Novel Perfluoroalkylation of Alkenes with Perfluoroalkanesulphonyl Chlorides Catalysed by a Ruthenium(II) Complex

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The perfluoroalkylation of acyclic and cyclic alkenes by perfluoroalkanesulphonyl chlorides 1 has been investigated in the presence of a ruthenium(II) catalyst. The addition reactions proceeded smoothly, with extrusion of sulphur dioxide, in alkenes possessing either an electron-donating or an electron-withdrawing group, at 120 °C to give the corresponding chloroperfluoroalkylated compounds in high yield.

Recently, much attention has been focussed on fluoroalkylated compounds, owing to the characteristic features of the fluorine atoms, particularly in the field of medicinal and agricultural chemistry, and materials science.[1] However, the introduction of a perfluoroalkyl group into alkenes or aromatic compounds is not easy since the usual methods for alkylation cannot be applied to perfluoroalkylation. Therefore, efficient synthetic methods for this transformation have been the subject of much research. New methods or reagents for perfluoroalkylation of alkenes have been developed: e.g., metal complexes of perfluoroalkyl halides,[2] radical reactions of a perfluoroalkyl iodide initiated by photochemical or thermal means,[3] radical reaction of a perfluoroalkanesulphonyl chloride initiated either by peroxide or photochemically,[4] thermal reactions of a perfluoroalkanesulphonyl bromide[5] and of a (perfluoroalkyl)-phenyliodonium trifluoromethanesulphonate (FITS reagent),[6] radical reactions of thiohydroxamic esters,[7] electrochemical methods with trifluoroacetic acid,[8] and electron-transfer reactions of (perfluoroalkanoyl) peroxides[9] have been developed. Perfluoroalkylation of alkynes by a perfluoroalkyl iodide,[10] or by FITS reagent,[6b] has also been reported. However, these methods do not give satisfactory yields of products, often suffer from side reactions, and some require air-sensitive or sophisticated compounds which are hence troublesome to handle. Previously, we have reported a novel chlorotrifluoromethylation of alkenes with trifluoromethane-sulphonyl chloride catalysed by a ruthenium complex as a preliminary communication.[11] We now give a full account of this novel chloroperfluoroalkylation of acyclic and cyclic alkenes.

Results and Discussion

When a solution containing trifluoromethanesulphonyl chloride 1a (2.0 mmol), styrene 2a (2.0 mmol) and dichloro-tris(triphenylphosphine)ruthenium(II) (0.02 mmol) in benzene (4 cm³) was degassed and heated at 120 °C for 24 h, the reaction proceeded smoothly with extrusion of sulphur dioxide, and 3-chloro-1,1,1-trifluoro-3-phenylpropane 3a was obtained in 70% yield without formation of any side-reaction products [eqn. (1)].

$$CF_3SO_2Cl + PhCH=CH_2 \xrightarrow[120\,°C]{RuCl_2(PPh_3)_3}$$

$$\begin{array}{cc} \textbf{1a} & \textbf{2a} \end{array}$$

$$PhCHClCH_2CF_3 + SO_2 \quad (1)$$

$$\textbf{3a}$$

However, when the reaction was carried out at temperatures lower than 120 °C, the yield of compound 3a was lower, and the product was accompanied by 1-phenyl-2-(trifluoromethyl-sulphonyl)ethene 4 as a side-reaction product [eqn. (2)]. Therefore, reaction temperatures higher than 120 °C are required to extrude sulphur dioxide sufficiently and to obtain the alkane derivative 3a selectively. The yield of compound 3a was improved (87%) when the reaction substrate 1a was carried out with an excess of styrene at 120 °C. The results are summarized in Table 1.

$$CF_3SO_2Cl + PhCH=CH_2 \xrightarrow[80-100\,°C]{RuCl_2(PPh_3)_3}$$

$$\begin{array}{cc} \textbf{1a} & \textbf{2a} \end{array}$$

$$(2)$$

The catalytic effects of other metals or metal complexes, such as palladium, nickel, rhodium, and ruthenium, were investigated; however, these catalysts were much less effective or did not show any catalytic effect, as shown in Table 2. These results showed that dichlorotris(triphenylphosphine)-ruthenium(II) is the sole effective catalyst among these metal catalysts examined.

The time-course in the reaction of substrate 1a with styrene was studied in the presence of dichlorotris(triphenylphosphine)-ruthenium(II) at 100 °C and 120 °C, and the results are shown in Fig. 1, which indicates that the reaction is complete within 10 h, giving the alkane derivative 3a in high yield at 120 °C, whereas in the reaction at 100 °C the required reaction time is > 15 h, and even then the yield of product 3a did not exceed ca. 60%.

The reaction conditions giving the highest yield of adduct 3a having been revealed, perfluoroalkylations of some vinylarenes and alk-1-enes with substrate 1a were studied in benzene in the presence of the ruthenium(II) catalyst at 120 °C. Similarly, reactions of perfluorohexanesulphonyl chloride 1b with olefins were also investigated under similar conditions [eqn. (3)]. The results are summarized in Table 3.

$$R_FSO_2Cl + RCH=CH_2 \xrightarrow[C_6H_6,\,120\,°C]{RuCl_2(PPh_3)_3}$$

$$\begin{array}{cc} \textbf{1} & \textbf{2} \end{array}$$

1a $R_F = CF_3$
1b $R_F = C_6F_{13}$

$$RCHClCH_2R_F + \quad \begin{array}{c} R \\ H \end{array}\!\!C=C\!\!\begin{array}{c} H \\ R_F \end{array} + PhC_6F_{13} \quad (3)$$

$$\begin{array}{ccc} \textbf{3} & \textbf{5} & \textbf{6} \end{array}$$

Table 1 Reaction of trifluoromethanesulphonyl chloride with styrene catalysed by dichlorotris(triphenylphosphine)ruthenium(II)[a]

CF_3SO_2Cl (mmol)	$PhCH=CH_2$ (mmol)	Conditions		Product yield (%)[b]	
		Temp. (T/°C)	Time (t/h)	3a	4
2.0	2.0	80	24	58	11
2.0	2.0	100	24	59	3
2.0	2.0	120	24	70	0
2.0	4.0	120	16	84	0
2.0	5.0	120	16	87	0

[a] The reactions were carried out in benzene solution in a degassed sealed tube. [b] The product yield was determined by GC, with undecane as internal standard, based on the trifluoromethanesulphonyl chloride employed.

