Electronic Supplementary Information

for

Halogen-Bonding-Mediated Synthesis of Amides and Peptides

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Table of Contents

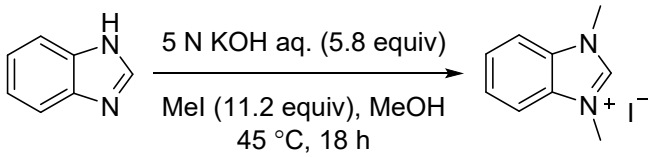
1 General information

The ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were measured at 100 MHz using a Bruker AV 400 instrument with $CDCl_3$ and DMSO-d_6 as the solvent.^{1}H NMR chemical shifts (δ) were determined relative to internal standard TMS (δ=0.0 ppm) and the solvents (DMSO-d_6, ^{1}H: δ = 2.50 ppm); ^{13}C NMR chemical shifts (δ) were measured with the solvents as references (For $CDCl_3$, ^{13}C: δ = 77.00 ppm; for DMSO-d_6, ^{13}C: δ = 39.53 ppm). The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiple, br = broad and coupling constants (J) were in Hertz (Hz). IR spectra were recorded on a FT-IR Bruker EQUINOX55 spectrometer in KBr pellets. Mass spectra were acquired on Agilent 6520 Q-TOF LC/MS and Varian 7.0T FTMS. Reactions were monitored by thin layer chromatography (TLC) carried out on Huanghai HSGF254 plates. Preparative TLC was performed on Xincheng GF254 preparative TLC plates. Silica gel (200-300 mesh) was purchased from Anhui Liangchen Co.; China. Unless otherwise noted, all reactions were performed under Argon protection. High performance liquid chromatography (HPLC) analysis was conducted using Shimadzu LC-10 AD coupled diode array-detector SPD-MA-10A-VP and chiral column of Daicel CHIRALCEL OD-H (4.6 mm-25 cm), AD-H (4.6 mm-25 cm), or AS-H (4.6 mm-25 cm). Melting points were recorded on a RY-1 type apparatus. All solvents were obtained from commercial sources and were purified according to standard procedures.

Materials: All solvents were purified according to the purification handbook *Purification of Laboratory Chemicals* before using. Other reagents and starting materials were synthesized or purchased from commercial sources and used as received.

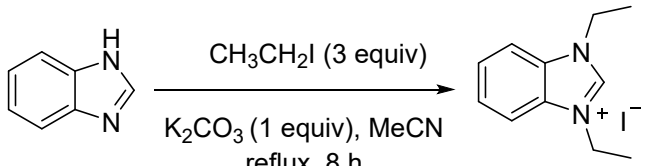
2 The Preparation of carbene precursors

Carbene precursor **3a** is commercially available.



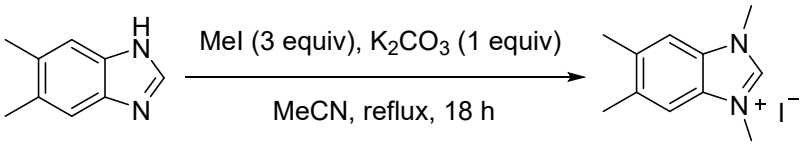
3b, 92%

1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3b): The carbene precursor was performed according to the reported procedures[1]. Benzimidazole (2 g, 16.93 mmol) was dissolved in 20 ml 5 N KOH solution and 10 ml MeOH, and MeI (26.91 g, 189.62 mmol) was added dropwise. The temperature was maintained at 45 ℃ for 18 hours, and then returned to room temperature and left overnight to filter the white crystals (4.26 g, 92% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.67 (s, 1H), 8.04 – 7.99 (m, 2H), 7.71 – 7.67 (m, 2H), 4.08 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.09, 131.64, 126.43, 113.43, 33.32.



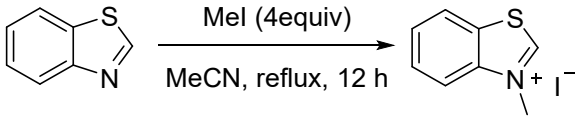
3c, 74%

1,3-diethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3c): The carbene precursor was performed according to the reported procedures[2]. Benzimidazole (1.0 g, 8.46 mmol), CH_3CH_2I (3.96 g, 25.39 mmol) and K_2CO_3 (1.17 g, 8.46 mmol) were heated under reflux conditions in acetonitrile for 8 h. The solvent of the resulting suspension was removed under reduced pressure, and the residue was resuspended in dichloromethane and filtered to remove the formed potassium iodide. The filtrate was evaporated under reduced pressure, the residue was resuspended in tetrahydrofuran and filtered to give the pure product (1.88 g, 74% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.88 (s, 1H), 8.17 – 8.04 (m, 2H), 7.77 – 7.63 (m, 2H), 4.53 (q, J = 7.3 Hz, 4H), 1.55 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.60, 130.94, 126.44, 113.65, 99.51, 42.06, 14.18.



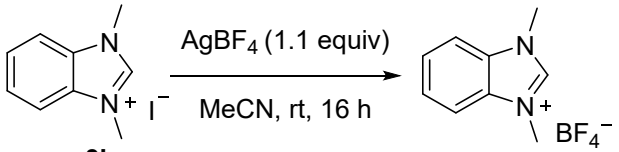
3d, 82%

1,3,5,6-tetramethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3d): The carbene precursor was performed according to the reported procedures[2-3]. 5,6-dimethylbenzimidazole (2.0 g, 13.68 mmol) and K_2CO_3 (1.89 g, 13.68 mmol) were dissolved in MeCN and MeI (5.83 g, 41.04 mmol) was added dropwise and the reaction mixture was heated under reflux conditions in acetonitrile for 18 h. The solvent of the resulting suspension was removed under reduced pressure, and the residue was resuspended in dichloromethane and filtered to remove the formed potassium iodide. The filtrate was evaporated under reduced pressure, the residue was resuspended in ethyl acetate and filtered to give the pure product (3.39 g, 82% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.51 (s, 1H), 7.80 (s, 2H), 4.02 (s, 6H), 2.42 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.77, 136.02, 130.09, 112.90, 33.11, 19.95.



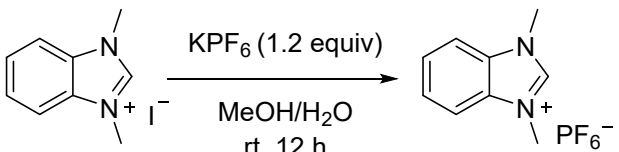
3e, 56%

3-methylbenzo[*d*]thiazol-3-ium iodide (3e): The carbene precursor was performed according to the reported procedures[4]. Benzothiazole (2.0 g, 14.79 mmol) and MeI (8.4 g, 59.18 mmol) were heated under reflux conditions in acetonitrile for 12 h and then cooled to room temperature and the precipitated solid was filtered, which was washed with ethyl acetate to give pure product (2.24, 56% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.55 (s, 1H), 8.53 (d, J = 8.1 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 7.95 (dd, J = 11.4, 4.1 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 4.41 (s, 3H).^{13}C NMR (100 MHz, DMSO-d_6) δ 164.86, 141.01, 131.09, 129.43, 128.31, 125.02, 117.13.



3b **3f**, 84%

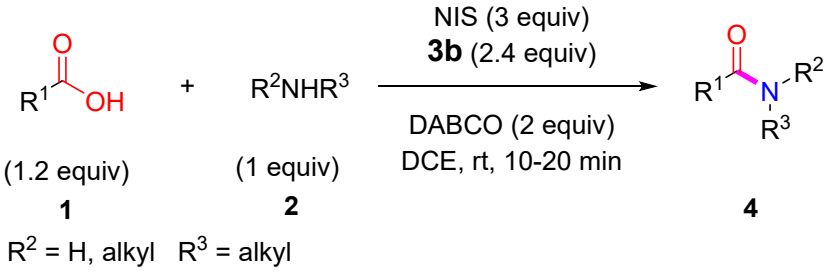
1,3-dimethylbenzimidazolium tetrafluoroborate (3f): The carbene precursor was performed according to the reported procedures[5]. **3b** (500 mg, 1.82 mmol) was dissolved in acetonitrile (15 mL). A solution of $AgBF_4$ (391mg, 2.0 mmol) in acetonitrile (5 mL) was then added dropwise leading to the precipitation of silver iodide. The suspension was stirred for 16 hours in absence of light and the precipitate was eliminated by filtration. The filtrate was removed under reduced pressure, and the white residue was dissolved in dichloromethane and then filtered to remove insoluble impurities. The filtrate was removed under reduced pressure, and the white residue was dissolved in dichloromethane and then *n*-pentane was added. After filtration and several washings with *n*-pentane to give pure product (1.430 g, 84% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.59 (s, 1H), 8.00 (dd, J = 6.1, 3.1 Hz, 2H), 7.70 (dd, J = 6.2, 3.0 Hz, 2H), 4.08 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.15, 131.69, 126.45, 113.38, 33.10.



3b **3g**, 81%

1,3-dimethyl-benzimidazolium hexafluorophosphate (3g): The carbene precursor was performed according to the reported procedures[6]. **3b** (500 mg, 1.82 mmol) was dissolved in MeOH (10 mL), a solution of KPF_6 (403 mg, 2.19 mmol) in MeOH (1 ml) and H_2O (6 mL) was then added dropwise and the whole mixture was stirred at room temperature for overnight. The white precipitated solid was washed with methanol and then dried in air to afford product (430 mg, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.60 (d, J = 14.2 Hz, 1H), 8.18 – 7.90 (m, 2H), 7.86 – 7.57 (m, 2H), 4.06 (d, J = 14.4 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.17, 131.70, 126.45, 113.38, 33.10.

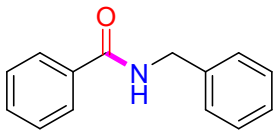
3 General Procedure for preparation of amides



Carboxylic acid **1** (0.12 mmol), amine **2** (0.1 mmol) and DABCO (22.4 mg, 0.2 mmol) were placed in a 10 ml two-neck round bottom flask, and DCE (3 ml) was added in argon atmosphere. After 5 min, NIS (67.5 mg, 0.3 mmol) and **3b** (65.8 mg, 0.24 mmol) were added in sequence at rt. The resulting mixture was stirred at room temperature and monitored by TLC. After amine was fully consumed, the reaction was quenched with 5% sodium thiosulfate solution (5 mL) and extracted with DCM (6 mL x 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the pure amide product **4**.

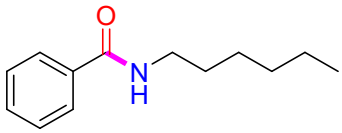
3.1. Characterization of the obtained amides

***N*-benzylbenzamide (4aa)**[7]



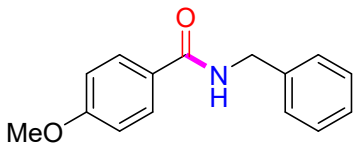
White solid, 99% yield (22.4 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 2H), 7.52 – 7.46 (m, 1H), 7.44 – 7.39 (m, 2H), 7.38 – 7.25 (m, 5H), 6.49 (br s, 1H), 4.64 (d, J = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.32, 138.17, 134.37, 131.51, 128.76, 128.56, 127.89, 127.59, 126.93, 44.10.

***N*-hexylbenzamide (4ab)**[8]



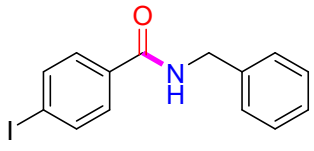
White solid, 96% yield (21.1 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.50 – 7.40 (m, 3H), 6.21 (br s, 1H), 3.44 (dd, J = 13.2, 7.0 Hz, 2H), 1.60 (dd, J = 14.6, 7.4 Hz, 2H), 1.42 – 1.28 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.50, 134.86, 131.25, 128.50, 126.80, 40.09, 31.48, 29.61, 26.64, 22.53, 13.98.

***N*-benzyl-4-methoxybenzamide (4ba)**[7]



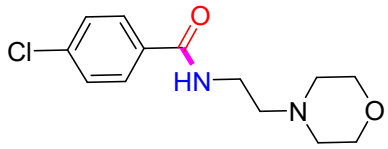
White solid, 88% yield (21.2 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.68 (m, 2H), 7.39 – 7.26 (m, 5H), 6.94 – 6.84 (m, 2H), 6.45 (br s, 1H), 4.62 (d, *J* = 5.7 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.84, 162.16, 138.38, 128.74, 128.70, 127.86, 127.49, 126.58, 113.70, 55.36, 44.01.

***N*-benzyl-4-iodobenzamide (4ca)**[7]



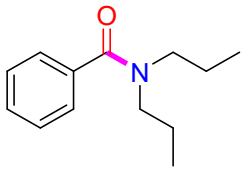
White solid, 90% yield (30.6 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.2 Hz, 2H), 7.50 (d, *J* = 6.3 Hz, 2H), 7.39 – 7.26 (m, 5H), 6.45 (br s, 1H), 4.68 – 4.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.52, 137.88, 137.77, 133.73, 128.82, 128.55, 127.92, 127.72, 98.48, 44.19.

4-chloro-*N*-(2-morpholinoethyl)benzamide (4dc)[7]



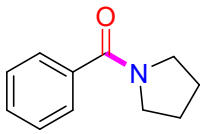
White solid, 99% yield (26.5 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.79 (br s, 1H), 3.79 – 3.66 (m, 4H), 3.55 (dd, *J* = 11.2, 5.6 Hz, 2H), 2.61 (t, *J* = 6.0 Hz, 2H), 2.55 – 2.46 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.27, 137.59, 132.91, 128.78, 128.31, 66.93, 56.75, 53.27, 36.02.

***N*, *N*-dipropylbenzamide (4ad)**[9]



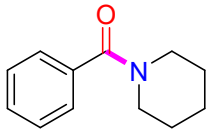
Colorless oil, 99% yield (20.3 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 5H), 3.46 (s, 2H), 3.16 (s, 2H), 1.69 (d, *J* = 5.8 Hz, 2H), 1.52 (d, *J* = 5.6 Hz, 2H), 0.98 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.73, 137.38, 128.93, 128.30, 126.40, 77.32, 77.00, 76.68, 50.63, 46.22, 21.86, 20.67, 11.38, 10.97.

phenyl(pyrrolidin-1-yl)methanone (4ae)[10]



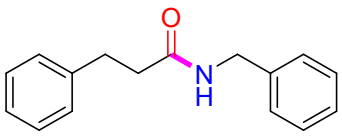
White solid, 94% yield (16.4 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.44 – 7.34 (m, 3H), 3.65 (t, *J* = 6.9 Hz, 2H), 3.43 (t, *J* = 6.5 Hz, 2H), 1.97 (dt, *J* = 13.2, 6.6 Hz, 2H), 1.87 (dt, *J* = 13.2, 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.72, 137.23, 129.73, 128.21, 127.05, 77.32, 77.00, 76.68, 49.57, 46.13, 26.36, 24.44.

phenyl(piperidin-1-yl)methanone (4af)[10]



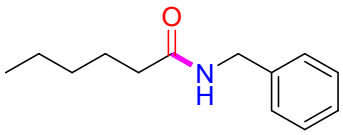
White solid, 99% yield (19.8 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 5H), 3.71 (s, 2H), 3.34 (s, 2H), 1.67 (s, 4H), 1.52 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.26, 136.49, 129.28, 128.34, 126.74, 77.32, 48.71, 43.08, 26.48, 25.59, 24.56.

***N*-benzyl-3-phenylpropanamide (4ea)**[11]



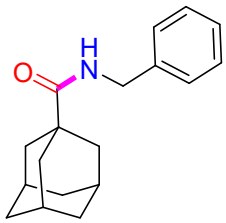
White solid, 99% yield (23.7 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 5H), 7.20 (t, *J* = 7.7 Hz, 3H), 7.13 (d, *J* = 6.7 Hz, 2H), 5.72 (br s, 1H), 4.38 (d, *J* = 5.6 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.84, 140.72, 138.10, 128.60, 128.51, 128.36, 127.68, 127.40, 126.21, 43.51, 38.44, 31.67.

_N_-benzylhexanamide (4fa)[7]



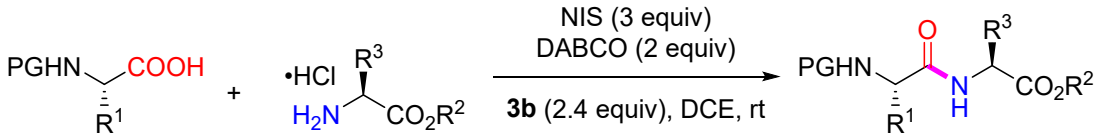
White solid, 99% yield (20.4 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 5H), 5.81 (br s, 1H), 4.43 (d, *J* = 5.6 Hz, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.51 (m, 2H), 1.29 (t, *J* = 11.9 Hz, 4H), 0.89 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.96, 138.42, 128.65, 127.78, 127.44, 43.53, 36.73, 31.45, 25.42, 22.36, 13.90.

(3r,5r,7r)-_N_-benzyladamantane-1-carboxamide (4ga)[12]



White solid, 98% yield (27.1 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 5H), 5.90 (br s, 1H), 4.43 (d, *J* = 5.5 Hz, 2H), 2.04 (s, 3H), 1.89 (s, 6H), 1.72 (dd, *J* = 20.7 Hz, *J* = 12.4 Hz,6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.75, 138.65, 128.64, 127.59, 127.33, 43.27, 40.60, 39.26, 36.46, 28.08.

4 General Procedure for the preparation of dipeptides



5 (1.2 equiv)
PG = Cbz, Boc, Fmoc

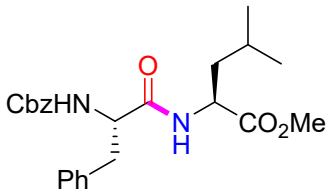
6 (1 equiv)

7

Amino acids **5** (0.12 mmol), amino acids **6** (0.1 mmol) and DABCO (22.4 mg, 0.2 mmol) were placed in a 10 ml two-neck round bottom flask, and DCE (3 ml) was added in argon atmosphere. After 5 min, NIS (67.5 mg, 0.3 mmol) and **3b** (65.8 mg, 0.24 mmol) were added in sequence at rt. The resulting mixture was stirred at room temperature and monitored by TLC. After amine was fully consumed, the reaction was quenched with 5% sodium thiosulfate solution (5 mL) and extracted with DCM (6 mL x 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the desired product **7**.

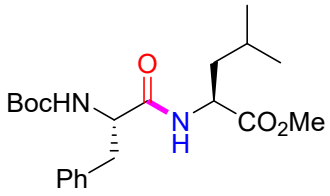
4.1 Characterization of the obtained dipeptides

Cbz-L-Phe-L-Leu-OMe (7aa)[13]



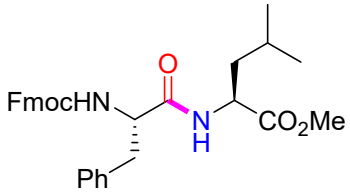
White solid, 95% yield (40.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.26 – 7.21 (m, 3H), 7.20 – 7.13 (m, 2H), 6.41 (br s, 1H), 5.45 (d, *J* = 6.7 Hz, 1H), 5.07 (s, 2H), 4.60 – 4.42 (m, 2H), 3.68 (s, 3H), 3.07 (d, *J* = 6.7 Hz, 2H), 1.62 – 1.41 (m, 3H), 0.87 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.77, 170.61, 155.88, 136.22, 136.06, 129.32, 128.55, 128.46, 128.12, 127.93, 126.92, 66.97, 55.92, 52.20, 50.72, 41.33, 38.32, 24.62, 22.61, 21.83.

Boc-L-Phe-L-Leu-OMe (7ba)[14]



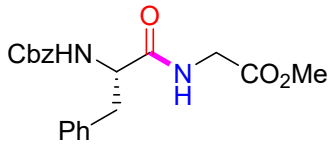
White solid, 83% yield (32.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.25 – 7.19 (m, 3H), 6.30 (d, *J* = 8.1 Hz, 1H), 5.03 (br s, 1H), 4.56 (dd, *J* = 8.2, 5.0 Hz, 1H), 4.36 (d, *J* = 6.1 Hz, 1H), 3.69 (s, 3H), 3.07 (d, *J* = 6.8 Hz, 2H), 1.63 – 1.45 (m, 3H), 1.41 (s, 9H), 0.90 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.78, 170.90, 155.35, 136.54, 129.34, 128.58, 126.87, 80.16, 55.61, 52.20, 50.68, 41.53, 38.01, 28.19, 24.60, 22.70, 21.83.

Fmoc-L-Phe-L-Leu-OMe (7ca)[15]



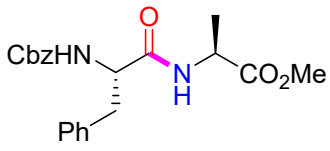
White solid, 81% yield (41.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.60 – 7.47 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.25 – 7.14 (m, 3H), 6.17 (s, 1H), 5.38 (d, *J* = 7.0 Hz, 1H), 4.55 (td, *J* = 8.5, 5.3 Hz, 1H), 4.44 (dd, *J* = 10.5, 7.1 Hz, 2H), 4.37 – 4.25 (m, 1H), 4.19 (t, *J* = 6.9 Hz, 1H), 3.69 (s, 3H), 3.08 (dd, *J* = 23.4, 5.8 Hz, 2H), 1.64 – 1.37 (m, 3H), 0.87 (dd, *J* = 9.6, 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.70, 170.44, 155.93, 143.73, 143.64, 141.27, 136.20, 129.38, 128.66, 127.72, 127.06, 125.06, 124.98, 119.97, 67.09, 55.97, 52.26, 50.80, 47.07, 41.47, 38.39, 24.67, 22.64, 21.87.

Cbz-L-Phe-L-Gly-OMe (7ab)[13]



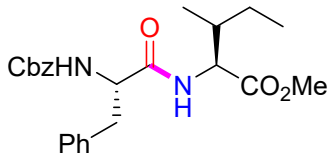
White solid, 98% yield (36.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 8H), 7.20 – 7.13 (m, 2H), 6.66 (br s, 1H), 5.57 (s, 1H), 5.04 (q, *J* = 12.3 Hz, 2H), 4.52 (d, *J* = 5.7 Hz, 1H), 4.05 – 3.81 (m, 2H), 3.69 (s, 3H), 3.20 – 2.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.33, 169.86, 155.99, 136.29, 136.02, 129.21, 128.56, 128.44, 128.09, 127.89, 126.92, 66.97, 55.92, 52.28, 41.06, 38.33.

Cbz-L-Phe-L-Ala-OMe (7ac)[16]



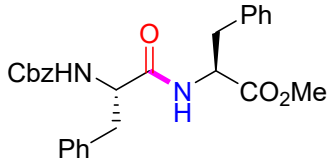
White solid, 85% yield (32.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 8H), 7.24 – 7.14 (m, 2H), 6.37 (br s, 1H), 5.36 (d, *J* = 6.4 Hz, 1H), 5.08 (s, 2H), 4.57 – 4.36 (m, 2H), 3.71 (s, 3H), 3.15 – 3.00 (m, 2H), 1.32 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.76, 170.30, 155.85, 136.15, 129.32, 128.65, 128.53, 128.50, 128.48, 128.17, 128.01, 127.04, 67.04, 55.97, 52.44, 48.11, 38.47, 18.25.

Cbz-L-Phe-L-Ile-OMe (7ad)[14]



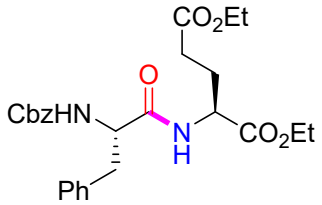
White solid, 97% yield (41.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 7.28 – 7.22 (m, 3H), 7.21 – 7.15 (m, 2H), 6.38 (br s, 1H), 5.43 (d, *J* = 6.7 Hz, 1H), 5.08 (s, 2H), 4.49 (dt, *J* = 10.3, 5.2 Hz, 2H), 3.68 (s, 3H), 3.17 – 2.98 (m, 2H), 1.84 – 1.78 (m, 1H), 1.37 – 1.28 (m, 1H), 1.14 – 0.96 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.66, 170.58, 155.89, 136.23, 136.09, 129.28, 128.63, 128.48, 128.14, 127.96, 126.96, 67.01, 56.51, 56.10, 52.02, 38.34, 37.74, 25.05, 15.22, 11.46.

Cbz-L-Phe-L-Phe-OMe (7ae)[17]



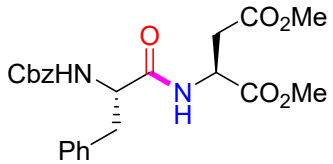
White solid, 97% yield (44.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 7.26 – 7.18 (m, 6H), 7.15 (d, *J* = 6.6 Hz, 2H), 6.96 (d, *J* = 4.1 Hz, 2H), 6.30 (d, *J* = 6.7 Hz, 1H), 5.30 (d, *J* = 6.7 Hz, 1H), 5.11 – 4.98 (m, 2H), 4.78 (dd, *J* = 13.5, 6.0 Hz, 1H), 4.42 (d, *J* = 6.6 Hz, 1H), 3.66 (s, 3H), 3.14 – 2.89 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.27, 170.33, 155.81, 136.17, 135.50, 129.30, 129.14, 128.64, 128.49, 128.15, 127.96, 127.08, 127.00, 67.01, 55.95, 53.25, 52.25, 38.26, 37.84.

Cbz-L-Phe-L-Glu(OEt)-OEt (7af)



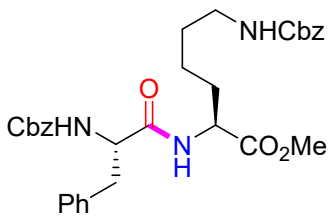
White solid, 97% yield (47.1 mg). m.p.: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 8H), 7.22 – 7.08 (m, 2H), 6.57 (br s, 1H), 5.33 (s, 1H), 5.09 (s, 2H), 4.50 (d, *J* = 24.7 Hz, 2H), 4.13 (dd, *J* = 20.1, 6.6 Hz, 4H), 3.08 (s, 2H), 2.39 – 2.09 (m, 3H), 1.93 (s, 1H), 1.26 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.69, 171.14, 170.69, 155.80, 136.08, 129.30, 128.65, 128.49, 128.15, 128.01, 127.03, 67.05, 61.64, 60.67, 56.03, 51.76, 38.32, 30.00, 27.20, 14.12, 14.07. IR(KBr): 3435, 1580, 1418, 1368, 1025, 649 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{26}H_{32}N_2O_7$ $[M+H]^+$: 485.22823, Found: 485.22776.

Cbz-L-Phe-L-Asp(OMe)-OMe(7ag)



White solid, 80% yield (33.6 mg). m.p.: 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 7.27 – 7.21 (m, 3H), 7.20 – 7.13 (m, 2H), 6.84 (d, *J* = 7.2 Hz, 1H), 5.32 (br s, 1H), 5.07 (s, 2H), 4.89 – 4.70 (m, 1H), 4.48 (d, *J* = 5.5 Hz, 1H), 3.71 (s, 3H), 3.64 (s, 3H), 3.09 (d, *J* = 5.8 Hz, 2H), 2.98 (dd, *J* = 17.2, 3.6 Hz, 1H), 2.81 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.17, 170.63, 170.57, 155.76, 136.11, 135.97, 129.29, 128.63, 128.48, 128.14, 127.99, 126.99, 67.01, 55.86, 52.77, 52.00, 48.54, 38.38, 35.88. IR(KBr): 3427, 1639, 1570, 1414, 1368, 1051, 1022, 644, 525 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{23}H_{26}N_2O_7$ $[M+H]^+$: 443.18128, Found: 443.18088.

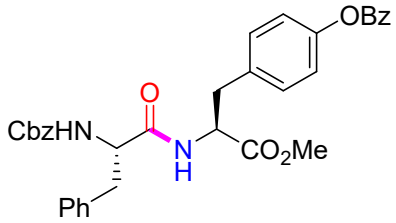
Cbz-L-Phe-L-Lys(Cbz)-OMe (7ah)



White solid, 97% yield (56.2 mg). m.p.: 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 7H), 7.28 – 7.19 (m, 6H), 7.15 (d,

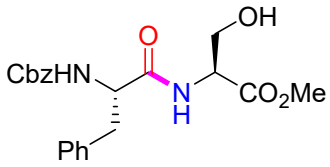
J = 6.9 Hz, 2H), 6.52 (br s, 1H), 5.43 (br s, 1H), 5.17 – 4.95 (m, 5H), 4.62 – 4.33 (m, 2H), 3.69 (s, 3H), 3.23 – 2.92 (m, 4H), 1.81 – 1.58 (m, 2H), 1.52 – 1.38 (m, 2H), 1.31 – 1.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.11, 170.93, 156.53, 156.02, 136.53, 136.23, 136.07, 129.25, 128.58, 128.47, 128.45, 128.12, 128.06, 127.96, 126.93, 99.92, 67.01, 66.59, 56.08, 52.35, 51.97, 40.33, 38.30, 31.64, 29.11, 21.99. IR(KBr): 3468, 3413, 1638, 1614, 1566, 1414, 1022, 623 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{32}H_{37}N_3O_7$ $[M+H]^+$: 576.27043, Found: 576.26986.

Cbz-L-Phe-L-Tyr(Bz)-OMe (7ai)[18]



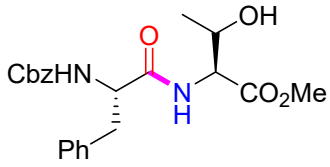
White solid, 96% yield (54.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.34 – 7.25 (m, 7H), 7.24 – 7.13 (m, 4H), 6.91 – 6.78 (m, 4H), 6.21 (d, J = 7.2 Hz, 1H), 5.25 (br s, 1H), 5.07 (t, J = 13.5 Hz, 2H), 4.99 (s, 2H), 4.73 (dd, J = 13.3, 5.9 Hz, 1H), 4.41 (d, J = 6.6 Hz, 1H), 3.66 (s, 3H), 3.12 – 2.86 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.33, 170.24, 157.90, 155.84, 136.89, 136.18, 130.20, 129.34, 128.68, 128.54, 128.53, 128.19, 127.99, 127.94, 127.71, 127.46, 127.03, 114.88, 69.92, 67.07, 55.99, 53.38, 52.27, 38.26, 37.00.

Cbz-L-Phe-L-Ser-OMe (7aj)[14]



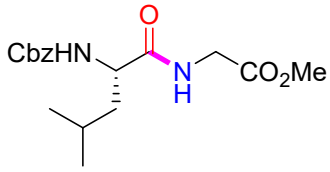
White solid, 84% yield (32.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 7.25 – 7.14 (m, 5H), 7.05 (br s, 1H), 5.58 (d, J = 6.6 Hz, 1H), 5.02 (dd, J = 27.6, 12.2 Hz, 2H), 4.64 – 4.42 (m, 2H), 3.87 (s, 2H), 3.71 (s, 3H), 3.22 (s, 1H), 3.12 (dd, J = 13.9, 6.1 Hz, 1H), 3.02 (dd, J = 13.6, 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.40, 170.50, 156.28, 136.13, 135.95, 129.27, 128.62, 128.48, 128.18, 127.99, 127.03, 77.32, 67.15, 62.69, 56.19, 54.79, 52.68, 38.35.

Cbz-L-Phe-L-Thr-OMe (7ak) [14]



Colorless oil, 92% yield (36.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 10H), 7.00 (br s, 1H), 5.60 (br s, 1H), 5.12 – 4.93 (m, 2H), 4.64 – 4.48 (m, 2H), 4.26 (s, 1H), 3.68 (s, 3H), 3.27 – 2.89 (m, 3H), 1.11 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.67, 171.06, 156.11, 136.18, 136.04, 129.32, 128.52, 128.45, 128.12, 127.93, 126.91, 68.08, 67.04, 57.37, 56.07, 52.53, 38.21, 19.72.

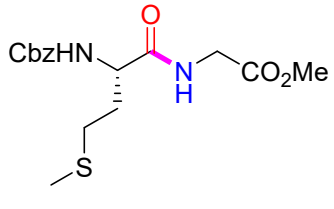
Cbz-L-Leu-Gly-OMe (7db)[13]



White solid, 95% yield (32.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 5H), 6.79 (br s, 1H), 5.40 (d, J = 6.0 Hz, 1H), 5.10 (d, J = 7.0 Hz, 2H), 4.28 (s, 1H), 4.02 (s, 2H), 3.73 (s, 3H), 1.68 (d, J = 5.5 Hz, 2H), 1.59 – 1.48 (m, 1H), 0.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.57, 170.12, 156.26, 136.08, 128.48, 128.15, 127.99, 67.06, 53.34, 52.31, 41.30, 41.07, 24.60, 22.88, 21.87.

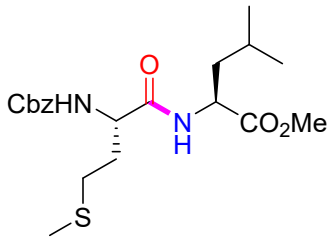
Cbz-L-Met-Gly-OMe (7eb)[13]

White solid, 87% yield (30.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 6.93 (br s,



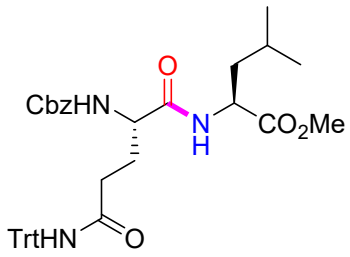
1H), 5.76 (d, J = 8.0 Hz, 1H), 5.10 (q, J = 12.2 Hz, 2H), 4.45 (dd, J = 14.1, 7.0 Hz, 1H), 4.15 – 3.88 (m, 2H), 3.73 (s, 3H), 2.59 (t, J = 7.2 Hz, 2H), 2.16 – 2.01 (m, 4H), 1.98 (dd, J = 14.4, 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.58, 169.98, 156.11, 136.02, 128.48, 128.17, 128.01, 67.08, 53.61, 52.34, 41.06, 31.53, 29.87, 15.11.

Cbz-L-Met-L-Leu-OMe (7ea)



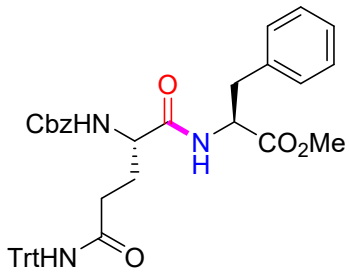
White solid, 88% yield (35.1 mg). m.p.: 83-85 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 6.61 (d, J = 7.8 Hz, 1H), 5.59 (d, J = 8.1 Hz, 1H), 5.11 (s, 2H), 4.59 (td, J = 8.8, 4.9 Hz, 1H), 4.43 (dd, J = 14.5, 7.0 Hz, 1H), 3.73 (s, 3H), 2.61 (t, J = 7.0 Hz, 2H), 2.15 – 1.93 (m, 5H), 1.70 – 1.48 (m, 3H), 0.93 (d, J = 2.3 Hz, 3H), 0.91 (d, J = 2.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.99, 170.87, 155.92, 136.10, 128.51, 128.18, 128.01, 67.02, 53.36, 52.30, 50.78, 41.19, 31.56, 29.80, 24.78, 22.73, 21.77, 14.95. IR(KBr): 3429, 1639, 1565, 1413, 1050, 1022, 804, 644, 523 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{19}H_{28}N_2O_5S$ $[M+H]^+$: 411.19482, Found: 411.19439.

Cbz-L-Gln(Trt)-L-Leu-OMe (7fa)



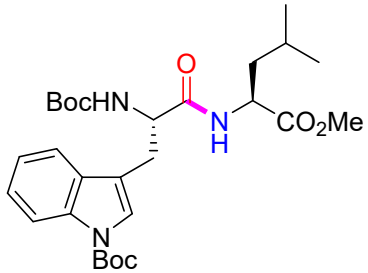
White solid, 80% yield (51.9 mg). m.p.: 68-70 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.17 (m, 20H), 7.04 – 6.84 (m, 2H), 5.79 (d, J = 6.3 Hz, 1H), 5.17 – 5.00 (m, 2H), 4.45 (td, J = 9.3, 4.6 Hz, 1H), 4.16 (dd, J = 13.2, 6.6 Hz, 1H), 3.66 (s, 3H), 2.55 (t, J = 6.1 Hz, 2H), 2.15 – 1.92 (m, 2H), 1.59 – 1.36 (m, 3H), 0.85 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.16, 171.94, 171.29, 156.03, 144.48, 136.31, 128.65, 128.46, 128.07, 128.01, 127.94, 127.01, 70.66, 66.81, 53.56, 52.19, 50.88, 40.51, 33.33, 29.64, 24.61, 22.73, 21.56. IR(KBr): 3425, 1643, 1581, 1414, 1368, 1051, 1022, 699, 644, 524 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{39}H_{43}N_3O_6$ $[M+H]^+$: 650.32246, Found: 650.32172.

Cbz-L-Gln(Trt)-L-Phe-OMe (7fe)



White solid, 97% yield (61.7 mg). m.p.: 68-70 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.10 (m, 24H), 7.03 (d, J = 5.8 Hz, 2H), 6.93 (s, 1H), 5.81 (d, J = 6.4 Hz, 1H), 5.15 – 4.96 (m, 2H), 4.68 (dd, J = 13.2, 7.6 Hz, 1H), 4.11 (dd, J = 14.2, 7.0 Hz, 1H), 3.65 (s, 3H), 3.05 (dd, J = 13.9, 5.4 Hz, 1H), 2.89 (dd, J = 13.8, 7.7 Hz, 1H), 2.41 (s, 2H), 2.04 – 1.89 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.64, 171.79, 171.13, 156.08, 144.44, 136.25, 135.87, 129.11, 128.64, 128.49, 128.43, 128.05, 127.99, 127.91, 126.99, 126.94, 70.63, 66.82, 53.85, 53.58, 52.25, 37.50, 33.18, 29.47, 29.00. IR(KBr): 3466, 3412, 1638, 1614, 1413, 1022, 624 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{42}H_{41}N_3O_6$ $[M+H]^+$: 684.30681, Found: 684.30605.

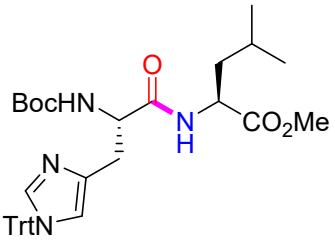
Boc-L-Trp(Boc)-L-Leu-OMe (7ga)



White solid, 85% yield (45.1 mg). m.p.: 56-58 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.7 Hz,

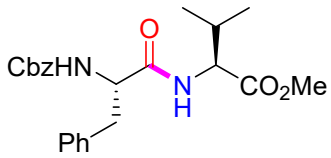
1H), 7.46 (s, 1H), 7.31 (t, J = 7.3 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 6.28 (d, J = 8.2 Hz, 1H), 5.16 (br s, 1H), 4.54 (td, J = 8.5, 5.1 Hz, 1H), 4.45 (d, J = 6.1 Hz, 1H), 3.66 (s, 3H), 3.31 – 2.98 (m, 2H), 1.66 (s, 9H), 1.54 (dd, J = 10.3, 4.0 Hz, 2H), 1.43 (s, 10H), 0.87 (t, J = 6.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.65, 170.85, 155.35, 149.51, 135.48, 130.23, 124.51, 124.35, 122.64, 119.03, 115.40, 115.19, 83.51, 80.18, 54.42, 52.18, 50.70, 41.62, 28.21, 28.15, 27.80, 24.60, 22.66, 21.84. IR(KBr): 3417, 2960, 2934, 1733, 1658, 1568, 1369, 1256, 1160, 1087, 1052, 766, 747 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{28}H_{41}N_3O_7$ $[M+H]^+$: 532.30173, Found: 532.30131.

Boc-L-His(Trt)-L-Leu-OMe (7ha)



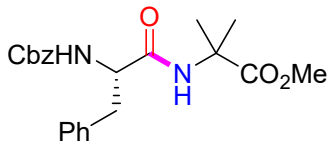
White solid, 71% yield (44.1 mg). m.p.: 57-59 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.44 (m, 1H), 7.37 – 7.29 (m, 10H), 7.10 (dd, J = 6.7, 3.0 Hz, 6H), 6.66 (s, 1H), 6.23 (br s, 1H), 4.64 – 4.35 (m, 2H), 3.66 (s, 3H), 3.09 – 2.89 (m, 2H), 1.64– 1.47 (m, 3H), 1.43 (s, 9H), 0.87 (dd, J = 5.9, 3.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.35, 173.04, 171.52, 155.77, 142.29, 138.30, 136.93, 129.71, 128.02, 128.00, 119.40, 79.62, 75.26, 54.27, 52.06, 50.77, 41.39, 30.24, 29.64, 28.29, 24.69, 22.74, 21.89. IR(KBr): 3467, 3413, 1637, 1614, 1413, 622 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{37}H_{44}N_4O_5$ $[M+H]^+$: 625.33845, Found: 625.33769.

Cbz-L-Phe-L-Val-OMe (7al)[19]



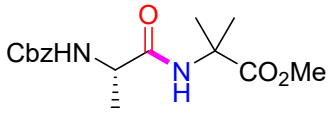
White solid, 97% yield (40.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.15 (m, 10H), 6.32 (d, J = 5.4, 1H), 5.38 (d, J = 5.7, 1H), 5.18 – 5.01 (m, 2H), 4.45 (dd, J = 8.6, 5.1 Hz, 2H), 3.68 (s, 3H), 3.18 – 2.98 (m, 2H), 2.08 (dq, J = 13.5, 6.8 Hz, 1H), 0.84 (d, J = 6.9 Hz, 3H), 0.80 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.68, 170.72, 155.92, 136.25, 136.11, 129.30, 128.66, 128.50, 128.16, 128.00, 127.00, 67.05, 57.27, 56.19, 52.07, 38.30, 31.17, 18.75, 17.72.

Cbz-L-Phe-Aib-OMe (7am)[14]



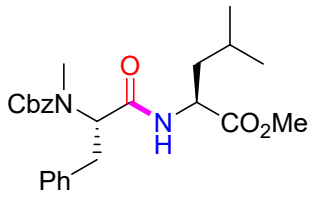
White solid, 73% yield (29.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 6H), 7.27 – 7.20 (m, 4H), 6.19 (s, 1H), 5.41 (br s, 1H), 5.09 (s, 2H), 4.37 (d, J = 6.1 Hz, 1H), 3.69 (s, 3H), 3.13 (dd, J = 13.5, 5.6 Hz, 1H), 2.99 (dd, J = 13.7, 7.8 Hz, 1H), 1.43 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.45, 169.72, 155.87, 136.48, 136.20, 129.45, 128.64, 128.49, 128.15, 127.97, 127.02, 66.98, 56.51, 56.22, 52.58, 38.64, 24.54, 24.41.

Cbz-L-Ala-Aib-OMe (7im) [14]



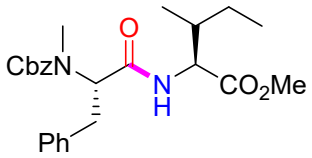
Colorless oil, 73% yield (23.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 6.66 (br s, 1H), 5.37 (br s, 1H), 5.12 (s, 2H), 4.22 (s, 1H), 3.72 (s, 3H), 1.53 (s, 3H), 1.52 (s, 3H), 1.37 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.73, 171.40, 155.99, 136.20, 128.50, 128.48, 128.17, 128.00, 66.97, 56.48, 52.63, 50.46, 24.67, 24.63, 18.39.

Cbz-L-*N*MePhe-L-Leu-OMe (7ja)



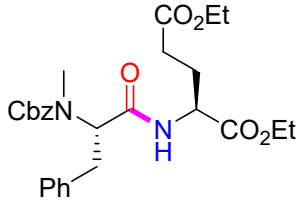
Colorless oil, 95% yield (42.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 3H), 7.29 – 7.11 (m, 7H), 6.42 (d, *J* = 7.1 Hz, 0.58H), 6.12 (s, 0.34H), 5.14 – 4.81 (m, 3H), 4.58 (s, 1H), 3.70 (s, 3H), 3.40 – 3.25 (m, 1H), 3.07 – 2.90 (m, 1H), 2.84 (s, 3H), 1.56 (ddd, *J* = 24.4, 12.2, 5.8 Hz, 3H), 0.90 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.97, 172.84, 169.91, 169.68, 157.11, 155.96, 137.34, 137.08, 136.35, 135.90, 128.87, 128.48, 128.14, 128.02, 127.60, 126.57, 67.73, 67.45, 61.07, 60.07, 52.24, 50.71, 41.16, 34.04, 33.81, 31.28, 30.56, 24.85, 22.73, 21.72. IR(KBr): 3469, 3414, 1677, 1638, 1614, 1411, 1264, 1023, 747, 622, 474 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{25}H_{33}N_2O_5$ $[M+H]^+$: 441.23840, Found: 441.23768.

Cbz-L-*N*MePhe-L-Ile-OMe (7jd)[14]



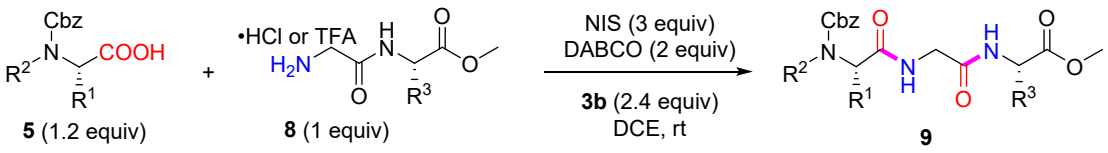
Colorless oil, 95% yield (41.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 3H), 7.26 – 7.11 (m, 7H), 6.56 (d, *J* = 8.2 Hz, 0.61H), 6.26 (d, *J* = 7.2 Hz, 0.33H), 5.11 (dd, *J* = 19.4, 12.6 Hz 2H), 5.02 – 4.78 (m, 1H), 4.54 (dd, *J* = 8.3, 5.0 Hz, 1H), 3.70 (s, 3H), 3.39 – 3.25 (m, 1H), 3.10 – 2.90 (m, 1H), 2.85 (d, *J* = 8.5 Hz, 3H), 1.81 (d, *J* = 39.4 Hz, 1H), 1.43 – 1.28 (m, 1H), 1.14 – 0.98 (m, 1H), 0.91 – 0.80 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.81, 169.91, 169.61, 157.12, 155.94, 137.33, 137.11, 136.38, 135.91, 128.86, 128.49, 128.11, 128.00, 127.64, 126.56, 67.75, 67.46, 61.13, 60.22, 56.33, 52.03, 37.63, 34.14, 33.83, 31.33, 30.65, 24.95, 15.40, 11.44.

Cbz-L-*N*MePhe-L-Glu(OEt)-OEt (7jf)[18]



Colorless oil, 94% yield (46.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 4H), δ 7.25 – 7.10 (m, 6H), 6.77 – 6.55 (m, 1H), 5.16 – 4.75 (m, 3H), 4.53 (d, *J* = 5.4 Hz, 1H), 4.25 – 4.01 (m, 4H), 3.32 (dd, *J* = 14.2, 6.6 Hz, 1H), 3.08 – 2.91 (m, 1H), 2.84 (s, 3H), 2.40 – 2.09 (m, 3H), 2.04 – 1.85 (m, 1H), 1.32 – 1.16 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.58, 171.26, 170.11, 156.96, 155.85, 137.37, 137.12, 136.40, 136.05, 128.85, 128.46, 128.08, 127.96, 127.61, 126.56, 67.62, 67.43, 61.56, 61.26, 60.61, 52.01, 51.71, 34.13, 33.95, 31.73, 31.57, 30.97, 30.06, 27.09, 26.84, 14.10, 14.06.

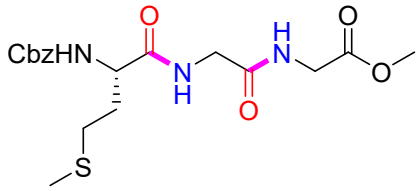
5 General Procedure for the preparation of tripeptides



Amino acids **5** (0.12 mmol), dipeptides **8** (0.1 mmol) and DABCO (22.4 mg, 0.2 mmol) were placed in a 10 ml two-neck round bottom flask, and DCE (3 ml) was added in argon atmosphere. After 5 min, NIS (67.5 mg, 0.3 mmol) and **3b** (65.8 mg, 0.24 mmol) were added in sequence at rt. The resulting mixture was stirred at room temperature and monitored by TLC. After amine was fully consumed, the reaction was quenched with 5% sodium thiosulfate solution (5 mL) and extracted with DCM (6 mL x 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the desired product **9**.

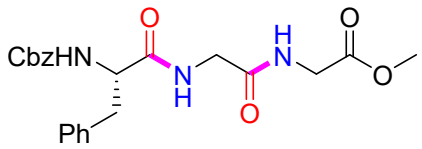
5.1. Characterization of the obtained tripeptides

Cbz-L-Met-Gly-Gly-OMe (9aa)



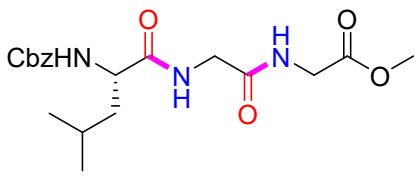
White solid, 98% yield (40.0 mg). m.p.: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.12 (m, 7H), 6.02 (br s, 1H), 5.08 (dd, J = 24.9, 12.1 Hz, 2H), 4.39 (d, J = 6.3 Hz, 1H), 4.01 (dt, J = 27.9, 13.8 Hz, 4H), 3.70 (s, 3H), 2.55 (t, J = 6.8 Hz, 2H), 2.17 – 2.02 (m, 4H), 1.95 (dd, J = 13.8, 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.21, 170.22, 169.19, 156.41, 136.00, 128.50, 128.20, 128.00, 67.14, 54.18, 52.32, 42.92, 41.04, 31.40, 30.03, 15.22. IR(KBr): 3456, 3418, 1637, 1615, 1413, 749 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{18}H_{25}N_3O_6$ $[M+H]^+$: 412.15368, Found: 412.15326.

Cbz-L-Phe-Gly-Gly-OMe (9ba)



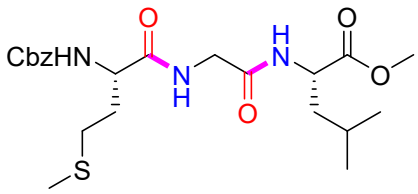
Brown solid, 88% yield (37.1 mg). m.p.: 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 11H), 7.06 (s, 1H), 5.79 (d, J = 7.0 Hz, 1H), 5.01 (q, J = 12.3 Hz, 2H), 4.50 (d, J = 6.9 Hz, 1H), 4.05 – 3.80 (m, 4H), 3.68 (s, 3H), 3.11 (dd, J = 13.8, 6.3 Hz, 1H), 2.99 (dd, J = 13.5, 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.93, 170.13, 169.11, 156.25, 136.27, 136.00, 129.17, 128.58, 128.52, 128.49, 128.45, 128.12, 127.89, 126.96, 67.03, 56.35, 52.25, 42.88, 40.99, 38.25. IR(KBr): 3470, 3413, 1639, 1615, 1561, 1412, 1261, 749 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{22}H_{25}N_3O_6$ $[M+H]^+$: 428.18161, Found: 428.18117.

Cbz-L-Leu-Gly-Gly-OMe (9ca)



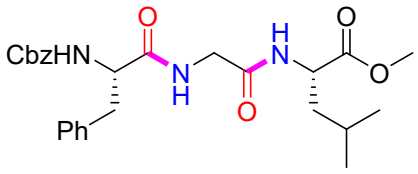
Brown oil, 92% yield (36.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 7H), 5.73 (d, J = 7.0 Hz, 1H), 5.06 (dd, J = 29.9, 12.2 Hz, 2H), 4.22 (s, 1H), 4.09 – 3.86 (m, 4H), 3.70 (s, 3H), 1.72 – 1.49 (m, 3H), 0.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.23, 170.20, 169.36, 156.53, 136.04, 128.48, 128.16, 127.92, 67.07, 53.84, 52.24, 42.91, 41.14, 41.01, 24.63, 22.86, 21.79. IR(KBr): 3417, 1639, 1613, 1567, 1412, 1274, 1022, 750, 643 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{19}H_{27}N_3O_6$ $[M+H]^+$: 394.19726, Found: 394.19689.

Cbz-L-Met-Gly-L-Leu-OMe (9ab)



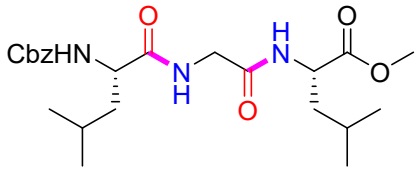
White solid, 86% yield (40.2 mg). m.p.: 83-85 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 7.14 (s, 1H), 6.89 (br s, 1H), 5.77 (br s, 1H), 5.10 (dd, *J* = 28.8, 12.1 Hz, 2H), 4.60 (dd, *J* = 12.7, 8.1 Hz, 1H), 4.37 (dd, *J* = 13.7, 7.1 Hz, 1H), 4.15 – 4.01 (m, 1H), 3.89 (dd, *J* = 16.5, 4.5 Hz, 1H), 3.70 (s, 3H), 2.56 (t, *J* = 7.0 Hz, 2H), 2.14 – 1.92 (m, 5H), 1.72 – 1.51 (m, 3H), 0.92 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.27, 171.84, 168.46, 156.25, 135.97, 128.59, 128.54, 128.25, 128.08, 67.22, 54.14, 52.30, 50.82, 43.07, 41.19, 31.24, 30.07, 24.78, 22.74, 21.83, 15.24. IR(KBr): 3420, 1640, 1567, 1413, 1022, 750 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{22}H_{33}N_3O_6S$ $[M+H]^+$: 468.21628, Found: 468.21589.

Cbz-L-Phe-Gly-L-Leu-OMe (9bb)



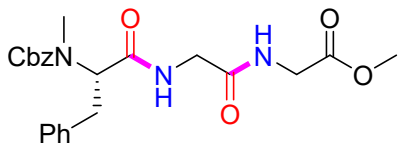
Yellow solid, 95% yield (46.0 mg). m.p.: 90-92 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 6H), 7.26 – 7.20 (m, 2H), 7.15 (d, *J* = 6.8 Hz, 2H), 6.96 – 6.81 (m, 2H), 5.47 (d, *J* = 7.1 Hz, 1H), 5.04 (q, *J* = 12.2 Hz, 2H), 4.66 – 4.53 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 1H), 4.18 – 4.00 (m, 1H), 3.76 (dd, *J* = 16.7, 4.4 Hz, 1H), 3.69 (s, 3H), 3.13 (dd, *J* = 13.8, 6.3 Hz, 1H), 3.02 (dd, *J* = 13.5, 7.7 Hz, 1H), 1.66 – 1.55 (m, 3H), 0.92 (dd, *J* = 5.7, 2.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.28, 171.52, 168.43, 156.13, 136.14, 135.86, 129.13, 128.73, 128.51, 128.24, 128.06, 127.10, 67.15, 56.53, 52.31, 50.75, 43.00, 41.04, 37.93, 24.72, 22.77, 21.78. IR(KBr): 3469, 3415, 1638, 1615, 1566, 1413, 1368, 1022, 750, 641 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{26}H_{33}N_3O_6$ $[M+H]^+$: 484.24421, Found: 484.24376.

Cbz-L-Leu-Gly-L-Leu-OMe (9cb)



White solid, 96% yield (42.9 mg). m.p.: 92-94 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 7.19 (s, 1H), 7.07 (d, *J* = 6.5 Hz, 1H), 5.52 (d, *J* = 5.6 Hz, 1H), 5.13 (d, *J* = 12.1 Hz, 1H), 5.03 (d, *J* = 12.2 Hz, 1H), 4.59 (dd, *J* = 12.8, 8.0 Hz, 1H), 4.26 – 4.05 (m, 2H), 3.86 (dd, *J* = 16.6, 4.6 Hz, 1H), 3.69 (s, 3H), 1.66 – 1.53 (m, 6H), 0.96 – 0.86 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.31, 172.96, 168.74, 156.35, 135.99, 128.50, 128.19, 128.01, 67.10, 53.74, 52.26, 50.78, 43.05, 41.16, 41.04, 24.72, 24.63, 22.88, 22.73, 21.84, 21.80. IR(KBr): 3465, 3417, 2957, 1641, 1614, 1564, 1413, 1261, 1023, 750, 643 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{23}H_{35}N_3O_6$ $[M+H]^+$: 450.25986, Found: 450.25955.

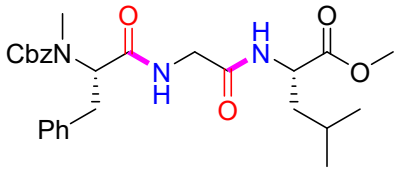
Cbz-L-*N*MePhe-Gly-Gly-OMe (9da)



Colorless oil, 95% yield (42.1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 3H), 7.28 – 7.08 (m, 7H), 7.03 – 6.73 (m, 2H), 5.09 (s, 1H), 5.01 – 4.83 (m, 1H), 4.79 – 4.67 (m, 1H), 4.12 – 3.82 (m, 4H), 3.72 (s, 3H), 3.38 (dd, *J* = 14.2, 5.6 Hz, 1H), 3.13 – 2.92 (m, 1H), 2.89 – 2.76 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.82, 170.12, 169.15, 168.74, 157.01, 155.94, /9137.17, 136.20, 135.90, 128.92, 128.52, 128.45, 128.04, 127.61,

126.64, 67.52, 61.76, 61.11, 52.28, 42.91, 40.96, 34.10, 32.36, 31.56. IR(KBr): 3464, 3415, 1639, 1615, 1568, 1412, 1022, 642 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{23}H_{27}N_3O_6$ $[M+H]^+$: 442.19726, Found: 442.19702.

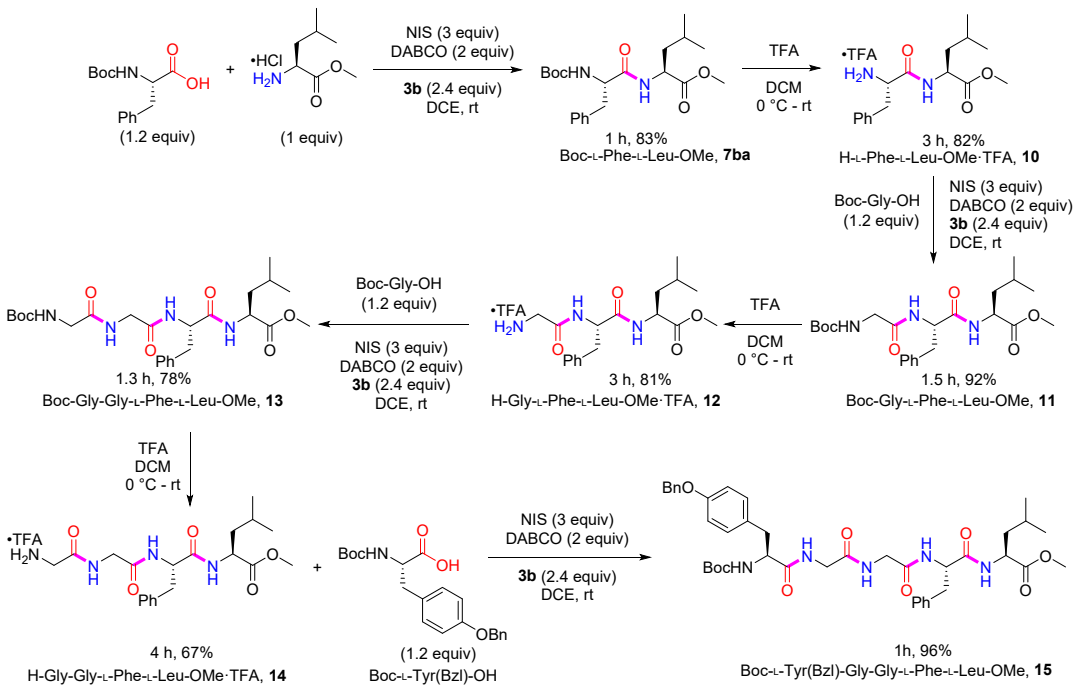
Cbz-L-*N*MePhe-Gly-L-Leu-OMe (9db)



Yellow oil, 83% yield (41.4 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 4H), 7.25 – 7.08 (m, 6H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 5.1 Hz, 1H), 6.78 – 6.61 (m, 1H), 5.17 – 4.86 (m, 2H), 4.66 – 4.49 (m, 2H), 4.20 (dd, *J* = 16.8, 6.7 Hz, 1H), 4.05 – 3.82 (m, 1H), 3.79 – 3.64 (m, 4H), 3.43 – 3.36 (m, 1H), 3.10 (dd, *J* = 14.1, 10.3 Hz, 1H), 2.98 – 2.85 (m, 1H), 2.73 (s, 2H), 1.72 – 1.61 (m, 3H), 0.94 (t, *J* = 5.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.44, 173.16, 170.52, 168.75, 168.35, 156.86, 155.76, 137.38, 136.17, 128.95, 128.81, 128.54, 128.50, 128.48, 128.46, 128.12, 127.86, 126.63, 67.64, 62.81, 61.01, 52.19, 50.72, 43.01, 40.94, 33.97, 33.43, 24.72, 22.78, 21.72. IR(KBr): 3327, 2957, 1744, 1679, 1581, 1438, 1408, 1369, 1333, 1206, 1153, 1024, 980, 750, 700 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{27}H_{35}N_3O_6$ $[M+H]^+$: 498.25986, Found: 498.25989.

6 Synthetic applications

6.1 The Synthesis of Protected Leu-enkephalin



H-L-Phe-L-Leu-OMe•TFA (**10**)[14]: Boc-L-Phe-L-Leu-Me (**7ba**, 313.99 mg, 0.8 mmol) was dissolved in 4 mL of DCM and TFA (4 mL) was added dropwise at 0 °C. After 1 h, the mixture was

allowed to warm to room temperature and stirred for 2 h. After the reaction was finished, the solvent was removed under reduced pressure and the addition of DCM and ether to the residue led to the precipitation of a white crystal, which was washed with ether and dried in vacuo to give product **10** (218.7 mg，82% yield) . ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.85 (d, J = 7.6 Hz, 1H), 8.16 (s, 3H), 7.31 (dt, J = 23.5, 7.4 Hz, 5H), 4.35 (dd, J = 14.4, 8.1 Hz, 1H), 4.05 (t, J = 6.5 Hz, 1H), 3.63 (s, 3H), 3.12 (dd, J = 14.1, 5.4 Hz, 1H), 2.94 (dd, J = 14.0, 7.8 Hz, 1H), 1.73 – 1.47 (m, 3H), 0.89 (dd, J = 16.8, 6.4 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.17, 168.22, 134.73, 129.52, 128.54, 127.19, 53.22, 52.07, 50.44, 36.87, 24.04, 22.72, 21.29.

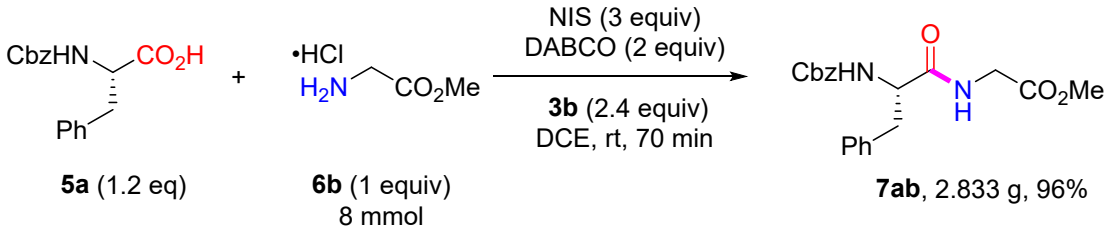
Boc-Gly-L-Phe-L-Leu-OMe (**11**)[20]: Boc-Gly-OH (21.0mg, 0.12 mmol), H-L-Phe-L-Leu-OH•TFA (**10**, 10.64mg, 0.1 mmol) and DABCO (22.4 mg, 0.2 mmol) were placed in a 10 ml two-neck round bottom flask, and DCE (3 ml) was added in argon atmosphere. After 5 min, NIS (67.5 mg, 0.3 mmol) and **3b** (65.8 mg, 0.24 mmol) were added in sequence at rt. The resulting mixture was stirred at room temperature and monitored by TLC. After amine was fully consumed, the reaction was quenched with 5% sodium thiosulfate solution (5 mL) and extracted with DCM (6 mL x 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the desired product **11** (41.3 mg，92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 3H), 7.21 – 7.18 (m, 2H), 6.93 (d, J = 8.0 Hz, 1H), 6.64 (d, J = 6.7 Hz, 1H), 5.30 (t, J = 5.4 Hz, 1H), 4.75 (q, J = 6.8 Hz, 1H), 4.57 – 4.46 (m, 1H), 3.85 – 3.71 (m, 2H), 3.69 (s, 3H), 3.14 – 3.01 (m, 2H), 1.63 – 1.45 (m, 3H), 1.43 (s, 9H), 0.88 (d, J = 5.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.69, 170.44, 169.36, 155.98, 136.24, 129.33, 128.53, 126.94, 80.20, 54.08, 52.19, 50.85, 44.20, 41.13, 38.08, 28.22, 24.64, 22.62, 21.82.

Boc-Gly-Gly-L-Phe-L-Leu-OMe (**13**)[14]: Boc-Gly-OH (21.0mg, 0.12 mmol), H-Gly-L-Phe-L-Leu-OMe•TFA (**12**, 44.65mg, 0.1 mmol) and DABCO (22.4 mg, 0.2 mmol) were placed in a 10 ml two-neck round bottom flask, and DCE (3 ml) was added in argon atmosphere. After 5 min, NIS (67.5 mg, 0.3 mmol) and **3b** (65.8 mg, 0.24 mmol) were added in sequence at rt. The resulting mixture was stirred at room temperature and monitored by TLC. After amine was fully consumed, the reaction was quenched with 5% sodium thiosulfate solution (5 mL) and extracted with DCM (6 mL x 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the desired product **13** (39.7 mg，78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.35 (m, 3H), 7.25 – 7.12 (m, 5H), 5.75 (br s, 1H), 5.01 (d, J = 5.6 Hz, 1H), 4.59 (d, J = 4.7 Hz, 1H), 3.92 (dd, J = 36.2, 14.4 Hz, 4H), 3.70 (s, 3H), 3.12 (dd, J = 13.3, 4.6 Hz, 1H), 2.97 (dd, J = 13.4, 7.6 Hz, 1H), 1.70 – 1.51 (m, 3H), 1.45 (s, 9H), 0.89 (d, J = 4.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.01, 171.05, 169.76, 168.49, 156.12, 136.40, 129.38, 128.32, 126.77, 79.85, 54.15, 52.19, 50.80, 43.77, 42.94, 40.89, 38.88, 28.33, 24.76, 22.69, 21.83.

Boc-L-Tyr(Bzl)-Gly-Gly-L-Phe-L-Leu-OMe (**15**): Boc-L-Tyr(Bzl)-OH (45.0mg, 0.12 mmol), H-Gly-Gly-L-Phe-L-Leu-OMe •TFA (**14**, 50.3mg, 0.1 mmol) and DABCO (22.4 mg, 0.2 mmol) were placed in a 10 ml two-neck round bottom flask, and DCE (3 ml) was added in argon atmosphere. After 5 min, NIS (67.5 mg, 0.3 mmol) and **3b** (65.8 mg, 0.24 mmol) were added in sequence at rt.

The resulting mixture was stirred at room temperature and monitored by TLC. After amine was fully consumed, the reaction was quenched with 5% sodium thiosulfate solution (5 mL) and extracted with DCM (6 mL x 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the desired product **15** (72.5 mg，96% yield). m.p.: 148-150 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.39 (d, J = 7.6 Hz, 1H), 8.18 (t, J = 5.4 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 5.4 Hz, 1H), 7.45 – 7.23 (m, 8H), 7.17 (t, J = 10.2 Hz, 3H), 6.94 – 6.89 (m, 2H), 5.05 (s, 2H), 4.62 – 4.50 (m, 1H), 4.28 (dd, J = 12.8, 9.5 Hz, 1H), 4.18 – 4.05 (m, 1H), 3.82 – 3.53 (m, 6H), 3.02 (dd, J = 13.9, 4.1 Hz, 1H), 2.93 (dd, J = 13.8, 3.8 Hz, 1H), 2.80 – 2.61 (m, 2H), 1.67 – 1.41 (m, 3H), 1.35 – 1.16 (m, 10H), 0.87 (dd, J = 21.9, 6.3 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.75, 172.14, 171.24, 168.98, 168.31, 156.88, 155.35, 137.70, 137.26, 130.34, 130.21, 129.21, 128.41, 128.04, 127.75, 127.62, 126.28, 114.34, 78.09, 69.12, 55.97, 53.55, 51.86, 50.35, 42.09, 41.72, 37.62, 36.49, 28.15, 24.20, 22.75, 21.34. IR(KBr): 3468, 3415, 1637, 1615, 1581, 1414, 1021, 749, 640 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{41}H_{53}N_5O_9$ $[M+Na]^+$: 782.37410, Found: 782.37400.

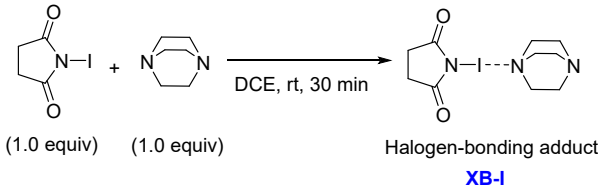
7 The gram-scale synthesis of 7ab



Cbz-L-Phe-Gly-OMe (**7ab**): Cbz-L-Phe-OH (2.873g, 9.6 mmol), H-Gly-OMe·HCl (1.004 g, 8 mmol) and DABCO (1.794 g, 16 mmol) were placed in a 100 ml two-neck round bottom flask, and DCE (35 ml) was added in argon atmosphere. After 5 min, NIS (5.399 g, 24 mmol) and **3b** (6.578 g, 24 mmol) were added in sequence at rt. The resulting mixture was stirred at room temperature and monitored by TLC. After 70 min, the reaction was quenched with 5% sodium thiosulfate solution (20 mL) and extracted with DCM (30 mL x 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the desired product **7ab** (2.833 g, 96% yield).

8 Experimental mechanism studies

8.1 Synthesis of intermediate XB-I



DABCO (22.4 mg, 0.2 mmol) was placed in a 10ml two-neck round bottom flask, and DCE (3ml) was added in argon atmosphere. After 10 min, NIS (67.5 mg, 0.2 mmol) was added at rt. The resulting mixture was stirred at room temperature for 20 min and the precipitated solid was filtered, which was washed with ether to give intermediate I. ^{13}C NMR (100 MHz, $CDCl_3$) was recorded subsequently (Figures S1).

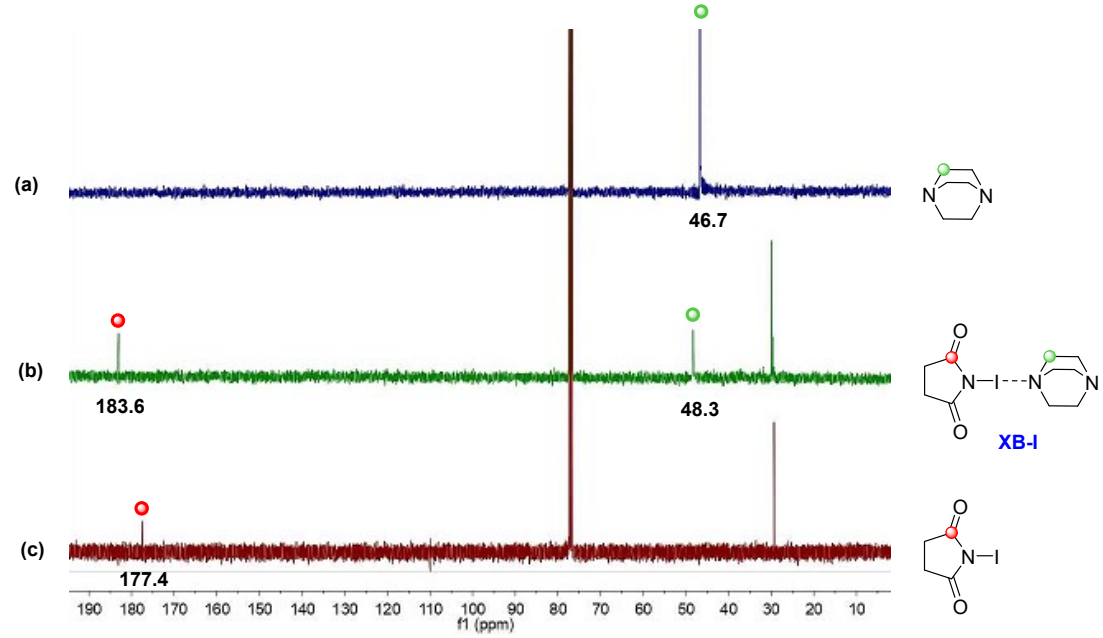


Figure S1. ^{13}C NMR spectra of (a) DABCO, (b) intermediate I and (c) NIS

8.2 ^{13}C NMR analysis

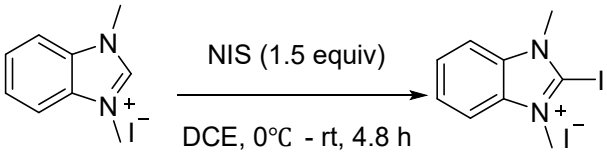
Analysis of complex I showed that the signal of NIS carbonyl carbon moved down 6.2 ppm from 177.4 ppm to 183.6 ppm and the signal of DABCO carbon atom down 1.6 ppm from 46.7 ppm to 48.3 ppm.

8.3 Detection of I_2

1) preparation of 0.5% aqueous starch solution: placed 0.5g of soluble starch in a 10ml round bottom flask, followed by 5ml of cold water and stirred well. Added slowly dropwise to 100ml of 100°C water, continued to heat for 5 minutes, cooled to room temperature and set aside.
2) Taking 3 ml of ready-made aqueous starch solution in a 10 ml glass vial, subsequently added a drop of reaction solution to it and shaken well. We could observe that the aqueous starch solution turned blue, which was consistent with the color of I_2 in the aqueous starch solution. Thus, it was proved that our reaction system generated I_2 (Figure S2).

Figure S2. Color comparison of reaction mixture and I_2 in aqueous starch solution

8.4 Synthesis of intermediate IM5a



3b **IM5a**

3b (66.0 mg, 0.24 mmol) was placed in a 10 ml two-neck round bottom flask, and DCE (3ml) was added in an ice bath argon atmosphere. After 30 min, NIS (81.0 mg, 0.36 mmol) was added. After

15 min, the resulting mixture returned to room temperature and stirred at room temperature for 4 h and the precipitated solid was filtered, which was washed with EtOAc to give intermediate **IM5a**. m.p.: 210-212 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (dd, J = 6.2, 3.1 Hz, 2H), 7.62 (dd, J = 6.2, 3.1 Hz, 2H), 4.08 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 133.27, 126.16, 118.68, 113.23, 36.11. IR(KBr): 3550.19, 3473.39, 3415.11, 3237.39, 1638.30, 1616.26, 1578.73, 1416.00, 748.59, 622.36 cm^{-1}. HRMS (ESI): m/z Calcd. For $C_{41}H_{53}N_5O_9$ $[M]^+$: 272.98832, Found: 272.98810.

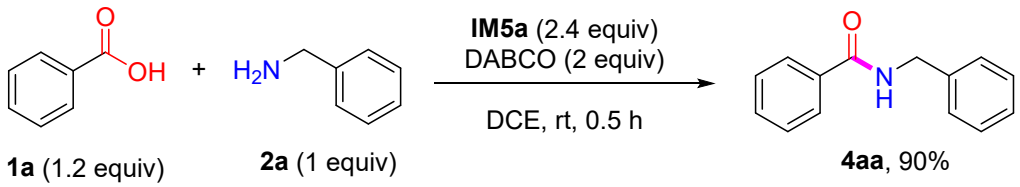
8.5 Screening of base equivalents

Table S1. Screening of base equivalents for synthesizing dipeptides

Entry	Base (*x* equiv)	NHC precursor (**3b**)	Solvent	Time (h)	Yield[a] [%]
1	DABCO (2 equiv)	2.4 equiv	DCE	1.2	99
2	DABCO (1.5 equiv)	2.4 equiv	DCE	7.5	93
3	DABCO (1 equiv)	2.4 equiv	DCE	7.5	93
4	DABCO (0.5 equiv)	2.4 equiv	DCE	7.5	86
5	DABCO (0.3 equiv)	2.4 equiv	DCE	7.5	82
6	-	2.4 equiv	DCE	7.5	78

When we found that Intermediate **IM5a** could be synthesized even under base-free room temperature conditions, we screened for base equivalents (Table S1). It was observed from the Table S1 that the reaction yield dropped when decreasing the base equivalents, and the reaction time was greatly prolonged. Therefore, we concluded that the optimal reaction conditions for a 2 equivalents amount of DABCO.

8.6 Synthesis of 4aa by intermediate IM5a

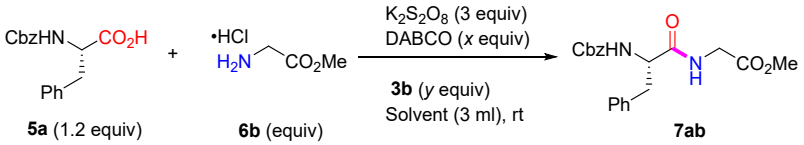


Benzoic acid (14.66 mg, 0.12 mmol), benzylamine (10.72 mg, 0.1 mmol) and DABCO (23 mg, 0.2 mmol) were placed in a 10ml two-neck round bottom flask, and DCE (3ml) was added in argon atmosphere. After 5 min, **IM5a** (96 mg, 0.24 mmol) was added at rt. The resulting mixture was stirred at room temperature and monitored by TLC. After amine was fully consumed, the reaction was quenched with 5% sodium thiosulfate solution (5 mL) and extracted with DCM (6 mL x 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the pure amide product **4aa** (19 mg，90% yield).

9 Optimization of the reaction conditions

We began our work by constructing the peptide bond between Cbz-L-Phe-OH and H-Gly-OMe•HCl to yield **7ab** employing $K_2S_2O_8$-**3b**-DABCO as coupling system (Table S2). We first probed the reaction solvent and found that DCM was more effective than other solvents, with a yield of 64% for **7ab** (entries 1-9). Then, we investigated the effect of various bases on the reaction (entries 10–14). Inorganic bases, the likes of K_2CO_3 and Cs_2CO_3, did not react well, probably due to poor solubility (entries 13-14). It was observed that organic bases gave better results than inorganic bases (entries 10–12). When increasing the equivalent of DABCO to 7 equivalents, the **7ab** was obtained in good yield (entry 15), whereas, the reaction effect did not improve when the equivalents were continued to be increased (entry 16). We subsequently examined the equivalence of carbene precursor **3b**, and found that the desired product was obtained in 84% yield when the carbene precursor was 4 equivalents (entry 18).

