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Photo-induced intramolecular arene-olefin *meta*-cycloaddition of 5-phenyl-fluorinated-pent-1-enes

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Dedicated to Prof. Yoshiro Kabayashi on the occasion of his 75th birthday

Abstract

A series of fluorinated angular and linear triquinanes and their aza-analogues have been synthesized by photo-induced intramolecular *meta*-cycloaddition of 5-phenyl-fluorinated-pent-1-enes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Fluorinated triquinanes; Intramolecular *meta*-cycloaddition; Photochemistry

1. Introduction

The *meta*- or 1,3-photoaddition of olefins to arenes is unique among the cycloaddition reactions. From the readily available materials under mild conditions, it provides a cycloadduct having three new rings and up to six stereocenters which can hardly be prepared by usual methods [1]. There are a variety of excellent examples of the synthetic use of the intramolecular *meta*-cycloaddition, but the synthetic potential of the reaction has by no means been fully exploited [2,3]. Thus, the intramolecular *meta*-cycloaddition of 5-phenylpent-1-ene derivatives has been recently used elegantly as the key step in the synthesis towards polyquinanes and fenestranes [4,5]. The former is the general skeleton for numerous natural products and the latter of theoretical importance with potential for use in materials and medicinal research [6,7]. In connection with the special character of fluorine atom, the introduction of fluorine into this intramolecular *meta*-cycloaddition would be of interest. However, to the best of our knowledge, no attempt has been made to introduce fluorine into the side chain of 5-phenyl-pent-1-ene system although several examples of fluorine atom or trifluoromethyl group fixed on the different position of the phenyl ring giving the normal photo adducts have been reported [8,9]. Herein, we present the results on the photochemistry of 5-phenyl-fluorinated-pent-1-ene and its aza-analogues.

2. Results and discussion

The vinyl bromide **1** was prepared by aldol condensation of *o*-anisaldehyde and acetone followed by saturation of the double bond with bromine and dehydrobromination with Et_3N. Two isomers **1a** and **1b** were obtained but not separated by usual flash chromatography. In connection with our previous finding that some inexpensive trifluoromethylating agents, such as $FSO_2CF_2CO_2Me$, $FO_2SCF_2CF_2OCF_2CO_2Me$ and XCF_2CO_2Me (X=Cl, Br, I) can successfully replace halogen in vinyl, allyl, aryl and alkyl halides. Here, $FSO_2CF_2CO_2Me$ was found the most suitable as the trifluoromethylating agent to the halides **1a** and **1b** giving the corresponding products **2a** and **2b** in high yields because of its lower decomposition temperature (80°C) as compared with other trifluoromethylating agents [10–13]. Hydrogenation of a mixture of **2a** and **2b** in the presence of Ranny nickel resulted in **3a** and **3b**, which then reacted with vinyl magnesium bromide to give the photo precursors **4a** and **4b** (Scheme 1).

Irradiation (500 W Hg lamp, quartz vessel) of **4a** and **4b** as a 0.2% (W/V) solution in hexane caused the rapid disappearance of the bichromophores and the clean formation of intramolecular *meta* adducts, angular triquinane **5a** and **5b** (Scheme 2) in 2.0 h. At this step, **5a** and **5b** can be successfully separated by flash chromatography.

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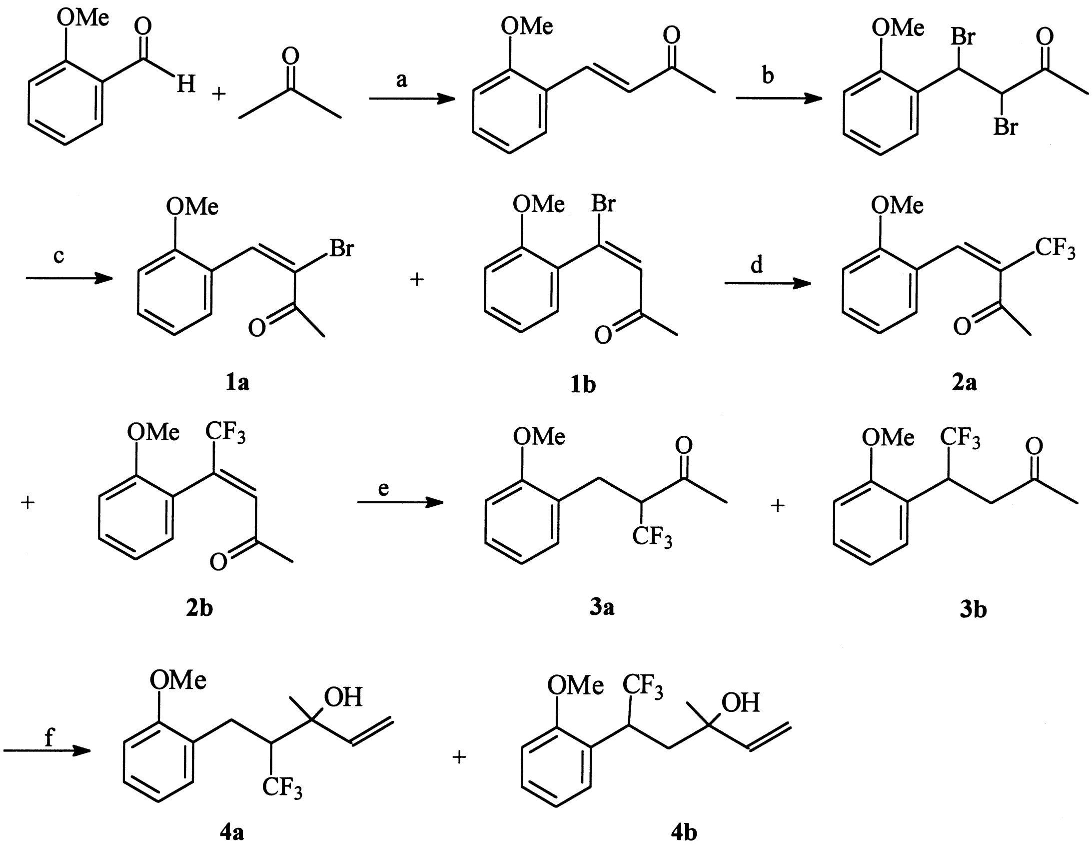
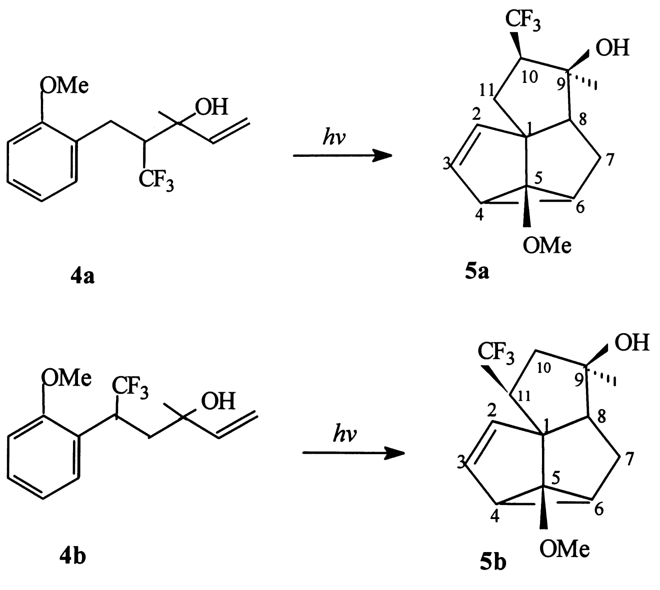
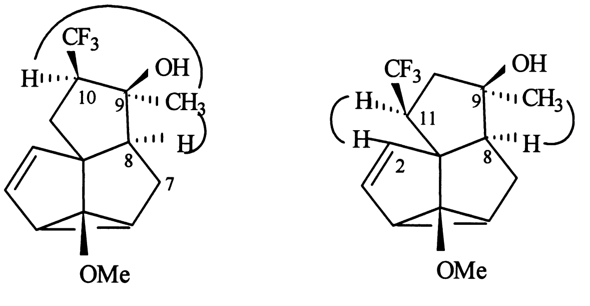


