Electronic Supplementary Information

Metal-free Functionalization of Tyrosine Residue in Short Peptides and Study of Morphological Alterations

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1. General Information

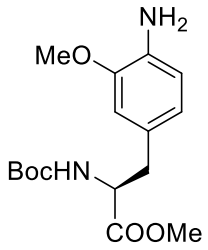
All chemicals have been purchased from commercial sources and were used without further purification unless otherwise noted. All solvents are reagent grade or HPLC grade. Anhydrous acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2) and *N*,*N*-dimethylformamide (DMF) were obtained from a dry solvent system. Dichloromethane was freshly distilled from CaH_2 and anhydrous tetrahydrofuran (THF) was freshly distilled from sodium-benzophenone. The synthetic transformations have been monitored by thin layer chromatography (TLC). TLC was performed on silica gel 60 F254 plates (glass plates). Concentration under reduced pressure was performed by rotary evaporation below 45 °C. Column chromatography was performed using silica gel (100-200 mesh) packed in glass columns. Yields refer to spectroscopically pure compounds after isolation. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-*d6* using 300, 400 or 500 MHz (^{1}H) and 101 or 126 or 151 MHz (^{13}C). Chemical shifts (δ-values) are reported in ppm, spectra were calibrated related to solvents' residual proton chemical shifts ($CDCl_3$, δ = 7.26) or (DMSO-*d6*, 2.5) and solvents' residual carbon chemical shifts ($CDCl_3$, δ = 77.16) or (DMSO-*d6*, δ = 39.52), multiplicity is reported as follows: s = singlet, brs = broad singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, t = triplet, m = multiplet or unresolved and coupling constant *J* in Hz. Melting points (mp) were determined in open capillaries and are uncorrected. Infrared spectra (IR) were recorded on a 0.1 mm KBr demountable cell. High-resolution mass spectra (HRMS) were obtained by electrospray ionization using a Q-TOF mass spectrometer in positive ion mode ([M+H], [M+Na] or [M-Boc]) as indicated.

2. Experimental Procedure for Compounds 2a, 4a-i and 5-8

General Procedure for Synthesis of Compounds 2a, 4a-i

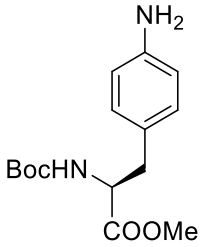
To a solution of **1a** and **3a-i** (0.33 mmol, 1.0 equiv) in MeOH (2 mL) was added $PhI(OAc)_2$ (PIDA) (0.66 mmol, 2.0 equiv) at 0 ºC. After 0.5 h, to the mixture was added a solution of glycine (0.39 mmol, 1.2 equiv) and Et_3N (0.66 mmol, 2.0 equiv) in MeOH (3 mL) and the reaction was kept stirring at 100 ºC for 2 h. The reaction mixture was warmed to room temperature and MeOH was evaporated using rotary evaporator. The reaction mixture was then quenched by saturated aqueous NH_4Cl solution (5 mL) and extracted with DCM (2 x 10 mL). The organic layer was separated and washed with water (10 mL) followed by brine solution (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by chromatography on silica gel to afford products **2a** and **4a-i**.

Methyl-(*S*)-3-(4-amino-3-methoxyphenyl)-2-((*tert*-butoxycarbonyl)amino)propanoate (2a)



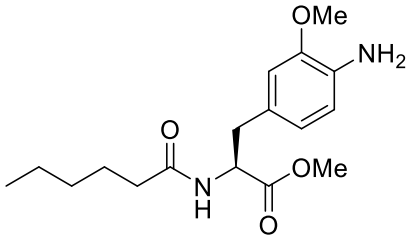
Following the general procedure, the reaction is performed with ***N***-Boc-L-Tyr-OMe **1a** (100 mg, 0.33 mmol) using PIDA (213 mg, 0.66 mmol), glycine (29.26 mg, 0.39 mmol) and Et_3N (0.9 mL, 0.66 mmol) in MeOH (5 mL) at given condition for 2 h. The residue was purified by silica gel column chromatography (20% EtOAc/hexanes) to afford **2a** as yellow liquid (89 mg, 81%); ^{1}H NMR (400 MHz, DMSO-*d6*): δ 7.16 (d, J = 7.9 Hz, 1H), 6.67 (s, 1H), 6.56 – 6.49 (m, 2H), 4.57 (brs, 2H), 4.08 (td, J = 9.2, 5.5 Hz, 1H), 3.73 (s, 3H), 3.60 (s, 3H), 2.82 (dd, J = 13.7, 5.3 Hz, 1H), 2.70 (dd, J = 13.7, 9.5 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (151 MHz, DMSO-*d6*): δ 173.3, 155.7, 146.6, 136.4, 125.6, 121.8, 114.1, 111.9, 78.7, 56.2, 55.6, 52.2, 36.7, 28.6; IR ($CHCl_3$): ν_{max} 3448, 3346, 2638, 1736, 1709, 1411, 1286, 1247, 910, 782, 653 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{16}H_{25}N_2O_5$: 325.1755, found 325.1754.

Methyl (*tert*-butoxycarbonyl)-L-tyrosine (2a′)



To a solution of methyl (*tert*-butoxycarbonyl)-L-tyrosine (100 mg, 0.33 mmol, 1.0 equiv) in MeOH (3.0 mL) was added PIDA (131 mg, 0.41 mmol, 1.2 equiv) at 0 ºC. After 0.5 h, MeOH (3 mL) was evaporated using rotary evaporator. Then glycine (30 mg, 0.41 mmol, 1.2 equiv) and Et_3N (0.09 mL, 0.4 mmol, 2.0 equiv) was added to the reaction mixture in MeCN (2 mL) at 80 ºC. After completion of the reaction 16 h, reaction mixture was quenched by H_2O (2 mL) and was allowed to cool at room temperature. The reaction mixture was extracted with EtOAc (2 x 5 mL), and the organic layer was separated and washed with water (10 mL) followed by brine solution (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by chromatography (20% EtOAc/hexanes) on silica gel to afford **2a′** as yellow liquid (70 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (d, J = 8.3 Hz, 2H), 6.63 – 6.59 (m, 2H), 4.94 (d, J = 7.6 Hz, 1H), 4.50 (dd, J = 13.4, 5.9 Hz, 1H), 3.70 (s, 3H), 3.62 (brs, 2H), 3.00 – 2.92 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.7, 155.3, 145.5, 130.3, 125.8, 115.4, 80.0, 54.7, 52.3, 37.6, 28.5; IR ($CHCl_3$): ν_{max} 3346, 3224, 1736, 1709, 1411, 1232, 782, 653 cm^{-1}. HRMS (ESI): m/z calculated for $[M+H]^+$ $C_{15}H_{23}N_2O_4$ 295.3547, found 295.3587.

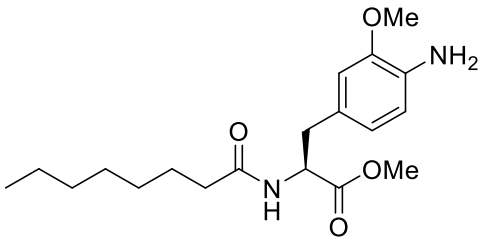
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-hexanamidopropanoate (4a)



Following the general procedure, the reaction is performed with methyl hexanoyl-L-tyrosinate **3a** (100 mg, 0.34 mmol) using PIDA (219 mg, 0.68 mmol), glycine (30.71 mg, 0.40 mmol) and Et_3N (0.95 mL, 0.68 mmol) in MeOH (5 mL) at given condition for 2 h. The residue was purified by silica gel column chromatography (40% EtOAc/hexanes) to afford **4a** as yellow liquid (82.4 mg, 75%); ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.15 (d, J = 7.7 Hz, 1H), 6.67 (s, 1H), 6.53 – 6.49 (m, 2H), 4.61 (brs, 2H), 4.36 (td, J = 9.0, 5.5 Hz, 1H), 3.73 (s, 3H), 3.59 (s, 3H), 2.85 (dd, J = 13.7,

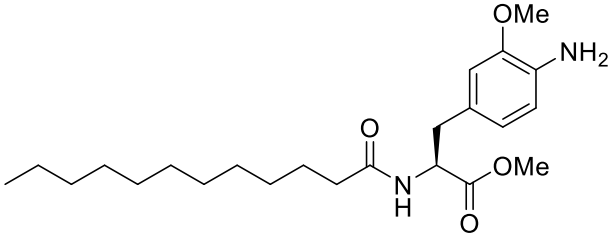
5.4 Hz, 1H), 2.72 (dd, *J* = 13.7, 9.3 Hz, 1H), 2.05 (t, *J* = 7.4 Hz, 2H), 1.44 – 1.38 (m, 2H), 1.26 – 1.20 (m, 4H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-*d6*): δ 172.5, 172.3, 146.1, 135.9, 124.9, 121.3, 113.6, 111.5, 55.1, 54.0, 51.7, 36.5, 34.9, 30.7, 24.9, 21.9, 13.9; IR ($CHCl_3$): ν_{max} 3616, 3369, 2957, 2930, 1737, 1517, 1369, 1250, 1170, 1038, 931, 859, 758, 668 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + H]^+$ $C_{17}H_{27}N_2O_4$ 323.1965 found 323.1960.

Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-octanamidopropanoate (4b)



Following the general procedure, the reaction is performed with methyl octanoyl-L-tyrosinate **3b** (100 mg, 0.31 mmol) using PIDA (200 mg, 0.62 mmol), glycine (28.06 mg, 0.37 mmol) and Et_3N (0.86 mL, 0.62 mmol) in MeOH (5 mL) at given condition for 2 h. The residue was purified by silica gel column chromatography (40% EtOAc/hexanes) to afford **4b** as yellow liquid (81.7 mg, 75%); ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.16 (d, *J* = 7.8 Hz, 1H), 6.67 (s, 1H), 6.52 (dt, *J* = 7.9, 4.7 Hz, 2H), 4.87 (brs, 2H), 4.36 (ddd, *J* = 9.0, 7.9, 5.5 Hz, 1H), 3.73 (s, 3H), 3.59 (s, 3H), 2.85 (dd, *J* = 13.8, 5.4 Hz, 1H), 2.72 (dd, *J* = 13.8, 9.2 Hz, 1H), 2.06 (t, *J* = 7.4 Hz, 2H), 1.44 – 1.38 (m, 2H), 1.25 – 1.17 (m, 8H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-*d6*): δ 172.5, 172.3, 146.3, 135.4, 125.4, 121.3, 113.9, 111.5, 55.2, 54.0, 51.7, 36.5, 35.0, 31.2, 28.5, 25.2, 22.1, 14.0; IR ($CHCl_3$): ν_{max} 2924, 2854, 1800, 1737, 1711, 1464, 1374, 1215, 1180, 1032, 951, 756, 722, 679 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{19}H_{31}N_2O_4$ 351.2284, found 351.2276.

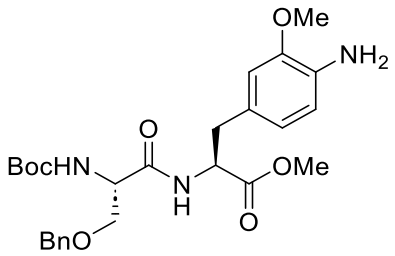
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-dodecanamidopropanoate (4c)



Following the general procedure, the reaction is performed with methyl dodecanoyl-L-tyrosinate **3c** (100 mg, 0.26 mmol) using PIDA (168 mg, 0.52 mmol), glycine (23.87 mg, 0.31 mmol) and Et_3N (0.73 mL, 0.53 mmol) in MeOH (5 mL) at given condition for 2 h. The residue was purified by silica gel column chromatography (40% EtOAc/hexanes) to afford **4c** as yellow liquid (77.5

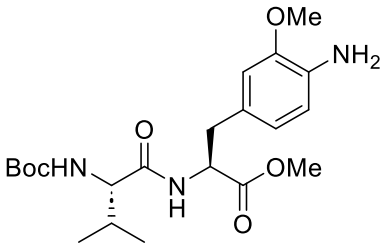
mg, 72%); ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.15 (d, *J* = 7.7 Hz, 1H), 6.65 (s, 1H), 6.55 – 6.45 (m, 2H), 4.58 (brs, 2H), 4.35 (td, *J* = 8.8, 5.6 Hz, 1H), 3.72 (s, 3H), 3.58 (s, 3H), 2.84 (dd, *J* = 13.8, 5.5 Hz, 1H), 2.72 (dd, *J* = 13.8, 9.2 Hz, 1H), 2.05 (t, *J* = 7.3 Hz, 2H), 1.43 – 1.37 (m, 2H), 1.27 – 1.21 (m, 16H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-*d6*): δ 172.5, 172.4, 146.2, 135.9, 125.0, 121.3, 113.6, 111.5, 55.2, 54.0, 51.7, 36.6, 35.0, 31.4, 29.1, 29.1, 29.0, 28.8, 28.8, 28.6, 25.2, 22.2, 14.0; IR ($CHCl_3$): ν_{max} 3616, 3369, 3170, 2924, 2854, 1800, 1736, 1710, 1464, 1374, 1215, 1180, 1116, 1032, 951, 758, 722, 679 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{23}H_{39}N_2O_4$ 407.2904, found 407.2895.

Methyl-(*S*)-3-(4-amino-3-methoxyphenyl)-2-((S)-3-(benzyloxy)-2-((*tert*-butoxycarbonyl)amino)propanamido)propanoate (4d)



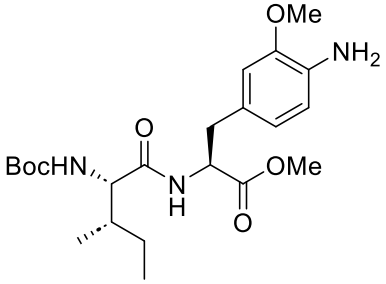
Following the general procedure, the reaction is performed with methyl *o*-benzyl-*N*-(*tert*-butoxycarbonyl)-L-seryl-L-tyrosinate **3d** (100 mg, 0.21 mmol) using PIDA (136 mg, 0.42 mmol), glycine (19.08 mg, 0.25 mmol) and Et_3N (0.6 mL, 0.42 mmol) in MeOH (5 mL) at given condition for 2 h. The residue was purified by silica gel column chromatography (45% EtOAc/hexanes) to afford **4d** as yellow liquid (83.8 mg, 79%); ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.16 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.27 (m, 5H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.63 (d, *J* = 1.4 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.47 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.59 (brs, 2H), 4.47 – 4.40 (m, 3H), 4.28 (dd, *J* = 12.6, 7.7 Hz, 1H), 3.72 (s, 3H), 3.56 (s, 3H), 3.51 (dd, *J* = 16.7, 9.3 Hz, 2H), 2.89 – 2.78 (m, 2H), 1.37 (s, 9H); ^{13}C NMR (151 MHz, DMSO-*d6*): δ 171.8, 169.8, 155.2, 146.2, 138.2, 136.1, 128.2, 127.5, 127.4, 124.4, 121.3, 113.7, 111.5, 78.3, 72.0, 70.0, 55.2, 54.2, 54.0, 51.8, 36.6, 28.2; IR ($CHCl_3$): ν_{max} 3362, 3320, 2975, 2938, 2344, 1867, 1715, 1694, 1642, 1456, 1378, 1281, 1225, 1041, 1010, 932, 873, 842 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + H]^+$ $C_{26}H_{36}N_3O_7$ 502.2540, found 502.2553.

Methyl-(*S*)-3-(4-amino-2-methoxyphenyl)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methylbutanamido)propanoate (4e)



Following the general procedure, the reaction is performed with *N*-Boc-L-Val-L-Tyr-OMe **3e** (100 mg, 0.25 mmol) using PIDA (161.4 mg, 0.5 mmol), glycine (22.5 mg, 0.30 mmol) and Et_3N (0.6 mL, 0.50 mmol) in MeOH (5 mL) at given condition for 2 h. The residue was purified by silica gel column chromatography (40% EtOAc/hexanes) to afford **4e** as yellow liquid (81.59 mg, 76%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.62 (d, J = 7.8 Hz, 1H), 6.58 – 6.46 (m, 2H), 6.24 (d, J = 6.8 Hz, 1H), 5.02 (d, J = 9.4 Hz, 1H), 4.82 (dt, J = 7.8, 5.7 Hz, 1H), 3.88 (dd, J = 8.7, 6.1 Hz, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.03 (t, J = 5.9 Hz, 2H), 2.12 – 2.01 (m, 1H), 1.44 (s, 9H), 0.93 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 171.3, 155.8, 147.6, 135.3, 130.6, 125.6, 121.8, 115.7, 115.1, 111.5, 80.0, 60.1, 55.6, 53.4, 52.4, 37.8, 31.2, 28.4, 19.3, 17.8; IR ($CHCl_3$): ν_{max} 3456, 3223, 2868, 1778, 1735, 1669, 1532, 1452, 1375, 1229, 1178, 1109, 1016, 838, 756, 665 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + H]^+$ $C_{21}H_{34}N_3O_6$ 424.2442, found 424.2436.

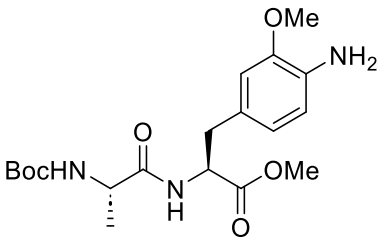
Methyl-(*S*)-3-(4-amino-2-methoxyphenyl)-2-((2*S*,3*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methylpentanamido)propanoate (4f)



Following the general procedure, the reaction is performed with *N*-Boc-L-Ile-L-Tyr-OMe **3f** (100 mg, 0.24 mmol) using PIDA (155 mg, 0.48 mmol), glycine (21.77 mg, 0.29 mmol) and Et_3N (0.6 mL, 0.48 mmol) in MeOH (5 mL) at given condition for 2 h. The residue was purified by silica gel column chromatography (35% EtOAc/hexanes) to afford **4f** as colorless liquid (83.54 mg,

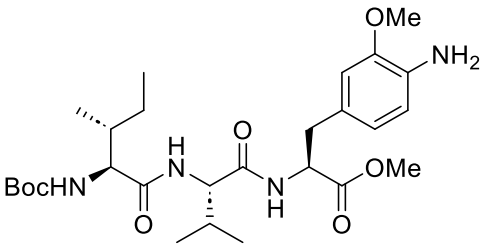
78%); ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.14 (d, *J* = 7.7 Hz, 1H), 6.66 (s, 1H), 6.57 – 6.43 (m, 2H), 4.59 (brs, 2H), 4.36 (ddd, *J* = 9.0, 7.9, 5.4 Hz, 1H), 3.80 (t, *J* = 9.2 Hz, 1H), 3.73 (s, 3H), 3.59 (s, 3H), 2.85 (dd, *J* = 13.7, 5.5 Hz, 1H), 2.72 (dd, *J* = 13.7, 9.2 Hz, 1H), 1.41 (m, 1H), 1.32 – 1.17 (m, 10H), 1.15 (m, 1H), 0.89 – 0.79 (m, 6H); ^{13}C NMR (101 MHz, DMSO-*d6*): δ 172.5, 172.3, 146.1, 121.3, 113.6, 111.5, 55.2, 54.0, 51.7, 36.5, 34.9, 30.7, 29.0, 24.9, 21.9, 13.8; IR ($CHCl_3$): ν_{max} 3478, 3235, 3056, 1738, 1665, 1514, 1453, 1375, 1228, 1167, 1104, 1014, 839, 767, 665 cm^{-1}; HRMS(ESI): *m/z* calculated for $[M + H]^+$ $C_{22}H_{36}N_3O_6$ 438.2599, found 438.2592.

Methyl-(*S*)-3-(4-amino-3-methoxyphenyl)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino) propanamido)propanoate (4g)



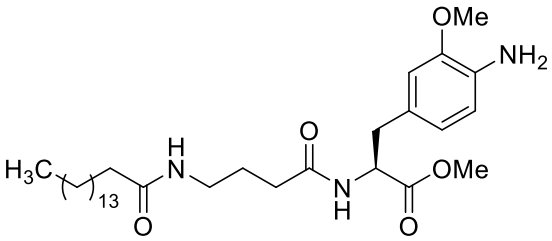
Following the general procedure, the reaction is performed with *N*-Boc-L-Ala-L-Tyr-OMe **3g** (100 mg, 0.27 mmol) using PIDA (174 mg, 0.54 mmol), glycine (24.02 mg, 0.32 mmol) and Et_3N (0.75 ml, 0.54 mmol) in MeOH (5 mL) at given condition for 2 h. The residue was purified by silica gel column chromatography (30% EtOAc/hexanes) to afford **4g** as yellow liquid (72.3 mg, 67%); ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.01 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.70 (s, 1H), 6.62 – 6.48 (m, 2H), 5.38 (brs, 2H), 4.41 (dd, *J* = 13.6, 7.4 Hz, 1H), 4.06 – 3.92 (m, 1H), 3.76 (s, 3H), 3.58 (s, 3H), 2.84 (t, *J* = 7.2 Hz, 2H), 1.36 (s, 9H), 1.13 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-*d6*): δ 172.8, 172.0, 154.9, 146.8, 134.1, 126.0, 121.3, 114.7, 111.7, 78.0, 55.3, 53.8, 51.8, 49.5, 36.5, 28.2, 18.1; IR ($CHCl_3$): ν_{max} 3401, 3224, 2966, 1740, 1738, 1660, 1512, 1449, 1373, 1232, 1158, 1109, 1016, 844, 756 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + H]^+$ $C_{19}H_{30}N_3O_6$ 396.1880, found 396.1892.

Methyl-(6*S*,9*S*,12*S*)-12-(4-amino-3-methoxybenzyl)-6-((*R*)-sec-butyl)-9-isopropyl-2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (4h)



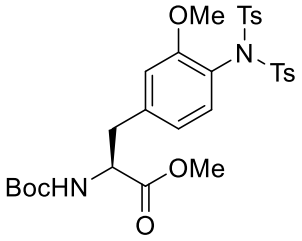
Following the general procedure, the reaction is performed with *N*-Boc-L-Ile-L-Val-L-Tyr-OMe **3h** (100 mg, 0.19 mmol) using (PIDA) (123 mg, 0.38 mmol), glycine (17.26 mg, 0.23 mmol) and Et_3N (0.5 mL, 0.38 mmol) in MeOH (5 mL) at given condition for 3.5 h. The residue was purified by silica gel column chromatography (70% EtOAc/hexanes) to afford **4h** as colourless liquid (75.06 mg, 71%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 – 7.02 (m, 1H), 6.62 (d, J = 7.8 Hz, 1H), 6.55 – 6.49 (m, 2H), 6.28 (d, J = 7.9 Hz, 1H), 5.02 (d, J = 7.0 Hz, 1H), 4.81 – 4.77 (m, 1H), 4.27 – 4.20 (m, 1H), 3.93 – 3.90 (m, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 3.11 – 3.09 (m, 1H), 3.06 – 2.95 (m, 3H), 2.14 – 2.07 (m, 1H), 1.89 – 1.84 (m, 1H), 1.53 – 1.48 (m, 1H), 1.44 (s, 9H), 1.16 – 1.10 (m, 1H), 0.92 – 0.88 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 171.8, 170.5, 147.6, 135.4, 130.2, 122.1, 121.8, 115.1, 111.4, 58.5, 55.6, 53.6, 53.5, 52.4, 37.7, 29.8, 28.4, 24.9, 19.2, 18.0, 15.7, 11.5; IR ($CHCl_3$) $\nu_{max:}$ 3289, 2924, 2860, 1694, 1642, 1518, 1456, 1378, 1282, 1227, 1167, 1032 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + H]^+$ $C_{27}H_{45}N_4O_7$ 537.3288, found 537.3281.

Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-(4-Palmitamidobutanamido) propanoate (4i)



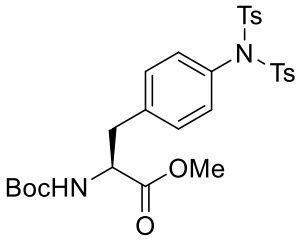
Following the general procedure, the reaction is performed with compound **3i** (100 mg, 0.19 mmol, 1.0 equiv) using PIDA (123 mg, 0.38 mmol, 2.0 equiv), glycine (17 mg, 0.23 mmol, 1.2 equiv) and Et_3N (0.05 mL, 0.38 mmol, 2.0 equiv) in MeOH (5 mL) at given condition for 2 h. The residue was purified by silica gel column chromatography (75% EtOAc/hexanes) to afford **4i** as yellow liquid (77.5 mg, 72%). ^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.21 (d, J = 7.7 Hz, 1H), 7.71 (t, J = 5.5 Hz, 1H), 6.65 (s, 1H), 6.52 – 6.48 (m, 2H), 4.54 (brs, 2H), 4.36 (td, J = 8.6, 5.8 Hz, 1H), 3.72 (s, 3H), 3.59 (s, 3H), 2.96 (dd, J = 12.9, 6.6 Hz, 2H), 2.85 (dd, J = 13.8, 5.6 Hz, 1H), 2.73 (dd, J = 13.8, 9.0 Hz, 1H), 2.07 (td, J = 7.4, 3.9 Hz, 2H), 2.02 (t, J = 7.5 Hz, 2H), 1.54 (dd, J = 14.3, 7.2 Hz, 2H), 1.48 – 1.44 (m, 2H), 1.23 (s, 24H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-*d6*): δ 172.4, 172.0, 171.9, 146.1, 136.0, 124.8, 121.3, 113.6, 111.4, 55.2, 54.1, 51.7, 38.0, 36.6, 35.4, 32.6, 31.3, 29.1, 29.0, 28.8, 28.7, 25.5, 25.3, 22.1, 14.0; IR ($CHCl_3$): ν_{max} 3706, 3487, 3452, 3367, 3999, 3170, 3018, 2920, 2850, 1743, 1646, 1548, 1215, 753, 670 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + H]^+$ $C_{31}H_{54}N_3O_5$ 548.4063, found 548.4074.

Methyl-(S)-2-((*tert*-butoxycarbonyl)amino)-3-(3-methoxy-4-((4-methylphenyl)sulfonamido)phenyl)propanoate (5)



To a solution of **2a** (100 mg, 0.31 mmol, 1.0 equiv) in DCM (5 mL), Et_3N (0.086 mL, 0.62 mmol, 2.0 equiv) followed by *p*-toluenesulfonyl chloride (88 mg, 0.46 mmol, 1.5 equiv) was added at 0 °C under nitrogen atmosphere. The solution was stirred for 12 h at room temperature. After completion of the reaction (monitored by TLC), reaction mixture was then quenched by addition of saturated aqueous NH_4Cl (10 mL) and then washed with saturated $NaHCO_3$ (10 mL). The organic layer was separated, evaporated and the residue was purified through column chromatography to obtain the required product **5** (155 mg, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.3 Hz, 4H), 7.30 (d, J = 8.4 Hz, 4H), 7.01 (d, J = 8.0 Hz, 1H), 6.70 (d, J = 7.9 Hz, 1H), 6.61 (d, J = 1.6 Hz, 1H), 5.04 (d, J = 8.0 Hz, 1H), 4.61 (dd, J = 13.3, 6.5 Hz, 1H), 3.70 (s, 3H), 3.39 (s, 3H), 3.14 – 3.02 (m, 2H), 2.45 (s, 6H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 157.5, 155.1, 144.6, 140.6, 137.1, 133.1, 129.2, 128.9, 121.5, 112.8, 80.2, 55.1, 54.2, 52.3, 38.7, 28.4, 21.7; IR ($CHCl_3$): ν_{max} 2938, 2344, 1867, 842, 784, 668 cm^{-1}; HRMS (ESI): m/z calculated for $[M + Na]^+$ $C_{30}H_{36}N_2O_9S_2Na$ 655.1760, found 655.1765.

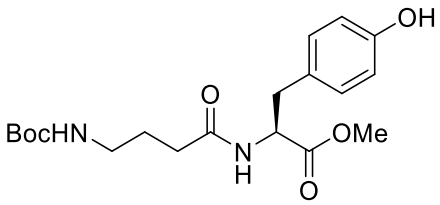
Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-((4-methyl-N-tosylphenyl)sulfonamido)phenyl)propanoate (5′)



To a solution of **2a′** (100 mg, 0.34 mmol, 1.0 equiv) in DCM (5 mL), Et_3N (0.094 mL, 0.68 mmol, 2.0 equiv) followed by *p*-toluenesulfonyl chloride (97 mg, 0.51 mmol, 1.5 equiv) was added at 0 °C under nitrogen atmosphere. The solution was stirred for 12 h at room temperature. After completion of the reaction (monitored by TLC), reaction mixture was then quenched by addition of saturated aqueous NH_4Cl (10 mL) and then washed with saturated $NaHCO_3$ solution (10 mL).

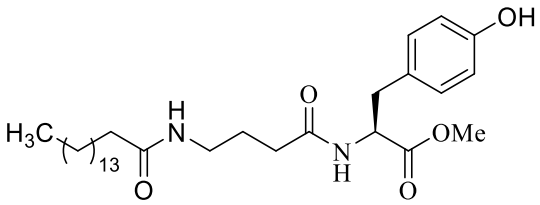
The organic layer was separated, evaporated and the residue was purified through column chromatography to obtain the required product **5′** (181 mg, 89%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.4 Hz, 4H), 7.33 (d, J = 8.1 Hz, 4H), 7.12 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 5.04 (d, J = 7.9 Hz, 1H), 4.60 (dd, J = 13.1, 6.2 Hz, 1H), 3.69 (s, 3H), 3.15-3.04 (m, 2H), 2.47 (s, 6H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1, 155.1, 145.0, 138.7,136.6, 133.2, 131.5, 130.0, 129.6, 128.6, 80.2, 54.3, 52.3, 38.2, 29.7, 28.3, 21.7; IR ($CHCl_3$) ν_{max} 2924, 2862, 1867, 842 cm-1. HRMS (ESI): m/z calculated for m/z calculated for $[M + Na]^+$ $C_{29}H_{34}N_2O_8S_2Na$ 625.1654, found 625.1656.

Methyl (4-((*tert*-butoxycarbonyl)amino) butanoyl)-L-tyrosinate (S1)



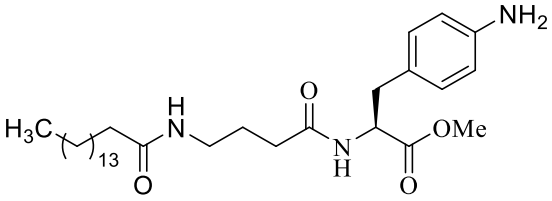
To the solution of N-Boc-GABA-OH (3.2 g, 15.7 mmol, 1.0 equiv) in DCM (50 mL), EDC.HCl (6.0 g, 31.5 mmol, 2.0 equiv) and HOBt (3.19 g, 23.6 mmol, 1.5 equiv) were added at 0 ºC under nitrogen atmosphere. The solution was stirred for 10 min. and a mixture of $HCl.NH_2$-Tyr-OMe (4.65 g, 15.7 mmol, 1.0 equiv) and DIPEA (11.3 mL, 63.01 mmol, 4.0 equiv) was added. After completion of the reaction (TLC analysis), reaction mixture was then quenched by adding saturated aqueous NH_4Cl (2 x 50 mL) and then washed with saturated $NaHCO_3$. The organic layer was separated, evaporated and the residue was purified through column chromatography (50% EtOAc/hexanes) to obtain the dipeptide **S1** as a yellow liquid (5.2 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 7.2 Hz, 1H), 4.85 – 4.78 (m, 2H), 4.73 (brs, 1H), 3.72 (s, 3H), 3.25 (dd, J = 12.4, 6.1 Hz, 1H), 3.17 (dd, J = 14.0, 5.7 Hz, 1H), 3.10 – 3.02 (m, 1H), 2.58 (t, J = 7.3 Hz, 1H), 2.22-2.18 (m, 1H), 1.96 – 1.89 (m, 1H), 1.77 – 1.68 (m , 1H), 1.42 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$); δ 172.3, 156.6, 149.8, 133.9, 130.3, 121.7, 79.5, 53.4, 52.5, 39.6, 37.3, 33.4, 28.5, 25.4; IR ($CHCl_3$): ν_{max} 3362, 3320, 2975, 2938, 1743, 1684, 1520, 1440, 1366, 1248, 1163, 1041, 1010, 932, 873, 842, 784, 668 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + H]^+$ $C_{19}H_{29}N_2O_6$ 381.2025, found 381.2028.

Methyl-(4-palmitamidobutanoyl) L-tyrosinate (3i):



To a solution of methyl (4-aminobutanoyl)-L-tyrosinate **S1** (1.0 g, 3.57 mmol, 1.0 equiv) in DCM (20 mL), Et_3N (1.0 mL, 7.14 mmol, 2.0 equiv) followed by Palmitoyl chloride (1.1 mL, 3.57 mmol, 1equiv) was added at 0 °C under nitrogen atmosphere. The solution was stirred for 2 h at 0 °C. After completion of the reaction (TLC analysis), reaction mixture was then quenched by addition of saturated aqueous NH_4Cl (2 x 50 mL) and then washed with saturated $NaHCO_3$. The organic layer was separated, evaporated and the residue was purified through column chromatography (70% EtOAc/hexanes) to obtain the required product **3i** (1.1 gm, 59%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (brs, 1H), 6.95 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 8.1 Hz, 1H), 6.23 (t, J = 5.7 Hz, 1H), 4.86 – 4.80 (m, 1H), 3.73 (s, 3H), 3.19 – 3.08 (m, 3H), 2.93 – 2.96 (dd, J = 14.1, 7.5 Hz 1H), 2.21 – 2.13 (m, 4H), 1.77 – 1.68 (m, 2H), 1.64 – 1.56 (m, 2H), 1.25 (s, 24H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.4, 172.9, 172.3, 155.9, 130.2, 127.0, 115.7, 53.4, 52.4, 38.8, 37.1, 36.8, 33.6, 31.9, 29.7, 29.6, 29.4, 25.8, 25.4, 22.7, 14.1; IR ($CHCl_3$): ν_{max} 3298, 3020, 2920, 2851, 1743, 1644, 1545, 1516, 1443, 1371, 1215, 828, 755, 668 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + Na]^+$ $C_{30}H_{50}N_2O_5Na$ 541.3617, found 541.3632.

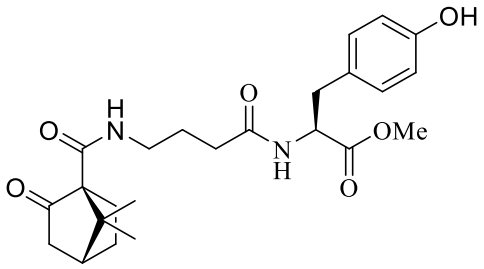
Methyl (*S*)-3-(4-aminophenyl)-2-(4-palmitamidobutanamido)propanoate (6)



To a solution of compound **3i** (100 mg, 0.19 mmol, 1.0 equiv) in MeOH (3.0 mL) was added PIDA (61.5 mg, 0.19 mmol, 1.0 equiv) at 0 °C. After 0.5 h, MeOH (3 mL) was evaporated using rotary evaporator. Then glycine (17 mg, 0.23 mmol, 1.2 equiv) and Et_3N (0.054 mL, 0.38 mmol, 2.0 equiv) was added to the reaction mixture in MeCN (2 mL) at 80 °C. After completion of the reaction 16 h, reaction mixture was quenched by H_2O (2 mL) and was allowed to cool at room

temperature. The reaction mixture was extracted with EtOAc (2 x 5 mL), and the organic layer was separated and washed with water (10 mL) followed by brine solution (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by chromatography (75% EtOAc/hexanes) on silica gel to afford **6** as yellow liquid (47 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 7.9 Hz, 1H), 5.93 (t, J = 5.4 Hz, 1H), 4.87 (dt, J = 7.4, 6.0 Hz, 1H), 3.73 (s, 3H), 3.26 – 3.14 (m, 3H), 3.09 – 3.02 (m, 1H), 2.54 (t, J = 7.5 Hz, 2H), 2.22-2.13 (m, 4H), 1.78-1.70 (m, 4H), 1.26-1.24 (m, 24H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$); δ 172.7, 172.2, 171.9, 156.5, 156.1, 149.7, 133.8, 130.2, 121.6, 115.6, 79.3, 53.3, 52.4, 39.8, 39.5 , 37.1, 33.3, 31.6, 28.4, 26.3, 25.3; IR ($CHCl_3$): ν_{max} 3020, 2920, 2851, 2938, 1743, 1684, 1520, 1440, 1366, 1248, 855, 746, 670 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + H]^+$ $C_{30}H_{52}N_3O_4$ 518.3957, found 518.3960.

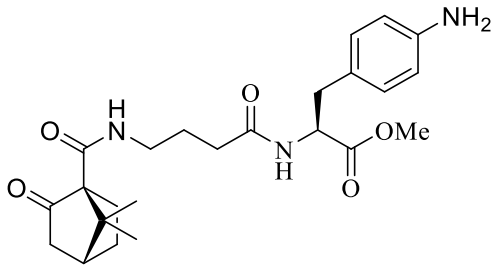
Methyl (4-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxamido)butanoyl)-L-tyrosinate (7)



To the solution of ketopinic acid (100 mg, 0.55 mmol, 1.0 equiv) in DCM (10 mL), EDC.HCl (210 mg, 1.1 mmol, 2.0 equiv) and HOBt (111 mg, 23.6 mmol, 1.5 equiv) were added at 0 ºC under nitrogen atmosphere. The solution was stirred for 10 min. and a mixture of TFA salt of NH_2-GABA-Tyr-OMe **S1** (304 mg, 0.55 mmol, 1.0 equiv) and DIPEA (0.4 mL, 2.2 mmol, 4.0 equiv) was added. After completion of the reaction (monitored by TLC), reaction mixture was quenched by adding saturated aqueous NH_4Cl (10 mL) and then washed with saturated $NaHCO_3$ (10 mL). The organic layer was separated, evaporated and the residue was purified through column chromatography (70% EtOAc/hexanes) to obtain the dipeptide **7** as a white liquid (120 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (t, J = 5.8 Hz, 1H), 7.56 (brs, 1H), 6.99 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.1 Hz, 1H), 6.75 (d, J = 8.5 Hz, 2H), 4.82 (m, 1H), 3.72 (s, 3H), 3.35 (m, 1H), 3.24 – 3.16 (m, 1H), 3.15 – 3.09 (m, 1H), 2.59 – 2.53.(m, 1H), 2.52 – 2.47 (m, 2H), 2.20 – 2.14 (m, 3H), 2.10 (t, 1H), 1.99 (d, J = 18.8 Hz, 1H), 1.82 – 1.75 (m, 2H), 1.64 – 1.56 (m, 1H), 1.48 – 1.39 (m,

1H), 1.25 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 217.3, 172.8, 172.6, 169.9, 155.7, 130.2, 127.2, 115.6, 64.9, 53.6, 52.4, 50.2, 43.81, 43.3, 38.1, 37.0, 33.3, 28.2, 27.7, 25.8, 21.0, 20.6; IR ($CHCl_3$): ν_{max} 2945, 2833, 1657, 1450, 1114, 1021, 932, 873, 842, 679 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + Na]^+$ $C_{24}H_{32}N_2O_6Na$ 467.2158, found 467.2171.

Methyl (*S*)-3-(4-aminophenyl)-2-(4-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxamido)butanamido)propanoate (8)

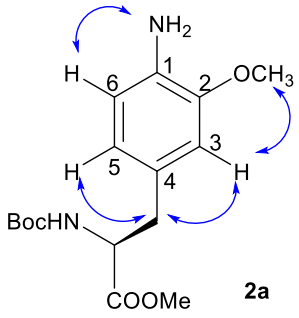


To a solution of compound **7** (100 mg, 0.22 mmol, 1.0 equiv) in MeOH (3.0 mL) was added PIDA (71 mg, 0.22 mmol, 1.0 equiv) at 0 ºC. After 0.5 h, MeOH (3 mL) was evaporated using rotary evaporator. Then glycine (20 mg, 0.27 mmol, 1.2 equiv) and Et_3N (0.063 mL, 0.45 mmol, 2.0 equiv) was added to the reaction mixture in MeCN (2 mL) at 80 ºC. After completion of the reaction 16 h, reaction mixture was quenched by H_2O (2 mL) and was allowed to cool at room temperature. The reaction mixture was extracted with EtOAc (2 x 5 mL), and the organic layer was separated and washed with water (10 mL) followed by brine solution (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by chromatography (75% EtOAc/hexanes) on silica gel to afford **8** (44 mg, 44%) as yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (t, *J* = 5.7 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 2H), 4.86 – 4.79 (m, 1H), 3.73 (s, 3H), 3.36 – 3.31 (m, 1H), 3.21 – 3.10 (m, 2H), 2.93 (dd, *J* = 14.0, 7.9 Hz, 1H), 2.58-2.53 (m, 1H), 2.52-2.48 (m, 1H), 2.19 – 2.08 (m, 4H), 1.99 (d, *J* = 18.8 Hz, 1H), 1.79 (d, *J* = 5.7 Hz, 1H), 1.76 (d, *J* = 6.7 Hz, 3H), 1.63-1.56 (m, 1H), 1.47-1.42 (m, 1H), 1.25 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 217.4 , 172.6, 172.5, 169.9, 155.5, 130.3, 127.6, 115.7, 64.9, 53.5, 52.4, 50.2, 43.8, 43.3, 38.0, 37.0, 33.3, 28.3, 27.7, 25.8, 21.0, 20.6; IR ($CHCl_3$): ν_{max} 2950, 2878, 1658, 1488, 1114, 932, 873, 756, 722, 679 cm^{-1}; HRMS (ESI): *m/z* calculated for $[M + H]^+$ $C_{24}H_{34}N_3O_5$ 444.2498, found 444.2500.

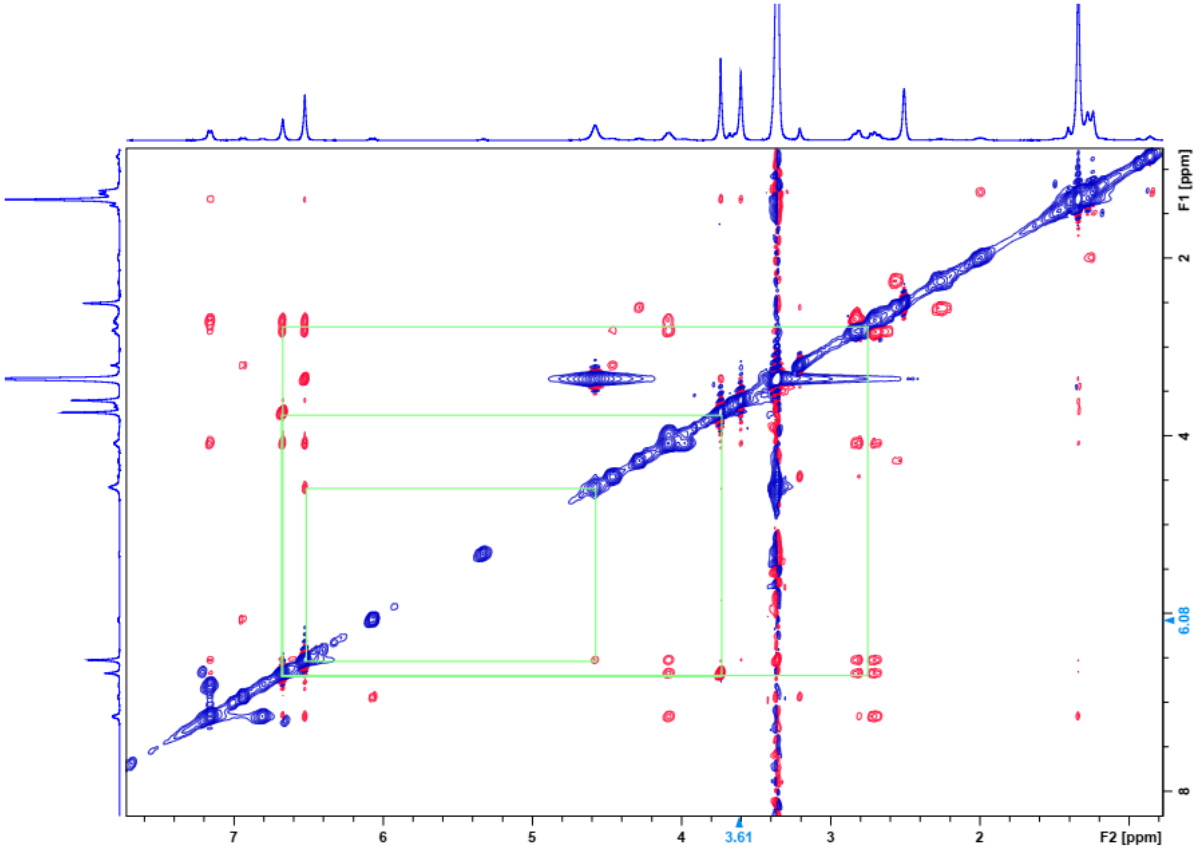
3. NOESY NMR Spectra of Compounds 2a, 4c and 5

NOESY NMR Spectrum of Compound 2a

The presence of nOe correlation between H3/OCH3 and H3/benzylic protons & H6/aryl NH2 and H5/benzylic protons confirms the structure of the regioisomer **2a**.

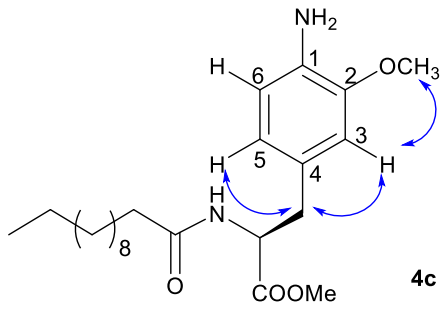


2a

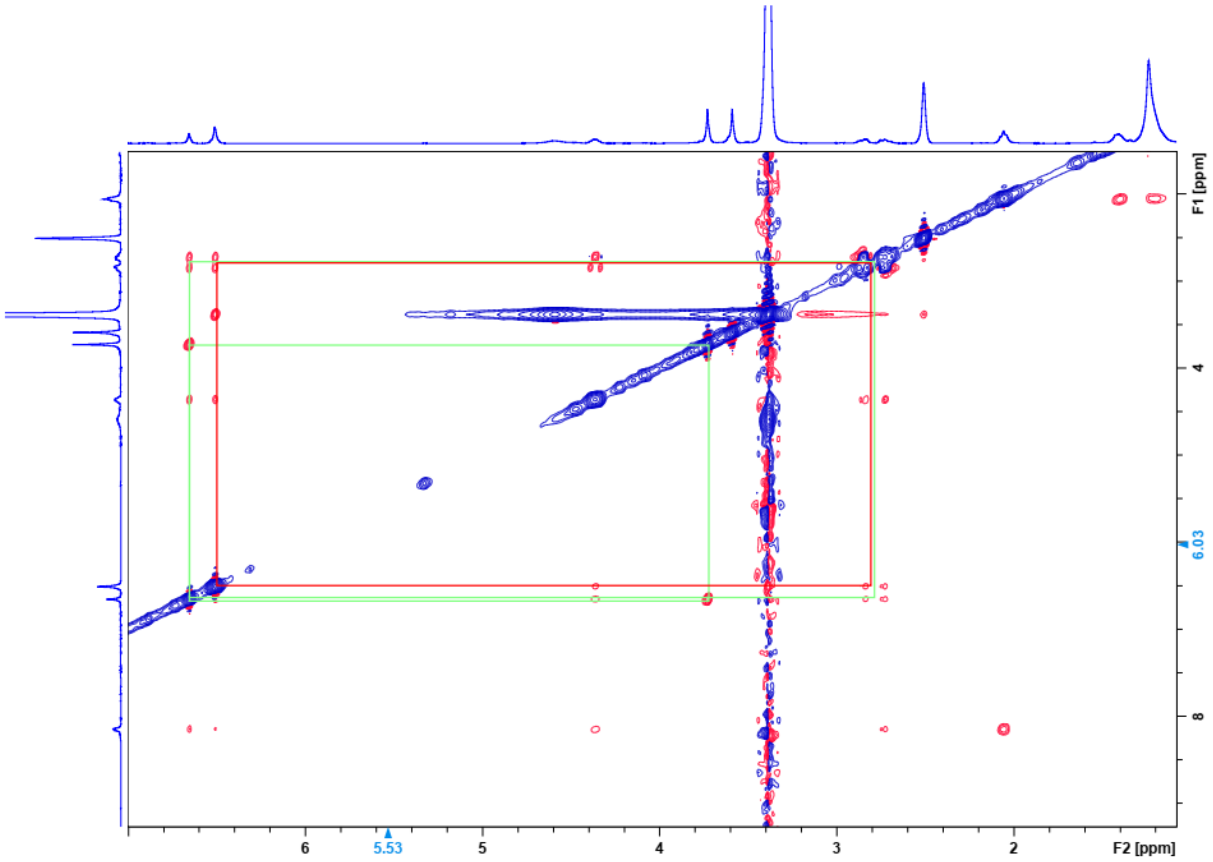


NOESY NMR Spectrum of Compound 4c

The presence of nOe correlation between H3/OCH3 and H3/benzylic protons & H5/benzylic protons confirms the structure of the regioisomer **4c**.

