Supplementary Material

Mixed functionalization of organic ligands in UiO-66: a tool to design metal-organic frameworks for tailored microextraction

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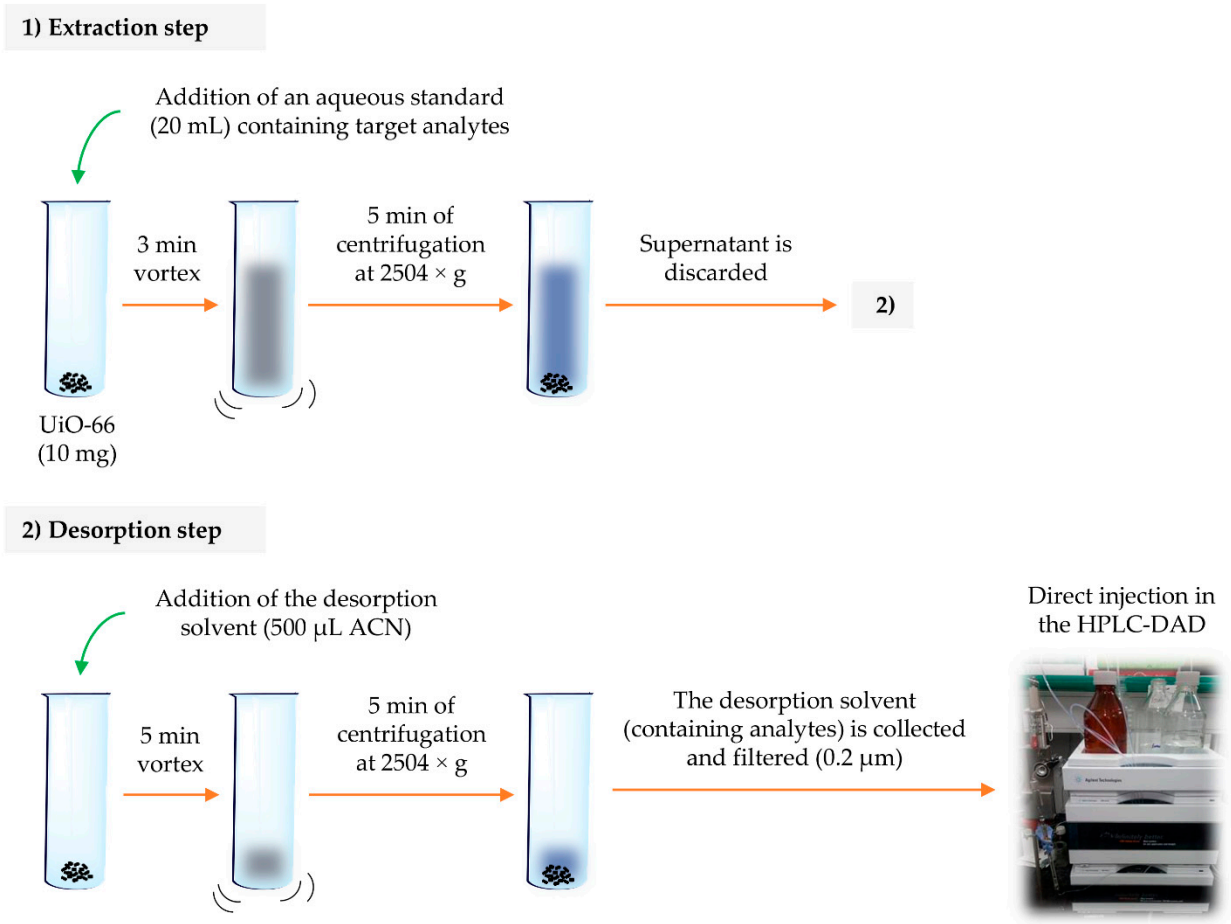

Figure S1. Scheme of the D-µSPE-HPLC-DAD method using optimum conditions.

