

**Supporting Information for:
Discovery of Novel N-(4-Hydroxybenzyl)valine Hemoglobin
Adducts in Human Blood**

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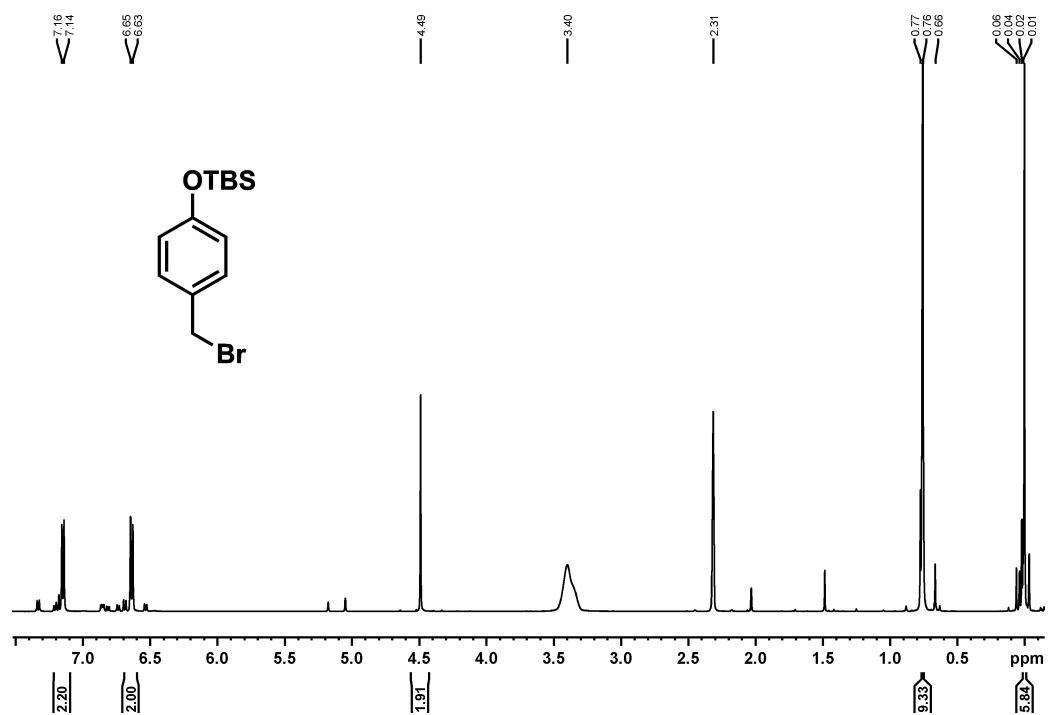
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Supporting Information containing:

