tert-Butyl(3-cyano-4,6-dimethylpyridin-2-yl)carbonate as a green and chemoselective *N*-*tert*-butoxycarbonylation reagent

Fangyu Du [1], Qifan Zhou [1], Yang Fu, Hanqi Zhao, Yuanguang Chen, Guoliang Chen *

Key Laboratory of Structure-Based Drug Design & Discovery of Ministry of Education, Shenyang Pharmaceutical University, No.103 Wenhua Road, Shenhe District, Shenyang 110016, P. R. of China

* Corresponding author: spucgl@163.com

[1] Authors contributed equally to this work.

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General information

All of the starting materials, reagents, and solvents are commercially available and used without further purification. Melting points were determined with a X-4 apparatus and were uncorrected. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 600 MHz or 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 using tetramethylsilane (TMS) as an internal standard. Electrospray ionization mass spectrometry (ESI-MS) analyses were recorded in an Agilent 1100 Series MSD Trap SL (Santa Clara, CA, USA). The reactions were monitored by thin-layer chromatography (TLC: HG/T2354-92, GF254), and compounds were visualized on TLC with UV light.

tert-butyl (3-cyano-4,6-dimethylpyridin-2-yl) carbonate is abbreviated as BCMP.

Synthesis of 4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile

To a solution of potassium carbonate (13.8 g, 0.1 mol), acetylacetone (11.0 g, 0.1 mol) in water (100 mL) were added 2-cyanoacetamide (8.4 g, 0.1 mol) in portion at room temperature. The mixture was stirred at room temperature for 24 h. The precipitate that formed was collected by filtration, washed with water (20 mL×3) and dried under infrared light to give crude product. The crude product was recrystallized from methanol (1 L) to obtain a white needle solid (13.0 g, 88 % yield) exhibiting the following spectroscopic characteristics. mp 280~281 ^{o}C (lit [1]: 286℃); ESI-MS (m/z): $[M+H]^+$=149.1, ^{1}H NMR (600 MHz, DMSO-d_6) δ: 6.16 (s, 1H), 2.30 (s, 3H), 2.22 (s, 3H).

Synthesis of *tert*-butyl (3-cyano-4,6-dimethylpyridin-2-yl) carbonate (BCMP)

To a mixture of 4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (2.0 g, 13.5 mmol) and DMAP (0.02 g, 0.135 mmol) in THF (20 mL) were added a solution of

Boc_2O (3.2 g, 14.8 mmol) in THF (2 mL) at. The reaction mixture was stirred at 0 ºC for 2 h and then diluted with water, extracted with ethyl acetate (20 mL×3). The organic layer was washed with citric acid aqueous (20 mL×2), water (20 mL×2) and once with brine (25 mL), dried over anhydrous sodium sulfate and concentrated in *vacuo* to give *tert*-butyl (3-cyano-4,6-dimethylpyridin-2-yl) carbonate as a white solid (2.7 g, 81%).^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.07 (s, 1H), 2.55 (s, 3H), 2.54 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.91, 158.25, 154.78, 149.88, 122.87, 113.33, 100.66, 85.34, 27.58, 24.39, 20.14. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{13}H_{16}N_2O_3Na$: 271.1053; found: 271.1055.

React IR Experiment

React IR experiments were conducted using Mettler Toledo ReactIR 15 (SN: 23267) with MCT detector using HappGenzel; DiComp (Diamond) probe (SN: 23146) connected *via* AgX×9.5 mm×1.5 m Fiber (Silver Halide). iC IR 4.3 Reaction Analysis Software was used during data collection and analysis.

To a 50 mL, 3-neck flask equipped with a magnetic stirrer was inserted the ReactIR 15 DiComp probe. IR spectra were obtained every 15 seconds. Data collection began at the beginning of the experiment. To a solution of 4-aminophenol (0.20 g, 1.83 mmol) in acetonitrile (10 mL) and ethanol (2 mL) at room temperature was added BCMP (0.46 g, 1.83 mmol). The resulting solution was gradually heated to 65 ºC and allowed to stir for 60 minutes. The workup was consistent with general procedure of method A.

General procedure

Method A：A mixture of BCMP (2.02 mmol) and substituted amine (2.02 mmol) in ethanol (10 mL) was heated under reflux for 1 h. The reaction mixture was concentrated under reduced pressure. The residue was suspended in *tert*-butyl methyl ether (10 mL), filtered, and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography on silica gel to give the title compound.

Method B: A mixture of BCMP (2.02 mmol), potassium carbonate (2.02 mmol), substituted amine (2.02 mmol) in water (10 mL) was heated under reflux for 1 h. The residue was suspended in *tert*-butyl methyl ether (10 mL), filtered, and the organic layer was concentrated *in vacuo* to give the crude product. The crude product was purified by flash column chromatography on silica gel to give the title compound.

The recycle of Boc carrier

After the reaction was completed, the mixture was cooled to room temperature, and concentrated under reduced pressure. The residue was stirred in *tert*-butyl methyl ether. Then, the needle crystal was collected by filtration in 95% recovery rate which could directly use in the preparation of BCMP without any purification.

Data of ^{1}H, ^{13}C NMR and MS

tert-Butyl (4-hydroxyphenyl)carbamate (**3a**)

White solid, 97% yield. mp 145-146 ^{o}C (lit [2]: 146 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.18 (d, *J*=6.9 Hz, 2H), 6.74 (d, *J*=8.8 Hz, 2H), 6.34 (br, 1H), 5.14 (br, 1H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 155.87, 139.03, 128.81, 128.57, 126.40, 79.20, 41,79, 36,23, 28.42. ESI HRMS: m/z $[M-H]^-$ calcd for $C_{11}H_{14}NO_3N$: 208.0979; found: 208.0983.

tert-Butyl (3-hydroxyphenyl)carbamate (**3b**)

Colorless oil, 94% yield. mp 129-130 ^{o}C (lit [3]: 130-131 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.12-7.10 (m, 2H), 6.73-6.71 (dd, *J*=1.2 Hz, 8.0 Hz, 1H), 6.55-6.53 (m, 2H), 6.03 (br, 1H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 156.55, 152.96, 139.39, 129.91, 110.74, 110.34, 106.05, 80.90, 28.36. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{11}H_{15}NO_3Na$: 232.0944; found: 232.0946.

tert-Butyl phenethylcarbamate (**3c**)

White solid, 99% yield. mp 50-52 ^{o}C (lit [4]: 56.1-56.4 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.31-7.29 (m, 2H), 7.23-7.21 (m, 1H), 7.20-7.18 (m, 2H), 4.54 (br, 1H), 3.37

(t, *J*=6.7 Hz, 2H), 2.79 (t, *J*=7.1 Hz, 2H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 155.87, 139.03, 128.81, 128.57, 126.40, 79.20, 41.79, 36.23, 28.42.

ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{13}H_{19}NO_2Na$: 244.1308; found: 244.1310.

tert-Butyl phenylcarbamate (**3d**)

White solid, 97% yield. mp 136-138 °C (lit [5]: 132-133 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.36-7.35 (m, 2H), 7.30-7.26 (m, 2H), 7.04-7.02 (m, 1H), 6.46 (br, 1H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 152.76, 138.35, 128.98, 123.03, 118.55, 80.50, 28.36. ESI MS: m/z 216.1 $[M+Na]^+$. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{11}H_{15}NO_2Na$: 216.1000; found: 216.0995.

tert-Butyl cyclohexylcarbamate (**3e**)

White solid, 98% yield. mp 74-76 °C (lit [6]: 79-80 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 4.42 (br, 1H), 3.41 (s, 1H), 1.93-1.91 (m, 2H), 1.71-1.68 (m, 2H), 1.60-1.57 (m, 2H), 1.44 (s, 9H), 1.36-1.29 (m, 2H), 1.18-1.06 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 155.20, 78.96, 49.43, 35.55, 28.44, 25.56, 24.90. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{11}H_{21}NO_2Na$: 222.1465; found: 222.1466.

tert-Butyl (4-methoxyphenyl)carbamate (**3f**)

White solid, 100% yield. mp 93-95 °C (lit [2]: 92-94 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.27-7.25 (m, 2H), 6.85-6.82 (m, 2H), 6.34 (br, 1H), 3.78 (s, 3H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 155.71, 153.17, 131.45, 120.63, 114.21, 80.25, 55.52, 28.38. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{12}H_{17}NO_3Na$: 246.1101; found: 246.1110.

tert-Butyl benzylcarbamate (**3g**)

White solid, 97% yield. mp 47-49 °C (lit [7]: 57 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.34-7.32 (m, 2H), 7.29-7.25 (m, 3H), 4.83 (m, 1H), 4.32 (s, 2H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 155.90, 138.95, 128.60, 127.49, 127.32, 79.47, 44.72, 28.42. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{12}H_{17}NO_2Na$: 230.1157; found: 230.1160.

tert-Butyl (2-hydroxyphenyl)carbamate (**3h**)

Yellow solid, 89% yield. mp 141-142 °C (lit [4]: 142 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.13 (br, 1H), 7.06-7.03 (m, 2H), 6.98-6.97 (m, 1H), 6.87-6.84 (m, 1H), 6.63 (br, 1H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 155.03, 147.40, 125.63, 125.55, 121.36, 120.77, 118.75, 82.07, 28.27. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{11}H_{15}NO_3Na$: 232.0944; found: 232.0945.

tert-Butyl (4-mercaptophenyl)carbamate (**3i**)

White solid, 91% yield. mp 179-180 °C (lit [4]: 179-180 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.40 (d, *J*=8.5 Hz, 2H), 7.30 (d, *J*=8.2 Hz, 2H), 6.48 (br, 1H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 152.47, 138.41, 131.00, 130.85, 118.92, 80.87, 28.31. ESI MS: m/z 248.3 $[M+Na]^+$. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{11}H_{15}NO_2SNa$: 248.0721; found: 248.0726.

tert-butyl *p*-tolylcarbamate (**3j**)

white solid, 95% yield. mp 93-94 °C (lit [8]: 92-92.8 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.22 (d, *J*=7.7 Hz, 2H), 7.08 (d, *J*=8.3 Hz, 2H), 6.39 (s, 1H), 2.29 (s, 3H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 152.92, 135.76, 132.54, 129.46, 118.72, 80.30, 28.38, 20.72. ESI MS: m/z 230.4 $[M+Na]^+$. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{12}H_{17}NO_2Na$: 230.1157; found: 230.1166.

tert-Butyl (2-aminophenyl)carbamate (**3k**)

Brown solid, 85% yield. mp 103-104 °C (lit [2]: 110-113 °C). ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 8.27 (br, 1H), 7.16 (d, *J*=7.4 Hz, 1H), 6.84-6.81 (td, *J*=1.5 Hz, 7.9 Hz, 1H), 6.68-6.66 (dd, *J*=1.3 Hz, 7.9 Hz, 1H), 6.53-6.50 (td, *J*=1.4 Hz, 7.7 Hz, 1H), 4.81 (s, 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 153.83, 139.44, 126.14, 124.83, 124.73, 119.63, 117.62, 80.52, 28.35. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{11}H_{16}N_2O_2Na$: 231.1104; found: 231.1111.

tert-Butyl (4-cyanophenyl)carbamate (**3l**)

Yellow solid, 36% yield. mp 97-99 °C (lit [9]: 113-114 °C). ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 9.90 (s, 1H), 7.71 (d, *J*=8.8 Hz, 2H), 7.63 (d, *J*=8.8 Hz, 2H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 151.97, 142.61, 133.29, 118.10,

105.78, 81.69, 28.23. ESI HRMS: m/z $[M-H]^-$ calcd for $C_{12}H_{13}N_2O_2$: 217.0983; found: 217.0984.

tert-Butyl 4-oxopiperidine-1-carboxylate (**3m**)

White solid, 96% yield. mp 71-72 °C (lit [10]: 73-75 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 3.72 (t, *J*=6.1Hz, 4H), 2.44 (t, *J*=6.1 Hz, 4H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 207.73, 154.46, 80.41, 43.00, 41.15, 28.35. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{10}H_{17}NO_3Na$: 222.1101; found: 222.1105.

tert-Butyl 4-(2-hydroxyethyl)piperidine-1-carboxylate (**3n**)

Light-yellow oil, 95% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) : 4.09-4.07 (dt, *J*=2.3 Hz, 13.2 Hz, 2H), 3.71 (t, *J*=6.6 Hz, 2H), 2.72-2.67 (td, *J*=2.6 Hz, 13.1 Hz, 2H), 1.68-1.66 (m, 2H), 1.63-1.56 (m, 1H), 1.54-1.51 (m, 3H), 1.45 (s, 9H), 1.16-1.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 154.92, 79.29, 60.07, 44.03, 39.29, 32.53, 32.12, 28.45. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{12}H_{23}NO_3Na$: 252.1570; found: 252.1580.

tert-Butyl (3-nitrophenyl)carbamate (**3o**)

Yellow solid, 18% yield. mp 180-182 °C (lit [11]: 181-183 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) : 8.30 (t, *J*=2.1 Hz, 1H), 7.89-7.87 (m, 1H), 7.44 (t, *J*=8.2 Hz, 1H), 6.70 (br, 1H), 1.54 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 152.25, 148.78, 139.64, 129.72, 123.92, 117.64, 113.14, 81.65, 28.25. ESI HRMS: m/z $[M-H]^-$ calcd for $C_{11}H_{13}N_2O_4$: 237.0881; found: 237.0880.

Di-*tert*-butyl 1,3-phenylenedicarbamate (**3p**)

White solid, 88% yield. mp 144-146 °C (lit [12]: 142-144 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) : 7.50 (s, 1H), 7.20 (t, *J*=8.1 Hz, 1H), 7.02-7.01 (m, 2H), 1.51 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 152.65, 139.06, 129.47, 113.00, 108.52, 80.53, 28.33. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{16}H_{24}N_2O_4Na$: 331.1628; found: 331.1644.

tert-Butyl (2-(1*H*-indol-3-yl)ethyl)carbamate (**3q**)

White solid, 92% yield. mp 91-92 °C (lit [13]: 88-90 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.08 (br, 1H), 7.61 (d, *J*=7.9 Hz, 1H), 7.37 (d, *J*=8.1 Hz, 1H), 7.21-7.19 (m, 1H), 7.13-7.11 (m, 1H), 7.02 (s, 1H), 3.46 (t, *J*=5.8 Hz, 2H), 2.95 (t, *J*=6.8 Hz, 2H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 156.02, 136.41, 127.41, 122.14, 122.02, 119.42, 118.84, 113.19, 111.18, 79.14, 40.87, 28.45, 25.81. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{15}H_{20}N_2O_2Na$: 283.1417; found: 283.1430.

tert-Butyl isopropylcarbamate (**3r**)

White solid, 98% yield. mp 72-73 °C (lit [14]: 70.5-72.5 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) : 3.74 (t, *J*=5.6 Hz, 1H), 1.44 (s, 9H), 1.13 (d, *J*=6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 155.17, 78.97, 42.58, 28.46, 23.12. ESI MS: Not responding.

tert-butyl (2-chloro-4-hydroxyphenyl)carbamate (**3s**)

Light yellow solid, 98% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.78 (d, *J*=7.6 Hz, 1H), 6.84 (d, *J*=2.8 Hz, 1H), 6.68 (dd, *J*=8.9, 2.8 Hz, 2H), 5.32 (br, 1H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 153.44, 152.27, 127.87, 124.65, 122.95, 116.22, 114.85, 81.11, 28.35. ESI HRMS: m/z $[M-H]^-$ calcd for $C_{11}H_{13}ClNO_3$: 242.0584, 244.0558; found: 242.0585, 244.0558.

methyl 4-((tert-butoxycarbonyl)amino)benzoate (**3t**)

White solid, 55% yield. mp 154-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99-7.95 (m, 2H), 7.43 (d, *J*=8.8 Hz, 2H), 6.71 (s, 1H), 3.89 (s, 3H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 166.74, 155.19, 142.71, 130.89, 124.40, 117.36, 81.22, 51.92, 28.28. HRMS: m/z $[M+Na]^+$ calcd for $C_{13}H_{17}NO_4Na$: 274.1055; found: 274.1050.

methyl 3-((tert-butoxycarbonyl)amino)benzoate (**3u**)

White solid, 70% yield. mp 110-112 °C (lit [15]: 111-113 °C) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 (d, J=1.6 Hz, 1H), 7.72-7.67 (m, 2H), 7.36 (t, J=7.9 Hz, 1H), 6.67 (s, 1H), 3.91 (s, 3H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 166.86, 152.64, 138.68, 130.90, 129.08, 124.11, 122.87, 119.42, 80.88, 52.19, 28.32. ESI

HRMS: m/z $[M+Na]^+$ calcd for $C_{13}H_{17}NO_4Na$: 274.1055; found: 274.1050.Methyl (*tert*-butoxycarbonyl)-*L*-tryptophanate (**5a**)

White solid, 91% yield. mp 168-170 °C (lit [16]: 151-152 °C). ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.13 (br, 2H), 7.56 (d, *J*=7.9 Hz, 2H), 7.36 (d, *J*=8.1 Hz, 2H), 7.19 (t, *J*=7.3 Hz, 2H), 7.12 (t, *J*=7.5 Hz, 2H), 7.00 (s, 2H), 5.08 (d, *J*=7.0 Hz, 2H), 4.65 (d, *J*=7.0 Hz, 2H), 3.67 (s, 6H), 3.32-3.28 (m, 4H), 1.43 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 172.77, 155.26, 136.14, 127.71, 122.72, 122.22, 119.63, 118.77, 111.17, 110.29, 79.84, 54.19, 52.23, 28.34, 28.01. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{17}H_{22}N_2O_4Na$: 341.1472; found: 341.1494.

Methyl 2-((*tert*-butoxycarbonyl)amino)-2-phenylacetate (**5b**)

Yellow solid, 86% yield. mp 101-103 °C (lit [17]: 103-105 °C). ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.36-7.31 (m, 5H), 5.55 (d, *J*=5.6 Hz, 1H), 3.72 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 171.68, 154.81, 136.92, 130.91, 128.91, 128.44, 127.14, 80.18, 57.60, 52.69, 28.31. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{14}H_{19}NO_4Na$: 288.1206; found: 288.1207.

tert-Butyl (*tert*-butoxycarbonyl)-*L*-valinate (**5c**)

Colorless oil, 97% yield. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 5.03 (d, *J*=8.2 Hz, 1H), 4.11-4.09 (q, *J*=8.8 Hz, 4.4 Hz, 1H), 2.14-2.09 (m, 1H), 1.47 (s, 9H), 1.45 (s, 9H), 0.96 (d, *J*=6.8 Hz, 3H), 0.90 (d, *J*=6.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ (ppm): 171.49, 155.71, 81.60, 79.43, 58.84, 31.47, 28.31, 28.04, 18.90, 17.46. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{14}H_{27}NO_4Na$: 296.1832; found: 296.1848.

Methyl (*tert*-butoxycarbonyl)glycinate (**5d**)

Colorless liquid, 96% yield. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 5.30 (br, 1H), 3.91 (d, *J*=5.6 Hz, 2H), 3.75 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.87, 155.76, 79.87, 63.65, 52.10, 42.22, 29.61, 28.23. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_8H_{15}NO_4Na$: 212.0893; found: 212.0898.

Methyl 2-((*tert*-butoxycarbonyl)amino)-2-(2-chlorophenyl)acetate (**5e**)

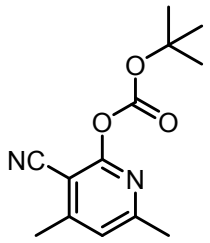
White solid, 95% yield. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.40-7.35 (m, 2H), 7.28-

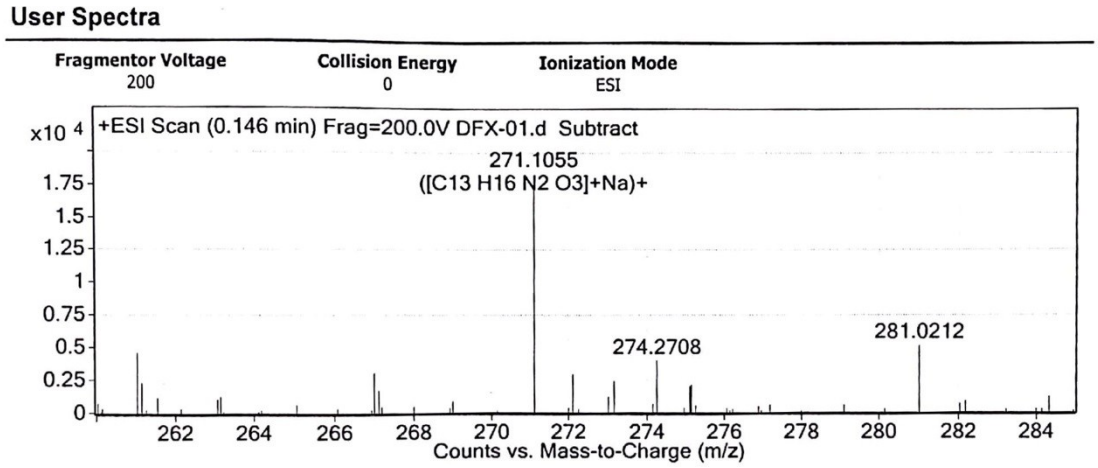
7.26 (m, 2H), 5.69 (d, *J*=7.2 Hz, 1H), 5.65 (br, 1H), 3.73 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 171.04, 154.84, 135.27, 133.58, 130.06, 129.77, 129.57, 127.23, 80.15, 60.30, 55.57, 52.82, 28.25, 20.95, 14.16. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_{14}H_{18}ClNO_4Na$: 322.0817; found: 322.0830.

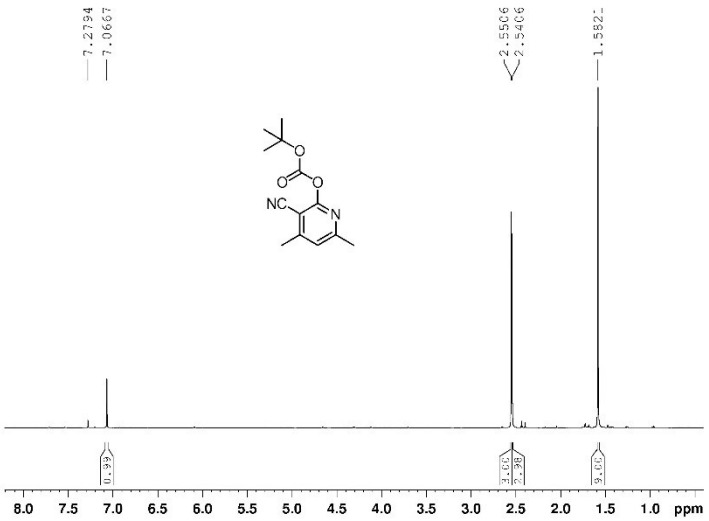
Methyl 3-((*tert*-butoxycarbonyl)amino)propanoate (**5f**)

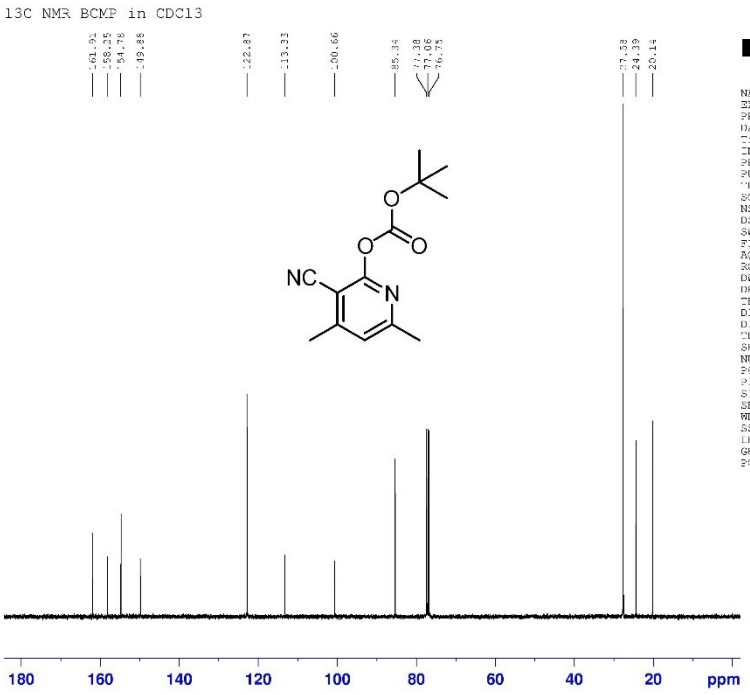
Colorless oil, 91% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 5.06 (br, 1H), 3.70 (s, 3H), 3.40 (d, *J*=5.8 Hz, 2H), 2.53 (t, *J*=6.0 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 172.90, 155.78, 79.33, 51.70, 36.06, 34.42, 28.35. ESI HRMS: m/z $[M+Na]^+$ calcd for $C_9H_{17}O_4Na$: 226.1050; found: 226.1059.