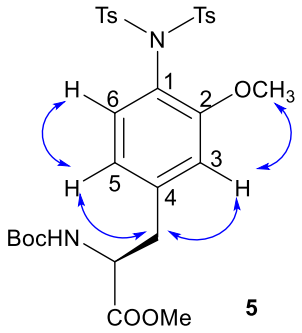


4c

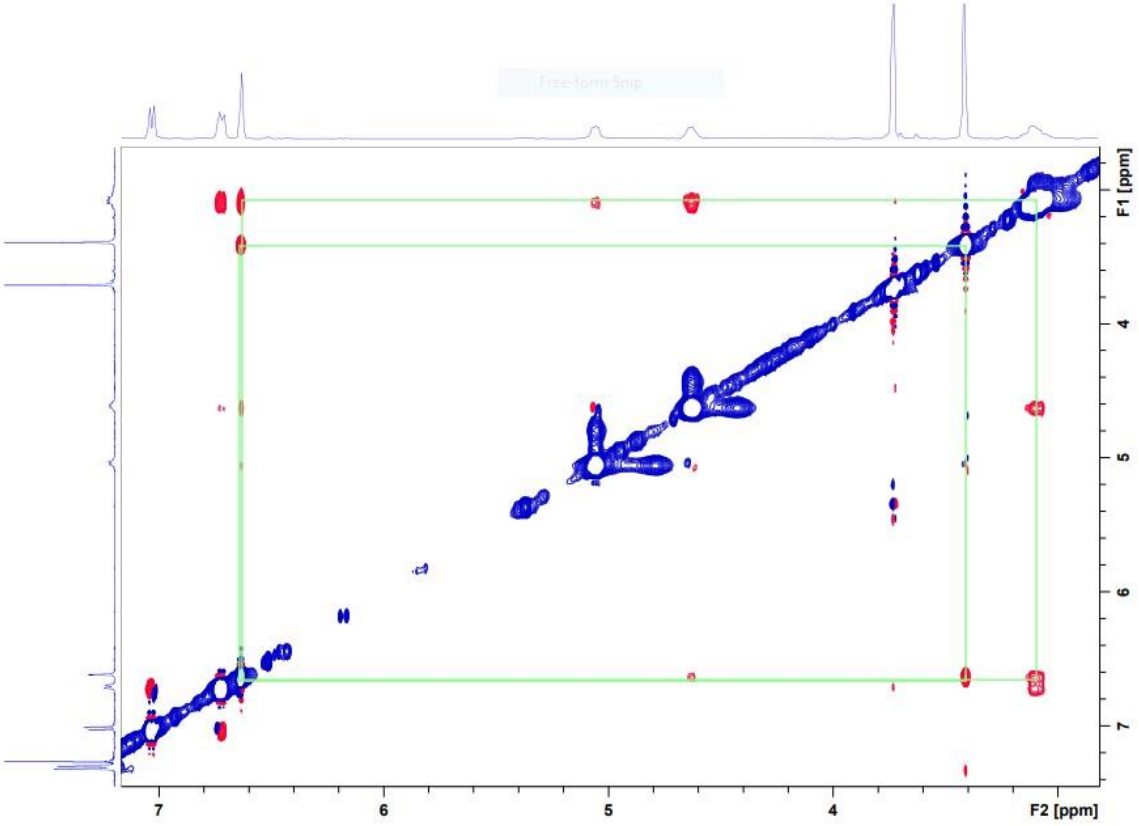


NOESY NMR Spectrum of Ditosyl Derivative 5

The presence of nOe correlation between H3/OCH3 and H3/benzylic protons & H5/H6 and H5/benzylic protons confirms the structure of the regioisomer **5**.



5



4. Morphological Studies

Microscopic Analysis: Scanning electron microscopy (SEM) measurements on powder samples of **3i** and **4i** were taken directly on copper substrate and performed using FESEM (JEOL 7610F FESEM equipped with an OXFORD EDAX detector). Transmission electron microscopy (TEM) was carried out using FEI Talos 200KV. For TEM measurements, samples were prepared in cyclohexane and drop-casted the suspension on carbon coated copper grids (200 mesh) directly at 25 °C.

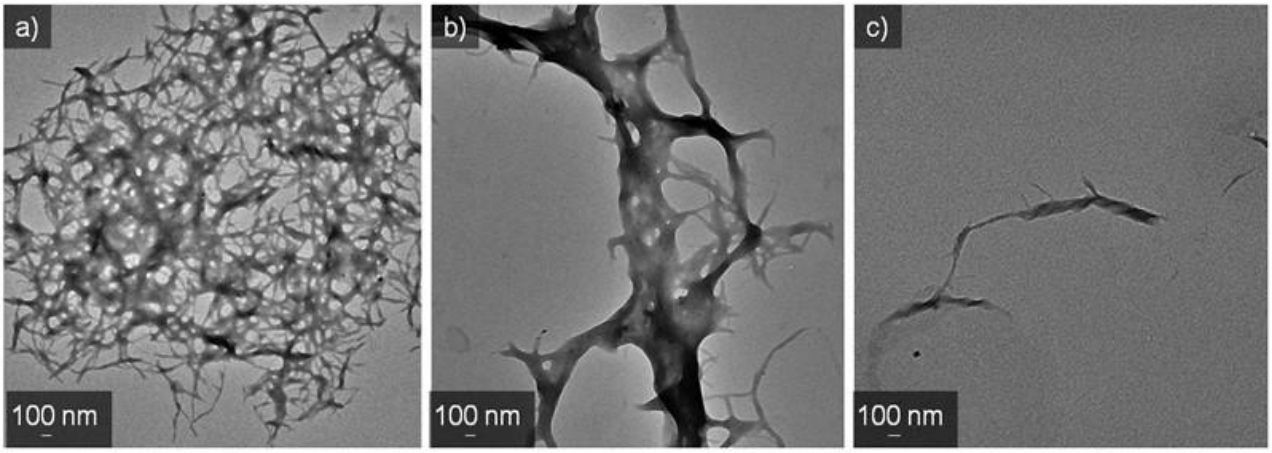


Figure S1. a-c) Transmission electron microscopic (TEM) images of **3i** from cyclohexane drop-casted on carbon coated copper grid. (c) High resolution image has seen clearly the twisted nanofibers.

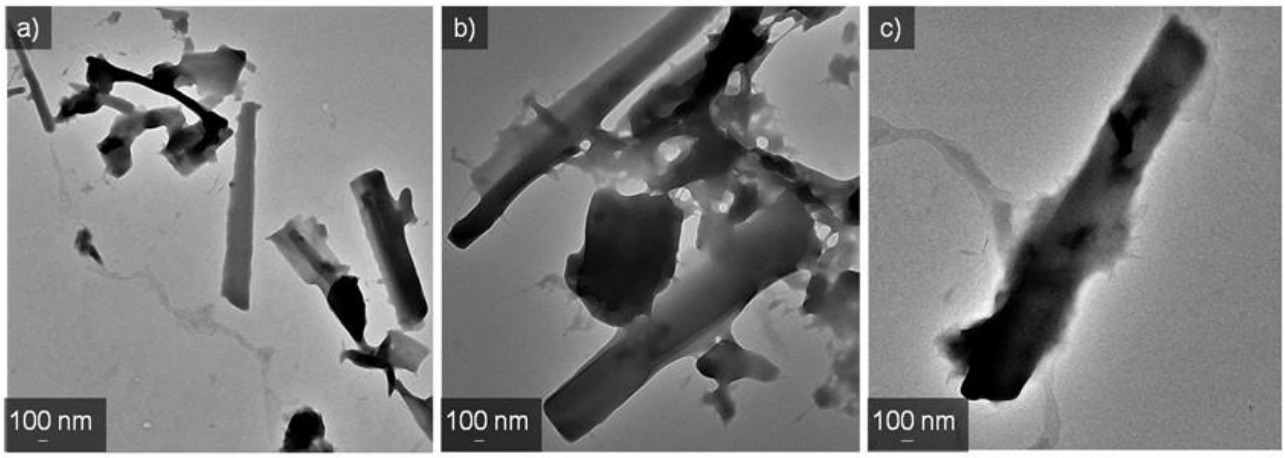
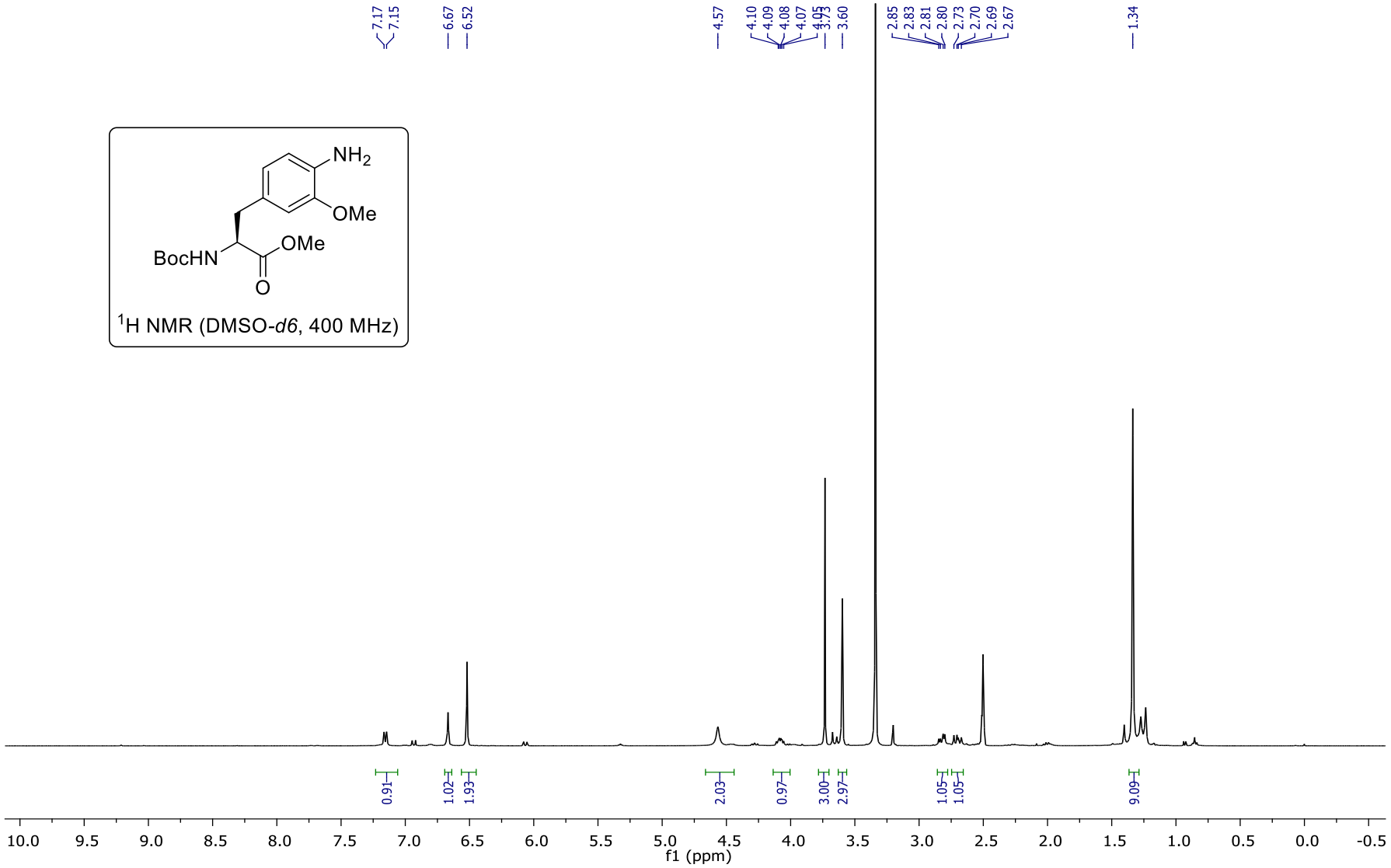


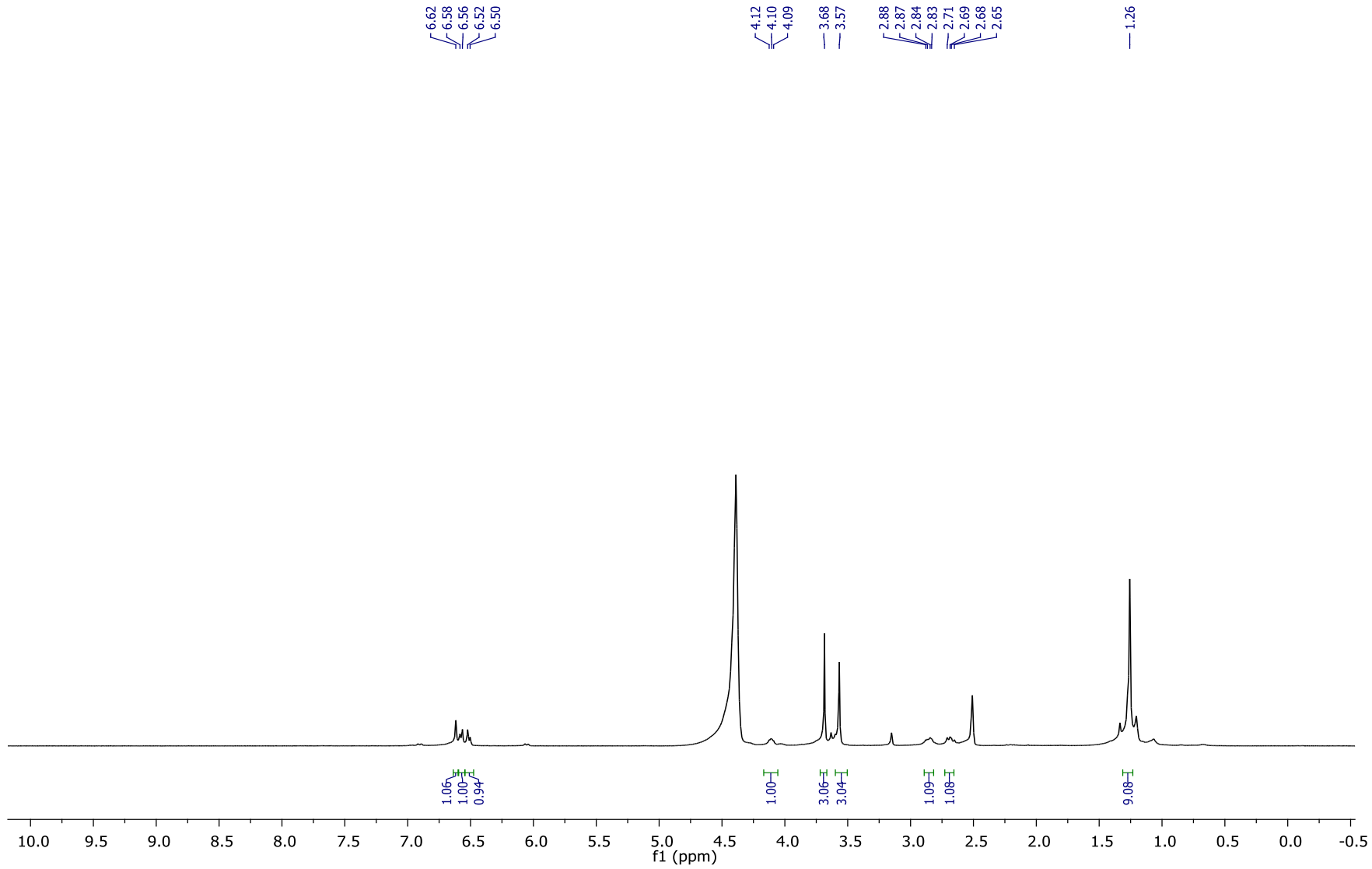
Figure S2. a-c) Transmission electron microscopic (TEM) images of **4i** from cyclohexane drop-casted on carbon coated copper grid.

5. ^{1}H NMR and ^{13}C NMR Spectra of Compounds

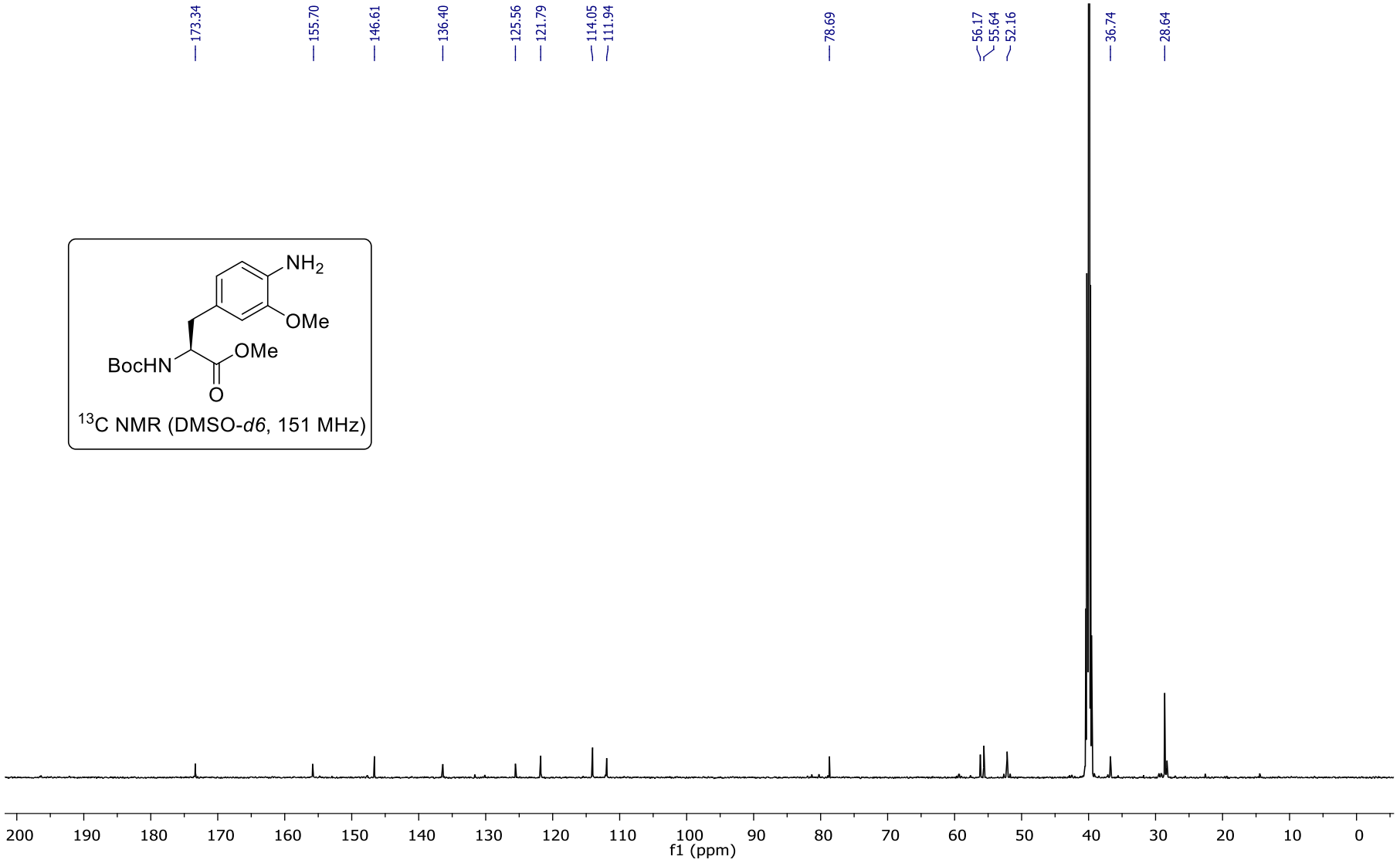
Methyl-(*S*)-3-(4-amino-3-methoxyphenyl)-2-((*tert*-butoxycarbonyl)amino)propanoate (2a)



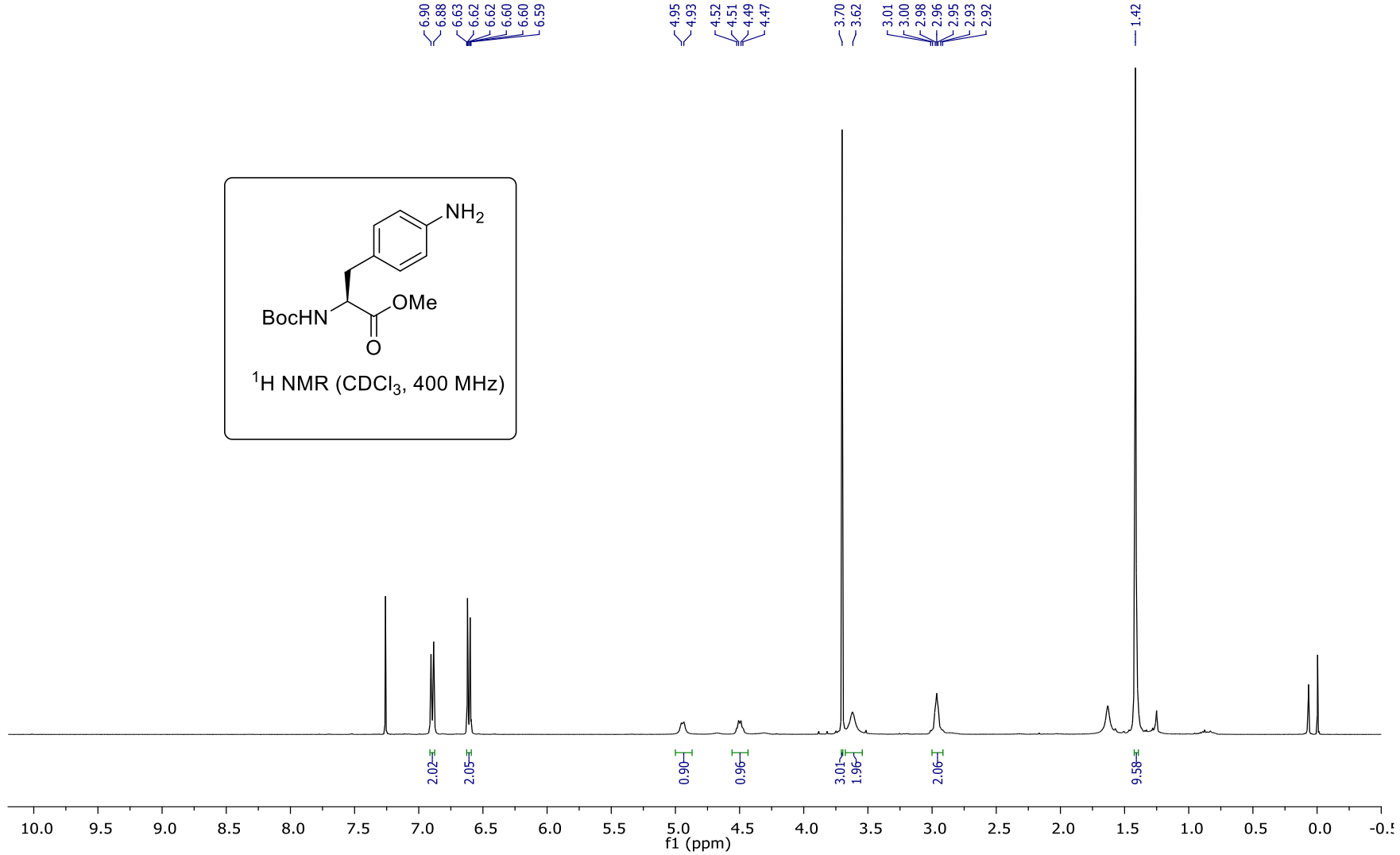
D_2O Exchange NMR Spectrum of Compound 2a



