

Supporting Information

Defluorophosphorylation of Fluoroalkyl Peroxides for the Synthesis of Highly Substituted Furans

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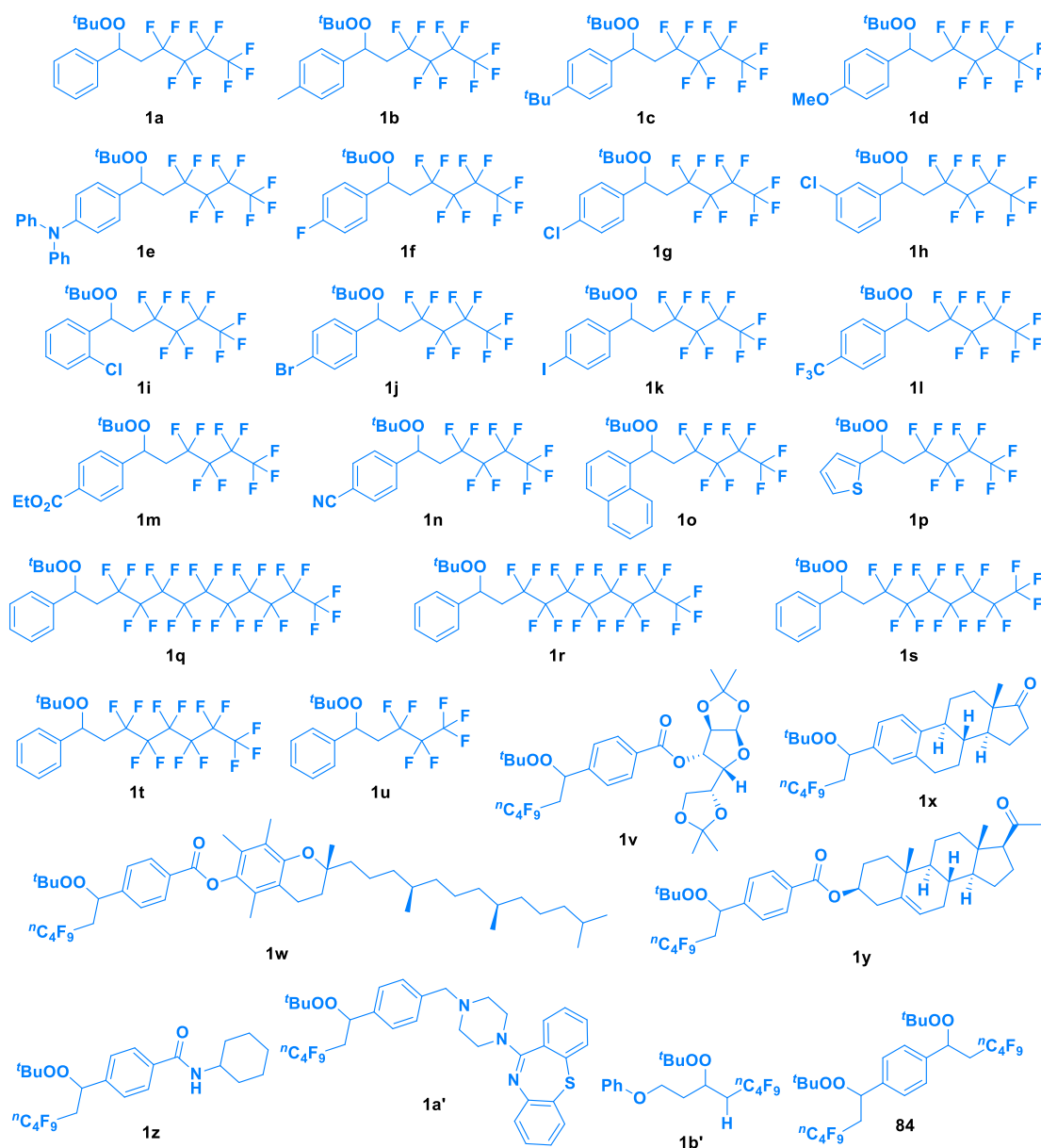
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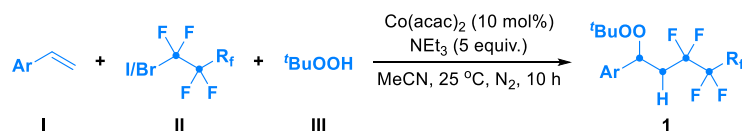
1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under air atmosphere using undistilled solvent. Melting points were recorded on an electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^1H , ^{19}F , ^{31}P , and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker Avance or Joel 400 MHz spectrometers. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QToF) using electrospray ionization (ESI) in positive or negative mode. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

2. General procedure for the synthesis of polyfluoroalkyl peroxides

Various polyfluoroalkyl peroxides 1:





According to previously reported methods,^[1-2] to an oven-dried vial equipped with a stir bar was added alkene (**I**, 2.0 mmol), polyfluoroalkyl halide (**II**, 4.0 mmol), ^tBuOOH (**III**, 1.545 g, 70% in water, 12.0 mmol), and Co(acac)₂ (51.4 mg, 0.2 mmol) at room temperature under air. The vial was capped with a rubber septum, evacuated and refilled with nitrogen (3 times). Anhydrous MeCN (8.0 mL) and NEt₃ (1.012 g, 10.0 mmol) were added by syringe and the resulting brown solution was stirred at room temperature for 10 h. The reaction vial was opened to air and then quenched with a saturated Na₂SO₃ solution (approximate 25 wt.%, 20 mL) to consume excess ^tBuOOH. The resulting mixture was extracted with EtOAc (20 mL x 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate as eluent to afford the purified peroxides **1** (17%-91% isolated yields).

Polyfluoroalkyl peroxides **1a**,^[1-2] **1d**,^[1] **1g**,^[1] **1f**,^[1] and **1j**^[1] are known substrates.

Representative examples:

1-(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (1a). This compound was prepared as a light yellow oil from styrene (208.3 mg, 2.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (1.384 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 76% yield (630.1 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.39 – 7.30 (m, 5H), 5.28 (dd, *J* = 7.0, 5.6 Hz, 1H), 2.90 – 2.71 (m, 1H), 2.56 – 2.35 (m, 1H), 1.22 (s, 9H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.14 (t, *J* = 10.4 Hz, 3F), -111.31 – -113.42 (m, 2F), -124.42 (q, *J* = 9.7 Hz, 2F), -125.92 (t, *J* = 12.2 Hz, 2F) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 139.5, 128.6, 128.5, 126.9, 80.8, 78.9 (t, *J* = 2.4 Hz), 36.0 (t, *J* = 21.0 Hz), 26.3 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

This is a known compound. The spectral data match those in the literature.^[1]

1-(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-4-methylbenzene (1b). This compound was prepared as a light yellow oil from 1-methyl-4-vinylbenzene (236.4 mg, 2.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (1.384 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 58% yield (498.7 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.35 – 7.29 (m, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.32 (t, *J* = 6.3 Hz, 1H), 2.99 – 2.81 (m, 1H), 2.61 – 2.43 (m, 1H), 2.40 (s, 3H), 1.28 (s, 9H) ppm.

1-(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-4-methoxybenzene (1d). This compound was prepared as a light yellow oil from 1-methoxy-4-vinylbenzene (268.4 mg, 2.0

mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (1.384 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 15:1) in 41% yield (363.9 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.31 – 7.26 (m, 2H), 6.93 – 6.89 (m, 2H), 5.22 (t, *J* = 6.3 Hz, 1H), 3.82 (s, 3H), 2.99 – 2.73 (m, 1H), 2.58 – 2.40 (m, 1H), 1.22 (s, 9H) ppm.

This is a known compound. The spectral data match that in the literature.^[1]

4-(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-*N,N*-diphenylaniline (1e). This compound was prepared as a light yellow oil from *N,N*-diphenyl-4-vinylaniline (542.7 mg, 2.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (1.384 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 45% yield (520.6 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.33 – 7.27 (m, 6H), 7.17 – 7.06 (m, 8H), 5.30 (t, *J* = 6.2 Hz, 1H), 3.04 – 2.83 (m, 1H), 2.65 – 2.47 (m, 1H), 1.31 (s, 9H) ppm.

1-(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-4-chlorobenzene (1g). This compound was prepared as a light yellow oil from 1-chloro-4-vinylbenzene (277.2 mg, 2.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (1.384 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 66% yield (588.6 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.42 – 7.29 (m, 4H), 5.28 (t, *J* = 6.3 Hz, 1H), 2.90 – 2.68 (m, 1H), 2.52 – 2.33 (m, 1H), 1.23 (s, 9H) ppm.

This is a known compound. The spectral data match that in the literature.^[1]

1-(1-((*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-3-chlorobenzene (1h). This compound was prepared as a light yellow oil from 1-chloro-3-vinylbenzene (277.2 mg, 2.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (1.384 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 68% yield (610.5 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.36 (q, *J* = 1.3 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.27 – 7.22 (m, 1H), 5.25 (dd, *J* = 7.5, 4.9 Hz, 1H), 2.87 – 2.63 (m, 1H), 2.55 – 2.29 (m, 1H), 1.22 (s, 9H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.04 (d, *J* = 10.7 Hz, 3F), -109.96 – -114.16 (m, 2F), -124.35 (q, *J* = 9.6 Hz, 2F), -125.90 (q, *J* = 11.5 Hz, 2F) ppm.

1-Bromo-4-(1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (1j). This compound was prepared as a light yellow oil from 1-bromo-4-vinylbenzene (366.1 mg, 2.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (1.384 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 91% yield (892.0 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.55 – 7.49 (m, 2H), 7.28 – 7.21 (m, 2H), 5.24 (dd, *J* = 7.2, 5.4

Hz, 1H), 2.89 – 2.64 (m, 1H), 2.54 – 2.28 (m, 1H), 1.22 (s, 9H) ppm.

This is a known compound. The spectral data match that in the literature.^[1]

4-(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzonitrile (1n). This compound was prepared as a light yellow oil from 4-vinylbenzonitrile (258.3 mg, 2.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (1.384 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 10:1) in 17% yield (148.9 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.74 – 7.65 (m, 2H), 7.52 – 7.46 (m, 2H), 5.32 (dd, *J* = 7.6, 4.8 Hz, 1H), 2.84 – 2.56 (m, 1H), 2.52 – 2.26 (m, 1H), 1.21 (s, 9H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.02 (t, *J* = 8.0 Hz, 3F), -110.24 – -113.67 (m, 2F), -124.31 (q, *J* = 9.7 Hz, 2F), -125.86 (d, *J* = 12.5 Hz, 2F) ppm.

(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)benzene (1r). This compound was prepared as a white solid from styrene (208.3 mg, 2.0 mmol), 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptafluoro-8-iodooctane (2.184 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 56% yield (689.1 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.42 – 7.31 (m, 5H), 5.28 (dd, *J* = 7.1, 5.4 Hz, 1H), 2.90 – 2.72 (m, 1H), 2.58 – 2.36 (m, 1H), 1.22 (s, 9H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -80.70 (t, *J* = 10.1 Hz, 3F), -110.56 – -113.50 (m, 2F), -121.51 (q, *J* = 14.3 Hz, 2F), -121.64 – -122.13 (m, 4F), -122.50 – -122.92 (m, 2F), -123.38 (t, *J* = 14.4 Hz, 2F), -125.86 – -126.42 (m, 2F) ppm.

(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentafluorononyl)benzene (1s). This compound was prepared as a light yellow oil from styrene (208.3 mg, 2.0 mmol), 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7-pentafluoro-7-iodoheptane (1.984 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 77% yield (866.4 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.43 – 7.32 (m, 5H), 5.31 – 5.25 (m, 1H), 2.91 – 2.71 (m, 1H), 2.59 – 2.34 (m, 1H), 1.23 (s, 9H) ppm.

(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzene (1t). This compound was prepared as a light yellow oil from styrene (208.3 mg, 2.0 mmol), 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane (1.784 g, 4.0 mmol), and ^tBuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 62% yield (633.3 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.31 – 7.18 (m, 5H), 5.17 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.83 – 2.59 (m, 1H), 2.47 – 2.24 (m, 1H), 1.12 (s, 9H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -80.88 (t, *J* = 10.2 Hz, 3F), -110.64 – -113.43 (m, 2F), -121.48 – -122.35 (m, 2F), -122.69 – -123.27 (m, 2F), -123.31 – -123.89 (m, 2F), -126.18 (td, *J* =

14.8, 6.0 Hz, 2F) ppm.

(3aR,5R,6S,6aR)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-(1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzoate (1v). This compound was prepared as a white solid from (3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-vinylbenzoate (390.4 mg, 1.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (691.9 g, 2.0 mmol), and ^tBuOOH (772.5 mg, 70% in water, 6.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 6:1) in 43% yield (300.0 mg).

¹H NMR (400 MHz, CDCl₃): δ = 8.03 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 5.92 (d, *J* = 3.7 Hz, 1H), 5.48 (d, *J* = 2.7 Hz, 1H), 5.32 (dd, *J* = 7.4, 5.1 Hz, 1H), 4.60 (d, *J* = 3.7 Hz, 1H), 4.40 – 4.28 (m, 2H), 4.15 – 4.03 (m, 2H), 2.82 – 2.60 (m, 1H), 2.54 – 2.24 (m, 1H), 1.53 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H), 1.25 (s, 3H), 1.19 (s, 9H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.14 (t, *J* = 8.8 Hz, 3F), -110.53 – -113.60 (m, 2F), -124.41 (q, *J* = 10.8 Hz, 2F), -125.96 (t, *J* = 12.3 Hz, 2F) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.7, 145.2, 130.0, 129.6, 126.8, 112.3, 109.4 (d, *J* = 0.9 Hz), 105.1, 83.3, 81.0 (d, *J* = 3.0 Hz), 79.9, 78.1, 76.7, 72.5, 67.2, 35.9 (m), 26.7, 26.6, 26.1, 26.0, 25.1 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

(8R,9S,13S,14S)-3-(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (1x). This compound was prepared as a white solid from (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (280.4 mg, 1.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (691.9 g, 2.0 mmol), and ^tBuOOH (772.5 mg, 70% in water, 6.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 55% yield (324.6 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.32 (d, *J* = 8.1 Hz, 1H), 7.17 (dt, *J* = 8.2, 2.6 Hz, 1H), 7.11 (dd, *J* = 3.1, 2.0 Hz, 1H), 5.26 (dd, *J* = 7.0, 5.3 Hz, 1H), 3.04 – 2.75 (m, 3H), 2.60 – 2.40 (m, 3H), 2.34 (td, *J* = 10.5, 3.7 Hz, 1H), 2.20 – 1.97 (m, 4H), 1.70 – 1.47 (m, 6H), 1.26 (s, 9H), 0.93 (s, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.02 – -81.22 (m, 3F), -111.05 – -113.52 (m, 2F), -124.42 (q, *J* = 10.3 Hz, 2F), -125.80 – -126.05 (m, 2F) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 220.4, 140.0, 136.6 (t, *J* = 2.1 Hz), 127.3, 125.5, 124.1, 124.1, 80.6, 78.6 (m), 50.5, 47.8, 44.4, 37.9 (d, *J* = 1.6 Hz), 35.8 (t, *J* = 21.0 Hz), 31.5, 29.3 (d, *J* = 3.8 Hz), 26.8, 26.4 (d, *J* = 1.9 Hz), 26.2, 25.5, 21.4, 13.7 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

(3S,8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl

4-(1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzoate (1y). This compound was prepared as a white solid from (3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 4-vinylbenzoate (446.3 mg, 1.0 mmol),

1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (691.9 g, 2.0 mmol), and ^tBuOOH (772.5 mg, 70% in water, 6.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 37% yield (278.3 mg).

¹H NMR (400 MHz, CDCl₃): δ = 8.06 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 5.33 (t, *J* = 6.4 Hz, 1H), 5.03 – 4.86 (m, 1H), 2.83 – 2.66 (m, 1H), 2.51 – 2.34 (m, 2H), 2.13 – 2.01 (m, 1H), 1.99 – 1.91 (m, 2H), 1.82 – 1.51 (m, 9H), 1.33 – 1.21 (m, 17H), 0.95 – 0.83 (m, 8H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.01 (t, *J* = 9.1 Hz, 3F), -111.13 – -113.35 (m, 2F), -124.34 (q, *J* = 9.8 Hz, 2F), -125.87 (t, *J* = 12.4 Hz, 2F) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 221.1, 165.6, 144.3, 130.9, 129.8, 126.6, 125.9, 114.4, 80.9, 78.2, 74.1, 54.2, 51.3, 47.7, 44.6, 36.7, 35.7 (t, *J* = 21.0 Hz), 35.6, 35.0, 34.0, 31.5, 30.7, 29.6, 28.2, 27.4, 26.1, 21.7, 20.4, 13.7, 12.2 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

4-(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-*N*-cyclohexylbenzamide (1z). This compound was prepared as a light yellow oil from *N*-cyclohexyl-4-vinylbenzamide (229.3 mg, 1.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (691.9 g, 2.0 mmol), and ^tBuOOH (772.5 mg, 70% in water, 6.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 20:1) in 23% yield (122.5 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.54 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.16 (d, *J* = 8.2 Hz, 1H), 5.22 (t, *J* = 6.2 Hz, 1H), 4.22 – 4.10 (m, 1H), 3.40 – 3.26 (m, 1H), 2.80 – 2.61 (m, 1H), 2.42 – 2.22 (m, 1H), 1.87 – 1.73 (m, 5H), 1.24 – 1.03 (m, 11H), 0.74 – 0.63 (m, 2H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.21 (t, *J* = 9.4 Hz, 3F), -112.10 – -112.60 (m, 2F), -124.51 (q, *J* = 10.0 Hz, 2F), -126.03 (t, *J* = 12.5 Hz, 2F) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 169.6, 154.1, 142.0, 137.1, 126.9 (d, *J* = 55.5 Hz), 80.7, 78.3, 55.9, 49.6, 35.8 (t, *J* = 21.0 Hz), 31.9, 30.5 (d, *J* = 3.4 Hz), 26.0, 25.1 (d, *J* = 3.8 Hz), 24.3 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

11-(4-(4-(1-(*tert*-Butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzyl)piperazin-1-yl)dibenzo[*b,f*][1,4]thiazepine (1a'). This compound was prepared as a white solid from 11-(4-(4-vinylbenzyl)piperazin-1-yl)dibenzo[*b,f*][1,4]thiazepine (411.6 mg, 1.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (691.9 g, 2.0 mmol), and ^tBuOOH (772.5 mg, 70% in water, 6.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 10:1) in 42% yield (304.7 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.49 (dd, *J* = 6.5, 2.7 Hz, 1H), 7.41 – 7.26 (m, 9H), 7.19 – 7.12 (m, 1H), 7.06 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.90 – 6.83 (m, 1H), 5.31 – 5.21 (m, 1H), 3.80 – 3.18 (m, 6H), 2.88 – 2.70 (m, 1H), 2.63 – 2.34 (m, 4H), 1.21 (s, 9H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -80.92 (t, *J* = 10.1 Hz, 3F), -111.27 – -113.37 (m, 2F), -124.30 (q, *J* = 9.6 Hz, 2F), -125.79 (t, *J* = 12.4 Hz, 2F) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 160.8, 148.9, 139.9, 138.4, 138.2, 134.2, 132.2, 132.1, 130.7, 129.3, 129.1, 129.0, 128.2, 128.0, 126.8, 125.3, 122.7, 80.8, 78.7, 62.7, 52.9, 46.7 (m), 35.8 (t, *J* = 20.9 Hz), 26.3 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

1,4-Bis(1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (84). This compound was prepared as a light yellow oil from 1,4-divinylbenzene (130.2 mg, 1.0 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (1.384 g, 4.0 mmol), and *t*BuOOH (1.545 g, 70% in water, 12.0 mmol) according to the general procedure for the synthesis of polyfluoroalkyl peroxides (purified by silica gel column chromatography; eluent: petroleum ether/ethyl acetate = 50:1) in 24% yield (179.2 mg).

¹H NMR (400 MHz, CDCl₃): δ = 7.41 (d, *J* = 4.2 Hz, 4H), 5.33 (dd, *J* = 7.5, 4.9 Hz, 2H), 2.90 – 2.69 (m, 2H), 2.58 – 2.35 (m, 2H), 1.25 (s, 18H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.26 (dd, *J* = 20.6, 9.4 Hz, 3F), -109.22 – -115.73 (m, 2F), -124.53 (q, *J* = 9.5 Hz, 2F), -126.08 (t, *J* = 12.4 Hz, 2F) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 139.9 (d, *J* = 1.7 Hz), 127.1, 80.9 (t, *J* = 1.6 Hz), 78.6 (m), 36.0 (t, *J* = 21.1 Hz), 26.2 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

3. General procedure for the synthesis of diphosphinylated furan derivatives

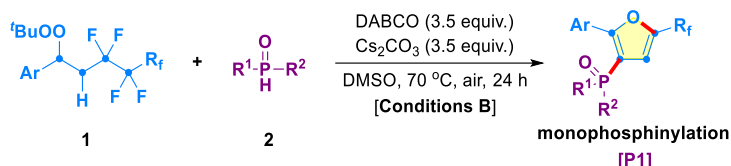


0.15 mmol scale: To an oven-dried vial equipped with a stir bar was added polyfluoroalkyl peroxide **1** (0.36 mmol), phosphine oxide **2** (0.3 mmol), triethylenediamine (DABCO, 84.1 mg, 0.75 mmol), Cs₂CO₃ (244.4 mg, 0.75 mmol), and DCE (2.0 mL) at room temperature under air and the vial was sealed with a rubber septum. The vial containing the pale-yellow reaction mixture was placed in an oil bath at 70 °C and stirred for 24 h.

0.3 mmol scale: To an oven-dried vial equipped with a stir bar was added polyfluoroalkyl peroxide **1** (0.72 mmol),^[1-2] phosphine oxide **2** (0.6 mmol), triethylenediamine (DABCO, 168.3 mg, 1.5 mmol), Cs₂CO₃ (488.7 mg, 1.5 mmol), and DCE (4.0 mL) at room temperature under air and the vial was sealed with a rubber septum. The vial containing the pale-yellow reaction mixture was placed in an oil bath at 70 °C and stirred for 24 h.

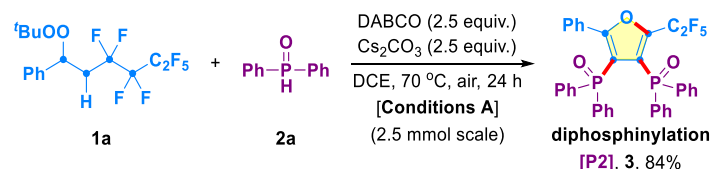
Upon completion of the reaction (indicated by TLC analysis), the vial was cooled to room temperature and opened to air. The resulting black mixture was then quenched with a saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (1/1) or dichloromethane/methanol (20/1) as eluent to afford the purified products.

4. General procedure for the synthesis of monophosphinylated furan derivatives



To an oven-dried vial equipped with a stir bar was added polyfluoroalkyl peroxide **1** (0.3 mmol), phosphine oxide **2** (0.9 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol), Cs_2CO_3 (342.1 mg, 1.05 mmol), and DMSO (2.0 mL) at room temperature under air and the vial was sealed with a rubber septum. The vial was placed in an oil bath at 70 °C and stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the resulting black mixture was cooled to room temperature and opened to air. Next, the reaction was quenched with a saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The combined organic layer was washed twice with saturated brine (20 mL), dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (1/1) or dichloromethane/methanol (20/1) as eluent to afford the purified products.

5. General procedure for the scale-up synthesis of diphosphinylated furan **3**



To an oven-dried vial equipped with a stir bar was added (1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluoro-1-hexyl)benzene (**1a**, 2.473 g, 6 mmol), diphenylphosphine oxide (**2a**, 1.011 g, 5 mmol), triethylenediamine (DABCO, 1.402 g, 12.5 mmol), Cs_2CO_3 (4.073 g, 12.5 mmol), and DCE (10.0 mL) at room temperature under air and the vial was sealed with a rubber septum. The vial with the pale-yellow reaction mixture was placed in an oil bath at 70 °C and stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis) the vial was cooled to room temperature and opened to air. The resulting black mixture was then quenched by saturated NH_4Cl solution (50 mL) and extracted with EtOAc (50 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using dichloromethane/methanol (20/1) as eluent to afford the purified product **3** (1.391 g, 84% yield, white solid).

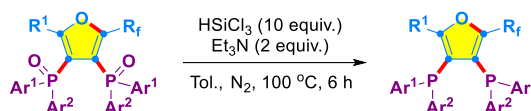
6. General procedure for the scale-up synthesis of monophosphinylated furan **4**



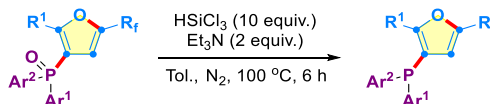
To an oven-dried vial equipped with a stir bar was added (1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluoro-1-hexyl)benzene (**1a**, 1.649 g, 4 mmol), diphenylphosphine oxide (**2a**, 2.426 g, 12 mmol), triethylenediamine (DABCO, 1.57 g, 14 mmol),

Cs₂CO₃ (4.561 g, 14 mmol), and DMSO (10.0 mL) at room temperature under air and the vial was sealed with a rubber septum. The pale-yellow reaction mixture in the vial was placed in an oil bath at 70 °C and stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis) the vial was cooled to room temperature and opened to air. The resulting black mixture was then quenched by saturated NH₄Cl solution (50 mL) and extracted with EtOAc (50 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using dichloromethane/methanol (20/1) as eluent to afford the purified product **4** (1.276 g, 69% yield, white solid).

7. General procedures for the synthesis of tri(hetero)arylphosphines 87-93



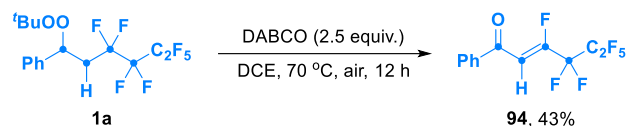
To an oven-dried vial equipped with a stir bar was added diphosphinylated furan derivative (0.3 mmol) at room temperature under air. The vial was capped with a rubber septum, evacuated and refilled with nitrogen (3 times). Anhydrous toluene (5 mL), trichlorosilane (406.3 mg, 3 mmol), and Et₃N (60.7 mg, 0.6 mmol) were added sequentially via syringe. The clear reaction mixture was placed in an oil bath at 100 °C and stirred for 6 h until full conversion of the diphosphinylated furan was detected by TLC analysis. The reaction vial cooled to room temperature, opened to air and then quenched with saturated NH₄Cl solution (20 mL). The resulting mixture was extracted with EtOAc (20 mL x 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether as eluent to afford the purified products.



To an oven-dried vial equipped with a stir bar was added monophosphinylated furan derivative (0.3 mmol) at room temperature under ai. The vial was capped with a rubber septum, evacuated and refilled with nitrogen (3 times). Anhydrous toluene (5 mL), trichlorosilane (406.3 mg, 3 mmol), and Et₃N (60.7 mg, 0.6 mmol) were added sequentially via syringe. The clear reaction mixture was placed in an oil bath at 100 °C and stirred for 6 h until full conversion of the monophosphinylated furan was detected by TLC analysis. After cooling the vial to room temperature, the reaction vial was opened to air and quenched with saturated NH₄Cl solution (20 mL). The resulting mixture was extracted with EtOAc (20 mL x 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether as eluent to afford the pure products.

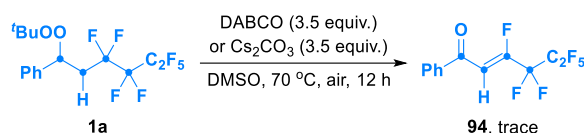
8. Mechanistic studies

1) Possible reaction intermediate: (Z)-3,4,4,5,5,6,6,6-octafluoro-1-phenylhex-2-en-1-one (**94**)^[3]



To an oven-dried vial equipped with a stir bar was added (1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (**1a**, 123.7 mg, 0.3 mmol), triethylenediamine (DABCO, 84.1 mg, 0.75 mmol), and DCE (2.0 mL) at room temperature under air. The vial, containing a pale-yellow reaction mixture, was sealed with a rubber septum, placed in an oil bath at 70 °C and stirred for 12 h. Upon completion of the reaction (indicated by TLC analysis), the resulting black mixture was cooled to room temperature, opened to air, quenched with saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1 to 20/1) as eluent to afford the product **94**^[3] (41.0 mg, 43% yield, yellow oil).

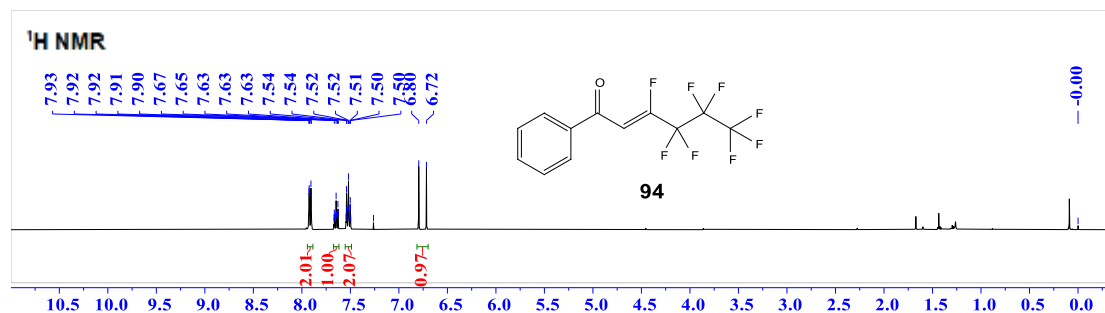
This result suggested that compound **94** is a possible intermediate for the diphosphinylation reaction.

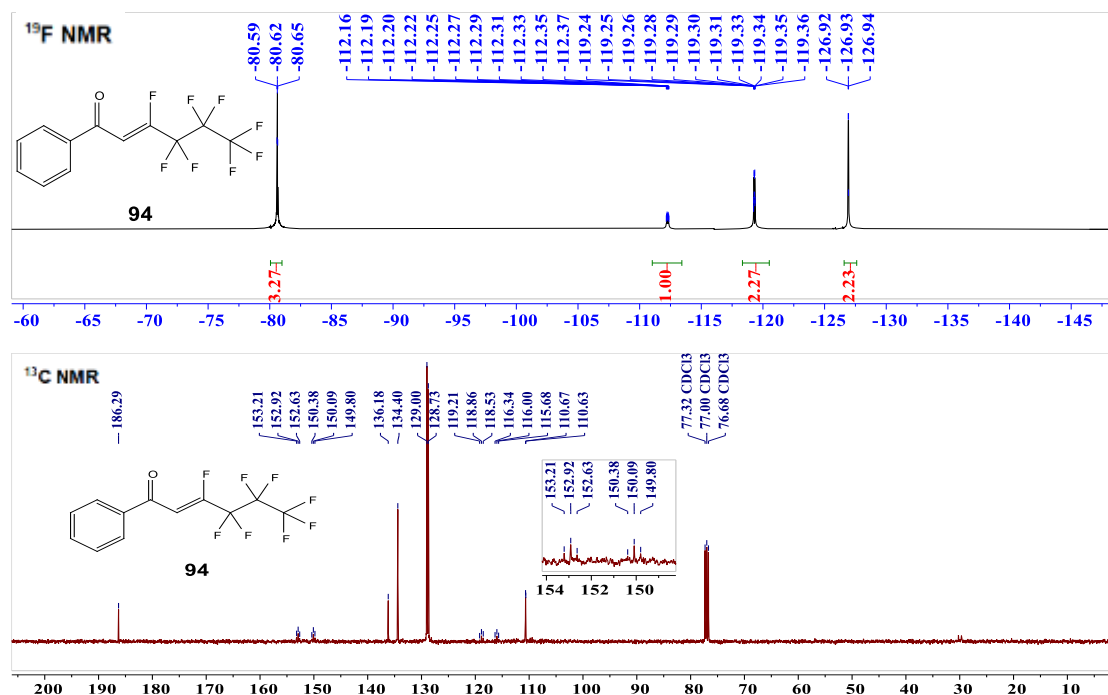


To an oven-dried vial equipped with a stir bar was added (1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (**1a**, 123.7 mg, 0.3 mmol), base (DABCO or Cs_2CO_3 , 1.05 mmol), and DMSO (2.0 mL) at room temperature under air and the vial was sealed with a rubber septum. The pale-yellow reaction mixture was placed in an oil bath at 70 °C and stirred for 12 h. Upon completion of the reaction (indicated by TLC analysis), the vial was cooled to room temperature and the septum removed. The resulting black mixture was then quenched with saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO_4 , filtered, and concentrated under reduced pressure.

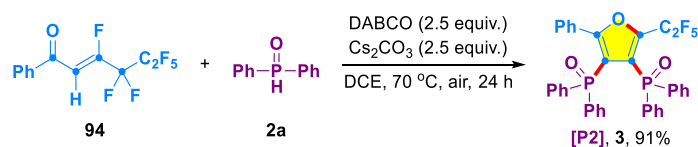
Analysis of the ^{19}F NMR spectra of the residue indicated that there was no desired compound **94** formed under the reaction conditions. This result might be attributed to the instability of the compound **94** in DMSO.^[3]

NMR spectra of (Z)-3,4,4,5,5,6,6,6-octafluoro-1-phenylhex-2-en-1-one (**94**) in CDCl_3



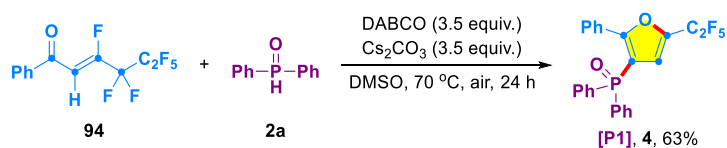


2) Control experiments of (Z)-3,4,4,5,5,6,6,6-octafluoro-1-phenylhex-2-en-1-one (**94**) with diphenylphosphine oxide (**2a**)



To an oven-dried vial equipped with a stir bar was added (Z)-3,4,4,5,5,6,6,6-octafluoro-1-phenylhex-2-en-1-one (**94**, 114.5 mg, 0.36 mmol), diphenylphosphine oxide (**2a**, 60.7 mg, 0.3 mmol), triethylenediamine (DABCO, 84.1 mg, 0.75 mmol), Cs₂CO₃ (244.4 mg, 0.75 mmol), and DCE (2.0 mL) at room temperature under air and the vial was sealed with a rubber septum. The pale-yellow reaction mixture was placed in an oil bath at 70 °C and stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the reaction was cooled to room temperature, opened to air and the resulting black mixture was then quenched by saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine (20 mL) twice, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using dichloromethane/methanol (20/1) as eluent to afford the pure product **3** (90.4 mg, 91% yield, white solid).

This result suggested that compound **94** is a possible reaction intermediate for the diphosphinylation.