Table 2 Catalytic effect of transition metal catalyst in the reaction of trifluoromethanesulphonyl chloride with styrene[a]

Transition metal catalyst	Yield of product (3a) (%)[b]
$Pd(PPh_3)_4$	4
$Pd(dba)_2$[c]	trace
$PdCl_2$	0
$PdCl_2(MeCN)_2$	trace
$Pd(OAc)_2$	13
$NiCl_2(PPh_3)_3$	0
$RhCl(PPh_3)_3$	2
$RuCl_3·3HCl$	0
$RuCl_2(PPh_3)_3$	87

[a] The reactions were carried out in a degassed sealed tube containing 1a (2.0 mmol), styrene (5.0 mmol) and metal catalyst (0.02 mmol) in benzene (4 cm³) at 120 °C. [b] The yield was determined by GC based on the chloride 1a employed. [c] Dibenzylideneacetonepalladium(o).
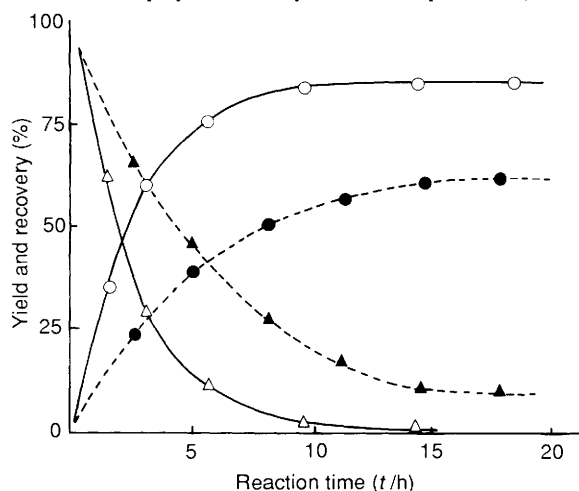
Fig. 1 Time-course in the reaction of CF_3SO_2Cl with styrene catalysed by $RuCl_2(PPh_3)_3$. —O—O— Yield of product 3a at 120 °C. —△—△— Recovery of styrene at 120 °C. --●---●-- Yield of product 3a at 100 °C. --▲--▲-- Recovery of styrene at 100 °C.

The reactions of substrate 1a with vinylarenes 2a–2d and alk-1-enes 2g–2i in the presence of the ruthenium(II) catalyst afforded the corresponding chloroperfluoroalkylated compounds in high yield. In the reaction of compound 1a with p-methylstyrene 2b, 3,3,3-trifluoro-1-(p-tolyl)propene 5c was obtained in 16% yield together with 3-chloro-1,1,1-trifluoro-3-(p-tolyl)propane 3c. Product 5c may be formed by dehydrochlorination of compound 3c aided by the ruthenium catalyst. We have previously reported the ruthenium(II)-catalysed dehydrochlorination of (E)-2-chloro-2-(p-tolyl)ethyl styryl sulphone to give (E,E)-p-methylstyryl styryl sulphone under similar reaction conditions.[12] It seems that dehydrochlorination tends to occur in cases where the product formed would be conjugated with and stabilized by the aromatic ring. Similar results were observed in the reactions of the sulphonyl

chloride 1b with alkenes 2a–2c as shown in Table 3. Reaction of compound 1b with alk-1-enes 2e–2g also afforded the corresponding chloroperfluoroalkylated compound in high yield. In the reactions of compound 1b, (perfluorohexyl)benzene 6 was formed in 5–19% yield; however, benzotrifluoride was not observed in the reactions of the trifluoromethyl compound 1a, since the b.p. of benzotrifluoride is low (101–102 °C) and it is difficult to separate it from an excess of the solvent (benzene) by GC or gel-permeation chromatography. Product 6 may be formed by reaction of the chloride 1b with solvent benzene.

The reaction of sulphonyl chlorides 1 with alkenes possessing an electron-withdrawing group (7a–d) was also investigated in the presence of the ruthenium(II) complex under similar conditions [eqn. (4)]. As shown in Table 4, the corresponding chloroperfluoroalkylated products 8a–f were obtained in good yield. The results show that the present method is a useful reaction for perfluoroalkylation of alkenes possessing both electron-donating and electron-withdrawing groups, whereas the reported methods, for example perfluoroalkylation by electrochemical methods, can be applied only to such alkenes possessing electron-withdrawing groups,[8] and by an electron-transfer reaction using (perfluoroalkanoyl) peroxides, is useful only for electron-rich alkenes.[9]

$$R_FSO_2Cl + R(R^1)C=CH_2 \xrightarrow[C_6H_6, 120 °C]{RuCl_2(PPh_3)_3}$$

$$\mathbf{1} \qquad\qquad \mathbf{7}$$

$$R(R')CClCH_2R_F + 6 \quad (4)$$

$$\mathbf{8}$$
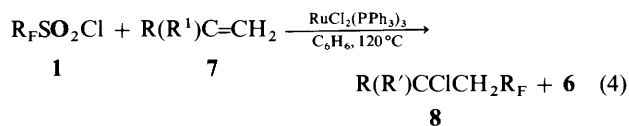
The reaction of compound 1a with internal olefins such as (E)-β-methylstyrene was found to give 3-chloro-1,1,1-trifluoro-2-methyl-3-phenylpropane 9 in 52% yield under similar conditions [eqn. (5)]. Reaction of compound 1a with 1-phenylbuta-1,3-diene in the presence of the ruthenium(II) complex afforded 5,5,5-trifluoro-1-phenylpenta-1,3-diene 10 although the yield was low (11%) [eqn. (6)]. In this case, it seems that a chlorotrifluoromethylated compound, 1-chloro-5,5,5-trifluoro-1-phenylpent-2-ene or 3-chloro-5,5,5-trifluoro-1-phenylpent-1-ene, once formed was completely dehydrochlorinated under the reaction conditions. Reaction of compound 1a with phenylacetylene did not give the expected 1-chloro-3,3,3-trifluoro-1-phenylpropene 11 at all under similar conditions [eqn. (7)].

$$CF_3SO_2Cl + \underset{H}{\overset{Ph}{>}}C=C\underset{Me}{\overset{H}{<}} \xrightarrow[120 °C, 17 h]{RuCl_2(PPh_3)_3}$$

$$PhCHClCH(Me)CF_3 \quad (5)$$

$$\mathbf{9}$$

$$CF_3SO_2Cl + PhCH=CHCH=CH_2 \xrightarrow[120 °C, 17 h]{RuCl_2(PPh_3)_3}$$

$$PhCH=CHCH=CHCF_3 \quad (6)$$

$$\mathbf{10}$$
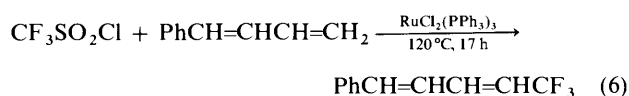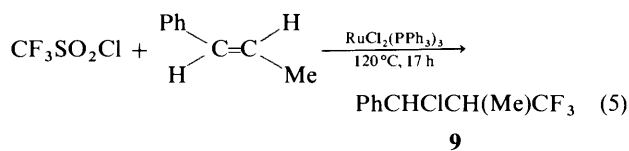
Table 3 Reaction of perfluoroalkanesulphonyl chlorides with vinyl arenes and alk-1-enes catalysed by ruthenium(II) phosphine complex [a]

