenesulfonyl chloride



Scheme 5. Radical cyclisation of 1,6-dienes using methanesulfonyl chloride

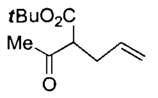
Following the successful removal of the manganese halide by-products from the organic products in the biphasic radical reactions, our efforts focussed on applying these conditions to the initiation of novel sequential reactions. The aim was to perform a decacarbonyldimanganese-mediated radical addition reaction to give an intermediate that could then undergo an ionic cyclisation promoted by the biphasic conditions. Of particular interest was the formation of substituted cyclopropanes by elaboration of allyl-substituted 1,3-dicarbonyls such as the malonate **18** (Scheme 6).

Following manganese carbonyl-promoted radical addition of $BrCCl_3$ or CBr_4 to the double bond of **18**, it was envisaged that the intermediate secondary bromide or chloride could be deprotonated to give an enolate, which could then undergo a 3-*exo*-tet anionic cyclisation leading to **19** or **20**.[14] Initial reactions centred on the photolysis of **18** with various quantities of $Mn_2(CO)_{10}$ and $BrCCl_3$ (3 equivalents) followed, after 6 hours by addition of DBU to initiate the formation of the cyclopropane ring (Table 2, entries 1−3). These one-pot reactions produced good-to-excellent yields of the desired cyclopropane **19**, together with small amounts of the bromide **21**, formed on reaction of the enolate derived from **18** with $BrCCl_3$ [as confirmed by a control reaction in the absence of $Mn_2(CO)_{10}$]. However, the formation of **18** can be minimised by ensuring that the base is added to the reaction mixture after completion of the radical addition, which can be facilitated by increasing the number of equivalents of $Mn_2(CO)_{10}$. The use of CBr_4 instead of $BrCCl_3$ gave a similar result, providing the tribromocyclopropane **20** in 56% yield (Table 2, entry 4). By comparison, the use of biphasic conditions afforded the desired cyclic products **19** and **20** in excellent yields of 80% and 88%, respectively (Table 2, entries 5 and 6).

Table 2. Reaction of diethyl allyl malonate (**18**) with $BrCCl_3$ or CBr_4 and $Mn_2(CO)_{10}$

Entry	X	$Mn_2(CO)_{10}$ [eq.]	Base	**19** or **20** [%]	**21** [%]
1	Cl	0.1	DBU	60	13
2	Cl	0.2	DBU	72	7
3	Cl	0.3	DBU	75	<5
4	Br	0.1	DBU	56	28
5	Cl	0.3	NaOH	80	0
6	Br	0.3	NaOH	88	0

This methodology can be used to prepare cyclopropanes from other 1,3-dicarbonyls. For example, photolysis of the β-keto ester **22** with $Mn_2(CO)_{10}$ and $BrCCl_3$, followed by addition of base, gave the trichloride **23** in 60% yield as a 1:1 mixture of diastereomers.



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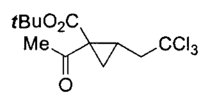

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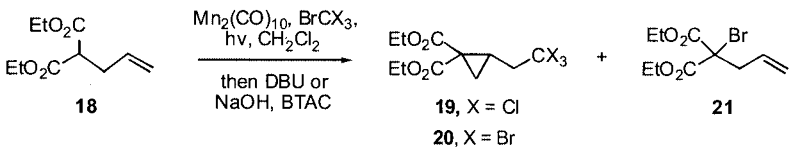
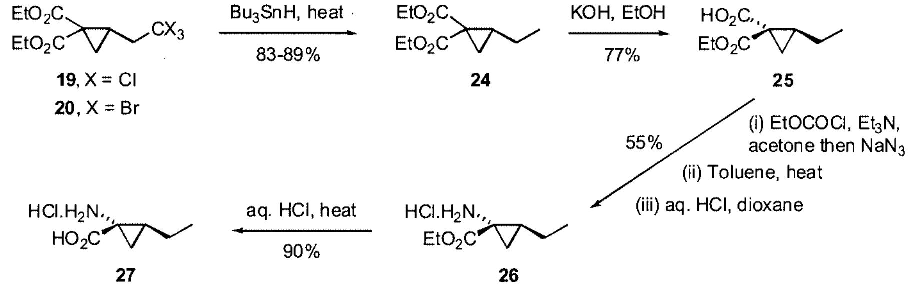
The resulting halogenated cyclopropanes are useful synthetic intermediates. For example, the cyclopropanes **19** and **20** can be elaborated to the hydrochloride salt of (±)-coronamic acid **27** (a constituent amino acid of the plant toxin coronatine),[15] using conventional methodology, as shown in Scheme 7. Hence, reduction of **19** and **20** using tributyltin



Scheme 6. Formation of halogenated cyclopropanes



Scheme 7. Synthesis of (±)-coronamic acid (**27**)

hydride afforded the cyclopropane **24** in 83−89% yield, which on reaction with potassium hydroxide in ethanol resulted in selective hydrolysis of the less hindered ester to give **25**.[16] Formation of the mixed anhydride by treatment of the acid with ethyl chloroformate followed by Curtius rearrangement and hydrolysis led to the amine hydrochloride salt **26** in a 55% yield (unoptimised). Finally, heating **26** in hydrochloric acid afforded the amino acid hydrochloride salt **27**. The overall yield of this short approach to racemic **27** from diethyl allylmalonate **18** is 28% (using CBr_4 in the radical addition step) or 27% (using $BrCCl_3$).

Conclusion

This work has demonstrated, for the first time, that decacarbonyldimanganese mediated radical reactions can be performed under biphasic conditions. The presence of aqueous sodium hydroxide and BTAC can successfully remove pentacarbonylmanganese halide by-products produced from radical reactions of alkyl halides. Moreover, reactions under biphasic conditions using $XMn(CO)_5$ instead of $Mn_2(CO)_{10}$ have been shown to work efficiently, and the in situ formation of $Mn_2(CO)_{10}$ has been established. This may be explained by the intermediate formation of the pentacarbonylmanganese anion, which could also explain the formation of an organomanganese adduct on reaction with benzyl bromide. Application of the biphasic conditions to a range of couplings, cyclisations and intermolecular addition reactions has been successfully achieved, and $Mn_2(CO)_{10}$ has been shown to react with $BrCCl_3$, CBr_4 and sulfonyl chlorides to produce electrophilic radicals that can add to electron-rich alkenes. This has been exploited for the formation of cyclopropanes using a new radical addition−ionic cyclisation sequence, which has been applied to a concise synthesis of (±)-coronamic acid (**27**).

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectra were recorded on Jeol EX 270, Jeol ECX 400, Bruker DMX 300 or Bruker AMX 500 spectrometers. Carbon spectra were recorded at 67.5 MHz and assigned using DEPT experiments. Coupling constants are recorded to the nearest 0.5 Hz. Samples were prepared as solutions in $CDCl_3$ and contained an internal tetramethylsilane standard to which chemical shifts are referenced. IR spectra were recorded on an ATI Mattson Genesis Series FT IR spectrometer, and samples were prepared as thin films or as solutions in $CHCl_3$ or CH_2Cl_2. Mass spectra were recorded on a Fisons Instruments VG Analytical Autospec Spectrometer system as low and high resolution EI and CI (NH_3) spectra. Photolysis reactions were performed with visible light (λ > 400 nm) using an ICL 302 UV xenon lamp (300 W). Melting points were recorded on a Gallenkamp melting point apparatus. Thin layer chromatography (TLC) was performed using Merck 5554 aluminium-backed silica gel plates; compounds were visualised by either UV lamp irradiation or staining with alkaline aqueous potassium permanganate solution. Column chromatography was carried out under gravity using Fisons Matrex Silica 60 (70−200 microns) or ICN Biomedicals GmbH flash silica 60 (32−63 microns) and the specified eluent.