The spectra of ^{1}H, ^{13}C NMR and MS



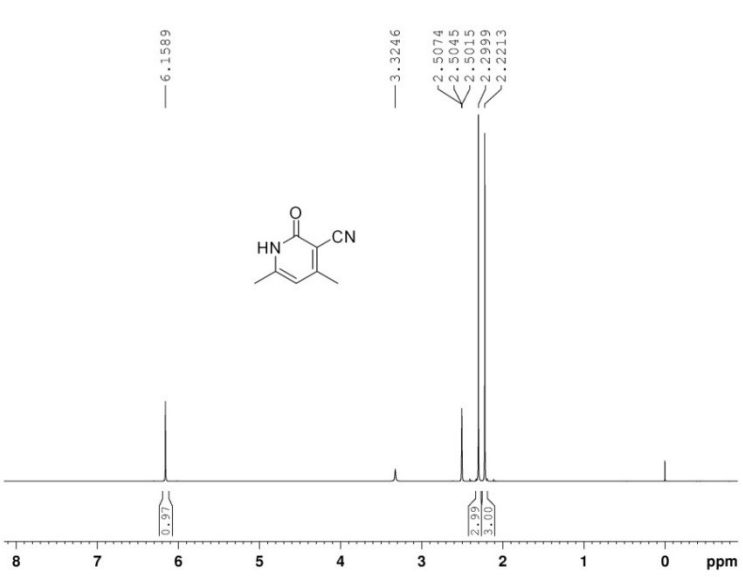






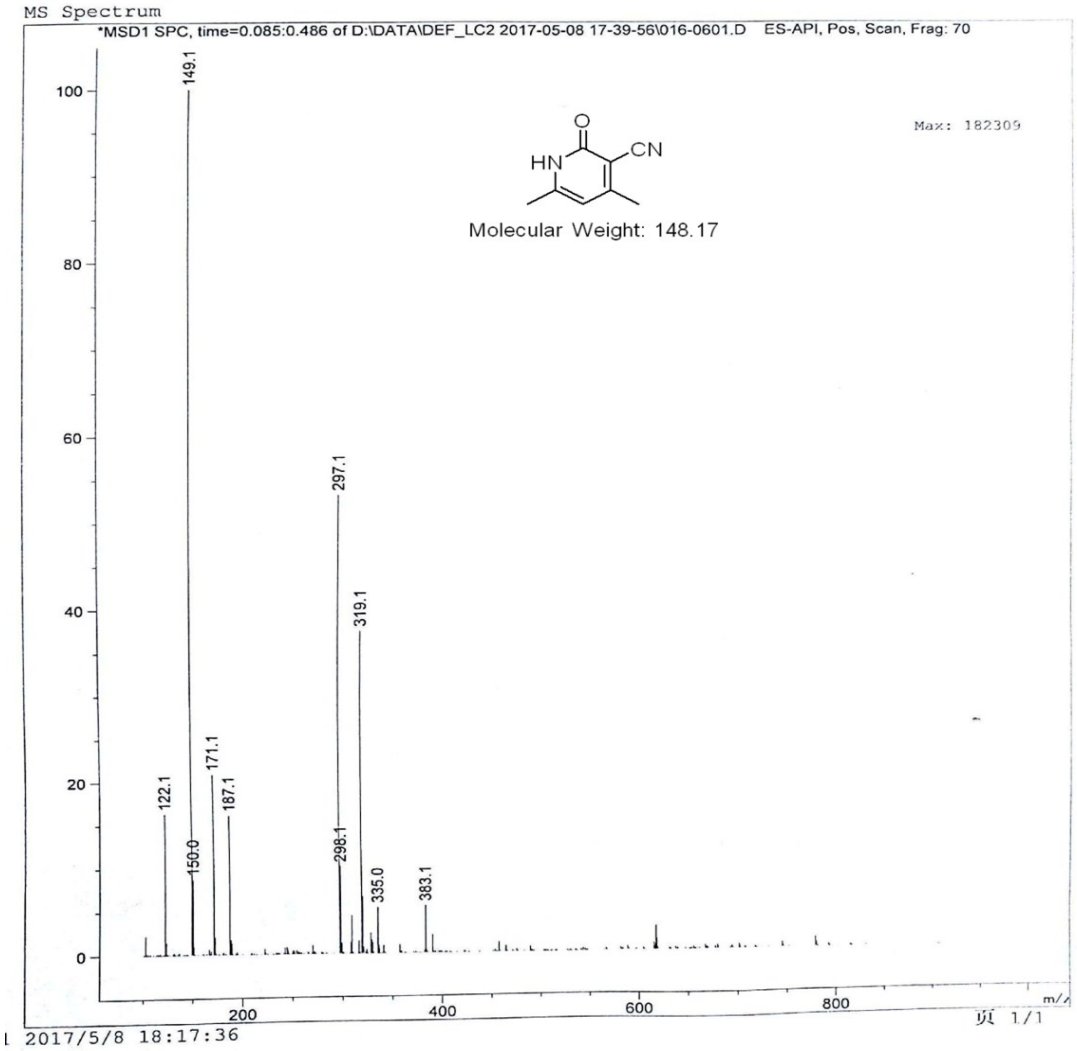
BRUKER

NAME	BCMP
EXPNO	10
PROCNO	1
Date_	20190218
Time	14.14 h
INSTRUM	spect
PROBHD	Z116098_0801 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	230
DS	4
SWH	24038.461 Hz
FIDRES	0.733596 Hz
AQ	1.3631988 sec
RG	200.9
DW	20.800 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	100.6354036 MHz
NUC1	13C
P0	3.33 usec
P1	10.00 usec
SI	32768
SF	100.6253419 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

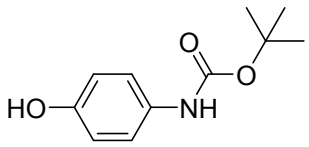


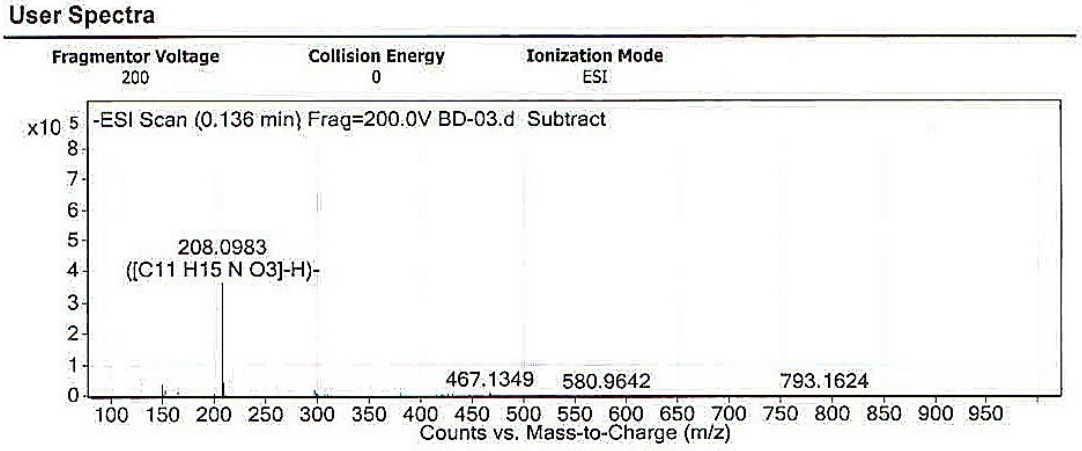
BRUKER

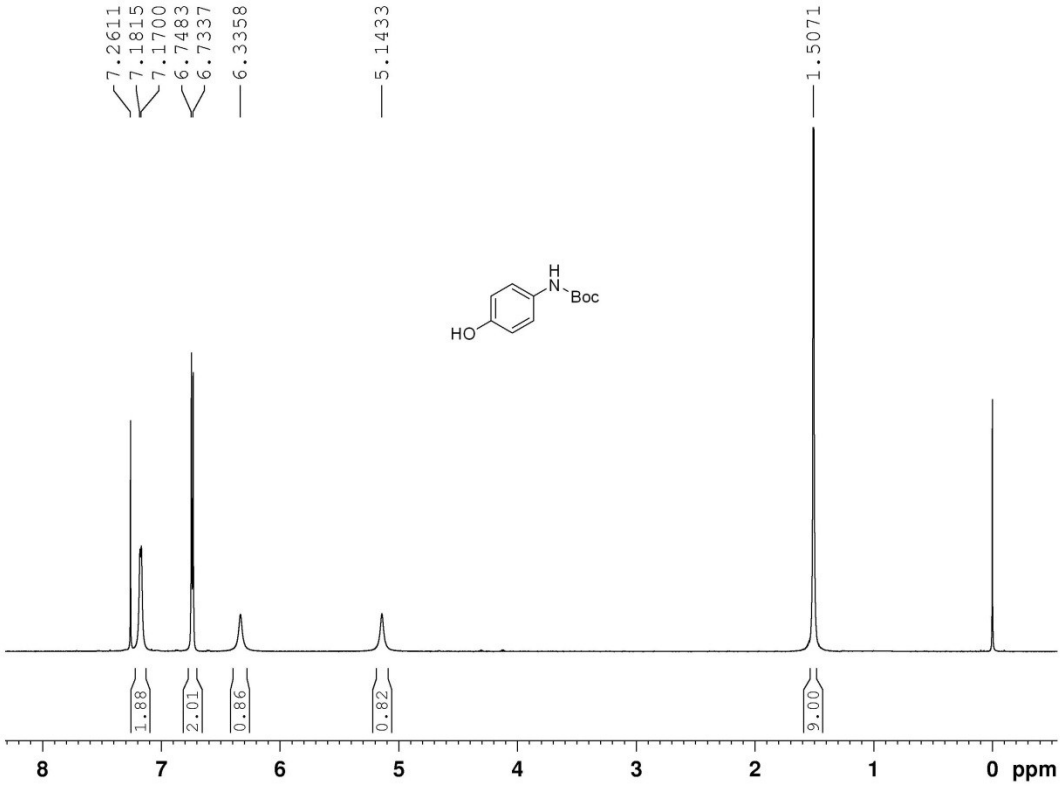
NAME	PYT-A-01
EXPNO	1
PROCNO	1
Date_	20170510
Time	14.50
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	16
DS	2
SWH	12335.526 Hz
FIDRES	0.188225 Hz
AQ	2.6564426 se
RG	174.88
DW	40.533 us
DE	6.50 us
TE	297.9 K
D1	1.00000000 se
======== CHANNEL f1 ======	
NUC1	1H
P1	12.85 us
SI	65536
SF	600.1300044 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

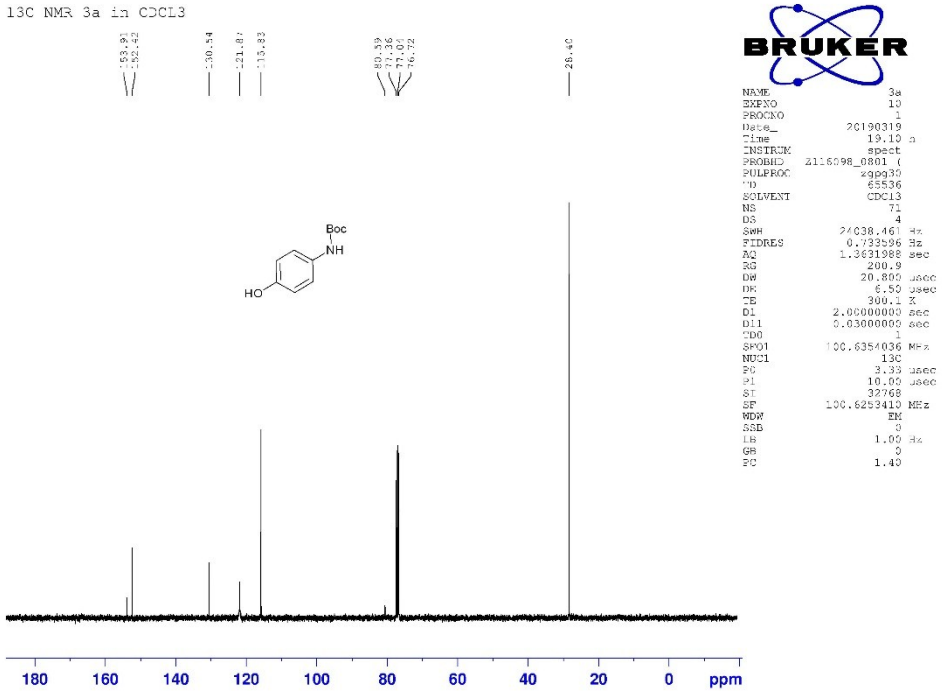


tert-Butyl (4-hydroxyphenyl)carbamate (**3a**)



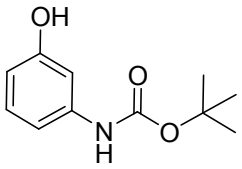


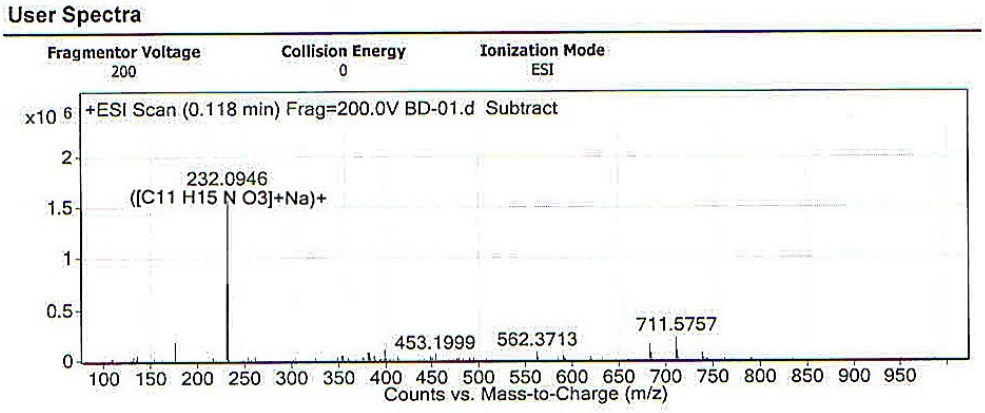


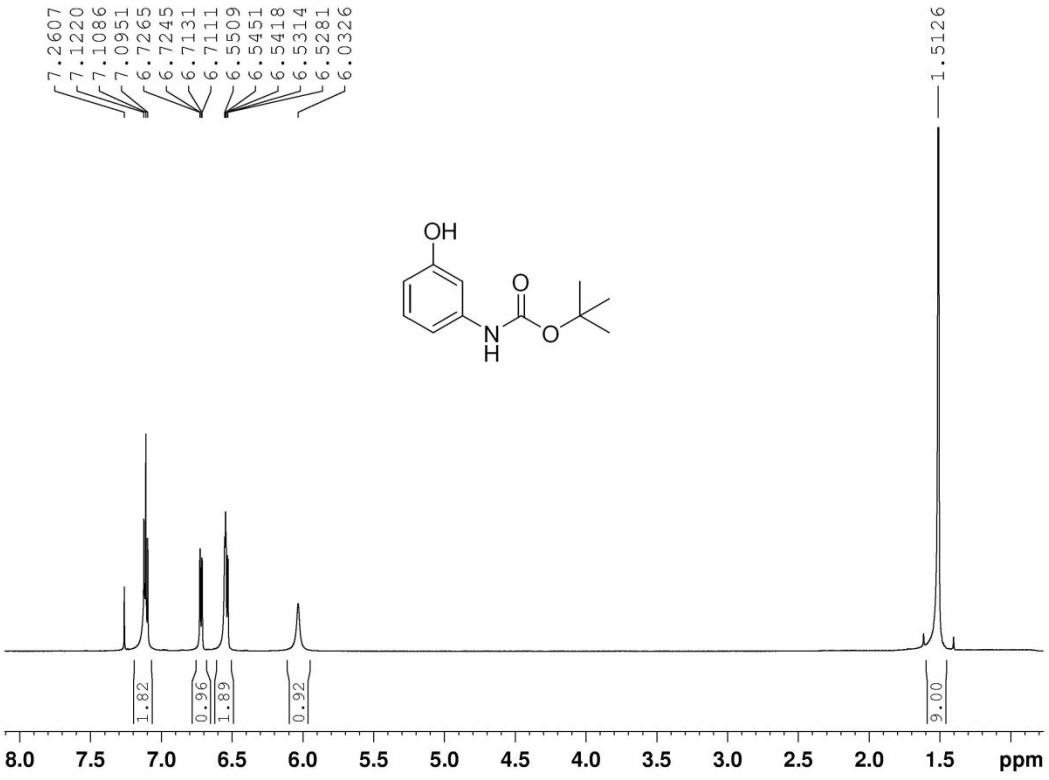


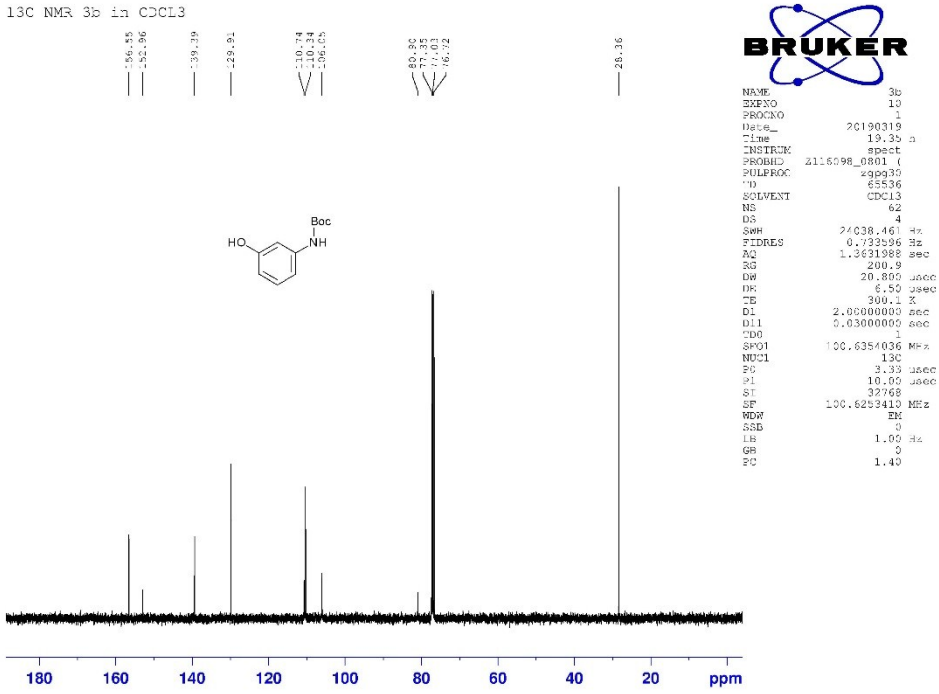
NAME	3a
EXPNO	10
PROCNO	1
Date_	20190319
Time	19.10 h
INSTRUM	spect
PROBHD	Z116098_0801 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	72
DS	4
SWH	24038.461 Hz
FIDRES	0.733596 Hz
AQ	1.3631988 sec
RG	200.9
DW	20.800 usec
DE	6.50 usec
TE	300.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	100.6354036 MHz
NUC1	13C
PC	3.33 usec
P1	10.00 usec
SI	32768
SF	100.6253419 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

tert-Butyl (3-hydroxyphenyl)carbamate (**3b**)

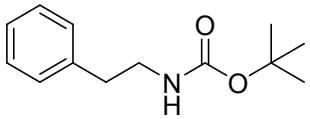

OH
O
N
H
O

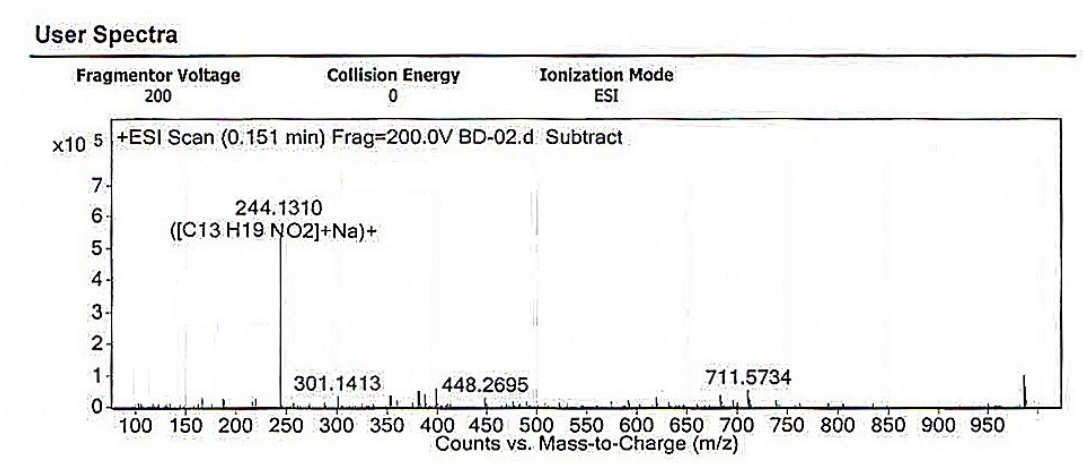

User Spectra
Fragmentor Voltage
200
Collision Energy
0
Ionization Mode
ESI
x10 6
+ESI Scan (0.118 min) Frag=200.0V BD-01.d Subtract
232.0946
([C11 H15 N O3]+Na)+
453.1999
562.3713
711.5757
Counts vs. Mass-to-Charge (m/z)

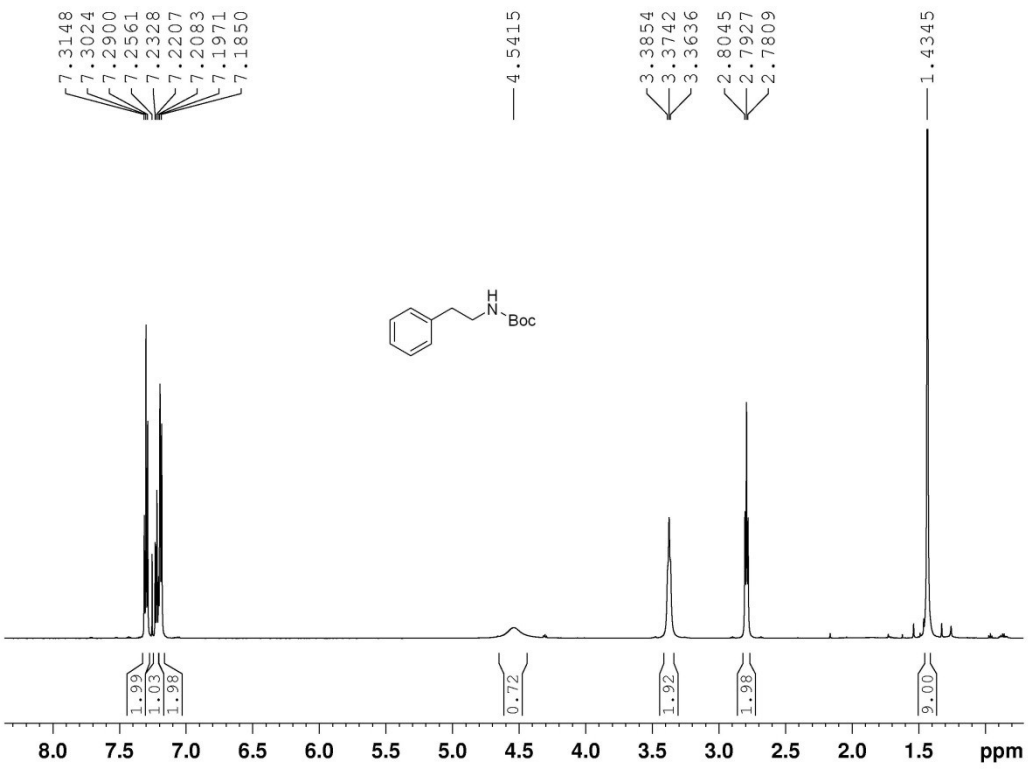

7.2607
7.1220
7.1086
7.0951
6.7265
6.7245
6.7131
6.7111
6.5509
6.5451
6.5418
6.5314
6.5281
6.0326
1.5126
OH
O
N
H
O
1.82
0.96
1.89
0.92
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

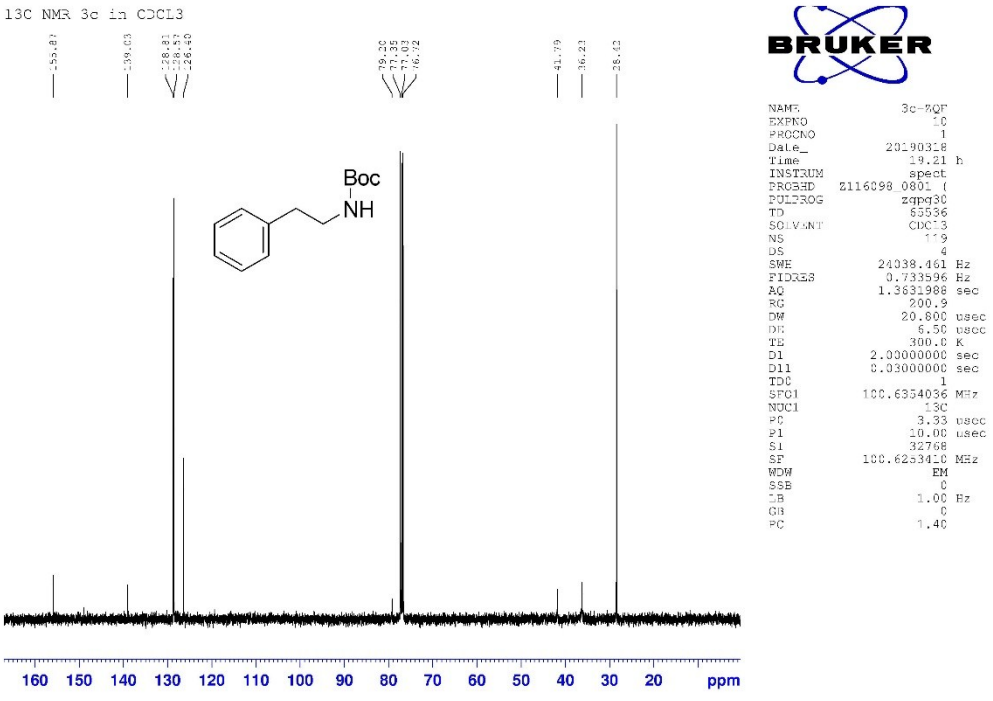


tert-Butyl phenethylcarbamate (**3c**)

