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Supporting Information

Copper-Catalyzed Pentafluoroethylation of Aryl/Alkenyl Iodides

with Pentafluoroethylsilane

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Experimental Procedures and Spectral Data

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I. General Experimental.

Unless otherwise noted, reactions were carried out in a 10 mL glass tube with magnetic stirring. Reactions that require heating were carried out in the oil bath. Analytical thin layer chromatography (TLC) was performed with Merck silica gel 60 F_{254} aluminum plates. Visualization was done under a UV lamp (254 nm) and by immersion in potassium permanganate (KMnO₄), followed by heating using a heat gun. Organic solutions were concentrated by rotary evaporation at 23-35 °C. Purification of reaction products were generally done by flash column chromatography with Silicycle 60-230 mesh silica gel.

II. Materials.

Halocarbon 125-Pentafluoroethane (Purity: 99.0% min., 9.1kg in 16 L size cylinder) was purchased from SCIENTIFIC GAS ENGINEERING CO., LTD. Copper(I) iodide (extra pure, 99.99%) was purchased from Acros. Potassium fluoride (97%) and anhydrous DMF was purchased from J&K Scientific. Other chemicals for substrates preparation were purchased from Acros, J&K Scientific, Aldrich, Bide and Dikemann.

III. Instrumentation.

Proton nuclear magnetic resonance spectra (¹H NMR), carbon nuclear magnetic resonance spectra (¹³C NMR) and fluorine nuclear magnetic resonance spectra (¹⁹F NMR) were recorded at 23 °C on Bruker 400 MHz or 500 MHz spectrometer in CDCl₃. Chemical shifts of ¹H NMR spectra were reported as parts per million in δ scale using residual solvent signal (CDCl₃: 7.26 ppm) or tetramethylsilane (0.00 ppm) as internal standard. Chemical shifts of ¹³C NMR spectra were reported using residual solvent signal of CDCl₃ (77.16 ppm) on the δ scale. Chemical shifts of ¹⁹F NMR were reported as parts per million in δ scale using benzotrifluoride (-63.72 ppm) as internal standard. Data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J*, Hz) and integration. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95XL GC Mass Spectrometer or a Thermo Scientific Q Exactive Focus Mass Spectrometer or a Bruker SolariX 9.4T FTMS with Q Exactive Focus Orbitrap.

Substrates 1 (Aryl iodides)



Note: Substrates **1a-1l**, **1o**, **1v**, **1x**, **1z-1af** are commercially available. Substrates **1m**, **1n**,**1p-1u**, **1w**, **1y** can be prepared from literature procedures¹⁻¹⁰.

Substrates 3 (Alkenyl iodides)



Note: Substrate **3h** is commercially available. Substrates **3a-3g** can be prepared according to general procedures.

IV. Experimental Procedures

General Procedure (I) (cf. Scheme 4) for the synthesis of alkenyl iodides (3a-3f).



Alkenyl iodides (**3a-3f**) were synthesized according to the literature procedure¹¹. To a solution of Et₂O was added NaHMDS/LiHMDS (1.0 M solution in THF, 3.0 equiv.) dropwise at -78 °C under Argon. CH₂I₂ (1.5 equiv.) was added dropwise at the same temperature. After 20-30 min, benzyl bromide (1.0 equiv.) was added and the reaction system was allowed to stir at -78 °C for 1-1.5h and then warm up to room temperature. DBU (1.0 equiv.) was added at room temperature and the reaction system was stirred for another 1h. When the reaction was completed (monitored by TLC), it was diluted by Et₂O and filtered through a pad of Celite. The residue was dried over Na₂SO₄ and the solvent was removed by reduced pressure. Purification on column chromatography afforded the corresponding product.

General Procedure (II) (cf. Scheme 4) for the synthesis of alkenyl iodide (3g).



Alkenyl iodide (**3g**) was synthesized according to the literature procedure¹². A round bottom flask charged with $ZrCp_2Cl_2$ (1.46 g, 5 mmol) was added 5 ml THF. The superhydried solution (1.0 M in THF, 5 mmol) was added dropwise. The solution was stirred in the dark for 2 h before a solution of the but-3-yn-1-ylbenzene (325 mg, 2.5 mmol) in THF (5 ml) was added. The reaction stirred for 15 min and cooled to 0°C, then the NIS (1.13 g, 5 mmol) in 5 ml THF solution was added dropwise. The reaction mixture was stirred for 2 h then quenched by NH₄Cl solution. The reaction mixture was extracted with Et₂O (3 × 30 ml). The combined organic layers were washed with H₂O (3 × 10 ml), then brine (3 × 10 ml), dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford products **3g** (335 mg, 52%).

General Procedure (III) (cf. Scheme 5) for the synthesis of aryl iodide (5).



Aryl iodide (5) was synthesized according to the literature procedure¹³. A round bottom flask charged with 4-iodobenzaldehyde (1.160 g, 5 mmol) and 4-bromobenzylamine (930 mg, 5 mmol) was dissolved in MeOH/AcOH (60 ml, v / v = 99:1) solution. Sodium borohydride (285 mg, 7.5 mmol) was added to the stirring solution slowly. The reaction mixture was stirred at room temperature for 12 h then poured into NaHCO₃ solution. The reaction mixture was extracted with Ethyl acetate (3×30 ml). The combined organic layers were washed with H₂O (3×10 ml), then brine (3×10 ml), dried over MgSO₄ and concentrated in vacuo. The obtained yellow solid was used directly without further purification. A round

bottom flask charged with 4-Toluenesulfonyl chloride (1.14 g, 6 mmol), K_2CO_3 (828 mg, 6mmol) and previous obtained solid were dissolved in 20 ml acetone then stirred at room temperature for 12 h. The reaction mixture was extracted with Ethyl acetate (3 × 30 ml). The combined organic layers were washed with H₂O (3 × 10 ml), then brine (3 × 10 ml), dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (EA : Hexane = 1: 6) on silica gel to afford product **5** as white solid (675 mg, 49%).

General Procedure (IV) for the synthesis of Et₃SiCF₂CF₃.

Et₃SiCl + HCF₂CF₃
$$\xrightarrow{n-BuLi (1.25 equiv)}$$
 Et₃SiCF₂CF₃ Et₂O, -78 °C to rt, 12 h

Et₃SiCF₂CF₃ was synthesized according to the literature procedure.¹⁴ To a round bottom flask, 250 ml diethyl ether was cooled down to -78 °C. Pentafluoroethane was bubbled into diethyl ether for 3 hours followed by adding a solution of *n*-BuLi (100 ml, 2.5 M in hexane, 250 mmol, 1.25 equiv) carefully so that the temperature of the reaction system didn't exceed -60 °C. After stirring for 1 h, the solution of triethylchlorosilane (21.72 g, 200 mmol, 1 equiv) in diethyl ether was added within 5 min. The mixture was allowed to warm up to room temperature slowly for 12 h. The mixture was filtered through a pad of Celite and concentrated to dryness to afford the crude product. The product was purified by distillation in vacuo and obtained a colorless liquid (33.7 g, 72%). The purity of the product was determined by ¹H NMR and ¹⁹F NMR. The spectra are in full accordance with the literature report.¹⁴

General procedure (V) (*cf.* Scheme 3&4) for copper-catalyzed pentafluoroethylation of aryl/alkenyl iodides



To an oven-dried glass tube equipped with a stir bar was added aryl iodide **1** or **3** (0.2 mmol, if it was a solid substrate), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in the glovebox. The reaction vial was sealed with a rubber septum and removed from the glovebox. Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol), iodide **1** or **3** (if it was a liquid substrate) and DMF (2.0 ml) was then added to the vial through the syringe under argon. The resulting mixture was stirred at 90°C for 36 hours. After cooling to room temperature, the crude sample was analyzed by ¹⁹F NMR using benzotrifluoride (12 μ L, 0.1 mmol) as internal standard. The reaction mixture was extracted with CH₂Cl₂ (3 × 10 ml). The combined organic layers were washed with H₂O (2 × 10 ml), then brine (2 × 10 ml), dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford products **2** or **4**.

