

Palladium(II)-catalysed oxidation of alcohols under an oxygen atmosphere in a fluorous biphasic system (FBS)

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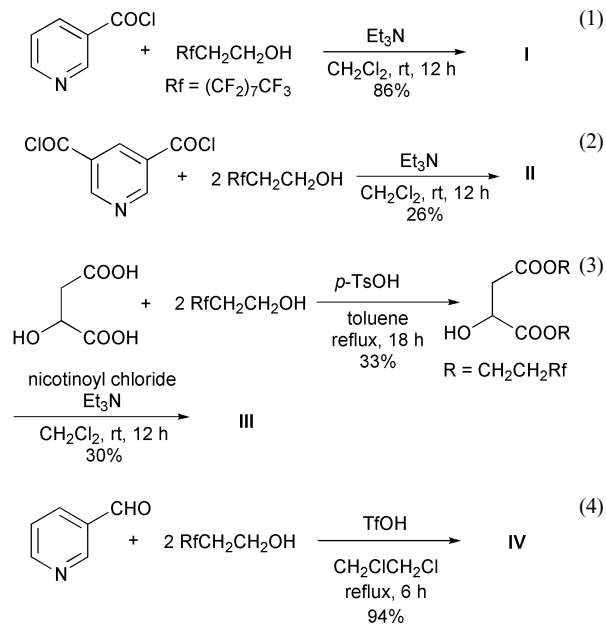
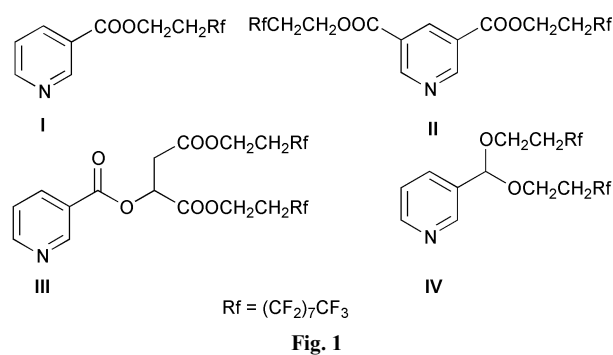
Palladium(II) acetate catalyses the aerobic oxidation of alcohols into the corresponding aldehydes and ketones in the presence of a catalytic amount of a novel perfluoroalkylated-pyridine as a ligand using molecular oxygen in a fluorous biphasic system (FBS) composed of toluene and perfluorodecalin. This catalytic system is applicable to various benzylic and aliphatic alcohols. The fluorous phase containing the active palladium species is easily separated and can be reused several times without a significant loss of catalytic activity.

Introduction

Recently, transition metal-catalysed reactions in a fluorous biphasic system (FBS) have become one of the most important methods for facile catalyst separation from the reaction mixture and recycling of the catalyst.¹ In this two-phase system, the metal catalyst coordinated by perfluoroalkylated ligands can dissolve into the fluorous phase and be easily recovered by the separation of the organic phase containing the product after the reaction. Furthermore, FBS has the advantage of possible use for water-sensitive reactions unlike aqueous biphasic systems.² In a variety of reactions using FBS,³ we have paid attention to the oxidation of organic compounds,⁴ because perfluorocarbon has unique properties such as chemical inertness, resistance to oxidation and, in particular, high O₂-solubility.⁵ However, examples of oxidation using molecular oxygen as the final oxidant have been limited.^{6–8} As for the oxidation of alcohols in FBS, copper-catalysed oxidation using perfluoroalkylated-bipyridine as a ligand was reported by Knochel *et al.* quite recently.^{6a} We reported the aerobic oxidation of alcohols in toluene to give the corresponding aldehydes and ketones using a catalytic amount of Pd(OAc)₂, pyridine and 3 Å molecular sieves under an oxygen atmosphere.⁹ The heterogenization of a homogeneous catalytic system is also of importance from the standpoint of environmental and economical concerns.¹⁰ We have now focused on the application of our catalytic system to the fluorous biphasic conditions by considering recent advances in FBS. We report herein the simple preparation of novel perfluoroalkylated-pyridine derivatives and the palladium-catalysed aerobic oxidation of alcohols in FBS using these derivatives as ligands.

