

Supporting Information

Defluorinative Phosphorylation of Perfluoroalkyl Ketones: Synthesis of Fluoroalkylated and Phosphorylated Furan Derivatives

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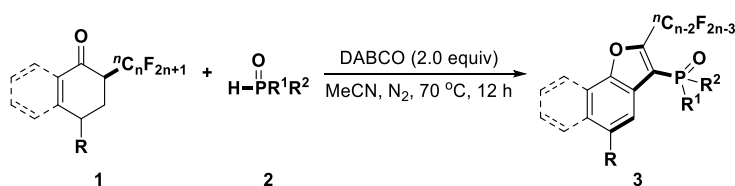
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1. General information

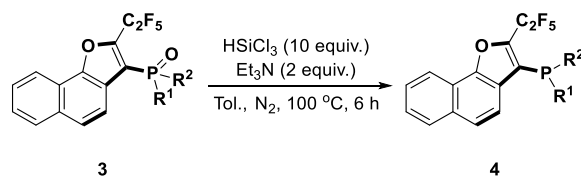
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under N₂ atmosphere using undistilled solvent. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ¹H, ¹⁹F, ³¹P, and ¹³C NMR spectra were recorded in CDCl₃ 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 spectra (HRMS) were obtained using a commercial apparatus (ESI or EI Source). Column chromatography was generally performed on silica gel (300-400 mesh) or alkali alumina (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

2. General procedures for the synthesis of tri(hetero)arylphosphine oxides



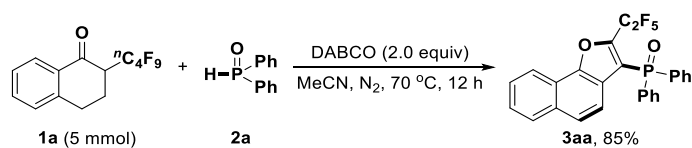
A solution of α -perfluoroalkyl ketone **1**^[1-2] (0.3 mmol), *P*-nucleophile **2** (0.36 mmol), and triethylenediamine (DABCO, 67 mg, 0.60 mmol) in MeCN (2.0 mL) was stirred under nitrogen atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate or dichloromethane/methanol as eluent to afford the pure products **3**.

3. The synthesis of tri(hetero)arylphosphines **4**^[3]



After removal of the solvent of above reaction mixture, the formed crude perfluoroalkylated naphtho[1,2-*b*]furan/benzofuran derivative **3** was directly used in the next step without further purification. Trichlorosilane (406 mg, 3 mmol), Et₃N (71 mg, 0.6 mmol), and toluene (5 mL) was added to the above reaction mixture and stirred under nitrogen atmosphere at 100 °C for 6 h. Upon completion of the reaction (indicated by TLC), the reaction 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 twice, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether as eluent to afford the pure products **4**.

4. Scale-up synthesis of product 3aa

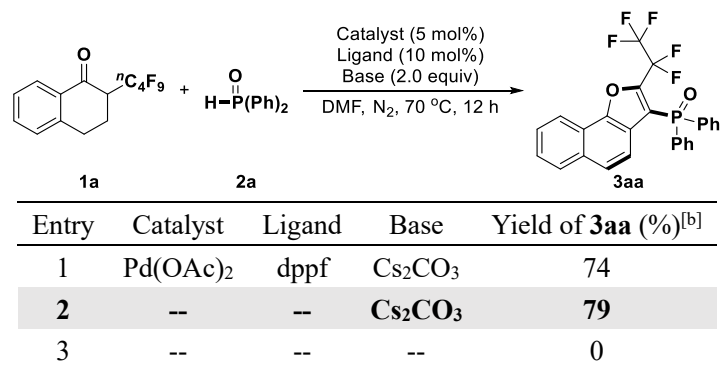


A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**, 1.82 g, 5 mmol), diphenylphosphine oxide (**2a**, 1.21 g, 6 mmol), and triethylenediamine (DABCO, 1.12 g, 10 mmol) in MeCN (30.0 mL) was stirred under nitrogen atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH₄Cl solution (150 mL) and extracted with EtOAc (100 mL x 3). The organic layer was washed with saturated brine twice, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate or dichloromethane/methanol as eluent to afford the pure products **3aa** (2.07 g, 85% yield).

5. Optimization of reaction conditions

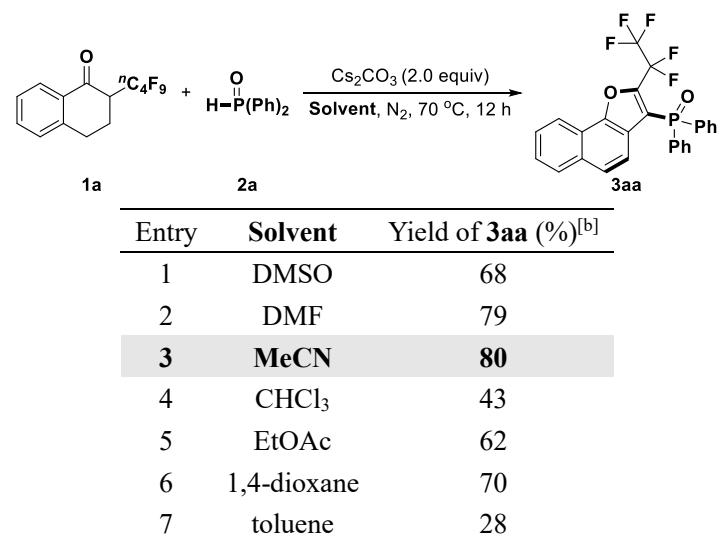
1) Optimization of reaction conditions of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1a**) with diphenylphosphine oxide (**2a**)

Table S1. Initial attempts for the desired reaction^[a]

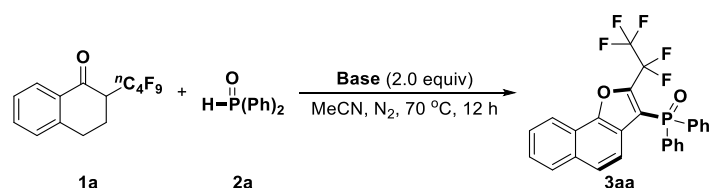


^[a] Reaction conditions: 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1a**, 0.3 mmol), diphenylphosphine oxide (**2a**, 0.36 mmol), catalyst (0.015 mmol), ligand (0.03 mmol), and base (0.6 mmol) in DMF (2.0 mL) at 70 °C under N₂ for 12 h. ^[b] Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard.

Table S2. Optimization of the reaction solvent^[a]

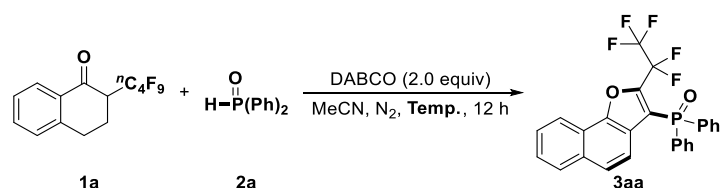


^[a] Reaction conditions: 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1a**, 0.3 mmol), diphenylphosphine oxide (**2a**, 0.36 mmol), and Cs₂CO₃ (0.6 mmol) in solvent (2.0 mL) at 70 °C under N₂ for 12 h. ^[b] Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard.

Table S3. Optimization of the reaction base^[a]

Entry	Base	Yield of 3aa (%) ^[b]
1	CS ₂ CO ₃	80
2	K ₂ CO ₃	65
3	NaOH	trace
4	K ₃ PO ₄	33
5	DABCO	87 (86) ^[c]
6	DBU	38

^[a] Reaction conditions: 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**, 0.3 mmol), diphenylphosphine oxide (**2a**, 0.36 mmol), and base (0.6 mmol) in MeCN (2.0 mL) at 70 °C under N₂ for 12 h. ^[b] Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard. ^[c] Isolated yield.

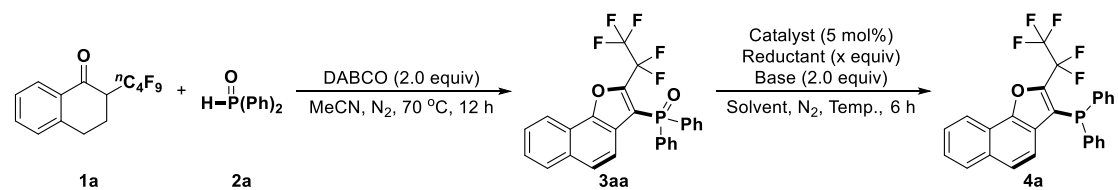
Table S4. Optimization of the reaction temperature^[a]

Entry	Temperature (°C)	Yield of 3aa (%) ^[b]
1	25	68
2	50	83
3	70	87 (86) ^[c]

^[a] Reaction conditions: 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**, 0.3 mmol), diphenylphosphine oxide (**2a**, 0.36 mmol), and DABCO (0.6 mmol) in MeCN (2.0 mL) at 25-70 °C under N₂ for 12 h. ^[b] Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard. ^[c] Isolated yield.

