Supporting Information

Total Synthesis and Biological Activity of Dolastatin 16

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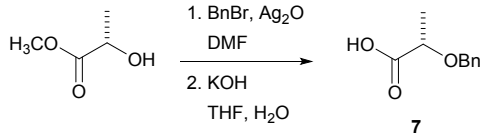
Experimental Procedures

General Methods. Tetrahydrofuran (THF), methanol (CH_3OH), and acetonitrile (CH_3CN) were purchased from Kanto Chemical Co. Inc. Dichloromethane (CH_2Cl_2) and triethylamine (Et_3N) were distilled from CaH_2. All commercially obtained reagents were used as received.

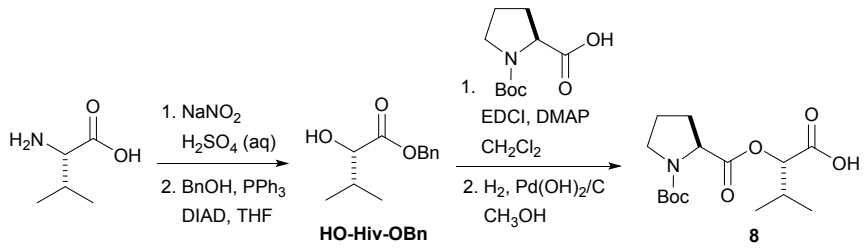
Analytical TLC was carried out using pre-coated silica gel plates (Merck TLC silica gel $60F_{254}$). Wakogel 60N 63-212 μm was used for column chromatography. IR spectra were recorded on a JASCO FTIR-4100 Type A spectrometer using a NaCl cell. ^1H and ^{13}C NMR spectra were recorded using a JNM-EX 400 (400 MHz and 100 MHz) spectrometer. Chemical shifts are reported in ppm relative to $CHCl_3$ (δ = 7.26) in $CDCl_3$ for ^1H NMR, and $CDCl_3$ (δ = 77.0) for ^{13}C NMR. Splitting patterns are designated as s, d, t, q, and m, indicating singlet, doublet, triplet, quartet, and multiplet, respectively.



7

BnO-Lac-OH (7). To a solution of methyl L-lactate (HO-Lac-OMe) (100 mg, 0.961 mmol) in DMF (4.8 mL) was added BnBr (0.137 mL, 1.15 mmol) and Ag_2O (134 mg, 0.577 mmol) under Ar atmosphere. After 16 h of stirring at room temperature, the reaction mixture was quenched with CH_3OH, filtered through celite, and concentrated in vacuo. The crude product was purified using column chromatography (1% EtOAc in hexane) to afford BnO-Lac-OMe as a colorless oil (81.6 mg, 0.420 mmol, 44%): $[\alpha]^{23}_D$ = –88.3 (*c* 1.30, $CHCl_3$); IR (neat) 3734, 2873, 2360, 2341, 1750, 1456, 1275, 1206, 1143, 1065, 1025, 740, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.42 (3H, d, *J* = 6.8 Hz), 3.74 (3H, s), 4.06 (1H, q, *J* = 6.8 Hz), 4.44 (1H, d, *J* = 11.7 Hz), 4.70 (1H, d, *J* = 11.7 Hz), 7.24-7.34 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.7, 51.9, 72.0, 73.9, 127.8, 127.9, 128.4, 137.5, 173.7; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{14}O_3Na$ 217.0835; Found 217.0836.

To a solution of BnO-Lac-OMe (81.6 mg, 0.420 mmol) in THF (7.7 mL) at 0 °C was added a solution of KOH (324 mg, 5.77 mmol) in H_2O (7.7 mL). The mixture was stirred for 16 h at room temperature, quenched with 3 M HCl (2.8 mL, 8.40 mmol), extracted with EtOAc, washed with brine, and concentrated in vacuo. The crude product was purified using column chromatography (10% EtOAc in hexane) to afford **7** as a colorless oil (63.5 mg, 0.352 mmol, 84%): $[\alpha]^{23}_D$ = –71.9 (*c* 7.62, $CHCl_3$); IR (neat) 3734, 3033, 2939, 2877, 2360, 2341, 1456, 1209, 1118, 1063, 1015, 738, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.45 (3H, d, *J* = 6.8 Hz), 4.06 (1H, q, *J* = 6.8 Hz), 4.46 (1H, d, *J* = 11.7 Hz), 4.68 (1H, d, *J* = 11.7 Hz), 7.24-7.33 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.4, 72.0, 73.4, 127.9, 128.0, 128.4, 137.0, 179.0; HRMS (ESI) m/z: $[M – H]^–$ Calcd for $C_{10}H_{11}O_3$ 179.0714; Found 179.0714.



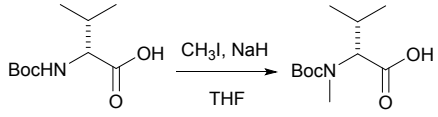
*Boc-Pro-O-Hiv-OH (**8**)*. To a solution of L-valine (2.0 g, 17.1 mmol) in 0.5 M H_2SO_4 (68.3 mL) at 0 °C was slowly added a solution of $NaNO_2$ (7.08 g, 103 mmol) in H_2O (16.2 mL). The mixture was stirred for 3 h at 0 °C, then stirred at room temperature for 24 h. The reaction mixture was extracted with Et_2O, washed with brine, dried over Na_2SO_4, and concentrated in vacuo to afford (S)-2-hydroxyisovaleric acid (HO-Hiv-OH) as a colorless oil (1.56 g, 13.2 mmol, 77%): $[\alpha]^{23}_D$ = +36.8 (*c* 1.40, $CHCl_3$); IR (neat) 3626, 2967, 1714, 1556, 1455, 1215 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.90 (3H, d, *J* = 6.8 Hz), 1.04 (3H, d, *J* = 6.8 Hz), 2.09-2.18 (1H, m), 4.13 (1H, d, *J* = 3.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.8, 18.7, 32.0, 74.8, 179.3; HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_5H_9O_3$ 117.0557; Found 117.0555.

To a solution of HO-Hiv-OH (1.91 g, 16.2 mmol) in THF (81 mL) were added BnOH (1.68 mL, 16.2 mmol) and PPh_3 (6.37 g, 24.3 mmol). DIAD (12.8 mL, 24.3 mmol) was added at 0°C under Ar atmosphere. The mixture was stirred at room temperature for 16 h, quenched with saturated $NaHCO_3$, extracted with EtOAc, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified using column chromatography (5% EtOAc in hexane) to afford HO-Hiv-OBn as a colorless oil (2.60 g, 12.5 mmol, 77%): $[\alpha]^{23}_D$ = –8.50 (*c* 1.40, $CHCl_3$); IR (neat) 3508, 3034, 2964, 2933, 2875, 1955, 1878, 1733, 1608, 1587, 1498, 1456, 1388, 1370, 1261, 1214, 1178, 1138, 1106, 1070, 1029, 988, 913, 888, 831, 751, 698, 651 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.79 (3H, d, *J* = 6.8 Hz), 0.96 (3H, d, *J* = 6.8 Hz), 2.02-2.07 (1H, m), 2.96 (1H, s), 4.03 (1H, d, *J* = 3.9 Hz), 5.13 (1H, d, *J* = 12.2 Hz), 5.18 (1H, d, *J* = 12.2 Hz), 7.29-7.32 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.8, 18.6, 32.0, 67.0, 74.9, 128.2, 128.3, 128.4, 135.1, 174.6; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{16}O_3$ 208.1099; Found 208.1095.

To a solution of HO-Hiv-OBn (1.42 g, 6.82 mmol) and Boc-Pro-OH (1.47 g, 6.82 mmol) in CH_2Cl_2 (34 mL) were added DMAP (83.3 mg, 0.682 mmol) and EDCI (1.96 g, 10.2 mmol) under Ar atmosphere. The mixture was stirred for 16 h at room temperature, quenched with saturated NH_4Cl solution, extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified using column chromatography (5% EtOAc in hexane) to afford Boc-Pro-O-Hiv-OBn as a colorless oil (2.54 g, 6.26 mmol, 92%): $[\alpha]^{23}_D$ = –77.0 (*c* 2.32, $CHCl_3$); IR (neat) 3734, 2973, 2879, 2360, 2341, 1749, 1700, 1395, 1366, 1258, 1166, 1128, 1089, 1017, 917, 889, 753, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, mixture of rotamers) δ 0.92 (3H, d, *J* = 6.8 Hz), 0.97 (3H, d, *J* = 6.8 Hz), 1.37-1.45 (9H, m), 1.70-1.84 (2H, m), 2.00-2.18 (2H, m), 2.19-2.26 (1H, m), 3.29-3.41 (1H, m),

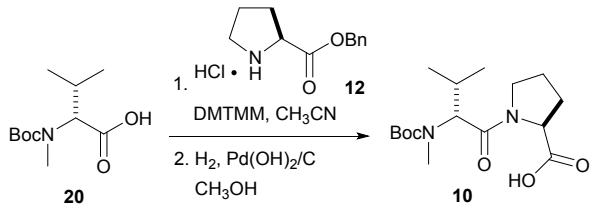
3.48-3.54 (1H, m), 4.27-4.31 (0.6H, m), 4.37-4.42 (0.4H, m), 4.88 (0.6 H, d, J = 4.4 Hz), 4.92 (0.4H, d, J = 3.9 Hz), 5.05-5.10 (1H, m), 5.16-5.20 (1H, m), 7.31-7.34 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, mixture of rotamers) δ 17.0, 17.2, 18.6, 18.8, 23.3, 24.0, 28.3, 28.4, 29.5, 30.0, 30.1, 30.5, 46.3, 46.5, 58.2, 58.4, 66.8, 67.0, 76.9, 79.7, 79.8, 128.39, 128.44, 128.47, 128.53, 128.6, 135.1, 135.2, 153.8, 154.4, 169.2, 169.5, 172.4, 172.7; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{31}NO_6Na$ 428.2044; Found 428.2040.

To a solution of Boc-Pro-O-Hiv-OBn (162 mg, 0.400 mmol) in CH_3OH (2.0 mL) was carefully added 10% Pd/C (16.2 mg, 10 wt%) under Ar atmosphere. The solution was purged with H_2 gas and stirring was continued under H_2 atmosphere at room temperature for 16 h. The solution was filtered through celite and concentrated in vacuo. The crude product was purified using column chromatography (30% EtOAc in hexane) to afford **8** as a colorless oil (125 mg, 0.396 mmol, 99%): $[\alpha]^{23}_D$ = –48.6 (*c* 0.43, $CHCl_3$); IR (neat) 3734, 2974, 2880, 2360, 2341, 1749, 1699, 1419, 1167, 1015, 772, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, mixture of rotamers) δ 0.94-1.03 (6H, m), 1.38-1.45 (9H, m), 1.80-1.95 (2H, m), 2.06-2.16 (1H, m), 2.18-2.36 (2H, m), 3.39-3.47 (1H, m), 3.48-3.60 (1H, m), 4.33 (0.4H, dd, J = 3.4, 8.8 Hz), 4.40 (0.6H, dd, J = 4.4, 8.5 Hz), 4.88 (0.4H, d, J = 3.9 Hz), 5.06 (0.6H, d, J = 3.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, mixture of rotamers) δ 16.8, 17.0, 18.8, 18.9, 23.3, 24.4, 28.2, 28.4, 29.9, 30.0, 30.3, 30.6, 46.3, 46.8, 58.6, 59.0, 76.4, 76.9, 78.7, 80.1, 81.2, 153.9, 155.8, 171.3, 172.7; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{25}NO_6Na$ 338.1574; Found 338.1577.



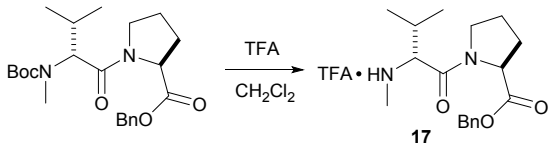
20

*Boc-D-MeVal-OH (**20**).* To a stirring solution of *N*-Boc-D-valine (4.78 g, 22.0 mmol) and CH_3I (13.7 mL, 220 mmol) in THF (81 mL) was added NaH (60% mineral oil dispersion, 8.80 g, 220 mmol) in several portions. The mixture was stirred for 24 h at room temperature, quenched by adding EtOAc (5.0 mL) and H_2O (5.0 mL), and concentrated in vacuo. The residue was partitioned between Et_2O and H_2O. The aqueous layer was extracted with Et_2O. The Et_2O extracts were washed with saturated $NaHCO_3$. The aqueous layers were combined and acidified with 5% citric acid to pH 3 and extracted with EtOAc. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated in vacuo to afford Boc-D-MeVal-OH (**20**) as a colorless oil (4.07 g, 17.6 mmol, 80%): $[\alpha]^{23}_D$ = +77.1 (*c* 2.70, $CHCl_3$); IR (neat) 3734, 2973, 1741, 1699, 1669, 1558, 1507, 1473, 1456, 1393, 1368, 1309, 1258, 1153, 1051, 934, 878, 770, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (3H, d, J = 6.8 Hz), 1.01 (3H, d, J = 6.8 Hz), 1.45 (9H, s), 2.15-2.26 (1H, m), 2.85 (3H, s), 4.07-4.15 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.0, 19.1, 19.7, 20.1, 27.4, 27.8, 28.3, 31.1, 32.6, 65.0, 65.8, 80.6, 81.0, 155.6, 157.0, 175.3, 176.5; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{21}NO_4Na$ 254.1363; Found 254.1361.



*Boc-D-MeVal-Pro-OH (**10**)*. To a solution of Boc-D-MeVal-OH (1.72 g, 7.43 mmol) and HCl·H-Pro-OBn (**12**) (1.80 g, 7.43 mmol) in THF (37 mL) was added DMTMM (2.06 g, 7.43 mmol) under Ar atmosphere. After 16 h of stirring at room temperature, the mixture was concentrated in vacuo. The residue was purified using column chromatography (10% EtOAc in hexane) to afford Boc-D-MeVal-Pro-OBn as a colorless oil (2.14 g, 5.11 mmol, 69%): $[\alpha]^{23}_{D} = +25.5$ (*c* 1.60, $CHCl_3$); IR (neat) 2966, 2874, 1746, 1687, 1651, 1432, 1382, 1305, 1148, 887, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, mixture of rotamers) δ 0.74-0.92 (6H, m), 1.39-1.47 (9H, m), 1.69-2.00 (3H, m), 2.12-2.23 (1H, m), 2.24-2.35 (1H, m), 2.65 (2H, s), 2.66 (0.6H, s), 2.72 (0.2H, s), 2.73 (0.2H, s), 3.51-3.58 (1H, m), 3.60-3.67 (1H, m), 4.06 (0.08H, d, *J* = 10.7 Hz), 4.24 (0.24H, d, *J* = 10.7 Hz), 4.32 (0.08H, d, *J* = 10.7 Hz), 4.47-4.53 (1.6H, m), 5.08 (1H, d, *J* = 12.2 Hz), 5.17 (1H, d, *J* = 12.2 Hz), 7.24-7.35 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, mixture of rotamers) δ 17.8, 18.0, 18.15, 18.20, 19.3, 19.6, 20.0, 20.3, 22.1, 25.0, 25.1, 26.5, 26.7, 26.8, 26.9, 28.28, 28.33, 28.4, 28.86, 28.90, 29.0, 29.4, 31.0, 31.1, 42.7, 46.0, 46.1, 46.4, 46.7, 58.6, 58.8, 58.9, 59.2, 61.1, 61.4, 62.6, 62.9, 66.7, 66.8, 67.0, 67.3, 77.4, 79.7, 79.8, 79.9, 80.0, 80.6, 128.0, 128.1, 128.16, 128.22, 128.3, 128.49, 128.50, 128.52, 128.7, 130.2, 135.58, 135.62, 135.7, 155.2, 156.2, 156.4, 168.6, 168.7, 169.1, 169.6, 171.7, 171.9, 172.1, 175.5; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{34}N_2O_5Na$ 441.2360; Found 441.2357.

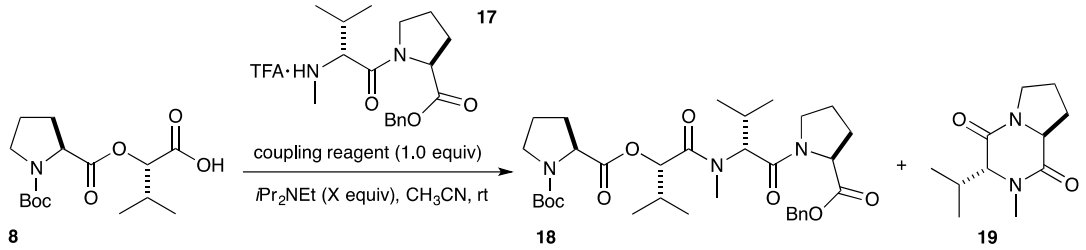
To a solution of Boc-D-MeVal-Pro-OBn (152 mg, 0.363 mmol) in CH_3OH (1.8 mL) was carefully added 10% Pd/C (15.2 mg, 10 wt%) under Ar atmosphere. The solution was purged with H_2 gas and stirring was continued under H_2 atmosphere at room temperature for 16 h. The solution was filtered through celite and concentrated in vacuo. The crude product was purified using column chromatography (30% EtOAc in hexane) to afford **10** as a colorless oil (90.6 mg, 0.276 mmol, 76%): $[\alpha]^{23}_{D} = +15.8$ (*c* 0.56, $CHCl_3$); IR (neat) 3489, 2968, 1743, 1687, 1652, 1446, 1393, 1367, 1306, 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.86 (3H, d, *J* = 6.8 Hz), 0.90 (3H, d, *J* = 6.8 Hz), 1.38-1.50 (9H, m), 1.80-2.10 (3H, m), 2.26-2.37 (2H, m), 2.74 (2.8H, s), 2.76 (0.2H, s), 3.58-3.62 (1H, m), 3.63-3.70 (1H, m), 4.29 (0.20H, d, *J* = 10.7 Hz), 4.35 (0.04H, d, *J* = 10.7 Hz), 4.50-4.60 (1.76H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.9, 19.6, 20.0, 24.9, 26.7, 26.9, 27.3, 27.6, 28.3, 28.4, 29.4, 47.1, 47.8, 59.9, 61.2, 62.7, 80.3, 156.3, 172.3, 172.5; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{28}N_2O_5Na$ 351.1890; Found 351.1889.



17

*TFA·H-D-MeVal-Pro-OBn (**17**)*. To Boc-D-MeVal-Pro-OBn (54.4 mg, 0.130 mmol) was added TFA/CH_2Cl_2 (1:4 v/v, 4.3 mL). After 1 h of stirring at room temperature, the solution was concentrated in vacuo to afford crude TFA·H-D-MeVal-Pro-OBn (**17**), which was used in the next step without further purification.

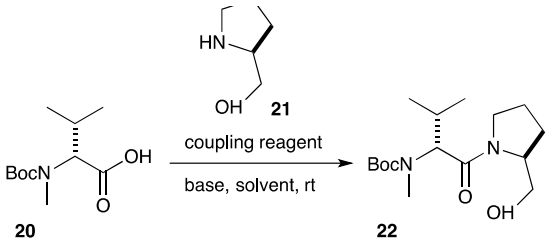
Optimization for the synthesis of 18[a]



entry	coupling reagent	X	yield (%) of **18**[b]	yield (%) of **19**[b]
1	DMTMM	2	47	0[c]
2	DMTMM	6	46	0[c]
3	DMTMM	10	2	0[c]
4	PyBroP	2	12	16
5	PyBroP	6	28	45
6	PyBroP	10	28	62

[a]Reaction conditions: **8** (0.130 mmol), **17** (1.0 equiv), coupling reagent (1.0 equiv), CH_3CN, rt, 16 h, otherwise mentioned. [b]Isolated yield. [c]Complex mixture.