R_F in substrate 1	R in alkene 2	Reaction time (t/h)	Product yield (%) [b]
1a CF_3	2a Ph	16	3a 87
1b C_6F_{13}	2a Ph	18	3b 70, 5b 13, 6 5
1a CF_3	2b p-MeC_6H_4 [c]	16	3c 46, 5c 16
1b C_6F_{13}	2b p-MeC_6H_4	18	3d 34, 5d 42, 6 9
1a CF_3	2c p-ClC_6H_4	16	3e 74
1b C_6F_{13}	2c p-ClC_6H_4	18	3f 67, 5e 11, 6 11
1a CF_3	2d m-$NO_2C_6H_4$	16	3g 79
1b C_6F_{13}	2e $Me[CH_2]_3$	18	3h 66, 6 14
1b C_6F_{13}	2f $Me[CH_2]_4$	18	3i 68, 6 19
1a CF_3	2g $Me[CH_2]_5$	14	3j 66
1b C_6F_{13}	2g $Me[CH_2]_5$	18	3k 76, 6k 19
1a CF_3	2h $Me[CH_2]_7$	14	3l 72
1a CF_3	2i $Me[CH_2]_9$	15	3m 70

[a] The reaction was carried out in a degassed sealed tube containing 1 (2.0 mmol), 2 (4.0 mmol) and the ruthenium(II) catalyst (0.02 mmol) in benzene (4 cm³) at 120 °C. [b] The yield was determined by GC base on substrate 1 employed. [c] p-Methylstyrene (10 mmol) was added.

Table 4 Reaction of perfluoroalkanesulphonyl chlorides with alk-1-enes possessing an electron-withdrawing group [a]

R_F in substrate 1	R and R' in alkenes 7		Amount of alkene 7 (mmol)	Reaction Time (t/h)	Product yield (%)
	R	R'			
1a CF_3	7a EtO_2C	H	4.0	14	8a 41
1a CF_3	7a EtO_2C	H	10.0	14	8a 70
1b C_6F_{13}	7a EtO_2C	H	4.0	18	8b 67, 6 25
1a CF_3	7a MeO_2CCH_2	MeO_2C	6.0	14	8c 64
1b C_6F_{13}	7c $EtCO_2$	H	4.0	18	8d 54, 6 34
1a CF_3	7d $PhCO_2$	H	6.0	24	8e 49
1b C_6F_{13}	7d $PhCO_2$	H	4.0	18	8f 56, 6 22

[a] The reaction was carried out in a degassed sealed tube containing 1 (2.0 mmol), alkene 7, and the ruthenium(II) catalyst (0.02 mmol) in benzene (4 cm³) at 120 °C. [b] The yield was determined by GC based on substrate 1 employed.

$$CF_3SO_2Cl + PhC\equiv CH \xrightarrow[\substack{120°C, 16 h}]{RuCl_2(PPh_3)_3 //} PhCCl=CHCF_3 \quad (7)$$
$$11$$
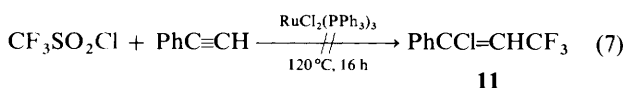
The chlorotrifluoromethylated products were treated with with aq. potassium hydroxide. When 3-chloro-1,1,1-trifluoro-3-phenylpropane **3a** or 3-chloro-1,1,1-trifluoro-2-methyl-3-phenylpropane **9** was allowed to react with aq. potassium hydroxide at 50 °C for 3 h, the starting material was completely consumed and (E)-3,3,3-trifluoro-1-phenylpropene **5a** or 3,3,3-trifluoro-2-methyl-1-phenylpropene **12** was isolated in 62 and 71% yield, respectively [eqns. (8) and (9)]. Thus, the combination of chloroperfluoroalkylation and dehydrochlorination can be regarded as the equivalent of a substitution reaction by the perfluoroalkyl group on the terminal carbon atom of an olefin, and this provides an excellent and novel preparative method for perfluoroalkylated compounds.

$$PhCHClCH_2CF_3 \xrightarrow[50°C, 3 h]{KOH} \underset{H}{\overset{Ph}{>}}C=C\underset{CF_3}{\overset{H}{<}} \quad (8)$$
$$3a \qquad\qquad 5a$$

$$PhCHClCH(Me)CF_3 \xrightarrow[50°C, 3 h]{KOH} PhCH=C\underset{CF_3}{\overset{Me}{<}} \quad (9)$$
$$9 \qquad\qquad 12$$
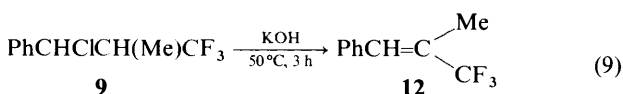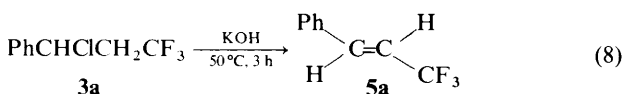
The reaction mechanism for these chloroperfluoroalkylations is given in Scheme 1. The redox-transfer reaction between perfluoroalkanesulphonyl chloride **1** and the ruthenium(II) catalyst affords the anion radical of compound **1** (**13**), which cleaves homolytically to give perfluoroalkanesulphonyl radical **14** and Ru^{III}–Cl. Perfluoroalkyl radical **15**, formed from radical **14** by extrusion of sulphur dioxide, adds to alkene **2** to give
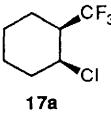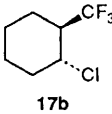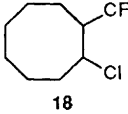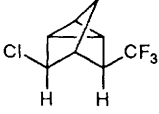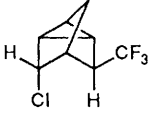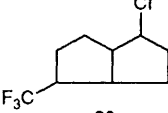
carbon radical **16**. The subsequent chlorine-atom abstraction, by radical **16**, from Ru^{III}–Cl species affords chloroalkylated product **3**, and the ruthenium(II) catalyst is regenerated. We believe that the radicals, formed by the interaction between a polyhalogenoalkane and a metal catalyst, lie in the co-ordination sphere of the metal, and that their reactivity is restricted compared with that of ordinary free radicals intitiated by peroxides or diazo compounds and by photoirradiation, and therefore a high product yield is observed.[13] The high product yield of chloroperfluoroalkylation in the present reaction, and the absence of formation of side-reaction products such as telomers, even for such easily polymerizable alkenes as styrene, is further evidence that the radicals lie in the co-ordination sphere of the ruthenium.

