Supporting Information

Direct γ-C(sp^3)-H Alkylation of Carbonyls through Visible Light Photoredox Catalysis

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General Considerations

Commercial reagents and anhydrous solvents were purchased from *Sigma-Aldrich*, *Alfa* and *TCI*, and were used as received unless otherwise indicated. All catalytic reactions were carried out under N_2 with oven-dried vials. Thin layer chromatography was performed on SiliCycle® 250 um, 60A plates. Column chromatography was performed on *SiliCycle*®*SilicaFlash*® P60, 40-63 um, 60A. Visualization was accomplished with I_2-silica first, then with phosphomolybdate stain.

^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on a Bruker 500 Hz (126 Hz, 202 Hz and 471 Hz for ^{13}C, ^{31}P and ^{19}F, respectively) spectrometer at ambient temperature. All NMR spectra are referenced to the residual solvent ($CHCl_3$) signal. Data for ^{1}H, ^{19}F and ^{31}P NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported as follows: chemical shift (δ ppm). Several spectra are from mixtures of rotamers and deconvolution is not possible.

High resolution mass spectra (HRMS) were obtained from Columbia University Mass Spectrometry Facility on a JOEL JMSHX110HF mass spectrometer using ESI+/ESI$^-$/ASAP$^-$ ionization model. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FI-IR spectrometer.

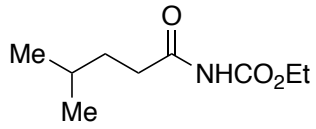
All acrylates (except methyl 2-phenylacrylate[1] and 2-benzylacrylate[2]), methyl vinyl ketone, *N,N*-dimethylacrylamide, phenyl vinyl sulfone, diethyl vinylphosphate and dimethyl maleate were purchased from Aldrich and used as received. All amide substrates were synthesized according to the general methods as shown below.

Amide Synthesis and Characterization

Procedure A: To a solution of carboxylic acid (1.0 equiv.) and 3 drops of anhydrous DMF in anhydrous CH_2Cl_2 (0.2 M) at 0 ˚C, oxalyl chloride (1.2 equiv.) was added dropwise over 5 mins. The reaction was vigorously stirred at room temperature for 3 h. After removal of the solvent, the resulting acyl chloride was redissolved in anhydrous toluene (1.0 M), followed by addition of ethyl carbamate (2.0 equiv.) The slurry was vigorously stirred at 80 ˚C overnight. After cooling down to room temperature, the solvent was removed and the residue was purified by flash column chromatography using hexane/EtOAc as the eluent.

Procedure B: To a solution of carboxylic acid (1.0 equiv.) and Et_3N (1.2 equiv.) in anhydrous THF (0.1 M) at 0 ˚C, ethyl chloroformate (1.1 equiv.) was added dropwise over 5 mins. The slurry was stirred for 1 h at 0 ˚C. Then 28-35% *aq.* NH_3 (2 mL per mmol of mixed anhydride) was added dropwise. The mixture was then warmed up to room temperature and vigorously stirred overnight. The mixture was diluted with EtOAc, then the organic and aqueous layer were separated. The aqueous layer was extracted with EtOAc three times (5 mL per mmol of amide). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo*. The crude amide was pure enough for direct use in further steps.

To a solution of crude amide (1.0 equiv.) and ethyl chloroformate (1.1 equiv.) or benzoyl chloride (1.1 equiv.) or (-)-menthyl chloroformate (1.1 equiv) in anhydrous THF (0.2 M) at -78˚C, LiO^tBu (1.2 equiv., 1.0M in THF,) was added dropwise over 10 mins. The reaction was gradually allowed to warm to room temperature over 3 h, and then was stirred for another hour before being carefully quenched by slow addition of sat. aq. NH_4Cl (5 mL per mmol of amide). The mixture was diluted with EtOAc (5 mL per mmol of amide), separated, and the aqueous layer was extracted with EtOAc three times (5 mL per mmol of amide). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo*. The residue was purified by flash column chromatography using mixed hexane/EtOAc as the eluent.



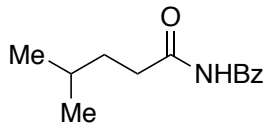
Prepared according to ***Procedure A*** from commercially available 4-methyl pentanoic acid (1.16g, 10.0 mmol). Colorless oil (1.39g, 74% yield for 2 steps). R_f = 0.40 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.79 – 2.74 (m, 2H), 1.68 – 1.52 (m, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 151.8, 62.2, 34.1, 33.1, 27.7, 22.3, 14.2.

HRMS m/z calcd. for $C_9H_{18}NO_3$ $[M+H]^+$ 188.1287, found 188.1287.

IR (cm^{-1}) 3279 (br), 2957, 2871, 1760, 1706, 1514, 1203, 1055.



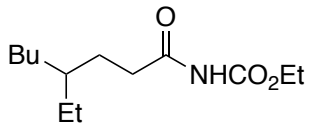
Prepared according to ***Procedure B*** from commercially available 4-methyl pentanoic acid (348, 3.0 mmol). White solid (378 mg, 57% yield for 2 steps). R_f = 0.37 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (brs, 1H), 8.01 – 7.79 (m, 2H), 7.66 – 7.60 (m, 1H), 7.55 – 7.49 (m, 2H), 3.11 – 2.99 (m, 2H), 1.73 – 1.59 (m, 3H), 0.97 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.8, 165.6, 133.2, 132.9, 128.9, 127.7, 35.7, 32.9, 27.7, 22.4.

HRMS m/z calcd. for $C_{13}H_{16}NO_2$ $[M-H]^-$ 218.1181, found 218.1178.

IR (cm^{-1}) 3063 (br), 1780, 1723, 1690, 1451, 1210, 1037, 778, 701, 686.



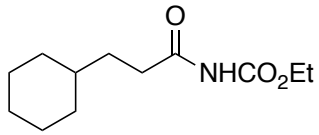
Prepared according to ***Procedure A*** from commercially available 4-ethyloctanoic acid (516 mg, 3.0 mmol). Colorless oil (568 mg, 78% yield for 2 steps). R_f = 0.41 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.82 – 2.59 (m, 2H), 1.64 – 1.57 (m, 2H), 1.36 – 1.20 (m, 12H), 0.91 – 0.82 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 151.7, 62.2, 38.5, 33.6, 32.6, 28.8, 27.6, 25.6, 23.0, 14.2, 14.1, 10.7.

HRMS m/z calcd. for $C_{13}H_{26}NO_3$ $[M+H]^+$ 244.1913, found 244.1915.

IR (cm^{-1}) 3279 (br), 2958, 2927, 1760, 1696, 1499, 1200, 1073.



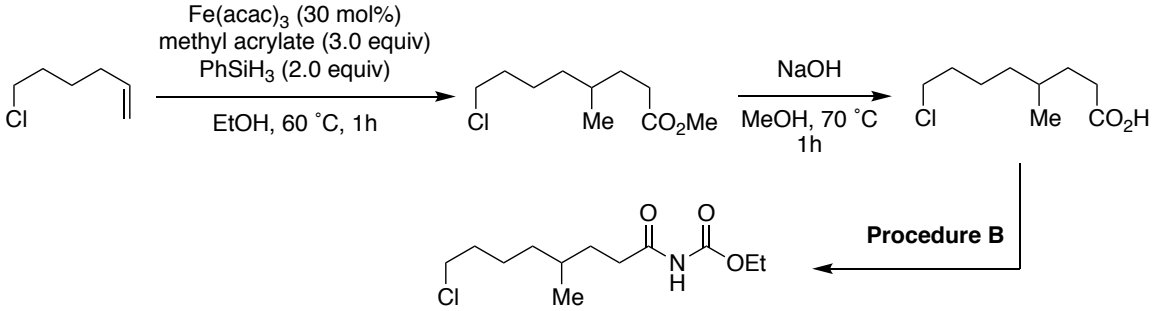
Prepared according to ***Procedure A*** from commercially available 3-cyclohexanepropionic acid (1.56g, 10.0 mmol). Colorless oil (1.87g, 82% yield for 2 steps). R_f = 0.35 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.77 (t, *J* = 7.9 Hz, 2H), 1.77 – 1.68 (m, 4H), 1.67 – 1.62 (m, 1H), 1.59 – 1.52 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.28 – 1.12 (m, 4H), 0.98 – 0.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 151.8, 62.2, 37.2, 33.7, 33.0, 31.6, 26.5, 26.2, 14.2.

HRMS m/z calcd. for $C_{12}H_{22}NO_3$ $[M+H]^+$ 228.1600, found 228.1595.

IR (cm^{-1}) 3279 (br), 2927, 2851, 1759, 1695, 1497, 1198, 1050.

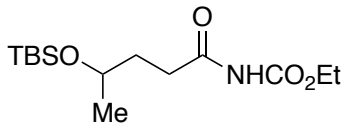


Methyl 8-chloro-4-methyloctanoate was synthesized according to Baran's procedure.[3] To a solution of 6-chlorohex-1-ene (0.59g, 5.0 mmol, 1.0 equiv), methyl acrylate (1.36 mL, 15.0 mmol, 3.0 equiv) and $Fe(acac)_3$ (0.53g, 1.5 mmol, 0.30 equiv) in

25 mL of anhydrous EtOH at 60 ˚C, $PhSiH_3$ (1.23 mL, 10.0 mmol, 2.0 equiv) was added dropwise. The mixture was then vigorously stirred at the same temperature for 1h. After cooling down to room temperature, the solvent was removed *in vacuo* and the residue was directly subjected to flash chromatography using 5% EtOAc in hexane as the eluent to give the crude methyl 8-chloro-4-methyloctanoate with a large amount of $PhSi(OEt)H_2$.

The crude methyl 8-chloro-4-methyloctanoate was then dissolved in 10.0 mL of MeOH before 3.0 mL of 2.0 M aq. NaOH was added dropwise. The mixture was vigorously stirred at 70 ˚C for 1h. After cooling down to room temperature, the mixture was carefully acidified by slow addition of 10% HCl until pH = 2. The mixture was extracted with CH_2Cl_2 (20 mL×3). The organic layer was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give the crude 8-chloro-4-methyloctanoic acid as a light yellow oil, which was pure enough for further steps.

Ethyl (8-chloro-4-methyloctanoyl)carbamate was then synthesized according to ***Procedure B***. Colorless oil (411mg, 49% yield for 5 steps). R_f = 0.21 (9:1 hex:EtOAc).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (brs, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.95 – 2.65 (m, 2H), 1.82 – 1.66 (m, 3H), 1.57 – 1.27 (m, 8H), 1.24 – 1.14 (m, 1H), 0.92 (d, *J* = 6.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 151.8, 62.2, 45.1, 35.9, 33.8, 32.8, 32.3, 31.1, 24.3, 19.3, 14.2.
HRMS m/z calcd. for $C_{12}H_{23}NO_3Cl$ $[M+H]^+$ 264.1367, found 264.1367.
IR (cm^{-1}) 3280 (br), 2956, 2857, 1760, 1695, 1493, 1120, 1074, 835, 773.



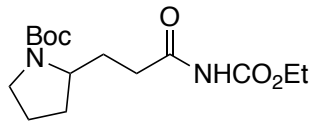
Prepared according to ***Procedure B*** from 4-([tert-butyldimethylsilyl]oxy)pentanoic acid (740 mg, 3.2 mmol).[4] Colorless oil (209 mg, 22% for 2 steps). R_f = 0.35 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.95 – 3.86 (m, 1H), 2.86 – 2.79 (m, 2H), 1.85 – 1.80 (m, 1H), 1.78 – 1.71 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 6.0 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 151.6, 67.6, 62.1, 33.6, 32.4, 25.9, 23.7, 18.1, 14.2, -4.5, -4.8.

HRMS m/z calcd. for $C_{14}H_{30}NO_4Si$ $[M+H]^+$ 304.1944, found 304.1940.

IR (cm^{-1}) 3280 (br), 2956, 2857, 1760, 1695, 1493, 1120, 1074, 835, 773.



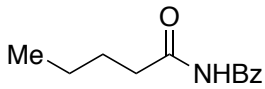
Prepared according to ***Procedure B*** from 4-(1-[tert-butoxycarbonyl]pyrrolidin-2-yl)butanoic acid (1.22g, 5.0 mmol).[5] Colorless oil (about 60:40 mixture of rotamers, 0.97g, 62% yield for 2 steps). R_f = 0.25 (2:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 0.44H), 7.54 (s, 0.42H), 4.35 – 4.03 (m, 2H), 4.00 – 3.78 (m, 1H), 3.51 – 3.23 (m, 2H), 2.88 – 2.52 (m, 2H), 2.03 – 1.80 (m, 4H), 1.78 – 1.62 (m, 2H), 1.47 (s, 9H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 173.8, 155.5, 154.7, 151.8, 151.6, 79.3, 62.1, 61.8, 56.5, 56.2, 46.5, 46.0, 33.7, 33.1, 30.7, 30.5, 30.0, 29.1, 28.4, 23.6, 23.0, 14.2.

HRMS m/z calcd. for $C_{15}H_{25}N_2O_5$ $[M-H]^-$ 313.1764, found 313.1763.

IR (cm^{-1}) 3274 (br), 2974, 1755, 1688, 1512, 1480, 1392, 1201, 1168, 1100, 1073, 773.



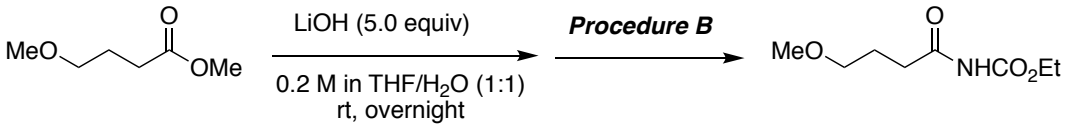
Prepared according to ***Procedure B*** from commercially available valeric acid (501mg, 5.0 mmol). Colorless oil (653 mg, 64% yield for 2 steps). R_f = 0.29 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.97 – 7.85 (m, 2H), 7.65 – 7.55 (m, 1H), 7.52 – 7.44 (m, 2H), 3.00 (*t*, J = 7.5 Hz, 2H), 1.74 – 1.63 (m, 2H), 1.48 – 1.36 (m, 2H), 0.95 (*t*, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.8, 165.7, 133.1, 132.9, 128.9, 127.80, 37.4, 26.2, 22.3, 13.9.

HRMS m/z calcd. for $C_{12}H_{16}NO_2$ $[M+H]^+$ 206.1136, found 206.1175.

IR (cm^{-1}) 3289 (br), 2954, 2870, 1678, 1468, 1241, 706.



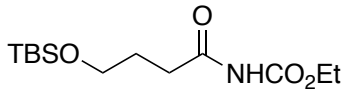
To a solution of methyl 4-methoxybutyrate (1.32g, 10 mmol) in 50 mL of mixed THF/H_2O (1:1) at room temperature, LiOH (1.20 g, 50 mmol) was added in portions. The mixture was vigorously stirred overnight before being carefully quenched and acidified until pH = 2. The mixture was extracted with CH_2Cl_2 (30 mL×3), and the organic layer was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give crude 4-methoxybutanoic acid, which was directly used for next step without further purification. Ethyl (4-methoxybutanoyl)carbamate was then synthesized according to ***Procedure B***. Colorless oil (392 mg, 21%yield for 3 steps). R_f = 0.25 (2:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.43 (t, *J* = 6.2 Hz, 2H), 3.32 (s, 3H), 2.80 (t, *J* = 7.3 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.29 (t, *J* = 7.1 H, 3Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 151.8, 71.6, 62.1, 58.5, 33.0, 24.1, 14.2.

HRMS m/z calcd. for $C_8H_{14}NO_4$ $[M-H]^-$ 188.0923, found 188.0918.

IR (cm^{-1}) 3255 (br), 2932, 2857, 1758, 1690, 1495, 1210, 1055.



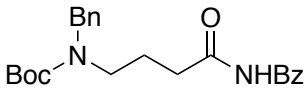
Prepared according to ***Procedure B*** from 4-((tert-butyldimethylsilyl)oxy)butanoic acid (1.09g, 5.0 mmol).[10] Colorless oil (377 mg, 26% yield). R_f = 0.35 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.69 (t, *J* = 6.1 Hz, 2H), 2.81 (t, *J* = 7.2 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 151.8, 62.2, 62.1, 32.8, 27.2, 25.9, 18.3, 14.2, -5.4.

HRMS m/z calcd. for $C_{13}H_{26}NO_4Si$ $[M-H]^-$ 288.1631, found 288.1628.

IR (cm^{-1}) 3246 (br), 2930, 2858, 1758, 1691, 1502, 1204, 1075, 845, 772.



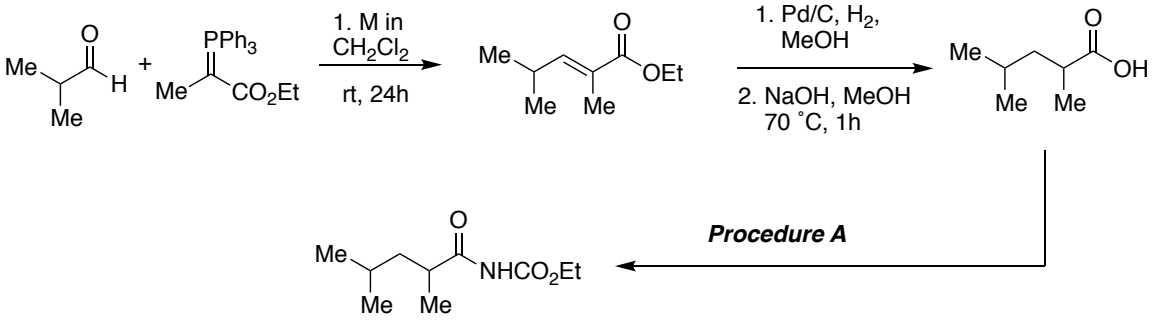
Prepared according to ***Procedure B*** from 4-(benzyl(tert-butoxycarbonyl)amino)butanoic acid (587 mg, 2.0 mmol).[11] Colorless oil (~ 4:5 mixture of rotamers, 344 mg, 43% yield). R_f = 0.25 (3:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.42 (brs, 0.47H), 8.85 (brs, 0.38H), 7.99 – 7.82 (m, 2H), 7.65 – 7.56 (m, 1H), 7.55 – 7.45 (m, 2H), 7.37 – 7.30 (m, 2H), 7.30 – 7.20 (m, 3H), 4.55 – 4.40 (m, 2H), 3.40 – 3.20 (m, 2H), 3.04 – 2.82 (m, 2H), 2.01 – 1.88 (m, 2H), 1.52 (s, 4H), 1.46 (s, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 174.9, 165.5, 156.1, 138.3, 133.2, 133.0, 129.0, 128.8, 128.5, 127.8, 127.7, 127.2, 80.1, 79.8, 50.5, 49.8, 45.6, 45.4, 34.8, 28.4, 22.9, 22.5.

HRMS m/z calcd. for $C_{23}H_{27}N_2O_4$ $[M-H]^-$ 395.1971, found 395.1978.

IR (cm^{-1}) 3275 (br), 2974, 2929, 1686, 1468, 1415, 1240, 1157, 700.



A solution of isobutyraldehyde (0.72g, 10.0 mmol) and ethyl 2-(triphenylphosphoranylidene)propionate (4.35g, 12.0 mmol) in 10 mL of anhydrous CH_2Cl_2 was vigorously stirred at room temperature for 24h. After removal of CH_2Cl_2, 100 mL of pentane was added and the mixture was sonicated until light yellow precipitate formed. The slurry was filtered and the filtrate was concentrated *in vacuo*. Repeated the

Sonication (with Pentane)-Filter Procedure three more time to give crude ethyl *(E)*-2,4-dimethylpent-2-enoate as a light yellow oil, which was pure enough for direct use in the next step.

To a solution of the above ethyl *(E)*-2,4-dimethylpent-2-enoate in 100 mL of anhydrous MeOH, 10% Pd/C (500 mg) was added in one portion. The black slurry was stirred under a H_2 atmosphere (balloon) overnight before being filtered through celite. The filtrate was concentrated to about 20 mL, then 6.0 mL of 2.0 M aq. NaOH was added dropwise. The mixture was vigorously stirred at 70 ˚C for 1h. After cooling down to room temperature, the mixture was carefully acidified by slow addition of 10% HCl until pH = 2. The mixture was extracted with CH_2Cl_2 (20 mL×3). The organic layer was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give crude 2,4-dimethylpentanoic acid as a light yellow oil.

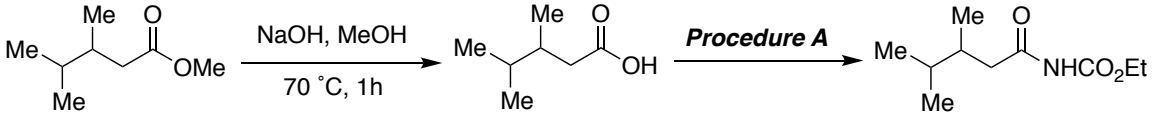
Ethyl (2,4-dimethylpentanoyl)carbamate was then synthesized according ***Procedure A***. Colorless oil (407 mg, 20% yield for 5 steps). R_f = 0.40 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.31 – 3.21 (m, 1H), 1.73 – 1.59 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.30 – 1.22 (m, 1H), 1.17 (d, *J* = 6.9 Hz, 3H), 0.91 (dd, *J* = 6.5, 5.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.9, 151.4, 62.2, 42.5, 37.5, 25.7, 22.8, 22.3, 17.4, 14.2.

HRMS m/z calcd. for $C_{10}H_{20}NO_3$ $[M+H]^+$ 202.1443, found 202.1444.

IR (cm^{-1}) 3273 (br), 2957, 2873, 1760, 1705, 1516, 1184, 1039.



To a solution of methyl 3,4-dimethylpentanoate[6] (0.72g, 5.0 mmol) in 10 mL of MeOH, 3.0 mL of 2.0 M aq. NaOH was added dropwise. The mixture was vigorously stirred at 70 ˚C for 1h. After cooling down to room temperature, the mixture was carefully acidified by slow addition of 10% HCl until pH = 2. The mixture was extracted with CH_2Cl_2 (10 mL×3). The organic layer was combined, washed with brine, dried over

anhydrous Na_2SO_4, and concentrated in vacuum to give crude 2,4-dimethylpentanoic acid as a light yellow oil, which was directly used for next step without further purification.

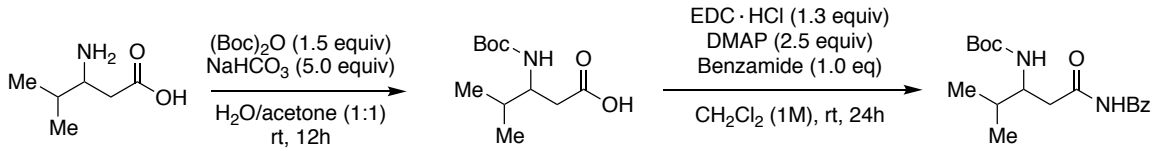
Ethyl (3,4-dimethylpentanoyl)carbamate was then synthesized according to ***Procedure A***. Colorless oil (285 mg, 28% yield for 3 steps). R_f = 0.41 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.77 (dd, *J* = 15.7, 4.8 Hz, 1H), 2.54 (dd, *J* = 15.7, 9.2 Hz, 1H), 1.98 (ddt, *J* = 9.5, 7.1, 4.7 Hz, 1H), 1.69 – 1.58 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.90 (dd, *J* = 7.0, 2.3 Hz, 6H), 0.87 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 151.8, 62.1, 40.6, 35.0, 32.1, 19.9, 18.2, 15.6, 14.2.

HRMS m/z calcd. for $C_{10}H_{20}NO_3$ $[M+H]^+$ 202.1443, found 202.1446.

IR (cm^{-1}) 3278 (br), 2960, 2875, 1760, 1704, 1506, 1198, 1053.



To a solution of DL-β-Leucine (1.31g, 10.0 mmol) in 50 mL of 1:1 mixed H_2O/acetone at room temperature, $NaHCO_3$ (4.2g, 50.0 mmol) and $(Boc)_2O$ (3.27g, 15.0 mmol) were added sequentially. The mixture was then vigorously stirred overnight. After being carefully acidified by aq. HCl (0.5 M) until pH = 2. The mixture was extracted by CH_2Cl_2 (30 mL × 3). The combined organic layer was washed by brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give a light yellow solid as the crude Boc-protected DL-β-Leucine, which was pure enough for the next step.

A mixture of EDC·HCl (500 mg, 2.6 mmol) and DMAP (611 mg, 5.0 mmol) in 2 mL of anhydrous CH_2Cl_2 was stirred at room temperature for 30 min. Then crude Boc-protected DL-β-Leucine (462 mg, 2.0 mmol) and benzamide (243 mg, 2.0 mmol) were then added and the resulting solution was vigorously stirred for 24h. After being quenched and acidified by aq. HCl (0.5 M) until pH = 2, the reaction was diluted with 50 mL of CH_2Cl_2 and washed with H_2O (30 mL) and brine (30 mL). The organic layer was then dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was directly

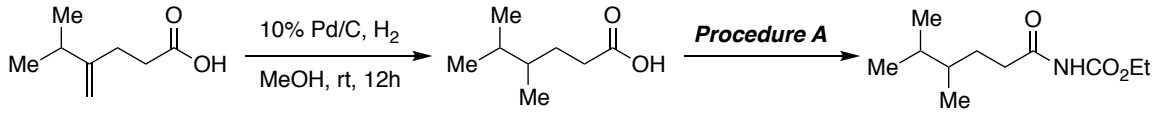
subjected to flash silica gel chromatography to give pure tert-butyl (1-benzamido-4-methyl-1-oxopentan-3-yl)carbamate as a white solid (128mg, 19% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.90 – 7.87 (m, 2H), 7.62 – 7.54 (m, 1H), 7.52 – 7.46 (m, 2H), 4.91 (*d*, J = 9.5 Hz, 1H), 3.98 – 3.82 (m, 1H), 3.20 – 3.01 (m, 2H), 1.96 – 1.84 (m, 1H), 1.39 (s, 10H), 0.97 (d, *J* = 1.2 Hz, 3H), 0.95 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 165.8, 155.8, 133.2, 132.8, 128.9, 127.9, 79.3, 53.1, 40.5, 32.2, 28.4, 19.2, 18.3.

HRMS m/z calcd. for $C_{18}H_{25}N_2O_4$ $[M-H]^-$ 333.1814, found 333.1807.

IR (cm^{-1}) 3294 (br), 2966, 1687, 1506, 1485, 1244, 1169, 710.



To a solution of 5-methyl-4-methylenehexanoic acid[7] (0.71g, 5.0 mmol) in 50 mL of anhydrous MeOH, 10% Pd/C (250 mg) was added in one portion. The black slurry was stirred under a H_2 atmosphere (balloon) overnight before being filtered through celite. The filtrate was concentrated to give 4,5-dimethylhexanoic acid as a light yellow oil.

