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Grubbs–Hoveyda Second-Generation Catalysts Activated by the Introduction of a Light Fluorous Tag onto the Bidentate Ligands

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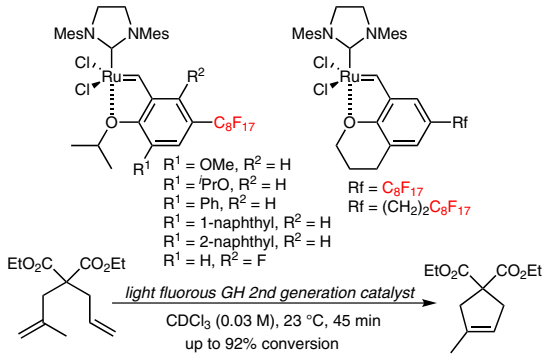

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Abstract Various novel Grubbs–Hoveyda second-generation catalysts activated by a fluorous tag on the ligands were prepared. The catalyst bearing the 1-naphthyl group on the bidentate ligand exhibited the highest catalytic activity among the studied catalysts for the ring-closing-metathesis reaction of diethyl 2-allyl-2-(2-methylallyl)malonate.

Key words catalyst, metathesis, ligands, fluorous, activation

Olefin metathesis is one of the most attractive and powerful tool for the formation of C=C bonds in the field of synthetic organic chemistry.[1] Among the ruthenium-based complexes that are able to catalyze this transformation, first and second generation Grubbs–Hoveyda catalysts (GH I: **1a**[2] and GH II: **2a**[3]) are particularly suited for this process because they exhibit high functional group tolerance, excellent air tolerance, and thermodynamic stability (Figure 1).[4]

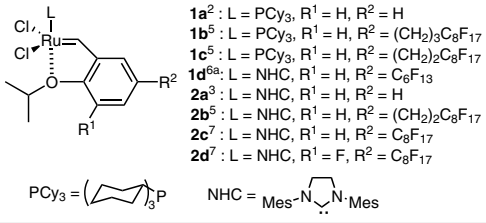


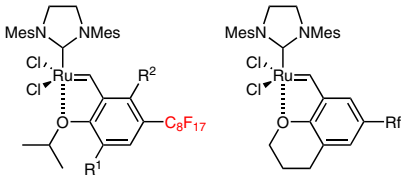
Figure 1 Grubbs–Hoveyda first- (GH I) and second-generation (GH II) catalysts **1a** and **2a**, and known light fluorous GH catalyst variants **1b–d** and **2b–d**

Since we introduced a light fluorous tag into **2a** for the first time in 2005,[5] several light fluorous-tagged ruthenium-based catalysts for olefin metathesis with improved recyclability and activation have been reported.[6] Several representative light fluorous GH catalysts are shown in Figure 1 (**1b**, **1c**, and **2b–d**). Among these catalysts, **2d** exhibits the highest catalytic activity for the ring-closing metathesis (RCM) reaction.[7] To the best of our knowledge, **2d** has the highest activity among all the known light fluorous catalysts. Since the light fluorous tag can be employed as an electron-withdrawing group, it is possible to shift the equilibrium of the ligation to the dissociated state, thus improving the reaction rate.[8] Furthermore, the perfluoroalkyl group exhibits strong hydrophobicity, and it may be separated from the organic component by its fluorophilicity via fluorous solid-phase extraction.[9] Thus, the introduction of the light fluorous tag allows the creation of interesting and useful metathesis catalytic systems.

Using these characteristics, we recently developed a fluorous GH second-generation catalyst supported on Teflon powder, where the catalyst could be shuttled between the solid Teflon phase and the liquid DMF phase by simply controlling the water content of the reaction media.[10] Here, we present a comparison of the catalytic activities of various novel light fluorous-tagged GH II type catalysts.

The new set of light fluorous catalysts **2e–j** used in this study are shown in Figure 2. The light fluorous catalysts **2e–i** are all characterized by the presence of a bulky substituent *ortho* to the isopropoxyl group. Blechert et al. reported that an increase in steric hindrance *ortho* to the isopropoxyl group on the ligand enhances the rate of metathesis reactions.[11] In the case of catalyst **2j**, the perfluoroalkyl substituent on the aromatic ring of the fluorous ligand is retained in the same position that it occupies in the known catalyst **2d**; however, the *ortho* fluoro group is replaced to the *meta* position. Concurrently, we also prepared the light fluorous chromane-ligand catalysts **3a** and **3b** based on Glrela's pioneering work,[12] which revealed that the conformational

constraint of the chelating ether linkage leads to an unexpected disturbance of the catalyst geometry and a vast improvement in activity.



2e: R^1 = OMe, R^2 = H
2f: R^1 = ^{i}PrO, R^2 = H
2g: R^1 = Ph, R^2 = H
2h: R^1 = 1-naphthyl, R^2 = H
2i: R^1 = 2-naphthyl, R^2 = H
2j: R^1 = H, R^2 = F

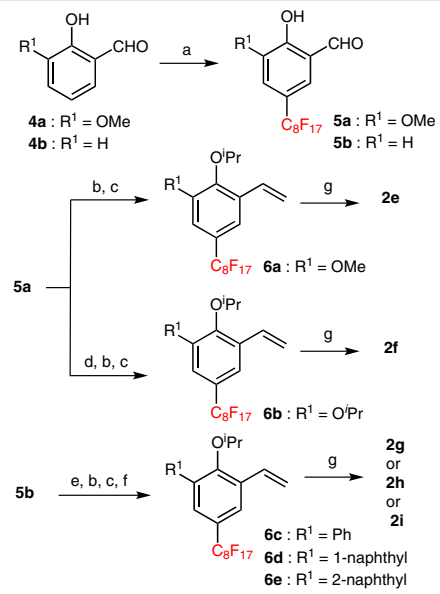
3a: Rf = C_8F_{17}
3b: Rf = $(CH_2)_2C_8F_{17}$

Figure 2 Novel light fluorous GH second-generation catalysts used in this study

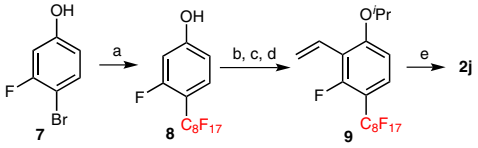
Scheme 1 shows the synthetic route to the light fluorous catalysts **2e–i**. In all cases, the light fluorous tag was introduced by direct perfluoroalkylation[13] via phenoxyl radical formation of **4** with the radical initiator V-70 L,[14] which we have developed previously.[15] The perfluoroalkylation of **4a** and salicylaldehyde (**4b**) under mildly basic conditions provided the monoperfluoroalkylated compounds **5a** and **5b** in 59% and 36% yield, respectively. In the synthesis of **2e**, isopropyl ether formation followed by Wittig olefination[16] provided ligand **6a** in 69% yield over the two steps. Ligand exchange with a standard Grubbs second-generation catalyst (not the GH catalyst) provided the target catalyst **2e** in 37% yield. In the synthesis of catalyst **2f**, demethylation of **5a**, diisopropyl ether formation, and subsequent Wittig olefination provided ligand **6b** in 66% yield over the three steps. Then, ligand exchange provided **2f** in 50% yield. The other catalysts **2g–i** were prepared via a synthetic route using Suzuki–Miyaura coupling[17] as the key reaction. After bromination of **5b**, isopropyl ether formation, and Wittig olefination, the subsequent Suzuki–Miyaura coupling with each corresponding aryl borate provided the ligands **6c–e** in 30 to 65% yields over the four steps. Then, ligand exchange provided **2g–i** in 25–46% yields.

The synthesis of catalyst **2j** is shown in Scheme 2. The coupling of 4-bromo-3-fluorophenol (**7**) with perfluorooctyl iodide by the Ullmann reaction[18] provided perfluorophenol **8** in 73% yield. Subsequent regioselective monobromination and isopropylation of the phenolic hydroxyl group, followed by Suzuki–Miyaura coupling using potassium vinyltrifluoroborate, provided the *ortho*-fluorinated fluorous ligand **9** in 49% yield over the three steps. A similar ligand exchange with the standard Grubbs II catalyst provided **2j** in 41% yield.

The fluorous chromane-ligand catalysts **3a** and **3b** were synthesized according to Glrela's method,[12] as shown in Scheme 3. The coupling reaction of 4-bromophenol (**10**) with perfluorooctyl iodide or perfluorooctylethyl iodide by

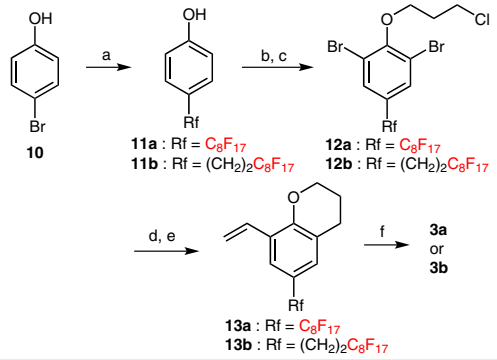


Scheme 1 Synthesis of the light fluorous GH second-generation catalysts **2e–i**. *Reagents and conditions*: (a) V-70L (1.0 equiv), $C_8F_{17}I$ (1.5 equiv), Cs_2CO_3 (8.0 equiv), DMF, r.t., 18–20 h, **5a**: 59%, **5b**: 36%; (b) *i*-PrI (10.0 equiv), K_2CO_3 (8.0 equiv), DMF, 60 °C, 2 h; (c) $(Ph_3PMe)Br$ (4.0 equiv), NaHMDS (8.0 equiv), anhyd THF, –78 °C → r.t., 3 h, **6a**: 69% (2 steps), **6b**: 66% (3 steps); (d) BBr_3 (10.0 equiv), CH_2Cl_2, r.t., 20 h; (e) Br_2 (10.0 equiv), AcOH, 50 °C, 3 h; (f) $R^1B(OH)_2$ (1.3–1.5 equiv), K_2CO_3 (3 equiv), $Pd(OAc)_2$/S-Phos (0.05 equiv), 1,4-dioxane, 90 °C, 6–7 h, **6c**: 57%, **6d**: 65%, **6e**: 30% (4 steps); Grubbs II catalyst (0.9–1.1 equiv), CuCl (2 equiv), anhyd CH_2Cl_2, r.t., 3 h, **2e**: 37%, **2f**: 50%, **2g**: 25%, **2h**: 34%, **2i**: 46%.