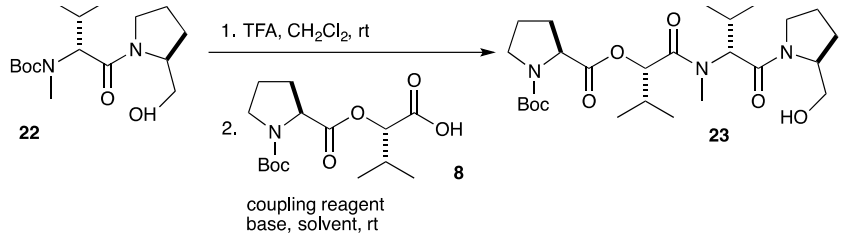
Optimization for the synthesis of 22[a]



entry	coupling reagent	base	solvent	yield (%)[b]
1	PyBOP	$^{i}Pr_2NEt$	CH_3CN	0[c]
2	DECP	Et_3N	CH_3CN	65
3[d]	HATU/HOAt	$^{i}Pr_2NEt$	CH_3CN	69[e]
4	DMTMM		CH_3CN	95[e]
5	DMTMM	Et_3N	CH_3CN	99[e]
6[d]	EDCI/HOAt	$NaHCO_3$	$CHCl_3$	87
7[d]	EDCI/HOAt	$NaHCO_3$	CH_3CN	91
8[d]	EDCI/HOAt	$NaHCO_3$	CH_2Cl_2	92
9[d]	EDCI/HOAt	$NaHCO_3$	THF	93
10[d,f]	EDCI/HOAt	$NaHCO_3$	THF	94

[a]Reaction conditions: **20** (0.220 mmol), **21** (1.0 equiv), coupling reagent (1.0 equiv), base (1.0 equiv), rt, 16 h, otherwise mentioned. [b]Isolated yield. [c]Complex mixture. [d]1.0 equiv of HOAt was used. [e]Contains inseparable impurities. [f]**20** (2.63 mmol).

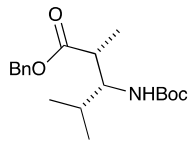
Optimization for the synthesis of 23[a]



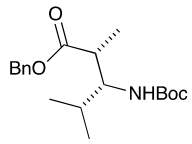
entry	coupling reagent	base	solvent	yield (%)[b]
1[c]	Triphosgene	$^{i}Pr_2NEt$, 2,4,6-collidine	CH_3CN	0
2[d]	HATU/HOAt	$^{i}Pr_2NEt$	CH_3CN	2
3	DECP	Et_3N	CH_3CN	9
4[d]	EDCI/HOAt	Et_3N	CH_3CN	10
5	DMTMM	$^{i}Pr_2NEt$	CH_3CN	54[e]
6	DMTMM	Et_3N	CH_3CN	63[e]
7	PyBroP	Et_3N	CH_3CN	40
8	PyBroP	$^{i}Pr_2NEt$	THF	46
9	PyBroP	$^{i}Pr_2NEt$	CH_3CN	60
10[f]	PyBroP	$^{i}Pr_2NEt$	CH_3CN	76

[a]Reaction conditions: **8** (0.130 mmol), **22** (1.0 equiv), coupling reagent (1.0 equiv), base (6.0 equiv), rt, 16 h, otherwise mentioned. [b]Isolated yield. [c]2,4,6-collidine (1.0 equiv) was added. [d]1.0 equiv of HOAt was used. [e]Mixture of diastereomers. [f]1.5 equiv of coupling reagent and 10 equiv of $^{i}Pr_2NEt$ were used.

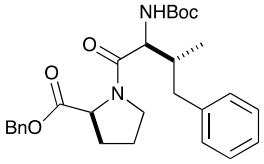
NMR Spectra



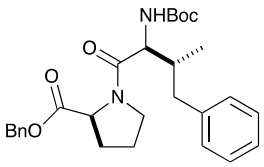
Boc-DmI-OBn



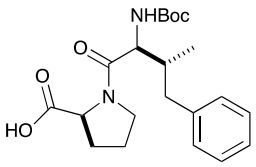
Boc-DmI-OBn



Boc-Dpv-Pro-OBn



Boc-Dpv-Pro-OBn


NHBoc
O
O
N
HO

14

6.31
0.82
1.00
0.90
0.85
1.01
1.01
0.94
0.81
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2.11
9.93
3.03
PPM
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7
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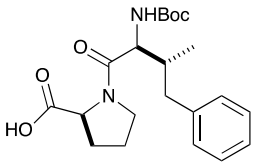
NHBoc
O
O
N
HO