General Procedure for the Homocoupling Reaction of Benzyl Bromide under Biphasic Conditions: Benzyl bromide (0.25 g, 1.46 mmol) was added to a stirred solution of $Mn_2(CO)_{10}$ (0.14−0.40 g, 0.36−1.46 mmol) or $Mn(CO)_5X$ (X = Br, Cl, I) (0.73−2.92 mmol) in degassed dichloromethane (10 cm^3). An aqueous solution of sodium hydroxide (5 M, 10 cm^3) containing benzyltriethylammonium chloride (0−0.04 g, 0−0.18 mmol) was then added and the mixture was photolysed under an atmosphere of nitrogen for 2−27 h. The organic layer was separated, washed with water and dried over $MgSO_4$. The crude mixture was then adsorbed onto silica. Column chromatography (silica, petroleum ether) gave bibenzyl (**2**)[2] (11−80%) as a white solid and benzylpentacarbonylmanganese (**3**)[12] (0−56%) as an orange solid.

Benzylpentacarbonylmanganese (3): R_f = 0.22 (petroleum ether). m.p. 37−39 °C. ^1H NMR (270 MHz, $CDCl_3$): δ = 7.25−7.16 (m, 4 H, aromatics H_{ortho}/H_{meta}), 6.96 (m, 1 H, aromatic H_{para}), 2.40 (s, 2 H, CH_2) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 151.8 (*C*=CH), 128.6 (C=*C*H), 125.8 (*C*H=CH), 123.4 (CH=*C*H), 11.1 (*C*H_2Mn) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2107 (m), 2043 (w), 2016 (C=O, s), 2007 (C=O, s) cm^{-1}. MS (EI): *m/z* (%) = 287 (100) [M$^+$], 231 (40), 180 (36), 91 (86). HRMS for $MnC_{12}H_7O_5$: calcd. 286.9752 [M$^+$]; found 286.9746.

5-[2-(1,3-Benzodioxol-5-yl)ethyl]-1,3-benzodioxole (4): $Mn_2(CO)_{10}$ (0.18 g, 0.45 mmol) was added to a stirred solution of 5-(bromomethyl)-1,3-benzodioxole (0.20 g, 0.90 mmol) in degassed dichloromethane (10 cm^3) under nitrogen. An aqueous solution of NaOH (5 M, 10 cm^3) containing BTAC (0.02 g, 0.11 mmol) was then added and the mixture was irradiated under nitrogen until disappearance of the starting material. After the reaction time, the organic layer was separated, washed with water and dried over $MgSO_4$. The crude mixture was adsorbed onto silica; column chromatography (silica, petroleum ether/ethyl acetate, 6:1) afforded **4**[13b] (56 mg, 47%) as a white solid.

1,2,3-Trimethoxy-5-(3,4,5-trimethoxyphenethyl)benzene (5): $Mn_2(CO)_{10}$ (0.15 g, 0.38 mmol) was added to a stirred solution of 3,4,5-

trimethoxybenzyl bromide (0.20 g, 0.77 mmol) in degassed dichloromethane (10 cm^3) under nitrogen. An aqueous solution of NaOH (5 M, 10 cm^3) containing BTAC (0.02 g, 0.09 mmol) was added and the mixture was irradiated under nitrogen until disappearance of the starting material, as indicated by TLC. After the reaction time, the organic layer was separated, washed with water and dried over $MgSO_4$. The crude mixture was then adsorbed onto silica and column chromatography (silica, petroleum ether/ethyl acetate, 6:1) afforded **5**[17] (51 mg, 36%) as a white solid.

2,3-Diphenylbutane (6): 1-Bromoethylbenzene (0.27 g, 1.46 mmol) was added to a stirred solution of $Mn_2(CO)_{10}$ (0.28 g, 0.73 mmol) in degassed dichloromethane (10 cm^3). An aqueous solution of sodium hydroxide (5 M, 10 cm^3) containing BTAC (0.03 g, 0.18 mmol) was added and the mixture photolysed under an atmosphere of nitrogen for 2 h. After the reaction time, the organic layer was separated, washed with water and dried over $MgSO_4$. The crude mixture was adsorbed onto silica; column chromatography (silica, petroleum ether) afforded **6**[18] (111 mg, 75%) as an inseparable mixture of two diastereomers in a 1:1 ratio, as indicated by the ^1H NMR spectrum.

2,3-Dimethyl-2,3-diphenylbutane (7): 1-(1-Bromo-1-methylethyl)-benzene (0.29 g, 1.46 mmol) was added to a stirred solution of $Mn_2(CO)_{10}$ (0.28 g, 0.73 mmol) in degassed dichloromethane (10 cm^3). An aqueous solution of sodium hydroxide (5 M, 10 cm^3) containing BTAC (0.03 g, 0.18 mmol) was added and the mixture photolysed under an atmosphere of nitrogen for 4 h. After the reaction time, the organic layer was separated, washed with water and dried over $MgSO_4$. The crude mixture was adsorbed onto silica; column chromatography (silica, petroleum ether) afforded **7**[19] (40 mg, 25%) as a colourless oil.

General Procedure for Bromine-Atom Transfer Reactions Using $BrCCl_3$ under Biphasic Conditions: $Mn_2(CO)_{10}$ (0.11 g, 0.28 mmol) or $Mn(CO)_5Br$ (0.15 g, 0.56 mmol) was added to a stirred solution of $BrCCl_3$ (0.51 g, 2.56 mmol) and the diene **8a−c** (0.08−0.22 g, 0.86 mmol) in dichloromethane (20 cm^3) under an atmosphere of nitrogen. An aqueous solution of sodium hydroxide (5 M, 20 cm^3) containing BTAC (0.01 g, 0.07 mmol) was added and the mixture photolysed under an atmosphere of nitrogen for 2 h. After the reaction time, the organic layer was separated, washed with water and dried over $MgSO_4$. The crude mixture was adsorbed onto silica; column chromatography afforded products **9a**,[3a] **9b**[3a] and **9c** (0.24−0.45 g, 64−99%), as colourless oils, as mixtures of diastereomers in the ratio 2.5−18:1, as indicated by the ^1H NMR spectra.

