Supporting Information

Combinatorial identification of a highly soluble phase-selective organogelator with high gelling capacity for crude oil gelation

Juntong Li,[†] Yanping Huo*[†] and Huaqiang Zeng*[‡]

[†] Faculty of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, Guangdong, China 510006
[‡] Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos, Singapore 138669

Corresponding Authors: yphuo@gdut.edu.cn and hqzeng@ibn.a-star.edu.sg

1. **General Remarks**……..………………………...………………..………..……..……….**S2**

2. **Synthetic Scheme Synthesis of PSOG Library**………………………………………......**S3**

3. **Experimental Procedures and Compound Characterizations**…….………….……….**S3**

4. **(B)MGC Determinations of 116 PSOGs**…………………………………………….….**S45**

5. **Table S1: Gelling Properties of Gelators**…...…………………..……...……………….**S46**

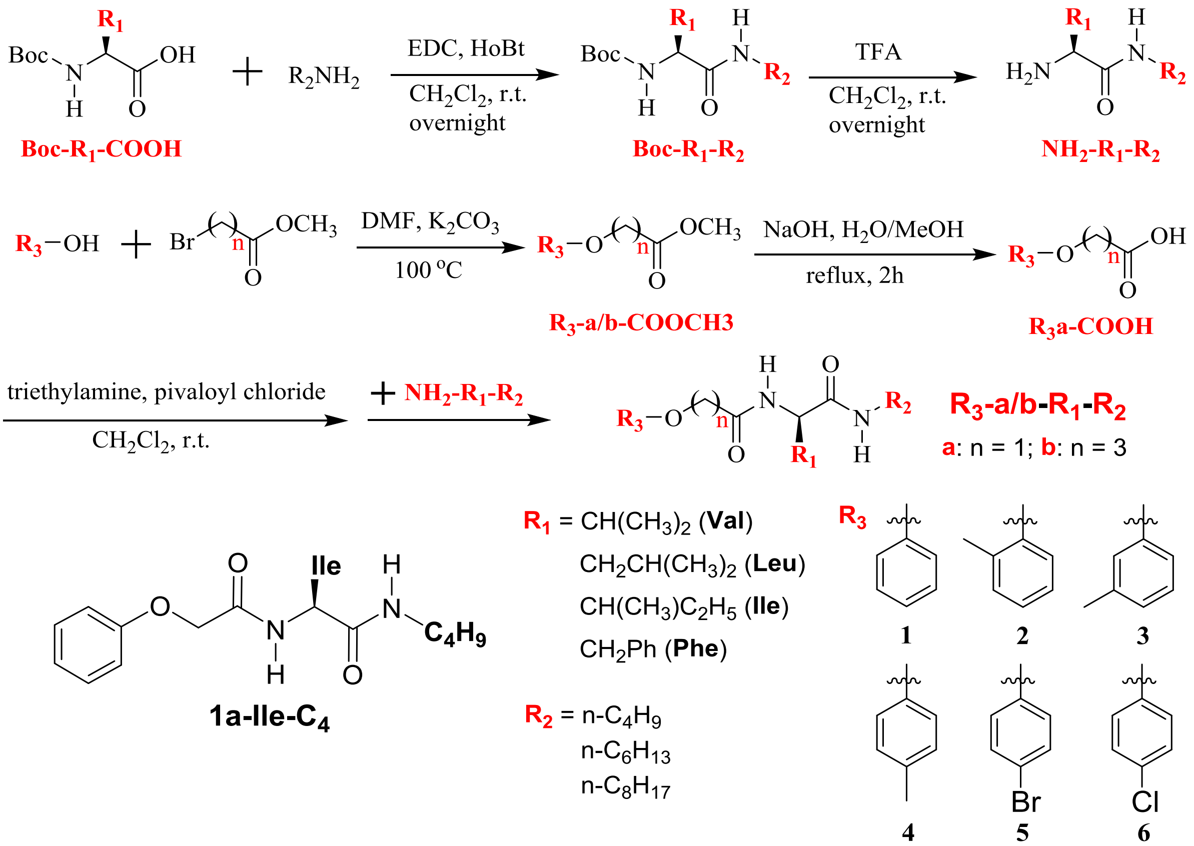
6. **Figures S1: SEM Micrographs and Rheological Data**…………………………..…..**S50**

7. **^{1}H and ^{13}C NMR for 116 PSOGs**………..……………………………………...….**S51**

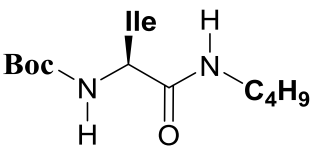
General Remarks

All the reagents were obtained from commercial suppliers and used as received unless otherwise noted. Aqueous solutions were prepared from MilliQ water. The organic solutions from all liquid extractions were dried over anhydrous Na_2SO_4 for a minimum of 15 minutes before filtration. Flash column chromatography was performed using pre-coated 0.2 mm silica plates from Selecto Scientific. Chemical yield refers to pure isolated substances. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker ACF-400 spectrometer. The solvent signal of $CDCl_3$ was referenced at δ= 7.26 ppm. Coupling constants (*J* values) are reported in Hertz (Hz). ^{1}H NMR data are recorded in the order: chemical shift value, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), number of protons that gave rise to the signal and coupling constant, where applicable. ^{13}C spectra are proton-decoupled and recorded on Bruker ACF400 (400 MHz). The solvent, $CDCl_3$, was referenced at δ= 77 ppm. $CDCl_3$ (99.8%-Deuterated) was purchased from Aldrich and used without further purification. Mass spectra were acquired with Shimazu LCMS-2010EV. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-7400F electron microscope (5 kV). Rheological studies of gels at biphasic MGCs (BMGCs) were performed using an ARES-G2 rheometer (TA Instruments, U.S.A.) equipped with a plate (8 mm diameter).

Synthetic scheme



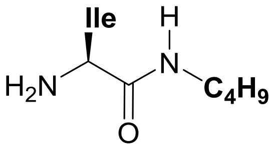
Synthetic procedure: **1a-Ile-C4** is used to illustrate typical synthetic procedures for a total of 116 gelators.



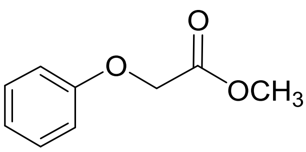
Boc-Ile-C₄

Boc-Ile-COOH (524 mg, 2.1 mmol), n-butyl amine (146.2 mg, 2.0 mmol), EDC (422 mg, 2.2 mmol) and HoBt (298 mg, 2.2 mmol) were dissolved in dichloromethane (20 mL). The reaction was stirred at room temperature overnight. Unreacted amine was extracted twice using 1M HCl (30 mL x 2), and unreacted acid removing by wshing twice with saturated sodium bicarbonate aqueous solution (50 mL x 2). The organic phase was finally washed using saturated brine (50 mL) and dried over anhydrous sodium sulphate.

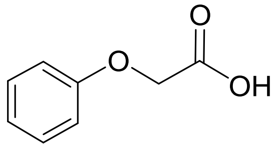
Removal of organic solvent under vacuum yielded the pure product **Boc-Ile-C4** as a white solid .Yield: 544 mg, 95%. ^{1}H NMR (400 MHz, CDCl3) δ 5.86 (s, 1H), 5.08 (d, J = 7.2 Hz, 1H), 3.85 (m, 1H), 3.27 (m, 2H), 2.41 – 2.30 (m, 1H), 1.48 (dd, J = 5.3, 3.1 Hz, 2H), 1.44 (s, 9H), 1.37 – 1.31 (m, 2H), 0.98 (d, J = 6.8 Hz, 2H), 0.92 (m, 9H).



NH_2-Ile-C_4 To a solution of **Boc-Ile-C4** (286 mg, 1.0 mmol) in dichloromethane (10 mL) was added trifluoroacetic acid (TFA, 0.8 mL, 10 mmol) dropwise at 0 ℃. The reaction solution was allowed to rise to room temperature slowly by simply removing ice-water bath, and further stirred at room temperature for 5 h. Saturated sodium carbonate aqueous solution (30 mL) was then added slowly into solution under constant stirring to quench TFA, followed by adding solid sodium carbonate (500 mg) to achieve full neutralization. Dichloromethane (15 mL × 3) was used to extract final product three times. The organic layer was combined, washed over distilled water (20 mL) once, and dried over sodium sulphate, concentrated by rotary evaporation to afford Boc-deprotected compound **H_2N-Ile-C4**. Yield: 166 mg, 90%. ^{1}H NMR (400 MHz, DMSO) δ 8.18 (d, J = 5.3 Hz, 1H), 6.20 (s, 2H), 3.36 (d, J = 5.5 Hz, 1H), 2.94 (ddt, J = 77.3, 12.7, 6.4 Hz, 2H), 2.16 (s, 1H), 1.71 (dt, J = 13.3, 6.5 Hz, 2H), 1.48 – 1.04 (m, 2H), 0.90 (d, J = 7.0 Hz, 2H), 0.85 (t, J = 7.5 Hz, 9H).

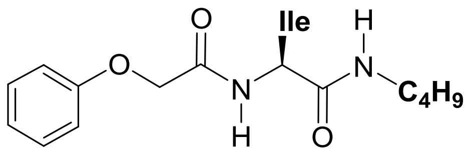


1a-$COOCH_3$ Phenol (aromatic motif **1**, 198 mg, 2.0 mmol) was dissolved in dried N, N-dimethylformamide (30 mL), following by adding anhydrous potassium carbonate (691 mg, 5 mmol) and methyl bromoacetate (2 mL, 2.0 mmol). The reaction mixture was heated to 100 ℃ overnight after which time the reaction mixture was filtered and the solvent was removed under vacuum. The crude product was dissolved in dichloromethane (40 mL), washed with distilled water (3x 30 mL) and dried over sodium sulphate. Removal of solvent under vacuum to give crude product that was crystallized from methanol to yield alkylated intermediate **1a-COOCH$_3$** as a white solid. Yield: 299 mg, 90%. ^{1}H NMR (400 MHz, DMSO) δ 7.29 (t, J = 7.8 Hz, 2H), 6.95 (dd, J = 18.5, 7.7 Hz, 3H), 4.78 (s, 2H), 3.70 (s, 3H).



1a-COOH

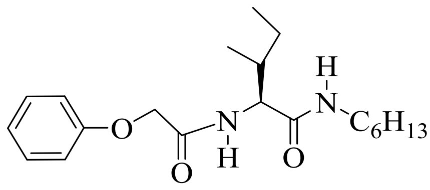
Next, the alkylated intermediate **1a-COOCH$_3$** (166 mg, 1 mmol) obtained was dissolved in hot methanol (15 ml), and 1M NaOH aqueous solution (4 ml, 4 mmol) was added. The mixture was heated under reflux for 2 hours and then distilled water (50 mL) was added. The aqueous layer was neutralized with 1M HCl (6 mL). The precipitated crude product was collected by filtration and recrystallized from methanol to yield acid **1a-COOH**. Yield: 140 mg, 92%. ^{1}H NMR (400 MHz, DMSO) δ 12.96 (s, 1H), 7.29 (t, J = 7.7 Hz, 2H), 6.99 – 6.86 (m, 3H), 4.66 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 170.6, 158.2, 129.9, 121.4, 114.90, 64.9.



1a-Ile-C$_4$

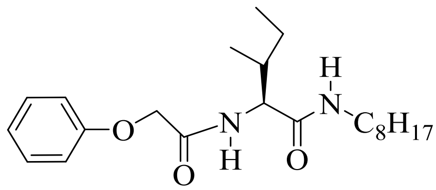
Triethylamine (105 μL, 0.75 mmol) and **1a-COOH** (95 mg, 0.625 mmol) were mixed in 10 mL of anhydrous dichloromethane in a tightly capped reaction flask. After flushing the flaks with nitrogen to remove the air inside the bottle, the reaction solution was cooled to zero degrees in an ice-water bath. 1 mL of anhydrous methylene chloride solution containing pivaloyl chloride (93 μL, 0.75 mmol) was slowly injected with a syringe into the reaction flask in 3-5 minutes. The reaction mixture was then allowed to rise to room temperature with the ice-water bath removed, and kept at room temperature for 30 min. To this solution was added **H$_2$N-Ile-C4** (116 mg, 0.625 mmol), followed by slowly adding triethylamine (105 μL, 0.75 mmol) dissolved in 5 ml of anhydrous dichloromethane over 3-5 min. The reaction was then stirred at room temperature for 2 hours under N$_2$. 5 ml of 1M HCl was added into the reaction solution, which was stirred for another

1-2 min. The separated dichloromethane was successively washed using 5 mL of 1 M HCl, 5 mL of 1 M NaOH and 15 mL of deionized water. After drying the organic layer, the organic solvent was removed to give pure **1a-Ile-C4** as a white solid. Yield: 177 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.07 (t, J = 5.6 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.00 – 6.89 (m, 3H), 4.63 – 4.49 (m, 2H), 4.19 (dd, J = 8.9, 7.7 Hz, 1H), 3.14 – 2.94 (m, 3H), 1.77 – 1.65 (m, 1H), 1.51 – 1.18 (m, 6H), 0.81 (ddd, J = 12.3, 11.0, 6.4 Hz, 9H). ^{13}C NMR (101 MHz, DMSO) δ 170.8, 167.7, 158.1, 129.9, 121.5, 115.0, 66.9, 58.8, 38.5, 37.3, 31.5, 24.8, 19.9, 15.8, 14.1, 11.4. MS-ESI: calculated for $[M+Na]^+$ ($C_{18}H_{28}N_2O_3Na$): m/z 342.43, found: m/z 342.20.



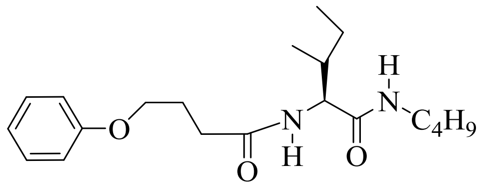
1a-Ile-C6

Yield: 196 mg, 90%. ^{1}H NMR (400 MHz, DMSO) δ 8.07 (t, *J* = 5.5 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.31 – 7.25 (m, 2H), 6.98 – 6.91 (m, 3H), 4.61 – 4.51 (m, 2H), 4.19 (dd, *J* = 8.9, 7.6 Hz, 1H), 3.15 – 2.92 (m, 2H), 1.76 – 1.64 (m, 1H), 1.51 – 1.14 (m, 10H), 0.81 (dq, *J* = 7.3, 6.3 Hz, 9H). ^{13}C NMR (101 MHz, DMSO) δ 170.8, 167.7, 158.1, 129.9, 121.6, 115.0, 66.9, 56.8, 38.8, 37.4, 31.4, 29.3, 26.5, 24.8, 22.5, 15.8, 14.4, 11.4. MS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{32}N_2O_3Na$): m/z 371.49, found: m/z 371.30.



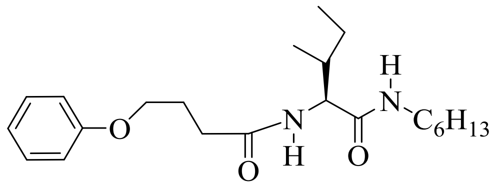
1a-Ile-C8

Yield: 209 mg, 89%. ^{1}H NMR (400 MHz, DMSO) δ 8.09 (t, *J* = 5.5 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.31 – 7.25 (m, 2H), 6.94 (ddd, *J* = 8.6, 4.6, 0.9 Hz, 3H), 4.60 – 4.50 (m, 2H), 4.19 (dd, *J* = 8.9, 7.7 Hz, 1H), 3.12 – 2.93 (m, 3H), 1.71 (td, *J* = 10.2, 3.3 Hz, 1H), 1.43 – 1.18 (m, 14H), 0.86 – 0.75 (m, 10H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{36}N_2O_3Na$): m/z 399.54, found: m/z 399.20.



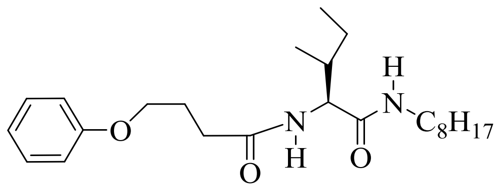
1b-Ile-C4

Yield: 191 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.01 – 7.93 (m, 0H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.30 – 7.23 (m, 2H), 6.93 – 6.87 (m, 3H), 4.12 (t, *J* = 8.5 Hz, 1H), 3.96 – 3.88 (m, 2H), 3.13 – 2.91 (m, 2H), 2.37 – 2.25 (m, 2H), 1.91 (p, *J* = 7.0 Hz, 2H), 1.73 – 1.61 (m, 1H), 1.52 – 1.11 (m, 6H), 0.80 (ddd, *J* = 12.5, 10.9, 6.5 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{32}N_2O_3Na$): *m/z* 371.49, found: *m/z* 371.15.



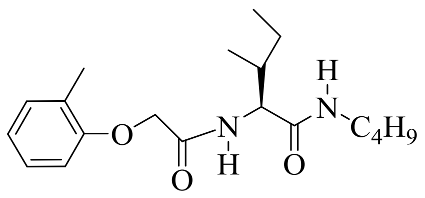
1b-Ile-C6

Yield: 208 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 7.95 (d, *J* = 5.6 Hz, 0H), 7.91 (d, *J* = 9.0 Hz, 0H), 7.29 – 7.25 (m, 2H), 6.93 – 6.89 (m, 3H), 4.11 (t, *J* = 8.5 Hz, 1H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.13 – 2.93 (m, 2H), 2.32 (ddd, *J* = 12.0, 9.5, 4.6 Hz, 2H), 1.94 – 1.89 (m, 2H), 1.67 (ddd, *J* = 16.7, 7.8, 3.4 Hz, 1H), 1.46 – 1.08 (m, 8H), 0.88 – 0.74 (m, 9H). MS-ESI: calculated for $[M+H]^+$ ($C_{20}H_{37}N_2O_3$): m/z 377.54, found: m/z 377.35.



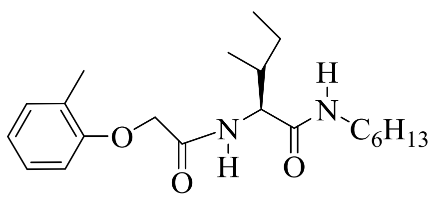
1b-Ile-C8

Yield: 223 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 7.90 (s, 1H), 7.86 (s, 1H), 7.27 (s, 2H), 6.91 (s, 3H), 4.12 (s, 1H), 3.93 (s, 2H), 3.08 – 2.98 (m, 2H), 2.31 (d, J = 4.9 Hz, 2H), 1.93 (s, 2H), 1.68 (d, J = 5.7 Hz, 1H), 1.37 (s, 2H), 1.23 (s, 8H), 1.11 (d, J = 4.2 Hz, 4H), 0.86 (s, 3H), 0.80 (s, 3H), 0.79 (s, 3H). MS-ESI: calculated for [M+Na]+ ($C_{24}H_{40}N_2O_3Na$): *m/z* 427.60, found: *m/z* 427.25.



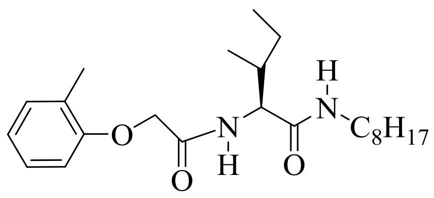
2a-Ile-C4

Yield: 181 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 8.09 (t, *J* = 5.5 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.18 – 7.09 (m, 2H), 6.86 (dd, *J* = 13.3, 7.6 Hz, 2H), 4.61 – 4.51 (m, 2H), 4.22 (dd, *J* = 8.9, 7.2 Hz, 1H), 3.16 – 2.94 (m, 2H), 2.21 (s, 3H), 1.71 (ddd, *J* = 16.1, 6.9, 3.4 Hz, 1H), 1.51 – 1.08 (m, 6H), 0.83 (dt, *J* = 12.9, 7.2 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{30}N_2O_3Na$): *m/z* 357.46, found: *m/z* 357.15.



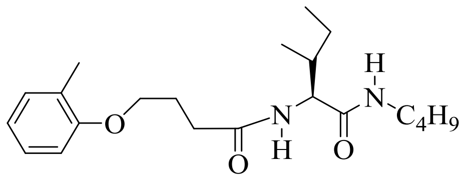
2a-Ile-C6

Yield: 180 mg, 86%. [1]H NMR (400 MHz, DMSO) δ 8.07 (t, J = 5.1 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.12 (s, 2H), 6.83 (s, 2H), 4.68 (s, 2H), 4.57 (s, 1H), 3.13 – 3.07 (m, 2H), 2.22 (s, 2H), 2.18 – 2.16 (m, 3H), 1.73 (s, 1H), 1.38 (s, 2H), 1.19 (d, J = 6.6 Hz, 2H), 1.08 (d, J = 14.3 Hz, 4H), 0.81 (dd, J = 13.3, 6.7 Hz, 9H). MS-ESI: calculated for [M+Na]+ ($C_{21}H_{34}N_2O_3Na$): m/z 385.51, found: m/z 385.35.



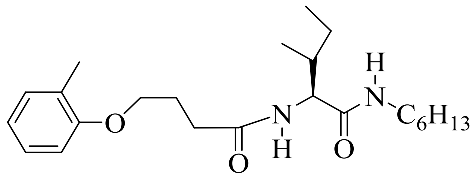
2a-Ile-C8

Yield: 217 mg, 89%. [1]H NMR (400 MHz, DMSO) δ 8.08 (t, *J* = 5.6 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.13 (ddd, *J* = 9.6, 9.2, 4.3 Hz, 2H), 6.86 (dd, *J* = 12.9, 8.0 Hz, 2H), 4.62 – 4.51 (m, 2H), 4.22 (dd, *J* = 9.0, 7.0 Hz, 1H), 3.16 – 2.95 (m, 2H), 2.21 (s, 3H), 1.71 (dtd, *J* = 13.0, 6.5, 3.1 Hz, 1H), 1.46 – 1.17 (m, 14H), 0.82 (dq, *J* = 7.3, 6.2 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{38}N_2O_3Na$): *m/z* 412.57, found: *m/z* 412.20.



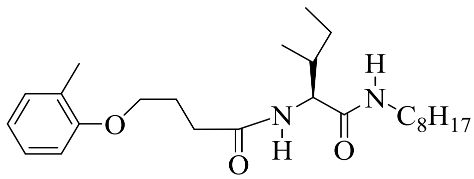
2b-Ile-C4

Yield: 204 mg, 90%. ^{1}H NMR (400 MHz, DMSO) δ 8.02 – 7.94 (m, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.14 – 7.08 (m, 2H), 6.86 (dd, *J* = 6.1, 2.6 Hz, 1H), 6.81 (td, *J* = 7.4, 0.8 Hz, 1H), 4.11 (t, *J* = 8.5 Hz, 1H), 3.98 – 3.88 (m, 2H), 3.13 – 2.92 (m, 2H), 2.40 – 2.26 (m, 2H), 2.15 (s, 3H), 1.99 – 1.87 (m, 2H), 1.70 – 1.61 (m, 1H), 1.42 – 1.05 (m, 6H), 0.81 (dt, *J* = 13.9, 7.3 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): *m/z* 385.51, found: *m/z* 385.20.



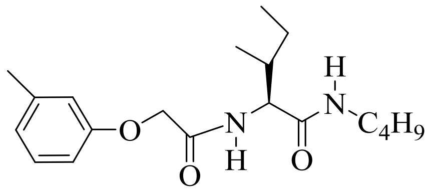
2b-Ile-C6

Yield: 215 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 7.86 (s, 1H), 7.13 (s, 2H), 7.05 (d, J = 8.9 Hz, 1H), 6.90 (s, 1H), 6.80 (s, 1H), 4.10 (s, 1H), 3.96 (s, 2H), 3.03 (dd, J = 36.1, 5.7 Hz, 2H), 2.41 (s, 2H), 2.14 (s, 3H), 1.96 (s, 2H), 1.76 (s, 1H), 1.38 (s, 2H), 1.18 (s, 2H), 1.10 (s, 6H), 0.85 (s, 3H), 0.81 (d, J = 6.3 Hz, 3H), 0.79 (s, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{38}N_2O_3Na$): *m/z* 412.57, found: *m/z* 412.20.



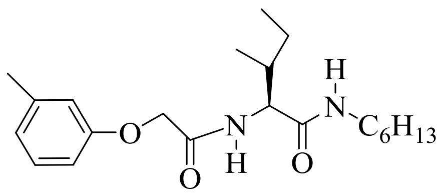
2b-Ile-C8

Yield: 232 mg, 89%. ^{1}H NMR (400 MHz, DMSO) δ 7.95 (d, J = 8.3 Hz, 1H), 7.84 (s, 1H), 7.13 (s, 1H), 6.87 – 6.80 (m, 3H), 4.27 (d, J = 7.7 Hz, 1H), 3.97 (s, 2H), 3.05 – 2.97 (m, 2H), 2.41 (s, 2H), 2.31 (d, J = 7.3 Hz, 1H), 2.15 (s, 3H), 1.94 (s, 2H), 1.36 (s, 2H), 1.23 (s, 8H), 1.10 (s, 4H), 0.85 (s, 3H), 0.84 (s, 3H), 0.81 (d, J = 6.5 Hz, 3H). MS-ESI: calculated for [M+Na]+ ($C_{25}H_{42}N_2O_3Na$): *m/z* 441.62, found: *m/z* 441.25.



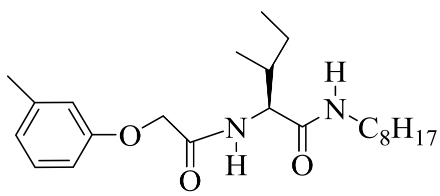
3a-Ile-C4

Yield: 183 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 8.06 (s, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.12 (s, 1H), 6.84 – 6.78 (m, 3H), 4.68 (s, 2H), 4.56 (d, J = 2.5 Hz, 1H), 3.13 – 2.99 (m, 2H), 2.22 (s, 2H), 2.19 (s, 3H), 1.71 (s, 1H), 1.29 (s, 2H), 1.06 (s, 2H), 0.85 – 0.79 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{30}N_2O_3Na$): m/z 357.46, found: m/z 357.15.



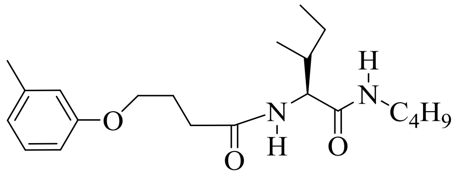
3a-Ile-C6

Yield: 200 mg, 88%. [1]H NMR (400 MHz, DMSO) δ 8.08 (t, *J* = 5.5 Hz, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.80 – 6.68 (m, 3H), 4.58 – 4.47 (m, 2H), 4.19 (dd, *J* = 9.0, 7.7 Hz, 1H), 3.14 – 2.93 (m, 2H), 2.26 (s, 3H), 1.71 (ddd, *J* = 16.4, 7.3, 3.3 Hz, 1H), 1.45 – 1.18 (m, 10H), 0.89 – 0.76 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): *m/z* 385.51, found: *m/z* 385.20.



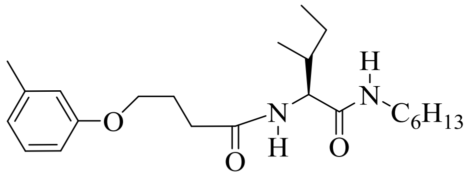
3a-Ile-C8

Yield: 214 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 8.07 (t, *J* = 5.5 Hz, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.74 (ddd, *J* = 10.5, 8.5, 5.4 Hz, 3H), 4.58 – 4.48 (m, 2H), 4.22 – 4.15 (m, 1H), 3.14 – 2.93 (m, 2H), 2.26 (s, 3H), 1.75 – 1.66 (m, 1H), 1.48 – 1.11 (m, 14H), 0.87 – 0.74 (m, 9H). [13]C NMR (101 MHz, DMSO) δ 170.8, 167.8, 158.1, 139.4, 129.6, 122.3, 115.5, 112.1, 66.9, 56.8, 38.8, 37.3, 31.7, 29.4, 29.1, 26.8, 24.7, 22.6, 21.5, 15.8, 14.4, 11.4. MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{38}N_2O_3Na$): *m/z* 413.57, found: *m/z* 413.20.



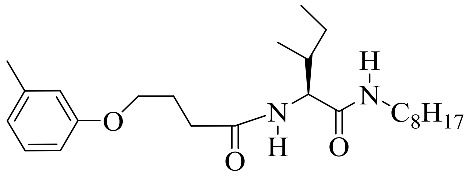
3b-Ile-C4

Yield: 201 mg, 89%. ^{1}H NMR (400 MHz, DMSO) δ 7.91 (t, J = 5.6 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.16 – 7.07 (m, 1H), 6.70 (dd, J = 8.4, 6.2 Hz, 3H), 4.12 (t, J = 8.4 Hz, 1H), 3.98 – 3.89 (m, 2H), 3.14 – 2.91 (m, 2H), 2.31 – 2.26 (m, 3H), 1.91 (dd, J = 13.9, 6.9 Hz, 2H), 1.73 – 1.63 (m, 1H), 1.45 – 1.36 (m, 2H), 1.23 (s, 4H), 1.09 (dd, J = 13.7, 5.5 Hz, 2H), 0.82 (ddd, J = 18.0, 6.7, 3.2 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): *m/z* 385.51, found: *m/z* 385.20.



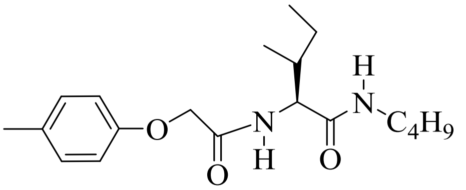
3b-Ile-C6

Yield: 218 mg, 89%. ^{1}H NMR (400 MHz, DMSO) δ 8.05 (s, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.15 (s, 1H), 6.75 (d, J = 7.3 Hz, 3H), 4.59 (s, 2H), 4.20 (s, 1H), 3.10 (s, 2H), 2.26 (s, 3H), 1.71 (d, J = 6.5 Hz, 1H), 1.38 (s, 2H), 1.24 (s, 8H), 1.10 – 1.04 (m, 4H), 0.92 – 0.81 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{38}N_2O_3Na$): *m/z* 412.57, found: *m/z* 412.20.



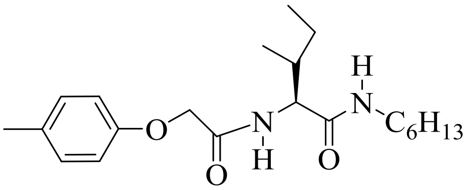
3b-Ile-C8

Yield: 231 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 7.98 – 7.93 (m, 1H), 7.91 (d, *J* = 9.1 Hz, 1H), 7.13 (dd, *J* = 8.1, 5.3 Hz, 1H), 6.73 – 6.68 (m, 3H), 4.15 – 4.08 (m, 1H), 3.93 (dd, *J* = 11.1, 4.7 Hz, 2H), 3.12 – 2.92 (m, 2H), 2.30 – 2.25 (m, 5H), 1.93 – 1.87 (m, 2H), 1.72 – 1.63 (m, 1H), 1.48 – 1.11 (m, 14H), 0.87 – 0.75 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{25}H_{42}N_2O_3Na$): m/z 441.62, found: m/z 441.25.



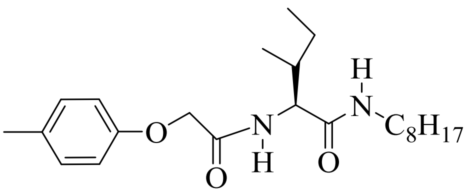
4a-Ile-C4

Yield: 183 mg, 88%.[1]H NMR (400 MHz, DMSO) δ 8.06 (t, *J* = 5.6 Hz, 1H), 7.83 (d, *J* = 9.1 Hz, 1H), 7.11 – 7.04 (m, 2H), 6.85 – 6.79 (m, 2H), 4.57 – 4.46 (m, 2H), 4.18 (dd, *J* = 8.9, 7.7 Hz, 1H), 3.13 – 2.94 (m, 2H), 2.22 (s, 3H), 1.70 (ddd, *J* = 16.4, 7.3, 3.4 Hz, 1H), 1.51 – 1.14 (m, 6H), 0.81 (ddd, *J* = 13.1, 11.8, 6.1 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{30}N_2O_3Na$): *m/z* 357.46, found: *m/z* 357.15.



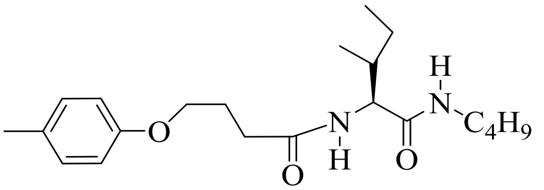
4a-Ile-C6

Yield: 204 mg, 90%. [1]H NMR (400 MHz, DMSO) δ 8.07 (t, *J* = 5.4 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.56 – 4.46 (m, 2H), 4.19 (t, *J* = 8.3 Hz, 1H), 3.14 – 2.93 (m, 2H), 2.22 (s, 3H), 1.77 – 1.64 (m, 1H), 1.50 – 1.08 (m, 10H), 0.81 (ddd, *J* = 11.9, 10.1, 5.9 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): m/z 385.51, found: m/z 385.25.



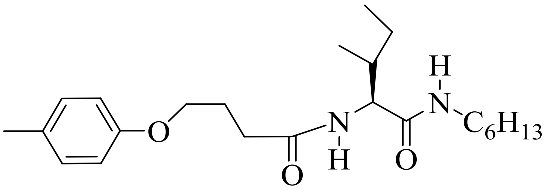
4a-Ile-C8

Yield: 208 mg, 85%. [1]H NMR (400 MHz, DMSO) δ 8.08 (t, *J* = 5.6 Hz, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.83 – 6.79 (m, 2H), 4.55 – 4.46 (m, 2H), 4.18 (dd, *J* = 8.9, 7.7 Hz, 1H), 3.14 – 2.93 (m, 2H), 2.22 (s, 3H), 1.74 – 1.65 (m, 1H), 1.43 – 1.17 (m, 14H), 0.89 – 0.77 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{38}N_2O_3Na$): *m/z* 413.57, found: *m/z* 413.25.



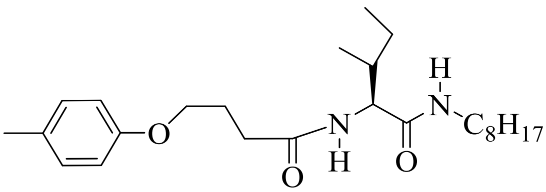
4b-Ile-C4

Yield: 202 mg, 89%. [1]H NMR (400 MHz, DMSO) δ 8.06 (s, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.11 (d, J = 7.8 Hz, 2H), 6.80 (d, J = 8.1 Hz, 2H), 4.68 (s, 2H), 4.56 (d, J = 2.5 Hz, 1H), 3.13–2.99 (m, 2H), 2.22 (s, 2H), 2.19 (s, 3H), 1.75 (s, 1H), 1.38 (s, 2H), 1.28 – 1.23 (m, 2H), 1.10 (s, 4H), 0.85 – 0.79 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): *m/z* 385.51, found: *m/z* 385.20.



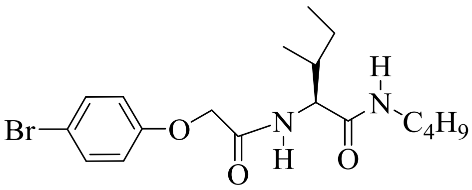
4b-Ile-C6

Yield: 217 mg, 89%. [1]H NMR (400 MHz, DMSO) δ 7.94 (d, J = 8.3 Hz, 1H), 7.84 (t, J = 5.5 Hz, 1H), 7.08 (s, 2H), 6.78 (d, J = 2.1 Hz, 2H), 4.26 (dd, J = 15.3, 8.1 Hz, 1H), 3.88 (dd, J = 6.5, 1.9 Hz, 2H), 3.03 (ddd, J = 20.6, 12.0, 5.8 Hz, 2H), 2.37 (d, J = 7.3 Hz, 2H), 2.18 (s, 3H), 1.88 (d, J = 6.9 Hz, 2H), 1.52 (dq, J = 12.8, 6.4 Hz, 1H), 1.39 – 1.33 (m, 2H), 1.22 (s, 6H), 1.10 (s, 2H), 0.86 – 0.78 (m, 9H). MS-ESI: calculated for $[M+H]^+$ ($C_{23}H_{39}N_2O_3$): *m/z* 391.57, found: *m/z* 391.15.



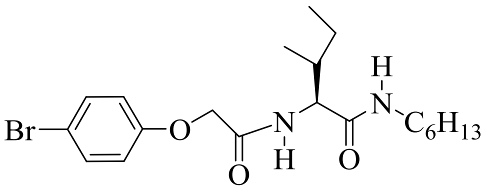
4b-Ile-C8

Yield: 228 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 7.87 (d, J = 9.8 Hz, 1H), 7.84 (s, 1H), 7.02 (s, 2H), 6.79 – 6.77 (m, 2H), 4.10 (s, 1H), 3.91 (s, 2H), 3.09 – 2.99 (m, 2H), 2.36 (s, 2H), 2.22 (s, 3H), 1.88 (s, 2H), 1.76 (s, 1H), 1.37 – 1.33 (m, 2H), 1.23 – 1.18 (m, 8H), 1.07 (s, 4H), 0.85 (s, 3H), 0.82 (s, 3H), 0.79 (s, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{25}H_{42}N_2O_3Na$): *m/z* 441.62, found: *m/z* 441.25.



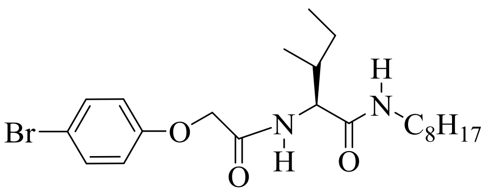
5a-Ile-C4

Yield: 210 mg, 84%.[1]H NMR (400 MHz, DMSO) δ 8.06 (t, *J* = 5.5 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.49 – 7.40 (m, 2H), 6.94 – 6.85 (m, 2H), 4.59 (t, *J* = 8.5 Hz, 2H), 4.21 – 4.13 (m, 1H), 3.15 – 2.93 (m, 2H), 1.78 – 1.64 (m, 1H), 1.45 – 1.20 (m, 6H), 0.81 (ddd, *J* = 12.3, 10.9, 6.4 Hz, 9H). [13]C NMR (101 MHz, DMSO) δ 170.8, 167.4, 157.5, 132.5, 117.3, 112.9, 67.1, 56.9, 38.5, 37.2, 31.5, 24.8, 20.0, 15.8, 14.1, 11.4. MS-ESI: calculated for [M+Na]+ ($C_{18}H_{27}BrN_2O_3Na$): *m/z* 422.33, found: *m/z* 422.25.



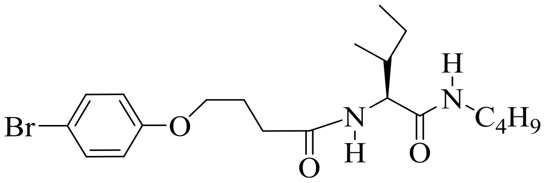
5a-Ile-C6

Yield: 226 mg, 84%.[1]H NMR (400 MHz, DMSO) δ 8.06 (t, *J* = 5.5 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.48 – 7.42 (m, 2H), 6.93 – 6.86 (m, 2H), 4.57 (d, *J* = 2.0 Hz, 2H), 4.23 – 4.11 (m, 1H), 3.03 (ddd, *J* = 18.7, 13.1, 6.0 Hz, 2H), 2.50 (s, 2H), 1.71 (d, *J* = 6.0 Hz, 1H), 1.46 – 1.35 (m, 2H), 1.28 – 1.18 (m, 6H), 0.81 (dq, *J* = 7.3, 6.2 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{31}BrN_2O_3Na$): *m/z* 450.38, found: *m/z* 450.25.



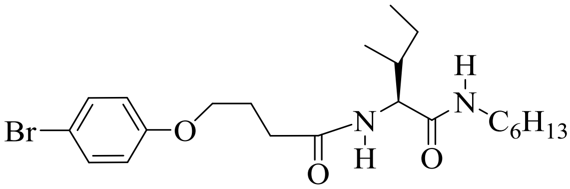
5a-Ile-C8

Yield: 244 mg, 86%.[1]H NMR (400 MHz, DMSO) δ 8.08 (t, *J* = 5.6 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.47 – 7.42 (m, 2H), 6.92 – 6.87 (m, 2H), 4.62 – 4.51 (m, 2H), 4.17 (dd, *J* = 8.8, 7.8 Hz, 1H), 3.13 – 2.92 (m, 2H), 1.70 (ddd, *J* = 14.2, 10.1, 5.0 Hz, 1H), 1.43 – 1.17 (m, 14H), 0.87 – 0.76 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{35}BrN_2O_3Na$): m/z 479.44, found: m/z 479.10.



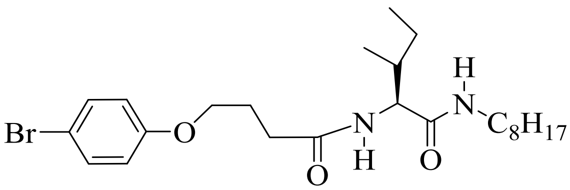
5b-Ile-C4

Yield: 234 mg, 85%. ^{1}H NMR (400 MHz, DMSO) δ 8.03 (t, J = 5.6 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.43 (s, 2H), 6.91 (s, 2H), 4.68 – 4.66 (m, 2H), 4.58 (d, J = 1.4 Hz, 1H), 4.00 (s, 2H), 3.10 – 2.98 (m, 2H), 2.09 (s, 1H), 1.98 – 1.94 (m, 2H), 1.35 (s, 2H), 1.12 (s, 2H), 1.06 (d, J = 5.8 Hz, 2H), 0.82 (dd, J = 17.9, 6.1 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{31}BrN_2O_3Na$): *m/z* 450.38, found: *m/z* 450.10.



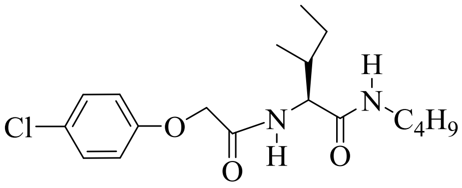
5b-Ile-C6

Yield: 245 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 8.03 (t, J = 5.5 Hz, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.49 – 7.45 (m, 2H), 6.88 (dd, J = 6.2, 4.0 Hz, 2H), 4.68 (s, 2H), 4.57 (d, J = 1.6 Hz, 1H), 4.28 – 3.93 (m, 2H), 3.13 – 2.96 (m, 2H), 1.82 – 1.68 (m, 1H), 1.38 (d, J = 6.1 Hz, 2H), 1.31 – 1.15 (m, 8H), 1.10 (s, 4H), 0.90 – 0.79 (m, 9H). ^{13}C NMR (101 MHz, DMSO) δ 171.8, 171.3, 158.3, 132.5, 117.1, 112.2, 67.6, 57.2, 38.8, 36.9, 31.8, 31.4, 29.4, 26.5, 25.3, 24.9, 22.5, 15.8, 14.4, 11.4. MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{35}BrN_2O_3Na$): *m/z* 478.44, found: *m/z* 478.15.



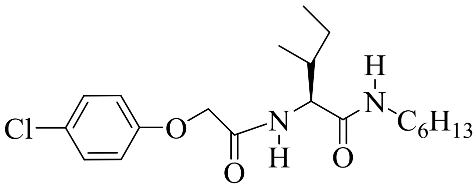
5b-Ile-C8

Yield: 261 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 7.97 (d, *J* = 5.7 Hz, 1H), 7.94 (d, *J* = 9.1 Hz, 1H), 7.44 – 7.41 (m, 2H), 6.91 – 6.86 (m, 2H), 4.10 (t, *J* = 8.5 Hz, 1H), 3.97 – 3.90 (m, 2H), 3.10 – 2.90 (m, 2H), 2.31 (dd, *J* = 13.6, 6.2 Hz, 2H), 1.93 – 1.87 (m, 2H), 1.65 (dd, *J* = 15.1, 8.5 Hz, 1H), 1.43 – 1.09 (m, 14H), 0.88 – 0.72 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{24}H_{39}BrN_2O_3Na$): *m/z* 507.49, found: *m/z* 507.20.



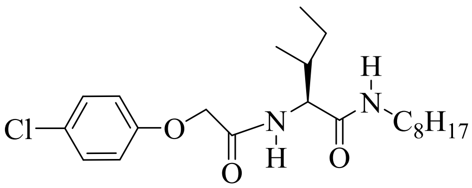
6a-Ile-C4

Yield: 189 mg, 85%. ^{1}H NMR (400 MHz, DMSO) δ 8.03 (t, J = 5.4 Hz, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.04 – 6.95 (m, 2H), 4.68 (s, 2H), 4.58 (d, J = 1.5 Hz, 1H), 3.14 – 2.98 (m, 2H), 1.70 (dd, J = 11.5, 4.6 Hz, 1H), 1.38 (d, J = 6.0 Hz, 2H), 1.20 (s, 2H), 1.09 (d, J = 12.9 Hz, 2H), 0.80 (dd, J = 14.0, 8.5 Hz, 9H). MS-ESI: calculated for $[M+Na]^{+}$ ($C_{18}H_{27}ClN_2O_3Na$): *m/z* 377.88, found: *m/z* 377.10.



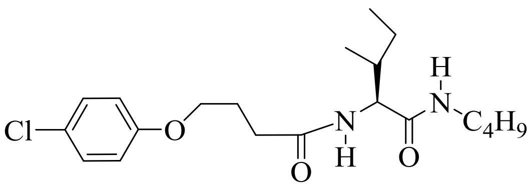
6a-Ile-C6

Yield: 205 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 8.06 (t, *J* = 5.6 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.35 – 7.29 (m, 2H), 6.98 – 6.92 (m, 2H), 4.62 – 4.53 (m, 2H), 4.17 (dd, *J* = 8.8, 7.8 Hz, 1H), 3.15 – 2.92 (m, 2H), 1.75 – 1.65 (m, 1H), 1.49 – 1.15 (m, 10H), 0.81 (dq, *J* = 7.4, 6.2 Hz, 9H). MS-ESI: calculated for $[M+Na]^{+}$ ($C_{20}H_{31}ClN_2O_3Na$): *m/z* 3405.93, found: *m/z* 405.10.



6a-Ile-C8

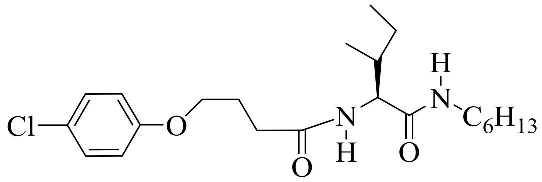
Yield: 223 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.08 (t, *J* = 5.6 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.35 – 7.30 (m, 2H), 6.97 – 6.92 (m, 2H), 4.64 – 4.51 (m, 2H), 4.22 – 4.13 (m, 1H), 3.12 – 2.93 (m, 2H), 1.71 (td, *J* = 10.2, 3.3 Hz, 1H), 1.50 – 1.20 (m, 14H), 0.86 – 0.76 (m, 9H). MS-ESI: calculated for $[M+Na]^{+}$ ($C_{22}H_{35}ClN_2O_3Na$): *m/z* 422.98, found: *m/z* 422.15.



6b-Ile-C4

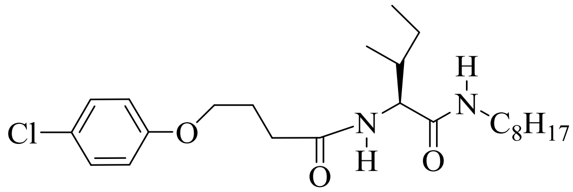
Yield: 207 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ

7.98 – 7.89 (m, 1H), 7.86 (s, 1H), 7.32 (s, 2H), 6.93 (d, J = 2.3 Hz, 2H), 4.11 – 4.05 (m, 1H), 3.95 – 3.79 (m, 2H), 3.12 – 2.95 (m, 2H), 2.39 (s, 2H), 1.99 (s, 1H), 1.89 (s, 2H), 1.36 – 1.27 (m, 2H), 1.16 (s, 2H), 1.10 (s, 2H), 0.86 – 0.78 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{31}ClN_2O_3Na$): m/z 405.93, found: m/z 405.15.



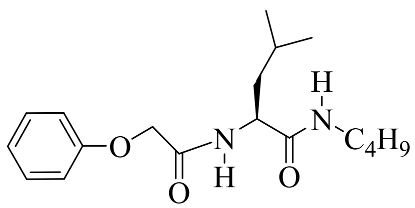
6b-Ile-C6

Yield: 224 mg, 87%. ^1H NMR (400 MHz, DMSO) δ 7.86 (t, J = 5.4 Hz, 1H), 7.32 (d, J = 2.1 Hz, 2H), 7.05 (d, J = 8.9 Hz, 1H), 6.94 (s, 2H), 4.10 (t, J = 8.6 Hz, 1H), 3.95 (s, 2H), 3.04 (d, J = 47.9 Hz, 2H), 2.35 (s, 2H), 1.90 (d, J = 7.0 Hz, 2H), 1.77 (d, J = 6.6 Hz, 1H), 1.41 – 1.35 (m, 2H), 1.24 (s, 6H), 1.07 (s, 2H), 0.91 – 0.73 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{35}ClN_2O_3Na$): *m/z* 424.98, found: *m/z* 424.25.



6b-Ile-C8

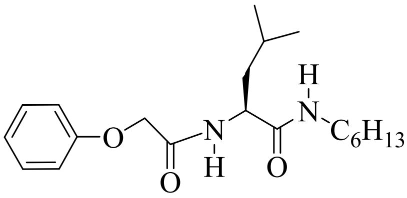
Yield: 237 mg, 86%. ^1H NMR (400 MHz, DMSO) δ 7.91 (d, J = 5.5 Hz, 1H), 7.88 (d, J = 9.2 Hz, 1H), 7.32 (d, J = 2.8 Hz, 2H), 6.94 – 6.89 (m, 2H), 4.11 (t, J = 8.4 Hz, 1H), 3.92 (dd, J = 10.2, 3.6 Hz, 2H), 3.13 – 2.93 (m, 2H), 2.36 – 2.29 (m, 2H), 1.93 (dd, J = 13.8, 6.9 Hz, 4H), 1.67 (d, J = 6.1 Hz, 1H), 1.37 (d, J = 4.5 Hz, 2H), 1.22 (s, 8H), 1.11 – 1.04 (m, 2H), 0.85 – 0.72 (m, 9H). MS-ESI: calculated for $[M+H]^+$ ($C_{24}H_{40}ClN_2O_3$): *m/z* 441.04, found: *m/z* 441.15.



1a-Leu-C4

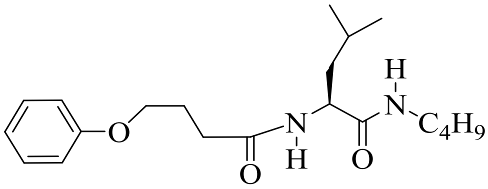
Yield: 169 mg, 85%. ^1H NMR (400 MHz, DMSO) δ 8.04 (t, J = 5.3 Hz, 1H), 7.84 (d, J = 9.3 Hz, 1H), 7.27 (d, J = 0.7 Hz, 2H), 6.97 – 6.93 (m, 3H), 4.66 (s, 2H), 4.56 (d, J = 1.8 Hz, 1H), 3.13–2.98 (m, 2H), 1.74 (s, 1H), 1.30 (dd, J = 16.3, 9.1 Hz, 2H), 1.05 (d, J = 7.2 Hz, 2H), 0.90 – 0.80 (m, 9H). MS-ESI: calculated for $[M+Na]^+$

($C_{18}H_{28}N_2O_3Na$): m/z 342.43, found: m/z 342.15.



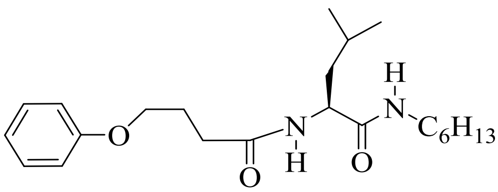
1a-Leu-C6

Yield: 186 mg, 85%. [1]H NMR (400 MHz, DMSO) δ 7.99 (d, J = 8.4 Hz, 1H), 7.94 (t, J = 4.9 Hz, 1H), 7.27 (s, 2H), 6.97 (s, 3H), 4.66 (s, 2H), 4.53 (s, 1H), 3.04 (dd, J = 18.0, 6.5 Hz, 2H), 1.50 – 1.45 (m, 2H), 1.37 (s, 1H), 1.18 (s, 2H), 1.10 (s, 6H), 0.87 (s, 3H), 0.85 (s, 3H), 0.82 (s, 3H). MS-ESI: calculated for [M+Na]+ ($C_{20}H_{32}N_2O_3Na$): *m/z* 371.49, found: *m/z* 371.20.



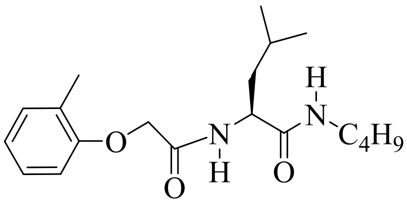
1b-Leu-C4

Yield: 186 mg, 86%. [1]H NMR (400 MHz, DMSO) δ 7.66 (t, J = 5.2 Hz, 1H), 7.29 (s, 2H), 7.23 (s, 1H), 6.90 (d, J = 2.8 Hz, 3H), 4.27 (td, J = 9.1, 5.1 Hz, 1H), 3.95 (s, 2H), 3.13 – 2.90 (m, 2H), 2.36 (s, 2H), 1.91 (d, J = 7.0 Hz, 2H), 1.55 (d, J = 9.9 Hz, 1H), 1.41 – 1.34 (m, 2H), 1.25 (dd, J = 15.1, 7.2 Hz, 2H), 1.10 – 1.06 (m, 2H), 0.88 – 0.79 (m, 9H). MS-ESI: calculated for $[M+Na]^+$) ($C_{20}H_{32}N_2O_3Na$): *m/z* 371.43, found: *m/z* 371.15.

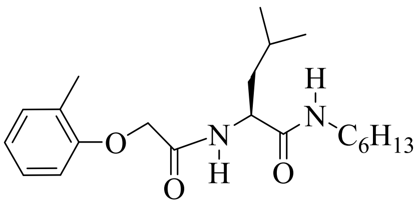


1b-Leu-C6

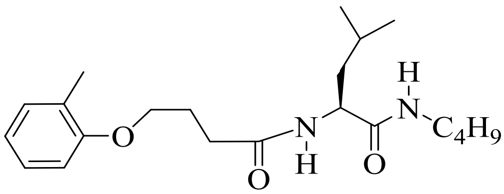
Yield: 203 mg, 87%.1H NMR (400 MHz, DMSO) δ 7.98 (d, J = 8.3 Hz, 1H), 7.87 (s, 1H), 7.26 (s, 2H), 6.93 (s, 3H), 4.29 (s, 1H), 3.98 (s, 2H), 3.07 – 3.00 (m, 2H), 2.37 (s, 2H), 1.93 (s, 2H), 1.56 (s, 1H), 1.37 (s, 2H), 1.22 – 1.20 (m, 2H), 1.11 (s, 6H), 0.87 (s, 3H), 0.85 (s, 3H), 0.82 (d, J = 6.1 Hz, 3H). MS-ESI: calculated for [M+Na]+) ($C_{22}H_{36}N_2O_3Na$): *m/z* 377.54, found: *m/z* 377.25.



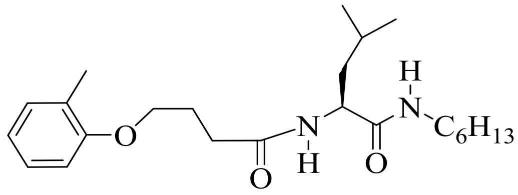
2a-Leu-C4 Yield: 181 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.03 (t, J = 5.3 Hz, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 3.4 Hz, 2H), 6.98 – 6.95 (m, 2H), 4.69 (s, 2H), 4.58 (d, J = 1.7 Hz, 1H), 4.06 (s, 2H), 2.09 (s, 1H), 1.99 (s, 3H), 1.32 (d, J = 24.7 Hz, 2H), 1.16 (s, 4H), 0.87 – 0.78 (m, 9H). MS-ESI: calculated for $[M+Na]^+$) ($C_{19}H_{30}N_2O_3Na$): *m/z* 357.36, found: *m/z* 357.15.



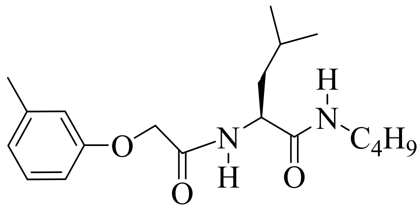
2a-Leu-C6 Yield: 196 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 7.98 (t, J = 5.1 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.12 (s, 2H), 6.82 (d, J = 9.4 Hz, 2H), 4.68 (s, 2H), 4.54 (d, J = 3.4 Hz, 1H), 3.10 – 2.98 (m, 2H), 2.19 (s, 3H), 1.50 (d, J = 11.9 Hz, 1H), 1.37 (d, J = 6.1 Hz, 2H), 1.24 (s, 2H), 1.11 (s, 6H), 0.85 (dd, J = 10.2, 6.4 Hz, 9H). MS-ESI: calculated for [M+Na]+) ($C_{21}H_{34}N_2$O3Na): m/z 385.51, found: m/z 385.20.



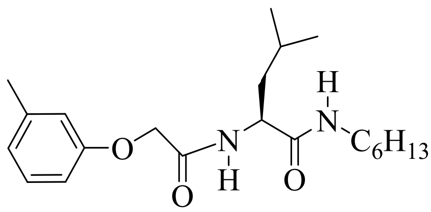
2b-Leu-C4 Yield: 195 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 7.97 (t, J = 5.5 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.11 (d, J = 7.7 Hz, 2H), 6.86 (dd, J = 12.3, 5.3 Hz, 2H), 4.68 (s, 2H), 4.53 (s, 1H), 4.05 (d, J = 7.1 Hz, 2H), 2.19 (s, 3H), 2.09 (s, 2H), 1.99 – 1.96 (m, 2H), 1.58 – 1.51 (m, 1H), 1.35 – 1.26 (m, 2H), 1.16 (s, 2H), 1.10 (s, 2H), 0.87 – 0.81 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): m/z 385.52, found: m/z 385.20.



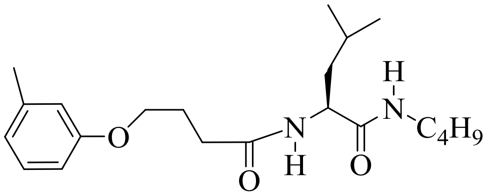
2b-Leu-C6 Yield: 209 mg, 86%. [1]H NMR (400 MHz, DMSO) δ 7.67 (s, 1H), 7.24 (d, J = 8.5 Hz, 1H), 7.12 (s, 2H), 6.89 (s, 1H), 6.80 (s, 1H), 4.27 (d, J = 8.3 Hz, 1H), 3.98 (s, 2H), 3.02 (dd, J = 12.5, 6.2 Hz, 2H), 2.41 (s, 2H), 2.14 (s, 3H), 1.96 (s, 2H), 1.54 (s, 1H), 1.40 (s, 2H), 1.22 – 1.20 (m, 2H), 1.10 (s, 6H), 0.88 (s, 3H), 0.84 (s, 3H), 0.82 (s, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{38}N_2O_3Na$): *m/z* 412.57, found: *m/z* 412.20.



3a-Leu-C4 Yield: 180 mg, 86%. [1]H NMR (400 MHz, DMSO) δ 7.97 (d, J = 8.6 Hz, 1H), 7.94 (t, J = 5.7 Hz, 1H), 7.13 (s, 1H), 6.69 (dd, J = 8.2, 2.1 Hz, 3H), 4.63 (s, 2H), 4.51 (d, J = 3.4 Hz, 1H), 3.05 (tq, J = 12.8, 6.3 Hz, 2H), 2.23 (s, 3H), 1.50 (dd, J = 11.4, 7.3 Hz, 2H), 1.40 – 1.33 (m, 2H), 1.25 (dd, J = 14.9, 7.2 Hz, 2H), 1.10 (s, 1H), 0.84 (dd, J = 14.1, 5.4 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{30}N_2O_3Na$): *m/z* 357.46, found: *m/z* 357.10.

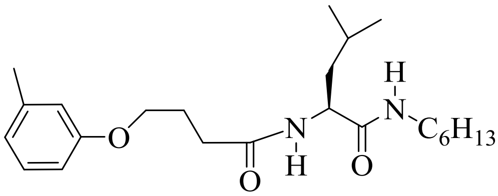


3a-Leu-C6 Yield: 194 mg, 85%. [1]H NMR (400 MHz, DMSO) δ 8.00 – 7.95 (m, 1H), 7.93 (d, J = 5.2 Hz, 1H), 7.16 (d, J = 6.1 Hz, 1H), 6.70 (s, 3H), 4.62 – 4.59 (m, 2H), 4.50 (s, 1H), 3.04 (dd, J = 14.3, 7.5 Hz, 2H), 2.26 – 2.21 (m, 3H), 1.53 (d, J = 9.9 Hz, 1H), 1.36 (d, J = 6.4 Hz, 2H), 1.23 (s, 6H), 1.06 (s, 2H), 0.86 – 0.81 (m, 9H). MS-ESI: calculated for [M+Na]+ ($C_{21}H_{34}N_2O_3Na$): *m/z* 385.51, found: *m/z* 385.20.



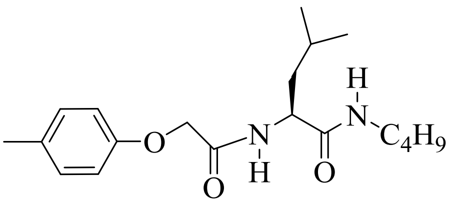
3b-Leu-C4

Yield: 196 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 7.96 (d, J = 8.3 Hz, 1H), 7.86 (t, J = 5.6 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 6.70 (d, J = 2.9 Hz, 3H), 4.29 (dd, J = 14.9, 8.4 Hz, 1H), 3.90 (d, J = 6.5 Hz, 2H), 3.10 – 2.96 (m, 2H), 2.39 (d, J = 7.3 Hz, 2H), 2.31 (d, J = 6.9 Hz, 3H), 1.92 (dt, J = 6.9, 3.1 Hz, 4H), 1.55 (dt, J = 13.3, 6.6 Hz, 1H), 1.42 – 1.35 (m, 2H), 1.25 (dd, J = 14.9, 7.2 Hz, 2H), 0.87 – 0.79 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): *m/z* 385.51, found: m/z 385.20.



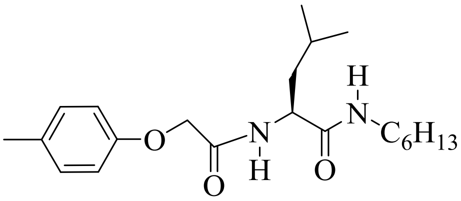
3b-Leu-C6

Yield: 210 mg, 86%. [1]H NMR (400 MHz, DMSO) δ 7.67 (s, 1H), 7.24 (d, J = 8.5 Hz, 1H), 7.12 (s, 2H), 6.89 (s, 1H), 6.80 (s, 1H), 4.27 (d, J = 8.3 Hz, 1H), 3.98 (s, 2H), 3.02 (dd, J = 12.5, 6.2 Hz, 2H), 2.41 (s, 2H), 2.14 (s, 3H), 1.96 (s, 2H), 1.54 (s, 1H), 1.40 (s, 2H), 1.22 – 1.20 (m, 2H), 1.10 (s, 6H), 0.88 (s, 3H), 0.84 (s, 3H), 0.82 (s, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{38}N_2O_3Na$): *m/z* 413.57, found: *m/z* 413.20.



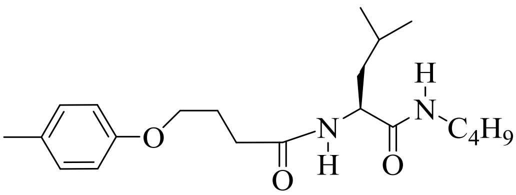
4a-Leu-C4

Yield: 176 mg, 85%. [1]H NMR (400 MHz, DMSO) δ 7.92 (t, J = 13.0 Hz, 1H), 7.09 (s, 2H), 6.83 (d, J = 8.4 Hz, 1H), 6.80 (s, 2H), 4.60 (s, 2H), 4.48 (s, 1H), 3.02 (tq, J = 19.7, 6.5 Hz, 2H), 2.23 (s, 3H), 1.51 – 1.44 (m, 1H), 1.43 – 1.31 (m, 2H), 1.23 (s, 2H), 1.10 (s, 2H), 0.96–0.66 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{30}N_2O_3Na$): *m/z* 357.46, found: *m/z* 357.15.



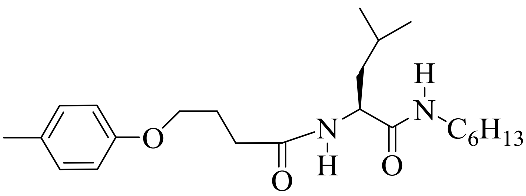
4a-Leu-C6

Yield: 193 mg, 85%. ^{1}H NMR (400 MHz, DMSO) δ 8.06 (t, J = 4.8 Hz, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.10 (s, 2H), 6.88 (d, J = 7.6 Hz, 2H), 4.68 – 4.67 (m, 2H), 4.56 (s, 1H), 3.13 – 2.94 (m, 2H), 2.22 (s, 3H), 1.72 (d, J = 6.5 Hz, 1H), 1.39 (s, 2H), 1.24 (s, 6H), 1.11 – 1.02 (m, 2H), 0.84 (dd, J = 18.0, 6.2 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): *m/z* 385.51, found: *m/z* 385.15.



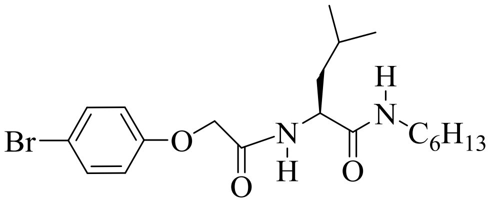
4b-Leu-C4

Yield: 195 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 7.94 (d, J = 8.2 Hz, 1H), 7.83 (t, J = 5.6 Hz, 1H), 7.08 (s, 2H), 6.79 (s, 2H), 4.25 (dd, J = 14.9, 8.4 Hz, 1H), 3.87 (d, J = 9.3 Hz, 2H), 2.35 (s, 2H), 2.22 – 2.16 (m, 3H), 1.91 – 1.84 (m, 6H), 1.52 (dt, J = 14.0, 6.0 Hz, 1H), 1.36 (dd, J = 14.1, 7.0 Hz, 2H), 1.24 (dd, J = 14.9, 7.4 Hz, 2H), 0.96 – 0.75 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): *m/z* 385.51, found: *m/z* 385.25.



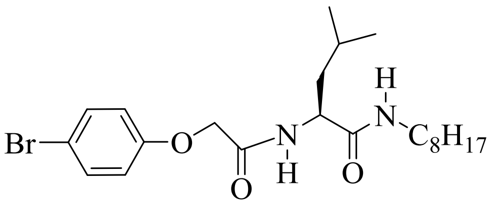
4b-Leu-C6

Yield: 213 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 7.67 (s, 1H), 7.24 (d, J = 8.3 Hz, 1H), 7.06 (s, 2H), 6.80 (s, 2H), 4.26 (d, J = 7.6 Hz, 1H), 3.89 (s, 2H), 3.07 – 2.99 (m, 2H), 2.38 (s, 2H), 2.22 (s, 3H), 1.93 (s, 2H), 1.54 (s, 1H), 1.38 (d, J = 7.2 Hz, 2H), 1.25 (s, 2H), 1.10 (s, 6H), 0.88 (s, 3H), 0.85 (s, 3H), 0.82 (s, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{38}N_2O_3Na$): *m/z* 413.57, found: *m/z* 413.15.



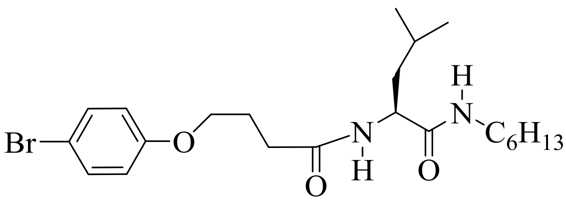
5a-Leu-C6

Yield: 225 mg, 84%. [1]H NMR (400 MHz, DMSO) δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.96 (t, *J* = 5.6 Hz, 1H), 7.45 – 7.42 (m, 4H), 6.88 (dt, *J* = 6.8, 3.4 Hz, 4H), 4.65 (s, 2H), 4.58 – 4.49 (m, 2H), 3.09 – 2.94 (m, 2H), 1.53 – 1.41 (m, 3H), 1.37 – 1.18 (m, 8H), 0.90 – 0.77 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{31}BrN_2O_3Na$): *m/z* 450.38, found: *m/z* 450.35.



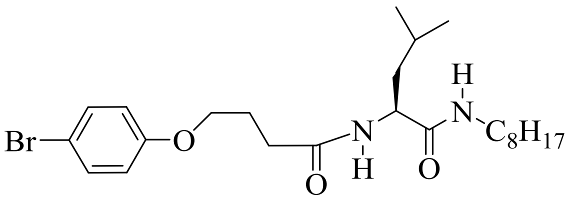
5a-Leu-C8

Yield: 246 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.98 (t, *J* = 5.6 Hz, 1H), 7.47 – 7.41 (m, 2H), 6.93 – 6.88 (m, 2H), 4.59 – 4.49 (m, 2H), 4.31 (dt, *J* = 14.2, 7.2 Hz, 1H), 3.10 – 2.92 (m, 2H), 1.52 – 1.40 (m, 3H), 1.40 – 1.30 (m, 2H), 1.24 (d, *J* = 16.2 Hz, 10H), 0.88 – 0.79 (m, 9H). MS-ESI: calculated for [M+Na]+ ($C_{22}H_{35}BrN_2O_3Na$): *m/z* 478.44, found: *m/z* 478.50.



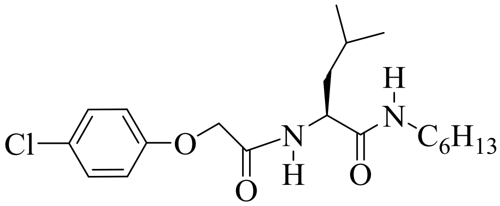
5b-Leu-C6

Yield: 244 mg, 85%. [1]H NMR (400 MHz, DMSO) δ 7.94 (d, J = 8.3 Hz, 1H), 7.84 (t, J = 5.5 Hz, 1H), 7.44 (s, 2H), 6.88 (d, J = 2.4 Hz, 2H), 4.25 (dd, J = 15.4, 7.8 Hz, 1H), 3.94 – 3.85 (m, 2H), 3.00 (dt, J = 20.0, 6.6 Hz, 2H), 2.35 (s, 2H), 1.95 (d, J = 6.8 Hz, 2H), 1.51 (dd, J = 13.4, 6.8 Hz, 1H), 1.38 (d, J = 7.2 Hz, 2H), 1.23 (dd, J = 9.2, 5.9 Hz, 6H), 1.10 (s, 2H), 0.87 – 0.80 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{35}BrN_2O_3Na$): *m/z* 478.44, found: *m/z* 478.50.



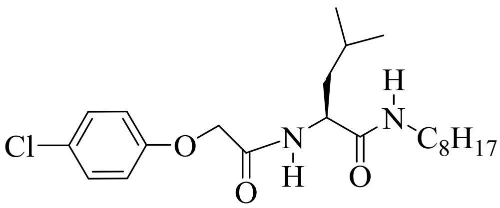
5b-Leu-C8

Yield: 267 mg, 88%. [1]H NMR (400 MHz, DMSO) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.90 (t, *J* = 5.6 Hz, 1H), 7.44 – 7.40 (m, 2H), 6.90 – 6.85 (m, 2H), 4.24 (dt, *J* = 15.1, 7.6 Hz, 1H), 3.96 – 3.85 (m, 2H), 3.07 – 2.89 (m, 2H), 2.26 (t, *J* = 7.6 Hz, 2H), 1.94 – 1.85 (m, 2H), 1.49 (dt, *J* = 12.9, 6.5 Hz, 1H), 1.40 – 1.29 (m, 4H), 1.23 (d, *J* = 17.3 Hz, 10H), 0.91 – 0.74 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{24}H_{39}BrN_2O_3Na$): *m/z* 506.39, found: *m/z* 506.20.



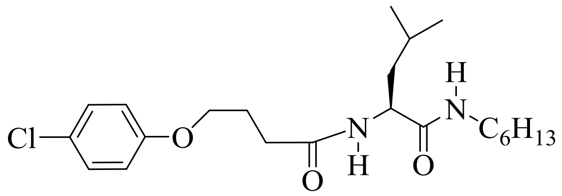
6a-Leu-C6

Yield: 208 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 7.88 (t, J = 5.3 Hz, 1H), 7.44 (s, 2H), 7.06 (d, J = 8.8 Hz, 1H), 6.91 (d, J = 3.4 Hz, 2H), 4.10 (t, J = 8.6 Hz, 1H), 3.98 (d, J = 6.4 Hz, 2H), 3.17 – 2.92 (m, 2H), 2.35 (s, 2H), 1.92 (s, 2H), 1.76 (dd, J = 8.3, 5.4 Hz, 1H), 1.40 (dd, J = 13.1, 7.2 Hz, 2H), 1.23 – 1.20 (m, 2H), 1.10 – 1.01 (m, 2H), 0.83 (ddd, J = 10.4, 9.0, 4.4 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{31}ClN_2O_3Na$): *m/z* 405.93, found: *m/z* 405.15.