14

200
175
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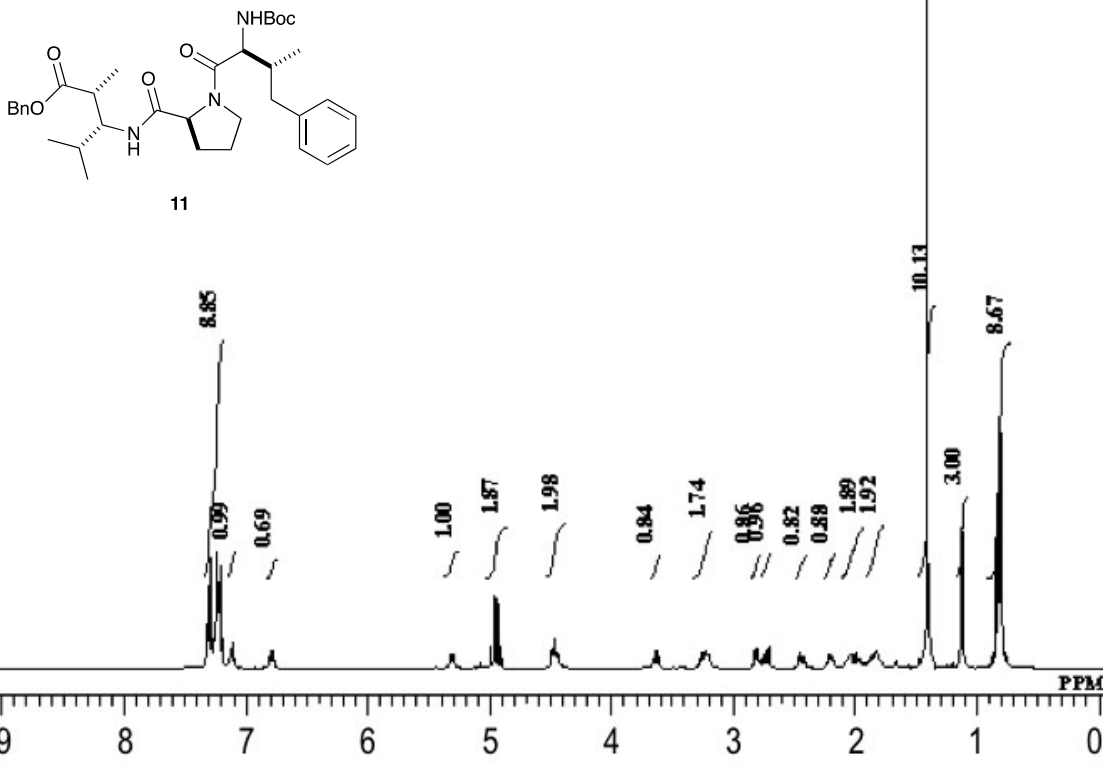
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O
O
BnO
O
N
H
N
11
8.85
0.99
0.69
1.00
1.87
1.98
0.84
1.74
0.86
0.82
0.88
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10.13
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7
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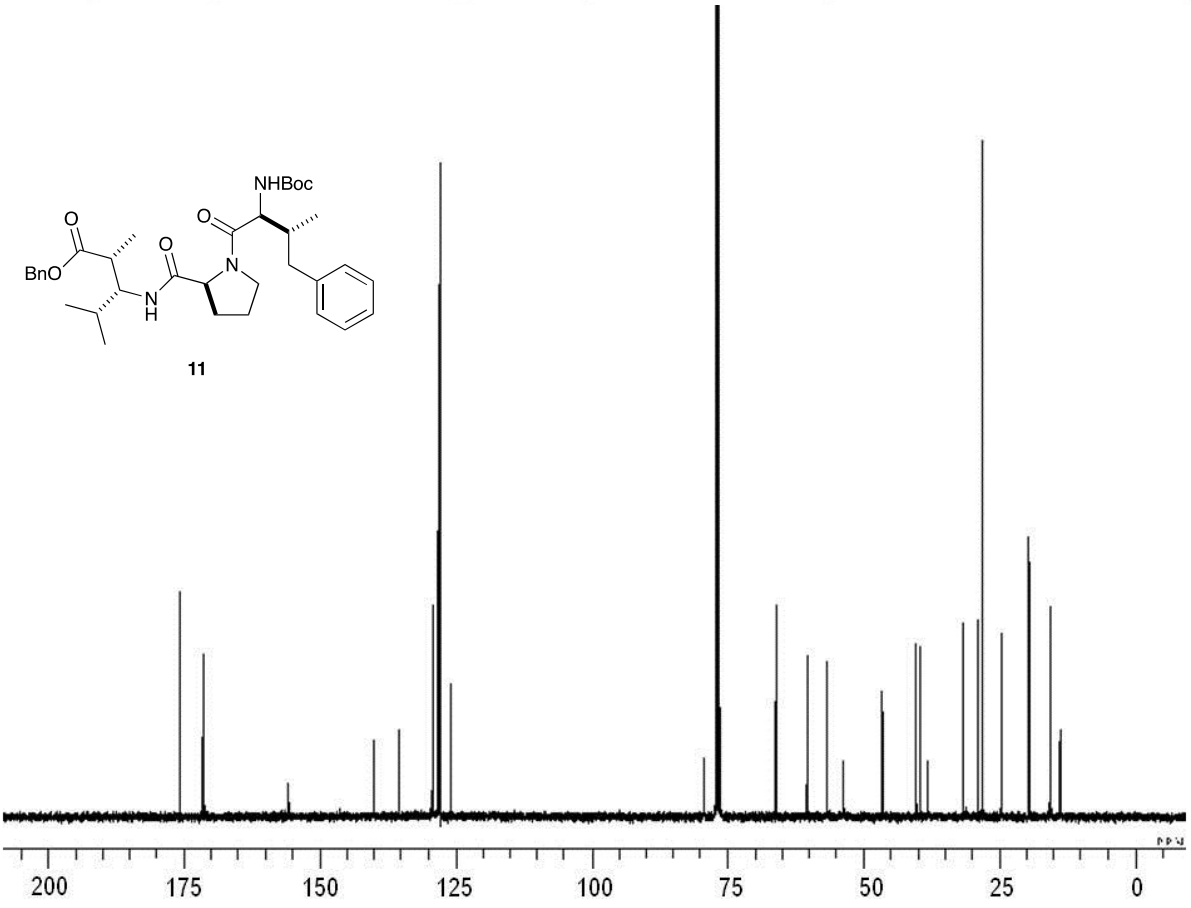
NHBoc
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O
BnO
O
N
H
N
11
200
175
150
125
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25
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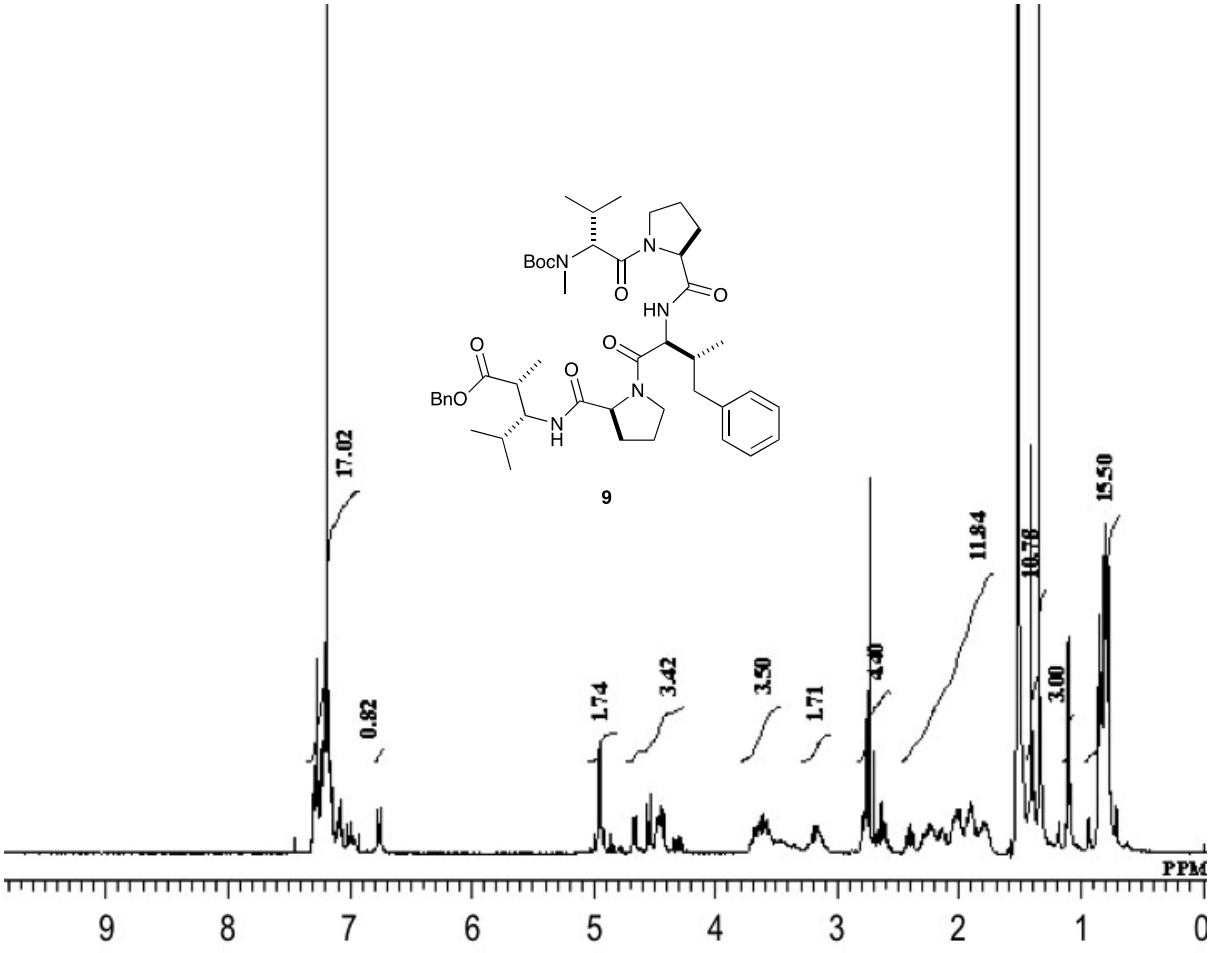
BocN
BnO
HN
N
O
H
9
17.02
0.82
1.74
3.42
3.50
1.71
4.40
11.84
10.78
3.00
15.50
PPM
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8
7
6
5
4
3
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1
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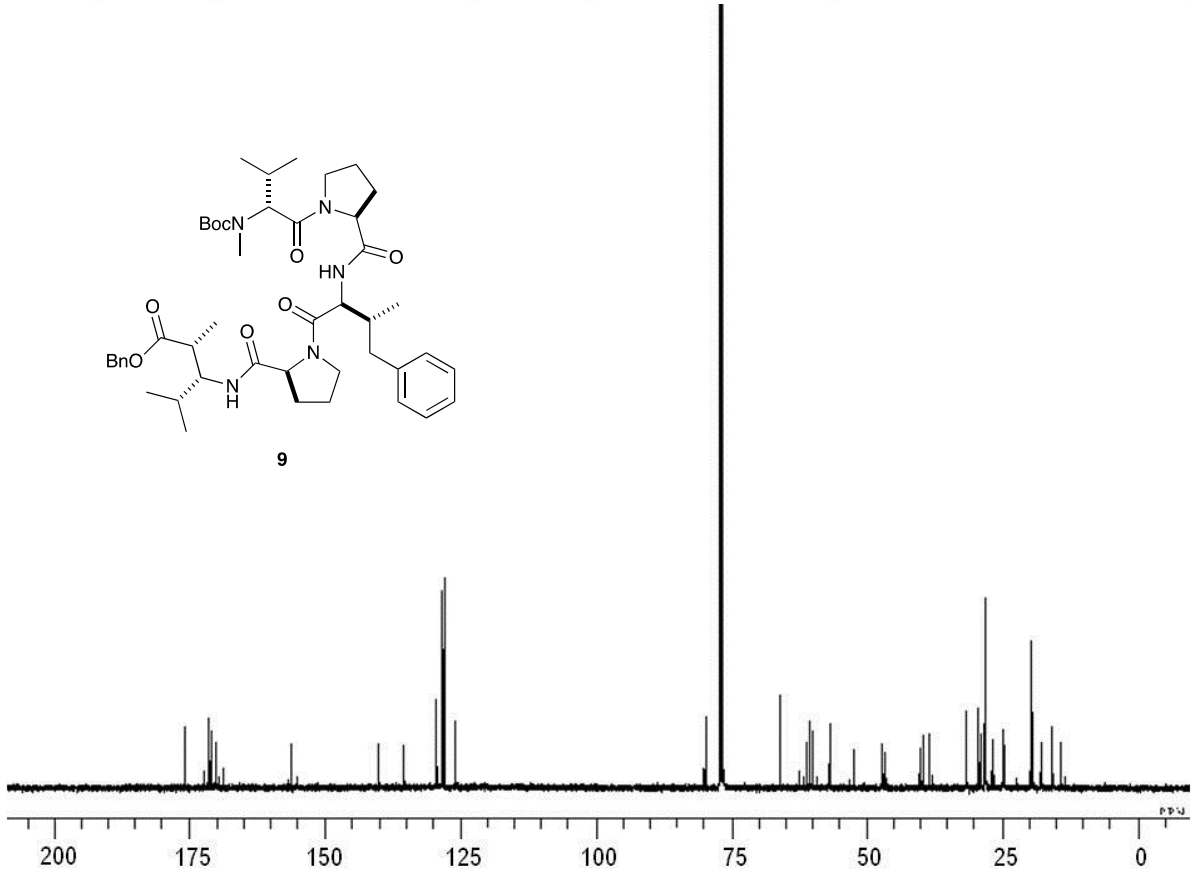
BocN
BnO
HN
N
O
H
9
200
175
