Supplementary Information

Etched stainless steel wire modified with conjugated microporous polymers-F6 for jacket-free stir bar sorptive extraction of benzoylureas in juice sample

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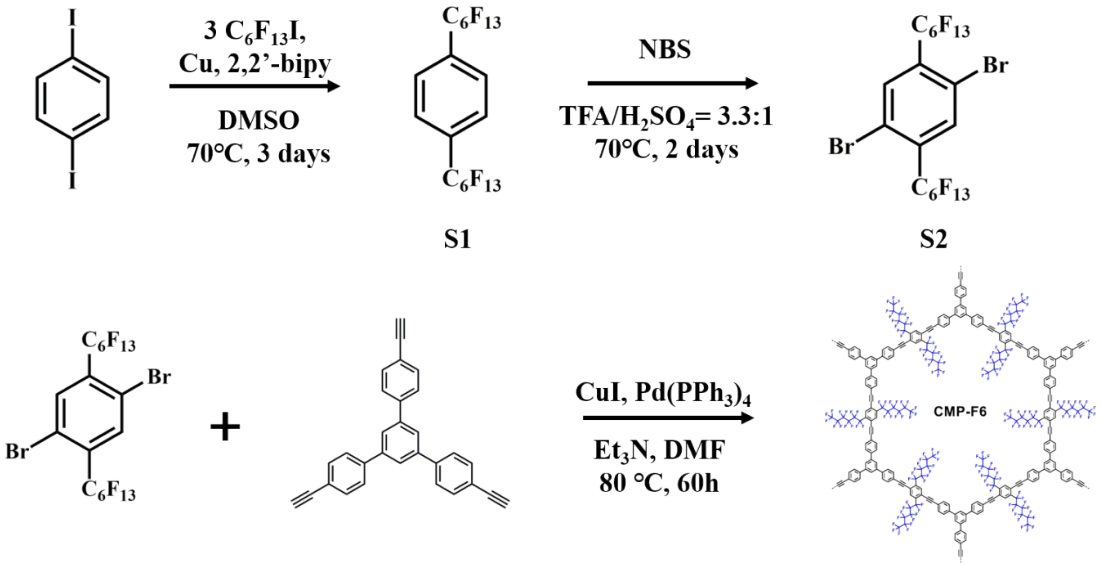


Fig. S1. The synthetic route of CMP-F6.

1,4-bis(perfluorohexyl)benzene (S1). A 100 ml round-bottom flask equipped with a stir bar was flame-dried and then charged with 1,4-diiodobenzene (3.30 g, 10 mmol), Cu powder (5.08 g, 80 mmol), and 2,2'-bipy (156 mg, 1 mmol). The flask was evacuated and backfilled with argon three times. Anhydrous DMSO (30 mL) was added via a syringe. Perfluorohexyl iodide (6.5 mL, 30 mmol) was added dropwise while stirring. Upon completion of addition, the reaction mixture was heated to 70 °C for 72 hours then removed from heat. At the end of the reaction, 100 mL of ethyl acetate and 100 mL of primary water were used to extract the mixture after the reaction. After the solution was stratified, it was observed that the upper organic phase was blue and the lower aqueous phase had a large amount of insoluble matter. The organic layer was further dried with anhydrous $MgSO_4$, followed by evaporation of the ethyl acetate from the organic phase by a rotary evaporator to give **S1** as white solids.

1,4-dibromo-2,5-bis(perfluorohexyl) benzene (S2). A 50 mL round-bottom flask was charged with S1 (2.00 g, 2.80 mmol), trifluoroacetic acid (20.0 mL), and concentrated H_2SO_4 (6.0 mL). The reaction mixture was heated to 60 °C, and N-bromosuccinimide (1.50 g, 8.43 mmol) was added in portions (250 mg/hr) over 6 hours. The stirring was continued for 48 hours at 60 °C. After reaction, the reaction mixture was poured into ice water and extracted three times with ethyl acetate. The organic layer was further dried with anhydrous magnesium sulfate, and the ethyl acetate from the organic phase was then steamed through a rotary evaporator to obtain **S2** as yellow solids.