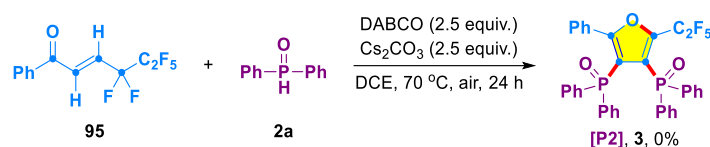


To an oven-dried vial equipped with a stir bar was added (Z)-3,4,4,5,5,6,6,6-octafluoro-1-phenylhex-2-en-1-one (**94**, 95.4 mg, 0.3 mmol),

diphenylphosphine oxide (**2a**, 182.0 mg, 0.9 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol), Cs₂CO₃ (342.1 mg, 1.05 mmol), and DMSO (2.0 mL) at room temperature under air and the vial was sealed with a rubber septum. The pale-yellow reaction mixture was placed in an oil bath at 70 °C and stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the vial was cooled to room temperature, opened to air, and the resulting black mixture was then quenched by saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine (20 mL) twice, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using dichloromethane/methanol (20/1) as eluent to afford the pure product **4** (87.4 mg, 63% yield, white solid).

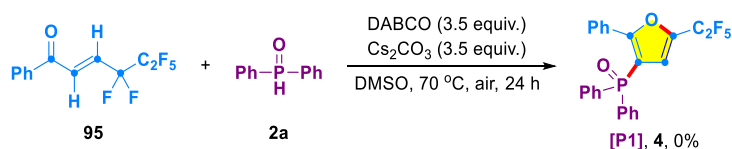
*This result suggested that compound **94** is a possible reaction intermediate for the monophosphinylation.*

3) Control experiments of (*E*)-4,4,5,5,6,6,6-heptafluoro-1-phenylhex-2-en-1-one (**95**)^[4] with diphenylphosphine oxide (**2a**)



To an oven-dried vial equipped with a stir bar was added (*E*)-4,4,5,5,6,6,6-heptafluoro-1-phenylhex-2-en-1-one (**95**^[4], 108.1 mg, 0.36 mmol), diphenylphosphine oxide (**2a**, 60.7 mg, 0.3 mmol), triethylenediamine (DABCO, 84.1 mg, 0.75 mmol), Cs₂CO₃ (244.4 mg, 0.75 mmol), and DCE (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture placed in an oil bath at 70 °C and the reaction mixture stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the vial was opened to air, the resulting black mixture was quenched with saturated NH₄Cl solution (20 mL) and it was extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure.

*Analysis of the ³¹P NMR spectra of the residue indicated that there was no desired product **3** formed under the reaction conditions. This result suggested that the β-fluorine atom of polyfluoroalkyl ketone substrate **94** plays a vital role for the diphosphinylation.*

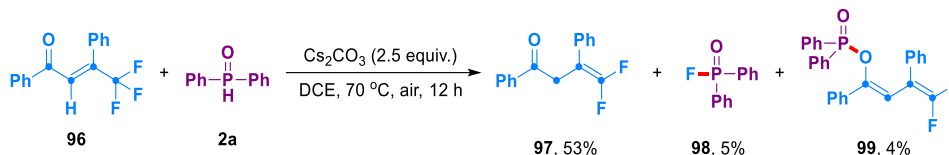


To an oven-dried vial equipped with a stir bar was added (*E*)-4,4,5,5,6,6,6-heptafluoro-1-phenylhex-2-en-1-one (**95**, 90.1 mg, 0.3 mmol), diphenylphosphine oxide (**2a**, 182.0 mg, 0.9 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol, DABCO), Cs₂CO₃ (342.1 mg, 1.05 mmol), and DMSO (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture was placed in an oil bath at 70 °C and it was stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the vial was opened to air, the resulting black mixture was then quenched with saturated NH₄Cl solution (20 mL) and it was extracted with EtOAc (20 mL x 3). The organic layer was

washed twice with saturated brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure.

Analysis of the ³¹P NMR spectra of the residue indicated that there was no desired product 4 formed under the reaction conditions. This result suggested that the β-fluorine atom of polyfluoroalkyl ketone substrate 94 plays a vital role for the monophosphinylation.

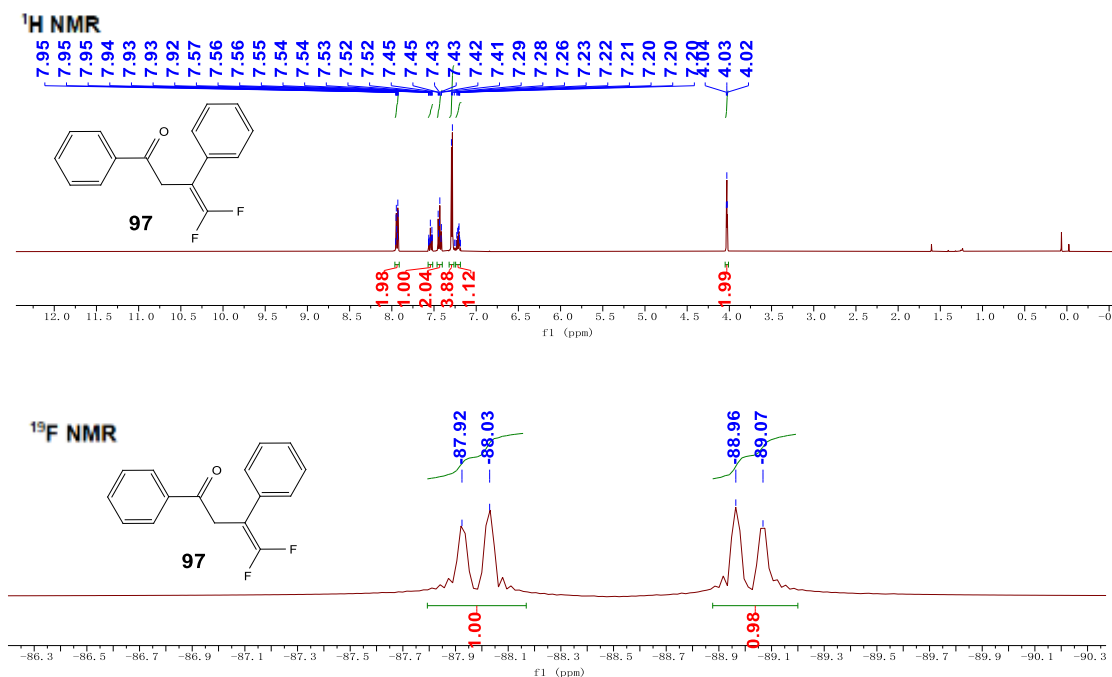
4) Control experiment of (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one (96)^[5] with diphenylphosphine oxide (2a)

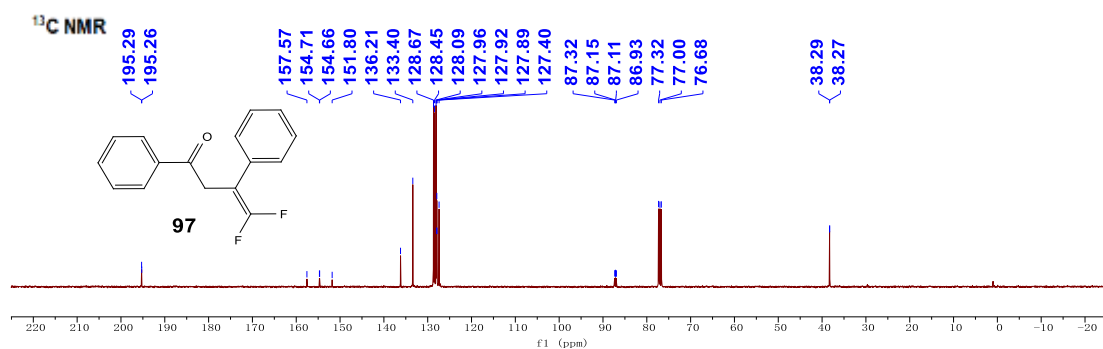


To an oven-dried vial equipped with a stir bar was added (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one (**96**, 82.9 mg, 0.3 mmol), diphenylphosphine oxide (**2a**, 151.6 mg, 0.75 mmol), Cs₂CO₃ (244.4 mg, 0.75 mmol), and DCE (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture was placed in an oil bath at 70 °C and it was stirred for 12 h. Upon completion of the reaction (indicated by TLC analysis), the vial was opened to air, the resulting black mixture was then quenched by saturated NH₄Cl solution (20 mL) and the resulting solution extracted with EtOAc (20 mL x 3). The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (500/1~1/1) as eluent to afford the pure product **97**^[5] (41.1 mg, 53% yield, yellow oil), **98**^[6] (3.3 mg, 5% yield, colorless oil), and **99** (5.5 mg, 4% yield, yellow oil).

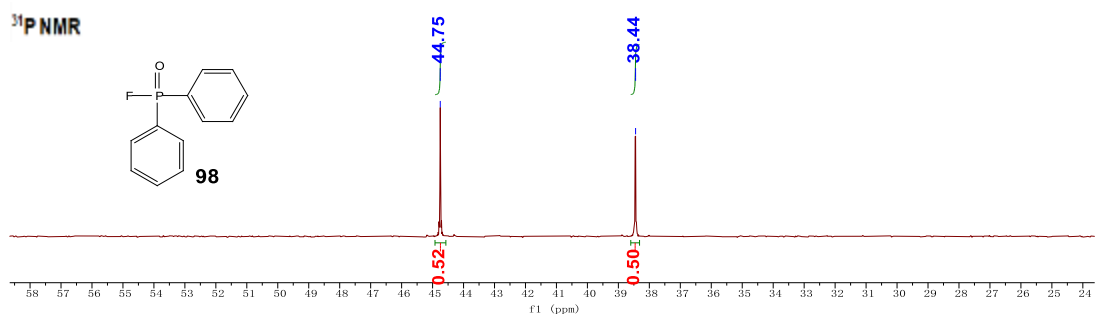
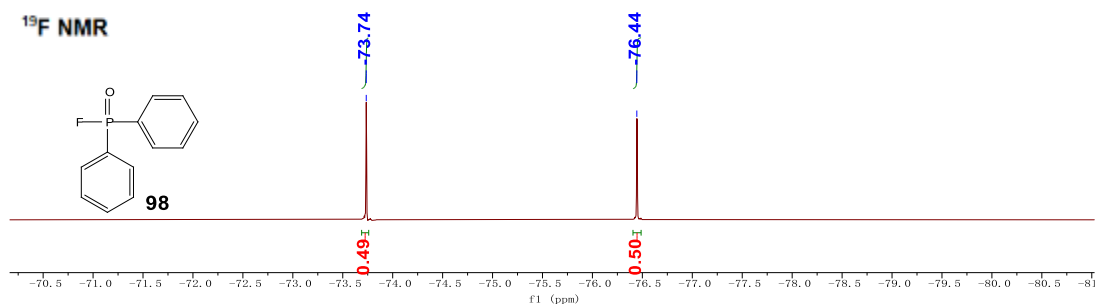
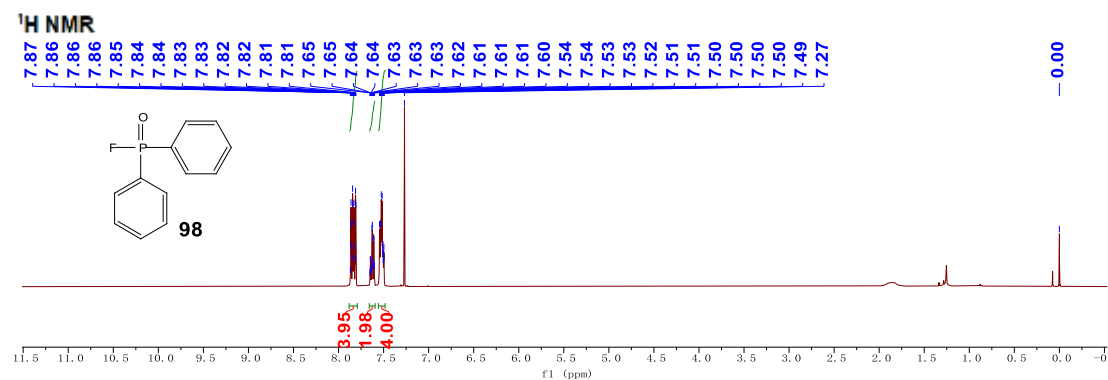
This result suggested that diphenylphosphine oxide (2a) serves as a defluorinative reagent for the phosphinylation.

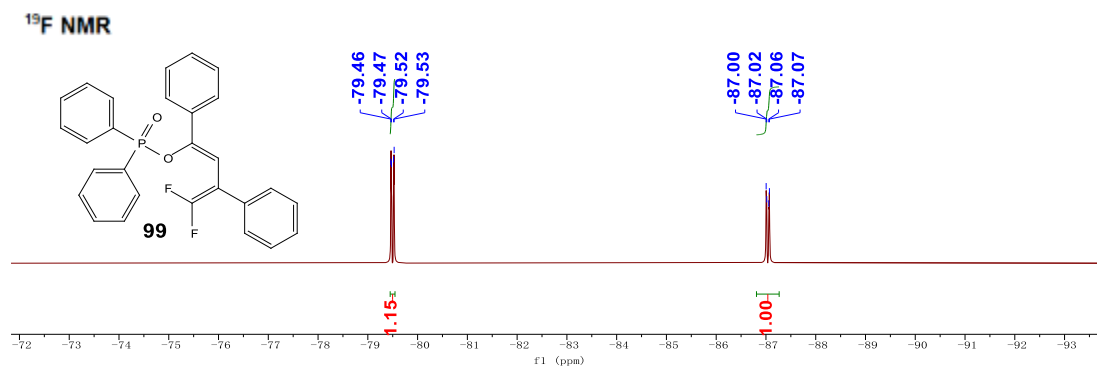
NMR spectra of 4,4-difluoro-1,3-diphenylbut-3-en-1-one (97)

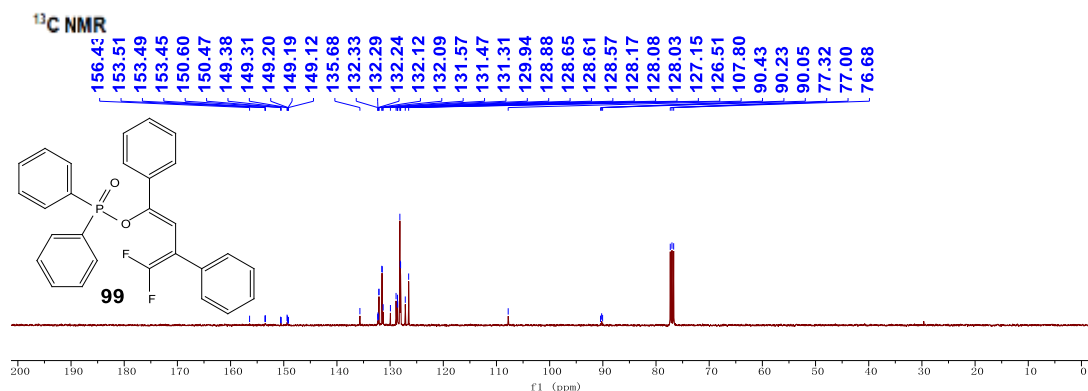




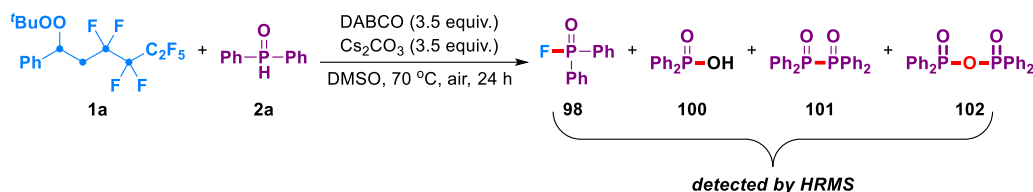
NMR spectra of diphenylphosphinic fluoride (98)







5) Detection of possible reaction intermediates by HRMS



To an oven-dried vial equipped with a stir bar was added (1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (**1a**, 123.7 mg, 0.3 mmol), diphenylphosphine oxide (**2a**, 182.0 mg, 0.9 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol), Cs_2CO_3 (342.1 mg, 1.05 mmol), and DMSO (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture was placed in an oil bath at 70 °C and the solution was stirred for 24 h. Upon completion of the reaction, the vial was cooled to room temperature, the cap was removed, the mixture was passed through a short pad of Celite and it was rinsed with MeCN. A sample was taken from the filtrate and was directly analyzed by HRMS.

HRMS analysis of the reaction mixture suggested the involvement of intermediates **98**, **100**, **101**, and **102**.



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

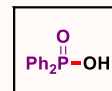
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 10-25 H: 10-22 O: 1-2 P: 1-2

slw-1112-1 (1.388) Is (1.00,1.00) C₁₂H₁₁O₂P

2: TOF MS ES+



100

Calcd for C₁₂H₁₂O₂P⁺ [M+H]⁺

Exact Mass: 219.0569



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
219.0575	219.0575	0.0	0.0	7.5	75.5	n/a	n/a	C12 H12 O2 P

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

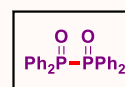
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 24-25 H: 20-22 O: 1-2 P: 1-2

slw-1112-1 (2.071) Is (1.00,1.00) C₂₄H₂₀O₂P₂

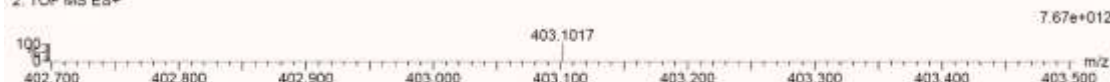
2: TOF MS ES+



101

Calcd for C₂₄H₂₁O₂P₂⁺ [M+H]⁺

Exact Mass: 403.1011



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
403.1017	403.1017	0.0	0.0	15.5	75.7	n/a	n/a	C24 H21 O2 P2

Elemental Composition Report

Page 1

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

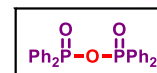
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 22-25 H: 19-22 O: 2-4 P: 1-2

3002-2 256 (1.845)

1: TOF MS ES+



102

Calcd for C₂₄H₂₁O₃P₂⁺ [M+H]⁺

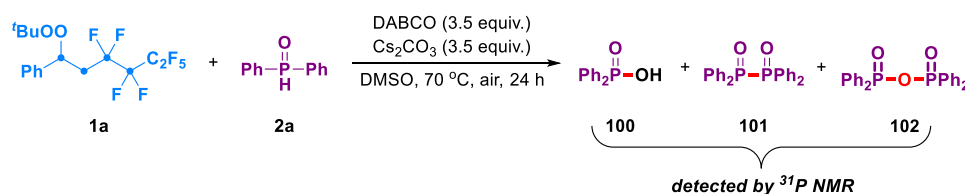
Exact Mass: 419.0960



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
419.0960	419.0966	-0.6	-1.4	15.5	33.7	n/a	n/a	C24 H21 O3 P2

6) Detection of possible reaction intermediates by ³¹P NMR

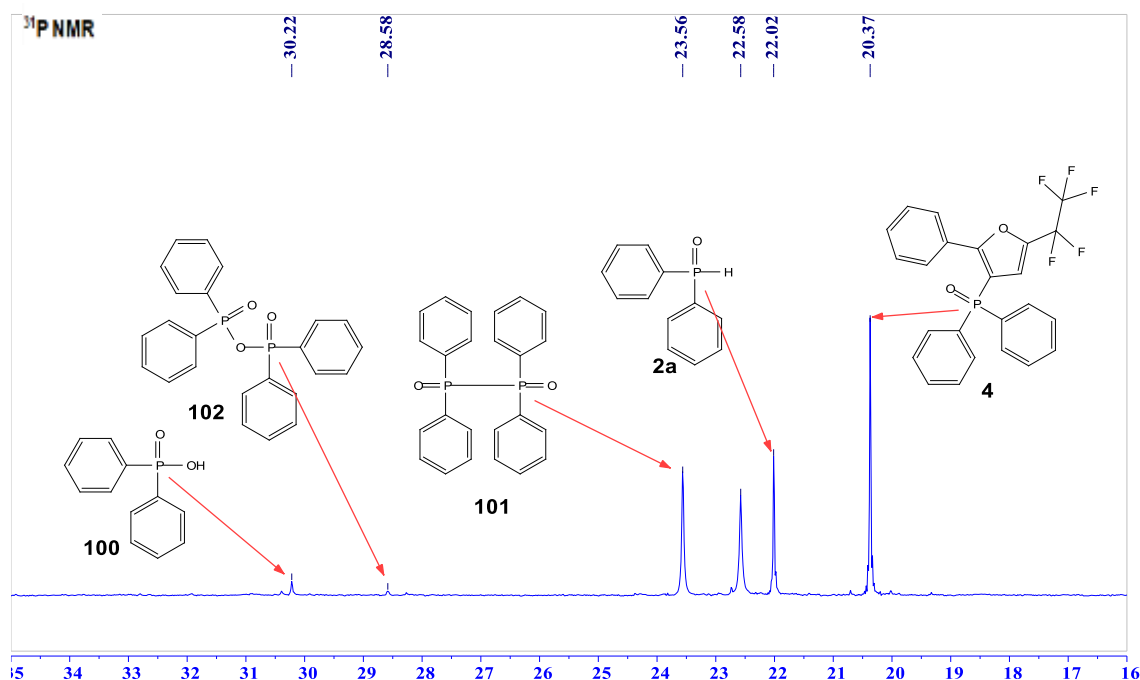


To an oven-dried vial equipped with a stir bar was added

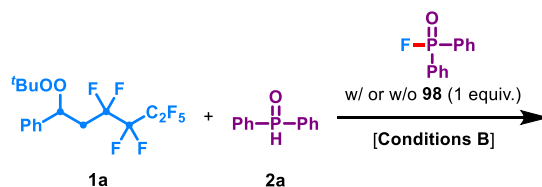
(1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (**1a**, 123.7 mg, 0.3 mmol), diphenylphosphine oxide (**2a**, 182.0 mg, 0.9 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol), Cs₂CO₃ (342.1 mg, 1.05 mmol), and DMSO (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum. the pale-yellow reaction mixture was placed in an oil bath at 70 °C and the solution was stirred for 2 h. Upon completion of the reaction (indicated by TLC analysis), the vial was cooled to room temperature, the cap was removed, the resulting black mixture was then quenched with saturated NH₄Cl solution (20 mL) and it was extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure.

Analysis of the ³¹P NMR spectra of the residue suggested the involvement of intermediate **100**,^[7] intermediate **101**^[8], and intermediate **102**.^[9] The intermediates **101** and **102** were formed by the reaction of diphenylphosphine oxide (**2a**) and diphenylphosphinic fluoride (**98**).^[8-9] Diphenylphosphinic fluoride (**98**) was unstable under the reaction conditions due to the presence of a variety of nucleophiles and was not detected by ³¹P NMR.

Crude ³¹P NMR spectra of the reaction



7) Control experiment in the presence of diphenylphosphinic fluoride (**98**)

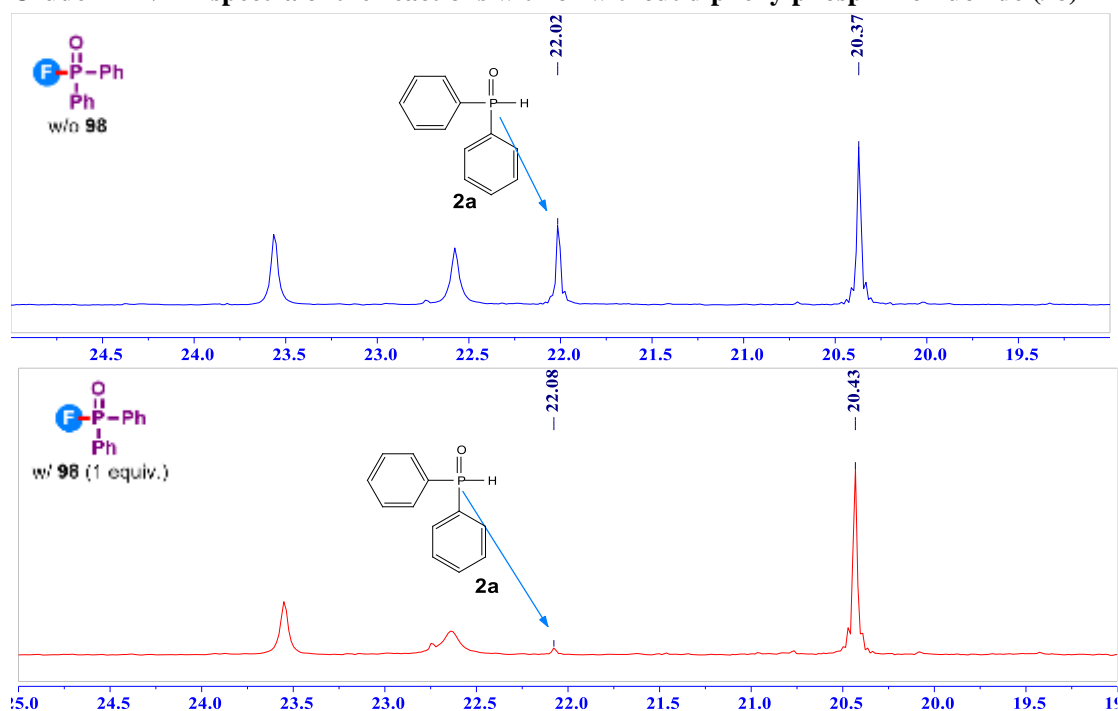


To an oven-dried vial equipped with a stir bar was added (1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (**1a**, 123.7 mg, 0.3 mmol), diphenylphosphine oxide (**2a**, 182.0 mg, 0.9 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol), Cs₂CO₃ (342.1 mg, 1.05 mmol), diphenylphosphinic fluoride (**98**, 0 or 0.3 mmol), and DMSO (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the

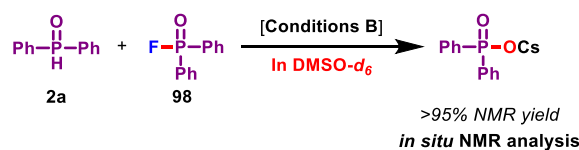
pale-yellow reaction mixture was placed in an oil bath at 70 °C and the solution was stirred for 2 h. Upon completion of the reaction (indicated by TLC analysis), the reaction vial was cooled to room temperature, opened to air, and the resulting black mixture was then quenched with saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure.

Analysis of the ³¹P NMR spectra of two reaction mixtures suggested the consumption of diphenylphosphine oxide (2a) through its reaction with diphenylphosphinic fluoride (98). No diphenylphosphinic fluoride (98) was recovered due to its high reactivity in the reaction.

Crude ³¹P NMR spectra of the reactions with or without diphenylphosphinic fluoride (98)



8) Control experiments of diphenylphosphine oxide (2a) with diphenylphosphinic fluoride (98)

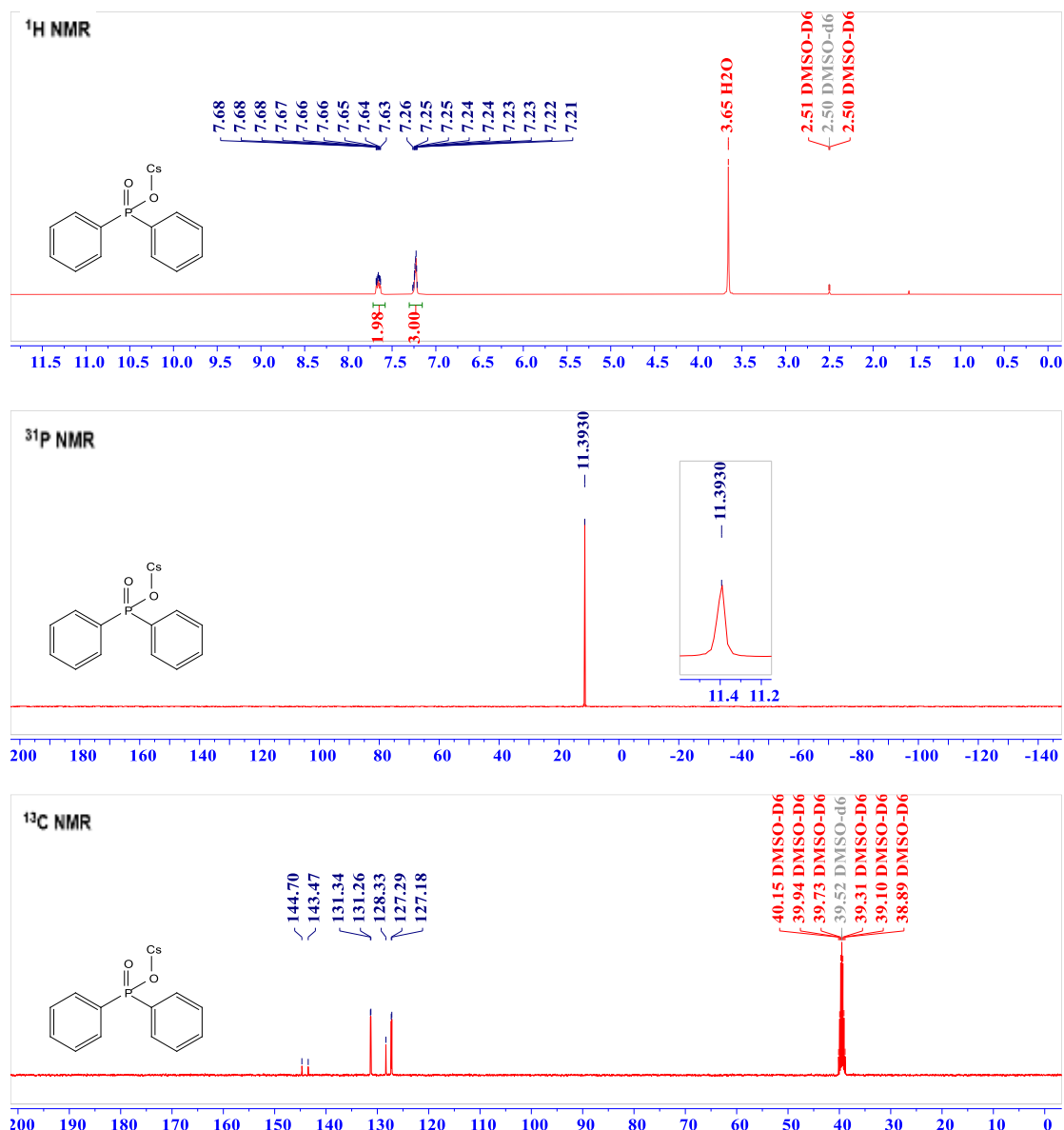


To an oven-dried vial equipped with a stir bar was added diphenylphosphine oxide (**2a**, 60.7 mg, 0.3 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol), Cs₂CO₃ (342.1 mg, 1.05 mmol), diphenylphosphinic fluoride (**98**, 66.1 mg, 0.3 mmol), and DMSO-*d*₆ (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture was placed in an oil bath at 70 °C and stirred for 12 h. The vial was cooled to room temperature, opened to air, and the residue was directly analyzed by NMR.

95% NMR yield of cesium diphenylphosphinate was determined by ³¹P NMR analysis of residue using triphenylphosphine oxide as an internal standard (based on the combination of 2a and 98).

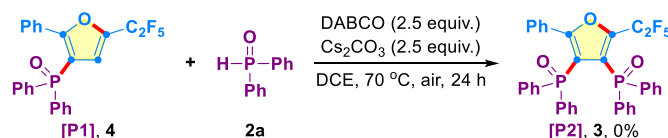
Diphenylphosphinic fluoride (98) was unstable under the reaction conditions.

NMR spectra of cesium diphenylphosphinate



In addition, diphenylphosphinic fluoride (98) was sensitive to air and moisture.

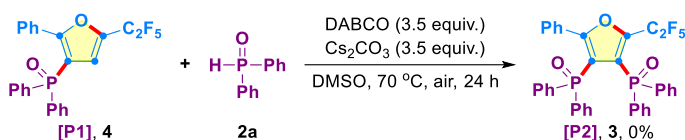
9) Control experiments of (5-(perfluoroethyl)-2-phenylfuran-3-yl)diphenylphosphine oxide (4) with diphenylphosphine oxide (2a)



To an oven-dried vial equipped with a stir bar was added (5-(perfluoroethyl)-2-phenylfuran-3-yl)diphenylphosphine oxide (**4**, 166.4 mg, 0.36 mmol), diphenylphosphine oxide (**2a**, 60.7 mg, 0.3 mmol), triethylenediamine (DABCO, 84.1 mg, 0.75 mmol), Cs₂CO₃ (244.4 mg, 0.75 mmol), and DCE (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture was placed in an oil bath at 70 °C and the solution was stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the vial was removed from the bath, cooled, and opened to air. The resulting black

mixture was then quenched with saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure.

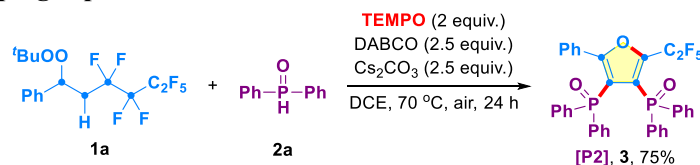
Analysis of the ³¹P NMR spectra of the residue indicated that there was **no desired product 3** formed under the reaction conditions. This result suggested that compound 4 is not the intermediate in the formation of product 3.



To an oven-dried vial equipped with a stir bar was added (5-(perfluoroethyl)-2-phenylfuran-3-yl)diphenylphosphine oxide (**4**, 138.7 mg, 0.3 mmol), diphenylphosphine oxide (**2a**, 182.0 mg, 0.9 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol), Cs₂CO₃ (342.1 mg, 1.05 mmol), and DMSO (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture was placed in an oil bath at 70 °C and the solution was stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the vial was removed from the bath, cooled to room temperature, and opened to air. The resulting black mixture was then quenched with saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure.

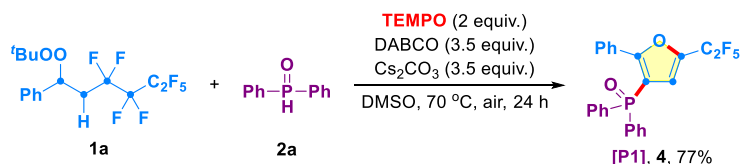
Analysis of the ³¹P NMR spectra of the residue indicated that there was **no desired product 3** formed under the reaction conditions. This result suggested that compound 4 is not the intermediate for the formation of product 3.

10) Radical trapping experiments



To an oven-dried vial equipped with a stir bar was added (1-(tert-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (**1a**, 148.4 mg, 0.36 mmol), diphenylphosphine oxide (**2a**, 60.7 mg, 0.3 mmol), triethylenediamine (DABCO, 84.1 mg, 0.75 mmol), Cs₂CO₃ (244.4 mg, 0.75 mmol), 2,2,6,6-tetramethylpiperidinoxy (TEMPO, 93.8 mg, 0.6 mmol), and DCE (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture was placed in an oil bath at 70 °C and the solution was stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the vial was removed from the bath, cooled to room temperature and the resulting black mixture was quenched with saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using dichloromethane/methanol (20/1) as eluent to afford the pure product **3** (74.5 mg, 75% yield, white solid).

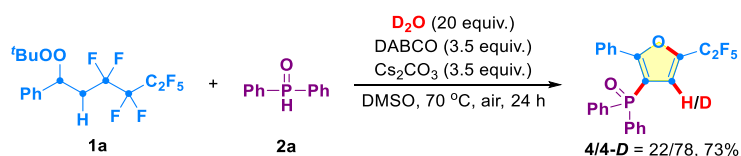
This result suggested that radical processes are not the main pathway for the diphosphinylation.