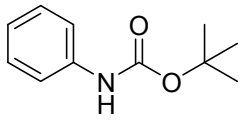


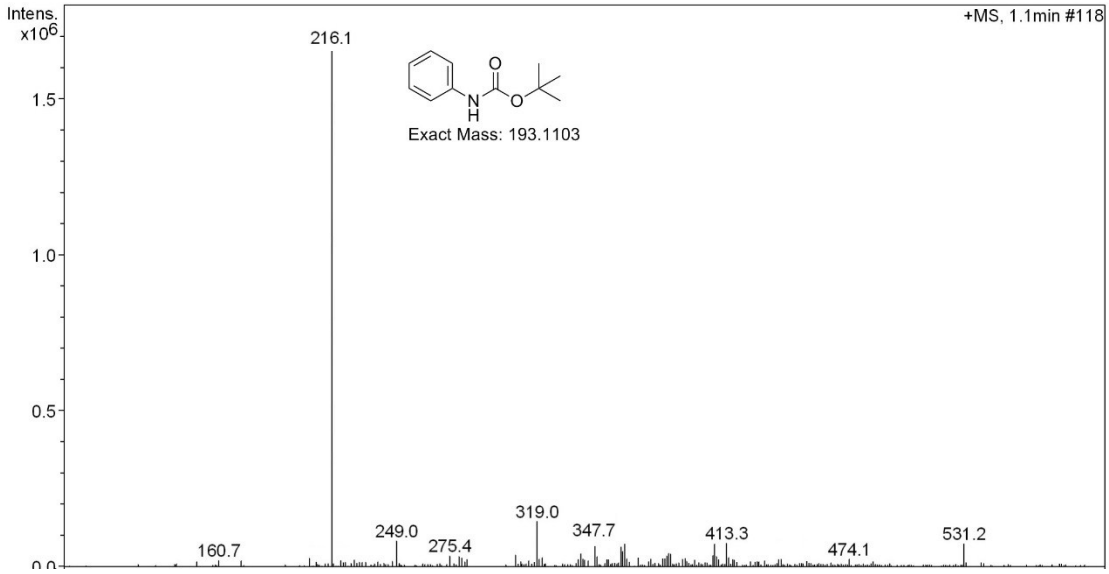


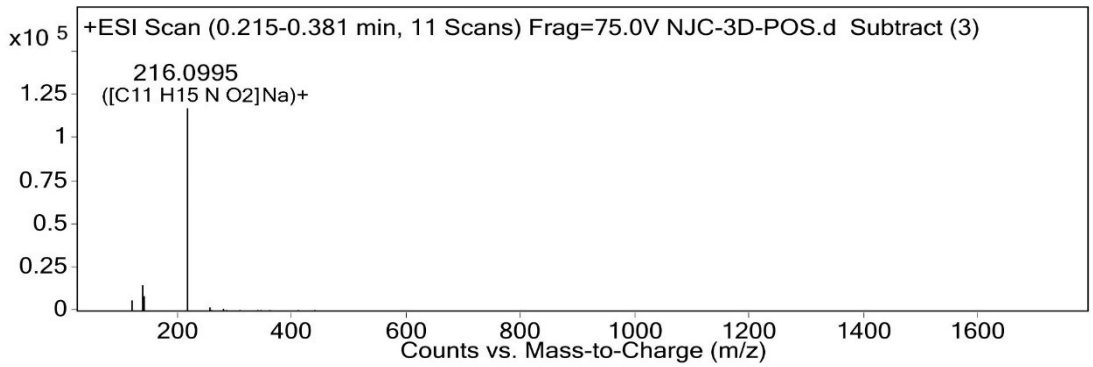


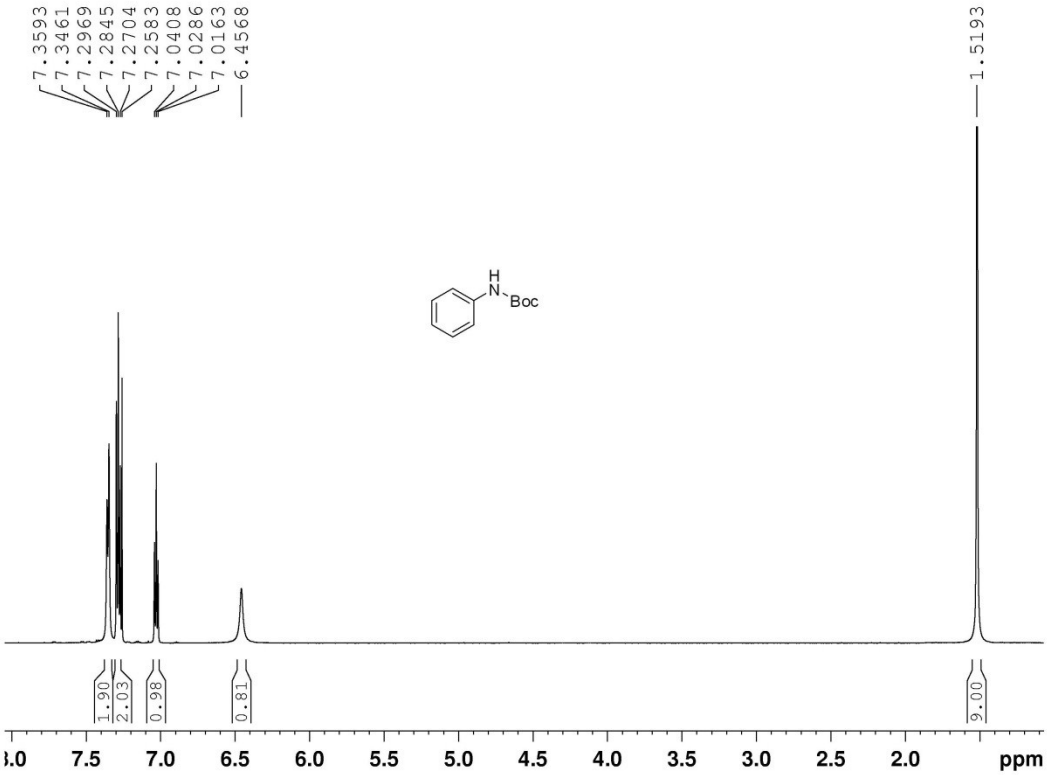


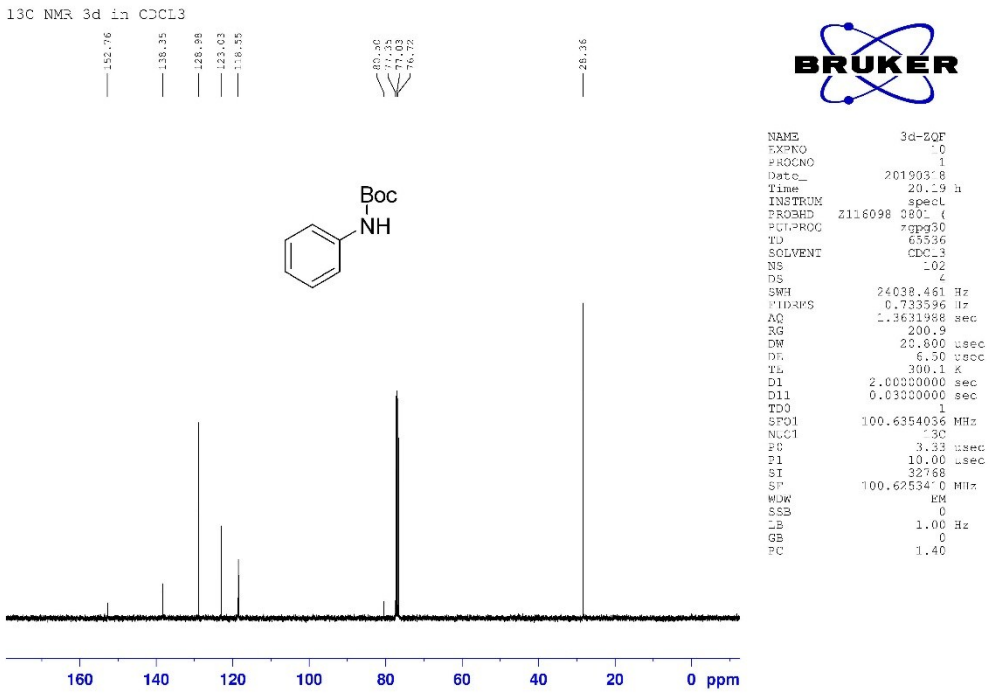
tert-Butyl phenylcarbamate (**3d**)



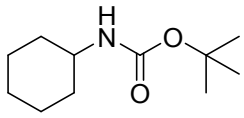

Intens.
x10^6
+MS, 1.1min #118
216.1
Exact Mass: 193.1103
1.5
1.0
0.5
160.7
249.0
275.4
319.0
347.7
413.3
474.1
531.2


x10 5
+ESI Scan (0.215-0.381 min, 11 Scans) Frag=75.0V NJC-3D-POS.d Subtract (3)
216.0995
([C11 H15 N O2]Na)+
1.25
1
0.75
0.5
0.25
0
200
400
600
800
1000
1200
1400
1600
Counts vs. Mass-to-Charge (m/z)

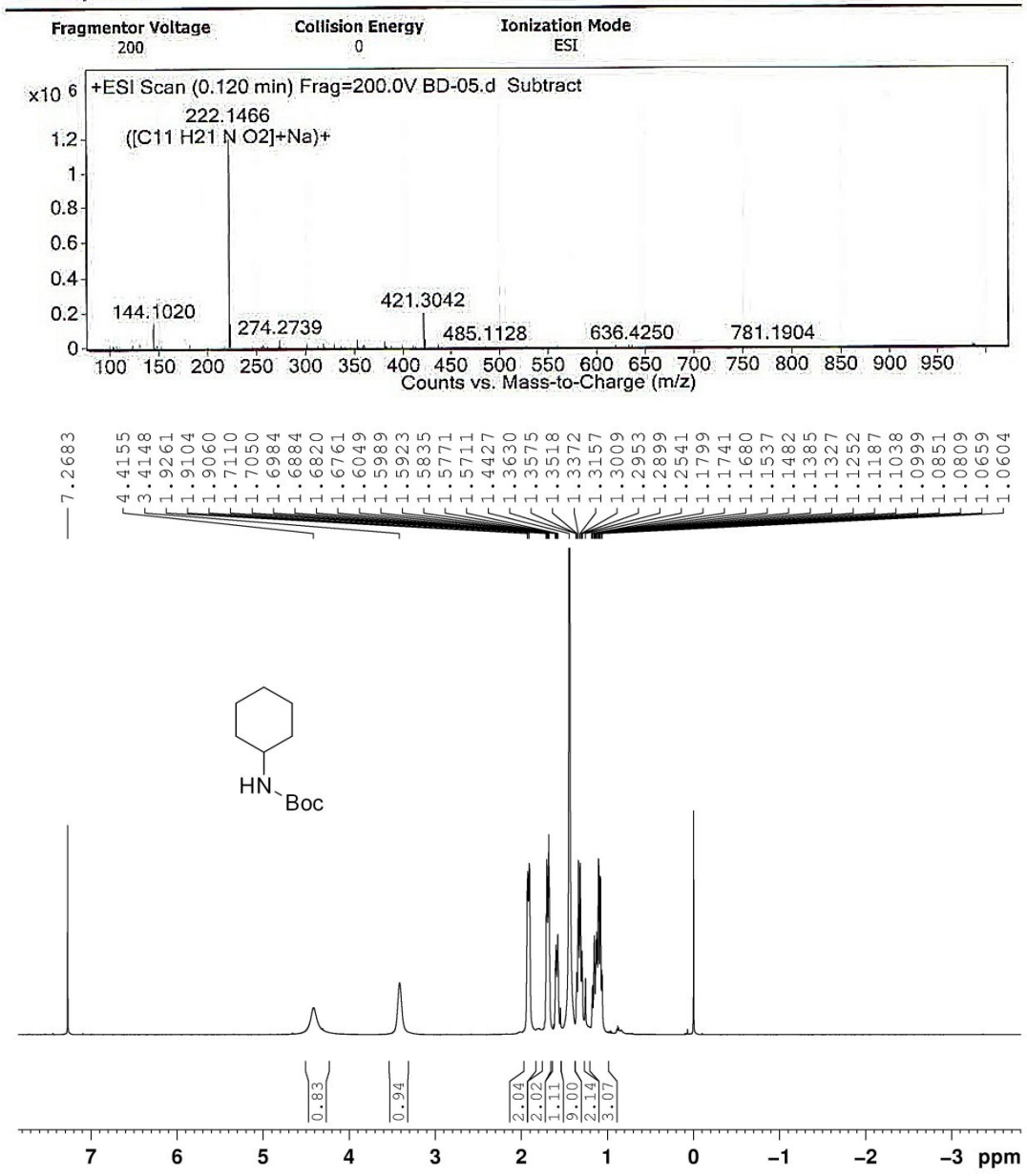


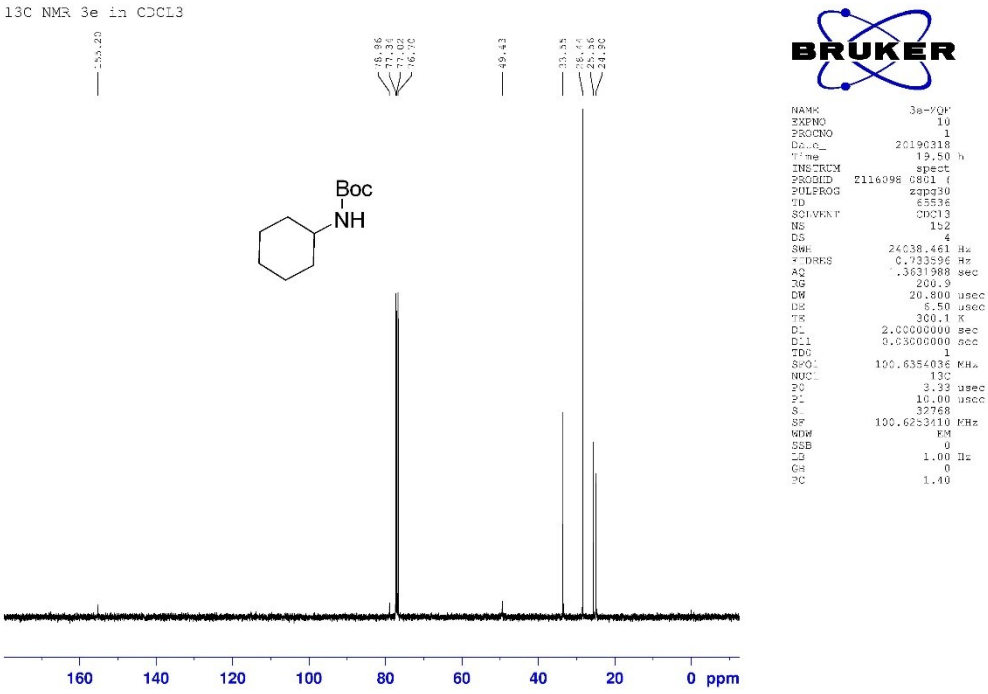


tert-Butyl cyclohexylcarbamate (**3e**)

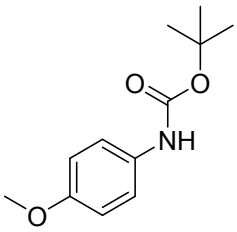


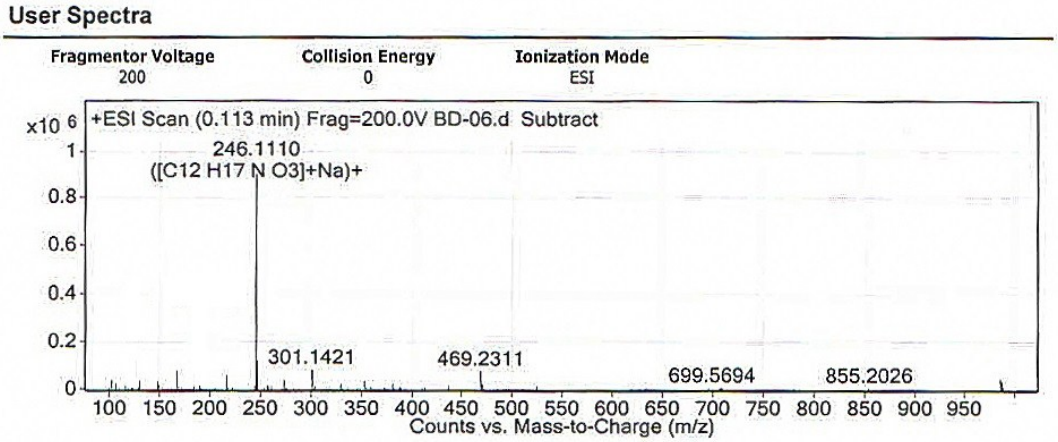
User Spectra

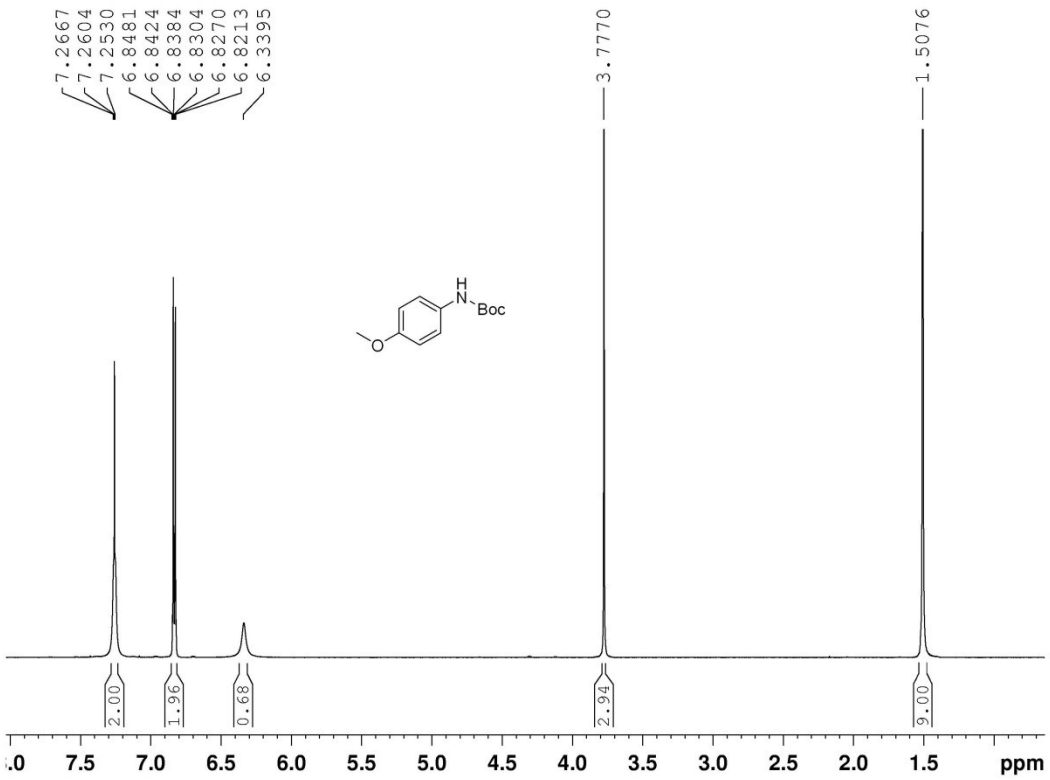


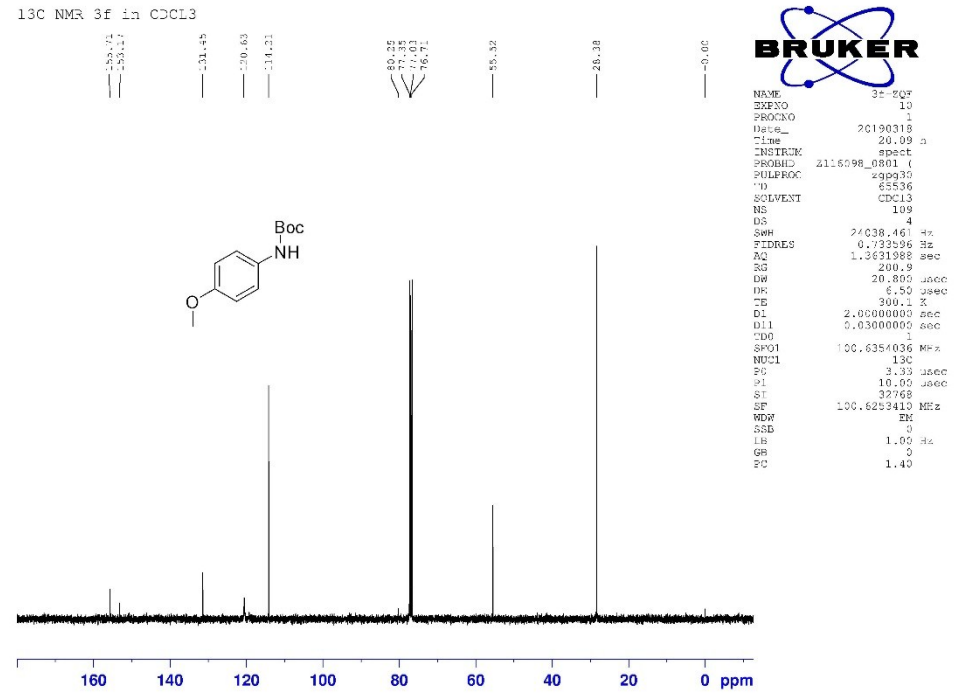


tert-Butyl (4-methoxyphenyl)carbamate (**3f**)

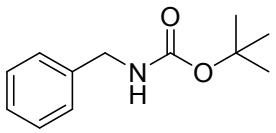


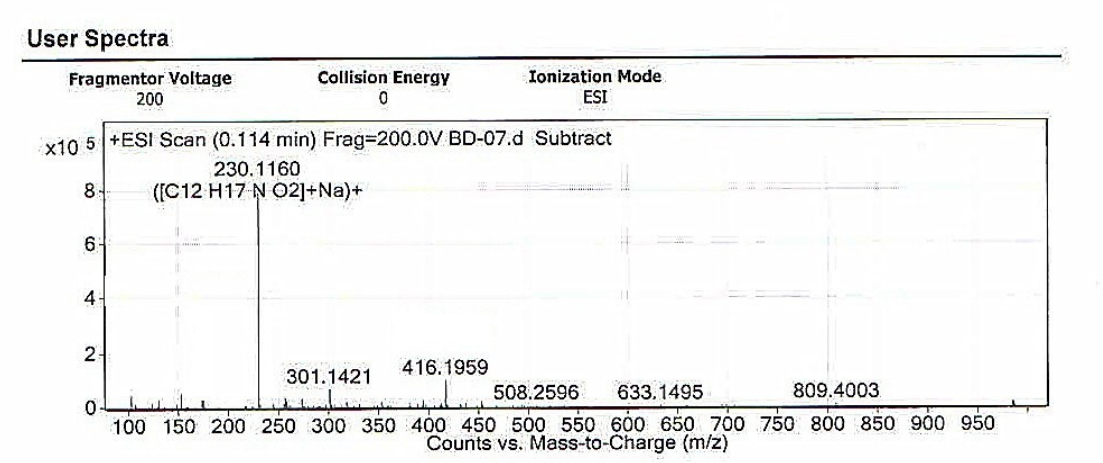


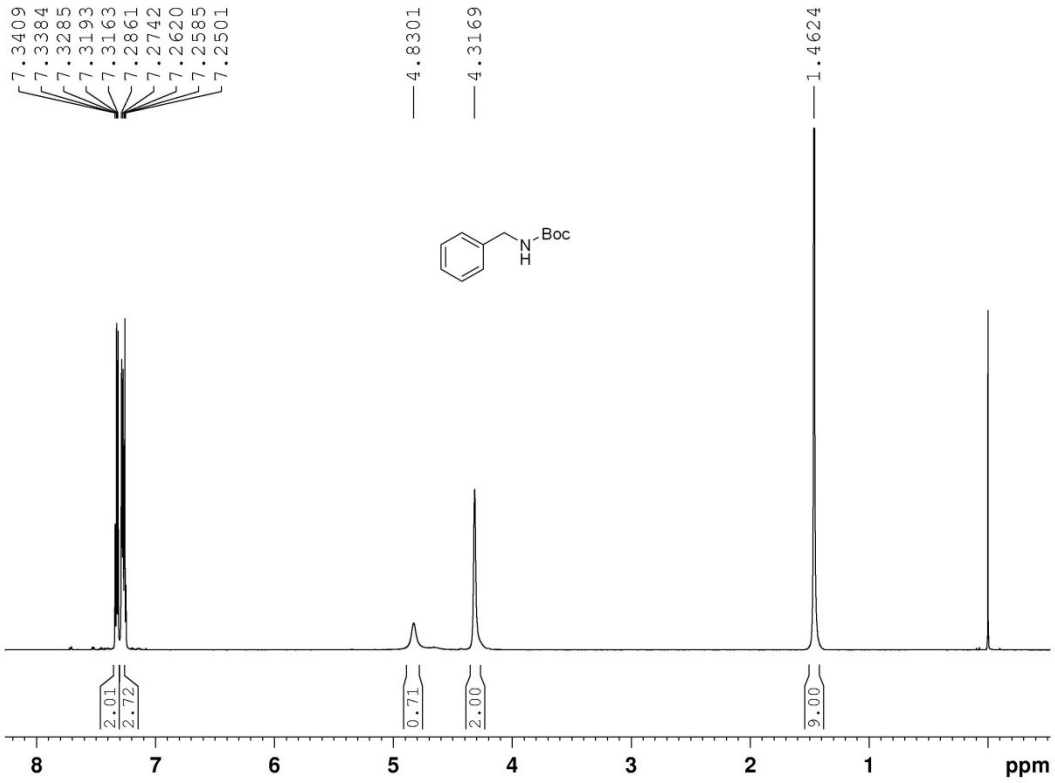


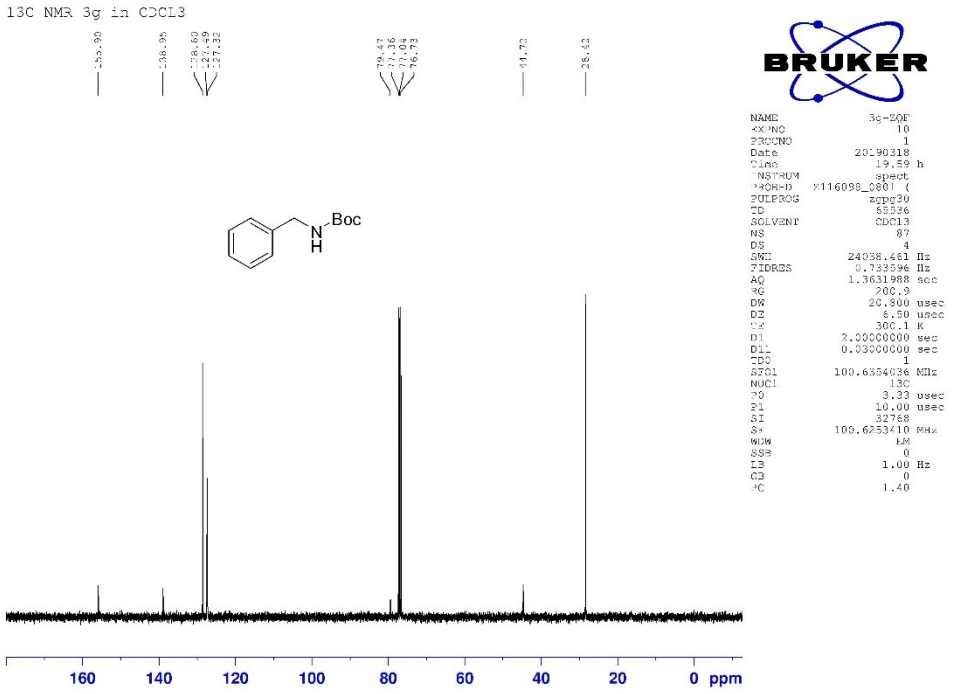


tert-Butyl benzylcarbamate (**3g**)