4 mmol scale synthesis of 2b:



To an oven-dried round bottom flask equipped with a stir bar was added aryl iodide **1b** (1.12 g, 4.0 mmol), CuI (152.0 mg, 0.8 mmol), 1,10-Phenanthroline (144.0 mg, 0.8 mmol) and Potassium fluoride (928.0 mg, 16 mmol) in the glovebox. The reaction vial was sealed with a rubber septum and removed from the glovebox. Pentafluoroethyl triethylsilane (3.748 g, 16 mmol) and DMF (40.0 ml) was then added to the vial through the syringe under argon. The resulting mixture was stirred at 90°C for 36 hours. After cooling to room temperature, the crude sample was analyzed by ¹⁹F NMR using benzotrifluoride (12 μ L, 0.1 mmol) as internal standard. The reaction mixture was extracted with CH₂Cl₂ (3 × 30 ml). The combined organic layers were washed with H₂O (2 × 30 ml), then brine (2 × 30 ml), dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford product **2b** (990.8 mg, 91%).

1 mmol scale synthesis of 2ab:



To an oven-dried round bottom flask equipped with a stir bar was added aryl iodide **1ab** (369.2 mg, 1.0 mmol), CuI (38.0 mg, 0.2 mmol), 1,10-Phenanthroline (36.0 mg, 0.2 mmol) and Potassium fluoride (232.0 mg, 4.0 mmol) in the glovebox. The reaction vial was sealed with a rubber septum and removed from the glovebox. Pentafluoroethyl triethylsilane (937.0 mg, 4.0 mmol) and DMF (10.0 ml) was then added to the vial through the syringe under argon. The resulting mixture was stirred at 90°C for 36 hours. After cooling to room temperature, the crude sample was analyzed by ¹⁹F NMR using benzotrifluoride (12 μ L, 0.1 mmol) as internal standard. The reaction mixture was extracted with CH₂Cl₂ (3 × 30 ml). The combined organic layers were washed with H₂O (2 × 30 ml), then brine (2 × 30 ml), dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford product **2ab** (346.5 mg, 96%).

3 mmol scale synthesis of 4g:



To an oven-dried round bottom flask equipped with a stir bar was added aryl iodide **3g** (774 mg, 3.0 mmol), CuI (114.0 mg, 0.6 mmol), 1,10-Phenanthroline (108.0 mg, 0.6 mmol) and Potassium fluoride (696.0 mg, 12.0 mmol) in the glovebox. The reaction vial was sealed with a rubber septum and removed

from the glovebox. Pentafluoroethyl triethylsilane (2.811 g, 12.0 mmol) and DMF (30.0 ml) was then added to the vial through the syringe under argon. The resulting mixture was stirred at 90 °C for 36 hours. After cooling to room temperature, the crude sample was analyzed by ¹⁹F NMR using benzotrifluoride (12 μ L, 0.1 mmol) as internal standard. The reaction mixture was extracted with CH₂Cl₂ (3 × 30 ml). The combined organic layers were washed with H₂O (2 × 30 ml), then brine (2 × 30 ml), dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford product **4g** (525.0 mg, 70%).

Suzuki Reaction (cf. Scheme 5)



To an oven-dried glass tube equipped with a stir bar was added Pd(PPh₃)₄ (4.2 mg, 0.00365 mmol), 3methoxyphenylboronic acid (26.6 mg, 0.175 mmol) and K₂CO₃ (48.3 mg, 0.350 mmol). The tube was sealed with a septum, evacuated and refilled with argon three times. A solution of **6** and **6'** (80.0 mg, 0.146 mmol) in 0.6 mL dioxane and 120 μ L H₂O was added under argon through syringe. The resulting mixture was heated at 95 °C with stirring in an oil bath for 12 h. After cooling to room temperature, the reaction mixture was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were washed with H₂O (2 × 10 mL), then brine (2 × 10 mL), dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford product **7** as a white solid (62.8 mg, 72% yield).

General procedure (VI) (cf. Scheme 7) for photocatalyzed hydrodefluorination reaction of 2



To an oven-dried glass tube equipped with a stir bar was added pentafluoroethyl benzene **2** (0.2 mmol, if it was a solid substrate), Ammonium formate (50.4mg, 0.8 mmol) and 1-Napth-PTH (7.5 mg, 0.02 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon three times, pentafluoroethyl benzene **2** (0.2 mmol, if it was a liquid substrate) and DMSO (1.0 mL) was added through syringe under argon. The mixture was exposed to a blue LED (Aijiadian, 440-450 nm, $\lambda_d = 444.9$ nm, $\lambda_p = 437.9$ nm, 99.3% purity) and stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was extracted with CH₂Cl₂ (3 × 10 ml). The combined organic layers were washed with H₂O (2 × 10 ml), then brine (2 × 10 ml), dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford products **8**.

Figure 1. Potocatalyzed hydrodefluorination reaction equipment set up



V. Optimization Tables





 $X = Ph \text{ or } NO_2$



	Substrate	CuX	Ligand	TESC ₂ F ₅	F source	T /°C	Time/ h	Yield ^a
1	X = Ph	Cul (10 mol%)	L1 (10 mol%)	2 equiv	KF (2 equiv)	60	24	31%
2	X = Ph	CuCl (10 mol%)	L1 (10 mol%)	2 equiv	KF (2 equiv)	60	24	30%
3	X = Ph	CuOAc (10mol%)	L1 (10 mol%)	2 equiv	KF (2 equiv)	60	24	0%
4	X = Ph	Cul (10 mol%)	L2 (10 mol%)	2 equiv	KF (2 equiv)	60	24	80%
5	X = Ph	Cul (10 mol%)	L3 (10 mol%)	2 equiv	KF (2 equiv)	60	24	7%
6	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	KF (2 equiv)	60	24	87%
7	X = Ph	Cul (10 mol%)	L5 (10 mol%)	2 equiv	KF (2 equiv)	60	24	64%
8	X = Ph	Cul (10 mol%)	L6 (10 mol%)	2 equiv	KF (2 equiv)	60	24	30%
9	X = Ph	Cul (10 mol%)	BINAP(10 mol%)	2 equiv	KF (2 equiv)	60	24	15%
10	X = Ph	Cul (5 mol%)	L4 (10 mol%)	2 equiv	KF (2 equiv)	60	24	87%
11	X = Ph	Cul (10 mol%)	١	2 equiv	KF (2 equiv)	60	24	15%
12	X = Ph	Phen-Cu-I (10 mol%) ^b	١	2 equiv	KF (2 equiv)	60	24	61%
13	X = Ph	Cul (10 mol%)	L4 (10 mol%)	1 equiv	KF (1 equiv)	60	24	37%
14	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2.5 equiv	KF (2.5 equiv)	60	24	55%
15	X = Ph	Cul (10 mol%)	L4 (10 mol%)	3 equiv	KF (3 equiv)	60	24	19%
16	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	KF (1 equiv)	60	24	50%
17	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	KF (4 equiv)	60	24	55%
16	X = Ph	CuCl (10 mol%)	L4 (10 mol%)	2 equiv	KF (2 equiv)	60	24	70%
17	X = Ph	Cul (10 mol%)	L4(10 mol%)	2 equiv	KF (2 equiv)	75	24	99%
18	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	KF (2 equiv)	90	24	96%
19	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	KF (2 equiv)	r.t.	24	33%
20	X = Ph	Cul (5 mol%)	L4 (5 mol%)	2 equiv	KF (2 equiv)	75	24	18%
21	X = Ph	Cul (2.5 mol%)	L4 (2.5 mol%)	2 equiv	KF (2 equiv)	75	24	23%
22	X = Ph	Cul (1 mol%)	L4 (1 mol%)	2 equiv	KF (2 equiv)	75	24	4%
23	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	/	75	24	4%
24	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	K ^t OBu (2 equiv)	75	24	4%