3-(Bromomethyl)-1-(trichloroacetyl)-4-(2,2,2-trichloroethyl)-pyrrolidine (9c): Major (*cis*) isomer: $R_f = 0.3$ (petroleum ether/ethyl acetate, 9:1). ^1H NMR (270 MHz, $[D_8]$Tol, 80 °C): $\delta = 4.41$ (br. s, 2 H, C*H*$_2$N), 4.04 (dd, 2 H, *J* = 6 and 12 Hz, C*H*$_2$N), 3.57 (dd, 1 H, *J* = 4.5 and 10 Hz, C*H*Br), 3.35 (1 H, apparent t, *J* = 10 Hz, C*H*Br), 3.18−3.12 (m, 1 H, C*H*Cl), 3.02−2.88 (m, 3 H, C*H*Cl and 2 × C*H*CH$_2$) ppm. ^{13}C NMR (67.5 MHz, $[D_8]$Tol, 80 °C): $\delta = 159.6$ (*C*=O), 99.7 (*C*Cl$_3$CH$_2$), 96.6 (*C*Cl$_3$C=O), 54.0 and 53.8 (*C*H$_2$CCl$_3$ and 2 × *C*H$_2$N), 45.2 (*C*HCH$_2$Br), 40.0 (*C*HCH$_2$CCl$_3$), 30.8 (*C*H$_2$Br) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2964 (w), 2890 (w), 1674 (C=O, s), 1408 (m), 1245 (w), 1180 (w), 850 (m), 812 (s) cm^{-1}. MS (CI/NH$_3$): *m*/*z* (%) = 455 (24) [$^{79,35}M + NH_4^+$], 438 (31) [$^{79,35}M + H^+$], 442 (100), 320 (31). HRMS ($C_9H_{11}BrCl_6NO$): calcd. 437.8155 [$^{79,35}M + H^+$]; found 437.8153. Minor (*trans*) isomer: $R_f = 0.2$ (petroleum ether/ethyl acetate, 9:1). ^1H NMR (270 MHz, $[D_8]$Tol, 80 °C): $\delta = 4.85$ (1 H, br. s, C*H*N), 4.49 (1 H, br. s, C*H*N), 3.98−3.91 (m, 2 H, C*H*$_2$N), 3.66−3.57 (m, 1 H, C*H*Br), 3.45−3.38 (m, 1 H, C*H*Br), 3.20−3.11 (m, 1 H, C*H*Cl), 2.99−2.84 (m, 3 H, C*H*Cl and 2 × C*H*CH$_2$) ppm. ^{13}C NMR (67.5 MHz, $[D_8]$Tol, 80 °C): $\delta = 159.0$ (*C*=O), 99.3 (*C*Cl$_3$CH$_2$), 94.8 (*C*Cl$_3$C=O), 58.5, 56.3 and 53.9 (*C*H$_2$CCl$_3$ and 2 × *C*H$_2$N), 50.2 (*C*HCH$_2$Br), 47.6 (*C*HCH$_2$CCl$_3$), 35.5 (*C*H$_2$Br) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3031 (w), 2958 (br., w), 2888 (br., w), 1674 (C=O, s), 1406 (m), 1230 (m) cm^{-1}. MS (CI/NH$_3$): *m*/*z* (%) = 455 (27) [$^{79,35}M + NH_4^+$], 438 (34) [$^{79,35}M + H^+$], 442 (100), 320 (33). HRMS ($C_9H_{11}BrCl_6NO$): calcd. 437.8155 [$^{79,35}M + H^+$]; found 437.8148.

Typical Procedure for the Cyclisation of Dienes 8a,b in the Presence of Benzenesulfonyl Chloride: $Mn_2(CO)_{10}$ (0.11 g, 0.28 mmol) was added to a stirred solution of benzenesulfonyl chloride (0.45 g, 2.56 mmol) and the diene **8a**,**b** (0.86 mmol) in degassed dichloromethane (20 cm^3) under nitrogen. An aqueous solution of NaOH (5 M, 20 cm^3) containing BTAC (0.03, 0.21 mmol) was added and the mixture photolysed for 2 h. After the reaction time, the organic layer was separated, washed with water and dried over $MgSO_4$. The crude product was adsorbed onto silica; column chromatography afforded the inseparable products **14a**,**b** and **15a**,**b** as oils.

Diethyl 3-(Chloromethyl)-4-[(phenylsulfonyl)methyl]-1,1-cyclopentanedicarboxylate (14a) and Diethyl 3-methyl-4-[(phenylsulfonyl)-methyl]-1,1-cyclopentanedicarboxylate (15a): Pale yellow oil; R_f = 0.4 (petroleum ether/ethyl acetate, 2:1). IR ($CHCl_3$) (as an 8:1 mixture of **14a** and **15a**, as indicated by the ^1H NMR spectrum): $\tilde{\nu}$ = 3031 (m), 2984 (m), 1725 (C=O, vs), 1447 (w), 1307 (s), 1266 (s), 1228 (s), 1185 (m), 1151 (s), 1087 (w), 908 (s) cm^{-1}. Compound **14a**: Yield: 78%, 2:1 ratio of diastereomers (as indicated by the ^1H NMR spectrum). Major (*cis*) isomer: ^1H NMR (270 MHz, $CDCl_3$): $\delta = 7.89−7.47$ (m, 5 H, aromatics), 4.18−4.06 (q, *J* = 7 Hz, 4 H, 2 × C*H*$_2$CH$_3$), 3.43 (d, *J* = 7 Hz, 1 H, C*H*SO$_2$), 3.31−3.01 (m, 2 H, C*H*SO$_2$ and C*H*Cl), 2.69−1.89 (m, 7 H, C*H*Cl, 2 × C*H*CH$_2$ and 2 × CHC*H*$_2$), 1.23−1.17 (m, 6 H, 2 × CH$_2$C*H*$_3$) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 172.5$ (*C*=O), 172.3 (*C*=O), 139.9 (*C*=CH), 134.5 (C=*C*H), 130.0 (CH=*C*H), 128.6 (CH=*C*H), 62.4 (*C*H$_2$CH$_3$), 59.1 [*C*(CO$_2$Et)$_2$], 56.2 (*C*H$_2$SO$_2$), 44.9 (*C*HCH$_2$Cl), 44.4 (*C*H$_2$Cl), 38.9 (*C*HCH$_2$SO$_2$), 37.8 (*C*H$_2$), 36.4 (*C*H$_2$) ppm. The presence of the minor (*trans*) isomer was indicated by: ^1H NMR (270 MHz, $CDCl_3$): $\delta = 3.33$ (m, 1 H, C*H*SO$_2$ or C*H*Cl) ppm. MS (CI, NH$_3$): *m*/*z* (%) = 434 (82) [$^{35}M + NH_4^+$], 400 (100). HRMS ($C_{19}H_{28}ClNO_6S$): calcd. 434.1404 [$^{35}M + NH_4^+$]; found 434.1398. Compound **15a**: Yield: 10%, 15:1 ratio of diastereomers (as indicated by the ^1H NMR spectrum). The presence of the major (*cis*) isomer was indicated by: ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.79$ (d, *J* = 7 Hz, 3 H, C*H*$_3$) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 37.4$ (CH-CH$_3$), 15.6 (*C*H$_3$). The presence of the minor (*trans*) isomer was indicated by: ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.91$ (d, 3 H, *J* = 7 Hz, C*H*$_3$) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 38.0$ (*C*HCH$_3$), 14.5 (*C*H$_3$) ppm.

3-(Chloromethyl)-4-[(phenylsulfonyl)methyl]tetrahydrofuran (14b) and 3-Methyl-4-[(phenylsulfonyl)methyl]tetrahydrofuran (15b): Pale yellow oil; R_f = 0.4 (petroleum ether/ethyl acetate, 2:1). IR ($CHCl_3$) (as an inseparable 7:1 mixture of **14b**:**15b**, as indicated by the ^1H NMR spectrum): $\tilde{\nu}$ = 3033 (w), 2927 (m), 2856 (w), 1447 (w), 1308 (s), 1228 (s), 1150 (s), 1185 (m), 1087 (m) cm^{-1}. Compound **14b**: Yield: 42%, 1.7:1 ratio of diastereomers (as indicated by the ^1H NMR spectrum). Major (*cis*) isomer: ^1H NMR (270 MHz, $CDCl_3$): $\delta = 7.94−7.57$ (m, 5 H, aromatics), 4.15−4.08 (m, 1 H, OC*H*), 4.00−3.87 (m, 2 H, 2 × OC*H*), 3.79−3.67 (m, 1 H, OC*H*), 3.52−3.49 (m, 1 H, PhSO$_2$C*H*$_A$H$_B$), 3.34−3.30 (m, 1 H, PhSO$_2$-CH$_A$*H*$_B$), 3.22−3.03 (m, 1 H, ClC*H*$_A$H$_B$), 2.96−2.70 (m, 3 H, ClCH$_A$*H*$_B$ and 2 × OCH$_2$C*H*) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 139.6$ (*C*=CH), 134.7 (C=*C*H), 130.1 (CH=*C*H),

128.6 (CH=*C*H), 71.5 (O*C*H_2), 71.3 (O*C*H_2), 54.9 (Cl*C*H_2), 44.5 (*C*HCH_2Cl), 36.7 (*C*HCH_2SO_2Ph), 30.3 (PhSO_2*C*H_2). The presence of the minor (*trans*) isomer was indicated by: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.65−3.55 (m, 1 H, PhSO_2C*H*) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 55.9 (Cl*C*H_2), 47.9 (*C*HCH_2Cl) ppm. MS (CI/NH_3): *m*/*z* (%) = 292 (100) [^{35}M + NH_4^+], 258 (40), 241 (6). HRMS ($C_{12}H_{19}ClNO_3S$): calcd. 292.0774 [^{35}M + NH_4^+]; found 292.0773. Compound **15b**: Yield: 6%, 4:1 ratio of diastereomers (as indicated by the ^{1}H NMR spectrum). The presence of the major (*cis*) isomer was indicated by: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.93 (d, *J* = 7 Hz, 3 H, C*H_3*) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 38.6 (*C*HCH_3), 14.8 (*C*H_3) ppm. The presence of the minor (*trans*) isomer was indicated by: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.02 (d, 3 H, *J* = 7 Hz, C*H_3*) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 14.0 (*C*H_3) ppm.

