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Tandem Carbonyl Ene Cyclization-Cycloalkylation: A Route to Trifluoromethyl Diterpenoids.

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Summary: A new sequential carbonyl-ene cyclization/cycloalkylation of trifluoromethyl ketones catalyzed by aluminum Lewis acids is described. From ketone **1**, the 4-CF_3-4-OH *cis*-octahydrophenanthrene **6** is obtained in 50 % yield. From ketone **2**, with $MeAlCl_2$ a total stereoselective route to the 4-CF_3-*trans*-10-methyl podocarpatrienol **8** (90 % yield) has been found. These studies also exhibited some striking results in the stereochemical outcome of ene cyclizations.

Among the different strategies for the construction of C-aromatic ring diterpenoids, the acid-catalyzed intramolecular polycyclization constitutes one of the most widely developed.[1] The sequential ring closure of polyunsaturated acyclic chains can be initiated by various functionalities such as olefins,[2] epoxides,[3] alcohols,[4] acetals,[5] diazoketones.[6] Surprisingly, despite successful intramolecular ene reactions performed on aldehydes and ketones,[7] these functionalities had never been used as initiators of a sequential intramolecular ring closure.

As part of our interest in the ene reactions of trifluoromethyl ketones,[8] we investigated the sequential ene-reaction/cycloalkylation of ketones **1** and **2** to construct the trifluoromethylated diterpenoid skeleton[9] (Figure 1). Assuming that a concerted process in the initial carbonyl-ene reaction would preclude subsequent cycloalkylation, we set out to find conditions which could favor an ionic process. In a general way, enhancement of the electrophilicity of an enophile accelerates stepwise reactions more than concerted ones.[7c] For a given enophile, this can be achieved by the use of a stronger Lewis acid, by increasing the number of

catalyst equivalents and/or by increasing reaction temperature. From our previous results on the ene-cyclization of ω-ethylenic ketones,[8] we felt that an ionic process could be favored from **1**, since a concerted process involving the type I hydrogen[10,11] is unlikely due to steric constraints in the required 6-membered ring transition state. However, competition between 5- and 6-membered ring closures both leading to secondary cationic centers could occur. From **2** (R = CH_3), the presence of a type II allylic hydrogen should favor a concerted process in a 6-member ring closure as previously shown in the decalin series[8b] (Figure 1).

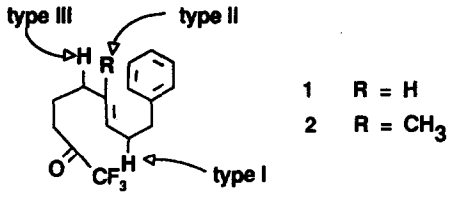
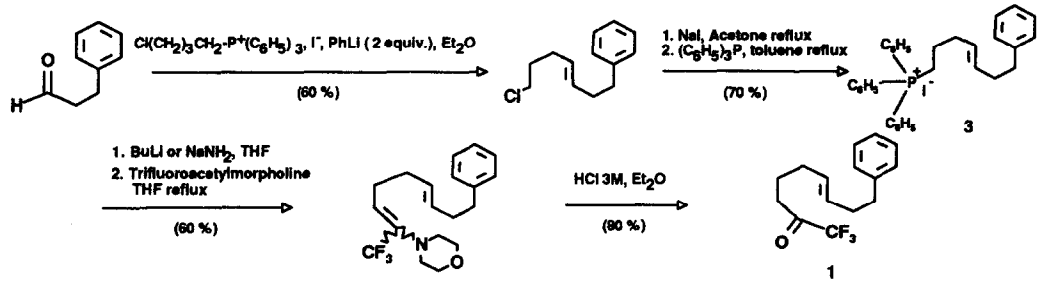


Figure 1

Results and Discussion

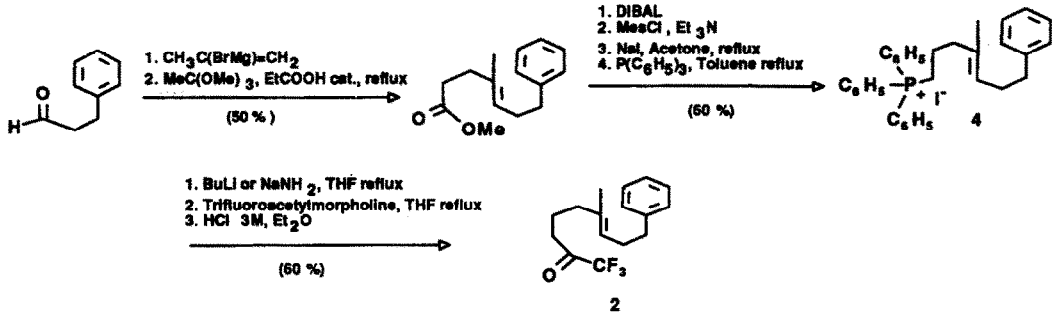
Preparation of ketones 1 and 2.

In both cases, the trifluoromethyl ketone functionality is introduced as the final synthetic step, using our described Wittig condensation of a phosphorane with N-trifluoroacetylmorpholine followed by acidic hydrolysis.[12] The desired *E* isomer of the phosphonium salt **3** was obtained using Schlosser's procedure[13] (Scheme 1) but when the same strategy was applied to the synthesis of phosphonium **4**, a 60:40 mixture of *Z* and *E* isomers was obtained.



Scheme 1

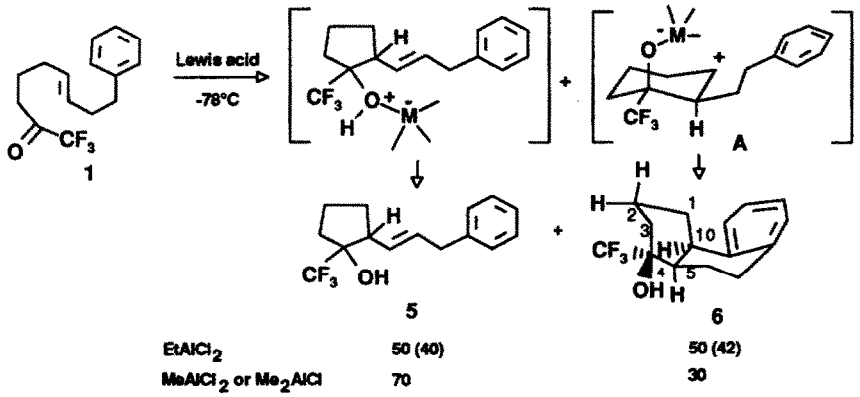
The *E* isomer of **4** was prepared by another strategy based on a stereoselective Claisen rearrangement[14] (Scheme 2).