2) Optimization of reaction conditions for the synthesis of phosphines 4

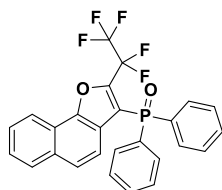
Table S5. Initial attempts for the desired reaction^[a]



Entry	Catalyst	Reductant (x equiv.)	Base	Solvent	Temp. (°C)	Yield of 4a (%) ^[b]
1	--	TMDS (5)	DABCO	MeCN	70	trace
2	Cu(OTf) ₂	TMDS (5)	DABCO	MeCN	70	trace
3	--	--	--	MeCN	70	trace
4	--	HSiCl₃ (10)	Et₃N	toluene	100	67
5	--	HSiCl ₃ (10)	Et ₃ N	toluene	100	77 ^[c]

^[a] Reaction conditions: **step 1**: 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1a**, 0.30 mmol), diphenylphosphine oxide (**2a**, 0.36 mmol), and DABCO (0.6 mmol) in MeCN (2.0 mL) at 70 °C under N₂ for 12 h; **step 2**: catalyst (0.015 mmol), reductant (1.5-3.0 mmol), and base (0.6 mmol) were added and stirred under N₂ at 70-100 °C in solvent (2.0 mL) for 6 h; TMDS = 1,1,3,3-tetramethyl disilazane. ^[b] Isolated Yield. ^[c] 0.3 mmol of **3aa** was directly used for reduction.

6. Characterization data for products



(2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide (3aa):

Yield = 86% (125 mg). Yellow solid. M.p. 199.7–200.9 °C.

IR (KBr): $\nu = 3056, 1546, 1438, 1333, 1203, 1146, 1124, 1036, 934, 754 \text{ cm}^{-1}$.

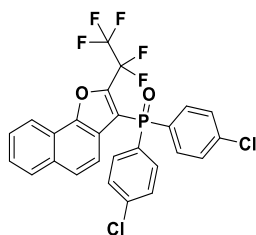
¹H NMR (400 MHz, CDCl₃): $\delta = 8.31$ (d, $J = 8.1$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), $7.84 - 7.75$ (m, 4H), $7.65 - 7.54$ (m, 5H), $7.53 - 7.46$ (m, 4H), 7.23 (d, $J = 8.9$ Hz, 1H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.09 - -82.73$ (m, 3F), $-107.67 - -108.41$ (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 20.2$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.3$ (d, $J = 11.1$ Hz), 145.0 (m), $132.6, 132.5$ (d, $J = 2.8$ Hz), $132.3, 131.6, 131.5, 128.6$ (d, $J = 12.9$ Hz), $128.1, 127.2$ (d, $J = 6.9$ Hz), $125.5, 123.9$ (d, $J = 7.8$ Hz), $120.4, 120.3, 119.9, 118.1$ (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₆H₁₇F₅O₂P [M+H]⁺ 487.0881, found: 487.0889.



Bis(4-chlorophenyl)(2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)phosphine oxide (3ab):

Yield = 99% (165 mg). Orange solid. M.p. 72.1–73.7 °C.

IR (KBr): $\nu = 3060, 1583, 1553, 1483, 1389, 1330, 1210, 1087, 1014, 937, 761 \text{ cm}^{-1}$.

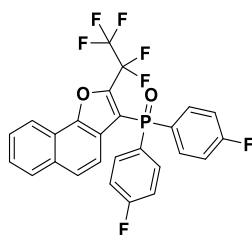
¹H NMR (400 MHz, CDCl₃): $\delta = 8.33$ (d, $J = 8.1$ Hz, 1H), 7.91 (d, $J = 7.9$ Hz, 1H), $7.74 - 7.67$ (m, 4H), $7.66 - 7.57$ (m, 3H), $7.53 - 7.46$ (m, 4H), 7.35 (d, $J = 8.9$ Hz, 1H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.29$ (t, $J = 3.4$ Hz, 3F), $-107.47 - -107.83$ (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 19.6$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.5$ (m), 145.0 (m), 139.5 (d, $J = 3.6$ Hz), 133.0 (d, $J = 11.6$ Hz), $132.5, 130.3$ (m), $129.2, 129.1, 128.2, 127.4$ (d, $J = 9.2$ Hz), $125.9, 123.7$ (m), $120.4, 120.4, 119.7, 117.2$ (d, $J = 107.2$ Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₆H₁₅Cl₂F₅O₂P [M+H]⁺ 555.0101, found: 555.0109.



Bis(4-fluorophenyl)(2-(perfluoroethyl)naphtho[1,2-b]furan-3-yl)phosphine oxide (3ac):

Yield = 94% (147 mg). Yellow solid. M.p. 72.1–73.7 °C.

IR (KBr): $\nu = 3066, 1592, 1500, 1333, 1240, 1204, 1123, 1067, 935, 803 \text{ cm}^{-1}$.

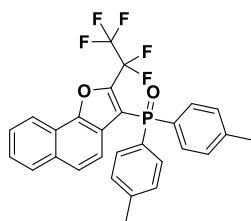
¹H NMR (400 MHz, CDCl₃): $\delta = 8.33 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 7.91 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 7.85 - 7.74 \text{ (m, 4H)}, 7.70 - 7.55 \text{ (m, 3H)}, 7.39 \text{ (d, } J = 8.9 \text{ Hz, 1H)}, 7.22 \text{ (t, } J = 7.9 \text{ Hz, 4H)}$ ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.08 - -82.64 \text{ (m, 3F)}, -104.30 - -105.35 \text{ (m, 2F)}, -107.29 - -108.30 \text{ (m, 2F)}$ ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 19.4$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 165.4 \text{ (m)}, 151.5 \text{ (m)}, 144.8 \text{ (m)}, 134.2 \text{ (m)}, 132.5, 128.2, 128.1 \text{ (m)}, 127.4, 127.3, 125.8, 123.9 \text{ (d, } J = 7.7 \text{ Hz)}, 120.4, 120.4, 119.8, 117.7 \text{ (m)}, 116.2 \text{ (m)}$ ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₆H₁₅F₇O₂P [M+H]⁺ 523.0692, found: 523.0701.



(2-(Perfluoroethyl)naphtho[1,2-b]furan-3-yl)di-*p*-tolylphosphine oxide (3ad):

Yield = 80% (123 mg). Yellow oil.

IR (KBr): $\nu = 2923, 1602, 1553, 1513, 1329, 1220, 1118, 936, 808 \text{ cm}^{-1}$.

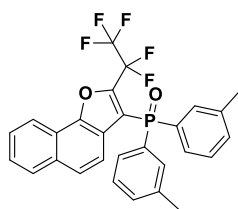
¹H NMR (400 MHz, CDCl₃): $\delta = 8.35 - 8.29 \text{ (m, 1H)}, 7.87 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 7.71 - 7.53 \text{ (m, 7H)}, 7.33 - 7.26 \text{ (m, 5H)}, 2.41 \text{ (s, 6H)}$ ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -81.98 - -82.70 \text{ (m, 3F)}, -107.74 - -108.12 \text{ (m, 2F)}$ ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 21.1$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.2 \text{ (m)}, 144.9 \text{ (m)}, 143.0 \text{ (m)}, 132.4, 131.7, 131.6, 129.4, 129.3, 129.1 \text{ (m)}, 128.1 \text{ (m)}, 127.1 \text{ (m)}, 125.4 \text{ (m)}, 124.0 \text{ (m)}, 120.4, 120.2 \text{ (m)}, 118.6 \text{ (m)}, 21.5$ ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₈H₂₁F₅O₂P [M+H]⁺ 515.1194, found: 515.1204.



(2-(Perfluoroethyl)naphtho[1,2-b]furan-3-yl)di-*m*-tolylphosphine oxide (3ae):

Yield = 92% (142 mg). Yellow oil.

IR (KBr): $\nu = 3088, 1735, 1552, 1513, 1329, 1208, 1116, 1034, 936, 811 \text{ cm}^{-1}$.

