Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Peptide-functionalized semiconductor surfaces: Strong surface electronic effects from minor alterations to backbone composition

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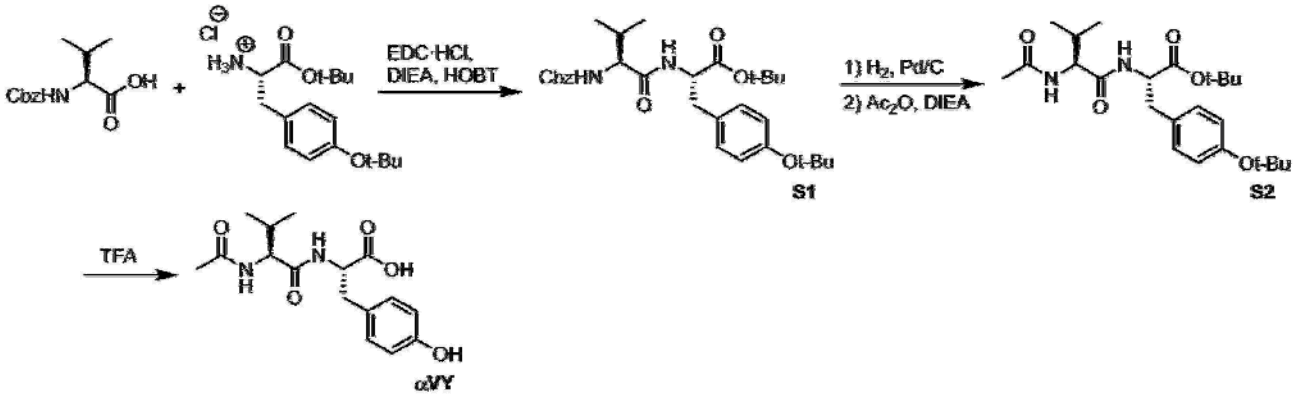
Materials:

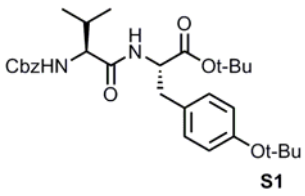
2-(6-chloro-1H-benzotriazole-1-yl)-1,1,3,3-tetramethylaminium hexafluorophosphate (HCTU) and 9-fluorenylmethyl *N*-succinimidyl carbonate (Fmoc-OSu) were purchased from Novabiochem. Ac-Tyr-OH and Cbz-Val-OH were purchased from Chem-Impex. Solvents and all other reagents were purchased from Aldrich, AnaSpec, Baker, Fisher, or TCI and used as received without further purification. Flash chromatography was performed using SorbTech silica gel (60 Å, 40-63 μm). (2*S*, 3*S*)-3-azido-2,4-dimethylpentanoic acid (**S3**) and (2*R*, 3*S*)-3-((butoxycarbonothioyl)amino)-2,4-dimethylpentanoic acid (**S6**) were synthesized using published protocols.[1]

Dipeptide Synthesis:



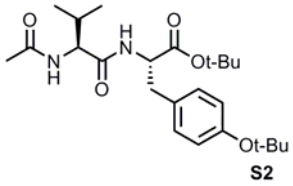
General Procedure A:

To a stirred solution of amino acid or azido acid (1 equiv) in dichloromethane (0.2 M) was added HOBT•H_2O (1 equiv), EDC•HCl (1 equiv), and DIEA (2.9 equiv). The reaction was allowed to stir for 5 minutes to allow activation of the carboxylic acid. After this time, H-Tyr(*t*-Bu)-O*t*-Bu•HCl (0.9 equiv) was added and the reaction stirred 4 h. The reaction was then diluted with ethyl acetate, washed with 5% aqueous sodium bisulfite, 5% aqueous sodium bicarbonate, and brine. The organics were dried with magnesium sulfate, concentrated, purified using column chromatography, and dried under vacuum to afford the desired dipeptide.



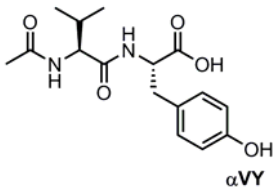
Cbz-Val-Tyr(*t*Bu)-O*t*-Bu (S1): General Procedure A was followed using 500 mg Cbz-Val-OH (1.99 mmol), 304 mg HOBT•H_2O (1.99 mmol), 10 mL dichloromethane, EDC•HCl (1.99 mmol), 1.00 mL DIEA (5.74 mmol), and 597 mg H-Tyr(*t*-Bu)-O*t*-Bu•HCl (1.81 mmol). Column chromatography (25% ethyl acetate in hexanes) afforded the product as a white solid (719 mg, 1.37 mmol, 69% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.42 (m, 5H), 7.06 (d, *J*

= 8.3 Hz, 2 H), 6.91 (d, *J* = 8.3 Hz, 2 H), 6.27 (d, *J* = 7.0 Hz, 1 H), 5.33 (d, *J* = 7.4 Hz, 1 H), 5.13 (s, 2 H), 4.73 (dt, *J* = 7.7 Hz, 6.2 Hz,1 H), 4.02 (m, 1 H), 3.04 (m, 2 H), 2.12 (m, 1 H), 1.39 (s, 9 H), 1.33 (s, 9 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (133 MHz, $CDCl_3$) δ 170.5, 170.3, 156.3, 154.4, 136.3, 130.8, 129.9, 128.5, 128.2, 128.0, 124.1, 82.4, 78.4, 67.0, 60.3, 53.6, 37.5, 31.1, 28.8, 27.9, 19.1, 17.7. $[\alpha]_D$ = +26 (*c* = 1.0, $CHCl_3$). HRMS *m*/*z* calculated for $C_{30}H_{43}N_2O_6$ $[M+H]^+$ 527.3121; found 527.3167.



S2

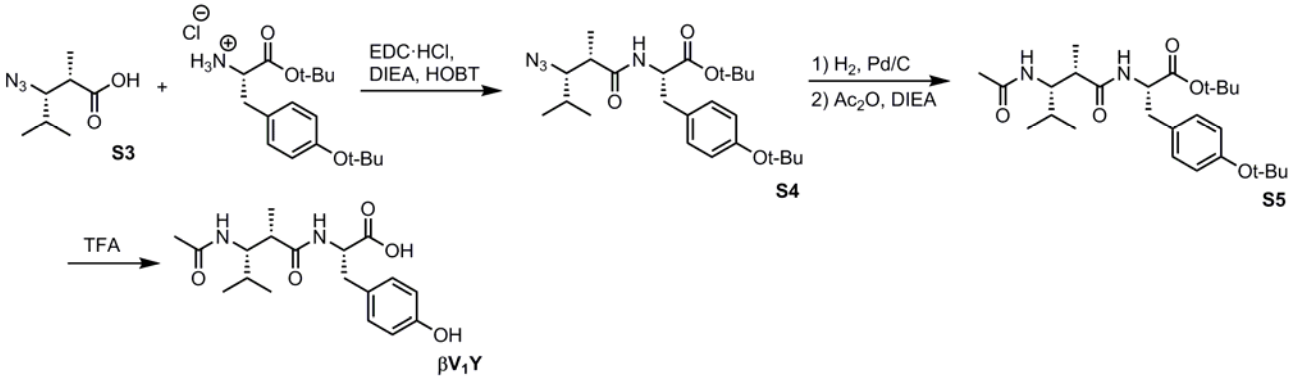
Ac-Val-Tyr(*t*Bu)-O*t*-Bu (S2): To a stirred solution of 633 mg **S1** (1.20 mmol, 1 equiv) in 25 mL methanol was added 125 mg 10 wt% Pd/C (10% w/w). The flask was fitted with a hydrogen-filled balloon and the reaction was allowed to stir at room temperature for 1.5 h. The reaction mixture was then flushed with nitrogen, filtered over Celite, washed with methanol, and concentrated. To a stirred solution of the crude mixture in 12 mL dichloromethane was added 836 µL DIEA (4.80 mmol, 4 equiv) and 454 µL acetic anhydride (4.80 mmol, 4 equiv). The reaction was allowed to stir for 2 h and was then diluted with 100 mL ethyl acetate and washed with 5% aqueous sodium bisulfite, 5% aqueous sodium bicarbonate, and brine. The organics were dried with magnesium sulfate and concentrated. The crude material was purified using column chromatography (20% → 67% ethyl acetate in hexanes) and dried under vacuum to afford the product as a white solid (340 mg, 0.782 mmol, 65% yield over 2 steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.3 Hz, 2 H), 6.87 (d, *J* = 8.3 Hz, 2 H), 6.64 (d, *J* = 7.7 Hz, 1 H), 6.44 (d, *J* = 8.9 Hz, 1 H), 4.67 (dt, *J* = 7.4 Hz, 6.6 Hz, 1 H), 4.31 (dd, *J* = 8.7 Hz, 6.8 Hz, 1 H), 2.99 (m, 2 H), 2.00-2.09 (m, 1 H), 1.98 (s, 3 H), 1.34 (s, 9 H), 1.29 (s, 9 H), 0.92 (d, *J* = 6.6 Hz, 3 H), 0.91 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.2, 170.0, 154.3, 130.8, 129.9, 124.1, 82.1, 78.3, 53.8, 37.5, 31.3, 28.8, 27.8, 23.1, 19.0, 18.2. $[\alpha]_D$ = +24 (*c* = 0.50, $CHCl_3$). HRMS *m*/*z* calculated for $C_{24}H_{39}N_2O_5$ $[M+H]^+$ 435.2859; found 435.2889.