To an oven-dried vial equipped with a stir bar was added (1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (**1a**, 123.7 mg, 0.3 mmol), diphenylphosphine oxide (**2a**, 182.0 mg, 0.9 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol), Cs_2CO_3 (342.1 mg, 1.05 mmol), 2,2,6,6-tetramethylpiperidinoxy (TEMPO, 93.8 mg, 0.6 mmol), and DMSO (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture was placed in an oil bath at 70 °C and the solution was stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the vial was removed from the bath, cooled to room temperature, and opened to air. The resulting black mixture was quenched with saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using dichloromethane/methanol (20/1) as eluent to afford the pure product **4** (106.8 mg, 77% yield, white solid).

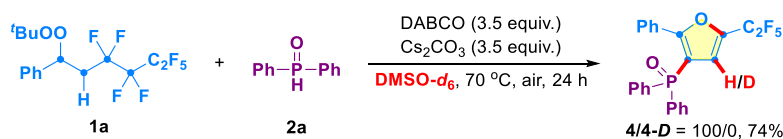
This result suggested that radical process is not the main pathway for the monophosphinylation.

11) Deuterium experiments



To an oven-dried vial equipped with a stir bar was added (1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (**1a**, 123.7 mg, 0.3 mmol), diphenylphosphine oxide (**2a**, 182.0 mg, 0.9 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol), Cs_2CO_3 (342.1 mg, 1.05 mmol), D_2O (120.2 mg, 6 mmol), and DMSO (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture was placed in an oil bath at 70 °C and the solution stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the vial was removed from the bath, allowed to cool to room temperature, and the septum was removed, opening the reaction mixture to air. The resulting black mixture was then quenched with saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using dichloromethane/methanol (20/1) as eluent to afford the pure product **4** and **4-D** (101.2 mg, 73% yield, $4/4\text{-D} = 22/78$, white solid).

This result suggested that the hydrogen atom in product 4 comes from water.

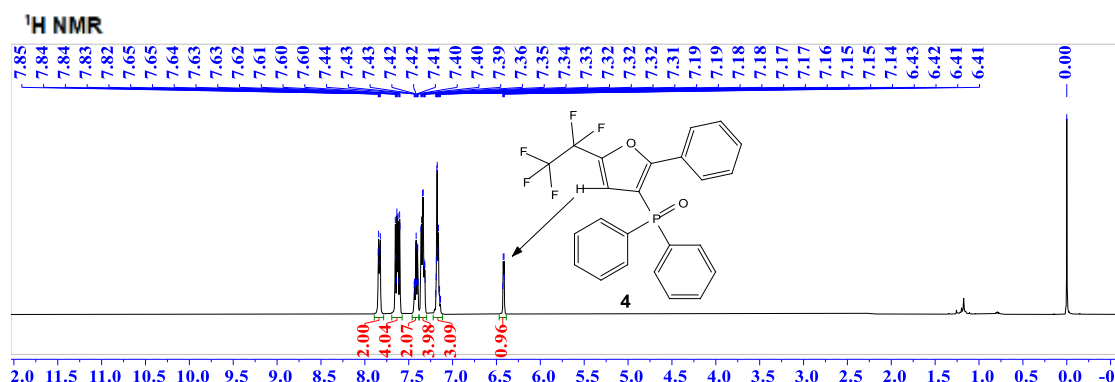


To an oven-dried vial equipped with a stir bar was added (1-(*tert*-butylperoxy)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (**1a**, 123.7 mg, 0.3 mmol),

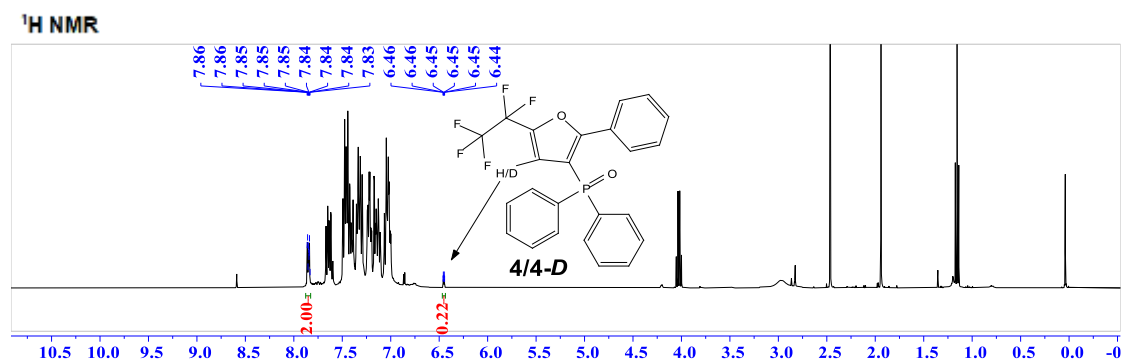
diphenylphosphine oxide (**2a**, 182.0 mg, 0.9 mmol), triethylenediamine (DABCO, 117.8 mg, 1.05 mmol), Cs₂CO₃ (342.1 mg, 1.05 mmol), and DMSO-*d*₆ (2.0 mL) at room temperature under air. The vial was sealed with a rubber septum, the pale-yellow reaction mixture was placed in an oil bath at 70 °C and the solution was stirred for 24 h. Upon completion of the reaction (indicated by TLC analysis), the resulting black mixture was removed from the bath, cooled to room temperature, and opened to air. Next, the reaction was quenched with saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed twice with saturated brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using dichloromethane/methanol (20/1) as eluent to afford the pure product **4** (102.6 mg, 74% yield, white solid).

This result suggested that the hydrogen atom in product 4 doesn't come from DMSO.

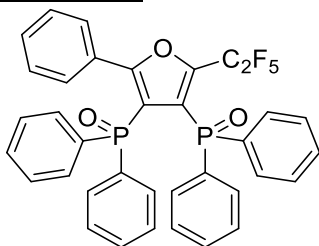
¹H NMR spectra of product 4



Crude ¹H NMR spectra of product 4 and its isomer 4-D (with 20 equiv. of D₂O)



9. Characterization data for products



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(diphenylphosphine oxide) (3):

Yield = 87% (86.5 mg, 0.15 mmol scale). Yield = 87% (172.9 mg, 0.3 mmol scale). White solid.

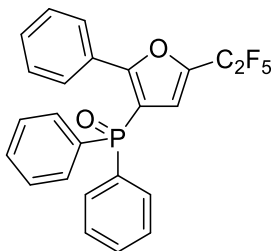
^1H NMR (400 MHz, CDCl_3): δ = 7.58 – 7.44 (m, 8H), 7.44 – 7.33 (m, 4H), 7.32 – 7.26 (m, 4H), 7.25 – 7.17 (m, 3H), 7.17 – 7.04 (m, 6H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -81.98 (s, 3F), -105.88 (s, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 23.54 (s, 1P), 23.42 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 164.3 (m), 144.7 (m), 133.3, 132.2 (m), 132.0 (d, J = 2.9 Hz), 131.9 (d, J = 1.9 Hz), 131.8 (d, J = 2.4 Hz), 131.4 (d, J = 2.9 Hz), 131.2, 130.2, 129.7, 128.1, 127.7 (m), 127.7, 126.3 (m), 117.4 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{36}\text{H}_{26}\text{F}_5\text{O}_3\text{P}_2$ $[\text{M}+\text{H}]^+$ 663.1272, found: 663.1277.



(5-(Perfluoroethyl)-2-phenylfuran-3-yl)diphenylphosphine oxide (4):

Yield = 78% (108.2 mg, 0.3 mmol scale). White solid.

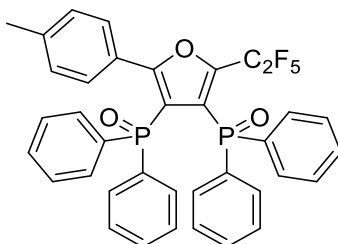
^1H NMR (400 MHz, CDCl_3): δ = 7.89 – 7.79 (m, 2H), 7.69 – 7.58 (m, 4H), 7.46 – 7.38 (m, 2H), 7.37 – 7.30 (m, 4H), 7.22 – 7.11 (m, 3H), 6.47 – 6.39 (m, 1H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -83.85 (t, J = 4.4 Hz, 3F), -114.21 (s, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 20.55 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 162.7 (m), 139.4 (m), 132.2 (d, J = 2.8 Hz), 131.6 (d, J = 109.6 Hz), 131.4 (d, J = 10.0 Hz), 130.2, 128.7, 128.6, 128.3, 128.1, 128.0, 119.1 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{17}\text{F}_5\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$ 463.0881, found: 463.0888.



(2-(Perfluoroethyl)-5-(*p*-tolyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (5):

Yield = 86% (174.6 mg, 0.3 mmol scale). Yellow oil.

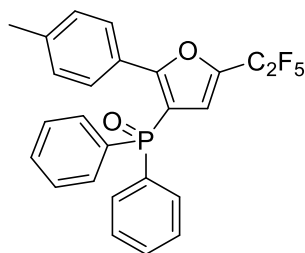
¹H NMR (400 MHz, CDCl₃): δ = 7.60 – 7.43 (m, 9H), 7.43 – 7.37 (m, 2H), 7.30 – 7.20 (m, 7H), 7.15 – 7.06 (m, 4H), 6.94 (d, *J* = 7.8 Hz, 2H), 2.24 (s, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.99 (s, 3F), -105.82 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 24.05 (t, *J* = 13.5 Hz, 1P), 23.36 (t, *J* = 13.2 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.7 (m), 144.6 (m), 140.6, 133.4, 132.4, 132.3, 131.9 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 23.7 Hz), 131.3 (d, *J* = 2.8 Hz), 129.6, 128.4, 127.8 (d, *J* = 13.2 Hz), 127.5 (d, *J* = 12.9 Hz), 126.1 (m), 125.3, 116.9 (m), 21.3 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₇H₂₈F₅O₃P₂ [M+H]⁺ 677.1428, found: 677.1437.



(5-(Perfluoroethyl)-2-(*p*-tolyl)furan-3-yl)diphenylphosphine oxide (6):

Yield = 56% (80.0 mg, 0.3 mmol scale). White solid.

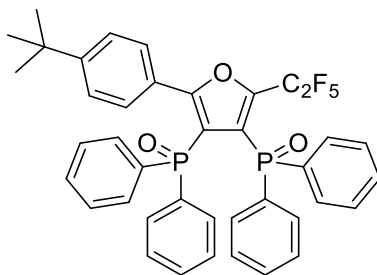
¹H NMR (400 MHz, CDCl₃): δ = 7.85 – 7.79 (m, 2H), 7.75 – 7.65 (m, 4H), 7.52 – 7.45 (m, 2H), 7.44 – 7.37 (m, 4H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.50 – 6.43 (m, 1H), 2.24 (s, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.88 (t, *J* = 3.5 Hz, 3F), -114.08 – -114.30 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.60 (t, *J* = 15.4 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.9 (m), 140.5, 139.0 (m), 132.1 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 109.6 Hz), 131.4 (d, *J* = 10.3 Hz), 129.0, 128.7, 128.5, 128.0, 125.3, 119.1 (m), 21.3 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₅H₁₉F₅O₂P [M+H]⁺ 477.1037, found: 477.1045.



(2-(4-(*tert*-Butyl)phenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (7):

Yield = 71% (153.1 mg, 0.3 mmol scale). Yellow oil.

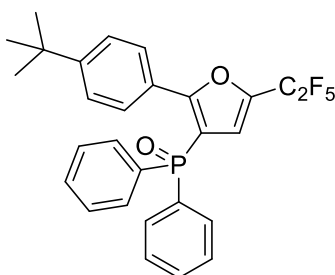
¹H NMR (400 MHz, CDCl₃): δ = 7.57 – 7.44 (m, 9H), 7.41 – 7.36 (m, 2H), 7.29 – 7.24 (m, 5H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.14 – 7.04 (m, 6H), 1.21 (s, 9H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.92 (s, 3F), -105.88 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 23.50 (s, 1P), 23.37 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.3 (m), 153.4, 144.7 (m), 132.9 (d, *J* = 89.6 Hz), 132.1 (d, *J* = 8.6 Hz), 132.0, 131.9 (m), 131.8, 131.3 (d, *J* = 2.8 Hz), 129.5, 128.3 (m), 127.7 (d, *J* = 13.1 Hz), 127.5 (d, *J* = 12.9 Hz), 125.1, 124.7, 116.7 (m), 30.9, 30.8 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₄₀H₃₄F₅O₃P₂ [M+H]⁺ 719.1898, found: 719.1903.



(2-(4-(*tert*-Butyl)phenyl)-5-(perfluoroethyl)furan-3-yl)diphenylphosphine oxide (8):

Yield = 49% (76.2 mg, 0.3 mmol scale). White solid.

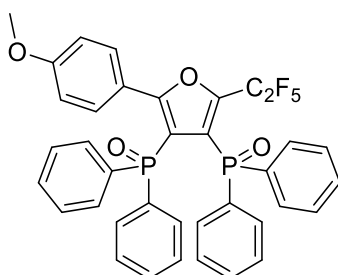
¹H NMR (400 MHz, CDCl₃): δ = 7.83 – 7.77 (m, 2H), 7.75 – 7.67 (m, 4H), 7.54 – 7.46 (m, 2H), 7.45 – 7.38 (m, 4H), 7.30 – 7.23 (m, 2H), 6.54 – 6.48 (m, 1H), 1.24 (s, 9H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.84 – -83.90 (m, 3F), -114.03 – -114.34 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.60 (t, *J* = 13.0 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.9 (m), 153.6, 139.1 (m), 132.4, 132.1 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 10.0 Hz), 131.3, 128.6 (d, *J* = 12.5 Hz), 127.9, 125.3, 125.2, 119.0 (m), 34.7, 30.9 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₈H₂₅F₅O₂P [M+H]⁺ 519.1507, found: 519.1503.



(2-(4-Methoxyphenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (9):

Yield = 72% (149.6 mg, 0.3 mmol scale). Yellow oil.

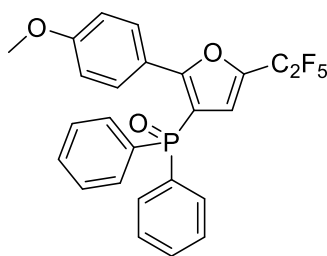
¹H NMR (400 MHz, CDCl₃): δ = 7.61 – 7.51 (m, 4H), 7.48 – 7.33 (m, 8H), 7.30 – 7.25 (m, 4H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.16 – 7.05 (m, 4H), 6.66 (d, *J* = 8.7 Hz, 2H), 3.72 (s, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.01 (s, 3F), -105.85 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 24.28 (t, *J* = 14.5 Hz, 1P), 23.31 (t, *J* = 14.5 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.6 (m), 161.0, 144.1 (m), 133.5, 132.4 (d, *J* = 10.1 Hz), 132.0 (d, *J* = 10.4 Hz), 131.9 (m), 131.8 (d, *J* = 10.6 Hz), 131.3, 131.2, 127.8 (d, *J* = 13.1 Hz), 127.5 (d, *J* = 12.9 Hz), 126.0 (m), 120.5, 116.0 (m), 113.3, 55.2 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₇H₂₈F₅O₄P₂ [M+H]⁺ 693.1377, found: 693.1388.



(2-(4-Methoxyphenyl)-5-(perfluoroethyl)furan-3-yl)diphenylphosphine oxide (10):

Yield = 44% (65.0 mg, 0.3 mmol scale). White solid.

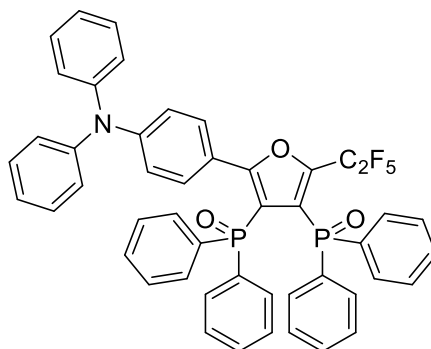
¹H NMR (400 MHz, CDCl₃): δ = 7.94 – 7.86 (m, 2H), 7.75 – 7.65 (m, 4H), 7.55 – 7.47 (m, 2H), 7.46 – 7.39 (m, 4H), 6.80 – 6.73 (m, 2H), 6.46 – 6.40 (m, 1H), 3.74 (s, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.86 (t, *J* = 3.0 Hz, 3F), -114.06 – -114.13 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.85 (t, *J* = 13.6 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.9 (m), 161.1, 138.7 (m), 132.4, 132.2 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 10.0 Hz), 131.3, 129.8, 128.7 (d, *J* = 14.0 Hz), 120.8, 119.2 (m), 113.8, 55.2 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₂₅H₁₉F₅O₃P [M+H]⁺ 493.0986, found: 493.0992.



(2-(4-(Diphenylamino)phenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (11):

Yield = 60% (149.4 mg, 0.3 mmol scale). Yellow oil.

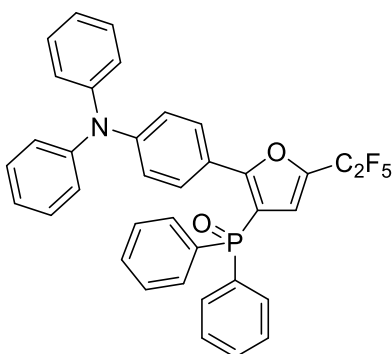
¹H NMR (400 MHz, CDCl₃): δ = 7.60 – 7.44 (m, 8H), 7.44 – 7.37 (m, 2H), 7.31 – 7.23 (m, 12H), 7.18 – 7.10 (m, 4H), 7.09 – 7.04 (m, 2H), 7.04 – 6.98 (m, 4H), 6.74 (d, *J* = 8.4 Hz, 2H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.92 (s, 3F), -105.92 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 23.7-22.8 (m, 2P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.4 (m), 149.6, 146.6, 144.2 (m), 132.6 (m), 131.9, 131.9 (d, *J* = 10.2 Hz), 131.3, 130.7, 129.3, 127.8 (d, *J* = 12.9 Hz), 127.6 (d, *J* = 12.8 Hz), 125.3, 124.0, 120.5, 116.0 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₄₈H₃₅F₅NO₃P₂ [M+H]⁺ 830.2007, found: 830.2012.



(2-(4-(Diphenylamino)phenyl)-5-(perfluoroethyl)furan-3-yl)diphenylphosphine oxide (12):

Yield = 42% (79.3 mg, 0.3 mmol scale). White solid.

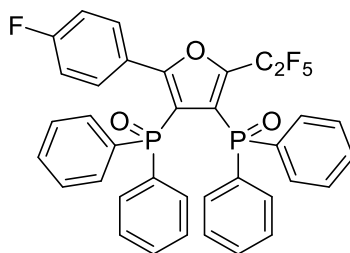
¹H NMR (400 MHz, CDCl₃): δ = 7.79 – 7.67 (m, 6H), 7.56 – 7.49 (m, 2H), 7.48 – 7.39 (m, 4H), 7.24 (t, *J* = 7.8 Hz, 4H), 7.09 – 6.96 (m, 6H), 6.91 – 6.83 (m, 2H), 6.52 – 6.44 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.81 (t, *J* = 2.7 Hz, 3F), -114.03 (q, *J* = 2.4 Hz, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.48 (t, *J* = 13.9 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.9 (m), 149.5, 146.6, 138.6 (m), 132.5, 132.0 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 9.9 Hz), 131.4, 129.3, 129.0, 128.6 (d, *J* = 12.5 Hz), 125.1, 123.8, 121.2, 120.8, 119.1 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₃₆H₂₆F₅NO₂P [M+H]⁺ 630.1616, found: 630.1619.



(2-(4-Fluorophenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (13):

Yield = 70% (142.9 mg, 0.3 mmol scale). Orange solid.

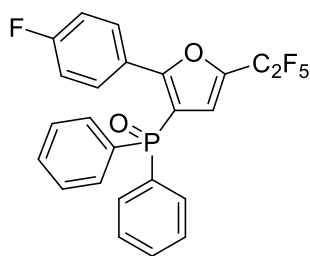
¹H NMR (400 MHz, CDCl₃): δ = 7.66 – 7.54 (m, 4H), 7.50 – 7.40 (m, 8H), 7.36 – 7.21 (m, 6H), 7.21 – 7.09 (m, 4H), 6.87 (t, *J* = 7.8 Hz, 2H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.05 (s, 3F), -105.94 (s, 2F), -108.78 (s, 1F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 24.01 (s, 1P), 23.28 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 163.7 (m), 163.7 (d, *J* = 250.2 Hz), 144.3 (m), 132.7 (d, *J* = 103.7 Hz), 132.2, 132.0, 131.9 (d, *J* = 6.5 Hz), 131.7 (d, *J* = 10.6 Hz), 131.5 (d, *J* = 3.0 Hz), 131.1, 127.9 (d, *J* = 13.0 Hz), 127.6 (d, *J* = 12.9 Hz), 126.1 (m), 124.4, 118.2 (m), 115.0 (d, *J* = 52.0 Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₃₆H₂₅F₆O₃P₂ [M+H]⁺ 681.1178, found: 681.1178.



(2-(4-Fluorophenyl)-5-(perfluoroethyl)furan-3-yl)diphenylphosphine oxide (14):

Yield = 60% (86.5 mg, 0.3 mmol scale). White solid.

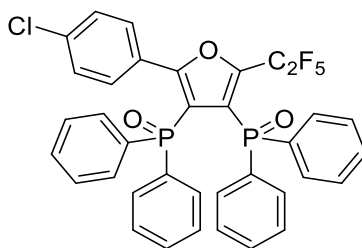
¹H NMR (400 MHz, CDCl₃): δ = 8.00 – 7.90 (m, 2H), 7.77 – 7.63 (m, 4H), 7.55 – 7.47 (m, 2H), 7.46 – 7.37 (m, 4H), 6.99 – 6.88 (m, 2H), 6.47 (d, *J* = 3.7 Hz, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.89 (t, *J* = 2.6 Hz, 3F), -108.85 – -108.99 (m, 1F), -114.25 (q, *J* = 2.3 Hz, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.54 (t, *J* = 13.7 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 163.7 (d, *J* = 250.5 Hz), 161.7 (m), 139.4 (m), 132.3 (d, *J* = 2.8 Hz), 132.0, 131.4 (d, *J* = 10.0 Hz), 130.9, 130.4 (d, *J* = 8.6 Hz), 128.7 (d, *J* = 8.6 Hz), 124.3 (d, *J* = 12.5 Hz), 119.1 (m), 115.5 (d, *J* = 21.9 Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₂₄H₁₆F₆O₂P [M+H]⁺ 481.0787, found: 481.0797.



(2-(4-Chlorophenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (15):

Yield = 72% (150.5 mg, 0.3 mmol scale). Yellow oil.

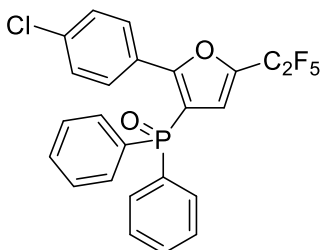
¹H NMR (400 MHz, CDCl₃): δ = 7.65 – 7.55 (m, 4H), 7.46 – 7.35 (m, 8H), 7.32 – 7.22 (m, 6H), 7.19 – 7.10 (m, 6H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.07 (s, 3F), -105.97 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 24.05 (t, *J* = 13.6 Hz, 1P), 23.46 (t, *J* = 13.2 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 163.5 (m), 144.4 (m), 136.6, 133.2, 132.2, 132.0 (d, *J* = 9.0 Hz), 131.8, 131.7, 131.5, 131.1 (m), 128.0 (d, *J* = 4.4 Hz), 127.9 (d, *J* = 12.5 Hz), 127.6 (d, *J* = 12.8 Hz), 126.7, 126.1 (m), 118.3 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₃₆H₂₅ClF₅O₃P₂ [M+H]⁺ 697.0882, found: 697.0875.



(2-(4-Chlorophenyl)-5-(perfluoroethyl)furan-3-yl)diphenylphosphine oxide (16):

Yield = 67% (99.9 mg, 0.3 mmol scale). White solid.

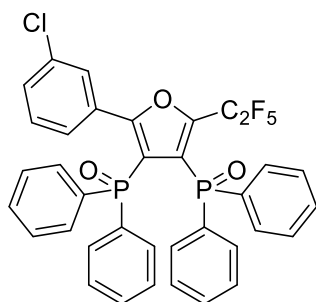
¹H NMR (400 MHz, CDCl₃): δ = 7.96 – 7.87 (m, 2H), 7.74 – 7.63 (m, 4H), 7.54 – 7.46 (m, 2H), 7.45 – 7.38 (m, 4H), 7.24 – 7.18 (m, 2H), 6.49 – 6.44 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.88 (t, *J* = 2.8 Hz, 3F), -114.26 (t, *J* = 2.4 Hz, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.56 (t, *J* = 12.3 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 161.3 (m), 139.6 (m), 136.4, 132.4 (d, *J* = 2.8 Hz), 131.9, 131.4 (d, *J* = 10.0 Hz), 130.8, 129.3, 128.7 (d, *J* = 14.4 Hz), 128.6, 126.4, 119.2 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₂₄H₁₆ClF₅O₂P [M+H]⁺ 497.0491, found: 497.0502.



(2-(3-Chlorophenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (17):

Yield = 76% (158.9 mg, 0.3 mmol scale). Yellow oil.

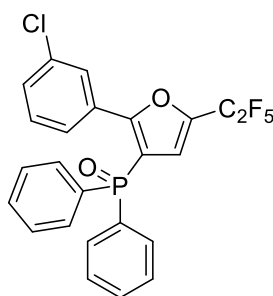
¹H NMR (400 MHz, CDCl₃): δ = 7.63 – 7.34 (m, 11H), 7.31 – 7.25 (m, 4H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.16 – 7.04 (m, 6H), 6.99 (d, *J* = 7.5 Hz, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.09 (s, 3F), -105.97 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 22.79 (s, 1P), 21.49 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 160.5 (m), 141.4 (m), 134.3, 133.6, 132.9, 132.1, 132.0, 131.8 (d, *J* = 10.4 Hz), 131.4 (d, *J* = 11.7 Hz), 130.2, 129.7, 129.3, 129.0, 127.9 (m), 127.8 (d, *J* = 13.0 Hz), 127.6 (d, *J* = 13.0 Hz), 126.0, 119.6 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₃₆H₂₅ClF₅O₃P₂ [M+H]⁺ 697.0882, found: 697.0884.



(2-(3-Chlorophenyl)-5-(perfluoroethyl)furan-3-yl)diphenylphosphine oxide (18):

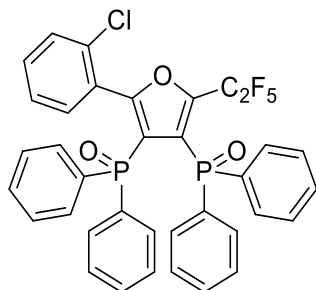
Yield = 59% (87.9 mg, 0.3 mmol scale). White solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.70 – 7.60 (m, 4H), 7.45 – 7.38 (m, 3H), 7.37 – 7.29 (m, 4H), 7.21 – 7.11 (m, 2H), 7.04 – 6.97 (m, 1H), 6.90 – 6.85 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.89 (t, *J* = 3.0 Hz, 3F), -114.35 (q, *J* = 2.9 Hz, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 18.16 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 159.9 (m), 141.0 (m), 134.0, 133.1, 132.1 (d, J = 11.7 Hz), 131.8, 131.5, 131.3 (d, J = 10.1 Hz), 130.7, 129.4, 128.4 (d, J = 12.4 Hz), 127.3, 126.2, 117.3 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{16}\text{ClF}_5\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$ 497.0491, found: 497.0500.



(2-(2-Chlorophenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (19):

Yield = 69% (144.3 mg, 0.3 mmol scale). Yellow oil.

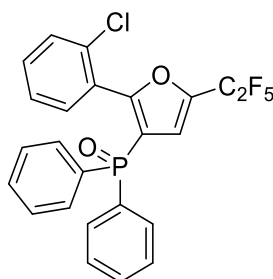
^1H NMR (400 MHz, CDCl_3): δ = 7.62 – 7.40 (m, 10H), 7.35 – 7.20 (m, 9H), 7.18 – 7.07 (m, 5H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -81.98 (s, 3F), -105.96 (s, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 23.63 – 22.46 (m, 2P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 162.5 (m), 144.9 (m), 133.6, 133.0, 132.2, 132.0 (d, J = 2.8 Hz), 131.8 (d, J = 10.5 Hz), 131.6 (d, J = 2.9 Hz), 131.0, 130.3, 129.7, 129.7, 129.0, 128.0, 127.9 (d, J = 13.2 Hz), 127.6 (d, J = 13.2 Hz), 126.4 (m), 119.3 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{36}\text{H}_{25}\text{ClF}_5\text{O}_3\text{P}_2$ $[\text{M}+\text{H}]^+$ 697.0882, found: 697.0891.



(2-(2-Chlorophenyl)-5-(perfluoroethyl)furan-3-yl)diphenylphosphine oxide (20):

Yield = 75% (111.8 mg, 0.3 mmol scale). White solid.

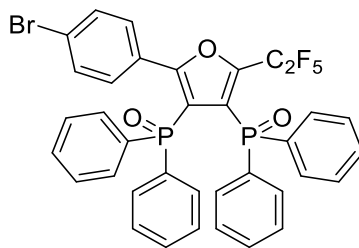
^1H NMR (400 MHz, CDCl_3): δ = 7.91 – 7.85 (m, 2H), 7.76 – 7.67 (m, 4H), 7.56 – 7.49 (m, 2H), 7.48 – 7.40 (m, 4H), 7.25 – 7.21 (m, 1H), 7.20 – 7.14 (m, 1H), 6.54 – 6.49 (m, 1H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -83.84 (t, J = 3.2 Hz, 3F), -114.26 (q, J = 3.0 Hz, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 19.91 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 160.8 (m), 139.9 (m), 134.3, 132.4 (d, J = 2.9 Hz), 131.8, 131.4 (d, J = 10.0 Hz), 130.7, 130.2, 129.6, 129.5, 128.7 (d, J = 12.9 Hz), 127.8, 126.4, 119.1 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{16}\text{ClF}_5\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$ 497.0491, found: 497.0499.



(2-(4-Bromophenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (21):

Yield = 65% (144.6 mg, 0.3 mmol scale). Yellow oil.

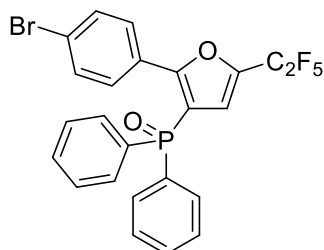
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.64 – 7.56 (m, 4H), 7.47 – 7.37 (m, 6H), 7.34 – 7.23 (m, 10H), 7.19 – 7.08 (m, 4H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -82.06 (s, 3F), -105.97 (s, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 24.20 (s, 1P), 23.50 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 163.6 (m), 144.2 (m), 133.2, 132.1 (d, J = 10.4 Hz), 132.1, 132.1 (d, J = 3.0 Hz), 131.8 (d, J = 10.6 Hz), 131.6 (d, J = 2.9 Hz), 131.3, 131.0, 127.9 (d, J = 13.1 Hz), 127.6 (d, J = 12.9 Hz), 127.2, 126.1 (m), 125.1, 119.0 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{36}\text{H}_{25}\text{BrF}_5\text{O}_3\text{P}_2$ $[\text{M}+\text{H}]^+$ 741.0377, found: 741.0383.



(2-(4-Bromophenyl)-5-(perfluoroethyl)furan-3-yl)diphenylphosphine oxide (22):

Yield = 91% (147.8 mg, 0.3 mmol scale). White solid.

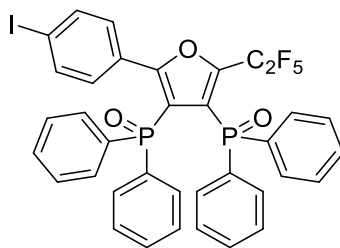
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.88 – 7.81 (m, 2H), 7.74 – 7.64 (m, 4H), 7.56 – 7.49 (m, 2H), 7.48 – 7.35 (m, 6H), 6.49 – 6.43 (m, 1H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -83.86 (t, J = 3.0 Hz, 3F), -114.24 – -114.33 (m, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 20.62 (t, J = 12.9 Hz, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 161.4 (m), 139.6 (m), 132.4 (d, J = 2.9 Hz), 131.9, 131.6, 131.4 (d, J = 10.0 Hz), 130.8, 129.5, 128.7 (d, J = 12.8 Hz), 126.9, 124.9, 119.2 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{16}\text{BrF}_5\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$ 540.9986, found: 540.9998.



(2-(4-Iodophenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (23):

Yield = 85% (124.7 mg, 0.186 mmol scale). Yellow oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.65 – 7.51 (m, 6H), 7.48 – 7.38 (m, 6H), 7.35 – 7.23 (m, 6H),

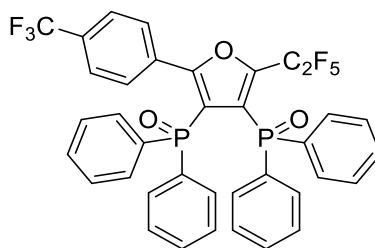
7.21 – 7.08 (m, 6H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -82.05 (s, 3F), -105.93 (s, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 24.50 (t, J = 14.8 Hz, 1P), 23.25 (t, J = 13.3 Hz, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 163.7 (m), 144.4 (m), 136.9, 133.1, 132.1, 132.0 (d, J = 10.3 Hz), 132.0 (d, J = 3.2 Hz), 131.7 (d, J = 10.8 Hz), 131.5 (d, J = 2.9 Hz), 131.2, 131.0, 127.9 (d, J = 13.2 Hz), 127.6 (d, J = 13.1 Hz), 126.1 (m), 118.3 (m), 97.3 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{36}\text{H}_{25}\text{F}_5\text{IO}_3\text{P}_2$ $[\text{M}+\text{H}]^+$ 789.0238, found: 789.0236.



(2-(Perfluoroethyl)-5-(4-(trifluoromethyl)phenyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (24):

Yield = 65% (142.5 mg, 0.3 mmol scale). Yellow oil.

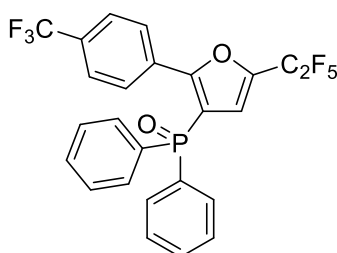
^1H NMR (400 MHz, CDCl_3): δ = 7.71 – 7.54 (m, 6H), 7.52 – 7.39 (m, 8H), 7.37 – 7.23 (m, 6H), 7.22 – 7.09 (m, 4H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -63.08 (s, 3F), -82.09 (t, J = 2.8 Hz, 3F), -106.00 (s, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 24.49 (s, 1P), 23.27 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 163.0 (m), 144.7 (m), 132.2, 132.1 (d, J = 10.5 Hz), 132.0 (d, J = 6.2 Hz), 131.9, 131.8, 131.7, 131.7, 130.9, 130.3, 128.0 (d, J = 13.3 Hz), 127.7 (d, J = 13.2 Hz), 126.2 (m), 124.7 (q, J = 9.6 Hz), 123.5 (q, J = 270.3 Hz), 119.5 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{37}\text{H}_{25}\text{F}_8\text{O}_3\text{P}_2$ $[\text{M}+\text{H}]^+$ 731.1146, found: 731.1151.



