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Perfluoroalkylation through Cross-Metathesis between Alkenes and (Perfluoroalkyl)propenes

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A new approach to perfluoroalkylated compounds based on cross-metathesis between perfluoropropenes and terminal alkenes has been developed. The reaction is catalysed with high efficiency and selectivity by the Hoveyda–Grubbs second-generation catalyst under mild reaction conditions. The method is applicable to a wide range of compounds, such as vinylaromatics, isoprenoids and saccharides.

Introduction

Fluorine-containing compounds are ever more popular targets of the pharmaceutical and specialty chemicals industries.[1] This stems from the fact that the presence of fluorine or fluorinated functional groups with their unique properties gives the target molecules special (desirable) properties (e.g., metabolic stability, increased lipophilicity etc.).[2] Although there have been considerable advances in perfluoroalkylation reactions,[3] there is still demand for development and introduction of new methodologies in this area of chemistry.

Alkene metathesis, which allows double bonds to be coupled under mild reaction conditions, is one of the most widely exploited methods in organic synthesis.[4] Because of its generality it is not surprising that it has also been applied, in a few cases, in organofluorine chemistry for the synthesis of homoallyl,[5] allyl[6] or vinyl fluorides,[7] and also for perfluoroalkylation through the use of (perfluoroalkyl)*ethenes*.[8,9] In the report by Blechert et al.[9] it is demonstrated that (perfluoroalkyl)ethenes can be used as substrates in ruthenium-catalysed cross-metathesis reactions for the synthesis of perfluoroalkylated compounds. Although this is a useful method, for the successful execution of the reaction it was necessary to use at least a tenfold excess of the corresponding (perfluoroalkyl)ethene with respect to the substrate and also to run the reaction in trifluorotoluene to overcome solubility problems. This approach has been recently used for the synthesis of perfluoroalkylated cyclodextrins.[10] Since it has been demonstrated that the inductive effects of perfluoroalkyl groups change profoundly with the distance from the reaction centre [e.g., different reactivities of $R_FCH{=}CH_2$ and $R_FCH_2CH{=}CH_2$,[11a] and also of $R_F(CH_2)_nCH_2I$[11b]], we were interested in the reactivities and scope of (perfluoroalkyl)*propenes* in cross-metathesis reactions.

Results and Discussion

Since metathesis between alkenes and highly fluorinated substrates is a rather unexplored area, and because related compounds – (perfluoroalkyl)propenes – can be easily accessible from simple starting materials, we decided to study their synthetic potential in cross-metathesis reactions and their potential use in the synthesis of fluoroalkyl compounds. As representatives of (perfluoroalkyl)propenes we chose 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononon-1-ene [(perfluorohexyl)propene, **1a**], 4,4,5,5,6,6,6-heptafluorohex-1-ene [(perfluoropropyl)propene, **1b**] and 4-(trifluoromethyl)-4,5,5,5-tetrafluoropent-1-ene [(perfluoroisopropyl)propene, **1c**]. Initially, compound **1a** was synthesized by a two-step procedure based on the copper-catalysed addition of perfluorohexyl iodide to allyl alcohol,[12] followed by elimination promoted by zinc under acidic conditions.[13] Later, a more convenient one-step procedure based on the radical reactions between the appropriate perfluoroalkyl iodides and allyltributylstannane was used.[14]

We found that cross-metathesis reactions between the prepared (perfluoroalkyl)propenes and various terminal alkene substrates could be conveniently carried out not only in dichloromethane at reflux in the presence of the Hoveyda–Grubbs second-generation catalyst (Figure 1), but also that a (perfluoroalkyl)propene/substrate ratio of 2:1 was sufficient to achieve reasonable yields of the desired compounds (Scheme 1).

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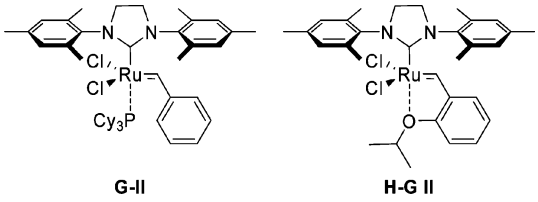
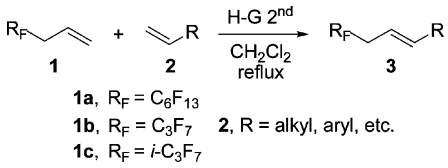


Figure 1. The Grubbs second-generation (G-II) and the Hoveyda–Grubbs second-generation (H-G II) catalysts.



Scheme 1. Cross-metathesis between **1** and **2** to afford **3**.

To determine the scope of the perfluoroalkylation procedure with respect to structural variation of the substrates, we tested the metathesis reactions with a wide range of terminal alkenes **2**, and the results are summarized in Table 1. All reactions were carried out until the disappearance of the starting material **2** or until progress of the reaction was no longer observable. With regard to homodimerization of the starting compounds, this was not detected for substrates **2**; only perfluoroalkenes **1** underwent the reaction in isolable amounts.

Initially, all reactions were carried out with (perfluorohexyl)propene (**1a**). Metathesis with 1- and 2-vinylnaphthalene (**2a** and **2b**) thus afforded rather low yields of the corresponding perfluoroalkylated alkenes **3** (17%) and **4** (15%); however, these low yields could be attributed to the propensities of **2a** and **2b** to undergo polymerization (Entries 1 and 2). A considerably better result was obtained with vinylferrocene (**2c**), with the product **5** being obtained in a reasonable 48% yield (Entry 3). The metathesis reaction also proceeded very well with alkenes such as **2d**,[15] with the corresponding product **6** being obtained in 66% yield (Entry 4). These positive results prompted us to shift our attention to perfluoroalkylation of more complex compounds such as isoprenoids. The reaction was thus carried out with alkene **2e**, obtained from lithocholic acid (Entry 5), and the product **7a** was isolated in a very good 75% yield.