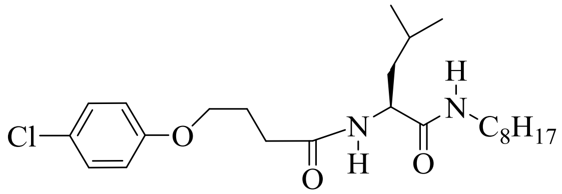
6a-Leu-C8

Yield: 224 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.98 (t, *J* = 5.6 Hz, 1H), 7.34 – 7.29 (m, 2H), 6.98 – 6.92 (m, 2H), 4.59 – 4.49 (m, 2H), 4.31 (dt, *J* = 14.2, 7.1 Hz, 1H), 3.01 (dq, *J* = 13.0, 6.2 Hz, 2H), 1.54 – 1.41 (m, 3H), 1.39 – 1.31 (m, 2H), 1.28 – 1.16 (m, 10H), 0.90 – 0.77 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{35}ClN_2O_3Na$): *m/z* 422.98, found: *m/z* 422.15.



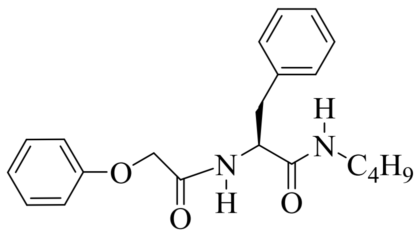
6b-Leu-C6

Yield: 219 mg, 85%. [1]H NMR (400 MHz, DMSO) δ 7.67 (t, J = 5.4 Hz, 1H), 7.33 (d, J = 3.5 Hz, 2H), 7.24 (d, J = 8.4 Hz, 1H), 6.96 (d, J = 3.5 Hz, 2H), 4.27 (td, J = 9.2, 5.2 Hz, 1H), 3.95 (s, 2H), 3.03 (dd, J = 18.7, 6.0 Hz, 2H), 2.35 (s, 2H), 1.90 (d, J = 6.9 Hz, 2H), 1.54 (s, 1H), 1.39 – 1.33 (m, 2H), 1.25 – 1.18 (m, 6H), 1.07 (s, 2H), 0.89 – 0.82 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{35}ClN_2O_3Na$): *m/z* 422.98, found: *m/z* 422.15.



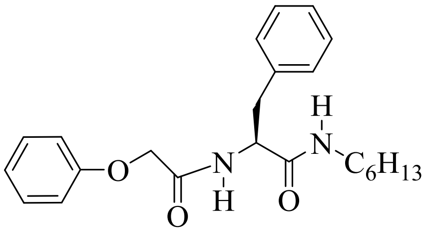
6b-Leu-C8

Yield: 237 mg, 86%. [1]H NMR (400 MHz, DMSO) δ 7.67 (t, J = 5.4 Hz, 1H), 7.33 (d, J = 3.5 Hz, 2H), 7.24 (d, J = 8.4 Hz, 1H), 6.93 (d, J = 2.6 Hz, 2H), 4.31 – 4.24 (m, 1H), 3.95 – 3.85 (m, 2H), 3.07 – 2.98 (m, 2H), 2.35 (s, 2H), 1.89 (s, 2H), 1.56 (d, J = 16.7 Hz, 1H), 1.45 – 1.38 (m, 2H), 1.23 (s, 8H), 1.11 (s, 4H), 0.86 – 0.77 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{24}H_{39}ClN_2O_3Na$): *m/z* 461.04, found: *m/z* 461.20.

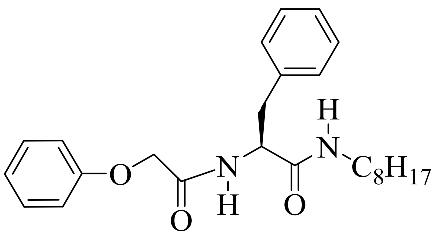


1a-Phe-C4

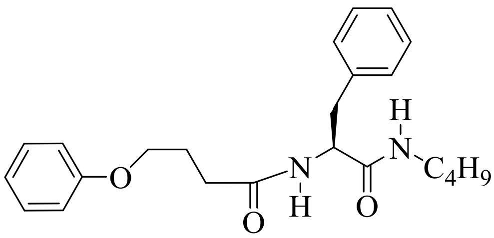
Yield: 196 mg, 89%. [1]H NMR (400 MHz, DMSO) δ 8.09 (d, J = 8.5 Hz, 1H), 7.99 (t, J = 5.3 Hz, 1H), 7.24 – 7.16 (m, 5H), 6.97 – 6.87 (m, 3H), 6.83 (d, J = 7.9 Hz, 2H), 4.66 (s, 1H), 4.45 (s, 2H), 3.13 – 3.00 (m, 2H), 1.37 – 1.30 (m, 2H), 1.25 – 1.18 (m, 2H), 0.99 (s, 2H), 0.85 (td, J = 7.2, 3.5 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{26}N_2O_3Na$): *m/z* 377.45, found: *m/z* 377.20.



1a-Phe-C6 Yield: 210 mg, 88%.[1]H NMR (400 MHz, DMSO) δ 8.23 – 8.11 (m, 1H), 8.06 (d, *J* = 2.1 Hz, 1H), 7.31 – 7.14 (m, 7H), 6.98 – 6.89 (m, 1H), 6.81 (dd, *J* = 5.8, 1.8 Hz, 2H), 4.54 (dd, *J* = 6.6, 3.9 Hz, 1H), 4.49 – 4.39 (m, 2H), 3.11 – 2.81 (m, 4H), 1.27 (d, *J* = 46.9 Hz, 8H), 0.91 – 0.79 (m, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{30}N_2O_3Na$): *m/z* 405.50, found: *m/z* 405.15.

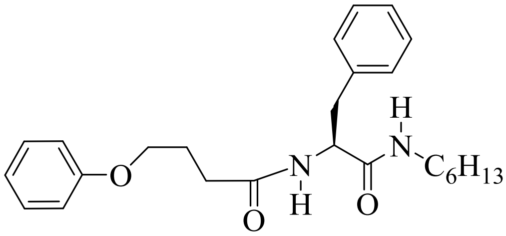


1a-Phe-C8 Yield: 229 g, 89%. ^{1}H NMR (400 MHz, DMSO) δ 8.14 (d, *J* = 8.5 Hz, 1H), 8.03 (t, *J* = 5.6 Hz, 1H), 7.27 – 7.19 (m, 8H), 6.98 – 6.91 (m, 1H), 6.82 (dd, *J* = 8.7, 0.9 Hz, 2H), 4.54 (td, *J* = 8.8, 5.2 Hz, 1H), 4.49 – 4.37 (m, 2H), 3.07 – 2.83 (m, 3H), 1.34 (dd, *J* = 13.7, 6.8 Hz, 2H), 1.24 (d, *J* = 10.3 Hz, 10H), 0.85 (t, *J* = 6.9 Hz, 4H). ^{13}C NMR (101 MHz, DMSO) δ 170.8, 167.7, 158.1, 138.1, 129.9, 129.7, 128.5, 126.8, 121.5, 114.9, 66.9, 54.0, 39.0, 38.3, 31.7, 29.4, 29.2, 29.1, 26.8, 22.6, 14.4. MS-ESI: calculated for $[M+Na]^+$ ($C_{25}H_{34}N_2O_3Na$): *m/z* 433.56, found: *m/z* 433.15.



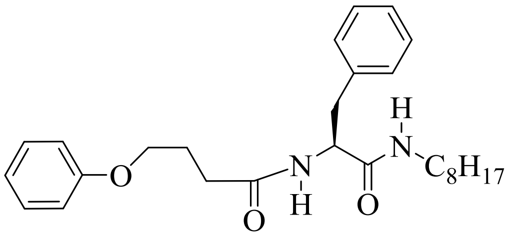
1b-Phe-C4 Yield: 209 mg, 87%.[1]H NMR (400 MHz, DMSO) δ 8.09 (d, *J* = 8.5 Hz, 1H), 8.00 (t, *J* = 5.5 Hz, 1H), 7.27 – 7.19 (m, 7H), 6.89 (dd, *J* = 21.5, 13.5 Hz, 3H), 4.66 (s, 1H), 4.45 (s, 2H), 3.08 – 2.87 (m, 4H), 1.37 – 1.30 (m, 2H), 1.22 (d, *J* = 4.8

Hz, 4H), 1.11 (s, 2H), 0.86 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{30}N_2O_3Na$): *m/z* 405.50, found: *m/z* 405.15.



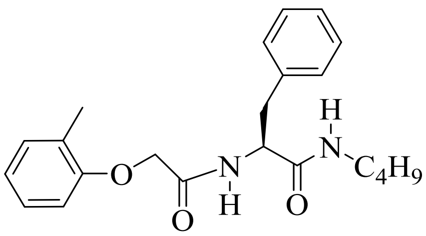
1b-Phe-C6

Yield: 223 mg, 87%.^{1}H NMR (400 MHz, DMSO) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.94 (t, *J* = 5.6 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.21 (t, *J* = 4.3 Hz, 3H), 7.17 – 7.12 (m, 1H), 6.94 – 6.84 (m, 4H), 4.47 (td, *J* = 9.3, 5.3 Hz, 1H), 3.80 (t, *J* = 6.6 Hz, 2H), 3.03 – 2.71 (m, 4H), 2.25 – 2.16 (m, 2H), 1.87 – 1.75 (m, 2H), 1.36 – 1.16 (m, 8H), 0.84 (t, *J* = 7.0 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{25}H_{34}N_2O_3Na$): *m/z* 433.56, found: *m/z* 433.15.



1b-Phe-C8

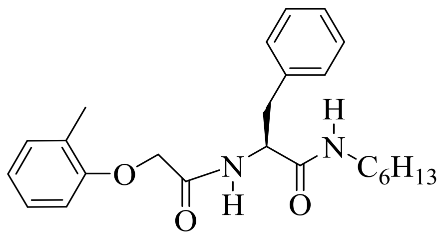
Yield: 241 mg, 88%.^{1}H NMR (400 MHz, DMSO) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.93 (t, *J* = 5.6 Hz, 1H), 7.33 – 7.10 (m, 7H), 6.94 – 6.83 (m, 3H), 4.47 (td, *J* = 9.3, 5.3 Hz, 1H), 3.80 (t, *J* = 6.6 Hz, 2H), 3.06 – 2.72 (m, 4H), 2.27 – 2.13 (m, 2H), 1.81 (p, *J* = 7.0 Hz, 2H), 1.42 – 1.08 (m, 12H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{27}H_{38}N_2O_3Na$): *m/z* 461.61, found: *m/z* 461.20.



2a-Phe-C4

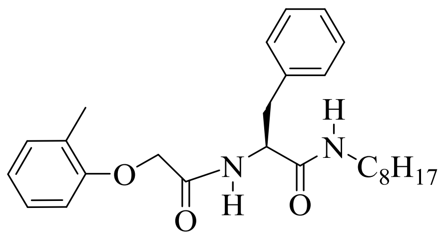
Yeild: 202 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.05 (t, *J* = 5.6 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.16 (m, 5H), 7.14 (dd, *J* = 7.3, 0.8 Hz, 1H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 6.85 (td, *J* = 7.4, 0.8 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 4.55 (td,

J = 8.5, 5.2 Hz, 1H), 4.52 – 4.42 (m, 2H), 3.00 (dtd, J = 39.3, 13.4, 5.6 Hz, 4H), 2.16 (s, 3H), 1.30 (dddd, J = 22.5, 15.0, 8.3, 4.2 Hz, 4H), 0.85 (t, J = 7.3 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{28}N_2O_3Na$): *m/z* 391.48, found: *m/z* 391.15.



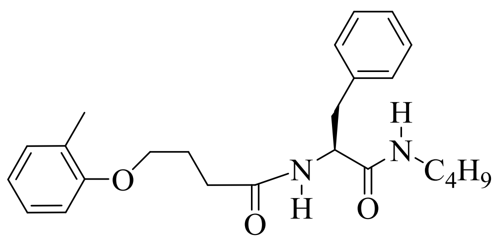
2a-Phe-C6

Yield: 216 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.06 (t, J = 5.6 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.27 – 7.17 (m, 5H), 7.14 (dd, J = 7.3, 0.7 Hz, 1H), 7.06 (td, J = 7.6, 1.3 Hz, 1H), 6.85 (td, J = 7.4, 0.7 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 4.55 (td, J = 8.4, 5.3 Hz, 1H), 4.51 – 4.42 (m, 2H), 3.08 – 2.84 (m, 4H), 2.15 (s, 3H), 1.39 – 1.17 (m, 8H), 0.86 (t, J = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{24}H_{32}N_2O_3Na$): *m/z* 419.53, found: *m/z* 419.20.



2a-Phe-C8

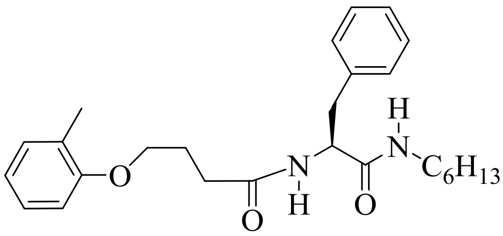
Yield: 234 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.05 (t, J = 5.6 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.28 – 7.17 (m, 5H), 7.13 (d, J = 7.3 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 6.85 (t, J = 7.1 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 4.56 (td, J = 8.4, 5.3 Hz, 1H), 4.51 – 4.41 (m, 2H), 3.12 – 2.84 (m, 4H), 2.16 (s, 3H), 1.38 – 1.16 (m, 12H), 0.85 (t, J = 6.8 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{26}H_{36}N_2O_3Na$): *m/z* 447.59, found: *m/z* 447.20.



2b-Phe-C4

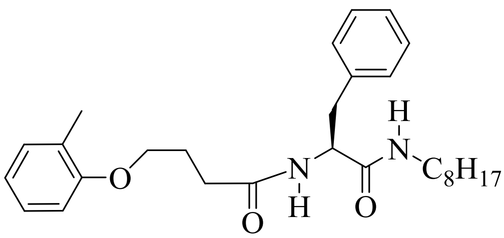
Yield: 0211 mg, 85%. ^{1}H NMR (400 MHz, DMSO) δ 8.13 (d, J = 8.6 Hz, 1H), 7.94 (t, J = 5.6 Hz, 1H), 7.20 (t, J = 6.6 Hz, 4H), 7.17 – 7.09 (m, 3H), 6.81 (dd, J = 7.8, 5.4 Hz, 2H), 4.47 (td, J = 9.2, 5.3 Hz, 1H), 3.81 (t, J = 6.5 Hz, 2H), 3.08 –

2.71 (m, 4H), 2.28 – 2.19 (m, 2H), 2.14 (s, 3H), 1.83 (p, J = 7.0 Hz, 2H), 1.37 – 1.14 (m, 4H), 0.83 (t, J = 7.3 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{24}H_{32}N_2O_3Na$): m/z 419.53, found: m/z 419.20.



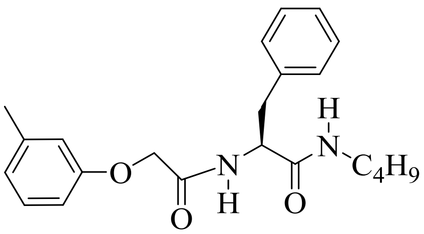
2b-Phe-C6

Yield: 233 mg, 88%. ^1H NMR (400 MHz, DMSO) δ 8.12 (d, J = 8.5 Hz, 1H), 7.92 (t, J = 5.5 Hz, 1H), 7.21 – 7.12 (m, 6H), 6.89 – 6.81 (m, 3H), 3.97 (t, J = 6.3 Hz, 2H), 3.82 (s, 1H), 3.04 – 2.73 (m, 4H), 2.42 (s, 2H), 2.15 (s, 3H), 1.97 (t, J = 6.8 Hz, 2H), 1.36 – 1.30 (m, 2H), 1.23 – 1.19 (m, 4H), 1.12 – 1.11 (m, 2H), 0.85 (dd, J = 8.7, 5.1 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{26}H_{36}N_2O_3Na$): m/z 447.59, found: m/z 447.20.



2b-Phe-C8

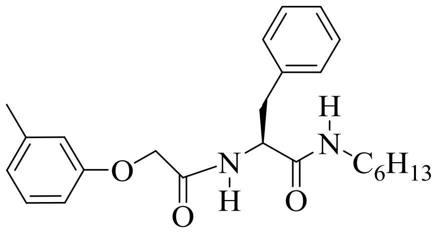
Yield: 248 mg, 88%. ^1H NMR (400 MHz, DMSO) δ 8.14 (d, J = 8.6 Hz, 1H), 7.94 (t, J = 5.6 Hz, 1H), 7.19 (dd, J = 9.4, 3.9 Hz, 4H), 7.15 – 7.09 (m, 3H), 6.84 – 6.78 (m, 2H), 4.47 (td, J = 9.2, 5.3 Hz, 1H), 3.81 (t, J = 6.5 Hz, 2H), 3.06 – 2.73 (m, 4H), 2.28 – 2.19 (m, 2H), 2.13 (s, 3H), 1.83 (p, J = 7.0 Hz, 2H), 1.34 – 1.14 (m, 12H), 0.85 (t, J = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{28}H_{40}N_2O_3Na$): m/z 475.64, found: m/z 475.25.



3a-Phe-C4

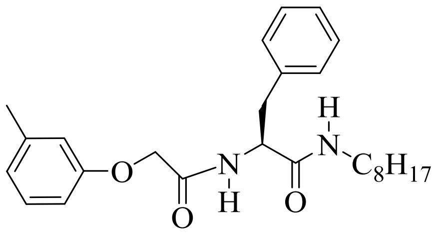
Yield: 199 mg, 86%. ^1H NMR (400 MHz, DMSO) δ 8.06 (d, J = 8.4 Hz, 1H), 8.00 (t, J = 5.5 Hz, 1H), 7.18 (dd, J = 12.5, 7.5 Hz, 5H), 6.74 (d, J = 9.4 Hz, 4H), 4.61 (s, 2H), 4.43 (s, 1H), 2.98 (ddd, J = 38.5, 23.7, 8.4 Hz, 4H), 2.26 (s, 3H), 1.32 – 1.22

(m, 2H), 1.12 (s, 2H), 0.87 – 0.83 (m, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{28}N_2O_3Na$): *m/z* 391.48, found: *m/z* 391.15.



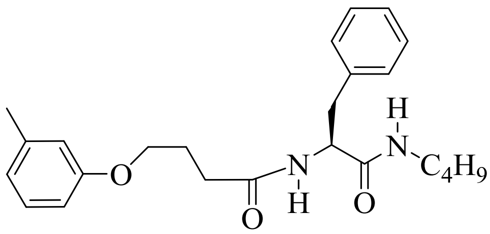
3a-Phe-C6

Yield: 218 mg, 88%.[1]H NMR (400 MHz, DMSO) δ 8.12 (d, *J* = 8.5 Hz, 1H), 8.05 (t, *J* = 5.6 Hz, 1H), 7.27 – 7.10 (m, 6H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.70 (s, 1H), 6.61 (dd, *J* = 8.2, 2.5 Hz, 1H), 4.53 (td, *J* = 8.7, 5.3 Hz, 1H), 4.40 (d, *J* = 14.7 Hz, 2H), 3.08 – 2.82 (m, 4H), 2.25 (s, 3H), 1.36 – 1.17 (m, 8H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{24}H_{32}N_2O_3Na$): *m/z* 419.53, found: *m/z* 419.20.



3a-Phe-C8

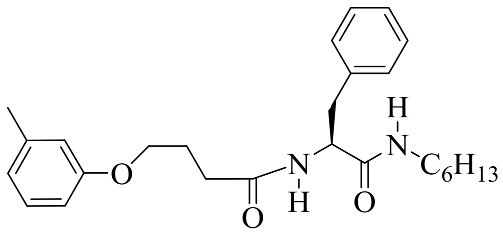
Yield: 233 mg, 88%. [1]H NMR (400 MHz, DMSO) δ 8.10 (d, *J* = 8.5 Hz, 1H), 8.02 (t, *J* = 5.6 Hz, 1H), 7.24 – 7.11 (m, 7H), 6.78 – 6.60 (m, 4H), 4.53 (td, *J* = 8.7, 5.3 Hz, 1H), 4.40 (d, *J* = 14.8 Hz, 2H), 3.06 – 2.81 (m, 3H), 2.25 (s, 3H), 1.33 (dt, *J* = 14.0, 7.1 Hz, 2H), 1.24 (d, *J* = 11.0 Hz, 10H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{26}H_{36}N_2O_3Na$): *m/z* 447.59, found: *m/z* 447.20.



3b-Phe-C4

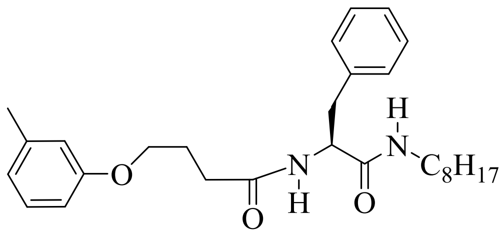
Yield: 216 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 8.10 (d, *J* = 8.5 Hz, 1H), 7.91 (t, *J* = 5.5 Hz, 1H), 7.22 (s, 2H), 7.14 (d, *J* = 1.6 Hz, 2H), 6.74 – 6.69 (m, 5H), 3.94 (d, *J* = 6.4 Hz, 2H), 3.79 (d, *J* = 6.5 Hz, 1H), 3.06 – 2.76 (m, 4H), 2.37 (d, *J* = 7.3 Hz, 2H), 2.23 (d, *J* = 7.4 Hz, 3H), 1.92 – 1.83 (m, 2H), 1.31 – 1.21 (m, 2H), 1.12 – 1.10

(m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{24}H_{32}N_2O_3Na$): *m/z* 419.53, found: *m/z* 419.20.



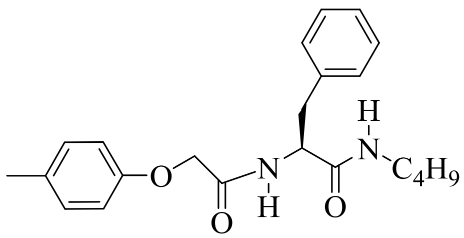
3b-Phe-C6

Yield: 235 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.90 (t, *J* = 5.5 Hz, 1H), 7.22 – 7.12 (m, 6H), 6.72 – 6.66 (m, 3H), 3.94 (d, *J* = 6.4 Hz, 1H), 3.79 (t, *J* = 6.5 Hz, 2H), 3.04 – 2.73 (m, 4H), 2.26 (s, 3H), 1.86 (dd, *J* = 37.9, 6.9 Hz, 2H), 1.31 (s, 2H), 1.21 (s, 2H), 1.11 (s, 6H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{26}H_{36}N_2O_3Na$): *m/z* 447.59, found: *m/z* 447.20.



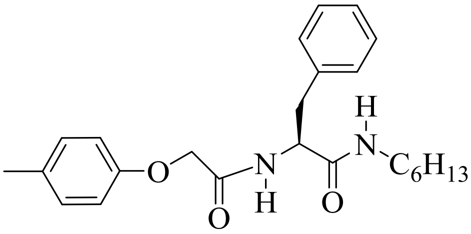
3b-Phe-C8

Yield: 250 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.93 (t, *J* = 5.6 Hz, 1H), 7.20 (dd, *J* = 9.0, 4.8 Hz, 4H), 7.17 – 7.11 (m, 2H), 6.69 (ddd, *J* = 17.7, 8.2, 3.2 Hz, 3H), 4.47 (td, *J* = 9.2, 5.3 Hz, 1H), 3.78 (t, *J* = 6.6 Hz, 2H), 3.05 – 2.72 (m, 4H), 2.26 (s, 3H), 2.18 (dd, *J* = 14.3, 7.3 Hz, 2H), 1.80 (p, *J* = 7.0 Hz, 2H), 1.36 – 1.15 (m, 12H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{28}H_{40}N_2O_3Na$): *m/z* 475.64, found: *m/z* 475.25.



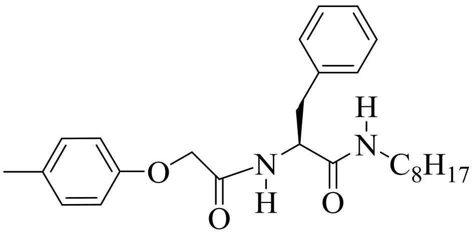
4a-Phe-C4

Yield: 196 mg, 85%. ^{1}H NMR (400 MHz, DMSO) δ 8.03 (d, *J* = 8.5 Hz, 1H), 7.97 (t, *J* = 5.5 Hz, 1H), 7.22 (t, *J* = 6.7 Hz, 5H), 7.04 (s, 2H), 6.74 (s, 2H), 4.60 – 4.59 (m, 2H), 4.40 (s, 1H), 3.02 – 2.96 (m, 2H), 2.22 – 2.19 (m, 3H), 1.31 – 1.23 (m, 2H), 1.11 (s, 2H), 0.99 – 0.98 (m, 2H), 0.88 – 0.85 (m, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{28}N_2O_3Na$): *m/z* 391.48, found: *m/z* 391.15.



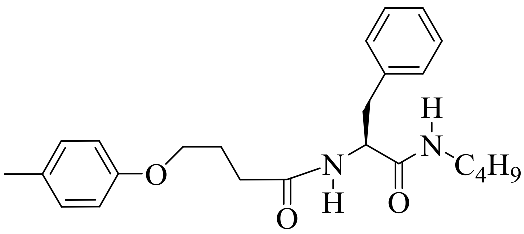
4a-Phe-C6

Yield: 213 mg, 86%.^{1}H NMR (400 MHz, DMSO) δ 8.08 (d, *J* = 8.5 Hz, 1H), 8.02 (t, *J* = 5.6 Hz, 1H), 7.27 – 7.16 (m, 5H), 7.07 – 7.02 (m, 2H), 6.76 – 6.70 (m, 2H), 4.58 – 4.50 (m, 1H), 4.38 (d, *J* = 15.2 Hz, 2H), 2.98 (dqd, *J* = 22.6, 13.3, 7.9 Hz, 4H), 2.22 (s, 3H), 1.36 – 1.16 (m, 8H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{24}H_{32}N_2O_3Na$): *m/z* 419.53, found: *m/z* 419.20.



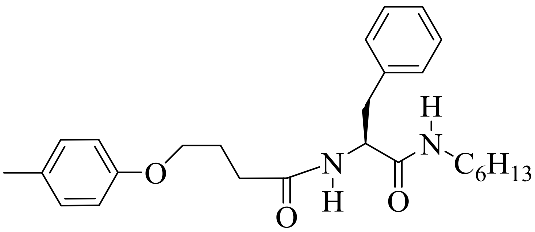
4a-Phe-C8

Yield: 232 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.08 (d, *J* = 8.5 Hz, 1H), 8.01 (t, *J* = 5.6 Hz, 1H), 7.22 (tdd, *J* = 6.9, 5.1, 3.9 Hz, 5H), 7.04 (dd, *J* = 8.6, 0.5 Hz, 2H), 6.75 – 6.69 (m, 2H), 4.53 (td, *J* = 8.8, 5.3 Hz, 1H), 4.39 (s, 2H), 2.98 (dddd, *J* = 41.2, 36.3, 13.4, 5.4 Hz, 4H), 2.22 (s, 3H), 1.36 – 1.17 (m, 12H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{26}H_{36}N_2O_3Na$): *m/z* 447.59, found: *m/z* 447.20.



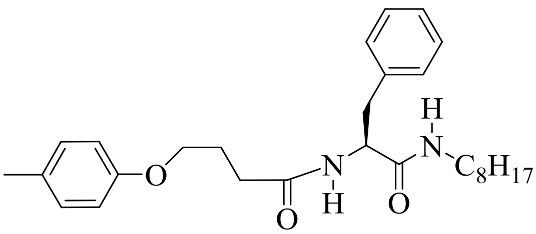
4b-Phe-C4

Yield: 216 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.93 (t, *J* = 5.6 Hz, 1H), 7.25 – 7.13 (m, 5H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.77 – 6.73 (m, 2H), 4.47 (td, *J* = 9.3, 5.3 Hz, 1H), 3.76 (t, *J* = 6.6 Hz, 2H), 3.05 – 2.71 (m, 4H), 2.26 – 2.14 (m, 5H), 1.79 (p, *J* = 7.0 Hz, 2H), 1.36 – 1.26 (m, 2H), 1.24 – 1.15 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{24}H_{32}N_2O_3Na$): *m/z* 419.53, found: *m/z* 419.20.



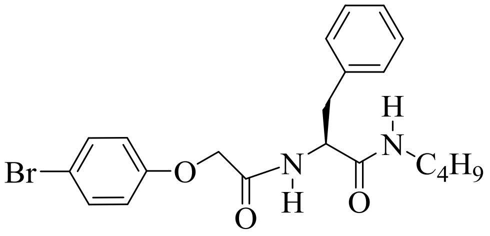
4b-Phe-C6

Yield: 234 mg, 88%. ¹H NMR (400 MHz, DMSO) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.90 (t, *J* = 4.4 Hz, 1H), 7.21 (s, 2H), 7.07 (d, *J* = 8.3 Hz, 5H), 6.76 (s, 2H), 3.92 (s, 2H), 3.77 (s, 1H), 3.01 – 2.94 (m, 2H), 2.36 (s, 2H), 2.22 – 2.21 (m, 3H), 1.91 (s, 2H), 1.34 – 1.29 (m, 2H), 1.20 (s, 4H), 1.11 – 1.10 (m, 2H), 0.99 (s, 2H), 0.85 (d, *J* = 3.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{26}H_{36}N_2O_3Na$): *m/z* 447.59, found: *m/z* 447.25.



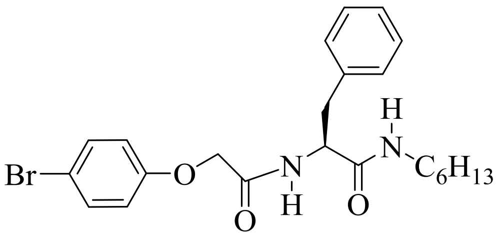
4b-Phe-C8

Yield: 248 mg, 87%. ¹H NMR (400 MHz, DMSO) δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.89 (t, *J* = 5.5 Hz, 1H), 7.22 – 7.07 (m, 6H), 6.78 (d, *J* = 11.7 Hz, 3H), 3.92 (d, *J* = 6.4 Hz, 2H), 3.77 (s, 1H), 2.97 (dd, *J* = 16.8, 5.4 Hz, 2H), 2.36 (d, *J* = 7.3 Hz, 2H), 2.22 – 2.21 (m, 3H), 2.08 – 2.08 (m, 2H), 1.91 – 1.80 (m, 2H), 1.35 – 1.29 (m, 2H), 1.22 – 1.16 (m, 6H), 1.11 (s, 2H), 0.99 (s, 2H), 0.85 (d, *J* = 6.4 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{28}H_{40}N_2O_3Na$): *m/z* 475.64, found: *m/z* 475.20.



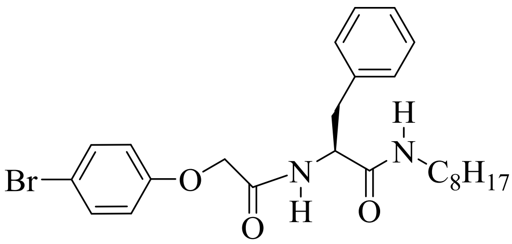
5a-Phe-C4

Yield: 240 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.20 (d, *J* = 8.5 Hz, 1H), 8.02 (t, *J* = 5.6 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.27 – 7.17 (m, 5H), 6.81 – 6.75 (m, 2H), 4.52 (td, *J* = 9.0, 5.2 Hz, 1H), 4.49 – 4.42 (m, 2H), 2.98 (dtd, *J* = 49.7, 13.4, 5.3 Hz, 4H), 1.33 (tdd, *J* = 13.8, 9.6, 4.2 Hz, 2H), 1.21 (dq, *J* = 14.1, 7.1 Hz, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{25}BrN_2O_3Na$): *m/z* 456.35, found: *m/z* 456.25.



5a-Phe-C6

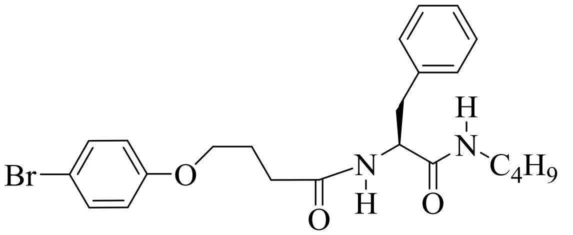
Yield: 250 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.23 (d, *J* = 8.5 Hz, 1H), 8.05 (t, *J* = 5.6 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.26 – 7.16 (m, 5H), 6.80 – 6.75 (m, 2H), 4.56 – 4.48 (m, 1H), 4.44 (d, *J* = 15.2 Hz, 2H), 3.09 – 2.78 (m, 4H), 1.36 – 1.16 (m, 8H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{29}BrN_2O_3Na$): *m/z* 484.40, found: *m/z* 484.15.



5a-Phe-C8

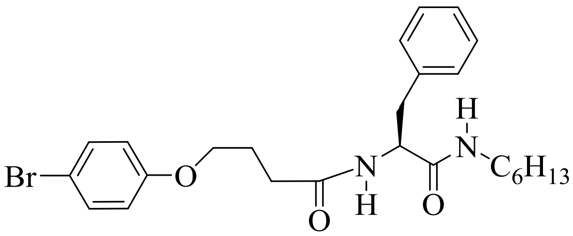
Yield: 265 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 8.20 (d, *J* = 8.5 Hz, 1H), 8.03 (t, *J* = 5.6 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.27 – 7.15 (m, 5H), 6.81 – 6.75 (m, 2H), 4.53 (td, *J* = 9.0, 5.2 Hz, 1H), 4.44 (d, *J* = 15.1 Hz, 2H), 3.12 – 2.80 (m, 4H), 1.34 (dd, *J* = 13.4, 7.0 Hz, 2H), 1.27 – 1.15 (m, 10H), 0.85 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR

(101 MHz, DMSO) δ 170.8, 167.4, 157.5, 138.1, 132.5, 129.6, 128.5, 126.7, 117.3, 112.9, 67.1, 54.1, 39.0, 38.3, 31.7, 29.4, 29.2, 26.8, 22.6, 14.5. MS-ESI: calculated for $[M+H]^+$ ($C_{25}H_{34}BrN_2O_3$): *m/z* 489.45, found: *m/z* 489.30.



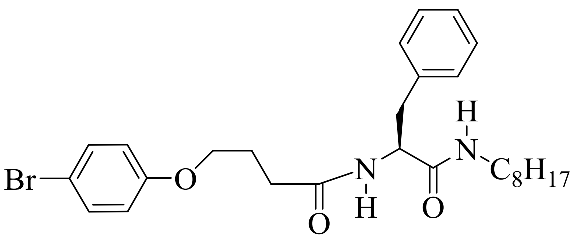
5b-Phe-C4

Yield: 244 mg, 85%. ^{1}H NMR (400 MHz, DMSO) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.94 (t, *J* = 5.6 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.25 – 7.11 (m, 5H), 6.88 – 6.80 (m, 2H), 4.47 (td, *J* = 9.2, 5.3 Hz, 1H), 3.79 (t, *J* = 6.5 Hz, 2H), 3.07 – 2.70 (m, 4H), 2.26 – 2.13 (m, 2H), 1.80 (p, *J* = 6.9 Hz, 2H), 1.36 – 1.14 (m, 4H), 0.83 (t, *J* = 7.3 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{29}BrN_2O_3Na$): *m/z* 484.40, found: *m/z* 484.15.



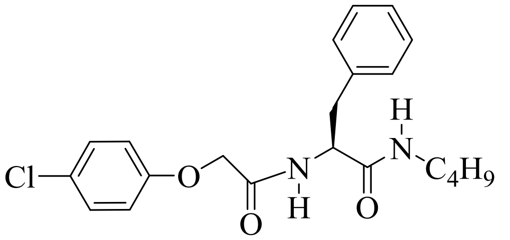
5b-Phe-C6

Yield: 267 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.15 (d, *J* = 8.6 Hz, 1H), 7.97 (t, *J* = 5.5 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.21 (t, *J* = 4.3 Hz, 4H), 6.87 – 6.79 (m, 2H), 4.47 (td, *J* = 9.3, 5.2 Hz, 1H), 3.78 (t, *J* = 6.6 Hz, 2H), 3.08 – 2.70 (m, 4H), 2.26 – 2.13 (m, 2H), 1.80 (p, *J* = 7.0 Hz, 2H), 1.35 – 1.14 (m, 8H), 0.84 (t, *J* = 7.0 Hz, 3H). MS-ESI: calculated for $[M+H]^+$ ($C_{25}H_{34}BrN_2O_3$): *m/z* 489.45, found: *m/z* 489.30.



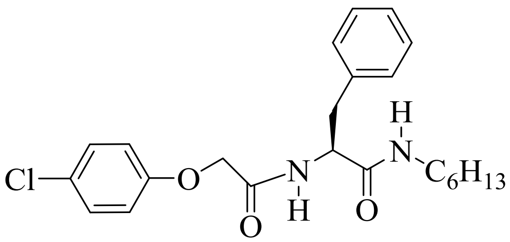
5b-Phe-C8

Yield: 277 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.94 (t, *J* = 5.6 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.23 – 7.14 (m, 5H), 6.88 – 6.80 (m, 2H), 4.47 (td, *J* = 9.2, 5.3 Hz, 1H), 3.79 (t, *J* = 6.6 Hz, 2H), 3.04 – 2.69 (m, 5H), 2.27 – 2.12 (m, 2H), 1.88 – 1.73 (m, 2H), 1.38 – 1.11 (m, 12H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{27}H_{37}BrN_2O_3Na$): *m/z* 540.45, found: *m/z* 540.15.



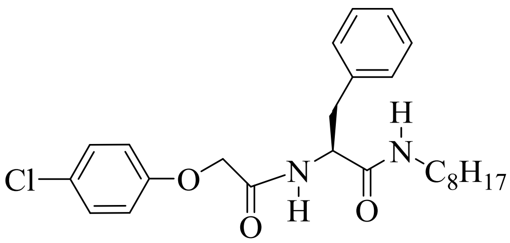
6a-Phe-C4

Yield: 208 mg, 85%. ^{1}H NMR (400 MHz, DMSO) δ 8.20 (d, *J* = 8.5 Hz, 1H), 8.02 (t, *J* = 5.6 Hz, 1H), 7.30 – 7.15 (m, 7H), 6.88 – 6.77 (m, 2H), 4.52 (td, *J* = 9.0, 5.2 Hz, 1H), 4.46 (s, 2H), 3.09 – 2.80 (m, 4H), 1.33 (tdd, *J* = 13.8, 9.6, 4.2 Hz, 2H), 1.25 – 1.15 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 170.8, 167.5, 157.0, 138.1, 129.6, 128.5, 126.7, 125.2, 116.7, 67.1, 54.1, 38.7, 38.3, 31.5, 19.5, 14.2. MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{25}ClN_2O_3Na$): *m/z* 411.89, found: *m/z* 411.15.



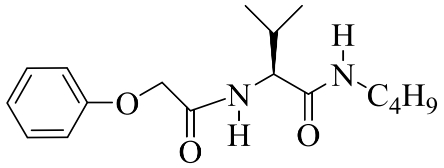
6a-Phe-C6

Yield: 223 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 8.22 (d, *J* = 8.5 Hz, 1H), 8.05 (t, *J* = 5.6 Hz, 1H), 7.30 – 7.16 (m, 7H), 6.88 – 6.79 (m, 2H), 4.57 – 4.49 (m, 1H), 4.49 – 4.41 (m, 2H), 3.09 – 2.79 (m, 4H), 1.38 – 1.14 (m, 8H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+K]^+$ ($C_{23}H_{29}ClN_2O_3K$): *m/z* 455.95, found: *m/z* 455.20.



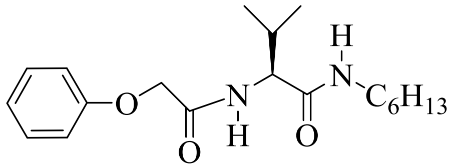
6a-Phe-C8

Yield: 244 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.20 (d, *J* = 8.5 Hz, 1H), 8.03 (t, *J* = 5.6 Hz, 1H), 7.32 – 7.14 (m, 7H), 6.87 – 6.79 (m, 2H), 4.52 (d, *J* = 5.0 Hz, 1H), 4.46 (s, 2H), 3.09 – 2.80 (m, 4H), 1.39 – 1.13 (m, 12H), 0.85 (t, *J* = 6.9 Hz, 3H). MS-ESI: calculated for $[M+K]^+$ ($C_{23}H_{29}ClN_2O_3K$): *m/z* 468.00, found: *m/z* 468.15.



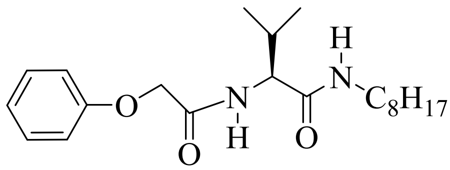
1a-Val-C4

Yield: 166 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.04 (t, *J* = 5.3 Hz, 1H), 7.84 (d, *J* = 9.3 Hz, 1H), 7.27 (d, *J* = 0.7 Hz, 2H), 6.97 – 6.93 (m, 3H), 4.66 (s, 2H), 4.56 (d, *J* = 1.8 Hz, 1H), 3.13 – 2.98 (m, 2H), 1.74 (s, 1H), 1.30 (dd, *J* = 16.3, 9.1 Hz, 2H), 1.05 (d, *J* = 7.2 Hz, 2H), 0.90 – 0.80 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{17}H_{26}N_2O_3Na$): *m/z* 329.41, found: *m/z* 329.15.



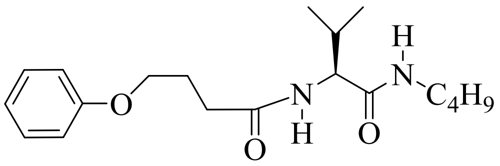
1a-Val-C6

Yield: 182 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.09 (t, *J* = 5.5 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.00 – 6.87 (m, 3H), 4.63 – 4.52 (m, 2H), 4.16 (dd, *J* = 9.0, 6.9 Hz, 1H), 3.15 – 2.93 (m, 2H), 1.94 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.42 – 1.18 (m, 8H), 0.82 (dt, *J* = 11.9, 6.6 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{30}N_2O_3Na$): *m/z* 357.46, found: *m/z* 346.15.



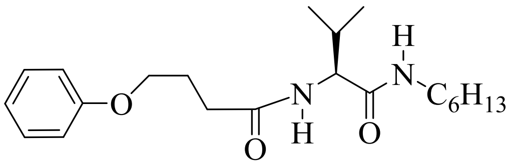
1a-Val-C8

Yield: 198 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 4.66 (s, 1H), 4.57 (d, *J* = 1.3 Hz, 2H), 1.24 (s, 6H), 0.00 (s, 4H), 0.00 (dt, *J* = 12.4, 6.6, 6.6 Hz, 9H), 0.00 (t, *J* = 5.5, 5.5 Hz, 1H), 1.41 – 1.35 (m, 2H), 0.00 (d, *J* = 9.0 Hz, 1H), 0.00 (dd, *J* = 13.5, 6.8 Hz, 1H), 0.00 (d, *J* = 6.9 Hz, 2H), 3.14 – 2.95 (m, 2H), 0.00 (dd, *J* = 7.7, 6.8 Hz, 3H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): *m/z* 385.51, found: *m/z* 385.20.



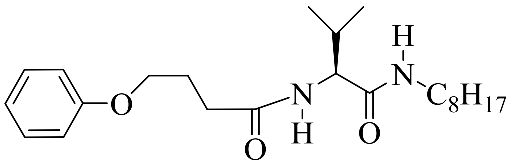
1b-Val-C4

Yield: 171 mg, 85%. ^{1}H NMR (400 MHz, DMSO) δ 8.03 (t, *J* = 5.2 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.29 (t, *J* = 7.0 Hz, 2H), 6.96 – 6.87 (m, 3H), 4.66 (s, 1H), 4.57 (d, *J* = 1.6 Hz, 2H), 3.17 – 2.95 (m, 2H), 1.95 (dq, *J* = 20.1, 6.6 Hz, 1H), 1.45 – 1.34 (m, 2H), 1.24 (s, 4H), 1.11 (s, 2H), 0.82 (dt, *J* = 12.4, 6.5 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{30}N_2O_3Na$): *m/z* 343.43, found: *m/z* 343.10.



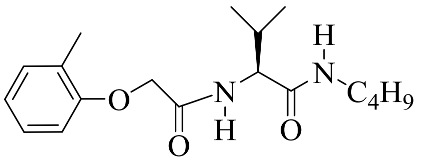
1b-Val-C6

Yield: 193 mg, 85%. ^{1}H NMR (400 MHz, DMSO) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.70 (dd, *J* = 19.2, 6.9 Hz, 2H), 7.55 (d, *J* = 15.1 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.27 (td, *J* = 9.2, 5.3 Hz, 2H), 3.03 – 2.96 (m, 2H), 1.55 (d, *J* = 9.2 Hz, 2H), 1.41 (s, 2H), 1.23 (s, 4H), 1.11 (s, 6H), 0.85 – 0.76 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}N_2O_3Na$): *m/z* 385.51, found: *m/z* 385.20.

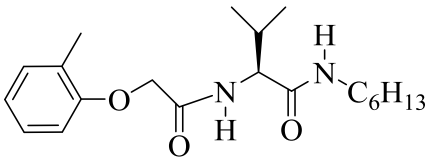


1b-Val-C8

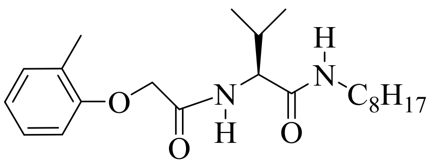
Yield: 210 mg, 86%.^{1}H NMR (400 MHz, DMSO) δ 8.03 (t, *J* = 5.4 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.30 – 7.26 (m, 2H), 6.95 – 6.89 (m, 3H), 4.66 (s, 1H), 4.57 (d, *J* = 1.8 Hz, 2H), 4.02 (t, *J* = 7.1 Hz, 2H), 3.15 – 2.92 (m, 2H), 2.09 (s, 1H), 1.99 – 1.91 (m, 2H), 1.38 (dq, *J* = 13.8, 6.9 Hz, 2H), 1.27 (dd, *J* = 18.6, 10.9 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 4H), 1.11 (s, 4H), 0.88 – 0.74 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{23}H_{38}N_2O_3Na$): *m/z* 413.57, found: *m/z* 413.20.



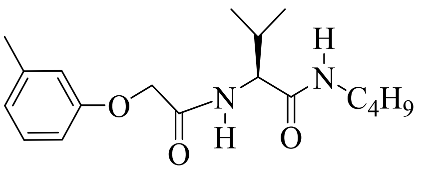
2a-Val-C4 Yield: 176 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.04 (t, *J* = 5.4 Hz, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.14 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.69 (ddd, *J* = 10.5, 8.8, 4.1 Hz, 3H), 4.63 (s, 1H), 4.59 – 4.50 (m, 2H), 3.18 – 2.91 (m, 2H), 2.26 (s, 3H), 2.02 – 1.90 (m, 1H), 1.47 – 1.31 (m, 2H), 1.29 – 1.16 (m, 2H), 0.91 – 0.73 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{18}H_{28}N_2O_3Na$): *m/z* 343.43, found: *m/z* 343.10.



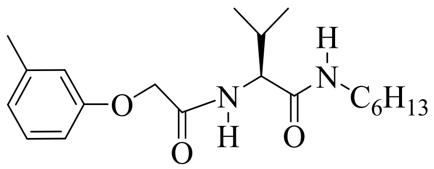
2a-Val-C6 Yield: 186 mg, 85%. ^{1}H NMR (400 MHz, DMSO) δ 8.09 (t, *J* = 5.6 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.19 – 7.09 (m, 2H), 6.86 (t, *J* = 7.6 Hz, 2H), 4.63 – 4.52 (m, 2H), 4.21 (dd, *J* = 9.0, 6.3 Hz, 1H), 3.17 – 2.93 (m, 2H), 2.22 (s, 3H), 1.96 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.43 – 1.18 (m, 8H), 0.94 – 0.72 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{32}N_2O_3Na$): *m/z* 371.49, found: *m/z* 371.15.



2a-Val-C8 Yield: 208 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.08 (t, *J* = 5.5 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.18 – 7.09 (m, 2H), 6.86 (t, *J* = 7.7 Hz, 2H), 4.62 – 4.53 (m, 2H), 4.21 (dd, *J* = 8.9, 6.3 Hz, 1H), 3.15 – 2.94 (m, 2H), 2.22 (s, 3H), 1.96 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.46 – 1.17 (m, 12H), 0.93 – 0.71 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{36}N_2O_3Na$): *m/z* 399.54, found: *m/z* 399.20.

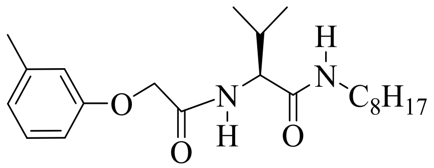


3a-Val-C4 Yield: 175 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.04 (t, *J* = 5.4 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.15 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.71 (ddd, *J* = 10.5, 8.8, 4.1 Hz, 3H), 4.63 (s, 1H), 4.55 (d, *J* = 3.3 Hz, 2H), 3.14 – 2.94 (m, 2H), 2.26 (s, 3H), 2.01 – 1.87 (m, 1H), 1.41 – 1.23 (m, 4H), 0.88 – 0.78 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{18}H_{28}N_2O_3Na$): *m/z* 343.43, found: *m/z* 343.15.



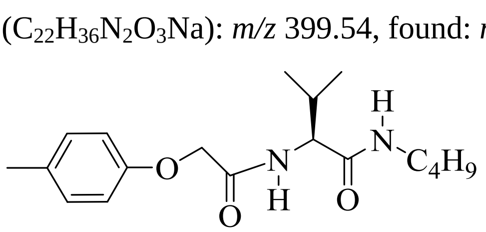
3a-Val-C6

Yield: 192 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.03 (t, *J* = 5.4 Hz, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.16 (d, *J* = 1.3 Hz, 1H), 6.76 – 6.70 (m, 3H), 4.63 (s, 2H), 4.55 (d, *J* = 2.7 Hz, 1H), 3.13 – 2.97 (m, 2H), 2.27 – 2.26 (m, 3H), 1.46 (s, 1H), 1.41 – 1.35 (m, 2H), 1.24 (s, 4H), 1.11 (s, 2H), 0.86 – 0.79 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{32}N_2O_3Na$): *m/z* 371.49, found: *m/z* 371.15.



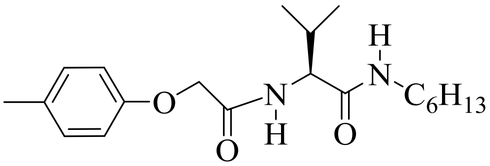
3a-Val-C8

Yield: 205 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.06 (t, *J* = 5.6 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.81 – 6.69 (m, 3H), 4.60 – 4.48 (m, 2H), 4.17 (dd, *J* = 9.0, 6.8 Hz, 1H), 3.16 – 2.92 (m, 2H), 2.26 (s, 3H), 1.94 (q, *J* = 6.8 Hz, 1H), 1.43 – 1.31 (m, 2H), 1.31 – 1.14 (m, 10H), 0.82 (dt, *J* = 12.3, 6.7 Hz, 9H). ^{13}C NMR (101 MHz, DMSO) δ 170.7, 167.9, 158.1, 139.4, 129.7, 129.7, 122.3, 115.6, 112.1, 66.9, 57.7, 38.8, 31.7, 31.3, 29.4, 29.1, 26.8, 22.6, 21.5, 19.6, 18.5, 14.4. MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{36}N_2O_3Na$): *m/z* 399.54, found: *m/z* 399.20.



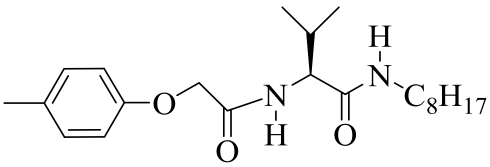
4a-Val-C4

Yield: 173 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 8.06 (t, *J* = 5.6 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.86 – 6.79 (m, 2H), 4.57 – 4.47 (m, 2H), 4.16 (dd, *J* = 9.0, 6.9 Hz, 1H), 3.17 – 2.93 (m, 2H), 2.22 (s, 3H), 1.94 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.43 – 1.31 (m, 2H), 1.26 (dq, *J* = 14.0, 7.0 Hz, 2H), 0.88 – 0.75 (m, 9H). ^{13}C NMR (101 MHz, DMSO) δ 170.7, 167.9, 156.0, 130.3,130.3, 114.8, 67.1, 57.7, 38.5, 31.5, 31.3, 20.5, 20.0, 19.6, 18.5, 14.1. MS-ESI: calculated for $[M+Na]^+$ ($C_{18}H_{28}N_2O_3Na$): *m/z* 343.43, found: *m/z* 343.15.



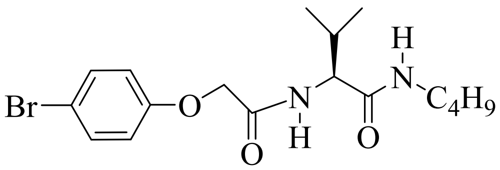
4a-Val-C6

Yield: 191 mg, 88%. ^{1}H NMR (400 MHz, DMSO) δ 8.03 (t, *J* = 5.4 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.09 (d, *J* = 2.3 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.61 (s, 2H), 4.52 (s, 1H), 3.16 – 2.94 (m, 2H), 2.23 (s, 3H), 2.09 (s, 1H), 1.42 – 1.33 (m, 2H), 1.30 – 1.20 (m, 6H), 0.83 (dt, *J* = 12.3, 6.6 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{32}N_2O_3Na$): *m/z* 371.49, found: *m/z* 371.15.



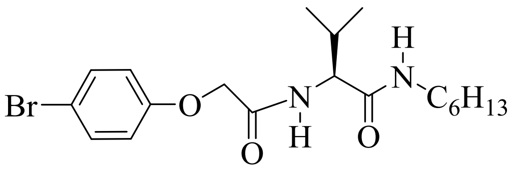
4a-Val-C8

Yield: 202 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 8.05 (t, *J* = 5.5 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.87 – 6.79 (m, 2H), 4.57 – 4.46 (m, 2H), 4.16 (dd, *J* = 9.0, 6.9 Hz, 1H), 3.16 – 2.96 (m, 2H), 2.22 (s, 3H), 1.94 (td, *J* = 13.5, 6.8 Hz, 1H), 1.48 – 1.15 (m, 12H), 0.82 (dt, *J* = 11.9, 6.7 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{22}H_{36}N_2O_3Na$): *m/z* 399.54, found: *m/z* 399.20.



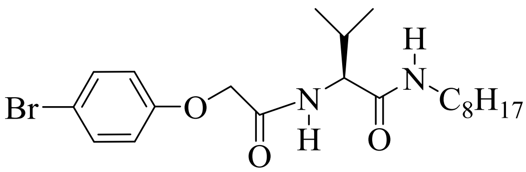
5a-Val-C4

Yield: 207 mg, 86 %. ^{1}H NMR (400 MHz, DMSO) δ 8.03 (t, *J* = 5.4 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.31 (d, *J* = 3.5 Hz, 2H), 6.94 – 6.89 (m, 2H), 4.68 (s, 2H), 4.59 (d, *J* = 2.1 Hz, 1H), 3.12 – 2.97 (m, 2H), 2.05 – 1.96 (m, 1H), 1.36 – 1.27 (m, 2H), 1.11 (s, 2H), 0.86 – 0.73 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{17}H_{25}BrN_2O_3Na$): *m/z* 408.30, found: *m/z* 408.05.



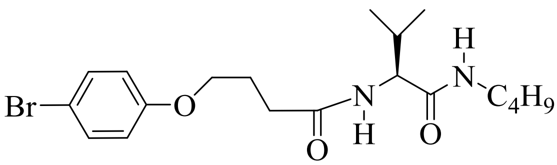
5a-Val-C6

Yield: 223 mg, 86%. [1]H NMR (400 MHz, DMSO) δ 8.07 (t, *J* = 5.6 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.47 – 7.41 (m, 2H), 6.93 – 6.87 (m, 2H), 4.63 – 4.53 (m, 2H), 4.14 (dd, *J* = 8.9, 7.0 Hz, 1H), 3.14 – 2.92 (m, 2H), 1.93 (dq, *J* = 13.7, 6.8 Hz, 1H), 1.40 – 1.19 (m, 8H), 0.82 (dt, *J* = 9.5, 6.7 Hz, 9H). [13]C NMR (101 MHz, DMSO) δ 171.9, 171.3, 158.3, 132.5, 117.2, 112.2, 67.7, 58.3, 31.8, 31.4, 30.8, 29.4, 26.4, 25.3, 22.5, 19.6, 18.8, 14.3. MS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{29}BrN_2O_3Na$): *m/z* 437.36, found: *m/z* 437.10.



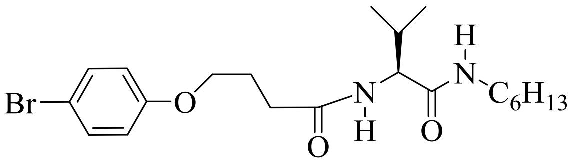
5a-Val-C8

Yield: 240 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 8.05 (t, *J* = 5.5 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.47 – 7.41 (m, 2H), 6.94 – 6.87 (m, 2H), 4.63 – 4.53 (m, 2H), 4.15 (dd, *J* = 8.9, 7.0 Hz, 1H), 3.15 – 2.92 (m, 2H), 1.94 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.42 – 1.32 (m, 2H), 1.29 – 1.18 (m, 10H), 0.82 (dt, *J* = 9.6, 6.7 Hz, 9H). [13]C NMR (101 MHz, DMSO) δ 170.7, 167.5, 157.5, 132.5, 117.3, 112.9, 67.1, 57.9, 38.8, 31.7, 31.2, 29.4, 29.1, 26.8, 22.6, 19.6, 18.6, 14.4. MS-ESI: calculated for $[M+H]^+$ ($C_{21}H_{34}BrN_2O_3$): *m/z* 442.41, found: *m/z* 442.10.



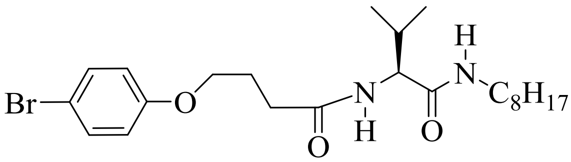
5b-Val-C4

Yield: 252 mg, 87%. [1]H NMR (400 MHz, DMSO) δ 8.00 – 7.86 (m, 2H), 7.45 – 7.40 (m, 2H), 6.93 – 6.85 (m, 2H), 4.08 (dd, *J* = 8.9, 7.4 Hz, 1H), 3.99 – 3.89 (m, 2H), 3.14 – 2.92 (m, 2H), 2.31 (td, *J* = 7.3, 3.7 Hz, 2H), 1.96 – 1.86 (m, 3H), 1.41 – 1.21 (m, 4H), 0.87 – 0.78 (m, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{29}BrN_2O_3Na$): *m/z* 437.36, found: *m/z* 437.10.



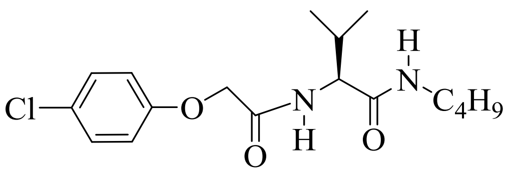
5b-Val-C6

Yield: 255 mg, 83%. ^{1}H NMR (400 MHz, DMSO) δ 7.98 – 7.90 (m, 2H), 7.44 – 7.41 (m, 2H), 6.90 – 6.87 (m, 2H), 4.14 – 4.05 (m, 1H), 3.95 (dd, *J* = 12.5, 6.1 Hz, 2H), 3.11 – 2.93 (m, 2H), 2.32 – 2.29 (m, 1H), 1.91 (dq, *J* = 14.0, 6.9 Hz, 4H), 1.38 – 1.19 (m, 8H), 0.82 (dt, *J* = 6.8, 4.3 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{33}BrN_2O_3Na$): *m/z* 464.41, found: *m/z* 464.10.



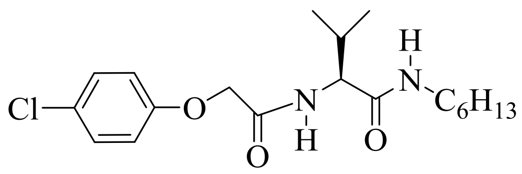
5b-Val-C8

Yield: 272 mg, 84%. ^{1}H NMR (400 MHz, DMSO) δ 7.91 (dd, *J* = 13.6, 7.4 Hz, 2H), 7.43 – 7.41 (m, 2H), 6.88 (dd, *J* = 6.3, 2.8 Hz, 2H), 4.09 (dd, *J* = 10.3, 2.9 Hz, 1H), 3.98 – 3.92 (m, 2H), 3.09 – 2.92 (m, 2H), 2.36 – 2.28 (m, 2H), 1.97 – 1.84 (m, 4H), 1.37 – 1.33 (m, 2H), 1.32 – 1.15 (m, 8H), 0.93 – 0.71 (m, 9H). MS-ESI: calculated for $[M+H]^+$ ($C_{23}H_{38}BrN_2O_3$): *m/z* 470.46, found: *m/z* 470.10.



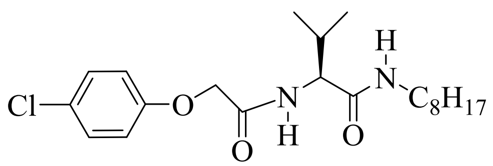
6a-Val-C4

Yield: 185 mg, 87%. ^{1}H NMR (400 MHz, DMSO) δ 8.05 (t, *J* = 5.5 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.38 – 7.26 (m, 2H), 7.03 – 6.86 (m, 2H), 4.65 – 4.54 (m, 2H), 4.15 (dd, *J* = 8.9, 7.0 Hz, 1H), 3.16 – 2.92 (m, 2H), 2.00 – 1.88 (m, 1H), 1.42 – 1.19 (m, 4H), 0.97 – 0.67 (m, 9H). ^{13}C NMR (101 MHz, DMSO) δ 170.7, 167.5, 157.1, 129.7, 125.2, 116.8, 67.2, 57.8, 38.5, 31.5, 31.2, 20.0, 19.6, 18.6, 14.1. MS-ESI: calculated for $[M+Na]^+$ ($C_{17}H_{25}BrN_2O_3Na$): *m/z* 362.85, found: *m/z* 362.10.



6a-Val-C6

Yield: 200 mg, 87%.[1]H NMR (400 MHz, DMSO) δ 8.08 (t, *J* = 5.6 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.35 – 7.31 (m, 2H), 6.98 – 6.93 (m, 2H), 4.65 – 4.53 (m, 2H), 4.15 (dd, *J* = 9.0, 7.0 Hz, 1H), 3.15 – 2.93 (m, 2H), 1.94 (dq, *J* = 13.7, 6.8 Hz, 1H), 1.39 – 1.20 (m, 8H), 0.82 (dt, *J* = 9.8, 6.6 Hz, 9H). MS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{29}BrN_2O_3Na$): *m/z* 391.90, found: *m/z* 391.10.



6a-Val-C8

Yield: 215 mg, 86%. ^{1}H NMR (400 MHz, DMSO) δ 8.05 (t, *J* = 5.6 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.35 – 7.30 (m, 2H), 6.99 – 6.93 (m, 2H), 4.64 – 4.54 (m, 2H), 4.15 (dd, *J* = 8.9, 7.0 Hz, 1H), 3.14 – 2.93 (m, 2H), 1.94 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.45 – 1.33 (m, 2H), 1.30 – 1.16 (m, 10H), 0.82 (dt, *J* = 9.9, 6.7 Hz, 9H). ^{13}C NMR (101 MHz, DMSO) δ 170.7, 167.5, 157.1, 129.7, 125.2, 116.8, 67.2, 57.9, 38.8, 31.7, 31.2, 29.4, 29.1, 26.8, 22.6, 19.6, 18.6, 14.4. MS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{33}BrN_2O_3Na$): *m/z* 397.96, found: *m/z* 397.20.

(B)MGC Determinations of PSOGs

A. Stable to Inversion Method for MGC Determinations

The minimum gelation concentration (MGC in % w/v, i.e., mg/100 μL of oil) in oil was determined by the "stable to inversion" method. In a typical experiment, we added 10.0 mg of gelator (e.g. **Ac-Ile-C8**) into 500 μL of oil (e.g. diesel) in a sealed sample vial, which was heated on the hotplate until all gelator molecules were dissolved. The solution was then cooled to room temperature under ambient conditions. The sample was regarded as a gel if no flow was observed within 30 sec after inverting the sample vial. If gel formed, a small increment of 30-50 μL of oil was added into the sample vial with the heating-cooling cycle repeated until flow was observed when the sample vial was inverted. For **Ac-Ile-C8** in diesel, 10 mg of **Ac-Ile-C8** can gel 1470 μL of diesel, giving rise to a MGC value of 0.68% w/v (10 mg / 1470 μL).

B. Determination of BMGC (biphasic minimum gelling concentration) using a Biphasic System

Phase-selective gelation of oil in the presence of seawater was carried out using gelator in a biphasic gelation system, which comprises 0.5 mL of oil on top and 2 mL of seawater at the bottom. Incremental amounts of geltaor-containing solution were added into oil with gentle shaking of the system to simulate the choppy wave motion. The BMGC values correspond to the amounts at which point complete phase-selective gelation of oil could be reached at room temperature within minutes under shaking. The gelator-containing solutions were prepared in ethyl acetate/ethanol (v:v, 3:2) with a gelator concentration of 150 mg/mL.

C. Determination of Solubility of gelators in ethanol:ethyl acetate (2:3, v:v)

The solubility was determined using a trial and error-correcting process. Firstly, a fixed amount of 100 mg of gelator was heated in 500 μL ethanol:ethyl acetate (2:3, v:v) in a sealed 2 mL vial for 1 min, followed by cooling to keeping at room temperature for 5 min. Depending on whether solution is clear or not, gelators are divided into two groups. For gelators having a solubility of ≥ 200 mg/mL, gelators were added at 10 mg per portion until it can't dissolve; then solvents were added at 5 μL per portion until solution just becomes clear. For gelators having a solubility of < 200 mg/mL, solvents were added at 50 μL per portion until all gelator fully dissolve; then gelator was added at 2 mg per portion until it just gets dissolved in solution. The total amount of solvents and gelators used were employed to calculate the solubility with values rounded off to the nearest 5s or 10s.

Table S1. Gelation abilities (MGC and BMGC values in % w/v, mg/100 μL) of gelators in oils of varying types.

Gelators	Solubility	Diesel		Mineral oil		Silicone oil	
		MGC	BMGC	MGC	BMGC	MGC	BMGC
1a-Ile-C4	360 mg	0.48	0.92	0.68	0.68	2.69	2.69
1a-Ile-C6	350 mg	1.84	2.88	1.34	1.90	P	2.21
1a-Ile-C8	350 mg	0.56	1.33	0.62	0.61	0.48	0.53
1b-Ile-C4	190 mg	0.87	0.73	0.66	0.70	0.61	0.59
1b-Ile-C6	300 mg	4.84	S	1.66	S	P	S
1b-Ile-C8	280 mg	0.45	1.36	0.54	1.77	1.13	1.83
2a-Ile-C4	210 mg	2.63	3.84	3.63	3.88	0.68	0.41
2a-Ile-C6	345 mg	1.26	1.64	2.43	2.21	1.17	1.66
2a-Ile-C8	210 mg	1.23	1.26	1.52	0.83	1.31	0.64
2b-Ile-C4	260 mg	1.95	2.85	1.88	1.83	1.61	0.93
2b-Ile-C6	200 mg	S	S	S	2.67	P	1.60
2b-Ile-C8	340 mg	1.53	1.93	0.64	1.41	0.53	0.88
3a-Ile-C4	280 mg	2.34	S	2.74	S	1.75	2.36
3a-Ile-C6	360 mg	1.63	0.80	2.65	0.61	P	0.63
3a-Ile-C8	150 mg	0.39	0.53	0.81	0.42	1.22	0.89
3b-Ile-C4	220 mg	2.23	2.21	2.06	2.03	1.85	2.21
3b-Ile-C6	150 mg	3.43	0.94	1.62	0.66	P	0.57
3b-Ile-C8	340 mg	2.21	S	1.63	2.39	1.58	1.90
4a-Ile-C4	340 mg	0.78	1.66	0.67	1.89	0.59	0.63
4a-Ile-C6	265 mg	3.43	2.65	1.46	1.40	1.61	1.33
4a-Ile-C8	260 mg	2.41	S	1.80	2.63	2.11	2.77
4b-Ile-C4	180 mg	1.78	3.32	1.86	4.29	1.69	0.83
4b-Ile-C6	215 mg	4.33	S	3.31	S	3.60	S
4b-Ile-C8	335 mg	1.47	1.77	0.89	1.31	0.64	0.88
5a-Ile-C4	360 mg	0.85	0.88	0.73	1.15	0.48	0.72
5a-Ile-C6	350 mg	1.78	2.88	1.83	2.60	P	2.63
5a-Ile-C8	300 mg	0.82	1.65	0.54	0.63	0.52	1.24
5b-Ile-C4	365 mg	2.23	S	2.85	S	P	S
5b-Ile-C6	360 mg	0.62	0.55	0.48	0.48	0.73	0.73
5b-Ile-C8	300 mg	0.55	1.73	0.44	1.69	0.39	1.44
6a-Ile-C4	370 mg	2.74	S	2.81	S	0.88	S
6a-Ile-C6	360 mg	1.19	0.91	0.85	0.63	0.67	1.13
6a-Ile-C8	350 mg	0.43	1.13	0.41	0.78	0.51	0.63
6b-Ile-C4	365 mg	1.33	1.78	1.38	1.64	1.74	1.46
6b-Ile-C6	340 mg	S	2.58	S	2.26	S	2.18
6b-Ile-C8	300 mg	2.25	1.11	1.23	1.24	0.68	0.84
1a-Leu-C4	300 mg	S	S	S	S	S	S
1a-Leu-C6	325 mg	3.63	S	2.67	S	P	S

1b-Leu-C4	320 mg	4.38	3.38	5.33	S	S	2.60
1b-Leu-C6	340 mg	S	3.30	2.80	1.38	S	S
2a-Leu-C4	335 mg	S	S	S	S	P	S
2a-Leu-C6	370 mg	4.43	4.43	2.87	2.87	S	3.69
2b-Leu-C4	355 mg	4.36	S	3.76	S	S	S
2b-Leu-C6	390 mg	S	3.66	S	2.84	P	1.68
3a-Leu -C4	300 mg	3.84	S	4.03	S	P	S
3a-Leu -C6	300 mg	5.27	4.87	S	3.90	P	3.22
3b-Leu-C4	335 mg	5.22	S	4.87	S	P	S
3b-Leu-C6	320 mg	3.85	2.79	1.91	1.47	1.76	1.26
4a-Leu-C4	325 mg	S	S	4.88	S	P	S
4a-Leu-C6	370 mg	3.15	4.08	1.25	2.66	1.33	1.93
4b-Leu-C4	370 mg	S	S	4.39	S	3.67	S
4b-Leu-C6	370 mg	4.66	S	3.68	S	3.81	2.61
5a-Leu-C6	320 mg	3.33	3.31	3.57	2.78	P	1.60
5a-Leu-C8	330 mg	2.36	1.79	3.21	2.52	P	0.82
5b-Leu-C6	370 mg	P	2.96	4.86	2.75	P	2.30
5b-Leu-C8	380 mg	2.77	2.54	4.15	2.69	P	2.18
6a-Leu-C6	370 mg	S	S	S	S	S	2.84
6a-Leu-C8	330mg	2.15	2.37	2.77	1.88	2.60	1.35
6b-Leu-C6	380 mg	3.84	S	2.40	S	1.27	2.38
6b-Leu-C8	370 mg	4.22	2.88	2.88	2.96	2.74	0.64
1a-Phe-C4	270 mg	1.63	3.38	2.43	3.66	1.37	3.37
1a-Phe-C6	300 mg	0.63	1.13	0.66	0.77	0.53	0.85
1a-Phe-C8	280 mg	0.58	0.43	0.47	0.68	0.51	0.67
1b-Phe-C4	265 mg	2.81	S	1.99	S	2.65	1.65
1b-Phe-C6	300 mg	2.46	3.36	2.52	2.52	2.31	2.31
1b-Phe-C8	340 mg	2.41	0.66	2.43	0.81	2.29	0.83
2a-Phe-C4	260 mg	P	S	P	S	1.34	1.84
2a-Phe-C6	300 mg	1.37	0.68	1.13	1.21	0.88	0.56
2a-Phe-C8	180 mg	0.83	1.67	0.71	1.24	0.70	0.88
2b-Phe-C4	220 mg	3.88	S	3.89	S	P	S
2b-Phe-C6	210 mg	3.68	2.77	2.66	2.41	2.36	1.89
2b-Phe-C8	250 mg	3.12	2.55	2.55	2.32	2.33	2.65
3a-Phe-C4	270 mg	3.74	2.74	2.89	2.89	P	P
3a-Phe-C6	350 mg	3.44	1.87	2.63	2.13	1.77	0.88
3a-Phe-C8	340 mg	2.68	2.67	2.54	2.49	1.57	2.15
3b-Phe-C4	280 mg	1.18	S	0.77	2.66	1.07	1.73
3b-Phe-C6	300 mg	4.19	0.86	4.24	0.57	3.42	0.62
3b-Phe-C8	280 mg	3.92	3.03	3.28	2.87	2.48	2.55
4a-Phe-C4	260 mg	3.59	S	2.66	S	2.74	0.74
4a-Phe-C6	345 mg	2.92	3.28	2.36	2.74	2.14	2.32
4a-Phe-C8	360 mg	2.52	0.49	2.18	0.81	2.09	0.83
4b-Phe-C4	340 mg	S	S	S	S	P	P

4b-Phe-C6	340 mg	4.21	2.23	3.57	2.34	3.88	0.67
4b-Phe-C8	360 mg	3.88	0.54	3.31	0.35	2.29	0.47
5a-Phe-C4	315 mg	P	S	P	S	0.76	S
5a-Phe-C6	360 mg	2.81	S	2.77	S	0.62	0.86
5a-Phe-C8	120 mg	0.53	0.66	0.47	0.63	0.44	1.26
5b-Phe-C4	390 mg	2.57	0.85	2.74	1.24	P	1.28
5b-Phe-C6	350 mg	1.85	0.87	1.66	0.94	P	0.86
5b-Phe-C8	330 mg	1.64	0.77	1.58	0.83	P	0.82
6a-Phe-C4	380 mg	0.72	0.65	0.56	0.57	0.51	0.64
6a-Phe-C6	350 mg	1.18	0.67	0.61	0.69	0.82	0.53
6a-Phe-C8	300 mg	1.36	1.16	1.27	1.30	0.85	0.77
1a-Val-C4	220 mg	0.62	1.16	0.85	0.83	0.64	0.75
1a-Val-C6	360 mg	S	0.67	2.53	0.63	2.73	0.49
1a-Val-C8	300 mg	1.28	0.72	0.37	0.66	0.55	0.93
1b-Val-C4	340 mg	1.83	1.26	0.72	1.31	0.52	1.19
1b-Val-C6	340 mg	P	0.87	2.35	1.36	0.75	0.74
1b-Val-C8	370 mg	S	0.79	3.16	0.84	0.85	0.82
2a-Val-C6	300 mg	2.36	1.94	2.14	1.67	1.89	0.88
2a-Val-C8	230 mg	2.20	3.32	1.86	2.88	0.41	0.41
3a-Val-C4	200 mg	1.25	0.74	0.68	0.82	0.66	1.25
3a-Val-C6	150 mg	0.71	0.63	0.66	0.53	0.83	0.67
3a-Val-C8	360 mg	0.66	0.86	0.44	0.64	0.41	0.71
4a-Val-C4	340 mg	0.56	0.64	0.53	0.66	0.52	0.57
4a-Val-C6	270 mg	S	2.66	2.27	2.13	2.58	1.41
4a-Val-C8	340 mg	P	P	2.21	2.43	1.45	1.54
5a-Val-C4	350 mg	P	0.78	1.28	0.73	0.66	0.64
5a-Val-C6	150 mg	0.78	0.67	0.63	0.70	0.55	0.63
5a-Val-C8	140 mg	0.88	0.64	0.47	0.66	0.73	0.68
5b-Val-C4	360 mg	1.20	0.71	1.14	0.87	0.52	0.62
5b-Val-C6	350 mg	1.18	0.84	1.24	0.88	P	0.65
5b-Val-C8	370 mg	1.63	0.61	1.57	0.96	0.83	0.66
6a-Val-C4	370 mg	1.27	0.73	1.35	0.75	0.64	0.68
6a-Val-C6	330 mg	1.68	0.73	1.25	0.92	0.88	0.70
6a-Val-C8	150 mg	0.46	0.59	0.53	0.58	0.65	0.61

S = soluble, and P = precipitate

Scanning Electron Microscopy (SEM) Study

A small amount of petrol gel was placed on copper tape attached aluminum stub, and allowed to dry overnight under ambient conditions. Later, sample was sputter-coated with a thin layer of Pt, and subjected to SEM observation on a JEOL JSM-7400F electron microscope at an accelerating voltage of 5 kV.