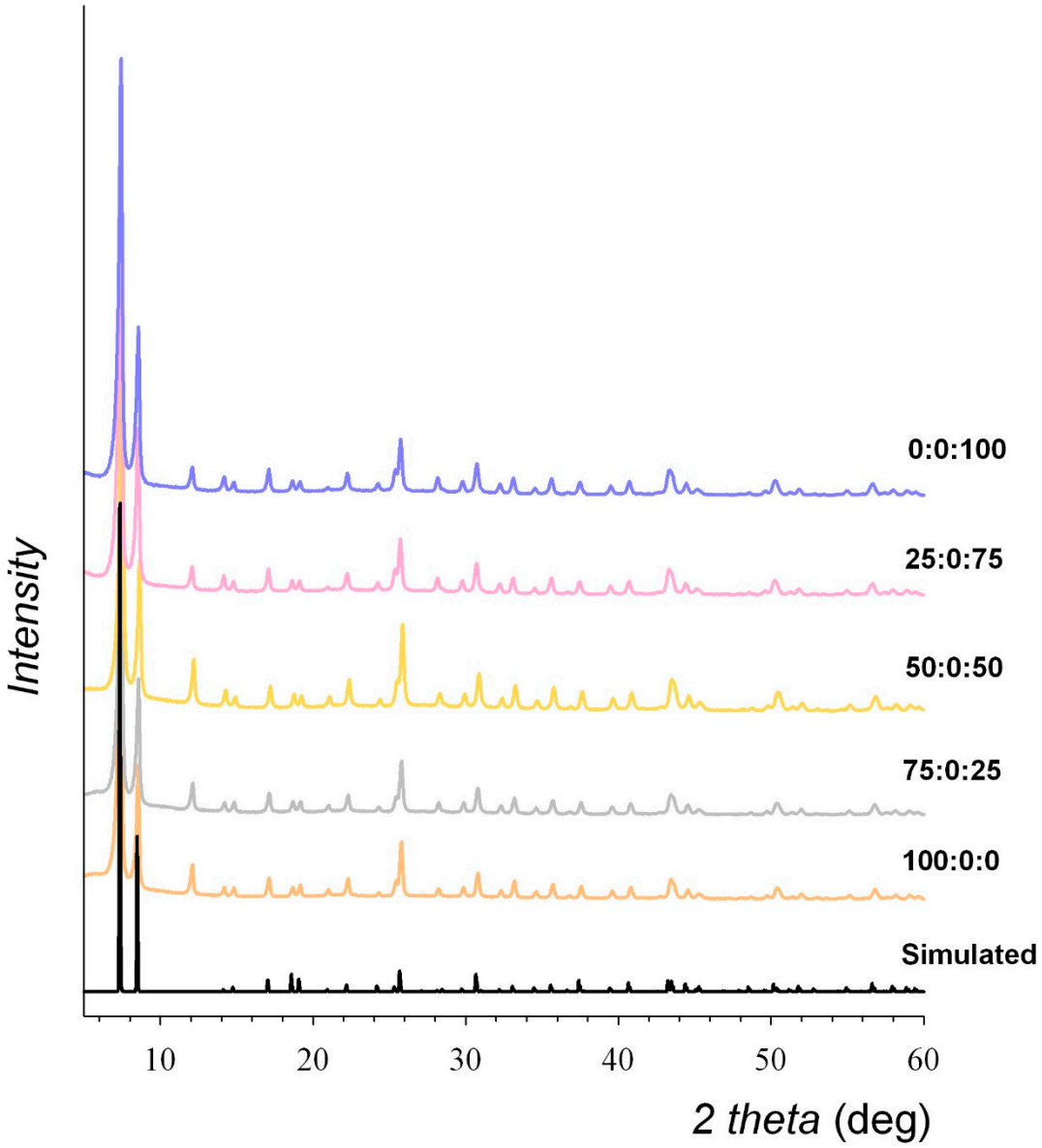

Figure S2. XRD patterns of the H-bdc/NO_2-bdc series of UiO-66.