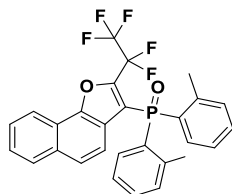
¹H NMR (400 MHz, CDCl₃): $\delta = 8.36 - 8.30 \text{ (m, 1H)}, 7.92 - 7.86 \text{ (m, 1H)}, 7.72 - 7.62 \text{ (m, 3H)}, 7.61 - 7.55 \text{ (m, 2H)}, 7.52 - 7.45 \text{ (m, 2H)}, 7.43 - 7.34 \text{ (m, 4H)}, 7.25 \text{ (d, } J = 9.0 \text{ Hz, 1H)}, 2.37 \text{ (s, 6H)}$ ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.33 \text{ (t, } J = 4.0 \text{ Hz, 3F)}, -107.77 - -108.21 \text{ (m, 2F)}$ ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 21.51$ ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 151.3 (m), 145.0 (m), 138.7 (d, J = 12.6 Hz), 133.3 (d, J = 2.9 Hz), 132.7, 132.4, 132.1 (d, J = 10.2 Hz), 131.6 (m), 128.7 (d, J = 11.1 Hz), 128.4 (d, J = 13.8 Hz), 128.2, 127.2 (d, J = 7.5 Hz), 125.4, 124.1 (m), 120.5, 120.3 (d, J = 21.2 Hz), 118.4 (m), 117.9 (m), 21.3 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{28}\text{H}_{21}\text{F}_5\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$ 515.1194, found: 515.1204.



(2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)di-*o*-tolylphosphine oxide (3af):

Yield = 68% (105 mg). Yellow oil.

IR (KBr): ν = 3061, 2963, 2927, 2856, 1594, 1453, 1211, 1126, 1034, 936, 808 cm^{-1} .

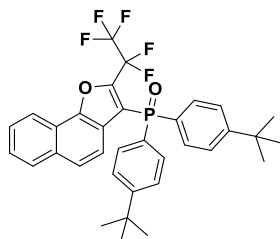
^1H NMR (400 MHz, CDCl_3): δ = 8.38 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.52 – 7.45 (m, 2H), 7.38 – 7.32 (m, 2H), 7.28 (d, J = 9.0 Hz, 1H), 7.22 – 7.15 (m, 4H), 2.61 (s, 6H) ppm.

^{19}F NMR (376 MHz, CDCl_3): δ = -82.35 (t, J = 2.8 Hz, 3F), -107.92 – 107.84 (m, 2F) ppm.

^{31}P NMR (162 MHz, CDCl_3): δ = 27.1 ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 151.4 (m), 143.8 (d, J = 8.3 Hz), 132.5, 132.5, 132.3 (m), 132.2, 132.2, 132.1, 130.1 (d, J = 109.8 Hz), 128.2, 127.3 (d, J = 6.9 Hz), 125.6, 125.5, 124.3 (d, J = 7.5 Hz), 120.6, 120.5, 120.0, 118.3 (d, J = 102.0 Hz), 21.7 (d, J = 4.4 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{28}\text{H}_{21}\text{F}_5\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$ 515.1194, found: 515.1204.



Bis(4-(*tert*-butyl)phenyl)(2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)phosphine oxide (3ag):

Yield = 93% (167 mg). Yellow oil.

IR (KBr): ν = 2964, 2870, 1719, 1599, 1553, 1394, 1212, 1137, 1034, 937, 829 cm^{-1} .

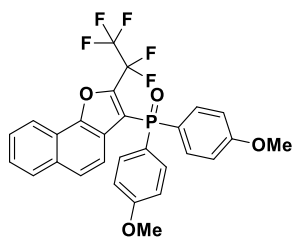
^1H NMR (400 MHz, CDCl_3): δ = 8.32 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.75 – 7.67 (m, 4H), 7.63 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 6.9 Hz, 2H), 7.54 – 7.47 (m, 4H), 7.35 (d, J = 8.9 Hz, 1H), 1.33 (s, 18H) ppm.

^{19}F NMR (376 MHz, CDCl_3): δ = -81.69 – -82.94 (m, 3F), -107.12 – -108.59 (m, 2F) ppm.

^{31}P NMR (162 MHz, CDCl_3): δ = 21.2 ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 156.1 (d, J = 3.1 Hz), 151.3 (m), 132.4, 131.7, 131.5, 129.0 (m), 128.1, 127.1 (d, J = 7.8 Hz), 125.6, 125.5, 125.3, 124.3 (m), 120.5, 120.4, 120.4, 118.6 (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 $\text{C}_{34}\text{H}_{33}\text{F}_5\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$ 599.2133, found: 599.2136.



Bis(4-methoxyphenyl)(2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)phosphine oxide (3ah):

Yield = 79% (129 mg). Yellow oil.

IR (KBr): $\nu = 3063, 2934, 2840, 1907, 1598, 1504, 1259, 1208, 1120, 1033, 935, 805 \text{ cm}^{-1}$.

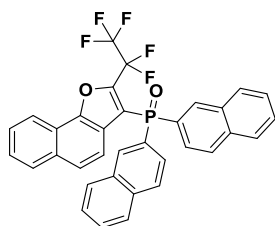
¹H NMR (400 MHz, CDCl₃): $\delta = 8.36 - 8.29$ (m, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.74 – 7.66 (m, 4H), 7.65 – 7.54 (m, 3H), 7.33 (d, $J = 8.9$ Hz, 1H), 7.03 – 6.97 (m, 4H), 3.84 (s, 6H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.25 - -82.37$ (m, 3F), $-107.77 - -107.93$ (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 34.21$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 162.8$ (d, $J = 2.9$ Hz), 151.2 (m), 144.7 (m), 133.5 (d, $J = 12.1$ Hz), 132.4, 128.1, 127.1 (d, $J = 5.2$ Hz), 125.4, 124.1 (m), 123.7 (d, $J = 118.0$ Hz), 120.4, 120.3, 120.2, 118.9 (m), 114.1 (d, $J = 14.0$ Hz), 55.3 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₈H₂₁F₅O₄P [M+H]⁺ 547.1092, found: 547.1098.



Di(naphthalen-2-yl)(2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)phosphine oxide (3ai):

Yield = 78% (137 mg). Pink solid. M.p. 259.1–260.8 °C.

IR (KBr): $\nu = 3744, 3057, 1591, 1551, 1380, 1330, 1216, 1165, 1034, 935, 774 \text{ cm}^{-1}$.

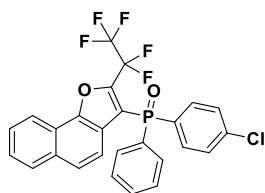
¹H NMR (400 MHz, CDCl₃): $\delta = 8.91$ (d, $J = 8.2$ Hz, 2H), 8.33 (d, $J = 8.1$ Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 2H), 7.91 (d, $J = 7.9$ Hz, 2H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.57 – 7.29 (m, 11H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.35$ (t, $J = 3.0$ Hz, 3F), $-107.00 - -110.20$ (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 28.4$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.4$ (d, $J = 11.1$ Hz), 145.3 (m), 134.0 (d, $J = 8.7$ Hz), 133.9 (d, $J = 1.9$ Hz), 133.8 (d, $J = 4.6$ Hz), 133.0 (d, $J = 12.9$ Hz), 132.5, 128.9 (d, $J = 1.3$ Hz), 128.2, 128.1 (d, $J = 109.6$ Hz), 127.4, 127.3 (d, $J = 5.7$ Hz), 127.2 (d, $J = 9.1$ Hz), 126.7, 125.6, 124.3, 124.2, 124.2, 125.0, 120.4, 120.1, 118.4 (d, $J = 104.6$ Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₄H₂₁F₅O₂P [M+H]⁺ 587.1194, found: 587.1188.



(4-Chlorophenyl)(2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)(phenyl)phosphine oxide (3aj):

Yield = 82% (128 mg). Yellow solid. M.p. 146.4–147.4 °C.

IR (KBr): $\nu = 3027, 1578, 1513, 1383, 1328, 1206, 1167, 1086, 1034, 802, 778 \text{ cm}^{-1}$.

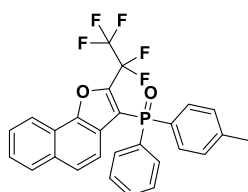
¹H NMR (400 MHz, CDCl₃): $\delta = 8.33$ (d, $J = 8.1$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.82 – 7.69 (m, 4H), 7.68 – 7.57 (m, 4H), 7.56 – 7.45 (m, 4H), 7.30 (d, $J = 8.9$ Hz, 1H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.55$ – -82.40 (m, 3F), -107.72 – -107.84 (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 20.2$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.4$ (m), 145.0 (m), 139.2 (d, $J = 3.4$ Hz), 133.1 (d, $J = 11.5$ Hz), 132.8 (d, $J = 3.0$ Hz), 132.5, 132.3, 131.6 (d, $J = 10.7$ Hz), 131.3 (d, $J = 16.3$ Hz), 130.3, 129.0 (d, $J = 13.5$ Hz), 128.8 (d, $J = 13.0$ Hz), 128.2, 127.4 (d, $J = 8.2$ Hz), 125.7, 123.9 (d, $J = 7.6$ Hz), 120.5, 120.4, 119.8, 117.7 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₆H₁₆ClF₅O₂P [M+H]⁺ 521.0491, found: 521.0493.



(2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)(phenyl)(*p*-tolyl)phosphine oxide (3ak):

Yield = 73% (110 mg). Light-pink solid. M.p. 148.0–149.0 °C.