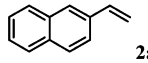
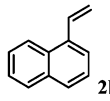
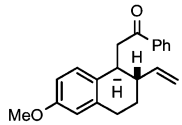
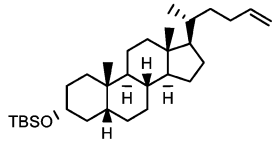
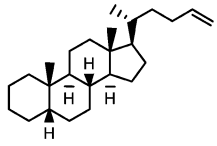
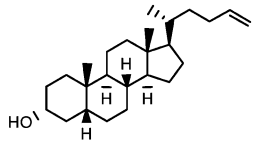
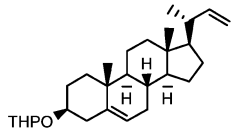
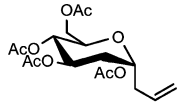
Metathesis between **2e** and **1a** was also carried out in the presence of the Grubbs second-generation catalyst in order to compare the catalytic activities and selectivities of the two catalysts. It proceeded well enough, affording the expected product **7a** in 59% yield, but the formation of a minor amount of homodimer *dim*-**2e** (10%) was also observed.

Metathesis was then also carried out with compound **2f** (Entry 6), giving the expected product **8** in a good 64% yield. Gratifyingly, the metathesis also proceeded with compound **2g**, possessing a free hydroxy group (Entry 7), to yield the desired product **9a** in a good 70% yield. Under the same conditions a reaction was also performed with compound **2h** (Entry 8), to give product **10a** in a good yield of 79%. Finally, the metathesis reaction was carried out with the 1-allylglucose derivative **2i** and yielded the expected compound **11** in 64% yield (Entry 9).

Metathesis with substrate **2e** was also carried out in the presence of 5 and 2 mol-% of catalyst. In the former case the conversion of the starting material was quantitative and in the latter 80% (according to ^{1}H NMR analysis of the reaction mixtures).

In addition, metathesis reactions between **1b** or **1c** and selected substrates were carried out. The reaction between **2e** and **1c** gave **7c** in a good 63% yield (Entry 5). Also, me-

Table 1. Synthesis of perfluoroalkylated compounds by cross-metathesis.[a]

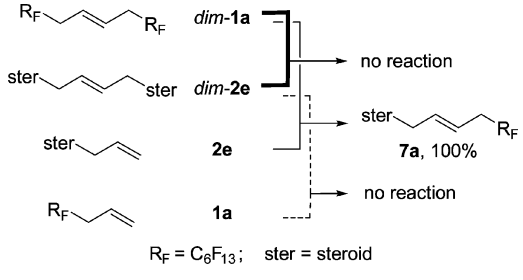
Entry	1	2	R_F⁄⁄R 3-11	E/Z	Yield [%][b]
1	**1a**	 **2a**	**3**	*E*	17
2	**1a**	 **2b**	**4**	*E*	15
3	**1a**	 **2c**	**5**	*E*	48
4	**1a**	 **2d**	**6**	*E*	66
5	**1a**	 **2e**	**7a**	*E*	75 (59)[c]
	1c		**7c**	7/1	63
6	**1a**	 **2f**	**8**	4/1	64
7	**1a**	 **2g**	**9a**	2/1	70
	1b		**9b**	1.5/1	71
	1c		**9c**	1.5/1	75
8	**1a**	 **2h**	**10a**	*E*	79
	1b		**10b**	*E*	81
9	**1a**	 **2i**	**11**	*E*	64

[a] All reactions were catalysed with the Hoveyda–Grubbs second-generation catalyst (10 mol-%) unless noted (reaction time 3 h). [b] Isolated yields. [c] The Grubbs second-generation catalyst (10 mol-%) was used.

tathesis between **2g** and **1b** or **1c** yielded the corresponding products **9b** and **9c** in good yields of 71 and 75%, respectively (Entry 7). A similar result was observed in the reaction between **1b** and **2h**, which afforded the corresponding product **10b** in 81% yield (Entry 8).

In most cross-metathesis reactions *E*/*Z* selectivity can be a critical issue, especially when the double bond of the obtained alkene is intended for further elaboration. Fortunately, though, we were pleased to find that in most cases the cross-metathesis proceeded with a high degree of *E* selectivity (>98%). In fact, we did not usually observe any signals that could be attributed to *Z* isomers in the NMR spectra. An exception from this general trend was the metathesis between the protected alkene derivative **2e** and (perfluoroisopropyl)propene (**1c**), which gave product **7c** as a mixture of *E*/*Z* isomers in 7:1 ratio. Interestingly, the reactions between alkene **2g**, bearing a free hydroxy group, and **1a**–**1c** also gave the corresponding products **9a**–**9c** as mixtures of double bond isomers with unhelpful *E*/*Z* ratios (1.5–2:1).

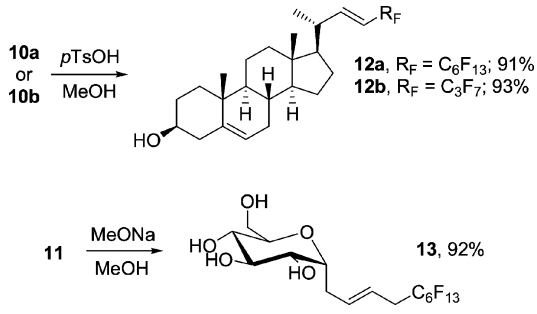
Since the homodimer of (perfluorohexyl)propene (dimer *dim*-**1a**) was the major side product in cross-metathesis reactions involving **1a** and the steroid homodimer (*dim*-**2e**) was a side product in cross-metathesis between **1a** and **2e** catalysed by the Grubbs second-generation catalyst (Entry 5), we were interested in whether these compounds could also participate in cross-metathesis. A larger quantity of *dim*-**2e** was synthesized from **2e** in the presence of the Grubbs second-generation catalyst (the Hoveyda–Grubbs second-generation catalyst did not promote the reaction). Three cross-metathesis reactions were then investigated: i) between *dim*-**2e** and *dim*-**1a**, ii) between **2e** and *dim*-**1a**, and iii) between *dim*-**2e** and **1a** (Scheme 2). In the first case, the reaction did not take place. In the second case, a smooth reaction was observed, affording the desired cross-metathesis product **7a** in quantitative yield (^{1}H NMR yield). In the last case (i.e., the attempted reaction between *dim*-**2e** and **1a**), again no reaction was observed. Cross-metathesis between *dim*-**1a** and vinylferrocene (**2c**) was also investigated. The reaction proceeded with full conversion of **2c** and yielded **5** in 42% isolated yield (homodimerization of **2c** was not observed).



Scheme 2. Cross-reactions between terminal and internal alkenes.