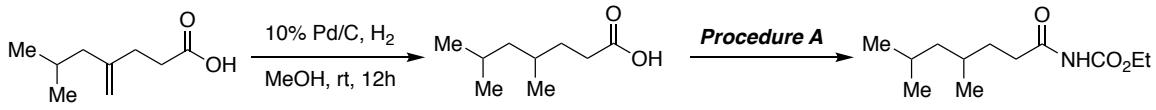
Ethyl (4,5-dimethylhexanoyl)carbamate was then synthesized according to ***Procedure A***. Colorless oil (283 mg, 26% yield for 3 steps). R_f = 0.45 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.90 – 2.68 (m, 2H), 1.80 – 1.55 (m, 2H), 1.51 – 1.42 (m, 1H), 1.41 – 1.35 (m, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.85 (dd, *J* = 5.9, 5.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 151.7, 62.2, 38.2, 34.3, 31.9, 28.5, 20.1, 17.9, 15.1, 14.2.

HRMS m/z calcd. for $C_{11}H_{22}NO_3$ $[M+H]^+$ 216.1600, found 216.1598.

IR (cm^{-1}) 3279 (br), 2959, 2873, 1759, 1702, 1499, 1201, 1058.



To a solution of 6-methyl-4-methyleneheptanoic acid[7] (0.78g, 5.0 mmol) in 50 mL of anhydrous MeOH, 10% Pd/C (250 mg) was added in one portion. The black slurry was stirred under a H_2 atmosphere (balloon) overnight before being filtered through celite. The filtrate was concentrated to give 4,6-dimethylheptanoic acid as a light yellow oil.

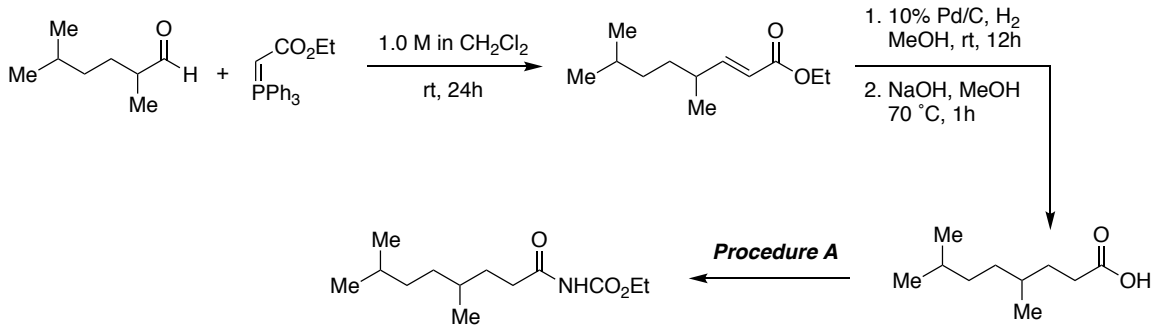
Ethyl (4,6-dimethylheptanoyl)carbamate was then synthesized according to ***Procedure A***. Colorless oil (323 mg, 28% yield for 3 steps). R_f = 0.45 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.85 – 2.58 (m, 2H), 1.71 – 1.60 (m, 2H), 1.58 – 1.49 (m, 1H), 1.47 – 1.38 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.16 – 1.08 (m, 1H), 1.06 – 0.97 (m, 1H), 0.86 (d, J = 6.6 Hz, 6H), 0.83 (d, J = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 151.9, 62.1, 46.4, 33.8, 31.5, 30.0, 25.2, 23.3, 22.2, 19.4, 14.2.

HRMS m/z calcd. for $C_{12}H_{22}NO_3$ $[M-H]^-$ 228.1600, found 228.1598.

IR (cm^{-1}) 3279 (br), 2955, 2870, 1760, 1697, 1467, 1200, 1053.



The mixture of 2,5-dimethylhexanal[8] (0.64g, 5.0 mmol) and ethyl (triphenylphosphoranylidene)acetate (2.09g, 6.0 mmol) in 5.0 mL of anhydrous CH_2Cl_2 was vigorously stirred at room temperature for 24h. After removal of CH_2Cl_2, 50 mL of pentane was added and the mixture was sonicated until light yellow precipitate formed. The slurry was filtered and the filtrate was concentrated in vacuum. Repeated the *Sonication (with Pentane)-Filter Procedure* three more time to give crude ethyl *(E)*-4,7-dimethyloct-2-enoate as a light yellow oil, which was pure enough for direct use in the next step.

To a solution of the above ethyl *(E)*-4,7-dimethyloct-2-enoate in 50 mL of anhydrous MeOH, 10% Pd/C (250 mg) was added in one portion. The black slurry was stirred under a H_2 atmosphere (balloon) overnight before being filtered through celite. The filtrate was concentrated to about 10 mL, then 3.0 mL of 2.0 M aq. NaOH was added dropwise. The mixture was vigorously stirred at 70 ˚C for 1h. After cooling down to room temperature, the mixture was carefully acidified by slow addition of 10% HCl until pH = 2. The mixture was extracted with CH_2Cl_2 (10 mL×3). The organic layer was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give crude 4,7-dimethyloctanoic acid as a light yellow oil.

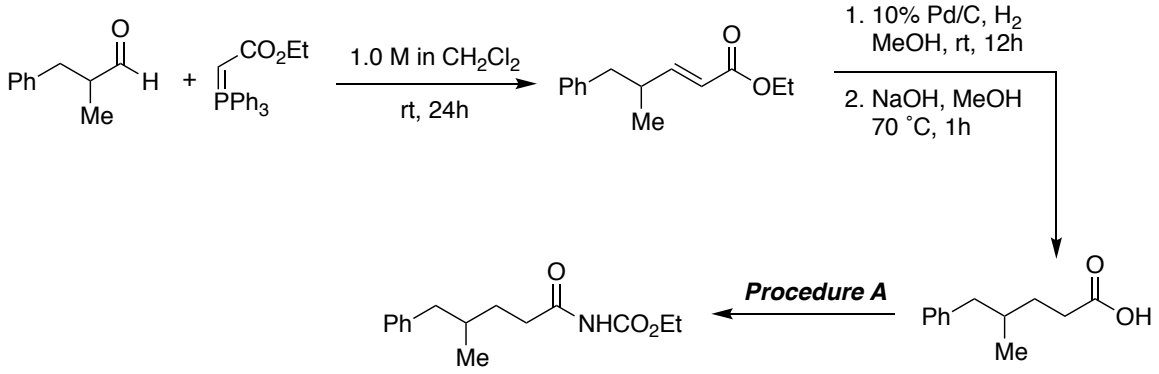
Ethyl (4,7-dimethyloctanoyl)carbamate was then synthesized according to ***Procedure A***. Colorless oil (359 mg, 30% yield for 5 steps). R_f = 0.45 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.83 – 2.67 (m, 2H), 1.76 – 1.64 (m, 1H), 1.52 – 1.39 (m, 3H), 1.35 – 1.27 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.22 – 1.09 (m, 3H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.86 (dd, *J* = 6.6, 2.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 151.8, 62.1, 36.2, 34.4, 33.9, 32.7, 31.2, 28.2, 22.7, 22.5, 19.4, 14.2.

HRMS m/z calcd. for $C_{13}H_{24}NO_3$ $[M\text{-}H]^-$ 242.1756, found 242.1750.

IR (cm^{-1}) 3279 (br), 2954, 2870, 1760, 1697, 1498, 1200, 1053.



The mixture of 2-methyl-3-phenylpropanal[9] (0.72g, 5.0 mmol) and Ethyl (triphenylphosphoranylidene)acetate (2.09g, 6.0 mmol) in 20.0 mL of anhydrous CH_2Cl_2 was vigorously stirred at room temperature for 24h. After removal of CH_2Cl_2, 50 mL of pentane was added and the mixture was sonicated until light yellow precipitate formed.

The slurry was filtered and the filtrate was concentrated *in vacuo*. Repeated the *Sonication with Pentane-Filter Procedure* three more time to give crude ethyl *(E)*-4-methyl-5-phenylpent-2-enoate as a light yellow oil, which was pure enough for direct use in the next step.

To a solution of the above ethyl *(E)*-4-methyl-5-phenylpent-2-enoate in 50 mL of anhydrous MeOH, 10% Pd/C (250 mg) was added in one portion. The black slurry was stirred under a H_2 atmosphere (balloon) overnight before being filtered through celite. The filtrate was concentrated to about 10 mL, then 3.0 mL of 2.0 M aq. NaOH was added dropwise. The mixture was vigorously stirred at 70 ˚C for 1h. After cooling down to room temperature, the mixture was carefully acidified by slow addition of 10% HCl until pH = 2. The mixture was extracted with CH_2Cl_2 (10 mL×3). The organic layer was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give crude 4-methyl-5-phenylpentanoic acid as a light yellow oil.

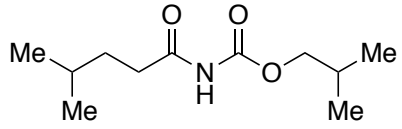
Ethyl (4-methyl-5-phenylpentanoyl)carbamate was then synthesized according to ***Procedure A***. Colorless oil (718 mg, 58% yield for 5 steps). R_f = 0.25 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.31 – 7.27 (m, 2H), 7.22 – 7.15 (m, 3H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.87 (ddd, *J* = 16.3, 9.8, 5.7 Hz, 1H), 2.79 (ddd, *J* = 16.2, 9.8, 5.7 Hz, 1H), 2.70 (dd, *J* = 13.4, 6.0 Hz, 1H), 2.44 (dd, *J* = 13.4, 8.1 Hz, 1H), 1.89 – 1.73 (m, 2H), 1.60 – 1.51 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 151.8, 140.9, 129.2, 128.2, 125.8, 62.2, 43.4, 34.6, 33.9, 30.9, 19.1, 14.2.

HRMS m/z calcd. for $C_{15}H_{20}NO_3$ $[M-H]^-$ 262.1443, found 262.1437.

IR (cm^{-1}) 3278 (br), 2958, 2925, 1759, 1703, 1494, 1199, 1049, 739, 700.



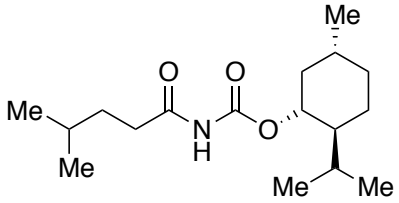
Prepared according to ***Procedure B*** from commercially available 4-methyl pentanoic acid (580 mg, 5.0 mmol). Colorless oil (537 mg, 50% yield). R_f = 0.35 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 3.94 (d, *J* = 6.7 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.03 – 1.91 (m, 1H), 1.67 – 1.49 (m, 3H), 0.95 (d, *J* = 6.8 Hz, 6H), 0.92 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 152.0, 72.1, 34.1, 33.0, 27.7, 27.6, 22.3, 18.9.

HRMS m/z calcd. for $C_{11}H_{20}NO_3$ $[M-H]^-$ 214.1443, found 214.1440.

IR (cm^{-1}) 3268 (br), 2957, 2873, 1757, 1687, 1501, 1215, 1050.



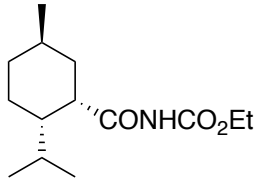
Prepared according to ***Procedure B*** from commercially available 4-methyl pentanoic acid (348 mg, 3.0 mmol). Colorless oil (407 mg, 46% yield). R_f = 0.42 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (brs, 1H), 4.64 (td, *J* = 10.9, 4.4 Hz, 1H), 2.89 – 2.65 (m, 2H), 2.08 (dtd, *J* = 11.9, 4.0, 1.7 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.75 – 1.46 (m, 6H), 1.39 (ddt, *J* = 12.5, 10.7, 3.1 Hz, 1H), 1.15 – 0.99 (m, 2H), 0.93 (dd, *J* = 8.9, 6.7 Hz, 13H), 0.81 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 151.5, 47.0, 40.9, 34.2, 34.1, 33.0, 31.4, 27.7, 26.3, 23.4, 22.3, 22.0, 20.7, 16.4.

HRMS m/z calcd. for $C_{17}H_{32}NO_3$ $[M+H]^+$ 298.2382, found 298.2385.

IR(cm^{-1}) 3270(br), 2953, 2927, 1754, 1694, 1467, 1207, 1178.



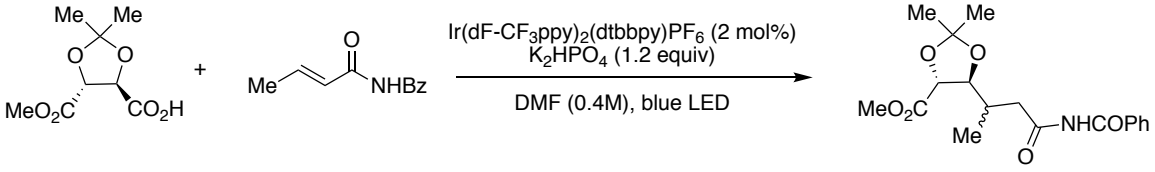
Prepared according to ***Procedure B*** from (1S,2S,5R)-2-isopropyl-5-methylcyclohexane-1-carboxylic acid (295 mg, 1.6 mmol).[12] White solid (257 mg, 59% yield). R_f = 0.40 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.54 (brs, 1H), 1.96 – 1.84 (m, 2H), 1.82 – 1.75 (m, 1H), 1.75 – 1.63 (m, 2H), 1.62 – 1.52 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.26 (ddd, *J* = 13.9, 12.5, 5.8 Hz, 1H), 1.03 (ddt, *J* = 12.3, 9.6, 4.3 Hz, 1H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.86 (dd, *J* = 10.3, 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 151.5, 62.0, 46.5, 41.5, 37.8, 35.2, 30.0, 27.1, 26.0, 22.3, 21.5, 21.4, 14.2.

HRMS m/z calcd. for $C_{14}H_{24}NO_3$ $[M\text{-}H]^-$ 254.1756, found 254.1753.

IR (cm^{-1}) 3271 (br), 2953, 2924, 2871, 1759, 1696, 1517, 1222, 1050, 929.



Methyl (4R,5S)-5-(4-benzamido-4-oxobutan-2-yl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate was synthesized according to MacMillan's procedure.[13] A solution of (4R,5R)-5-(methoxycarbonyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylic acid[14] (613 mg, 3.0 mmol), (*E*)-N-(but-2-enoyl)benzamide (568 mg, 3.0 mmol), Ir(dF-CF_3ppy)(dtbbpy)PF_6 (34 mg, 0.03 mmol) and K_2HPO_4 (627 mg, 3.6 mmol) in 7.5 mL of anhydrous DMF. The mixture was then degassed with nitrogen gas for 15 mins before being tightly capped. The reaction was illuminated with a blue LED (Kessil, 34W) for 12h (the distance between the vial and the LED was about 10 cm and the temperature was about 45 ˚C). The mixture was diluted with ether (50 mL) and filtered through celite before being concentrated *in vacuo*. The residue was directly subjected to flash silica gel chromatography for purification (EtOAc/hexane = 5:1) to give methyl (4R,5S)-5-(4-benzamido-4-oxobutan-2-yl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate as a colorless oil (392 mg, 38% yield).

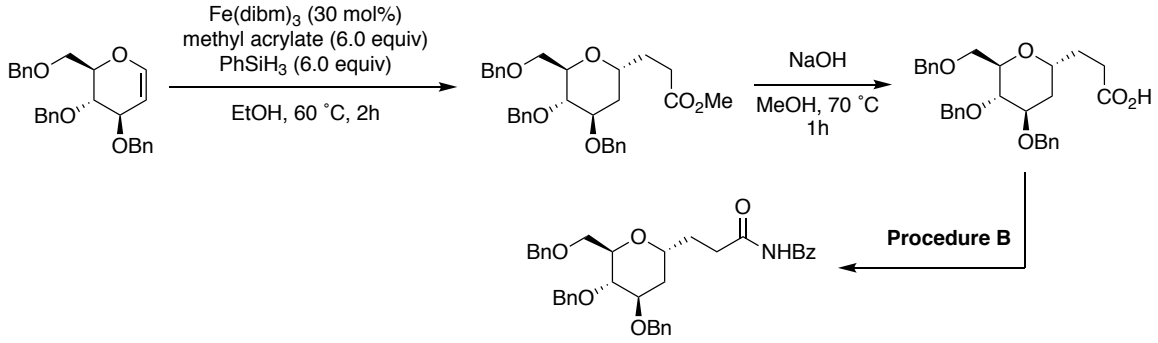
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (brs, 0.5H), 8.92 (brs, 0.5H), 7.91 – 7.87 (m, 2H), 7.65 – 7.59 (m, 1H), 7.55 – 7.48 (m, 2H), 4.39 (d, *J* = 7.2 Hz, 0.5H), 4.35 (d, *J* = 6.6 Hz, 0.5H), 4.26 – 4.21 (m, 1H), 3.80 (s, 1.5H), 3.79 (s, 1.5H), 3.28 – 3.20 (m, 1H), 3.02 –

2.92 (m, 1H), 2.61 – 2.47 (m, 1H), 1.49 (s, 1.5H), 1.48 (s, 1.5H), 1.44 (s, 1.5H), 1.43 (s, 1.5H), 1.14 – 1.08 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 174.8, 172.0, 171.8, 165.5, 165.5, 133.3, 133.2, 132.8, 132.7, 129.0, 129.0, 127.7, 111.2, 111.0, 82.4, 81.9, 77.2, 76.6, 52.4, 52.4, 41.4, 40.5, 32.8, 31.4, 27.0, 26.80, 25.6, 25.6, 16.1, 14.5.

HRMS m/z calcd. for $C_{18}H_{24}NO_6$ $[M+H]^+$ 350.1604, found 350.1605.

IR (cm^{-1}) 3290 (br), 2988, 1681, 1469, 1239, 1207, 1095, 708.



Methyl 3-((2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate was synthesized according to Baran's procedure.[3] To a solution of Methyl 3-((2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (1.09g, 2.0 mmol) in 10 mL of MeOH, 2.0 mL of 2.0 M aq. NaOH was added dropwise. The mixture was vigorously stirred at 70 ˚C for 1h. After cooling down to room temperature, the mixture was carefully acidified by slow addition of 10% HCl until pH = 2. The mixture was extracted with CH_2Cl_2 (20 mL×3). The organic layer was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum to give the crude 3-((2R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)propanoic acid as a light yellow oil, which was pure enough for further steps.

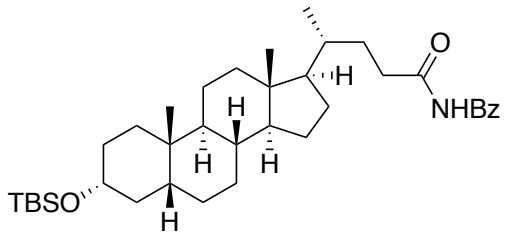
N-(3-((2R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)propanoyl)benzamide was then synthesized according to ***Procedure B***. Colorless oil (617mg, 53% yield). R_f = 0.37 (2:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (brs, 0.5H), 8.92 (brs, 0.5H), 7.91 – 7.87 (m, 2H), 7.65 – 7.59 (m, 1H), 7.55 – 7.48 (m, 2H), 4.39 (d, *J* = 7.2 Hz, 0.5H), 4.35 (d, *J* = 6.6 Hz, 0.5H), 4.26 – 4.21 (m, 1H), 3.80 (s, 1.5H), 3.79 (s, 1.5H), 3.28 – 3.20 (m, 1H), 3.02 – 2.92 (m, 1H), 2.61 – 2.47 (m, 1H), 1.49 (s, 1.5H), 1.48 (s, 1.5H), 1.44 (s, 1.5H), 1.43 (s, 1.5H), 1.14 – 1.08 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 13C NMR (126 MHz, Chloroform-d) δ 175.9, 165.7, 138.5, 138.4, 138.2, 133.1, 132.9, 128.9, 128.5, 128.4, 128.4, 128.0, 127.9, 127.9, 127.7, 127.7, 127.6, 77.0, 76.7, 74.1, 73.4, 72.6, 71.5, 70.2, 69.2, 34.2, 33.5, 26.6.

HRMS m/z calcd. for $C_{37}H_{40}NO_6$ $[M+H]^+$ 594.2856, found 594.2851.

IR (cm^{-1}) 3280 (br), 2924, 2865, 1681, 1453, 1241, 1092, 1071, 746, 696.



Prepared according to ***Procedure B*** from TBS-protected lithocholic acid (491 mg, 1.0 mmol).[15] White solid (366 mg, 62% yield). R_f = 0.38 (4:1 hex:EtOAc).

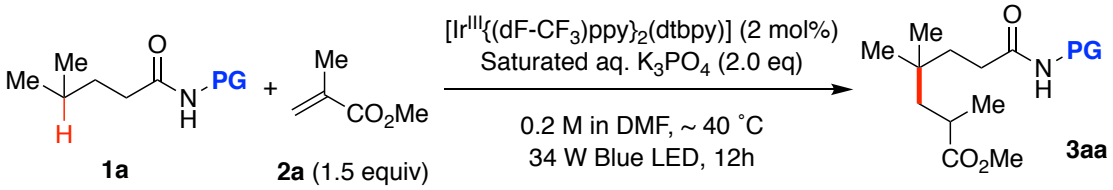
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (brs, 1H), 7.92 – 7.88 (m, 2H), 7.65 – 7.60 (m, 1H), 7.55 – 7.49 (m, 2H), 3.60 (tt, *J* = 10.9, 4.6 Hz, 1H), 3.07 (ddd, *J* = 16.5, 10.5, 4.9 Hz, 1H), 2.94 (ddd, *J* = 16.3, 10.1, 5.7 Hz, 1H), 2.01 – 1.73 (m, 6H), 1.62 – 1.03 (m, 20H), 1.00 (d, J = 6.5 Hz, 3H), 0.92 (s, 3H), 0.91 (s, 9H), 0.67 (s, 3H), 0.08 (s, 6H).

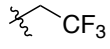
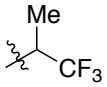
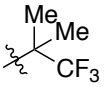
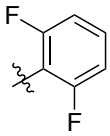
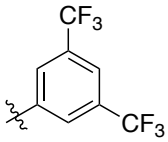
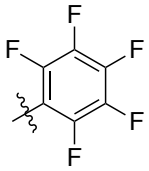
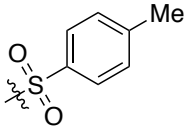
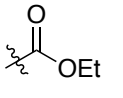
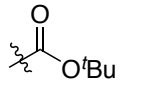
^{13}C NMR (126 MHz, $CDCl_3$) δ 177.1, 165.5, 133.1, 132.9, 129.0, 127.7, 72.8, 56.4, 56.1, 42.8, 42.3, 40.2, 40.1, 36.9, 35.9, 35.6, 35.6, 34.8, 34.6, 31.0, 30.2, 28.3, 27.3, 26.4, 26.0, 24.3, 23.4, 20.8, 18.5, 18.3, 12.1, -4.6.

HRMS m/z calcd. for $C_{37}H_{58}NO_3Si$ $[M-H]^-$ 592.4186, found 592.4184.

IR (cm^{-1}) 2925, 2860, 1698, 1658, 1275, 1250, 1097, 870, 773, 706, 697.

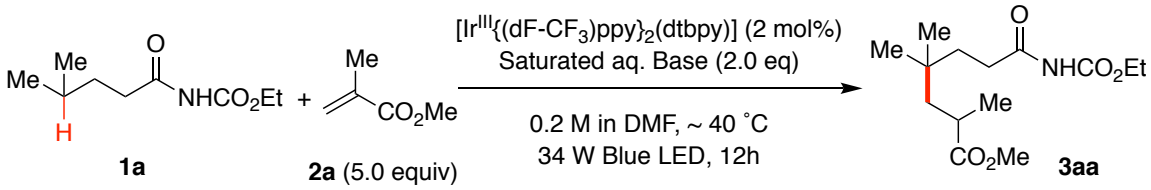
Examination of Protecting Groups



				
No product	No product	5%	18%	10%
				
No product	No product	R = Me, 32% R = Ph, 37%	**41% (76%)[c]**	23%

Note:
[a]0.10 mmol scale reaction.
[b]NMR yields were presented using trimethoxylbenzene as the internal standard.
[c]5.0 equiv of methyl methacrylate was used.

Examination of Bases



Entry	Base	Conv. %	NMR Yield %[b]
1	K_2CO_3	90	48
2	Na_2CO_3	65	38
3	Cs_2CO_3	95	66
4	Na_3PO_4	77	53
5	K_2HPO_4	80	11
6	KH_2PO_4	<10	trace
7	$KHCO_3$	35	26
8	$NaHCO_3$	<10	trace
9	KOH	80	trace
10	NaOH	50	trace
11	Quinuclidine	<10	trace
12	1.1 equiv of K_3PO_4	95	83

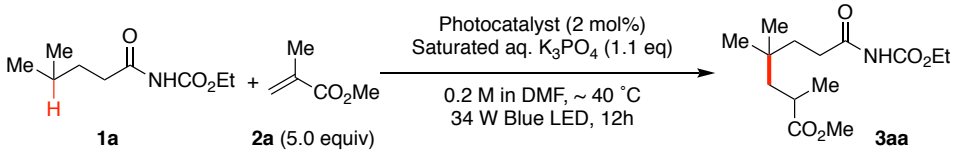
Note:

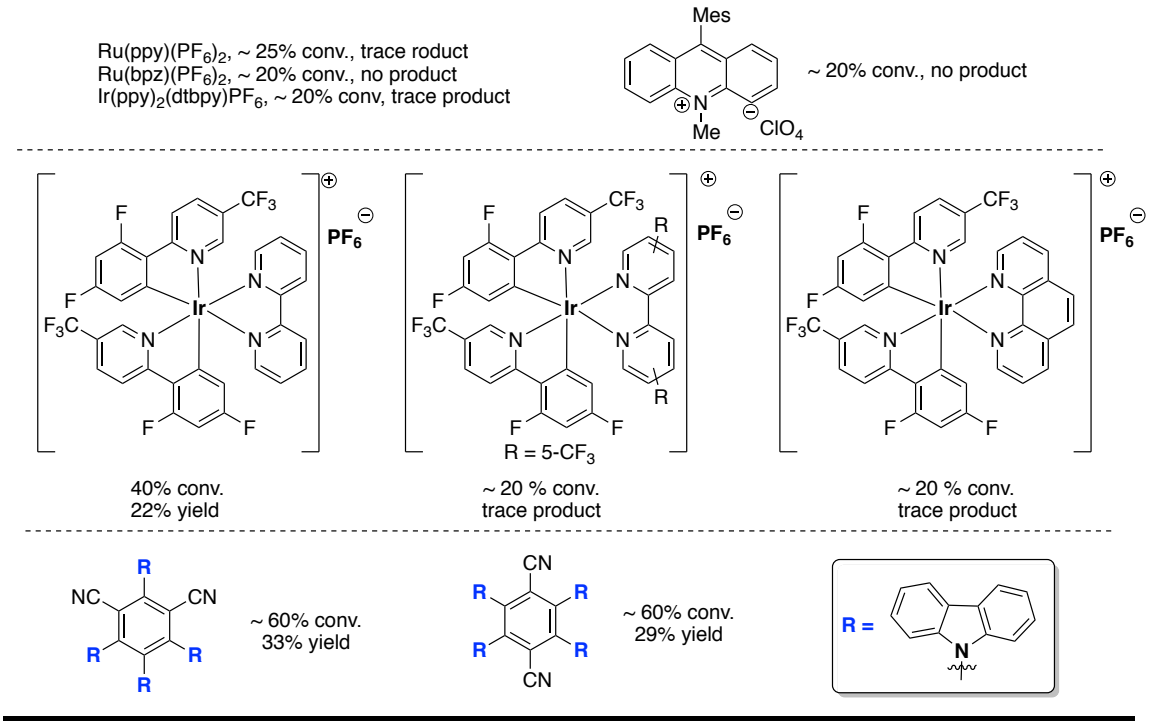
[a]0.10 mmol scale reactions.