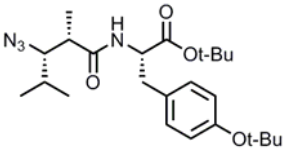


αVY

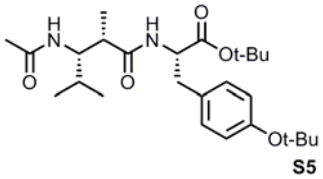
Ac-Val-Tyr-OH (αVY): To a stirred solution of 313 mg **S2** (0.720 mmol) in 3 mL dichloromethane was added 3 mL trifluoroacetic acid. The solution was allowed to stir for 4 h, and was then concentrated and co-evaporated twice with chloroform. The crude material was purified by column chromatography (75% ethyl acetate in hexanes → 10% methanol in dichloromethane) and lyophilized from 50% acetonitrile in water and to afford the product as a white solid (167 mg, 0.518 mmol, 72% yield). ^{1}H NMR (500 MHz, MeOD) δ 8.17 (d, *J* = 8.0 Hz, 1 H), 7.03 (d, *J* = 8.7 Hz, 2 H), 6.67 (d, *J* = 8.7 Hz, 2 H), 4.60 (m, 1 H), 4.15 (d, *J* = 7.9 Hz, 1 H), 3.08 (dd, *J* = 14.0 Hz, 5.2 Hz, 1 H), 2.87 (dd, *J* = 14.0 Hz, 8.5 Hz, 1 H), 1.99

(m, 1 H), 1.96 (s, 3 H), 0.92 (d, J = 6.8 Hz, 3 H), 0.91 (d, J = 6.8 Hz, 3 H). ^{13}C NMR (166 MHz, MeOD) δ 174.5, 173.6, 173.5, 173.2, 157.3, 131.4, 128.9, 116.1, 60.2, 60.2, 55.2, 55.1, 37.7, 37.7, 31.8, 22.4, 19.7, 18.7. $[\alpha]_D$ = +1.7 (c = 0.50, $CHCl_3$:MeOH (1:1)). HRMS m/z calculated for $C_{16}H_{21}N_2O_5$ $[M-H]^-$ 321.1450; found 321.1485.



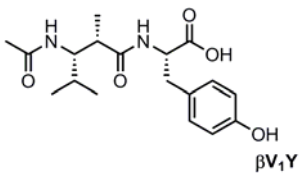

S4

anti **Azido-β^{2,3}-VA-Tyr(*t*-Bu)-O*t*-Bu (S4):** General Procedure A was followed using 288 mg **S3** (1.68 mmol), 257 mg HOBT•H_2O (1.68 mmol), 8 mL dichloromethane, 322 mg EDC•HCl (1.68 mmol), 853 µL DIEA (4.90 mmol), and 505 mg H-Tyr(*t*Bu)-O*t*-Bu•HCl (1.53 mmol). Column chromatography (14% ethyl acetate in hexanes) afforded the product as a white solid (480 mg, 1.07 mmol, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, J = 8.7 Hz, 2 H), 6.90 (d, J = 8.7 Hz, 2 H), 6.18 (d, J = 7.5 Hz, 1 H), 4.73 (dt, J = 7.5 Hz, 6.0 Hz, 1 H), 3.40 (dd, J = 8.7 Hz, 4.5 Hz, 1 H), 3.05 (m, 2 H), 2.34 (m, 1 H), 1.87 (m, 1 H), 1.40 (s, 9 H), 1.31 (s, 9 H), 1.10 (d, J = 7 Hz, 3 H), 1.02 (d, J = 7.2 Hz, 3 H), 0.84 (d, J = 6.8 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 170.7, 154.2, 131.1, 129.9, 124.0, 82.1, 78.3, 71.3, 53.5, 44.0, 37.4, 29.7, 28.8, 27.9, 20.6, 16.0, 15.5. $[\alpha]_D$ = +11 (c = 1.0, $CHCl_3$). HRMS m/z calculated for $C_{24}H_{39}N_4O_4$ $[M+H]^+$ 447.2971; found 447.3005.

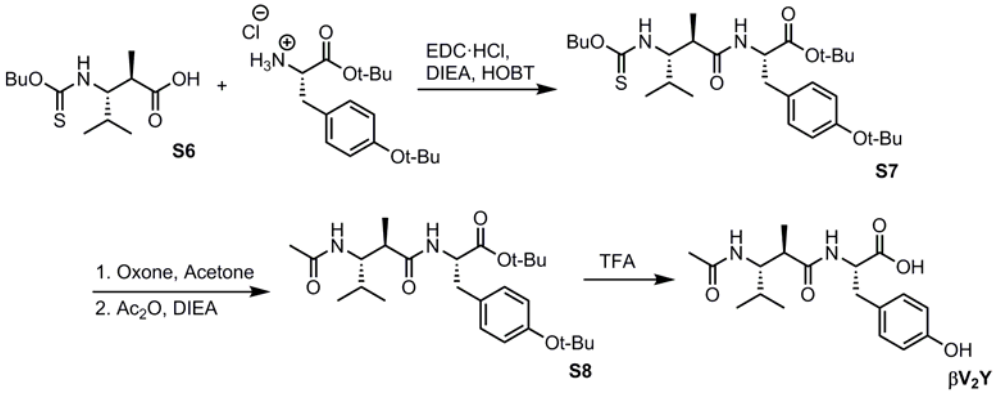

S5

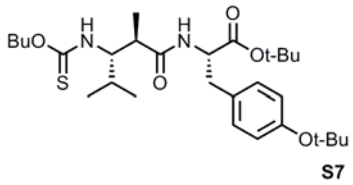
anti **Ac-β^{2,3}-VA-Tyr(*t*-Bu)-O*t*-Bu (S5):** To a stirred solution of 474 mg **S4** (1.06 mmol, 1 equiv) in 10 mL methanol was added 52 mg 20 wt% $Pd(OH)_2$/C (10% w/w). The flask was fitted with a hydrogen-filled balloon and the reaction was allowed to stir overnight. The reaction mixture was then filtered through Celite, eluting with methanol, and concentrated. To a stirred solution of the crude mixture in 4 mL dichloromethane was added 700 µL DIEA (4.02 mmol, 4 equiv) and 380 µL

acetic anhydride (4.02 mmol, 4 equiv). The reaction was allowed to stir for 2 h and was then diluted with 100 mL ethyl acetate and washed with 5% aqueous sodium bisulfate solution, 5% aqueous sodium bicarbonate solution, and brine. The organics were dried with magnesium sulfate and concentrated. The crude material was purified by column chromatography (50% → % 100 ethyl acetate in hexanes) and dried under vacuum to afford the product as a white solid (196 mg, 0.424 mmol, 40% yield over 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.5 Hz, 2 H), 6.98 (d, *J* = 9.8 Hz, 1 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 6.13 (d, *J* = 7.9 Hz, 1 H), 4.65 (dt, *J* = 7.9 Hz, 6.5 Hz, 1 H), 3.65 (td, *J* = 9.5 Hz, 3.3 Hz, 1 H), 3.06 (dd, *J* = 14.0 Hz, 6.3 Hz, 1 H), 2.96 (dd, *J* = 14.0 Hz, 6.5 Hz, 1 H), 2.52 (qd, *J* = 7.1 Hz, 3.5 Hz, 1 H), 1.99 (s, 3 H), 1.59-1.67 (m, 1 H), 1.40 (s, 9 H), 1.30 (s, 9 H), 1.07 (d, *J* = 7.1 Hz, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H), 0.87 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (166 MHz, $CDCl_3$) δ 175.3, 170.4, 170.3, 154.3, 130.8, 129.8, 124.1, 82.5, 78.4, 57.6, 53.1, 40.4, 37.2, 31.8, 28.7, 27.9, 23.4, 20.0, 19.7, 16.8. $[\alpha]_D$ = +20.2 (*c* = 1.00, $CHCl_3$). HRMS *m*/*z* calculated for $C_{26}H_{43}N_2O_5$ $[M+H]^+$ 463.3172; found 463.3186.



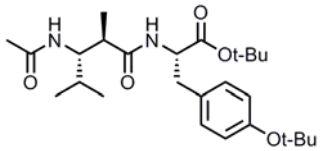
***anti* Ac-β^{2,3}-VA-Tyr-OH (βV$_1$Y):** To a stirred solution of 196 mg **S5** (0.424 mmol, 1 equiv) in 5 mL dichloromethane was added 5 mL trifluoroacetic acid. The reaction was allowed to stir overnight and was then dried under nitrogen. The crude mixture was dissolved in 7 mL 20% acetonitrile in water, purified using reverse-phase HPLC, and lyophilized to afford the product as a white solid (89 mg, 0.25 mmol, 60% yield). ^{1}H NMR (400 MHz, 50% MeOD/$CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 1 H), 7.34 (d, *J* = 9.8 Hz, 1 H), 6.99 (d, *J* = 8.5 Hz, 2 H), 6.70 (d, *J* = 8.5 Hz, 2 H), 4.58-4.62 (m, 1 H), 3.60 (m, 1 H), 3.10 (dd, *J* = 14.1 Hz, 5.3 Hz, 1 H), 2.87 (dd, *J* = 14.3 Hz, 8.3 Hz, 1 H), 2.60 (m, 1 H), 1.96 (s, 3 H), 1.67 (m, 1 H), 0.97 (d, *J* = 6.8 Hz, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H), 0.81 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (133 MHz, 50% MeOD/$CDCl_3$) δ 176.7, 174.1, 172.2, 156.3, 130.7, 128.0, 115.7, 58.3, 53.8, 53.7, 40.9, 37.0, 31.5, 30.1, 23.1, 23.0, 20.1, 19.1, 16.5. $[\alpha]_D$ = +3.4 (*c* = 0.50, MeOH). HRMS *m*/*z* calculated for $C_{18}H_{25}N_2O_5$ $[M-H]^-$ 349.1763; found 349.1728.





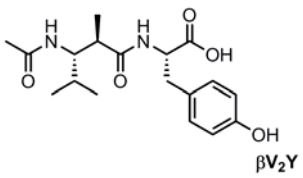
S7

***syn* β^{2,3}-VA-Tyr(*t*-Bu)-O*t*-Bu Thiocarbamate (S7):** General Procedure A was followed using 50 mg **S6** (0.19 mmol), 29 mg HOBT•H_2O (0.19 mmol), 1 mL dichloromethane, 37 mg EDC•HCl (0.17 mmol), 97 µL DIEA (0.56 mmol), and 57 mg H-Tyr(*t*Bu)-O*t*-Bu•HCl (0.17 mmol). Column chromatography (20% ethyl acetate in hexanes) afforded the product as a white solid (65 mg, 0.12 mmol, 64% yield). This compound exists as a series of conformers in slow exchange on the NMR time scale; NMR spectra are attached. $[\alpha]_D$ = +47.6 (*c* = 1.00, $CHCl_3$). HRMS *m*/*z* calculated for $C_{29}H_{49}N_2O_5S$ $[M+H]^+$ 537.3362; found 537.3362.