Scheme 1. a. 5% NaOH, H_2O; b. Br_2CCl_4, hv; c. Et_3N, CH_2Cl_2; d. $FSO_2CF_2CO_2$ Me, CuI, DMF, 80°C; e. Ranny Ni, 50 atm, MeOH; f. $CH_2 = CHBr$, Mg, THF.

The structures of the photo adducts were established by 1D- and 2D-NMR measurements. The triquinane skeleton of **5a** and **5b** was determined by ^1H, ^1H COSY and ^{13}C, ^1H COSY. NOESY data confirmed the relative stereochemistry of the products. In **5a**, crosspeaks were observed due to H(10)–Me(9) and H(8)–Me(9) interactions establishing that H(8), Me(9) and H(10) were positioned *cis* with each other. Similarly, in compound **5b**, crosspeaks were also observed for H(2)–H(11) and H(8)–Me(9), showing that the positions of H(8), Me(9) and H(11) were *cis* with each other.

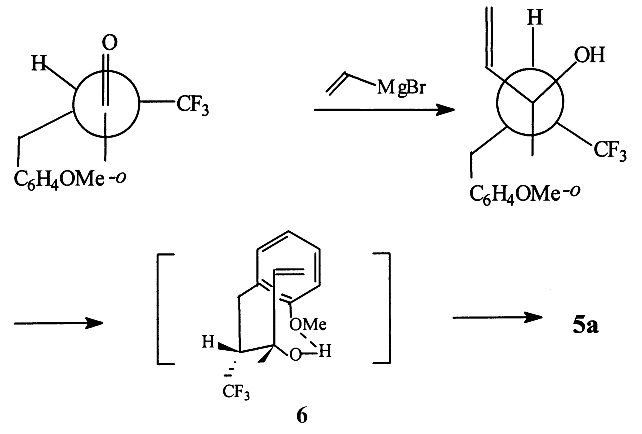


Scheme 2.



5a **5b**

Interestingly, the *cis* relationship between CF_3 and OH groups was also found in both **5a** and **5b**. The *cis* relationship of **5a** can be ascribed to the preparation of photo precursor **4**. **4** was prepared by the Grignard reaction of vinyl bromide with ketone **3** (Scheme 1). In our opinion, the nucleophilic attack may follow the Felkin–Anh Model [14], that is, the Grignard reagent attacks the carbonyl group opposite to more steric hindered benzyl group to give the conformer **6**, in which the relative stereochemistry of CF_3



Scheme 3.

and OH is fixed due to the hydrogen bonding between OH and MeO groups. The *cis* relationship between CF_3 and OH is, thus, retained during the photo reaction (Scheme 3).

The relationship between OH and MeO was also only *cis* due to an intramolecular hydrogen bonding between the two groups when the addition reaction took place as shown in **6**, which is similar to that in the non-fluorinated systems reported by Zhang et al. [15,16] and Crimmins and Choy [17].

The formation of angular product **5** can be described as bonding between C(2) and C(4) (Scheme 4). The regioselectivity controlled by the donating MeO group at the benzene ring is understandable because this group strongly stabilizes the partial positive charge of the zwitterion **7**.

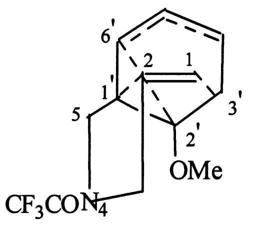
When 5-(*o*-methoxyphenyl)pent-1-en-3-ols or their trifluoroacetates, **8** , were irridiated under the same conditions as above, both angular adduct **9** and linear adduct **10** were obtained (Scheme 5).

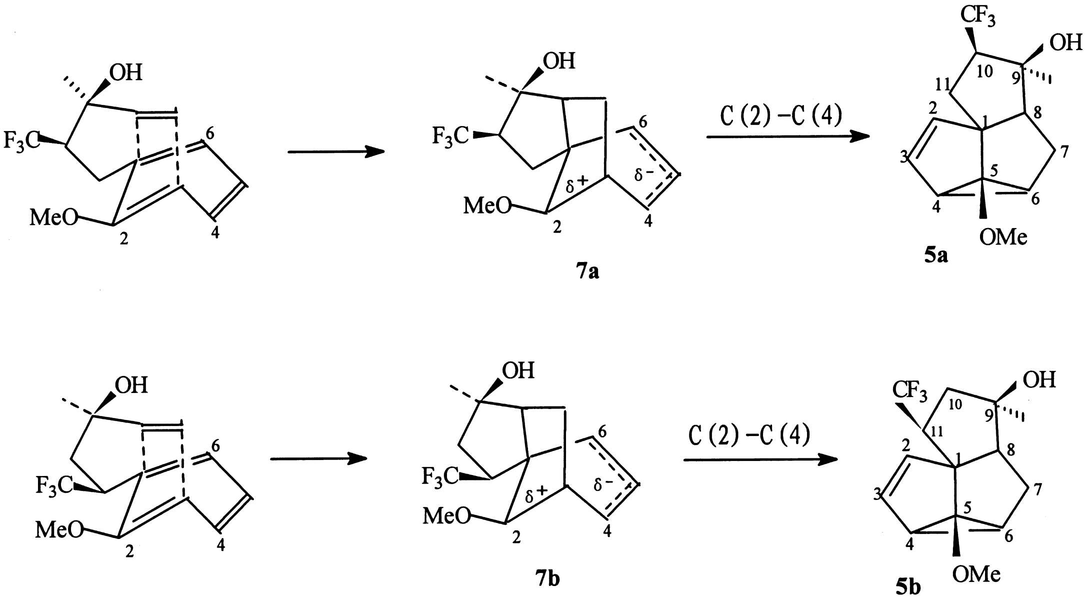
There is no big difference in the intramolecular *meta*-photocycloaddition reaction between alcohols and their trifluoroacetates except that the ratio of **9**:**10** rises from 1:2 to 1:1 when trifluoroacetates were employed instead of alcohols (Fig. 1).