25	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	KOAc(2 equiv)	75	24	12%
26	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	K ₃ PO ₄ (2 equiv)	75	24	29%
27	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	Li ^t OBu(2 equiv)	75	24	14%
28	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	AgF(2 equiv)	75	24	19%
29	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	FeF3 (2equiv)	75	24	0%
30	X = Ph	Cul (10 mol%)	L4 (10 mol%)	2 equiv	KF (2 equiv)	90	36	>99%(85%) ^c
31	$X = NO_2$	Cul (10 mol%)	L1 (10 mol%)	2 equiv	KF (2 equiv)	90	36	47%
32	X = NO ₂	Cul (10 mol%)	L2 (10 mol%)	2 equiv	KF (2 equiv)	90	36	39%
33	$X = NO_2$	Cul (10 mol%)	L4 (10 mol%)	2 equiv	KF (2 equiv)	90	36	40%
34	$X = NO_2$	Cul (10 mol%)	L5 (10 mol%)	2 equiv	KF (2 equiv)	90	36	27%
35	$X = NO_2$	Cul (10 mol%)	L6 (10 mol%)	2 equiv	KF (2 equiv)	90	36	20%
36	$X = NO_2$	Cul (10 mol%)	PCy₃(10 mol%)	2 equiv	KF (2 equiv)	90	36	18%
37	$X = NO_2$	Cul (10 mol%)	Xantphos (10 mol%)	2 equiv	KF (2 equiv)	90	36	13%
38	$X = NO_2$	CuCl (10 mol%)	IPr (10 mol%)	2 equiv	KF (2 equiv)	90	36	0%
39	$X = NO_2$	CuCl (10 mol%)	IMes (10 mol%)	2 equiv	KF (2 equiv)	90	36	0%
40	$X = NO_2$	CuCl (10 mol%)	SIMes (10 mol%)	2 equiv	KF (2 equiv)	90	36	11%
41	$X = NO_2$	CuCl (10 mol%)	L1 (10 mol%)	2 equiv	KF (2 equiv)	90	36	38%
42	$X = NO_2$	CuCl (10 mol%)	L5 (10 mol%)	2 equiv	KF (2 equiv)	90	36	38%
43	$X = NO_2$	Cul (10 mol%)	L4 (10 mol%)	2 equiv	KF (2 equiv)	60	36	23%
44	$X = NO_2$	Cul (20 mol%)	L4 (20 mol%)	2 equiv	KF (2 equiv)	90	36	50%
45	$X = NO_2$	Cul (20 mol%)	L1 (20 mol%)	2 equiv	KF (2 equiv)	90	36	69%
46	$X = NO_2$	Cul (20 mol%)	L1 (40 mol%)	2 equiv	KF (2 equiv)	90	36	44%
47	$X = NO_2$	Cul (20 mol%)	L1 (20 mol%)	4 equiv	KF (4 equiv)	90	36	81%
48	$X = NO_2$	Phen-Cu-I (10mol%) [♭]	١	2 equiv	KF (2 equiv)	90	36	35%

^a Unless specified otherwise, reactions were carried out in DMF (0.1 M). The product yield was determined by ¹⁹F NMR using

benzotrifluoride as an internal standard. ^bPhen-Cu-I was synthesized according to literature report and used directly without characterization. ^cisolated yield in bracket.

Table2. Reaction condition optimization for photocatalyzed hydrodefluorination of 2f

		F, CF ₃ HCO ₂ M Photocatalyst Additives CO ₂ Et 0.1 mmol 2f	$\overset{H}{\longrightarrow} \overset{CF_{3}}{\underset{CO_{2} \text{Et}}{\overset{H}{\longrightarrow}}}$	+ E	CF_3 CO ₂ Et 8a'		
Entry ^a	HCO ₂ M	Photocatalyst	Additives	Solvent	Time / h	8a ^a	8a'
1	HCO ₂ Cs (4 equiv)	10 mol% PTH	10 mol% CySH	DMSO	12	35%	44%
2	HCO ₂ Cs (4 equiv)	10 mol% 1-Napth-PTH	10 mol% CySH	DMSO	12	51%	15%
3	HCO ₂ Na (4 equiv)	10 mol% 1-Napth-PTH	10 mol% CySH	DMSO	12	42%	14%
4	HCO ₂ K (4 equiv)	10 mol% 1-Napth-PTH	10 mol% CySH	DMSO	12	41%	34%
5	HCO ₂ NH ₄ (4 equiv)	10 mol% 1-Napth-PTH	10 mol% CySH	DMSO	12	99%	0
6	HCO ₂ NH ₄ (3 equiv)	10 mol% 1-Napth-PTH	10 mol% CySH	DMSO	12	55%	8%
7	HCO ₂ NH ₄ (2 equiv)	10 mol% 1-Napth-PTH	10 mol% CySH	DMSO	12	79%	1%
8	HCO ₂ NH ₄ (4 equiv)	10 mol% 1-Napth-PTH	λ	DMSO	12	99%	0
9	HCO ₂ NH ₄ (4 equiv)	5 mol% 1-Napth-PTH	١	DMSO	12	70%	12%
10	HCO ₂ NH ₄ (4 equiv)	2 mol% 1-Napth-PTH	١	DMSO	12	0	0
11	HCO ₂ NH ₄ (4 equiv)	5 mol% 4-CZIPN	١	DMSO	12	0	56%
12	HCO ₂ NH ₄ (8 equiv)	5 mol% 4-CZIPN	١	DMSO	36	55%	44%
13	HCO ₂ NH ₄ (4 equiv)	5 mol% 3DPAFINPN	١	DMSO	12	60%	36%
14	HCO ₂ NH ₄ (4 equiv)	5 mol% 3DPA2FIBN	١	DMSO	12	99%	0
15	HCO ₂ NH ₄ (4 equiv)	5 mol% Acridinium BF4	١	DMSO	12	0	0
16	HCO ₂ NH ₄ (4 equiv)	5 mol% Ru(bpy) ₃ Cl ₂ ·6H ₂ O	١	DMSO	12	0	0
17 ^b	HCO ₂ NH ₄ (4 equiv)	10 mol% 1-Napth-PTH	١	DMSO	12	0	0
18	HCO ₂ NH ₄ (4 equiv)	Ι	١	DMSO	12	0	15%
19°	HCO ₂ NH ₄ (4 equiv)	10 mol% 1-Napth-PTH	١	DMSO	12	0	0
20	HCO ₂ NH ₄ (4 equiv)	10 mol% 1-Napth-PTH	١	EA	12	0	0
21	HCO ₂ NH ₄ (4 equiv)	10 mol% 1-Napth-PTH	١	CH₃CN	12	0	34%
22	HCO ₂ NH ₄ (4 equiv)	10 mol% 1-Napth-PTH	١	Toluene	12	0	4%
23	HCO ₂ NH ₄ (4 equiv)	10 mol% 1-Napth-PTH	١	DMF	12	0	0
24	HCO ₂ NH ₄ (4 equiv)	10 mol% 1-Napth-PTH	١	THF	12	0	0
25	HCO ₂ NH ₄ (4 equiv)	10 mol% 1-Napth-PTH	١	Acetone	12	0	11%

a: Reactions were under argon, yields are determined by ¹⁹F NMR with PhCF₃ as an internal standard; **b**: with art blue I_{3} EP as a second data (air)

without blue LED; c: In sealed tube (air).



General procedure for synthesis of 8a' in 0.2 mmol scale



To an oven-dried glass tube equipped with a stir bar was charged with ammonium formate (50.4 mg, 0.8 mmol) and 4-CZIPN (7.9 mg, 0.01 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon three times, pentafluoroethyl benzene **2f** (53.6 mg, 0.2 mmol) and DMSO (2.0 mL) was added through syringe under argon. The mixture was exposed to a blue LED and stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was analyzed by ¹⁹F NMR with using benzotrifluoride as an internal standard and got 38% crude ¹⁹F NMR yield. The reaction mixture was subjected to GC-MS analysis.

Crude ¹⁹F NMR spectrum of the reaction with benzotrifluoride as an internal standard



¹⁹F NMR chemical shift



GC-MS analysis of the reaction mixture.