(5-(Perfluoroethyl)-2-(4-(trifluoromethyl)phenyl)furan-3-yl)diphenylphosphine oxide (25):

Yield = 64% (101.8 mg, 0.3 mmol scale). White solid.

^1H NMR (400 MHz, CDCl_3): δ = 8.08 (d, J = 8.2 Hz, 2H), 7.78 – 7.64 (m, 4H), 7.58 – 7.50 (m, 4H), 7.49 – 7.41 (m, 4H), 6.55 – 6.47 (m, 1H) ppm.

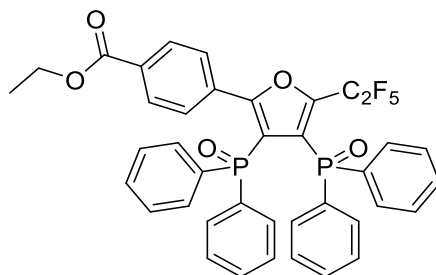
$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -62.99 (s, 3F), -83.82 (t, J = 3.1 Hz, 3F), -114.32 – -114.39 (m, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 20.66 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 160.7 (m), 140.3 (m), 132.6, 131.8, 131.5, 131.4, 131.1 (m), 128.9, 128.8, 128.4, 125.4 (q, J = 3.8 Hz), 123.6 (q, J = 270.6 Hz), 119.3 (m) ppm; carbons

corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₅H₁₆F₈O₂P [M+H]⁺ 531.0755, found: 531.0760.



Ethyl 4-(3,4-bis(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzoate (26):

Yield = 81% (178.5 mg, 0.3 mmol scale). Yellow oil.

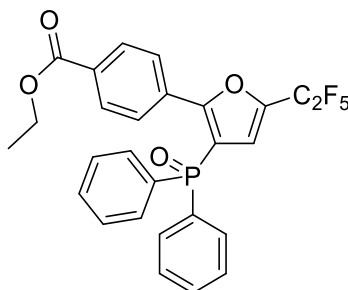
¹H NMR (400 MHz, CDCl₃): δ = 7.85 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.55 (m, 4H), 7.53 – 7.37 (m, 8H), 7.35 – 7.18 (m, 6H), 7.17 – 7.05 (m, 4H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.03 (t, *J* = 2.8 Hz, 3F), -105.94 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 24.33 (s, 1P), 23.32 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 165.6, 163.4 (m), 144.7 (m), 133.1, 132.2, 132.1 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 10.3 Hz), 131.7 (d, *J* = 10.7 Hz), 131.6, 131.6 (d, *J* = 2.8 Hz), 131.0, 129.8, 128.8, 127.9 (d, *J* = 13.1 Hz), 127.6 (d, *J* = 13.0 Hz), 126.2 (m), 119.2 (m), 61.1, 14.1 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₉H₃₀F₅O₅P₂ [M+H]⁺ 735.1483, found: 735.1487.



Ethyl 4-(3-(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzoate (27):

Yield = 62% (99.4 mg, 0.3 mmol scale). White solid.

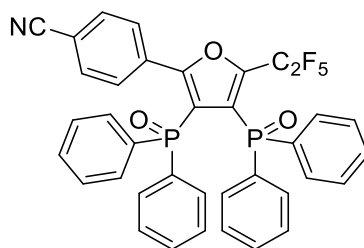
¹H NMR (400 MHz, CDCl₃): δ = 8.02 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.76 – 7.62 (m, 4H), 7.53 – 7.34 (m, 6H), 6.48 (d, *J* = 3.6 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.89 (s, 3F), -114.33 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.46 (t, *J* = 13.1 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 165.6, 161.1 (m), 140.0 (m), 132.4 (d, *J* = 2.9 Hz), 131.8, 131.6, 131.5, 131.3 (d, *J* = 10.1 Hz), 130.7, 129.4, 128.4 (d, *J* = 12.5 Hz), 127.8, 119.3 (m), 61.1, 14.1 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₇H₂₁F₅O₄P [M+H]⁺ 535.1092, found: 535.1096.



4-(3,4-Bis(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzonitrile (28):

Yield = 68% (140.3 mg, 0.3 mmol scale). Yellow oil.

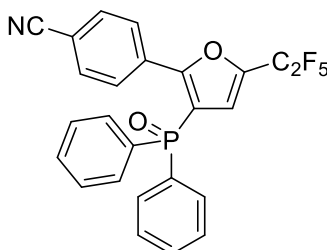
¹H NMR (400 MHz, CDCl₃): δ = 7.73 – 7.62 (m, 6H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.41 – 7.24 (m, 10H), 7.21 – 7.12 (m, 4H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.12 (s, 3F), -106.07 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 25.23 (t, *J* = 13.1 Hz, 1P), 23.30 (t, *J* = 13.4 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.7 (m), 144.4 (m), 133.0, 132.6, 132.1 (d, *J* = 10.2 Hz), 131.9 (d, *J* = 3.5 Hz), 131.8 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 10.9 Hz), 131.4, 130.8, 130.5, 128.0 (d, *J* = 13.3 Hz), 127.7 (d, *J* = 13.0 Hz), 126.1 (m), 120.4 (m), 118.0, 113.7 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₃₇H₂₅F₅NO₃P₂ [M+H]⁺ 688.1224, found: 688.1234.



4-(3-(Diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzonitrile (29):

Yield = 49% (71.6 mg, 0.3 mmol scale). White solid.

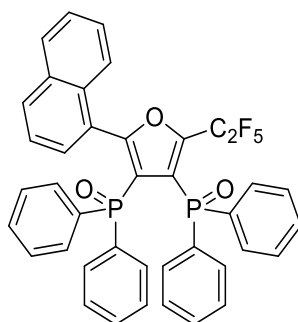
¹H NMR (400 MHz, CDCl₃): δ = 8.17 – 8.09 (m, 2H), 7.74 – 7.64 (m, 4H), 7.60 – 7.52 (m, 4H), 7.50 – 7.42 (m, 4H), 6.52 – 6.47 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.80 (t, *J* = 3.0 Hz, 3F), -114.37 – -114.44 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.57 (t, *J* = 13.0 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 159.9 (m), 140.6 (m), 132.7 (d, *J* = 2.9 Hz), 132.1, 131.8, 131.5, 131.4 (d, *J* = 10.1 Hz), 130.4, 128.9 (d, *J* = 12.8 Hz), 128.5, 119.3 (m), 118.1, 113.4 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₂₅H₁₆F₅NO₂P [M+H]⁺ 488.0833, found: 488.0845.



2-(Naphthalen-1-yl)-5-(perfluoroethyl)furan-3,4-diylbis(diphenylphosphine oxide) (30):

Yield = 53% (113.3 mg, 0.3 mmol scale). Yellow oil.

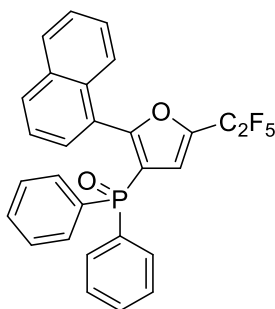
¹H NMR (400 MHz, CDCl₃): δ = 7.80 – 7.71 (m, 4H), 7.70 – 7.64 (m, 2H), 7.46 – 7.37 (m, 5H), 7.36 – 7.27 (m, 6H), 7.23 – 7.11 (m, 5H), 7.05 – 6.95 (m, 2H), 6.90 – 6.80 (m, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.91 (s, 3F), -106.00 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 22.82 (s, 1P), 21.32 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.2 (m), 143.1 (m), 132.9, 132.7, 132.3 (d, *J* = 10.5 Hz), 132.0, 132.0, 131.6, 131.2, 131.1, 130.9, 130.4, 128.1, 127.8 (d, *J* = 13.2 Hz), 127.2 (d, *J* = 12.9 Hz), 126.9, 126.3, 125.6 (m), 125.5, 124.7, 124.3, 119.8 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₄₀H₂₈F₅O₃P₂ [M+H]⁺ 713.1428, found: 713.1434.



(2-(Naphthalen-1-yl)-5-(perfluoroethyl)furan-3-yl)diphenylphosphine oxide (31):

Yield = 74% (113.8 mg, 0.3 mmol scale). White solid.

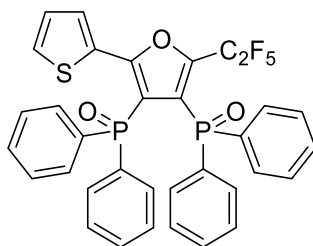
¹H NMR (400 MHz, CDCl₃): δ = 7.76 – 7.68 (m, 2H), 7.66 – 7.53 (m, 6H), 7.52 – 7.43 (m, 2H), 7.31 – 7.24 (m, 2H), 7.24 – 7.12 (m, 5H), 7.05 – 7.00 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.75 (t, *J* = 3.0 Hz, 3F), -114.13 (q, *J* = 2.2 Hz, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 18.47 (t, *J* = 14.1 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.3 (m), 140.7 (m), 133.0, 131.8 (d, *J* = 2.8 Hz), 131.7, 131.3, 131.1 (d, *J* = 10.0 Hz), 130.9, 130.6, 130.5, 128.2, 128.1 (d, *J* = 12.7 Hz), 127.1, 126.1, 125.1, 124.6, 124.4, 117.8 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₈H₁₉F₅O₂P [M+H]⁺ 513.1037, found: 513.1052.



(2-(Perfluoroethyl)-5-(thiophen-2-yl)furan-3,4-diyl)bis(diphenylphosphine oxide) (32):

Yield = 76% (152.4 mg, 0.3 mmol scale). Yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.64 – 7.55 (m, 4H), 7.49 – 7.39 (m, 6H), 7.37 – 7.33 (m, 2H), 7.32 – 7.25 (m, 6H), 7.20 – 7.12 (m, 4H), 6.85 – 6.79 (m, 1H) ppm.

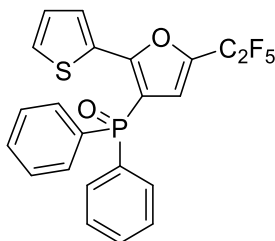
¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.99 (s, 3F), -105.75 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 25.36 (t, *J* = 14.8 Hz, 1P), 23.71 (t, *J* = 13.5 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 158.4 (m), 144.0 (m), 132.8 (d, *J* = 12.1 Hz), 132.2, 132.1, 132.0, 131.8 (d, *J* = 10.7 Hz), 131.7, 131.6 (d, *J* = 2.9 Hz), 131.1, 130.1, 128.6, 127.9 (d, *J* = 13.0

Hz), 127.6 (d, $J = 13.0$ Hz), 127.3, 126.4 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{34}H_{24}F_5O_3P_2S$ $[M+H]^+$ 669.0836, found: 669.0834.



(5-(Perfluoroethyl)-2-(thiophen-2-yl)furan-3-yl)diphenylphosphine oxide (33):

Yield = 63% (88.5 mg, 0.3 mmol scale). White solid.

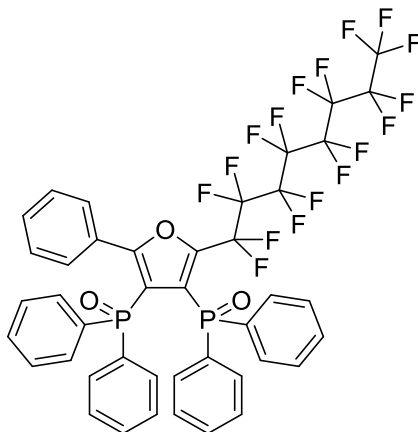
1H NMR (400 MHz, $CDCl_3$): $\delta = 7.90 - 7.85$ (m, 1H), 7.78 – 7.65 (m, 4H), 7.59 – 7.40 (m, 6H), 7.34 – 7.30 (m, 1H), 6.93 – 6.87 (m, 1H), 6.46 – 6.37 (m, 1H) ppm.

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): $\delta = -83.86$ (t, $J = 3.0$ Hz, 3F), -114.08 – -114.27 (m, 2F) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 20.70$ (t, $J = 15.3$ Hz, 1P) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 157.8$ (m), 138.6 (m), 132.4 (d, $J = 2.9$ Hz), 131.9, 131.4 (d, $J = 10.2$ Hz), 130.9, 130.8, 129.5, 129.1, 128.7 (d, $J = 12.6$ Hz), 128.1, 119.0 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{22}H_{15}F_5O_2PS$ $[M+H]^+$ 469.0445, found: 469.0453.



(2-(Perfluorooctyl)-5-phenylfuran-3,4-diyl)bis(diphenylphosphine oxide) (34):

Yield = 82% (236.8 mg, 0.3 mmol scale). Yellow oil.

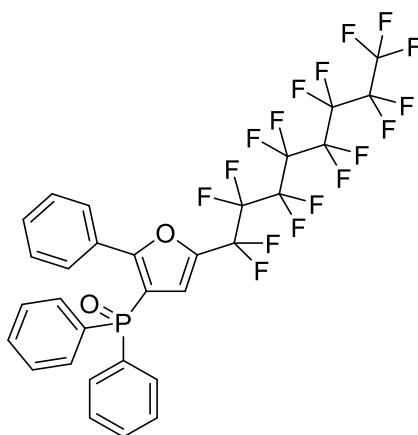
1H NMR (400 MHz, $CDCl_3$): $\delta = 7.62 - 7.53$ (m, 4H), 7.51 – 7.38 (m, 8H), 7.34 – 7.06 (m, 13H) ppm.

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): $\delta = -80.71$ (t, $J = 9.9$ Hz, 3F), -103.22 (t, $J = 14.1$ Hz, 2F), -119.53 – -119.96 (m, 2F), -121.32 – -122.19 (m, 6F), -122.50 – -122.94 (m, 2F), -125.98 – -126.34 (m, 2F) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 23.90$ (t, $J = 14.9$ Hz, 1P), 23.57 (t, $J = 13.2$ Hz, 1P) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 165.0$ (m), 144.5 (m), 133.6, 132.5, 131.9 (m), 131.9, 131.8, 131.3 (d, $J = 2.9$ Hz), 130.2, 129.8, 128.3, 127.9, 127.8, 127.5 (d, $J = 12.9$ Hz), 126.4 (m), 117.5 (m) ppm; carbons corresponding to the C_8F_{17} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{42}H_{26}F_{17}O_3P_2$ $[M+H]^+$ 963.1080, found: 963.1086.



(5-(Perfluorooctyl)-2-phenylfuran-3-yl)diphenylphosphine oxide (35):

Yield = 44% (100.6 mg, 0.3 mmol scale). White solid.

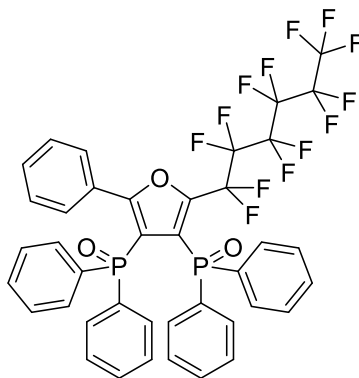
¹H NMR (400 MHz, CDCl₃): δ = 7.98 – 7.89 (m, 2H), 7.77 – 7.66 (m, 4H), 7.55 – 7.37 (m, 6H), 7.30 – 7.22 (m, 3H), 6.51 (d, *J* = 3.7 Hz, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -80.79 (t, *J* = 10.2 Hz, 3F), -111.27 (t, *J* = 13.2 Hz, 2F), -121.38 – -122.05 (m, 6F), -122.11 – -122.39 (m, 2F), -122.55 – -122.99 (m, 2F), -126.04 – -126.23 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.51 (t, *J* = 13.2 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.9 (m), 139.6 (m), 132.3, 132.2, 131.4 (d, *J* = 10.0 Hz), 131.1, 130.2, 128.6 (d, *J* = 12.6 Hz), 128.4, 128.1, 128.0, 119.6 (m) ppm; carbons corresponding to the C₈F₁₇ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₃₀H₁₇F₁₇O₂P [*M*+H]⁺ 763.0689, found: 763.0695.



(2-(Perfluorohexyl)-5-phenylfuran-3,4-diyl)bis(diphenylphosphine oxide) (36):

Yield = 77% (199.3 mg, 0.3 mmol scale). Yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.62 – 7.53 (m, 4H), 7.52 – 7.39 (m, 8H), 7.34 – 7.07 (m, 13H) ppm.

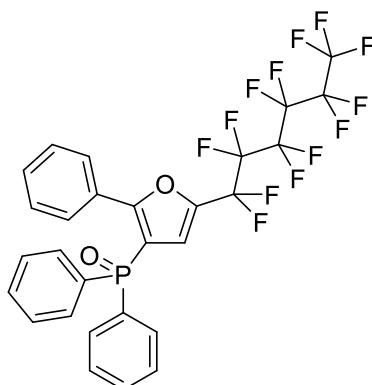
¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -80.69 (t, *J* = 9.8 Hz, 3F), -103.21 (t, *J* = 14.5 Hz, 2F), -119.38 – -120.22 (m, 2F), -121.38 – -122.00 (m, 2F), -122.39 – -123.09 (m, 2F), -125.56 – -126.49 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 23.91 (t, *J* = 12.1 Hz, 1P), 23.56 (t, *J* = 15.0 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.9 (m), 144.5 (m), 133.6, 132.5, 132.0, 131.9 (m), 131.8 (d, *J* = 14.8 Hz), 131.3 (d, *J* = 2.9 Hz), 130.2, 129.8, 128.3, 127.9, 127.8, 127.5 (d, *J* = 12.9

Hz), 126.4 (m), 117.5 (m) ppm; carbons corresponding to the C₆F₁₃ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₄₀H₂₆F₁₃O₃P₂ [M+H]⁺ 863.1144, found: 863.1149.



(5-(Perfluorohexyl)-2-phenylfuran-3-yl)diphenylphosphine oxide (37):

Yield = 56% (111.3 mg, 0.3 mmol scale). White solid.

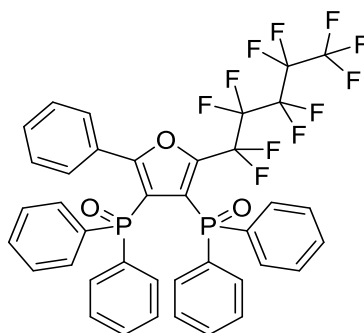
¹H NMR (400 MHz, CDCl₃): δ = 7.99 – 7.90 (m, 2H), 7.77 – 7.67 (m, 4H), 7.55 – 7.37 (m, 6H), 7.30 – 7.22 (m, 3H), 6.54 – 6.48 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -80.77 (t, *J* = 10.1 Hz, 3F), -111.28 (t, *J* = 13.2 Hz, 2F), -121.69 – -121.94 (m, 2F), -122.15 – -122.43 (m, 2F), -122.62 – -122.98 (m, 2F), -125.91 – -126.67 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.47 (t, *J* = 9.6 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.8 (m), 139.5 (m), 132.3, 132.2 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 10.0 Hz), 131.2, 130.2, 128.7, 128.4 (d, *J* = 23.4 Hz), 128.1, 128.0, 119.6 (m) ppm; carbons corresponding to the C₆F₁₃ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₈H₁₇F₁₃O₂P [M+H]⁺ 663.0753, found: 663.0757.



(2-(Perfluoropentyl)-5-phenylfuran-3,4-diyl)bis(diphenylphosphine oxide) (38):

Yield = 81% (197.5 mg, 0.3 mmol scale). Yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.62 – 7.52 (m, 4H), 7.51 – 7.38 (m, 8H), 7.36 – 7.05 (m, 13H) ppm.

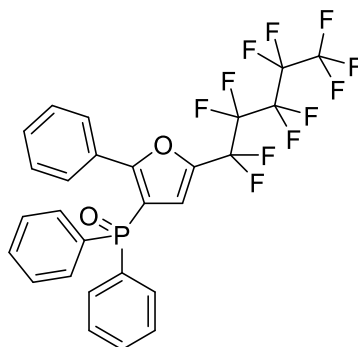
¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -80.67 (t, *J* = 10.0 Hz, 3F), -102.98 – -103.49 (m, 2F), -119.91 (t, *J* = 13.6 Hz, 2F), -122.28 – -122.76 (m, 2F), -125.94 – -126.47 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 23.87 (s, 1P), 23.56 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 165.0 (m), 144.6 (m), 133.6, 132.5, 131.9 (m), 131.9 (d, *J* = 19.3 Hz), 131.8, 131.3 (d, *J* = 2.9 Hz), 130.2, 129.8, 128.3, 127.9, 127.8, 127.5 (d, *J* = 12.9 Hz),

126.5 (m), 117.5 (m) ppm; carbons corresponding to the C₅F₁₁ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₉H₂₆F₁₁O₃P₂ [M+H]⁺ 813.1176, found: 813.1185.



(5-(Perfluoropentyl)-2-phenylfuran-3-yl)diphenylphosphine oxide (39):

Yield = 77% (141.5 mg, 0.3 mmol scale). White solid.

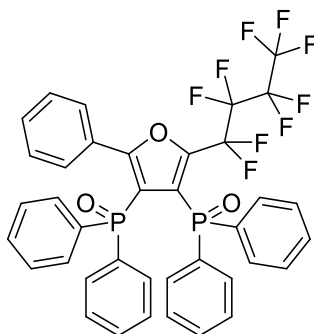
¹H NMR (400 MHz, CDCl₃): δ = 7.97 – 7.87 (m, 2H), 7.76 – 7.63 (m, 4H), 7.51 – 7.35 (m, 6H), 7.27 – 7.18 (m, 3H), 6.49 (d, *J* = 3.8 Hz, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -80.76 (t, *J* = 9.9 Hz, 3F), -111.23 – -111.44 (m, 2F), -122.34 – -122.53 (m, 2F), -122.57 – -122.78 (m, 2F), -126.08 – -126.36 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.46 (t, *J* = 12.3 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.8 (m), 139.5 (m), 132.2, 132.2 (d, *J* = 2.8 Hz), 131.4 (d, *J* = 10.0 Hz), 131.1, 130.2, 128.6 (d, *J* = 12.5 Hz), 128.3, 128.1, 128.0, 119.6 (m) ppm; carbons corresponding to the C₅F₁₁ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₇H₁₇F₁₁O₂P [M+H]⁺ 613.0785, found: 613.0796.



(2-(Perfluorobutyl)-5-phenylfuran-3,4-diyl)bis(diphenylphosphine oxide) (40):

Yield = 87% (199.0 mg, 0.3 mmol scale). Yellow oil.

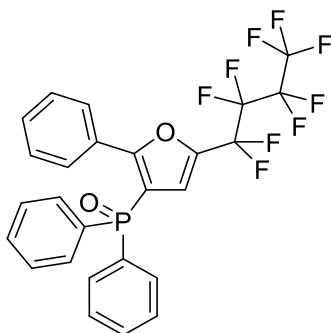
¹H NMR (400 MHz, CDCl₃): δ = 7.61 – 7.52 (m, 4H), 7.51 – 7.43 (m, 4H), 7.44 – 7.37 (m, 4H), 7.34 – 7.24 (m, 5H), 7.24 – 7.19 (m, 2H), 7.19 – 7.07 (m, 6H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -80.86 (t, *J* = 9.7 Hz, 3F), -103.34 (t, *J* = 13.5 Hz, 2F), -120.69 (q, *J* = 10.4 Hz, 2F), -125.80 (t, *J* = 11.0 Hz, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 23.84 (t, *J* = 13.1 Hz, 1P), 23.49 (t, *J* = 13.0 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.8 (m), 144.5 (m), 133.5, 132.4 (d, *J* = 3.3 Hz), 131.9 (d, *J* = 10.4 Hz), 131.9 (m), 131.8 (d, *J* = 14.4 Hz), 131.3 (d, *J* = 3.0 Hz), 130.2, 129.8, 128.2, 127.9, 127.7, 127.5 (d, *J* = 12.9 Hz), 126.5 (m), 117.4 (m) ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₈H₂₆F₉O₃P₂ [M+H]⁺ 763.1208, found: 763.1197.



(5-(Perfluorobutyl)-2-phenylfuran-3-yl)diphenylphosphine oxide (41):

Yield = 62% (104.6 mg, 0.3 mmol scale). White solid.

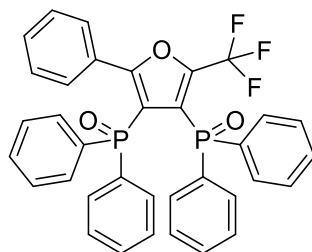
¹H NMR (400 MHz, CDCl₃): δ = 7.98 – 7.88 (m, 2H), 7.77 – 7.66 (m, 4H), 7.56 – 7.38 (m, 6H), 7.32 – 7.20 (m, 3H), 6.50 (d, *J* = 3.8 Hz, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -80.94 (t, *J* = 9.4 Hz, 3F), -111.45 (t, *J* = 12.4 Hz, 2F), -123.21 (q, *J* = 10.4 Hz, 2F), -125.94 – -126.12 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.48 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.8 (m), 139.4 (m), 132.2, 132.2, 131.4 (d, *J* = 10.0 Hz), 131.1, 130.2, 128.6 (d, *J* = 12.7 Hz), 128.3, 128.1, 127.9, 119.6 (m) ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₆H₁₇F₉O₂P [M+H]⁺ 563.0817, found: 563.0825.



(2-Phenyl-5-(trifluoromethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (42):

Yield = 59% (108.4 mg, 0.3 mmol scale). Orange solid.

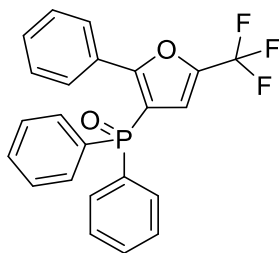
¹H NMR (400 MHz, CDCl₃): δ = 7.65 – 7.55 (m, 4H), 7.47 – 7.37 (m, 6H), 7.32 – 7.25 (m, 6H), 7.24 – 7.17 (m, 3H), 7.14 – 7.05 (m, 6H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -58.3 (s, 3F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 23.00 (s, 1P), 22.51 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.8 (m), 141.9 (m), 132.8 (m), 132.1, 132.0, 131.7 (d, *J* = 110.3 Hz), 131.5 (d, *J* = 2.7 Hz), 130.9 (m), 130.1, 129.7, 128.0, 127.9, 127.7, 127.6, 124.0 (q, *J* = 202.8 Hz), 117.1 (m) ppm.

HRMS (m/z): calcd for C₃₅H₂₆F₃O₃P₂ [M+H]⁺ 613.1304, found: 613.1310.



Diphenyl(2-phenyl-5-(trifluoromethyl)furan-3-yl)phosphine oxide (43):

Yield = 41% (50.7 mg, 0.3 mmol scale). Orange solid.

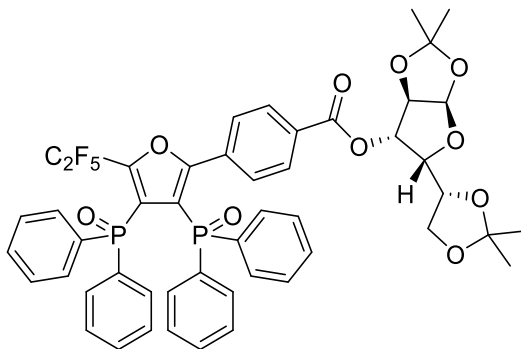
^1H NMR (400 MHz, CDCl_3): δ = 7.97 – 7.89 (m, 2H), 7.77 – 7.66 (m, 4H), 7.55 – 7.47 (m, 2H), 7.45 – 7.37 (m, 4H), 7.28 – 7.21 (m, 3H), 6.48 – 6.42 (m, 1H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -63.80 (s, 3F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 20.56 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 161.8 (m), 140.3 (m), 132.2 (d, J = 2.8 Hz), 131.4 (d, J = 10.0 Hz), 131.1, 130.1, 128.7, 128.6, 128.3, 128.1, 128.0, 123.6 (q, J = 202.8 Hz), 117.2 (m) ppm.

HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{17}\text{F}_3\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$ 413.0913, found: 413.0921.



(3aR,5R,6S,6aR)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-(3,4-bis(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzoate (44):

Yield = 49% (139.4 mg, 0.3 mmol scale). Orange solid.

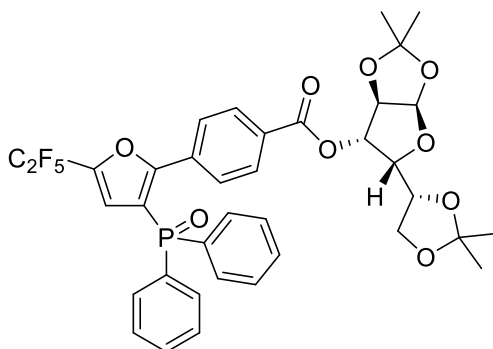
^1H NMR (400 MHz, CDCl_3): δ = 7.82 (d, J = 8.2 Hz, 2H), 7.67 – 7.49 (m, 6H), 7.40 – 7.22 (m, 11H), 7.18 – 7.05 (m, 5H), 5.85 (d, J = 3.6 Hz, 1H), 5.42 (s, 1H), 4.50 (d, J = 3.6 Hz, 1H), 4.28 – 4.19 (m, 2H), 4.06 – 3.96 (m, 2H), 1.47 (s, 3H), 1.33 (s, 3H), 1.24 (s, 3H), 1.19 (s, 3H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -82.10 (s, 3F), -105.97 (s, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 25.35 (s, 1P), 23.29 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 164.2, 163.5 (m), 144.4 (m), 133.1 (d, J = 4.9 Hz), 133.0, 132.3 (d, J = 3.5 Hz), 132.1 (m), 132.0 (m), 131.7, 131.6 (m), 130.9 (m), 130.7, 130.1, 129.0, 128.0 (d, J = 3.5 Hz), 127.6 (d, J = 3.5 Hz), 119.8 (m), 112.3, 109.3, 105.0, 83.2, 79.8, 76.6, 72.4, 67.1, 26.8, 26.6, 26.1, 25.1 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{49}\text{H}_{44}\text{F}_5\text{O}_{10}\text{P}_2$ $[\text{M}+\text{H}]^+$ 949.2324, found: 949.2321.



(3aR,5R,6S,6aR)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-(3-(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzoate (45):

Yield = 43% (96.6 mg, 0.3 mmol scale). Orange solid.

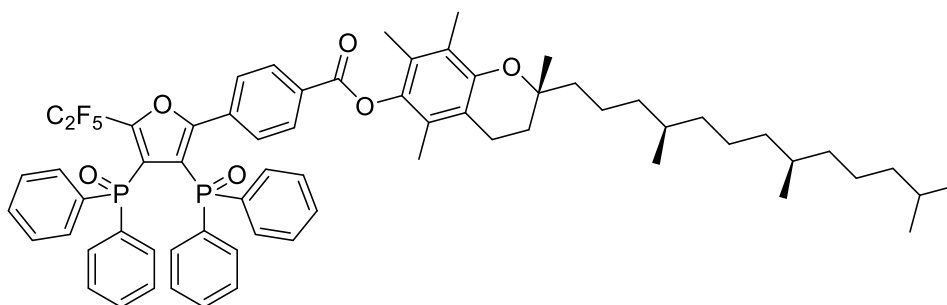
¹H NMR (400 MHz, CDCl₃): δ = 8.11 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.6 Hz, 2H), 7.77 – 7.68 (m, 4H), 7.60 – 7.52 (m, 2H), 7.52 – 7.43 (m, 4H), 6.51 (d, J = 3.7 Hz, 1H), 5.95 (d, J = 3.7 Hz, 1H), 5.47 (d, J = 2.2 Hz, 1H), 4.62 (d, J = 3.7 Hz, 1H), 4.36 – 4.29 (m, 2H), 4.14 – 4.05 (m, 2H), 1.56 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.84 (t, J = 2.5 Hz, 3F), -114.37 (q, J = 2.0 Hz, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.74 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.3, 160.8 (m), 140.2 (m), 132.5 (m), 132.2, 131.7 (d, J = 3.9 Hz), 131.3 (m), 130.6 (d, J = 3.9 Hz), 130.4, 129.6, 128.8 (m), 128.0, 119.3 (m), 112.2, 109.3, 105.0, 83.2, 79.8, 76.7, 72.4, 67.2, 26.7, 26.6, 26.1, 25.1 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₇H₃₅F₅O₉P [M+H]⁺ 749.1933, found: 749.1934.



(R)-2,5,7,8-Tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(3,4-bis(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzoate (46):

Yield = 45% (151.1 mg, 0.3 mmol scale). Orange solid.

¹H NMR (400 MHz, CDCl₃): δ = 8.08 (d, J = 8.5 Hz, 2H), 7.69 – 7.57 (m, 6H), 7.50 – 7.40 (m, 6H), 7.36 – 7.29 (m, 4H), 7.29 – 7.24 (m, 2H), 7.20 – 7.12 (m, 4H), 2.61 (t, J = 6.6 Hz, 2H), 2.11 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.88 – 1.73 (m, 2H), 1.57 – 1.48 (m, 2H), 1.44 – 1.36 (m, 3H), 1.32 – 1.21 (m, 11H), 1.17 – 1.01 (m, 7H), 0.89 – 0.82 (m, 13H) ppm.

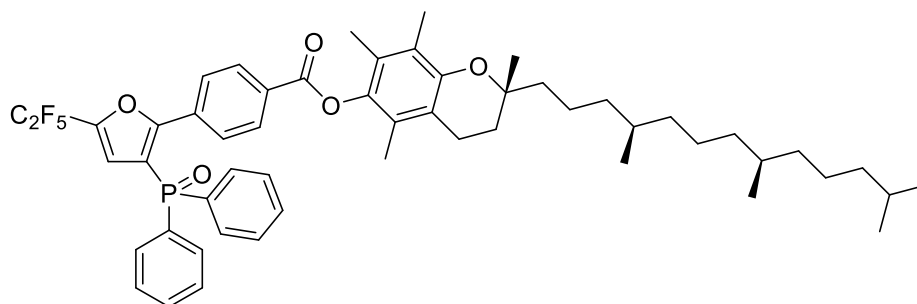
¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.04 (t, J = 2.4 Hz, 3F), -105.93 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 24.48 (s, 1P), 23.32 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.3, 163.5 (m), 149.5, 144.6 (m), 140.4, 132.9, 132.2, 132.2, 132.1, 132.1 (m), 131.8 (d, J = 10.7 Hz), 131.7 (d, J = 2.7 Hz), 131.0 (m), 130.9, 130.1, 129.5, 128.0 (d, J = 13.2 Hz), 127.7 (d, J = 13.0 Hz), 126.7, 124.9, 123.1, 119.5 (m), 117.5, 75.1 (d, J = 0.8 Hz), 39.3, 37.3 (m), 32.8, 32.7, 32.7 (m), 27.9, 24.8, 24.8, 24.4, 24.1, 23.7, 22.7, 22.6,

21.0, 20.6, 19.7, 19.7, 19.6 (m), 13.0, 12.1, 11.8 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₆₆H₇₄F₅O₆P₂ [M+H]⁺ 1119.4875, found: 1119.4881.



(R)-2,5,7,8-Tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(3-(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzoate (47):

Yield = 40% (110.3 mg, 0.3 mmol scale). Orange solid.