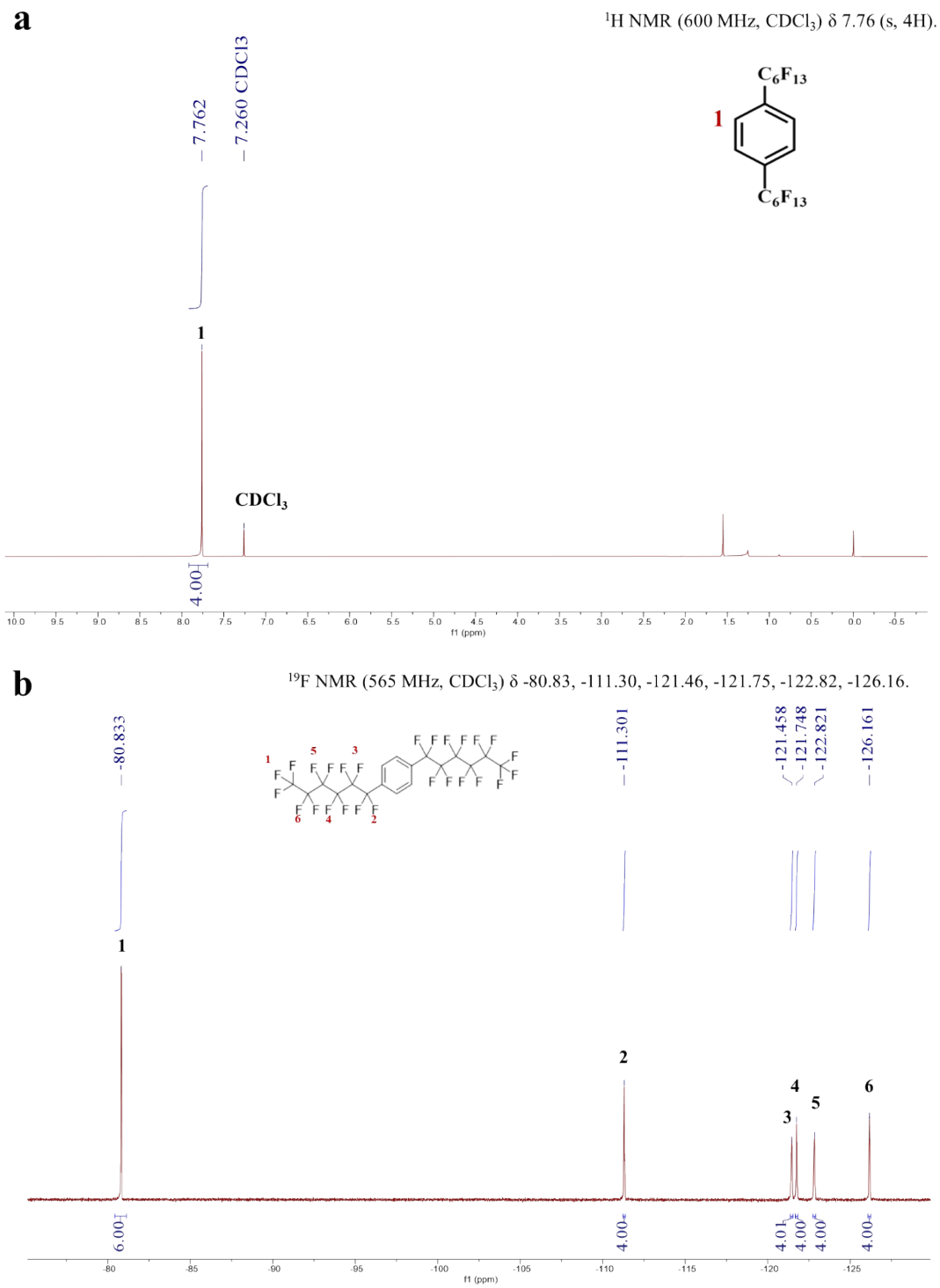


Fig. S2. The (a) ^{1}H-NMR and (b) ^{19}F-NMR of **S1**

(a) ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.76 (s, 4H); (b) ^{19}F-NMR (565 MHz, $CDCl_3$): δ = -80.833, -111.301, -121.458, -121.748, -122.821, -126.161.