Rheology Experiment

Rheological studies of gels at biphasic MGCs (BMGCs) were performed using an ARES-G2 rheometer (TA Instruments, U.S.A.) equipped with a plate (8 mm diameter). The gels were equilibrated at 25 ℃ between the plates that were adjusted to a gap of 2.0 mm. The storage modulus (G’) and loss modulus (G”) of gels were first measured in strain sweep (0.01–100%) modes at a constant frequency of 1 Hz, followed by a frequency scan of 1.0 to 100 rad/s under the controlled strain of 0.1%. Experiments were repeated twice to ensure the reproducibility.

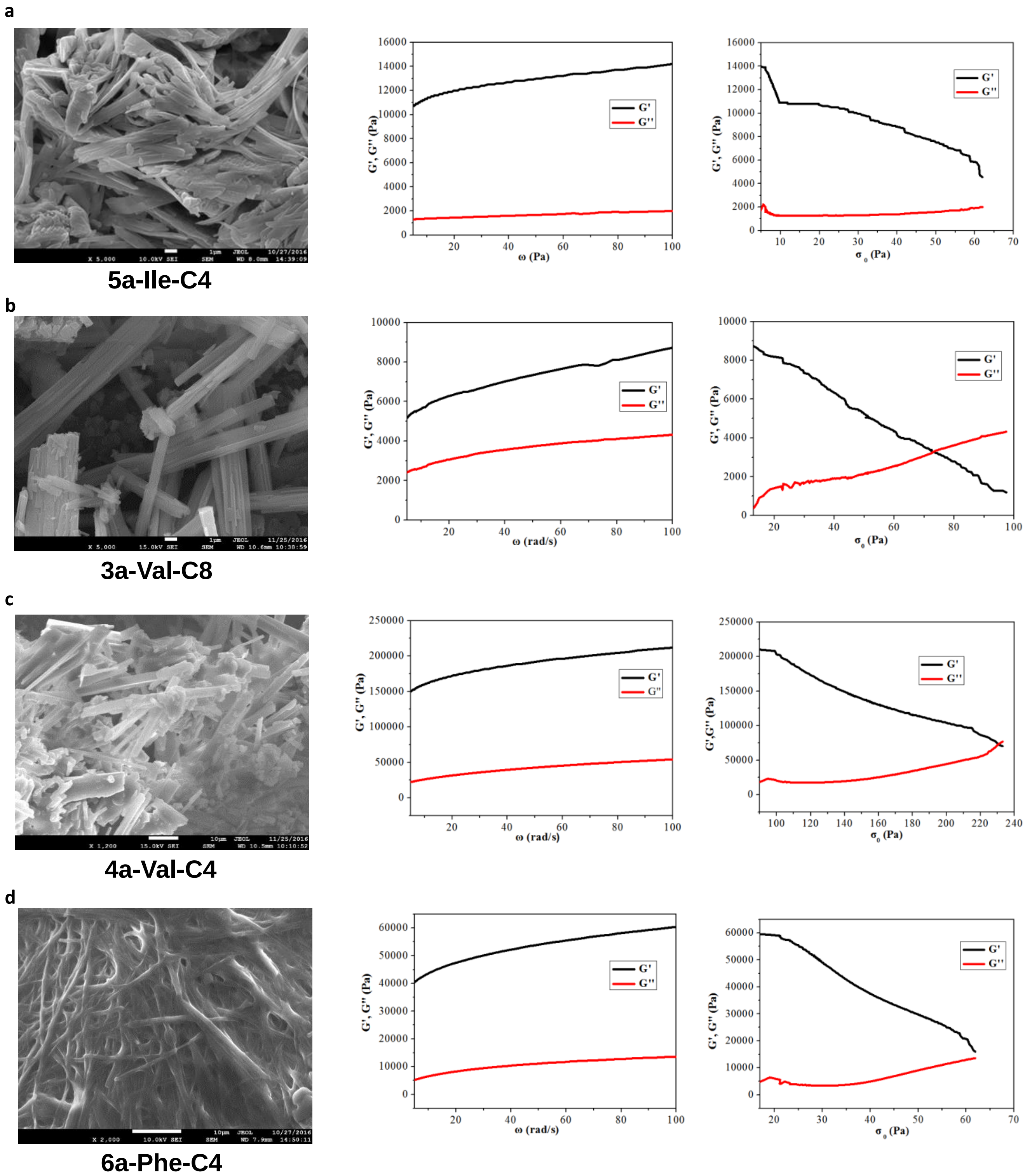
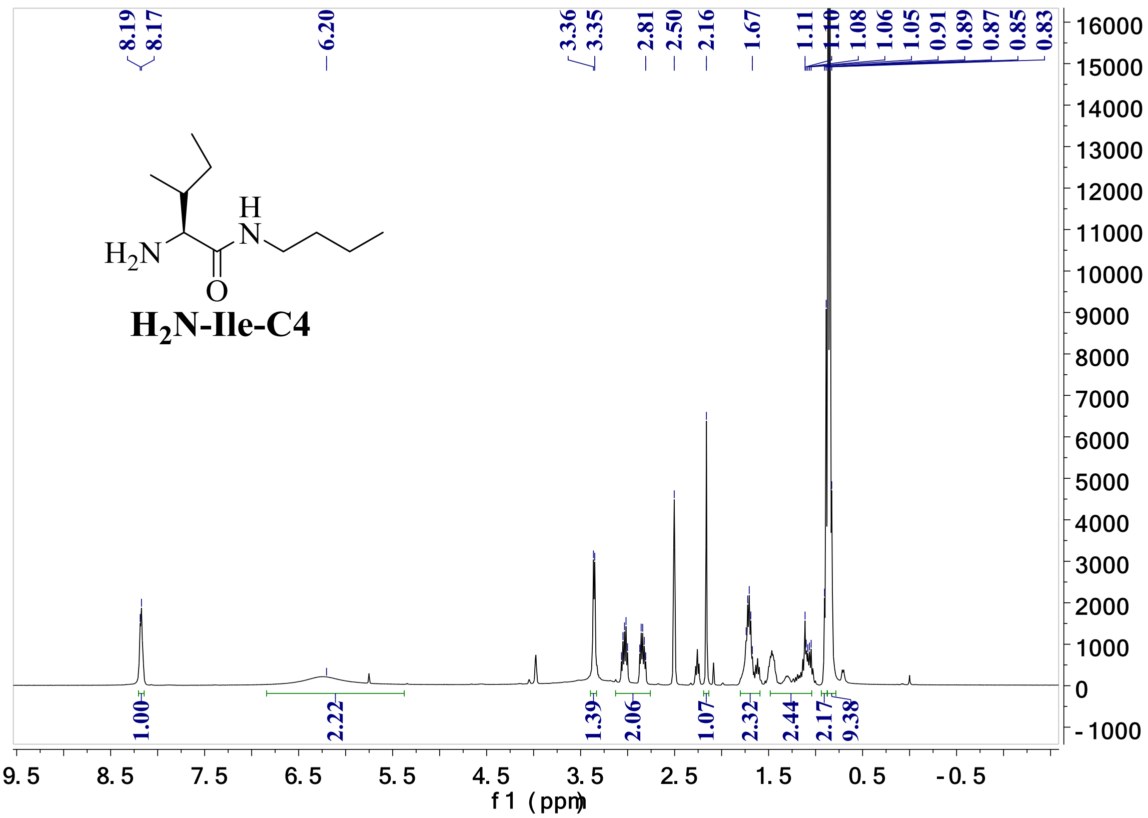
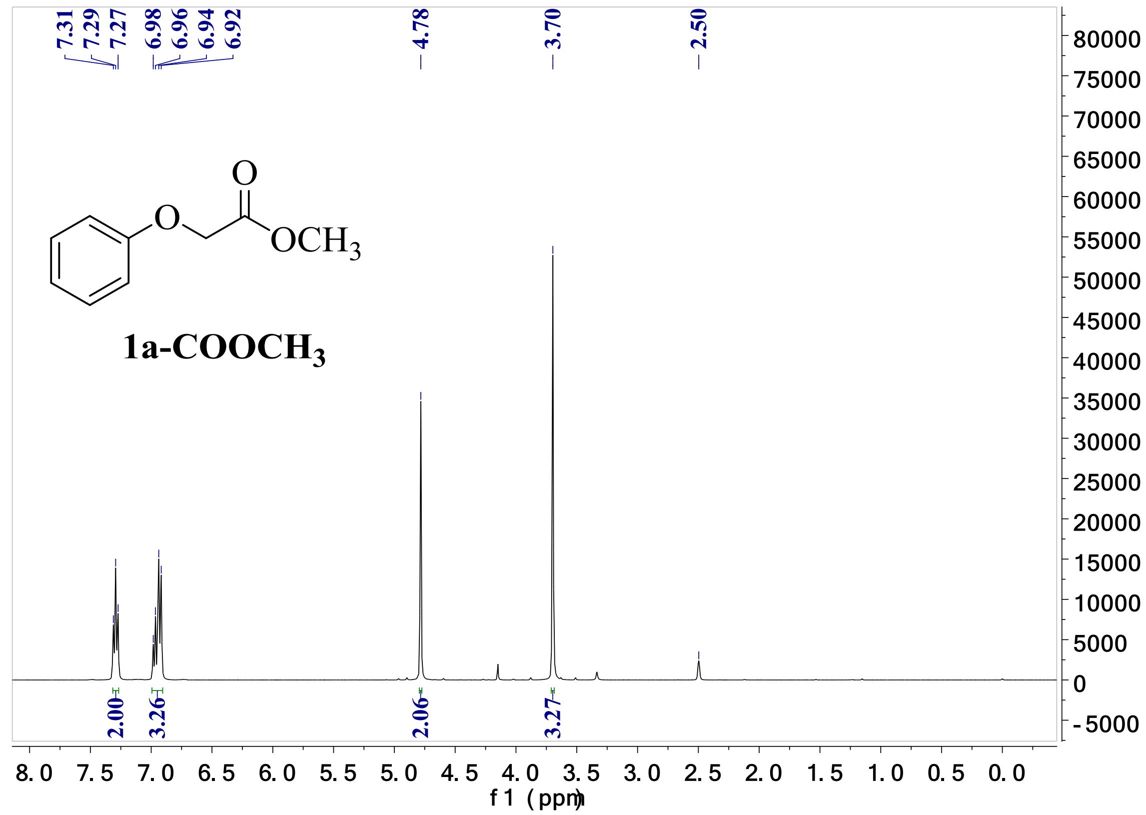
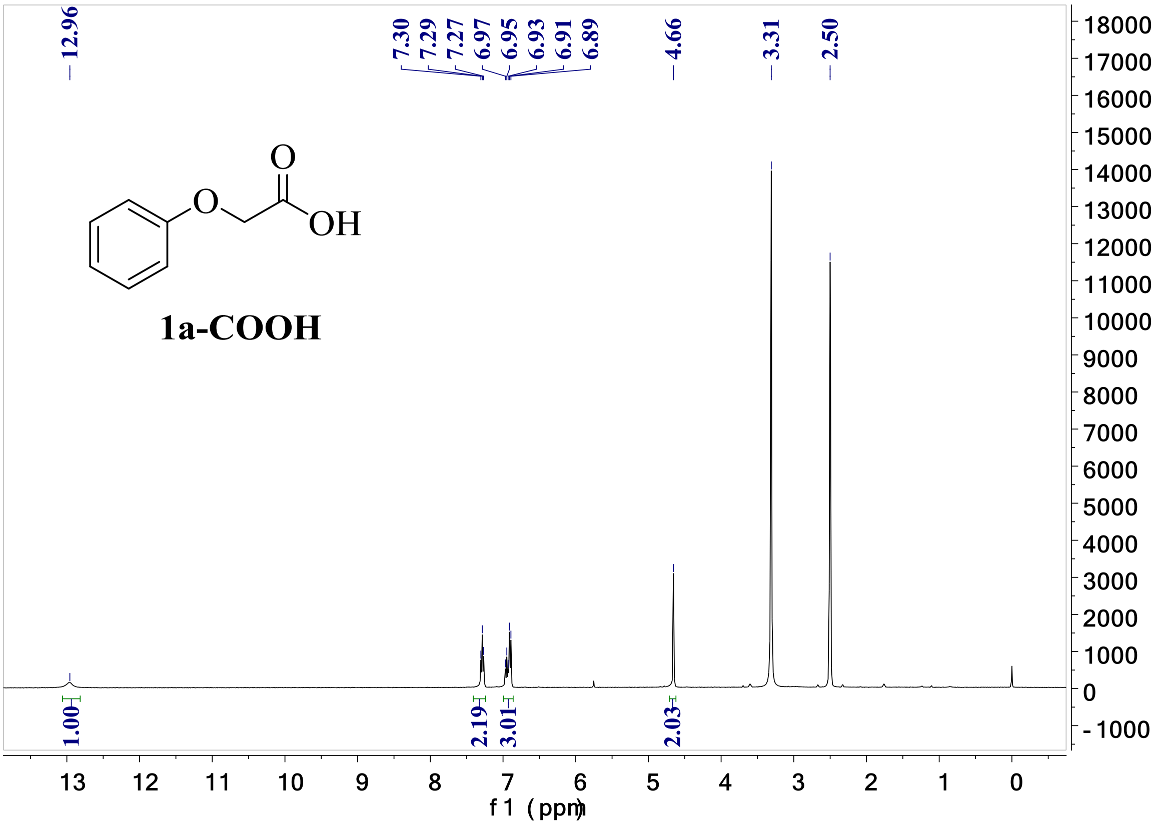


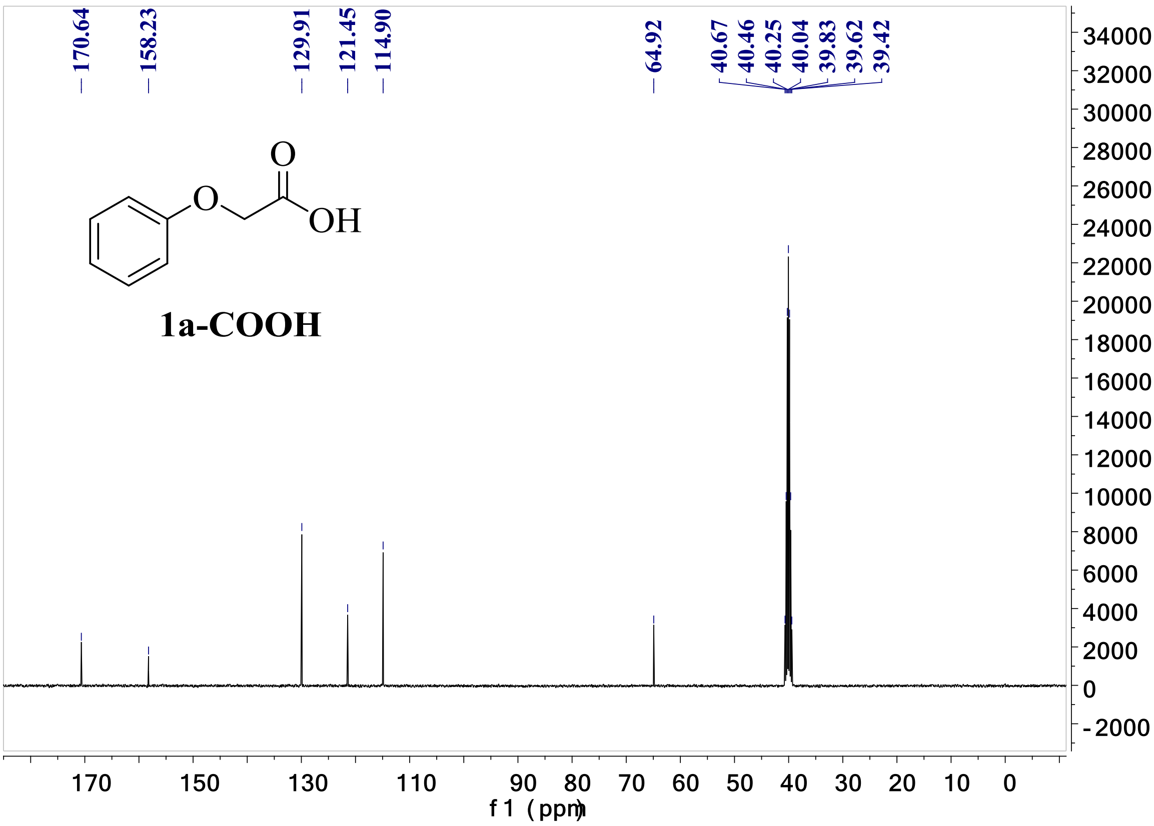
Figure S1. SEM micrographs and rheological data of the as-formed diesel gels of **5a-Ile-C4**, **3a-Val-C8**, **4a-Val-C4** and **6a-Phe-C4** at 1.5% w/v; G' = storage modulus, G" = loss modulus, frequency sweep = ω, and stress amplitude = σ_0.

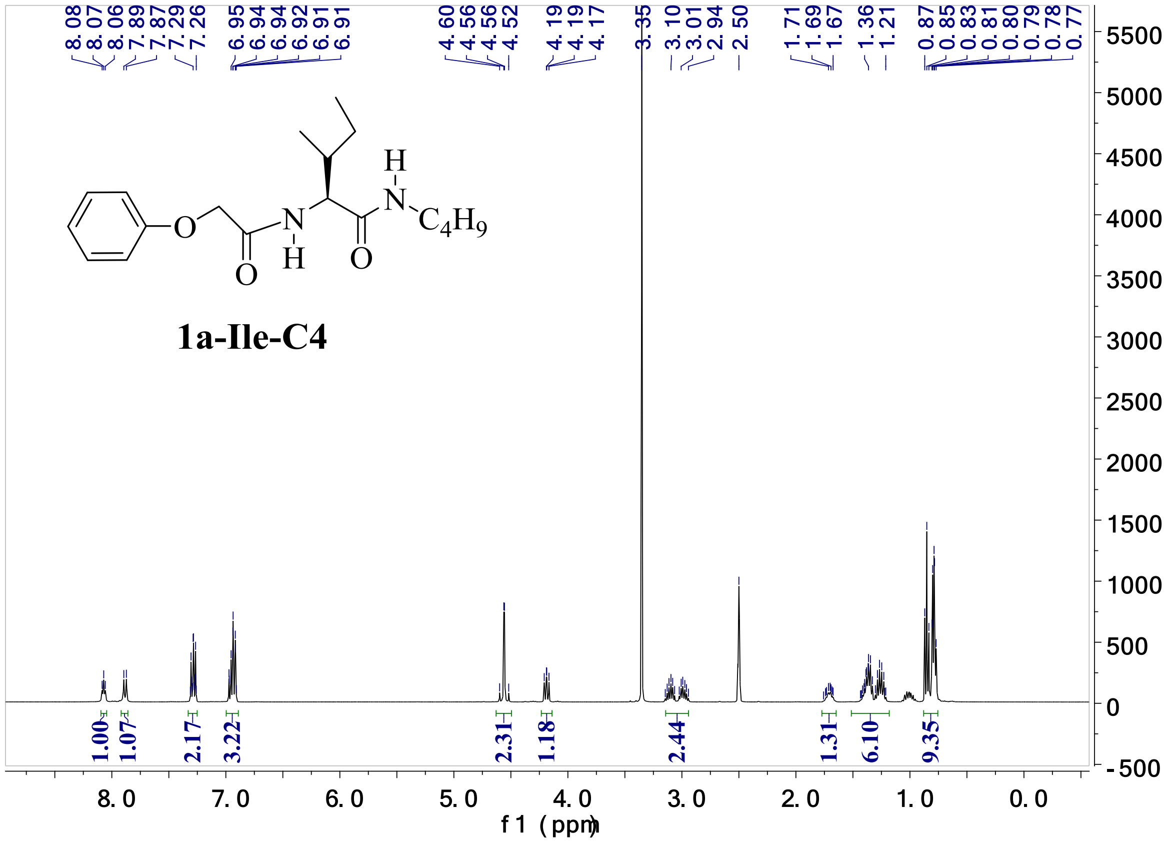
[1]H and [13]C NMR Spectra for 116 representative PSOGs

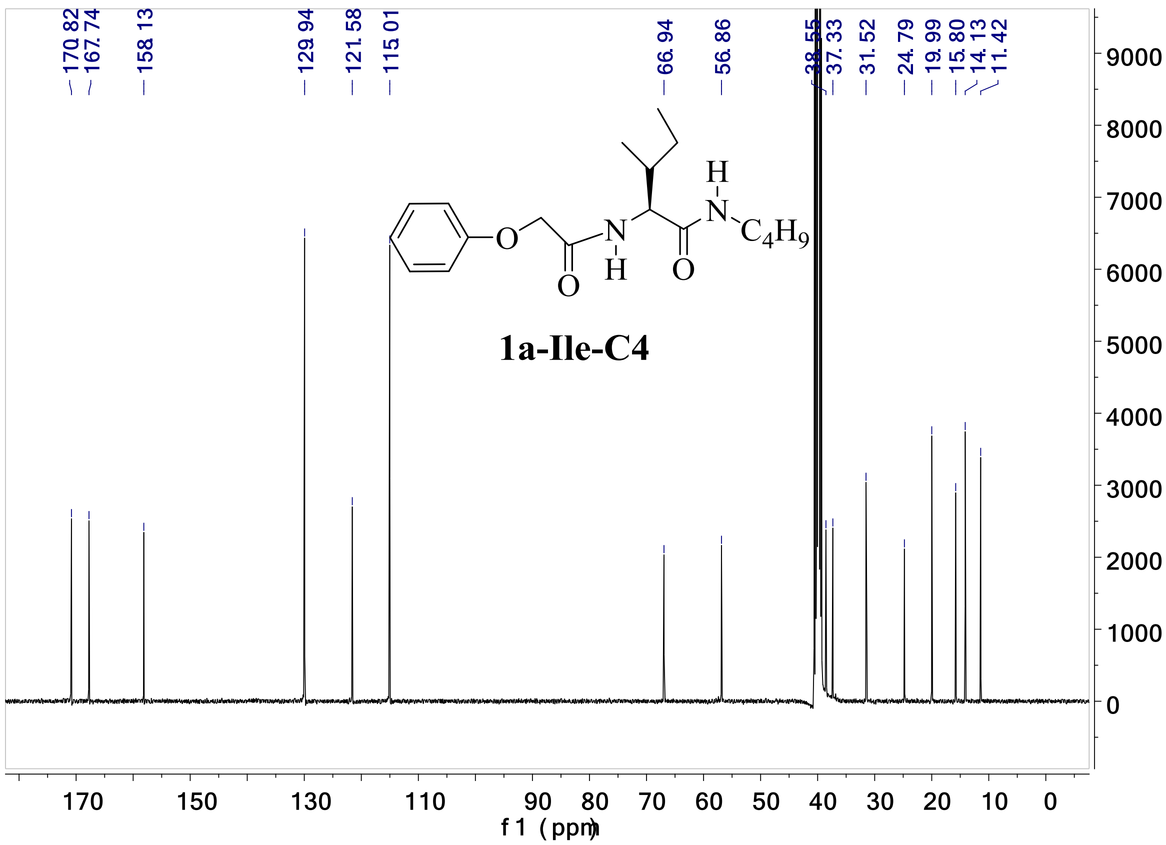


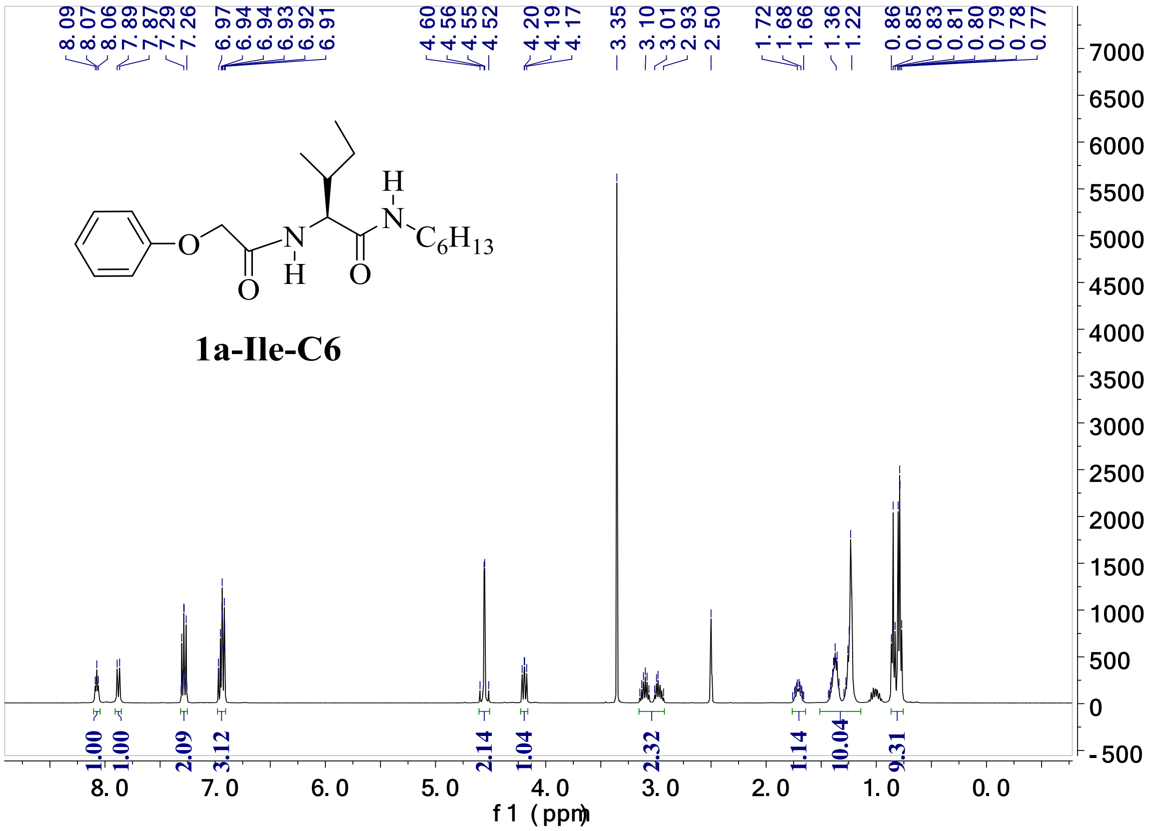


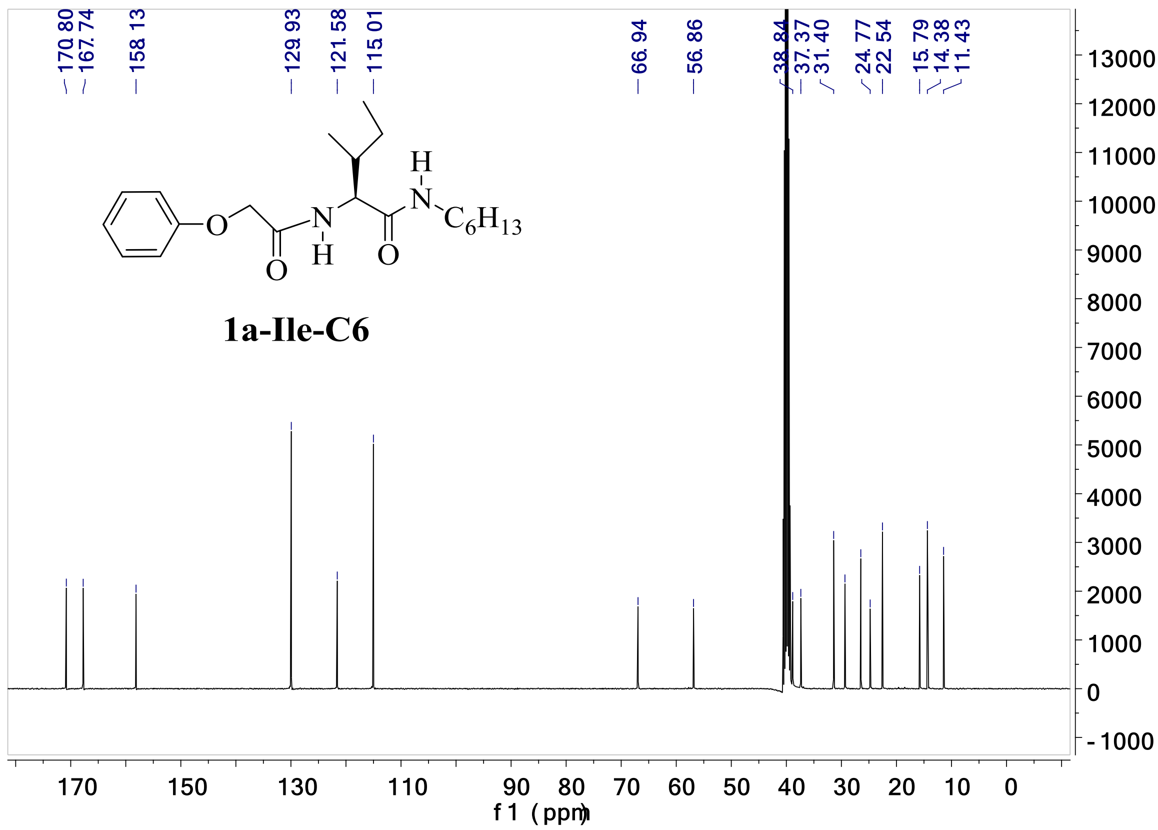

12.96
7.30
7.29
7.27
6.97
6.95
6.93
6.91
6.89
4.66
3.31
2.50
O
O
OH
1a-COOH
1.00
2.19
3.01
2.03
f1 (ppm)

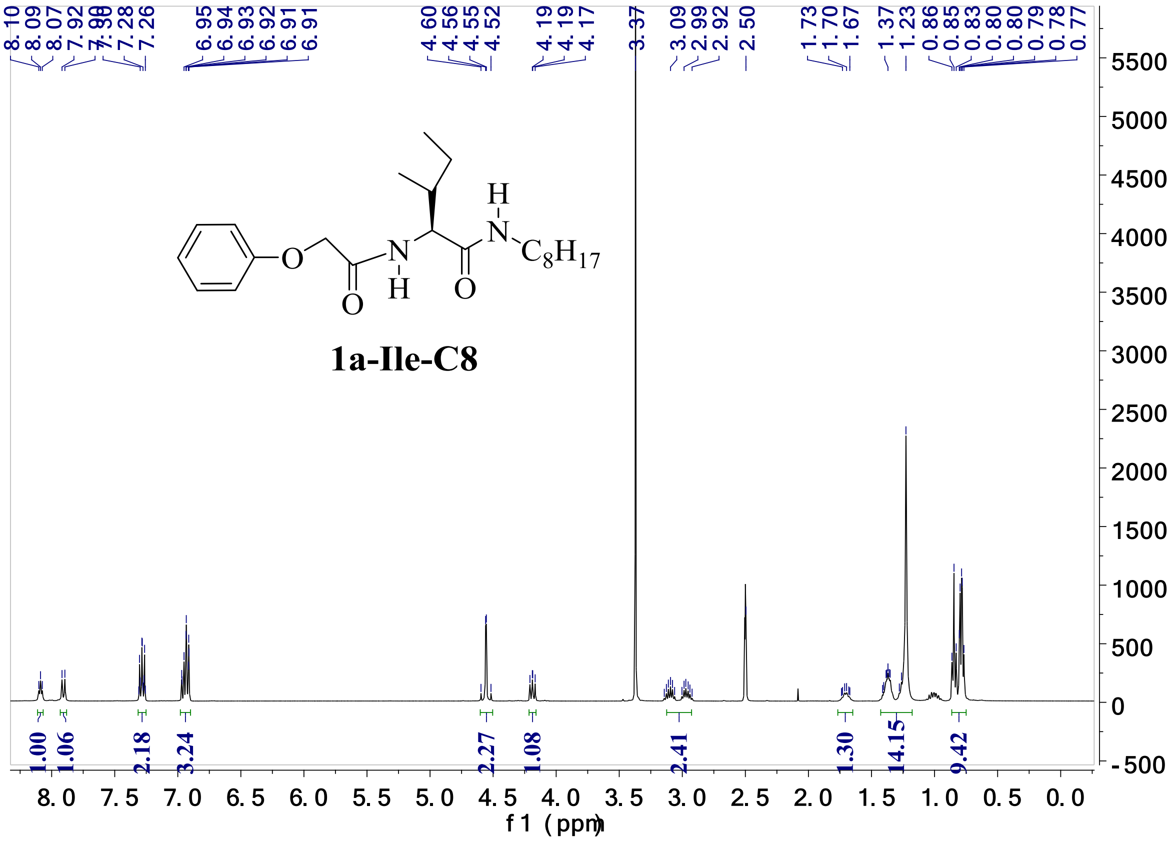

170.64
158.23
129.91
121.45
114.90
64.92
40.67
40.46
40.25
40.04
39.83
39.62
39.42
O
O
OH
1a-COOH
f1 (ppm)


8.08
8.07
8.06
7.89
7.87
7.29
7.26
6.95
6.94
6.94
6.92
6.91
6.91
4.60
4.56
4.56
4.52
4.19
4.19
4.17
3.35
3.10
3.01
2.94
2.50
1.71
1.69
1.67
1.36
1.21
0.87
0.85
0.83
0.81
0.80
0.79
0.78
0.77
1a-Ile-C4
1.00
1.07
2.17
3.22
2.31
1.18
2.44
1.31
6.10
9.35
f1 (ppm)

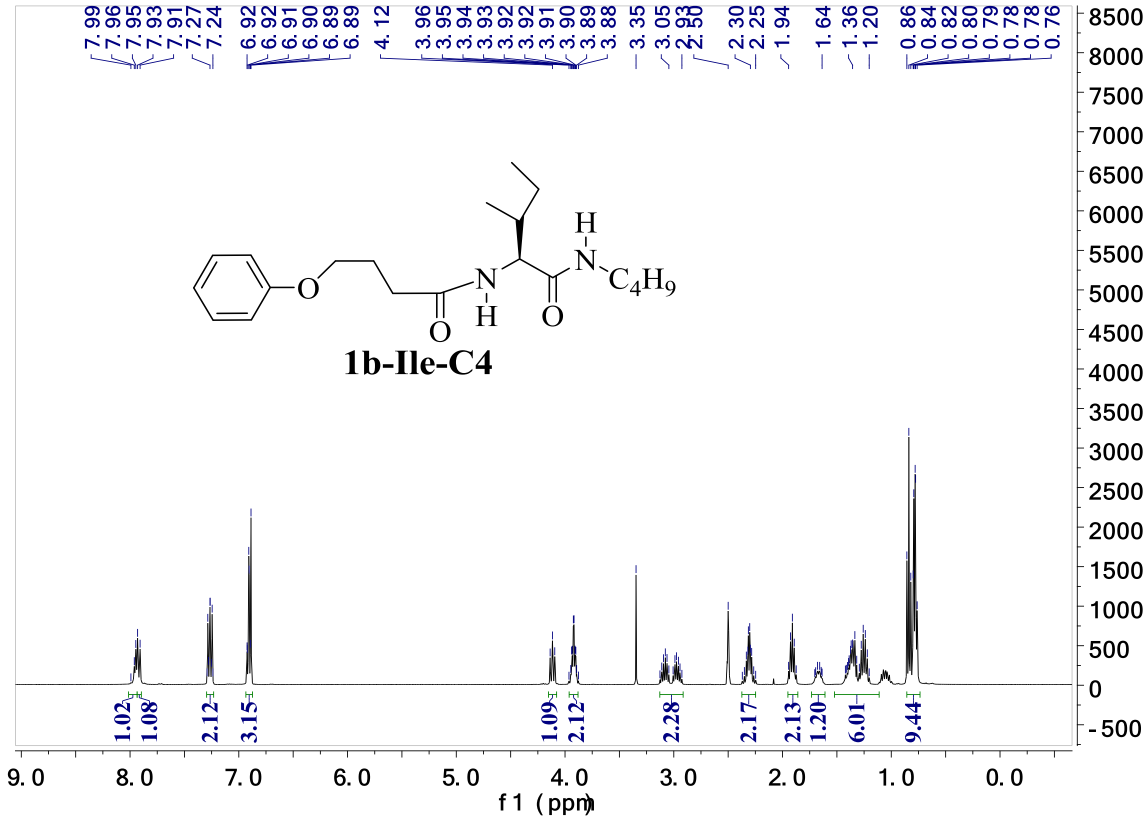

170.82
167.74
158.13
129.94
121.58
115.01
66.94
56.86
38.55
37.33
31.52
24.79
19.99
15.80
14.13
11.42
1a-Ile-C4
f1 (ppm)


8.09
8.07
8.06
7.89
7.87
7.29
7.26
6.97
6.94
6.94
6.93
6.92
6.91
4.60
4.56
4.55
4.52
4.20
4.19
4.17
3.35
3.10
3.01
2.93
2.50
1.72
1.68
1.66
1.36
1.22
0.86
0.85
0.83
0.81
0.80
0.79
0.78
0.77
1a-Ile-C6
1.00
1.00
2.09
3.12
2.14
1.04
2.32
1.14
10.04
9.31
f1 (ppm)

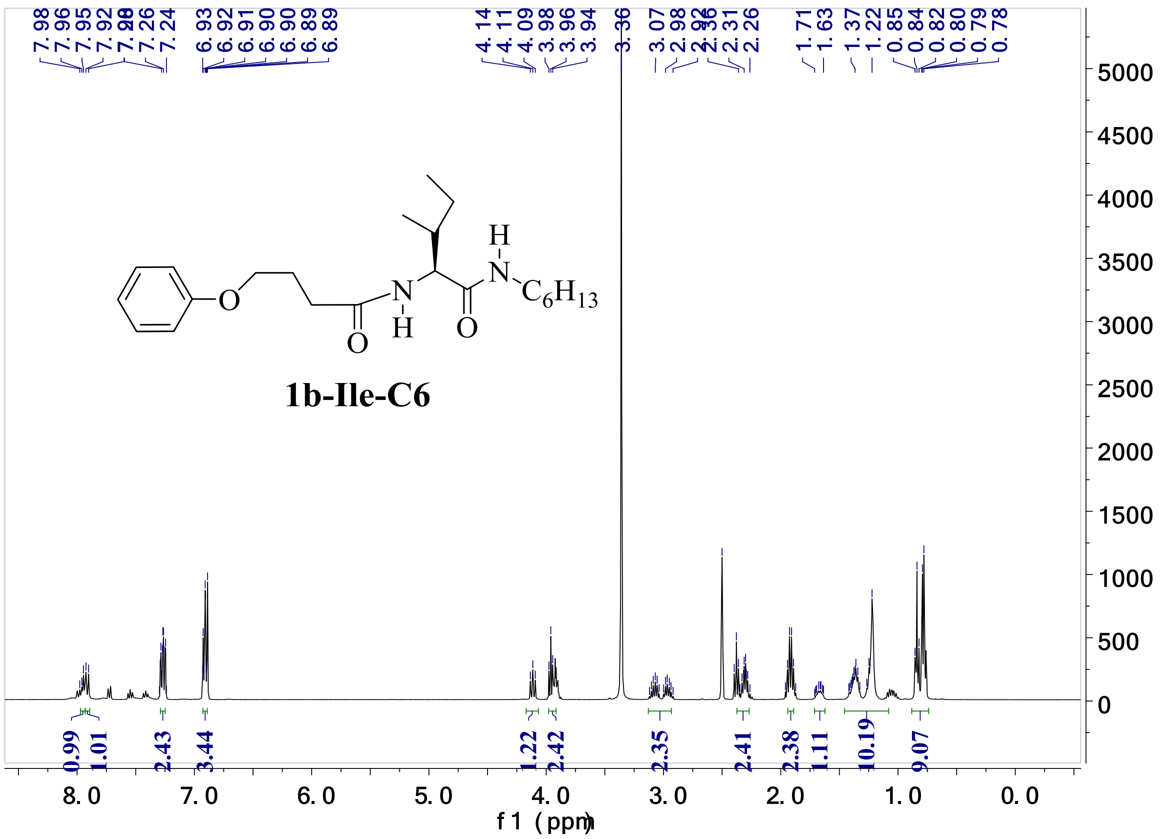

170.80
167.74
158.13
129.93
121.58
115.01
66.94
56.86
38.84
37.37
31.40
24.77
22.54
15.79
14.38
11.43
1a-Ile-C6
f1 (ppm)

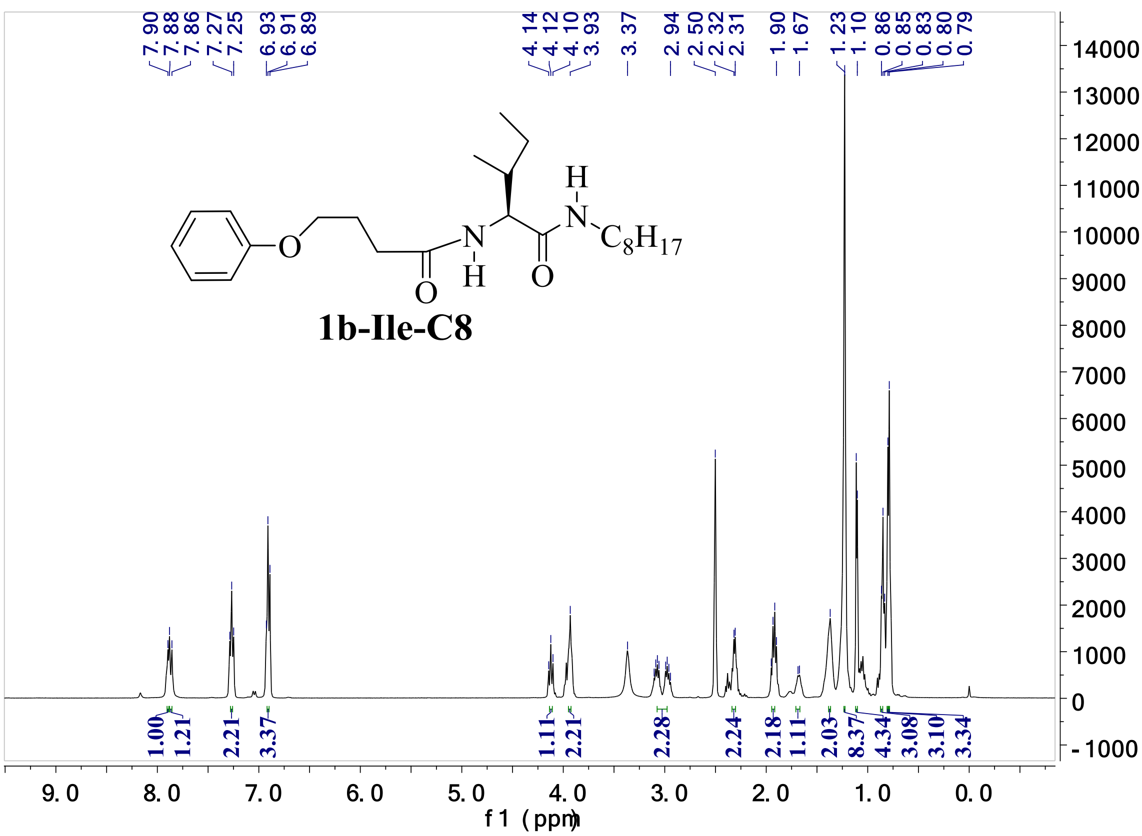


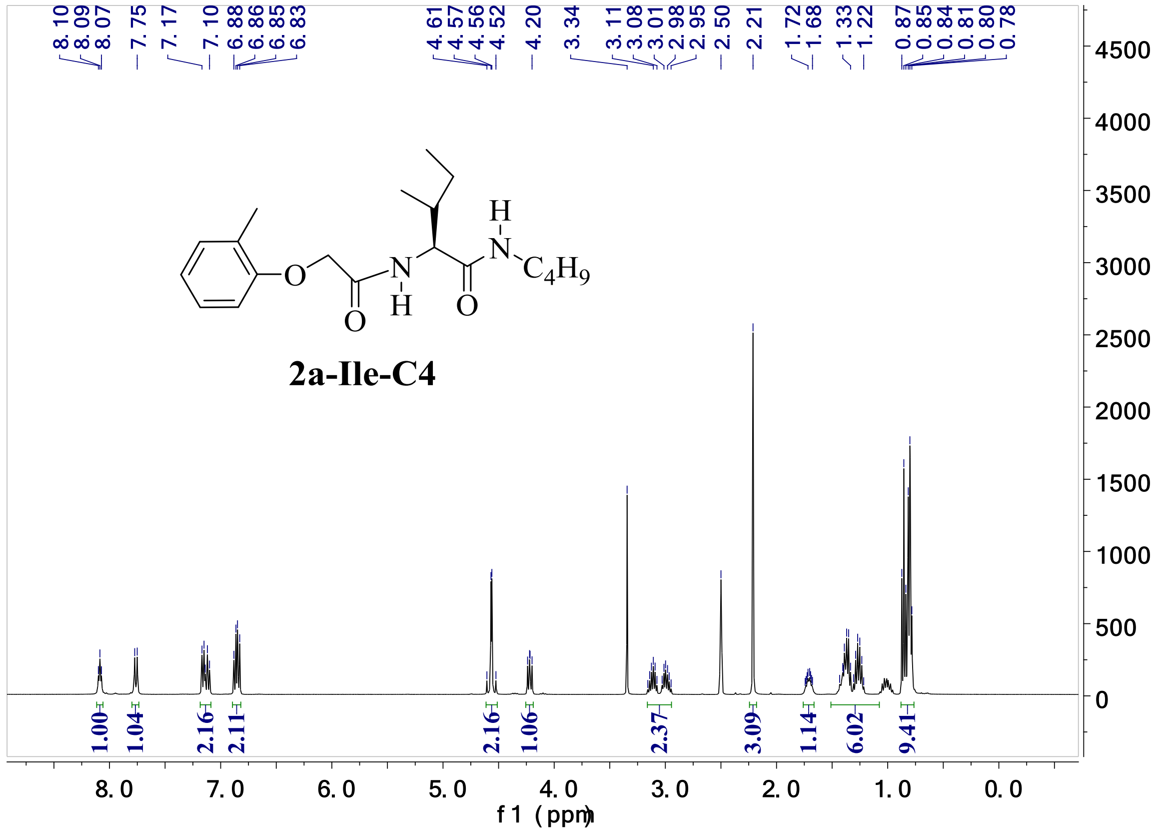
1a-Ile-C8



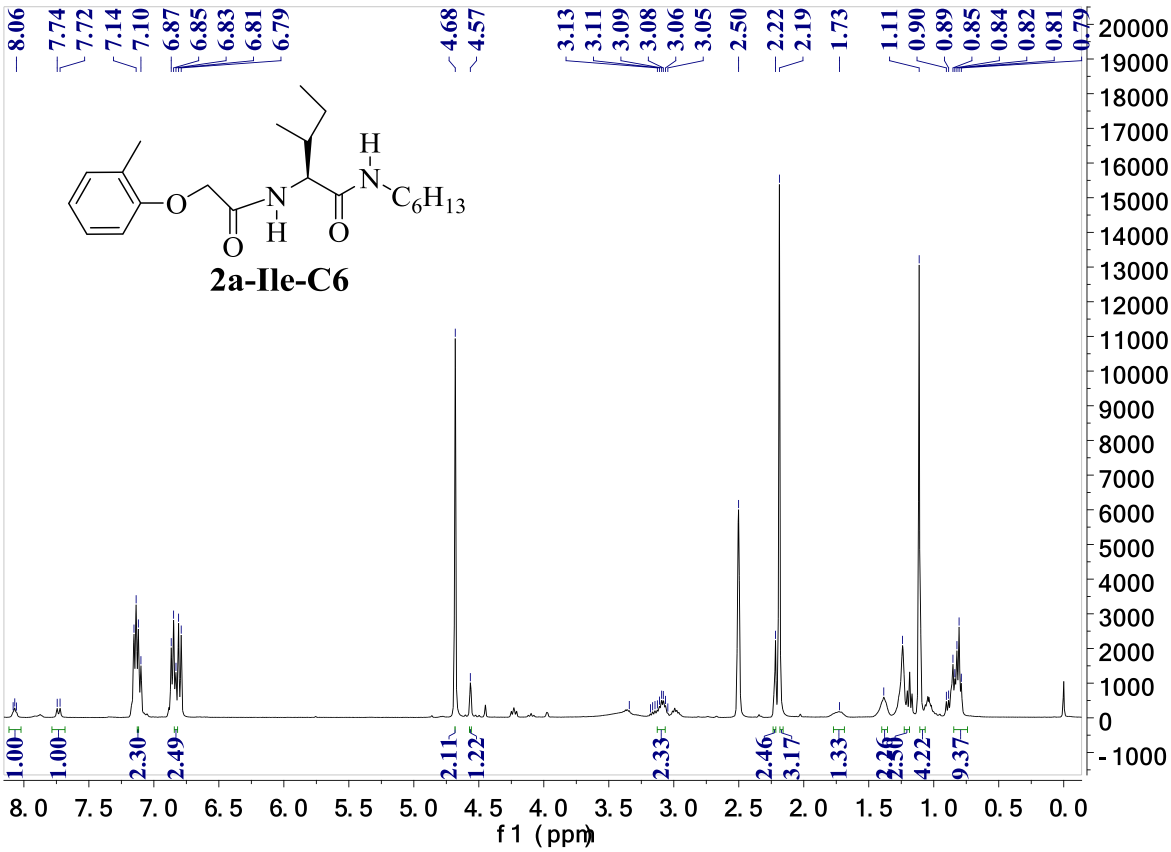
1b-Ile-C4


1b-Ile-C6
f1 (ppm)

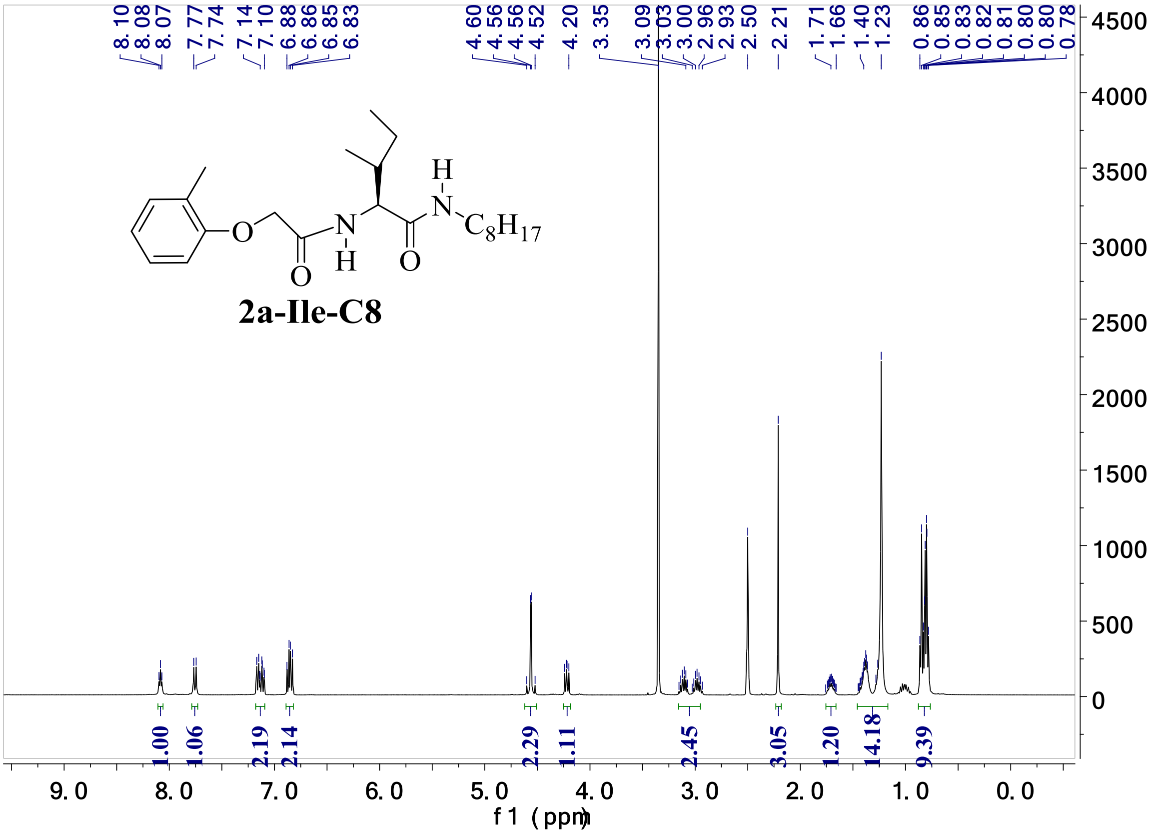

1b-Ile-C8
f1 (ppm)



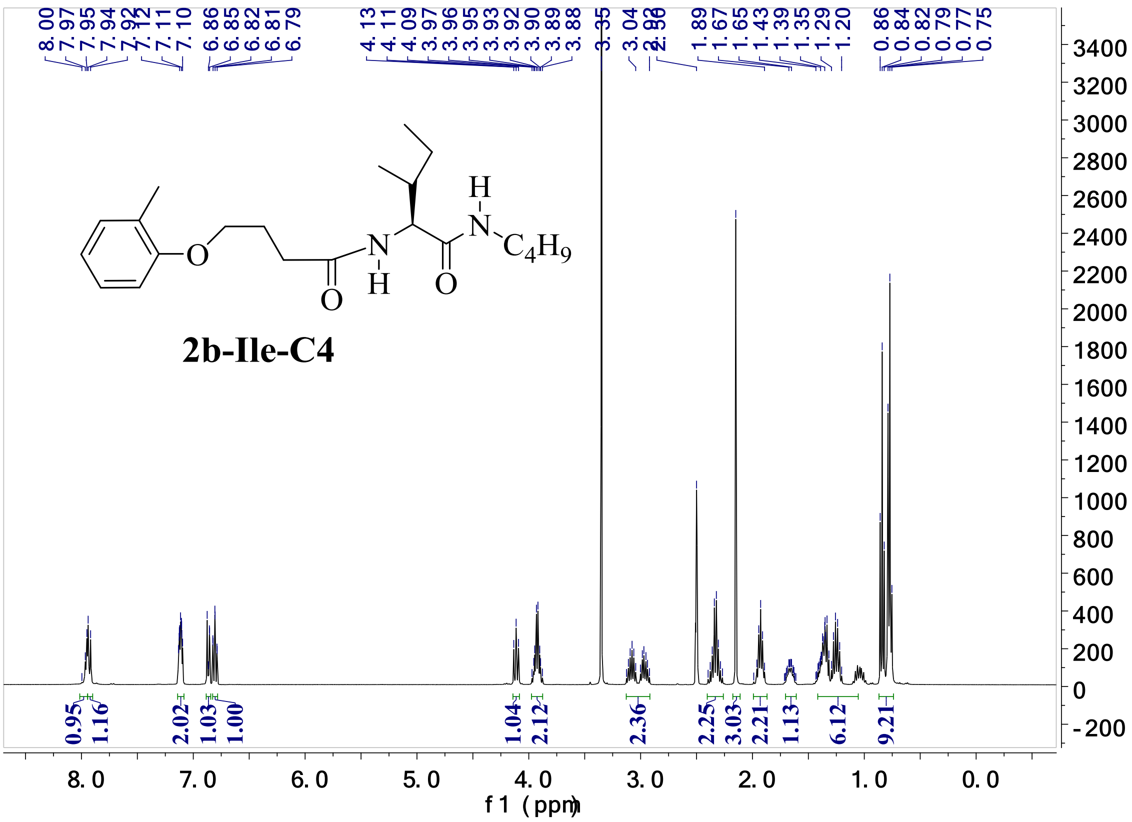
2a-Ile-C4



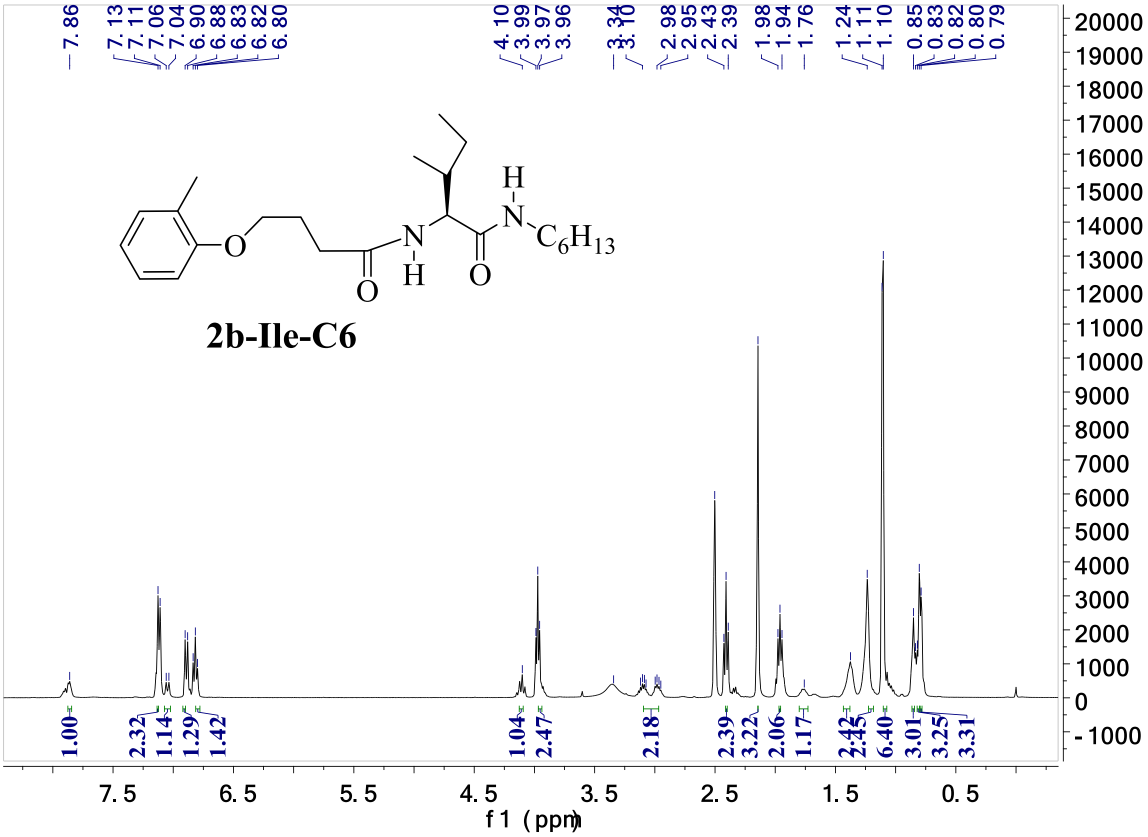
2a-Ile-C6



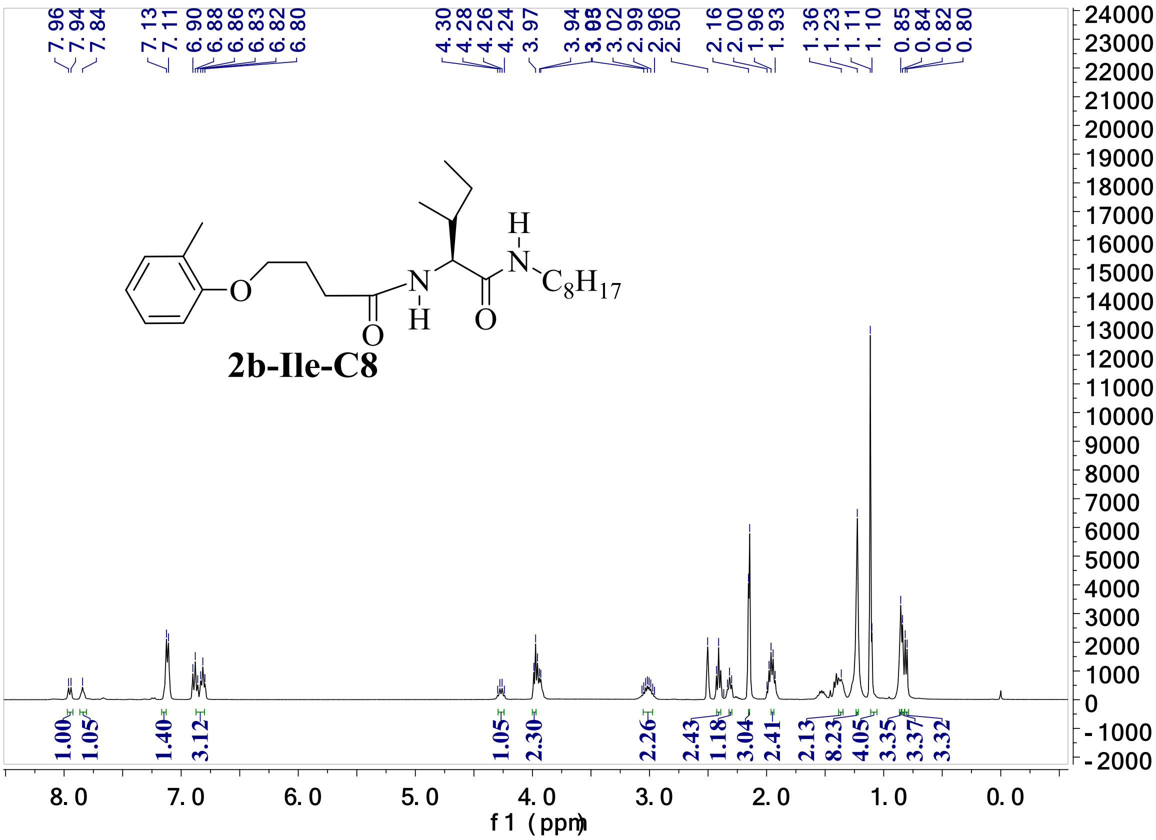
2a-Ile-C8
f1 (ppm)



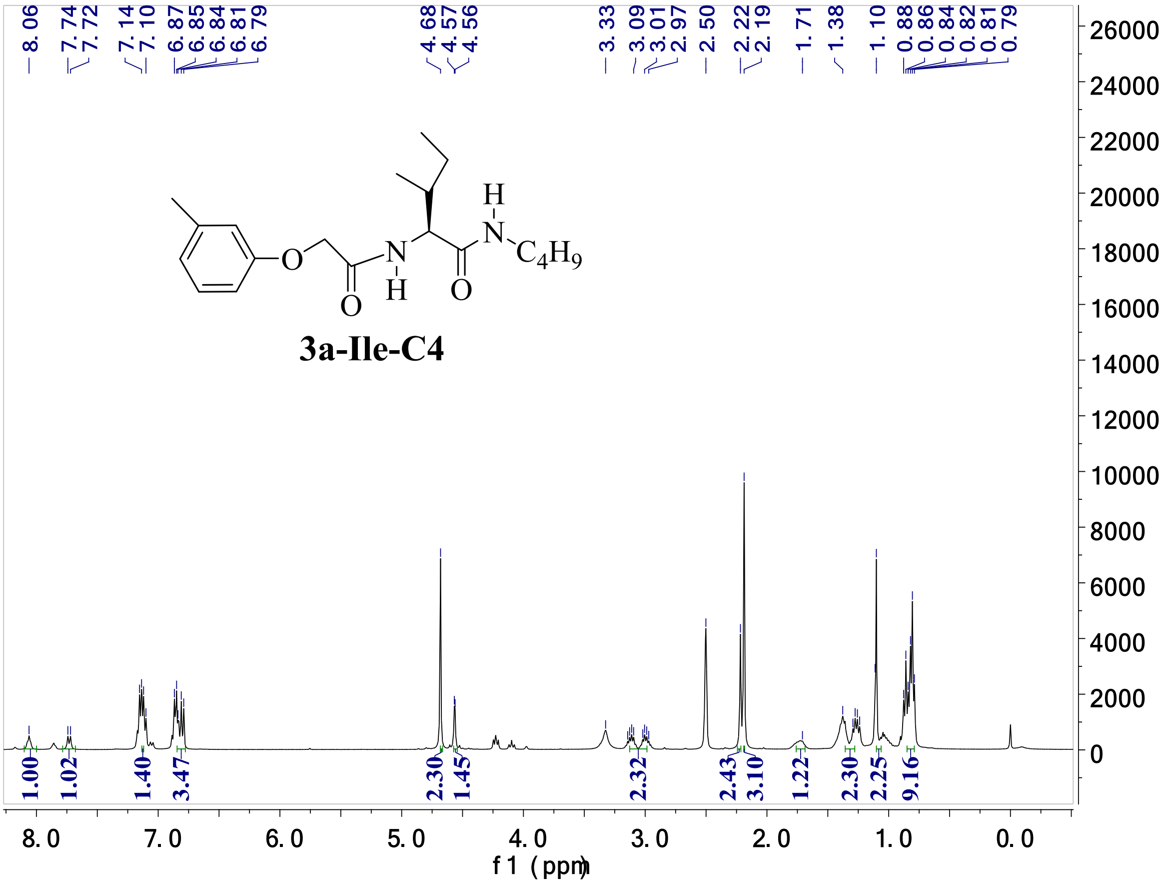
2b-Ile-C4
f1 (ppm)