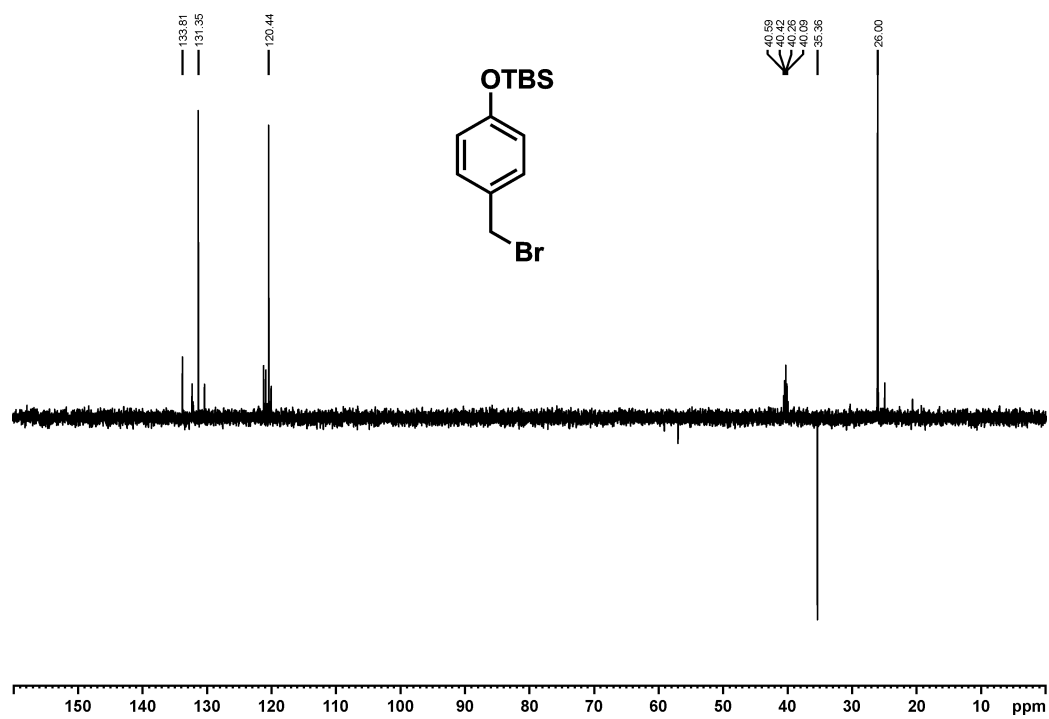
¹H and ¹³⁵DEPT NMR spectra of the synthesized 4-QM precursor, ¹H and HSQC NMR spectra of synthesized 4-OHBn-ValpNA, Bn-Val, 2-OHBn-Val, 3-OHBn-Val, 4-OHBn-Val, and proposed MS fragments of 4-OHBn-Val-FTH.

Supplemental Figure 1. NMR spectrum of 4-QM precursor (compound **3**).