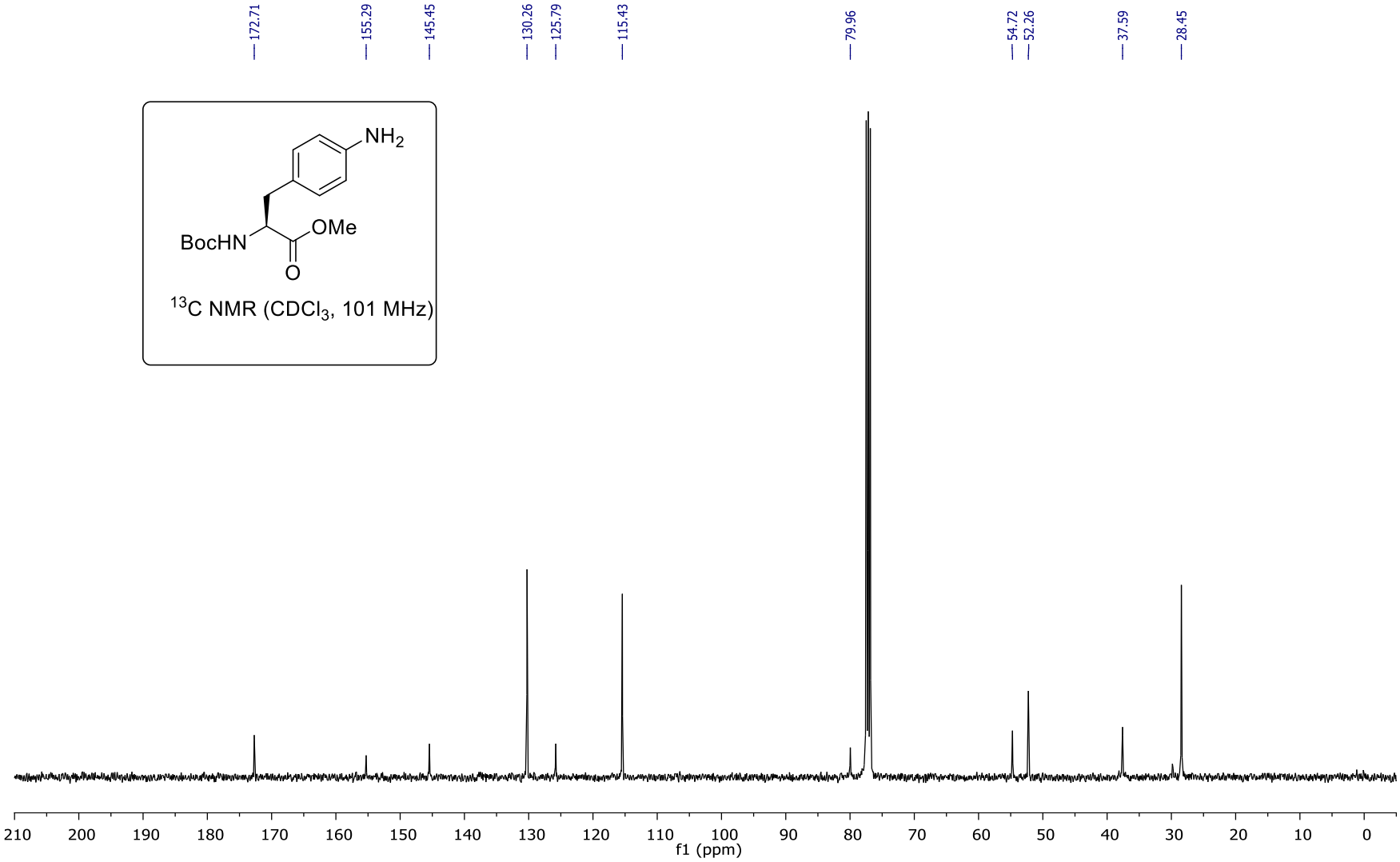
Methyl-(*S*)-3-(4-amino-3-methoxyphenyl)-2-((*tert*-butoxycarbonyl)amino)propanoate (2a)



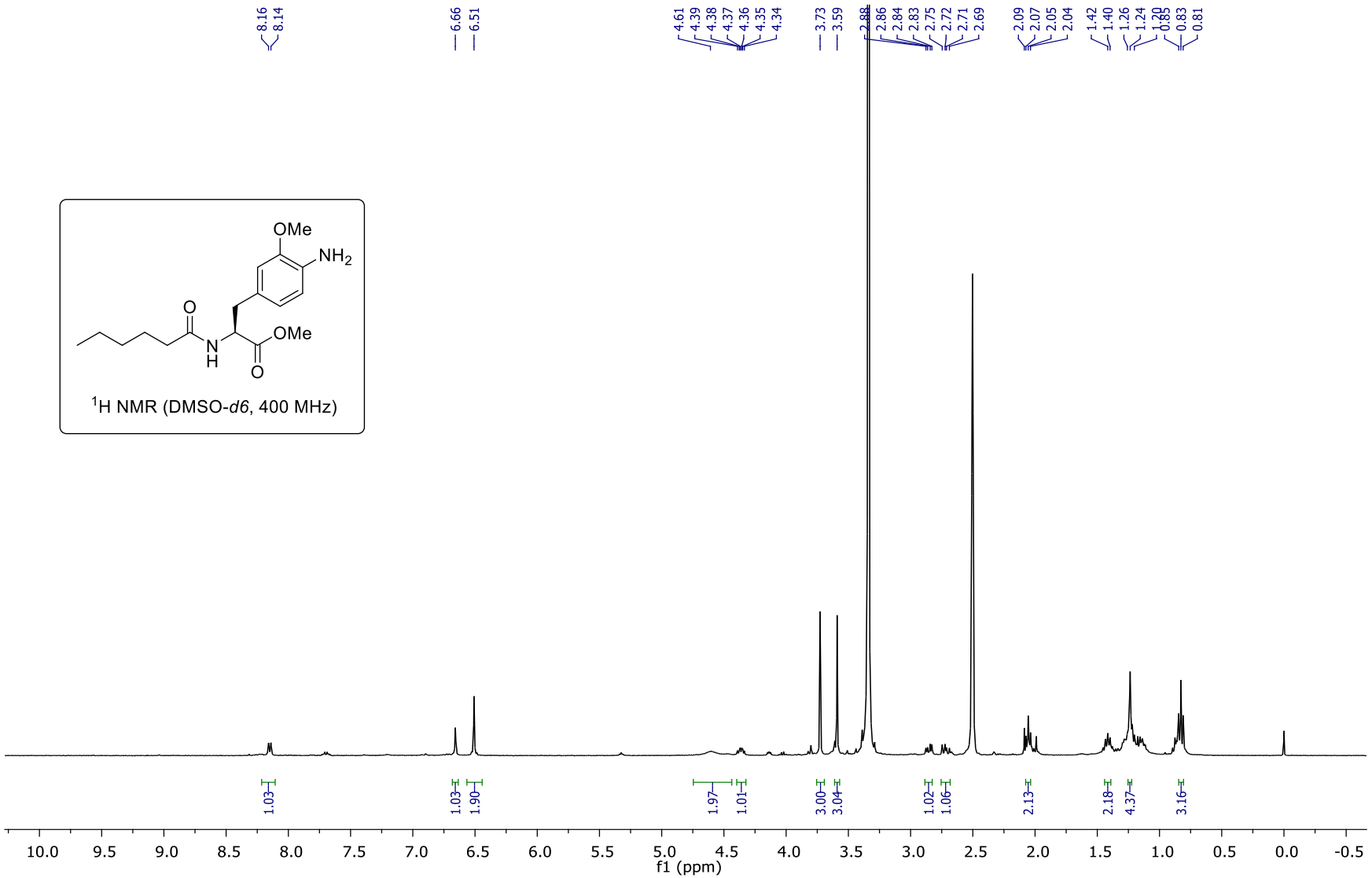
Methyl (*tert*-butoxycarbonyl)-L-tyrosine (2a′)



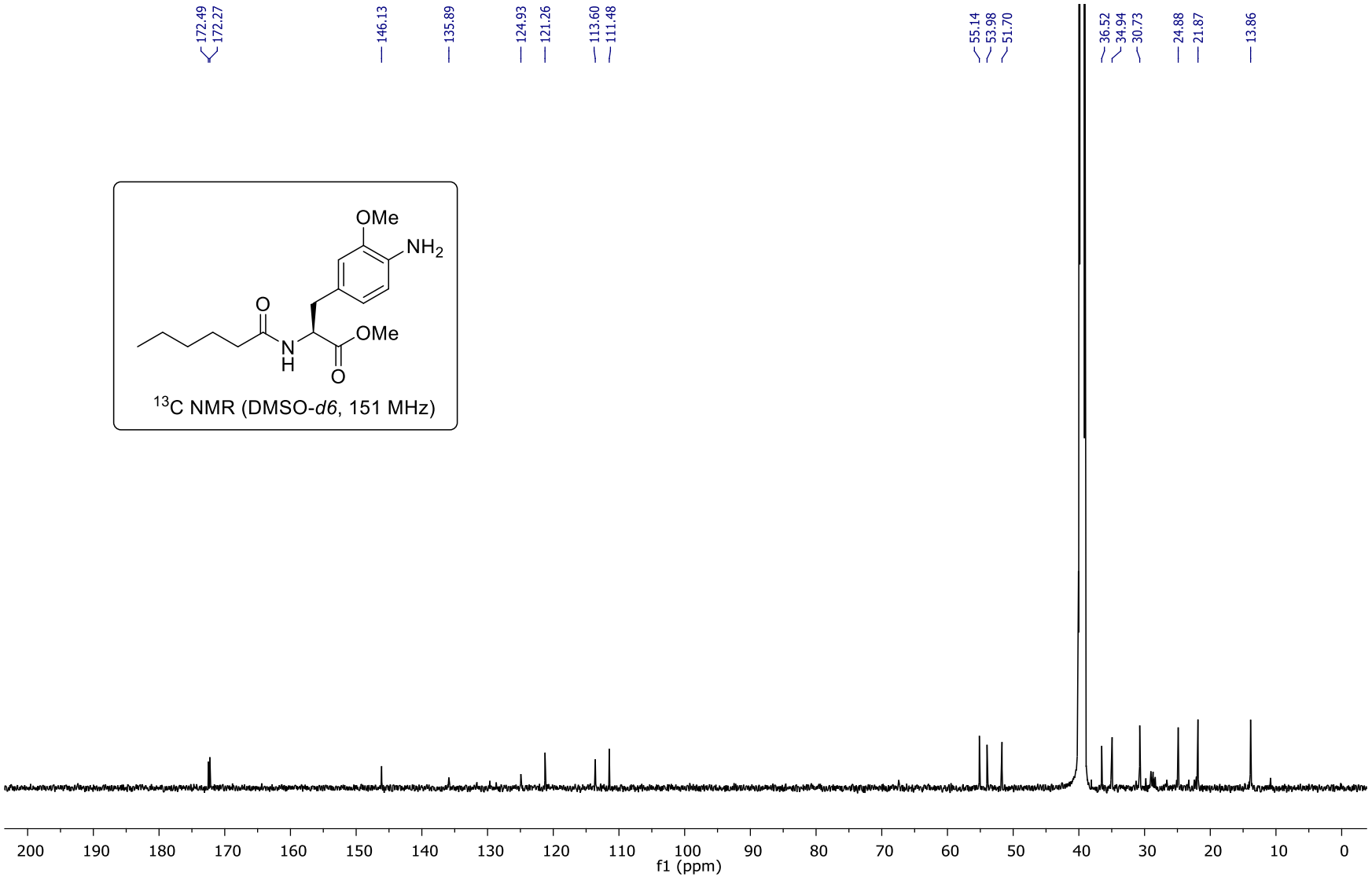
Methyl (*tert*-butoxycarbonyl)-L-tyrosine (2a′)



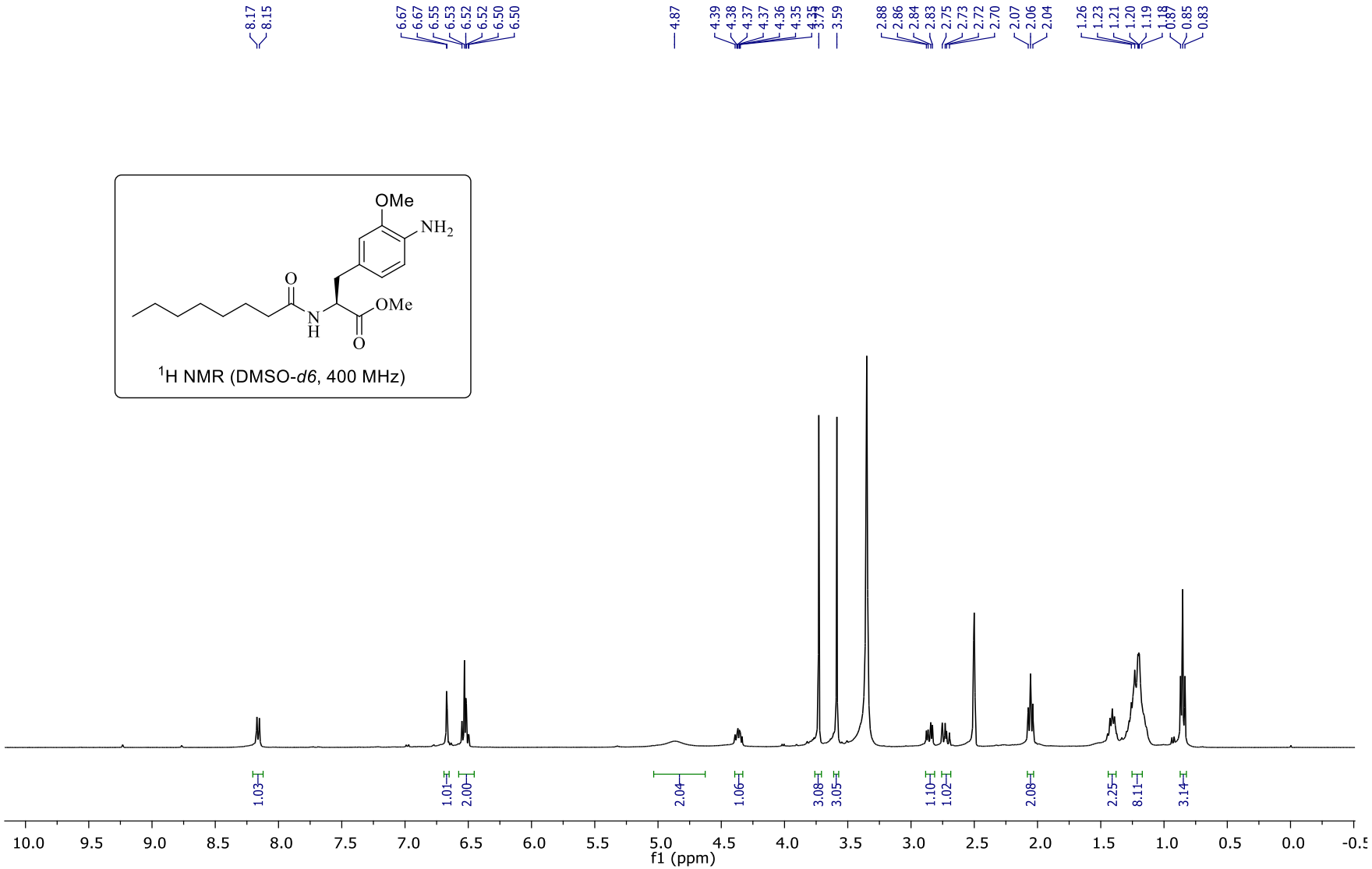
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-hexanamidopropanoate (4a)



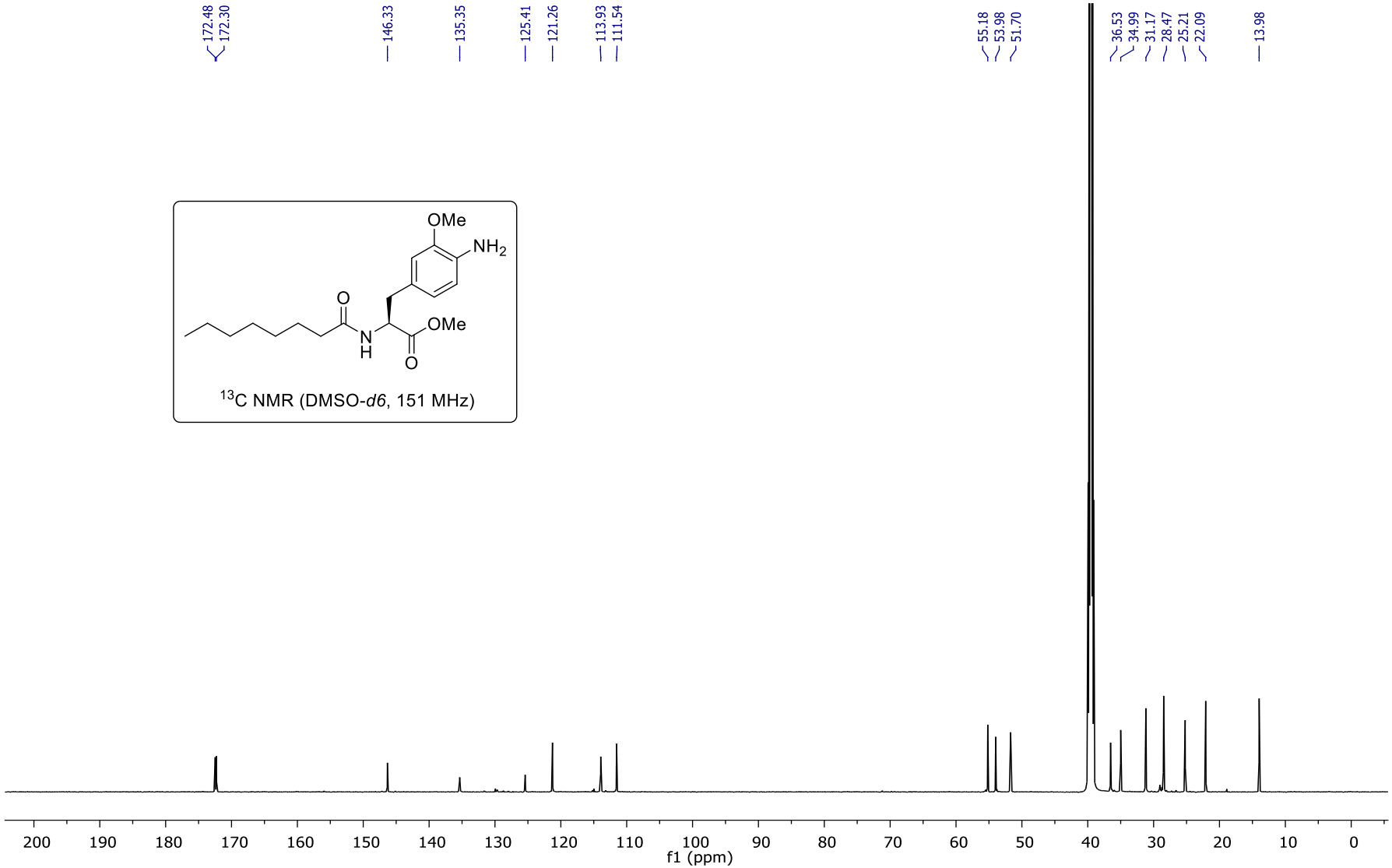
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-hexanamidopropanoate (4a)



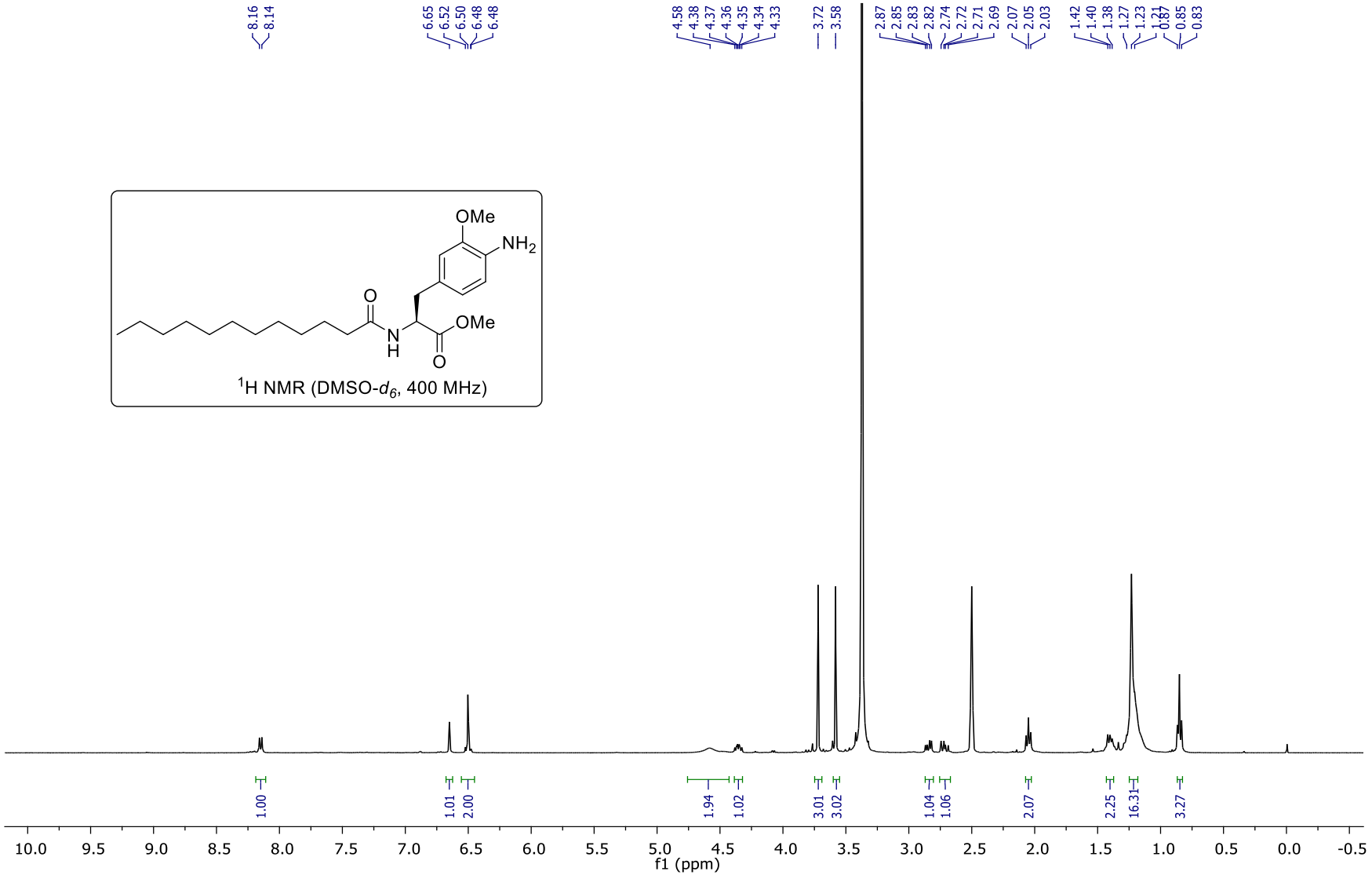
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-octanamidopropanoate (4b)