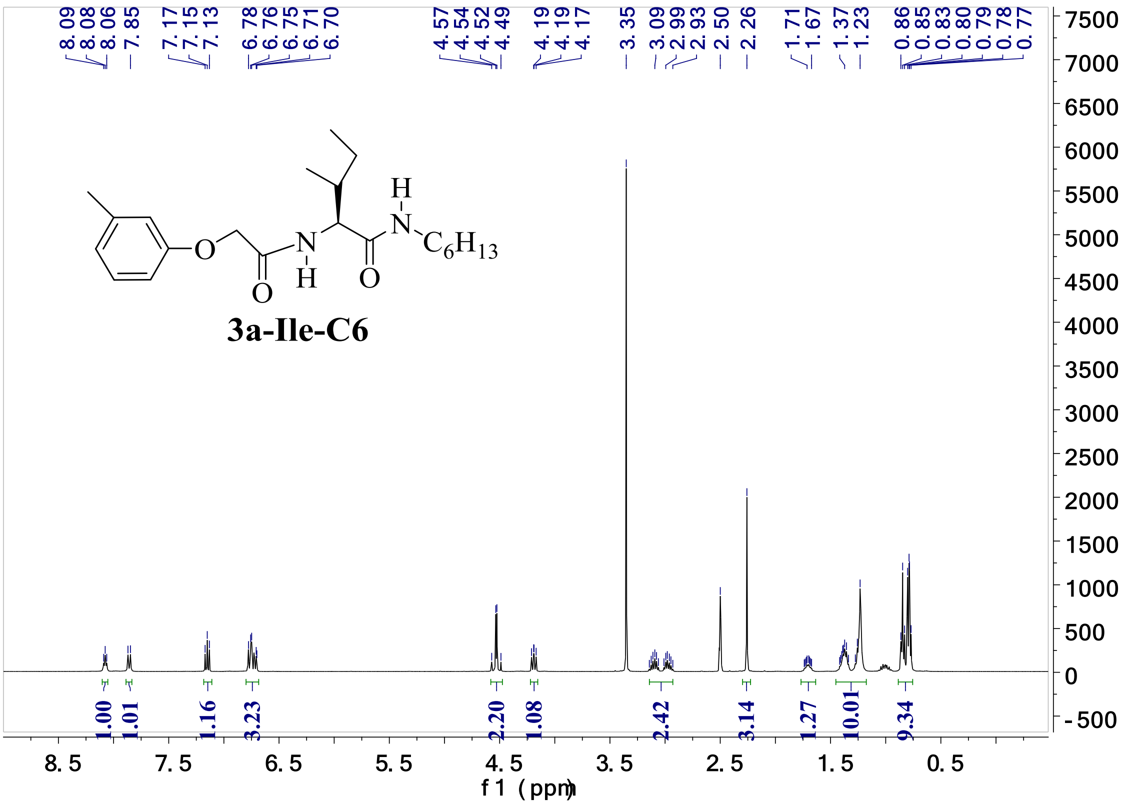


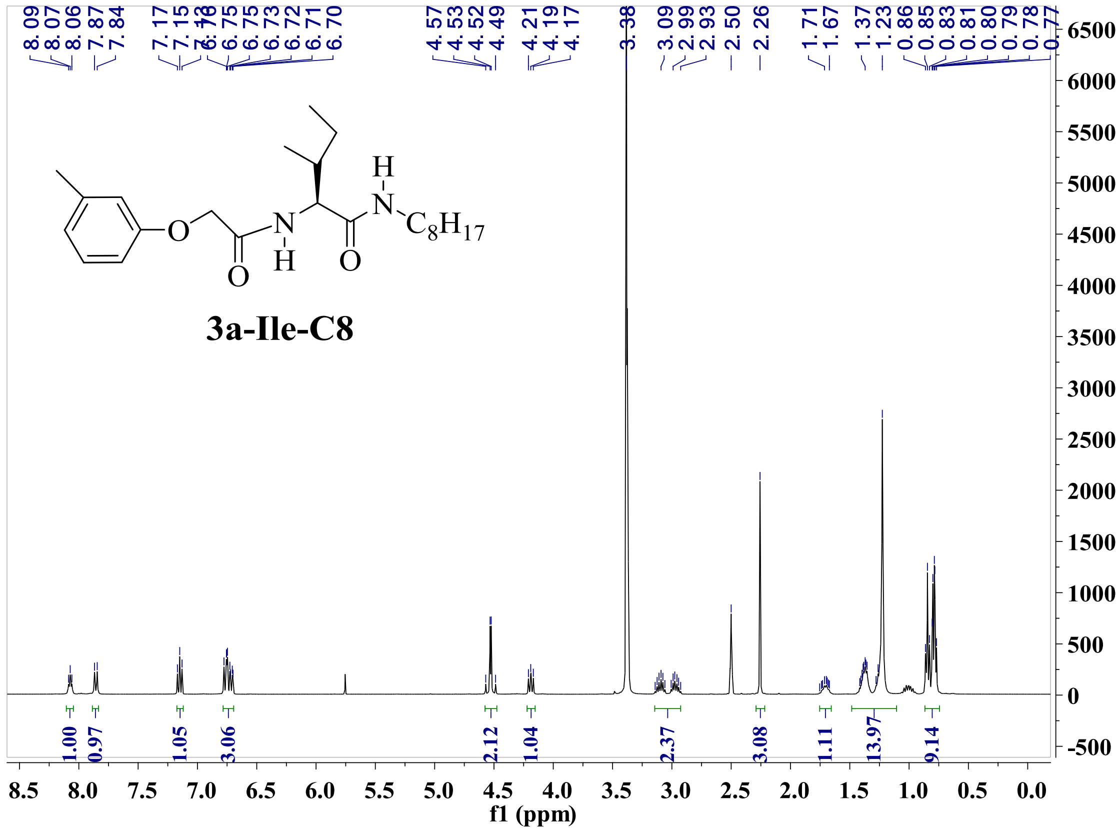
2b-Ile-C6

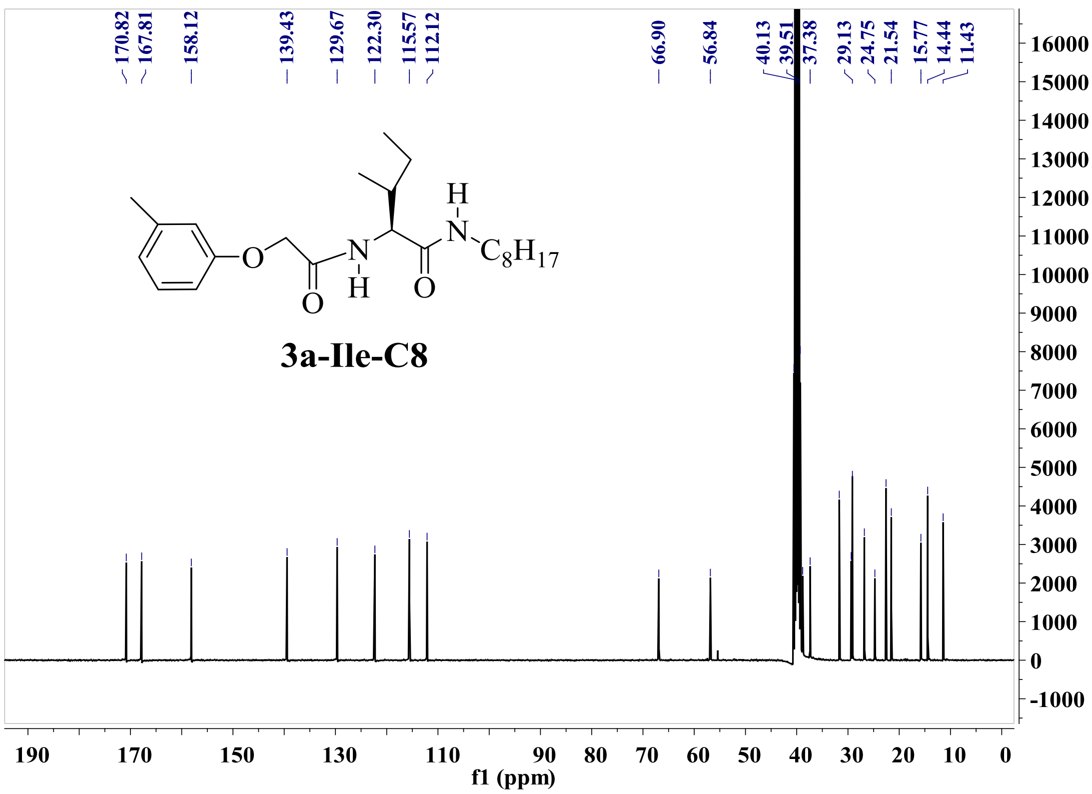


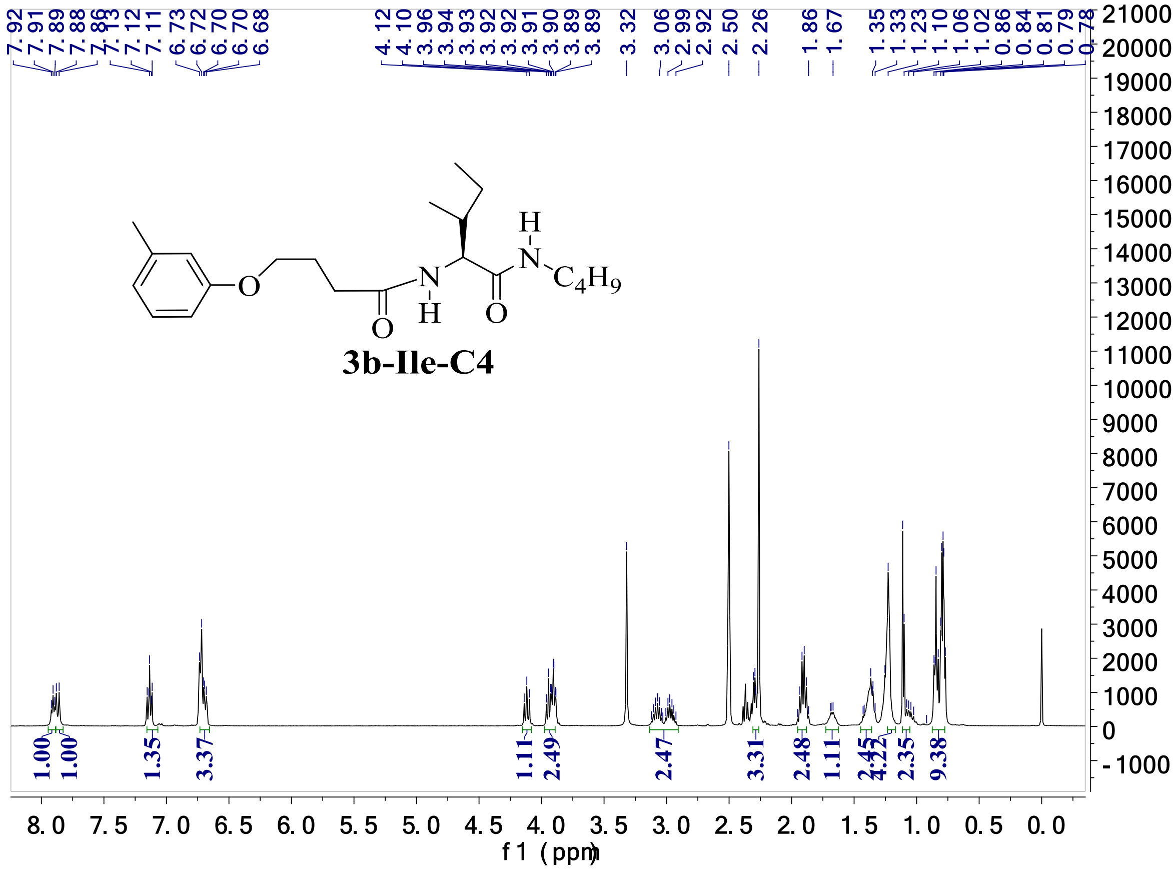
2b-Ile-C8

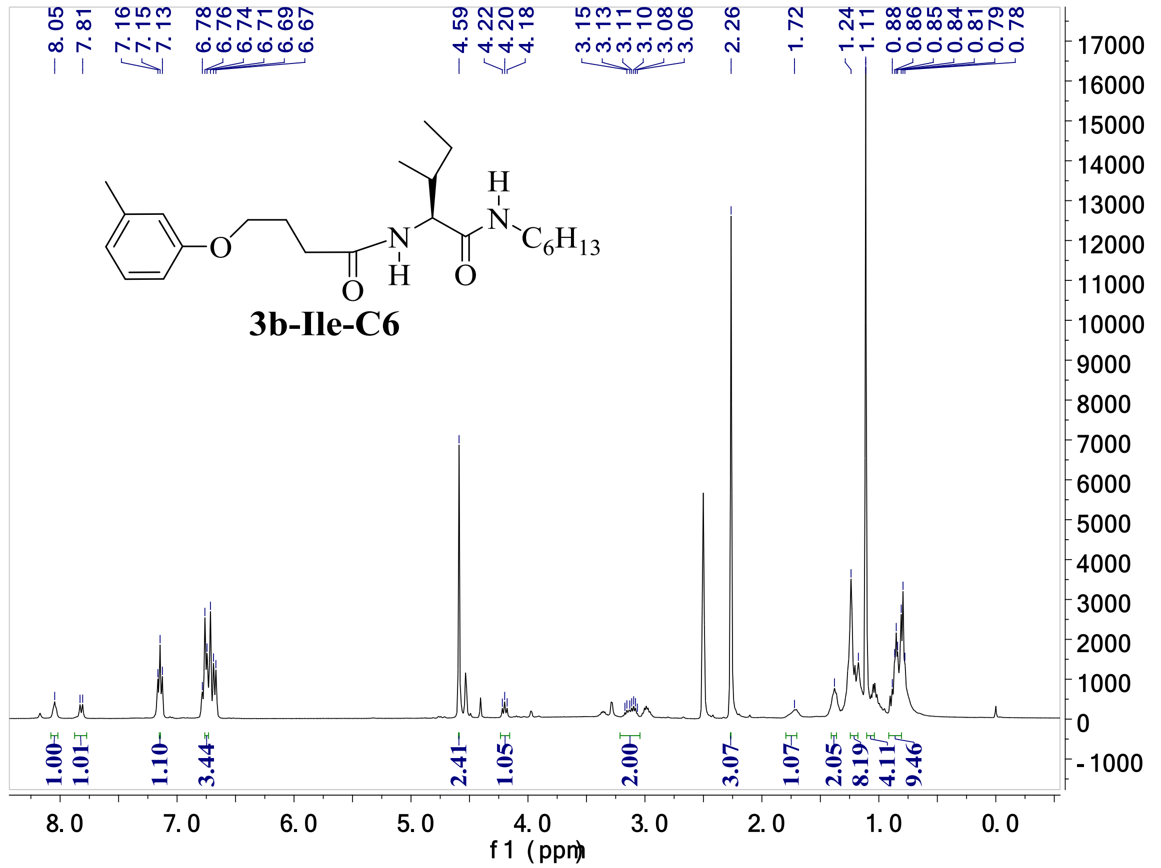

3a-Ile-C4
f1 (ppm)

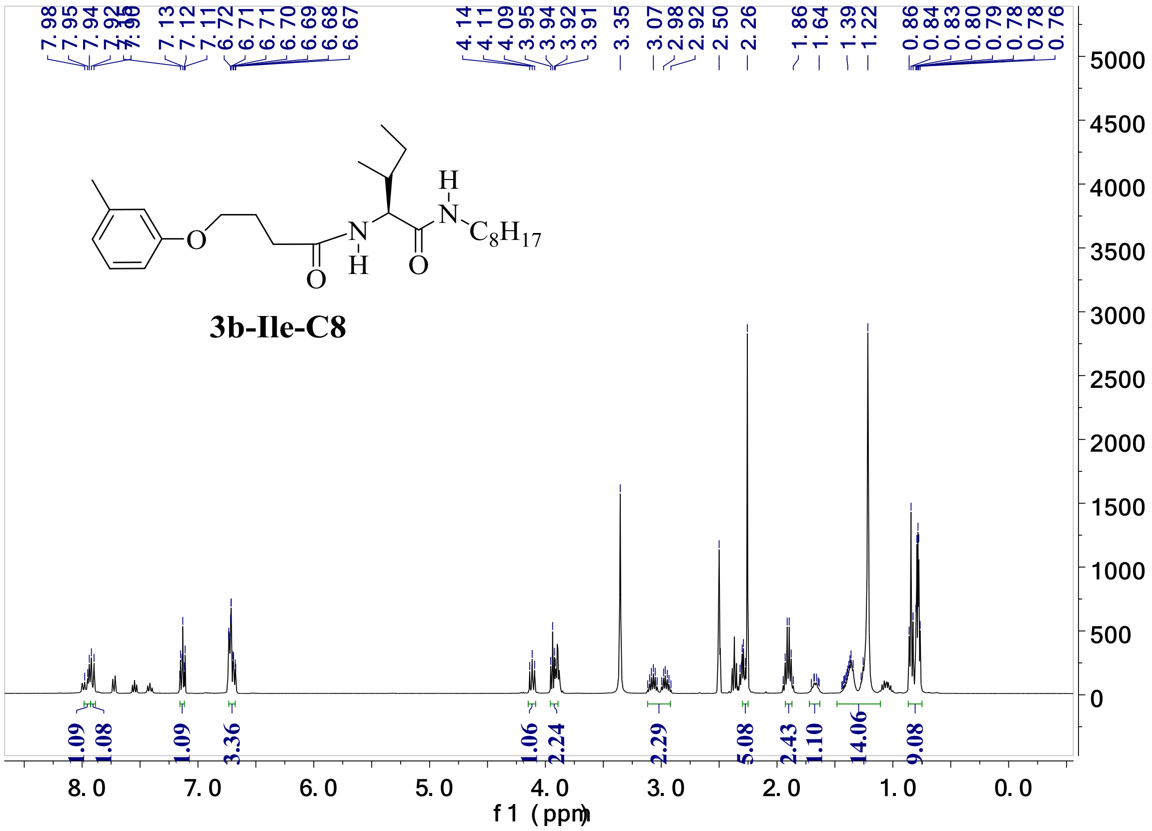

3a-Ile-C6
f1 (ppm)

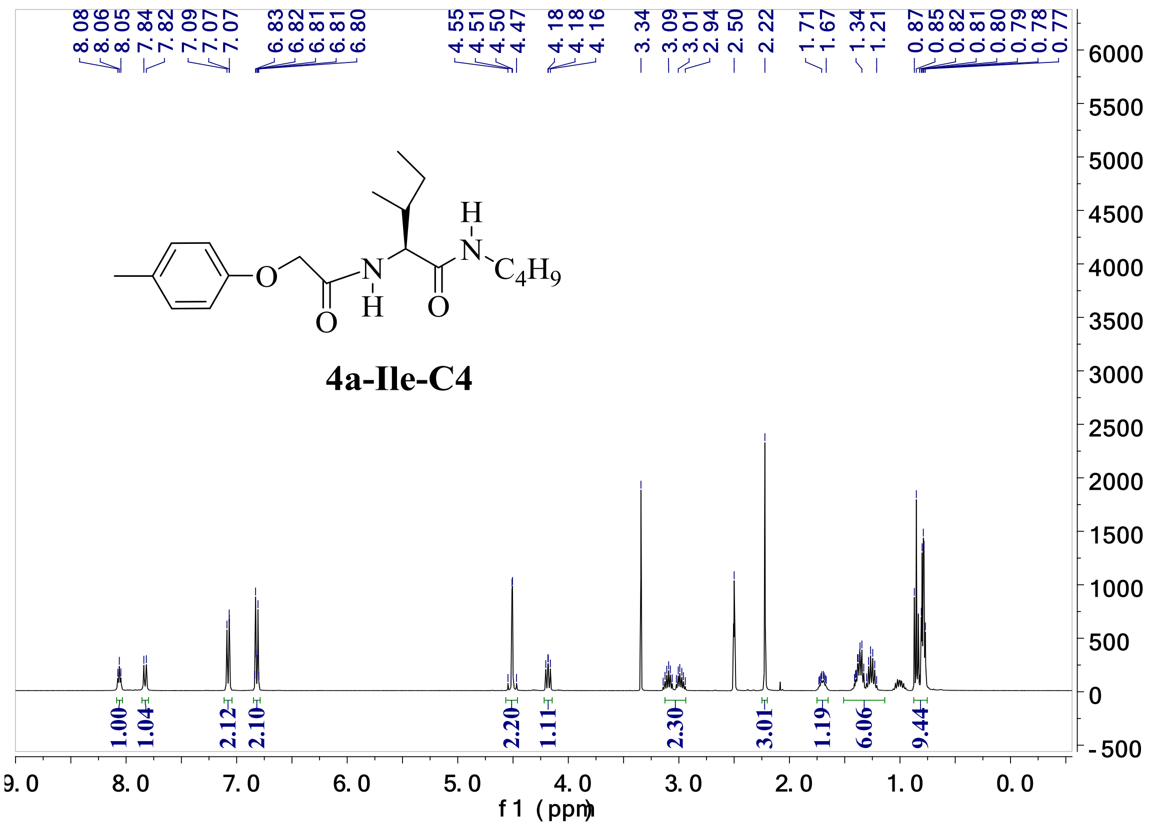

3a-Ile-C8
H
N
C8H17
O
N
H
O
O
f1 (ppm)

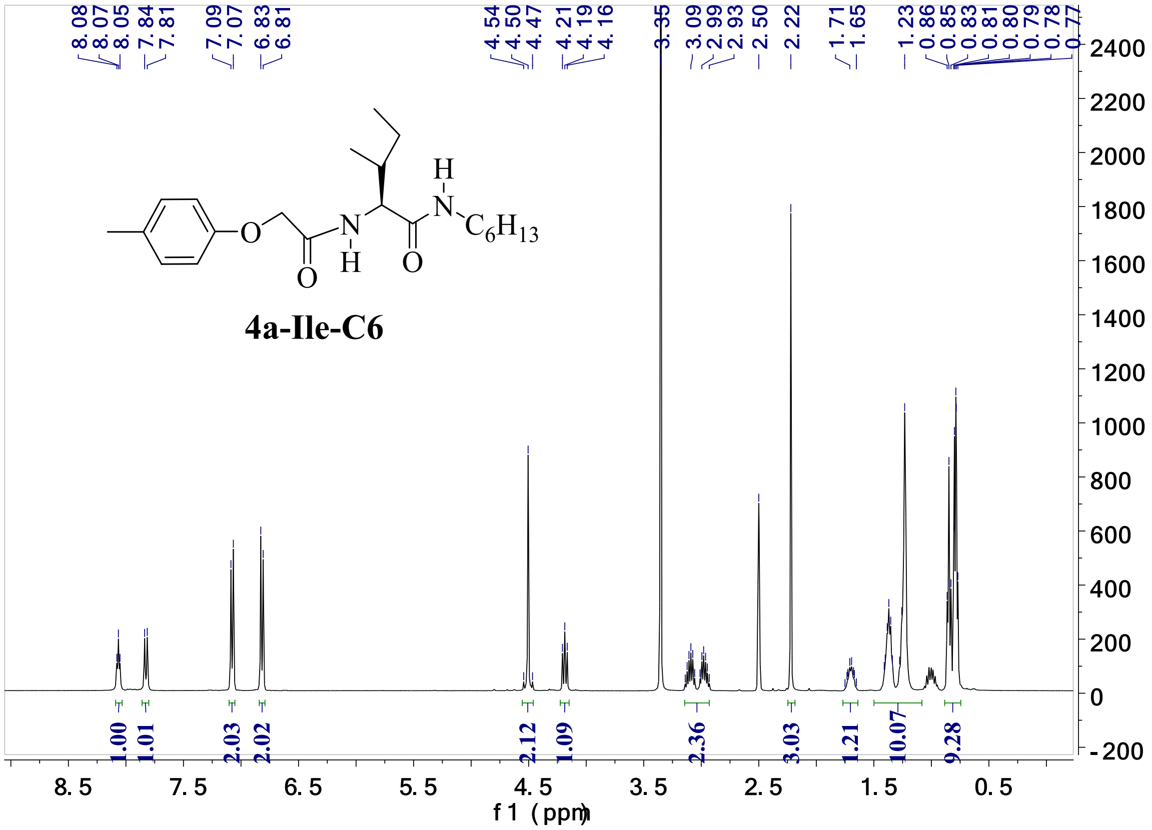

3a-Ile-C8
H
N
C8H17
O
N
H
O
O
f1 (ppm)

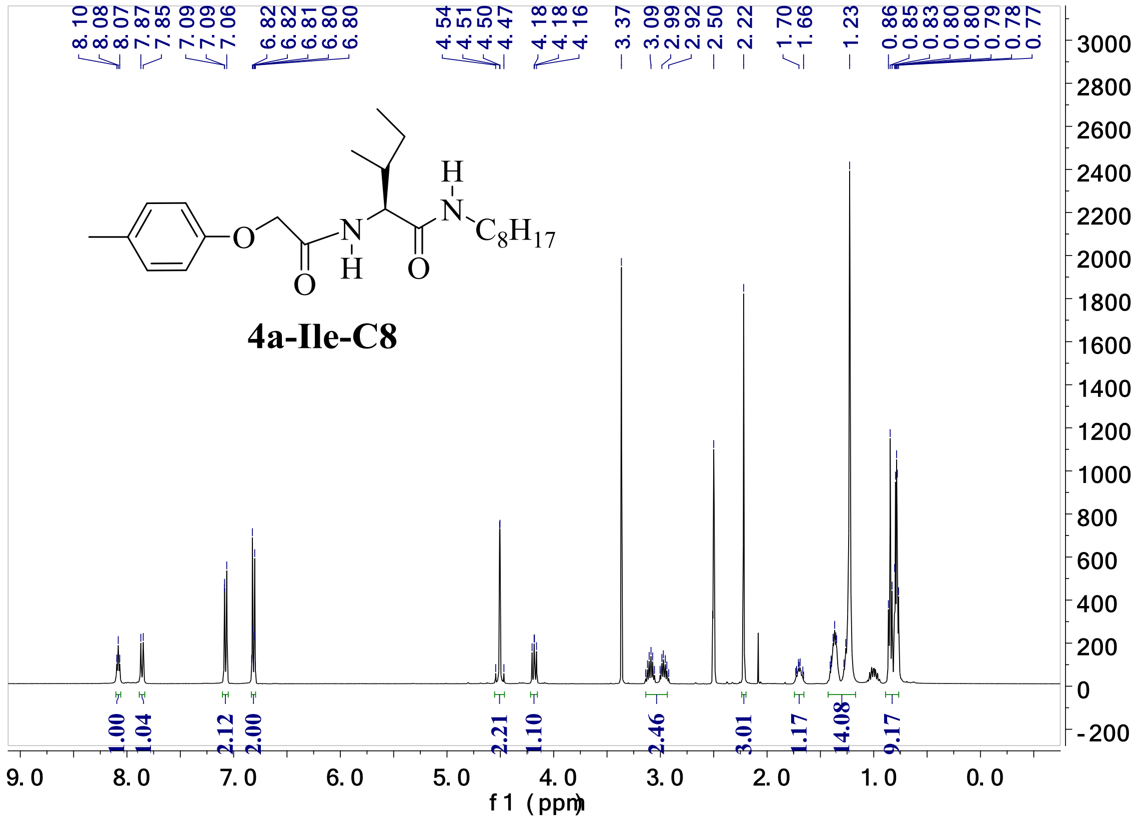


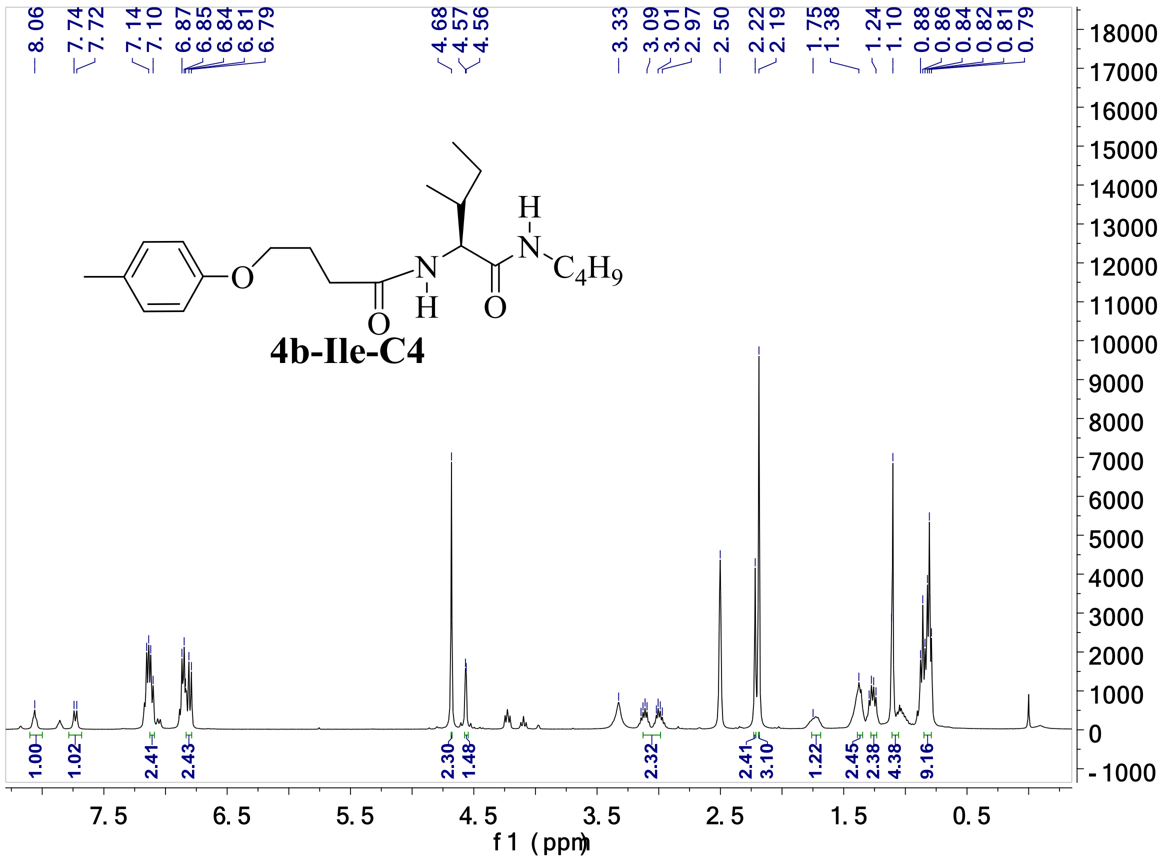



3b-Ile-C8
f1 (ppm)

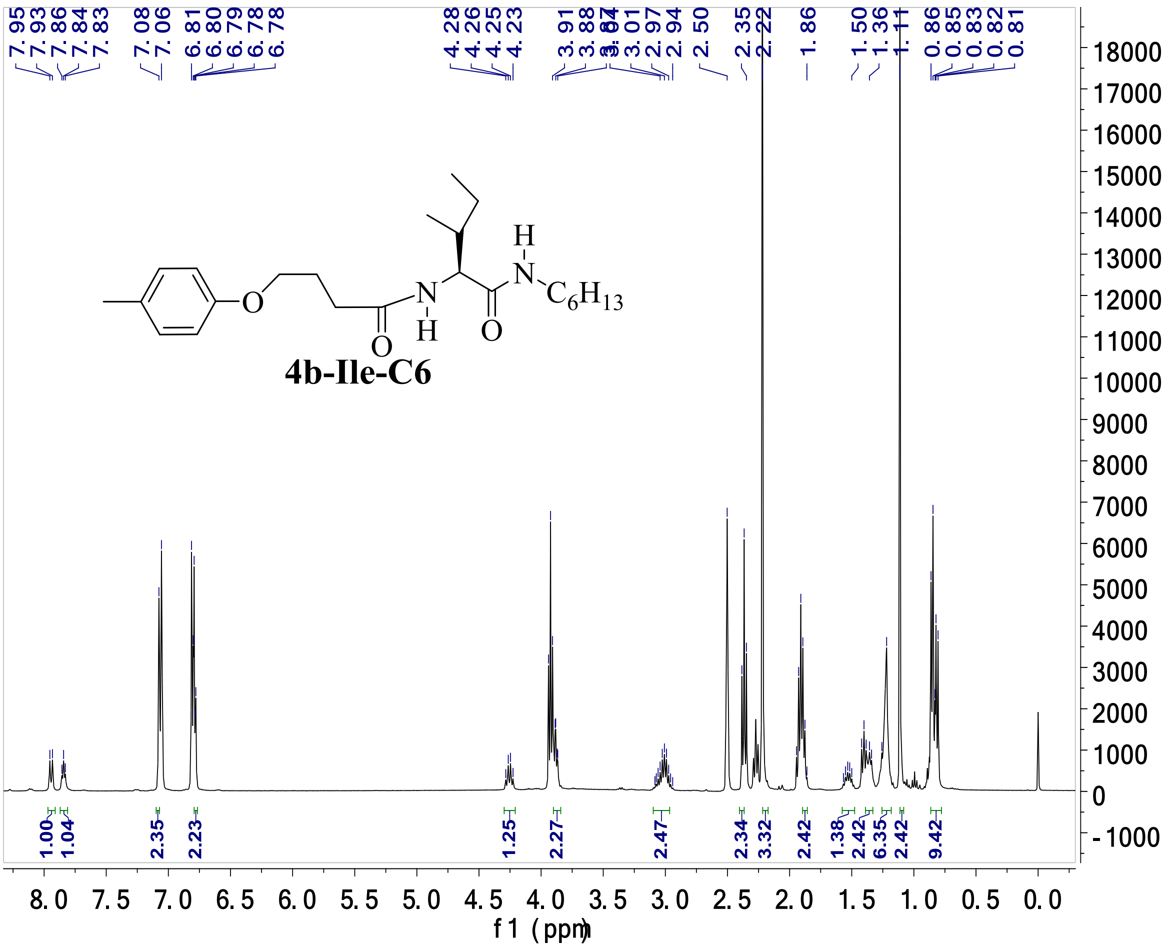

4a-Ile-C4
f1 (ppm)


4a-Ile-C6
f1 (ppm)

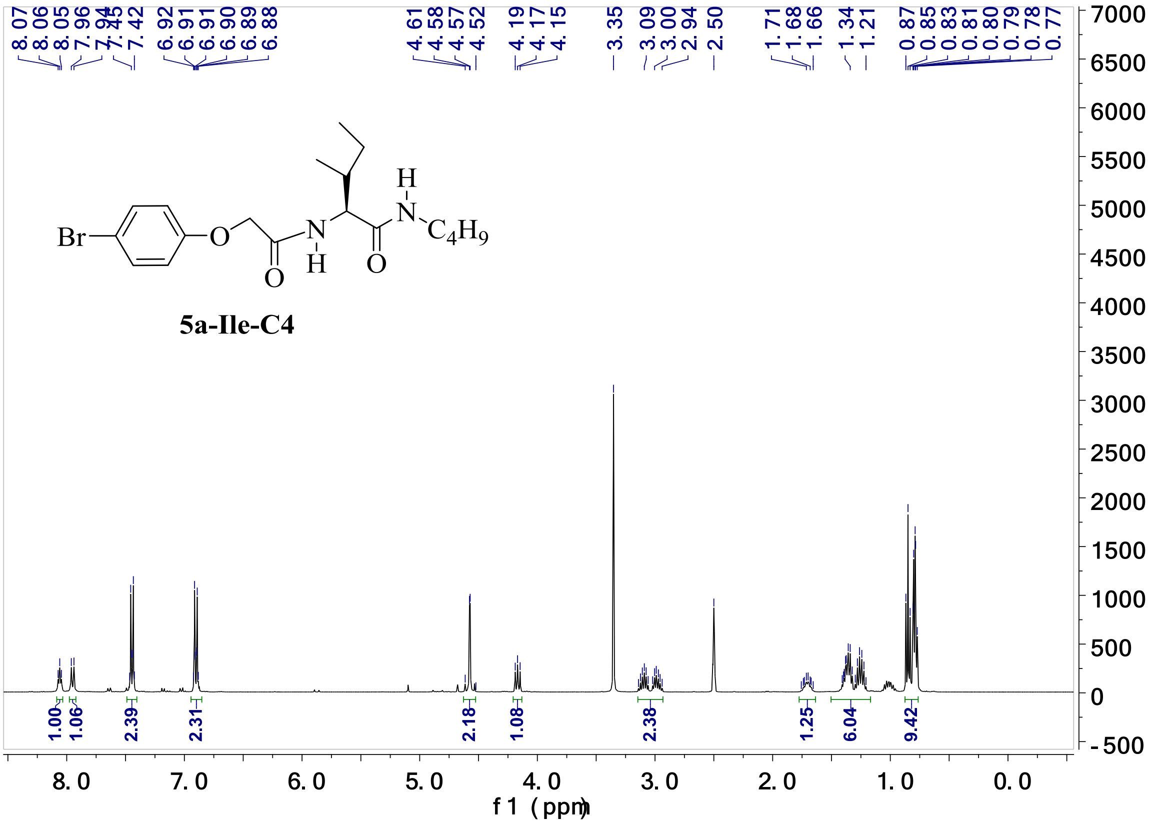

4a-Ile-C8
f1 (ppm)

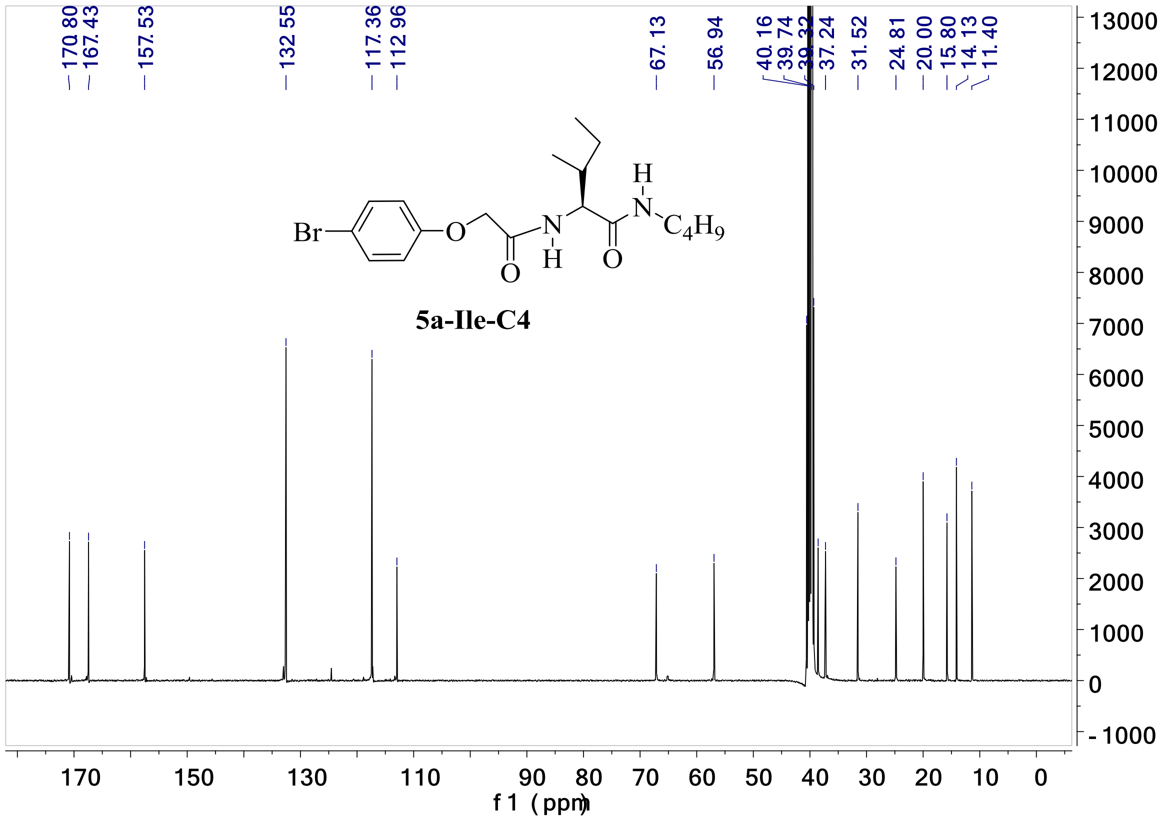


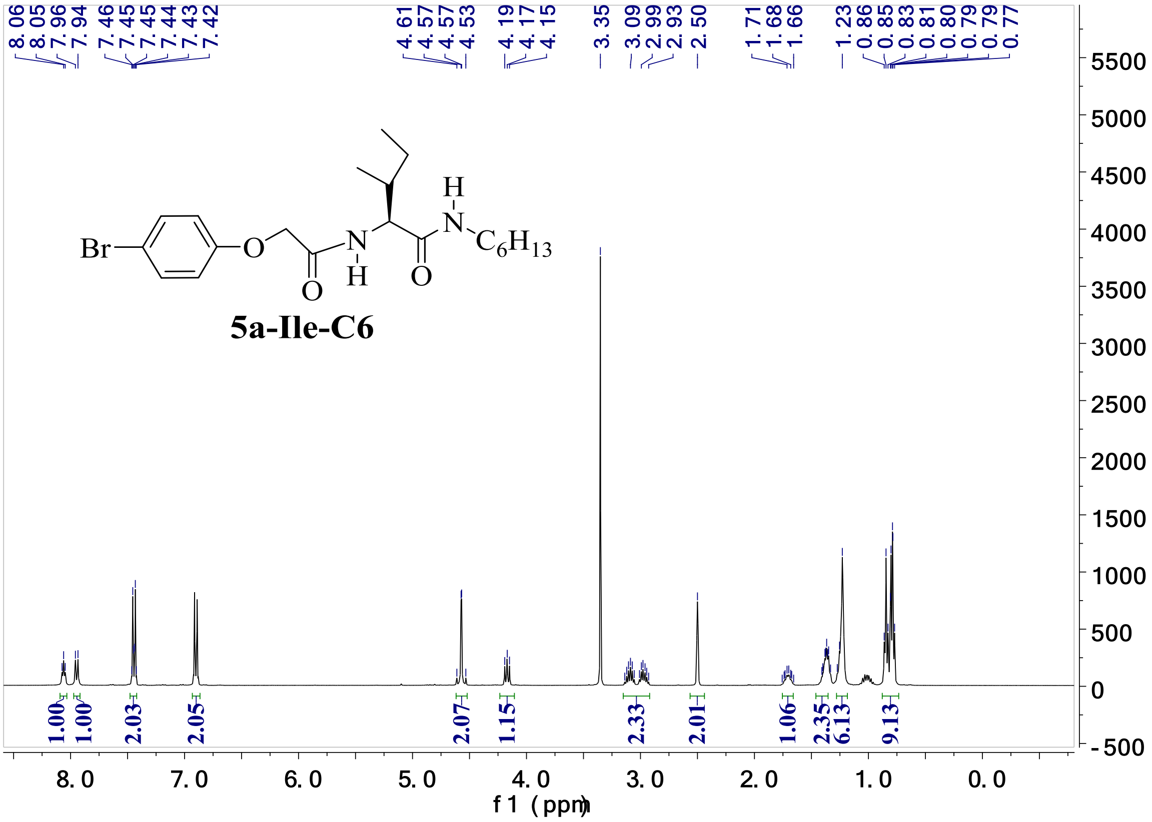
4b-Ile-C4
f1 (ppm)

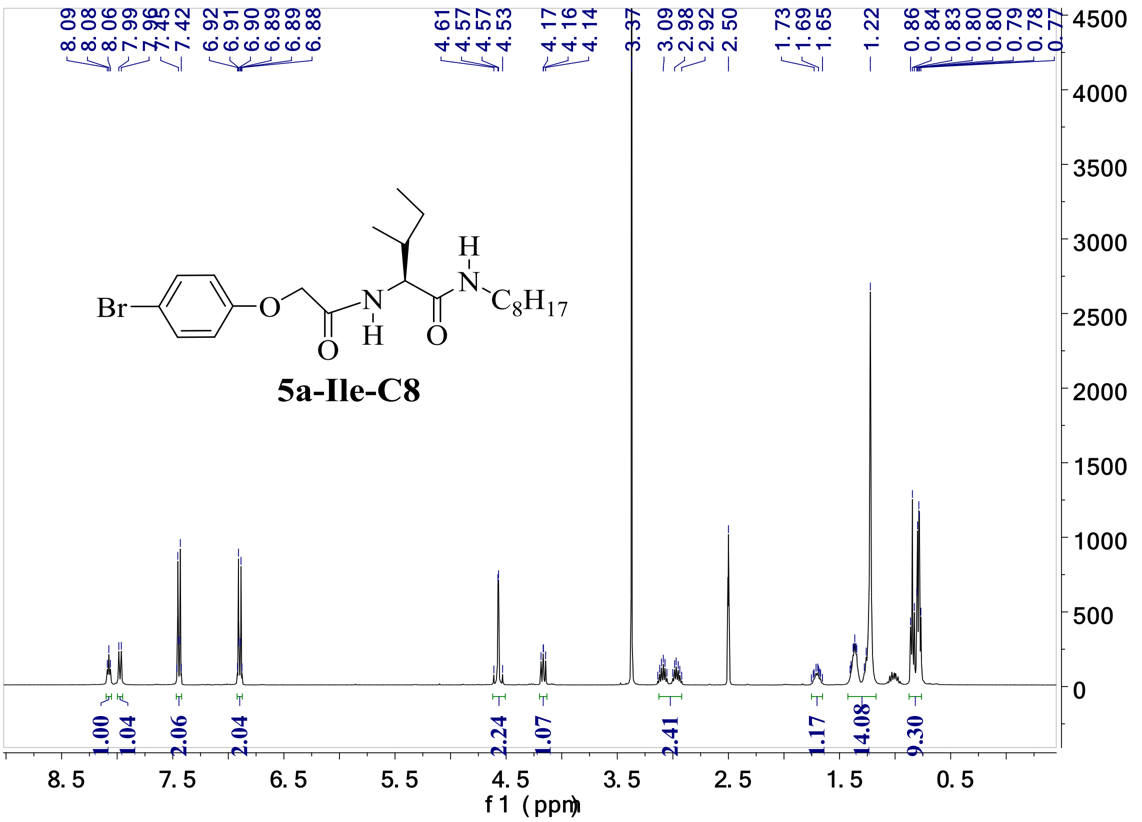


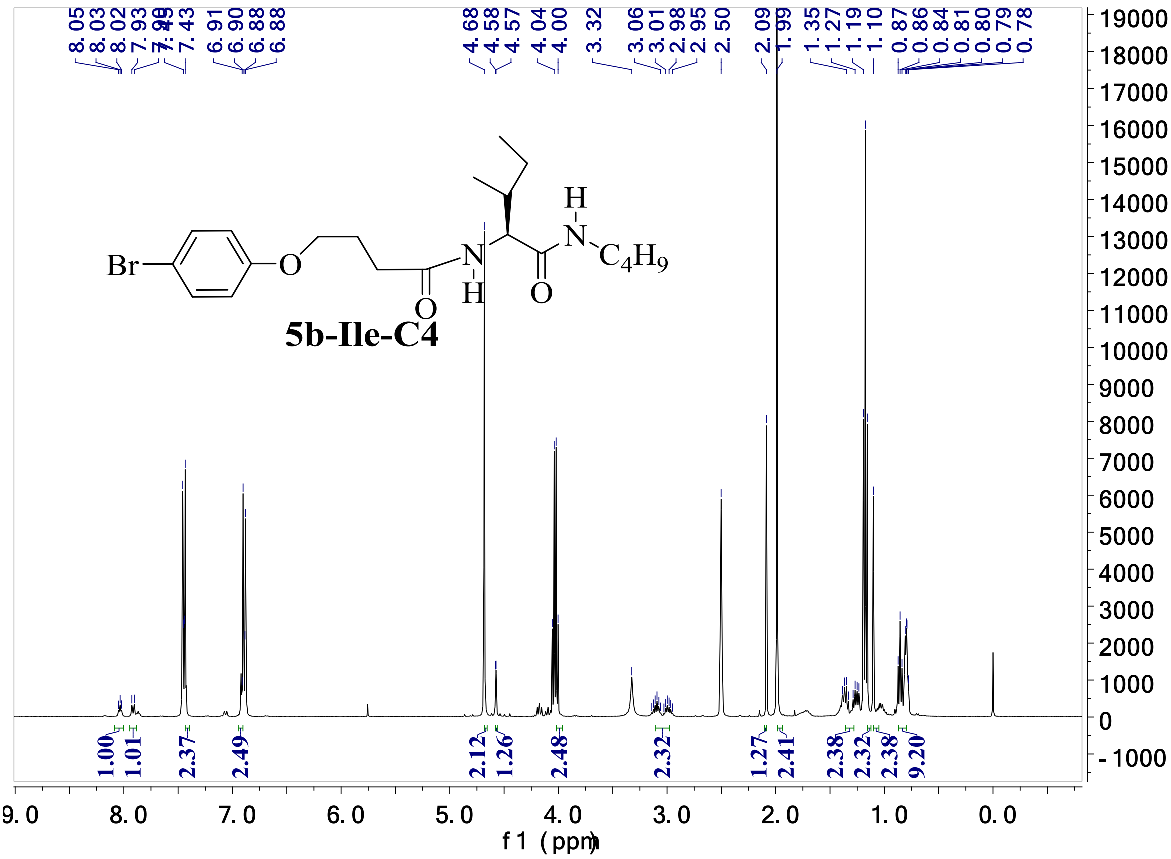
4b-Ile-C6
f1 (ppm)


8.07
8.06
8.05
7.96
7.94
7.45
7.42
6.92
6.91
6.91
6.90
6.89
6.88
4.61
4.58
4.57
4.52
4.19
4.17
4.15
3.35
3.09
3.00
2.94
2.50
1.71
1.68
1.66
1.34
1.21
0.87
0.85
0.83
0.81
0.80
0.79
0.78
0.77
5a-Ile-C4
1.00
1.06
2.39
2.31
2.18
1.08
2.38
1.25
6.04
9.42
f1 (ppm)

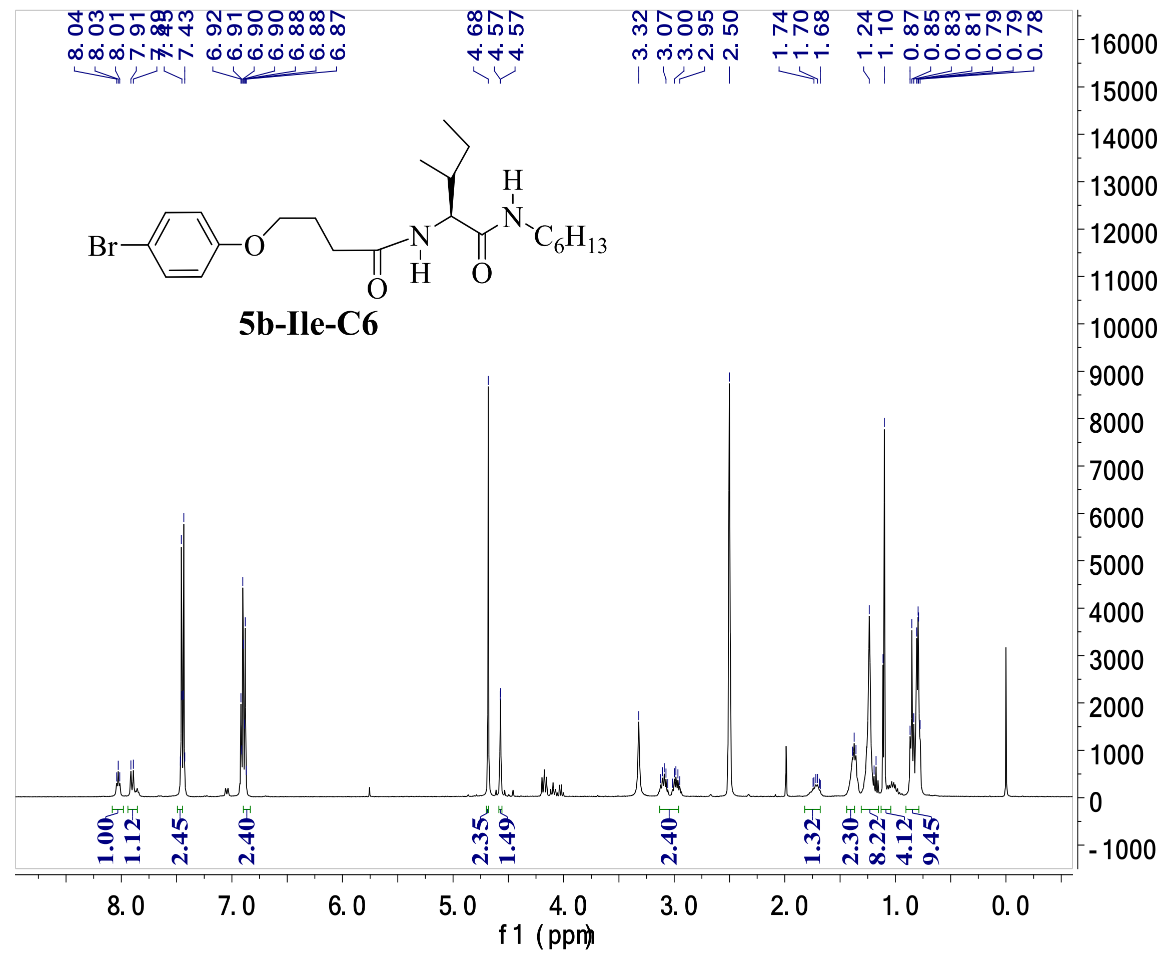

170.80
167.43
157.53
132.55
117.36
112.96
67.13
56.94
40.16
39.74
39.32
37.24
31.52
24.81
20.00
15.80
14.13
11.40
5a-Ile-C4
f1 (ppm)


5a-Ile-C6

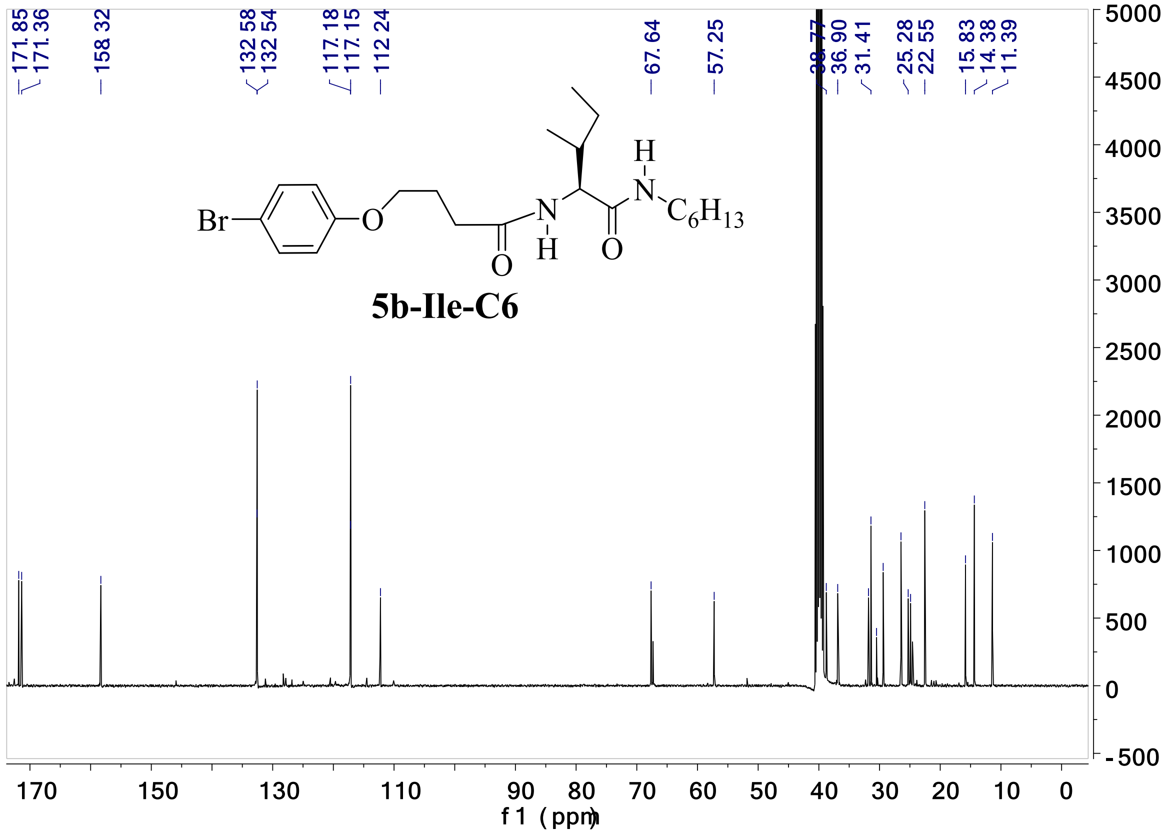

5a-Ile-C8

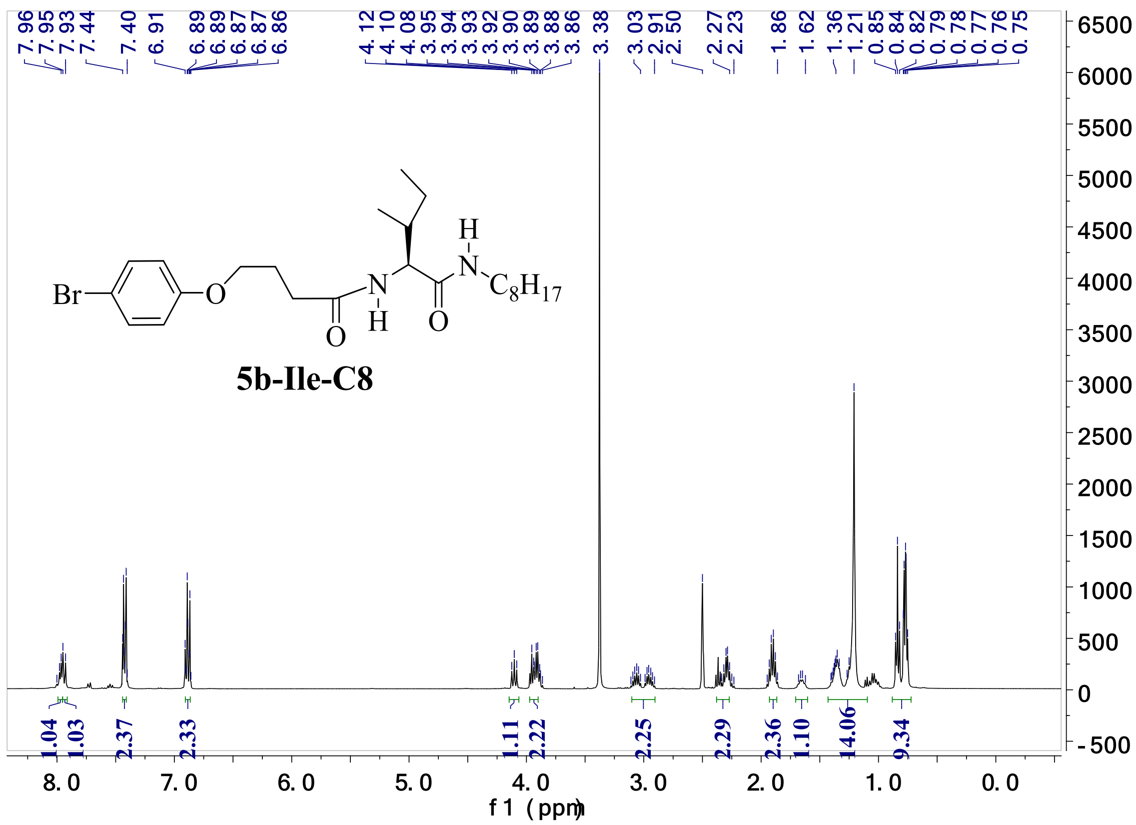


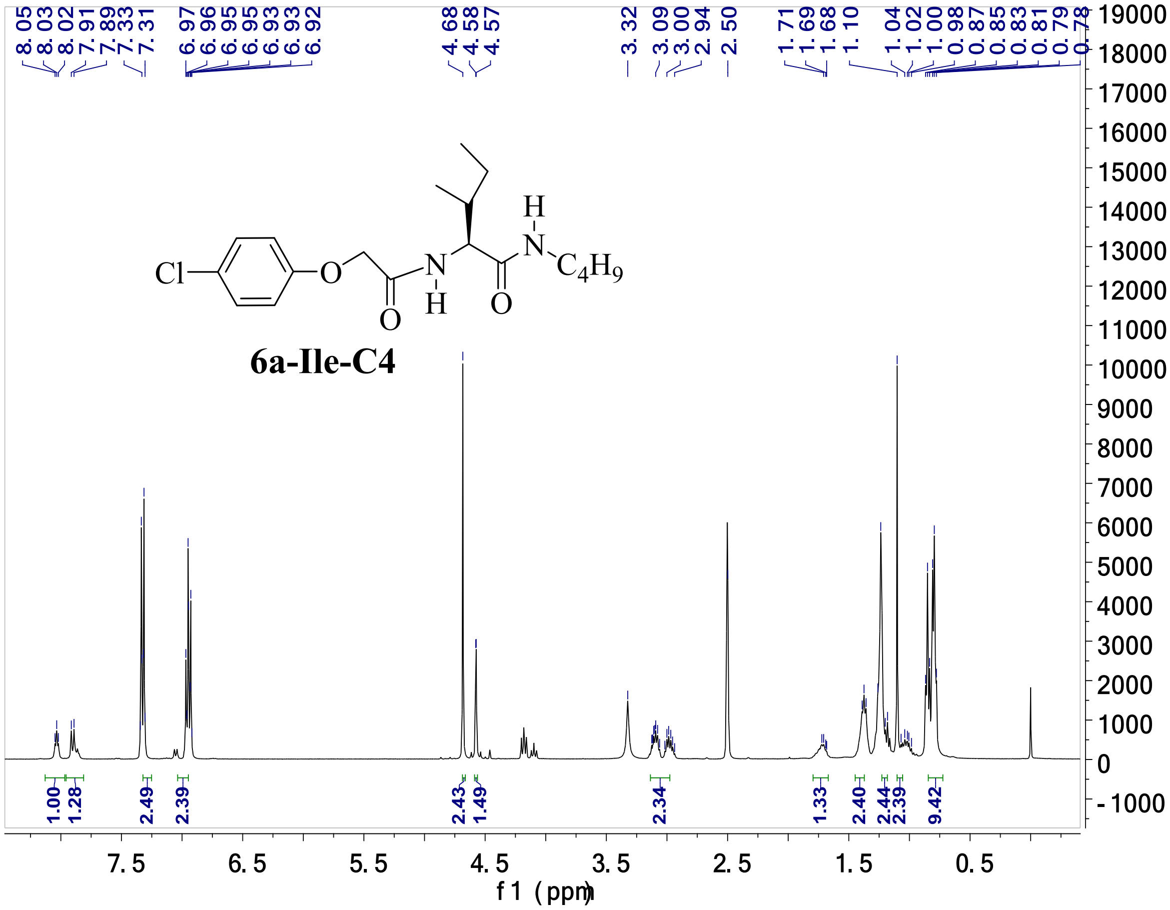
5b-Ile-C4

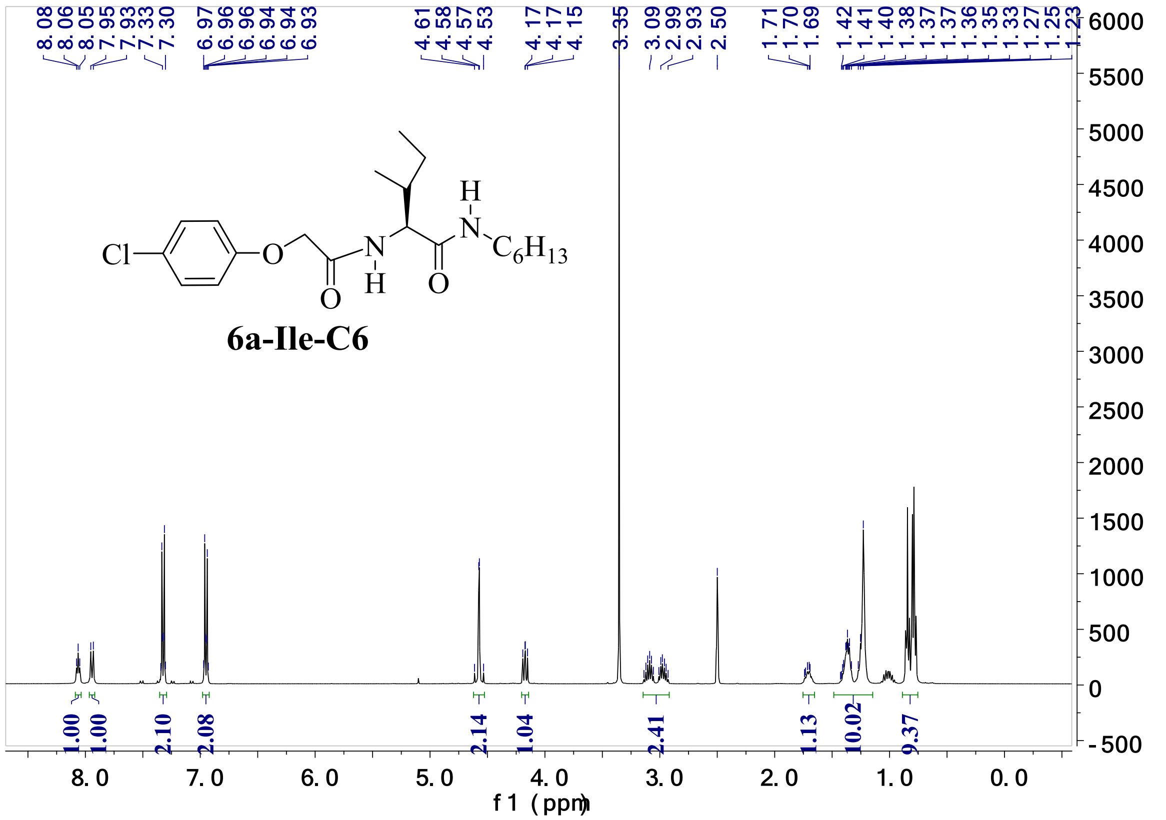


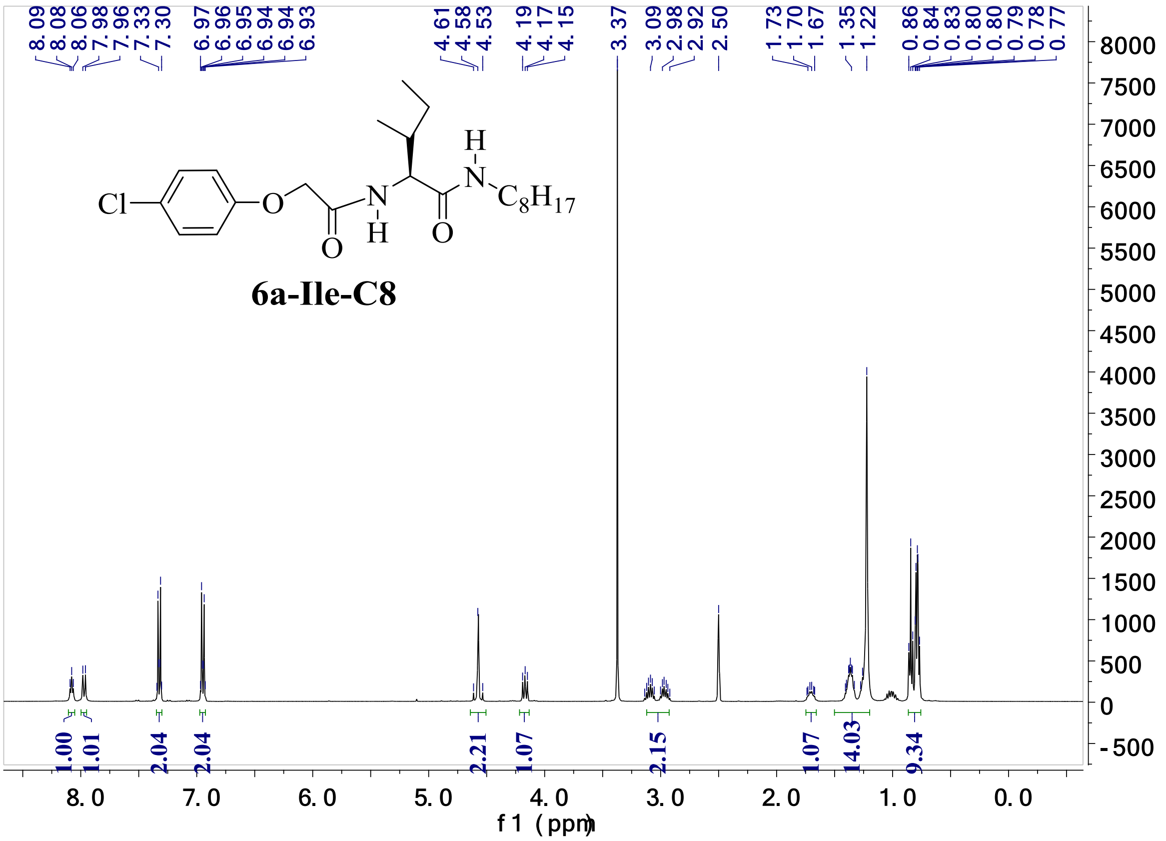
5b-Ile-C6

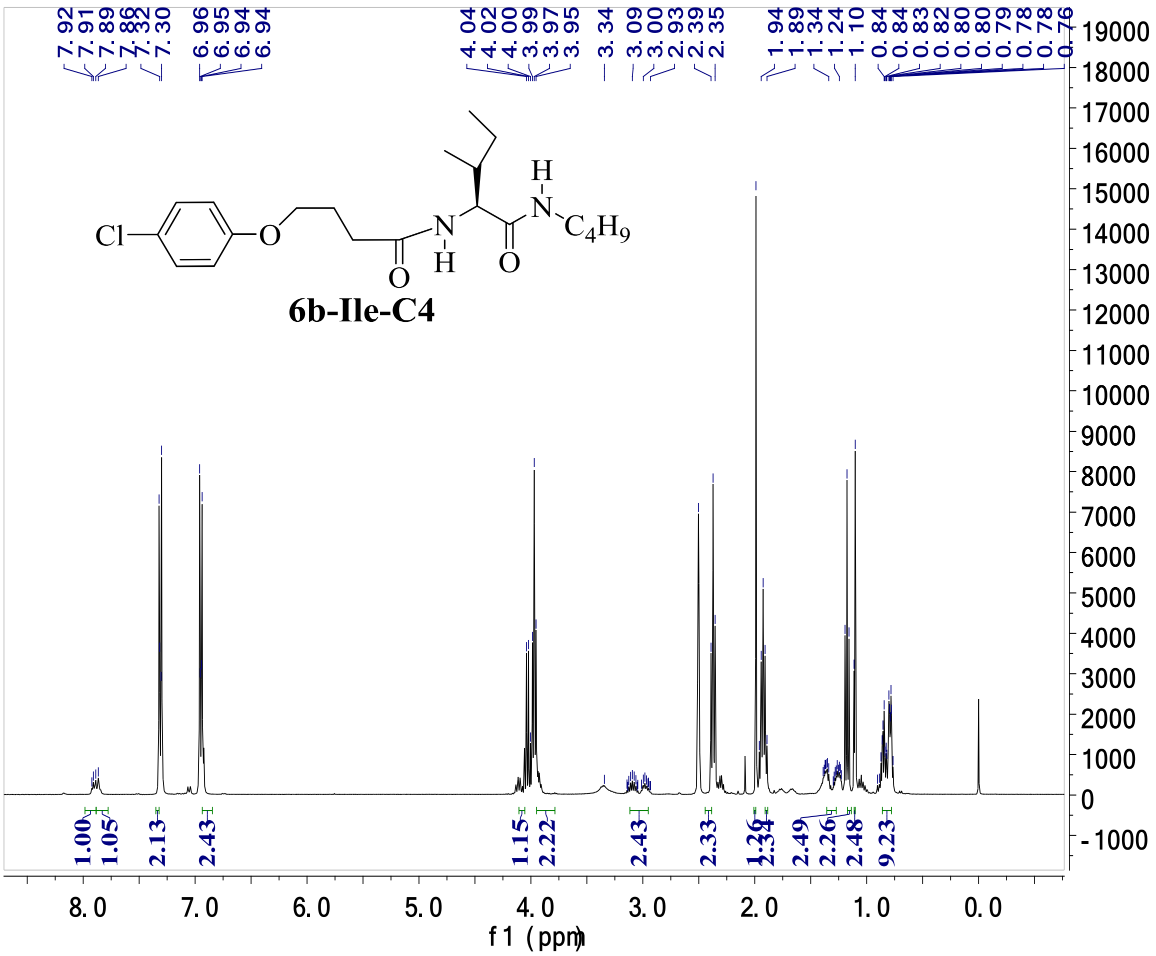

5b-Ile-C6

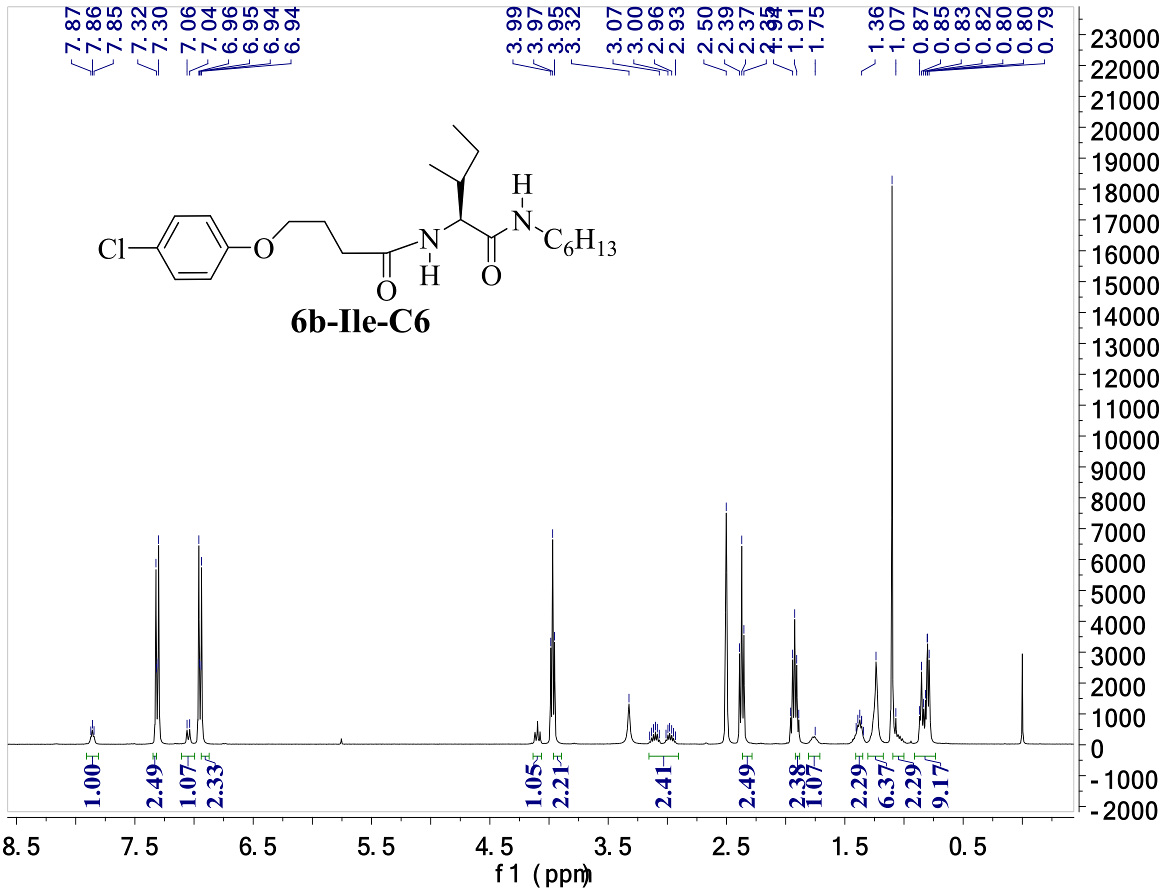

5b-Ile-C8

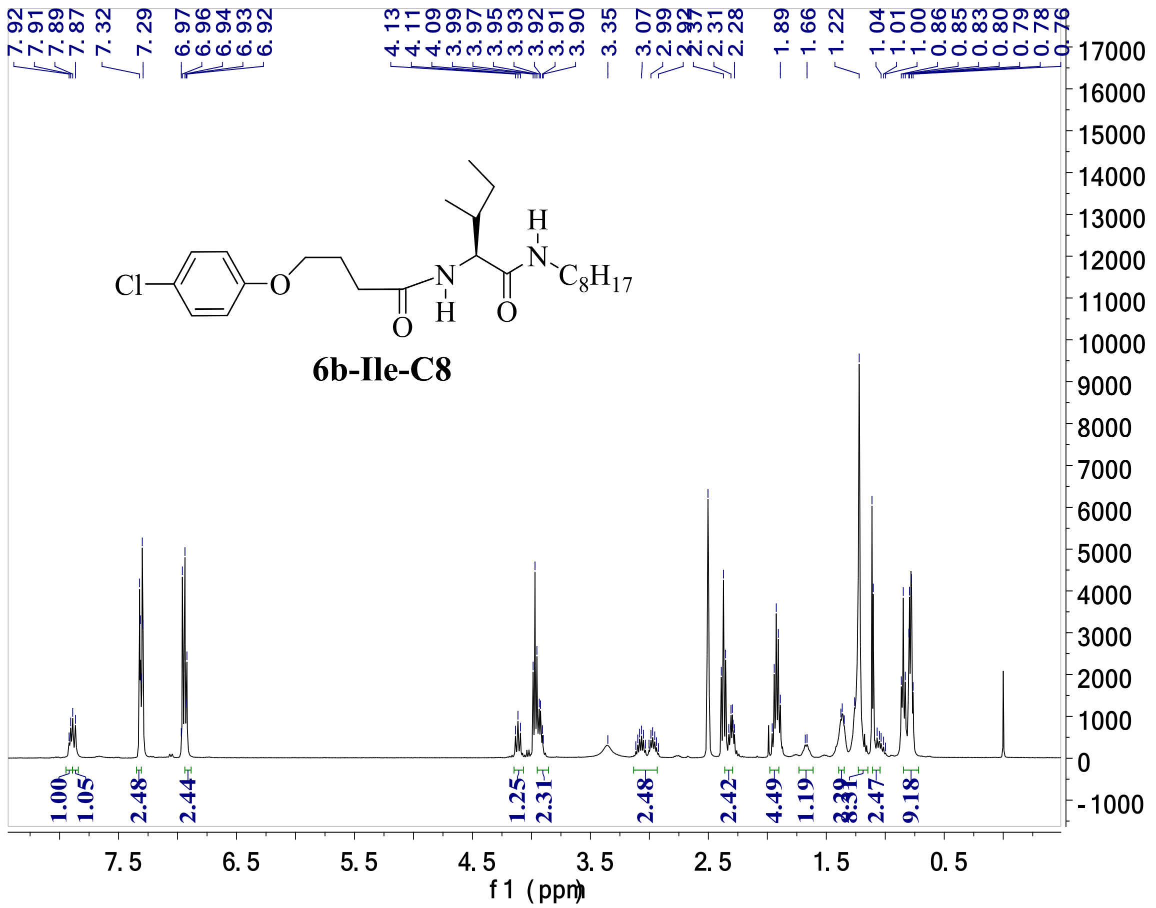


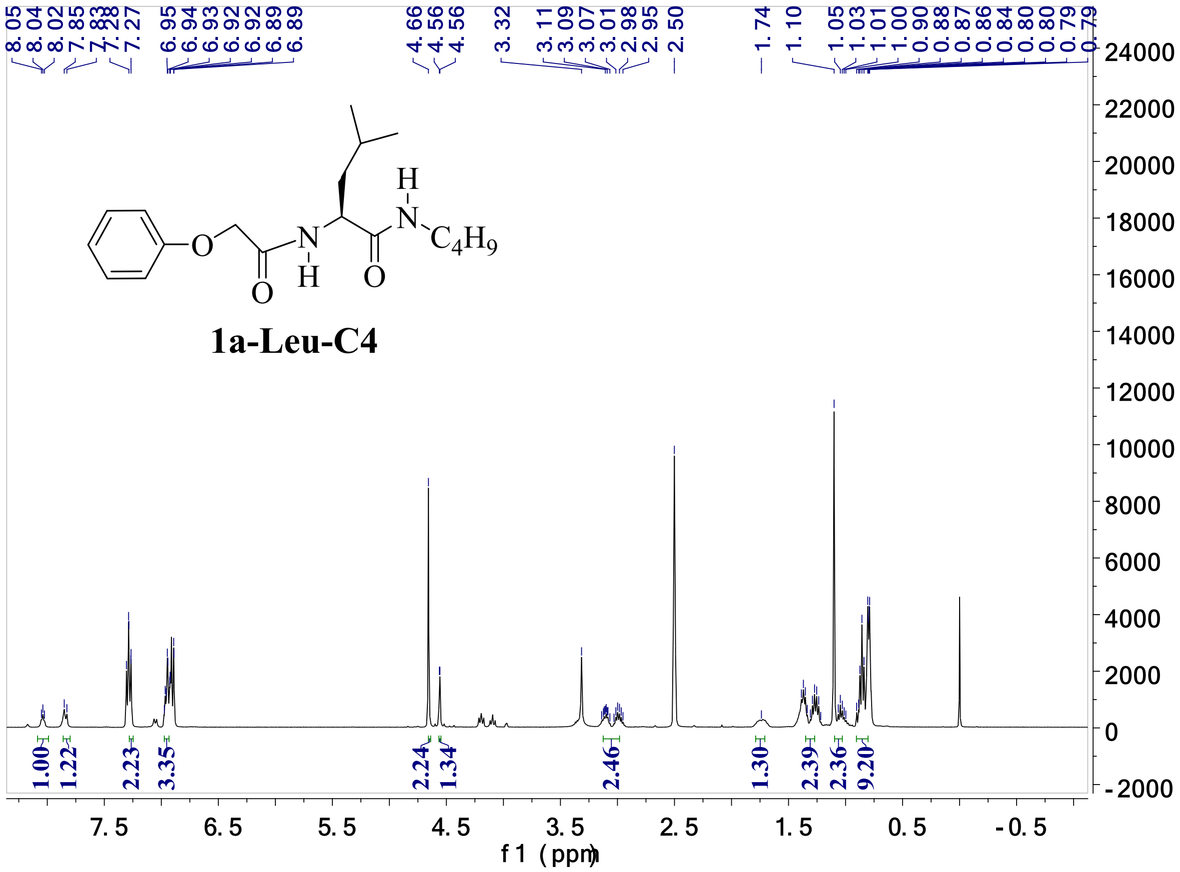


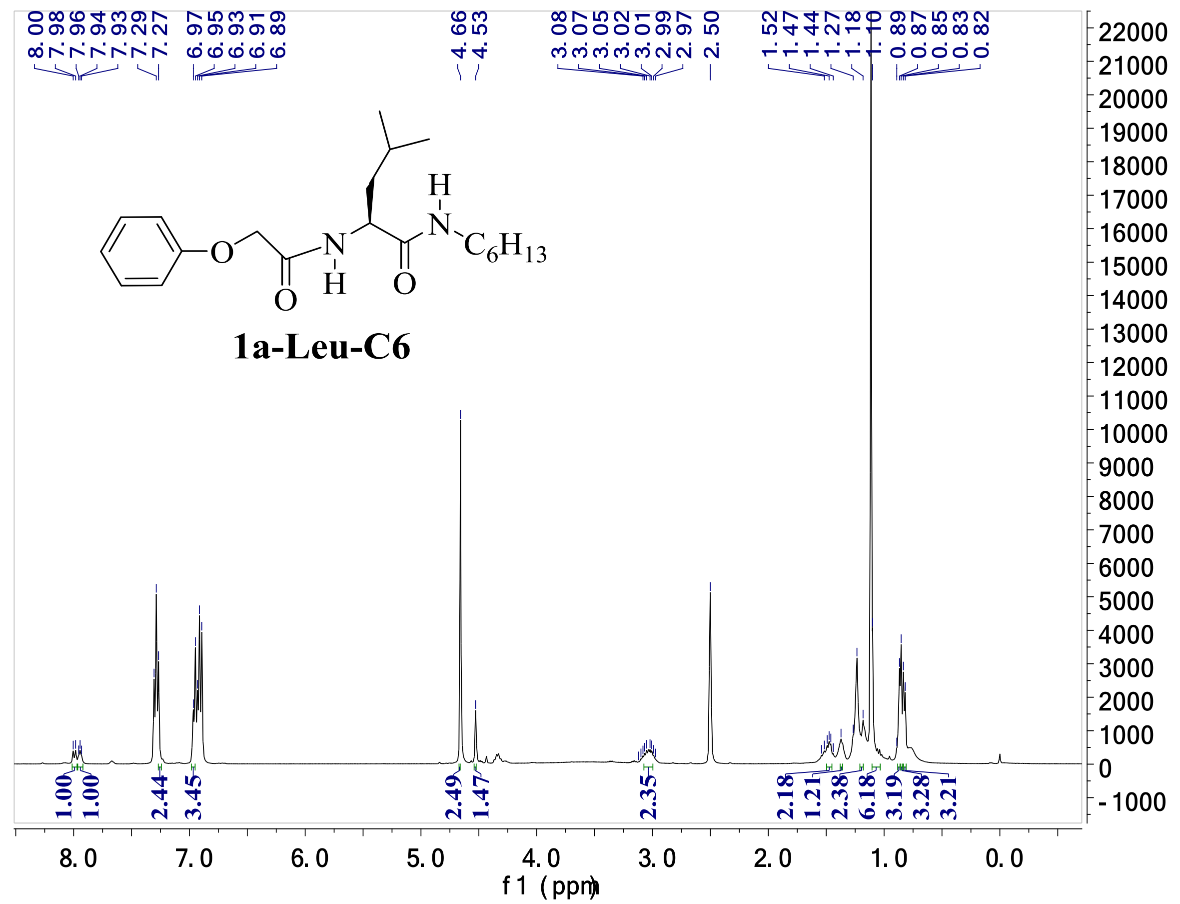

6a-Ile-C8
Cl
O
N
H
C8H17
f1 (ppm)