Typical Procedure for the Cyclisation of the Dienes 8a,b,d,e in the Presence of Methanesulfonyl Chloride: $Mn_2(CO)_{10}$ (0.11 g, 0.28 mmol) was added to a stirred solution of methanesulfonyl chloride (0.29 g, 2.56 mmol) and the diene **8a,b,d,e** (0.86 mmol) in degassed dichloromethane (20 cm^3) under nitrogen. The mixture was then photolysed until disappearance of the starting material, as indicated by thin layer chromatography. After the reaction time, an aqueous solution of sodium hydroxide (5 M, 20 cm^3) containing BTAC (0.03 g, 0.21 mmol) was added and the solution stirred for 1 h. The organic layer was separated, washed with water and dried ($MgSO_4$). The crude mixture was adsorbed onto silica; column chromatography afforded the desired chlorine-atom transfer products **16a,b,d,e** (29−62%) and hydrogen-atom transfer products **17a,b,d,e** (20−35%) as oils.

Diethyl 3-(Chloromethyl)-4-[(methylsulfonyl)methyl]-1,1-cyclopentanedicarboxylate (16a) and Diethyl 3-Methyl-4-[(methylsulfonyl)-methyl]-1,1-cyclopentanedicarboxylate (17a): Yellow oil; R_f = 0.24 (ethyl acetate-petroleum ether, 1:1). IR ($CHCl_3$) (as an inseparable 2:1 mixture of **16a** and **17a**, as indicated by the ^{1}H NMR spectrum): ṽ = 3058 (vs), 1767 (C=O; s), 1368 (s), 1312 (vs), 1230 (vs) cm^{-1}. Compound **16a**: Yield: 62%, 2.5:1 ratio of diastereomers (as indicated by the ^{1}H NMR spectrum). Major (*cis*) isomer: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.23 (q, *J* = 7 Hz, 4 H, 2 × C*H_2*CH_3), 3.59 (d, *J* = 7 Hz, 1 H, C*H*SO_2), 3.33−2.99 (m, 2 H, C*H*SO_2 and CH_AH_BCl), 3.00 (s, 3 H, C*H_3*SO_2), 2.89−1.96 (m, 7 H, CH_AH_BCl, 2 × C*H*CH_2 and 2 × CHC*H_2*), 1.28 (t, *J* = 7 Hz, 6 H, 2 × CH_2C*H_3*) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 172.2 (*C*=O), 171.9 (*C*=O), 61.8 (2 × *C*H_2CH_3), 58.6 [*C*(CO_2Et)], 55.0 (*C*H_2SO_2), 53.9 (*C*H_2SO_2), 46.3 (*C*H_2Cl), 44.5 (CH*C*H_3), 43.9 (*C*HCH_2Cl), 41.7 (*C*H_2CH), 38.5 (*C*H_2CH), 35.6 (*C*HCH_2SO_2), 14.0 (2 × CH_2*C*H_3). The presence of the minor (*trans*) isomer was indicated by: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.00 (s, 3 H, C*H_3*SO_2) ppm. MS (CI, NH_3): *m*/*z* (%) = 372 (55) [^{35}M + NH_4^+], 355 (13) [^{35}M + H^+], 338 (100), 321 (27), 292 (13). HRMS ($C_{14}H_{27}ClNO_6S$): calcd. 373.1248 [^{35}M + NH_4^+]; found 372.1247. Compound **17a**: Yield: 20% (as indicated by the ^{1}H NMR spectrum); 18:1 ratio of diastereomers (as indicated by the ^{1}H NMR spectrum). The presence of the major (*cis*) isomer was indicated by: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.94 (d, *J* = 7 Hz, 3 H, C*H_3*) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 41.0 (*C*H_2CH), 37.9 (*C*H_2CH), 36.9 (*C*HCH_3), 36.4 (*C*HCH_2SO_2), 16.0 (CH*C*H_3). The presence of the minor (*trans*) isomer was indicated by: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 7 Hz, 3 H, C*H_3*) ppm. HRMS ($C_{14}H_{28}NO_6S$): calcd. 338.1637 [M + NH_4^+]; found 338.1633.

3-(Chloromethyl)-4-[(methylsulfonyl)methyl]tetrahydrofuran (16b): Yield: 35%; pale yellow oil; R_f = 0.3 (ethyl acetate-petroleum ether, 2:1); 2.5:1 ratio of diastereomers as indicated by the ^{1}H NMR spectrum. IR ($CHCl_3$): ṽ = 3029 (s), 2956 (s), 2931 (s), 2873 (s), 1305 (vs), 1232 (vs) cm^{-1}. Major (*cis*) isomer: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.08−3.93 (m, 3 H, OC*H* and 2 × OC*H*), 3.83−3.72 (m, 2 H, OC*H* and ClC*H_A*H_B), 3.69−3.59 (m, 1 H, SO_2CH_A*H_B*), 3.54 (d, *J* = 8 Hz, 1 H, ClCH_A*H_B*), 3.33−3.26 (m, 1 H, SO_2CH_A*H_B*), 3.14−2.73 (m, 2 H, 2 × C*H*CH_2), 2.95 (s, 3 H, C*H_3*SO_2) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 72.2 (*C*H_2O), 71.2 (*C*H_2O), 53.0 (*C*H_2SO_2), 44.5 (*C*HCH_2Cl), 43.3 (*C*H_2Cl), 42.1 (*C*H_3), 38.3 (*C*HCH_2SO_2). The presence of the minor (*trans*) isomer was indicated by: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.14 (dd, 1 H, *J* = 7 and 9.5 Hz, OC*H*), 2.93 (s, 3 H, C*H_3*SO_2) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 73.6 (*C*H_2O), 71.5 (*C*H_2O), 58.2 (*C*H_2SO_2), 47.8 (*C*HCH_2Cl), 46.4 (*C*H_2Cl), 42.2 (*C*H_3), 39.9 (*C*HCH_2SO_2) ppm. MS (CI, NH_3): *m*/*z* (%) = 230 (100) [^{35}M + NH_4^+]. HRMS ($C_7H_{17}ClNO_3S$): calcd. 230.0617 [^{35}M + NH_4^+]; found 230.0617.