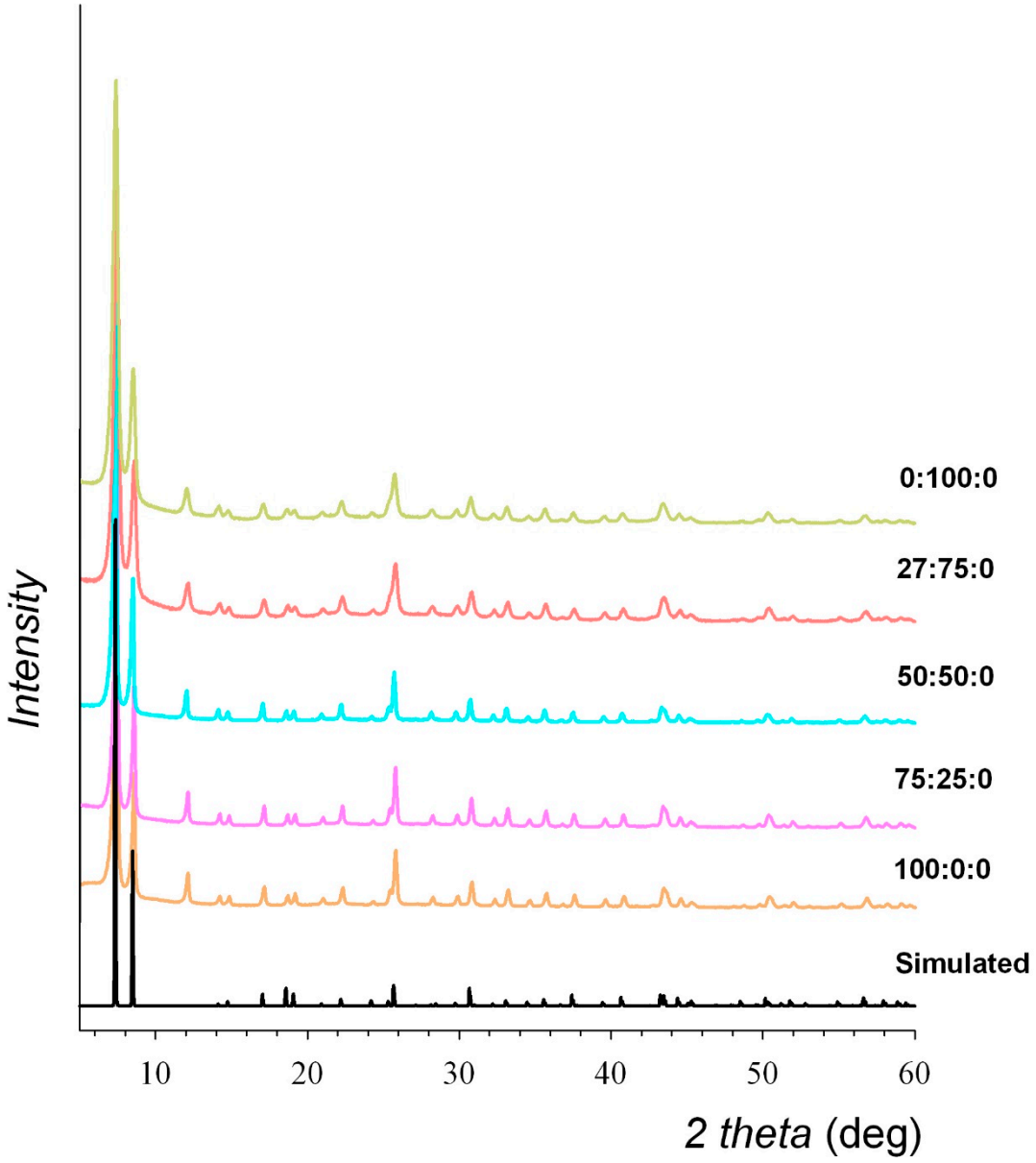

Figure S3. XRD patterns of the H-bdc/NH_2-bdc series of UiO-66.