a) ^1H NMR spectrum

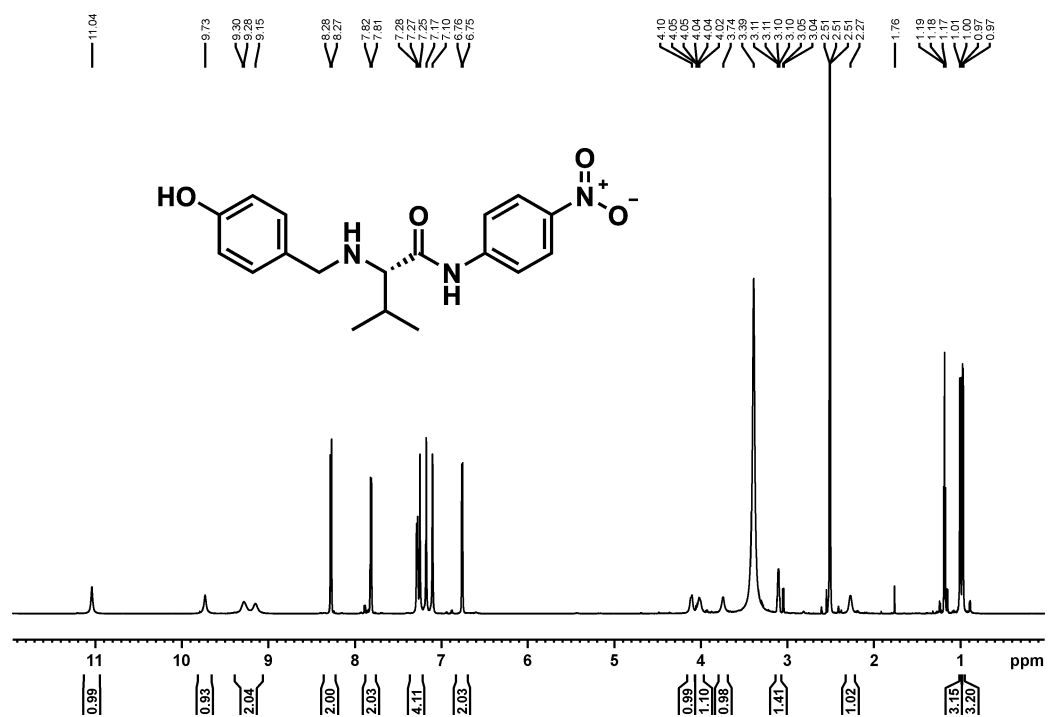


b) $^{135}\text{DEPT}$ NMR spectrum