3-Methyl-4-[(methylsulfonyl)methyl]tetrahydrofuran (17b): Yield: 59%; pale yellow oil; R_f = 0.25 (ethyl acetate-petroleum ether, 2:1); 6:1 ratio of diastereomers as indicated by the ^{1}H NMR spectrum. IR ($CHCl_3$): ṽ = 3013 (s), 2966 (s), 2932 (s), 2870 (s), 1311 (vs), 1231 (s), 1141 (vs) cm^{-1}. Major (*cis*) isomer: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.07 (dd, 1 H, *J* = 7 and 9, OC*H*), 3.94 (dd, *J* = 6.5 and 8.5 Hz, 1 H, 1 × OC*H*), 3.68 (dd, 1 H, *J* = 8 and 9, SO_2C*H*-$_A$$H_B$), 3.46 (q, 1 H, *J* = 17, 1 × OC*H*), 3.18 (dd, 1 H, *J* = 5 and 13.5, 1 × OC*H*), 3.01−2.93 (m, 1 H, SO_2CH_A*H_B*), 2.94 (s, 3 H, C*H_3*SO_2), 0.98 (d, *J* = 7 Hz, 3 H, C*H_3*) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 75.2 (*C*H_2O), 71.6 (*C*H_2O), 54.0 (*C*H_2SO_2), 42.2 (SO_2*C*H_3), 36.7 (*C*HCH_3), 36.5 (*C*HCH_2SO_2), 14.0 (*C*H_3). The presence of the minor (*trans*) isomer was indicated by: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.14 (dd, 1 H, *J* = 7 and 9, OC*H*), 3.31 (dd, 1 H, *J* = 5 and 13, OC*H*), 2.93 (s, 3 H, C*H_3*SO_2), 1.09 (d, *J* = 7 Hz, 3 H, C*H_3*) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 57.9 (*C*H_2SO_2), 41.4 (SO_2*C*H_3), 16.7 (*C*H_3) ppm. MS (CI, NH_3): *m*/*z* (%) = 196 (100) [M + NH_4^+], 179 (13). HRMS ($C_7H_{18}NO_3S$): calcd. 196.1007 [M + NH_4^+]; found 196.1008.

***cis*- and *trans*-3-(Chloromethyl)-4-[(methylsulfonyl)methyl]-1-(phenylsulfonyl)pyrrolidine (16d):** Yield: 29%; colourless oil; R_f = 0.5 (ethyl acetate); 3:1 ratio of diastereomers as indicated by the ^{1}H NMR spectrum. IR ($CHCl_3$): ṽ = 2965 (w), 2930 (w), 2867 (w), 1349 (m), 1315 (vs), 1167 (s), 1095 (w) cm^{-1}. Major isomer: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.87−7.54 (m, 5 H, aromatics), 3.67−2.40 (m, 10 H, C*H_2*SO_2, C*H_2*Cl, C*H*CH_2SO_2, C*H*CH_2Cl, NC*H_2*, NC*H_2*), 2.93 (s, 3 H, C*H_3*SO_2), 0.79 (d, *J* = 7 Hz, 3 H, CHC*H_3*) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 136.8 (*C*-SO_2), 133.7, 130.0, 128.1 (5 × *C*H=CH, aromatic), 52.6 (*C*H_2N), 51.9 (*C*H_2N), 50.7 (*C*H_2SO_2), 45.2 (*C*HCH_2Cl), 43.7 (*C*H_2Cl), 42.8 (*C*H_3SO_2), 35.3 (*C*HCH_2SO_2). The presence of the minor isomer was indicated by: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.61 (dd, 1 H, *J* = 7 and 9, C*H*N) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 133.4, 139.9, 128.3 (5 × *C*H=CH, aromatic), 57.4 (*C*H_2N), 53.4 (*C*H_2N), 46.1 (*C*HCH_2Cl), 42.4 (*C*H_3SO_2), 36.4 (*C*HCH_2SO_2) ppm. MS (CI, NH_3): *m*/*z* (%) = 369 (41) [^{35}M + NH_4^+], 352 (100) [^{35}M + H^+], 318 (9), 130 (20). HRMS ($C_{13}H_{19}ClNO_4S_2$): calcd. 352.0444 [^{35}M + H^+]; found 352.0446.

3-Methyl-4-[(methylsulfonyl)methyl]-1-(phenylsulfonyl)pyrrolidine (17d): Yield: 27%; colourless oil; R_f = 0.4 (ethyl acetate); 5:1 ratio of diastereomers as indicated by the ^{1}H NMR spectrum. IR ($CHCl_3$): ṽ = 2968 (m), 2928 (m), 2857 (w), 1348 (m), 1312 (s), 1167 (s), 1147 (m), 1095 (m), 1047 (w) cm^{-1}. Major (*cis*) isomer: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.82−7.51 (m, 5 H, aromatics), 3.58−2.32 (m, 8 H, C*H_2*SO_2, C*H*CH_2SO_2, C*H*CH_3, NC*H_2*, NC*H_2*), 2.87 (s, 3 H, C*H_3*SO_2), 0.79 (d, *J* = 7 Hz, 3 H, CHC*H_3*)

ppm. ^{13}C NMR (67.5 MHz, CDCl$_3$): δ = 137.3 (*C*SO$_2$), 133.5 (*C*H=CH, aromatic), 129.8 (*C*H=CH, aromatic), 128.0 (*C*H=CH, aromatic), 54.7 (*C*H$_2$N), 53.6 (*C*H$_2$N), 51.1 (*C*H$_2$SO$_2$), 42.4 (*C*HCH$_3$), 39.4 (*C*HSO$_2$), 36.1 (*C*H$_3$SO$_2$), 13.9 (CH*C*H$_3$). The presence of the minor (*trans*) isomer was indicated by: ^{1}H NMR (270 MHz, CDCl$_3$): δ = 0.94 (d, *J* = 7 Hz, 3 H, CHC*H*$_3$) ppm. ^{13}C NMR (67.5 MHz, CDCl$_3$): δ = 130.5 (*C*H=CH, aromatic), 128.1 (*C*H=CH, aromatic), 57.3 (*C*H$_2$N), 54.1 (*C*H$_2$N), 42.0 (*C*HCH$_3$), 40.0 (*C*HSO$_2$), 30.3 (*C*H$_3$SO$_2$), 14.8 (CH*C*H$_3$) ppm. MS (CI, NH$_3$): *m*/*z* (%) = 335 (19) [M + NH$_4^+$], 318 (100) [M + H$^+$], 176 (13), 96 (16). HRMS (C$_{13}$H$_{20}$NO$_4$S$_2$): calcd. 318.0834 [M + H$^+$]; found 318.0833.

1-Benzoyl-3-(chloromethyl)-4-[(methylsulfonyl)methyl]pyrrolidine (16e): Yield: 41%; colourless oil; *R*$_f$ = 0.2 (ethyl acetate); 1.5:1 ratio of diastereomers as indicated by the ^{1}H NMR spectrum. IR (CHCl$_3$): ṽ = 3020 (w), 2958 (w), 2929 (w), 1625 (CO; s), 1577 (m), 1148 (m), 1423 (s), 1313 (s), 1216 (m), 1143 (m) cm^{-1}. Major isomer: ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.60−7.48 (m, 2 H, aromatics), 7.46−7.42 (m, 3 H, aromatics), 3.93−2.45 (m, 10 H, 2 × C*H*$_2$N, C*H*$_2$SO$_2$, C*H*$_2$Cl, C*H*CH$_2$SO$_2$, C*H*CH$_2$Cl), 2.95 (s, 3 H, C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 169.9 (*C*=O), 135.8 (*C*=CH, aromatic), 130.2 (*C*H=CH, aromatic), 128.4 (*C*H=CH, aromatic), 127.2 (*C*H=CH, aromatic), 52.7 (*C*H$_2$SO$_2$), 51.9 (*C*H$_2$N), 48.8 (*C*H$_2$N), 43.0 (*C*H$_2$Cl), 41.6 (*C*HCH$_2$Cl), 41.8 (*C*H$_3$SO$_2$), 35.2 (*C*HCH$_2$SO$_2$CH$_3$). The presence of the minor isomer was indicated by: ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.02 (s, 3 H, C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 52.4 (*C*H$_2$N), 49.9 (*C*H$_2$N), 42.4 (*C*H$_2$Cl), 42.9 (*C*HCH$_2$Cl), 33.8 (*C*HCH$_2$SO$_2$CH$_3$) ppm. MS (CI, NH$_3$): *m*/*z* (%) = 316 (100) [^{35}M + H$^+$], 282 (30), 222 (9), 105 (27). HRMS (C$_{14}$H$_{19}$ClNO$_3$S): calcd. 316.0774 [^{35}M + H$^+$]; found 316.0771.