[b]Trimethoxybenzene as the internal standard.

[c]Isolated yield.

Examination of Photocatalysts



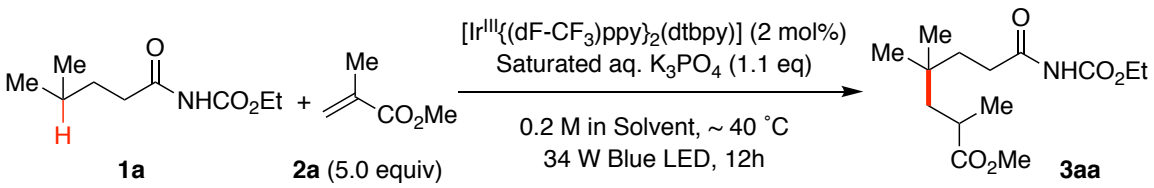


Note:

[a]0.10 mmol scale reactions.

[b]NMR yields were presented using trimethoxybenzene as the internal standard.

Examination of Solvents



1a **2a** (5.0 equiv) **3aa**

Entry	Solvent	Conv. %	NMR Yield %[b]
1	DMA	88	76
2	DMSO	90	63
3	MeCN	87	33
4	$PhCF_3$	80	trace
5	Toluene	40	trace
6	$CHCl_3$	75	44
7	DCE	75	45
8	Acetone	60	35
9	THF	50	trace
10[c]	**DMF/t-AmylOH (1:1)**	**95**	**84(74)**[d]

Note:

[a]0.10 mmol scale reactions.

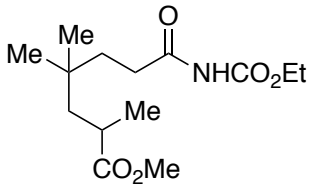
[b]Trimethoxybenzene as the internal standard.

[c]3.0 equiv of methyl methacrylate was used.

[d]Isolated yield.

Photoredox-Catalyzed γ-C(sp^3)-H Alkylation (Alkene and Amide Scope)

Procedure C: A magnet stir bar, the amide (0.1 mmol, 1.0 equiv.), alkene (1.2 – 3.0 equiv.), sat. aq. K_3PO_4 (1.1 equiv.) and [Ir{dF-(CF_3)ppy}$_2$(dtbbpy)]PF_6 (2 mol %) were charged into an oven-dried vial (4 mL), followed by 1.0 mL of 1:1 mixed DMF:*t*-AmylOH. The vial was then bubbled with nitrogen gas for 15 mins before being tightly capped. The reaction was illuminated with a blue LED (Kessil, 34W) for 12h (the distance between the vial and the LED was about 15 cm and the temperature was ~40 ˚C). The mixture was diluted with ether (5.0 mL) and filtered through celite before being concentrated *in vacuo*. The residue was directly subjected to flash silica gel chromatography for purification, using hexane and EtOAc (or acetone) as the eluent.



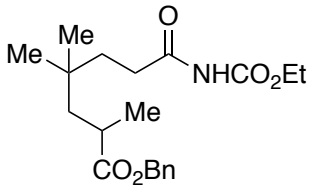
Prepared according to ***Procedure C*** (with 3.0 equiv. of methyl methacrylate). Colorless oil (21.3 mg, 74% yield). R_f = 0.20 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.68 (s, 3H), 2.73 – 2.65 (m, 2H), 2.59 – 2.50 (m, 1H), 1.91 (dd, *J* = 14.2, 9.5 Hz, 1H), 1.60 – 1.50 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.23 – 1.14 (m, 4H), 0.89 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.3, 174.8, 151.6, 62.1, 51.7, 45.3, 36.0, 35.6, 32.9, 31.5, 26.8, 26.7, 20.4, 14.2.

HRMS m/z calcd. for $C_{14}H_{26}NO_5$ $[M+H]^+$ 288.1811, found 288.1814.

IR (cm^{-1}) 3286 (br), 2956, 2874, 1759, 1736, 1710, 1494, 1198, 1049.



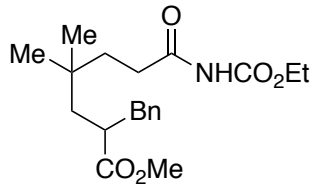
Prepared according to ***Procedure C*** (with 1.5 equiv. of benzyl methacrylate). Colorless oil (25.6 mg, 70% yield). R_f = 0.25 (3:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (brs, 1H), 7.41 – 7.31 (m, 5H), 5.14 (d, *J* = 12.3 Hz, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.77 – 2.66 (m, 2H), 2.60 (dqd, *J* = 9.9, 7.0, 2.9 Hz, 1H), 1.95 (dd, *J* = 14.3, 9.3 Hz, 1H), 1.61 – 1.52 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.26 – 1.13 (m, 4H), 0.88 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.7, 174.8, 151.6, 136.0, 128.5, 128.2, 128.2, 66.3, 62.2, 45.2, 36.0, 35.7, 33.0, 31.5, 26.8, 26.7, 20.4, 14.3.

HRMS m/z calcd. for $C_{20}H_{30}NO_5$ $[M+H]^+$ 364.2124, found 364.2114.

IR (cm^{-1}) 3285 (br), 2959, 1758, 1707, 1495, 1199, 1074, 750, 698.



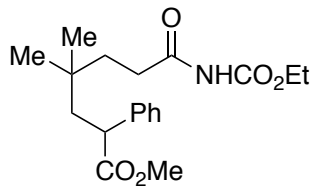
Prepared according to ***Procedure C*** (with 1.5 equiv. of methyl 2-benzylacrylate). Colorless oil (24.7 mg, 68% yield). R_f = 0.25 (3:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (brs, 1H), 7.31 – 7.26 (m, 2H), 7.23 – 7.14 (m, 3H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.56 (s, 3H), 2.91 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.80 – 2.57 (m, 3H), 2.50 (ddd, *J* = 16.2, 11.3, 5.5 Hz, 1H), 1.89 (dd, J = 14.3, 10.0 Hz, 1H), 1.59 – 1.43 (m, 2H), 1.37 – 1.30 (m, 4H), 0.85 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.1, 174.7, 151.6, 138.9, 129.0, 128.4, 126.4, 62.1, 51.5, 43.7, 42.7, 40.9, 35.7, 32.8, 31.4, 26.9, 26.8, 14.3.

HRMS m/z calcd. for $C_{20}H_{30}NO_5$ $[M+H]^+$ 364.2124, found 364.2120.

IR (cm^{-1}) 3288(br), 2955, 1733, 1704, 1494, 1198, 1074, 735, 700.



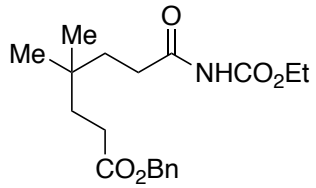
Prepared according to ***Procedure C*** (with 1.5 equiv. of methyl 2-phenylacrylate). Colorless oil (25.0 mg, 72% yield). R_f = 0.20 (3:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.37 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.70 (dd, *J* = 9.2, 3.8 Hz, 1H), 3.66 (s, 3H), 2.82 – 2.53 (m, 2H), 2.36 (dd, *J* = 14.2, 9.2 Hz, 1H), 1.63 – 1.57 (m, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.93 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2, 174.7, 151.6, 140.6, 128.7, 127.8, 127.1, 62.2, 52.2, 47.5, 44.9, 35.9, 33.2, 31.5, 26.9, 14.3.

HRMS m/z calcd. for $C_{19}H_{28}NO_5$ $[M+H]^+$ 350.1967, found 350.1962.

IR (cm^{-1}) 3286 (br), 2955, 1758, 1734, 1494, 1202, 1074, 775, 732, 700.



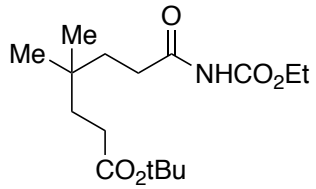
Prepared according to ***Procedure C*** (with 1.2 equiv. of benzyl acrylate). Colorless oil (21.4 mg, 61% yield). R_f = 0.25 (3:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.32 (m, 6H), 5.13 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.75 (t, *J* = 8.3 Hz, 2H), 2.37 (t, J = 8.3 Hz, 2H), 1.67 – 1.56 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 174.0, 151.6, 136.0, 128.5, 128.2, 128.2, 66.2, 62.2, 36.2, 35.5, 32.2, 31.3, 29.7, 26.4, 14.2.

HRMS m/z calcd. for $C_{19}H_{28}NO_5$ $[M+H]^+$ 350.1967, found 350.1969.

IR (cm^{-1}) 3278 (br), 2923, 2854, 1733, 1705, 1496, 1198, 1074, 738, 698.



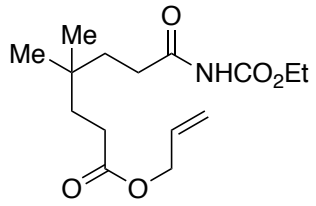
Prepared according to ***Procedure C*** (3.0 equiv. of *tert*-butyl acrylate). Colorless oil (20.9 mg, 66% yield). R_f = 0.38 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (brs, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.89 – 2.58 (m, 2H), 2.37 – 1.98 (m, 2H), 1.61 – 1.53 (m, 4H), 1.45 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 173.6, 151.7, 80.1, 62.2, 36.3, 35.6, 32.2, 31.4, 30.7, 28.1, 26.5, 14.2.

HRMS m/z calcd. for $C_{16}H_{29}NO_5Na$ $[M+Na]^+$ 338.1943, found 338.1946

IR (cm^{-1}) 3277 (br), 2971, 2933, 1762, 1727, 1519, 1152, 1042.



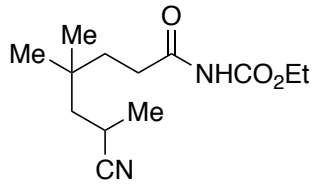
Prepared according to ***Procedure C*** (with 2.0 equiv. of allyl acrylate). Colorless oil (18.6 mg, 62% yield). R_f = 0.30 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (brs, 1H), 5.94 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 1H), 5.34 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.25 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.59 (d, *J* = 5.7, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.79 – 2.70 (m, 2H), 2.40 – 2.26 (m, 2H), 1.65 – 1.53 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 173.8, 151.7, 132.2, 118.2, 65.1, 62.2, 36.2, 35.5, 32.2, 31.3, 29.5, 26.4, 14.2.

HRMS m/z calcd. for $C_{15}H_{24}NO_5$ $[M-H]^-$ 298.1654, found 298.1656.

IR (cm^{-1}) 3281 (br), 2958, 1757, 1735, 1706, 1492, 1199, 1074, 775.



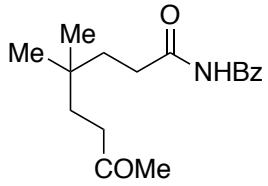
Prepared according to ***Procedure C*** (with 3.0 equiv. of methacrylonitrile). Colorless oil (15.7 mg, 62% yield). R_f = 0.20 (2:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (brs, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.83 – 2.70 (m, 2H), 2.65 (dtt, *J* = 10.2, 7.1, 3.6 Hz, 1H), 1.79 (dd, *J* = 14.3, 10.3 Hz, 1H), 1.67 (qdd, *J* = 13.9, 10.0, 6.2 Hz, 2H), 1.40 – 1.30 (m, 7H), 1.04 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 151.7, 124.2, 62.3, 45.9, 35.9, 33.0, 31.3, 26.9, 26.6, 20.7, 20.5, 14.2.

HRMS m/z calcd. for $C_{13}H_{21}N_2O_3$ $[M-H]^-$ 253.1552, found 253.1554.

IR (cm^{-1}) 3290 (br), 2952, 2115, 1730, 1599, 1456, 1424, 1219, 1191, 630.



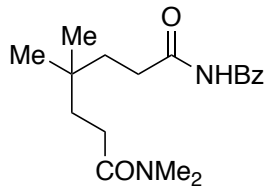
Prepared according to ***Procedure C*** (with 1.5 euqiv. of methyl vinyl ketone). Colorless oil (12.7 mg, 44% yield). R_f = 0.25 (2:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (brs, 1H), 7.90 – 7.84 (m, 2H), 7.68 – 7.59 (m, 1H), 7.56 – 7.50 (m, 2H), 3.04 – 2.88 (m, 2H), 2.54 – 2.39 (m, 2H), 2.19 (s, 3H), 1.70 – 1.63 (m, 2H), 1.62 – 1.55 (m, 2H), 0.95 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4, 176.5, 165.4, 133.3, 132.8, 129.0, 127.6, 38.8, 35.4, 35.0, 32.9, 32.1, 30.0, 26.7.

HRMS m/z calcd. for $C_{17}H_{22}NO_3$ $[M-H]^-$ 288.1600, found 288.1606.

IR (cm^{-1}) 3284 (br), 2955, 2868, 1710, 1682, 1504, 1471, 1241, 710.



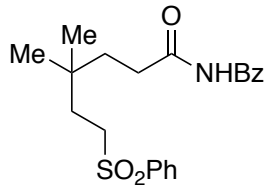
Prepared according to ***Procedure C*** (with 2.0 equiv. of *N,N′*-dimethylacrylamide). Colorless oil (19.2 mg, 60% yield). R_f = 0.25 (1:2 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.93 – 7.84 (m, 2H), 7.65 – 7.59 (m, 1H), 7.56 – 7.48 (m, 2H), 3.05 (s, 3H), 2.99 – 2.89 (m, 5H), 2.40 – 2.28 (m, 2H), 1.73 – 1.59 (m, 4H), 0.98 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 173.5, 165.4, 133.2, 132.9, 129.0, 127.6, 37.4, 36.3, 35.5, 33.0, 32.4, 28.3, 26.8.

HRMS m/z calcd. for $C_{18}H_{25}N_2O_3$ $[M-H]^-$ 317.1865, found 317.1868.

IR (cm^{-1}) 3262 (br), 2924, 2858, 1685, 1626, 1504, 1481, 1245, 1142, 712.



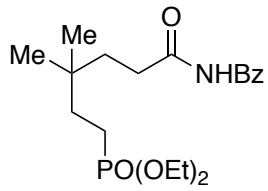
Prepared according to ***Procedure C*** (with 1.5 equiv. of vinyl phenyl sulfone) White solid (21.4 mg, 55% yield). R_f = 0.30 (1:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (brs, 1H), 8.01 – 7.92 (m, 2H), 7.90 – 7.83 (m, 2H), 7.69 – 7.62 (m, 2H), 7.61 – 7.57 (m, 2H), 7.56 – 7.50 (m, 2H), 3.21 – 3.11 (m, 2H), 2.98 – 2.85 (m, 2H), 1.75 – 1.68 (m, 2H), 1.65 – 1.55 (m, 2H), 0.94 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 165.3, 139.2, 133.6, 133.3, 132.7, 129.3, 129.1, 128.1, 127.6, 52.3, 35.2, 33.4, 32.6, 32.4, 26.6.

HRMS m/z calcd. for $C_{21}H_{24}NO_4S$ $[M-H]^-$ 386.1426, found 386.1425.

IR (cm^{-1}) 3290 (br), 2957, 1684, 1473, 1301, 1242, 1148, 1075, 711, 689.



Prepared according to ***Procedure C*** (with 1.5 equiv. of vinyl phosphonate). Colorless oil (29.8 mg, 78% yield). R_f = 0.35 (5:1 hex:acetone).

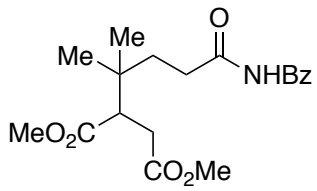
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (brs, 1H), 8.01 – 7.84 (m, 2H), 7.68 – 7.58 (m, 1H), 7.56 – 7.45 (m, 2H), 4.28 – 4.00 (m, 4H), 3.05 – 2.83 (m, 2H), 1.79 – 1.68 (m, 2H), 1.68 – 1.62 (m, 2H), 1.60 – 1.53 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 6H), 0.95 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.4, 165.5, 133.2, 132.9, 128.9, 127.7, 61.5 (d, *J* = 6.5 Hz), 35.1, 33.6 (d, *J* = 5.0 Hz), 32.9, 32.6 (d, J = 16.4 Hz), 26.3, 20.6 (d, *J* = 141.2 Hz), 16.5 (d, *J* = 6.0 Hz).

^{31}P NMR (202 Hz, $CDCl_3$) δ 33.6.

HRMS m/z calcd. for $C_{19}H_{29}NO_5P$ $[M-H]^-$ 382.1783, found 382.1779.

IR (cm^{-1}) 3239 (br), 2956, 2869, 1684, 1508, 1477, 1242, 1025, 961, 711.



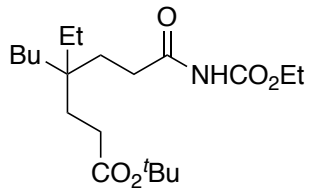
Prepared according to the ***Procedure C*** (with 1.5 equiv. of dimethyl maleate). Colorless oil (17.2 mg, 47% yield; 8.9 mg starting material was recovered). R_f = 0.20 (3:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (brs, 1H), 7.93 – 7.85 (m, 2H), 7.68 – 7.59 (m, 1H), 7.53 (dd, *J* = 8.4, 7.2 Hz, 2H), 3.72 (s, 3H), 3.68 (s, 3H), 3.13 – 2.95 (m, 2H), 2.91 – 2.80 (m, 2H), 2.55 (dd, *J* = 14.7, 0.9 Hz, 1H), 1.81 – 1.68 (m, 2H), 1.03 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 174.4, 173.0, 165.4, 133.3, 132.7, 129.0, 127.6, 51.8, 51.6, 49.4, 34.9, 34.6, 32.7, 32.2, 25.0, 24.6.

HRMS m/z calcd. for $C_{19}H_{24}NO_6$ $[M-H]^-$ 362.1604, found 362.1609.

IR (cm^{-1}) 3273 (br), 2967, 1727, 1682, 1469, 1435, 1239, 1159, 1075, 707, 694.



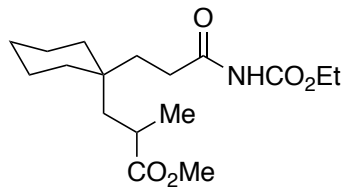
Prepared according to ***Procedure C*** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless oil (25.2 mg, 68% yield). R_f = 0.38 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (brs, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.77 – 2.55 (m, 2H), 2.24 – 2.06 (m, 2H), 1.59 – 1.49 (m, 4H), 1.46 (s, 9H), 1.37 – 1.13 (m, 11H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 173.7, 151.6, 80.1, 62.1, 36.7, 35.4, 30.6, 30.4, 29.9, 29.8, 28.2, 28.1, 25.1, 23.5, 14.2, 14.1, 7.5.

HRMS m/z calcd. for $C_{20}H_{37}NO_5Na$ $[M+Na]^+$ 394.2570, found 394.2564.

IR (cm^{-1}) 3283 (br), 2960, 2871, 1759, 1709, 1495, 1201, 1152, 1074.



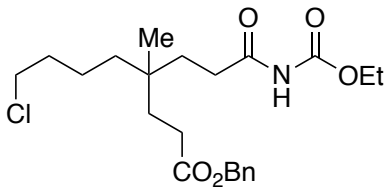
Prepared according to ***Procedure C*** (with 3.0 equiv. of methyl methacrylate). Colorless oil (22.0 mg, 67% yield). R_f = 0.22 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (brs, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 3H), 2.85 – 2.44 (m, 2H), 1.94 (dd, *J* = 14.7, 9.5 Hz, 1H), 1.67 (ddd, *J* = 14.3, 12.0, 5.4 Hz, 1H), 1.52 (ddd, *J* = 14.3, 11.9, 4.6 Hz, 1H), 1.48 – 1.35 (m, 6H), 1.34 – 1.28 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.28 – 1.21 (m, 3H), 1.18 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 174.7, 151.6, 62.1, 51.8, 35.7, 35.5, 35.1, 34.6, 30.7, 26.2, 21.5, 21.4, 20.5, 14.2.

HRMS m/z calcd. for $C_{17}H_{30}NO_5$ $[M+H]^+$ 328.2124, found 328.2126.

IR (cm^{-1}) 3285 (br), 2924, 2852, 1757, 1706, 1495, 1195, 1073.



Prepared according to ***Procedure C*** (with 1.5 equiv. of benzyl acrylate). Colorless oil

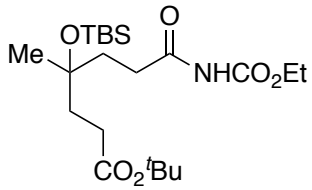
(23.0 mg, 54% yield). R_f = 0.28 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 5H), 5.13 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.55 (t, *J* = 6.7 Hz, 2H), 2.77 – 2.67 (m, 2H), 2.38 – 2.30 (m, 2H), 1.79 – 1.72 (m, 2H), 1.67 – 1.57 (m, 3H), 1.44 – 1.36 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.29 – 1.21 (m, 3H), 0.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 173.9, 151.6, 136.0, 128.6, 128.2, 66.3, 62.3, 44.9, 38.1, 34.5, 33.6, 33.2, 33.0, 30.8, 29.0, 24.2, 20.8, 14.2.

HRMS m/z calcd. for $C_{22}H_{33}NO_5Cl$ $[M+H]^+$ 426.2047, found 426.2042.

IR (cm^{-1}) 3283 (br), 2936, 1705, 1496, 1201, 1074, 740, 699.



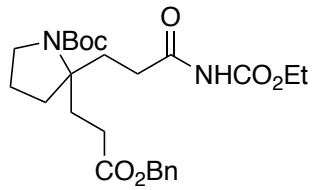
Prepared according to ***Procedure C*** (with 2.0 equiv. of *tert*-butyl acrylate). Colorless oil (30.7 mg, 71% yield). R_f = 0.33 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (brs, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.82 (dd, *J* = 9.0, 7.2 Hz, 2H), 2.41 – 2.24 (m, 2H), 1.89 – 1.73 (m, 4H), 1.46 (s, 12H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.12 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 173.3, 151.6, 80.1, 74.4, 62.2, 37.1, 36.0, 31.3, 30.6, 28.1, 27.1, 25.9, 18.2, 14.2, -2.0, -2.1.

HRMS m/z calcd. for $C_{21}H_{41}NO_6Si$ $[M+Na]^+$ 454.2601, found 454.2603.

IR (cm^{-1}) 3283 (br), 2930, 2857, 1760, 1710, 1495, 1202, 1153, 1053, 835, 773.



Prepared according to ***Procedure C*** (with 1.2 equiv. of benzyl acrylate). Colorless oil

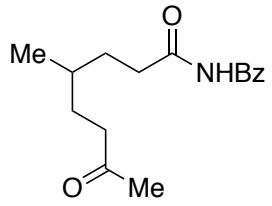
(24.4 mg, 51% yield). R_f = 0.18 (2:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (brs, 0.37H), 7.43 – 7.32 (m, 6H), 5.14 (s, 1.2H), 5.13 (s, 0.8H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.57 – 3.34 (m, 2H), 2.87 (ddd, *J* = 16.6, 11.9, 5.0 Hz, 0.5H), 2.72 – 2.58 (m, 1H), 2.56 – 2.47 (m, 0.55H), 2.44 – 2.19 (m, 4H), 2.10 – 2.00 (m, 1H), 1.98 – 1.84 (m, 2H), 1.82 – 1.69 (m, 3H), 1.46 (s, 9H), 1.35 – 1.28 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1, 173.6, 173.3, 173.2, 154.0, 153.9, 151.6, 151.5, 1136.0, 135.9, 128.6, 128.3, 128.3, 128.2, 128.2, 80.1, 79.3, 66.4, 66.3, 64.7, 63.9, 62.3, 62.0, 49.0, 48.8, 35.8, 34.6, 33.8, 33.0, 32.6, 31.5, 29.8, 29.7, 28.5, 28.4, 21.8, 21.7, 14.2.

HRMS m/z calcd. for $C_{15}H_{35}N2O_7$ $[M-H]^-$ 475.2444, found 475.2449.

IR (cm^{-1}) 3276 (br), 2972, 1731, 1685, 1497, 1390, 1201, 1163, 1075, 699.



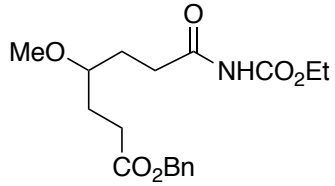
Prepared according to ***Procedure C*** (with 1.5 equiv. of methyl vinyl ketone). Colorless oil (3.9 mg, 14% yield). R_f = 0.18 (2:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (brs, 1H), 7.87 – 7.82 (m, 2H), 7.65 – 7.57 (m, 1H), 7.53 – 7.47 (m, 2H), 3.08 – 2.92 (m, 2H), 2.55 – 2.38 (m, 2H), 2.15 (s, 3H), 1.81 – 1.64 (m, 2H), 1.60 – 1.42 (m, 3H), 0.94 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.2, 176.1, 165.4, 133.2, 132.8, 129.0, 127.6, 41.3, 35.2, 32.1, 30.7, 30.4, 29.9, 19.3.

HRMS m/z calcd. for $C_{16}H_{22}NO_3$ $[M+H]^+$ 276.1600, found 276.1599.

IR (cm^{-1}) 3286 (br), 2925, 1708, 1681, 1471, 1241, 709.



Prepared according to ***Procedure C*** (0.10 mmol of benzyl acrylate and 1.2 equiv. of the

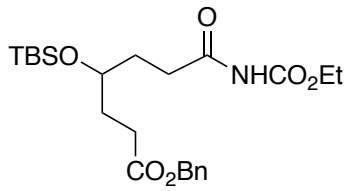
amide). Colorless oil (27.1 mg, 77% yield). R_f = 0.20 (2:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (brs, 1H), 7.42 – 7.32 (m, 5H), 5.14 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.32 (s, 3H), 3.32 – 3.25 (m, 1H), 2.92 – 2.75 (m, 2H), 2.47 (t, *J* = 7.6 Hz, 2H), 1.92 – 1.77 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1, 173.4, 151.6, 136.0, 128.5, 128.2, 128.2, 78.9, 66.2, 62.2, 56.7, 31.9, 30.0, 28.4, 27.6, 14.2.