150
125
100
75
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25
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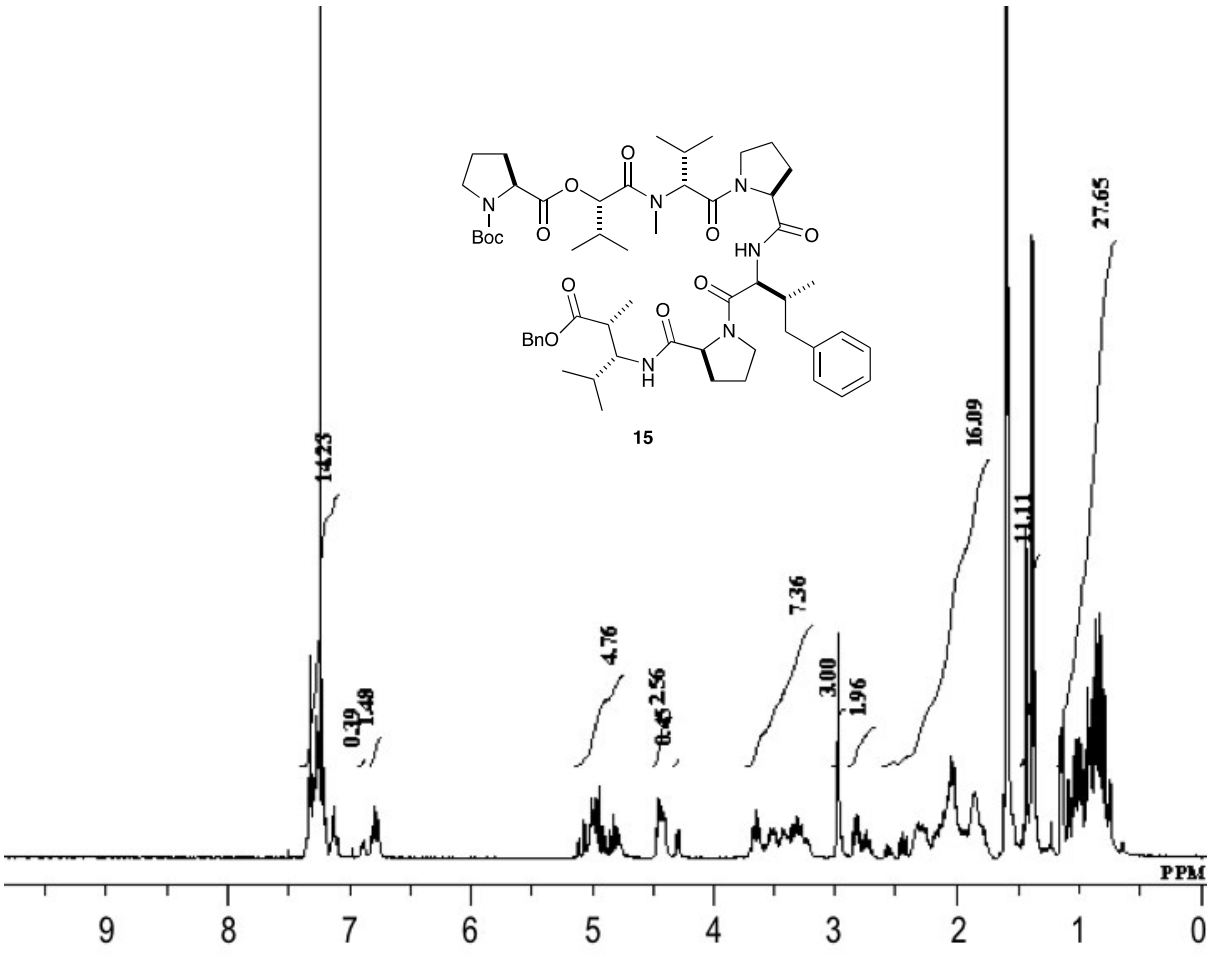
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14.23
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1.48
4.76
2.56
7.36
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16.09
11.11
27.65
PPM
9
8
7
6
5
4
3
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1
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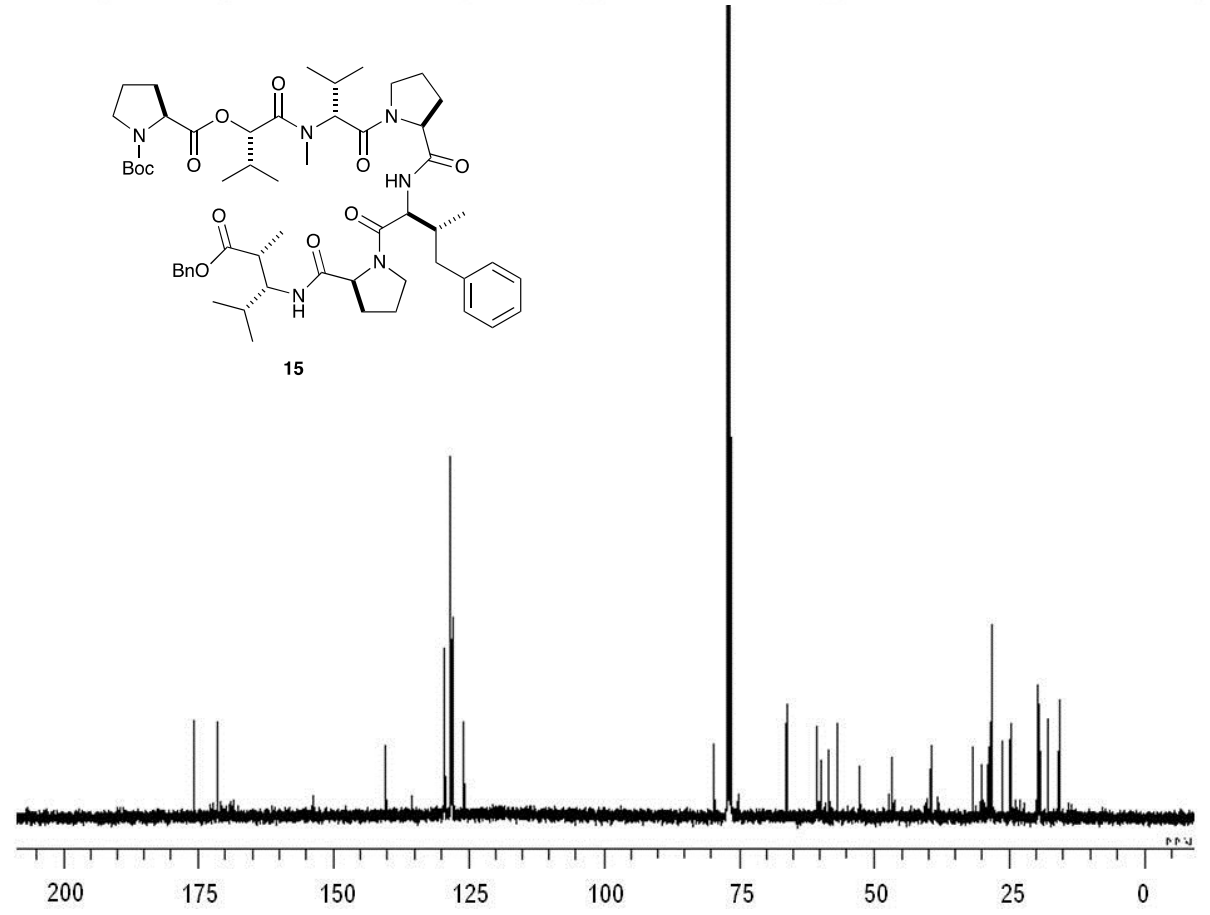
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200
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150
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100
75
50
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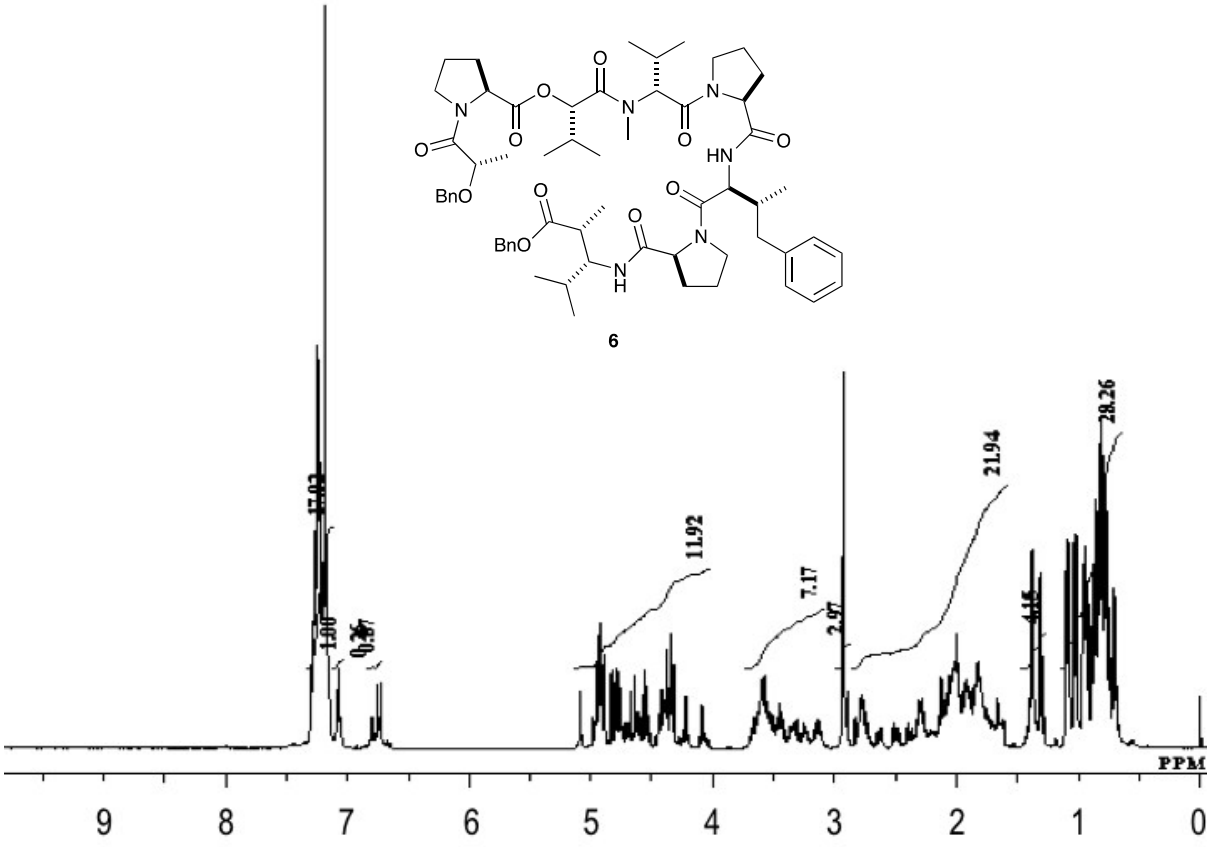
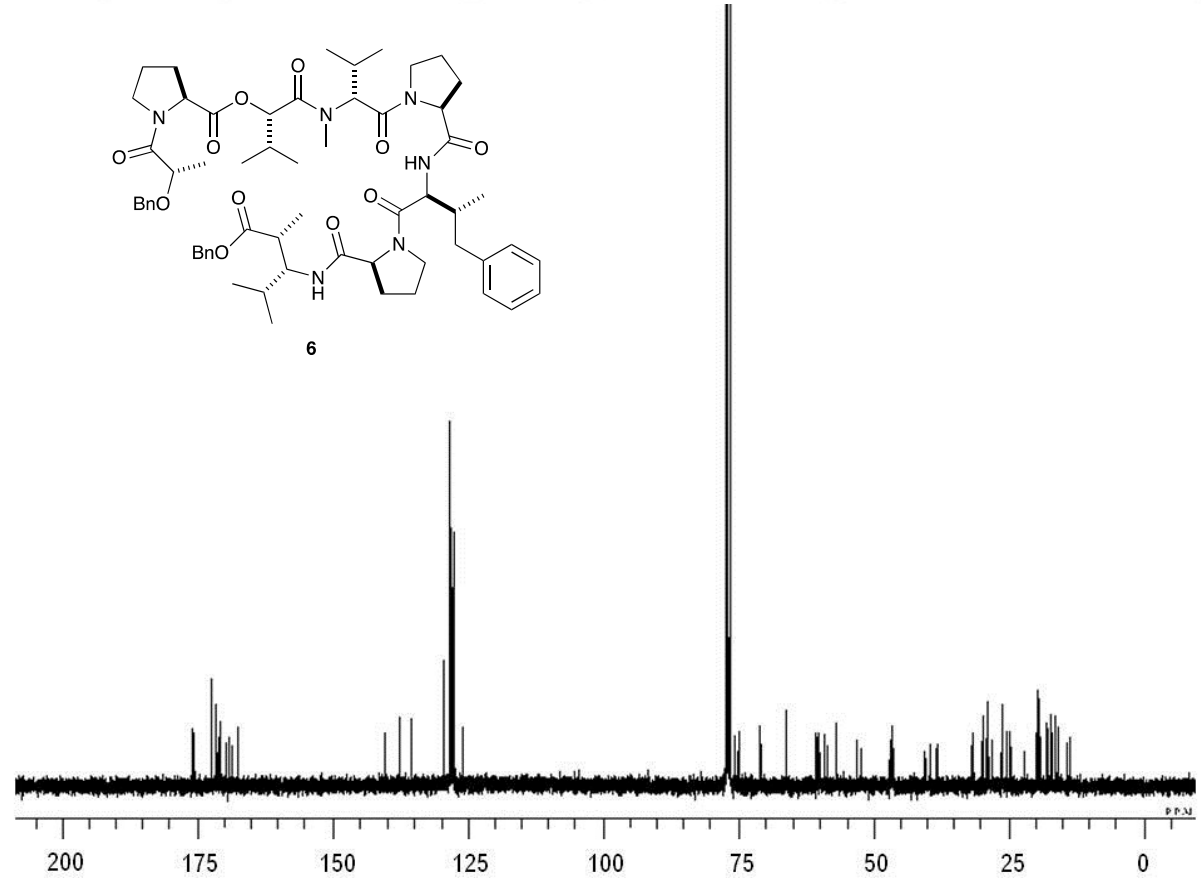
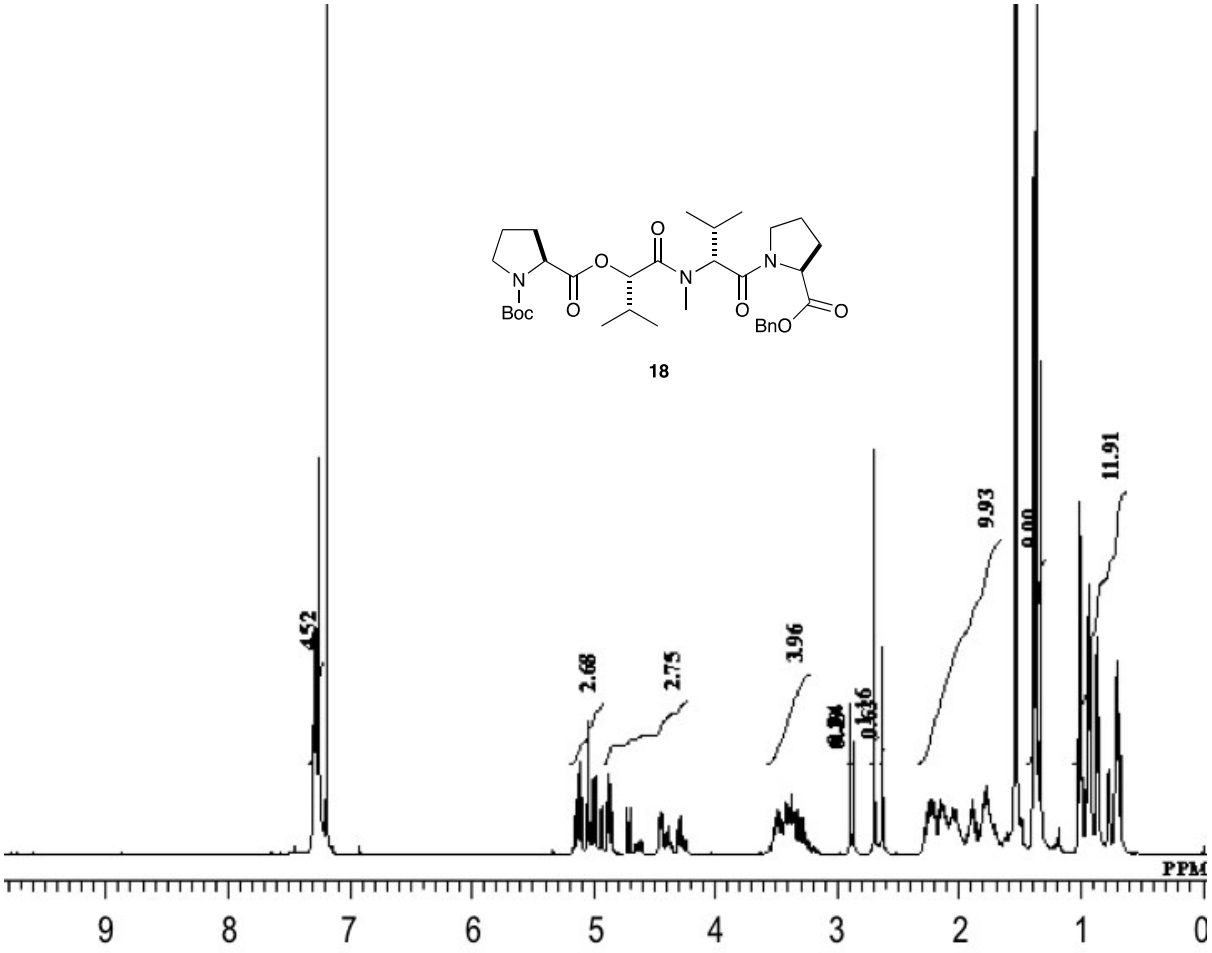
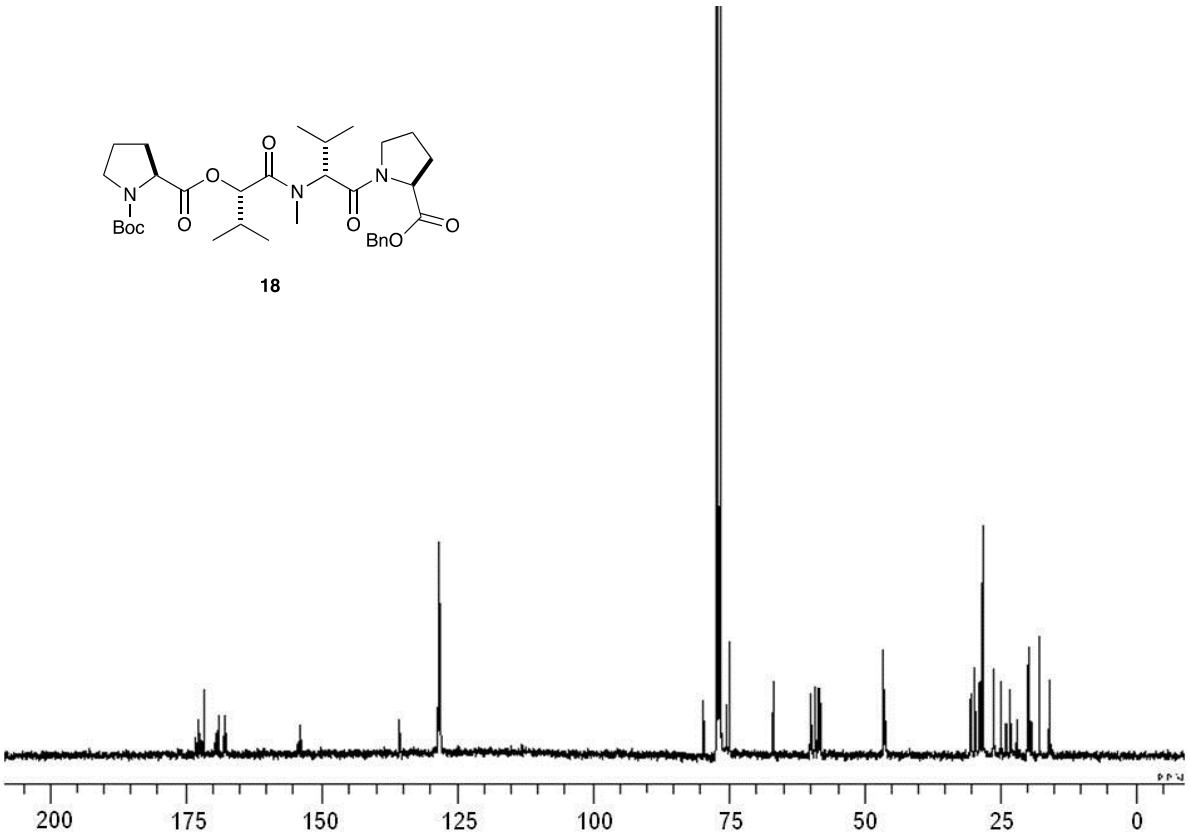
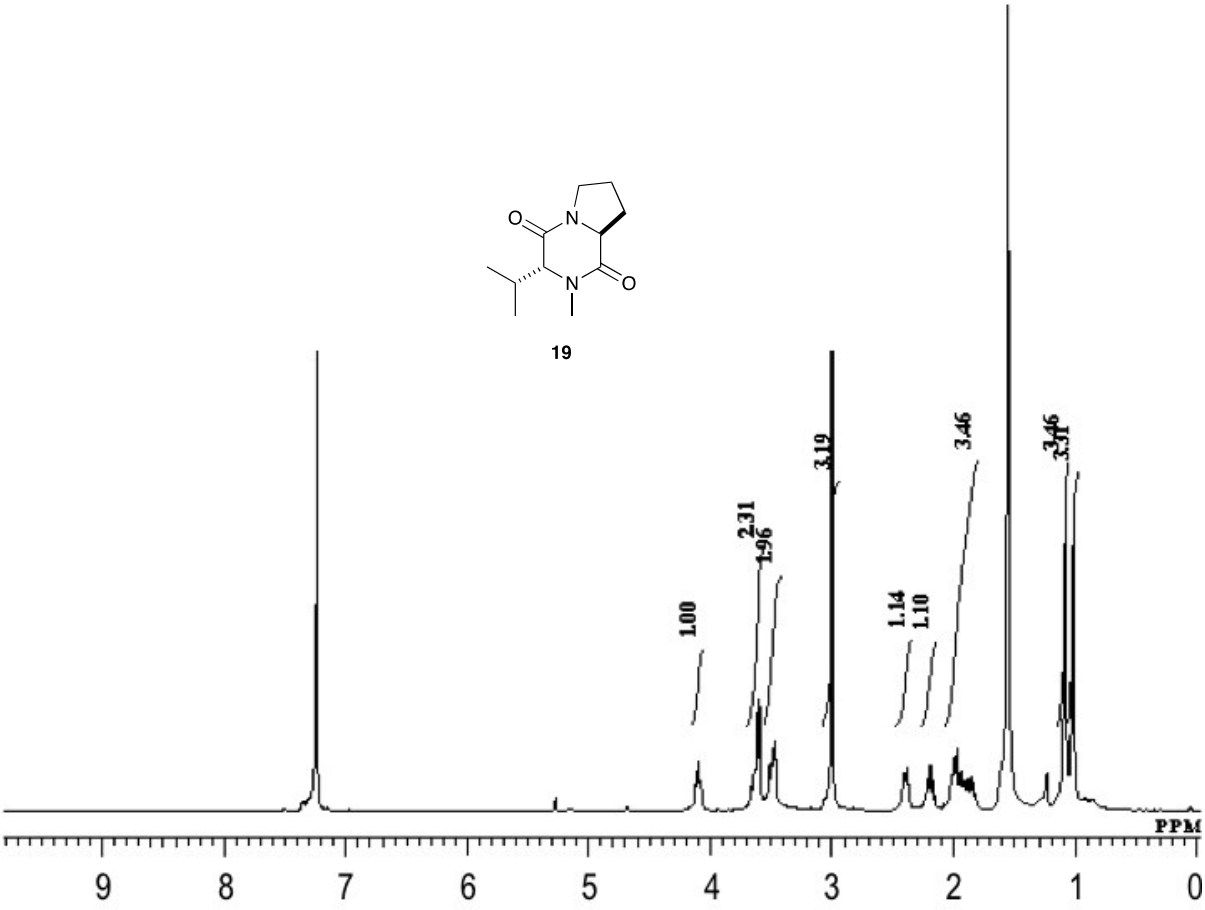
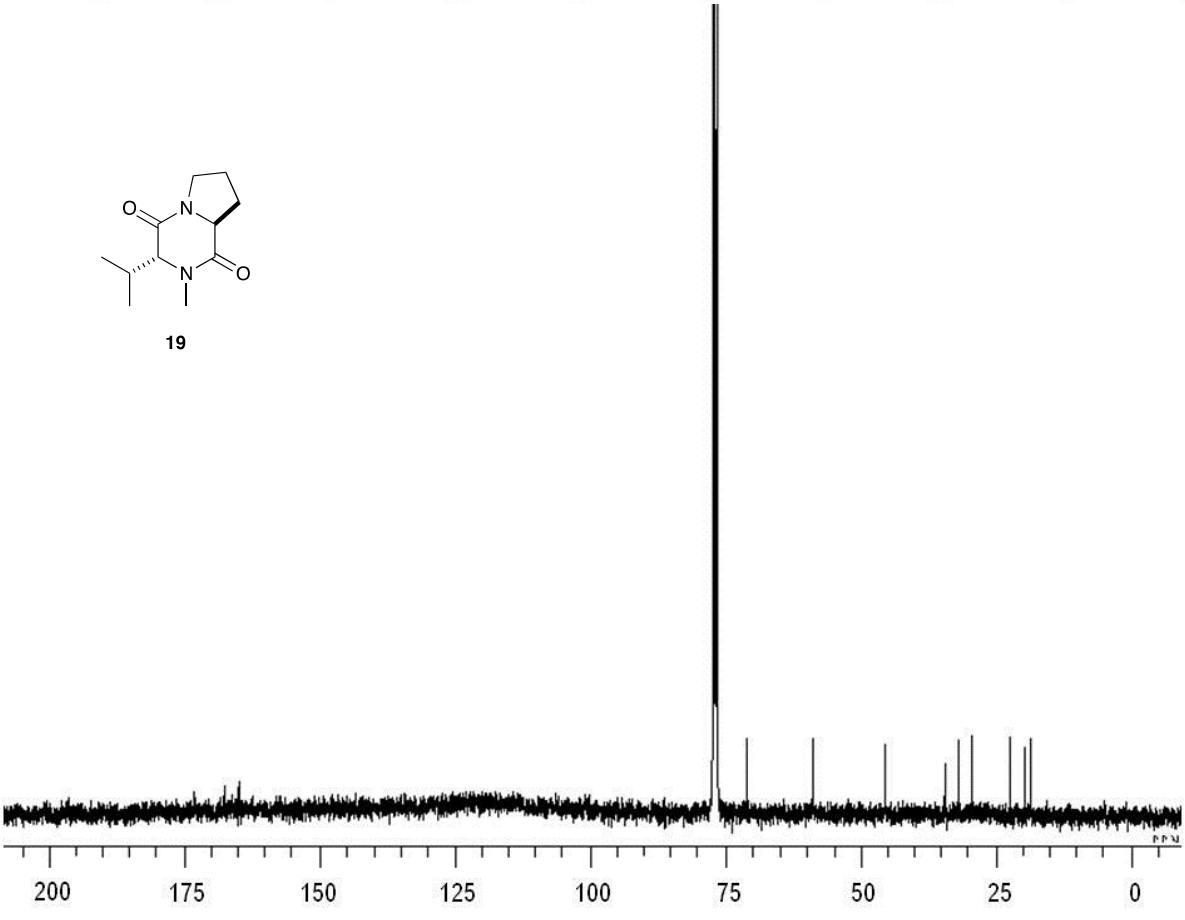