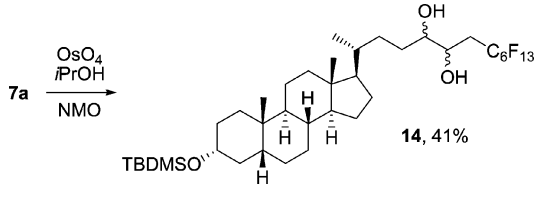
In view of the above findings, the classification of (perfluoroalkyl)*propenes* with respect to (perfluoroalkyl)*ethenes* according to the Grubbs categorization of alkenyl substrates becomes a desirable issue.[16] The obtained results showed that (perfluorohexyl)propene (**1a**) could undergo easy dimerization to *dim*-**2a**, which could also participate in metathesis reactions. Therefore, **1a** and other (perfluoroalkyl)propenes could be classified as Type I olefins. Since (perfluoroalkyl)ethenes are classified as Type II olefins, it is obvious that there are considerable differences in their reactivities. These differences could be attributable to the presence of the methylene group as the spacer between the double bond and the perfluoroalkyl moiety, diminishing its inductive effect. Nonetheless, one should keep in mind that the Grubbs categorization was based on reactions carried out with different types of catalysts (the ruthenium-based Grubbs first- and Grubbs second-generation catalysts and the molybdenum-based Schrock catalyst) from those used in our case.

Removal of the protecting TBDMS group from **7a** with $Et_3N{\cdot}3\,HF$[17] afforded compound **9a** in 63% yield. Removal of the THP protecting group from **10a** and **10b** (Scheme 3) with *p*-TsOH in MeOH proceeded quantitatively, affording substances **12a** and **12b** in very good 91 and 93% isolated yields, respectively. Analogously, deprotection of the saccharide derivative **11** under basic conditions (MeONa/MeOH) afforded **13** in a good 92% yield.



Scheme 3. Deprotection of **10** and **11**.

Easy functionalization of the obtained perfluoroalkylated alkenes was demonstrated by catalytic dihydroxylation of the double bonds. Dihydroxylation of **7a** with osmium tetraoxide under standard conditions (Scheme 4)[18] afforded the corresponding dihydroxy compound **14** as a 1:1 diastereoisomeric mixture in 41% isolated yield.



Scheme 4. Catalytic dihydroxylation of **7a** to afford **14**.

Conclusions

In summary, the metathesis reactions between (perfluoroalkyl)propenes and various terminal alkenes including terpenes and saccharides proceeded in all cases in good to excellent yields under mild reaction conditions (reflux in DCM) and with favourable (perfluoroalkyl)propene/substrate ratios (2:1). The reaction conditions and the known tolerance of the catalysts used for a wide range of functional groups enabled metathesis also to be carried out with substrates possessing unprotected hydroxy groups, thus allowing direct perfluoroalkylation and avoiding often lengthy and problematic protection/deprotection reaction sequences. In addition, (perfluoroalkyl)propenes can be classified as Type I olefins, unlike (perfluoroalkyl)ethenes, which behave rather like Type II olefins (according to the Grubbs categorization). This reaction thus provides a simple pathway for introduction of perfluoroalkyl groups into compounds with various degrees of complexity.

Experimental Section

General Procedure for Cross-Metathesis between Terminal Alkenes and (Perfluoroalkyl)propenes: The Hoveyda–Grubbs second-generation catalyst (10 mol-%) was added under argon to a mixture of a terminal alkene (**2a**–**2j**, 1 equiv.) and a (perfluoroalkyl)propene (**1a**–**c**, 2 equiv.) in DCM. The resulting solution was stirred at 42 °C for 3 h. Removal of the solvent in vacuo gave a brown oil, which could be purified by flash chromatography.

2-[(*E*)-4′,4′,5′,5′,6′,6′,7′,7′,8′,8′,9′,9′,9′-Tridecafluorononen-1′-enyl]-naphthalene (3): The reaction was carried out with **2a** (154 mg, 1 mmol) and (perfluorohexyl)propene (**1a**, 720 mg, 2 mmol) by the General Procedure. Column chromatography on silica gel (hexane/heptane, 1:1) afforded compound **3** (81 mg, 17%) as a white foam: $[\alpha]_D^{20}$ = +3.0 (*c* = 0.26, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 3.07 (br. td, *J* = 18.1, 7.2 Hz, 2 H), 6.26 (dt, *J* = 15.8, 7.3 Hz, 1 H), 6.78 (br. d, *J* = 15.8 Hz, 1 H), 7.47 (m, 2 H), 7.60 (dd, *J* = 8.6, 1.8 Hz, 1 H), 7.74 (d, *J* = 1.7 Hz, 1 H), 7.81 (m, 3 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 35.27 (t, $J_{C,F}$ = 22.6 Hz, CH_2), 116.31 (t, *J* = 4.4 Hz, CH), 123.29 (CH), 126.17 (CH), 126.41 (CH), 126.64 (CH), 127.68 (CH), 128.05 (CH), 128.36 (CH), 133.18 (C), 133.45 (C), 133.61 (C), 137.33 (CH) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3061, 3010, 1657, 1628, 1599, 1509, 1364, 1347, 1243, 1145, 969 cm^{-1}. MS (FAB): *m*/*z* = 487 $[M + H]^+$ (12), 361 (7), 312 (3), 233 (5), 207 (46), 156 (32). HR-MS (FAB) calcd. for $C_{19}H_{12}F_{13}$ $[M + H]^+$ 487.0731; found 487.0717. R_f(hexane) = 0.53.

1-[(*E*)-4′,4′,5′,5′,6′,6′,7′,7′,8′,8′,9′,9′,9′-Tridecafluorononen-1′-enyl]-naphthalene (4): The reaction was carried out with **2b** (154 mg, 1 mmol) and **1a** (720 mg, 2 mmol) by the General Procedure. Column chromatography on silica gel (hexane/heptane, 1:1) afforded compound **4** (75 mg, 15%) as a white foam: $[\alpha]_D^{20}$ = +10.9 (*c* = 0.21, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.14 (m, 2 H), 6.16 (dt, *J* = 15.6, 7.2 Hz, 1 H), 7.37 (dt, *J* = 15.7, 1.5 Hz, 1 H), 7.45 (m, 1 H), 7.51 (m, 2 H), 7.58 (m, 1 H), 7.81 (m, 1 H), 7.86 (m, 1 H), 8.06 (m, 1 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 35.48 (t, $J_{C,F}$ = 22.5 Hz, CH_2), 119.37 (t, $J_{C,F}$ = 4.4 Hz, CH), 123.61 (CH), 124.24 (CH), 125.58 (CH), 125.91 (CH), 126.27 (CH), 128.49 (CH), 128.58 (CH), 130.98 (C), 133.55 (C), 134.09 (C), 134.88 (CH) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3064, 3050, 1592, 1510, 1344, 1344, 1267, 1243, 1145, 969 cm^{-1}. MS (FAB): *m*/*z* = 486 $[M]^+$ (22), 467 (4), 196 (3), 167 (32), 153 (23). HR-MS (FAB) calcd. for $C_{19}H_{11}F_{13}$ $[M]^+$ 486.0653; found 486.0631. R_f(hexane) = 0.53.