HRMS m/z calcd. for $C_{18}H_{24}NO_6$ $[M-H]^-$ 350.1604, found 350.1609.

IR (cm^{-1}) 3285 (br), 2931, 1702, 1691, 1497, 1200, 1074, 750, 698.



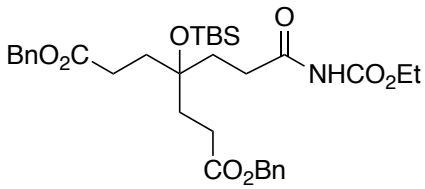
Prepared according to ***Procedure C*** (0.10 mmol of benzyl acrylate and 1.2 equiv. of the amide). Colorless oil (22.2mg, 49% yield). R_f = 0.29 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 6H), 5.14 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.87 – 3.77 (m, 1H), 2.90 – 2.76 (m, 2H), 2.45 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 2H), 1.92 – 1.72 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 173.5, 151.6, 136.0, 128.5, 128.2, 128.2, 70.0, 66.2, 62.2, 31.9, 31.6, 30.8, 29.8, 25.9, 18.0, 14.2, -4.6, -4.6.

HRMS m/z calcd. for $C_{23}H_{36}NO_6Si$ $[M-H]^-$ 450.2312, found 450.2318.

IR (cm^{-1}) 3288 (br), 2928, 2855, 1734, 1705, 1702, 1495, 1200, 1073, 836, 750, 697.



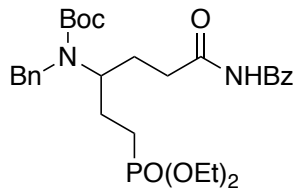
Prepared according to ***Procedure C*** (with 2.0 equiv. of benzyl acrylate). Colorless oil (22.3 mg, 36% yield). R_f = 0.20 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 11H), 5.13 (s, 4H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.88 – 2.76 (m, 2H), 2.49 – 2.39 (m, 4H), 1.92 – 1.78 (m, 6H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 9H), 0.13 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 173.3, 151.5, 135.9, 128.5, 128.2, 128.2, 76.1, 66.4, 62.3, 34.0, 33.1, 31.0, 29.0, 26.0, 18.5, 14.2, -1.9.

HRMS m/z calcd. for $C_{33}H_{46}NO_8Si$ $[M-H]^-$ 612.2993, found 612.2999.

IR (cm^{-1}) 3288 (br), 2928, 2854, 1735, 1496, 1200, 1163, 1098, 835, 774, 697.



Prepared according to ***Procedure C*** (with 2.0 equiv. of vinyl phosphate). Colorless oil (21.2 mg, 38% yield; 20.0 mg starting material was recovered). R_f = 0.20 (5:1 hex:acetone).

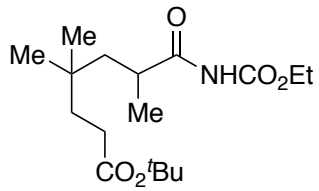
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (brs, 0.5H), 8.39 (brs, 0.5H), 7.92 – 7.78 (m, 2H), 7.68 – 7.58 (m, 1H), 7.57 – 7.47 (m, 2H), 7.40 – 7.15 (m, 5H), 4.50 (brd, *J* = 15.4 Hz, 0.5H), 4.40 – 4.30 (m, 1.5H), 4.09 – 3.84 (m, 4H), 2.95 – 2.70 (m, 2H), 2.05 – 1.39 (m, 15H), 1.30 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 174.7, 165.2, 165.1, 156.5, 156.4, 139.3, 139.3, 133.2, 133.1, 132.8, 129.0, 128.9, 128.5, 127.6, 127.5, 127.4, 127.1, 80.4, 80.4, 61.5, 61.5, 56.4, 56.0, 47.2, 34.3, 28.5, 28.4, 27.4, 27.3, 26.5, 26.1, 23.5, 22.4, 16.5, 16.4.

^{31}P NMR (202 MHz, $CDCl_3$) δ 31.9, 31.7.

HRMS m/z calcd. for $C_{29}H_{40}N_2O_7P$ $[M-H]^-$ 559.2573, found 559.2570.

IR (cm^{-1}) 3270 (br), 2976, 2930, 1683, 1453, 1365, 1242, 1161, 1026, 961, 705.



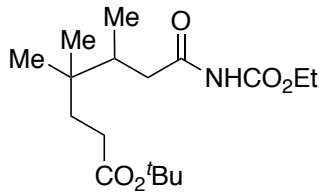
Prepared according to ***Procedure C*** (with 1.5 equiv. of *tert*-butyl acrylate). Colorless oil (21.8 mg, 66% yield). R_f = 0.37 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (brs, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.36 (brs, 1H), 2.22 – 2.16 (m, 2H), 2.08 (dd, *J* = 14.3, 8.9 Hz, 1H), 1.54 – 1.49 (m, 2H), 1.45 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.20 (d, *J* = 7.0 Hz, 3H), 1.16 (dd, *J* = 14.3, 2.9 Hz, 1H), 0.87 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 173.6, 151.4, 80.0, 62.2, 44.6, 37.0, 32.9, 30.8, 28.1, 26.8, 26.7, 20.7, 14.2.

HRMS m/z calcd. for $C_{17}H_{31}NO_5Na$ $[M+Na]^+$ 352.2100, found 352.2102.

IR (cm^{-1}) 3278 (br), 2970, 1756, 1719, 1501, 1201, 1155, 1045.



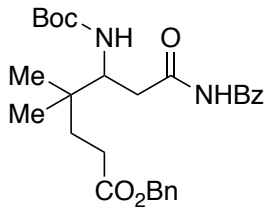
Prepared according to ***Precedure C*** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless oil (18.7 mg, 57% yield). R_f = 0.40 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (brs, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.84 (dd, *J* = 16.1, 2.8 Hz, 1H), 2.52 (dd, *J* = 16.0, 10.8 Hz, 1H), 2.21 (dd, *J* = 8.9, 7.7 Hz, 2H), 1.98 (dqd, *J* = 13.5, 6.8, 2.8 Hz, 1H), 1.65 – 1.51 (m, 2H), 1.46 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.87 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 173.8, 151.6, 80.1, 62.2, 38.5, 36.6, 34.8, 34.7, 30.4, 28.1, 28.1, 24.2, 24.0, 14.5, 14.2.

HRMS m/z calcd. for $C_{17}H_{31}NO_5Na$ $[M+Na]^+$ 352.2100, found 352.2094.

IR (cm^{-1}) 3283 (br), 2970, 1760, 1725, 1499, 1202, 1153, 1047.



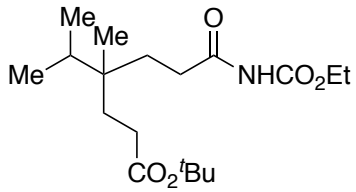
Prepared according to the ***Procedure C*** (with 1.2 equiv. of Benzyl acrylate). Colorless oil (21.1 mg, 43% yield; 14.2 mg starting material was recovered). R_f = 0.22 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (brs, 1H), 7.92 – 7.81 (m, 2H), 7.65 – 7.59 (m, 1H), 7.56 – 7.46 (m, 2H), 7.44 – 7.31 (m, 5H), 5.13 (s, 2H), 4.78 (d, *J* = 10.2 Hz, 1H), 4.12 (td, *J* = 10.5, 3.7 Hz, 1H), 3.26 (dd, *J* = 13.8, 3.6 Hz, 1H), 2.92 (dd, *J* = 13.8, 10.5 Hz, 1H), 2.51 – 2.39 (m, 2H), 1.80 – 1.61 (m, 2H), 1.38 (s, 9H), 0.97 (d, *J* = 10.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 173.7, 165.7, 155.8, 136.0, 133.2, 132.9, 128.9, 128.5, 128.2, 128.1, 127.8, 79.4, 66.3, 54.4, 39.0, 37.2, 33.8, 29.2, 28.3, 23.4, 23.1.

HRMS m/z calcd. for $C_{28}H_{35}N_2O_6$ $[M-H]^-$ 495.2495, found 495.2498.

IR (cm^{-1}) 3298 (br), 2967, 1712, 1681, 1502, 1474, 1242, 1161, 709, 697.



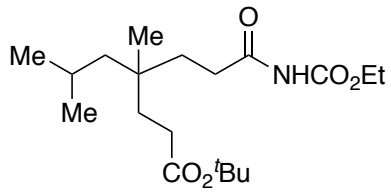
Prepared according to ***Procedure C*** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless oil (14.5 mg, 42% yield; 7.9 mg starting material was recovered). R_f = 0.41 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (brs, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.76 – 2.64 (m, 2H), 2.24 – 2.21 (m, 2H), 1.69 – 1.51 (m, 5H), 1.46 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 3H), 0.86 (s, 3H), 0.81 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 173.7, 151.6, 80.1, 62.2, 36.6, 33.6, 31.1, 30.8, 30.6, 30.1, 28.1, 20.6, 17.0, 17.0, 14.2.

HRMS m/z calcd. for $C_{18}H_{33}NO_5Na$ $[M+Na]^+$ 366.2256, found 366.2249.

IR (cm^{-1}) 3283 (br), 2967, 2875, 1758, 1709, 1495, 1200, 1152, 1073.



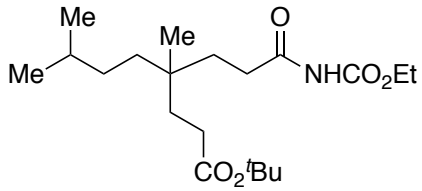
Prepared according to ***Procedure C*** (with 2.0 equiv. of *tert*-butyl acrylate). Colorless oil (23.1 mg, 65% yield). R_f = 0.40 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (brs, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.82 – 2.62 (m, 2H), 2.31 – 2.04 (m, 2H), 1.75 – 1.65 (m, 1H), 1.64 – 1.51 (m, 4H), 1.45 (s, 9H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 5.3 Hz, 2H), 0.94 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 173.6, 151.7, 80.1, 62.2, 47.9, 35.2, 34.3, 33.6, 31.0, 30.4, 28.1, 25.51, 24.7, 23.7, 14.2.

HRMS m/z calcd. for $C_{19}H_{34}NO_5$ $[M-H]^-$ 356.2437, found 356.2439.

IR (cm^{-1}) 3282 (br), 2956, 2870, 1759, 1709, 1493, 1367, 1200, 1151, 1074.



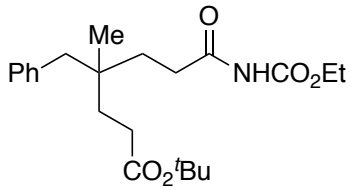
Prepared according to ***Procedure C*** (with 2.0 equiv. of *tert*-butyl acrylate). Colorless oil (24.8 mg, 67% yield). R_f = 0.42 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (brs, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.75 – 2.63 (m, 2H), 2.24 – 2.10 (m, 2H), 1.60 – 1.52 (m, 4H), 1.50 – 1.40 (m, 1H), 1.46 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.24 – 1.17 (m, 2H), 1.15 – 1.08 (m, 2H), 0.90 (s, 3H), 0.89 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 173.7, 151.6, 80.1, 62.2, 36.5, 34.3, 33.8, 33.1, 32.3, 30.9, 30.3, 28.7, 28.1, 24.3, 22.7, 14.2.

HRMS m/z calcd. for $C_{20}H_{36}NO_5$ $[M-H]^-$ 370.2593, found 370.2593.

IR (cm^{-1}) 3282 (br), 2955, 2929, 2869, 1759, 1709, 1468, 1366, 1200, 1151, 1074.



Prepared according to the ***Procedure C*** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless

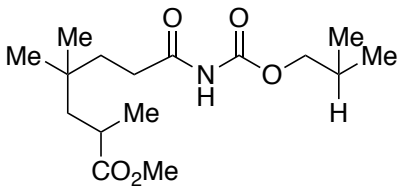
oil (16.9 mg, 43% yield; 12.1 mg starting material was recovered). R_f = 0.22 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (brs, 1H), 7.31 – 7.26 (m, 2H), 7.24 – 7.20 (m, 1H), 7.17 – 7.13 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.88 – 2.72 (m, 2H), 2.57 (s, 2H), 2.40 – 2.19 (m, 2H), 1.68 – 1.54 (m, 4H), 1.47 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 173.4, 151.6, 138.1, 130.6, 127.9, 126.1, 80.2, 62.2, 45.6, 36.0, 33.3, 32.8, 31.0, 30.4, 28.1, 24.0, 14.2.

HRMS m/z calcd. for $C_{22}H_{32}NO_5$ $[M-H]^-$ 390.2281, found 390.2285.

IR (cm^{-1}) 3280 (br), 2975, 2928, 1758, 1709, 1494, 1367, 1200, 1150, 1074, 737, 703.



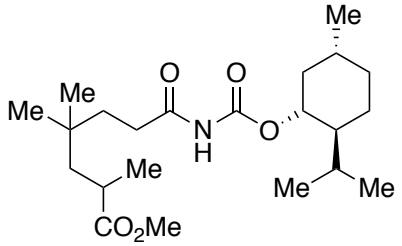
Prepared according to ***Procedure C*** (with 3.0 equiv. of methyl methacrylate). Colorless oil (19.8 mg, 63% yield). R_f = 0.20 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (brs, 1H), 3.95 (d, *J* = 6.6 Hz, 2H), 3.68 (s, 3H), 2.71 (ddd, *J* = 10.0, 5.5, 2.3 Hz, 2H), 2.60 – 2.50 (m, 1H), 2.07 – 1.84 (m, 2H), 1.62 – 1.50 (m, 2H), 1.23 – 1.15 (m, 4H), 0.97 (d, *J* = 6.8 Hz, 6H), 0.89 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.3, 174.8, 151.8, 72.1, 51.7, 45.3, 36.0, 35.6, 32.9, 31.5, 27.7, 26.8, 26.7, 20.4, 18.9.

HRMS m/z calcd. for $C_{16}H_{28}NO_5$ $[M-H]^-$ 314.1966, found 314.1967.

IR (cm^{-1}) 3280 (br), 2957, 2875, 1736, 1497, 1199, 1075.



Prepared according to ***Procedure C*** (with 3.0 equiv. of methyl methacrylate). Colorless

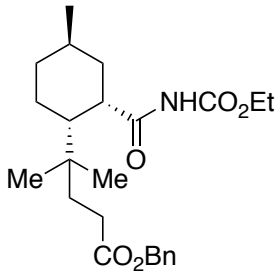
oil (~1:1 mixed diastereomers, 24.7 mg, 62% yield). R_f = 0.23 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (brd, 1H), 4.63 (td, *J* = 10.9, 4.4 Hz, 1H), 3.67 (s, 3H), 2.77 – 2.64 (m, 2H), 2.55 (tt, *J* = 9.9, 6.9 Hz, 1H), 2.11 – 2.03 (m, 1H), 1.97 – 1.84 (m, 2H), 1.74 – 1.65 (m, 2H), 1.60 – 1.45 (m, 3H), 1.43 – 1.33 (m, 1H), 1.24 – 1.14 (m, 4H), 1.12 – 0.97 (m, 2H), 0.95 – 0.86 (m, 13H), 0.80 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.3, 178.3, 175.0, 151.4, 151.4, 51.7, 51.7, 47.0, 45.4, 40.9, 40.9, 36.0, 36.0, 35.6, 34.1, 32.9, 31.5, 31.5, 31.4, 26.8, 26.7, 26.3, 26.3, 23.4, 23.4, 22.0, 20.7, 20.4, 16.4, 16.4.

HRMS m/z calcd. for $C_{22}H_{38}NO_5$ $[M-H]^-$ 396.2750, found 396.2749.

IR (cm^{-1}) 3276 (br), 2953, 1737, 1457, 1370, 1201, 1178.



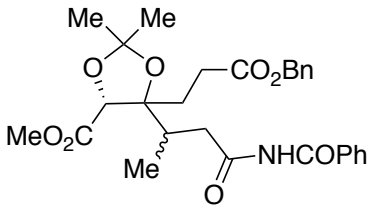
Prepared according to ***Procedure C*** (1.2 equiv. of benzyl accrylate). Colorless oil (22.6 mg, 54% yield). R_f = 0.24 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 6H), 5.12 (d, *J* = 1.6 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.32 (brs, 1H), 2.40 (ddd, *J* = 16.5, 11.6, 5.2 Hz, 1H), 2.32 (ddd, *J* = 16.1, 11.6, 5.3 Hz, 1H), 1.93 – 1.86 (m, 1H), 1.86 – 1.79 (m, 2H), 1.76 – 1.63 (m, 2H), 1.52 (ddd, *J* = 14.0, 11.5, 5.2 Hz, 1H), 1.42 – 1.28 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.23 - 1.13 (m, 1H), 1.13 – 1.04 (m, 1H), 1.00 – 0.93 (m, 1H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.87 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 174.2, 151.4, 136.1, 128.5, 128.2, 128.1, 66.1, 62.2, 43.3, 40.8, 35.9, 35.9, 34.5, 31.8, 29.2, 26.7, 26.1, 25.2, 22.1, 14.2.

HRMS m/z calcd. for $C_{24}H_{34}NO_5$ $[M-H]^-$ 416.2437, found 416, 2439.

IR (cm^{-1}) 3271 (br), 2949, 1759, 1735, 1704, 1498, 1159, 1182, 1045, 749, 697.



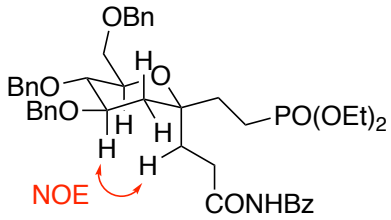
Prepared according to ***Procedure C*** (1.2 equiv. of benzyl accrylate). Colorless oil (18.8 mg, 37% yield; 20.0 mg starting material was recovered). R_f = 0.24 (3:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 – 8.66 (m, 1H), 7.92 – 7.84 (m, 2H), 7.66 – 7.58 (m, 1H), 7.56 – 7.47 (m, 2H), 7.41 – 7.32 (m, 5H), 5.22 – 4.98 (m, 2H), 4.75 – 4.42 (m, 1H), 3.86 – 3.69 (m, 3H), 3.57 – 3.21 (m, 1H), 3.06 – 2.44 (m, 4H), 2.34 – 1.91 (m, 2H), 1.64 – 1.53 (m, 3H), 1.49 – 1.36 (m, 3H), 1.18 – 0.89 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 174.9, 174.6, 173.8, 173.5, 173.3, 173.0, 169.8, 169.4, 168.9, 165.4, 165.4, 165.3, 165.3, 135.9, 133.3, 133.2, 133.1, 133.1, 133.0, 132.7, 129.0, 129.0, 129.0, 129.0, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 127.6, 127.6, 127.6, 127.6, 110.4, 110.1, 109.6, 109.5, 87.0, 86.3, 86.3, 80.7, 79.8, 66.5, 66.5, 66.3, 52.4, 52.4, 40.5, 40.5, 40.3, 39.7, 37.2, 35.1, 32.7, 32.6, 29.7, 29.4, 28.9, 28.9, 28.7, 28.5, 28.1, 27.8, 27.7, 27.6, 27.2, 27.0, 27.0, 26.6, 26.5, 26.5, 16.0, 15.2, 15.2, 15.1.

HRMS m/z calcd. for $C_{28}H_{34}NO_8$ $[M+H]^+$ 512.2285, found 512, 2295.

IR (cm^{-1}) 3292 (br), 2935, 1731, 1680, 1467, 1382, 1240, 1207, 1173, 1102, 699.



Prepared according to ***Procedure C*** (with 2.0 equiv of ethyl phosphate). Light yellow oil (~4.4:1 mixture of diastereomers, 30.8 mg, 41% yield; 30.1 mg starting material was recovered). R_f = 0.41 (1:4 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 0.77H), 8.71 (s, 0.17H), 7.88 – 7.80 (m, 2H), 7.65 – 7.58 (m, 1H), 7.54 – 7.47 (m, 3H), 7.40 – 7.20 (m, 15H), 4.90 (d, *J* = 10.9 Hz, 0.79H), 4.74 – 4.43 (m, 5.2H), 4.25 – 4.20 (m, 0.17H), 4.15 – 4.02 (m, 4H), 3.93 – 3.85 (m,

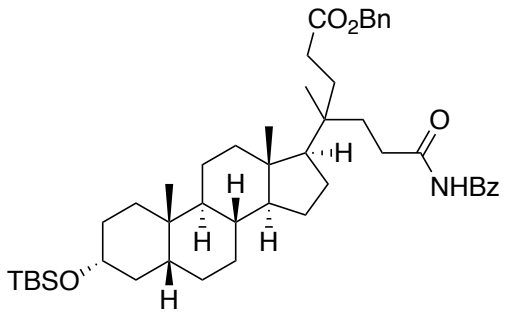
0.79H), 3.77 – 3.40 (m, 4H), 3.11 – 2.88 (m, 2H), 2.75 – 2.65 (m, 0.18H), 2.23 – 2.12 (m, 0.82H), 2.09 – 1.98 (m, 1.80H), 1.93 – 1.62 (m, 5H), 1.35 – 1.29 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 165.4, 138.5, 138.4, 138.4, 133.1, 132.9, 129.0, 128.9, 128.4, 128.4, 128.4, 128.3, 128.3, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 78.9, 78.3, 75.2, 75.1, 75.0, 73.8, 73.4, 73.3, 72.8, 72.5, 72.4, 72.2, 71.8, 71.2, 70.1, 69.9, 67.5, 61.7, 61.7, 61.6, 61.5, 37.7, 33.0, 32.2, 32.1, 31.1, 29.7, 28.0, 25.6, 25.6, 19.6, 18.4, 16.5, 16.5.

^{31}P NMR (202 MHz, $CDCl_3$) δ 33.5, 32.9.

HRMS m/z calcd. for $C_{43}H_{53}NO_9P$ $[M+H]^+$ 758.3458, found 758, 3454.

IR (cm^{-1}) 3249 (br), 2927, 1686, 1453, 1246, 1097, 1058, 1027, 964, 738, 699.



Prepared according to ***Procedure C*** (with 1.5 equiv of benzyl acrylate). White solid (~3:4 mixture of diastereomers, 42.1 mg, 56% yield; 19.9 mg starting material was recovered). R_f = 0.28 (4:1 hex:EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (brs, 0.48H), 8.61 (brs, 0.36H), 7.90 – 7.84 (m, 2H), 7.65 – 7.60 (m, 1H), 7.56 – 7.49 (m, 2H), 7.44 – 7.30 (m, 5H), 5.16 – 5.11 (m, 2H), 3.64 – 3.53 (m, 1H), 3.02 – 2.87 (m, 2H), 2.49 – 2.29 (m, 2H), 2.06 – 1.99 (m, 1H), 1.93 – 1.03 (m, 26H), 1.02 – 0.98 (m, 3H), 0.94 – 0.89 (m, 12H), 0.79 (s, 3H), 0.10 – 0.06 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 174.2, 165.3, 136.1, 136.1, 133.2, 133.2, 132.9, 132.9, 129.0, 129.0, 128.6, 128.5, 128.1, 128.1, 128.1, 127.6, 127.6, 127.6, 72.7, 72.7, 66.2, 66.1, 56.7, 56.6, 43.9, 43.9, 42.2, 40.9, 40.8, 40.2, 40.2, 38.4, 36.9, 35.6, 35.4, 34.6, 33.5, 33.2, 32.8, 32.6, 32.3, 32.2, 31.0, 29.3, 29.0, 27.3, 26.3, 26.0, 26.0, 23.7, 23.4, 22.9, 22.7, 22.6, 20.7, 18.3, 15.0, -4.6, -4.6.

HRMS m/z calcd. for $C_{47}H_{68}NO_5Si$ $[M-H]^-$ 754.4867, found 754.4855.

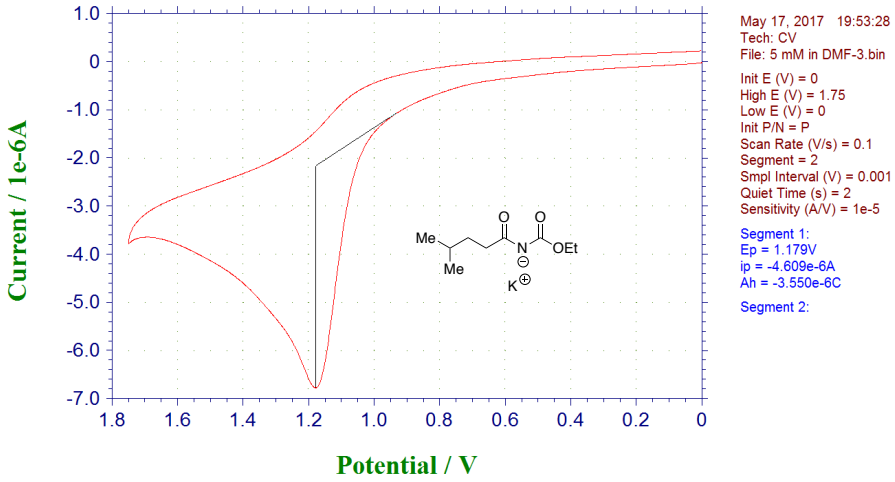
IR (cm^{-1}) 3278 (br), 2927, 2856, 1735, 1712, 1680, 1469, 1249, 1160, 1094, 1078, 835, 774, 707.

Mechanistic Investigations

1. Cyclic Voltammetry (CV) Study: a glassy electrode, a Pt mesh counter electrode and an Ag/AgCl reference electrode were used and measurement was taken in a 5 mM solution of a specific compound in DMF containing 0.1 M NBu_4PF_6.

(a) CV study of amide **1a**: no oxidation was observed even at voltage >2V vs Ag/AgCl, suggesting that neutral **1a** cannot be oxidized by the excited Ir^{III} complex (1.21V vs SCE in MeCN).

(b) CV study of **1a** potassium salt: **1a** potassium salt was prepared by treatment of **1a** with 1.0 equiv of KO^tBu in DMF (0.1 M). As shown below, E_p and $E_{1/2}$ of **1a** potassium salt were determined to be 1.18 V and 1.09 V vs Ag/AgCl (i.e. 1.13 V and 1.04 V vs SCE in DMF), which suggest that single electron oxidation of **1a** potassium salt by the excited Ir^{III} complex is feasible (1.21 V vs SCE in MeCN).



