

## Covalent Organic Frameworks Anchored with Frustrated Lewis Pairs for Hydrogenation of Alkynes with H<sub>2</sub>

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1. Results and discussion

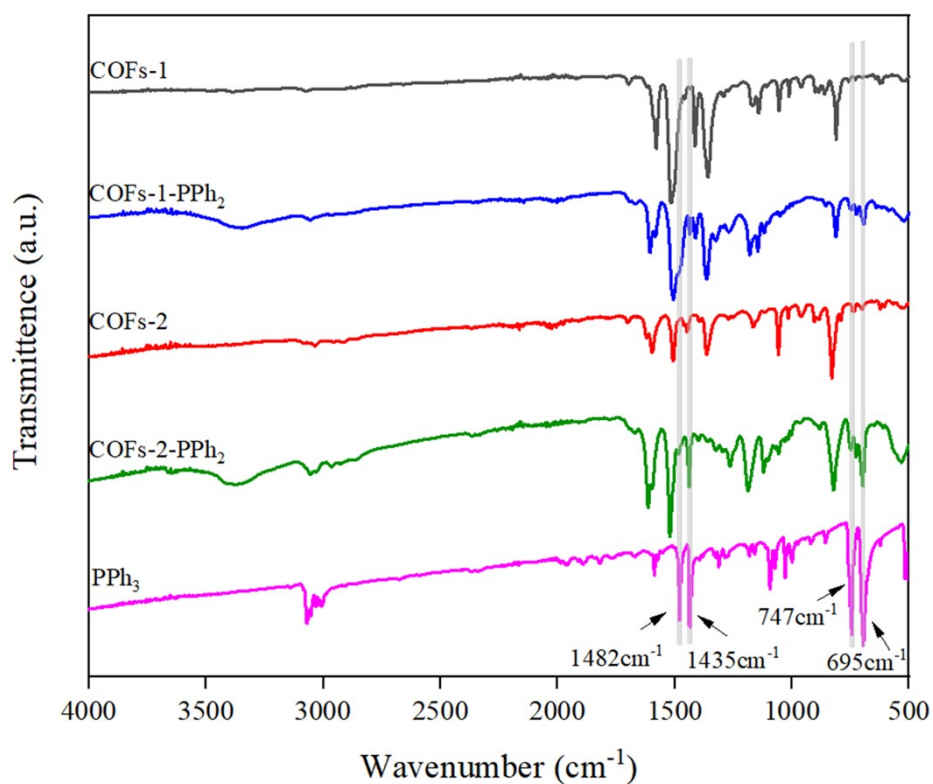


Figure S1. The FT-IR spectra of COFs-1, COFs-1-PPh<sub>2</sub>, COFs-2, COFs-2-PPh<sub>2</sub> and PPh<sub>3</sub>.

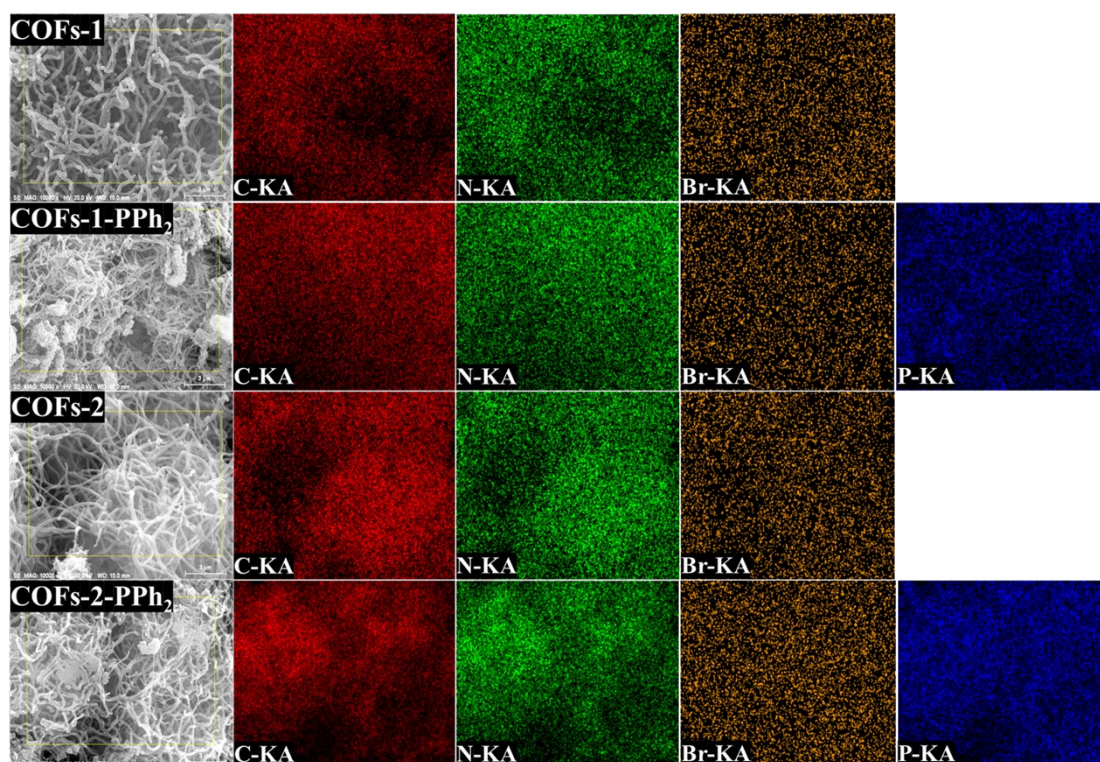


Figure S2. The EDX mapping images of COFs-1, COFs-1-PPh<sub>2</sub>, COFs-2 and COFs-2-PPh<sub>2</sub>.

Table S1. Elemental contents of COFs-1, COFs-2, COFs-1-PPh<sub>2</sub> and COFs-2-PPh<sub>2</sub>.

		C <sup>[a]</sup>	H <sup>[a]</sup>	N <sup>[a]</sup>	Br <sup>[b]</sup>	P <sup>[b]</sup>	Cu <sup>[b]</sup>
		(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
COFs-1	Exp.	52.8	2.5	10.9	30.5±4.2	~	~
	Theo.	53.7	2.4	11.4	32.5	~	~
COFs-1-PPh <sub>2</sub>	Exp.	70.6	4.6	9.8	14.3±3.1	4.7±1.1	0.05±0.01
	Theo.	78.6	4.6	8.0	0	8.8	~
COFs-2	Exp.	57.8	2.7	5.6	31.2±5.1	~	~
	Theo.	58.8	2.9	5.7	32.7	~	~
COFs-2-PPh <sub>2</sub>	Exp.	68.1	4.7	5.3	8.9±1.9	3.5±0.8	0.08±0.02
	Theo.	82.3	4.9	4.0	0	8.9	~

[a] Determined by elemental analyses. [b] Determined by EDX equipped on SEM (Take the average of the five tests).

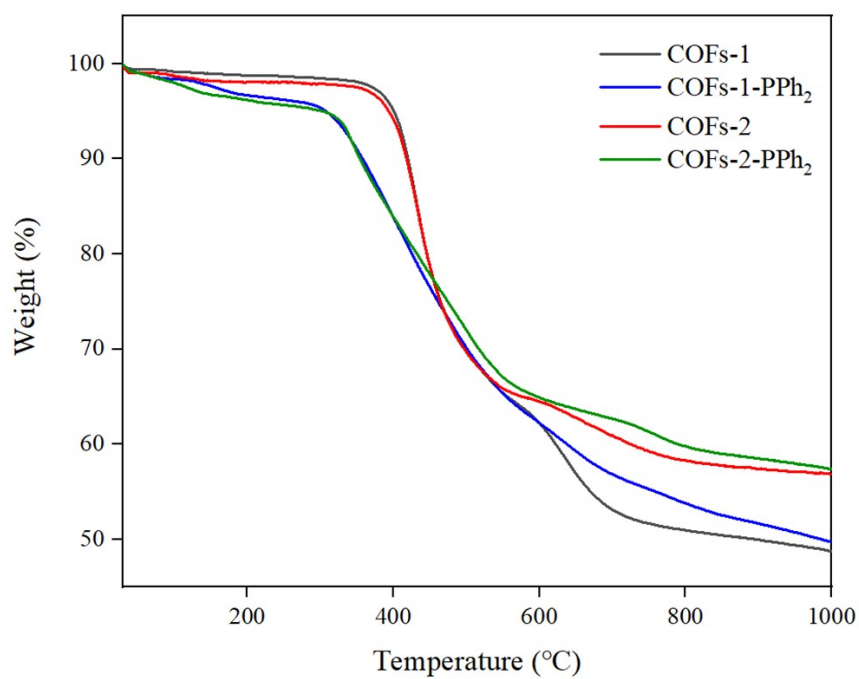


Figure S3. TGA of COFs-1, COFs-1-PPh<sub>2</sub>, COFs-2 and COFs-2-PPh<sub>2</sub>.