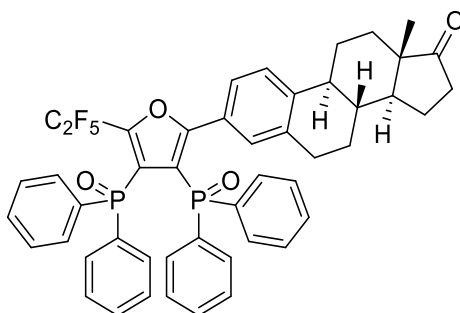
¹H NMR (400 MHz, CDCl₃): δ = 8.21 – 8.09 (m, 4H), 7.80 – 7.68 (m, 4H), 7.57 – 7.51 (m, 2H), 7.50 – 7.42 (m, 4H), 6.57 – 6.52 (m, 1H), 2.70 – 2.52 (m, 2H), 2.12 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.87 – 1.75 (m, 2H), 1.60 – 1.38 (m, 7H), 1.31 – 1.22 (m, 10H), 1.19 – 1.03 (m, 7H), 0.89 – 0.85 (m, 12H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.79 (t, *J* = 3.0 Hz, 3F), -114.29 (q, *J* = 2.5 Hz, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.55 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.3, 161.0 (m), 149.4, 140.3, 140.2 (m), 132.4 (d, *J* = 2.7 Hz), 132.2, 131.9, 131.4 (d, *J* = 10.1 Hz), 130.8, 130.6, 130.0, 128.8 (d, *J* = 12.6 Hz), 128.1, 126.6, 124.9, 123.1, 119.3, 117.4, 75.0, 40.3 (m), 39.5 (m), 39.3, 37.4, 37.4 (m), 37.3 (m), 32.7 (d, *J* = 1.7 Hz), 32.6 (m), 31.0 (m), 27.9, 24.7 (d, *J* = 1.5 Hz), 24.4, 23.8 (m), 22.6 (d, *J* = 9.6 Hz), 20.9, 20.5, 19.7 (d, *J* = 6.6 Hz), 19.5 (m), 12.9, 12.1, 11.8 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₅₄H₆₅F₅O₅P [M+H]⁺ 919.4484, found: 919.4490.



(8R,9S,13S,14S)-3-(3,4-bis(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (48):

Yield = 55% (138.4 mg, 0.3 mmol scale). Yellow oil.

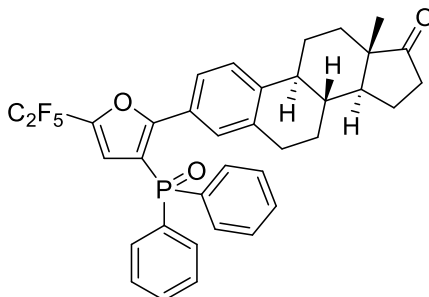
¹H NMR (400 MHz, CDCl₃): δ = 7.58 – 7.40 (m, 10H), 7.33 – 7.28 (m, 4H), 7.25 – 7.07 (m, 8H), 7.01 (d, *J* = 1.8 Hz, 1H), 2.77 – 2.62 (m, 2H), 2.57 – 2.44 (m, 1H), 2.38 – 2.28 (m, 1H), 2.23 – 1.89 (m, 5H), 1.69 – 1.55 (m, 1H), 1.53 – 1.31 (m, 5H), 0.90 (s, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.99 (s, 3F), -105.85 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 23.14 (s, 1P), 22.93 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 220.7, 164.6 (m), 144.6 (m), 142.2, 135.8, 133.6, 132.5 (m), 132.0 (m), 131.8 (m), 127.8 (d, J = 13.2 Hz), 127.4 (d, J = 12.9 Hz), 126.8, 126.6 (d, J = 9.8 Hz), 125.6, 124.9, 117.2 (m), 50.3, 47.8, 44.3, 37.6, 35.7, 31.4, 28.9, 26.1, 25.4, 21.5, 13.7 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₄₈H₄₂F₅O₄P₂ [M+H]⁺ 839.2473, found: 839.2471.



(8*R*,9*S*,13*S*,14*S*)-3-(3-(Diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (49):

Yield = 33% (63.2 mg, 0.3 mmol scale). Orange solid.

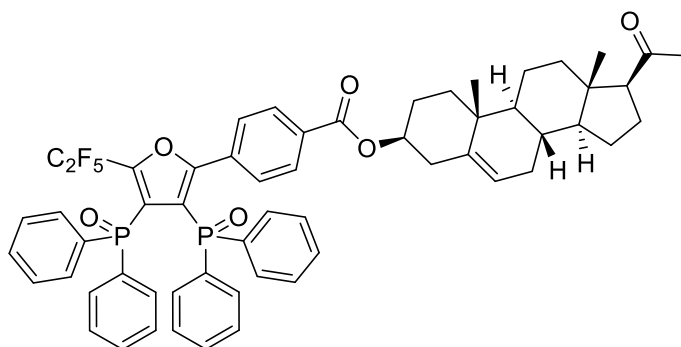
¹H NMR (400 MHz, CDCl₃): δ = 7.77 – 7.69 (m, 4H), 7.68 – 7.63 (m, 1H), 7.59 (s, 1H), 7.55 – 7.48 (m, 2H), 7.48 – 7.40 (m, 4H), 7.18 (d, J = 8.3 Hz, 1H), 6.51 (d, J = 3.7 Hz, 1H), 2.79 (dd, J = 8.3, 3.6 Hz, 2H), 2.50 (dd, J = 18.9, 8.6 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.23 – 1.93 (m, 5H), 1.64 – 1.33 (m, 6H), 0.89 (s, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.84 (t, J = 3.6 Hz, 3F), -114.16 (q, J = 3.6 Hz, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.20 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 220.6, 162.8 (m), 142.2, 139.0 (m), 136.5, 132.3 (d, J = 4.2 Hz), 132.1 (t, J = 2.4 Hz), 131.3 (m), 131.2 (d, J = 4.4 Hz), 128.7, 128.6 (d, J = 3.8 Hz), 128.5 (d, J = 3.8 Hz), 125.4, 125.3, 119.0, 50.3, 47.8, 44.3, 35.7, 31.4, 29.0, 26.1, 25.3, 21.4, 13.7 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₆H₃₃F₅O₃P [M+H]⁺ 639.2082, found: 639.2087.



(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl

4-(3,4-bis(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzoate (50):

Yield = 43% (129.6 mg, 0.3 mmol scale). Orange solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.80 (d, J = 7.9 Hz, 2H), 7.62 – 7.50 (m, 4H), 7.41 (d, J = 8.0 Hz, 2H), 7.41 – 7.30 (m, 6H), 7.28 – 7.14 (m, 6H), 7.13 – 7.00 (m, 4H), 5.34 (s, 1H), 4.86 – 4.66 (m, 1H), 2.47 (t, J = 8.7 Hz, 1H), 2.36 (d, J = 7.7 Hz, 2H), 2.20 – 2.02 (m, 4H), 2.01 – 1.77 (m,

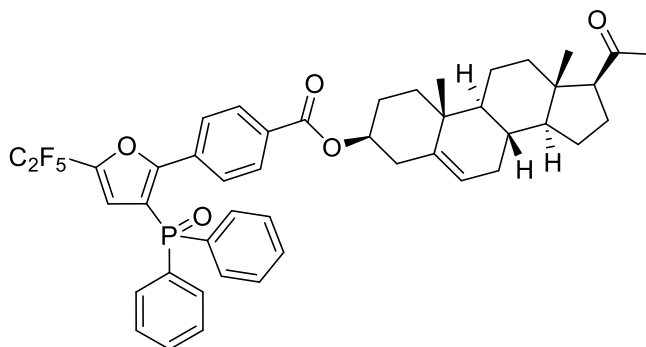
4H), 1.69 – 1.32 (m, 7H), 1.25 – 1.03 (m, 4H), 1.02 – 0.90 (m, 4H), 0.56 (s, 3H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -82.04 (s, 3F), -105.92 (s, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 24.63 (s, 1P), 23.31 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 209.5, 165.0, 163.5 (m), 139.4, 133.1 (m), 132.1 (m), 132.0 (m), 131.9, 131.8, 131.7, 131.6 (m), 131.0 (m), 129.8, 128.8, 127.9 (d, J = 13.1 Hz), 127.6 (d, J = 13.0 Hz), 126.1 (m), 122.5, 119.8 (m), 74.6, 63.5, 56.7, 49.7, 43.9, 38.6, 37.9, 36.8, 36.5, 31.7, 31.6, 31.5, 27.7, 24.4, 22.7, 20.9, 19.2, 13.1 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{58}\text{H}_{56}\text{F}_5\text{O}_6\text{P}_2$ $[\text{M}+\text{H}]^+$ 1005.3467, found: 1005.3472.



(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradehydro-1*H*-cyclopenta[*a*]phenanthren-3-yl

4-(3-(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzoate (51):

Yield = 22% (53.1 mg, 0.3 mmol scale). Orange solid.

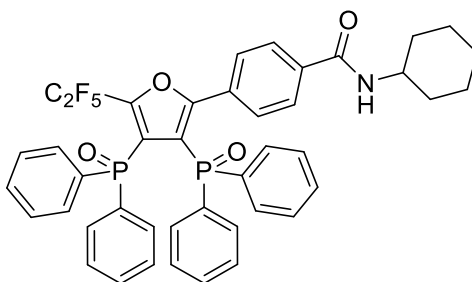
^1H NMR (400 MHz, CDCl_3): δ = 8.08 – 8.04 (m, 2H), 7.97 – 7.92 (m, 2H), 7.75 – 7.68 (m, 4H), 7.56 – 7.51 (m, 2H), 7.49 – 7.43 (m, 4H), 6.52 – 6.47 (m, 1H), 5.45 – 5.38 (m, 1H), 4.89 – 4.77 (m, 1H), 2.56 (t, J = 8.9 Hz, 1H), 2.47 – 2.41 (m, 2H), 2.23 – 2.16 (m, 1H), 2.14 (s, 3H), 2.10 – 1.88 (m, 5H), 1.79 – 1.42 (m, 9H), 1.28 – 1.16 (m, 3H), 1.07 (s, 3H), 0.65 (s, 3H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -83.81 (t, J = 4.0 Hz, 3F), -114.30 (q, J = 3.8 Hz, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 20.62 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 209.5, 165.1, 161.1 (m), 140.0 (m), 139.4, 132.4 (d, J = 2.8 Hz), 131.8, 131.7, 131.6, 131.4 (d, J = 10.1 Hz), 130.7, 129.5, 128.8 (d, J = 12.5 Hz), 127.9, 122.5, 119.3 (m), 74.7, 63.6, 56.7, 49.8, 43.9, 38.7, 38.0, 36.9, 36.5, 31.7, 31.7, 31.5, 27.7, 24.4, 22.7, 21.0, 19.3, 13.2 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{46}\text{H}_{47}\text{F}_5\text{O}_5\text{P}$ $[\text{M}+\text{H}]^+$ 805.3076, found: 805.3076.



4-(3,4-Bis(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)-*N*-cyclohexylbenzamide (52):

Yield = 53% (125.2 mg, 0.3 mmol scale). Orange solid.

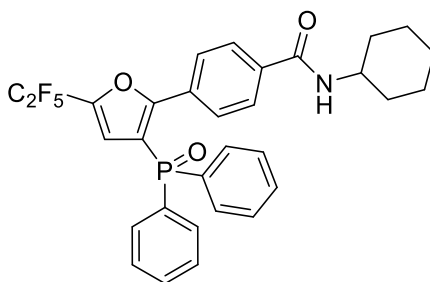
¹H NMR (400 MHz, CDCl₃): δ = 7.66 – 7.58 (m, 4H), 7.57 – 7.53 (m, 2H), 7.50 – 7.39 (m, 8H), 7.37 – 7.30 (m, 4H), 7.24 – 7.18 (m, 2H), 7.17 – 7.05 (m, 4H), 6.11 (d, J = 7.4 Hz, 1H), 4.00 – 3.85 (m, 1H), 2.19 – 2.06 (m, 1H), 2.02 – 1.91 (m, 2H), 1.80 – 1.69 (m, 2H), 1.67 – 1.59 (m, 1H), 1.45 – 1.35 (m, 2H), 1.26 – 1.19 (m, 2H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.04 (s, 3F), -106.01 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 25.39 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 165.6, 164.3 (m), 145.0 (m), 136.7, 132.5, 132.1, 132.0 (m), 131.9, 131.9 (m), 131.8, 131.7, 130.1, 128.2 (d, J = 13.4 Hz), 127.8 (d, J = 13.0 Hz), 126.3, 118.7 (m), 48.8, 33.0, 25.4, 24.8 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₄₃H₃₇F₅NO₄P₂ [M+H]⁺ 788.2112, found: 788.2128.



***N*-Cyclohexyl-4-(3-(diphenylphosphoryl)-5-(perfluoroethyl)furan-2-yl)benzamide (53):**

Yield = 41% (72.3 mg, 0.3 mmol scale). Orange solid.

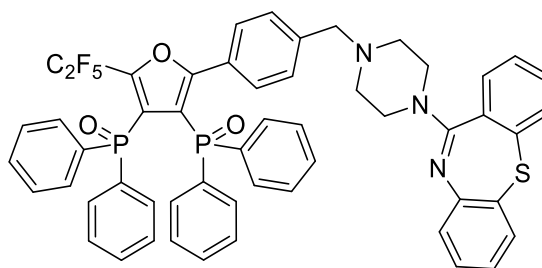
¹H NMR (400 MHz, CDCl₃): δ = 8.01 (d, J = 8.2 Hz, 2H), 7.73 – 7.64 (m, 6H), 7.54 (t, J = 7.4 Hz, 2H), 7.50 – 7.41 (m, 4H), 6.47 (d, J = 3.7 Hz, 1H), 6.23 (d, J = 8.0 Hz, 1H), 3.98 – 3.85 (m, 1H), 2.04 – 1.93 (m, 2H), 1.78 – 1.69 (m, 2H), 1.68 – 1.56 (m, 2H), 1.37 – 1.19 (m, 4H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.85 – -84.70 (m, 3F), -113.14 – -115.36 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.94 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 165.7, 161.3 (m), 139.8 (m), 136.2, 132.5 (d, J = 2.8 Hz), 131.9, 131.4 (d, J = 10.1 Hz), 130.8, 130.3, 128.8 (d, J = 12.5 Hz), 128.1, 127.0, 119.3 (m), 48.8, 33.8, 33.0, 25.6, 25.4, 24.8 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₁H₂₈F₅NO₃P [M+H]⁺ 588.1721, found: 588.1727.



(2-(4-((4-(Dibenzo[*b,f*][1,4]thiazepin-11-yl)piperazin-1-yl)methyl)phenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphine oxide) (54):

Yield = 68% (197.9 mg, 0.3 mmol scale). Yellow oil.

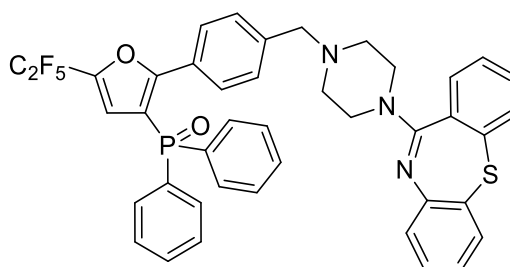
¹H NMR (400 MHz, CDCl₃): δ = 7.66 – 7.34 (m, 14H), 7.32 – 7.24 (m, 7H), 7.21 – 7.02 (m, 10H), 6.86 (t, J = 7.4 Hz, 1H), 3.90 – 3.10 (m, 6H), 2.60 – 2.19 (m, 4H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.92 (s, 3F), -105.87 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 23.48 (s, 1P), 23.26 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.4 (m), 160.6, 148.7, 140.5 (m), 139.7, 133.9, 133.4 (m), 132.2 (m), 132.0, 132.0 (m), 131.9 (m), 131.8, 131.7, 131.3 (m), 130.7, 129.7, 129.0, 128.9, 128.4, 128.2, 127.8, 127.8 (d, *J* = 13.1 Hz), 127.5 (d, *J* = 12.9 Hz), 126.9 (m), 125.2, 122.7, 118.5 (m), 62.3 (m), 52.7 (m, 4C) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₅₄H₄₃F₅N₃O₃P₂S [M+H]⁺ 970.2415, found: 970.2421.



(2-(4-((4-(Dibenzo[*b,f*][1,4]thiazepin-11-yl)piperazin-1-yl)methyl)phenyl)-5-(perfluoroethyl)furan-3-yl)diphenylphosphine oxide (55):

Yield = 49% (113.1 mg, 0.3 mmol scale). Orange solid.

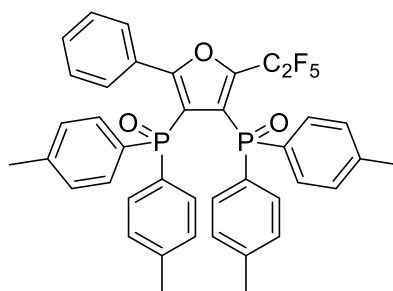
¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, *J* = 8.1 Hz, 2H), 7.66 – 7.58 (m, 4H), 7.45 – 7.36 (m, 4H), 7.35 – 7.28 (m, 5H), 7.25 – 7.11 (m, 5H), 7.06 (t, *J* = 7.1 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.82 – 6.73 (m, 1H), 6.46 – 6.37 (m, 1H), 3.85 – 2.95 (m, 6H), 2.55 – 2.16 (m, 4H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.80 (t, *J* = 3.0 Hz), -114.14 (d, *J* = 2.2 Hz) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.42 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.6 (m), 160.7, 148.8, 140.3, 139.7, 139.3 (m), 134.0, 132.5 (d, *J* = 2.9 Hz), 132.2, 132.1 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 2.4 Hz), 131.4 (d, *J* = 10.0 Hz), 131.1, 130.7, 130.6 (d, *J* = 11.5 Hz), 129.0, 128.9 (d, *J* = 11.9 Hz), 128.6 (d, *J* = 12.5 Hz), 128.2, 128.1, 127.9, 126.9, 125.2, 122.7, 119.1 (m), 62.4, 52.7 (m), 46.4 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₄₂H₃₄F₅N₃O₂PS [M+H]⁺ 770.2024, found: 770.2029.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(di-*p*-tolylphosphine oxide) (56):

Yield = 71% (153.1 mg, 0.3 mmol scale). Yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.43 – 7.32 (m, 9H), 7.29 – 7.22 (m, 2H), 7.17 – 7.05 (m, 6H), 6.90 (d, *J* = 7.7 Hz, 4H), 2.34 (s, 6H), 2.23 (s, 6H) ppm.

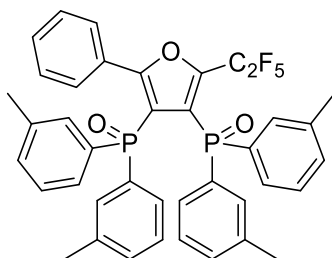
¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.91 (s, 3F), -105.78 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 24.64 (s, 1P), 23.86 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 163.9 (m), 141.9 (m), 132.1, 132.0, 131.9, 131.5 (m),

130.0 (m), 129.9, 129.8, 129.3 (m), 128.5, 128.3, 128.3, 128.1, 127.6, 118.3 (m), 21.5 (m), 21.4 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₄₀H₃₄F₅O₃P₂ [M+H]⁺ 719.1898, found: 719.1903.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(di-*m*-tolylphosphine oxide) (58):

Yield = 33% (35.2 mg, 0.15 mmol scale). Yellow solid.

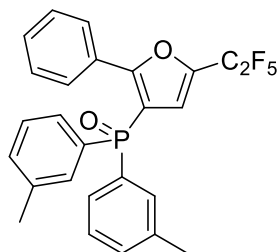
¹H NMR (400 MHz, CDCl₃): δ = 7.43 – 7.37 (m, 2H), 7.37 – 7.28 (m, 6H), 7.27 – 7.13 (m, 9H), 7.06 – 6.96 (m, 4H), 2.28 (s, 6H), 2.17 (s, 6H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.96 (s, 3F), -105.94 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 23.90 (s, 1P), 23.30 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.2 (m), 141.6 (m), 137.5 (d, *J* = 12.9 Hz), 137.1 (d, *J* = 12.9 Hz), 133.3, 132.7, 132.4 (d, *J* = 10.0 Hz), 132.2 (d, *J* = 10.0 Hz), 132.1, 131.3, 130.1, 129.8, 129.2 (d, *J* = 10.3 Hz), 128.9 (d, *J* = 11.1 Hz), 128.3, 127.6, 127.5, 127.3, 126.0 (m), 118.3 (m), 21.3, 21.2 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₄₀H₃₄F₅O₃P₂ [M+H]⁺ 719.1898, found: 719.1904.



(2-(Perfluoroethyl)-5-phenylfuran-3-yl)di-*m*-tolylphosphine oxide (59):

Yield = 32% (47.1 mg, 0.3 mmol scale). White solid.

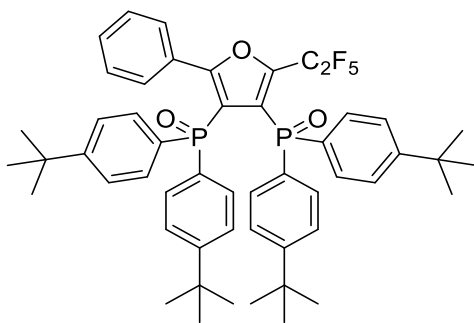
¹H NMR (400 MHz, CDCl₃): δ = 7.94 – 7.85 (m, 2H), 7.63 – 7.55 (m, 2H), 7.45 – 7.37 (m, 2H), 7.33 – 7.22 (m, 7H), 6.54 – 6.48 (m, 1H), 2.34 (s, 6H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.85 (t, *J* = 3.4 Hz, 3F), -114.16 – -114.32 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.86 (t, *J* = 13.4 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.5 (m), 139.3 (m), 138.6 (d, *J* = 12.4 Hz), 133.0 (d, *J* = 3.1 Hz), 132.1, 131.9 (d, *J* = 9.6 Hz), 131.0, 130.1, 128.5, 128.4 (d, *J* = 2.4 Hz), 128.3, 128.1, 128.1, 119.3 (m), 21.3 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₆H₂₁F₅O₂P [M+H]⁺ 491.1194, found: 491.1199.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(bis(4-(*tert*-butyl)phenyl)phosphine oxide) (60):

Yield = 50% (133.1 mg, 0.3 mmol scale). Yellow oil.

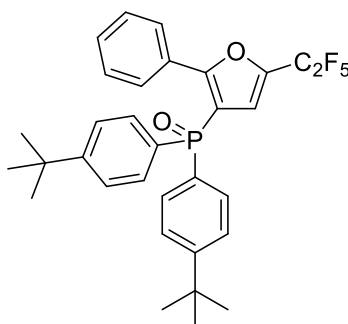
¹H NMR (400 MHz, CDCl₃): δ = 7.52 – 7.43 (m, 5H), 7.42 – 7.35 (m, 4H), 7.34 – 7.28 (m, 6H), 7.21 – 7.15 (m, 1H), 7.13 – 7.06 (m, 5H), 1.29 (s, 18H), 1.21 (s, 18H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.02 (s, 3F), -106.05 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 24.49 (s, 1P), 23.72 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 163.9 (m), 154.9 (d, *J* = 2.8 Hz), 154.1 (d, *J* = 2.9 Hz), 144.9 (m), 131.6 (d, *J* = 10.9 Hz), 131.4 (d, *J* = 10.2 Hz), 130.8, 130.1, 129.9, 129.8 (d, *J* = 19.5 Hz), 128.9, 128.5, 127.6, 124.8 (d, *J* = 10.7 Hz), 124.7 (d, *J* = 10.5 Hz), 117.9 (m), 34.8 (d, *J* = 0.9 Hz), 34.7 (d, *J* = 0.9 Hz), 31.0, 31.0 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₅₂H₅₈F₅O₃P₂ [*M*+H]⁺ 887.3776, found: 887.3781.



Bis(4-(*tert*-butyl)phenyl)(5-(perfluoroethyl)-2-phenylfuran-3-yl)phosphine oxide (61):

Yield = 36% (62.0 mg, 0.3 mmol scale). White solid.

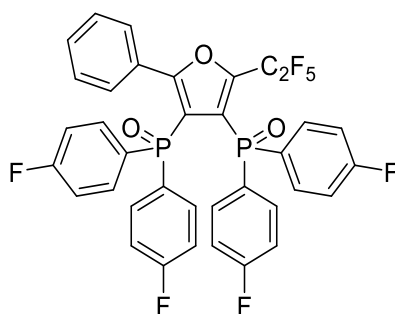
¹H NMR (400 MHz, CDCl₃): δ = 7.90 – 7.83 (m, 2H), 7.69 – 7.57 (m, 4H), 7.47 – 7.38 (m, 4H), 7.29 – 7.19 (m, 3H), 6.65 – 6.56 (m, 1H), 1.29 (s, 18H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.83 (s, 3F), -114.16 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.23 (t, *J* = 14.0 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.4 (m), 155.6 (d, *J* = 2.9 Hz), 139.3 (m), 131.4 (d, *J* = 10.4 Hz), 129.9, 129.1, 128.2, 128.2, 128.1, 128.0, 125.6 (d, *J* = 12.8 Hz), 119.2 (m), 35.0, 31.0 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₃₂H₃₃F₅O₂P [*M*+H]⁺ 575.2133, found: 575.2138.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(bis(4-fluorophenyl)phosphine oxide) (62):

Yield = 76% (167.5 mg, 0.3 mmol scale). Yellow oil.

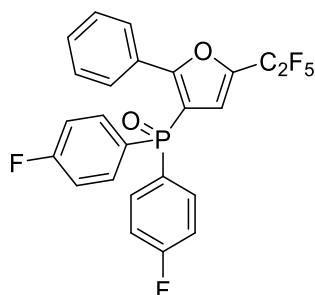
¹H NMR (400 MHz, CDCl₃): δ = 7.59 – 7.44 (m, 8H), 7.35 – 7.27 (m, 3H), 7.22 – 7.15 (m, 2H), 7.06 – 6.99 (m, 4H), 6.88 – 6.80 (m, 4H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.90 (s, 3F), -105.19 – -105.39 (m, 2F), -105.70 (s, 2F), -106.24 – -106.39 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 22.04 (t, *J* = 16.4 Hz, 1P), 21.58 (t, *J* = 16.3 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 166.3 (m), 164.5 (m), 163.8 (m), 145.3 (m), 134.6 (m), 130.6, 129.8, 129.0 (d, *J* = 3.4 Hz), 128.0, 127.8, 127.8, 126.9 (m), 126.6 (m), 117.1 (m), 115.5 (m), 115.2 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₆H₂₂F₉O₃P₂ [M+H]⁺ 735.0895, found: 735.0895.



Bis(4-fluorophenyl)(5-(perfluoroethyl)-2-phenylfuran-3-yl)phosphine oxide (63):

Yield = 80% (119.6 mg, 0.3 mmol scale). White solid.

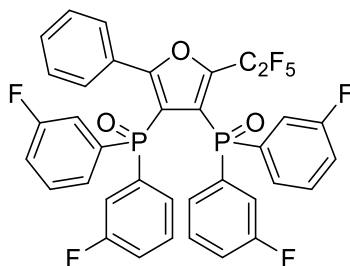
¹H NMR (400 MHz, CDCl₃): δ = 7.94 – 7.85 (m, 2H), 7.78 – 7.65 (m, 4H), 7.35 – 7.23 (m, 3H), 7.17 – 7.07 (m, 4H), 6.55 – 6.49 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.87 – -83.91 (m, 3F), -105.40 – -105.64 (m, 2F), -114.26 – -114.36 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 18.82 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 165.0 (m), 162.8 (m), 139.7 (m), 133.9 (m), 130.5, 128.4, 128.1, 127.7, 127.4 (m), 118.7 (m), 116.3 (d, *J* = 13.8 Hz), 116.1 (d, *J* = 3.4 Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₄H₁₅F₇O₂P [M+H]⁺ 499.0692, found: 499.0698.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(bis(3-fluorophenyl)phosphine oxide) (64):

Yield = 55% (121.2 mg, 0.3 mmol scale). Orange solid.

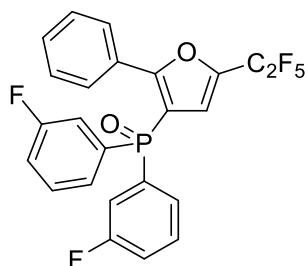
¹H NMR (400 MHz, CDCl₃): δ = 7.40 – 7.34 (m, 7H), 7.33 – 7.28 (m, 2H), 7.23 – 7.13 (m, 10H), 7.00 – 6.92 (m, 2H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.93 (t, J = 2.5 Hz, 3F), -105.97 (s, 2F), -110.67 (s, 2F), -111.03 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 21.01 (s, 1P), 20.22 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 165.0, 163.1 (m), 160.6 (m), 145.4 (m), 134.2 (m), 130.8, 130.2 (m), 130.0 (m), 129.8, 129.7, 128.0, 127.5 (m), 125.2 (m), 119.8 (m), 119.0 (m), 118.6 (m), 118.6 (m), 116.3 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₆H₂₂F₉O₃P₂ [M+H]⁺ 735.0895, found: 735.0895.



Bis(3-fluorophenyl)(5-(perfluoroethyl)-2-phenylfuran-3-yl)phosphine oxide (65):

Yield = 82% (122.6 mg, 0.3 mmol scale). Orange solid.

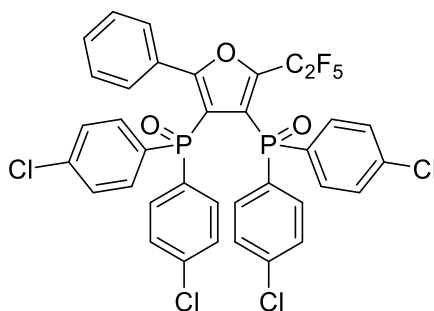
¹H NMR (400 MHz, CDCl₃): δ = 7.88 – 7.81 (m, 2H), 7.48 – 7.37 (m, 6H), 7.29 – 7.22 (m, 3H), 7.21 – 7.14 (m, 2H), 6.54 – 6.49 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.86 (t, J = 3.5 Hz, 3F), -109.57 – -110.54 (m, 2F), -113.91 – -114.74 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 18.04 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 163.2 (m), 162.5 (dd, J = 249.5, 17.7 Hz), 139.9 (m), 133.8 (dd, J = 109.5, 5.6 Hz), 130.8 (m), 130.6, 128.4, 128.1, 127.6, 127.1 (m), 119.7 (m), 118.6 (m), 118.3 (m), 112.2 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₄H₁₅F₇O₂P [M+H]⁺ 499.0692, found: 499.0698.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(bis(4-chlorophenyl)phosphine oxide) (66):

Yield = 65% (156.1 mg, 0.3 mmol scale). Yellow oil.

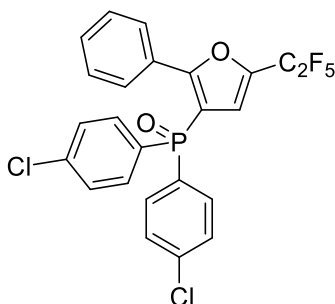
¹H NMR (400 MHz, CDCl₃): δ = 7.49 – 7.36 (m, 9H), 7.35 – 7.27 (m, 7H), 7.21 – 7.15 (m, 2H), 7.14 – 7.09 (m, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.86 (s, 3F), -105.70 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 22.45 – 21.56 (m, 2P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.7 (m), 145.4 (m), 139.4 (d, J = 3.5 Hz), 138.7 (d, J = 3.6 Hz), 133.3 (d, J = 11.4 Hz), 131.2, 130.7, 130.2, 130.0, 129.8, 129.0, 128.5 (d, J = 13.9 Hz), 128.2 (d, J = 6.9 Hz), 127.6, 125.6 (m), 116.7 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₆H₂₂Cl₄F₅O₃P₂ [M+H]⁺ 798.9713, found: 798.9718.



Bis(4-chlorophenyl)(5-(perfluoroethyl)-2-phenylfuran-3-yl)phosphine oxide (67):

Yield = 65% (103.6 mg, 0.3 mmol scale). White solid.

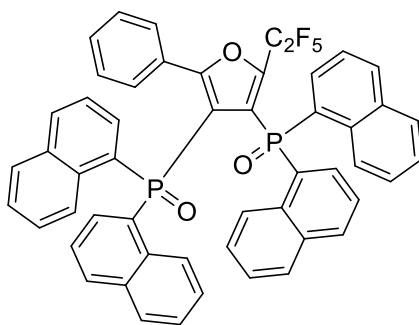
¹H NMR (400 MHz, CDCl₃): δ = 7.87 – 7.74 (m, 2H), 7.62 – 7.48 (m, 4H), 7.39 – 7.29 (m, 4H), 7.28 – 7.15 (m, 3H), 6.50 – 6.39 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.82 (t, J = 2.8 Hz, 3F), -114.20 – -114.35 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 18.96 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 163.0 (m), 139.8 (m), 139.1 (d, J = 3.5 Hz), 132.7 (d, J = 10.7 Hz), 130.6, 130.4, 129.3, 129.2 (d, J = 13.3 Hz), 128.5, 128.1, 127.7, 118.7 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₄H₁₅Cl₂F₅O₂P [M+H]⁺ 531.0101, found: 531.0107.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(di(naphthalen-1-yl)phosphine oxide) (68):

Yield = 73% (188.9 mg, 0.3 mmol scale). Orange solid.

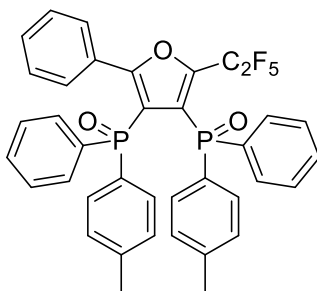
^1H NMR (400 MHz, CDCl_3): δ = 8.94 – 8.12 (m, 4H), 8.09 – 6.87 (m, 19H), 6.86 – 5.55 (m, 10H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -79.96 – -81.81 (m, 3F), -102.98 – -106.70 (m, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 32.51 (s, 1P), 29.95 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 161.0 (m), 149.4 (m), 137.9 (m), 134.6 (m), 134.5 (m), 134.0 (m), 133.7 (m), 133.6 (m), 133.4 (m), 133.3 (m), 133.2 (m), 132.4 (m), 131.9 (m), 131.5 (m), 129.5 (m), 129.0 (m), 128.6 (m), 128.4 (m), 127.7 (m), 126.8 (m), 126.5 (m), 125.8 (m), 125.2 (m), 123.7 (m), 123.5 (m), 122.9 (m), 120.0 (m), 117.1 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{52}\text{H}_{34}\text{F}_5\text{O}_3\text{P}_2$ $[\text{M}+\text{H}]^+$ 863.1898, found: 863.1903.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(phenyl(*p*-tolyl)phosphine oxide) (70):

Yield = 34% (70.4 mg, 0.3 mmol scale, dr = 1/1). Orange solid.