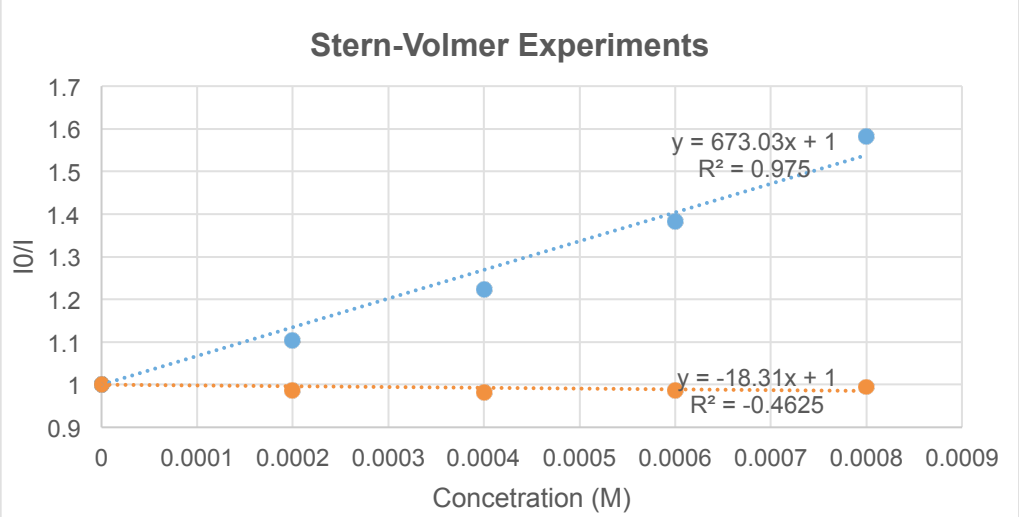
2. Stern-Volmer experiments were operated with different solutions containing 0.01 mM $Ir[(dF\text{-}CF_3)ppy]_2(dtbbpy)PF_6$ and x mM (x = 0. 0.2, 0.4, 0.6, 0.8) **1a** or potassium salt of **1a**, under irradiation at 380 nm. The luminescence was measured at 470 nm. Data from three different runs were collected.

(a) Stern-Volmer experiments of **1a**:

c (M)		0	0.0002	0.0004	0.0006	0.0008
I_0/I	Run 1	1	0.98628	0.97410	0.98015	0.99338
	Run 2	1	0.97995	0.99311	1.00396	1.00565
	Run 3	1	0.99323	0.97491	0.97853	0.98555
	Average	1	0.98641	0.98075	0.98757	0.99488

(b) Stern-Volmer experiments of potassium salt of **1a**:

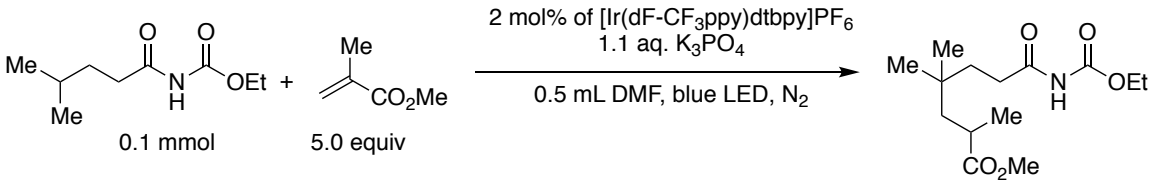
c (mM)		0	0.0002	0.0004	0.0006	0.0008
I_0/I	Run 1	1	1.10945	1.22282	1.38817	1.59465
	Run 2	1	1.10729	1.23392	1.38874	1.58631
	Run 3	1	1.09738	1.21584	1.37353	1.56921
	Average	1	1.10469	1.22443	1.38376	1.58334



•**1a** and $Ir[(dF\text{-}CF_3)ppy]_2(dtbbpy)PF_6$;

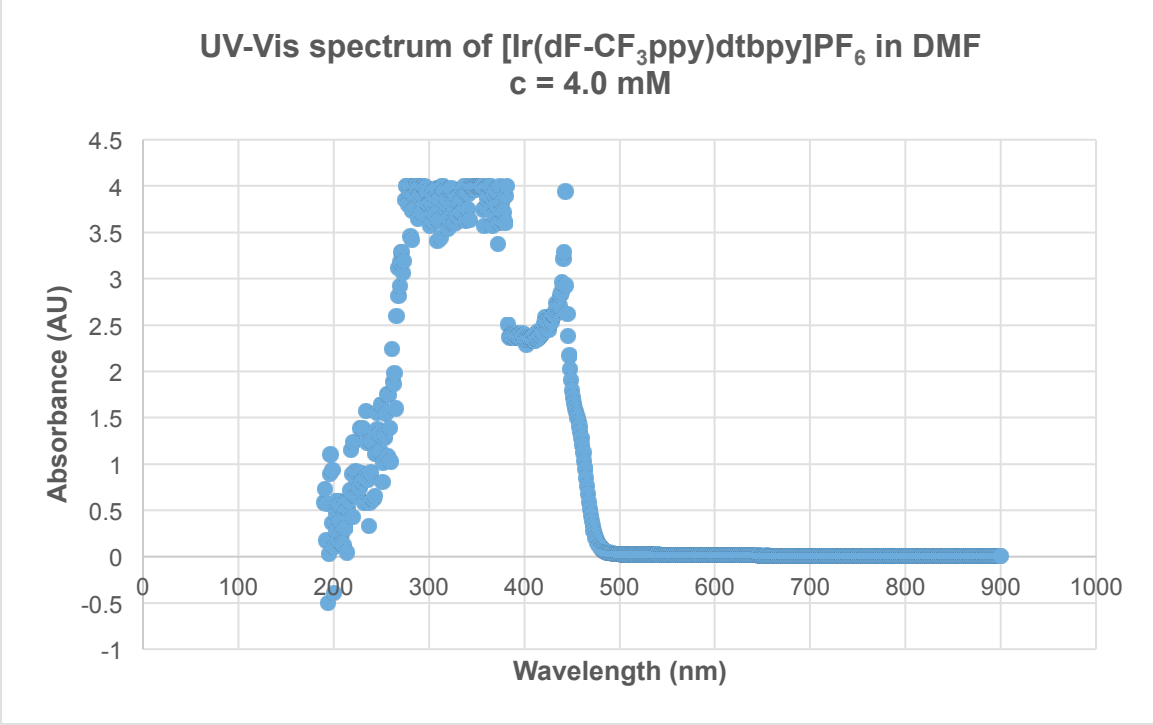
•Potassium salt of **1a** and $Ir[(dF\text{-}CF_3)ppy]_2(dtbbpy)PF_6$

3. Determination of quantum yield (Φ).



A magnetic stir bar, the amide substrate (0.1 mmol, 1.0 equiv.), methyl methacrylate (5.0 equiv), sat. aq. K_3PO_4 (1.1 equiv) and $[Ir\{dF\text{-}(CF_3)ppy\}_2(dtbbpy)]PF_6$ (2 mol %) were charged into an oven-dried NMR tube, followed by 0.5 mL of anhydrous DMF. The mixture was then bubbled with nitrogen gas for 15 mins before being tightly capped. The mixture was stirred and irradiated (λ = 419 nm) for 4h (14400 s). The yield was determined to be 4.7% by 1H NMR, using the trimethoxylbenzene as the internal standard. The quantum yield can be calculated by using the equation as shown below:

$$\Phi = \frac{\text{mol product}}{\text{photon flux} \cdot \text{f} \cdot \text{t}}$$



The absorbance of Ir(dF-CF_3ppy)dtbpy]PF_6 at 419 nm was determined to be 2.431427 according to its UV-Vis spectrum at the reaction concentration (4 mM). The fraction of light absorbed at 419 nm was calculated using the equation as shown below:

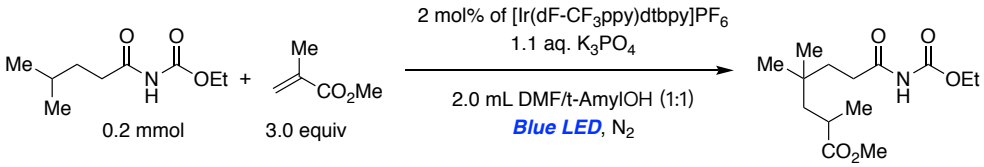
$$f = 1 - 10^{-A} = 1 - 10^{-2.431427} = 0.996297$$

The photon flux of the spectrophotometer (Newport TLS300XU) at 300 W and 419 nm was determined to be 5.2 x 10^{-9} einstein s^{-1} following the ferrioxalate actinometry procedure[16] in a NMR tube.

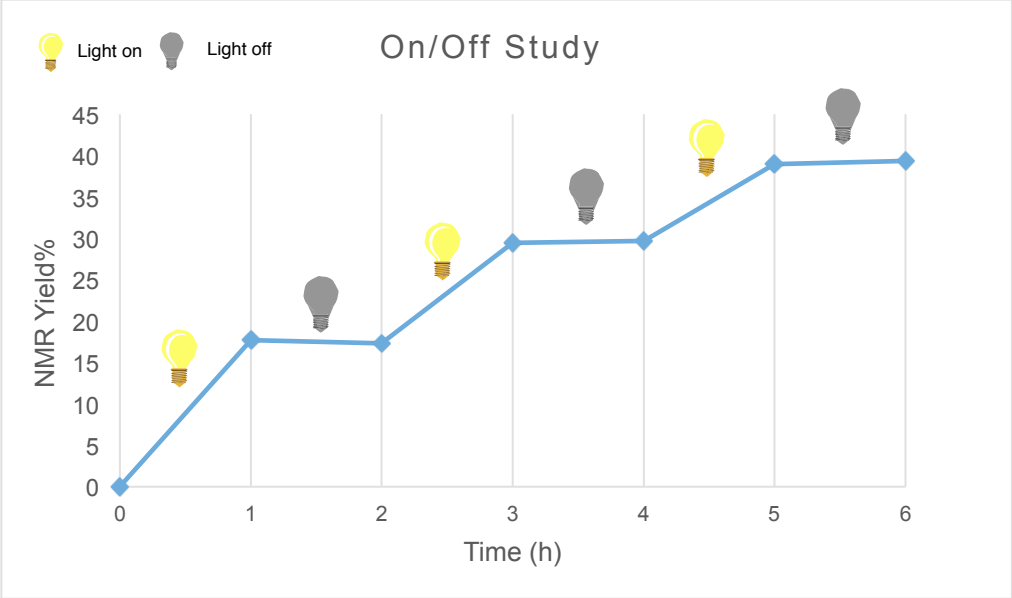
Thus, the quantum yield was:

$$\Phi = \frac{4.7\% \text{ x } 0.1/1000}{5.2 \text{ x } 10^{-9} \text{ x } 0.996297 \text{ x } 14400} = 6.3\%$$

4. On/off study.

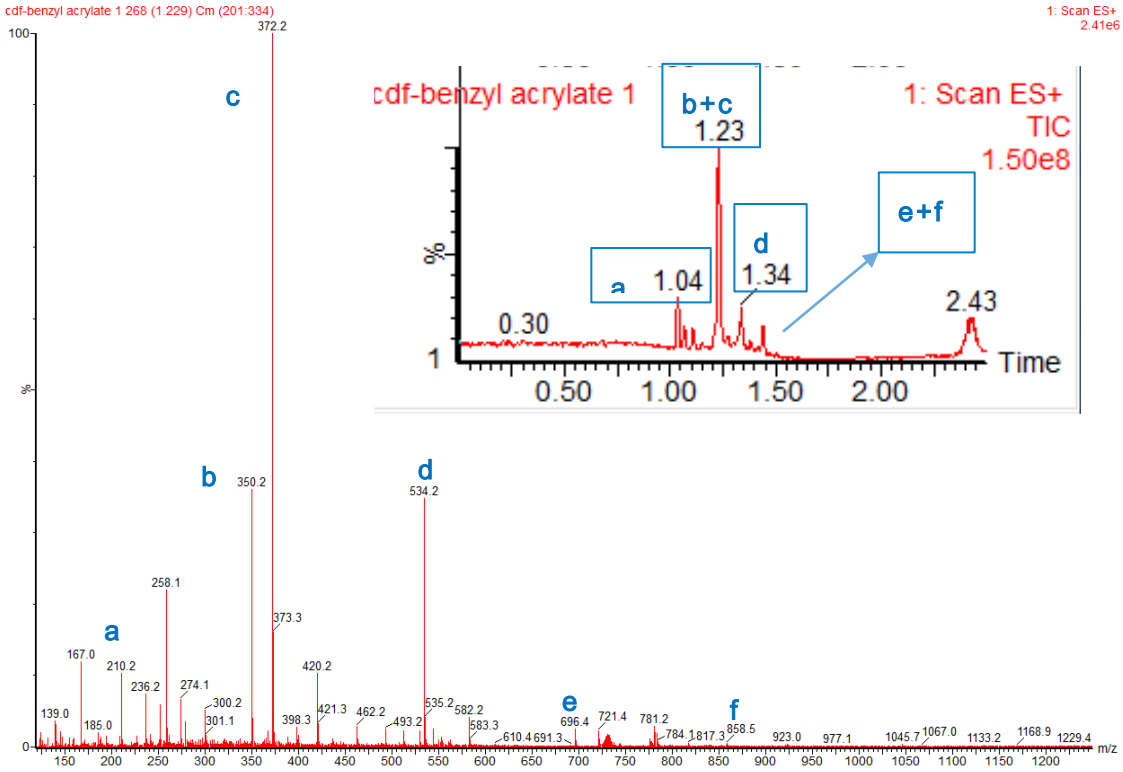


The reaction was set up on a 0.20 mmol scale according to the **General Procedure C**. The reaction mixture was irradiated for an hour. An aliquot (300 μL) was taken from the reaction mixture, filtered through a 1 cm-silica plug and washed with Et_2O (3.0 mL x 3). The filtrate was concentrated in vacuo and was redissolved in 0.50 mL of $CDCl_3$ containing trimethoxylbenzene (4.2 mg) as the internal standard. The yield of product was determined by 1H NMR. The reaction mixture was then degassed (by bubbling N_2 for 10 mins), tightly capped, wrapped by aluminum foil and re-subject to the Blue LED. The yields later on were determined in the same way after a 1 h light on or off.



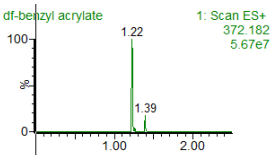
5. By-product analysis by UPLC.

5.1 Reaction of **1a** (0.10 mmol) and benzyl acrylate (2.0 equiv) under optimal conditions.

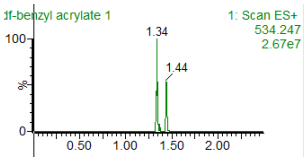


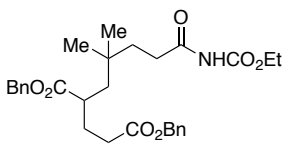
(1) **a** is assigned to starting material $[\mathbf{1a}+Na]^+$ (210.2), t_R = 1.04 min.

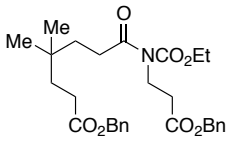
(2) **b** is assigned to product **3ae** (t_R = 1.22 min) and Michael product (t_R = 1.39 min) ($[M+H]^+$, 350.2); **c** is assigned to product **3ae** (t_R = 1.22 min) and Michael product (t_R = 1.39 min) ($[M+Na]^+$, 372.2).



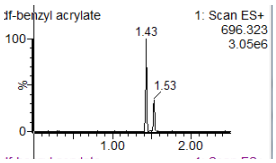
(3) **d** is assigned to two products ($[M+Na]^+$, 534.2) as shown below:

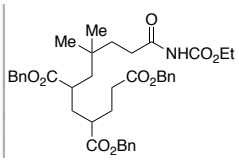


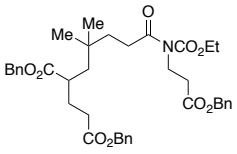




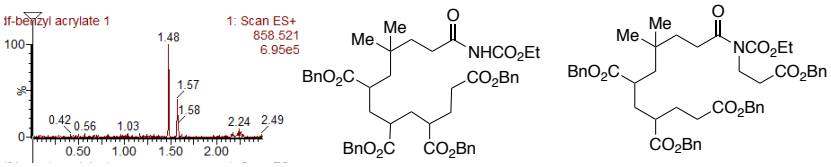
(4) **e** is assigned to two products ($[M+Na]^+$, 696.4) as shown below:



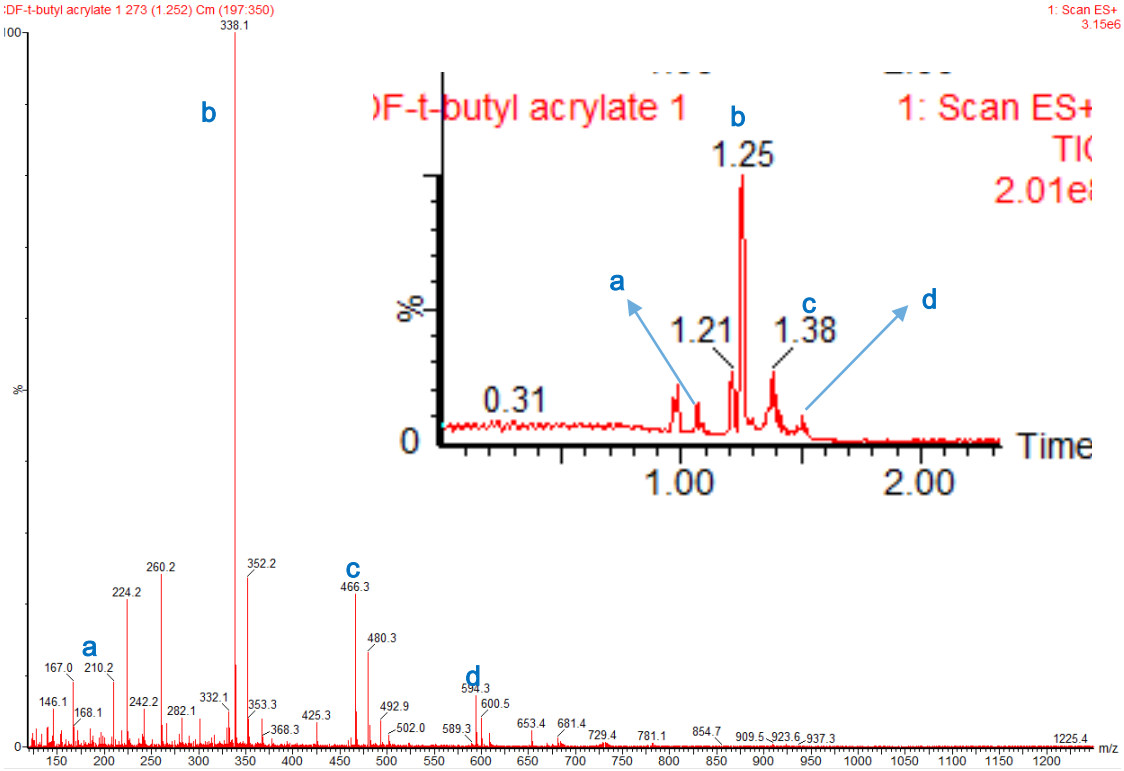




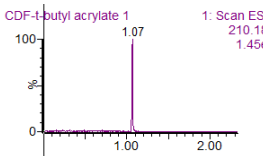
(5) **f** is assigned to two products ([M+Na]$^+$, 858.5) as shown below:



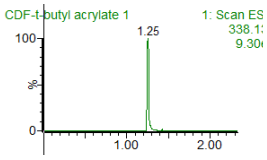
5.2 Reaction of **1a** (0.10 mmol) and *tert*-butyl acrylate (3.0 equiv) under optimal conditions.



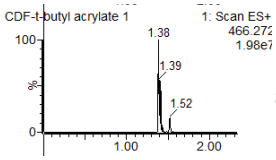
(1) **a** is assigned to starting material [**1a**+Na]$^+$ (210.2), t_R = 1.04 min.

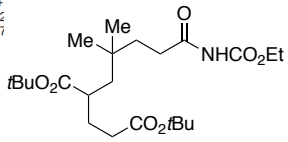


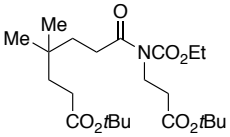
(2) **b** is assigned to product **3af** ([M+Na]$^+$, 338.1, t_R = 1.25 min) and trace Michael product.



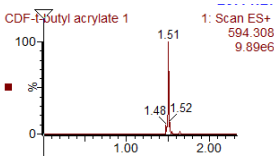
(3) **c** is assigned to two products ($[M+Na]^+$, 466.3, t_R = 1.39 min, 1.52 min) as shown below:

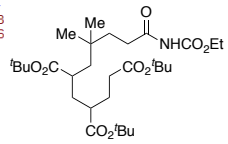


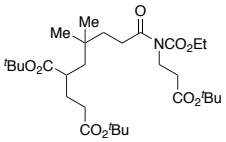




(4) **d** is assigned to two products ($[M+Na]^+$, 466.3, t_R = 1.39 min, 1.52 min) as shown below:







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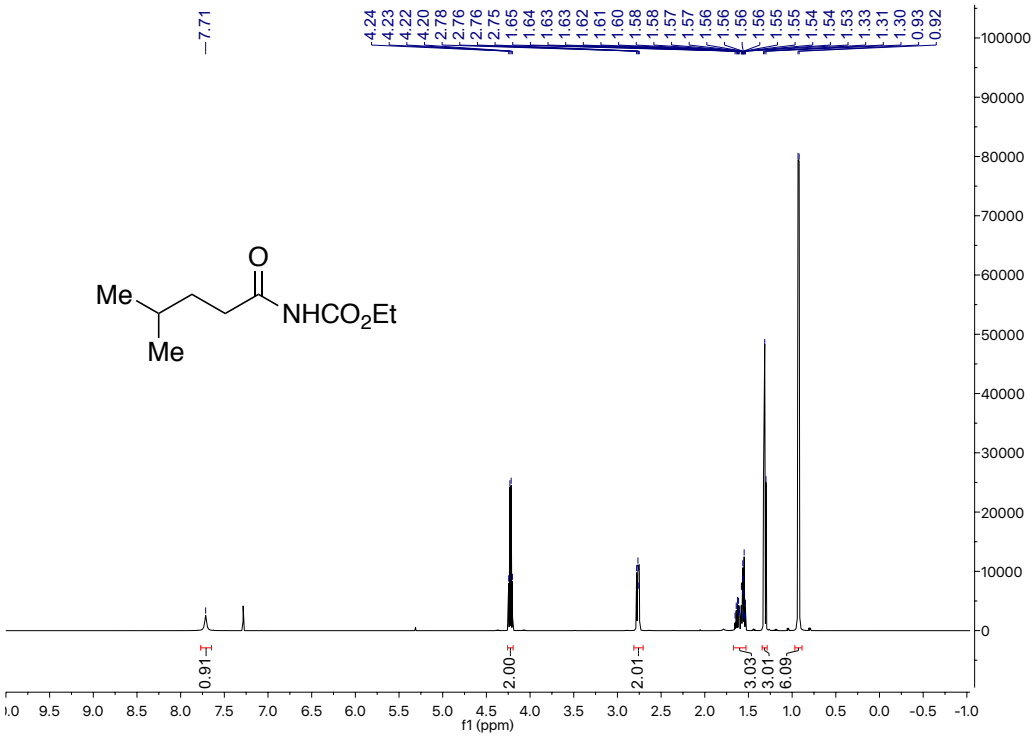
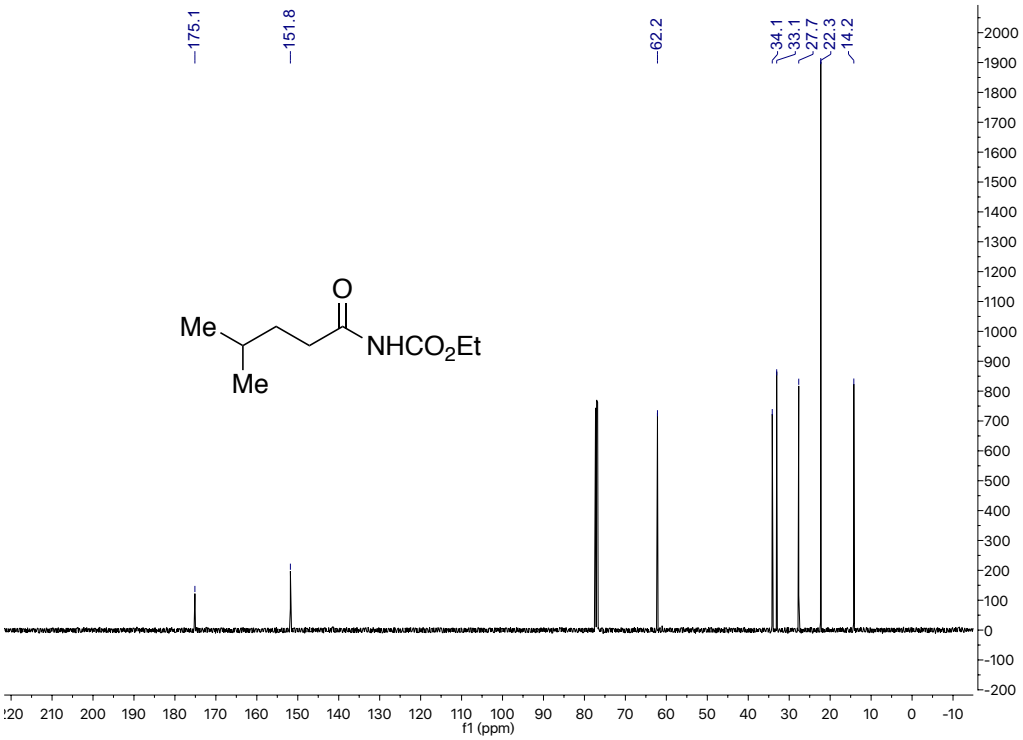
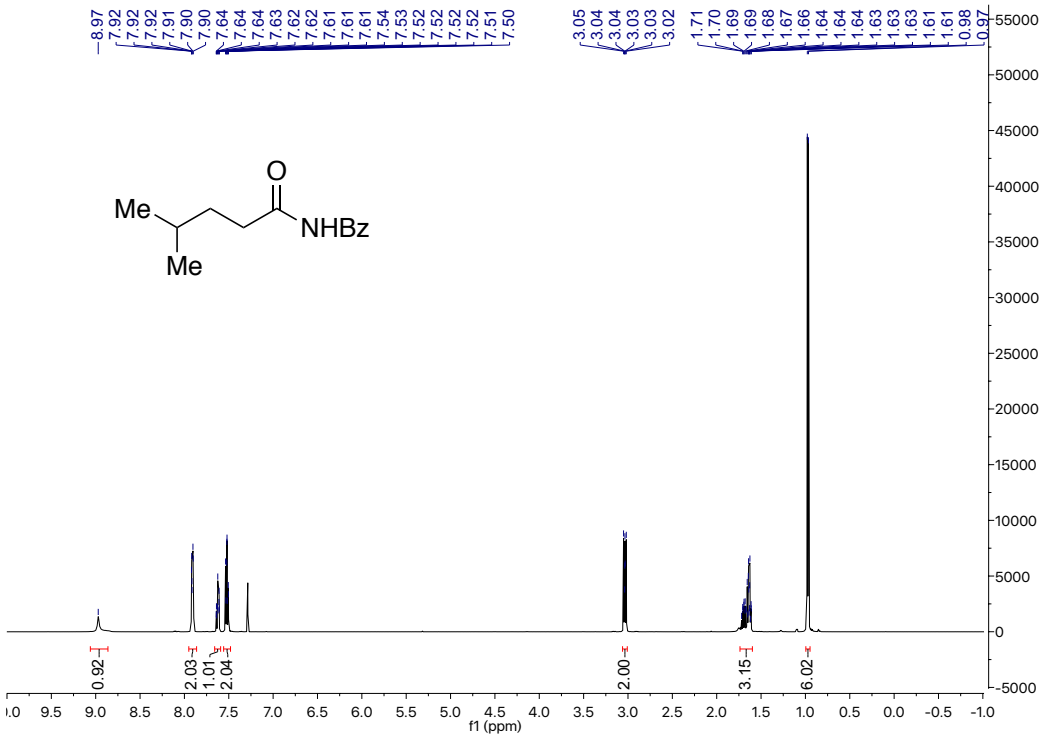
NMR Spectra