Results and discussion

First, we decided to prepare the novel perfluoroalkylated-pyridine derivatives (I–IV) shown in Fig. 1 and succeeded in this using the methods described in eqns. (1)–(4) using commercially available reagents. Pyridines I–III, which have perfluoroalkyl groups as ester moieties, were obtained in low to moderate overall yields [eqns. (1)–(3)], while pyridine IV was produced almost quantitatively by a simple acetalization in one step [eqn. (4)]. All the pyridines obtained were characterized by ¹H and ¹³C NMR, IR, and C, H combustion analysis. To evaluate the Pd(OAc)₂-catalysed oxidation of alcohols in this fluorous biphasic catalytic system using newly synthesized ligands I–IV, we carried out the oxidation of dodecan-2-ol, octadecan-1-ol and benzyl alcohol in a biphasic toluene and

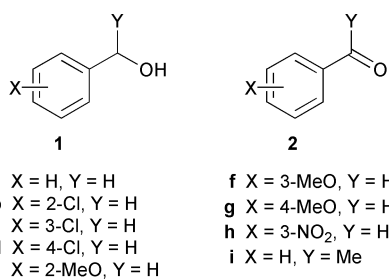


perfluorodecalin solvent in the presence of a catalytic amount of Pd(OAc)₂. The reaction procedure is as follows: to a mixture of 2.5 mol% Pd(OAc)₂, 20 mol% ligand, toluene (0.75 mL) and perfluorodecalin (1 mL) was added alcohol (0.5 mmol) in toluene (0.25 mL) and the resulting mixture was stirred at 80 °C for 6 h under an atmospheric pressure of oxygen. The results are summarized in Table 1. In the oxidation of dodecan-2-ol, ligand I was most effective to give dodecan-2-one in 70% yield (entry 1). The oxidation using II at 80 °C failed by the formation of a palladium black probably due to the weaker

Table 1 Pd(II)-Catalysed oxidation of alcohols under O₂ in FBS^a

Entry	Ligand	Catalyst (mol%)	Toluene (mL)/perfluorodecaline (mL)	t/h	Substrate	Product	Isolated yield (%) ^b
1	I	2.5	1.0/1.0	6			70 (71)
2 ^c	II	2.5	1.0/1.0	12			47 (68)
3	III	2.5	1.0/1.0	6			16 (24)
4	IV	2.5	1.0/1.0	6			42 (61)
5	I	2.5	1.0/1.0	6			55 (55)
6	IV	2.5	1.0/1.0	6			32 (47)
7	I	2.5	1.0/1.0	6			85 (98) ^d
8	IV	2.5	1.0/1.0	6			50 (53) ^d
9	IV	5.0	2.0/2.0	5			67 (71) ^d
10 ^e	IV	5.0	2.0/2.0	5			94 (95) ^d

^a Reaction conditions: alcohol (0.5 mmol), Pd(OAc)₂, ligand (20 mol%), solvent (toluene, perfluorodecalin), 80 °C, O₂. ^b The value in parentheses is the conversion of alcohol (%). ^c 60 °C. ^d GLC yield. ^e 3 Å molecular sieves (200 mg) were added.

**Fig. 2**

coordinative ability of ligand **II**, which has two electron-withdrawing substituents on an aromatic nuclei. However, the reaction could proceed at 60 °C to afford dodecan-2-one in moderate yield (entry 2). Ligand **III** gave a lower yield of the product (entry 3). When the oxidation was carried out using ligand **IV**, the reaction was slower, however in this case, the toluene (upper phase) was colourless after the reaction, suggesting that the palladium–**IV** complex could dissolve in the fluoruous phase (entry 4). In fact, the recovered fluoruous phase had a high catalytic activity (*vide infra*). The reaction mixture when stirred was always in an emulsion state (heterogeneous).¹¹ Similarly, in the oxidation of octadecan-1-ol and benzyl alcohol, ligand **I** gave the product in better yields than ligand **IV** (entries 5–8), but the recovered fluoruous phases showed a lower catalytic activity. Based on these results, we suppose that the oxidation proceeds mainly in the toluene phase by the palladium–**I** complex dissolved in toluene, resulting in a faster reaction, while the palladium–**IV** complex exists in the fluoruous phase and the reaction occurred at the interface. From these observations it was revealed that pyridine **IV** was the ligand of choice for our purpose to construct a recyclable catalytic system. Next, we looked for optimum conditions using **IV** as the ligand and eventually found that an increase in the proportion of both Pd(OAc)₂ and solvent and the addition of 3 Å molecular sieves gave a high yield of the product (entries 9 and 10).¹²

We carried out the oxidation of several benzylic alcohols (Fig. 2) using the optimum conditions and the results are given in Table 2. The oxidation of chlorobenzyl alcohols (**1b–1d**), in particular the *ortho*-substituted one (**1b**), proceeded more slowly than that of benzyl alcohol (**1a**), and the corresponding aldehydes were obtained in moderate to good yields (Table 2, entries 2–6). On the other hand, the oxidation of benzylic alcohols with an electron-donating substituent such as methoxybenzyl alcohols **1e–1g** smoothly proceeded to afford **2e–2g** in high yields within 5 h (entries 7–9). Secondary benzylic alcohol **1i** was also oxidised to give **2i** in 98% yield.