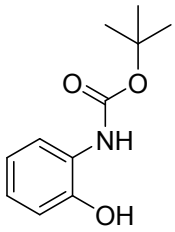


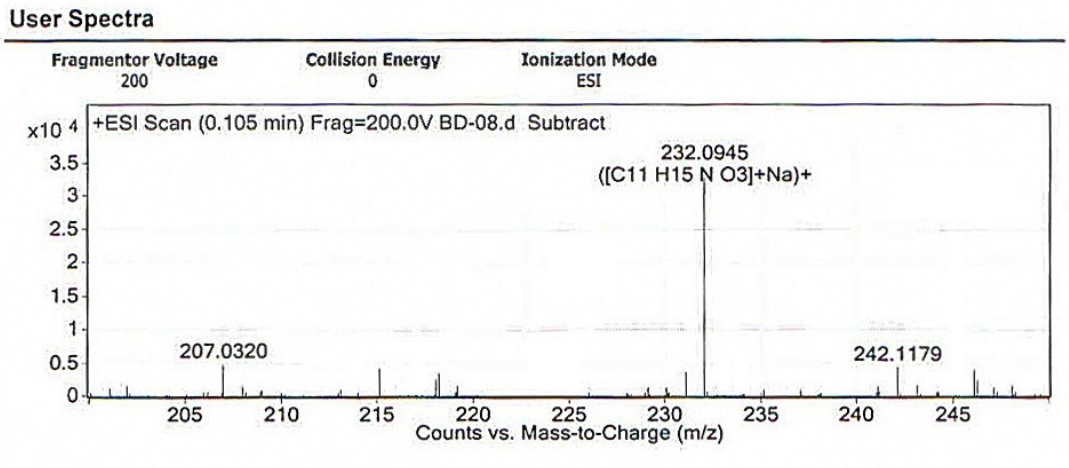

User Spectra
Fragmentor Voltage
200
Collision Energy
0
Ionization Mode
ESI
x10 5
+ESI Scan (0.114 min) Frag=200.0V BD-07.d Subtract
230.1160
([C12 H17 N O2]+Na)+
301.1421
416.1959
508.2596
633.1495
809.4003
Counts vs. Mass-to-Charge (m/z)

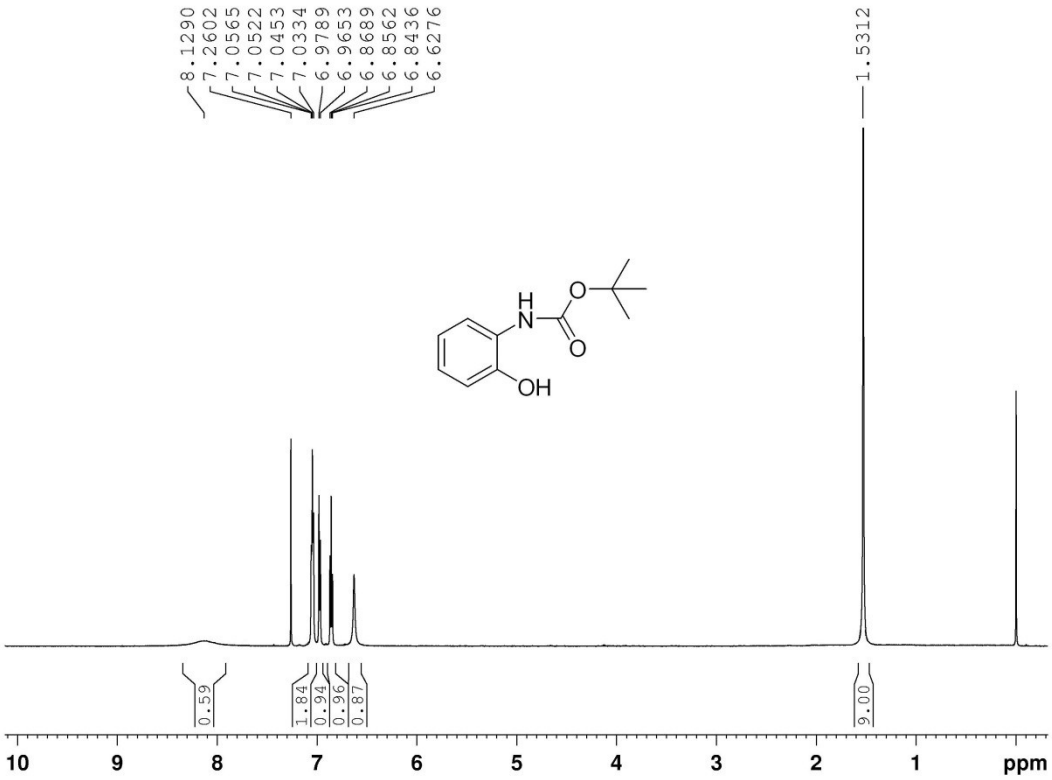

7.3409
7.3384
7.3285
7.3193
7.3163
7.2861
7.2742
7.2620
7.2585
7.2501
4.8301
4.3169
1.4624
Boc
2.01
2.72
0.71
2.00
9.00
ppm

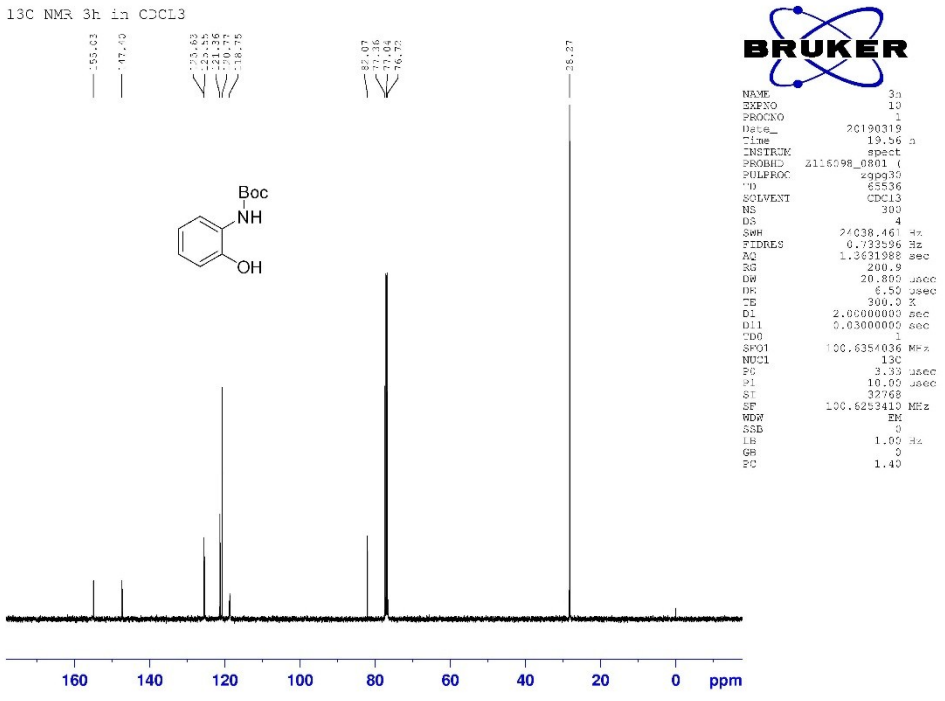


tert-Butyl (2-hydroxyphenyl)carbamate (**3h**)

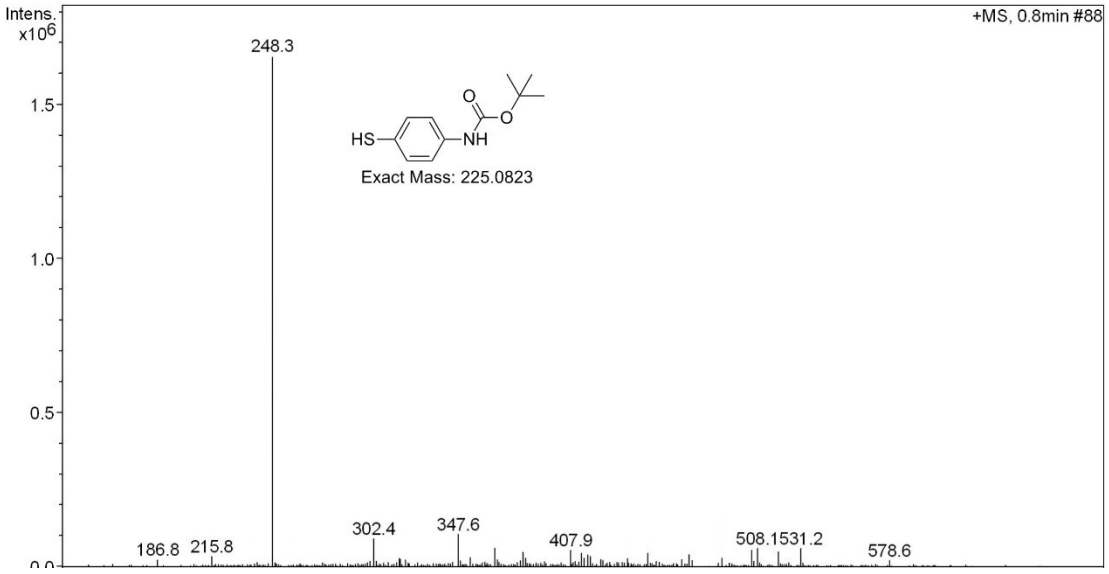


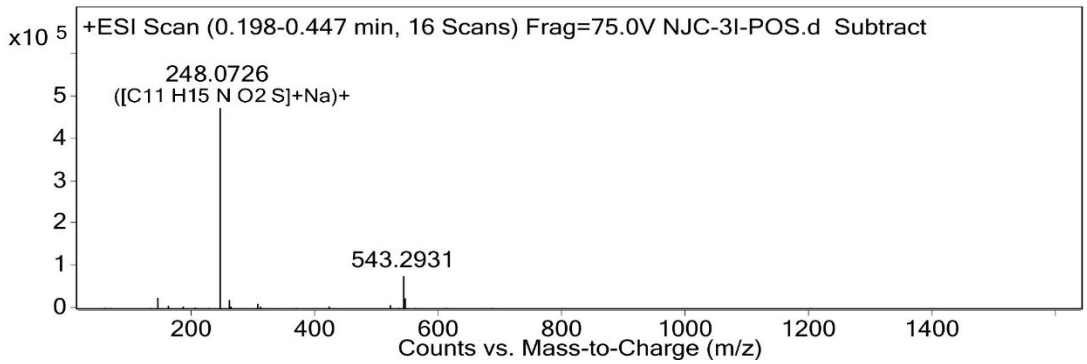


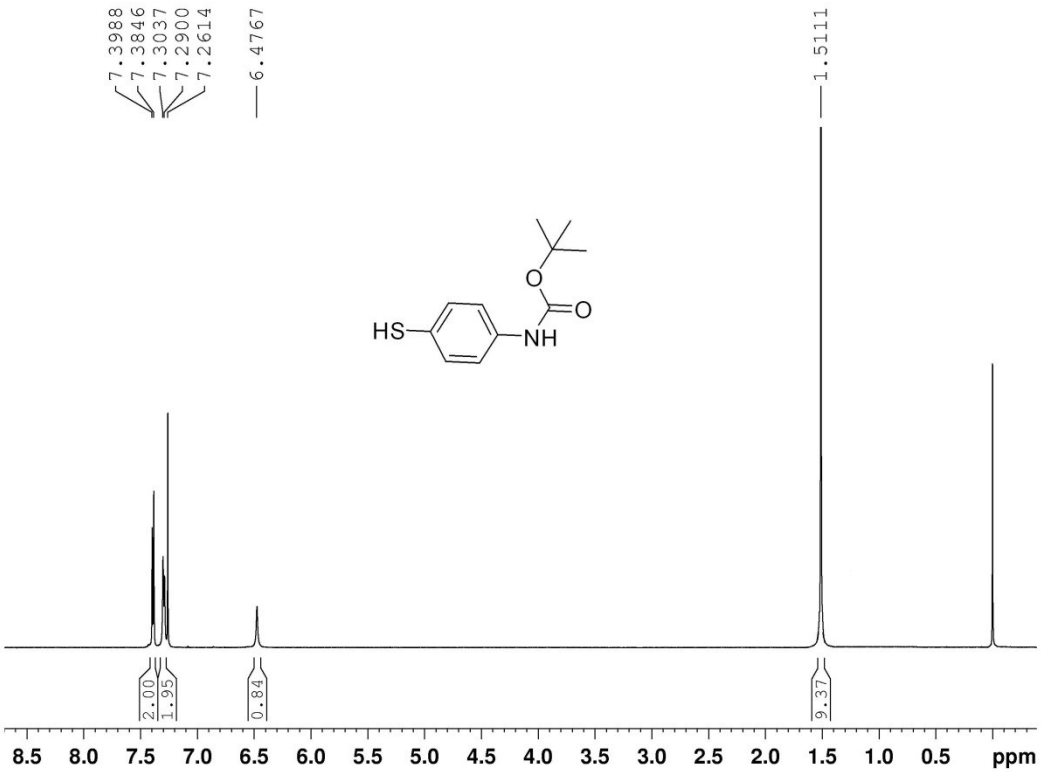


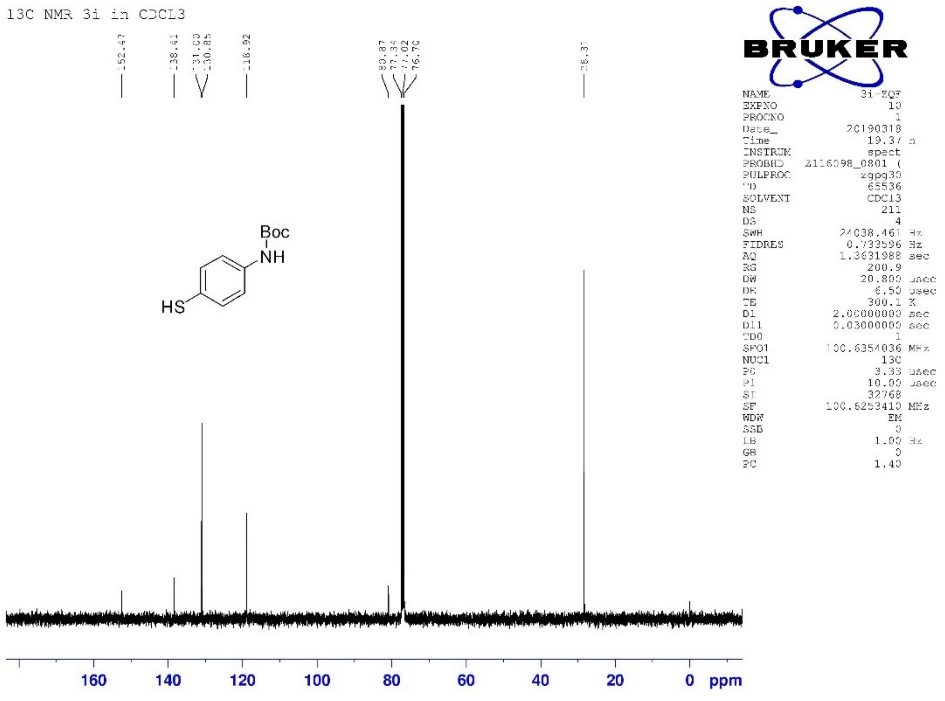


tert-Butyl (4-mercaptophenyl)carbamate (**3i**)

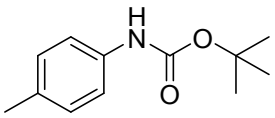

Intens.
x10^6
+MS, 0.8min #88
248.3
1.5
1.0
0.5
HS
NH
O
O
Exact Mass: 225.0823
186.8
215.8
302.4
347.6
407.9
508.1531.2
578.6

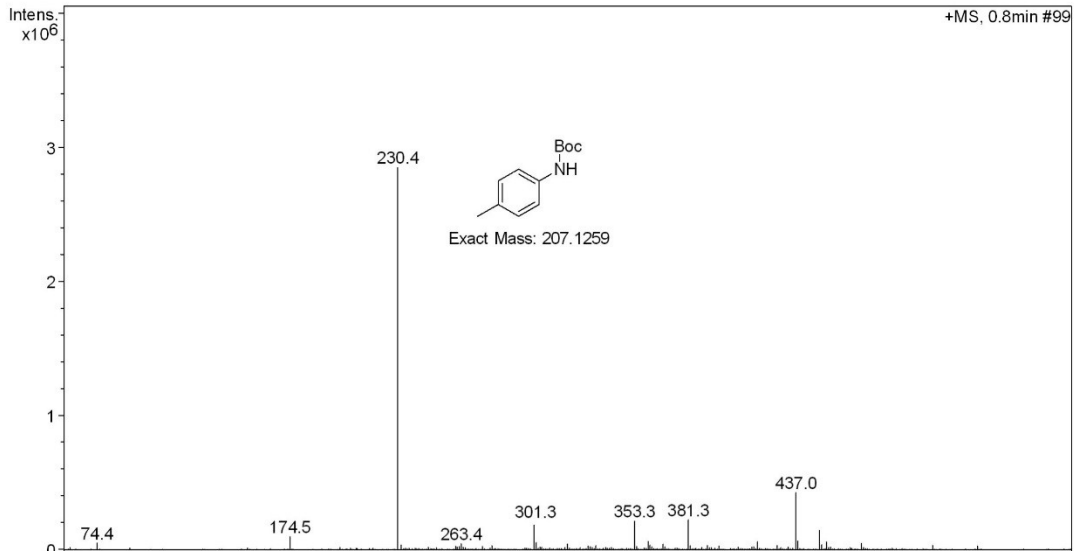

x10 5
+ESI Scan (0.198-0.447 min, 16 Scans) Frag=75.0V NJC-3I-POS.d Subtract
248.0726
([C11 H15 N O2 S]+Na)+
5
4
3
2
1
0
543.2931
200
400
600
800
1000
1200
1400
Counts vs. Mass-to-Charge (m/z)

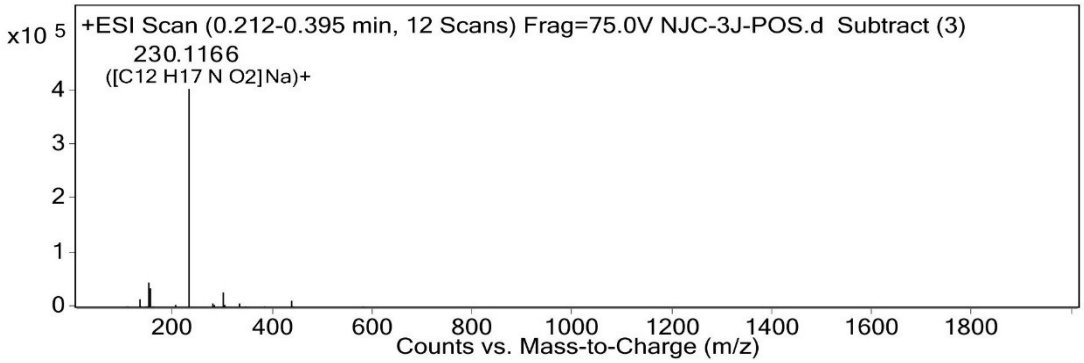


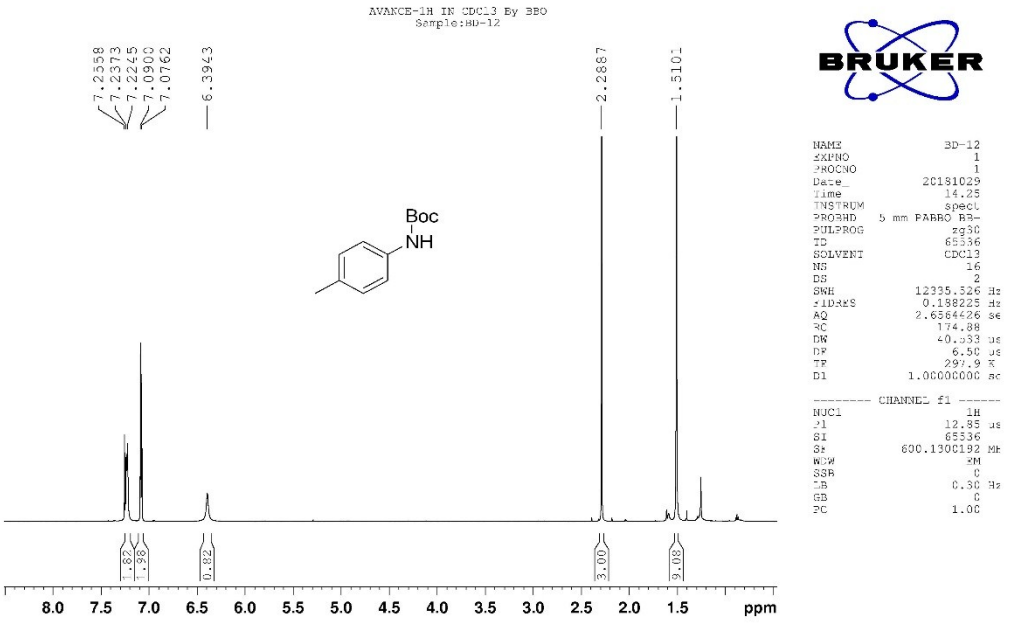


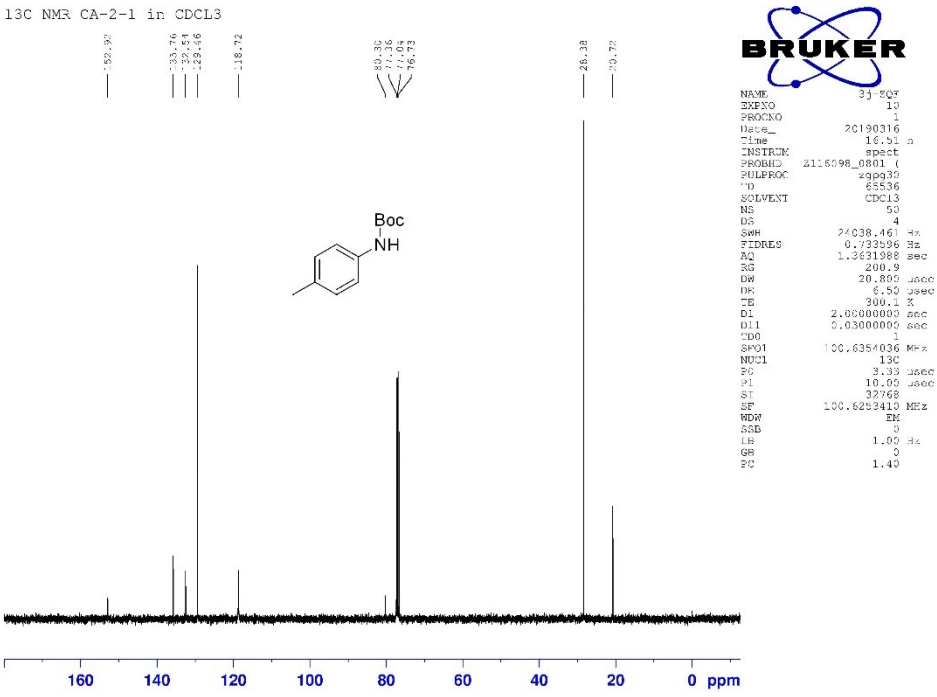
tert-Butyl *p*-tolylcarbamate (**3j**)


H
N
O
O

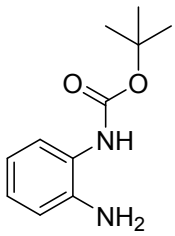

Intens.
x10^6
+MS, 0.8min #99
230.4
Boc
NH
Exact Mass: 207.1259
74.4
174.5
263.4
301.3
353.3
381.3
437.0

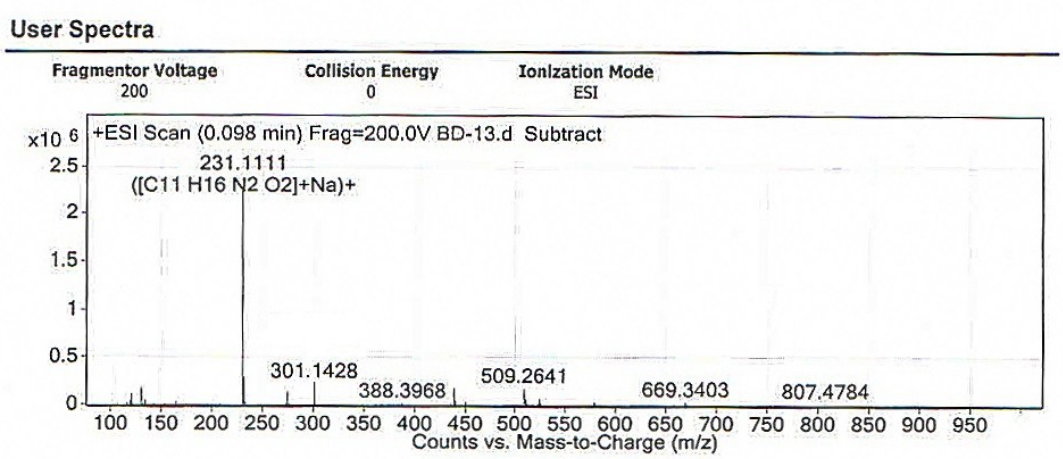

x10 5
+ESI Scan (0.212-0.395 min, 12 Scans) Frag=75.0V NJC-3J-POS.d Subtract (3)
230.1166
([C12 H17 N O2]Na)+
Counts vs. Mass-to-Charge (m/z)