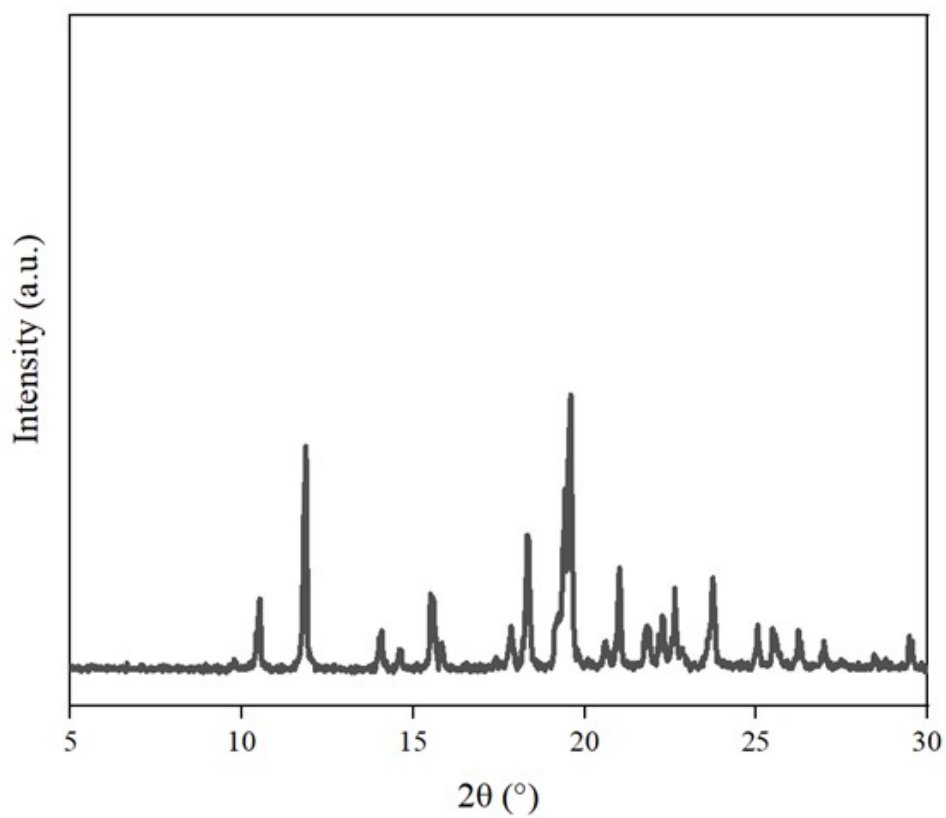


Figure S4. PXRD of PPh<sub>3</sub>.

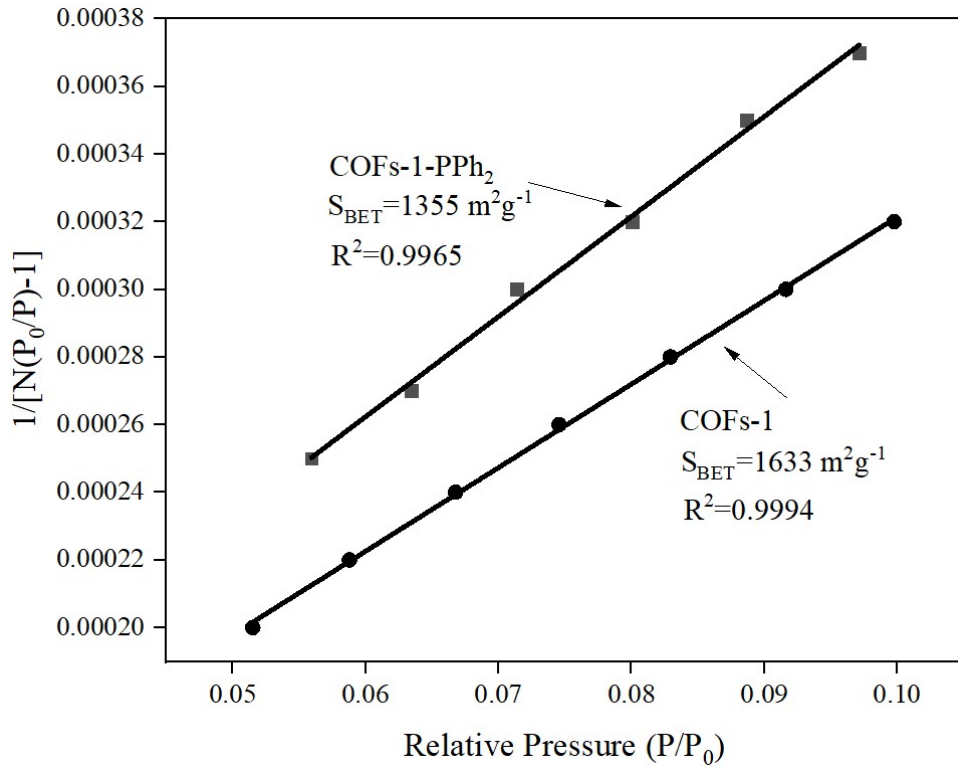


Figure S5. BET plot of COFs-1 and COFs-1-PPh<sub>2</sub>.

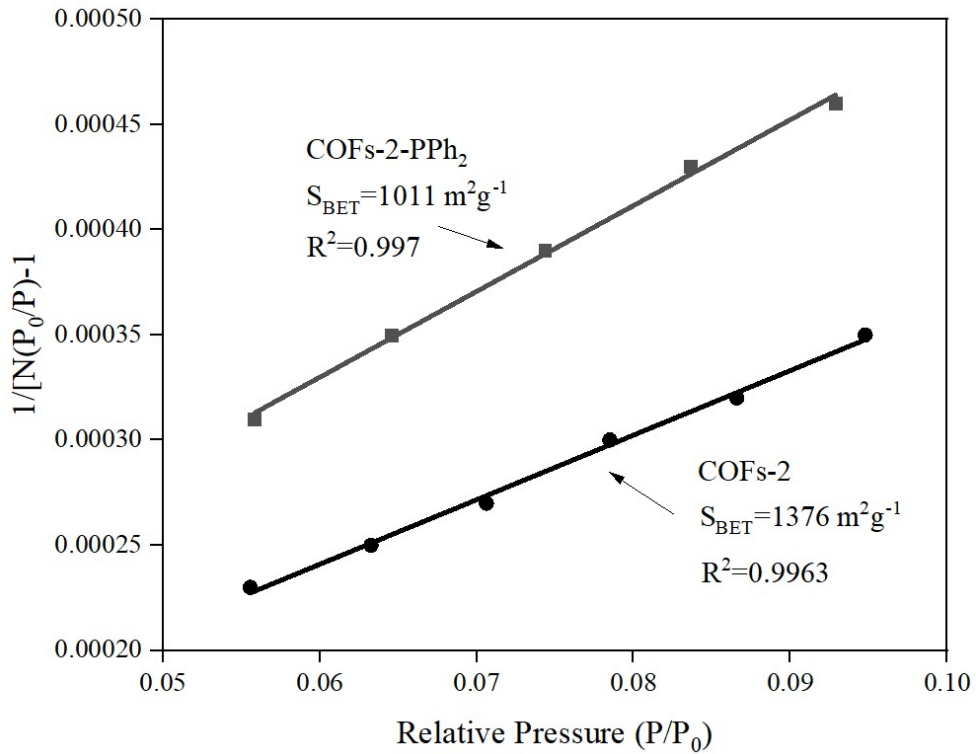


Figure S6. BET plot of COFs-2 and COFs-2-PPh<sub>2</sub>.

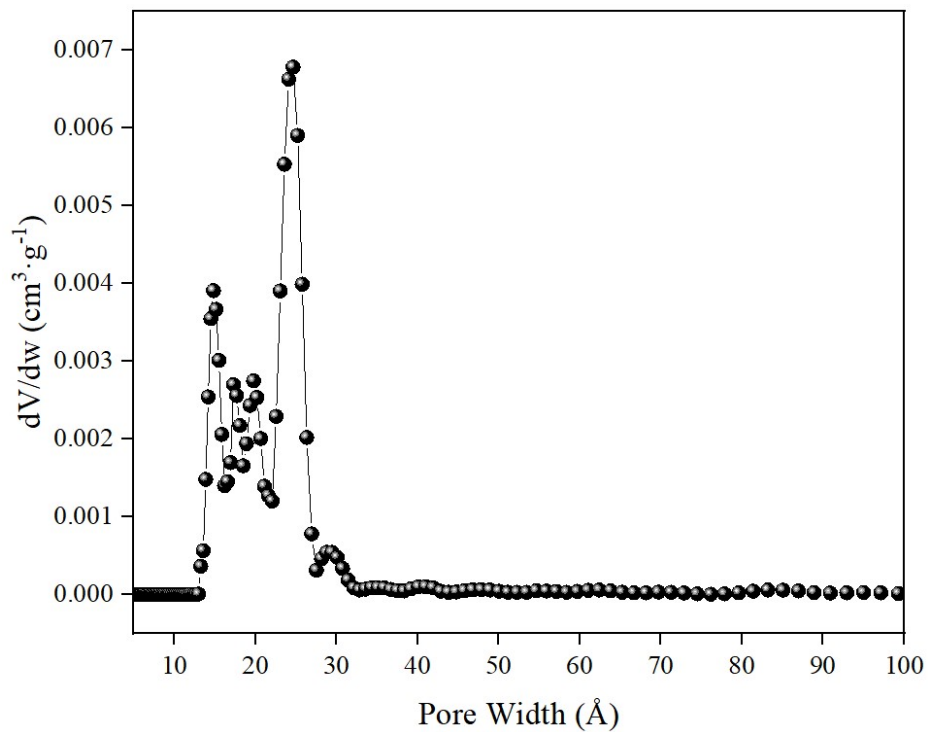


Figure S7. Pore size distribution profiles of COF-1.