Scheme 2 Synthesis of the light fluorous GH II catalyst **2j**. *Reagents and conditions*: Cu powder (25.4 equiv), $C_8F_{17}I$ (2.0 equiv), anhyd DMF, 110 °C, 3 h, 73%; (b) Br_2 (1.1 equiv), AcOH, 50 °C, 3 h; (c) *i*-PrI (10 equiv), K_2CO_3 (8.0 equiv), DMF, 60 °C, 2 h; (d) potassium vinyltrifluoroborate (1.1 equiv), Cs_2CO_3 (3.0 equiv), $Pd(PPh_3)_4$ (0.05 equiv), THF/H_2O, 85 °C, 22 h, 49% (3 steps); (e) Grubbs II catalyst (1.0 equiv), CuCl (2.0 equiv), anhyd CH_2Cl_2, 30 °C, 2 h, 41%.

the Ullmann reaction provided the corresponding perfluorophenols **11a** and **11b** in 61% and 28% yield, respectively. Subsequent *ortho*-dibromination and chloropropanation of the phenolic hydroxyl group gave **12a** and **12b** in 82% and 87% yield (two steps), respectively. Then, intramolecular cyclization and formylation via a lithiation process followed by Wittig reaction provided the fluorous ligands **13a** and **13b** in 15% and 29% yield (two steps), respectively. Finally, ligand exchange with the standard Grubbs II catalyst provided the target catalysts **3a** and **3b** in 35% and 78% yield, respectively.



Scheme 3 Synthesis of the light fluorous GH II chromane-type catalysts **3a** and **3b**. *Reagents and conditions*: Cu powder (19.9–45.9 equiv), $C_8F_{17}I$ or $C_8F_{17}(CH_2)_2I$ (2.0 equiv), anhyd DMF, 110 °C, 3 h, **11a**: 61%, **11b**: 28%; (b) Br_2 (10.0 equiv), AcOH, 50 °C, 3 h; (c) 1-bromo-3-chloropropane (10 equiv), Bu_4NHSO_4 (1.0 equiv), K_2CO_3 (8.0 equiv), MeCN, 45 °C, 20 h, **12a**: 82% (2 steps), **12b**: 87% (2 steps); (d) *n*-BuLi (10 equiv), anhyd THF, –78 °C, 10 min, anhyd DMF, –40 °C, 1 h; (e) $(Ph_3PMe)Br$ (4.0 equiv), NaHDMS (8.0 equiv), anhyd THF, –78 °C → r.t., 3 h, **13a**: 15% (2 steps), **13b**: 29% (2 steps); (f) Grubbs II catalyst (0.9 equiv), CuCl (2.0 equiv), anhyd CH_2Cl_2, 30 °C, 2 h, **3a**: 35%, **3b**: 78%.

The relative turnover rates of catalysts **2e** and **2f** were determined by comparing the RCM reaction rates of these catalysts in the conversion of diethyl 2-allyl-2-(2-methylallyl)malonate (**14**) to diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (**15**).[19] This substrate was used because of its moderate reactivity for the RCM reaction. It has suitable reactivity for comparison with the original catalyst, and the catalytic activities can be compared at room temperature (23 °C). The reactions were conducted with $CDCl_3$ as the solvent to allow for NMR monitoring of reaction aliquots. Separate reactions with the catalysts **2e** and **2f** were set up under identical conditions and with identical catalyst loadings (0.03 M). At given time points the percentage conversion of the reaction was determined by recording the ^1H NMR spectra of the reaction mixtures and calculating the relative integrals of the corresponding methylene protons of product **15**. A plot of percentage conversion versus time is shown in Figure 3, and confirms that **2e** exhibits slightly higher activity than **2f** in the RCM reaction of **14**. The data for GH II catalyst **2a** and fluorous catalyst **2c** are also plotted as controls in the same graph in Figure 3. The results indicate that the insertion of an alkoxy group *ortho* to the isopropoxyl group on the bidentate ligand is effective for activation during the first 50 minutes of the reaction. However, the activity of these catalysts begins to decrease at around 50 minutes. This is because the catalysts begin to decompose at this time, as indicated by the disappearance of their characteristic proton signals from the ^1H NMR spectra.

Similarly, the relative turnover rates of catalysts **2g–i**, which have an aromatic group at the *ortho* position to the isopropoxyl group on the bidentate ligand, were determined by comparing the same RCM reaction. The conditions and protocol were the same as those for the experiments conducted with **2e** and **2f**. The data for GH II catalyst **2a** and fluorous catalyst **2c** were also plotted as controls in this case. It is apparent that **2h** has the highest activity among the studied catalysts because it reaches 90% conversion after 40 minutes, whereas the control catalyst **2c** takes 55 minutes to reach the same conversion. The catalysts **2g** and **2i** are deactivated after 20 minutes of the reaction. The catalyst **2h** bearing a 1-naphthyl group shows higher reactivity than **2g** bearing a phenyl group (Figure 4). Thus, the introduction of the 1-naphthyl group onto the bidentate ligand is an effective means for improving catalytic activity. Furthermore, we added the result of the reaction in which the non-fluorous version (**2k**: R^1 = 1-naphthyl, R^2 = H, R^3 = H[20]) of catalyst **2h** was used, which we recently reported,[20] in order to evaluate the effect of the fluorous activation. It is clear that the introduction of the fluorous tag onto the ligand promotes the catalytic activity, as we have reported previously.[7] In the RCM reactions using the GH catalysts, the rate-determining step is the release step of the biden-

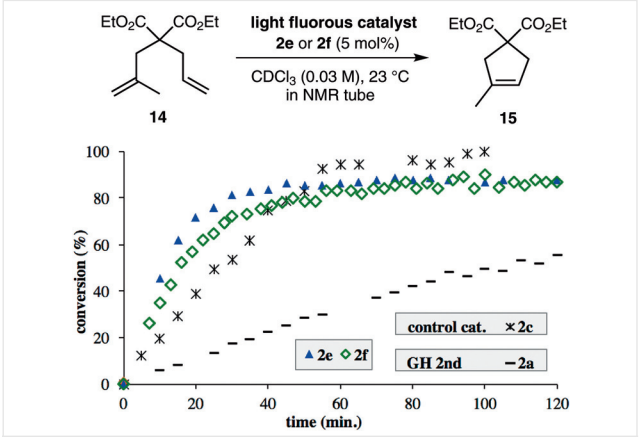


Figure 3 Comparison of the catalytic activities of **2e** and **2f** for the RCM reaction of **14**

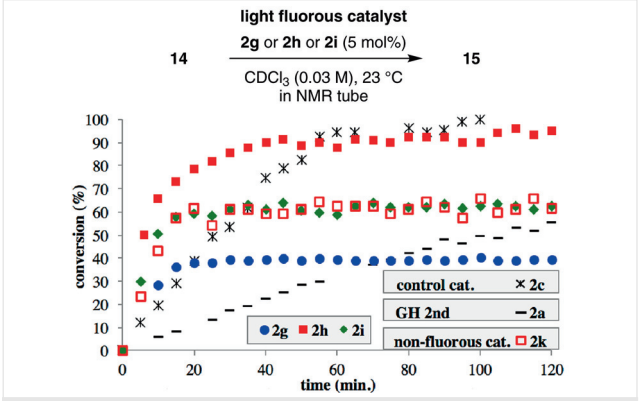


Figure 4 Comparison of the catalytic activities of **2g**, **2h**, and **2i** for the RCM reaction of **14**

tate ligand on ruthenium,[8] and the reaction rate is thus influenced by the ligation ability. We believe that the electron-withdrawing effect of the fluorous tag contributes to the decrease in the ligation ability on ruthenium. This fluorous activation effect was also obtained in the RCM reaction of **14** using deuterated dichloromethane (Figure 5).