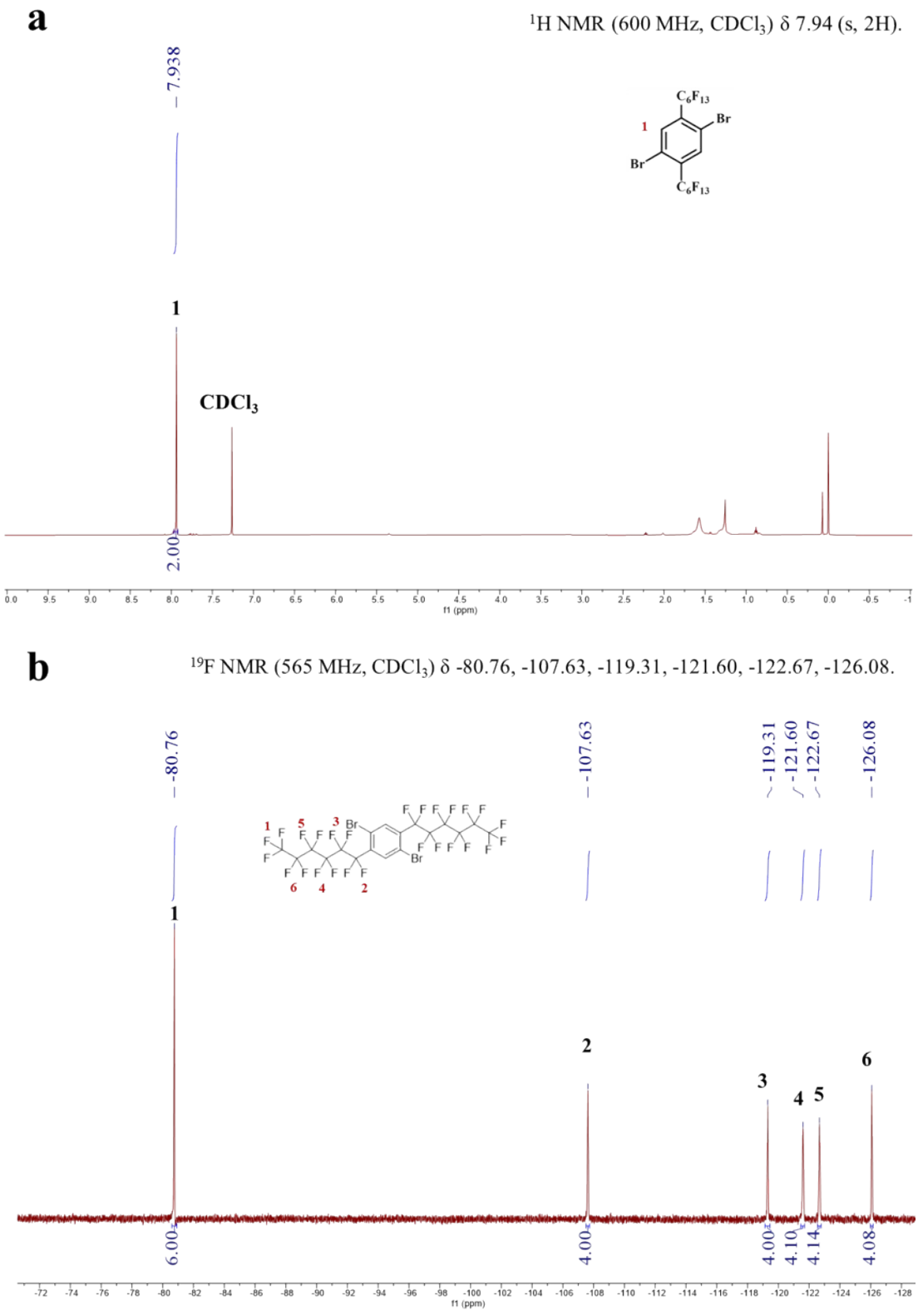


Fig. S3. The (a) ^{1}H-NMR and (b) ^{19}F-NMR of **S2**

(a) ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.94 (s, 2H); (b) ^{19}F-NMR (565 MHz, $CDCl_3$): -80.759, -107.628, -119.312, -121.601, -122.673, -126.075.