VI. Proposed catalytic cycle

Scheme 1. Proposed catalytic cycle for Copper-Catalyzed Pentafluoroethylation of Aryl/Alkenyl Iodides



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VIII. Characterization

4-(perfluoroethyl)-1,1'-biphenyl (2b)

Following the general procedure V, reaction was run using aryl iodide **1b** (56.0 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (hexane) and obtained as a white solid (48.4 mg, 89% yield), $R_f = 0.55$ (hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.45 – 7.39 (m, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.7 (s, 3F), -115.7 (s, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 145.0 (t, J = 1.8 Hz), 139.8, 129.2, 128.4, 127.6, 127.4, 127.1 (t, J = 6.3 Hz), 127.6 (t, J = 24.3 Hz), 119.3 (qt, J = 286.0, 39.5 Hz), 115.2 (tq, J = 252.7, 38.2 Hz). The spectra are in full accordance with the literature report.¹⁵

4-(Perfluoroethyl)benzonitrile (2e)

Following the general procedure V, reaction was run using aryl iodide **1e** (45.8 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (DCM : Hexane = 1 : 5) and obtained as a yellow liquid (34.5 mg, 78% yield), R_f = 0.25 (DCM : Hexane = 1 : 5). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -85.1 (s, 3F), -116.2 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 133.0 (t, J = 24.2 Hz), 132.7, 127.5 (t, J = 6.4 Hz), 118.9 (qt, J = 284.4, 38.3 Hz), 117.5, 116.4, 112.8 (tq, J = 253.3, 38.3 Hz). The spectra are in full accordance with the literature report. ¹⁵

ethyl 4-(perfluoroethyl)benzoate (2f)



Following the general procedure V, reaction was run using aryl iodide **1f** (55.2 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (DCM / Hexane = 1:10) and obtained as a yellow liquid (40.7 mg, 76% yield), $R_f = 0.2$ (DCM / Hexane = 1:10). ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, J = 8.0, 2H), 7.67 (d, J = 8.3 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.7 (s, 3F), -115.4 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 165.6, 134.0, 132.8 (t, J = 23.9 Hz), 130.0, 126.7 (t, J = 6.2 Hz), 119.1 (qt, J = 285.9, 38.9 Hz), 113.2 (tq, J = 254.3, 38.3 Hz), 61.7, 14.4. The spectra are in full accordance with the literature report.¹⁵

benzyl 4-(perfluoroethyl)benzoate (2g)



Following the general procedure **V**, reaction was run using aryl iodide **1g** (67.2 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (DCM / Hexane = 1:10) and obtained as a yellow solid (29.7 mg, 45% yield), R_f = 0.35 (DCM / Hexane = 1:5). ¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.44 – 7.35 (m, 3H), 5.41 (s, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.6 (s, 3F), -115.4 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 165.3, 135.7, 133.7 (t, J = 2.1 Hz), 133.0 (t, J = 24.0 Hz), 130.1, 128.8, 128.6, 128.5, 126.8 (t, J = 6.3 Hz), 119.0 (qt, J = 286.1, 38.8 Hz), 113.2 (tq, J = 254.3, 38.5 Hz), 67.4. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₆H₁₁F₅O₂ 353.0571; Found 353.0567.

1-(benzyloxy)-4-(perfluoroethyl)benzene (2i)



Following the general procedure V, reaction was run using aryl iodide **1i** (62.0 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (hexane) and obtained as a white solid (39.0 mg, 65% yield), $R_f = 0.40$ (hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, J = 8.5 Hz, 2H), 7.47 – 7.31 (m, 5H), 7.06 (d, J = 8.5 Hz, 2H), 5.12 (s, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.9 (s, 3F), -113.9 (s, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 161.6, 136.4, 128.9, 128.4, 128.2 (t, J = 6.3 Hz), 127.6, 121.1 (t, J = 24.6 Hz), 115.1, 119.24 (qt, J = 286.0, 40.3 Hz), 113.4 (dq, J = 253.4, 38.2 Hz), 70.4. The spectra are in full accordance with the literature report.¹⁵

1-(benzyloxy)-2-(perfluoroethyl)benzene (2j)

Following the general procedure V, reaction was run using aryl iodide **1j** (62.0 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (hexane) and obtained as a colorless liquid (51.6 mg, 85% yield), $R_f = 0.40$ (hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, J = 7.9 Hz, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.37 – 7.31 (m, 1H), 7.10 – 7.04 (m, 2H), 5.17 (s, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -83.6 (s, 3F), -111.7 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 157.4 (t, J = 2.7 Hz), 136.5, 133.6, 129.2 (t, J = 8.5 Hz), 128.7, 128.1, 127.0, 120.7, 119.7(qt, J = 286.9, 39.1 Hz), 117.1 (t, J = 22.6 Hz),

114.0 (tq, *J* = 254.8, 39.6 Hz), 113.7, 70.6. **HRMS** (ESI) m/z: [M+Na]⁺ Calcd for C₁₅H₁₁F₅O 325.0622; Found 325.0624.

ethyl 2-(perfluoroethyl)benzoate (21)

Following the general procedure V, reaction was run using aryl iodide **11** (55.2 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (DCM / Hexane = 1:10) and obtained as a yellow liquid (31.1 mg, 58% yield), $R_f = 0.2$ (DCM / Hexane = 1:10). ¹H NMR (500 MHz, CDCl₃) δ 7.73 – 7.49 (m, 4H), 4.37 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -83.2 (s, 3F), -108.5 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 168.0, 133.7 (t, J = 3.3 Hz), 132.0, 130.3, 129.2, 128.3 (t, J = 7.2 Hz), 126.0 (t, J = 23.5 Hz), 119.1 (qt, J = 286.9, 38.7 Hz), 113.8 (tq, J = 255.4, 39.1 Hz), 62.2, 13.9. The spectra are in full accordance with the literature report.¹⁶

benzyl 2-(perfluoroethyl)benzoate (2m)



Following the general procedure V, reaction was run using aryl iodide **1m** (67.2 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (DCM / Hexane = 1:10) and obtained as a yellow oil (41.0 mg, 62% yield), R_f = 0.25 (DCM / Hexane = 1:5). ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.54 (m, 4H), 7.52 – 7.34 (m, 5H), 5.38 (s, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -83.1 (s, 3F), -108.5 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 167.6, 135.1, 133.1 (t, *J* = 3.2 Hz), 131.9, 130.4, 129.1, 128.7, 128.6, 128.6, 128.2 (t, *J* = 7.3 Hz), 126.0 (t, *J* = 23.6 Hz), 119.0 (qt, *J* = 287.0, 38.6 Hz), 113.6 (tq, *J* = 255.6, 39.1 Hz), 68.0. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₆H₁₁F₅O₂ 335.0571; Found 353.0571.

hexyl 2-(perfluoroethyl)benzoate (2n)

Following the general procedure **V**, reaction was run using aryl iodide **1n** (66.4 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA / Hexane = 1:20) and obtained as a yellow liquid (58.3 mg, 90% yield), R_f = 0.35 (EA / Hexane = 1:20). ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.48 (m, 4H), 4.31 (t, *J* = 6.8 Hz, 2H), 1.72 (p, *J* = 6.9 Hz, 2H), 1.51 – 1.15 (m, 6H), 1.01 – 0.75 (m, 3H). ¹⁹F NMR

(471 MHz, CDCl₃) δ -83.2 (s, 3F), -108.6 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 168.1, 133.7 (t, *J* = 3.2 Hz), 132.0, 130.3, 129.2, 128.3 (td, *J* = 7.3, 1.7 Hz), 126.0 (t, *J* = 23.6 Hz), 119.1 (qt, *J* = 286.9, 38.8 Hz), 113.7 (tq, *J* = 255.5, 39.2 Hz), 66.5, 31.5, 28.4, 25.6, 22.6, 14.1. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₅H₁₇F₅O₂ 347.1041; Found 347.1037.

2-(4-(perfluoroethyl)phenyl)-1,3-dioxolane (2p)



Following the general procedure V, reaction was run using aryl iodide **1p** (55.2 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA: hexane = 1:5) and obtained as a colorless oil (25.7 mg, 48% yield), R_f = 0.2 (EA: hexane = 1:5). ¹H NMR (500 MHz, CDCl₃) δ 7.62 (s, 4H), 5.87 (s, 1H), 4.39 – 3.89 (m, 4H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.7 (s, 3F), -114.9 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 142.2 (t, *J* = 1.5 Hz), 129.9, 129.5 (t, *J* = 24.0 Hz), 126.7 (t, *J* = 6.3 Hz), 119.2 (qt, *J* = 286.0, 39.3 Hz), 112.1 (tq, *J* = 254.5, 38.1 Hz), 102.9, 65.6. The spectra are in full accordance with the literature report.¹⁷

naphthalen-2-yl 2-(perfluoroethyl)benzoate (2q)



Following the general procedure **V**, reaction was run using aryl iodide **1q** (74.8 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (hexane) and obtained as a white solid (57.9 mg, 79% yield), R_f = 0.15 (hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.9 Hz, 1H), 7.92 – 7.83 (m, 3H), 7.78 – 7.70 (m, 2H), 7.72 – 7.64 (m, 2H), 7.58 – 7.48 (m, 2H), 7.41 (dd, *J* = 8.8, 2.3 Hz, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -83.9 (s, 3F), -107.9 (s, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 166.4, 148.3, 133.9, 132.6 (t, *J* = 3.1 Hz), 132.2, 131.8, 131.0, 129.8, 129.5, 128.6 (td, *J* = 7.3, 1.7 Hz), 127.9, 127.9, 126.8, 126.4 (t, *J* = 23.7 Hz), 126.1, 120.7, 119.4 (qt, *J* = 287.0, 38.7 Hz), 113.9 (tq, *J* = 255.6, 39.2 Hz). **HRMS** (ESI) m/z: [M+Na]⁺ Calcd for C₁₉H₁₁F₅NO₂ 389.0571; Found 389.0573.