7.71
4.24
4.23
4.22
4.20
2.78
2.76
2.76
2.75
1.65
1.64
1.63
1.63
1.62
1.61
1.60
1.58
1.58
1.57
1.57
1.56
1.56
1.56
1.56
1.55
1.55
1.54
1.54
1.53
1.33
1.31
1.30
0.93
0.92
Me
O
NHCO2Et
Me
0.91
2.00
2.01
3.03
3.01
6.09
f1 (ppm)


175.1
151.8
62.2
34.1
33.1
27.7
22.3
14.2
Me
O
NHCO2Et
Me
f1 (ppm)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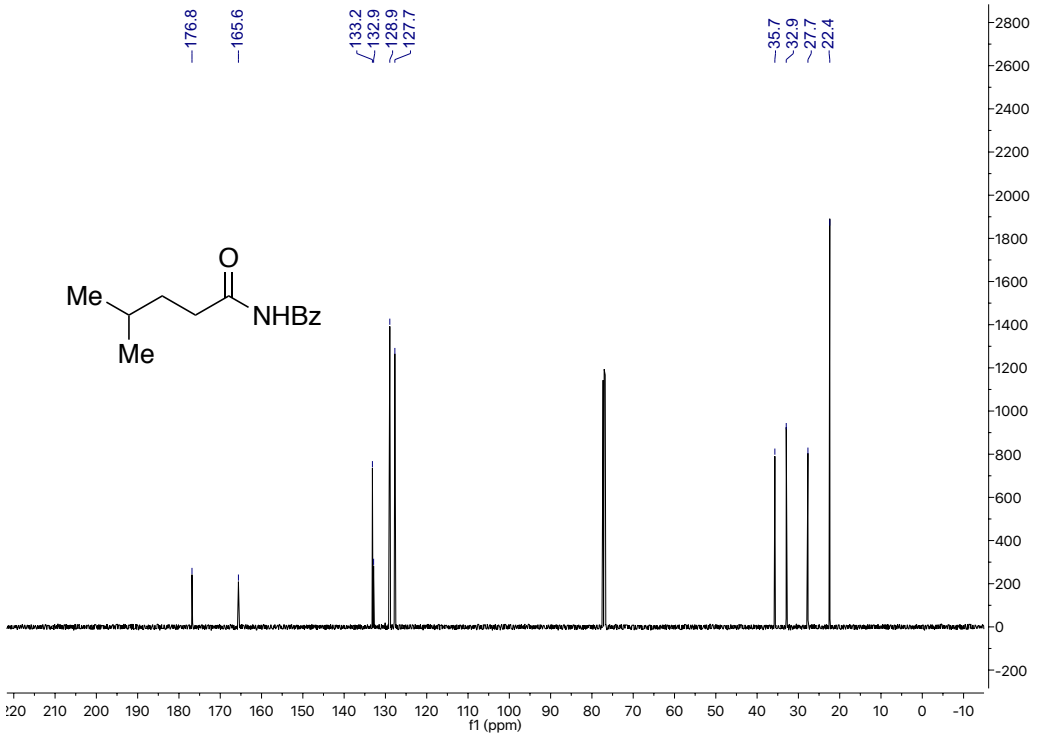
7.92
7.92
7.92
7.91
7.90
7.90
7.64
7.64
7.64
7.63
7.62
7.62
7.61
7.61
7.61
7.54
7.53
7.52
7.52
7.52
7.52
7.51
7.50
3.05
3.04
3.04
3.03
3.03
3.02
1.71
1.70
1.69
1.69
1.68
1.67
1.66
1.64
1.64
1.64
1.63
1.63
1.63
1.61
1.61
0.98
0.97
O
Me
NHBz
Me
0.92
2.03
1.01
2.04
2.00
3.15
6.02
f1 (ppm)


176.8
165.6
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132.9
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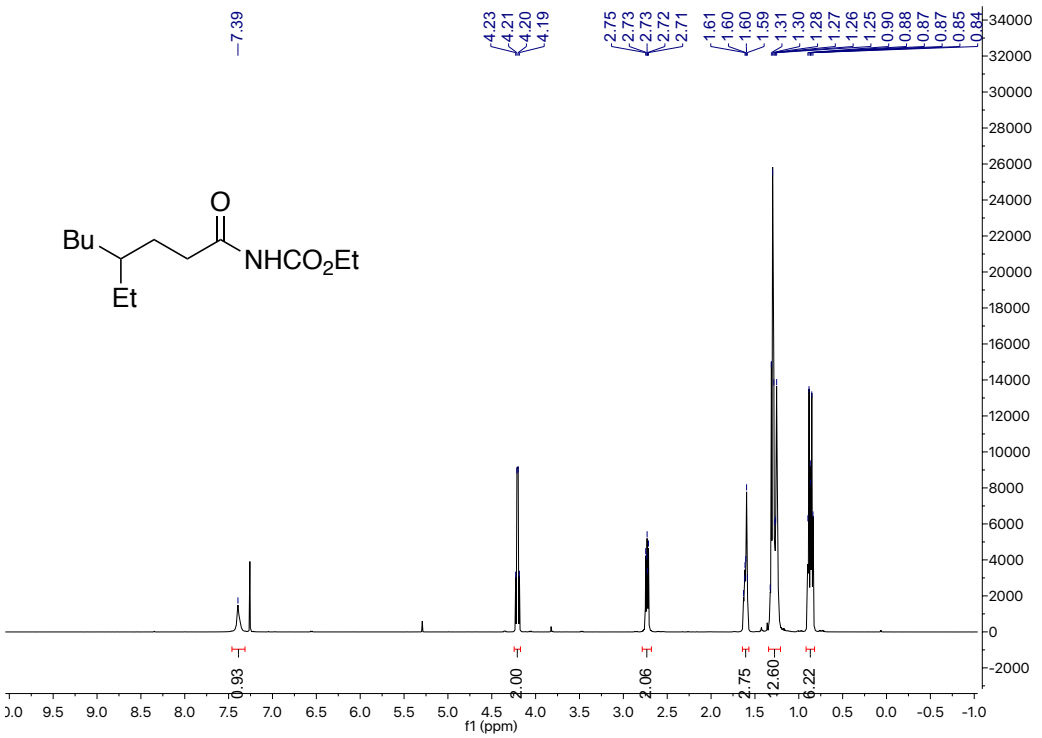
127.7
35.7
32.9
27.7
22.4
O
Me
NHBz
Me
f1 (ppm)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4.19
2.75
2.73
2.73
2.72
2.71
1.61
1.60
1.60
1.59
1.31
1.30
1.28
1.27
1.26
1.25
0.90
0.88
0.87
0.87
0.85
0.84
Bu
Et
O
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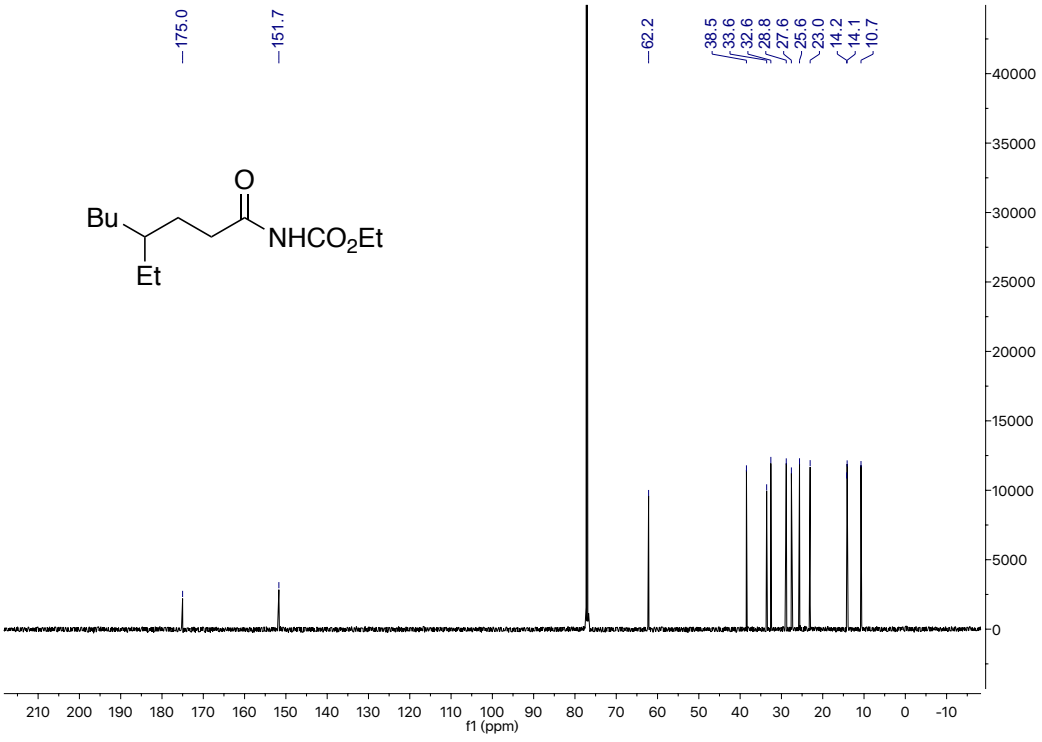
2.00
2.06
2.75
12.60
6.22
f1 (ppm)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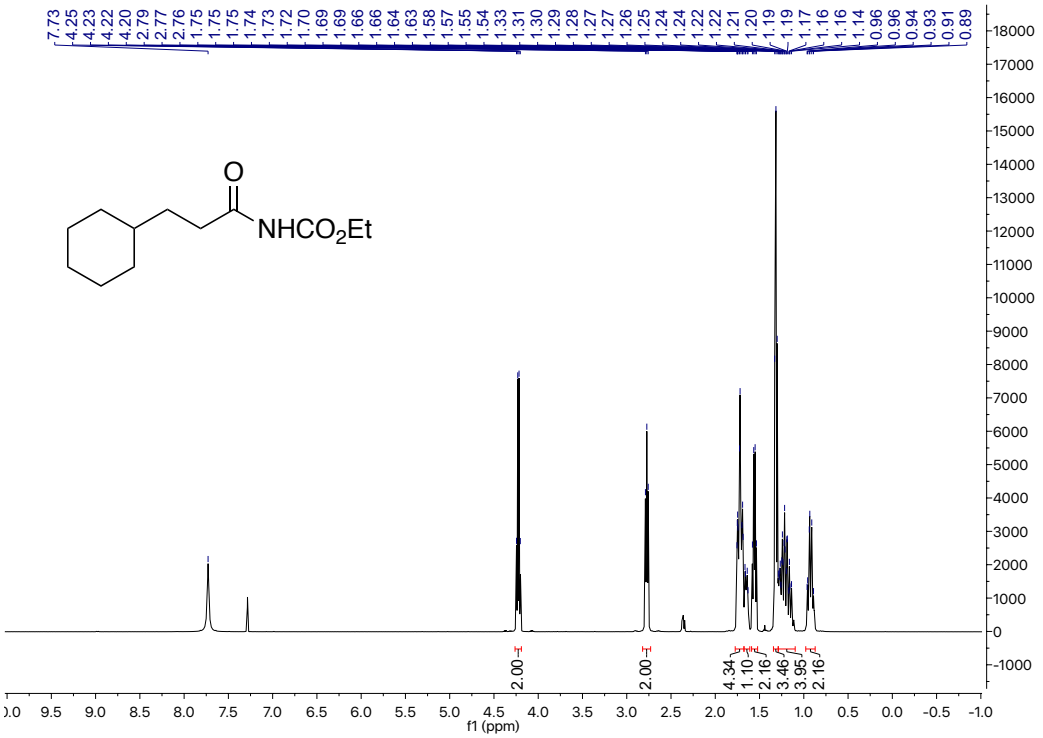
151.7
62.2
38.5
33.6
32.6
28.8
27.6
25.6
23.0
14.2
14.1
10.7
Bu
Et
O
NHCO2Et
f1 (ppm)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1.75
1.75
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1.63
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1.55
1.54
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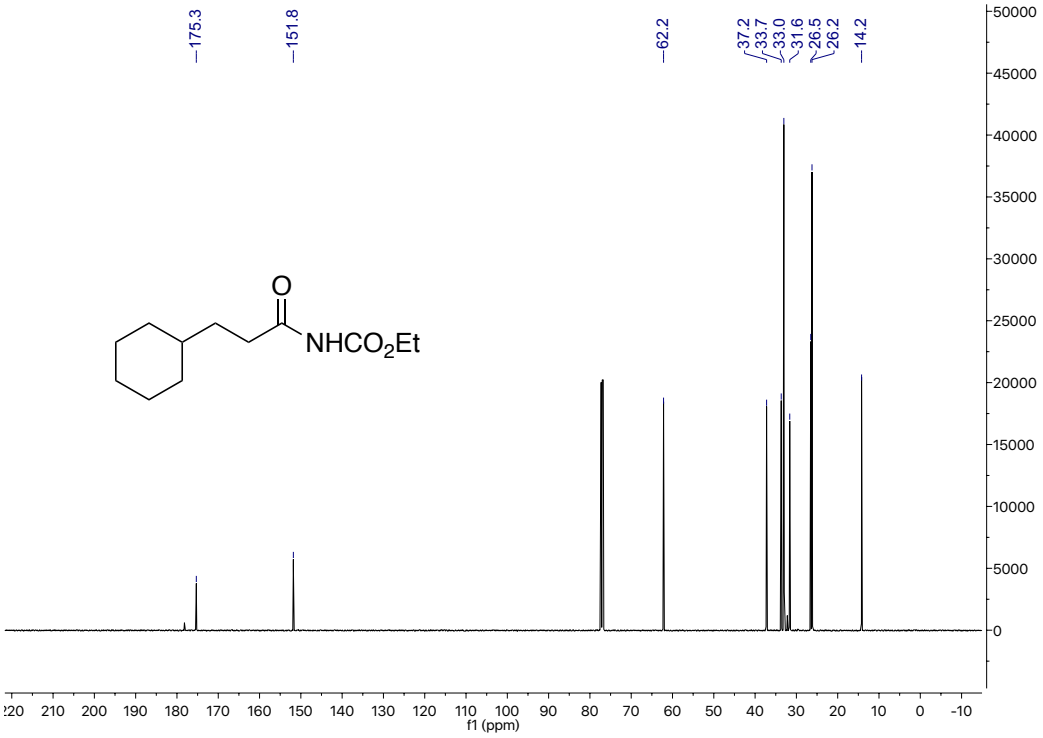
1.27
1.26
1.25
1.24
1.24
1.22
1.22
1.21
1.20
1.19
1.19
1.17
1.16
1.16
1.14
0.96
0.96
0.94
0.93
0.91
0.89
O
NHCO2Et
2.00
2.00
4.34
1.10
2.16
3.46
3.95
2.16
f1 (ppm)


175.3
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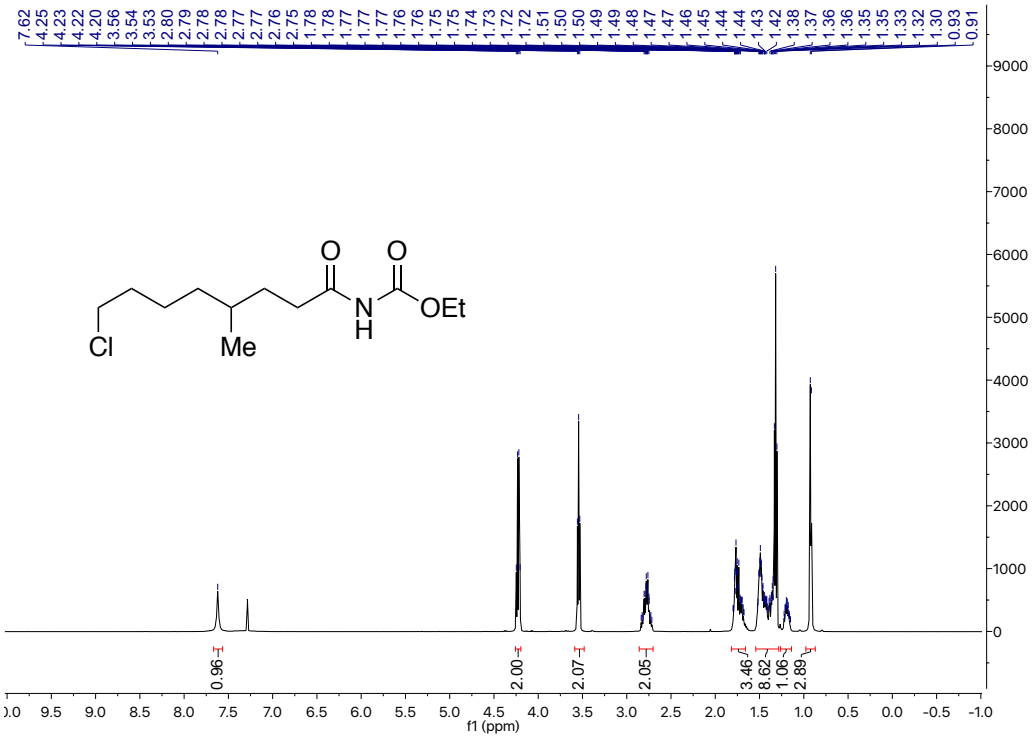
62.2
37.2
33.7
33.0
31.6
26.5
26.2
14.2
O
NHCO2Et
f1 (ppm)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4.25
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4.22
4.20
3.56
3.54
3.53
2.80
2.79
2.78
2.78
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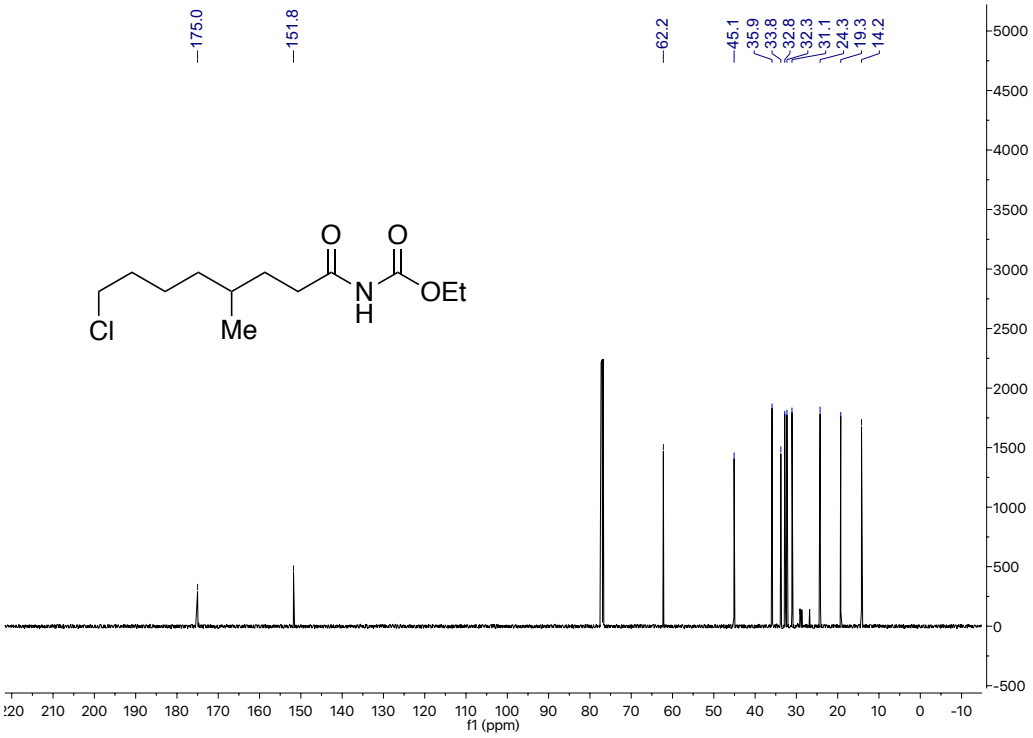
2.77
2.76
2.75
1.78
1.78
1.77
1.77
1.77
1.76
1.76
1.75
1.75
1.74
1.73
1.72
1.72
1.51
1.50
1.50
1.49
1.49
1.48
1.47
1.47
1.46
1.45
1.44
1.44
1.43
1.42
1.38
1.37
1.36
1.36
1.35
1.35
1.33
1.32
1.30
0.93
0.91
O
O
N
H
OEt
Cl
Me
0.96
2.00
2.07
2.05
3.46
8.62
1.06
2.89
f1 (ppm)


175.0
151.8
62.2
45.1
35.9
33.8
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31.1
24.3
19.3
14.2
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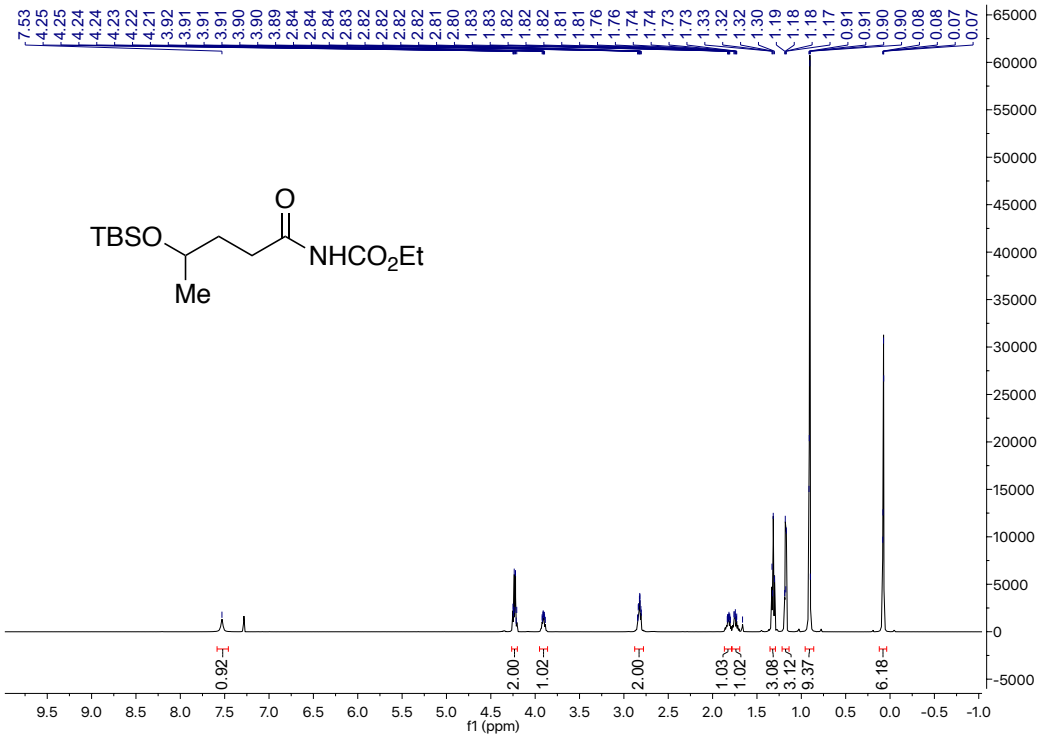
O
N
H
OEt
Cl
Me
f1 (ppm)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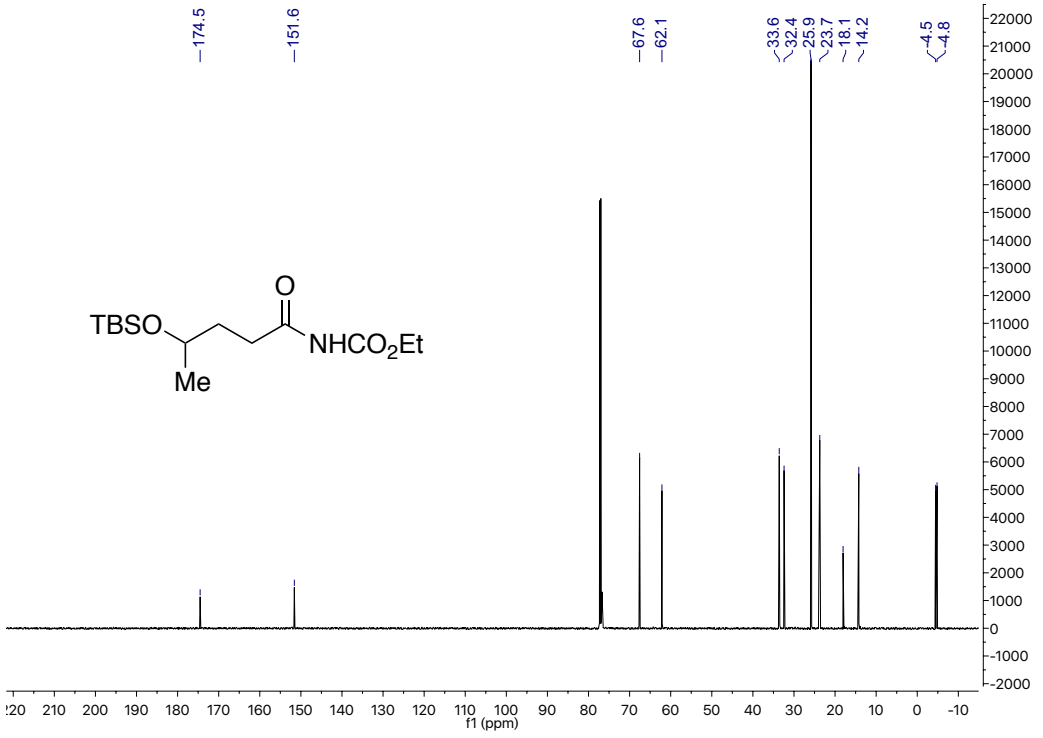
f1 (ppm)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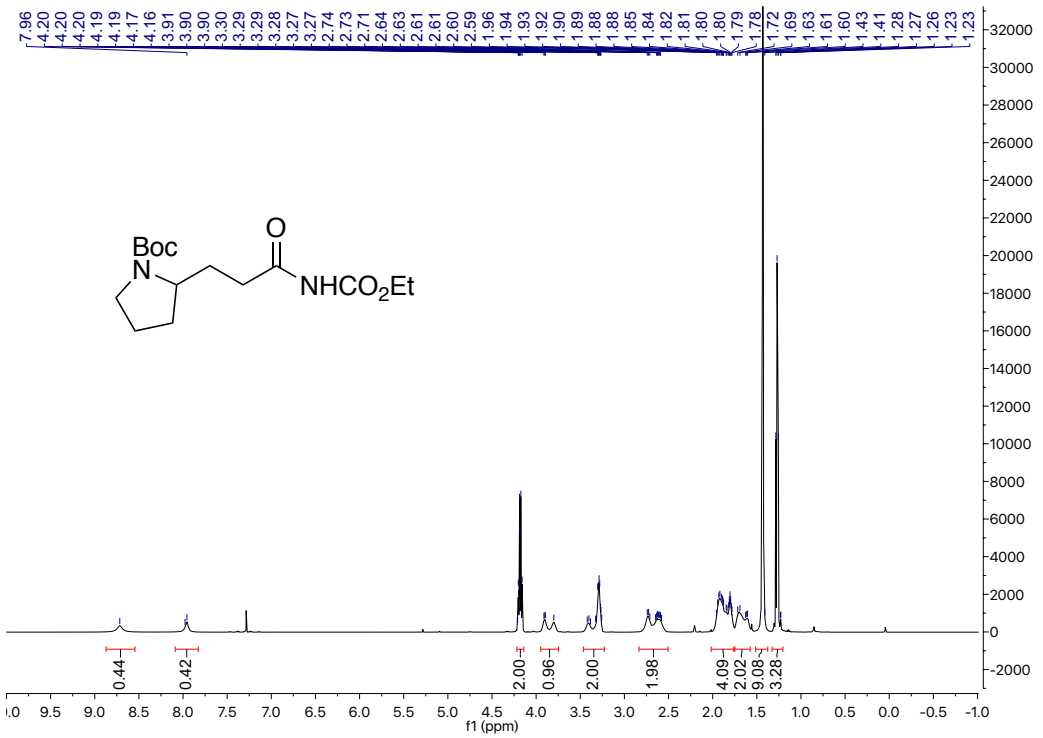
O
NHCO2Et
Me
f1 (ppm)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O
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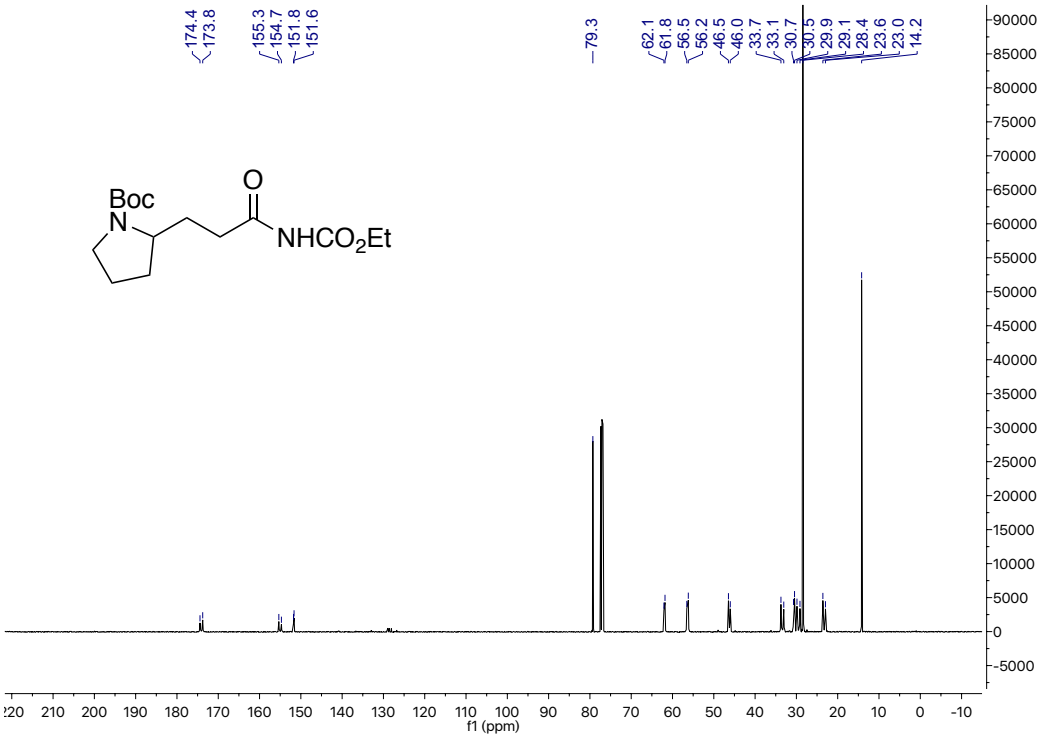
f1 (ppm)