Scheme 2

Cyclization of ketone 1

At - 78°C, $EtAlCl_2$-, Me_2AlCl- or $MeAlCl_2$-induced cyclization of **1** provided a mixture of mono- and dicyclization products **5** and **6** respectively with the best yield of **6** (42 %) obtained with $EtAlCl_2$. No noticeable increase in the yield of tricyclic compound **6** was observed when the reaction was performed with two equivalents of Lewis acid. When performed at 0°C, the reaction provided only traces of the tricyclic compound in a mixture of unidentified products. For **5**, spectral data clearly indicate the five membered-ring (^{13}C NMR $\delta_{C\text{-}1}$ = 81 ppm) and the position of the double bond but the stereochemistry at the hydroxy center remains speculative.



Scheme 3

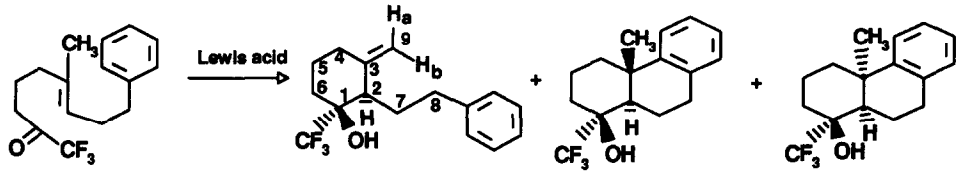
The structure of the tricyclic compound **6** has been deduced from NMR data. The *cis* relationship between H-5 and H-10 was shown by the coupling constant (4.8 Hz) in the homonuclear decoupling spectrum. Heteronuclear NOE experiments exhibit an enhancement of the H-5, H-10 and H-2_{ax} proton

integration (5 to 10 %) after irradiation of the fluorine atoms, demonstrating the *cis* configuration between these protons and the CF_3 group.

Cyclopentanol **5** could arise from a concerted process involving the type I hydrogen although the assignment of the C-1 configuration would be needed to support such a hypothesis. However, it is consistent with the general observation that, in a five membered ring ene cyclization, a concerted type I process is favored at -78°C while at higher temperatures the cationic process leading to the chloroalcohols becomes the favored pathway.[7c,7d,8a] The configuration of the hydroxylated carbon in **6** indicates that the ene cyclization proceeds with the oxygen of the enophile oriented towards the *pro*-C-10 carbon. In this conformation, the type I allylic hydrogen is not accessible and only an ionic process can occur leading to the six-membered ring carbenium A. This exclusive formation of the A/B *cis* system indicates that there is no anchimeric assistance from the phenyl group to the development of the positive charge on the *pro*-C-10 carbon. Such a result for a secondary cationic center was not anticipated.

Cyclization of ketone 2

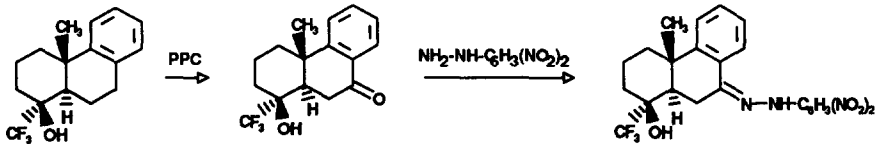
At - 78°C, $EtAlCl_2$-induced cyclization of **2** provided, after 0.5 h, the monocyclic compound **7** (75 %) and a 4/1 mixture of dicyclization products **8** and **9** (8 %) (Scheme 4). The ratio of **7** to (**8**+**9**) did not change even when the reaction time was prolonged or if the temperature was raised after the completion of the reaction. Conversely, when the reaction was performed at 0°C, instead of -78°C only dicyclization products **8** (65 %) and **9** (19 %) were isolated. With $MeAlCl_2$, at -78°C, after 0.5 h, a mixture of **7** and **8** (GC ratio 75:25) was obtained and after a prolonged reaction time (2 h), only the tricyclic compound **8** was isolated in a 90 % yield.



		7	8	(8 + 9)	9
$EtAlCl_2$	-78°C 0.5 h	85		15	
	2 h	85 (75)		15 (8)	
	0°C 0.5 h	0	75 (65)		25 (19)
$MeAlCl_2$	-78°C 0.5 h	75	25		0
	2 h	0	100 (90)		0

Scheme 4

The structure of **8** has been established by the X-ray crystallography of the 2,4-dinitrophenyl hydrazone **11**[15] of the ketone **10**, which was obtained by oxidation of compound **8** (Scheme 5). The A/B *cis* stereochemistry of **9** was assigned from its NMR data which displayed a coupling constant $J_{H\text{-}5,H\text{-}6ax}$ = 5 Hz instead of 12.5 Hz in **8**.. Furthermore, after irradiation of the fluorine atoms, NOE measurements exhibit an enhancement of the H-5 and H-6eq signals, indicating a *cis* relationship between these protons and the CF_3 group. The structure of **7** was determined by NMR data except the C-1 configuration which was deduced from our previous studies on carbonyl ene-cyclization:[8] Product **7** is the *cis* ene adduct expected in a concerted process involving the transfer of the type II hydrogen to the oxygen.



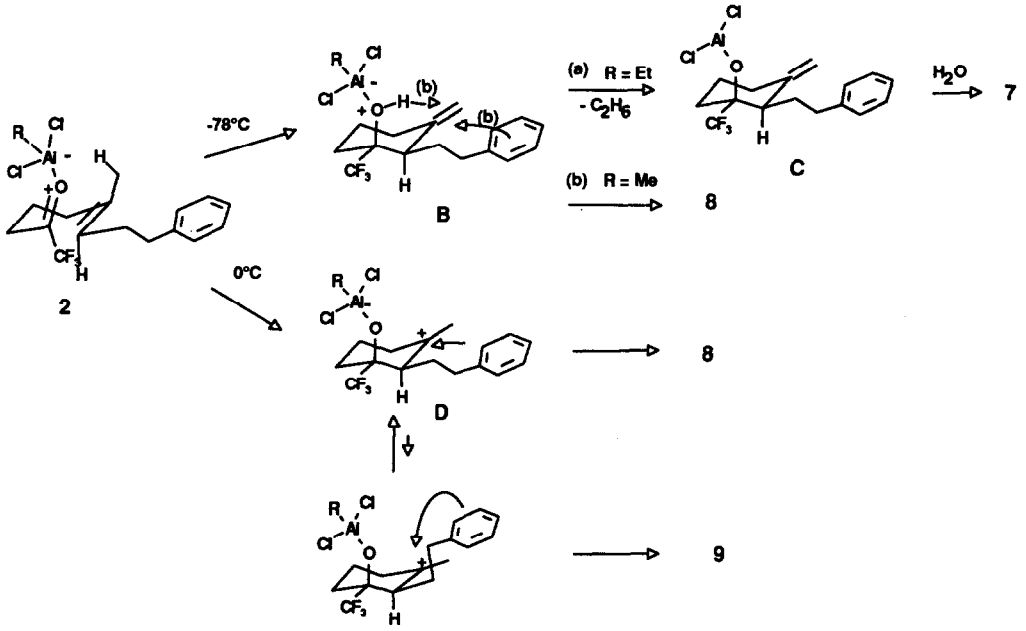
8 **10** **11**

Scheme 5

The outcome of the cyclisation is strongly sensitive to reaction conditions. However, the configuration of the hydroxylated carbon in **7**, **8** and **9**, indicates that in all cases the initial ene cyclization proceeds with the oxygen of the enophile oriented towards a type II hydrogen of the methyl group.