N,N-dibenzyl-4-(perfluoroethyl)benzamide (2r)



Following the general procedure V, reaction was run using aryl iodide 1r (85.5 mg, 0.2 mmol), CuI (7.6

mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA / Hexane = 1:10) and obtained as a yellow solid (43.5 mg, 52% yield), R_f = 0.2 (EA / Hexane = 1:5). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 4H), 7.46 – 7.27 (m, 8H), 7.15 (d, J = 7.4 Hz, 2H), 4.76 (s, 2H), 4.40 (s, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.6 (s, 3F), -115.1 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 170.9, 139.9, 136.6, 136.0, 129.9 (t, J = 24.2 Hz), 129.1, 128.9, 128.6, 128.0, 127.8, 127.2, 127.0 (t, J = 6.2 Hz), 119.0 (qt, J = 285.9, 39.0 Hz), 113.2 (tq, J = 254.2, 38.5 Hz), 51.6, 47.2. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₈F₅NO 442.1201; Found 442.1202.

N-methyl-4-(perfluoroethyl)-N-phenylbenzamide (2s)



Following the general procedure V, reaction was run using aryl iodide **1r** (67.4 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA : hexane = 1 : 10) and obtained as a yellow solid (65.2 mg, 99% yield), R_f = 0.23 (EA : hexane = 1: 6). ¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.37 (m, 4H), 7.21 (t, J = 7.4 Hz, 2H), 7.14 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 7.5 Hz, 2H), 3.50 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.9 (s, 3F), -115.3 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 169.1, 144.1, 139.7, 129.5 (t, J = 24.1 Hz), 129.4, 128.9, 127.1, 126.9, 126.0 (t, J = 6.2 Hz), 118.9 (qt, J = 286.0, 39.2 Hz), 113.0 (tq, J = 254.1, 38.3 Hz), 38.3. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₆H₁₂F₅NO 352.0731; Found 352.0731.

1-((4-(perfluoroethyl)phenyl)sulfonyl)pyrrolidine (2t)



Following the general procedure V, reaction was run using aryl iodide **1t** (67.4 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA : hexane = 1 : 20) and obtained as a white solid (57.6mg, 88% yield), R_f = 0.33 (EA : hexane = 1:10). ¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.1 Hz, 2H), 3.28 (m, 4H), 1.83 – 1.79 (m, 4H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.5 (s, 3F), -115.2 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 141.1, 132.6 (t, J = 24.2 Hz), 127.9, 127.5 (t, J = 6.2 Hz), 118.9 (qt, J = 286.1, 38.6 Hz), 112.9 (tq, J = 254.7, 38.6 Hz), 48.1, 25.4. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₂H₁₂F₅NO₂S 352.0401; Found 352.04012.

1-Fluoro-4-((4-(perfluoroethyl)phenyl)sulfonyl)benzene (2u)

Following the general procedure **V**, reaction was run using aryl iodide **1u** (72.4 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA / Hexane = 1:10) and obtained as a yellow solid (53.8 mg, 76% yield), R_f = 0.30 (EA / Hexane = 1:10). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.3 Hz, 2H), 8.03 – 7.93 (m, 2H), 7.75 (d, J = 8.3 Hz, 2H), 7.21 (t, J = 8.5 Hz, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ - 84.5 (s, 3F), -102.9 (m, 1F), -115.4 (s, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 166.0 (d, J = 257.3 Hz), 145.4, 136.7 (d, J = 3.2 Hz), 133.6 (t, J = 24.3 Hz), 131.0 (d, J = 9.6 Hz), 128.1, 127.9 (t, J = 6.2 Hz), 118.8 (qt, J = 286.0, 38.4 Hz), 117.1 (d, J = 22.9 Hz), 112.8 (tq, J = 255.1, 38.7 Hz). The spectra are in full accordance with the literature report.¹⁵

4-nitro-4'-(perfluoroethyl)-1,1'-biphenyl (2v)

Following the general procedure V, reaction was run using aryl iodide **1ab** (65.0 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (DCM / Hexane = 1:10) and obtained as a white solid (57.5 mg, 91% yield), R_f = 0.25 (DCM / Hexane = 1:10). ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.83 (m, 2H), 7.38 – 7.23 (m, 6H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.7 (s, 3F), -115.0 (s, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 147.8, 146.1, 142.6, 129.2 (t, *J* = 24.2 Hz), 128.3, 127.9, 127.4 (t, *J* = 6.3 Hz), 124.4, 119.2 (tq, *J* = 286.0, 39.2 Hz), 113.4 (tq, *J* = 253.9, 38.3 Hz). HRMS (ESI) m/z: [M+Na]⁺ Calcd for C_{14H8F5NO2} 340.0367; Found 340.0369.

(E)-1-(4-(perfluoroethyl)phenyl)-3-phenylprop-2-en-1-one (2w)



Following the general procedure **V**, reaction was run using aryl iodide **1w** (66.8 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (DCM : Hexane = 1:10) and obtained as a yellow solid (39.8 mg, 61% yield), R_f = 0.25 (DCM : Hexane = 1:5). ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.70 – 7.61 (m, 2H), 7.56 – 7.38 (m, 4H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.6 (s, 3F), -115.3 (s, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 189.8, 146.3, 141.4, 134.7, 132.5 (t, *J* = 24.0 Hz), 131.1, 129.2, 128.8, 128.7, 127.0 (t, *J* = 6.3 Hz), 121.7, 119.1 (qt, *J* = 286.1, 38.9 Hz), 113.3 (tq, *J* = 254.0, 38.4 Hz) HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₇H₁₁F₅O 327.0803; Found 327.0805

6-(perfluoroethyl)quinoline (2x)



Following the general procedure V, reaction was run using aryl iodide **1x** (51.0 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA : Hexane = 1:10) and obtained as a yellow solid (32.0 mg, 65% yield), R_f = 0.30 (EA : Hexane = 1:5). ¹H NMR (500 MHz, CDCl₃) δ 9.04 (s, 1H), 8.25 (t, J = 9.0 Hz, 2H), 8.12 (s, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.52 (dd, J = 7.8, 3.8 Hz, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.5 (s, 3F), -114.4 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 152.6, 149.1, 137.2, 130.6, 127.6 (t, J = 7.0 Hz), 127.4, 127.0 (t, J = 24.0 Hz), 126.2 (t, J = 5.6 Hz), 122.4, 119.2 (qt, J = 285.8, 39.2 Hz)), 112.4 (tq, J = 254.2, 38.3 Hz). The spectra are in full accordance with the literature report.¹⁵

5-(perfluoroethyl)-1-tosyl-1H-indole 20 (2y)



Following the general procedure **V**, reaction was run using aryl iodide **1y** (79.4 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA : hexane = 1:20) and obtained as a white solid (59.1 mg, 76% yield), R_f = 0.35 (EA : hexane = 1:20). ¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, J = 8.7 Hz, 1H), 7.82 (d, J = 8.3 Hz, 3H), 7.71 (d, J = 3.7 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.35 – 7.25 (m, 2H), 6.76 (d, J = 3.6 Hz, 1H), 2.38 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.7 (s, 3F), -113.3 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 145.7, 136.5, 135.1, 130.6, 130.3, 128.0, 127.0, 123.8 (t, J = 24.1 Hz), 122.4 (t, J = 6.2 Hz), 120.4 (t, J = 6.8 Hz), 119.3 (qt, J = 285.5. 39.9 Hz), 113.8 (tq, J = 253.9, 38.0 Hz), 113.7, 111.9, 108.9, 21.7. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₇H₁₂F₅O₂S 412.0401; Found 412.0404.