The structures of compounds **9** and **10** were determined by NMR. An X-ray crystal diffraction of **9b** was also obtained, which gave the most direct support of the structure of the stereochemistry, especially of the relative positions of MeO and $OCOCF_3$ groups.

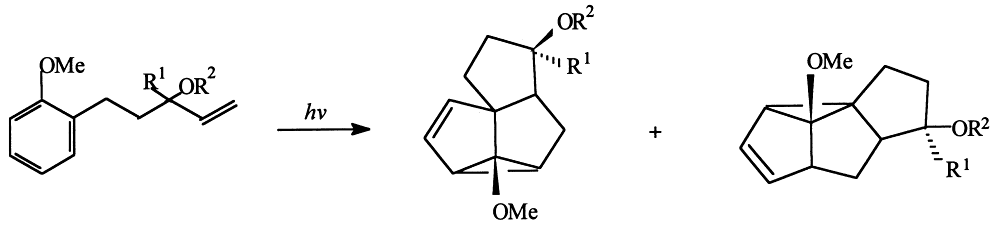
It is known that this photochemical methodology can also be applied to gain access to the potentially useful azatriquinanes [18,19]. How will trifluoroacetylated 3-benzylaminopropene act in the photocycloaddition? It was found that photo precursor **11** underwent highly selective intramolecular *meta*-photocycloaddition yielding only the linear azatriquinane **12** (Scheme 6).

For bichromophores **11a** and **11b**, the shorter bond lengths and smaller angles of the $–CH_2–N–CH_2–$ tether, compared to hydrocarbon analogues, result in asymmetry of the S_1 arene [18,19]. In transition state of photo-precursor **11**, the intramolecular cycloaddition of the ethene to the S_1 benzene ring may not be a synchronous process. Thus C-1′ becomes tetrahedral before C-3′ and so cyclopropane ring formation between C-2′ and C-6′ is favored giving the linear isomer with high selectivity.





Scheme 4.



8 **9** **10**

8a: $R^1 = t$-Bu, $R^2 = H$	**9a** (23%)	**10a** (47%)
8b: $R^1 = t$-Bu, $R^2 = COCF_3$	**9b** (30%)	**10b** (28%)
8c: $R^1 =$ ethyl, $R^2 = H$	**9c** (28%)	**10c** (45%)
8d: $R^1 =$ ethyl, $R^2 = COCF_3$	**9d** (19%)	**10d** (21%)

Scheme 5.

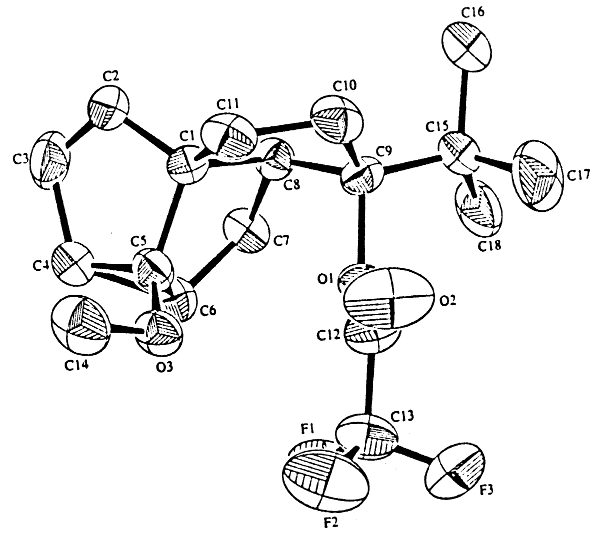
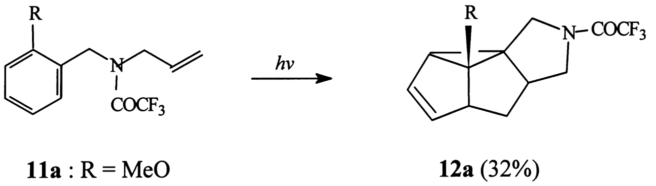


Fig. 1. X-ray crystal structure of **9b**.

For non-substituted **11c**, only fragmentation instead of intramolecular cycloaddition reaction occurred and gave no photo adducts. It shows that a donating substituent is essential to this reaction due to the introduction of trifluoroacetyl group into this system.

In conclusion, we have achieved the *meta*-photocycloaddition of side-chain trifluoromethylated or trifluoroacetylated arene to olefin and their aza-analogues. The facility and effectiveness of this methodology clearly suggest a significant role for this cycloaddition in the synthesis of polyquinanes and their fluorinated analogues.



11a : R = MeO	**12a** (32%)
11b : R = Me	**12b** (38%)
11c : R = H	----

Scheme 6.

3. Experimental

IR spectra were taken on Schimadzu-440 and Perkin-Elmer 983 spectrometers. ^{1}H NMR spectra were recorded on Varian EM-360A (60 MHz), FX-90Q (90 MHz) and Bruker AM 300 (300 MHz) NMR spectrometers. ^{19}F NMR spectra were recorded on a Varian EM-360L (56.4 MHz) NMR spectrometer. Chemical shifts were reported in parts per million relative to TMS as an internal standard for ^{1}H NMR and to CF_3COOH as an external standard for ^{19}F NMR. The solvent for NMR measurement was $CDCl_3$. MS and HRMS spectra were recorded on HP5989A and Finnigan MAT mass spectrometers. X-ray structure was recorded on Rigaku AFC7R diffractometer.

A 500 W medium pressure Hg lamp was used as the light source.