In this conformation, with $EtAlCl_2$, the competition between a concerted and an ionic process is dependent on temperature (Scheme 6). At - 78°C, **2** leads to the protonated complex **B** which is the ene adduct with a concerted transfer of the allylic hydrogen. A rapid loss of ethane provides the stable aluminum alkoxide **C**. At 0°C, the formation of dicyclization adducts **8** and **9** indicates that the cyclization proceeds through a cationic process leading to the tertiary carbenium ion **D** which is stable enough to allow a conformational equilibrium, before the nucleophilic attack by the phenyl group. The ratio 9:1 is similar to that observed in acidic cyclization of dienes which involves the intermediate formation of cyclohexyl carbenium ions similar to **D**?[2,16] This is a rare example of a favored ionic process in a conformation where the ene and enophile are oriented for an easy allylic hydrogen transfer. With $MeAlCl_2$, the second cyclization occurs even at -78°C providing only one diastereoisomer. The exclusive formation of the A/B *trans* isomer **8** and the observed transformation of the monocyclic adduct **B** into **8**, prompted us to envisage a different mechanism from the ionic process for the first ene cyclization. The ene cyclization occurs through a concerted process leading to **B**, but the required cationic center for the second cyclization cannot result from an intermolecular

protonation since alkyl aluminum halides are proton scavengers. The formation of **8** could thus result from an intramolecular protonation by the protonated aluminum complex. The selective formation of only one diastereoisomer **8** strongly suggests that this proton transfer from the "axial" face is synchronous with the equatorial nucleophilic attack by the phenyl group. This retro-transfer of a proton is quite usual in concerted retro-ene reactions but is unique in this case since it is not assisted by any fragmentation. The ease of this retro transfer can be attributed to the electron-withdrawing character of the CF_3 group which renders the alkoxide complex more acidic. However the difference in reactivity between ethyl aluminum compounds (loss of ethane) and methyl aluminum compound (loss of proton instead of methane) cannot be explained.



Scheme 6

In this study, trifluoromethyl ketones have been proved to be efficient initiators of polycyclization under reaction conditions which promote the generation of a cationic center in the first step of this tandem carbonyl-ene reaction/cycloalkylation.

From ketone **1**, the tricyclic compound **6** could be obtained in only 50 % yield. From ketone **2**, despite the presence of a type II allylic hydrogen which favors concerted ene cyclization, conditions were found to

provide a totally stereoselective route to the trifluoromethylated podocarpatriene ring system in an excellent yield.

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Experimental Section

^1H (200 or 300 MHz), ^{19}F (56 or 187 MHz) and ^{13}C NMR (50 or 75 MHz) were obtained with $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to Me_4Si and $CFCl_3$ (for ^{19}F NMR) as internal standards. In the case of determining of fine coupling constants an acquisition of 16 K data points, a Lorenz-Gauss transformation of the FID, and a zero filling to 64K were performed in order to obtain a minimum resolution of 0.2 Hz/pt (^1H and ^{19}F) or 0.5 Hz/pt (^{13}C). COSY, COSYLR, and XHCORR Bruker programs were used for 2D NMR experiments. GC/MS analyses were obtained at 70 eV, (capillary column CPSIL-5, 25 m). GC analysis was performed on a capillary column SE30, 10 or 25 m). $EtAlCl_2$, $MeAlCl_2$, Me_2AlCl (solutions in hexanes) were purchased from Aldrich Chemical Co. Chromatography was performed with Merck Kieselgel 60 (230-400 mesh ASTM).

***(E)*-9-Phenyl-1,1,1-trifluorononа-5-ene-2-one (1)**. Phenyllithium in Et_2O (13 mL of a 2 M solution in Et_2O, 0.026 mol) was added at 0° C, under Ar, to a suspension of phosphonium salt prepared from 1-bromo-4-chlorobutane and triphenylphosphine) in anhydrous THF (100 mL). After 30 min, the red solution was cooled to - 78°C and treated first with a solution of 3-phenylpropanal (3.4 g, 0.025 mol, 1.1 mol equiv) in THF (10 mL) and then again with PhLi (13 mL, 0.026 mmol) added dropwise. The resulting betaine ylid solution was allowed to warm to rt and stirred for 3 h. Most of the THF was evaporated and pentane (200 mL) was added in order to precipitate triphenylphosphine oxide. Filtration through silica gel and evaporation of solvent under reduced pressure gave a crude product (3.8 g). Chromatography on silica gel (pentane) gave the pure *(E)* 1-Chloro-7-phenylhept-4-ene (3.2 g, 60%): ^1H NMR δ 1.8 (m, 2H, -CH_2-CH_2-Cl), 2.0 (q, ^3J = 7.4 Hz, 2H, -CH_2-$(CH_2)_2$-Cl), 2.2 (q, ^3J = 7.5 Hz, 2H, C_6H_5-CH_2-CH_2-), 2.6 (t, ^3J = 7.5 Hz,2H, -CH_2-C_6H_5), 3.0 (t, ^3J = 7 Hz, 2H, -CH_2-Cl), 5.3 (m, ^3J = 17 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 2H, *CH=CH*), 7.3 (m, 5H, C_6H_5). A solution of this chloride (10 g, 0.048 mol) in acetone (100 mL) was treated at reflux for 12 h in the presence of NaI (10.8 g, 0.062 mol). After filtration of the produced sodium chloride and evaporation of acetone, the remaining oil was extracted with pentane. The solution was washed successively with an aqueous sodium thiosulfate solution and water, dried ($MgSO_4$) and filtered through silica gel (pentane). The *(E)*-1-iodo-7-phenyl-hept-4-ene (11.5 g, 80%) was isolated after evaporation of the pentane : ^1H NMR δ 1.8 (m, 2H, -CH_2-CH_2-Cl), 2.0 (q, ^3J = 7.4 Hz, 2H, -CH_2-$(CH_2)_2$-I), 2.2 (q, ^3J = 7.5 Hz, 2H, C_6H_5-CH_2-CH_2-), 2.6 (t, ^3J = 7.5 Hz, 2H, -CH_2-C_6H_5), 3.0 (t, ^3J = 7 Hz, 2H, -CH_2-I), 5.3 (m, 2H, *CH=CH*), 7.3 (m, 5H, C_6H_5). This crude iodide (10 g, 0.033 mol) and triphenylphosphine (9.6 g, 0.036 mol)