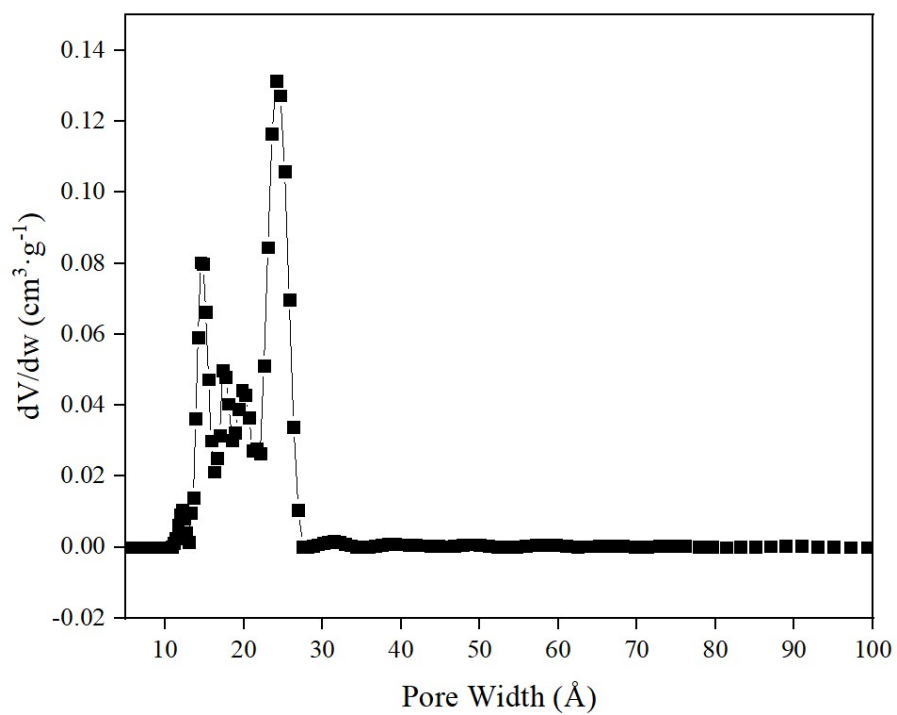


Figure S8. Pore size distribution profiles of COF-1-PPh<sub>2</sub>.

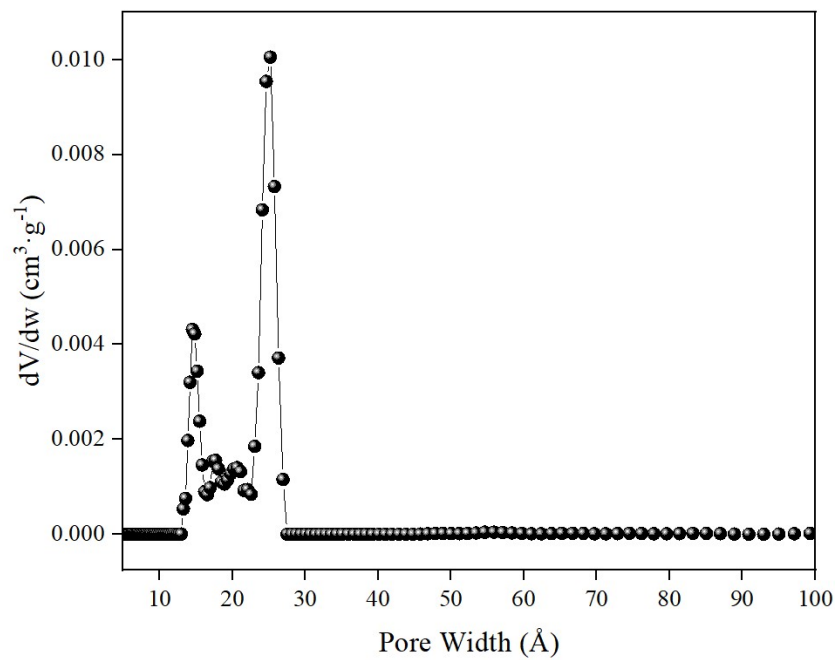


Figure S9. Pore size distribution profiles of COF-2.

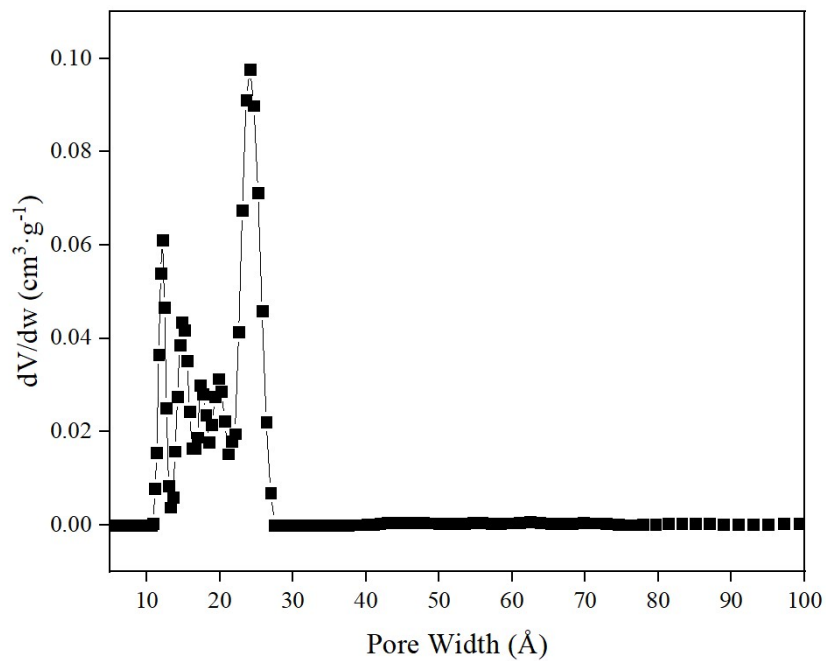


Figure S10. Pore size distribution profiles of COF-2-PPh<sub>2</sub>.

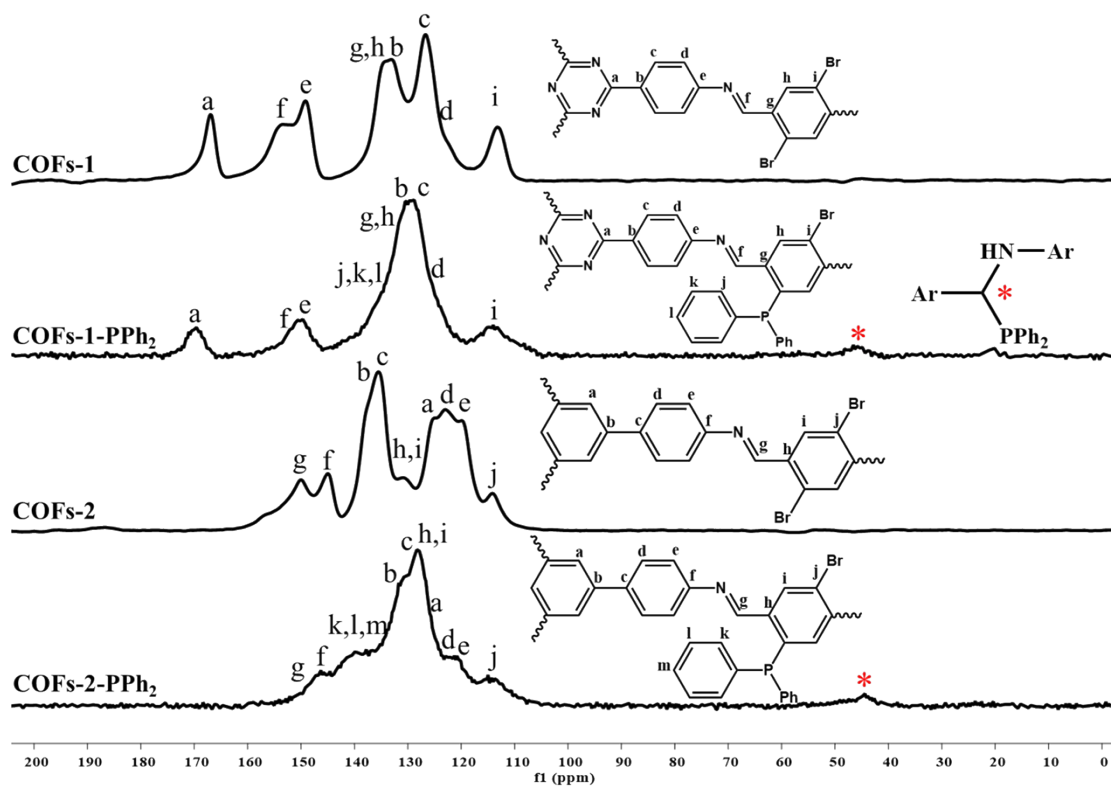


Figure S11. Solid-state  $^{13}\text{C}$  NMR spectral changes of COFs-1, COFs-1-PPh<sub>2</sub>, COFs-2 and COFs-2-PPh<sub>2</sub>.