3.1. *Trifluoromethylation of the vinyl bromide* 1

A mixture of vinyl bromide (**1**, 1.30 g, 5.1 mmol), CuI (970 mg, 5.1 mmol) and $FSO_2CF_2CO_2Me$ (4.86 g, 25.5 mmol) in dried DMF (10 ml) was stirred at 80°C under nitrogen for 15 h. Then, Cu was filtered off and the solution was poured into water. The mixture was extracted with ether (3×25 ml). The combined organic layer was washed with water (3×10 ml) and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude material was purified with flash chromatography (petroleum ether:ether=10:1) to give **2** (1.20 g) as light yellowish oil. Yield: 96%.

IR (Film), ν: 2470 (w), 1705 (vs), 1641 (m), 1600 (m), 1485 (s), 1465 (s), 1438 (m), 1294 (vs), 1281 (vs), 1179 (vs), 1159 (vs), 1026 (m), 756 (s) cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$) δ: 2.20 (s, 3H, *E*), 2.50 (s, 3H, *Z*), 3.90 (s, 3H), 6.90–7.60 (stack, 5H, **2b**), 6.90–7.60 (stack, 4H, **2b**), 8.07 (s, 1H, **2a**) ppm. ^{19}F NMR (56.4 MHz, $CDCl_3$) δ: −20.7 (s, **2b**),

−15.0 (s, **2a**) ppm. EIMS (*m/z*): 245 (M^++1, 20), 244 (M^+, 7.8), 229 (M^+–Me, 16), 213 (M^+–OMe, 100), 195 (5.7), 151 (8.9), 133 (7.6), 109 (5.2), 89 (3.9), 77 (2.3). HRMS Calc. for $C_{12}H_{11}O_2F_3$ (M^+): 244.0711; Found: 244.0695.

3.2. *Preparation of* 3

A mixture of **2a** and **2b** (2.28 g, 9.34 mmol, **2a**:**2b**=3:2) in MeOH (15 ml) was hydrogenated under freshly made Ranny Ni at 50 atm for 6 h, then, the catalyst was filtered off and the solvent was removed under vacuum. The crude material was purified with flash chromatography (petroleum ether:ether=15:1) to give **3** (1.20 g **3a**:**3b**=3:2) as colorless oil. Yield: 100%.

IR (Film), ν: 2950 (m), 1730 (s), 1600 (m), 1500 (s), 1470 (s), 1440 (m), 1360 (s), 1250 (vs), 1160 (s), 1105 (vs), 1050 (m), 1030 (m), 760 (s) cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$) δ: 2.10 (s, 3H), 2.25 (m, 1H), 3.08 (d, 1H), 3.52 (d, 1H), 3.85 (s, 3H), 6.80–7.20 (stack, 4H) ppm. ^{19}F NMR (56.4 MHz, CCl_4) δ: −10.7 (d, *J*=8 Hz) ppm. EIMS (*m/z*): 246 (M^+, 100), 213 (4.4), 203 (18), 183 (6.0), 177 (5.8), 151 (7.1), 121 (88), 108 (16), 91 (59), 77 (13), 43 (79).

3.3. *Preparation of* 4

A mixture of **3a** and **3b** (550 mg, 2.2 mmol) in dried THF (5.0 ml) was added dropwise to Grignard reagent prepared from Mg (840 mg,35 mmol) and vinyl bromide (3.2 g, 30 mmol) in THF (45 ml). sat. NH_4Cl (50 ml) was added after stirring for 3 h and stirred for another 10 min. The mixture was extracted with ether (3×20 ml). The combined organic layer was washed with brine (3×10 ml) and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude material was purified with flash chromatography (petroleum ether:ether=5:1) to give **4** (630 mg, **4a**:**4b**=3:2) as light yellowish oil. Yield: 87%.

IR (Film), ν: 3481 (br), 2952 (m), 2845 (w), 1800 (m), 1497 (s), 1467 (m), 1371 (w), 1246 (s), 1142 (m), 1096 (s), 1028 (m), 930 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.29 (s, 3H, Me, **4b**), 1.43 (s, 3H, Me, **4a**), 1.50 (s, 1H, OH), 2.62–2.82 (stack, 2H), 3.12 (m, 1H), 3.78 (s, 3H, OMe, **4a**), 3.81 (s, 3H, OMe, **4b**), 5.16 (ddd, 1H, *J*=26.7, 10.5, 1.0 Hz), 5.39 (ddd, 1H, *J*=24.0, 17.1, 1.1 Hz), 6.04 (m, 1H), 6.83–6.94 (stack, 2H), 7.15–7.25 (stack, 2H) ppm. ^{19}F NMR (56.4 MHz, $CDCl_3$) δ: −14.5 (d, *J*=8 Hz, **4b**), −15.7 (d, *J*=8 Hz, **4a**) ppm. EIMS (*m/z*): 274 (M^+, 6.9), 256 (M^+–H_2O, 4.1), 236 (21), 216 (17), 201 (5.4), 185 (4.6), 173 (3.5), 149 (3.5), 121 (50), 108 (12), 91 (57), 77 (15), 71 (100). HRMS Calc. for $C_{14}H_{17}O_2F_3$ (M^+): 274.1181; Found: 274.1149.

3.4. *Irradiation of* 4

A solution of **4a** and **4b** (780 mg, 2.8 mmol) in 450 ml hexane was irradiated in a quartz vessel for 2.0 h. After removal of the solvent, the crude material was separated by flash chromatography (petroleum ether:ether =10:1∼5:1) to give **5a** and **5b** as light yellowish oil.

5a. Yield: 250 mg (32%). IR (Film), ν: 3490 (br), 2941 (m), 2834 (w), 1592 (m), 1497 (s), 1246 (vs), 1141 (m), 1105 (s), 1026 (m), 754 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ^{1}H, ^{1}H COSY, ^{13}C, ^{1}H COSY and NOESY), δ: 1.25 (s, 3H, Me), 1.53 (dd, 1H, *J*=13.2, 7.4 Hz, H-7), 2.00–2.10 (stack, 2H, H-11,H-11), 2.08–2.15 (stack, 2H, H-6, H-8), 2.19 (m, 1H, H-4), 2.44 (dd, 1H, *J*=14.5, 9.8 Hz, H-7), 2.65 (m, 1H, H-10), 3.36 (s, 3H, OMe), 5.54 (d, 1H, *J*=1.0 Hz, H-2), 5.58 (m, 1H, H-3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.44 (t), 23.64 (q, Me), 24.60 (t), 35.56 (d), 40.43 (d), 53.76 (q, C-10, *J*=24 Hz), 57.07 (q, OMe), 65.64 (s), 68.86 (d), 80.22 (s), 90.07 (s), 125.59 (d), 128.07 (q, CF_3, *J*=280 Hz), 137.00 (d) ppm. ^{19}F NMR (56.4 MHz, CCl_4), δ: −12.7 (d, *J*=8.0 Hz) ppm. EIMS (*m/z*): 274 (M^+, 18), 257 (M^+-OH, 16), 256 (M^+–H_2O, 11), 236 (M^+-2F, 44), 216 (27), 201 (7.7), 187 (8.4), 151 (7.5), 121 (100), 109 (9.3), 91 (50), 77 (11), 71 (57). HRMS: Calc. for $C_{14}H_{17}O_2F_3$ (M^+): 274.1181; Found: 274.1195.