IR (KBr): $\nu = 3059, 2924, 1549, 1438, 1328, 1225, 1202, 1119, 1057, 936, 808 \text{ cm}^{-1}$.

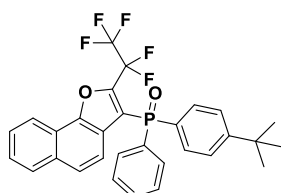
¹H NMR (400 MHz, CDCl₃): $\delta = 8.33$ (d, $J = 8.1$ Hz, 1H), 7.89 (d, $J = 8.1$ Hz, 1H), 7.82 – 7.74 (m, 2H), 7.71 – 7.55 (m, 6H), 7.53 – 7.45 (m, 2H), 7.31 (dd, $J = 8.0, 2.9$ Hz, 2H), 7.27 – 7.24 (m, 1H), 2.42 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.32$ (t, $J = 2.8$ Hz, 3F), -107.87 – -107.96 (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 21.09$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.3$ (m), 145.0 (m), 143.2 (d, $J = 3.0$ Hz), 132.5 (m), 132.5, 132.4, 131.7 (d, $J = 4.9$ Hz), 131.6 (d, $J = 4.5$ Hz), 129.4 (d, $J = 13.4$ Hz), 128.8 (m), 128.6 (d, $J = 12.8$ Hz), 128.2, 127.3, 127.2, 124.1 (m), 120.5, 120.4, 120.1, 118.4 (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 C₂₇H₁₉F₅O₂P [M+H]⁺ 501.1037, found: 501.1042.



(4-(*tert*-Butyl)phenyl)(2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)(phenyl)phosphine oxide

(3al):

Yield = 83% (135 mg). Yellow oil.

IR (KBr): $\nu = 2964, 1763, 1552, 1438, 1213, 1133, 1035, 936, 811 \text{ cm}^{-1}$.

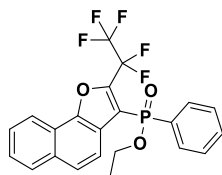
¹H NMR (400 MHz, CDCl₃): $\delta = 8.32 \text{ (d, } J = 8.2 \text{ Hz, 1H)}, 7.89 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 7.82 - 7.69 \text{ (m, 4H)}, 7.66 - 7.62 \text{ (m, 1H)}, 7.61 - 7.55 \text{ (m, 3H)}, 7.54 - 7.46 \text{ (m, 4H)}, 7.29 \text{ (d, } J = 8.9 \text{ Hz, 1H)}, 1.34 \text{ (s, 9H)}$ ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.36 \text{ (t, } J = 3.8 \text{ Hz, 3F)}, -107.32 - -108.48 \text{ (m, 2F)}$ ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 21.25$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 156.2 \text{ (d, } J = 2.9 \text{ Hz)}, 151.3 \text{ (m)}, 144.9 \text{ (m)}, 131.6 \text{ (m)}, 132.4 \text{ (m)}, 132.4, 131.6 \text{ (m)}, 128.6 \text{ (m)}, 128.5, 128.1, 128.0, 127.2 \text{ (d, } J = 7.5 \text{ Hz)}, 125.8, 125.6, 125.4, 124.1 \text{ (m)}, 120.5, 120.4, 120.2, 118.4 \text{ (m)}, 35.0 \text{ (d, } J = 1.0 \text{ Hz)}, 31.0$ ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₀H₂₅F₅O₂P [M+H]⁺ 543.1507, found: 543.1501.

**Ethyl (2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)(phenyl)phosphinate (3am):**

Yield = 58% (264 mg, 1 mmol scale). Yellow oil.

IR (KBr): $\nu = 3062, 2985, 1594, 1559, 1439, 1222, 1125, 1035, 936, 814 \text{ cm}^{-1}$.

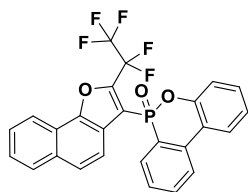
¹H NMR (400 MHz, CDCl₃): $\delta = 8.32 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 8.19 \text{ (d, } J = 8.8 \text{ Hz, 1H)}, 7.97 \text{ (d, } J = 7.8 \text{ Hz, 1H)}, 7.92 - 7.84 \text{ (m, 2H)}, 7.80 \text{ (d, } J = 8.9 \text{ Hz, 1H)}, 7.70 - 7.60 \text{ (m, 2H)}, 7.58 - 7.52 \text{ (m, 1H)}, 7.50 - 7.43 \text{ (m, 2H)}, 4.26 \text{ (q, } J = 6.7 \text{ Hz, 2H)}, 1.46 \text{ (t, } J = 7.0 \text{ Hz, 3H)}$ ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.66 \text{ (t, } J = 3.5 \text{ Hz, 3F)}, -108.80 - -110.42 \text{ (m, 2F)}$ ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 23.47$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.3 \text{ (m)}, 144.6 \text{ (m)}, 132.7 \text{ (m)}, 131.5 \text{ (m)}, 131.2 \text{ (d, } J = 10.9 \text{ Hz)}, 128.8 \text{ (m)}, 128.7, 128.5, 128.3, 127.2, 125.8, 123.7 \text{ (m)}, 120.6, 120.4, 120.4, 117.0 \text{ (m)}, 61.8 \text{ (d, } J = 5.8 \text{ Hz)}, 16.3 \text{ (d, } J = 6.9 \text{ Hz)}$ ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₂H₁₇F₅O₃P [M+H]⁺ 455.0830, found: 455.0834.

**6-(2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)dibenzo[*c,e*][1,2]oxaphosphinine 6-oxide (3an):**

Yield = 19% (95 mg, 1 mmol scale). Brown solid. M.p. 85.0–86.0 °C.

IR (KBr): $\nu = 3630, 1560, 1478, 1331, 1209, 1120, 1036, 945, 752 \text{ cm}^{-1}$.

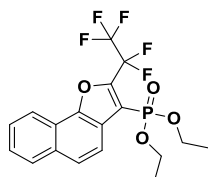
¹H NMR (400 MHz, CDCl₃): $\delta = 8.35 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 8.29 \text{ (d, } J = 8.8 \text{ Hz, 1H)}, 8.13 - 8.08 \text{ (m, 1H)}, 8.06 \text{ (dd, } J = 8.0, 1.4 \text{ Hz, 1H)}, 8.00 \text{ (d, } J = 7.6 \text{ Hz, 1H)}, 7.84 \text{ (d, } J = 8.8 \text{ Hz, 1H)}, 7.75 - 7.63 \text{ (m, 4H)}, 7.46 - 7.39 \text{ (m, 2H)}, 7.36 - 7.28 \text{ (m, 2H)}$ ppm.

^{19}F NMR (376 MHz, CDCl_3): $\delta = -82.13 - -83.28$ (m, 3F), $-110.35 - -111.90$ (m, 2F) ppm.

^{31}P NMR (162 MHz, CDCl_3): $\delta = 14.15$ (d, $J = 14.8$ Hz) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 151.4$ (m), 148.8 (d, $J = 8.2$ Hz), 134.9 (d, $J = 6.1$ Hz), 133.5 , 133.5 , 132.8 , 130.7 , 130.6 (d, $J = 12.4$ Hz), 128.4 , 128.4 , 128.3 , 127.4 (d, $J = 7.4$ Hz), 126.2 , 125.8 (t, $J = 1.1$ Hz), 125.0 (d, $J = 0.9$ Hz), 124.8 , 124.4 , 124.3 (d, $J = 9.9$ Hz), 123.5 (d, $J = 10.6$ Hz), 121.2 (d, $J = 12.0$ Hz), 120.5 , 120.5 , 120.5 , 120.4 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{26}\text{H}_{15}\text{F}_5\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$ 501.0673, found: 501.0685.



Diethyl (2-(perfluoroethyl)naphtho[1,2-b]furan-3-yl)phosphonate (3ao):

Yield = 25% (32 mg). Yellow oil.

IR (KBr): $\nu = 3065, 2985, 2931, 2857, 1729, 1566, 1332, 1261, 1220, 1137, 1036, 976, 817$ cm^{-1} .

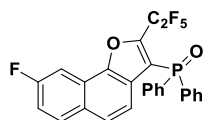
^1H NMR (400 MHz, CDCl_3): $\delta = 8.38 - 8.31$ (m, 1H), 8.22 (d, $J = 8.8$ Hz, 1H), 7.98 (d, $J = 7.7$ Hz, 1H), 7.82 (d, $J = 8.9$ Hz, 1H), $7.70 - 7.60$ (m, 2H), $4.35 - 4.14$ (m, 4H), 1.37 (t, $J = 7.1$ Hz, 6H) ppm.

^{19}F NMR (376 MHz, CDCl_3): $\delta = -82.84$ (t, $J = 3.4$ Hz, 3F), -111.07 (p, $J = 3.4$ Hz, 2F) ppm.