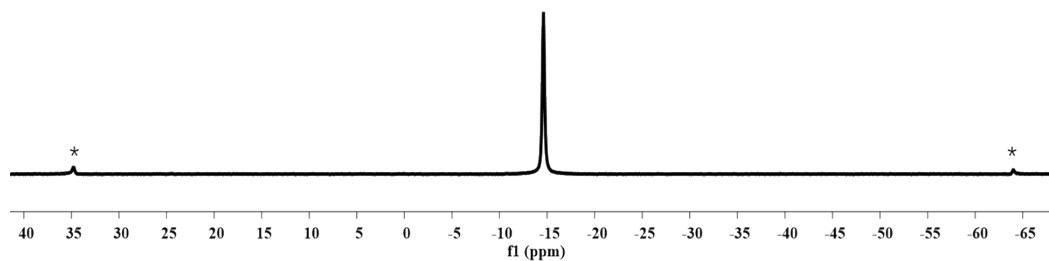


Figure S12. Solid-state  $^{31}\text{P}$  NMR spectral of Br-free-COFs-1-P. Asterisks denote spinning sidebands

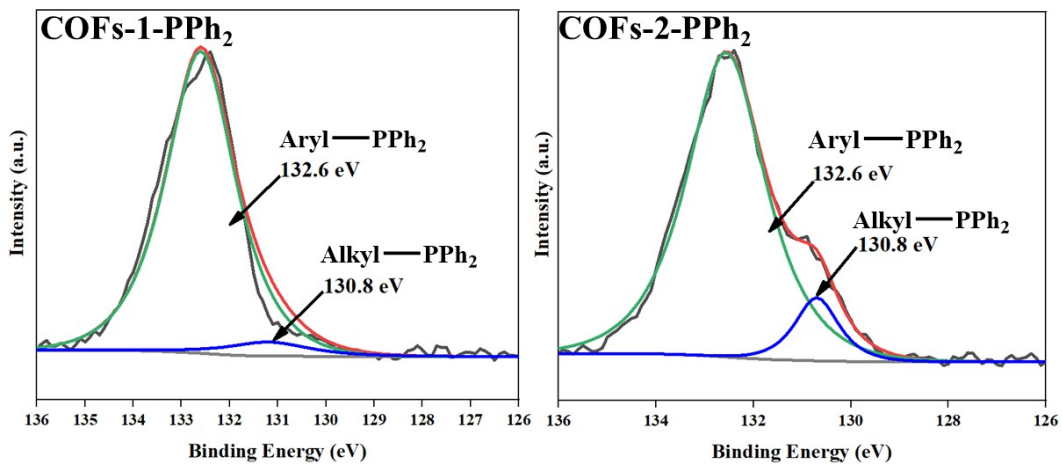


Figure S13.  $P_{2p}$  XPS spectra of COFs-1- $PPh_2$  and COFs-2- $PPh_2$ .

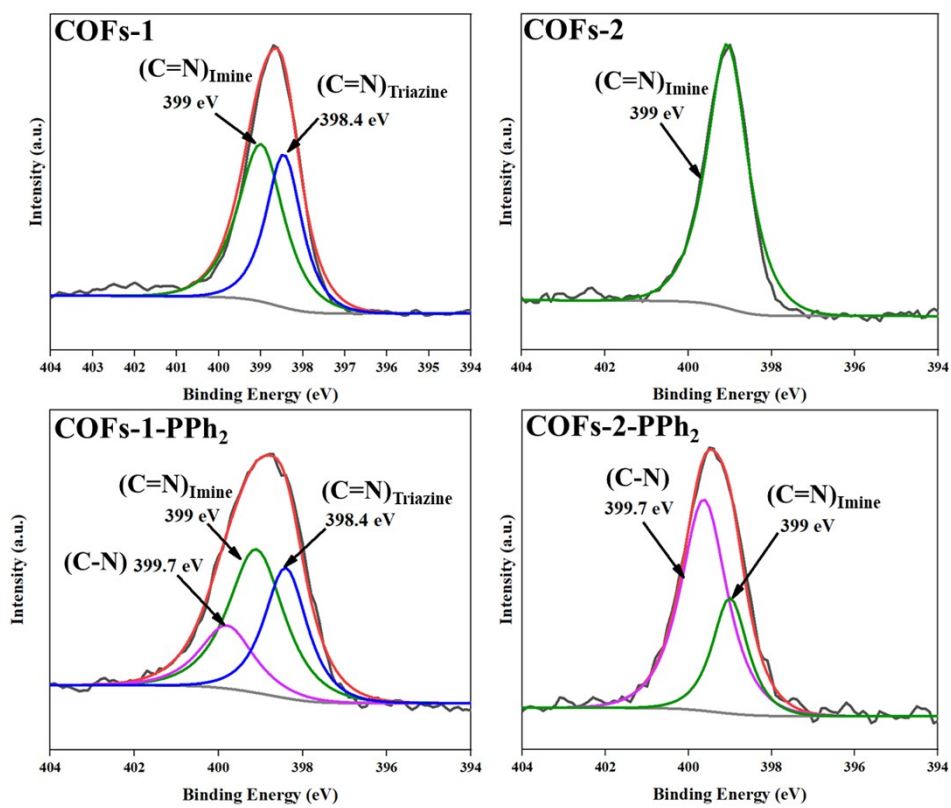


Figure S14.  $N_{1s}$  XPS spectra of COFs-1, COFs-1- $PPh_2$ , COFs-2 and COFs-2- $PPh_2$ .



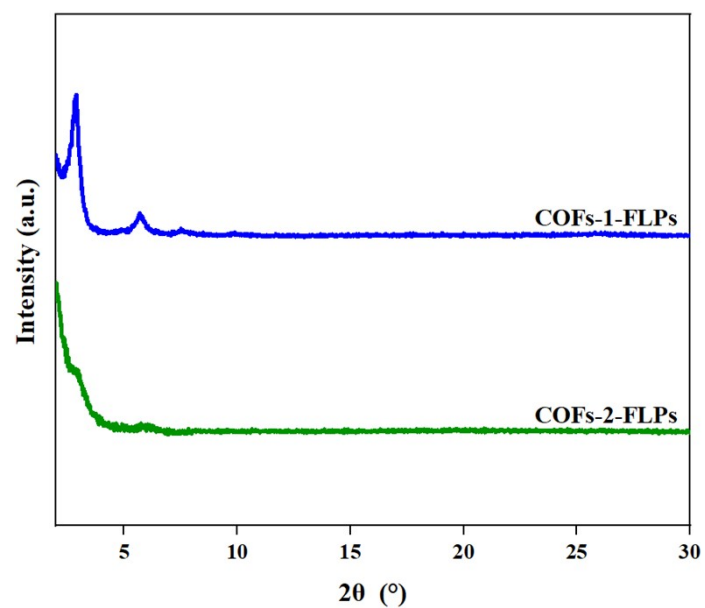


Figure S15. PXRD of COFs-1-FLPs and COFs-2-FLPs before hydrogenation reaction.

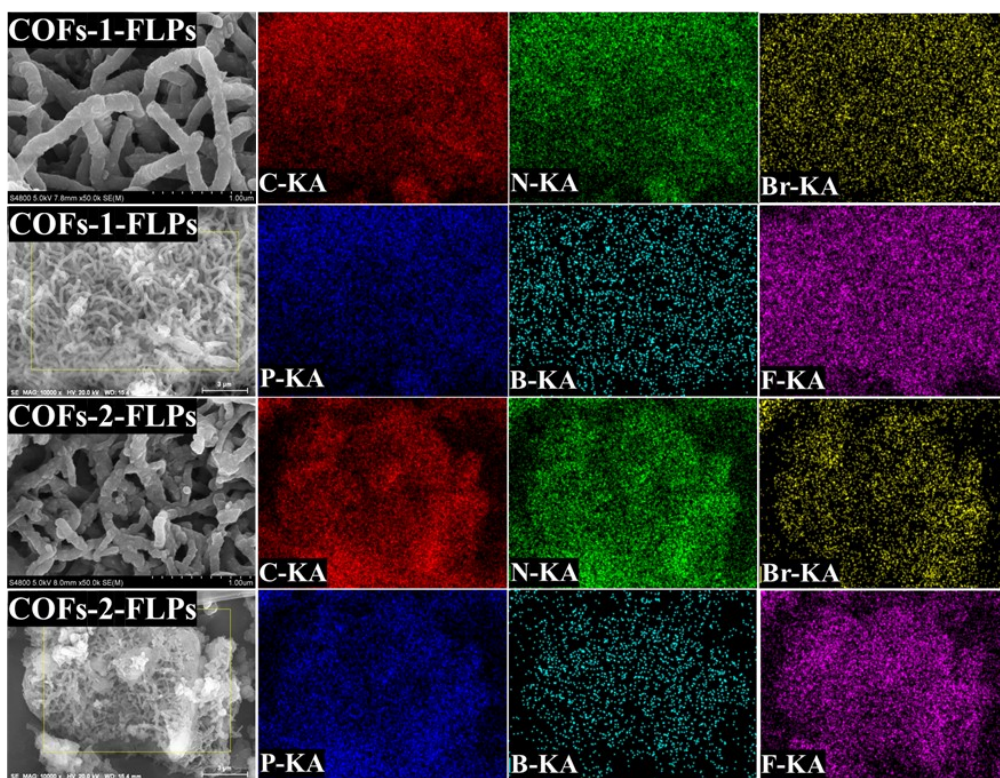


Figure S16. The SEM and EDX mapping images of COFs-1-FLPs and COFs-2-FLPs.