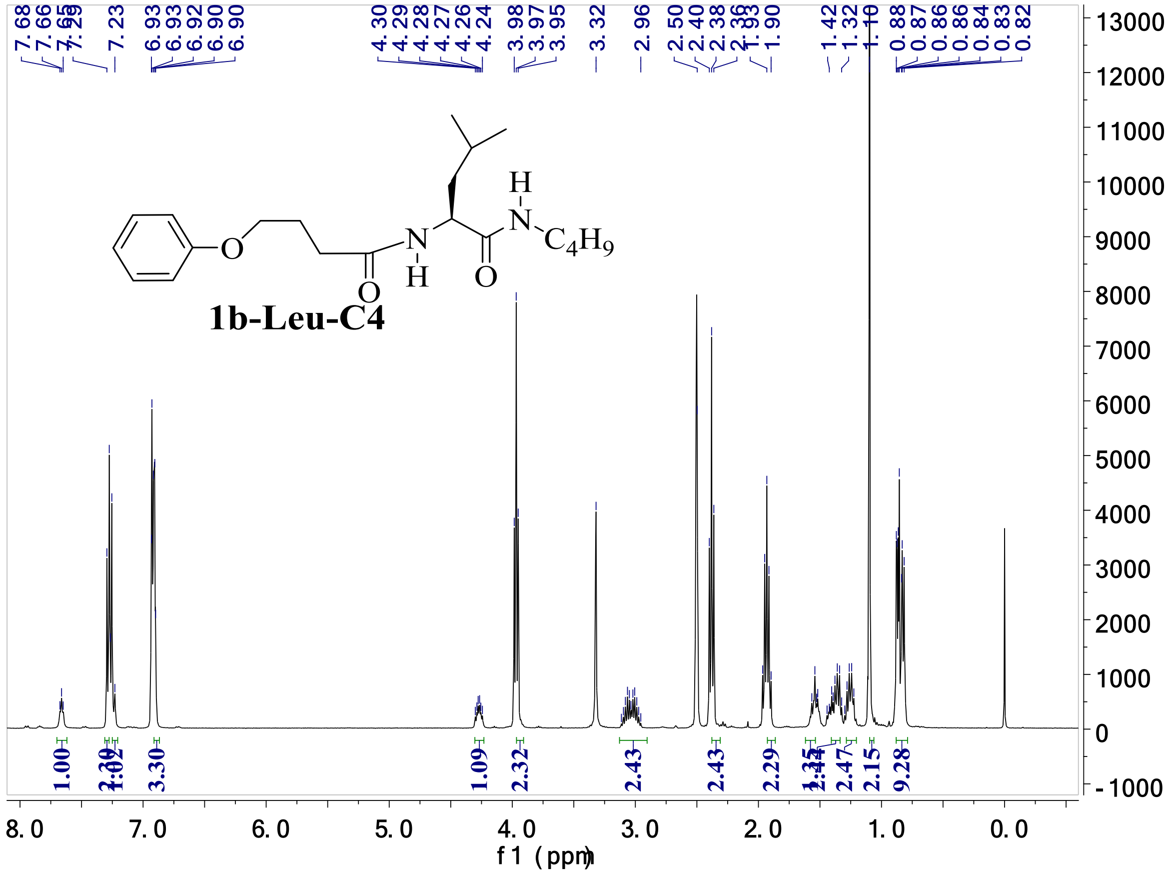

6b-Ile-C4
Cl
O
N
H
C4H9
f1 (ppm)

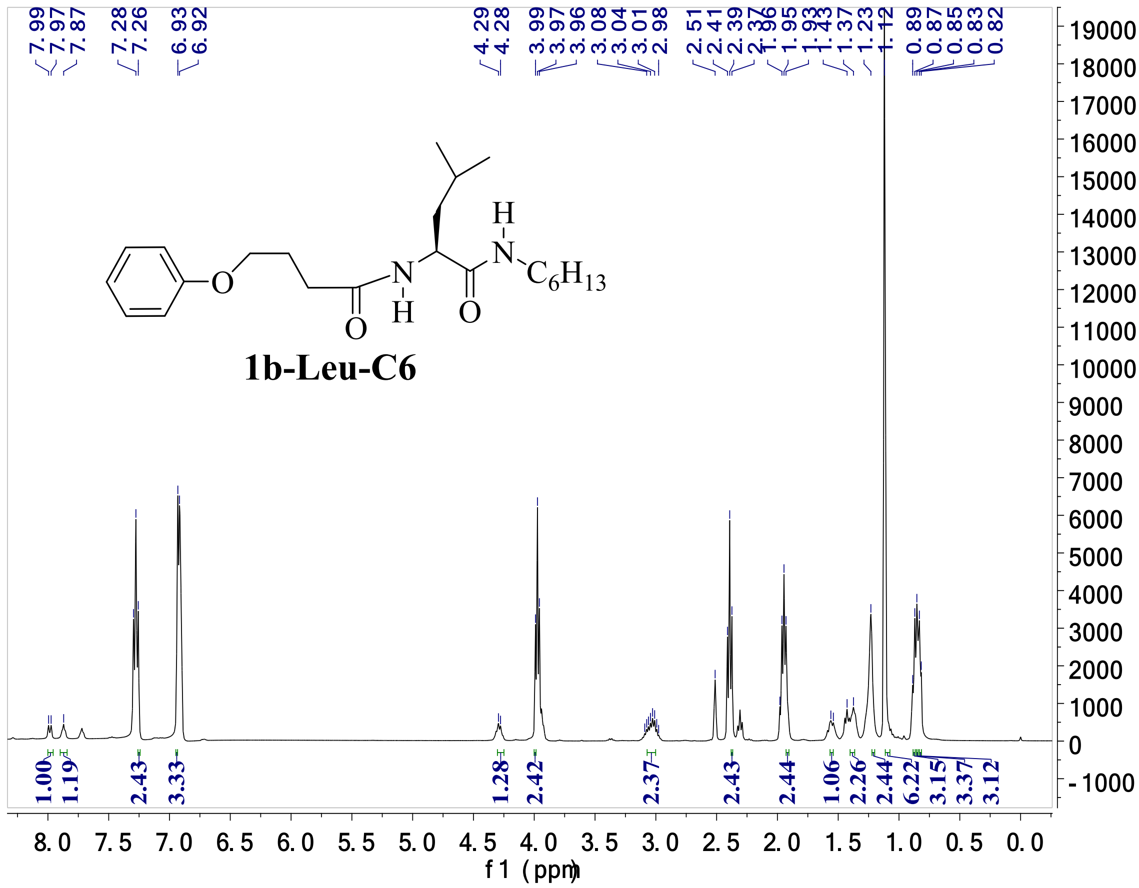


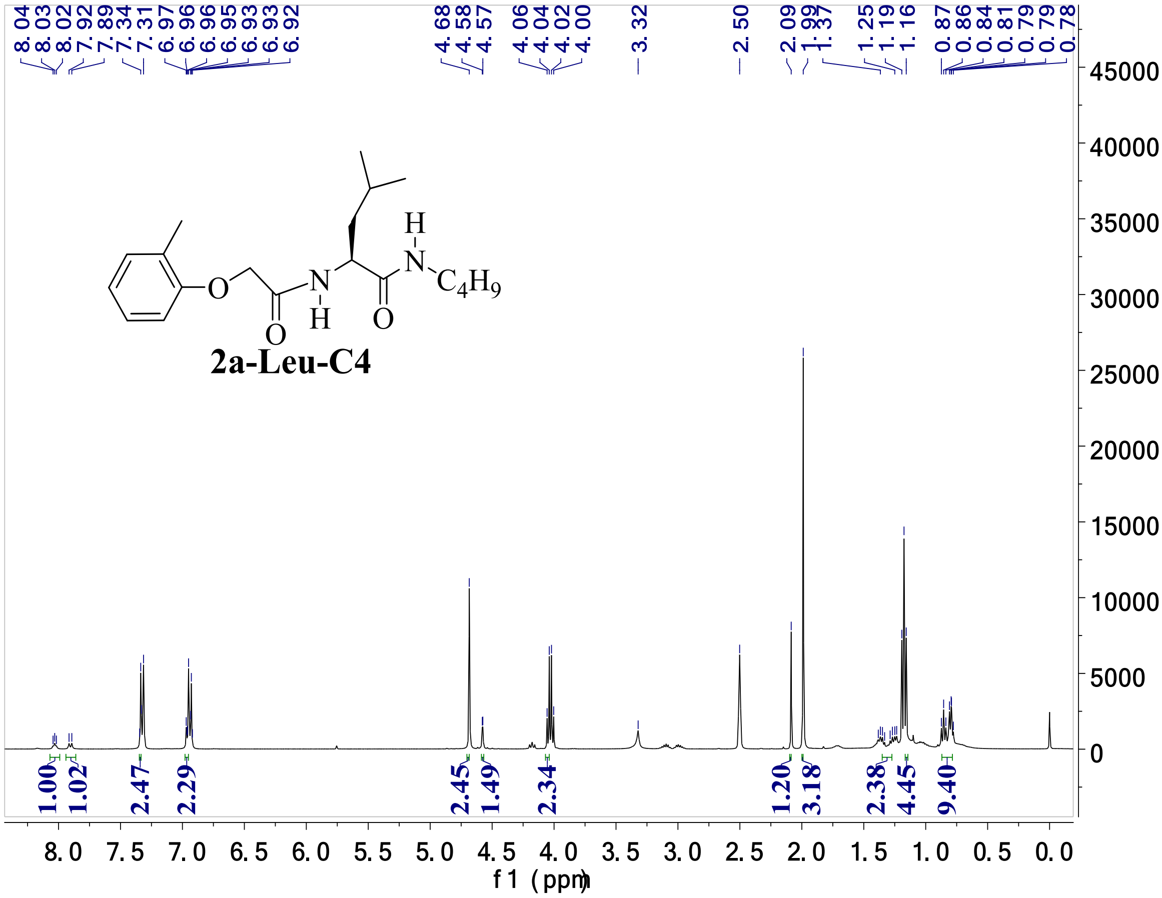


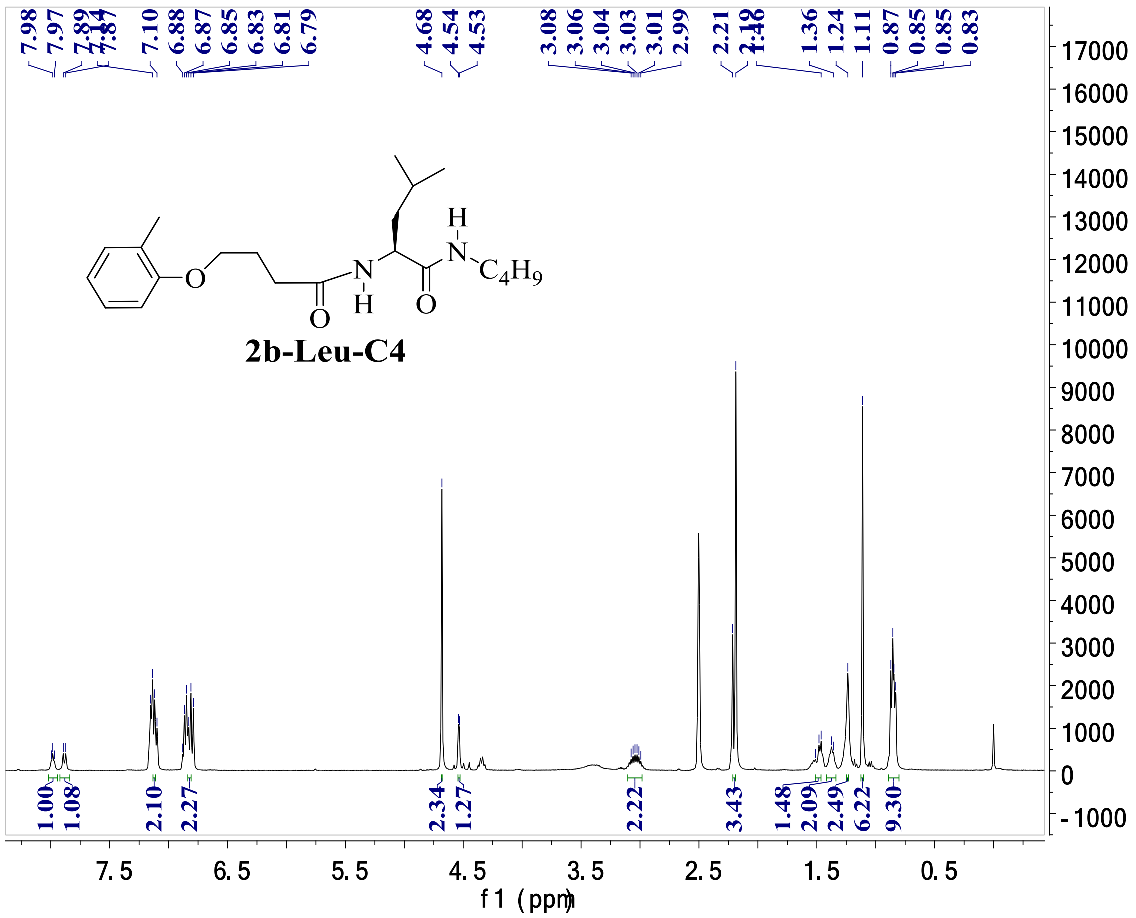

1a-Leu-C4
f1 (ppm)

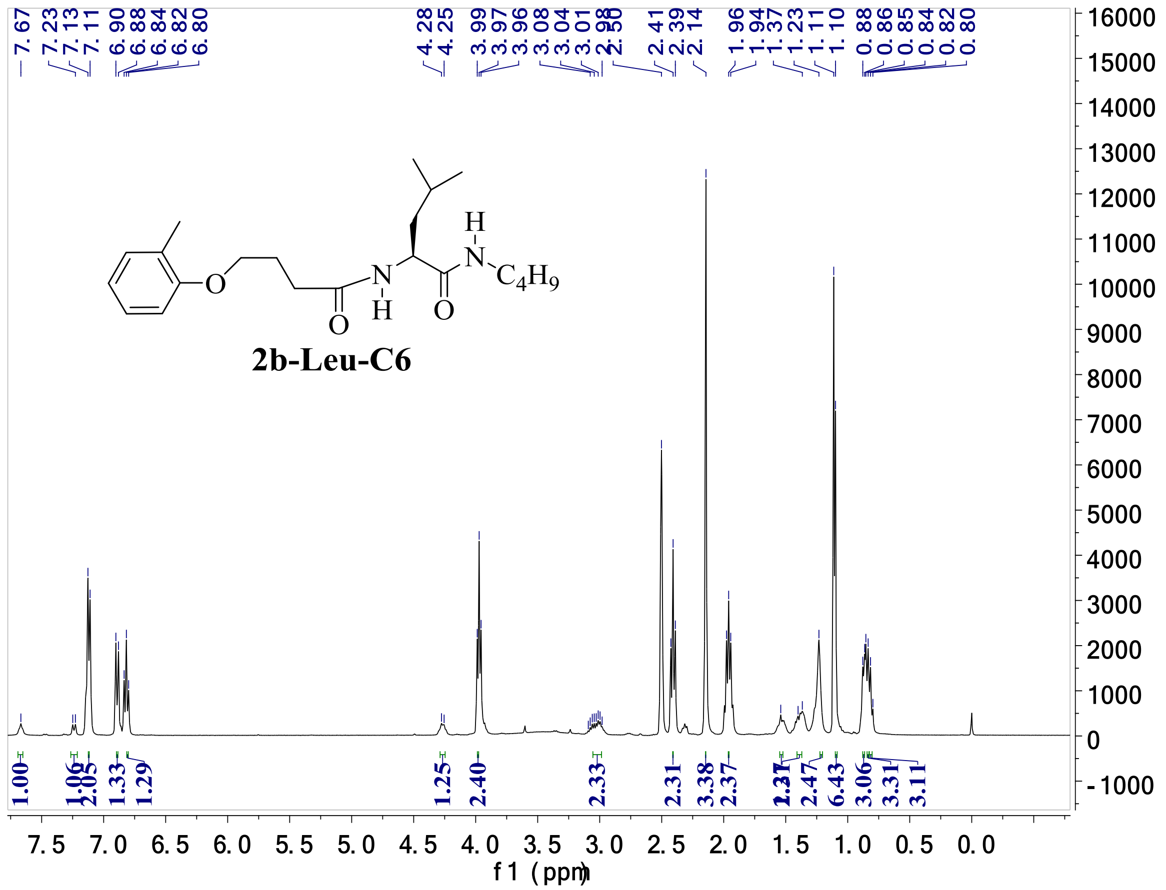

1a-Leu-C6
f1 (ppm)

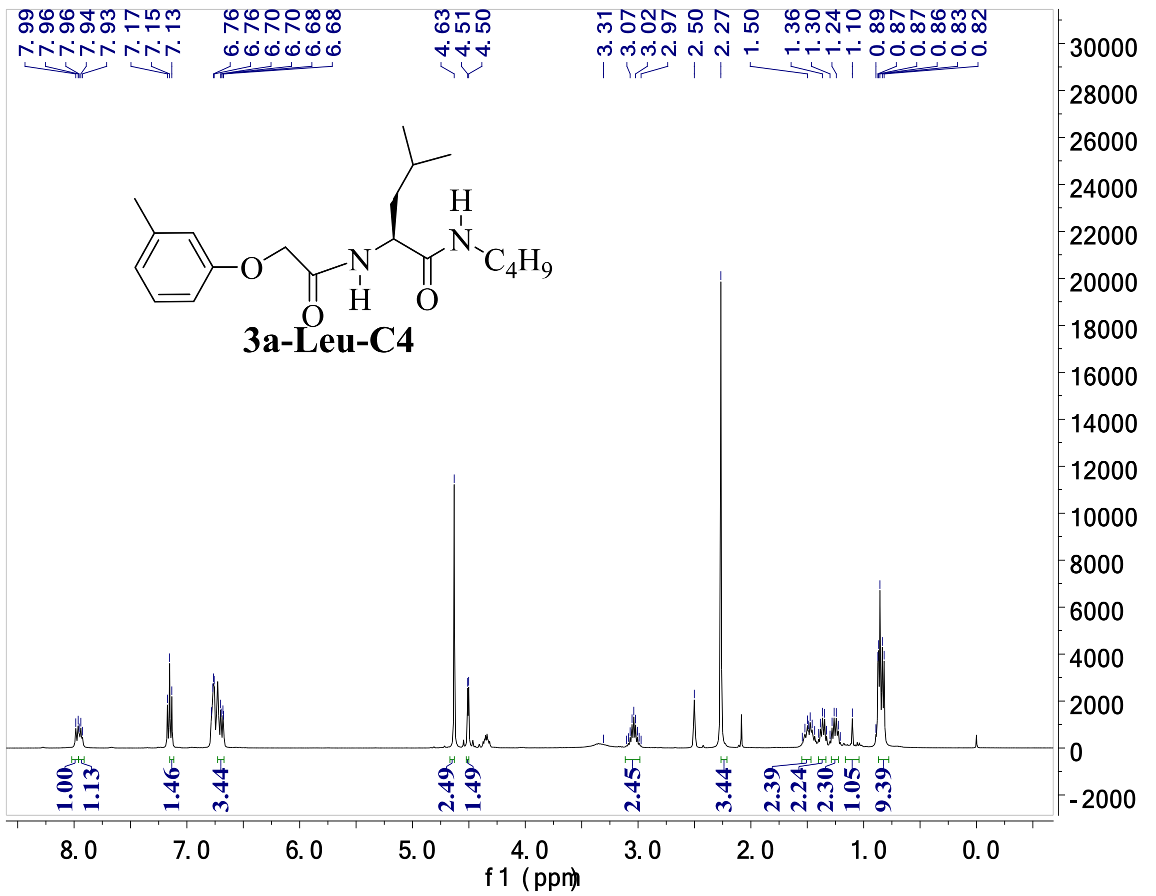


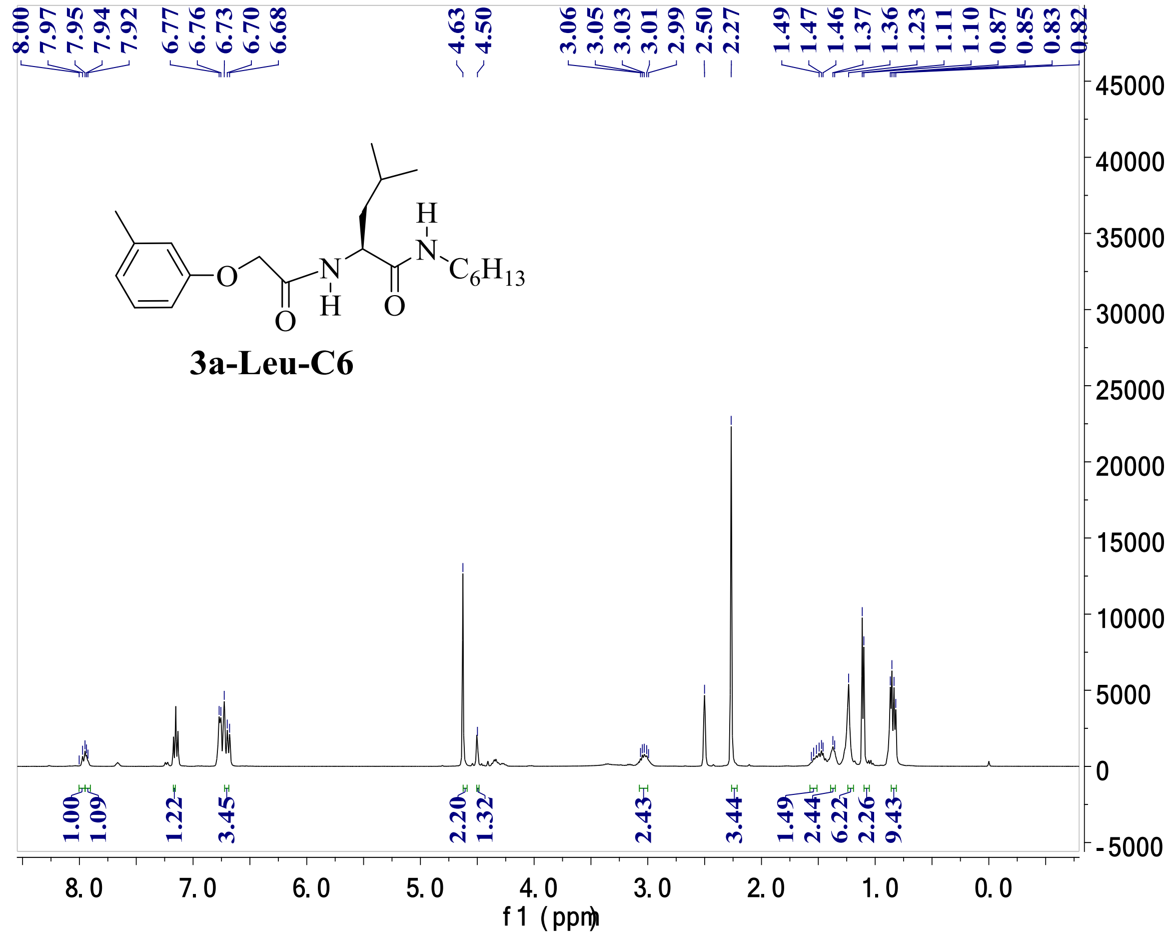


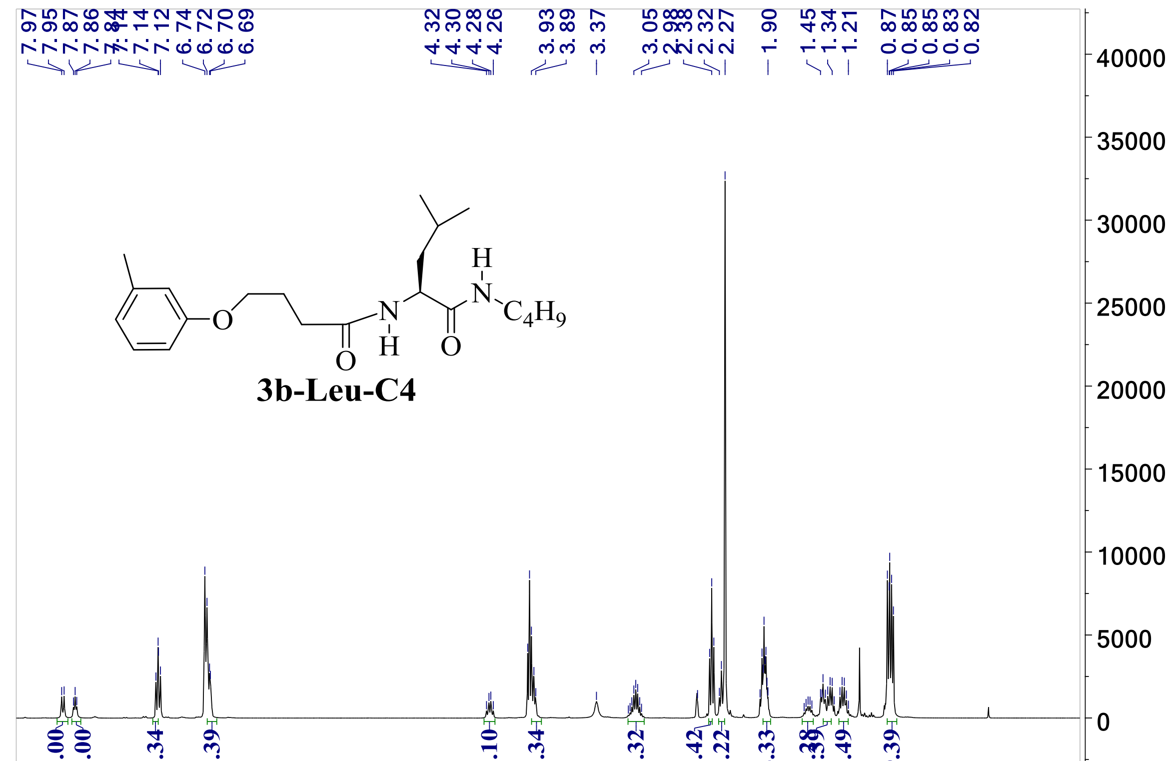

2a-Leu-C4
f1 (ppm)

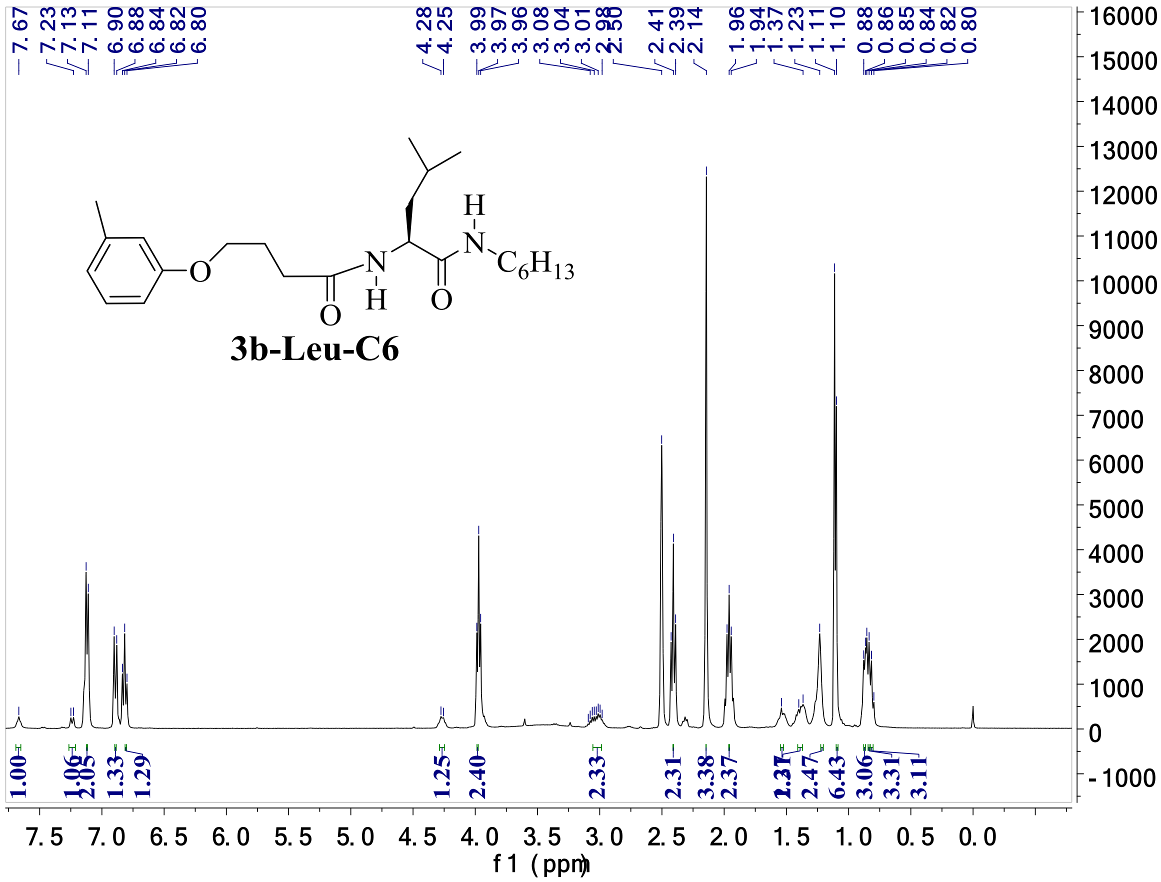

2b-Leu-C4
f1 (ppm)

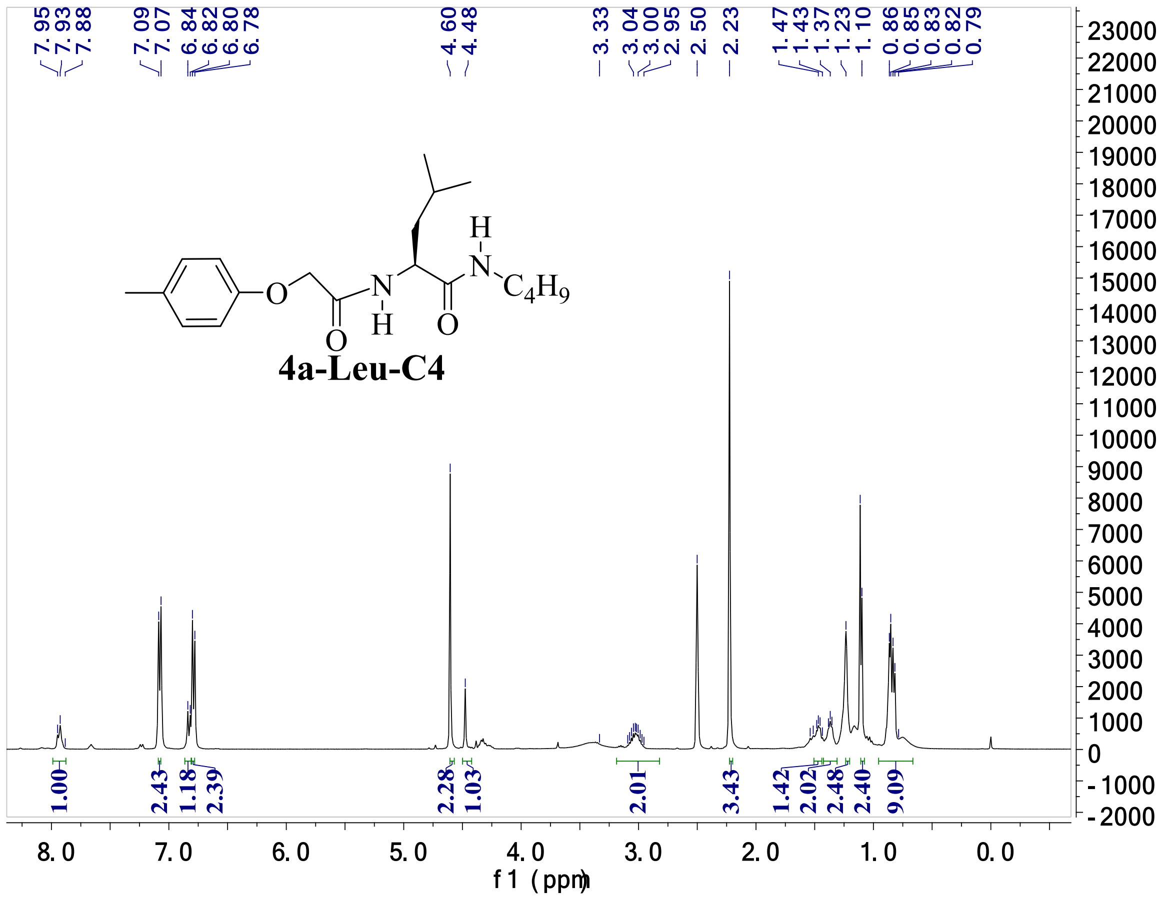

2b-Leu-C6
f1 (ppm)

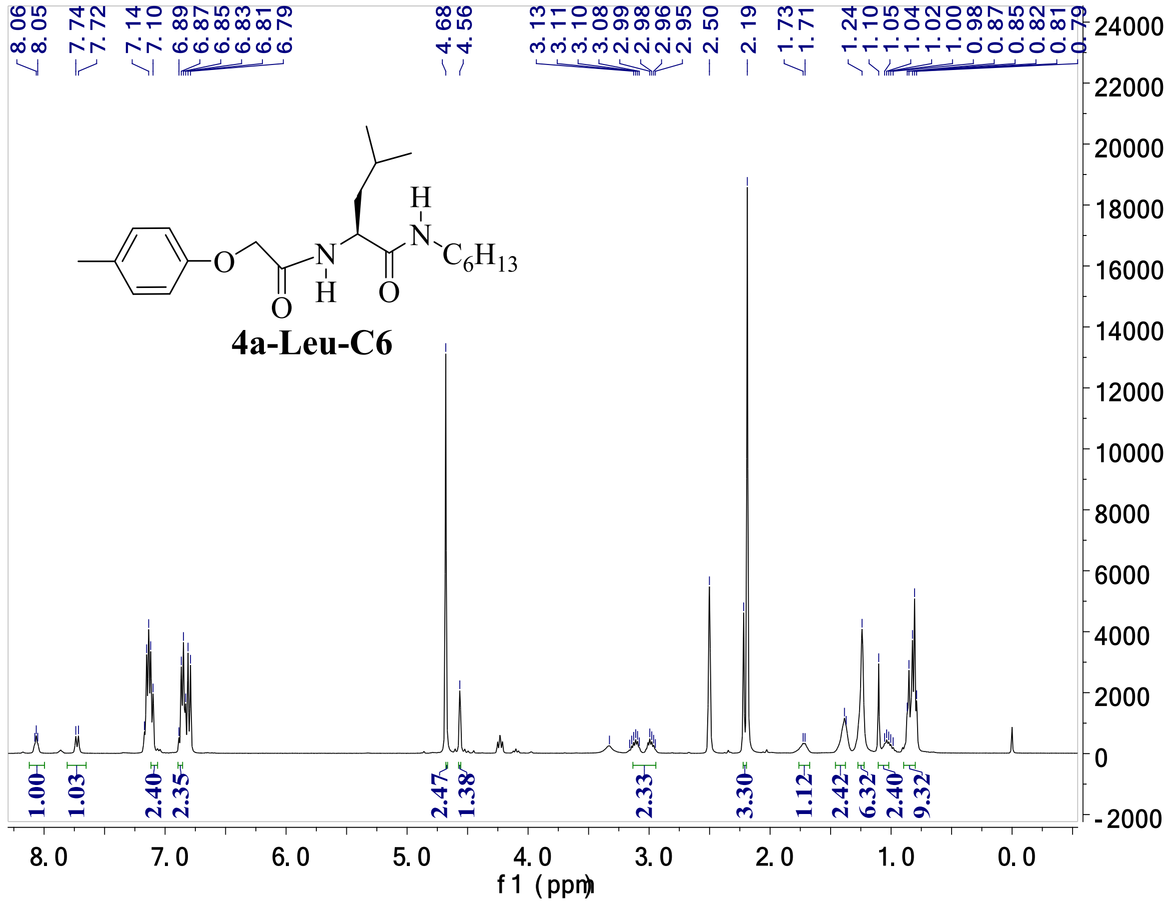

3a-Leu-C4
f1 (ppm)


3a-Leu-C6
f1 (ppm)

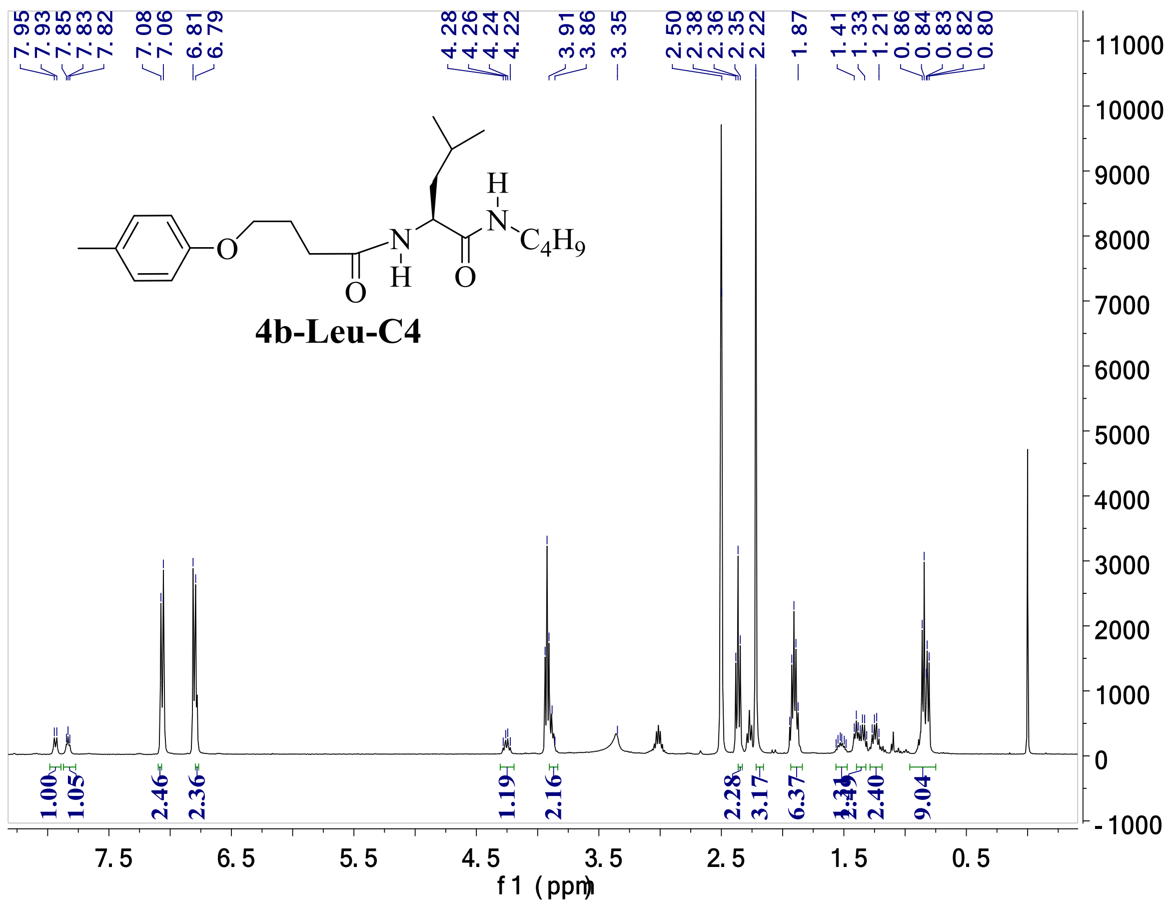

3b-Leu-C4
f1 (ppm)


3b-Leu-C6
f1 (ppm)

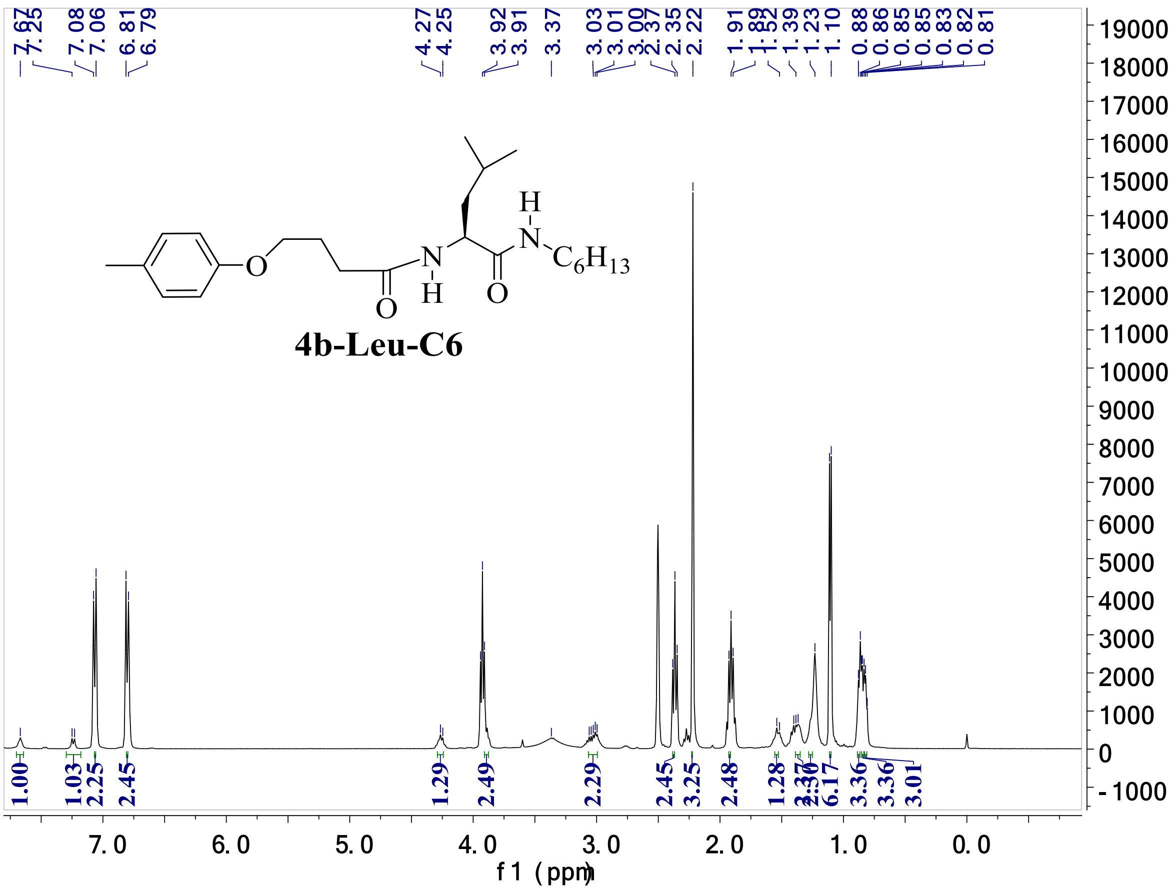

4a-Leu-C4
f1 (ppm)



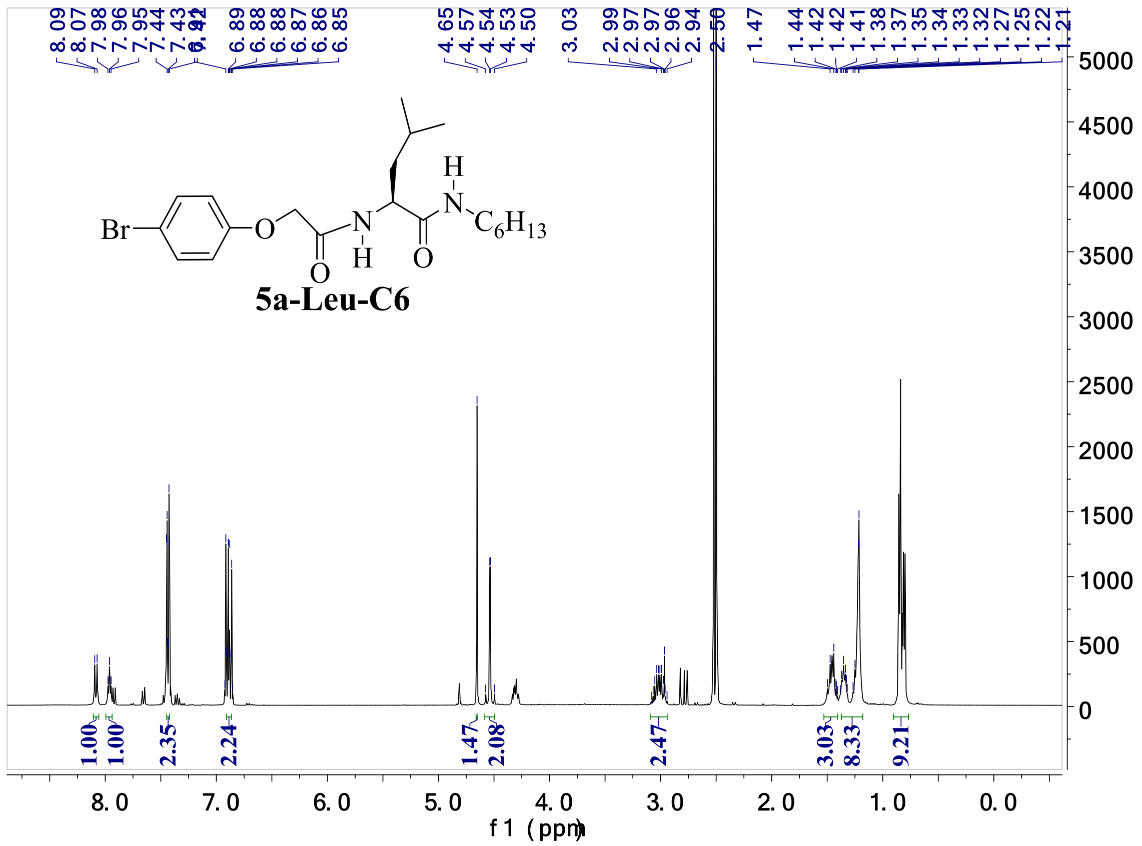
4a-Leu-C6



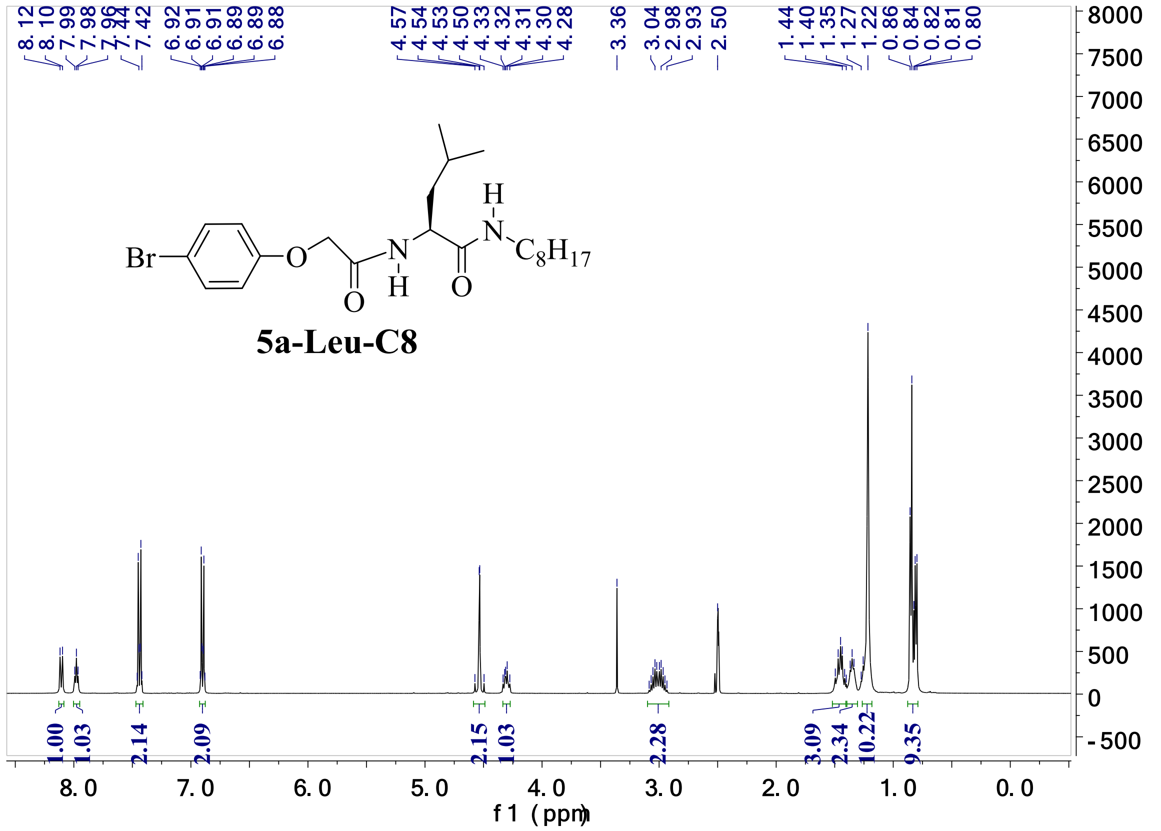
4b-Leu-C4



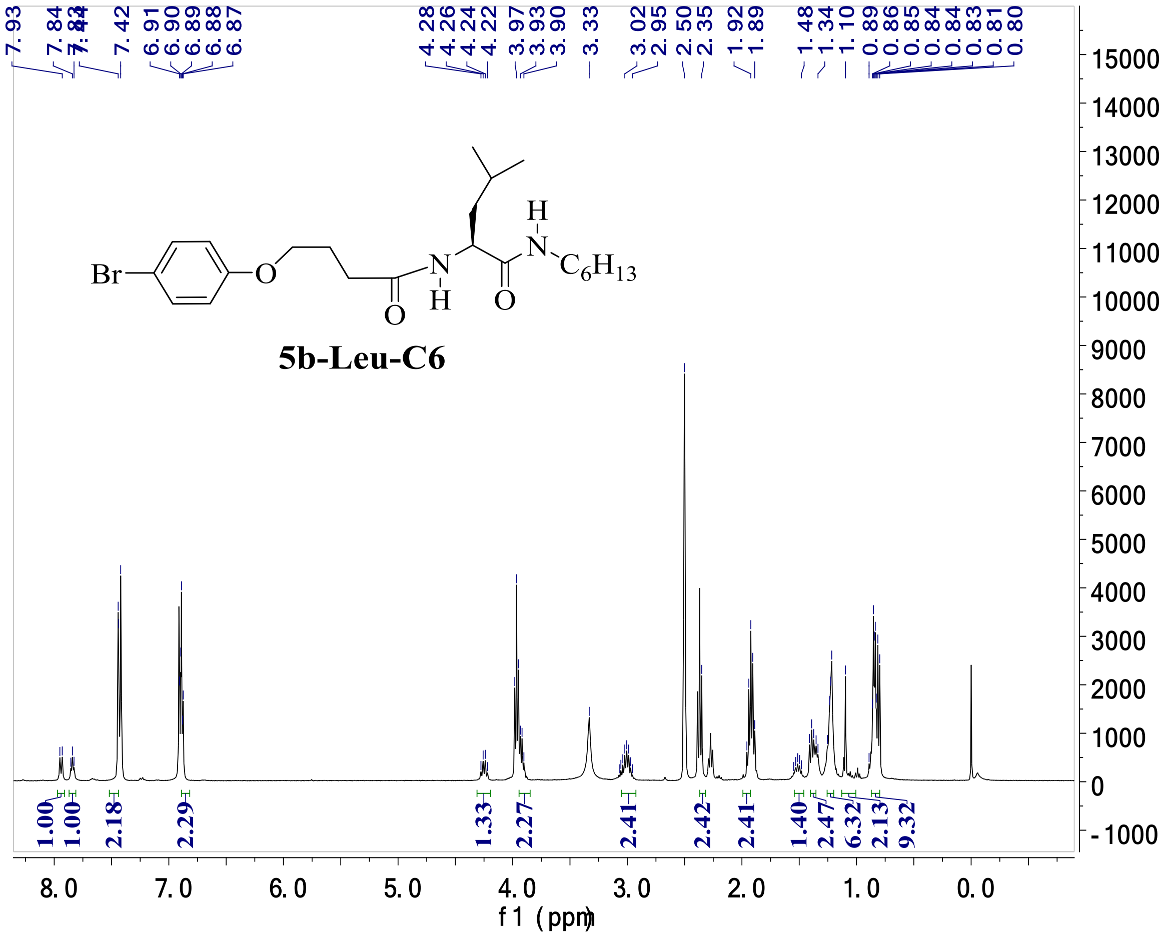
4b-Leu-C6
f1 (ppm)



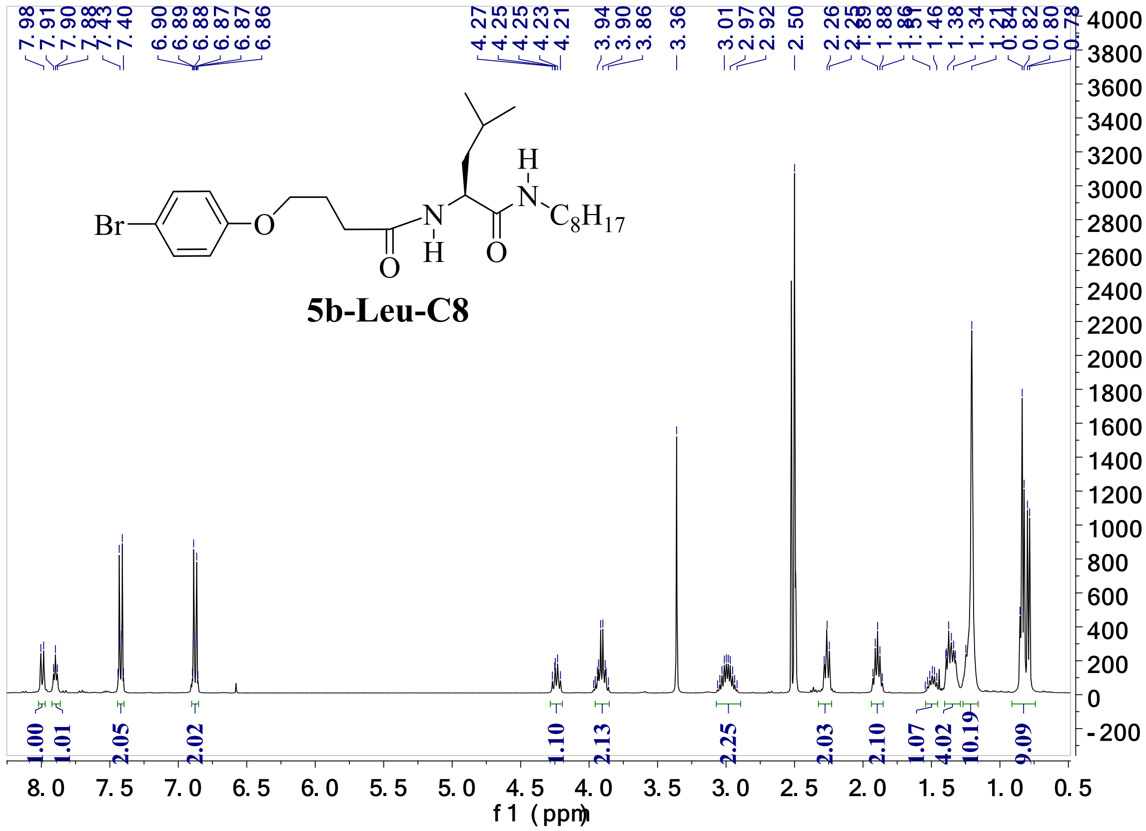
5a-Leu-C6
f1 (ppm)