^{31}P NMR (162 MHz, CDCl_3): $\delta = 8.57$ ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 151.2$ (m), 144.6 (t, $J = 20.7$ Hz), 132.7 , 128.4 , 127.2 , 125.8 , 123.8 (m), 120.5 , 120.4 , 120.4 , 113.9 (m), 109.2 (d, $J = 40.8$ Hz), 62.8 (d, $J = 5.6$ Hz), 16.2 (d, $J = 6.9$ Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{18}\text{H}_{17}\text{F}_5\text{O}_4\text{P}$ $[\text{M}+\text{H}]^+$ 423.0779, found: 423.0789.



(8-Fluoro-2-(perfluoroethyl)naphtho[1,2-b]furan-3-yl)diphenylphosphine oxide (3ba):

Yield = 88% (280 mg, 0.63 mmol scale). Light-yellow solid. M. p. $169.8-170.4$ $^\circ\text{C}$.

IR (KBr): $\nu = 3063, 1547, 1518, 1437, 1347, 1207, 1168, 1123, 1029, 956, 835, 727, 701$ cm^{-1} .

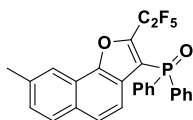
^1H NMR (400 MHz, CDCl_3): $\delta = 7.94-7.86$ (m, 2H), $7.83-7.75$ (m, 4H), $7.65-7.56$ (m, 3H), 7.51 (td, $J = 7.5, 3.2$ Hz, 4H), $7.36-7.31$ (m, 1H), $7.28-7.25$ (m, 1H) ppm.

^{19}F NMR (376 MHz, CDCl_3): $\delta = -82.36$ (s, 3F), -108.04 (s, 2F), -110.82 (s, 1F) ppm.

^{31}P NMR (162 MHz, CDCl_3): $\delta = 21.07$ ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 161.3$ (d, $J = 247.2$ Hz), 150.8 (m), 145.4 (m), 132.6 (d, $J = 2.8$ Hz), 132.0 (d, $J = 110.8$ Hz), 131.6 (d, $J = 10.6$ Hz), 130.8 (d, $J = 9.1$ Hz), 129.3 , 128.6 (d, $J = 12.8$ Hz), 125.2 , 124.8 (d, $J = 7.4$ Hz), 121.2 (d, $J = 10.0$ Hz), 119.3 , 118.3 (s), 117.2 (d, $J = 24.5$ Hz), 104.7 (d, $J = 23.5$ Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{26}\text{H}_{16}\text{F}_6\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$ 505.0787, found: 505.0787.



(8-Methyl-2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide (3ca):

Yield = 88% (176 mg, 0.4 mmol scale). Brown solid. M. p. 152.2-153.4 °C.

IR (KBr): $\nu = 3059, 2923, 2853, 1546, 1436, 1333, 1205, 1122, 1041, 946, 834, 753, 726 \text{ cm}^{-1}$.

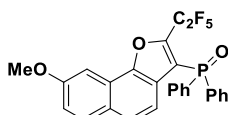
¹H NMR (400 MHz, CDCl₃): $\delta = 8.09$ (dd, $J = 1.9, 1.0 \text{ Hz}$, 1H), 7.83–7.75 (m, 5H), 7.63–7.57 (m, 2H), 7.54–7.47 (m, 5H), 7.41 (dd, $J = 8.4, 1.7 \text{ Hz}$, 1H), 7.11 (d, $J = 8.9 \text{ Hz}$, 1H), 2.57 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.32$ (s, 3F), -107.97 (s, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 20.99$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.1$ (d, $J = 11.0 \text{ Hz}$), 145.0 (m), 137.4, 132.7, 132.5 (d, $J = 2.9 \text{ Hz}$), 131.6 (d, $J = 10.6 \text{ Hz}$), 131.6, 130.6, 129.4, 128.6 (d, $J = 12.6 \text{ Hz}$), 128.0, 125.3, 124.0 (d, $J = 7.5 \text{ Hz}$), 120.6, 119.1 (d, $J = 55.0 \text{ Hz}$), 118.0 (m), 21.8 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₇H₁₉F₅O₂P [M+H]⁺ 501.1037, found: 501.1041.



(8-Methoxy-2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide (3da):

Yield = 84% (65 mg, 0.15 mmol scale). Brown solid. M. p. 153.8-154.6 °C.

IR (KBr): $\nu = 3058, 2962, 1559, 1516, 1439, 1331, 1224, 1209, 1198, 1177, 955, 832, 728 \text{ cm}^{-1}$.

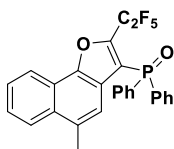
¹H NMR (400 MHz, CDCl₃): $\delta = 7.82$ –7.74 (m, 5H), 7.64–7.56 (m, 3H), 7.54–7.47 (m, 5H), 7.23 (dd, $J = 8.9, 2.6 \text{ Hz}$, 1H), 7.01 (d, $J = 8.8 \text{ Hz}$, 1H), 3.99 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.32$ (s, 3F), -108.15 (s, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 20.87$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 158.8, 150.9$ (d, $J = 11.2 \text{ Hz}$), 145.1 (m), 132.8, 132.5 (d, $J = 3.0 \text{ Hz}$), 131.7 (d, $J = 10.2 \text{ Hz}$), 129.9, 128.7, 128.6, 127.6, 125.2, 124.5 (d, $J = 7.6 \text{ Hz}$), 121.5, 119.5, 117.4, 99.2, 55.5 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₇H₁₉F₅O₃P [M+H]⁺ 517.0986, found: 517.0985.



(5-Methyl-2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide (3ea):

Yield = 56% (42 mg, 0.15 mmol scale). Light-yellow solid. M. p. 238.8-239.1 °C.

IR (KBr): $\nu = 3060, 2943, 1547, 1441, 1332, 1224, 1202, 1124, 1038, 934, 754, 701, 567 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.38$ –8.32 (m, 1H), 8.05–8.00 (m, 1H), 7.78 (dd, $J = 12.8, 7.5 \text{ Hz}$, 4H), 7.70–7.59 (m, 4H), 7.55–7.48 (m, 4H), 7.10 (s, 1H), 2.54 (s, 3H) ppm.

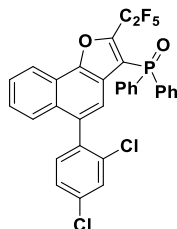
¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.40$ (s, 3F), -107.84 (s, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = 21.66$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 150.6$ (d, $J = 10.6 \text{ Hz}$), 144.4, 132.8, 132.5 (d, $J = 2.7 \text{ Hz}$), 131.9,

131.8, 131.7, 131.7, 128.6 (d, $J = 12.6$ Hz), 127.0 (d, $J = 33.3$ Hz), 124.9, 123.7 (d, $J = 7.3$ Hz), 120.9, 120.5, 119.8, 117.7 (m), 19.9 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{27}H_{19}F_5O_2P$ $[M+H]^+$ 501.1037, found: 501.1036.



(5-(2,4-Dichlorophenyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide (3fa):

Yield = 63% (60 mg, 0.15 mmol scale). Light-yellow solid. M. p. 213.9-214.7 °C.

IR (KBr): $\nu = 2989, 1551, 1437, 1329, 1210, 1121, 1042, 931, 773, 728, 694, 565, 540$ cm^{-1} .

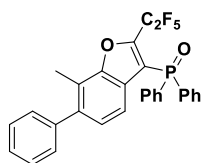
1H NMR (400 MHz, $CDCl_3$): $\delta = 8.43$ (d, $J = 8.1$ Hz, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.79 (dd, $J = 12.7, 7.2$ Hz, 4H), 7.70 (t, $J = 7.5$ Hz, 1H), 7.65–7.57 (m, 3H), 7.56–7.47 (m, 5H), 7.33 (d, $J = 1.6$ Hz, 1H), 7.16 (dd, $J = 8.1, 1.9$ Hz, 1H), 7.09 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -82.37$ (s, 3F), -108.27 (s, 2F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 21.16$ ppm.

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.3$ (d, $J = 10.1$ Hz), 145.4 (m), 139.8, 135.4, 132.7, 132.4, 131.8, 131.7, 131.7, 131.5, 130.5, 130.1, 129.4, 128.8 (d, $J = 12.2$ Hz), 127.7, 127.4, 126.3, 123.5 (d, $J = 6.2$ Hz), 121.1, 120.9, 120.7, 118.4 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{32}H_{19}Cl_2F_5O_2P$ $[M+H]^+$ 631.0414, found: 631.0418.



(7-Methyl-2-(perfluoroethyl)-6-phenylbenzofuran-3-yl)diphenylphosphine oxide (3ga):

Yield = 60% (32 mg, 0.1 mmol scale). Yellow oil.

IR (KBr): $\nu = 2925, 2854, 1560, 1480, 1438, 1329, 1213, 1168, 1120, 1040, 935, 774, 701$ cm^{-1} .

