Postsynthetic Modification: A Versatile Approach Towards Multifunctional Metal-Organic Frameworks

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SUPPORTING INFORMATION

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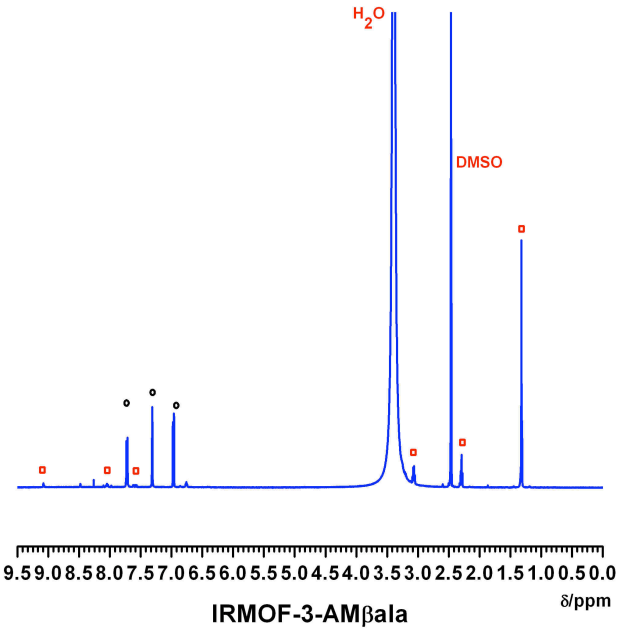

Figure S1. ^{1}H NMR spectra of digested IRMOF-3 modified with Boc-β-alanine anhydride for 2 days. NH_2-BDC resonances are denoted by black circles and RCONH-BDC resonances by red squares.

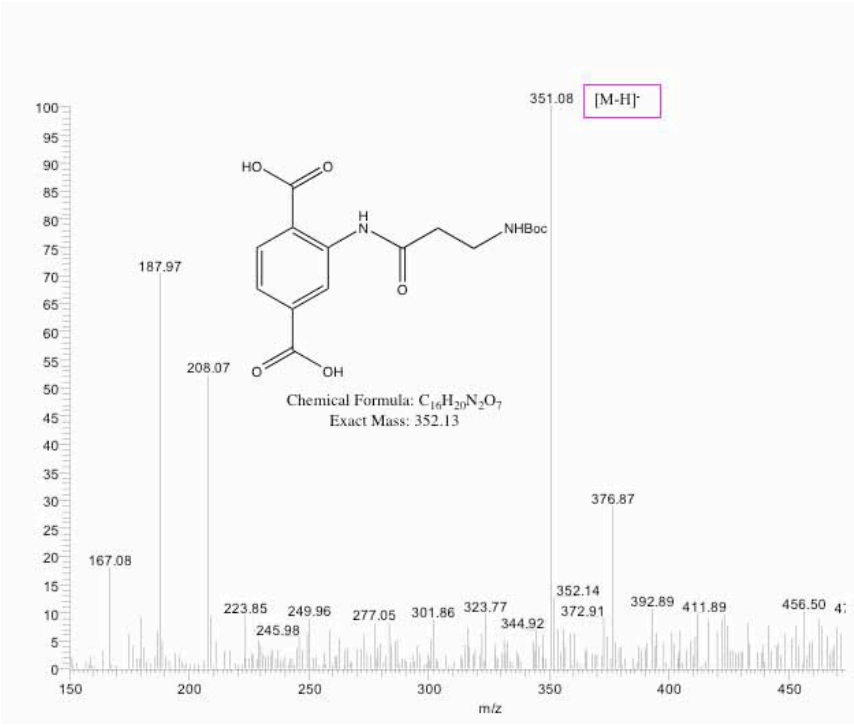

Figure S2. ESI-MS (negative ion mode) of the digested IRMOF-3-AMβala.

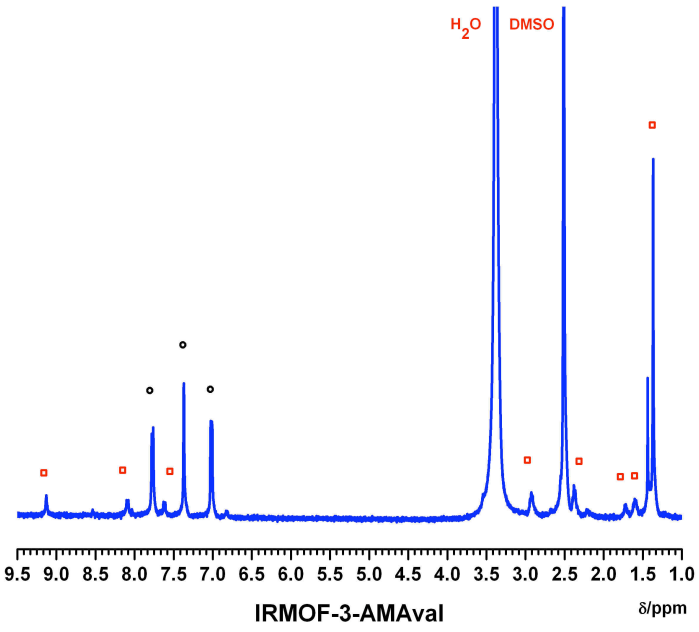

Figure S3. ^{1}H NMR spectra of digested IRMOF-3 modified with Boc-aminovaleric anhydride for 2 days. NH_2-BDC resonances are denoted by black circles and RCONH-BDC resonances by red squares.