1-Benzoyl-3-methyl-4-[(methylsulfonyl)methyl]pyrrolidine (17e). Yield: 26%; colourless oil; *R*$_f$ = 0.1 (ethyl acetate); 1.3:1 ratio of diastereomers as indicated by the ^{1}H NMR spectrum. IR (film): ṽ = 3056 (m), 2968 (m), 2929 (m), 2879 (m), 1720 (m), 1626 (CO, s), 1577 (m), 1423 (s), 1305 (s), 1267 (s), 1137 (s) cm^{-1}. Major (*cis*) isomer: ^{1}H NMR (270 MHz, CDCl$_3$): δ = 7.52−7.48 (m, 2 H, aromatics), 7.45−7.41 (m, 3 H, aromatics), 3.95−2.51 (m, 8 H, 2 × C*H*$_2$N, C*H*$_2$SO$_2$, C*H*CH$_2$SO$_2$, C*H*CH$_3$), 2.92 (s, 3 H, C*H*$_3$SO$_2$), 0.95 (d, *J* = 7 Hz, 3 H, CHC*H*$_3$) ppm. ^{13}C NMR (67.5 MHz, CDCl$_3$): δ = 170.5 (*C*=O), 136.4 (*C*=CH, aromatic), 130.2, 128.5 and 127.2 (5 × *C*H=CH, aromatics), 56.3 (*C*H$_2$SO$_2$), 53.6 (*C*H$_2$N), 51.9 (*C*H$_2$N), 41.8 (*C*H$_3$SO$_2$), 35.7 and 34.6 (C*H*CH$_3$ and *C*HCH$_2$SO$_2$CH$_3$), 13.2 (CH*C*H$_3$). The presence of the minor (*trans*) isomer was indicated by: ^{1}H NMR (270 MHz, CDCl$_3$): δ = 2.99 (s, 3 H, C*H*$_3$SO$_2$), 1.07 (d, *J* = 7 Hz, 3 H, CHC*H*$_3$) ppm. ^{13}C NMR (67.5 MHz, CDCl$_3$): δ = 53.1 (*C*H$_2$N), 52.3 (*C*H$_2$N), 36.1 and 34.3 (*C*HCH$_3$ and *C*HCH$_2$SO$_2$CH$_3$), 13.8 (CH*C*H$_3$) ppm. MS (CI, NH$_3$): *m*/*z* (%) = 282 (100) [M + H$^+$], 188 (12), 105 (22). HRMS (C$_{14}$H$_{20}$NO$_3$S): calcd. 282.1164 [M + H$^+$]; found 282.1163.

General Procedure for Sequential Radical Addition−Ionic Cyclisation Using DBU: The unsaturated 1,3-dicarbonyl compound **18** or **22** (0.50−4.94 mmol) and bromotrichloromethane (0.29−2.85 g, 1.5−14.82 mmol) or carbon tetrabromide (0.49−4.92 g, 1.5−14.82 mmol) was added to a stirred solution of Mn$_2$(CO)$_{10}$ (0.07−0.65 g, 0.15−1.48 mmol) in degassed dichloromethane (10−100 cm^3). The mixture was photolysed under nitrogen until reaction completion, as indicated by TLC. DBU (0.17−1.64 g, 1.10−10.8 mmol) was added dropwise and the mixture stirred overnight. Column chromatography afforded the desired cyclopropanes **19**, **20** and **23** (0.11−0.83 g, 60−76%) as oils.

General Procedure for Sequential Radical Addition−Ionic Cyclisation under Biphasic Conditions: Diethyl allylmalonate (**18**) (0.20 g, 0.99 mmol) and bromotrichloromethane (0.57 g, 2.97 mmol) or carbon tetrabromide (0.99 g, 2.97 mmol) were added to a stirred solution of Mn$_2$(CO)$_{10}$ (0.13 g, 0.30 mmol) in degassed dichloromethane (20 cm^3). The mixture was photolysed under nitrogen until reaction completion, as indicated by TLC. An aqueous solution of NaOH (5 M, 10−100 cm^3) containing BTAC (0.02 g, 0.11 mmol) was added, and the biphasic system stirred vigorously overnight. Column chromatography afforded the desired cyclopropanes **19** and **20** (0.28−0.39 g, 80−88%) as oils.

Diethyl 2-(2,2,2-Trichloroethyl)-1,1-cyclopropanedicarboxylate (19): Yield: 75%; colourless oil; *R*$_f$ = 0.3 (petroleum ether/ethyl acetate, 9:1). IR (film): ṽ = 2983 (m), 2937 (w), 2908 (w), 1726 (C=O, br. vs), 1465 (w), 1446 (w), 1398 (m), 1369 (s), 1321 (s), 1282 (s), 1213 (s), 1132 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.33−4.14 (m, 4 H, 2 × C*H*$_2$CH$_3$), 3.12 (dd, 1 H, *J* = 4 and 15 Hz, C*H*$_A$H$_B$CCl$_3$), 2.48 (ddd, 1 H, *J* = 1, 9 and 15 Hz, CH$_A$*H*$_B$CCl$_3$), 2.36−2.28 (m, 1 H, C*H*CH$_2$), 1.65−1.60 (m, 2 H, CC*H*$_2$CH), 1.32−1.24 (m, 6 H, 2 × CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 169.1 (*C*=O), 167.6 (*C*=O), 98.4 (*C*Cl$_3$), 61.7 (*C*H$_2$CH$_3$), 61.6 (*C*H$_2$CH$_3$), 52.8 (*C*H$_2$CCl$_3$), 32.5 [*C*(CO$_2$Et)$_2$], 24.2 (*C*HCH$_2$), 20.7 (C*C*H$_2$CH), 14.0 (CH$_2$*C*H$_3$), 13.9 (CH$_2$*C*H$_3$) ppm. MS (CI, NH$_3$): *m*/*z* (%) = 317 (100) [^{35}M + H$^+$], 283 (20). HRMS (C$_{11}$H$_{16}$Cl$_3$O$_4$): calcd. 317.0114 [^{35}M + H$^+$]; found 317.0113.

Diethyl 2-(2,2,2-Tribromoethyl)-1,1-cyclopropanedicarboxylate (20): Yield: 76%; yellow oil; *R*$_f$ = 0.3 (petroleum ether/ethyl acetate, 9:1). IR (film) ṽ = 2981 (m), 2937 (w), 2906 (w), 1726 (C=O, br. vs), 1466 (w), 1444 (w), 1394 (m), 1369 (s), 1319 (s), 1278 (s), 1211 (s), 1130 (s) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 4.26−4.16 (m, 4 H, 2 × C*H*$_2$CH$_3$), 3.46 (dd, 1 H, *J* = 4 and 15 Hz, C*H*$_A$H$_B$CBr$_3$), 2.77 (dd, 1 H, *J* = 9 and 15 Hz, CH$_A$*H*$_B$CBr$_3$), 2.35−2.29 (m, 1 H, C*H*CH$_2$), 1.73−1.67 (m, 2 H, CC*H*$_2$CH), 1.36−1.24 (m, 6 H, 2 × CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 169.1 (*C*=O), 167.6 (*C*=O), 61.6 (2 × *C*H$_2$CH$_3$), 57.1 (*C*H$_2$CBr$_3$), 38.7 (*C*Br$_3$), 32.3 [*C*(CO$_2$Et)$_2$], 26.9 (*C*HCH$_2$), 21.1 (C*C*H$_2$CH), 14.0 (CH$_2$*C*H$_3$), 13.9 (CH$_2$*C*H$_3$) ppm. MS (CI, NH$_3$): *m*/*z* (%) = 449 (31) [^{79,79,79}M + H$^+$], 451 (100) [^{81,79,79}M + H$^+$], 453 (95) [^{81,81,79}M + H$^+$], 455 (30) [^{81,81,81}M + H$^+$], 173 (18). HRMS (C$_{11}$H$_{16}$Br$_3$O$_4$): calcd. 448.8599 [^{79,79,79}M + H$^+$]; found 448.8601.