were refluxed in toluene (100 mL) for 30 h. The solid phosphonium salt was filtered and washed several times with toluene and then Et_2O. After drying under vacuum, *(E)*-(7-Phenylhept-4-ene)-triphenylphosphonium iodide (**3**) (15.7 g, 84%) was obtained, (mp = 178°C). The corresponding phosphonium ylide was prepared[12] by refluxing this phosphonium salt (9.7 g, 17.3 mmol) and $NaNH_2$ (0.75 g, 1.1 equiv) in THF (50 mL) with hexamethyldisilazane (0.2 mL) as catalyst, for 2 h. N-Trifluoroacetylmorpholine (3.3 g, 18 mmol) was added via a syringe to the red ylid solution. Heating and stirring were maintained until the red color disappeared (about 24 h). The mixture was concentrated under reduced pressure, and triphenylphosphine oxide was precipitated by addition of pentane (150 mL). The solution was filtered through a silica gel column. Solvents were removed under reduced pressure and the remaining oil was chromatographied on silica gel (pentane-ether (80:20)) to give the *(Z)*/*(E)* 2-morpholino 9-phenyl 1,1,1-trifluorononon-2.6-diene (3.5 g, 60%): ^{19}F NMR δ -60 and 63.8 (*E*/*Z* = 60:40); ^1H δ 2.0 (q, ^3J = 7.5 Hz, 2 H), 2.2 (m, 4 H); 2.6 (m, 6 H), 3.7 (m, 4 H, 5.35 (t, ^3J = 7 Hz), 5.4 (m, 2 H),7.1 (m, 5 H). A solution of these enamines (2.8 g, 5 mmol) in Et_2O (10 mL) was stirred with 3 M HCl (3.4 mL, 2 equiv) for 40 h at rt. After extraction (Et_2O), the organic layer was washed (brine) and dried (Na_2SO_4). Evaporation of the solvent and chromatography on SiO_2 (pentane-Et_2O 90:10) gave the ketone **1** (1.3 g, 80 %): ^{19} F NMR δ - 79.2; ^1H NMR δ 1.8 (m, 2 H), 2.0 (q,^3J = 7.5 Hz, 2 H), 2.2 (q, ^3J 7.4 Hz, 2 H), 2.6 (m, 4 H), 5.3 (m, ^3J = 17 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 2 H), 7.1 (m, 5 H); ^{13}C NMR δ 22.0, 25.9, 35.5, 35.7, 115.4 (q, ^1J = 292 Hz,CF_3), 125.7, 128.2, 128.4, 130.4, 140.0, 144.0, 194.0 (q, ^2J = 34 Hz, *C*O-CF_3); MS *m/e* 270 (8, M^+), 252 (6), 158 (11), 129 (10), 117 (16), 104 (18), 91 (100). Anal. Calc. for $C_{15}H_{17}F_3O$: C, 66.65; H, 6.34. Found: C, 67.00; H, 6.40.

***(E)*-6-Methyl-9-phenyl-1,1,1-trifluorononan-6-ene-2-one (2).** A solution of 2-bromopropene (18.0 g, 0.15 mol) in THF (40 mL) was added dropwise to a suspension of magnesium (5 equiv) in THF (10 mL), under Ar. After 1 h a solution of 3-phenylpropanal (13.4 g, 0.1 mole) in solution in THF (10 mL) was added dropwise at -15°C to the Grignard solution. Reaction mixture was stirred at rt for 2 h. Aqueous NH_4Cl was added slowly at 0°C and the aqueous layer was extracted three times with diethyl ether. The combined extracts were washed with brine until neutral, dried ($MgSO_4$) and concentrated to give the crude 2-methyl-5-phenylpent-1-ene-3-ol (14.0 g, 80%): ^1H NMR δ 1.7 (s, 3H), 1.8 (m, 2H), 2.28 (br s, 1 H, OH), 2.6 (m, 2H), 4.0 (t, ^3J = 6.5 Hz, 1H), 4.8 (br s, 1H), 4.94 (br s, 1H), 7.2 (m, 5H). This alcohol (8.0 g, 0.045 mol) was refluxed with freshly distilled trimethyl orthoformate (32.8 g, 0.27 mol), and propionic acid (0.3 g, 4 mmol) for 15 h. After evaporation of trimethyl orthoformate, the residual oil was extracted with Et_2O, washed (brine) and concentrated. Distillation under vacuum gave 6 g (60 %) of methyl *(E)*-4-methyl-7-phenyl hept-4-ene-oate: bp = 118-120°C (0.8 mm Hg): ^1H NMR δ 1.5 (s, 3H), 2.2 (m, 6H), 2.5 (t, ^3J = 7.6 Hz, 2H), 3.6 (s, 3H), 5.15 (tq, ^3J = 6.3 Hz, ^4J = 1.2 Hz, 1H), 7.2 (m, 5H). At 0°C, 4 g (0.017 mol) of this ester in solution in Et_2O (10 mL) was added dropwise to a suspension of $LiAlH_4$ (0.6 g, 0.015 mol) in Et_2O (20 mL). Excess of $LiAlH_4$ was destroyed with wet Et_2O. Organic layer was extracted (Et_2O), washed (brine), dried ($MgSO_4$) and concentrated. The residual oil was filtered on SiO_2 (Pentane-Et_2O 50:50) to give, after evaporation of solvent, the *(E)*-4-methyl-7-phenyl-heptan-4-ene-1-ol (3.35 g, 96%): ^1H NMR δ 1.5 (s, 3H), 1.6 (m, 2H), 2.0 (t, ^3J = 7.5 Hz, 2H), 2.15 (br s, 1H, OH), 2.25 (q, ^3J = 7.6 Hz, 2H), 2.6 (t, ^3J = 7.5 Hz, 2H), 3.55 (t, ^3J = 6.5 Hz, 2H), 5.2 (br t, ^3J = 7 Hz, 1H), 7.2 (m, 5H). Methanesulfonyl

