

Supporting Information
for
**Synthesis and synthetic applications of (4-hydroxyphenyl)perfluoroalkyl-
methanols**

Kyu Terashima,¹ Tomoko Kawasaki-Takasuka,¹ Ichiro Minami,² Takashi Yamazaki*¹

¹ Division of Applied Chemistry, Institute of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei 184-8588, Japan.

² Division of Machine Elements, Luleå University of Technology, Luleå SE-97187, Sweden.

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1. General information

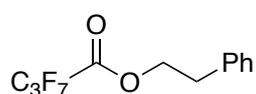
Most of reactions where an organic solvent was employed were performed under argon with magnetic stirring using flame-dried glassware. Unless otherwise noted, materials were obtained from commercial suppliers including anhydrous THF, Et₂O, and CH₂Cl₂, and were used without further purification. Analytical thin-layer chromatography (TLC) was routinely used for monitoring reactions by generally using a mixture of hexane and ethyl acetate. Spherical neutral silica gel (63–210 nm) was employed for usual column chromatography.

¹H (300.40 MHz), ¹³C (75.45 Hz), and ¹⁹F (282.65 Hz) NMR spectra were recorded in CDCl₃ unless otherwise noted, and chemical shifts were reported in parts per million (ppm), downfield from internal tetramethylsilane (Me₄Si: δ 0.00, for ¹H and ¹³C) or hexafluorobenzene (C₆F₆: δ –163.00 for ¹⁹F). Data were tabulated in the following order: number of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sex, sextet; m, multiplet; br, broad peak), coupling constants in Hertz. In the case of ¹³C NMR for the compounds with C₃F₇ and C₆F₁₃ groups, because multiple coupling of fluorine-possessing carbon atoms made their observation difficult even after long data acquisition time, these data are not shown. Infrared (IR) spectra were reported in wave numbers (cm⁻¹). High resolution mass spectrometry was performed by the positive ionization mode.

1-(Allyloxy)-4-bromobenzene [1], 1-(allyloxy)-3-bromobenzene [2], 1-(allyloxy)-2-bromobenzene [3], and 1-bromo-4-((tetrahydro-2H-pyran-2-yl)oxy)benzene [4] were synthesized following to the reported procedures.

2. Synthetic procedure and characterization of new compounds

2.1. 2-Phenylethyl 2,2,3,3,4,4,4-heptafluorobutyrate

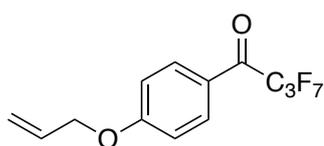


To a 30 mL round-bottomed flask, 2-phenylethanol (2.4463 g, 20.025 mmol) and heptafluorobutyric acid (4.7318 g, 22.107 mmol) were introduced, where conc. H₂SO₄ (0.60 mL, 11 mmol) was added slowly at 0 °C. After stirring for 24 h at room temperature, the reaction mixture was treated with sat. NaHCO₃ aq. at 0 °C, and after stirring for 15 min. at the same temperature, the solution was extracted with CH₂Cl₂. After the organic layer was washed with sat. NaCl aq. and dried over anhydrous Na₂SO₄, concentration *in vacuo* afforded the crude product (referred to as usual work up) which was purified by column chromatography (hexane:AcOEt=15:1) to give the desired product (5.9953 g, 18.842 mmol, 94%).

R_f=0.68 (hexane:AcOEt=8:1). ¹H NMR: δ 3.05 (2H, t, *J*=7.2 Hz), 4.57 (2H, t, *J*=7.2 Hz), 7.21-7.36 (5H, m). ¹³C NMR: δ 34.5, 68.8, 127.1, 128.7, 128.9, 136.1, 158.2 (t, *J*=29.8 Hz).

^{19}F NMR: δ -128.36 (2F, s), -120.74 (1F, d, $J=9.0$ Hz), -120.68 (1F, d, $J=9.0$ Hz), -82.11 (3F, t, $J=9.0$ Hz). IR (CHCl_3) ν 3068, 3031, 2966, 1779, 1305, 1237, 1146, 969, 758 cm^{-1} . HRMS (FAB+, m/z): $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_9\text{F}_7\text{NaO}_2$, 341.0383; Found, 341.0376.

2.2 1-{4-(Allyloxy)phenyl}-2,2,3,3,4,4,4-heptafluorobutan-1-one (3a)

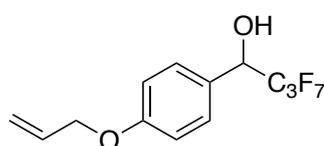


To a 30 mL two-necked round-bottomed flask were added 1-(allyloxy)-4-bromobenzene (0.2579 g, 1.209 mmol) and THF (1 mL), where BuLi (a 1.53 M hexane solution, 0.72 mL, 1.1 mmol) was dropped slowly at -80 $^\circ\text{C}$, and the mixture was stirred for 30 min at the same temperature. To this mixture was added a solution of 2-phenylethyl 2,2,3,3,4,4,4-heptafluorobutyrate (0.3185 g, 1.000 mmol) in THF (1.0 mL) via a syringe. After 1 h at the same temperature, the reaction mixture was quenched with 1 M HCl and extracted with AcOEt three times. After usual workup, the resultant crude product was purified by column chromatography (hexane) to give the desired product **3a** (0.2920 g, 0.8327 mmol, 83%) as a colorless oil.

Rf=0.13 (hexane). ^1H NMR: δ 4.65 (2H, dt, $J=5.4$, 1.5 Hz), 5.36 (1H, dq, $J=10.5$, 1.5 Hz), 5.44 (1H, dq, $J=17.4$, 1.5 Hz), 6.05 (1H, ddt, $J=17.4$, 10.5, 5.4 Hz), 6.98-7.03 (2H, m), 8.07 (2H, d, $J=8.7$ Hz). ^{13}C NMR: δ 69.1, 115.0, 118.4, 124.4, 131.9, 132.86, 132.91, 133.0, 164.4, 181.3 (t, $J=25.4$ Hz). ^{19}F NMR: δ -126.84 (2F, m), -114.60 (1F, d, $J=9.0$ Hz), -114.53 (1F, d, $J=9.0$ Hz), -81.43 (3F, t, $J=9.0$ Hz). IR (CHCl_3) ν 3087, 2988, 2938, 2873, 1696, 1599, 1234, 1163, 909, 732 cm^{-1} . HRMS (FAB+, m/z): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{10}\text{F}_7\text{O}_2$, 331.0564; Found, 331.0601.

2.3 *In situ* MPV reduction by using commercially available MgBr_2 [5]

2.3.1. 1-{4-(Allyloxy)phenyl}-2,2,3,3,4,4,4-heptafluorobutan-1-ol (4ab)



To a 30 mL two-necked round-bottomed flask were added 1-(allyloxy)-4-bromobenzene (0.2579 g, 1.209 mmol) and THF (1 mL), where BuLi (a 1.53 M hexane solution, 0.72 mL, 1.1 mmol) was dropped slowly at -80 $^\circ\text{C}$, and the mixture was stirred for 30 min at the same temperature. To this mixture was added a solution of 2-phenylethyl 2,2,3,3,4,4,4-heptafluorobutyrate (0.3185 g, 1.000 mmol) in THF (1.0 mL) via a syringe. After 1 h at the same temperature, anhydrous MgBr_2 (0.2035 g, 1.103 mmol) was added to the solution and the whole was stirred for 30 min at -80 $^\circ\text{C}$. To the solution was added *i*-PrOH (0.23 mL, 3.0 mmol) and the mixture was stirred for 1 h at 80 $^\circ\text{C}$. After usual workup, the resultant crude product was purified by column chromatography (hexane: AcOEt=10:1 \rightarrow 8:1) to give the desired product **4ab** as a yellow oil (0.2947 g, 0.8872 mmol,

89%).

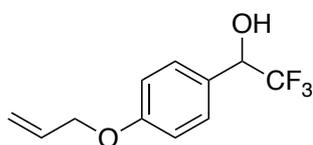
2.4. *In situ* MPV reduction by using MgBr₂ prepared *in situ* (General procedure 1)

To a 30 mL two-necked round-bottomed flask were added ArBr (1.2 mmol, 1.2 eq.) and THF (1 mL), where BuLi (a 2.7 M hexane solution, 0.40 mL, 1.1 mmol, 1.1 eq.) was dropped slowly at –80 °C, and the mixture was stirred for 30 min at the same temperature. To this mixture was added a solution of the perfluorinated ester (1 mmol, 1.0 eq.) in THF (1.0 mL) via a syringe. After 1 h at the same temperature, the reaction mixture was transferred via cannula to the other 30 mL two-necked round-bottomed flask which was filled with a THF solution of MgBr₂ prepared from Mg (0.0528 g, 2.20 mmol) and 1,2-dibromoethane (0.19 mL, 2.2 mmol) in THF (1 mL) mixing for 1 h at room temperature under argon. After 30 min., to the solution was added *i*-PrOH (0.23 mL, 3.0 mmol) and the mixture was stirred for a further period (see Table 2) at 80 °C. After usual workup, the resultant crude product was purified by column chromatography to give desired product.

Following to this “General procedure 1” by using 1-(allyloxy)-4-bromobenzene (0.2552 g, 1.209 mmol) and ethyl heptafluorobutyrate (0.175 mL, 1.01 mmol), **4ab** was obtained as a yellow oil (0.2950 g, 0.8880 mmol, 89%).

R_f=0.42 (hexane:AcOEt=5:1). ¹H NMR: δ 2.39 (1H, d, *J*=4.8 Hz), 4.56 (2H, d, *J*=4.5 Hz), 5.14 (1H, dt, *J*=17.7, 5.7 Hz), 5.39 (1H, d, *J*=10.5 Hz), 5.43 (1H, d, *J*=17.4 Hz), 6.01 (1H, ddt, *J*=17.1, 10.8, 5.1 Hz), 6.94-7.02 (2H, m), 7.39 (2H, d, *J*=8.4 Hz). ¹³C NMR: δ 68.8, 71.4 (dd, *J*=29.2, 22.3 Hz), 114.7, 117.8, 126.3, 129.3, 132.8, 159.4. ¹⁹F NMR: δ –128.18 (1F, dm, *J*=285.2 Hz), –127.52 (1F, dm, *J*=290.8 Hz), –126.13 (1F, dm, *J*=290.8 Hz), –120.01 (1F, dm, *J*=281.8 Hz), –82.11 (3F, m). IR (CHCl₃) ν 3432, 3025, 2938, 2870, 1618, 1510, 1231, 1178, 1119, 792 cm⁻¹. HRMS (FAB+, *m/z*): [M]⁺ Calcd for C₁₃H₁₁F₇O₂, 332.0642; Found, 331.0644.

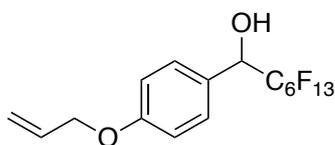
2.4.1. 1-{4-(Allyloxy)phenyl}-2,2,2-trifluoroethan-1-ol (**4aa**) [6]



Following to the “General procedure 1” using 1-(allyloxy)-4-bromobenzene (0.2552 g, 1.198 mmol) and ethyl trifluoroacetate (0.12 mL, 1.00 mmol), 0.1500 g (0.6460 mmol) of **4aa** was obtained in 65% yield.

R_f=0.27 (hexane:AcOEt=6:1). ¹H NMR: δ 2.62 (1H, brs), 4.56 (2H, dt, *J*=5.4, 1.5 Hz), 4.96 (1H, q, *J*=6.9 Hz), 5.30 (1H, dq, *J*=10.5, 1.5 Hz), 5.42 (1H, dq, *J*=17.1, 1.5 Hz), 6.05 (1H, ddt, *J*=17.1, 10.5, 5.4 Hz), 6.92-6.96 (2H, m), 7.37-7.39 (2H, m). ¹³C NMR: δ 68.8, 72.4 (q, *J*=32.2 Hz), 114.8, 117.9, 124.3 (q, *J*=281.0 Hz), 126.2, 128.7, 159.4. ¹⁹F NMR: δ –79.81 (d, *J*=6.8 Hz).

2.4.2. 1-{4-(Allyloxy)phenyl}-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-ol (4ad)

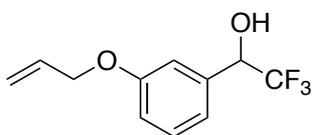


Following to the “General procedure 1” using 1-(allyloxy)-4-bromobenzene (0.2552 g, 1.198 mmol) and methyl tridecafluoroheptanoate (0.3786 mL, 1.00 mmol), 0.3121 g (0.6472 mmol) of **4ad** was obtained in 65% yield as a yellow solid.

solid.

mp. 50.4-52.1 °C. Rf=0.33 (hexane:AcOEt=6:1). ¹H NMR: δ 2.38 (1H, d, *J*=5.1 Hz), 4.56 (2H, dt, *J*=5.1, 1.5 Hz), 5.15 (1H, dt, *J*=17.7, 6.0 Hz), 5.31 (1H, dq, *J*=10.5, 1.5 Hz), 5.42 (1H, dq, *J*=17.1, 1.5 Hz), 6.06 (1H, ddt, *J*=17.1, 10.5, 5.4 Hz), 6.93-6.98 (2H, m), 7.38 (2H, d, *J*=8.7 Hz). ¹³C NMR: δ 68.9, 71.8 (dd, *J*=27.6, 21.7 Hz), 114.8, 117.9, 126.3, 129.4, 132.8, 159.6. ¹⁹F NMR: δ -128.06 (1F, dm, *J*=292.0 Hz), -127.21 (1F, dm, *J*=280.0 Hz), -126.81 (1F, dm, *J*=292.0 Hz), -124.15 ~ -124.02 (2F, m), -123.34 (2F, m), -122.52 (2F, m), -119.49 (1F, dm, *J*=282.9 Hz), -82.12 ~ -82.05 (3F, m). IR (CHCl₃) ν 3458, 3088, 3023, 2924, 2857, 1897, 1614, 1517, 1214, 935 cm⁻¹. HRMS (FAB+, *m/z*): [M]⁺ Calcd for C₁₆H₁₁F₁₃O₂, 482.0546; Found, 482.0567.

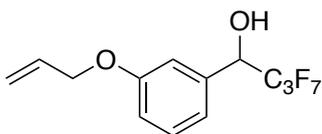
2.4.3. 1-{3-(Allyloxy)phenyl}-2,2,2-trifluoroethan-1-ol (4ba)



Following to the “General procedure 1” using 1-(allyloxy)-3-bromobenzene (0.2552 g, 1.198 mmol) and ethyl trifluoroacetate (0.12 mL, 1.00 mmol), 0.1583 g (0.6817 mmol) of **4ba** was obtained in 68% yield as a yellow oil.

Rf=0.27 (hexane:AcOEt=6:1). ¹H NMR: δ 2.65 (1H, brs), 4.55 (2H, dt, *J*=5.4, 1.5 Hz), 4.98 (1H, q, *J*=7.2 Hz), 5.30 (1H, dq, *J*=10.5, 1.5 Hz), 5.42 (1H, dq, *J*=17.4, 1.5 Hz), 6.06 (1H, ddt, *J*=17.1, 10.5, 5.4 Hz), 6.96 (1H, ddd, *J*=8.4, 2.4, 1.2 Hz), 7.03-7.05 (2H, m), 7.31 (1H, t, *J*=8.4 Hz). ¹³C NMR: δ 68.8, 71.4 (q, *J*=32.2 Hz), 114.8, 117.9, 124.3 (q, *J*=281.2 Hz), 126.2, 128.73, 128.75, 132.8, 159.4. ¹⁹F NMR: δ -79.5 (d, *J*=6.8 Hz). IR (CHCl₃) ν 3440, 3085, 2926, 2867, 1589, 1258, 1171, 1121, 932, 713 cm⁻¹. HRMS (FAB+, *m/z*): [M]⁺ Calcd for C₁₁H₁₂F₃O₂, 232.0706; Found, 232.0736.

2.4.4. 1-{3-(Allyloxy)phenyl}-2,2,3,3,4,4,4-heptafluorobutan-1-ol (4bb)

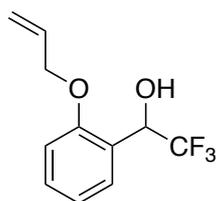


Following to the “General procedure 1” using 1-(allyloxy)-3-bromobenzene (0.2552 g, 1.198 mmol) and ethyl heptafluorobutyrate (0.175 mL, 1.01 mmol), 0.2870 g (0.8639 mmol) of **4bb** was obtained in 86% yield as a yellow oil.

Rf=0.33 (hexane:AcOEt=6:1). ¹H NMR: δ 2.53 (1H, d, *J*=5.4 Hz), 4.55 (2H, dt, *J*=5.4, 1.5 Hz), 5.16 (1H, dt, *J*=17.7, 5.7 Hz), 5.22 (1H, dq, *J*=10.5, 1.5 Hz), 5.42 (1H, dq, *J*=17.4,

1.5 Hz), 6.06 (1H, ddt, $J=17.4, 10.5, 5.4$ Hz), 6.97 (1H, ddd, $J=8.4, 2.4, 1.2$ Hz), 7.02-7.04 (2H, m), 7.29-7.35 (1H, m). ^{13}C NMR: δ 68.9, 71.8 (dd, $J=29.2, 21.0$ Hz), 114.4, 116.0, 117.9, 120.6, 129.5, 132.8, 135.5, 158.6. ^{19}F NMR: δ -128.00 (1F, dm, $J=287.5$ Hz), -127.55 (1F, dm, $J=292.0$ Hz), -126.09 (1F, dm, $J=294.2$ Hz), -119.75 (1F, dm, $J=282.9$ Hz), -82.1 ~ -82.0 (3F, m). IR (CHCl_3) ν 3447, 3088, 3028, 2916, 2872, 1589, 1344, 1227, 1115, 792 cm^{-1} . HRMS (FAB+, m/z): $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{11}\text{F}_7\text{O}_2$, 332.0642; Found, 332.0670.

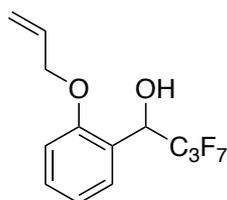
2.4.5. 1-{2-(Allyloxy)phenyl}-2,2,2-trifluoroethan-1-ol (4ca)



Following to the “General procedure 1” using 1-(allyloxy)-2-bromobenzene (0.2552 g, 1.198 mmol) and ethyl trifluoroacetate (0.12 mL, 1.00 mmol), 0.1707 g (0.7351 mmol) of **4ca** was obtained in 74% yield as a yellow oil.

$R_f=0.33$ (hexane:AcOEt=6:1). ^1H NMR: δ 3.70 (1H, d, $J=7.8$ Hz), 4.61 (2H, dt, $J=5.4, 1.5$ Hz), 5.28 (1H, dq, $J=8.1, 7.4$ Hz), 5.32 (1H, dq, $J=10.2, 1.5$ Hz), 5.41 (1H, dq, $J=17.4, 1.5$ Hz), 6.04 (1H, ddt, $J=17.4, 10.5, 5.4$ Hz), 6.93 (1H, d, $J=8.1$ Hz), 6.94-7.04 (1H, td, $J=7.5, 1.2$ Hz), 7.35 (1H, ddd, $J=8.4, 7.8, 1.8$ Hz), 7.39 (1H, d, $J=7.5$ Hz). ^{13}C NMR: δ 68.2, 69.4 (q, $J=32.8$ Hz), 112.3, 118.0, 121.1, 122.3, 124.6 (q, $J=282.3$ Hz), 129.2, 130.4, 132.4, 156.4. ^{19}F NMR: δ -79.3 (d, $J=7.1$ Hz). IR (CHCl_3) ν 3481, 3074, 3022, 2932, 2877, 1494, 1247, 1217, 1171, 756 cm^{-1} . HRMS (FAB+, m/z): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_2$, 233.0706; Found, 233.0715.

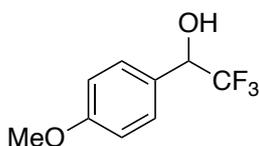
2.4.6. 1-{2-(Allyloxy)phenyl}-2,2,3,3,4,4,4-heptafluorobutan-1-ol (4cb)



Following to the “General procedure 1” using 1-(allyloxy)-2-bromobenzene (0.2552 g, 1.200 mmol) and ethyl heptafluorobutyrate (0.175 mL, 1.01 mmol), 0.2655 g (0.7992 mmol) of **4cb** was obtained in 80% yield as a yellow oil.

$R_f=0.26$ (hexane:AcOEt=6:1). ^1H NMR: δ 3.83 (1H, d, $J=8.7$ Hz), 4.62 (2H, d, $J=5.1$ Hz), 5.32 (1H, d, $J=10.6$ Hz), 5.41 (1H, d, $J=17.4$ Hz), 5.47 (1H, ddd, $J=20.7, 8.7, 5.0$ Hz), 6.04 (1H, ddt, $J=17.4, 10.5, 5.4$ Hz), 6.95 (1H, d, $J=8.7$ Hz), 7.03 (1H, t, $J=7.5$ Hz), 7.34-7.38 (2H, m). ^{13}C NMR: δ 69.1 (dd, $J=29.4, 22.2$ Hz), 69.3, 112.4, 118.0, 121.1, 122.0, 129.9, 130.5, 132.3, 156.8. ^{19}F NMR: δ -128.64 (1F, dm, $J=280.4$ Hz), -128.15 (1F, dm, $J=290.9$ Hz), -126.59 (1F, dm, $J=282.9$ Hz), -119.44 (1F, dm, $J=280.7$ Hz), -82.13 ~ -82.06 (3F, m). IR (CHCl_3) ν 3466, 3077, 3028, 2927, 2872, 1594, 1230, 1191, 1120, 756 cm^{-1} . HRMS (FAB+, m/z): $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{11}\text{F}_7\text{O}_2$, 332.0642; Found, 332.0679.

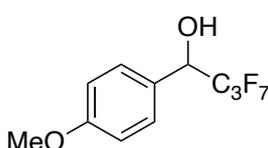
2.4.7. 2,2,2-Trifluoro-1-(4-methoxyphenyl)ethan-1-ol (4da) [7]



Following to the “General procedure 1” using 4-bromoanisole (0.2244 g, 1.200 mmol) and ethyl trifluoroacetate (0.12 mL, 1.00 mmol), 0.1366 g (0.6626 mmol) of **4da** was obtained in 66% yield as a yellow oil.

Rf=0.26 (hexane:AcOEt=6:1). $^1\text{H NMR}$: δ 2.60 (1H, d, $J=7.8$ Hz), 3.82 (3H, s), 4.97 (1H, q, $J=6.9$ Hz), 6.91-6.96 (2H, m), 7.38-7.41 (2H, m). $^{13}\text{C NMR}$: δ 55.2, 72.2 (q, $J=31.6$ Hz), 113.9, 124.3 (q, $J=281.6$ Hz), 126.2, 128.8, 160.2. $^{19}\text{F NMR}$: δ -79.82 (d, $J=6.8$ Hz).

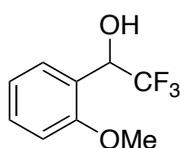
2.4.8. 2,2,3,3,4,4,4-Heptafluoro-1-(4-methoxyphenyl)butan-1-ol (4db)



Following to the “General procedure 1” using 4-bromoanisole (0.2244 g, 1.200 mmol) and ethyl heptafluorobutyrate (0.175 mL, 1.01 mmol), 0.2421 g (0.7907 mmol) of **4db** was obtained in 79% yield as a yellow solid.

mp. 43.9-44.8 °C. Rf=0.26 (hexane:AcOEt=6:1). $^1\text{H NMR}$: δ 2.44 (1H, d, $J=4.8$ Hz), 3.83 (3H, s), 5.14 (1H, dt, $J=17.4, 5.4$ Hz), 6.91-6.96 (2H, m), 7.39 (2H, d, $J=8.7$ Hz). $^{13}\text{C NMR}$: δ 55.2, 71.5 (dd, $J=28.5, 22.3$ Hz), 113.9, 126.1, 129.3, 160.4. $^{19}\text{F NMR}$: δ -128.28 (1F, dm, $J=282.9$ Hz), -127.50 (1F, dm, $J=294.2$ Hz), -126.12 (1F, dm, $J=294.2$ Hz), -119.86 (1F, dm, $J=282.9$ Hz), -82.14 ~ -82.07 (3F, m). IR (CHCl₃) ν 3496, 3014, 2966, 2943, 2844, 1613, 1518, 1349, 1233, 843 cm⁻¹. HRMS (FAB+, m/z): [M+H]⁺ Calcd for C₁₃H₁₀F₇O₂, 307.0564; Found, 307.0600.

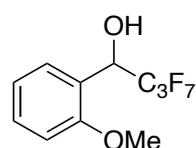
2.4.9. 2,2,2-Trifluoro-1-(2-methoxyphenyl)ethan-1-ol (4ea) [7]



Following to the “General procedure 1” using 2-bromoanisole (0.2244 g, 1.200 mmol) and ethyl trifluoroacetate (0.12 mL, 1.00 mmol), 0.1331 g (0.6456 mmol) of **4ea** was obtained in 65% yield as a yellow oil.

Rf=0.26 (hexane:AcOEt=6:1). $^1\text{H NMR}$: δ 3.66 (1H, d, $J=7.8$ Hz), 3.89 (3H, s), 5.27 (1H, dq, $J=7.2, 6.9$ Hz), 6.94-7.04 (2H, m), 7.35-7.40 (2H, m). $^{13}\text{C NMR}$: δ 55.6, 69.3 (q, $J=32.9$ Hz), 111.2, 120.9, 122.0, 124.6 (q, $J=281.9$ Hz), 129.1, 130.5, 157.4. $^{19}\text{F NMR}$: δ -79.35 (d, $J=6.8$ Hz).