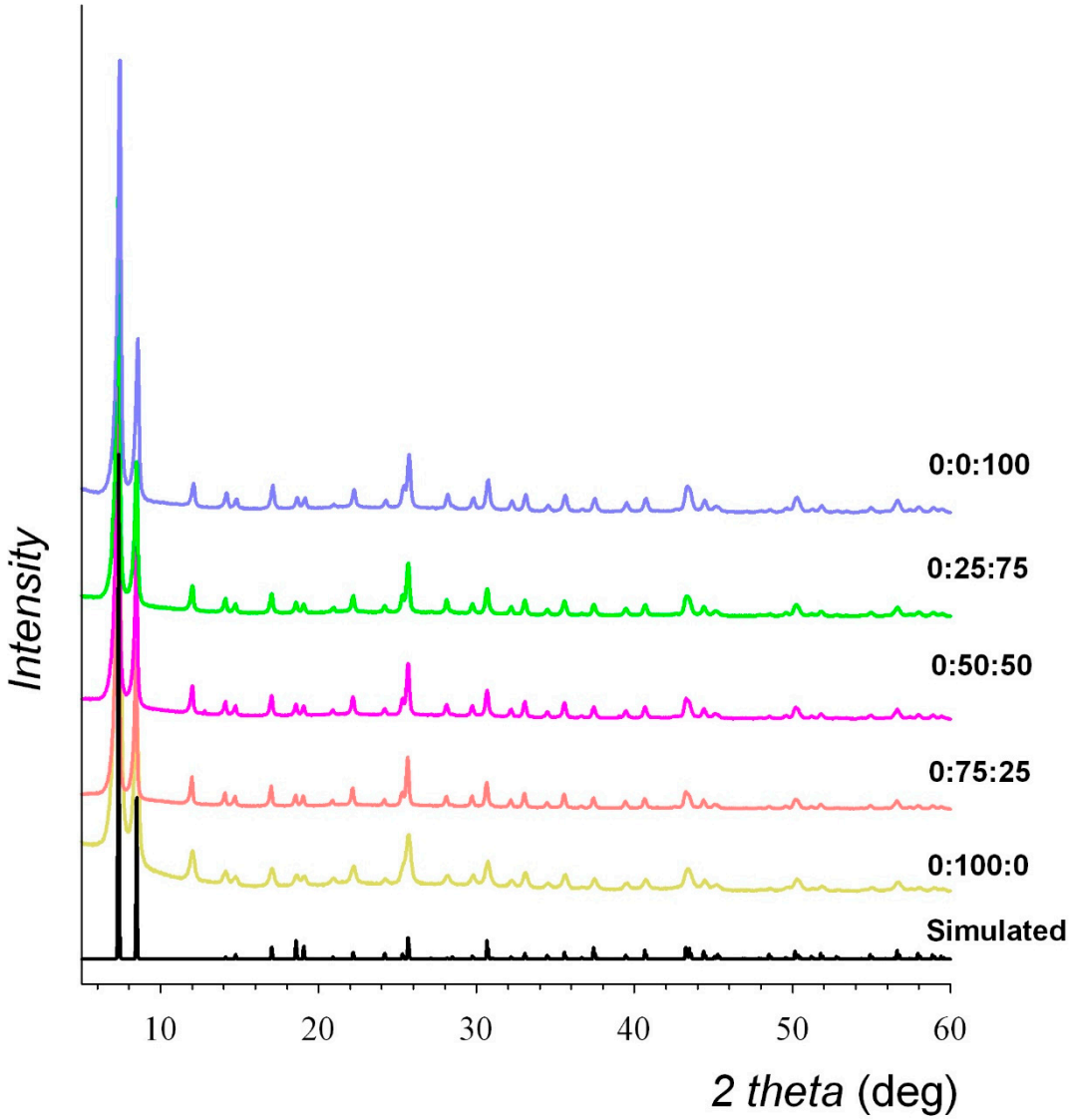

Figure S4. XRD patterns of the NH_2-bdc/NO_2-bdc series of UiO-66.

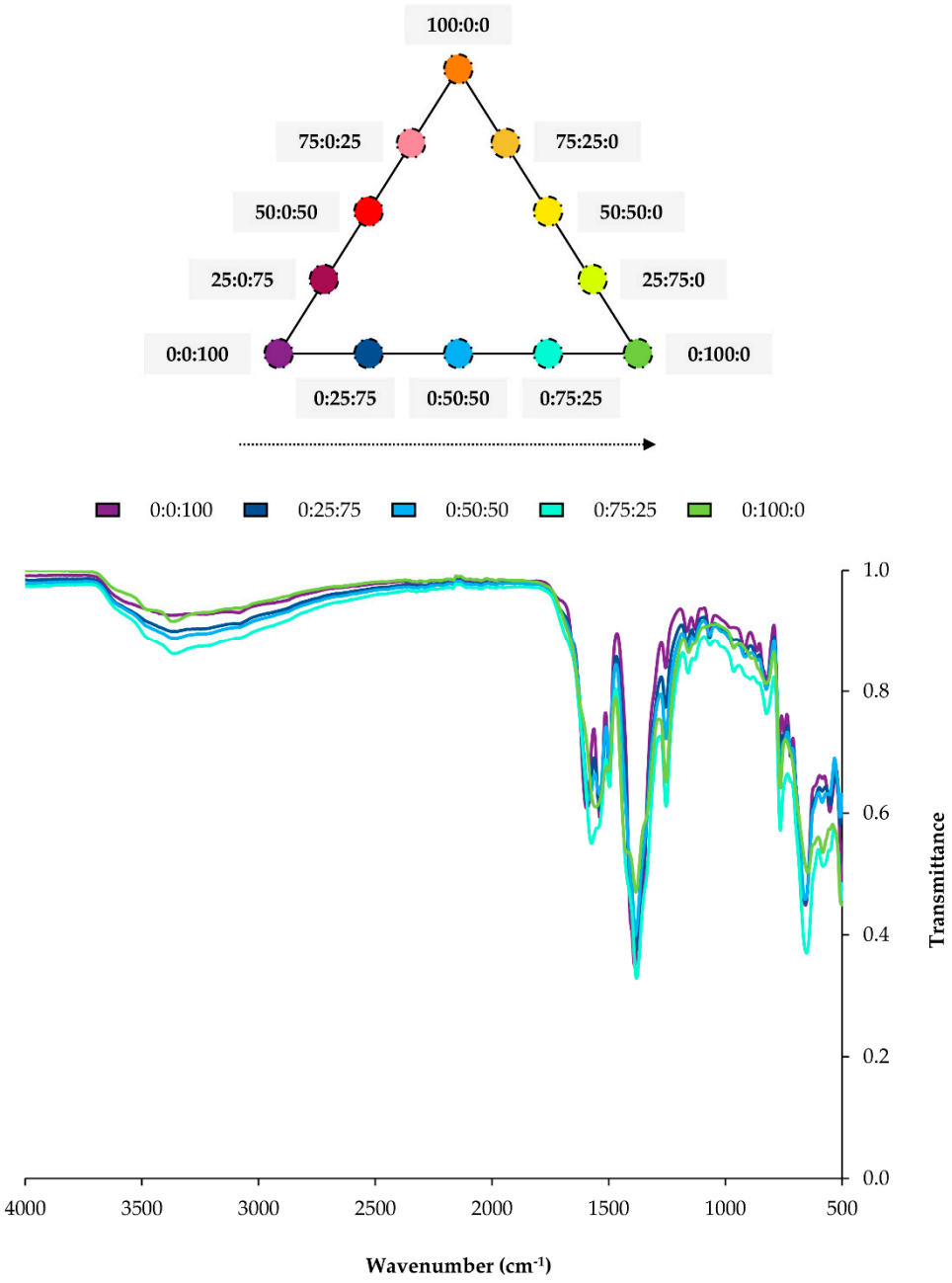

Figure S5. Infrared spectra for the NH_2-bdc/NO_2-bdc series. The code H-bdc:NH_2-bdc:NO_2-bdc is included for each MOF.