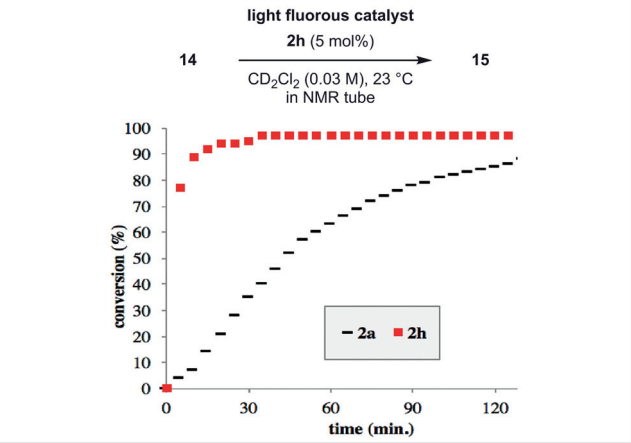


Figure 5 Comparison of the catalytic activities of **2a** and **2h** for the RCM reaction of **14** in CD_2Cl_2

Next, we present the results for the RCM reaction of **14** using catalyst **2j** under the same conditions, together with the data for the control catalyst **2c** and the regioisomeric catalyst **2d** (Figure 6). Although **2j** shows slightly higher catalytic activity than the GH II catalyst **2a**, it shows lower activity than catalyst **2d.** We conclude that the introduction of a fluoro group *ortho* to the isopropoxyl group is an important factor that dramatically improves the catalytic activity.

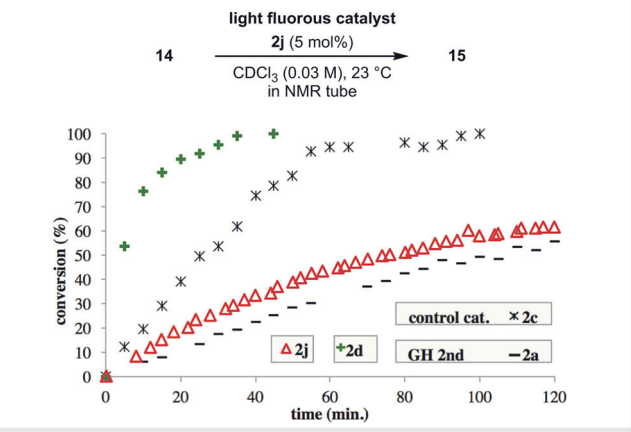


Figure 6 Comparison of the catalytic activities of **2a**, **2c**, **2d**, and **2j** for the RCM reaction of **14**

We then compared the catalytic activities of the fluorous chromane-ligand catalysts **3a** and **3b** and the control catalyst **2a**. We have been working towards improving the catalytic activity of the chromane-ligand catalysts by insertion of a fluorous tag. However, fluorous introduction to the catalyst did not result in any improvement of the catalytic activity, as shown in Figure 7.

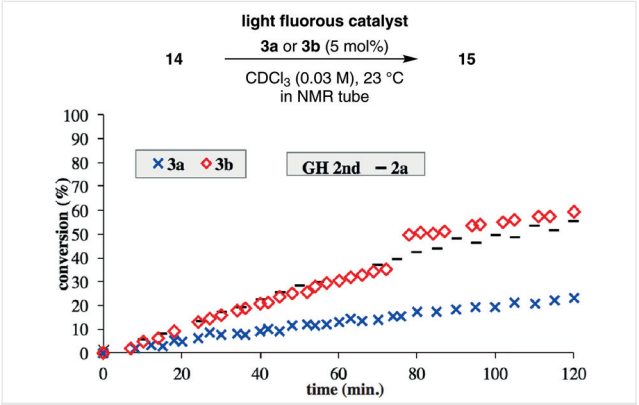


Figure 7 Comparison of the catalytic activities of **3a** and **3b** for the RCM reaction of **14**

Using a 45 minute time scale, the conversion rates of the fluorous GH II catalysts were reassessed, which confirmed their high catalytic activity for the RCM reaction (Figure 8). The known highly active light fluorous catalyst **2d** is also plotted in the same graph for comparison. Catalyst **2h** shows activity comparable to **2e**.

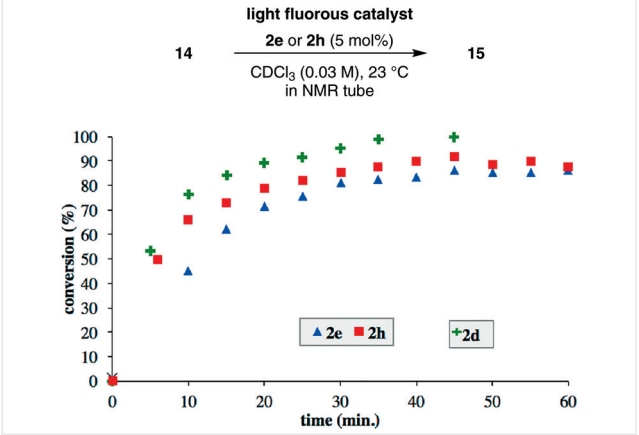


Figure 8 Comparison of the catalytic activities of **2e** and **2h** for the RCM reaction of **14**

In the RCM reaction of 4-methyl-*N*,*N*-bis(2-methylallyl)benzenesulfonamide[21] providing a tetra-substituted cyclic olefin,[20] a similar difference in catalytic activity was observed between GH II catalyst **2a** and **2h**. Although the tetra-substituted cyclic olefin was obtained in 9% yield when **2a** (5 mol%) was used under the 0.1 M condition in chloroform at 58 °C, the corresponding cyclic olefin was obtained in 19% yield when **2h** was used.

In summary, we have synthesized eight light fluorous GH second-generation catalysts **2e–j**, **3a**, and **3b**. Among these catalysts, **2h** exhibited the highest catalytic activity. We have established that the insertion of a light fluorous tag onto the bidentate ligand is an effective method for improving the catalytic activity of GH second-generation-type catalysts for the first 20 minutes of the reaction. However, this strategy was not successful for the chromane-type catalysts **3a**,**b**. The catalyst **2h** bearing a 1-naphthyl group on the bidentate ligand was found to exhibit high activity. At present, we believe that **2h** is one of the most useful light fluorous GH second-generation catalysts, and is easily synthesized.

All laboratory chemicals were purchased from Wako, TCI, Aldrich, and Kanto Kagaku Co., Ltd. NMR spectra were recorded on Jeol JNM-EX270 (^{1}H: 270 MHz, ^{13}C: 67.8 MHz) and Jeol ECA-500 (^{1}H: 400 MHz, ^{19}F: 466 MHz, ^{13}C: 124.5 MHz) spectrometers. Chemical shifts (δ) are given in units of ppm, and coupling constants (*J*) are given in Hz. IR spectra were recorded on a Shimadzu FT/IR-4200 spectrometer. The signals of IR spectra are expressed in wavenumbers (cm^{-1}). HRMS was performed by FAB and EI using a magnetic sector analyzer. The spectra were calibrated with Ultramark 1621® and PFK prior to data acquisition. The elemental analyses were performed using a Yanaco CHN Corder MT-6 instrument.

Synthesis of Catalyst 2e

2-Hydroxy-3-methoxy-5-(perfluorooctyl)benzaldehyde (5a)

To a solution of 2-hydroxy-3-methoxybenzaldehyde (**4a**; 300 mg, 1.97 mmol), perfluorooctyl iodide (1.62 g, 2.96 mmol), and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70L; 308 mg, 1.97 mmol) in DMF (10 mL) was added Cs_2CO_3 (6.39 g, 19.68 mmol) at r.t. The mixture was stirred for 20 h at the same temperature. After the addition of aq 1.0 M HCl and dilution with Et_2O, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give **5a** as pale yellow crystals; yield: 1.90 g (59%); mp 69.5–73.3 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.98 (s, 3 H), 7.22 (s, 1 H), 7.47 (s, 1 H), 9.98 (s, 1 H), 11.43 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 56.6, 105–120 (m, C_8F_{17}), 114.9, 120.1, 120.4, 123.5 149.0, 154.6, 195.9.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –109.9 (2 F), –121.0 (2 F), –122.5 (2 F), –125.9 (2 F), –127.7 (6 F).

HRMS (EI): *m*/*z* calcd for $C_{16}H_7F_{17}O_3$: 570.0124; found: 570.0127.

1-Isopropoxy-6-methoxy-4-(perfluorooctyl)-2-vinylbenzene (6a)

2-Isopropoxy-3-methoxy-5-(perfluorooctyl)benzaldehyde

To a solution of **5a** (300 mg, 0.52 mmol) and 2-iodopropane (894.4 mg, 5.26 mmol) in DMF (10 mL) was added K_2CO_3 (581.7 mg, 4.20 mmol) under N_2 and the mixture was stirred at 60 °C for 2 h. After the addition of aq 1.0 M HCl and dilution with Et_2O, the organic layer was washed with H_2O and and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to give 2-isopropoxy-3-methoxy-5-(perfluorooctyl)benzaldehyde as pale yellow crystals; yield: 283.4 mg (88%); mp 56.6–57.9 °C.

^{1}H NMR (270 MHz, CDCl3): δ = 1.36 (d, *J* = 6.2 Hz, 6 H), 3.94 (s, 3 H), 4.73–4.87 (m, 1 H), 7.24 (d, *J* = 1.8 Hz, 1 H), 7.69 (d, *J* = 2.4 Hz, 1 H), 10.46 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 22.4, 56.3, 76.9, 105–124 (m, C_8F_{17}), 115.1, 118.4, 124.2, 130.5, 153.4, 153.6, 189.5.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –110.2 (2 F), –121.2 (2 F), –21.5 (2 F), –121.8 (4 F), –122.7 (2 F), –126.1 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{13}F_{17}O_3$: 612.0593; found: 612.0582;

Anal. Calcd for $C_{19}H_{13}F_{17}O_3$: C, 37.27; H, 2.14. Found: C, 37.07; H, 2.28.