6
11.92
7.17
21.94
28.26
PPM
9
8
7
6
5
4
3
2
1
0


6
200
175
150
125
100
75
50
25
0


Boc
BnO
18
4.52
2.68
2.75
3.96
9.93
0.00
11.91
PPM
9
8
7
6
5
4
3
2
1
0


Boc
BnO
18
200
175
150
125
100
75
50
25
0


19
1.00
2.31
1.96
3.19
1.14
1.10
3.46
3.46
3.41
PPM
9
8
7
6
5
4
3
2
1
0


19
200
175
150
125
100
75
50
25
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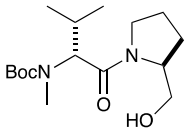
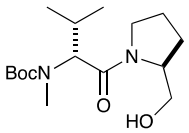

BocN
N
O
HO

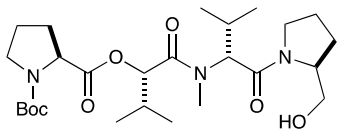
22

8.64
3.00
2.71
2.68
1.82
1.74
1.59
1.19
0.92
0.90
0.65
0.64
0.56
0.22
PPM
9
8
7
6
5
4
3
2
1
0


BocN
N
O
HO

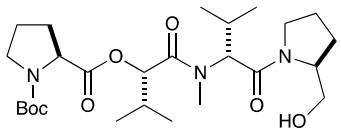
22

200
175
150
125
100
75
50
25
0


N
Boc
O
O
O
O
N
N
O
HO

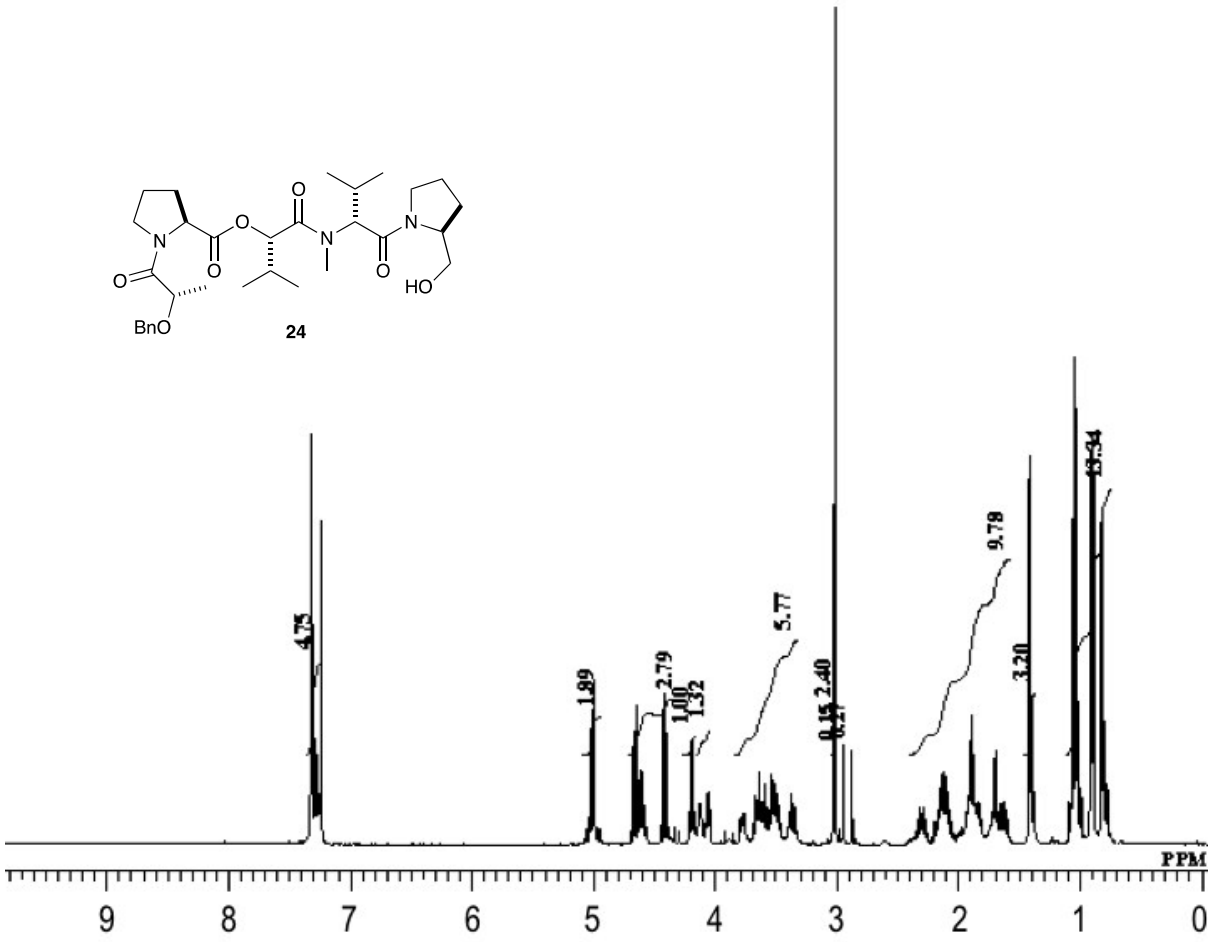
23

1.58
1.03
0.79
5.36
3.00
9.62
10.56
13.25
PPM
9
8
7
6
5
4
3
2
1
0


N
Boc
O
O
O
O
N
N
O
HO

23

200
175
150
125
100
75
50
25
0


BnO
HO
24
4.75
1.89
2.79
1.00
1.32
5.77
0.15
2.40
0.21
9.78
3.20
13.34
PPM
9
8
7
6
5
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3
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1
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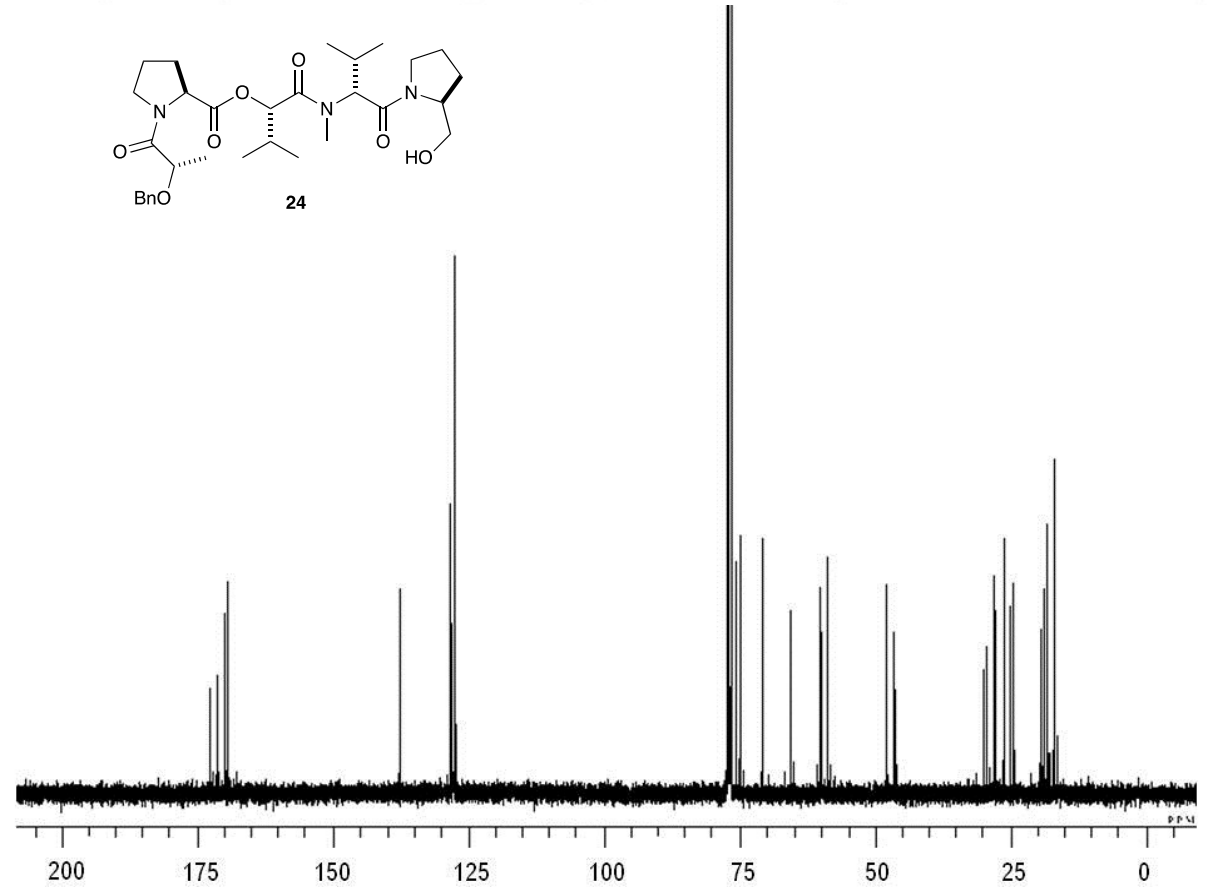
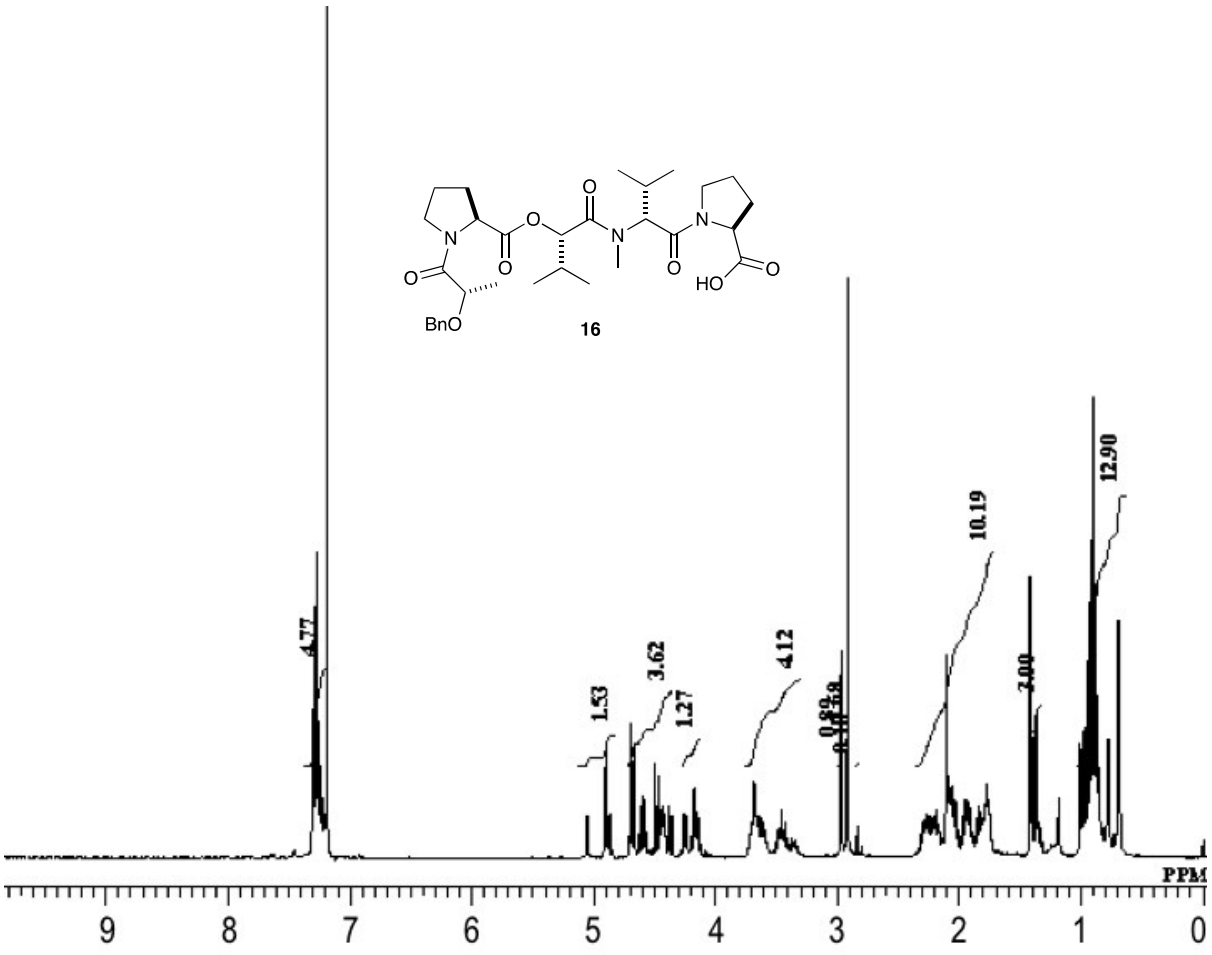
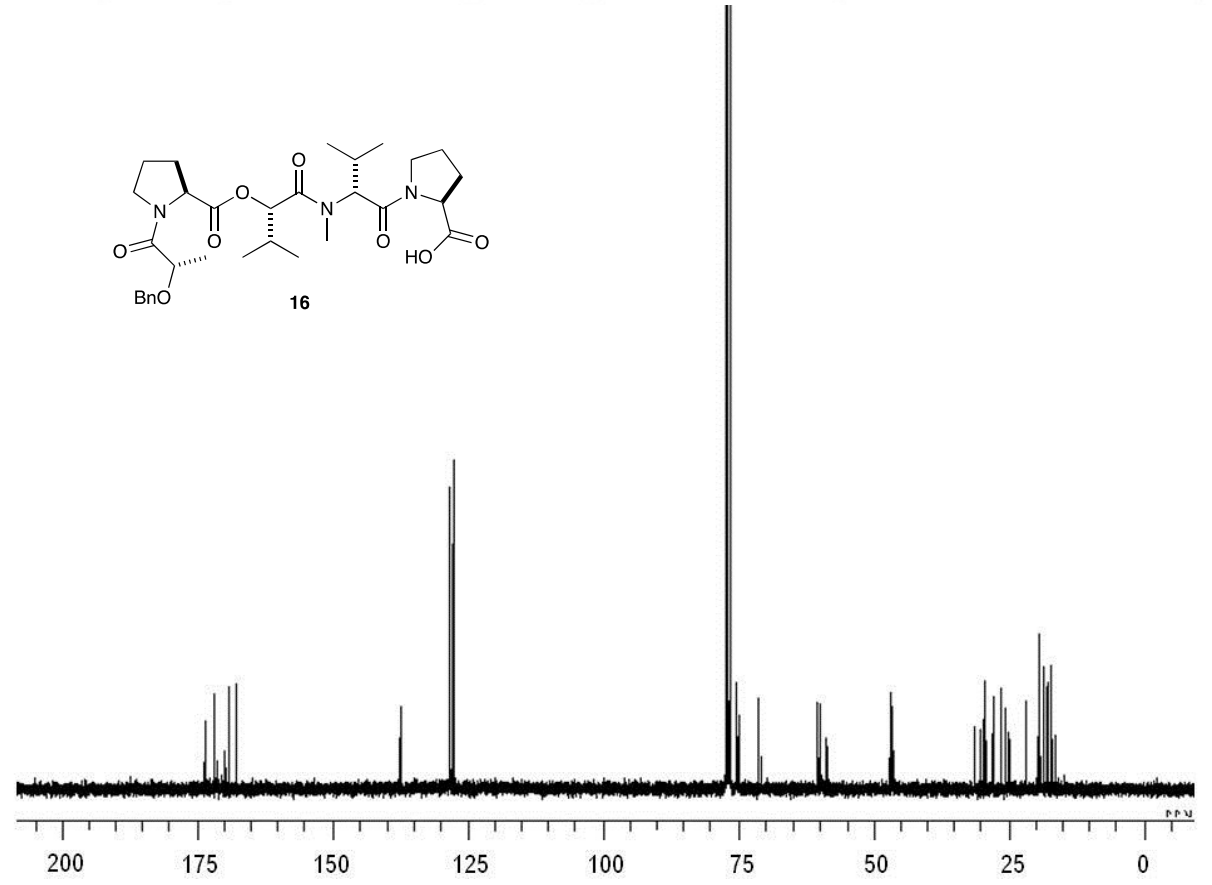
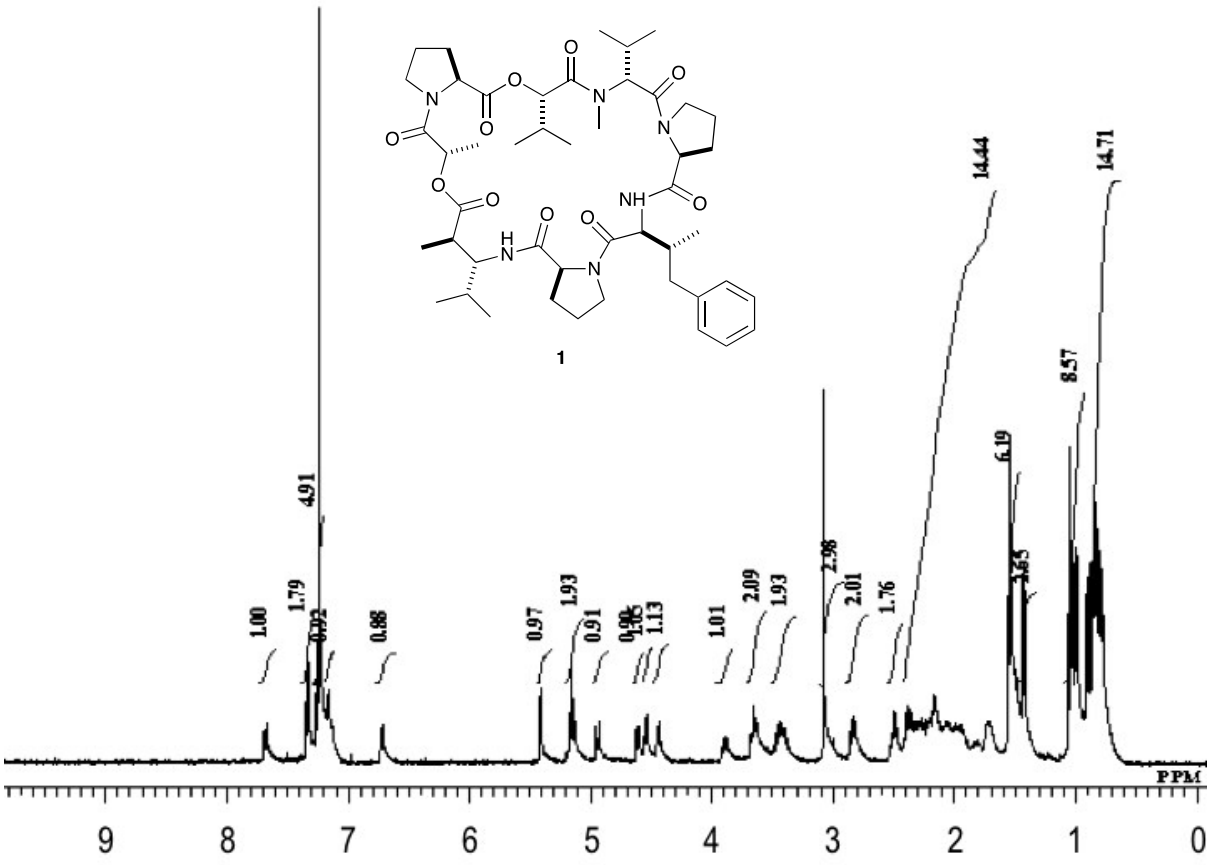
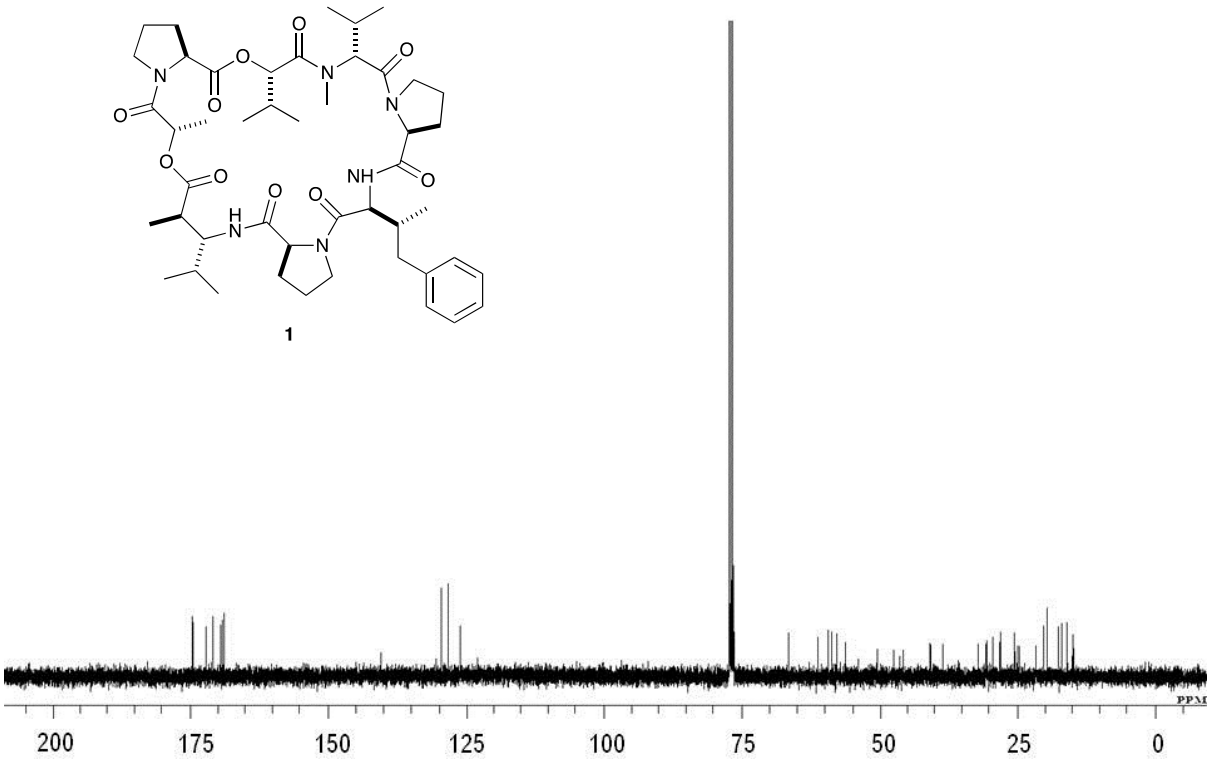
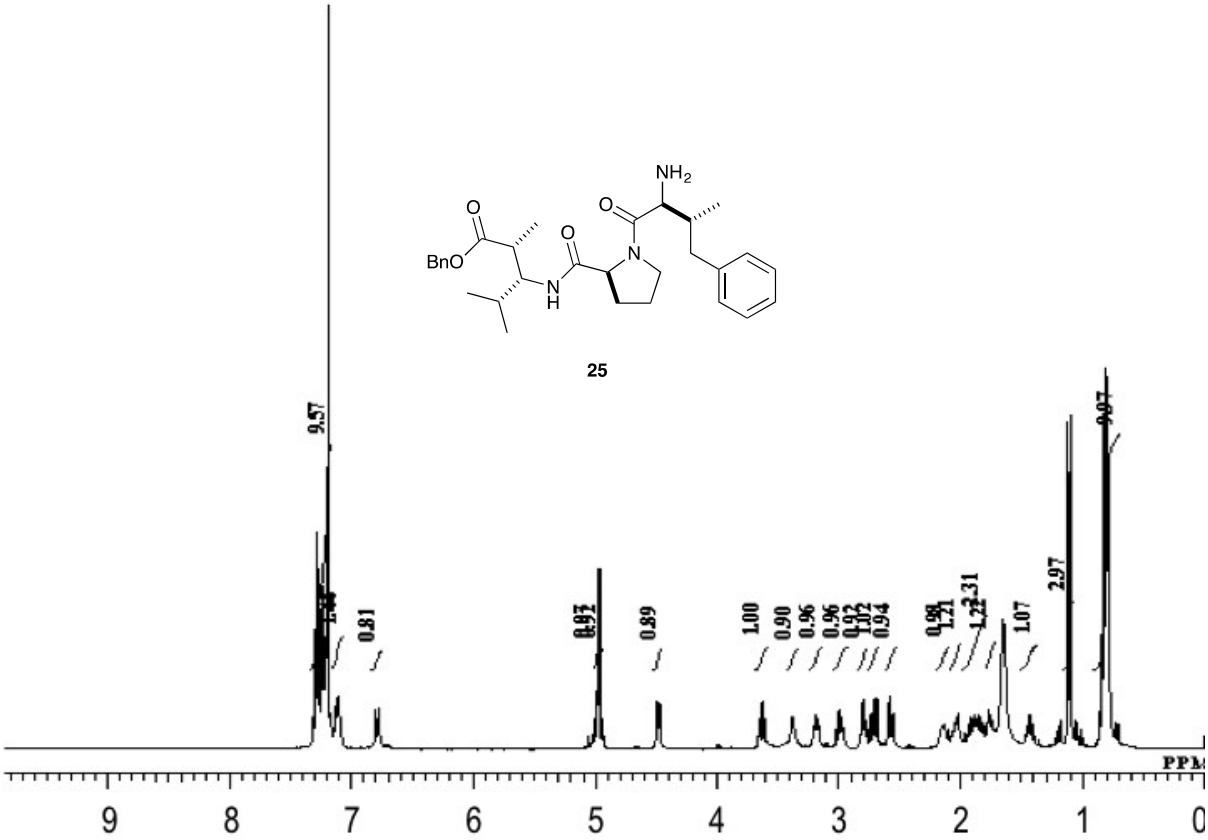