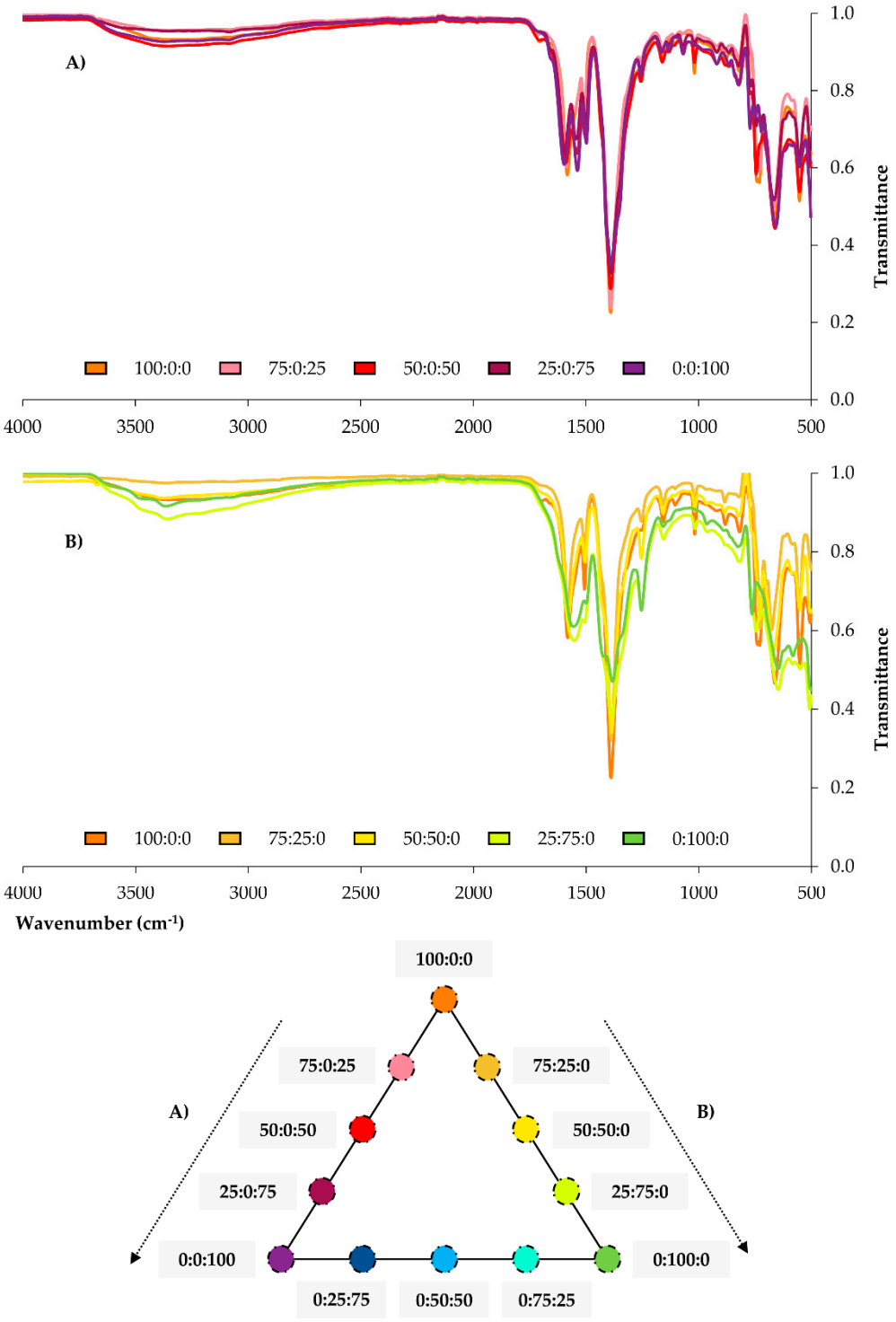

Figure S6. Infrared spectra for **A)** H-bdc/NO_2-bdc and **B)** H-bdc/NH_2-bdc series. The code H-bdc:NH_2-bdc:NO_2-bdc is included for each MOF. The small band at around 1700 cm^{-1} in the FTIR can be linked to DMF moieties retained inside the porous structure strongly adsorbed.