S8

***syn* Ac-β^{2,3}-VA-Tyr(*t*-Bu)-O*t*-Bu (S8):** To a stirred solution of 62 mg **S7** (0.12 mmol, 1 equiv) in 1.2 mL 3:1:1 acetone/tetrahydrofuran/water was added 110 mg Oxone (0.17 mmol, 1.5 equiv). The reaction was stirred for 30 minutes, then the solution was adjusted to pH 11 using saturated aqueous sodium carbonate solution. The solution was saturated with solid sodium chloride and the aqueous layer extracted 6 times with chloroform. The organics were combined, dried with magnesium sulfate, and concentrated. To a stirred solution of the crude mixture in 2 mL dichloromethane was added 80 µL DIEA (0.46 mmol, 4 equiv) and 44 µL acetic anhydride (0.46 mmol, 4 equiv). The reaction was stirred overnight and then diluted with 50 mL ethyl acetate and washed with 5% aqueous sodium bisulfate solution, 5% aqueous sodium bicarbonate solution, and brine. The organics were dried with magnesium sulfate and concentrated. The crude mixture was purified using column chromatography (50% → 66% → 100% ethyl acetate in hexanes) and dried under vacuum to afford the product as a white solid (32 mg, 0.07 mmol, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.2 Hz, 2 H), 6.90 (d, *J* = 8.0 Hz, 2 H), 6.50 (d, *J* = 7.5 Hz, 1 H), 5.67 (d, *J* = 10.0 Hz, 1 H), 4.72 (m, 1 H), 4.11 (m, 1 H), 3.03 (d, *J* = 6.3 Hz, 2 H), 2.45 (m, 1 H), 2.00 (s, 3 H), 1.74 (m, 1 H), 1.38 (s, 9 H), 1.31 (s, 9 H), 1.09 (d, *J* = 6.9 Hz, 3 H), 0.89 (d, *J* = 6.5 Hz, 3 H), 0.82 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (133 MHz, $CDCl_3$) 174.0, 171.0, 170.4, 154.4, 131.5, 130.0, 124.2, 82.2, 55.9, 53.6, 43.8, 37.6, 30.0, 29.0, 28.1, 23.5, 20.6, 17.3, 14.1. $[\alpha]_D$ = +40.9 (*c* = 1.00, $CHCl_3$). HRMS *m*/*z* calculated for $C_{26}H_{42}N_2O_5Na$ $[M+Na]^+$ 485.2991; found 485.3017.



βV$_2$Y

***syn* Ac-β^{2,3}-VA-Tyr-OH (βV$_2$Y):** To a stirred solution of 87 mg **S8** in 5 mL dichloromethane was added 5 mL trifluoroacetic acid. The reaction was allowed to stir overnight and was then dried under nitrogen. The crude mixture was dissolved in 4 mL 20% acetonitrile in water, purified using

reverse-phase HPLC, and lyophilized to afford the product as a white solid (33 mg, 0.094 mmol, 50% yield). ^{1}H NMR (400 MHz, MeOD) δ 7.53 (d, *J* = 10.16 Hz, 1 H), 7.05 (d, *J* = 8.41 Hz, 2 H), 6.89 (d, *J* = 8.53 Hz, 2 H), 4.69 (dd, *J* = 10.67, 4.64 Hz, 1 H), 3.99 (m, 1 H), 3.17 (dd, *J* = 14.18, 4.52 Hz, 1 H), 2.80 (dd, *J* = 14.18, 10.67 Hz, 1 H), 2.42 (m, 1 H), 1.95 (s, 3 H), 1.27 (m, 1 H), 1.03 (d, *J* = 6.78 Hz, 3 H), 0.71 (d, *J* = 6.78 Hz, 3 H), 0.65 (d, *J* = 6.78 Hz, 3 H). ^{13}C NMR (175 MHz, MeOD) 177.5, 175.1, 173.8, 157.5, 131.3, 129.4, 116.3, 57.2, 54.8, 44.4, 37.6, 31.0, 22.6, 21.1, 16.3, 15.8. $[\alpha]_D$ = +17 (*c* = 0.25, MeOH). HRMS *m*/*z* calculated for $C_{18}H_{26}N_2O_5Na$ $[M+Na]^+$ 373.1739; found 373.1747.

Peptide characterization in solution:

The identity and purity of products confirmed by ^{1}H-NMR, ^{13}C-NMR, and high-resolution MS. Optical rotations were measured on a Perkin-Elmer 241 digital polarimeter with a sodium lamp at ambient temperature. NMR spectra of synthetic small molecules were recorded on a Bruker Avance-300, Bruker Avance-400 spectrometer or Bruker Avance-500 spectrometer.Concentration-dependent NMR spectra (Figure S1) were obtained in acetonitrile-d_3. After initial measurement at 1 mM concentration, samples were diluted 10x to a final concentration of 0.1 mM and re-measured. Solution FT-IR measurements were obtained using a Bruker VERTEX-70LS system. All peptides were measured at a concentration of 1 mM in acetonitrile with a sodium chloride cell using a 0.5 mm Teflon spacer.

Functionalization of GaAs substrates:

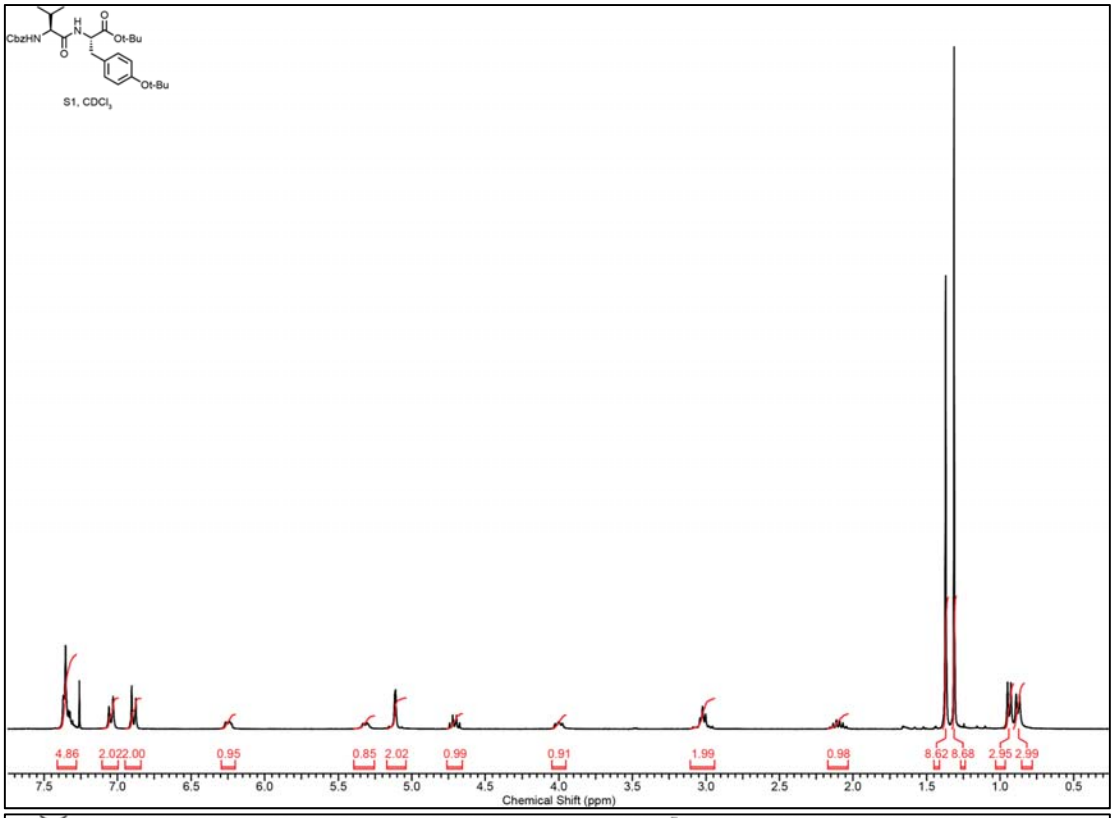
~1 cm^2 samples were cut from Si doped (4.9×10^{16} cm^{-3}) GaAs (100) wafers (2.6×10^{-2} Ω·cm resistivity, Institute of Electronic Materials Technology, Poland). Samples were cleaned using heated sonication bath in ethanol:acetone 50:50 (v/v) for 15 minutes, followed by 35 minutes UV/ozone treatment (Novascan Industries Ltd., USA). Samples were then etched in basic

solution (NH_4OH: water 1:9 v:v) for 1 minute, and rinsed in water for 1 minute. Immediately after cleaning the samples were transferred into a glove box (O_2<0.1ppm, H_2O<1ppm, MBRAUN, MB 20G, USA) and were immersed in 1 mM solution of the dipepetides or single amino acid in acetonitrile. After overnight assembly, the samples were thoroughly washed in water and dried in a vacuum chamber for 1 hour. Assembly was verified by ATR-FTIR spectroscopy (Bruker, Equinox-55) using a liquid nitrogen cooled mercury cadmium telluride (MCT) detector.

Surface electronic properties characterizations:

CPD was measured in a contactless manner using the Kelvin probe technique (Kelvin probe S, Besocke, Germany with reference gold electrode [WF_{Au}=5 eV]).[2] Fresh samples were mounted in a dark Faraday cage operated under a nitrogen flow (less than 15% relative humidity) in order to minimize effects of oxidation and artifacts obtained due to changes in the humidity. Contact to a grounded sample holder was achieved by scratching the back of the sample and introduction of a layer of eutectic InGa solution. Dark CPD values were recorded after equilibration and averaged for at least three different samples for each peptide assembly.