2.4.10. 2,2,3,3,4,4,4-Heptafluoro-1-(2-methoxyphenyl)butan-1-ol (4eb)

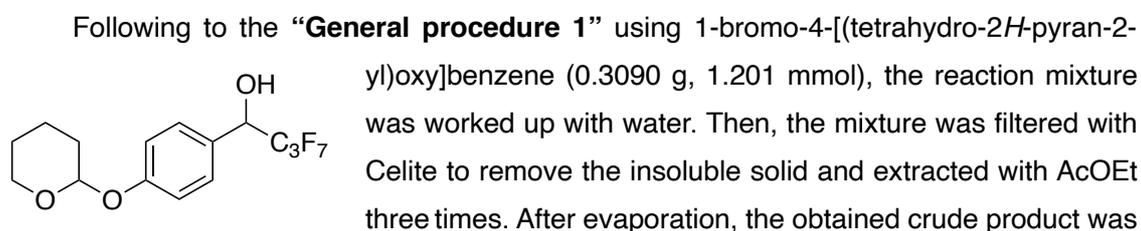


Following to the “General procedure 1” using 2-bromoanisole (0.2244 g, 1.200 mmol) and ethyl heptafluorobutyrate (0.175 mL, 1.01 mmol), 0.2514 g (0.8212 mmol) of **4eb** was obtained in 82% yield as a yellow solid.

mp. 50.1-52.7 °C. Rf=0.30 (hexane:AcOEt=6:1). ¹H NMR: δ 3.79 (1H, d, *J*=9.0 Hz), 3.89 (3H, s), 5.43 (1H, ddd, *J*=20.6, 6.4, 5.4 Hz), 6.96 (1H, d, *J*=8.1 Hz), 7.02 (1H, td, *J*=7.5, 0.9 Hz), 7.33-7.41 (2H, m). ¹³C NMR: δ 55.7, 69.4 (dd, *J*=29.1, 22.3 Hz), 111.3, 121.0, 121.6, 129.9, 130.6, 157.8. ¹⁹F NMR: δ -128.44 (1F, dm, *J*=280.7 Hz), -128.12 (1F, dm, *J*=295.2 Hz), -126.48 (1F, dm, *J*=292.0 Hz), -119.28 (1F, dm, *J*=280.6 Hz), -82.09 ~ -82.02 (3F, m). IR (CHCl₃) ν 3466, 3011, 2940, 2841, 2051, 1602, 1467, 1440, 1351, 822 cm⁻¹. HRMS (FAB+, *m/z*): [M+H]⁺ Calcd for C₁₁H₁₀F₇O₂, 307.0564; Found, 307.0593.

2.5. *In situ* MPV reduction by using MgBr₂ prepared *in situ* (General procedure 2)

2.5.1. 2,2,3,3,4,4,4-Heptafluoro-1-[4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl]butan-1-ol (4fb)

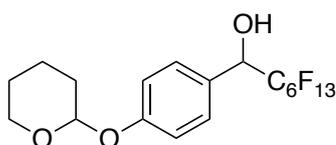


Following to the “General procedure 1” using 1-bromo-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]benzene (0.3090 g, 1.201 mmol), the reaction mixture was worked up with water. Then, the mixture was filtered with Celite to remove the insoluble solid and extracted with AcOEt three times. After evaporation, the obtained crude product was dissolved in a minimum volume of CH₂Cl₂ where hexane was added until white precipitation was generated. After washing the solid with hexane, 0.2974 g (0.7904 mmol, 79%) of the desired product **4fb** was obtained as a white solid (1:1 diastereomeric mixture) (Starting from 1-bromo-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]benzene (1.5427 g, 6.0000 mmol) and ethyl heptafluoroacetate ((1.2111 g, 5.0027 mmol), 1.6760 g (3.7537 mmol, 75%) of **4fb** was obtained).

mp. 104.2-105.1 °C. Rf=0.30 (hexane:AcOEt=6:1). ¹H NMR: δ 1.57-2.06 (6H, m), 2.43 (1H, d, *J*=5.1 Hz), 3.59-3.63 (1H, m), 3.83-3.94 (1H, m), 5.14 (1H, dt, *J*=17.4, 6.0 Hz), 5.44-5.46 (1H, m), 7.07-7.10 (2H, m), 7.36-7.39 (2H, m). ¹³C NMR: δ 18.7, 25.0, 30.2, 62.2, 71.5 (dd, *J*=29.2, 22.0 Hz) and 71.6 (dd, *J*=29.2, 22.0 Hz) (diastereomer pair), 96.28 and 96.33 (diastereomer pair), 116.3 and 116.4 (diastereomer pair), 127.0, 129.2, 157.9. ¹⁹F NMR: δ -128.42 (1F, dm, *J*=287.5 Hz), -127.61 (1F, dm, *J*=294.2 Hz), -126.17 (1F, dm, *J*=297.6 Hz), -119.96 (1F, dm, *J*=279.4 Hz), -82.15 (3F, m). IR (KBr) ν 3363, 2955, 2881, 1612, 1514, 1346, 1226, 1121, 970, 795 cm⁻¹. HRMS (FAB+, *m/z*): [M-H]⁺ Calcd for C₁₅H₁₄F₇O₃, 375.0826; Found, 375.0803.

2.5.2. 2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-[4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl]heptan-1-ol (4fd)

Following to the “General procedure 2” using 1-bromo-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]benzene (1.5427 g, 6.0000 mmol) and methyl tridecafluoroheptanoate (1.8914 g,

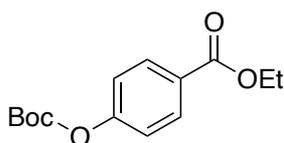


5.0025 mmol), 1.9729 g (3.748 mmol) of **4fd** was obtained in 75% yield (1:1 diastereomere mixture as a white solid.

mp. 113.5-114.6 °C. Rf=0.30 (hexane:AcOEt=6:1). ¹H

NMR: δ 1.54-2.10 (6H, m), 2.42 (1H, brs), 3.60-3.64 (1H, m), 3.86-3.93 (1H, m), 5.17 (1H, dt, *J*=18.0, 5.4 Hz), 5.43-5.47 (1H, m), 7.08-7.10 (2H, m), 7.37-7.40 (2H, m). ¹³C NMR (acetone-*d*₆): δ 19.5, 25.9, 31.0, 62.4, 71.8 (dd, *J*=29.2, 21.8 Hz) and 71.9 (dd, *J*=29.2, 21.8 Hz) (diastereomer pair), 96.9 and 97.0 (diastereomer pair), 116.88 and 116.91 (diastereomer pair), 129.1, 130.3, 158.7. ¹⁹F NMR: δ -128.09 (1F, dm, *J*=298.8 Hz), -127.33 (1F, dm, *J*=285.2 Hz), -126.79 (1F, dm, *J*=298.8 Hz), -124.11 (2F, m), -123.34 (2F, m), -122.52 (2F, m), -119.35 (1F, dm, *J*=280.7 Hz), -82.05 (3F, m). IR (KBr) ν 3371, 2949, 2889, 1904, 1610, 1586, 1514, 1232, 1032, 972 cm⁻¹. HRMS (FAB+, *m/z*): [M]⁺ Calcd for C₁₈H₁₅F₁₃O₃, 526.0808; Found, 526.0846.

2.6 Ethyl 4-[(1,1-dimethylethoxy)carbonyl]oxybenzoate (**6**)



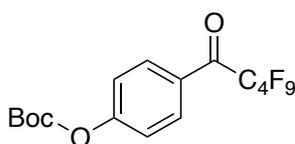
To a 30 mL two-necked round-bottomed flask were added ethyl 4-hydroxybenzoate (3.3242 g, 20.004 mmol), *N,N*-dimethyl-4-aminopyridine (0.2451 g, 2.006 mmol), CH₂Cl₂ (20 mL), triethylamine (3.0 mL, 22 mmol), and di-*t*-butyl dicarbonate (4.4830

g, 20.540 mmol), and the mixture was stirred for 30 min. at room temperature. The reaction mixture was quenched with 0.5 M NaHSO₄ and extracted with CH₂Cl₂ three times. After usual workup, the obtained crude product was purified by column chromatography (hexane:AcOEt=15:1) to give desired product **6** (5.0909 g, 19.118 mmol, 96%) as a white solid.

mp. 66.8-67.6 °C. Rf=0.40 (hexane:AcOEt=20:1). ¹H NMR: δ 1.39 (3H, t, *J*=7.2 Hz), 1.57 (9H, s), 4.37 (2H, q, *J*=7.2 Hz), 7.22-7.27 (2H, m), 8.04-8.09 (2H, m). ¹³C NMR: δ 14.2, 27.5, 60.9, 83.9, 121.0, 127.8, 131.0, 151.0, 154.4, 165.6. IR (CHCl₃) ν 3067, 3052, 2988, 2938, 2909, 1767, 1721, 1303, 1018, 898 cm⁻¹. HRMS (FAB+, *m/z*): [M+H]⁺ Calcd for C₁₄H₁₉O₅, 276.1227; Found, 276.1253.

2.7. 1-[4-[(1,1-Dimethylethoxy)carbonyl]oxy]phenyl]-2,2,3,3,4,4,5,5,5-nonafluoropentan-1-one (**3b**)

To a 50 mL two-necked round-bottomed flask were added ethyl 4-[(1,1-dimethylethoxy)carbonyl]oxybenzoate (0.2668 g, 1.002 mmol), C₄F₉I (0.5223 g, 1.510 mmol) and

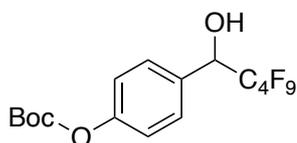


Et₂O (5 mL), where MeLi-LiBr complex (a 1.5 M Et₂O solution, 1.0 mL, 1.5 mmol) was dropped slowly at -80 °C. After 1 h at the same temperature, the reaction mixture was quenched with H₂O and the solution was extracted with Et₂O. After the Et₂O layer was washed

with sat. NaCl aq. and dried over anhydrous Na₂SO₄, concentration *in vacuo* afforded the crude product which was purified by column chromatography (hexane:CH₂Cl₂=1:1) to give the desired product **3b** as colorless liquid (0.4006 g, 0.9099 mmol, 91%).

R_f=0.57 (hexane:CH₂Cl₂=1:1). ¹H NMR: δ 1.58 (9H, s), 7.38 (2H, d, *J*=8.7 Hz), 8.12 (2H, dt, *J*=8.7 Hz). ¹³C NMR: δ 27.5, 84.7, 121.8, 128.6, 132.1, 150.5, 156.4, 181.9 (t, *J*=26.1 Hz). ¹⁹F NMR: δ -126.47 (2F, m), -123.16 (2F, m), -114.18 (2F, m), -82.18 (3F, t, *J*=9.3 Hz). IR(CHCl₃) ν 3021, 2985, 1761, 1709, 1602, 1372, 1216, 1138, 841, 757 cm⁻¹. HRMS (FAB+, *m/z*): [M+H]⁺ Calcd for C₁₆H₁₄F₉O₄, 441.0743; Found, 441.0734.

2.8. 1-[4-[(1,1-Dimethylethoxy)carbonyl]oxy]phenyl]-2,2,3,3,4,4,5,5,5-nonafluoropentan-1-ol (**4gc**)

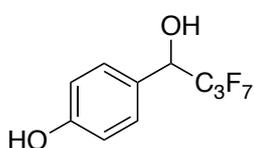


To a 30 mL two-necked round-bottomed flask were added ethyl 4-[(1,1-dimethyl-ethoxy)carbonyl]oxybenzoate (0.2664 g, 1.000 mmol), C₄F₉I (0.5191 g, 1.501 mmol) and Et₂O (2 mL), where MeLi-LiBr complex (a 1.5 M Et₂O solution, 1.0 mL, 1.5 mmol) was dropped slowly at -80 °C. After 1 h at the same temperature, via cannula, the reaction mixture was transferred to the another 30 mL two-necked round-bottomed flask which was filled with a Et₂O solution of the MgBr₂ prepared from a mixture of Mg (0.0730 g, 3.00 mmol) and 1,2-dibromoethane (0.5642 g, 3.003 mmol) in Et₂O (1 mL) for 1 h at room temperature under argon. After 30 min., to the solution was added *i*-PrOH (0.23 mL, 3.0 mmol) and the mixture was stirred for 1 h at 50 °C. After usual workup, the resultant crude product was purified by column chromatography (hexane:AcOEt=6:1) to give 0.2914 g (0.6650 mmol) of the desired product **4gc** in 67% yield.

mp. 103.8-105.1 °C. R_f=0.42 (hexane:AcOEt=4:1). ¹H NMR: δ 1.57 (9H, s), 2.51 (1H, d, *J*=5.1 Hz), 5.21 (1H, dt, *J*=17.7, 5.1 Hz), 7.22-7.26 (2H, m), 7.48 (2H, d, *J*=8.4 Hz). ¹³C NMR (acetone-*d*₆): δ 27.8, 71.5 (dd, *J*=28.5, 21.7Hz), 83.7, 122.0, 130.3, 133.7, 152.4, 152.7. ¹⁹F NMR: δ -128.21 (1F, dm, *J*=291.8 Hz), -127.43 (1F, dm, *J*=284.9 Hz), -126.72 (1F, dm, *J*=293.1 Hz), -123.4 (2F, m), -119.23 (1F, dm, *J*=280.4 Hz), -82.18 (3F, m). IR (KBr) ν 2990, 2942, 1924, 1732, 1600, 1510, 1375, 1315, 901 cm⁻¹. HRMS (FAB+, *m/z*): [M+H]⁺ Calcd for C₁₆H₁₅F₉O₄, 443.0899; Found, 443.0903.

2.9. General procedure for the deprotection of the allyl group (General procedure 3)

2.9.1. 2,2,3,3,4,4,4-Heptafluoro-1-(4-hydroxyoxyphenyl)butan-1-ol (**2ab**)



To a 9 mL ACE GLASS[®] were added **4ab** (0.0999 g, 0.0301 mmol), MeCN (1.5 mL), and NaI (1.8 mmol, 6.0 eq.). After charged with Ar gas, TMSCl (0.23 mL, 1.8 mmol, 6.0 eq.) was added to the

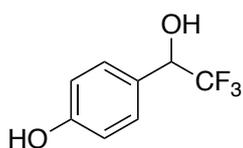
mixture and stirred at 50 °C for 1 h. The reaction mixture was quenched with sat. Na₂S₂O₃ aq. and extracted with Et₂O three times. After usual workup, the resultant crude product was purified by column chromatography (hexane:AcOEt=3:1) to give the desired product **2ab** (0.0639 g, 0.219 mmol, 73%) as a white solid.

2.10. General procedure for the deprotection of the THP group (General procedure 4)

To a 50 mL round-bottomed flask were added **4fb** (1.8814 g, 5.0000 mmol), MeOH (15 mL) and *p*-TsOH·H₂O (0.0978 g, 0.514 mmol, 10 mol%) and the mixture was stirred at r.t. for 1 h. Then, sat. NaHCO₃ aq. was added to the mixture and MeOH was removed *in vacuo*. The residue was extracted with Et₂O three times and the Et₂O layer was dried over anhydrous Na₂SO₄. The solvent was concentrated *in vacuo* and the precipitate was washed with hexane to give the desired product **2ab** as white solid (1.3305 g, 4.5542 mmol, 91%).

mp. 107.1-109.8 °C. Rf=0.33 (hexane:AcOEt=3:1). ¹H NMR: δ 2.39 (1H, d, *J*=5.1 Hz), 4.93 (1H, s), 5.14 (1H, dt, *J*=17.4, 5.1 Hz), 6.85-6.90 (2H, m), 7.35 (2H, d, *J*=8.4 Hz). ¹³C NMR (DMSO-*d*₆): δ 69.8 (dd, *J*=29.1, 21.0 Hz), 114.9, 125.7, 129.6, 158.1. ¹⁹F NMR: δ -128.16 (1F, dm, *J*=284.9 Hz), -127.53 (1F, dm, *J*=295.4 Hz), -126.12 (1F, dm, *J*=298.5 Hz), -120.07 (1F, dm, *J*=282.7 Hz), -82.12 (3F, m). IR (KBr) ν 3270, 2817, 2697, 1906, 1604, 1241, 1125, 1015, 918, 807 cm⁻¹. HRMS (FAB+, *m/z*): [M+H]⁺ Calcd for C₁₀H₈F₇O₂, 293.0407; Found, 293.0444.

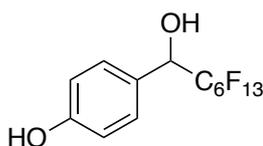
2.9.2. 2,2,2-Trifluoro-1-(3-hydroxyoxyphenyl)ethan-1-ol (**2aa**) [8]



Following to the “General procedure 3” using **4aa** (0.1447 g, 0.3077 mmol), 0.0415 g (0.216 mmol) of **2aa** was obtained in 72% yield as a white solid.

Rf=0.30 (hexane:AcOEt=3:1). ¹H NMR (acetone-*d*₆): δ 5.06 (1H, qd, *J*=7.2, 5.4 Hz), 5.76 (1H, d, *J*=5.4 Hz), 6.85 (2H, d, *J*=8.4 Hz), 7.34 (2H, d, *J*=8.1 Hz), 8.68 (1H, s). ¹³C NMR (acetone-*d*₆): δ 72.2 (q, *J*=29.7 Hz), 115.7, 115.8, 126.1 (q, *J*=277.9 Hz), 129.8, 158.8. ¹⁹F NMR (acetone-*d*₆): δ -77.38 (d, *J*=6.8 Hz).

2.9.3. 2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-(4-hydroxyphenyl)heptan-1-ol (**2ad**)



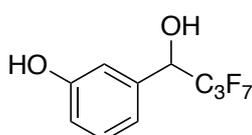
Following to the “General procedure 3” using **4ad** (0.1447 g, 0.3077 mmol), 0.0930g (0.216 mmol) of **2ad** was obtained in 70% yield as a white solid.

Following to the “General procedure 4” using **4fd** (2.6315 g, 5.0000 mmol), 2.1012 g (4.7520 mmol) of **2ad** was obtained in 95% yield as a white solid.

mp. 111.1-113.1 °C. Rf=0.33 (hexane:AcOEt=3:1). ¹H NMR: δ 2.43 (1H, d, *J*=5.1 Hz),

4.97 (1H, brs), 5.16 (1H, dt, $J=18.6, 5.1$ Hz), 6.88 (2H, d, $J=8.4$ Hz), 7.35 (2H, d, $J=8.1$ Hz). ^{13}C NMR (acetone- d_6): δ 72.0 (dd, $J=29.1, 21.7$ Hz), 115.9, 127.0, 130.5, 159.1. ^{19}F NMR: δ -128.95 (1F, dm, $J=288.6$ Hz), -128.17 (1F, dm, $J=280.7$ Hz), -126.65 (1F, dm, $J=283.9$ Hz), -123.93 (2F, m), -123.21 (2F, m), -122.43 (2F, m), -129.07 (1F, dm, $J=280.7$ Hz), -81.96 (3F, m). IR (KBr) ν 3411, 3037, 1899, 1698, 1615, 1519, 1455, 1365, 1229, 1066 cm^{-1} . HRMS (FAB+, m/z): $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_8\text{F}_{13}\text{O}_2$, 442.0233; Found, 442.0250.

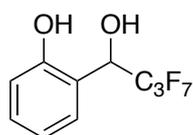
2.9.4. 2,2,3,3,4,4,4-Heptafluoro-1-(3-hydroxyoxyphenyl)butan-1-ol (2bb)



Following to the “General procedure 3” using **4bb** (0.0996 g, 0.300 mmol), 0.0779 g (0.268 mmol) of **2bb** was obtained in 89% yield as a white solid.

mp. 84.2-86.3 °C. Rf=0.33 (hexane:AcOEt=3:1). ^1H NMR: δ 3.71 (1H, s), 5.11 (1H, dd, $J=17.7, 6.0$ Hz), 6.87-6.91 (1H, dd, $J=8.1, 2.7$ Hz), 6.94 (1H, s), 6.99 (1H, d, $J=7.2$ Hz), 7.26 (H, t, $J=7.2$ Hz). ^{13}C NMR (acetone- d_6): δ 71.8 (dd, $J=28.5, 21.0$ Hz), 116.0, 116.8, 120.2, 130.0, 137.7, 158.2. ^{19}F NMR: δ -128.04 (1F, dm, $J=276.4$ Hz), -127.58 (1F, dm, $J=290.9$ Hz), -126.11 (1F, dm, $J=290.8$ Hz), -119.84 (1F, dm, $J=282.9$ Hz), -82.14 ~ -82.07 (3F, m). IR (KBr) ν 3270, 2817, 2697, 1906, 1604, 1241, 1125, 1015, 918, 807 cm^{-1} . HRMS (FAB+, m/z): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{10}\text{H}_8\text{F}_7\text{O}_2$, 293.0407; Found, 293.0452.

2.9.5. 2,2,3,3,4,4,4-Heptafluoro-1-(2-hydroxyoxyphenyl)butan-1-ol (2cb)

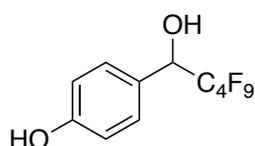


Following to the “General procedure 3” using **4cb** (0.0997 g, 0.300 mmol), (0.0358 g, 0.1225 mmol) of **2cb** was obtained in 41% yield as a white solid.

mp. 61.5-62.9 °C. Rf=0.30 (hexane:AcOEt=3:1). ^1H NMR: δ 3.53 (1H, d, $J=6.9$ Hz), 5.36-5.47 (1H, m), 6.28 (s, 1H), 6.88 (1H, dd, $J=7.5, 1.2$ Hz), 6.96 (1H, td, $J=7.5, 1.2$ Hz), 7.20 (d, $J=7.8$ Hz), 7.26-7.32 (1H, m). ^{13}C NMR (acetone- d_6): δ 65.5 (dd, $J=28.5, 21.0$ Hz), 116.1, 120.4, 122.5, 130.2, 130.8, 156.1. ^{19}F NMR: δ -128.16 (1F, dm, $J=284.9$ Hz), -127.53 (1F, dm, $J=295.4$ Hz), -126.12 (1F, dm, $J=298.5$ Hz), -120.07 (1F, dm, $J=282.7$ Hz), -82.12 (3F, m). IR (KBr) ν 3257, 2924, 2854, 1615, 1600, 1461, 1351, 1224, 1116, 917 cm^{-1} . HRMS (FAB+, m/z): $[\text{M}]^+$ Calcd for $\text{C}_{10}\text{H}_8\text{F}_7\text{O}_2$, 292.0329; Found, 292.0335.

2.11. 2,2,3,3,4,4,5,5,5-Nonafluoro-1-(4-hydroxyphenyl)pentan-1-ol (2ac)

To a 30 mL round-bottomed flask were added **4gc** (0.4427 g, 1.0010 mmol) and MeOH (5 mL), where 10 M NaOH (1 mL) was dropped slowly at -10 °C, and



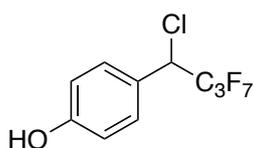
the mixture was stirred for 1 h at room temperature. Then, the reaction mixture was quenched with 4 M HCl at -10 °C and the

mixture was extracted with Et₂O three times. The combined Et₂O layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed *in vacuo* to give 0.3393 g (0.9919 mmol) of the white solid **2ac** which was found to be almost pure. (99% yield).

mp. 107.1-109.8 °C. Rf=0.40 (CHCl₃:acetone=8:1). ¹H NMR: δ 2.40 (1H, d, *J*=4.8 Hz), 4.94 (1H, brs), 5.15 (1H, dt, *J*=17.1, 5.4 Hz), 6.88 (2H, d, *J*=8.7 Hz), 7.36 (2H, d, *J*=8.4 Hz). ¹³C NMR (DMSO-*d*₆): δ 70.2 (dd, *J*=29.2, 21.7 Hz), 115.0, 125.8, 129.6, 158.2. ¹⁹F NMR: δ -128.13 (1F, dm, *J*=287.7 Hz), -127.34 (1F, dm, *J*=282.9 Hz), -126.76 (1F, dm, *J*=288.4 Hz), -123.48 (2F, m), -119.70 (1F, dm, *J*=285.2 Hz), -82.18 (3F, m). IR (KBr) ν 3426, 3038, 1901, 1615, 1519, 1456, 1353, 1135, 1038, 889 cm⁻¹. HRMS (FAB+, *m/z*): [M]⁺ Calcd for C₁₁H₇F₉O₂, 342.0297; Found, 342.0268.

2.12. General procedure for the chlorination of the benzylic alcohols (General procedure 5)

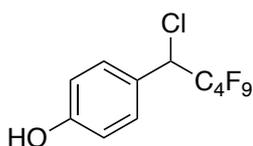
2.12.1. 4-(1-Chloro-2,2,3,3,4,4,4-heptafluorobutyl)phenol (**7b**)



To a 30 mL two-necked round-bottomed flask equipped with reflux condenser were added **2ab** (0.5843 g, 2.000 mmol) and THF (6 mL), where a solution containing SOCl₂ (0.20 mL, 2.4 mmol) and pyridine (0.18 ml, 2.2 mmol) in THF (2.0 mL) was introduced slowly at -10 °C, and the mixture was stirred for 1 h at the same temperature. Then, DMF (0.0143 g, 0.196 mmol) in THF (1 mL) was added and the reaction mixture was stirred at 80 °C for 1 h. The reaction mixture was quenched with H₂O and the mixture was extracted with Et₂O three times, and the usual workup afforded a crude product **7b** which was used in the next reaction without further purification. Because this chlorinated product was gradually decomposed, it must be used for the next reaction as soon as possible.