Scheme 1
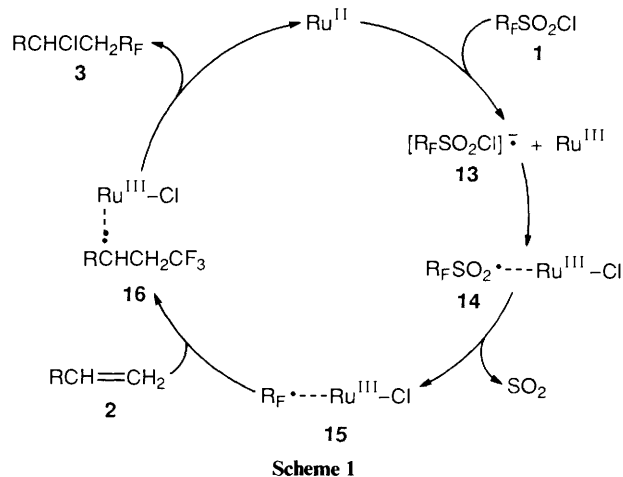
Table 5 Reaction of trifluoromethanesulphonyl chloride with cyclic olefins and dienes catalysed by ruthenium(ii) complex [a]

Substrate (mmol)	Reaction time (t/h)	Product yield (%)
	4.0	18	17a 7 17b 16
	4.0	18	18 25
	4.0	21	None
	4.0	16	19a 16 19b 17
	5.0	42	20 19

[a] The reaction was carried out in a degassed sealed tube containing sulphonyl chloride 1a (2.0 mmol), cycloalkene, and ruthenium(ii) catalyst (0.02 mmol) in benzene (4 cm³) at 120 °C. [b] The yield refers to pure isolated product based on the chloride 1a employed.

The reaction of the chloride 1a with some cycloalkenes and cycloalkadienes in the presence of the ruthenium(ii) catalyst was also studied. In the reaction with cyclohexene, cis-1-chloro-2-(trifluoromethyl)cyclohexane 17a and trans-1-chloro-2-(trifluoromethyl)cyclohexane 17b were isolated in 7 and 16% yield, respectively. On the other hand, the stereoisomers of 1-chloro-2-(trifluoromethyl)cyclooctane 18 formed by the reaction of compound 1a with cyclooctene under similar conditions could not be separated, and the total yield of the mixture was 25%. Although the yield was low, a chlorotrifluoromethylated product was formed from these two

(10)

19

(11)

20

cycloalkenes, whereas no reaction was observed in the reaction of compound 1a with bicyclo[2.2.1]hept-2-ene in the presence of the ruthenium(ii) complex under similar conditions. The reaction of compound 1a with bicyclo[2.2.1]hepta-2,5-

diene catalysed by the ruthenium(ii) complex gave exo-3-chloro-exo-5-(trifluoromethyl)tricyclo[2.2.1.0²·⁶] heptane 19a and endo-3-chloro-exo-5-(trifluoromethyl)tricyclo[2.2.1.0²·⁶]-heptane 19b in 16 and 17% yield, respectively [eqn. (10)]; no corresponding 1,2-adduct such as 5-chloro-6-(trifluoromethyl)bicyclo[2.2.1]hept-2-ene was detected. Similarly, reaction of compound 1a with cycloocta-1,5-diene afforded 2-chloro-6-(trifluoromethyl)bicyclo[3.3.0]octane 20 in 19% yield [eqn. (11)]. The results are summarized in Table 5. The formation of these bicyclocompounds 19 and 20 is accounted for by an addition of trifluoromethyl radical to the alkenes.

In conclusion, the present reaction of perfluoroalkanesulphonyl chlorides with alkenes catalysed by a ruthenium(ii) complex was found to be an excellent method for perfluoroalkylation. The method has the following characteristic features: (a) the yield is high, (b) the reaction can be achieved without use of special apparatus such as electrochemical equipment, (c) trifluoromethanesulphonyl chloride is a liquid (b.p. 29–32 °C) and can be easily handled at room temperature, whereas trifluoromethyl iodide, a well known trifluoromethylating reagent, is a gas (b.p. −22.5 °C) and troublesome to use in laboratories, (d) the ruthenium(ii) catalyst is required in only catalytic amounts, in contrast to the situation in previously reported stoichiometric metal-activated reactions.

Experimental

1 m stainless steel column. Gel-permeation chromatography was performed using a JAI LC-08 liquid chromatograph with two JAIGEL-1 H columns (20 mm × 600 mm) with chloroform as eluent.

All solvents were distilled and stored under nitrogen. Palladium dichloride, ruthenium trichloride and rhodium trichloride (Wako Chemicals) were used without further purification. Dichlorotris(triphenylphosphine)ruthenium(II),[14] chlorotris(triphenylphosphine)rhodium(I),[15] tetrakis(triphenylphosphine)palladium(0),[16] dibenzylideneacetonepalladium(0),[17] palladium diacetate,[18] dichlorobis(acetonitrile)palladium(II),[19] and dichlorobis(triphenylphosphine)nickel(II),[20] were prepared by the methods described in the literature. Trifluoromethanesulphonylchloride and perfluorohexanesulphonyl chloride (Fluorochem) were used without further purification. Styrene derivatives, alk-1-enes, α,β-unsaturated esters, and cyclic alkenes (Tokyo Kasei Chemicals) were purified by distillation prior to use and were stored under nitrogen.

General Procedure for the Reaction of Perfluoroalkanesulphonyl Chlorides 1 *with Alkenes.*—A solution containing a perfluoroalkanesulphonyl chloride 1 (2.0 mmol), alkene (4–10 mmol), and dichlorotris(triphenylphosphine)ruthenium(II) (0.02 mmol) in dry benzene (4 cm^3) was degassed by a freeze–pump–thaw cycle, sealed in an ampoule, and heated at 120 °C for 24 h. The reaction mixture was subjected to short-column chromatography on Florisil with benzene as eluent to remove the metal complex. The products were isolated from the reaction mixture by the use of gel-permeation chromatography and/or column chromatography over silica gel (Wakogel C-60), and were identified by IR, NMR and MS. The yields of the products were determined by GC with undecane as internal standard.