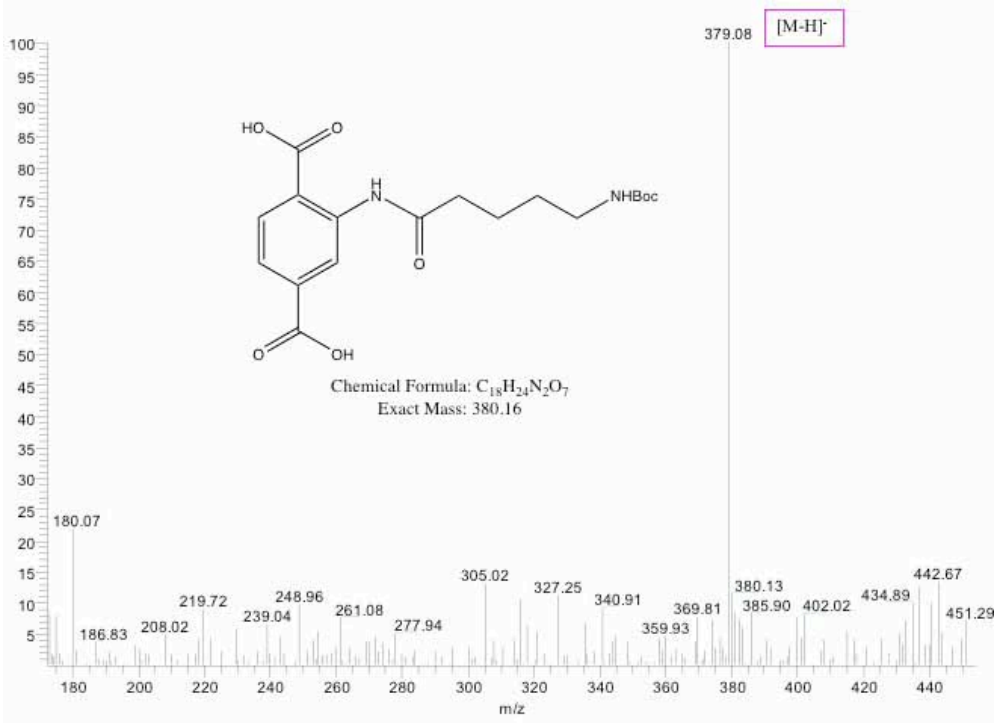

Figure S4. ESI-MS (negative ion mode) of the digested IRMOF-3-AMAval.

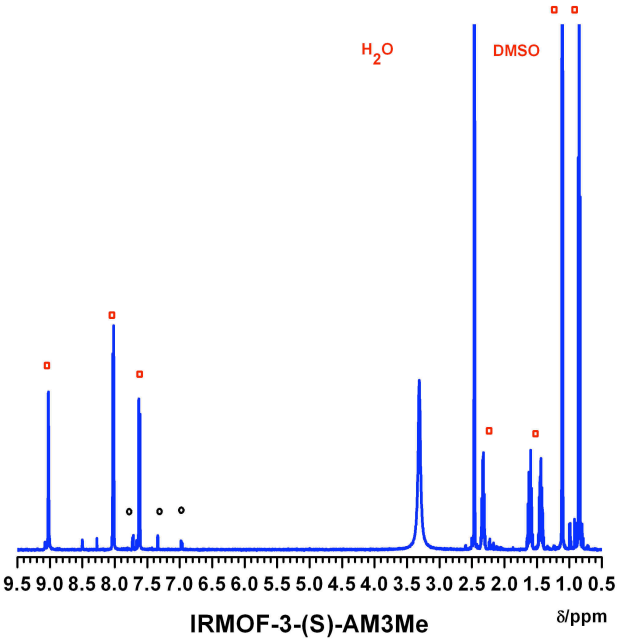

Figure S5. ^{1}H NMR spectra of digested IRMOF-3 modified with (*S*)-(+)-2-methyl butyric anhydride for 5 days. NH_2-BDC resonances are denoted by black circles and RCONH-BDC resonances by red squares.

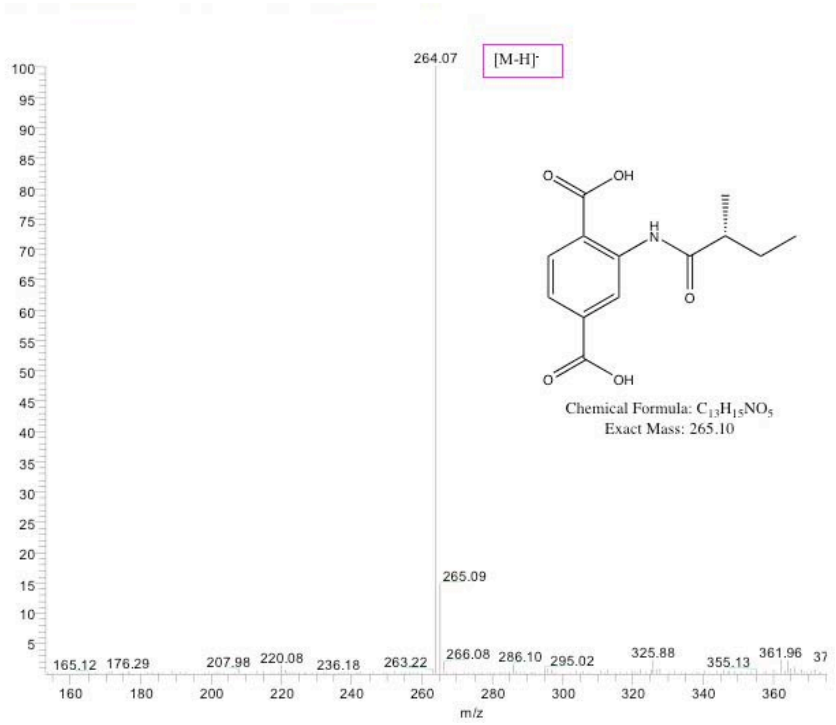

Figure S6. ESI-MS (negative ion mode) of the digested IRMOF-3-(*S*)-AM3Me.