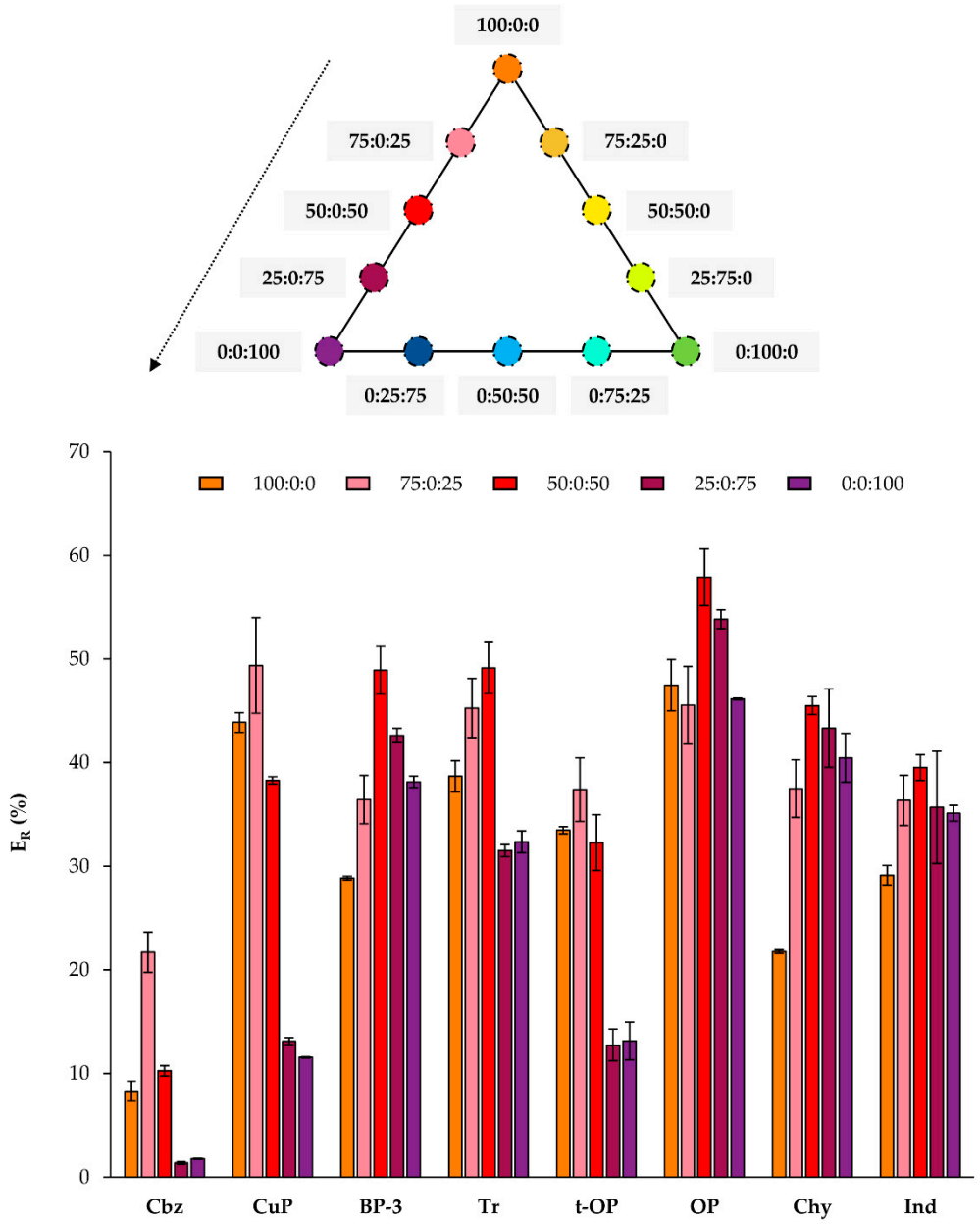

Figure S7. Analytical performance when using the H-bdc/NO_2-bdc series of UiO-66 as sorbents in D-μSPE-HPLC-DAD, expressed in terms of extraction efficiency (E_R, %) for the target analytes. The code H-bdc:NH_2-bdc:NO_2-bdc is included for each MOF. Experiments were performed in triplicate, with the conditions described in section 2.3.2.