BnO
HO
24
200
175
150
125
100
75
50
25
0

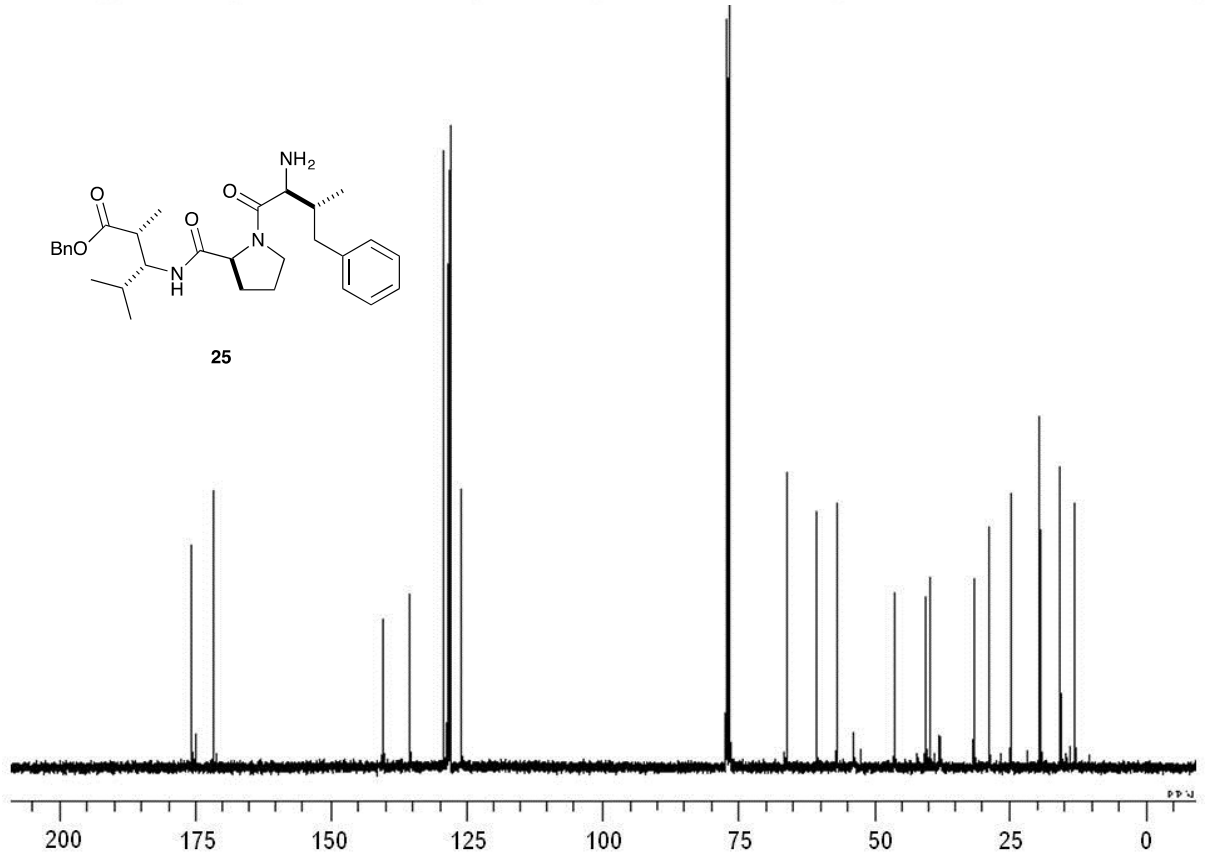

BnO
16
4.77
1.53
3.62
1.27
4.12
10.19
2.00
12.90
PPM
9
8
7
6
5
4
3
2
1
0

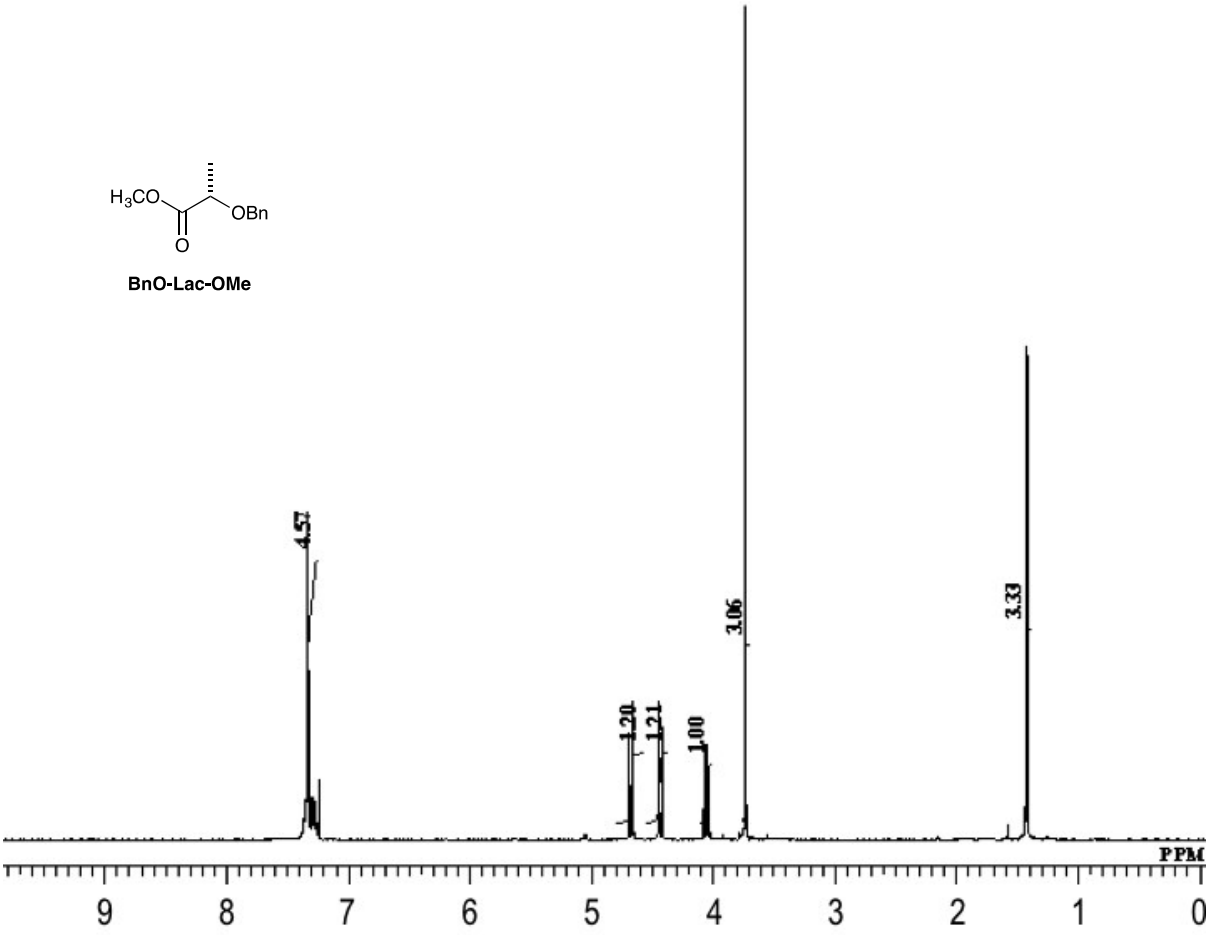

BnO
16
200
175
150
125
100
75
50
25
0

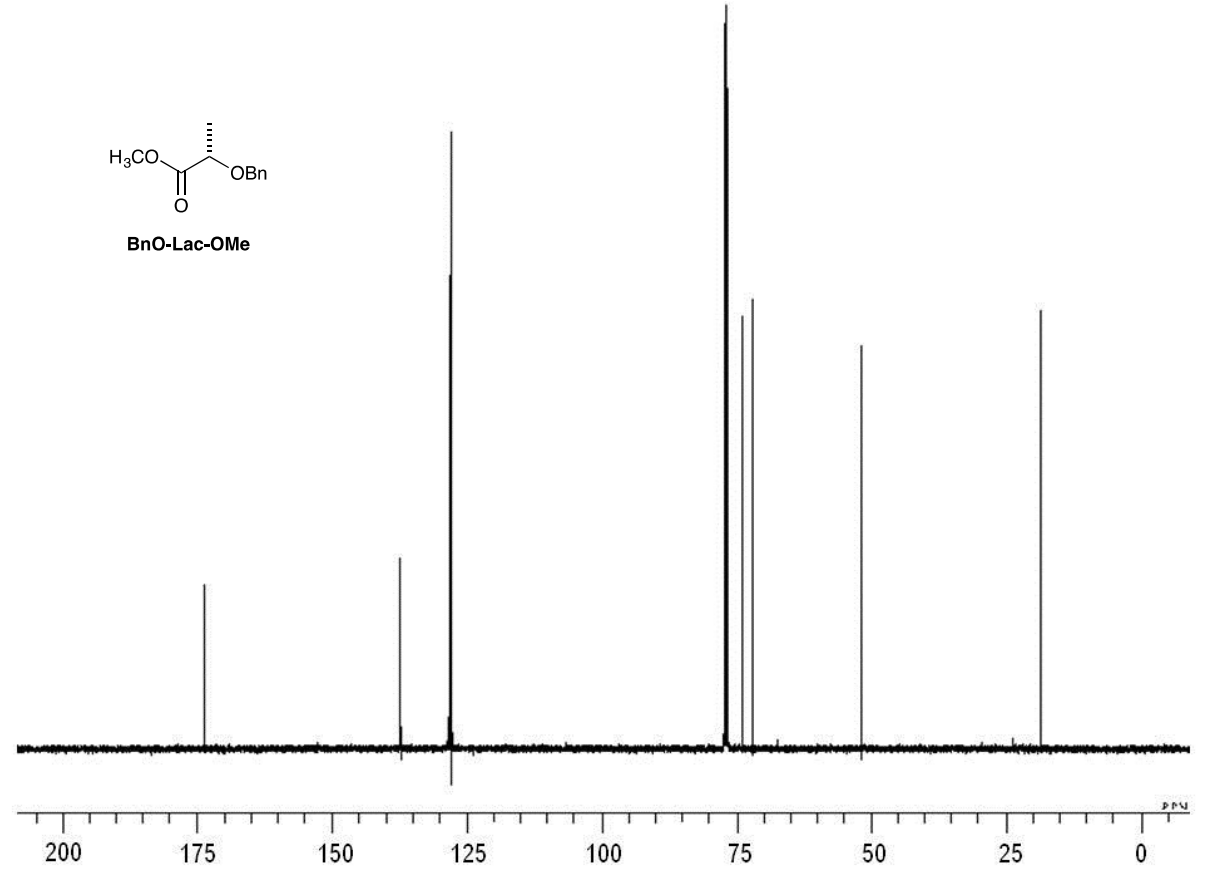

1
1.00
1.79
4.91
0.88
0.97
1.93
0.91
1.13
1.01
2.09
1.93
2.98
2.01
1.76
14.44
6.19
3.65
8.57
14.71
PPM
9
8
7
6
5
4
3
2
1
0