SPV spectra were recorded by illuminating the samples at a wavelength range of 1600-600 nm using the output of quartz-tungsten-halogen (QTH) light source transferred through a double monochromator (MS 257, Newport, USA) and long pass filters (in order to eliminate second order reflections). Spectra were collected, using Tracq 32 software (Newport, USA) for a freshly prepared set of samples of hybrids of all the library members in one day. At least three sets of experiments were conducted showing the same trends but with some variations in the overall signal magnitude. Representative results of one of the batches are presented.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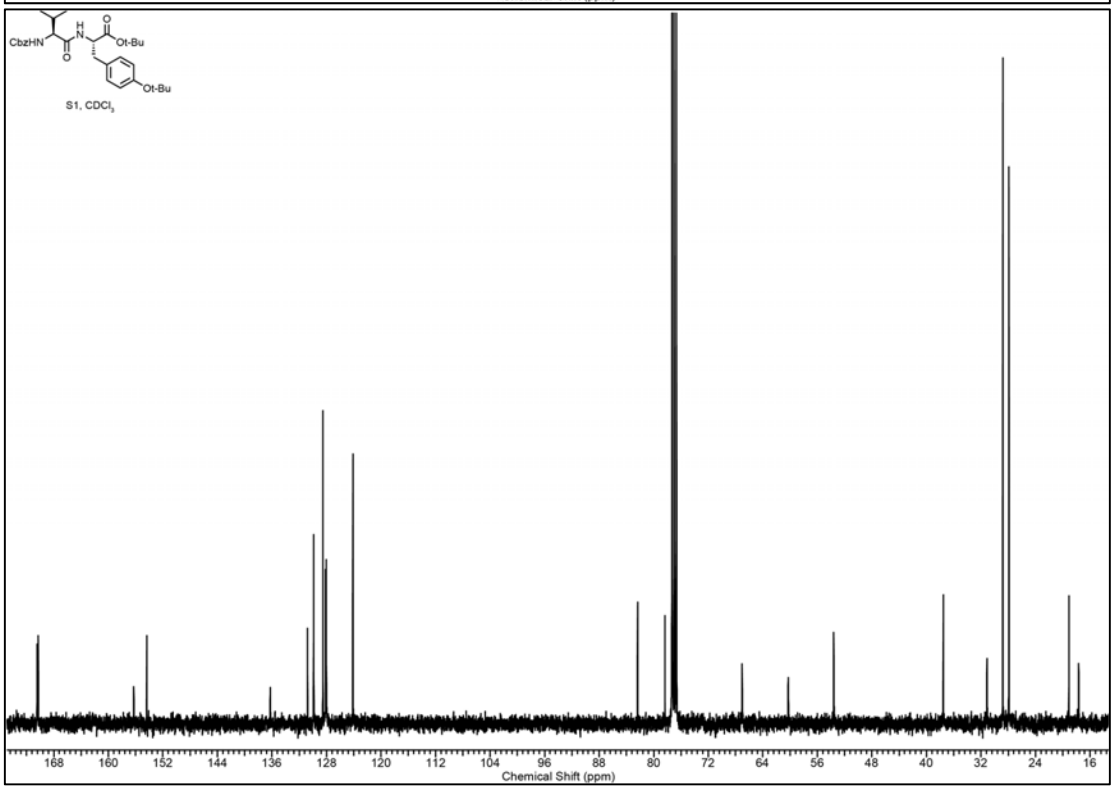
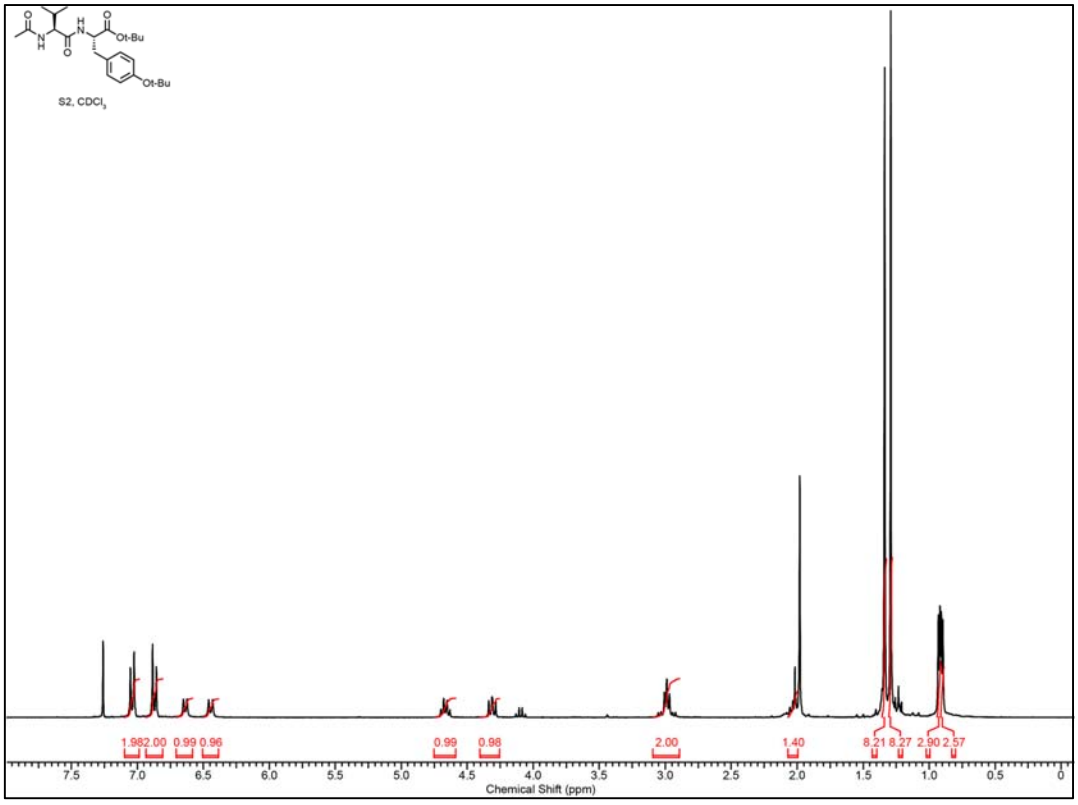
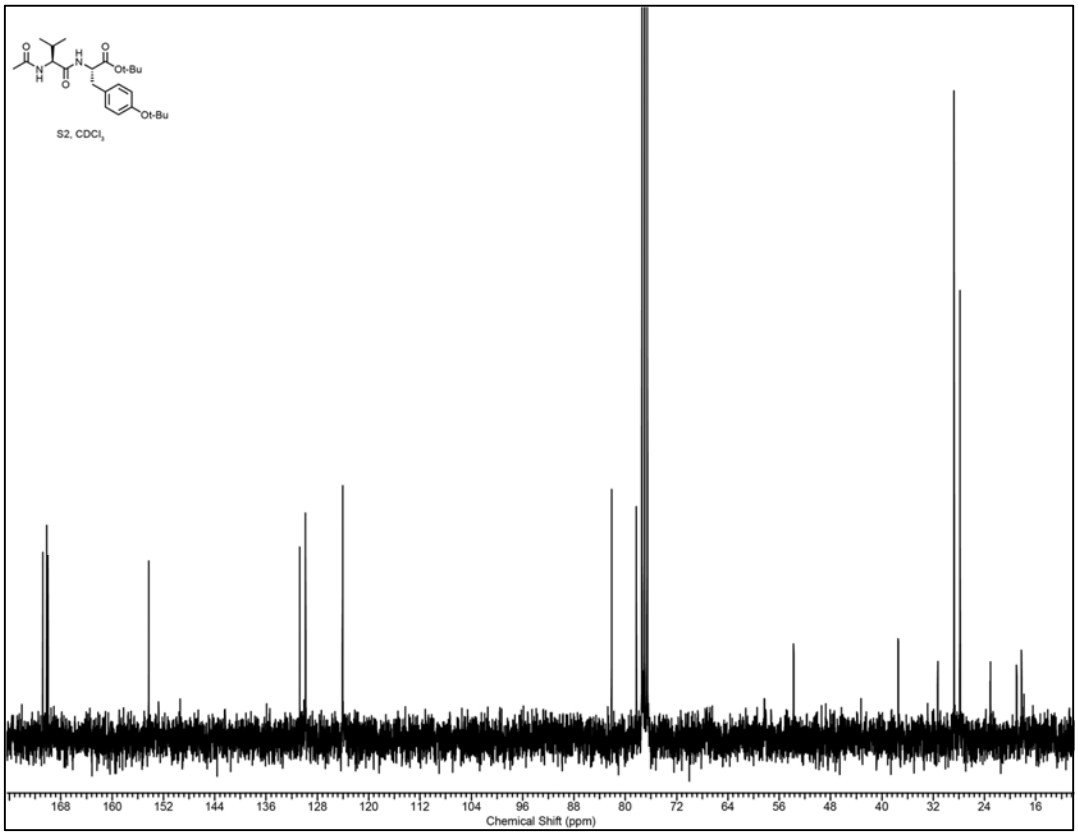
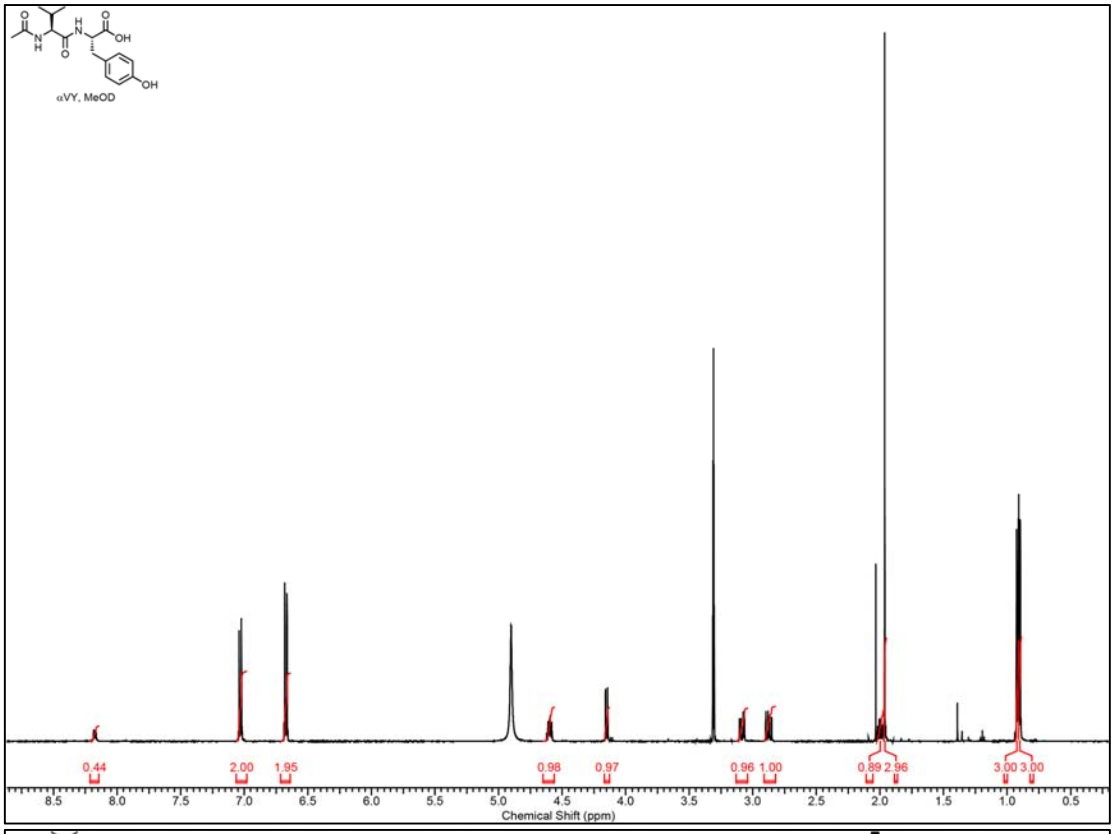
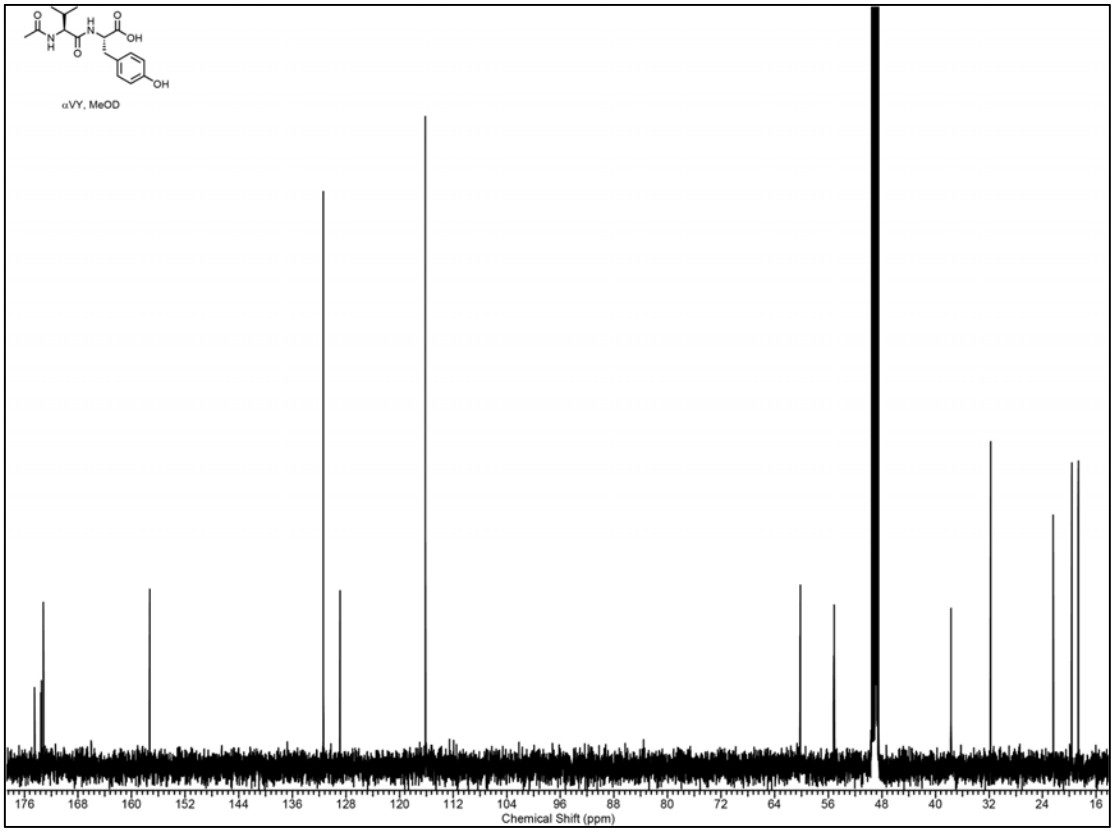
Chemical Shift (ppm)