Dehydrochlorination of the Adducts 3a *and* 9.—A mixture containing 3-chloro-1,1,1-trifluoro-3-phenylpropane 3a (133 mg, 0.64 mmol), potassium hydroxide (101 mg, 1.08 mmol) and methanol (6 cm^3) was stirred at 50 °C for 3 h. After removal of methanol under reduced pressure, the organic residue was extracted with 1,1-dichloroethane, and the extracts were dried over anhydrous magnesium sulphate. (*E*)-3,3,3-Trifluoro-1-phenylpropene 5a was obtained in pure form after removal of the solvent under reduced pressure (68 mg, 62%). Similarly, 3,3,3-trifluoro-2-methyl-1-phenylpropene 12 was formed in 71% yield from 3-chloro-1,1,1-trifluoro-2-methyl-1-phenylpropane 9 under similar conditions.

The following compounds were thus prepared.

3-*Chloro*-1,1,1-*trifluoro*-3-*phenylpropane* 3a. An oil; v$_{max}$-(neat)/cm^1 3030, 1380, 1270 and 1140; δ$_H$(CDCl$_3$) 2.50–3.28 (2 H, m), 5.40 (1 H, t, *J* 7.2) and 7.26 (5 H, s); *m/z* 208 (M$^+$), 173, 125, 109 and 105 (Found: M$^+$, 208.0267. C$_9$H$_8$ClF$_3$ requires M, 208.0267).

8-*Chloro*-1,1,1,2,2,3,3,4,4,5,5,6,6-*tridecafluoro*-8-*phenyloctane* 3b. An oil; v$_{max}$(neat)/cm^{-1} 1360; δ$_H$(CDCl$_3$) 2.53–3.37 (2 H, m), 5.20 (1 H, t, *J* 7.2) and 7.33 (5 H, s); δ$_C$(CDCl$_3$) 41.0 (t, *J*$_{CCF}$ 20.8), 54.1, 126.9 (2C), 129.2 (3 C) and 140.4; *m/z* 458 (M$^+$) and 423 (Found: M$^+$, 458.0135. C$_{14}$H$_8$ClF$_{13}$ requires M, 458.0107).

3-*Chloro*-1,1,1-*trifluoro*-3-(p-*tolyl*)*propane* 3c. An oil; v$_{max}$(neat)/cm^{-1} 3020, 2920, 1610, 1510, 1420, 1380, 1260 and 1140; δ$_H$(CDCl$_3$) 2.30 (3 H, s), 2.50–3.23 (2 H, m), 5.01 (1 H, t, *J* 6.6) and 7.08 and 7.14 (4 H, ABq, *J* 8.7); *m/z* 222 (M$^+$), 187, 139, 123 and 117 (Found: M$^+$, 222.0430. C$_{10}$H$_{10}$ClF$_3$ requires M, 222.0423).

8-*Chloro*-1,1,1,2,2,3,3,4,4,5,5,6,6-*tridecafluoro*-8-(p-*tolyl*)-*octane* 3d. An oil; v$_{max}$(neat)/cm^{-1} 3030, 2930, 1615, 1515, 1440 and 1365; δ$_H$(CDCl$_3$) 2.35 (3 H, s), 2.51–3.37 (2 H, m), 5.20 (1 H, t, *J* 6.9), and 7.16 and 7.27 (4 H, ABq, *J* 8.1); δ$_C$(CDCl$_3$) 21.1, 40.8

(t, *J*$_{CCF}$ 22.0), 54.0, 126.7 (2C), 129.7 (2C), 137.4 and 139.1; *m/z* 472 (M$^+$), 437, 167, 139, 123 and 69 (Found: M$^+$, 472.0301. C$_{15}$H$_{10}$ClF$_{13}$ requires M, 472.0263).

3-*Chloro*-3-(p-*chlorophenyl*)-1,1,1-*trifluoropropane* 3e. An oil; v$_{max}$(neat)/cm^{-1} 1900, 1600, 1490, 1380, 1260 and 1140; δ$_H$(CDCl$_3$) 2.46–3.21 (2 H, m), 4.98 (1 H, t, *J* 7.2) and 7.18 (4 H, s); *m/z* 242 (M$^+$), 207, 161 and 143 (Found: M$^+$, 241.9879. C$_9$H$_7$Cl$_2$F$_3$ requires M, 241.9877).

8-*Chloro*-8-(p-*chlorophenyl*)-1,1,1,2,2,3,3,4,4,5,5,6,6-*tridecafluorooctane* 3f. An oil; v$_{max}$(neat)/cm^{-1} 1600, 1490, 1420 and 1365; δ$_H$(CDCl$_3$) 2.50–3.33 (2 H, m), 5.19 (1 H, t, *J* 6.9), and 7.33 (4 H, s); δ$_C$(CDCl$_3$) 41.0 (t, *J*$_{CCF}$ 20.8), 53.3 (t, *J*$_{CCCF}$ 3.1), 128.3 (2C), 129.4 (2C), 135.3 and 138.9; *m/z* 492 (M$^+$), 457, 159, 143, 138 and 69 (Found: M$^+$, 491.9745. C$_{14}$H$_7$Cl$_2$F$_{13}$ requires M, 491.9717).

3-*Chloro*-1,1,1-*trifluoro*-3-(m-*nitrophenyl*)*propane* 3g. Pale yellow oil; v$_{max}$(neat)/cm^{-1} 3070, 1530, 1350, 1250 and 1140; δ$_H$(CDCl$_3$) 2.60–3.22 (2 H, m), 5.13 (1 H, t, *J* 6.6) and 7.14–8.31 (4 H, m); *m/z* 253 (M$^+$), 218, 154, 103 and 77 (Found: M$^+$, 253.0087. C$_9$H$_7$ClF$_3$NO$_2$ requires M, 253.0117).

8-*Chloro*-1,1,1,2,2,3,3,4,4,5,5,6,6-*tridecafluorododecane* 3h. An oil; v$_{max}$(neat)/cm^{-1} 2960, 2930, 2870, 1470, 1440 and 1360; δ$_H$(CDCl$_3$) 0.72–2.13 (9 H, m), 2.16–3.03 (2 H, m) and 4.26 (1 H, quintet, *J* 6.2); δ$_C$(CDCl$_3$) 13.8, 22.2, 28.3, 38.7, 39.7 (t, *J*$_{CCF}$ 22.6) and 53.5; *m/z*, 402 (M$^+$ − 36) and 69 [Found: (M$^+$ − HCl), 402.0641. C$_{12}$H$_{11}$F$_{13}$ (M$^+$ − HCl) requires *m/z*, 402.0653].