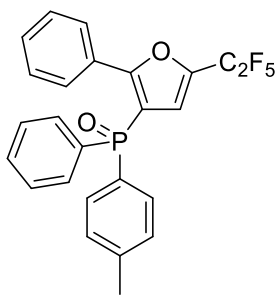
^1H NMR (400 MHz, CDCl_3): δ = 7.61 – 7.27 (m, 15H), 7.19 – 7.12 (m, 4H), 7.10 – 7.04 (m, 2H), 6.92 – 6.83 (m, 2H), 2.34 (s, 3H), 2.22 (d, J = 10.6 Hz, 3H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -81.96 (t, J = 2.4 Hz, 3F), -105.84 (s, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 24.25 – 23.53 (m, 2P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 164.3 (m), 142.0 (m), 133.6 (d, J = 3.4 Hz), 132.8 (m), 132.4 (d, J = 8.2 Hz), 132.2 (d, J = 1.7 Hz), 132.0 (d, J = 9.6 Hz), 131.9 (m), 131.8 (m), 131.3 (m), 130.1 (d, J = 8.3 Hz), 129.8, 128.8 (d, J = 13.5 Hz), 128.6 (d, J = 6.8 Hz), 128.4 (d, J = 7.0 Hz), 128.3 (m), 128.2 (d, J = 3.3 Hz), 127.9 (d, J = 4.1 Hz), 127.8 (d, J = 0.9 Hz), 127.7 (m), 127.5 (d, J = 2.4 Hz), 126.5 (m), 117.1 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{38}\text{H}_{30}\text{F}_5\text{O}_3\text{P}_2$ $[\text{M}+\text{H}]^+$ 691.1585, found: 691.1599.



(5-(Perfluoroethyl)-2-phenylfuran-3-yl)(phenyl)(p-tolyl)phosphine oxide (71):

Yield = 32% (45.7 mg, 0.3 mmol scale). White solid.

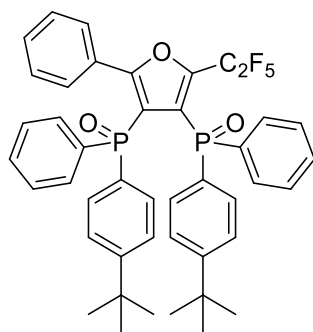
¹H NMR (400 MHz, CDCl₃): δ = 7.96 – 7.90 (m, 2H), 7.73 – 7.65 (m, 2H), 7.62 – 7.55 (m, 2H), 7.53 – 7.47 (m, 1H), 7.45 – 7.38 (m, 2H), 7.30 – 7.21 (m, 5H), 6.52 – 6.48 (m, 1H), 2.38 (s, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.85 (t, *J* = 3.2 Hz, 3F), -114.19 (q, *J* = 3.0 Hz, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 20.74 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.5 (m), 142.9, 139.3 (m), 132.5, 132.1 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 10.5), 131.4 (d, *J* = 10.0), 130.1, 129.5 (d, *J* = 12.9 Hz), 128.9, 128.6 (d, *J* = 12.5 Hz), 128.3, 128.1, 128.0, 127.8, 119.3 (m), 21.6 (d, *J* = 1.4 Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₅H₁₉F₅O₂P [M+H]⁺ 477.1037, found: 477.1044.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis((4-(tert-butyl)phenyl)(phenyl)phosphine oxide) (72):

Yield = 26% (60.4 mg, 0.3 mmol scale, dr = 1/1). Orange solid.

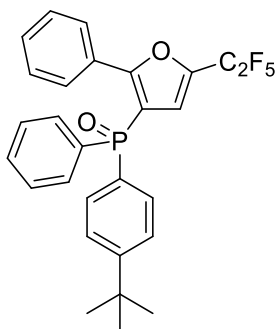
¹H NMR (400 MHz, CDCl₃): δ = 7.52 – 7.43 (m, 7H), 7.40 – 7.27 (m, 8H), 7.21 – 7.02 (m, 8H), 1.31 (s, 9H), 1.18 (s, 9H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.92 – -82.04 (m, 3F), -105.85 – -106.05 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 22.94 (s, 1P), 21.73 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.3 (m), 139.4 (m), 132.5 (m), 132.0 (m), 131.9 (m), 131.9 (m), 131.8 (m), 131.7 (m), 131.4 (m), 131.2 (m), 130.6 (m), 130.1 (m), 129.9 (m), 127.8 (m), 127.7 (m), 127.6 (m), 127.4 (m), 125.2 (m), 125.0 (m), 124.9 (m), 124.7 (m), 117.9 (m), 34.8 (m), 31.0 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₄₄H₄₂F₅O₃P₂ [M+H]⁺ 775.2524, found: 775.2526.



(4-(*tert*-Butyl)phenyl)(5-(perfluoroethyl)-2-phenylfuran-3-yl)(phenyl)phosphine oxide (73):

Yield = 27% (42.0 mg, 0.3 mmol scale). White solid.

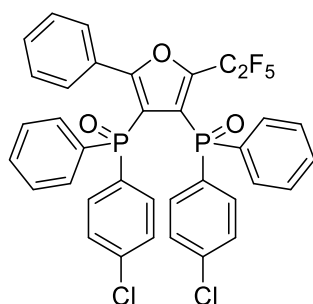
^1H NMR (400 MHz, CDCl_3): δ = 7.92 – 7.86 (m, 2H), 7.75 – 7.67 (m, 2H), 7.66 – 7.58 (m, 2H), 7.53 – 7.46 (m, 1H), 7.46 – 7.38 (m, 4H), 7.30 – 7.20 (m, 3H), 6.57 – 6.52 (m, 1H), 1.30 (s, 9H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -83.83 (t, J = 2.7 Hz, 3F), -114.18 (s, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 20.38 (t, J = 13.1 Hz, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 162.5 (m), 155.8 (d, J = 12.9 Hz), 139.4 (m), 132.5, 132.1 (d, J = 2.9 Hz), 131.5 (d, J = 10.0 Hz), 131.4 (d, J = 10.5 Hz), 130.1, 128.8, 128.6 (d, J = 12.5 Hz), 128.3, 128.2, 128.1, 127.7, 125.7 (d, J = 12.9 Hz), 119.2 (m), 35.0 (d, J = 1.2 Hz), 31.0 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{28}\text{H}_{25}\text{F}_5\text{O}_2\text{P}$ [$\text{M}+\text{H}$] $^+$ 519.1507, found: 519.1520.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis((4-chlorophenyl)(phenyl)phosphine oxide) (74):

Yield = 62% (136.1 mg, 0.3 mmol scale, dr = 1/1). Orange solid.

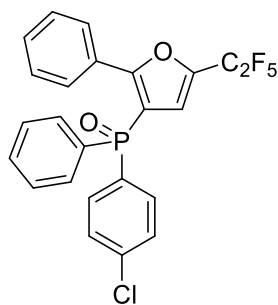
^1H NMR (400 MHz, CDCl_3): δ = 7.65 – 7.47 (m, 5H), 7.44 – 7.27 (m, 12H), 7.25 – 7.13 (m, 4H), 7.06 – 7.01 (m, 1H), 6.98 – 6.92 (m, 1H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -81.92 (d, J = 9.6 Hz, 3F), -105.76 (d, J = 20.2 Hz, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 23.04 – 22.58 (m, 2P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 164.5 (m), 145.1 (m), 138.8 (m), 138.1 (m), 133.5 (d, J = 11.7 Hz), 133.4 (d, J = 11.3 Hz), 133.3 (d, J = 11.2 Hz), 132.8, 132.4 (m), 131.8 (m), 131.7 (m), 130.9 (m), 130.5 (d, J = 1.7 Hz), 129.8, 128.3 (d, J = 6.2 Hz), 128.2 (m), 128.1 (m), 128.0, 127.9, 127.9 (d, J = 2.0 Hz), 127.8 (d, J = 6.0 Hz), 127.7, 125.9 (m), 117.0 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{36}\text{H}_{24}\text{Cl}_2\text{F}_5\text{O}_3\text{P}_2$ [$\text{M}+\text{H}$] $^+$ 731.0492, found: 731.0504.



(4-Chlorophenyl)(5-(perfluoroethyl)-2-phenylfuran-3-yl)(phenyl)phosphine oxide (75):

Yield = 78% (116.2 mg, 0.3 mmol scale). White solid.

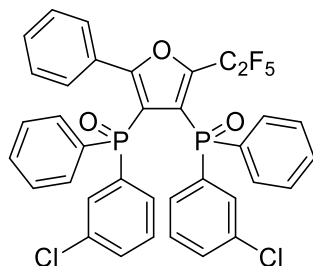
¹H NMR (400 MHz, CDCl₃): δ = 7.94 – 7.88 (m, 2H), 7.75 – 7.60 (m, 4H), 7.55 – 7.49 (m, 1H), 7.47 – 7.37 (m, 4H), 7.30 – 7.22 (m, 3H), 6.54 – 6.50 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -83.85 (t, *J* = 2.7 Hz, 3F), -114.24 (s, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 19.69 (t, *J* = 13.0 Hz, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 162.8 (m), 139.6 (m), 138.9 (d, *J* = 3.7 Hz), 132.8 (d, *J* = 10.7 Hz), 132.4 (d, *J* = 2.9 Hz), 131.8, 131.3 (d, *J* = 10.1 Hz), 130.7 (d, *J* = 9.6 Hz), 130.4, 129.6, 128.9 (d, *J* = 24.9 Hz), 128.8 (d, *J* = 24.9 Hz), 128.4, 128.1, 127.8, 118.9 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₄H₁₆ClF₅O₂P [M+H]⁺ 497.0491, found: 497.0503.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis((3-chlorophenyl)(phenyl)phosphine oxide) (76):

Yield = 64% (140.4 mg, 0.3 mmol scale, dr = 1/1). Orange solid.

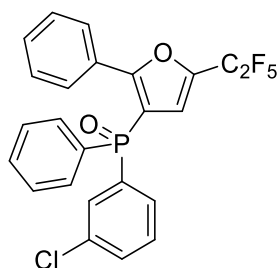
¹H NMR (400 MHz, CDCl₃): δ = 7.59 – 7.46 (m, 6H), 7.44 – 7.34 (m, 8H), 7.32 – 7.25 (m, 3H), 7.23 – 7.14 (m, 5H), 7.11 – 7.01 (m, 1H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -81.79 – -82.05 (m, 3F), -105.74 – -106.00 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 22.16 (s, 1P), 21.99 (s, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.6 (m), 145.2 (m), 135.6 (d, *J* = 5.3 Hz), 134.6 (m), 134.4 (d, *J* = 3.8 Hz), 134.3, 134.0 (m), 133.8 (d, *J* = 5.1 Hz), 133.5 (m), 133.0, 132.6, 132.4 (m), 131.8 (m), 131.7 (m), 131.3 (d, *J* = 14.7 Hz), 130.9 (m), 130.6 (m), 130.4 (m), 130.2 (m), 129.7, 129.3 (m), 129.0 (m), 128.1 (m), 127.9 (m), 127.9, 127.7 (m), 125.2 (m), 116.8 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₆H₂₄Cl₂F₅O₃P₂ [M+H]⁺ 731.0492, found: 731.0498.



(3-Chlorophenyl)(5-(perfluoroethyl)-2-phenylfuran-3-yl)(phenyl)phosphine oxide (77):

Yield = 63% (93.9 mg, 0.3 mmol scale). Orange solid.

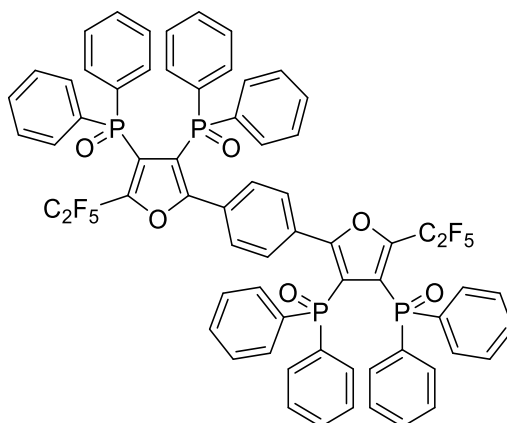
^1H NMR (400 MHz, CDCl_3): δ = 7.93 – 7.85 (m, 2H), 7.77 – 7.67 (m, 3H), 7.61 – 7.50 (m, 2H), 7.49 – 7.42 (m, 3H), 7.38 – 7.32 (m, 1H), 7.31 – 7.23 (m, 3H), 6.58 – 6.51 (m, 1H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -83.84 (t, J = 3.4 Hz, 3F), -113.28 – -115.23 (m, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 19.17 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 162.9 (m), 139.7 (m), 135.1 (d, J = 16.3 Hz), 134.6, 133.5, 131.5, 131.4 (m), 131.3 (d, J = 10.1 Hz), 131.3 (d, J = 10.9 Hz), 130.4, 130.3, 130.0 (d, J = 13.5 Hz), 129.4 (d, J = 9.5 Hz), 128.8 (d, J = 12.9 Hz), 128.4, 128.1, 127.8, 118.8 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{16}\text{ClF}_5\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$ 497.0491, found: 497.0497.



Compound (85):

Yield = 44% (82.3 mg, 0.15 mmol scale). Orange solid.

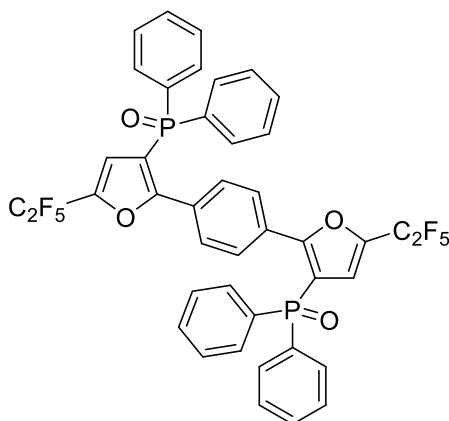
^1H NMR (400 MHz, CDCl_3): δ = 7.53 – 7.42 (m, 10H), 7.41 – 7.32 (m, 12H), 7.28 – 7.19 (m, 10H), 7.16 – 7.10 (m, 6H), 7.07 – 6.99 (m, 6H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -81.86 – -82.24 (m, 3F), -105.72 – -106.12 (m, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 23.78 (s, 1P), 23.26 (s, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 163.4 (m), 144.6 (m), 133.1, 132.0 (d, J = 11.4 Hz), 131.8 (d, J = 4.5 Hz), 131.7 (m), 131.3 (m), 131.0 (m), 129.8, 128.7 (m), 127.9 (d, J = 13.1 Hz), 127.6 (d, J = 12.9 Hz), 126.1 (m), 119.3 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{66}\text{H}_{45}\text{F}_{10}\text{O}_6\text{P}_4$ $[\text{M}+\text{H}]^+$ 1247.2001, found: 1247.2023.



(1,4-phenylenebis(5-(perfluoroethyl)furan-2,3-diyl))bis(diphenylphosphine oxide) (86):

Yield = 38% (96.5 mg, 0.3 mmol scale). Orange solid.

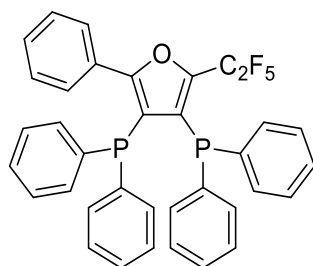
^1H NMR (400 MHz, CDCl_3): δ = 7.96 – 7.87 (m, 4H), 7.73 – 7.64 (m, 8H), 7.55 – 7.49 (m, 4H), 7.48 – 7.38 (m, 8H), 6.48 – 6.43 (m, 2H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -83.85 (t, J = 3.2 Hz, 6F), -114.29 (q, J = 2.8 Hz, 4F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 20.78 (s, 2P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 161.1 (m), 139.7 (m), 132.4 (d, J = 2.8 Hz), 131.8, 131.4 (d, J = 10.1 Hz), 130.7, 129.2, 128.7 (d, J = 12.6 Hz), 127.9, 119.3 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{42}\text{H}_{27}\text{F}_{10}\text{O}_4\text{P}_2$ $[\text{M}+\text{H}]^+$ 847.1219, found: 847.1231.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(diphenylphosphane) (87):

Yield = 90% (170.2 mg, 0.3 mmol scale). Orange solid.

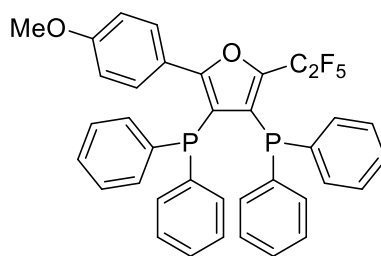
^1H NMR (400 MHz, CDCl_3): δ = 7.27 – 7.15 (m, 6H), 7.14 – 7.02 (m, 11H), 7.01 – 6.89 (m, 8H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -82.65 – -82.75 (m, 3F), -108.32 – -108.53 (m, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = -27.46 (d, J = 30.4 Hz, 1P), -28.76 – -29.64 (m, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 161.6 (m), 144.8 (m), 134.0 (m), 132.5 (d, J = 19.3 Hz), 132.1 (d, J = 19.2 Hz), 129.5 (m), 129.2, 128.9, 128.72, 128.69, 128.2, 127.90, 127.87, 127.84, 127.6, 119.2 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{36}\text{H}_{26}\text{F}_5\text{OP}_2$ $[\text{M}+\text{H}]^+$ 631.1374, found: 631.1379.



(2-(4-Methoxyphenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphane) (88):

Yield = 52% (103.1 mg, 0.3 mmol scale). Orange solid.

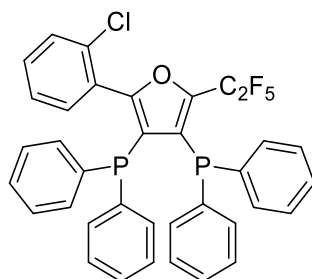
¹H NMR (400 MHz, CDCl₃): δ = 7.23 – 7.15 (m, 7H), 7.10 – 7.02 (m, 10H), 6.99 – 6.93 (m, 5H), 6.50 (d, J = 9.0 Hz, 2H), 3.59 (s, 3H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.65 – -82.80 (m, 3F), -108.19 – -108.50 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = -27.31 – -27.52 (m, 1P), -28.77 – -29.65 (m, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 161.8 (m), 160.2, 144.2 (m), 134.2 (m), 134.0 (m), 132.4 (m), 132.1 (m), 130.1 (d, J = 3.6 Hz), 129.4 (m), 128.5 (m), 128.1, 127.9 (d, J = 1.4 Hz), 127.8 (m), 121.5, 117.5 (m), 113.1, 55.2 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₇H₂₈F₅O₂P₂ [M+H]⁺ 661.1479, found: 661.1490.



(2-(2-Chlorophenyl)-5-(perfluoroethyl)furan-3,4-diyl)bis(diphenylphosphane) (89):

Yield = 63% (125.7 mg, 0.3 mmol scale). Orange solid.

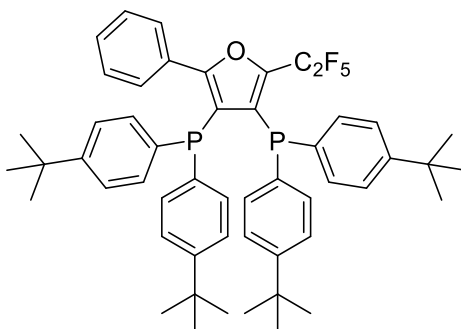
¹H NMR (400 MHz, CDCl₃): δ = 7.27 – 7.23 (m, 4H), 7.09 – 7.06 (m, 8H), 7.02 – 6.99 (m, 10H), 6.91 – 6.85 (m, 2H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.81 – -82.88 (m, 3F), -108.57 – -108.79 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = -28.21 – -29.23 (m, 2P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 159.6 (m), 145.3 (m), 133.7 (m), 133.6 (m), 133.5, 132.6 (d, J = 3.5 Hz), 132.5 (m), 132.1 (d, J = 15.6 Hz), 132.0 (d, J = 19.5 Hz), 130.5, 129.1, 128.8, 128.3, 128.0, 127.9 (d, J = 5.9 Hz), 127.7 (d, J = 56.4 Hz), 126.8 (d, J = 2.6 Hz), 120.4 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₆H₂₅ClF₅OP₂ [M+H]⁺ 665.0984, found: 665.0989.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(bis(4-(*tert*-butyl)phenyl)phosphane) (90):

Yield = 47% (120.6 mg, 0.3 mmol scale). Orange solid.

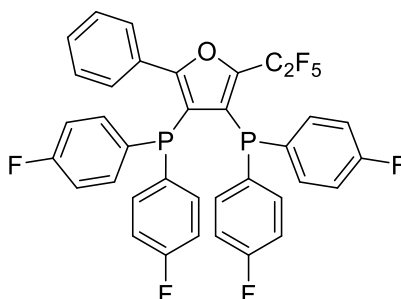
¹H NMR (400 MHz, CDCl₃): δ = 7.28 – 7.25 (m, 2H), 7.23 – 7.16 (m, 9H), 7.11 – 7.03 (m, 10H), 1.26 (s, 18H), 1.23 (s, 18H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.85 – -82.93 (m, 3F), -108.32 – -108.52 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = -29.73 (d, *J* = 37.1 Hz, 1P), -30.85 – -31.65 (m, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 161.1 (m), 150.9 (d, *J* = 20.0 Hz), 144.2 (m), 132.4 (d, *J* = 1.9 Hz), 132.2 (d, *J* = 1.6 Hz), 132.2 (d, *J* = 1.9 Hz), 132.1 (d, *J* = 1.7 Hz), 131.5 (m), 131.3 (m), 129.4, 128.9, 128.8 (d, *J* = 3.5 Hz), 127.5, 124.9 (d, *J* = 1.7 Hz), 124.8 (d, *J* = 2.0 Hz), 120.3 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₅₂H₅₈F₅OP₂ [M+H]⁺ 855.3878, found: 855.3883.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(bis(4-fluorophenyl)phosphane) (91):

Yield = 92% (193.9 mg, 0.3 mmol scale). Orange solid.

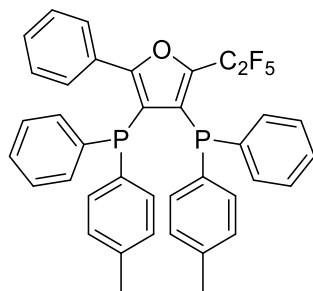
¹H NMR (400 MHz, CDCl₃): δ = 7.27 – 7.21 (m, 7H), 7.15 – 7.04 (m, 6H), 6.94 – 6.86 (m, 4H), 6.82 – 6.74 (m, 4H) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -82.74 – -82.88 (m, 3F), -108.09 – -108.55 (m, 2F), -112.05 – -112.25 (m, 2F), -112.41 – -112.70 (m, 2F) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = -27.90 – -28.45 (m, 1P), -29.55 – -30.50 (m, 1P) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 163.2 (d, *J* = 247.5 Hz), 163.0 (d, *J* = 247.4 Hz), 160.6 (m), 144.8 (m), 134.5 (m), 134.1 (m), 129.5, 129.1 (m), 128.9 (m), 128.8 (d, *J* = 3.2 Hz), 128.6, 127.8 (m), 127.8, 118.7 (m), 115.4 (m), 115.2 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (*m/z*): calcd for C₃₆H₂₂F₉OP₂ [M+H]⁺ 703.0997, found: 703.0995.



(2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(phenyl(*p*-tolyl)phosphane) (92):

Yield = 54% (106.7 mg, 0.3 mmol scale, dr = 1/1). Orange solid.

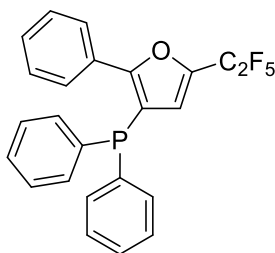
^1H NMR (400 MHz, CDCl_3): δ = 7.25 – 7.16 (m, 4H), 7.14 – 7.04 (m, 8H), 7.03 – 6.90 (m, 7H), 6.90 – 6.82 (m, 2H), 6.81 – 6.73 (m, 2H), 2.22 – 2.08 (m, 6H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -81.89 – -83.68 (m, 3F), -106.51 – -110.82 (m, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = -27.60 – -28.12 (m, 1P), -29.20 – -30.00 (m, 1P) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 161.4 (m), 143.2 (m), 138.1 (d, J = 9.9 Hz), 137.8 (d, J = 7.0 Hz), 134.7 (m), 134.6 (m), 134.5 (m), 132.8 (m), 132.6 (m), 132.4 (m), 132.0 (m), 131.9 (m), 130.2 (m), 129.9 (m), 129.0 (m), 128.7 (d, J = 6.6 Hz), 128.6, 128.6 (m), 128.0 (m), 127.8, 127.7 (m), 127.6, 127.6, 119.5 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{38}\text{H}_{30}\text{F}_5\text{OP}_2$ [$\text{M}+\text{H}$] $^+$ 659.1687, found: 659.1692.



(5-(Perfluoroethyl)-2-phenylfuran-3-yl)diphenylphosphane (93):

Yield = 99% (132.6 mg, 0.3 mmol scale). Orange solid.

^1H NMR (400 MHz, CDCl_3): δ = 7.87 – 7.82 (m, 2H), 7.39 – 7.34 (m, 13H), 6.49 – 6.47 (m, 1H) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -83.77 (t, J = 3.3 Hz, 3F), -113.83 (q, J = 3.2 Hz, 2F) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = -29.69 (s, 1P) ppm.

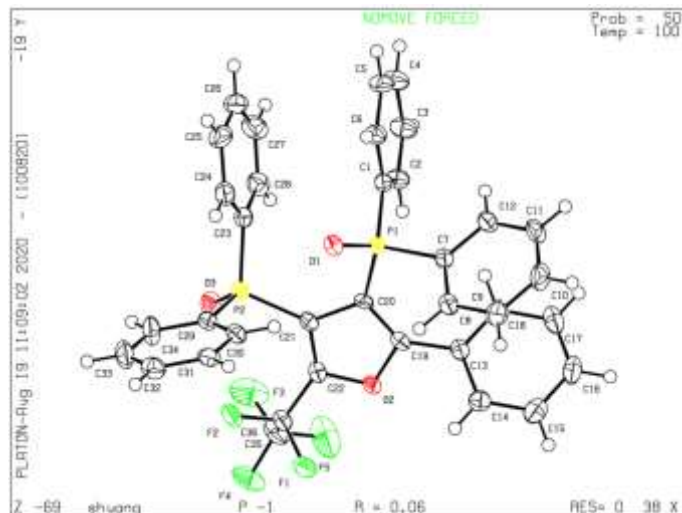
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 160.3 (m), 139.8 (m), 136.1 (d, J = 8.2 Hz), 133.2 (d, J = 19.5 Hz), 129.34, 129.27, 129.0 (d, J = 27.7 Hz), 128.8, 128.6, 127.3 (d, J = 9.2 Hz), 119.2 (m), 115.5 (d, J = 18.4 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{17}\text{F}_5\text{OP}$ [$\text{M}+\text{H}$] $^+$ 447.0932, found: 447.0940.

10. The X-ray crystal structures of products

The single crystals were grown from the mixed solution of DCM and EtOAc (v/v = 1:3) by slowly evaporating the above solvents at room temperature

1) (2-(Perfluoroethyl)-5-phenylfuran-3,4-diyl)bis(diphenylphosphine oxide) (3):



CCDC number: 2024117

Crystal data and structure refinement for product 3

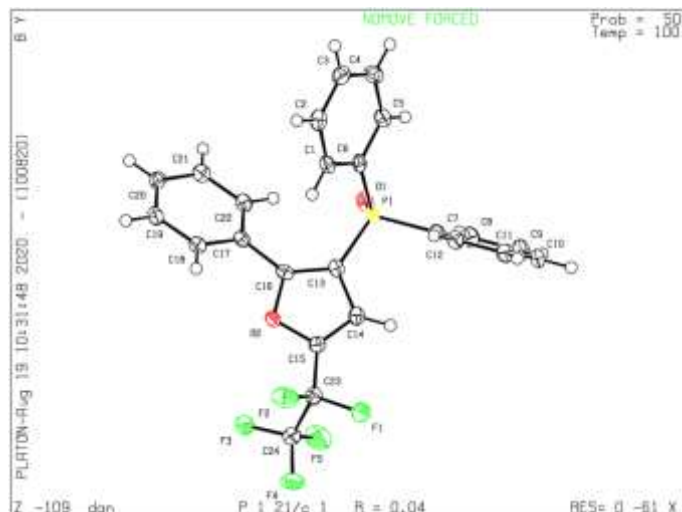
Empirical formula	C ₃₆ H ₂₅ F ₅ O ₃ P ₂
Formula weight	662.50
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.3450(6)
b/Å	12.0953(6)
c/Å	14.1162(7)
α /°	89.245(4)
β /°	77.498(4)
γ /°	62.787(5)
Volume/Å ³	1673.56(16)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.315
μ/mm^{-1}	0.192
F(000)	680.0
Crystal size/mm ³	0.15 × 0.13 × 0.12
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	4.126 to 50
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -16 ≤ l ≤ 15
Reflections collected	14757

Independent reflections 5685 [$R_{\text{int}} = 0.0532$, $R_{\text{sigma}} = 0.0682$]
 Data/restraints/parameters 5685/0/415
 Goodness-of-fit on F^2 1.068
 Final R indexes [$I \geq 2\sigma(I)$] $R_1 = 0.0556$, $wR_2 = 0.1543$
 Final R indexes [all data] $R_1 = 0.0701$, $wR_2 = 0.1719$
 Largest diff. peak/hole / $e \text{ \AA}^{-3}$ 0.47/-0.54

Crystal structure determination of product 3

Crystal Data for $\text{C}_{36}\text{H}_{25}\text{F}_5\text{O}_3\text{P}_2$ ($M = 662.50 \text{ g/mol}$): triclinic, space group P-1 (no. 2), $a = 11.3450(6) \text{ \AA}$, $b = 12.0953(6) \text{ \AA}$, $c = 14.1162(7) \text{ \AA}$, $\alpha = 89.245(4)^\circ$, $\beta = 77.498(4)^\circ$, $\gamma = 62.787(5)^\circ$, $V = 1673.56(16) \text{ \AA}^3$, $Z = 2$, $T = 100.01(10) \text{ K}$, $\mu(\text{Mo K}\alpha) = 0.192 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.315 \text{ g/cm}^3$, 14757 reflections measured ($4.126^\circ \leq 2\theta \leq 50^\circ$), 5685 unique ($R_{\text{int}} = 0.0532$, $R_{\text{sigma}} = 0.0682$) which were used in all calculations. The final R_1 was 0.0556 ($I > 2\sigma(I)$) and wR_2 was 0.1719 (all data).