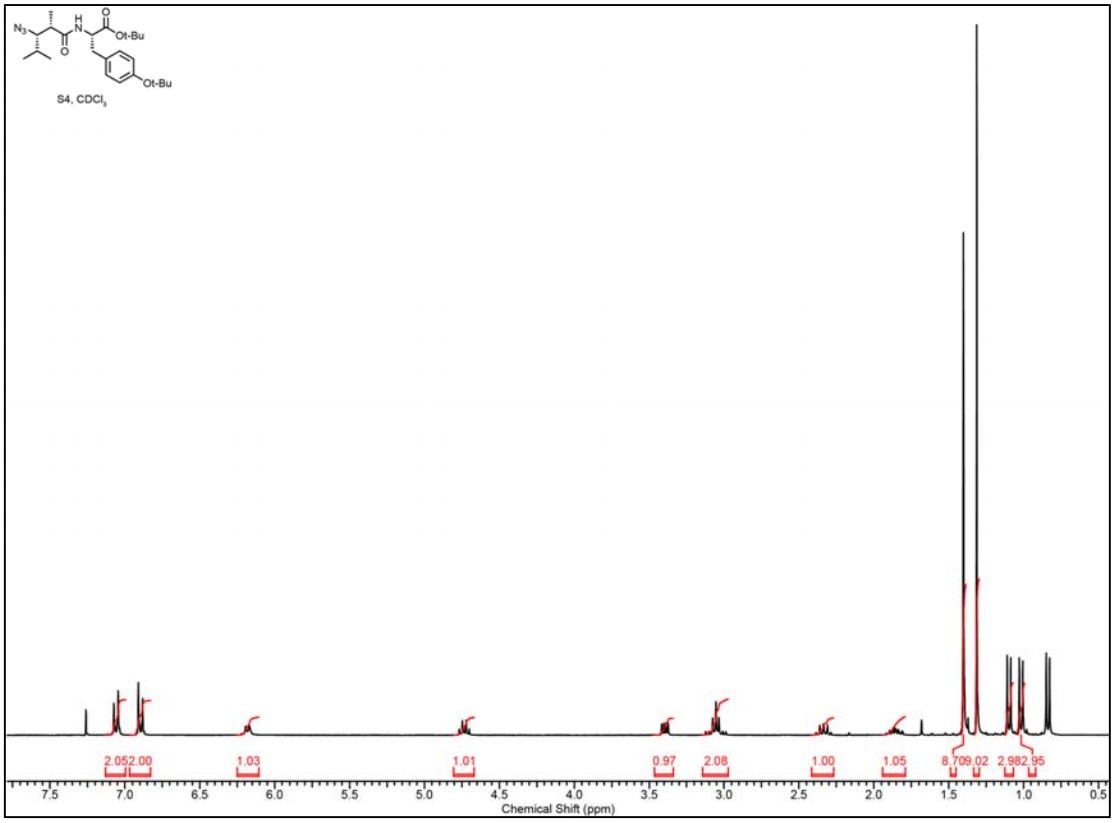

CbzHN
Ot-Bu
Ot-Bu
S1, CDCl3
Chemical Shift (ppm)

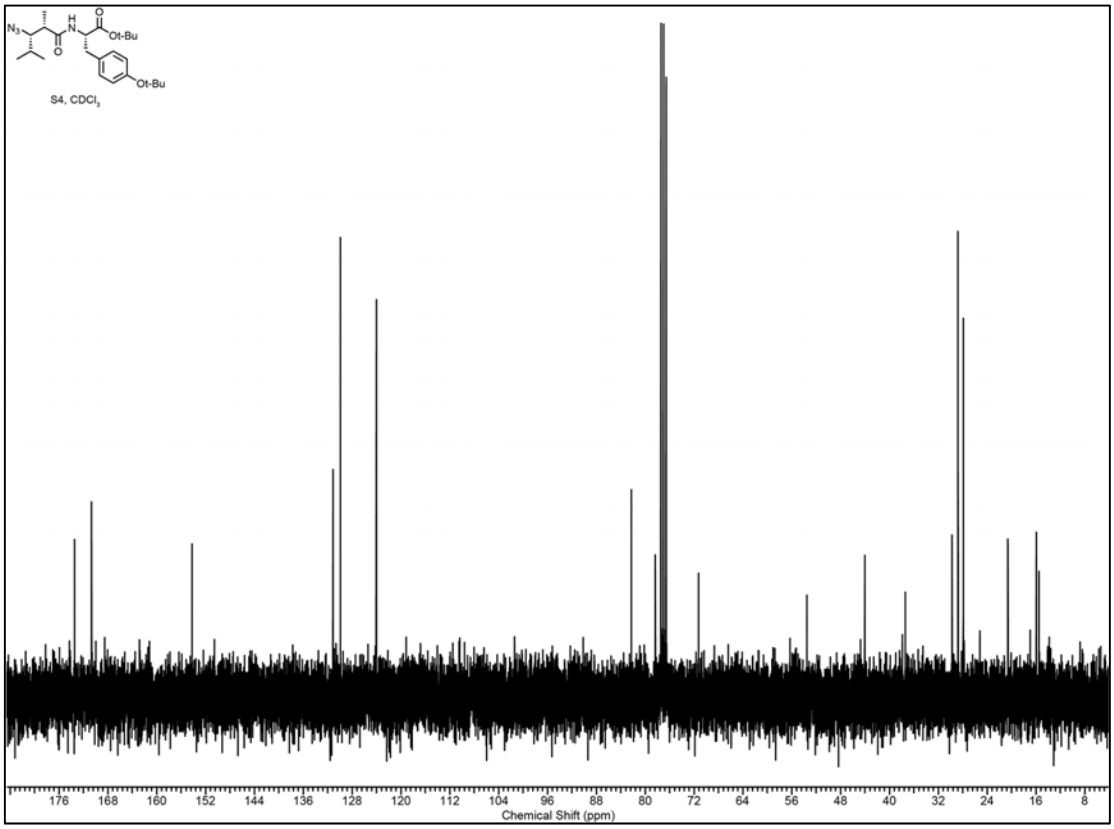

S2, CDCl3
Ot-Bu
Ot-Bu
1.98 2.00 0.99 0.96 0.99 0.98 2.00 1.40 8.21 8.27 2.90 2.57
Chemical Shift (ppm)