1-[(*E*)-4′,4′,5′,5′,6′,6′,7′,7′,8′,8′,9′,9′,9′-Tridecafluorononen-1′-enyl]-ferrocene (5): The reaction was carried out with **2c** (106 mg, 0.5 mmol) and **1a** (360 mg, 1 mmol) by the General Procedure. Column chromatography on silica gel (toluene) and crystallization (CH_2Cl_2/hexane) yielded compound **5** (130 mg, 48%) as orange crystals: m.p. 91–92 °C. $[\alpha]_D^{20}$ = +6.9 (*c* = 0.17, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 2.87 (dt, *J* = 18.0, 7.3 Hz, 2 H), 4.11 (s, 5 H), 4.23 (m, 2 H), 4.35 (m, 2 H), 5.70 (dt, *J* = 15.6, 7.3 Hz, 1 H), 6.37 (br. d, *J* = 15.7 Hz, 1 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 35.25 (t, $J_{C,F}$ = 45.3 Hz, CH_2), 66.85 (2 C, 2×CH), 68.95 (2 C, 2×CH), 69.18 (5 C, 5×CH), 81.74 (CH), 112.46 (t, $J_{C,F}$ = 4.3 Hz, CH), 135.20 (CH) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3099, 3011, 1657, 1412, 1347, 1243, 1145, 1106, 962 cm^{-1}. MS (FAB): *m*/*z* = 544 $[M]^+$ (28), 274 (17), 256 (13), 232 (12), 181 (76), 149 (22). HR-MS (FAB) calcd. for $C_{19}H_{13}F_{13}Fe$ $[M]^+$ 544.0159; found 544.0154. R_f(hexane) = 0.31.

2-[6′-Methoxy-2′-((*E*)-4′′,4′′,5′′,5′′,6′′,6′′,7′′,7′′,8′′,8′′,9′′,9′′,9′′-tridecafluorononen-1′′-enyl)-1′,2′,3′,4′-tetrahydronaphthalen-1′-yl]-1-phenylethanone (6): The reaction was carried out with **2d** (100 mg, 0.33 mmol) and **1a** (238 mg, 0.66 mmol) by the General Procedure. Column chromatography on silica gel (hexane/diethyl ether 20:1) and on fluorinated silica gel (first elution MeOH/water 4:1, washing of the non-fluorinated starting material, second elution diethyl ether, washing of the product) yielded compound **6** (144 mg, 66%) as a yellowish oil: $[\alpha]_D^{20}$ = +2.0 (*c* = 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.73 (m, 1 H), 1.99 (dtd, *J* = 13.5, 6.7, 3.5 Hz, 1 H), 2.52 (m, 1 H), 2.73 (td, *J* = 18.1, 7.0 Hz, 2 H), 2.80 (t, *J* = 6.5 Hz, 2 H), 3.25 (dd, *J* = 17.7, 5.2 Hz, 1 H), 3.36 (dd, *J* = 17.7, 7.0 Hz, 1 H), 3.50 (m, 1 H), 5.47 (dtd, *J* = 15.4, 7.1, 0.8 Hz, 1 H), 5.72 (ddt, *J* = 15.4, 8.2, 1.3 Hz, 1 H), 6.62 (d, *J* = 2.8 Hz, 1 H), 6.68 (dd, *J* = 8.5, 2.8 Hz, 1 H), 7.00 (d, *J* = 8.5 Hz, 1 H), 7.45 (m, 2 H), 7.56 (m, 1 H), 7.95 (m, 2 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 26.07 (CH_2), 27.09 (CH_2), 34.82 (t, $J_{C,F}$ = 22.6 Hz, CH_2), 37.35 (CH), 41.95 (CH), 45.76 (CH_2), 55.14 (CH_3), 112.55 (CH), 113.36 (CH), 117.07 (t, $J_{C,F}$ = 4.2 Hz, CH), 128.01 (2 C, 2×CH), 128.60 (2 C, 2×CH), 129.61 (CH), 130.96 (C), 133.07 (CH), 137.13 (C), 137.59 (C), 141.79 (CH), 157.61 (C), 199.11 (C) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3088, 3061, 3028, 2839, 1685, 1609, 1598, 1449, 1352, 1242, 1145, 1120, 974, 598 cm^{-1}. MS (FAB): *m*/*z* = 639 $[M + H]^+$ (3), 595 (2), 519 (21), 262 (8), 253 (9), 155 (22). HR-MS (FAB) calcd. for $C_{28}H_{24}F_{13}O_2$ $[M]^+$ 639.1569; found 639.1562. R_f(hexane/Et_2O, 20:1) = 0.25.

(1′′,1′′-Dimethylethyl)dimethyl{[(3*α*)-20-(6′,6′,7′,7′,8′,8′,9′,9′,10′,10′,11′,11′,11′-tridecafluoroundec-3′(*E*)-en-1′-yl)pregnan-3-yl]oxy}silane (7a): The reaction was carried out with **2e** (95 mg, 0.2 mmol) and **1a** (144 mg, 0.4 mmol) by the General Procedure. Column chromatography on silica gel (hexane/toluene, 20:1) yielded compound **7a** (121 mg, 75%) as a colourless oil: $[\alpha]_D^{20}$ = +21.0 (*c* = 0.27, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.06 (s, 6 H), 0.62 (s, 3 H), 0.89 (s, 9 H), 0.90 (s, 3 H), 0.91 (d, *J* = 6.4 Hz, 3 H), 2.13 (m, 1 H), 2.78 (dt, *J* = 18.2, 6.8 Hz, 2 H), 3.58 (m, 1 H), 5.38 (m, 1 H), 5.69 (m, 1 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = –4.62 (2 C, 2×CH_3), 11.92 (CH_3), 18.36 (C), 18.38 (CH_3), 20.79 (CH_2), 23.38 (CH_3), 24.20 (CH_2), 25.97 (3 C, 3×CH_3), 26.40 (CH_2), 27.29 (CH_2), 28.29 (CH_2), 29.33 (CH_2), 31.01 (CH_2), 34.58 (C), 34.82 (t, $J_{C,F}$ = 22.6 Hz, CH_2), 35.13 (CH_2), 35.28 (CH), 35.57 (CH_2), 35.84 (CH), 36.91 (CH_2), 40.15 (CH_2), 40.18 (CH), 42.29 (CH), 42.70 (C), 56.17 (CH), 56.41 (CH), 72.85 (CH), 115.85 (t, $J_{C,F}$ = 4.0 Hz, CH), 139.64 (CH) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2931, 2859, 1672, 1471, 1373, 1243, 1071, 972 cm^{-1}.

