

Supporting Information

Palladium-Catalyzed Defluorinative Alkynylation of Polyfluoroalkyl Ketones with Alkynes for the Synthesis of Fluorinated Fused Furans

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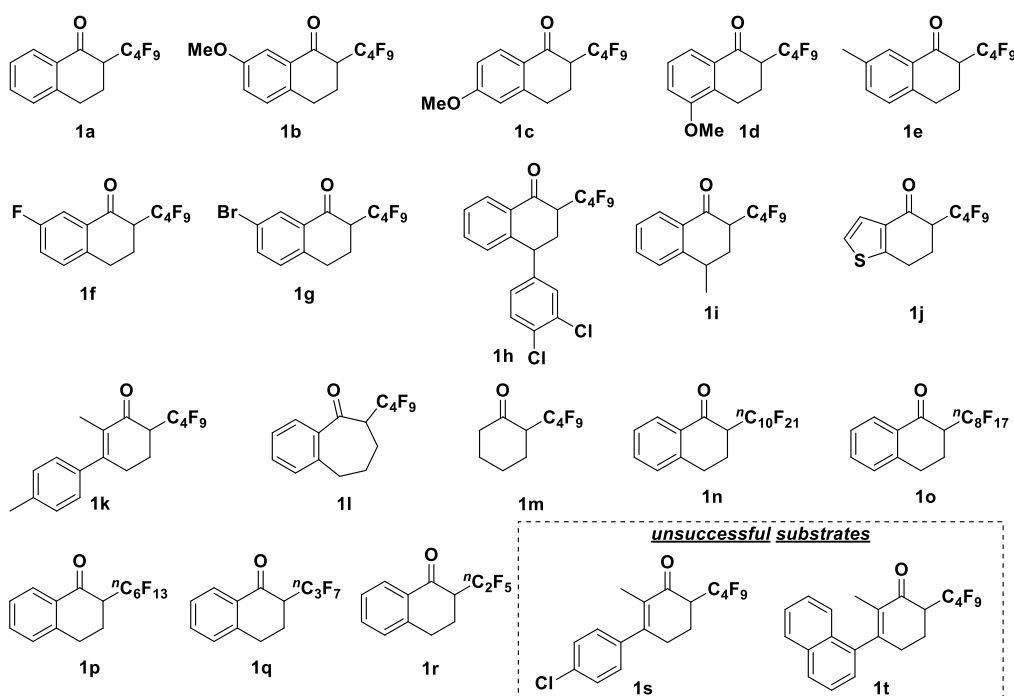
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1. General information

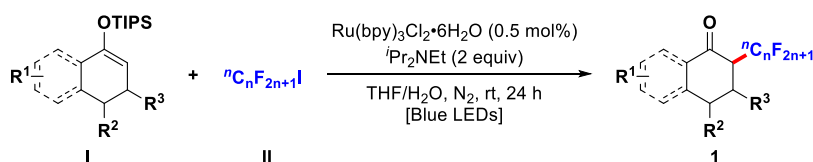
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under N₂ atmosphere using undistilled solvent. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ¹H, ¹⁹F, 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 Source). 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 procedures for the synthesis of α -perfluoroalkyl ketones

Various α -perfluoroalkyl ketones:



General procedure A^[1]



According to MacMillan's reported method, a solution of enilsilane **I** (1.2 mmol), Ru(bpy)₃Cl₂·6H₂O (4.5 mg, 0.006 mmol, 0.5 mol%), *N*-ethyl-*N*-isopropylpropan-2-amine (424.0 μ L, 2.4 mmol), perfluoroalkyl iodide **II** (12 mmol), H₂O (32.0 μ L, 17.8 mmol) in THF (6.0 mL) was stirred under nitrogen atmosphere (by 3 times' vacuum evacuation/N₂ backfill cycles) by irradiation with 8 W Blue LEDs at room temperature for 24 h. Upon completion of the reaction (indicated by TLC), solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (1:500) as eluent to afford the α -perfluoroalkyl ketone **1**.

Representative examples:

2-(Perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (1a)^[1]

¹H NMR (400 MHz, CDCl₃): δ = 8.08 – 8.01 (m, 1H), 7.57 – 7.49 (m, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.28 (s, 1H), 3.49 – 3.35 (m, 1H), 3.23 – 3.15 (m, 1H), 3.08 – 2.98 (m, 1H), 2.55 – 2.36 (m, 2H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -80.45 – -81.25 (m, 3F), -108.96 – -113.38 (m, 2F), -118.78 – -121.94 (m, 2F), -125.80 – -126.50 (m, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 190.3 (m), 142.9, 134.2, 132.3 (m), 128.7, 127.9, 127.0, 49.3 (t, J = 20.3 Hz), 27.1, 22.9 (m) ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

2,4'-Dimethyl-4-(perfluorobutyl)-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (1k)

¹H NMR (400 MHz, CDCl₃): δ = 7.25 – 7.20 (m, 2H), 7.13 – 7.08 (m, 2H), 3.36 – 3.22 (m, 1H), 2.87 – 2.75 (m, 1H), 2.72 – 2.60 (m, 1H), 2.38 (s, 3H), 1.77 (t, J = 1.9 Hz, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -80.77 (t, J = 9.8 Hz, 3F), -109.70 – -114.25 (m, 2F), -119.29 – -122.06 (m, 2F), -125.98 (t, J = 15.4 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 191.7 (t, J = 1.4 Hz), 156.6, 138.4, 137.3, 132.1, 129.1, 127.0, 47.6 (t, J = 20.2 Hz), 30.7, 22.0 (m), 21.2, 13.3 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

4'-Chloro-2-methyl-4-(perfluorobutyl)-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (1s)

¹H NMR (400 MHz, CDCl₃): δ = 7.34 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 3.35 – 3.20 (m, 1H), 2.83 – 2.71 (m, 1H), 2.70 – 2.58 (m, 1H), 2.46 – 2.29 (m, 2H), 1.79 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -80.80 – -80.92 (m, 3F), -110.28 – -114.09 (m, 2F), -119.53 – -121.96 (m, 2F), -125.96 – -126.14 (m, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 191.2, 154.9, 138.6, 134.2, 132.4, 128.6, 128.4, 47.6 (t, J = 20.6 Hz), 30.4, 21.8, 12.9 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

2-Methyl-3-(naphthalen-1-yl)-6-(perfluorobutyl)cyclohex-2-en-1-one (1t)

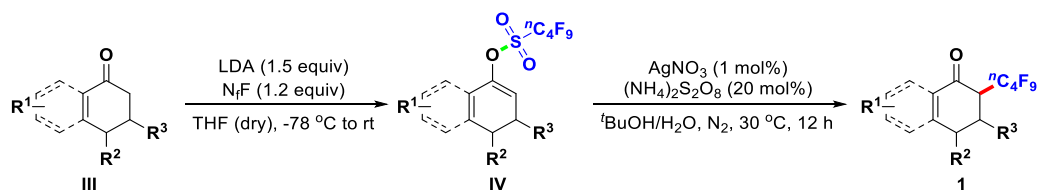
¹H NMR (400 MHz, CDCl₃): δ = 7.93 – 7.86 (m, 1H), 7.83 (d, J = 8.3 Hz, 1H), 7.69 – 7.56 (m, 1H), 7.54 – 7.46 (m, 3H), 7.24 – 7.18 (m, 1H), 3.55 – 3.31 (m, 1H), 2.96 – 2.78 (m, 1H), 2.78 – 2.58 (m, 1H), 2.50 (d, J = 5.4 Hz, 2H), 1.56 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -80.80 (s, 3F), -109.50 – -113.97 (m, 2F), -119.36 – -122.12 (m, 2F), -125.92 (t, J = 12.4 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 191.3 (m), 156.2 (d, J = 18.6 Hz), 138.1 (d, J = 5.1 Hz), 134.2 (d, J = 9.4 Hz), 133.6, 129.1 (d, J = 9.3 Hz), 128.7 (d, J = 9.2 Hz), 128.2 (d, J = 7.5 Hz), 126.8 (d, J = 16.2 Hz), 126.2 (d, J = 5.1 Hz), 125.4 (d, J = 11.6 Hz), 124.3 (d, J = 4.8 Hz), 123.6 (d, J = 3.6 Hz), 47.7 (q, J = 20.0 Hz), 31.1 (d, J = 23.2 Hz), 22.3 (m), 12.9 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

5-(Perfluorobutyl)-6,7-dihydrobenzo[*b*]thiophen-4(5H)-one (**1j**), 2-(perfluorodecyl)-3,4-dihydronaphthalen-1(2H)-one (**1n**), 2-(perfluorooctyl)-3,4-dihydronaphthalen-1(2H)-one (**1o**), 2-(perfluorohexyl)-3,4-dihydronaphthalen-1(2H)-one (**1p**), and 2-(perfluoroethyl)-3,4-dihydronaphthalen-1(2H)-one (**1r**) were synthesized according to general procedure A.

General procedure B^[2]



Step 1: The solution of ketone **III** (5 mmol) in dry THF (25 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and then lithium diisopropylamide (LDA, 3.75 mL, 7.5 mmol, 2.0 mol/L in THF/hexane) was dropwise added to the reaction mixture. Nonfluorobutanesulfonyl fluoride (1.1 mL, 6 mmol) was added slowly by a syringe over 10 min. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) on Et_3N -treated silica gel eluting with petroleum ether to afford enol nonaflate **IV**.

Step 2: A solution of enol nonaflate **IV** (0.8 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.16 mmol, 37 mg), and AgNO_3 (0.008 mmol, 1.4 mg) in $t\text{BuOH}$ (2.0 mL) and H_2O (2.0 mL) was stirred vigorously under nitrogen atmosphere (by 3 times' vacuum evacuation/ N_2 backfill cycles) at $30\text{ }^{\circ}\text{C}$ for 12 h. Upon completion of the reaction (indicated by TLC), the reaction mixture was extracted with dichloromethane. The organic layer was separated and the aqueous layer was washed with dichloromethane (3×10 mL). The combined organic layers were dried over Na_2SO_4 . The solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate as eluent to afford α -perfluoroalkyl ketone **1**.

Representative examples:

7-Methoxy-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1b**)

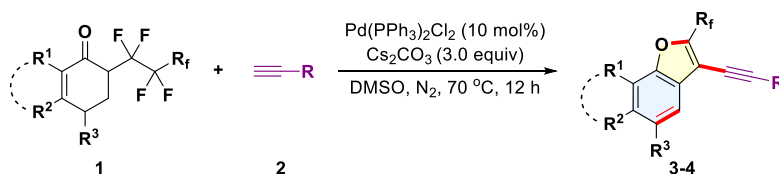
^1H NMR (400 MHz, CDCl_3): δ = 8.02 (d, J = 8.8 Hz, 1H), 6.86 (dd, J = 8.8, 2.5 Hz, 1H), 6.70 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 3.44 – 3.30 (m, 1H), 3.20 – 3.10 (m, 1H), 3.00 – 2.91 (m, 1H), 2.50 – 2.34 (m, 2H) ppm.

^{19}F NMR (376 MHz, CDCl_3): δ = -80.45 – -81.24 (m, 3F), -108.98 – -113.48 (m, 2F), -118.81 – -121.88 (m, 2F), -125.99 – -126.55 (m, 2F) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 188.8 (m), 164.1, 145.5, 130.3, 125.8, 113.7, 112.3, 55.4, 48.9 (t, J = 20.4 Hz), 27.3, 23.0 ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

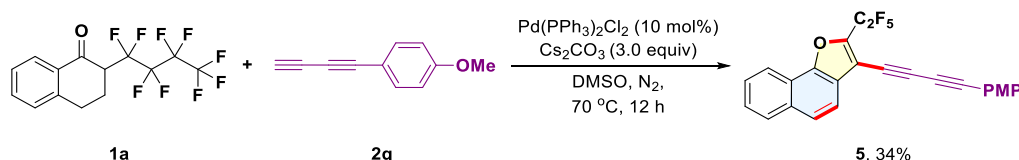
6-Methoxy-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1c**), 5-methoxy-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1d**), 7-methyl-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1e**), 7-fluoro-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1f**), 7-bromo-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1g**), 4-(3,4-dichlorophenyl)-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1h**), 4-methyl-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1i**), 6-(perfluorobutyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (**1j**), 2-(perfluorobutyl)cyclohexan-1-one (**1m**), and 2-(perfluoropropyl)-3,4-dihydronaphthalen-1(2H)-one (**1r**) were synthesized according to general procedure B.

3. General procedures for the synthesis of naphtho[1,2-*b*]furan derivatives



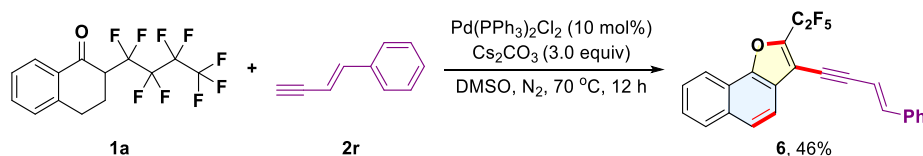
A solution of fluoroalkyl ketones **1** (0.3 mmol), alkyne **2** (0.45 mmol), Pd(PPh₃)₂Cl₂ (21 mg, 0.03 mmol), and Cs₂CO₃ (293 mg, 0.9 mmol) in DMSO (3.0 mL) was stirred under N₂ atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH₄Cl solution (20 mL) and extracted with EtOAc (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 (500/1 ~ 50/1) as eluent to afford the pure products **3-4**.

4. General procedure for the reaction of α -perfluorobutyl tetralone (1a) with 1-(buta-1,3-diy-1-yl)-4-methoxybenzene (2q)



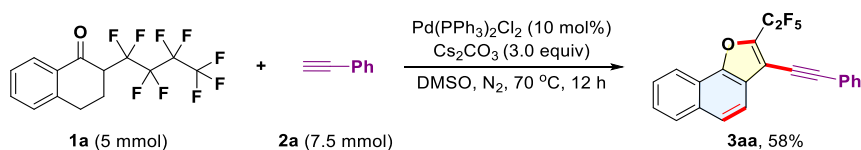
A solution of α -perfluorobutyl tetralone (**1a**, 73 mg, 0.2 mmol), 1-(buta-1,3-diy-1-yl)-4-methoxybenzene (**2q**, 47 mg, 0.3 mmol), Pd(PPh₃)₂Cl₂ (14 mg, 0.02 mmol), and Cs₂CO₃ (196 mg, 0.6 mmol) in DMSO (2.0 mL) was stirred under N₂ atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated 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 (500/1 ~ 100/1) as eluent to afford the pure product **5** (30 mg, 34% yield).