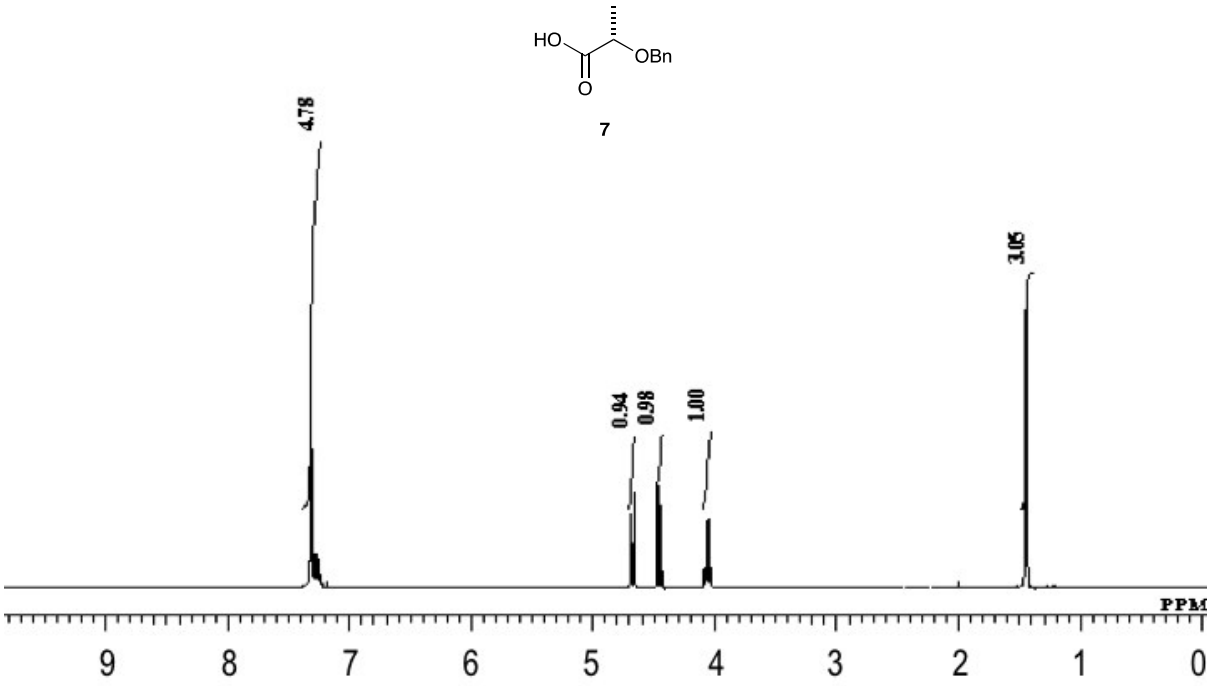

1
PPM
200
175
150
125
100
75
50
25
0

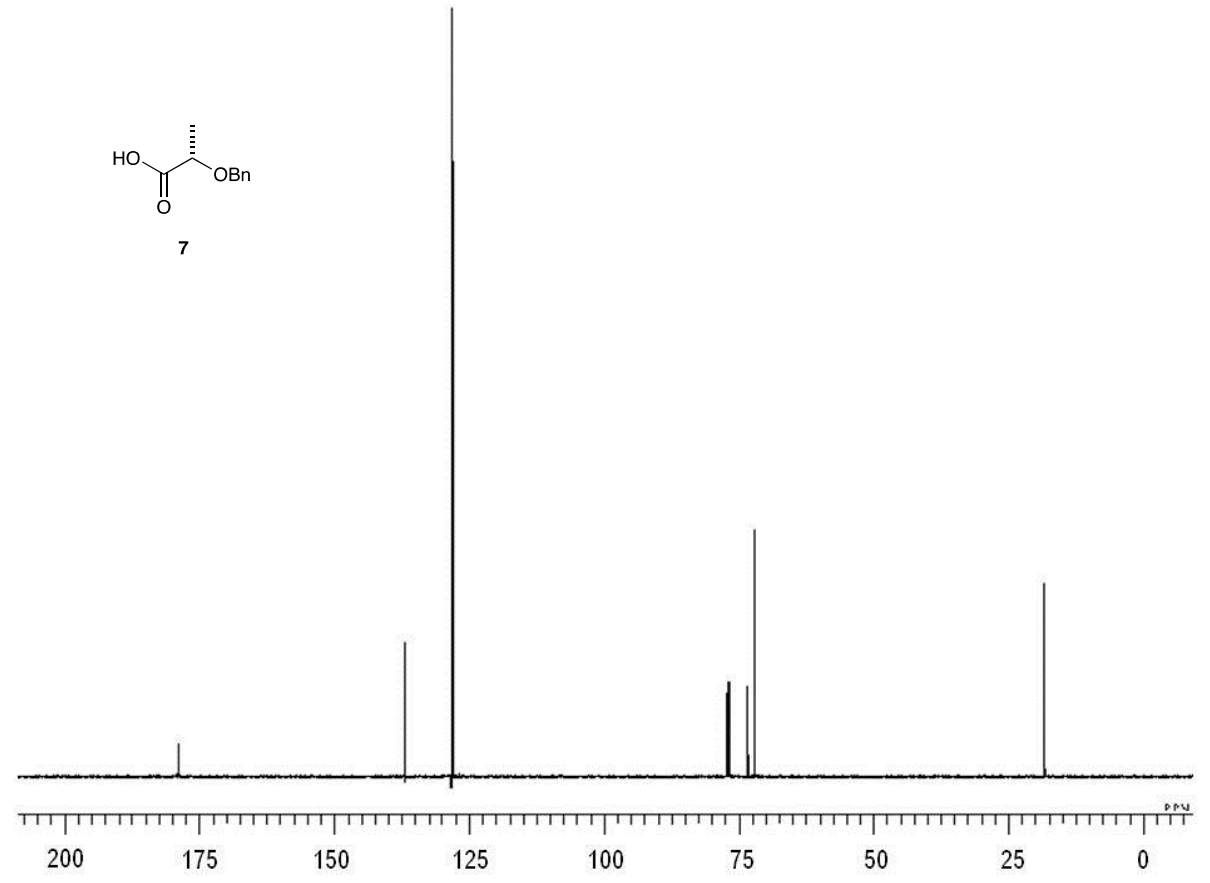

NH2
O
O
BnO
O
N
N
H
25
9.57
0.81
0.89
1.00
0.90
0.96
0.96
1.07
2.97
9.07
9
8
7
6
5
4
3
2
1
0

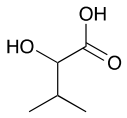

NH2
O
O
BnO
O
N
N
H
25
200
175
150
125
100
75
50
25
0


H3CO
OBn
O
BnO-Lac-OMe
4.57
1.20
1.21
1.00
3.06
3.33
PPM
9
8
7
6
5
4
3
2
1
0

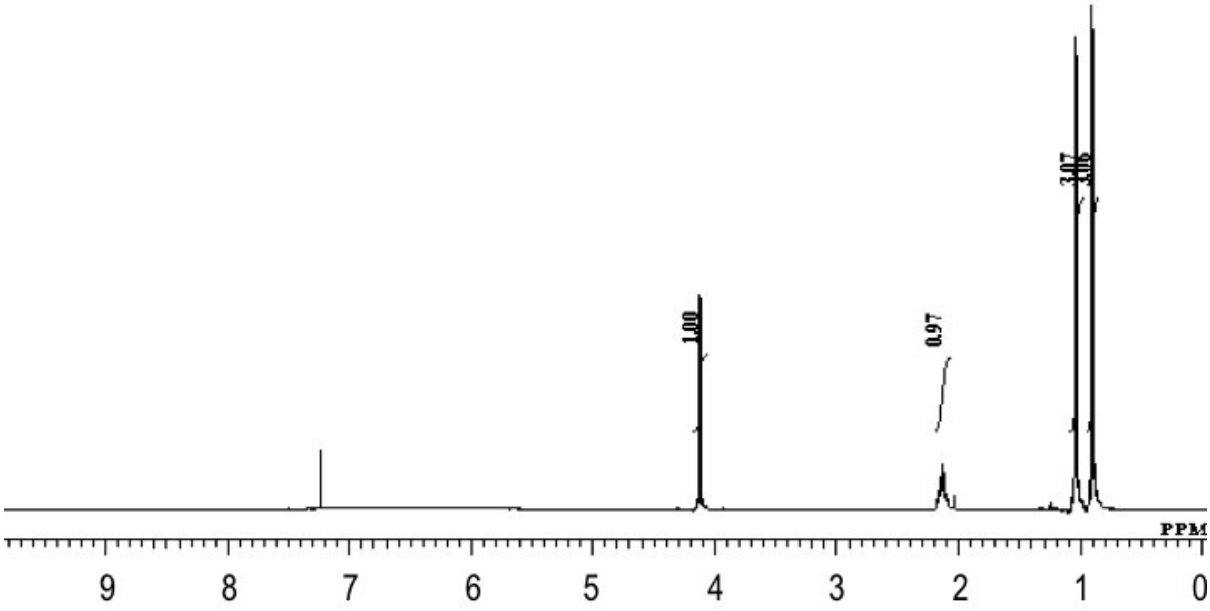

H3CO
OBn
O
BnO-Lac-OMe
200
175
150
125
100
75
50
25
0

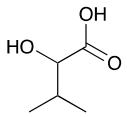

HO
OBn
O
7
4.78
0.94
0.98
1.00
3.05
PPM
9
8
7
6
5
4
3
2
1
0


HO
OBn
O
7
PPM
200
175
150
125
100
75
50
25
0

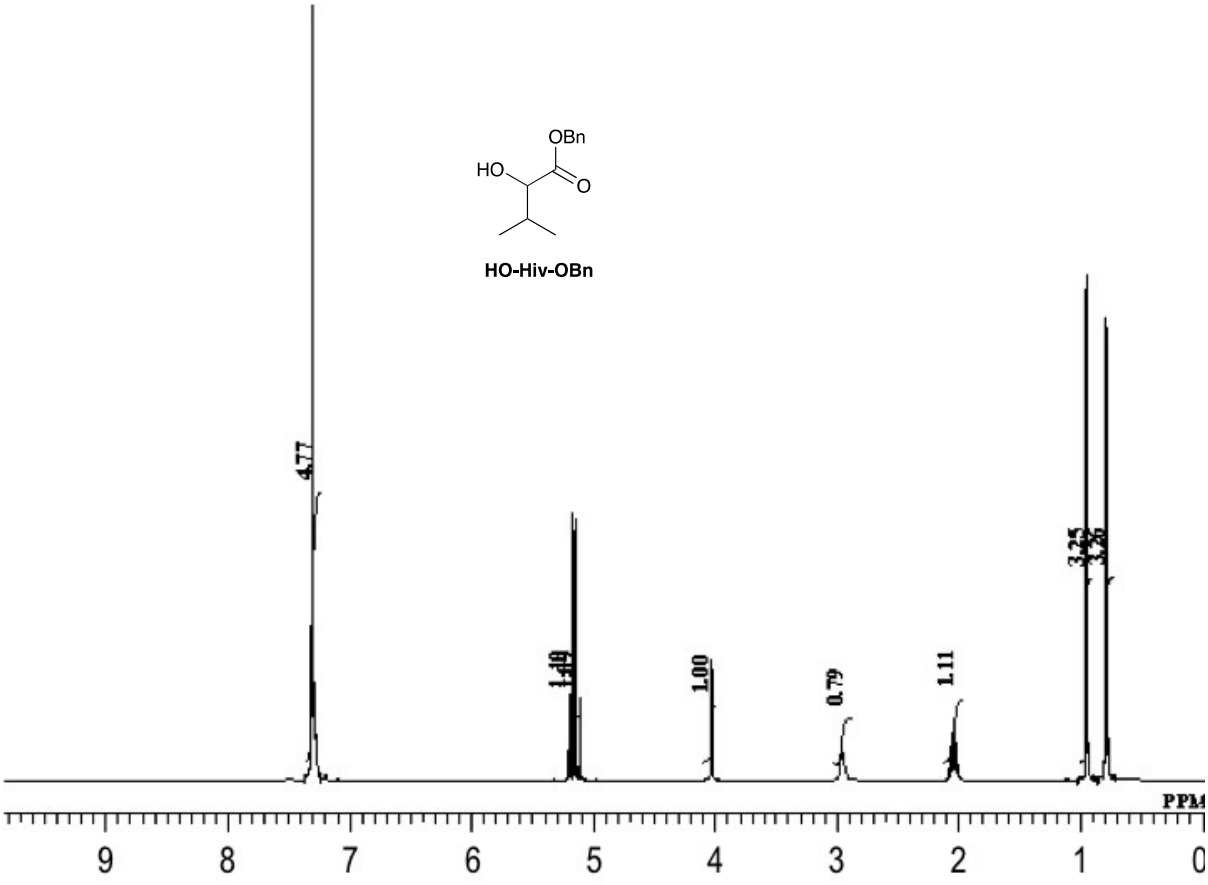


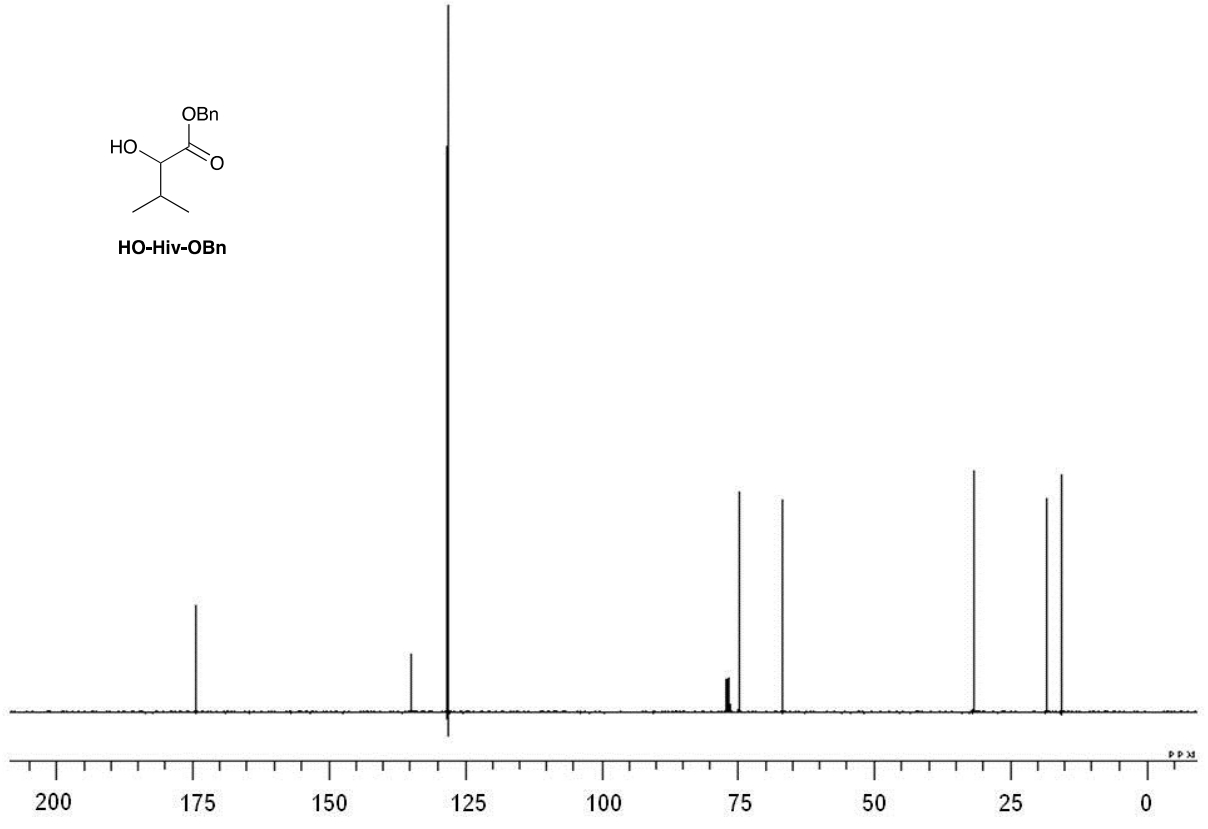
HO-Hiv-OH

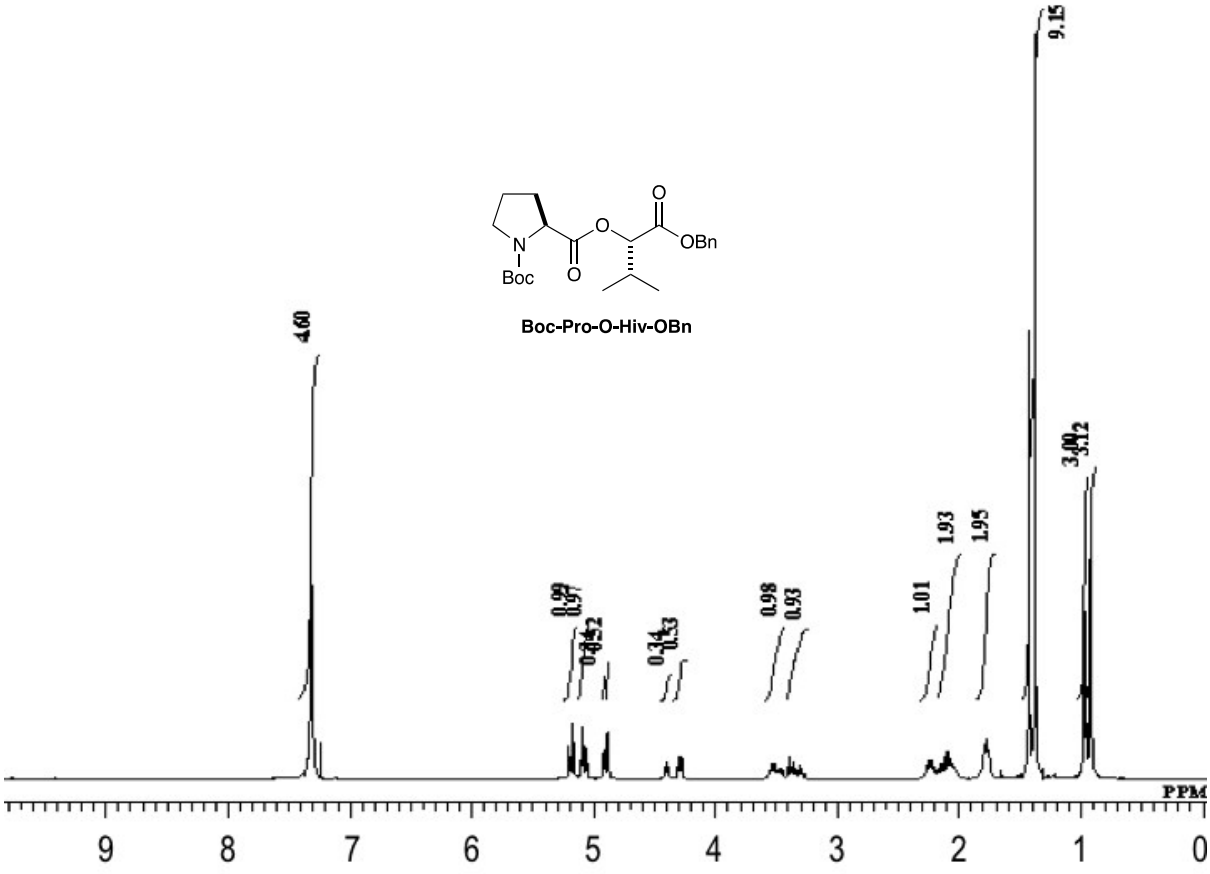


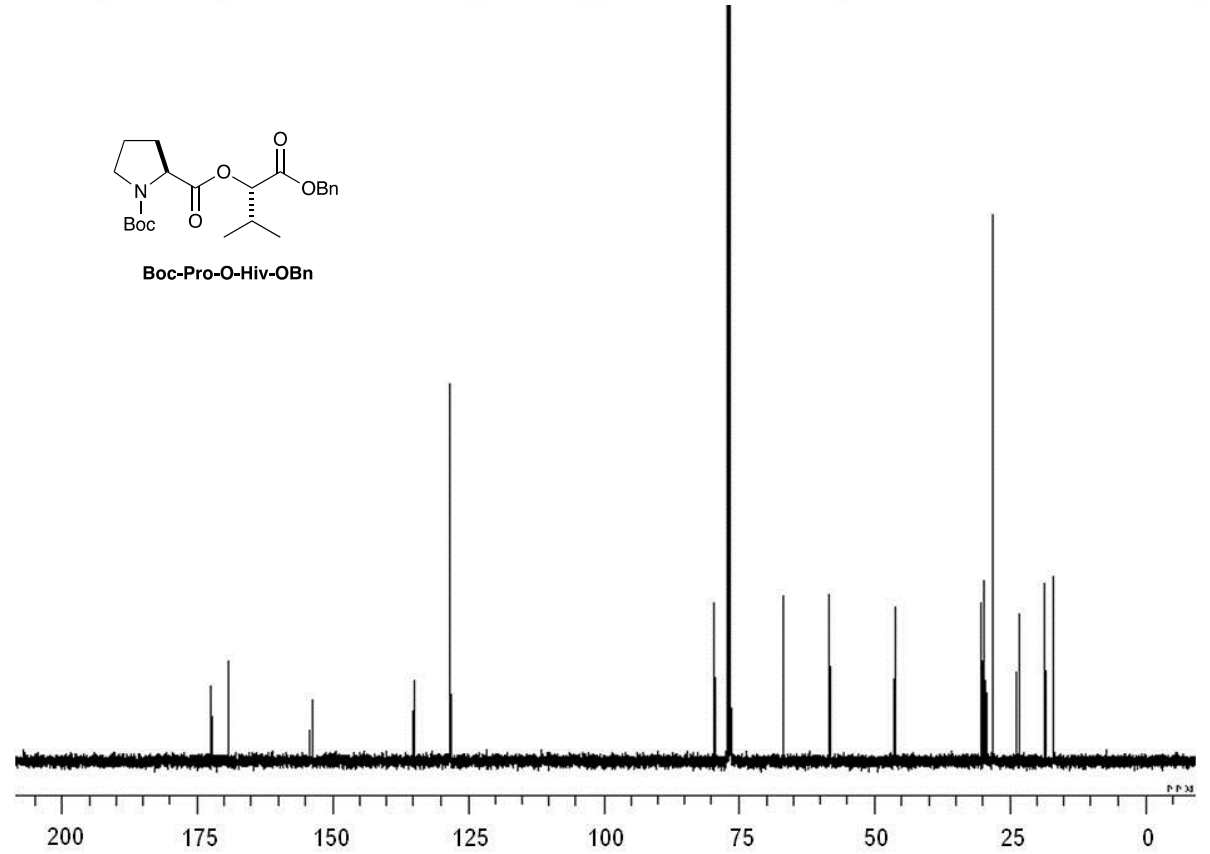


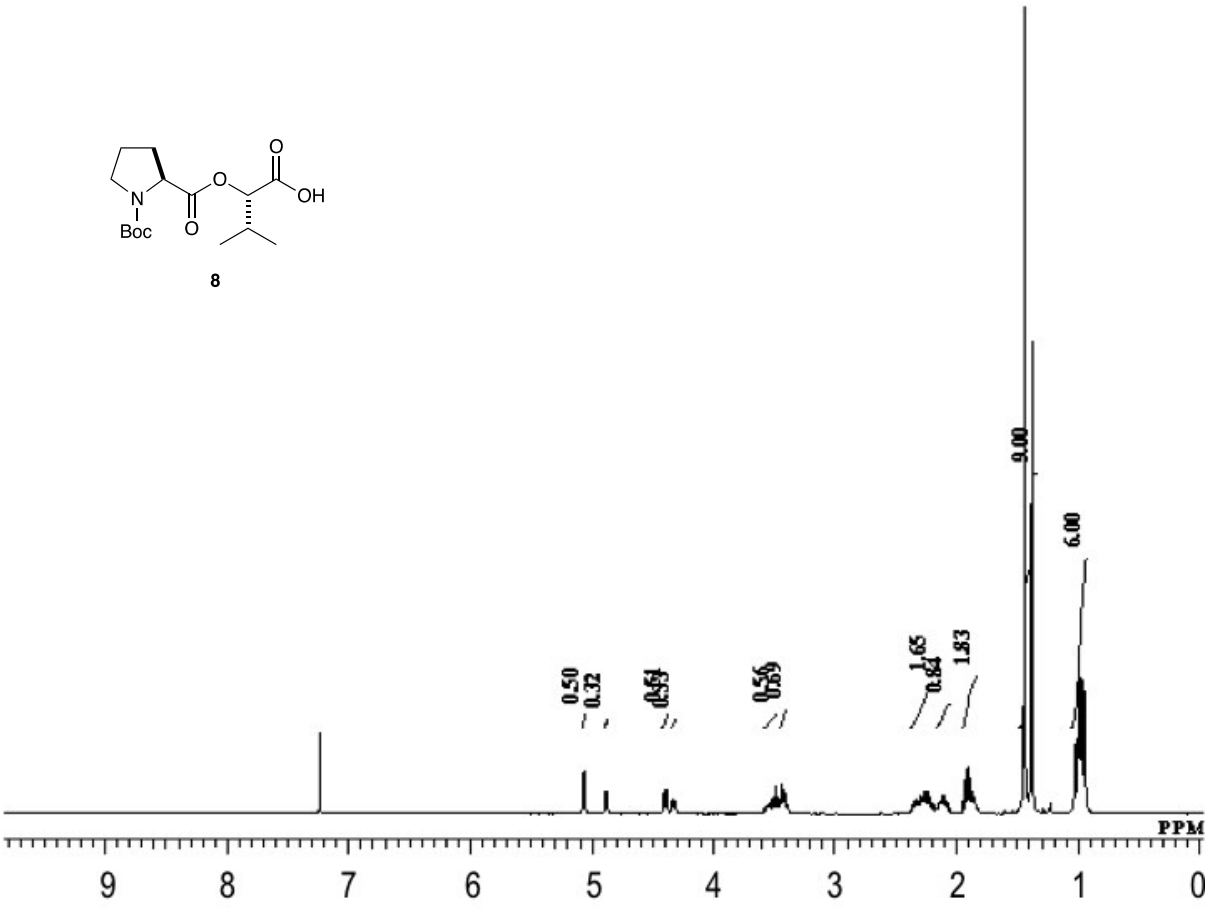
HO-Hiv-OH

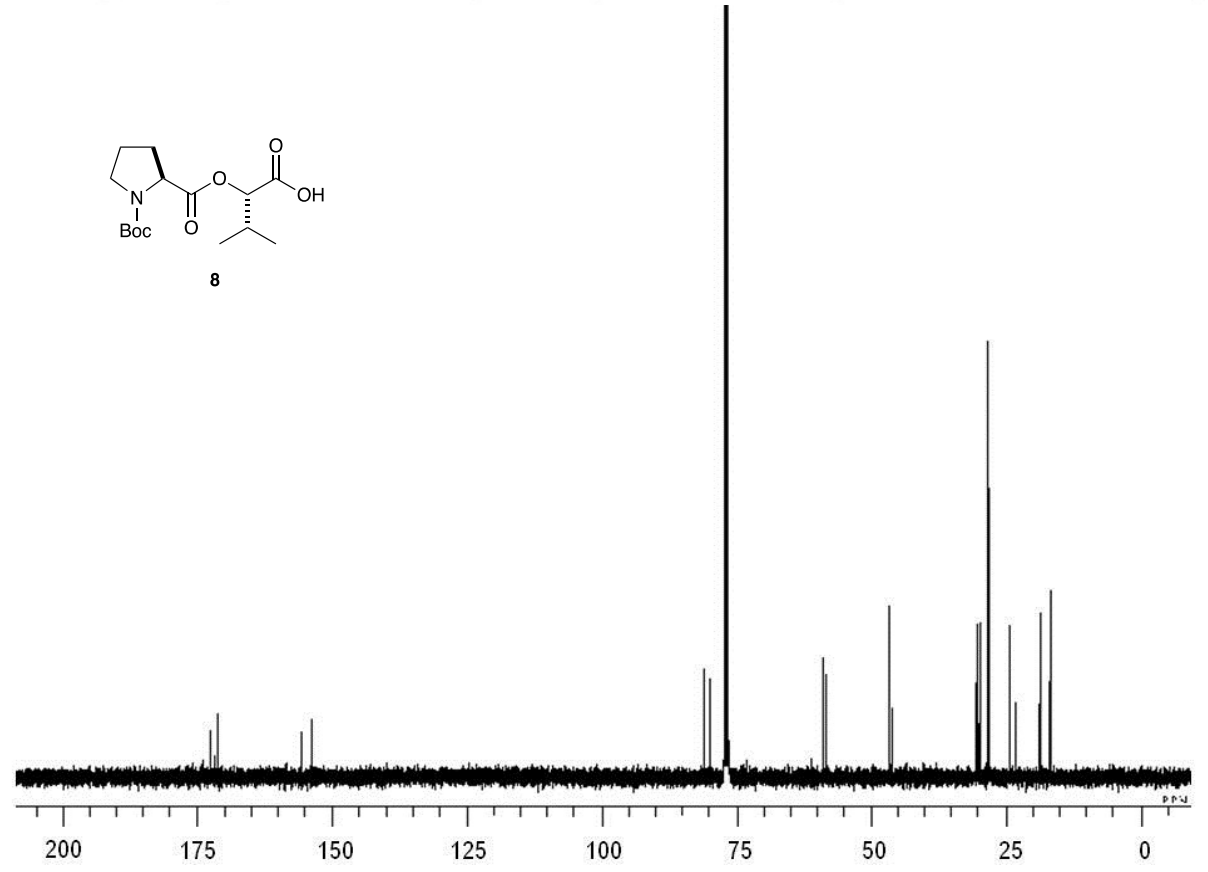

OBn
HO
O
HO-Hiv-OBn
4.77
1.49
1.00
0.79
1.11
3.25
3.26
PPM
9
8
7
6
5
4
3
2
1
0

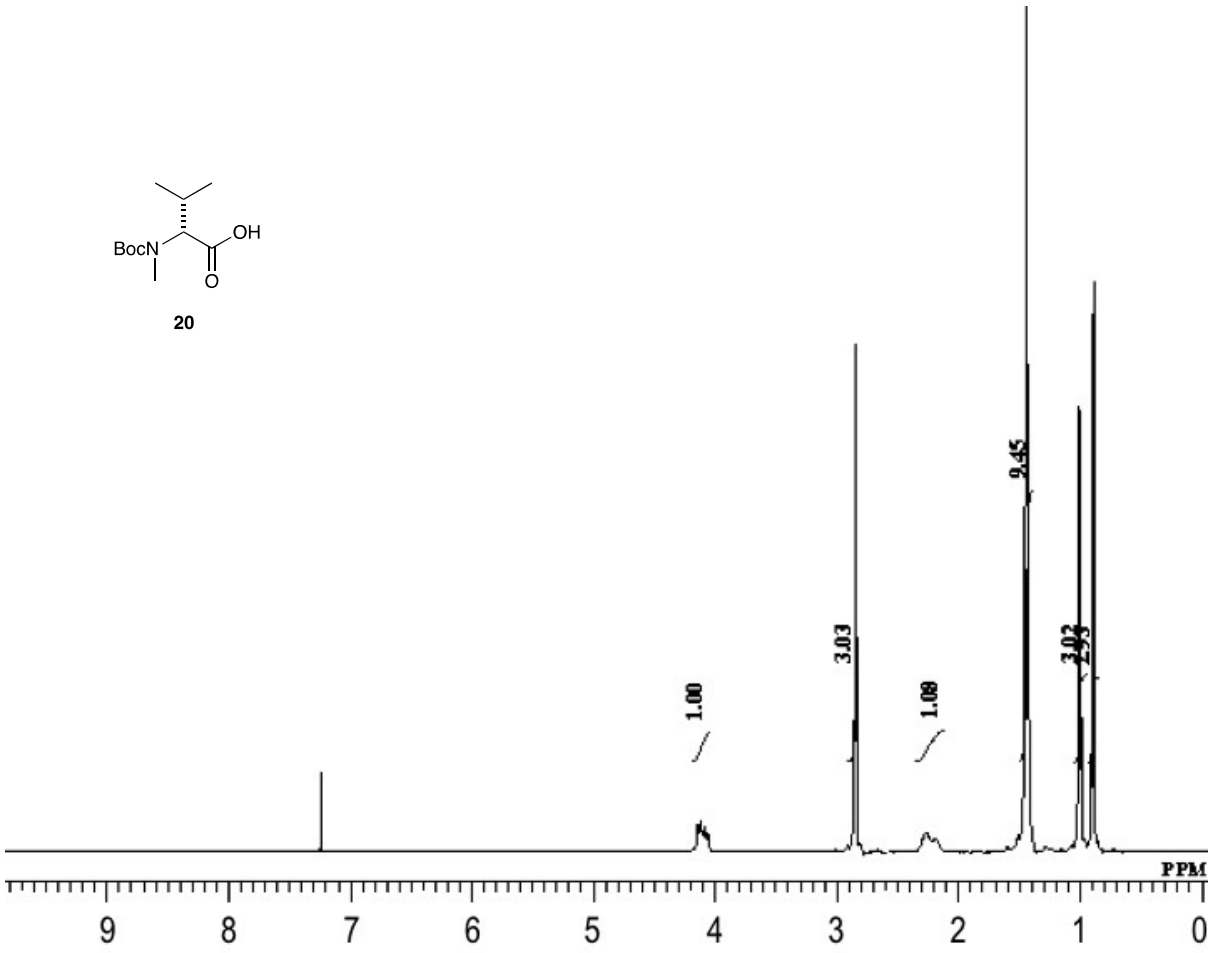

OBn
HO
O
HO-Hiv-OBn
200
175
150
125
100
75
50
25
0


Boc-Pro-O-Hiv-OBn
4.60
9.15
1.93
1.95
1.01
0.98
0.93
PPM
9
8
7
6
5
4
3
2
1
0


Boc-Pro-O-Hiv-OBn
200
175
150
125
100
75
50
25
0


O
O
OH
N
Boc
O
8
0.50
0.32
0.56