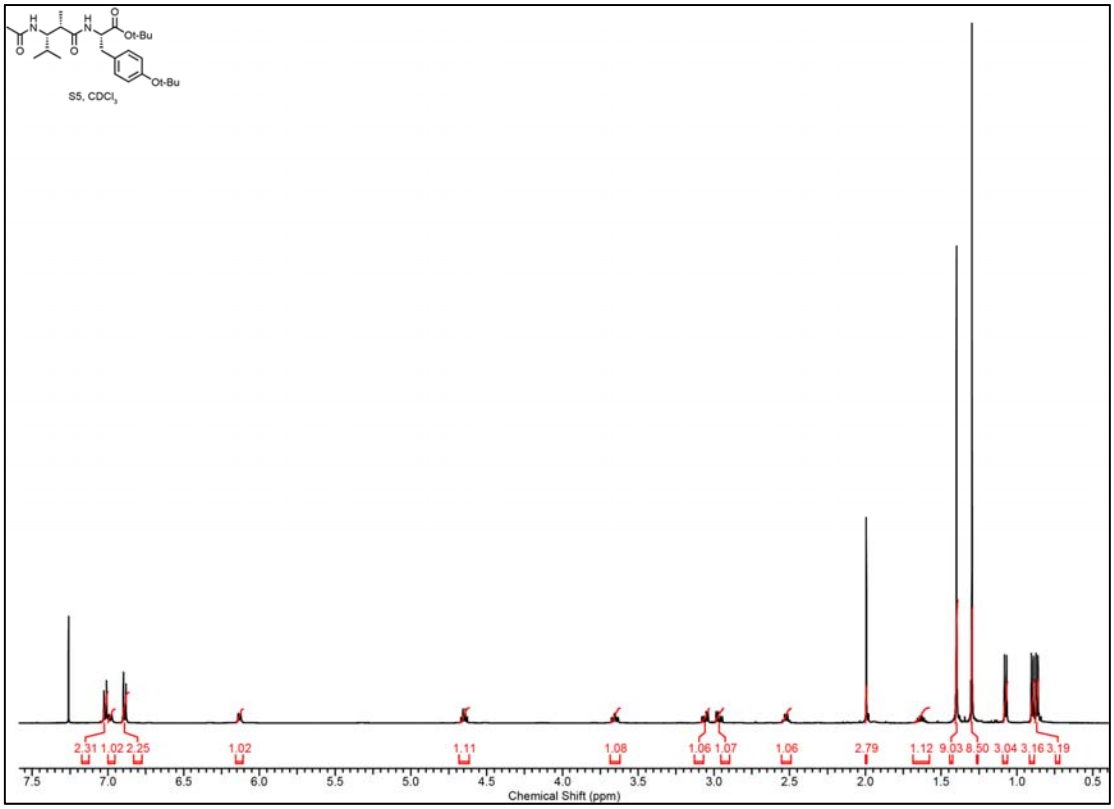

S2, CDCl3
Ot-Bu
Ot-Bu
Chemical Shift (ppm)

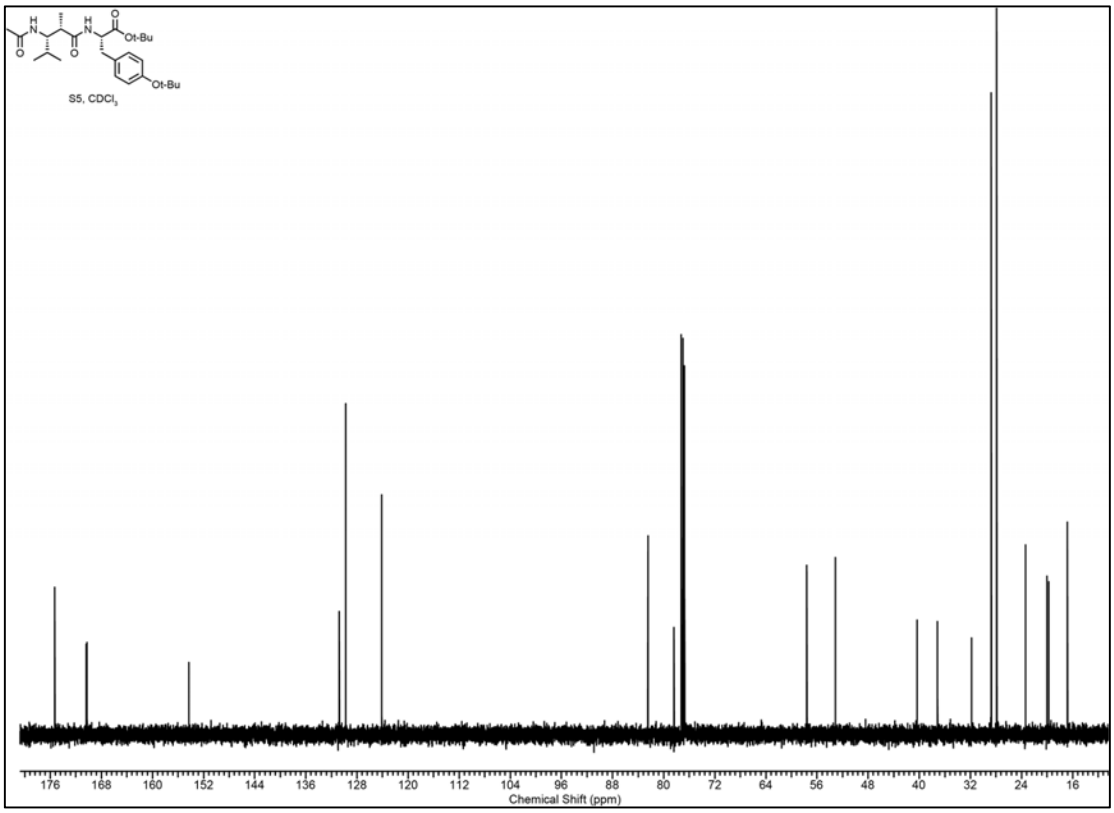

αVY, MeOD
0.44
2.00
1.95
0.98
0.97
0.96
1.00
0.89
2.96
3.00
3.00
Chemical Shift (ppm)

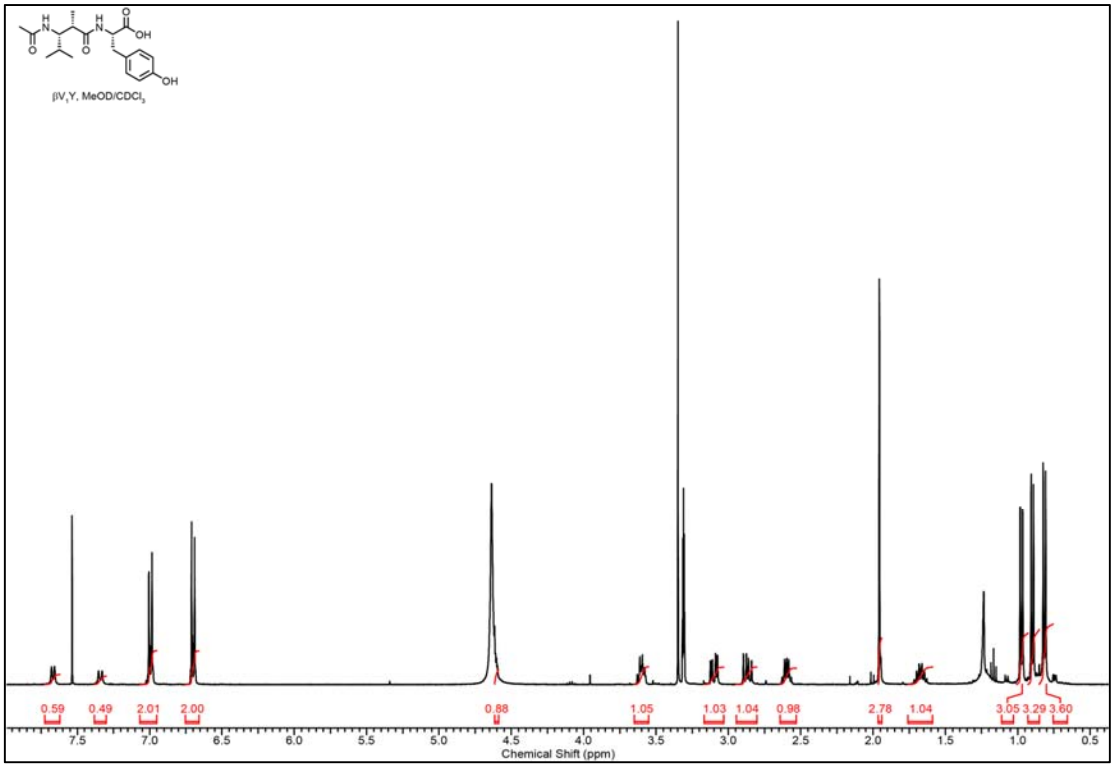

αVY, MeOD
Chemical Shift (ppm)

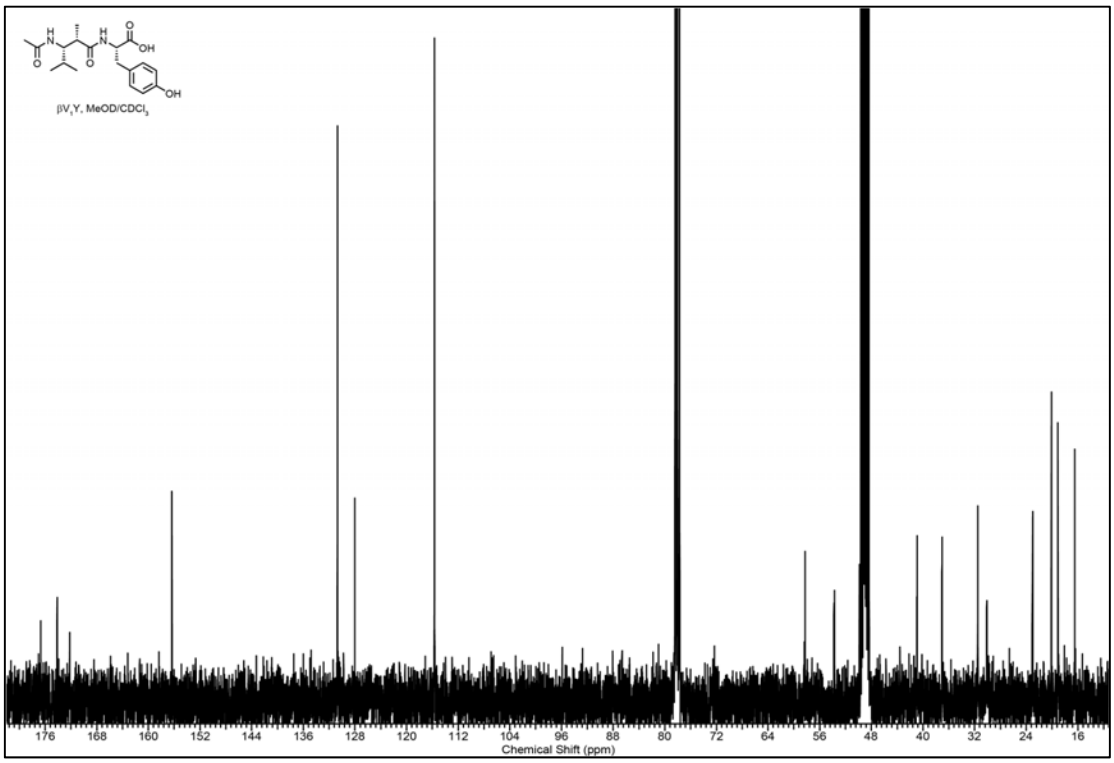

S4, CDCl3
2.05
2.00
1.03
1.01
0.97
2.08
1.00
1.05
8.70
9.02
2.98
2.95
Chemical Shift (ppm)