Rf=0.58 (CH₂Cl₂). ¹H NMR: δ 5.08 (1H, brs), 5.20 (1H, t, *J*=12.6 Hz), 6.82-6.85 (2H, m), 7.34-7.37 (2H, m). ¹⁹F NMR: δ -125.03 (2F, s), -118.07 (1F, d, *J*=278.1 Hz), -116.28 (1F, d, *J*=273.6 Hz), -82.01 (3F, t, *J*=8.5 Hz).

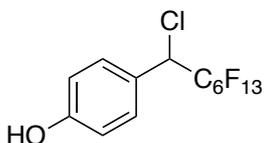
2.12.2. 4-(1-Chloro-2,2,3,3,4,4,5,5,5-nonafluoropentyl)phenol (**7c**)



Following to the “General procedure 5”, DMF (0.0296 g, 0.409 mmol) and **2ac** (0.6842 g, 2.000 mmol) were used for the synthesis of **7c**.

Rf=0.58 (CH₂Cl₂). ¹H NMR: δ 5.06 (1H, brs), 5.22 (1H, t, *J*=12.3 Hz), 6.82-6.87 (2H, m), 7.34-7.37 (2H, m). ¹⁹F NMR: δ -127.27 (1F, dm, *J*=15.0 Hz), -127.16 (1F, dm, *J*=15.0 Hz), -121.56 (2F, m), -117.47 (1F, dm, *J*=277.0 Hz), -115.64 (1F, dm, *J*=274.7 Hz), -82.14 (3F, m).

2.12.3. 4-(1-Chloro-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluorohexyl)phenol (**7d**)

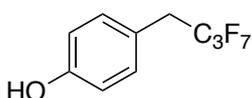


Following to the “General procedure 5”, DMF (0.0296 g, 0.409 mmol) and **2ad** (0.8843 g, 2.000 mmol) were used for the synthesis of **7d**.

Rf=0.58 (CH₂Cl₂). ¹H NMR: δ 5.10 (1H, brs), 5.22 (1H, t, *J*=12.6 Hz), 6.82-6.86 (2H, m), 7.34-7.37 (2H, m). ¹⁹F NMR: δ -127.49 (2F, m), -124.08 (2F, m), -123.13 (2F, m), -120.66 (2F, m), -117.31 (1F, dm, *J*=278.3 Hz), -115.61 (1F, dm, *J*=273.6 Hz), -82.07 (3F, m).

2.13. The reduction of the benzylic chlorides (General procedure 6)

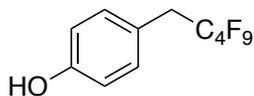
2.13.1. 4-(2,2,3,3,4,4,4-Heptafluorobutyl)phenol (**8b**)



To a 30 mL two-necked round-bottomed flask equipped with reflux condenser containing NaBH₄ (0.1644 g, 3.998 mmol) was added THF (5 mL), where **7b** prepared from **2ab** (0.5843 g, 2.000 mmol) in THF (2 mL) was introduced slowly at -10 °C, and the mixture was stirred for 30 min at room temperature and then 1 h at 80 °C. The reaction mixture was quenched with 1 M HCl at 0 °C and the usual workup afforded the crude product which was purified by column chromatography (CH₂Cl₂) to give 0.5120 g (1.854 mmol) of the desired product **8b** in 93% 2-step yield from **2ab** as a white solid.

mp. 76.6-78.0 °C. Rf=0.43 (CH₂Cl₂). ¹H NMR: δ 3.28 (2H, t, *J*=18.9 Hz), 4.84 (1H, s), 6.82 (2H, d, *J*=8.4 Hz), 7.16 (2H, d, *J*=8.1 Hz). ¹³C NMR (acetone-*d*₆): δ 36.2 (t, *J*=22.3 Hz), 116.3, 120.5, 133.0, 158.3. ¹⁹F NMR: δ -128.34 (2F, s), -124.89 (2F, m), -82.64 (3F, m). IR (KBr) ν 3403, 3049, 2947, 1899, 1616, 1518, 1449, 1348 1261, 845 cm⁻¹. HRMS (FAB+, *m/z*): [M]⁺ Calcd for C₁₀H₇F₇O, 276.0380; Found, 276.0390.

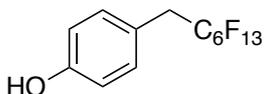
2.13.2. 4-(2,2,3,3,4,4,5,5,5-Nonafluoropentyl)phenol (**8c**)



Following to the “General procedure 6”, **8c** was prepared from **2ac** (0.6842 g, 2.000 mmol) and 0.6347 g (1.946 mmol) of **8c** was isolated in 97% 2-step yield from **2ac** as a white solid.

mp. 72.1-74.8 °C. Rf=0.43 (CH₂Cl₂). ¹H NMR: δ 3.29 (2H, t, *J*=18.9 Hz), 4.87 (1H, s), 6.83 (2H, d, *J*=8.4 Hz), 7.16 (2H, d, *J*=8.4 Hz). ¹³C NMR (acetone-*d*₆): δ 36.2 (t, *J*=21.7 Hz), 116.2, 120.5, 133.0, 158.2. ¹⁹F NMR: δ -127.25 (2F, m), -125.16 (2F, m), -114.99 (2F, m), -82.31 (3F, m). IR (KBr) ν 3409, 3058, 2956, 1898, 1615, 1517, 1450, 1351, 1245, 845 cm⁻¹. HRMS (FAB+, *m/z*): [M]⁺ Calcd for C₁₀H₇F₉O, 326.0348; Found, 326.0354.

2.13.3. 4-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluorohexyl)phenol (**8d**)

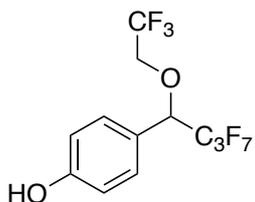


Following to the “**General procedure 6**”, **8d** was prepared from **2ad** (0.8844 g, 2.000 mmol) and 0.7618 g (1.788 mmol) of **8d** was isolated in 89% 2-step yield from **2ad** as a white solid.

mp. 91.7-93.0 °C. Rf=0.43 (CH₂Cl₂). ¹H NMR: δ 3.29 (2H, t, *J*=18.9 Hz), 4.85 (1H, s), 6.83 (2H, d, *J*=8.4 Hz), 7.16 (2H, d, *J*=8.4 Hz). ¹³C NMR (acetone-*d*₆): δ 36.4 (t, *J*=21.7 Hz), 116.2, 120.4, 133.0, 158.3. ¹⁹F NMR: δ -127.42 (2F, m), -124.21 (4F, m), -123.15 (2F, m), -114.77 (2F, m), -82.07 (3F, m). IR (KBr) ν 3351, 3029, 2956, 1897, 1616, 1517, 1453, 1358, 1233, 788 cm⁻¹. HRMS (FAB+, *m/z*): [M]⁺ Calcd for C₁₃H₇F₁₃O, 426.0284; Found, 426.0258.

2.14. The introduction of a polyfluoroalkoxy group (General procedure 7)

2.14.1. 4-(2,2,3,3,4,4,4-Heptafluoro-1-(2,2,2-trifluoroethoxy))butylphenol (**9ab**)

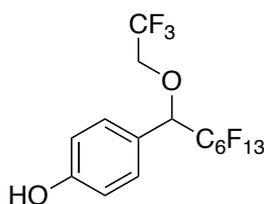


To a 30 mL two-necked round-bottomed flask equipped with reflux condenser containing NaH (55% dispersion in paraffin liquid, 0.1922 g, 4.4068 mmol) was added DME (2 mL), where 2,2,2-trifluoroethanol (0.4808 g, 4.806 mmol) in DME (3 mL) was introduced slowly and the reaction mixture was stirred for 30 min at the same temperature. Then, **7b** prepared from **2ab** (0.5843 g, 2.000 mmol) in DME (3 mL) was added slowly and the reaction mixture was stirred for 12 h at 80 °C. The reaction mixture was quenched with 1 M HCl at 0 °C and the mixture was extracted with Et₂O three times. The usual workup afforded the crude product which was purified by column chromatography (CH₂Cl₂) to give 0.6741 g (1.8016 mmol) of the desired product **9ab** in 90% 2-step yield from **2ab** as a yellow solid.

mp. 73.2-75.1 °C. Rf=0.27 (hexane:CH₂Cl₂=1:2). ¹H NMR: δ 3.71 (1H, dq, *J*=12.0, 8.4 Hz), 3.83 (1H, dq, *J*=12.0, 8.4 Hz), 4.89 (1H, dd, *J*=18.6, 3.3 Hz), 4.99 (1H, brs), 6.90 (2H, d, *J*=8.4 Hz), 7.32 (2H, d, *J*=8.4 Hz). ¹³C NMR (acetone-*d*₆): δ 66.6 (q, *J*=34.1 Hz), 79.6 (dd, *J*=31.6, 20.4 Hz), 116.6, 121.6, 126.6 (q, *J*=276.1 Hz), 131.6, 160.1. ¹⁹F NMR: δ -128.53 (1F, dm, *J*=287.5 Hz), -128.38 (1F, dm, *J*=295.4 Hz), -126.15 (1F, dm, *J*=288.6 Hz), -117.95 (1F, dm, *J*=287.5 Hz), -82.20 (3F, m), -75.26 (3F, t, *J*=9.0 Hz). IR (KBr) ν 3316, 3034, 2947, 2713, 2459, 2114, 1904, 1516, 1227, 945 cm⁻¹. HRMS (FAB+, *m/z*): [M+H]⁺ Calcd for C₁₂H₉F₁₀O₂, 375.0437; Found, 375.0480.

2.14.2. 4-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-(2,2,2-trifluoroethoxy)heptyl)phenol (**9ad**)

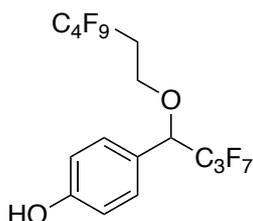
Following to the “**General procedure 7**”, **9ad** was prepared from **2ad** (0.8844 g, 2.000 mmol) and 0.9567 g (1.778 mmol) of **9ad** was obtained in 89% 2-step yield from **7c** as a



yellow solid.

mp. 83.2-85.6 °C. Rf=0.30 (hexane:AcOEt=3:1). ¹H NMR: δ 3.70 (1H, dq, *J*=12.0, 8.4 Hz), 3.82 (1H, dq, *J*=12.0, 8.4 Hz), 4.92 (1H, dd, *J*=18.6, 4.2 Hz), 5.02 (1H, brs), 6.91 (2H, d, *J*=8.7 Hz), 7.32 (2H, d, *J*=8.7 Hz). ¹³C NMR (acetone-*d*₆): δ 66.7 (q, *J*=35.0 Hz), 79.9 (dd, *J*=32.2, 21.1 Hz), 116.7, 121.7, 126.6 (q, *J*=277.2 Hz), 131.6, 160.3. ¹⁹F NMR: δ -128.30 (1F, dm, *J*=298.8 Hz), -127.27 (1F, dm, *J*=284.9 Hz), -126.75 (1F, dm, *J*=289.7 Hz), -124.86 (1F, dm, *J*=294.2 Hz), -124.23 (1F, dm, *J*=305.0 Hz), -123.46 (1F, dm, *J*=287.5 Hz), -122.95 (2F, m), -122.83 (1F, dm, *J*=292.0 Hz), -117.54 (1F, dm, *J*=289.7 Hz) -82.20 (3F, m), -75.30 (3F, t, *J*=9.0 Hz). IR (KBr) ν 3392, 3044, 2944, 2710, 2466, 2149, 1901, 1516, 1223, 943 cm⁻¹. HRMS (FAB+, *m/z*): [M+H]⁺ Calcd for C₁₅H₉F₁₆O₂, 525.0342; Found, 525.0343.

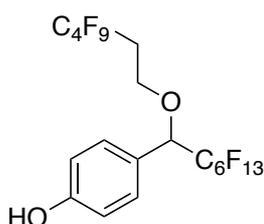
2.14.3. 4-{2,2,3,3,4,4,4-Heptafluoro-1-(3,3,4,4,5,5,6,6,6-nonafluorohexyloxy)butyl}phenol (9bb)



Following to the “**General procedure 7**”, 3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (1.2682 g, 4.8021 mmol) was used instead of 2,2,2-trifluoroethanol and 0.7729 g (1.4744mmol) of **9bb** was obtained in 74% 2-step yield from **2ab** as a brown liquid.

Rf=0.27 (hexane:CH₂Cl₂=1:2). ¹H NMR: δ 2.43 (2H, tt, *J*=18.6, 6.3 Hz), 3.57 (1H, dt, *J*=9.9, 6.3 Hz), 3.72 (1H, dt, *J*=9.9, 6.3 Hz), 4.70 (1H, dd, *J*=18.0, 3.3 Hz), 4.97 (1H, brs), 6.89 (2H, d, *J*=8.7 Hz), 7.30 (2H, d, *J*=8.4 Hz). ¹³C NMR (acetone-*d*₆): δ 31.7 (t, *J*=21.0 Hz), 62.1 (t, *J*=4.3 Hz), 79.0 (dd, *J*=31.0, 20.4 Hz), 116.3, 122.6, 131.3, 159.8. ¹⁹F NMR: δ -128.41 (1F, dm, *J*=290.2 Hz), -128.34 (1F, dm, *J*=294.5 Hz), -127.39 (2F, m), -125.97 (1F, dm, *J*=285.2 Hz), -125.95 (2F, m), -117.80 (1F, dm, *J*=287.5 Hz), -115.09 (2F, m), -82.36 ~ -82.11 (6F, m). IR (CHCl₃) ν 3337, 3023, 2900, 1614, 1516, 1425, 1220, 1136, 880, 760 cm⁻¹. HRMS (FAB+, *m/z*): [M]⁺ Calcd for C₁₆H₁₀F₁₆O₂, 538.0420; Found, 538.0443.

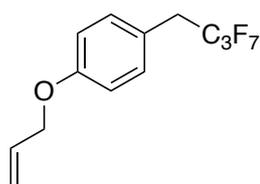
2.14.4. 4-{2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-(3,3,4,4,5,5,6,6,6-nonafluorohexyloxy)heptyl}phenol (9bd)



Following to the “**General procedure 7**”, 3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (1.2684 g, 4.803 mmol) and **7d** prepared from **2ad** (0.8843 g, 2.000 mmol) were used, and after purification by column chromatography (CH₂Cl₂), the obtained solid was washed with hexane to give 0.6352 g (0.9229 mmol) of the desired product **9bd** in 46% 2-step yield from **2ad** as a white solid.

mp. 90.0-90.5 °C. Rf=0.40 (hexane:AcOEt=3:1). ¹H NMR: δ 2.43 (2H, tt, *J*=18.3, 6.3 Hz), 3.57 (1H, dt, *J*=9.9, 6.3 Hz), 3.63 (1H, dt, *J*=9.9, 6.3 Hz), 4.73 (1H, dd, *J*=18.9, 3.3 Hz), 4.93 (1H, brs), 6.89 (2H, d, *J*=8.7 Hz), 7.31 (2H, d, *J*=8.1 Hz). ¹³C NMR (Acetone-*d*₆): δ 31.5 (t, *J*=21.1 Hz), 62.0 (t, *J*=4.0 Hz), 79.1 (dd, *J*=31.6, 21.0 Hz), 116.2, 122.5, 131.3, 159.7. ¹⁹F NMR: δ -128.27 (1F, dm, *J*=305.5 Hz), -127.42 (2F, m), -126.72 (1F, dm, *J*=297.9 Hz), -125.99 (2F, m), -125.96 (1F, dm, *J*=307.8 Hz), -124.80 (1F, dm, *J*=283.2 Hz), -124.25 (1F, dm, *J*=282.9 Hz), -123.54 (1F, dm, *J*=290.3 Hz), -123.41 (1F, dm, *J*=287.6 Hz), -122.86 (1F, dm, *J*=288.3 Hz), -122.26 (1F, dm, *J*=285.2 Hz), -117.35 (1F, dm, *J*=289.7 Hz), -115.09 (2F, m), -82.33 (3F, m), -82.11 (3F, m). IR (KBr) ν 3213, 2969, 2707, 2491, 1617, 1517, 1368, 1233, 1136, 878 cm⁻¹. HRMS (FAB+, *m/z*): [M]⁺ Calcd for C₁₉H₁₀F₂₂O₂, 688.0324; Found, 688.0352.

2.15. 1-(Allyloxy)-4-(2,2,3,3,4,4,4-heptafluorobutyl)benzene (**10**)

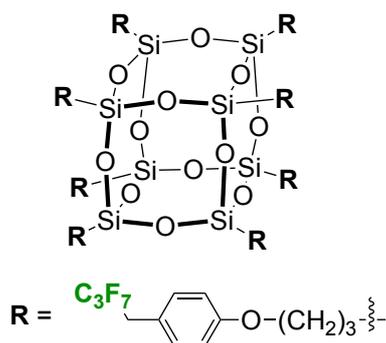


To a 30 mL two-necked round-bottomed flask equipped with reflux condenser, K₂CO₃ (0.1970, 1.425 mmol), **8b** (0.2762 g, 1.000 mmol) and acetone (4 mL/mmol) were introduced, where allyl bromide (0.12 mL, 1.4 mmol) was added. After stirring for 12 h under reflux temperature, the solvent was removed *in vacuo* where 1 M HCl was added and the mixture was extracted with Et₂O. After usual workup, the crude product was purified by column chromatography (hexane:AcOEt=1:40 to 20:1) to give the desired product **10** as a colorless liquid (0.3110 g, 0.9835 mmol, 98%).

Rf=0.53 (hexane:AcOEt=20:1). ¹H NMR: δ 3.29 (2H, t, *J*=18.6 Hz), 4.54 (2H, dt, *J*=5.1, 1.5 Hz), 5.30 (1H, ddt, *J*=10.7, 2.7, 1.5 Hz), 5.42 (1H, ddt, *J*=17.1, 2.7, 1.5 Hz), 6.06 (1H, ddt, *J*=17.1, 10.5, 5.4 Hz), 6.89-6.93 (2H, m), 7.20 (2H, d, *J*=8.4 Hz). ¹³C NMR: δ 36.0 (t, *J*=22.3 Hz), 68.8, 114.8, 117.7, 120.9, 131.9, 133.1, 158.6. ¹⁹F NMR: δ -125.54 (2F, m), -115.69 (2F, m), -81.76 (3F, t, *J*=9.0 Hz). IR (CHCl₃) ν 3013, 2938, 1614, 1514, 1353, 1667, 1171, 1115, 940, 849 cm⁻¹. HRMS (FAB +, *m/z*): [M]⁺ Calcd for C₁₃H₁₁F₇O, 316.0693; Found, 316.0726.

2.16. F-POSS (**11b**)

To a 10 mL two-necked round-bottomed were added **10** (0.3075 g, 0.9725 mmol), **11a** [9] (0.0427 g, 0.101 mmol), and H₂PtCl₆·6H₂O (0.0054 g, 0.010 mmol, *i*-PrOH (0.10 mL) solution). After stirring for 18 h under 90 °C, the mixture was filtered with Celite (washed with Et₂O) and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (hexane:AcOEt=10:1 to 6:1) to give the desired product **11b** as a white solid (0.0886 g, 0.0302 mmol, 30%).



mp. 98.6-99.8 °C. R_f=0.21 (hexane:AcOEt=10:1).

¹H NMR: δ 0.76 (16H, m), 1.87 (16H, m), 3.21 (16H, t, J=18.9 Hz), 3.94 (16H, t, J=6.3 Hz), 6.83 (16H, d, J=8.4 Hz), 7.12 (16H, d, J=8.1 Hz). ¹³C NMR: δ 8.1, 22.7, 35.9 (t, J=22.3 Hz), 69.3, 114.4, 120.6, 131.8, 158.9. ¹⁹F NMR: δ -128.66 (16F, m), -115.76 (16F, m), -81.88 (24F, t, J=9.3 Hz). IR (KBr) ν 3040, 2942, 2867, 2297, 1893, 1614, 1515, 1354, 1219, 1118 cm⁻¹. Anal. Calcd for C₁₀₄H₉₆F₅₆O₁₉Si₈

C, 42.51; H, 3.29; F, 36.21; O, 10.35; Si, 7.65. Found: C, 42.72; H, 3.17.

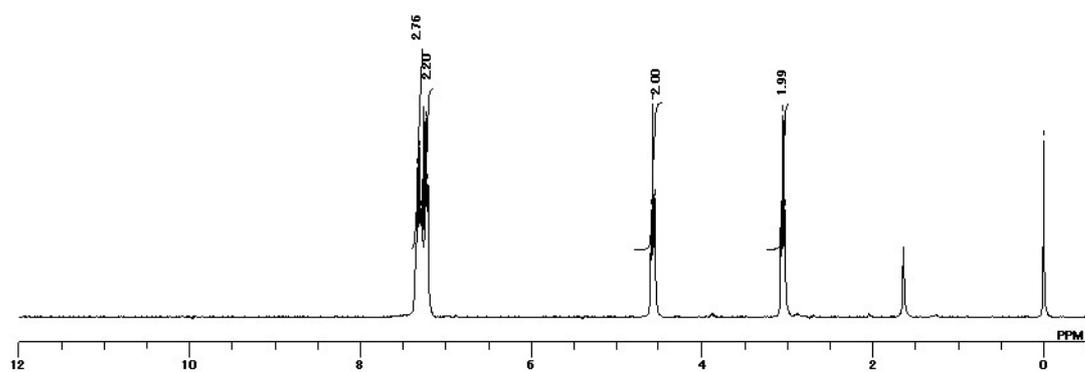
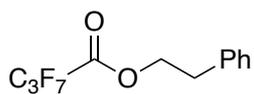
2.17. References

1. Mori, A.; Mizusaki, T.; Miyakawa, Y.; Ohashi, E.; Haga, T.; Maegawa, T.; Monguchi, Y.; Saiki, H. *Tetrahedron* **2006**, *62*, 11925–11932.
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3. Senboku, H.; Michinishi, J.-Y.; Hara, S. *Synlett* **2011**, 1567–1572.
4. Bergueiro, J.; Montenegro, J.; Saa, C.; Lopez, S. *RSC Adv.* **2014**, *4*, 14475–14479.
5. Sometimes we noticed that MgBr₂ shortly after opening did not affect this reaction.
6. Wu, S.; Zeng, W.; Wang, Q.; Chen, F.-X. *Org. Biomol. Chem.* **2012**, *10*, 9334–9337.
7. Pistritto, V. A.; Paolillo, J. M.; Bisset, K. A.; Leadbeater, N. E. *Org. Biomol. Chem.* **2018**, *16*, 4715–4719.
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9. Liu, L.-K.; Dare, O., E. *J. Chin. Chem. Soc.* **2004**, *51*, 175–182.