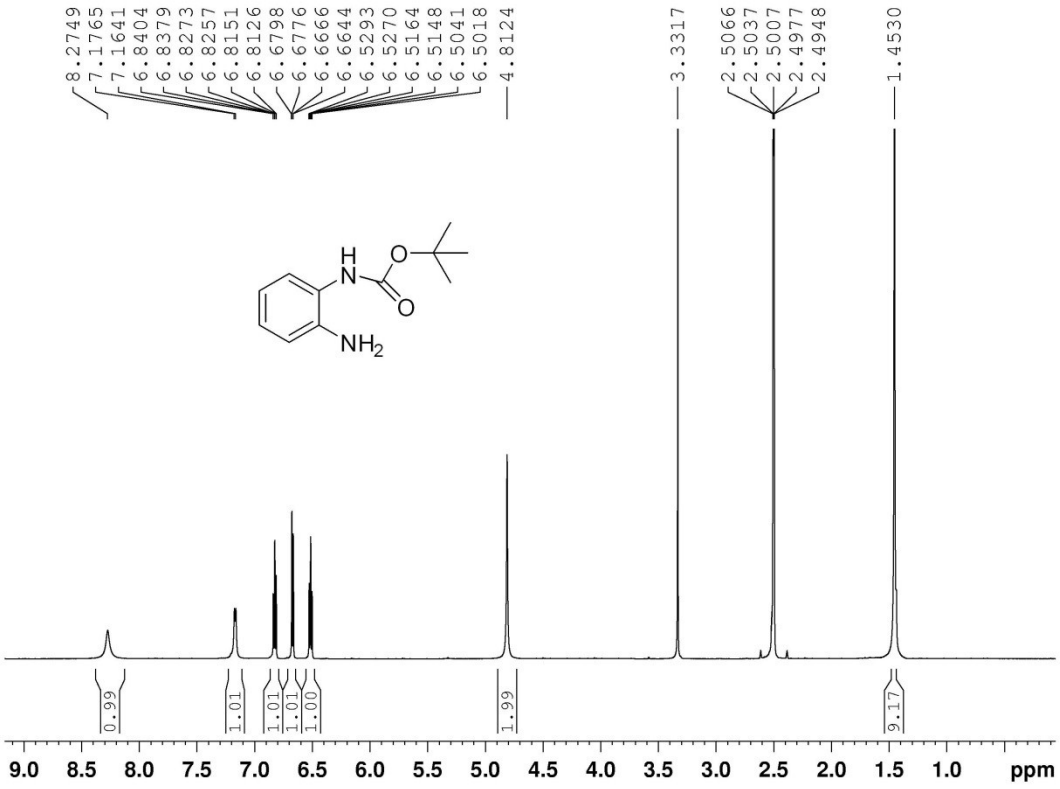


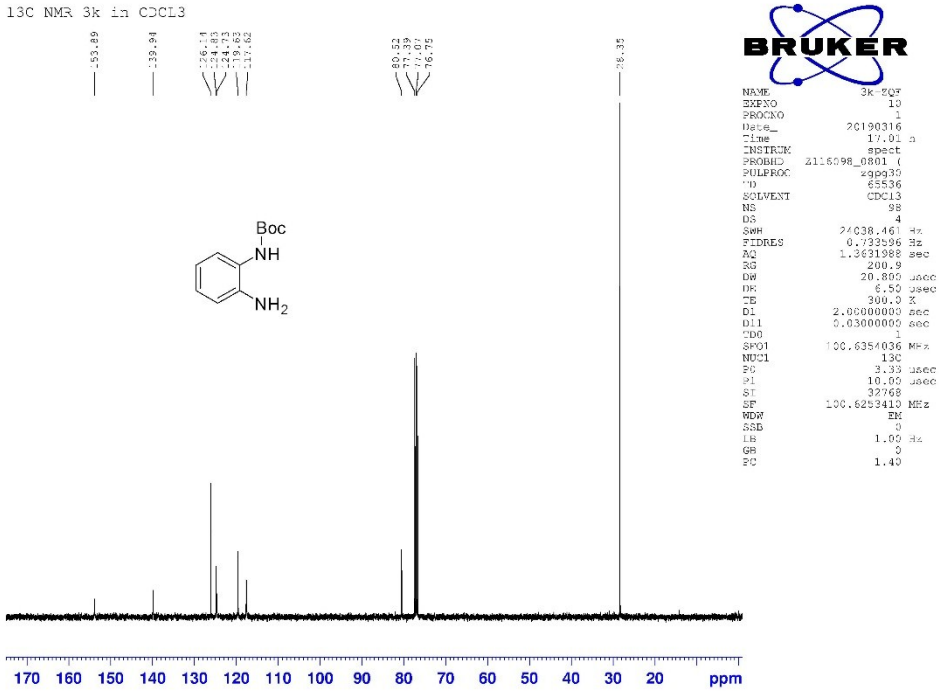


tert-Butyl (2-aminophenyl)carbamate (**3k**)

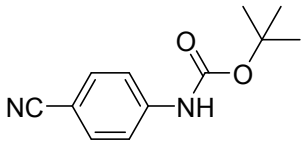

O
O
NH
NH2

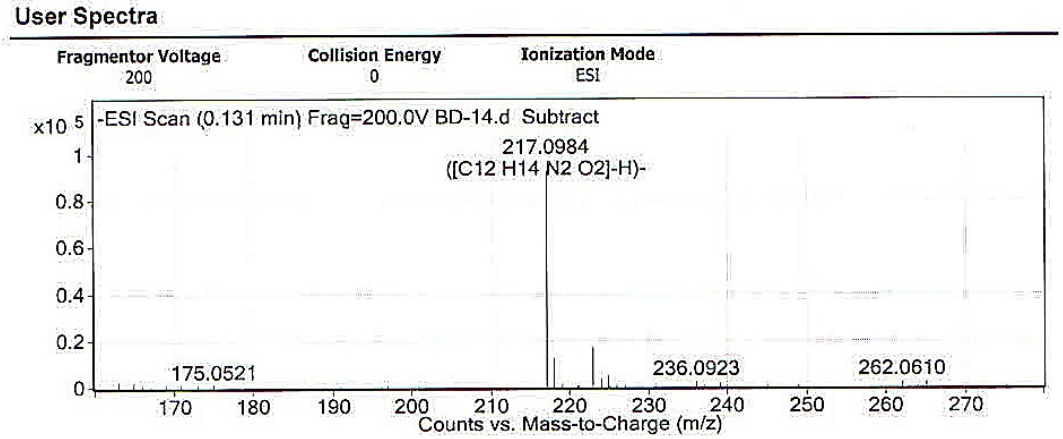

User Spectra
Fragmentor Voltage
200
Collision Energy
0
Ionization Mode
ESI
+ESI Scan (0.098 min) Frag=200.0V BD-13.d Subtract
x10 6
231.1111
([C11 H16 N2 O2]+Na)+
301.1428
388.3968
509.2641
669.3403
807.4784
Counts vs. Mass-to-Charge (m/z)

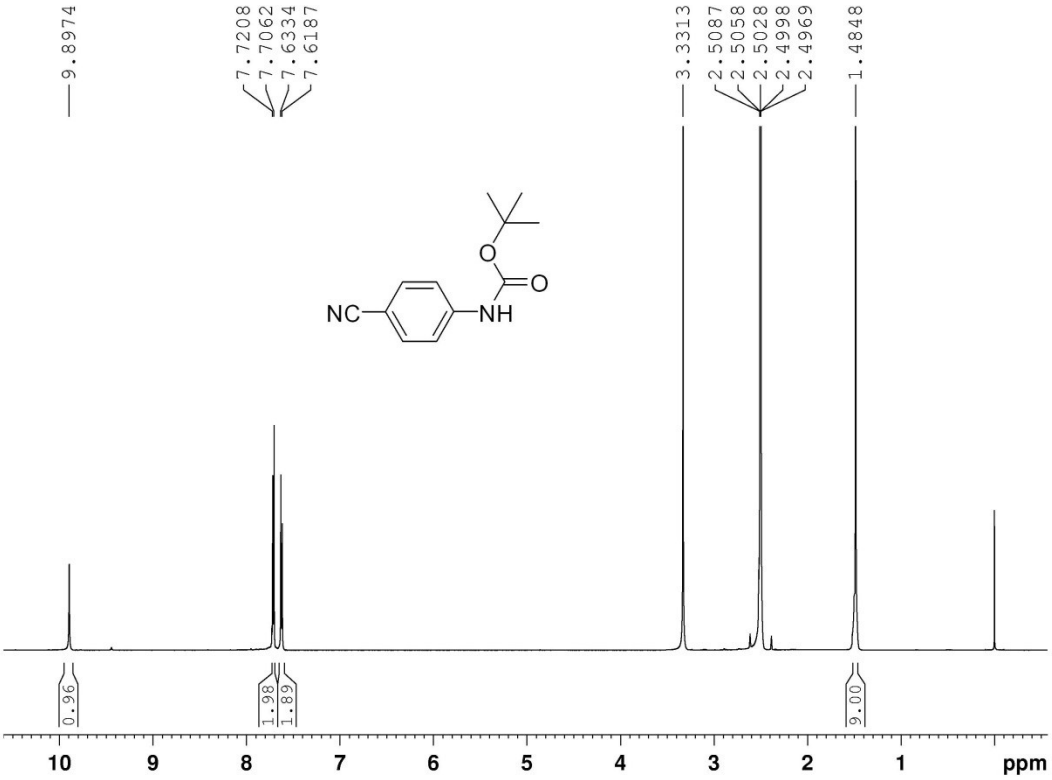

8.2749
7.1765
7.1641
6.8404
6.8379
6.8273
6.8257
6.8151
6.8126
6.6798
6.6776
6.6666
6.6644
6.5293
6.5270
6.5164
6.5148
6.5041
6.5018
4.8124
3.3317
2.5066
2.5037
2.5007
2.4977
2.4948
1.4530
0.99
1.01
1.01
1.01
1.00
1.99
9.17
ppm

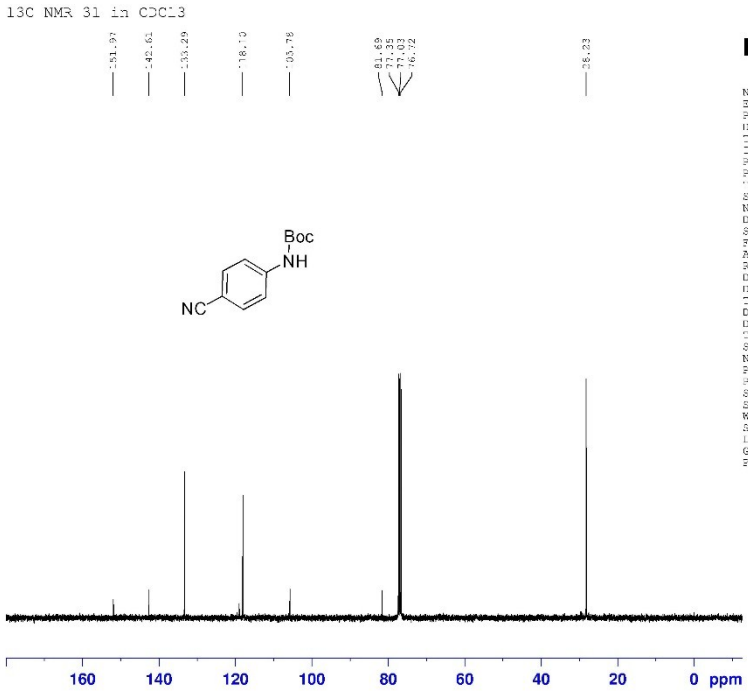


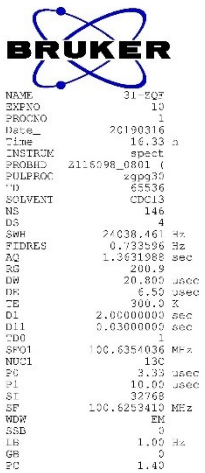
tert-Butyl (4-cyanophenyl)carbamate (**3l**)



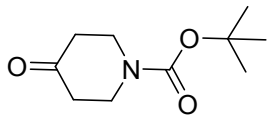


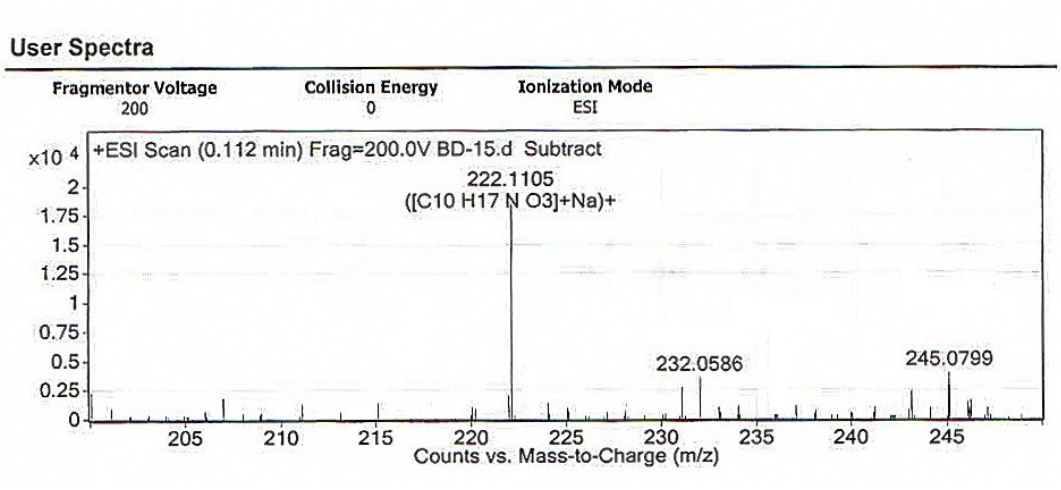


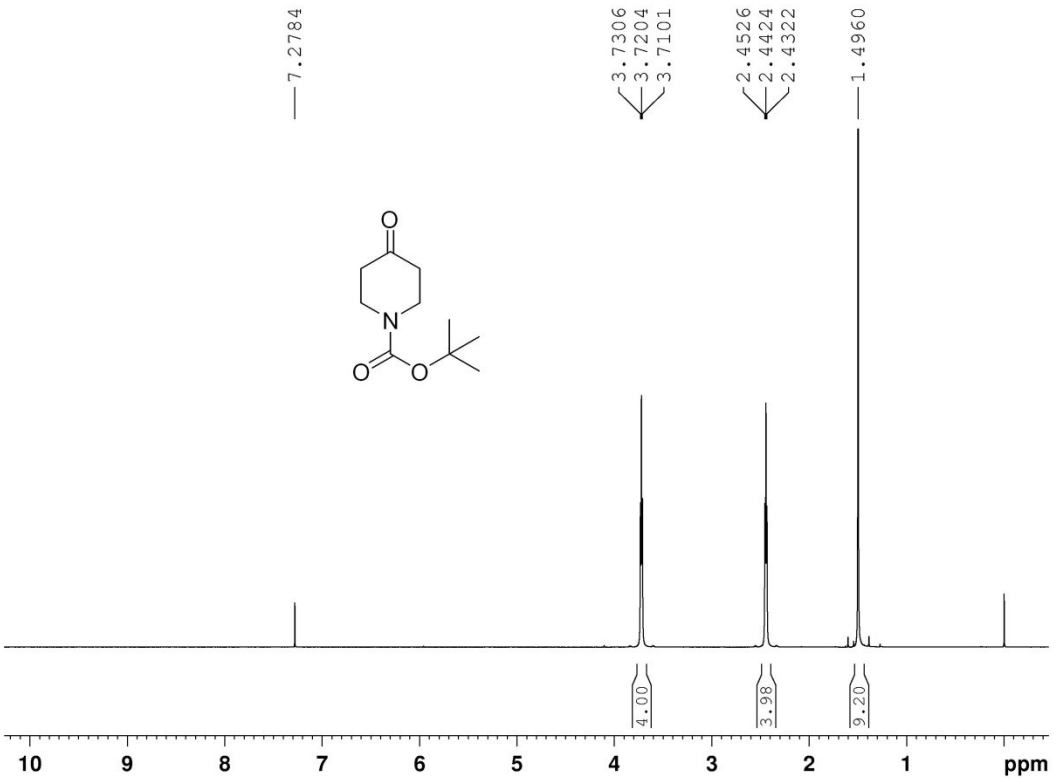


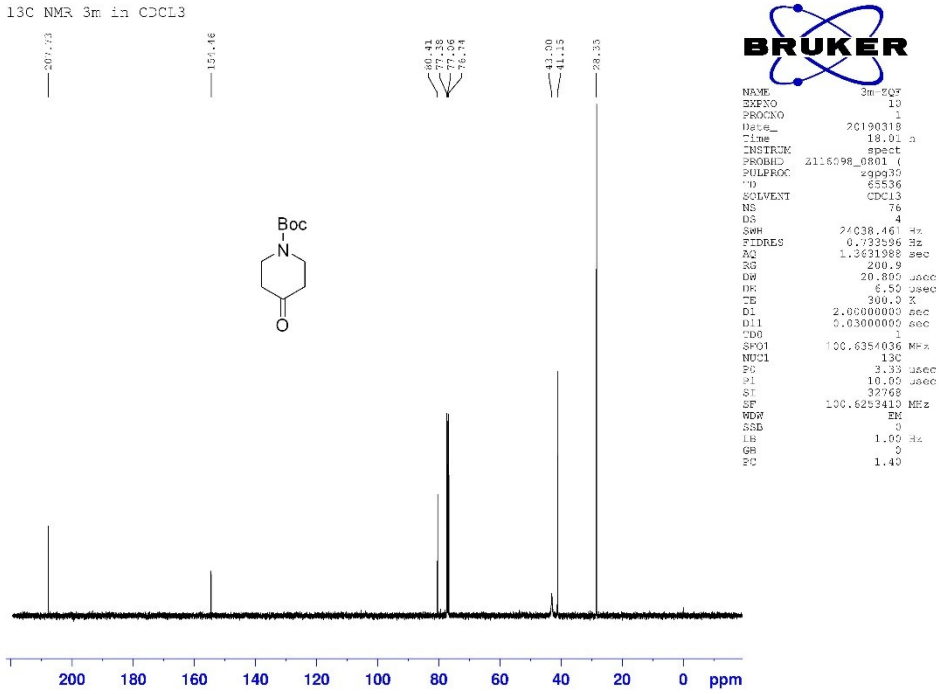


tert-Butyl 4-oxopiperidine-1-carboxylate (**3m**)

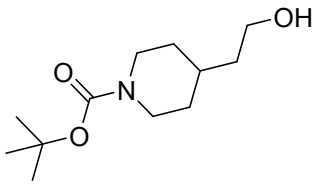


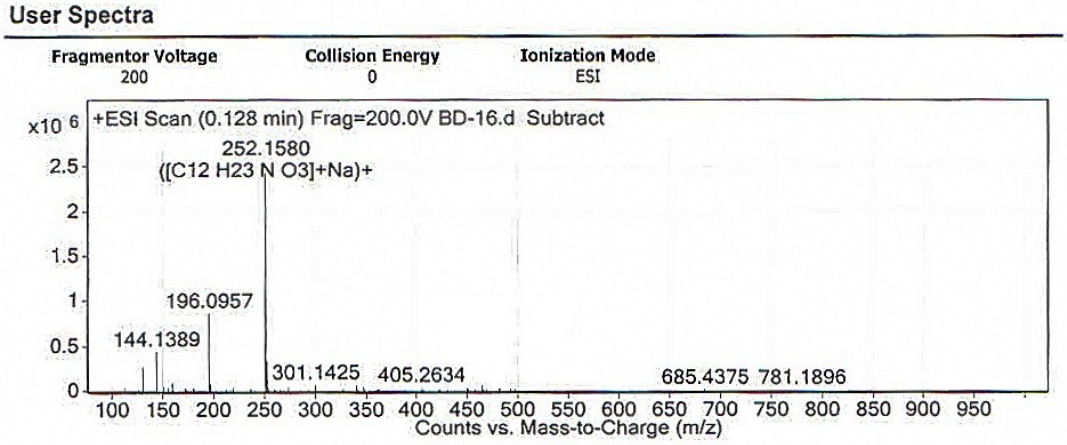

User Spectra
Fragmentor Voltage
200
Collision Energy
0
Ionization Mode
ESI
x10 4
+ESI Scan (0.112 min) Frag=200.0V BD-15.d Subtract
222.1105
([C10 H17 N O3]+Na)+
232.0586
245.0799
Counts vs. Mass-to-Charge (m/z)

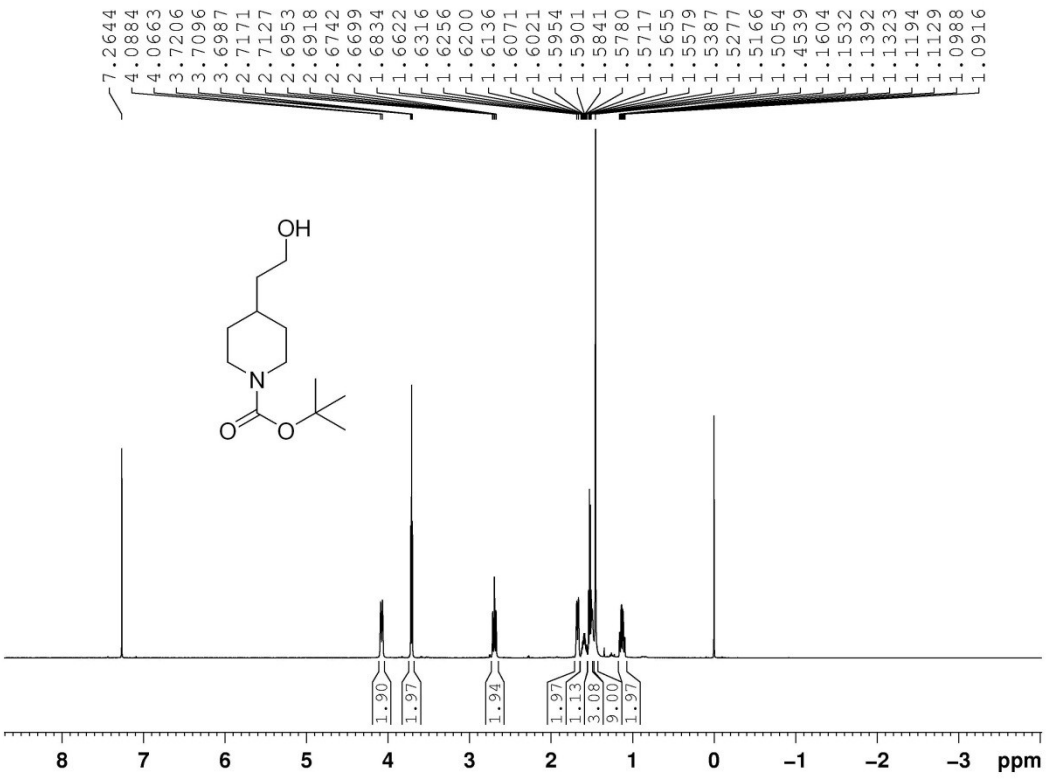

7.2784
3.7306
3.7204
3.7101
2.4526
2.4424
2.4322
1.4960
4.00
3.98
9.20
ppm

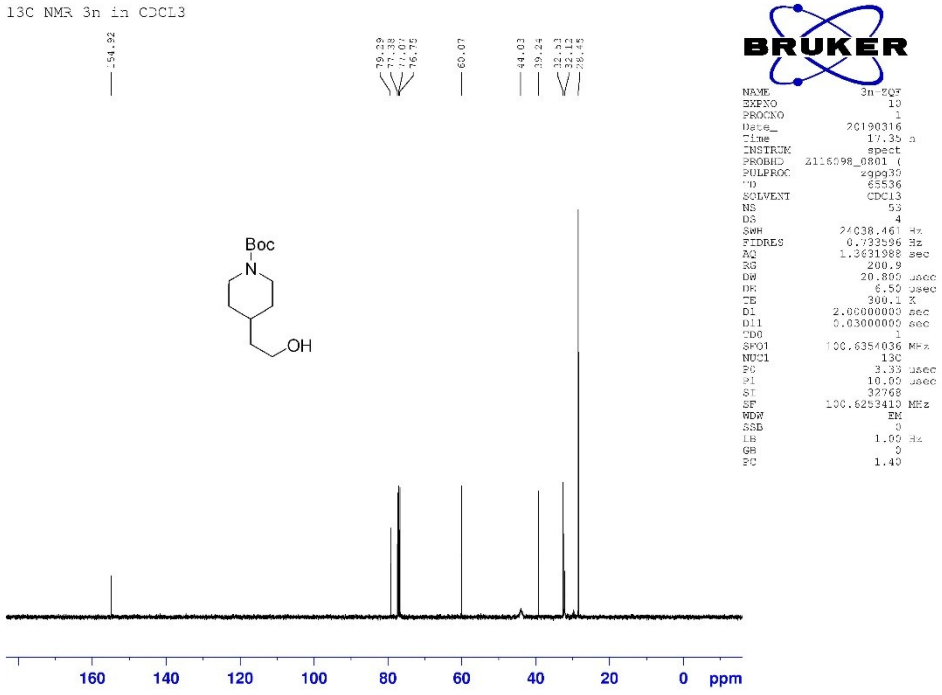


tert-Butyl 4-(2-hydroxyethyl)piperidine-1-carboxylate **(3n)**

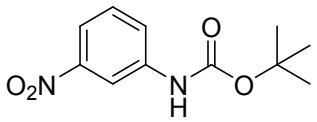




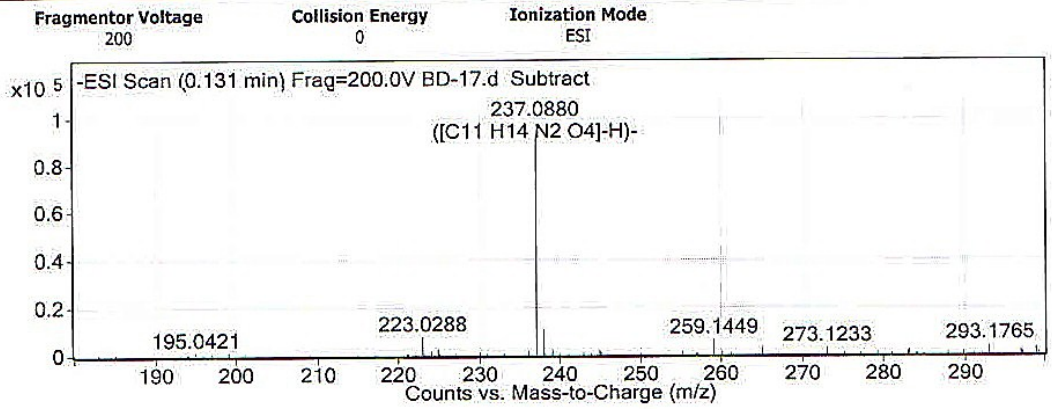


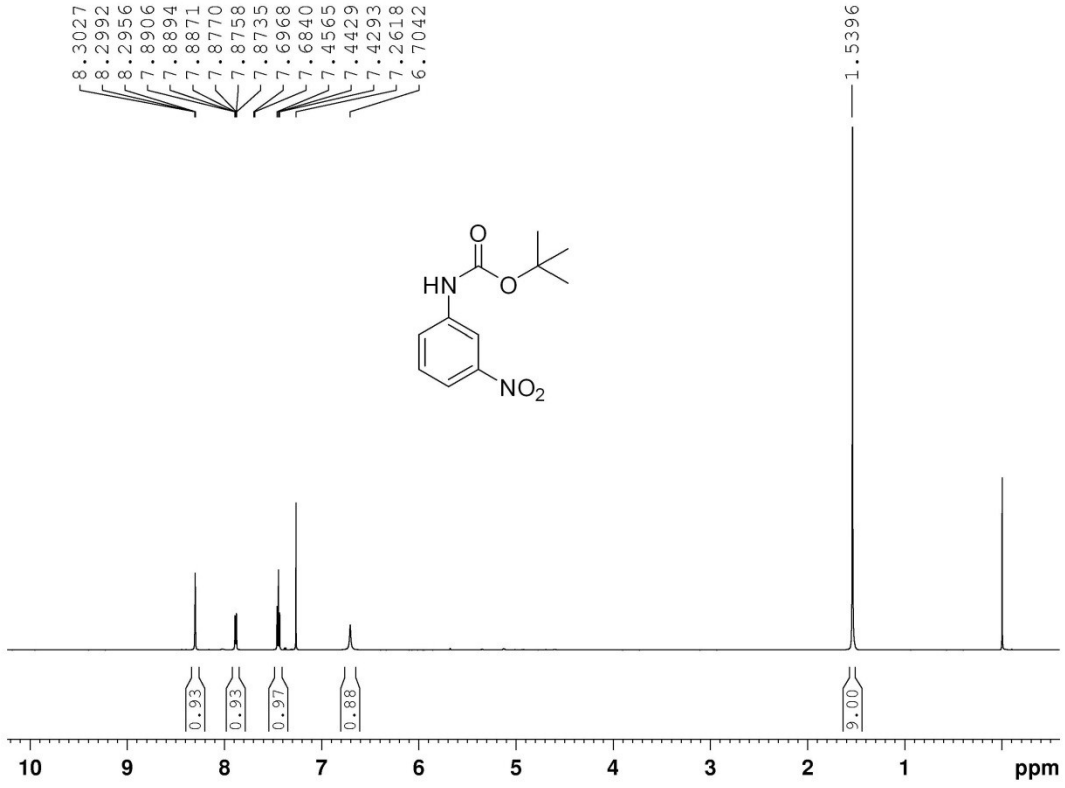


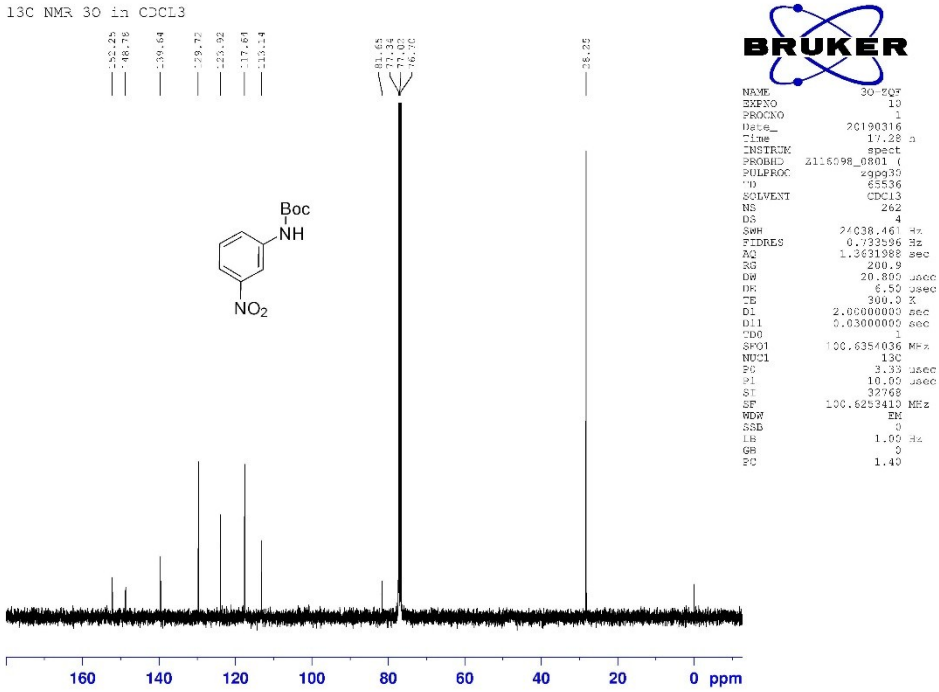
tert-Butyl (3-nitrophenyl)carbamate (**3o**)