MS (FAB): *m*/*z* = 804 [M]$^+$ (2), 672 (4), 654 (3), 630 (1), 315 (9), 280 (20). R_f(hexane/toluene, 10:1) = 0.42.

Mixture of (1′′,1′′-Dimethylethyl)dimethyl{(3α)-20-[(6′-trifluoromethyl-6′,7′,7′,7′-tetrafluorohept-3′(*E*/*Z*)-en-1′-yl)pregnan-3-yl]-oxy}silane (7c): The reaction was carried out with **2e** (80 mg, 0.17 mmol) and **1c** (72 mg, 0.34 mmol) by the General Procedure. Column chromatography on silica gel (heptane) afforded the title compound **7c** (69 mg, 63%, inseparable 7:1 mixture of *E*/*Z* isomers) as a colourless oil: $[\alpha]_D^{20}$ = +31.5 (*c* = 0.21, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2931, 2859, 1671, 1471, 1374, 1244, 1091, 974 cm^{-1}. MS (FAB): *m*/*z* = 653 [M – H]$^+$ (2), 521 (5), 463 (2), 413 (1), 337 (9), 236 (4). HR-MS (FAB) calcd. for $C_{35}H_{56}OF_7Si$ [M – H]$^+$ 653.3989; found 653.3971. R_f(heptane) = 0.45.

Isomer (*E*)-7c: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.06 (s, 6 H), 0.62 (s, 3 H), 0.89 (s, 9 H), 0.89 (d, *J* = 6.8 Hz, 3 H), 0.90 (s, 3 H), 2.13 (m, 1 H), 2.79 (br. dd, *J* = 20.0, 7.2 Hz, 2 H), 3.58 (m, 1 H), 5.36 (dm, *J* = 15.2 Hz, 1 H), 5.65 (dm, *J* = 15.2 Hz, 1 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = –4.62 (2 C, 2 × CH_3), 11.92 (CH_3), 18.32 (CH_3), 18.36 (C), 20.79 (CH_2), 23.38 (CH_3), 24.21 (CH_2), 25.97 (3 C, 3 × CH_3), 26.40 (CH_2), 27.29 (CH_2), 28.27 (CH_2), 29.20 (CH_2), 31.00 (CH_2), 34.58 (d, $J_{C,F}$ = 20.9 Hz, CH_2), 34.58 (C), 35.07 (CH_2), 35.19 (CH), 35.57 (CH_2), 35.84 (CH), 36.90 (CH_2), 40.14 (CH_2), 40.17 (CH), 42.28 (CH), 42.70 (C), 56.16 (CH), 56.40 (CH), 72.85 (CH), 116.97 (d, $J_{C,F}$ = 5.6 Hz, CH), 138.93 (CH) ppm.

Isomer (*Z*)-7c: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.06 (s, 6 H), 0.63 (s, 3 H), 0.89 (s, 9 H), 0.89 (d, *J* = 6.8 Hz, 3 H), 0.90 (s, 3 H), 2.13 (m, 1 H), 2.86 (br. dd, *J* = 19.6, 7.6 Hz, 2 H), 3.58 (m, 1 H), 5.36 (dm, *J* = 15.2 Hz, 1 H), 5.65 (dm, *J* = 15.2 Hz, 1 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = –4.62 (2 C, 2 × CH_3), 11.92 (CH_3), 18.32 (CH_3), 18.36 (C), 20.79 (CH_2), 23.38 (CH_3), 24.21 (CH_2), 25.97 (3 C, 3 × CH_3), 26.40 (CH_2), 27.29 (CH_2), 28.27 (CH_2), 29.20 (CH_2), 31.00 (CH_2), 34.58 (d, $J_{C,F}$ = 20.9 Hz, CH_2), 34.58 (C), 35.07 (CH_2), 35.19 (CH), 35.57 (CH_2), 35.84 (CH), 36.90 (CH_2), 40.14 (CH_2), 40.17 (CH), 42.28 (CH), 42.70 (C), 56.16 (CH), 56.40 (CH), 72.85 (CH), 116.05 (d, $J_{C,F}$ = 5.6 Hz, CH), 136.84 (CH) ppm.

Mixture of 20-(6′,6′,7′,7′,8′,8′,9′,9′,10′,10′,11′,11′,11′-Tridecafluoroundec-3′(*E*/*Z*)-en-1′-yl)pregnane (8): The reaction was carried out with **2f** (75 mg, 0.22 mmol) and **1a** (158 mg, 0.44 mmol) by the General Procedure. Column chromatography on silica gel (heptane) afforded the title compound **8** (95 mg, 64%, inseparable 4:1 mixture of *E*/*Z* isomers) as a colourless oil: $[\alpha]_D^{20}$ = +39.6 (*c* = 0.11, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2931, 2863, 1673, 1375, 1363, 1242, 1145, 973 cm^{-1}. MS (APCI): *m*/*z* = 674 [M]$^+$ (1), 607 (65), 551 (52), 495 (36), 439 (9), 391 (7), 278 (4). R_f(heptane) = 0.80.

