

Figure S1. EIC for PK20 and [Ile⁹]PK20 generated for $m/z = 1357.40 \pm 0.20$ showing peak of quantified compounds.

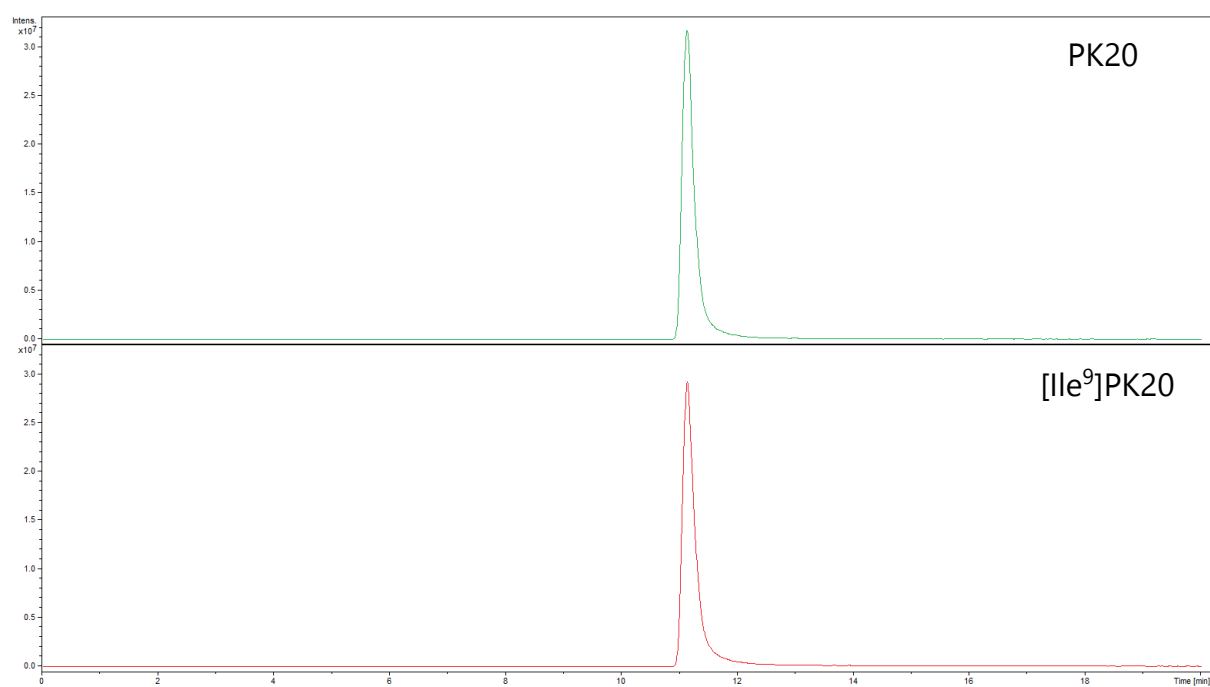


Figure S2. MS spectra recorded for PK20 (A) and [Ile⁹]PK20 (B).