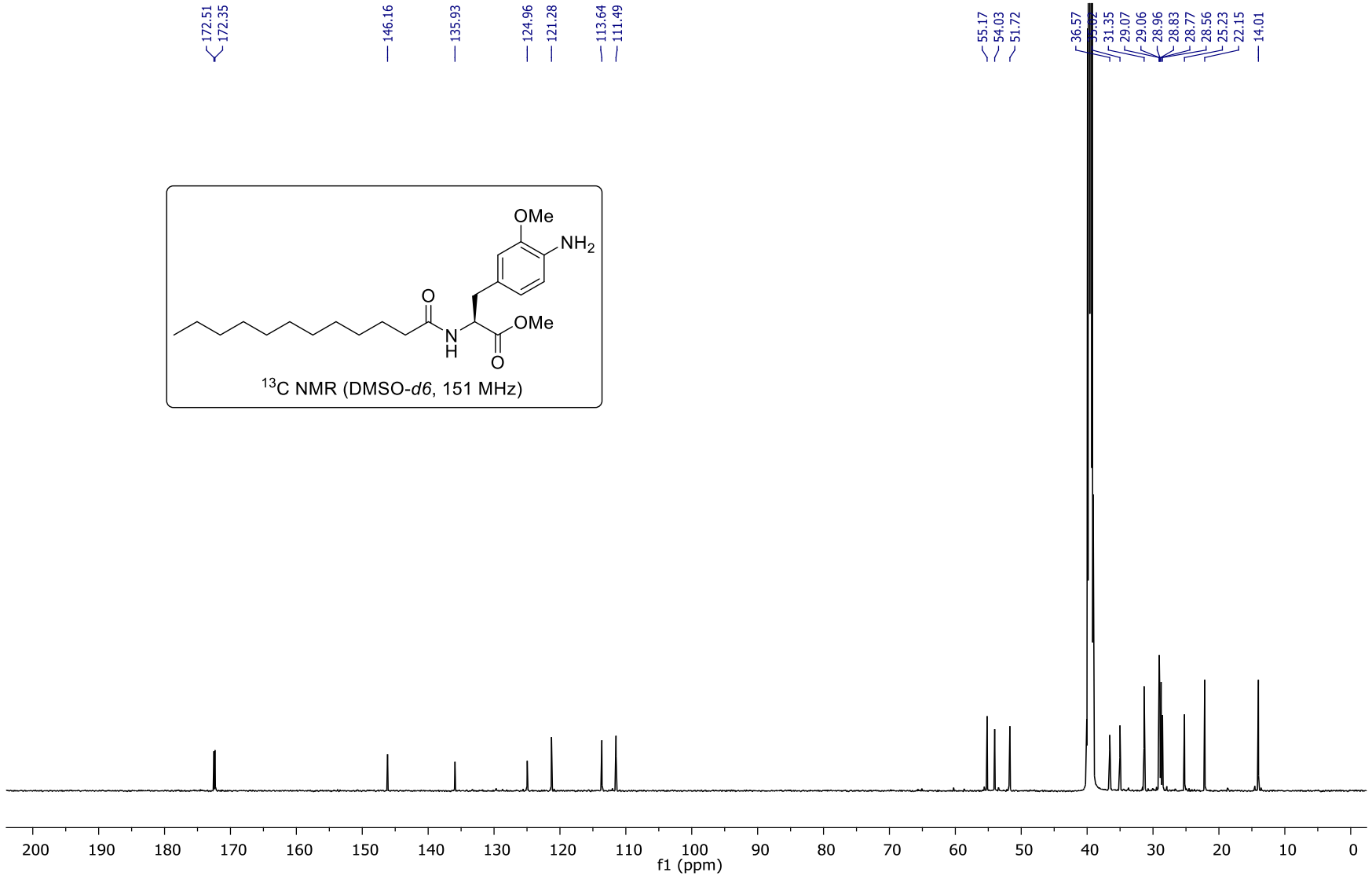
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-octanamidopropanoate (4b)



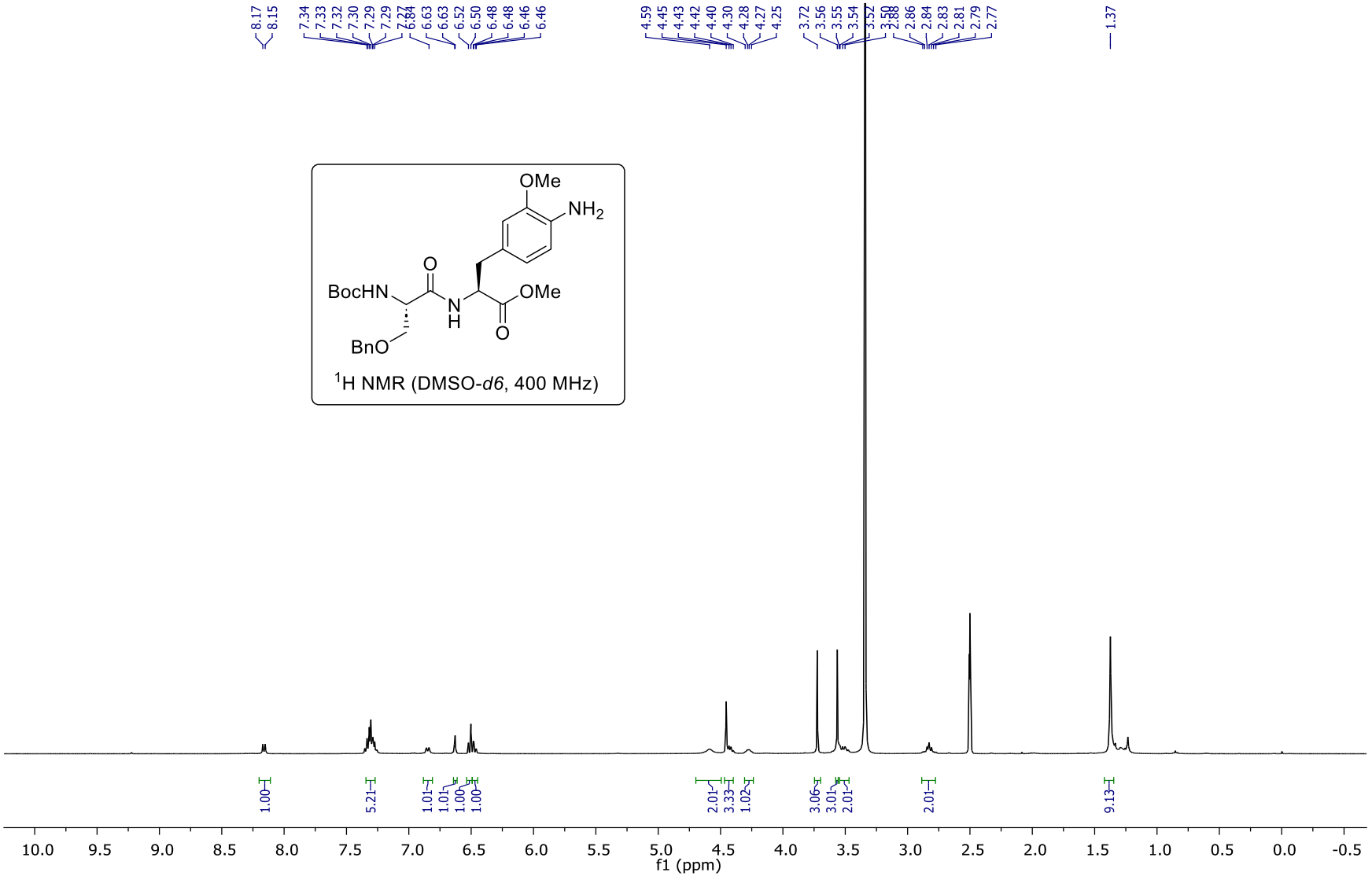
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-dodecanamidopropanoate (4c)



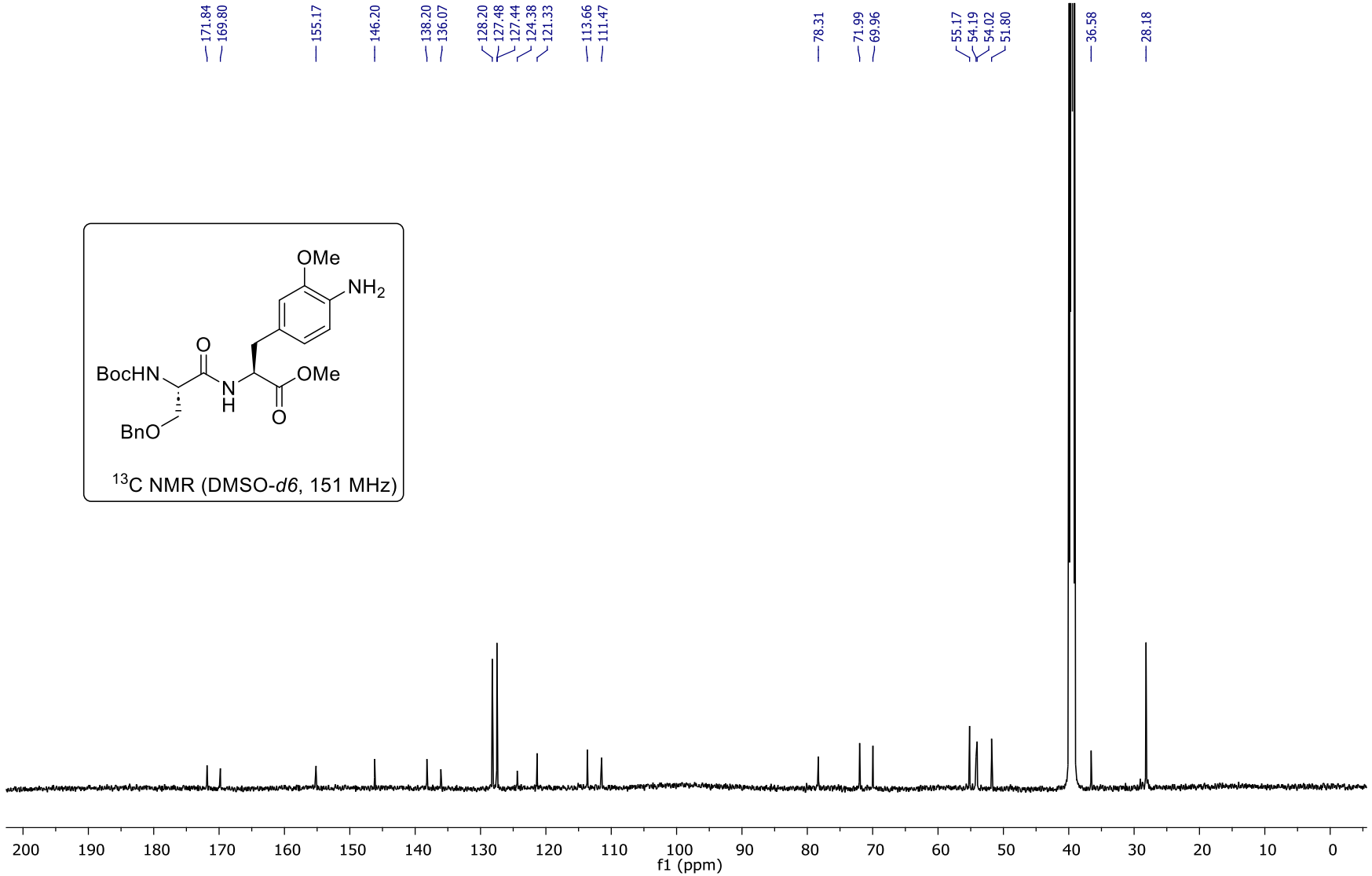
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-dodecanamidopropanoate (4c)



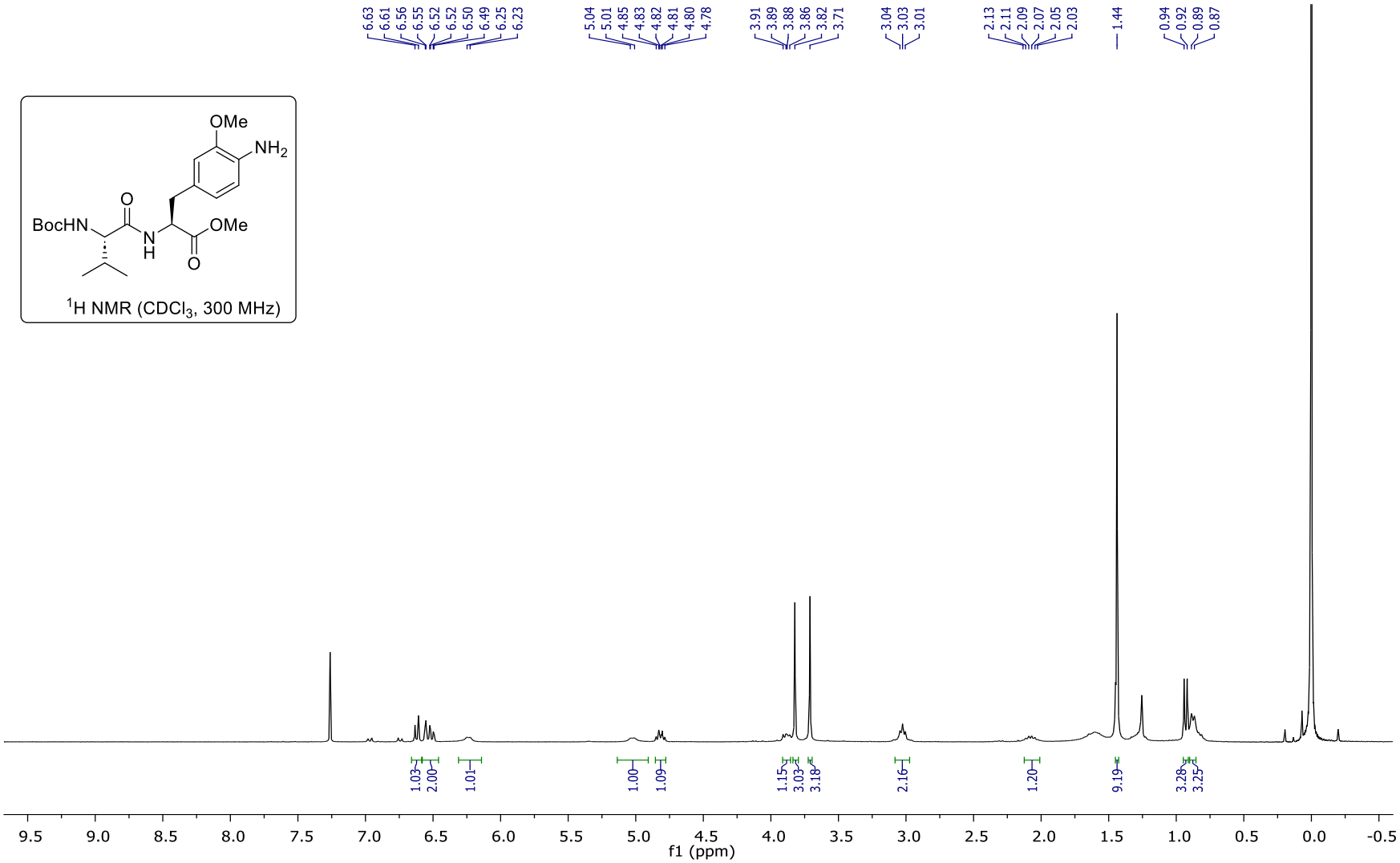
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-((S)-3-(benzyloxy)-2-((*tert*-butoxycarbonyl)amino)propanamido)propanoate (4d)



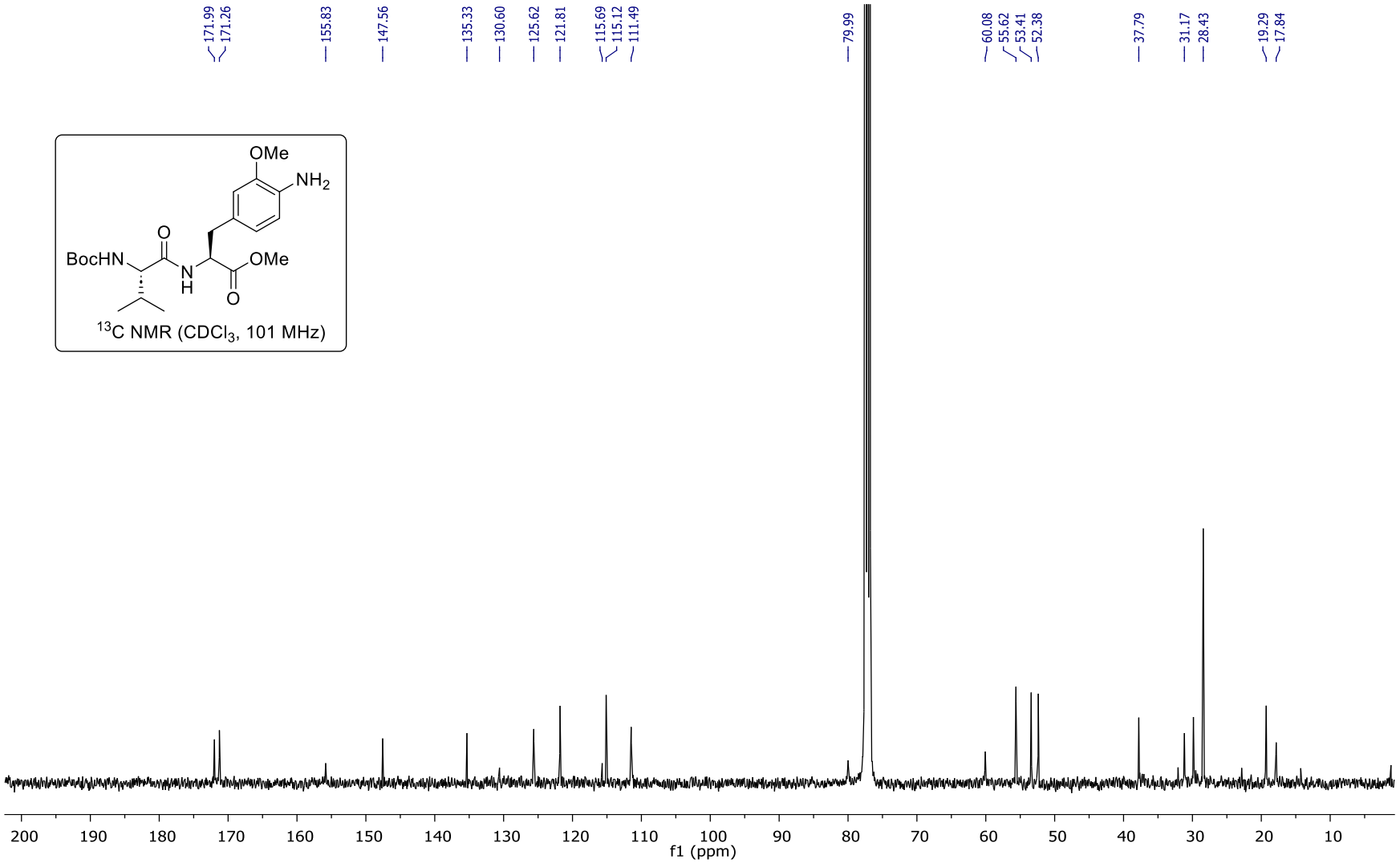
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-((*S*)-3-(benzyloxy)-2-((*tert*-butoxycarbonyl)amino)propanamido)propanoate (4d)



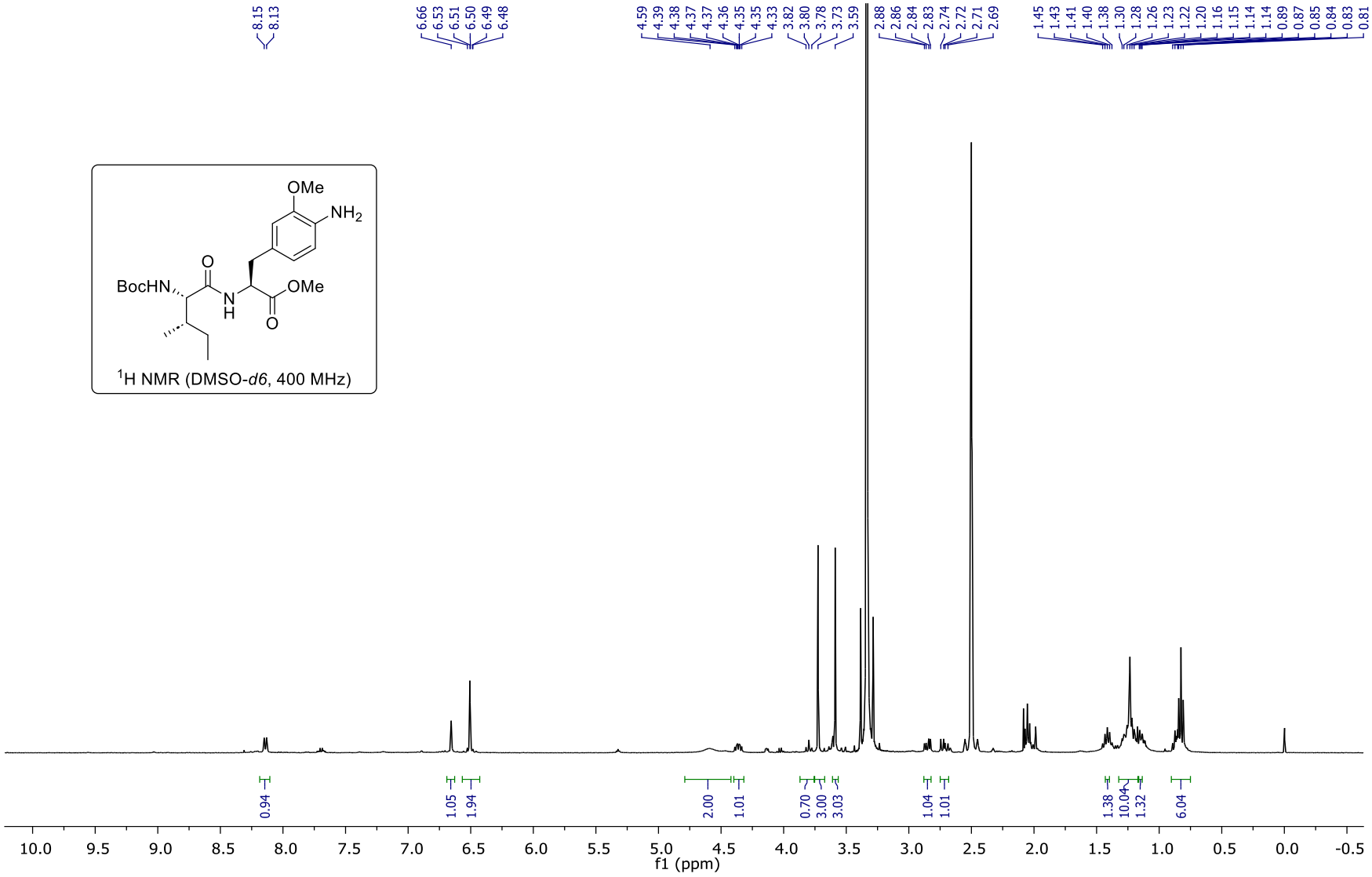
Methyl-(*S*)-3-(4-amino-2-methoxyphenyl)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methylbutanamido)propanoate (4e)