Table S2. Optimization of the reaction conditions of peptide synthesis

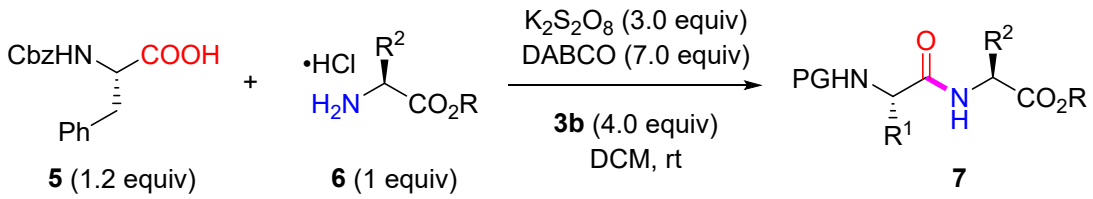


Entry	NHC precursor **3b** (*y* equiv)	Base (*x* equiv)	Solvent	Time (h)	Yield [a] (%)
1	2.4	DABCO (6)	DCE	12	59
2	2.4	DABCO (6)	DCM	12	64

3	2.4	DABCO (6)	PhF	14.5	26
4	2.4	DABCO (6)	$CHCl_3$	14	37
5	2.4	DABCO (6)	MeOH	14	trace
6	2.4	DABCO (6)	$MeNO_2$	12	trace
7	2.4	DABCO (6)	$PhNO_2$	12	50
8	2.4	DABCO (6)	1,4-Dioxane	14	42
9	2.4	DABCO (6)	THF	12	trace
10	2.4	DMAP (6)	DCM	14	50
11	2.4	NMM (6)	DCM	12	62
12	2.4	Et_3N (6)	DCM	12	41
13	2.4	K_2CO_3 (6)	DCM	13	34
14	2.4	Cs_2CO_3 (6)	DCM	14	trace
15	2.4	DABCO (7)	DCM	11	74%
16	2.4	DABCO (8)	DCM	9	73%
17	3.0	DABCO (7)	DCM	11	73%
18	4.0	DABCO (7)	DCM	7	84%

Reaction conditions: **5a** (0.12 mmol, 1.2 equiv), **6b** (0.10 mmol, 1.0 equiv), $K_2S_2O_8$ (0.3mmol, 3.0 equiv), DABCO (*x* equiv), **3b** (*y* equiv), DCM (3.0 mL). [a]Isolated yield.

10 General Procedure for the preparation of dipeptides



Amino acids **5** (0.12 mmol), amino acids **6** (0.1 mmol) and DABCO (78.5 mg, 0.7 mmol) were placed in a 10 ml two-neck round bottom flask, and DCE (3 ml) was added in argon atmosphere. After 5 min, $K_2S_2O_8$ (81.1 mg, 0.3 mmol) and **3b** (109.6 mg, 0.4) were added in sequence at rt. The resulting mixture was stirred at room temperature and monitored by TLC. After amine was fully consumed, the reaction was quenched with 5% sodium thiosulfate solution (5 mL) and extracted with DCM (6 mL x 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the pure dipeptides product **7**.

11 Computational details of the mechanism

Quantum chemical calculations were performed using the Gaussian 09 suite of programs.[21] Geometry optimizations and frequencies were calculated with the M06-2X density functional and a mixed basis set of SDD for I and 6-31G(d) for other atoms in conjunction with the SMD implicit solvation model to account for the solvation effects of dichloroethane and dichloromethane. The recently corrected radius for iodine was used for SMD calculations (the radius of iodine was set to 2.74 Å using the modifysph command).[22] Optimized geometries were verified by frequency computations as minima (zero imaginary frequencies) or transition structures (a single imaginary frequency) at the same level of theory. Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition structure and intermediates. More accurate electronic energies were obtained by single point energy calculations at the SMD-M06-2X/6-311+G(d,p)+Def2-TZVP(I) level of theory. A factor of RTln(24.46) was added to free energy for each species to account for the 1 atm to 1 M standard state change. All Gibbs energies in solution reported throughout the text are in kilocalories per mole, and the bond lengths are in angstroms. The structures were generated by CYL view.[23]

Calculated cartesian coordinates

11.1 NIS-3a-DABCO system

XB-I (DABCO-NIS)

C	2.53382900	1.34936500	-0.35075400
C	4.08779200	1.32615600	-0.36811400
H	2.11778700	1.61454800	-1.32700300
H	2.14300100	2.05159000	0.39132400
H	4.46708400	1.57167100	-1.36432500
H	4.49272400	2.05603200	0.33888700
C	2.53185400	-0.97797400	-0.99179200
H	2.11422100	-1.95547300	-0.73417400
H	2.14127900	-0.68447700	-1.97032800
C	4.08577400	-0.98386300	-0.96445500
H	4.46362700	-1.96962600	-0.67825400
H	4.49018400	-0.73801900	-1.95058800
C	4.08710200	-0.34560800	1.33368100
H	4.49034000	-1.32352200	1.61238500
H	4.46748800	0.39375800	2.04449700
C	2.53311100	-0.36979700	1.34443000
H	2.14073500	-1.36319300	1.58049000
H	2.11837300	0.34340900	2.06257600
N	4.58862100	-0.00132400	0.00012000
N	2.03261600	0.00102200	0.00090500
I	-0.41476900	0.00095100	-0.00099900
C	-4.80855000	-0.76536900	0.00175400

C	-4.80943500	0.76259000	0.00211400
H	-5.28162500	-1.20175700	0.88502100
H	-5.28362700	-1.20131500	-0.88065600
H	-5.28270400	1.19795600	0.88578600
H	-5.28533000	1.19845700	-0.87988700
N	-2.57364500	-0.00008400	-0.00115900
C	-3.33463500	-1.15286100	0.00000000
C	-3.33596600	1.15180100	0.00015300
O	-2.89174900	-2.28254100	-0.00034000
O	-2.89439800	2.28199300	-0.00015600

Zero-point correction= 0.256843 (Hartree/Particle)
Thermal correction to Energy= 0.272827
Thermal correction to Enthalpy= 0.273771
Thermal correction to Gibbs Free Energy= 0.209458
SCF Done: E(RM062X) = -1002.96273998

NIS

C	2.76946100	-0.76590000	0.00036700
C	2.76946200	0.76589700	-0.00029000
H	3.24547700	-1.19825100	-0.88286400
H	3.24469900	-1.19737700	0.88445900
H	3.24476800	1.19737600	-0.88434200
H	3.24540900	1.19824300	0.88298200
N	0.55475700	0.00000200	-0.00000500
I	-1.49669900	0.00000000	-0.00000600
C	1.30844700	-1.17609400	0.00004600
C	1.30844600	1.17609200	-0.00008400
O	0.84540500	-2.28863100	-0.00000200
O	0.84541100	2.28863300	-0.00001300

Zero-point correction= 0.077951 (Hartree/Particle)
Thermal correction to Energy= 0.085618
Thermal correction to Enthalpy= 0.086562
Thermal correction to Gibbs Free Energy= 0.043353
SCF Done: E(RM062X) = -657.650151870

DABCO

C	0.77793200	-1.37555600	-0.08891500
C	-0.77820800	-1.37544600	-0.08822600
H	1.17503100	-1.82634400	-1.00476300
H	1.17563000	-1.93957200	0.76149300
H	-1.17618900	-1.82698500	-1.00332000
H	-1.17522600	-1.93865700	0.76303200
C	0.77807600	0.76464800	-1.14666700

H	1.17526600	1.78304700	-1.07851300
H	1.17560300	0.31032500	-2.06046200
C	-0.77796700	0.76424200	-1.14701100
H	-1.17572600	1.78249300	-1.07996400
H	-1.17484000	0.30887800	-2.06057200
C	-0.77794100	0.61143300	1.23523700
H	-1.17484500	1.63036000	1.29714800
H	-1.17601900	0.04452400	2.08367800
C	0.77810800	0.61068900	1.23549900
H	1.17596600	1.62918000	1.29844900
H	1.17535100	0.04264600	2.08357500
N	-1.28709800	0.00013000	0.00007600
N	1.28709800	-0.00012300	0.00002700

Zero-point correction= 0.176565 (Hartree/Particle)
Thermal correction to Energy= 0.183185
Thermal correction to Enthalpy= 0.184129
Thermal correction to Gibbs Free Energy= 0.145574
SCF Done: E(RM062X) = -345.281590045

NHC precursor (3b)

C	0.01139200	2.52448800	0.69955300
C	0.01139200	2.52448800	-0.69955300
C	-0.04208500	3.70751000	-1.43654600
C	-0.09462200	4.88401100	-0.70494100
C	-0.09462200	4.88401100	0.70494100
C	-0.04208500	3.70751000	1.43654600
H	-0.04153500	3.70171300	-2.52120500
H	-0.13711200	5.83189900	-1.23064800
H	-0.13711200	5.83189900	1.23064800
H	-0.04153500	3.70171300	2.52120500
N	0.07369300	1.19378100	-1.09242400
N	0.07369300	1.19378100	1.09242400
C	0.09985500	0.71189400	-2.46817100
H	0.12559100	-0.37739400	-2.44988700
H	-0.79890300	1.05235900	-2.98482700
C	0.09985500	0.71189400	2.46817100
H	-0.79890300	1.05235900	2.98482700
H	0.12559100	-0.37739400	2.44988700
C	0.11142900	0.43602800	0.00000000
H	0.98971900	1.09751700	2.96829700
H	0.98971900	1.09751700	-2.96829700
H	0.15430600	-0.65163100	0.00000000
I	-0.03442600	-3.45706600	0.00000000

Zero-point correction= 0.180855 (Hartree/Particle)
Thermal correction to Energy= 0.192184
Thermal correction to Enthalpy= 0.193128
Thermal correction to Gibbs Free Energy= 0.140944
SCF Done: E(RM062X) = -756.699240474

IM1a

I	1.32941900	0.63408400	-0.26346800
C	-2.76889100	1.75470500	-1.48677100
C	-2.66806700	2.52153900	-0.16826000
H	-3.59977000	1.04412100	-1.51319300
H	-2.85482300	2.40382000	-2.36191200
H	-3.45853600	2.27231300	0.54456200
H	-2.66629200	3.60693400	-0.29962600
N	-0.69241700	1.27329500	-0.47991600
C	-1.46439000	0.97999500	-1.59421500
C	-1.32370900	2.11996100	0.41946800
O	-1.13972000	0.22013900	-2.48163300
O	-0.86570300	2.46543700	1.48706700
I	4.40369200	-0.45725900	0.11228100
H	-0.16418600	-1.49798900	1.83774000
C	-1.11961100	-1.37344500	1.34632300
N	-1.42727000	-1.86370700	0.14811600
N	-2.15294800	-0.71222900	1.86242700
C	-2.74397400	-1.52342800	-0.13384800
C	-0.53999800	-2.59987300	-0.74781600
C	-3.20807000	-0.78673700	0.96118200
C	-2.18886500	-0.04116300	3.15801200
C	-3.55665700	-1.80484900	-1.23344400
H	0.40925700	-2.77087300	-0.24016400
H	-1.00395900	-3.55541600	-0.99831600
H	-0.38145600	-2.00185700	-1.64828900
C	-4.51459400	-0.29737400	1.01979500
H	-2.95495500	-0.50606600	3.78068000
H	-1.21148700	-0.14535700	3.62811600
H	-2.40882600	1.01692900	3.00659900
C	-4.85556300	-1.32506200	-1.17304200
H	-3.18734000	-2.36697800	-2.08410600
C	-5.32555500	-0.58352400	-0.06760000
H	-4.87186900	0.26857200	1.87353700
H	-5.53020000	-1.52062800	-1.99962100
H	-6.35095700	-0.22984400	-0.06966400

Zero-point correction= 0.259875 (Hartree/Particle)

Thermal correction to Energy= 0.281386
Thermal correction to Enthalpy= 0.282330
Thermal correction to Gibbs Free Energy= 0.204704
SCF Done: E(RM062X) = -1414.37592470

TS1a

I	1.68432200	-0.63670400	0.01781100
C	-3.17478300	-2.01543400	1.27268800
C	-2.54183900	-2.68298500	0.05613000
H	-4.10857800	-1.49178000	1.04768400
H	-3.37104600	-2.70240800	2.10058000
H	-3.11277200	-2.55383500	-0.86783500
H	-2.35281000	-3.75245700	0.18381200
N	-1.02579900	-1.02570400	0.88511300
C	-2.12204400	-0.98675100	1.70935600
C	-1.20416200	-1.95772000	-0.06569400
O	-2.27471200	-0.23458000	2.66386000
O	-0.36407200	-2.21055100	-0.94175700
I	4.40448600	0.47205300	0.02404600
H	-0.10012900	2.18552100	-0.35878400
C	-1.11359000	1.81576800	-0.42854300
N	-2.05711800	2.03291800	0.48087500
N	-1.58703800	1.08733500	-1.43586700
C	-3.21904700	1.40616000	0.05571200
C	-1.89382200	2.74505300	1.74242900
C	-2.91609600	0.79276000	-1.16482400
C	-0.83396600	0.62426700	-2.59640400
C	-4.48885200	1.32772000	0.62734800
H	-0.88235900	3.14839100	1.78065300
H	-2.61952000	3.55869000	1.79132000
H	-2.04529900	2.03268300	2.55466200
C	-3.86802800	0.06015000	-1.87573600
H	-1.39974700	0.85933900	-3.49957000
H	0.12249900	1.14643400	-2.61888100
H	-0.67046300	-0.45252700	-2.51083500
C	-5.43815900	0.60943300	-0.08322700
H	-4.71167800	1.79810900	1.57865000
C	-5.13189800	-0.01722400	-1.30982000
H	-3.62715000	-0.42137400	-2.81756600
H	-6.44230400	0.51848600	0.31715600
H	-5.90783600	-0.57476000	-1.82363900

Zero-point correction= 0.258966 (Hartree/Particle)
Thermal correction to Energy= 0.279901

Thermal correction to Enthalpy= 0.280845
Thermal correction to Gibbs Free Energy= 0.204794
SCF Done: E(RM062X) = -1414.34799181

I_2

I	0.00000000	0.00000000	1.40961100
I	0.00000000	0.00000000	-1.40961100

Zero-point correction= 0.000424 (Hartree/Particle)
Thermal correction to Energy= 0.003367
Thermal correction to Enthalpy= 0.004312
Thermal correction to Gibbs Free Energy= -0.025490
SCF Done: E(RM062X) = -595.271049000

XB-II (DABCO-I_2)

C	-4.01068300	-1.34968400	0.26096900
C	-2.46004900	-1.39337700	0.15943800
H	-4.33570500	-1.64803200	1.26128500
H	-4.45300400	-2.03828100	-0.46339200
H	-2.00105700	-1.81275300	1.05735500
H	-2.11872200	-1.96205200	-0.70891400
C	-4.01096200	0.90270000	1.03686400
H	-4.33545900	1.91816100	0.79467100
H	-4.45475700	0.62017800	1.99493400
C	-2.46030600	0.83611800	1.12701600
H	-2.00153500	1.82363300	1.04138300
H	-2.12006100	0.36792200	2.05395100
C	-2.45824400	0.56004700	-1.28639600
H	-2.11748000	1.59676300	-1.34303700
H	-1.99725800	-0.00627900	-2.09858400
C	-4.00887600	0.44821900	-1.30181700
H	-4.45240700	1.41899200	-1.53772400
H	-4.33197400	-0.27057400	-2.05963000
N	-1.96017200	0.00056500	0.00046200
N	-4.51065500	0.00063600	-0.00170900
I	0.35685100	-0.00150900	0.00161200
I	3.42560000	0.00075000	-0.00085700

Zero-point correction= 0.179324 (Hartree/Particle)
Thermal correction to Energy= 0.190231
Thermal correction to Enthalpy= 0.191176
Thermal correction to Gibbs Free Energy= 0.138180
SCF Done: E(RM062X) = -940.584800001

IM2a

C	-2.52209400	0.70059500	0.00001600
C	-2.52206200	-0.70060600	-0.00001900
C	-3.70707100	-1.43545800	0.00000200
C	-4.88612900	-0.70452800	0.00006500
C	-4.88616100	0.70441000	0.00010200
C	-3.70713600	1.43539300	0.00007900
H	-3.70138800	-2.52039100	-0.00002900
H	-5.83478800	-1.23098200	0.00008400
H	-5.83484400	1.23082100	0.00015000
H	-3.70150100	2.52032700	0.00010700
N	-1.18859900	-1.09093400	-0.00008200
N	-1.18864900	1.09098500	-0.00002500
C	-0.67674000	-2.45706600	-0.00014900
H	0.41640500	-2.41321000	-0.00021400
H	-1.03007600	-2.97519800	0.89334300
C	-0.67685300	2.45714000	0.00000600
H	-1.03025700	2.97520500	0.89351000
H	0.41629200	2.41333000	-0.00000100
C	-0.42706300	0.00004200	-0.00008100
H	-1.03027200	2.97525700	-0.89346200
H	-1.03017900	-2.97514600	-0.89363000
H	0.68229900	0.00005900	-0.00012400
C	4.80315300	-0.76229800	0.00026400
C	4.80312300	0.76234700	-0.00000100
H	5.27616400	-1.20468800	-0.88131300
H	5.27598600	-1.20438200	0.88209000
H	5.27610700	1.20444900	-0.88173700
H	5.27595000	1.20475500	0.88166600
N	2.53090200	-0.00001800	-0.00009600
C	3.30728000	-1.11468800	0.00016800
C	3.30723700	1.11467800	-0.00019200
O	2.89014400	-2.27303400	0.00036400
O	2.89005800	2.27301100	-0.00043500

Zero-point correction= 0.257173 (Hartree/Particle)
Thermal correction to Energy= 0.274569
Thermal correction to Enthalpy= 0.275513
Thermal correction to Gibbs Free Energy= 0.208768
SCF Done: E(RM062X) = -819.061981904

TS2a

C	-2.42819000	0.69938400	-0.00004900
C	-2.42818600	-0.69938500	0.00008600
C	-3.61364400	-1.43272900	0.00004700

C	-4.79632500	-0.70362900	-0.00011900
C	-4.79632800	0.70361500	-0.00024600
C	-3.61365100	1.43272100	-0.00021000
H	-3.60957700	-2.51801800	0.00014700
H	-5.74450200	-1.23149700	-0.00015400
H	-5.74450800	1.23147800	-0.00037100
H	-3.60959100	2.51801000	-0.00029900
N	-1.09331200	-1.08056100	0.00024100
N	-1.09331600	1.08056600	0.00002500
C	-0.62993900	-2.45982800	0.00037800
H	0.46260800	-2.45742300	0.00036200
H	-0.99957700	-2.97232700	0.89208300
C	-0.62994700	2.45983500	0.00004700
H	-0.99962300	2.97241300	0.89169200
H	0.46260000	2.45743200	0.00008600
C	-0.28977200	0.00000400	0.00017700
H	-0.99954800	2.97242300	-0.89162300
H	-0.99957700	-2.97249400	-0.89123200
H	1.11394200	0.00000600	0.00003800
C	4.65969800	-0.76329500	-0.00024700
C	4.65968800	0.76331400	0.00003800
H	5.13284800	-1.20239600	-0.88259800
H	5.13301000	-1.20276500	0.88183100
H	5.13291700	1.20276600	-0.88209400
H	5.13290600	1.20244700	0.88233400
N	2.40770500	-0.00000600	-0.00018900
C	3.17635800	-1.13203900	-0.00022100
C	3.17634300	1.13203600	0.00008200
O	2.74448400	-2.27632400	-0.00023400
O	2.74445300	2.27631600	0.00032000

Zero-point correction= 0.252751 (Hartree/Particle)
Thermal correction to Energy= 0.269763
Thermal correction to Enthalpy= 0.270707
Thermal correction to Gibbs Free Energy= 0.206277
SCF Done: E(RM062X) = -819.049036204

IM3a (NHC)

C	-0.16291600	0.69959400	-0.00000100
C	-0.16291600	-0.69959400	-0.00000100
C	-1.34936900	-1.42979500	0.00000300
C	-2.53642800	-0.70234700	0.00000200
C	-2.53642800	0.70234700	0.00000200
C	-1.34936900	1.42979500	0.00000300

H	-1.34746600	-2.51546400	0.00000700
H	-3.48393700	-1.23196900	0.00000200
H	-3.48393700	1.23196900	0.00000200
H	-1.34746600	2.51546400	0.00000800
N	1.17454700	-1.07115900	-0.00000800
N	1.17454700	1.07115900	-0.00000800
C	1.60944300	-2.45403100	-0.00000200
H	2.69895000	-2.46477300	-0.00013500
H	1.24046500	-2.97067100	0.89088100
C	1.60944300	2.45403100	-0.00000200
H	1.24046600	2.97067000	0.89088200
H	2.69895000	2.46477300	-0.00013600
C	2.02184100	0.00000000	0.00001300
H	1.24024500	2.97073900	-0.89075300
H	1.24024700	-2.97073800	-0.89075400

Zero-point correction= 0.167364 (Hartree/Particle)
Thermal correction to Energy= 0.176980
Thermal correction to Enthalpy= 0.177924
Thermal correction to Gibbs Free Energy= 0.133076
SCF Done: E(RM062X) = -458.396946502

IM4a

I	-0.57571000	-0.69139600	-0.02879100
C	-6.04026000	0.43282300	0.06522500
C	-5.34584000	-0.92116700	0.09537400
H	-6.68405700	0.58032000	-0.80636000
H	-6.63869600	0.64352200	0.95602200
H	-5.58373700	-1.56410100	-0.75692000
H	-5.53339700	-1.49811900	1.00562500
N	-3.65297700	0.78057000	-0.01185100
C	-4.86694900	1.42512200	-0.00084500
C	-3.86614500	-0.53618800	0.03941800
O	-5.02406900	2.63761200	-0.03821100
O	-2.97947400	-1.42234100	0.04476000
C	1.50739300	-0.19853800	-0.06763500
N	2.52402700	-1.07238500	-0.05200600
N	1.99962900	1.04854900	-0.05914800
C	3.72211600	-0.36992200	-0.00653100
C	2.43265200	-2.52735000	-0.02416300
C	3.38759600	0.98607400	-0.01173700
C	1.22455500	2.28547500	-0.04605100
C	5.04732800	-0.80327500	0.04410900
H	1.48355400	-2.84041300	-0.45646500

H	3.24780800	-2.93453800	-0.62315600
H	2.50989700	-2.88335700	1.00548900
C	4.36341000	1.98235900	0.03747000
H	0.31405900	2.15019300	-0.62872400
H	0.97392000	2.55739100	0.98147700
H	1.82488100	3.07056600	-0.50514100
C	6.01760900	0.18607100	0.08974300
H	5.30113100	-1.85754400	0.05579500
C	5.68120700	1.55397200	0.08626700
H	4.10469700	3.03530000	0.04297600
H	7.06319900	-0.09966100	0.13296300
H	6.47491900	2.29239000	0.12712000

Zero-point correction= 0.247355 (Hartree/Particle)
Thermal correction to Energy= 0.266596
Thermal correction to Enthalpy= 0.267540
Thermal correction to Gibbs Free Energy= 0.195851
SCF Done: E(RM062X) = -1116.08273392

IM5a

C	1.78554800	-0.69927300	-0.01189900
C	1.78555000	0.69927000	-0.01189900
C	2.97271300	1.43529500	0.00462200
C	4.14838000	0.70504100	0.01908900
C	4.14837800	-0.70504800	0.01908800
C	2.97271100	-1.43529900	0.00462000
H	2.97531200	2.51926300	0.01311200
H	5.09617200	1.23198400	0.03451200
H	5.09616900	-1.23199200	0.03451000
H	2.97530800	-2.51926800	0.01311000
N	0.45276200	1.09948800	-0.02482000
N	0.45275900	-1.09948700	-0.02481700
C	-0.03091700	2.47900800	-0.01194300
H	-0.78209100	2.60749800	-0.79190500
H	-0.45002300	2.71452800	0.96803400
C	-0.03093000	-2.47900400	-0.01194400
H	-0.45010200	-2.71450000	0.96801100
H	-0.78205400	-2.60750400	-0.79195200
C	-0.30348900	0.00000200	-0.02512300
H	0.81098200	-3.13541200	-0.22305400
H	0.81098600	3.13540600	-0.22312500
I	-2.38352800	0.00000100	0.00940600

Zero-point correction= 0.170405 (Hartree/Particle)
Thermal correction to Energy= 0.181885

Thermal correction to Enthalpy= 0.182829
Thermal correction to Gibbs Free Energy= 0.131655
SCF Done: E(RM062X) = -755.894520464

Succinimide

C	-0.76592500	-1.25505700	0.00035100
C	0.76592500	-1.25505700	-0.00028500
H	-1.19946000	-1.73274600	-0.88163800
H	-1.19860100	-1.73200000	0.88318000
H	1.19860800	-1.73207200	-0.88307000
H	1.19945200	-1.73267000	0.88174900
N	0.00000100	0.95928700	-0.00001300
C	-1.16596000	0.21093500	0.00004100
C	1.16595800	0.21093700	-0.00009400
O	-2.28344400	0.67304500	0.00002900
O	2.28344500	0.67304400	-0.00005200
H	-0.00000300	1.97522300	-0.00001400

Zero-point correction= 0.088329 (Hartree/Particle)
Thermal correction to Energy= 0.094429
Thermal correction to Enthalpy= 0.095373
Thermal correction to Gibbs Free Energy= 0.058033
SCF Done: E(RM062X) = -360.648745644

Succinimide anion

C	-0.76001400	-1.22481400	0.00035300
C	0.76001400	-1.22481500	-0.00025200
H	-1.20669700	-1.69622200	-0.88065900
H	-1.20583900	-1.69553000	0.88218100
H	1.20584100	-1.69556000	-0.88206300
H	1.20669400	-1.69619200	0.88077800
N	0.00000000	1.06476600	-0.00003100
C	-1.10798100	0.27754400	0.00004500
C	1.10798100	0.27754500	0.00002800
O	-2.27585600	0.66858600	0.00002800
O	2.27585600	0.66858600	-0.00016100

Zero-point correction= 0.075941 (Hartree/Particle)
Thermal correction to Energy= 0.081700
Thermal correction to Enthalpy= 0.082644
Thermal correction to Gibbs Free Energy= 0.046069
SCF Done: E(RM062X) = -360.161263945

$PhCO_2H$

C	-2.56208000	0.04189200	-0.00005700

C	-1.83716900	1.23283300	-0.00008600
C	-0.44583500	1.20204000	0.00005100
C	0.21782300	-0.02760900	0.00021200
C	-0.50884600	-1.22077500	0.00019800
C	-1.89829000	-1.18517100	-0.00002200
H	-3.64769800	0.06963700	-0.00012400
H	-2.35587300	2.18630700	-0.00037300
H	0.12409700	2.12490400	-0.00024700
H	0.02728500	-2.16440100	0.00013500
H	-2.46453700	-2.11118400	0.00001000
C	1.70291200	-0.11756100	0.00012700
O	2.32673500	-1.15559500	-0.00030800
O	2.30309000	1.08267400	0.00002000
H	3.26704500	0.92421400	0.00036300

Zero-point correction= 0.110813 (Hartree/Particle)
Thermal correction to Energy= 0.118186
Thermal correction to Enthalpy= 0.119130
Thermal correction to Gibbs Free Energy= 0.078662
SCF Done: E(RM062X) = -420.787251524

Benzoate ($PhCOO^-$)

C	2.52843100	0.00001500	-0.00001000
C	1.82743400	1.20609500	-0.02099800
C	0.43388300	1.20145800	-0.01802500
C	-0.27766600	-0.00000200	0.00000100
C	0.43390500	-1.20147800	0.01804000
C	1.82743000	-1.20609200	0.02099900
H	3.61508200	-0.00000200	-0.00001300
H	2.36948700	2.14811600	-0.03945300
H	-0.13196700	2.12806100	-0.03164100
H	-0.13196400	-2.12806700	0.03169000
H	2.36952900	-2.14808700	0.03944900
C	-1.81977600	0.00000600	0.00000200
O	-2.36324800	-1.12698100	-0.04815100
O	-2.36325300	1.12697700	0.04814100

Zero-point correction= 0.098485 (Hartree/Particle)
Thermal correction to Energy= 0.105577
Thermal correction to Enthalpy= 0.106521
Thermal correction to Gibbs Free Energy= 0.066607
SCF Done: E(RM062X) = -420.310061800

IM6a

C	-0.32540000	1.68165900	0.23520700

C	-0.50405900	0.78157400	1.28846900
C	-1.69178500	0.73754600	2.02284400
C	-2.68087100	1.63236000	1.65168800
C	-2.49856900	2.54036200	0.58786800
C	-1.32237300	2.58312600	-0.14121700
H	-1.84009000	0.02813100	2.82929300
H	-3.62654400	1.62477800	2.18319700
H	-3.30795000	3.21357200	0.32565400
H	-1.19114500	3.26479800	-0.97377800
N	0.66066200	0.02853900	1.37290000
N	0.93793900	1.43890200	-0.29038200
C	0.83311000	-1.17984900	2.16746900
H	0.75795300	-2.03891600	1.49643600
H	1.79814500	-1.15706200	2.67528300
C	1.47018600	2.04364600	-1.50698900
H	2.54356800	2.20083300	-1.39946100
H	1.23196700	1.37604300	-2.33801100
C	1.47182900	0.42751900	0.39182100
H	0.98627200	3.00992400	-1.64369900
H	0.04134200	-1.21281900	2.91411600
I	3.31996600	-0.43182700	-0.01830600
O	0.13546000	-1.54616700	-0.93057300
C	-0.74977300	-0.85033300	-1.48904400
C	-2.17857200	-1.02693100	-0.95956600
O	-0.59667000	-0.00830400	-2.40469300
C	-2.45838000	-1.97334100	0.02964400
C	-3.21205400	-0.21565200	-1.42975000
C	-3.74598600	-2.10423200	0.54465000
H	-1.64603000	-2.59976100	0.38648700
C	-4.50245600	-0.33795600	-0.91595400
H	-2.97901700	0.51558700	-2.19757900
C	-4.77138500	-1.28173300	0.07495600
H	-3.95330700	-2.84442500	1.31284100
H	-5.29875000	0.30252200	-1.28562900
H	-5.77589900	-1.37926100	0.47696800

Zero-point correction= 0.269690 (Hartree/Particle)
Thermal correction to Energy= 0.290070
Thermal correction to Enthalpy= 0.291014
Thermal correction to Gibbs Free Energy= 0.217717
SCF Done: E(RM062X) = -1176.23074033

TS3a

C	-1.86395200	1.57706200	0.63195500

C	-1.95163400	1.49498100	-0.75970200
C	-2.35439900	2.58031800	-1.52987500
C	-2.65677000	3.75401800	-0.84509100
C	-2.55726500	3.83796200	0.55173600
C	-2.15488100	2.74877100	1.31885000
H	-2.43040100	2.51917500	-2.60990000
H	-2.97497800	4.62513100	-1.40815400
H	-2.79698600	4.77349000	1.04616200
H	-2.06801300	2.81082000	2.39817400
N	-1.57736500	0.19671900	-1.10307900
N	-1.46004800	0.32589200	1.09009300
C	-1.41347100	-0.32594200	-2.44982100
H	-0.46757600	-0.86816500	-2.49939200
H	-2.24596800	-0.98104700	-2.71815800
C	-0.95516300	0.09864100	2.43210100
H	-0.79626100	-0.96782000	2.58930500
H	-0.00902900	0.63714900	2.53813200
C	-1.22404800	-0.45086100	0.01927100
H	-1.68602100	0.46358300	3.15530000
H	-1.37523600	0.51458100	-3.14248600
I	-1.30351200	-2.57028600	0.12032800
O	0.92231800	-0.57134900	-0.14307500
C	1.54126200	0.52140300	0.07640300
C	3.05898700	0.43957100	-0.01708800
O	1.02932700	1.61574300	0.35943500
C	3.69995700	-0.76060500	-0.33081700
C	3.82382500	1.58368500	0.21835500
C	5.08980700	-0.81647600	-0.40967600
H	3.09552200	-1.64363500	-0.51201900
C	5.21313500	1.53136300	0.14080500
H	3.30921100	2.50800100	0.46084400
C	5.84854900	0.32966700	-0.17292600
H	5.58281600	-1.75298900	-0.65415400
H	5.80197700	2.42525300	0.32544800
H	6.93217600	0.28683200	-0.23332800

Zero-point correction= 0.268922 (Hartree/Particle)
Thermal correction to Energy= 0.288773
Thermal correction to Enthalpy= 0.289718
Thermal correction to Gibbs Free Energy= 0.217761
SCF Done: E(RM062X) = -1176.21650711

Iodide (I^-)

I	0.00000000	0.00000000	0.00000000

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016848
SCF Done: E(RM062X) = -297.804510770

IM7a

C	-2.68189500	-0.64513000	-0.23361500
C	-2.76360600	0.71958200	0.06160700
C	-3.97936300	1.34311800	0.33285100
C	-5.10504900	0.53338700	0.29733700
C	-5.02223900	-0.84122300	0.00368400
C	-3.81081400	-1.46069900	-0.26675800
H	-4.03644300	2.40177700	0.56128500
H	-6.07616500	0.97073800	0.50311400
H	-5.93148700	-1.43259500	-0.00943100
H	-3.74159300	-2.51994800	-0.48910900
N	-1.46415100	1.21775300	0.02282200
N	-1.33746700	-0.92720000	-0.45873200
C	-1.06380800	2.59615500	0.28998100
H	0.01588300	2.67451600	0.17098100
H	-1.56409800	3.25470600	-0.42134500
C	-0.77949200	-2.22898200	-0.80899700
H	-1.44475500	-2.69639900	-1.53515300
H	0.20119800	-2.08537400	-1.26319600
C	-0.65711400	0.20494700	-0.28789400
H	-0.69672100	-2.84651200	0.08655100
H	-1.34610800	2.85452800	1.31156400
O	0.65519500	0.34501400	-0.45331700
C	1.48733800	-0.31976600	0.48115800
O	0.99889900	-0.95386100	1.36900400
C	2.90851800	-0.10345400	0.18091700
C	3.83500100	-0.69001800	1.05105100
C	3.33382800	0.64924300	-0.91919000
C	5.19303400	-0.52120200	0.81806900
H	3.48083100	-1.26977900	1.89741500
C	4.69580400	0.81092900	-1.14377100
H	2.61165100	1.10008000	-1.59083600
C	5.62141700	0.22850700	-0.27813900
H	5.91720700	-0.97214700	1.48830400
H	5.03595700	1.39177700	-1.99458100
H	6.68387100	0.35918100	-0.45943500

Zero-point correction= 0.271225 (Hartree/Particle)

Thermal correction to Energy= 0.289029
Thermal correction to Enthalpy= 0.289973
Thermal correction to Gibbs Free Energy= 0.224356
SCF Done: E(RM062X) = -878.450724441

$BnNH_2$

C	2.31536800	0.31245200	-0.06801100
C	1.38632200	1.34383700	0.05255500
C	0.02467700	1.05746200	0.13913800
C	-0.42776200	-0.26364600	0.10380100
C	0.51131400	-1.29157100	-0.02514100
C	1.87262300	-1.00913000	-0.10561200
H	3.37594900	0.53600100	-0.13597900
H	1.72167100	2.37684400	0.07912900
H	-0.70147000	1.85905600	0.23047600
H	0.16962100	-2.32370400	-0.06465900
H	2.58787200	-1.82063000	-0.20515900
C	-1.90008400	-0.59690900	0.22955700
H	-2.13170500	-0.77945800	1.28645900
H	-2.08687000	-1.54621700	-0.29568400
N	-2.75127100	0.50365900	-0.22170700
H	-2.64570700	0.60952900	-1.23011900
H	-3.72521300	0.24799500	-0.07023800

Zero-point correction= 0.140015 (Hartree/Particle)
Thermal correction to Energy= 0.147472
Thermal correction to Enthalpy= 0.148416
Thermal correction to Gibbs Free Energy= 0.107701
SCF Done: E(RM062X) = -326.862309793

TS4a

C	0.16524200	1.44271500	-0.56785400
O	-0.44783900	1.46458800	-1.60751400
N	1.46872400	-0.07978000	-0.77814500
H	0.87392500	-0.88637800	-0.98556800
H	1.96272300	0.14300300	-1.64486900
C	1.11886900	2.48261400	-0.07894000
C	1.45468400	2.63211300	1.26825600
C	2.36214700	3.61995600	1.64323600
C	2.93217000	4.45072400	0.68040700
C	2.59252800	4.29952600	-0.66388300
C	1.68486100	3.31717400	-1.04513100
H	1.00795800	1.98861600	2.01850400
H	2.62172700	3.74107100	2.69021600

H	3.63900300	5.21910900	0.97805900
H	3.03131100	4.95010100	-1.41377300
H	1.40324900	3.19159700	-2.08618700
C	2.42402600	-0.39688000	0.29728300
H	3.14929500	0.42090600	0.33446500
H	1.87309600	-0.39492500	1.24376500
C	3.11340300	-1.72618200	0.09516500
C	2.75060400	-2.83893100	0.85625500
C	4.09394700	-1.86729900	-0.89228200
C	3.35966900	-4.07449700	0.63868900
H	1.99263100	-2.73422900	1.62980500
C	4.70171900	-3.09948200	-1.11283400
H	4.38387000	-1.00274400	-1.48597100
C	4.33483800	-4.20663100	-0.34679300
H	3.07371500	-4.93186300	1.24068800
H	5.46568300	-3.19665900	-1.87841500
H	4.81192400	-5.16716700	-0.51604100
C	-3.26438200	-1.25093100	0.23719100
C	-3.80985200	-0.00325400	-0.08284600
C	-5.15088500	0.14494100	-0.42645700
C	-5.91824200	-1.01205700	-0.43192600
C	-5.36961200	-2.26654300	-0.10915600
C	-4.03216400	-2.41250500	0.23359000
H	-5.56862200	1.11383500	-0.67773100
H	-6.96880300	-0.94710300	-0.69446300
H	-6.00819700	-3.14321500	-0.13001200
H	-3.60250100	-3.37763200	0.47973600
N	-2.78101100	0.92609000	0.03052400
N	-1.92062000	-1.03757300	0.52520100
C	-2.89970900	2.36248100	-0.18846800
H	-2.05164100	2.86096400	0.28106500
H	-2.91031000	2.57359600	-1.25833700
C	-0.96286700	-2.05704100	0.93399500
H	-0.70906600	-2.69061600	0.08148800
H	-0.07183000	-1.56155300	1.31851100
C	-1.67107200	0.27108400	0.38670000
H	-1.41155200	-2.65839800	1.72636300
H	-3.82412900	2.70249300	0.28021900
O	-0.50124200	0.81784500	0.61754500

Zero-point correction= 0.413731 (Hartree/Particle)
Thermal correction to Energy= 0.438911
Thermal correction to Enthalpy= 0.439855
Thermal correction to Gibbs Free Energy= 0.357700

SCF Done: E(RM062X) = -1205.31585592

1,3-dimethylbenzididazol-2-one

C	0.46578200	-0.70332600	-0.00001200
C	0.46578200	0.70332600	-0.00001200
C	1.64846500	1.42590100	0.00002000
C	2.84371500	0.69815900	0.00005500
C	2.84371500	-0.69815900	0.00005600
C	1.64846500	-1.42590100	0.00002100
H	1.64459100	2.51145100	0.00002600
H	3.78812600	1.23303000	0.00008500
H	3.78812600	-1.23303000	0.00008500
H	1.64459100	-2.51145100	0.00002600
N	-0.85943200	1.10622900	-0.00005300
N	-0.85943200	-1.10622900	-0.00005300
C	-1.33613800	2.47027300	0.00000700
H	-2.42632000	2.43874400	-0.00013700
H	-0.98853200	2.99843700	0.89255800
C	-1.33613800	-2.47027300	0.00000800
H	-0.98853400	-2.99843600	0.89256000
H	-2.42632000	-2.43874400	-0.00013800
C	-1.69363900	0.00000000	-0.00002800
H	-0.98829800	-2.99858300	-0.89236400
H	-0.98829900	2.99858200	-0.89236500
O	-2.91589200	0.00000000	-0.00003500

Zero-point correction= 0.172009 (Hartree/Particle)
Thermal correction to Energy= 0.182793
Thermal correction to Enthalpy= 0.183737
Thermal correction to Gibbs Free Energy= 0.136033
SCF Done: E(RM062X) = -533.686663384

IM8a

C	-0.92917900	-1.76321200	-0.02370300
C	-1.53465400	-0.43561400	-0.19400100
O	-1.25569300	-2.61208400	0.75432200
C	-1.02114500	0.56435700	-1.03140900
C	-2.67725900	-0.18715600	0.58241200
C	-1.64998600	1.80227700	-1.08341100
H	-0.12717200	0.41780400	-1.62918400
C	-3.30142000	1.04930100	0.51809000
H	-3.06093900	-0.97011900	1.22811300
C	-2.78670900	2.04447700	-0.31374300
H	-1.24803400	2.57963800	-1.72429900

H	-4.18577700	1.24053800	1.11655100
H	-3.27243100	3.01411800	-0.36030900
N	0.25845200	-2.12934100	-0.89249200
C	1.58420000	-2.03959000	-0.14181900
H	0.11316600	-3.11041700	-1.17207300
H	0.31353900	-1.58216100	-1.76146400
C	1.92616400	-0.60504800	0.13276900
H	1.44846400	-2.62906800	0.76615500
H	2.31323700	-2.52540900	-0.79142300
C	2.59156300	0.14661700	-0.83944500
C	1.52273600	0.00185900	1.32410300
C	2.83976600	1.49973800	-0.62618100
H	2.91484100	-0.33111600	-1.76151900
C	1.77278300	1.35500100	1.53740400
H	1.00744800	-0.58684300	2.08012700
C	2.42677000	2.10407200	0.56093800
H	3.35882600	2.08055200	-1.38213300
H	1.45758700	1.82317800	2.46441400
H	2.62183600	3.15889600	0.72788900

Zero-point correction= 0.241645 (Hartree/Particle)
Thermal correction to Energy= 0.255139
Thermal correction to Enthalpy= 0.256083
Thermal correction to Gibbs Free Energy= 0.200705
SCF Done: E(RM062X) = -671.646509686

DABCO-H$^+$

C	0.80677800	0.17135000	1.36989500
C	-0.73414700	0.02847900	1.42079800
H	1.26997400	-0.57414600	2.01991400
H	1.11070300	1.16328100	1.71215800
H	-1.06010600	-0.90985700	1.87251100
H	-1.22669300	0.86353700	1.92024100
C	0.79510800	-1.28265800	-0.52814400
H	1.26639800	-1.47770800	-1.49387200
H	1.08144100	-2.07998500	0.16200600
C	-0.74420300	-1.23534400	-0.69357600
H	-1.05975100	-1.15509900	-1.73481900
H	-1.25170200	-2.07782600	-0.22280300
C	-0.71730700	1.22877400	-0.73085800
H	-1.21414000	1.25228900	-1.70147800
H	-1.02635200	2.09408100	-0.14238600
C	0.82099700	1.08734300	-0.83761700
H	1.11507300	0.88240400	-1.86978000

H	1.30259800	2.01486900	-0.52014300
N	-1.21718700	0.01235500	-0.00245300
N	1.29872200	-0.01337700	0.00247500
H	-2.24155100	0.02364800	-0.00468300

Zero-point correction= 0.190947 (Hartree/Particle)
Thermal correction to Energy= 0.197724
Thermal correction to Enthalpy= 0.198668
Thermal correction to Gibbs Free Energy= 0.159775
SCF Done: E(RM062X) = -345.744102875

4aa

C	-0.88446900	-0.95087400	-0.00128000
C	-2.18274700	-0.19339500	-0.02679500
O	-0.67546700	-1.82360100	0.83804000
C	-2.29862000	1.10002100	-0.54323900
C	-3.30196400	-0.81744900	0.52975500
C	-3.52871700	1.75277500	-0.51938900
H	-1.42971400	1.61920100	-0.93807500
C	-4.53194400	-0.16855600	0.54334200
H	-3.19118800	-1.81377600	0.94585300
C	-4.64705000	1.11788200	0.01710700
H	-3.61052000	2.76121300	-0.91300600
H	-5.40027700	-0.66314900	0.96777000
H	-5.60566900	1.62764400	0.03200100
N	0.01955100	-0.62243400	-0.95433300
C	1.32902700	-1.24989900	-1.03043700
C	2.41960800	-0.41965200	-0.38552300
H	1.24456500	-2.21671200	-0.52718700
H	1.56732000	-1.43189100	-2.08162700
C	3.54339100	-0.02380300	-1.10951300
C	2.30744100	-0.04466100	0.95795800
C	4.54610400	0.73451200	-0.50385800
H	3.63428600	-0.30946900	-2.15489900
C	3.30418100	0.71378200	1.56310100
H	1.43482400	-0.35919900	1.52608300
C	4.42767100	1.10543800	0.83255200
H	5.41636500	1.03706500	-1.07895100
H	3.20884200	0.99758400	2.60718000
H	5.20593100	1.69672700	1.30578200
H	-0.21935800	0.06389300	-1.65759500

Zero-point correction= 0.227503 (Hartree/Particle)
Thermal correction to Energy= 0.241415
Thermal correction to Enthalpy= 0.242359

Thermal correction to Gibbs Free Energy= 0.183423
SCF Done: E(RM062X) = -671.232032264

11.2 $K_2S_2O_8$-3a-DABCO system

3a

C	-2.57713100	0.68667500	-0.00010200
C	-2.44457900	-0.70647600	-0.00011200
C	-3.55358500	-1.55246900	-0.00020700
C	-4.79569500	-0.93699000	-0.00029200
C	-4.92959700	0.46629100	-0.00028700
C	-3.82686500	1.30667100	-0.00019100
H	-3.44412600	-2.63149400	-0.00021000
H	-5.69009300	-1.55079200	-0.00036500
H	-5.92400300	0.89955900	-0.00035700
H	-3.92643200	2.38656700	-0.00018500
N	-1.08154900	-0.97218900	-0.00000800
N	-1.28737500	1.20396500	0.00002000
C	-0.46903200	-2.29619200	0.00002100
H	0.61453800	-2.17271500	0.00006100
H	-0.78108600	-2.83691600	0.89499100
C	-0.93459900	2.61967000	0.00008000
H	-1.34330000	3.09205800	0.89475400
H	0.15220600	2.70323700	0.00018900
C	-0.42967500	0.18699500	0.00007300
H	-1.34312400	3.09209200	-0.89465600
H	-0.78101600	-2.83691700	-0.89497300
H	0.65414900	0.28193100	0.00016400
I	3.43696800	-0.01309600	0.00012500

Zero-point correction= 0.190632 (Hartree/Particle)
Thermal correction to Energy= 0.202528
Thermal correction to Enthalpy= 0.203472
Thermal correction to Gibbs Free Energy= 0.148913
SCF Done: E(RM062X) = -756.700062140

$K_2S_2O_8$

O	-2.73222000	0.46609300	-1.08165100
S	-1.86956600	0.63007000	0.10208300
O	-1.50433700	1.98284400	0.46984800
O	-2.29496500	-0.24129200	1.21353300
O	-0.49312700	-0.11546900	-0.51523400
O	0.49347200	-0.11518700	0.51563800
S	1.86977000	0.63034500	-0.10204900

O	1.50444300	1.98308800	-0.46983500
O	2.73267300	0.46647500	1.08151200
O	2.29487500	-0.24110700	-1.21353500
K	4.27339800	-1.41211300	0.06521500
K	-4.27391400	-1.41158200	-0.06535900

Zero-point correction= 0.037004 (Hartree/Particle)
Thermal correction to Energy= 0.050181
Thermal correction to Enthalpy= 0.051125
Thermal correction to Gibbs Free Energy= -0.006873
SCF Done: E(RM062X) = -2597.97706329

TS1b

O	-4.98306500	1.91799000	0.15093300
S	-3.85430600	1.24538600	-0.50210200
O	-4.25207800	0.14263200	-1.40487700
O	-2.87251000	2.16968500	-1.10777800
O	-3.11062000	0.54183300	0.74447700
O	-1.62444200	-0.29798500	0.02984900
S	-1.06819500	-0.99874300	1.50205100
O	-0.11162900	-2.03393600	1.11555000
O	-0.46040300	0.15880100	2.18560200
O	-2.27840600	-1.54468800	2.12139200
K	-3.85086200	-1.97754000	0.01748300
I	0.26843600	-0.39455300	-1.67093900
K	-0.85839600	2.21508900	0.49545200
H	1.67594100	-1.05600100	1.96404100
C	2.52062600	-0.65942400	1.41798900
N	3.00417900	0.57427400	1.54980100
N	3.19008600	-1.32354900	0.48190000
C	4.04699900	0.73255100	0.64587300
C	2.53852000	1.57547600	2.50098700
C	4.16444700	-0.48277200	-0.03790000
C	2.90109500	-2.67869200	0.02874600
C	4.87681100	1.81839800	0.36726300
H	1.61037100	1.21838000	2.94763100
H	3.29413900	1.72666000	3.27439000
H	2.36996400	2.51620500	1.97222400
C	5.11822700	-0.67558800	-1.03750200
H	3.72270100	-3.33992000	0.31062600
H	1.96907600	-2.99933500	0.49283500
H	2.77978700	-2.66697100	-1.05585900
C	5.82344300	1.62827300	-0.62804900
H	4.78492800	2.75695200	0.90349200

C	5.94153500	0.40449400	-1.31768700
H	5.20632700	-1.61995400	-1.56369000
H	6.49232500	2.44307900	-0.88370600
H	6.69839600	0.30643500	-2.08858100

Zero-point correction= 0.227284 (Hartree/Particle)
Thermal correction to Energy= 0.252458
Thermal correction to Enthalpy= 0.253402
Thermal correction to Gibbs Free Energy= 0.168729
SCF Done: E(RM062X) = -3354.67730483

IM1b

C	-0.20396100	0.69917000	0.00000200
C	-0.20396100	-0.69917000	0.00000200
C	-1.38775600	-1.43724100	0.00002600
C	-2.56448700	-0.70522800	0.00005100
C	-2.56448700	0.70522800	0.00005100
C	-1.38775600	1.43724100	0.00002600
H	-1.38132900	-2.52215900	0.00002700
H	-3.51365400	-1.23041500	0.00007100
H	-3.51365400	1.23041500	0.00007100
H	-1.38132900	2.52215900	0.00002700
N	1.12811700	-1.09308500	-0.00002300
N	1.12811700	1.09308500	-0.00002300
C	1.60458900	-2.47140600	-0.00002900
H	2.69383000	-2.45909600	-0.00005300
H	1.23842900	-2.97764200	0.89445300
C	1.60458900	2.47140600	-0.00002900
H	1.23842900	2.97764200	0.89445400
H	2.69383000	2.45909600	-0.00005300
C	1.88467800	0.00000000	-0.00003800
H	1.23838900	2.97764800	-0.89449100
H	1.23838900	-2.97764800	-0.89449200
H	2.96635100	0.00000000	-0.00006000

Zero-point correction= 0.190975 (Hartree/Particle)
Thermal correction to Energy= 0.200122
Thermal correction to Enthalpy= 0.201067
Thermal correction to Gibbs Free Energy= 0.157193
SCF Done: E(RM062X) = -458.880777939

IM2b

O	-0.34353600	0.91787500	0.00001700
S	-1.70003500	-0.07318600	-0.00000100
O	-1.59835500	-0.85901200	-1.23145400

O	-1.59836600	-0.85905000	1.23142900
O	-2.72761300	0.96990500	0.00000900
I	1.45931200	-0.00352400	0.00000000

Zero-point correction= 0.017367 (Hartree/Particle)
Thermal correction to Energy= 0.023209
Thermal correction to Enthalpy= 0.024153
Thermal correction to Gibbs Free Energy= -0.014955
SCF Done: E(RM062X) = -996.766200845

K_2SO_4

O	0.88478800	0.55209400	-1.08456600
S	0.00000000	0.00005100	-0.00020500
O	0.88444200	-0.55215800	1.08435600
O	-0.88457300	1.08459200	0.55183100
O	-0.88465500	-1.08433200	-0.55242000
K	-3.12076900	-0.00006300	0.00025500
K	3.12076800	-0.00006200	0.00025400

Zero-point correction= 0.018053 (Hartree/Particle)
Thermal correction to Energy= 0.026040
Thermal correction to Enthalpy= 0.026984
Thermal correction to Gibbs Free Energy= -0.020193
SCF Done: E(RM062X) = -1899.05709157

DABCO

C	-0.77810600	0.66846400	-1.20524700
C	0.77810400	0.66846800	-1.20524600
H	-1.17537800	0.14076900	-2.07885300
H	-1.17569100	1.68887400	-1.22062100
H	1.17538000	0.14077000	-2.07884800
H	1.17568500	1.68888000	-1.22062500
C	-0.77813000	-1.37808100	0.02375000
H	-1.17571800	-1.87070100	0.91753100
H	-1.17573700	-1.90186200	-0.85218200
C	0.77814300	-1.37807400	0.02375700
H	1.17572800	-1.87068600	0.91754300
H	1.17576200	-1.90185500	-0.85217000
C	0.77809700	0.70961900	1.18145900
H	1.17582900	0.21287900	2.07294900
H	1.17549200	1.73006500	1.16105200
C	-0.77810800	0.70960900	1.18145800
H	-1.17583600	0.21285900	2.07294500
H	-1.17551700	1.73005000	1.16105500
N	1.28717800	0.00000100	0.00004800

N	-1.28717800	-0.00001100	0.00004300

Zero-point correction= 0.186516 (Hartree/Particle)
Thermal correction to Energy= 0.192767
Thermal correction to Enthalpy= 0.193711
Thermal correction to Gibbs Free Energy= 0.155933
SCF Done: E(RM062X) = -345.282368404

TS2b

C	2.83733800	0.69289400	-0.00234100
C	2.77843000	-0.70341300	-0.00530200
C	3.93150300	-1.48742700	0.00807500
C	5.14325900	-0.80901500	0.02555500
C	5.20281500	0.59716300	0.03033200
C	4.05284100	1.37593400	0.01643700
H	3.88178000	-2.57146700	0.00480000
H	6.06818000	-1.37638600	0.03636700
H	6.17246000	1.08399700	0.04508300
H	4.09670200	2.46017500	0.02075100
N	1.42779100	-1.02559400	-0.02310700
N	1.51891700	1.13055000	-0.02074800
C	0.91733100	-2.38598200	-0.02826500
H	-0.17219800	-2.34262600	-0.03505900
H	1.26751600	-2.91344200	-0.91875900
C	1.13588400	2.53255300	-0.02885900
H	1.53203200	3.02180600	-0.92188500
H	0.04800200	2.59295100	-0.03246400
C	0.66429500	0.08676800	-0.03376500
H	1.52584800	3.02968100	0.86250400
H	1.25571900	-2.91518800	0.86573100
H	-0.82609000	0.07162200	-0.03268700
C	-2.49862100	-0.68172400	1.20926200
C	-4.04906800	-0.62661600	1.26317700
H	-2.12140000	-1.70623100	1.14613200
H	-2.03138200	-0.18926800	2.06621500
H	-4.46373400	-1.63131700	1.38011900
H	-4.38517900	-0.01890900	2.10760400
C	-2.54438000	-0.68878300	-1.21784200
H	-2.21972200	-0.11796200	-2.09170800
H	-2.06119900	-1.66941900	-1.24076300
C	-4.09031000	-0.79542100	-1.11941000
H	-4.55954600	-0.40305100	-2.02544700
H	-4.39891200	-1.83760200	-0.99980500
C	-4.12712100	1.35056200	-0.07441000

H	-4.49204400	1.75829600	-1.02095600
H	-4.56903300	1.93088500	0.73981200
C	-2.57756500	1.41632500	-0.01032800
H	-2.14618100	1.93511500	-0.87081800
H	-2.21966200	1.89510400	0.90535800
N	-4.58702700	-0.03716000	0.03292000
N	-2.05135700	0.02796700	-0.01535400

Zero-point correction= 0.374537 (Hartree/Particle)
Thermal correction to Energy= 0.391378
Thermal correction to Enthalpy= 0.392322
Thermal correction to Gibbs Free Energy= 0.329095
SCF Done: E(RM062X) = -804.156106691

DABCO-H$^+$

C	0.81939100	-1.24181400	-0.59022900
C	-0.72427200	-1.23321100	-0.71900300
H	1.27438700	-1.37066800	-1.57473200
H	1.14378700	-2.06558900	0.04988500
H	-1.06583600	-1.14444500	-1.75146800
H	-1.19893100	-2.09667700	-0.25144900
C	0.79630900	1.14104100	-0.79019400
H	1.24580700	2.06264200	-0.41385500
H	1.10977100	1.00313100	-1.82757500
C	-0.74782400	1.23131800	-0.69945100
H	-1.09250600	2.07741300	-0.10259200
H	-1.23478500	1.25221800	-1.67511200
C	-0.72896200	-0.01708300	1.42515800
H	-1.21696500	0.81319400	1.93697800
H	-1.05827500	-0.95972500	1.86505100
C	0.81332500	0.12205400	1.37294800
H	1.12251300	1.09214300	1.76905800
H	1.27829300	-0.66063300	1.97643800
N	-1.21712000	-0.01114700	0.00386400
N	1.29804700	0.01179800	-0.00434000
H	-2.24155300	-0.02138700	0.00734200

Zero-point correction= 0.201648 (Hartree/Particle)
Thermal correction to Energy= 0.208042
Thermal correction to Enthalpy= 0.208986
Thermal correction to Gibbs Free Energy= 0.171001
SCF Done: E(RM062X) = -345.743561760

IM3b (NHC)

C	0.00000000	-0.16302600	0.69957800

C	0.00000000	-0.16302600	-0.69957800
C	0.00000000	-1.34953600	-1.42972600
C	0.00000000	-2.53655700	-0.70235600
C	0.00000000	-2.53655700	0.70235600
C	0.00000000	-1.34953600	1.42972600
H	0.00000000	-1.34758000	-2.51540900
H	0.00000000	-3.48399400	-1.23212700
H	0.00000000	-3.48399400	1.23212700
H	0.00000000	-1.34758000	2.51540900
N	0.00000000	1.17439000	-1.07108200
N	0.00000000	1.17439000	1.07108200
C	0.00000000	1.60987000	-2.45384700
H	0.00000000	2.69937700	-2.46381100
H	0.89082000	1.24090500	-2.97060200
C	0.00000000	1.60987000	2.45384700
H	0.89082000	1.24090500	2.97060200
H	0.00000000	2.69937700	2.46381100
C	0.00000000	2.02171900	0.00000000
H	-0.89082000	1.24090500	2.97060200
H	-0.89082000	1.24090500	-2.97060200

Zero-point correction= 0.176714 (Hartree/Particle)
Thermal correction to Energy= 0.185896
Thermal correction to Enthalpy= 0.186840
Thermal correction to Gibbs Free Energy= 0.142775
SCF Done: E(RM062X) = -458.397915591

IM4b

O	-3.19207300	-0.67234100	-0.51212700
S	-4.24271100	0.23684600	0.20641900
O	-3.49148300	1.23122000	1.01840300
O	-5.04799700	0.88967300	-0.85941800
O	-5.07323800	-0.65577700	1.05693200
I	-0.93605300	-0.32598700	-0.23712900
C	1.27252100	-0.10941300	-0.07967900
N	2.16738100	-1.11002500	0.01481100
N	1.95088500	1.05221500	-0.06990700
C	3.45246400	-0.58685200	0.08630800
C	1.88822800	-2.53847400	0.05190200
C	3.31333600	0.80078700	0.02887500
C	1.39610500	2.39611700	-0.15454700
C	4.70166500	-1.19710300	0.18947500
H	0.81595400	-2.69711400	-0.04805200
H	2.40767500	-3.02925600	-0.77380600

H	2.23047600	-2.95072000	1.00348200
C	4.41578300	1.65318200	0.07073200
H	1.75829700	2.88170700	-1.06322500
H	0.30951000	2.33575000	-0.18033100
H	1.70671400	2.96870800	0.72185600
C	5.80180900	-0.35083600	0.23141500
H	4.80629900	-2.27583600	0.23377900
C	5.66152500	1.04841400	0.17273600
H	4.30334200	2.73111400	0.02487500
H	6.79556800	-0.77876700	0.31054000
H	6.55021700	1.66973300	0.20805500

Zero-point correction= 0.196216 (Hartree/Particle)
Thermal correction to Energy= 0.213177
Thermal correction to Enthalpy= 0.214121
Thermal correction to Gibbs Free Energy= 0.148258
SCF Done: E(RM062X) = -1455.21301855

Sulfate (SO_4^{2-})

O	1.38448300	0.14767800	-0.57275600
S	0.00014500	-0.00009300	-0.00010000
O	-0.22315200	1.05440800	1.05056400
O	-1.01782600	0.16245500	-1.09690500
O	-0.14379500	-1.36435500	0.61929700

Zero-point correction= 0.016094 (Hartree/Particle)
Thermal correction to Energy= 0.020071
Thermal correction to Enthalpy= 0.021015
Thermal correction to Gibbs Free Energy= -0.011360
SCF Done: E(RM062X) = -699.273522785

IM5a

C	0.01295800	1.78557400	0.69919300
C	0.01295800	1.78557400	-0.69919300
C	-0.00554000	2.97280700	-1.43535100
C	-0.02237500	4.14837800	-0.70513200
C	-0.02237500	4.14837800	0.70513200
C	-0.00554000	2.97280700	1.43535100
H	-0.01436600	2.97514800	-2.51936600
H	-0.03995100	5.09630600	-1.23179700
H	-0.03995100	5.09630600	1.23179700
H	-0.01436600	2.97514800	2.51936600
N	0.02759400	0.45278000	-1.09946200
N	0.02759400	0.45278000	1.09946200
C	0.01667500	-0.02969600	-2.47951300

H	0.78794600	-0.79039000	-2.60391600
H	-0.96702300	-0.43629600	-2.72147000
C	0.01667500	-0.02969600	2.47951300
H	-0.96702300	-0.43629600	2.72147000
H	0.78794600	-0.79039000	2.60391600
C	0.02812500	-0.30381300	0.00000000
H	0.24277900	0.81012700	3.13369200
H	0.24277900	0.81012700	-3.13369200
I	-0.01121600	-2.38397300	0.00000000

Zero-point correction= 0.180088 (Hartree/Particle)
Thermal correction to Energy= 0.191032
Thermal correction to Enthalpy= 0.191976
Thermal correction to Gibbs Free Energy= 0.142006
SCF Done: E(RM062X) = -755.894899587

$PhCO_2H$

C	-2.56205300	-0.04204800	0.00010200
C	-1.83683700	-1.23292000	0.00013200
C	-0.44562700	-1.20184700	0.00007400
C	0.21785600	0.02791100	-0.00001200
C	-0.50894200	1.22082800	-0.00004200
C	-1.89852100	1.18501700	0.00001400
H	-3.64769200	-0.07004500	0.00014700
H	-2.35533800	-2.18652500	0.00020200
H	0.12475800	-2.12448300	0.00009800
H	0.02693900	2.16459800	-0.00011100
H	-2.46479200	2.11103100	-0.00001100
C	1.70298800	0.11775700	-0.00007000
O	2.32689500	1.15539300	-0.00013000
O	2.30265200	-1.08266100	-0.00004700
H	3.26656300	-0.92462100	-0.00008700

Zero-point correction= 0.117015 (Hartree/Particle)
Thermal correction to Energy= 0.124065
Thermal correction to Enthalpy= 0.125009
Thermal correction to Gibbs Free Energy= 0.085092
SCF Done: E(RM062X) = -420.787966894

Benzoate ($PhCOO^-$)

C	-2.52848900	0.00000000	-0.00000400
C	-1.82744500	-1.20606000	-0.02096900
C	-0.43390200	-1.20140300	-0.01794100
C	0.27768700	0.00000000	0.00000100
C	-0.43390200	1.20140300	0.01794000

C	-1.82744500	1.20606000	0.02096300
H	-3.61519600	0.00000000	-0.00000600
H	-2.36944500	-2.14817300	-0.03951000
H	0.13223800	-2.12784500	-0.03156600
H	0.13223800	2.12784600	0.03156700
H	-2.36944600	2.14817300	0.03950200
C	1.82017400	0.00000000	0.00000300
O	2.36309600	1.12699900	-0.04793200
O	2.36309600	-1.12699900	0.04794000

Zero-point correction= 0.103982 (Hartree/Particle)
Thermal correction to Energy= 0.110771
Thermal correction to Enthalpy= 0.111715
Thermal correction to Gibbs Free Energy= 0.072330
SCF Done: E(RM062X) = -420.309542506

TS3b

C	1.86081700	1.58050700	-0.63082000
C	1.94991400	1.49795200	0.76069300
C	2.34879600	2.58464600	1.53113400
C	2.64597800	3.75981400	0.84679600
C	2.54532200	3.84406600	-0.54999100
C	2.14693300	2.75371000	-1.31733500
H	2.42560900	2.52361600	2.61111300
H	2.96073700	4.63200800	1.41016000
H	2.78080200	4.78086700	-1.04407500
H	2.05880900	2.81617800	-2.39653800
N	1.58111900	0.19790700	1.10354800
N	1.46134600	0.32806400	-1.08941800
C	1.41733900	-0.32566000	2.45006800
H	0.47067800	-0.86662700	2.49948500
H	2.24924200	-0.98195300	2.71740800
C	0.95533800	0.10022700	-2.43104300
H	0.79603900	-0.96627900	-2.58741500
H	0.00915300	0.63889500	-2.53567700
C	1.22955900	-0.45011200	-0.01898100
H	1.68562800	0.46468200	-3.15509700
H	1.38046900	0.51442800	3.14333600
I	1.30876900	-2.56873400	-0.12110600
O	-0.92219000	-0.57291700	0.14805900
C	-1.54268100	0.51730200	-0.07799800
C	-3.06044400	0.43473500	0.01696700
O	-1.03248600	1.61054400	-0.36909800
C	-3.70046700	-0.76528200	0.33318800

C	-3.82621700	1.57780100	-0.22056000
C	-5.09030600	-0.82212100	0.41221900
H	-3.09506300	-1.64734600	0.51603700
C	-5.21546700	1.52462100	-0.14251000
H	-3.31210900	2.50192900	-0.46488700
C	-5.84997600	0.32297800	0.17329200
H	-5.58261600	-1.75862500	0.65830900
H	-5.80500800	2.41779100	-0.32864400
H	-6.93360800	0.27940800	0.23377800

Zero-point correction= 0.283980 (Hartree/Particle)
Thermal correction to Energy= 0.303020
Thermal correction to Enthalpy= 0.303964
Thermal correction to Gibbs Free Energy= 0.233797
SCF Done: E(RM062X) = -1176.21821750

Iodide (I^-)

I	0.00000000	0.00000000	0.00000000

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016848
SCF Done: E(RM062X) = -297.803692692

IM6b

C	-0.31869100	1.67857600	0.24335100
C	-0.49454600	0.77663300	1.29541300
C	-1.68075600	0.73065100	2.03205100
C	-2.67107200	1.62569700	1.66483200
C	-2.49151300	2.53559100	0.60227200
C	-1.31699300	2.57994300	-0.12945600
H	-1.82738500	0.01896100	2.83680600
H	-3.61586900	1.61601700	2.19786400
H	-3.30204500	3.20843100	0.34262000
H	-1.18844600	3.26204100	-0.96208800
N	0.67094200	0.02420900	1.37616100
N	0.94327900	1.43679900	-0.28618900
C	0.84407500	-1.18702700	2.16615200
H	0.75839700	-2.04418700	1.49386200
H	1.81384500	-1.17072800	2.66509000
C	1.47032200	2.04171200	-1.50510100
H	2.54511700	2.19356000	-1.40436700
H	1.22264700	1.37691500	-2.33574200
C	1.47868100	0.42390200	0.39248700

H	0.98997500	3.01057800	-1.63632700
H	0.05914600	-1.21760800	2.92012600
I	3.32491300	-0.43646400	-0.02489000
O	0.12455400	-1.52357300	-0.93332000
C	-0.76401900	-0.83111000	-1.49086900
C	-2.19203800	-1.01581700	-0.96210700
O	-0.61463000	0.01414900	-2.40401000
C	-2.46858800	-1.97073700	0.01977700
C	-3.22803300	-0.20362800	-1.42507400
C	-3.75554200	-2.10966900	0.53430400
H	-1.65434300	-2.59811100	0.37052100
C	-4.51763600	-0.33349900	-0.91125100
H	-2.99759000	0.53392700	-2.18763900
C	-4.78346000	-1.28615200	0.07200400
H	-3.96038800	-2.85710400	1.29617600
H	-5.31600100	0.30770300	-1.27527100
H	-5.78754000	-1.38986900	0.47364300

Zero-point correction= 0.284872 (Hartree/Particle)
Thermal correction to Energy= 0.304389
Thermal correction to Enthalpy= 0.305333
Thermal correction to Gibbs Free Energy= 0.234189
SCF Done: E(RM062X) = -1176.23183226

IM7b

C	-2.68177200	-0.64519900	-0.23381700
C	-2.76403900	0.71944600	0.06160300
C	-3.98016800	1.34234200	0.33285900
C	-5.10548300	0.53206100	0.29734000
C	-5.02205600	-0.84246800	0.00353700
C	-3.81032300	-1.46134100	-0.26696500
H	-4.03805400	2.40091500	0.56153500
H	-6.07680900	0.96892700	0.50322100
H	-5.93105000	-1.43425600	-0.00957900
H	-3.74087500	-2.52059500	-0.48931100
N	-1.46461800	1.21811300	0.02294700
N	-1.33715300	-0.92669300	-0.45906500
C	-1.06453200	2.59668700	0.29008900
H	0.01528900	2.67501900	0.17205800
H	-1.56396200	3.25519000	-0.42195900
C	-0.77886200	-2.22835600	-0.80946800
H	-1.44427400	-2.69600900	-1.53535600
H	0.20156800	-2.08446200	-1.26418600
C	-0.65706700	0.20561800	-0.28790200

H	-0.69535700	-2.84579000	0.08611000
H	-1.34776900	2.85546300	1.31134600
O	0.65513800	0.34613600	-0.45319500
C	1.48756700	-0.31892500	0.48161500
O	0.99861200	-0.95259500	1.36938700
C	2.90869300	-0.10322800	0.18104800
C	3.83500500	-0.69114100	1.05053200
C	3.33421700	0.65020200	-0.91854200
C	5.19310500	-0.52294900	0.81741700
H	3.48050700	-1.27148200	1.89638700
C	4.69623800	0.81141100	-1.14312700
H	2.61212200	1.10193400	-1.58970600
C	5.62165500	0.22767400	-0.27812300
H	5.91716700	-0.97500200	1.48705100
H	5.03665900	1.39290600	-1.99341100
H	6.68416500	0.35796000	-0.45949100

Zero-point correction= 0.286413 (Hartree/Particle)
Thermal correction to Energy= 0.303423
Thermal correction to Enthalpy= 0.304367
Thermal correction to Gibbs Free Energy= 0.240394
SCF Done: E(RM062X) = -878.451609132

$BnNH_2$

C	-2.31524300	-0.31122500	-0.07022700
C	-1.38719400	-1.34328700	0.05318000
C	-0.02560600	-1.05787100	0.14230300
C	0.42792000	0.26294500	0.10683800
C	-0.51005800	1.29145500	-0.02464900
C	-1.87149500	1.00993500	-0.10780700
H	-3.37586200	-0.53408100	-0.14028800
H	-1.72338100	-2.37604700	0.07990200
H	0.70004100	-1.85975900	0.23531700
H	-0.16758800	2.32335300	-0.06427400
H	-2.58597000	1.82187900	-0.20953500
C	1.90057600	0.59395800	0.23512000
H	2.13371700	0.76364500	1.29387100
H	2.08764100	1.54914700	-0.27937200
N	2.75001700	-0.50232000	-0.22984900
H	2.64330900	-0.59684900	-1.23924600
H	3.72457800	-0.25051400	-0.07598100

Zero-point correction= 0.147830 (Hartree/Particle)
Thermal correction to Energy= 0.154976
Thermal correction to Enthalpy= 0.155921

Thermal correction to Gibbs Free Energy= 0.115578
SCF Done: E(RM062X) = -326.863190534

TS4b

C	-0.16750800	1.43656000	0.57072700
O	0.44566300	1.45576100	1.61042800
N	-1.47465600	-0.07674200	0.77854500
H	-0.88354400	-0.88511200	0.98972800
H	-1.96987300	0.14992100	1.64361700
C	-1.11269100	2.48333500	0.07952700
C	-1.44773600	2.63241400	-1.26796000
C	-2.34615200	3.62755900	-1.64528700
C	-2.90782800	4.46629400	-0.68439200
C	-2.56891200	4.31561800	0.66012900
C	-1.67030700	3.32581000	1.04373600
H	-1.00708900	1.98281900	-2.01657900
H	-2.60507700	3.74828900	-2.69249900
H	-3.60745300	5.24058200	-0.98384700
H	-3.00100500	4.97257400	1.40836000
H	-1.38887800	3.20067900	2.08491500
C	-2.42864600	-0.39332200	-0.29858800
H	-3.15163300	0.42631200	-0.33899400
H	-1.87528900	-0.39422500	-1.24364800
C	-3.12118900	-1.72086300	-0.09562700
C	-2.75998600	-2.83496900	-0.85549500
C	-4.10282900	-1.85925100	0.89112600
C	-3.37185100	-4.06909000	-0.63767300
H	-2.00083100	-2.73246700	-1.62826000
C	-4.71328000	-3.09003500	1.11207400
H	-4.39184800	-0.99372900	1.48387900
C	-4.34810700	-4.19849500	0.34709100
H	-3.08726200	-4.92745800	-1.23891100
H	-5.47813100	-3.18503600	1.87705200
H	-4.82750800	-5.15785100	0.51650600
C	3.26421600	-1.25753900	-0.23764200
C	3.80865200	-0.00964300	0.08332100
C	5.14966600	0.13939600	0.42662400
C	5.91817200	-1.01689200	0.43084400
C	5.37059200	-2.27157800	0.10725700
C	4.03316100	-2.41837800	-0.23535600
H	5.56670300	1.10838800	0.67874900
H	6.96873200	-0.95116300	0.69324100
H	6.00995700	-3.14771300	0.12722600

H	3.60451100	-3.38379700	-0.48222600
N	2.77888000	0.91903100	-0.02878200
N	1.92007800	-1.04492900	-0.52500200
C	2.89651000	2.35531900	0.19196400
H	2.04918100	2.85394700	-0.27878600
H	2.90468000	2.56549400	1.26205400
C	0.96232000	-2.06434400	-0.93360800
H	0.71388200	-2.70213200	-0.08262900
H	0.06828400	-1.56875300	-1.31119700
C	1.66923600	0.26352900	-0.38526500
H	1.40776500	-2.66164800	-1.73091600
H	3.82167500	2.69624800	-0.27460800
O	0.49895200	0.80870300	-0.61551700

Zero-point correction= 0.436966 (Hartree/Particle)
Thermal correction to Energy= 0.460919
Thermal correction to Enthalpy= 0.461863
Thermal correction to Gibbs Free Energy= 0.382384
SCF Done: E(RM062X) = -1205.31723815

1,3-dimethylbenzididazol-2-one

C	0.00000000	-0.46578200	0.70331800
C	0.00000000	-0.46578200	-0.70331800
C	0.00000000	-1.64845700	-1.42585600
C	0.00000000	-2.84373200	-0.69814200
C	0.00000000	-2.84373200	0.69814200
C	0.00000000	-1.64845700	1.42585600
H	0.00000000	-1.64461600	-2.51141700
H	0.00000000	-3.78814000	-1.23304300
H	0.00000000	-3.78814000	1.23304300
H	0.00000000	-1.64461600	2.51141700
N	0.00000000	0.85941100	-1.10619500
N	0.00000000	0.85941100	1.10619500
C	0.00000000	1.33621300	-2.47020400
H	0.00000000	2.42640000	-2.43847200
H	0.89245500	0.98850300	-2.99848500
C	0.00000000	1.33621300	2.47020400
H	0.89245500	0.98850300	2.99848500
H	0.00000000	2.42640000	2.43847200
C	0.00000000	1.69371400	0.00000000
H	-0.89245500	0.98850200	2.99848500
H	-0.89245500	0.98850200	-2.99848500
O	0.00000000	2.91571800	0.00000000

Zero-point correction= 0.181618 (Hartree/Particle)

Thermal correction to Energy= 0.191941
Thermal correction to Enthalpy= 0.192885
Thermal correction to Gibbs Free Energy= 0.146047
SCF Done: E(RM062X) = -533.687648298

IM8b

C	0.93220500	1.75935700	-0.02135700
C	1.54006000	0.43318300	-0.19197900
O	1.25489700	2.60873300	0.75749900
C	1.02598600	-0.56859100	-1.02688500
C	2.68545300	0.18777600	0.58140200
C	1.65681000	-1.80543800	-1.07940900
H	0.12926700	-0.42444400	-1.62118100
C	3.31171800	-1.04758600	0.51639800
H	3.06949800	0.97223000	1.22511700
C	2.79638400	-2.04459000	-0.31294800
H	1.25416000	-2.58442800	-1.71790300
H	4.19830300	-1.23661900	1.11228800
H	3.28367900	-3.01344800	-0.35986100
N	-0.25393900	2.12481800	-0.89400000
C	-1.58148700	2.03998000	-0.14574200
H	-0.10565400	3.10465200	-1.17621400
H	-0.30835000	1.57477900	-1.76109900
C	-1.92845900	0.60674300	0.12942800
H	-1.44552000	2.62995900	0.76190100
H	-2.30801200	2.52767600	-0.79690400
C	-2.59780300	-0.14291500	-0.84173900
C	-1.52737700	-0.00068200	1.32131500
C	-2.85327800	-1.49435900	-0.62623800
H	-2.92025500	0.33516200	-1.76396100
C	-1.78469300	-1.35208500	1.53677700
H	-1.00907800	0.58640900	2.07657700
C	-2.44334400	-2.09900400	0.56178900
H	-3.37613200	-2.07345300	-1.38091300
H	-1.47190800	-1.82046700	2.46450100
H	-2.64463100	-3.15233300	0.73077800

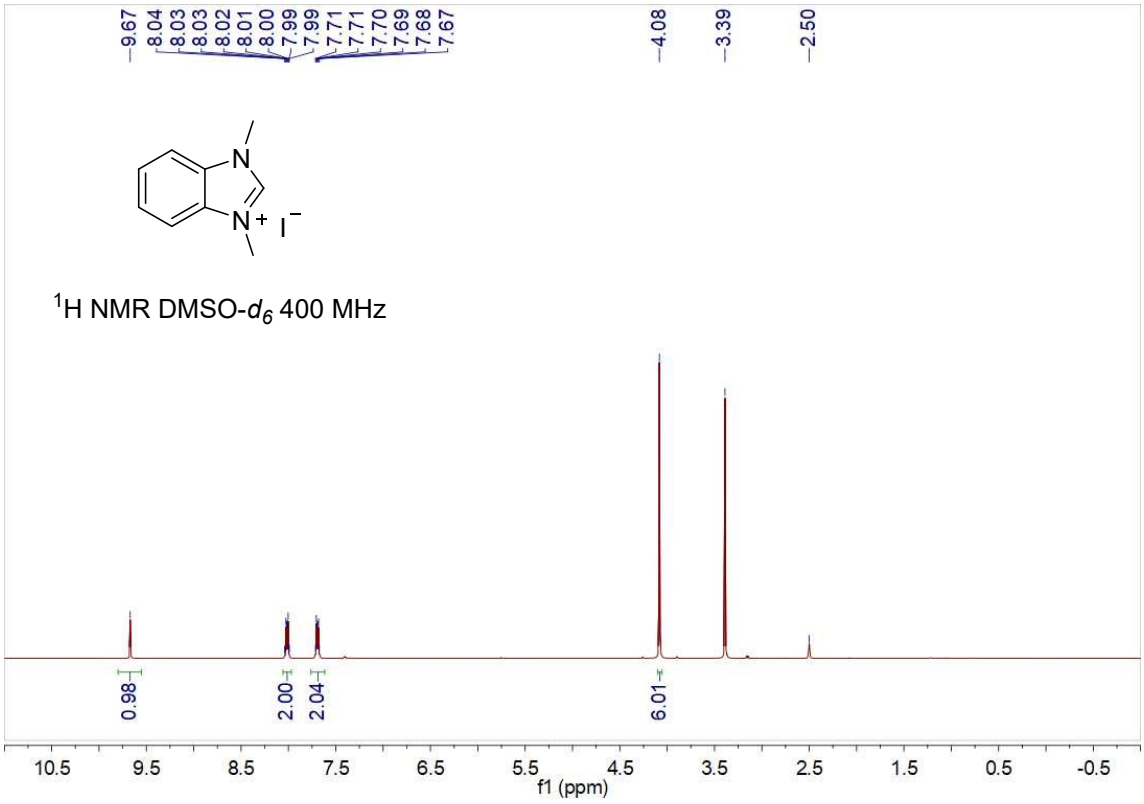
Zero-point correction= 0.255205 (Hartree/Particle)
Thermal correction to Energy= 0.268021
Thermal correction to Enthalpy= 0.268966
Thermal correction to Gibbs Free Energy= 0.214978
SCF Done: E(RM062X) = -671.646558292