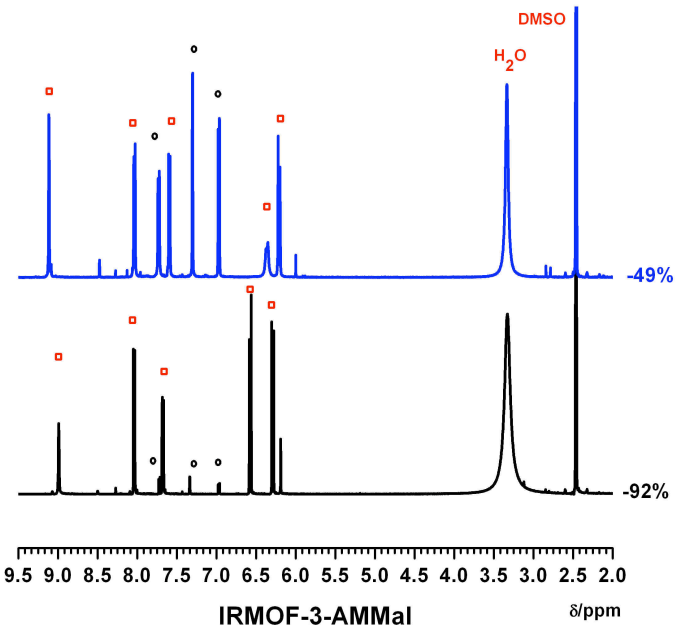

Figure S7. ^{1}H NMR spectra of digested IRMOF-3 modified with maleic anhydride for 5 days (bottom) and 1 day (top). NH_2-BDC resonances are denoted by black circles and RCONH-BDC resonances by red squares.

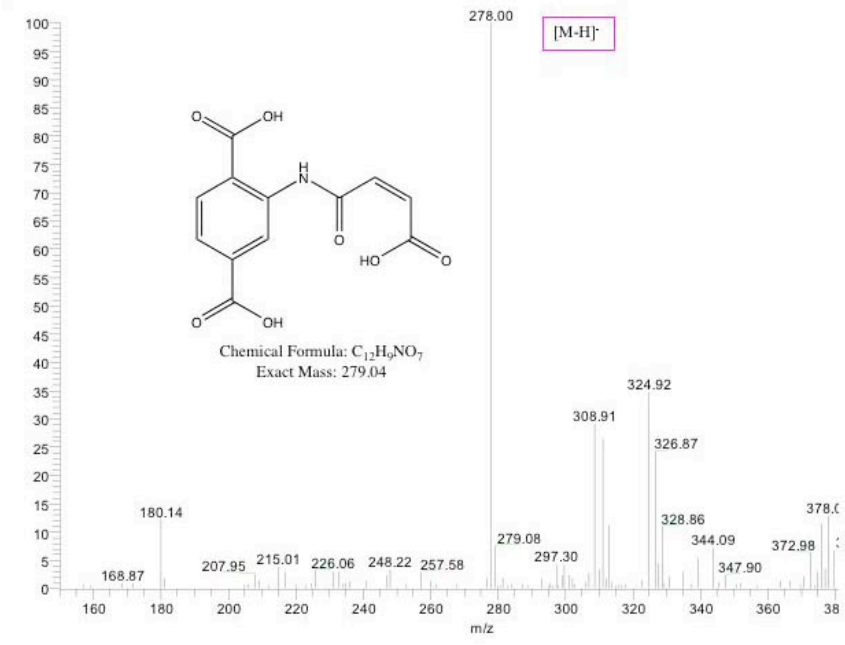

Figure S8. ESI-MS (negative ion mode) of the digested IRMOF-3-AMMal.

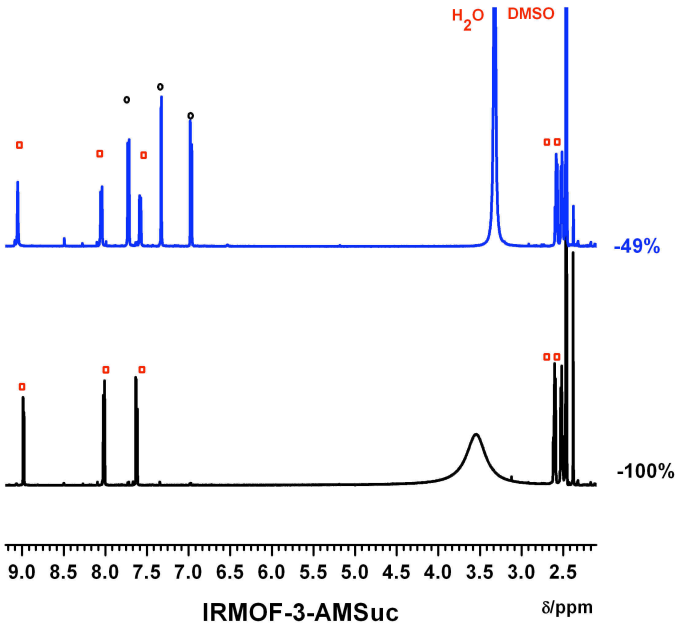

Figure S9. ^{1}H NMR spectra of digested IRMOF-3 modified with succinic anhydride for 5 days (bottom) and 1 day (top). NH_2-BDC resonances are denoted by black circles and RCONH-BDC resonances by red squares.

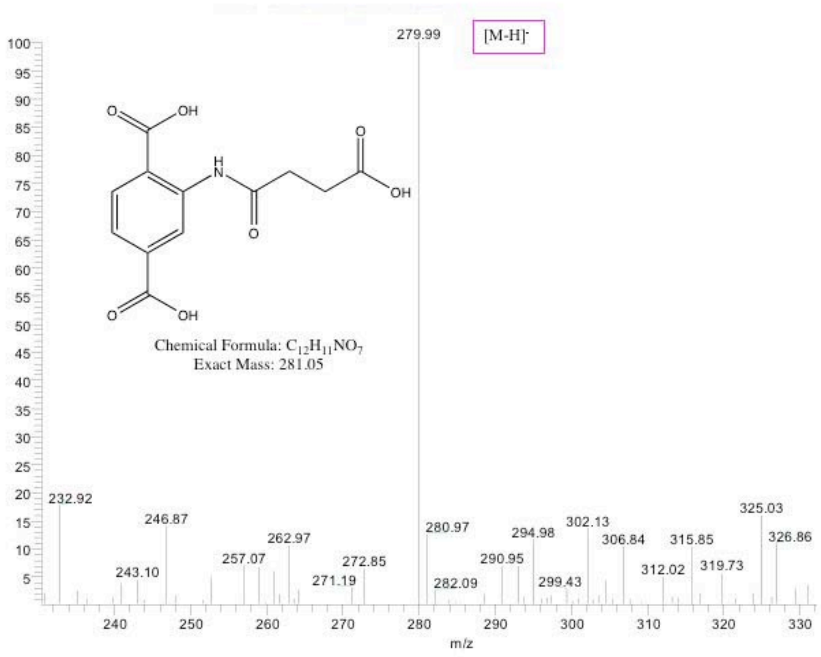

Figure S10. ESI-MS (negative ion mode) of the digested IRMOF-3-AMSuc.