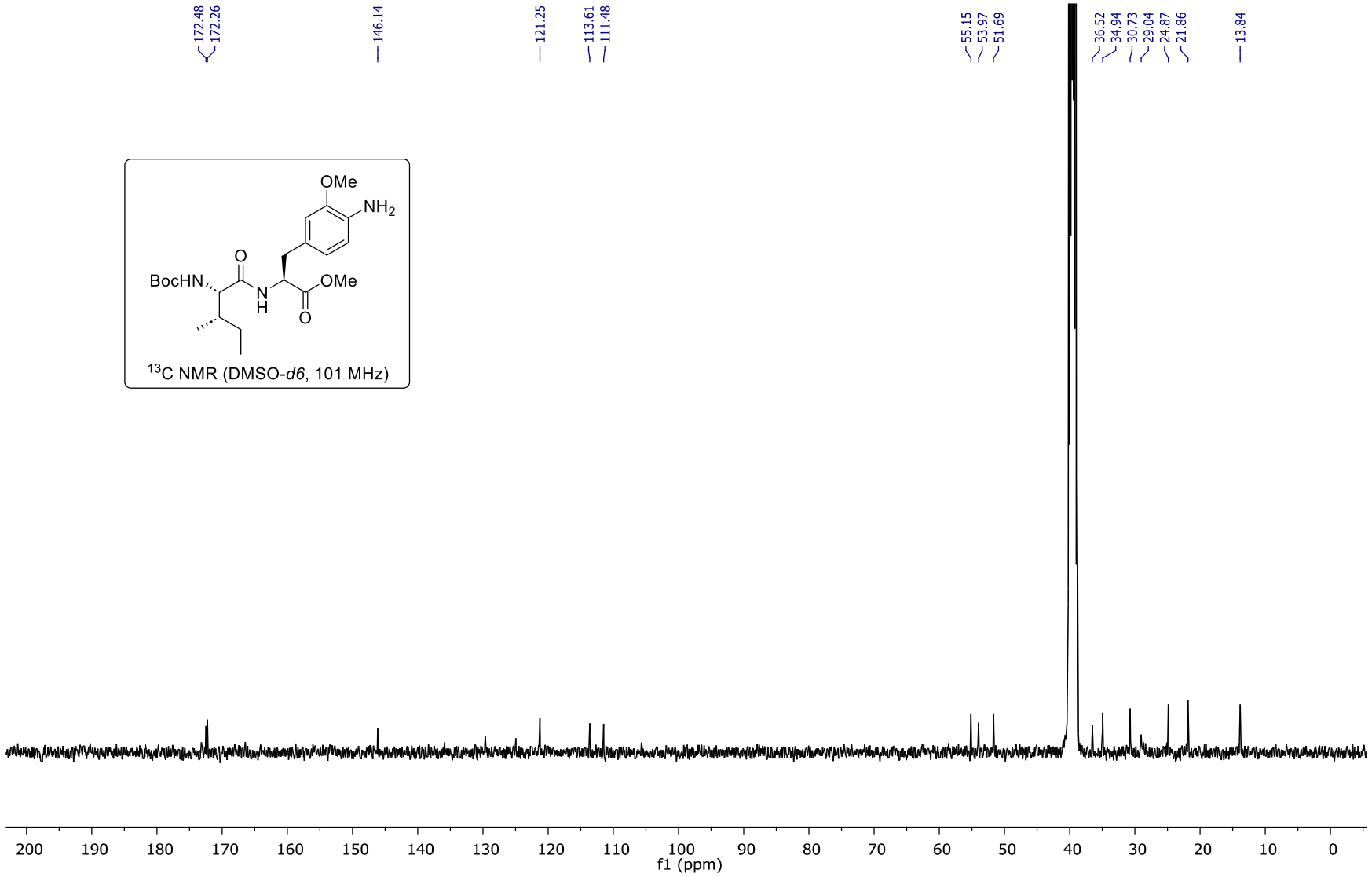
Methyl-(*S*)-3-(4-amino-2-methoxyphenyl)-2-((*S*)-2-((*tert*-butoxyc arbonyl)amino)-3-methylbutanamido)propanoate (4e)



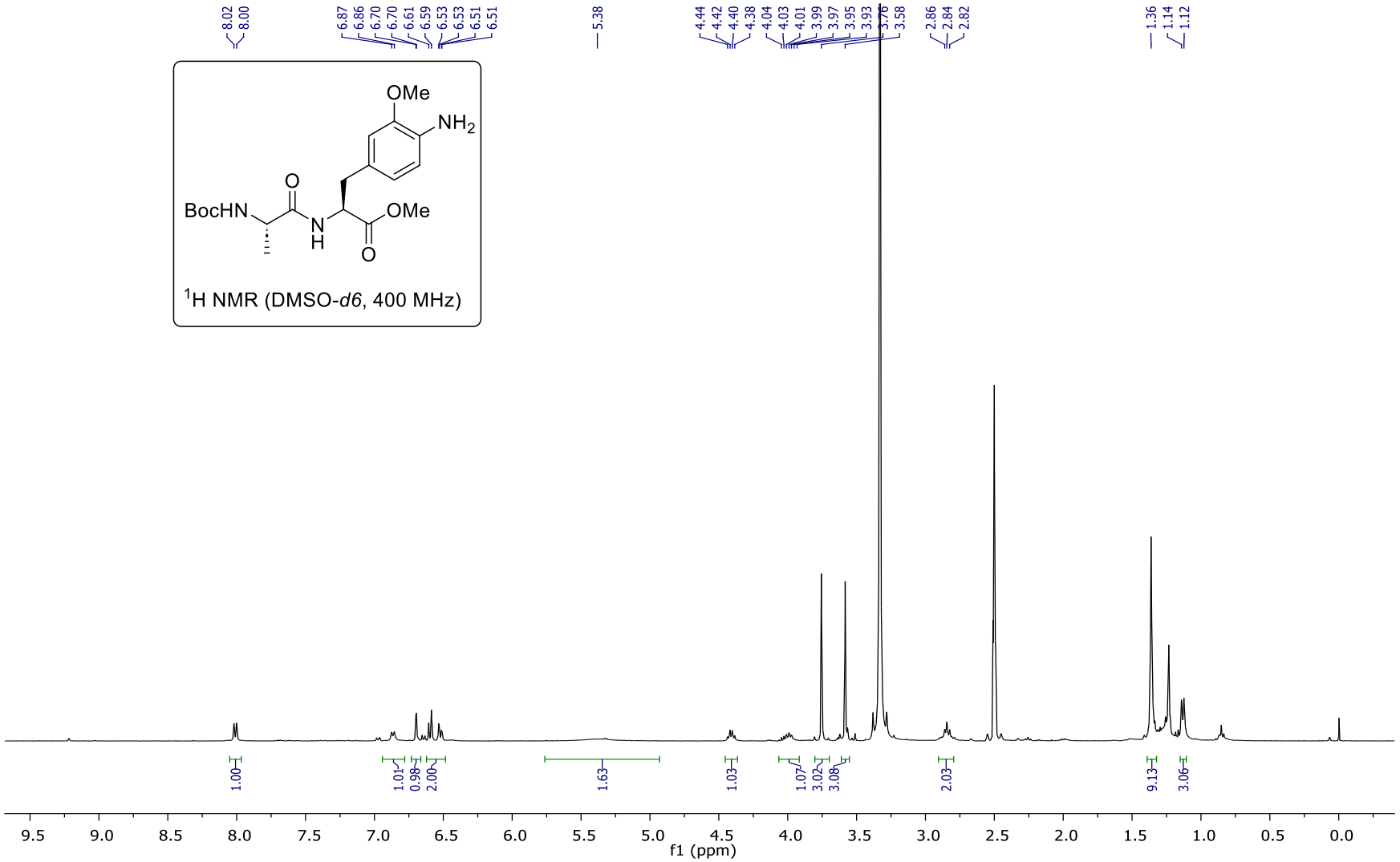
Methyl-(*S*)-3-(4-amino-2-methoxyphenyl)-2-((2*S*,3*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methylpentanamido)propanoate (4f)



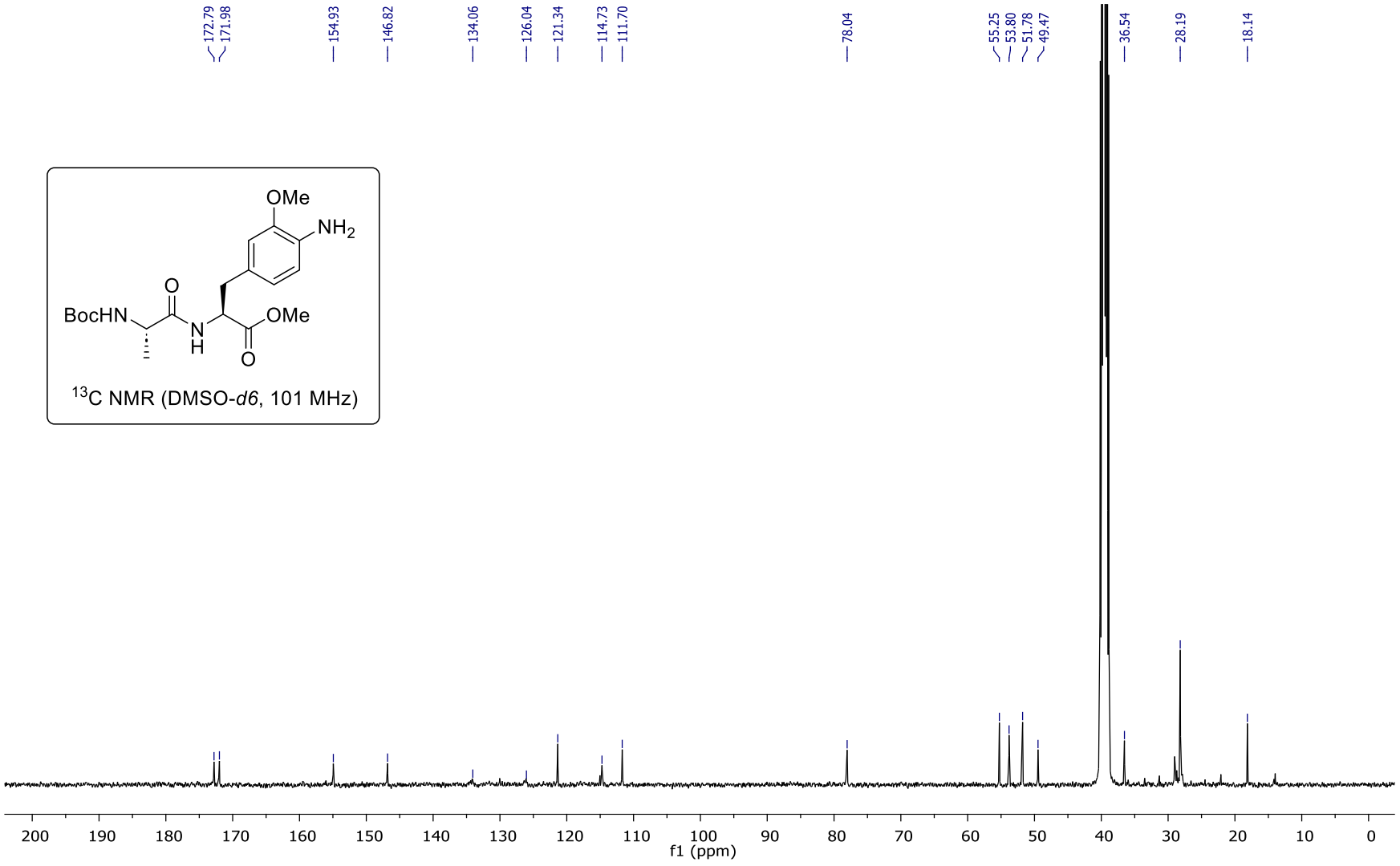
Methyl-(*S*)-3-(4-amino-2-methoxyphenyl)-2-((2*S*,3*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methylpentanamido)propanoate (4f)



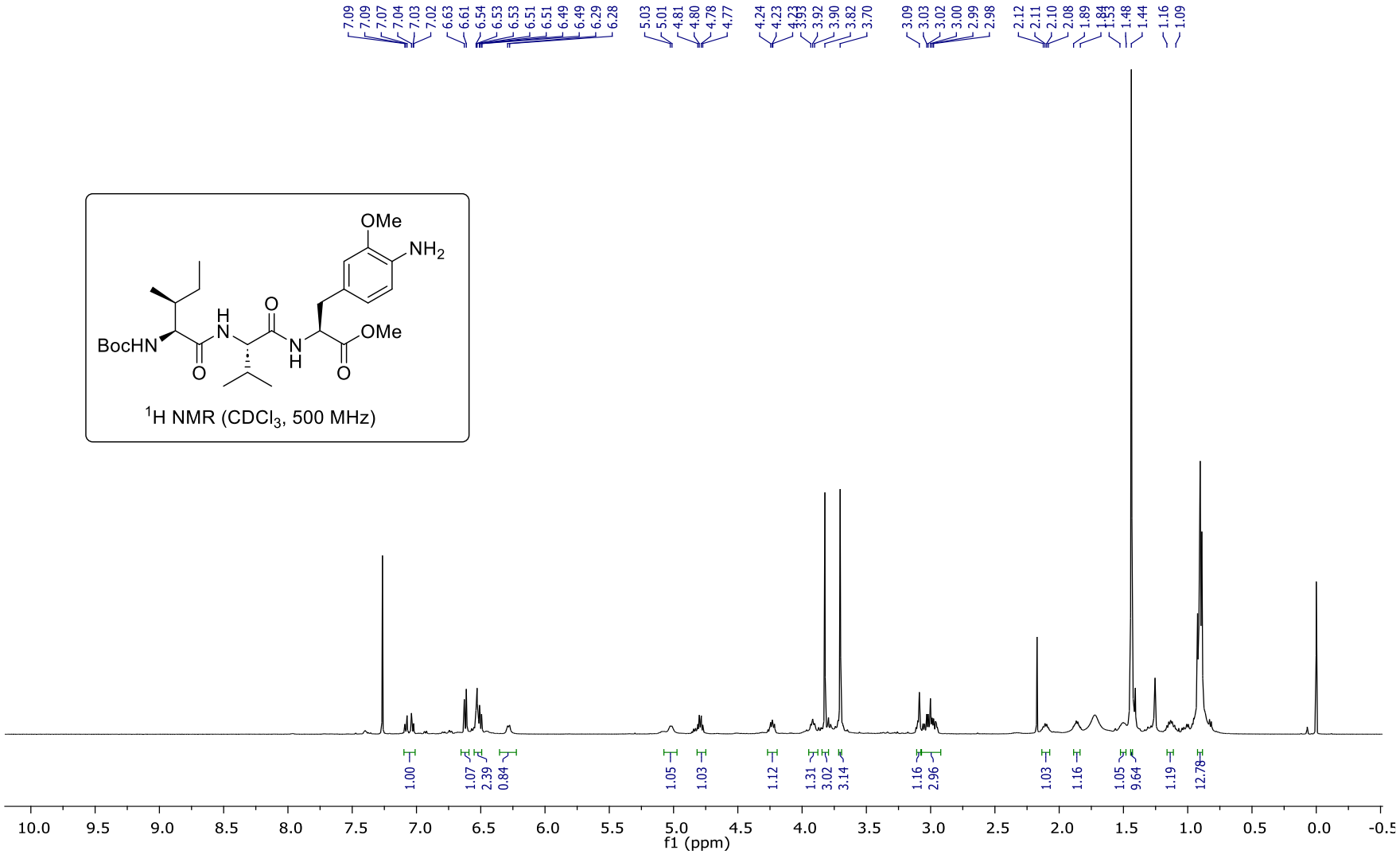
Methyl-(*S*)-3-(4-amino-3-methoxyphenyl)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino) propanamido)propanoate (4g)



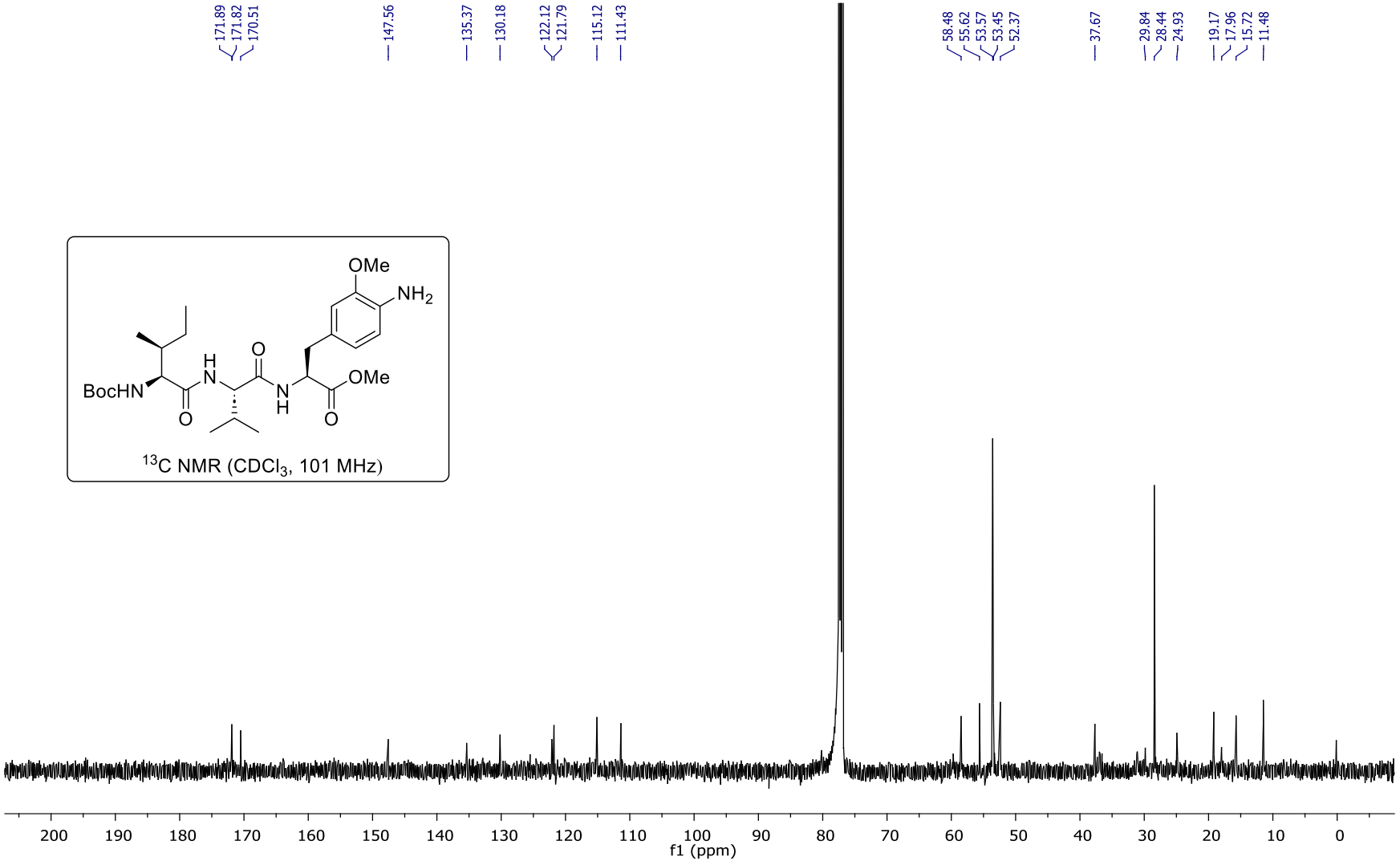
Methyl-(*S*)-3-(4-amino-3-methoxyphenyl)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino) propanamido)propanoate (4g)



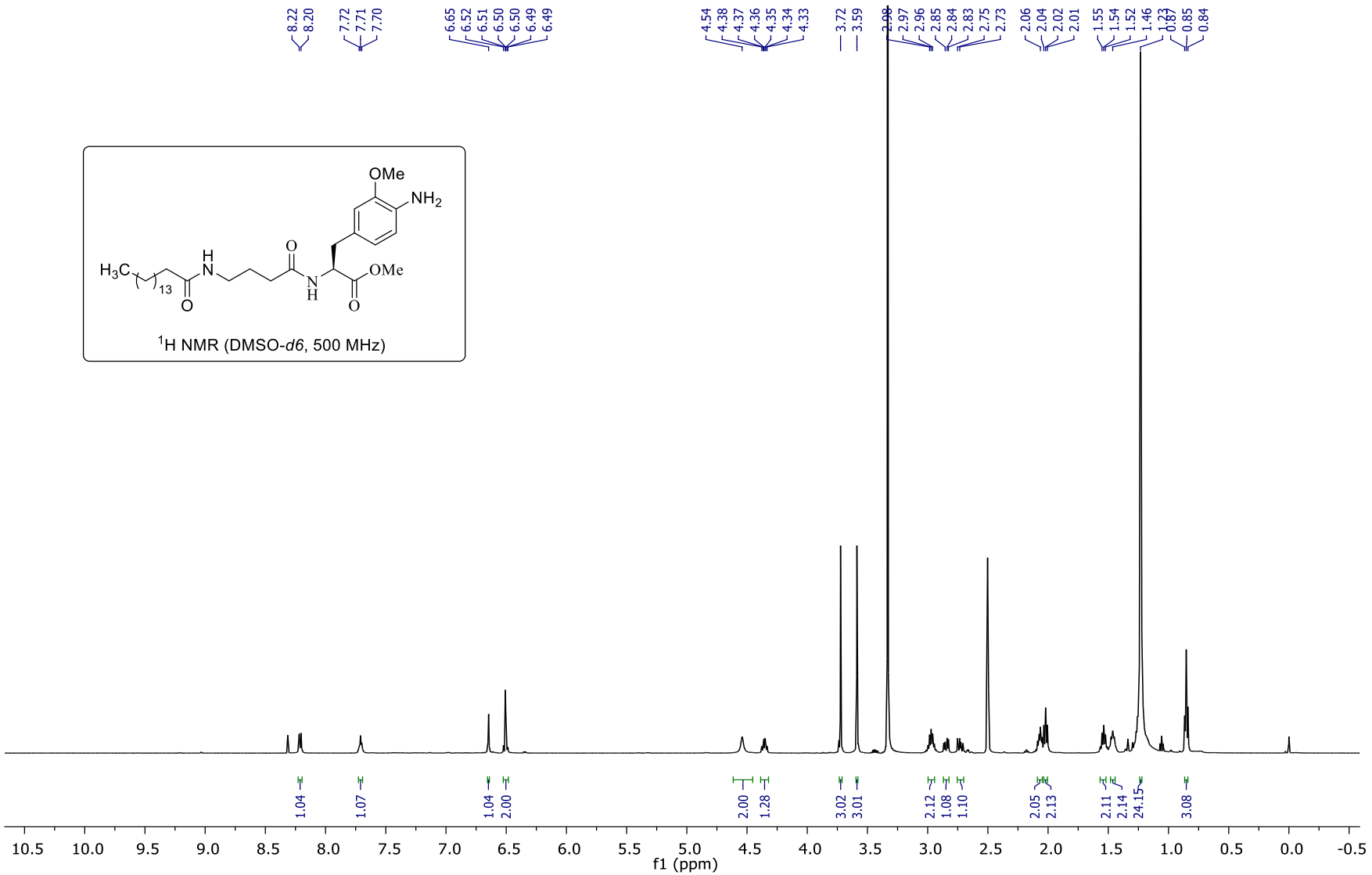
Methyl-(6*S*,9*S*,12*S*)-12-(4-amino-3-methoxybenzyl)-6-((*S*)-sec-butyl)-9-isopropyl-2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (4h)



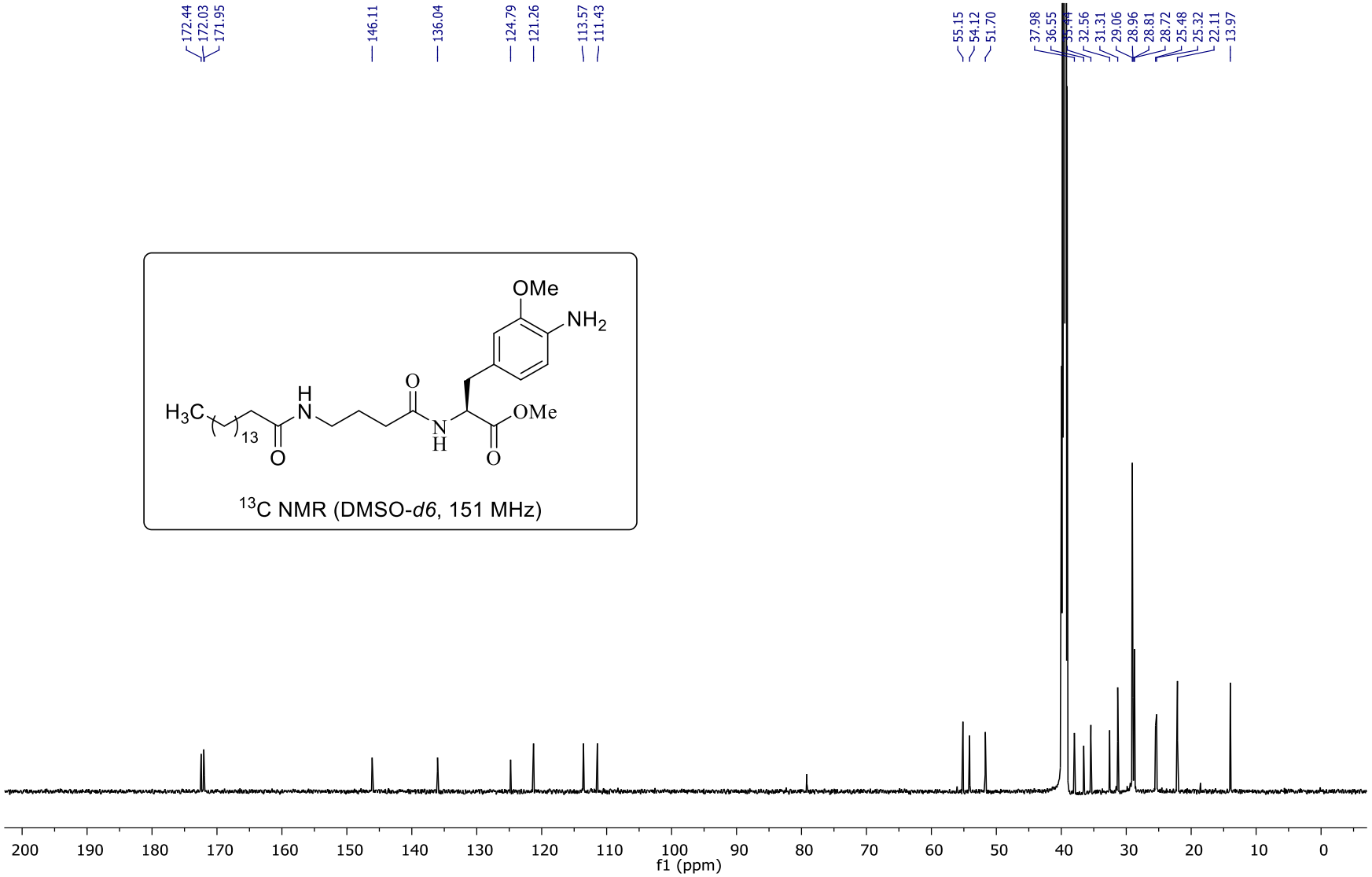
Methyl-(6*S*,9*S*,12*S*)-12-(4-amino-3-methoxybenzyl)-6-((*S*)-sec-butyl)-9-isopropyl-2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (4h)