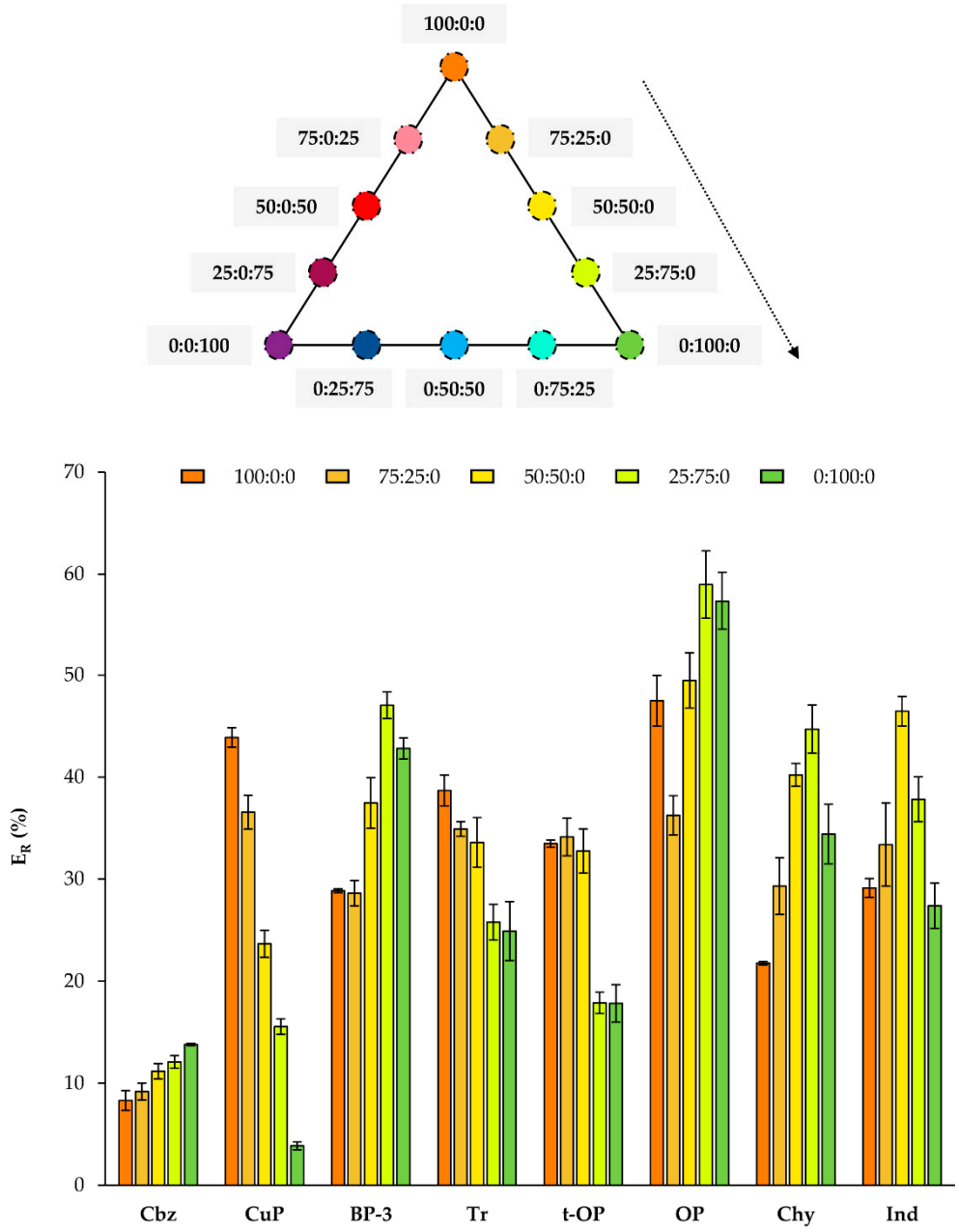

Figure S8. Analytical performance when using the H-bdc/NH_2-bdc series of MOFs as sorbents in D-μSPE-HPLC-DAD, expressed in terms of extraction efficiency (E_R, %) for the target analytes. The code H-bdc:NH_2-bdc:NO_2-bdc is included for each MOF. Experiments were performed in triplicate, with the conditions described in section 2.3.2.