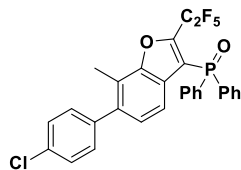
1H NMR (400 MHz, $CDCl_3$): $\delta = 7.74$ –7.65 (m, 4H), 7.57–7.50 (m, 2H), 7.44 (tt, $J = 7.5, 3.3$ Hz, 4H), 7.39–7.27 (m, 3H), 7.26–7.20 (m, 2H), 7.05 (dd, $J = 8.3, 3.6$ Hz, 1H), 6.91 (dd, $J = 8.3, 3.5$ Hz, 1H), 2.40 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -82.36$ (d, $J = 3.2$ Hz, 3F), -108.59 – -108.70 (m, 2F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 20.79$ ppm.

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.5$ (d, $J = 11.0$ Hz), 147.5 (m), 141.3, 140.0, 132.6 (d, $J = 2.7$ Hz), 132.6, 131.7 (d, $J = 10.5$ Hz), 131.6, 129.4, 128.7 (d, $J = 12.8$ Hz), 128.2, 127.3 (d, $J = 26.2$ Hz), 126.2 (d, $J = 7.9$ Hz), 120.3, 120.0, 117.2 (m), 12.8 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{29}H_{21}F_5O_2P$ $[M+H]^+$ 527.1194, found: 527.1199.



(6-(4-Chlorophenyl)-7-methyl-2-(perfluoroethyl)benzofuran-3-yl)diphenylphosphine oxide (3ha):

Yield = 77% (130 mg). Yellow oil.

IR (KBr): $\nu = 3058, 2984, 1560, 1478, 1438, 1329, 1212, 1120, 1089, 1038, 934, 752, 693 \text{ cm}^{-1}$.

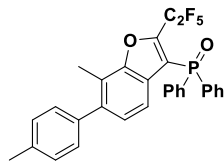
$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.68$ (dd, $J = 12.9, 7.5 \text{ Hz}$, 4H), 7.52 (t, $J = 7.2 \text{ Hz}$, 2H), 7.42 (td, $J = 7.6, 3.0 \text{ Hz}$, 4H), 7.31 (d, $J = 8.3 \text{ Hz}$, 2H), 7.15 (d, $J = 8.3 \text{ Hz}$, 2H), 6.99 (d, $J = 8.4 \text{ Hz}$, 1H), 6.91 (d, $J = 8.4 \text{ Hz}$, 1H), 2.37 (s, 3H) ppm.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3): $\delta = -82.36$ (s, 3F), -108.39 – 109.52 (m, 2F) ppm.

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): $\delta = 20.80$ ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 154.4$ (m), 146.5 (m), $139.9, 138.3, 133.5, 132.6, 132.6, 131.6$ (d, $J = 10.6 \text{ Hz}$), $131.5, 130.6, 128.6$ (d, $J = 12.9 \text{ Hz}$), $128.4, 126.8, 126.5$ (m), $120.5, 120.0, 12.7$ ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{29}\text{H}_{20}\text{ClF}_5\text{O}_2\text{P}$ [$\text{M}+\text{H}$] $^+$ 561.0804, found: 561.0809.



(7-Methyl-2-(perfluoroethyl)-6-(p-tolyl)benzofuran-3-yl)diphenylphosphine oxide (3ia):

Yield = 77% (125 mg). Yellow oil.

IR (KBr): $\nu = 3057, 2924, 1560, 1438, 1329, 1212, 1168, 1120, 1039, 935, 811, 727, 694 \text{ cm}^{-1}$.

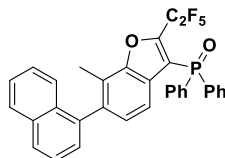
$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.74$ – 7.64 (m, 4H), 7.54 – 7.48 (m, 2H), 7.44 – 7.37 (m, 4H), 7.16 – 7.09 (m, 4H), 7.02 (dd, $J = 8.4, 1.3 \text{ Hz}$, 1H), 6.85 (d, $J = 8.3 \text{ Hz}$, 1H), 2.38 (s, 3H), 2.31 (s, 3H) ppm.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3): $\delta = -82.31$ – 82.40 (m, 3F), -108.68 (d, $J = 3.1 \text{ Hz}$, 2F) ppm.

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): $\delta = 20.79$ ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 154.5$ (d, $J = 10.6 \text{ Hz}$), 146.3 (m), $141.2, 137.1, 137.0, 132.7, 132.6$ (d, $J = 3.0 \text{ Hz}$), 131.7 (d, $J = 10.5 \text{ Hz}$), $129.2, 128.9, 128.7$ (d, $J = 12.9 \text{ Hz}$), $127.1, 126.0$ (d, $J = 7.8 \text{ Hz}$), $120.2, 119.9, 117.1$ (m), $21.1, 12.7$ ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{30}\text{H}_{23}\text{F}_5\text{O}_2\text{P}$ [$\text{M}+\text{H}$] $^+$ 541.1350, found: 541.1351.



(7-Methyl-6-(naphthalen-1-yl)-2-(perfluoroethyl)benzofuran-3-yl)diphenylphosphine oxide (3ja):

Yield = 44% (26 mg, 0.1 mmol scale). Yellow solid. M. p. 121.8–122.2 °C.

IR (KBr): $\nu = 3057, 1560, 1438, 1330, 1214, 1167, 1121, 1036, 932, 780, 725, 694, 552 \text{ cm}^{-1}$.

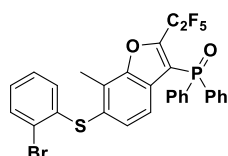
¹H NMR (400 MHz, CDCl₃): δ = 7.83 (t, J = 8.2 Hz, 2H), 7.78–7.68 (m, 4H), 7.55 (t, J = 7.4 Hz, 2H), 7.49–7.38 (m, 6H), 7.32 (d, J = 5.9 Hz, 2H), 7.23 (d, J = 7.0 Hz, 1H), 7.08–6.97 (m, 2H), 2.15 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -82.30 (s, 3F), -108.54 (s, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): δ = 20.87 ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 154.3 (d, J = 10.5 Hz), 146.0 (m), 139.8, 137.7, 133.5, 132.8 (d, J = 11.9 Hz), 132.6 (d, J = 2.5 Hz), 131.8, 131.7, 128.8 (d, J = 3.5 Hz), 128.7 (d, J = 3.8 Hz), 128.2 (d, J = 28.6 Hz), 127.7, 127.1, 126.6, 126.5, 126.1 (d, J = 33.6 Hz), 125.8, 125.2, 121.6, 120.3, 117.3 (m), 12.6 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₃H₂₃F₅O₂P [M+H]⁺ 577.1350, found: 577.1354.



6-((2-Bromophenyl)thio)-7-methyl-2-(perfluoroethyl)benzofuran-3-yl)diphenylphosphine oxide (3ka):

Yield = 34% (33 mg, 0.15 mmol scale). Yellow oil.

IR (KBr): ν = 2963, 1603, 1548, 1438, 1325, 1197, 1119, 1072, 979, 744, 725, 693, 575 cm⁻¹.

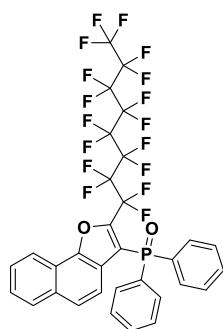
¹H NMR (400 MHz, CDCl₃): δ = 7.64–7.57 (m, 4H), 7.56–7.49 (m, 3H), 7.44–7.37 (m, 4H), 7.32 (d, J = 1.6 Hz, 1H), 7.18–7.13 (m, 1H), 7.08–7.02 (m, 3H), 2.30 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -81.71 (s, 3F), -104.47 (s, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): δ = 22.32 ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 155.3 (d, J = 11.8 Hz), 146.0 (m), 136.5 (d, J = 13.5 Hz), 134.7, 133.4, 133.1, 132.6 (d, J = 3.8 Hz), 132.1, 132.0, 130.6, 128.6, 128.5 (d, J = 13.2 Hz), 128.1, 126.7 (d, J = 7.4 Hz), 125.1, 118.6, 118.1 (m), 117.6, 112.1, 22.6 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₉H₂₀BrF₅O₂PS [M+H]⁺ 637.0020, found: 637.0018.



2-(Perfluorooctyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide (3ma):

Yield = 85% (201 mg). Yellow solid. M.p. 95.2–96.6 °C.

IR (KBr): ν = 3058, 1745, 1545, 1440, 1205, 1145, 992, 804, 725 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.34 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.84–7.73 (m, 4H), 7.69–7.56 (m, 5H), 7.54–7.45 (m, 4H), 7.35 (d, J = 8.9 Hz, 1H) ppm.