This catalytic system could be applied to the oxidation of aliphatic alcohols, as shown in Table 3, although a longer

Table 2 Pd(II)-Catalysed oxidation of benzylic alcohols under O₂ in FBS^a



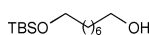
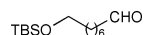


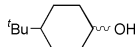
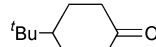


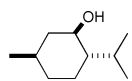
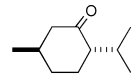
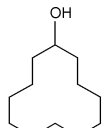
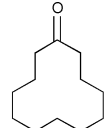
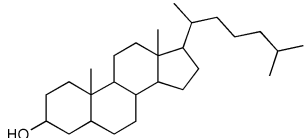
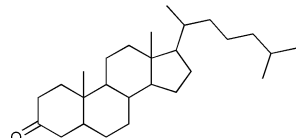
Entry	Substrate	t/h	Product	Conversion (%)	GLC yield (%) ^b
1	1a	5	2a	95	94
2	1b	5	2b	31	30
3	1b	24	2b	66	65
4	1c	5	2c	59	56
5 ^c	1c	15	2c	98	98
6	1d	5	2d	75	71
7	1e	5	2e	86	86
8	1f	5	2f	87	83
9	1g	5	2g	99	96 ^d
10	1h	5	2h	74	52 ^d
11	1i	5	2i	98	98

^a Reaction conditions: alcohol (0.5 mmol), Pd(OAc)₂ (0.025 mmol), ligand **IV** (0.1 mmol), 3 Å molecular sieves (200 mg), toluene (2 mL), perfluorodecalin (2 mL), 80 °C, O₂. ^b Based on alcohol employed (%). ^c Ligand **IV** (0.2 mmol). ^d Isolated yield.

reaction time was generally required. Dodecan-1-ol yielded dodecan-1-al in good yield (Table 3, entry 1). A primary alcohol with a hydroxy protecting group such as *tert*-butyldimethylsilyl (TBS) was easily oxidised to afford the corresponding aldehyde without affecting the protecting group (entry 2). Secondary alcohols including sterically hindered ones were also oxidised to give the corresponding ketones in high yields (entries 3–8). Next, we tried to oxidise allylic alcohols such as cinnamyl alcohol and geraniol, but they failed to be oxidised in this fluoruous biphasic catalytic system resulting in the precipitation of a palladium black.¹³ In our previous studies, the formation of a palladium black could be avoided by using an excess amount of pyridine.^{9b} Here, however, the oxidation of allylic alcohols failed even in the presence of an excess amount of ligand **IV**.

After the reaction of alcohols using ligand **IV**, the toluene phase was colourless, while the fluoruous phase turned to a yellow–white suspension (including molecular sieves), clearly showing that an active Pd(II) species is dissolving in it. In order to demonstrate the catalyst recycling, the fluoruous phase was reused in the oxidation of 1-phenylethanol. In our trials to keep the catalytic activity, we found that the addition of a small amount of the ligand once in every two runs was effective to avoid the formation of the black palladium precipitation (Table 4).¹⁴ Although a slight decrease of the catalytic activity was observed, 74% acetophenone was obtained even after six recycles. It is important to study the leaching problem in these catalyst recycling systems. Thus, we investigated the exact amount of palladium leaching into the toluene phase by ICP (inductively coupled plasma) atomic emission analysis. Leaching of only 0.8% of palladium to the toluene phase was

Table 3 Pd(II)-Catalysed oxidation of aliphatic alcohols under O₂ in FBS^a

Entry	Substrate	t/h	Product	Conversion (%)	Isolated yield (%) ^b
1		10		92	76
2		9		78	77
3		9		100	90
4		24		94	89
5		24		100	92
6		24		98	94
7		9		88	86
8		15		95	95

^a Reaction conditions: alcohol (0.5 mmol), Pd(OAc)₂ (0.025 mmol), ligand **IV** (0.1 mmol), 3 Å molecular sieves (200 mg), toluene (2 mL), perfluorodecalin (2 mL), 80 °C, O₂. ^b Based on alcohol employed (%).

detected after the first run. This result suggests that ligand **IV** works effectively as a ligand for palladium(II) and that its complex dissolves in perfluorodecalin to accomplish the effective recycling of the catalyst.