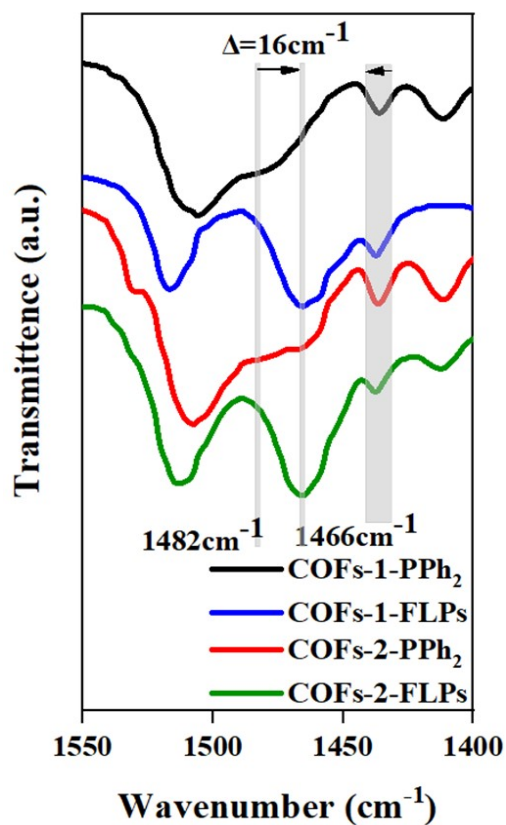
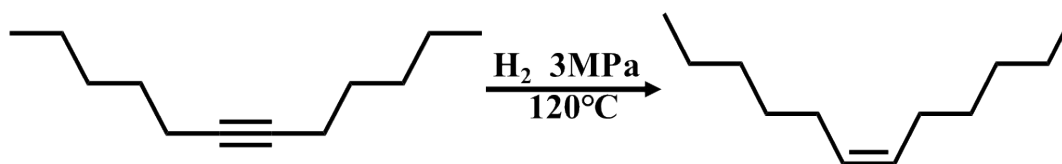


Figure S17. The FT-IR spectra of COFs-1-PPh<sub>2</sub>, COFs-1-FLPs, COFs-2-PPh<sub>2</sub> and COFs-2-FLPs.

Table S2. Investigation of COFs/BCF, COFs-FLPs and Br-free-COFs-1-P/BCF in the catalytic hydrogenation of 5-decyne to Z-5-decene.



Entry	Catalyst	T/h	Conversion/%
1	COFs-1/BCF	48	5
2	COFs-2/BCF	48	0
3	COFs-1-FLPs	36	88
4	COFs-2-FLPs	36	87
5	Br-free-COFs-1-P/BCF	48	14

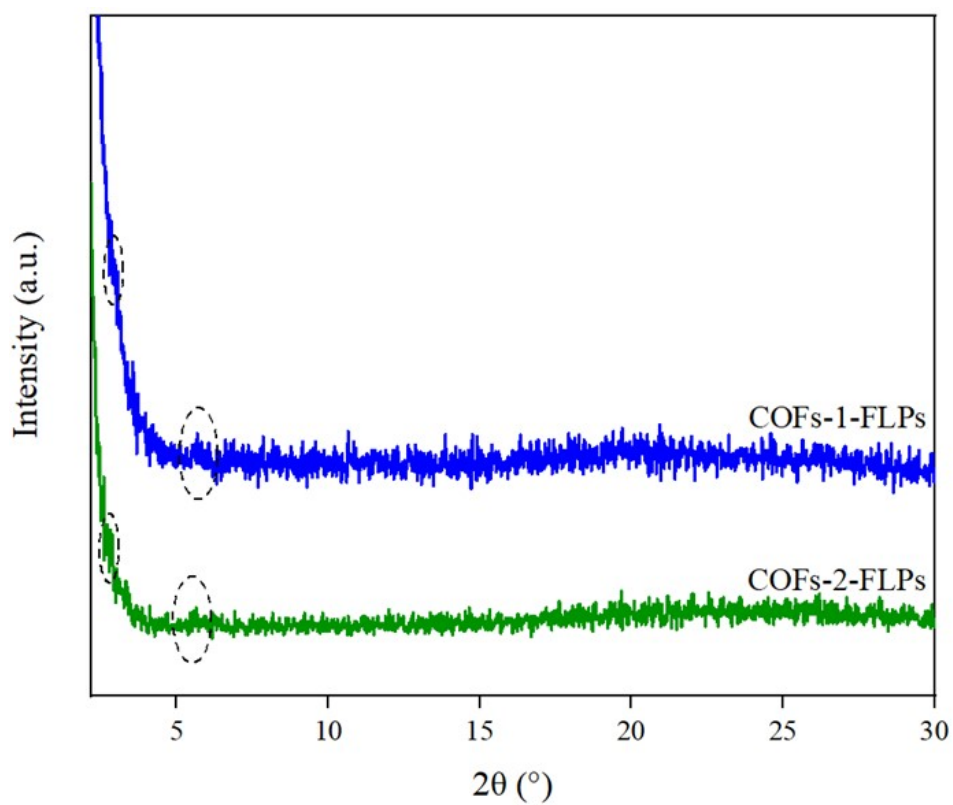


Figure S18. PXRD of COFs-1-FLPs and COFs-2-FLPs after 10 runs.

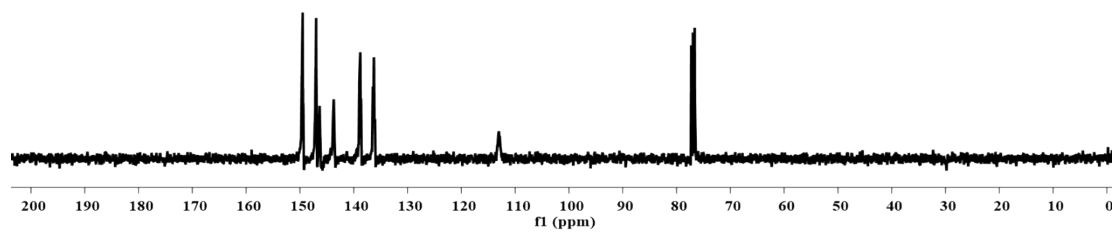


Figure S19. <sup>13</sup>C NMR spectrum of BCF (in CDCl<sub>3</sub>, 101 MHz).

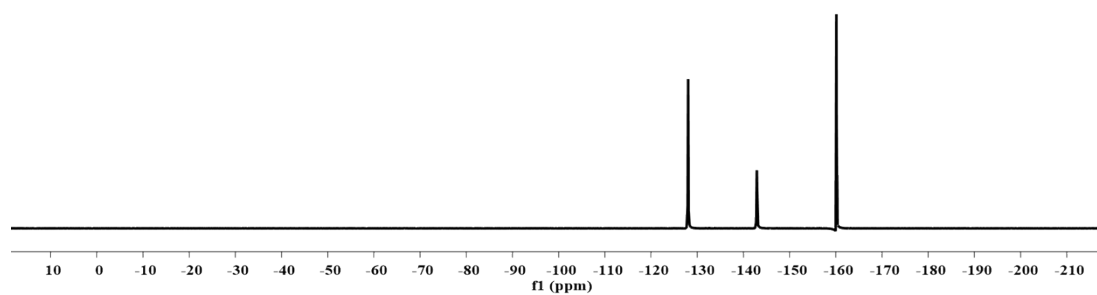


Figure S20.  $^{19}\text{F}$  NMR spectrum of BCF (in  $\text{CDCl}_3$ , 376 MHz).

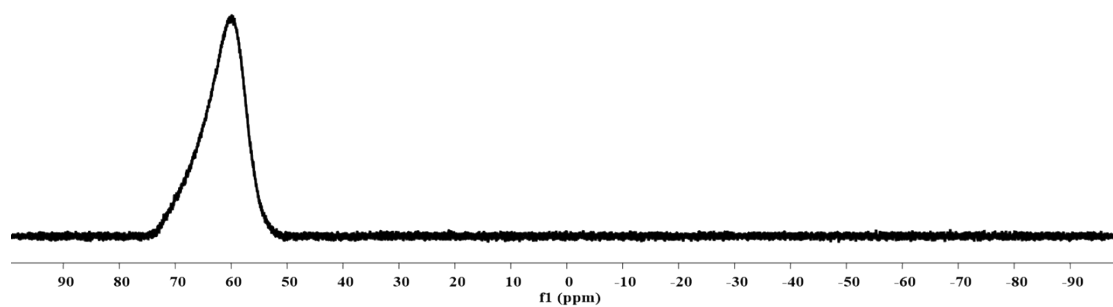


Figure S21.  $^{11}\text{B}$  NMR spectrum of BCF (in  $\text{CDCl}_3$ , 128 MHz).