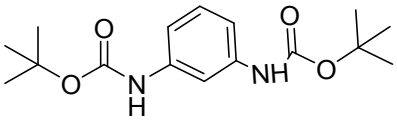
User Spectra

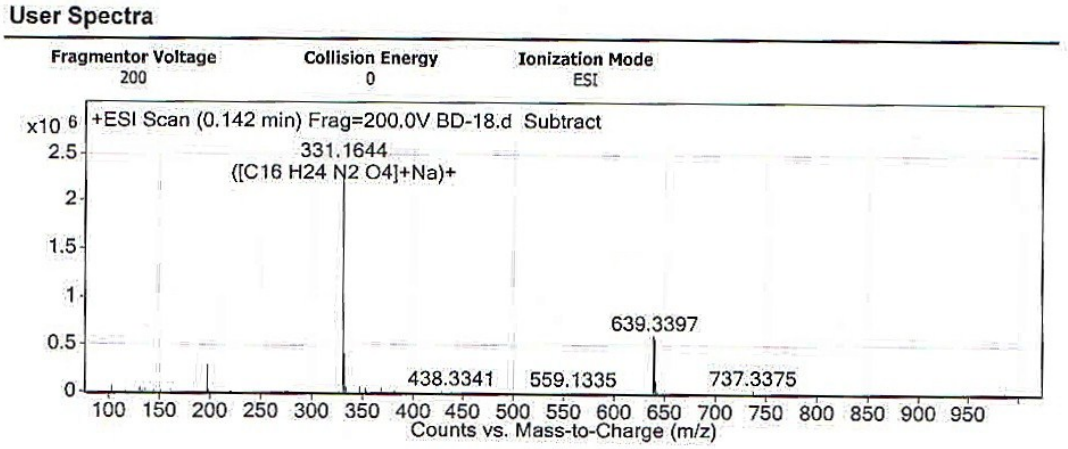


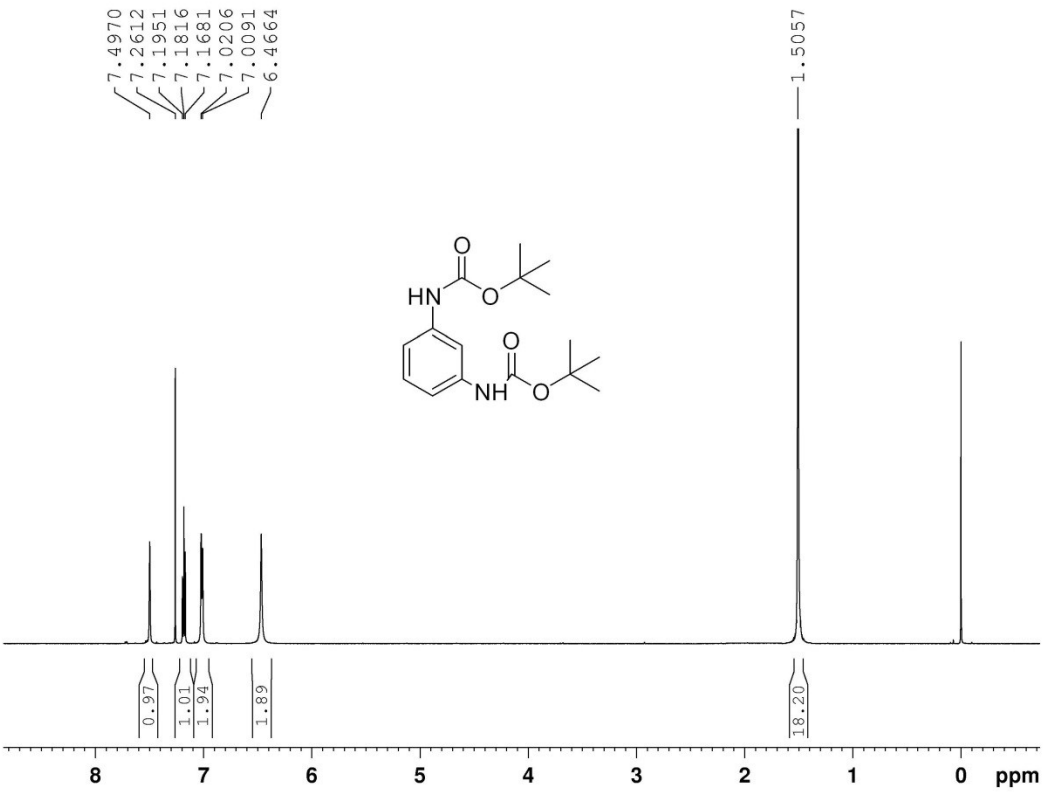


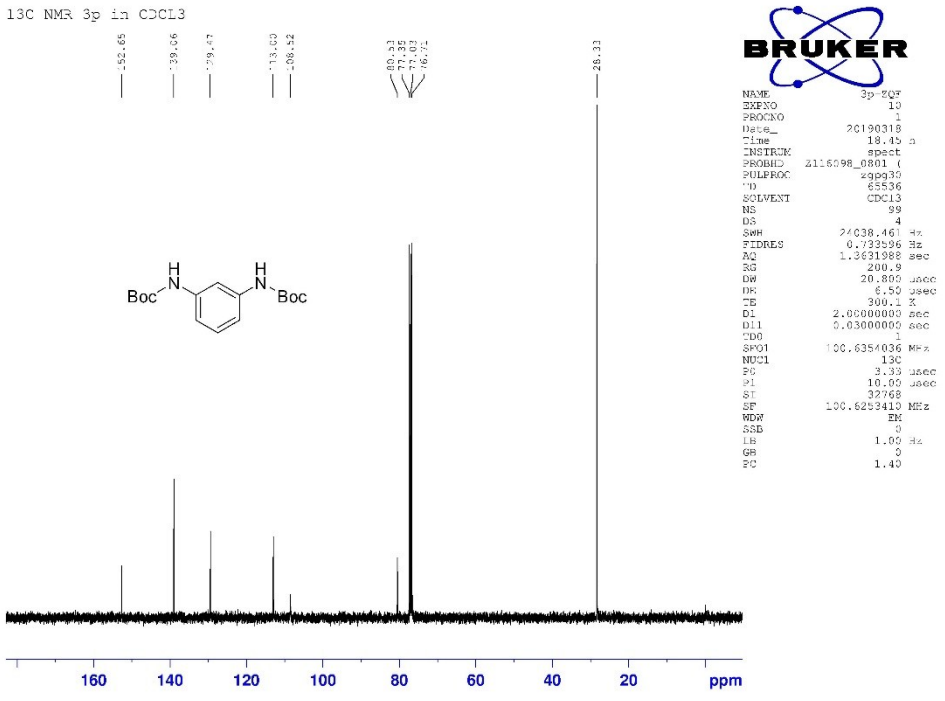


Di-*tert*-butyl 1,3-phenylenedicarbamate (**3p**)

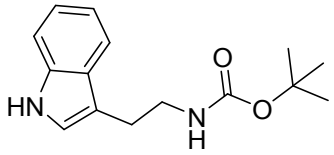


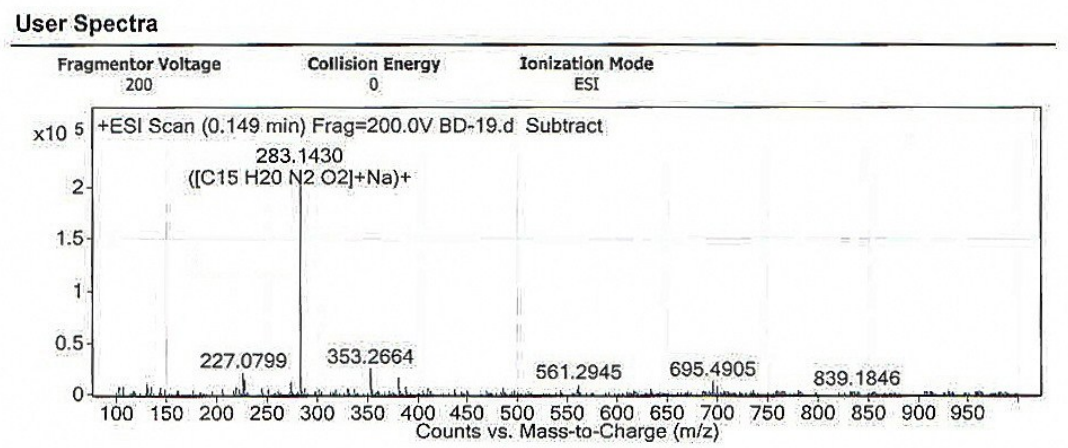


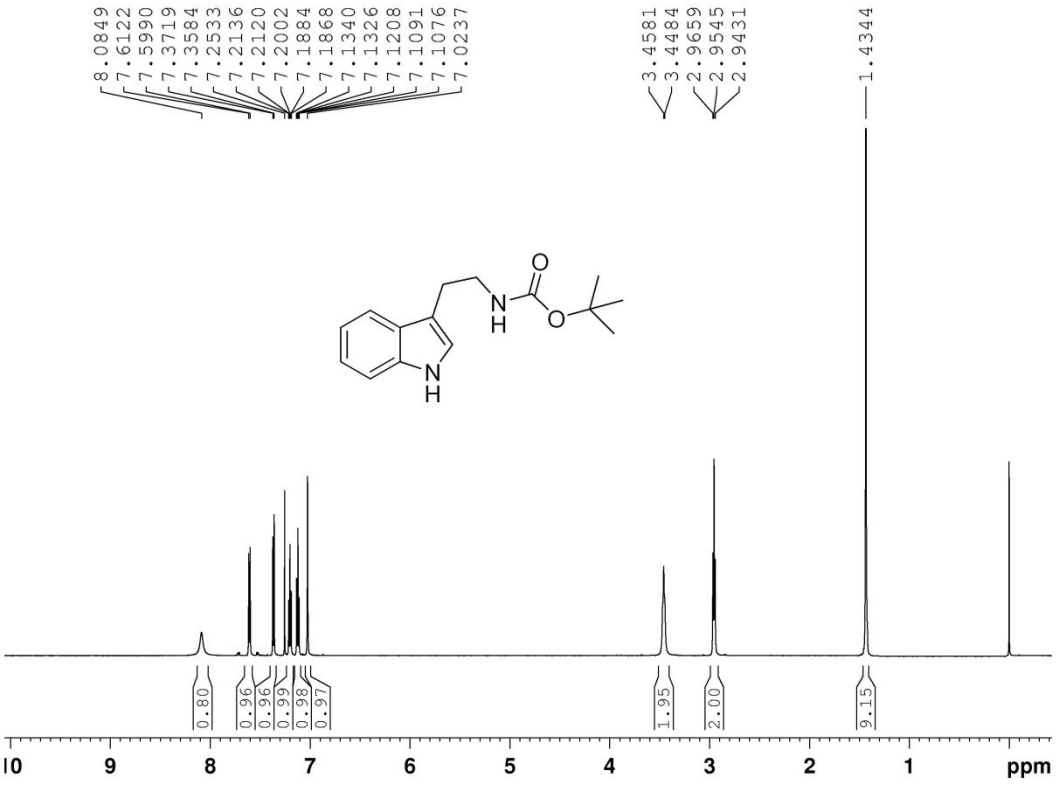


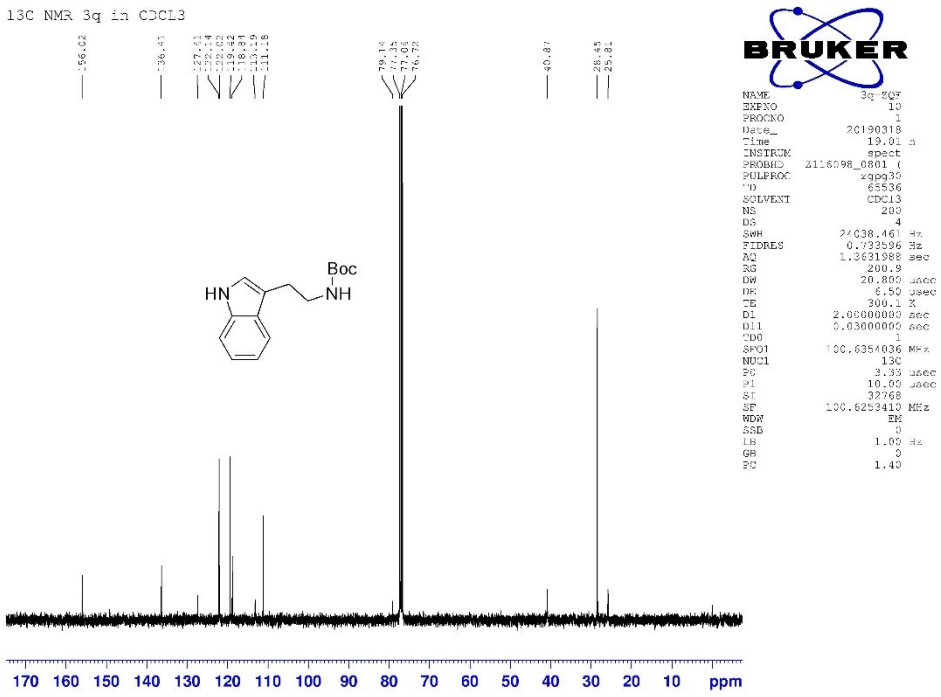


tert-Butyl (2-(1*H*-indol-3-yl)ethyl)carbamate (**3q**)

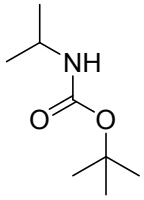

HN
O
N
H
O

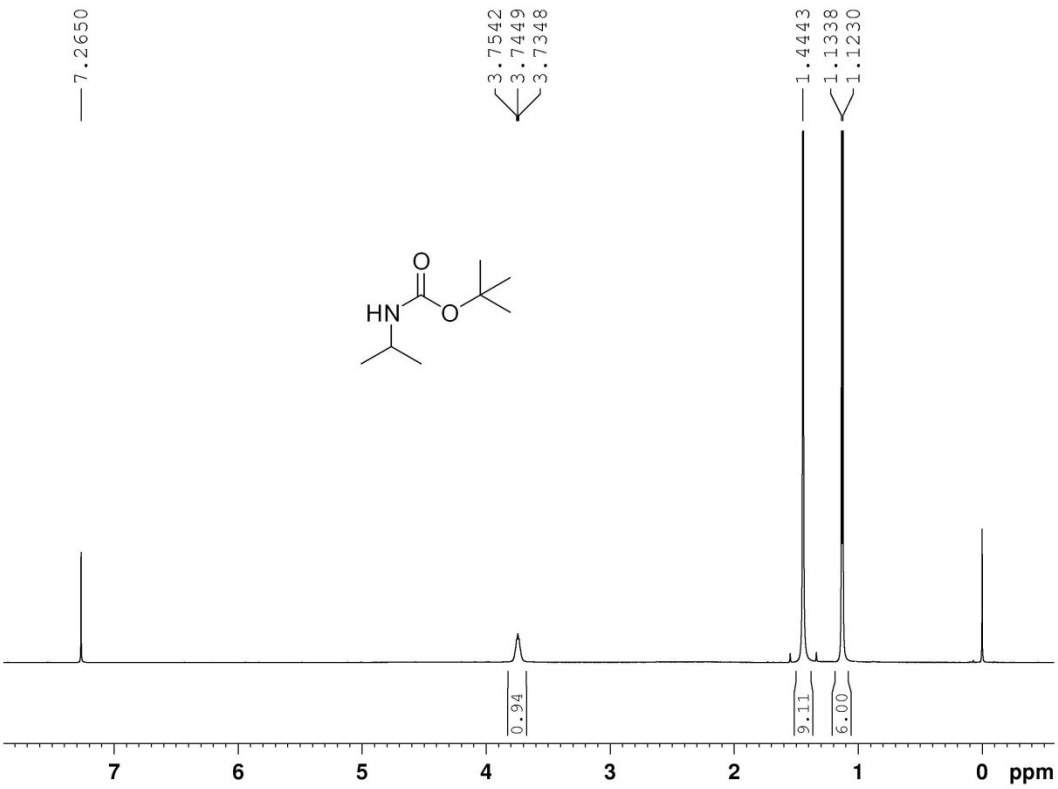

User Spectra
Fragmentor Voltage
200
Collision Energy
0
Ionization Mode
ESI
x10 5
+ESI Scan (0.149 min) Frag=200.0V BD-19.d Subtract
283.1430
([C15 H20 N2 O2]+Na)+
227.0799
353.2664
561.2945
695.4905
839.1846
Counts vs. Mass-to-Charge (m/z)

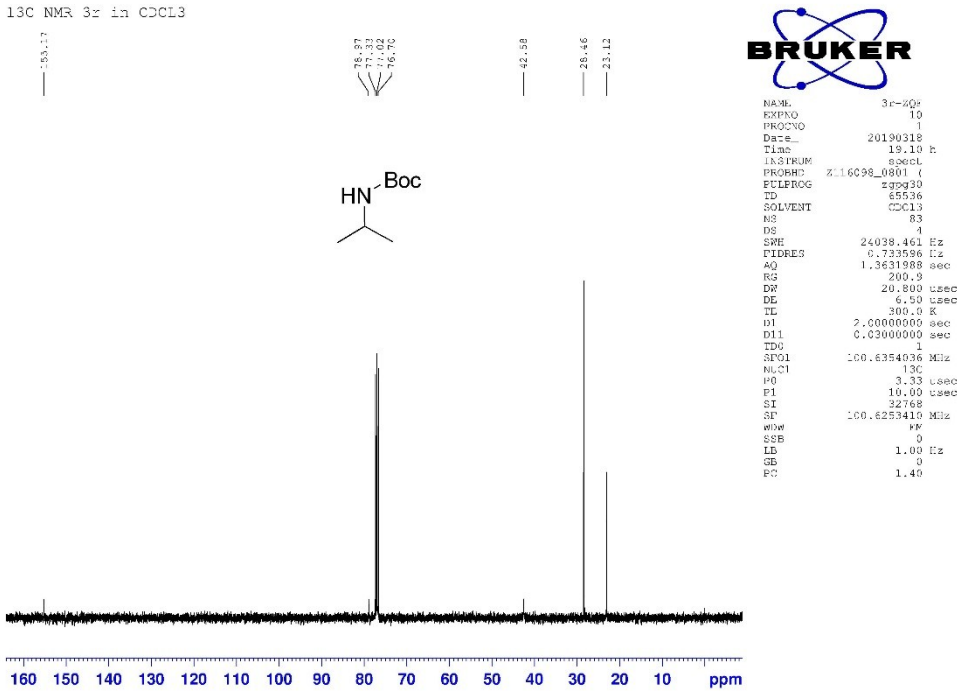

8.0849
7.6122
7.5990
7.3719
7.3584
7.2533
7.2136
7.2120
7.2002
7.1884
7.1868
7.1340
7.1326
7.1208
7.1091
7.1076
7.0237
3.4581
3.4484
2.9659
2.9545
2.9431
1.4344
O
N
H
O
N
H
0.80
0.96
0.96
0.99
0.98
0.97
1.95
2.00
9.15
10
9
8
7
6
5
4
3
2
1
ppm



tert-Butyl isopropylcarbamate (**3r**)

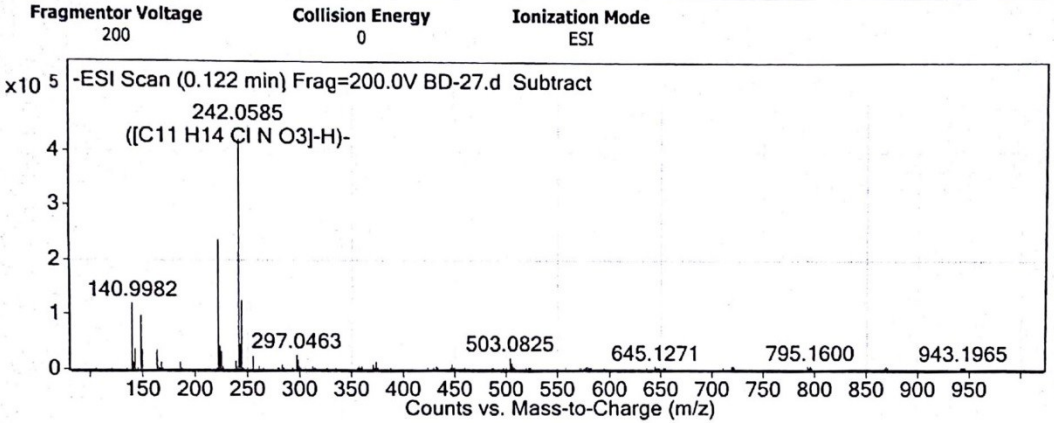


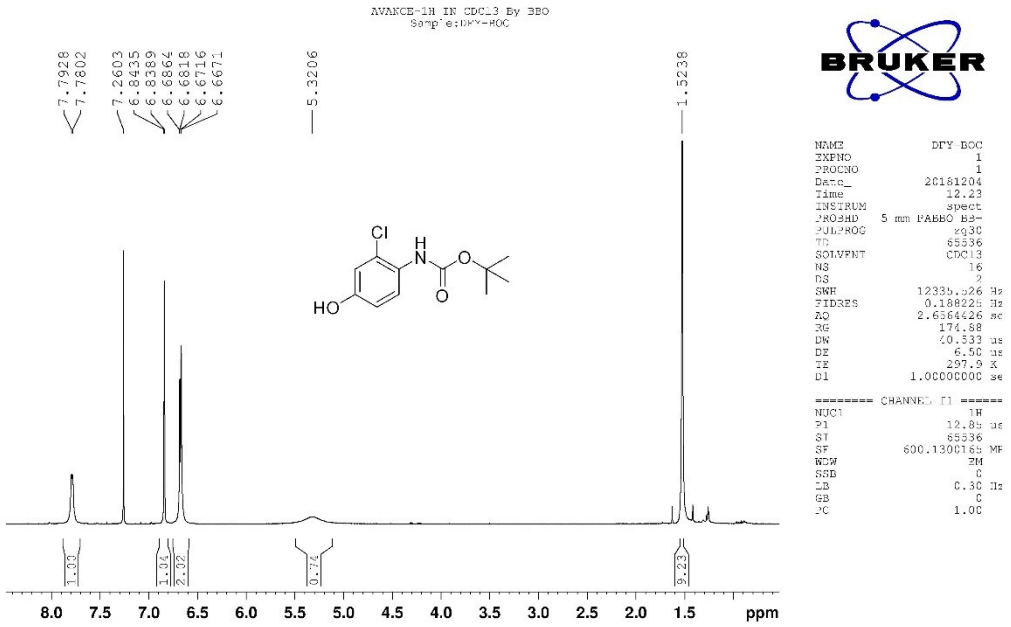


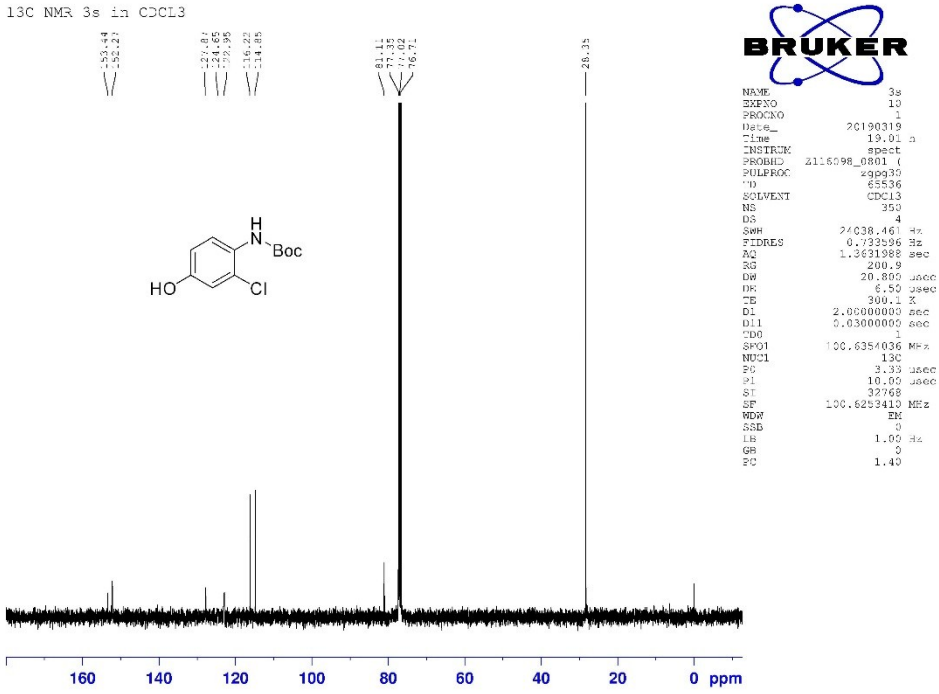


tert-butyl (2-chloro-4-hydroxyphenyl)carbamate (**3s**)