chloride (2 mL) in CH_2Cl_2 solution (10mL) was added dropwise to this crude alcohol in CH_2Cl_2 (10 mL), in presence of triethylamine (5 mL), at 0°C under Ar. The reaction mixture was stirred for 6 h at 0°C and then hydrolysed. After extraction with Et_2O, the organic layer was washed until neutral (brine), dried ($MgSO_4$) and concentrated to give the mesylate (3.5 g, 75%): ^1H NMR 1.5 (br s, 3H), 1.8 (m, 2H), 2.15 (t, ^3J = 7.5 Hz, 2H), 2.25 (q, ^3J = 7.6 Hz, 2H), 2.6 (t, ^3J = 7.4 Hz, 2H), 2.9 (s, 3H), 4.15 (t, ^3J = 6.4 Hz, 2H), 5.2 (tq, ^3J = 6 Hz, ^4J = 1 Hz, 1H), 7.2 (m, 5H). This crude mesylate (3.5 g, 0.012 mol) was refluxed with NaI (2 g, 0.013 mol) in acetone for 10 h. After filtration and evaporation of acetone, the residual oil was extracted with pentane, washed successively with aqueous sodium thiosulfate solution and water, dried ($MgSO_4$) and filtered through silica gel (pentane). The crude 1-iodo 4-methyl 7-phenylheptan-4-ene (3.7 g, 95%) was isolated after evaporation of the pentane: ^1H NMR δ 1.5 (3, 3H), 1.9 (m, 2H), 2.15 (t, ^3J = 7.6 Hz, 2H), 2.25 (q, ^3J = 7.5 Hz, 2H), 2.6 (t, ^3J = 7.5 Hz), 3.1 (t, ^3J = 7 Hz, 2H), 5.2 (br t, ^3J = 6.8 Hz, 1H), 7.2 (m, 5H). This crude iodide (3.7 g, 0.012 mol) was refluxed in toluene (20 mL) with triphenylphosphine (3.5 g, 0.013 mol) for 20 h. The white crystals were filtered, washed with Et_2O and dried under vacuum to give the (4-methyl 7-phenyl-*trans*-hept-4-ene) triphenylphosphonium iodide (**4**) (5.5 g, 80%), mp = 175°C: ^1H NMR δ 1.3 (s, 3H), 1.6 (m, 2H), 2.2 (m, 4H), 2.5 (t, ^3J = 7.3 Hz, 2H), 3.25 (m, 2H), 5.15 (t, ^3J = 6.9 Hz, 1H), 7.0 (m, 5H), 7.8 (m, 15 H); ^{31}P NMR δ (H_3PO_4) 19.5. According to the procedure described for **3**, phosphonium salt **4** (10 g, 17.3 mmol) gave 2.8 g (45%) of (*Z*/*E*) 6-methyl 2-morpholino 9-phenyl 1,1,1-trifluoronon-2,6-diene: ^1H NMR δ 1.5 (s, 3 H), 2.0 (br t, ^3J = 7.1 Hz, 2 H), 2.4 (m, 4 H), 2.75 (m, 6 H), 3.7 (m, 4 H), 5.15 (tq, ^3J = 7 Hz, ^4J = 1 H, 1 H), 5.25 and 5.9 (t, ^3J = 7 Hz, 1 H), 7.2 (m, 5 H); ^{19}F NMR δ -60 and -64 (*E*/*Z* = 65:35). As above described the acidic hydrolysis of enamines gave the (*E*)-6-Methyl-9-phenyl-1,1,1-trifluoronon-6-ene-2-one (**2**): ^1H NMR δ 1.5 (s, 3 H), 1.7 (m, 2 H), 2.0 (m, 2 H), 2.3 (q, ^3J = 7.5 Hz, 2 H), 2.6 (m, 4 H), 5.2 (tq, ^3J = 7 Hz, ^4J = 1 Hz, 1 H), 7.2 (m, 5 H); ^{19}F NMR δ - 79; ^{13}C NMR δ 15.5, 20.4, 29.9, 35.5, 36.0, 38.4, 115.7 (q, ^1J = 292.4 Hz, CF_3), 125.5, 125.9, 128.3, 134.2, 142.2, 192.0 (q, ^2J = 35 Hz, *C*O-CF_3); MS *m/e* 284 (3, M^+), 215 (2, M-CF_3), 175 (22), 91 (100), 81 (67). Anal. Calc. for $C_{16}H_{19}F_3O$: C, 67.59; H, 6.73. Found: C, 67.10; H, 6.71.

Lewis Acid Mediated Ketone Cyclization: General Procedure. Reactions were performed in anhydrous solvents under Ar, with the reaction volume adjusted to produce a solution about 0.04 M in ketone. The solution was cooled to the desired temperature and the Lewis acid in solution was added dropwise via syringe through a septum cap. When the starting material had disappeared (followed by GC after rapid quenching of samples), Et_2O (20 mL) was added and the mixture was hydrolyzed with saturated aqueous NH_4Cl and then allowed to warm to rt. The organic layer was washed with aqueous $NaHCO_3$ until neutral and then twice with brine, dried ($MgSO_4$), and concentrated by rotary evaporation or distillation. The crude product was further purified by column chromatography (silica gel 60, 70-230 mesh) using pentane and pentane-Et_2O mixtures as eluent.

Cyclization of 1. (a) With $EtAlCl_2$. **1** (0.200 g, 0.75 mmol) in CH_2Cl_2 (18 mL) treated with $EtAlCl_2$ (0.88 mL of a 1 M solution in hexanes, 0.77 mmol) at -78°C for 0.5 h afforded, after workup and purification, **5** (0.080 g, 40%) and **6** (0.084g, 42%).

(b) With $MeAlCl_2$ (or Me_2AlCl). **1** (0.100 g, 0.375 mmole) in CH_2Cl_2 (9 mL) treated with $MeAlCl_2$ or

$MeAlCl_2$ (0.41 mL of a 1 M solution in hexanes) at -78°C for 6 h afforded after workup and chromatography **5** (70 mg, 70%) and **6** (28 mg, 30%).