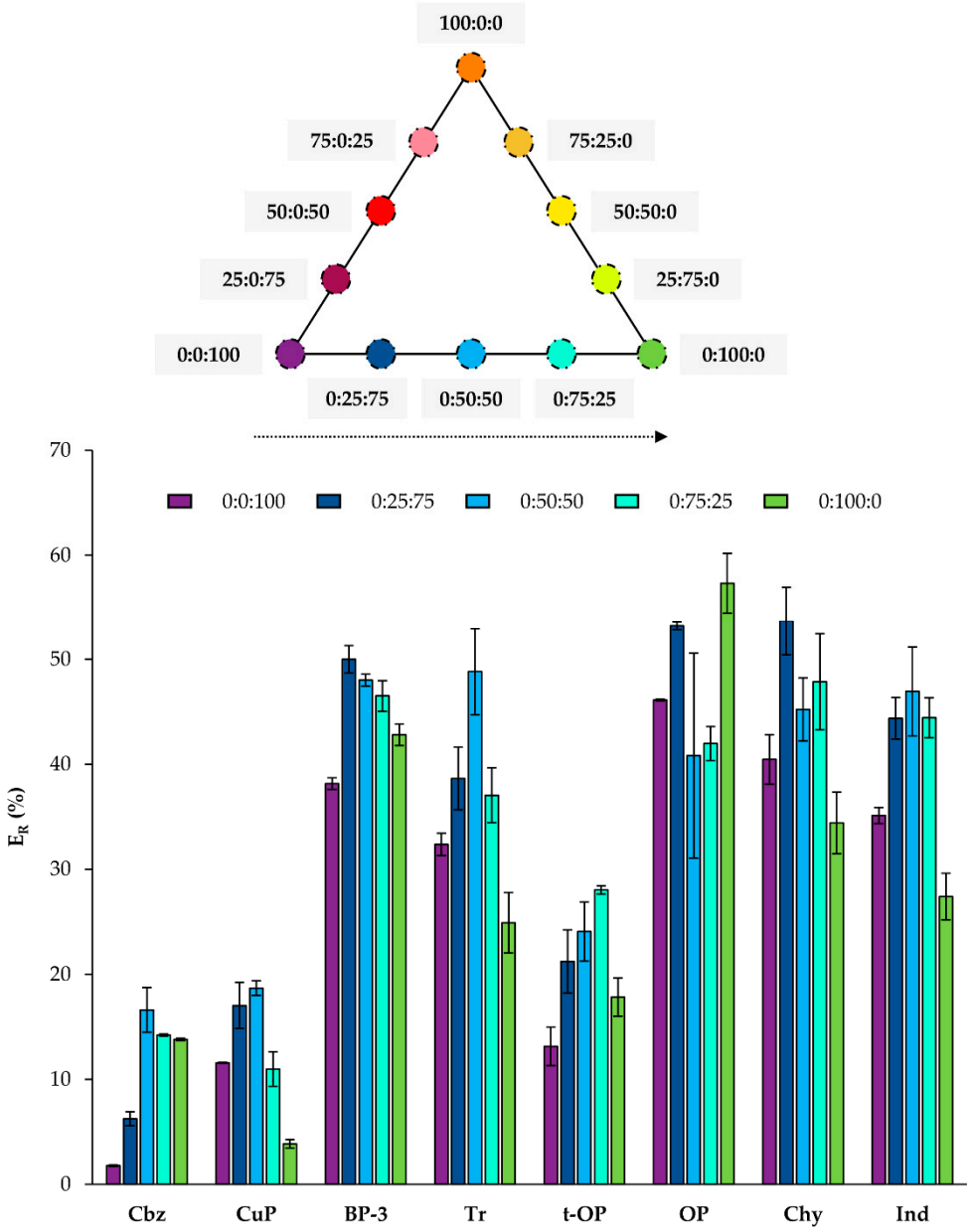

Figure S9. Analytical performance when using the NH_2-bdc/NO_2-bdc series of MOFs as sorbents in D-μSPE-HPLC-DAD, expressed in terms of extraction efficiency (E_R, %) for the target analytes. The code H-bdc:NH_2-bdc:NO_2-bdc is included for each MOF. Experiments were carried out in triplicate, with the conditions described in section 2.3.2.

Table S1. Adsorption data for all the synthesized UiO-66-based MOFs.

MOF (H-bdc:NH_2-bdc:NO_2-bdc)	Surface area	
	BET[1] ($m^2 \cdot g^{-1}$)	Langmuir[2] ($m^2 \cdot g^{-1}$)
100:0:0	1175	1480
75:25:0	938	1312
50:50:0	895	1444
25:75:0	757	1050
0:100:0	678	939
75:0:25	717	991
50:0:50	689	953
25:0:75	656	845
0:0:100	604	752
0:25:75	620	802
0:50:50	684	889
0:75:25	719	924

[1] Brunauer-Emmett-Teller multilayer gas adsorption model

[2] Langmuir monolayer gas adsorption model

Table S2. Elemental analysis data for all the synthesized UiO-66-based MOFs.

MOF (H-bdc:NH_2-bdc:NO_2-bdc)	Experimental / Calculated (%)		
	C	**N**	**H**
100:0:0	32.09 / 32.86	0.24 / 0.00	2.09 / 2.18
75:25:0	31.59 / 32.45	1.58 / 1.18	2.03 / 2.24
50:50:0	31.31 / 31.72	3.09 / 2.31	2.93 / 2.28
25:75:0	29.95 / 31.65	3.67 / 3.46	2.89 / 2.35
0:100:0	30.05 / 30.96	4.48 / 4.51	2.45 / 2.49
75:0:25	30.73 / 31.65	1.57 / 1.15	1.90 / 2.01
50:0:50	29.41 / 30.51	2.61 / 2.22	1.69 / 1.87
25:0:75	29.69 / 29.46	3.83 / 3.22	1.71 / 1.72
0:0:100	28.13 / 28.48	4.47 / 4.15	1.85 / 1.59
0:25:75	28.99 / 29.12	4.58 / 4.25	1.54 / 1.78
0:50:50	29.16 / 29.80	4.46 / 4.35	1.98 / 1.98
0:75:25	29.88 / 30.51	4.45 / 4.44	2.20 / 2.19