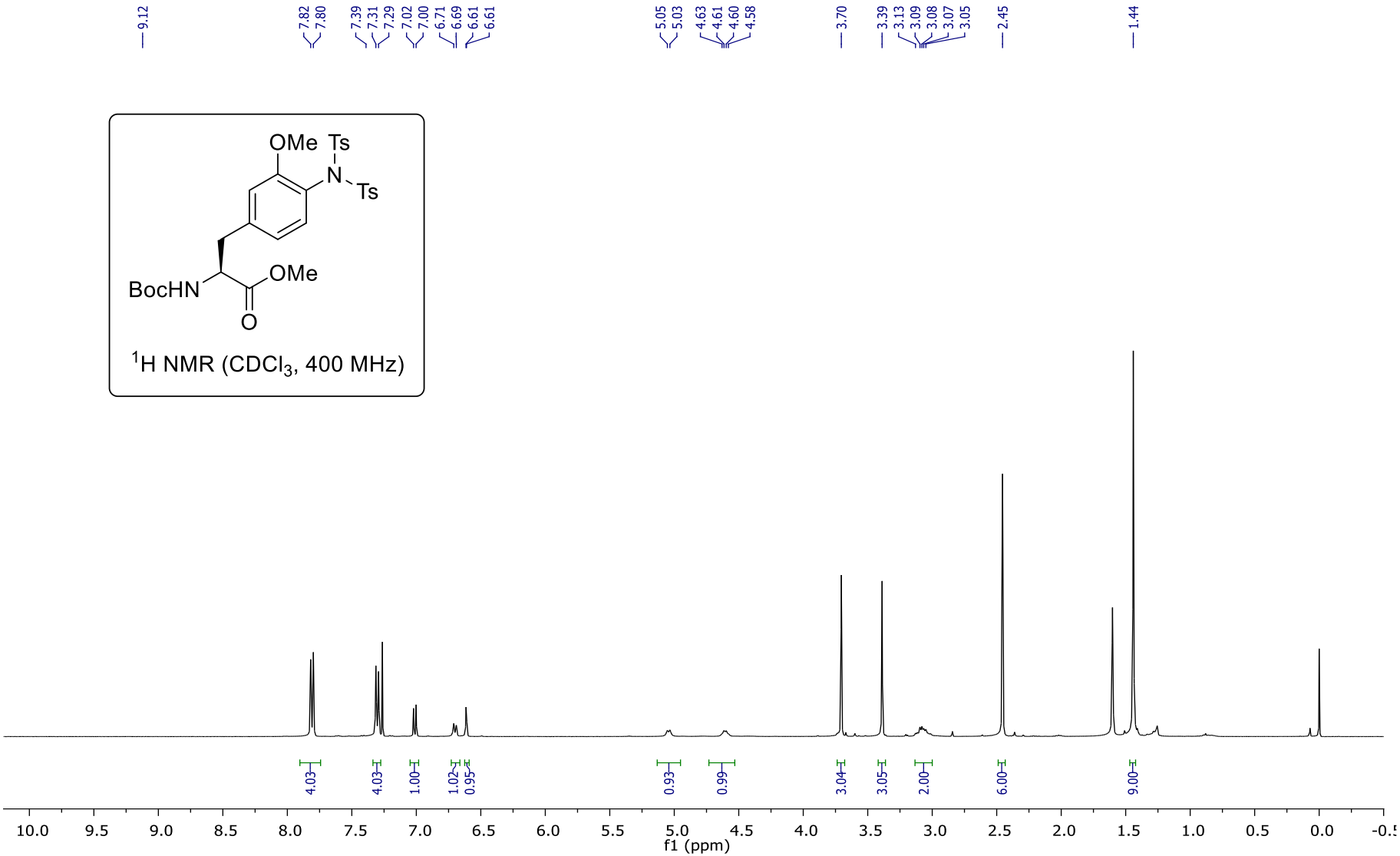
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-(4-palmitamidobutanamido)propanoate (4i)



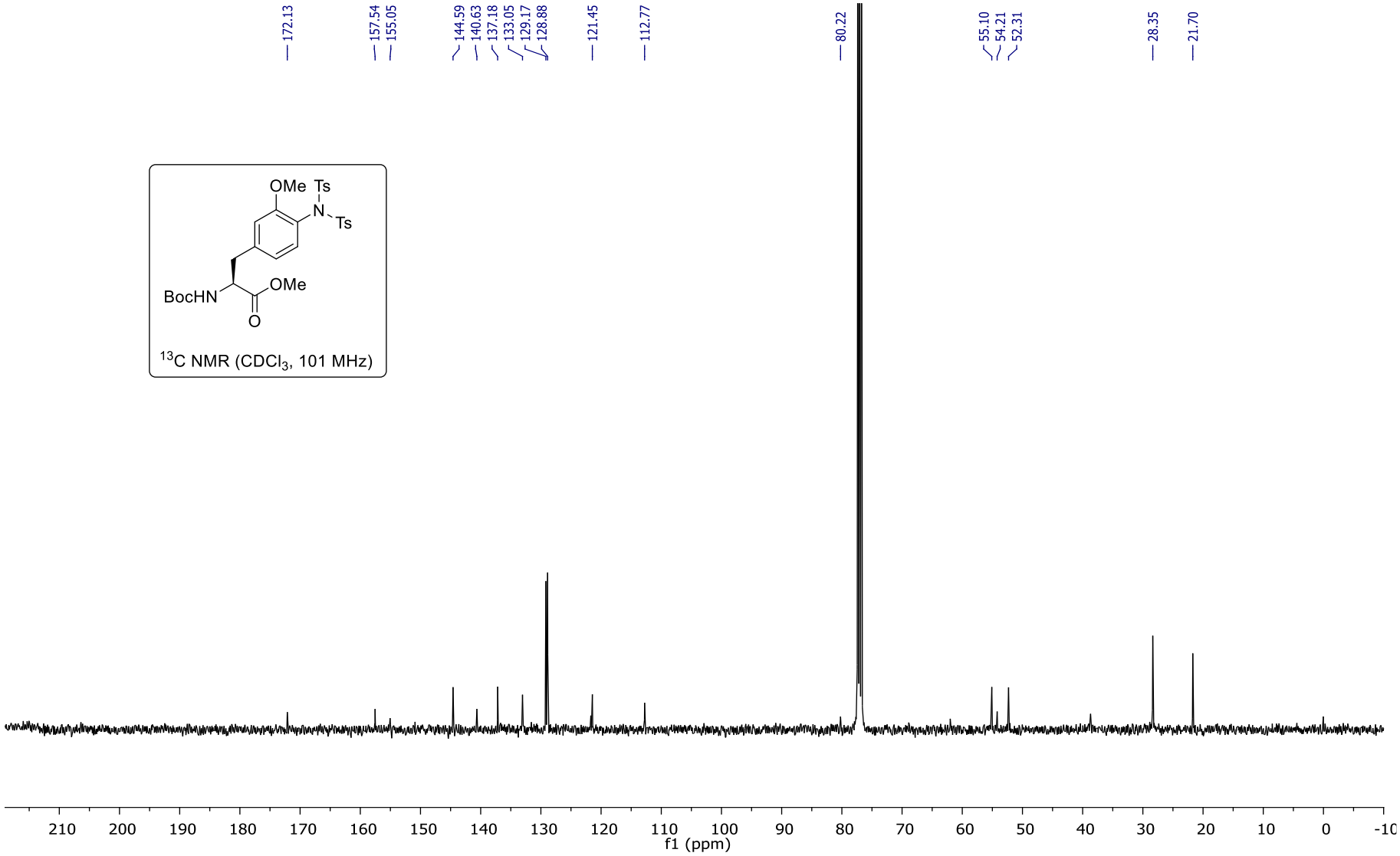
Methyl (*S*)-3-(4-amino-3-methoxyphenyl)-2-(4-Palmitamidobutanamido) propanoate (4i)



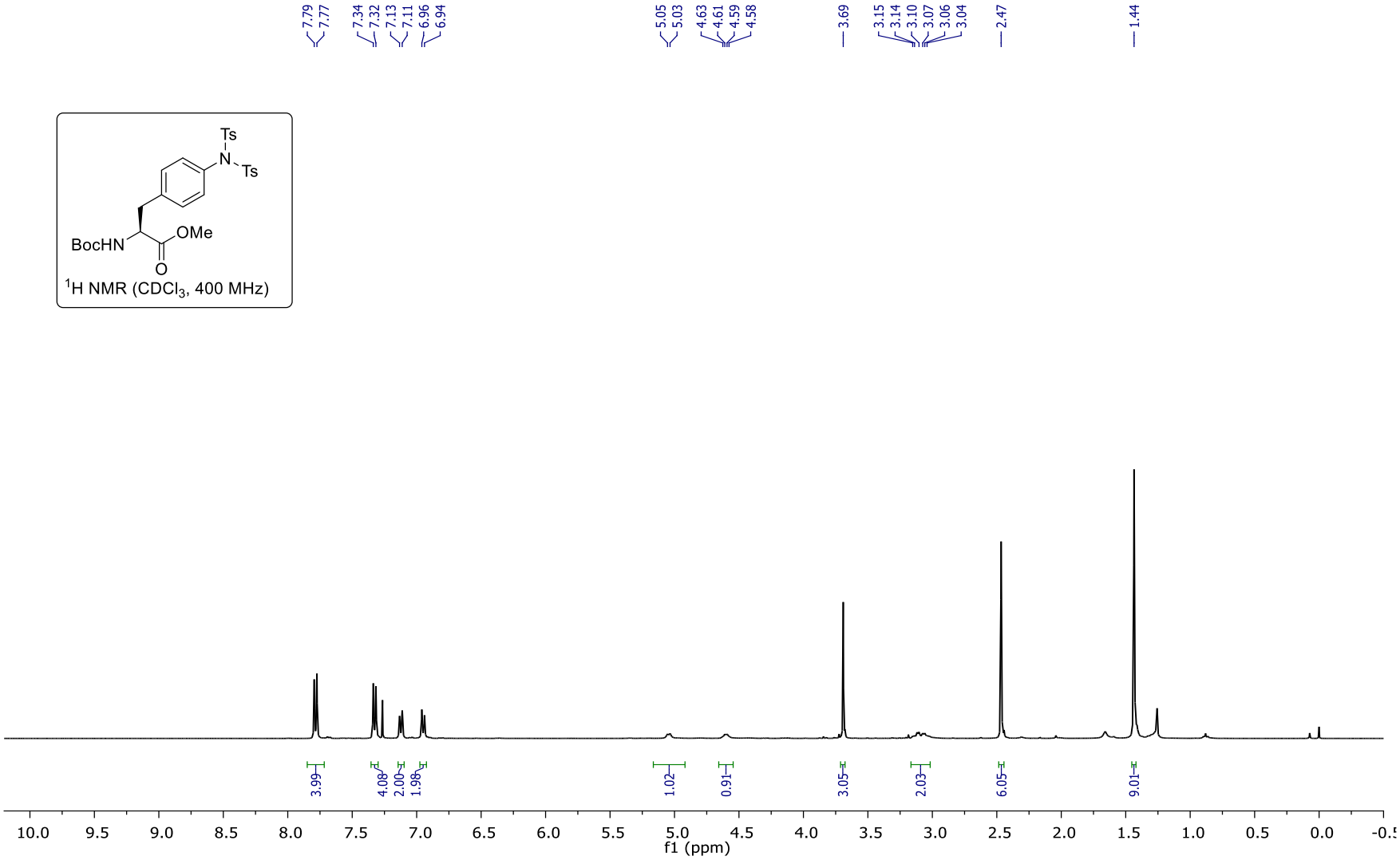
Methyl-(*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(3-methoxy-4-((4-methylphenyl)sulfonamido)phenyl)propanoate (5)



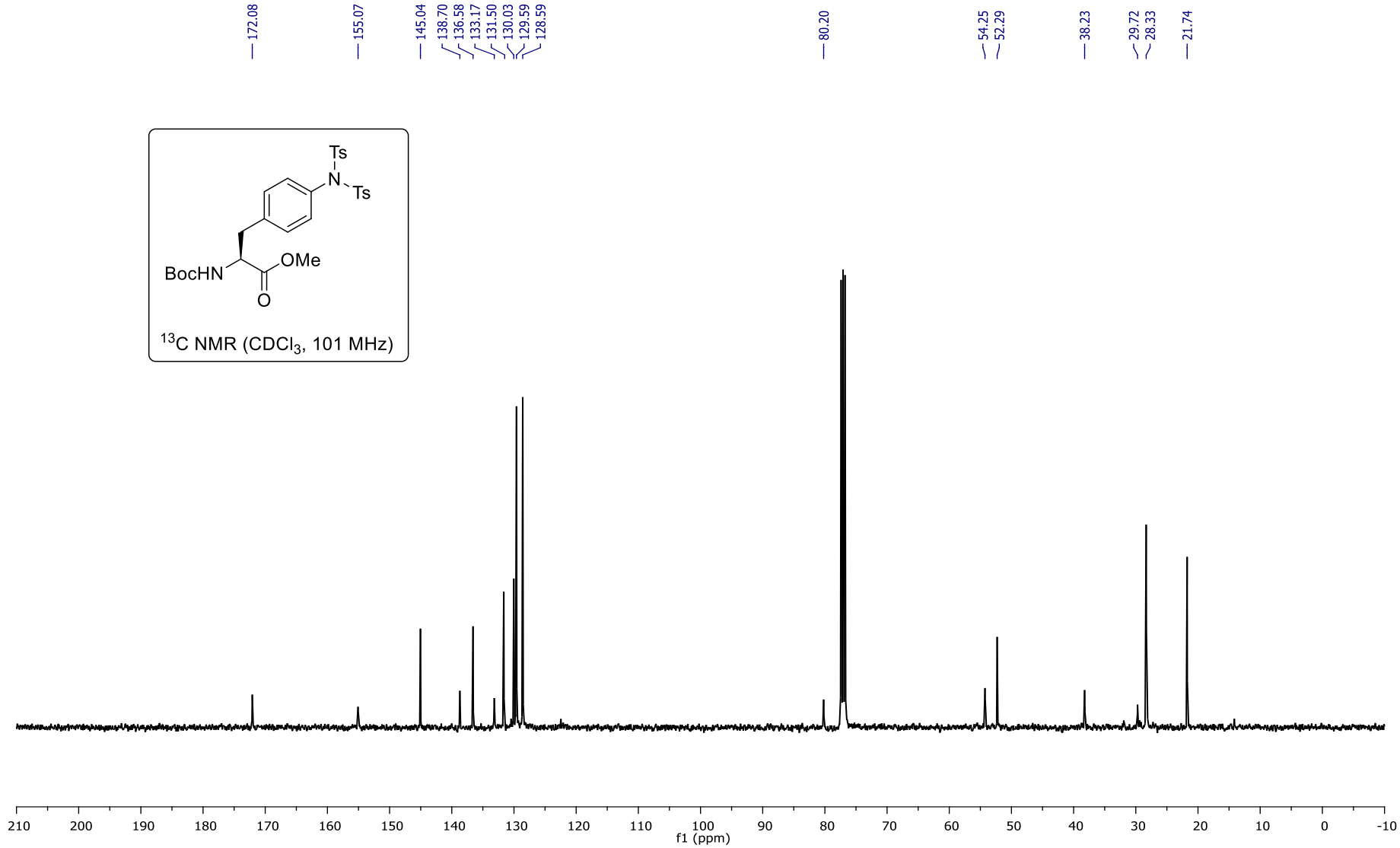
Methyl-(*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(3-methoxy-4-((4-methylphenyl)sulfonamido)phenyl)propanoate (5)



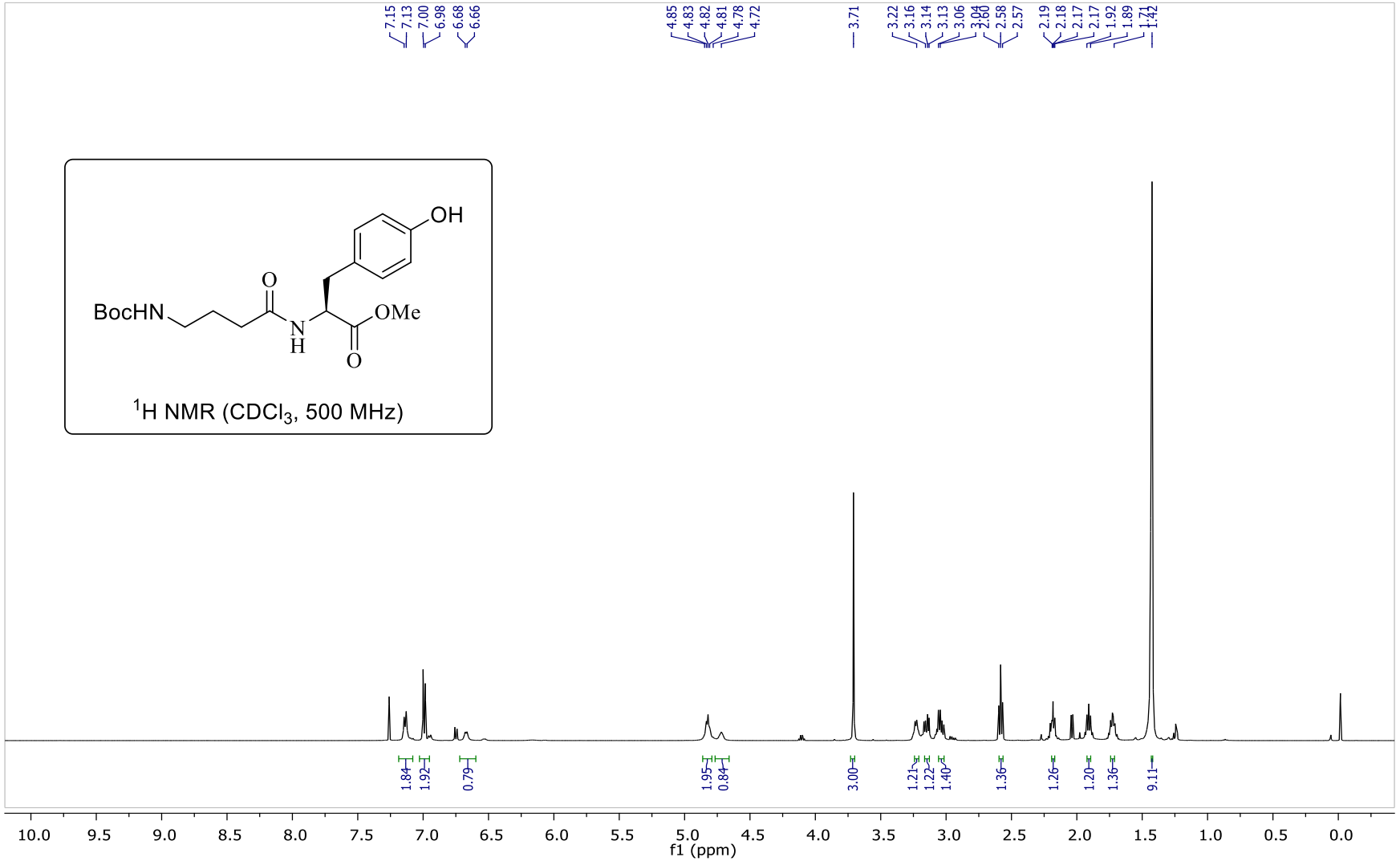
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-((4-methyl-*N*-tosylphenyl)sulfonamido)phenyl)propanoate (5′)



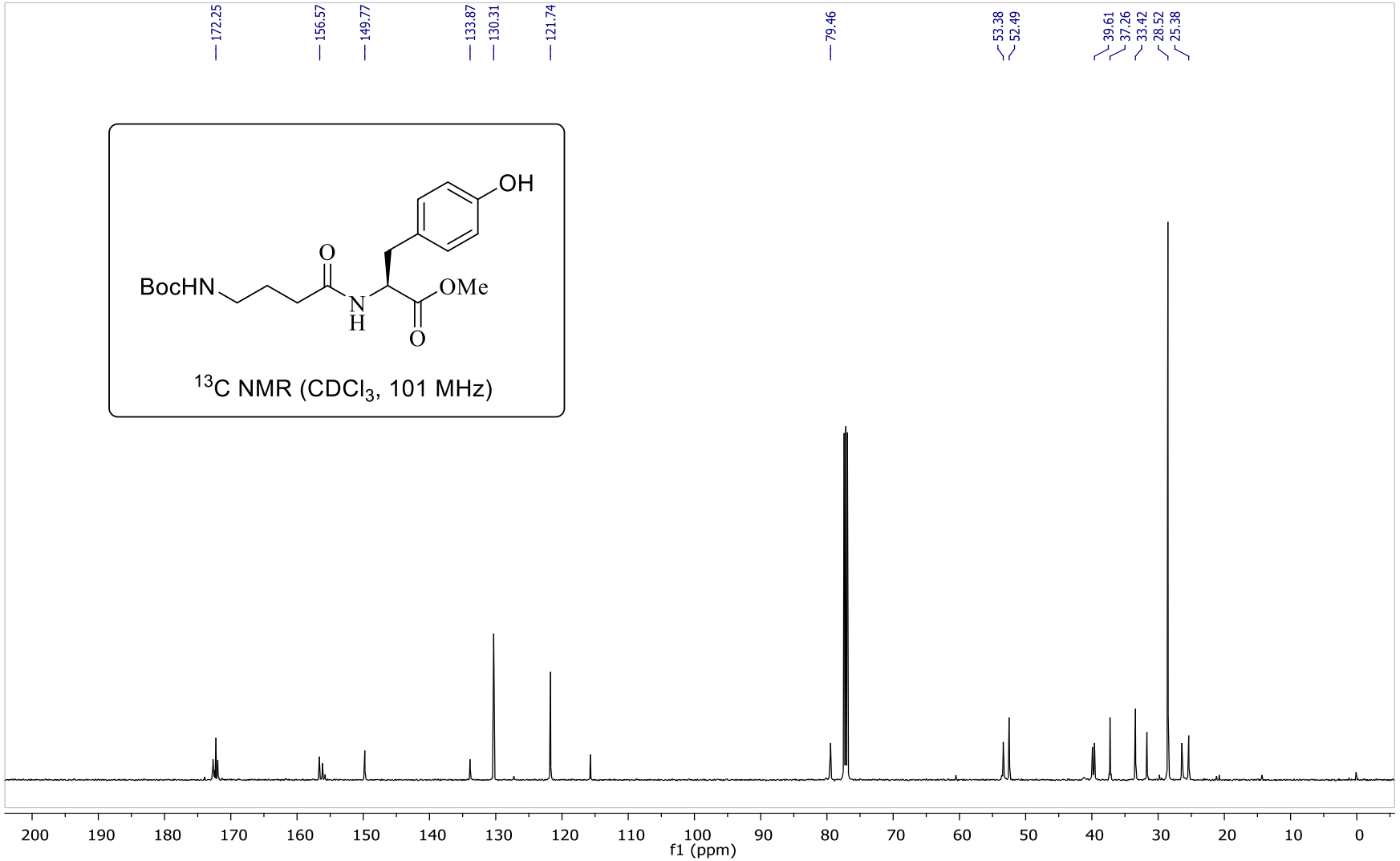
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-((4-methyl-*N*-tosylphenyl)sulfonamido)phenyl)propanoate (5′)