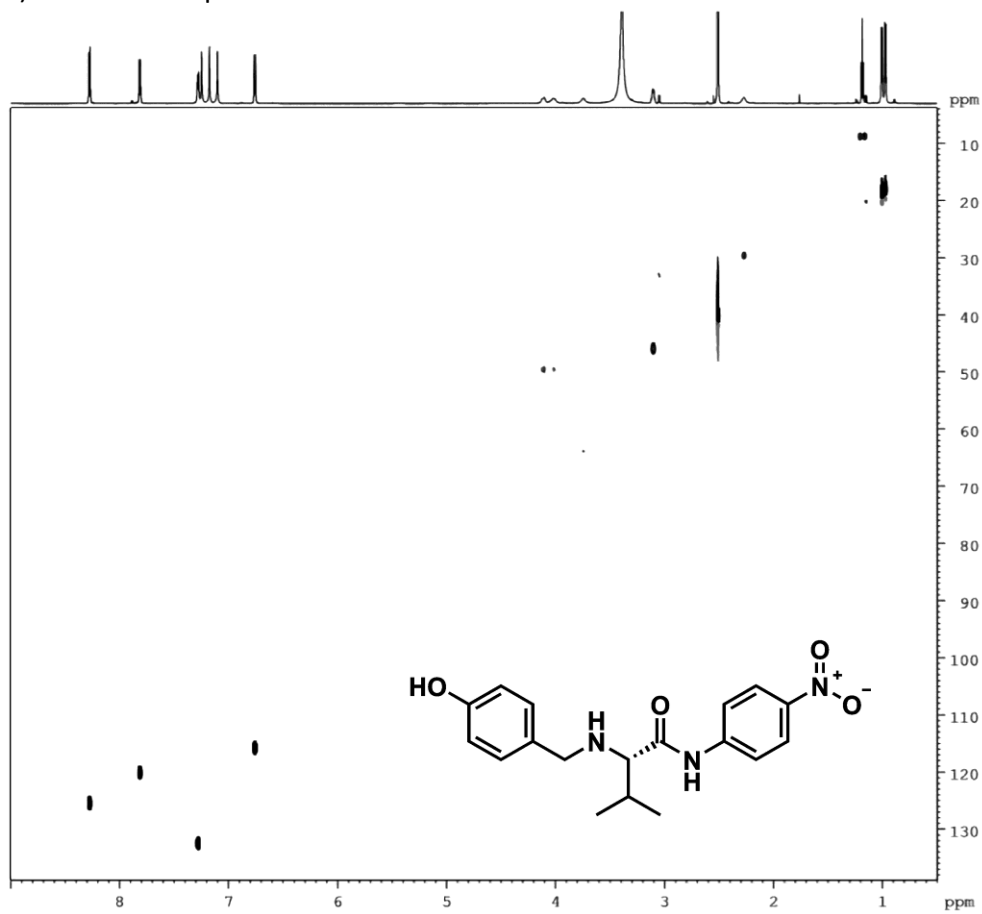


Supplemental Figure 2. NMR spectrum of 4-OHbn-ValpNA (compound **9**).