1-Trifluoromethyl-2(3-phenyl)prop-1-ene]cyclopentan-1-ol (5). ^1H NMR δ 1.6-1.9 (m, 4H+OH) ; 2.07-2.17 (m, 2H) ; 2.8 (m, $^3J_{H\text{-}2,H\text{-}3}$ = 10 Hz, $^3J_{H\text{-}6,H\text{-}2}$ = 7.2 Hz, 1H, H-2), 3.41 (br d, $^3J_{H\text{-}8,H\text{-}7}$ = 6.8 Hz, 2H, H-8), 5.58 (br ddt, $^3J_{H\text{-}6,H\text{-}7}$ = 15.5 Hz, $^3J_{H\text{-}6,H\text{-}2}$ = 7.2 Hz, $^4J_{H\text{-}6,H\text{-}8}$ = 1.4 Hz, 1H, H-6), 5.83 (br dtd, $^3J_{H\text{-}7,H\text{-}6}$ = 15.5 Hz, $^3J_{H\text{-}7,H\text{-}8}$ = 6.8 Hz, $^4J_{H\text{-}7,H\text{-}2}$ = 1.0 Hz, 1H, H-7), 7.16-7.4 (m, 5H); ^{19}F NMR δ -79.8; ^{13}C δ 22.1, 30.1, 34.7, 39.3, 47.3 (C-8), 81.1 (q, ^2J = 35 Hz, C-1) ; 126.2, 126.3 (q, ^1J = 283 Hz, CF_3), 127.0, 128.6, 128.8, 134.5, 140; S.M *m/e* 270 (56, M^+), 225 (22, M-H_2O), 183 (8, M-H_2O-CF_3), 141 (29), 117 (100, Ph-CH_2-CH=CH), 91 (5). Anal. Calc. for $C_{15}H_{17}F_3O$: C, 66.65; H, 6.34. Found: C, 65.90; H, 6.23.

4-Trifluoromethyl-4-hydroxy-cis-octahydrophenanthrene (6). ^1H NMR (C_6D_6) δ 1.2 (m, $^2J_{H\text{-}3ax,H\text{-}3eq}$ = 13.6 Hz, $^3J_{H\text{-}3ax,H\text{-}2ax}$ = 13.6 Hz, $^3J_{H\text{-}3ax,H\text{-}2eq}$ = 4.8 Hz, 1H, H-3_{ax}), 1.3 (m, 2H, H-2), 1.45 (br ddd, $^2J_{H\text{-}6ax,H\text{-}6eq}$ = 13.3 Hz, $^3J_{H\text{-}6ax,H\text{-}5}$ = 12.5 Hz, $^3J_{H\text{-}6ax,H\text{-}7ax}$ = 11.9 Hz, $^3J_{H\text{-}6ax,H\text{-}7eq}$ = 5.6 Hz, 1H, H-6_{ax}), 1.55 (m, 3H, H-1 and OH), 1.74 (m, $^2J_{H\text{-}3eq,H\text{-}3ax}$ = 13.6 Hz, $^3J_{H\text{-}3eq,H\text{-}2ax}$ = 3.8 Hz, $^3J_{H\text{-}3eq,H\text{-}2eq}$ = 3.8 Hz, $^4J_{H\text{-}3eq,H\text{-}1eq}$ = 1.4 Hz, 1H, H-3_{eq}), 1.83 (m, $^2J_{H\text{-}6eq,H\text{-}6ax}$ = 13.3 Hz, $^3J_{H\text{-}6eq,H\text{-}7ax}$ = 5.8 Hz, $^3J_{H\text{-}6eq,H\text{-}5}$ = 2.6 Hz, $^3J_{H\text{-}6eq,H\text{-}7eq}$ = 2.6 Hz, $^4J_{H\text{-}6eq,H\text{-}10}$ = 1.7 Hz, 1H, H-6_{eq}), 2.18 (br dt, $^3J_{H\text{-}5,H\text{-}6ax}$ = 12.5 Hz, $^3J_{H\text{-}5,H\text{-}10}$ = 4.8 Hz, $^3J_{H\text{-}5,H\text{-}6eq}$ = 2.5 Hz, 1H, H-5), 2.51 (m, $^2J_{H\text{-}7ax,H\text{-}7eq}$ = 17.1 Hz, $^3J_{H\text{-}7ax,H\text{-}6ax}$ = 11.9 Hz, $^3J_{H\text{-}7ax,H\text{-}6eq}$ = 5.8 Hz, 1H, H-7_{ax}), 2.65 (ddd, $^2J_{H\text{-}7ax,H\text{-}7eq}$ = 17.1 Hz, $^3J_{H\text{-}7eq,H\text{-}6ax}$ = 5.7 Hz, $^3J_{H\text{-}7eq,H\text{-}6eq}$ = 2.4 Hz, 1H, H-7_{eq}), 3.0 (m, $^3J_{H\text{-}10,H\text{-}1ax}$ = 12.8 Hz, $^3J_{H\text{-}10,H\text{-}5}$ = 4.7 Hz, $^3J_{H\text{-}10,H\text{-}1eq}$ = 4.4 Hz, 1H, H-10), 7.1 (m, 4H); ^{19}F NMR δ -76.5; ^{13}C NMR δ 17.6 (C-6), 21.5 (C-1), 28.5 (C-3), 29.5 (C-7), 30.1 (C-2), 37.9 (C-5), 38.1 (q, ^4J = 2.3 Hz, C-10), 74.3 (q, ^2J = 26.6 Hz, C-4), 123.4 (q, ^1J = 287 Hz, CF_3), 120.0, 126.2, 129.0, 192.4, 135.6 and 140.7 (C-8, C-9); S.M *m/e* 270 (40, M^+), 252 (100, M-H_2O), 237 (20), 183 (74, M-CF_3-H_2O), 155 (25), 141 (54), 129 (79), 115 (41), 91 (25). **Anal.** Calc. for $C_{15}H_{17}F_3O$: C, 66.65; H, 6.34. Found: C, 66.11, H, 6.20.

Cyclization of 2. (a) With $EtAlCl_2$. 2 (0.100 g, 0.35 mmol) in CH_2Cl_2 (10 mL) was treated at -78°C with $EtAlCl_2$ (0.4 mL of a 1 M solution in hexanes, 0.38 mmol) and stirred for 2 h. After workup, chromatography on SiO_2 afforded compound **7** (0.075g, 75%) and a mixture of **8** and **9** (0.008g, 8%) in a ratio (4:1).

The same reaction, performed at 0°C for 0.5 h, afforded compounds **8** (0.065 g, 65%) and **9** (0.019g, 19%).

(b) With $MeAlCl_2$. 2 (0.100 g, 0.35 mmole) in CH_2Cl_2 (10 mL) was treated with $MeAlCl_2$ (0.4 mL of a 1 M solution in hexanes) at -78°C for 2 h and afforded, after work-up and chromatography compound **8** (0.090g, 90%). After 0.5 h of reaction, GC analysis showed a mixture of monocyclic compound **7** and tricyclic compound **8** in a ratio (4:1).