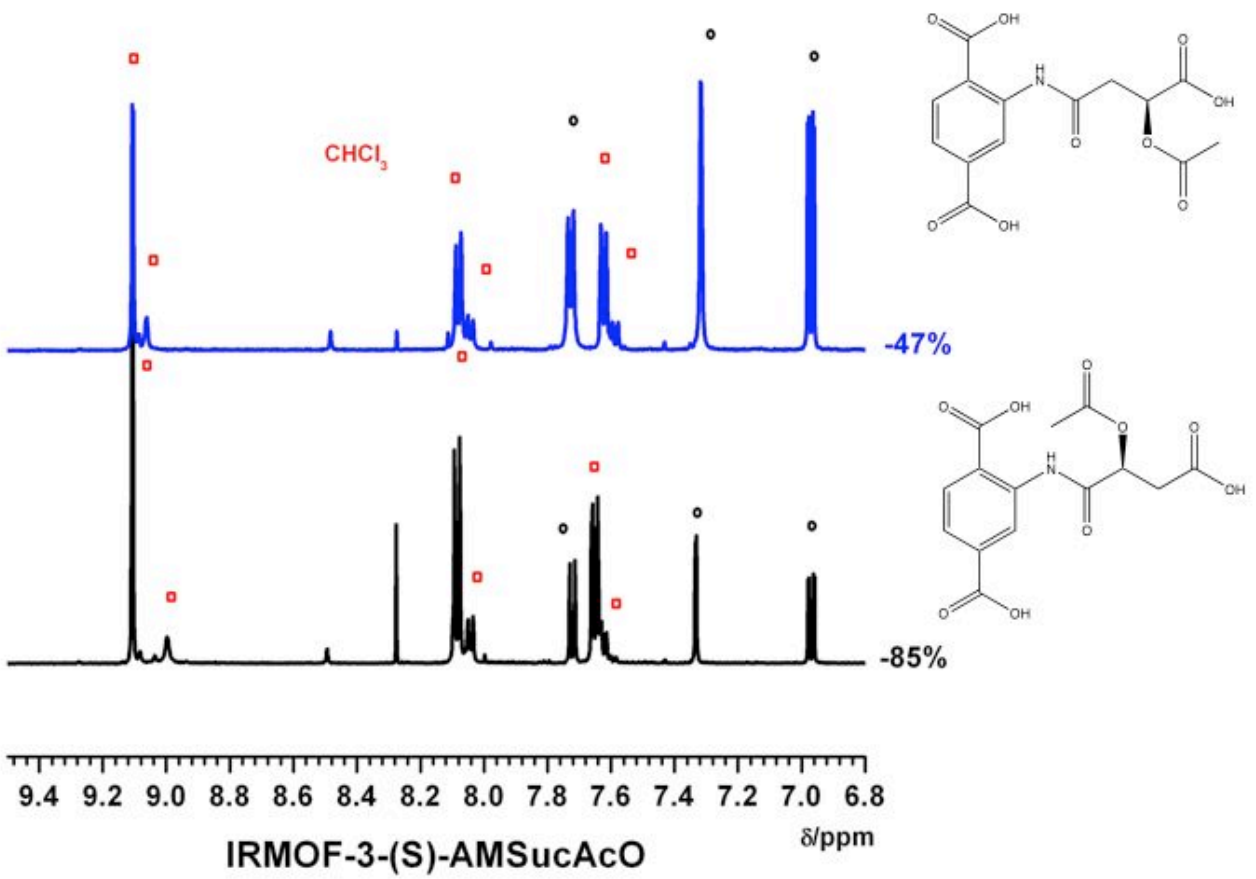

Figure S11. ^{1}H NMR spectra of digested IRMOF-3 modified with (*S*)-(-)-2-acetoxysuccunic anhydride for 1 days (top) and 5 days (bottom), respectively. The two amide products that can form are shown at the right (note that each spectra is a mixture of the two isomers). NH_2-BDC resonances are denoted by black circles and RCONH-BDC resonances by red squares.

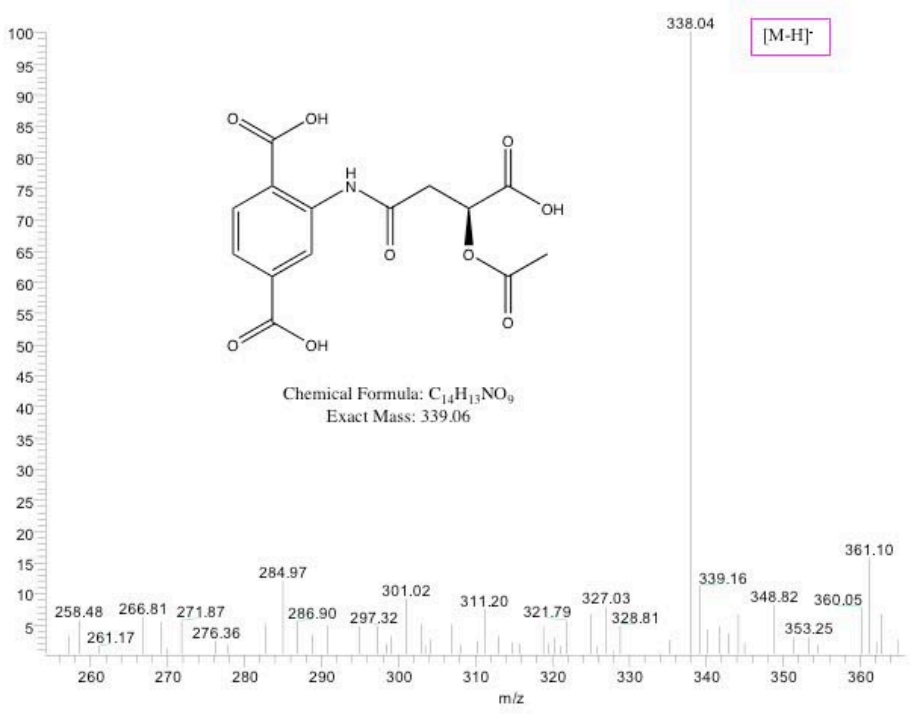

Figure S12. ESI-MS (negative ion mode) of the digested IRMOF-3-(*S*)-AMSucAcO.