0.65
1.65
0.84
1.83
9.00
6.00
PPM
9
8
7
6
5
4
3
2
1
0


O
O
OH
N
Boc
O
8
200
175
150
125
100
75
50
25
0


BocN
OH
O
20
1.00
3.03
1.08
9.45
3.02
2.93
PPM
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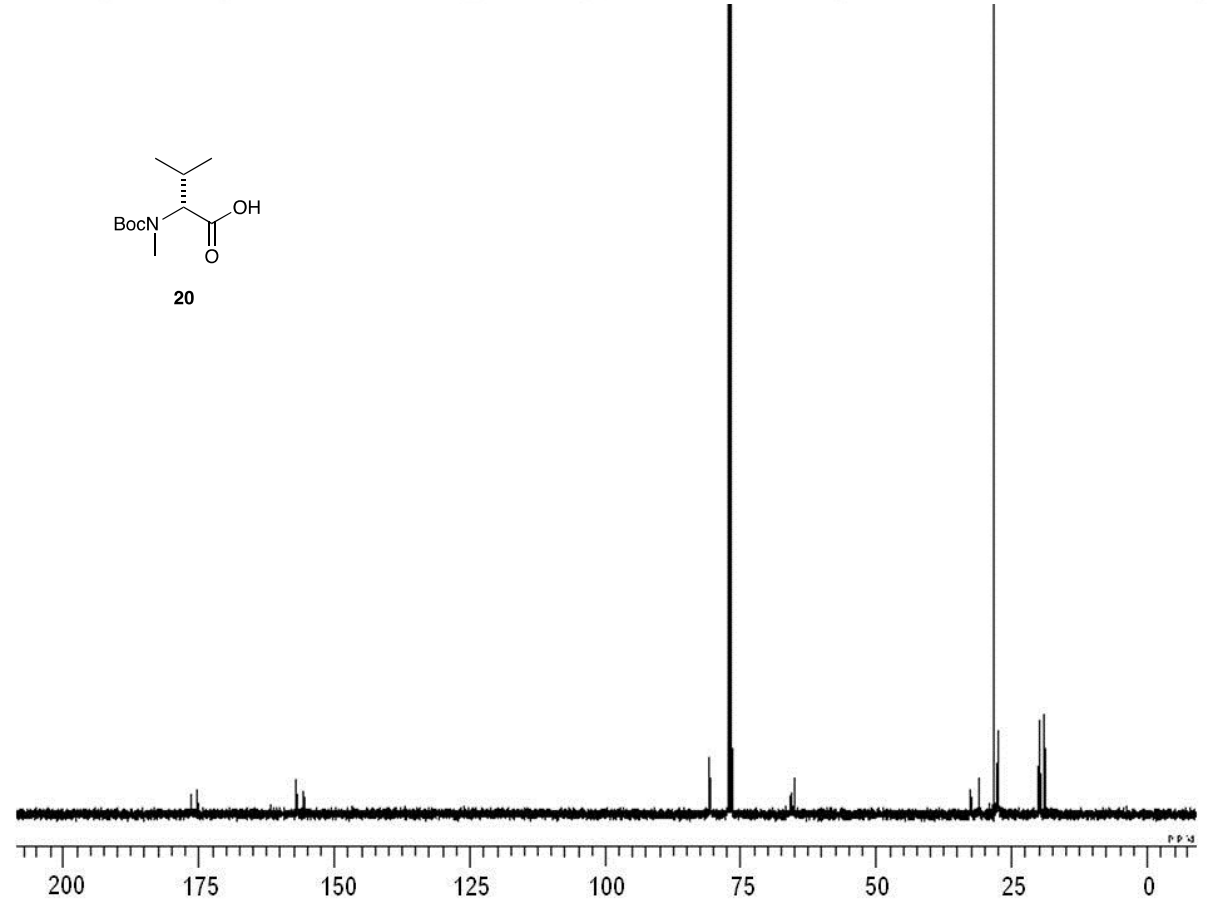
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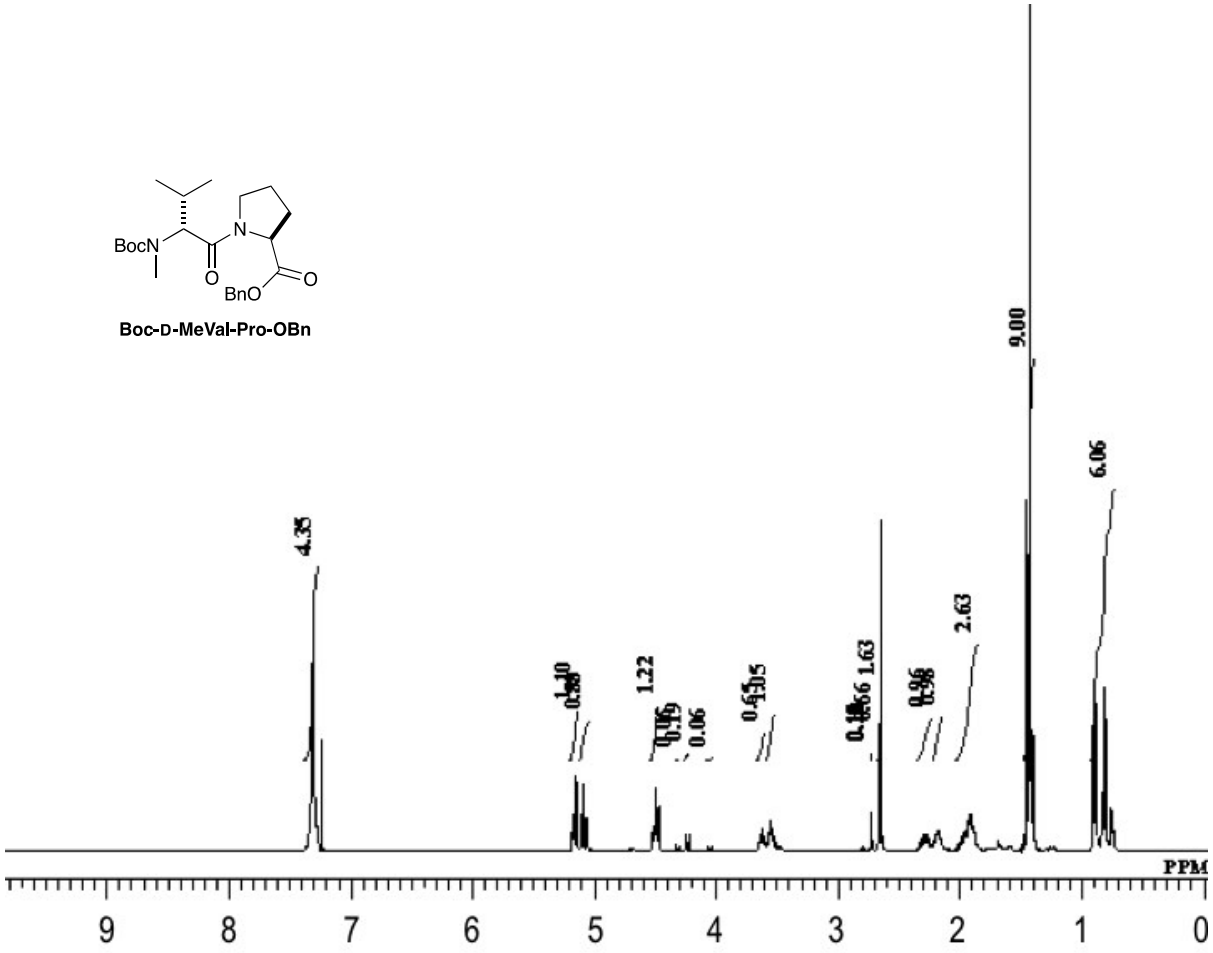
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BnO
O
Boc-D-MeVal-Pro-OBn
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PPM
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7
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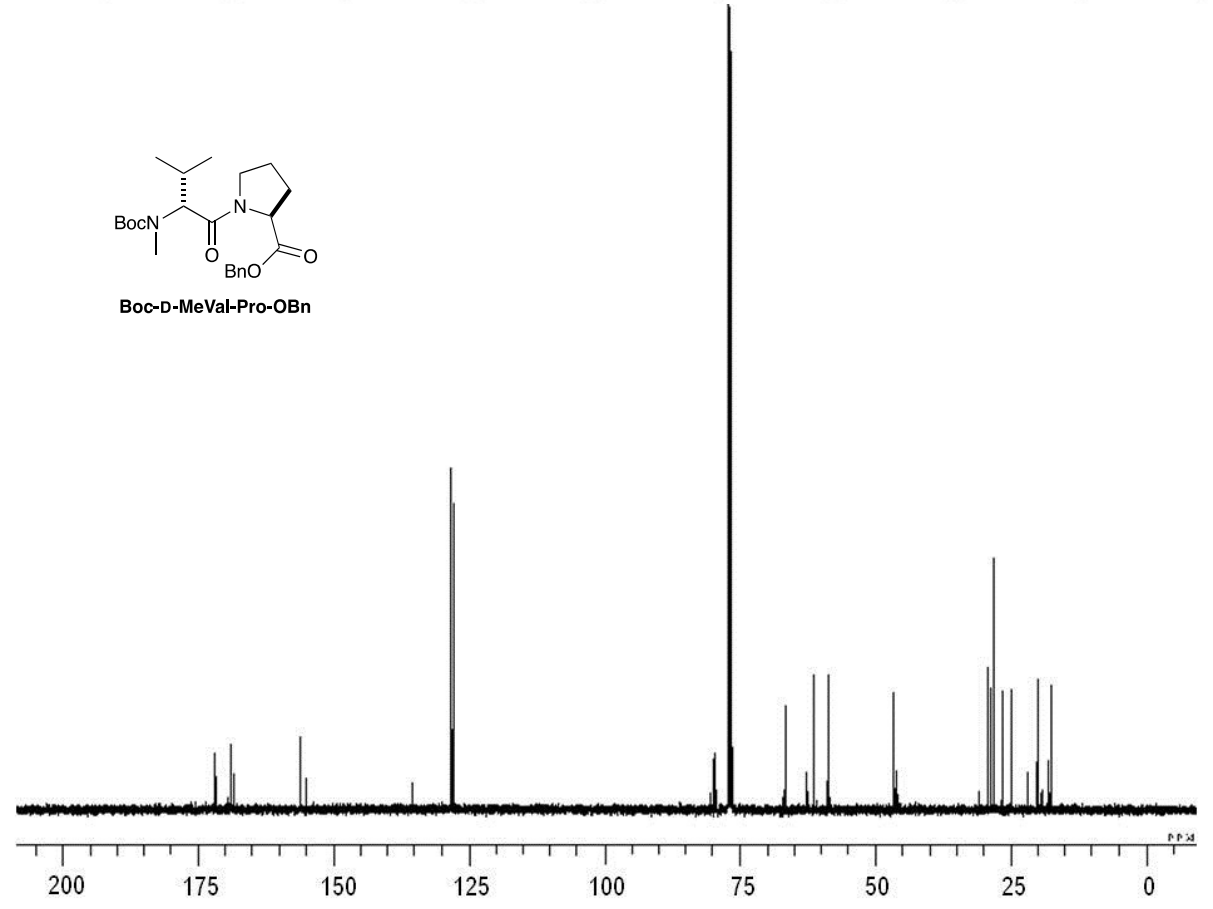
BocN
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BnO
O
Boc-D-MeVal-Pro-OBn
200
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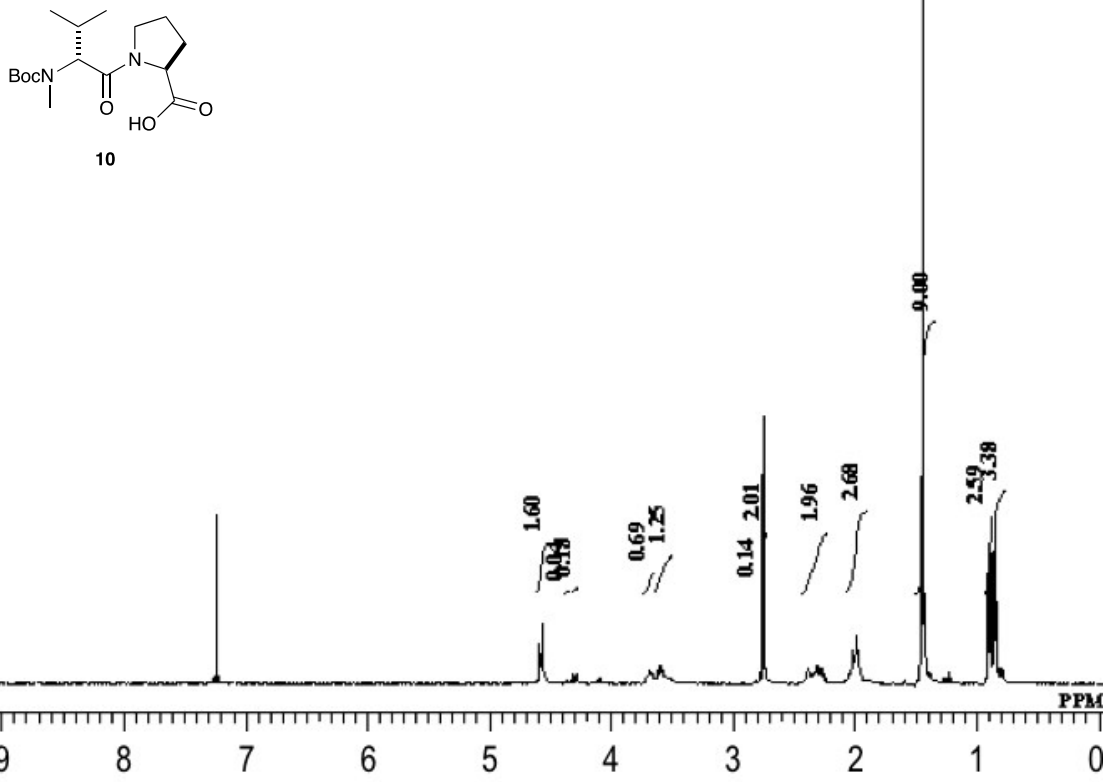
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HO
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1.25
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2.01
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9.00
2.59
3.38
PPM
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7
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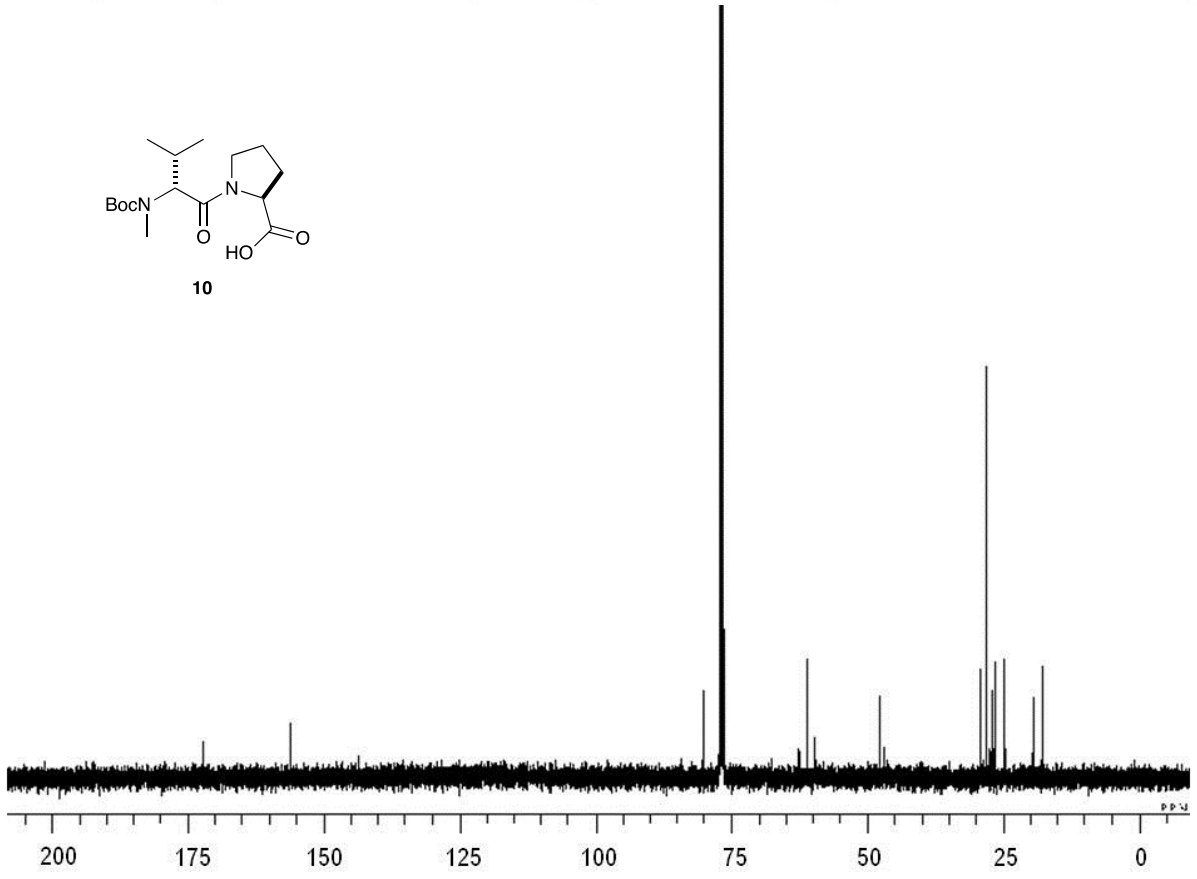
BocN
N
O
HO
O
10
200
175
150
125
100
75
50
25
0