4aa

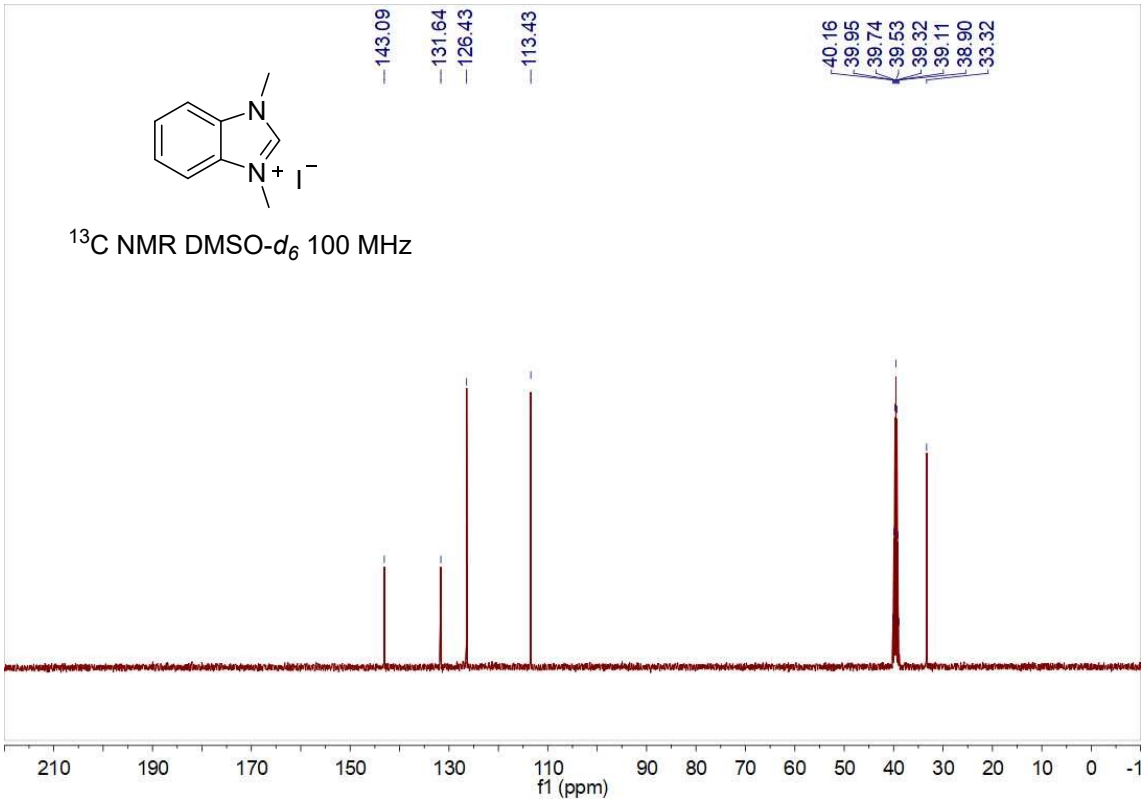
C	-0.88548400	-0.95644800	-0.00124500
C	-2.18111600	-0.19433900	-0.02738300
O	-0.67985900	-1.82991000	0.83790200
C	-2.29107500	1.10141700	-0.53930000
C	-3.30376100	-0.81611800	0.52478400
C	-3.51878500	1.75868600	-0.51566000
H	-1.41923600	1.61906900	-0.92984100
C	-4.53133700	-0.16268800	0.53813500
H	-3.19730400	-1.81422500	0.93778400
C	-4.64056000	1.12609900	0.01635600
H	-3.59596400	2.76897100	-0.90553900
H	-5.40235500	-0.65548500	0.95920000
H	-5.59732500	1.63939600	0.03122000
N	0.02008100	-0.63088400	-0.95413200
C	1.33000500	-1.25804400	-1.02615800
C	2.41884000	-0.42359700	-0.38364300
H	1.24512500	-2.22244800	-0.51843700
H	1.56974400	-1.44483200	-2.07624100
C	3.53721100	-0.01895900	-1.11108100
C	2.30929200	-0.05214800	0.96107200
C	4.53731300	0.74456100	-0.50762200
H	3.62605600	-0.30214100	-2.15735500
C	3.30340500	0.71141300	1.56405300
H	1.44070600	-0.37354100	1.53159200
C	4.42156300	1.11181100	0.83002700
H	5.40350800	1.05384600	-1.08530400
H	3.21029600	0.99229600	2.60914500
H	5.19790300	1.70699300	1.30158800
H	-0.21590600	0.05768400	-1.65612400

Zero-point correction= 0.240268 (Hartree/Particle)
Thermal correction to Energy= 0.253540
Thermal correction to Enthalpy= 0.254484
Thermal correction to Gibbs Free Energy= 0.196834
SCF Done: E(RM062X) = -671.233378812

12 ^{1}H NMR, ^{13}C NMR, and HPLC Spectrums



^{1}H NMR DMSO-d_6 400 MHz



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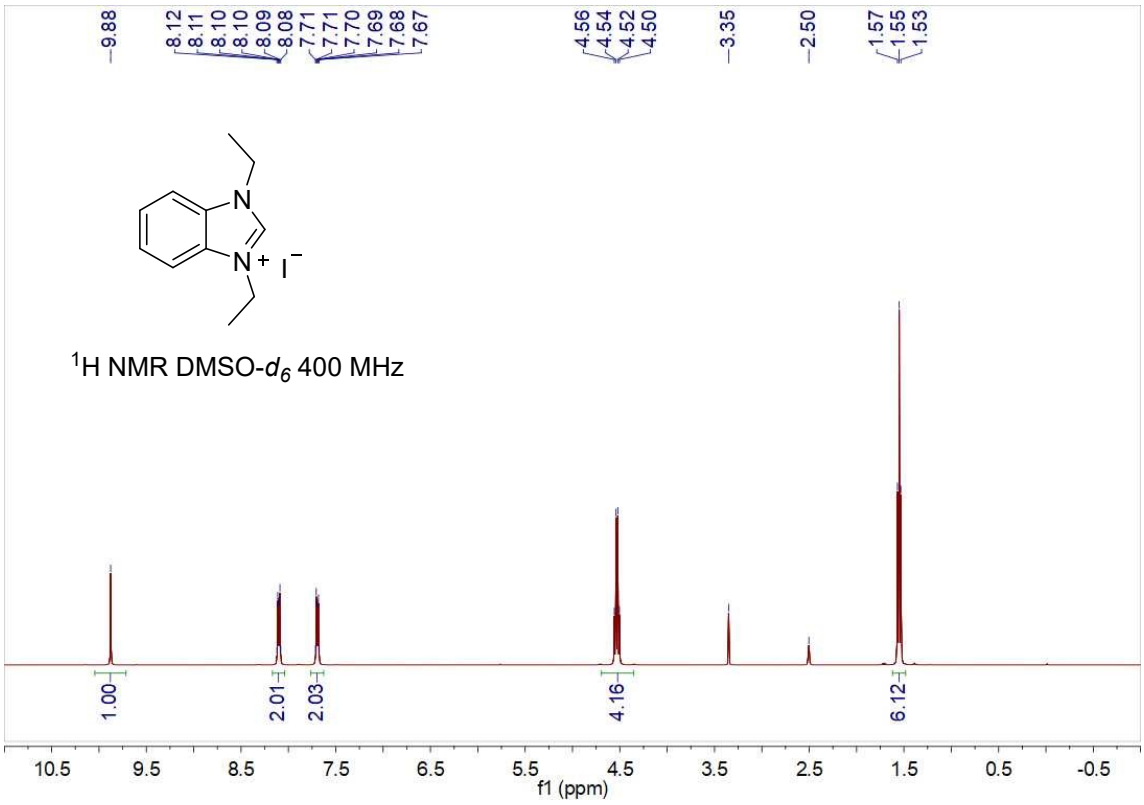

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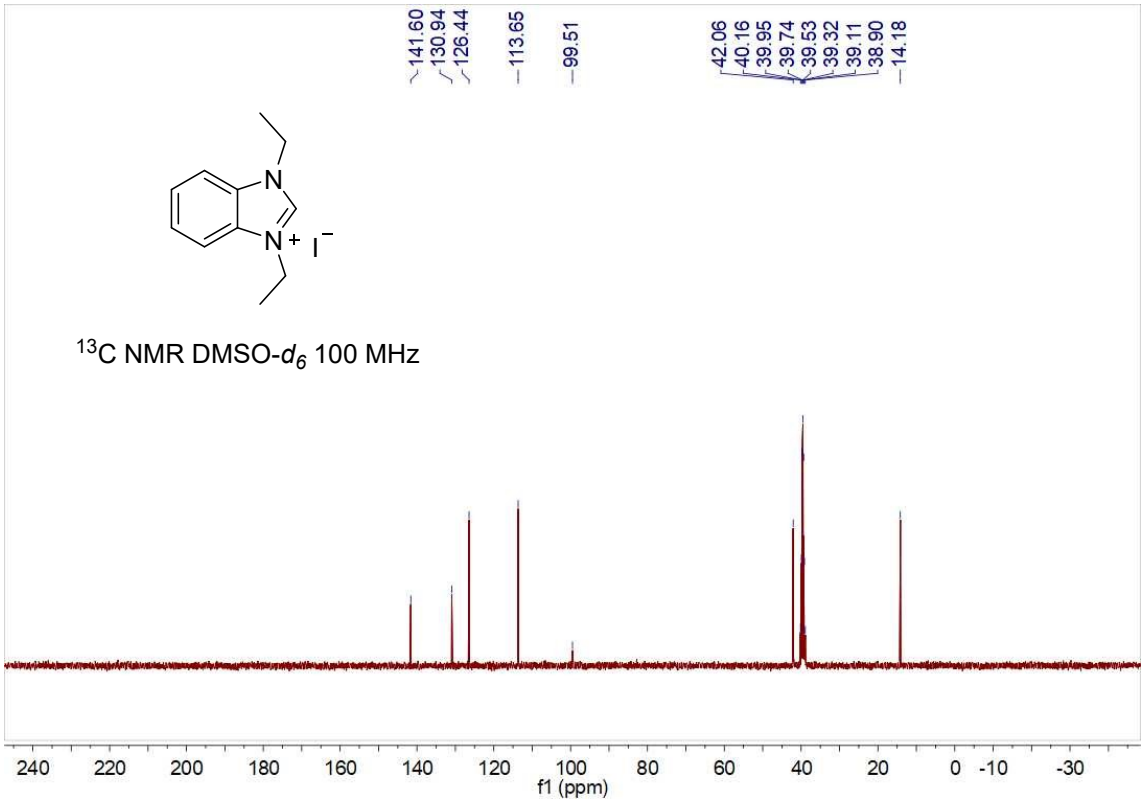

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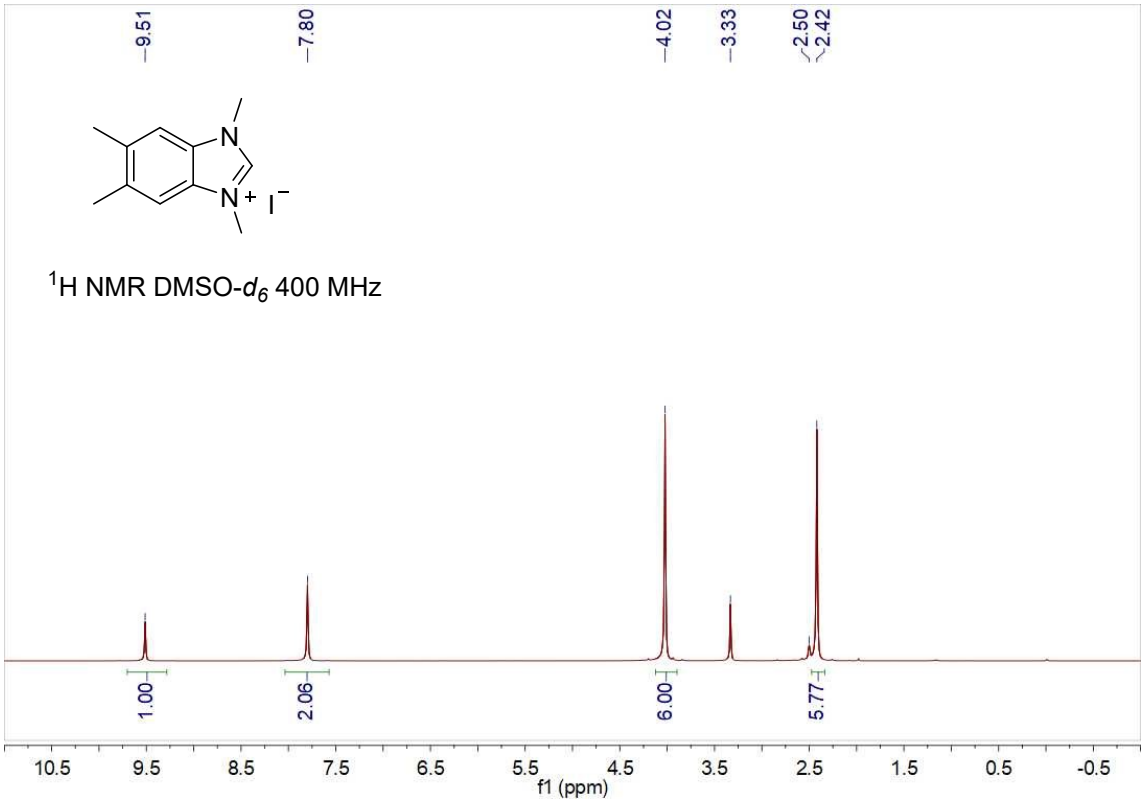
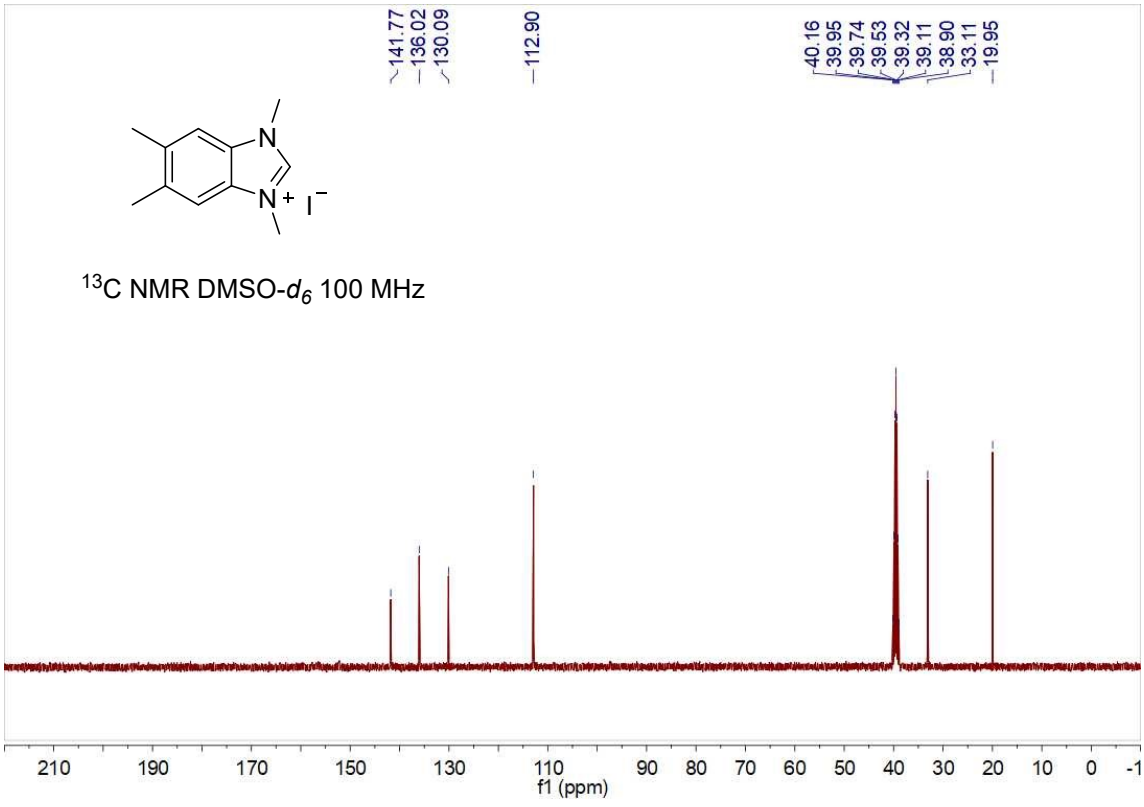
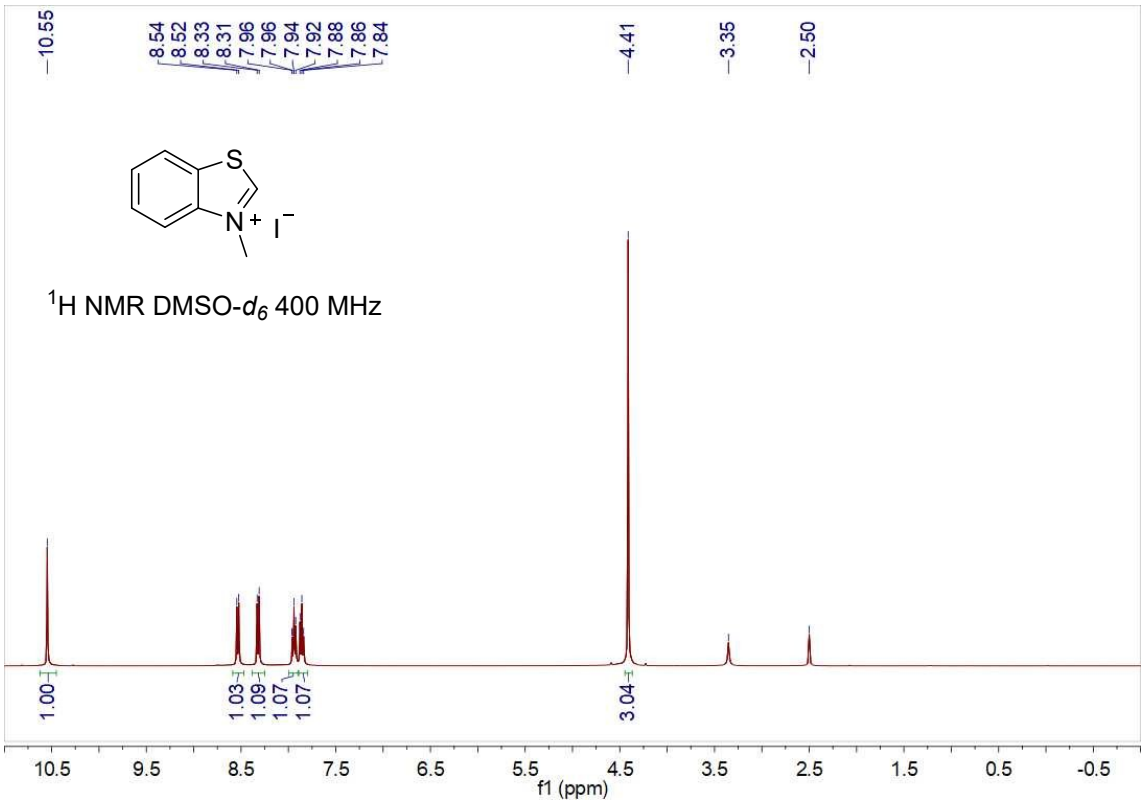


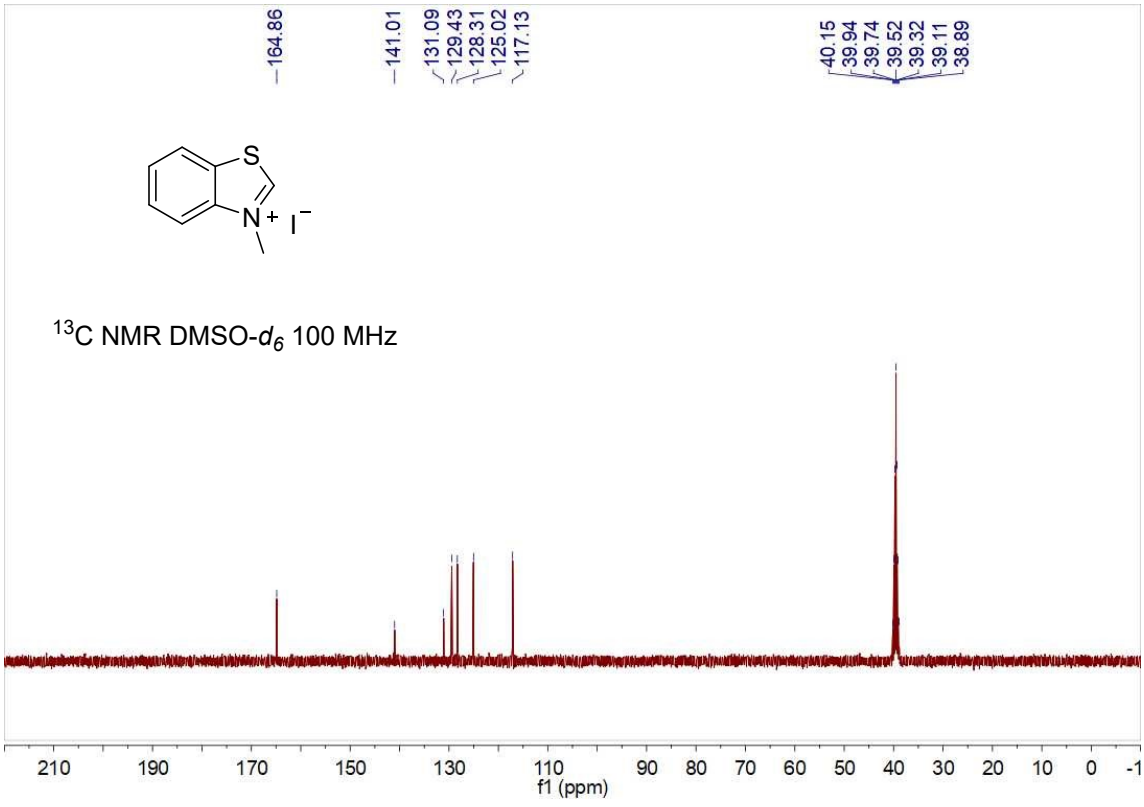
^{1}H NMR DMSO-d_6 400 MHz



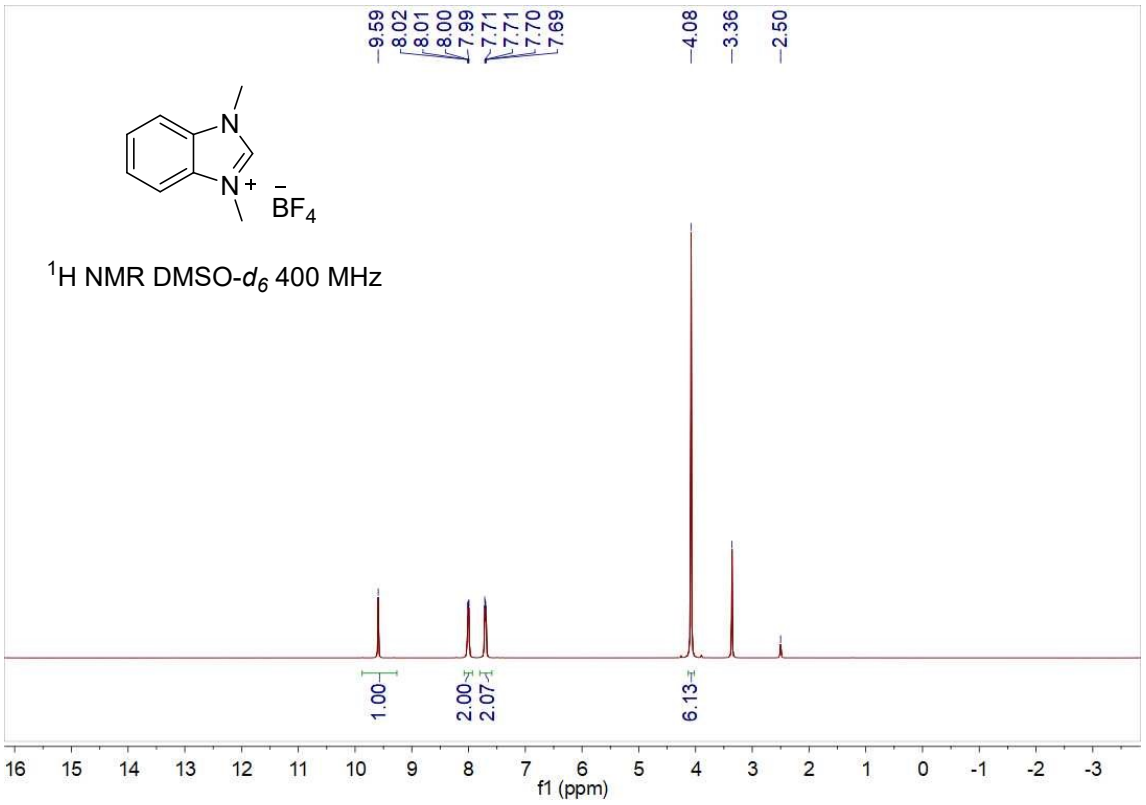
^{13}C NMR DMSO-d_6 100 MHz



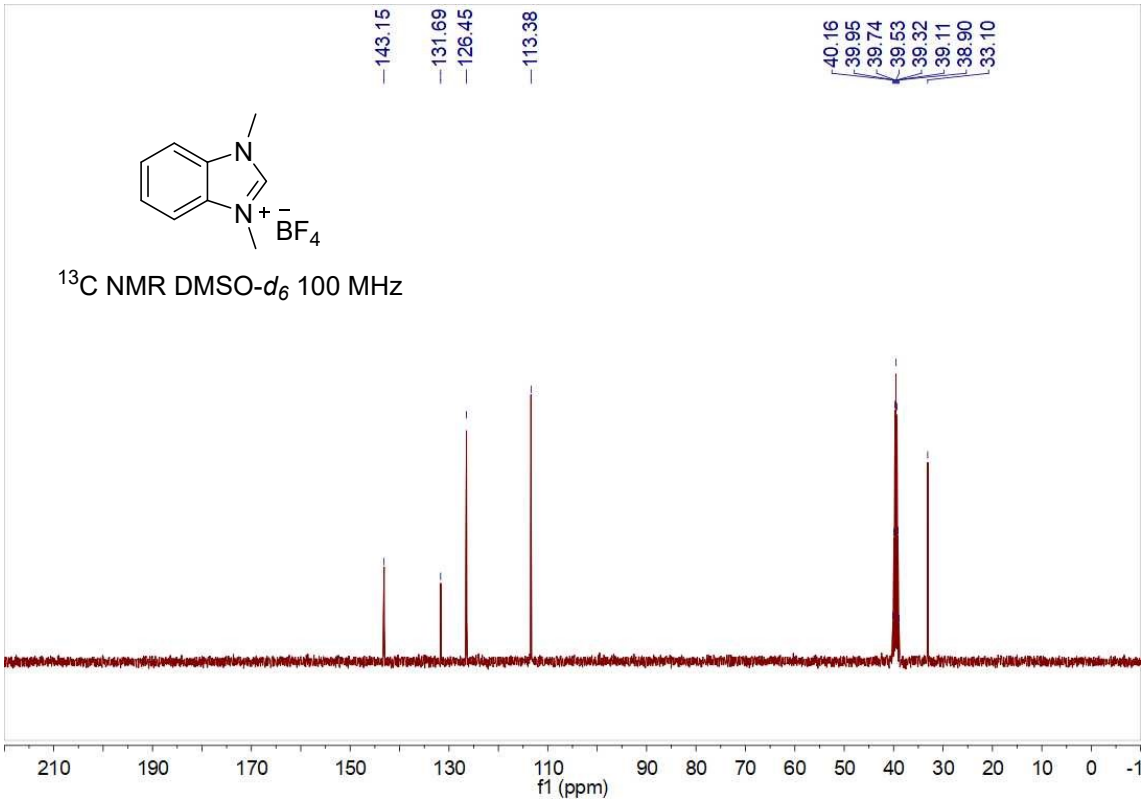
^{1}H NMR DMSO-d_6 400 MHz



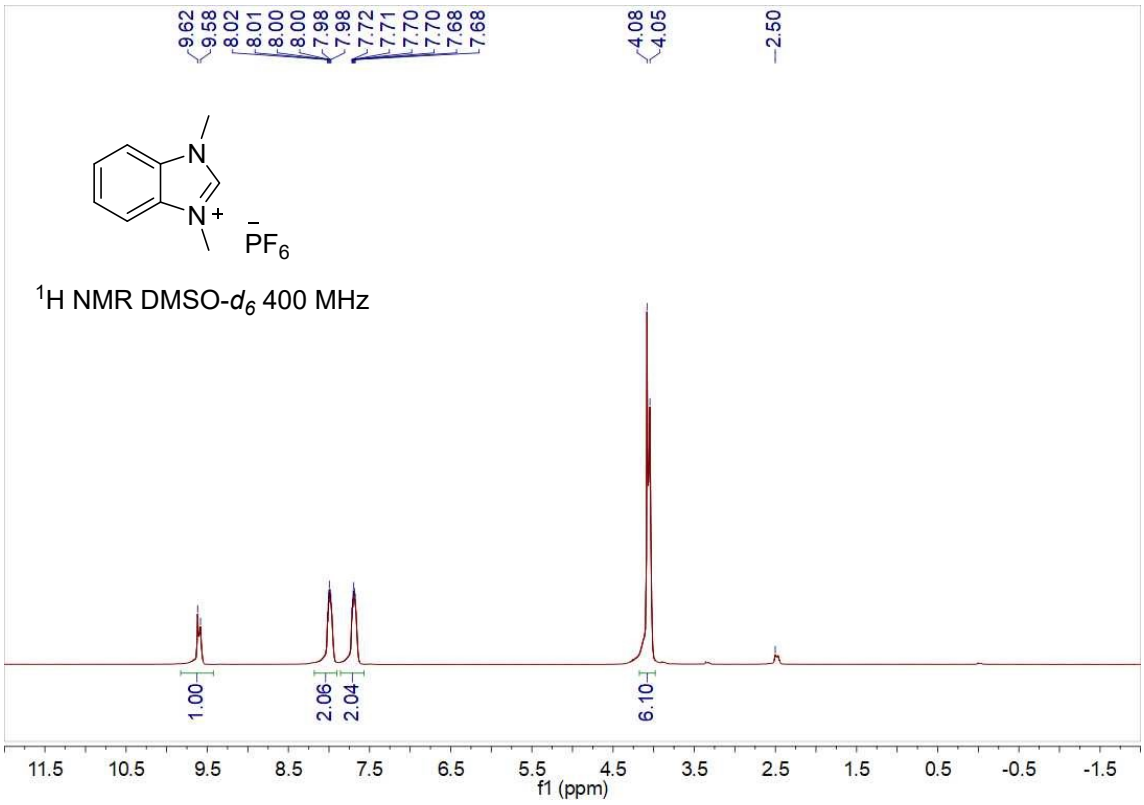
^{13}C NMR DMSO-d_6 100 MHz

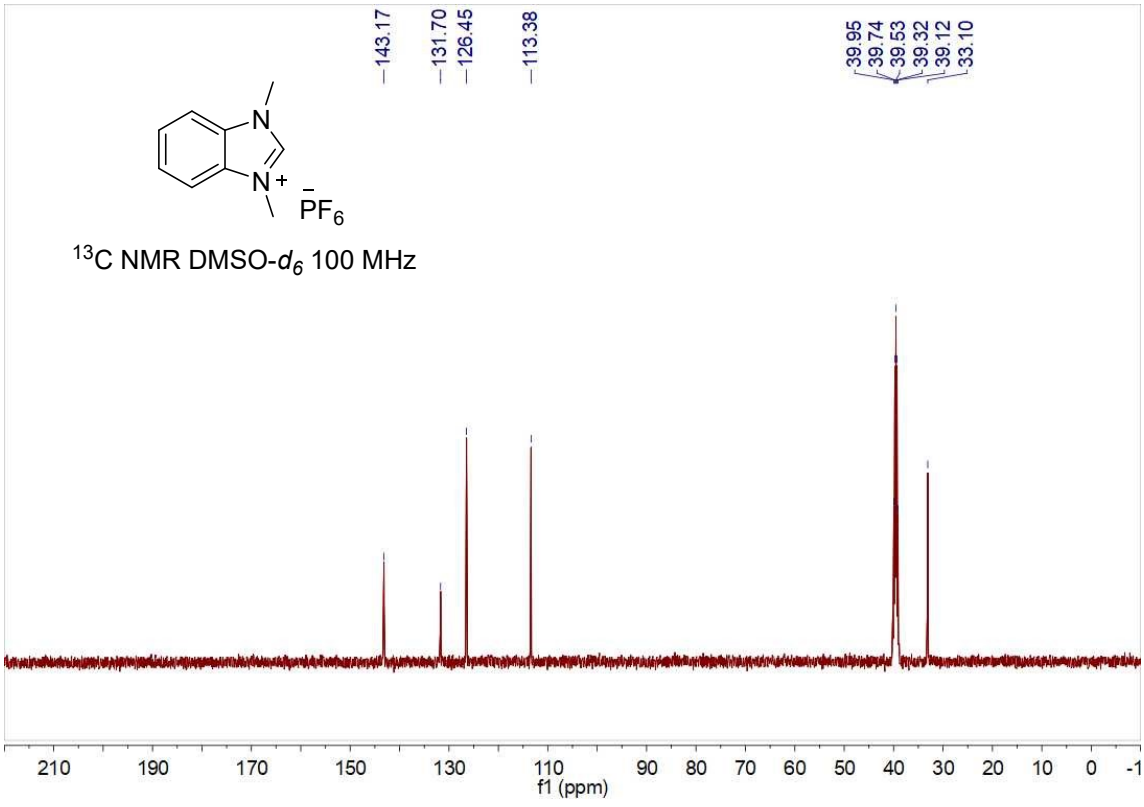


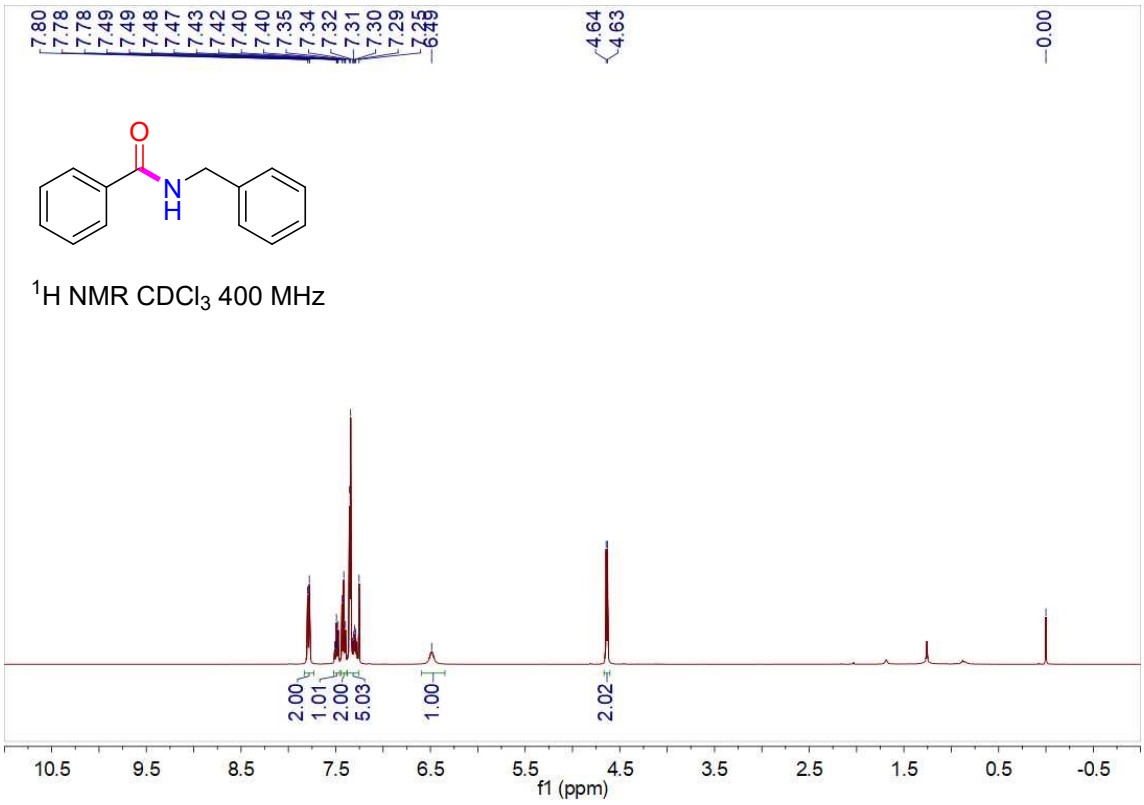
^{1}H NMR DMSO-d_6 400 MHz



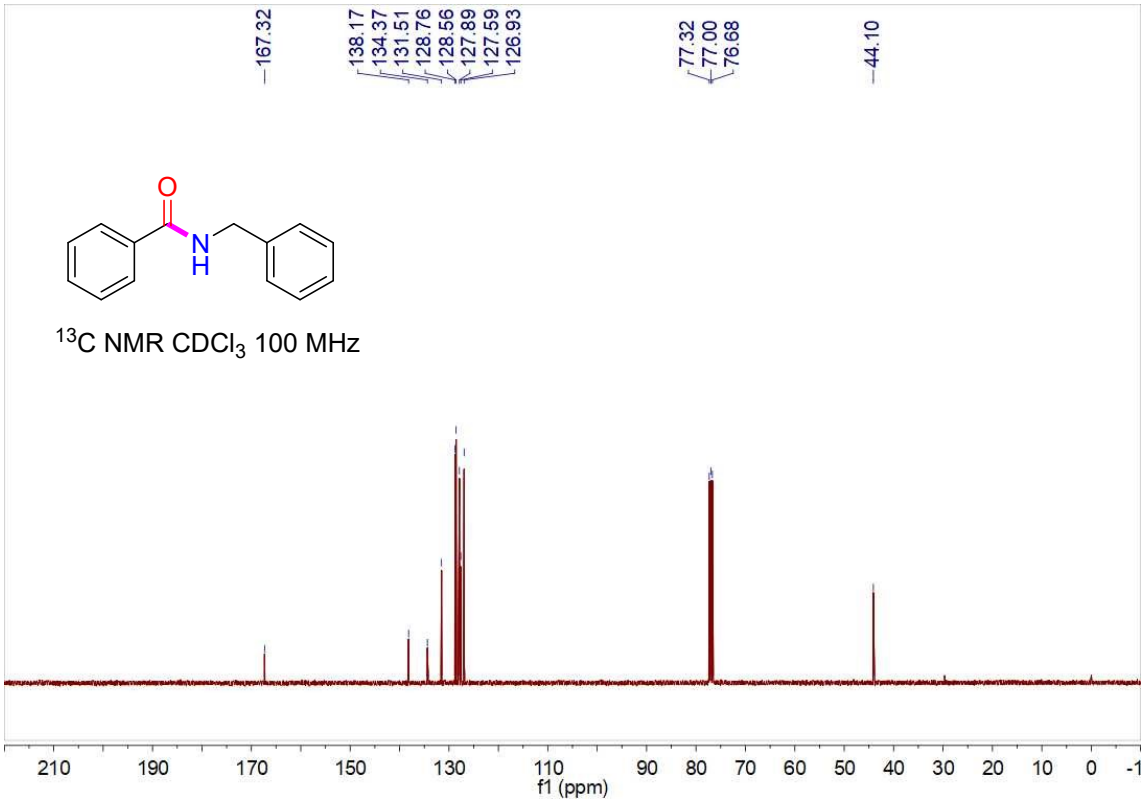
^{13}C NMR DMSO-d_6 100 MHz


9.62
9.58
8.02
8.01
8.00
8.00
7.98
7.98
7.72
7.71
7.70
7.70
7.68
7.68
4.08
4.05
2.50
N
N+
PF6
1H NMR DMSO-d6 400 MHz
1.00
2.06
2.04
6.10
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

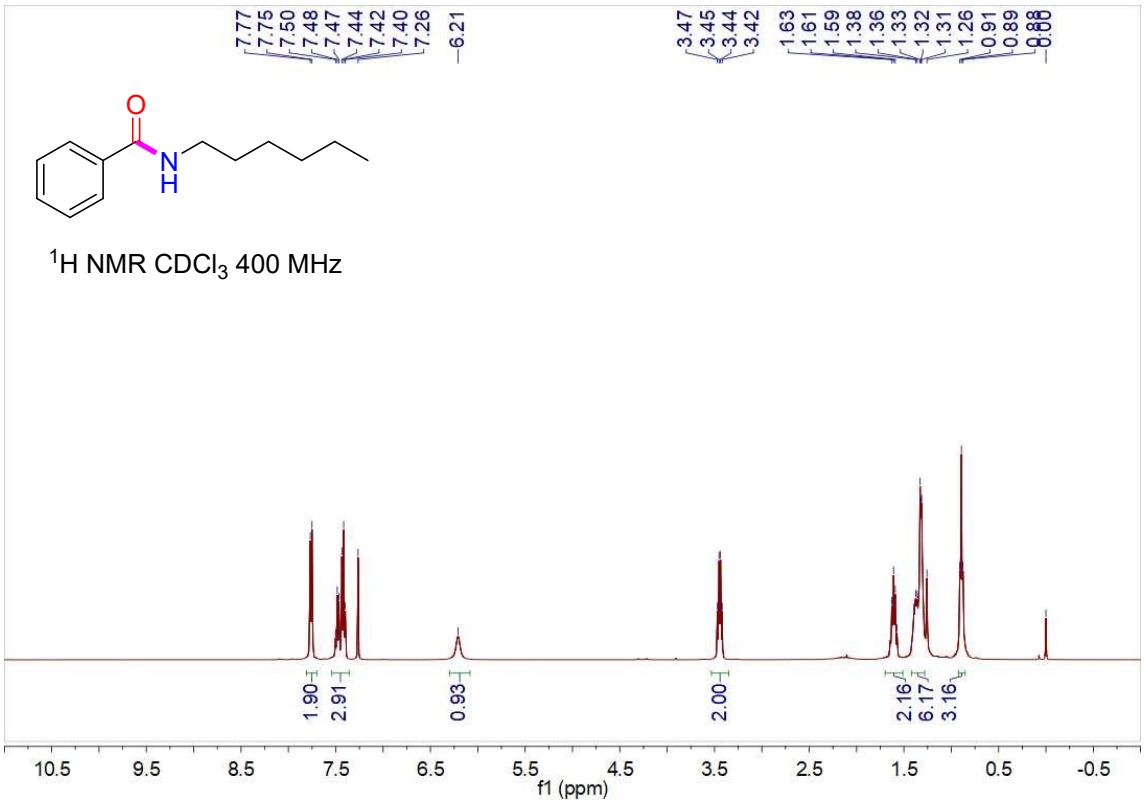

143.17
131.70
126.45
113.38
39.95
39.74
39.53
39.32
39.12
33.10
N
N+
PF6
13C NMR DMSO-d6 100 MHz
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



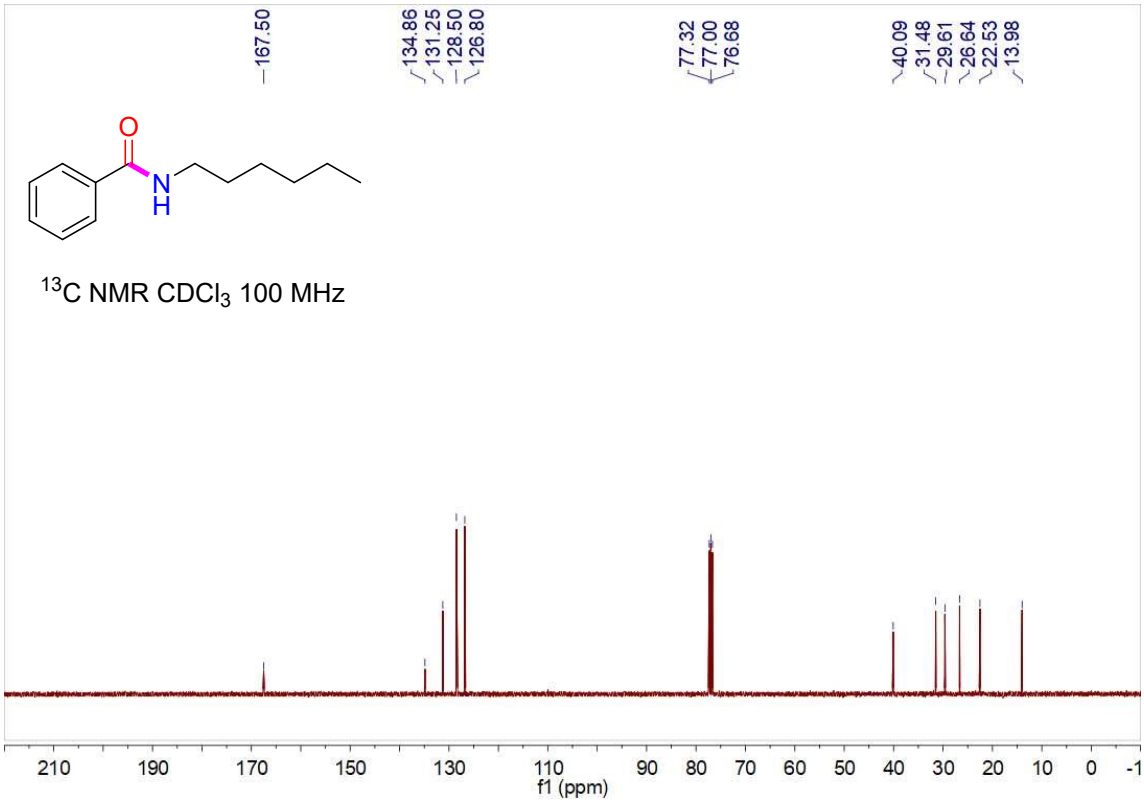
^{1}H NMR $CDCl_3$ 400 MHz



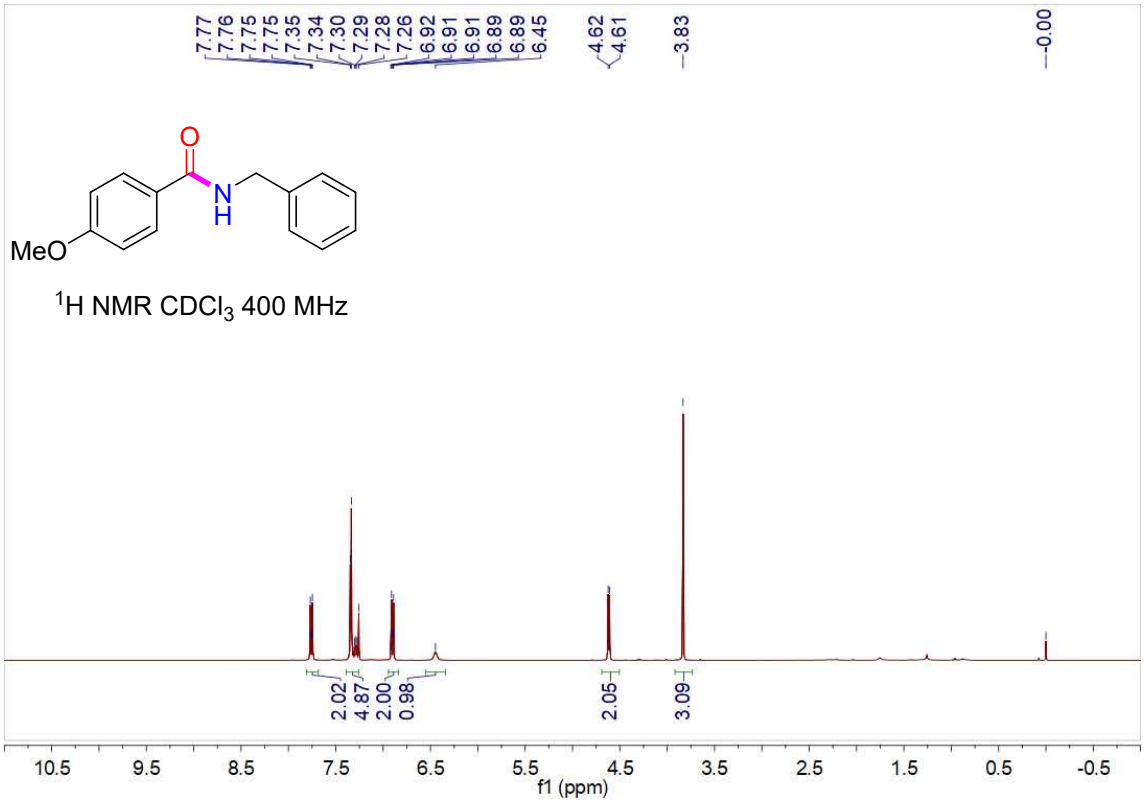
^{13}C NMR $CDCl_3$ 100 MHz



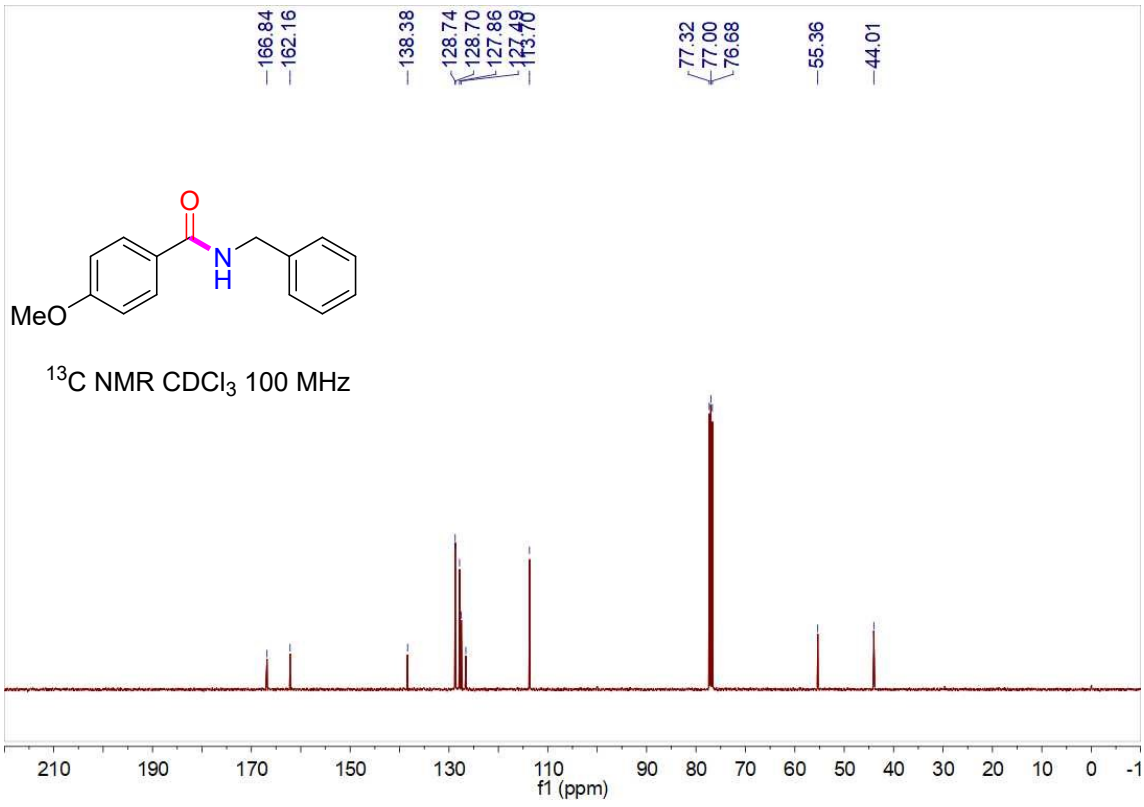
^{1}H NMR $CDCl_3$ 400 MHz



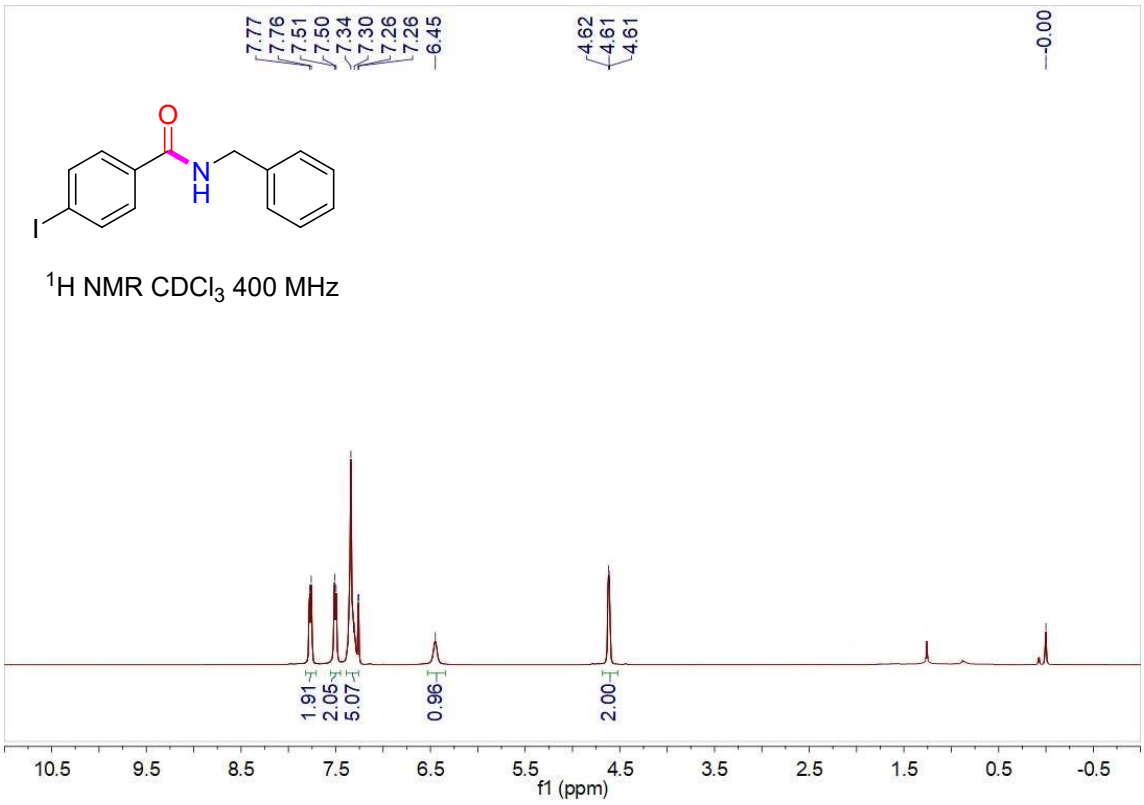
^{13}C NMR $CDCl_3$ 100 MHz



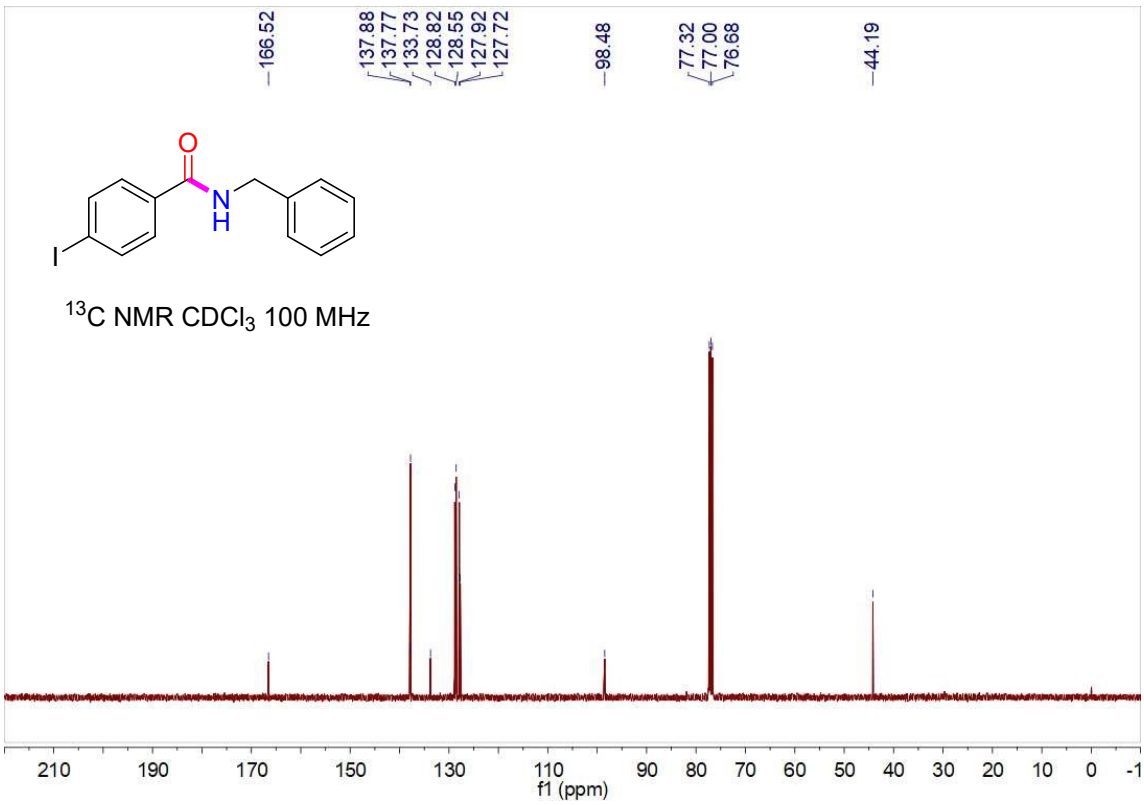
^{1}H NMR $CDCl_3$ 400 MHz



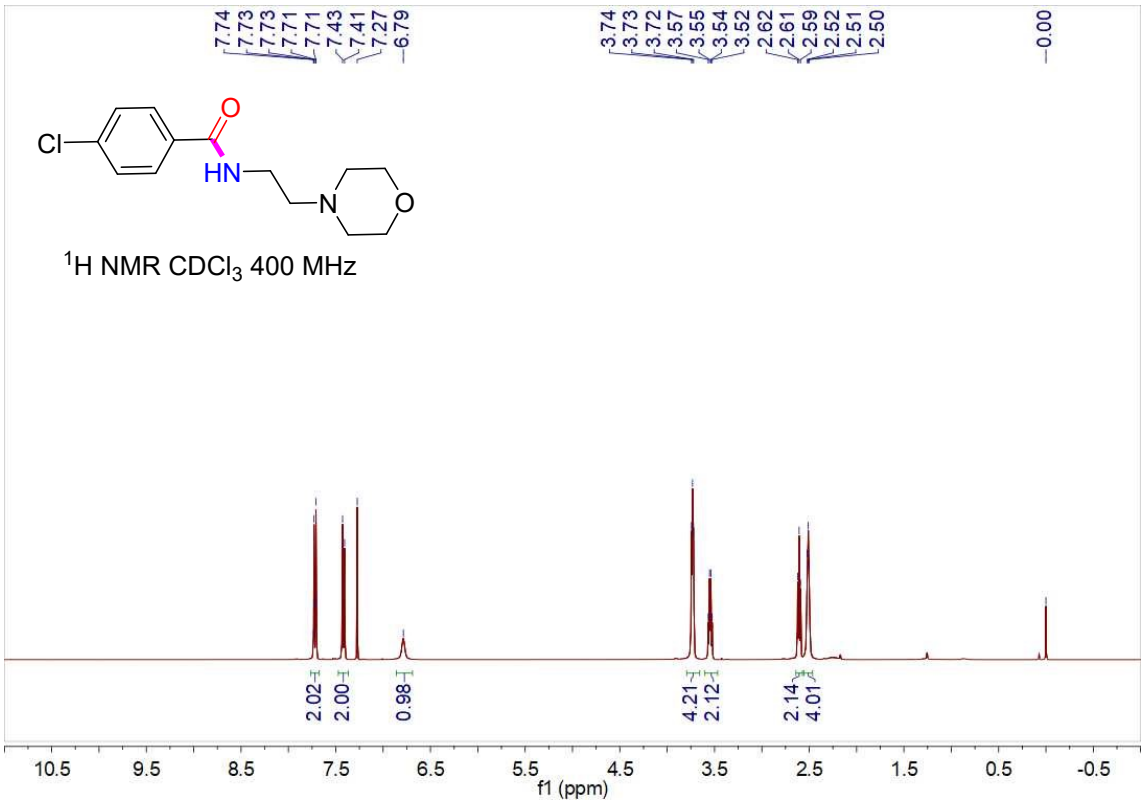
^{13}C NMR $CDCl_3$ 100 MHz



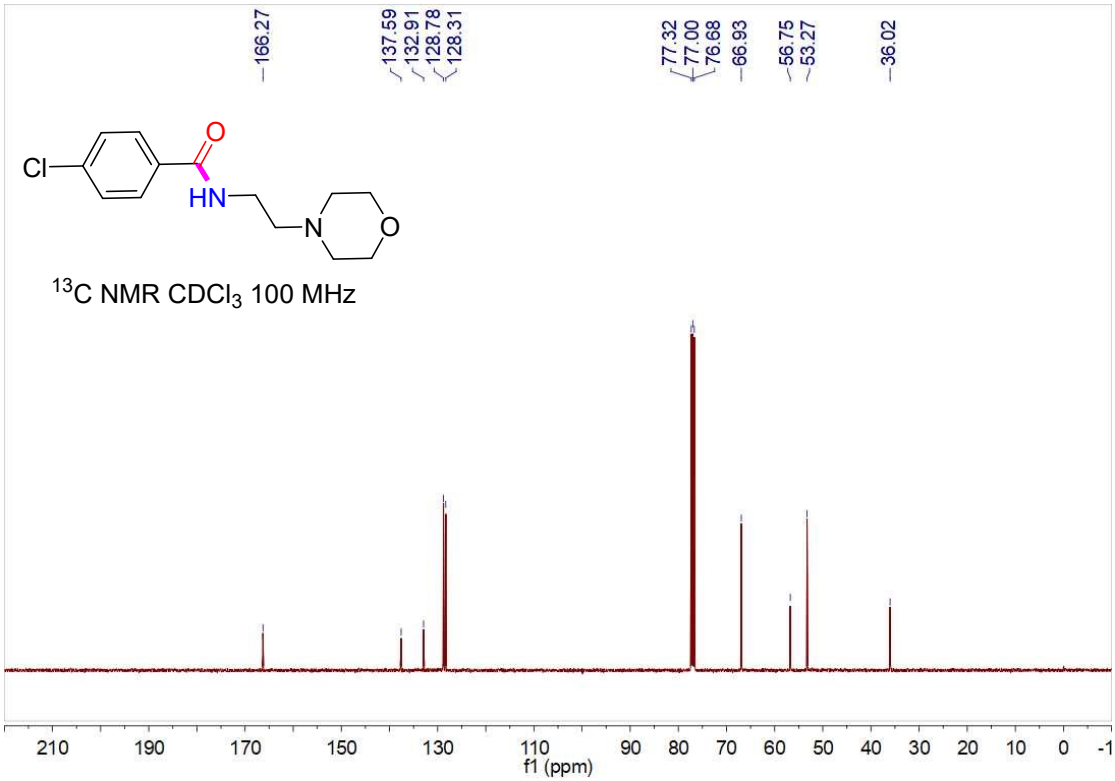
^{1}H NMR $CDCl_3$ 400 MHz



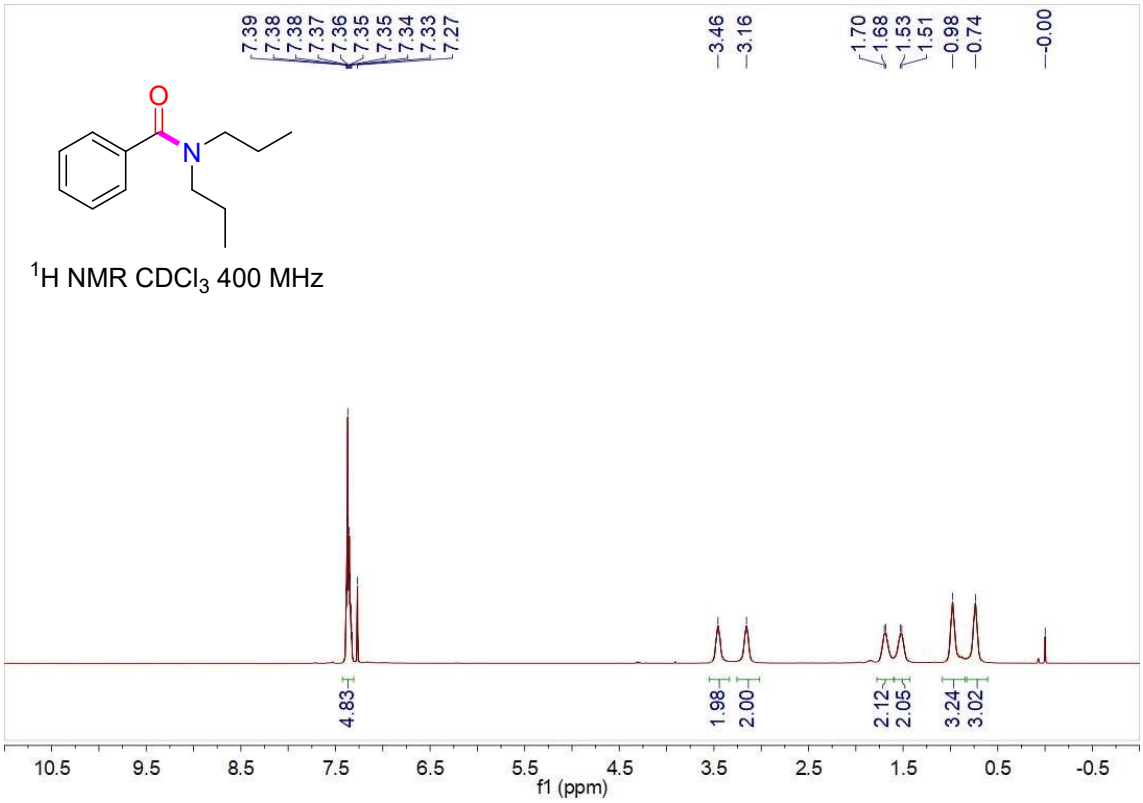
^{13}C NMR $CDCl_3$ 100 MHz



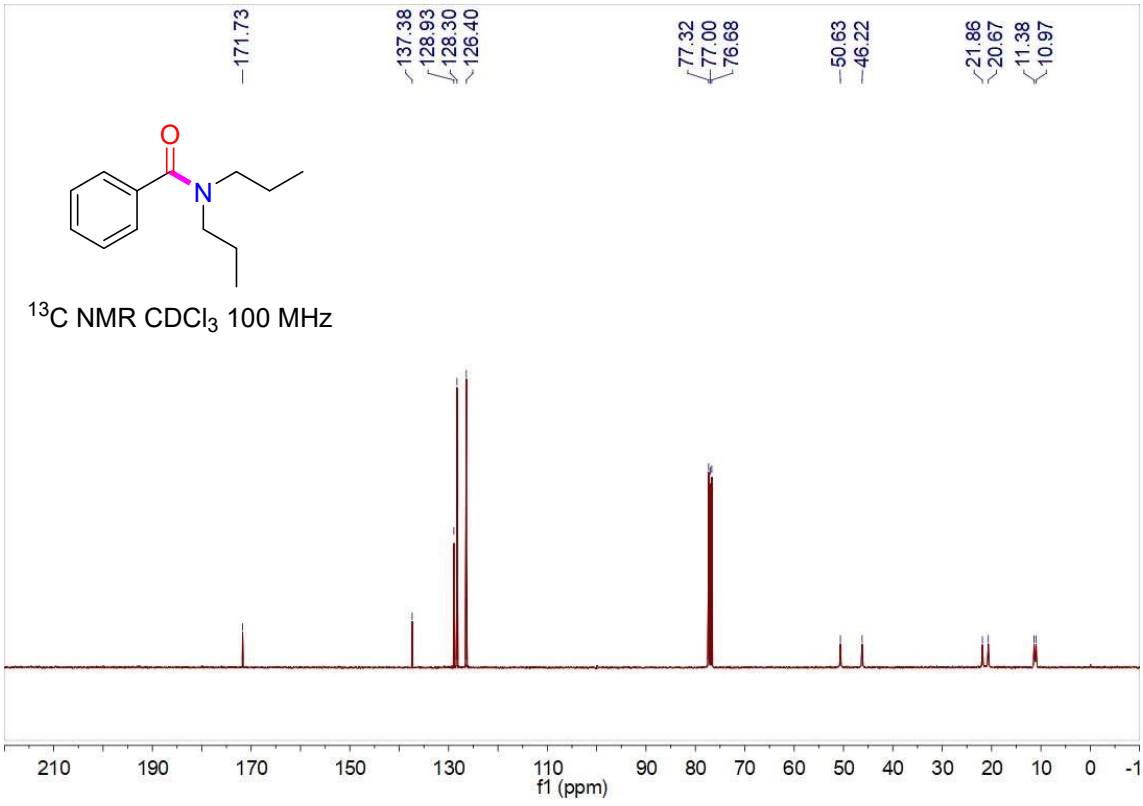
^{1}H NMR $CDCl_3$ 400 MHz



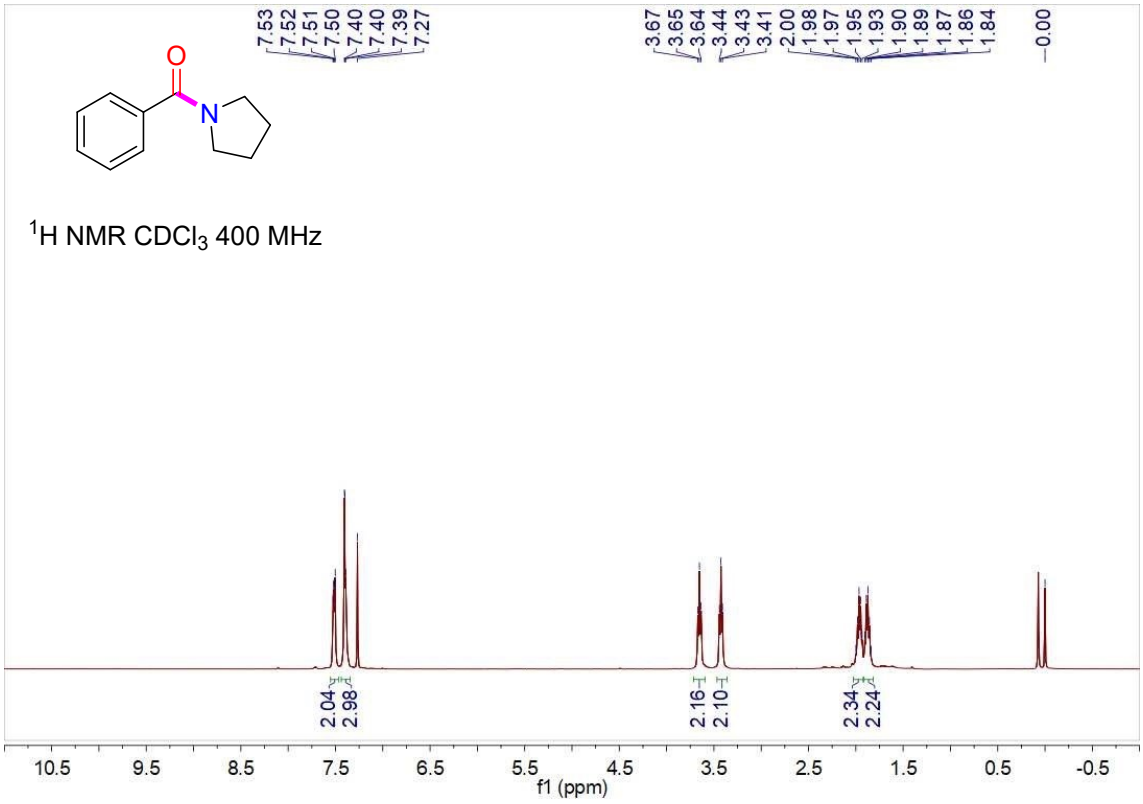
^{13}C NMR $CDCl_3$ 100 MHz



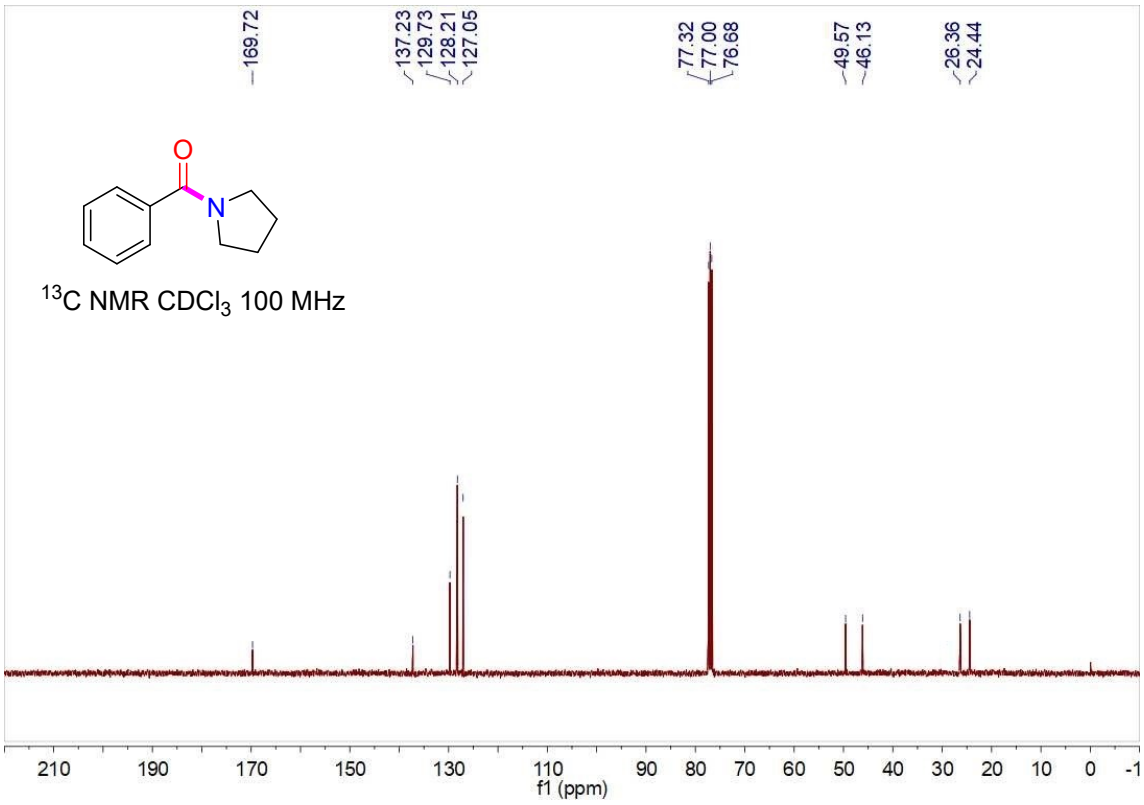
^{1}H NMR $CDCl_3$ 400 MHz

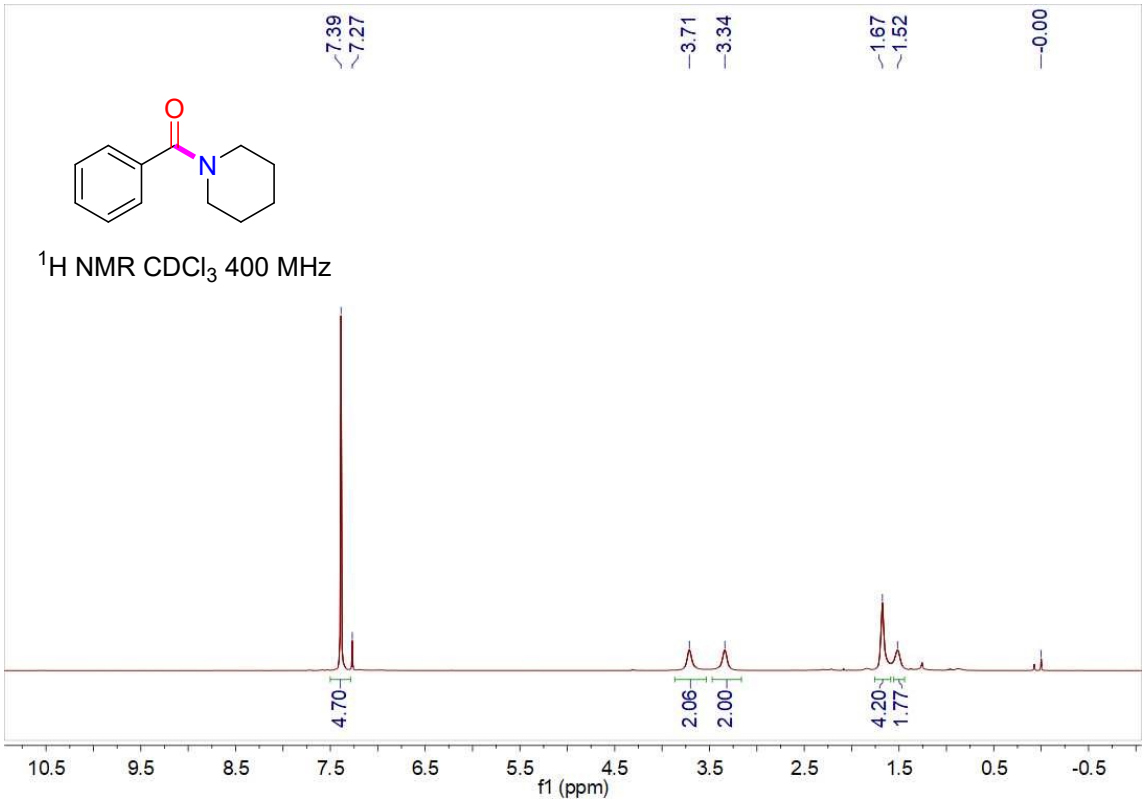


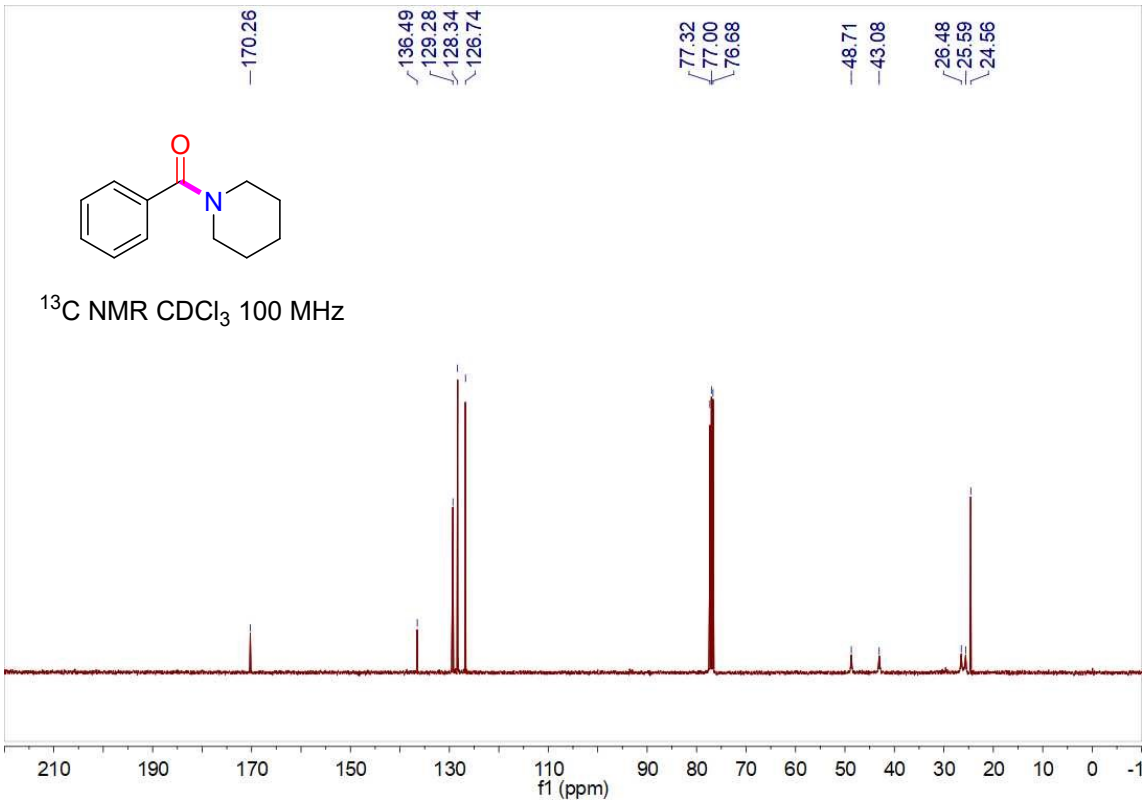
^{13}C NMR $CDCl_3$ 100 MHz



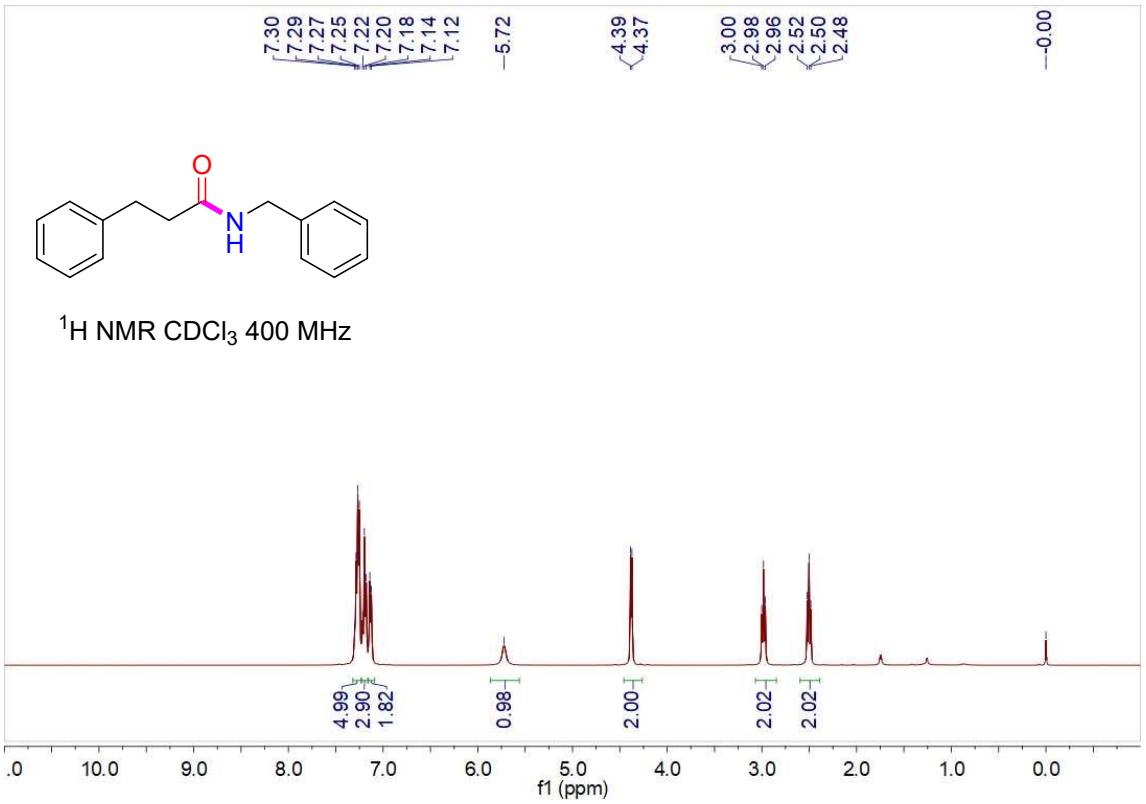
^{1}H NMR $CDCl_3$ 400 MHz


169.72
137.23
129.73
128.21
127.05
77.32
77.00
76.68
49.57
46.13
26.36
24.44
O
N
13C NMR CDCl3 100 MHz
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