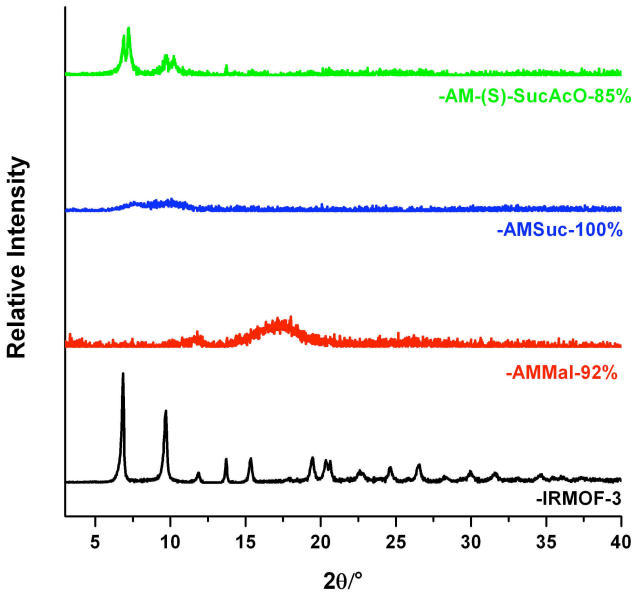

Figure S13. Powder X-ray diffraction (PXRD) patterns of cyclic anhydride modified IRMOF-3 samples at their respective conversions. Modified IRMOF-3 samples were soaked and exchanged with fresh $CHCl_3$ for 3 days. After decanting off the solvent, the samples were left drying in air for 10 min prior to PXRD analysis.

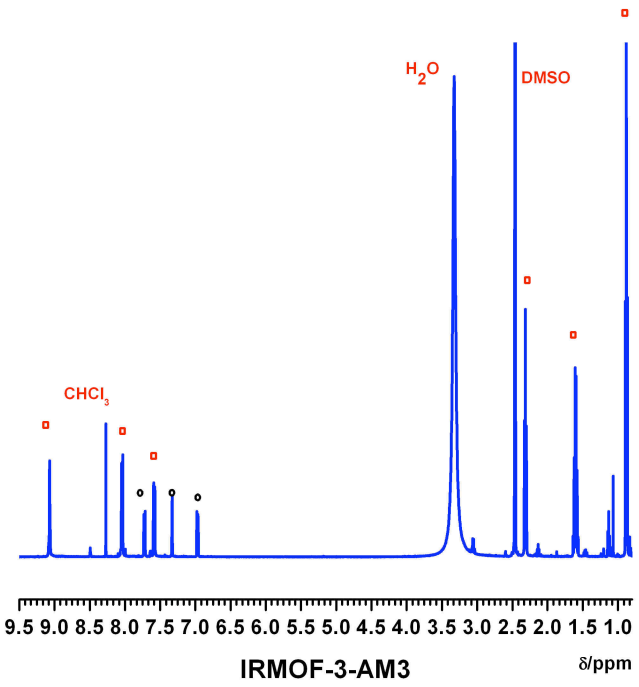

Figure S14. ^{1}H NMR spectra of digested IRMOF-3 modified with pivalic butyric anhydride for 3 days. NH_2-BDC resonances are denoted by black circles and RCONH-BDC resonances by red squares.

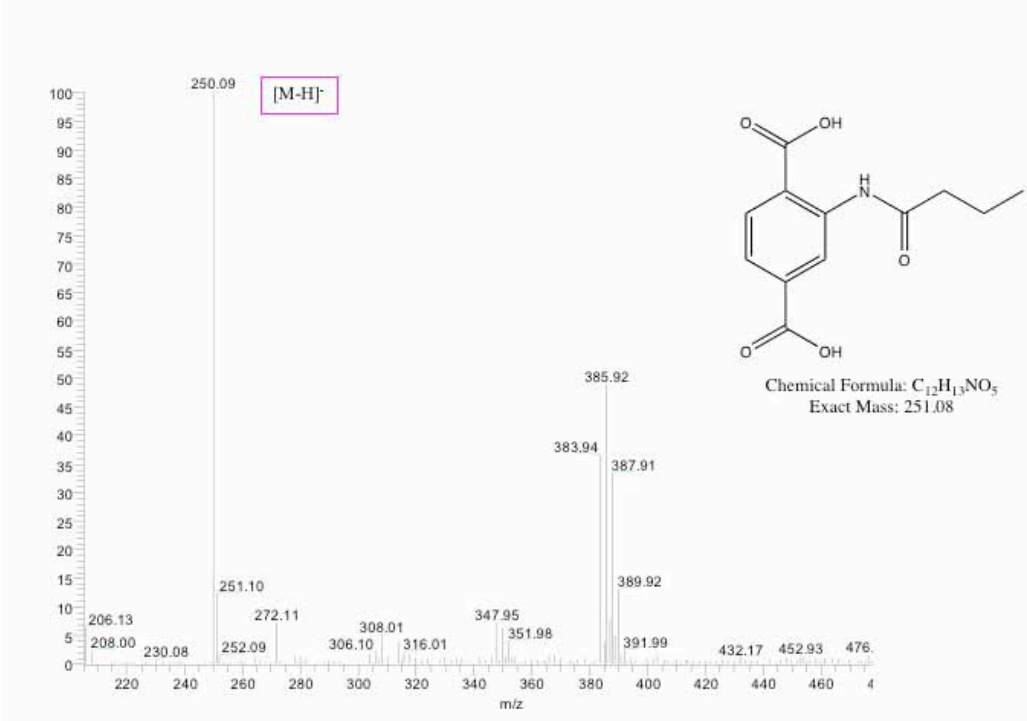

Figure S15. ESI-MS (negative ion mode) of the digested IRMOF-3-AM3.