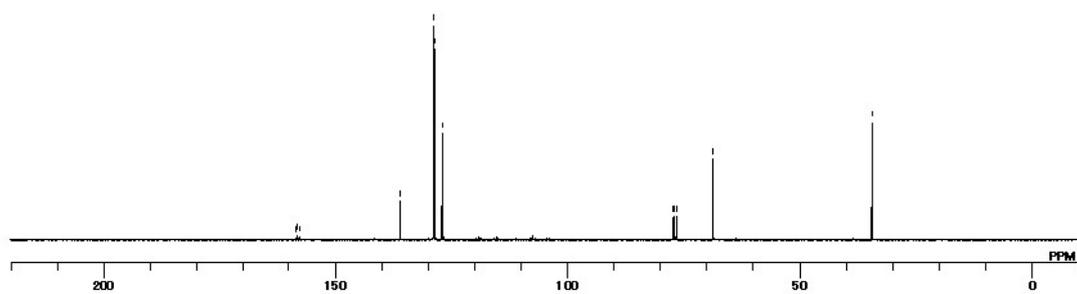
3. Spectral data

2-Phenylethyl 2,2,3,3,4,4,4-heptafluorobutyrate

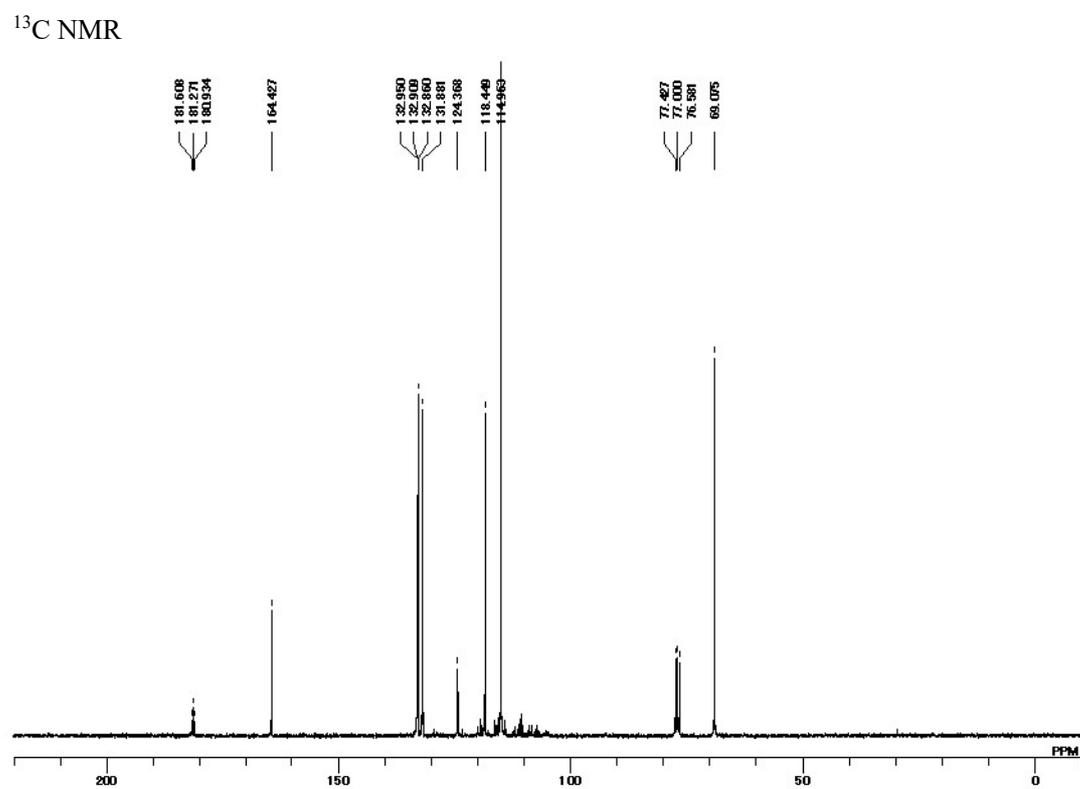
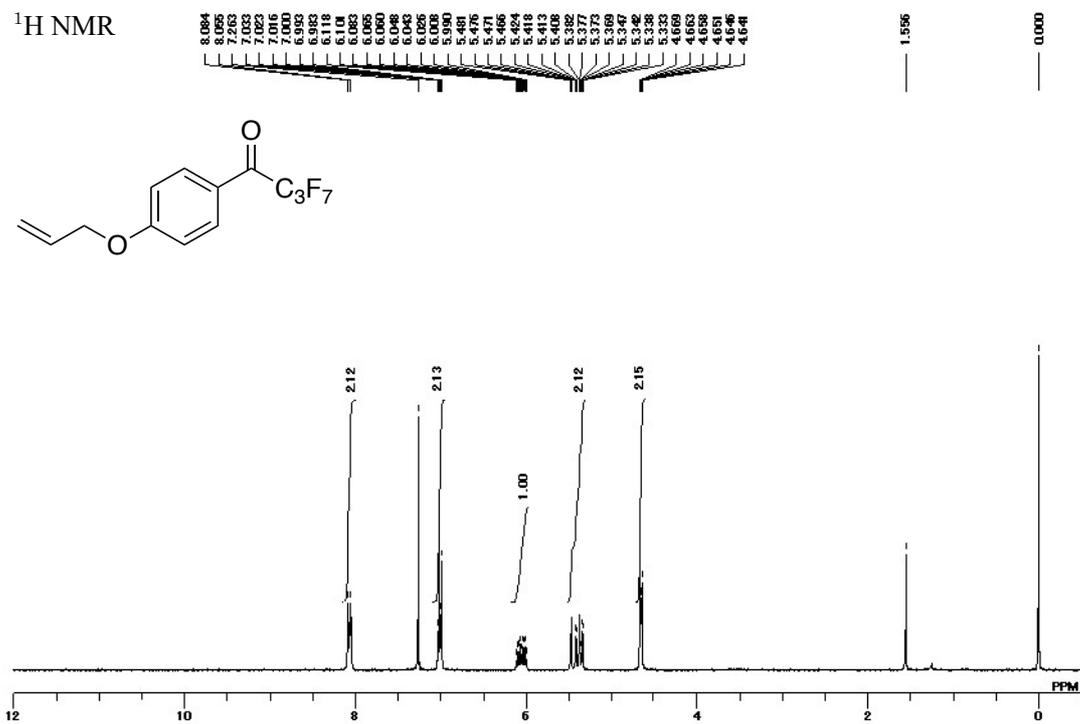
¹H NMR



¹³C NMR

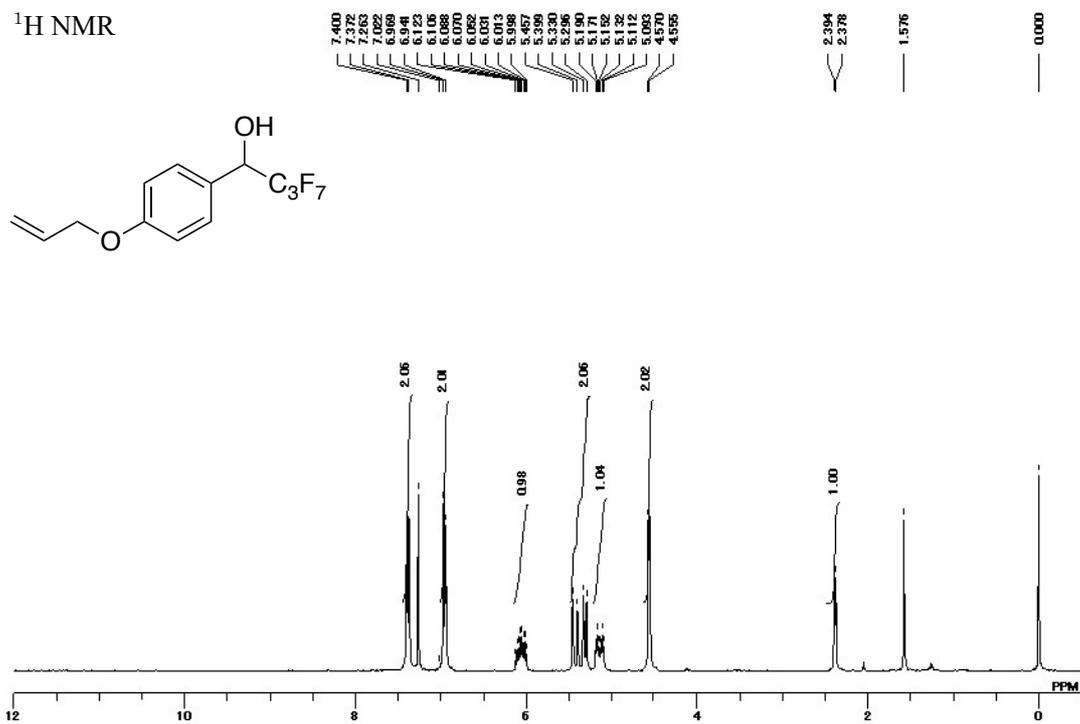


1-{4-(Allyloxy)phenyl}-2,2,3,3,4,4,4-heptafluorobutan-1-one (3a)

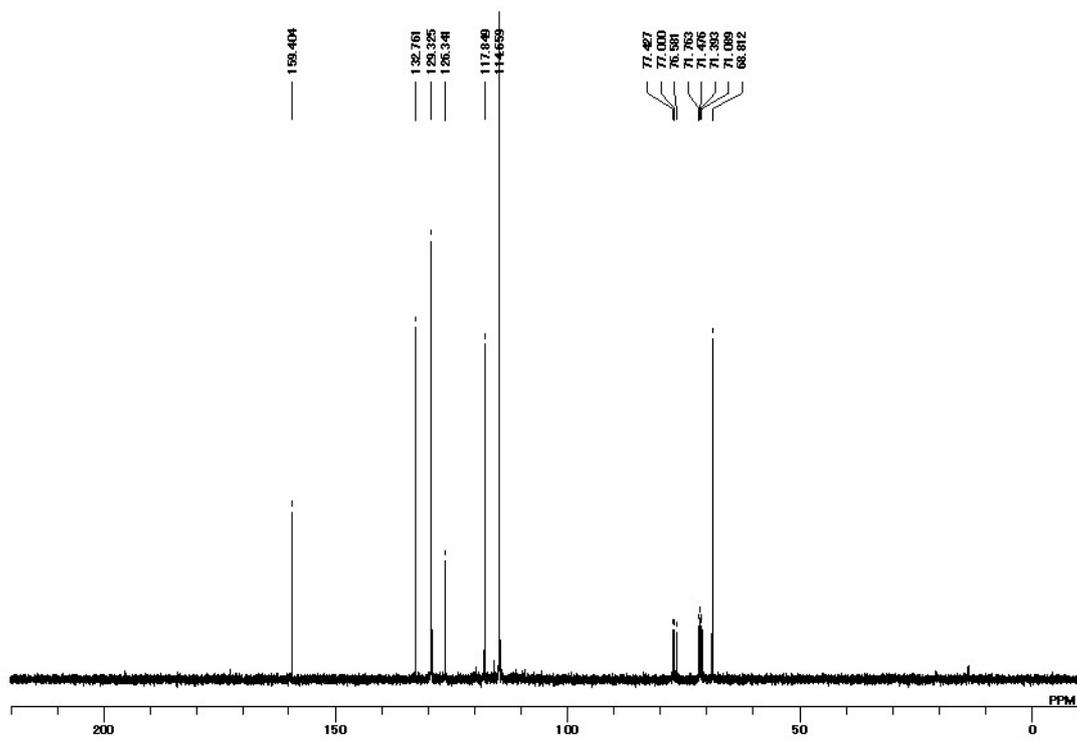


1-{4-(Allyloxy)phenyl}-2,2,3,3,4,4,4-heptafluorobutan-1-ol (4ab)

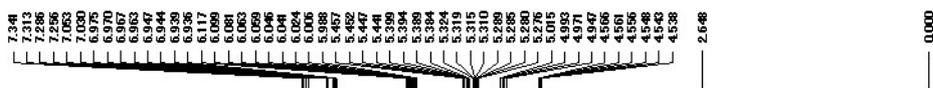
$^1\text{H NMR}$



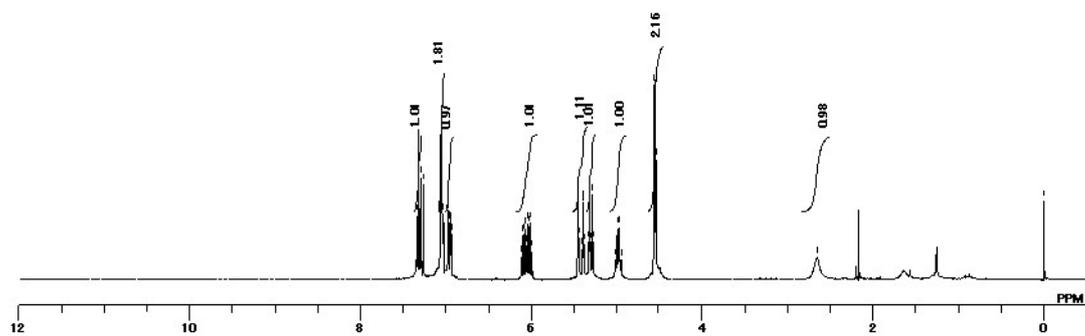
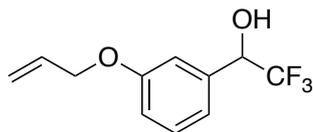
$^{13}\text{C NMR}$



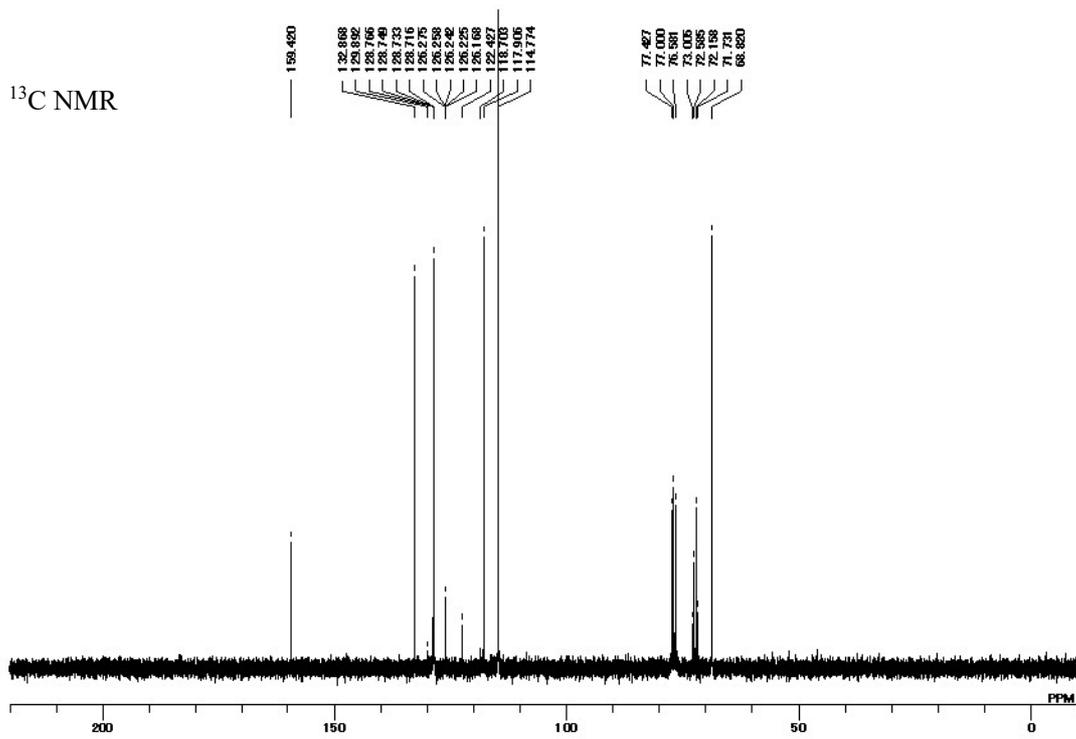
1-{3-(Allyloxy)phenyl}-2,2,2-trifluoroethan-1-ol (4ba)



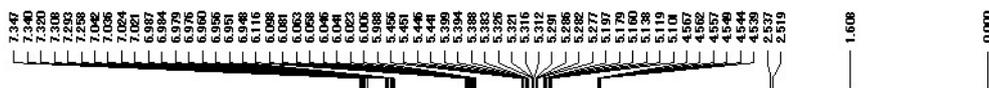
¹H NMR



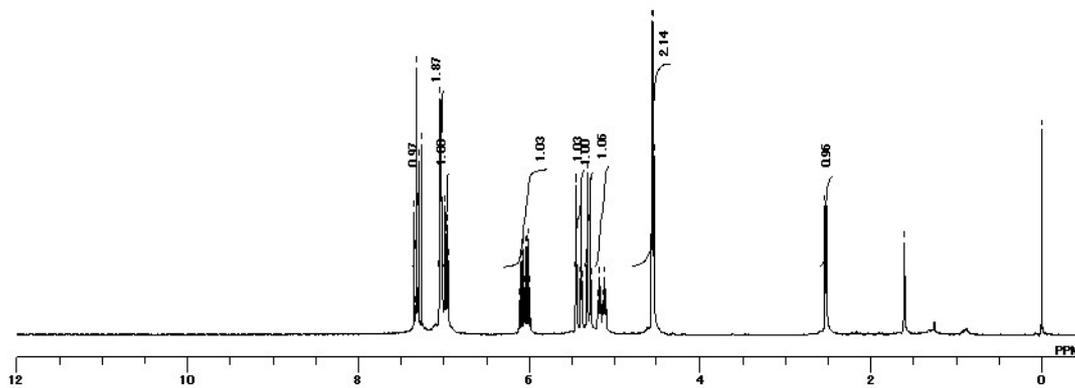
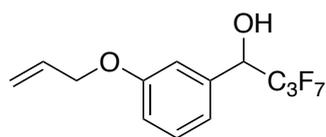
¹³C NMR



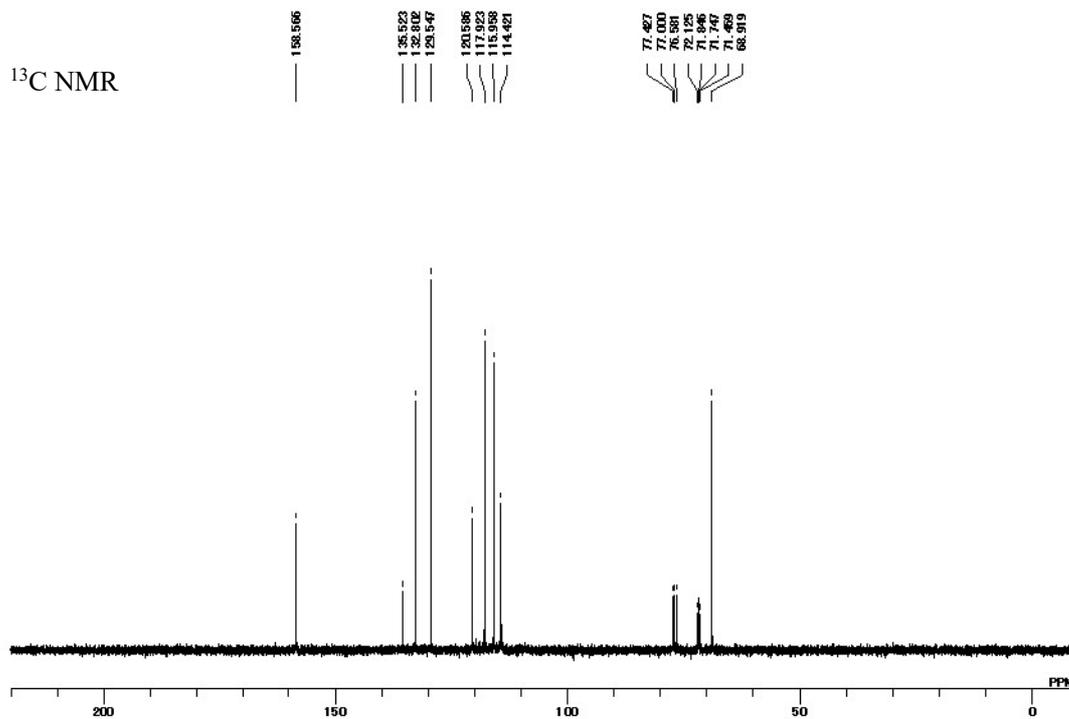
1-{3-(Allyloxy)phenyl}-2,2,3,3,4,4,4-heptafluorobutan-1-ol (4b)



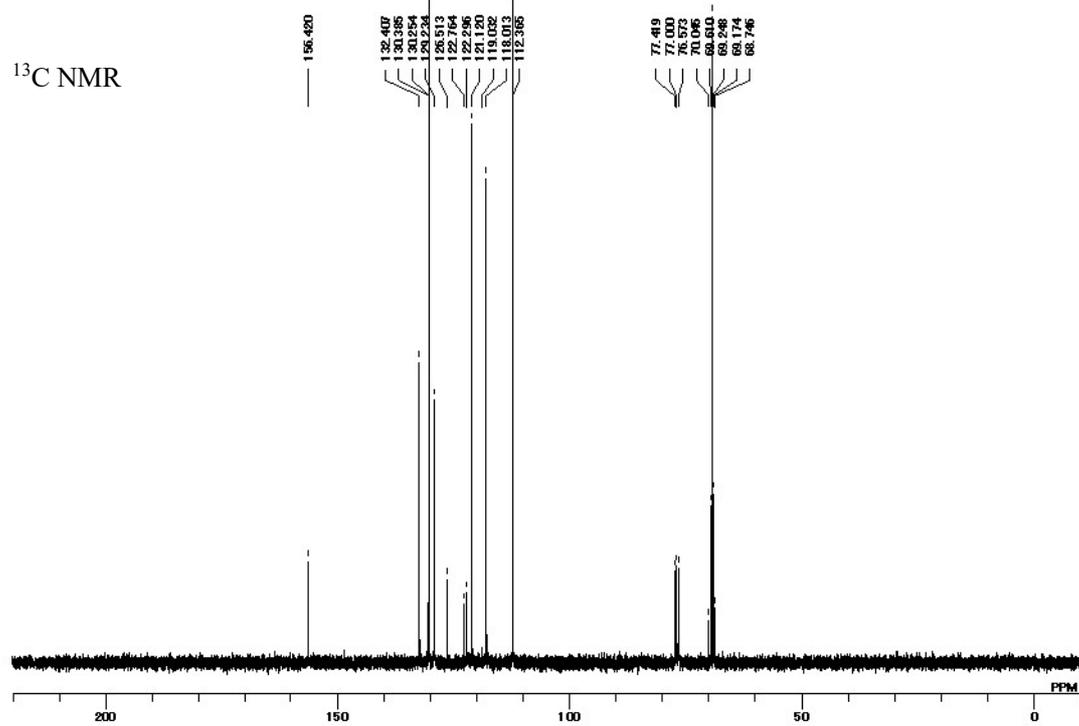
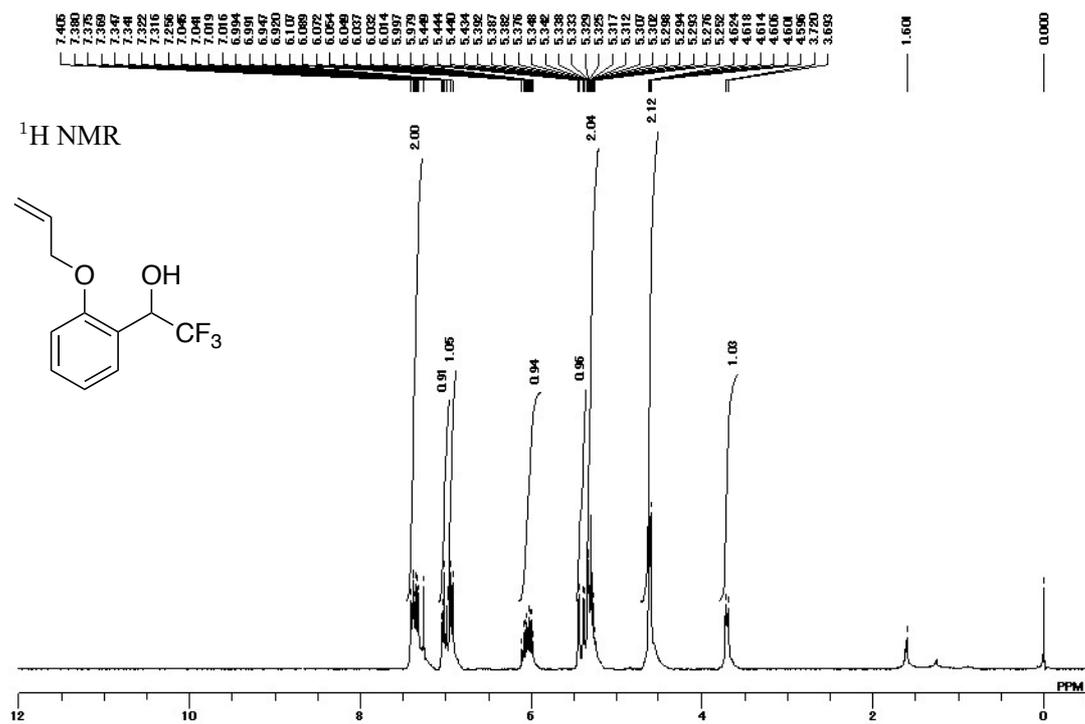
¹H NMR



¹³C NMR

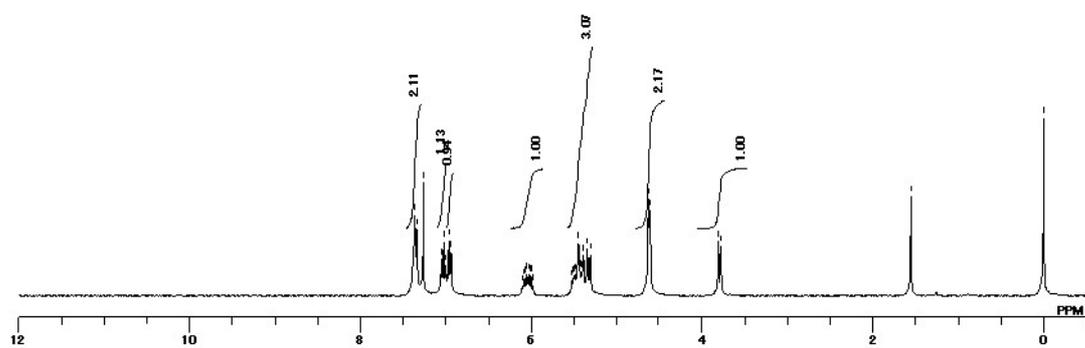
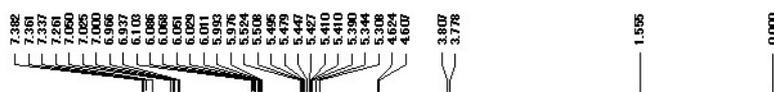
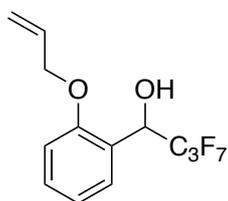


1-{2-(Allyloxy)phenyl}-2,2,2-trifluoroethan-1-ol (4ca)

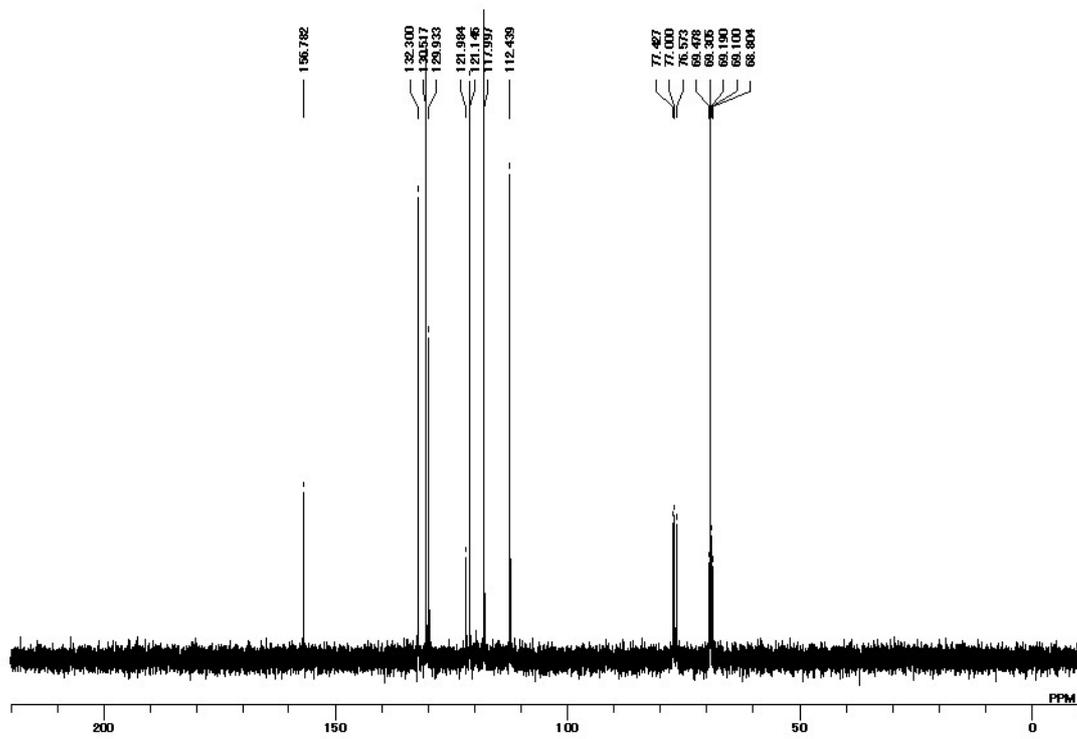


1-{2-(Allyloxy)phenyl}-2,2,3,3,4,4,4-heptafluorobutan-1-ol (4cb)