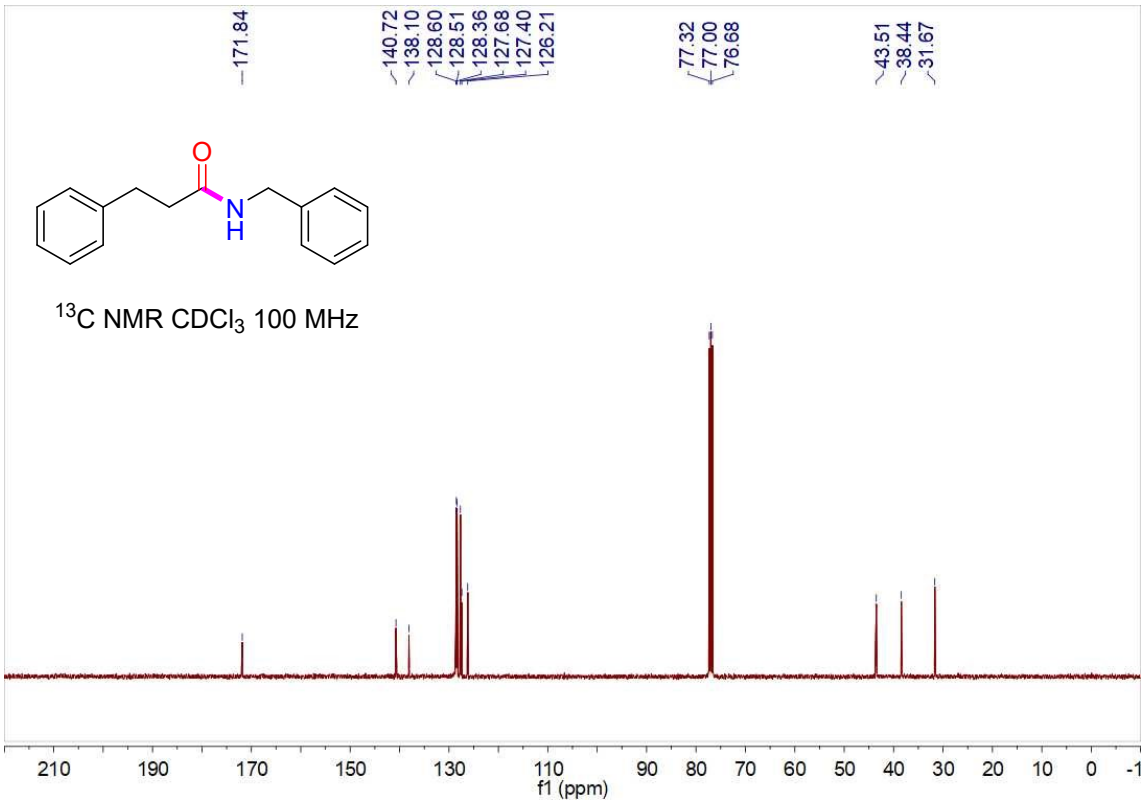

7.39
7.27
3.71
3.34
1.67
1.52
0.00
O
N
1H NMR CDCl3 400 MHz
4.70
2.06
2.00
4.20
1.77
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)



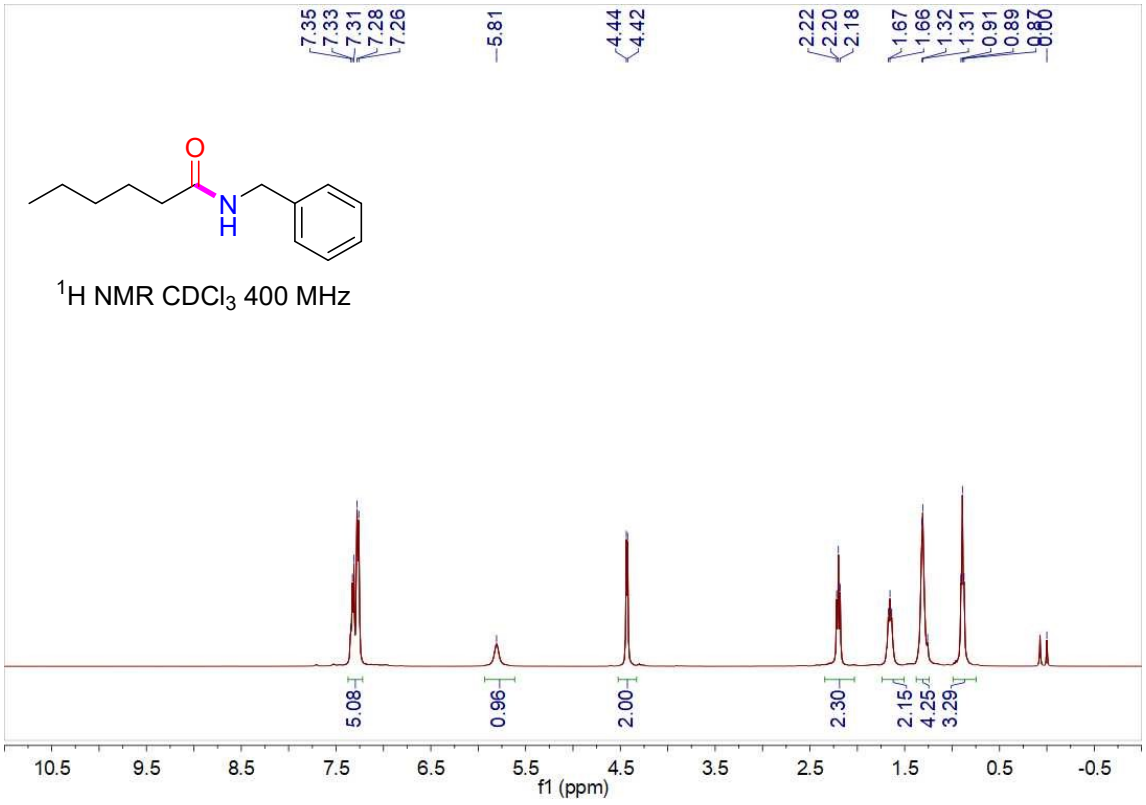
^{13}C NMR $CDCl_3$ 100 MHz



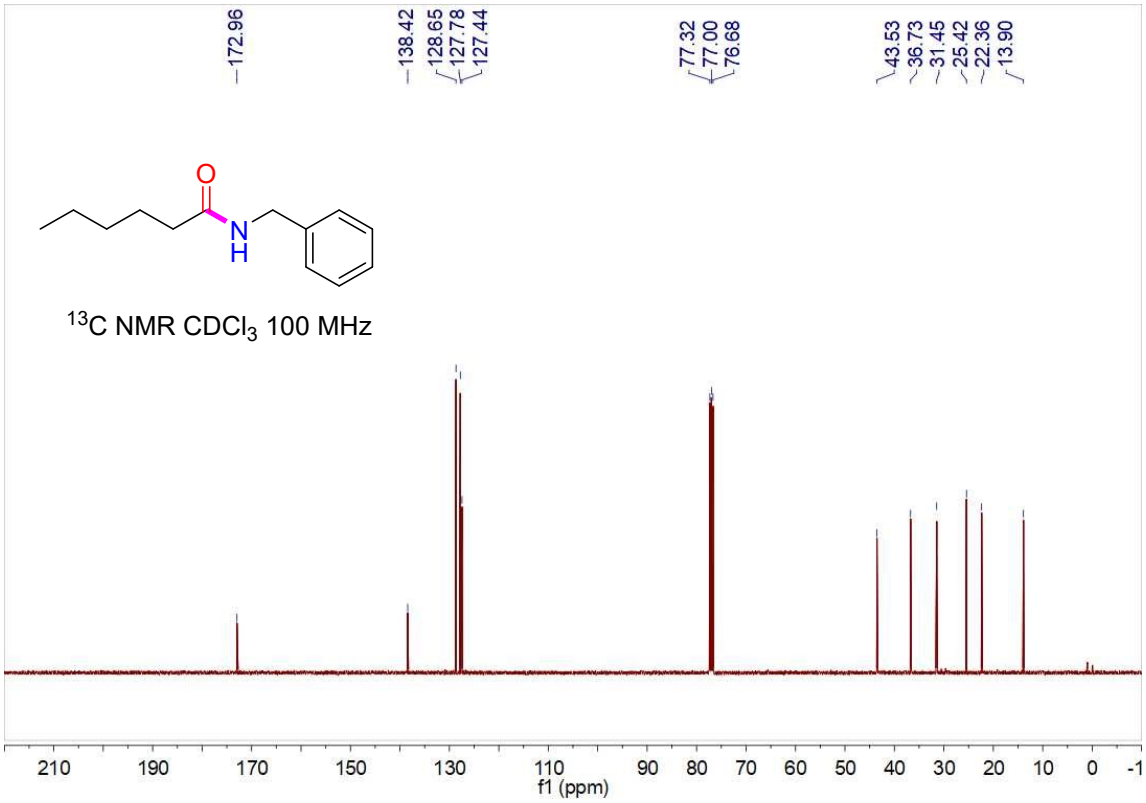
^{1}H NMR $CDCl_3$ 400 MHz



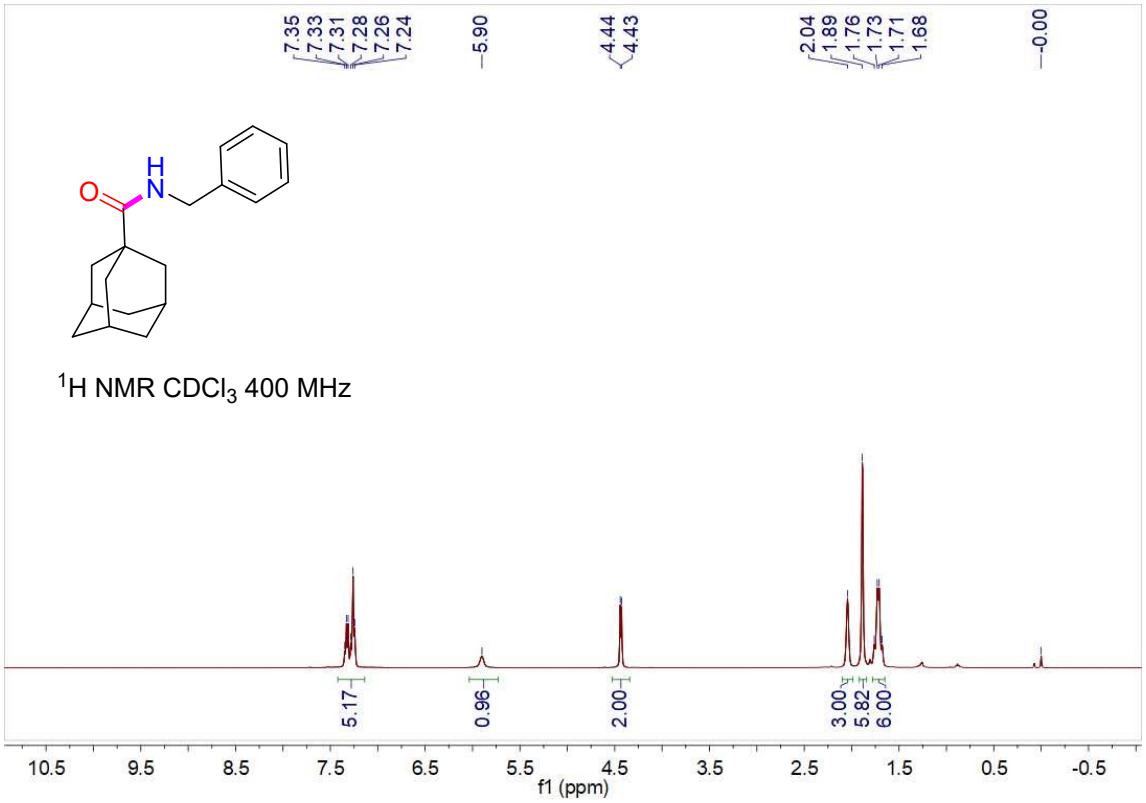
^{13}C NMR $CDCl_3$ 100 MHz



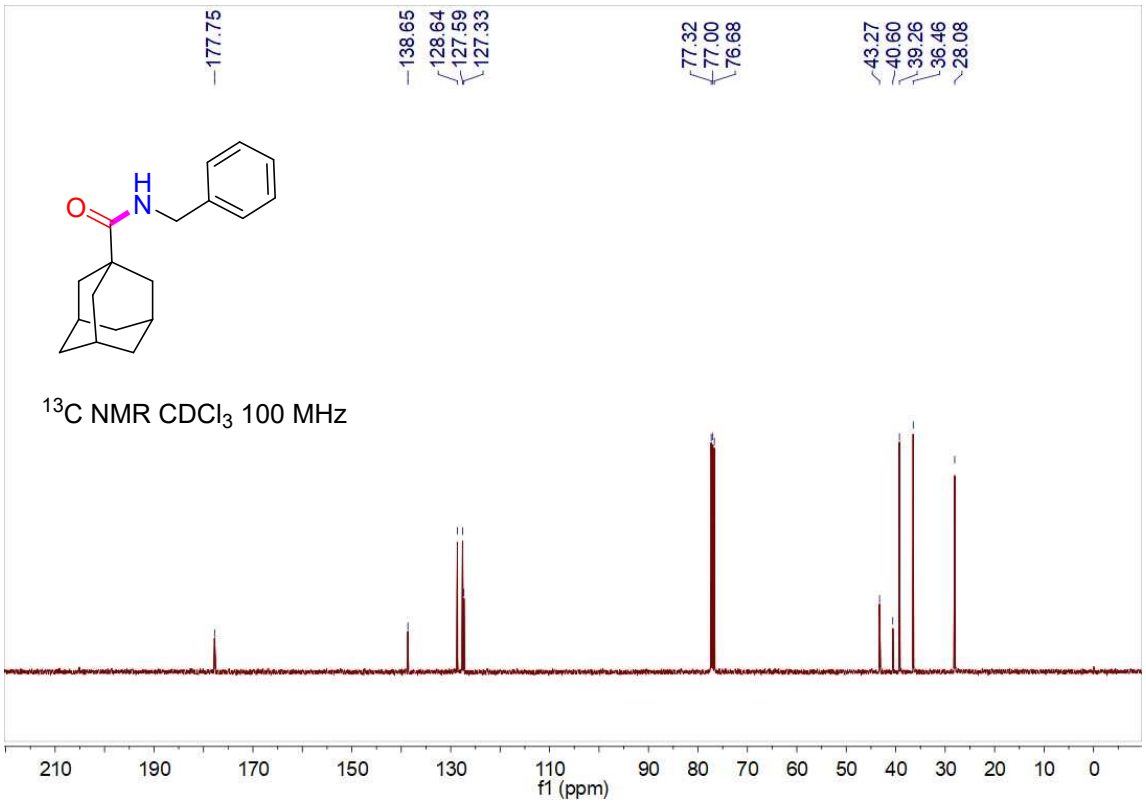
^{1}H NMR $CDCl_3$ 400 MHz

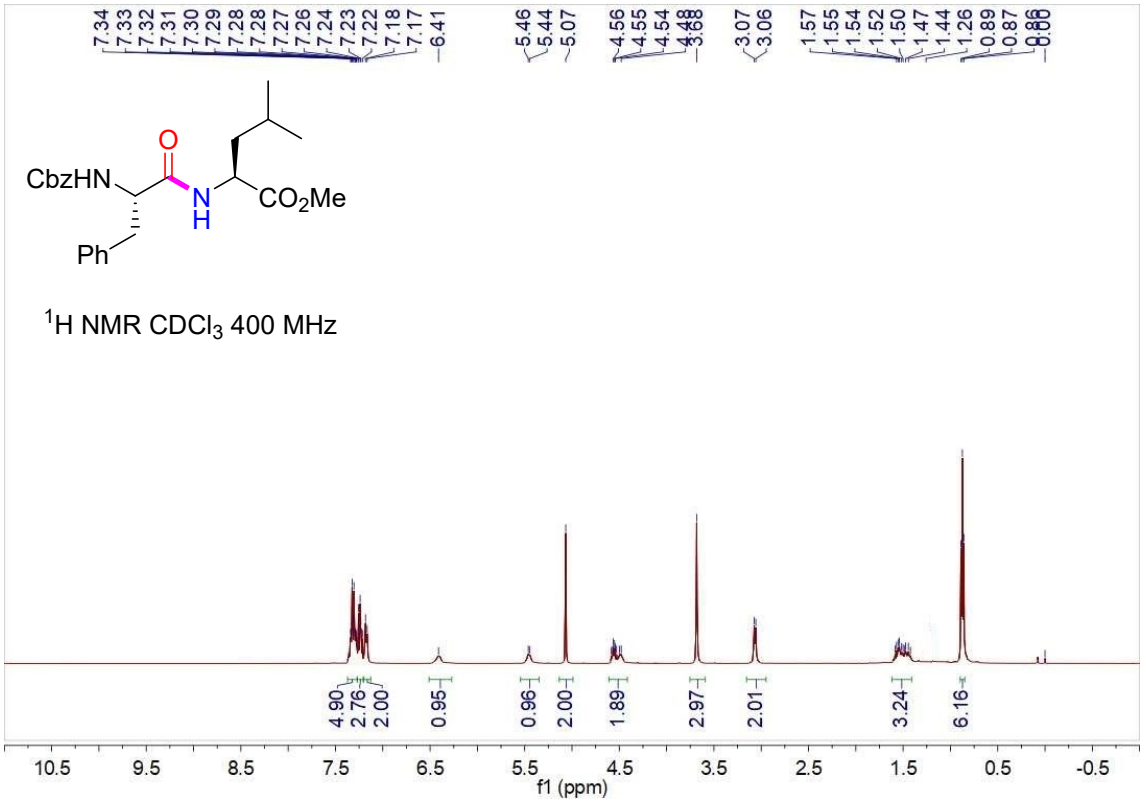


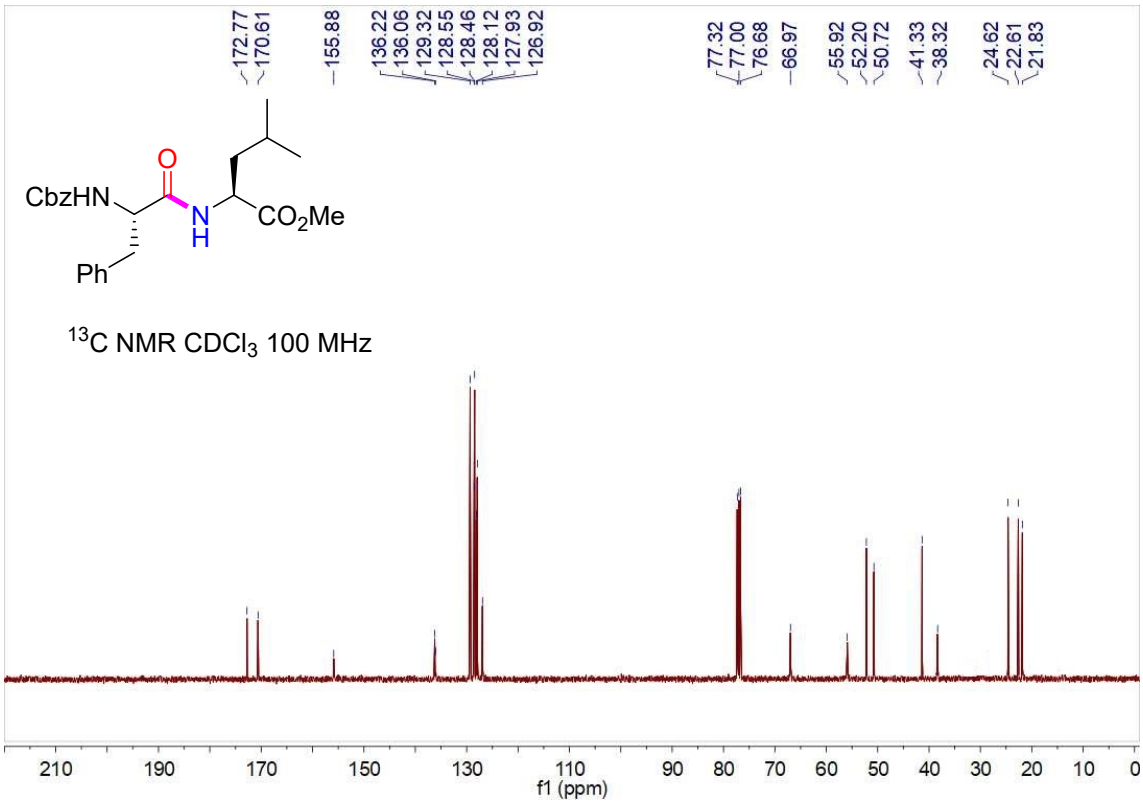
^{13}C NMR $CDCl_3$ 100 MHz



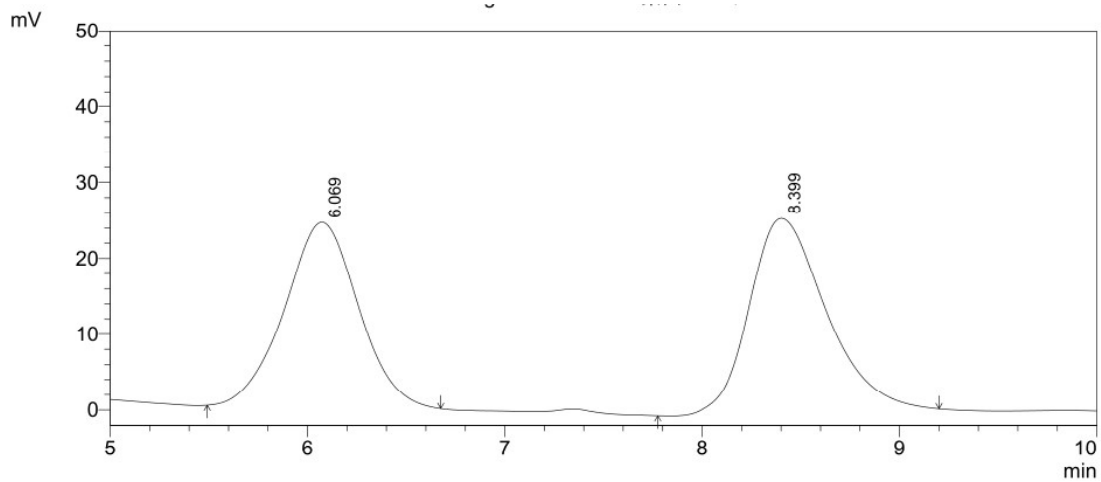
^{1}H NMR $CDCl_3$ 400 MHz


177.75
138.65
128.64
127.59
127.33
77.32
77.00
76.68
43.27
40.60
39.26
36.46
28.08
H
N
O
13C NMR CDCl3 100 MHz
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

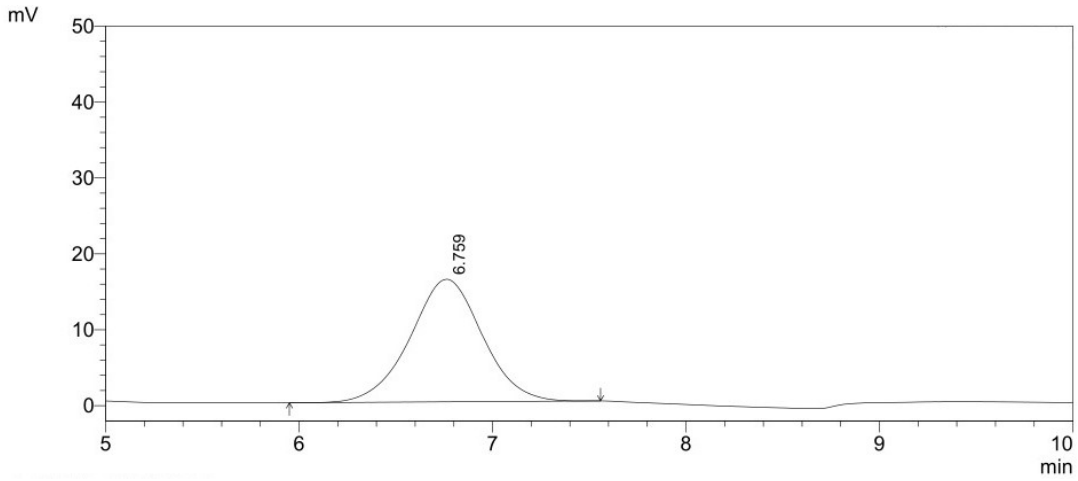

7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.24
7.23
7.22
7.18
7.17
6.41
5.46
5.44
5.07
4.56
4.55
4.54
3.68
3.07
3.06
1.57
1.55
1.54
1.52
1.50
1.47
1.44
1.26
0.89
0.87
O
CbzHN
N
H
CO2Me
Ph
1H NMR CDCl3 400 MHz
4.90
2.76
2.00
0.95
0.96
2.00
1.89
2.97
2.01
3.24
6.16
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)



Chromatogram (NIS-NHC)

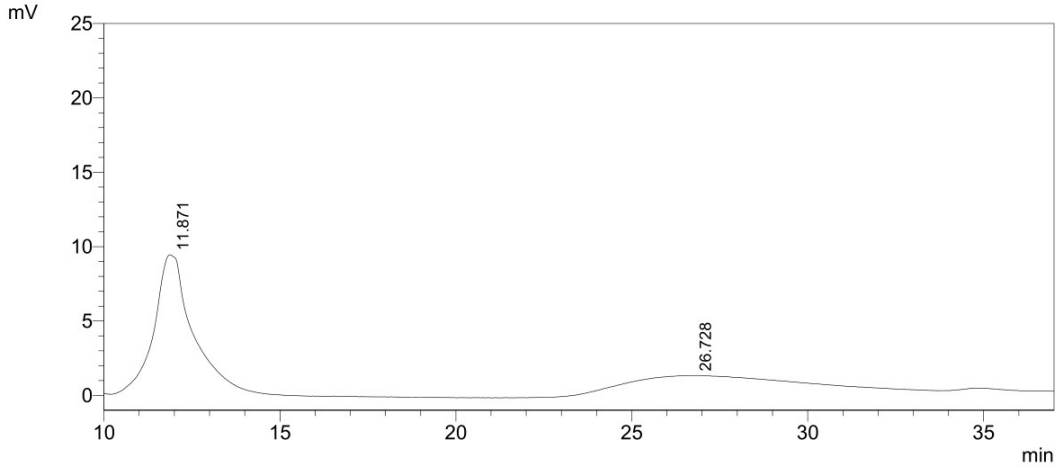


Peak No	Ret. Time	Area	Height	Area %	Height%
1	6.069	634854	24343	47.872	48.712
2	8.399	691301	25631	52.128	51.288
Total		1326155	49974	100.000	100.000

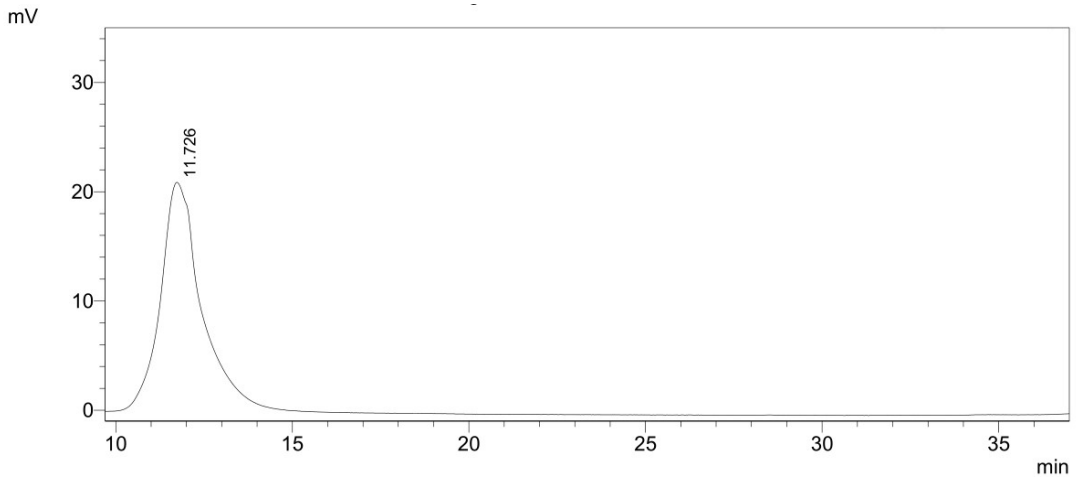


Peak No	Ret. Time	Area	Height	Area %	Height%
1	6.759	418648	16134	100.000	100.000
Total		418648	16134	100.000	100.000

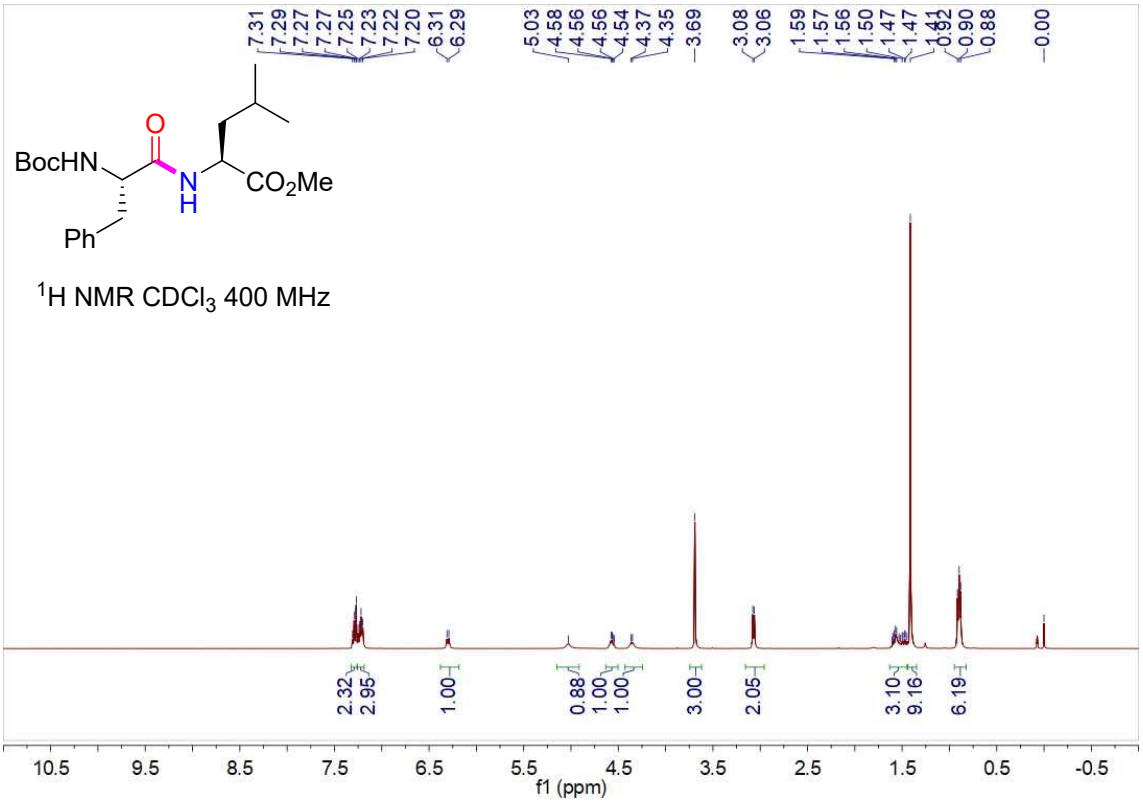
Chromatogram ($K_2S_2O_8$-NHC)

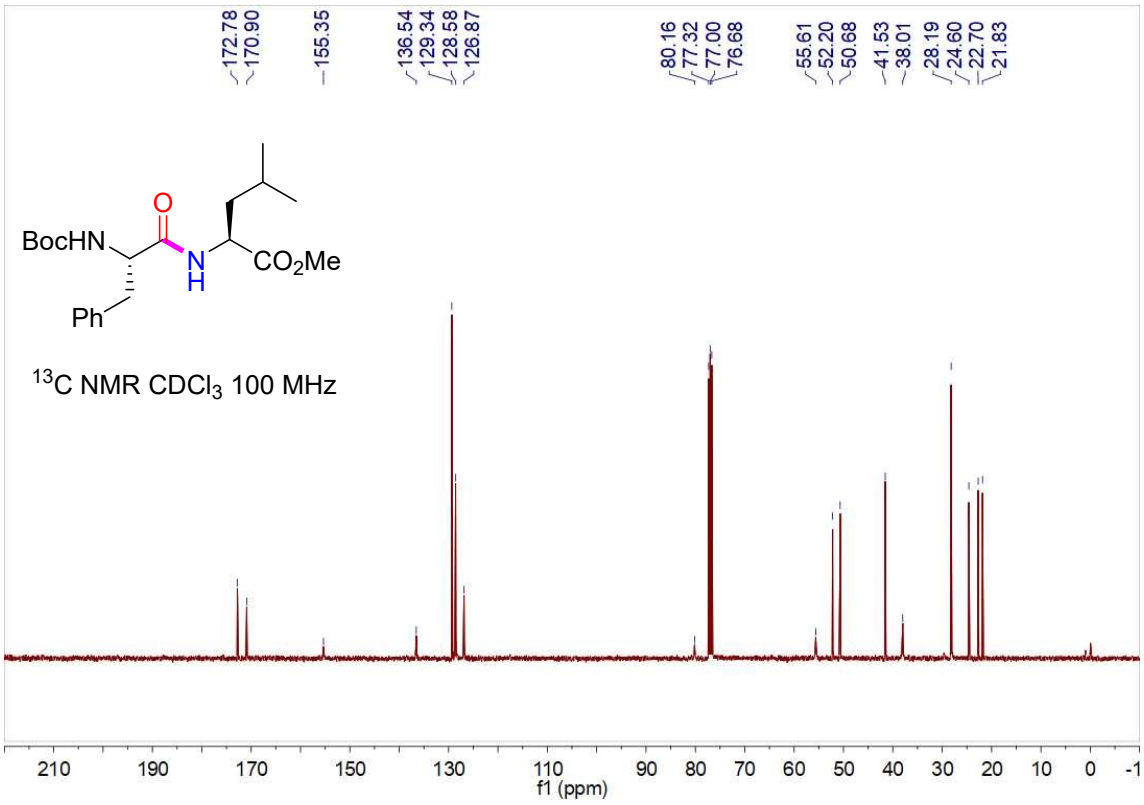


Peak No	Ret. Time	Area	Height	Area %	Height%
1	11.871	511582	8324	51.094	86.168
2	26.728	489678	1336	48.906	13.832
Total		1001260	9660	100.000	100.000

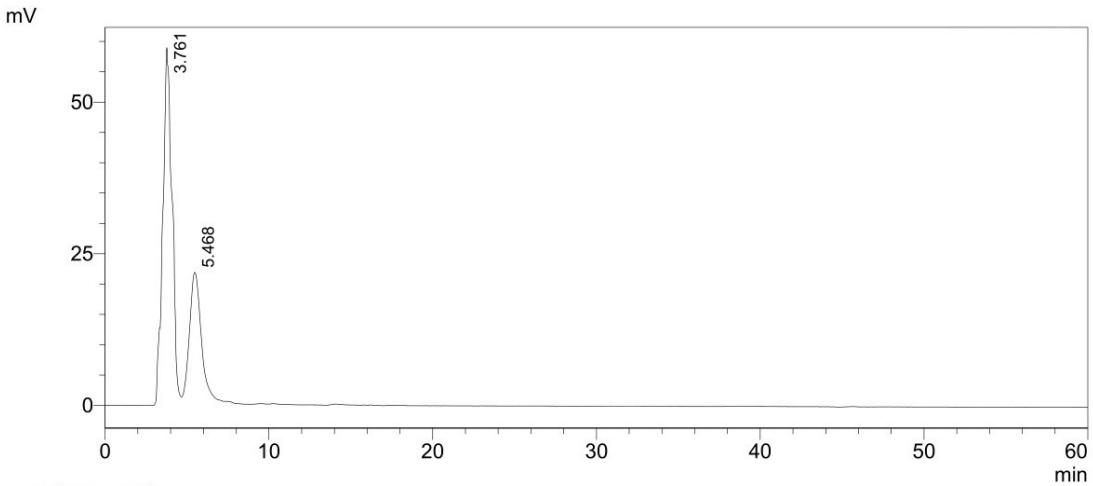


Peak No	Ret. Time	Area	Height	Area %	Height%
1	11.726	1654196	20784	100.000	100.000
Total		1654196	20784	100.000	100.000

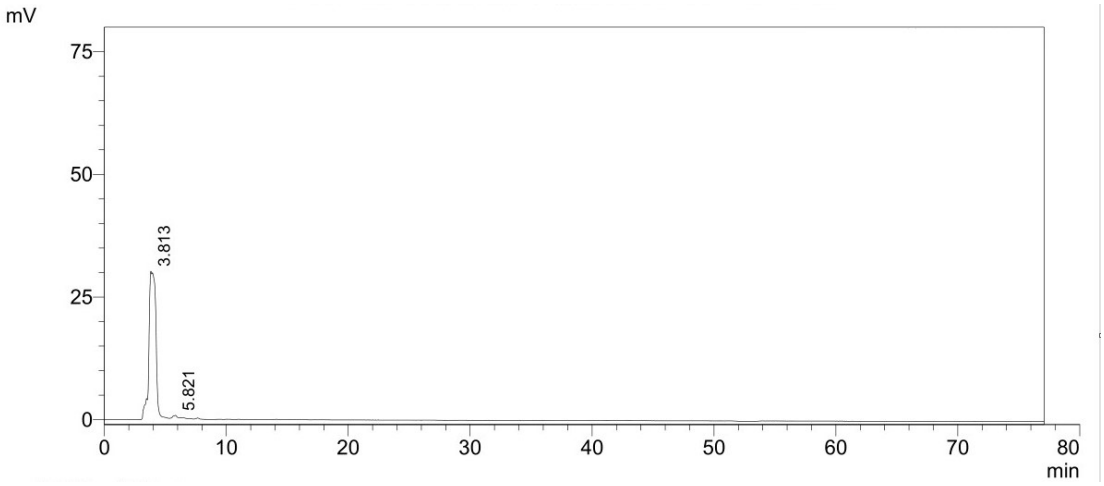




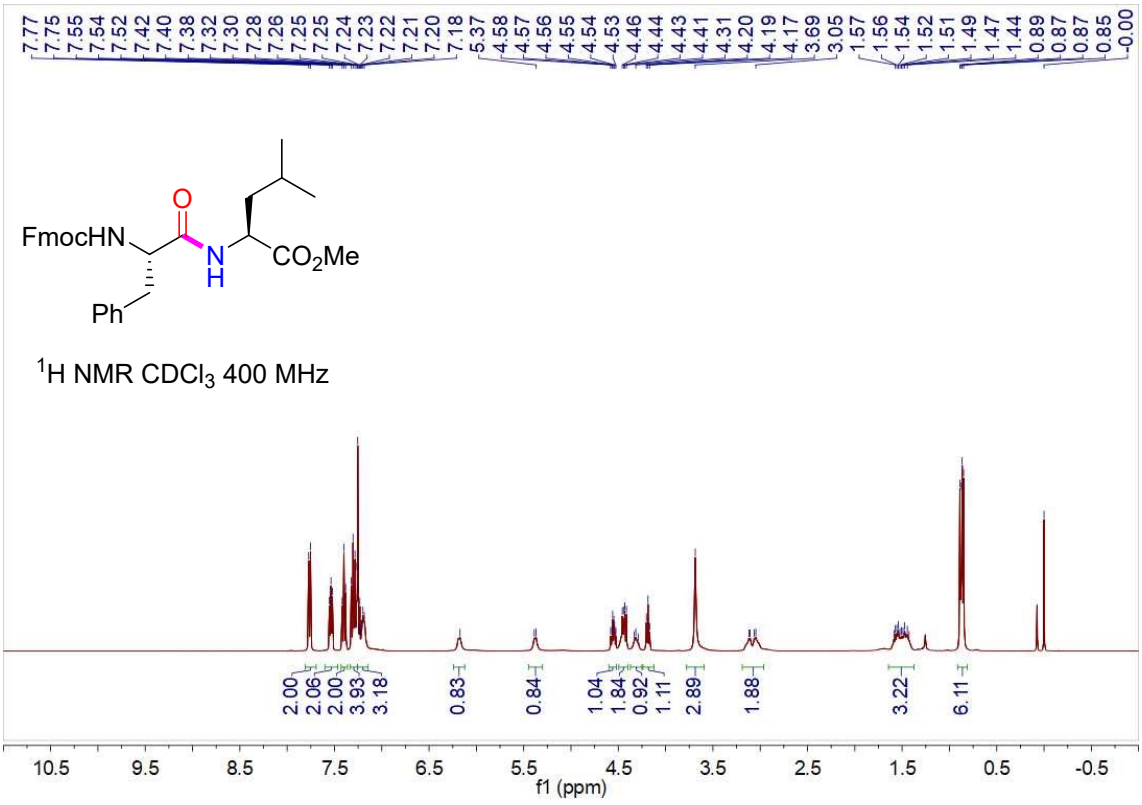
Chromatogram

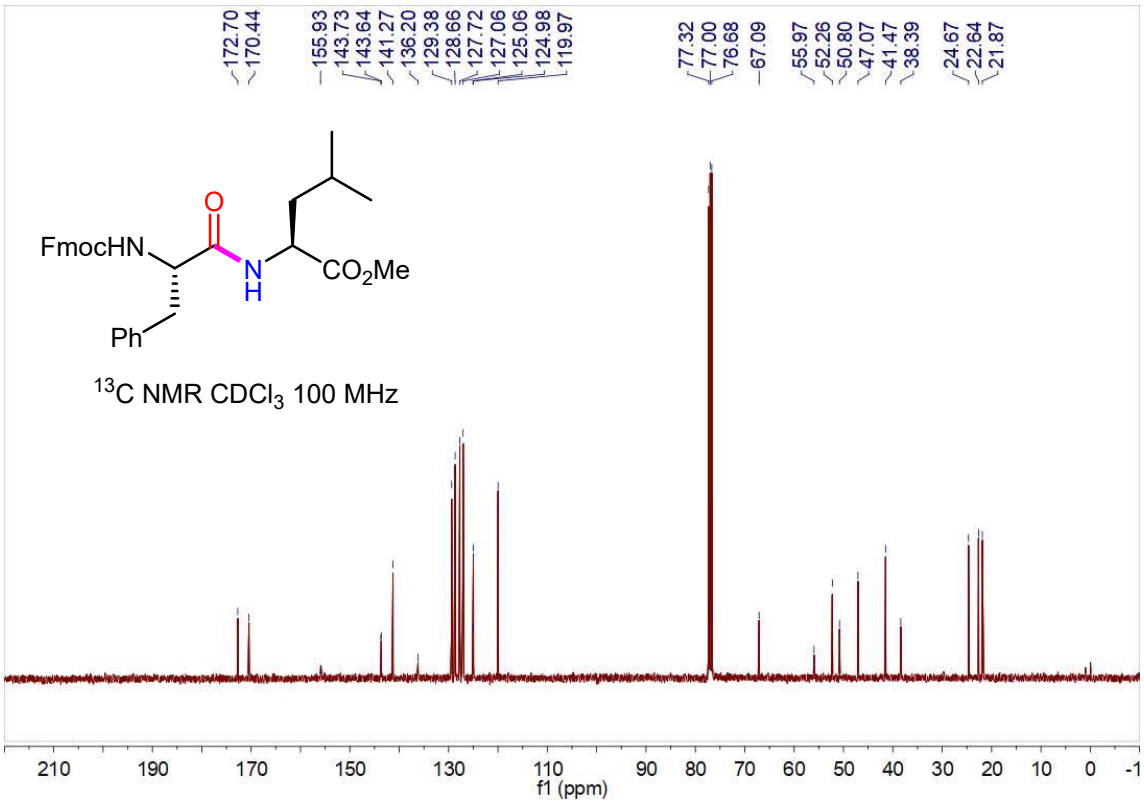


Peak No	Ret. Time	Area	Height	Area %	Height%
1	3.761	1160289	42338	53.928	67.132
2	5.468	991243	20728	46.072	32.868
Total		2151532	63066	100.000	100.000

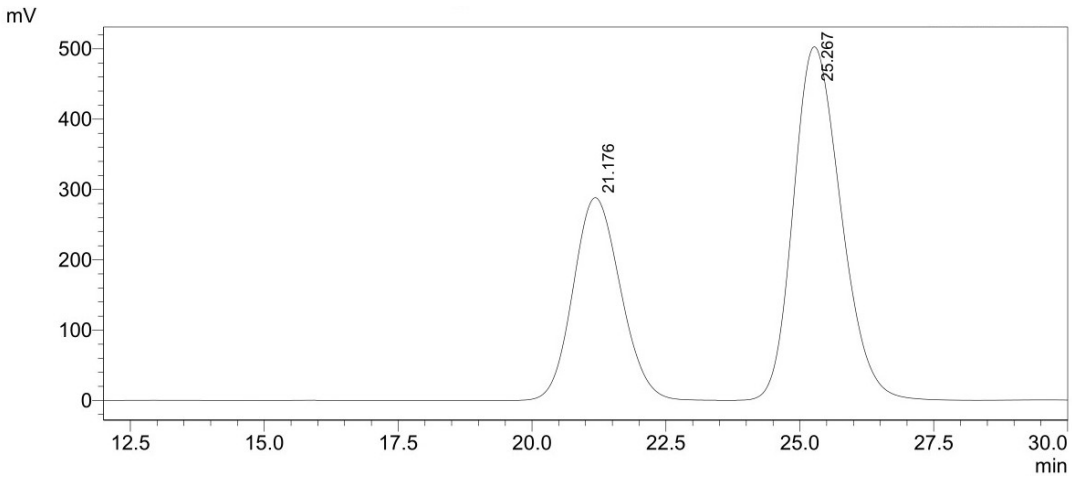


Peak No	Ret. Time	Area	Height	Area %	Height%
1	3.813	1003465	28048	98.095	97.790
2	5.821	19487	634	1.905	2.210
Total		1022952	28682	100.000	100.000

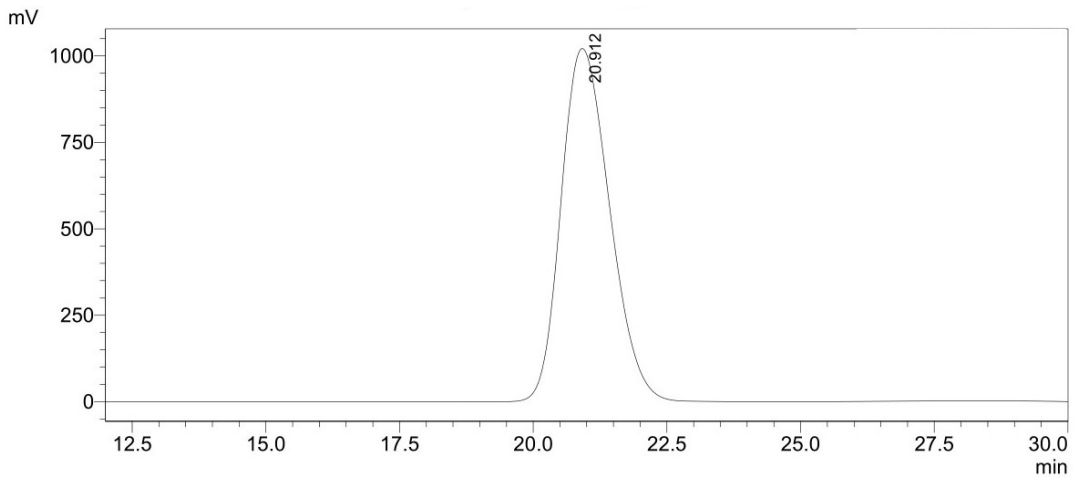




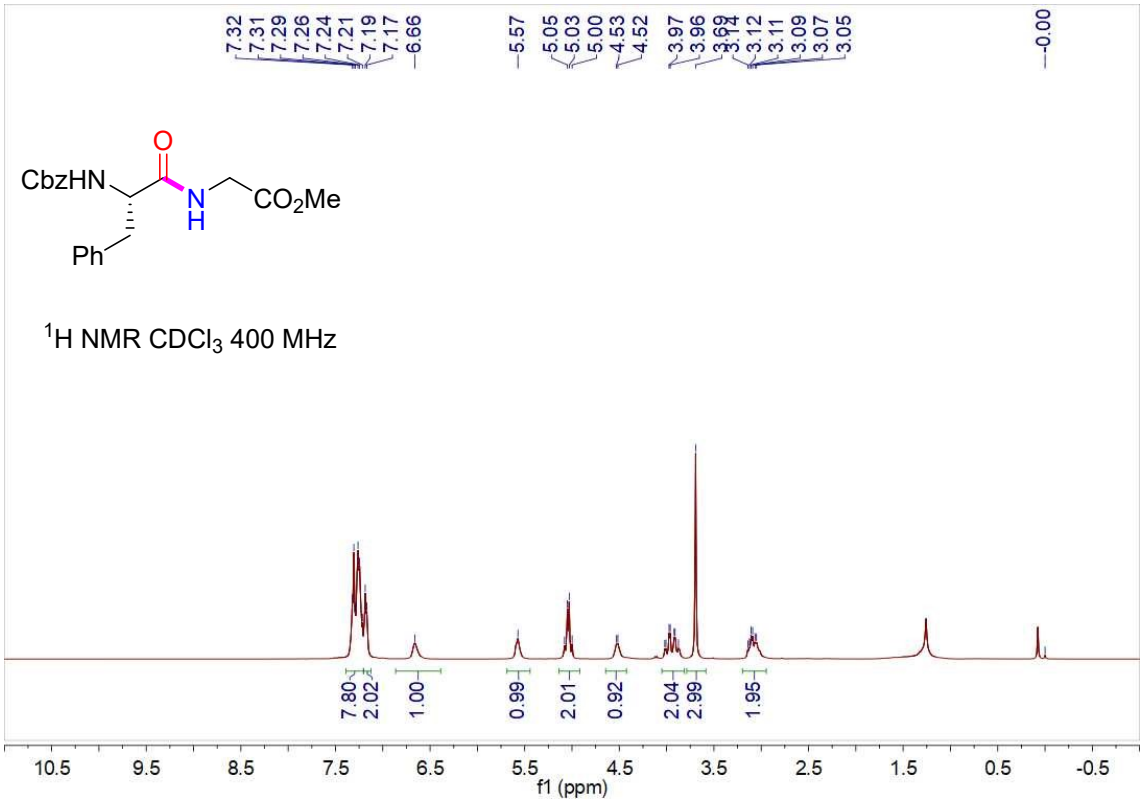
Chromatogram

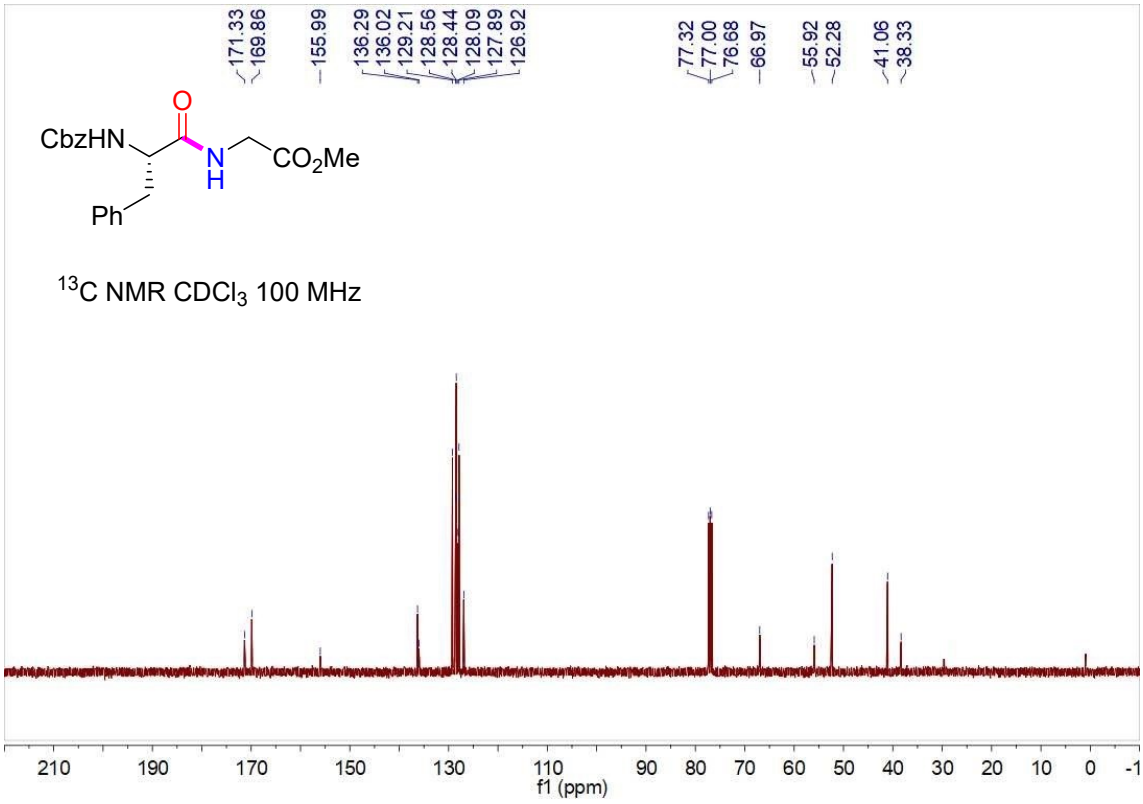


Peak No	Ret. Time	Area	Height	Area %	Height%
1	21.176	17494772	286935	36.068	36.343
2	25.267	31010482	502576	63.932	63.657
Total		48505254	789511	100.000	100.000

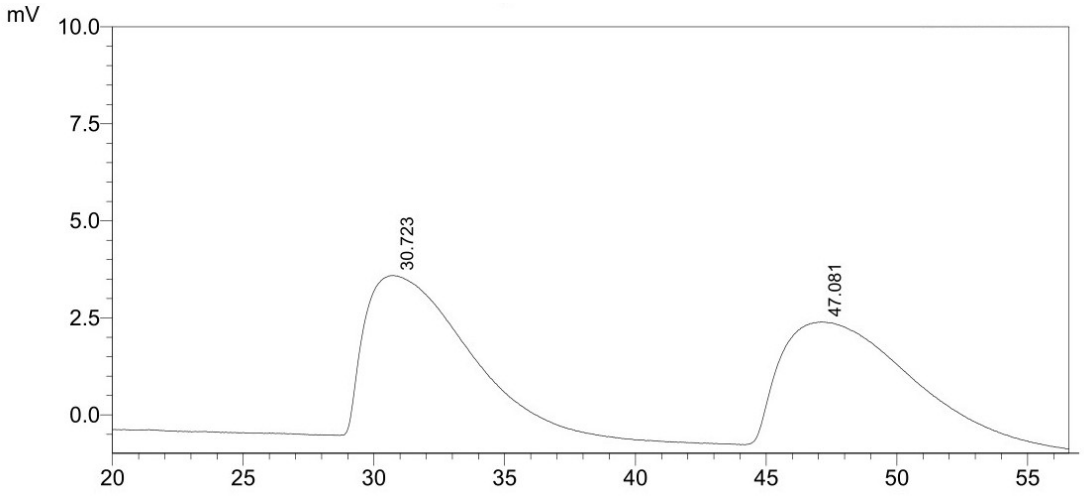


Peak No	Ret. Time	Area	Height	Area %	Height%
1	20.912	64404158	1021013	100.000	100.000
Total		64404158	1021013	100.000	100.000

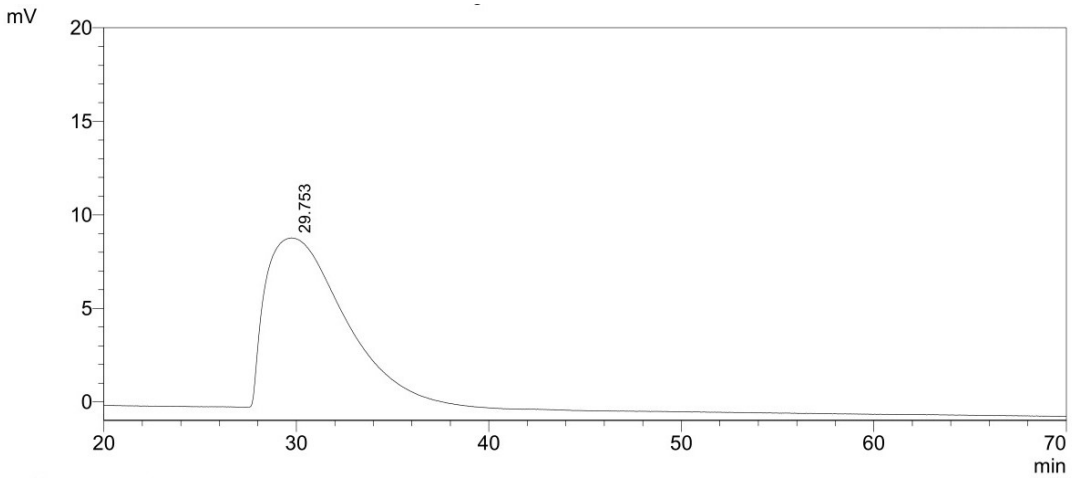




Chromatogram (NIS-NHC)

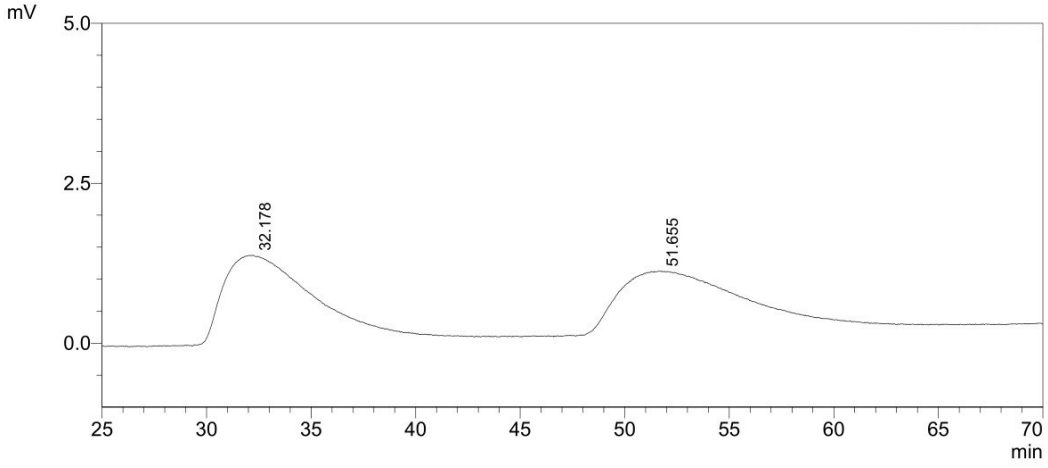


Peak No	Ret. Time	Area	Height	Area %	Height%
1	30.723	1119037	4119	50.087	56.387
2	47.081	1115156	3186	49.913	43.613
Total		22234193	7305	100.000	100.000

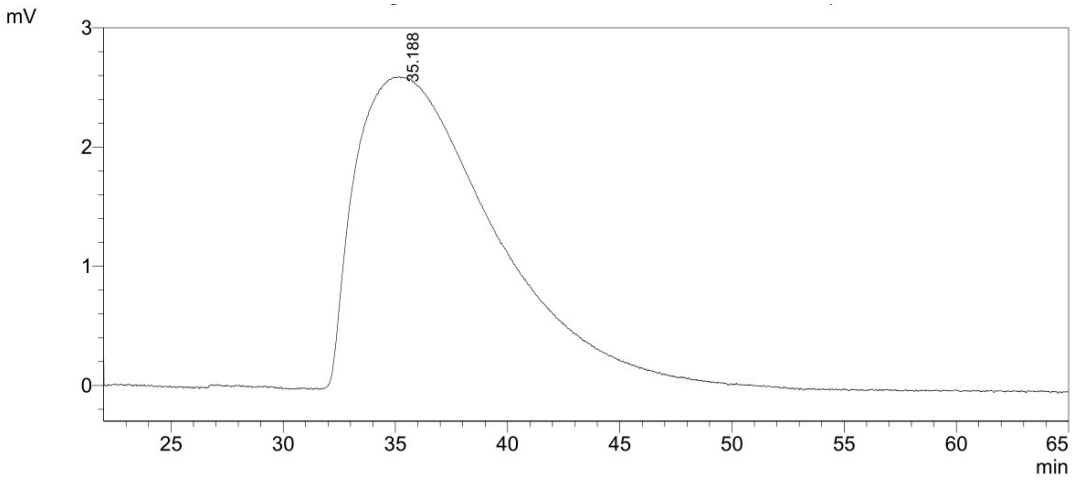


Peak No	Ret. Time	Area	Height	Area %	Height%
1	29.753	2648667	9076	100.000	100.000
Total		2648667	9076	100.000	100.000

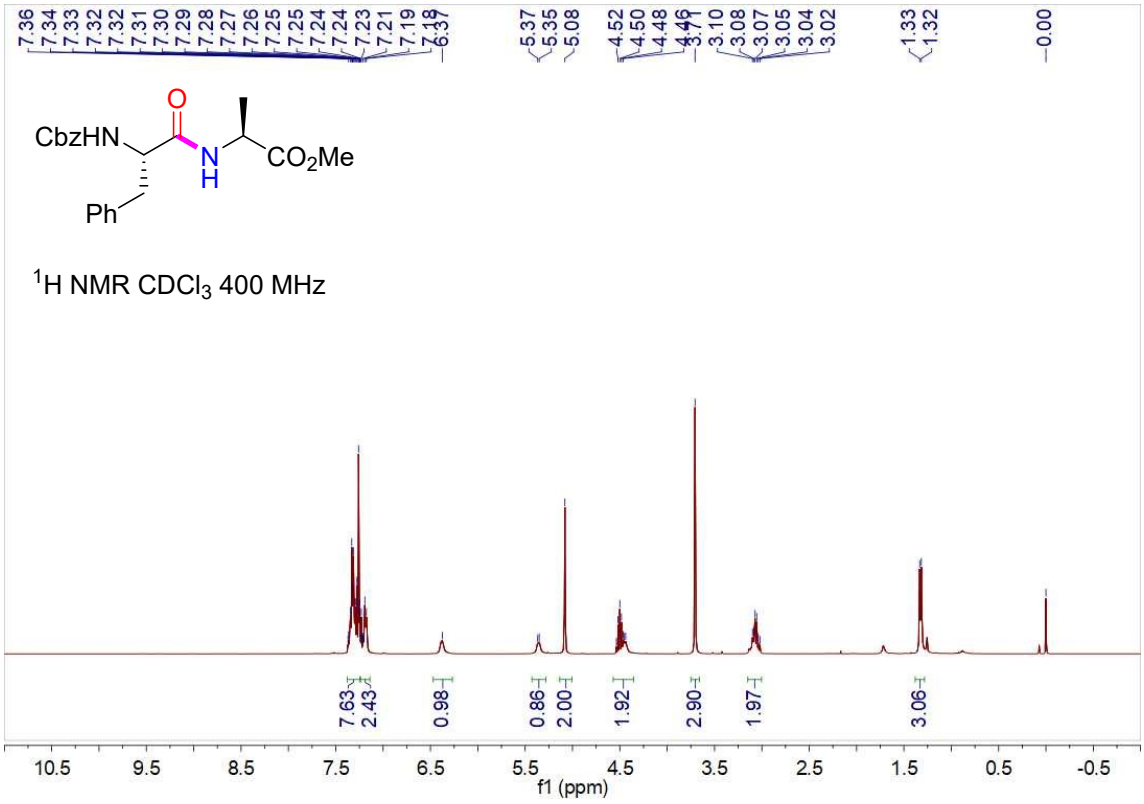
Chromatogram ($K_2S_2O_8$-NHC)

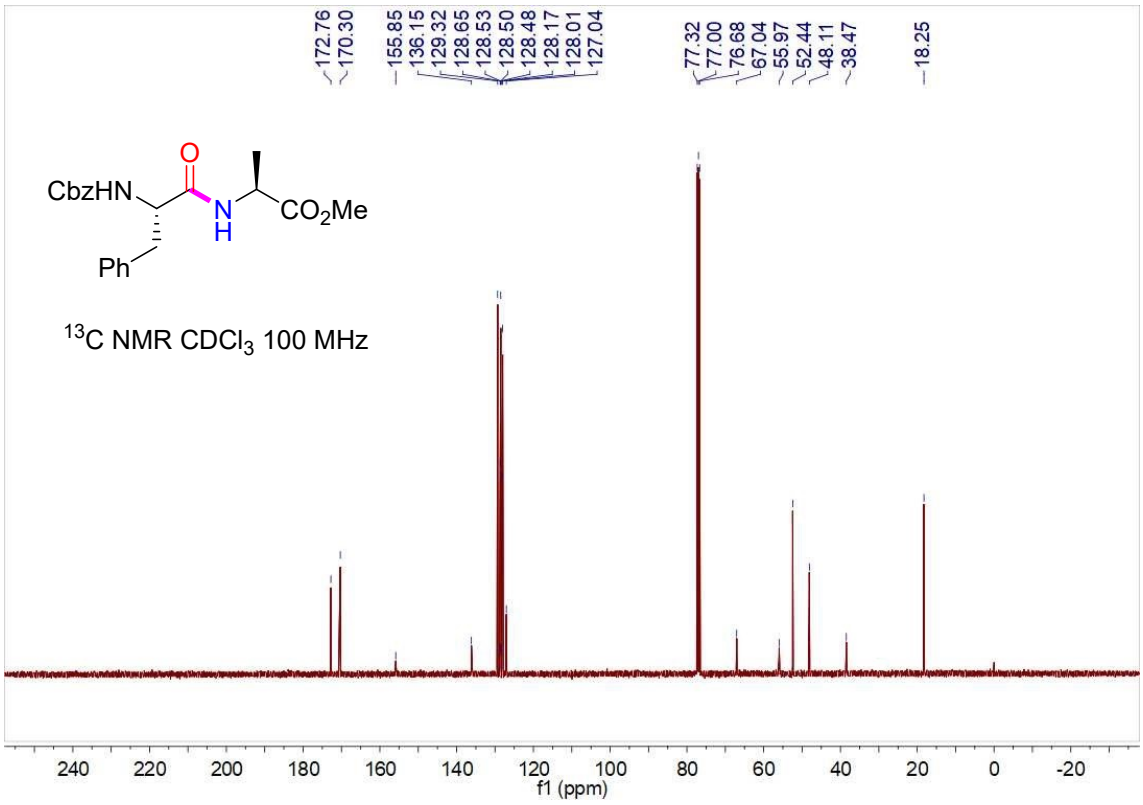


Peak No	Ret. Time	Area	Height	Area %	Height%
1	32.178	358275	1329	51.633	59.106
2	51.655	335612	920	48.367	40.894
Total		693887	2249	100.000	100.000

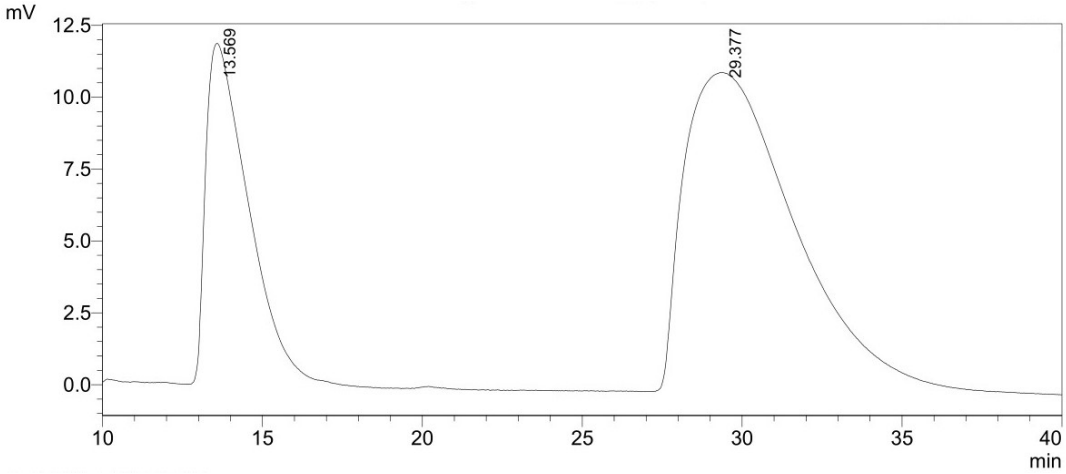


Peak No	Ret. Time	Area	Height	Area %	Height%
1	35.188	958365	2510	100.000	100.000
Total		958365	2510	100.000	100.000

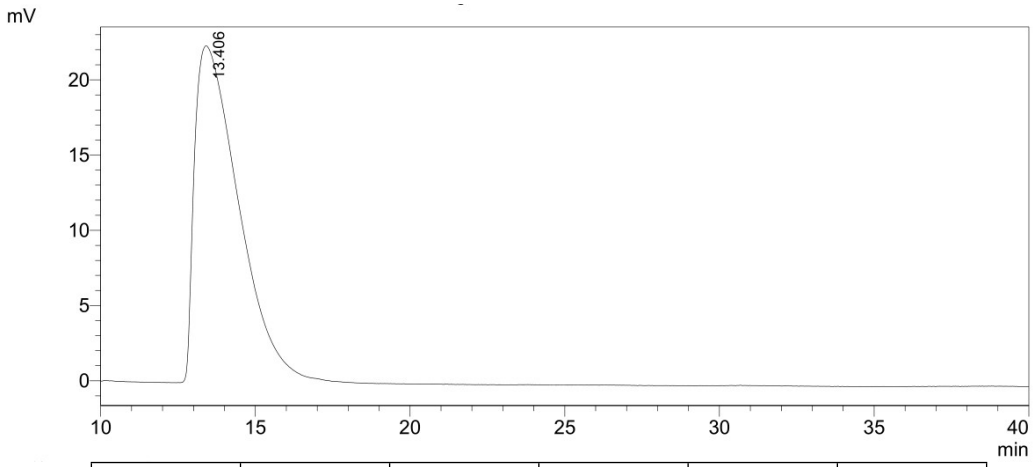




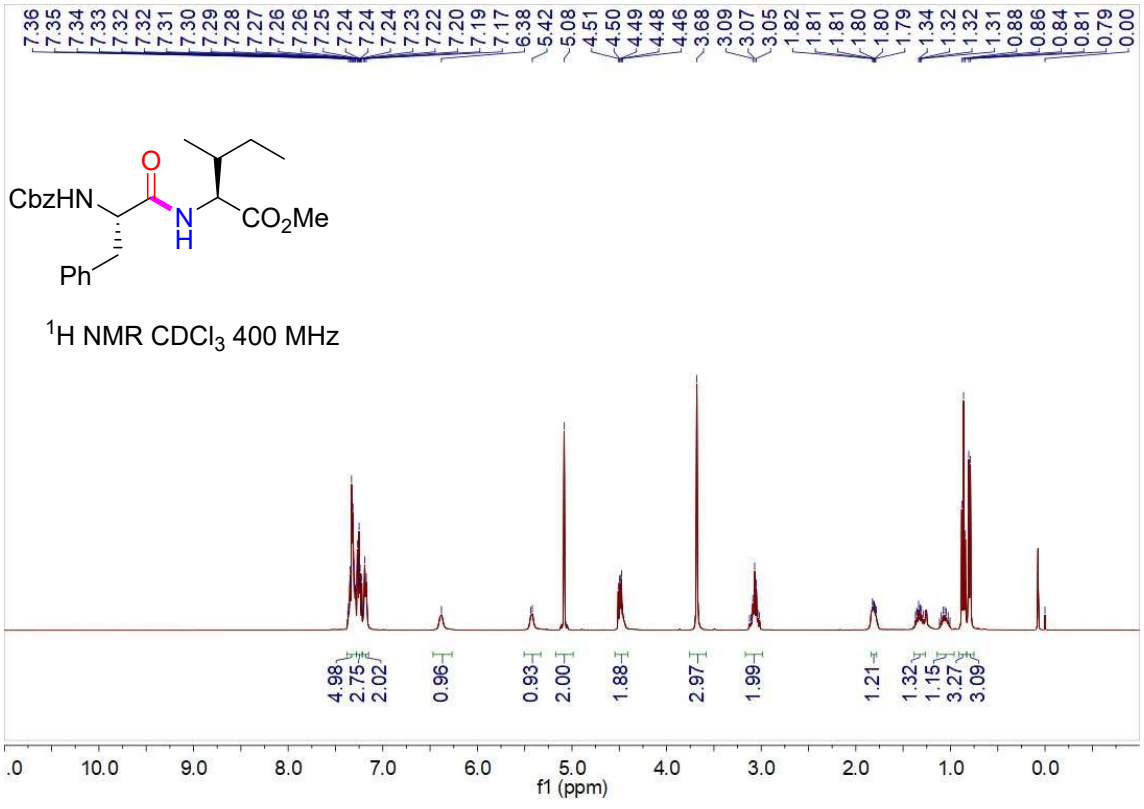
Chromatogram

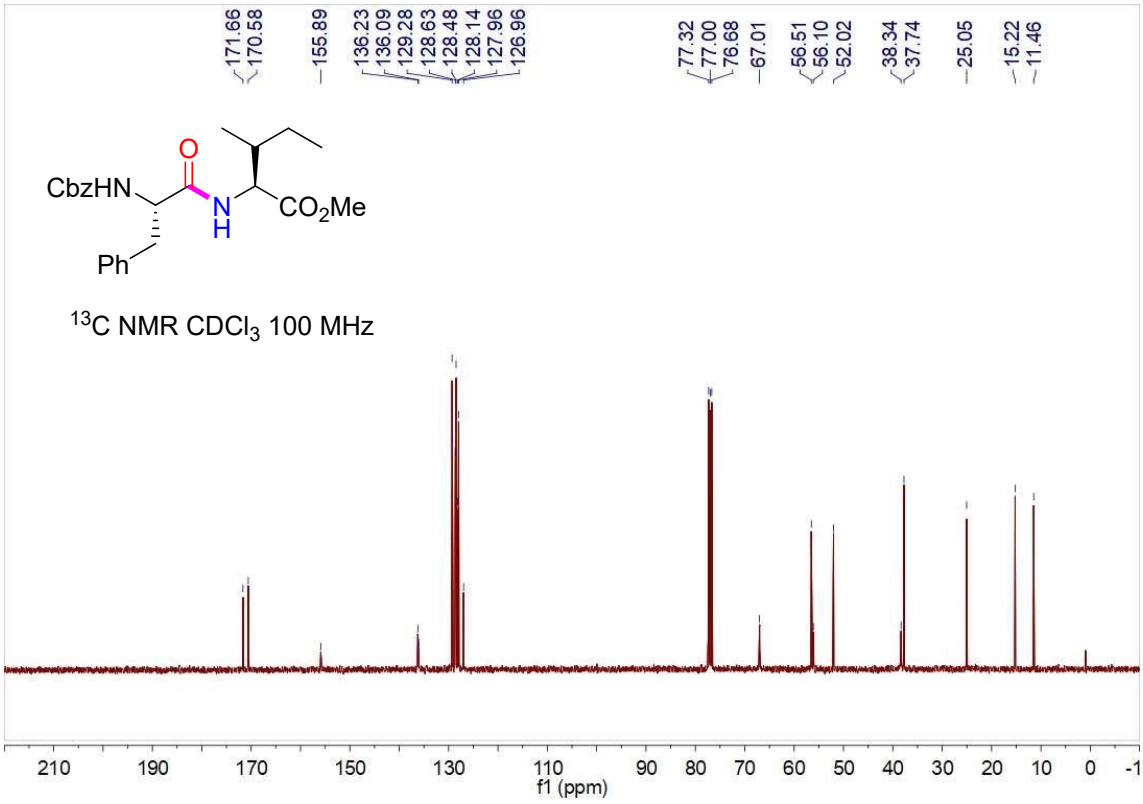


Peak No	Ret. Time	Area	Height	Area %	Height%
1	13.569	1106242	11838	50.683	64.159
2	29.377	1076442	6613	49.317	35.841
Total		2182684	18451	100.000	100.000