1-Trifluoromethyl-2(phenylethyl)methylenecyclohexan-1-ol (7): ^1H NMR (C_6D_6) δ 1.4 (m, 1 H, H-5_{ax}), 1.7 (m, $^2J_{H\text{-}7a,H\text{-}7b}$ = 13.3 Hz, $^3J_{H\text{-}7a,H\text{-}2}$ = 11.2 Hz, $^3J_{H\text{-}7a,H\text{-}8a}$ = 10.3 Hz, $^3J_{H\text{-}7a,H\text{-}8b}$ = 4.5 Hz, 1H, H-7a), 1.78 (m, $^4J_{H\text{-}6ax,F}$ = 1.5 Hz, 1H, H-6_{ax}), 1.85 (m, H-5_{eq}), 1.88 (m, H-6_{eq}), 2.10 (m, $^2J_{H\text{-}7b,H\text{-}7a}$ = 13.3 Hz, $^3J_{H\text{-}7b,H\text{-}8b}$ = 10.8 Hz, $^3J_{H\text{-}7b,H\text{-}8a}$ = 6.7 Hz, $^3J_{H\text{-}7b,H\text{-}2}$ = 3.4 Hz, 1H, H-7b), 2.14 (m, $^2J_{H\text{-}4ax,4eq}$ = 13.5 Hz, $^3J_{H\text{-}4ax,H\text{-}5ax}$ = 13.5 Hz, 1H, H-4_{ax}), 2.24 (m, $^2J_{H\text{-}4eq,H\text{-}4ax}$ = 13.5 Hz, $^3J_{H\text{-}4eq,H\text{-}5eq}$ = 6.9 Hz, $^3J_{H\text{-}4eq,H\text{-}5ax}$ = 2.7 Hz, 1H, H-4_{eq}), 2.45 (m, $^2J_{H\text{-}8a,H\text{-}8b}$ = 13.7 Hz, ^3J $H_{H\text{-}8a,H\text{-}7a}$ = 10.3 Hz, $^3J_{H\text{-}8a,H\text{-}7b}$ = 6.7 Hz, 1H, H-8a), 2.55 (br dd, $^3J_{H\text{-}2,H\text{-}7a}$ = 11.5 Hz, $^3J_{H\text{-}2,H\text{-}7b}$ = 3.4 Hz, 1H, H-2), 2.68 (m, $^2J_{H\text{-}8b,H\text{-}8a}$ = 13.7 Hz, $^3J_{H\text{-}8b,H\text{-}7b}$ = 10.8 Hz, $^3J_{H\text{-}8b,H\text{-}7a}$ = 4.8 Hz, 1H, H-8b), 4.83 (br d, $^2J_{H\text{-}9b,H\text{-}9a}$ = 1.7 Hz, $^4J_{H\text{-}9b,H\text{-}2}$ = $^4J_{H\text{-}9b,H\text{-}4ax}$ = 0.9 Hz, 1 H, H-9b),

4.98 (br d, $^2J_{H\text{-}9a,H\text{-}9b}$ = 1.7 Hz, $^4J_{H\text{-}9a,H\text{-}2}$ = 0.7 Hz, $^4J_{H\text{-}9a,H\text{-}4ax}$ = 0.7 Hz, 1H, H-9a); ^{19}F NMR δ -77.4; ; ^{13}C NMR δ 22.4 (C-5), 27.4 (C-7), 29.5 (q, ^3J = 2.1 Hz, C-6), 30.8 (C-4), 33.4 (C-8), 47.0 (C-2), 76.8 (q, ^2J = 30.1 Hz, C-1), 112.0 (CH_2=C), 124.0 (q, ^1J = 298 Hz, CF_3), 125.8, 128.36, 128.37, 142.0, 145.4 (C-3); SM *m/e* 193 (60, M-91), 104(100), 91(30). Anal. calc. for $C_{16}H_{19}F_3O$: C, 67.59; H, 6.73. Found: C, 66.90; H, 6.75.

4-Hydroxy-10-methyl-4-trifluoromethyl-*trans*-octahydrophenanthrene (8): ^{1}H NMR (C_6D_6) δ 1.2 (s, 3H, Me-15), 1.4-1.8 (m, 7 H + OH), 2 (m, 1H, H-1_{eq}), 2.15 (br dd, $^3J_{H\text{-}5,H\text{-}6ax}$ = 12.5 Hz, $^3J_{H\text{-}5,H\text{-}6eq}$ = 4.9 Hz, 1H, H-5), 2.4 (m, 2H, H-7), 7.2 (m, 4H); ^{19}F NMR δ - 77.9; ^{13}C NMR δ 17.0, 18.0, 24.3, 28.5, 32.0, 37.4, 37.6, 42.6, 76.3 (q, ^2J = 25.3 Hz, C-4), 124.0, 125.8, 125.9, 126.5 (q, ^1J = 289 Hz, CF_3), 128.9, 134.4 (C-8), 148.0 (C-9); SM *m/e* 284 (4, M^+), 269 (100, M-Me), 251 (72, M-Me-H_2O), 141 (20), 129 (42), 117 (32), 91 (22). Anal. Calc for $C_{16}H_{19}F_3O$: C, 67.59; H, 6.73; Found: C, 67.47; H, 6.86.

4-Hydroxy-10-methyl-4-trifluoromethyl-*cis*-octahydrophenanthrene (9). ^{1}H NMR (C_6D_6) δ 0.98 (s, 3H, Me-15), 1.05 (m, 1H, H-1_{ax}), 1.15 (m, 1H, H-3_{ax}), 1.30 (m, 1H, H-2_{ax}), 1.45 (m, 1H, H-3_{eq}), 1.55 (br s, 1H, OH), 1.60 (m, 1H, H-2_{eq}), 1.74 (br dd, $^3J_{H\text{-}5,H\text{-}6ax}$ = 5.1 Hz, $^3J_{H\text{-}5,H\text{-}6eq}$ = 2.7 Hz, 1H, H-5), 2.08 (m, $^2J_{H\text{-}6ax,H\text{-}6eq}$ = 15.1 Hz, $^3J_{H\text{-}6ax,H\text{-}7ax}$ = 11.9 Hz, $^3J_{H\text{-}6ax,H\text{-}7eq}$ = 8.7 Hz, $^3J_{H\text{-}6ax,H\text{-}5}$ = 5.1 Hz, 1H, H-6_{ax}), 2.15 (m, 1H, H-1_{eq}), 2.27 (m, $^2J_{H\text{-}6ax,H\text{-}6eq}$ = 15.1 Hz, $^3J_{H\text{-}6eq,H\text{-}7ax}$ = 8.2 Hz, $^3J_{H\text{-}6eq,H\text{-}5}$ = 2.7 Hz, $^3J_{H\text{-}6eqH\text{-}7eq}$ = 1.7 Hz, $^5J_{H\text{-}6eq,H\text{-}1eq}$ = 0.7 Hz, 1H, H-6_{eq}), 2.60 (m, $^2J_{H\text{-}7eq,H\text{-}7ax}$ = 17.9 Hz, $^3J_{H\text{-}7eq,H\text{-}6ax}$ = 8.4 Hz, $^3J_{H\text{-}7eq,H\text{-}6eq}$ = 1.7 Hz, $^4J_{H\text{-}7eq,H\text{-}14,}$ = 0.6 Hz, 1H, H-7_{eq}), 3.25 (m, $^2J_{H\text{-}7ax,H\text{-}7eq}$ = 17.9 Hz, $^3J_{H\text{-}7ax,H\text{-}6ax}$ = 11.9 Hz, $^3J_{H\text{-}7ax,H\text{-}6eq}$ = 8.12 Hz, $^4J_{H\text{-}7ax,H14}$ = 0.96 Hz, 1H, H-7_{ax}), 6.95 (m, 1H, H-14), 7.1 (m, 3H); ^{19}F NMR δ -78.8; ^{13}C NMR δ 16.9, 18.8, 26.1, 33.8, 35.6, 36.7, 37.3, 42.2, 77.1 (q, ^2J = 25.8 Hz, C-4), 124.0, 126.0, 126.1, 126.6 (q, ^1J = 290 Hz, CF_3), 129.6, 137.2 (C-8), 141.5 (C-9); SM *m/e* 284 (14, M^+), 269 (50, M-Me), 251 (56, M-Me-H_2O), 141 (24), 129 (42), 117 (27), 104 (59), 91 (22). Anal. calc. for $C_{16}H_{19}F_3O$: C, 67.59; H, 6.73. Found: C, 67.12; H, 6.69.