5. General procedure for the reaction of α -perfluorobutyl tetralone (1a) with (*E*)-but-1-en-3-yn-1-ylbenzene (2r)



A solution of α -perfluorobutyl tetralone (**1a**, 73 mg, 0.2 mmol), (*E*)-but-1-en-3-yn-1-ylbenzene (**2r**, 39 mg, 0.3 mmol), Pd(PPh₃)₂Cl₂ (14 mg, 0.02 mmol), and Cs₂CO₃ (196 mg, 0.6 mmol) in DMSO (2.0 mL) was stirred under N₂ 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 (500/1) as eluent to afford the pure product **6** (38 mg, 46% yield).

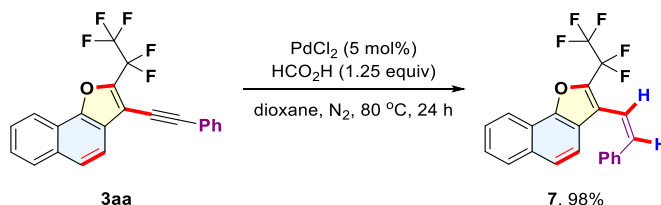
6. Large-scale synthesis of product 3aa



A solution of α -perfluorobutyl tetralone (**1a**, 1821 mg, 5 mmol), ethynylbenzene (**2a**, 766 mg, 7.5 mmol), Pd(PPh₃)₂Cl₂ (351 mg, 0.5 mmol), and Cs₂CO₃ (4887 mg, 15 mmol) in DMSO (50 mL) was stirred under N₂ atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH₄Cl solution (100 mL) and extracted with EtOAc (50 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 (500/1 ~ 200/1) as eluent to afford the pure product **3aa** (1130 mg, 58% yield).

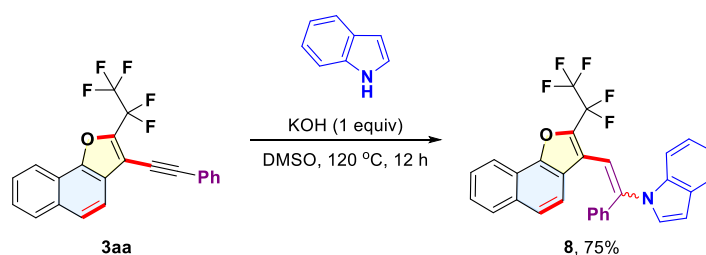
7. Further applications for the synthesis of complex molecules

1) Reduction reaction of product 3aa



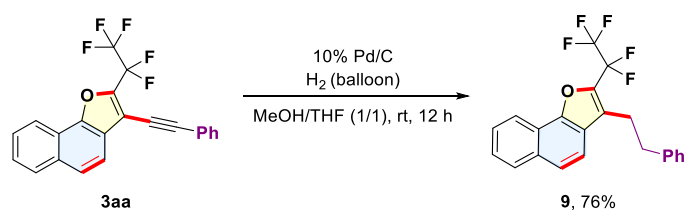
A solution of **3aa** (77 mg, 0.2 mmol), PdCl₂ (2 mg, 0.01 mmol), and HCO₂H (12 mg, 0.25 mmol) in 1,4-dioxane (2 mL) was stirred under N₂ atmosphere at 80 °C for 24 h. The reaction was then quenched by saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed 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 (500/1) as eluent to afford the pure product **7** (66 mg, 98% yield).

2) Hydroamination reaction of product 3aa with indole



A solution of **3aa** (77 mg, 0.2 mmol), indole (47 mg, 0.4 mmol), and KOH (56 mg, 0.2 mmol) in DMSO (1 mL) was stirred under N₂ atmosphere at 120 °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 (500/1 ~ 200/1) as eluent to afford the pure product **8** (58 mg, 75% yield).

3) Reduction reaction of product **3aa**



A solution of **3aa** (77 mg, 0.02 mmol) and 10% Pd/C (21 mg) in MeOH/THF (1 mL/1 mL) was stirred under H₂ atmosphere at room temperature for 12 h. The mixture was filtered through celite pad, and washed with EtOAc (10 ml x 3). The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (500/1) as eluent to afford the pure product **9** (60 mg, 76% yield).

4) Iodocyclization reaction of product **3ag**



A solution of **3ag** (42 mg, 0.1 mmol), InCl₃ (22 mg, 0.1 mmol), and I₂ (51 mg, 0.2 mmol) in DCM (3 mL) was stirred under N₂ atmosphere at 40 °C for 24 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 (200/1) as eluent to afford the pure product **10** (52 mg, 99% yield).

8. Optimization of reaction conditions

Table S1. Optimization of the reaction solvent^a

$\text{1a} + \text{2a} \xrightarrow[\text{solvent, N}_2, 70\text{ }^\circ\text{C, 12 h}]{\text{Pd(PPh}_3)_2\text{Cl}_2 (10\text{ mol\%}), \text{Cs}_2\text{CO}_3 (3.0\text{ equiv})}$

Entry	Solvent	Yield of 3aa (%) ^b
1	DMSO	58 (55) ^c
2	DMF	36
3	MeCN	14
4	CHCl ₃	trace
5	1,4-dioxane	trace
6	toluene	trace
7	DCE	trace
8	^t BuOAc	<5
9	^t BuOH	<5

^a Reaction conditions: 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1a**, 0.30 mmol), phenylacetylene (**2a**, 0.45 mmol), Pd(PPh₃)₂Cl₂ (0.03 mmol), and Cs₂CO₃ (0.90 mmol) in solvent (2.0 mL) at 70 °C for 12 h under N₂. ^b Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard. ^c Isolated yield.

Table S2. Optimization of the reaction temperature^a

$\text{1a} + \text{2a} \xrightarrow[\text{DMSO, N}_2, \text{Temp., 12 h}]{\text{Pd(PPh}_3)_2\text{Cl}_2 (10\text{ mol\%}), \text{Cs}_2\text{CO}_3 (3.0\text{ equiv})}$

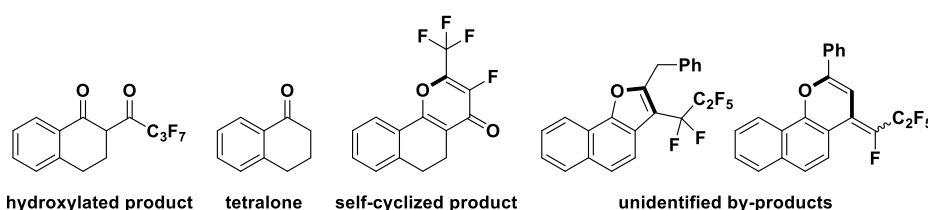
Entry	Temperature (°C)	Yield of 3aa (%) ^b
1	rt	34
2	50	52
3	70	58 (55) ^c
4	90	56

^a Reaction conditions: 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1a**, 0.30 mmol), phenylacetylene (**2a**, 0.45 mmol), Pd(PPh₃)₂Cl₂ (0.03 mmol), and Cs₂CO₃ (0.90 mmol) in DMSO (2.0 mL) at rt-90 °C for 12 h under N₂. ^b Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard. ^c Isolated yield.

21	Pd(PPh ₃) ₂ Cl ₂ (10)/Antioxidant 168 (20)	24 ^d
22	Pd(PPh ₃) ₂ Cl ₂ (10)/CuI (10)	49 ^d
23	Pd(PPh ₃) ₂ Cl ₂ (10)/CoBr ₂ (10)	54 ^d
24	Pd(PPh ₃) ₂ Cl ₂ (10)/ZnBr ₂ (10)	27 ^d
25	Pd(PPh ₃) ₂ Cl ₂ (10)/NaI (10)	52 ^d
26	Pd(PPh ₃) ₂ Cl ₂ (10)/TBAB (100)	trace
27	Pd(PPh₃)₂Cl₂ (10)	62 (58)^{c,d,e}

^a Reaction conditions: 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**, 0.3 mmol), phenylacetylene (**2a**, 0.36 mmol), catalyst (0.015-0.03 mmol), ligand (0-0.06 mmol), and Cs₂CO₃ (0.90 mmol) in DMSO (2.0 mL) at 70 °C for 12 h under N₂. ^b Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard.

^c Isolated yield. ^d 0.45 mmol of **2a** was used. ^e In 3.0 mL of DMSO.



Notice: Moderate yield of the model reaction was obtained under the optimal reaction conditions because the starting material of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**) is unstable under the palladium catalytic system. 2-(2,2,3,3,4,4,4-Heptafluorobutanoyl)-3,4-dihydronaphthalen-1(2*H*)-one (via hydrodefluorination of **1a**), tetralone (via C-C bond cleavage of **1a**), 3-fluoro-2-(trifluoromethyl)-5,6-dihydro-4*H*-benzo[*h*]chromen-4-one (via self-cyclization), and some unidentified by-products were observed.

Table S5. Optimization of the base^a

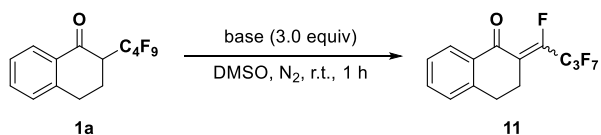


Entry	Base	Yield of 3aa (%) ^b
1	K ₂ CO ₃	24
2	DABCO	48
3	DBU	<5
4	Et ₃ N	30
5	NaOH	trace
6	CsF	58
7	^t BuOK	18

^a Reaction conditions: 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**, 0.3 mmol), phenylacetylene (**2a**, 0.45 mmol), Pd(PPh₃)₂Cl₂ (0.03 mmol), and base (0.90 mmol) in DMSO (3.0 mL) at 70 °C for 12 h under N₂. ^b Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard.

9. Mechanistic studies

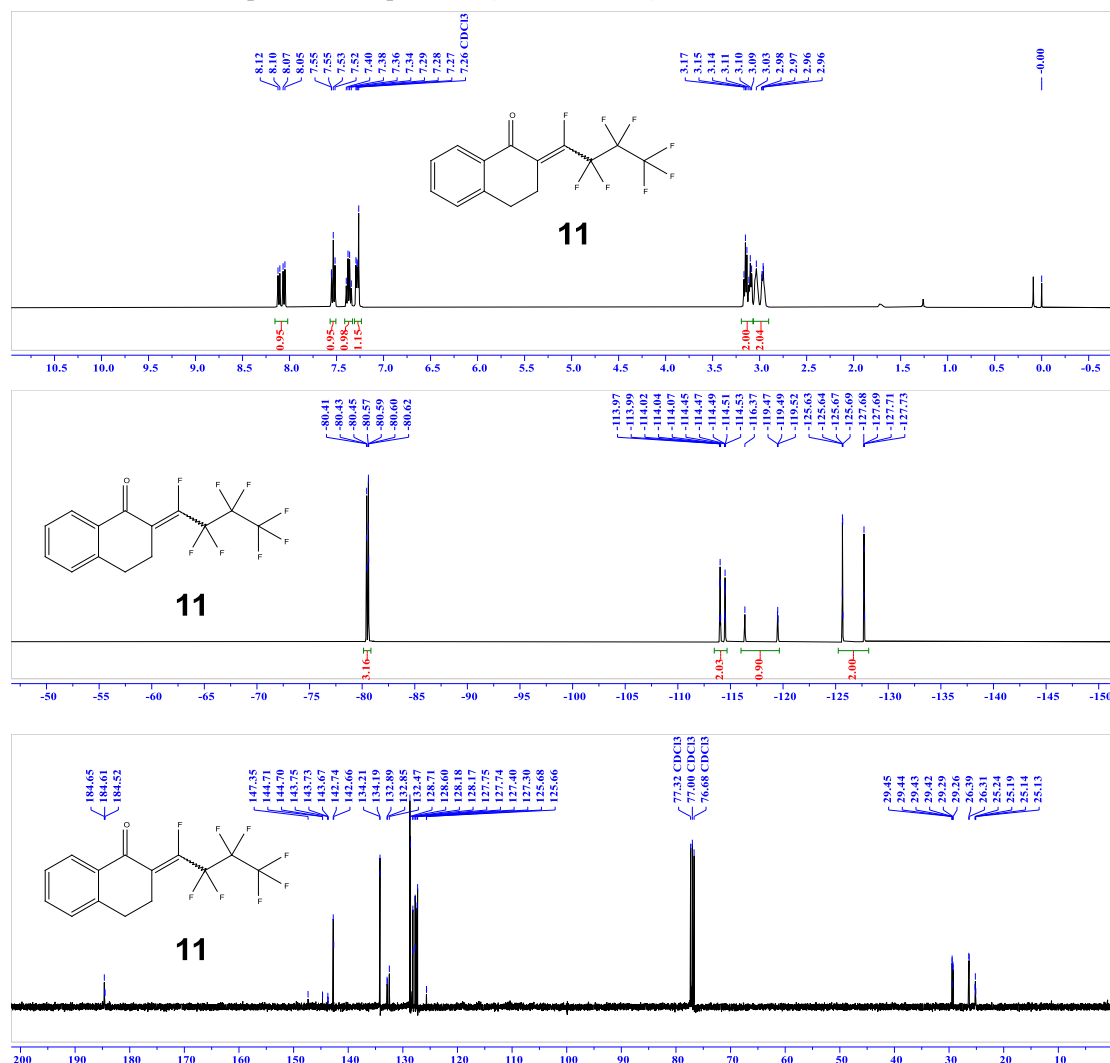
1) Detection of the key intermediate 2-(1,4,4,4,4,4-octafluoro-4 λ^8 -but-2-yn-1-ylidene)-3,4-dihydronaphthalen-1(2H)-one (**11**)



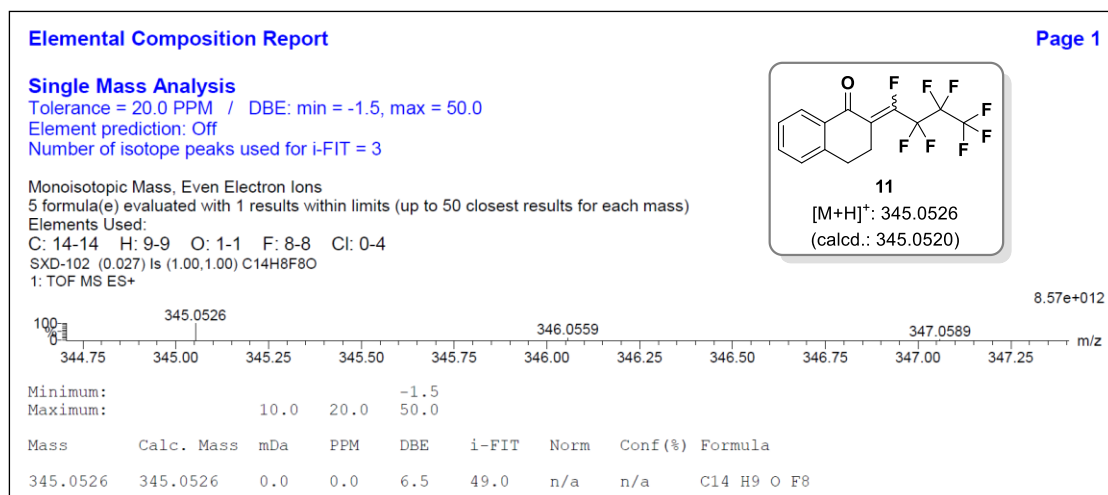
1a		base		11	
base	yield	base	yield	base	yield
Cs ₂ CO ₃	82% (Z/E = 1/1)	Et ₃ N	95% (Z/E = 1/3)	NaOH	51% (Z/E = 1/2.6)
DABCO	0%	^t BuOK	37% (Z/E = 1/2.5)	KHCO ₃	92% (Z/E = 1/1.2)

A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1a**, 73 mg, 0.2 mmol) and base (0.6 mmol) in DMSO (2.0 mL) was stirred under N₂ atmosphere at room temperature for 1 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 (500/1) as eluent to afford the pure 2-(1,4,4,4,4,4-octafluoro-4 λ^8 -but-2-yn-1-ylidene)-3,4-dihydronaphthalen-1(2H)-one (**11**, 0~95% yield, Z/E = 1/1 ~ 1/3). This result suggested that compound **11** was the possible reaction intermediate.