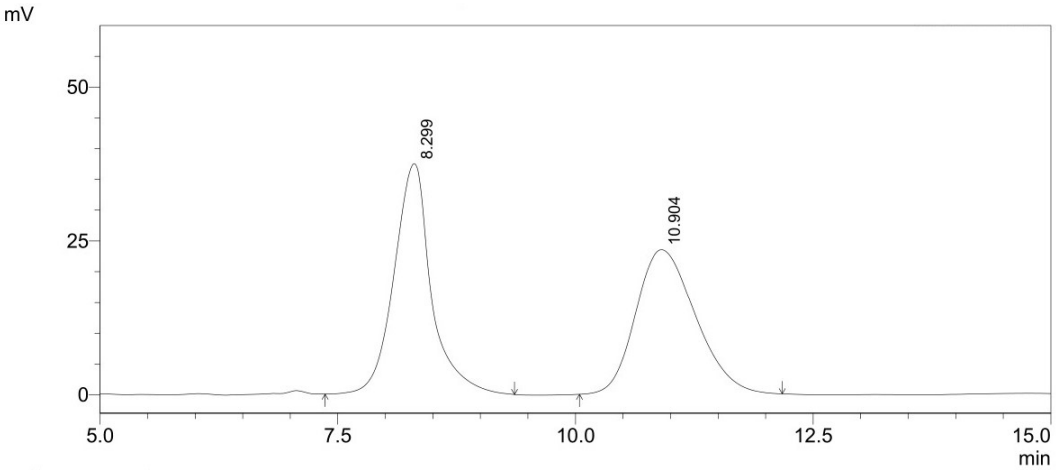


Peak No	Ret. Time	Area	Height	Area %	Height%
1	13.406	2210823	22364	100.000	100.000
Total		2210823	22364	100.000	100.000

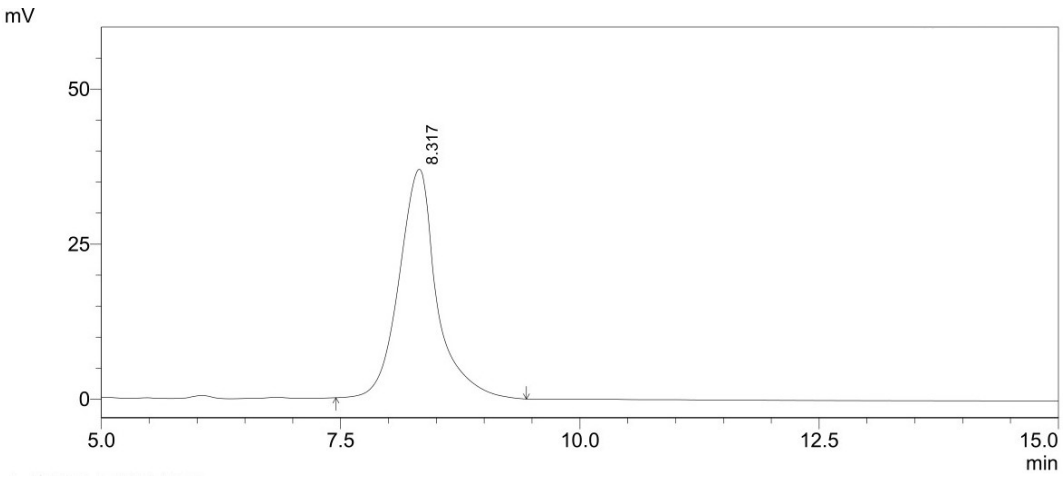




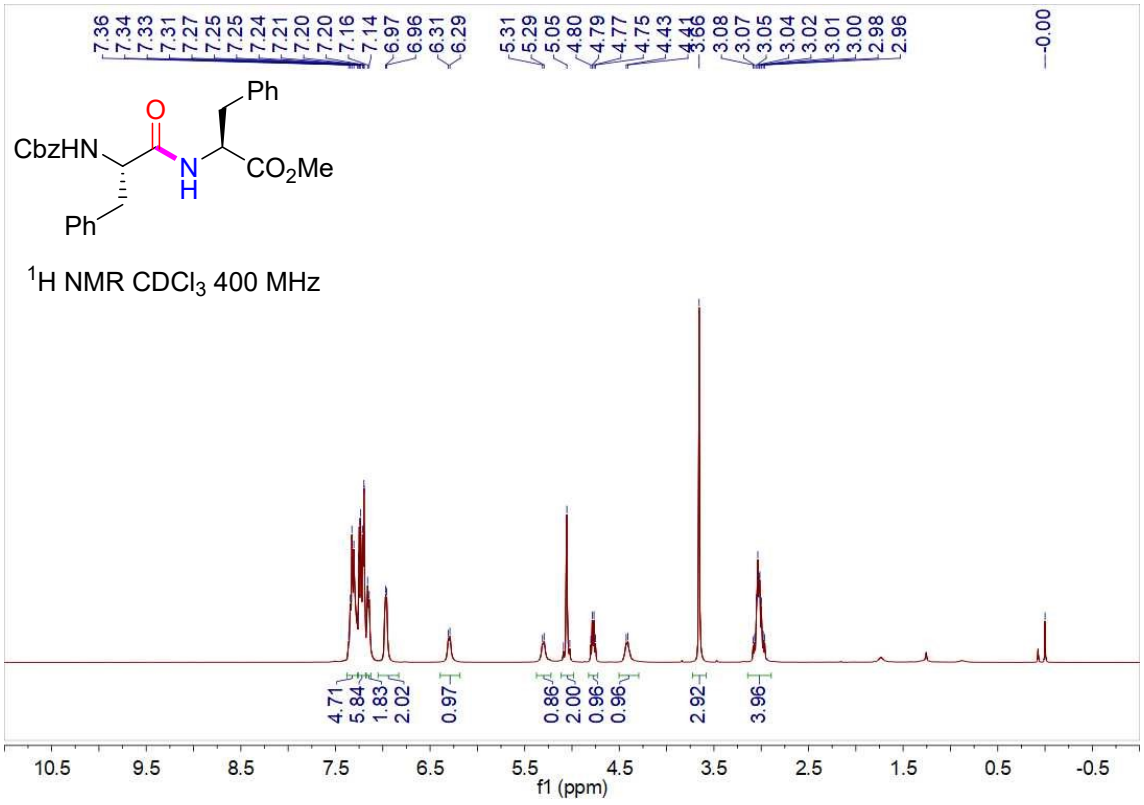
Chromatogram

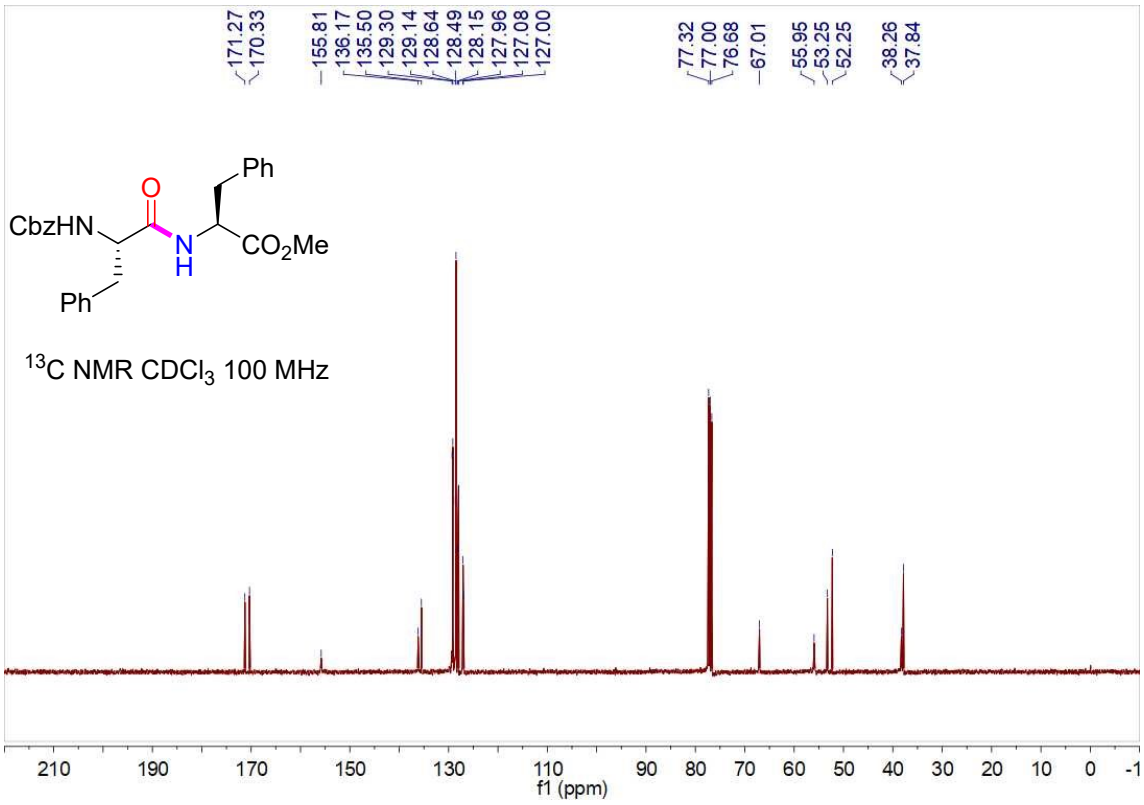


Peak No	Ret. Time	Area	Height	Area %	Height%
1	8.299	1022480	37476	49.934	61.477
2	10.904	1025200	23486	50.066	38.523
Total		2047680	60959	100.000	100.000

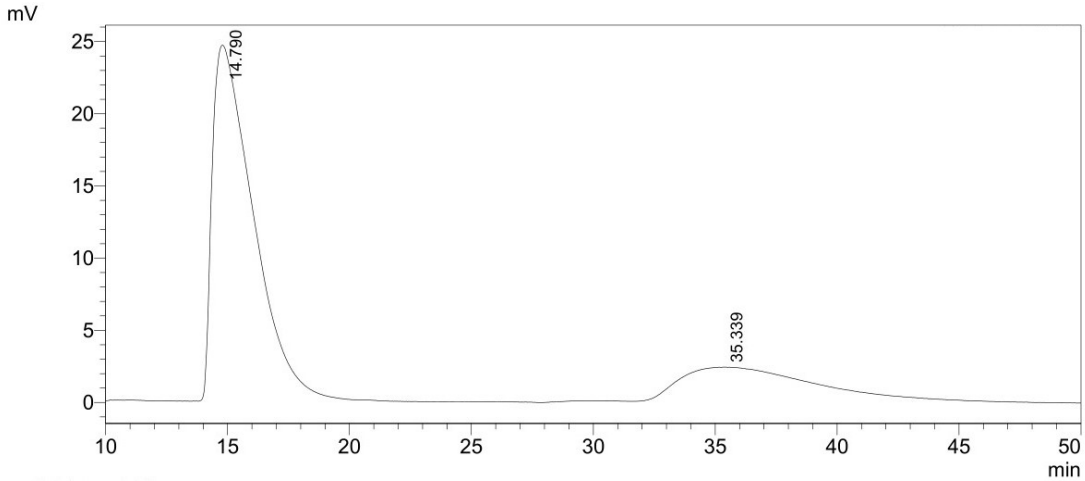


Peak No	Ret. Time	Area	Height	Area %	Height%
1	8.317	1016427	36919	100.000	100.000
Total		1016427	36919	100.000	100.000

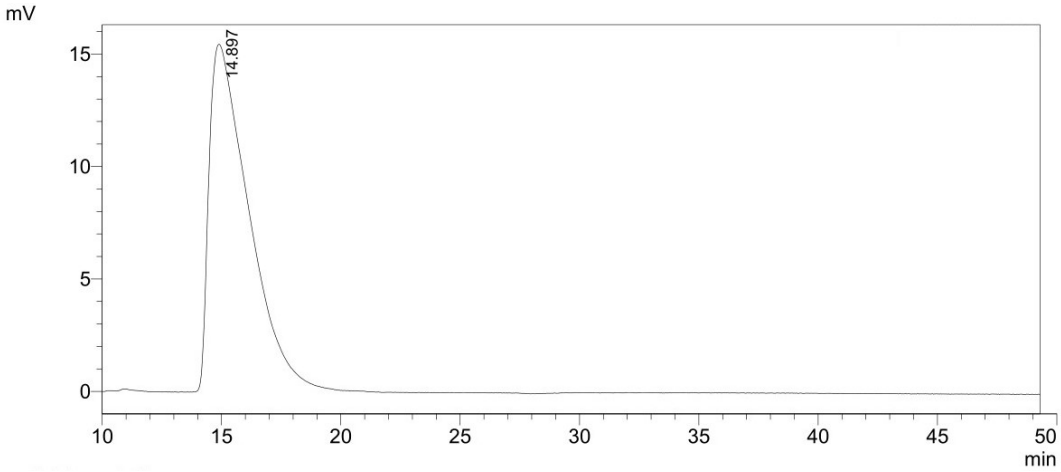




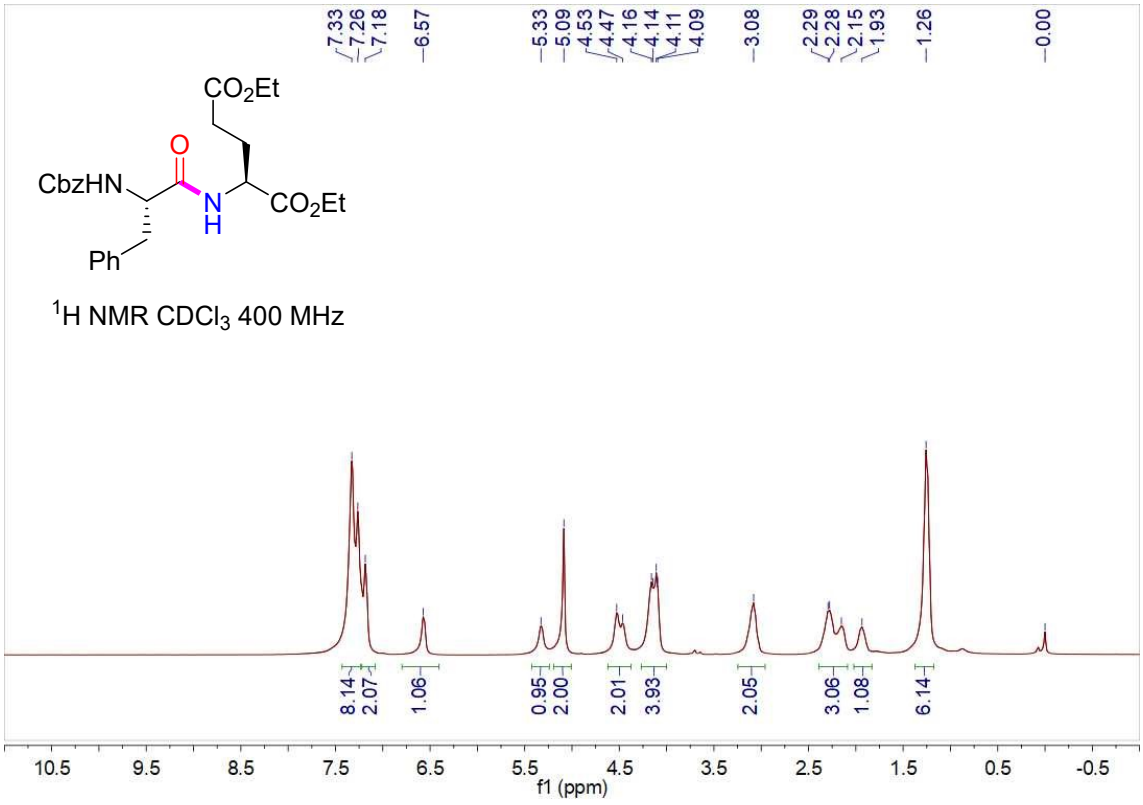
Chromatogram

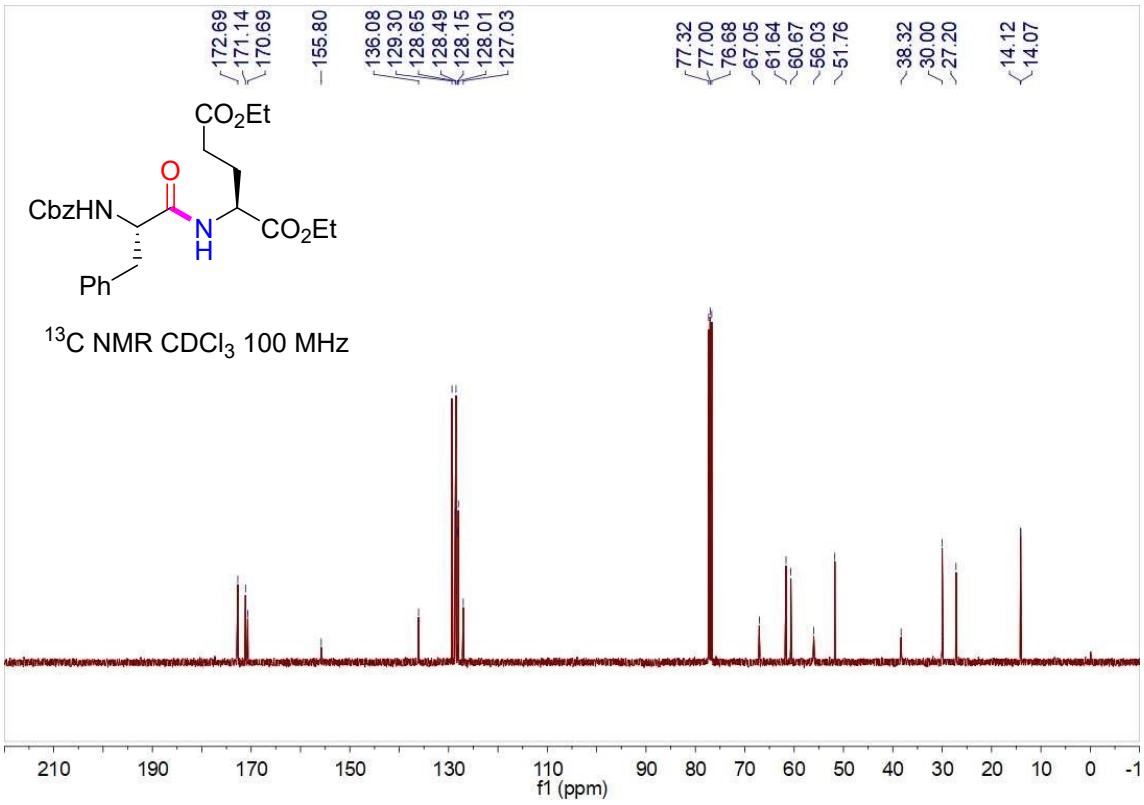


Peak No	Ret. Time	Area	Height	Area %	Height%
1	14.790	2784034	24498	74.995	91.176
2	35.339	928270	2371	25.005	8.824
Total		3712304	26869	100.000	100.000

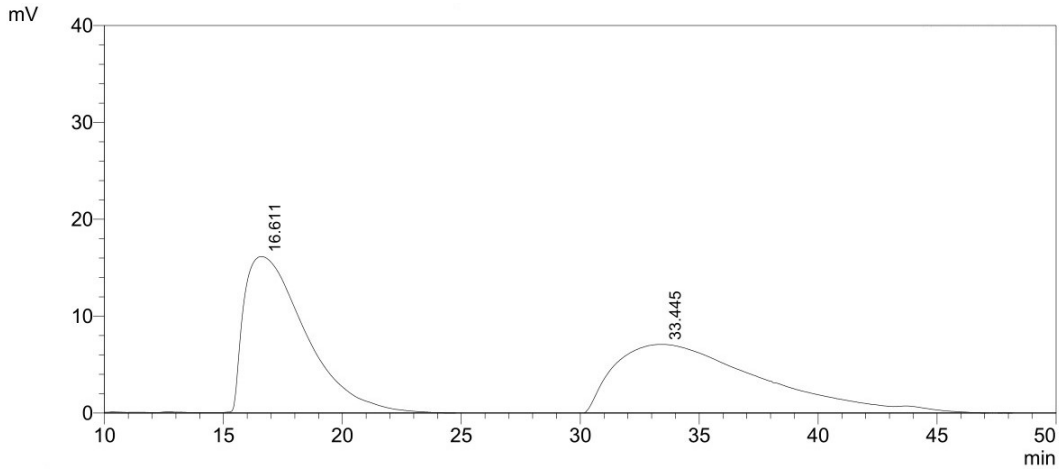


Peak No	Ret. Time	Area	Height	Area %	Height%
1	14.897	1736436	15392	100.000	100.000
Total		1736436	15392	100.000	100.000

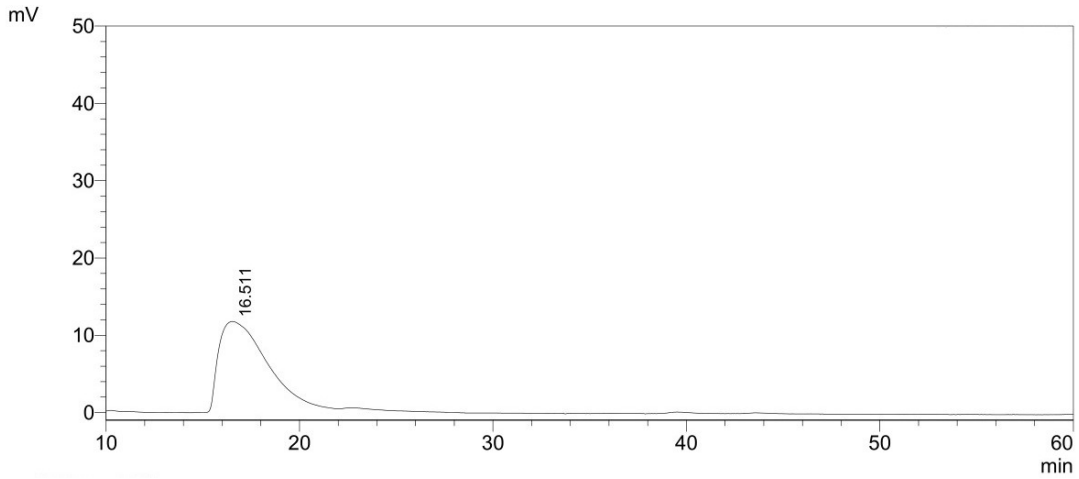




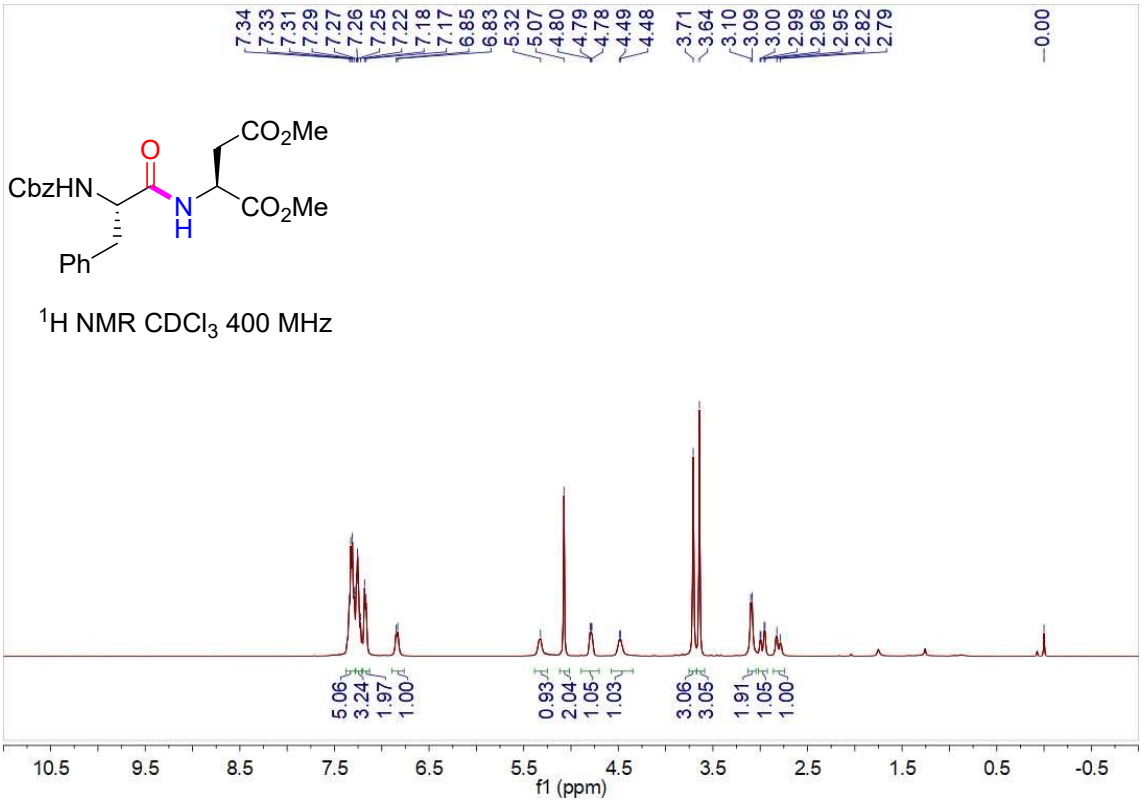
Chromatogram

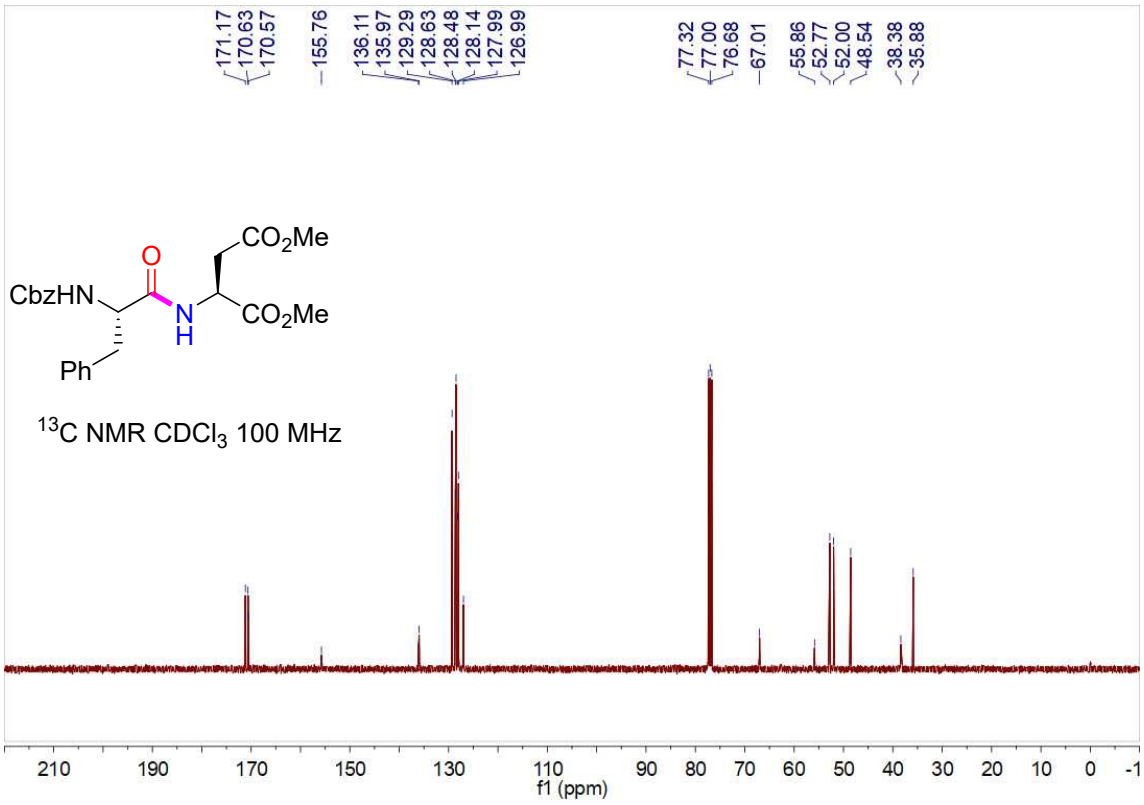


Peak No	Ret. Time	Area	Height	Area %	Height%
1	16.611	2817232	16021	51.212	69.686
2	33.445	2683929	6969	48.788	30.314
Total		5501161	22990	100.000	100.000

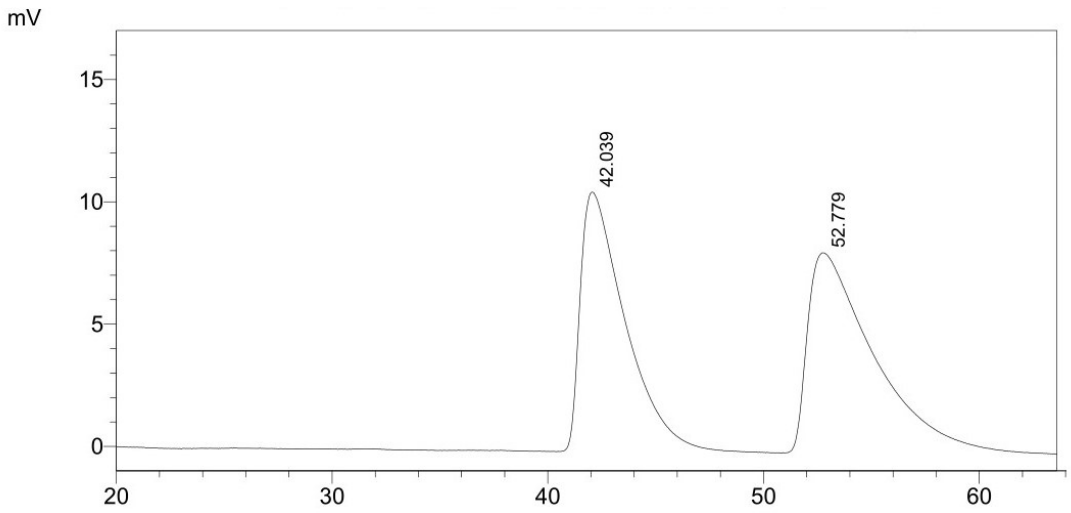


Peak No	Ret. Time	Area	Height	Area %	Height%
1	16.511	1989921	11656	100.000	100.000
Total		1989921	11656	100.000	100.000

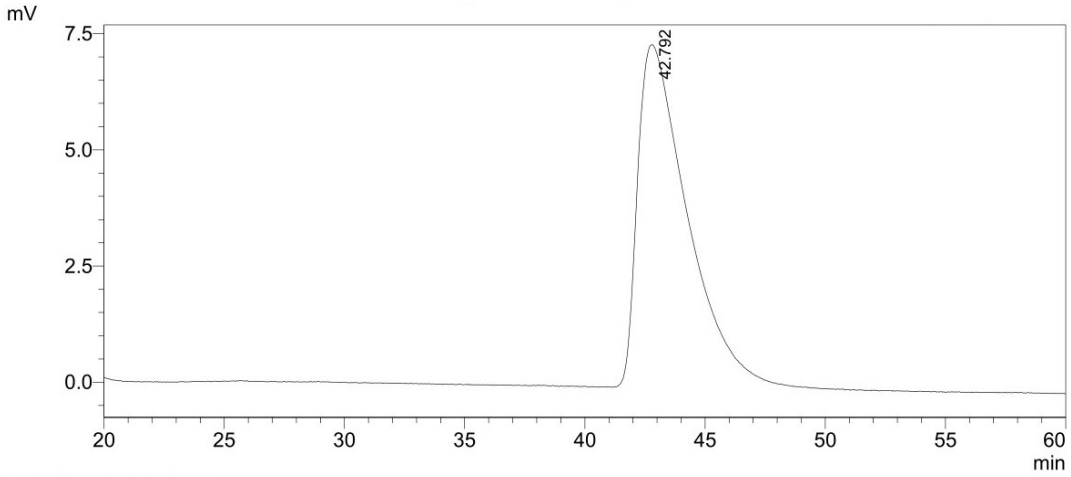




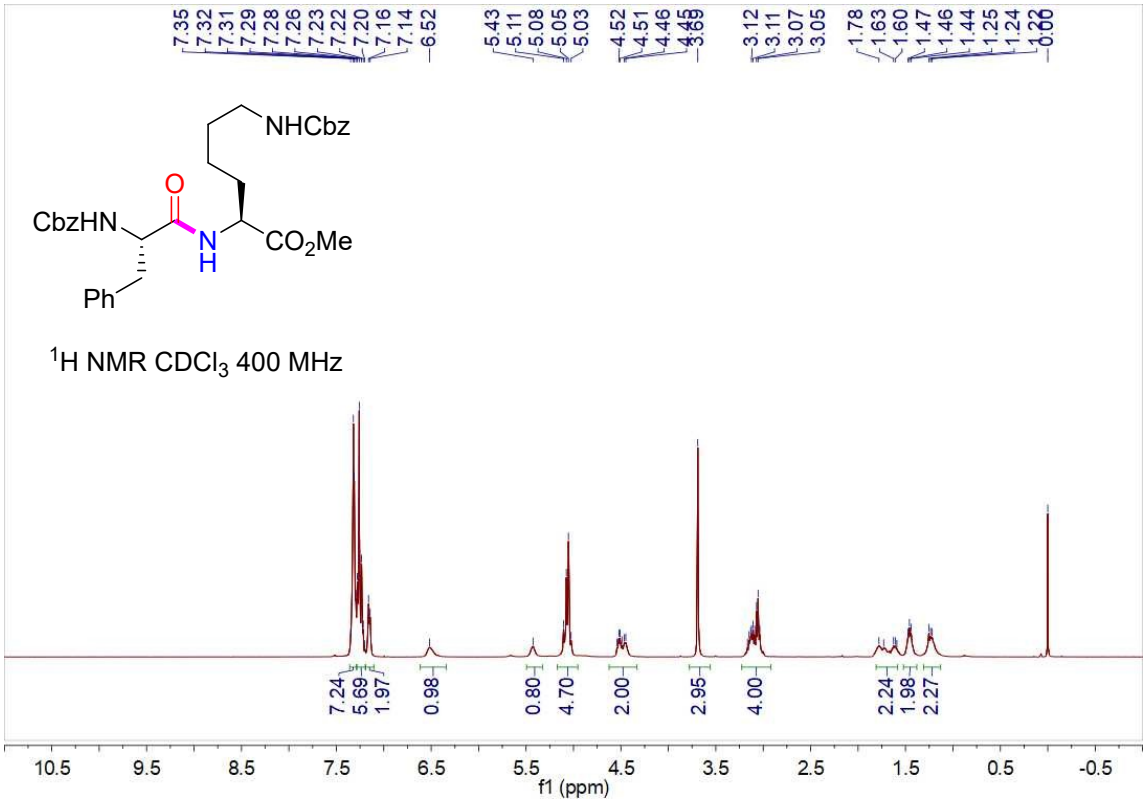
Chromatogram

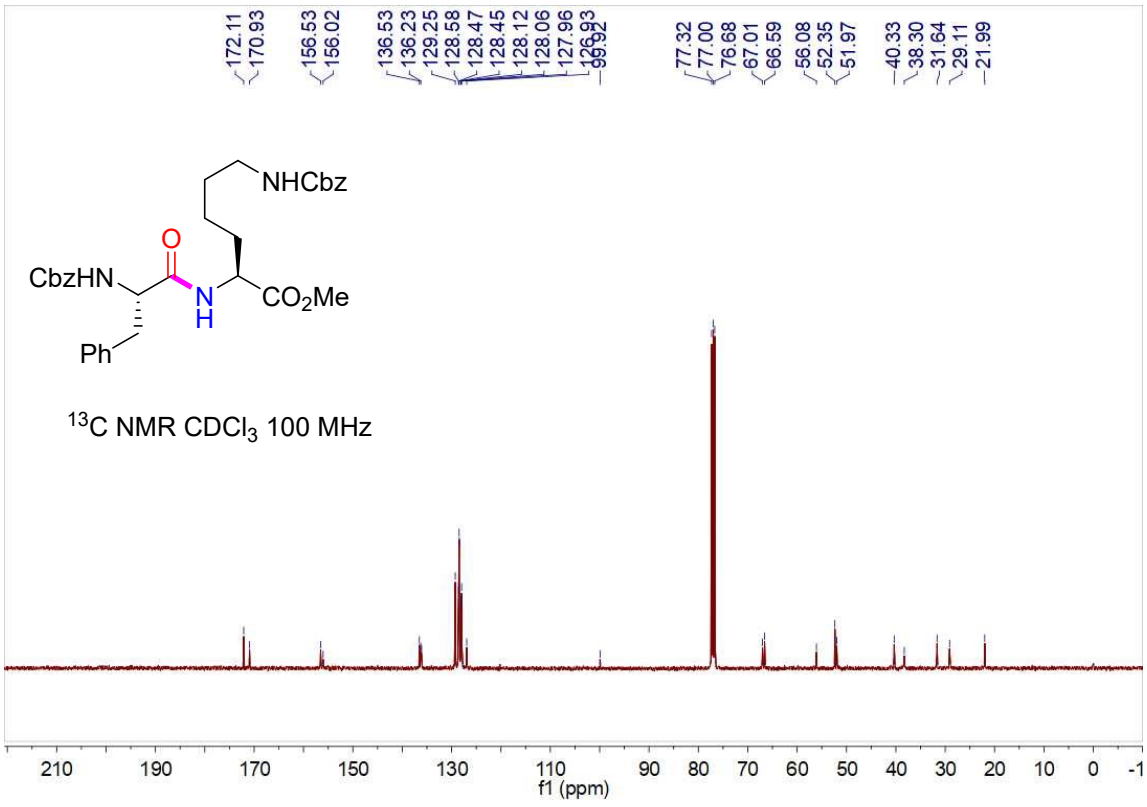


Peak No	Ret. Time	Area	Height	Area %	Height%
1	42.039	1496503	10559	51.519	58.263
2	52.779	1408274	7564	48.481	41.737
Total		2904777	18122	100.000	100.000

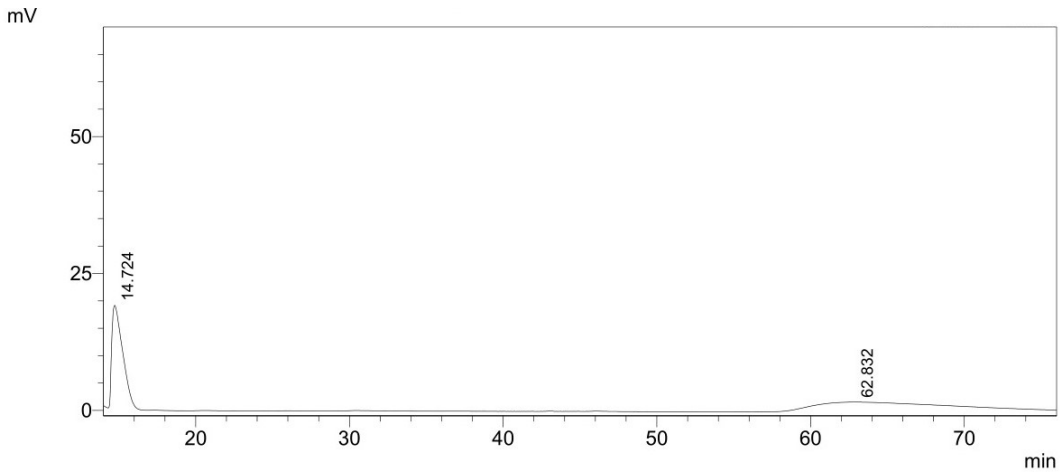


Peak No	Ret. Time	Area	Height	Area %	Height%
1	42.792	909497	6918	100.000	100.000
Total		909497	6918	100.000	100.000

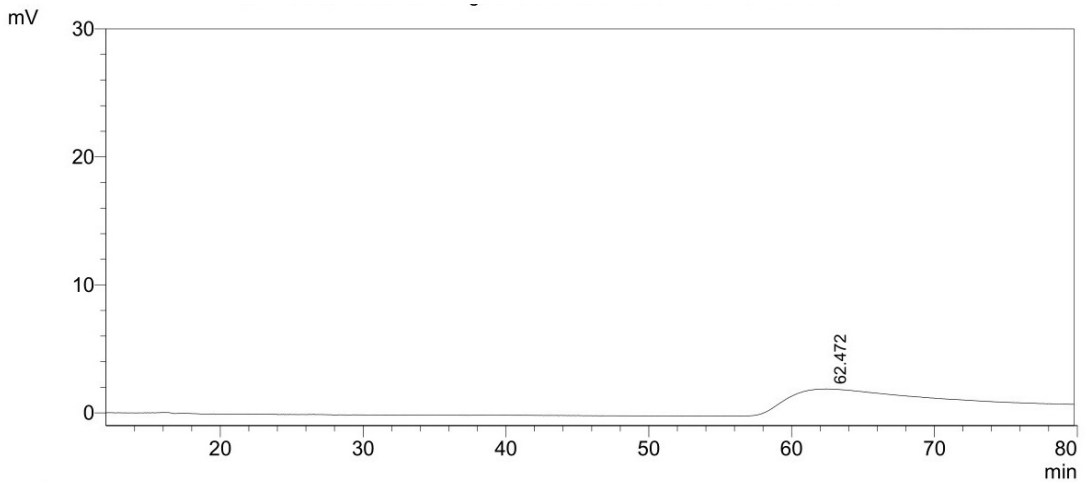




Chromatogram (NIS-NHC)

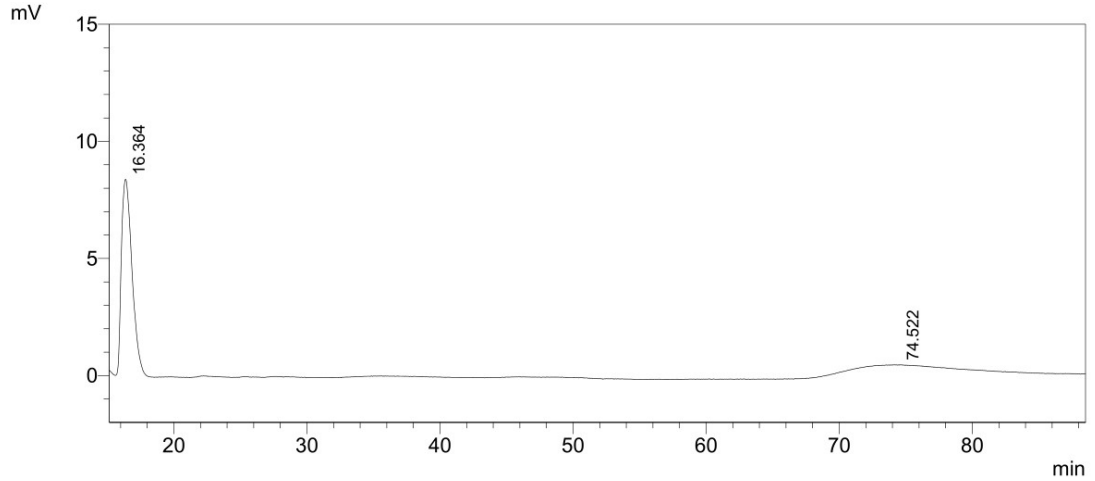


Peak No	Ret. Time	Area	Height	Area %	Height%
1	14.724	871845	18537	48.883	91.907
2	62.832	911696	1632	51.117	8.093
Total		1783541	20169	100.000	100.000

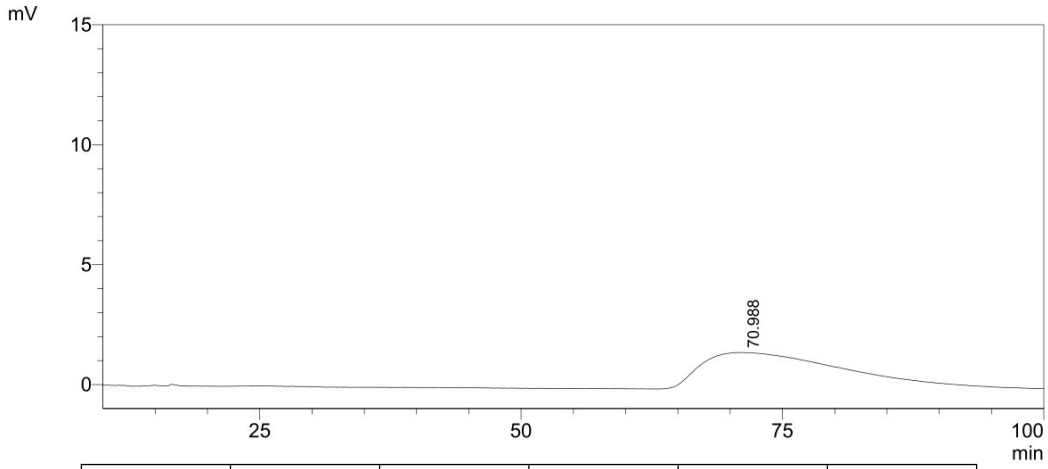


Peak No	Ret. Time	Area	Height	Area %	Height%
1	62.472	681376	1230	100.000	100.000
Total		681376	1230	100.000	100.000

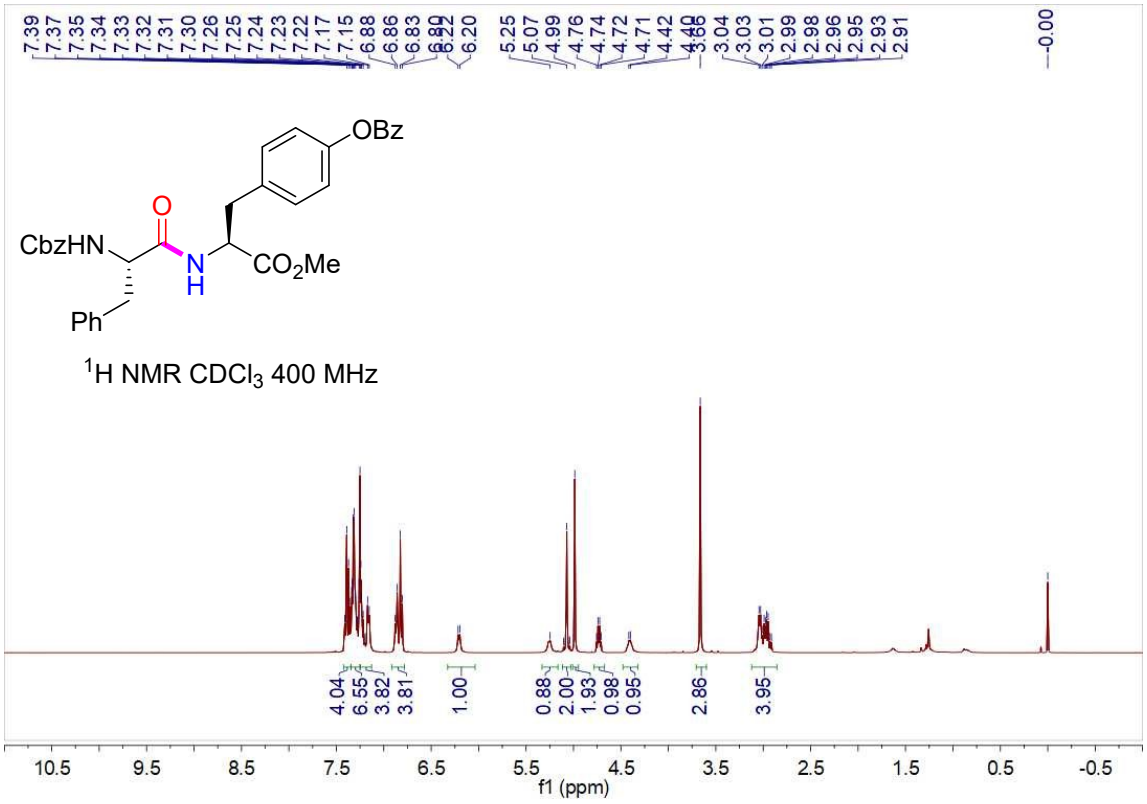
Chromatogram ($K_2S_2O_8$-NHC)

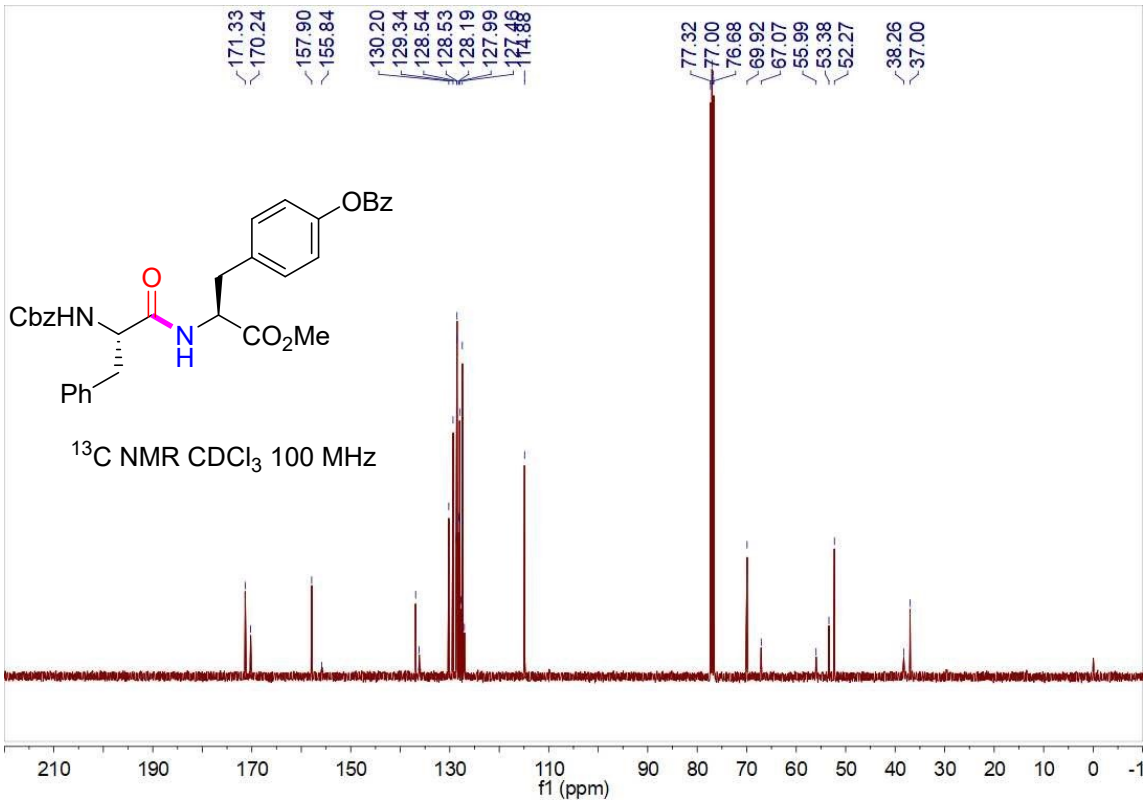


Peak No	Ret. Time	Area	Height	Area %	Height%
1	16.364	342408	7333	49.817	93.392
2	74.522	344920	519	50.183	6.608
Total		687328	7852	100.000	100.000

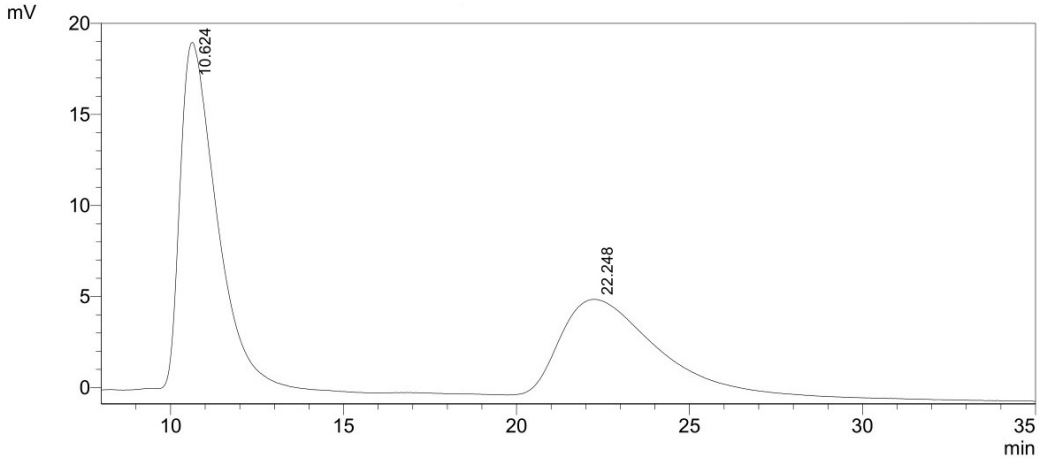


Peak No	Ret. Time	Area	Height	Area %	Height%
1	70.988	310789	564	100.000	100.000
Total		310789	564	100.000	100.000

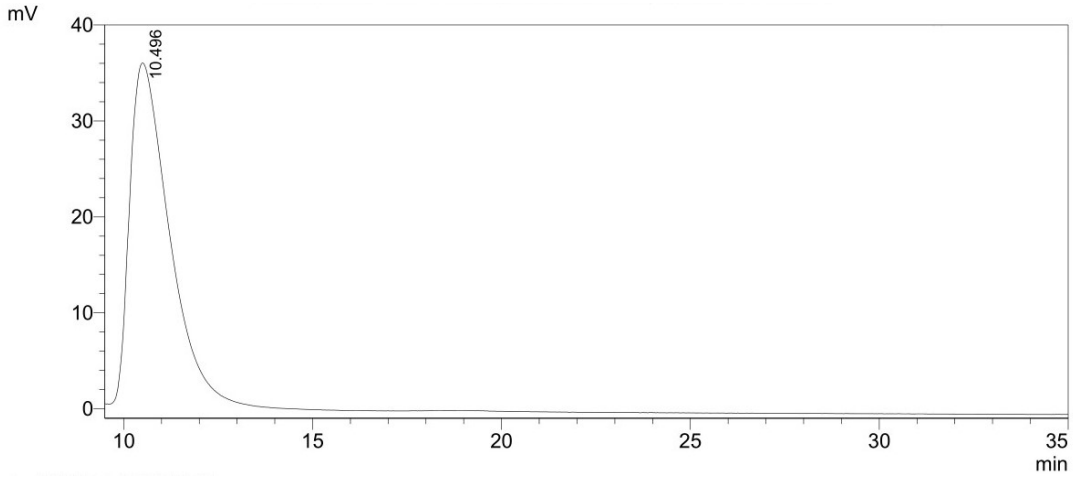




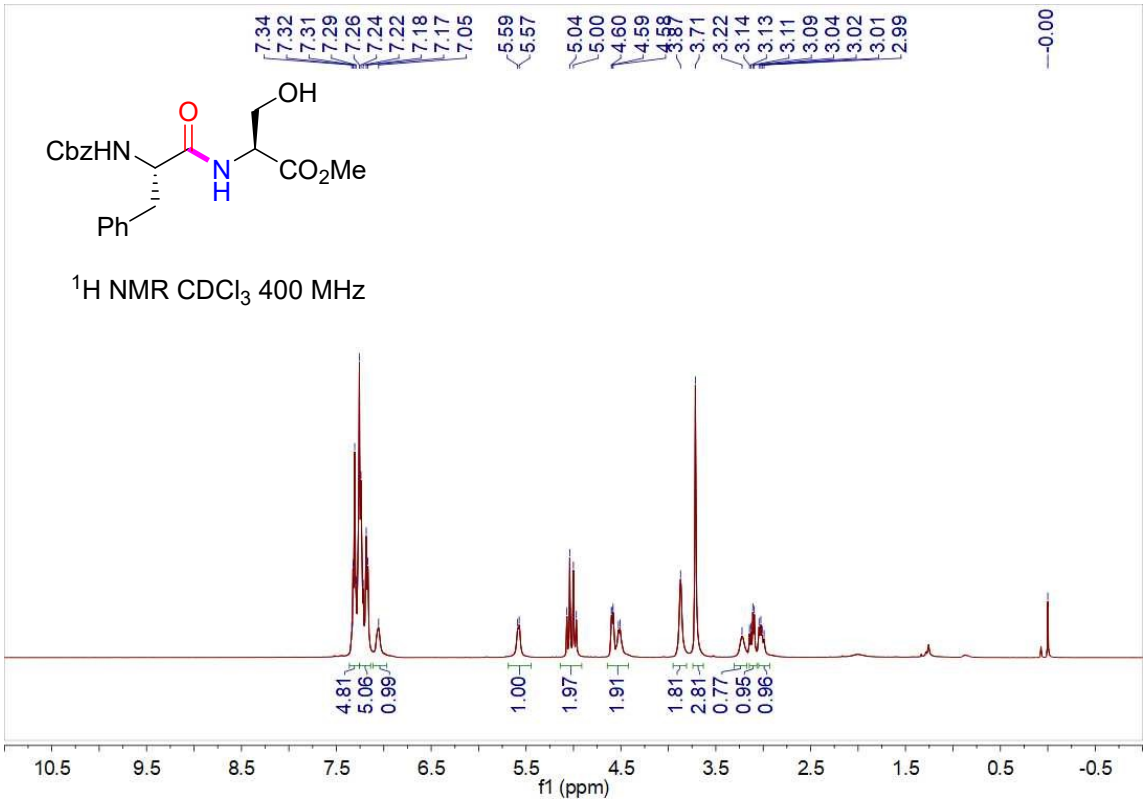
Chromatogram

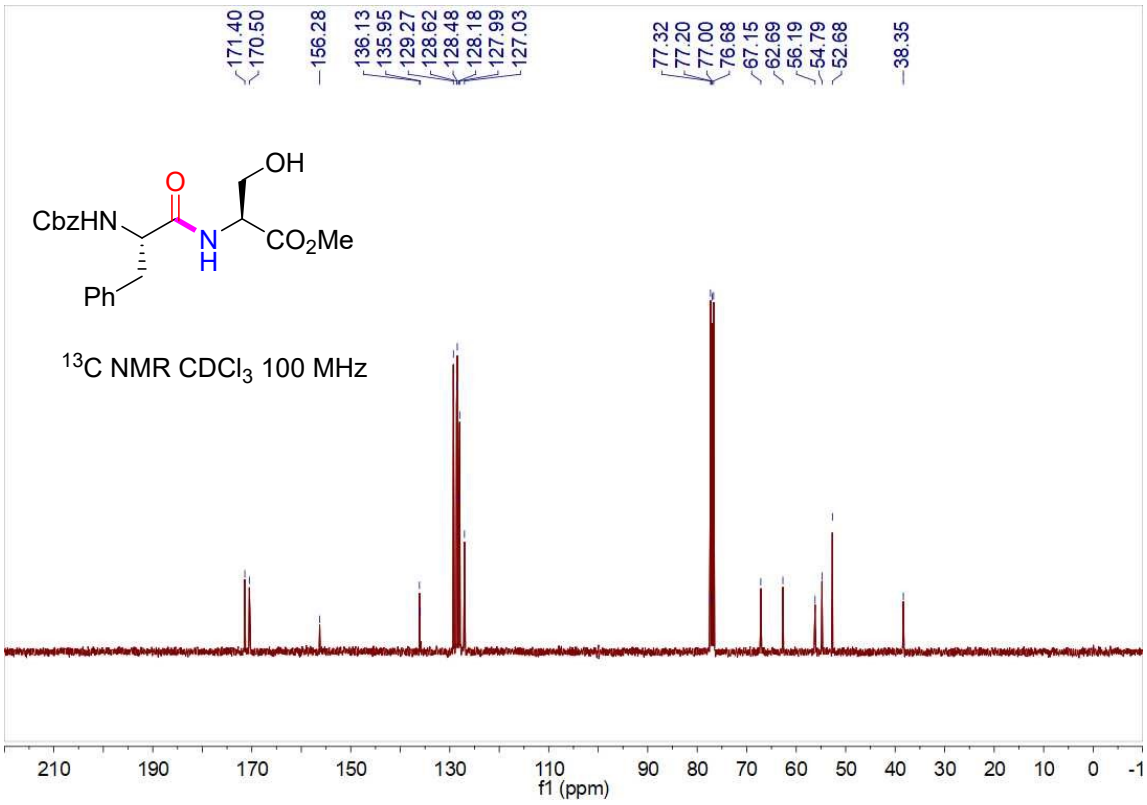


Peak No	Ret. Time	Area	Height	Area %	Height%
1	10.624	950869	15467	48.505	74.611
2	22.248	1009465	5263	51.495	25.389
Total		1960334	20731	100.000	100.000

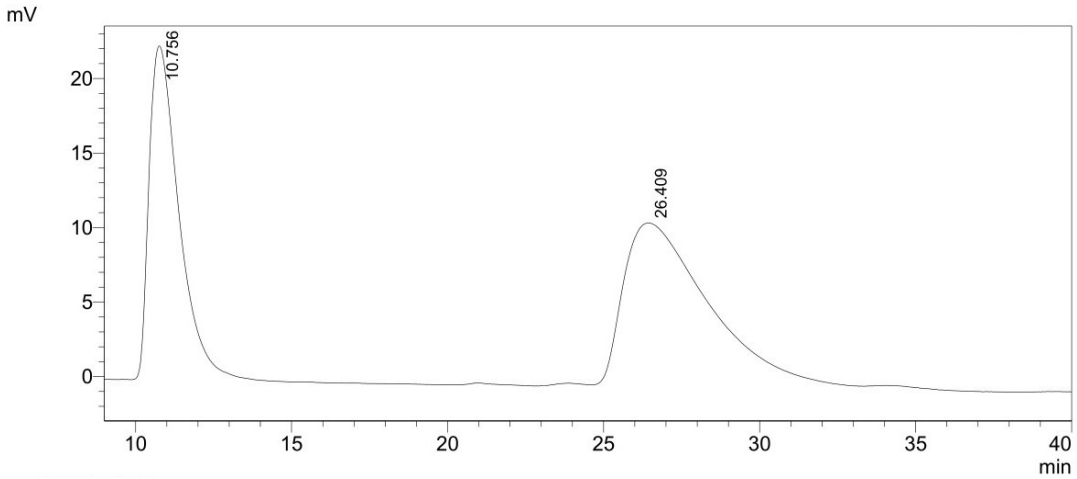


Peak No	Ret. Time	Area	Height	Area %	Height%
1	10.496	2485433	35377	100.000	100.000
Total		2485433	35377	100.000	100.000

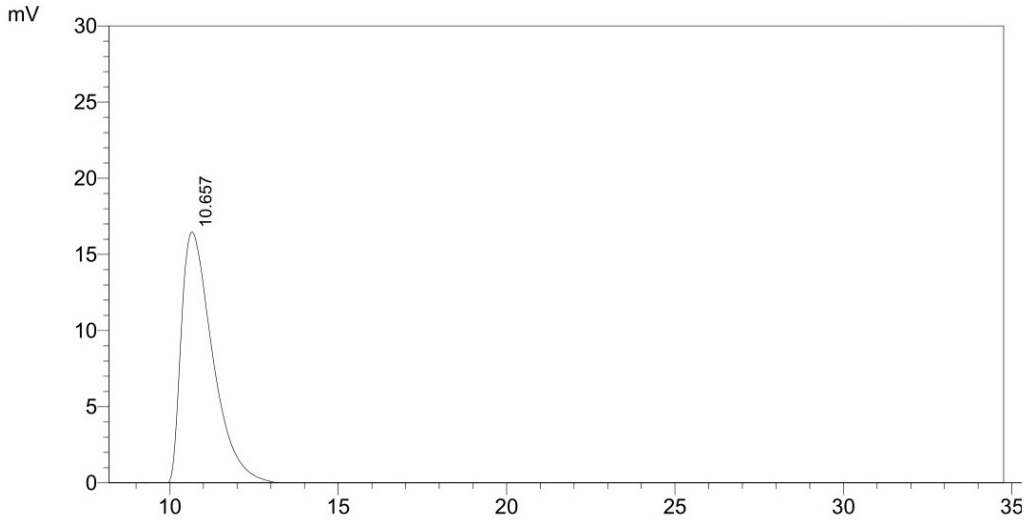




Chromatogram (NIS-NHC)

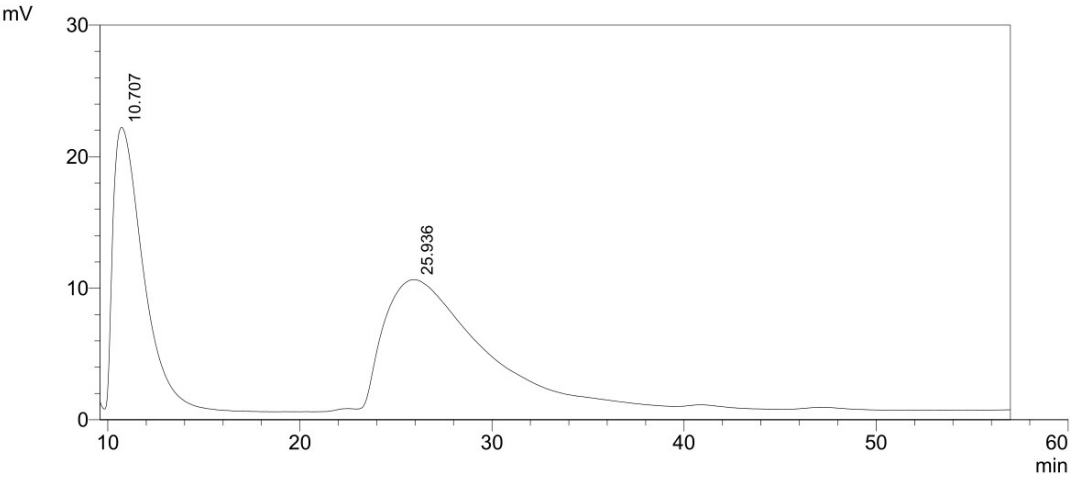


Peak No	Ret. Time	Area	Height	Area %	Height%
1	10.756	1497161	22414	45.900	68.147
2	26.409	1764651	10476	54.100	31.853
Total		3261812	32890	100.000	100.000

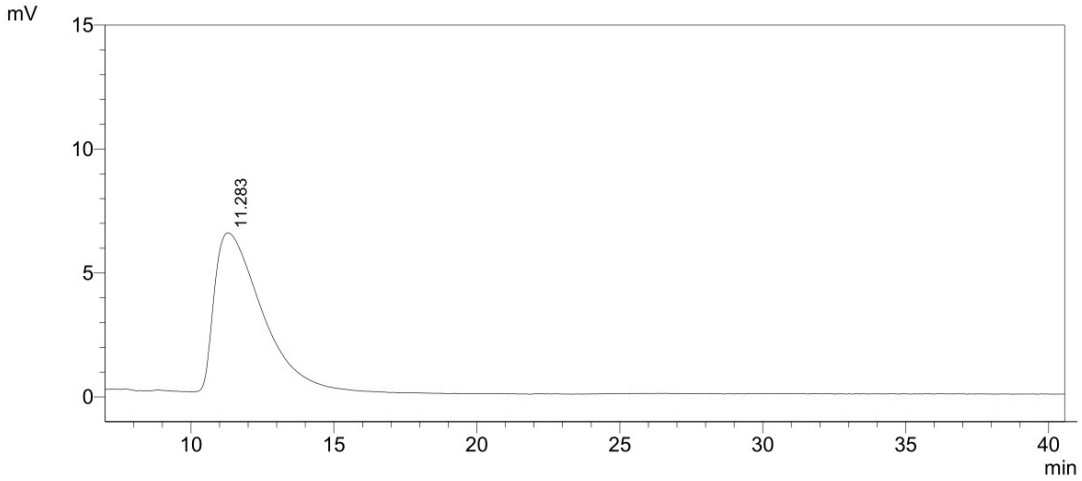


Peak No	Ret. Time	Area	Height	Area %	Height%
1	10.657	1077705	16534	100.000	100.000
Total		1077705	16534	100.000	100.000

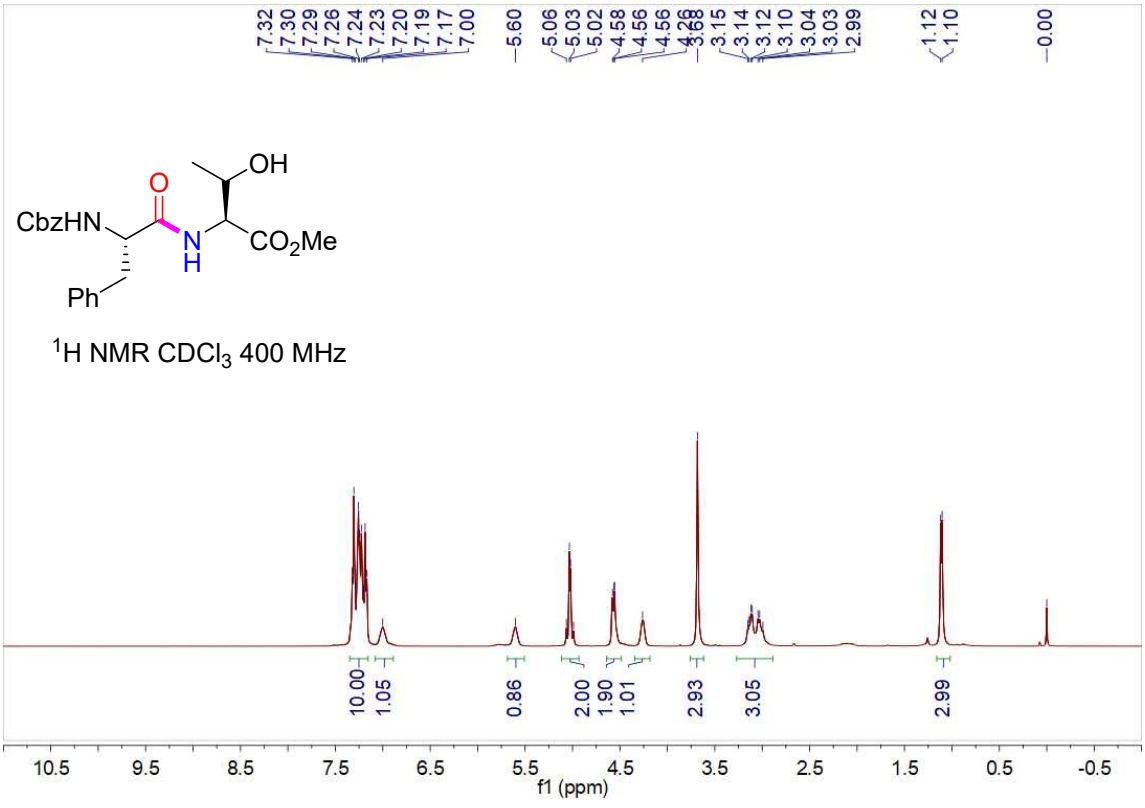
Chromatogram ($K_2S_2O_8$-NHC)

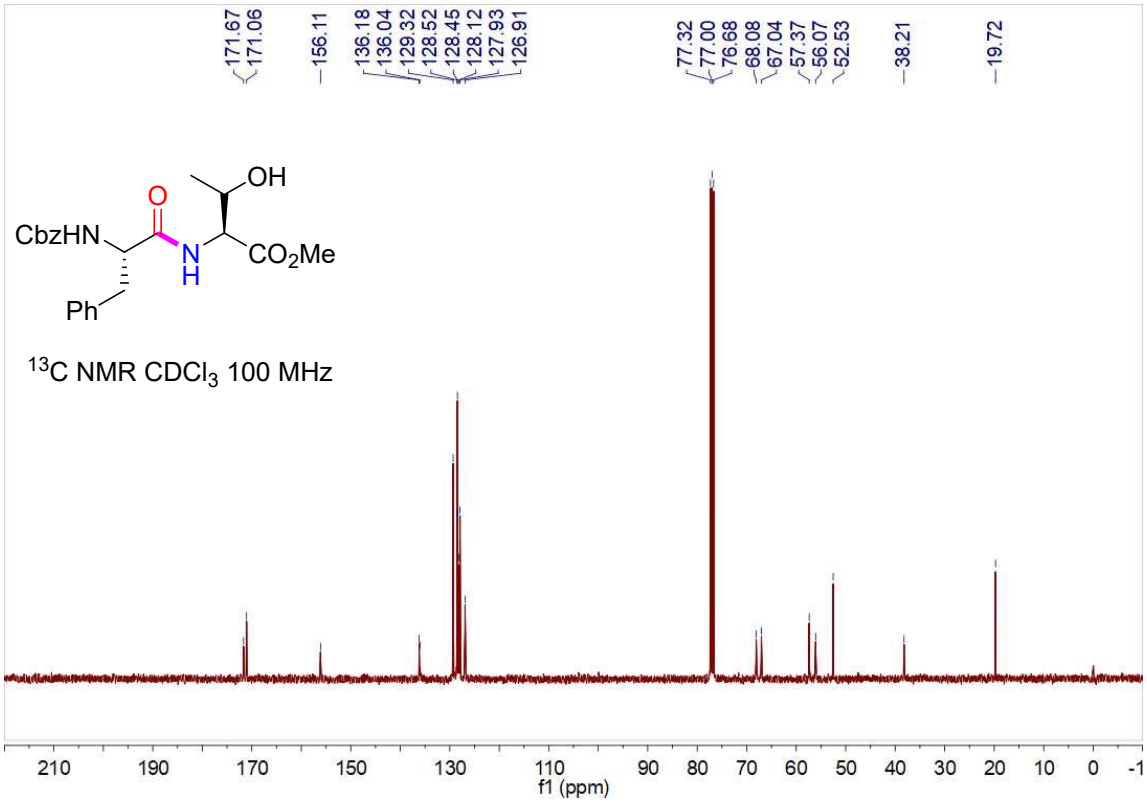


Peak No	Ret. Time	Area	Height	Area %	Height%
1	10.707	2306057	21374	49.234	71.764
2	25.936	2377809	8410	50.766	28.236
Total		4683865	29784	100.000	100.000

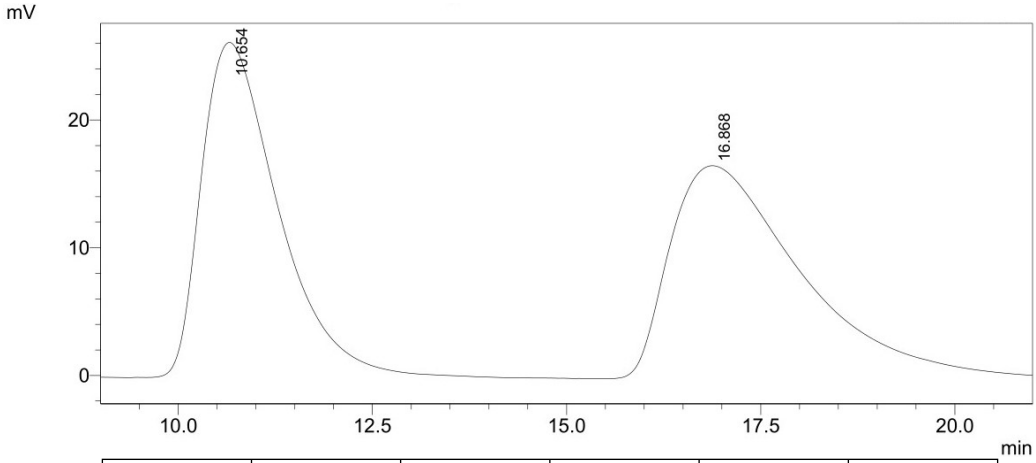


Peak No	Ret. Time	Area	Height	Area %	Height%
1	11.283	719815	6385	100.000	100.000
Total		719815	6385	100.000	100.000