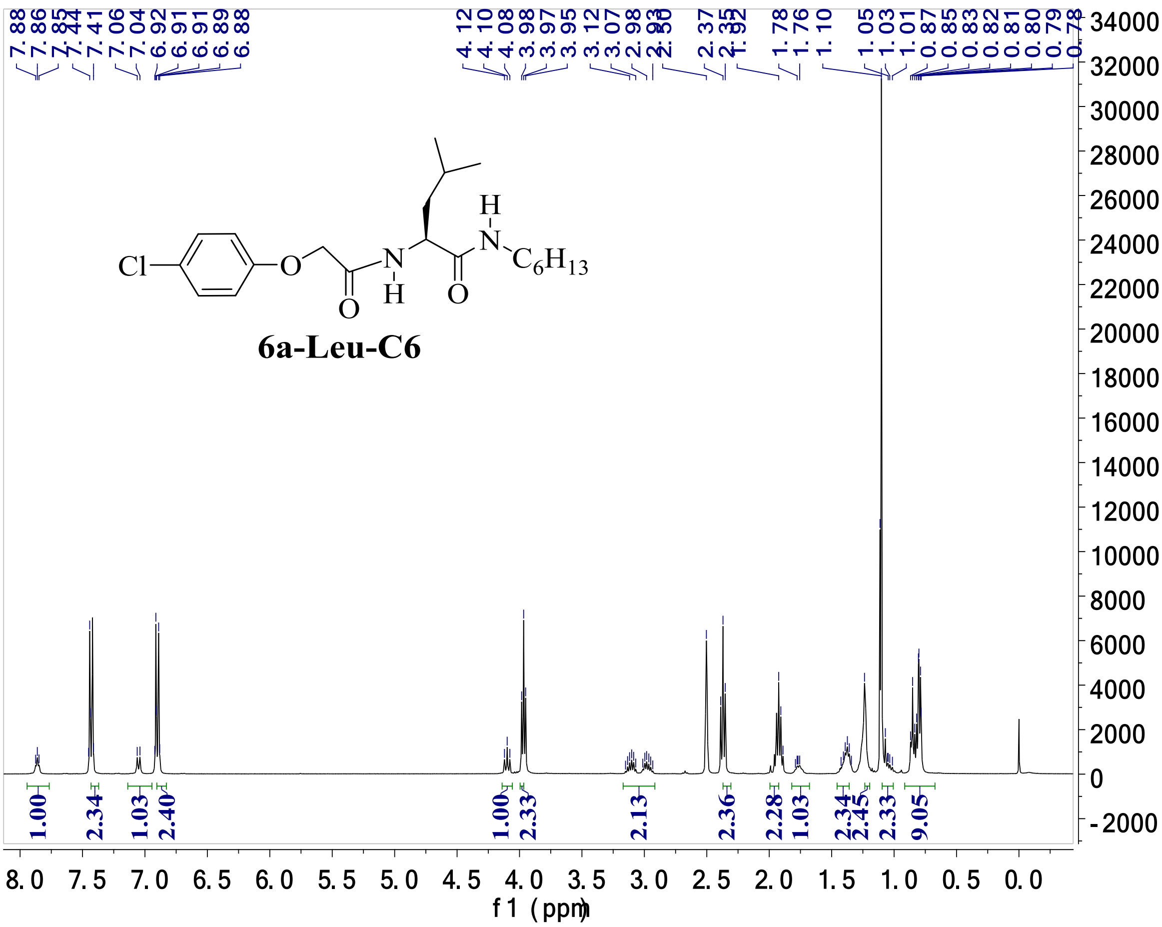
5a-Leu-C8



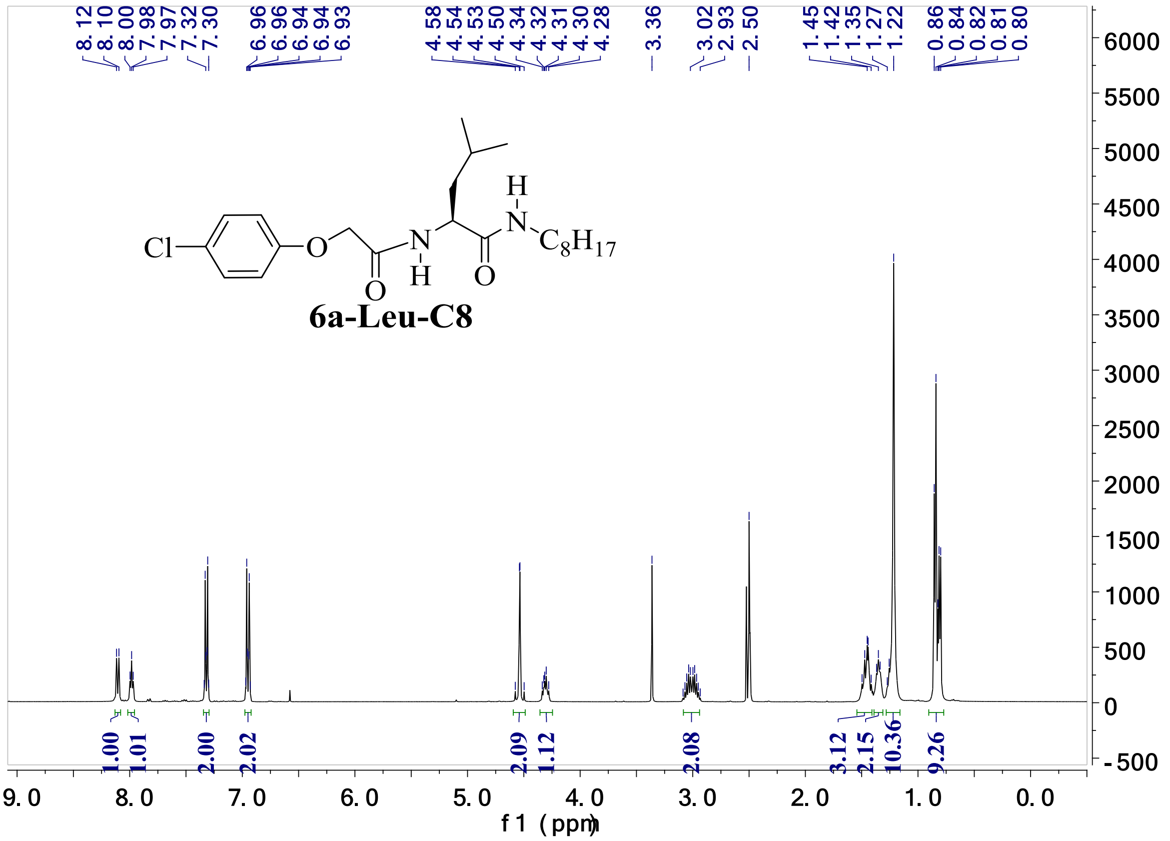
5b-Leu-C6

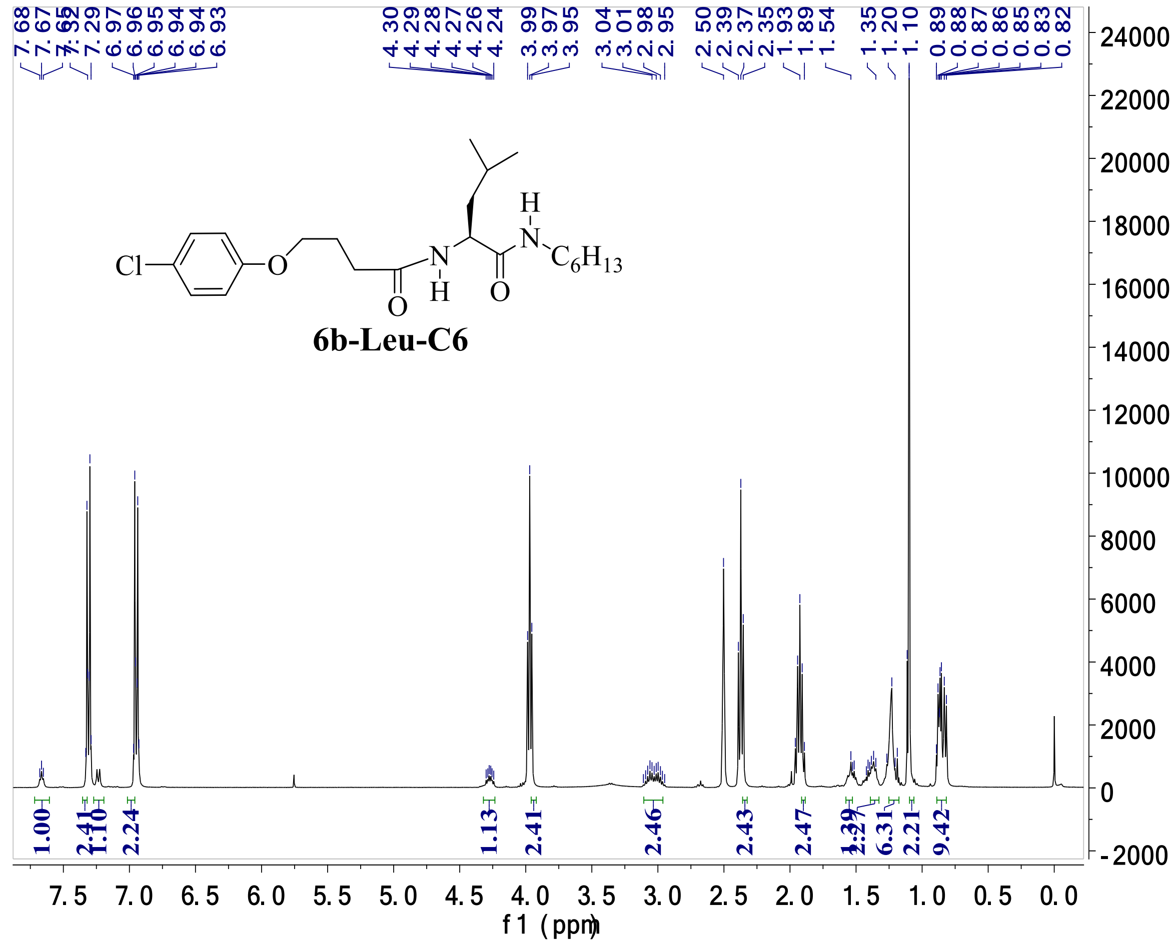


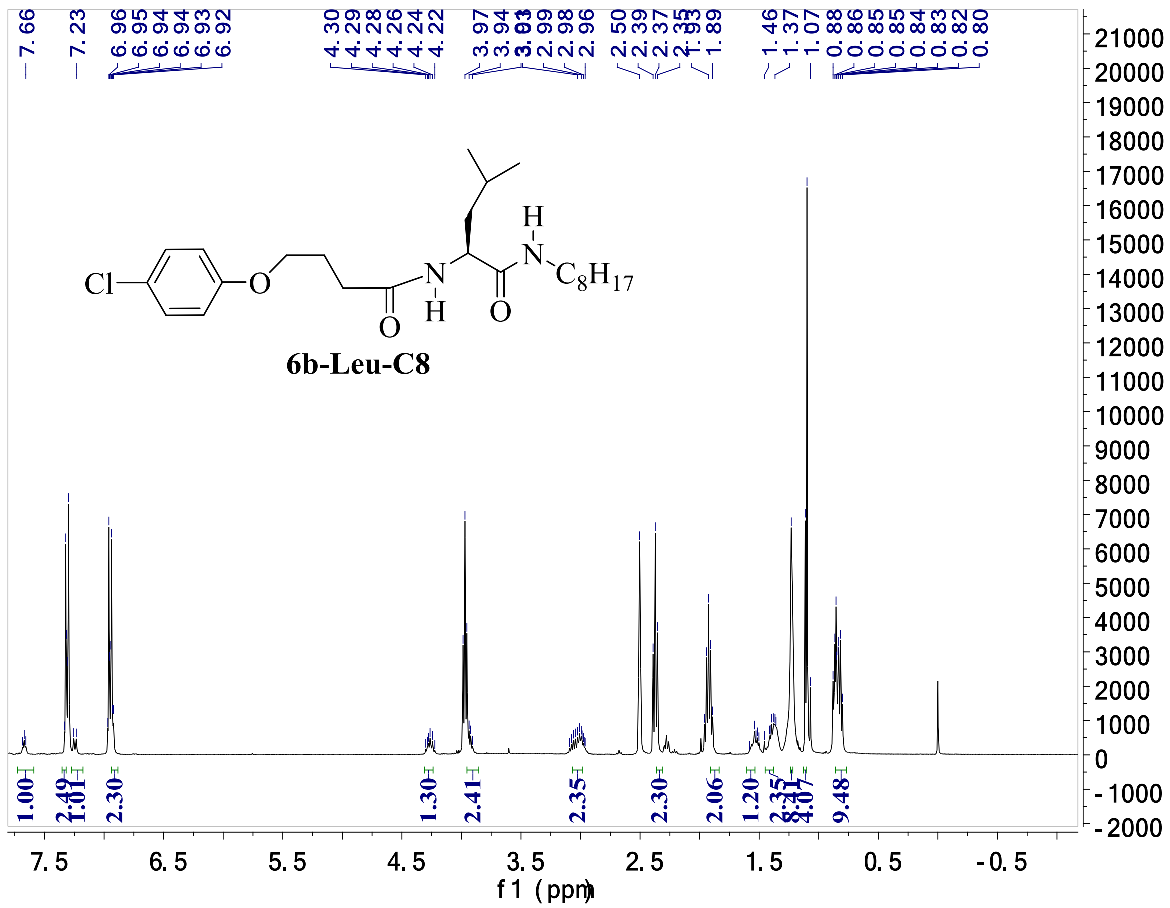
5b-Leu-C8

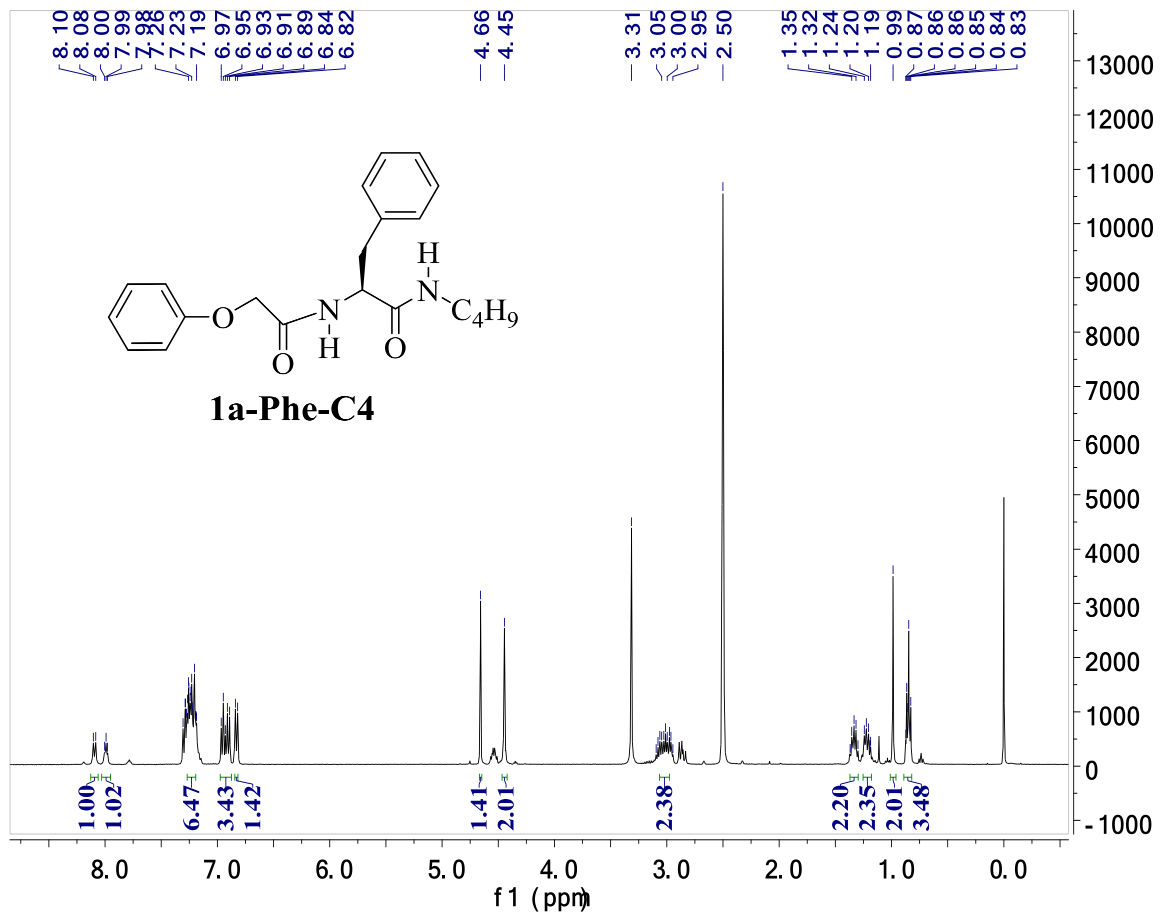


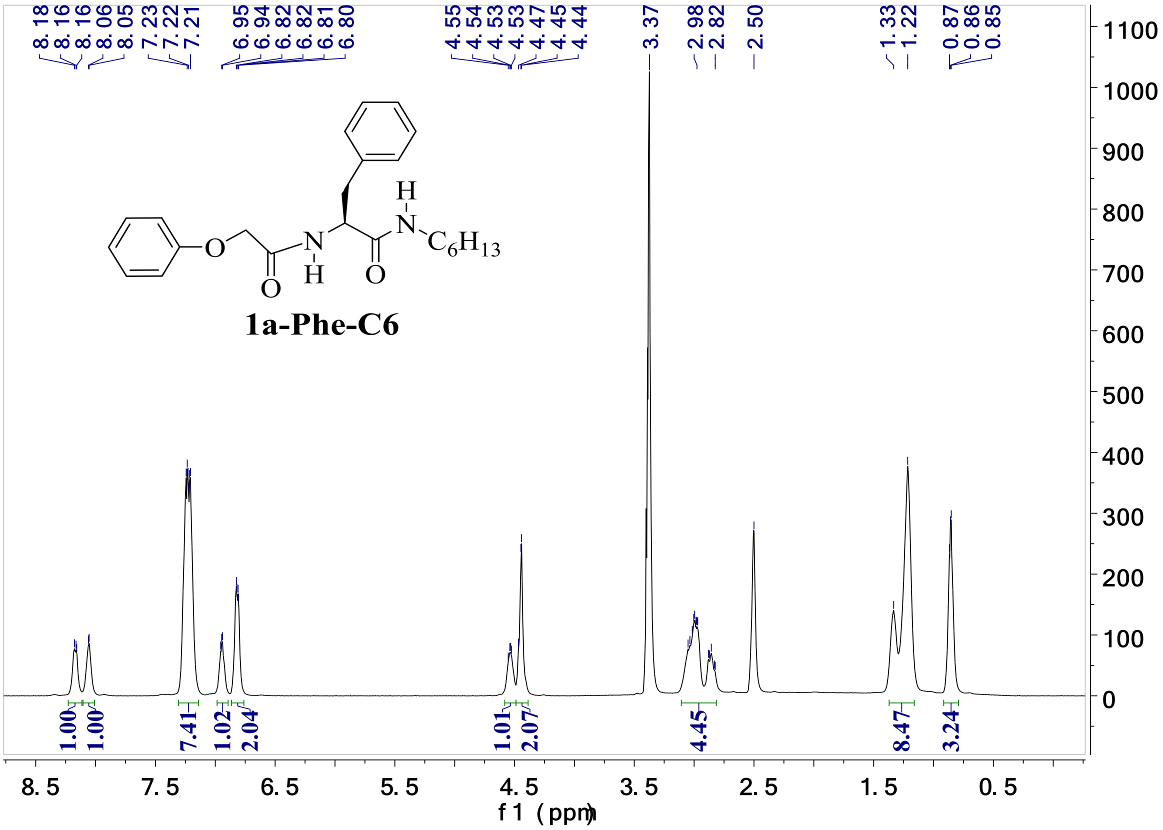
6a-Leu-C6


6a-Leu-C8
f1 (ppm)

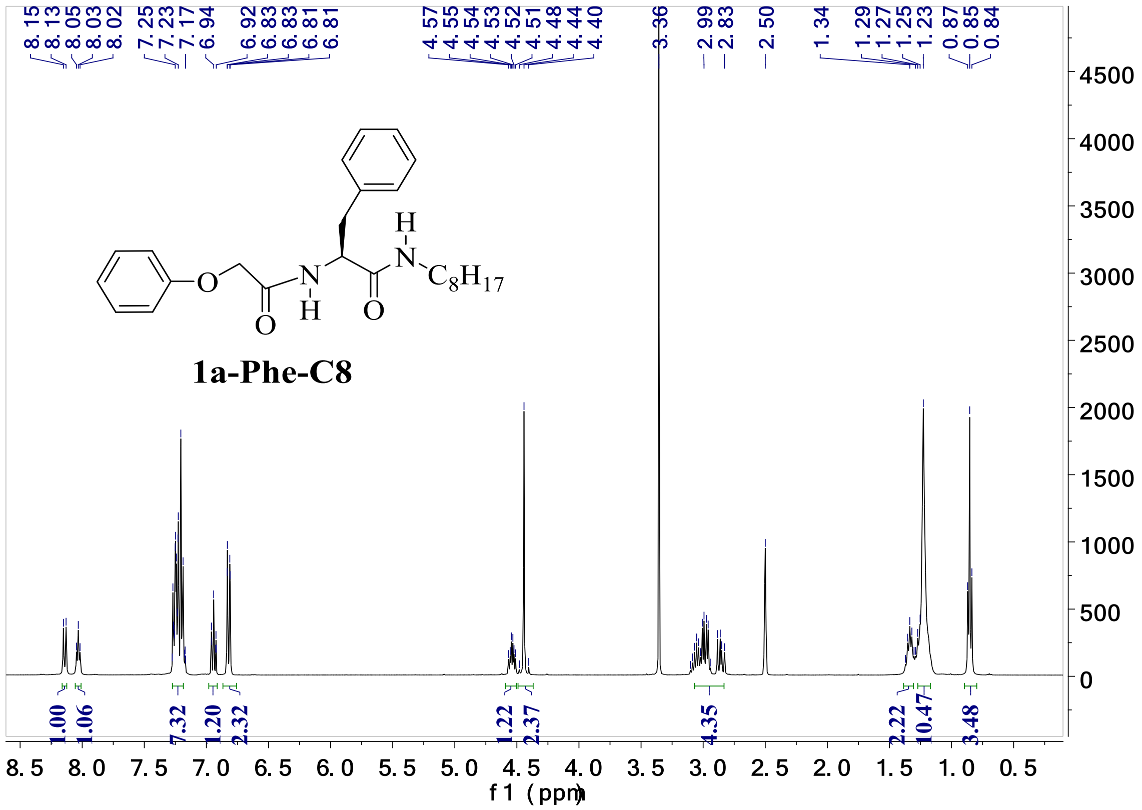

6b-Leu-C6
f1 (ppm)


6b-Leu-C8
f1 (ppm)

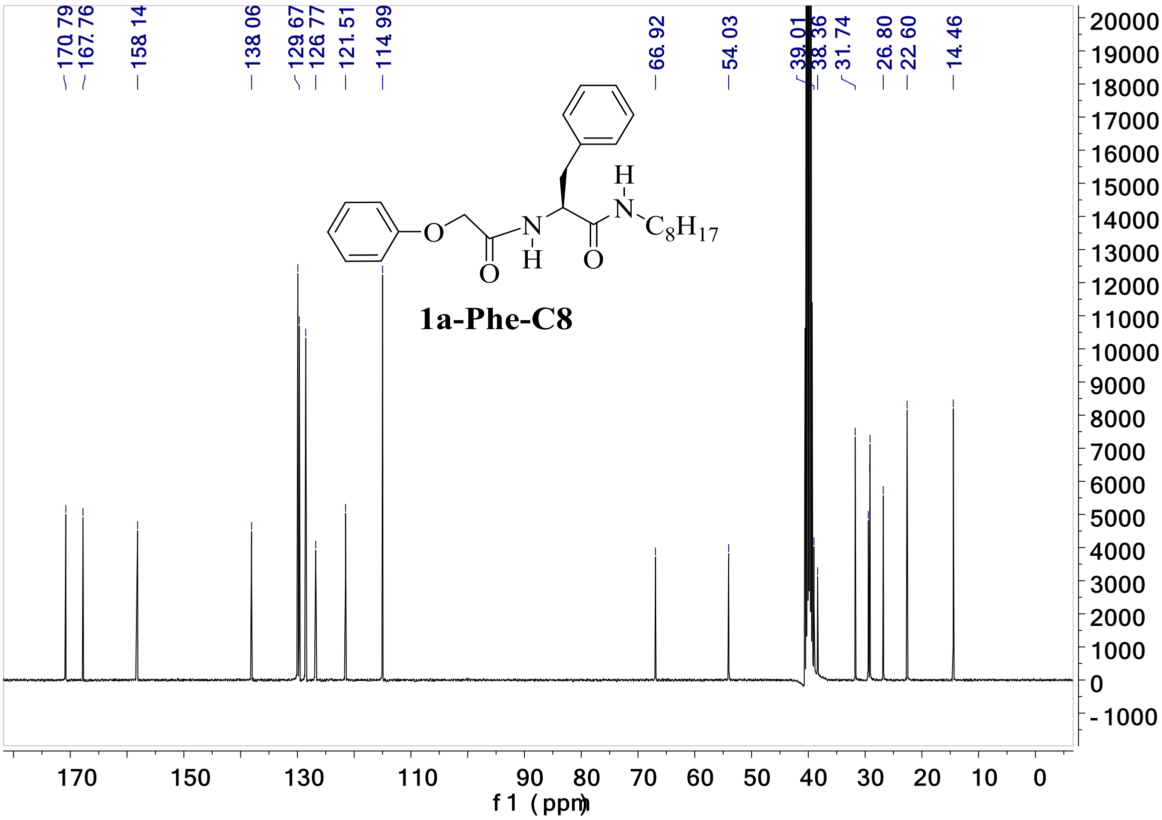

1a-Phe-C4
f1 (ppm)

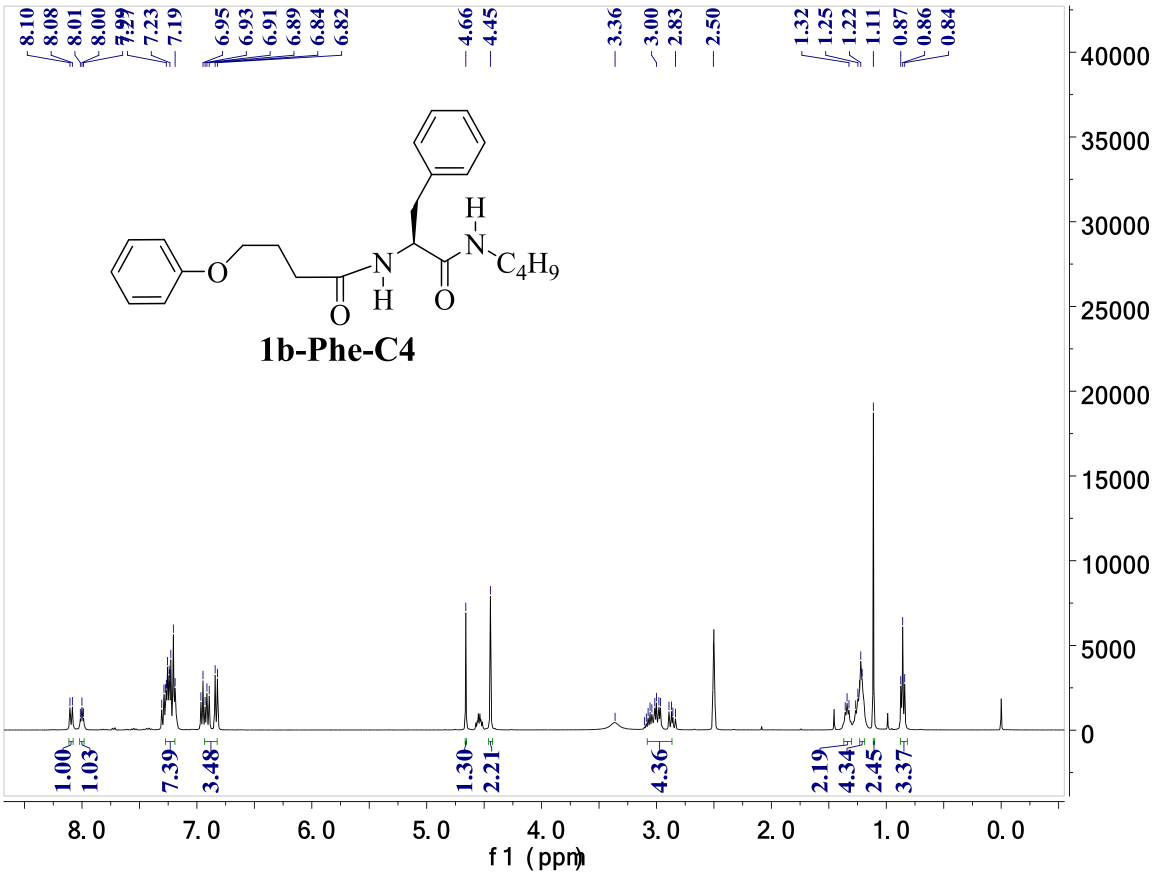


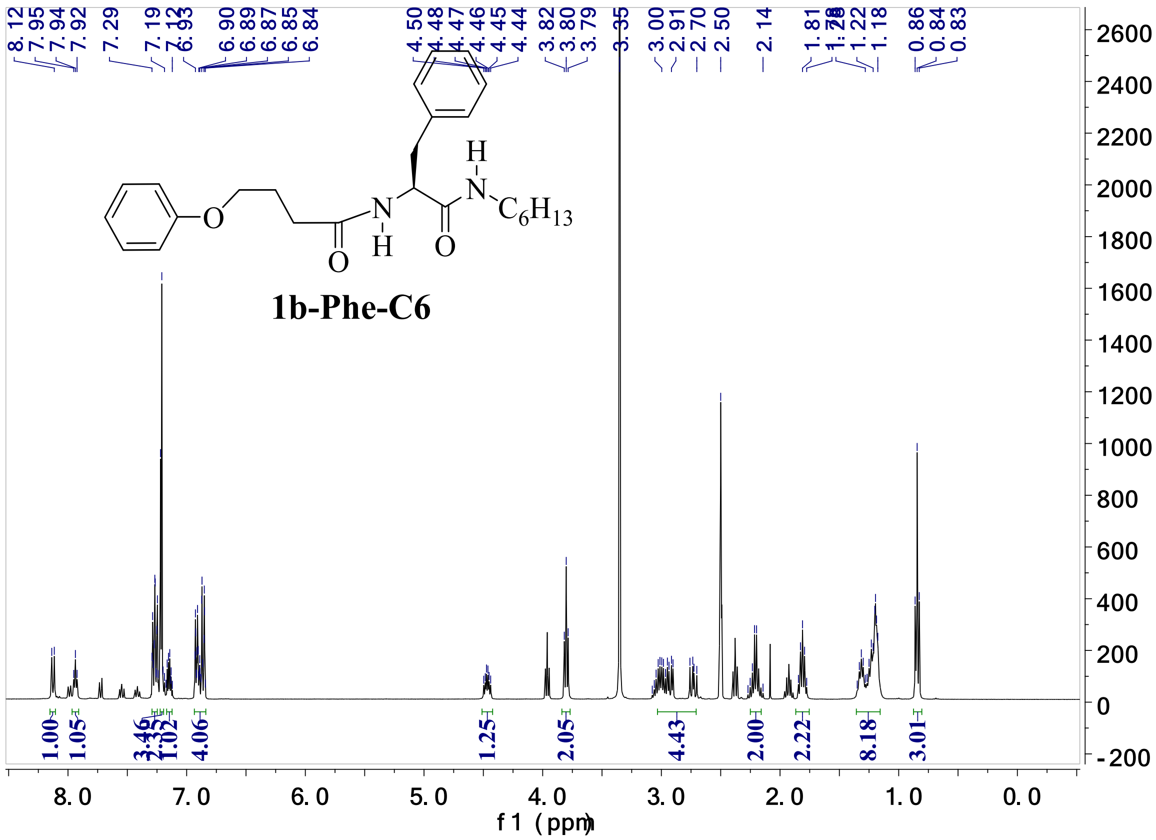
8.18
8.16
8.16
8.06
8.05
7.23
7.22
7.21
6.95
6.94
6.82
6.82
6.81
6.80
4.55
4.54
4.53
4.53
4.47
4.45
4.44
3.37
2.98
2.82
2.50
1.33
1.22
0.87
0.86
0.85
1a-Phe-C6
1.00
1.00
7.41
1.02
2.04
1.01
2.07
4.45
8.47
3.24
f1 (ppm)

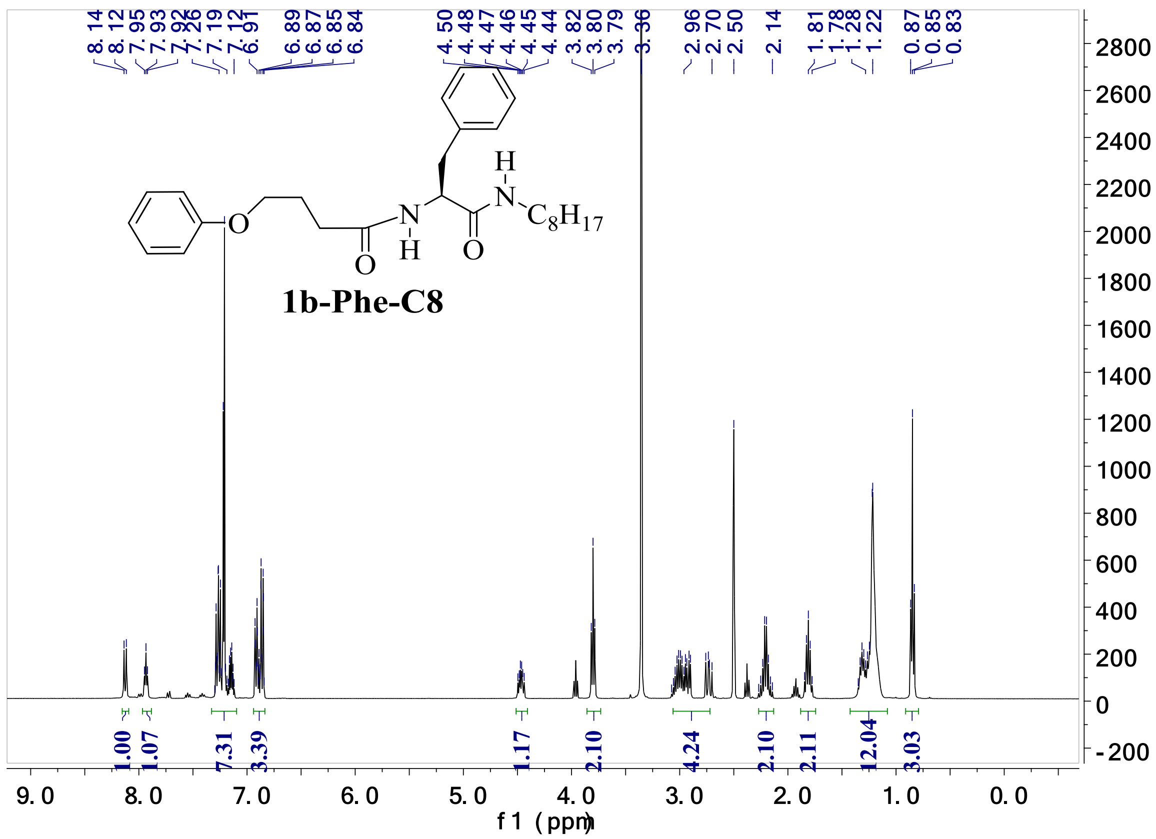


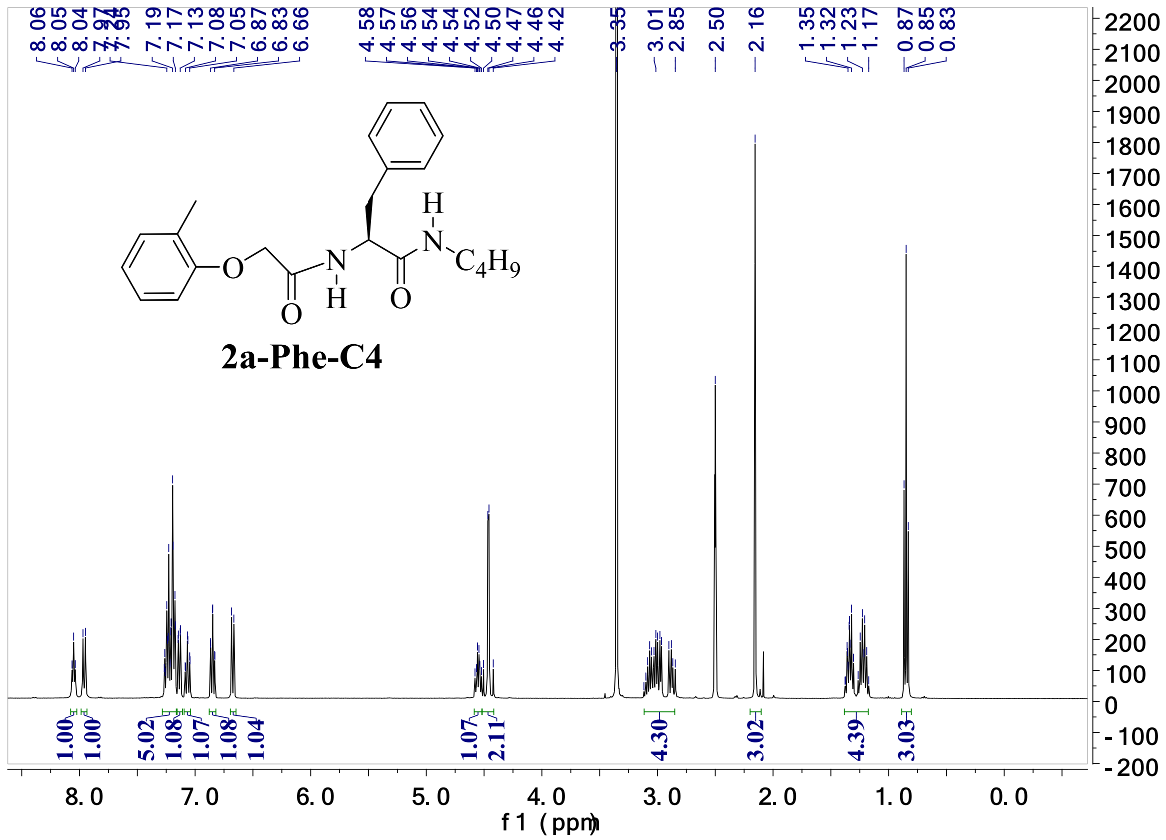
8.15
8.13
8.05
8.03
8.02
7.25
7.23
7.17
6.94
6.92
6.83
6.83
6.81
6.81
4.57
4.55
4.54
4.53
4.52
4.51
4.48
4.44
4.40
3.36
2.99
2.83
2.50
1.34
1.29
1.27
1.25
1.23
0.87
0.85
0.84
1a-Phe-C8
1.00
1.06
7.32
1.20
2.32
1.22
2.37
4.35
2.22
10.47
3.48
f1 (ppm)

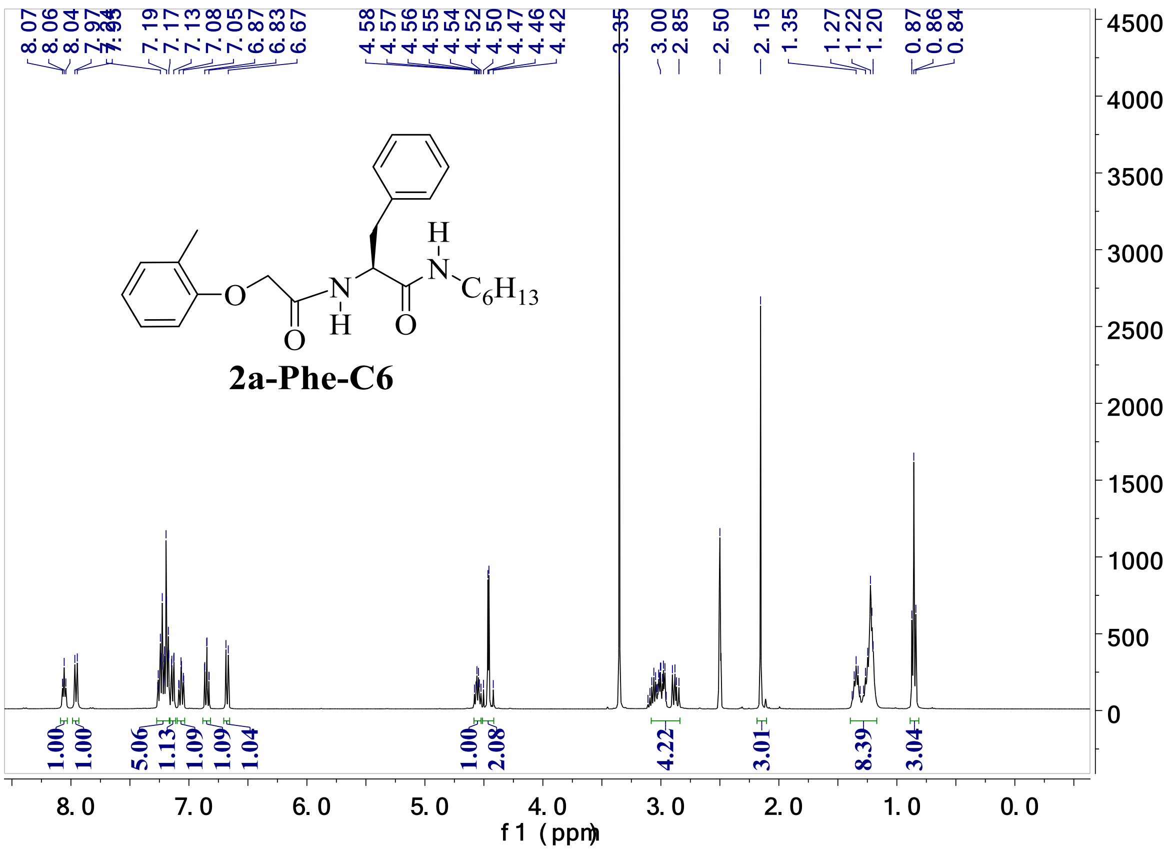

170.79
167.76
158.14
138.06
129.67
126.77
121.51
114.99
66.92
54.03
39.01
38.36
31.74
26.80
22.60
14.46
1a-Phe-C8
f1 (ppm)

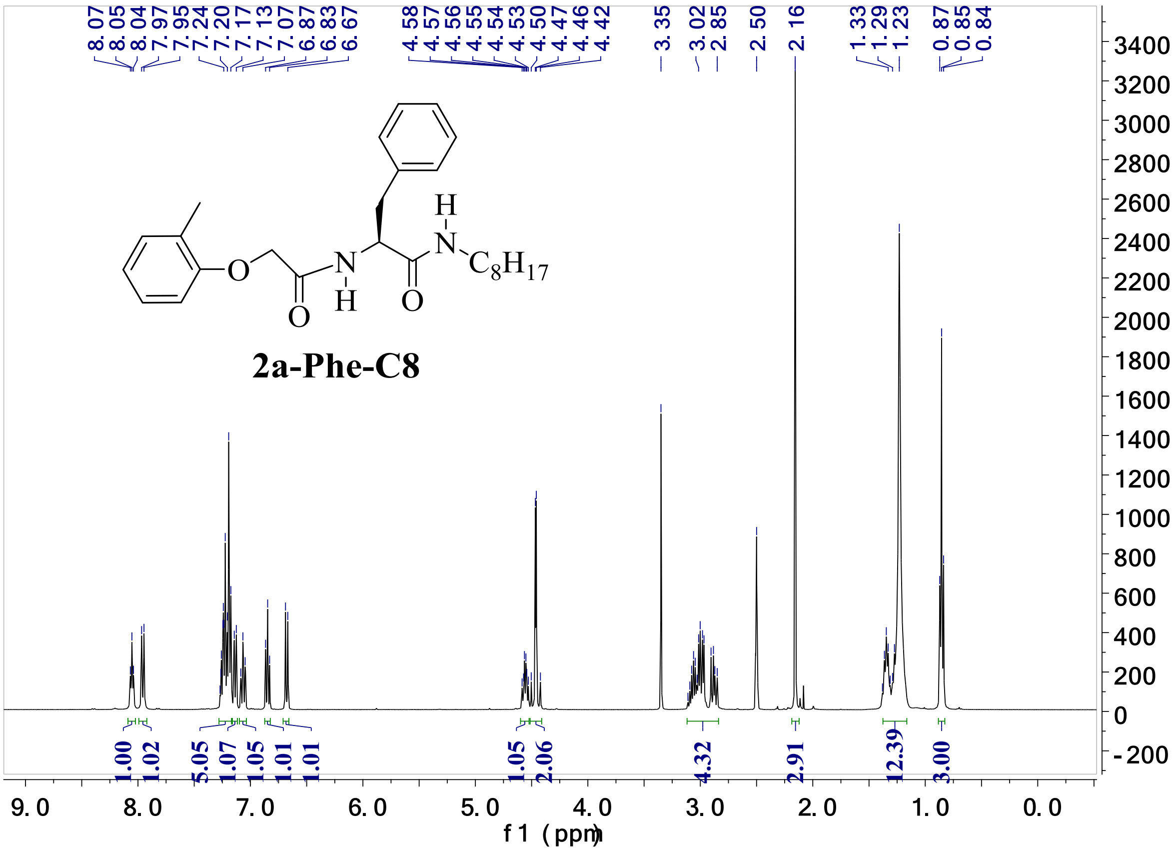

8.10
8.08
8.01
8.00
7.23
7.19
6.95
6.93
6.91
6.89
6.84
6.82
4.66
4.45
3.36
3.00
2.83
2.50
1.32
1.25
1.22
1.11
0.87
0.86
0.84
1b-Phe-C4
1.00
1.03
7.39
3.48
1.30
2.21
4.36
2.19
4.34
2.45
3.37
f1 (ppm)


1b-Phe-C6
f1 (ppm)

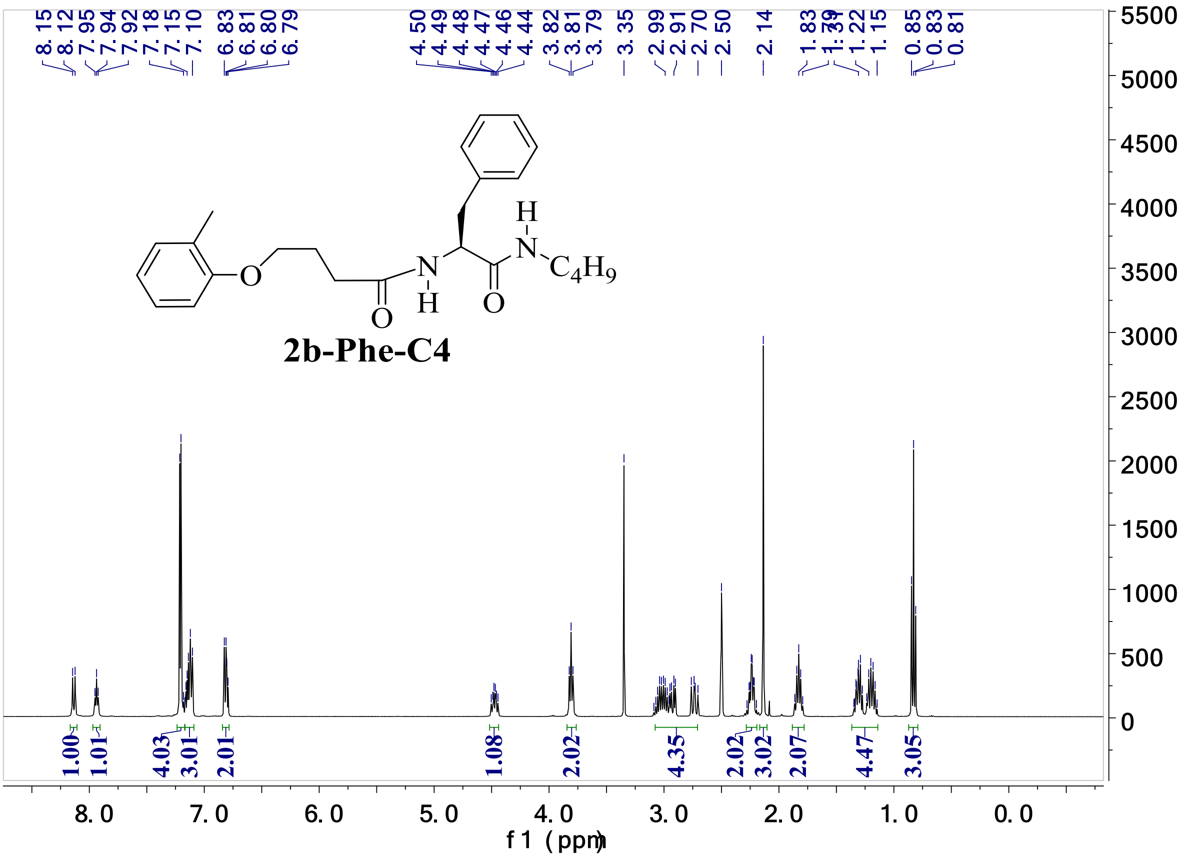

1b-Phe-C8
f1 (ppm)


2a-Phe-C4
f1 (ppm)

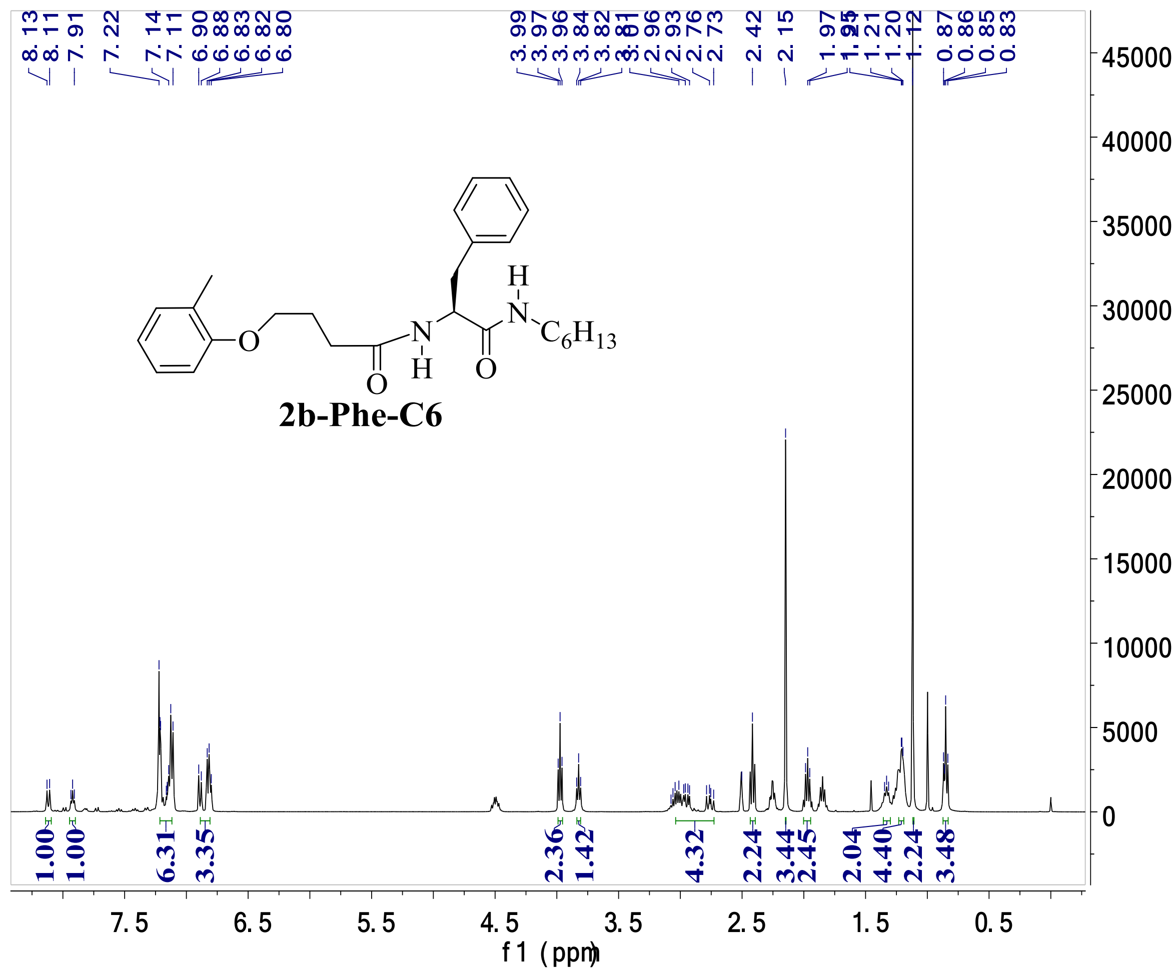

2a-Phe-C6
f1 (ppm)

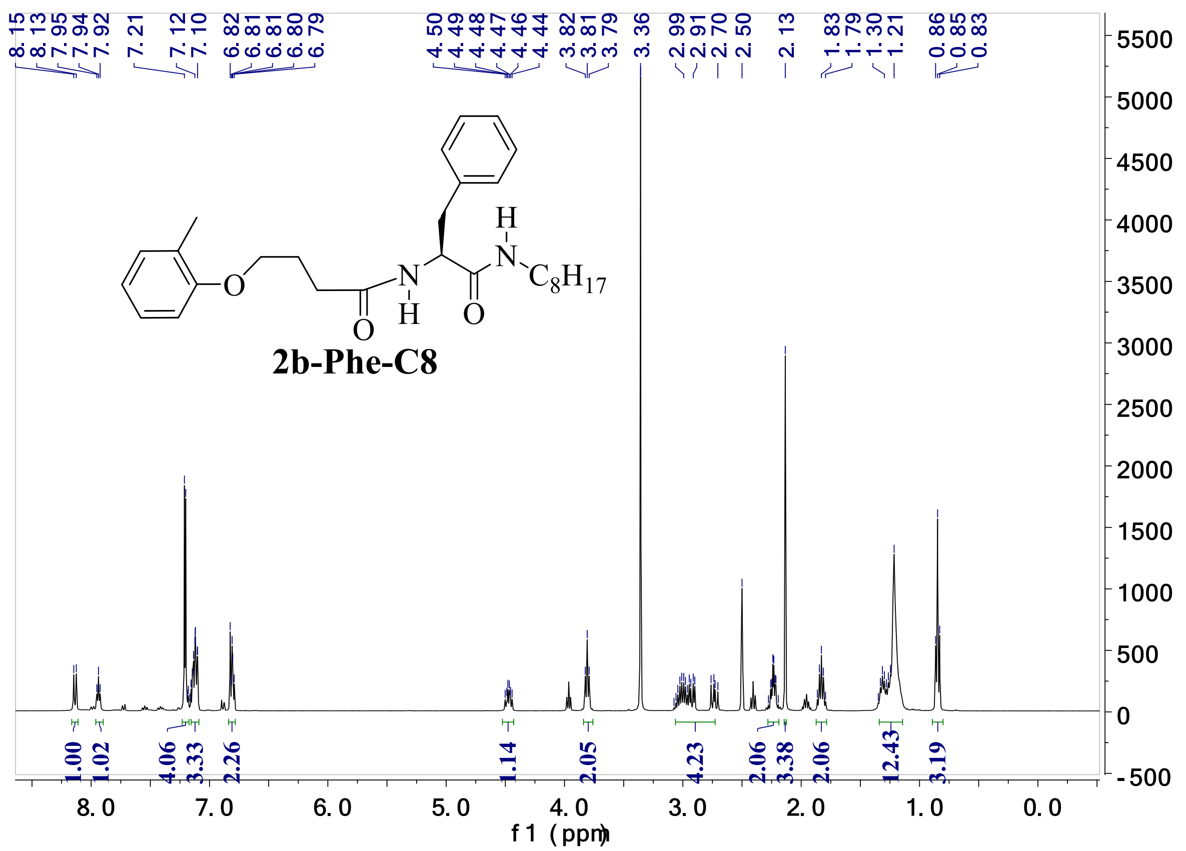


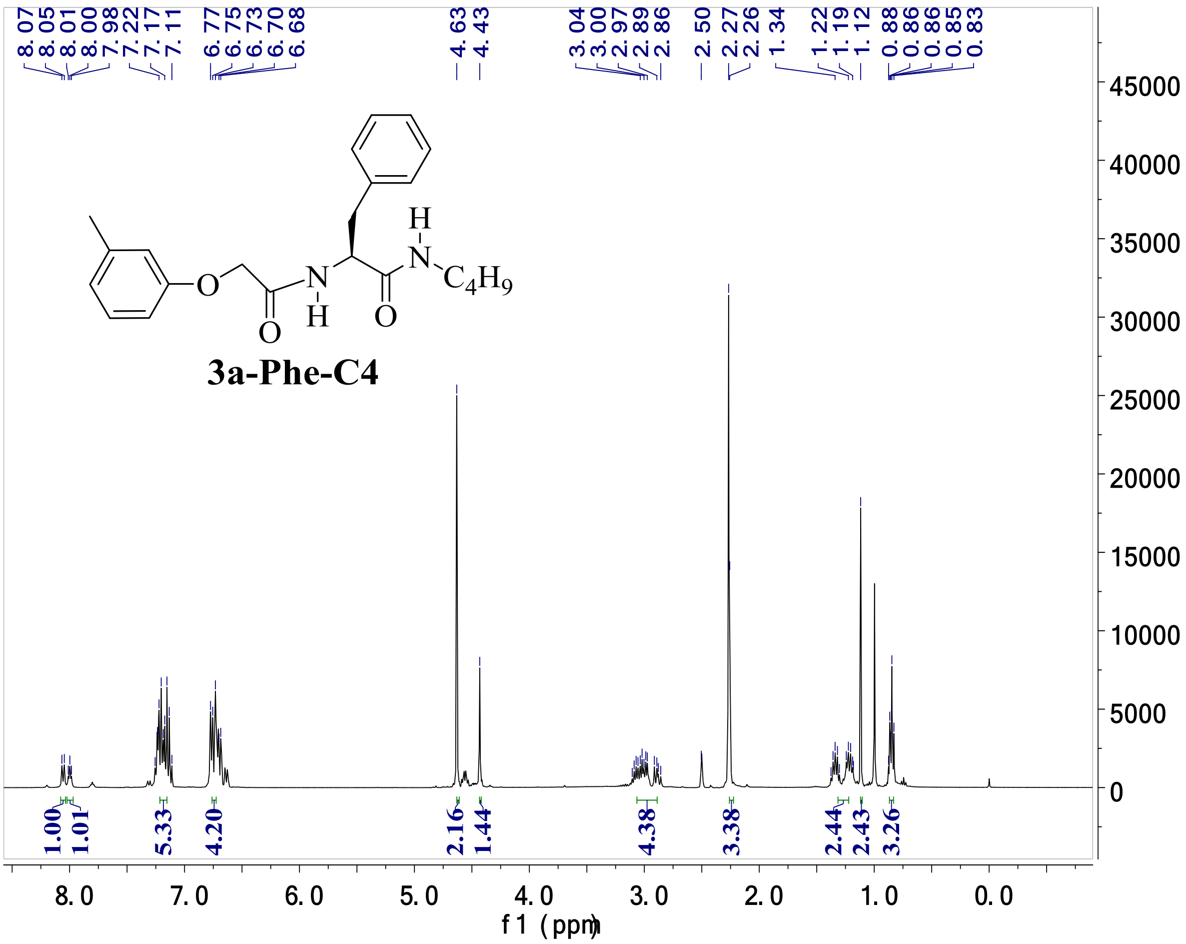
2a-Phe-C8

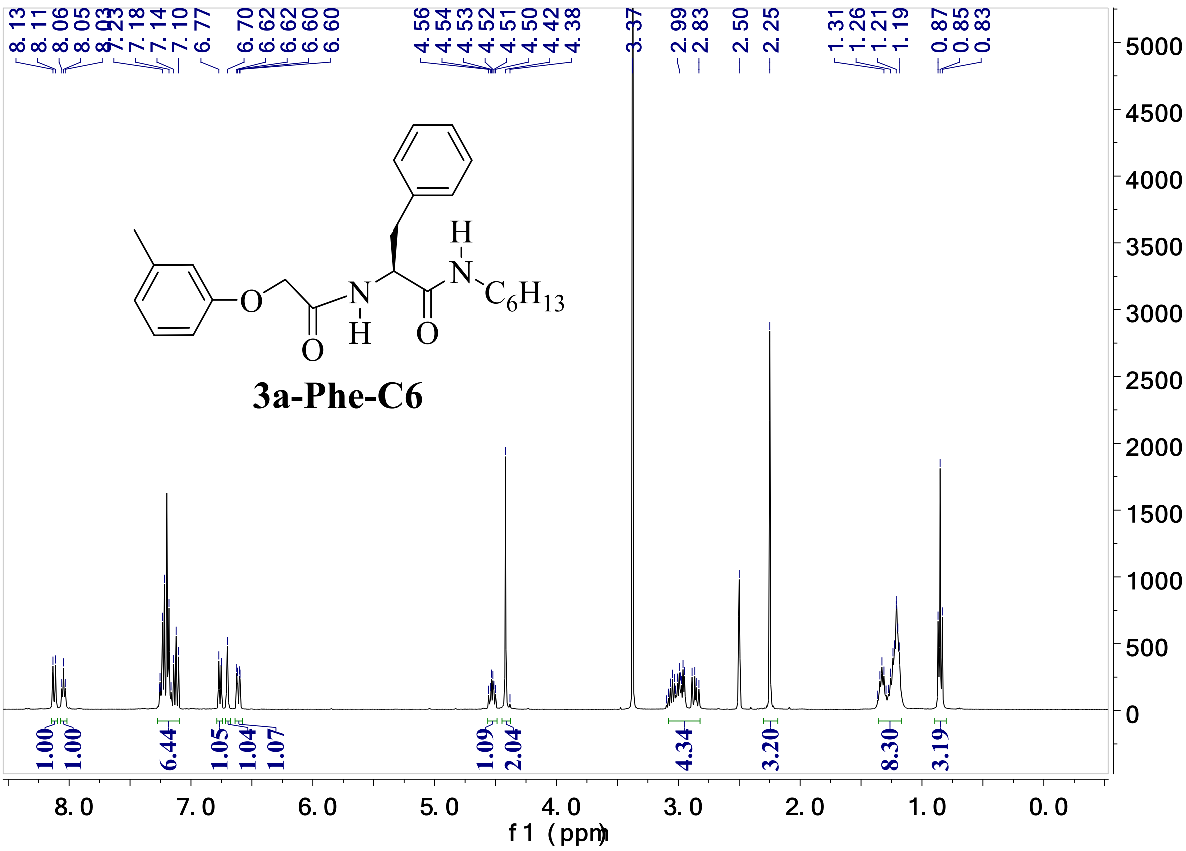


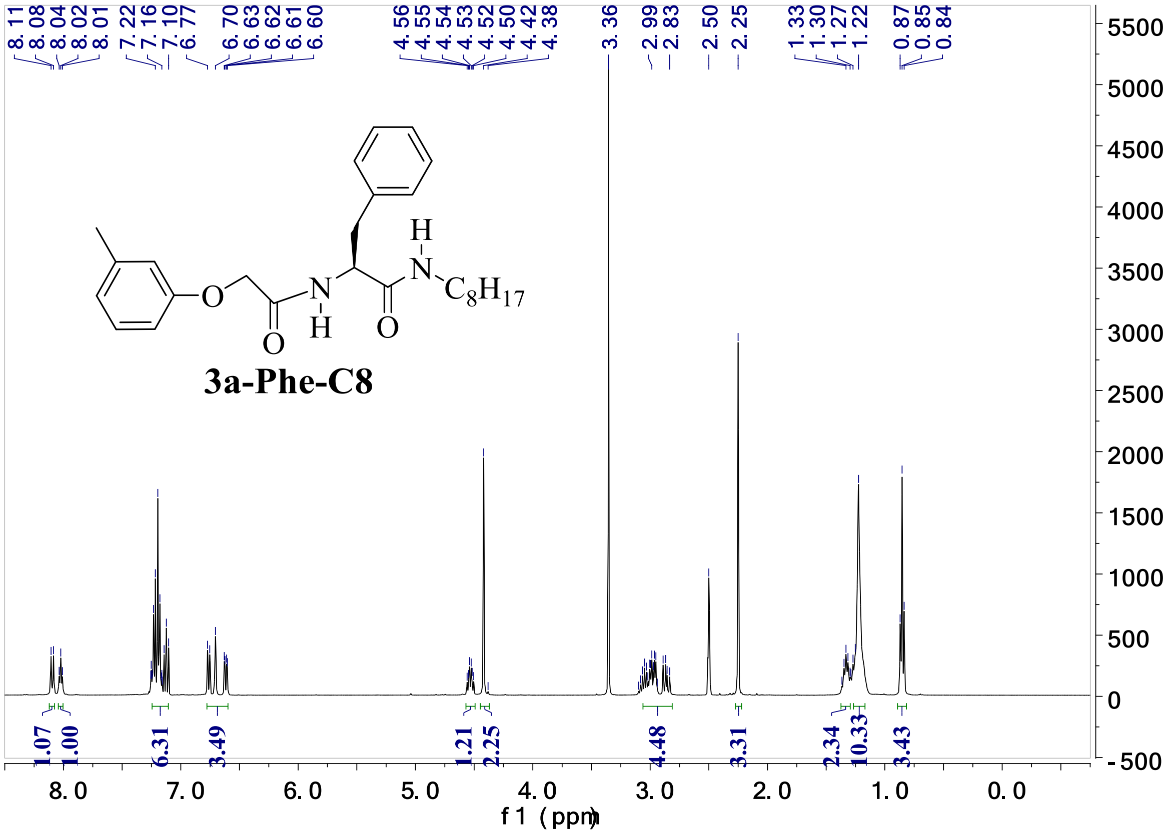
2b-Phe-C4


2b-Phe-C6
f1 (ppm)

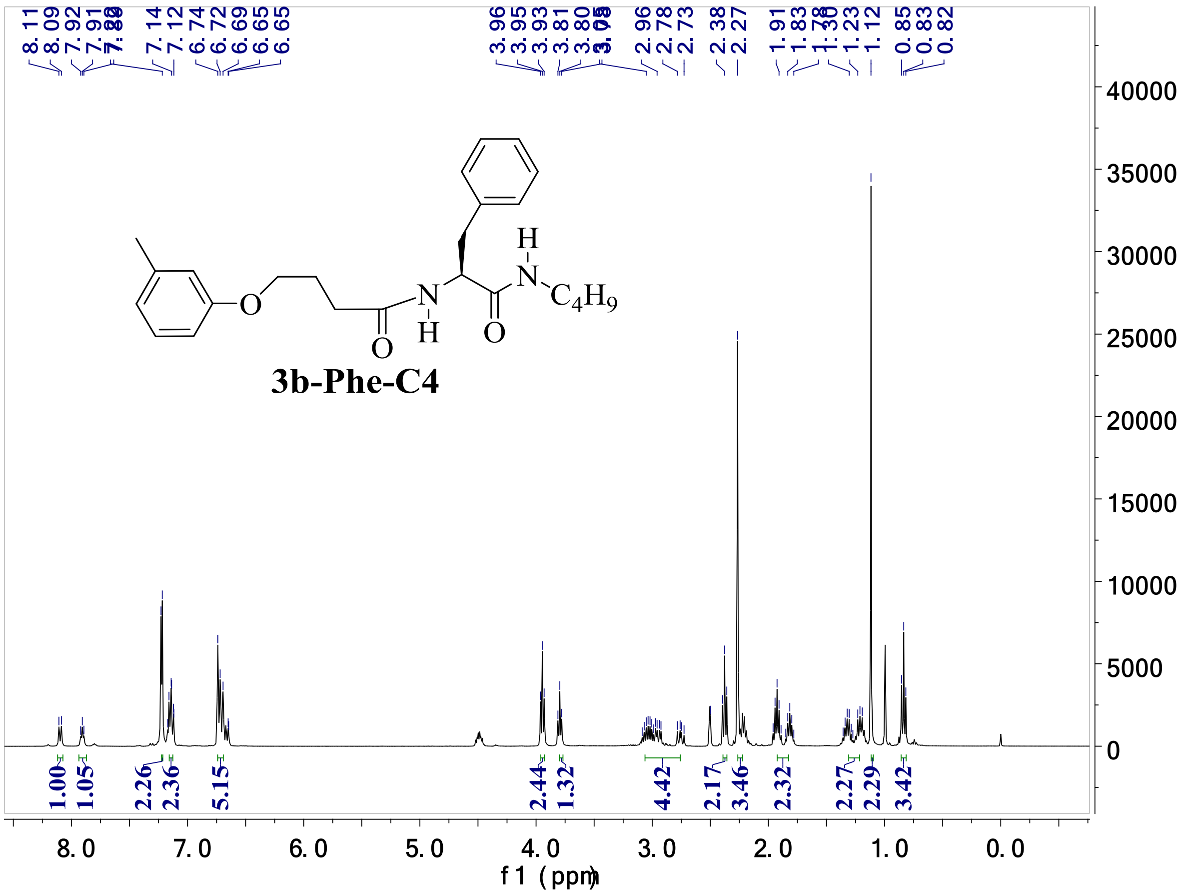

2b-Phe-C8
f1 (ppm)


3a-Phe-C4
f1 (ppm)

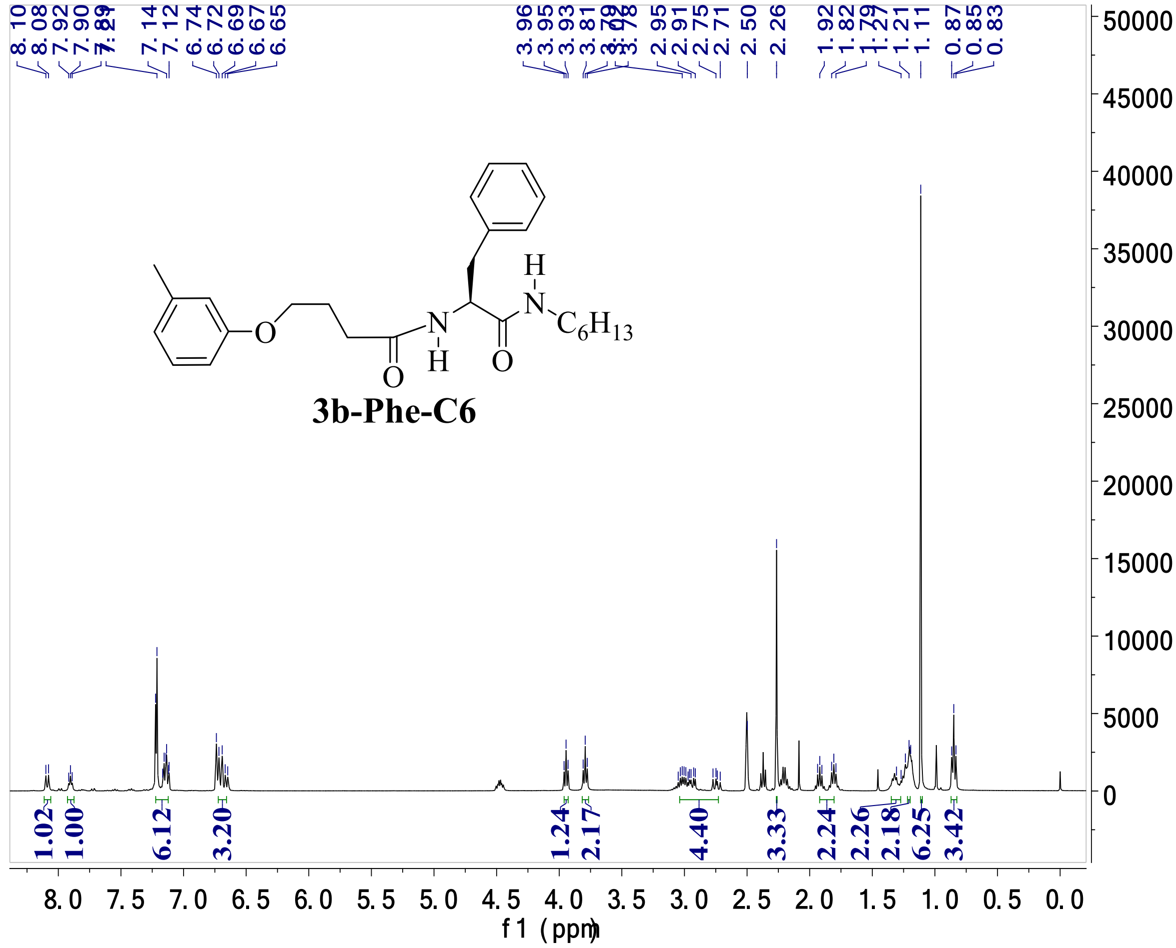

3a-Phe-C6
f1 (ppm)

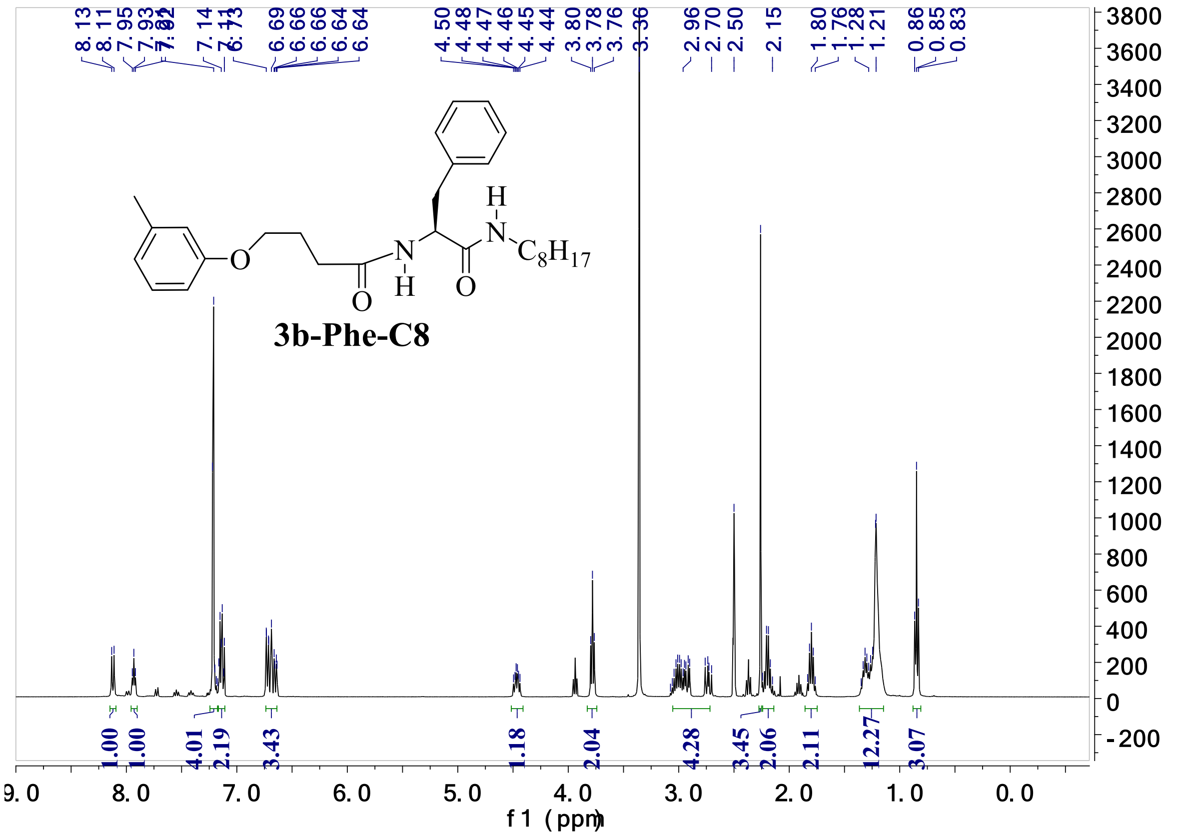


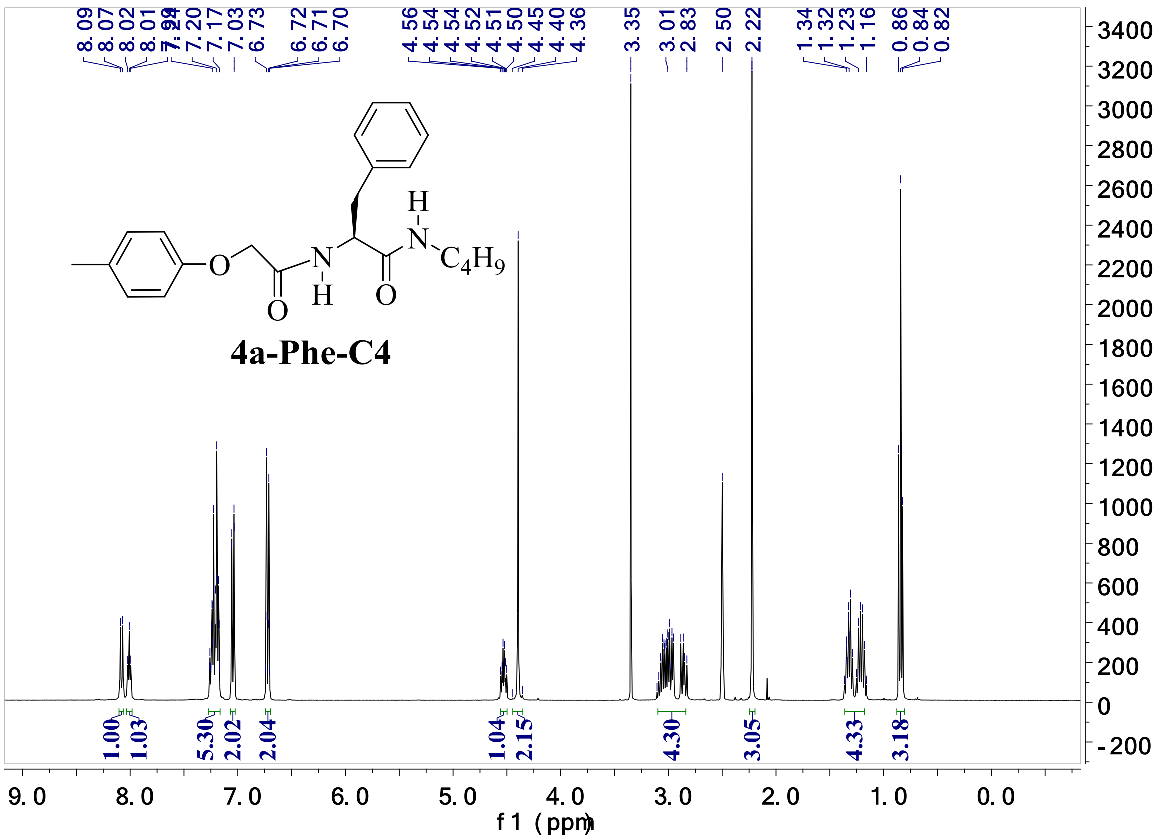
3a-Phe-C8
f1 (ppm)