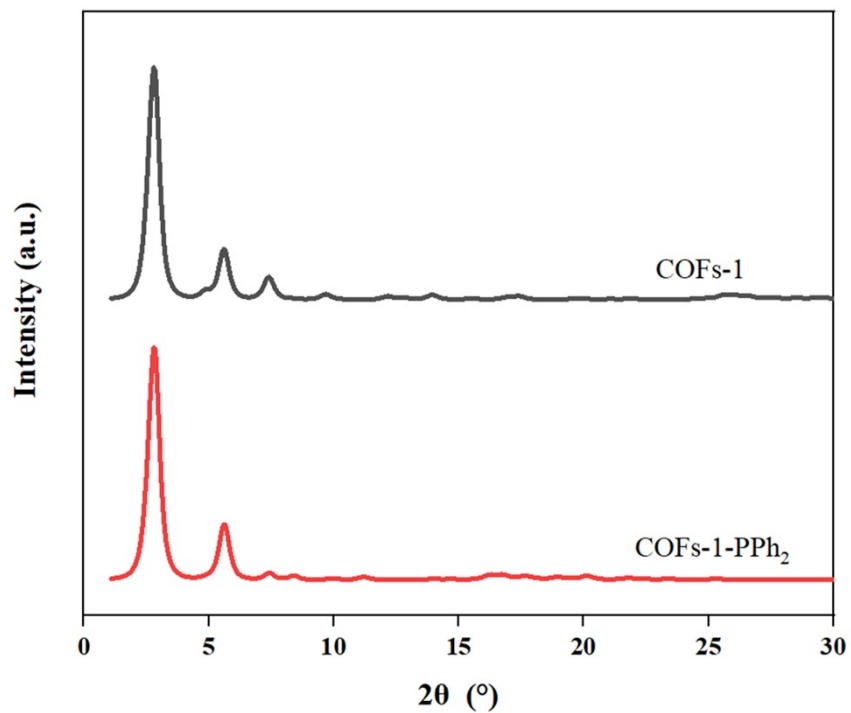
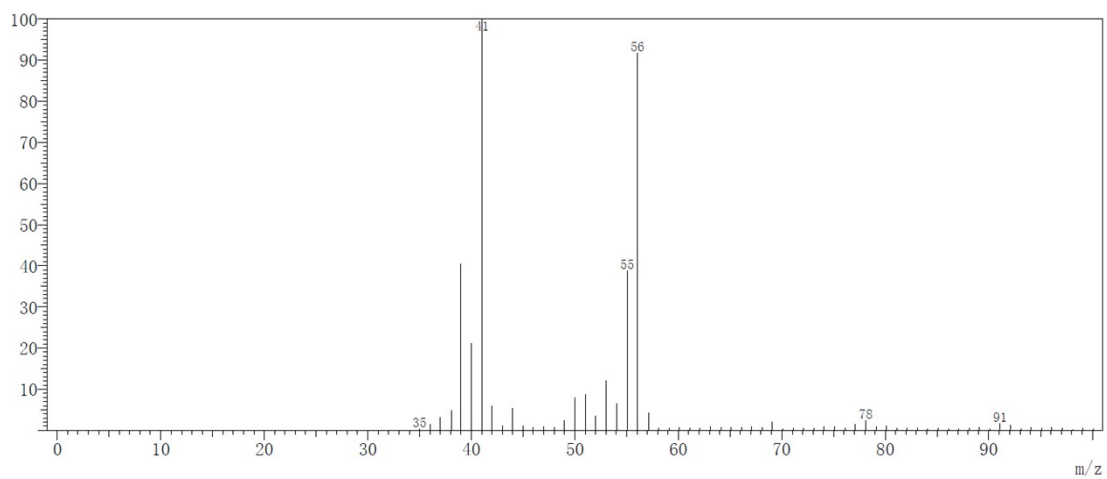


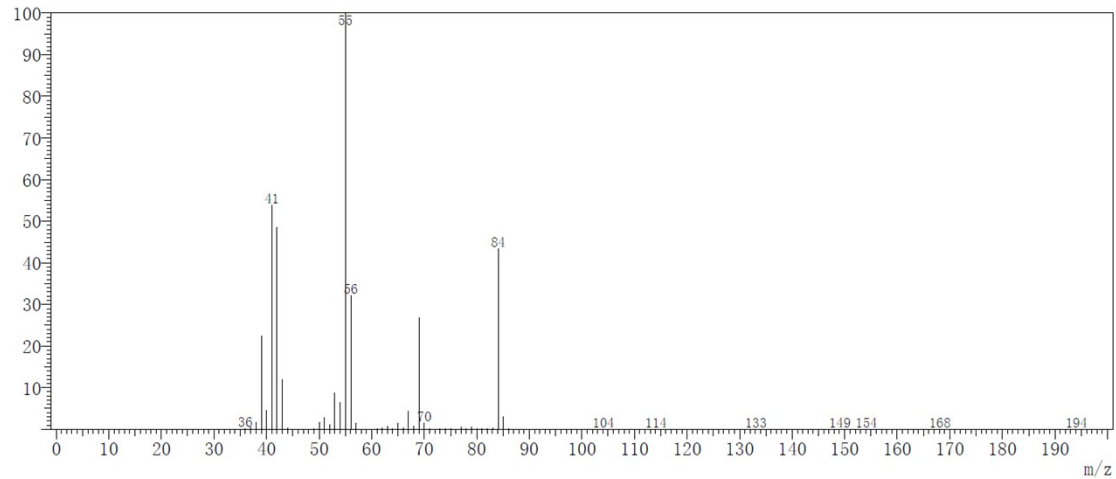
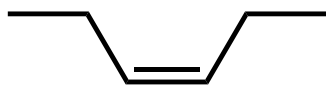
Figure S22. Simulated theoretical PXRD patterns of COFs-1 and COFs-1-PPh<sub>2</sub>. (Br was completely replaced by -PPh<sub>2</sub>)