Diethyl 2-Allyl-2-bromomalonate (21): Diethyl allylmalonate (**18**) (0.20 g, 0.98 mmol) and bromotrichloromethane (0.58 g, 2.94 mmol) were dissolved in degassed dichloromethane (20 cm^3). DBU (0.22 g, 1.47 mmol) was added and the mixture stirred overnight. The crude mixture was filtered through a silica plug to afford **21** (0.17 g, 54%) as a colourless oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.86−5.75 (m, 1 H, C*H*=CH$_2$), 5.20 (d, 2 H, *J* = 13 Hz, CH=C*H*$_2$), 4.27 (m, 4 H, 2 × C*H*$_2$CH$_3$), 3.04 (d, *J* = 6 Hz, 2 H, C*H*$_2$CBr), 1.29 (m, 6 H, 2 × CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 166.3 (2 × *C*=O), 131.2 (*C*H=CH$_2$), 120.2 (CH=*C*H$_2$), 62.9 (*C*H$_2$CBr), 61.8 (*C*Br), 42.4 (2 × *C*H$_2$CH$_3$), 13.9 (CH$_2$*C*H$_3$), 13.7 (CH$_2$*C*H$_3$) ppm. MS (CI, NH$_3$): *m*/*z* (%) = 296 (77) [^{79}M + NH$_4^+$], 279 (100) [^{79}M + H$^+$], 218 (21), 201 (43), 170 (21), 153 (29). HRMS (C$_{10}$H$_{16}$BrO$_4$): calcd. 279.0231 [^{79}M + H$^+$]; found 279.0230.

***tert*-Butyl 1-Acetyl-2-(2,2,2-trichloroethyl)cyclopropanecarboxylate (23):** Yield: 60%; separable mixture of two diastereomers in a 1:1 ratio, as indicated by the ^{1}H NMR spectrum. Diastereoisomer 1: pale yellow oil; *R*$_f$ = 0.4 (petroleum ether/diethyl ether, 9:1). IR (CHCl$_3$): ṽ = 3004 (m), 2979 (m), 2933 (m), 1724 (C=O, br., vs), 1429 (m), 1357 (s), 1290 (s), 1249 (s), 1166 (s), 1116 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (dd, 1 H, *J* = 5 and 15 Hz, $C\mathit{H}_AH_BCCl_3$), 2.54 (dd, 1 H, *J* = 5 and 15 Hz, $CH_A\mathit{H}_BCCl_3$), 2.43 (s, 3 H, $C\mathit{H}_3$), 2.38−2.22 (m, 1 H, $C\mathit{H}CH_2$), 1.73−1.66 (m, 1 H, $CC\mathit{H}_AH_BCH$), 1.51 [br. s, 10 H, $C(C\mathit{H}_3)_3$ and $CCH_A\mathit{H}_BCH$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.0 (*C*=O), 169.3 (*C*=O), 98.7 (*C*Cl_3), 82.5 [$\mathit{C}(CH_3)_3$], 51.5 ($\mathit{C}H_2CCl_3$), 40.2 (CO*C*CO), 31.0 ($\mathit{C}H_3CO$), 27.9 [$C(\mathit{C}H_3)_3$], 27.5 ($\mathit{C}HCH_2CCl_3$), 20.9 ($C\mathit{C}H_2CH$) ppm. MS (CI, NH_3): *m*/*z* (%) = 332 (2) [^{35}M + NH_4^+], 315 (10) [^{35}M + H^+], 276 (100), 259 (36). Diastereoisomer 2: pale yellow oil; R_f = 0.3 (petroleum ether/diethyl ether, 9:1). IR ($CHCl_3$): ṽ = 3004 (m), 2979 (m), 2933 (m), 1723 (C=O, vs), 1458 (m), 1369 (s), 1324 (s), 1241 (m), 1209 (m), 1167 (s), 1124 (vs) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.08 (dd, 1 H, *J* = 5 and 15 Hz, $C\mathit{H}_AH_BCCl_3$), 2.69 (dd, 1 H, *J* = 5 and 15 Hz, $CH_A\mathit{H}_BCCl_3$), 2.42 (s, 3 H, $C\mathit{H}_3$), 2.29−2.25 (m, 1 H, $C\mathit{H}CH_2$), 1.51 [br. s, 11 H, $C(C\mathit{H}_3)_3$, $CC\mathit{H}_AH_BCH$ and $CCH_A\mathit{H}_BCH$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.0 (*C*=O), 168.1 (*C*=O), 98.6 (*C*Cl_3), 82.9 [$\mathit{C}(CH_3)_3$], 52.3 ($\mathit{C}H_2CCl_3$), 40.7 (CO*C*CO), 29.4 ($\mathit{C}H_3CO$), 28.0 [$C(\mathit{C}H_3)_3$], 26.1 ($\mathit{C}HCH_2CCl_3$), 22.1 ($C\mathit{C}H_2CH$) ppm. MS (CI, NH_3): *m*/*z* (%) = 315 (7) [^{35}M + H^+], 276 (100), 259 (38), 183 (28). HRMS ($C_{12}H_{18}Cl_3O_3$): calcd. 315.0321 [^{35,35}M + H^+]; found 315.0321.

Reduction of Diethyl 2-(2,2,2-Trichloroethyl)-1,1-cyclopropanedicarboxylate (19) Using Tributyltin Hydride: The trichloride **19** (0.86 g, 2.72 mmol), *n*Bu_3SnH (4.75 g, 16.32 mmol) and AIBN (0.24 g, 1.36 mmol) were dissolved in degassed toluene (17 cm^3). The mixture was heated at 100 °C for 1 h, after which the mixture was cooled to room temp. and ethyl acetate (50 cm^3) added. A saturated aqueous solution of potassium fluoride (50 cm^3) was added and the biphasic mixture was stirred overnight. After separation and filtration of the organic layer, the filtrate was washed successively with water, brine, water and dried ($MgSO_4$). Column chromatography (flash silica, petroleum ether/ethyl acetate, 15:1) afforded **24** (0.52 g, 89%) as a colourless oil. R_f = 0.4 (petroleum ether/ethyl acetate, 9:1). IR (film): ṽ = 2979 (m), 2937 (m), 2877 (w), 1726 (C=O, s), 1465 (m), 1369 (m), 1321 (s), 1286 (s), 1207 (s), 1132 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.21−4.05 (m, 4 H, 2 × $C\mathit{H}_2CH_3$), 1.83−1.72 (m, 1 H, $CC\mathit{H}_AH_BCH$), 1.42−1.31 (m, 1 H, $CCH_A\mathit{H}_BCH$), 1.30−1.15 (m, 9 H, 2 × $CH_2C\mathit{H}_3$, $C\mathit{H}_2CH_3$ and $C\mathit{H}CH_2$), 0.94 (t, *J* = 7.5 Hz, 3 H, $C\mathit{H}_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5 (*C*=O), 168.3 (*C*=O), 61.2 (2 × $\mathit{C}H_2CH_3$), 34.3 [$\mathit{C}(CO)_2$], 29.8 ($\mathit{C}HCH_2$), 22.1 and 20.8 ($C\mathit{C}H_2CH$ and $\mathit{C}H_2CH_3$), 14.1 ($CH_2\mathit{C}H_3$), 14.0 ($CH_2\mathit{C}H_3$), 13.1 ($\mathit{C}H_3$) ppm. MS (CI, NH_3): *m*/*z* (%) = 232 (16) [M + NH_4^+], 215 (100) [M + H^+]. HRMS ($C_{11}H_{19}O_4$): calcd. 215.1283 [M + H^+]; found 215.1281.