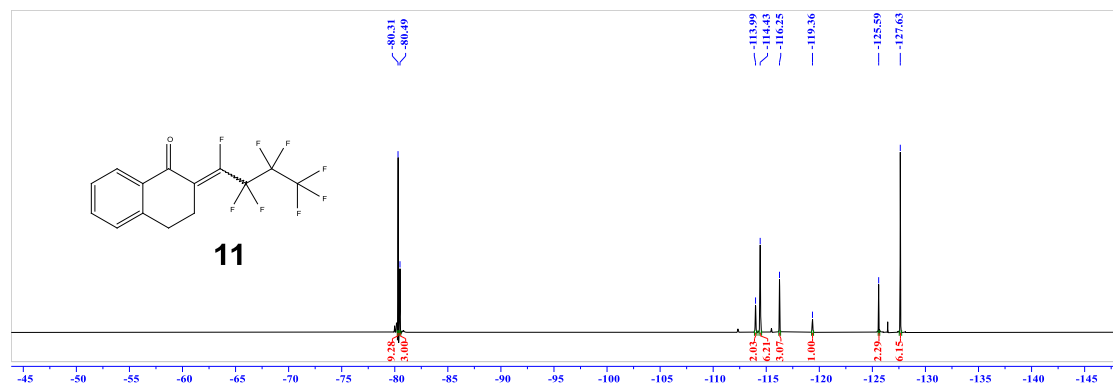
¹H, ¹⁹F, and ¹³C NMR spectra of compound **11** (Cs₂CO₃ as base):



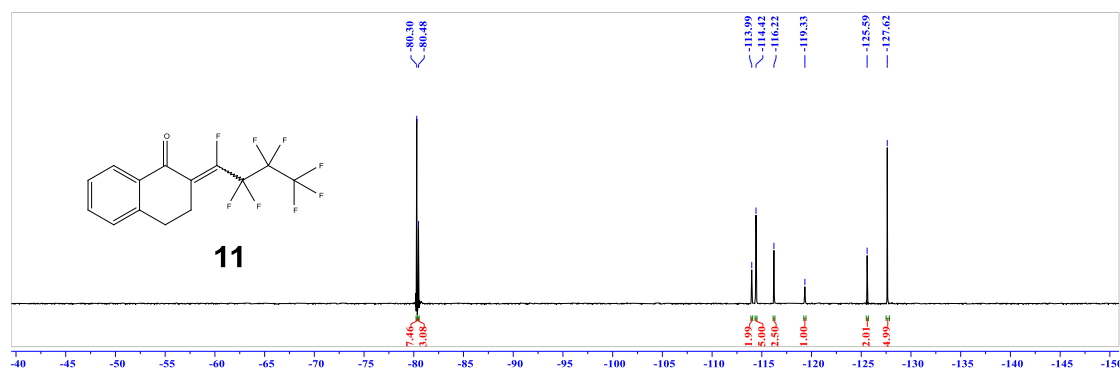
HRMS of compound 11:



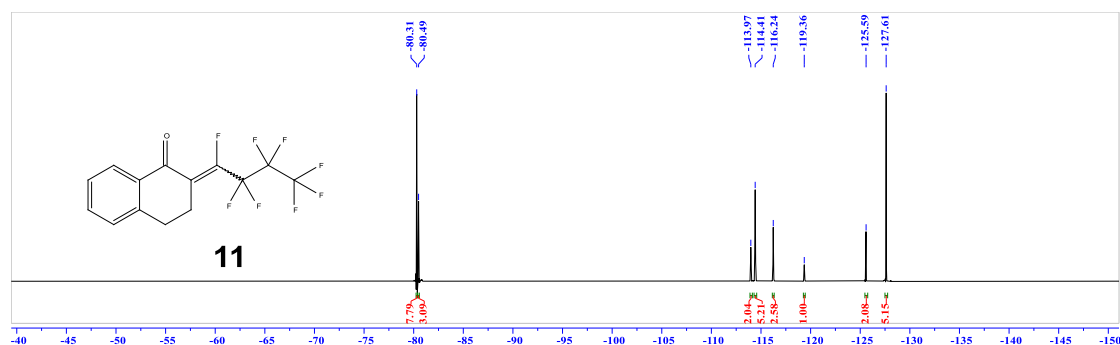
¹⁹F NMR spectra of compound 11 (Et₃N as base):



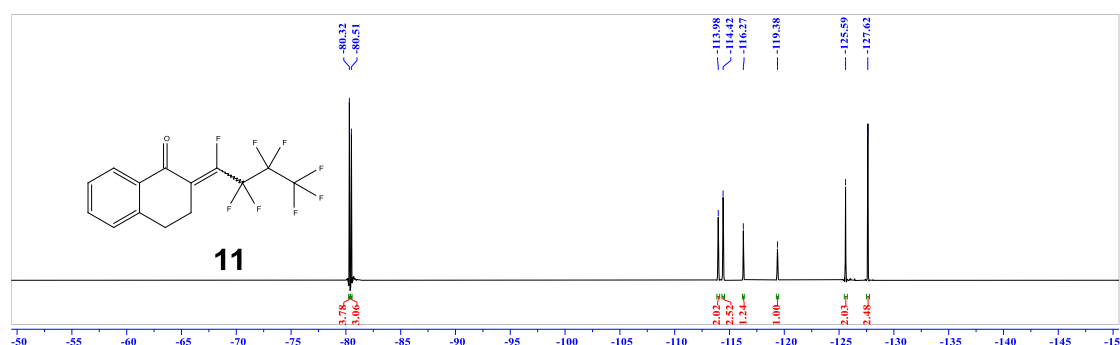
¹⁹F NMR spectra of compound 11 (tBuOK as base):



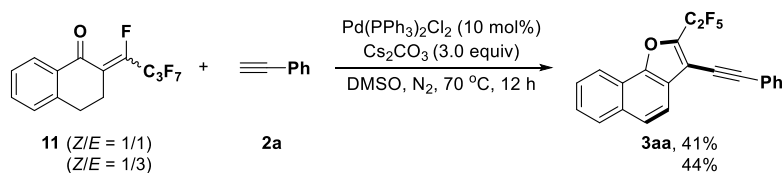
¹⁹F NMR spectra of compound **11** (NaOH as base):



¹⁹F spectra of compound **11** (KHCO₃ as base):

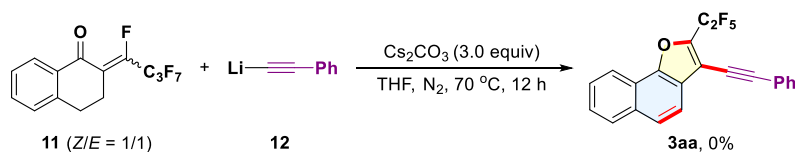


2) The reaction of compound **11** with ethynylbenzene (**2a**)



A solution of compound **11** (52 mg, 0.15 mmol), phenylacetylene (**2a**, 23 mg, 0.225 mmol), Pd(PPh₃)₂Cl₂ (11 mg, 0.015 mmol), and Cs₂CO₃ (147 mg, 0.45 mmol) in DMSO (2.0 mL) was stirred under N₂ 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 (200/1) as eluent to afford the pure product **3aa**. **This result further suggested that compound **11** was the possible reaction intermediate.**

3) The reaction of compound **11** with (phenylethynyl)lithium (**12**)

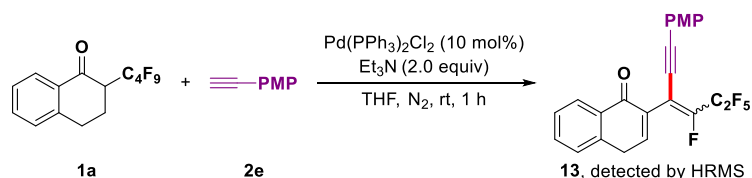


Step I: A solution of phenylacetylene (**2a**, 31 mg, 0.3 mmol) in dry THF (2 mL) was cooled to -78 °C and then *n*-butyllithium (*n*BuLi, 0.15 mL, 0.36 mmol, 2.5 mol/L in THF) was dropwise added to the reaction mixture over 1 h. After removal of the solvent of above reaction mixture, the formed crude (phenylethynyl)lithium (**12**) was directly

used in the next step without further purification.

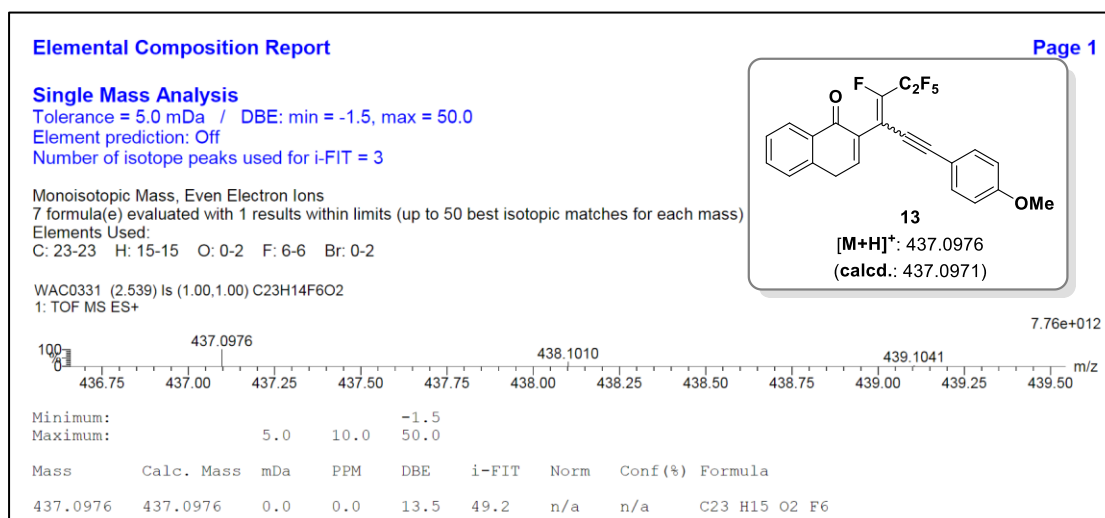
Step 2: A solution of compound **11** (69 mg, 0.2 mmol), (phenylethynyl)lithium (**12**), and Cs₂CO₃ (196 mg, 0.6 mmol) in THF (2.0 mL) was stirred under N₂ atmosphere at 70 °C for 12 h. No desired product **3aa** was obtained. **This result suggested that nucleophilic addition-elimination was not the main pathway for the intermolecular coupling.**

4) Detection of proposed endocyclic naphthalen-1(4H)-one **13**

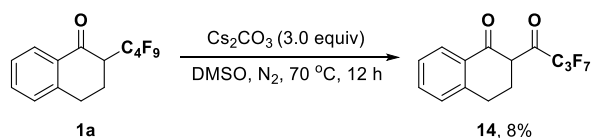


A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1a**, 109 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene (**2e**, 59 mg, 0.45 mmol), Pd(PPh₃)₂Cl₂ (21 mg, 0.03 mmol), and Et₃N (61 mg, 0.6 mmol) in THF (3.0 mL) was stirred under N₂ atmosphere at room temperature for 1 h. **Proposed endocyclic naphthalen-1(4H)-one **13** could be detected by HRMS, suggesting that intermediate **13** might be involved in the reaction.**

HRMS of intermediate **13**:



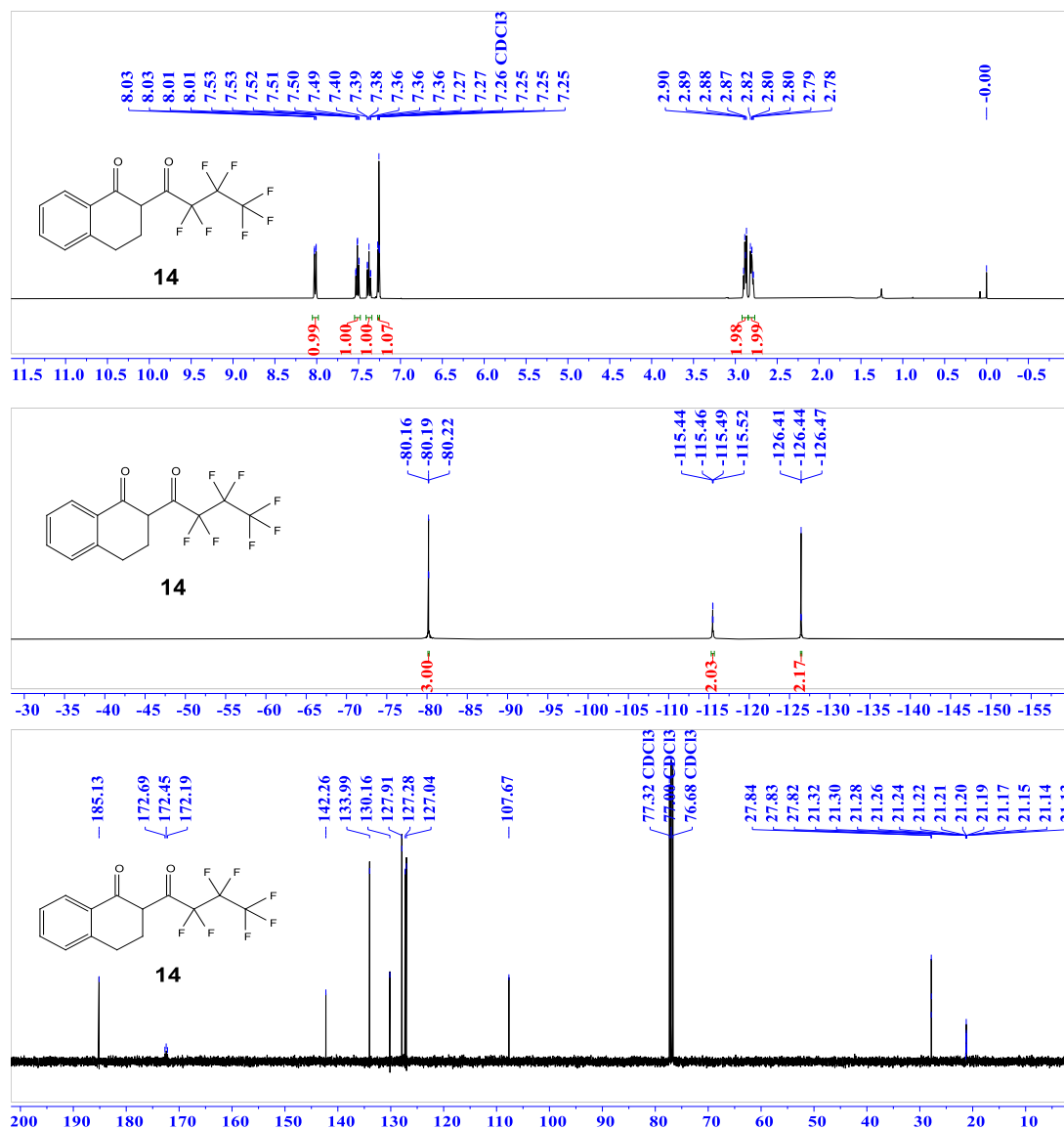
5) The formation of intermediate 2-(2,2,3,3,4,4,4-heptafluorobutanoyl)-3,4-dihydronaphthalen-1(2H)-one (**14**) in the absence of Pd(PPh₃)₂Cl₂ catalyst



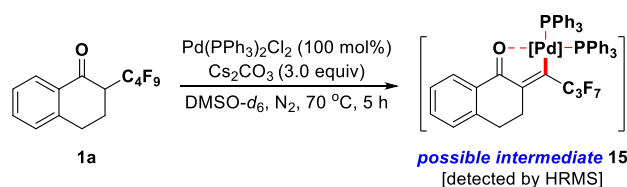
A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1a**, 109 mg, 0.3 mmol) and Cs₂CO₃ (293 mg, 0.9 mmol) in DMSO (3.0 mL) was stirred under N₂ atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH₄Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic 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 (200/1) as eluent to afford the pure product **14** (8 mg, 8% yield). **This result suggested that compound **14** may also come from base-**

promoted fluorine elimination of **11** without involving Pd species.

NMR spectra of compound **14**:

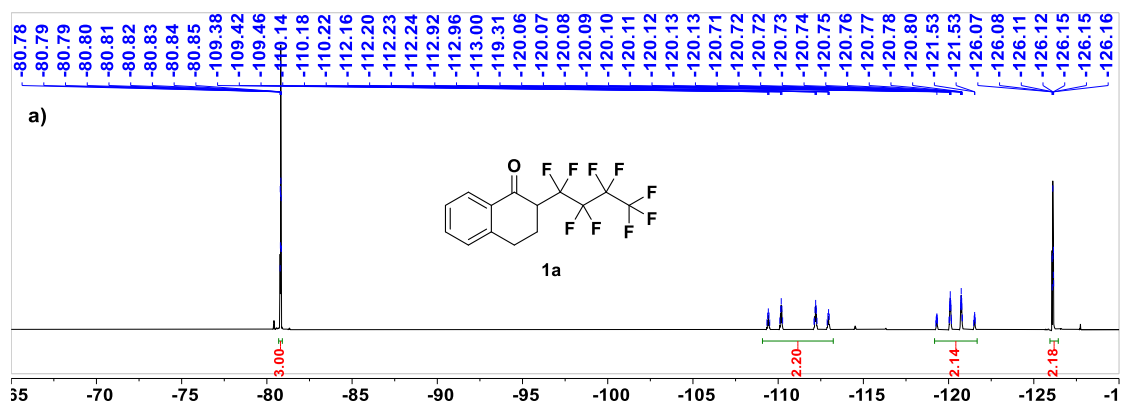


6) ^{19}F , ^{31}P NMR, and HRMS analysis of intermediate **15**

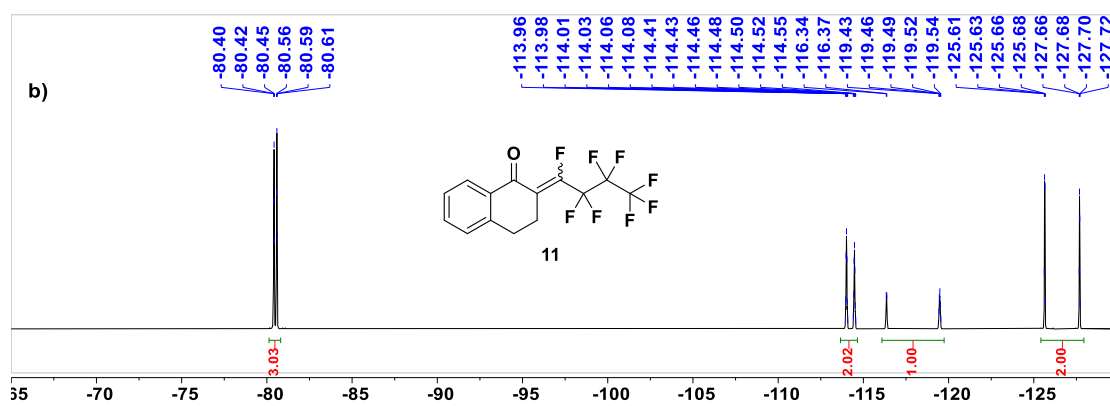


A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2H)-one (**1a**, 109 mg, 0.3 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (211 mg, 0.3 mmol), and Cs_2CO_3 (293 mg, 0.9 mmol) in $\text{DMSO-}d_6$ (3.0 mL) was stirred under N_2 atmosphere at 70 °C for 5 h. The reaction mixture was analyzed by ^{19}F and ^{31}P NMR.

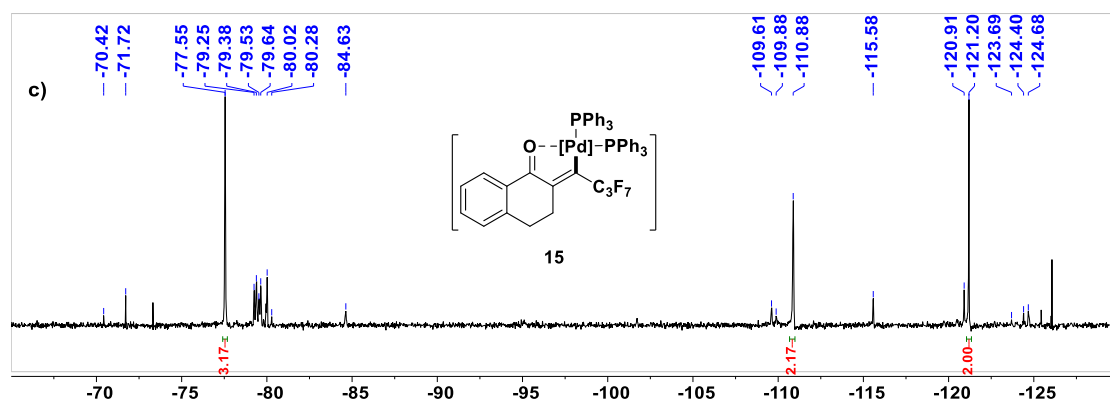
a) ^{19}F NMR spectra of compound 1a



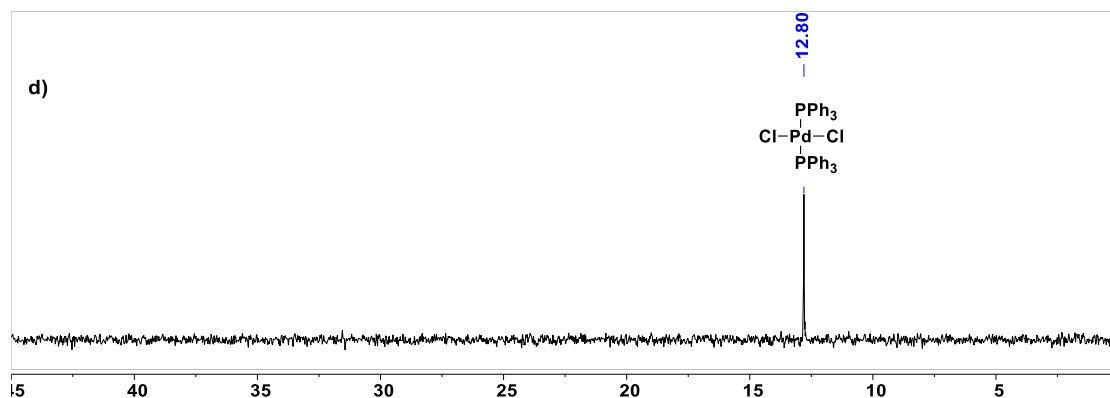
b) ^{19}F NMR spectra of intermediate 11



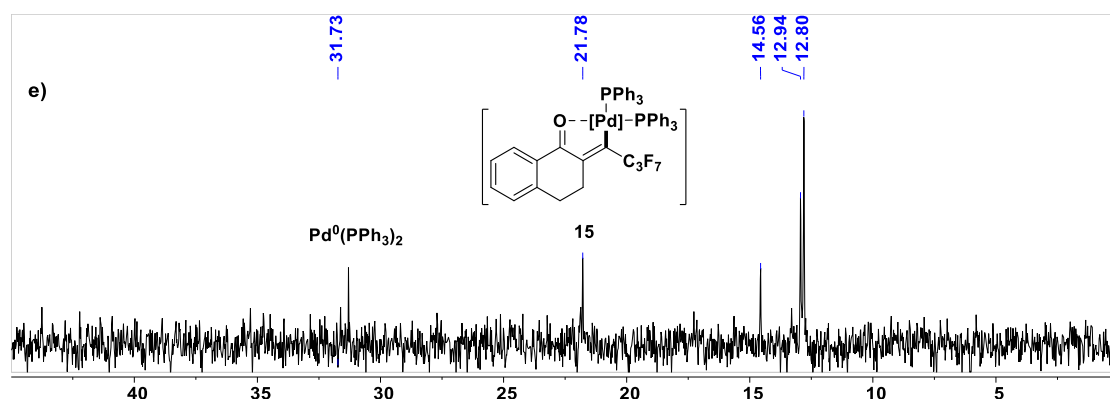
c) ^{19}F NMR spectra of reaction mixture



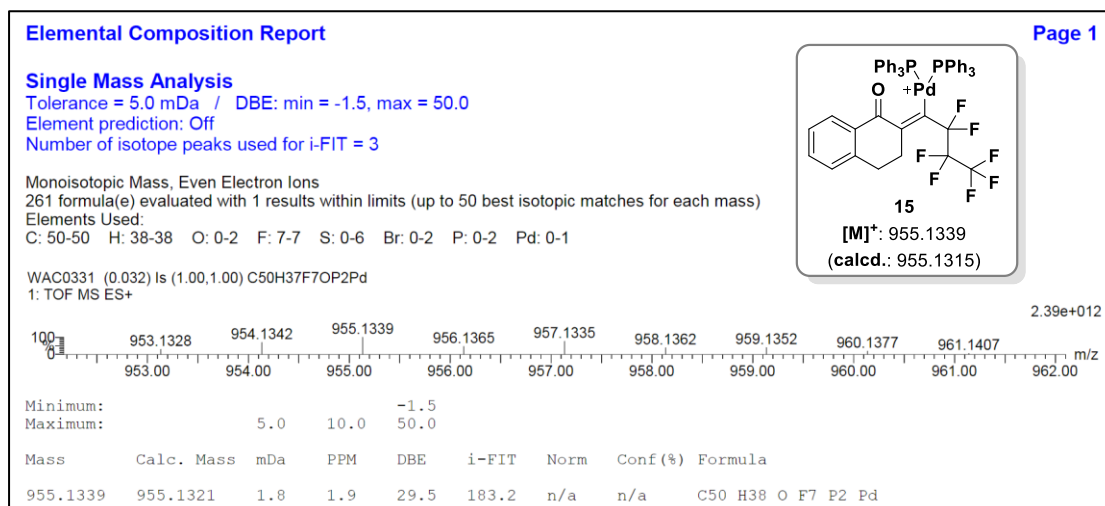
d) ^{31}P NMR spectra of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ ^[3]



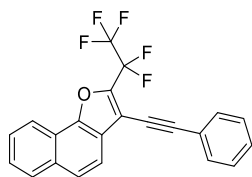
e) ^{31}P NMR spectra of reaction mixture^[3]



HRMS of vinylpalladium 15:



10. Characterization data for products



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

Yield = 58% (67 mg). White solid. M.p. 125.2–126.9 °C.

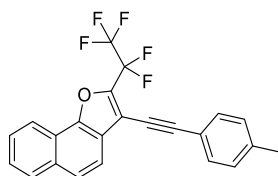
IR (KBr): $\nu = 3015, 2224, 1582, 808, 740 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.33 - 8.27$ (m, 1H), 7.97 – 7.90 (m, 1H), 7.76 (s, 2H), 7.65 – 7.54 (m, 4H), 7.40 – 7.35 (m, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.57$ (t, $J = 3.4$ Hz, 3F), -114.34 (q, $J = 3.4$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.0, 141.6$ (t, $J_{\text{C-F}} = 30.1$ Hz), 132.9, 132.5, 131.8, 129.1, 128.4, 127.1, 126.9, 125.3, 123.4, 122.3, 120.8, 120.3, 118.3, 109.4 (m), 98.1, 76.3 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₂H₁₂F₅O [M+H]⁺ 387.0803, found: 387.0805.