Boc
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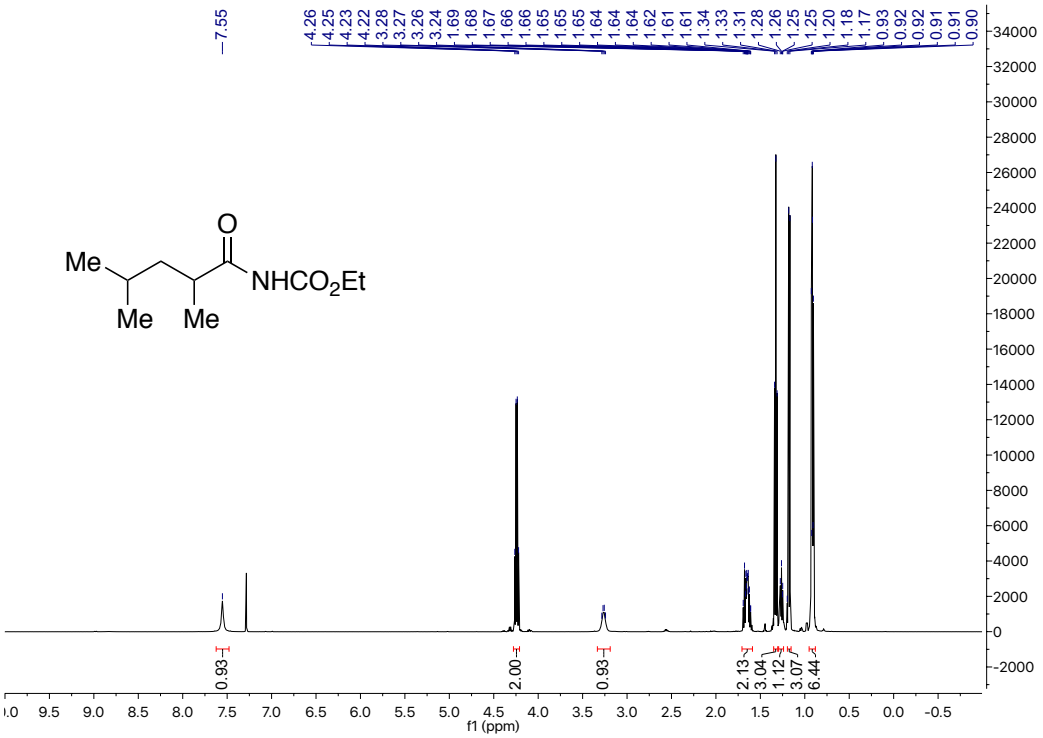
NHCO2Et
f1 (ppm)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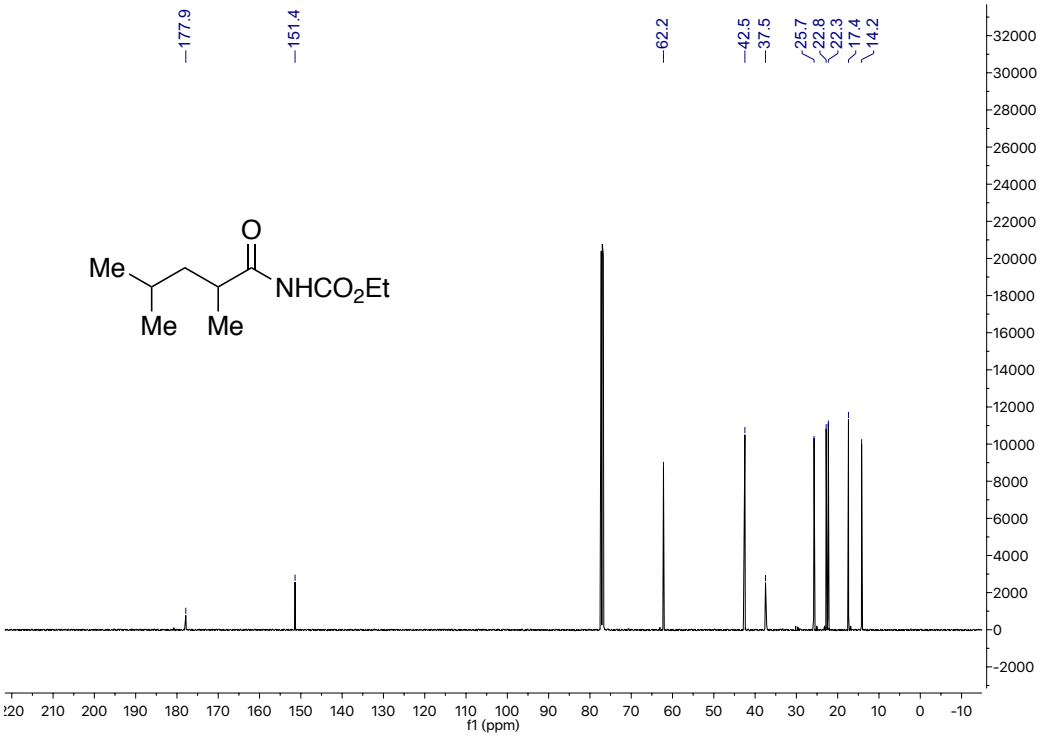
3.27
3.26
3.24
1.69
1.68
1.67
1.66
1.66
1.65
1.65
1.65
1.64
1.64
1.64
1.62
1.61
1.61
1.34
1.33
1.31
1.28
1.26
1.25
1.25
1.20
1.18
1.17
0.93
0.92
0.92
0.91
0.91
0.90
O
Me
NHCO2Et
Me
Me
0.93
2.00
0.93
2.13
3.04
1.12
3.07
6.44
f1 (ppm)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151.4
62.2
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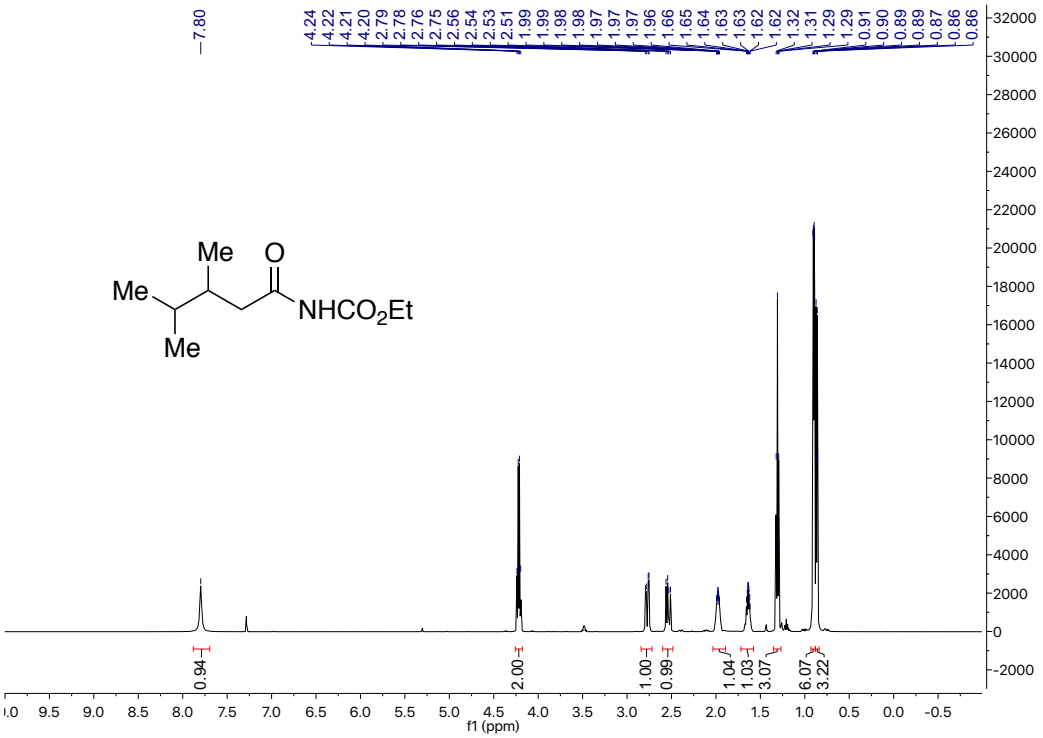
25.7
22.8
22.3
17.4
14.2
O
Me
NHCO2Et
Me
Me
f1 (ppm)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4.22
4.21
4.20
2.79
2.78
2.76
2.75
2.56
2.54
2.53
2.51
1.99
1.99
1.98
1.98
1.97
1.97
1.97
1.96
1.66
1.65
1.64
1.63
1.63
1.62
1.62
1.32
1.31
1.29
1.29
0.91
0.90
0.89
0.89
0.87
0.86
0.86
Me
O
Me
NHCO2Et
Me
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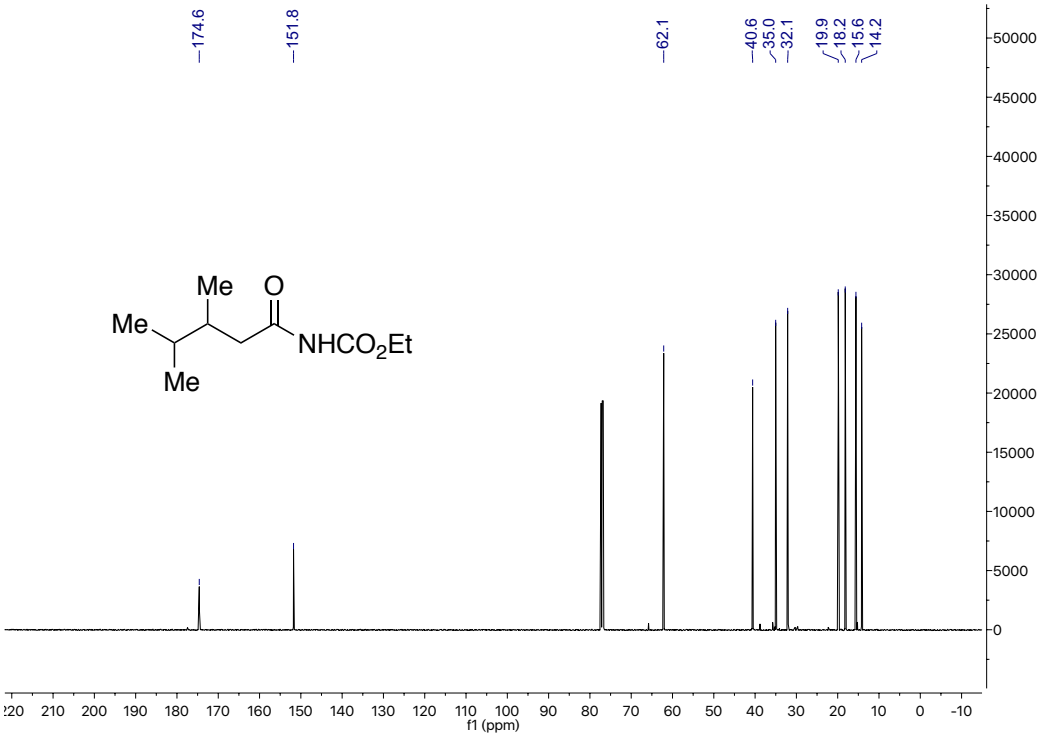
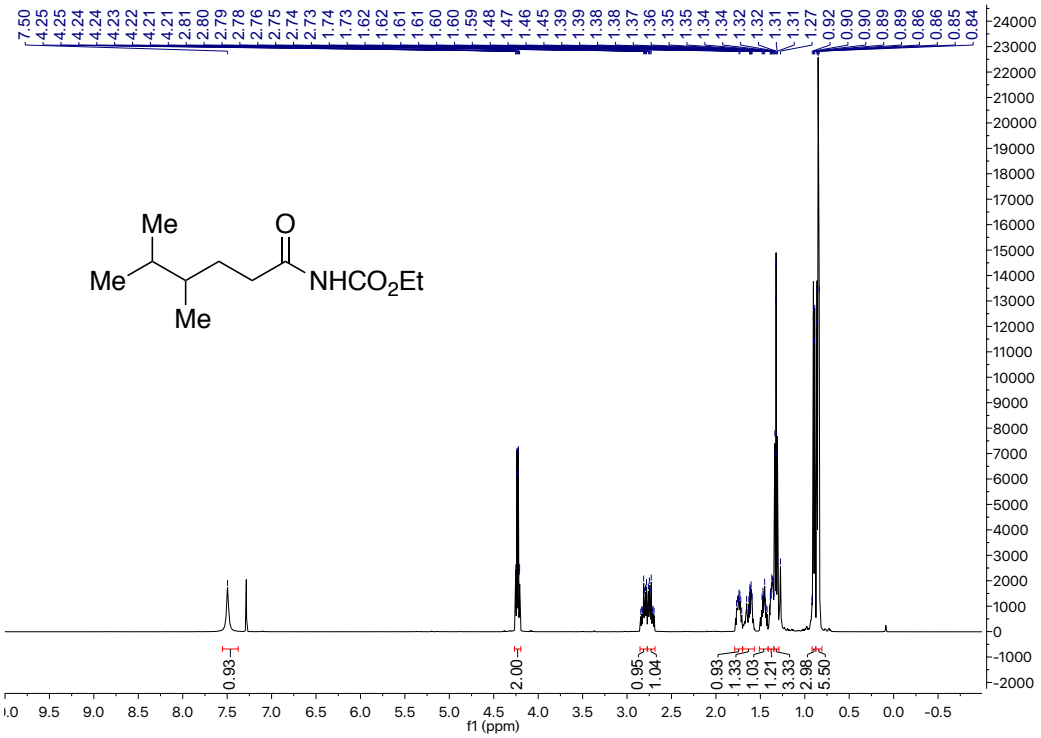
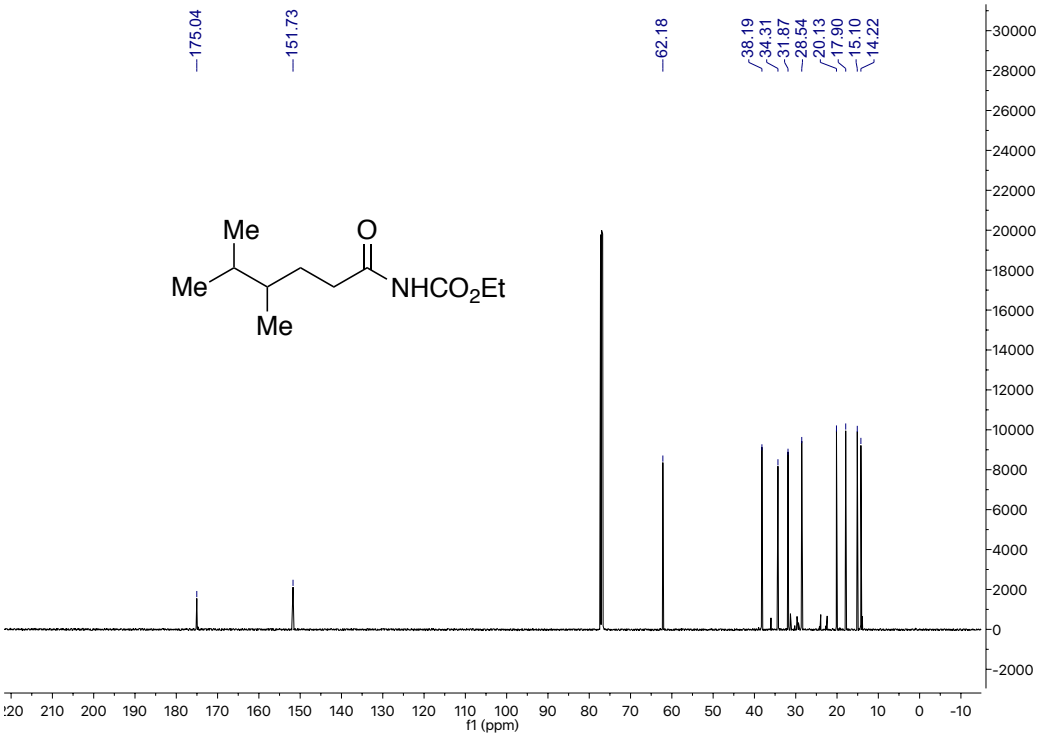
2.00
1.00
0.99
1.04
1.03
3.07
6.07
3.22
f1 (ppm)


174.6
151.8
62.1
40.6
35.0
32.1
19.9
18.2
15.6
14.2
Me
O
Me
NHCO2Et
Me
f1 (ppm)