5b. Yield: 180 mg (23%). R (Film), ν: 3477 (br), 2940 (m), 1800 (w), 1497 (s), 1466 (m), 1373 (m), 1315 (m), 1246 (vs), 1142 (s), 1107 (s), 1053 (m), 1032 (m), 932 (m), 754 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ^{1}H, ^{1}H COSY and ^{13}C, ^{1}H COSY) δ: 1.38 (s, 3H, Me), 1.63 (m, 2H, H-7, H-7), 2.03 (d, 1H, *J*=1.9 Hz, H-10), 2.06 (s, 1H, H-10), 2.21–2.25 (stack, 2H, H-4, H-6), 2.49 (dd, 1H, *J*=12.0, 6.8 Hz, H-8), 3.15 (m, 1H, H-11), 3.33 (s, 3H, OMe), 5.72 (dd, 1H, *J*=6.0, 2.2 Hz, H-2), 5.75 (m, 1H, H-3) ppm. ^{13}C NMR δ: 16.38 (t), 23.94 (q, Me), 27.91 (t), 35.08 (d), 35.24 (d), 57.10 (q, OMe), 60.67 (q, C_{11}, *J*=25 Hz), 65.88 (s), 73.89 (s), 75.24 (d), 88.14 (s), 125.94 (d), 129.07 (q, CF_3, *J*=276 Hz), 133.78 (d) ppm. ^{19}F NMR δ: −11.0 (d, *J*=8.0 Hz) ppm. EIMS (*m/z*): 275 (M^++1, 6.0), 245 (5.5), 233 (6.4), 222 (6.6), 207 (6.1), 195 (7.4), 177 (5.6), 149 (11), 128 (8.0), 119 (17), 95 (15), 91 (22), 77 (17), 57 (29), 44 (100). HRMS Calc. for $C_{14}H_{17}O_2F_3$ (M^+): 274.1181; Found: 274.1201.

1-(*o*-Methoxyphenyl)pentan-3-one and 5-(*o*-methoxyphenyl)-2,2-dimethyl-pentan-3-one were prepared by aldol condensation of *o*-anisaldehyde and 3,3-dimethylbutan-2-one or butan-2-one followed by catalytic hydrogenation according to standard procedures. These two ketones were used to prepare the respective **8a** and **8c** as follows:

3.5. *Preparation of* 8a *and* 8c

Ketone (4.5 mmol) in dried THF (5.0 ml) was added dropwise to Grignard reagent prepared from Mg (25 mmol) and vinyl bromide (22.5 mmol) in THF (20 ml). sat. NH_4Cl (20 ml) was added after stirring for 1 h and stirred for another 10 min. The mixture was extracted with ether (3×20 ml). The combined organic layer was washed with brine (3×10 ml) and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude material was purified with flash chromatography (petroleum ether:ether=15:1) to give **8** (980 mg) as colorless oil.

8a. Yield: 87%. IR (Film), ν: 3544 (br), 2959 (s), 1599 (m), 1495 (s), 1465 (m), 1242 (s), 1051 (m), 1034 (m), 920 (m), 754 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.93 (s, 9H, 3Me), 1.67 (br, 1H, OH), 1.82–1.87 (stack, 2H), 2.49–2.57 (stack, 2H), 3.83 (s, 3H, OMe), 5.28 (td, 2H, J=15, 1.6 Hz), 5.96 (dd, 1H, J=17, 11 Hz), 6.83–6.91 (stack, 2H), 7.12–7.18 (stack, 2H) ppm. EIMS (*m/z*): 248 (M^+, 0.25), 231 (M^+–OH, 2.0), 203 (M^+–3Me, 0.67), 191 (M^+–*t*-Bu, 46), 173 (2.2), 161 (2.0), 135 (4.7), 121 (100), 105 (2.7), 91 (31), 77 (5.2). Analysis Calc. for $C_{16}H_{24}O_2$, C, 77.37; H, 9.74; Found: C, 77.30; H, 10.02.

8c. Yield: 87%. IR (Film), ν: 3470 (br,m), 2935 (s), 2835 (s), 1600 (m), 1587 (m), 1495 (s), 1465 (m), 1245 (vs), 1054 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.92 (t, 3H, J=7.5 Hz,Me), 1.58–1.66 (stack, 2H), 1.78–1.85 (stack, 3H), 2.63–2.69 (dd, 2H, J=7.2,3.4 Hz), 3.84 (s, 3H, OMe), 5.18 (dd,1H, J=17.4, 1.2 Hz), 5.88 (dd, 1H, J=17.4, 10.9 Hz), 6.84–6.93 (stack, 2H), 7.14–7.22 (stack, 2H) ppm. EIMS (*m/z*): 220 (M^+, 2.1), 202 (M^+–H_2O, 2.6), 191 (M^+–Et, 11), 173 (M^+–H_2O–Et, 26), 136 (30), 121 (100), 107 (20), 91 (44), 77 (11). Analysis Calc. for $C_{14}H_{20}O_2$: C 76.31, H 9.15; Found: C 75.81, H 9.40.

3.6. Preparation of **8b** and **8d**

To **8a** or **8c** (1.0 mmol) was added $(CF_3CO)_2O$ (4.0 mmol), pyridine (3.0 mmol) and catalytic DMAP in dried CH_2Cl_2 (10 ml) at 0°C and stirred for 12 h, then, ether was added. The mixture was washed with sat. $NaHCO_3$, 2N HCl, $CuSO_4$ solution and brine, dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude material was purified with flash chromatography (petroleum ether:ether=15:1) to give **8b** or **8d** as light yellowish oil.

8b: Yield: 89%. IR (Film), ν: 2970 (m), 2953 (m), 1782 (s), 1610 (w), 1495 (m), 1244 (s), 1221 (s), 1169 (s), 752 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.14 (s, 9H, 3Me), 2.35–2.41 (stack, 2H), 2.60–2.66 (stack, 2H), 3.87 (s, 3H, OMe), 5.00 (d, 2H, J=7.1 Hz), 5.48 (t, 1H, J=7.1 Hz), 6.86–6.90 (stack, 2H), 7.12–7.26 (stack, 2H) ppm. ^{19}F NMR (56.4 MHz, $CDCl_3$) δ: −3.0 ppm. EIMS (*m/z*): 344 (M^+, 3.5), 241 (M^+–$OCOCF_3$, 0.77), 231 (0.76), 211 (0.88), 173 (3.2), 159 (1.2), 135 (1.8), 121 (100), 91 (34), 77 (3.7). HRMS Calc. for $C_{18}H_{23}O_3F_3$: 344.1599; Found: 344.1591.