6a

To a solution of (Ph_3PMe)Br (233.3 mg, 0.65 mmol) in anhyd THF (10.0 mL) was added a 1.9 mol/L THF solution of sodium bis(trimethylsilyl)amide (239.1 mg, 0.65 mL, 1.30 mmol) under N_2 at –78 °C and stirred for 30 min. The reaction temperature rose to –10 °C and the mixture was stirred for an additional 30 min. A solution of 2-isopropoxy-3-methoxy-5-(perfluorooctyl)benzaldehyde (100 mg, 0.16 mmol) in anhyd THF (8.0 mL) was then added and the stirring was continued for 5 h at r.t. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give **6a** as a pale yellow oil; yield: 65.3 mg (78%); 69% over 2 steps.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.29 (d, *J* = 6.21 Hz, 6 H), 3.87 (s, 3 H), 4.48–4.57 (m, 1 H), 5.35 (dd, *J* = 1.2, 11.2 Hz, 1 H), 5.76 (dd, *J* = 1.0, 17.8 Hz, 1 H), 6.97 (d, *J* = 1.6 Hz, 3 H), 7.02–7.23 (m, 1 H), 7.35 (d, *J* = 1.6 Hz, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 22.4, 56.1, 75.9, 106–124 (m, C_8F_{17}), 109.4, 116.0, 116.8, 123.9 131.2, 132.9, 147.4, 153.3.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –109.9 (2 F), –121.1 (2 F), –121.4 (2 F), –121.6 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{20}H_{15}F_{17}O_2$: 610.0801; found: 610.0784.

(1,3-Dimesitylimidazolidin-2-yl)[2-isopropoxy-3-methoxy-5-(perfluorooctyl)benzylidene]ruthenium(V) Chloride (2e)

To a solution of **6a** (45.0 mg, 0.07 mmol) in anhyd CH_2Cl_2 (6.0 mL) were added Grubbs II catalyst (53.4 mg, 0.06 mmol) and CuCl (13.9 mg, 0.14 mmol) under N_2 and the mixture was stirred at 30 °C for 3 h. The mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give **2e** as green crystals; yield: 28.9 mg (37%); mp 135–137 °C.

IR (FT-ATR): 3853, 3737, 3638, 2935, 2856, 2363, 2326, 1581, 1455, 1187, 1104, 898, 747 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.2 Hz, 10 H), 2.38–2.47 (m, 18 H), 3.79 (s, 3 H), 4.20 (s, 4 H), 5.80–5.75 (m, 1 H), 6.73 (s, 1 H), 7.06 (s, 4 H), 16.32 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.9, 22.5, 26.1, 26.4, 29.7, 30.3, 51.4, 56.0, 75.9, 76.2, 109.3, 116.8, 122.8, 123.8, 126.6, 127.6, 128.7, 132.8, 137.3, 139.1, 147.1, 149.6, 209.6, 295.0.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –109.9 (2 F), –121.1 (4 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{40}Cl_2F_{17}N_2O_2Ru$: 1076.1239; found: 1076.1250.

Synthesis of Catalyst 2f

1,2-Diisopropoxy-5-(perfluorooctyl)-3-vinylbenzene (6b)

2,3-Dihydroxy-5-(perfluorooctyl)benzaldehyde

To a mixture of **5a** (250.0 mg, 0.43 mmol) in anhyd CH_2Cl_2 (5.0 mL) was added a solution of BBr_3 (550 mg, 2.19 mmol) in CH_2Cl_2 (5.0 mL) under N_2 at 0 °C. The reaction temperature rose to r.t. and the mixture was stirred for 20 h. H_2O was slowly added to the resulting mixture and the stirring was continued for 30 min. After dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give 2,3-dihydroxy-5-(perfluorooctyl)benzaldehyde as a pale yellow powder; yield: 213.4 mg (87%); mp 128.4–129.1 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 5.84 (s, 1 H), 7.40 (d, *J* = 11.8 Hz, 2 H), 9.95 (s, 1 H), 11.45 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 106–123 (m, C_8F_{17}), 119.1, 119.9, 121.2, 123.1, 145.5, 151.1, 196.0.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –110.0 (2 F), –121.0 (2 F), –121.7 (6 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{15}H_5F_{17}O_3$: 555.9967; found: 555.9967.

2,3-Diisopropoxy-5-(perfluorooctyl)benzaldehyde

To a solution of 2,3-dihydroxy-5-(perfluorooctyl)benzaldehyde (100.0 mg, 0.17 mmol) and 2-iodopropane (305.6 mg, 1.79 mmol) in DMF (8 mL) was added K_2CO_3 (198.8 mg, 1.43 mmol) under N_2 and the mixture was stirred at 60 °C for 2 h. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give 2,3-diisopropoxy-5-(perfluorooctyl)benzaldehyde as a colorless oil; yield: 113.9 mg (99%).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.36 (d, *J* = 6.2 Hz, 6 H), 1.41 (d, *J* = 5.6 Hz, 6 H), 4.59–4.68 (m, 1 H), 4.77–4.86 (m, 1 H), 7.24 (sd, *J* = 2.9 Hz, 1 H), 7.67 (d, *J* = 2.4 Hz, 1 H), 10.46 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.7, 71.8, 106–119 (m, C_8F_{17}), 118.0, 119.2, 123.9, 130.7, 151.5, 154.3, 189.6.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –110.2 (2 F), –121.1 (2 F), –121.5 (2 F), –121.7 (4 F), –122.6 (2 F), –126.0 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{17}F_{17}O_3$: 640.0906; found: 640.0926.

6b

To a solution of $(Ph_3PMe)Br$ (252.8 mg, 0.70 mmol) in anhyd THF (7.0 mL) was added a 1.9 mol/L THF solution of sodium bis(trimethylsilyl)amide (259.3 mg, 0.7 mL, 1.41 mmol) under N_2 at –78 °C and the mixture was stirred for 30 min. The reaction temperature rose to –10 °C and was stirred for further 30 min. A solution of 2,3-diisopropoxy-5-(perfluorooctyl)benzaldehyde (117.0 mg, 0.17 mmol) in anhyd THF (7.0 mL) was then added and the stirring continued for 2 h at r.t. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give **6b** as a colorless oil; yield: 86.3 mg (76%); 66% over 3 steps.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.29 (d, *J* = 6.2 Hz, 6 H), 1.36 (d, *J* = 6.2 Hz, 6 H), 4.61–4.48 (m, 2 H), 5.32 (d, *J* = 11.3 Hz, 1 H), 5.74 (d, *J* = 17.8 Hz, 1 H), 6.95 (s, 1 H), 7.08 (q, *J* = 9.5 Hz, 1 H), 7.32 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.9, 22.6, 71.3, 75.8, 106–119 (m, C_8F_{17}), 112.8, 115.7, 116.7, 123.5, 125.6, 131.4, 135.8, 151.2.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –110.0 (2 F), –121.1 (2 F), –121.7 (6 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{22}H_{19}F_{17}O_2$: 638.1114; found: 638.1066.

[2,3-Diisopropoxy-5-(perfluorooctyl)benzylidene](1,3-dimesitylimidazolidin-2-yl)ruthenium(V) Chloride (2f)

To a solution of **6b** (31.0 mg, 0.048 mmol) in anhyd CH_2Cl_2 (5.0 mL) were added Grubbs II catalyst (37.0 mg, 0.052 mmol) and CuCl (9.6 mg, 0.097 mmol) under N_2 and the mixture was stirred at 30 °C for 1 h. The mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give **2f** as green crystals; yield: 27.0 mg (50%); mp 125–127 °C.

IR (FT-ATR): 3854, 3738, 3649, 2978, 2931, 2361, 2342, 1481, 1199, 1107, 1072, 910, 729 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.4 Hz, 6 H), 1.27 (d, *J* = 5.6 Hz, 6 H), 2.37 (s, 6 H), 2.47 (br s, 12 H), 4.19 (s, 4 H), 4.51–4.45 (m, 1 H), 5.89–5.80 (m, 1 H), 6.70 (d, *J* = 1.3 Hz, 1 H), 7.06 (s, 4 H), 7.18 (d, *J* = 1.6 Hz, 1 H), 16.31 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.5, 21.9, 22.5, 51.3, 75.7, 76.0, 113.7, 114.5, 116.6, 123.5, 125.5, 126.6, 127.5, 129.4, 139.0, 143.5, 147.4, 151.2, 209.8, 296.5.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.5 (3 F), –110.0 (2 F), –121.3 (4 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{42}H_{45}Cl_2F_{17}N_2O_2Ru$: 1104.1630; found: 1104.1637.

Synthesis of Catalyst 2g

1-Isopropoxy-6-phenyl-4-(perfluorooctyl)-2-vinylbenzene (6c)

2-Hydroxy-5-(perfluorooctyl)benzaldehyde (5b)[22]

To a solution of salicylaldehyde (**4b**; 300 mg, 2.46 mmol), perfluorooctyl iodide (2.0 g, 3.68 mmol), and V-70L (758.5 mg, 2.46 mmol) in DMF (16.0 mL) was added Cs_2CO_3 (6.41 g, 19.7 mmol) at r.t. The mixture was stirred for 20 h at the same temperature. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give **5b** as pale yellow crystals; yield: 476.4 mg (36%); mp 57–58 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 8.9 Hz, 1 H), 7.72 (d, *J* = 8.9 Hz, 1 H), 9.97 (s, 1 H), 11.33 (s, 1 H).