a) ^1H NMR spectrum

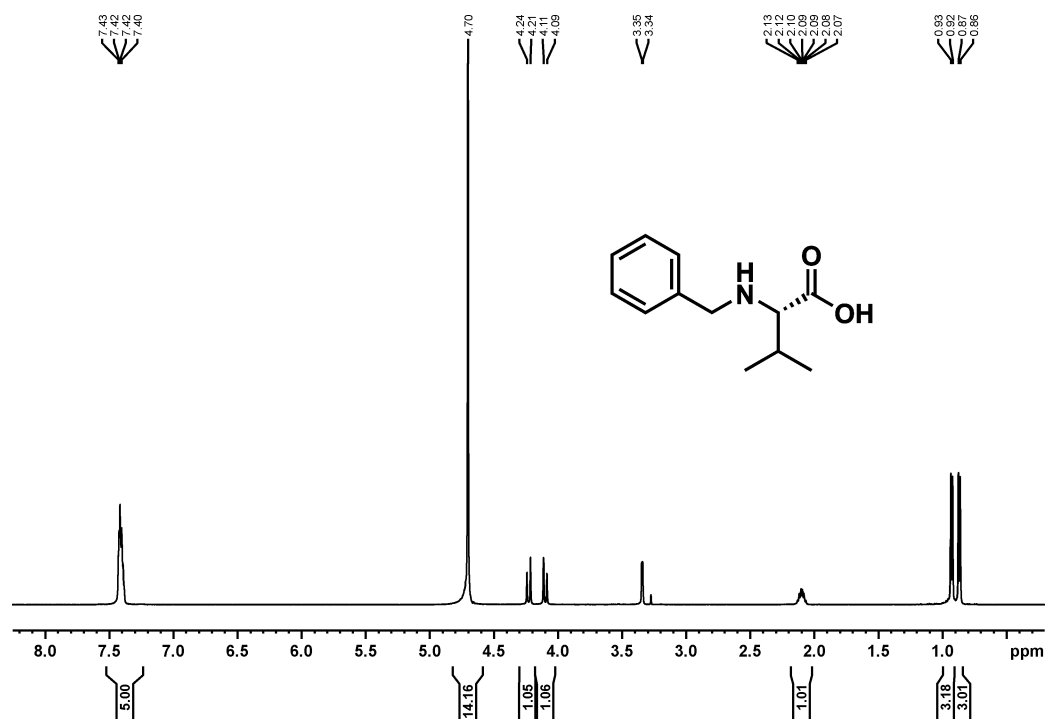


b) HSQC NMR spectrum

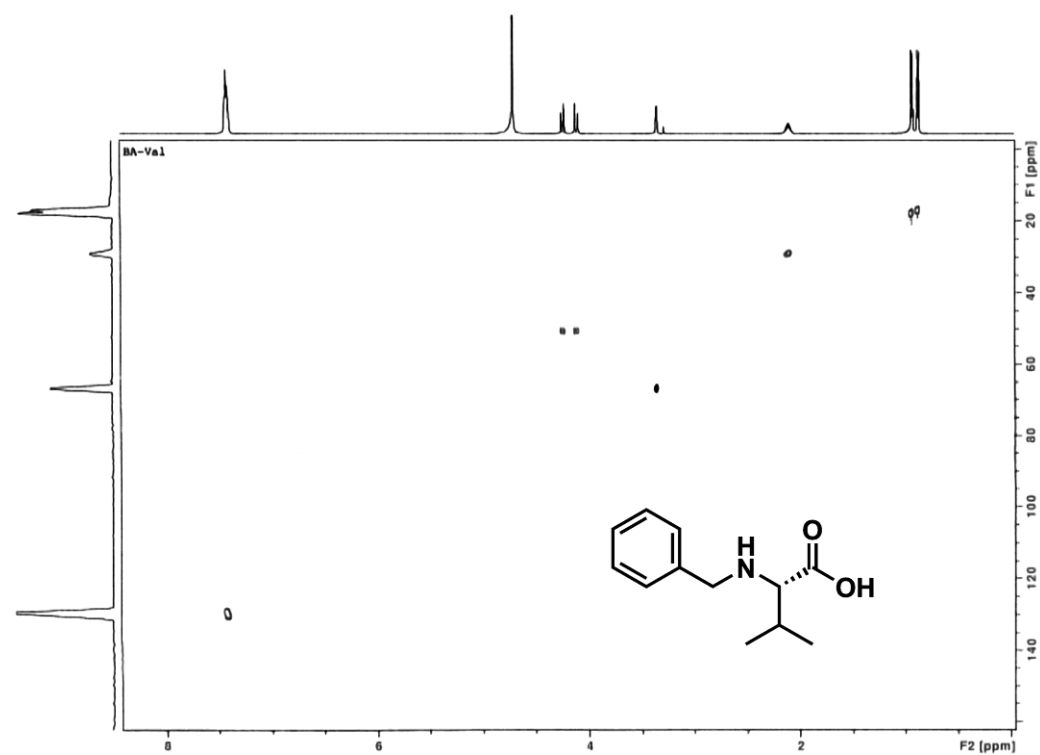


Supplemental Figure 3. NMR spectrum of N-benzylvaline (Bn-Val) (compound **11**) synthesized from benzaldehyde.