8d: Yield: 93%. IR (Film), ν: 3030 (m), 2971 (m), 1772 (vs), 1440 (m), 1221 (m), 1165 (s) cm^{-1}. ^{1}H NMR (90 MHz, CCl_4) δ: 1.05 (t, 3H, Me), 1.80–2.87 (stack, 6H), 3.97 (s, 3H, OMe), 5.42 (m, 1H), 5.58 (m, 1H), 6.17 (m, 1H), 6.82–7.27 (stack, 4H) ppm. ^{19}F NMR (56.4 MHz, $CDCl_3$) δ: −2.5 ppm. EIMS (*m/z*): 316 (M^+, 1.0), 220 (M^+–$COCF_3$, 9.8), 203 (M^+–$OCOCF_3$, 6.8), 192 (27), 173 (M^+–$OCOCF_3$–Et, 100), 158 (15), 135 (14), 121 (92), 91 (47).

3.7. Irradiation of **8**

A solution of **8** (4.0 mmol) in hexane (450 ml) was irradiated in a quartz vessel for 2.0 h. After removal of the solvent, the crude material was separated by flash chromatography (petroleum ether:ether=15:1∼10:1) to give **9** and **10**.

9a. Yield: 23%, yellow oil. IR (Film), ν: 3569 (m), 3493 (w), 3037 (w), 2962 (vs), 2955 (vs), 2941 (s), 1591 (w), 1439 (m), 1392 (m), 1215 (m), 1116 (m), 766 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.80 (s, 9H, 3Me), 1.39–1.50 (stack, 2H), 1.72 (m, 1H), 1.95–2.17 (stack, 6H), 3.38 (s, 3H, OMe), 5.40–5.44 (stack, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.28 (t), 25.69 (t), 25.88 (q, 3C), 35.82 (d), 37.59 (s), 39.45 (t), 40.32 (d), 57.05 (q, OMe), 63.08 (d), 68.58 (s), 86.45 (s), 89.97 (s), 124.73 (d), 138.18 (d) ppm. EIMS (*m/z*): 248 (M^+, 2.9), 231 (M^+–OH, 73), 217 (M^+–OMe, 46), 199 (51), 191 (M^+–*t*-Bu, 42), 173 (M^+–H_2O–*t*-Bu, 100), 159 (31), 143 (17), 131 (53), 121 (88), 105 (19), 91 (47). Analysis Calc. for $C_{16}H_{24}O_2$ C, 77.37; H, 9.74 Found: C, 77.19; H, 10.13.

10a. Yield: 47%, white crystal. IR (KBr) ν: 3460 (m), 2961 (s), 2907 (m), 2808 (m), 1584 (w), 1570 (m), 1556 (m), 1116 (m), 1072 (m), 741 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (s, 9H, 3Me), 1.39 (m, 1H), 1.48 (m, 1H), 1.76 (m, 1H), 1.98 (brs, 1H), 2.12–2.33 (stack, 4H), 3.34 (dd, 1H, J=5.2, 2.5 Hz), 3.40 (s, 3H, OMe), 5.52 (m, 1H), 5.60 (dd, 1H, J=5.5, 2.2 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 24.09 (t), 26.17 (q, 3C, *t*-Bu), 36.85 (s), 37.89 (t, 2C), 41.74 (d), 47.66 (d), 51.58 (s), 54.21 (d), 56.48 (q, OMe), 84.94 (s), 89.01 (s), 127.21 (d), 132.89 (d). EIMS (*m/z*): 248 (M^+, 1.0), 231 (M^+–OH, 14), 215 (M^+–H_2O–*t*-Bu, 21), 199 (16), 191 (M^+–Bu, 37), 173 (M^+–Bu–H_2O, 63), 159 (33), 147 (17), 131 (60), 121 (100), 105 (23), 91 (62). Analysis: Calc. for $C_{16}H_{24}O_2$ C, 77.37; H, 9.74; Found: C, 77.73; H, 10.26.

9b. Yield: 30%, white crystal. IR (Film), ν: 2974 (m), 2941 (m), 1776 (s), 1713 (w), 1601 (w), 1477 (w), 1460 (w), 1448 (w), 1373 (m), 1366 (m), 1215 (s), 1165 (s), 1155 (s), 1001 (w), 760 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (s, 9H, 3Me), 1.61–1.70 (stack, 3H), 2.06–2.28 (stack, 3H), 2.36–2.43 (stack, 2H), 3.25 (s, 3H, OMe),3.30 (m, 1H), 5.53–5.58 (stack, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.30 (t), 25.55 (t), 26.64 (q, 3C), 33.79 (t), 35.05 (d), 39.40 (s), 40.66 (d), 56.70 (q, OMe), 64.50 (d), 67.64 (s), 90.01 (s), 105.20 (s), 114.76 (q, CF_3, J=286 Hz), 125.80 (d), 137.42 (d), 156.78 (t, CO, J=41 Hz) ppm. ^{19}F NMR (56.4 MHz, CCl_4): −1.9 ppm. EIMS (*m/z*): 344 (M^+, 2.4), 287 (M^+–*t*-Bu, 3.3), 249 (5.2), 231 (M^+–$OCOCF_3$, 40), 215 (30), 199 (16), 183 (9.1), 173 (M^+–$OCOCF_3$–*t*-Bu, 100), 159 (17), 143 (20), 135 (32), 121 (32), 91 (35). Analysis Calc. for $C_{18}H_{23}O_3F_3$: C, 62.78; H, 6.73; Found: C, 62.91; H, 6.97.

X-Ray Details: $C_{18}H_{23}O_3F_3$; colorless, prismatic; Crystal System, orthorhombic; Lattice Type, Primitive; Lattice Parameter, a=13.264 A, b=15.203A, c=8.630A,

V=1740 A^3, Space Group, P2$_1$2$_1$2$_1$ (#19); Z value=4; No. Observations, I>3.00σ (I); Residuals, R=0.056, Rw=0.059.