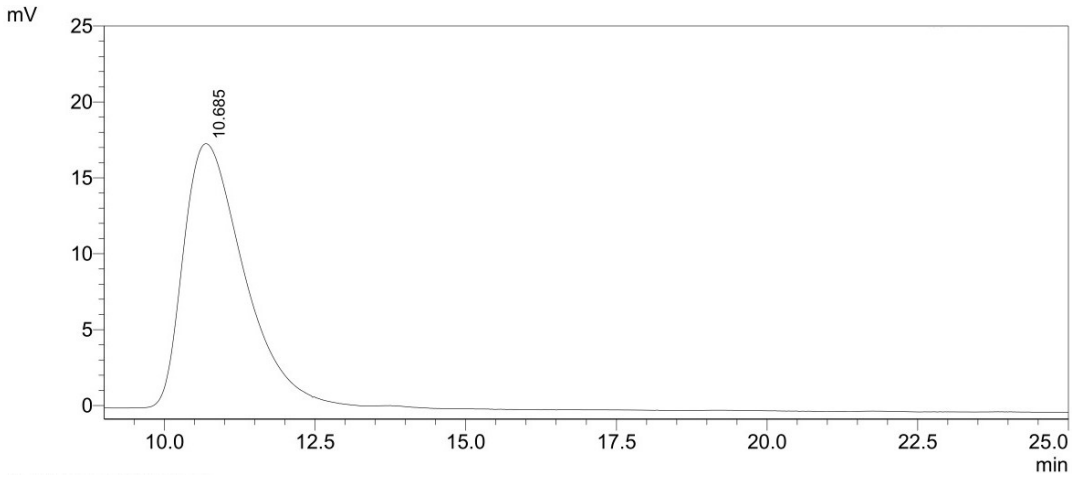




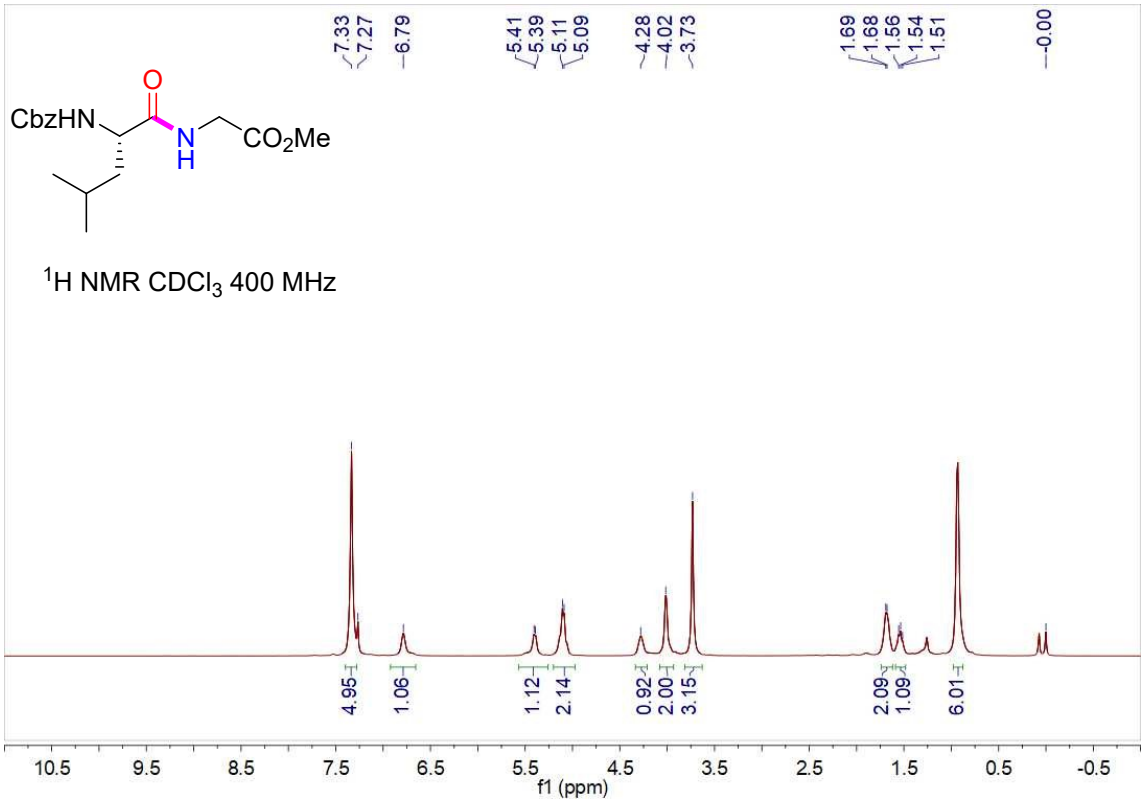
Chromatogram

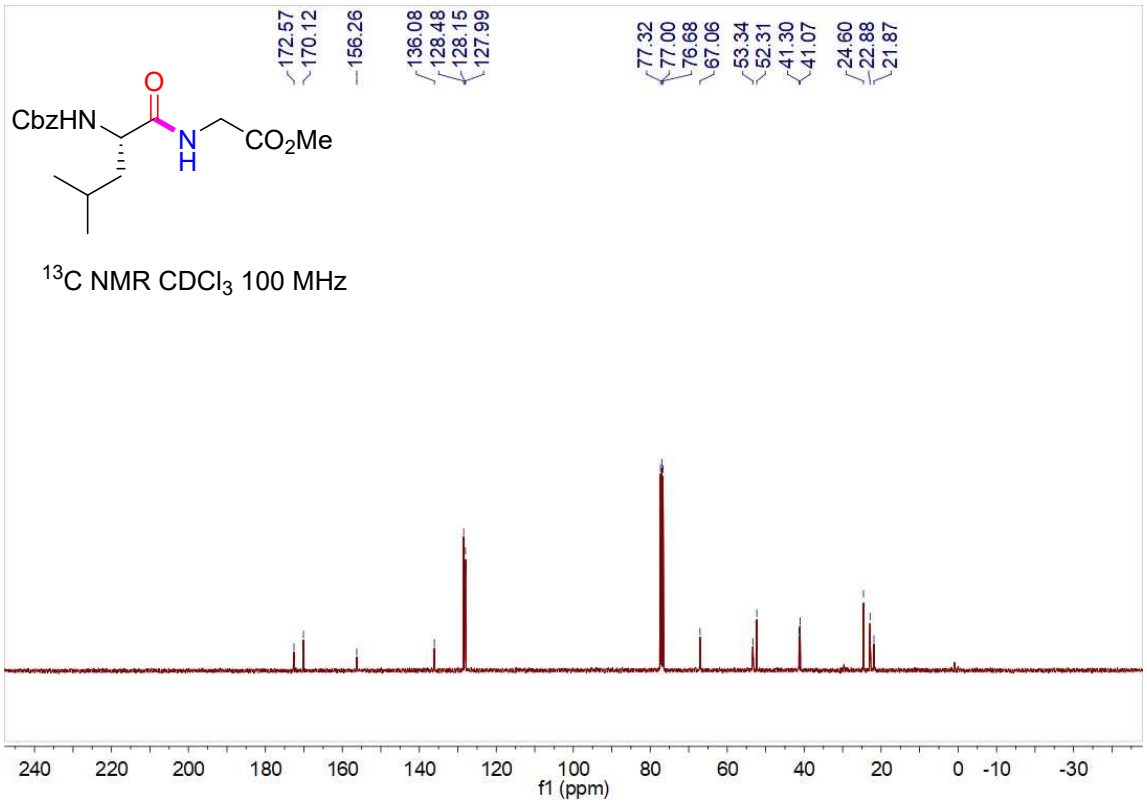


Peak No	Ret. Time	Area	Height	Area %	Height%
1	10.654	1782052	26173	48.418	61.217
2	16.868	1898543	16581	51.582	38.783
Total		3680586	42754	100.000	100.000

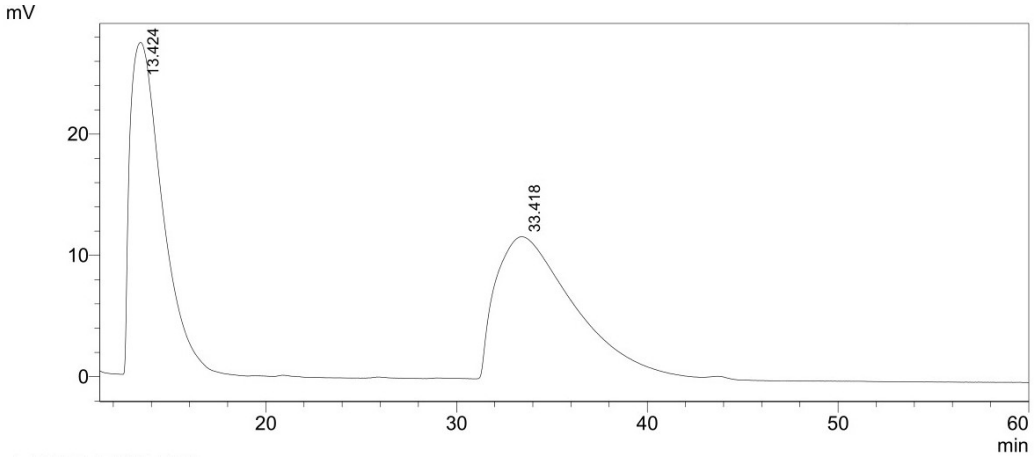


Peak No	Ret. Time	Area	Height	Area %	Height%
1	10.685	1213656	17379	100.000	100.000
Total		1213656	17379	100.000	100.000

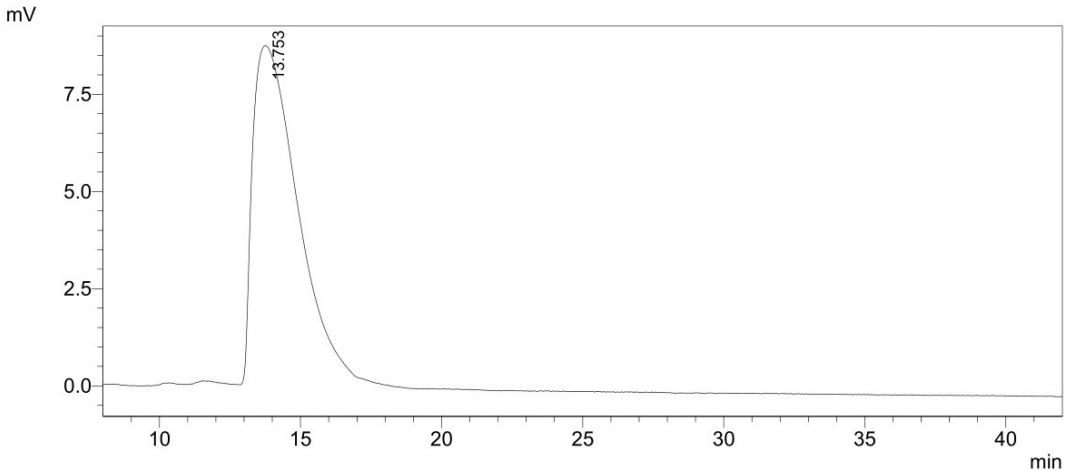




Chromatogram (NIS-NHC)

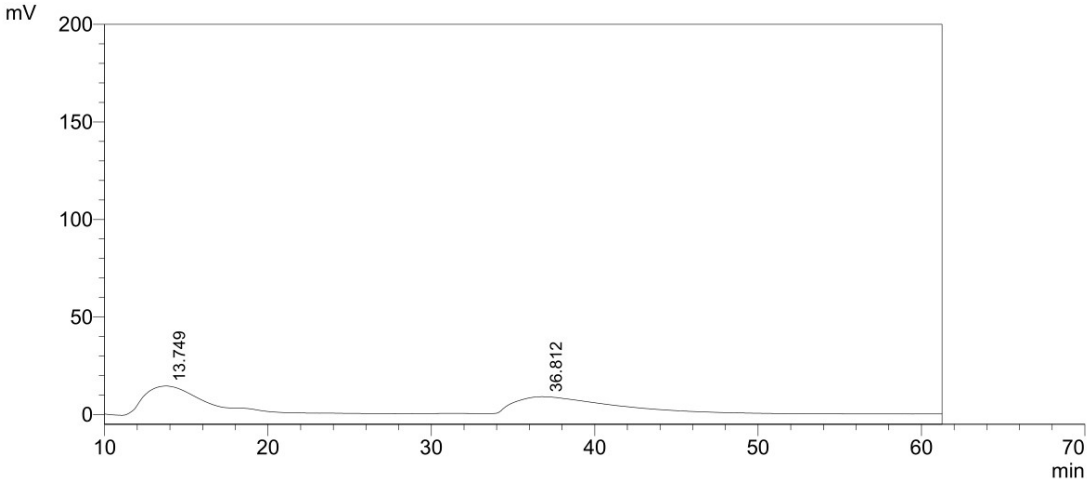


Peak No	Ret. Time	Area	Height	Area %	Height%
1	13.424	3204722	27348	50.831	70.407
2	33.418	3099924	11495	49.169	29.593
Total		6304645	38843	100.000	100.000

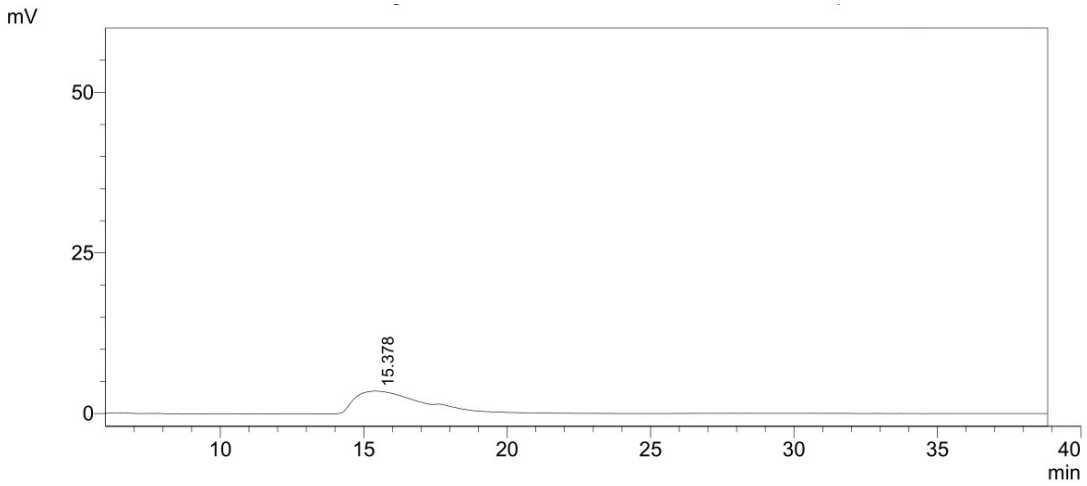


Peak No	Ret. Time	Area	Height	Area %	Height%
1	13.753	975018	8720	100.000	100.000
Total		975018	8720	100.000	100.000

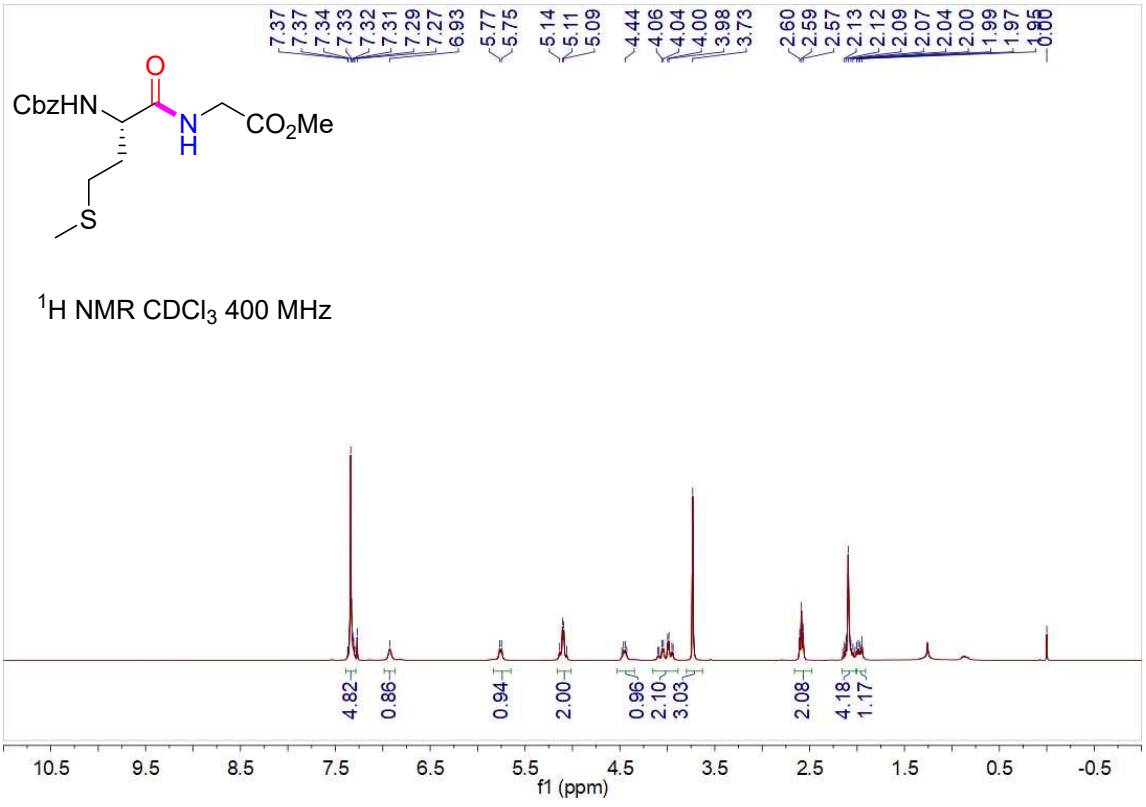
Chromatogram ($K_2S_2O_8$-NHC)

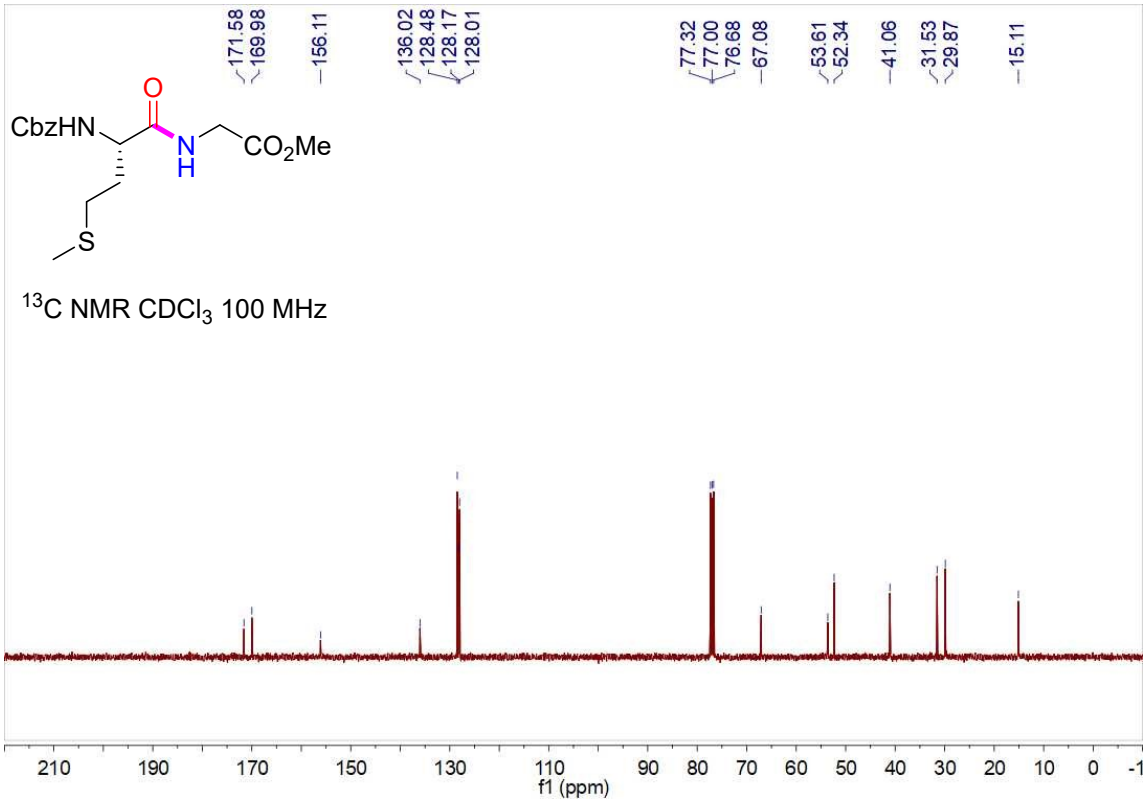


Peak No	Ret. Time	Area	Height	Area %	Height%
1	13.749	3121719	13975	49.711	62.424
2	36.812	3157987	8412	50.289	37.576
Total		6279707	22387	100.000	100.000

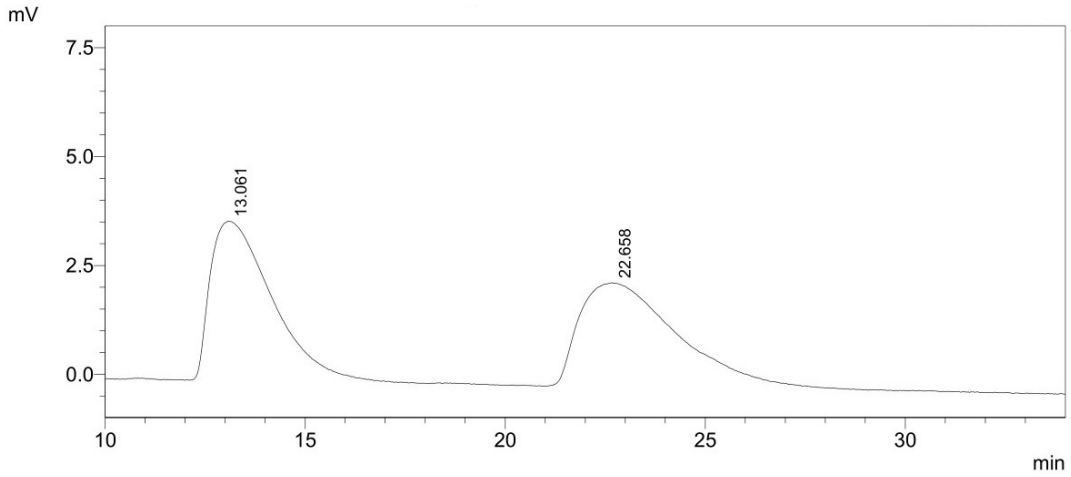


Peak No	Ret. Time	Area	Height	Area %	Height%
1	15.378	543566	3409	100.000	100.000
Total		543566	3409	100.000	100.000

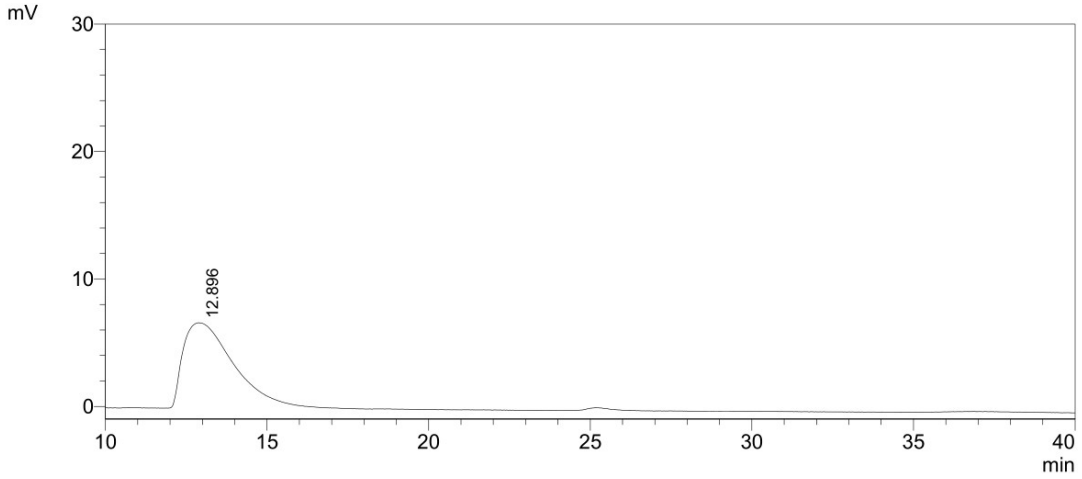




Chromatogram (NIS-NHC)

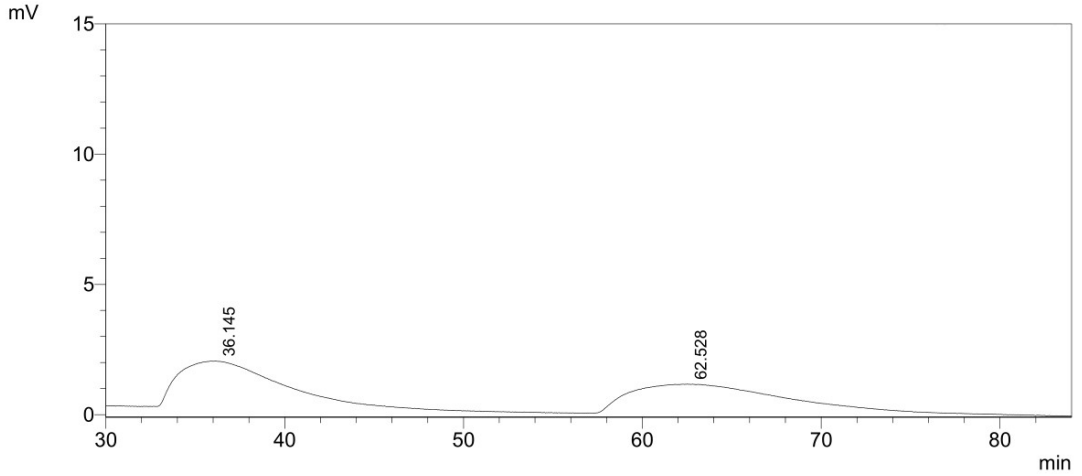


Peak No	Ret. Time	Area	Height	Area %	Height%
1	13.061	386048	3649	49.141	60.492
2	22.658	399537	2383	50.859	39.508
Total		785585	6032	100.000	100.000

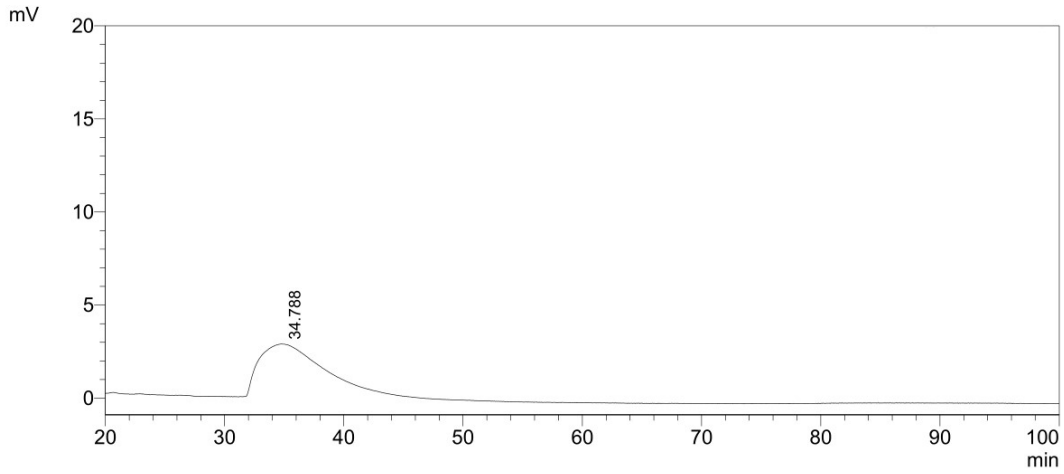


Peak No	Ret. Time	Area	Height	Area %	Height%
1	12.896	741451	6709	100.000	100.000
Total		741451	6709	100.000	100.000

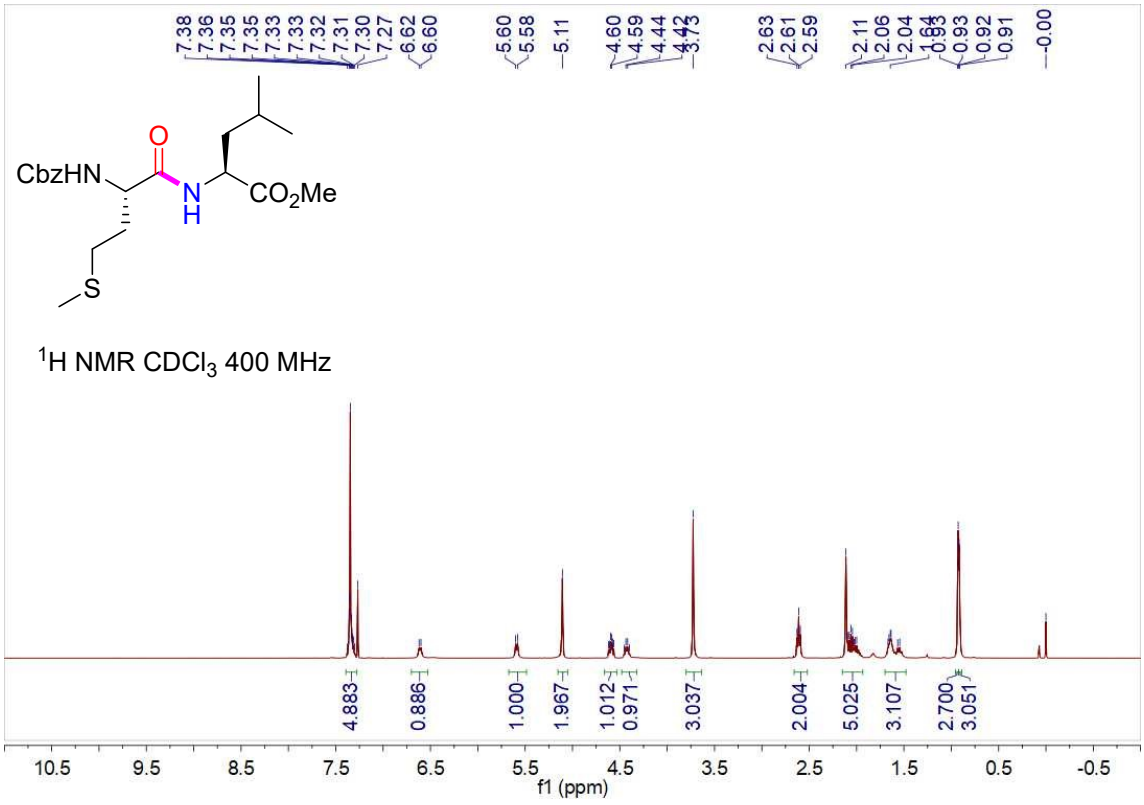
Chromatogram ($K_2S_2O_8$-NHC)

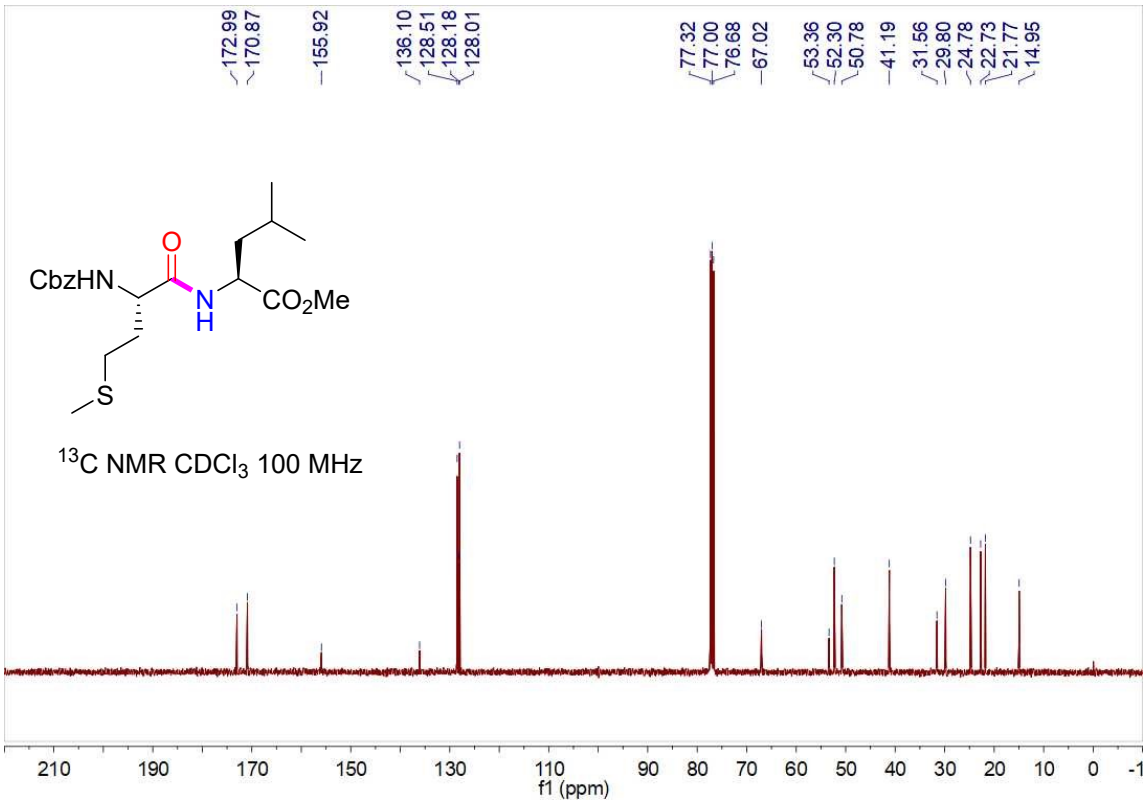


Peak No	Ret. Time	Area	Height	Area %	Height%
1	36.145	679181	1756	50.826	61.256
2	62.528	657112	1111	49.174	38.744
Total		1336293	2866	100.000	100.000

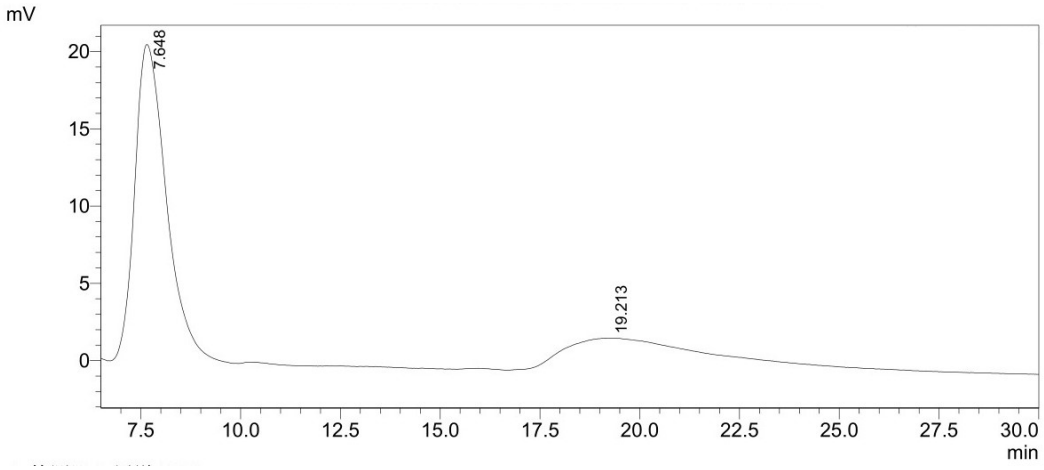


Peak No	Ret. Time	Area	Height	Area %	Height%
1	34.788	1111325	2849	100.000	100.000
Total		1111325	2849	100.000	100.000

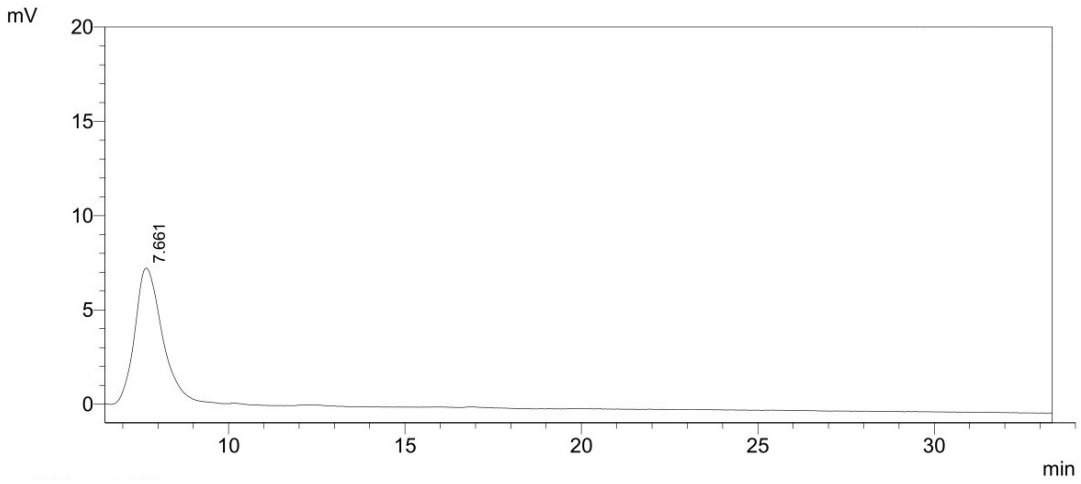




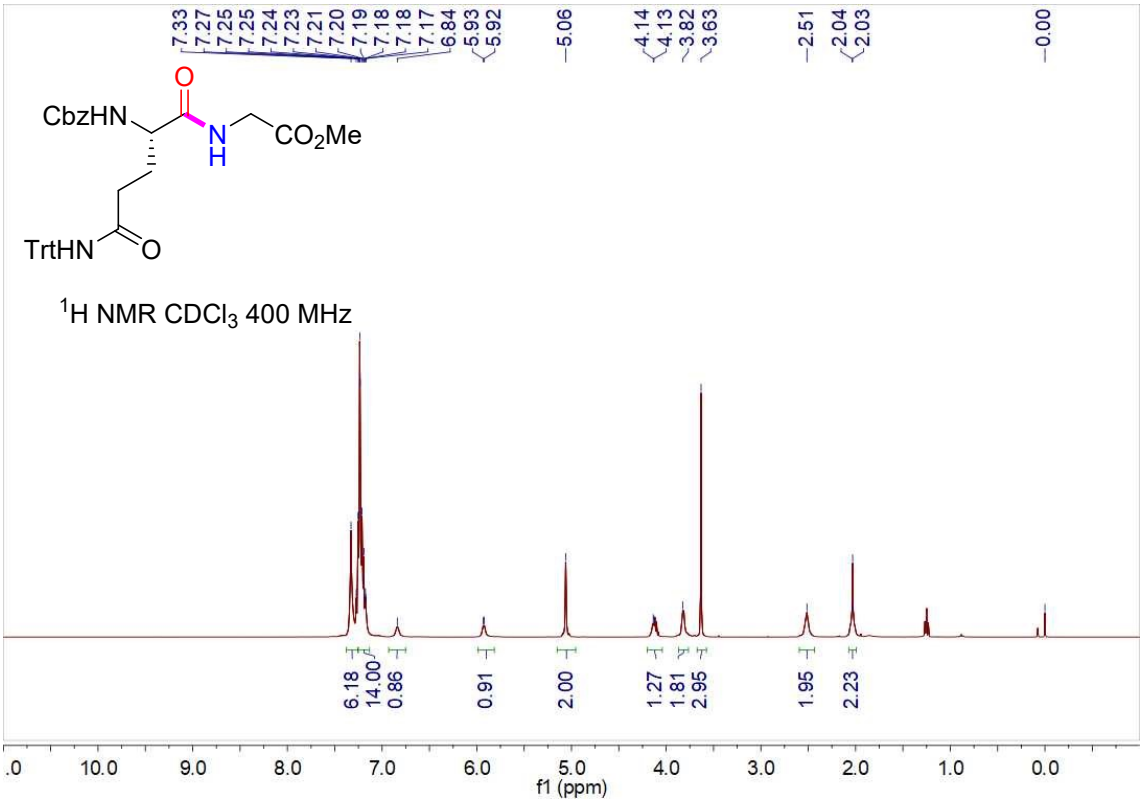
Chromatogram

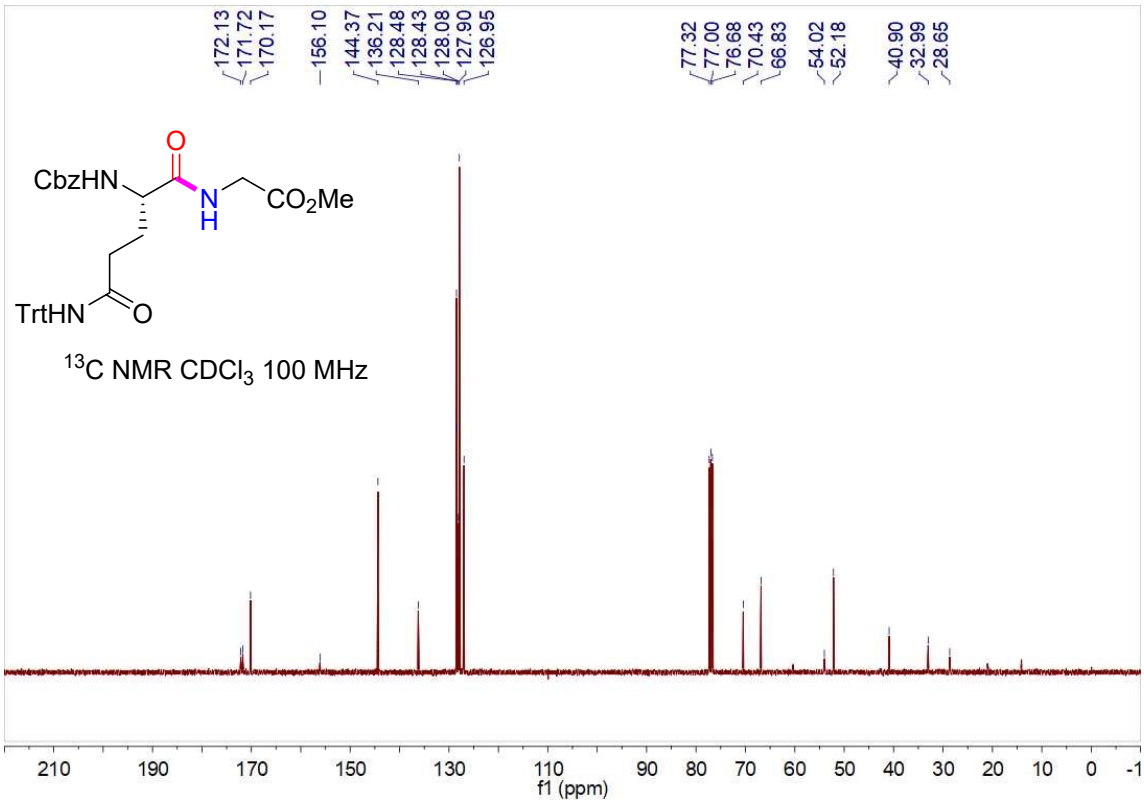


Peak No	Ret. Time	Area	Height	Area %	Height%
1	7.648	588791	14354	50.068	87.216
2	19.213	587200	2104	49.932	12.784
Total		1175992	16458	100.000	100.000

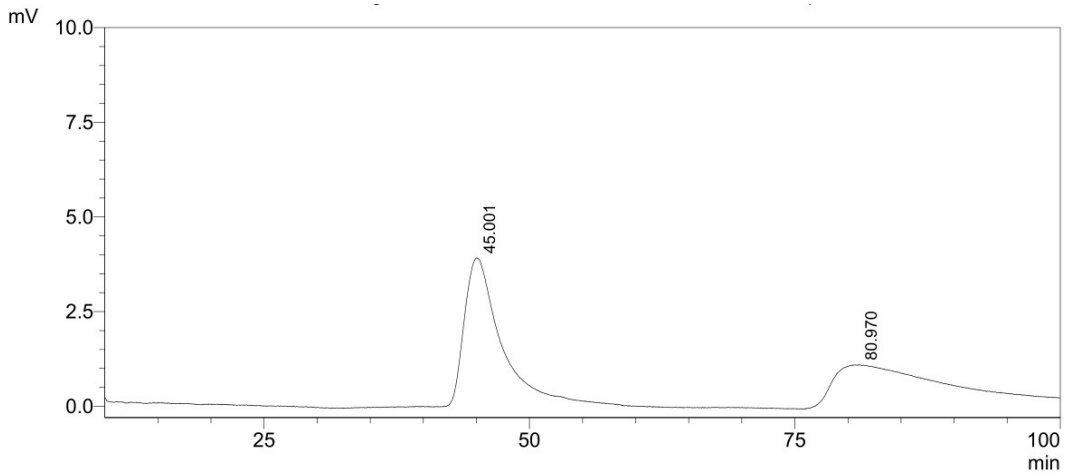


Peak No	Ret. Time	Area	Height	Area %	Height%
1	7.661	392674	7213	100.000	100.000
Total		392674	7213	100.000	100.000

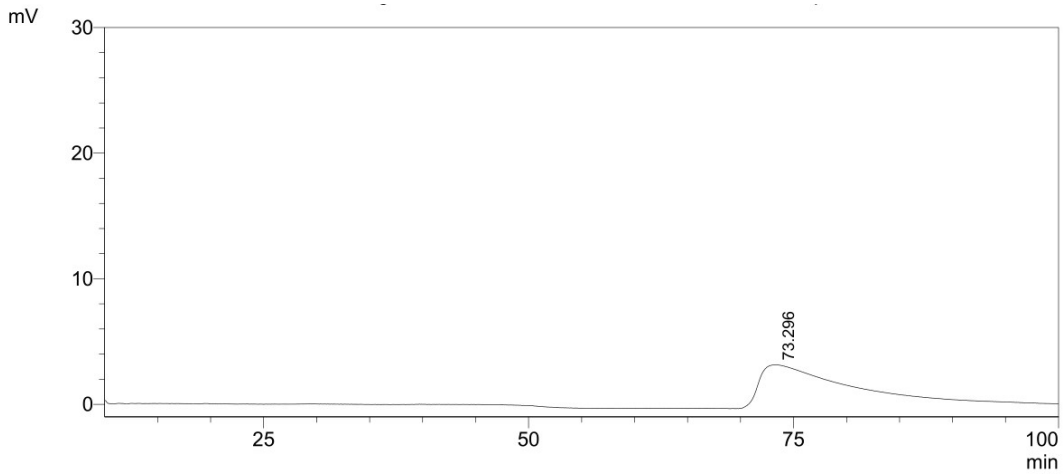




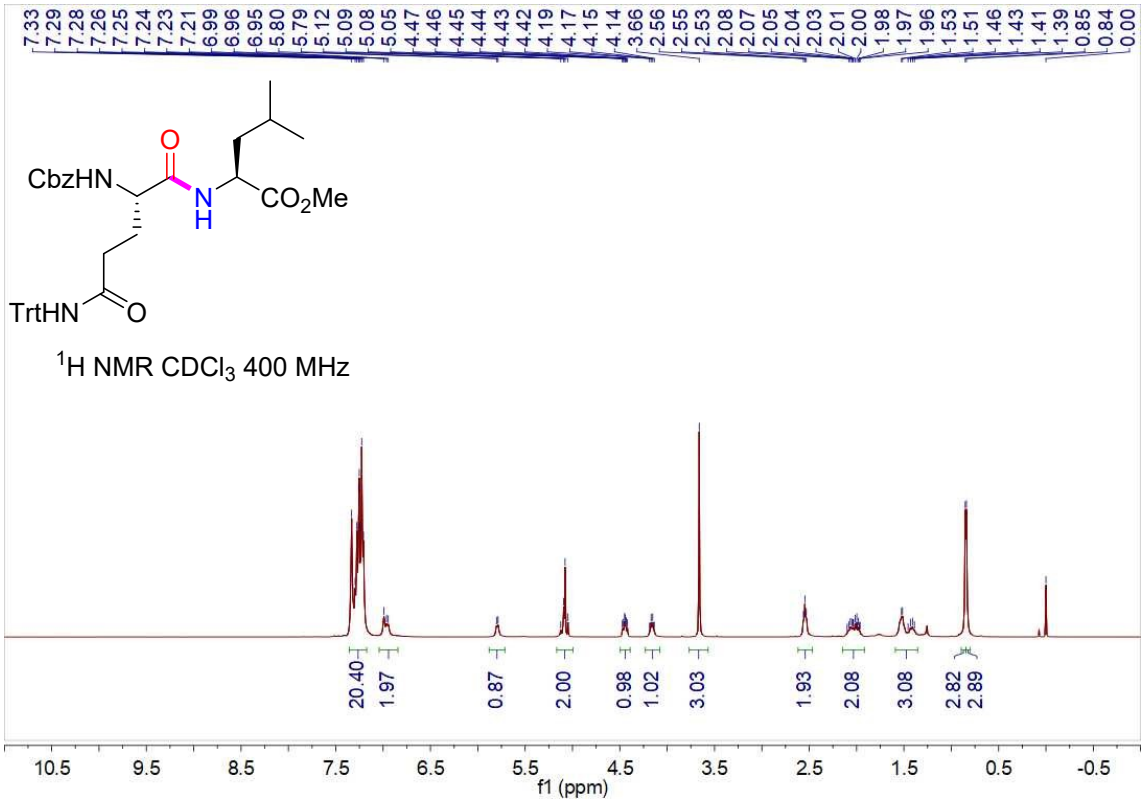
Chromatogram ($K_2S_2O_8$-NHC)

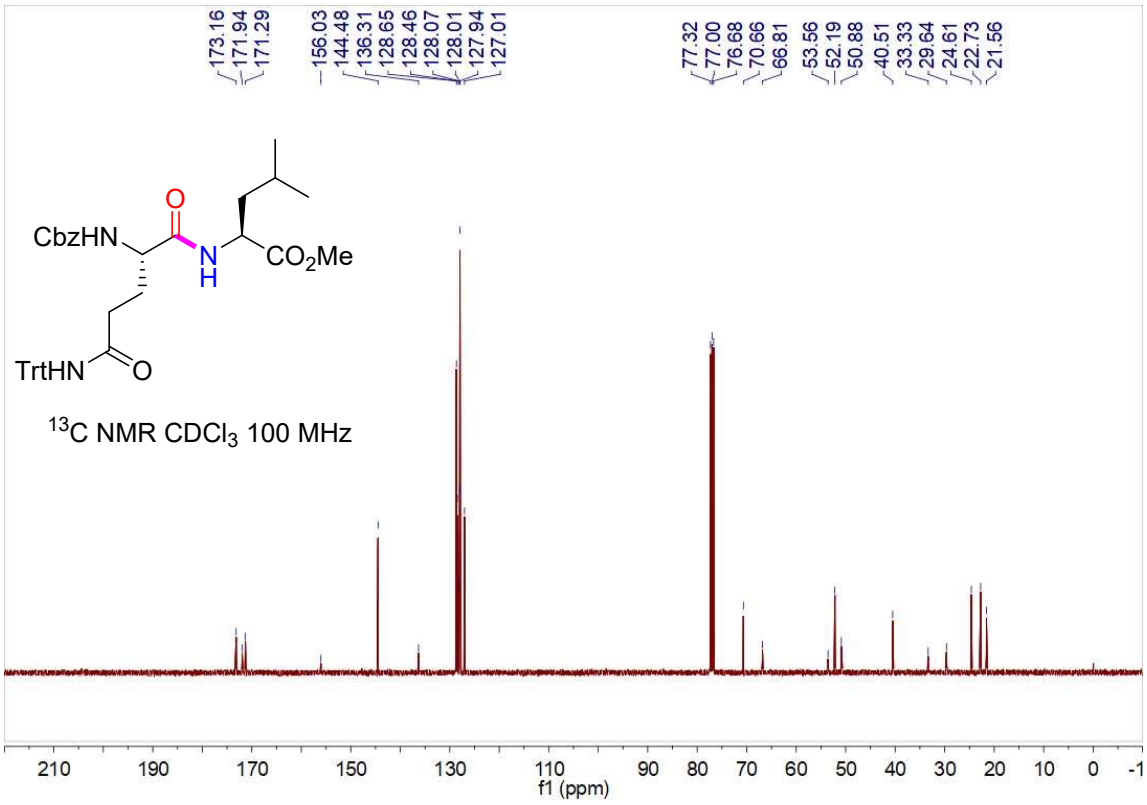


Peak No	Ret. Time	Area	Height	Area %	Height%
1	45.001	620433	3385	50.998	76.670
2	80.970	596142	1030	49.002	23.330
Total		1216575	4415	100.000	100.000

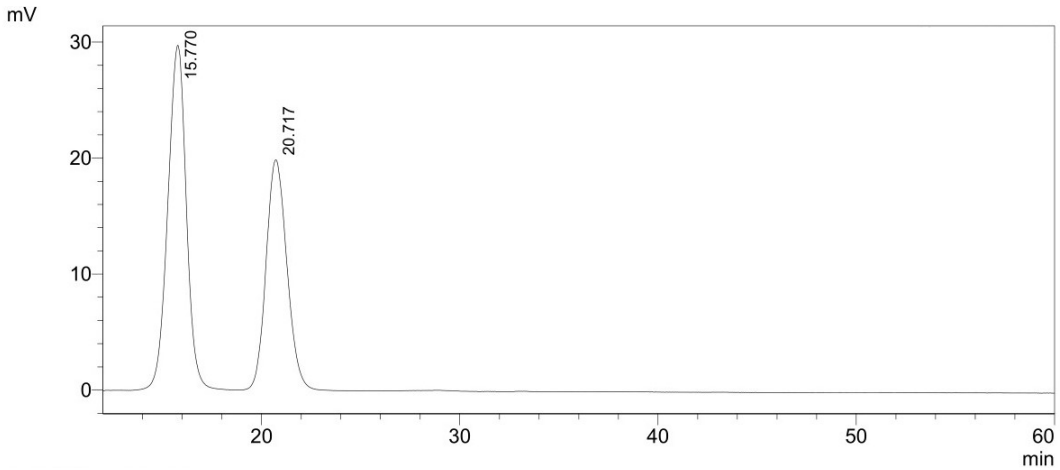


Peak No	Ret. Time	Area	Height	Area %	Height%
1	73.269	1938122	3293	100.000	100.000
Total		1938122	3293	100.000	100.000

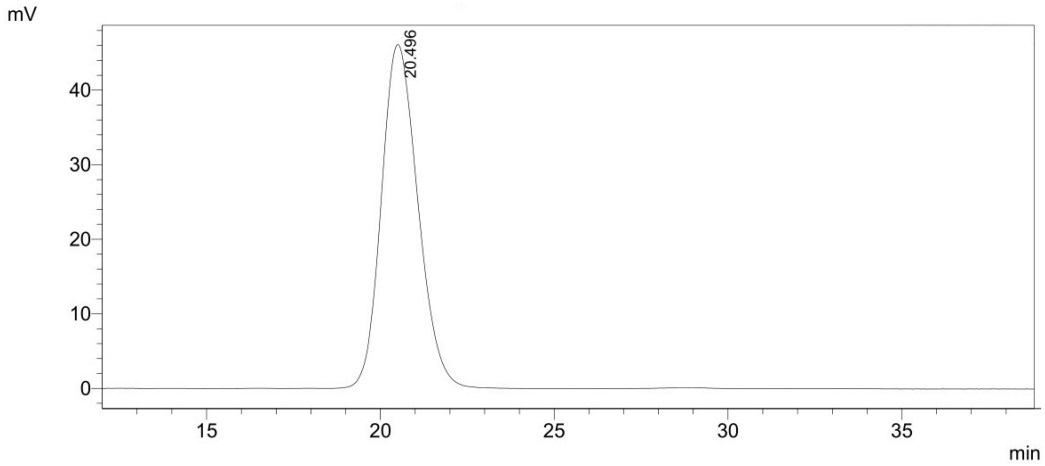




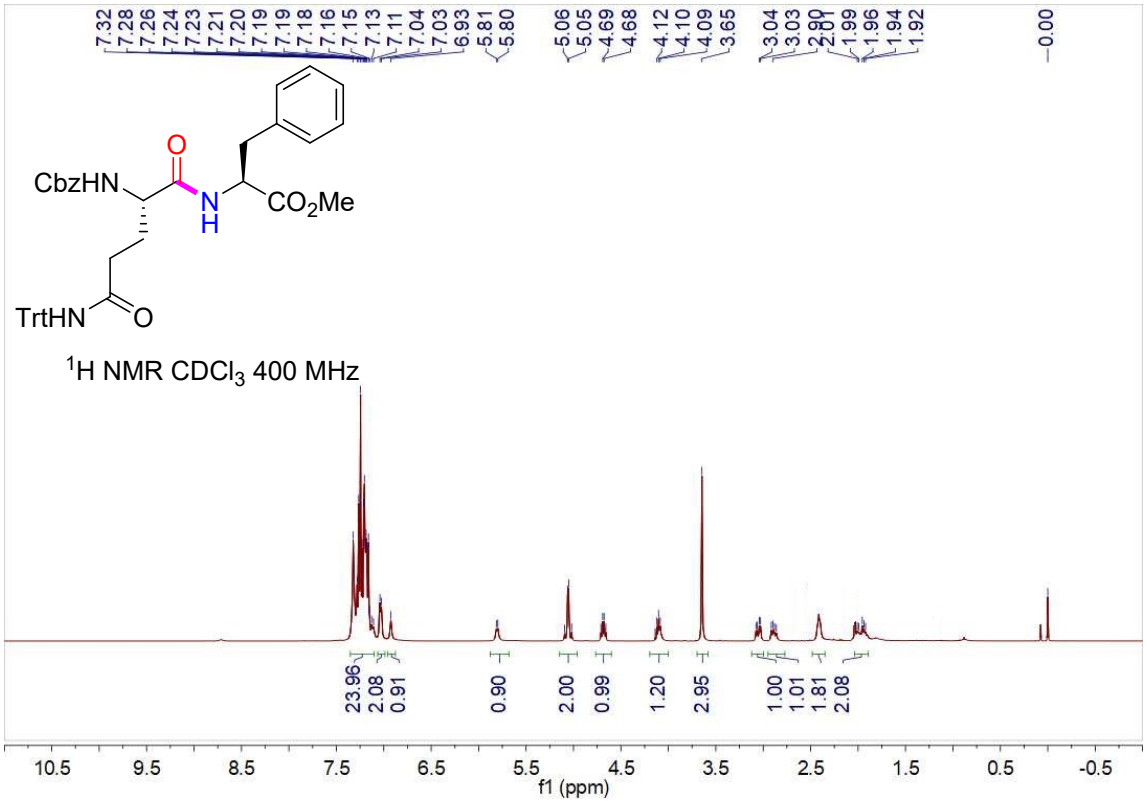
Chromatogram

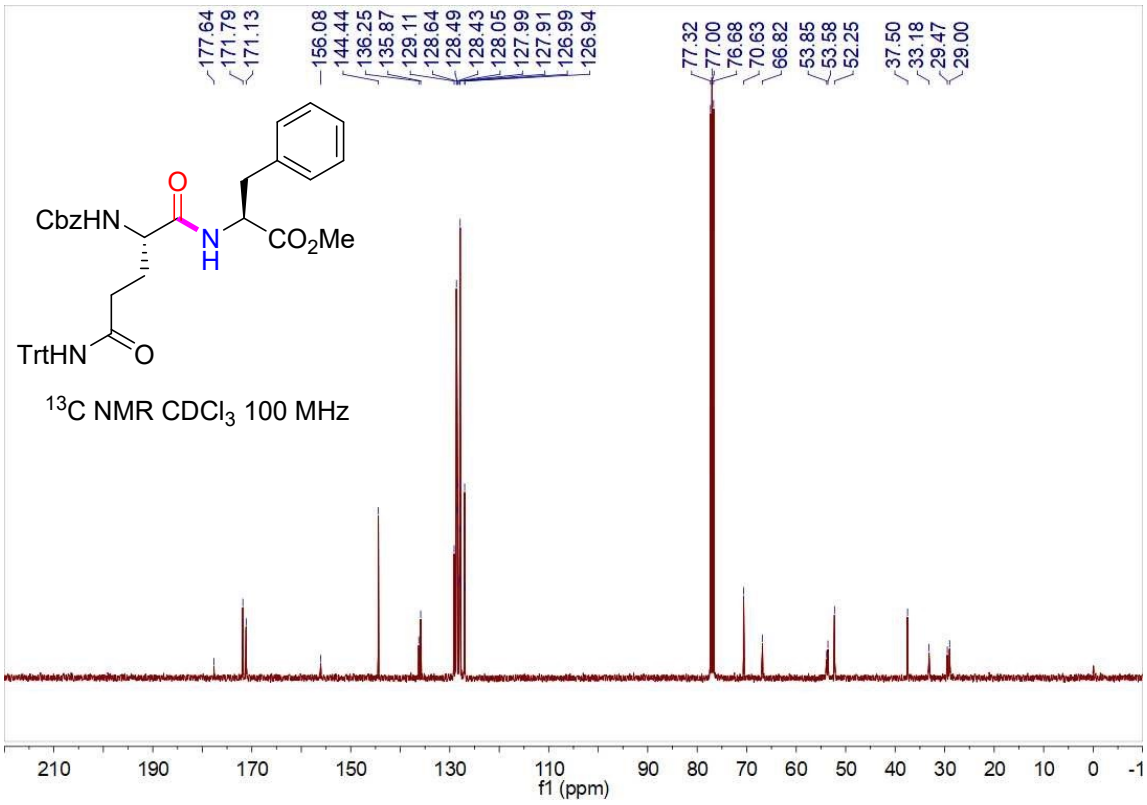


Peak No	Ret. Time	Area	Height	Area %	Height%
1	15.770	1900131	29602	56.592	59.837
2	20.717	1457476	19869	43.408	40.163
Total		3357607	49471	100.000	100.000

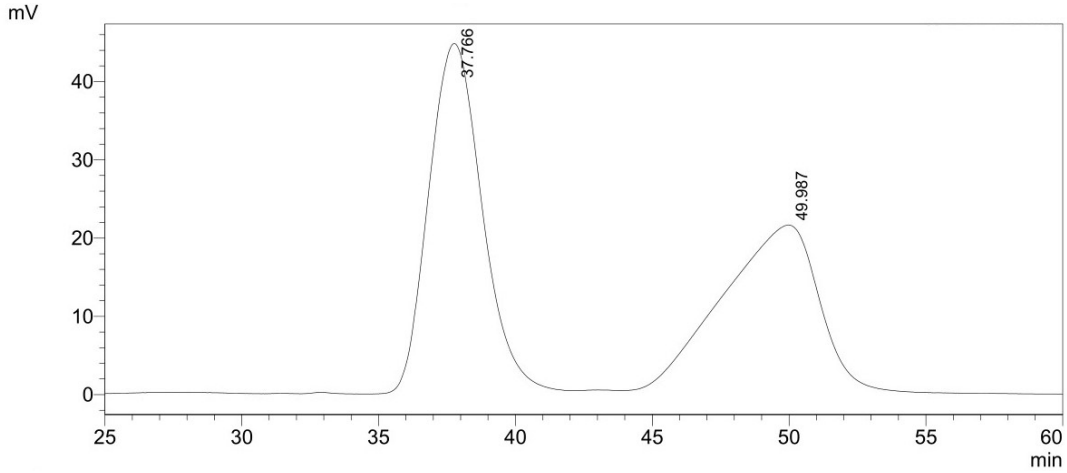


Peak No	Ret. Time	Area	Height	Area %	Height%
1	20.496	3361806	46082	100.000	100.000
Total		3361806	46082	100.000	100.000

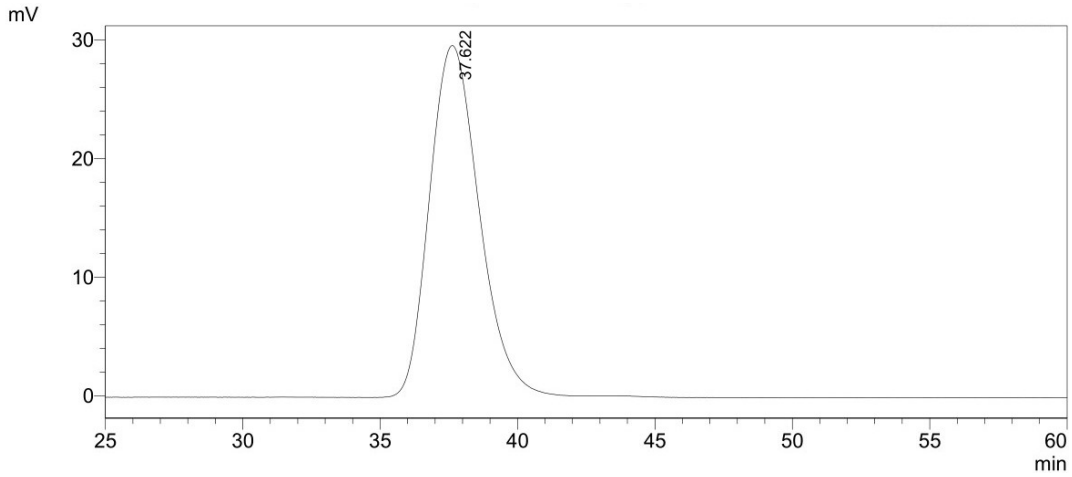




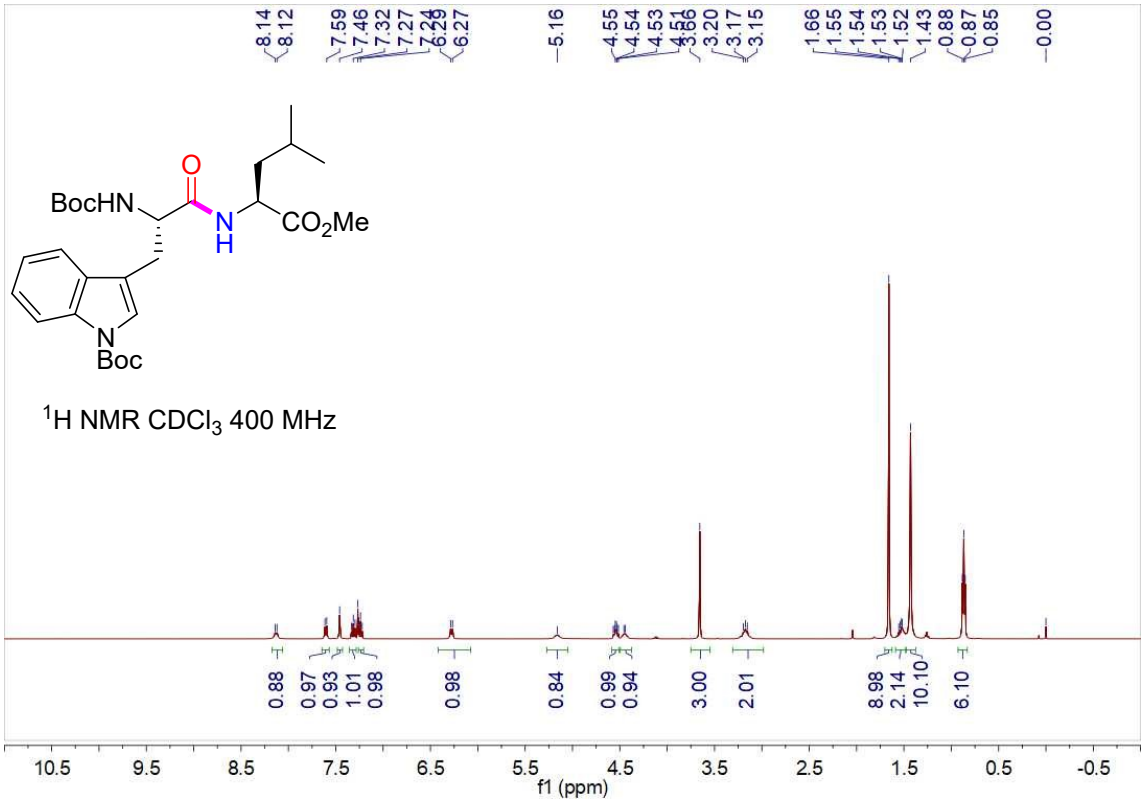
Chromatogram

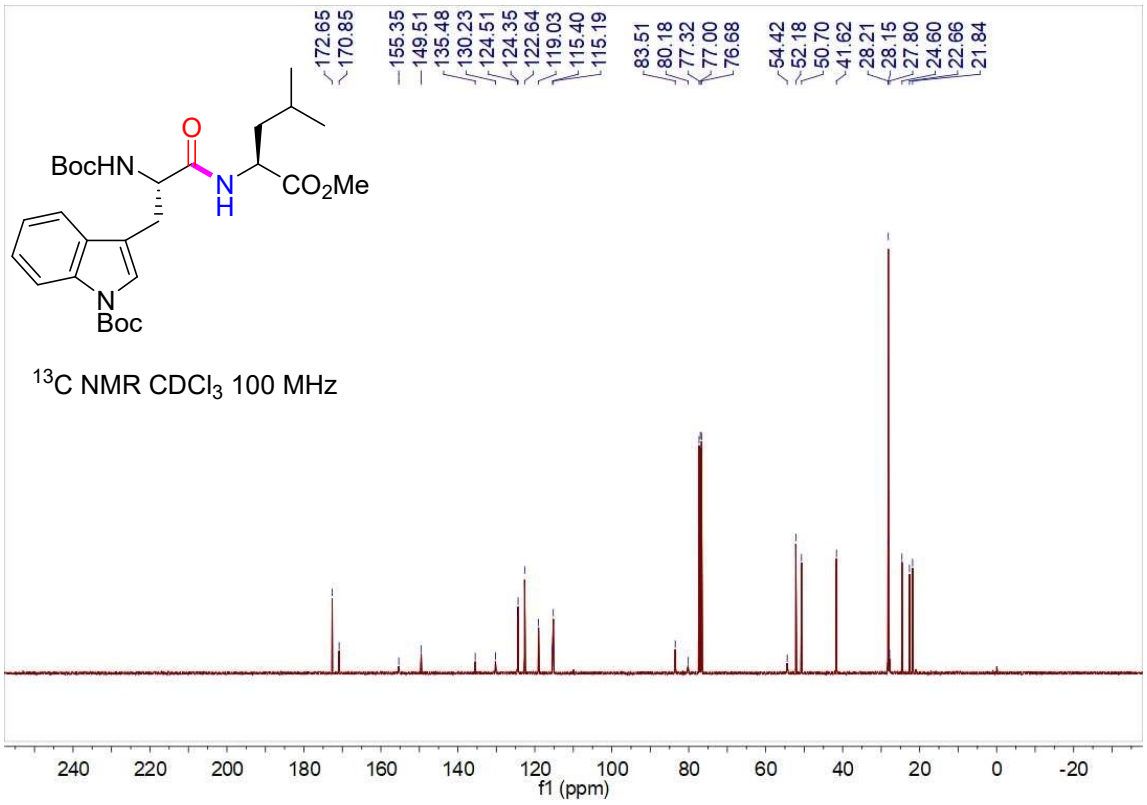


Peak No	Ret. Time	Area	Height	Area %	Height%
1	37.766	5984616	44512	54.241	67.935
2	49.987	5048678	21009	45.759	32.065
Total		11033294	65521	100.000	100.000

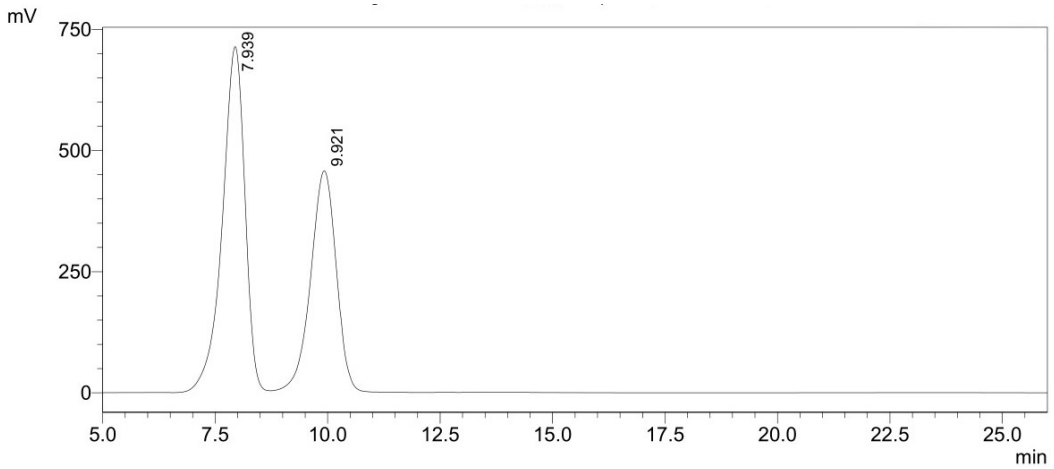


Peak No	Ret. Time	Area	Height	Area %	Height%
1	37.622	3663500	29492	100.000	100.000
Total		3663500	29492	100.000	100.000

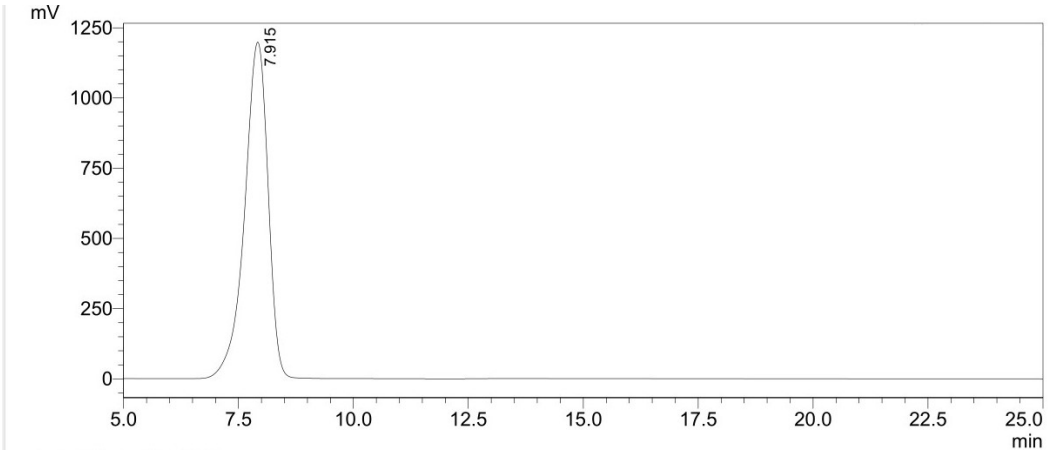




Chromatogram (NIS-NHC)

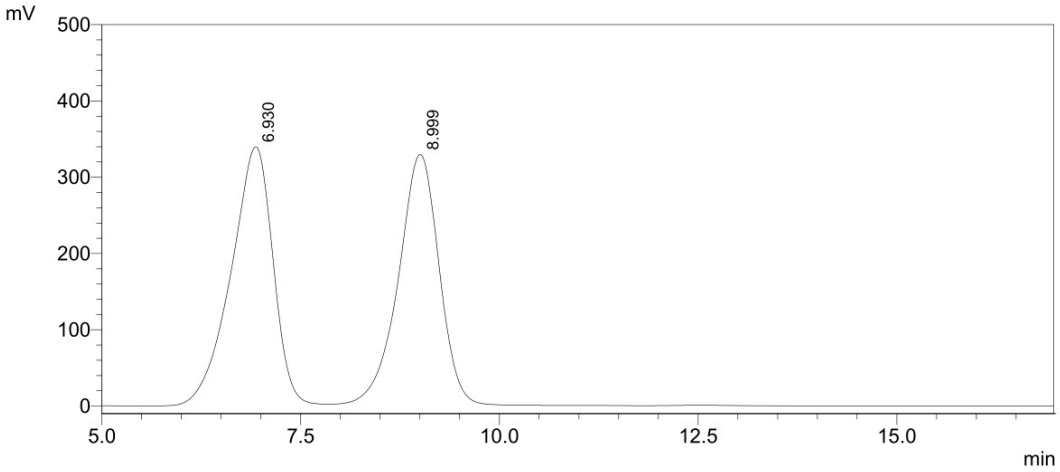


Peak No	Ret. Time	Area	Height	Area %	Height%
1	7.939	24350037	708356	58.436	61.137
2	9.921	17319500	450278	41.564	38.863
Total		41669537	1158634	100.000	100.000

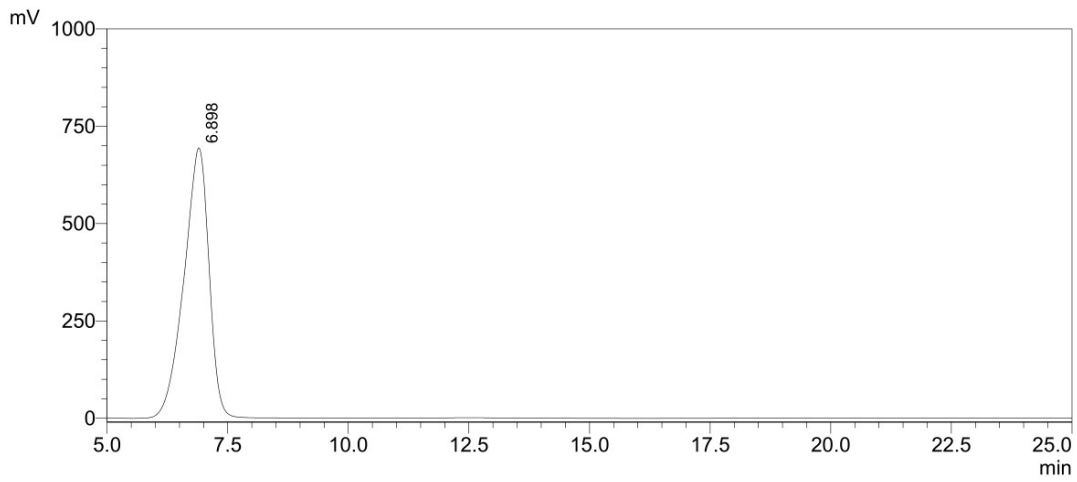


Peak No	Ret. Time	Area	Height	Area %	Height%
1	7.915	42549019	1198416	100.000	100.000
Total		42549019	1198416	100.000	100.000

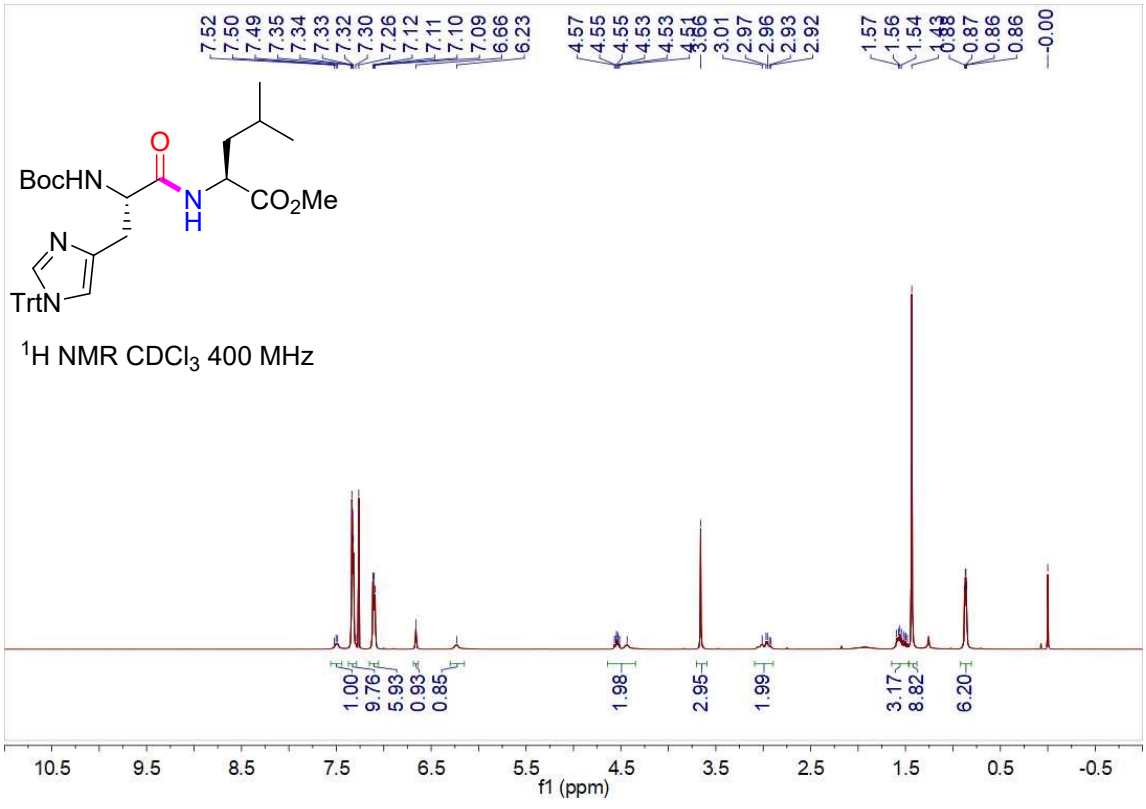
Chromatogram ($K_2S_2O_8$-NHC)