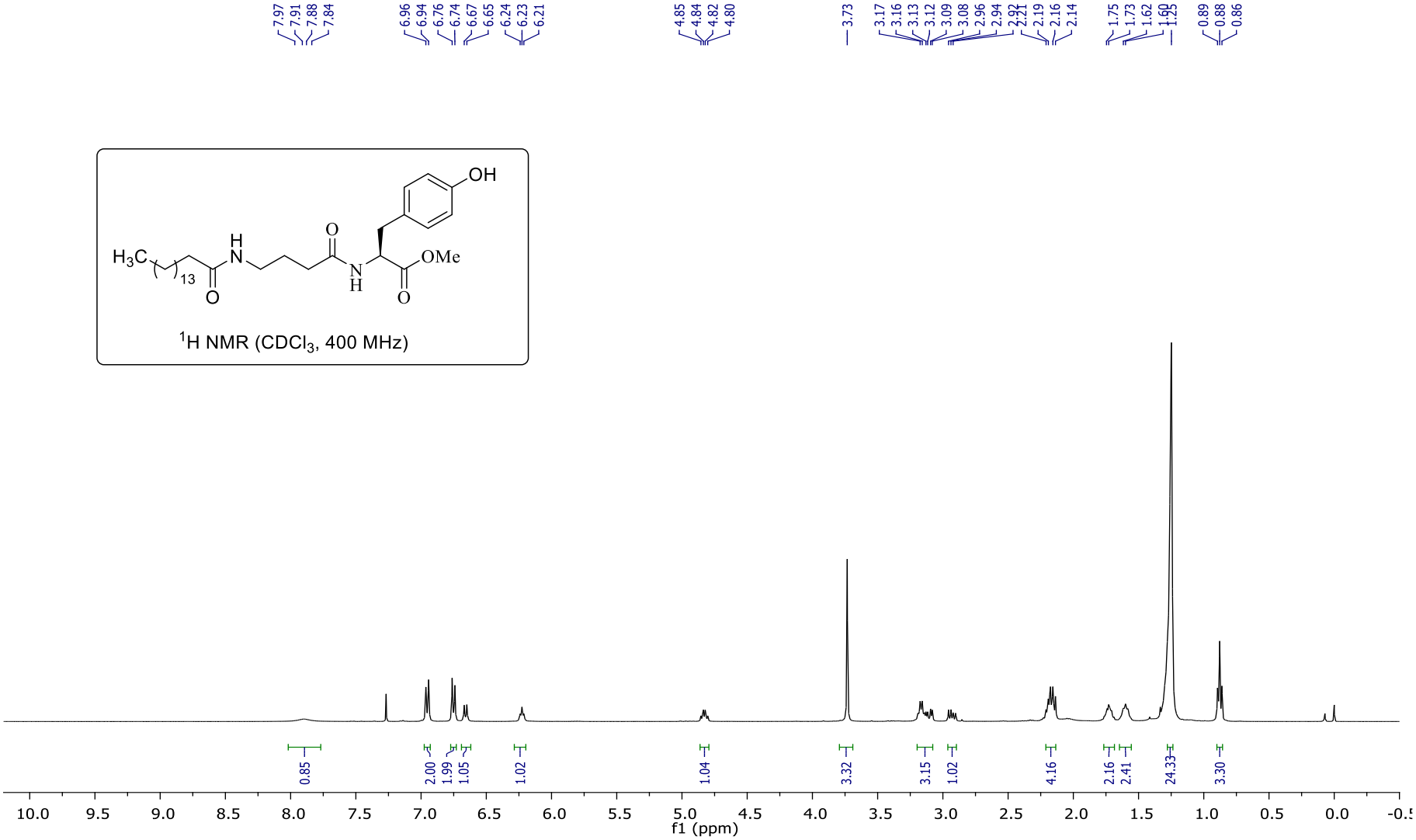
Methyl (4-((*tert*-butoxycarbonyl)amino)butanoyl)-L-tyrosinate (S1)



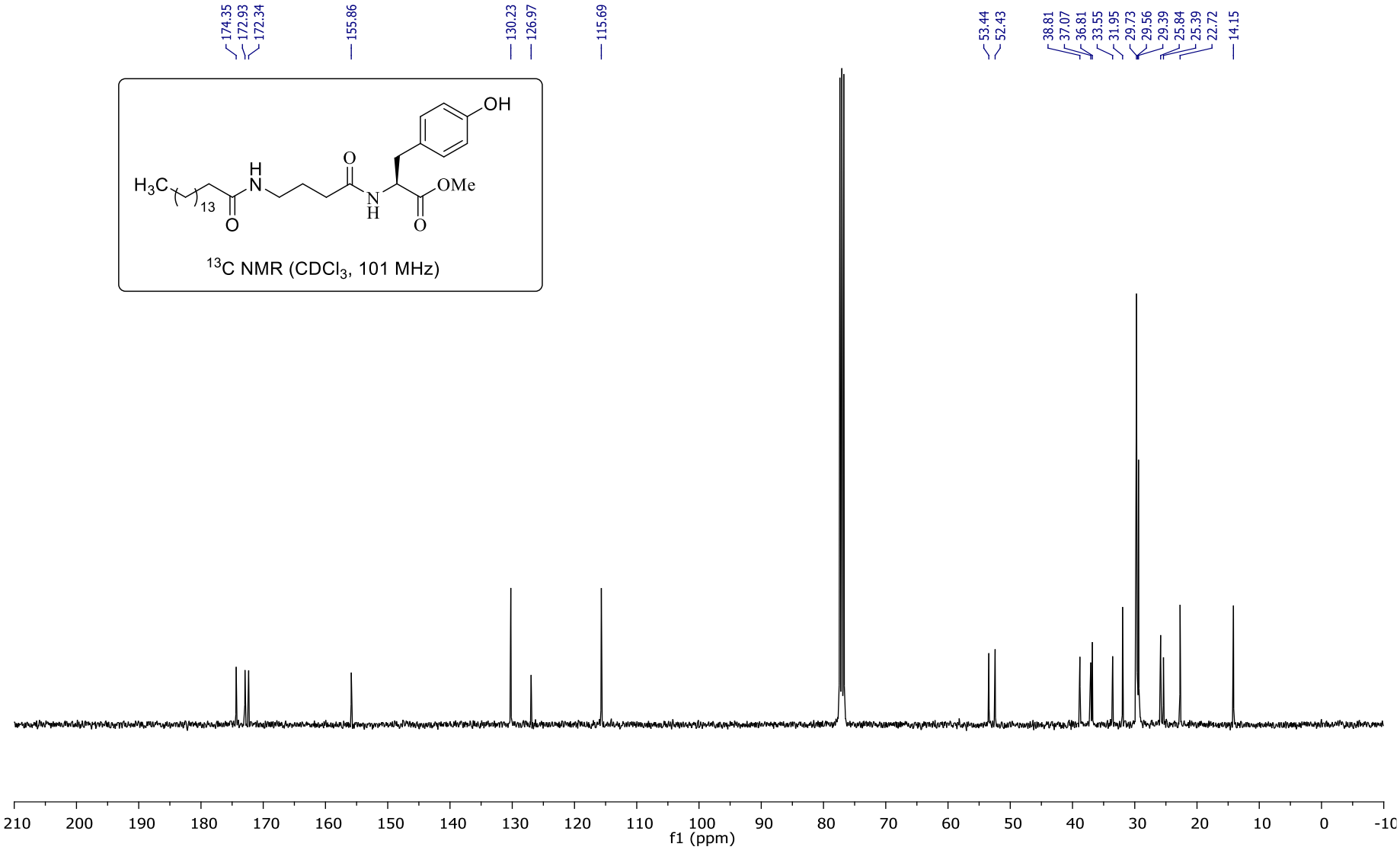
Methyl (4-((*tert*-butoxycarbonyl)amino)butanoyl)-L-tyrosinate (S1)



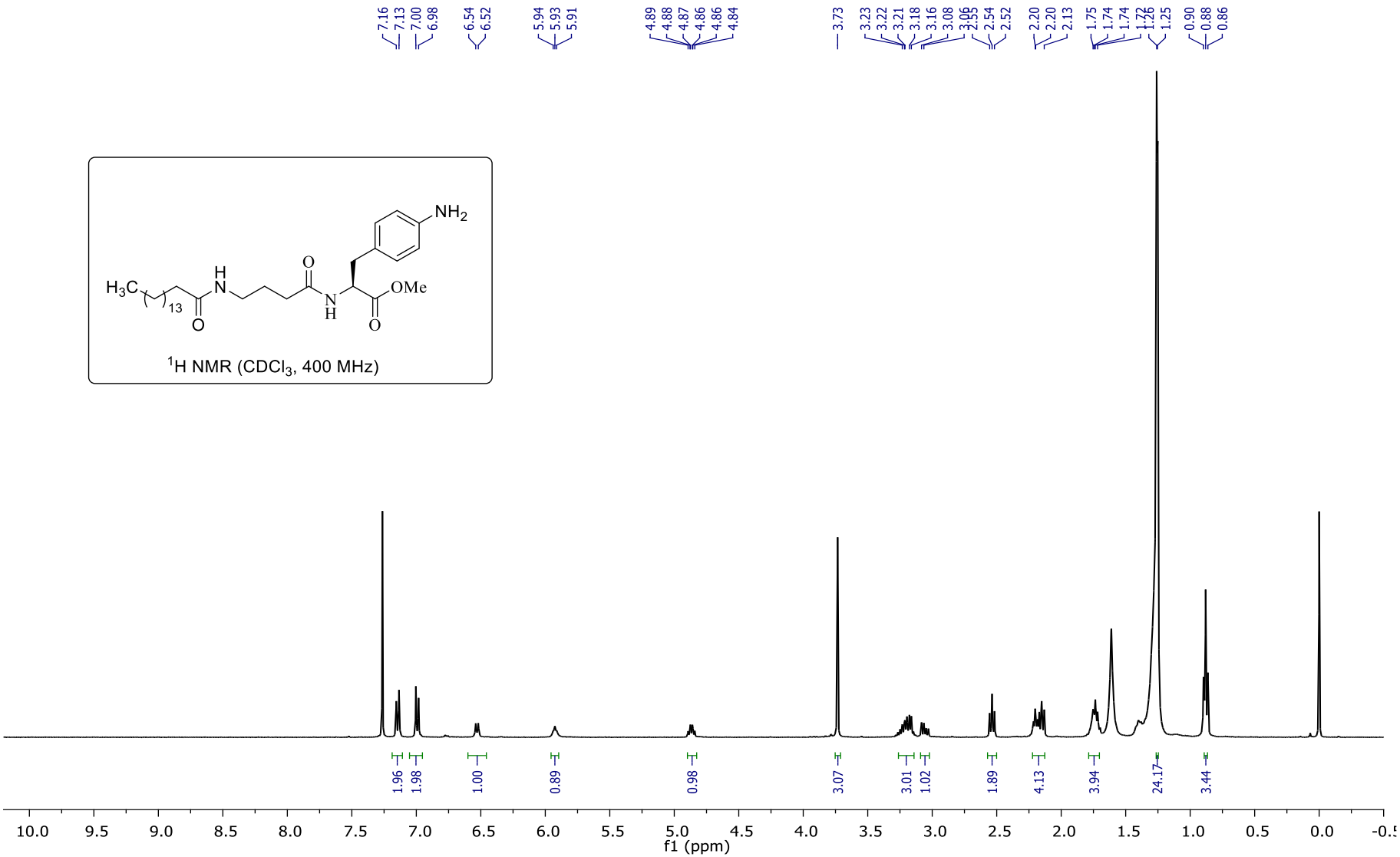
Methyl (4-palmitamidobutanoyl)-L-tyrosinate (3i)



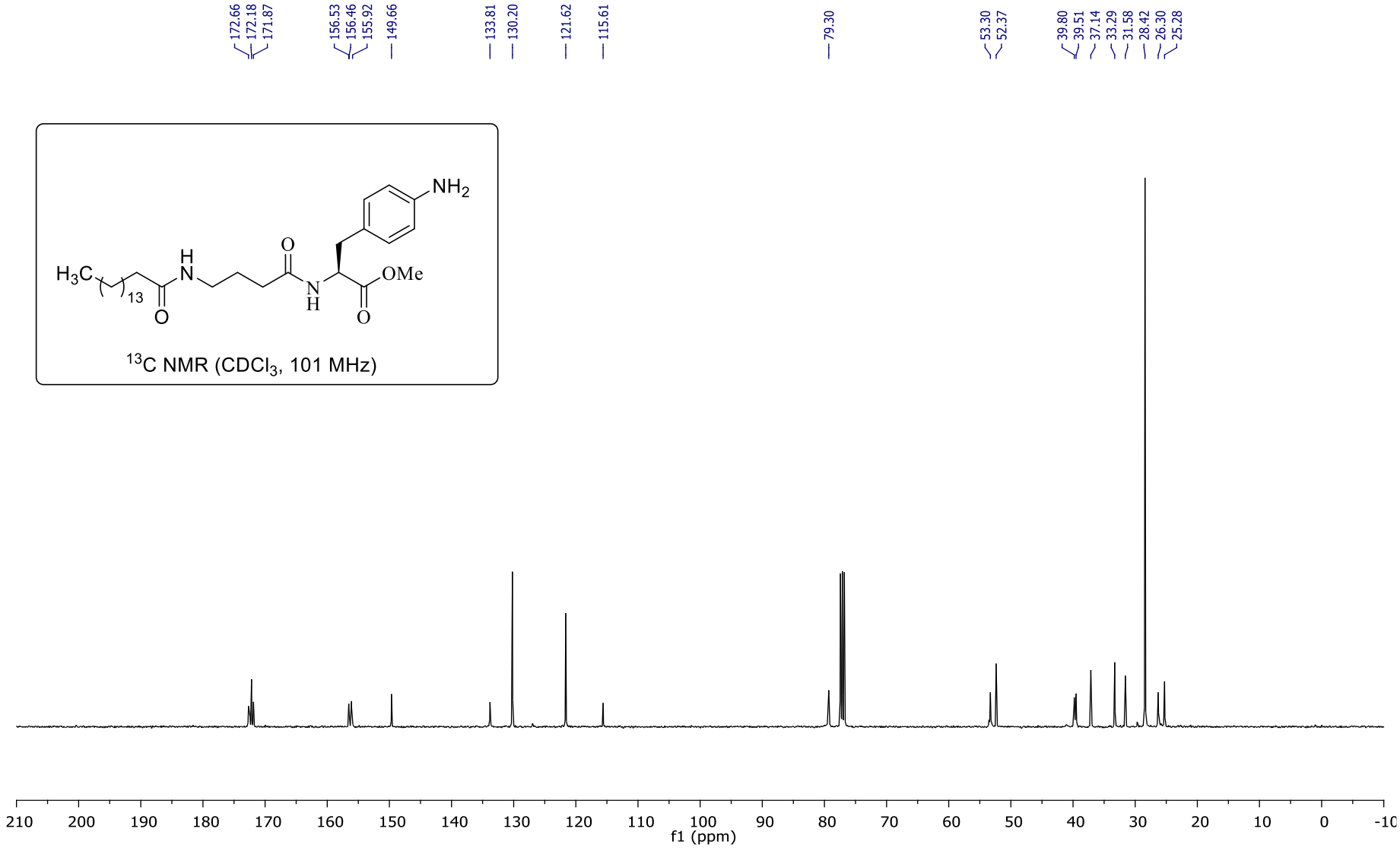
Methyl (4-palmitamidobutanoyl)-L-tyrosinate (3i)



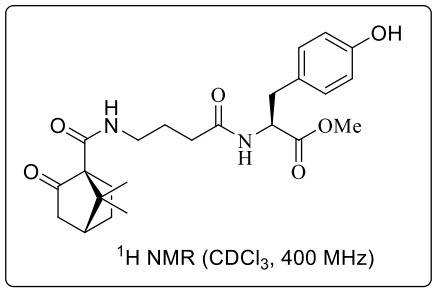
Methyl (*S*)-3-(4-aminophenyl)-2-(4-palmitamidobutanamido)propanoate (6)



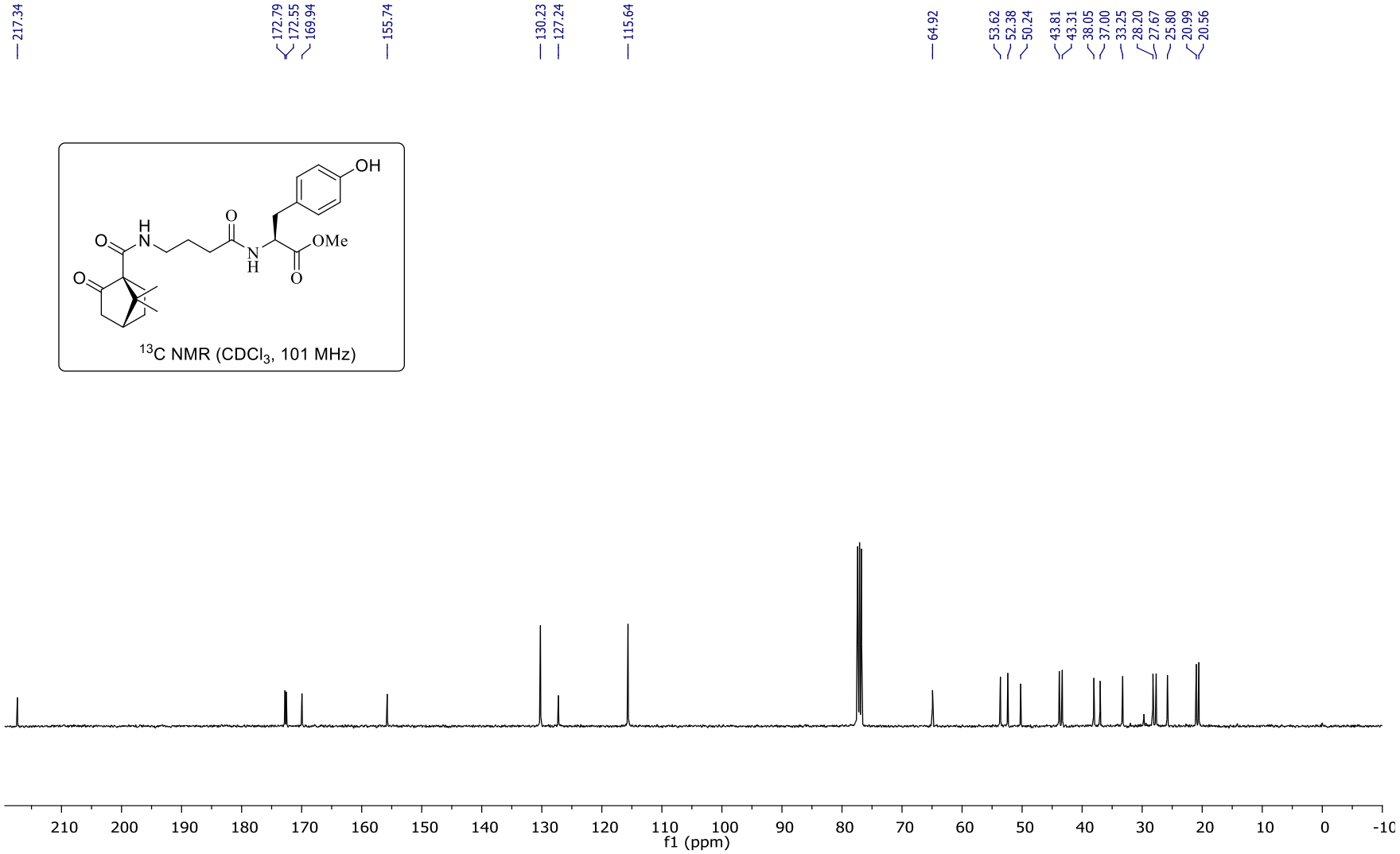
Methyl (*S*)-3-(4-aminophenyl)-2-(4-palmitamidobutanamido)propanoate (6)



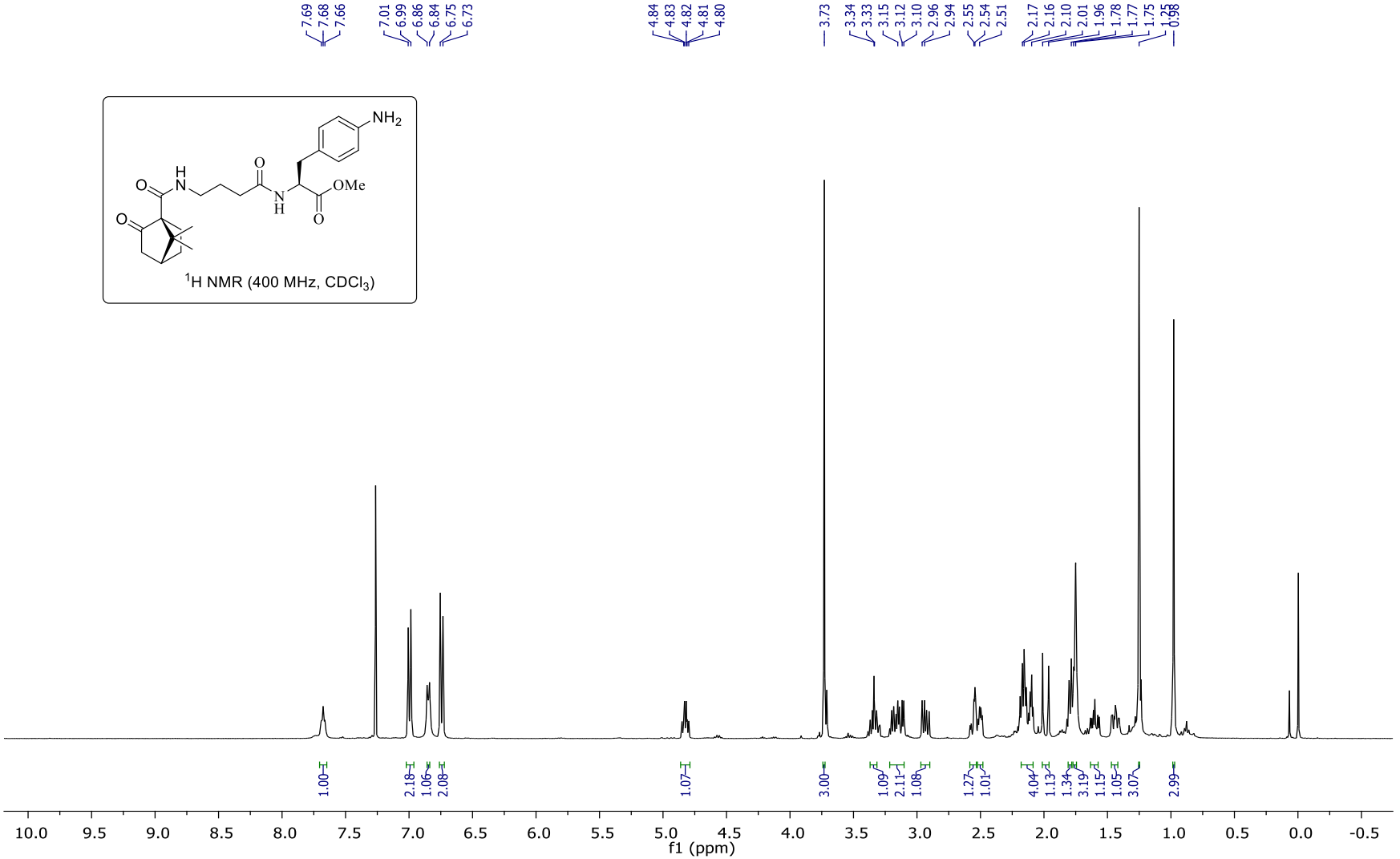
Methyl (4-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxamido)butanoyl)-L-tyrosinate (7)



Methyl (4-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxamido)butanoyl)-L-tyrosinate (7)



Methyl (*S*)-3-(4-aminophenyl)-2-(4-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxamido)butanamido)propanoate (8)



Methyl (*S*)-3-(4-aminophenyl)-2-(4-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxamido)butanamido)propanoate (8)