Conclusion

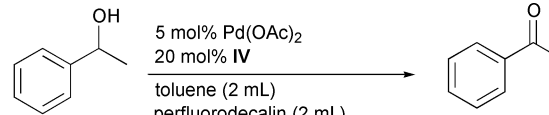
The novel fluoros biphase system of a combination of Pd(OAc)₂-perfluoroalkylated-pyridine-O₂ showed a high catalytic activity for the oxidation of benzylic and aliphatic alcohols to the corresponding ketones and aldehydes. The novel perfluoroalkylated-pyridine **IV** could be easily prepared from commercially available reagents in one step quantitatively and was found to act as an effective ligand in this catalytic oxidation. The recycling of the catalyst was possible at least 5 times without a significant loss of catalytic activity. Although our system has some limitations in substrates, we present a new mild catalytic recycling system for the aerobic oxidation of alcohols.

Experimental

General

NMR spectra were recorded on JEOL EX-400 (¹H NMR, 400 MHz; ¹³C NMR, 100 MHz) and JNM-AL-300 (¹H NMR, 300 MHz; ¹³C NMR, 75.5 MHz) instruments for solutions with Me₄Si as an internal standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. GLC analyses were performed on a Shimadzu GC-14A instrument (25 m × 0.33 mm, 5.0 mm film thickness, Shimadzu fused silica capillary column HiCap CBP10-S25-050) with a flame-ionization detector and helium as carrier gas. GLC yields were determined using bibenzyl or cyclododecane as an internal standard. Analytical thin layer chromatography (TLC) was performed with Merck silica gel 60 F-254 plates. Column chromatography was performed with Merck silica gel 60. Ele-

Table 4 Recycling of the fluoros phase

 <p>5 mol% Pd(OAc)₂ 20 mol% IV toluene (2 mL) perfluorodecalin (2 mL) MS3A (200 mg), 80 °C, 5 h, O₂</p>			
Run	GLC yield ^a	Run	GLC yield ^a
1	98 (98)	4	90 (91)
2	97 (98)	5 ^b	80 (81)
3 ^b	88 (90)	6	74 (74)

^a The value in parentheses is the conversion of alcohol (%). ^b Ligand **IV** (25 mg, 0.025 mmol) was added.

mental analyses were performed at the Microanalytical Center of Kyoto University. Inductively coupled plasma (ICP) atomic emission analysis to measure leaching of Pd was performed with a Shimadzu ICPS-1000 sequential plasma spectrometer.

Materials

Commercially available organic and inorganic compounds were used without further purification except for toluene, which was distilled by the usual method before use. 3 Å Molecular sieves (powder) were commercially available from Nacalai Tesque, and were activated by calcination just before use.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl nicotinate (**I**)

A mixture of nicotinic acid (1.23 g, 10 mmol) and thionyl chloride (5 mL) was stirred at 90 °C. After 6 h, the excess thionyl chloride was removed under reduced pressure and the resulting yellow-white solid was dissolved in CH₂Cl₂ (10 mL). Then, triethylamine (1 mL) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-

heptadecafluorodecanol (2.32 g, 5 mmol) were added to the mixture with stirring at 0 °C, and the mixture was allowed to warm to room temperature and stirred for 12 h. After the solvent was removed under reduced pressure to dryness, the resulting white solid was washed with water and dried under vacuum. The pure compound was obtained after column chromatography on SiO₂ with hexane–ethyl acetate (6:1) as eluent (2.48 g, 4.3 mmol, 86%) as a white solid; mp 47.2–48.0 °C; IR (KBr) 1722, 1590, 1298, 1202, 1147, 746, 705, 660 cm⁻¹; δ_{H} (300 MHz, CDCl₃) 2.63 (tt, $J_{\text{H-F}} = 18.2$ Hz, $J_{\text{H-H}} = 6.3$ Hz, 2H), 4.67 (t, $J = 6.3$ Hz, 2H), 7.41 (dd, $J = 7.9$, 5.0 Hz, 1H), 8.29 (d, $J = 7.9$ Hz, 1H), 8.81 (d, $J = 5.0$ Hz, 1H), 9.23 (s, 1H); δ_{C} (100 MHz, CDCl₃) 30.7 (t, $^2J_{\text{C-F}} = 22$ Hz), 57.4, 105–122 (m), 123.5, 125.7, 137.2, 151.1, 153.9, 165.0. Anal. Calc. for C₁₆H₈F₁₇NO₂: C, 33.76; H, 1.42. Found: C, 33.53; H, 1.19%.

Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl) pyridine-3,5-dicarboxylate(II)

A mixture of pyridine-3,5-dicarboxylic acid (0.33 g, 2 mmol) and thionyl chloride (2.2 mL) was stirred at 90 °C. After 6 h, the excess thionyl chloride was removed under reduced pressure and the resulting yellow–white solid was dissolved in CH₂Cl₂ (10 mL). Then, triethylamine (12 mL), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecanol (2.04 g, 4.4 mmol) and CH₂Cl₂ (4 mL) were added to the mixture with stirring at 0 °C, and the mixture was allowed to warm to room temperature and stirred. After 24 h, water was added and the mixture was diluted with CHCl₃. The organic layer was washed with water and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO₂ with hexane–ethyl acetate (7:3) as eluent to give a white solid. A small amount of impurities was removed by washing the solid with hexane and diethyl ether to give the pure compound as a white solid (0.54 g, 0.51 mmol, 26%); mp 123.5–124.5 °C; IR (KBr) 1730, 1602, 1205, 1147, 1115, 753, 703, 661, 561, 533 cm⁻¹; δ_{H} (270 MHz, CDCl₃) 2.65 (tt, $J_{\text{H-F}} = 18.1$ Hz, $J_{\text{H-H}} = 6.2$ Hz, 4H), 4.71 (t, $J = 6.2$ Hz, 4H), 8.84 (s, 1H), 9.50 (br s, 2H). Anal. Calc. for C₂₇H₁₁F₃₄NO₄: C, 30.61; H, 1.05. Found: C, 30.33; H, 0.91%.

Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl) malate

A mixture of (±)-malic acid (0.40 g, 5 mmol), toluene-*p*-sulfonic acid (50 mg), and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecanol (3.06 g, 6.6 mmol) in toluene (30 mL) was stirred at 130 °C using a Dean–Stark distillation apparatus. After 18 h, the mixture was allowed to cool to room temperature and the resulting solid was purified by column chromatography on SiO₂ using hexane–ethyl acetate (7:3) as eluent to give a white solid (1.03 g, 1.0 mmol, 33%); mp 64.6–65.3 °C; IR (KBr) 1749, 1200, 1142, 708, 666, 561, 536 cm⁻¹; δ_{H} (400 MHz, acetone-*d*₆) 2.59–2.85 (m, 7H), 4.42–4.60 (m, 5H). Anal. Calc. for C₂₄H₁₂F₃₄O₅: C, 28.09; H, 1.18. Found: C, 28.09; H, 0.99%.

Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl) 1-(pyridin-3-ylcarbonyloxy)succinate (III)

To a mixture of nicotinoyl chloride prepared as described above (3 mmol) and triethylamine (1 mL) in CH₂Cl₂ (10 mL) was added bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl) malate (1.03 g, 1 mmol) at 0 °C and the mixture was allowed to warm to room temperature and stirred for 12 h. The solvent was removed under reduced pressure and the resulting white solid was washed with water and CH₂Cl₂ and then dried under vacuum. The pure compound was obtained after column chromatography on SiO₂ with hexane–ethyl acetate (7:3) as eluent (0.34 g, 0.3 mmol, 30%) as a white solid; mp 74.0–75.0 °C; IR (KBr) 1770, 1739, 1723, 1592, 1204, 1147, 741, 714,

658, 560, 529 cm⁻¹; δ_{H} (300 MHz, CDCl₃) 2.42–2.56 (m, 4H), 3.04 (dd, $J = 16.7$, 5.0 Hz, 1H), 3.13 (dd, $J = 16.7$, 6.6 Hz, 1H), 4.44–4.61 (m, 4H), 5.75 (dd, $J = 6.6$, 5.0 Hz, 1H), 7.41 (dd, $J = 7.8$, 4.5 Hz, 1H), 8.29 (d, $J = 7.8$ Hz, 1H), 8.81 (d, $J = 4.5$ Hz, 1H), 9.24 (s, 1H); δ_{C} (100 MHz, CDCl₃) 30.3 (t, $^2J_{\text{C-F}} = 22$ Hz), 30.3 (t, $^2J_{\text{C-F}} = 22$ Hz), 35.7, 57.1, 57.8, 68.6, 105–122 (m), 123.6, 125.2, 138.0, 150.4, 153.2, 163.8, 167.8, 168.4. Anal. Calc. for C₃₀H₁₅F₃₄NO₆: C, 31.85; H, 1.34. Found: C, 31.55; H, 1.21%.