8-*Chloro*-1,1,1,2,2,3,3,4,4,5,5,6,6-*tridecafluorotridecane* 3i. An oil; v$_{max}$(neat)/cm^{-1} 2960, 2930, 2860, 1465, 1435 and 1360; δ$_H$(CDCl$_3$) 0.69–2.12 (11 H, m), 2.14–3.03 (2 H, m) and 4.24 (1 H, quintet, *J* 6.0); δ$_C$(CDCl$_3$) 13.9, 22.6, 25.8, 31.3, 39.0, 39.7 (t, *J*$_{CCF}$ 18.9) and 53.5; *m/z* 416 (M$^+$ − 36), 387 and 69 [Found: (M$^+$ − HCl), 416.0848. C$_{13}$H$_{13}$F$_{13}$ (M$^+$ − HCl) requires *m/z*, 416.0809].

3-*Chloro*-1,1,1-*trifluorononane* 3j. An oil; v$_{max}$(neat)/cm^{-1} 2930, 1460, 1380, 1260 and 1150; δ$_H$(CDCl$_3$) 0.64–2.04 (13 H, m), 2.39 and 2.68 (2 H, ABq, *J* 10.2 and 6.6) and 4.06 (1 H, quintet, *J* 6.6); δ$_C$(CDCl$_3$) 14.0, 22.6, 26.0, 28.7, 31.7, 38.2, 42.6 (q, *J*$_{CCF}$ 28.1), and 5.43 (q, *J*$_{CCCF}$ 3.7); *m/z* 216 (M$^+$), 180, 173, 151, 137, 83 and 73 (Found: M$^+$, 216.0858. C$_9$H$_{16}$ClF$_3$ requires M, 216.0893).

8-*Chloro*-1,1,1,2,2,3,3,4,4,5,5,6,6-*tridecafluorotetradecane* 3k. An oil; v$_{max}$(neat)/cm^{-1} 2960, 2940, 2870, 1470, 1435 and 1365; δ$_H$(CDCl$_3$) 0.67–2.09 (13 H, m), 2.13–3.01 (2 H, m) and 4.24 (1 H, quintet, *J* 6.2); δ$_C$(CDCl$_3$) 14.0, 22.6, 26.1, 28.7, 31.7, 38.9, 39.7 (t, *J*$_{CCF}$ 18.9) and 53.5; *m/z* 430 (M$^+$ − 36), 401 and 387 [Found: (M$^+$ − HCl), 430.0967. C$_{14}$H$_{15}$F$_{13}$ (M$^+$ − HCl) requires *m/z*, 430.0966].

3-*Chloro*-1,1,1-*trifluoroundecane* 3l. An oil; v$_{max}$(neat)/cm^{-1} 2920, 1460, 1380, 1260, 1240 and 1145; δ$_H$(CDCl$_3$) 0.60–2.07 (17 H, m), 2.38 and 2.68 (2 H, ABq, *J* 10.2 and 6.6) and 4.05 (1 H, quintet, *J* 6.6); δ$_C$(CDCl$_3$) 14.1, 22.8, 26.0, 29.0, 29.3, 29.5, 31.9, 38.2, 42.6 (q, *J*$_{CCF}$ 28.2) and 54.2 (q, *J*$_{CCCF}$ 3.7); *m/z* 224 (M$^+$), 175, 151, 137, 123, 98 and 85 (Found: M$^+$, 244.1306. C$_{11}$H$_{20}$ClF$_3$ requires M, 244.1206).

3-*Chloro*-1,1,1-*trichlorotridecane* 3m. An oil; v$_{max}$(neat)/cm^{-1} 2930, 1460, 1380, 1260, 1240 and 1150; δ$_H$ 0.60–2.00 (21 H, m), 2.39 and 2.67 (2 H, ABq, *J* 10.2 and 6.0), and 4.05 (1 H, quintet, *J* 6.0); δ$_C$(CDCl$_3$) 14.1, 22.8, 26.0, 29.0, 29.4, 29.5, 29.6, 29.7, 32.0, 38.2, 42.6 (q, *J*$_{CCF}$ 28.1) and 54.2 (q, *J*$_{CCCF}$ 3.1); *m/z* 272 (M$^+$), 173, 151, 137, 85, 71 and 56 (Found: M$^+$, 272.1525. C$_{13}$H$_{24}$ClF$_3$ requires M, 272.1519).

(E)-1-*Phenyl*-2-(*trifluoromethylsulphonyl*)*ethene* 4. M.p. 52–53 °C; v$_{max}$(KBr)/cm^{-1} 1370, 1220 and 1120; δ$_H$(CDCl$_3$) 6.73 (1 H, d, *J* 15.0), 7.44 (5 H, s) and 7.81 (1 H, d, *J* 15.0); *m/z* 236 (M$^+$), 167, 103 and 77 (Found: M$^+$, 236.0101. C$_9$H$_7$F$_3$SO$_2$ requires M, 236.0119).

(E)-3,3,3-*Trifluoro*-1-*phenylpropene*[21] 5a. An oil; v$_{max}$-(neat)/cm^{-1} 1670, 1580, 1500, 1450 and 1340; δ$_H$(CDCl$_3$) 5.80–

6.39 (1 H, m), 6.87–7.30 (1 H, m) and 7.30 (5 H, s); m/z 172 (M$^+$), 151, 145, 133, 122, 103 and 77.

(E)-3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-phenyloct-1-ene **5b.** An oil; ν_{max}(neat)/cm^{-1} 1660, 1585, 1500, 1450 and 1365; δ_H(CDCl$_3$) 5.73–6.55 (1 H, m), 7.09 (1 H, d, J 10.2) and 7.33 (5 H, s); δ_C(CDCl$_3$) 114.6 (t, J_{CCF} 23.2), 127.7 (2 C), 129.0 (2 C), 130.2, 133.8 and 139.9 (t, J_{CCCF} 9.8); m/z 422 (M$^+$), 403, 353, 153, 133 and 69 (Found: M$^+$, 422.0292. C$_{14}$H$_7$F$_{13}$ requires M, 422.0340).

3,3,3-Trifluoro-1-(p-tolyl)propane[21] **5c.** An oil; δ_H(CDCl$_3$) 2.33 (3 H, s), 5.90 and 6.18 (1 H, d, J 6.0), and 6.60–7.37 (5 H, m); m/z 186 (M$^+$), 165, 151, 117 and 91.