4-(perfluoroethyl)dibenzo[b,d]furan (2z)



Following the general procedure V, reaction was run using aryl iodide **1z** (58.8 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (hexane) and obtained as a white solid (51.5 mg, 90% yield), $R_f = 0.45$ (hexane). ¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, J = 7.7 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.66 (dd, J = 8.1, 3.2 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.5 (s, 3F), -113.4 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 156.4, 152.9 (t, J = 3.0 Hz), 128.2, 126.2, 125.5 (t, J = 7.3 Hz), 124.5, 123.4, 122.8, 122.6, 120.7, 117.1 (qt, J = 286.5, 38.9 Hz), 112.1, 111.2 (tq, J = 255.0 Hz, J = 39.8 Hz). The spectra are in full accordance with

the literature report.18

4-(perfluoroethyl)dibenzo[b,d]thiophene (2aa)



Following the general procedure V, reaction was run using aryl iodide **1aa** (62.0 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (hexane) and obtained as a yellow solid (40.0 mg, 67% yield), R_f = 0.40 (hexane). ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, J = 8.5 Hz, 1H), 8.21 – 8.15 (m, 1H), 7.91 – 7.85 (m, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.55 – 7.47 (m, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.3 (s, 3F), -113.9 (s, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 139.7 (t, J = 3.2 Hz), 137.9, 137.7, 134.2, 127.8, 126.3 (t, J = 7.2 Hz), 125.0, 124.9, 124.5, 123.4 (t, J = 24.9 Hz) 122.5, 121.8, 119.6 (qt, J = 286.8, 39.1 Hz), 114.5 (tq, J = 254.3, 38.8 Hz). The spectra are in full accordance with the literature report.¹⁵

3-(perfluoroethyl)-9-phenyl-9H-carbazole (2ab)



Following the general procedure **V**, reaction was run using aryl iodide **1ab** (73.8 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA: hexane = 1:20) and obtained as a white solid (65.7 mg, 91% yield), R_f = 0.25 (EA: hexane = 1:20). ¹H NMR (500 MHz, CDCl₃) δ 8.40 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.69 – 7.59 (m, 3H), 7.59 – 7.51 (m, 3H), 7.52 – 7.45 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.6 (s, 3F), -112.5 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 142.6, 141.8, 137.1, 130.2, 128.3, 127.3, 127.1, 123.9 (t, *J* = 6.3 Hz), 123.3, 122.9, 120.9, 120.7, 120.0 (t, *J* = 24.2 Hz), 119.3 (t, *J* = 6.8 Hz), 119.5 (qt, *J* = 284.1 Hz, 40.7 Hz), 116.0 (tq, *J* = 251.9, 38.1 Hz), 110.3, 110.1. The spectra are in full accordance with the literature report.¹⁵

2-(perfluoroethyl)-9H-fluorene (2ac)

Following the general procedure V, reaction was run using aryl iodide **1ab** (62.0 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (hexane) and obtained as a white solid (36.9 mg, 65% yield), $R_f = 0.45$ (hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.86 (m, 2H), 7.76 (s, 1H), 7.60 (m, 2H),

7.41 (m, 2H), 3.96 (s, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.7 (s, 3F), -113.8 (s, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 145.4, 144.0, 143.6, 140.4, 128.2, 127.2, 126.5 (t, *J* = 23.8 Hz), 125.4, 125.3, 123.2 (t, *J* = 6.4 Hz), 120.8, 120.1, 119.3 (qt, *J* = 286.8, 39.4 Hz), 113.9 (tq, *J* = 252.5, 38.4 Hz), 37.0. The spectra are in full accordance with the literature report.¹⁹

(E)-1-(benzyloxy)-4-(3,3,4,4,4-pentafluorobut-1-en-1-yl)benzene (4b)

Following the general procedure **V**, reaction was run using alkenyl iodide **3b** (61.2 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (hexane) and obtained as a white solid (51.2 mg, 86% yield), $R_f = 0.2$ (hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.70 – 7.62 (m, 4H), 7.59 (d, J = 7.9 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.26 (d, J = 15.9 Hz, 1H), 6.25 (dt, J = 16.1, 12.1 Hz, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -85.0 (s, 3F), -114.8 (d, J = 11.7 Hz, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 143.1, 140.2, 139.3 (t, J = 9.2 Hz), 132.6, 129.1, 128.2, 128.0, 127.7, 127.2, 119.2 (qt, J = 285.5, 38.5 Hz), 114.0 (t, J = 23.1 Hz), 113.0 (tq, J = 250.2, 38.4 Hz). The spectra are in full accordance with the literature report.²⁰

(E)-4-(3,3,4,4,4-pentafluorobut-1-en-1-yl)-1,1'-biphenyl (4c)



Following the general procedure V, reaction was run using alkenyl iodide **3c** (67.2 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (hexane) and obtained as a white solid (52.5 mg, 75% yield), $R_f = 0.15$ (EA : hexane = 1:20). ¹H NMR (500 MHz, CDCl₃) δ 7.51 – 7.41 (m, 6H), 7.42 – 7.35 (m, 1H), 7.16 (d, J = 16.2 Hz, 1H), 7.02 (d, J = 8.1 Hz, 2H), 6.07 (q, J = 12.7 Hz, 1H), 5.13 (s, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -85.1 (s, 3F), -114.3 (dd, J = 12.1, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 160.4, 139.1 (t, J = 9.2 Hz), 136.6, 129.3, 128.8, 128.3, 127.6, 126.6, 119.3 (qt, J = 285.6, 23.1 Hz), 113.1 (tq, J = 250.2, 38.5 Hz), 115.4, 111.7 (t, J = 23.1 Hz), 70.2. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₇H₁₃F₅O 351.0779; Found 351.0784.

(E)-1-nitro-4-(3,3,4,4,4-pentafluorobut-1-en-1-yl)benzene (4d)



Following the general procedure V, reaction was run using alkenyl iodide **3d** (53.4 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (DCM : hexane = 1:5) and obtained as a yellow solid (36.2 mg, 68% yield), $R_f = 0.25$ (DCM : hexane = 1:5). ¹H NMR (500 MHz, CDCl₃) δ 8.27 (d, J =

8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 16.2 Hz, 1H), 6.35 (dt, J = 16.2, 11.5 Hz, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -84.9 (s, 3F), -115.6 (d, J = 11.4 Hz, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 148.7, 139.6, 137.6 (t, J = 9.2 Hz), 128.5, 124.4, 118.6 (t, J = 23.4 Hz), 118.9 (qt, J = 285.5, 37.7 Hz), 112.3 (tq, J = 251.4, 38.9 Hz). The spectra are in full accordance with the literature report.²¹

hexyl (E)-4-(3,3,4,4,4-pentafluorobut-1-en-1-yl)benzoate (4e)



Following the general procedure **V**, reaction was run using alkenyl iodide **3e** (71.6 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (DCM : hexane = 1:10) and obtained as a colorless liquid (46.9 mg, 67% yield), R_f = 0.35 (DCM : hexane = 1:5). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.22 (dt, J = 16.3, 2.3 Hz, 1H), 6.27 (dt, J = 16.2, 11.7 Hz, 1H), 4.33 (t, J = 6.7 Hz, 2H), 1.77 (p, J = 6.9 Hz, 2H), 1.50 – 1.39 (m, 2H), 1.37 – 1.26 (m, 4H), 1.02 – 0.80 (m, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -85.0 (s, 3F), -115.2 (d, J = 11.7 Hz, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 166.1, 138.8 (t, J = 9.2 Hz), 137.6, 132.0, 130.3, 127.7, 119.5 (qt, J = 285.1, 37.0 HZ), 116.5 (t, J = 23.1 Hz), 112.6 (tq, J = 249.7, 39.3 Hz), 65.6, 31.6, 28.8, 25.8, 22.7, 14.1. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₇H₁₉F₅O₂ 572.0114; Found 572.0117.