Oxydation of 8: 4-Hydroxy-10-methyl-7-oxo-4-trifluoromethyl-*trans*-octahydrophenanthrene (10). **8** (0.165 g, 0.58 mmole) was refluxed in benzene (15 mL) with pyridinium chlorochromate (PCC) (0.624 g, 5 mol equiv.) and celite (1.4 g) for 14 h. Diethyl ether was added (60 mL) to the reaction mixture. After filtration on celite/$MgSO_4$ and evaporation of solvents, the crude product was chromatographied on SiO_2 (pentane/Et_2O: 80/20) and afforded compound **10** (0.1 g, 60%);^{1}H NMR (C_6D_6) δ 1.05 (m, $^2J_{H\text{-}1ax,H\text{-}1eq}$ = -13.6 Hz, $^3J_{H\text{-}1ax,H\text{-}2ax}$ = 13.6 Hz, $^3J_{H\text{-}1ax,H\text{-}2eq}$ = 3.0 Hz, 1H, H-1_{ax}), 1.13 (s, 3H, Me-15), 1.22 (m, $^2J_{H\text{-}2ax,H\text{-}2eq}$ = 13.6 Hz, $^3J_{H\text{-}2ax,H\text{-}1ax}$ = $^3J_{H\text{-}2ax,H\text{-}3ax}$ = 13.6 Hz, $^3J_{H\text{-}2ax,H\text{-}1eq}$ = 4.0 Hz, 1H, H-2_{ax}), 1.3 (m, 2H, H-3), 1.65 (m, $^2J_{H\text{-}2eq,H\text{-}2ax}$ = 13.6 Hz, $^3J_{H\text{-}2eq,H\text{-}3ax}$ = 3.0 Hz, $^3J_{H\text{-}2eq,H\text{-}1ax}$ = 3.0 Hz, $^3J_{H\text{-}2eq,H\text{-}3eq}$ = 4 Hz, $^3J_{H\text{-}2eq,H\text{-}1eq}$ = 4 Hz, 1H, H-2_{eq}), 1.84 (m, $^2J_{H\text{-}1eq,H\text{-}1ax}$ = 13.6 Hz, $^3J_{H\text{-}1eq,H\text{-}2ax}$ = $^3J_{H\text{-}1eq,H\text{-}2eq}$ = 4 Hz, $^4J_{H\text{-}1eq,H\text{-}3eq}$ = 1.4 Hz, 1H, H-6_{eq}), 2.05 (br dd, $^3J_{H\text{-}5,H\text{-}6ax}$ = 12.5 Hz, $^3J_{H\text{-}5,H\text{-}6eq}$ = 5.6 Hz, 1H, H-5), 2.86 (br dd, $^2J_{H\text{-}6ax,H\text{-}6eq}$ = 18.8 Hz, $^3J_{H\text{-}6ax,H\text{-}5}$ = 12.5 Hz, 1H, H-6_{ax}), 2.95 (br dd, $^2J_{H\text{-}6eq,H\text{-}6ax}$ = 18.8 Hz, $^3J_{H\text{-}6eq,H\text{-}5}$ = 5.6 Hz, 1H, H-6_{eq}), 6.97 (dt, $^3J_{H\text{-}13,H\text{-}14}$ = 7.6 Hz, $^3J_{H\text{-}13,H\text{-}12}$ = 7.6 Hz, $^4J_{H\text{-}13,H\text{-}11}$ = 1.2 Hz, 1H, H-13), 7.03 (dd, $^3J_{H\text{-}11,H\text{-}12}$ = 7.9 Hz, $^4J_{H\text{-}11,H\text{-}13}$ = 1.2 Hz, 1H, H-11), 7.17 (dt, $^3J_{H\text{-}12,H\text{-}11}$ = 7.7 Hz, $^3J_{H\text{-}12,H\text{-}13}$ = 7.7 Hz, $^4J_{H\text{-}12,H\text{-}14}$ = 1.6 Hz, H, H-12), 8.26 (dd, $^3J_{H\text{-}14,H\text{-}13}$ = 7.6 Hz, $^4J_{H\text{-}14,H\text{-}12}$ = 1.6 Hz, 1H, H-14); ^{19}F NMR δ -78.0; ^{13}C NMR δ 16.6 (C-2), 24.1 (Me), 31.7 (q, ^3J = 2.3 Hz, C-3), 35.4 (q, ^4J = 2.5 Hz, C-6), 36.03 (C-1), 37.5 (C-10), 41.5 (C-5), 75.2 (q, ^2J = 25.7 Hz, C-4), 123.1 (C-13), 126.5 (q, ^1J = 298 Hz, CF_3), 126.7 (C-12),

128 (C-11), 131.4 (C-9), 133.6 (C-14), 153.8 (C-8), 195.8 (C-7); SM *m/e* 298 (8, M^+), 284 (18), 283 (90, M-Me), 265 (100, M-Me-H_2O), 245 (18), 197 (8), 128 (38), 115 (43).

2,4-dinitrophenylhydrazone 11 : A solution of ketone **10** (0.1 g, 0.334 mmol) in CH_2Cl_2 (10 mL) reacted with 4 mL of a solution of 2,4-dinitrophenylhydrazine, 10 mL of MeOH and 4 mL of concentrated HCl. A filtration of the solid compound and recrystallisation (AcOEt/$CHCl_3$) afforded **11**: mp 285°C.[15]

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