(E)-3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-(p-tolyl)oct-1-ene **5d.** ν_{max}(neat)/cm^{-1} 3030, 2930, 1655, 1610, 1515, 1415 and 1365; δ_H 2.37 (3 H, s), 5.72–6.53 (1 H, m), 6.94–7.05 (1 H, m) and 7.18 and 7.34 (4 H, ABq, J 8.1); δ_C(CDCl$_3$) 21.3, 113.4 (t, J_{CCF} 23.2), 127.7 (2 C), 129.7 (2 C), 131.0, 139.8 (t, J_{CCCF} 9.2) and 140.6; m/z 436 (M$^+$), 417, 167, 147 and 69 (Found: M$^+$, 436.0521. C$_{15}$H$_9$F$_{13}$ requires M, 436.0496).

(E)-1-(p-Chlorophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-oct-1-ene **5e.** An oil; ν_{max}(neat)/cm^{-1} 1660, 1600, 1500, 1415 and 1365; δ_H(CDCl$_3$) 5.77–6.60 (1 H, m), 7.15 (1 H, d, J 14.4), and 7.40 (4 H, s); δ_C(CDCl$_3$) 115.2 (t, J_{CCF} 23.2), 128.9 (2 C), 129.3 (2 C), 132.1, 136.3 and 138.6 (t, J_{CCCF} 9.8); m/z 456 (M$^+$), 437, 187, 167, 151 and 69 (Found: M$^+$, 455.9954. C$_{14}$H$_6$ClF$_{13}$ requires M, 455.9950).

Tridecafluoro(phenyl)hexane **6.** Pale yellow oil; ν_{max}(neat)/cm^{-1} 1420, 1360, 1280, 1230, 1190 and 1140; δ_H(CDCl$_3$) 7.47 (5 H, s); δ_C(CDCl$_3$) 127.0 (2 C, t, J_{CCCF} 6.7), 128.8 and 132.1 (2 C); m/z 396 (M$^+$), 377, 158, 127 and 77 (Found: M$^+$, 396.0179. C$_{12}$H$_5$F$_{13}$ requires M, 396.0183).

Ethyl 2-chloro-4,4,4-trifluorobutanoate **8a.** An oil; ν_{max}(neat)/cm^{-1} 2980, 1750, 1370, 1260, 1150 and 1120; δ_H(CDCl$_3$) 1.31 (3 H, t, J 7.2), 2.29–3.33 (2 H, m), 4.23 (2 H, q, J 7.2) and 4.41 (1 H, t, J 7.2); δ_C(CDCl$_3$) 13.9, 39.2 (q, J_{CCF} 29.3), 49.0 (q, J_{CCCF} 2.4), 62.8 and 167.7; m/z 204 (M$^+$) 159, 133, 131, 78 and 69 (Found: M$^+$, 204.0167. C$_6$H$_8$ClF$_3$O$_2$ requires M, 204.0165).

Ethyl 2-chloro-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoate **8b.** An oil; ν_{max}(neat)/cm^{-1} 3000 and 1755; δ_H(CDCl$_3$) 1.27 (3 H, t, J 7.2), 2.09–3.69 (2 H, m), 4.28 (2 H, q, J 7.2) and 4.56 (1 H, t, J 7.2); δ_C(CDCl$_3$) 13.9, 36.8 (t, J_{CCF} 21.4), 48.4, 63.1 and 168.2; m/z 454 (M$^+$), 409 and 381 (Found: M$^+$, 454.0019. C$_{11}$H$_8$ClF$_{13}$O$_2$ requires M, 454.0005).

Dimethyl 2-chloro-2-(2,2,2-trifluoroethyl)butanedioate **8c.** An oil; ν_{max}(neat)/cm^{-1} 2950, 1740, 1440, 1360 and 1265; δ_H(CDCl$_3$) 3.20 (2 H, q, J 10.2), 3.28 (2 H, s), 3.67 (3 H, s) and 3.80 (3 H, s); δ_C(CDCl$_3$) 41.4, (q, J_{CCF} 29.3), 42.3, 52.1, 53.9, 60.5 (q, J_{CCCF} 2.4), 168.8 and 169.2; m/z 262 (M$^+$), 230, 183 and 109 (Found: M$^+$, 262.0290. C$_8$H$_{10}$ClF$_3$O$_4$ requires M, 262.0220).

1-Chloro-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl propanoate **8d.** An oil; ν_{max}(neat)/cm^{-1} 1755 and 1365; δ_H(CDCl$_3$) 1.17 (3 H, t, J 7.2), 2.42 (2 H, q, J 7.2), 2.29–3.60 (2 H, m) and 6.67–7.00 (1 H, m); δ_C(CDCl$_3$) 8.6, 27.6, 40.2 (t, J_{CCF} 20.8), 76.2 and 171.4; m/z 454 (M$^+$), 419, 397, 381, 361, 311 and 295 (Found: M$^+$, 453.9999. C$_{11}$H$_8$ClF$_{13}$O$_2$ requires M, 454.0005).

1-Chloro-3,3,3-trifluoropropyl benzoate **8e.** An oil; ν_{max}(neat)/cm^{-1} 1740, 1600, 1240, 1140, 1090 and 1060; δ_H(CDCl$_3$) 2.73–3.44 (2 H, m), 6.92 (1 H, dd, J 6.6 and 4.8) and 7.13–8.21 (5 H, m); m/z 252 (M$^+$), 217, 173, 140, 122, 105 and 77 (Found: M$^+$, 252.0165. C$_{10}$H$_8$ClF$_3$O$_2$ requires M, 252.0165).

1-Chloro-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl benzoate **8f.** An oil; ν_{max}(neat)/cm^{-1} 1750, 1600 and 1455; δ_H(CDCl$_3$) 2.65–3.54 (2 H, m), 6.92–7.23 (1 H, m), 7.27–7.70 (3 H, m), and 7.91–8.26 (2 H, m); δ_C(CDCl$_3$) 40.1 (t, J_{CCF} 20.7), 77.0, 128.5, 128.8 (2 C), 130.3 (2 C), 134.3 and 163.6; m/z 502 (M$^+$), 169, 105, 77 and 69 (Found: M$^+$, 502.0044. C$_{15}$H$_8$ClO$_2$F$_{13}$ requires M, 502.0005).

3-Chloro-1,1,1-trifluoro-2-methyl-3-phenylpropane **9.** An oil; ν_{max}(neat)/cm^{-1} 3000, 1450, 1360, 1260, 1170 and 1130;

δ_H(CDCl$_3$) 1.08 and 1.25 (3 H, d, J 7.2), 2.27–3.13 (1 H, m), 5.06 and 5.22 (1 H, d, J 6.6 and 4.2), and 7.03–7.47 (5 H, m); m/z 222 (M$^+$), 187, 127, 125 and 91 (Found: M$^+$, 222.0409. C$_{10}$H$_{10}$ClF$_3$ requires M, 222.0423).