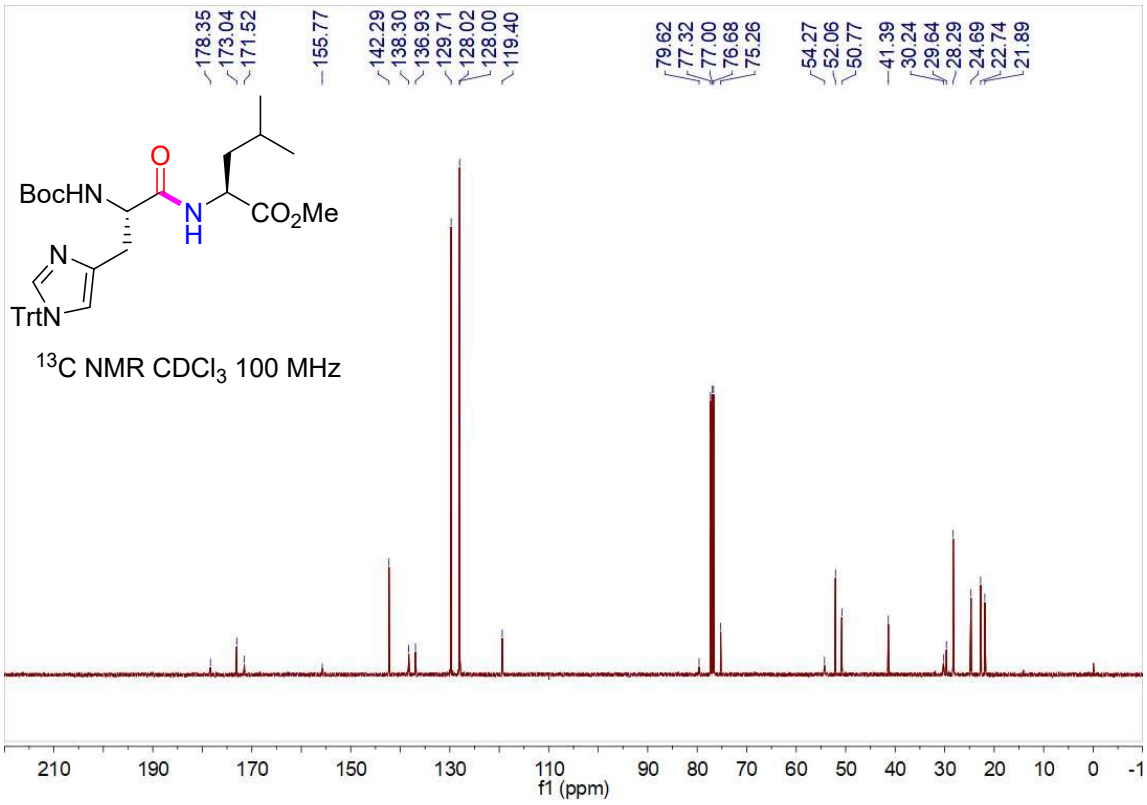


Peak No	Ret. Time	Area	Height	Area %	Height%
1	6.930	12252630	337386	51.425	50.707
2	8.999	11573624	327973	48.575	49.293
Total		23826253	665358	100.000	100.000

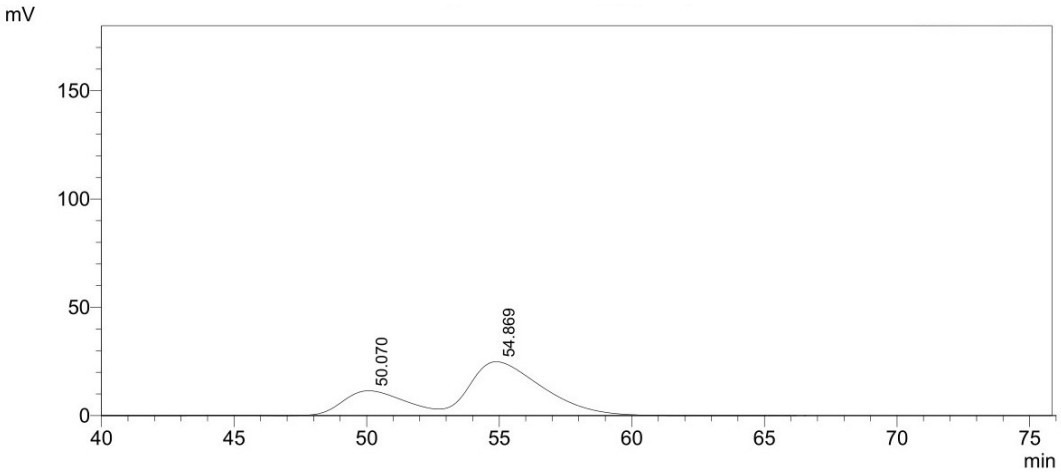


Peak No	Ret. Time	Area	Height	Area %	Height%
1	6.898	25078449	694260	100.000	100.000
Total		25078449	694260	100.000	100.000

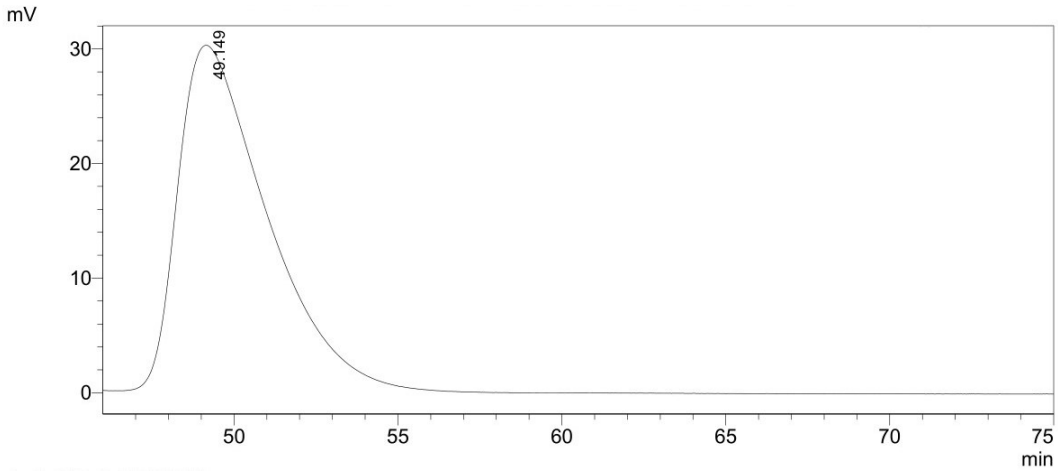




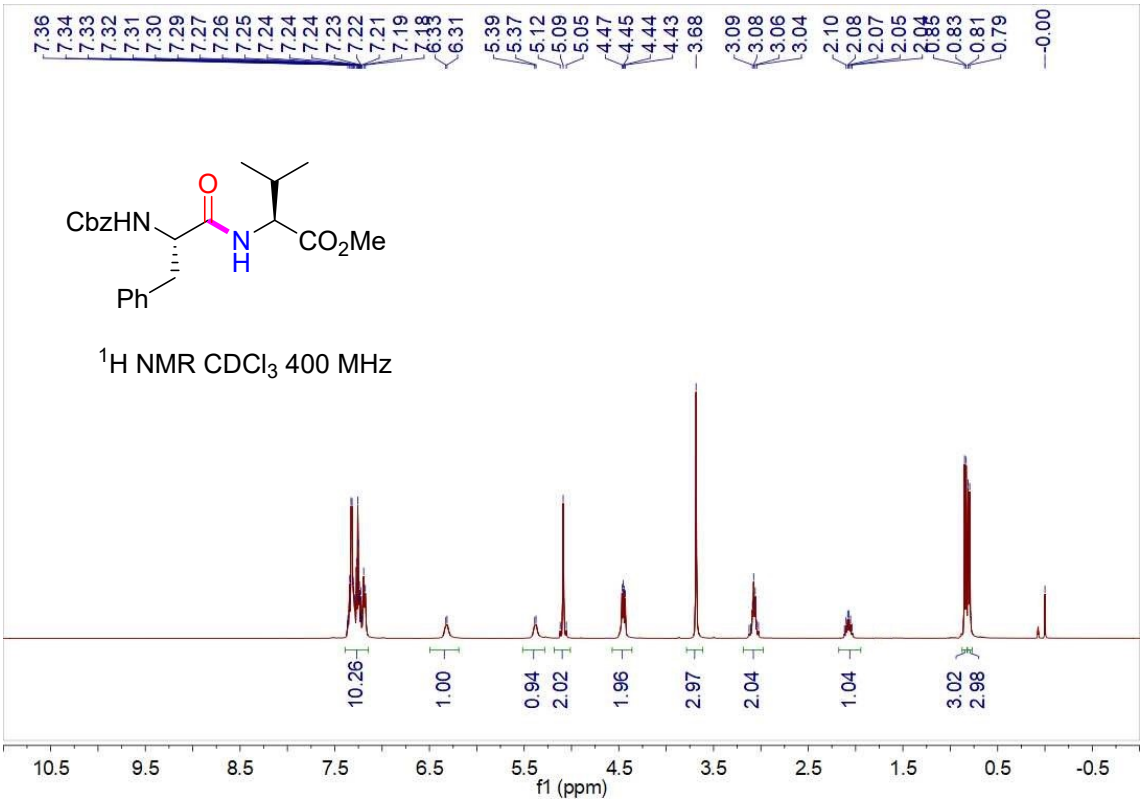
Chromatogram

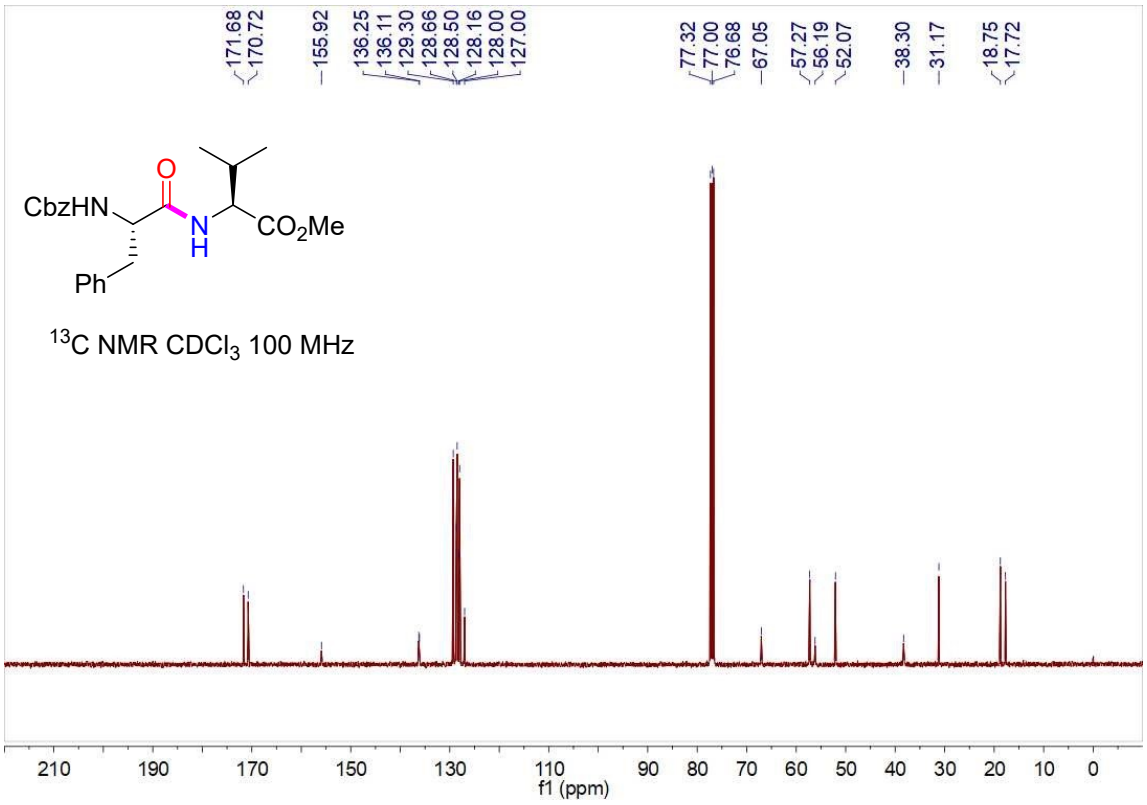


Peak No	Ret. Time	Area	Height	Area %	Height%
1	50.070	1416592	9968	26.342	30.616
2	54.869	3961160	22591	73.658	69.384
Total		5377752	32559	100.000	100.000

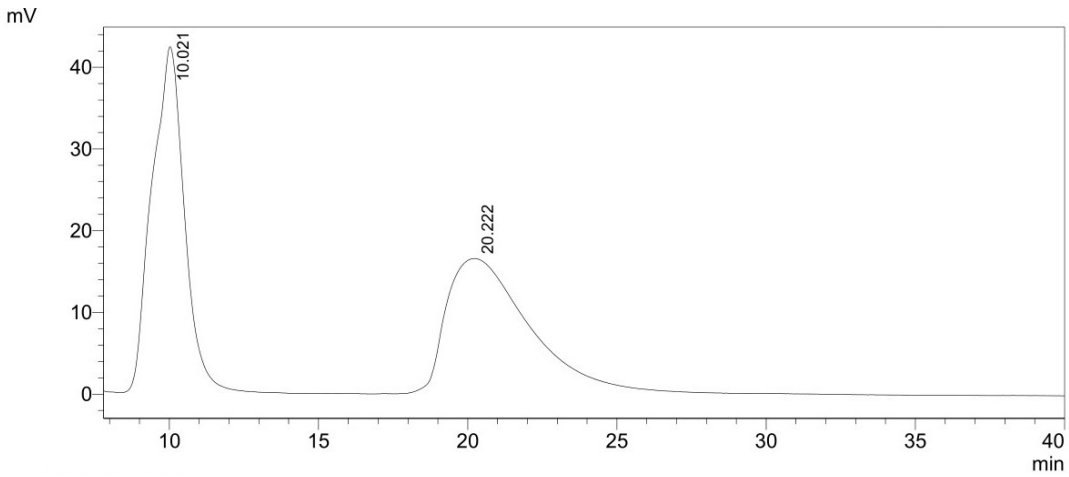


Peak No	Ret. Time	Area	Height	Area %	Height%
1	49.149	5661971	30105	100.000	100.000
Total		5661971	30105	100.000	100.000

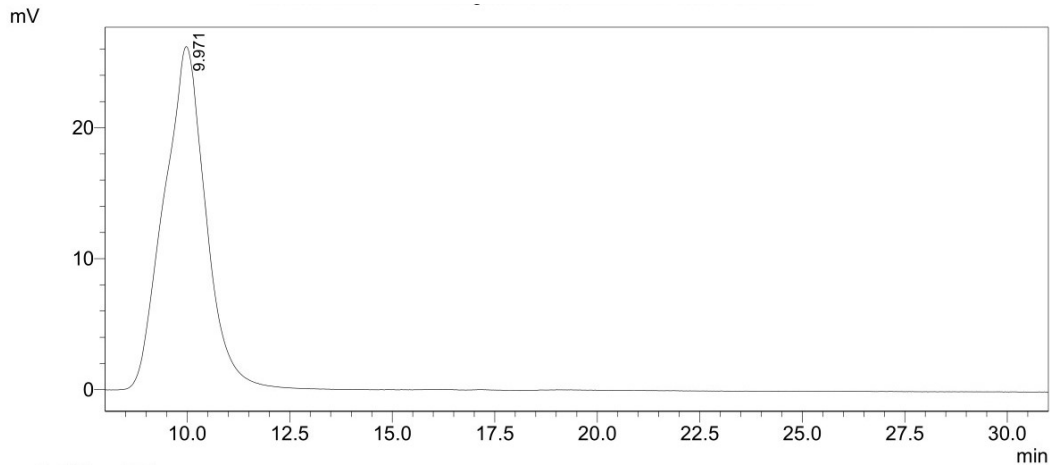




Chromatogram (NIS-NHC)

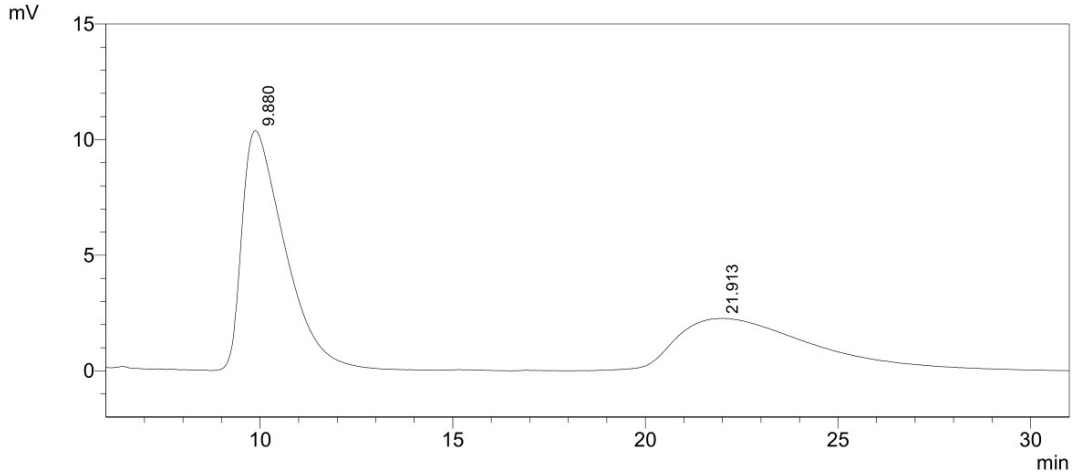


Peak No	Ret. Time	Area	Height	Area %	Height%
1	10.021	3179848	42268	51.895	72.330
2	20.222	2947589	16170	48.105	27.670
Total		6127437	58438	100.000	100.000

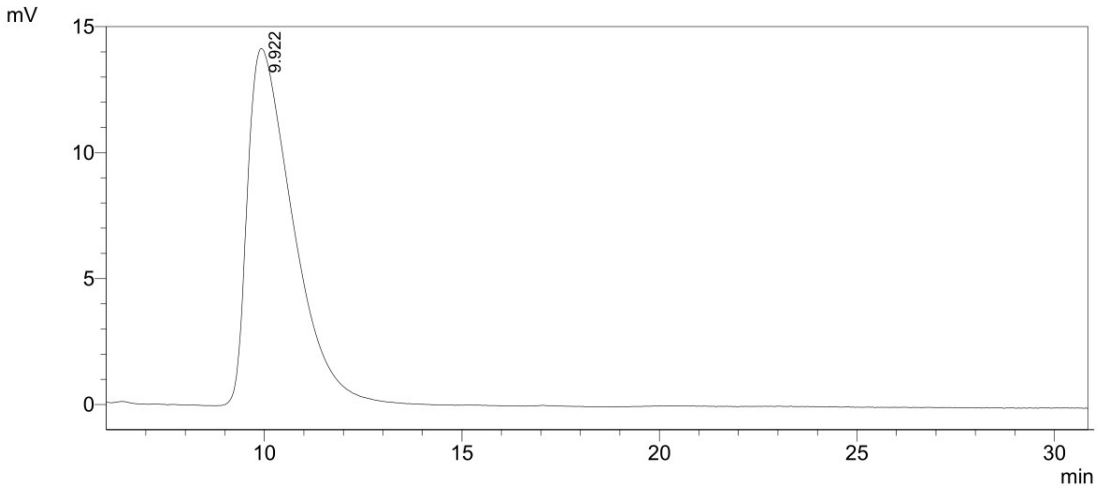


Peak No	Ret. Time	Area	Height	Area %	Height%
1	9.971	1832829	26123	100.000	100.000
Total		1832829	26123	100.000	100.000

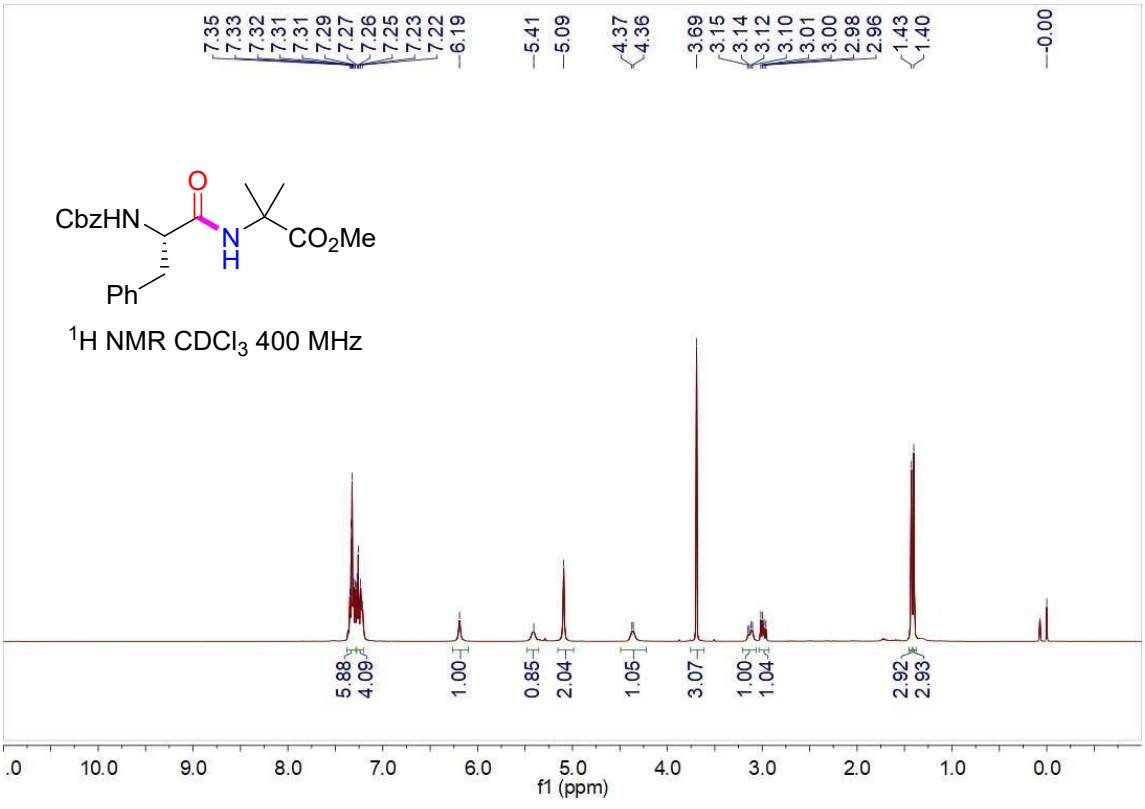
Chromatogram ($K_2S_2O_8$-NHC)

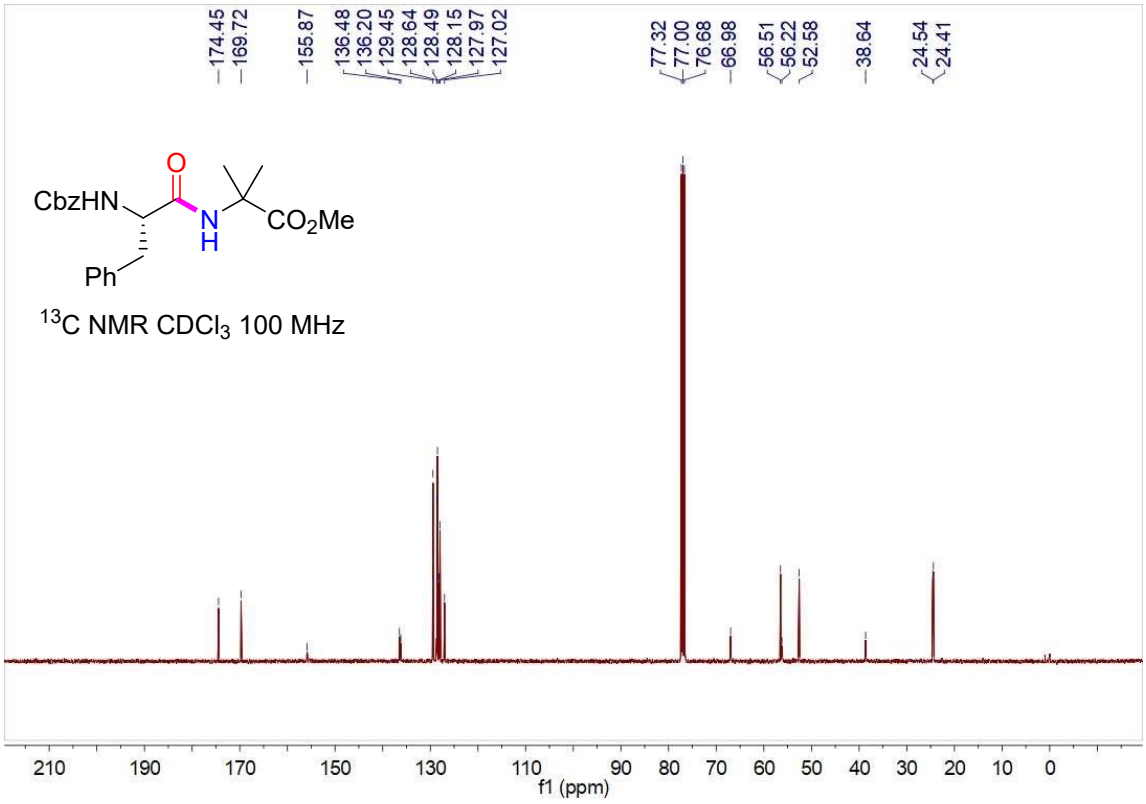


Peak No	Ret. Time	Area	Height	Area %	Height%
1	9.880	563807	8941	50.610	79.870
2	21.913	550205	2253	49.390	23.130
Total		1114012	11194	100.000	100.000

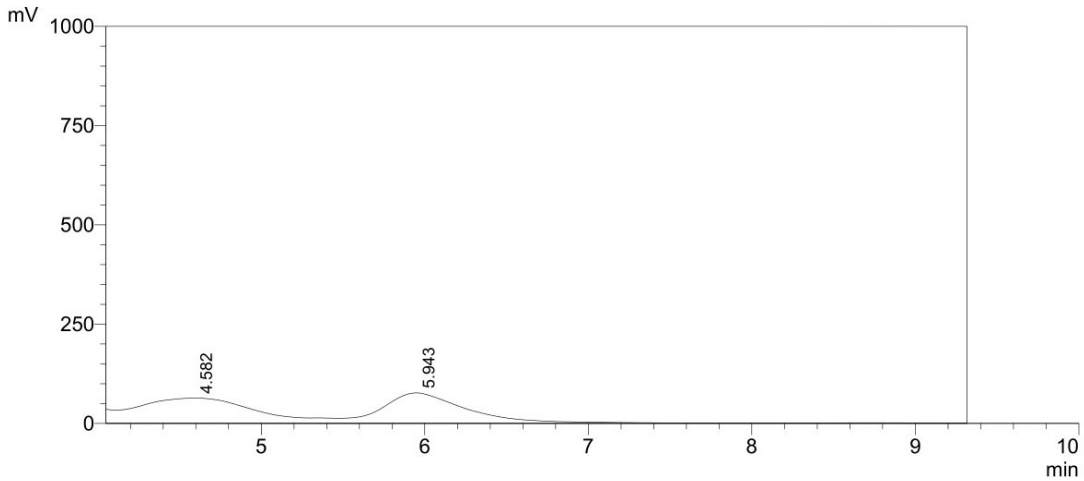


Peak No	Ret. Time	Area	Height	Area %	Height%
1	9.922	1121435	14143	100.000	100.000
Total		1121435	14143	100.000	100.000

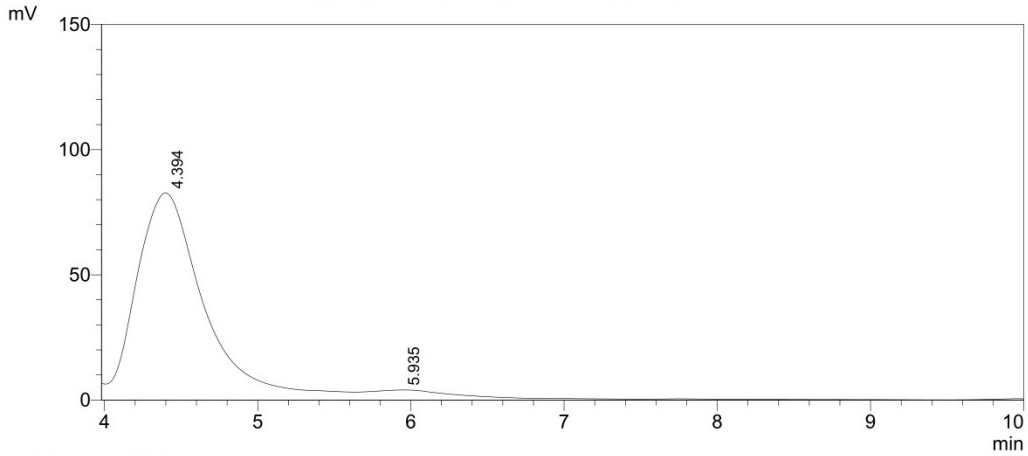




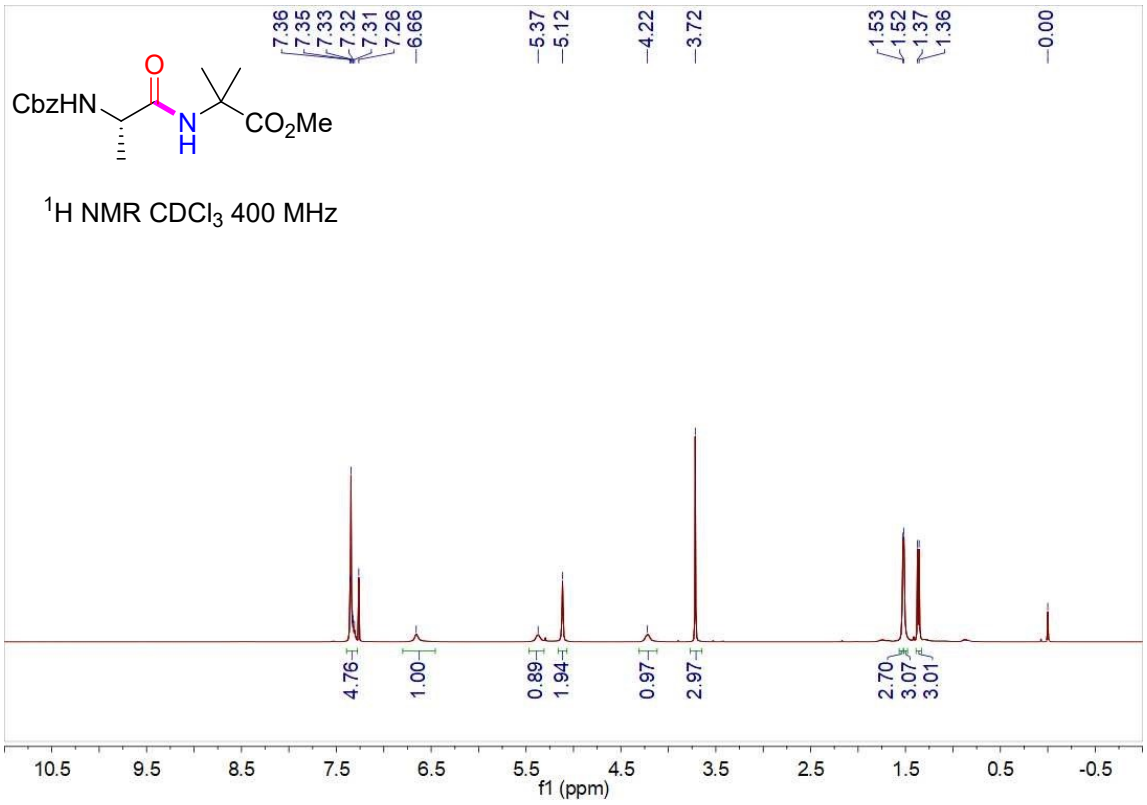
Chromatogram

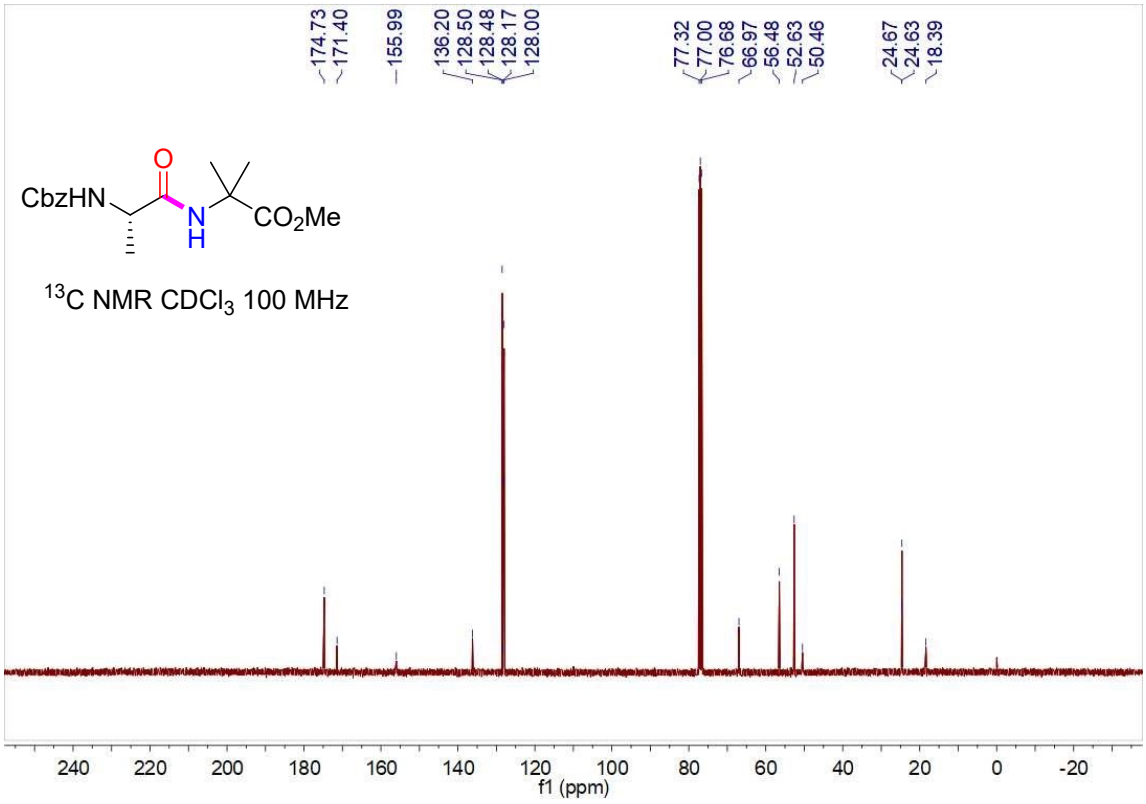


Peak No	Ret. Time	Area	Height	Area %	Height%
1	4.582	1346249	37291	40.982	36.130
2	5.943	1938713	65921	59.018	63.870
Total		3284962	103212	100.000	100.000

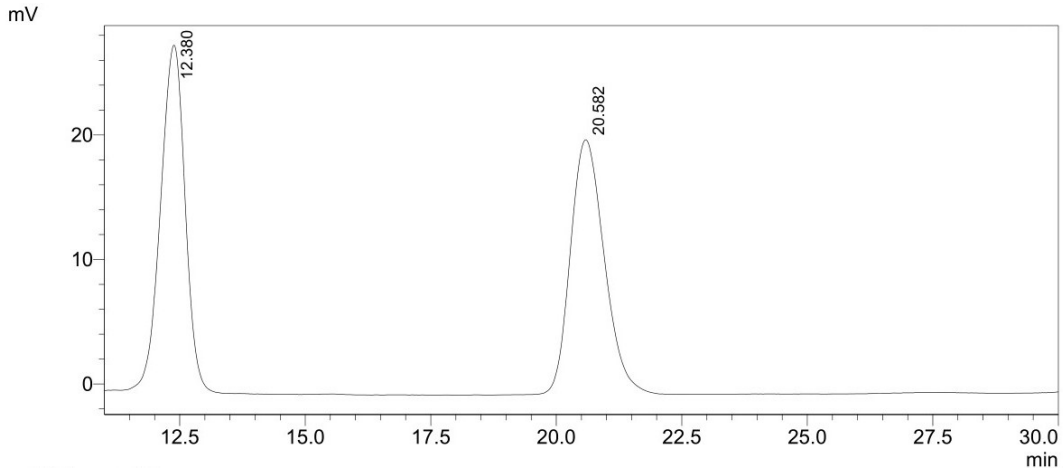


Peak No	Ret. Time	Area	Height	Area %	Height%
1	4.394	2066674	76662	98.064	97.973
2	5.935	40799	1586	1.936	2.027
Total		2107473	78248	100.000	100.000

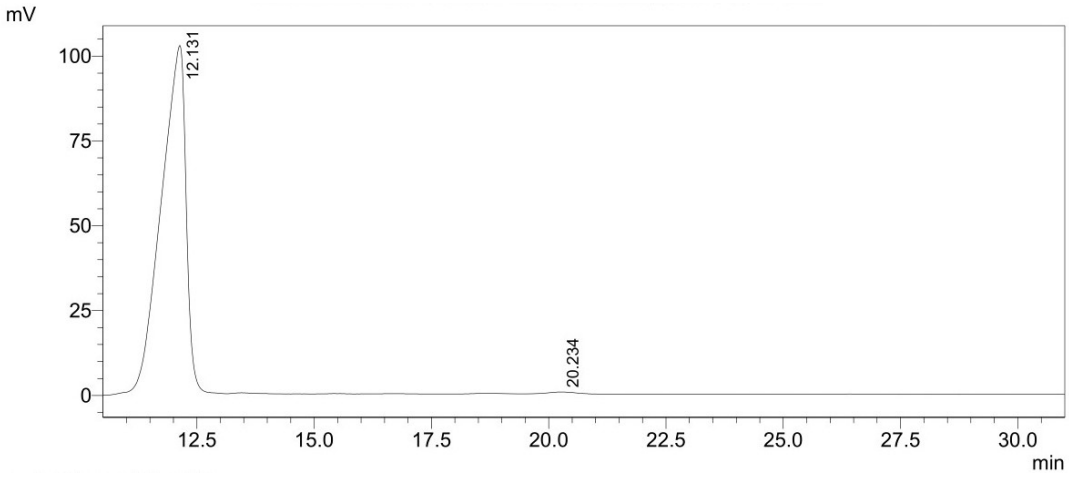




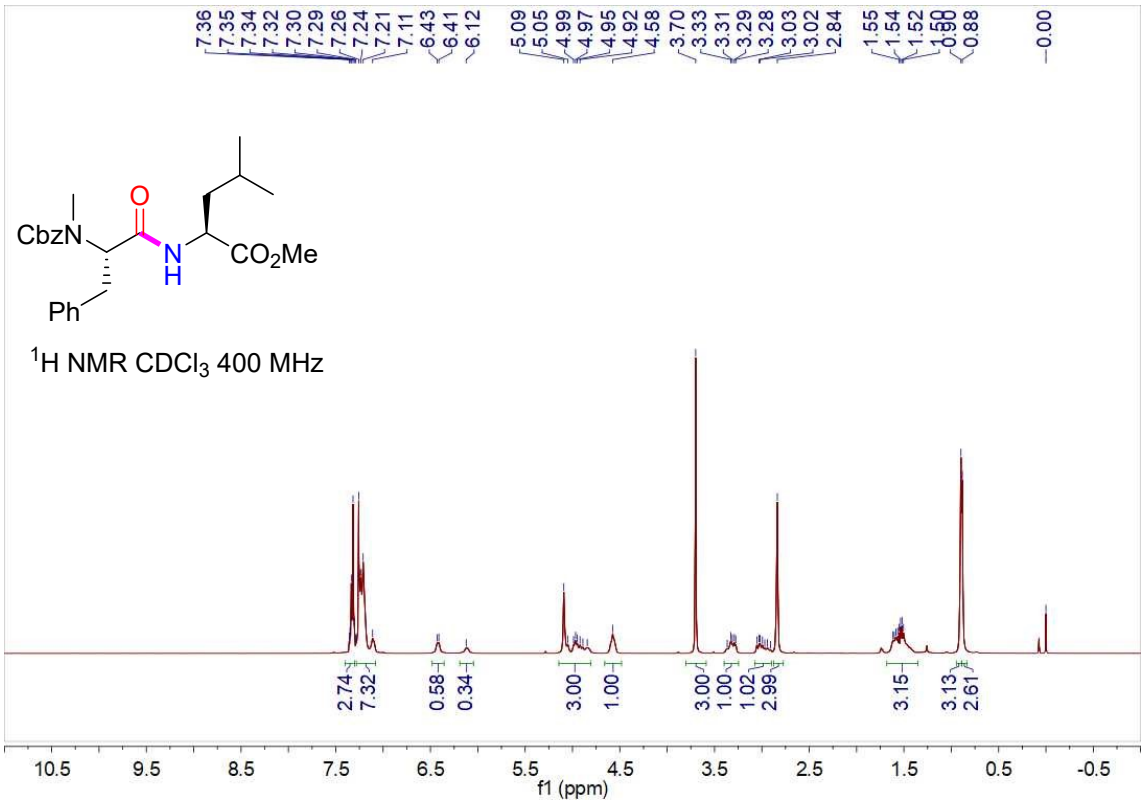
Chromatogram

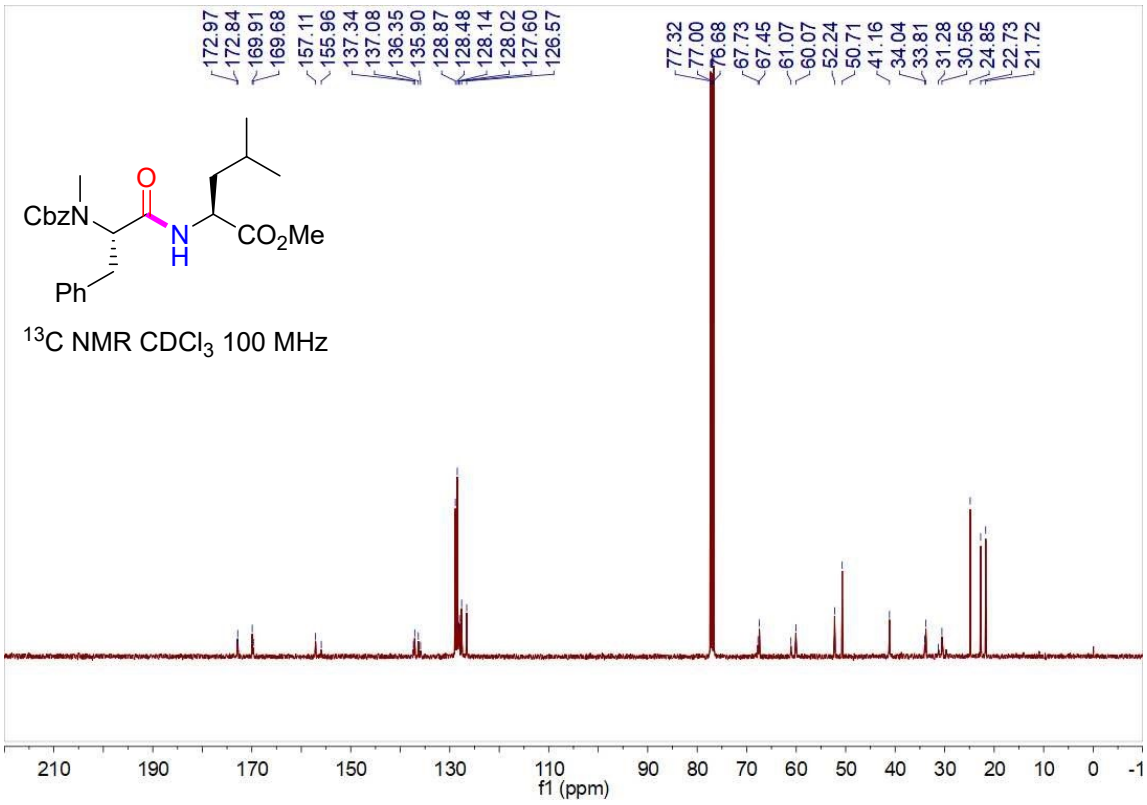


Peak No	Ret. Time	Area	Height	Area %	Height%
1	12.380	944128	27838	49560	57.655
2	20.582	960885	20455	50.440	42.356
Total		1905013	48293	100.000	100.000

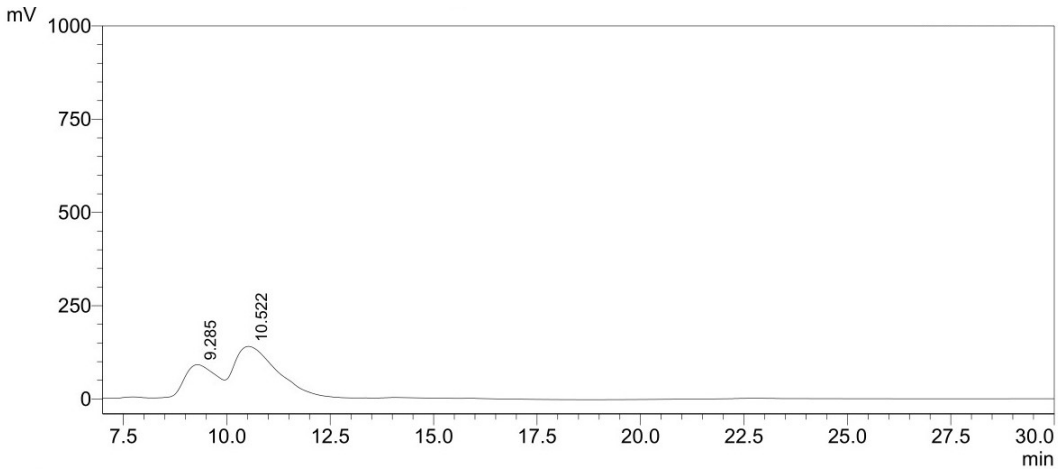


Peak No	Ret. Time	Area	Height	Area %	Height%
1	12.131	3788635	102742	99.363	99.433
2	20.234	24304	586	0.637	0.567
Total		3812939	103328	100.000	100.000

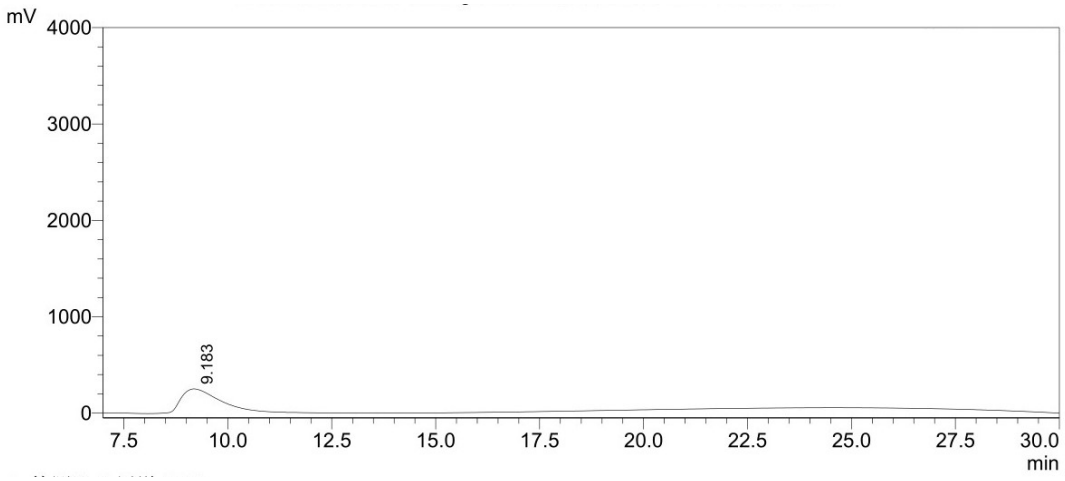




Chromatogram (NIS-NHC)

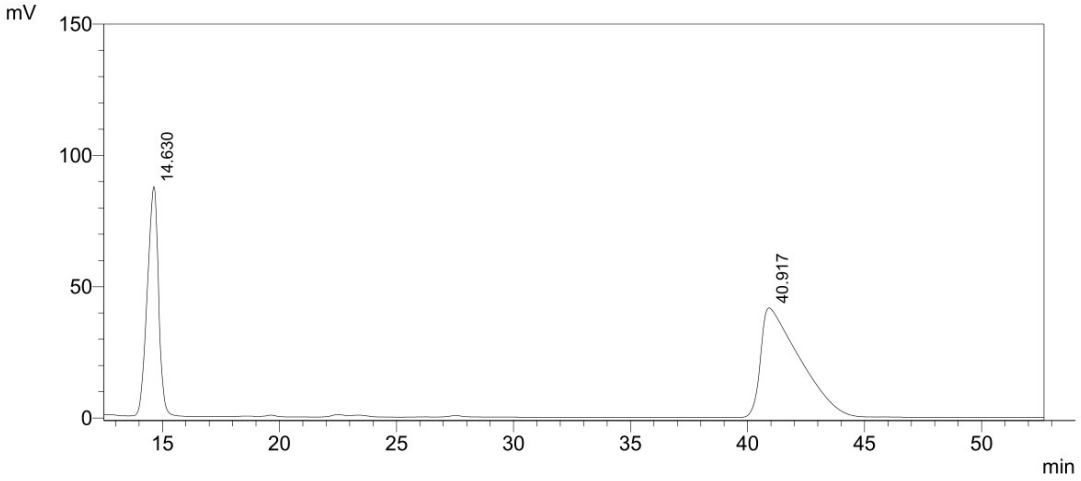


Peak No	Ret. Time	Area	Height	Area %	Height%
1	9.285	2447599	61188	48.784	53.906
2	10.522	2569612	52320	51.216	46.094
Total		5017211	113508	100.000	100.000

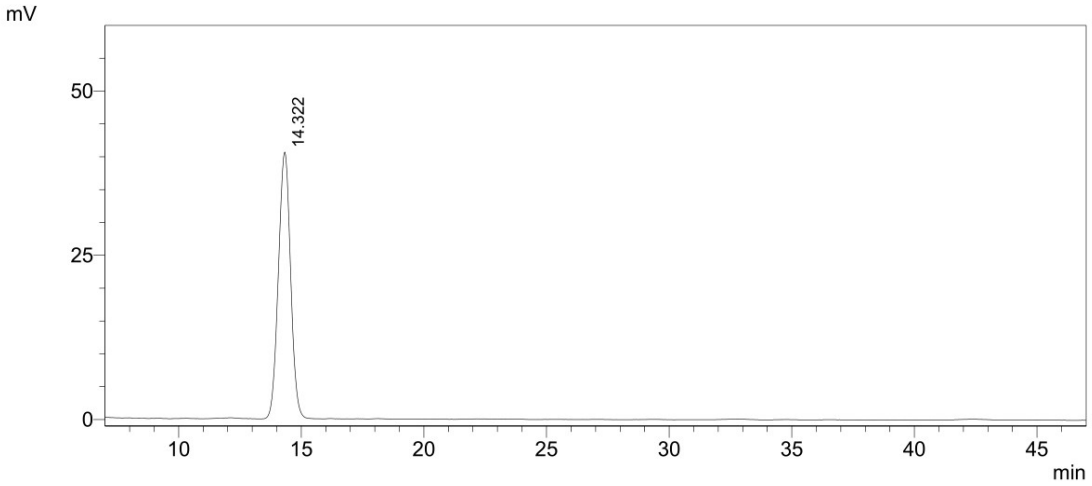


Peak No	Ret. Time	Area	Height	Area %	Height%
1	9.183	13164082	221017	100.000	100.000
Total		13164082	221017	100.000	100.000

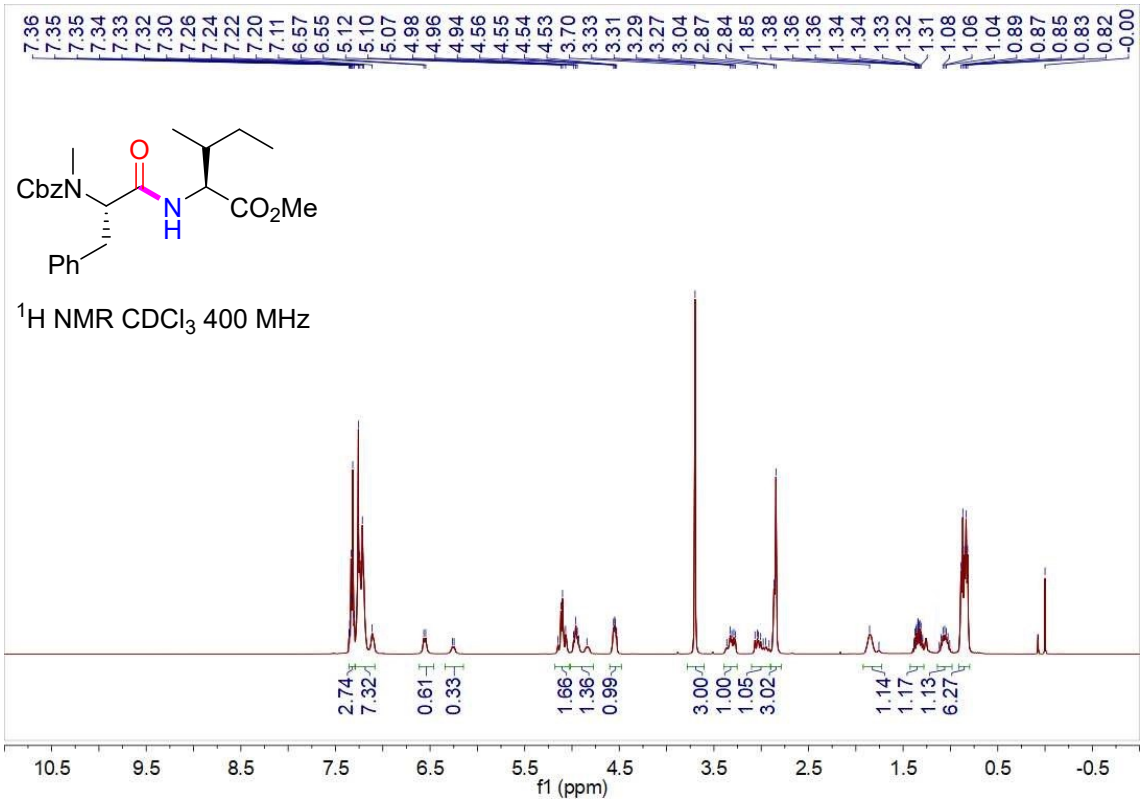
Chromatogram ($K_2S_2O_8$-NHC)

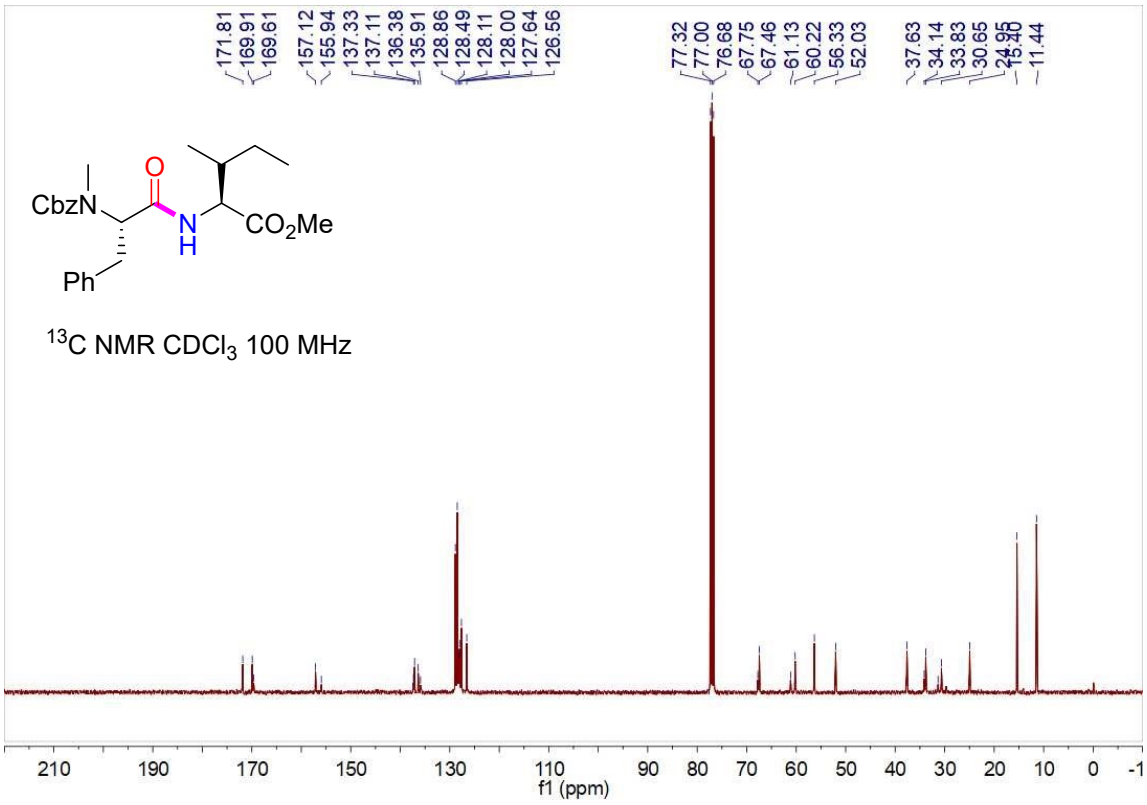


Peak No	Ret. Time	Area	Height	Area %	Height%
1	14.630	2897478	87422	50.461	73.941
2	40.917	2844538	30809	49.539	26.059
Total		5742017	118231	100.000	100.000

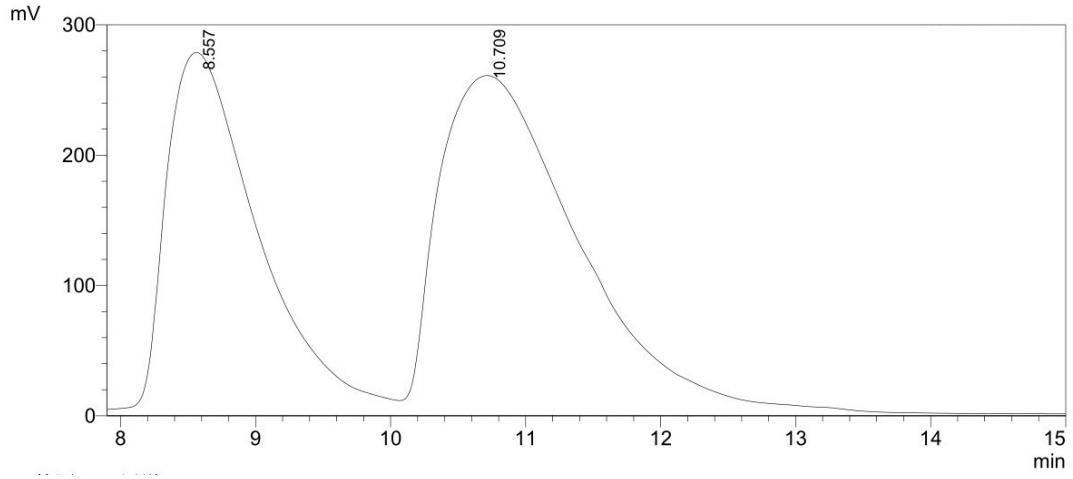


Peak No	Ret. Time	Area	Height	Area %	Height%
1	14.322	1402754	40593	100.000	100.000
Total		1402754	40593	100.000	100.000

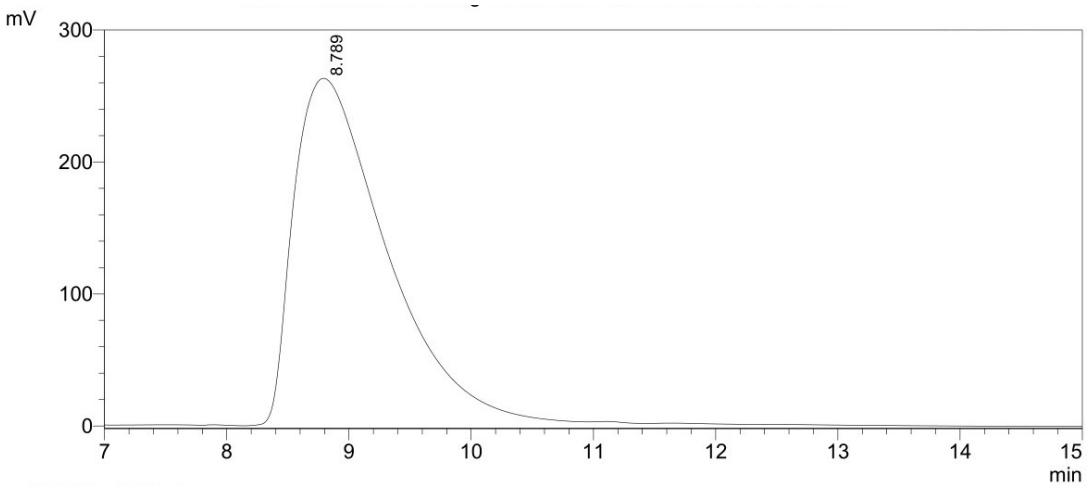




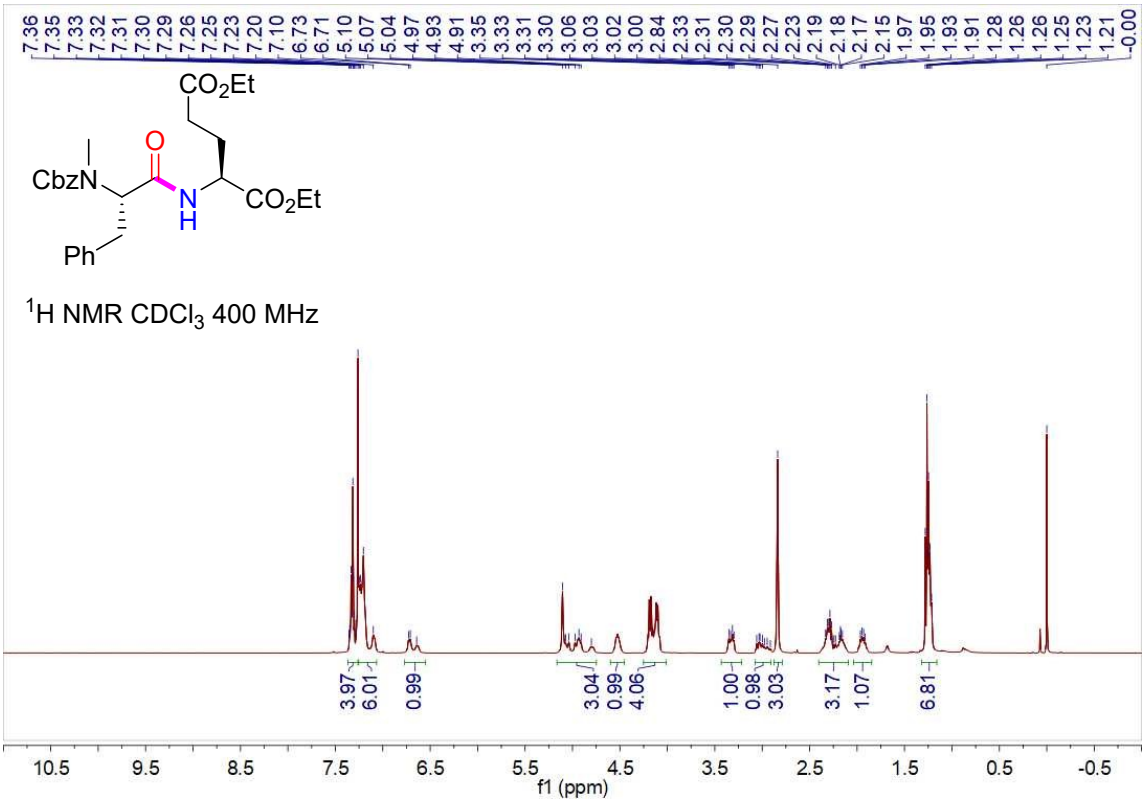
Chromatogram

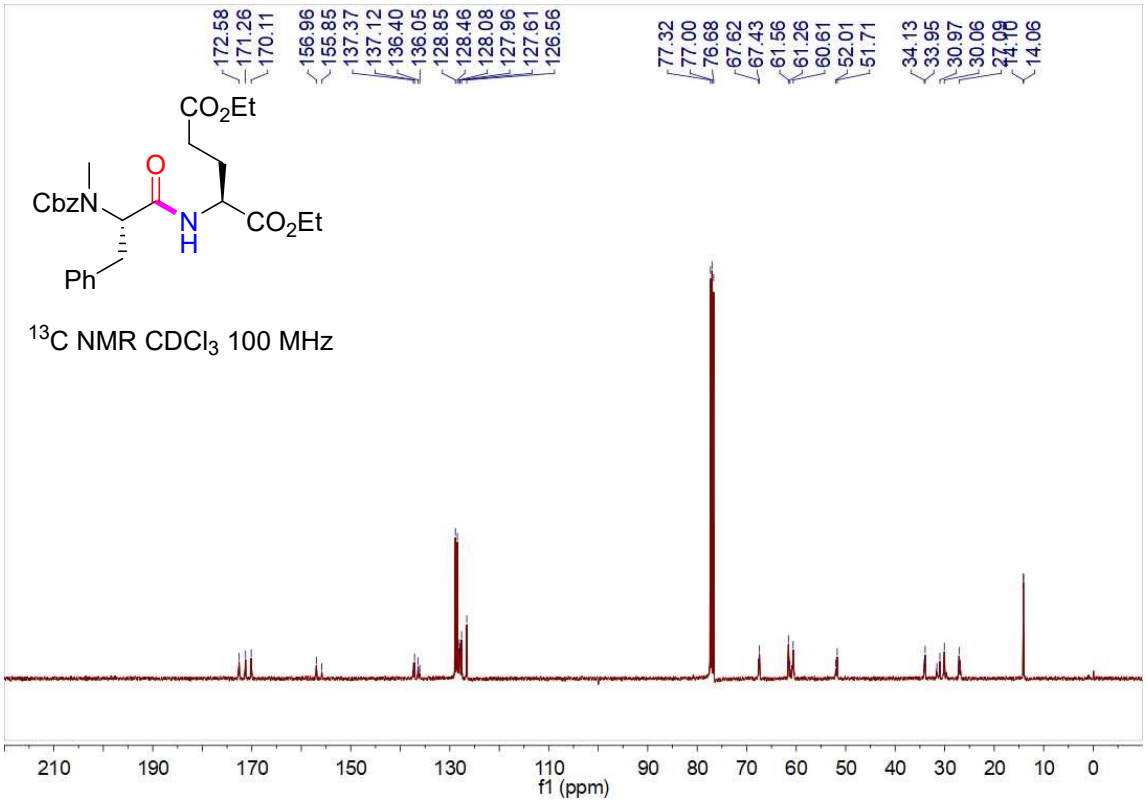


Peak No	Ret. Time	Area	Height	Area %	Height%
1	8.557	12316971	271826	48.535	56.135
2	10.709	13060579	212409	51.465	43.865
Total		25377551	484235	100.000	100.000

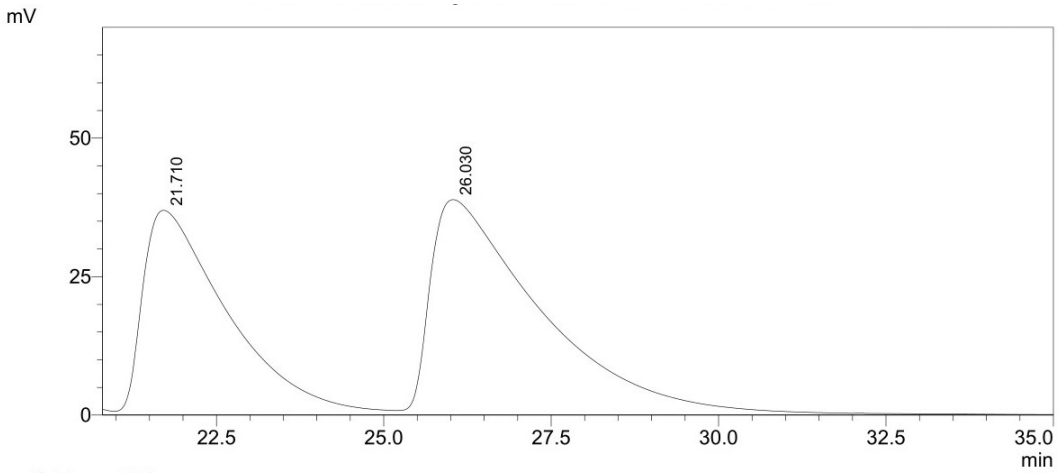


Peak No	Ret. Time	Area	Height	Area %	Height%
1	8.789	13746775	262348	100.000	100.000
Total		13746775	262348	100.000	100.000

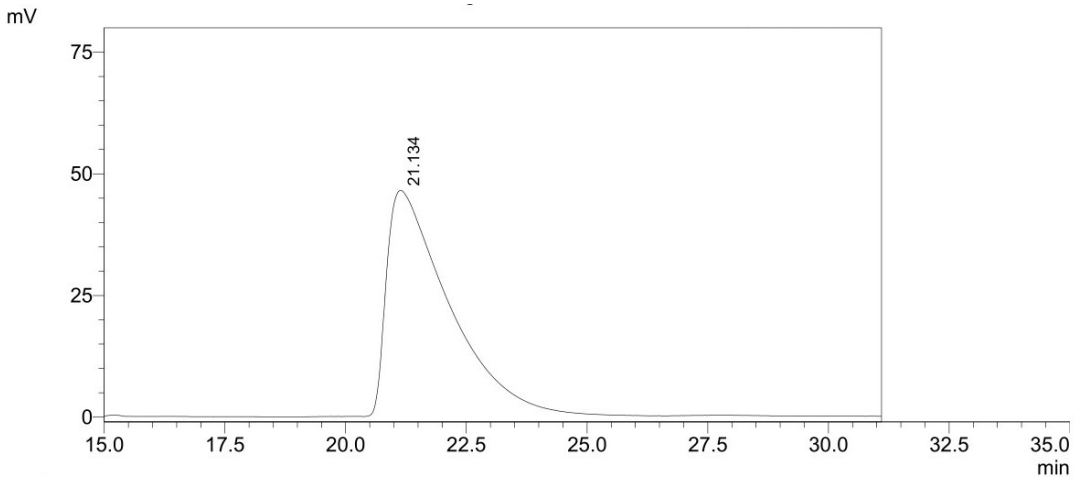




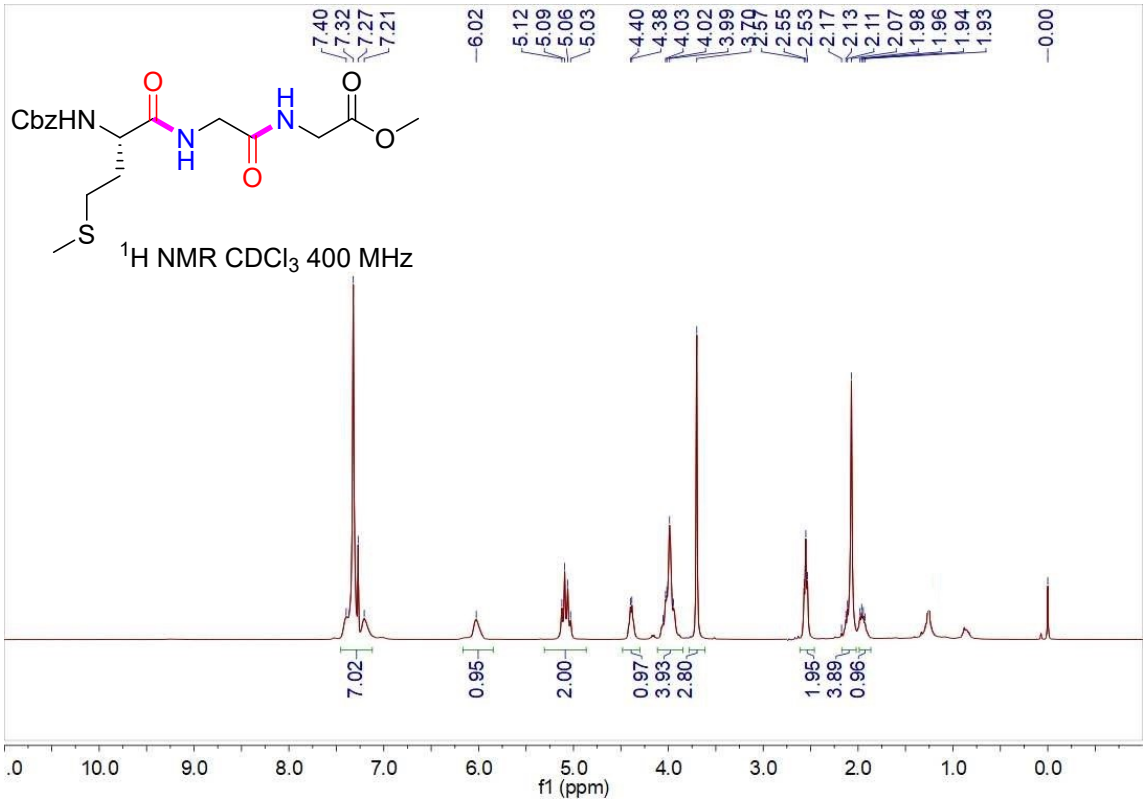
Chromatogram

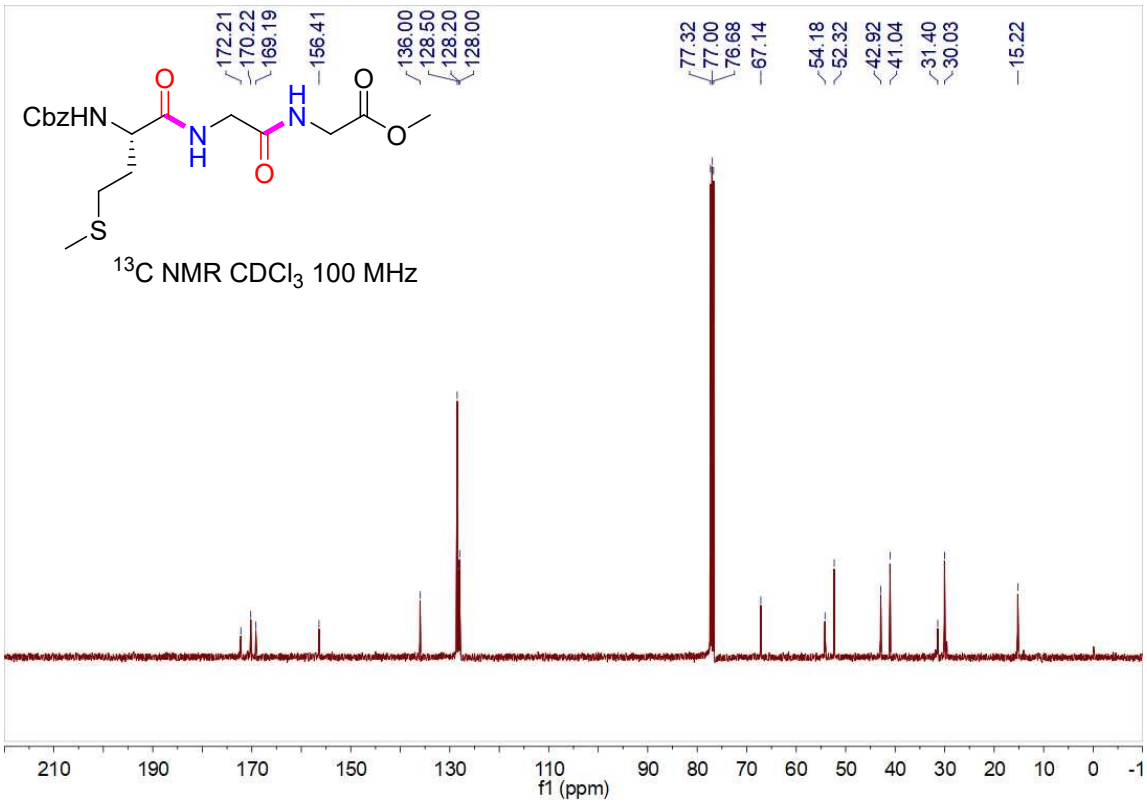


Peak No	Ret. Time	Area	Height	Area %	Height%
1	21.710	3076443	36179	49.426	51.961
2	26.030	3147895	33448	50.574	48.039
Total		6224338	69627	100.000	100.000

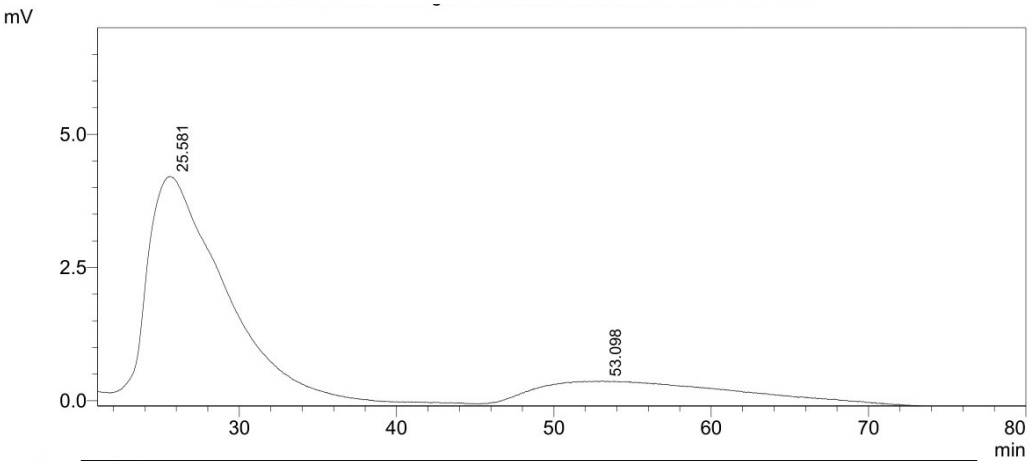


Peak No	Ret. Time	Area	Height	Area %	Height%
1	21.134	3045906	39105	100.000	100.000
Total		3045906	39105	100.000	100.000