Isomer (*E*)-8: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.64 (s, 3 H), 0.91 (d, *J* = 6.5 Hz, 3 H), 0.91 (s, 3 H), 2.78 (td, *J* = 18.7, 7.1 Hz, 2 H), 5.38 (m, 1 H), 5.69 (dtt, *J* = 15.4, 6.8, 1.4 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 11.97 (CH_3), 18.41 (CH_3), 20.82 (CH_2), 21.33 (CH_2), 24.23 (CH_2), 24.27 (CH_3), 27.03 (CH_2), 27.25 (CH_2), 27.52 (CH_2), 28.30 (CH_2), 29.32 (CH_2), 34.82 (t, $J_{C,F}$ = 22.4 Hz, CH_2), 35.17 (CH_2), 35.29 (CH), 35.36 (C), 35.88 (CH), 37.58 (CH_2), 40.30 (CH_2), 40.51 (CH), 42.74 (C), 43.73 (CH), 56.20 (CH), 56.63 (CH), 115.85 (CH), 139.65 (CH) ppm.

Isomer (*Z*)-8: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.65 (s, 3 H), 0.91 (d, *J* = 6.5 Hz, 3 H), 0.91 (s, 3 H), 2.78 (td, *J* = 18.7, 7.1 Hz, 2 H), 5.38 (m, 1 H), 5.69 (dtt, *J* = 15.4, 6.8, 1.4 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 11.97 (CH_3), 18.41 (CH_3), 20.82 (CH_2), 21.33 (CH_2), 24.23 (CH_2), 24.27 (CH_3), 27.03 (CH_2), 27.25 (CH_2), 27.52 (CH_2), 28.30 (CH_2), 29.32 (CH_2), 34.82 (t, $J_{C,F}$ = 22.4 Hz, CH_2), 35.17 (CH_2), 35.29 (CH), 35.36 (C), 35.88 (CH), 37.58 (CH_2), 40.30 (CH_2), 40.51 (CH), 42.74 (C), 43.73 (CH), 56.12 (CH), 56.20 (CH), 115.10 (CH), 137.70 (CH) ppm.

Mixture of (3α,5β)-20-(6′,6′,7′,7′,8′,8′,9′,9′,10′,10′,11′,11′,11′-Tridecafluoroundec-3′(*E*/*Z*)-en-1′-yl)pregnan-3-ol (9a): The reaction was carried out with **2g** (100 mg, 0.28 mmol) and **1a** (180 mg, 0.5 mmol) by the General Procedure. Column chromatography on silica gel (toluene/diethyl ether, 20:1) and on fluorinated silica gel (first elution 7:1 MeOH, water washing of the non-fluorinated starting material, second elution diethyl ether, washing of the product) afforded the title compound **9a** (135 mg, 70%, inseparable 2:1 mixture of *E*/*Z* isomers) as a colourless oil: $[\alpha]_D^{20}$ = +14.0 (*c* = 0.19, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3609, 2938, 2867, 1672, 1471, 1377, 1365, 1242, 1145, 1031, 1012, 973 cm^{-1}. MS (ESI): *m*/*z* = 690 [M]$^+$ (1), 663 (14), 610 (3), 648 (10), 426 (100), 316 (43), 288 (98). HR-MS (FAB) calcd. for $C_{32}H_{42}F_7$ [M – OH]$^+$ 673.3079; found 673.3089. R_f(toluene/diethyl ether, 20:1) = 0.25.

Isomer (*E*)-9a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.64 (s, 3 H), 0.91 (d, *J* = 6.6 Hz, 3 H), 0.92 (s, 3 H), 2.78 (dt, *J* = 18.2, 6.8 Hz, 2 H), 3.63 (m, 1 H), 5.38 (m, 1 H), 5.69 (m, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 11.95 (CH_3), 18.39 (CH_3), 20.81 (CH_2), 23.36 (CH_3), 24.19 (CH_2), 26.41 (CH_2), 27.18 (CH_2), 28.26 (CH_2), 30.53 (2 × CH_2), 34.55 (C), 34.82 (t, $J_{C,F}$ = 22.7 Hz, CH_2), 35.13 (CH_2), 35.26 (CH), 35.32 (CH_2), 35.83 (CH), 36.44 (CH_2), 40.19 (CH_2), 40.42 (CH), 42.08 (CH), 42.71 (C), 56.16 (CH), 56.51 (CH), 71.88 (CH), 115.89 (t, $J_{C,F}$ = 4.1 Hz, CH), 139.61 (CH) ppm.

Isomer (*Z*)-9a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.65 (s, 3 H), 0.91 (d, *J* = 6.6 Hz, 3 H), 0.92 (s, 3 H), 2.78 (dt, *J* = 18.2, 6.8 Hz, 2 H), 3.63 (m, 1 H), 5.38 (m, 1 H), 5.69 (m, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 12.01 (CH_3), 18.52 (CH_3), 20.81 (CH_2), 23.36 (CH_3), 24.19 (CH_2), 26.41 (CH_2), 27.18 (CH_2), 28.26 (CH_2), 29.31 (t, $J_{C,F}$ = 22.7 Hz, CH_2), 30.53 (CH_2), 34.55 (C), 35.13 (CH_2), 35.26 (CH), 35.32 (CH_2), 35.83 (CH), 36.44 (CH_2), 39.26 (CH_2), 40.19 (CH_2), 40.42 (CH), 42.08 (CH), 42.71 (C), 56.16 (CH), 56.51 (CH), 71.88 (CH), 117.49 (t, $J_{C,F}$ = 4.0 Hz, CH), 137.54 (CH) ppm.

Mixture of (3α,5β)-20-(6′,6′,7′,7′,8′,8′,8′-Heptafluorooct-3′(*E*/*Z*)-en-1′-yl)pregnan-3-ol (9b): The reaction was carried out with **2g** (80 mg, 0.22 mmol) and **1b** (105 mg, 0.5 mmol) by the General Procedure. Column chromatography on silica gel (toluene) afforded the title compound **9b** (80 mg, 71%, inseparable 1.5:1 mixture of *E*/*Z* isomers) as a white powder: m.p. 88–89 °C. $[\alpha]_D^{20}$ = +25.6 (*c* = 0.23, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3609, 2935, 2867, 1672, 1377, 1353, 1276, 1031, 1012, 972 cm^{-1}. MS (EI): *m*/*z* = 540 [M]$^+$ (1), 522 (8), 493 (3), 301 (3), 285 (31), 257 (12), 215 (36). HR-MS (EI) calcd. for $C_{29}H_{43}OF_7$ [M]$^+$ 540.3202; found 540.3228. R_f(toluene) = 0.29.