¹H NMR

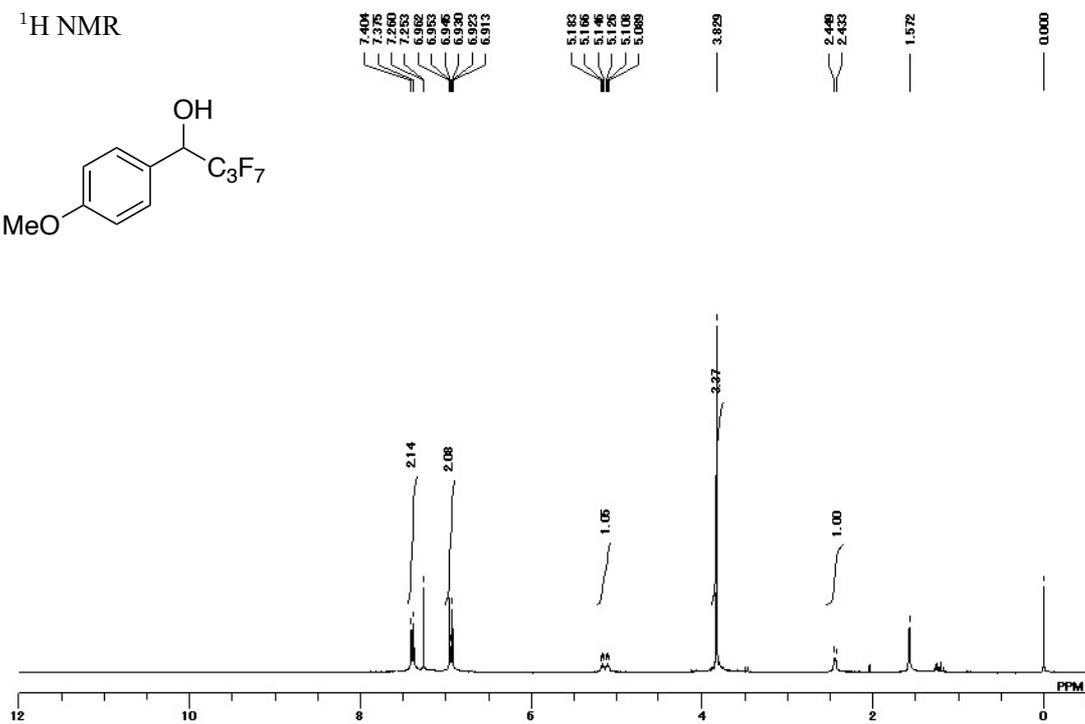
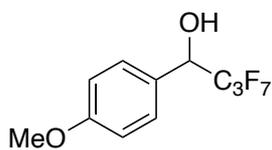


¹³C NMR

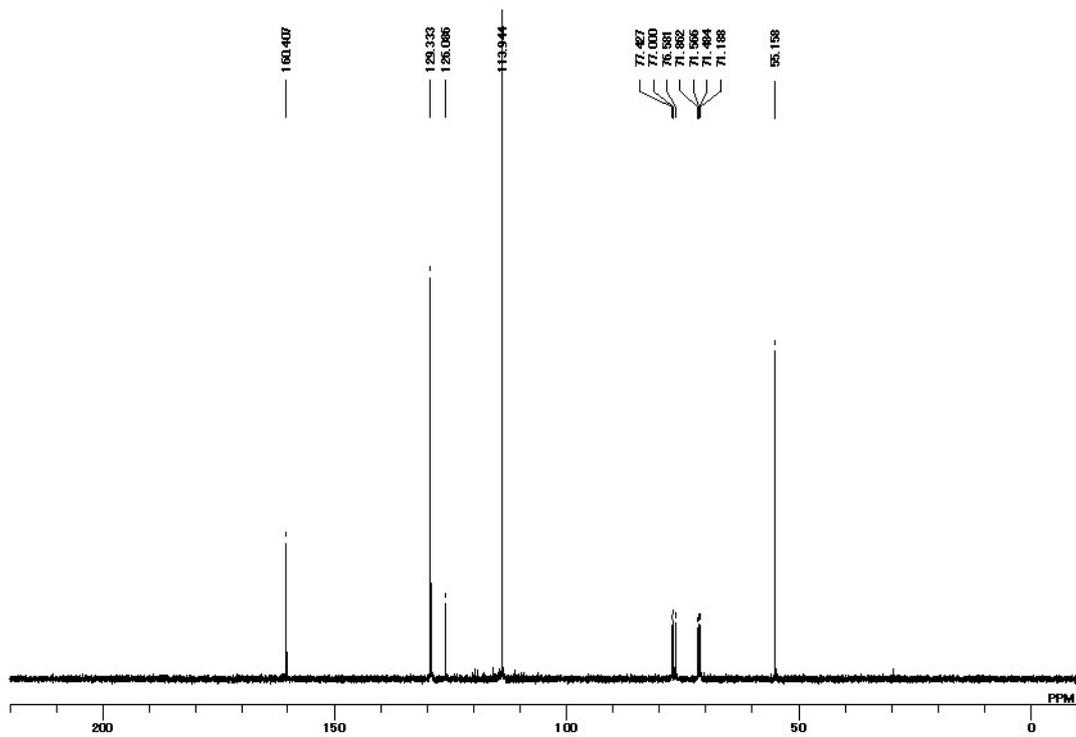


2,2,3,3,4,4,4-Heptafluoro-1-(4-methoxyphenyl)butan-1-ol (4db)

¹H NMR

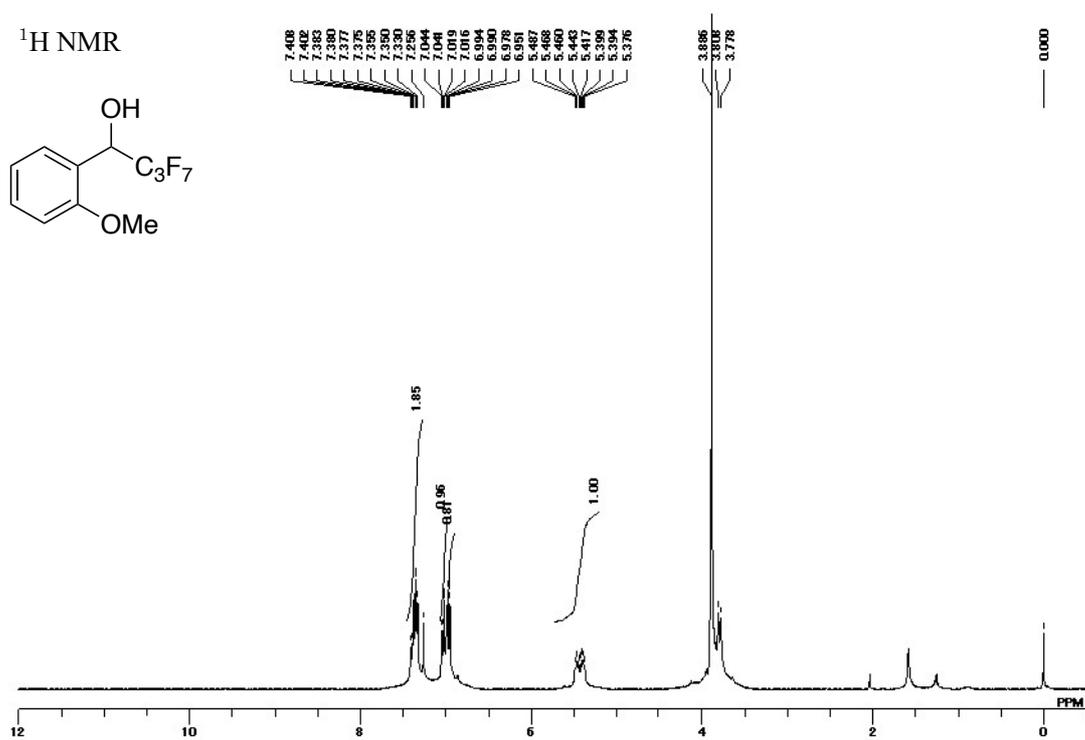
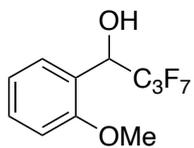


¹³C NMR

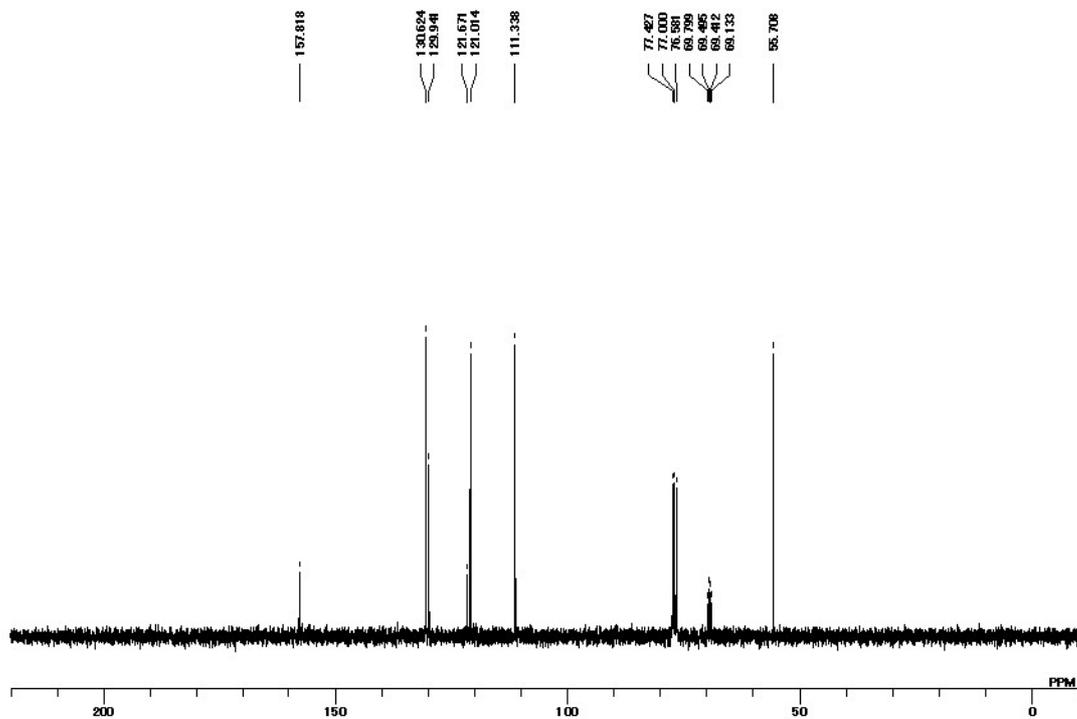


2,2,3,3,4,4,4-Heptafluoro-1-(2-methoxyphenyl)butan-1-ol (4b)

¹H NMR

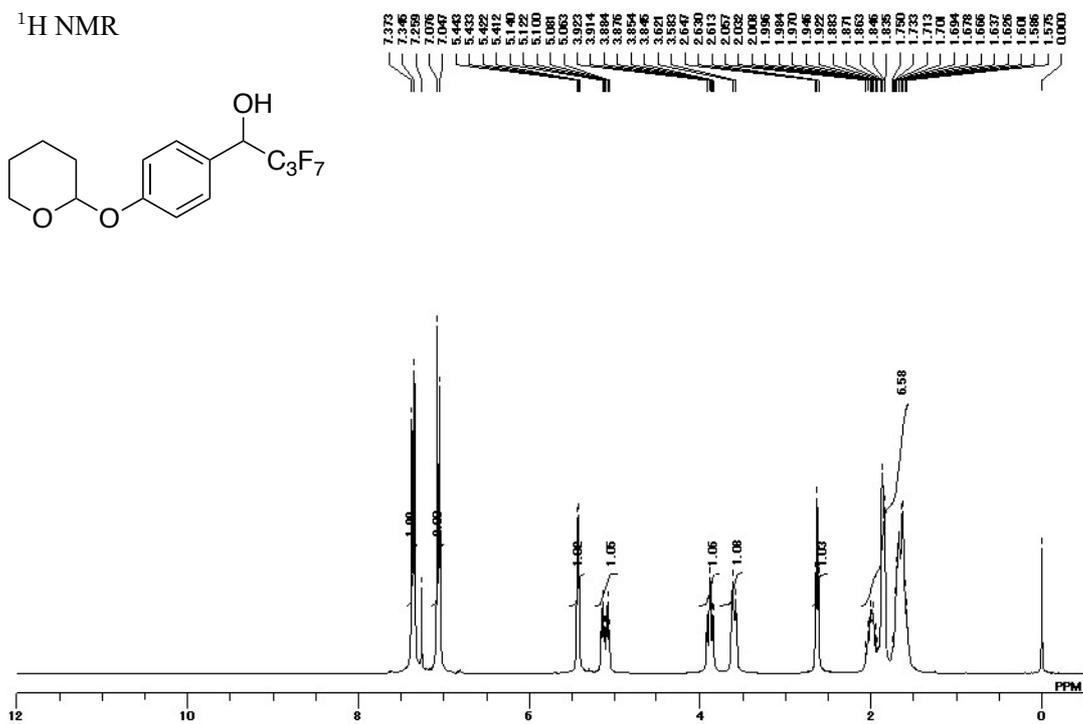
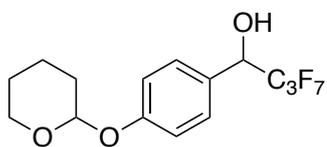


¹³C NMR

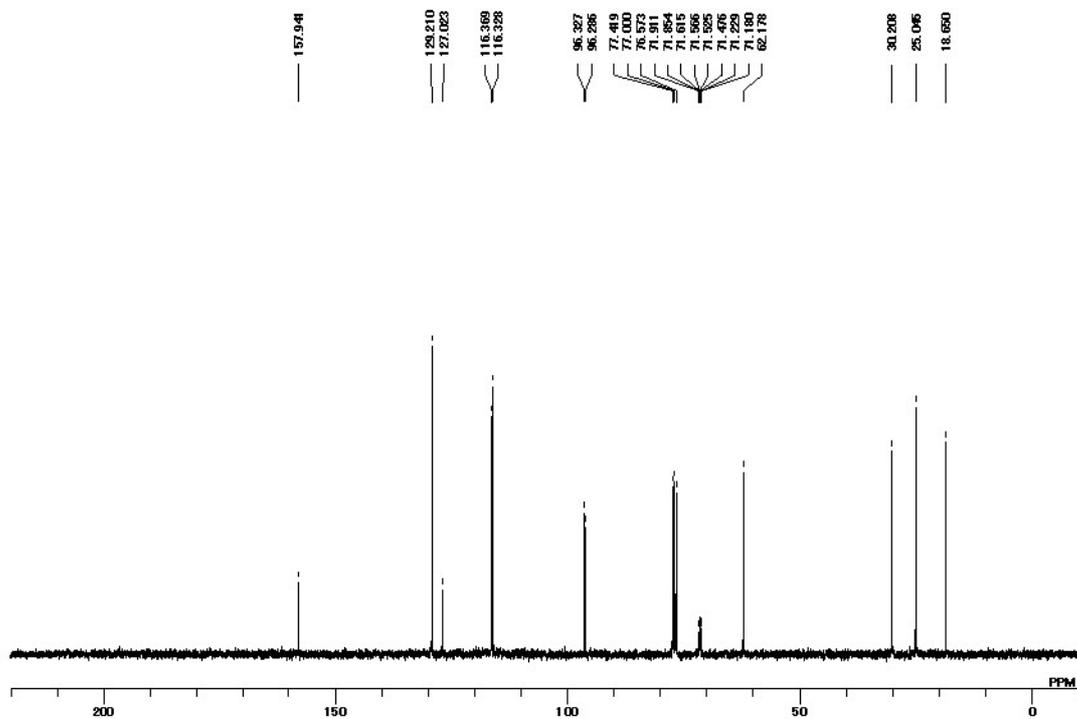


2,2,3,3,4,4,4-Heptafluoro-1-[4-{{tetrahydro-2H-pyran-2-yl}oxy}phenyl]butan-1-ol (4fb)

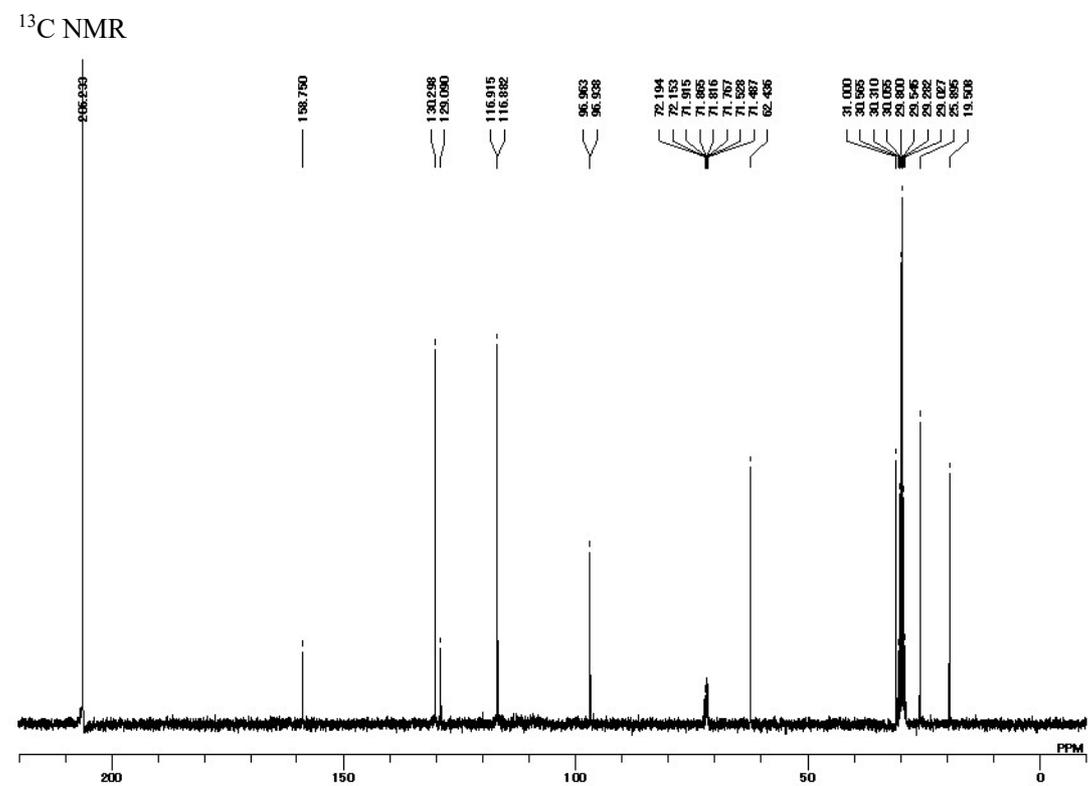
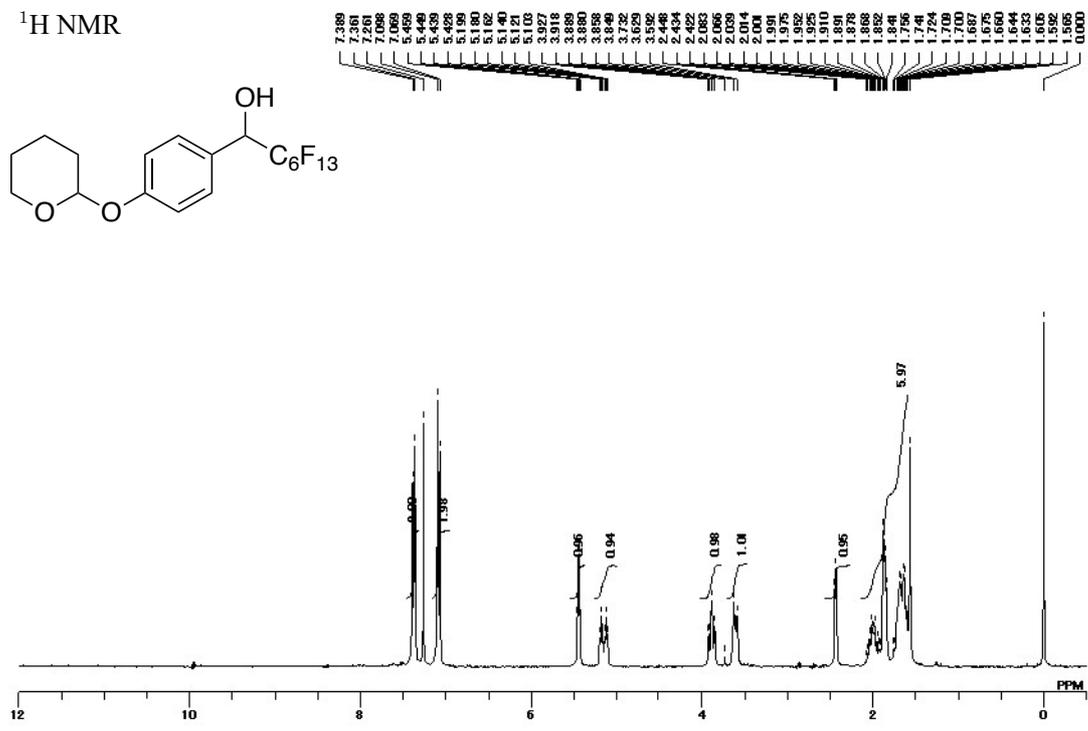
¹H NMR



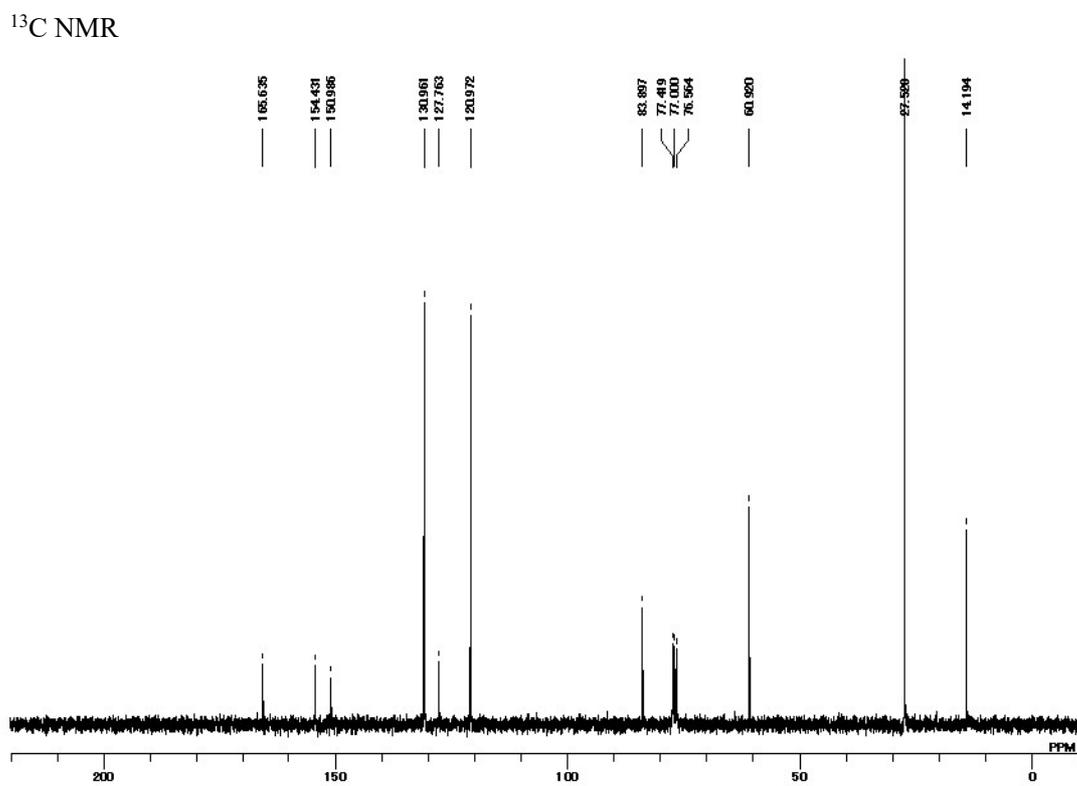
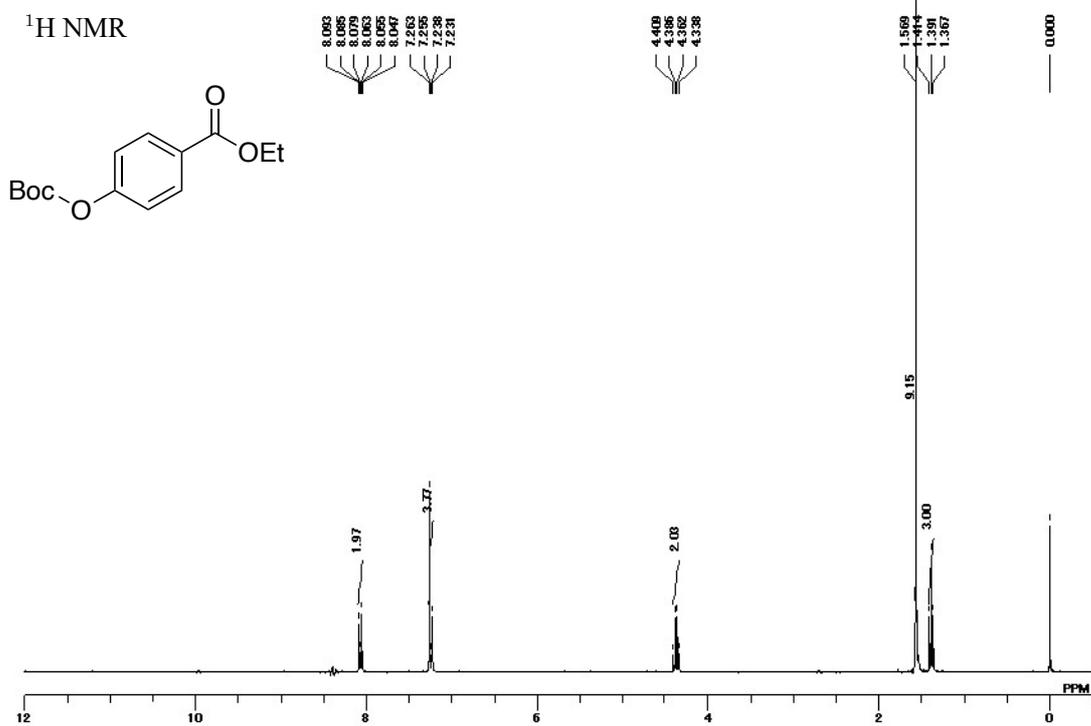
¹³C NMR