10b. Yield: 28%, yellow oil. IR (Film), ν: 2940 (m), 2934 (m), 1780 (s), 1364 (w), 1219 (m), 1169 (s), 1155 (s), 1128 (m), 745 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.97 (s, 9H, *t*-Bu), 1.58 (m, 1H), 1.67 (m, 1H), 1.95 (m, 1H), 2.13 (brs, 1H), 2.30–2.39 (stack, 4H), 3.28 (m, 1H), 3.39 (s, 3H, OMe), 5.54 (m, 1H), 5.67 (m, 1H) ppm. ^{19}F NMR (56.4 MHz, $CDCl_3$) δ: −4.0(s) ppm. EIMS (*m/z*): 344 (M$^+$, 2.6), 287 (M$^+$–*t*-Bu, 1.0), 247 (M$^+$–$COCF_3$, 1.0), 231 (M$^+$–1-$OCOCF_3$, 30), 230 (M$^+$–1-$OCOCF_3$, 30), 215 (40), 199 (42), 183 (9.3), 174 (M$^+$–$OCOCF_3$–*t*-Bu, 25), 173 (M$^+$–1-$OCOCF_3$–*t*-Bu, 100), 158 (22), 143 (24), 121 (29). HRMS Calc. for $C_{18}H_{23}O_3F_3$ (M$^+$): 344.1599; Found: 344.1608.

9c. Yield: 28%, yellow oil. IR (Film), ν: 3442 (m, br), 2937 (s), 1745 (m), 1462 (m), 1393 (m), 1215 (m), 1178 (m), 1019 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, 3H, Me, J=7.5 Hz), 1.24 (m, 1H), 1.42–1.56 (stack, 2H), 1.67–2.20 (stack, 8H), 2.45 (br, 1H), 3.30 (s, 3H, OMe), 5.48–5.52 (stack, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 8.76 (q, Me), 22.94 (t), 23.42 (t), 30.90 (t), 35.53 (d), 40.14 (t), 40.42 (d), 56.89 (q, OMe), 67.11 (d), 77.53 (s), 83.32 (s), 90.18 (s), 124.30 (d), 138.40 (d) ppm. EIMS (*m/z*): 220 (M$^+$, 5.3), 203 (M$^+$–OH, 15), 202 (M$^+$–H_2O, 8.7), 191 (M$^+$–Et, 22), 173 (M$^+$–H_2O–Et, 84), 159 (7.7), 135 (25), 121 (100), 105 (13), 91 (54), 85 (29). HRMS Calc. for $C_{14}H_{20}O_2$ (M$^+$): 220.1463; Found: 220.1437.

10c. Yield: 48%, white crystal. IR (Film), ν: 3458 (br, s), 3050 (w), 2934 (vs), 1661 (w), 1586 (w), 1451 (s), 1398 (s), 1298 (s), 1130 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, 3H, J=4.2 Hz), 1.43–1.57 (stack, 4H), 1.80–2.02 (stack, 4H), 2.14 (m, 1H), 3.32 (m,1H), 3.37 (s, 3H, OMe), 5.50 (m,1H), 5.59 (m,1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.36 (q, Me), 23.67 (t), 33.34 (t), 37.36 (t), 40.26 (d), 41.10 (t), 51.07 (d), 51.50 (s), 52.87 (d), 56.41 (q, OMe), 80.05 (s), 89.31 (s), 127.43 (d), 132.38 (d). EIMS (*m/z*): 220 (M$^+$, 2.3), 202 (M$^+$–H_2O, 20), 191 (M$^+$–Et, 100), 173 (M$^+$–Et–H_2O, 31), 171 (33), 170 (75), 169 (18), 160 (13), 159 (36), 155 (65), 141 (43), 129 (23), 115 (32), 105 (9.8), 91 (20), 77 (10). HRMS Calc. for $C_{14}H_{20}O_2$ (M$^+$): 220.1463; Found: 220.1451.

9d. Yield: 19%, yellow oil. IR (Film), ν: 2939 (m), 1772 (s), 1449 (m), 1378 (m), 1165 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.85 (t, 3H, Me), 1.62–1.77 (stack, 3H), 2.08–2.26 (stack, 6H), 2.76–2.87 (stack, 2H), 3.25 (s, 3H, OMe), 5.54 (m, 1H), 5.58 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 8.44 (q), 15.29 (d), 24.51 (t), 25.45 (t), 29.49 (t), 34.81 (d), 38.78 (t), 40.32 (d), 56.40 (q), 66.80 (d), 77.52 (s), 90.06 (s), 98.38 (s), 125.83 (d), 137.17 (d), 116.56 (q, CF_3), 156.48 (q, CO). ^{19}F NMR (56.4 MHz, $CDCl_3$) δ: −2.1 (s) ppm. EIMS (*m/z*): 316 (M$^+$, 1.5), 301 (M$^+$–Me, 0.5), 216 (M$^+$–Me–$COCF_3$+1,24), 203 (11), 191 (21), 173 (90), 154 (100), 131 (26), 121 (62), 105 (33), 91 (67), 77 (34).

10d. Yield: 21%, yellow oil. IR (Film), ν: 3040 (w), 2971 (m), 2939 (m), 1771 (vs), 1440 (m), 1378 (s), 1221 (vs), 1163 (vs), 1126 (m), 975 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86 (t, 3H, J=7.5 Hz), 1.67–1.75 (stack, 3H), 2.11–2.26 (stack, 6H), 2.80–2.90 (stack, 2H), 3.26 (s, 3H, OMe), 5.53 (dd, 1H, J=5.6, 1.2 Hz), 5.59 (dd, 1H, J=5.5, 2.4 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 7.70 (q, Me), 23.63 (t), 28.79 (t), 37.15 (t), 39.31 (d), 40.15 (t), 50.20 (d), 50.46 (s), 51.42 (d), 56.81 (q, OMe), 90.34 (s), 95.91 (s), 114.66 (q, CF_3, J=285 Hz), 128.30 (d), 132.21 (d), 156.12 (q, CO, J=12 Hz) ppm. ^{19}F NMR (56.4 MHz, $CDCl_3$) δ: −2.3 ppm. EIMS (*m/z*): 316 (M$^+$, 1.7), 302 (M$^+$–CH_2, 0.16), 285 (1.3), 251 (1.2), 219 (M$^+$–$OCOCF_3$, 2.0), 203 (12), 187 (16), 173 (100), 159 (19), 131 (19), 121 (35), 91 (38), 79 (13).

The elemental analyses of **9d** and **10d** could not be determined due to their slow decomposition at room temperature.

3.8. Preparation of compound 11

3-(*o*-Methoxybenzyl)aminoprop-1-ene (or 3-benzylaminoprop-1-ene) was prepared by condensation of *o*-anisaldehyde (or benzaldehyde) and allylic amine followed by reduction with $NaBH_4$ in MeOH according to standard procedures.