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –110.0 (2 F), –121.0 (2 F), –121.7 (6 F), –122.5 (2 F), –125.9 (2 F).

2-Hydroxy-3-bromo-5-(perfluorooctyl)benzaldehyde

To a solution of **5b** (1.8 g, 3.33 mmol) in AcOH (5.0 mL) was added a solution of Br_2 (5.0 g, 31.29 mmol) in AcOH (10.0 mL) at 50 °C and the mixture was stirred for 16 h. After the addition of aq $Na_2S_2O_3$ and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give 2-hydroxy-3-bromo-5-(perfluorooctyl)benzaldehyde as pale yellow crystals; yield: 1.8 g (86%); mp 45–46 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 2.4 Hz, 1 H), 7.99 (d, *J* = 1.9 Hz, 1 H), 9.94 (s, 1 H), 11.95 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 106–123 (m, C_8F_{17}), 112.4, 120.6, 121.7, 131.6, 137.7, 160.9, 195.4.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –110.0 (2 F), –121.0 (2 F), –121.3 (2 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{15}H_4BrF_{17}O_2$: 617.9123; found: 617.9135.

Anal. Calcd for $C_{15}H_4BrF_{17}O_2$: C, 29.10; H, 0.65. Found: C, 29.15; H, 0.93.

2-Isopropoxy-3-bromo-5-(perfluorooctyl)benzaldehyde

To a solution of 2-hydroxy-3-bromo-5-(perfluorooctyl)benzaldehyde (1.7 g, 2.67 mmol) and 2-iodopropane (4.5 g, 26.65 mmol) in DMF (25.0 mL) was added K_2CO_3 (3.0 g, 21.32 mmol) under N_2 and the mixture was stirred at 60 °C for 2 h. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give 2-isopropoxy-3-bromo-5-(perfluorooctyl)benzaldehyde as pale yellow crystals; yield: 1.7 g (96%); mp 75–76 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.43 (d, *J* = 6.2 Hz, 6 H), 4.65–4.74 (m, 1 H), 8.03 (dd, *J* = 8.9, 2.2 Hz, 2 H), 10.38 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 22.0, 79.7, 106–120 (m, C_8F_{17}), 119.3, 125.9, 126.5, 131.8, 137.3, 160.7, 188.2.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –110.3 (2 F), –121.1 (4 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{10}BrF_{17}O_2$: 659.9593; found: 659.9561.

Anal. Calcd for $C_{18}H_{10}BrF_{17}O_2$: C, 32.70; H, 1.52. Found: C, 32.63; H, 1.48.

1-Isopropoxy-6-bromo-4-(perfluorooctyl)-2-vinylbenzene

To a solution of (Ph_3PMe)Br (432.2 mg, 0.12 mmol) in anhyd THF (10.0 mL) was added a 1.9 mol/L THF solution of sodium bis(trimethylsilyl)amide (443.7 mg, 1.2 mL, 2.42 mmol) under N_2 at –78 °C and stirred for 30 min. The reaction temperature rose to –10 °C and the mixture was stirred for further 30 min. A solution of 2-isopropoxy-3-bromo-5-(perfluorooctyl)benzaldehyde (200.0 mg, 0.30 mmol) in anhyd THF (10.0 mL) was then added and stirring continued for 2 h at r.t. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give 1-isopropoxy-6-bromo-4-(perfluorooctyl)-2-vinylbenzene as a pale yellow oil; yield: (183.0 mg, 91%).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 6.5 Hz, 6 H), 4.50–4.61 (m, 1 H), 5.42 (d, *J* = 11.3 Hz, 1 H), 5.79 (d, *J* = 17.3 Hz, 1 H), 7.00 (dd, *J* = 17.6, 11.1 Hz, 1 H), 7.66 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 22.3, 77.8, 106–120 (m, C_8F_{17}), 117.2, 118.9, 124.3, 125.2, 131.0, 131.2, 134.4, 155.6.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –112.9 (2 F), –120.7 (2 F), –121.6 (6 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{12}BrF_{17}O$: 657.9800; found: 657.9768.

6c

A mixture of 1-isopropoxy-6-bromo-4-(perfluorooctyl)-2-vinylbenzene (50 mg, 0.076 mmol), phenylboronic acid (12.0 mg, 0.099 mmol), K_2CO_3 (31.5 mg, 0.23 mmol), $Pd(OAc)_2$ (0.85 mg, 0.0038 mmol), and S-Phos [dicyclohexyl(2′,6′-dimethoxy-[1,1′-biphenyl]-2-yl)phosphine; 3.9 mg, 0.0095 mmol] in anhyd 1,4-dioxane (4.0 mL) was stirred at 90 °C under N_2 for 20 h. After the addition of aq 1.0 M HCl, the catalyst was removed by filtration through a pad of Celite and washed with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/$CHCl_3$, 1:1) to give **6c** as a pale yellow oil; yield: 38.0 mg (76%); 57% over 4 steps.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.2 Hz, 6 H), 3.83–3.92 (m, 1 H), 5.46 (dd, *J* = 0.5, 10.8 Hz, 1 H), 6.00 (dd, *J* = 0.8, 17.8 Hz, 1 H), 7.21 (dd, *J* = 11.3, 17.8 Hz, 1 H), 7.40–7.64 (m, 6 H), 7.89 (d, *J* = 2.2 Hz, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.9, 76.2, 106–119 (m, C_8F_{17}), 123.8, 124.1, 125.5, 127.7 128.3, 128.7, 129.1, 131.6 133.4, 136.4, 138.1, 155.6.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –110.0 (2 F), –121.1 (2 F), –121.3 (2 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{17}F_{17}O$: 656.1008; found: 656.1004.

(1,3-Dimesitylimidazolidin-2-yl){[2-isopropoxy-5-(perfluorooctyl)-[1,1′-biphenyl]-3-yl)methylene}ruthenium(V) Chloride (2g)

To a solution of **6c** (38.0 mg, 0.058 mmol) in anhyd CH_2Cl_2 (6.0 mL) were added Grubbs II catalyst (44.5 mg, 0.052 mmol) and CuCl (5.8 mg, 0.058 mmol) under N_2 at 30 °C and the mixture was stirred for 2 h. The mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give **2g** as green crystals; yield: 16.4 mg (25%); mp 105–106 °C.

IR (FT-ATR): 3853, 3737, 3653, 3575, 2918, 2357, 1697, 1491, 1428, 1240, 1208, 1145, 909, 851, 715 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 6.2 Hz, 6 H), 2.41–2.56 (m, 19 H), 4.23 (s, 4 H), 4.41–4.50 (s, 1 H), 7.08 (s, 4 H), 7.36 (s, 6 H), 7.53 (d, *J* = 2.2 Hz, 1 H), 7.53 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 20.4, 20.8, 21.8, 78.7, 120.4, 123.8, 128.3, 128.4, 128.6, 128.8, 129.2, 129.4, 131.0, 131.5, 136.7, 137.5, 138.1, 139.1, 147.4, 151.3, 209.3, 296.5.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –109.4 (2 F), –121.1 (4 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{45}H_{42}Cl_2F_{17}N_2ORu$: 1121.1446; found: 1121.1476.

Synthesis of Catalyst 2h

1-Isopropoxy-6-(1-naphthyl)-4-(perfluorooctyl)-2-vinylbenzene (6d)

A similar procedure used for the preparation of **6c** was followed. A mixture of 1-isopropoxy-6-bromo-4-(perfluorooctyl)-2-vinylbenzene (155.0 mg, 0.2 mmol), 1-naphthylboronic acid (60.7 mg, 0.4 mmol), K_2CO_3 (97.5 mg, 0.7 mmol), $Pd(OAc)_2$ (2.6 mg, 0.02 mmol), and S-Phos (12.1 mg, 0.03 mmol) in anhyd 1,4-dioxane (14.0 mL) was stirred at 90 °C under N_2 for 6 h. After the addition of aq 1.0 M HCl, the catalyst was removed by filtration through a pad of Celite and washed with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/$CHCl_3$, 5:1) to give **6d** as a pale yellow oil; yield: 143.0 mg (86%); 65% over 4 steps.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.76 (dd, *J* = 49.4, 5.9 Hz, 6 H), 3.63–3.72 (m, 1 H), 5.48 (d, *J* = 11.3 Hz, 1 H), 6.06 (d, *J* = 17.8 Hz, 1 H), 7.25 (dd, *J* = 10.5, 17.8 Hz, 1 H), 7.49–7.65 (m, 6 H), 8.00 (s, 3 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.9, 22.1, 76.3, 106–119 (m, C_8F_{17}), 116.1, 125.2, 125.5, 125.9, 126.0, 126.0, 126.3, 127.7, 128.3, 128.4, 131.3, 131.7, 133.2, 133.7, 134.7, 135.8, 138.5, 156.5.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –110.0 (2 F), –121.1 (2 F), –121.4 (2 F), –121.7 (4 F), –122.6 (2 F), –126.0 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{19}F_{17}O$: 706.1164; found: 706.1165.

(1,3-Dimesitylimidazolidin-2-yl){[2-isopropoxy-5-(perfluorooctyl)-3-(naphthalen-1-yl)phenyl]methylene}ruthenium(V) Chloride (2h)

To a solution of **6d** (57.9 mg, 0.08 mmol) in anhyd CH_2Cl_2 (6.0 mL) were added Grubbs II catalyst (74.4 mg, 0.09 mmol) and CuCl (17.3 mg, 0.2 mmol) under N_2 and the mixture was stirred at 30 °C for 3 h. The mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give **2h** as green crystals; yield: 39.8 mg (34%); mp 129.3–131.3 °C.