a) ^1H NMR spectrum

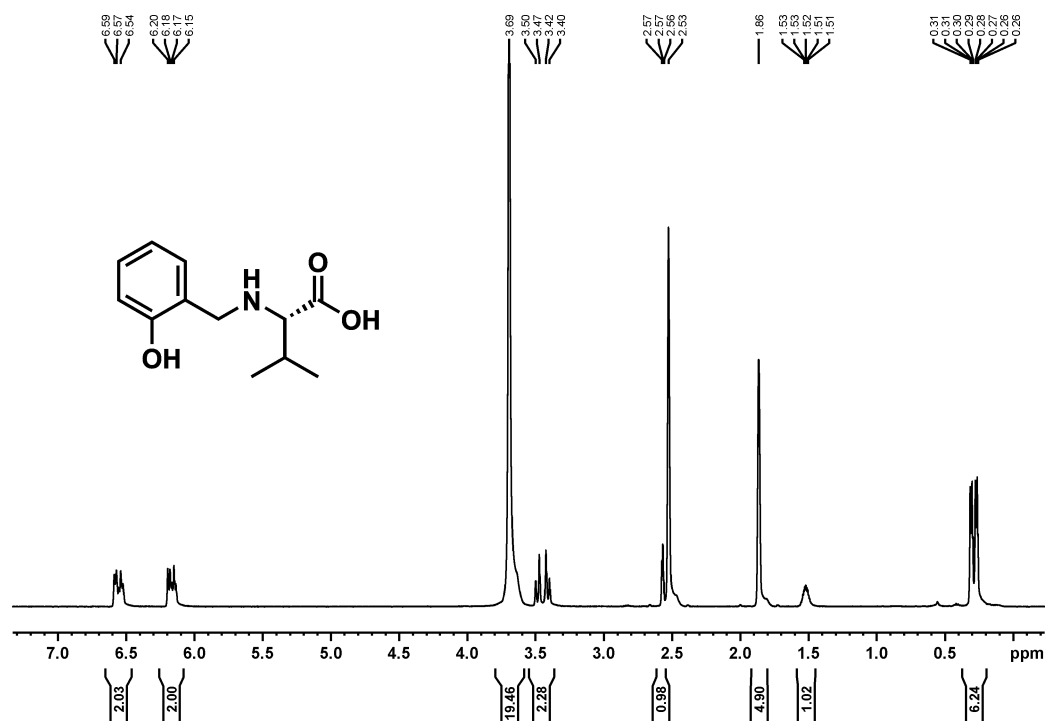


b) HSQC NMR spectrum

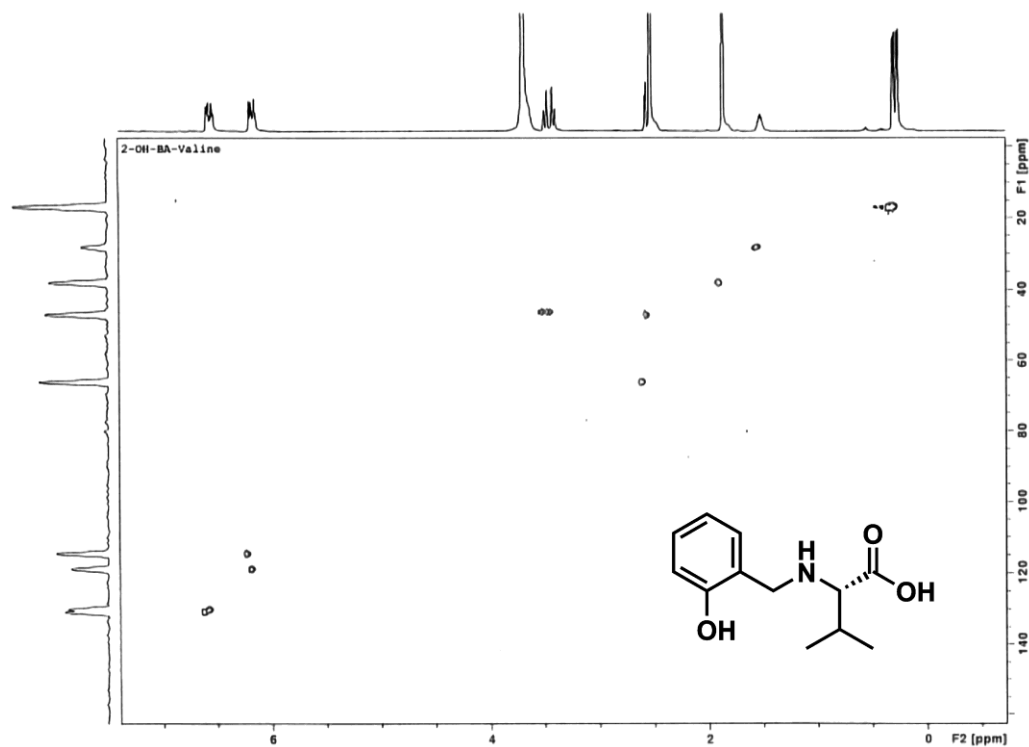


Supplemental Figure 4. NMR spectrum of N-(2-hydroxybenzyl)valine (2-OHBn-Val) (compound **12**) synthesized from 2-hydroxybenzaldehyde.