2-(Perfluoroethyl)-3-(*p*-tolylethynyl)naphtho[1,2-*b*]furan (3ab):

Yield = 64% (76 mg). White solid. M.p. 143.4-145.2 °C.

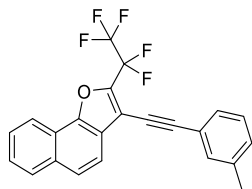
IR (KBr): $\nu = 3030, 2227, 1597, 1508, 809, 744 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.33$ (d, $J = 8.0$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.79 (t, $J = 9.0$ Hz, 2H), 7.69 – 7.63 (m, 1H), 7.62 – 7.56 (m, 1H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 7.9$ Hz, 2H), 2.39 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.56$ (t, $J = 3.9$ Hz, 3F), -114.31 (q, $J = 3.9$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.0$ (t, $J_{\text{C-F}} = 1.4$ Hz), 141.5 (t, $J_{\text{C-F}} = 30.1$ Hz), 139.4, 133.0, 131.7, 129.2, 128.5, 127.2, 126.9, 125.3, 123.5 (t, $J_{\text{C-F}} = 1.3$ Hz), 120.9, 120.4, 119.3, 118.4, 109.6 (m), 98.6 (t, $J_{\text{C-F}} = 1.4$ Hz), 75.7 (t, $J_{\text{C-F}} = 1.4$ Hz), 21.6 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₃H₁₄F₅O [M+H]⁺ 401.0959, found: 401.0957.



2-(Perfluoroethyl)-3-(*m*-tolylethynyl)naphtho[1,2-*b*]furan (3ac):

Yield = 65% (78 mg). Yellow solid. M.p. 119.2-119.9 °C.

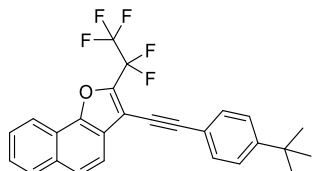
IR (KBr): $\nu = 2928, 2218, 1617, 807, 742 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta 8.28$ (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 7.9$ Hz, 1H), 7.74 (d, $J = 2.0$ Hz, 2H), 7.64 – 7.52 (m, 2H), 7.40 (d, $J = 7.0$ Hz, 2H), 7.25 (t, $J = 8.0$ Hz, 1H), 7.18 (t, $J = 6.0$ Hz, 1H), 2.36 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.51$ (t, $J = 3.5$ Hz, 3F), -114.24 (q, $J = 3.5$ Hz, 2F) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 151.0 (t, $J_{\text{C-F}}$ = 1.1 Hz), 141.5 (t, $J_{\text{C-F}}$ = 30.2 Hz), 138.2, 133.0, 132.3, 130.0, 128.9, 128.4, 128.4, 127.1, 126.9, 125.3, 123.5 (t, $J_{\text{C-F}}$ = 1.1 Hz), 122.1, 120.9, 120.3, 118.3, 109.5 (t, $J_{\text{C-F}}$ = 2.7 Hz), 98.4 (t, $J_{\text{C-F}}$ = 1.4 Hz), 75.9 (t, $J_{\text{C-F}}$ = 0.9 Hz), 21.2 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{14}\text{F}_5\text{O}$ $[\text{M}+\text{H}]^+$ 401.0959, found: 401.0959.



3-((4-(*tert*-Butyl)phenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3ad):

Yield = 64% (85 mg). Light yellow solid. M.p. 109.0-109.7 °C.

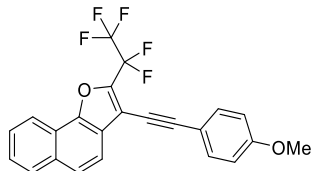
IR (KBr): ν = 2968, 2221, 1613, 812, 753 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 8.31 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 1.4 Hz, 2H), 7.66 – 7.51 (m, 4H), 7.41 (d, J = 8.4 Hz, 2H), 1.33 (s, 9H) ppm.

^{19}F NMR (376 MHz, CDCl_3): δ = -83.54 (t, J = 3.4 Hz, 3F), -114.29 (q, J = 3.4 Hz, 2F) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 152.6, 151.0 (m), 141.5 (t, $J_{\text{C-F}}$ = 31.9 Hz), 133.0, 131.6, 128.5, 127.1, 126.9, 125.5, 125.3, 123.5 (t, $J_{\text{C-F}}$ = 1.3 Hz), 120.9, 120.4, 119.3, 118.4, 109.5 (m), 98.3 (t, $J_{\text{C-F}}$ = 1.4 Hz), 75.7 (t, $J_{\text{C-F}}$ = 1.3 Hz), 34.9, 31.1 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{26}\text{H}_{20}\text{F}_5\text{O}$ $[\text{M}+\text{H}]^+$ 443.1429, found: 443.1427.



3-((4-Methoxyphenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3ae):

Yield = 69% (86 mg). Light yellow solid. M.p. 138.0-139.8 °C.

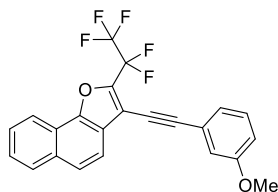
IR (KBr): ν = 3010, 2224, 1596, 1250, 834, 750 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 8.32 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.64 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.61 – 7.51 (m, 3H), 6.94 – 6.88 (m, 2H), 3.83 (s, 3H) ppm.

^{19}F NMR (376 MHz, CDCl_3): δ = -83.56 (t, J = 4.1 Hz, 3F), -114.27 (q, J = 4.1 Hz, 2F) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 160.3, 151.0 (t, $J_{\text{C-F}}$ = 1.3 Hz), 141.2 (t, $J_{\text{C-F}}$ = 31.6 Hz), 133.4, 133.0, 128.5, 127.1, 126.9, 125.2, 123.5 (t, $J_{\text{C-F}}$ = 1.2 Hz), 120.9, 120.4, 118.4, 114.4, 114.1, 109.6 (m), 98.3 (t, $J_{\text{C-F}}$ = 1.4 Hz), 75.1 (t, $J_{\text{C-F}}$ = 1.3 Hz), 55.3 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{14}\text{F}_5\text{O}_2$ $[\text{M}+\text{H}]^+$ 417.0908, found: 417.0906.



3-((3-Methoxyphenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3af):

Yield = 57% (71 mg). Light yellow solid. M.p. 95.9-96.1 °C.

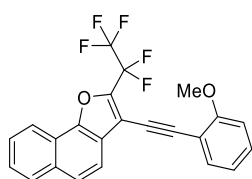
IR (KBr): $\nu = 3005, 2229, 1597, 1220, 815, 755 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.34 - 8.25$ (m, 1H), 7.97 – 7.89 (m, 1H), 7.76 (s, 2H), 7.67 – 7.53 (m, 2H), 7.29 (t, $J = 7.9$ Hz, 1H), 7.23 – 7.17 (m, 1H), 7.11 (dd, $J = 2.4, 1.3$ Hz, 1H), 6.94 (ddd, $J = 8.3, 2.6, 0.9$ Hz, 1H), 3.83 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.53$ (t, $J = 3.0$ Hz, 3F), -114.28 (q, $J = 3.0$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 159.4, 151.0$ (t, $J_{\text{C-F}} = 1.3$ Hz), 141.7 (t, $J_{\text{C-F}} = 31.2$ Hz), 133.0, 129.6, 128.5, 127.2, 126.9, 125.3, 124.4, 123.4 (t, $J_{\text{C-F}} = 1.2$ Hz), 123.3, 120.9, 120.3, 118.3, 116.6, 115.6, 109.3 (m), 98.0 (t, $J_{\text{C-F}} = 1.6$ Hz), 76.1 (t, $J_{\text{C-F}} = 1.3$ Hz), 55.3 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₃H₁₄F₅O₂ [M+H]⁺ 417.0908, found: 417.0904.



3-((2-Methoxyphenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3ag):

Yield = 66% (83 mg). Light yellow solid. M.p. 75.3-75.8 °C.

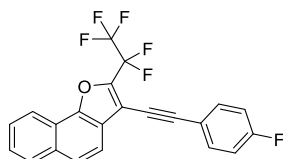
IR (KBr): $\nu = 2967, 2227, 1593, 1201, 806, 751 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.32$ (d, $J = 8.1$ Hz, 1H), 7.95 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 8.6$ Hz, 1H), 7.77 (d, $J = 8.6$ Hz, 1H), 7.67 – 7.61 (m, 1H), 7.60 – 7.52 (m, 2H), 7.39 – 7.31 (m, 1H), 7.02 – 6.88 (m, 2H), 3.95 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.53$ (t, $J = 3.3$ Hz, 3F), -114.26 (q, $J = 3.3$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 160.4, 151.0$ (t, $J_{\text{C-F}} = 1.3$ Hz), 141.3 (t, $J_{\text{C-F}} = 30.2$ Hz), 133.5, 133.0, 130.7, 128.5, 127.1, 126.8, 125.2, 123.7 (t, $J_{\text{C-F}} = 1.3$ Hz), 120.9, 120.5, 120.4, 118.6, 111.7, 110.8, 109.8 (m), 94.8 (t, $J_{\text{C-F}} = 1.4$ Hz), 80.3 (t, $J_{\text{C-F}} = 1.3$ Hz), 55.9 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₃H₁₄F₅O₂ [M+H]⁺ 417.0908, found: 417.0907.



3-((4-Fluorophenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3ah):

Yield = 56% (68 mg). Light yellow solid. M.p. 141.6-143.2 °C.

IR (KBr): $\nu = 3067, 2226, 1616, 1200, 811, 747 \text{ cm}^{-1}$.

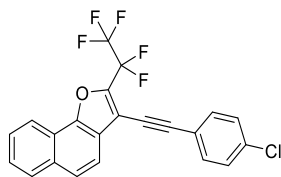
¹H NMR (400 MHz, CDCl₃): $\delta = 8.34 - 8.28$ (m, 1H), 7.95 (d, $J = 7.9$ Hz, 1H), 7.77 (d, $J = 2.1$ Hz, 2H), 7.64 (ddd, $J = 8.2, 7.0, 1.2$ Hz, 1H), 7.61 – 7.55 (m, 3H), 7.11 – 7.04 (m, 2H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.58$ (t, $J = 4.0$ Hz, 3F), -109.19 – -109.26 (m, 1F), -114.35 (q, $J = 4.0$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 163.0$ (d, $J_{\text{C-F}} = 249.7$ Hz), 151.0, 141.7 (t, $J_{\text{C-F}} = 30.5$ Hz), 133.8 (d, $J_{\text{C-F}} = 8.5$ Hz), 133.0, 128.5, 127.2, 127.0, 125.4, 123.4 (t, $J_{\text{C-F}} = 30.5$ Hz), 120.9, 120.4, 118.4 (d, $J_{\text{C-F}} = 3.5$ Hz), 118.2, 115.8 (d, $J_{\text{C-F}} = 22.1$ Hz), 110.0 – 109.2 (m), 97.0 (t, $J_{\text{C-F}} = 1.2$ Hz), 76.1 (q, $J_{\text{C-F}} = 1.3$ Hz) ppm; carbons corresponding to

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

HRMS (m/z): calcd for C₂₂H₁₁F₆O [M+H]⁺ 405.0709, found: 405.0713.



3-((4-Chlorophenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3ai):

Yield = 49% (62 mg); 53% (67 mg). Light yellow solid. M.p. 167.4-168.5 °C.

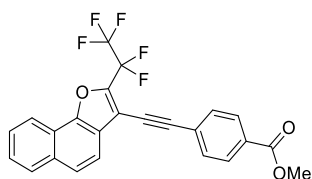
IR (KBr): ν = 3061, 2227, 1607, 1091, 824, 745 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.35 – 8.28 (m, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.81 – 7.73 (m, 2H), 7.67 – 7.62 (m, 1H), 7.61 – 7.56 (m, 1H), 7.54 – 7.48 (m, 2H), 7.38 – 7.32 (m, 2H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -83.56 (t, J = 4.1 Hz, 3F), -114.36 (q, J = 4.1 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 151.0 (t, J_{C-F} = 1.3 Hz), 141.8 (t, J_{C-F} = 31.8 Hz), 135.3, 133.0, 128.8, 128.5, 127.2, 127.0, 125.4, 123.3 (t, J_{C-F} = 1.3 Hz), 120.9, 120.8, 120.4, 120.2, 118.2, 109.0 (m), 96.8 (t, J_{C-F} = 1.7 Hz), 77.3 (t, J_{C-F} = 1.3 Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₂H₁₁ClF₅O [M+H]⁺ 421.0413, found: 421.0413.



Methyl 4-((2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)ethynyl)benzoate (3aj):

Yield = 57% (76 mg). Light yellow solid. M.p. 156.9-157.6 °C.

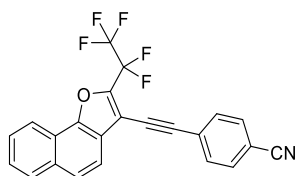
IR (KBr): ν = 2953, 2221, 1582, 1214, 812, 757 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.33 – 8.25 (m, 1H), 8.03 (d, J = 7.8 Hz, 2H), 7.98 – 7.90 (m, 1H), 7.82 – 7.71 (m, 2H), 7.66 – 7.55 (m, 4H), 3.93 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -83.55 (t, J = 3.1 Hz, 3F), -114.35 (t, J = 3.1 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 166.3, 151.1, 142.1 (t, J_{C-F} = 32.2 Hz), 133.0, 131.7, 130.3, 129.6, 128.5, 127.2, 127.0, 126.8, 125.5, 123.2, 120.8, 120.3, 118.1, 108.8 (m), 97.1, 79.0, 52.3 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₄H₁₄F₅O₃ [M+H]⁺ 445.0858, found: 445.0855.



4-((2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)ethynyl)benzonitrile (3ak):

Yield = 39% (48 mg); 45% (55 mg). Light yellow solid. M.p. 179.7-180.1 °C.

IR (KBr): ν = 2971, 2227, 1608, 813, 747 cm⁻¹.