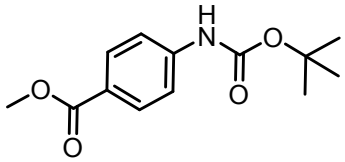
User Spectra

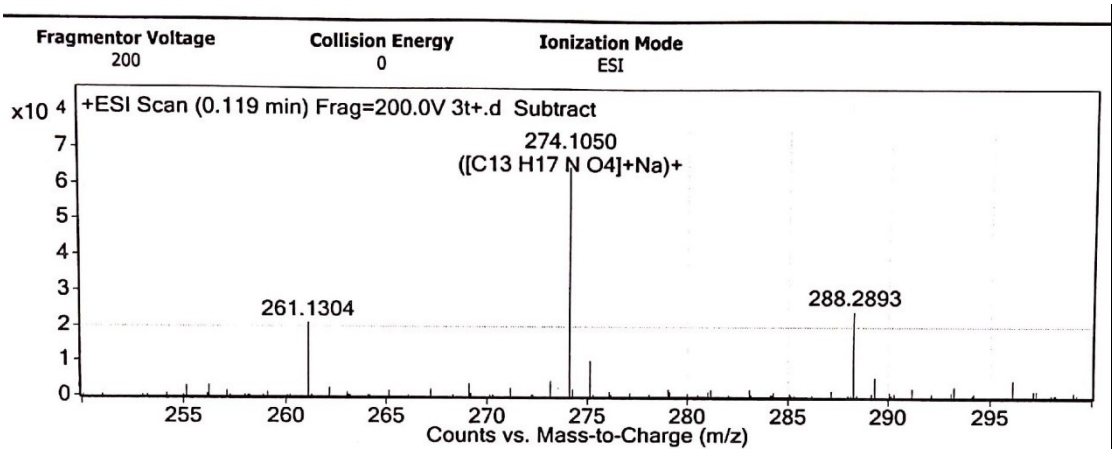


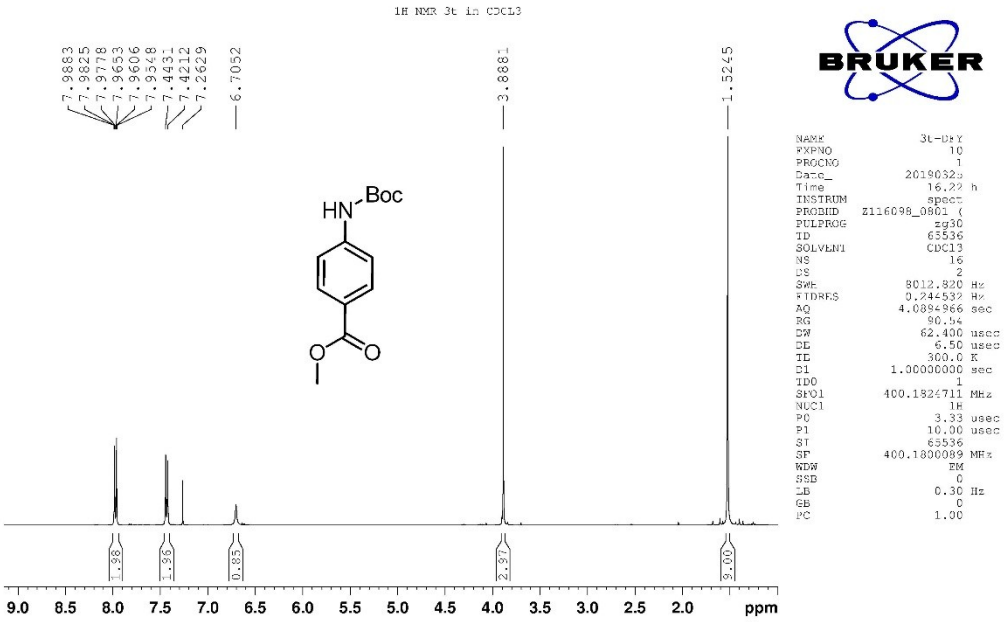


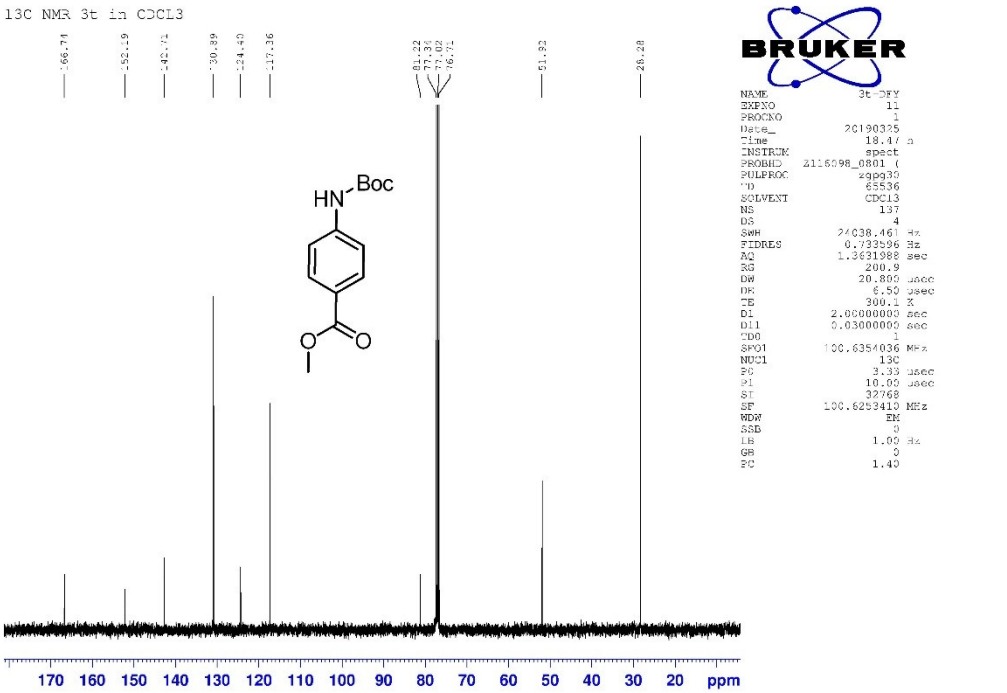


methyl 4-((tert-butoxycarbonyl)amino)benzoate (**3t**)

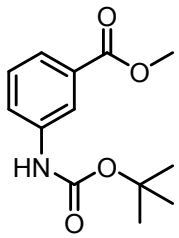


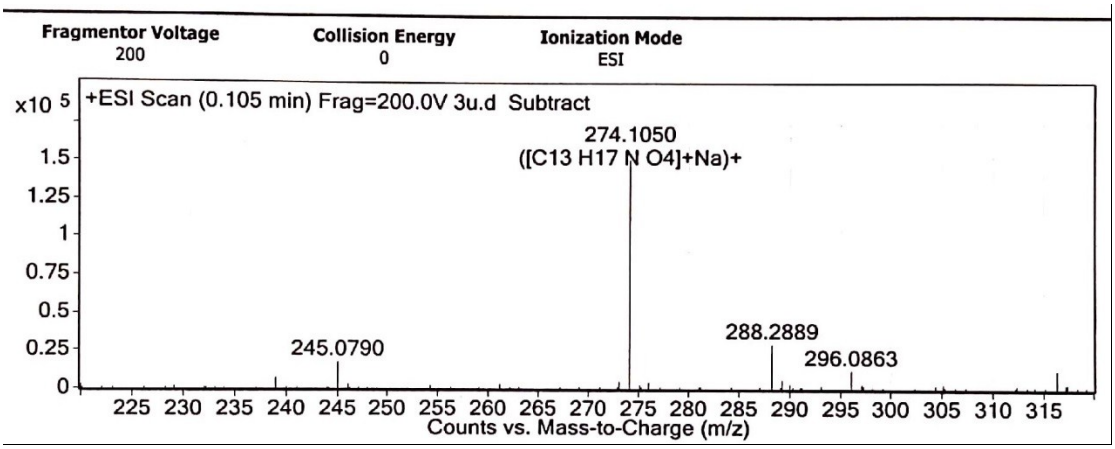


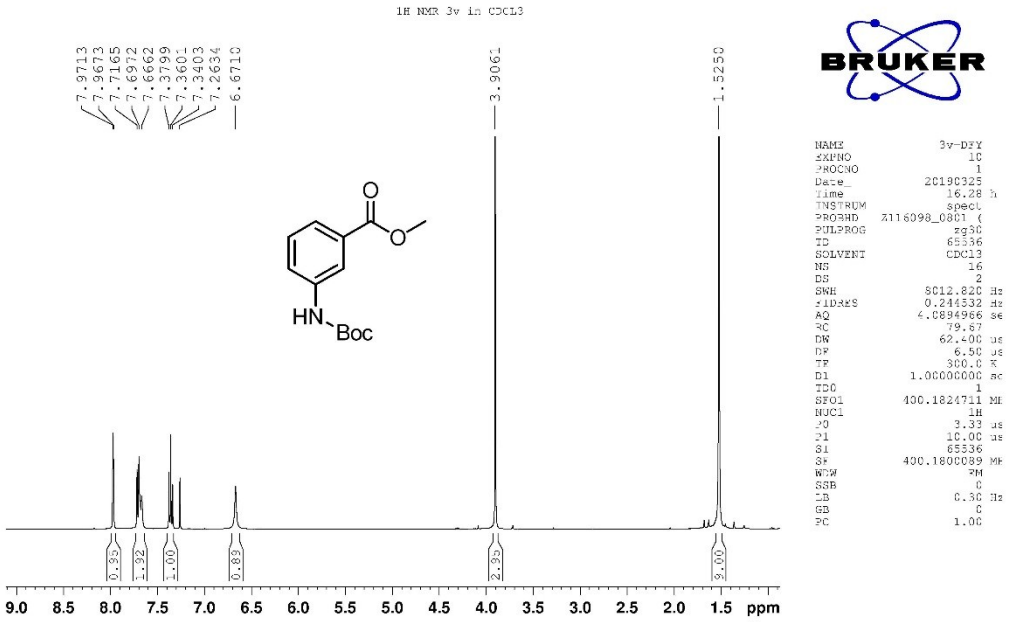


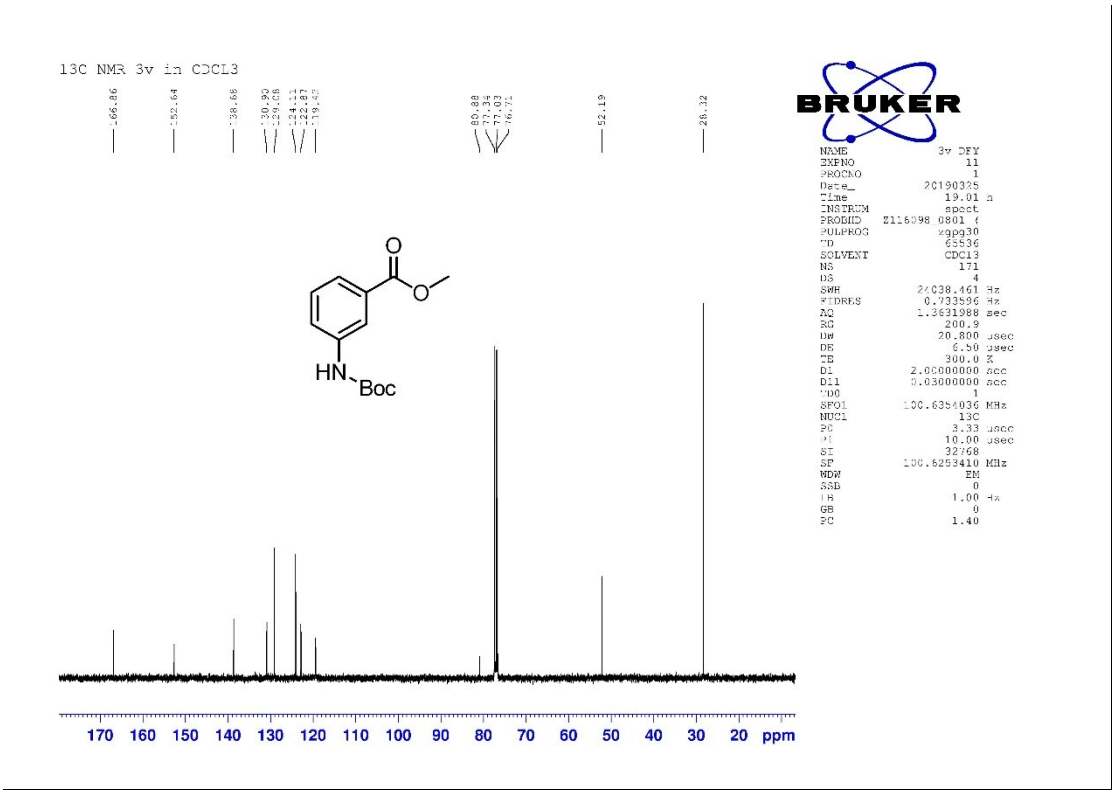


methyl 3-((tert-butoxycarbonyl)amino)benzoate (**3u**)

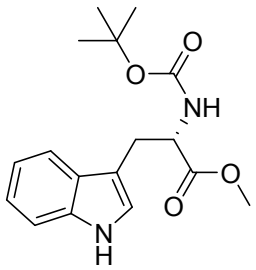


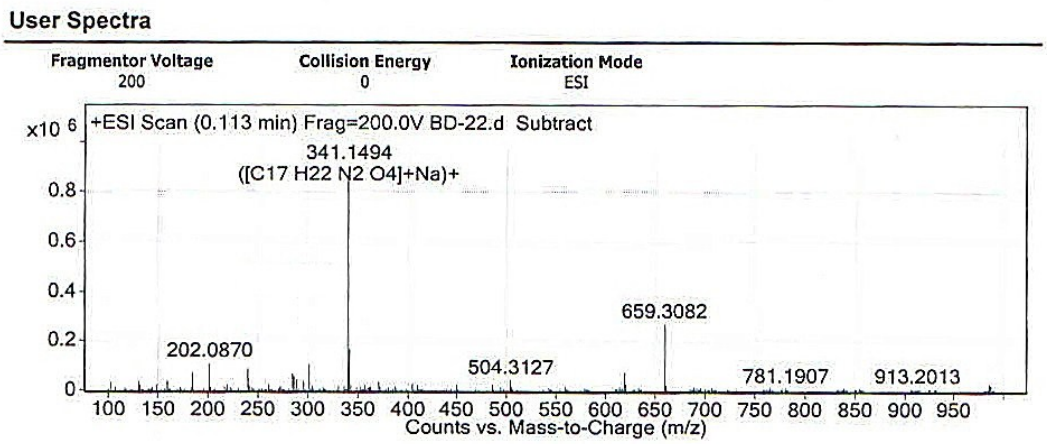

Fragmentor Voltage
200
Collision Energy
0
Ionization Mode
ESI
x10 5
+ESI Scan (0.105 min) Frag=200.0V 3u.d Subtract
274.1050
([C13 H17 N O4]+Na)+
245.0790
288.2889
296.0863
Counts vs. Mass-to-Charge (m/z)

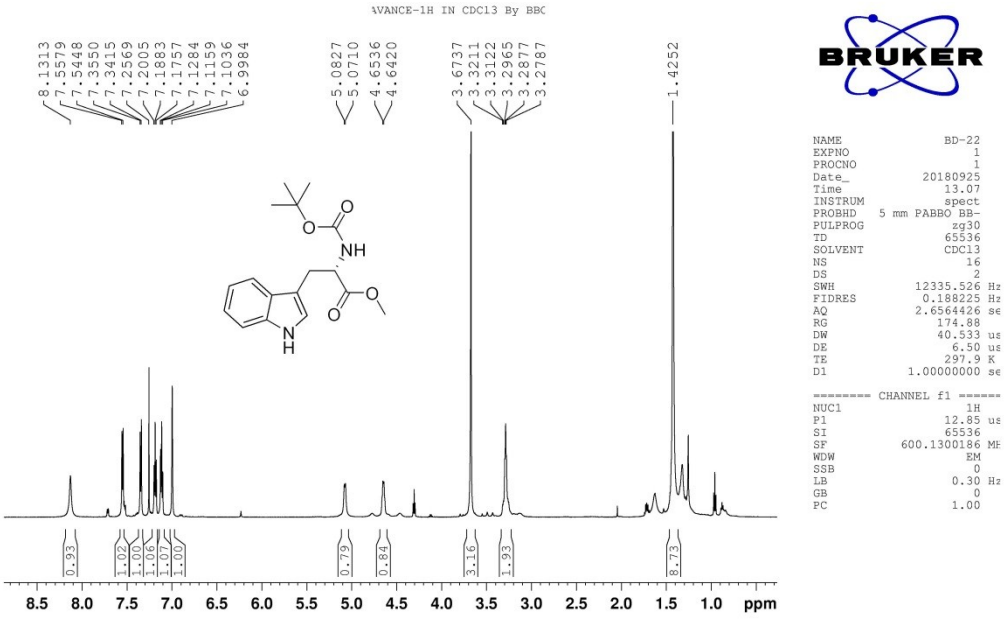

1H NMR 3v in CDCL3
7.9713
7.9673
7.7165
7.6972
7.6662
7.3799
7.3601
7.3403
7.2634
6.6710
3.9064
1.5250
HN
Boc
0.93
1.32
2.00
0.89
2.95
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
BRUKER
NAME 3v-DFY
EXPNO 10
PROCNO 1
Date_ 20190325
Time 16.28 h
INSTRUM spect
PROBHD Z116098_0801 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894966 se
RG 79.87
DW 62.400 us
DE 6.50 us
TE 300.0 K
D1 1.00000000 se
TD0 1
SFO1 400.1824711 MH
NUC1 1H
P0 3.33 us
P1 10.00 us
SI 65536
SF 400.1800089 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

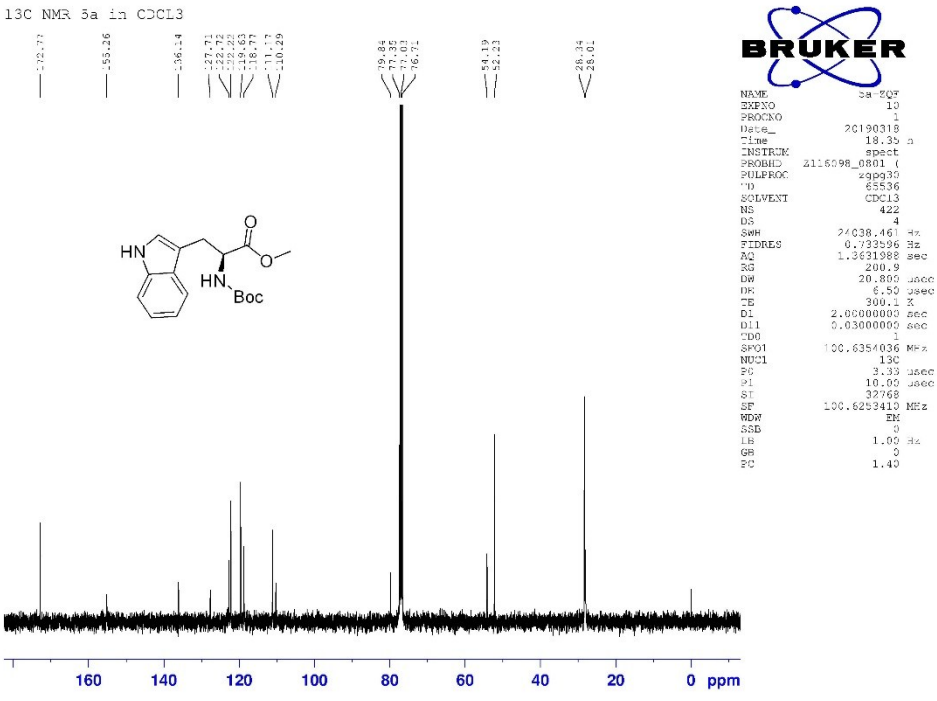


Methyl (*tert*-butoxycarbonyl)-*L*-tryptophanate (**5a**)

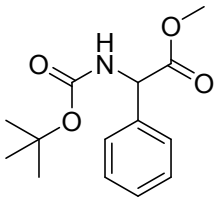


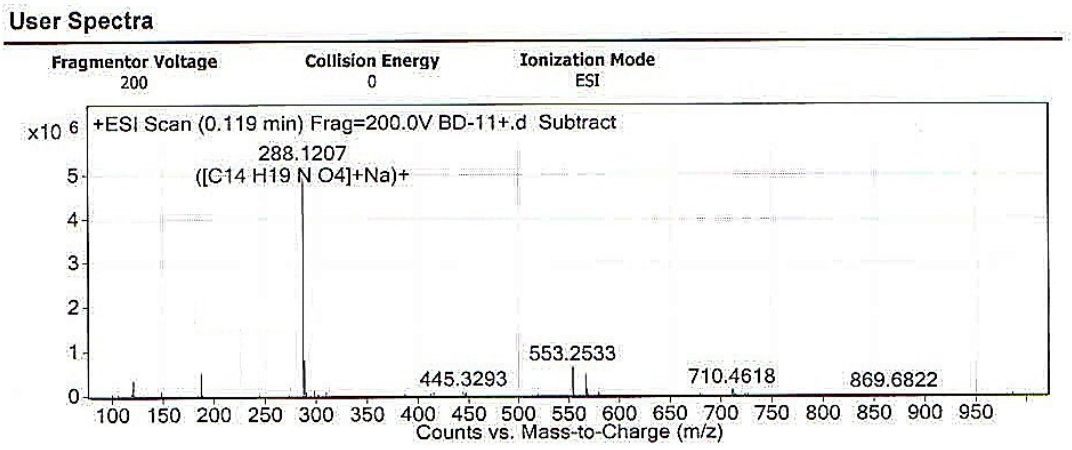


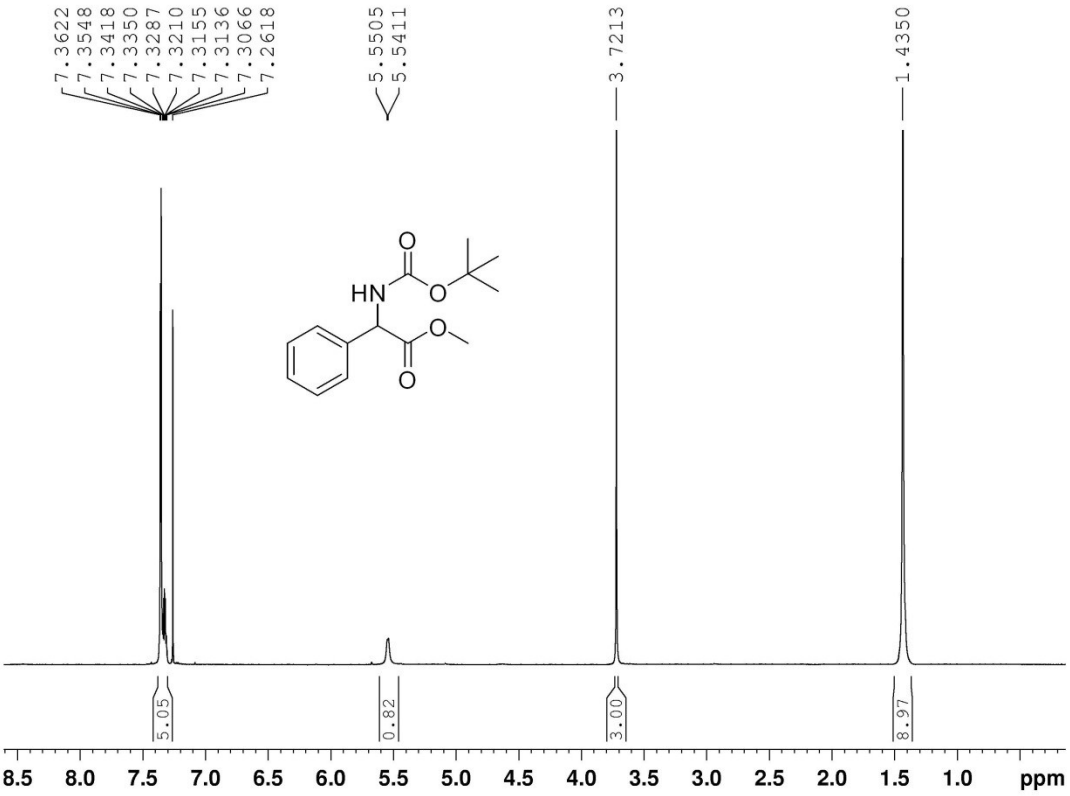


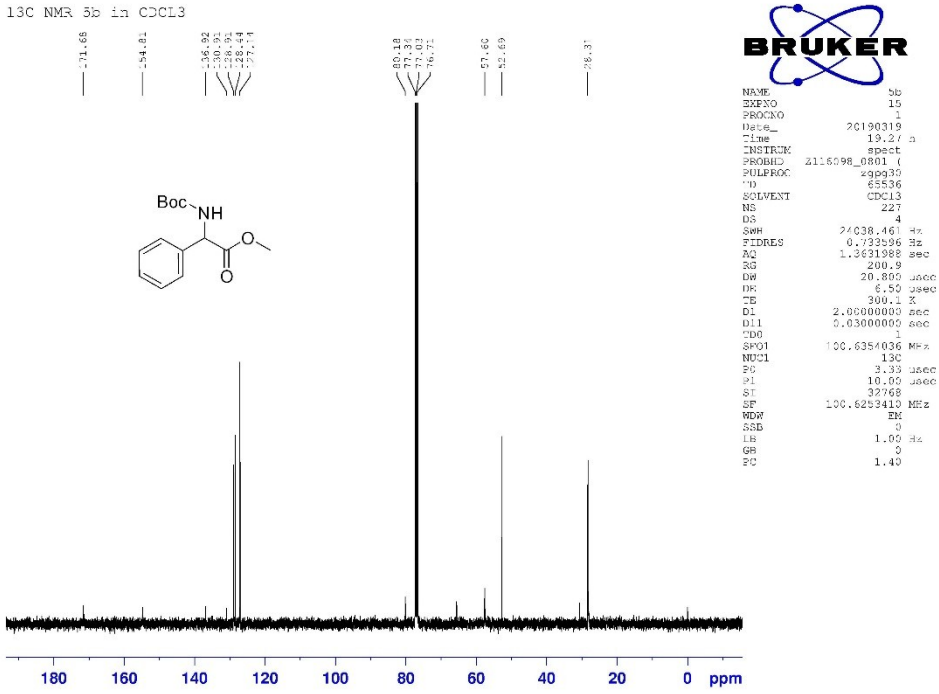


Methyl 2-((*tert*-butoxycarbonyl)amino)-2-phenylacetate (**5b**)