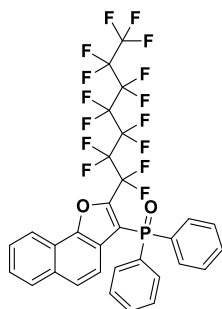
¹⁹F NMR (376 MHz, CDCl₃): δ = -80.74 (t, J = 9.8 Hz, 3F), -105.28 (t, J = 13.4 Hz, 2F), -119.89–120.43 (m, 2F), -121.44 (s, 2F), -121.65–122.16 (m, 4F), -122.66 (s, 2F), -125.94–126.36 (m,

2F) ppm.

³¹P NMR (162 MHz, CDCl₃): δ = 21.44 (m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 151.6 (d, J = 10.9 Hz), 145.0 (m), 132.8, 132.5, 132.5, 131.7 (d, J = 10.6 Hz), 128.7, 128.6, 128.2, 127.3 (d, J = 10.2 Hz), 125.5, 124.2 (d, J = 7.5 Hz), 120.5, 120.4, 120.3, 118.5 (d, J = 104.0 Hz) ppm; carbons corresponding to the C₈F₁₇ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₂H₁₇F₁₇O₂P [M+H]⁺ 787.0689, found: 787.0695.



(2-(Perfluoroheptyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide (3na):

Yield = 70% (155 mg). Yellow solid. M.p. 137.1–138.5 °C.

IR (KBr): ν = 3061, 1900, 1590, 1542, 1439, 1238, 1200, 1128, 1011, 874, 804, 701 cm⁻¹.

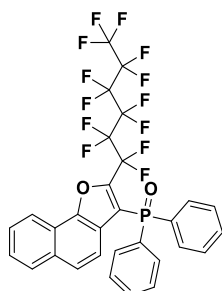
¹H NMR (400 MHz, CDCl₃): δ = 8.34 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.84 – 7.73 (m, 4H), 7.68 – 7.56 (m, 5H), 7.53 – 7.46 (m, 4H), 7.35 (d, J = 8.9 Hz, 1H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -80.73 (q, J = 10.0 Hz, 3F), -105.26 (t, J = 13.7 Hz, 2F), -119.90 – -120.34 (m, 2F), -121.47 (s, 2F), -121.92 (s, 2F), -122.65 (s, 2F), -125.89 – -126.21 (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): δ = 21.34 ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 151.6 (d, J = 11.1 Hz), 144.9 (m), 132.5, 132.5, 132.3 (d, J = 111.0 Hz), 131.8, 131.7, 128.6 (d, J = 12.8 Hz), 128.2, 127.3 (d, J = 10.1 Hz), 125.5, 124.2 (d, J = 7.6 Hz), 120.5, 120.4, 120.3, 118.5 (d, J = 104.6 Hz) ppm; carbons corresponding to the C₇F₁₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₁H₁₇F₁₅O₂P [M+H]⁺ 737.0721, found: 737.0729.



(2-(Perfluorohexyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide (3oa):

Yield = 85% (175 mg). Yellow solid. M.p. 163.4–164.2 °C.

IR (KBr): ν = 3058, 1899, 1542, 1439, 1237, 1200, 1120, 1068, 888, 804 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.34 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.84 – 7.74 (m, 4H), 7.68 – 7.55 (m, 5H), 7.54 – 7.45 (m, 4H), 7.33 (d, J = 8.9 Hz, 1H) ppm.

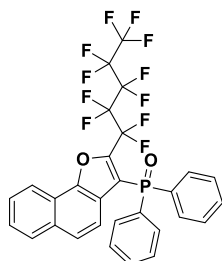
¹⁹F NMR (376 MHz, CDCl₃): δ = -80.74 (t, J = 10.0 Hz, 3F), -105.28 (t, J = 12.9 Hz, 2F), -119.90

-120.26 (m, 2F), -121.65 (s, 2F), -122.72 (s, 2F), -125.87 – -126.30 (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): δ = 21.37 ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 151.6 (m), 144.9 (m), 132.8, 132.5 (d, *J* = 3.2 Hz), 132.5, 131.8, 131.7, 128.6 (d, *J* = 13.0 Hz), 128.2, 127.3 (d, *J* = 10.0 Hz), 125.5, 124.2 (d, *J* = 7.9 Hz), 120.5, 120.4, 120.2, 118.5 (d, *J* = 104.5 Hz) ppm; carbons corresponding to the C₆F₁₃ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₀H₁₇F₁₃O₂P [M+H]⁺ 687.0753, found: 687.0765.



(2-(Perfluoropentyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide (3pa):

Yield = 66% (42 mg, 0.1 mmol scale). Yellow solid. M.p. 131.4–132.6 °C.

IR (KBr): ν = 3058, 1818, 1550, 1438, 1234, 1203, 1142, 1026, 790, 723 cm⁻¹.

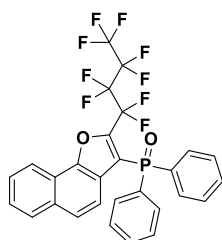
¹H NMR (400 MHz, CDCl₃): δ = 8.35 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.73 (m, 4H), 7.69 – 7.64 (m, 1H), 7.64 – 7.56 (m, 4H), 7.54 – 7.45 (m, 4H), 7.33 (d, *J* = 8.9 Hz, 1H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -80.06 – -81.14 (m, 3F), -104.48 – -106.25 (m, 2F), -119.38 – -120.83 (m, 2F), -121.64 – -123.11 (m, 2F), -125.31 – -127.02 (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): δ = 21.31 ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 151.6 (m), 145.0 (m), 132.8, 132.5 (d, *J* = 3.0 Hz), 131.8, 131.7, 128.7, 128.6, 128.2, 127.3 (d, *J* = 9.7 Hz), 125.5, 124.2 (d, *J* = 7.4 Hz), 120.5, 120.5, 120.3, 118.5 (m) ppm; carbons corresponding to the C₅F₁₁ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₉H₁₇F₁₁O₂P [M+H]⁺ 637.0785, found: 637.0793.



(2-(Perfluorobutyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide (3qa):

Yield = 59% (104 mg). Yellow solid. M.p. 98.9–99.5 °C.

IR (KBr): ν = 3057, 1592, 1542, 1438, 1244, 1198, 1135, 1072, 826, 700 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.34 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.74 (m, 4H), 7.68 – 7.56 (m, 5H), 7.53 – 7.46 (m, 4H), 7.32 (d, *J* = 8.9 Hz, 1H) ppm.

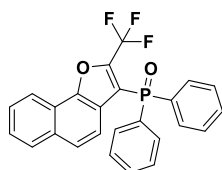
¹⁹F NMR (376 MHz, CDCl₃): δ = -80.85 (t, *J* = 10.2 Hz, 3F), -104.12 – -106.41 (m, 2F), -120.00 – -122.17 (m, 2F), -124.90 – -126.98 (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): δ = 21.34 ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 151.6 (m), 144.9 (m), 132.8, 132.5 (d, *J* = 3.1 Hz), 132.4, 131.8, 131.7, 128.6 (d, *J* = 13.0 Hz), 128.2, 127.3 (d, *J* = 9.9 Hz), 125.5, 124.2 (m), 120.5, 120.4, 120.2,

118.5 (d, $J = 104.5$ Hz) ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{17}F_9O_2P$ $[M+H]^+$ 587.0817, found: 587.0822.



Diphenyl(2-(trifluoromethyl)naphtho[1,2-*b*]furan-3-yl)phosphine oxide (3ra):

Yield = 45% (59 mg). White solid. M.p. 87.6–88.9 °C.

IR (KBr): $\nu = 3055, 1557, 1438, 1333, 1209, 1154, 1131, 997, 695, 571$ cm^{-1} .

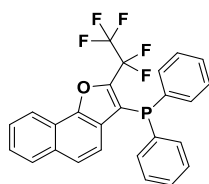
1H NMR (400 MHz, $CDCl_3$): $\delta = 8.39 - 8.33$ (m, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.83 – 7.75 (m, 4H), 7.67 – 7.57 (m, 5H), 7.54 – 7.48 (m, 4H), 7.20 (d, $J = 8.9$ Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -58.91$ (d, $J = 1.3$ Hz, 3F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 20.28$ ppm.

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.4$ (m), 146.2 (m), 132.6 (d, $J = 3.0$ Hz), 132.5, 131.9 (m), 131.7 (d, $J = 10.7$ Hz), 128.8 (d, $J = 12.30$ Hz), 128.3, 127.2 (d, $J = 6.3$ Hz), 125.6, 124.0 (d, $J = 7.6$ Hz), 120.6, 120.4, 119.9, 118.7 (q, $J = 269.1$ Hz), 115.6 (m) ppm.

HRMS (m/z): calcd for $C_{25}H_{17}F_3O_2P$ $[M+H]^+$ 437.0913, found: 437.0923.



(2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphane (4a):

Yield = 77% (109 mg, from **3aa**). White solid. M.p. 104.1–105.8 °C.