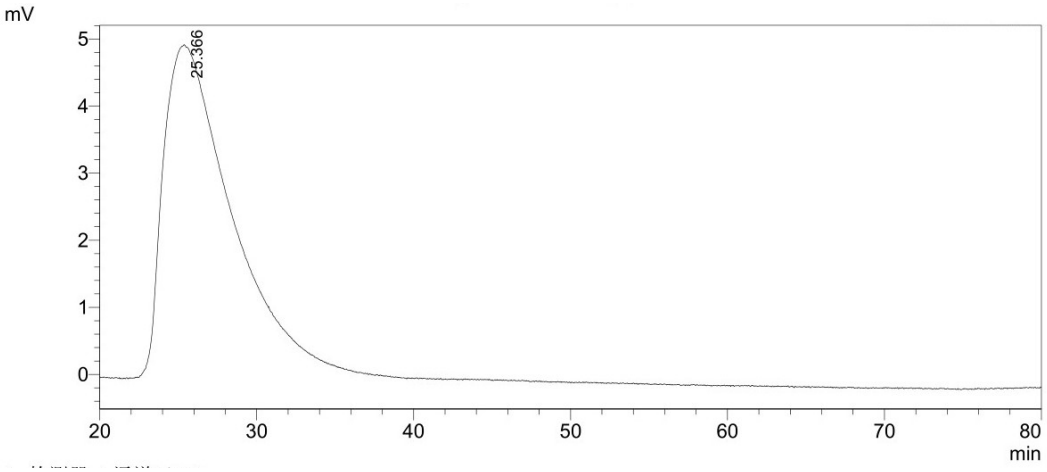




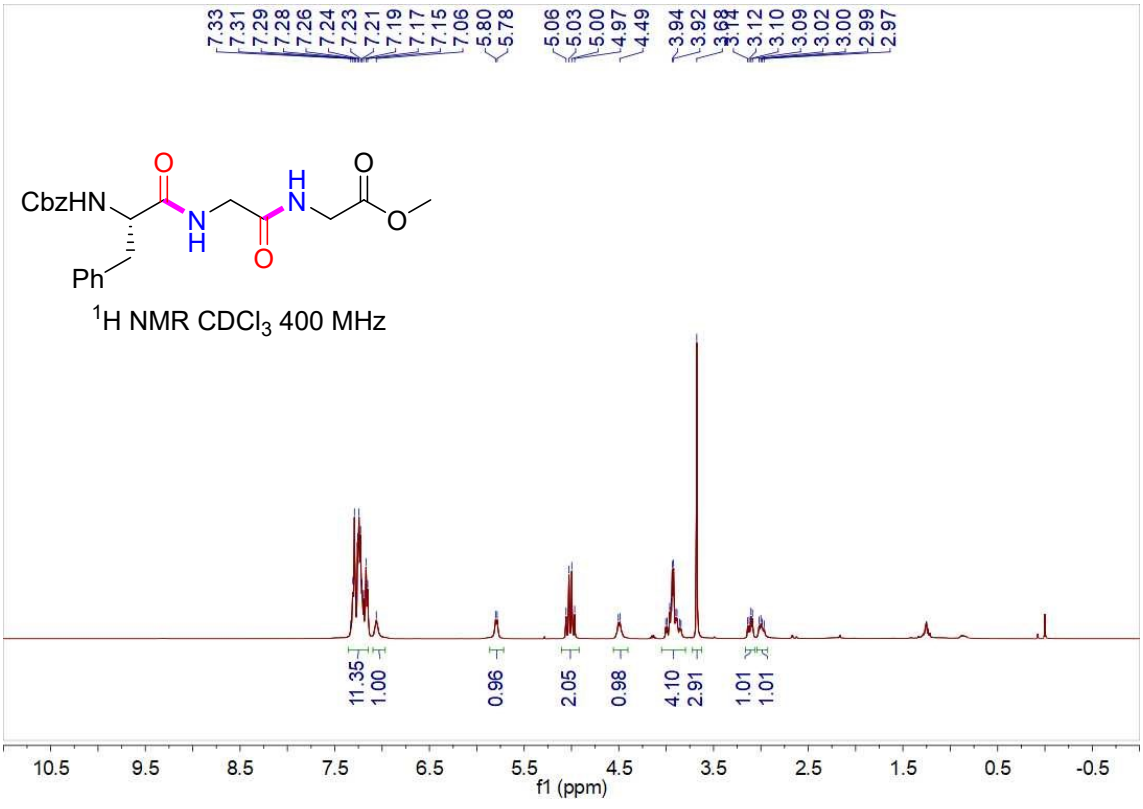
Chromatogram

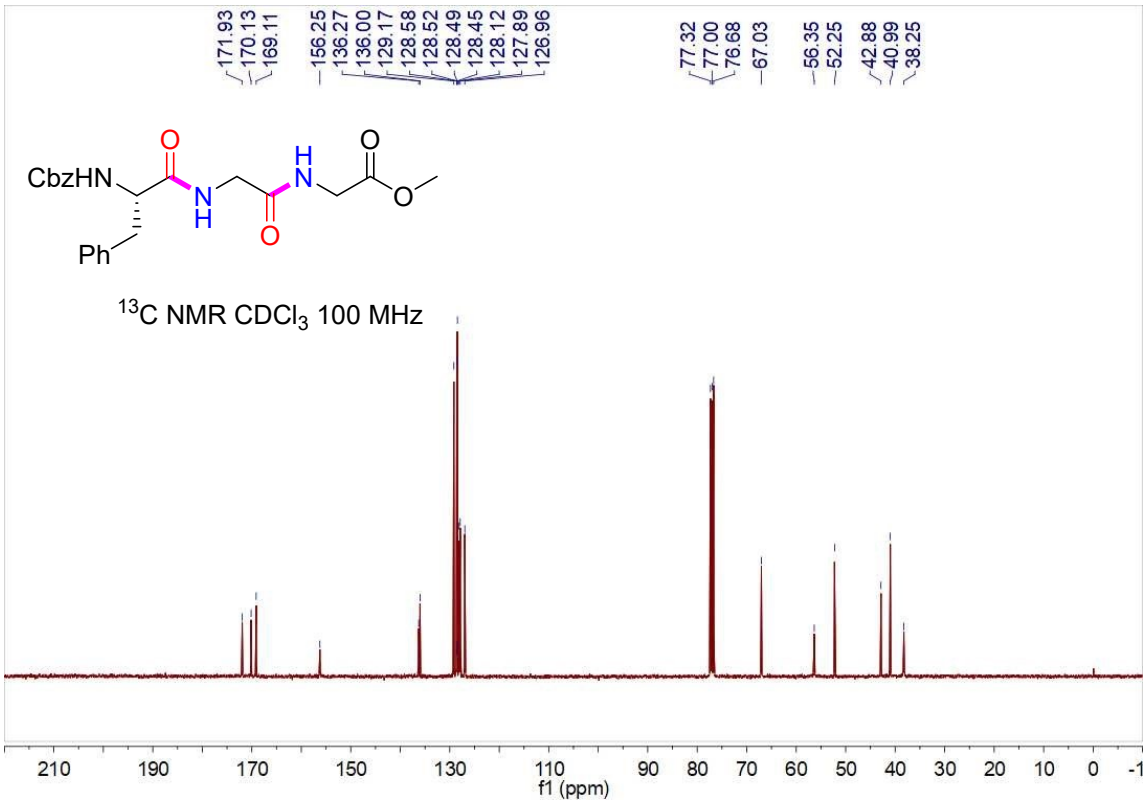


Peak No	Ret. Time	Area	Height	Area %	Height%
1	25.581	473010	2569	49.945	84.758
2	53.098	474047	462	50.055	15.242
Total		947057	3031	100.000	100.000



Peak No	Ret. Time	Area	Height	Area %	Height%
1	25.366	1295749	4802	100.000	100.000
Total		1295749	4802	100.000	100.000

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128.49
128.45
128.12
127.89
126.96
77.32
77.00
76.68
67.03
56.35
52.25
42.88
40.99
38.25
CbzHN
O
N
H
O
H
N
O
O
Ph
13C NMR CDCl3 100 MHz
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150
130
110
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80
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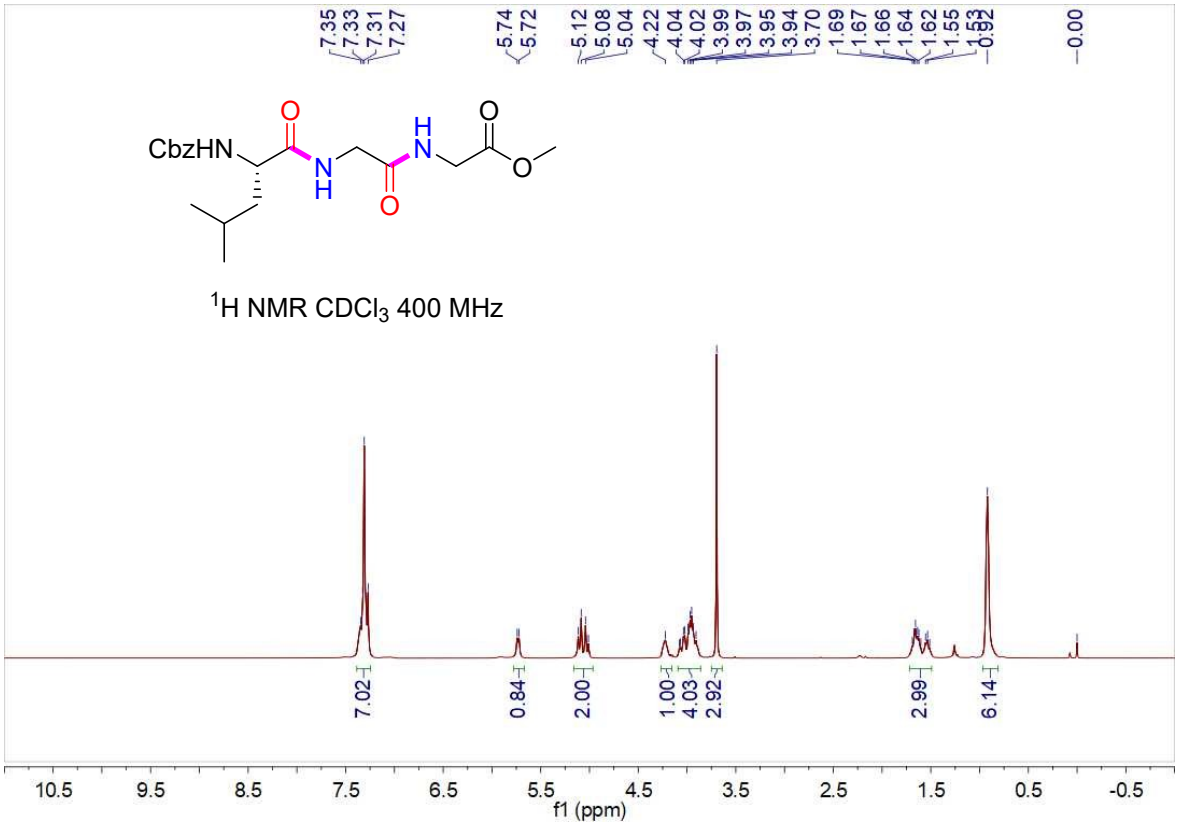
60
50
40
30
20
10
0
-1
f1 (ppm)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5.08
5.04
4.22
4.04
4.02
3.99
3.97
3.95
3.94
3.70
1.69
1.67
1.66
1.64
1.62
1.55
0.92
0.00
CbzHN
O
N
H
O
H
N
O
O
1H NMR CDCl3 400 MHz
7.02
0.84
2.00
1.00
4.03
2.92
2.99
6.14
10.5
9.5
8.5
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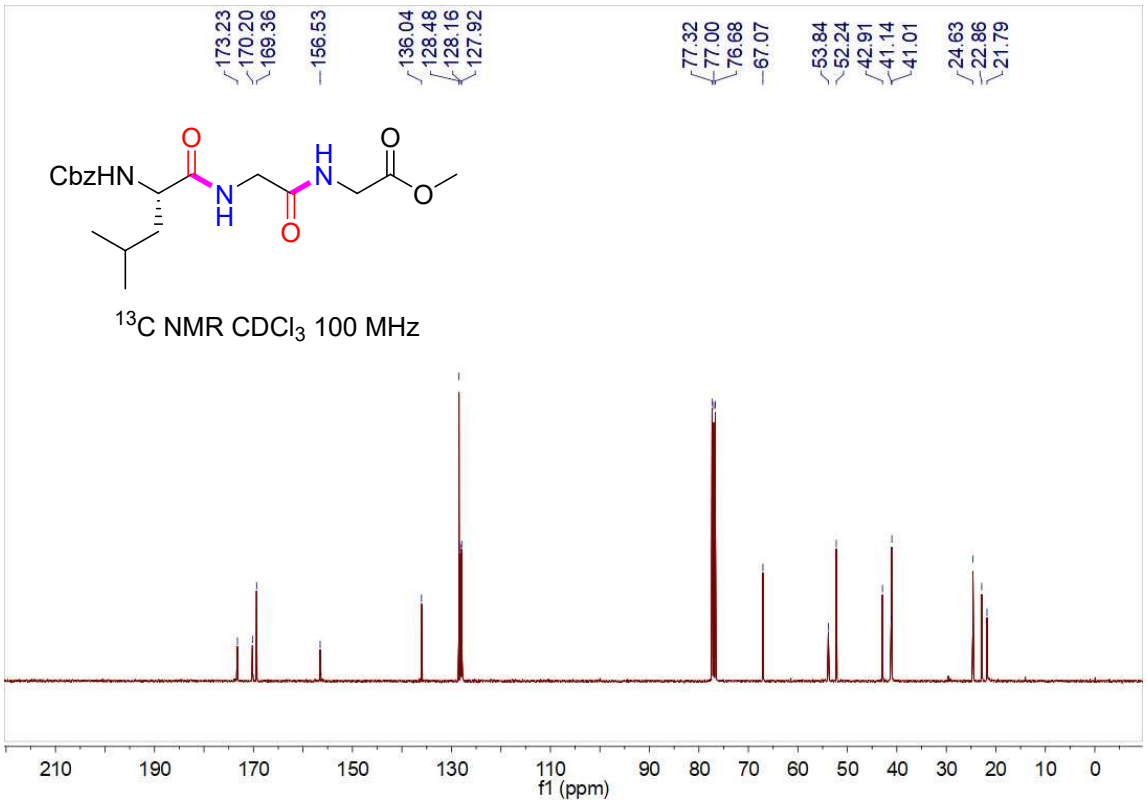
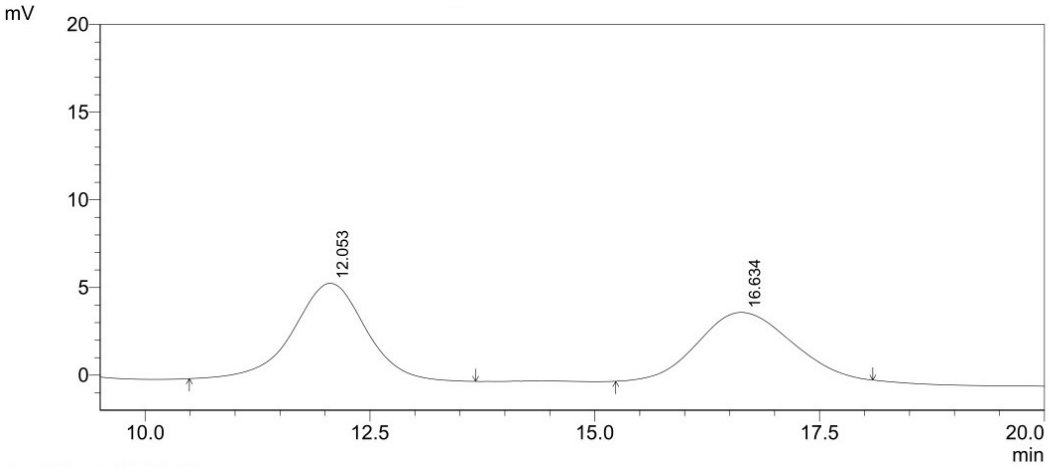
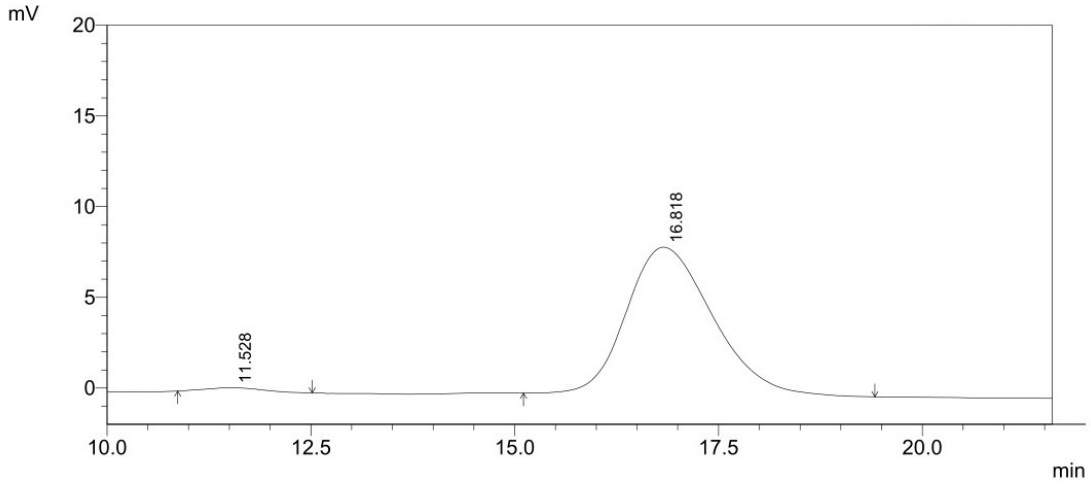
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)



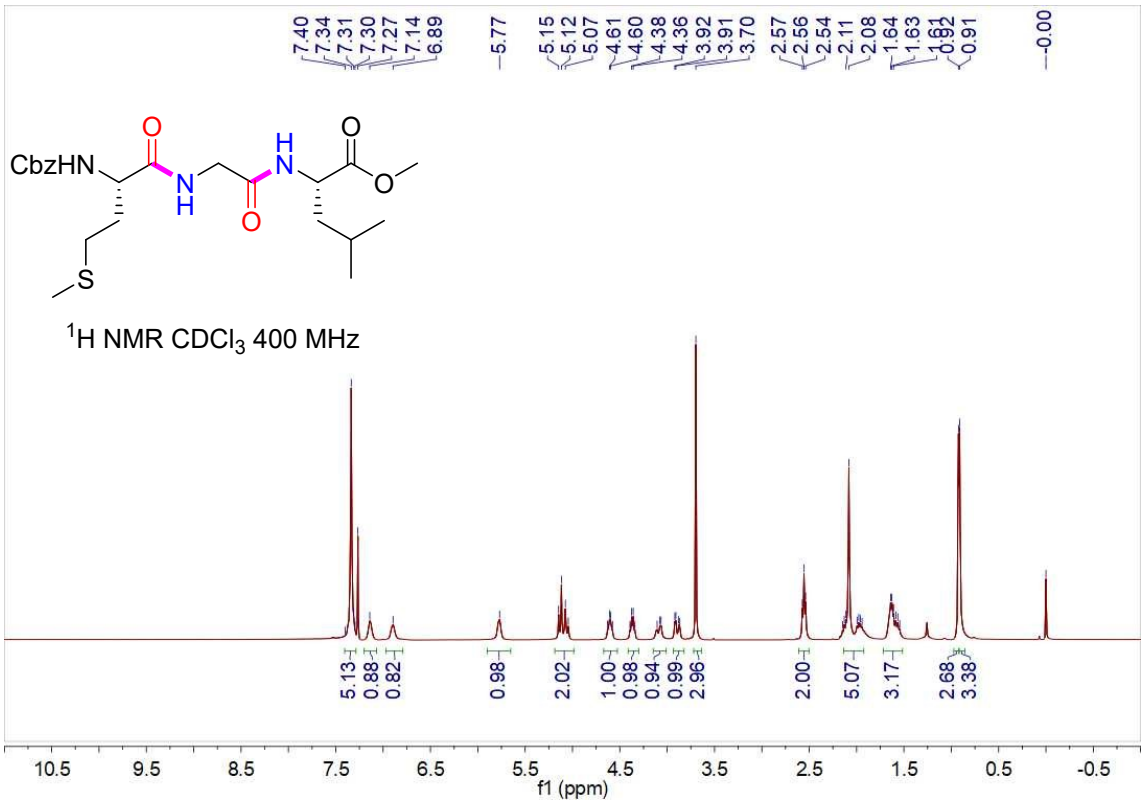
Chromatogram

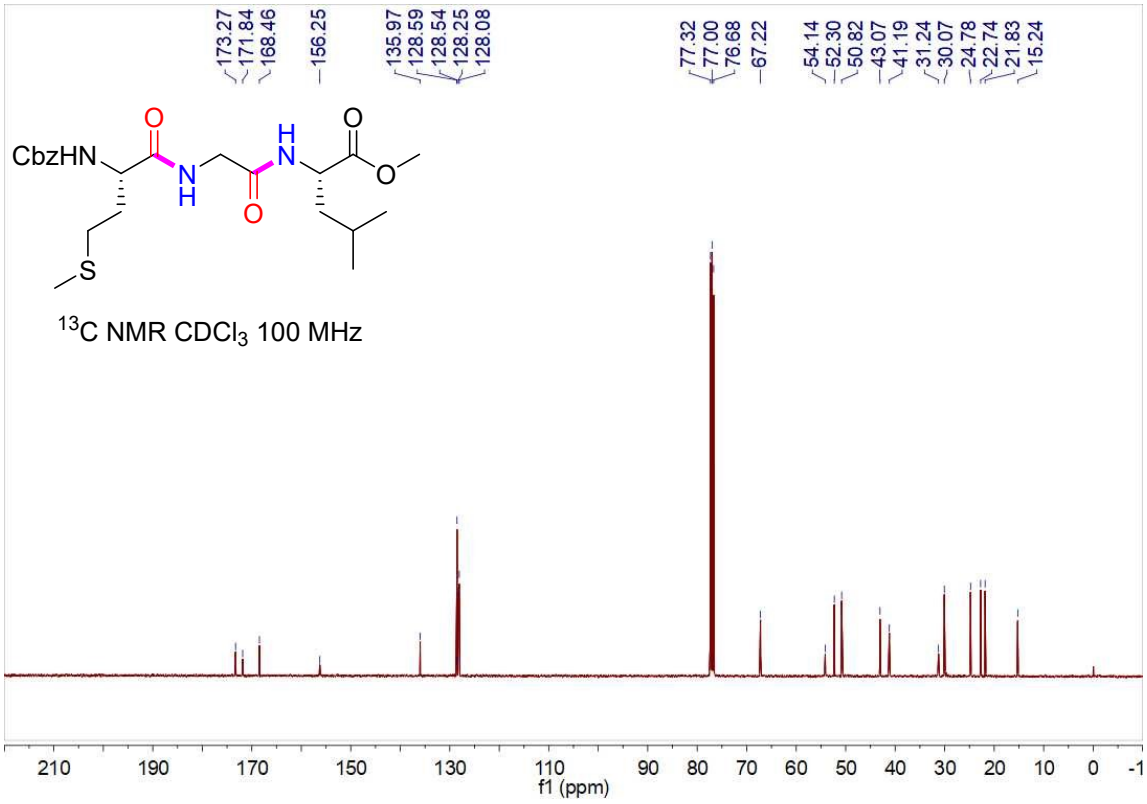


Peak No	Ret. Time	Area	Height	Area %	Height%
1	12.053	309409	5516	52.298	58.571
2	16.634	282217	3901	47.702	41.429
Total		591627	9417	100.000	100.000



Peak No	Ret. Time	Area	Height	Area %	Height%
1	11.528	10436	227	1.714	2.716
2	16.818	598374	8119	98.286	97.284
Total		608810	8346	100.000	100.000

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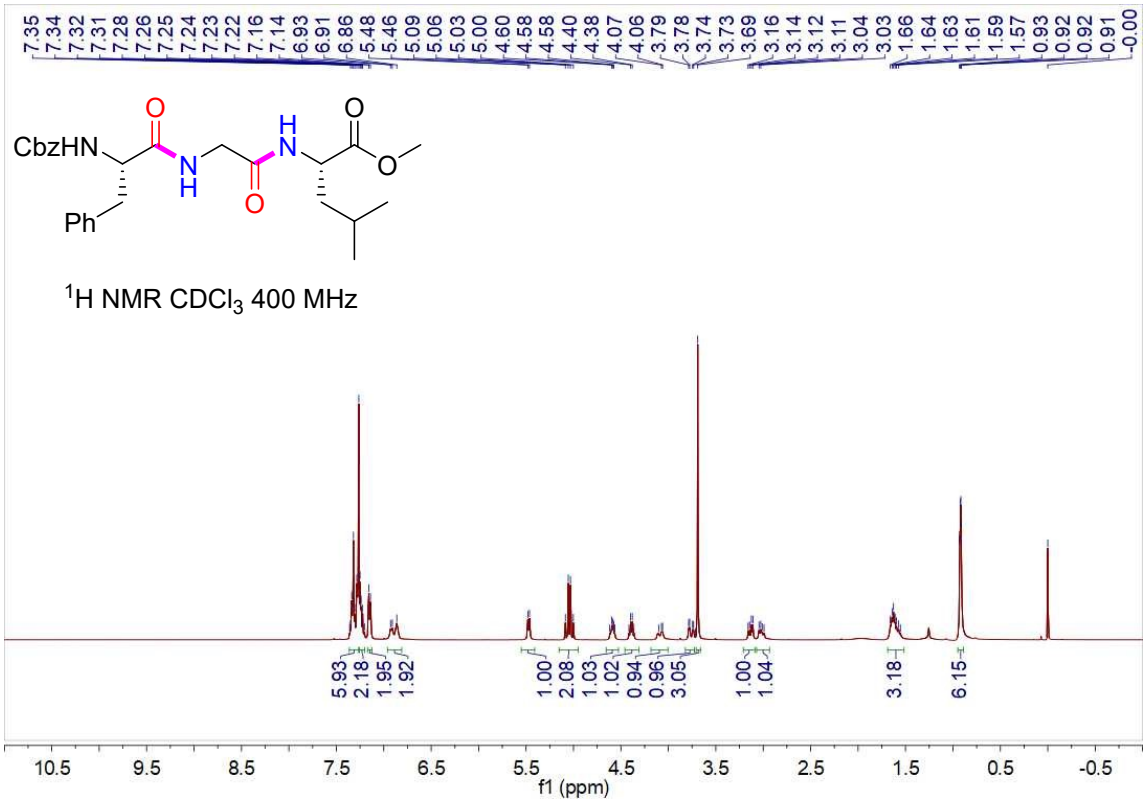
128.59
128.54
128.25
128.08
77.32
77.00
76.68
67.22
54.14
52.30
50.82
43.07
41.19
31.24
30.07
24.78
22.74
21.83
15.24
CbzHN
O
N
H
H
N
O
O
S
^{13}C NMR $CDCl_3$ 100 MHz
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.25
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7.22
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6.91
6.86
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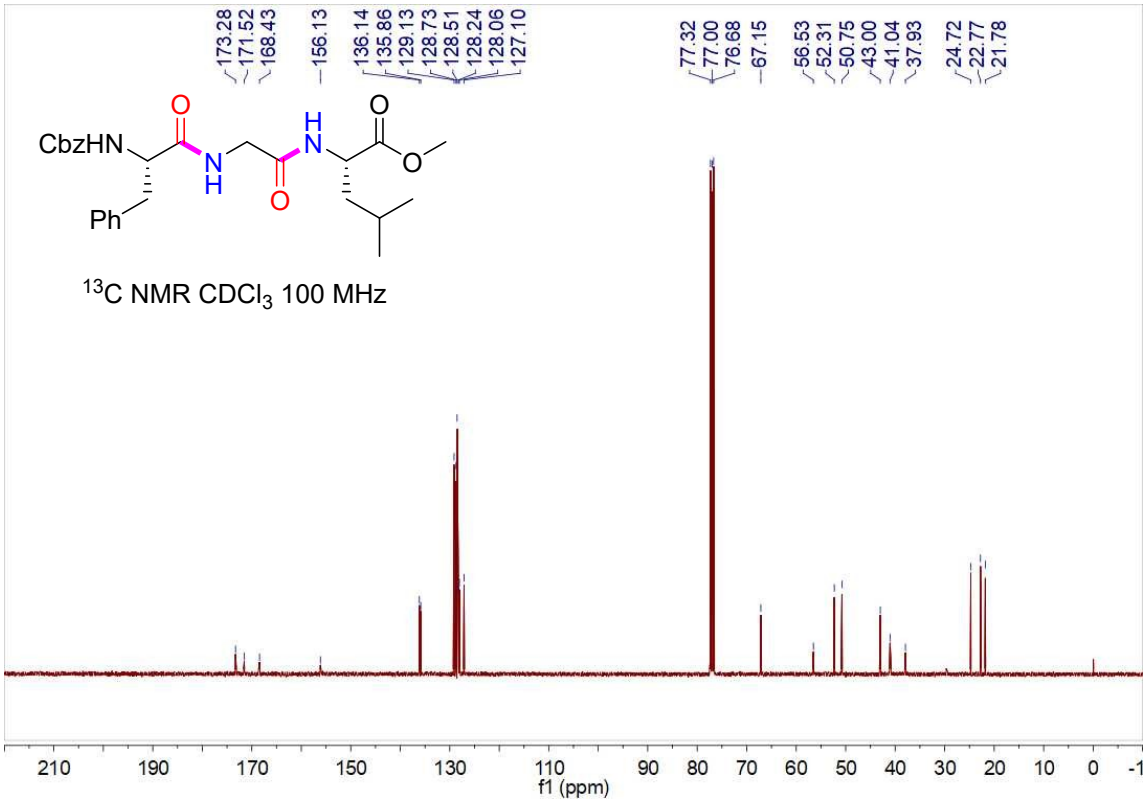
5.46
5.09
5.06
5.03
5.00
4.60
4.58
4.58
4.40
4.38
4.07
4.06
3.79
3.78
3.74
3.73
3.69
3.16
3.14
3.12
3.11
3.04
3.03
1.66
1.64
1.63
1.61
1.59
1.57
0.93
0.92
0.92
0.91
-0.00
CbzHN
O
N
H
H
N
O
O
Ph
^{1}H NMR $CDCl_3$ 400 MHz
5.93
2.18
1.95
1.92
1.00
2.08
1.03
1.02
0.94
0.96
3.05
1.00
1.04
3.18
6.15
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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135.86
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128.73
128.51
128.24
128.06
127.10
77.32
77.00
76.68
67.15
56.53
52.31
50.75
43.00
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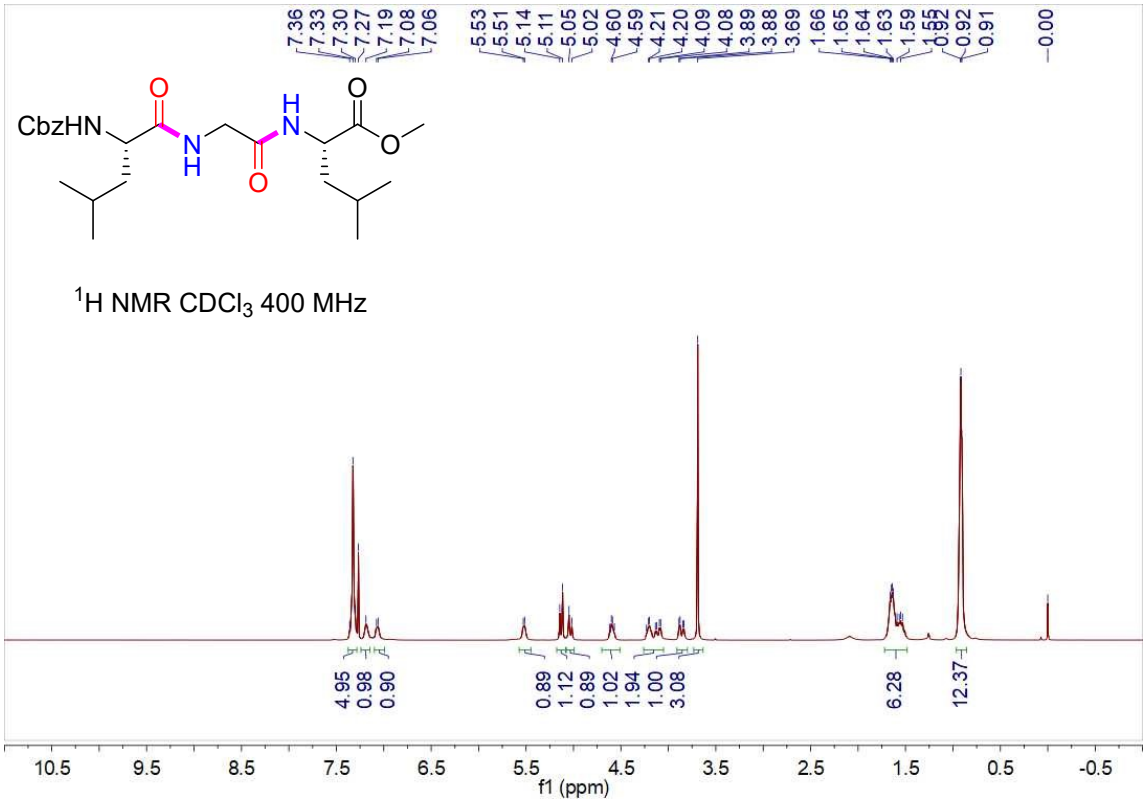
37.93
24.72
22.77
21.78
CbzHN
Ph
^{13}C NMR $CDCl_3$ 100 MHz
f1 (ppm)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7.33
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7.19
7.08
7.06
5.53
5.51
5.14
5.11
5.05
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4.59
4.21
4.20
4.09
4.08
3.89
3.88
3.69
1.66
1.65
1.64
1.63
1.59
0.92
0.91
0.00
CbzHN
^{1}H NMR $CDCl_3$ 400 MHz
4.95
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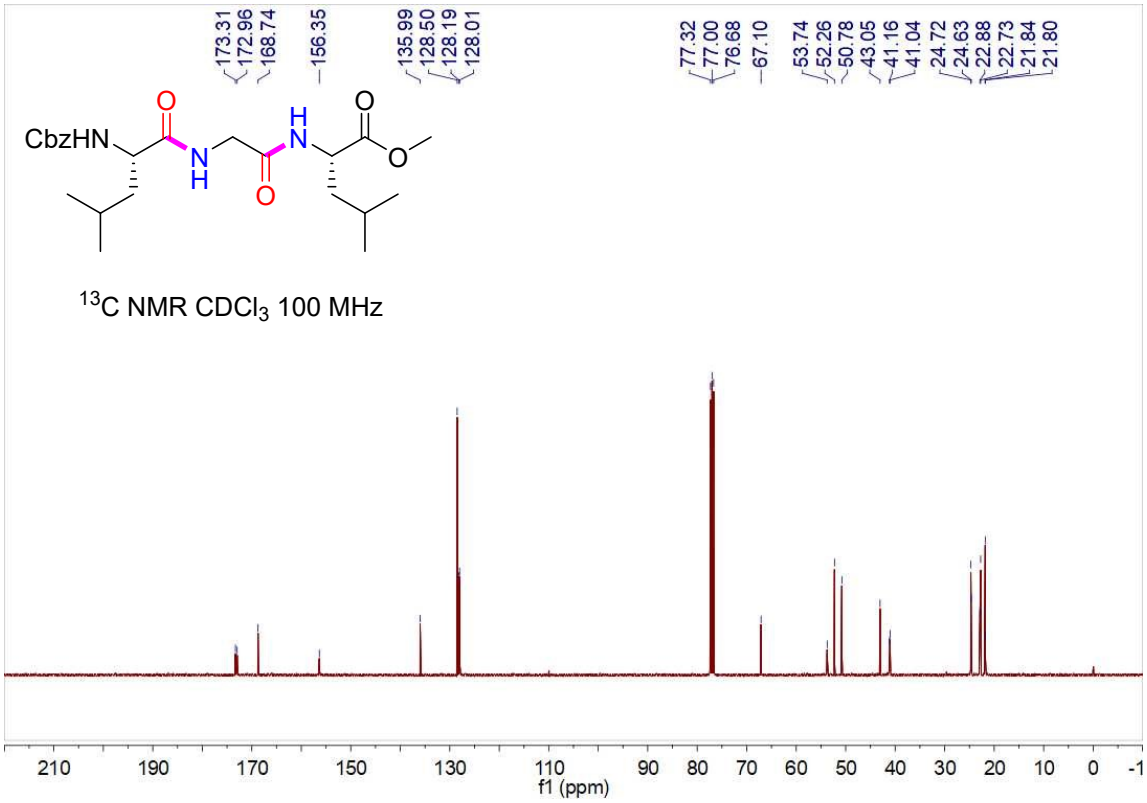
0.90
0.89
1.12
0.89
1.02
1.94
1.00
3.08
6.28
12.37
f1 (ppm)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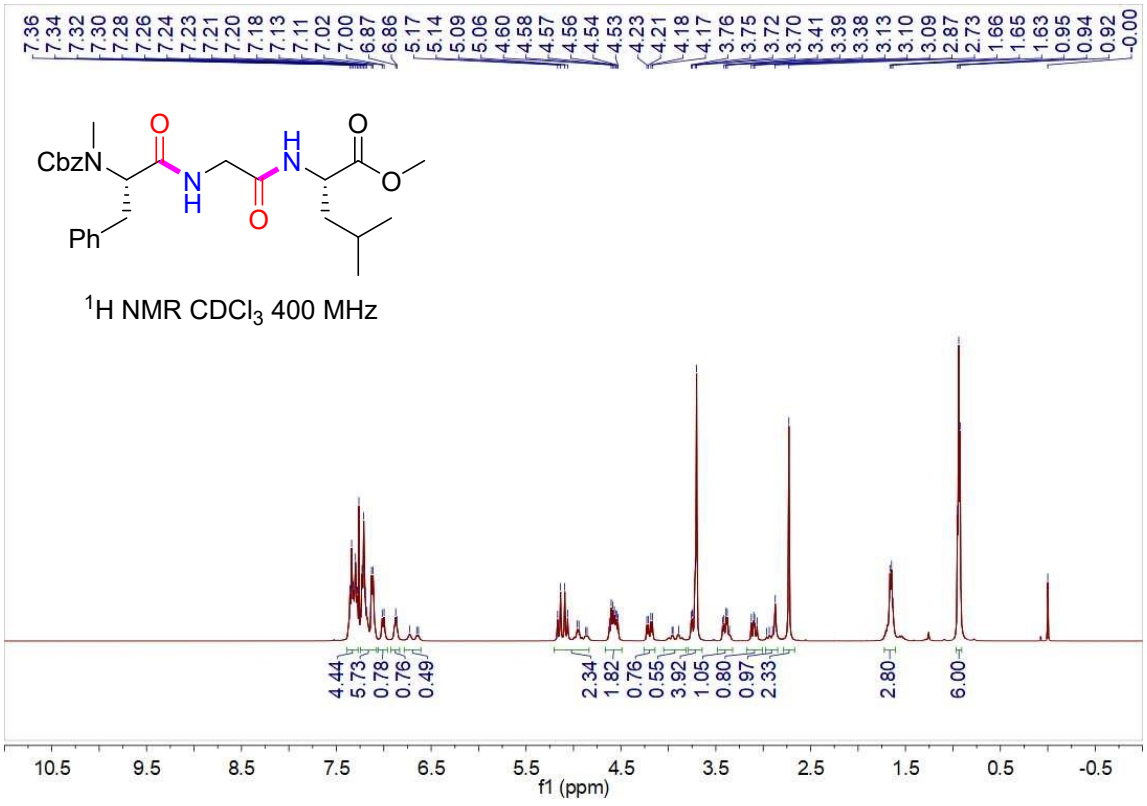
128.50
128.19
128.01
77.32
77.00
76.68
67.10
53.74
52.26
50.78
43.05
41.16
41.04
24.72
24.63
22.88
22.73
21.84
21.80
CbzHN
O
N
H
H
N
O
O
O
13C NMR CDCl3 100 MHz
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.26
7.24
7.23
7.21
7.20
7.18
7.13
7.11
7.02
7.00
6.87
6.86
5.17
5.14
5.09
5.06
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4.58
4.57
4.56
4.54
4.53
4.23
4.21
4.18
4.17
3.76
3.75
3.72
3.70
3.41
3.39
3.38
3.13
3.10
3.09
2.87
2.73
1.66
1.65
1.63
0.95
0.94
0.92
-0.00
CbzN
O
N
H
H
N
O
O
O
Ph
1H NMR CDCl3 400 MHz
4.44
5.73
0.78
0.76
0.49
2.34
1.82
0.76
0.55
3.92
1.05
0.80
0.97
2.33
2.80
6.00
10.5
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6.5
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4.5
3.5
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1.5
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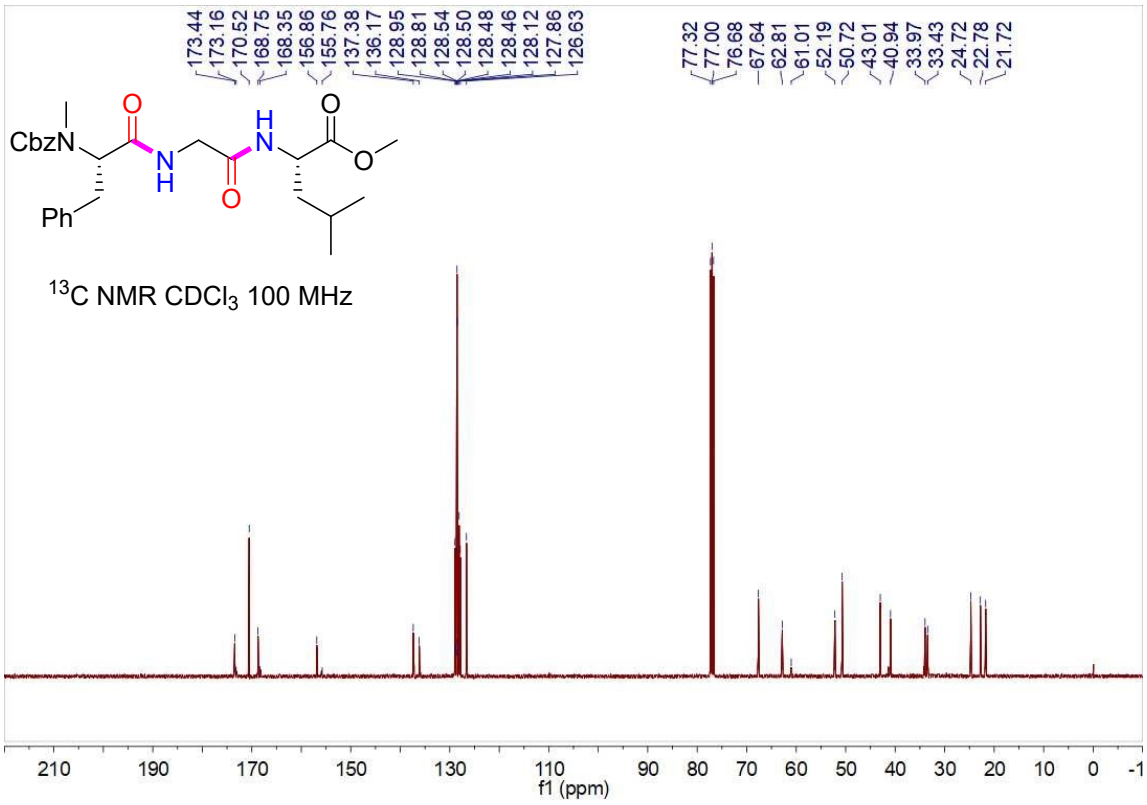
f1 (ppm)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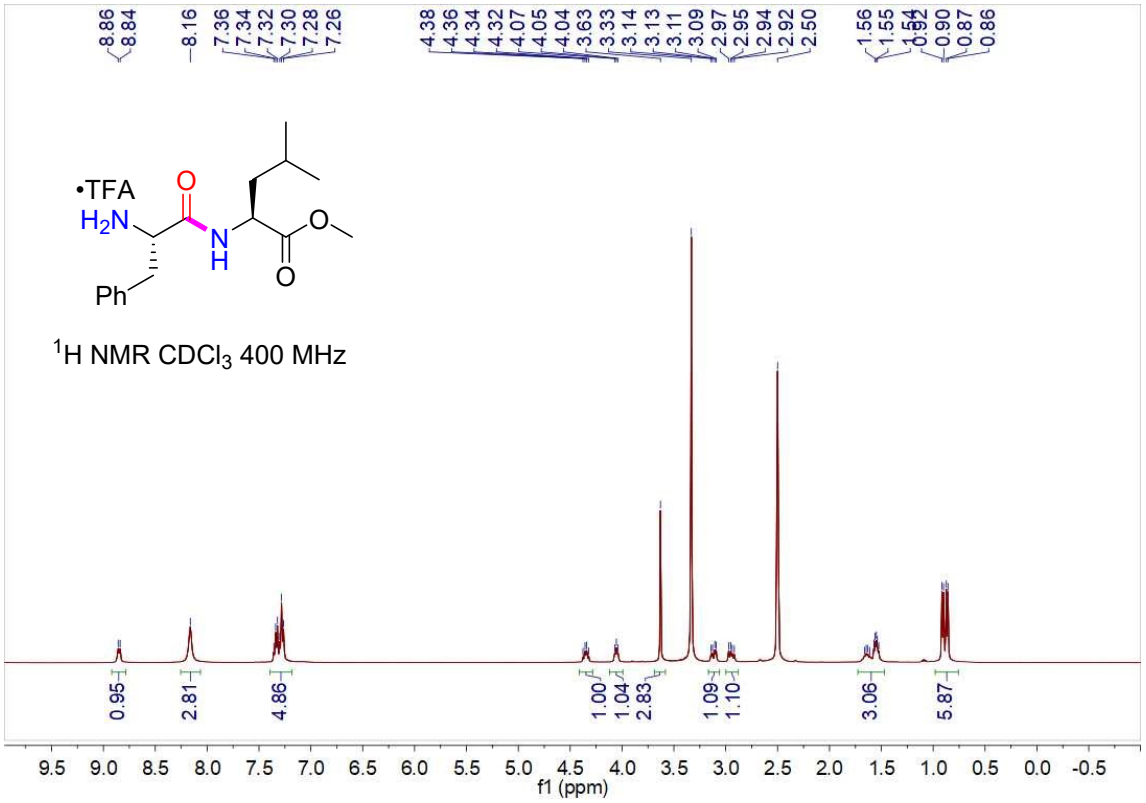
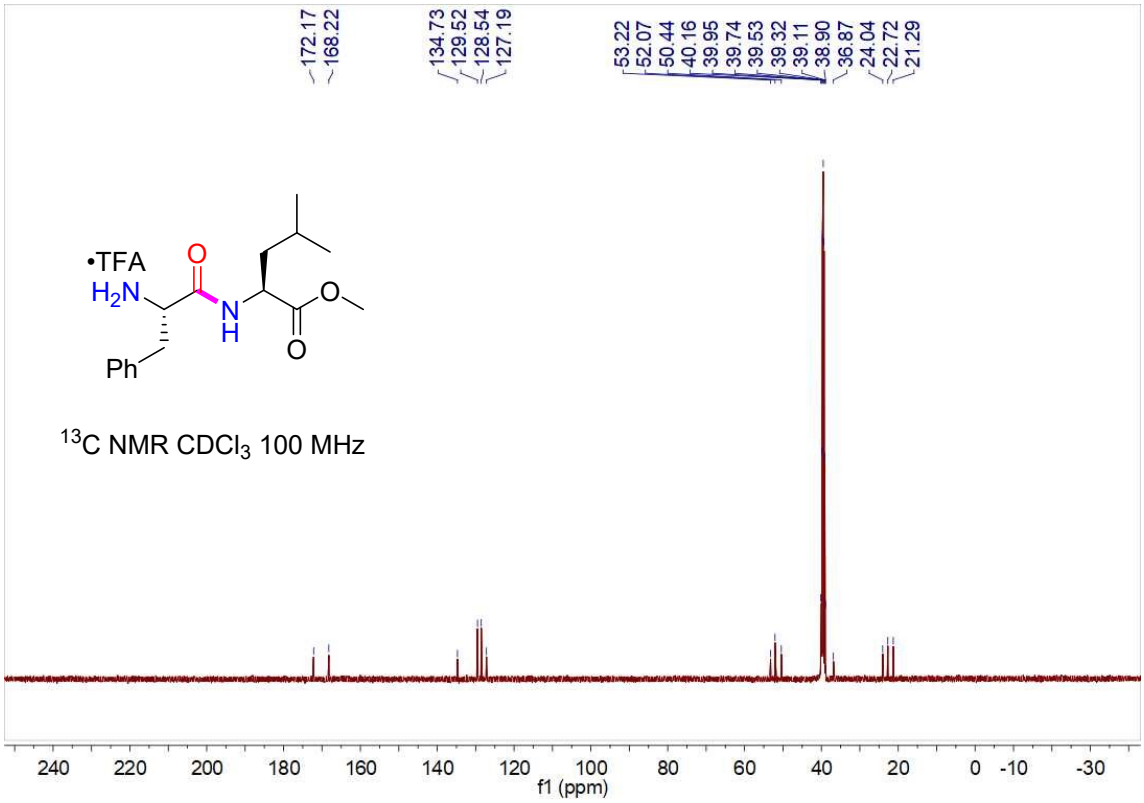
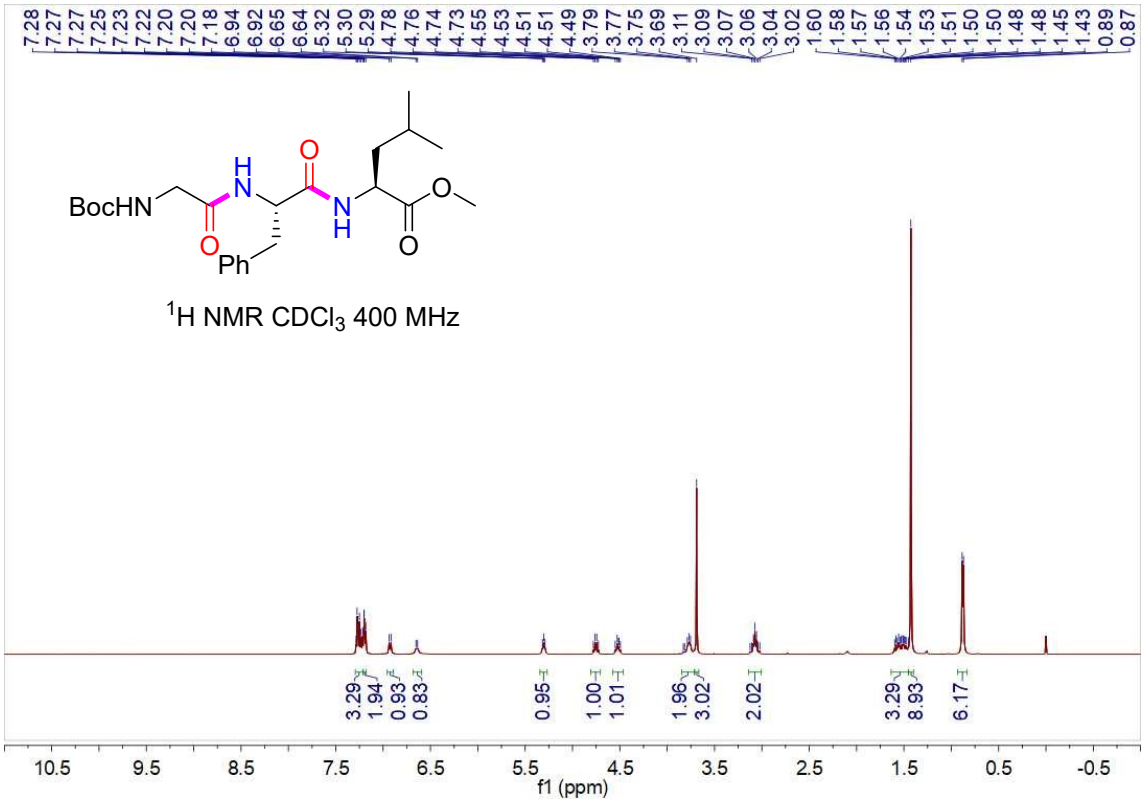
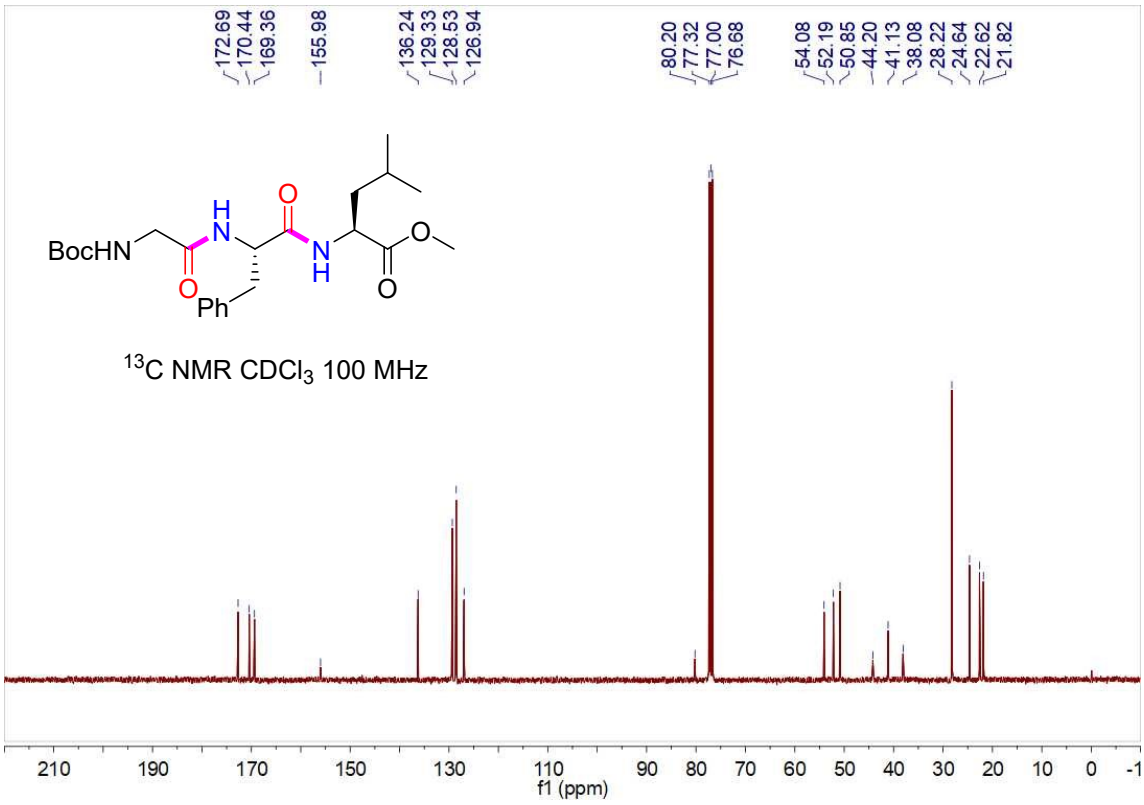
128.54
128.50
128.48
128.46
128.12
127.86
126.63
77.32
77.00
76.68
67.64
62.81
61.01
52.19
50.72
43.01
40.94
33.97
33.43
24.72
22.78
21.72
CbzN
Ph
^{13}C NMR $CDCl_3$ 100 MHz
f1 (ppm)

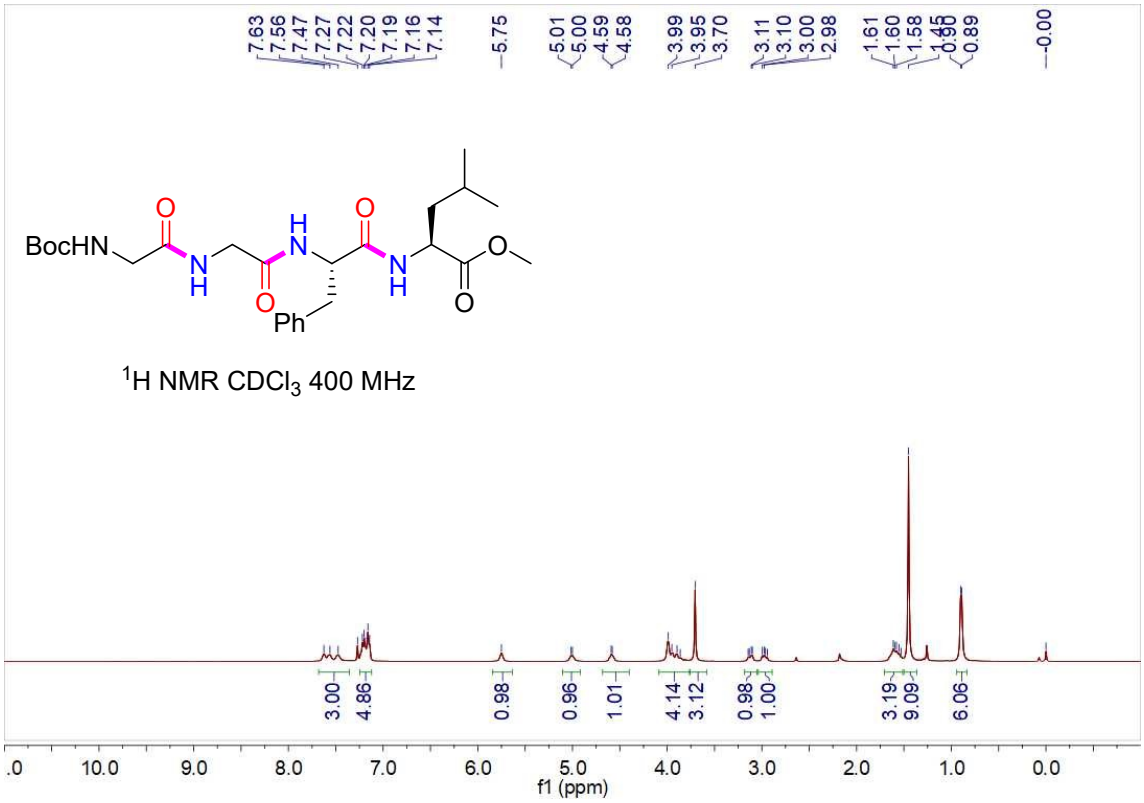

8.86
8.84
8.16
7.36
7.34
7.32
7.30
7.28
7.26
4.38
4.36
4.34
4.32
4.07
4.05
4.04
3.63
3.33
3.14
3.13
3.11
3.09
2.97
2.95
2.94
2.92
2.50
1.56
1.55
0.90
0.87
0.86
•TFA
Ph
^{1}H NMR $CDCl_3$ 400 MHz
0.95
2.81
4.86
1.00
1.04
2.83
1.09
1.10
3.06
5.87
f1 (ppm)


172.17
168.22
134.73
129.52
128.54
127.19
53.22
52.07
50.44
40.16
39.95
39.74
39.53
39.32
39.11
38.90
36.87
24.04
22.72
21.29
•TFA
H2N
O
N
H
O
O
Ph
13C NMR CDCl3 100 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
-10
-30
f1 (ppm)

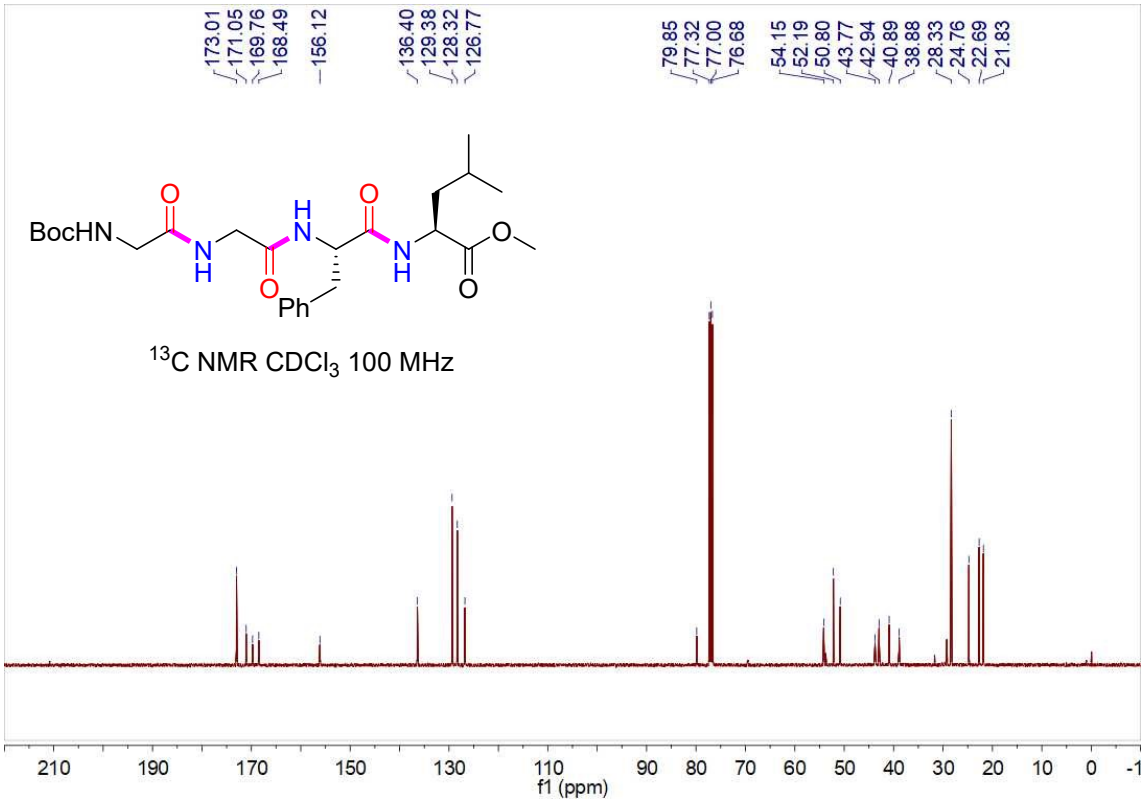

7.28
7.27
7.27
7.25
7.23
7.22
7.20
7.20
7.18
6.94
6.92
6.65
6.64
5.32
5.30
5.29
4.78
4.76
4.74
4.73
4.55
4.53
4.51
4.51
4.49
3.79
3.77
3.75
3.69
3.11
3.09
3.07
3.06
3.04
3.02
1.60
1.58
1.57
1.56
1.54
1.53
1.51
1.50
1.50
1.48
1.48
1.45
1.43
0.89
0.87
BocHN
H
N
O
O
N
H
O
O
Ph
1H NMR CDCl3 400 MHz
3.29
1.94
0.93
0.83
0.95
1.00
1.01
1.96
3.02
2.02
3.29
8.93
6.17
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)



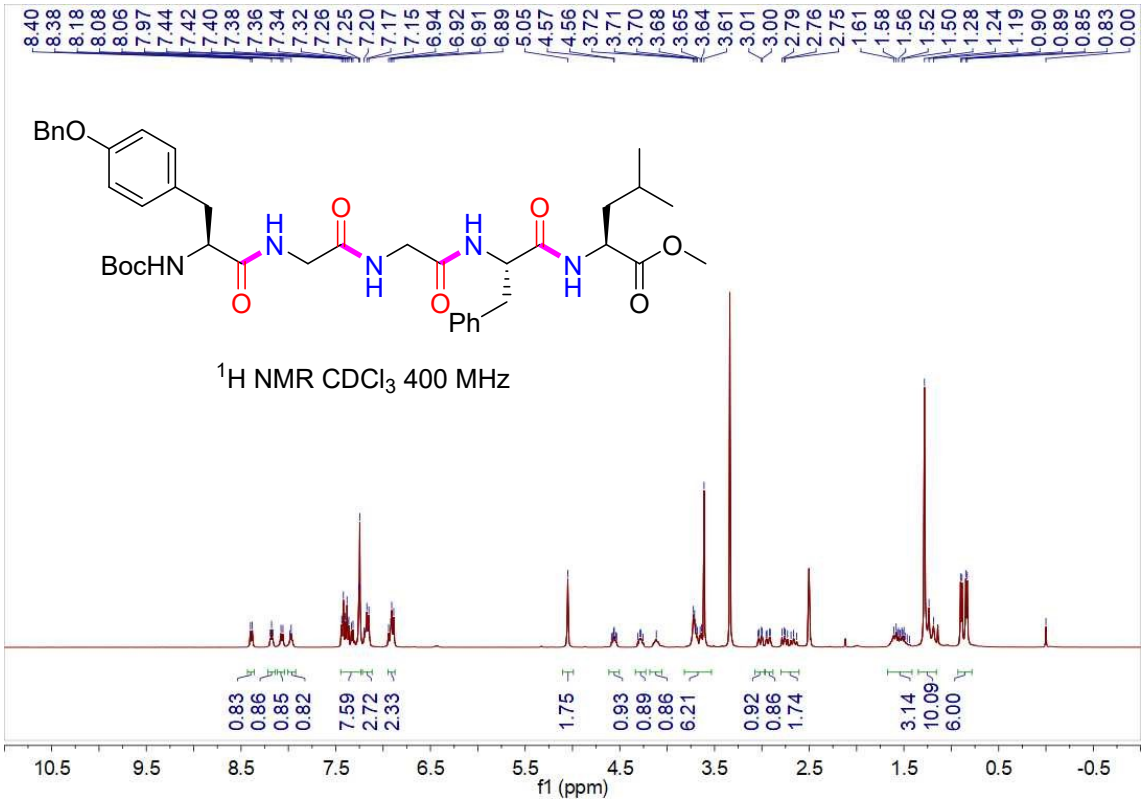
^{13}C NMR $CDCl_3$ 100 MHz



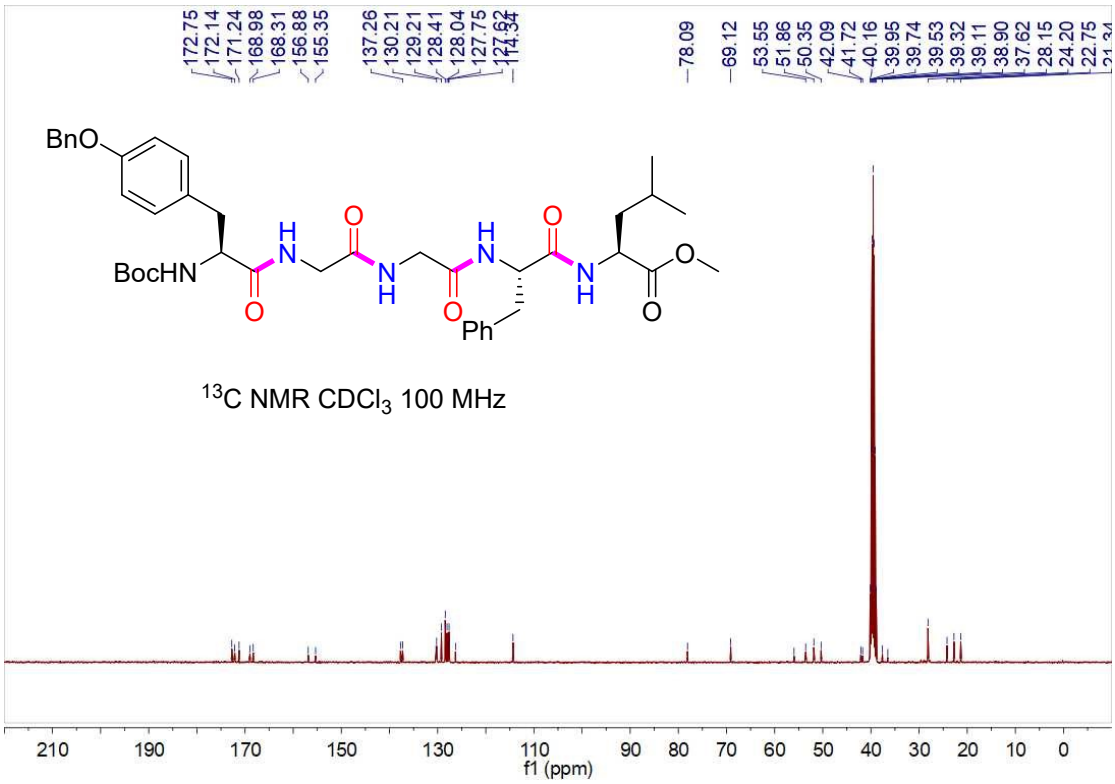
^{1}H NMR $CDCl_3$ 400 MHz



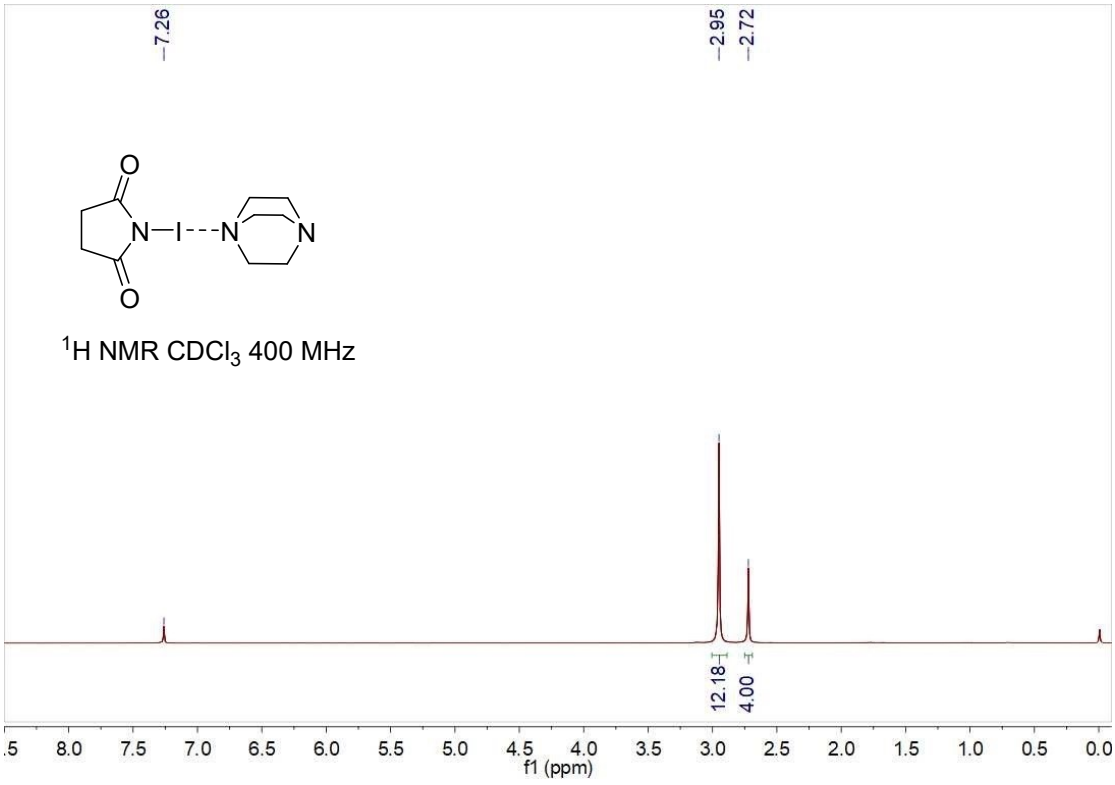
^{13}C NMR $CDCl_3$ 100 MHz



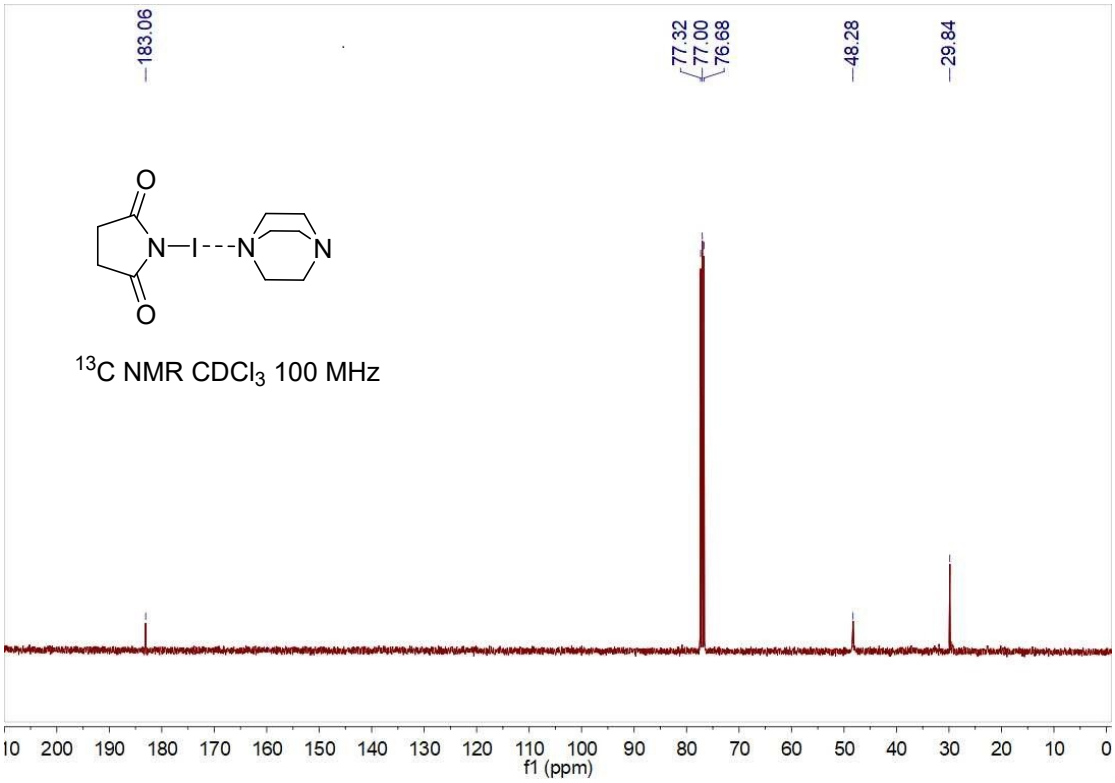
^{1}H NMR $CDCl_3$ 400 MHz



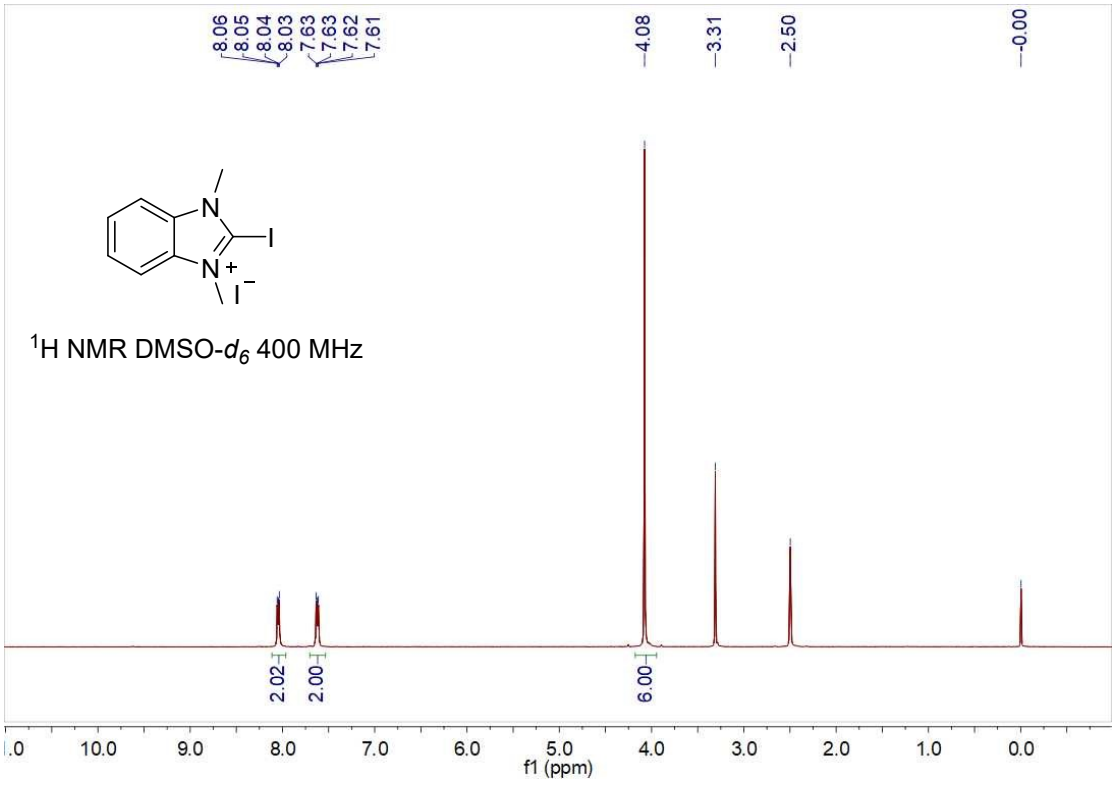
^{13}C NMR $CDCl_3$ 100 MHz



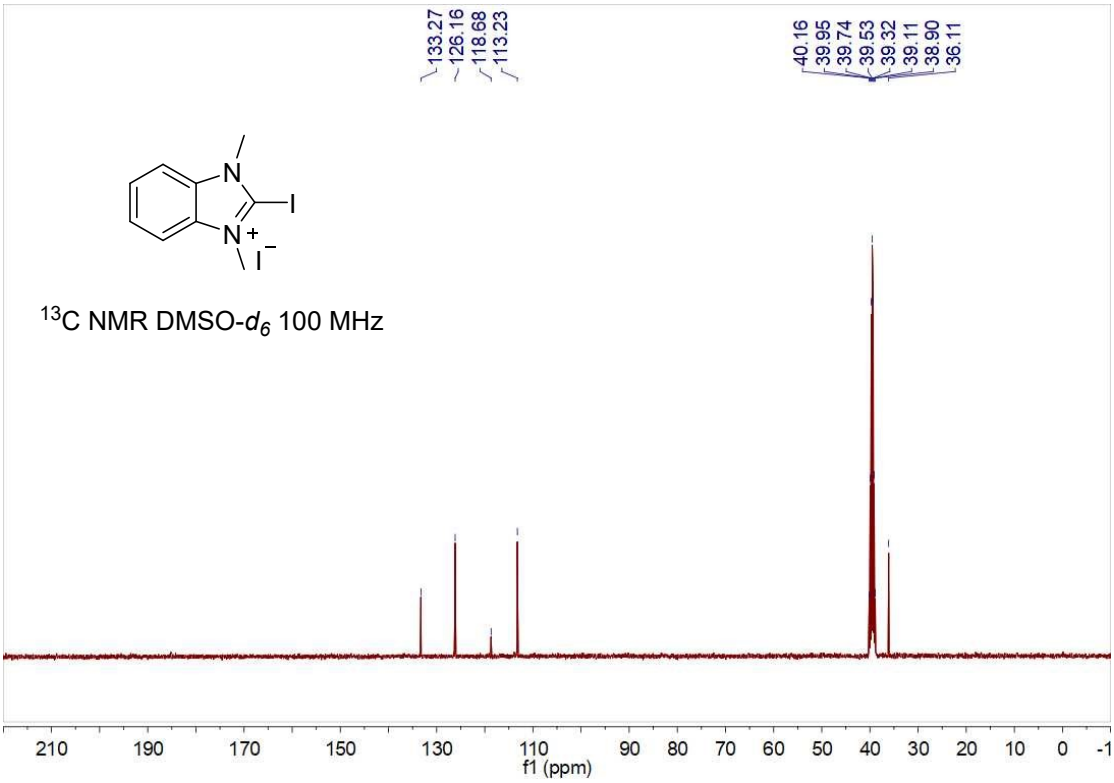
^{1}H NMR $CDCl_3$ 400 MHz



^{13}C NMR $CDCl_3$ 100 MHz



^{1}H NMR DMSO-d_6 400 MHz


133.27
126.16
118.68
113.23
40.16
39.95
39.74
39.53
39.32
39.11
38.90
36.11
N
I
N+
I−
13C NMR DMSO-d6 100 MHz
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

13 References

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