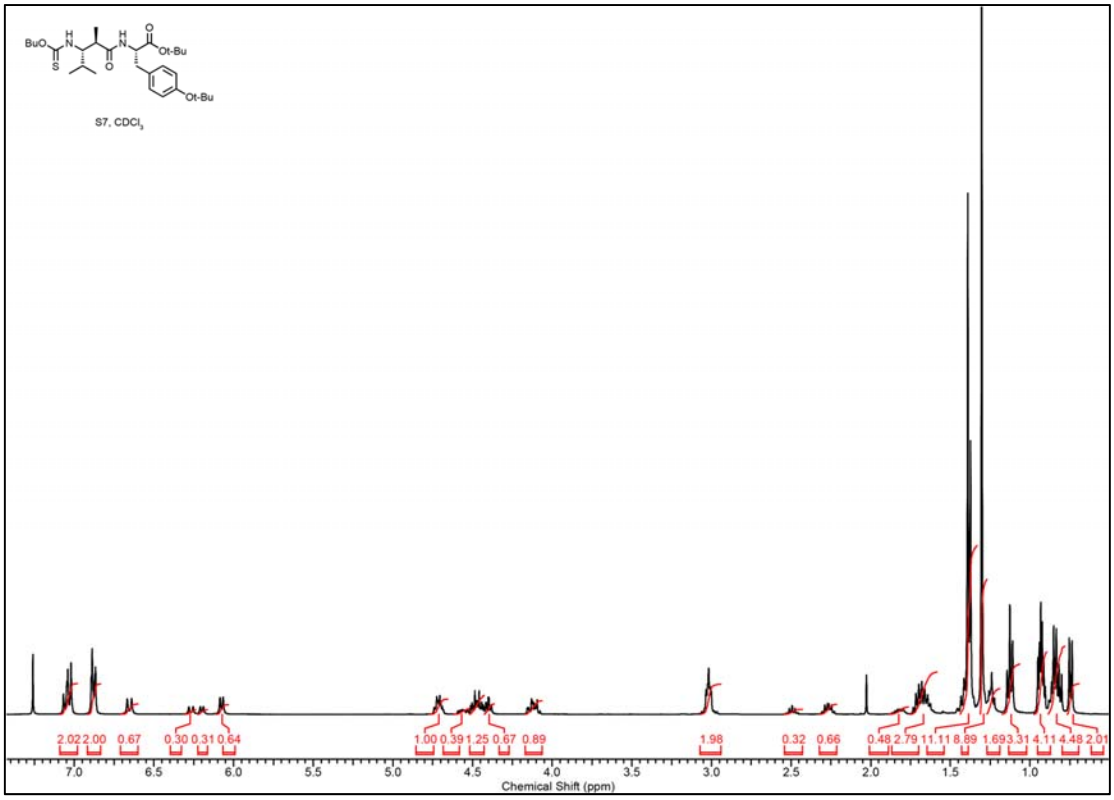

S4, CDCl3
Chemical Shift (ppm)

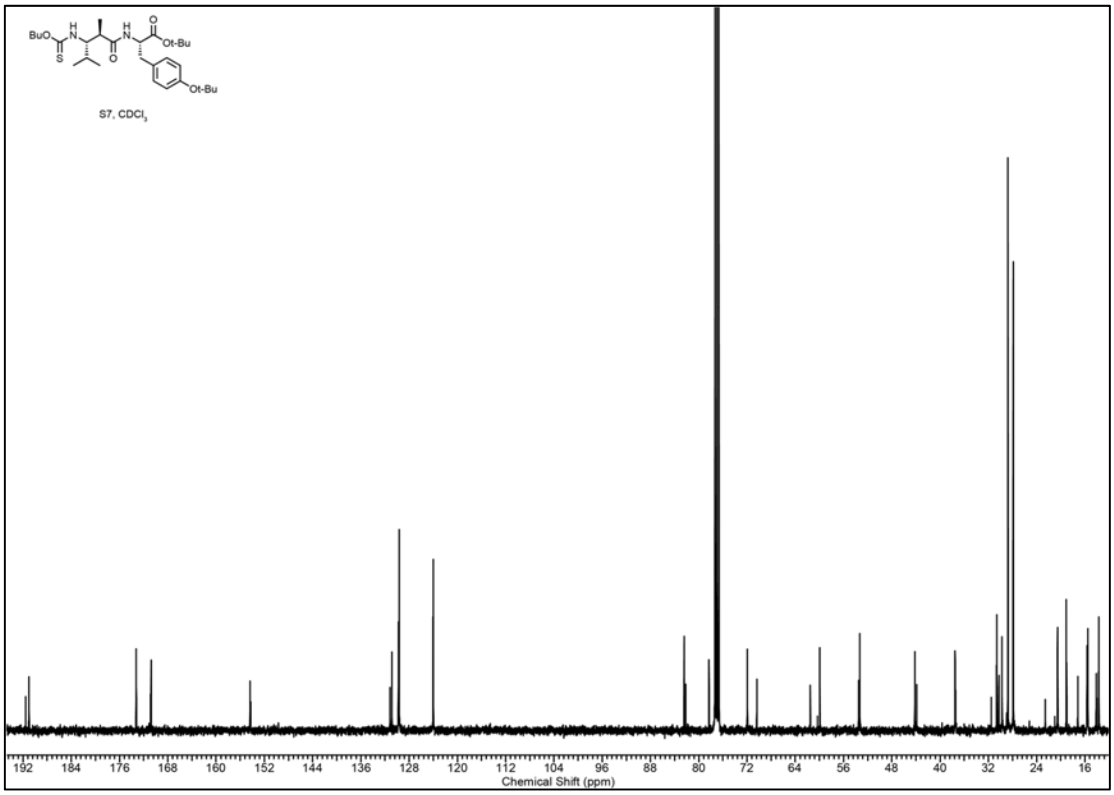

Ot-Bu
Ot-Bu
S5, CDCl3
2.31 1.02 2.25
1.02
1.11
1.08
1.06 1.07
1.06
2.79
1.12 9.03 8.50 3.04 3.16 3.19
Chemical Shift (ppm)

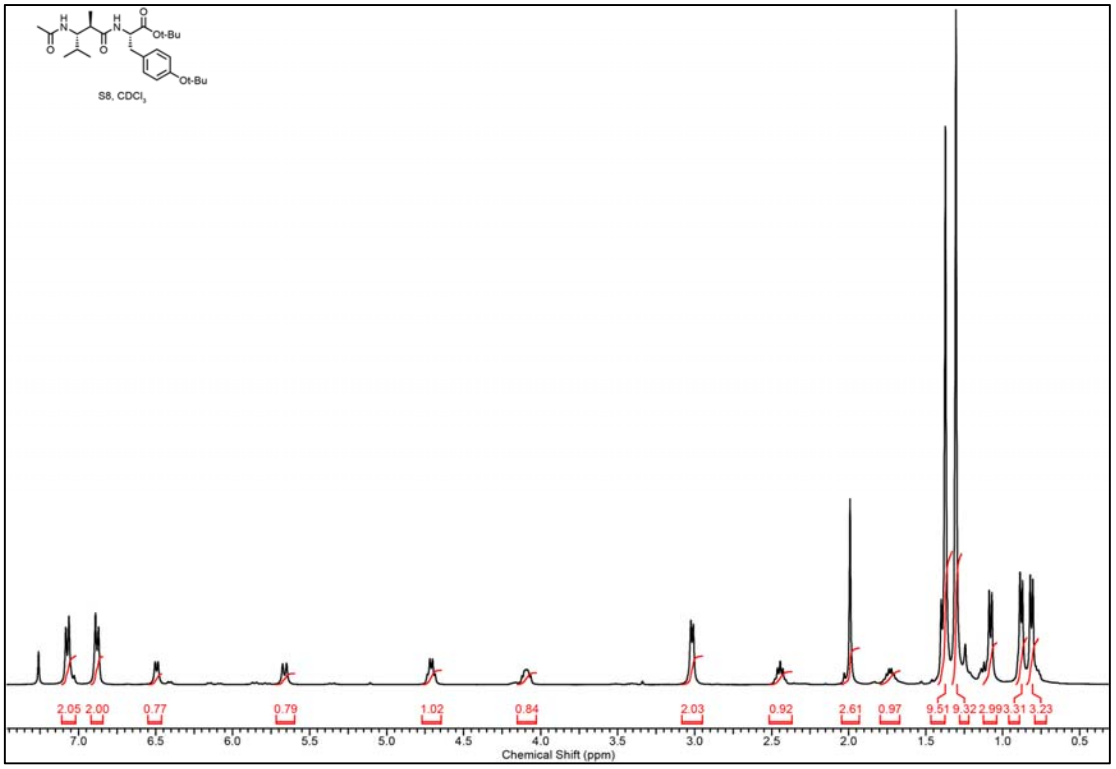

Ot-Bu
Ot-Bu
S5, CDCl3
Chemical Shift (ppm)