IR (KBr): $\nu = 3057, 1960, 1816, 1546, 1435, 1334, 1225, 1197, 1127, 930, 744, 697$ cm^{-1} .

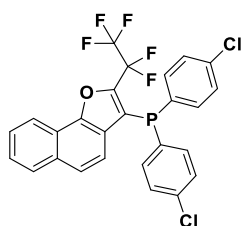
1H NMR (400 MHz, $CDCl_3$): $\delta = 8.34$ (d, $J = 8.2$ Hz, 1H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.63 – 7.56 (m, 1H), 7.55 – 7.49 (m, 1H), 7.46 – 7.37 (m, 5H), 7.35 – 7.29 (m, 6H), 6.74 (d, $J = 8.8$ Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -83.26 - -83.37$ (m, 3F), $-119.71 - -120.25$ (m, 2F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -30.40$ ppm.

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.1$ (m), 146.4 (m), 135.0 (m), 133.9 (d, $J = 16.8$ Hz), 132.6 (d, $J = 19.4$ Hz), 132.2, 128.9, 128.7, 128.7, 128.1, 126.9 (d, $J = 9.2$ Hz), 124.8 (m), 124.5, 121.1, 120.4, 119.9 (d, $J = 30.9$ Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{17}F_5OP$ $[M+H]^+$ 471.0932, found: 471.0940.



Bis(4-chlorophenyl)(2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)phosphane (4b):

Yield = 92% (149 mg, from **3ab**). White solid. M.p. 121.2–122.1 °C.

IR (KBr): $\nu = 3059, 2924, 1903, 1575, 1480, 1315, 1221, 1206, 1128, 1013, 806, 741 \text{ cm}^{-1}$.

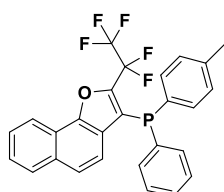
¹H NMR (400 MHz, CDCl₃): $\delta = 8.38 - 8.32$ (m, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.66 – 7.60 (m, 1H), 7.59 – 7.53 (m, 1H), 7.47 (d, $J = 8.8$ Hz, 1H), 7.36 – 7.29 (m, 8H), 6.76 (d, $J = 8.8$ Hz, 1H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.50 - -84.10$ (m, 3F), $-108.67 - -116.57$ (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = -31.54$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 152.2$ (m), 146.5 (m), 135.5 (m), 133.9, 133.7, 133.1 (m), 132.3, 129.1 (d, $J = 6.7$ Hz), 128.2, 127.2 (d, $J = 8.7$ Hz), 125.0, 124.2 (m), 121.1, 120.5, 119.8, 118.7 (d, $J = 30.0$ Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₆H₁₅Cl₂F₅OP [M+H]⁺ 539.0152, found: 539.0161.

**(2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)(phenyl)(*p*-tolyl)phosphane (4c):**

Yield = 78% (113 mg, from **3ak**). White solid. M.p. 101.4–102.7 °C.

IR (KBr): $\nu = 3017, 2925, 1435, 1314, 1216, 1205, 1130, 931, 808, 696 \text{ cm}^{-1}$.

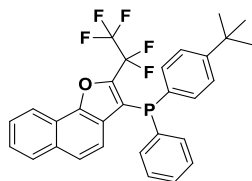
¹H NMR (400 MHz, CDCl₃): $\delta = 8.36 - 8.29$ (m, 1H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.62 – 7.57 (m, 1H), 7.55 – 7.49 (m, 1H), 7.43 – 7.37 (m, 3H), 7.36 – 7.29 (m, 5H), 7.17 – 7.11 (m, 2H), 6.77 (d, $J = 8.8$ Hz, 1H), 2.33 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.75 - -83.80$ (m, 3F), $-109.18 - -110.88$ (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = -30.96$ ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 152.1$ (m), 146.1 (m), 139.1, 135.5 (m), 132.9 (d, $J = 20.1$ Hz), 132.4 (d, $J = 19.0$ Hz), 132.2, 131.1 (m), 129.6 (d, $J = 7.1$ Hz), 128.7, 128.6, 128.1, 126.9 (d, $J = 9.6$ Hz), 124.8 (m), 124.5, 121.1, 120.5, 120.5, 120.3, 120.0, 21.3 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₇H₁₉F₅OP [M+H]⁺ 485.1088, found: 485.1095.

**(4-(*tert*-Butyl)phenyl)(2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)(phenyl)phosphane (4d):**

Yield = 72% (114 mg, from **3al**). White solid. M.p. 168.2–169.8 °C.

IR (KBr): $\nu = 3061, 2962, 2868, 1595, 1552, 1436, 1317, 1214, 1133, 1029, 814, 745 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.37 - 8.30$ (m, 1H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.62 – 7.56 (m, 1H), 7.54 – 7.48 (m, 1H), 7.42 – 7.29 (m, 10H), 6.76 (d, $J = 8.8$ Hz, 1H), 1.29 (s, 9H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -82.70 - -83.90$ (m, 3F), $-108.99 - -111.00$ (m, 2F) ppm.

³¹P NMR (162 MHz, CDCl₃): $\delta = -31.37$ ppm.

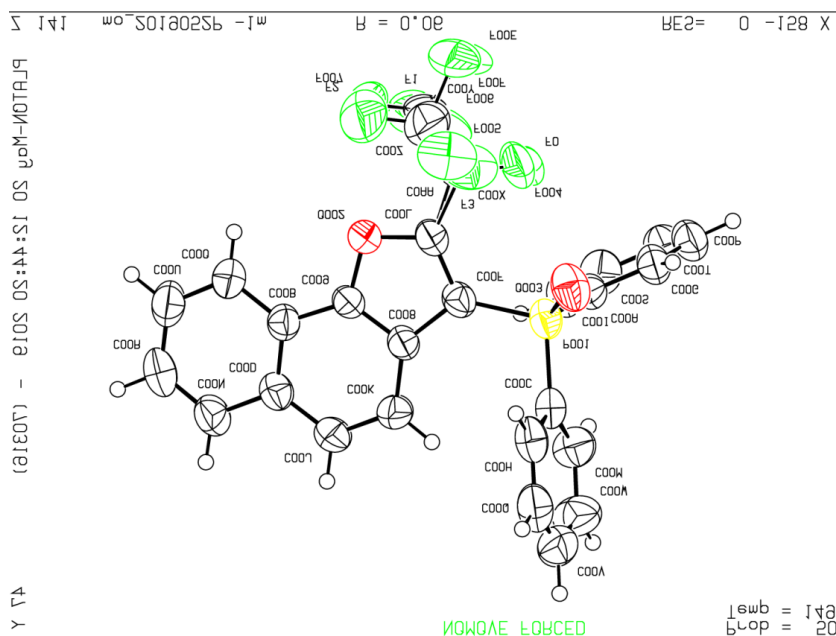
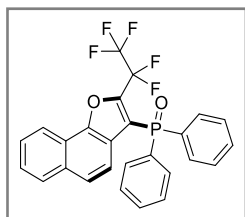
¹³C NMR (100 MHz, CDCl₃): δ = 152.2, 152.1 (m), 146.4 (m), 135.6 (m), 132.7 (d, J = 20.0 Hz), 132.4 (d, J = 18.9 Hz), 132.2, 131.0 (m), 128.6 (d, J = 6.3 Hz), 128.6, 128.1, 126.8 (d, J = 9.3 Hz), 125.8 (d, J = 7.0 Hz), 124.9 (m), 124.4, 121.1, 120.6, 120.5, 120.4, 120.1, 34.7, 31.2 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₀H₂₅F₅OP [M+H]⁺ 527.1558, found: 527.1557.

7. References

- [1] (a) P. V. Pham, D. A. Nagib, D. W. C. MacMillan, *Angew. Chem. Int. Ed.* **2011**, *50*, 6119–6122. (b) X. Su, H. Huang, Y. Yuan, Y. Li, *Angew. Chem., Int. Ed.* **2017**, *56*, 1338–1341.
- [2] (a) T. Xie, Y.-W. Zhang, L.-L. Liu, Z.-L. Shen, T.-P. Loh, X.-Q. Chu, *Chem. Commun.* **2018**, *54*, 12722–12725. (b) T. Xie, G.-Q. Wang, Y.-W. Wang, W. Rao, H. Xu, S. Li, Z.-L. Shen, X.-Q. Chu, *iScience* **2020**, *23*, 101259.
- [3] T. Liu, Y. Li, F. Cheng, X. Shen, J. Liu, J. Lin, *Green Chem.* **2019**, *21*, 3536–3541.

8. The X-ray crystal structure of product 3aa



(2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)diphenylphosphine oxide

Crystal Number: CCDC 1917241

Cell: a=10.260(5) b=10.582(5) c=11.990(6)

Chemical Formula: C₂₆H₁₆F₅O₂P

alpha=75.682(13)

beta=76.268(12)

Formula weight: 486.3778

gamma=62.415(12)

Space Group: P -1

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