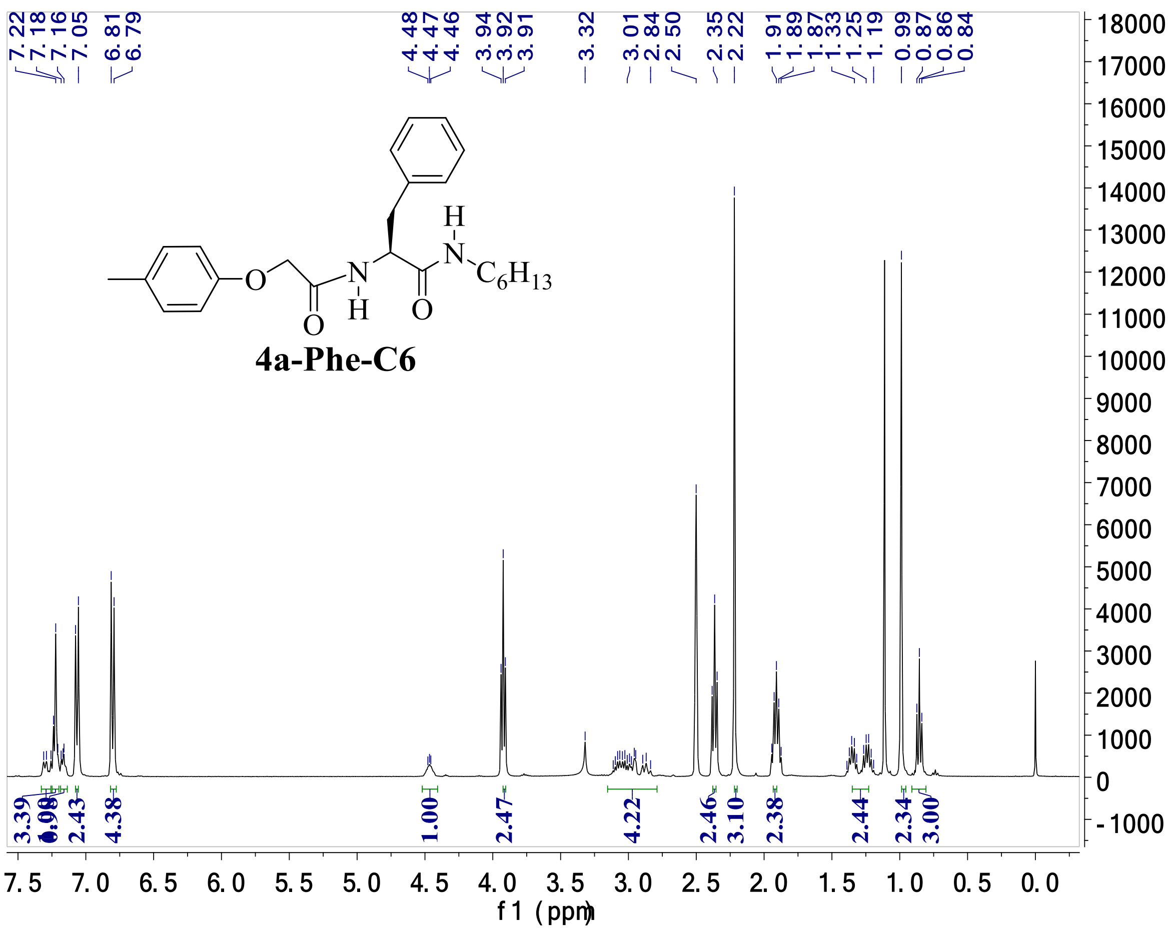


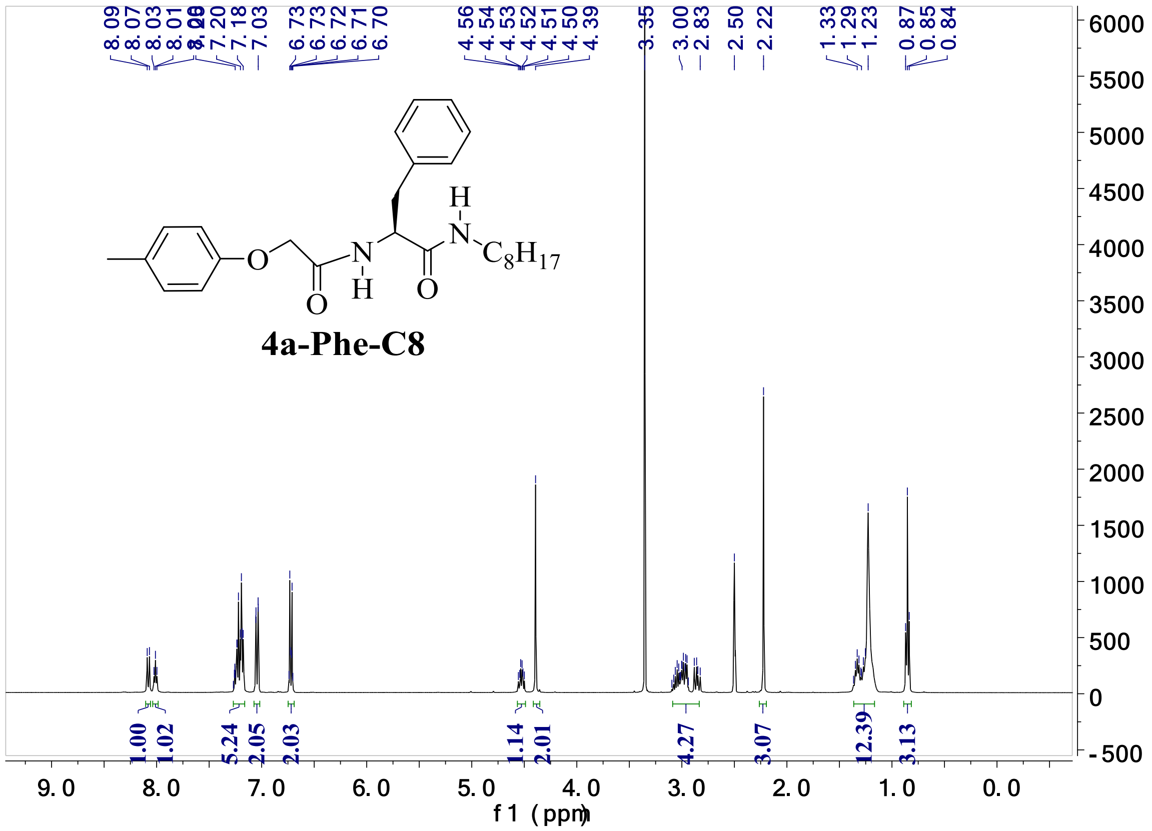
3b-Phe-C4
f1 (ppm)


3b-Phe-C6
f1 (ppm)

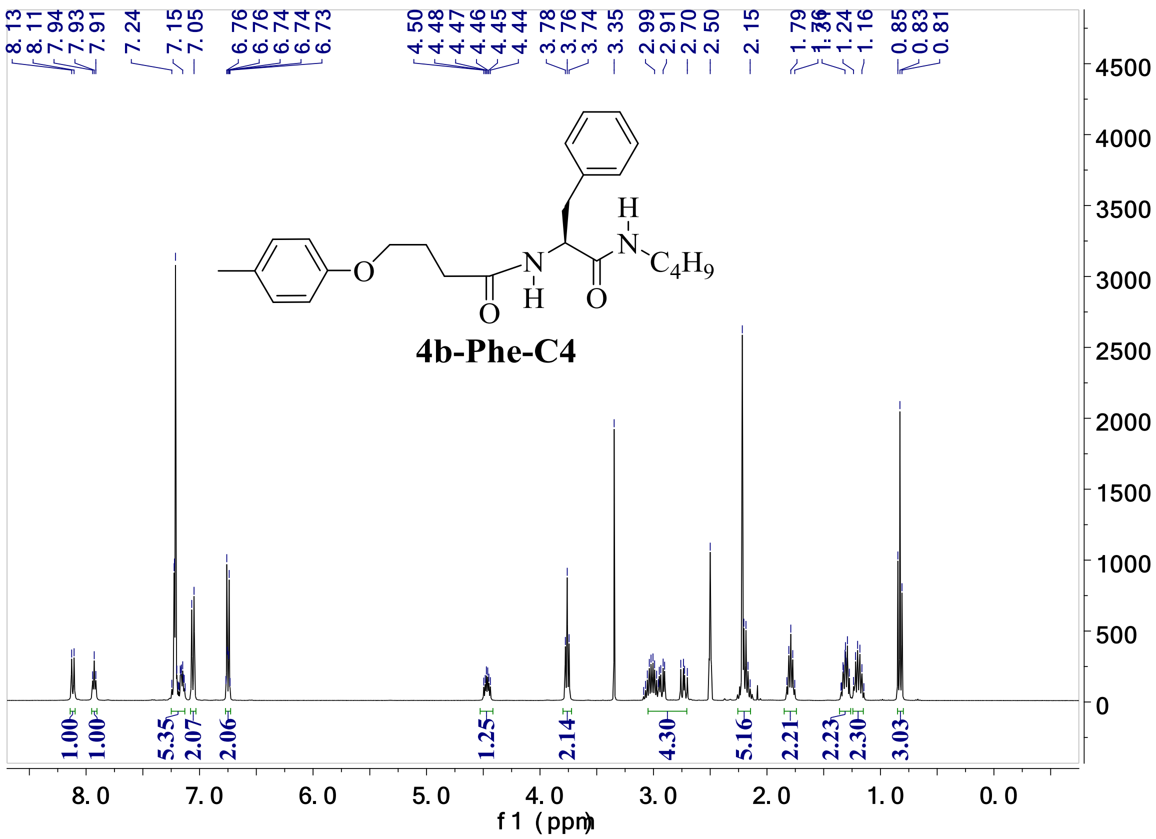

3b-Phe-C8
f1 (ppm)


4a-Phe-C4
f1 (ppm)

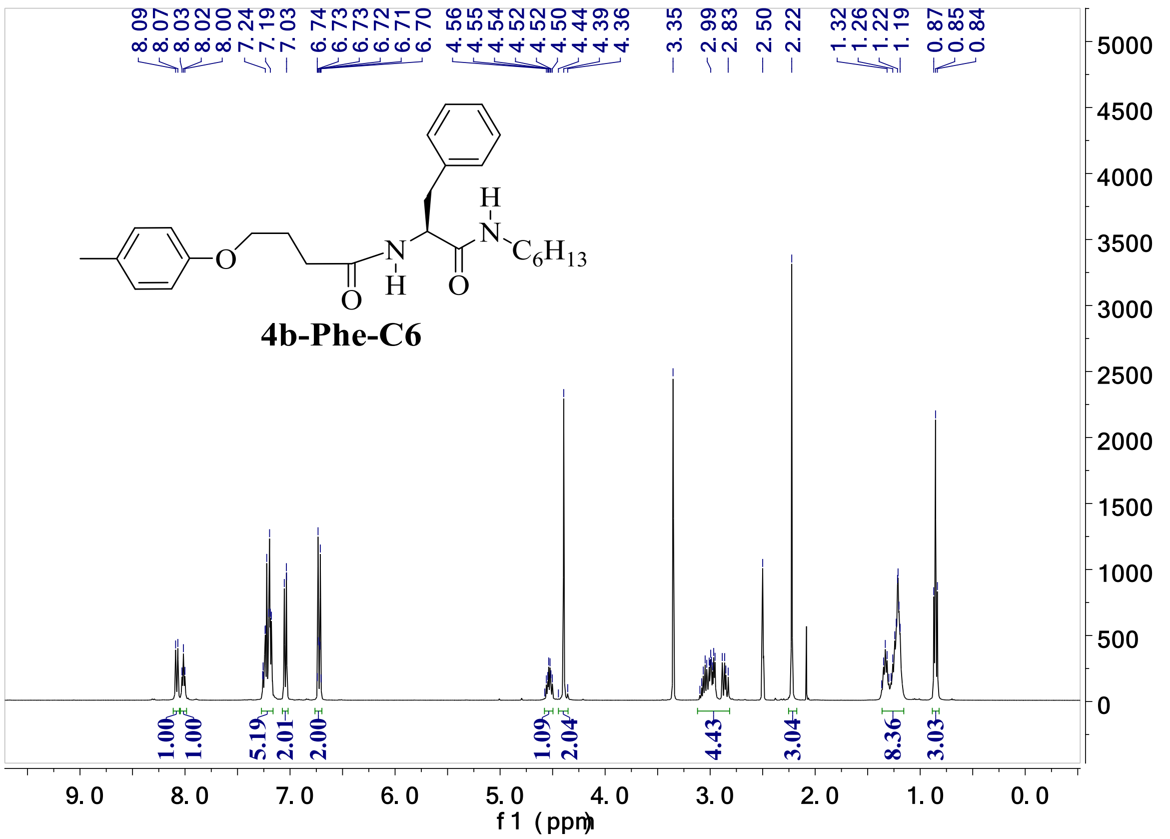

4a-Phe-C6
f1 (ppm)

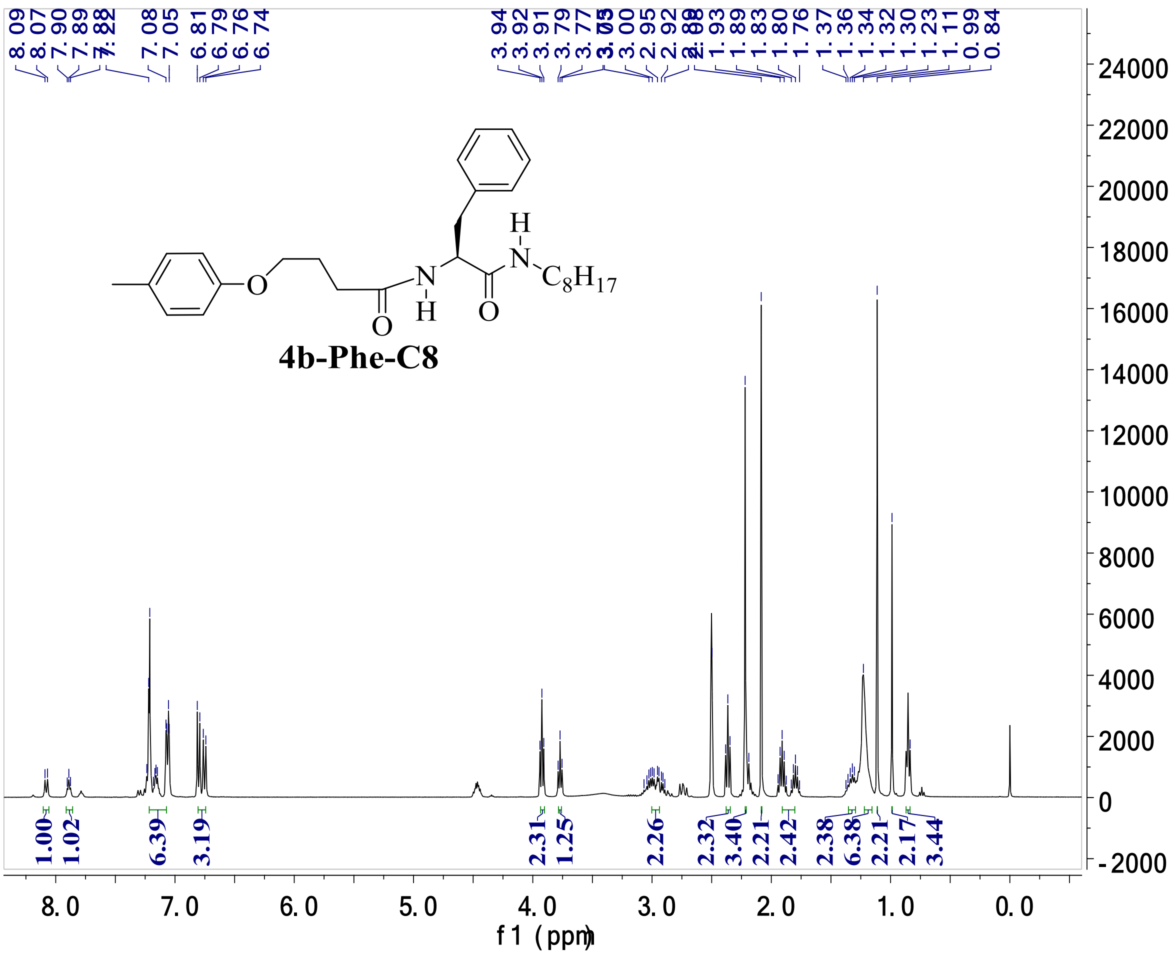


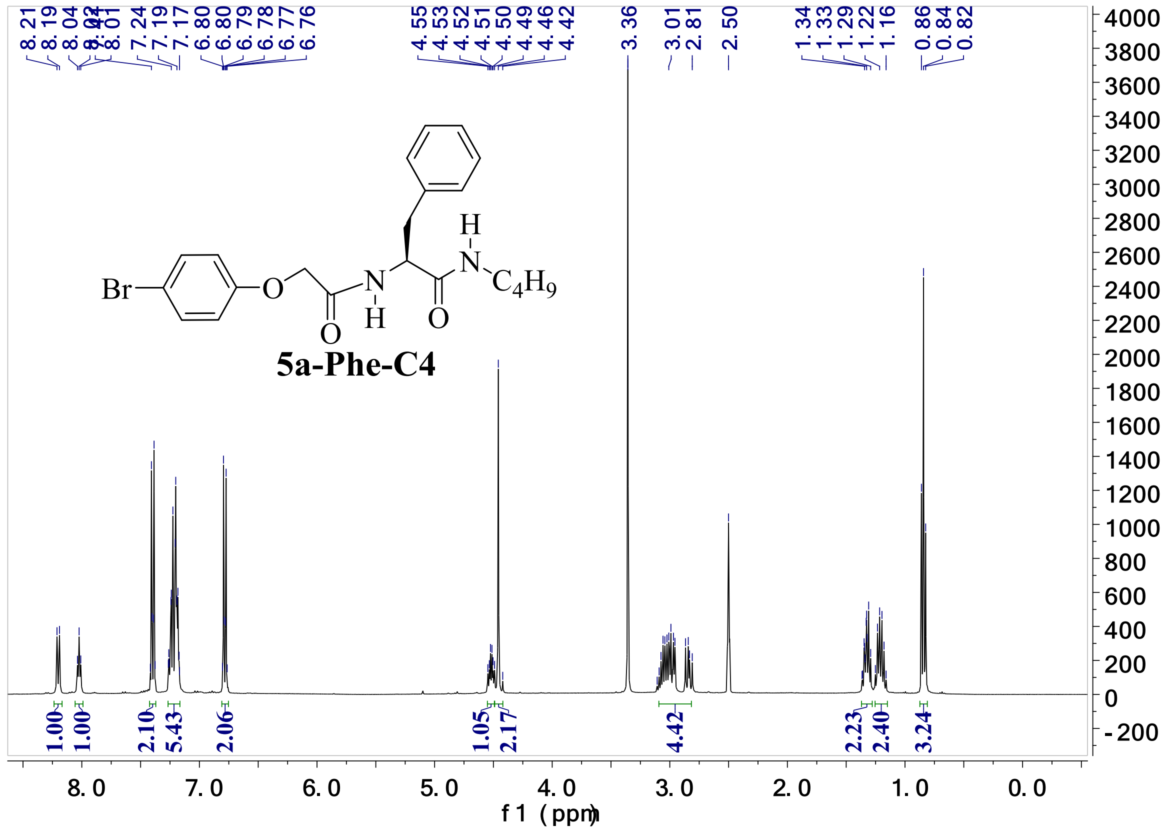
4a-Phe-C8



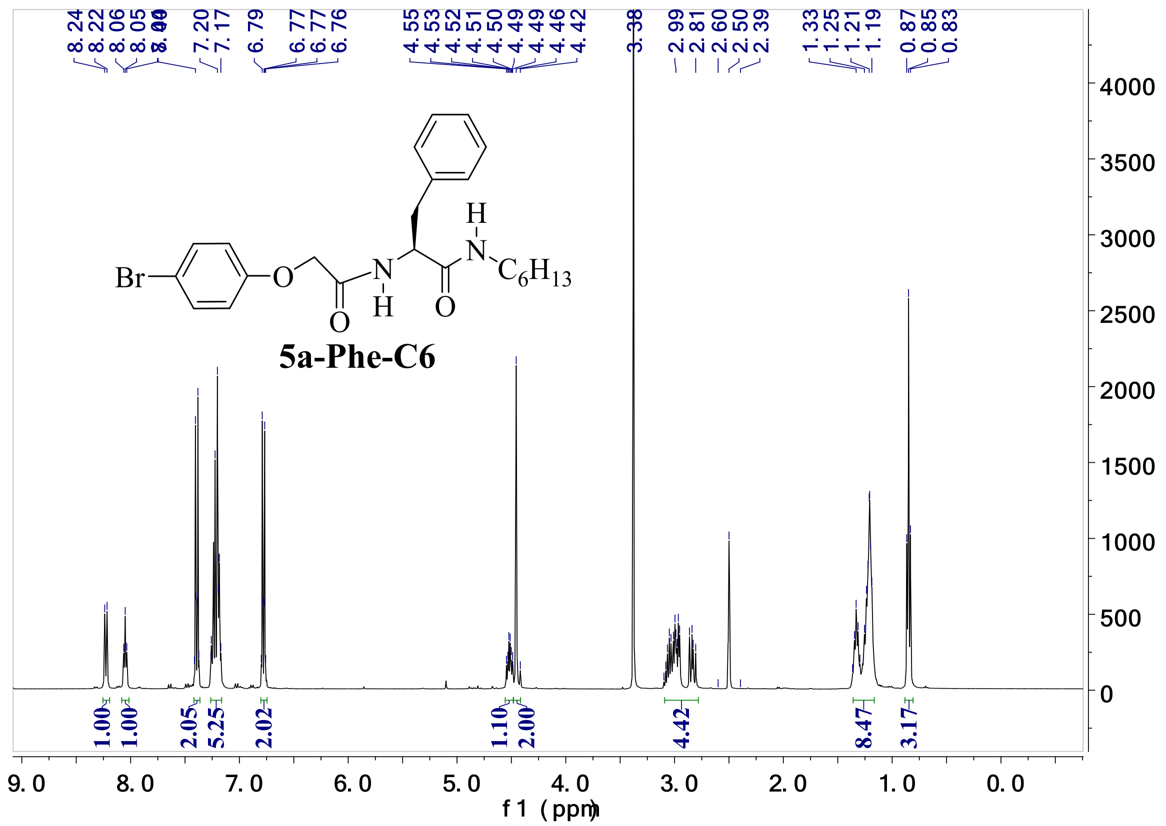
4b-Phe-C4


4b-Phe-C6
f1 (ppm)

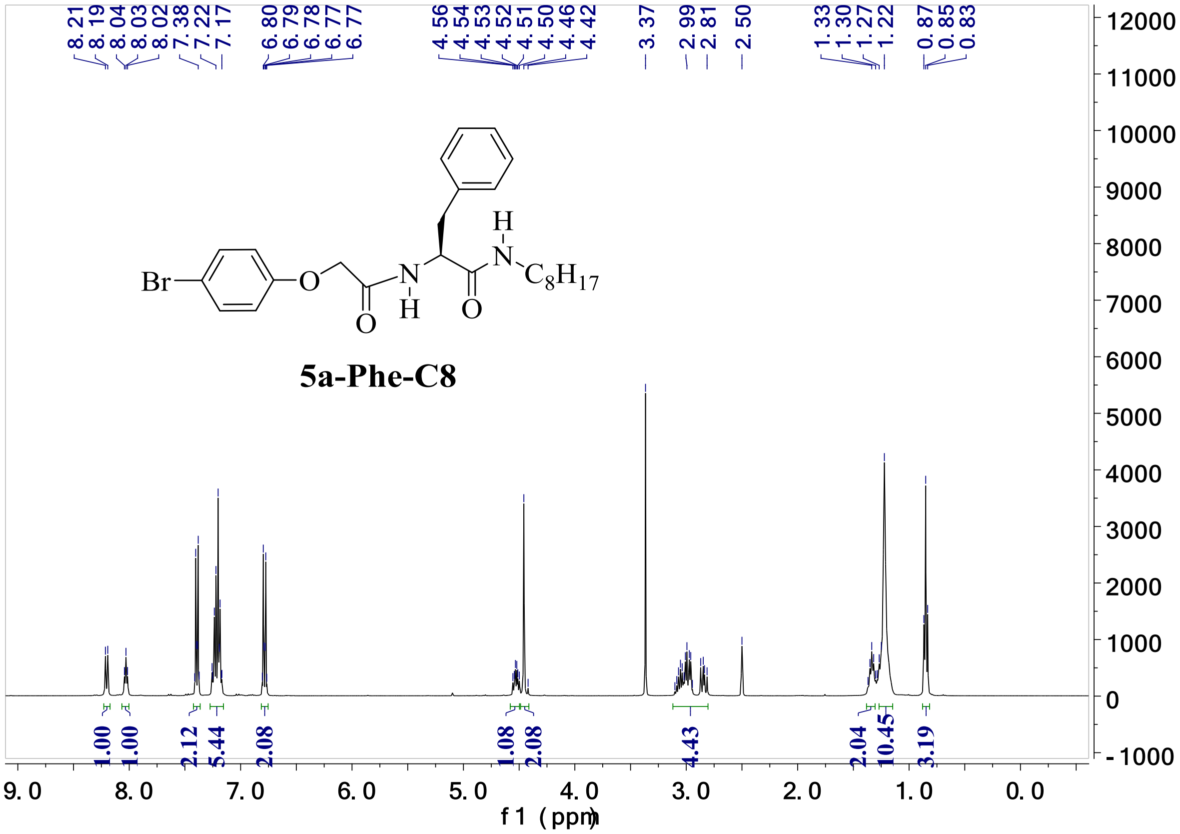

4b-Phe-C8
f1 (ppm)



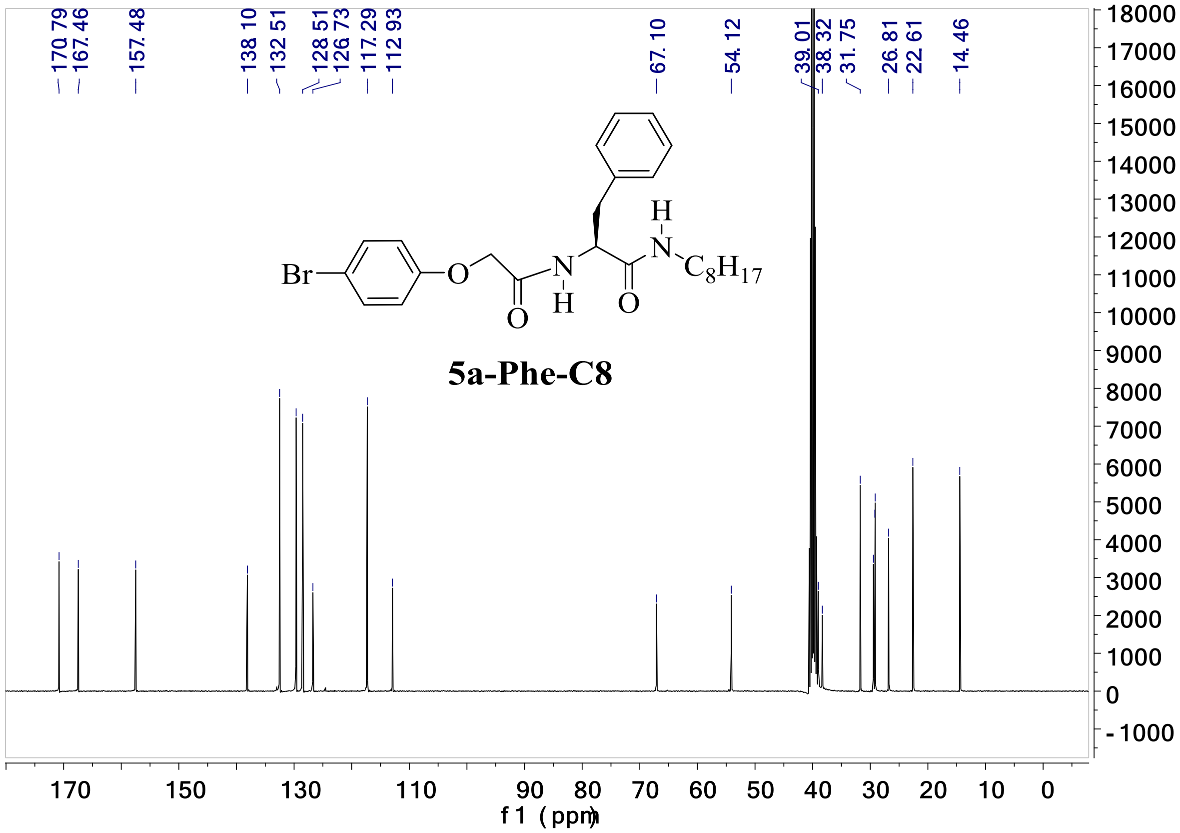
5a-Phe-C4



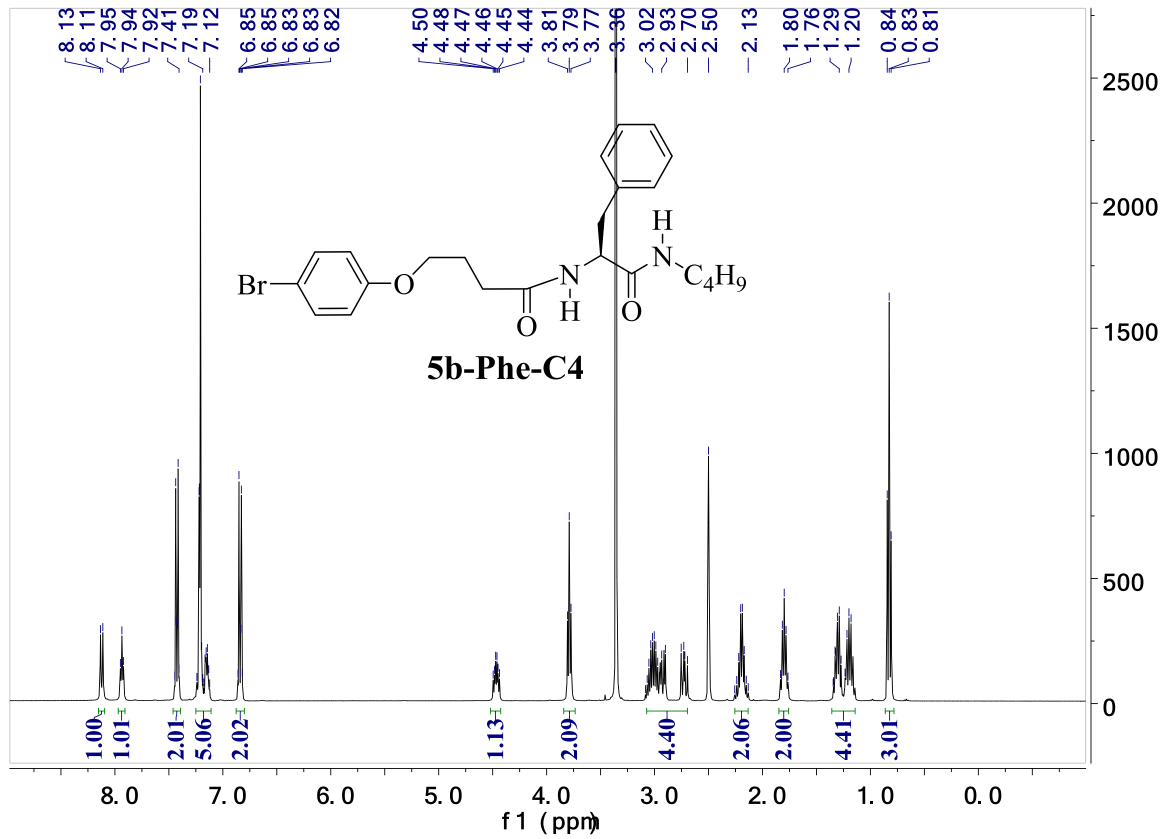
5a-Phe-C6

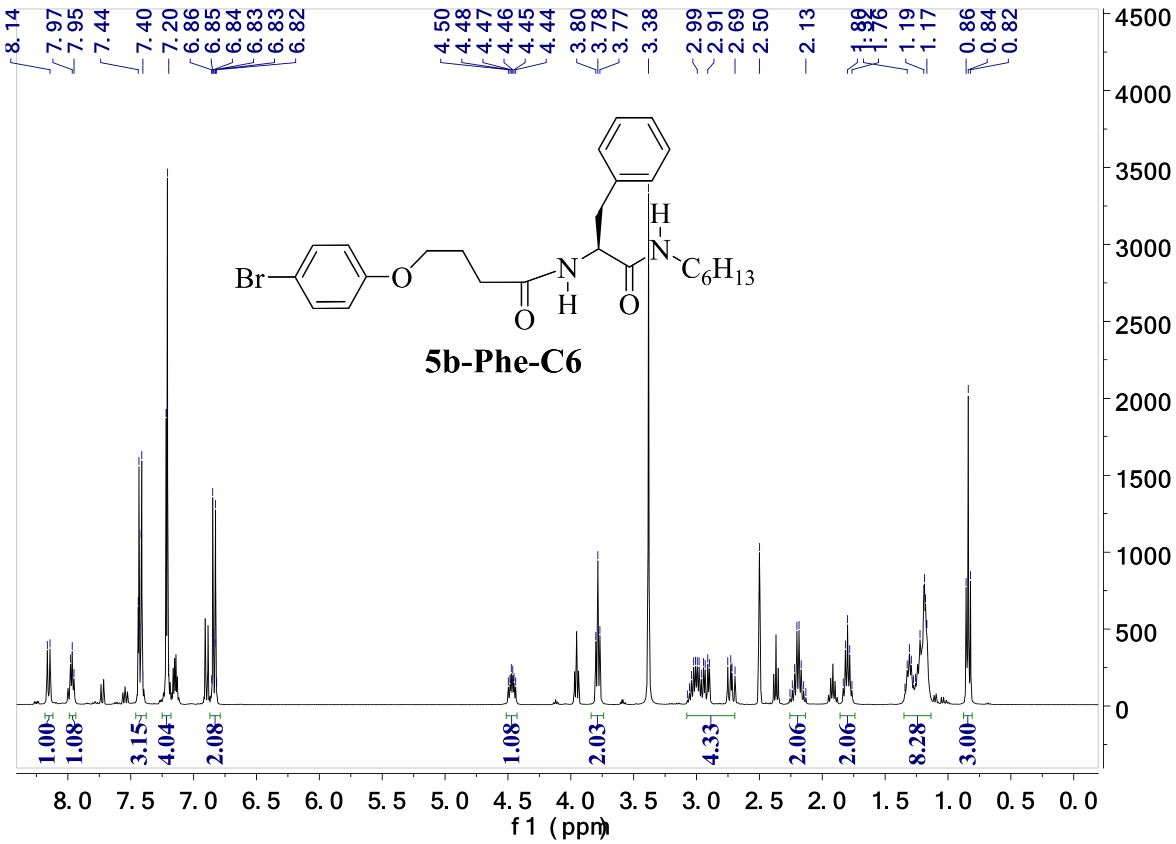


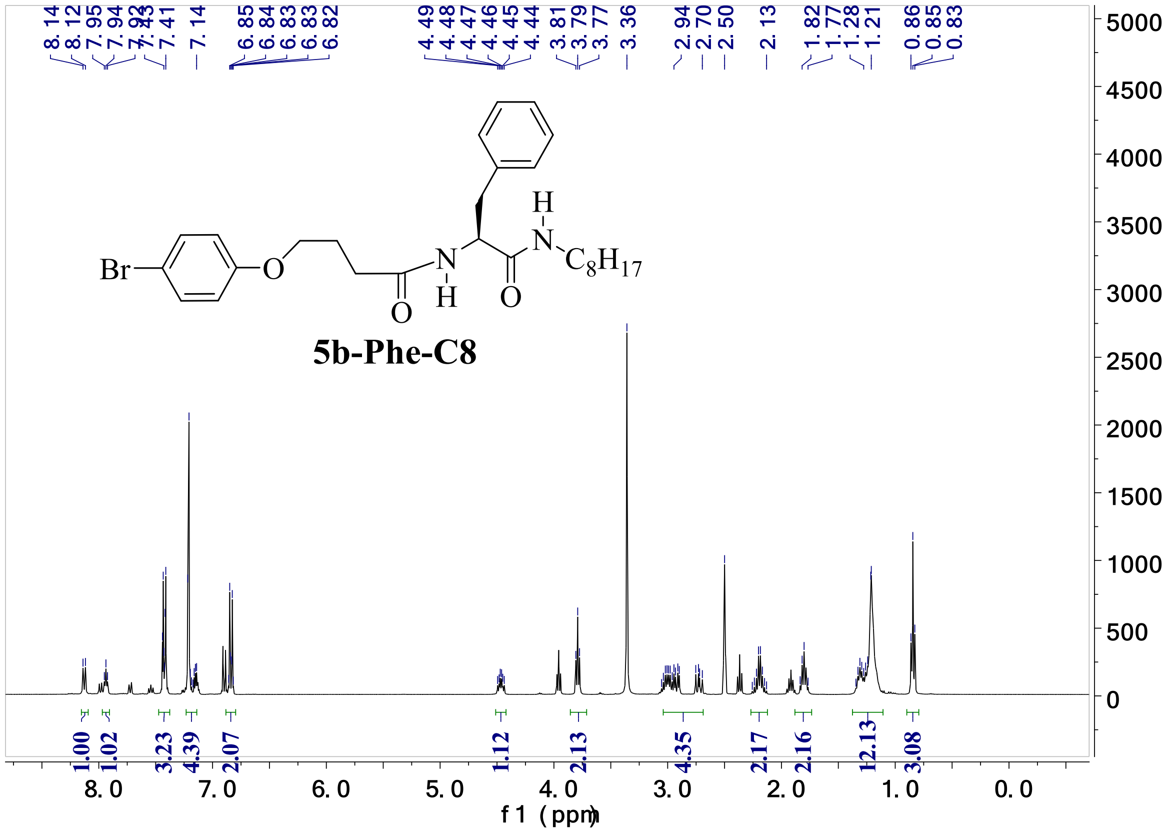
5a-Phe-C8

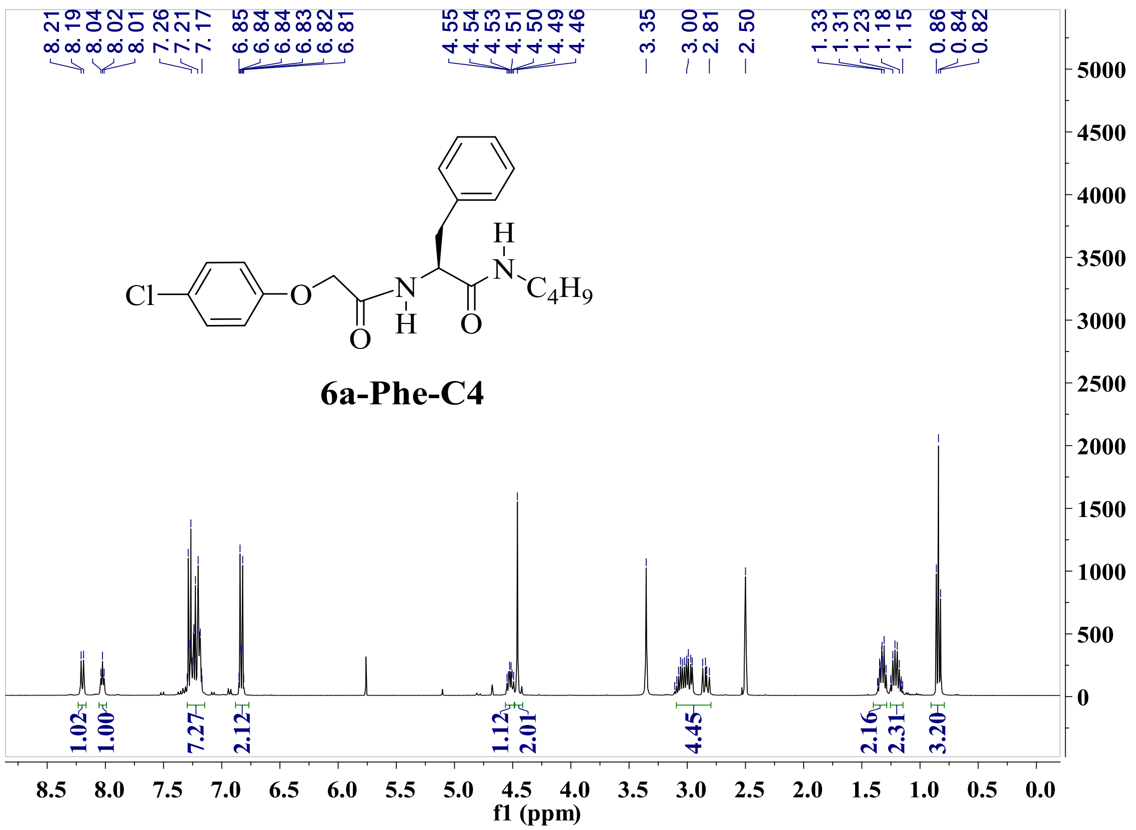


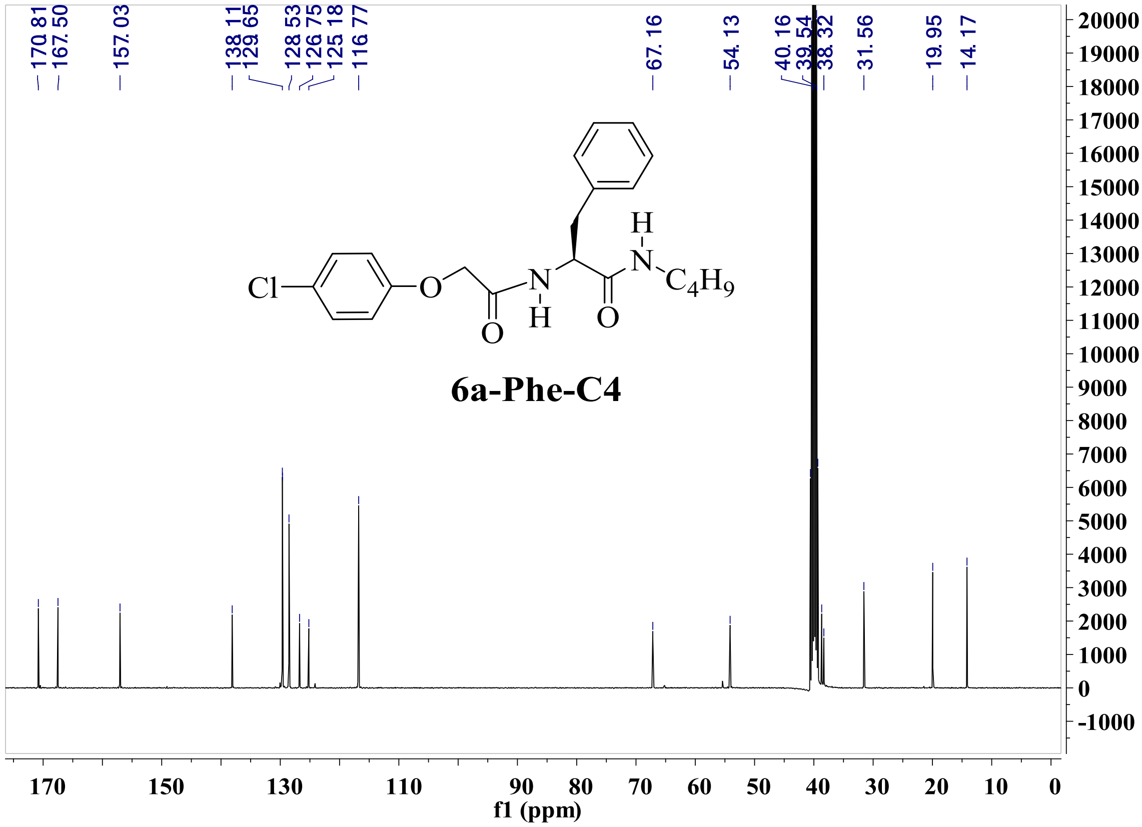
5a-Phe-C8

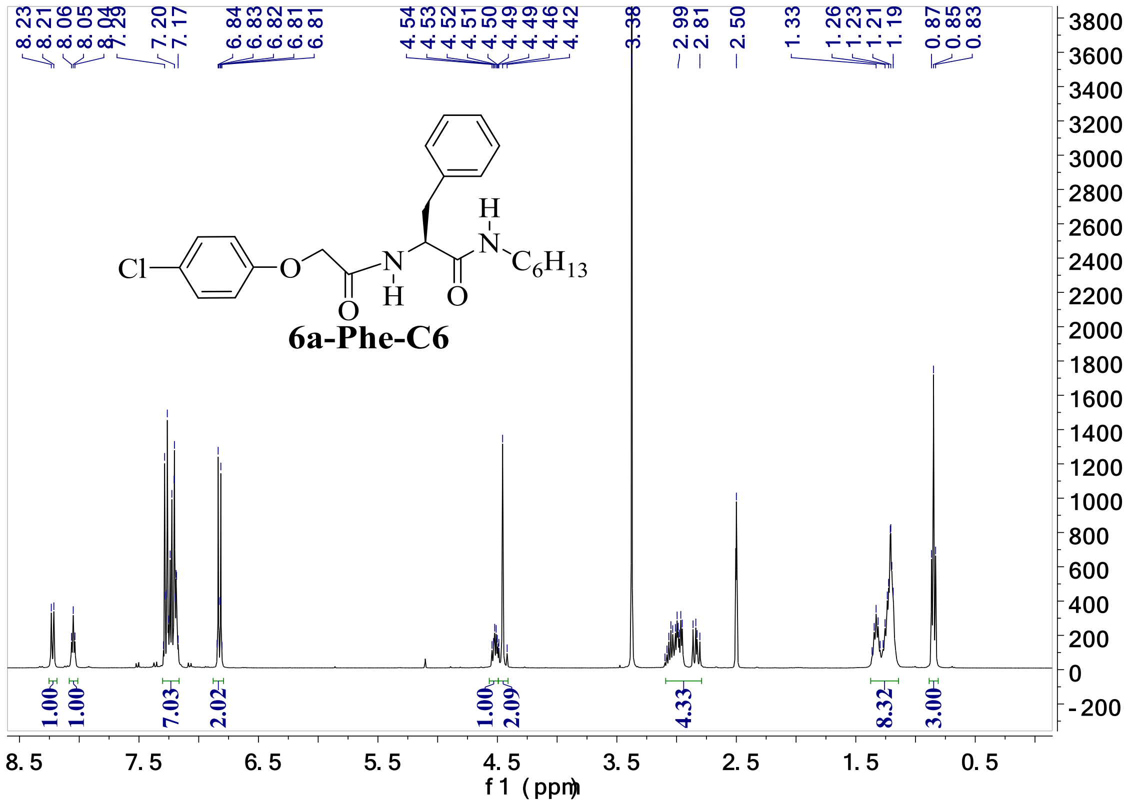

5b-Phe-C4

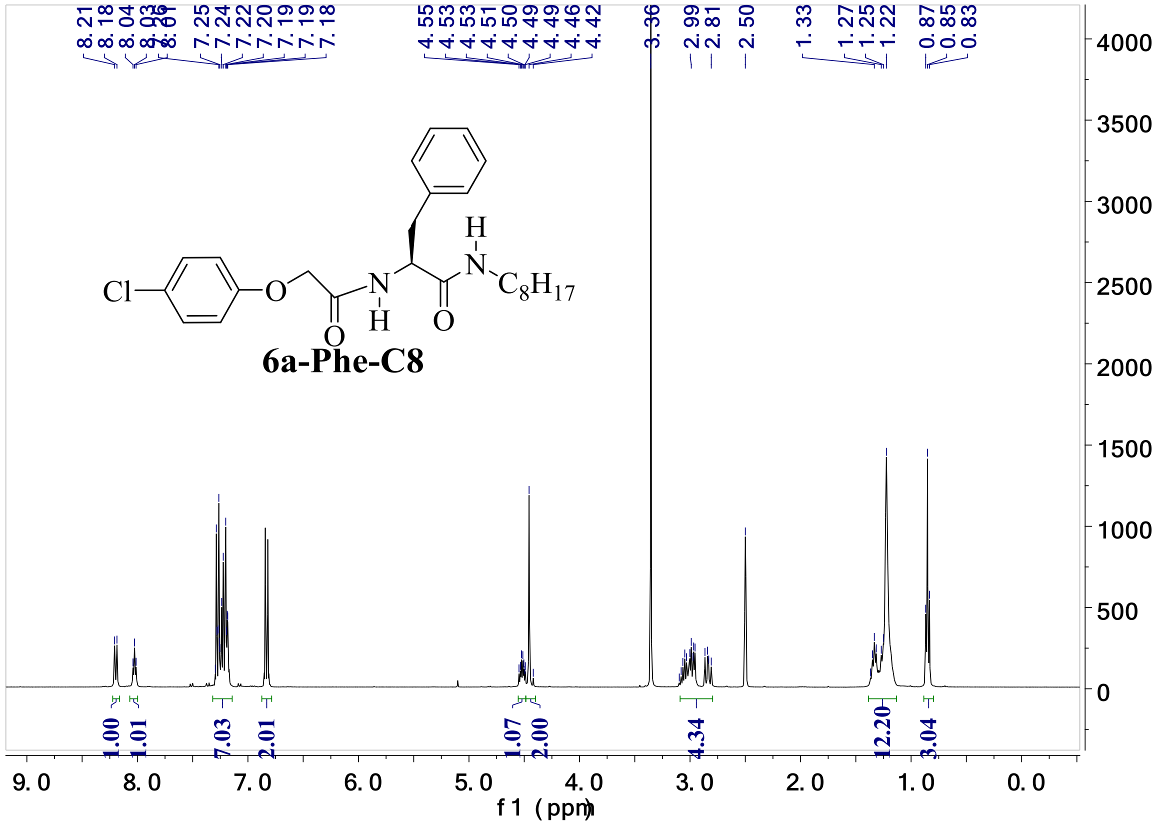

5b-Phe-C6


5b-Phe-C8
Br
O
N
H
C8H17
f1 (ppm)

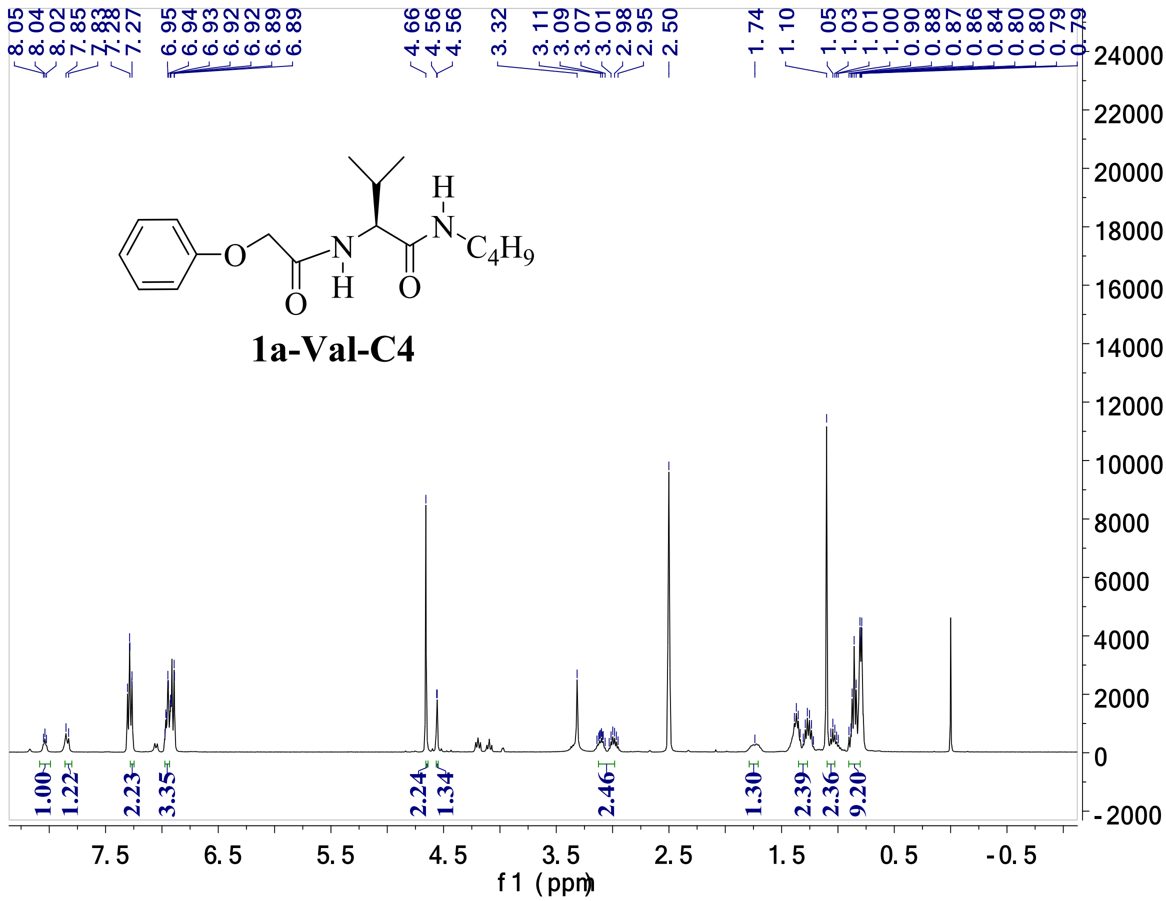

6a-Phe-C4
Cl
O
N
H
C4H9
f1 (ppm)


170.81
167.50
157.03
138.11
129.65
128.53
126.75
125.18
116.77
67.16
54.13
40.16
39.54
38.32
31.56
19.95
14.17
Cl
O
N
H
O
H
N
C_4H_9
O
6a-Phe-C4
f1 (ppm)

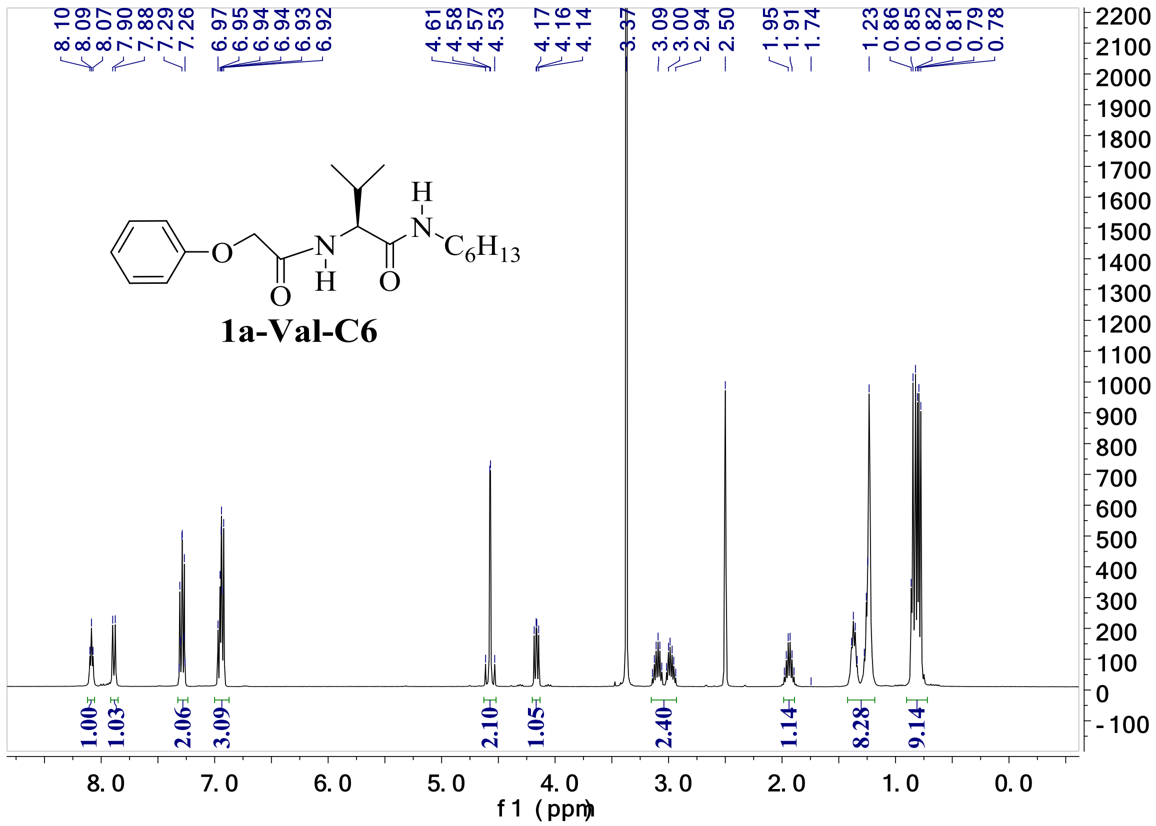

8.23
8.21
8.06
8.05
8.04
7.29
7.20
7.17
6.84
6.83
6.82
6.81
6.81
4.54
4.53
4.52
4.51
4.50
4.49
4.49
4.46
4.42
3.38
2.99
2.81
2.50
1.33
1.26
1.23
1.21
1.19
0.87
0.85
0.83
Cl
O
N
H
O
H
N
C_6H_{13}
O
6a-Phe-C6
1.00
1.00
7.03
2.02
1.00
2.09
4.33
8.32
3.00
f1 (ppm)

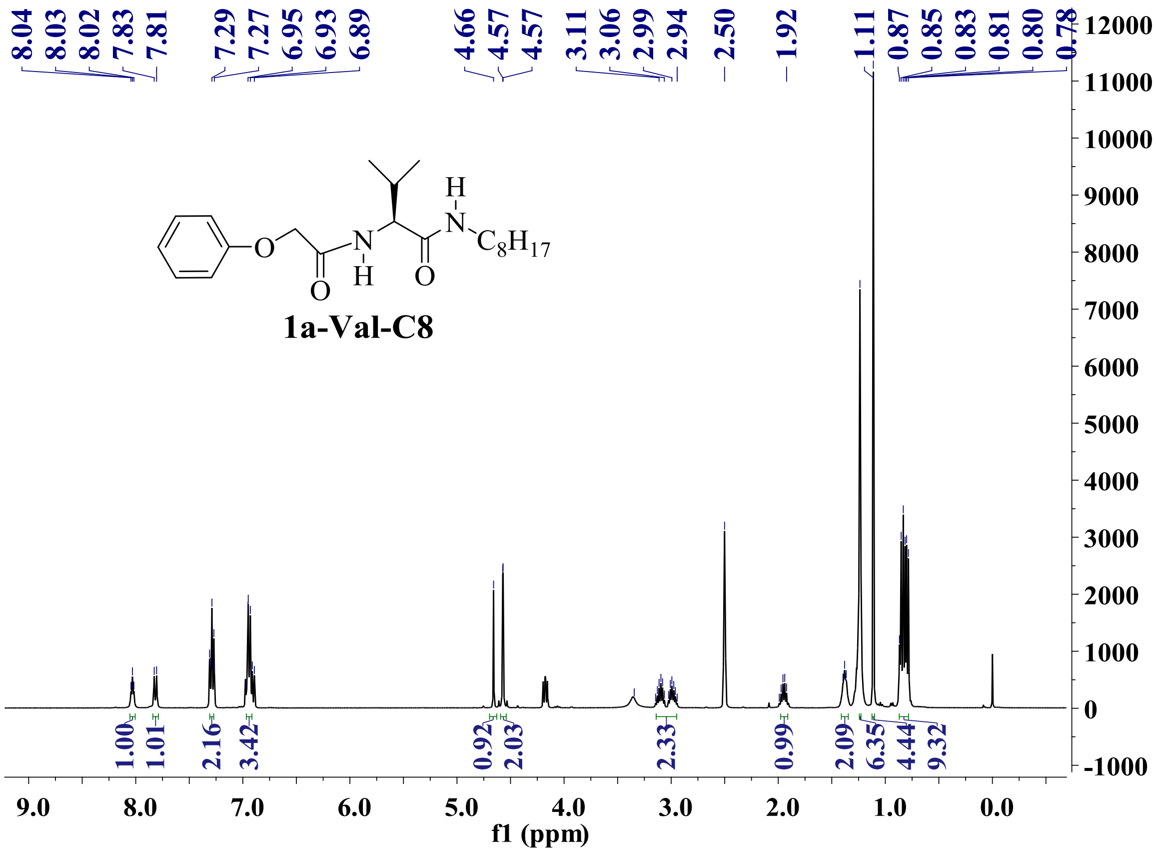


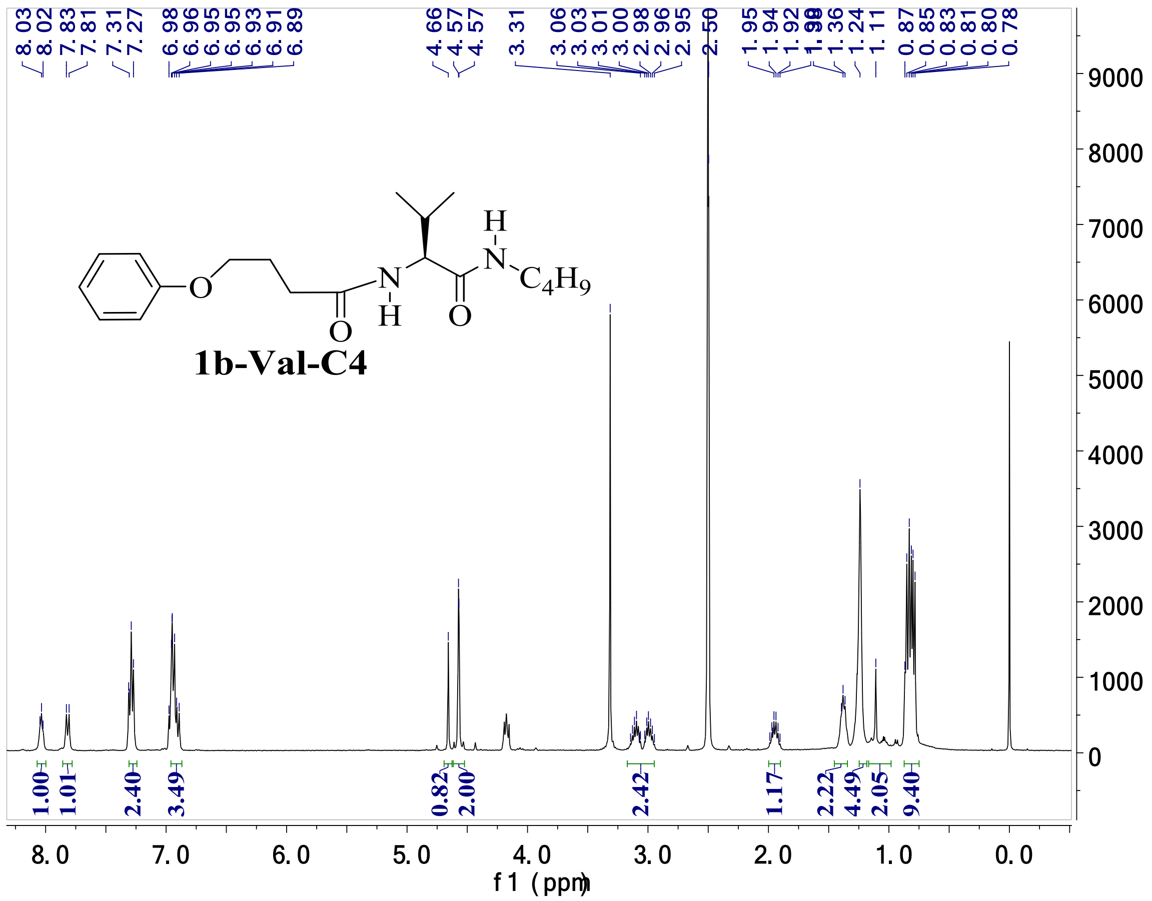
Cl
O
N
H
O
H
N
C_8H_{17}
O
6a-Phe-C8
f1 (ppm)

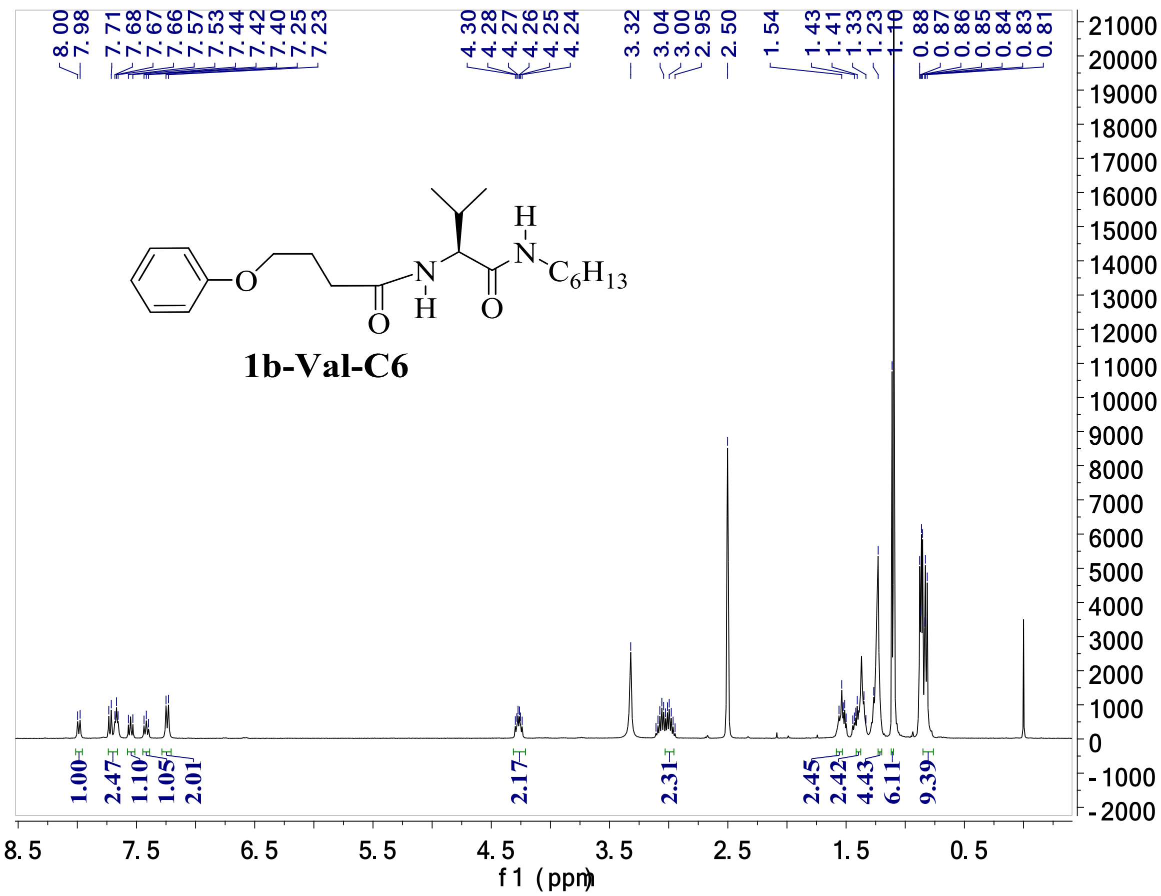


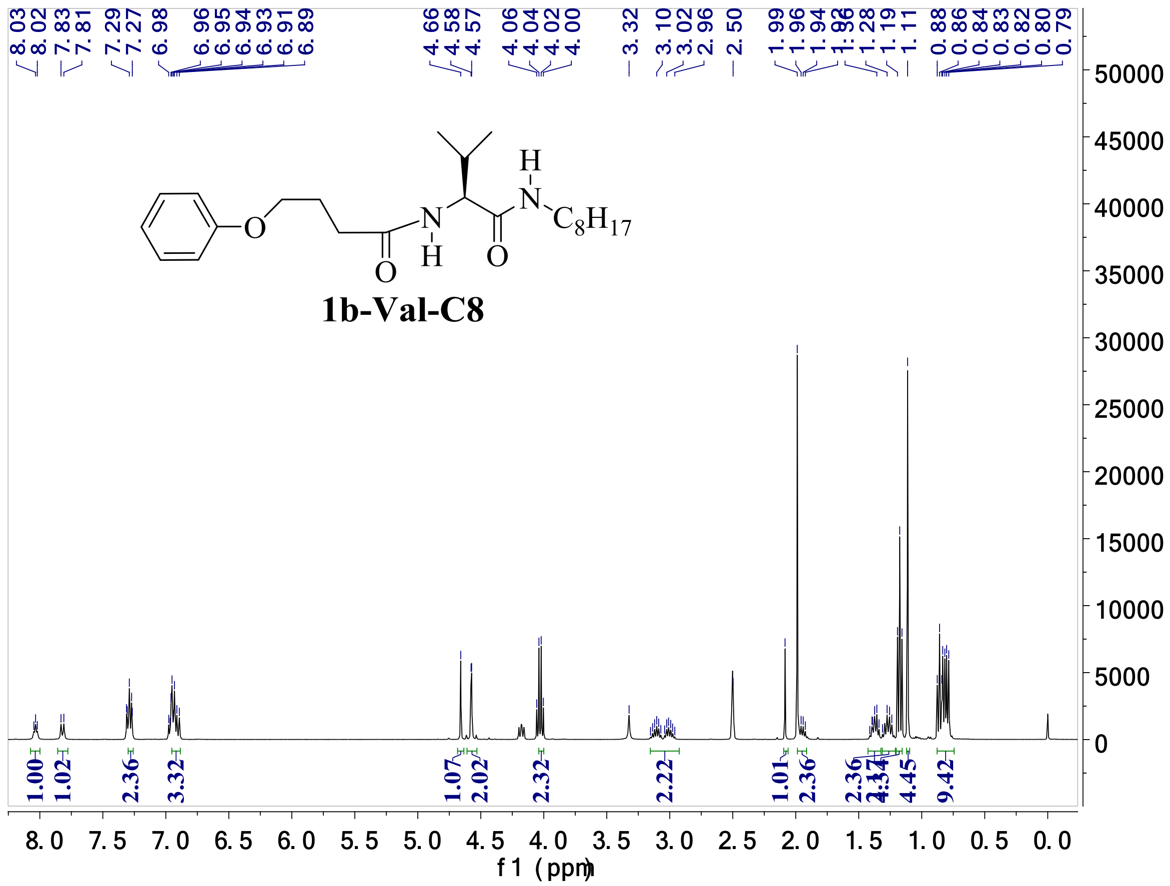
O
N
H
O
H
N
C_4H_9
O
1a-Val-C4
f1 (ppm)

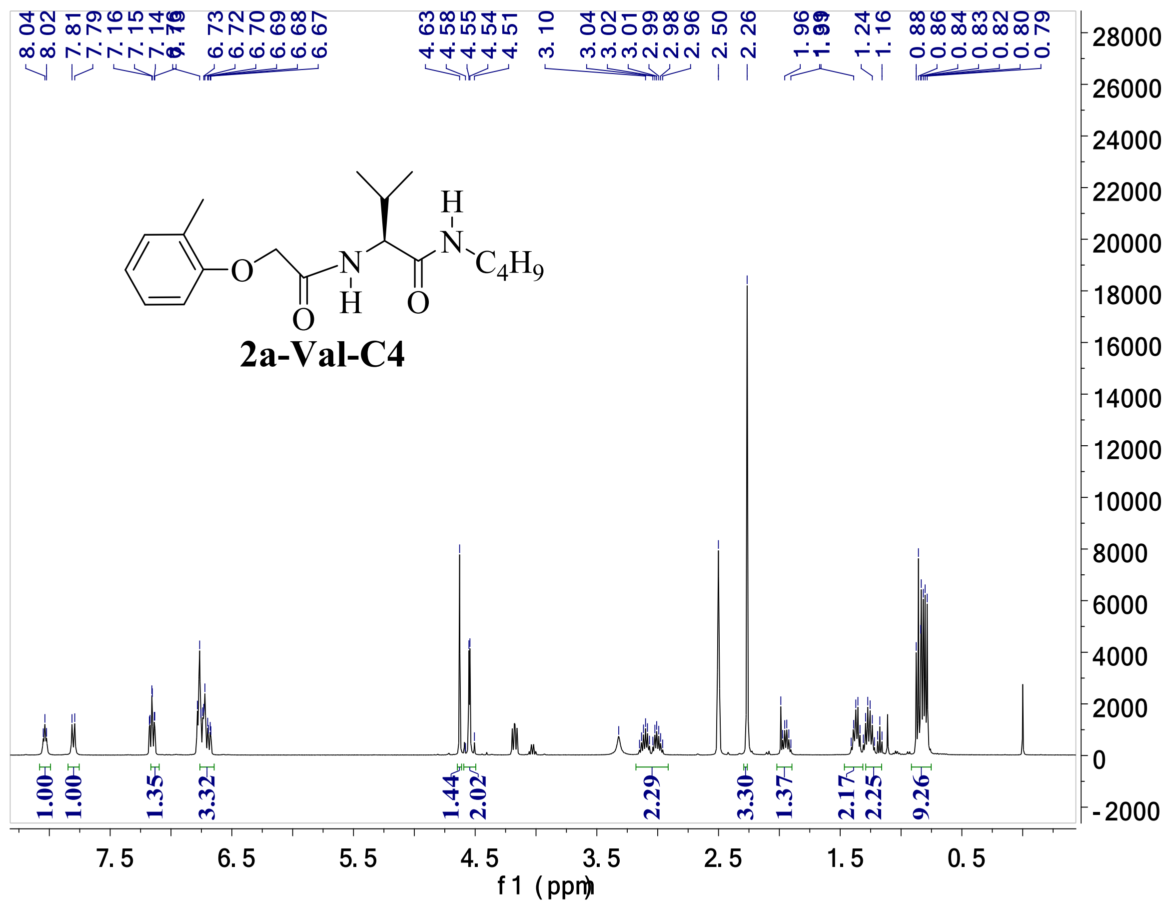

1a-Val-C6
f1 (ppm)

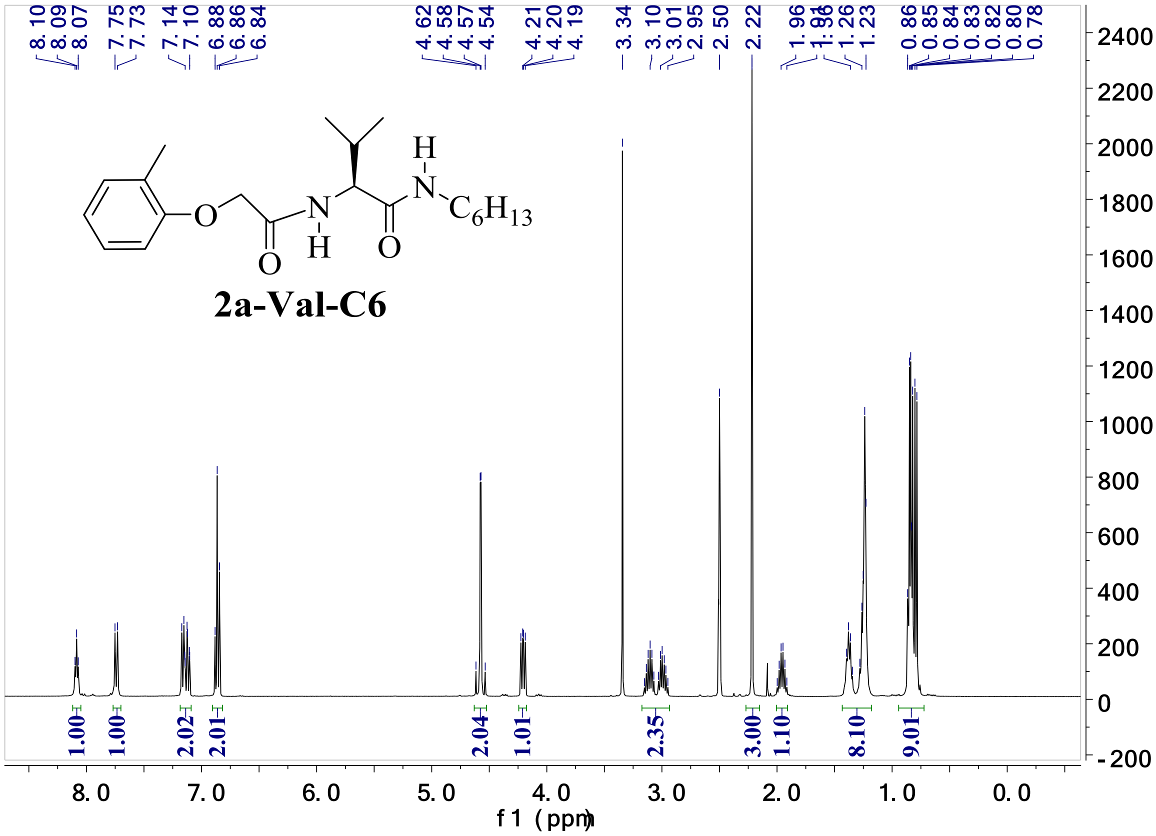

1a-Val-C8
f1 (ppm)