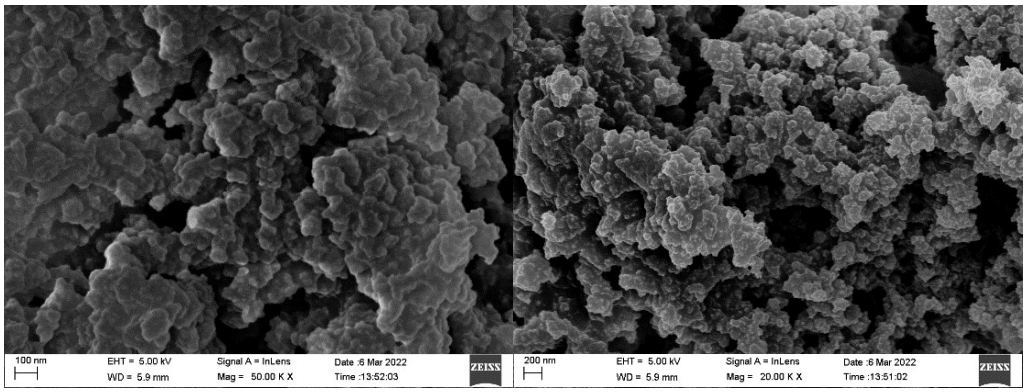


Fig. S4. SEM images of CMP-F6.

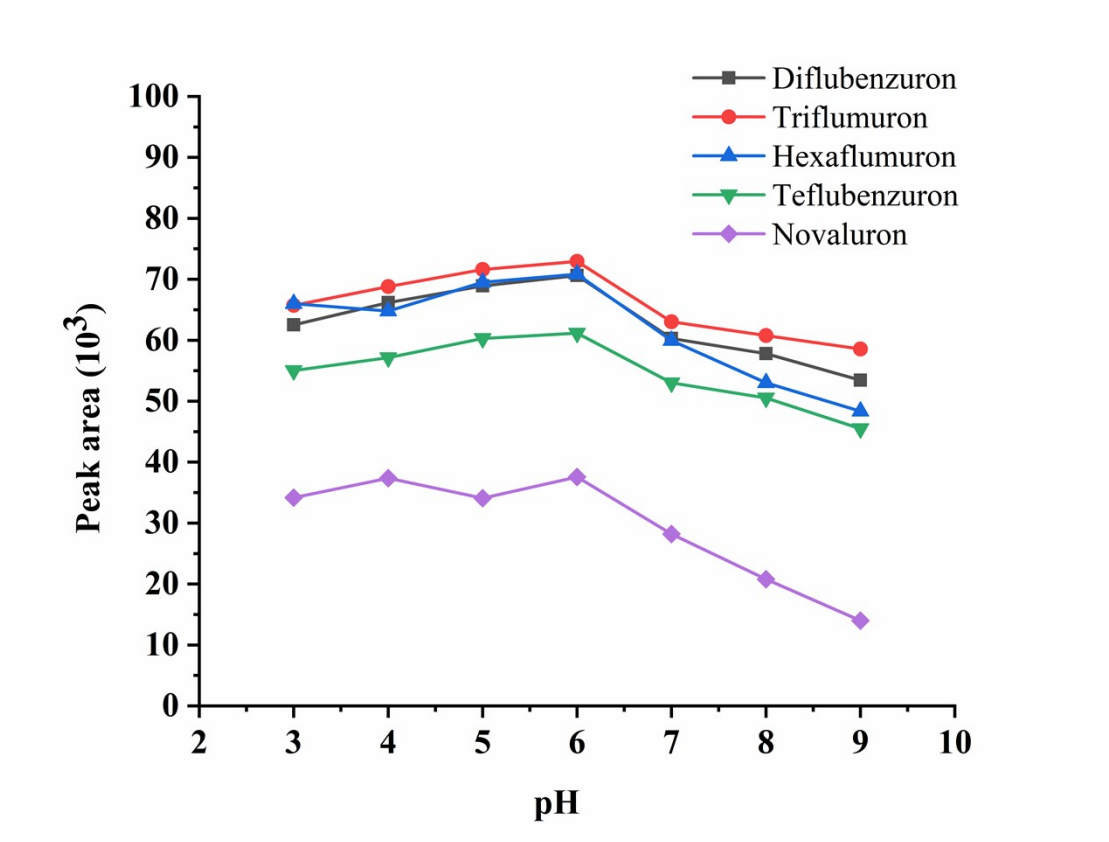


Fig. S5. Effects of pH on extraction efficiency.