2) (5-(Perfluoroethyl)-2-phenylfuran-3-yl)diphenylphosphine oxide (4):



CCDC number: 2024116

Table 1 Crystal data and structure refinement for product 4

Empirical formula	$\text{C}_{24}\text{H}_{16}\text{F}_5\text{O}_2\text{P}$
Formula weight	462.34
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	18.8874(14)
$b/\text{\AA}$	6.1813(5)
$c/\text{\AA}$	17.2323(11)
$\alpha/^\circ$	90
$\beta/^\circ$	91.402(6)
$\gamma/^\circ$	90

Volume/Å ³	2011.2(3)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.527
μ/mm^{-1}	0.203
F(000)	944.0
Crystal size/mm ³	0.14 × 0.13 × 0.12
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection/°	4.314 to 49.986
Index ranges	-22 ≤ h ≤ 17, -7 ≤ k ≤ 7, -19 ≤ l ≤ 20
Reflections collected	8029
Independent reflections	3550 [R_{int} = 0.0320, R_{sigma} = 0.0442]
Data/restraints/parameters	3550/0/289
Goodness-of-fit on F ²	1.053
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0413, wR_2 = 0.0952
Final R indexes [all data]	R_1 = 0.0522, wR_2 = 0.1029
Largest diff. peak/hole / e Å ⁻³	0.36/-0.38

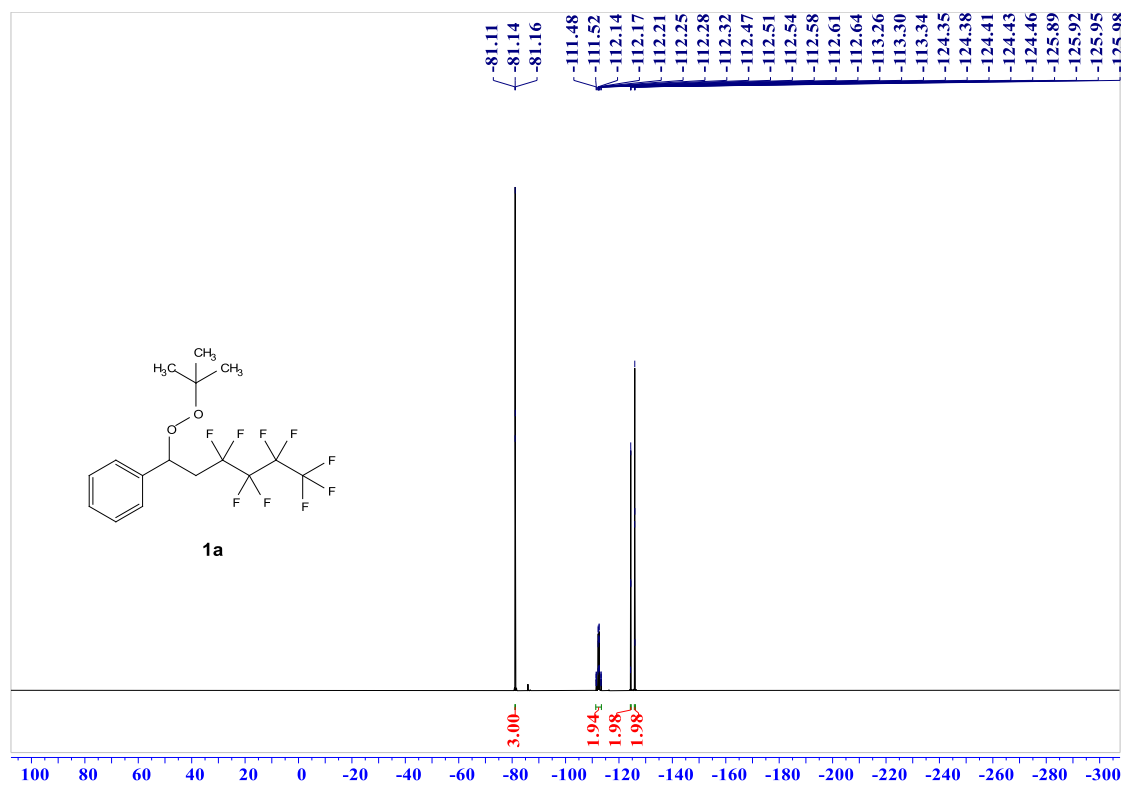
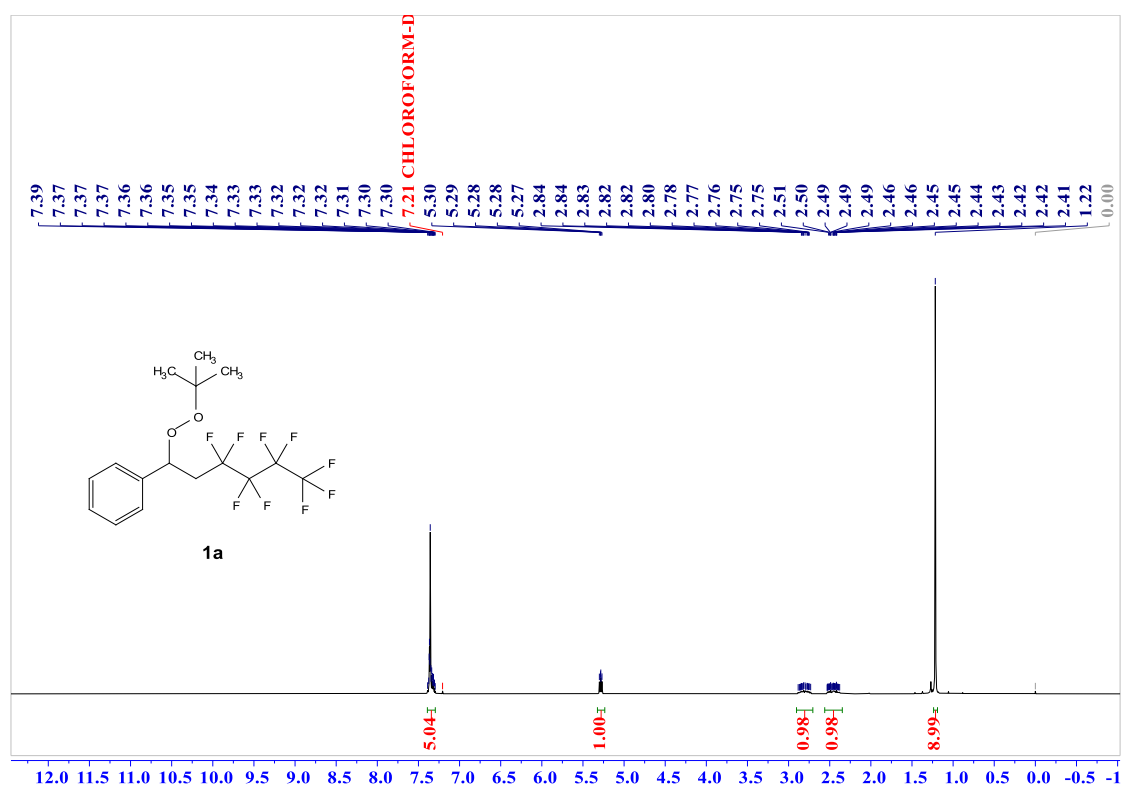
Crystal structure determination of product 4

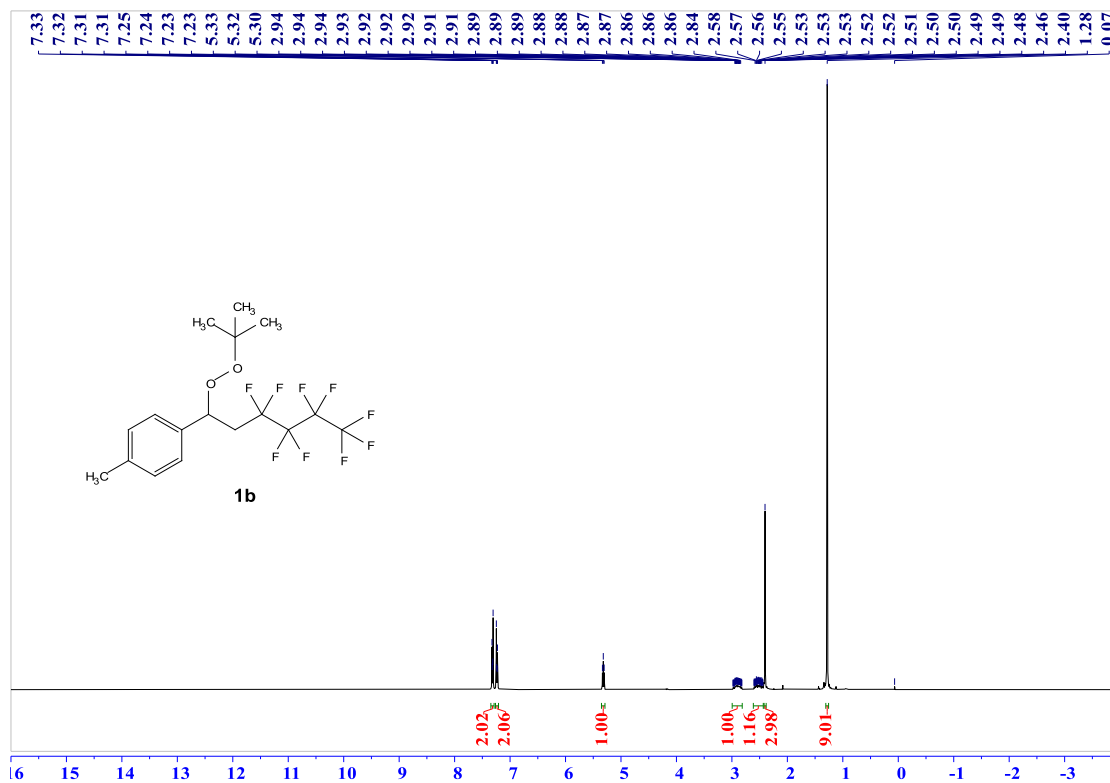
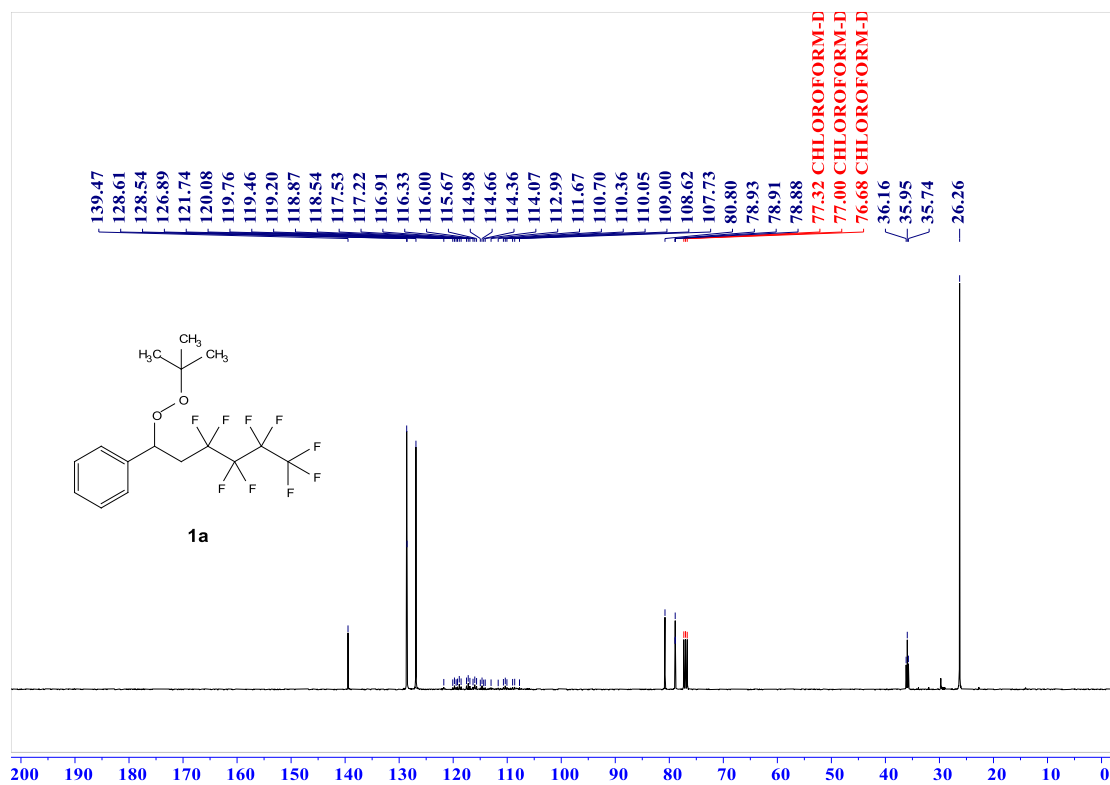
Crystal Data for C₂₄H₁₆F₅O₂P (M = 462.34 g/mol): monoclinic, space group P2₁/c (no. 14), a = 18.8874(14) Å, b = 6.1813(5) Å, c = 17.2323(11) Å, β = 91.402(6)°, V = 2011.2(3) Å³, Z = 4, T = 100.01(10) K, $\mu(\text{Mo K}\alpha)$ = 0.203 mm⁻¹, D_{calc} = 1.527 g/cm³, 8029 reflections measured (4.314° ≤ 2 Θ ≤ 49.986°), 3550 unique (R_{int} = 0.0320, R_{sigma} = 0.0442) which were used in all calculations. The final R_1 was 0.0413 ($I > 2\sigma(I)$) and wR_2 was 0.1029 (all data).

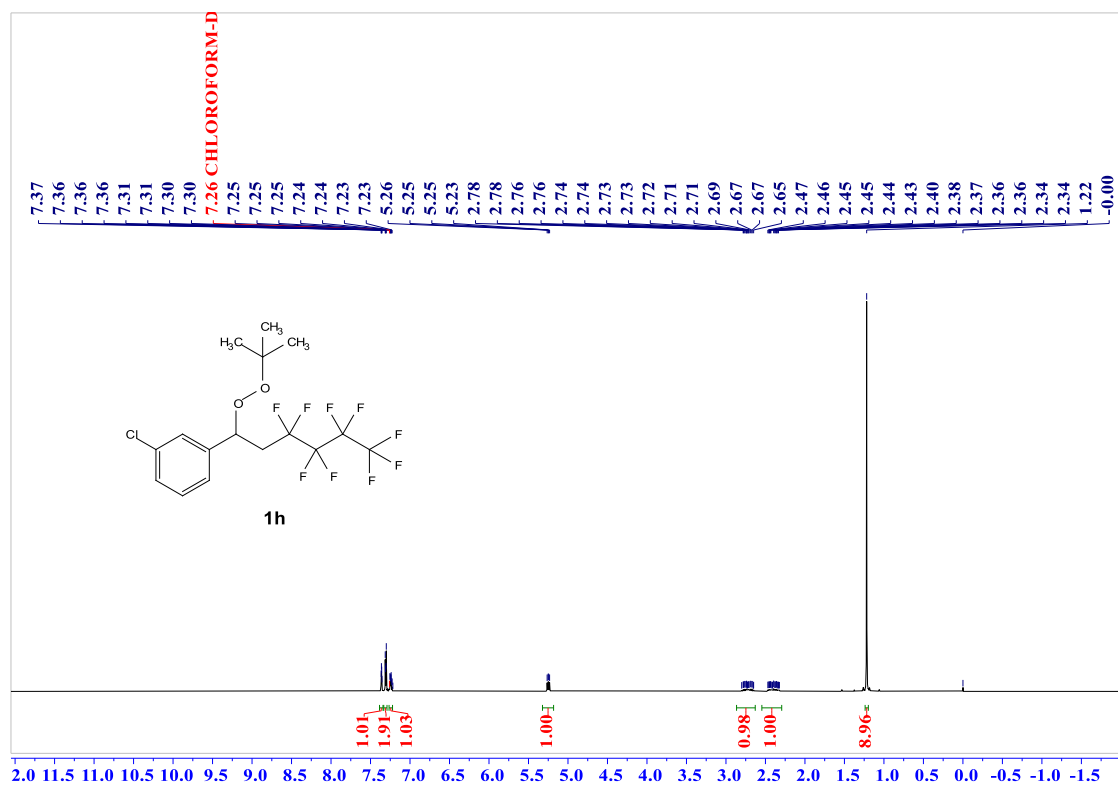
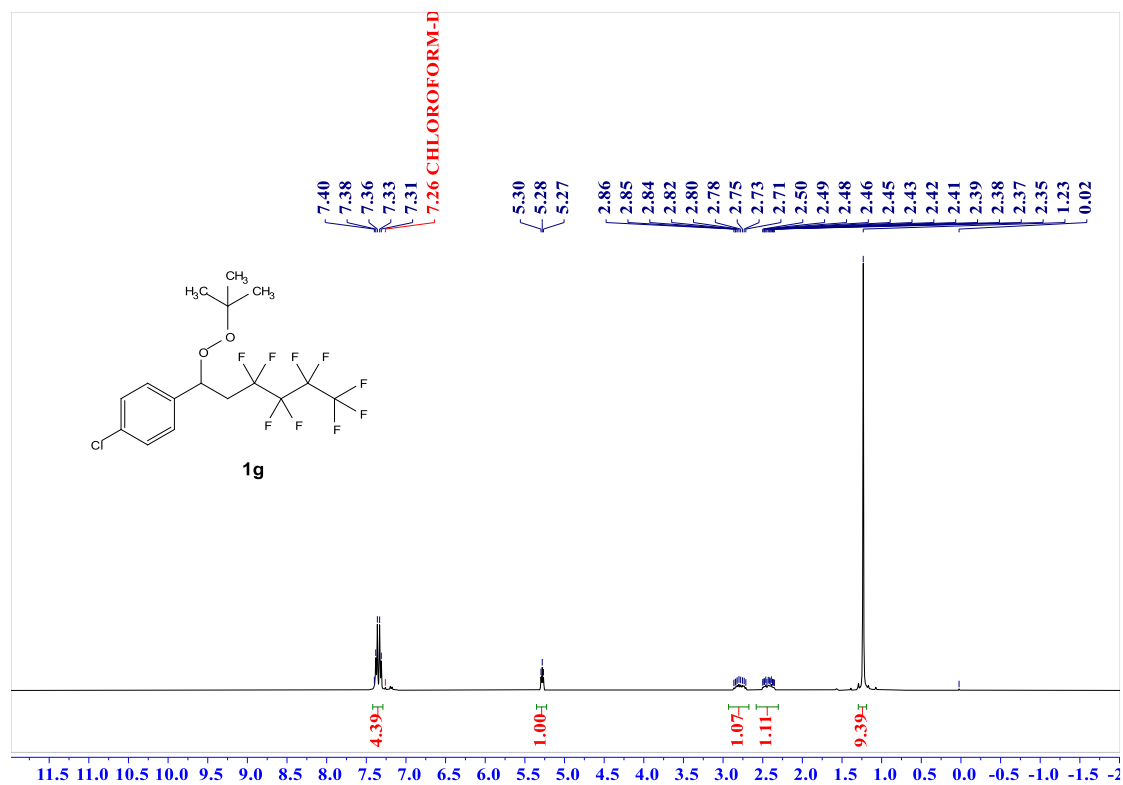
11. References

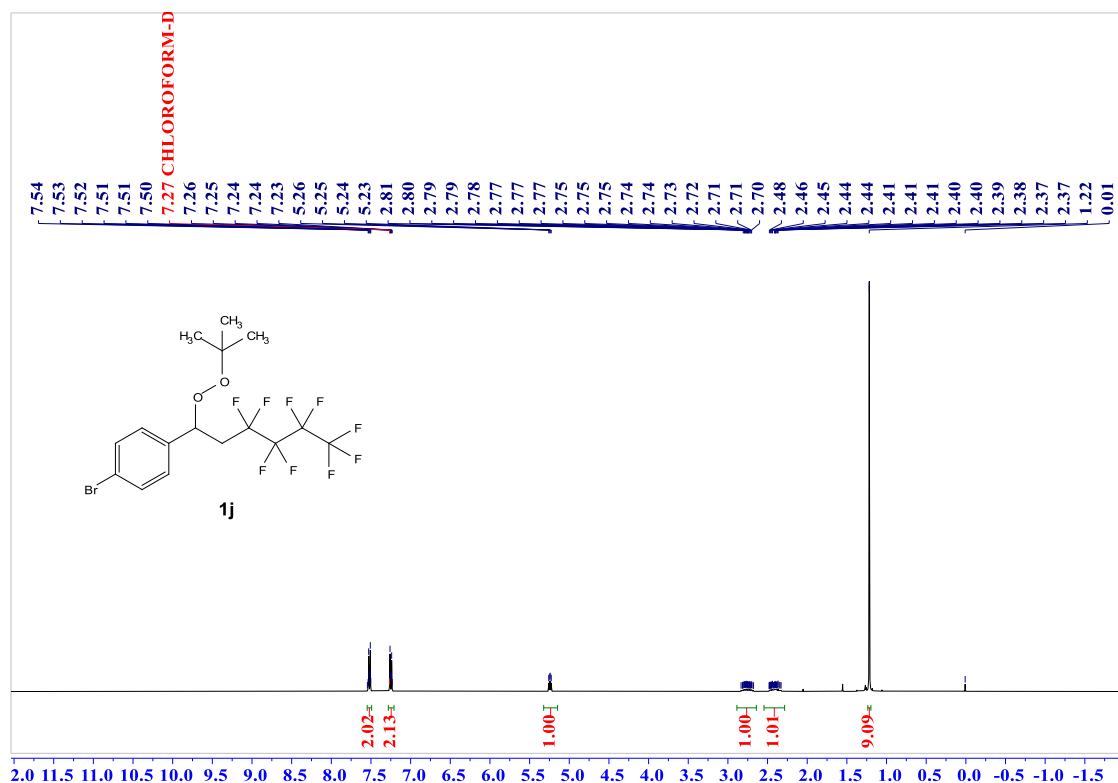
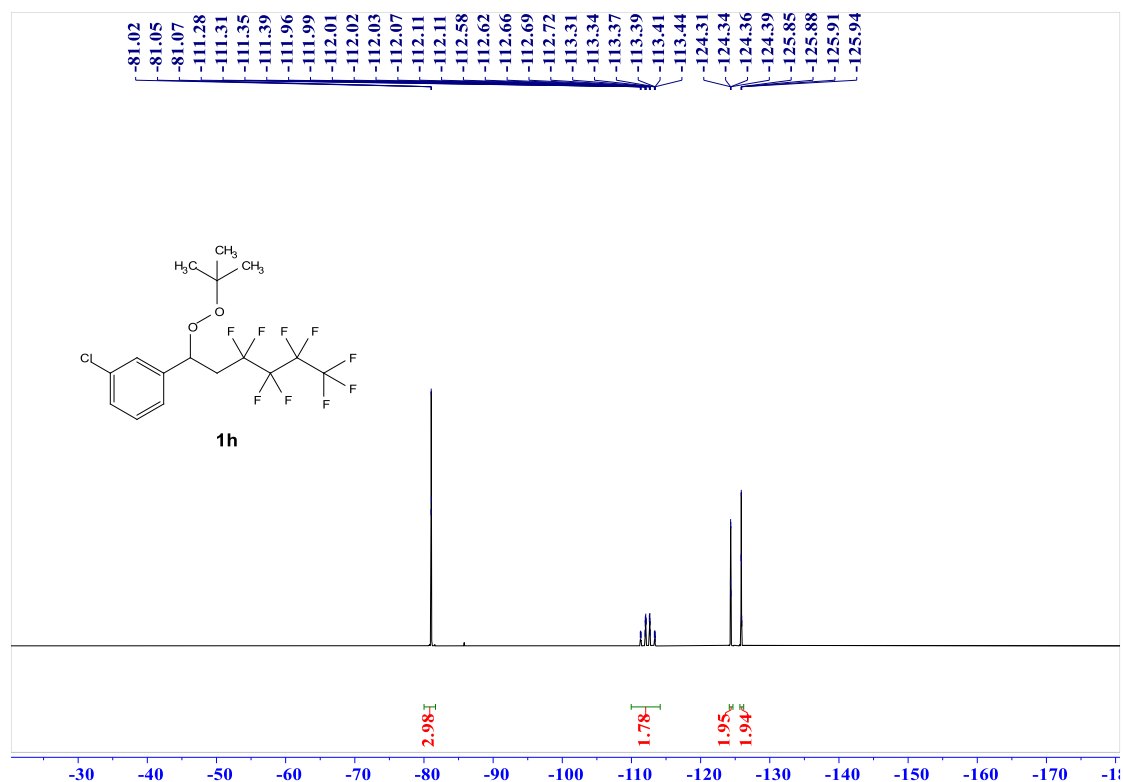
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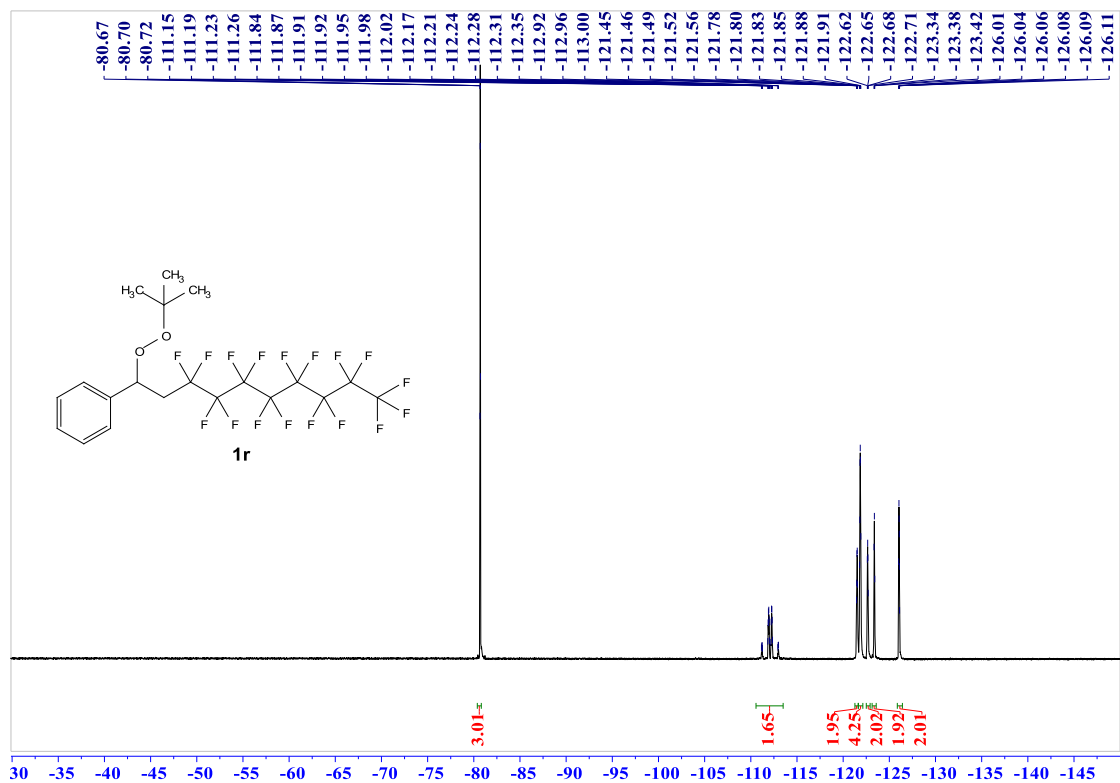
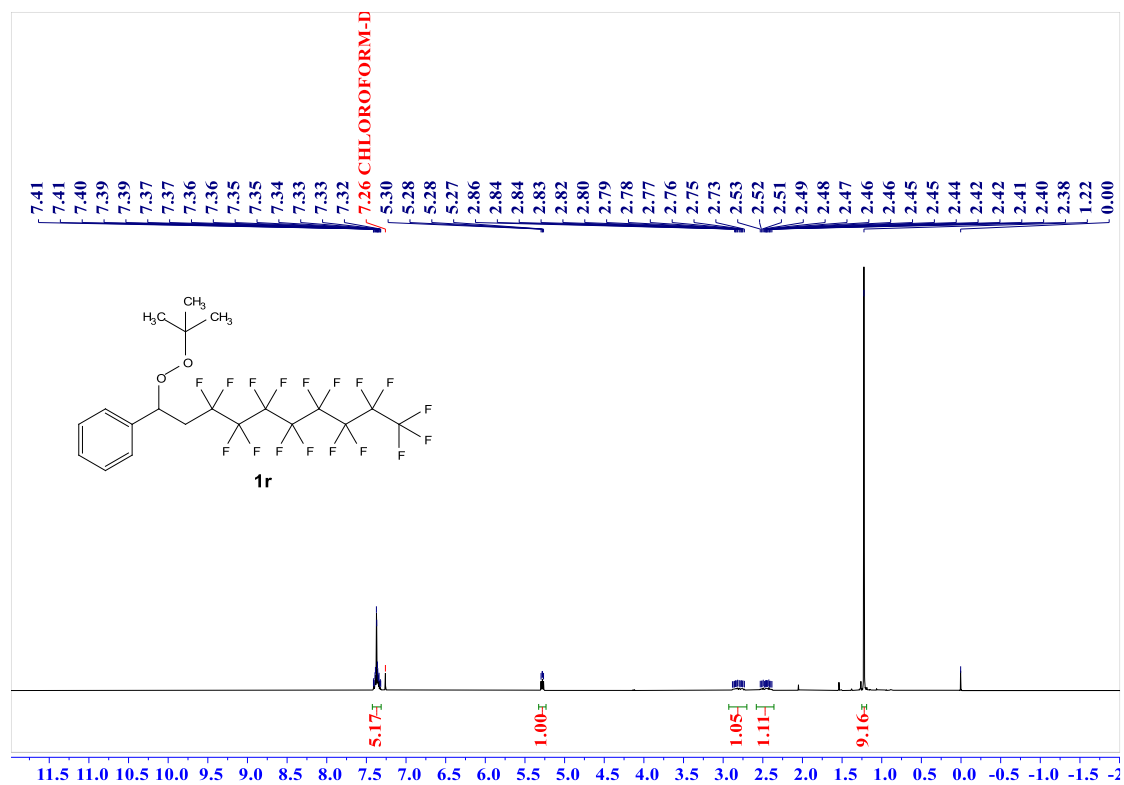
12. ^1H , ^{19}F , and ^{13}C NMR spectra of representative polyfluoroalkyl peroxides

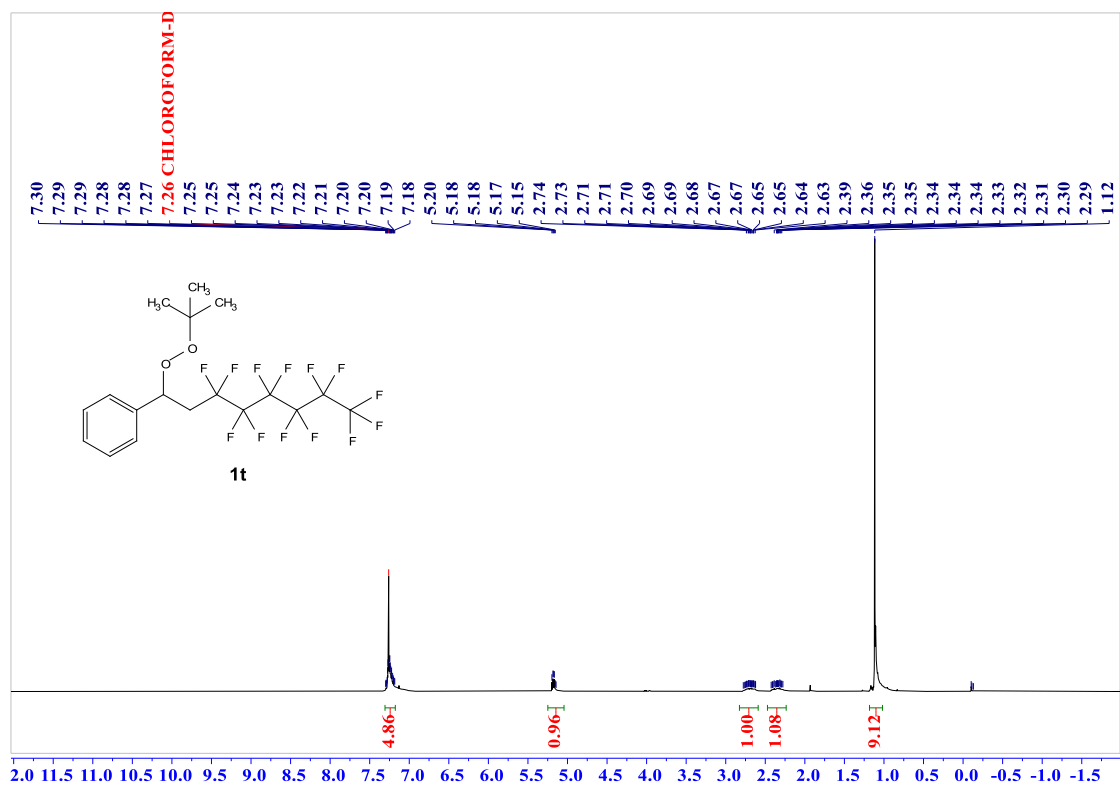
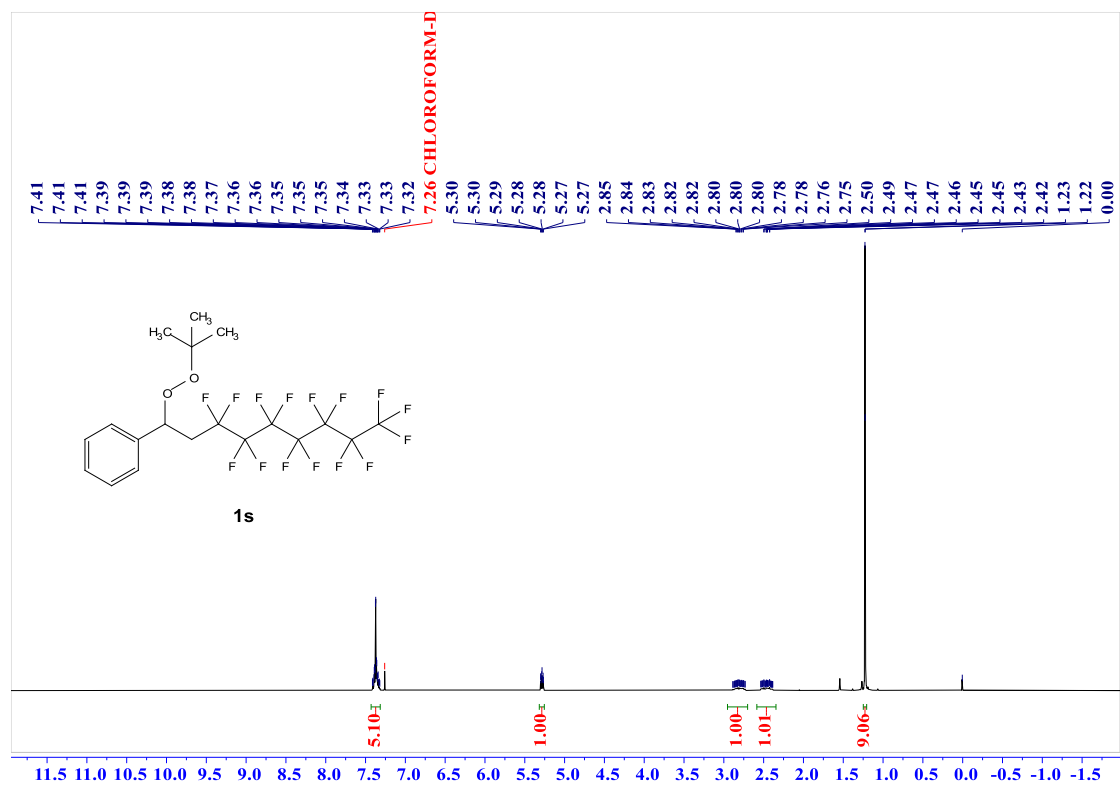


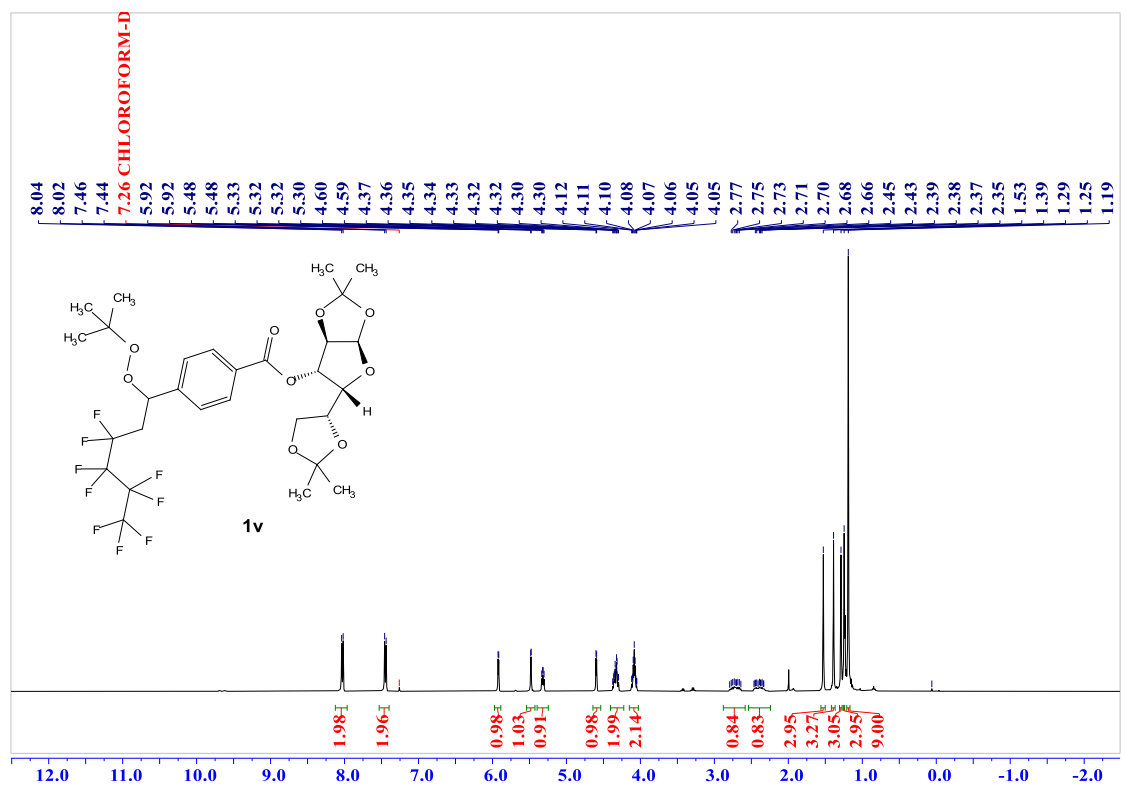
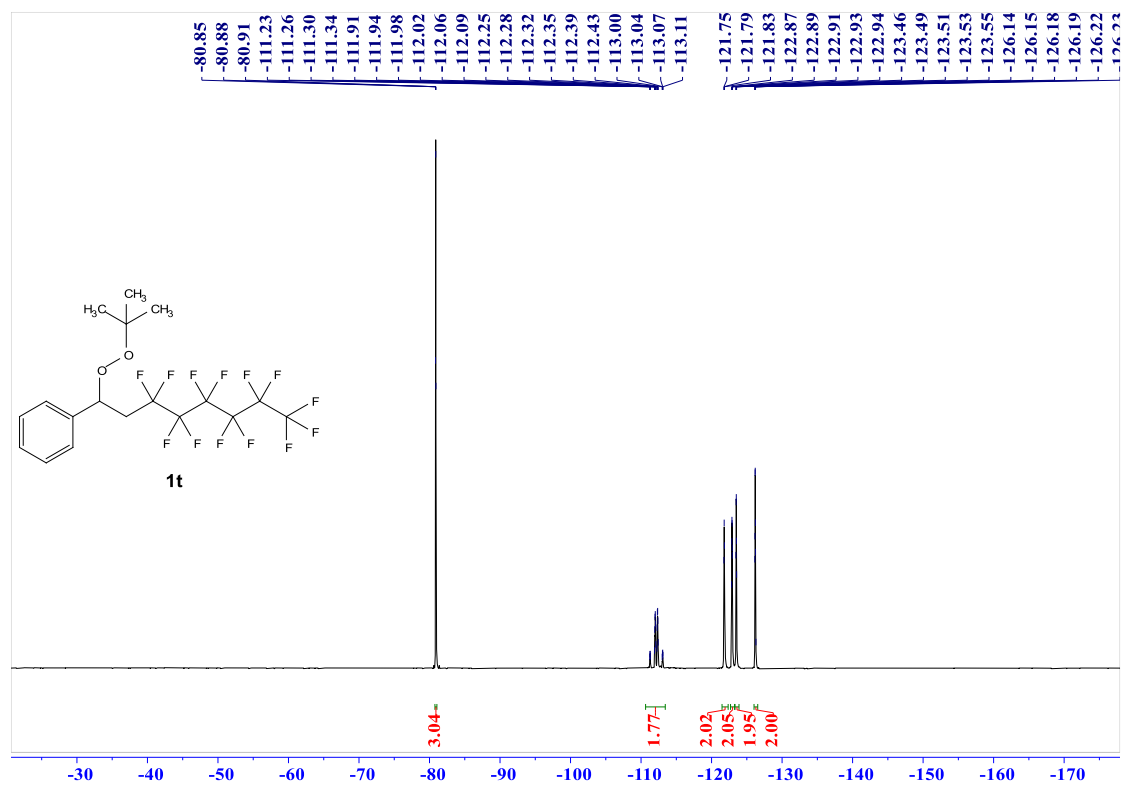