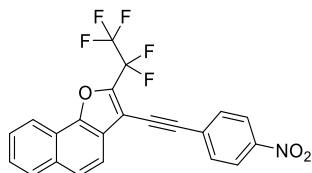
¹H NMR (400 MHz, CDCl₃): δ = 8.33 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.84 – 7.73 (m, 2H), 7.70 – 7.59

(m, 6H) ppm.

^{19}F NMR (376 MHz, CDCl_3): $\delta = -83.55$ (t, $J = 3.4$ Hz, 3F), -114.41 (q, $J = 3.4$ Hz, 2F) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 151.1$, 142.5 (t, $J_{\text{C-F}} = 30.2$ Hz), 133.0 , 132.2 , 132.1 , 128.5 , 127.4 , 127.2 , 127.0 , 125.7 , 123.1 (t, $J_{\text{C-F}} = 0.8$ Hz), 120.9 , 120.4 , 118.3 , 118.0 , 112.4 , 108.4 (m), 95.9 (t, $J_{\text{C-F}} = 1.4$ Hz), 80.5 (t, $J_{\text{C-F}} = 0.8$ Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{11}\text{F}_5\text{NO}$ $[\text{M}+\text{H}]^+$ 412.0755, found: 412.0755.



3-((4-Nitrophenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3al):

Yield = 33% (42 mg); 43% (55 mg). Yellow solid. M.p. 199.4-200.8 °C.

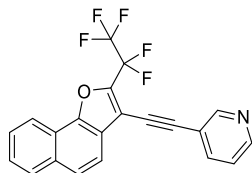
IR (KBr): $\nu = 2964$, 2227 , 1617 , 1519 , 811 , 748 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 8.36 - 8.30$ (m, 1H), $8.24 - 8.22$ (m, 2H), 7.99 (d, $J = 7.9$ Hz, 1H), 7.83 (d, $J = 8.6$ Hz, 1H), 7.78 (s, 1H), $7.72 - 7.69$ (m, 2H), $7.69 - 7.60$ (m, 2H) ppm.

^{19}F NMR (376 MHz, CDCl_3): $\delta = -83.53$ (t, $J = 3.5$ Hz, 3F), -114.40 (q, $J = 3.5$ Hz, 2F) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 151.2$ (t, $J_{\text{C-F}} = 1.2$ Hz), 147.5 , 142.6 (t, $J = 30.4$ Hz), 133.0 , 132.5 , 128.9 , 128.5 , 127.4 , 127.2 , 125.7 , 123.7 , 123.0 (t, $J_{\text{C-F}} = 1.0$ Hz), 120.8 , 120.3 , 117.9 , 108.3 (m), 95.7 (t, $J = 1.6$ Hz), 81.3 (t, $J = 1.2$ Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{22}\text{H}_{11}\text{F}_5\text{NO}_2$ $[\text{M}+\text{H}]^+$ 432.0654, found: 432.0661.



3-((2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)ethynyl)pyridine (3am):

Yield = 45% (52 mg). Light yellow solid. M.p. 128.7-129.3 °C.

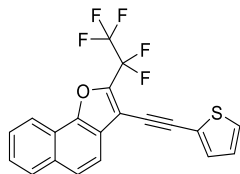
IR (KBr): $\nu = 3036$, 2206 , 1615 , 1577 , 802 , 759 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 8.85$ (s, 1H), 8.62 (d, $J = 3.7$ Hz, 1H), 8.34 (d, $J = 8.0$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.89 (dt, $J = 7.9$, 1.8 Hz, 1H), $7.85 - 7.76$ (m, 2H), $7.71 - 7.58$ (m, 2H), 7.34 (dd, $J = 7.7$, 5.0 Hz, 1H) ppm.

^{19}F NMR (376 MHz, CDCl_3): $\delta = -83.56$ (t, $J = 3.7$ Hz, 3F), -114.38 (q, $J = 3.7$ Hz, 2F) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 152.3$, 151.1 (t, $J_{\text{C-F}} = 1.2$ Hz), 149.4 , 142.2 (t, $J_{\text{C-F}} = 30.7$ Hz), 138.7 , 133.0 , 128.5 , 127.3 , 127.1 , 125.6 , 123.2 (t, $J_{\text{C-F}} = 1.2$ Hz), 123.1 (t, $J_{\text{C-F}} = 1.2$ Hz), 120.9 , 120.4 , 119.5 (m), 118.1 , 108.6 (m), 94.5 (t, $J_{\text{C-F}} = 1.4$ Hz), 79.6 (t, $J_{\text{C-F}} = 1.0$ Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{11}\text{F}_5\text{NO}$ $[\text{M}+\text{H}]^+$ 388.0755, found: 388.0757.



2-(Perfluoroethyl)-3-(thiophen-2-ylethynyl)naphtho[1,2-*b*]furan (3an):

Yield = 41% (48 mg); 49% (57 mg). Light yellow solid. M.p. 104.3-106.1 °C.

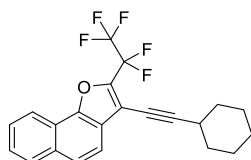
IR (KBr): $\nu = 2962, 2213, 1617, 1512, 811, 746 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.36 - 8.29$ (m, 1H), $8.00 - 7.92$ (m, 1H), 7.78 (d, $J = 1.2$ Hz, 2H), $7.68 - 7.55$ (m, 2H), $7.42 - 7.36$ (m, 2H), 7.06 (dd, $J = 5.1, 3.6$ Hz, 1H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.51$ (t, $J = 3.3$ Hz, 3F), -114.28 (q, $J = 3.3$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.0$ (d, $J_{\text{C-F}} = 1.0$ Hz), 141.6 (t, $J_{\text{C-F}} = 30.7$ Hz), $133.1, 133.0, 128.5, 128.5, 127.3, 127.2, 127.0, 125.4, 123.3$ (t, $J_{\text{C-F}} = 0.9$ Hz), $122.1, 120.9, 120.4, 118.3, 109.1$ (m), 91.2 (t, $J_{\text{C-F}} = 1.6$ Hz), 80.0 (t, $J_{\text{C-F}} = 1.1$ Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₀H₁₀F₅OS [M+H]⁺ 393.0367, found: 393.0370.



3-(Cyclohexylethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3ao):

Yield = 54% (64 mg). Light yellow solid. M.p. 130.1-130.3 °C.

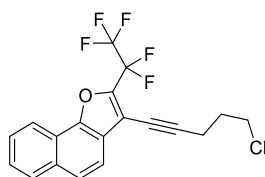
IR (KBr): $\nu = 2933, 2237, 1601, 810, 747 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.35 - 8.26$ (m, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), $7.77 - 7.68$ (m, 2H), $7.65 - 7.54$ (m, 2H), $2.77 - 2.71$ (m, 1H), $1.95 - 1.90$ (m, 2H), $1.83 - 1.77$ (m, 2H), $1.69 - 1.53$ (m, 3H), $1.47 - 1.37$ (m, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.69$ (t, $J = 3.8$ Hz, 3F), -114.43 (q, $J = 3.8$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 150.8$ (d, $J_{\text{C-F}} = 1.0$ Hz), 141.3 (t, $J_{\text{C-F}} = 30.2$ Hz), $132.9, 128.4, 127.0, 126.7, 125.0, 123.9$ (t, $J = 1.0$ Hz), $120.9, 120.4, 118.5, 110.0$ (m), 104.0 (t, $J_{\text{C-F}} = 1.3$ Hz), 67.6 (t, $J_{\text{C-F}} = 1.0$ Hz), $32.3, 29.9, 25.9, 24.6$ ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₂H₁₈F₅O [M+H]⁺ 393.1272, found: 393.1272.



3-(5-Chloropent-1-yn-1-yl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3ap):

Yield = 27% (32 mg); 33% (39 mg). Yellow solid. M.p. 57.0-57.6 °C.

IR (KBr): $\nu = 2962, 2242, 1600, 811, 749 \text{ cm}^{-1}$.

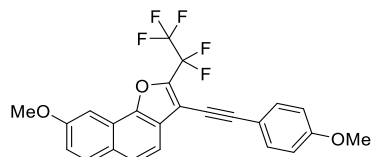
¹H NMR (400 MHz, CDCl₃): $\delta = 8.32$ (d, $J = 8.1$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), $7.80 - 7.68$ (m, 2H), $7.67 - 7.56$ (m, 2H), 3.77 (t, $J = 6.3$ Hz, 2H), 2.75 (t, $J = 6.8$ Hz, 2H), $2.17 - 2.10$ (m, 2H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.70$ (t, $J = 4.0$ Hz, 3F), -114.51 (q, $J = 4.0$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 150.9$ (t, $J_{\text{C-F}} = 1.1$ Hz), 141.6 (t, $J_{\text{C-F}} = 29.7$ Hz), $132.9, 128.5, 127.2, 126.9, 125.2, 123.7$ (t, $J_{\text{C-F}} = 1.1$ Hz), $120.9, 120.4, 118.3, 109.4$ (m), 97.6 (t, $J_{\text{C-F}} = 1.4$ Hz), 68.7 (t, $J_{\text{C-F}} = 1.1$ Hz), $43.4,$

31.1, 17.1 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₁₉H₁₃ClF₅O [M+H]⁺ 387.0570, found: 387.0571.



8-Methoxy-3-((4-methoxyphenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-b]furan (3be):

Yield = 61% (54 mg). White solid. M.p. 159.0-160.3 °C.

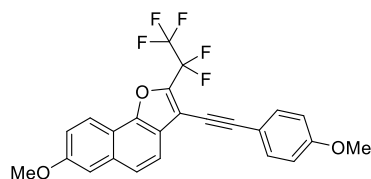
IR (KBr): $\nu = 2968, 2225, 1606, 1215, 835, 708 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.87$ (d, $J = 9.0$ Hz, 1H), 7.72 (d, $J = 8.5$ Hz, 1H), 7.65 (d, $J = 8.5$ Hz, 1H), $7.60 - 7.51$ (m, 3H), 7.23 (dd, $J = 8.9, 2.6$ Hz, 1H), $6.95 - 6.89$ (m, 2H), 4.02 (s, 3H), 3.85 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.57$ (t, $J = 3.6$ Hz, 3F), -114.39 (q, $J = 3.6$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 160.2, 158.7, 150.5$ (t, $J_{C-F} = 1.1$ Hz), 141.1 (t, $J_{C-F} = 31.6$ Hz), $133.4, 130.1, 128.1, 124.9, 124.0$ (t, $J_{C-F} = 1.2$ Hz), $121.9, 119.2, 115.9, 114.4, 114.1, 109.7$ (m), $99.0, 98.1$ (t, $J_{C-F} = 1.3$ Hz), 75.2 (t, $J_{C-F} = 1.1$ Hz), $55.6, 55.4$ ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₄H₁₆F₅O₃ [M+H]⁺ 447.1014, found: 447.1013.



7-Methoxy-3-((4-methoxyphenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-b]furan (3ce):

Yield = 66% (59 mg). Light yellow solid. M.p. 123.4-125.1 °C.

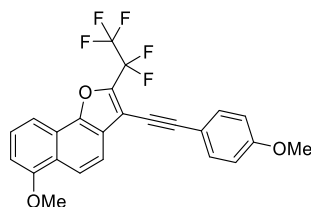
IR (KBr): $\nu = 2967, 2223, 1615, 1199, 830, 767 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.24$ (d, $J = 8.6$ Hz, 1H), 7.76 (d, $J = 8.6$ Hz, 1H), 7.69 (d, $J = 8.6$ Hz, 1H), $7.58 - 7.52$ (m, 2H), $7.34 - 7.27$ (m, 2H), $6.96 - 6.88$ (m, 2H), 3.96 (s, 3H), 3.85 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.59$ (t, $J = 3.5$ Hz, 3F), -114.20 (q, $J = 3.5$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 160.2, 158.5, 151.3$ (t, $J_{C-F} = 1.2$ Hz), 140.6 (t, $J_{C-F} = 30.7$ Hz), $134.6, 133.4, 124.3, 122.0, 121.9, 119.2, 119.1, 116.0, 114.5, 114.1, 109.6$ (m), $107.4, 98.1, 75.3, 55.4, 55.4$ ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₄H₁₆F₅O₃ [M+H]⁺ 447.1014, found: 447.1017.



6-Methoxy-3-((4-methoxyphenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-b]furan (3de):

Yield = 60% (53 mg). Yellow solid. M.p. 147.6-148.3 °C.

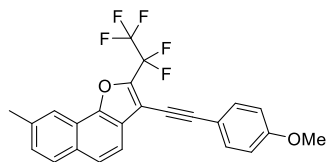
IR (KBr): $\nu = 2965, 2228, 1596, 1196, 800, 756 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.23$ (d, $J = 8.9$ Hz, 1H), 7.91 (d, $J = 8.3$ Hz, 1H), 7.77 (d, $J = 8.9$ Hz, 1H), $7.60 - 7.52$ (m, 3H), $6.99 - 6.89$ (m, 3H), 4.04 (s, 3H), 3.85 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -83.57 (t, *J* = 3.7 Hz, 3F), -114.36 (q, *J* = 3.7 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 160.2, 155.9, 150.9 (t, *J*_{C-F} = 1.2 Hz), 141.3 (t, *J*_{C-F} = 30.4 Hz), 133.4, 127.6, 124.6, 124.0, 121.9, 119.2, 117.5, 114.4, 114.1, 112.5, 109.6 (m), 105.4, 98.2 (t, *J*_{C-F} = 1.4 Hz), 75.2 (t, *J*_{C-F} = 1.1 Hz), 55.7, 55.4 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₄H₁₆F₅O₃ [M+H]⁺ 447.1014, found: 447.1013.



3-((4-Methoxyphenyl)ethynyl)-8-methyl-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3ee):

Yield = 63% (54 mg). Yellow solid. M.p. 138.4-139.8 °C.

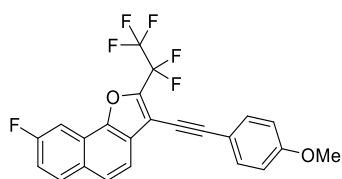
IR (KBr): ν = 3005, 2217, 1603, 1206, 810, 729 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.11 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.79 – 7.68 (m, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.47 – 7.39 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.60 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -83.57 (t, *J* = 3.4 Hz, 3F), -114.29 (q, *J* = 3.4 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 160.2, 150.7 (d, *J*_{C-F} = 1.3 Hz), 141.1 (t, *J*_{C-F} = 30.5 Hz), 137.3, 133.4, 131.2, 129.0, 128.3, 125.0, 123.6, 121.0, 119.5, 117.4, 114.4, 114.1, 109.6 (m), 98.1 (t, *J*_{C-F} = 1.3 Hz), 75.2 (t, *J*_{C-F} = 0.8 Hz), 55.3, 21.8 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₄H₁₆F₅O₂ [M+H]⁺ 431.1065, found: 431.1070.