(E,E)-5,5,5-Trifluoro-1-phenylpenta-1,3-diene **10.**[21] An oil; ν_{max}(neat)/cm^{-1} 1650, 1450, 1270, 1100 and 990; δ_H(CDCl$_3$) 5.27–6.07 (1 H, m), 6.50–7.00 (3 H, m) and 7.80–7.58 (5 H, m); δ_H(CDCl$_3$) 118.4, (q, J_{CCF} 34.2), 125.0, 127.1, 128.9, 129.0, 136.0, 137.6 (q, J_{CCCF} 7.3), and 139.3; m/z 198 (M$^+$), 177, 129, 115 and 78.

3,3,3-Trifluoro-2-methyl-1-phenylpropene **12.** An oil; ν_{max}(neat)/cm^{-1} 1490, 1440, 1360, 1320, 1290, 1160 and 1110; δ_H(CDCl$_3$) 1.84–2.17 (3 H, m), 6.63–7.08 (1 H, m) and 7.10–7.46 (5 H, m); m/z 186 (M$^+$), 165, 117, 115 and 91 (Found: M$^+$, 186.0680. C$_{10}$H$_9$F$_3$ requires M, 186.0656).

cis-1-Chloro-2-(trifluoromethyl)cyclohexane **17a.** An oil; ν_{max}(neat)/cm^{-1} 2940, 1270, 1140 and 1110; δ_H(CDCl$_3$; 500 MHz) 1.26–1.45 (1 H, m), 1.55–1.59 (1 H, m), 1.68–1.90 (5 H, m), 2.07–2.10 (1 H, m), 2.32–2.41 (1 H, m) and 4.55 (1 H, q, J 2.71) (the coupling constant between H–C–Cl and H–C–CF$_3$ was determined to be 2.71 Hz by spin decoupling); δ_C(CDCl$_3$) 19.2, 19.7 (q, J_{CCCF} 2.4), 24.7, 34.3, 47.0 (q, J_{CCF} 26.9) and 54.9 (q, J_{CCF} 2.4); m/z 186 (M$^+$), 150, 135 and 130 (Found: M$^+$, 186.0400. C$_7$H$_{10}$ClF$_3$ requires M, 186.0423).

trans-1-Chloro-2-(trifluoromethyl)cyclohexane **17b.** An oil; ν_{max}(neat)/cm^{-1} 2950, 1330, 1250, 1170, 1140 and 1090; δ_H(CDCl$_3$; 500 MHz) 1.31–1.46 (3 H, m), 1.66–1.82 (3 H, m), 2.10–2.13 (1 H, m), 2.24–2.27 (1 H, m), 2.31–2.38 (1 H, m) and 3.96 (1 H, td, J 9.91 and 4.21) (the coupling constant between H–C–Cl and H–C–CF$_3$ was determined to be 9.91 Hz by spin decoupling); δ_C(CDCl$_3$) 23.6, 24.8, 25.1 (q, J_{CCCF} 2.4), 36.6, 49.0 (q, J_{CCF} 25.6) and 55.7; m/z 150 (M$^+$ − 36), 135, 130 and 81 (Found: M$^+$, 186.0402. C$_7$H$_{10}$ClF$_3$ requires M, 186.0423).

1-Chloro-2-(trifluoromethyl)cyclooctane **18.** An oil; ν_{max}(neat)/cm^{-1} 2940, 1470, 1320, 1270, 1230, 1170 and 1110; δ_H(CDCl$_3$) 1.17–2.30 (12 H, m), 2.42–3.00 (1 H, m) and 4.06–4.50 (1 H, m); δ_C(CDCl$_3$) 23.7, 24.7 (q, J_{CCCF} 2.5), 25.4, 25.8, 28.9, 31.9, 50.9 (q, J_{CCF} 24.4) and 57.9 (q, J_{CCCF} 2.4); m/z 178 (M$^+$ − 36), 150, 109, 82 and 67 [Found: (M$^+$ − HCl), 178.0974. C$_9$H$_{13}$F$_3$ (M$^+$ − HCl) requires m/z 178.0969].

exo-3-Chloro-exo-5-(trifluoromethyl)tricyclo[2.2.1.0^{2,6}]heptane **19a.** An oil; ν_{max}(neat)/cm^{-1} 1390, 1280 and 1120; δ_H(CDCl$_3$) 1.40–2.66 (7 H, m) and 3.89 (1 H, br s); δ_C(CDCl$_3$) 11.9, 14.7 (q, J 2.5), 18.9, 27.0 (q, J 2.5), 38.3 (q, J 2.5), 46.6 (q, J 29.3) and 63.6; m/z 196 (M$^+$), 161, 147, 141, 134, 127 and 91 (Found: M$^+$, 196.0285. C$_8$H$_8$ClF$_3$ requires M, 196.0267).

endo-3-Chloro-exo-5-(trifluromethyl)tricyclo[2.2.1.0^{2,6}]-heptane **19b.** An oil; ν_{max}(neat)/cm^{-1} 1390, 1290, 1140 and 1110; δ_H(CDCl$_3$) 1.45 (1 H, d, J 11.4), 1.58 (3 H, s), 1.89 (1 H, d, J 11.4), 2.29 (1 H, s), 3.02 (1 H, q, J 9.8) and 3.97 (1 H, s); δ_C(CDCl$_3$) 12.1 (q, J 2.4), 14.5, 18.9, 29.0 (q, J 2.5), 38.5, 45.8 (q, J 29.3) and 64.8; m/z 196 (M$^+$), 161, 147, 141, 134, 127 and 91 (Found: M$^+$, 196.0259. C$_8$H$_8$ClF$_3$ requires M, 196.0267).

2-Chloro-6-(trifluoromethyl)bicyclo[3.3.0]octane **20.** An oil; ν_{max}(neat)/cm^{-1} 2950, 1390, 1270, 1160 and 1100; δ_H(CDCl$_3$) 0.70–3.24 (11 H, m) and 3.95–4.40 (1 H, m); δ_C(CDCl$_3$) 27.6 (q, J_{CCCF} 2.4), 30.1, 31.3, 35.1, 42.5 (q, J_{CCCF} 2.4), 51.1 (q, J_{CCF} 26.9), 55.0 and 65.6; m/z 212 (M$^+$), 176, 150, 135 and 81 (Found: M$^+$, 212.0616. C$_9$H$_{12}$ClF$_3$ requires M, 212.0579).

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