IR (FT-ATR): 2924, 2363, 1649, 1460, 1235, 1203, 1140, 773 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.75 (dd, *J* = 51.8, 6.2 Hz, 6 H), 2.46 (br s, 18 H), 4.13–4.22 (m, 5 H), 7.06–7.18 (m, 5 H), 7.42–7.49 (m, 5 H), 7.60–7.67 (m, 2 H), 7.85 (d, *J* = 7.8 Hz, 2 H), 16.53 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 18.4, 20.8, 20.8, 51.4, 79.1, 110–119 (m, C_8F_{17}), 120.9, 125.2, 125.9, 126.5, 127.5, 127.6, 128.2, 128.8, 129.0, 129.5, 131.7, 133.1, 135.6, 139.1, 147.2, 152.2, 209.5.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –109.5 (2 F), –121.1 (2 F), –121.3 (2 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{49}H_{44}Cl_2F_{17}N_2ORu$: 1172.1689; found: 1172.1677.

Synthesis of Catalyst 2i

1-Isopropoxy-6-(2-naphthyl)-4-(perfluorooctyl)-2-vinylbenzene (6e)

A similar procedure used for the preparation of **6c** was followed. A mixture of 1-isopropoxy-6-bromo-4-(perfluorooctyl)-2-vinylbenzene (135.0 mg, 0.2 mmol), 2-naphthylboronic acid (46.0 mg, 0.3 mmol), K_2CO_3 (85.5 mg, 0.6 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), and S-Phos (10.5 mg, 0.03 mmol) in anhyd 1,4-dioxane (11.0 mL) was stirred at 90 °C under N_2 for 3 h. After the addition of aq 1.0 M HCl, the catalyst was removed by filtration through a pad of Celite and washed with EtOAc. The aqueous phase was extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/$CHCl_3$, 5:1) to give **6e** as a pale yellow oil; yield: 57.3 mg (40%); 30% over 4 steps.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.96 (d, *J* = 5.9 Hz, 6 H), 3.79–3.88 (m, 1 H), 5.42 (d, *J* = 11.3 Hz, 1 H), 5.84 (d, *J* = 17.8 Hz, 1 H), 7.17 (dd, *J* = 10.5, 17.6 Hz, 1 H), 7.50–7.56 (m, 3 H), 7.71–7.74 (m, 2 H), 7.87–7.92 (m, 3 H), 8.02 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 22.1, 76.4, 106–119 (m, C_8F_{17}), 119.9, 123.9, 124.3, 124.7, 126.4, 127.3, 127.8, 127.9, 127.9, 128.2, 129.1, 131.7, 132.8, 133.5, 133.7, 135.8, 136.4, 155.9.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.7 (3 F), –110.0 (2 F), –121.1 (4 F), –121.7 (4 F), –122.6 (2 F), –126.0 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{19}F_{17}O$: 706.1164; found: 706.1168.

(1,3-Dimesitylimidazolidin-2-yl){[2-isopropoxy-5-(perfluorooctyl)-3-(naphthalen-2-yl)phenyl]methylene}ruthenium(V) Chloride (2i)

To a solution of **6e** (33.0 mg, 0.05 mmol) in anhyd CH_2Cl_2 (6.0 mL) were added Grubbs II catalyst (39.7 mg, 0.05 mmol) and CuCl (4.6 mg, 0.05 mmol) under N_2 and the mixture was stirred at 30 °C for 3 h. The reaction mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give **2i** as green crystals; yield: 25.2 mg (46%); mp 116.3–117.0 °C.

IR (FT-ATR): 2919, 2360, 1605, 1481, 1398, 1242, 1207, 1145, 1109, 1094, 743 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.2 Hz, 6 H), 2.50 (br s, 18 H), 4.23 (s, 4 H), 4.45–4.54 (m, 1 H), 7.07–7.12 (m, 6 H), 7.26–7.54 (m, 3 H), 7.62 (d, *J* = 2.2 Hz, 1 H), 7.80–7.87 (m, 4 H), 16.51 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 15.3, 22.1, 22.7, 66.0, 77.3, 110.3–119.9 (m, C_8F_{17}), 123.9, 124.3, 124.7, 126.4, 127.3, 127.7, 127.9, 128.2, 129.1, 131.7, 132.8, 133.5, 133.7, 135.8, 136.3, 155.8.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), 109.6 (2 F), –121.1 (4 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{49}H_{44}Cl_2F_{17}N_2ORu$: 1172.1689; found: 1172.1731.

Synthesis of Catalyst 2j

2-Fluoro-4-isopropoxy-1-(perfluorooctyl)-3-vinylbenzene (9)

3-Fluoro-4-(perfluorooctyl)phenol (8)

To a suspension of 4-bromo-3-fluorophenol (**7**; 750.0 mg, 3.92 mmol) and Cu powder (6.3 g, 99.49 mmol) in anhyd DMF (15.0 mL) was added perfluorooctyl iodide (4.2 g, 7.85 mmol) under N_2 and the mixture was stirred at 110 °C for 3 h. After the addition of H_2O, Cu powder was removed by filtration through a pad of Celite and washed with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give **8** as white crystals; yield: 1529 mg (73%); mp 58.3–58.8 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 5.43 (br s, 1 H), 6.65–6.74 (m, 2 H), 7.40 (t, *J* = 5.6 Hz, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 104.6, 107–120 (m, C_8F_{17}), 111.6, 130.3, 159.7, 160.7, 163.5.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.7 (3 F), –108.2 (2 F), –109.5 (1 F), –121.4 (2 F), –121.7 (6 F), –122.6 (2 F), –126.0 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{14}H_4F_{18}O$: 529.9975; found: 529.9926.

2-Bromo-3-fluoro-4-(perfluorooctyl)phenol

To a solution of **8** (500.0 mg, 0.94 mmol) in AcOH (5.0 mL) was added a solution of Br_2 (165.7 mg, 1.03 mmol) in AcOH (5.0 mL) and the mixture was stirred at 50 °C for 5 h. After the addition of aq $Na_2S_2O_3$ and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to give 2-bromo-3-fluoro-4-(perfluorooctyl)phenol as white crystals; yield: 535.3 mg (93%); mp 57–58 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.01 (br s, 1 H), 6.88 (d, *J* = 11.6 Hz, 1 H), 7.64 (d, *J* = 7.02 Hz, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 105.1, 105.2, 109–120 (m, C_8F_{17}), 131.8, 156.8, 158.9, 162.7.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –108.3 (2 F), –109.5 (1 F), –121.4 (2 F), –121.7 (6 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{14}H_3BrF_{18}O$: 607.9080; found: 607.9066.

2-Bromo-3-fluoro-1-isopropoxy-4-(perfluorooctyl)benzene

To a solution of 2-bromo-3-fluoro-4-(perfluorooctyl)phenol (360.0 mg, 0.59 mmol) and 2-iodopropane (1.0 g, 5.91 mmol) in DMF (25.0 mL) was added K_2CO_3 (654.0 mg, 21.32 mmol) under N_2 and the mixture was stirred at 60 °C for 2 h. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give 2-bromo-3-fluoro-1-isopropoxy-4-(perfluorooctyl)benzene as a colorless oil; yield: 306.7 mg (79%).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.43 (d, *J* = 5.9 Hz, 6 H), 4.54–4.63 (m, 1 H), 6.69 (d, *J* = 12.4 Hz, 1 H), 7.67 (d, *J* = 7.5 Hz, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.6, 72.8, 102.7, 107.6, 109–120 (m, C_8F_{17}), 132.7, 158.6, 158.8, 162.4.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –108.3 (2 F), –109.7 (1 F), –121.4 (2 F), –121.7 (6 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{17}H_9BrF_{18}O$: 649.9549; found: 649.9520.

9

2-Bromo-3-fluoro-1-isopropoxy-4-(perfluorooctyl)benzene (100.0 mg, 0.153 mmol), potassium vinyltrifluoroborate (22.5 mg, 0.16 mmol), $Pd(PPh_3)_4$ (8.84 mg, 0.0076 mmol), and Cs_2CO_3 (149.5 mg, 0.45 mmol) were added to THF/H_2O (9:1, 4.0 mL) under N_2 and the mixture was stirred at 85 °C for 22 h. After the addition of aq 1.0 M HCl, the catalyst was removed by filtration through a pad of Celite and washed with EtOAc. The aqueous phase was extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/$CHCl_3$, 10:1) to give **9** as white crystals; yield: 61.4 mg (67%); 49% over 3 steps; mp 43–44 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.40 (d, *J* = 5.9 Hz, 6 H), 4.53–4.62 (m, 1 H), 5.30 (d, *J* = 11.3 Hz, 1 H), 5.73 (d, *J* = 17.0 Hz, 1 H), 6.65 (d, *J* = 13.2 Hz, 1 H), 6.92 (q, *J* = 9.6 Hz, 1 H), 7.55 (d, *J* = 8.6 Hz, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.7, 71.4, 101.5, 104–119 (m, C_8F_{17}), 115.4, 124.0, 125.5, 126.6, 130.0, 159.0, 162.5.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –108.3 (2 F), –110.4 (1 F), –121.4 (2 F), –121.8 (6 F), –122.6 (2 F), –126.0 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{12}F_{18}O$: 598.0601; found: 598.0594.