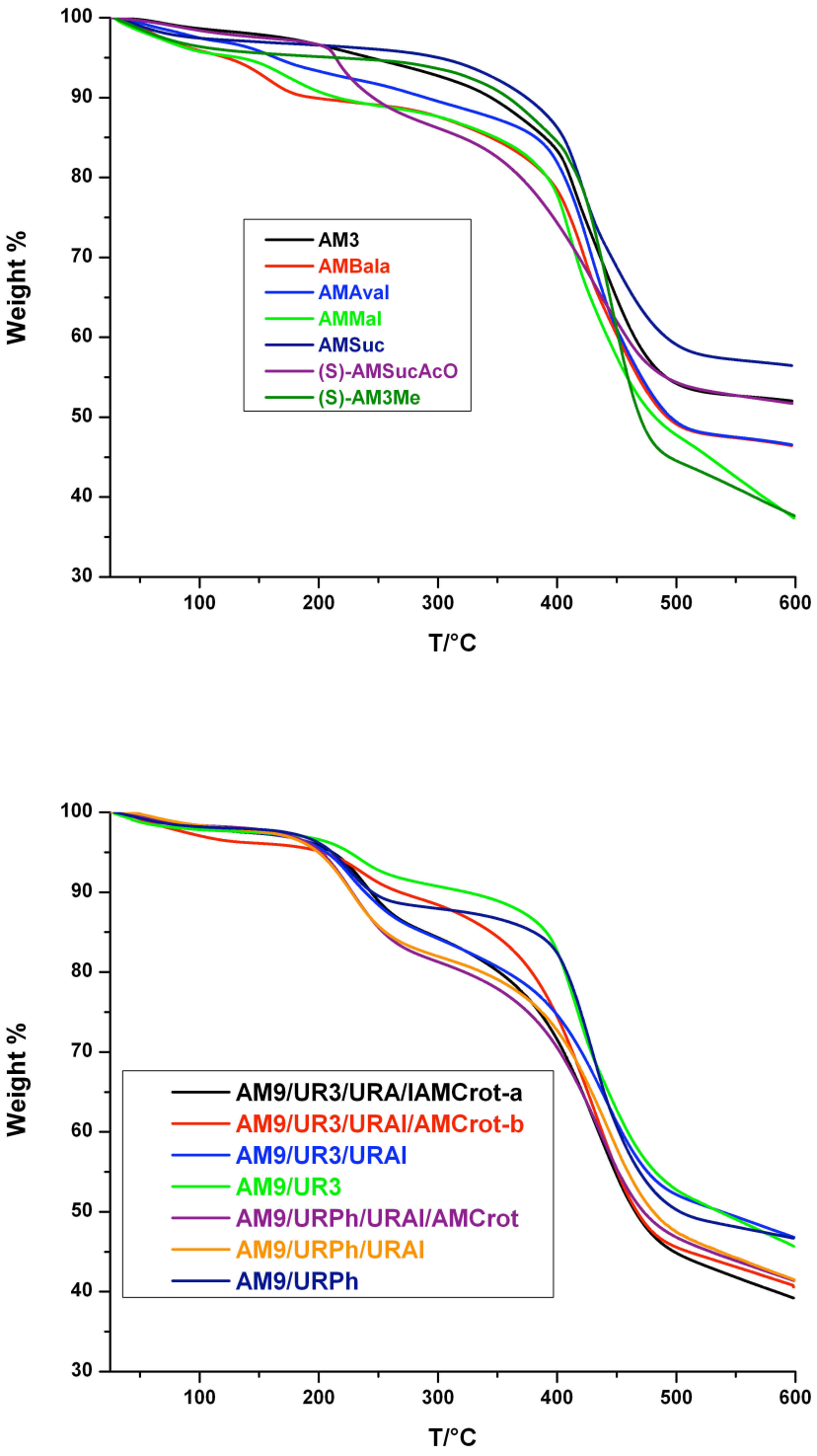

Figure S16. Thermogravimetric analysis (TGA) of modified IRMOF-3 samples. All samples were dried under vacuum for 8 h. Modified IRMOF-3 (10-20 mg) was heated at a scan rate of 5 °C/min from 25 to 600 °C.