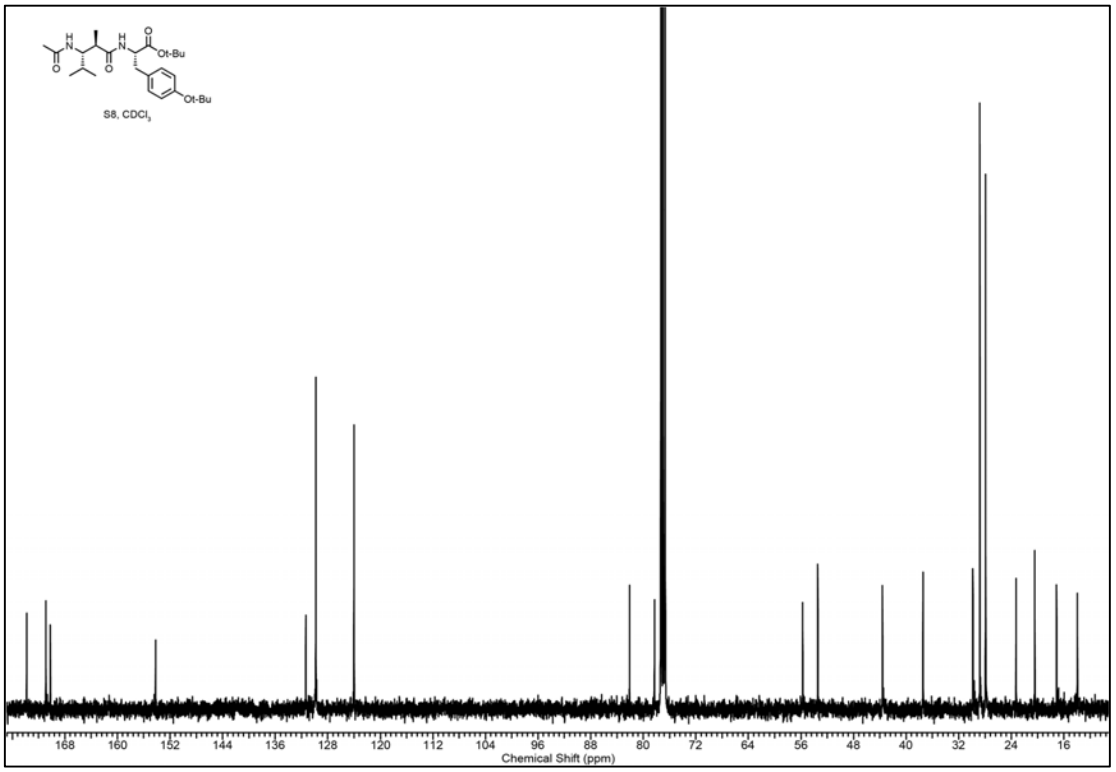

βV1Y, MeOD/CDCl3
0.59
0.49
2.01
2.00
0.88
1.05
1.03
1.04
0.98
2.78
1.04
3.05
3.29
3.60
Chemical Shift (ppm)


βV1Y, MeOD/CDCl3
Chemical Shift (ppm)

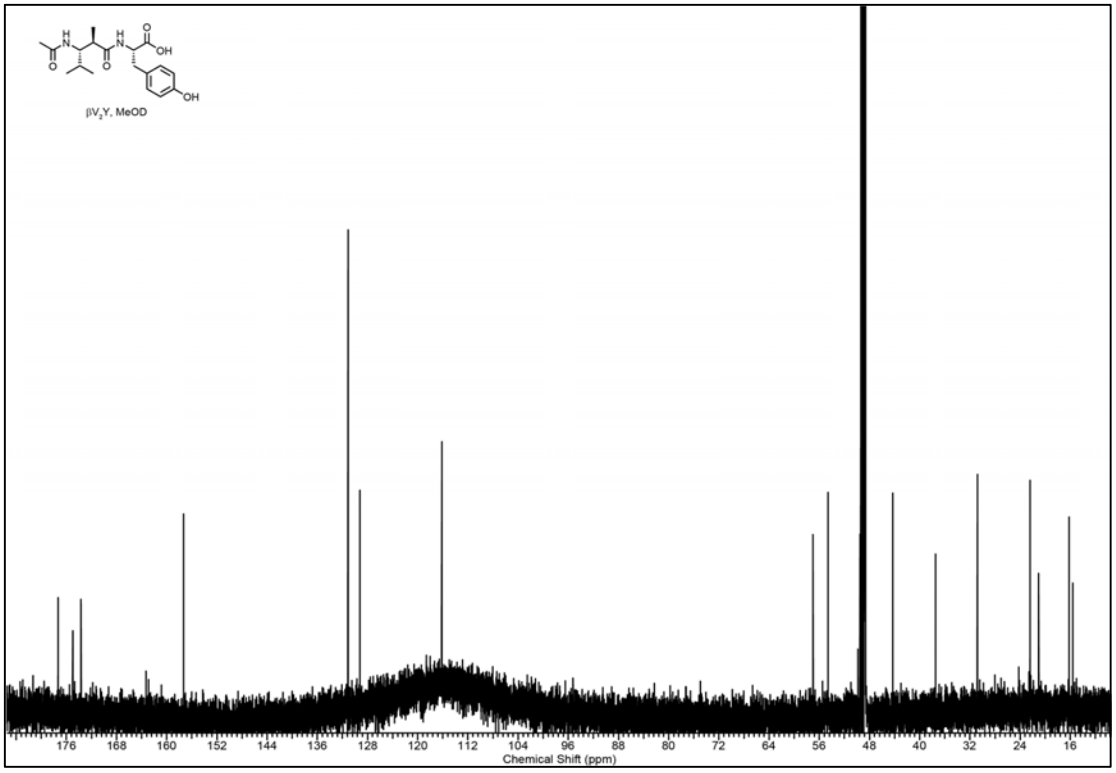

S7, CDCl3
2.02 2.00 0.67 0.30 0.31 0.64 1.00 0.39 1.25 0.67 0.89 1.98 0.32 0.66 0.48 2.79 11.11 8.89 1.69 3.31 4.11 4.48 2.01
Chemical Shift (ppm)


S7, CDCl3
Chemical Shift (ppm)


S8, CDCl3
Ot-Bu
Ot-Bu
2.05 2.00 0.77 0.79 1.02 0.84 2.03 0.92 2.61 0.97 9.51 9.32 2.99 3.31 3.23
Chemical Shift (ppm)


S8, CDCl3
Ot-Bu
Ot-Bu
Chemical Shift (ppm)


βV2Y, MeOD
0.44
2.04
2.00
1.01
0.98
1.09
1.02
1.00
2.99
1.36
3.00
3.00
3.06
Chemical Shift (ppm)


βV2Y, MeOD
Chemical Shift (ppm)

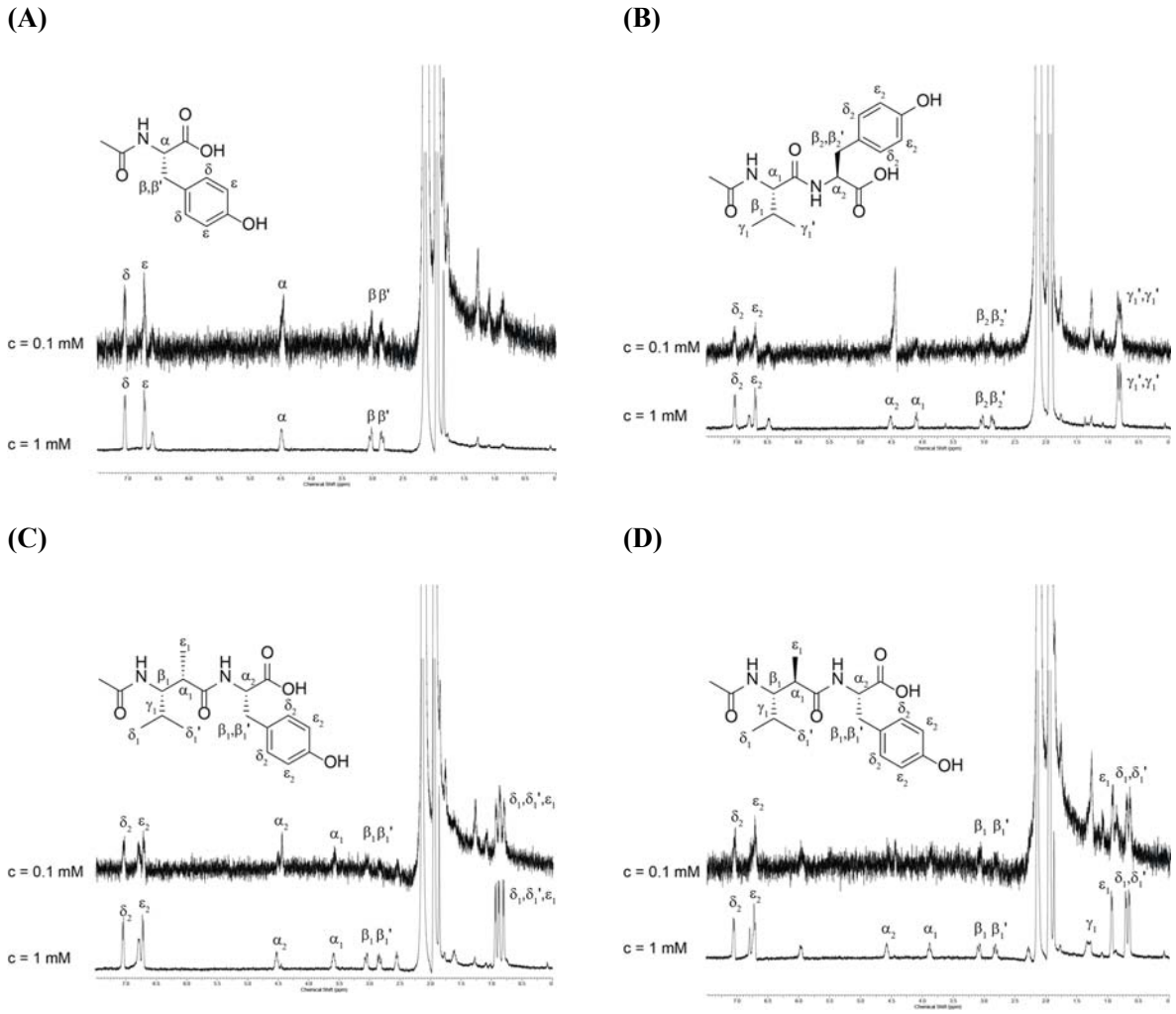


Figure S1. Concentration dependent NMR of (A) **αY**, (B) **αVY**, (C) **βV$_1$Y**, and (D) **βV$_2$Y**

References:

(1) Lengyel, G. A.; Frank, R. C.; Horne, W. S. *J Am Chem Soc* **2011**, *133*, 4246.
(2) Kronik, L.; Shapira, Y. *Surface Science Reports* **1999**, *37*, 1.