## 2. Original MS data

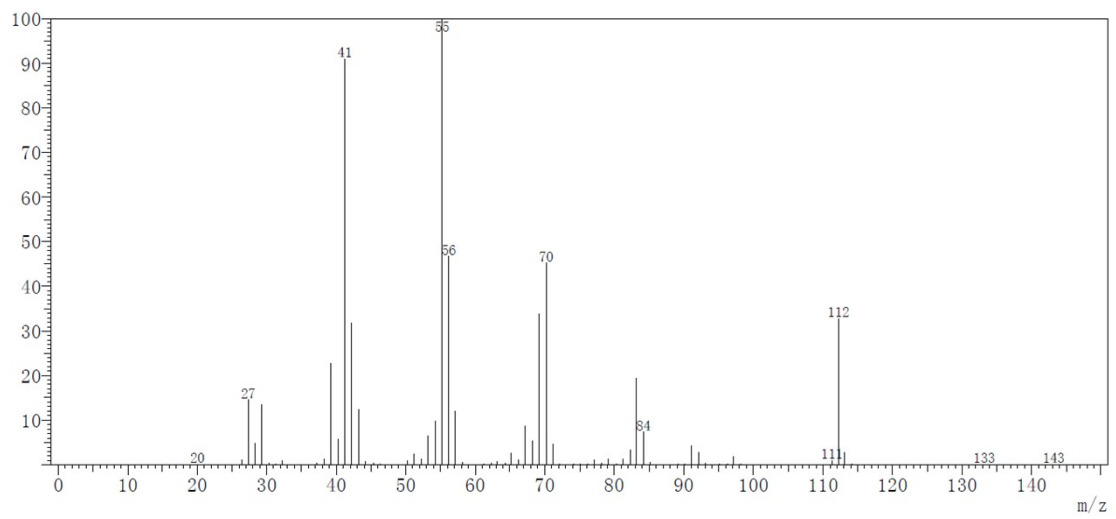
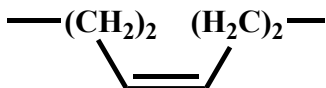
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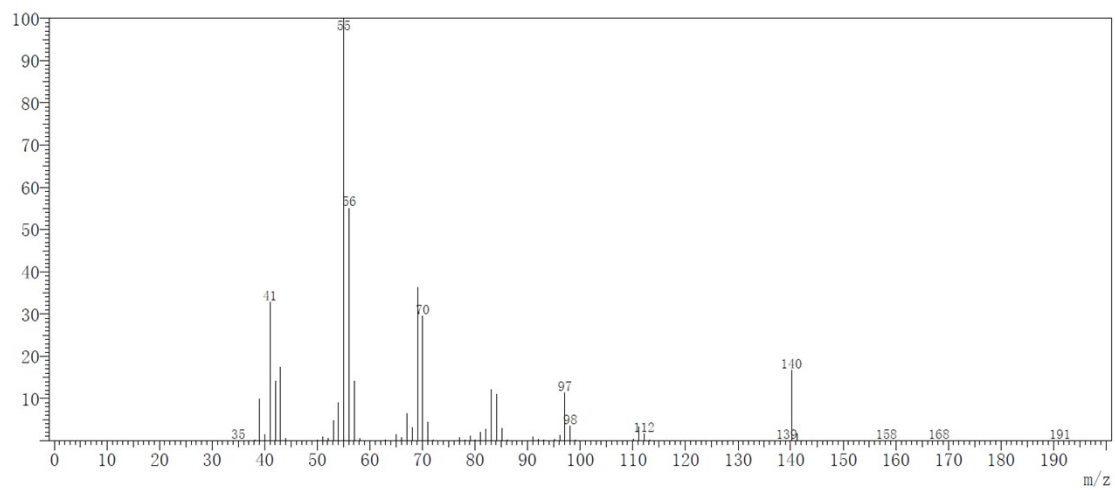
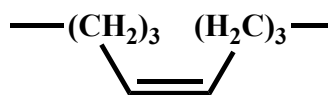
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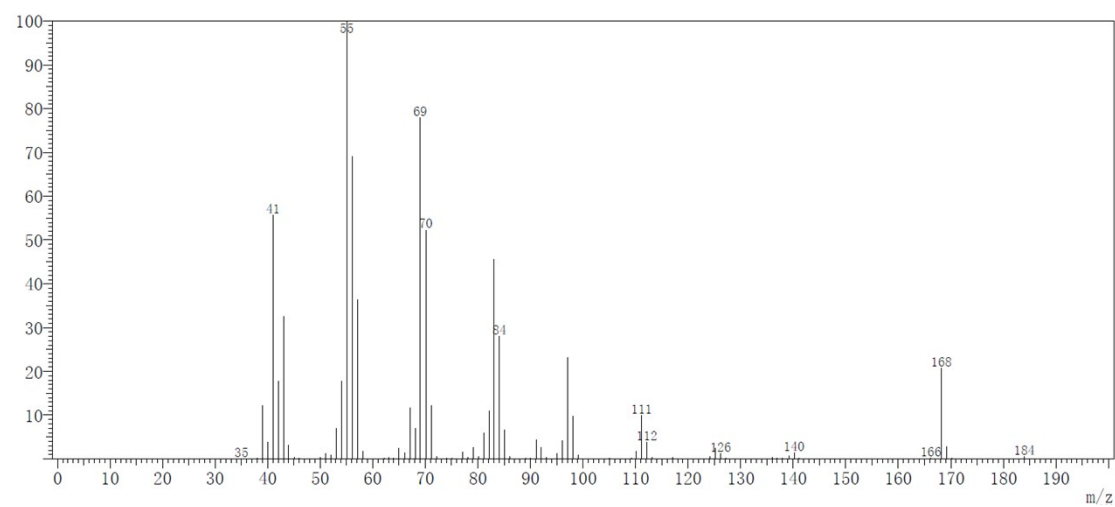
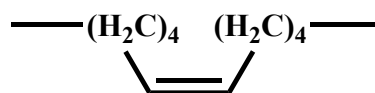
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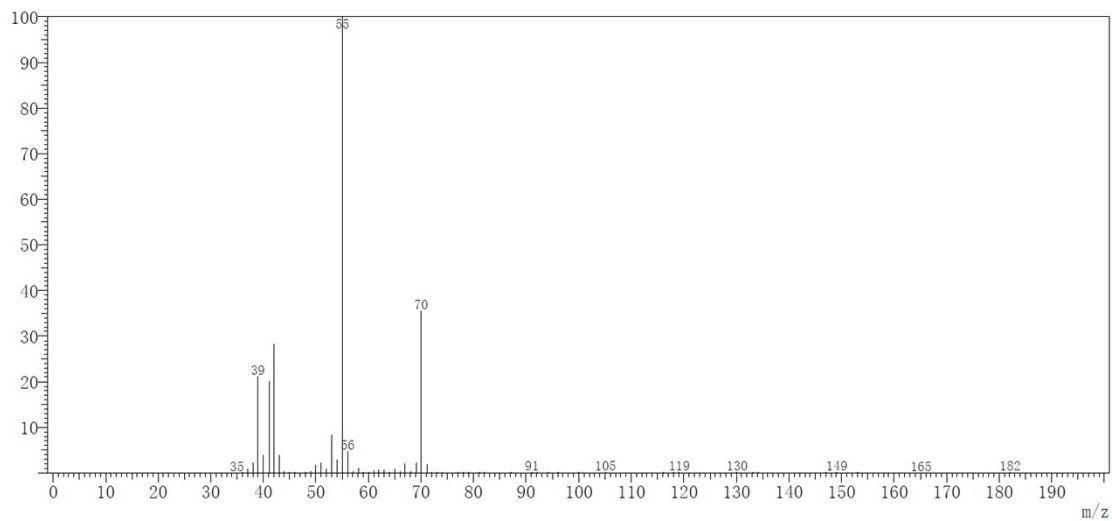
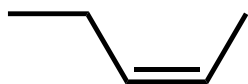
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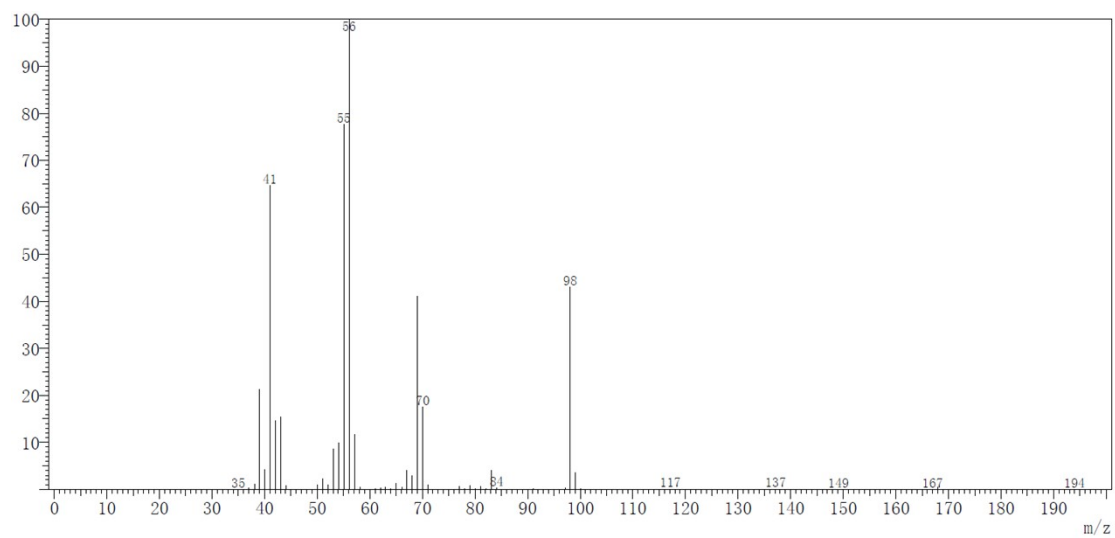
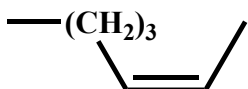
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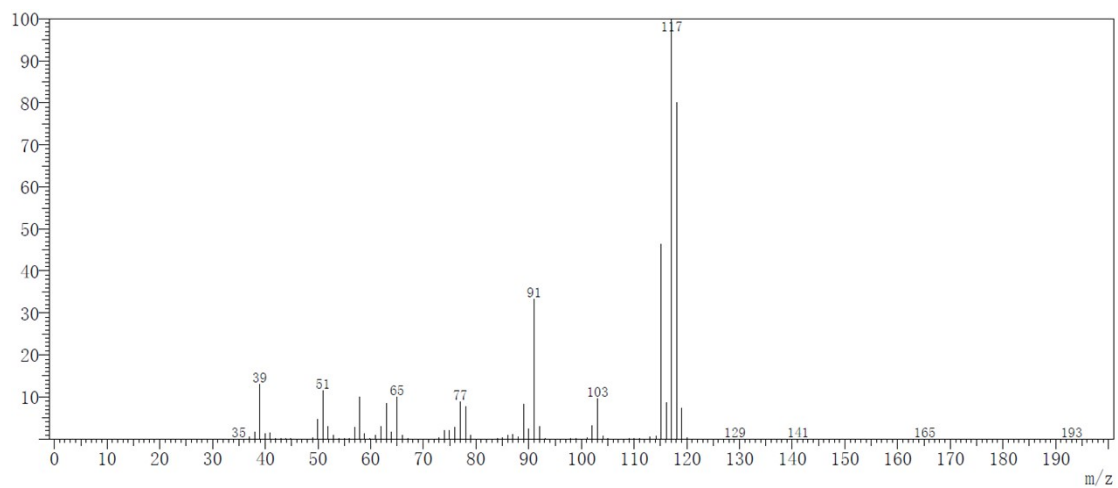
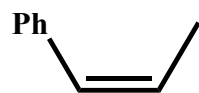