(E)-1-cyano-4-(3,3,4,4,4-pentafluorobut-1-en-1-yl)benzene (4f)

Following the general procedure **V**, reaction was run using alkenyl iodide **3f** (51.0 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA : hexane = 1:50) and obtained as a yellow liquid (36.9 mg, 75% yield), R_f = 0.4 (DCM : hexane = 1:30). ¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.20 (dt, J = 16.2, 2.4 Hz, 1H), 6.30 (dt, J = 16.3, 11.6 Hz, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -85.0 (s, 3F), -115.6 (d, J = 11.6 Hz, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 138.0 (t, J = 9.2 Hz), 137.7, 132.8, 128.2, 118.9 (qt, J = 285.7, 38.0 Hz), 118.3, 117.9 (t, J = 23.3 Hz), 113.7, 112.4 (tq, J = 251.3, 38.9 Hz). The spectra are in full accordance with the literature report.²⁰

(E)-(5,5,6,6,6-pentafluorohex-3-en-1-yl)benzene (4g)



Following the general procedure V, reaction was run using alkenyl bromide **3h** (51.8 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was

purified by flash column chromatography on silica gel (hexane) and obtained as a colorless liquid (35.0 mg, 70% yield), $R_f = 0.60$ (hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.46 – 7.30 (m, 2H), 7.33 – 7.28 (m, 1H), 7.27 – 7.22 (m, 2H), 6.69 – 6.36 (m, 1H), 5.66 (q, J = 13.4 Hz, 1H), 2.90 – 2.76 (m, 2H), 2.70 – 2.42 (m, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -85.4 (s, 3F), -115.2 (d, J = 11.4 Hz, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 142.1 (t, J = 8.7 Hz), 140.6 (d, J = 1.8 Hz), 128.7, 128.5, 126.4, 119.2 (qt, J = 285.5, 39.0 Hz), 117.5 (t, J = 23.1 Hz), 112.3 (tq, J = 250.3, 38.0 Hz), 34.5, 33.9. **HRMS** (APCI) m/z: [M+H]⁺ Calcd for C₁₂H₁₁F₅ 251.0854, Found 251.0849.

(3,3,4,4,4-pentafluorobut-1-ene-1,1-diyl)dibenzene (4h)



Following the general procedure V, reaction was run using alkenyl bromide **3h** (51.8 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (hexane) and obtained as a colorless liquid (51.3 mg, 86% yield), R_f = 0.28 (hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.34 (m, 6H), 7.34 – 7.20 (m, 4H), 6.12 (t, *J* = 14.4 Hz, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -85.2 (s, 3F), -107.6 (d, *J* = 13.3 Hz, 2F). ¹³C NMR (126 MHz, CDCl₃) δ 154.7, 140.7, 137.6, 129.7, 129.2 (t, *J* = 2.7 Hz), 128.6, 128.5, 128.1, 128.0, 119.3 (qt, *J* = 286.0, 37.6 Hz), 112.7 (t, *J* = 21.1 Hz), 112.5 (tq, *J* = 251.9, 37.9 Hz). HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₆H₁₁F₅ 299.0854; Found 299.0854.

N-(4-bromobenzyl)- N-(4-iodobenzyl)-4-methylbenzenesulfonamide (5)

The product was purified by flash column chromatography on silica gel (EA : hexane = 1:6) and obtained as a white solid (1.36 g, 49% yield), $R_f = 0.45$ (EA : hexane = 1:6). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, J = 7.1 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H), 7.37 – 7.28 (m, 4H), 6.89 (d, J = 7.9 Hz, 2H), 6.76 (d, J = 7.8 Hz, 2H), 4.33 – 3.98 (m, 4H), 2.46 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.8, 137.7, 137.3, 135.4, 134.7, 131.7, 130.5, 130.3, 130.0, 127.3, 121.9, 93.5, 50.5, 50.4, 21.7. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₁₉BrINO₂S 579.9238; Found 579.9237.

N-(4-bromobenzyl)-4-methyl-N-(4-(perfluoroethyl)benzyl)benzenesulfonamide (6)



Following the general procedure V, reaction was run using aryl iodide **5** (11.2 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), 1,10-Phenanthroline (7.2 mg, 0.04 mmol), Pentafluoroethyl triethylsilane (187.4 mg, 0.8 mmol) and Potassium fluoride (46.4 mg, 0.8 mmol) in 2 ml DMF for 36 h. The product was purified by flash column chromatography on silica gel (EA : hexane = 1:20) and obtained as a white solid (83.0 mg, 76% yield), R_f = 0.30 (EA : hexane = 1:20). ¹**H NMR** (500 MHz, CDCl₃) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.89

(d, J = 8.0 Hz, 2H), 4.33 (s, 2H), 4.26 (s, 2H), 2.46 (s, 3H).¹⁹**F NMR** (471 MHz, CDCl₃) δ -84.8 (s, 3F), -114.8 (s, 2F). ¹³**C NMR** (126 MHz, CDCl₃) δ 144.0, 140.3, 137.0, 134.5, 131.7, 130.3, 130.1, 128.8, 128.2 (t, J = 24.1 Hz), 127.3, 126.6 (t, J = 6.3 Hz), 122.0, 119.1 (qt, J = 285.9, 39.4 Hz), 112.4 (tq, J = 253.6, 38.1 Hz), 51.3, 51.1, 21.7. **HRMS** (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₉BrF₅NO₂S 572.0114; Found 572.0117.

N-((3'-methoxy-[1,1'-biphenyl]-4-yl)methyl)-4-methyl-N-(4-(perfluoroethyl)benzyl)benzenesulfonami de (7)



The product was purified by flash column chromatography on silica gel (EA : hexane = 1:20) and obtained as a white solid (60.5 mg, 72% yield), $R_f = 0.22$ (EA : hexane = 1:10). ¹**H** NMR (500 MHz, CDCl₃) δ 7.79 (d, J = 7.8 Hz, 2H), 7.45 (t, J = 8.0 Hz, 4H), 7.41 – 7.32 (m, 3H), 7.27 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 7.5 Hz, 3H), 7.09 (s, 1H), 6.93 (d, J = 8.2 Hz, 1H), 4.49 – 4.33 (m, 4H), 3.89 (s, 3H), 2.49 (s, 3H). ¹⁹**F** NMR (471 MHz, CDCl₃) δ -84.7 (s, 3F), -114.7 (s, 2F). ¹³**C** NMR (126 MHz, CDCl₃) δ 160.1, 143.8, 142.1, 140.8, 140.6, 137.2, 134.5, 130.0, 129.9, 129.2, 128.8, 128.0 (t, J = 24.0 Hz), 127.3, 127.2, 126.6 (t, J = 6.3 Hz), 119.6, 119.1 (qt, J = 286.0, 39.4 Hz), 113.4 (tq, J = 253.9, 37.8 Hz), 112.9, 112.8, 55.4, 51.4, 50.7, 21.6. **HRMS** (ESI) m/z: [M+Na]⁺ Calcd for C₃₀H₂₆F₅NO₃S 598.1446; Found 598.1453.





Following the general procedure VI, reaction was run using pentafluoroethyl benzene **2f** (51.8 mg, 0.2 mmol), Ammonium formate (50.4 mg, 0.8 mmol) and 1-Napth-PTH (7.5 mg, 0.02 mmol) in 1 ml DMSO for 12 h. The product was purified by flash column chromatography on silica gel (DCM : hexane = 1:10) and obtained as a colorless liquid (42.7 mg, 92% yield), R_f = 0.20 (DCM : hexane = 1:10). ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 3.43 (q, J = 10.7 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -65.6 (t, J = 10.7 Hz, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 135.1 (q, J = 3.0 Hz), 130.6, 130.3, 130.0, 125.6 (q, J = 276.9 Hz), 61.2, 40.3 (q, J = 30.0 Hz), 14.4. The spectra are in full accordance with the literature report.²²

benzyl 4-(2,2,2-trifluoroethyl)benzoate (8b)

ĊOOBn

Following the general procedure VI, reaction was run using pentafluoroethyl benzene **2g** (66.0 mg, 0.2 mmol), Ammonium formate (50.4 mg, 0.8 mmol) and 1-Napth-PTH (7.5 mg, 0.02 mmol) in 1 ml DMSO for 48 h. The product was purified by flash column chromatography on silica gel (DCM : hexane = 1:5) and obtained as a colorless liquid (41.8 mg, 71% yield), R_f = 0.15 (DCM : hexane = 1:5). ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, J = 8.4 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.43 – 7.33 (m, 5H), 5.38 (s, 2H), 3.43 (q, J = 10.7 Hz, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -65.6 (t, J = 10.6 Hz, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 166.1, 136.0, 135.3 (q, J = 3.0 Hz), 130.8, 130.4, 130.2, 128.8, 128.5, 128.3, 125.5 (q, J = 277.0 Hz), 67.0, 40.3 (q, J = 30.0 Hz). HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₆H₁₃F₃O₂ 317.0760; Found 317.0760.