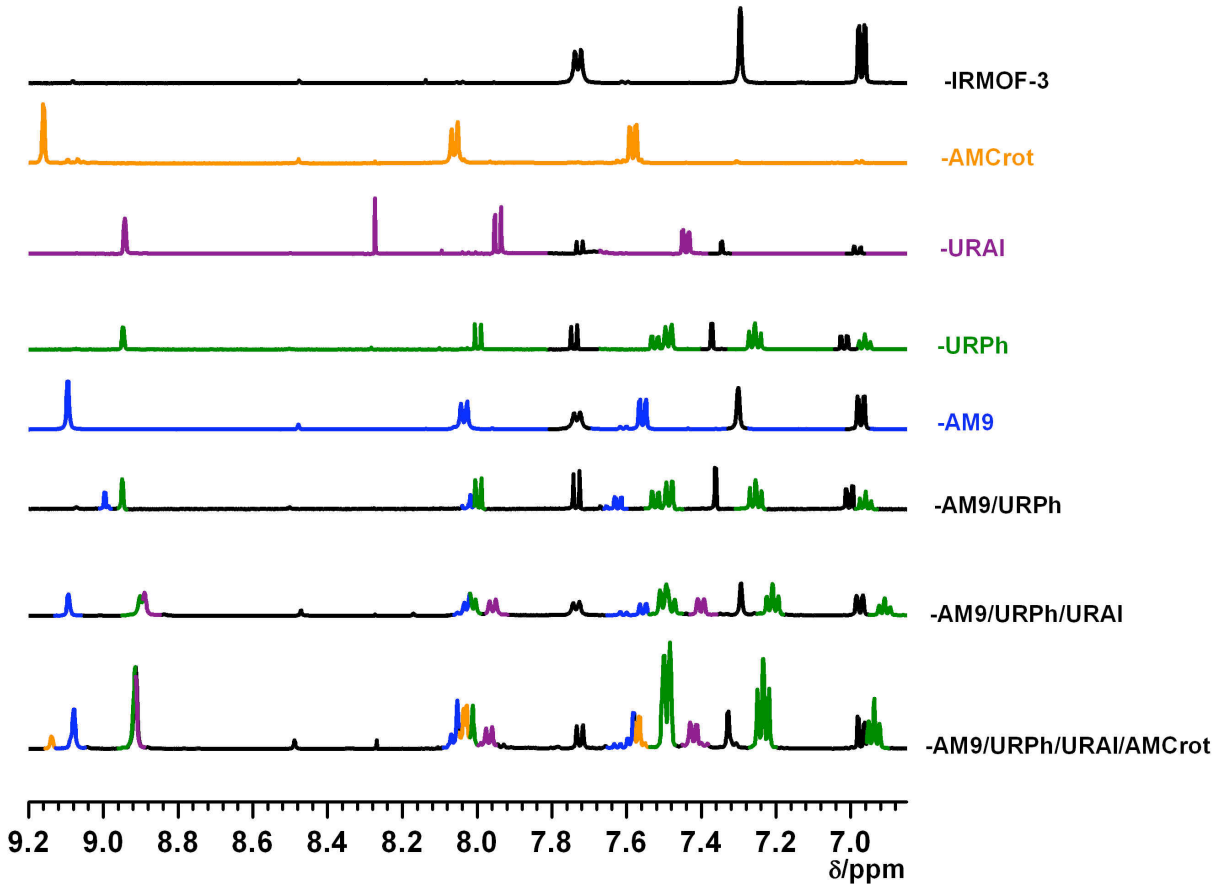

Figure S17. ^{1}H NMR spectra of multiple modified IRMOF-3 samples, IRMOF-3 samples modified with decanoic anhydride (blue, 51% conversion), phenyl isocyanate (green, 53% conversion), allyl isocyanate (purple, 75% conversion), crotonic anhydride (orange, 100% conversion), and unmodified IRMOF-3 (black) digested in DCl/D_2O and DMSO-d_6. Resonances in the spectra for IRMOF-3-AM9/URPh, IRMOF-3-AM9/URPh/URAl, and IRMOF-3-AM9/URPh/URAl/AMCrot-*a* are color coded corresponding to the top five spectra. IRMOF-3 resonances appear black in all spectra shown..

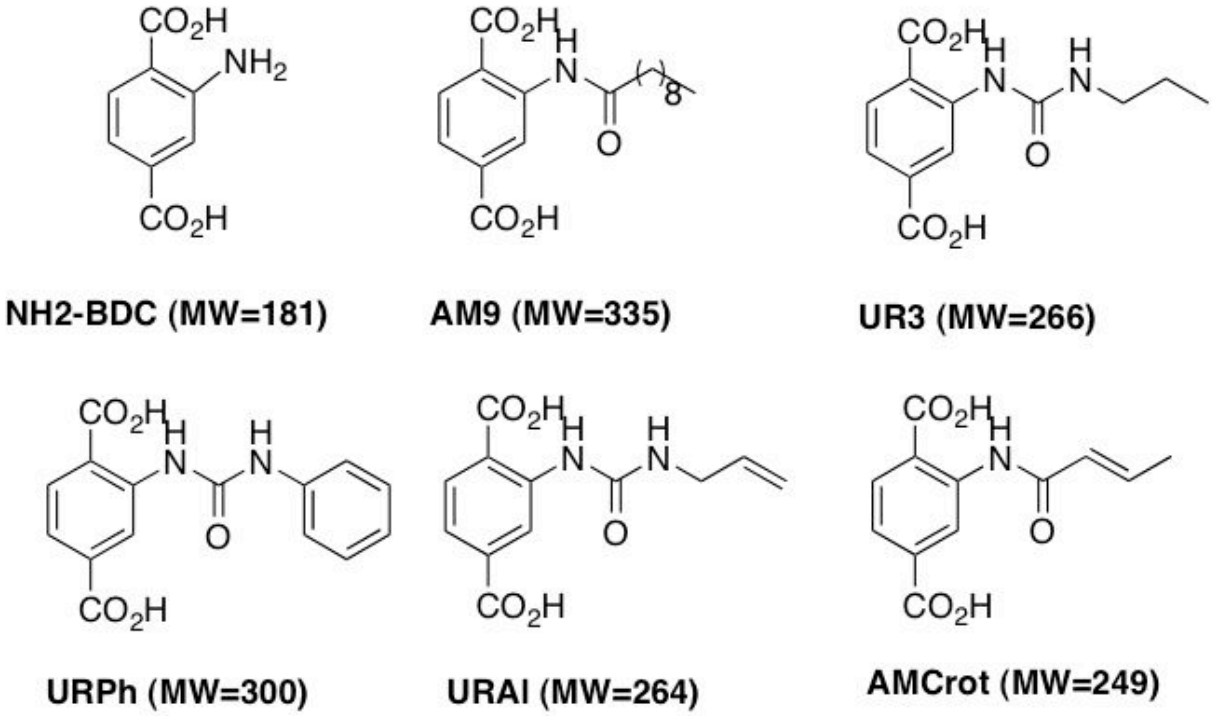

Figure S18. Expected molecular weight of unmodified, amide or urea products.