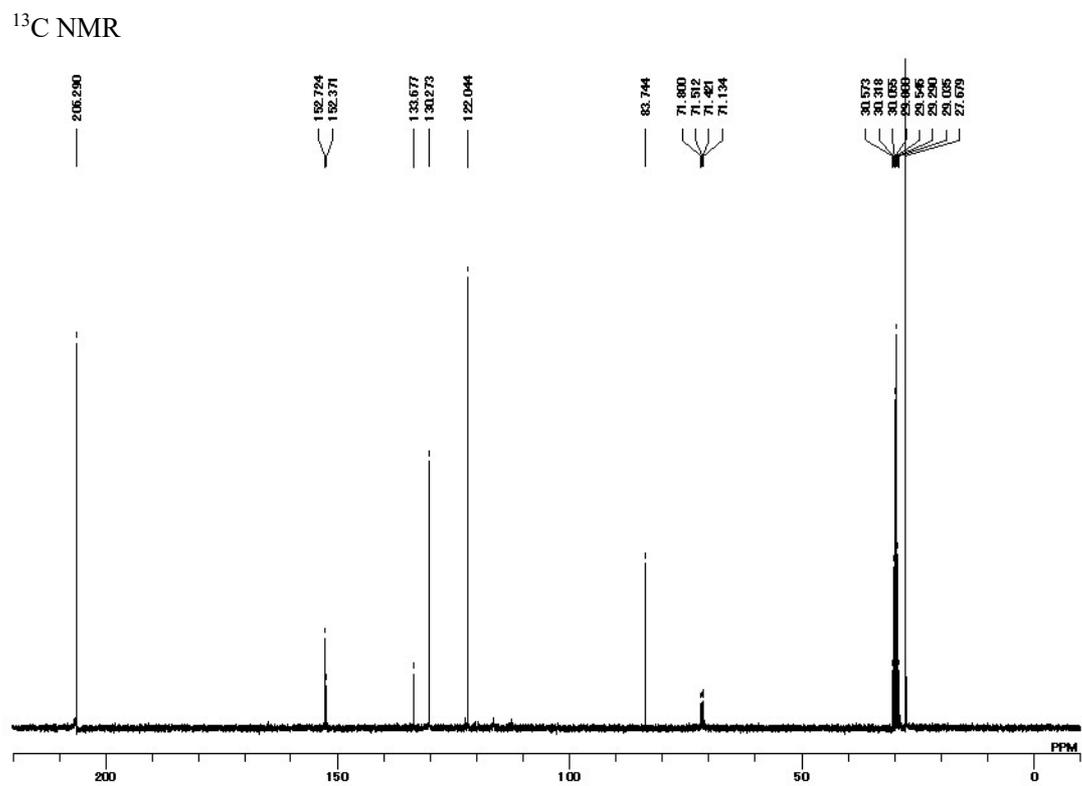
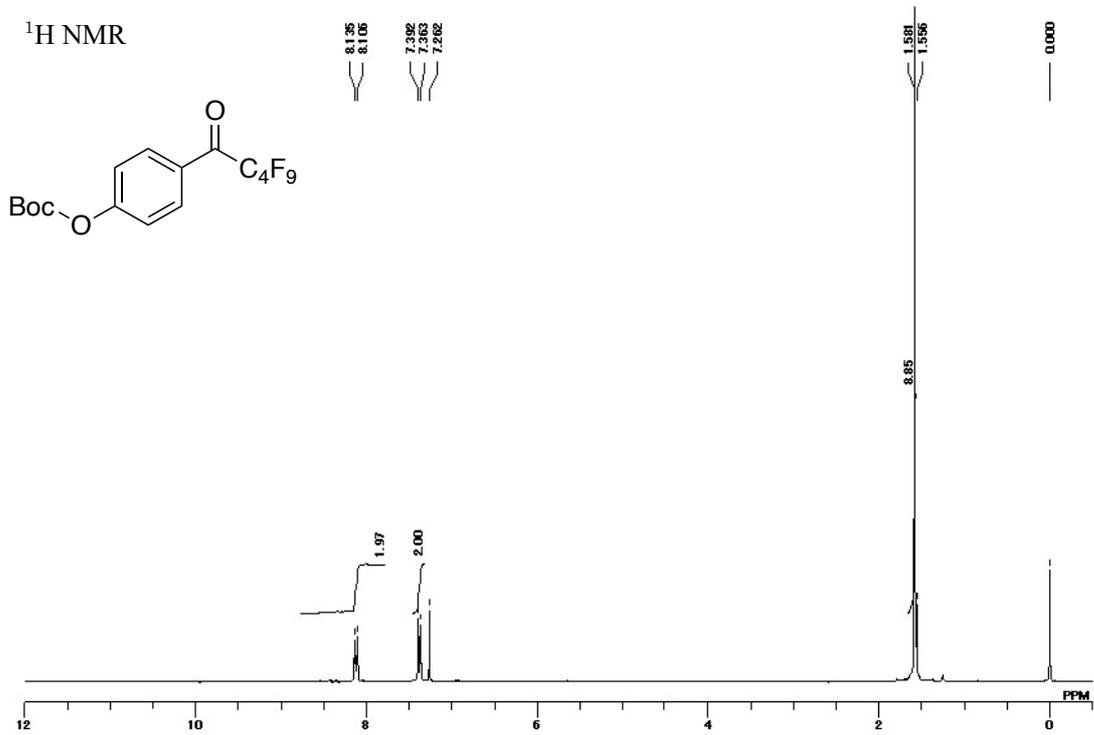
2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-[4-{{tetrahydro-2H-pyran-2-yl}oxy}phenyl]-heptan-1-ol
(4fd)



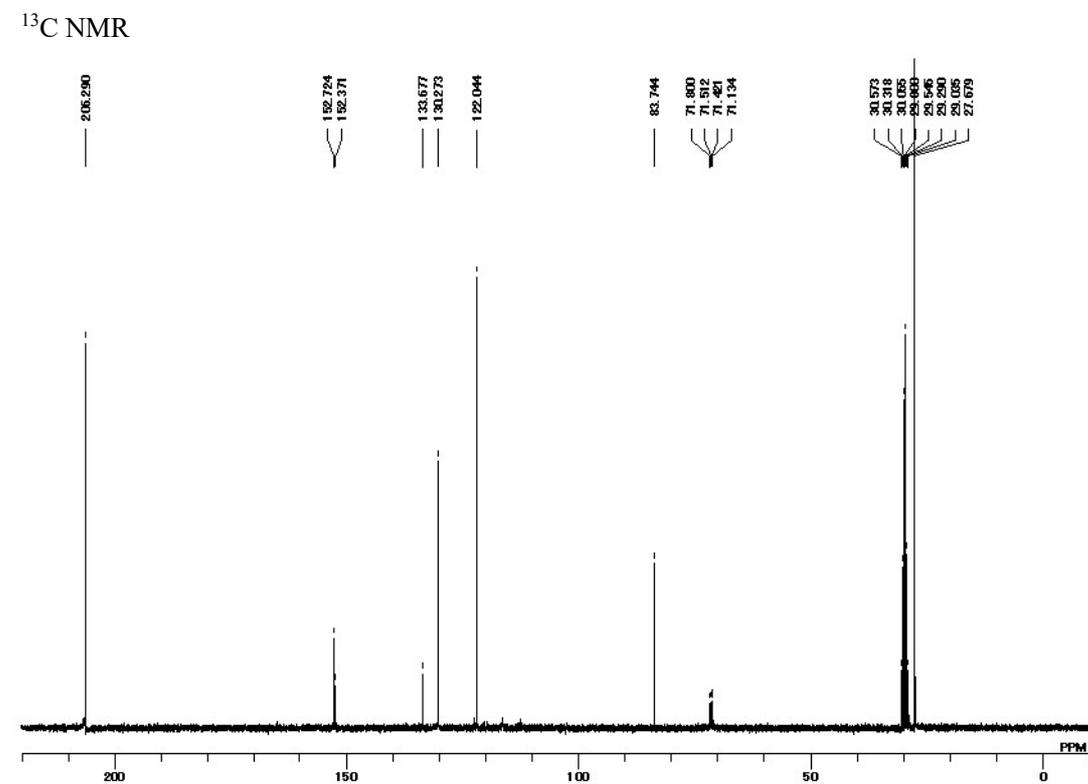
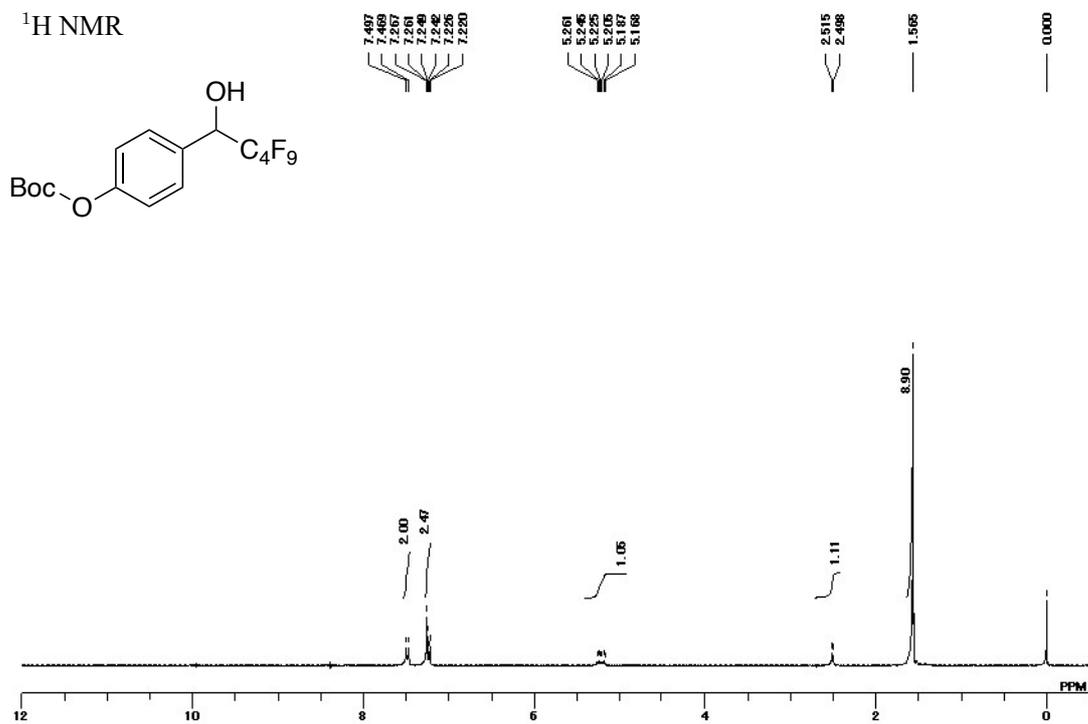
Ethyl 4-[(1,1-dimethylethoxy)carbonyl]oxy]benzoate (6)



1-[4-{{(1,1-Dimethylethoxy)carbonyl}oxy}phenyl]-2,2,3,3,4,4,5,5,5-nonafluoropentan-1-one (3b)

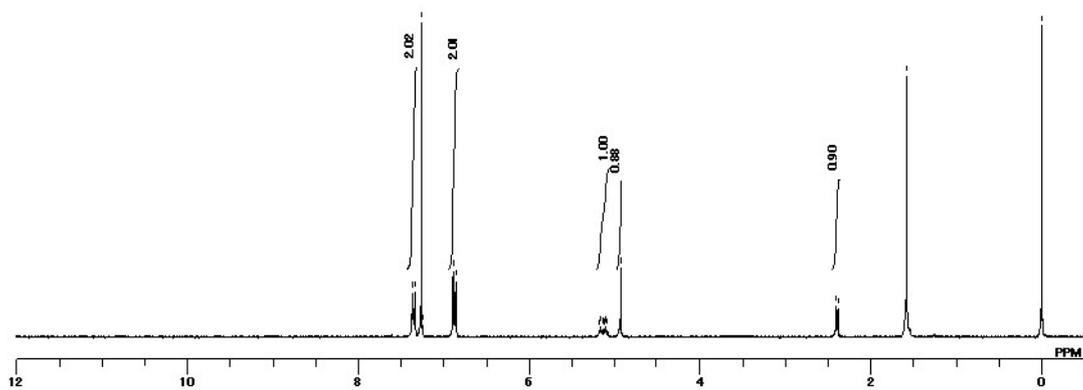
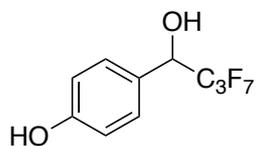


1-[4-{{(1,1-Dimethylethoxy)carbonyl}oxy}phenyl]-2,2,3,3,4,4,5,5,5-nonafluoropentan-1-ol (4gc)

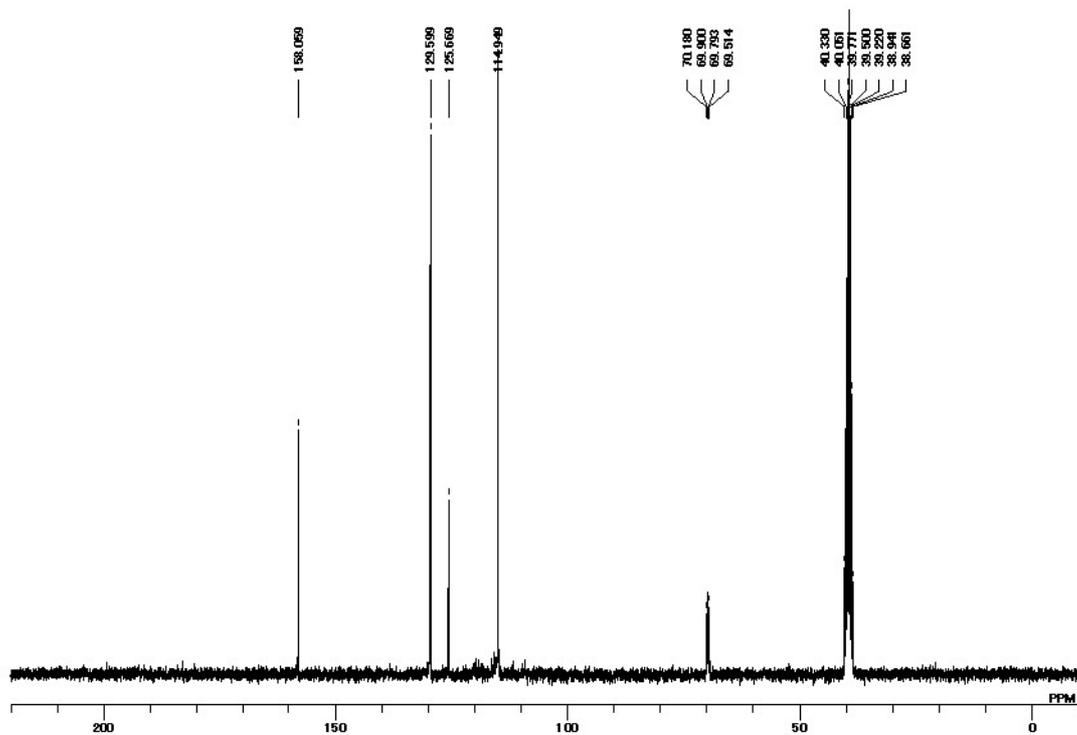


2,2,3,3,4,4,4-Heptafluoro-1-(4-hydroxyoxyphenyl)butan-1-ol (2ab)

¹H NMR

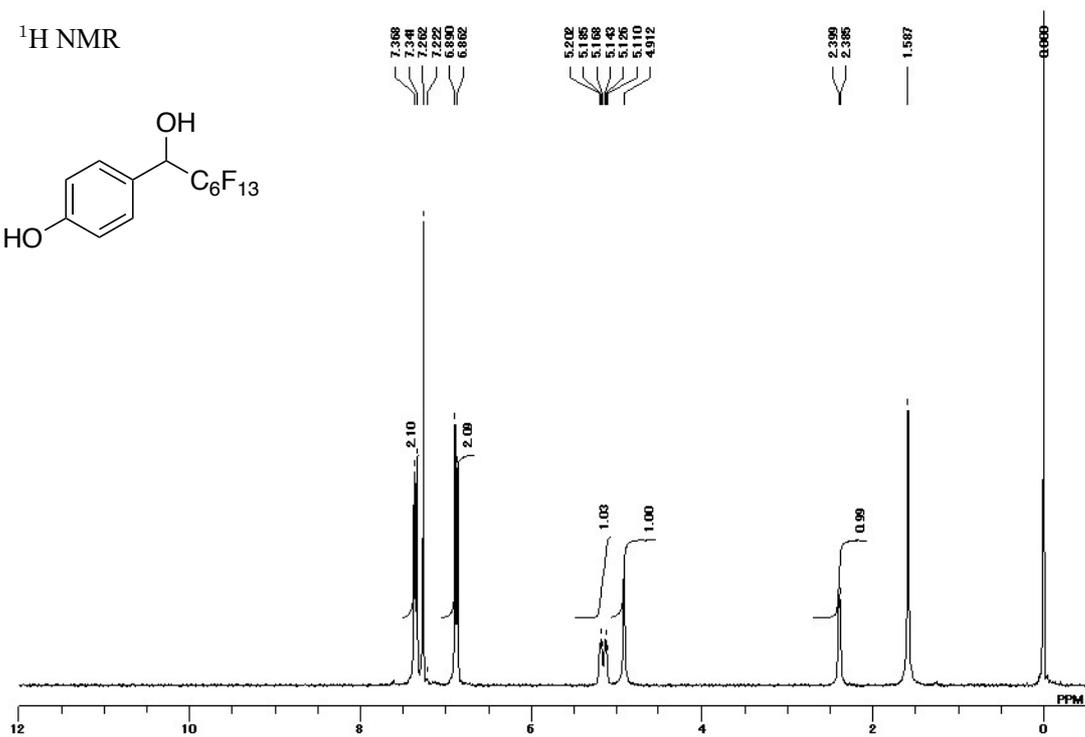
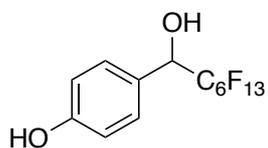


¹³C NMR

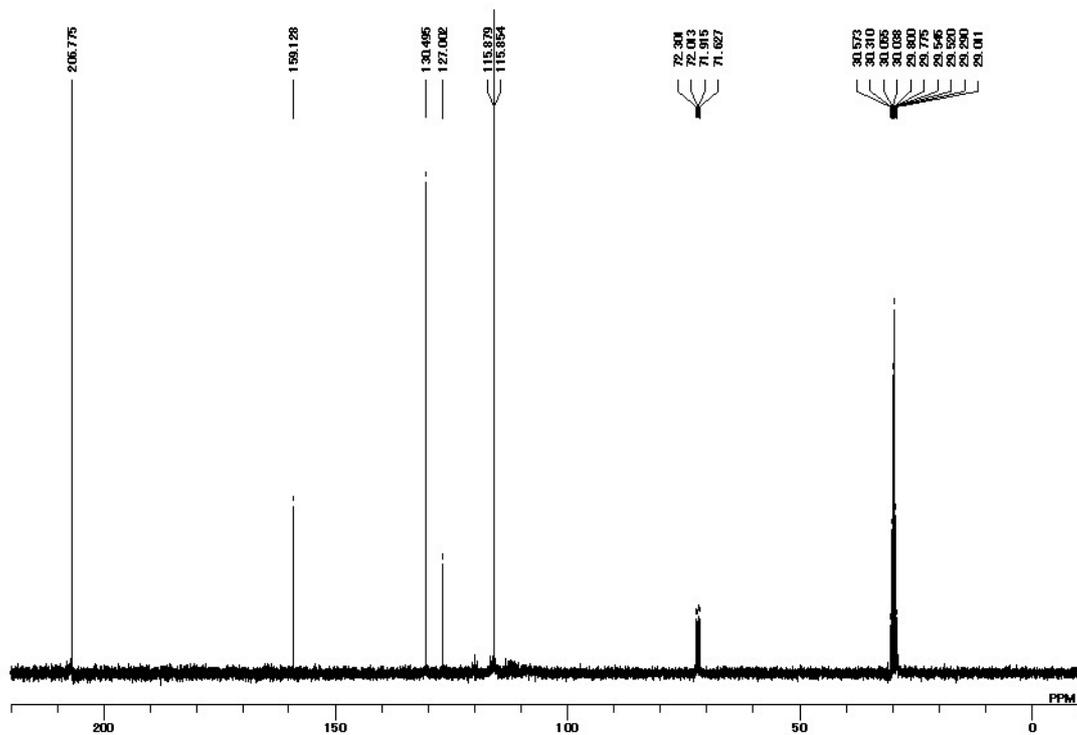


2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-(4-hydroxyphenyl)heptan-1-ol (2ad)

¹H NMR

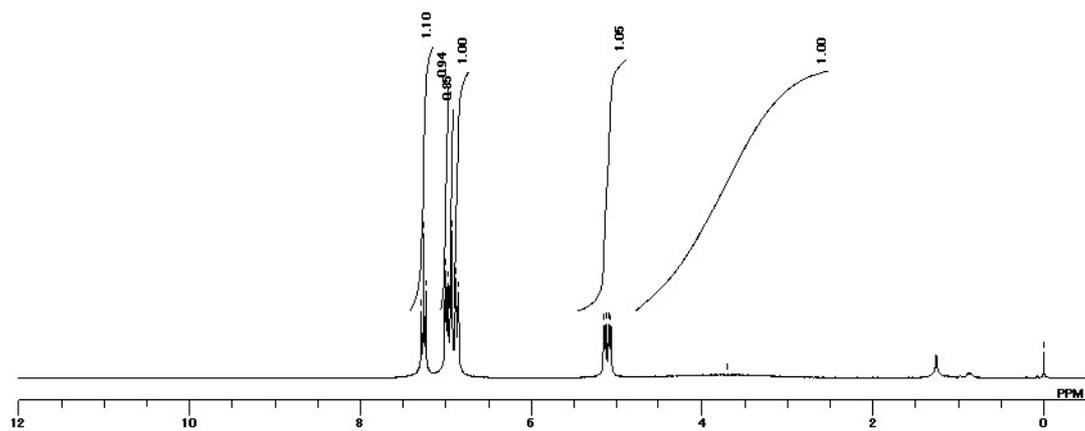
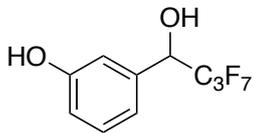


¹³C NMR

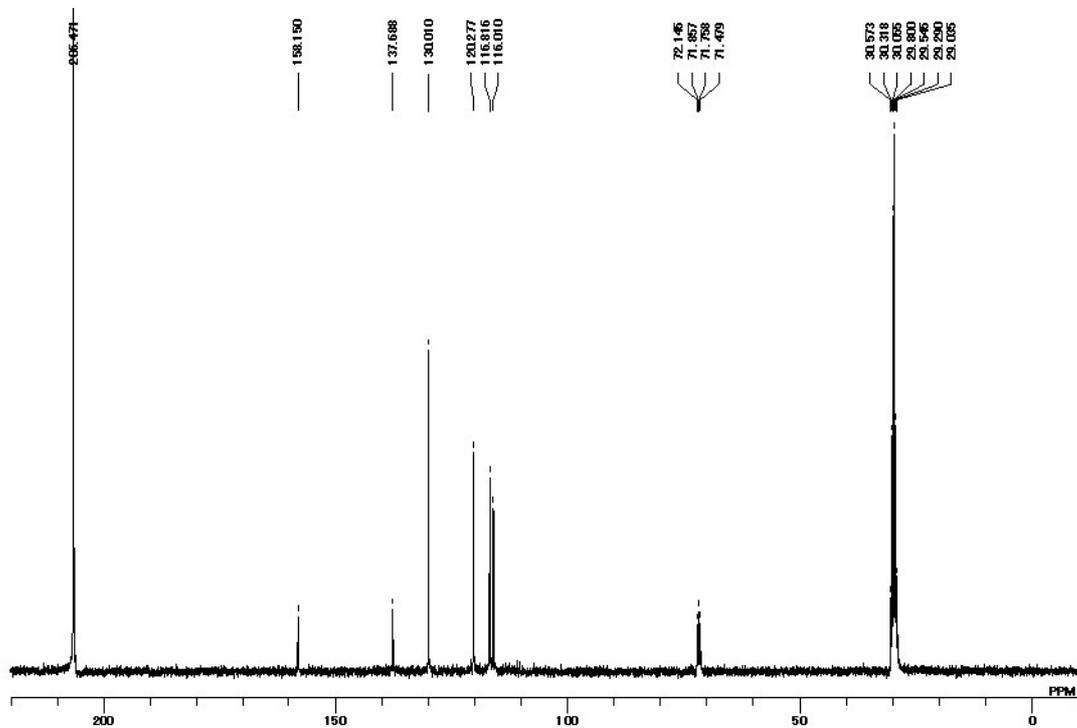


2,2,3,3,4,4,4-Heptafluoro-1-(3-hydroxyoxyphenyl)butan-1-ol (2bb)