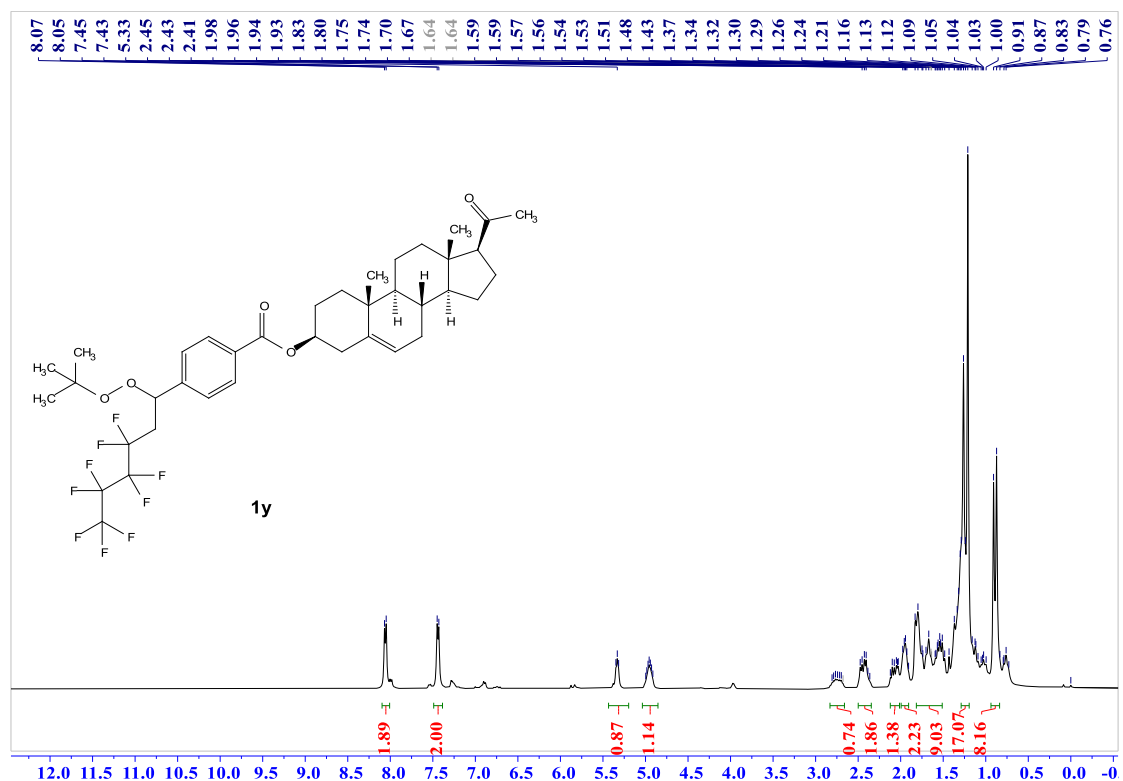
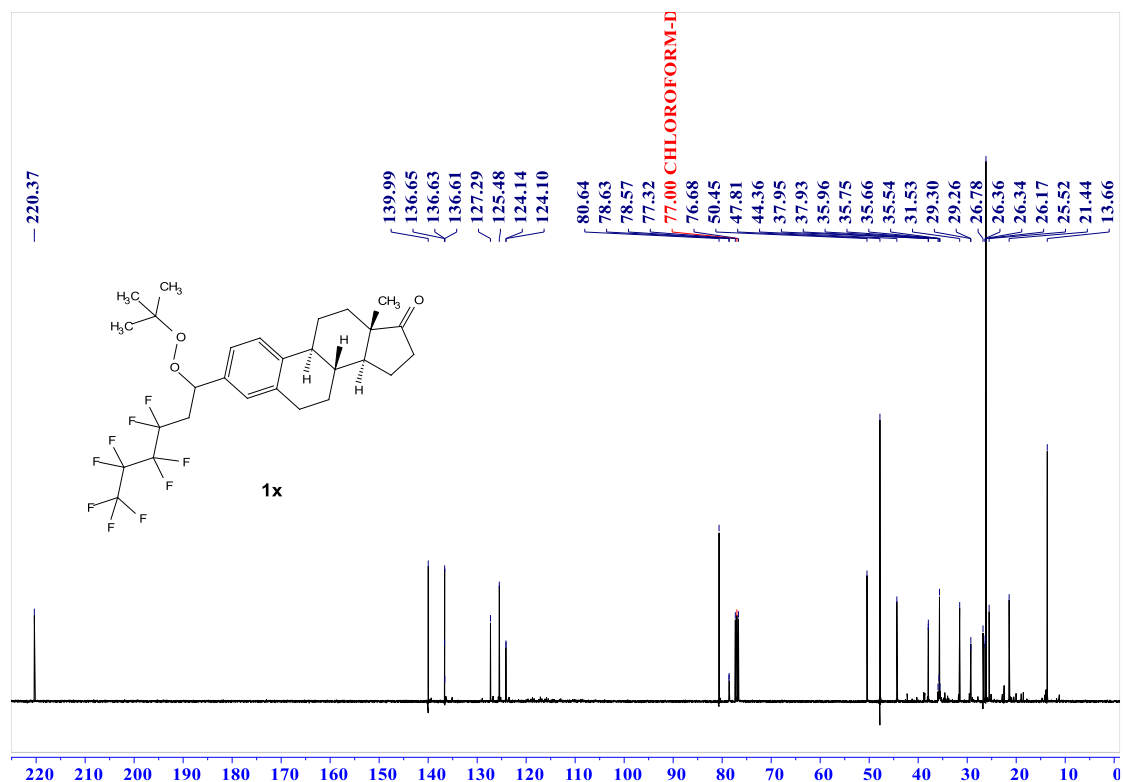


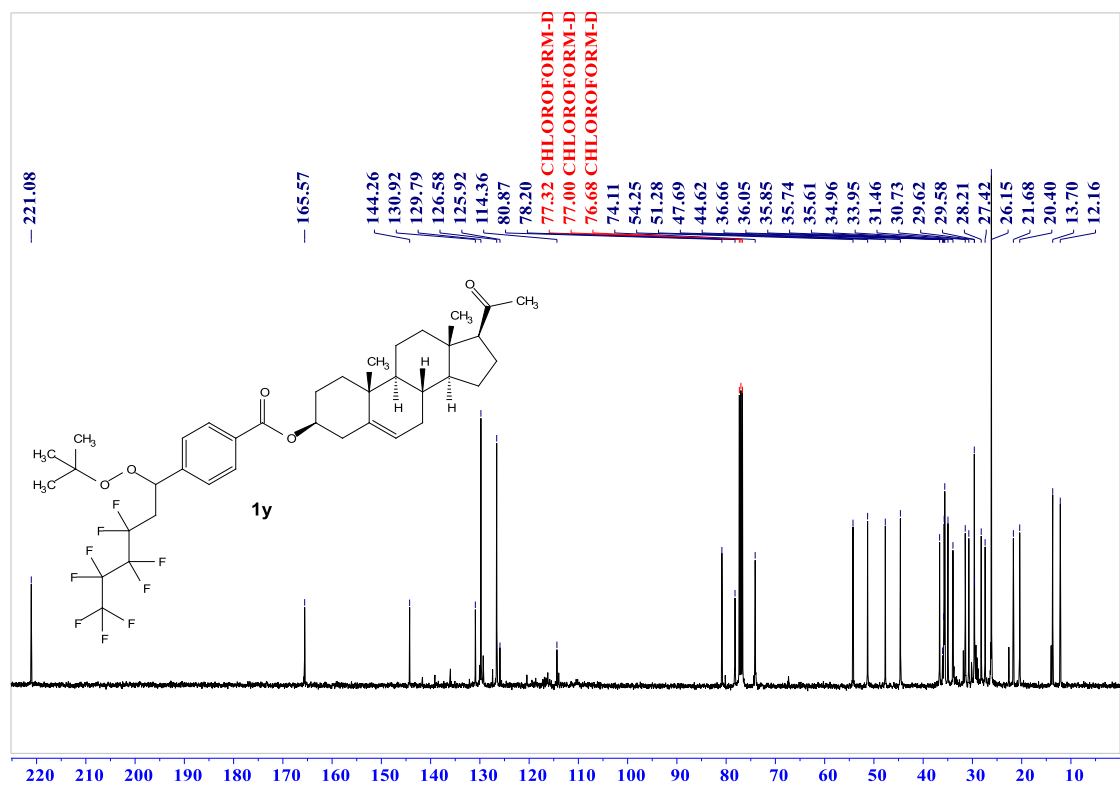
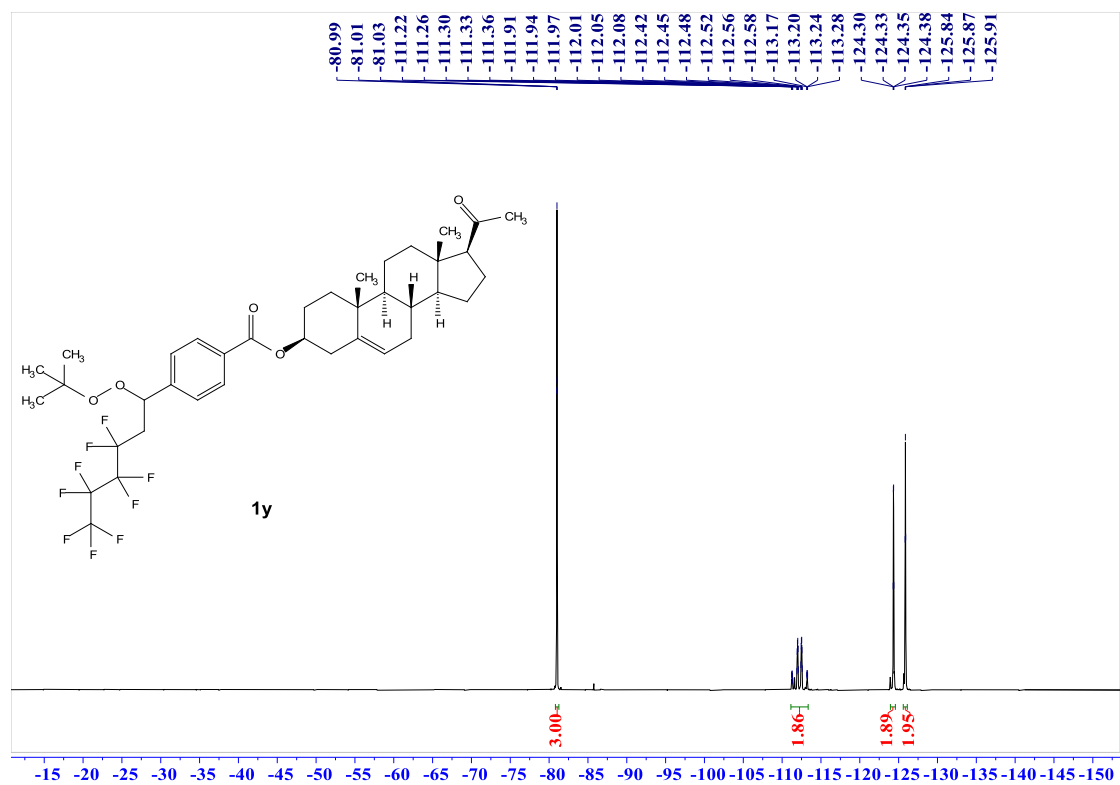


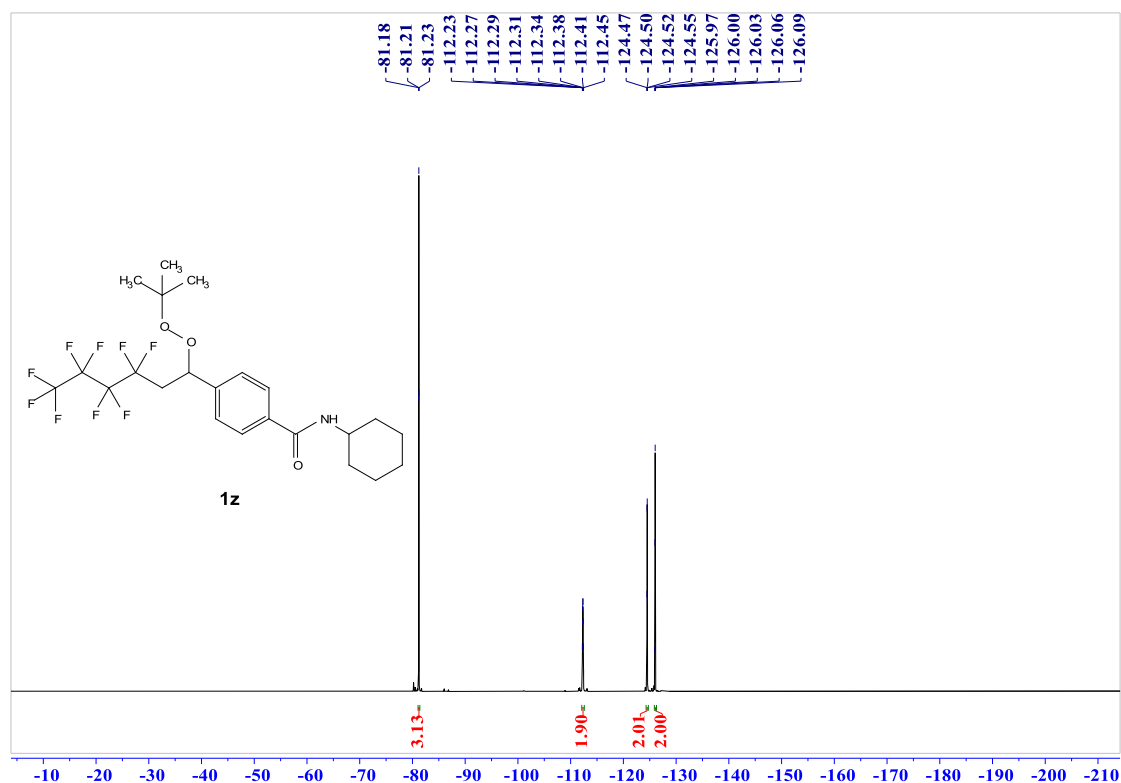
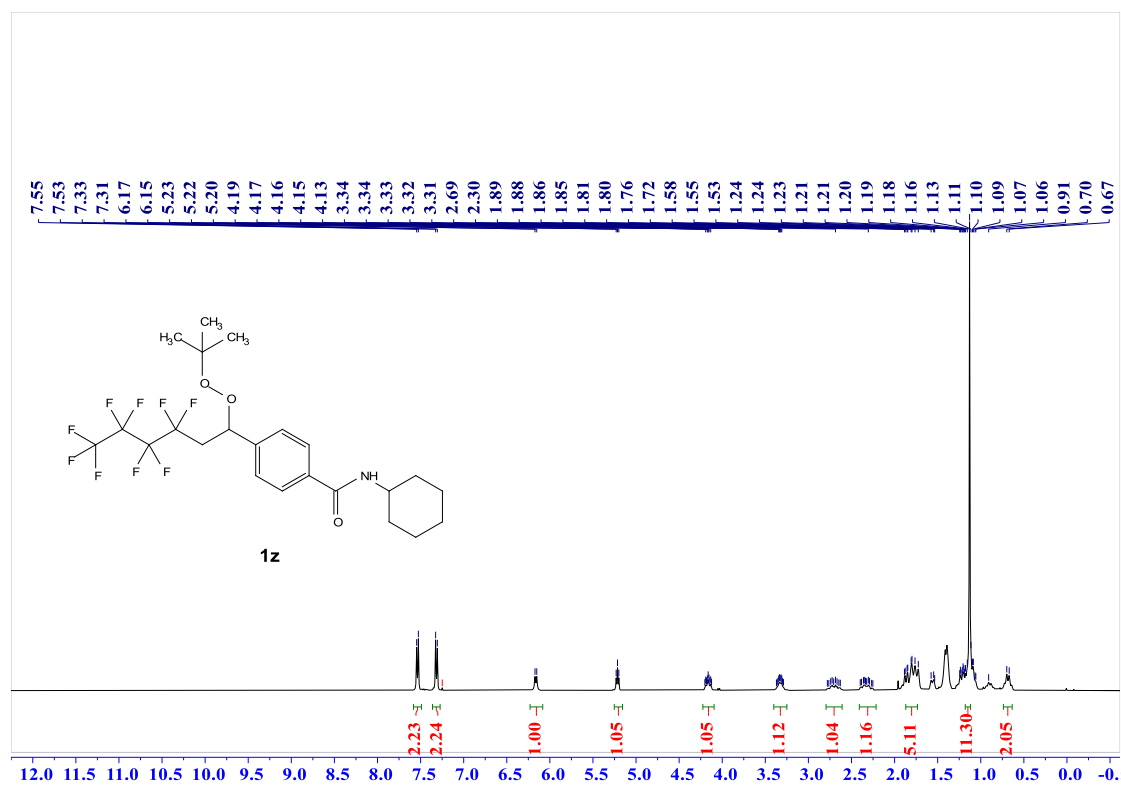


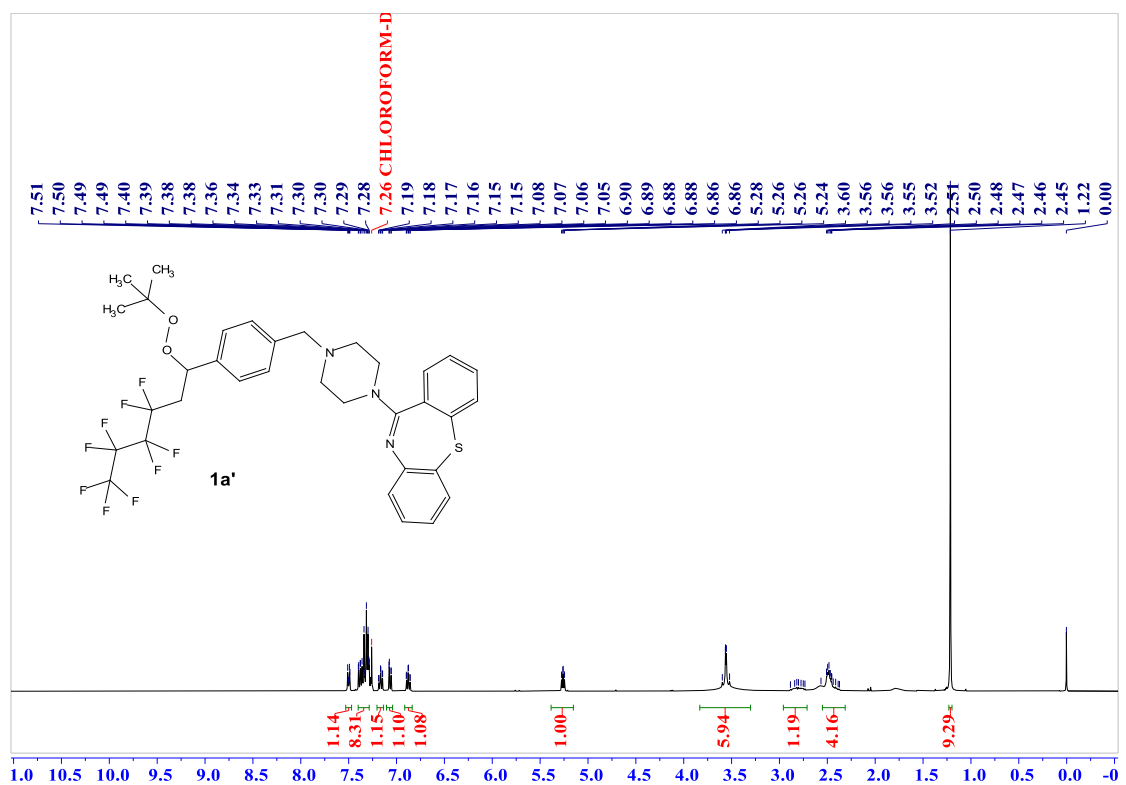
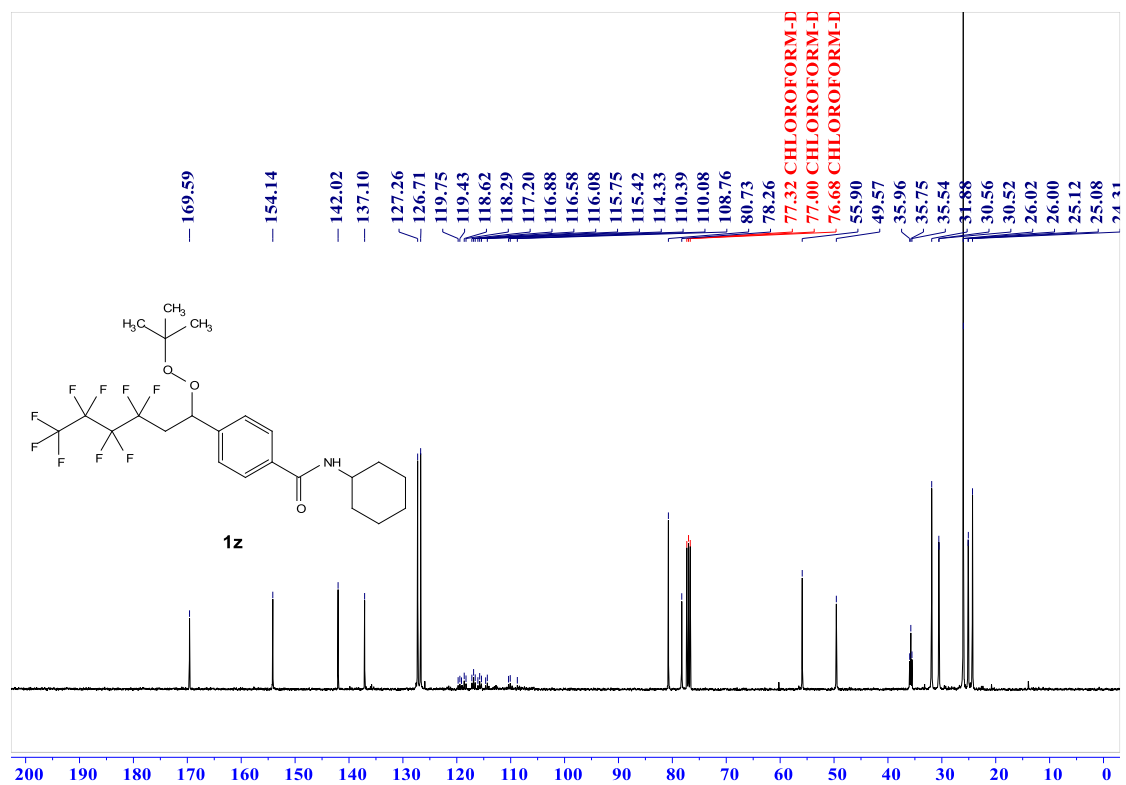


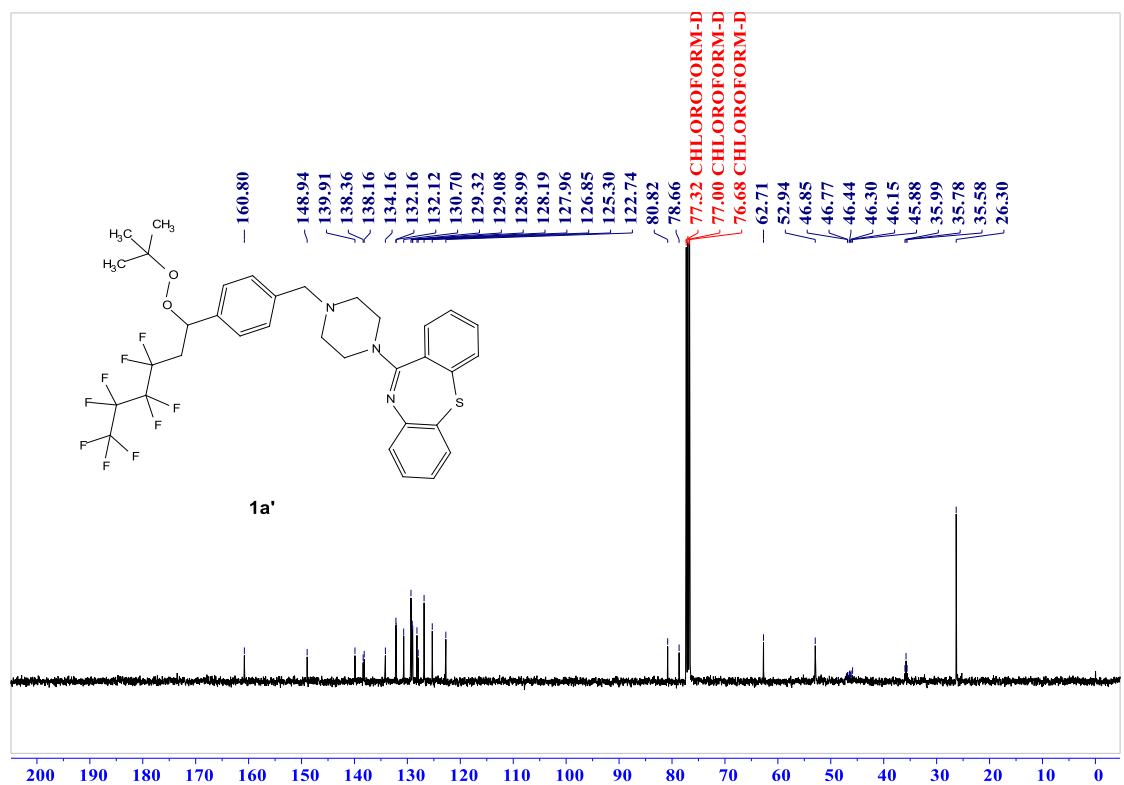


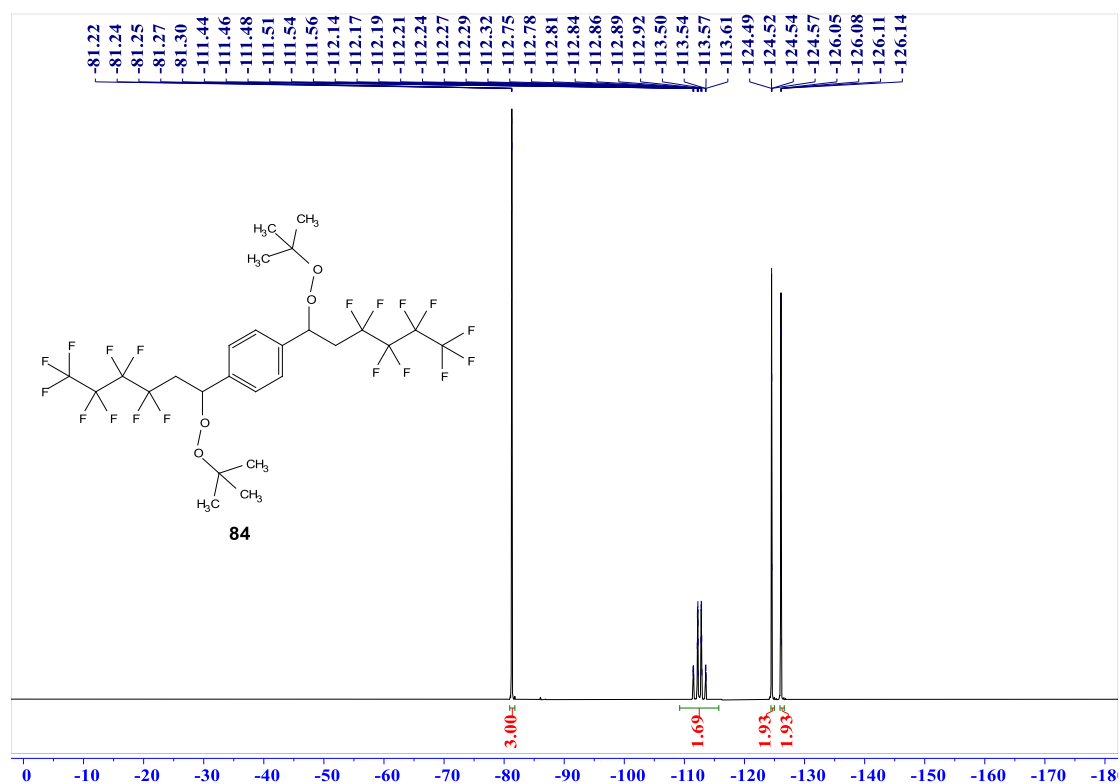
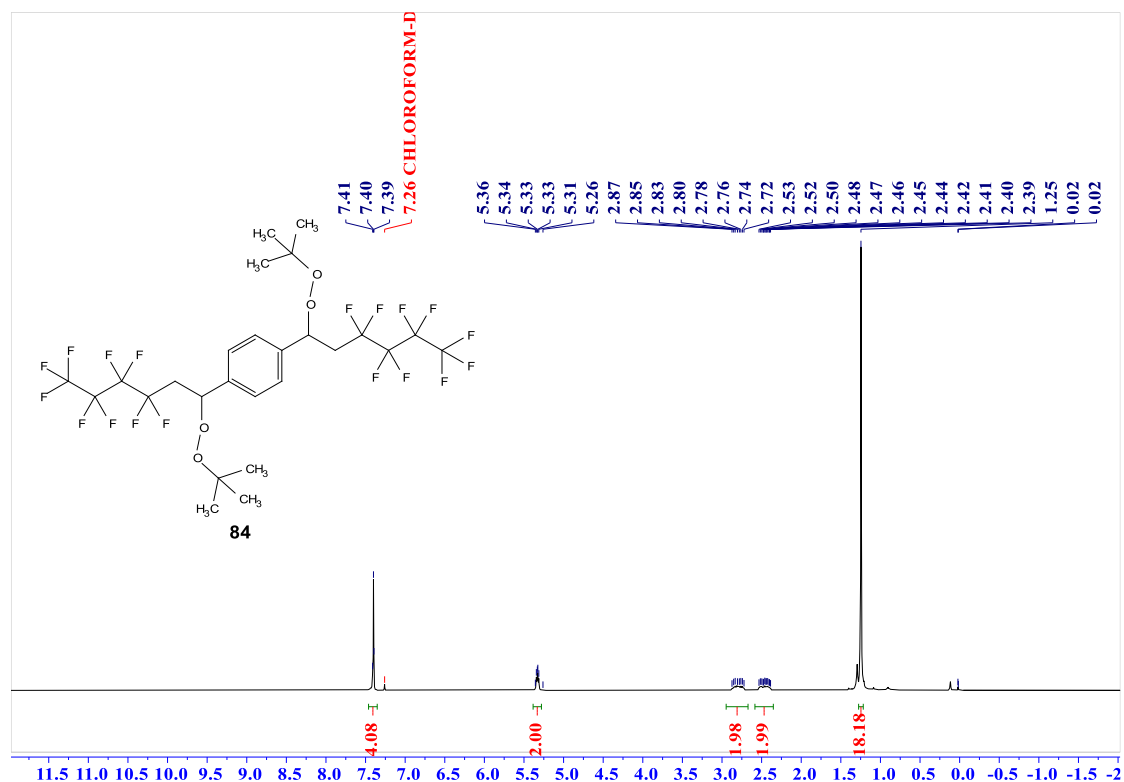


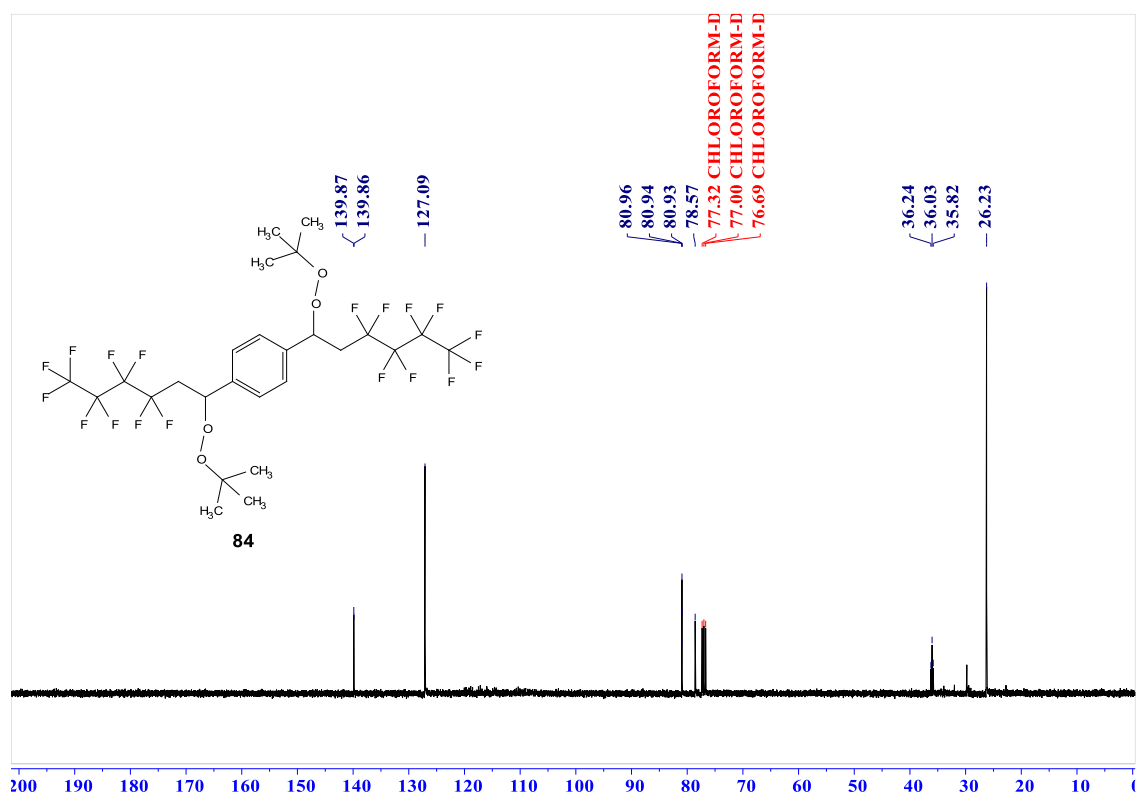












13. ^1H , ^{19}F , ^{31}P , and ^{13}C NMR spectra of products