(1,3-Dimesitylimidazolidin-2-yl)[2-fluoro-6-isopropoxy-3-(perfluorooctyl)benzylidene]ruthenium(V) Chloride (2j)

To a solution of **9** (59.7 mg, 0.098 mmol) in anhyd CH_2Cl_2 (6.0 mL) were added Grubbs II catalyst (75.3 mg, 0.088 mmol) and CuCl (19.8 mg, 0.20 mmol) under N_2 and the mixture was stirred at 30 °C for 3 h. The mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give **2j** as green crystals; yield: 43.2 mg (41%); mp 153–157 °C.

IR (FT-ATR): 3905, 3857, 3747, 3642, 3569, 2971, 2918, 2363, 2342, 1837, 1723, 1691, 1612, 1586, 1486, 1424, 1293, 1213, 1156, 1104, 1029, 915, 846 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.38 (s, 6 H), 2.45 (s, 12 H), 4.21 (s, 1 H), 4.90–4.82 (m, 1 H), 6.62 (d, *J* = 12.4 Hz, 1 H), 7.07 (s, 5 H), 16.22 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 19.4, 20.9, 51.4, 77.5, 102.8, 103.2, 122.3, 129.4, 139.1, 141.8, 155.8, 155.9, 158.3, 162.1, 209.2, 291.7.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –106.3 (1 F), –108.5 (2 F), –121.4 (2 F), –121.5 (2 F), –122.6 (4 F), –125.9 (2 F).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{39}H_{37}Cl_2F_{18}N_2ORu$: 1064.1039; found: 1064.1049.

Synthesis of Catalyst 3a

6-(Perfluorooctyl)-8-vinylchroman (13a)

4-(Perfluorooctyl)phenol (11a)[22]

To a suspension of 4-bromophenol (**10**; 1.0 g, 5.78 mmol) and Cu powder (7.3 g, 114.87 mmol) in anhyd DMF (10.0 mL) was added perfluorooctyl iodide (6.3 g, 11.56 mmol) under N_2 and the mixture was stirred at 120 °C for 3 h. After the addition of H_2O, Cu powder was removed by filtration through a pad of Celite and washed with EtOAc. The aqueous layer was extracted with EtOAc. The combined layers were washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give **11a** as white crystals; yield: 1.8 g (61%); mp 72.1–73.4 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 5.69 (s, 1 H), 6.94 (d, *J* = 8.6 Hz, 2 H), 8.04 (d, *J* = 9.4 Hz, 2 H).

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –112.3 (2 F), –120.7 (4 F), –121.3 (2 F), –121.8 (2 F), –122.5 (2 F), –125.9 (2 F).

2,6-Dibromo-4-(perfluorooctyl)phenol

To a solution of **11a** (1.8 g, 3.33 mmol) in AcOH (10.0 mL) was added a solution of Br_2 (2.8 g, 17.55 mmol) in AcOH (5.0 mL) and the mixture was stirred at 50 °C for 5 h. After the addition of aq $Na_2S_2O_3$ and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give 2,6-dibromo-4-(perfluorooctyl)phenol as white crystals; yield: 2.3 g (98%); mp 88.9–89.9 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.37 (br s, 1 H), 7.68 (s, 2 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 106–120 (m, C_8F_{17}), 110.2, 123.3, 130.9, 152.6.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –109.8 (2 F), –121.0 (2 F), –121.3 (2 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{14}H_3Br_2F_{17}O$: 667.8279; found: 667.8267.

1,3-Dibromo-2-(3-chloropropoxy)-5-(perfluorooctyl)benzene (12a)

To a solution of 2,6-dibromo-4-(perfluorooctyl)phenol (400.0 mg, 0.59 mmol), 3-bromopropyl chloride (939.9 mg, 5.97 mmol), and Bu_4NHSO_4 (202.6 mg, 0.59 mmol) in anhyd MeCN (25.0 mL) was added K_2CO_3 (660.0 mg, 4.77 mmol) under N_2 at 45 °C and stirred for 20 h. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give **12a** as white crystals; yield: 378.8 mg (84%); 82% over two steps; mp 55.6–56.6 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.30–2.39 (m, 2 H), 3.88 (t, *J* = 6.3 Hz, 2 H), 4.23 (t, *J* = 5.8 Hz, 2 H), 7.74 (s, 2 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 33.2, 41.3, 70.1, 106–119 (m, C_8F_{17}), 119.0, 127.2, 131.5, 156.3.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.5 (3 F), –110.2 (2 F), –121.1 (4 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{17}H_8Br_2ClF_{17}O$: 743.8359; found: 743.8380.

6-(Perfluorooctyl)chroman-8-carbaldehyde

Anhyd THF (8.0 mL) was added to a 1.6 mol/L solution of *n*-BuLi in hexane (2.4 mL, 3.8 mmol) under N_2 at –78 °C and the mixture was stirred for 10 min. A solution of **12a** (410.0 mg, 0.54 mmol) in anhyd THF (4.0 mL) was then added and the stirring continued for 40 min at the same temperature. Anhyd DMF (6.0 mL) was then added and the stirring continued for 1 h at –45 °C. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give 6-(perfluorooctyl)chroman-8-carbaldehyde as white crystals; yield: 203.4 mg (63%); mp 108–109 °C.

^{1}H NMR (495 MHz, $CDCl_3$): δ = 2.03–2.08 (m, 2 H), 2.84 (t, *J* = 3.5 Hz, 2 H), 4.33 (t, *J* = 2.9 Hz, 2 H), 7.39 (s, 1 H), 7.82 (s, 1 H), 10.35 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.2, 24.7, 67.5, 104–120 (m, C_8F_{17}), 120.4, 124.1, 124.5, 125.6, 133.6, 160.0, 188.7.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –110.0 (2 F), –121.1 (2 F), –121.4 (2 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_9F_{17}O_2$: 581.0331; found: 581.0382.

6-(Perfluorooctyl)-8-vinylchroman (13a)

To a solution of (Ph_3PMe)Br (246.2 mg, 0.68 mmol) in anhyd THF (10.0 mL) was added a 1.9 mol/L THF solution of sodium bis(trimethylsilyl)amide in THF (252.7 mg, 0.68 mL, 1.37 mmol) under N_2 at –78 °C and the mixture was stirred for 30 min. The reaction temperature rose to –10 °C and the mixture was stirred for an additional 30 min. A solution of 6-(perfluorooctyl)chroman-8-carbaldehyde (100 mg, 0.17 mmol) in anhyd THF (8.0 mL) was then added and the stirring continued for 2 h at r.t. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give **13a** as a colorless oil; yield: 23.4 mg (23%); 15% over two steps.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.89–1.98 (m, 2 H), 2.74 (t, *J* = 6.6 Hz, 2 H), 4.19 (t, *J* = 5.2 Hz, 2 H), 5.23 (dd, *J* = 0.8, 11.0 Hz, 1 H), 5.23 (dd, *J* = 0.8, 11.0 Hz, 1 H), 5.66 (dd, *J* = 1.3, 18.0 Hz, 1 H), 6.88 (q, *J* = 9.5 Hz, 1 H), 7.06 (s, 1 H), 7.36 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.7, 25.0, 66.8, 115.8, 117.0, 119.9, 122.5, 127.5, 130.7, 135.7, 154.8.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –109.6 (2 F), –121.1 (2 F), –121.5 (2 F), –121.7 (4 F), –122.5 (2 F), –125.9 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{11}F_{17}O$: 578.0538; found: 578.0564.

(1,3-Dimesitylimidazolidin-2-yl){[6-(perfluorooctyl)chroman-8-yl]methylene}ruthenium(V) Chloride (3a)

To a solution of **13a** (22.0 mg, 0.038 mmol) in anhyd CH_2Cl_2 (5.0 mL) were added Grubbs II catalyst (29.0 mg, 0.034 mmol) and CuCl (7.5 mg, 0.075 mmol) under N_2 and the mixture was stirred at 30 °C for 3 h. The mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give **3a** as green crystals; yield: 14.0 mg (35%); mp 178–183 °C (dec.).

IR (FT-ATR): 3979, 3857, 3747, 3685, 3417, 2956, 2918, 2363, 2336, 1596, 1481, 1413, 1240, 1208, 1140, 1046, 988, 904, 857, 809, 741, 720 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.09–2.00 (m, 2 H), 2.43 (d, *J* = 14.0 Hz, 18 H), 2.86 (t, *J* = 12.1 Hz, 2 H), 4.17 (s, 4 H), 4.27 (t, *J* = 10.2 Hz, 2 H), 6.91 (s, 1 H), 7.08 (s, 4 H), 7.43 (s, 1 H), 16.32 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 19.2, 21.0, 22.1, 23.6, 51.7, 70.2, 118.0, 123.3, 124.2, 127.1, 129.6, 136.1, 138.7, 139.0, 142.8, 143.2, 151.8, 209.2, 288.5.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.5 (3 F), –109.2 (2 F), –121.0 (2 F), –121.3 (2 F), –121.7 (4 F), –122.5 (2 F), –126.0 (2 F).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{39}H_{36}Cl_2F_{17}N_2ORu$: 1044.0977; found: 1044.0991.