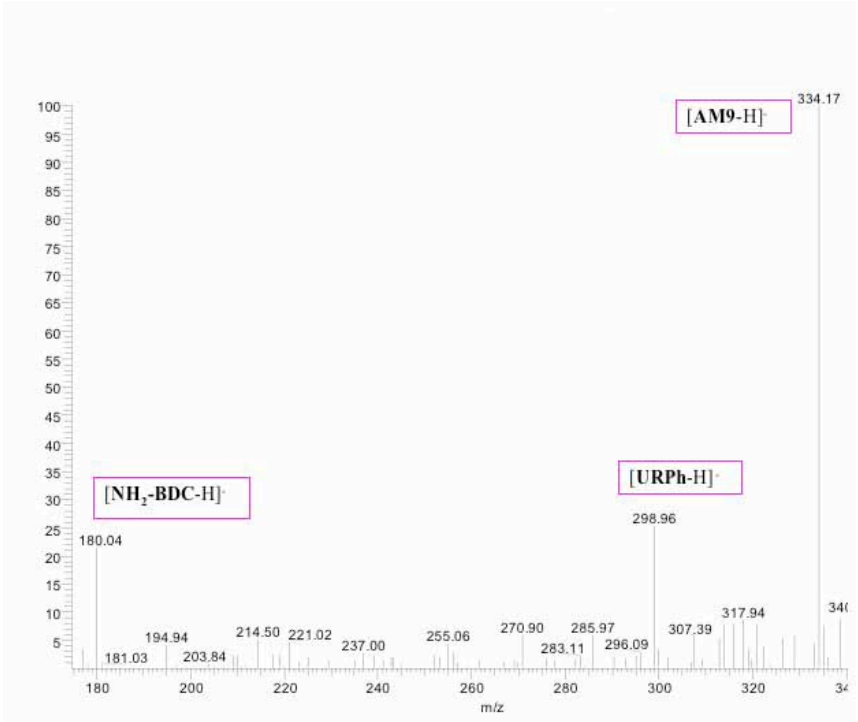

Figure S19 ESI-MS (negative mode) of a digested IRMOF-3-AM9/URPh single crystal.

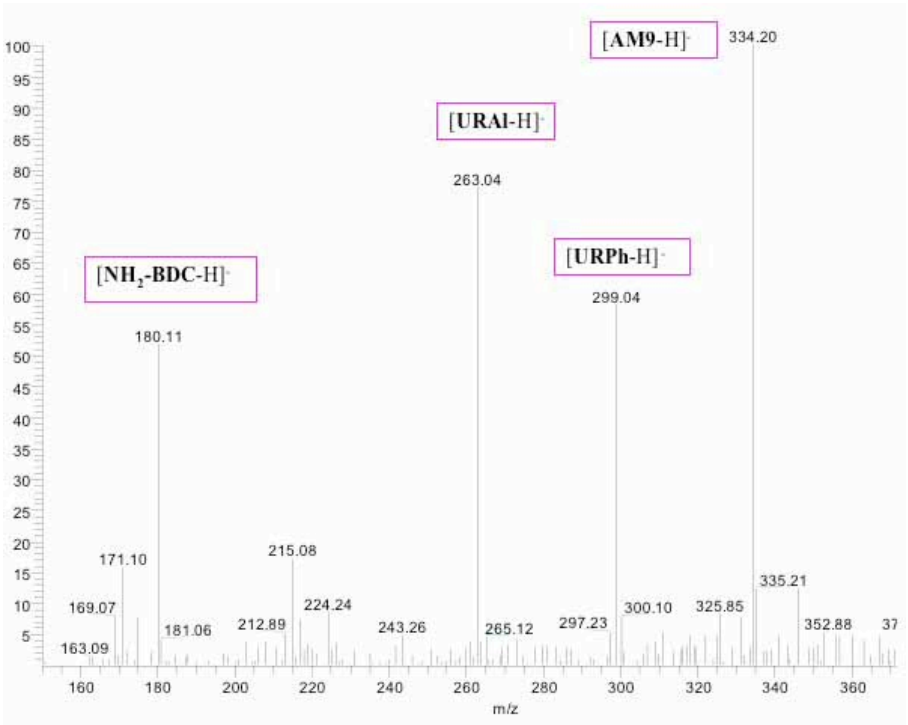

Figure S20. ESI-MS (negative mode) of a digested IRMOF-3-AM9/URPh/URAl single crystal.

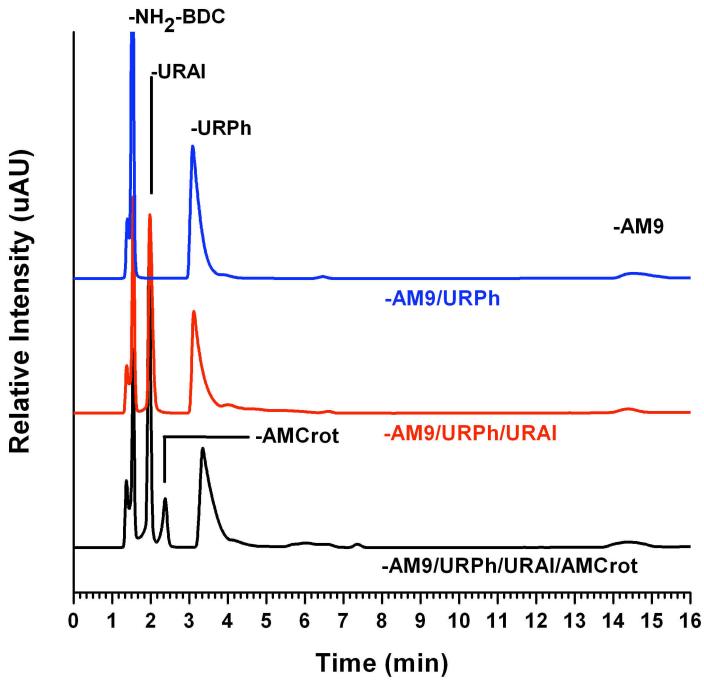

Figure S21. LC-UV/MS trace of IRMOF-3-AM9/URPh (blue), IRMOF-3-AM9/URPh/URAl (red), IRMOF-3-AM9/URPh/URAl/AMCrot-*a* (black).

Table S1. BET surface areas (m^2/g) of postsynthetic modified IRMOF-3, with varied percent conversions of cyclic anhydrides as determined by ^1H NMR. The results of two independent experiments are shown.

IRMOF-3-	AMMal (92%)	AMMal (49%)	AMSuc (99%)	AMSuc (49%)	(*S*)-AMSucAcO (47%)
Trial 1	29	2025	1.11	1558	1217
Trial 2	3	1785	3.17	1212	1021

Table S2. BET surface areas (m^2/g) of IRMOF-3 modified with multiple reagents. The results of two independent experiments are shown.

IRMOF-3-	AM9/UR3	AM9/URPh	AM9/UR3/URAl/AMCrot-*a*	AM9/UR3/URAl/AMCrot-*b*	AM9/URPh/URAl/AMCrot
Trial 1	1267	1671	427	1330	540
Trial 2	916	1441	482	1286	475