Table S1. The specific information of the BUs.

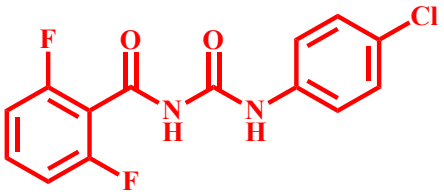
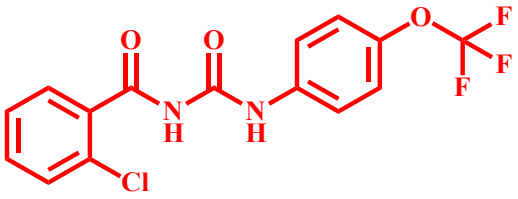
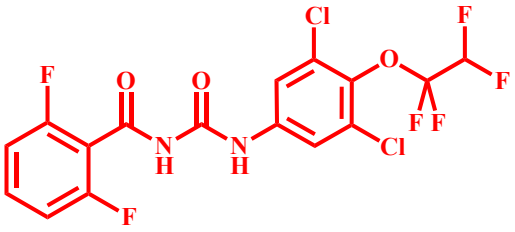
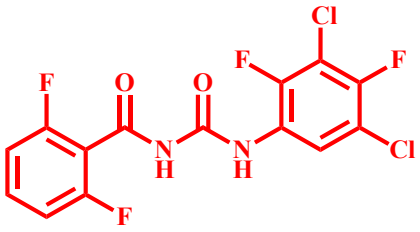
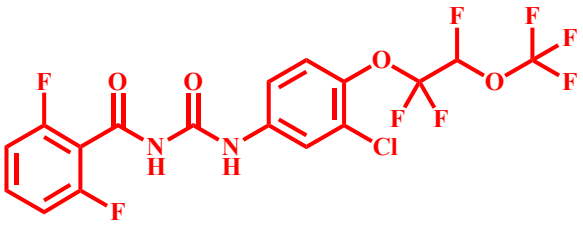
Compounds	Structural formulas	Log P
Diflubenzuron		3.859±0.416
Triflumuron		4.647±0.456
Hexaflumuron		5.673±0.652
Teflubenzuron		5.017±0.579
Novaluron		6.296±0.787

Table S2. The RSD values of the CMP-F6 based SBSE-HPLC-UV method.

Compounds	Intra-day (%, n=3)	Inter-day (%, n=3)	Between bars (%, n=3)
Diflubenzuron	3.16	2.47	2.21
Triflumuron	1.48	1.56	2.49
Hexaflumuron	5.03	0.03	1.44
Teflubenzuron	1.47	0.61	1.80
Novaluron	1.31	2.16	3.18

Table S3. Comparison of the CMP-F6@ SSW based SBSE method with other published methods for extraction of BUs.

Method	Sorbent	Matrix	LOD	Extraction time	Linear range	Ref.
IS-DLLME-HPLC/UV	Ionic liquid [N4444][PF6]	Honey	2.10-4.20 ng/g	about 3 mins	2-300 ng/g	[2]
Dissolvable LDHs-HPLC/UV	Mg/Al LDHs	Honey	5-20 ng/g	<6 min	3-2000 ng/g	[38]
FDME-HPLC/UV	1-dodecanol	Peach juice	1.52-2.72 ng/mL	35 s	10-10000 ng/mL	[12]
SDBS-LDHs-HPLC/UV	SDBS-LDH	Soft drink	0.1-0.3 ng/mL	25 min	0.3-200 ng/mL	[39]
MSPE-HPLC-UV	M-KAP	Honey and apple juice	0.5-1.5 ng/g	20 min	1.67-1000 ng/g	[40]
SBSE-HPLC-UV	CMP-F6	Apple juice	0.1-0.2 ng/mL	120 mins	0.5-300 ng/mL	This work

IS-DLLME: In-syringe dispersive liquid–liquid microextraction;

LDHs: Layered double hydroxides;

FDME: Floated organic drop microextraction;

MSPE: Magnetic solid phase micro extraction.