3-(*o*-Methylbenzyl)aminoprop-1-ene was prepared by condensation of *o*-methylbenzyl chloride and allylic amine followed by reduction with $LiAlH_4$ in dried THF according to standard procedures. The amines obtained were trifluoroacetylated to **11** as follows:

To the amine (8.1 mmol) was added $(CF_3CO)_2O$ (24 mmol), pyridine (8.1 mmol) and catalytic amount of DMAP in dried ether (10 ml) at 0°C and stirred or refluxed for 8–16 h, the mixture was poured into ice-water and extracted with ether(60 ml×3), washed with water until pH 7, then dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude material was purified with flash chromatography (petroleum ether: ether=15:1) to give **11** as colorless oil.

11a. Yield: 92%. IR (Film), ν: 2942 (w), 2840 (w), 1691 (s), 1603 (w), 1591 (w), 1495 (m), 1460 (m), 1442 (m), 1291 (w), 1207 (m), 1146 (s), 1115 (m), 757 (m) cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.83 (s, 3H, OMe), 3.97–4.14 (stack, 2H), 4.66 (s, 2H), 5.09–5.30 (stack, 2H), 5.77 (m, 1H), 6.88–7.09 (stack, 2H), 7.20–7.34 (stack, 2H) ppm. ^{19}F NMR (56.4 MHz, $CDCl_3$) δ: −9.3 ppm. EIMS (*m/z*): 273 (M$^+$-2, 10), 232 (100), 226 (0.82), 209 (1.3), 191 (0.63), 176 (1.6), 149 (4.8), 137 (5.1), 121 (31), 107 (62), 91 (52). Analysis: Calc. for $C_{13}H_{14}O_2NF_3$: C, 57.14; H, 5.16; N 5.13; Found: C, 56.79; H, 5.55; N, 5.04.

11b : Yield: 98%. IR (Film), ν: 2931 (w), 1693 (vs), 1450 (m), 1290 (s), 1207 (s), 1145 (s), 992 (m), 937 (w), 747 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.27 (s, 3H, Me), 3.94 (dd, 2H, J=20, 5.9 Hz), 4.68 (s, 2H), 5.09–5.33 (stack, 2H), 5.76 (m, 1H), 7.06–7.26 (stack, 4H) ppm. ^{19}F NMR

(56.4 MHz, $CDCl_3$) δ: -9.3 ppm. EIMS (*m/z*): 258 ($M^+{+}1$, 21), 257 (M^+, 22), 256 (M^+-1, 100), 216 (M^+-1-allyl, 10), 205 (3.0), 191 (3.3), 174 (4.8), 161 (2.0), 149 (4.2), 136 (16), 115 (3.8), 105 (15), 91 (4.9). Analysis Calc. for $C_{13}H_{14}ONF_3$: C, 60.69; H, 5.48; N 5.45; Found: C, 60.41; H, 5.40; N, 5.21.

11c. Yield: 78%. IR (Film), ν: 3067 (w), 3031 (w), 2933 (w), 1669 (vs), 1604 (w), 1456 (m), 1295 (w), 1207 (s), 1145 (s), 1004 (w) cm^{-1}. ^1H NMR (90 MHz, CCl_4) δ: 3.85 (d, 2H), 4.60 (s, 2H), 5.05–5.40 (stack, 2H), 5.75 (m, 1H), 7.05–7.45 (stack, 5H) ppm. ^{19}F NMR (60 MHz, $CDCl_3$) δ: -9.5 ppm. EIMS (*m/z*): 243 (M^+, 6.5), 217 (M^+–C_2H_2, 1.6), 202 (M^+-allyl, 100), 174 (M^+–CF_3, 0.74), 152 (3.5), 132 (7.1), 107 (18), 91 (67), 79 (19).

3.9. *Irradiation of* **11**

A solution of **11** (5.9 mmol) in hexane (450 ml) was irradiated in a quartz vessel for 2.0 h. After removal of the solvent, the crude material was separated by flash chromatography (petroleum ether:ether $=\sim$10:1) to give **12** as light yellowish oil.

12a. Yield: 32.5%. IR (Film), ν: 2938 (m), 1691 (vs), 1589 (w), 1516 (w), 1458 (m), 1350 (w), 1256 (m), 1207 (s), 1172 (s), 1145 (s), 760 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.86–2.07 (stack, 3H), 2.22 (m, 1H), 2.38 (m, 1H), 3.37 (s, 3H, OMe), 3.43–3.99 (stack, 6H), 5.60 (m, 1H), 5.66 (m, 1H) ppm. ^{19}F NMR (56.4 MHz, $CDCl_3$) δ: -6.0 ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 38.07 (d), 45.24 (t), 45.92 (t), 52.83 (d), 52.94 (t), 52.99 (d), 56.98 (q), 77.30 (s), 89.58 (s), 116.31 (q, CF_3, J=286 Hz). 127.35 (d), 133.28 (d), 154.60–156.06 (q, CO, J=36 Hz) ppm. EIMS (*m/z*): 273 (M^+, 3.0), 232 (31), 204 (1.9), 176 (3.1), 161 (5.4), 148 (3.3), 121 (15), 107 (21), 91 (40), 77 (20), 69 (100). Analysis: Calc. for $C_{13}H_{14}O_2NF_3$: C, 57.14; H, 5.16; N, 5.13; Found: C, 56.75; H,5.67; N, 5.05.

12b. Yield: 38%. IR (Film), ν: 3034 (w), 2928 (m), 2867 (m), 1796 (w), 1683 (vs), 1457 (m), 1256 (m), 1206 (s), 1142 (s), 756 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.31 (s, 3H, Me), 1.70–1.79 (stack, 2H), 1.93 (m, 1H), 2.53 (m, 1H), 2.98 (dd, 1H, J=5.1, 2.2 Hz), 3.43–3.94 (stack, 4H), 5.46 (m, 1H), 5.63 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.43 (q), 38.59 (d), 41.44 (d), 46.25 (t), 47.04 (t), 49.34 (s), 52.47 (t), 57.50 (d), 62.50 (s), 116.42 (q, CF_3, J=286 Hz), 127.76 (d), 133.36 (d), 155.25 (q, CO, J=37 Hz) ppm. ^{19}F NMR (60 MHz, $CDCl_3$) δ: -5.7 ppm. EIMS (*m/z*): 257(M^+, 3.6), 242 (M^+–Me, 3.4), 216 (56), 203 (0.75), 188 (3.2), 176 (8.5), 129 (6.9), 115 (8.9), 107 (22), 91 (100), 77 (11). Analysis: Calc. for $C_{13}H_{14}ONF_3$: C, 60.69; H, 5.48; N, 5.45; Found: C, 60.48; H, 5.43; N, 5.22.

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