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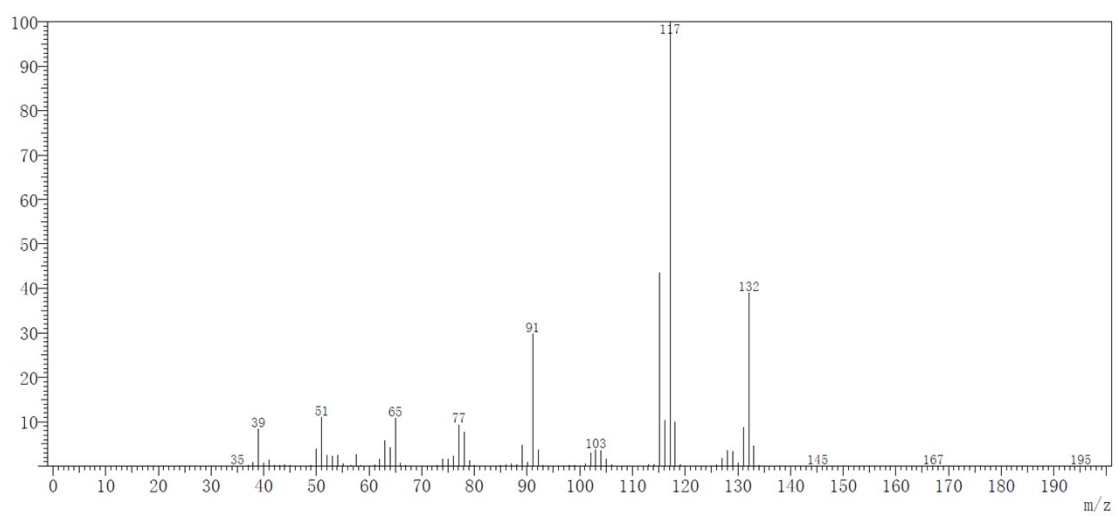




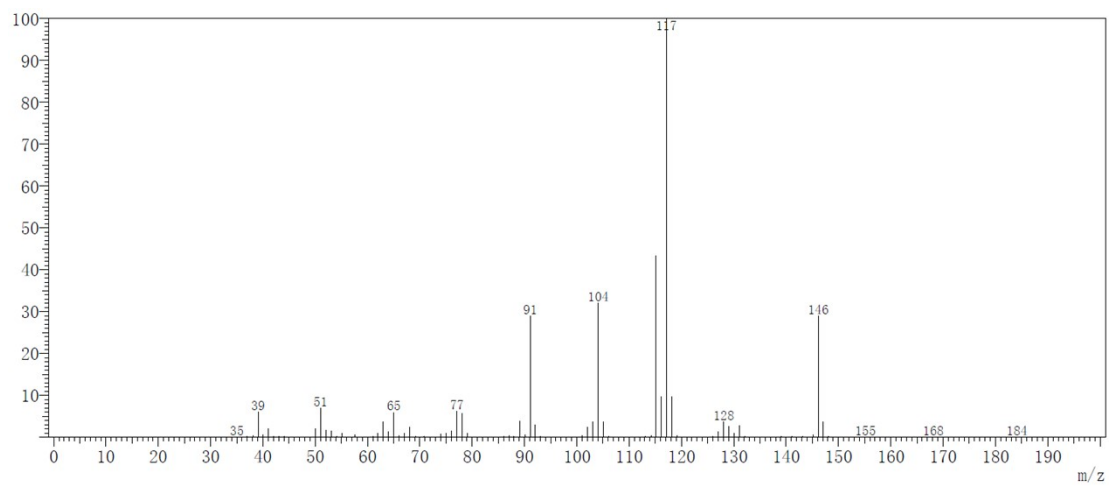
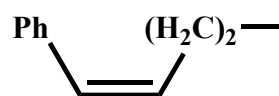
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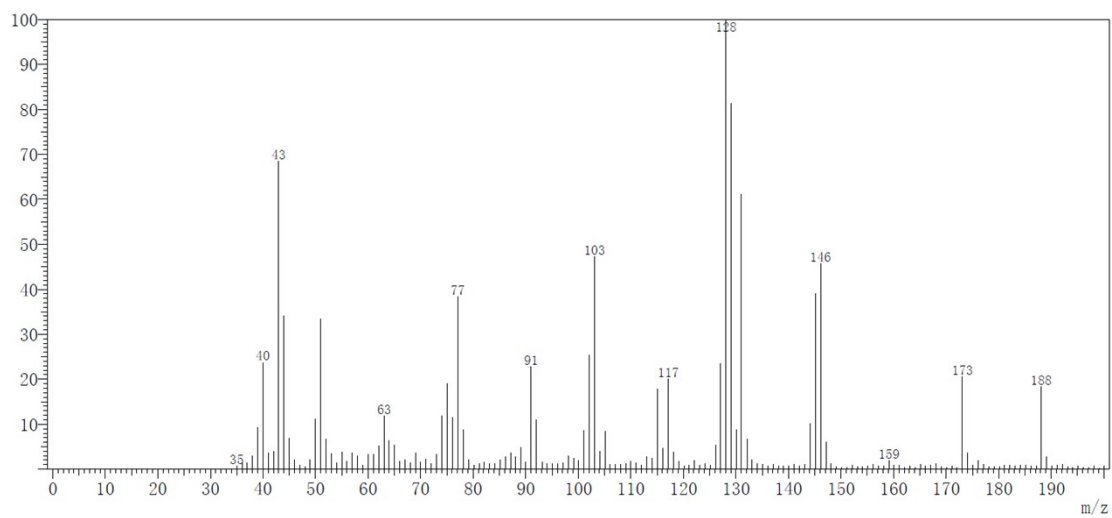
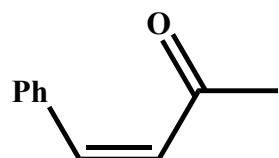
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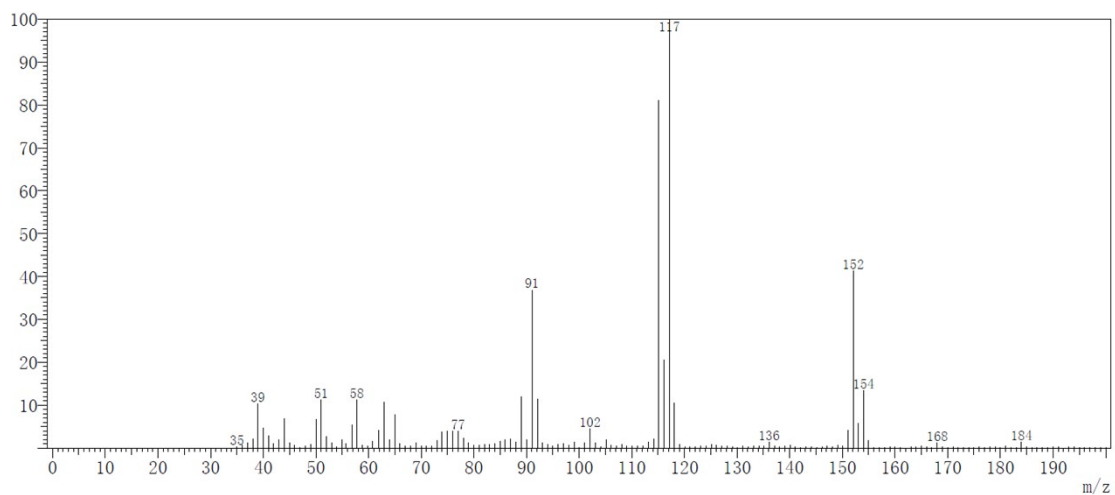
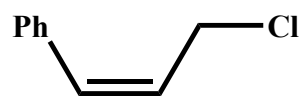
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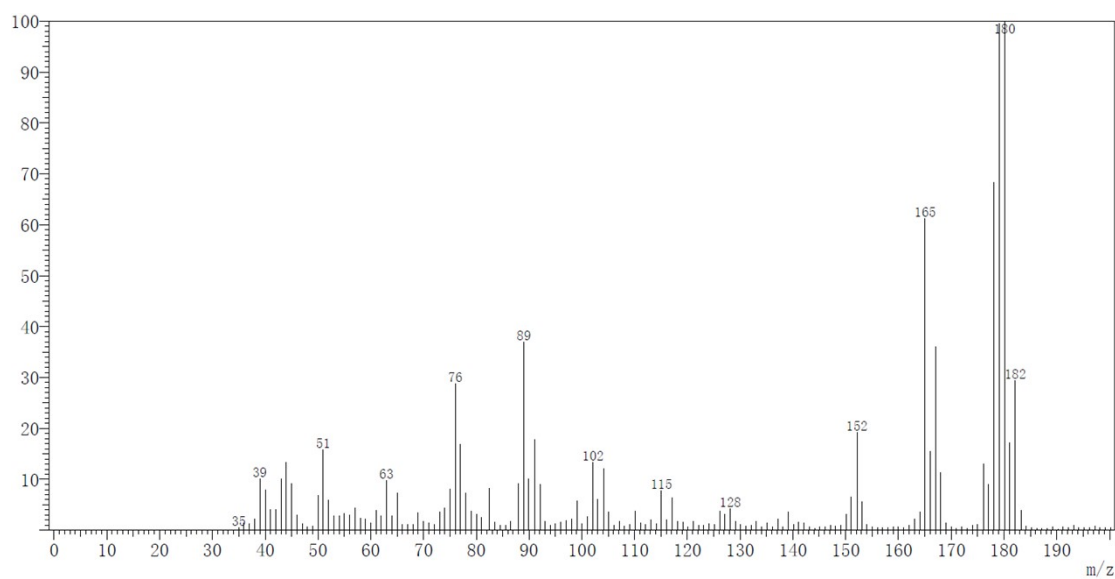
11.



12.



13.



Reference:

1. M. Ullrich, A. J. Lough, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 52–53.