4-(2,2,2-trifluoroethyl)benzonitrile (8c)



Following the general procedure VI, reaction was run using pentafluoroethyl benzene **2e** (44.2 mg, 0.2 mmol), Ammonium formate (50.4mg, 0.8 mmol) and 1-Napth-PTH (7.5 mg, 0.02 mmol) in 1 ml DMSO for 12 h. The product was purified by flash column chromatography on silica gel (DCM : hexane = 1:10) and obtained as a white solid (30.7 mg, 83% yield), R_f = 0.25 (DCM : hexane = 1:10). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 3.44 (q, J = 10.5 Hz, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -65.5 (t, J = 10.5 Hz, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 135.4 (q, J = 3.0 Hz), 132.6, 131.1, 125.3 (q, J = 277.0 Hz), 118.5, 112.5, 40.4 (q, J = 30.3 Hz). The spectra are in full accordance with the literature report.²³

ethyl 2-(2,2,2-trifluoroethyl)benzoate (8d)



Following the general procedure VI, reaction was run using pentafluoroethyl benzene **21** (51.8 mg, 0.2 mmol), Ammonium formate (50.4 mg, 0.8 mmol) and 1-Napth-PTH (7.5 mg, 0.02 mmol) in 1 ml DMSO for 12 h. The product was purified by flash column chromatography on silica gel (DCM : hexane = 1:10) and obtained as a colorless liquid (33.9 mg, 73% yield), $R_f = 0.20$ (DCM : hexane = 1:10). ¹H NMR (500 MHz, CDCl₃) δ 7.97 (dd, J = 7.8, 1.4 Hz, 1H), 7.50 (td, J = 7.5, 1.5 Hz, 1H), 7.41 (td, J = 7.6, 1.4 Hz, 1H), 7.37 (d, J = 7.7 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 4.00 (q, J = 10.8 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -65.2 (t, J = 10.6 Hz, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 167.4, 132.7, 132.1, 131.4, 131.3 (q, J = 3.1 Hz), 131.1, 128.3, 126.0 (q, J = 277.3 Hz), 61.4, 37.1 (q, J = 29.6 Hz), 14.3. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₁H₁₁F₃O₂ 255.0603; Found 255.0604.

benzyl 2-(2,2,2-trifluoroethyl)benzoate (8e)



Following the general procedure VI, reaction was run using pentafluoroethyl benzene **2m** (66.0 mg, 0.2 mmol), Ammonium formate (50.4mg, 0.8 mmol) and 1-Napth-PTH (7.5 mg, 0.02 mmol) in 1 ml DMSO for 48 h. The product was purified by flash column chromatography on silica gel (DCM : hexane = 1:5) and obtained as a colorless liquid (35.3 mg, 60% yield), R_f = 0.18 (DCM : hexane = 1:4). ¹H NMR (500 MHz, CDCl₃) δ 8.02 (dd, J = 7.9, 1.4 Hz, 1H), 7.51 (td, J = 7.5, 1.5 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.43 – 7.33 (m, 5H), 5.36 (s, 2H), 4.01 (q, J = 10.7 Hz, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -65.2 (t, J = 10.6 Hz, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 167.0, 135.8, 132.8, 132.3, 131.6 (q, J = 3.0 Hz), 131.3, 130.9, 128.8, 128.5, 128.4, 125.9 (q, J = 277.3 Hz), 67.2, 37.1 (q, J = 29.7 Hz). HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₆H₁₃F₃O₂ 317.0760; Found 317.0761.

hexyl 2-(2,2,2-trifluoroethyl)benzoate (8f)



Following the general procedure VI, reaction was run using pentafluoroethyl benzene **2n** (62.8 mg, 0.2 mmol), Ammonium formate (50.4mg, 0.8 mmol) and 1-Napth-PTH (7.5 mg, 0.02 mmol) in 1 ml DMSO for 12 h. The product was purified by flash column chromatography on silica gel (DCM : hexane = 1:10) and obtained as a yellow liquid (42.0 mg, 73% yield), $R_f = 0.2$ (DCM : hexane = 1:10). ¹H NMR (500 MHz, CDCl₃) δ 7.97 (dd, J = 7.8, 1.5 Hz, 1H), 7.50 (td, J = 7.5, 1.5 Hz, 1H), 7.41 (td, J = 7.7, 1.4 Hz, 1H), 7.37 (d, J = 7.7 Hz, 1H), 4.32 (t, J = 6.7 Hz, 2H), 4.01 (q, J = 10.8 Hz, 2H), 1.76 (p, J = 6.9 Hz, 2H), 1.49 – 1.39 (m, 2H), 1.38 – 1.29 (m, 4H), 0.98 – 0.82 (m, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ - 65.2 (t, J = 10.8 Hz, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 167.4, 132.7, 132.1, 131.4, 131.3 (q, J = 3.1 Hz), 131.1, 128.3, 126.0 (q, J = 277.4 Hz), 65.6, 37.1 (q, J = 29.6 Hz), 31.6, 28.7, 25.8, 22.7, 14.1. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₅H₁₉F₃O₂ 311.1229; Found 311.1225.

1-((4-(2,2,2-trifluoroethyl)phenyl)sulfonyl)pyrrolidine (8g)



Following the general procedure VI, reaction was run using pentafluoroethyl benzene **2t** (65.8 mg, 0.2 mmol), Ammonium formate (50.4 mg, 0.8 mmol) and 1-Napth-PTH (15.0 mg, 0.04 mmol) in 1 ml DMSO for 48 h. The product was purified by flash column chromatography on silica gel (EA : hexane = 1:10) and obtained as a yellow liquid (35.21 mg, 60% yield), R_f = 0.25 (EA : hexane = 1:10). ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 3.45 (q, J = 10.6 Hz, 2H), 3.39 – 3.22 (m, 4H), 1.88 – 1.63 (m, 4H). ¹⁹F NMR (471 MHz, CDCl₃) δ -65.5 (t, J = 10.5 Hz, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 137.2, 135.0 (q, J = 2.9 Hz), 131.0, 128.0, 125.4 (q, J = 277.1 Hz), 48.1, 40.2 (q, J = 30.1 Hz), 25.4. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₂H₁₄F₃NO₂S 316.0590; Found 316.0590.

1-fluoro-4-((4-(2,2,2-trifluoroethyl)phenyl)sulfonyl)benzene (8h)



Following the general procedure VI, reaction was run using pentafluoroethyl benzene **2u** (70.9 mg, 0.2 mmol), Ammonium formate (50.4 mg, 0.8 mmol) and 1-Napth-PTH (15.0 mg, 0.04 mmol) in 1 ml DMSO for 48 h. The product was purified by flash column chromatography on silica gel (EA : hexane = 1:10) and obtained as a yellow liquid (42.6 mg, 67% yield), $R_f = 0.3$ (EA : hexane = 1:10). ¹H NMR (500 MHz, CDCl₃) δ 8.00 – 7.94 (m, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.24 – 7.15 (m, 2H), 3.43 (q, J = 10.6 Hz, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -65.4 (t, J = 10.5 Hz, 3F), -101.6 – -105.6 (m, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 165.7 (d, J = 256.5 Hz), 141.6, 137.4 (d, J = 3.2 Hz), 135.9 (q, J = 2.9 Hz), 131.3, 130.7 (d, J = 9.6 Hz), 128.1, 125.3 (q, J = 277.2 Hz), 116.9 (d, J = 22.7 Hz), 40.2 (q, J = 30.0 Hz). HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₄H₁₀F₄O₂S 341.0230; Found 341.0228.

IX. Spectra



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)







S34



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)





S36



S37



2q ¹H NMR (500 MHz, CDCl₃)





2q ¹⁹F NMR (471 MHz, CDCl₃)



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)





7.41 7.33 7.33 7.33 7.23 7.23 7.24 7.24 7.20 7.01



¹H NMR (500 MHz, CDCl₃)



-3.50







S42



 C_2F_5 NO₂

2v ¹H NMR (400 MHz, CDCl₃)









2v ¹⁹F NMR (471 MHz, CDCl₃)

1		

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)





2w ¹H NMR (400 MHz, CDCl₃)







-2.38





4c ¹H NMR (500 MHz, CDCl₃)













S52



¹H NMR (500 MHz, CDCl₃)





S54





5 ¹³C NMR (126 MHz, CDCl₃)









7 ¹H NMR (500 MHz, CDCl₃)



-2.49



7 ¹⁹F NMR (471 MHz, CDCl₃)





S58



S59



8d ¹H NMR (500 MHz, CDCl₃)







20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)





S62



8f

¹H NMR (500 MHz, CDCl₃)









S64



-65.46 -65.48 -65.50

S65

F₃C Hu

8h ¹H NMR (500 MHz, CDCl₃)