Reduction of Diethyl 2-(2,2,2-Trichlorethyl)-1,1-cyclopropanedicarboxylate (20) Using Tributyltin Hydride: The tribromide **20** (0.36 g, 0.79 mmol) and *n*Bu_3SnH (1.38 g, 4.77 mmol) were mixed together without solvent. The mixture was heated to 80 °C under a nitrogen atmosphere for 3 h, then cooled to room temp. Ethyl acetate (20 cm^3), followed by a saturated aqueous solution of potassium fluoride (20 cm^3) were added, and the biphasic mixture stirred at room temp. overnight. After separation and filtration of the organic layer, the filtrate was washed successively with water, brine, water and dried ($MgSO_4$). Column chromatography (flash silica, petroleum ether/ethyl acetate, 15:1) afforded **24** (0.14 g, 83%) as a colourless oil.

(1*RS*,2*RS*)-1-(Ethoxycarbonyl)-2-ethylcyclopropanecarboxylic Acid (25): Potassium hydroxide (0.13 g, 2.38 mmol) in ethanol (2 cm^3) was added dropwise over 1 h to a stirred solution of the diester **24** (0.50 g, 2.38 mmol) in ethanol (1 cm^3). The solution was stirred at room temp. for 24 h and the solvent was then evaporated under reduced pressure. The residue was dissolved in water (1 cm^3) and extracted with dichloromethane (2 × 1 cm^3). The aqueous layer was cooled in ice and concentrated aqueous HCl (37%) was added dropwise until the mixture was acidic (as indicated by litmus paper). The combined organic extracts were dried over sodium sulfate and the solvents evaporated to afford **25** (0.21 g, 47%) as a colourless oil. IR (film): ṽ = 3300−2500 (br., s), 2969 (s), 2937 (s), 2879 (s), 1714 (C=O, br., vs), 1435 (m), 1373 (m), 1322 (m), 1209 (m), 1145 (m), 115 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.55 (br. s, 1 H, O*H*), 4.33−4.25 (m, 2 H, $C\mathit{H}_2CH_3$), 2.06 (1 H, apparent t, *J* = 7.5 Hz, $C\mathit{H}CH_2$), 1.90 (br. s, 1 H, $CC\mathit{H}_AH_BCH$), 1.70−1.68 (m, 1 H, $CCH_A\mathit{H}_BCH$), 1.63−1.54 (m, 2 H, $C\mathit{H}_2CH_3$), 1.32 (t, *J* = 7.5 Hz, 3 H, $OCH_2C\mathit{H}_3$), 0.99 (t, *J* = 7 Hz, 3 H, $C\mathit{H}_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.4 (*C*=O), 172.4 (*C*=O), 62.4 ($\mathit{C}H_2CH_3$), 38.4 ($\mathit{C}HCH_2$), 31.2 [$\mathit{C}(CO)_2$], 24.2 and 21.4 ($C\mathit{C}H_2CH$ and $\mathit{C}H_2CH_3$), 13.9 ($CH_2\mathit{C}H_3$), 13.1 ($\mathit{C}H_3$) ppm. MS (CI, NH_3): *m*/*z* (%) = 187 (5) [M + H^+], 122 (100). HRMS ($C_9H_{15}O_4$): calcd. 187.0970 [M + H^+]; found 187.0972.

[(1*RS*,2*RS*)-1-(Ethoxycarbonyl)-2-ethylcyclopropyl]ammonium Chloride (26): The carboxylic acid **25** (0.10 g, 0.52 mmol) was dissolved in acetone (10 cm^3) at 0 °C. Triethylamine (0.09 cm^3, 0.71 mmol) was added, followed by ethyl chloroformate (0.05 cm^3, 0.62 mmol). The solution was stirred for 25 min before the addition of a solution of sodium azide (0.06 g, 0.94 mmol) in water (5 cm^3). The solution was stirred for 15 min, diluted with ethyl acetate and washed with water. The organic layer was dried over sodium sulfate, filtered and the solvents evaporated. The residue was then dissolved in toluene (100 cm^3) and stirred at 90 °C for 1 h. The solvent was then removed, the residue dissolved in a mixture of dioxane/water/HCl (1:3:1, 20 cm^3) and stirred at room temp. for 20 min. Finally, the solvent was removed in vacuo to afford **26** (0.05 g, 53%) as a white solid. M.p. 110−112 °C. IR (film): ṽ = 3100−2600 (br., s), 2969 (s), 2935 (s), 2877 (s), 1731 (C=O, s), 1589 (m), 1529 (m), 1459 (m), 1379 (m), 1349 (m), 1249 (m), 1195 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01 (br. s, 2 H, $N\mathit{H}_2$), 4.49 (br. s, 2 H, $C\mathit{H}_2CH_3$), 1.92−1.26 (br. m, 8 H, $CC\mathit{H}_2$, $CH_2C\mathit{H}$, $CHC\mathit{H}_2$ and $CH_2C\mathit{H}_3$), 0.99 (br. s, 3 H, $CH_2C\mathit{H}_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1 (*C*=O), 62.4 ($\mathit{C}H_2CH_3$), 38.2 (N*C*CO), 30.2 ($\mathit{C}HCH_2$), 19.9 and 19.7 ($C\mathit{C}H_2CH$ and $\mathit{C}H_2CH_3$), 14.1 ($CH_2\mathit{C}H_3$), 13.2 (CH_3) ppm. MS (CI, NH_3): *m*/*z* (%) = 158 (100) [M + H^+ − HCl], 128 (26). HRMS ($C_8H_{16}NO_2$): calcd. 158.1181 [M + H^+−HCl]; found 158.1183.

[(1*RS*,2*RS*)-1-Carboxy-2-ethylcyclopropyl]ammonium Chloride [(±)-Coronamic Acid Hydrochloride] (27): The propanaminium chloride **26** (0.05 g, 0.26 mmol) was heated to reflux in 6 M HCl (5 cm^3) for 7 days. After cooling to room temp., the solvent was removed in vacuo to afford the title compound **27**[15c] (0.039 g, 90%) as a white solid. M.p. 200 °C (dec.) [ref.[15c] > 190 °C (sub.)]. IR (nujol): ṽ = 2925 (br., vs), 2857 (br., s), 2759 (w), 2669 (w), 2556 (w), 1984 (w), 1720 (C=O, s), 1591 (w), 1500 (m), 1459 (m), 1403 (m), 1252 (m). ^{1}H NMR (400 MHz, D_2O): δ = 1.75−1.64 (m, 2 H, $CC\mathit{H}_2CH$), 1.56−1.48 (3 H, $CH_2C\mathit{H}CH_2$ and $C\mathit{H}_2CH_3$), 0.93 (t, 3 H, *J* = 7 Hz, $CH_2C\mathit{H}_3$) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 169.7 (*C*=O), 37.9 ($\mathit{C}CO_2H$), 29.8 ($CH_2\mathit{C}HCH_2$), 19.6 ($\mathit{C}H_2$), 19.0 ($\mathit{C}H_2$), 12.5 ($\mathit{C}H_3$).

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