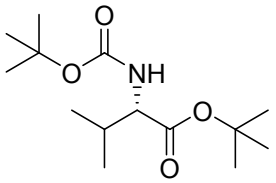


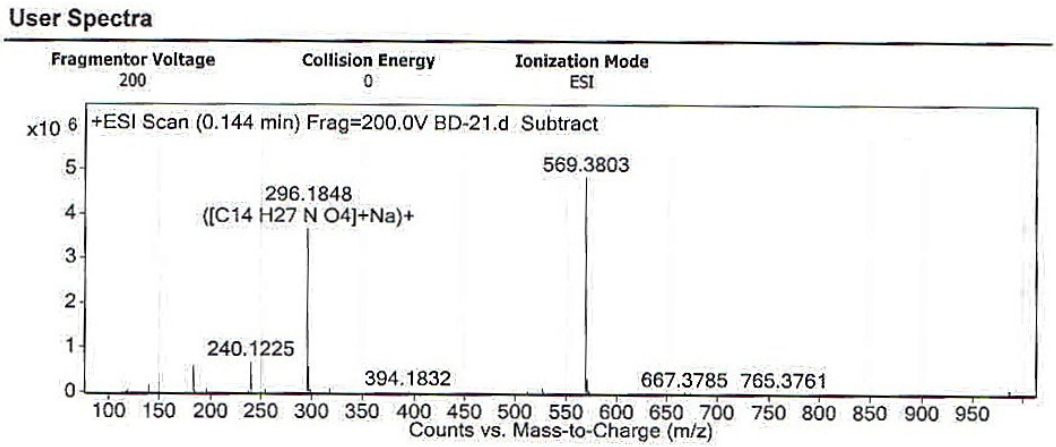

User Spectra
Fragmentor Voltage
200
Collision Energy
0
Ionization Mode
ESI
x10 6
+ESI Scan (0.119 min) Frag=200.0V BD-11+.d Subtract
288.1207
([C14 H19 N O4]+Na)+
553.2533
445.3293
710.4618
869.6822
Counts vs. Mass-to-Charge (m/z)

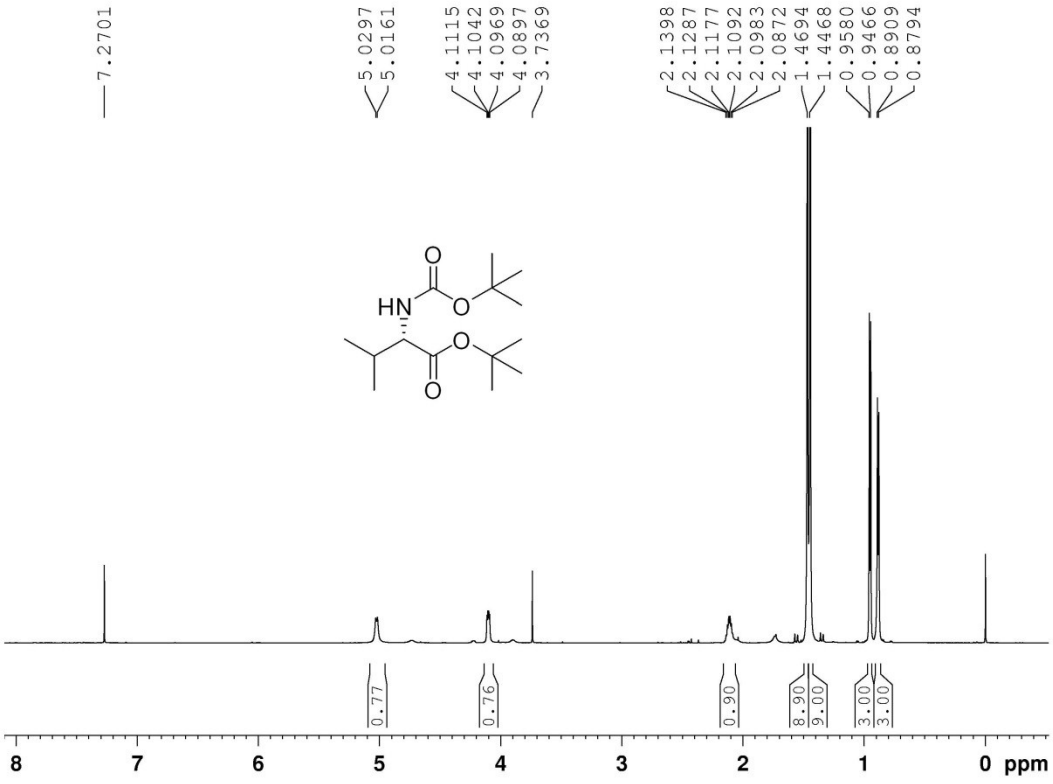

7.3622
7.3548
7.3418
7.3350
7.3287
7.3210
7.3155
7.3136
7.3066
7.2618
5.5505
5.5411
3.7213
1.4350
5.05
0.82
3.00
8.97
ppm

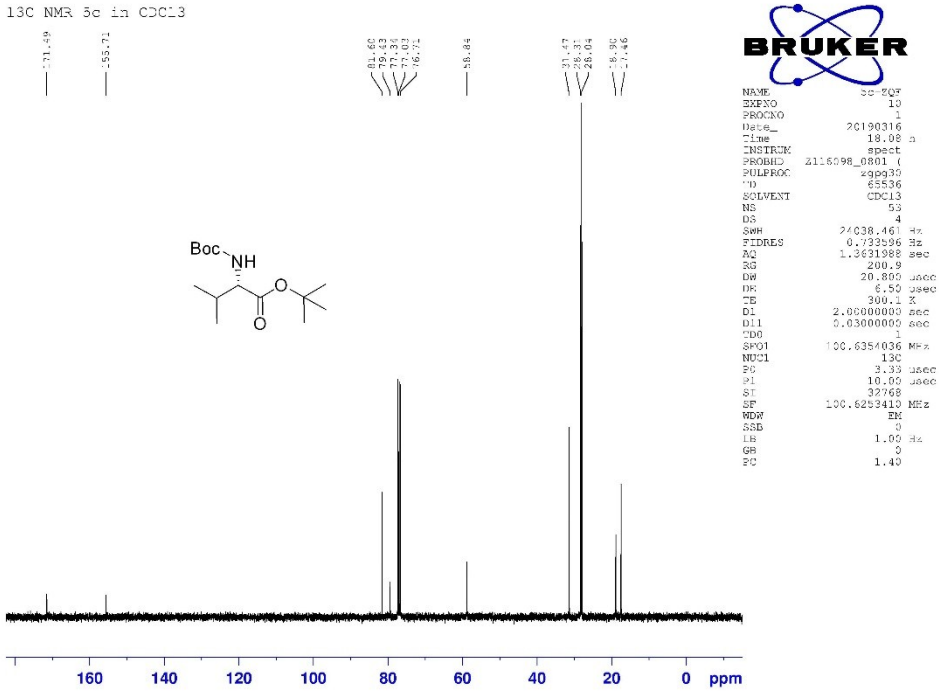


tert-Butyl (*tert*-butoxycarbonyl)-*L*-valinate (**5c**)

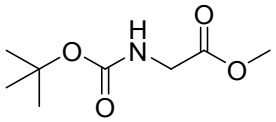




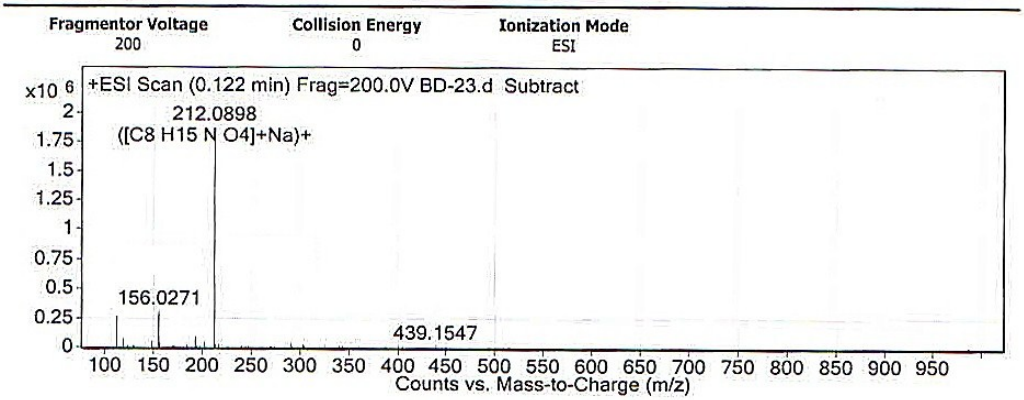


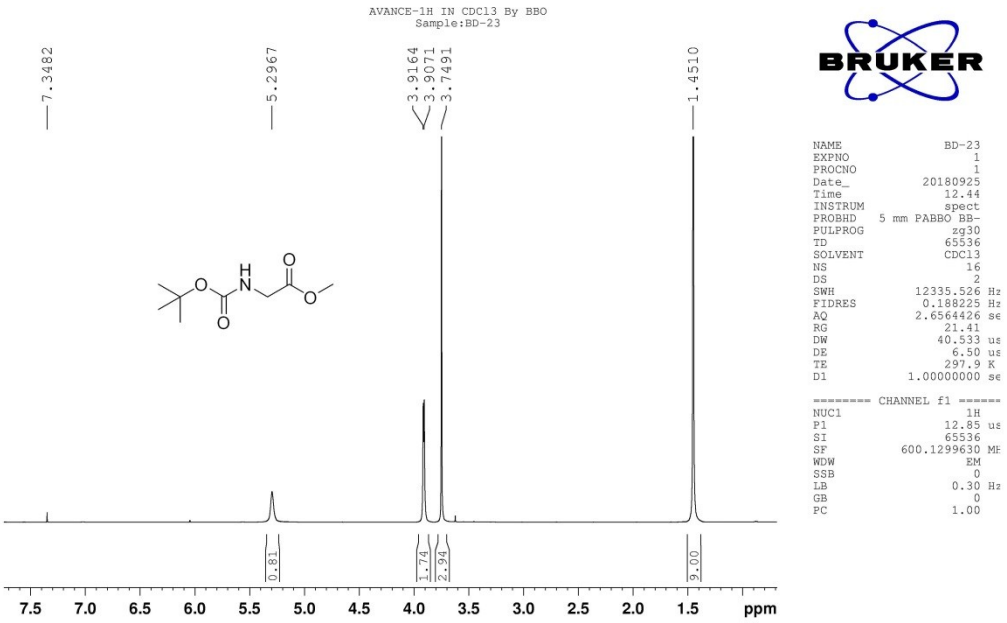


Methyl (*tert*-butoxycarbonyl)glycinate (**5d**)



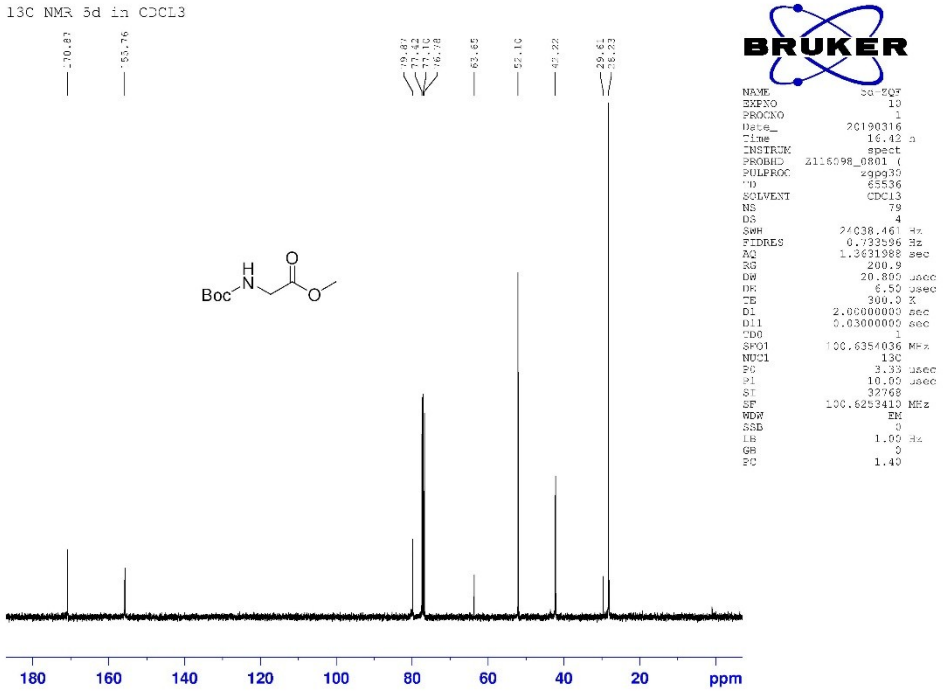
User Spectra



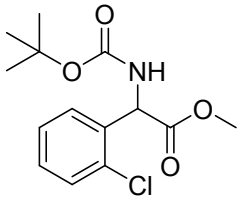


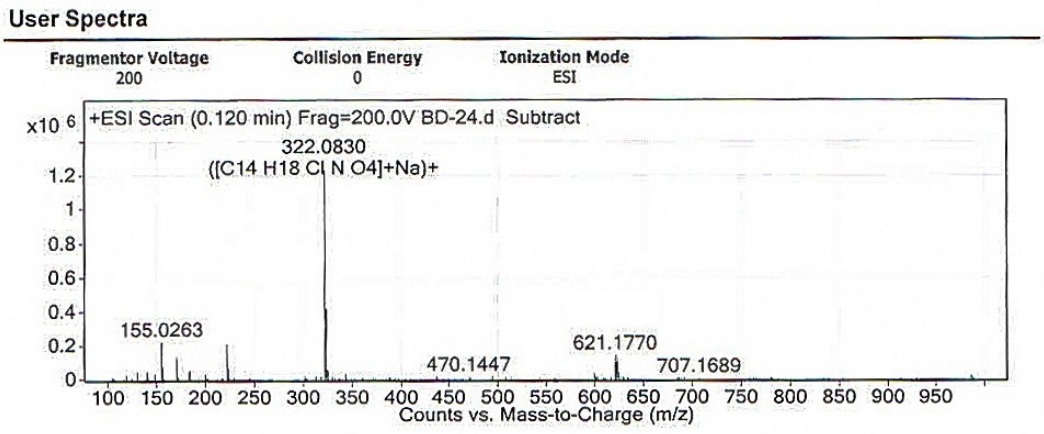
BRUKER

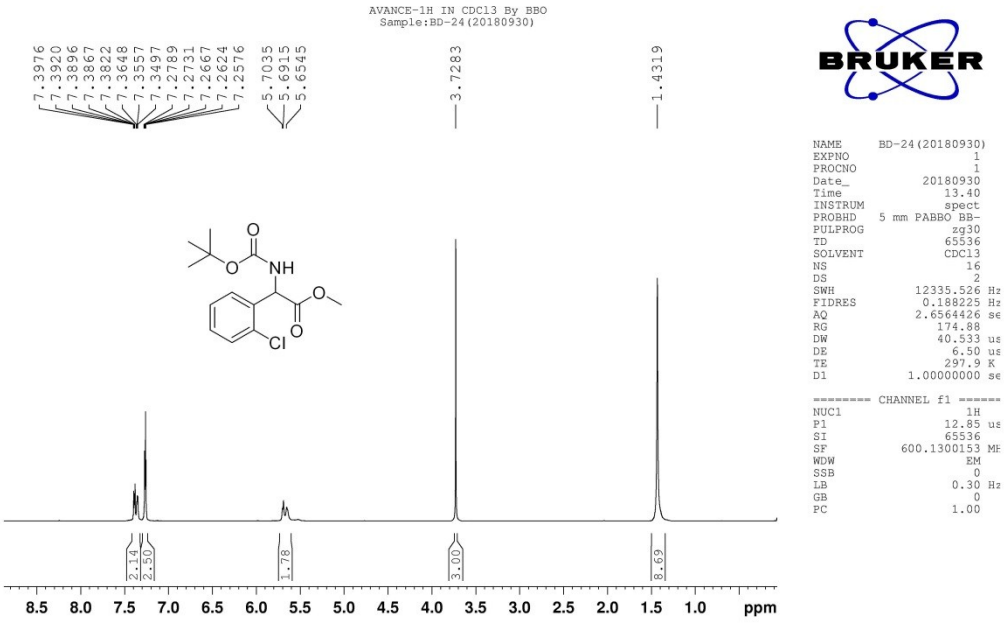
NAME	BD-23
EXPNO	1
PROCNO	1
Date_	20180925
Time	12.44
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	12335.526 Hz
FIDRES	0.188225 Hz
AQ	2.6564426 se
RG	21.41
DW	40.533 us
DE	6.50 us
TE	297.9 K
D1	1.00000000 se
======== CHANNEL f1 ======	
NUC1	1H
P1	12.85 us
SI	65536
SF	600.1299630 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

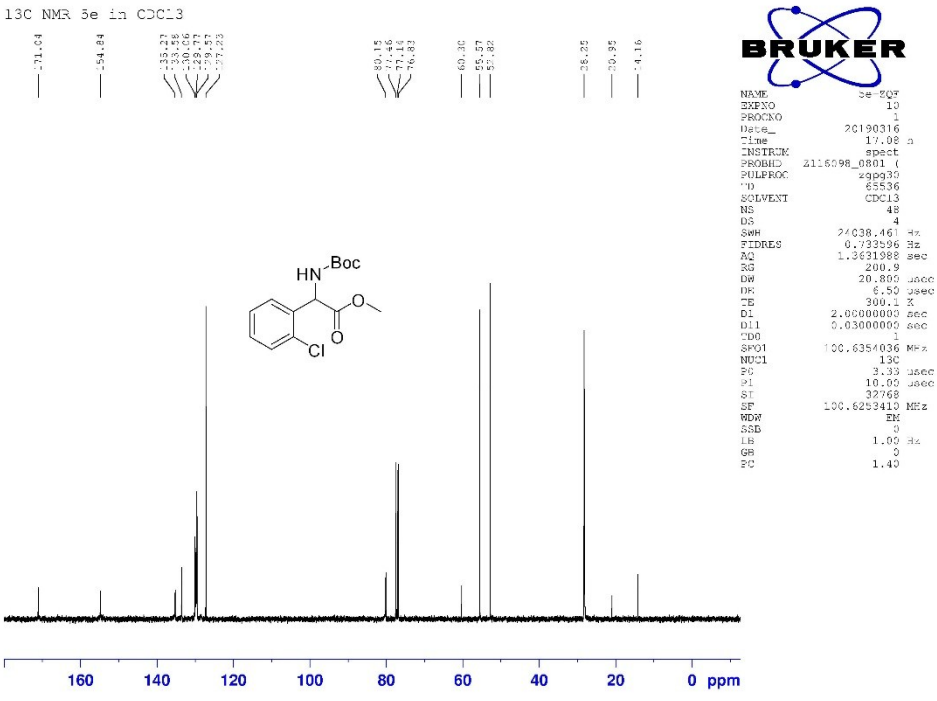


Methyl 2-((*tert*-butoxycarbonyl)amino)-2-(2-chlorophenyl)acetate (**5e**)

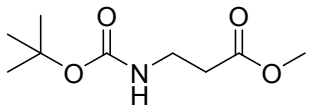






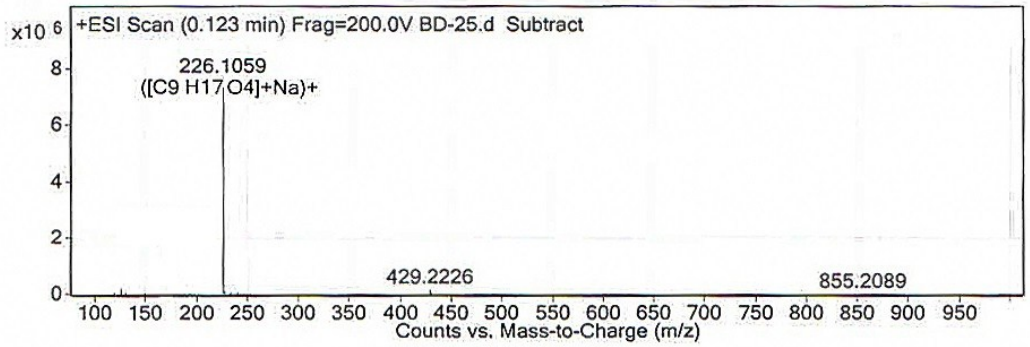


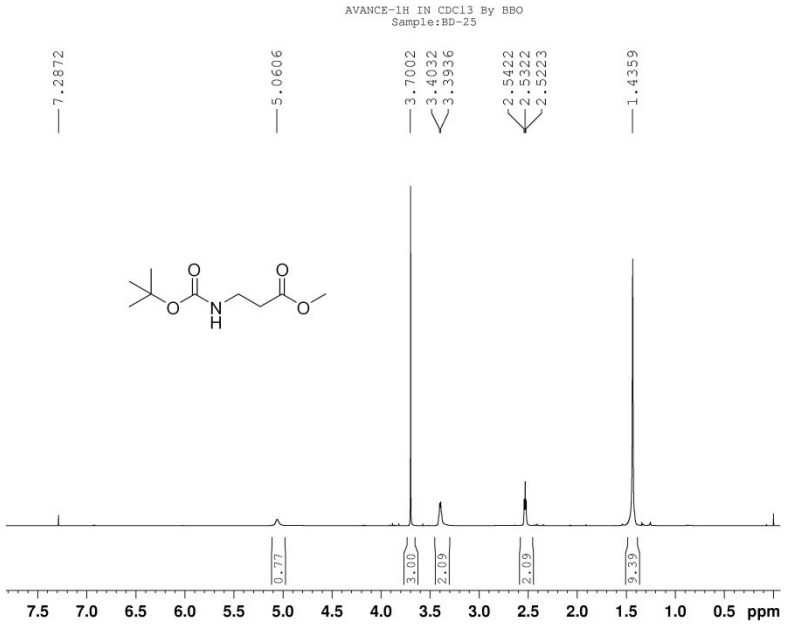
Methyl 3-((*tert*-butoxycarbonyl)amino)propanoate (**5f**)



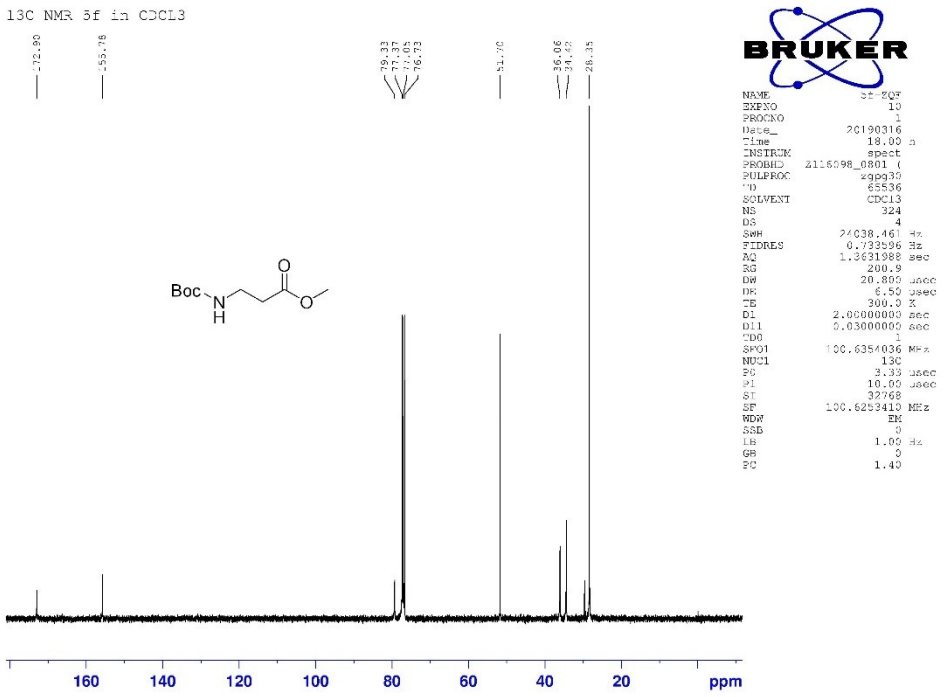
User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI





NAME	BD-25
EXPNO	1
PROCNO	1
Date_	20180925
Time	13.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	12335.526 Hz
FIDRES	0.188225 Hz
AQ	2.6564426 se
RG	83.13
DW	40.533 us
DE	6.50 us
TE	297.9 K
D1	1.00000000 se
======== CHANNEL f1 ======	
NUC1	1H
P1	12.85 us
SI	65536
SF	600.1300003 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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