Pyridine-3-carbaldehyde bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl) acetal (IV)

A mixture of pyridine-3-carbaldehyde (0.32 g, 3 mmol), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecanol (4.18 g, 9 mmol) and trifluoromethanesulfonic acid (0.1 mL, 1.1 mmol) in 1,2-dichloroethane (30 mL) was stirred at reflux in a 50 mL flask equipped with a dropping funnel, the top of which was attached with a reflux condenser, and 1,2-dichloroethane pooled in the dropping funnel was added dropwise to the reaction mixture. After 6 h, the reaction mixture was cooled to room temperature and then triethylamine (2 mL) was added to the solution, and the mixture was diluted with diethyl ether. The organic layer was washed with water and dried over MgSO₄. The solvent was removed under vacuum and the residue was subjected to column chromatography on SiO₂ with hexane–ethyl acetate (4:1) as eluent to give IV (2.85 g, 2.8 mmol, 94%) as a colorless oil; IR (neat) 1204, 1148, 1064, 980, 877, 787, 704, 657, 564, 529 cm⁻¹; δ_{H} (400 MHz, CDCl₃) 2.46 (tt, $J_{\text{H-F}} = 18.6$ Hz, $J_{\text{H-H}} = 6.4$ Hz, 4H), 3.77–3.81 (m, 4H), 5.67 (s, 1H), 7.34 (dd, $J = 7.8$, 4.9 Hz, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 8.62 (d, $J = 4.9$ Hz, 1H), 8.70 (s, 1H); δ_{C} (75.5 MHz, CDCl₃) 31.4 (t, $^2J_{\text{C-F}} = 21$ Hz), 57.4, 100.0, 105–122 (m), 123.3, 132.5, 134.3, 148.5, 150.3. Anal. Calc. for C₂₆H₁₃F₃₄NO₂: C, 30.70; H, 1.29. Found: C, 30.41; H, 1.54%.

Typical procedure for the palladium(II)-catalysed oxidation of alcohols under an oxygen atmosphere in a fluororous biphasic system

To a mixture of Pd(OAc)₂ (5.6 mg, 0.025 mmol) and toluene (1.5 mL) in a glass tube (\varnothing 15 mm × 180 mm) was added ligand IV (101 mg, 0.1 mmol) under vigorous stirring. After a few minutes, perfluorodecalin (2 mL) and molecular sieves were added and oxygen gas was introduced into the glass tube equipped with an O₂ balloon, and then the alcohol (0.5 mmol) in toluene (0.5 mL) was added. After stirring at 80 °C for the appropriate time under an atmospheric pressure of oxygen, the mixture was cooled to 0 °C in an ice bath and allowed to stand for *ca.* 5 min, and then the toluene phase was separated using a pipette. The amount of product was determined by GLC analysis using bibenzyl or cyclododecane as an internal standard. For isolation of the product the solvent was evaporated and the residue was purified by column chromatography on silica gel using hexane–ethyl acetate (95:5) as eluent.

Typical procedure for catalyst recycling

After the reaction as described above, octane (2 mL) was added at 0 °C and the mixture was allowed to stand for *ca.* 5 min without stirring, and then the toluene phase was separated using a pipette. The resulting fluororous phase (containing 3 Å molecular sieves) was ready for further runs: that is, the alcohol (0.5 mmol) in toluene (2 mL) was added to the fluororous phase and the mixture was stirred at 80 °C under O₂. The amount of palladium which had leached into the toluene phase in the oxidation of 1-phenylethanol under the conditions shown in Table 4 was estimated by ICP atomic emission analysis for a nitric acid solution of the residue after removing the solvent and the product from the separated toluene phase under reduced pressure (0.2 μmol, 0.8% based on Pd(OAc)₂ employed).

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- 13 We succeeded in the oxidation of allylic alcohols in our previous reported catalytic systems; refs. 9(b) and 10.
- 14 In several trials of the reaction using the recycled fluorine phase without the addition of a ligand, the precipitation of a palladium black was sometimes observed and the yield decreased. On the other hand, when further ligand was added for each run, the yield of the product gradually decreased, because a large excess of ligand lowered the reaction rate.