Synthesis of Catalyst 3b

4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Nonadecafluoroundecyl)phenol (11b)[5]

To a suspension of 4-bromophenol (**10**; 376.0 mg, 2.17 mmol) and Cu powder (6.3 g, 99.49 mmol) in anhyd DMF (15.0 mL) was added 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide (2.5 g, 4.35 mmol) under N_2 and the mixture was stirred at 120 °C for 3 h. After the addition of H_2O, Cu powder was removed by filtration through a pad of Celite and washed with EtOAc. The aqueous phase was extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give **11b** as white crystals; yield: 334.9 mg (28%); mp 82.8–83.3 °C.

^{1}H NMR (495 MHz, $CDCl_3$): δ = 2.37–2.28 (m, 2 H), 2.85–2.82 (m, 2 H), 4.66 (s, 1 H), 7.79–7.76 (m, 1 H), 7.08–7.06 (m, 2 H).

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –114.5 (2 F), –121.5 (2 F), –121.7 (4 F), –122.5 (2 F), –123.3 (2 F), –125.9 (2 F).

1,3-Dibromo-2-(3-chloropropoxy)-5-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-nonadecafluoroundecyl)benzene (12b)

2,6-Dibromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-nonadecafluoroundecyl)phenol

To a solution of **11b** (385.0 mg, 0.71 mmol) in AcOH (3.0 mL) was added a solution of Br_2 (1.1 g, 7.12 mmol) in AcOH (3.0 mL) at r.t. and the mixture was stirred for 20 h. After the addition of aq $Na_2S_2O_3$ and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give 2,6-dibromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-nonadecafluoroundecyl)phenol as white crystals; yield: 492.0 mg (99%); mp 56.2–56.7 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.23–2.42 (m, 2 H), 2.79–2.85 (m, 2 H), 5.81 (s, 1 H), 7.31 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 25.2, 32.8, 107–121 (m, C_8F_{17}), 110.8, 131.8, 133.6, 148.3.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –114.5 (2 F), –121.4 (2 F), –121.7 (4 F), –122.5 (2 F), –123.3 (2 F), –125.9 (2 F).

Anal. Calcd for $C_{16}H_7Br_2F_{17}O$: C, 27.53; H, 1.01. Found: C, 27.39; H, 1.13.

12b

To a solution of 2,6-dibromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-nonadecafluoroundecyl)phenol (490.0 mg, 0.70 mmol), 3-bromopropyl chloride (1.1 g, 7.01 mmol), and Bu_4NHSO_4 (238.0 mg, 0.70 mmol) in anhyd MeCN (20.0 mL) was added K_2CO_3 (775.0 mg, 5.60 mmol) under N_2 and the mixture was stirred at 40 °C for 20 h. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give **12b** as white crystals; yield: 477.7 mg (88%); 87% over two steps; mp 55.5–56.4 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.26–2.38 (m, 2 H), 2.81–2.87 (m, 2 H), 3.86 (t, *J* = 6.6 Hz, 2 H), 4.13 (t, *J* = 5.66 Hz, 2 H), 7.37 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 25.4, 32.7, 33.3, 41.5, 69.8, 106–122 (m, C_8F_{17}), 118.5, 132.6, 137.8, 151.8.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –114.4 (2 F), –121.4 (2 F), –121.7 (4 F), –122.5 (2 F), –123.2 (2 F), –125.9 (2 F).

Anal. Calcd for $C_{19}H_{12}Br_2ClF_{17}O$: C, 29.46; H, 1.56. Found: C, 29.25; H, 1.71.

6-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Nonadecafluoroundecyl)-8-vinylchroman (13b)

6-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Nonadecafluoroundecyl)chroman-8-carbaldehyde

Anhyd THF (6.0 mL) was added to a 1.6 mol/L solution of *n*-BuLi in hexane (1.8 mL, 2.8 mmol) under N_2 at –78 °C and the mixture was stirred for 10 min. A solution of **12b** (200.0 mg, 0.25 mmol) in anhyd THF (5.0 mL) was then added and the stirring continued for 40 min at the same temperature. Anhyd DMF (4.0 mL) was then added and the stirring continued for 1 h at –45 °C. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to give 6-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-nonadecafluoroundecyl)chroman-8-carbaldehyde as white crystals; yield: 136.3 mg (86%); mp 80.6–80.9 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.01–2.10 (m, 2 H), 2.29–2.36 (m, 2 H), 2.80–2.87 (m, 4 H), 4.30 (t, *J* = 5.2 Hz, 2 H), 7.12 (s, 1 H), 7.48 (s, 1 H), 10.39 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.7, 24.7, 25.4, 32.9, 66.9, 105–121 (m, C_8F_{17}), 124.0, 124.3, 125.6, 130.4, 136.0, 156.5, 189.8.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –114.4 (2 F), –121.4 (2 F), –121.7 (4 F), –122.5 (2 F), –123.3 (2 F), –125.9 (2 F).

Anal. Calcd for $C_{20}H_{13}F_{17}O_2$: C, 39.49; H, 2.15. Found: C, 39.17; H, 2.04.

13b

To a solution of $(Ph_3PMe)Br$ (465.8 mg, 1.304 mmol) in anhyd THF (13.0 mL) was added a 1.9 mol/L THF solution of sodium bis(trimethylsilyl)amide (477.3 mg, 1.29 mL, 2.603 mmol) under N_2 at –78 °C and the mixture was stirred for 30 min. The reaction temperature rose to –10 °C and the mixture was stirred for an additional 20 min. A solution of 6-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-nonadecafluoroundecyl)chroman-8-carbaldehyde (198 mg, 0.326 mmol) in anhyd THF (7.0 mL) was then added and the stirring was continued for 3 h at r.t. After the addition of aq 1.0 M HCl and dilution with EtOAc, the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/$CHCl_3$, 10:1) to give **13b** as a white powder; yield: 68.9 mg (34%); 29% over two steps; mp 33–34 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.95–2.04 (m, 2 H), 2.23–2.43 (m, 2 H), 2.74–2.83 (m, 4 H), 4.21 (t, *J* = 5.2 Hz, 2 H), 5.26 (dd, *J* = 1.35, 11.0 Hz, 1 H), 5.71 (t, *J* = 1.3, 17.8 Hz, 1 H), 6.80 (s, 1 H), 6.97 (q, *J* = 9.7 Hz, 1 H), 7.11 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 22.1, 25.0, 25.6, 33.3, 66.5, 104–119 (m, C_8F_{17}), 114.7, 122.6, 124.1, 126.2, 129.0, 130.1, 131.4, 150.9.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.6 (3 F), –114.5 (2 F), –121.5 (2 F), –121.7 (4 F), –122.5 (2 F), –123.3 (2 F), –126.0 (2 F).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{15}F_{17}O$: 606.0851; found: 606.0822.

(1,3-Dimesitylimidazolidin-2-yl){[6-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)chroman-8-yl]methylene}ruthenium(V) Chloride (3b)

To a solution of **13b** (40.0 mg, 0.065 mmol) in anhyd CH_2Cl_2 (6.0 mL) were added Grubbs II catalyst (50.3 mg, 0.059 mmol) and CuCl (13.0 mg, 0.13 mmol) under N_2 and the mixture was stirred at 30 °C for 3 h. The mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel (hexane/EtOAc, 2:1) to give **3b** as green crystals; yield: 55.5 mg (78%); mp 160–165 °C (dec.).

IR (FT-ATR): 3905, 3857, 3816, 3743, 3700, 3642, 3616, 3569, 3013, 2945, 2913, 2856, 2363, 2331, 1738, 1691, 1596, 1555, 1476, 1455, 1413, 1245, 1203, 1140, 1108, 1035, 993, 915, 857, 814, 730 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.01–2.04 (m, 2 H), 2.22–2.31 (m, 2 H), 2.43 (d, *J* = 14.8 Hz, 18 H), 2.77–2.87 (m, 4 H), 4.10–4.21 (m, 6 H), 6.51 (s, 1 H), 7.08 (s, 5 H), 16.43 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 19.2, 21.0, 22.5, 23.5, 51.7, 69.5, 77.5, 118.9, 124.1, 128.9, 129.5, 133.2, 136.3, 138.7, 143.7, 148.5, 210.7, 291.4.

^{19}F NMR (466 MHz, $CDCl_3$): δ = –80.5 (3 F), –114.4 (2 F), –121.5 (2 F), –121.8 (4 F), –122.5 (2 F), –123.3 (2 F), –126.0 (2 F).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{41}H_{40}Cl_2F_{17}N_2ORu$: 1072.1290; found: 1072.1320.

Ring-Closing Metathesis Reaction of 14 in $CDCl_3$; Diethyl 3-Methylcyclopent-3-ene-1,1-dicarboxylate (15);[19] Typical Procedure

Diethyl 2-allyl-2-(2-methylallyl)malonate (**14**; 13.4–40.5 mg, 0.053–0.159 mmol) and catalyst **2e** (5.0 mol%) were dissolved in $CDCl_3$ (0.03 M) in an NMR tube at 23 °C. The mixture was analyzed by ^{1}H NMR spectroscopy. Conversion was evaluated from the ^{1}H NMR spectra by integration of **14** and RCM product **15** signals; colorless oil.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.3 Hz, 6 H), 1.64 (s, 3 H), 2.83–2.90 (m, 4 H), 4.12 (q, *J* = 7.0, 14.3 Hz, 4 H), 5.12 (s, 1 H).

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Supporting Information

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