8-Fluoro-3-((4-methoxyphenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3fe):

Yield = 54% (47 mg). Yellow solid. M.p. 158.6-159.1 °C.

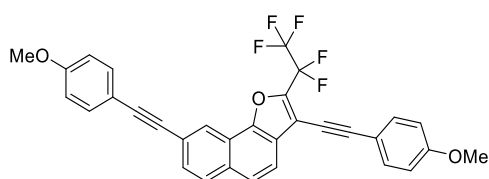
IR (KBr): ν = 2936, 2222, 1603, 1200, 832, 731 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.98 – 7.90 (m, 2H), 7.83 – 7.69 (m, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.35 (td, *J* = 8.8, 2.4 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -83.57 (t, *J* = 3.0 Hz, 3F), -111.15 – -111.21 (m, 1F), -114.45 (q, *J* = 3.0 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 161.4 (d, *J*_{C-F} = 247.5 Hz), 160.3, 150.5 (m), 141.6 (t, *J*_{C-F} = 31.8 Hz), 133.4, 131.1 (d, *J*_{C-F} = 9.0 Hz), 129.8, 125.0, 124.3, 121.7 (d, *J*_{C-F} = 10.0 Hz), 117.7, 116.8 (d, *J*_{C-F} = 24.5 Hz), 114.2, 114.1, 109.7 (m), 104.8 (d, *J*_{C-F} = 23.2 Hz), 98.5, 74.8, 55.4 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₃H₁₃F₆O₂ [M+H]⁺ 435.0814, found: 435.0815.



3,8-Bis((4-methoxyphenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3ge):

Yield = 39% (32 mg); 61% (50 mg). Yellow solid. M.p. 185.3-186.7 °C.

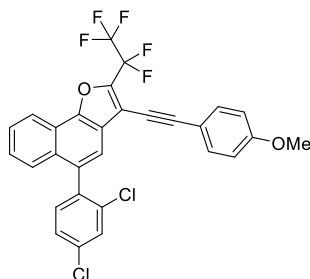
IR (KBr): $\nu = 2962, 2218, 1599, 1213, 832, 765 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.53 - 8.47$ (m, 1H), 7.94 (d, $J = 8.6$ Hz, 1H), 7.84 – 7.74 (m, 2H), 7.69 (dd, $J = 8.5, 1.6$ Hz, 1H), 7.59 – 7.51 (m, 4H), 6.96 – 6.88 (m, 4H), 3.87 – 3.85 (m, 6H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.56$ (t, $J = 3.2$ Hz, 3F), -114.44 (q, $J = 3.2$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 160.3, 159.8, 150.4$ (t, $J_{\text{C-F}} = 1.2$ Hz), 141.8 (t, $J_{\text{C-F}} = 32.8$ Hz), 133.4, 133.2, 131.9, 129.5, 128.5, 125.0, 124.1 (t, $J_{\text{C-F}} = 0.9$ Hz), 123.3, 122.5, 120.7, 119.0, 115.0, 114.3, 114.1, 114.1, 109.8 (m), 98.4 (t, $J_{\text{C-F}} = 1.3$ Hz), 91.1, 88.0, 74.9 (t, $J_{\text{C-F}} = 1.1$ Hz), 55.4, 55.3 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₂H₂₀F₅O₃ [M+H]⁺ 547.1327, found: 547.1329.

**5-(2,4-Dichlorophenyl)-3-((4-methoxyphenyl)ethynyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3he):**

Yield = 28% (32 mg); 30% (34 mg). Light yellow solid. M.p. 162.4-163.8 °C.

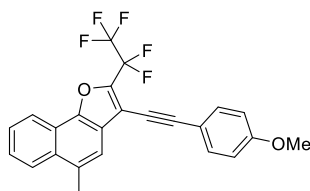
IR (KBr): $\nu = 2967, 2224, 1594, 1214, 823, 762 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.42$ (d, $J = 7.9$ Hz, 1H), 7.85 (d, $J = 8.5$ Hz, 1H), 7.73 – 7.66 (m, 2H), 7.63 – 7.50 (m, 5H), 7.35 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.93 – 6.86 (m, 2H), 3.84 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.55$ (t, $J = 3.2$ Hz, 3F), -114.39 (q, $J = 3.2$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 160.3, 150.8$ (t, $J_{\text{C-F}} = 1.4$ Hz), 141.6 (t, $J_{\text{C-F}} = 31.8$ Hz), 140.2, 135.3, 133.4, 132.6, 132.0, 131.9, 131.1, 130.3, 129.6, 127.4, 127.3, 126.6, 122.8 (t, $J_{\text{C-F}} = 1.3$ Hz), 121.1, 120.8, 119.4, 114.1, 114.1, 109.7 (m), 98.6 (t, $J_{\text{C-F}} = 1.3$ Hz), 74.8 (t, $J_{\text{C-F}} = 1.1$ Hz), 55.3 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₉H₁₆Cl₂F₅O₂ [M+H]⁺ 561.0442, found: 561.0436.

**3-((4-Methoxyphenyl)ethynyl)-5-methyl-2-(perfluoroethyl)naphtho[1,2-*b*]furan (3ie):**

Yield = 34% (29 mg); 35% (30 mg). Yellow solid. M.p. 137.8-139.6 °C.

IR (KBr): $\nu = 2918, 2222, 1612, 1217, 830, 756 \text{ cm}^{-1}$.

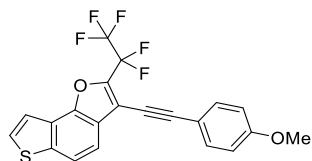
¹H NMR (400 MHz, CDCl₃): $\delta = 8.38 - 8.32$ (m, 1H), 8.11 – 8.04 (m, 1H), 7.69 – 7.60 (m, 3H), 7.58 – 7.53 (m, 2H), 6.96 – 6.89 (m, 2H), 3.85 (s, 3H), 2.77 (d, $J = 1.1$ Hz, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.59$ (t, $J = 3.8$ Hz, 3F), -114.22 (q, $J = 3.8$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 160.2, 150.2$ (t, $J_{\text{C-F}} = 1.4$ Hz), 141.0 (t, $J_{\text{C-F}} = 31.8$ Hz), 133.4, 132.2, 131.6, 128.3, 126.8, 126.7, 125.1, 123.0 (t, $J_{\text{C-F}} = 0.9$ Hz), 121.0, 120.9, 118.3, 114.5, 114.1, 98.0 (t, $J_{\text{C-F}} = 1.4$ Hz), 75.3 (t,

$J_{C-F} = 1.2$ Hz), 55.4, 19.8 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{16}F_5O_2$ $[M+H]^+$ 431.1065, found: 431.1064.



3-((4-Methoxyphenyl)ethynyl)-2-(perfluoroethyl)thieno[2,3-g]benzofuran (3je):

Yield = 58% (47 mg). White solid. M.p. 135.8-136.9 °C.

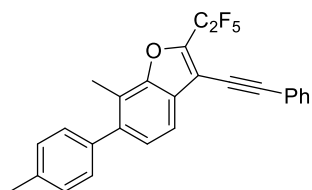
IR (KBr): $\nu = 2971, 2220, 1615, 1508, 1219, 828, 718$ cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): $\delta = 7.86$ (dd, $J = 8.5, 0.6$ Hz, 1H), 7.76 – 7.69 (m, 2H), 7.61 (d, $J = 5.5$ Hz, 1H), 7.57 – 7.51 (m, 2H), 6.95 – 6.88 (m, 2H), 3.85 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -83.59$ (t, $J = 4.2$ Hz, 3F), -114.46 (q, $J = 4.2$ Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 160.3, 149.5$ (t, $J_{C-F} = 1.0$ Hz), 140.6, 140.6 (t, $J_{C-F} = 30.2$ Hz), 133.4, 128.0, 125.3 (t, $J_{C-F} = 0.9$ Hz), 123.6, 119.0, 118.9, 117.1, 114.4, 114.1, 109.5 (m), 98.4 (t, $J_{C-F} = 1.5$ Hz), 75.1 (t, $J_{C-F} = 0.9$ Hz), 55.3 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{12}F_5O_2S$ $[M+H]^+$ 423.0473, found: 423.0474.



7-Methyl-2-(perfluoroethyl)-3-(phenylethynyl)-6-(p-tolyl)benzofuran (3ke):

Yield = 14% (12 mg). White solid. M.p. 62.7-63.9 °C.

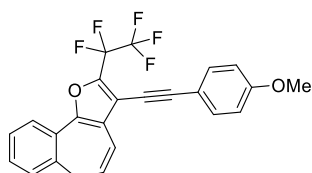
IR (KBr): $\nu = 3026, 2228, 1586, 1208, 806, 758$ cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): $\delta = 7.67$ (d, $J = 8.1$ Hz, 1H), 7.63 – 7.58 (m, 2H), 7.56 – 7.50 (m, 2H), 7.42 – 7.38 (m, 3H), 7.37 – 7.32 (m, 3H), 2.47 (s, 3H), 2.43 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -83.58$ (t, $J = 2.9$ Hz, 3F), -114.96 (q, $J = 2.9$ Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.4, 142.5$ (t, $J_{C-F} = 30.2$ Hz), 141.5, 137.2 (d, $J_{C-F} = 38.6$ Hz), 132.5, 131.8, 129.4, 129.1 (d, $J_{C-F} = 13.8$ Hz), 129.0, 128.4 (d, $J_{C-F} = 12.4$ Hz), 126.8, 125.8 (t, $J_{C-F} = 1.2$ Hz), 122.4, 121.0 (d, $J_{C-F} = 47.3$ Hz), 118.2, 108.5 (m), 81.5, 73.9, 21.2, 12.7 ppm; carbons corresponding to the C_8F_{17} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{18}F_5O$ $[M+H]^+$ 441.1272, found: 441.1279.



3-((4-Methoxyphenyl)ethynyl)-2-(perfluoroethyl)-6H-benzo[6,7]cyclohepta[1,2-b]furan (3le):

Yield = 26% (25 mg). White solid. M.p. 66.8-67.5 °C.

IR (KBr): $\nu = 2958, 2222, 1595, 1226, 834, 767$ cm^{-1} .

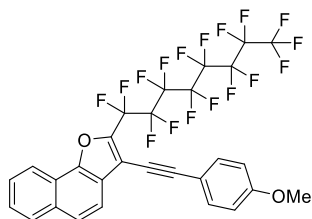
1H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$ (d, $J = 7.7$ Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 7.4$ Hz, 1H), 7.37

(t, $J = 7.5$ Hz, 1H), 7.28 (d, $J = 7.7$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 2H), 6.63 (d, $J = 9.8$ Hz, 1H), 5.99 – 5.86 (m, 1H), 3.84 (s, 3H), 3.24 (d, $J = 6.7$ Hz, 2H) ppm.

^{19}F NMR (376 MHz, CDCl_3): $\delta = -83.73$ (t, $J = 3.3$ Hz, 3F), -114.54 (q, $J = 3.3$ Hz, 2F) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 160.2$, 153.9 (t, $J_{\text{C-F}} = 2.1$ Hz), 139.0 (t, $J_{\text{C-F}} = 31.6$ Hz), 135.0, 133.3, 130.6, 128.7, 127.8, 126.6, 125.9, 125.0, 123.7, 119.9, 114.4, 114.0, 112.7 (m), 97.8 (t, $J_{\text{C-F}} = 1.4$ Hz), 75.2 (t, $J_{\text{C-F}} = 1.4$ Hz), 55.3, 34.1 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{16}\text{F}_5\text{O}_2$ $[\text{M}+\text{H}]^+$ 431.1065, found: 431.1064.



3-((4-Methoxyphenyl)ethynyl)-2-(perfluorooctyl)naphtho[1,2-*b*]furan (3ne):

Yield = 57% (81 mg). White solid. M.p. 125.6-125.9 °C.

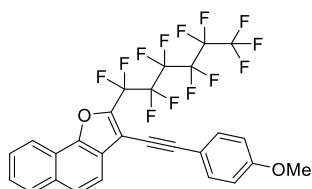
IR (KBr): $\nu = 2974$, 2226, 1612, 1212, 813, 748 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 8.34$ (d, $J = 8.0$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.82 – 7.78 (m, 2H), 7.70 – 7.64 (m, 1H), 7.62 – 7.58 (m, 1H), 7.57 – 7.51 (m, 2H), 6.95 – 6.89 (m, 2H), 3.85 (s, 3H) ppm.

^{19}F NMR (376 MHz, CDCl_3): $\delta = -80.65$ (t, $J = 9.9$ Hz, 3F), -110.89 – -111.23 (m, 2F), -121.45 – -121.96 (m, 6F), -122.01 – -122.24 (m, 2F), -122.44 – -122.85 (m, 2F), -125.90 – -126.28 (m, 2F) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 160.3$, 151.1 (t, $J_{\text{C-F}} = 1.0$ Hz), 141.4 (t, $J_{\text{C-F}} = 31.5$ Hz), 133.4, 133.0, 128.5, 127.2, 126.9, 125.2, 123.6, 121.0, 120.4, 118.5, 114.4, 114.1, 110.0 (m), 98.1 (t, $J_{\text{C-F}} = 1.5$ Hz), 75.1 (t, $J_{\text{C-F}} = 1.0$ Hz), 55.3 ppm; carbons corresponding to the C_8F_{17} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{29}\text{H}_{14}\text{F}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$ 717.0717, found: 717.0726.



3-((4-Methoxyphenyl)ethynyl)-2-(perfluorohexyl)naphtho[1,2-*b*]furan (3oe):

Yield = 48% (59 mg). Light yellow solid. M.p. 104.3-106.1 °C.

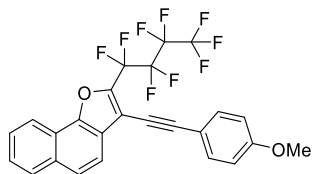
IR (KBr): $\nu = 2970$, 2221, 1610, 1216, 812, 719 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 8.34$ (d, $J = 8.0$ Hz, 1H), 7.97 (d, $J = 7.9$ Hz, 1H), 7.80 (d, $J = 1.2$ Hz, 2H), 7.69 – 7.63 (m, 1H), 7.60 (ddd, $J = 8.2$, 7.0, 1.3 Hz, 1H), 7.57 – 7.52 (m, 2H), 6.95 – 6.89 (m, 2H), 3.85 (s, 3H) ppm.