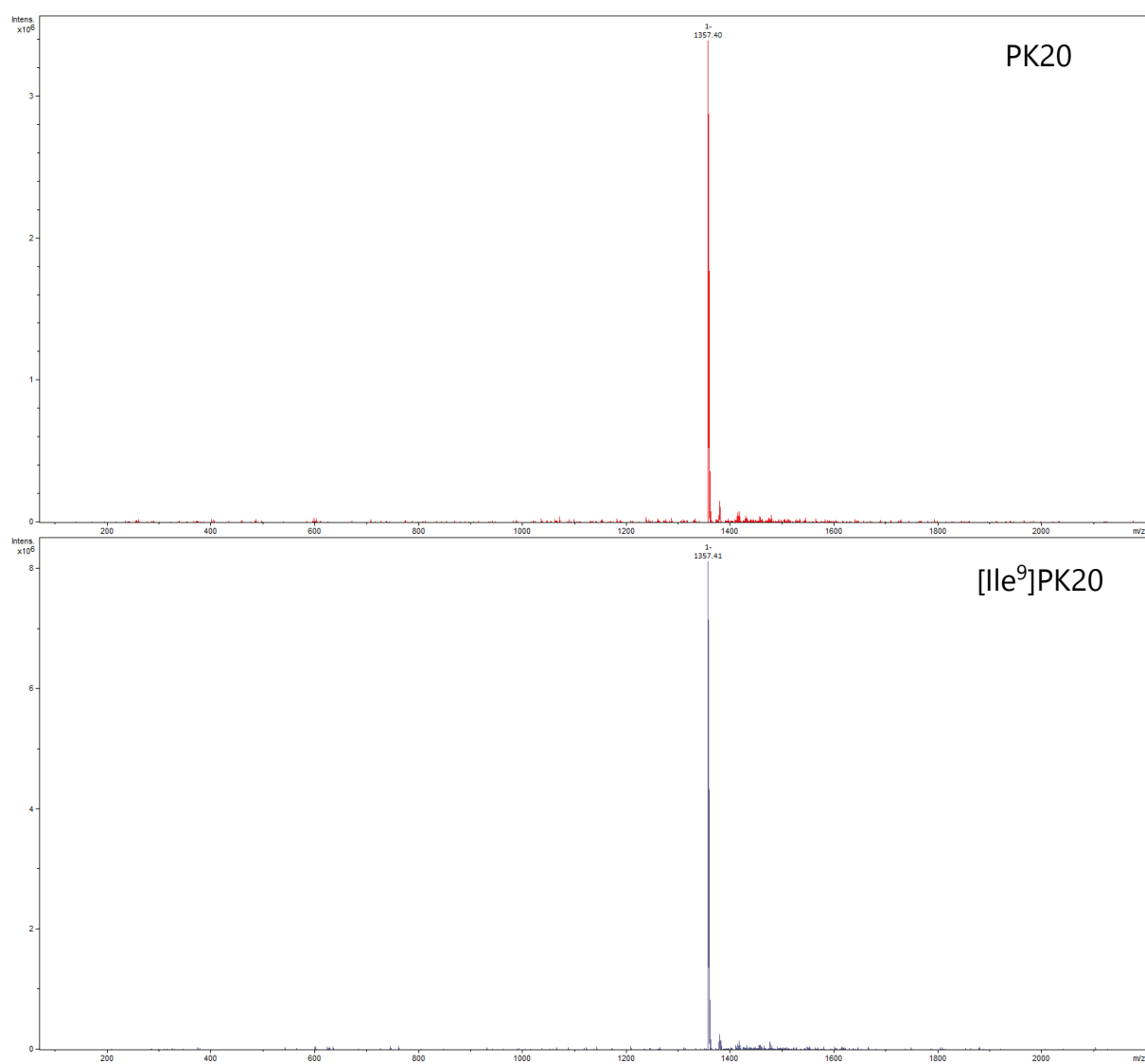


Figure S3. Calibration curves obtained for PK20 and [Ile⁹]PK20 as area for EIC ($m/z = 1357.40 \pm 0.20$) vs. ng of the peptide injected to LC column.