1b-Val-C4
f1 (ppm)

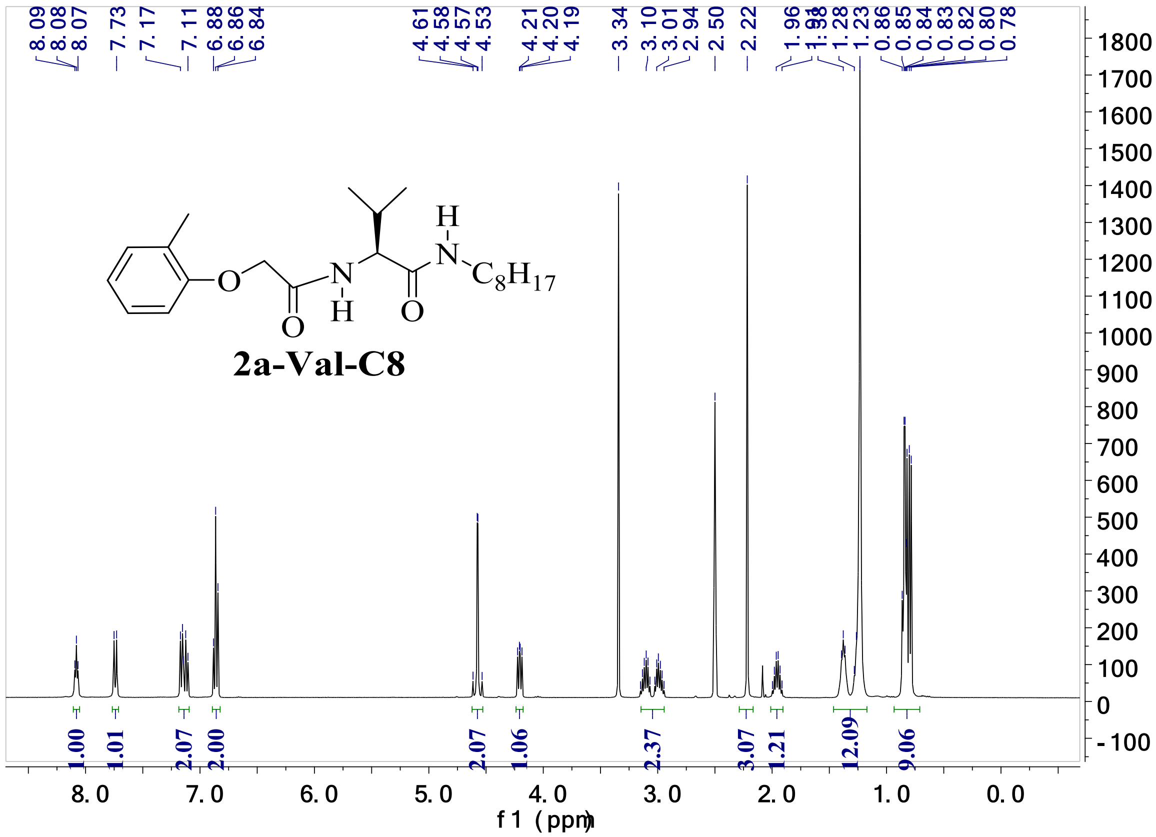

1b-Val-C6
f1 (ppm)


1b-Val-C8
f1 (ppm)

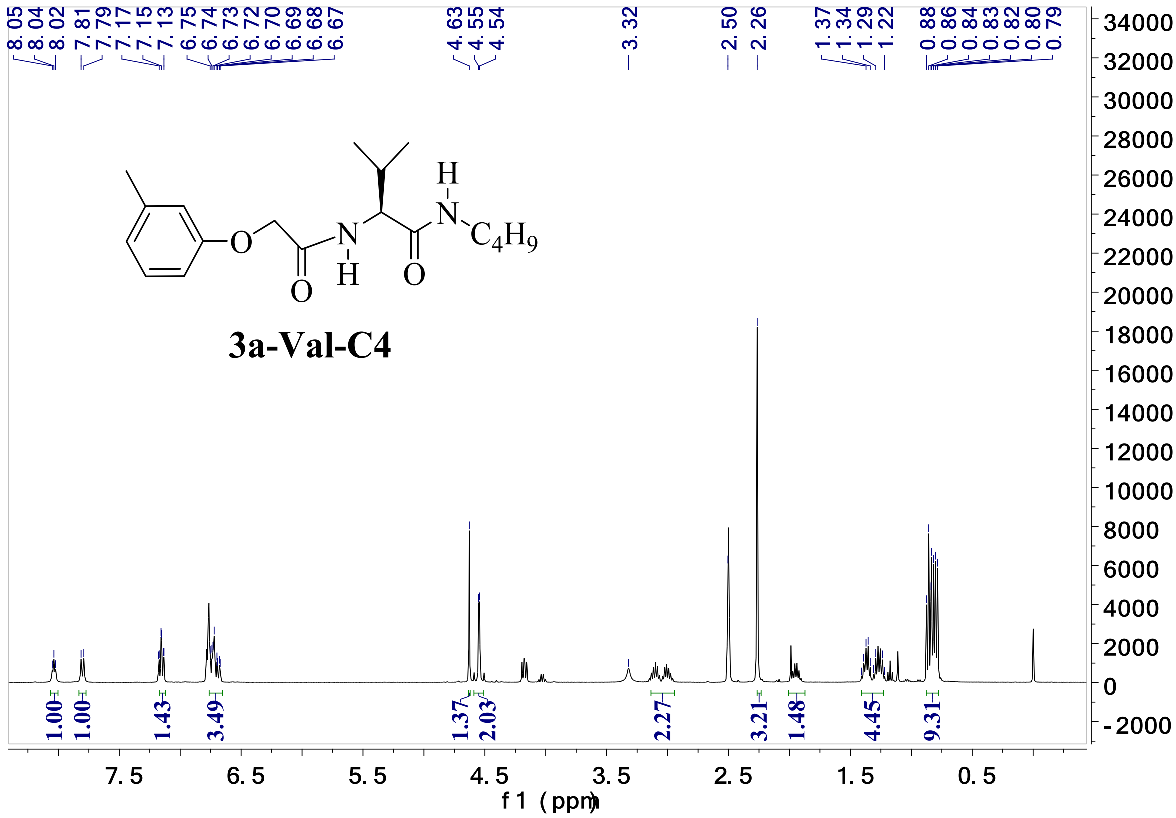

2a-Val-C4
f1 (ppm)



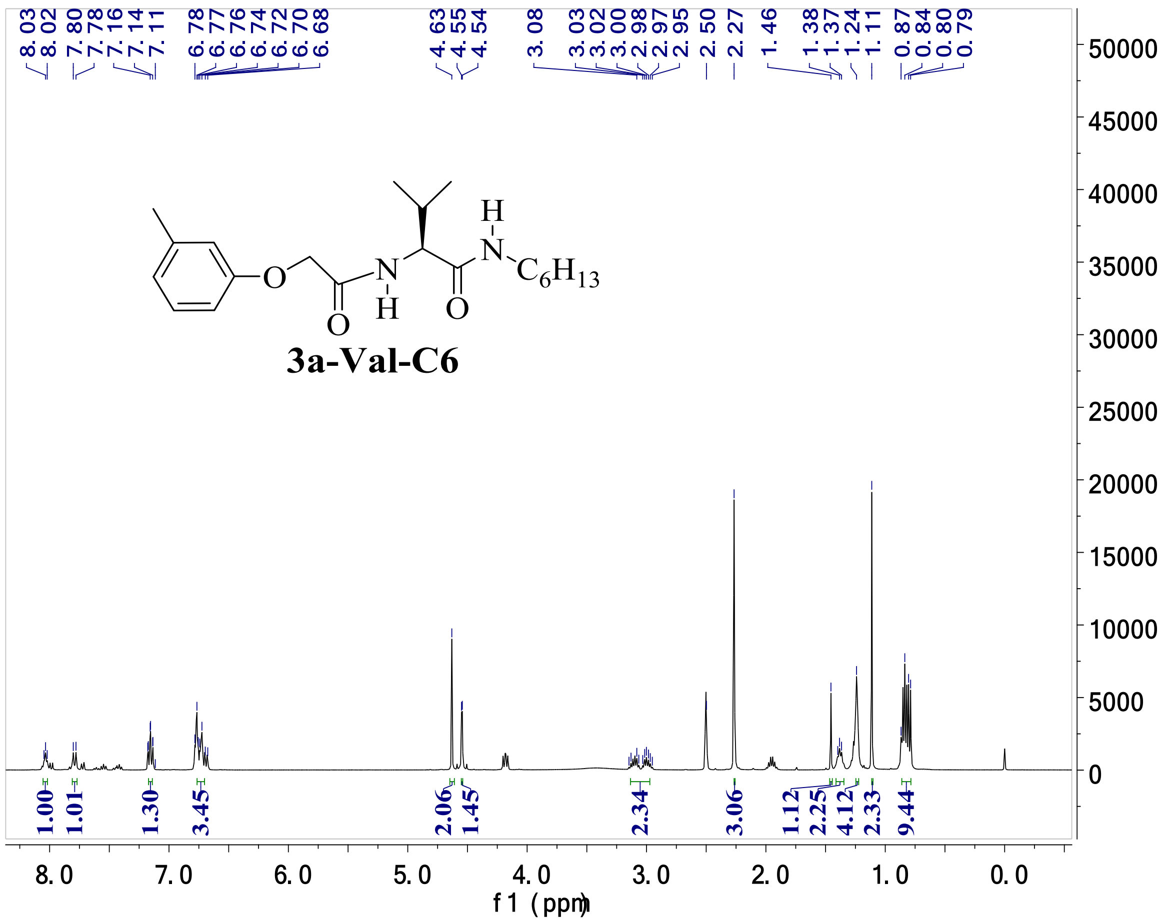
8.10
8.09
8.07
7.75
7.73
7.14
7.10
6.88
6.86
6.84
4.62
4.58
4.57
4.54
4.21
4.20
4.19
3.34
3.10
3.01
2.95
2.50
2.22
1.96
1.26
1.23
0.86
0.85
0.84
0.83
0.82
0.80
0.78
H
N
C_6H_{13}
O
N
H
O
O
2a-Val-C6
1.00
1.00
2.02
2.01
2.04
1.01
2.35
3.00
1.10
8.10
9.01
f1 (ppm)



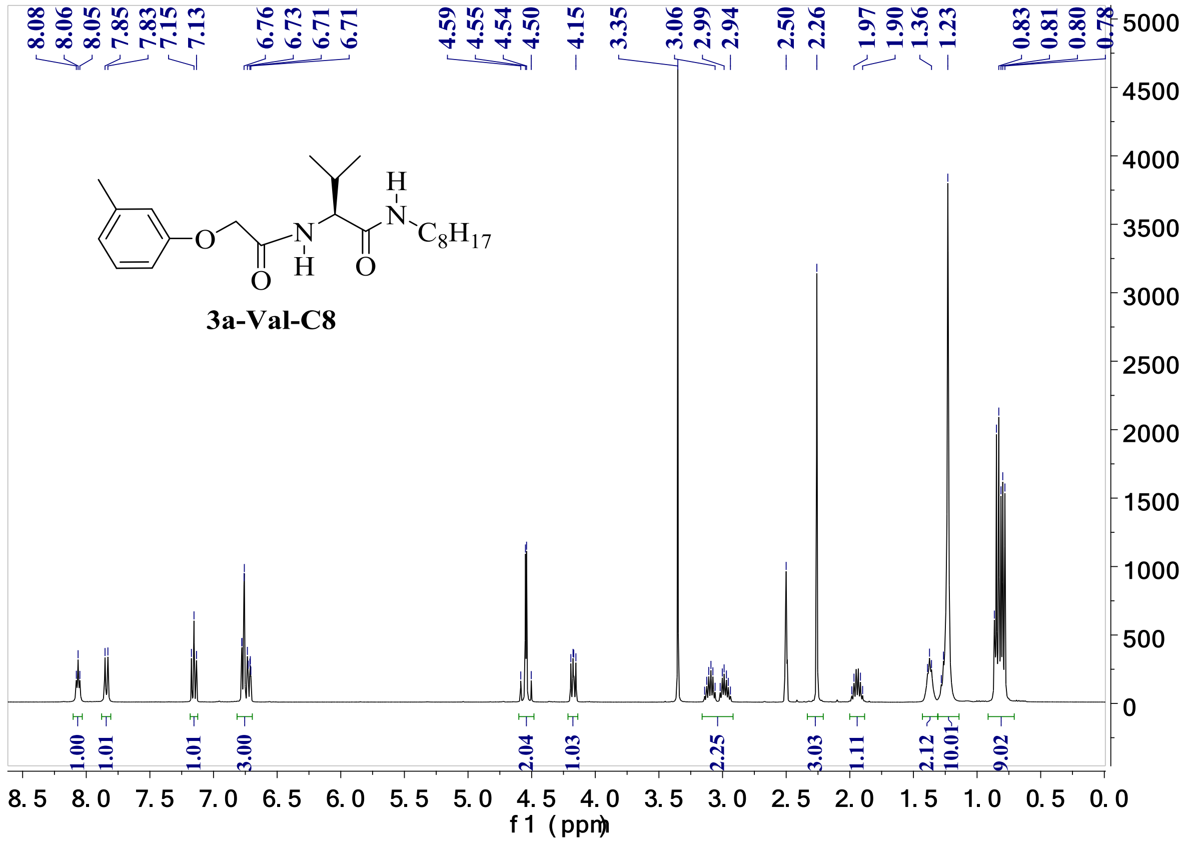
8.09
8.08
8.07
7.73
7.17
7.11
6.88
6.86
6.84
4.61
4.58
4.57
4.53
4.21
4.20
4.19
3.34
3.10
3.01
2.94
2.50
2.22
1.96
1.28
1.23
0.86
0.85
0.84
0.83
0.82
0.80
0.78
H
N
C_8H_{17}
O
N
H
O
O
2a-Val-C8
1.00
1.01
2.07
2.00
2.07
1.06
2.37
3.07
1.21
12.09
9.06
f1 (ppm)

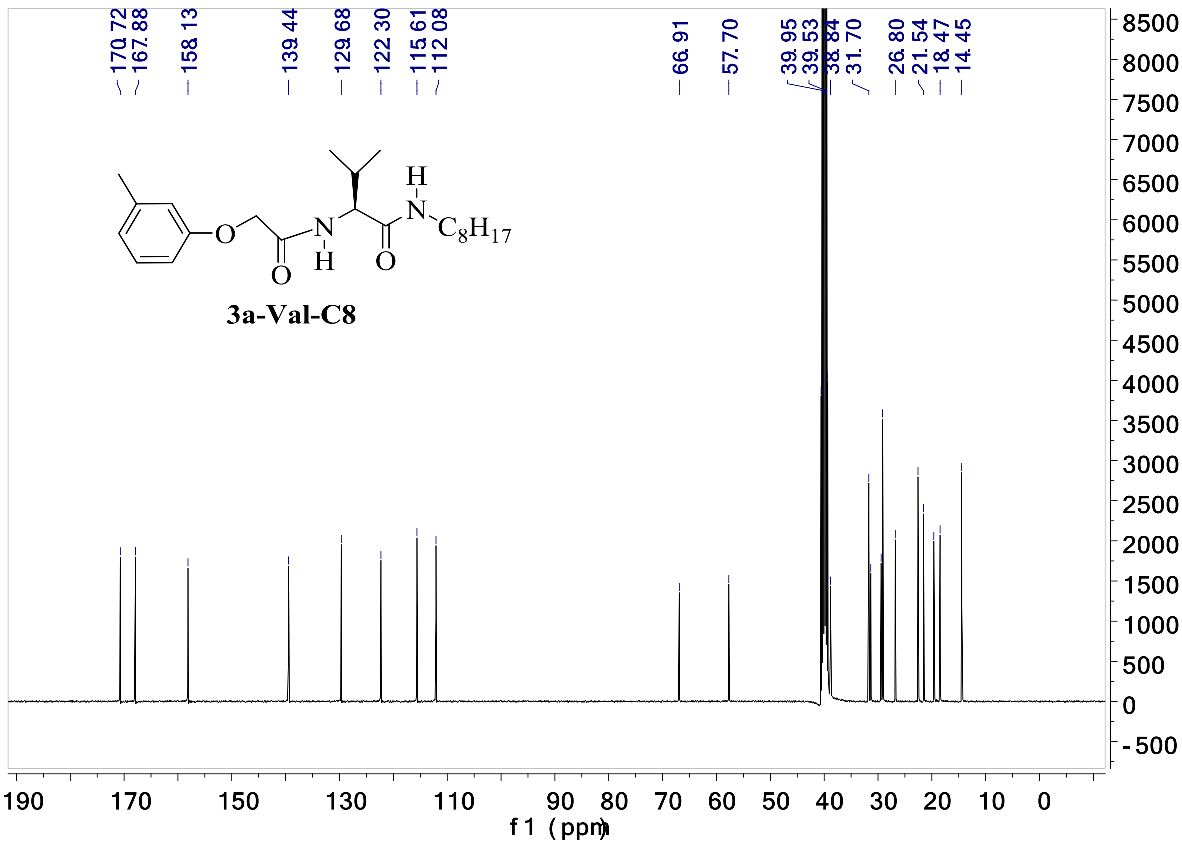


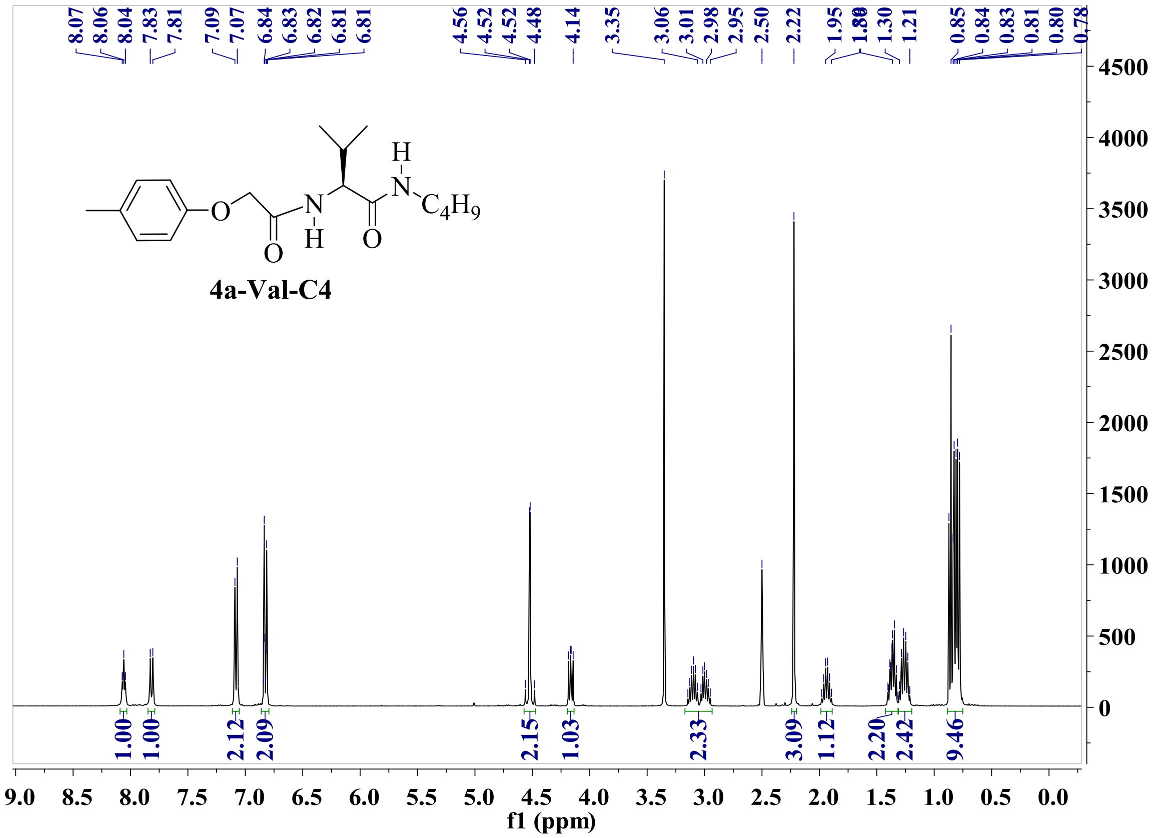
3a-Val-C4

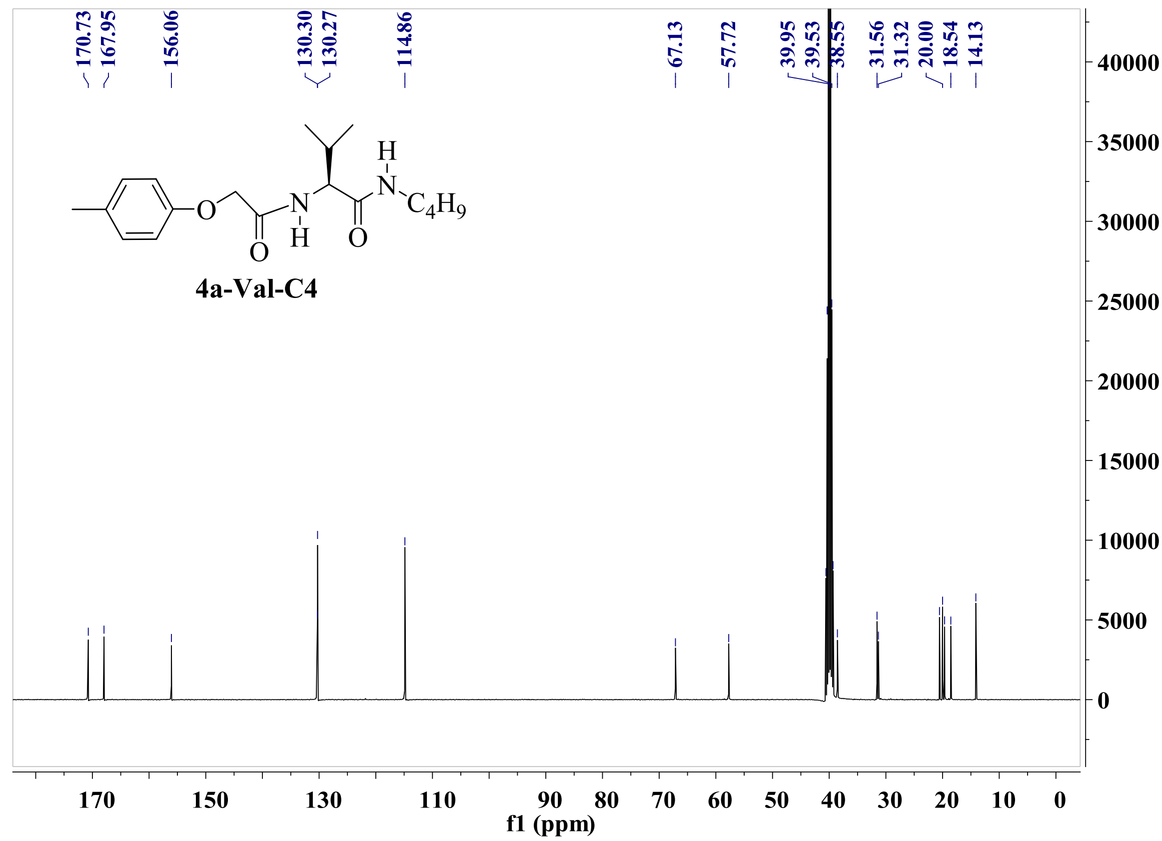


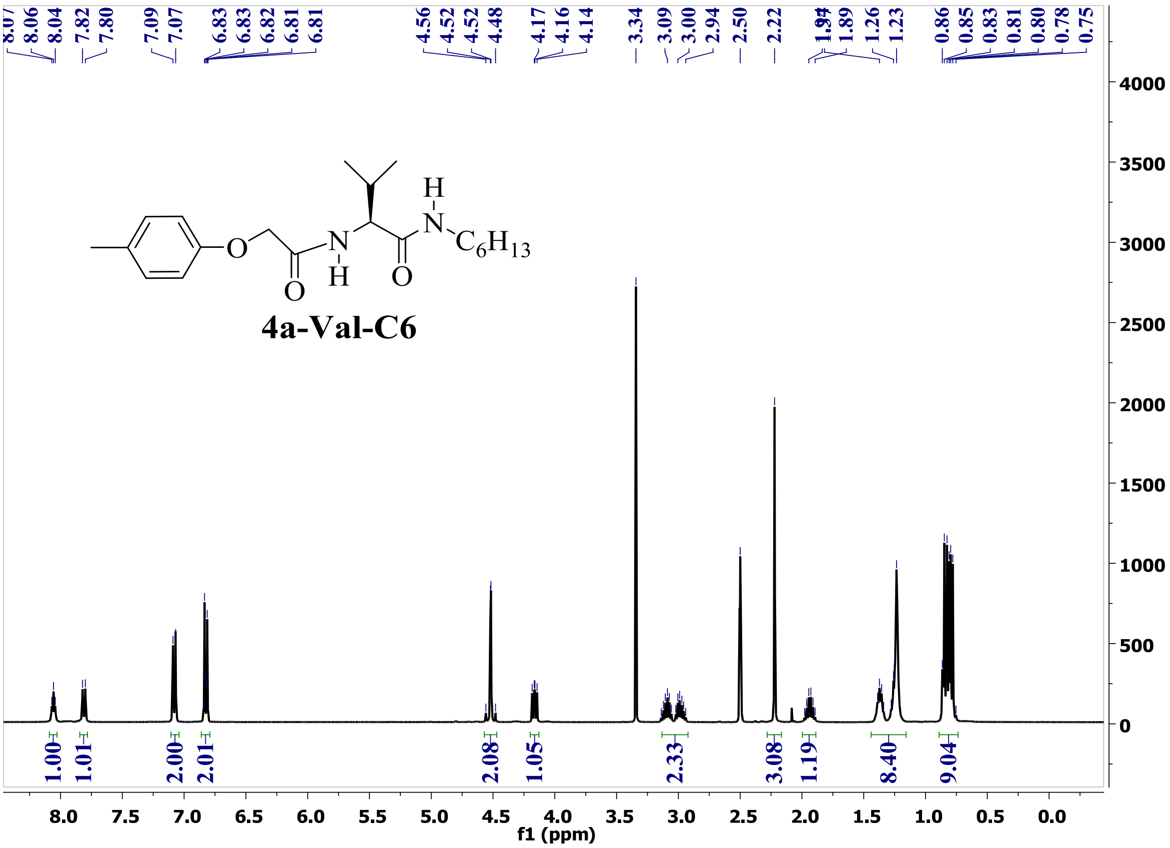
3a-Val-C6


8.08
8.06
8.05
7.85
7.83
7.15
7.13
6.76
6.73
6.71
6.71
4.59
4.55
4.54
4.50
4.15
3.35
3.06
2.99
2.94
2.50
2.26
1.97
1.90
1.36
1.23
0.83
0.81
0.80
0.78
3a-Val-C8
1.00
1.01
1.01
3.00
2.04
1.03
2.25
3.03
1.11
2.12
10.01
9.02
f1 (ppm)

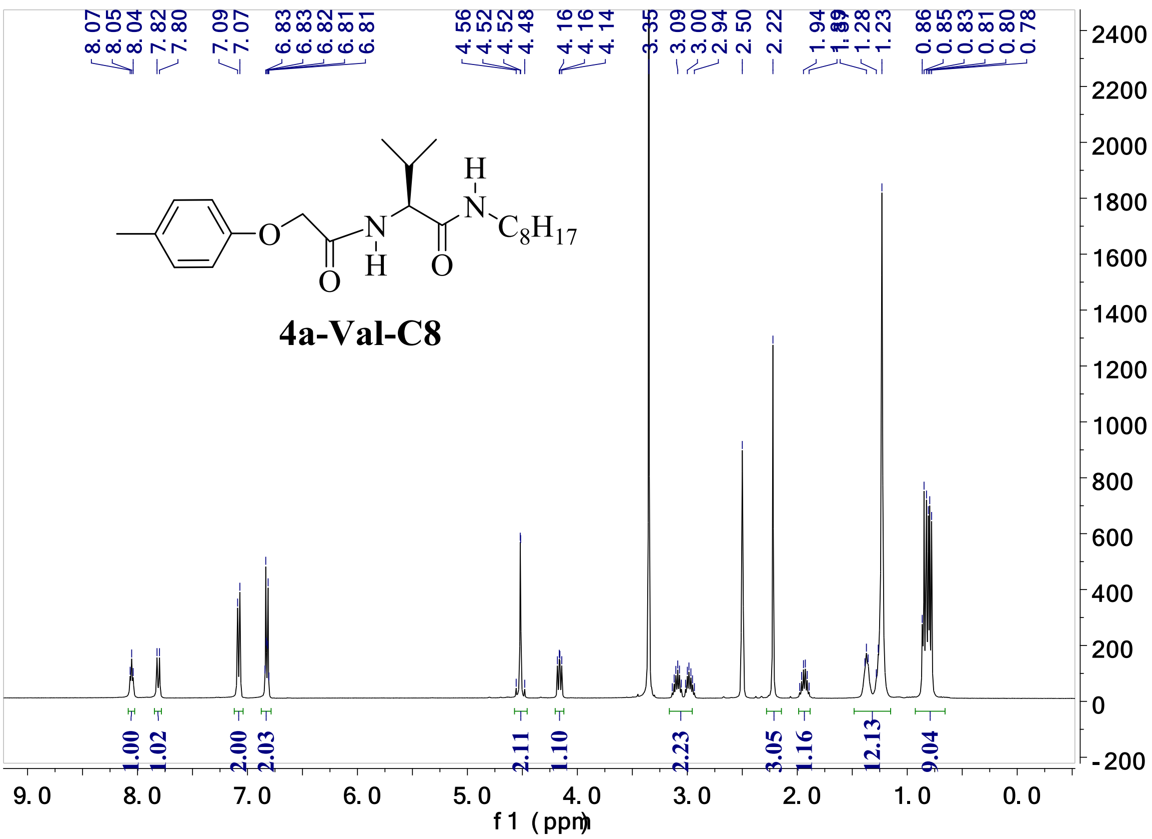

170.72
167.88
158.13
139.44
129.68
122.30
115.61
112.08
66.91
57.70
39.95
39.53
38.84
31.70
26.80
21.54
18.47
14.45
3a-Val-C8
f1 (ppm)


8.07
8.06
8.04
7.83
7.81
7.09
7.07
6.84
6.83
6.82
6.81
6.81
4.56
4.52
4.52
4.48
4.14
3.35
3.06
3.01
2.98
2.95
2.50
2.22
1.95
1.30
1.21
0.85
0.84
0.83
0.81
0.80
0.78
H
N
C_4H_9
O
N
H
O
O
4a-Val-C4
1.00
1.00
2.12
2.09
2.15
1.03
2.33
3.09
1.12
2.20
2.42
9.46
f1 (ppm)

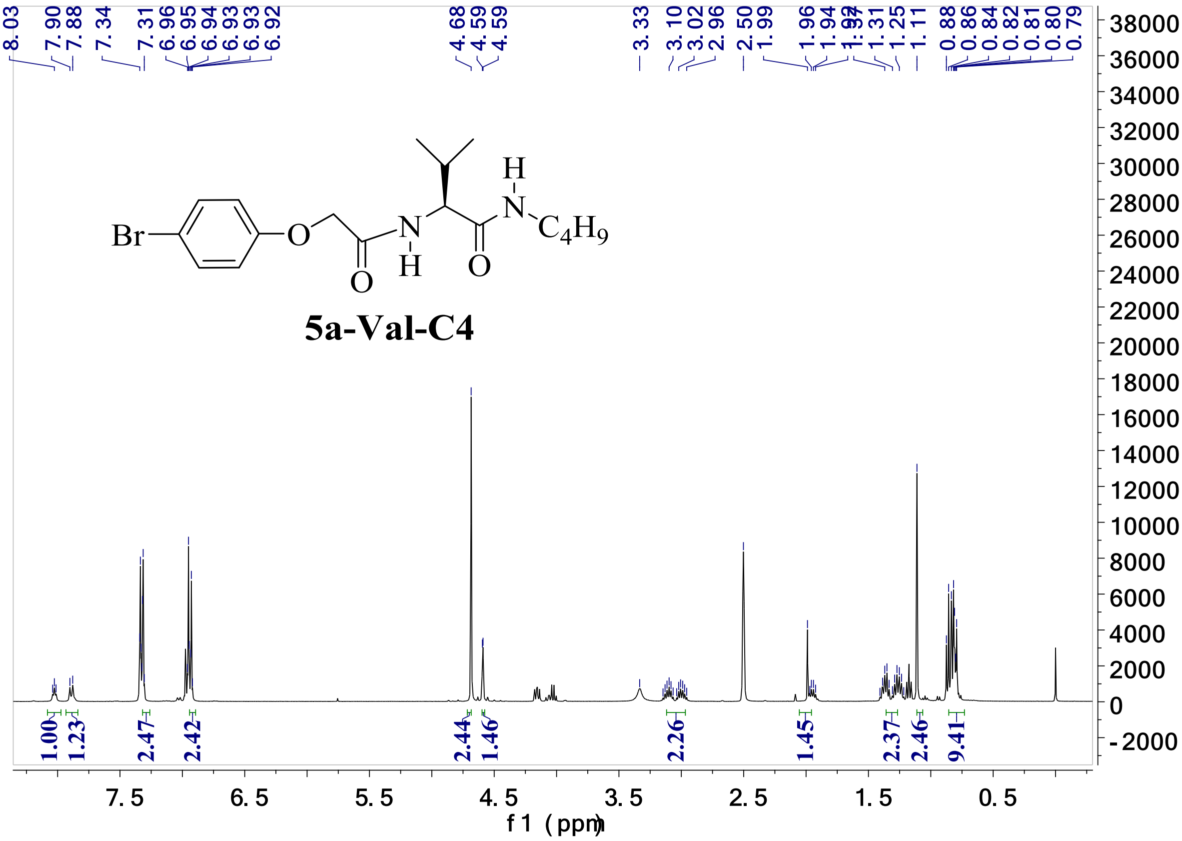

170.73
167.95
156.06
130.30
130.27
114.86
67.13
57.72
39.95
39.53
38.55
31.56
31.32
20.00
18.54
14.13
H
N
C_4H_9
O
N
H
O
O
4a-Val-C4
f1 (ppm)



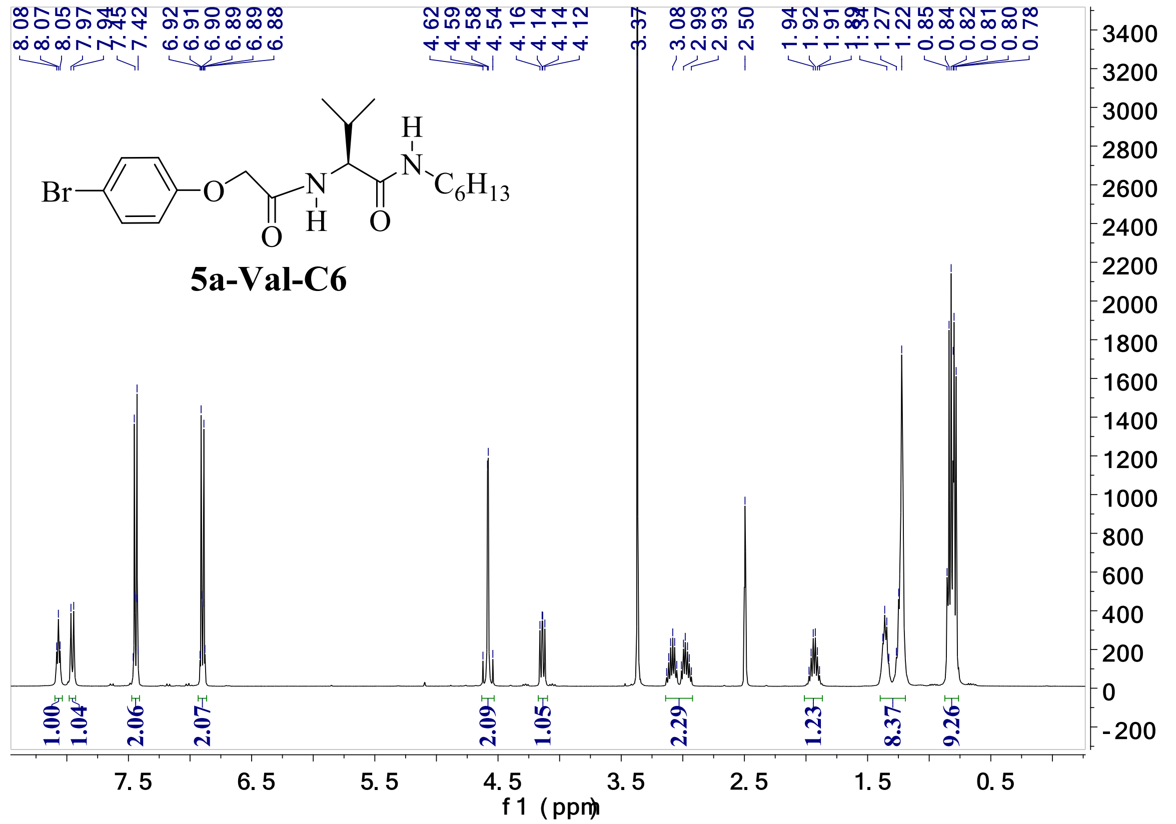
4a-Val-C6



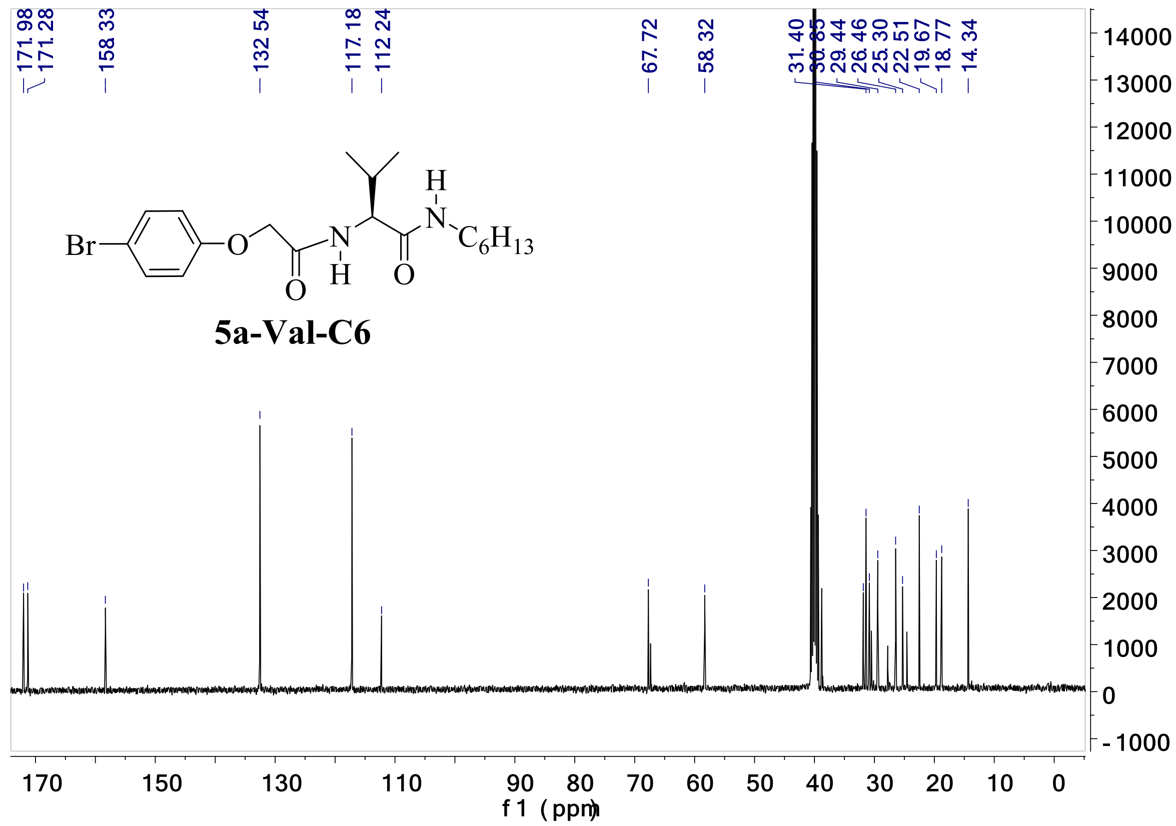
4a-Val-C8



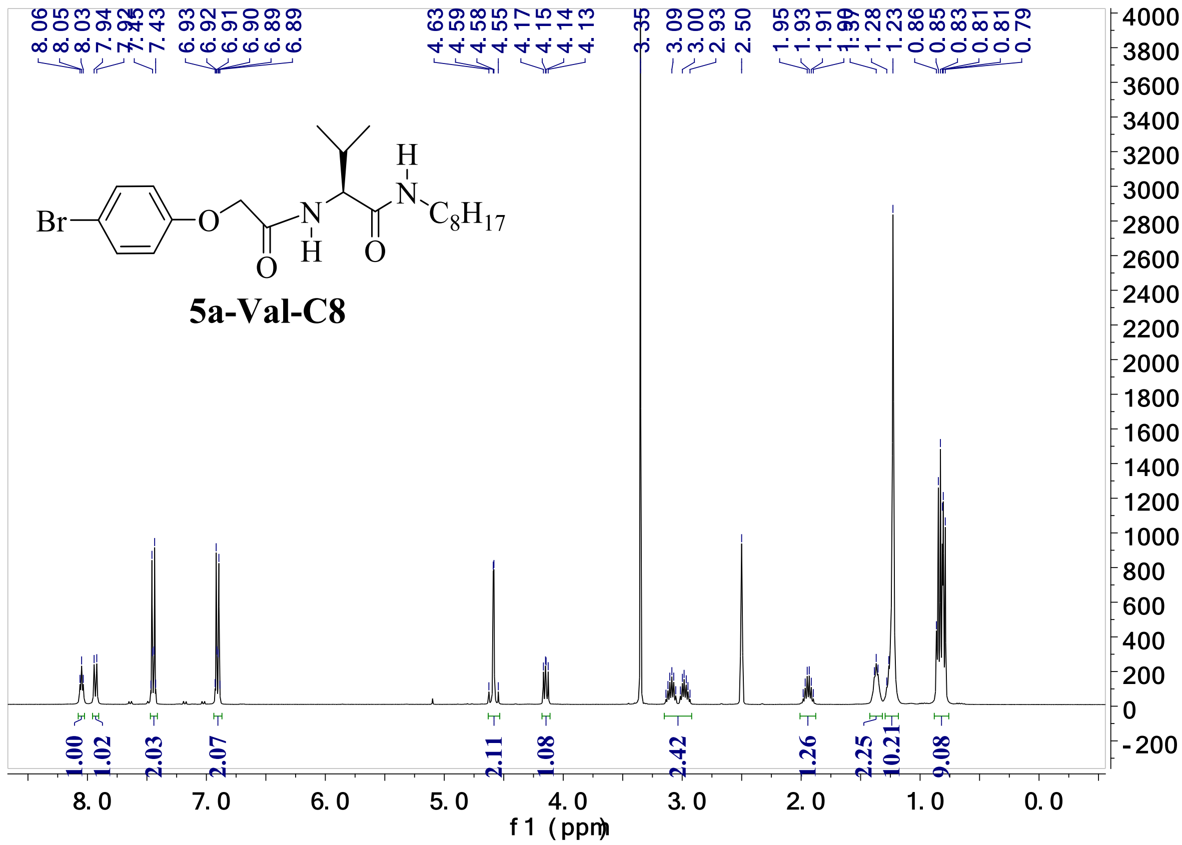
5a-Val-C4



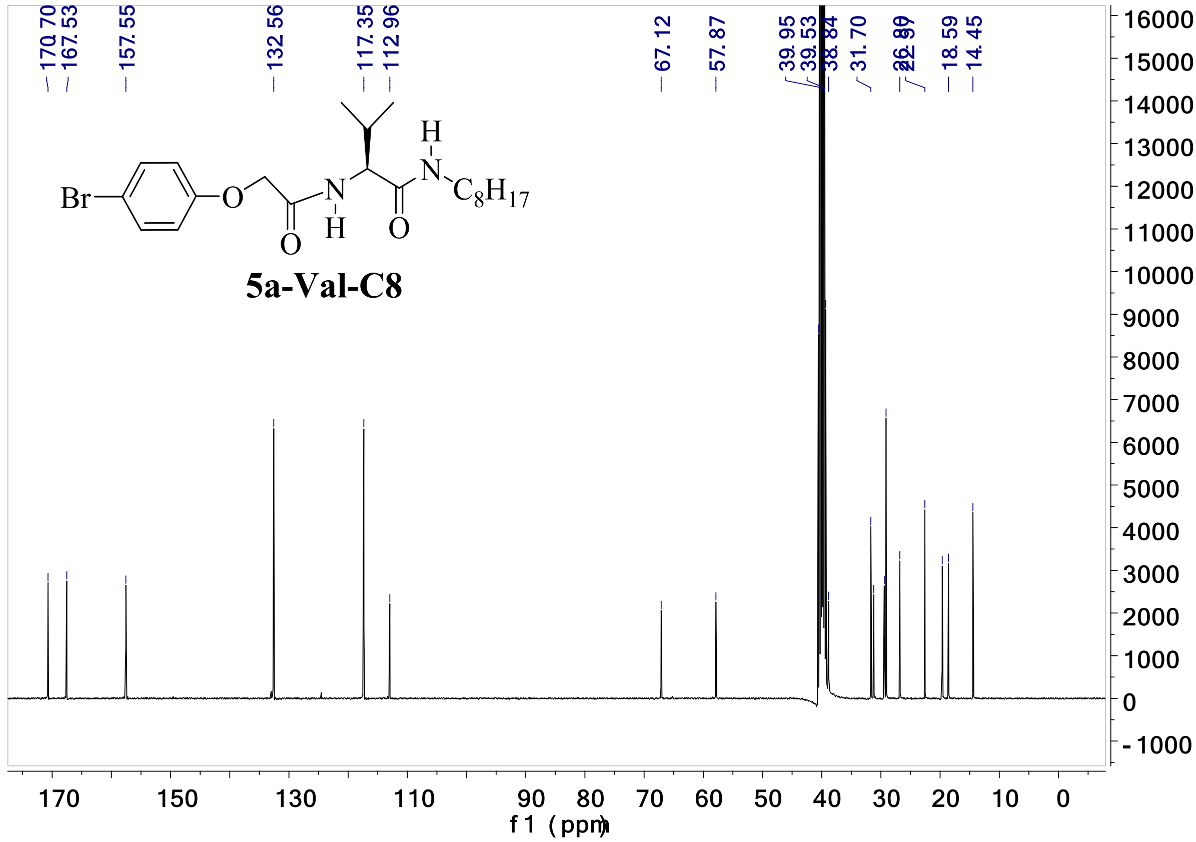
5a-Val-C6



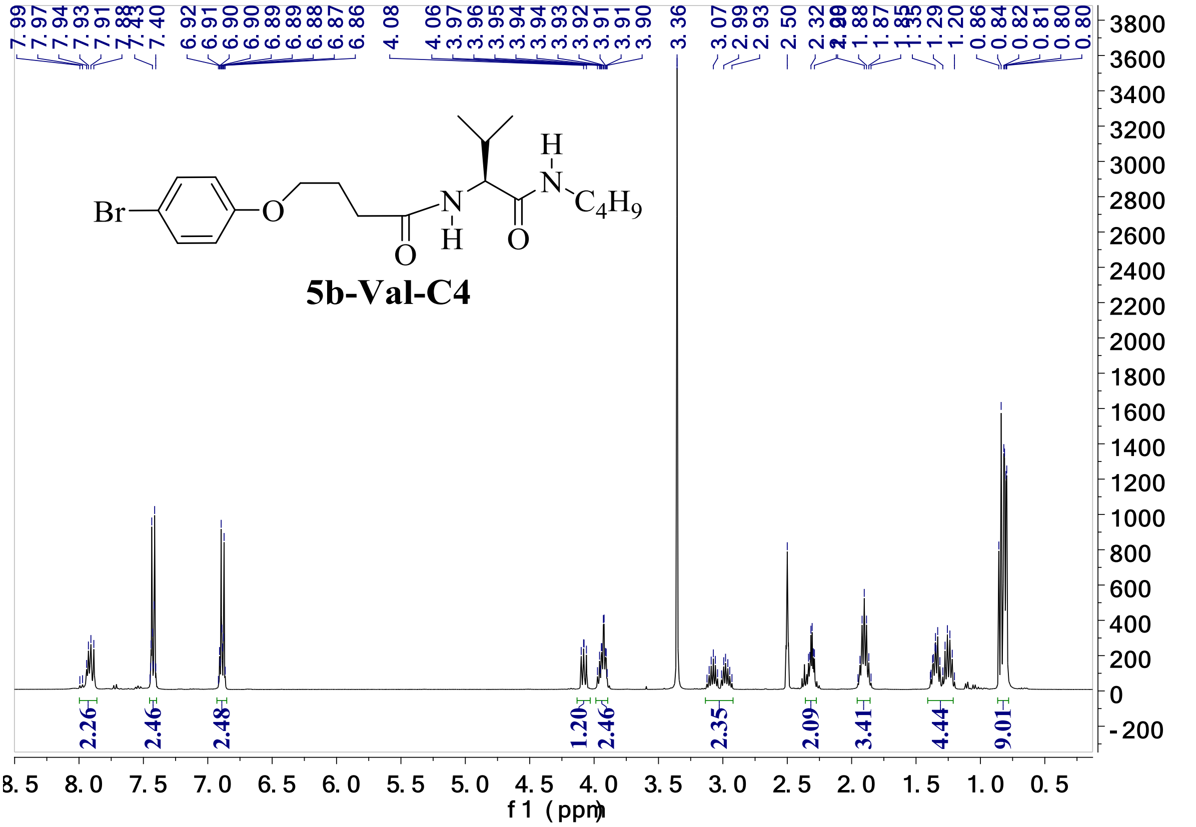
5a-Val-C6



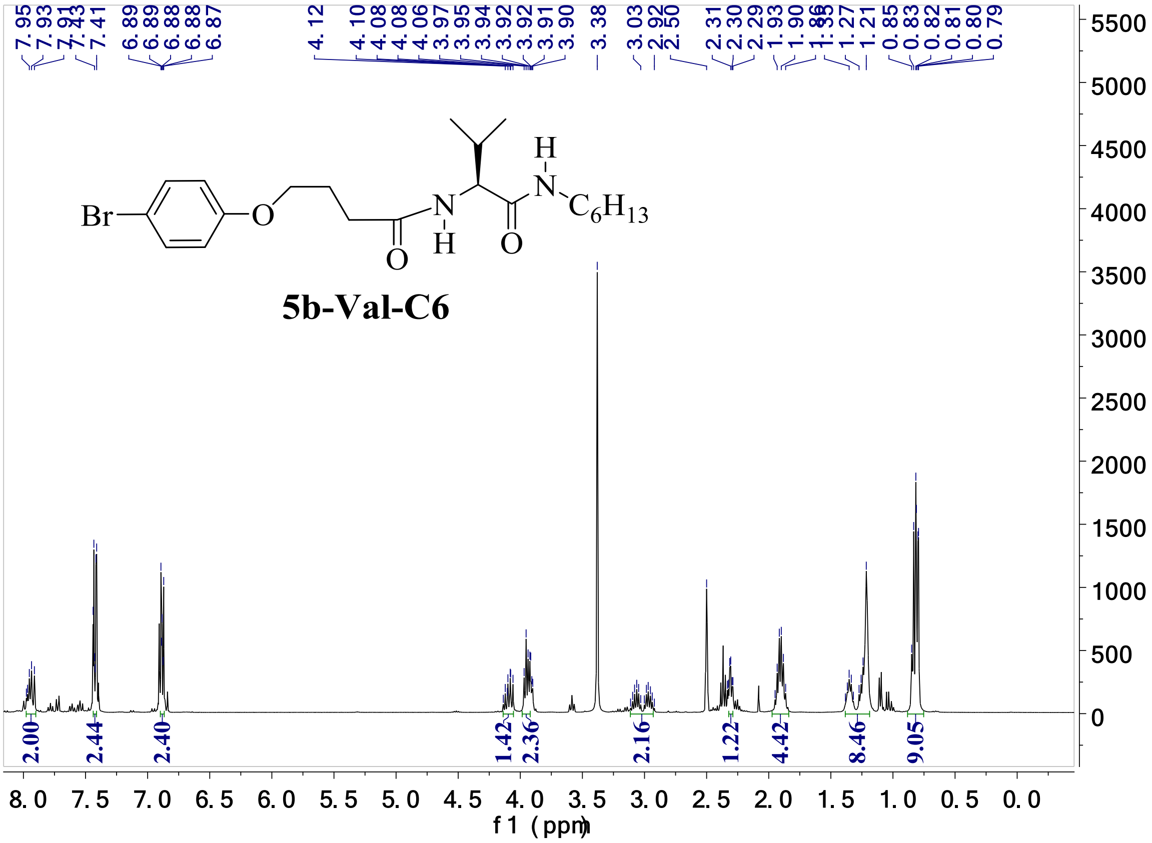
5a-Val-C8



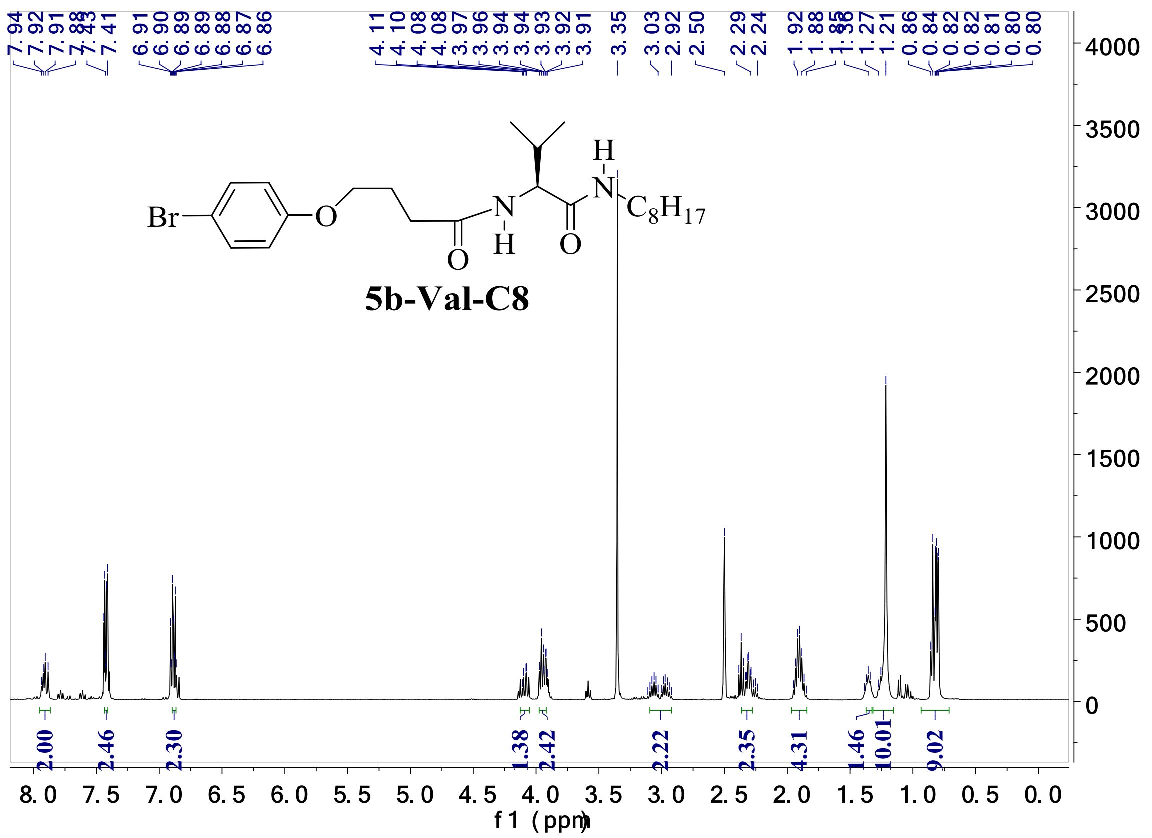
5a-Val-C8



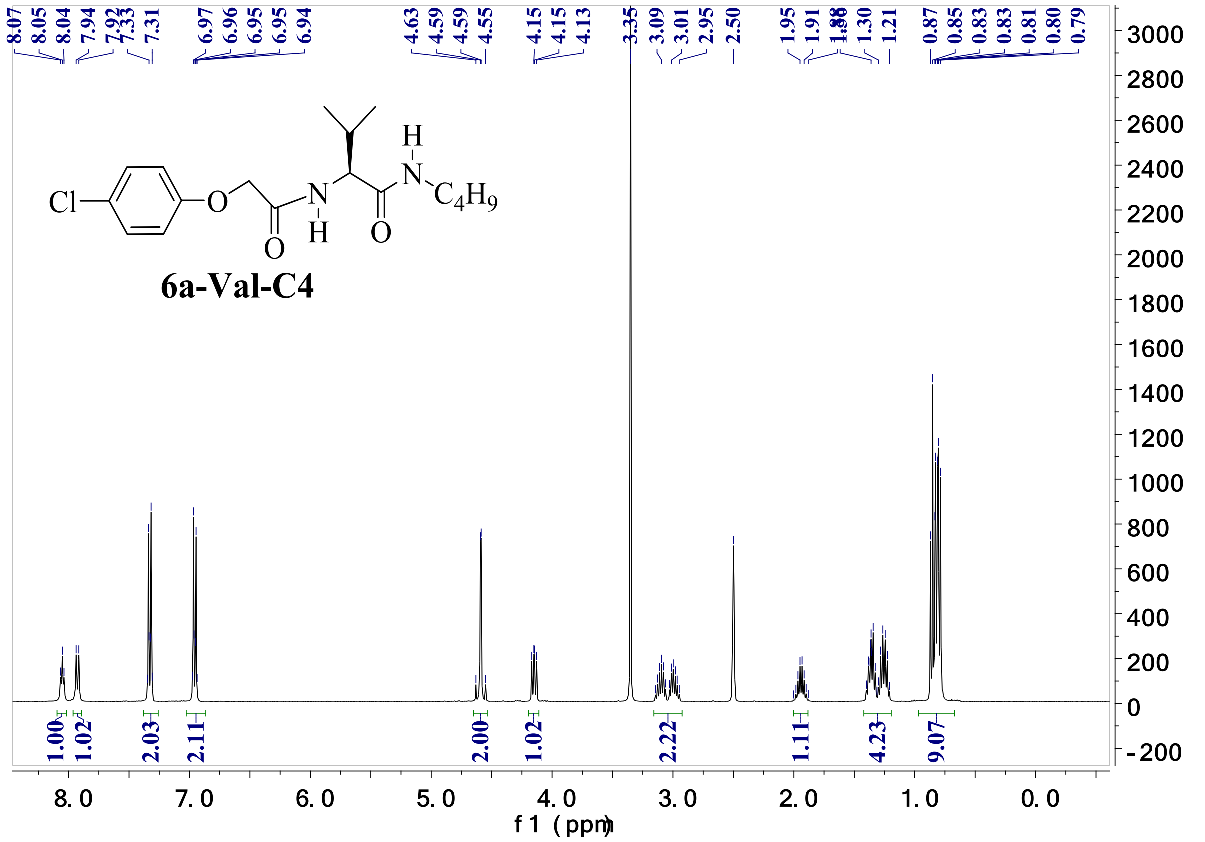
5b-Val-C4

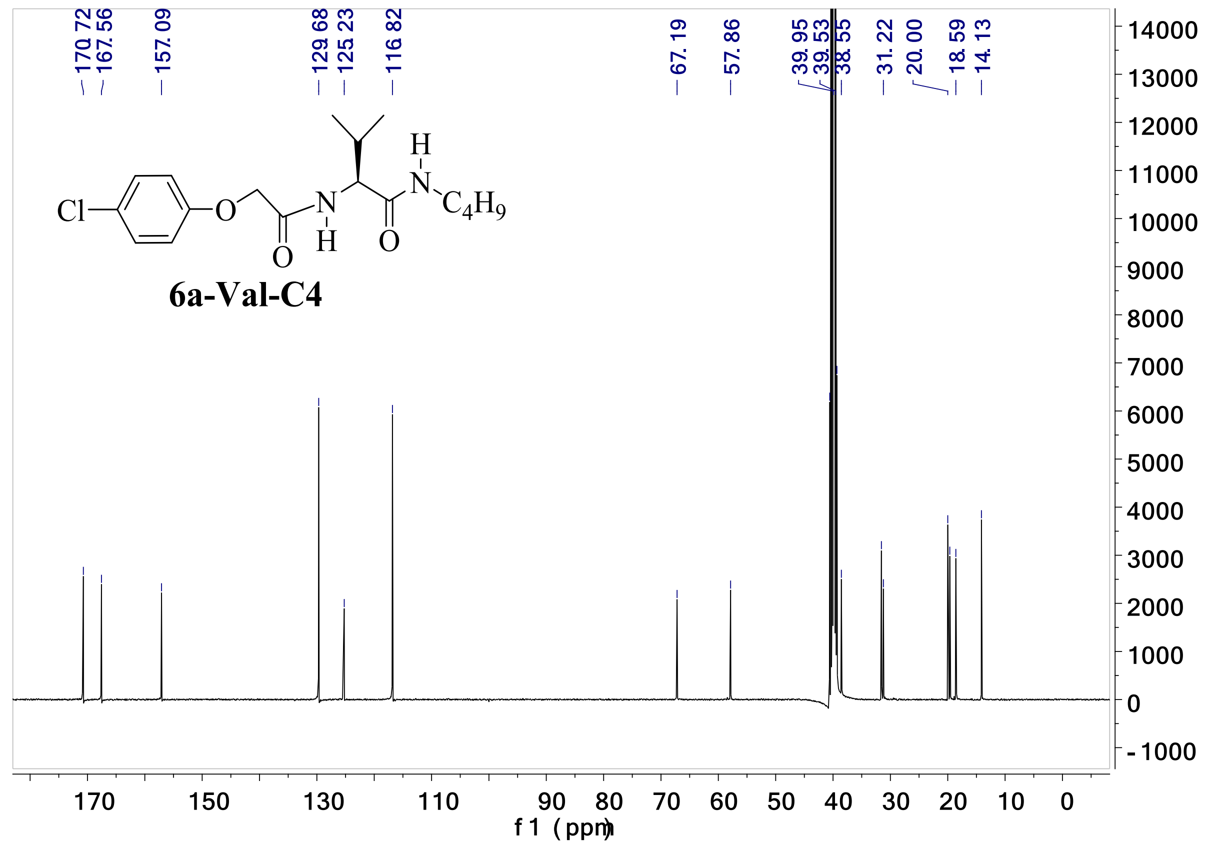


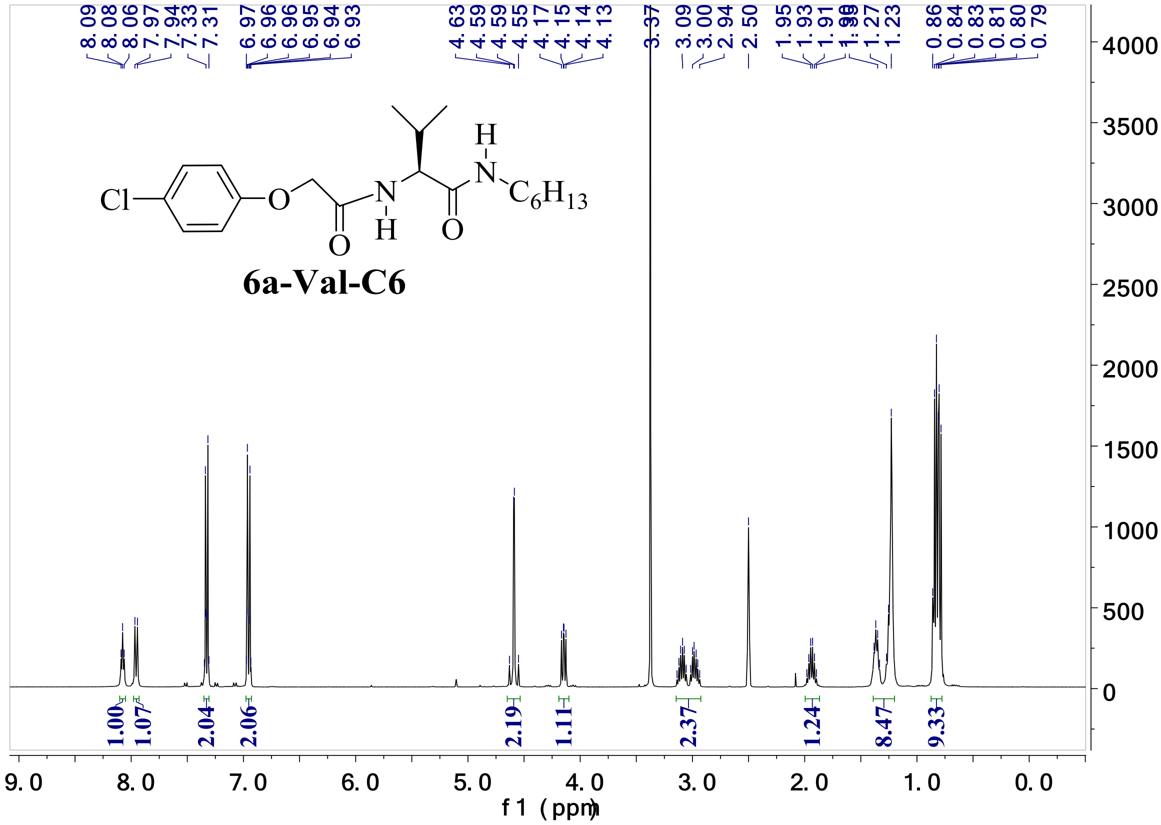
5b-Val-C6



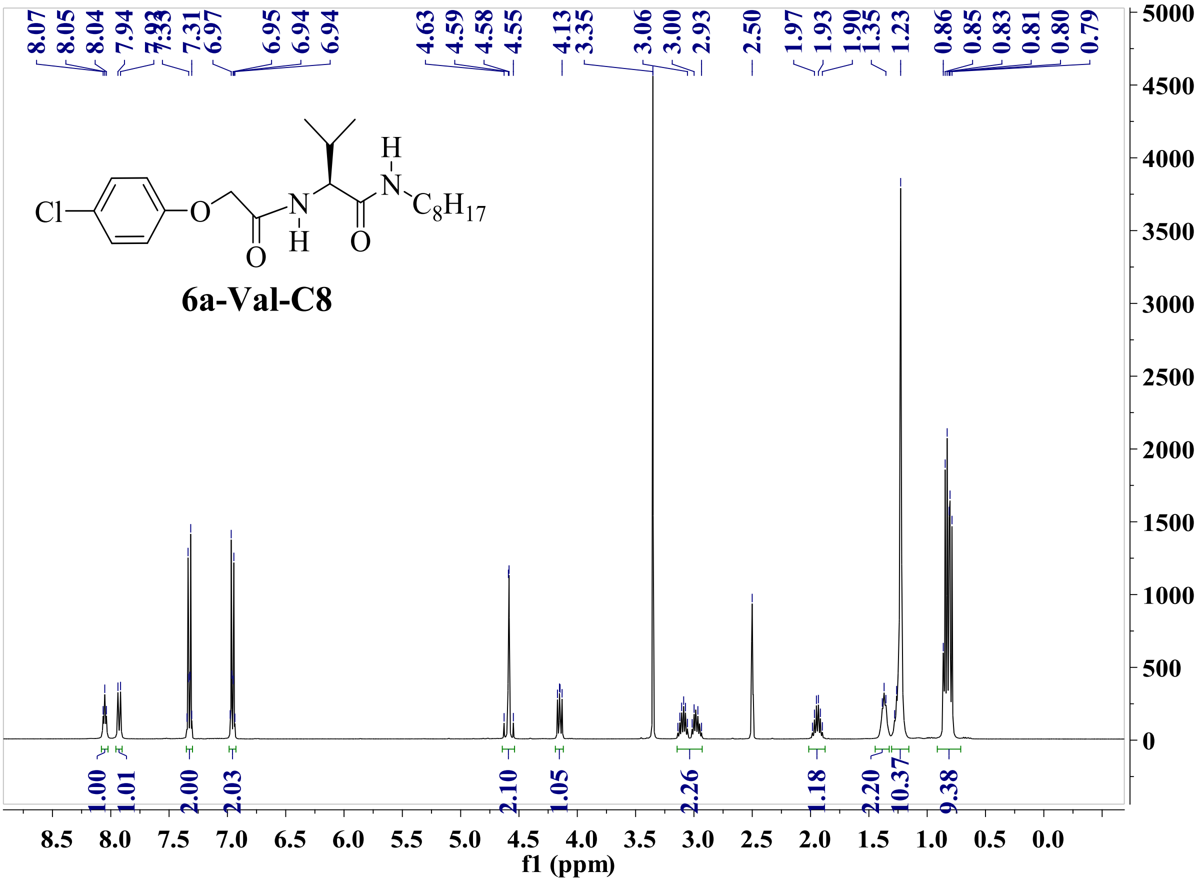
5b-Val-C8


6a-Val-C4
f1 (ppm)

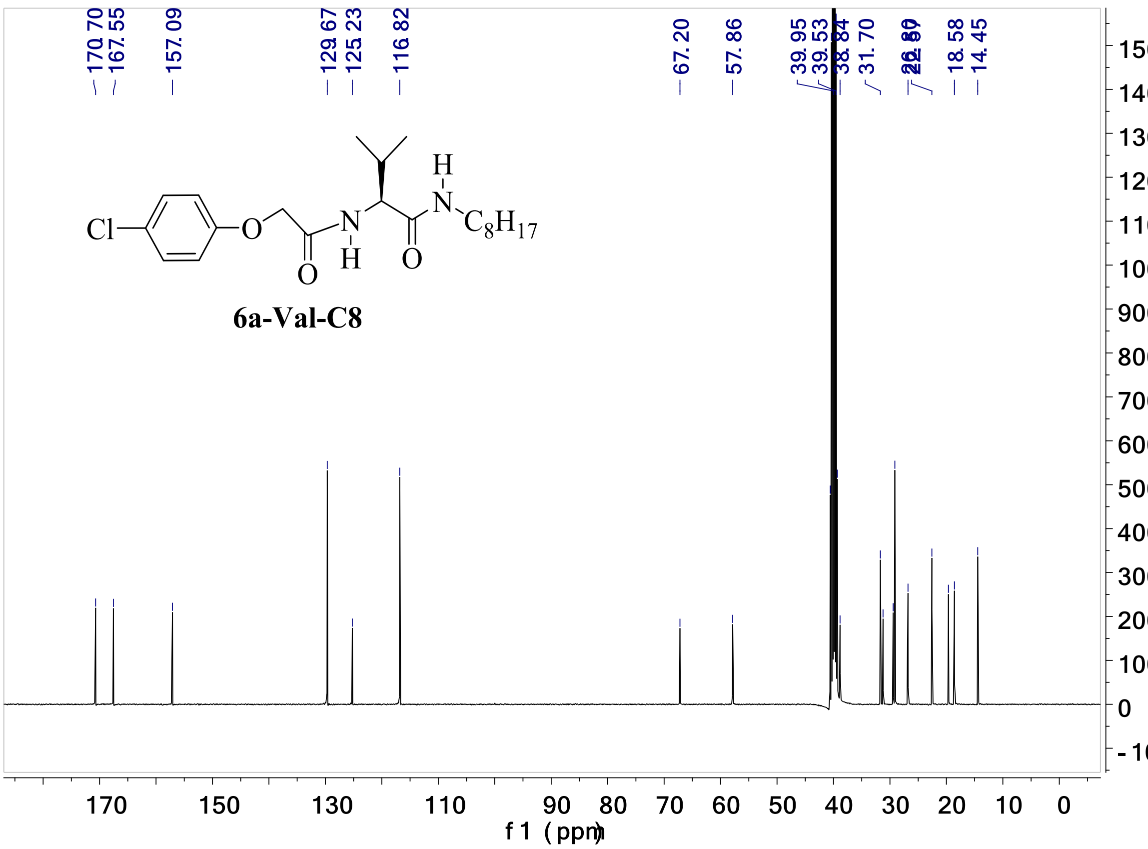

6a-Val-C4
f1 (ppm)



6a-Val-C6
f1 (ppm)



6a-Val-C8
f1 (ppm)



170.70
167.55
157.09
129.67
125.23
116.82
67.20
57.86
39.95
39.53
38.84
31.70
18.58
14.45
6a-Val-C8
f1 (ppm)