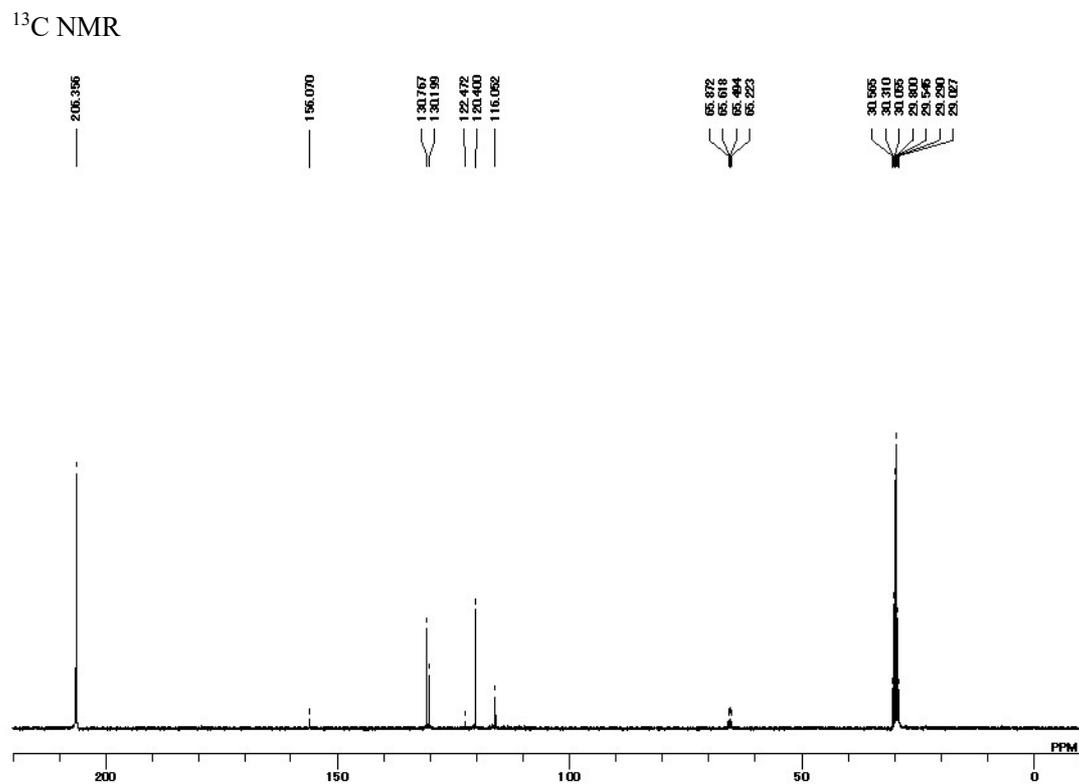
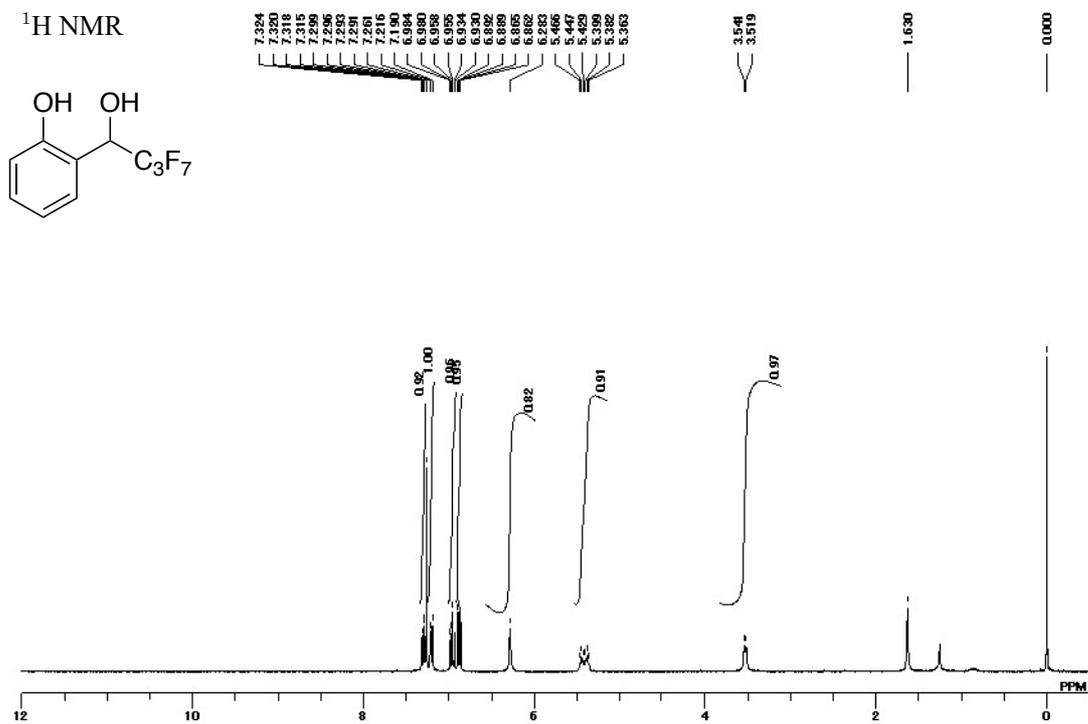
¹H NMR



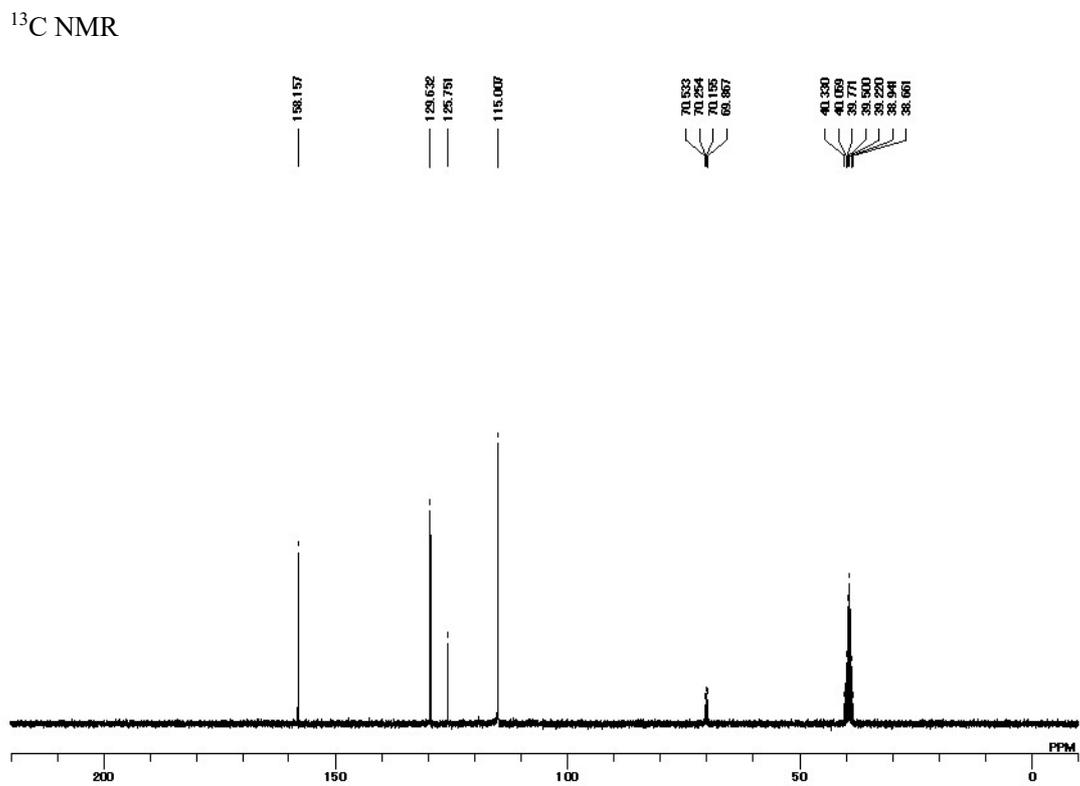
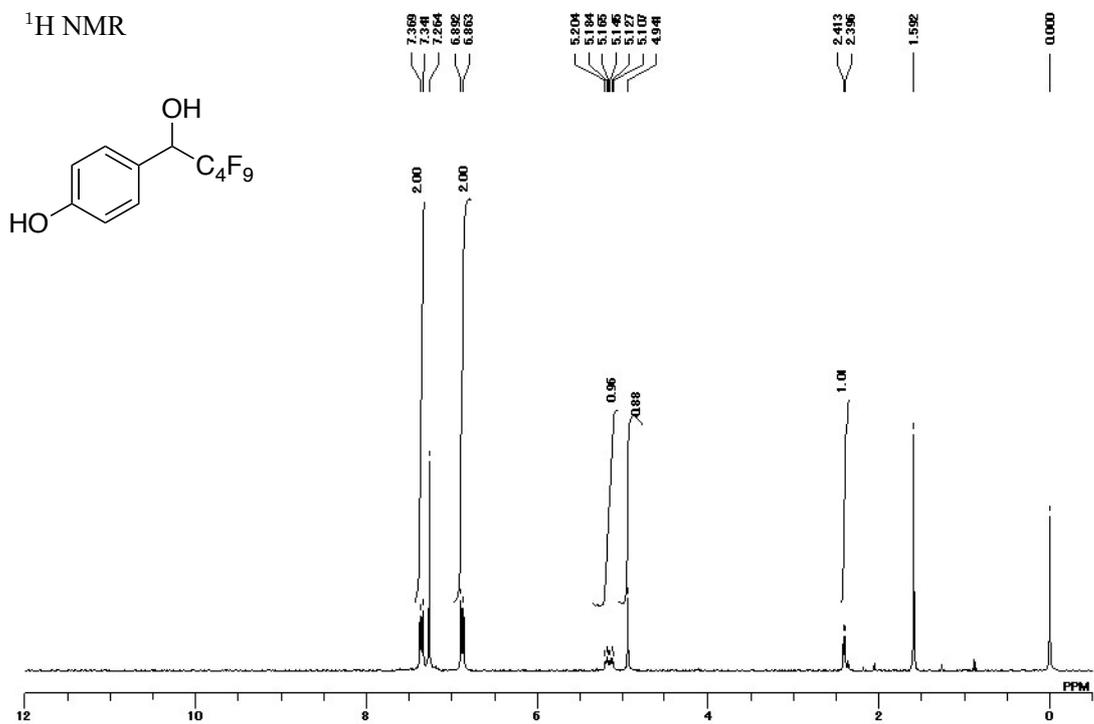
¹³C NMR



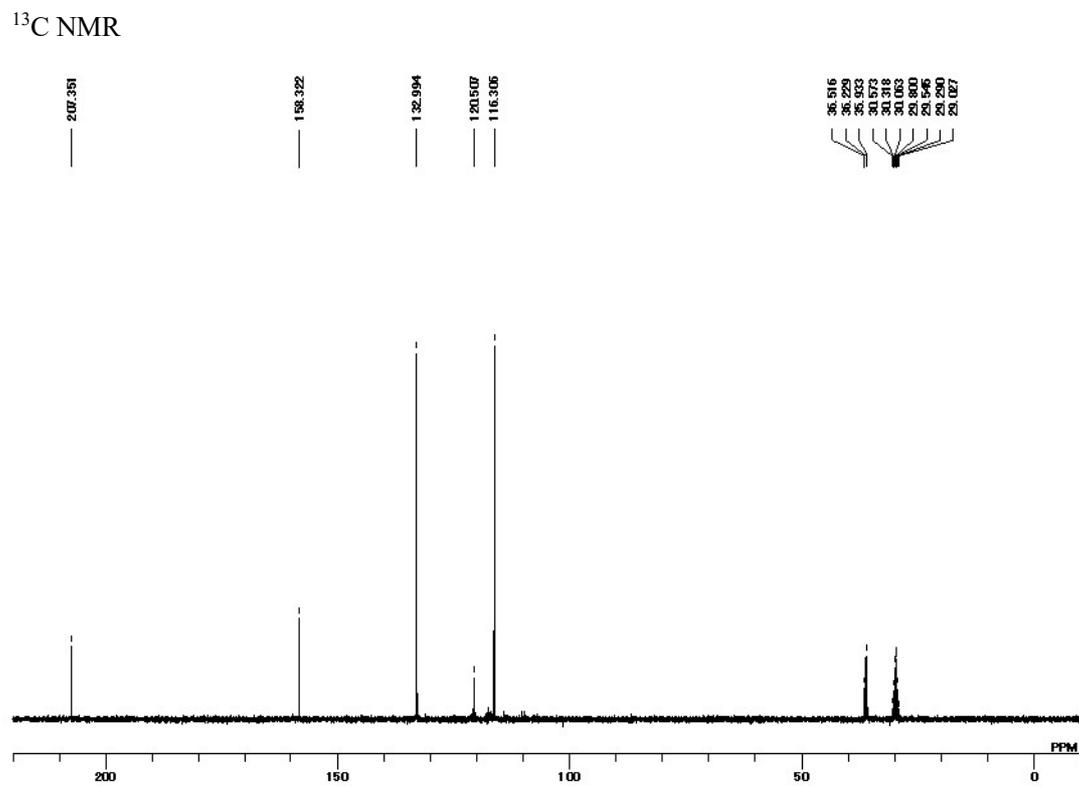
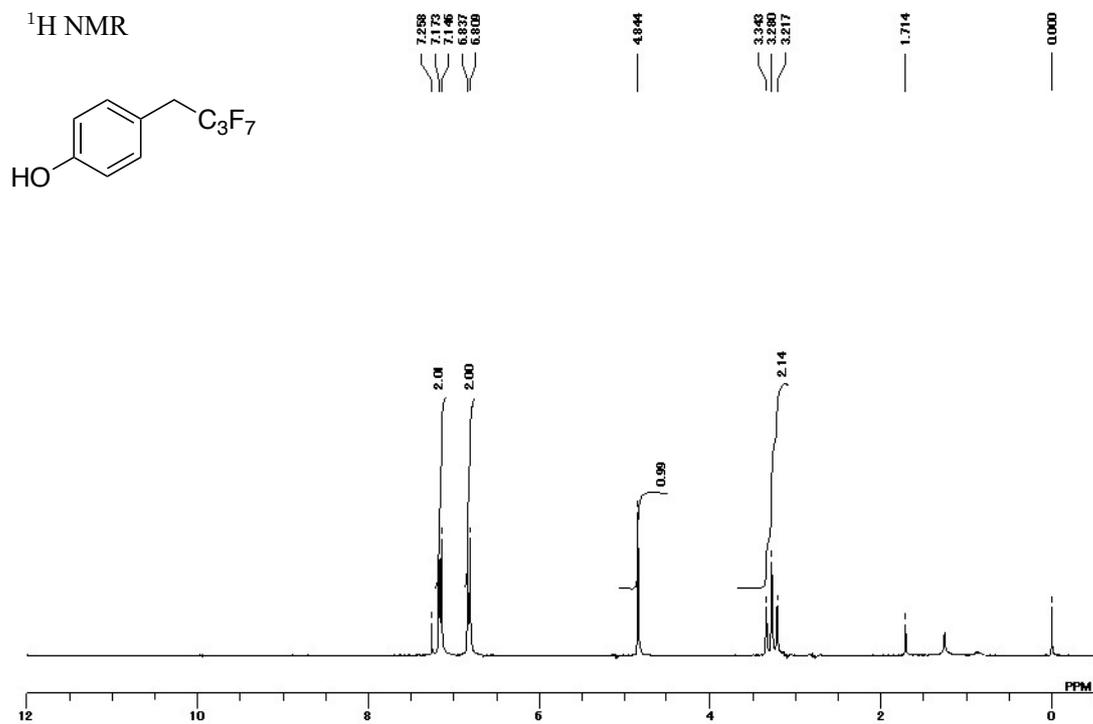
2,2,3,3,4,4,4-Heptafluoro-1-(2-hydroxyoxyphenyl)butan-1-ol (2cb)



2,2,3,3,4,4,5,5,5-Nonafluoro-1-(4-hydroxyphenyl)pentan-1-ol (2ac)

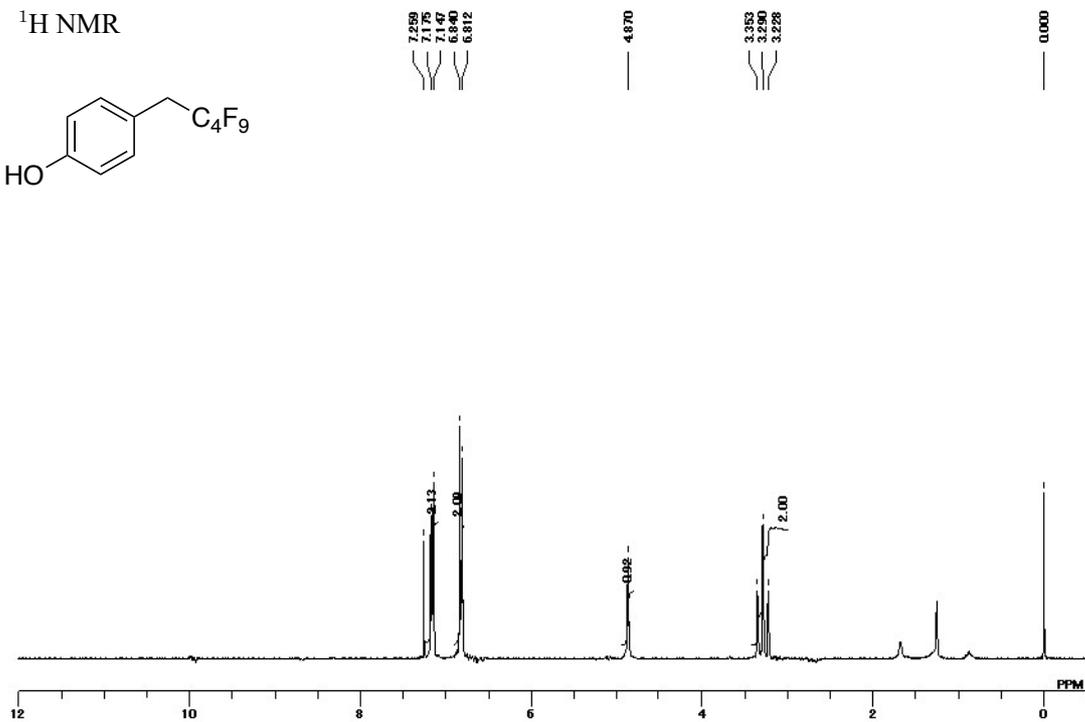
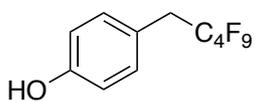


4-(2,2,3,3,4,4,4-Heptafluorobutyl)phenol (8b)

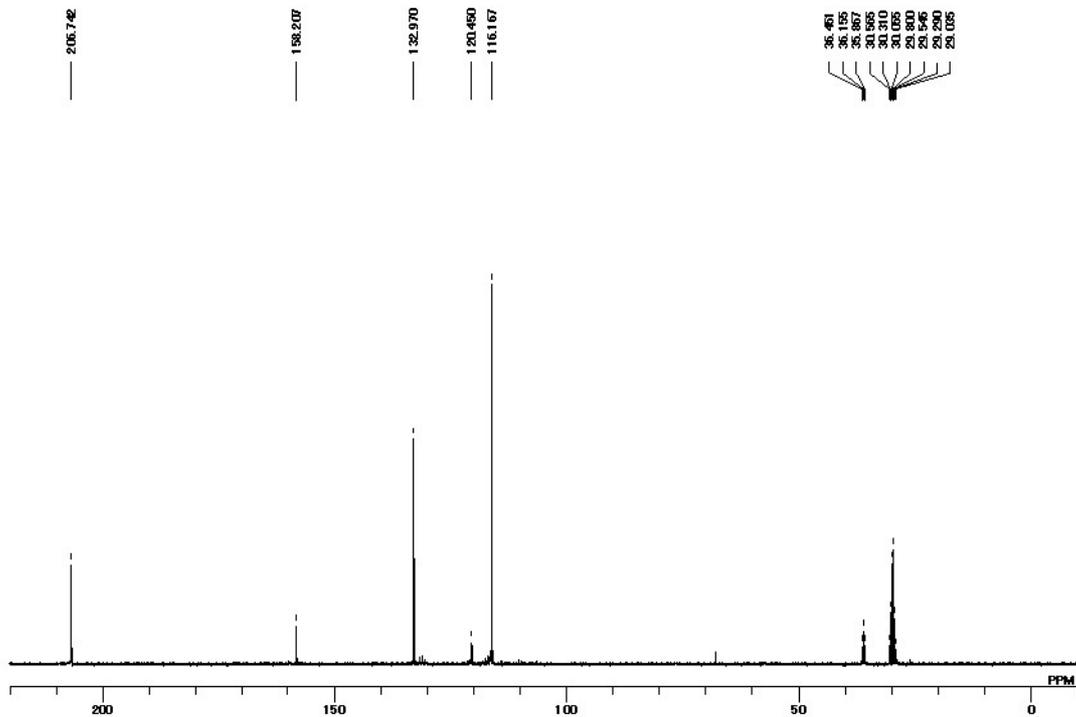


4-(2,2,3,3,4,4,5,5,5-Nonafluoropentyl)phenol (8c)

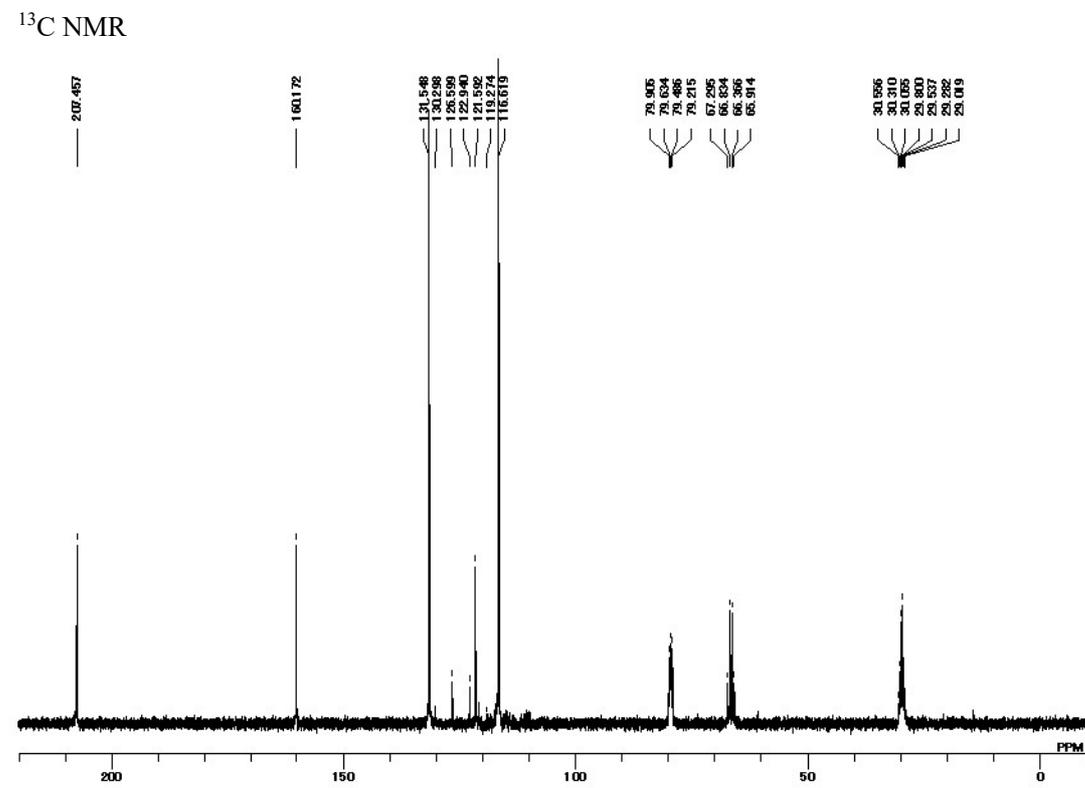
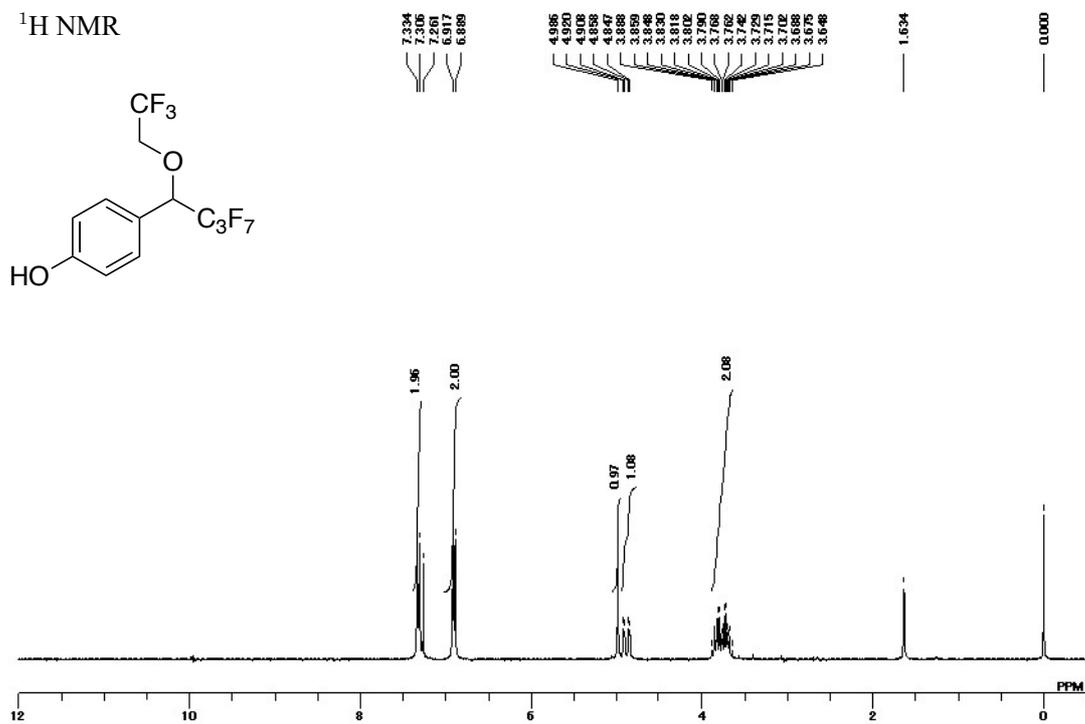
$^1\text{H NMR}$