Isomer (*E*)-9b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.64 (s, 3 H), 0.90 (d, *J* = 6.6 Hz, 3 H), 0.92 (s, 3 H), 2.78 (m, 2 H), 3.63 (m, 1 H), 5.37 (m, 1 H), 5.68 (m, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 11.99 (CH_3), 18.38 (CH_3), 20.81 (CH_2), 23.36 (CH_3), 24.20 (CH_2), 26.41 (CH_2), 27.19 (CH_2), 28.27 (CH_2), 30.54 (2 C, 2 × CH_2), 34.56 (m, CH_2), 35.13 (CH_2), 35.25 (CH), 35.33 (CH_2), 35.84 (CH), 36.44 (CH_2), 40.19 (CH_2), 40.43 (CH), 42.09 (CH), 42.71 (C), 56.17 (CH), 56.51 (CH), 71.86 (CH), 115.87 (CH), 139.56 (CH) ppm.

Isomer (*Z*)-9b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.65 (s, 3 H), 0.91 (d, *J* = 6.4 Hz, 3 H), 0.92 (s, 3 H), 2.78 (m, 2 H), 3.63 (m, 1 H), 5.37 (m, 1 H), 5.68 (m, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 12.04 (CH_3), 18.52 (CH_3), 20.81 (CH_2), 23.36 (CH_3), 24.20 (CH_2), 26.41 (CH_2), 27.19 (CH_2), 28.27 (CH_2), 29.31 (m, CH_2), 30.54 (CH_2), 35.13 (CH_2), 35.25 (CH), 35.33 (CH_2), 35.84 (CH), 36.44 (CH_2), 39.34 (CH_2), 40.19 (CH_2), 40.43 (CH), 42.09 (CH),

42.71 (C), 56.17 (CH), 56.45 (CH), 71.86 (CH), 117.43 (CH), 137.50 (CH) ppm.

(3α,5β)-20-[6′-(Trifluoromethyl)-6′,7′,7′,7′-tetrafluorohept-3′-en-1′-yl]pregnan-3-ol (9c): The reaction was carried out with **2g** (150 mg, 0.42 mmol) and **1c** (168 mg, 0.80 mmol) by the General Procedure. Column chromatography on silica gel (hexane/diethyl ether, 5:1) afforded the title compound **9c** (171 mg, 75%, inseparable 1:1 mixture of *E*/*Z* isomers) as a colourless oil. $[\alpha]_D^{20}$ = +19.6 (*c* = 0.16, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3610, 2937, 2867, 1671, 1376, 1365, 1286, 1030, 1012, 974 cm^{-1}. MS (FAB): *m*/*z* = 563 $[M + Na]^+$ (2), 523 (5), 507 (12), 337 (8), 263 (9), 233 (4), 179 (8). R_f(hexane/diethyl ether, 4:1) = 0.26.

Isomer (*E*)-9c: ^1H NMR (600 MHz, $CDCl_3$): δ = 0.63 (s, 3 H), 0.90 (d, *J* = 6.3 Hz, 3 H), 0.92 (s, 3 H), 2.80 (m, 2 H), 3.63 (m, 1 H), 5.36 (m, 1 H), 5.65 (m, 1 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 11.92 (CH_3), 18.29 (CH_3), 20.76 (CH_2), 23.34 (CH_3), 24.18 (CH_2), 26.38 (CH_2), 27.14 (CH_2), 28.24 (CH_2), 29.17 (CH_2), 30.45 (CH_2), 32.62 (d, $J_{C,F}$ = 20.9 Hz, CH_2), 34.52 (C), 35.02 (CH_2), 35.15 (CH), 35.28 (CH_2), 35.78 (CH), 36.35 (CH_2), 40.13 (CH_2), 40.35 (CH), 42.01 (CH), 42.67 (C), 56.10 (CH), 56.45 (CH), 71.85 (CH), 116.95 (d, $J_{C,F}$ = 5.4 Hz, CH), 138.89 (CH) ppm.

Isomer (*Z*)-9c: ^1H NMR (600 MHz, $CDCl_3$): δ = 0.64 (s, 3 H), 0.89 (d, *J* = 6.3 Hz, 3 H), 0.92 (s, 3 H), 2.80 (m, 2 H), 3.63 (m, 1 H), 5.36 (m, 1 H), 5.65 (m, 1 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 12.00 (CH_3), 18.47 (CH_3), 20.76 (CH_2), 23.34 (CH_3), 24.18 (CH_2), 26.38 (CH_2), 27.14 (CH_2), 28.24 (CH_2), 30.45 (CH_2), 32.54 (d, $J_{C,F}$ = 20.9 Hz, CH_2), 34.52 (C), 35.02 (CH_2), 35.15 (CH), 35.28 (CH_2), 35.78 (CH), 36.35 (CH_2), 39.12 (CH_2), 40.13 (CH_2), 40.35 (CH), 42.01 (CH), 42.64 (C), 55.60 (CH), 56.39 (CH), 71.85 (CH), 118.49 (d, $J_{C,F}$ = 5.6 Hz, CH), 136.79 (CH) ppm.

Tetrahydro-2′-{[(3β)-25,25,26,26,27,27,28,28,29,29,30,30,30-tridecafluorochola-5,22(*E*)-dien-3-yl]oxy}-2*H*-pyran (10a): The reaction was carried out with **2h** (82 mg, 0.2 mmol) and **1a** (144 mg, 0.4 mmol) by the General Procedure. Column chromatography on silica gel (hexane/diethyl ether, 20:1) and crystallization from acetone yielded the compound **10a** (115 mg, 79%) as white crystals: m.p. 144–145 °C. $[\alpha]_D^{20}$ = –25.2 (*c* = 0.20, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.70 (s, 3 H), 1.01 (s, 3 H), 1.04 (d, *J* = 6.6 Hz, 3 H), 2.75 (m, 2 H), 3.48 (m, 1 H), 3.53 (m, 1 H), 3.92 (m, 1 H), 4.72 (m, 1 H), 5.30 (br. dt, *J* = 15.2, 7.1 Hz, 1 H), 5.34 (m, 1 H), 5.55 (ddt, *J* = 15.3, 8.8, 1.3 Hz, 1 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 12.02 (CH_3), 19.37 (CH_3), 20.02 (CH_2), 20.10 (CH_2), 20.14 (CH_3), 21.00 (CH_2), 24.24 (CH_2), 25.46 (CH_2), 27.95 (CH_2), 28.24 (CH_2), 29.67 (CH_2), 31.25 (CH_2), 31.28 (CH_2), 31.84 (CH), 31.87 (CH_2), 34.74 (t, $J_{C,F}$ = 22.6 Hz, CH_2), 36.75 (C), 36.78 (C), 37.18 (CH_2), 37.42 (CH_2), 38.73 (CH_2), 39.60 (CH_2), 40.22 (CH + CH_2), 42.32 (C), 50.11 (CH), 50.15 (CH), 55.36 (CH), 56.70 (CH), 62.83 (CH_2), 62.95 (CH_2), 75.96 (CH), 96.81 (CH), 96.99 (CH), 113.58 (CH), 121.43 (CH), 121.51 (CH), 140.87 (C), 141.04 (C), 145.36 (CH) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3005, 2944, 2870, 1668, 1379, 1361, 1242, 975 cm^{-1}. MS (FAB): *m*/*z* = 745 $[M + H]^+$ (1), 663 (4), 341 (12), 207 (18). HR-MS (FAB) calcd. for $C_{35}H_{46}O_2F_{13}$ $[M^+ + H]$ 745.3290; found 745.3276. R_f(hexane/diethyl ether, 15:1) = 0.27.