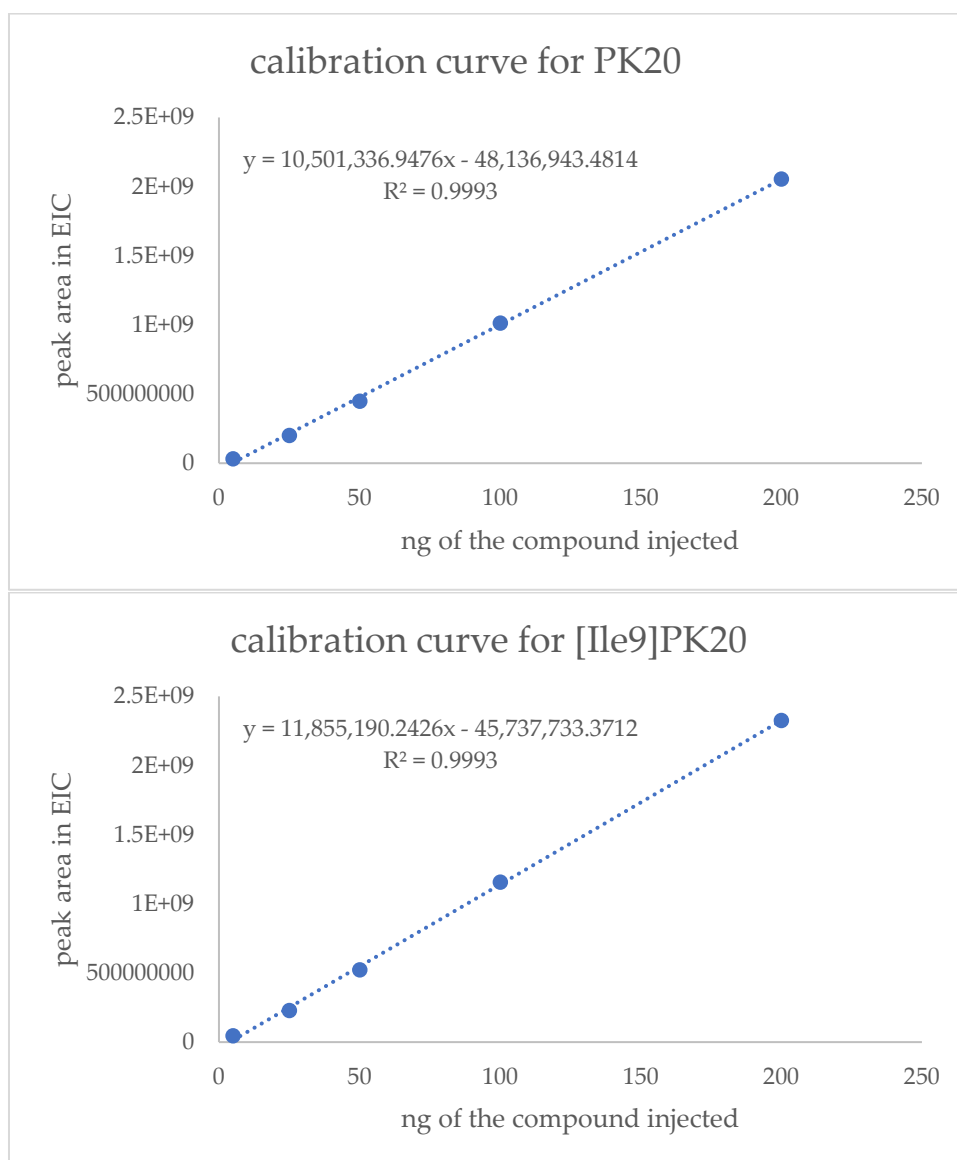


Table S1. Calibration and standard validation data for PK20 and [Ile⁹]PK20.

| Compound | Linear range /ng per injection | Calibration curve equation | Amount injected /ng | Intermediate precision /%CV | Recovery /% | LOD /ng per injection | LOQ /ng per injection |
|-------------------------|--------------------------------|------------------------------------|---------------------|-----------------------------|-------------|-----------------------|-----------------------|
| PK20 | 5-200 | $y = 10220837.313x - 32897298.173$ | 5 | 3.63 | 96.4 ± 0.7 | 2.92 | 8.84 |
| | | | 25 | 3.17 | | | |
| | | | 50 | 4.27 | 102.1 ± 0.6 | | |
| | | | 100 | 4.34 | | | |
| | | | 200 | 1.73 | 101.2 ± 0.5 | | |
| [Ile ⁹]PK20 | 5-200 | $y = 11633076.337x - 33670205.577$ | 5 | 1.79 | 95.6 ± 0.4 | 2.54 | 7.70 |
| | | | 25 | 2.60 | | | |
| | | | 50 | 0.77 | 99.4 ± 0.7 | | |
| | | | 100 | 2.12 | | | |
| | | | 200 | 2.77 | 101.3 ± 0.3 | | |