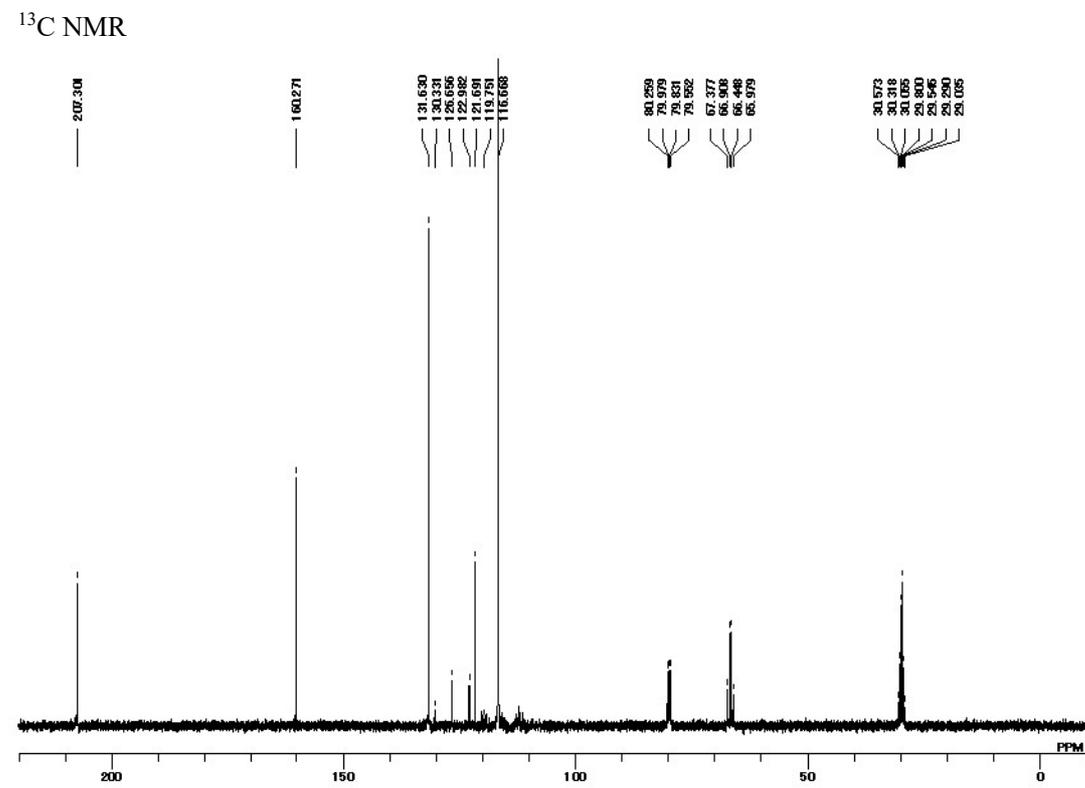
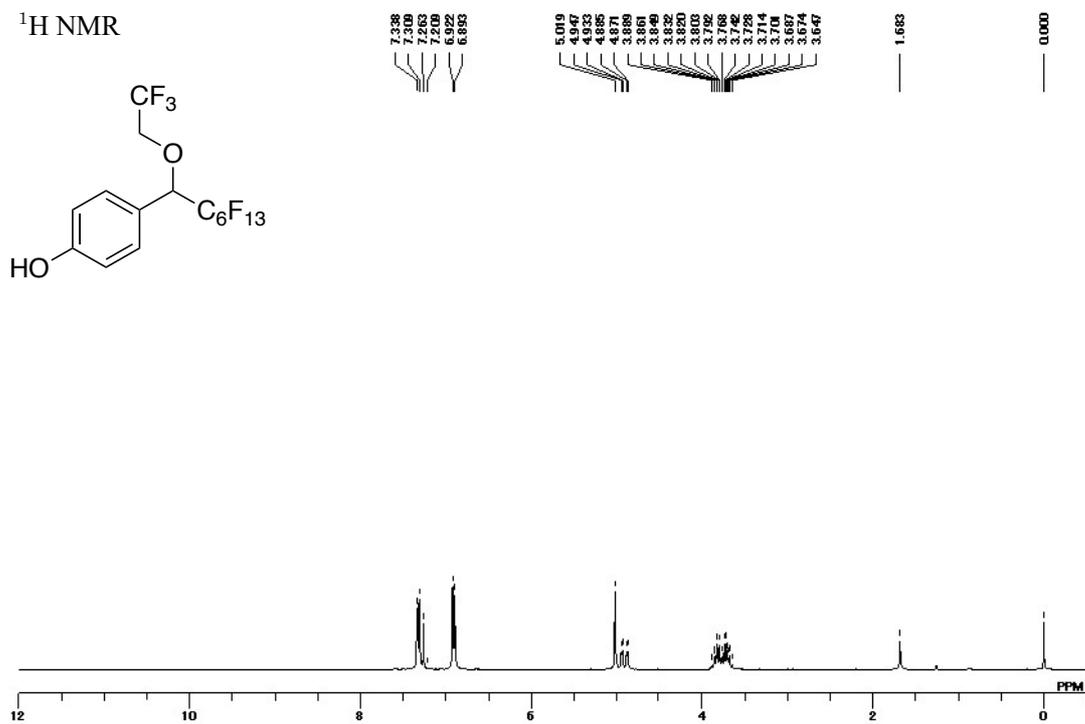
$^{13}\text{C NMR}$



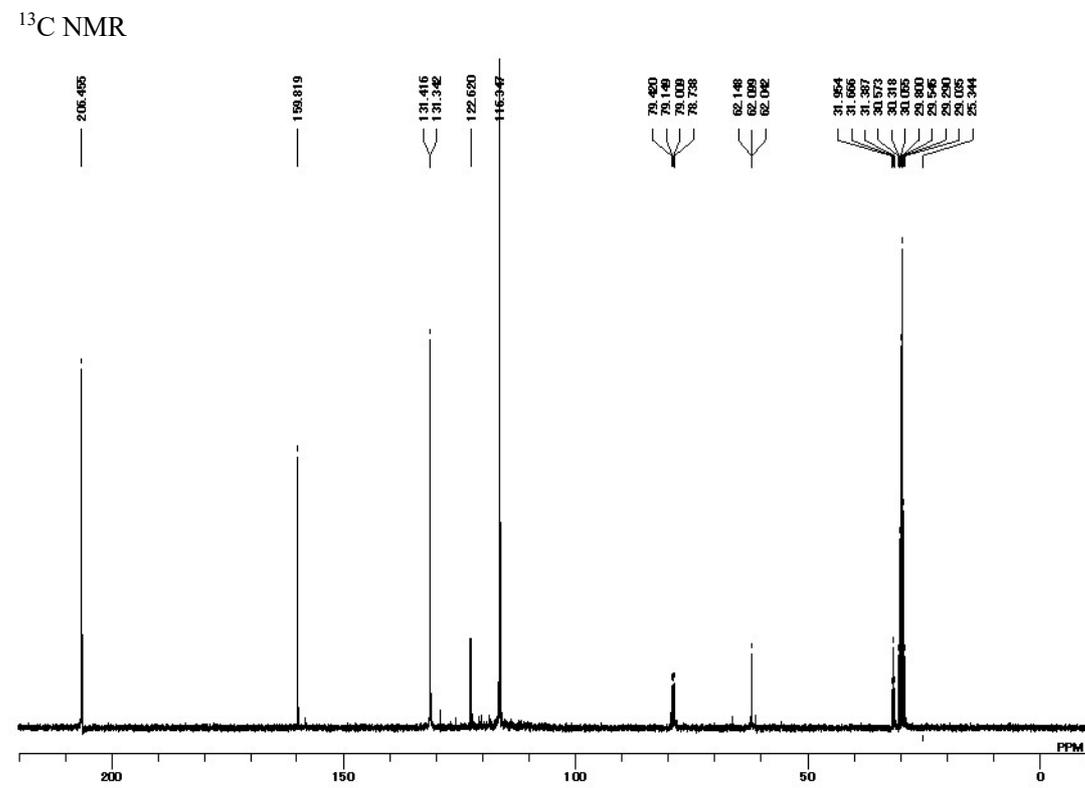
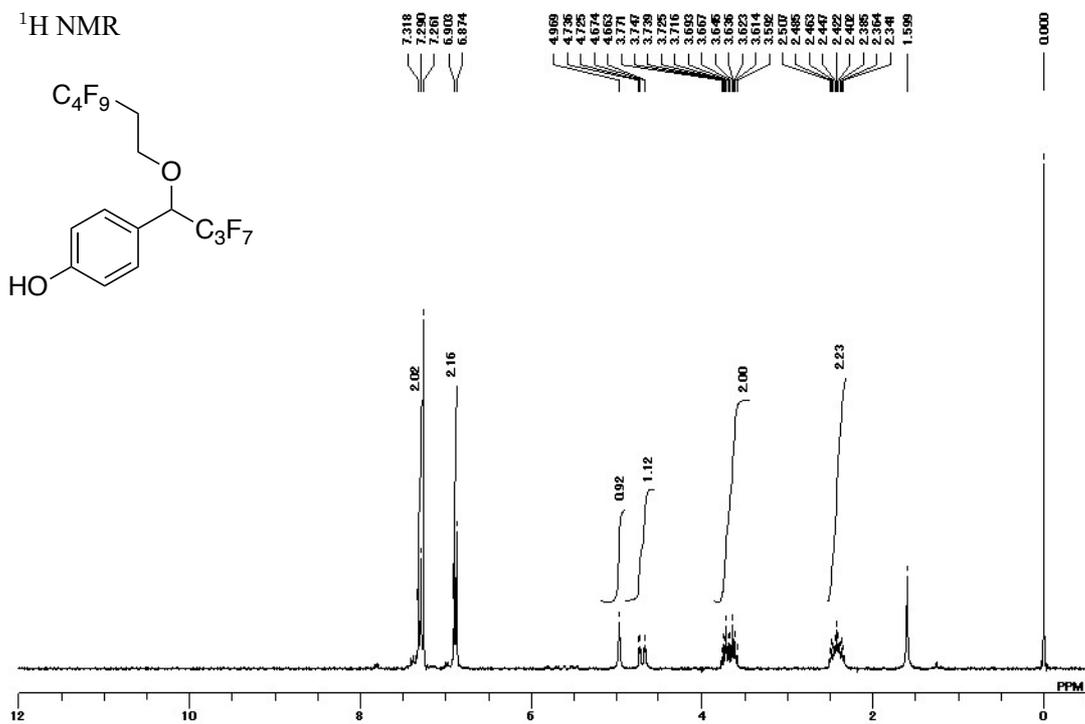
4-{2,2,3,3,4,4,4-Heptafluoro-1-(2,2,2-trifluoroethoxy)}butylphenol (9ab)



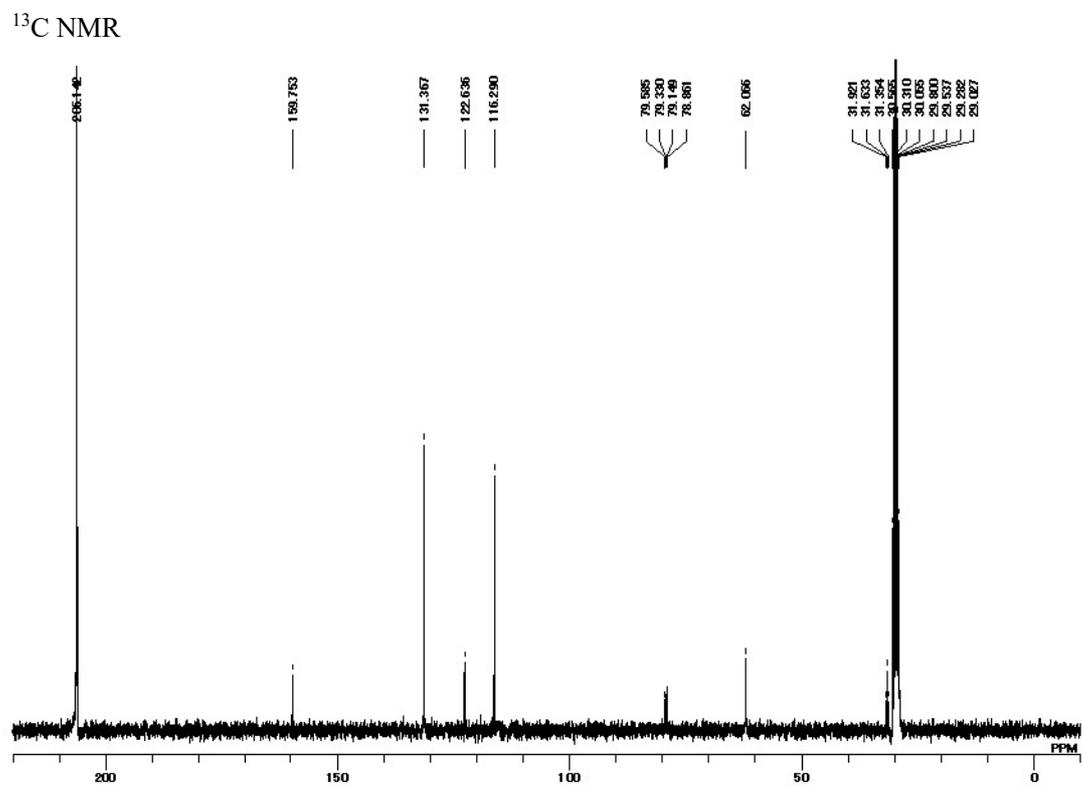
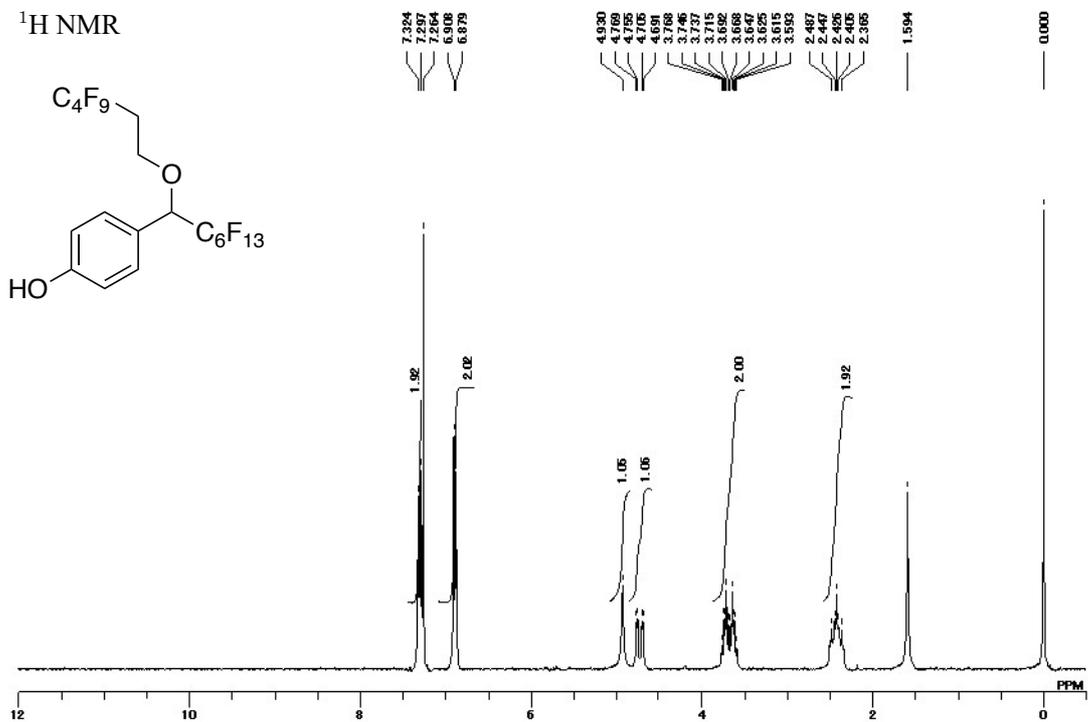
4-{2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-(2,2,2-trifluoroethoxy)heptyl}phenol (9ad)



4-{2,2,3,3,4,4,4-Heptafluoro-1-(3,3,4,4,5,5,6,6,6-nonafluorohexyloxy)butyl}phenol (9bb)

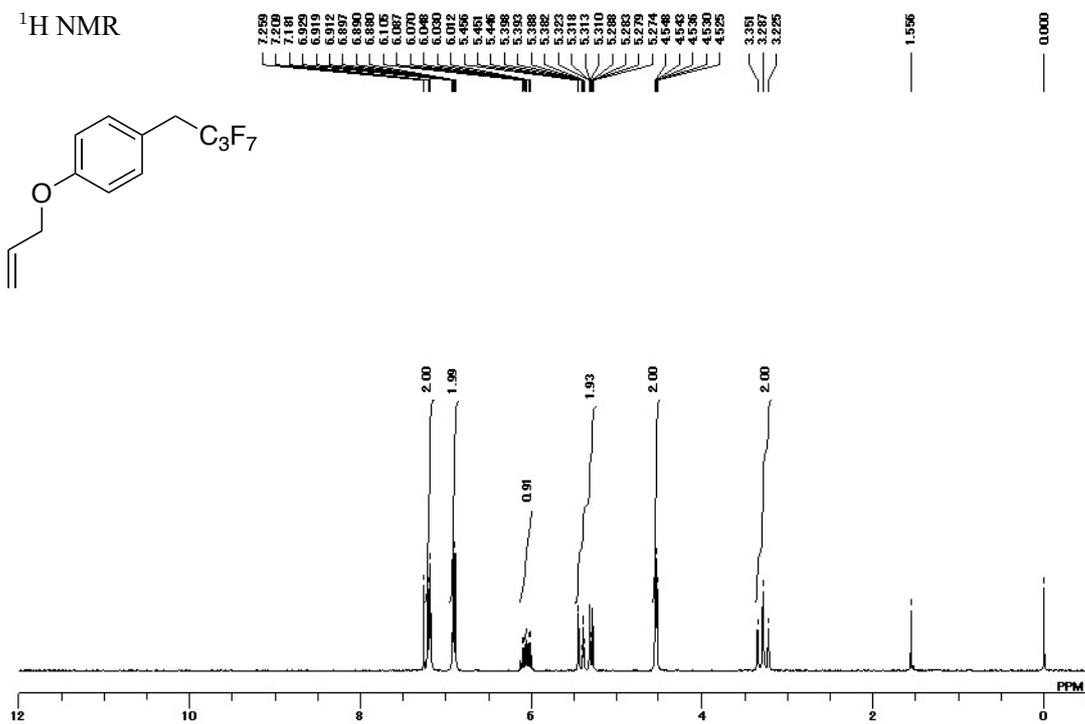


4-{2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-(3,3,4,4,5,5,6,6,6-nonafluoro-hexyloxy)heptyl}phenol
(9bd)

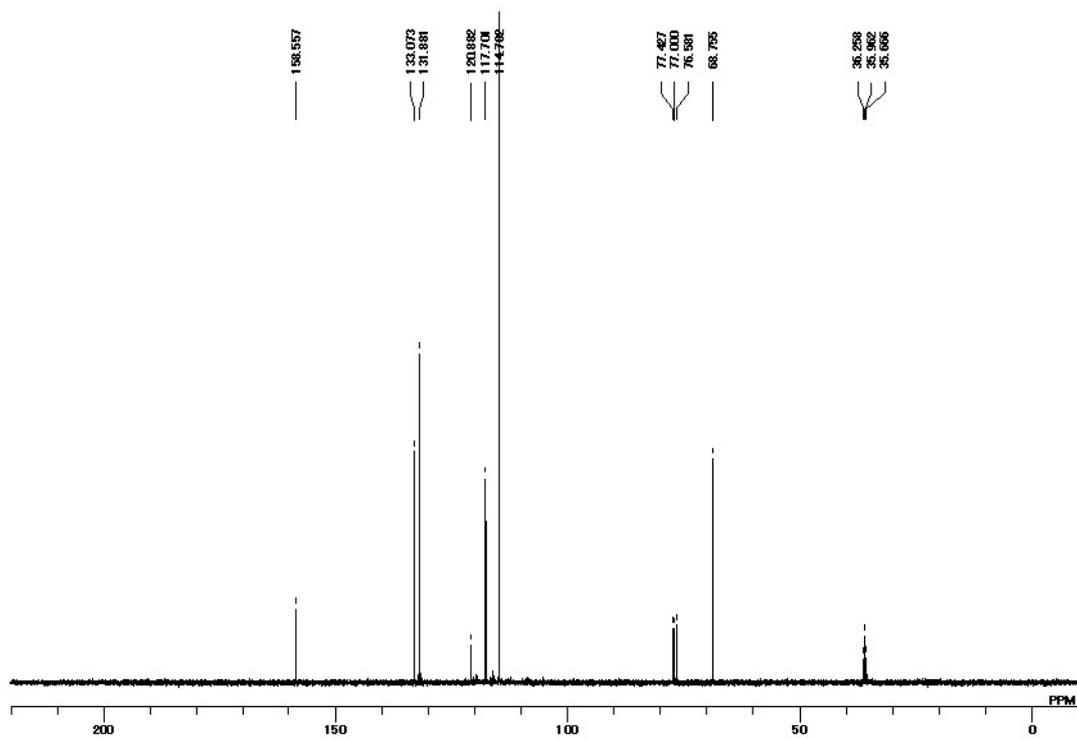


1-(Allyloxy)-4-(2,2,3,3,4,4,4-heptafluorobutyl)benzene (10)

¹H NMR

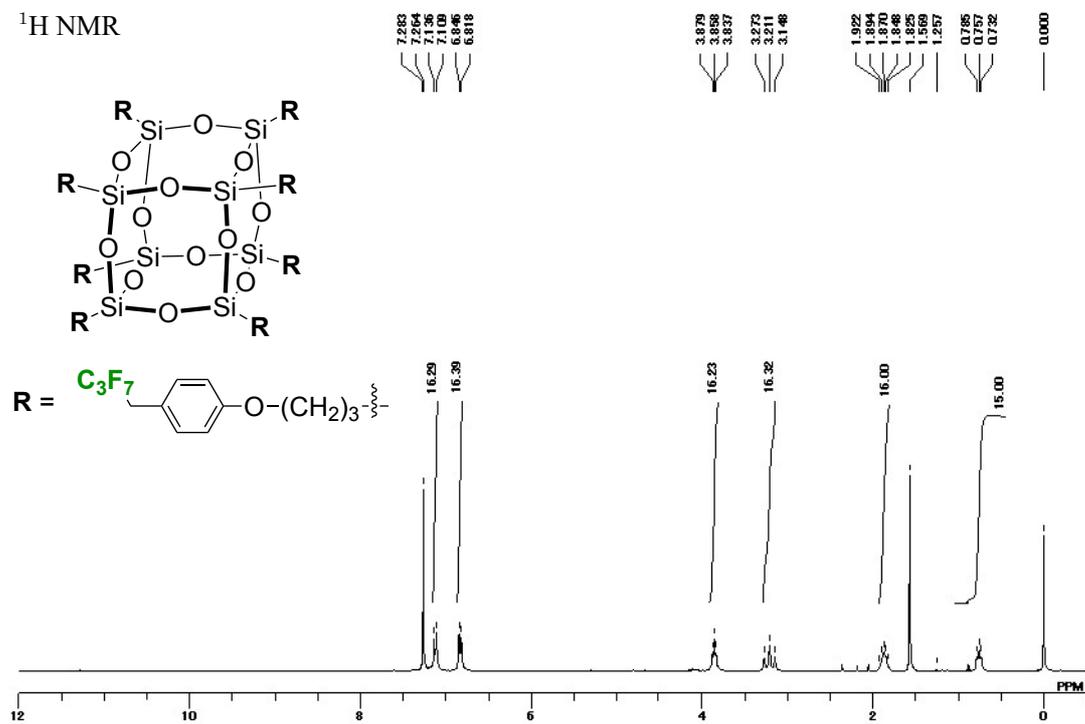


¹³C NMR



F-POSS (11b)

¹H NMR



¹³C NMR