a) ^1H NMR spectrum

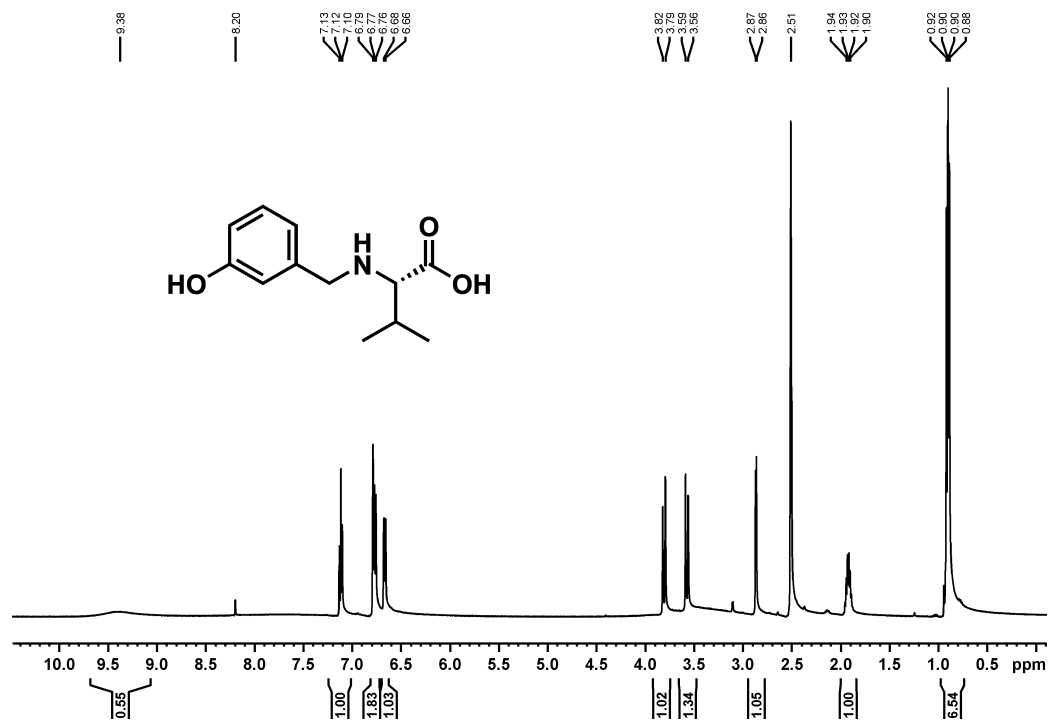


b) HSQC NMR spectrum

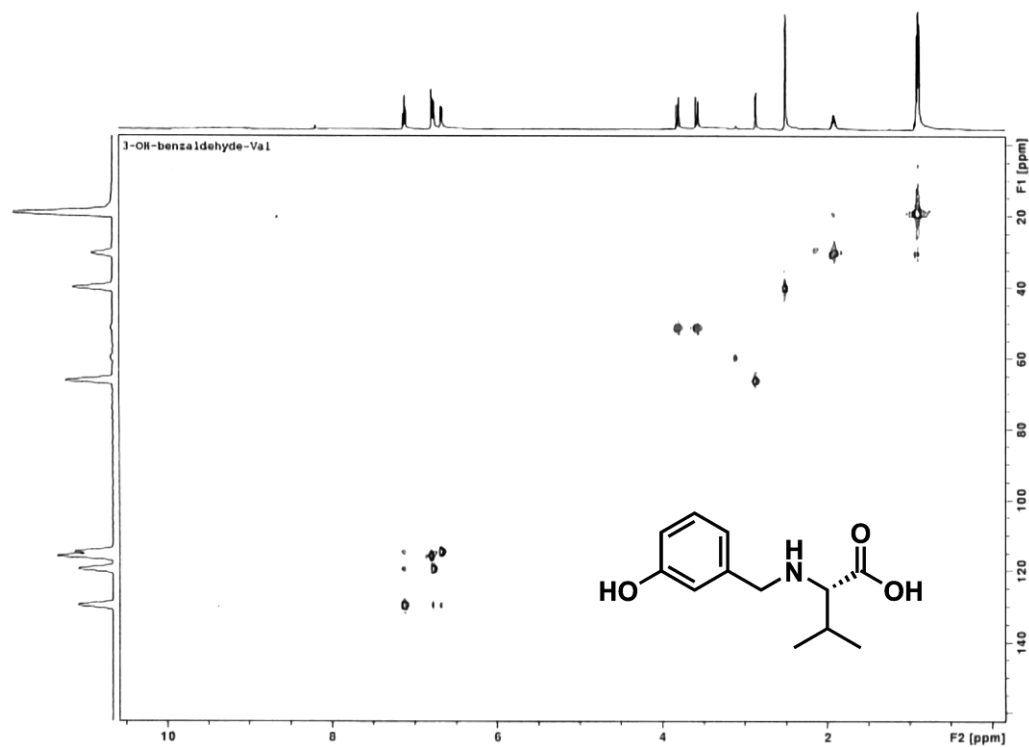


Supplemental Figure 5. NMR spectrum of N-(3-hydroxybenzyl)valine (3-OHBn-Val) (compound **13**) synthesized from 3-hydroxybenzaldehyde.