Tetrahydro-2′-{[(3β)-25,25,26,26,27,27,27-heptafluoro-chola-5,22(*E*)-dien-3-yl]oxy}-2*H*-pyran (10b): The reaction between **2g** (82 mg, 0.2 mmol) and **1a** (84 mg, 0.4 mmol) was carried out by the General Procedure. Column chromatography on silica gel (hexane/diethyl ether, 20:1) and crystallization from EtOH/$CHCl_3$ yielded compound **10b** (96 mg, 81%) as a mixture of diastereoisomers as white crystals: m.p. 159–160 °C. $[\alpha]_D^{20}$ = –42.3 (*c* = 0.24, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.70 (s, 3 H), 1.01 (s, 3 H), 1.04 (d, *J* = 6.6 Hz, 3 H), 2.74 (m, 2 H), 3.48 (m, 1 H), 3.53 (m, 1 H), 3.92 (m, 1 H), 4.72 (m, 1 H), 5.30 (br. dt, *J* = 15.2, 7.1 Hz, 1 H), 5.34 (m, 1 H), 5.55 (ddt, *J* = 15.3, 8.8, 1.3 Hz, 1 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 12.02 (CH_3), 19.36 (CH_3), 20.01 (CH_2), 20.10 (CH_2), 20.14 (CH_3), 20.98 (CH_2), 24.24 (CH_2), 25.46 (CH_2), 27.94 (CH_2), 28.24 (CH_2), 29.66 (CH_2), 31.24 (CH_2), 31.28 (CH_2), 31.84 (CH), 31.87 (CH_2), 34.48 (t, $J_{C,F}$ = 22.6 Hz, CH_2), 36.74 (C), 36.78 (C), 37.17 (CH_2), 37.42 (CH_2), 38.73 (CH_2), 39.60 (CH_2), 40.21 (2 C, CH and CH_2), 42.32 (C), 50.11 (CH), 50.14 (CH), 55.35 (CH), 56.69 (CH), 62.82 (CH_2), 62.94 (CH_2), 75.95 (CH), 96.81 (CH), 96.98 (CH), 113.56 (CH), 121.43 (CH), 121.50 (CH), 140.86 (C), 141.04 (C), 145.31 (CH) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3005, 2944, 2870, 1668, 1378, 1353, 1274, 976, 956 cm^{-1}. MS (FAB): *m*/*z* = 617 $[M + Na]^+$ (7), 571 (2), 529 (3), 507 (4), 309 (12), 253 (14). HR-MS (FAB) calcd. for $C_{32}H_{45}O_2F_7Na$ $[M + Na]^+$ 617.3205; found 617.3189. R_f(15:1 hexane/diethyl ether) = 0.27.

1-(2′,3′,4′,6′-Tetra-*O*-acetyl-α-D-glucopyranosyl)-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodec-2(*E*)-ene (11): The reaction between **2i** (93 mg, 0.25 mmol) and **1a** (180 mg, 0.5 mmol) was carried out by the General Procedure. Column chromatography on silica gel (hexane/EtOAc, 5:1) and crystallization from pentane/Et_2O yielded **11** (112 mg, 64%) as white crystals: m.p. 66–67 °C. $[\alpha]_D^{20}$ = +52.8 (*c* = 0.17, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.04 (s, 6 H), 2.06 (s, 3 H), 2.08 (s, 3 H), 2.36 (dt, *J* = 15.8, 4.9 Hz, 1 H), 2.62 (ddd, *J* = 15.8, 11.1, 7.3 Hz, 1 H), 2.83 (td, *J* = 18.2, 6.9 Hz, 2 H), 3.85 (ddd, *J* = 9.3, 5.0, 2.7 Hz, 1 H), 4.04 (dd, *J* = 12.3, 2.6 Hz, 1 H), 4.27 (m, 2 H), 5.00 (t, *J* = 9.1 Hz, 1 H), 5.10 (dd, *J* = 9.4, 5.7 Hz, 1 H), 5.32 (t, *J* = 9.1 Hz, 1 H), 5.58 (m, 1 H), 5.70 (m, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.60 (CH_3), 20.62 (CH_3), 20.65 (CH_3), 20.67 (CH_3), 29.29 (CH_3), 34.75 (t, $J_{C,F}$ = 22.3 Hz, CH_2), 62.01 (CH_2), 68.56 (CH), 68.94 (CH), 70.05 (CH), 70.21 (CH), 71.81 (CH), 119.86 (t, $J_{C,F}$ = 4.1 Hz, CH), 133.05 (CH), 169.49 (C), 169.58 (C), 170.11 (C), 170.61 (C) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2957, 1751, 1650, 1455, 1431, 1348, 1245, 1145, 972 cm^{-1}. MS (ESI): *m*/*z* = 704 $[M]^+$ (3), 667 (2), 645 (23), 525 (4), 483 (6), 314 (3), 288 (6). HR-MS (ESI) calcd. for $C_{24}H_{26}O_9F_{13}$ $[M + H]^+$ 705.1369; found 705.1395. R_f(hexane/diethyl ether, 2:1) = 0.21.

Supporting Information (see also the footnote on the first page of this article): Experimental details, spectral characteristics of compounds, copies of NMR spectroscopic data.

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