^{19}F NMR (376 MHz, CDCl_3): $\delta = -80.64$ (t, $J = 9.8$ Hz, 3F), -110.89 – -111.22 (m, 2F), -121.67 – -121.98 (m, 2F), -122.01 – -122.35 (m, 2F), -122.40 – -122.76 (m, 2F), -125.90 – -126.10 (m, 2F) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 160.3$, 151.1 (t, $J_{\text{C-F}} = 1.4$ Hz), 141.4 (t, $J_{\text{C-F}} = 31.1$ Hz), 133.4, 133.0, 128.5, 127.2, 126.9, 125.2, 123.5, 120.9, 120.4, 118.5, 114.4, 114.1, 110.0 (m), 98.1 (t, $J_{\text{C-F}} = 1.6$ Hz), 75.2 (t, $J_{\text{C-F}} = 1.0$ Hz), 55.3 ppm; carbons corresponding to the C_6F_{13} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $\text{C}_{27}\text{H}_{14}\text{F}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$ 617.0781, found: 617.0790.



3-((4-Methoxyphenyl)ethynyl)-2-(perfluorobutyl)naphtho[1,2-*b*]furan (3pe):

Yield = 58% (60 mg). Yellow solid. M.p. 85.6-87.2 °C.

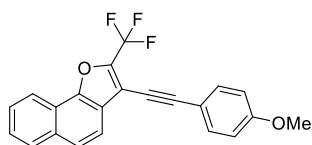
IR (KBr): $\nu = 2958, 2222, 1596, 1242, 896, 749 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.34$ (d, $J = 8.1$ Hz, 1H), 7.97 (d, $J = 7.8$ Hz, 1H), 7.80 (d, $J = 1.2$ Hz, 2H), 7.69 – 7.63 (m, 1H), 7.60 (ddd, $J = 8.2, 7.0, 1.4$ Hz, 1H), 7.57 – 7.52 (m, 2H), 6.97 – 6.88 (m, 2H), 3.85 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -80.73$ (t, $J = 9.7$ Hz, 3F), -111.28 (t, $J = 11.0$ Hz, 2F), -123.01 – -123.19 (m, 2F), -125.88 – -126.16 (m, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 160.3, 151.1$ (t, $J_{\text{C-F}} = 1.1$ Hz), 141.3 (t, $J_{\text{C-F}} = 30.9$ Hz), 133.4, 133.0, 128.5, 127.2, 126.9, 125.2, 123.5 (t, $J_{\text{C-F}} = 1.3$ Hz), 120.9, 120.4, 118.5, 114.4, 114.1, 110.0 (m), 98.1 (t, $J_{\text{C-F}} = 1.5$ Hz), 75.2 (t, $J_{\text{C-F}} = 1.4$ Hz), 55.3 ppm; carbons corresponding to the C₄F₉ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₅H₁₄F₉O₂ [M+H]⁺ 517.0845, found: 517.0845.



3-((4-Methoxyphenyl)ethynyl)-2-(trifluoromethyl)naphtho[1,2-*b*]furan (3qe):

Yield = 27% (20 mg); 51% (38 mg). Light yellow solid. M.p. 131.6-132.5 °C.

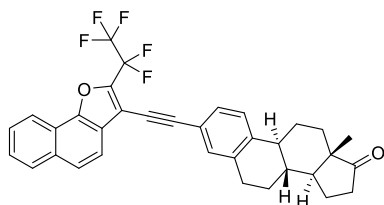
IR (KBr): $\nu = 2963, 2222, 1599, 1190, 808, 748 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.26$ (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.71 (s, 2H), 7.61 – 7.55 (m, 1H), 7.55 – 7.45 (m, 3H), 6.88 – 6.81 (m, 2H), 3.77 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -62.32$ (s, 3F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 160.3, 150.3$ (q, $J_{\text{C-F}} = 1.1$ Hz), 142.1 (t, $J_{\text{C-F}} = 30.0$ Hz), 133.4, 133.0, 128.5, 127.1, 126.8, 125.2, 123.3, 121.0, 120.4, 120.0 (q, $J_{\text{C-F}} = 267.3$ Hz), 118.6, 114.4, 114.1, 98.1 (q, $J_{\text{C-F}} = 1.6$ Hz), 75.1 (q, $J_{\text{C-F}} = 1.1$ Hz), 55.3 ppm.

HRMS (m/z): calcd for C₂₂H₁₄F₃O₂ [M+H]⁺ 367.0940, found: 367.0944.



(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-((2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)ethynyl)-

6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4):

Yield = 45% (60 mg). Light yellow solid. M.p. 178.2-179.8 °C.

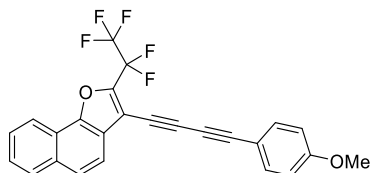
IR (KBr): $\nu = 2967, 2222, 1736, 1553, 1206, 817, 754 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.34$ (d, $J = 8.1$ Hz, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 7.80 (s, 2H), 7.70 – 7.57 (m, 2H), 7.43 – 7.28 (m, 3H), 3.02 – 2.89 (m, 2H), 2.56 – 2.39 (m, 2H), 2.38 – 2.27 (m, 1H), 2.22 – 1.95 (m, 4H), 1.68 – 1.45 (m, 6H), 0.93 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -83.55 (t, *J* = 3.6 Hz, 3F), -114.35 (q, *J* = 3.6 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 220.8, 151.0 (t, *J*_{C-F} = 1.1 Hz), 144.1 (t, *J*_{C-F} = 9.1 Hz), 141.3, 136.8, 132.9, 132.2, 129.1, 128.5, 127.2, 126.9, 125.5, 125.3, 123.5 (t, *J*_{C-F} = 1.0 Hz), 120.9, 120.4, 119.6, 118.4, 109.5 (m), 98.3 (t, *J*_{C-F} = 1.3 Hz), 75.6 (t, *J*_{C-F} = 0.8 Hz), 50.4, 47.9, 44.5, 37.9, 35.8, 31.5, 29.1, 26.3, 25.5, 21.5, 13.8 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₄H₂₈F₅O₂ [M+H]⁺ 563.2004, found: 563.2003.



3-((4-Methoxyphenyl)buta-1,3-diyne-1-yl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (5):

Yield = 34% (30 mg). Pink solid. M.p. 134.0-134.8 °C.

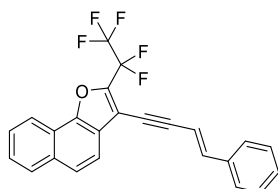
IR (KBr): ν = 2976, 2214, 1602, 1210, 828, 758 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.33 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.76 (m, 2H), 7.70 – 7.59 (m, 2H), 7.56 – 7.50 (m, 2H), 6.93 – 6.86 (m, 2H), 3.85 (s, 3H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -83.54 (t, *J* = 4.0 Hz, 3F), -114.51 (q, *J* = 4.0 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 160.7, 151.0 (t, *J*_{C-F} = 0.9 Hz), 143.4 (t, *J*_{C-F} = 30.0 Hz), 134.3, 133.0, 128.5, 127.3, 127.1, 125.6, 123.8, 120.9, 120.4, 118.3, 114.2, 113.0, 108.4 (m), 84.2, 82.5 (t, *J*_{C-F} = 1.7 Hz), 72.3 (t, *J*_{C-F} = 1.3 Hz), 67.6 (t, *J*_{C-F} = 1.0 Hz), 55.4 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₅H₁₄F₅O₂ [M+H]⁺ 441.0908, found: 441.0910.



(*E*)-2-(Perfluoroethyl)-3-(4-phenylbut-3-en-1-yn-1-yl)naphtho[1,2-*b*]furan (6):

Yield = 46% (38 mg). Light yellow solid. M.p. 139.7-141.5 °C.

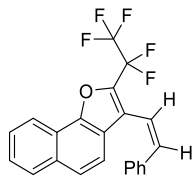
IR (KBr): ν = 3027, 2202, 1581, 809, 740 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.30 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 1.6 Hz, 2H), 7.67 – 7.54 (m, 2H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.29 (m, 3H), 7.15 (d, *J* = 16.3 Hz, 1H), 6.45 (d, *J* = 16.3 Hz, 1H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -83.54 (t, *J* = 2.7 Hz, 3F), -114.33 (q, *J* = 2.7 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 151.0 (t, *J* = 1.1 Hz), 143.1, 141.4 (t, *J*_{C-F} = 31.0 Hz), 135.8, 132.9, 129.1, 128.8, 128.4, 127.1, 126.9, 126.5, 125.3, 123.5 (t, *J*_{C-F} = 1.3 Hz), 120.9, 120.3, 118.3, 109.5 (m), 107.2, 97.5, 78.3 (t, *J* = 1.2 Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₄H₁₄F₅O [M+H]⁺ 413.0959, found: 413.0956.



(Z)-2-(Perfluoroethyl)-3-styrylnaphtho[1,2-*b*]furan (7):

Yield = 98% (66 mg). Yellow solid. M.p. 75.7-77.3 °C.

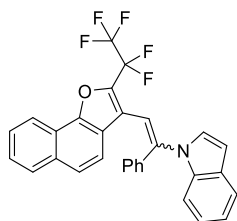
IR (KBr): $\nu = 3034, 1595, 814, 753 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.34$ (d, $J = 8.2$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.65 – 7.58 (m, 1H), 7.56 – 7.50 (m, 1H), 7.39 (d, $J = 8.8$ Hz, 1H), 7.17 (dd, $J = 7.2, 2.5$ Hz, 2H), 7.14 – 7.08 (m, 3H), 6.96 (d, $J = 12.2$ Hz, 1H), 6.91 (d, $J = 8.7$ Hz, 1H), 6.69 (dt, $J = 12.1, 3.5$ Hz, 1H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.73$ (t, $J = 3.6$ Hz, 3F), -114.21 (q, $J = 3.6$ Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 151.4$ (t, $J_{\text{C-F}} = 1.1$ Hz), 137.0 (t, $J_{\text{C-F}} = 30.4$ Hz), 136.3, 135.2 (t, $J_{\text{C-F}} = 1.6$ Hz), 132.4, 128.9, 128.3, 128.3, 127.8, 126.8, 126.6, 124.1, 123.4 (t, $J_{\text{C-F}} = 2.2$ Hz), 121.4 (t, $J_{\text{C-F}} = 1.0$ Hz), 121.0, 120.4, 119.8, 116.1 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₂H₁₄F₅O [M+H]⁺ 389.0959, found: 389.0953.



1-(2-(2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)-1-phenylvinyl)-1H-indole (8):

Yield = 75% (58 mg, *Z/E* = 1/3). White solid. M.p. 73.0-74.3 °C.

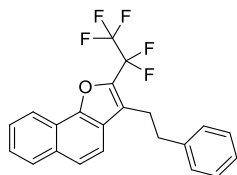
IR (KBr): $\nu = 3028, 1563, 1212, 810, 743 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.36 - 8.22$ (m, 1H), 7.83 – 7.65 (m, 1H), 7.64 – 7.31 (m, 7H), 7.27 – 7.22 (m, 1H), 7.19 – 6.97 (m, 5H), 6.94 – 6.85 (m, 1H), 6.67 – 6.38 (m, 2H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): $\delta = -83.35 - -83.55$ (m, 3F), $-113.20 - -113.85$ (m, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 150.9$ (m), 141.8 (t, $J_{\text{C-F}} = 1.4$ Hz), 137.3, 136.1, 135.5, 132.4, 129.7, 129.7, 129.2, 129.0, 128.8, 128.1, 127.5, 126.7, 126.5, 124.3, 122.4, 121.4 (m), 120.9, 120.7, 120.5, 120.3, 118.3, 112.2, 108.9 (m), 104.6 (m) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₃₀H₁₉F₅NO [M+H]⁺ 504.1381, found: 504.1378.



2-(Perfluoroethyl)-3-phenethylnaphtho[1,2-*b*]furan (9):

Yield = 76% (60 mg). Light yellow solid. M.p. 68.6-69.9 °C.

IR (KBr): $\nu = 3025, 1523, 802, 753 \text{ cm}^{-1}$.

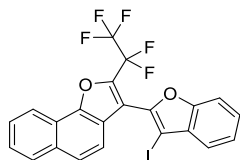
¹H NMR (400 MHz, CDCl₃): $\delta = 8.37 - 8.30$ (m, 1H), 7.97 – 7.92 (m, 1H), 7.69 (d, $J = 8.6$ Hz, 1H), 7.64 (t, $J = 7.1$ Hz, 1H), 7.60 – 7.55 (m, 1H), 7.50 (d, $J = 8.6$ Hz, 1H), 7.31 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 3.24 – 3.16 (m,

2H), 3.04 – 2.97 (m, 2H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -83.94 (t, J = 2.8 Hz, 3F), -113.65 (q, J = 2.8 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 151.1 (t, J_{C-F} = 1.2 Hz), 142.6 (t, J_{C-F} = 30.2 Hz), 140.8, 132.5, 128.5, 128.4, 128.3, 128.2, 126.9, 126.5, 126.3, 124.3, 123.3, 121.1, 120.5, 117.9, 36.7, 25.6 (t, J_{C-F} = 1.9 Hz) ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₂H₁₆F₅O [M+H]⁺ 391.1116, found: 391.1115.



3-(3-Iodobenzofuran-2-yl)-2-(perfluoroethyl)naphtho[1,2-b]furan (10):

Yield = 99% (52 mg). White solid. M.p. 118.3-119.7 °C.

IR (KBr): ν = 2923, 1537, 1220, 809, 745, 562 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.40 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.65 – 7.51 (m, 4H), 7.48 – 7.36 (m, 2H) ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ = -83.12 (t, J = 3.3 Hz, 3F), -114.03 (q, J = 3.3 Hz, 2F) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 154.9, 151.3, 145.8, 140.0 (t, J_{C-F} = 32.3 Hz), 132.9, 131.1, 128.5, 127.3, 127.1, 126.3, 125.4, 123.8, 122.2, 121.8, 121.0, 120.4, 119.4, 116.3 (m), 111.6, 68.5 ppm; carbons corresponding to the C₂F₅ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for C₂₂H₁₁F₅IO₂ [M+H]⁺ 528.9718, found: 528.9719.

11. References

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