a) ^1H NMR spectrum

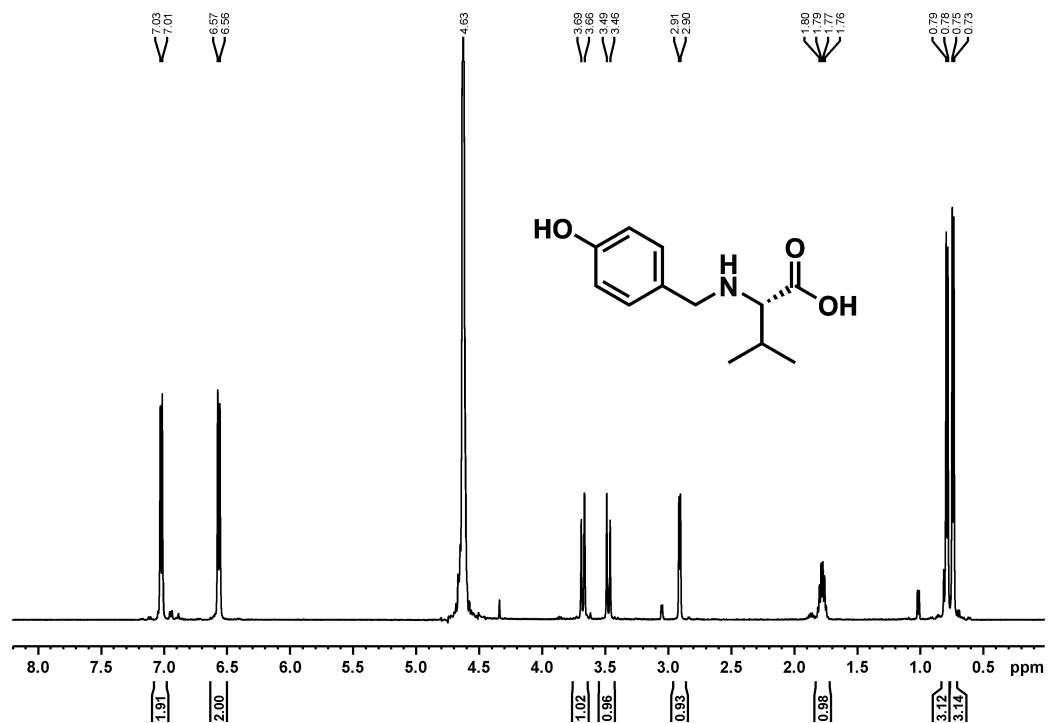


b) HSQC NMR spectrum

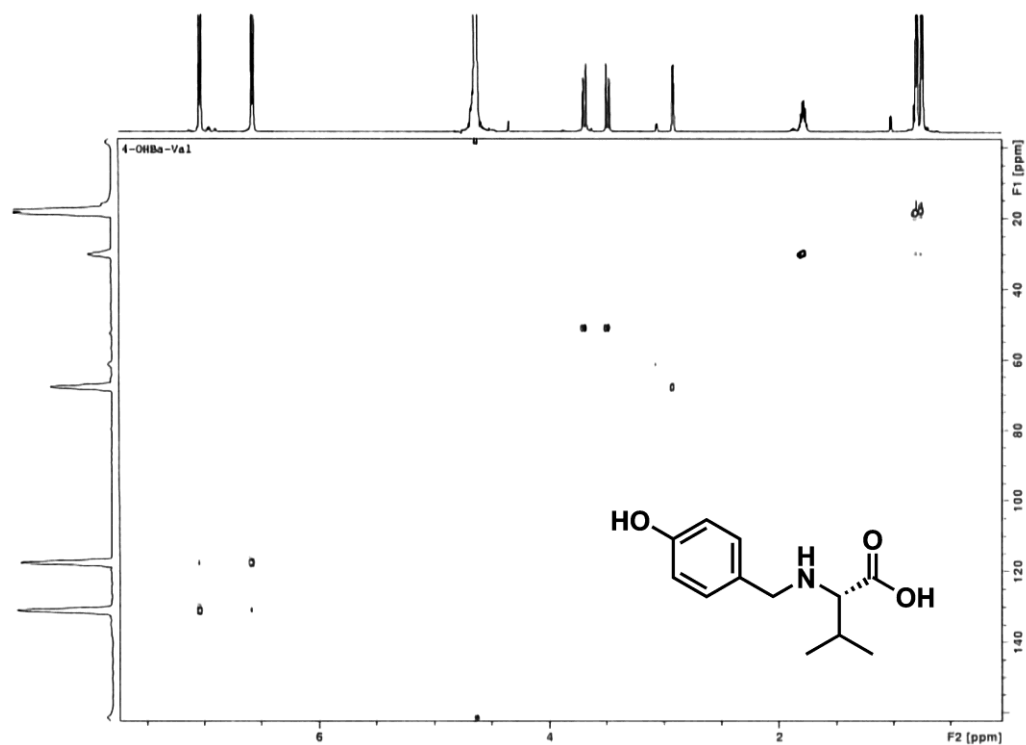


Supplemental Figure 6. NMR spectrum of N-(4-hydroxybenzyl)valine (4-OHBn-Val) (compound **14**) synthesized from 4-hydroxybenzaldehyde.

a) ^1H NMR spectrum



b) HSQC NMR spectrum



Supplemental Figure 7. Proposed MS fragments of 4-OHBn-Val-FTH (compound **10**) (cf. Figure 2B).