Me
O
Me
NHCO2Et
Me
f1 (ppm)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151.73
62.18
38.19
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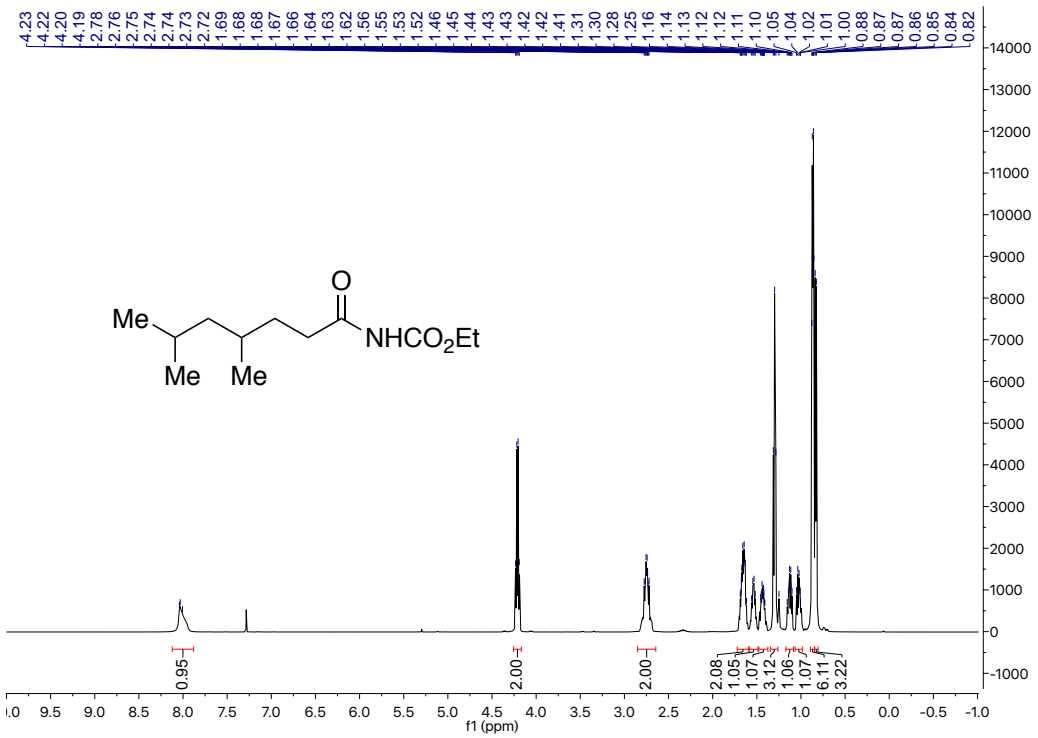
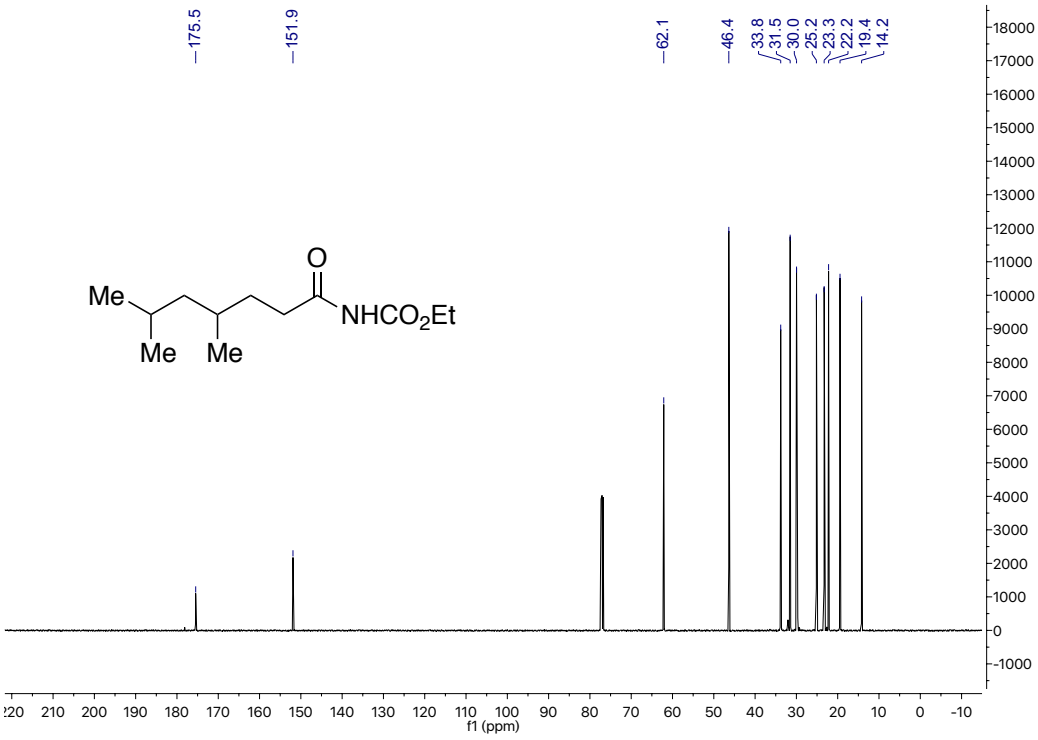
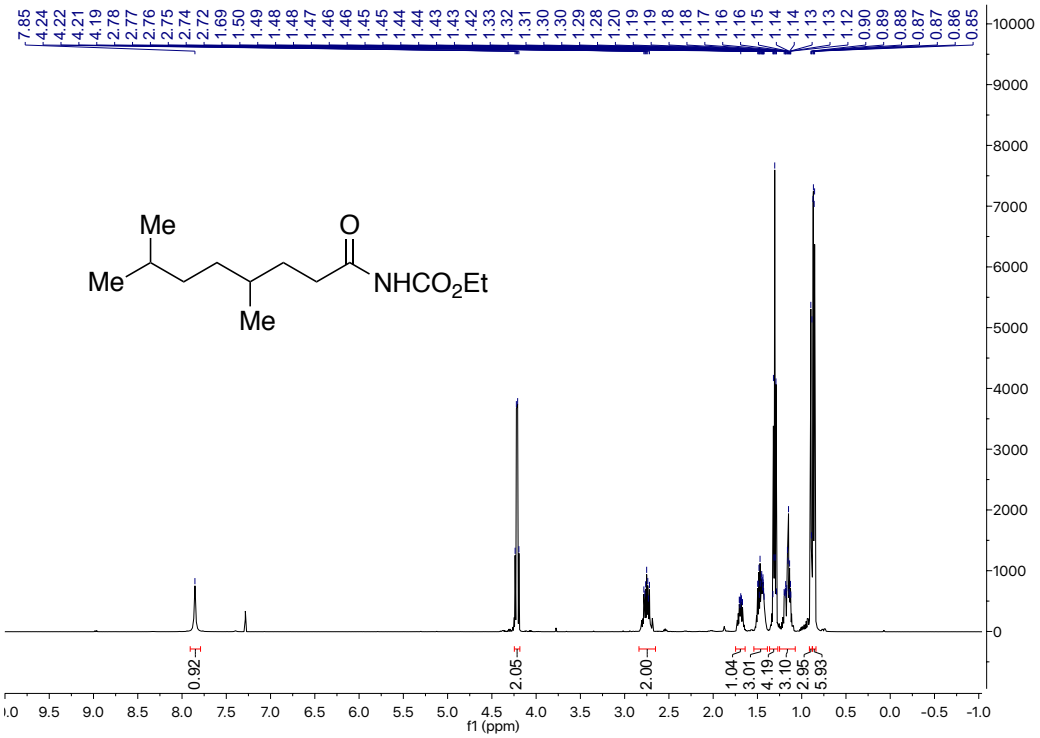
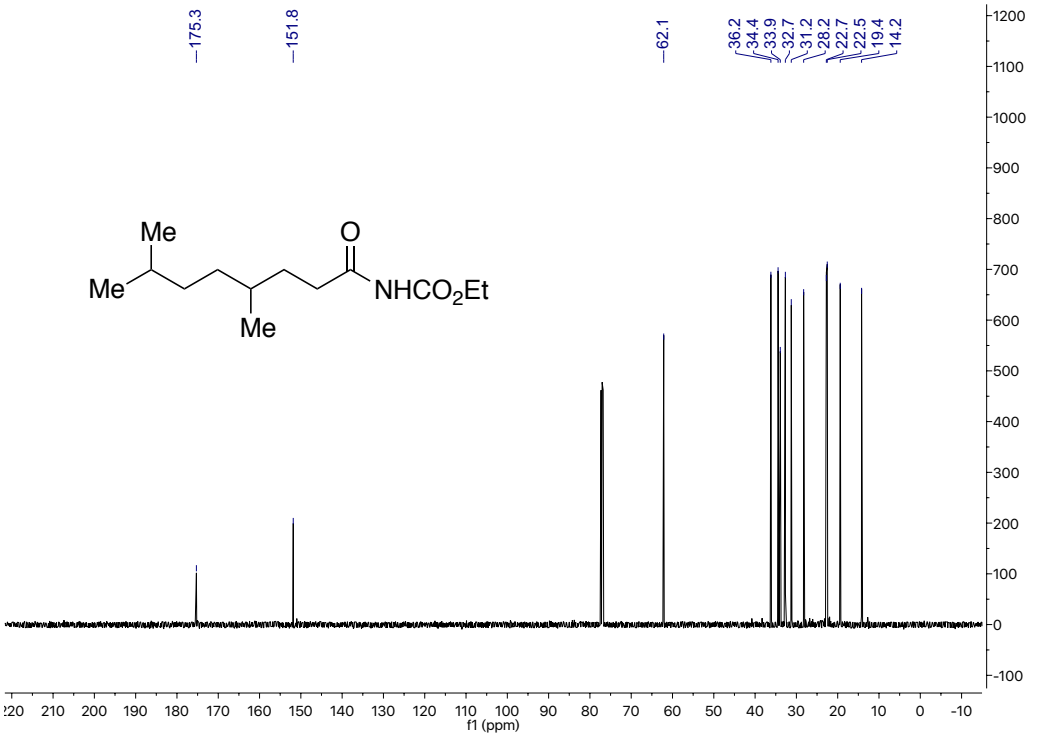
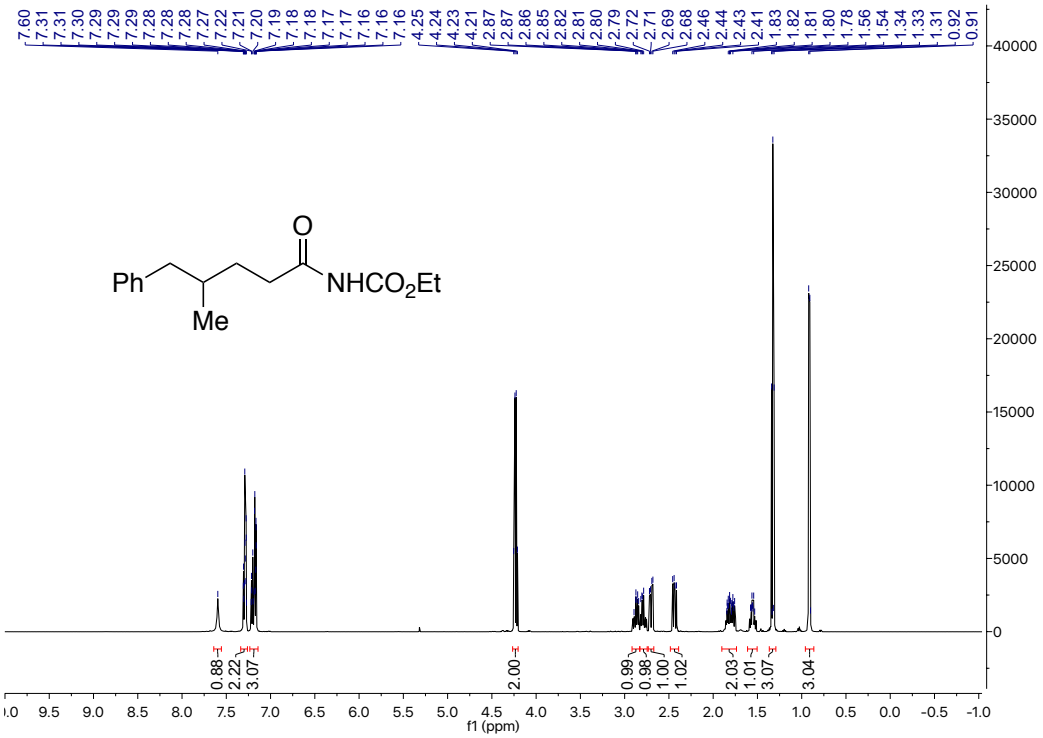
28.54
20.13
17.90
15.10
14.22
Me
O
Me
NHCO2Et
Me
f1 (ppm)

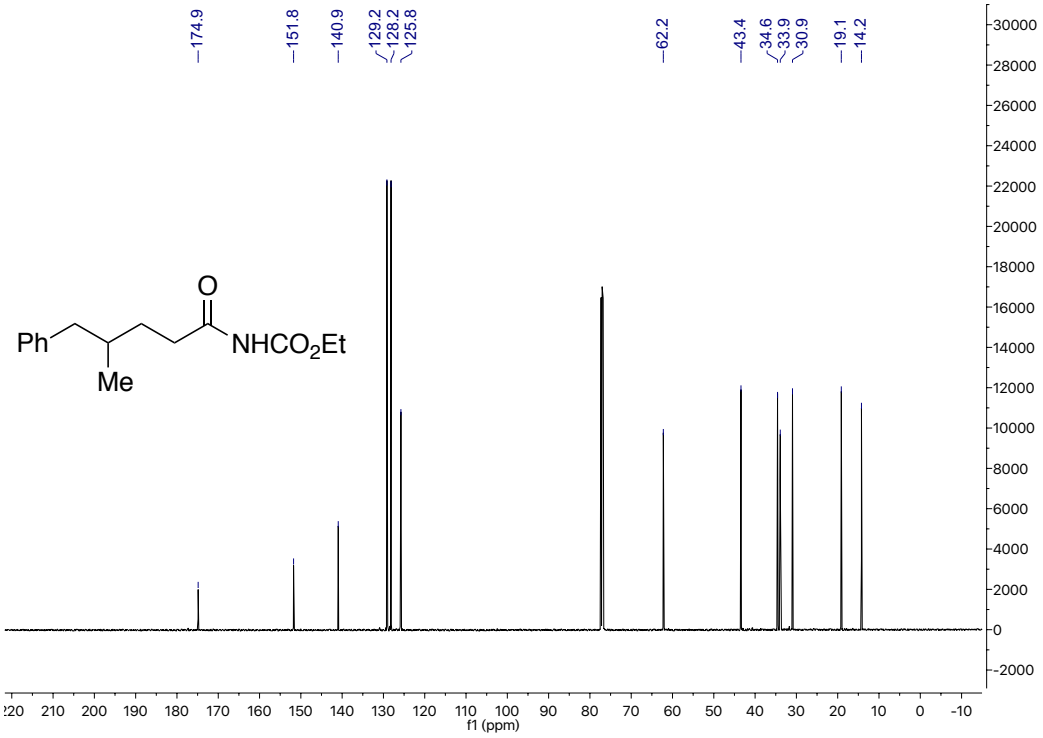

4.23 4.22 4.20 4.19 2.78 2.76 2.75 2.74 2.74 2.73 2.72 1.69 1.68 1.68 1.67 1.66 1.64 1.63 1.62 1.56 1.55 1.53 1.52 1.46 1.45 1.44 1.43 1.43 1.42 1.42 1.41 1.31 1.30 1.28 1.25 1.16 1.14 1.13 1.12 1.12 1.11 1.10 1.05 1.04 1.02 1.01 1.00 0.88 0.87 0.87 0.86 0.85 0.84 0.82
O
Me
NHCO2Et
Me
Me
0.95
2.00
2.00
2.08
1.05
1.07
3.12
1.06
1.07
6.11
3.22
f1 (ppm)

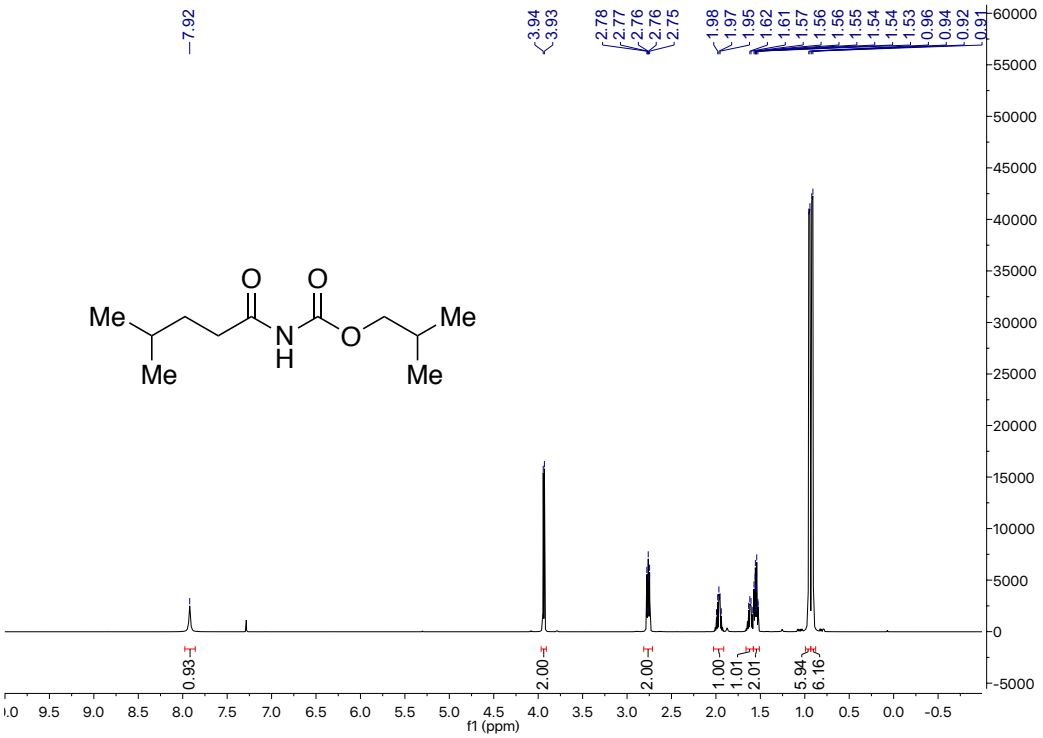

175.5
151.9
62.1
46.4
33.8
31.5
30.0
25.2
23.3
22.2
19.4
14.2
O
Me
NHCO2Et
Me
Me
f1 (ppm)


Me
O
Me
NHCO2Et
Me
f1 (ppm)


Me
O
Me
NHCO2Et
Me
f1 (ppm)


7.60 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.22 7.21 7.20 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.16
4.25 4.24 4.23 4.21 2.87 2.87 2.86 2.85 2.82 2.81 2.80 2.79 2.72 2.71 2.69 2.68 2.46 2.44 2.43 2.41 1.83 1.82 1.81 1.80 1.78 1.56 1.54 1.34 1.33 1.31 0.92 0.91
O
Ph
NHCO2Et
Me
0.88 2.22 3.07 2.00 0.99 0.98 1.00 1.02 2.03 1.01 3.07 3.04
f1 (ppm)


174.9 151.8 140.9 129.2 128.2 125.8 62.2 43.4 34.6 33.9 30.9 19.1 14.2
O
Ph
NHCO2Et
Me
f1 (ppm)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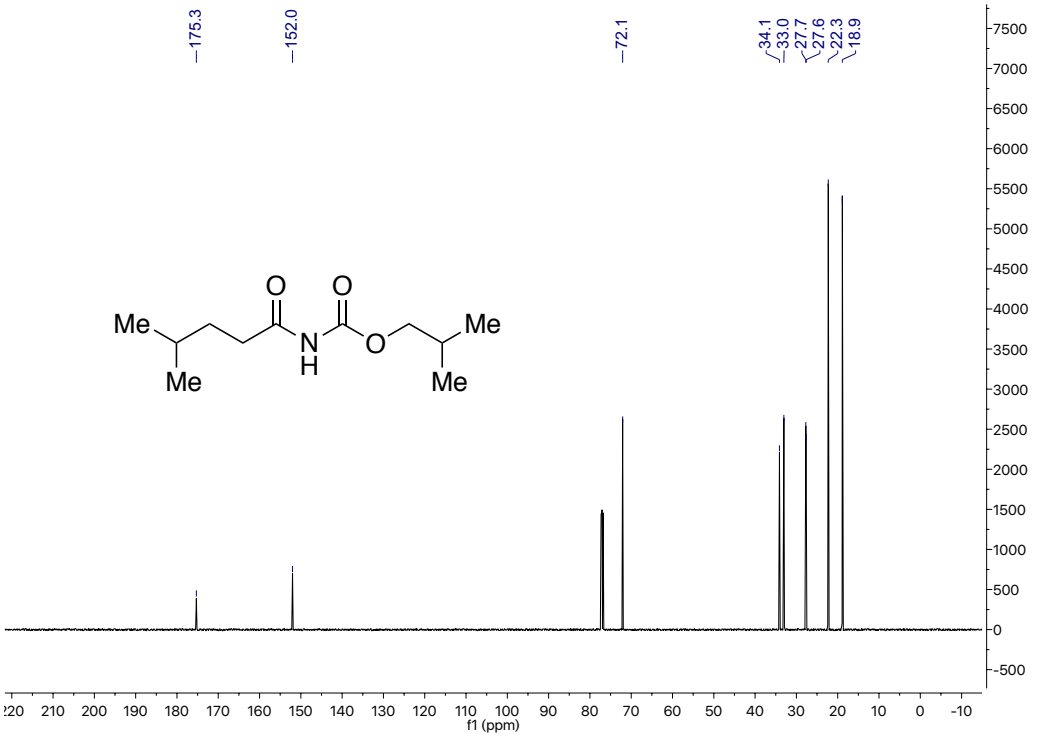
3.94
3.93
2.78
2.77
2.76
2.76
2.75
1.98
1.97
1.95
1.62
1.61
1.57
1.56
1.56
1.55
1.54
1.54
1.53
0.96
0.94
0.92
0.91
Me
Me
N
H
O
O
O
Me
Me
0.93
2.00
2.00
1.00
1.01
2.01
5.94
6.16
f1 (ppm)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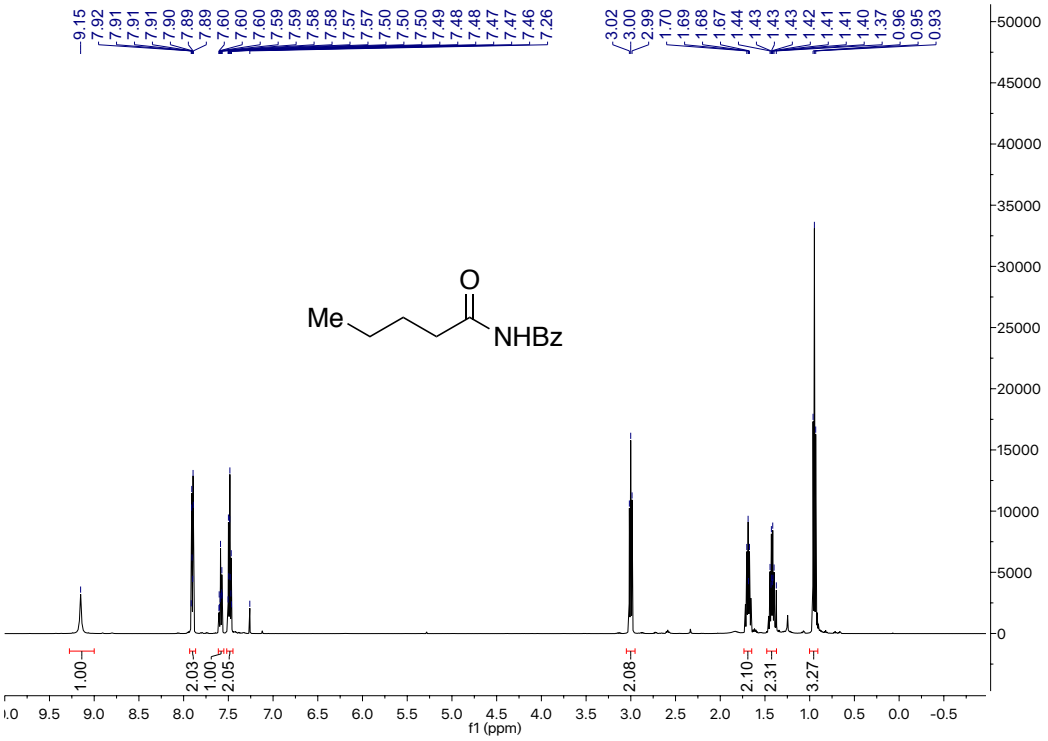
152.0
72.1
34.1
33.0
27.7
27.6
22.3
18.9
Me
Me
N
H
O
O
O
Me
Me
f1 (ppm)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7.90
7.89
7.89
7.60
7.60
7.60
7.59
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7.58
7.58
7.57
7.57
7.50
7.50
7.49
7.48
7.48
7.47
7.47
7.46
7.26
3.02
3.00
2.99
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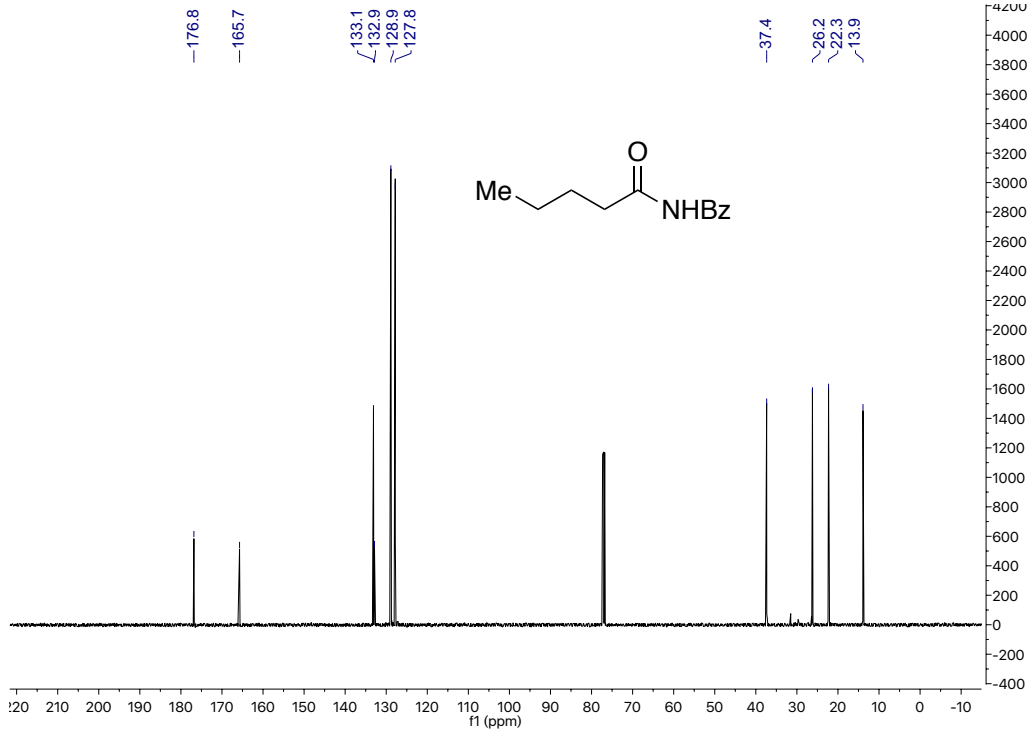
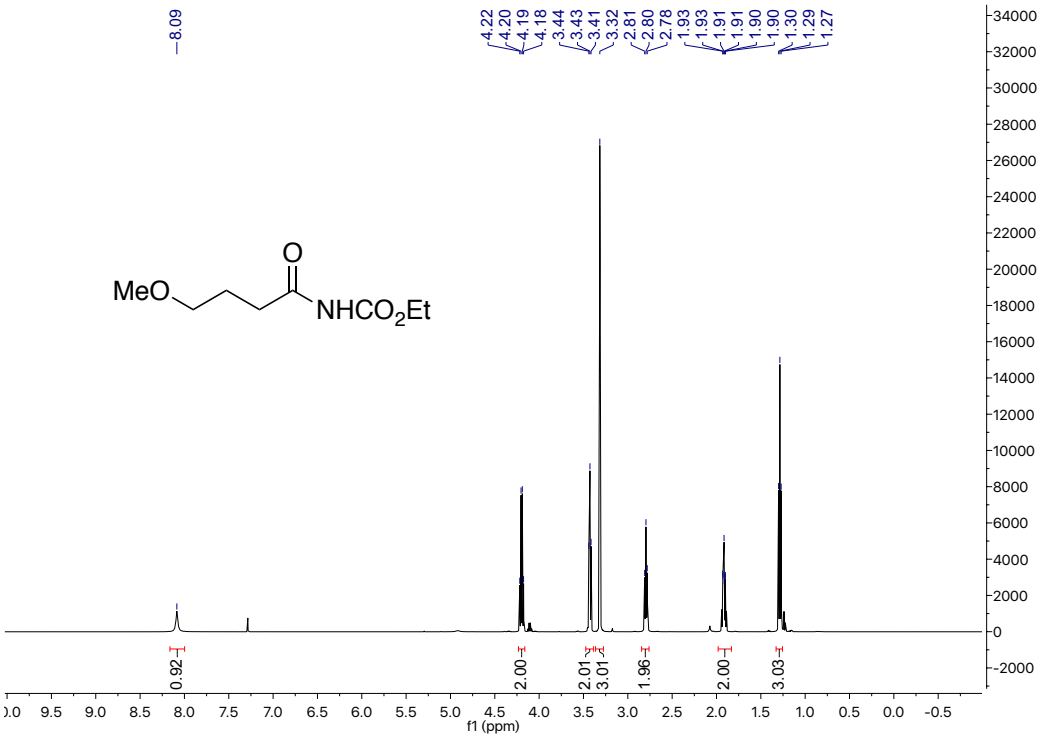
1.69
1.68
1.67
1.44
1.43
1.43
1.43
1.42
1.41
1.41
1.40
1.37
0.96
0.95
0.93
O
Me
NHBz
1.00
2.03
1.00
2.05
2.08
2.10
2.31
3.27
f1 (ppm)


176.8
165.7
133.1
132.9
128.9
127.8
37.4
26.2
22.3
13.9
O
Me
NHBz
f1 (ppm)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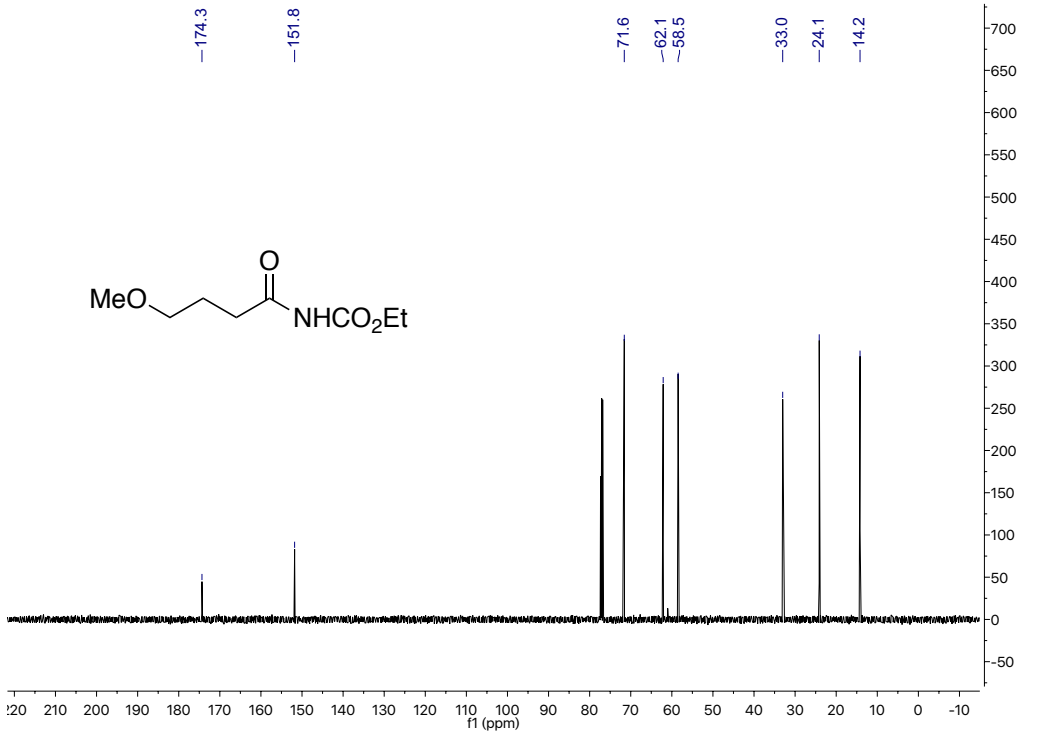
4.22
4.20
4.19
4.18
3.44
3.43
3.41
3.32
2.81
2.80
2.78
1.93
1.91
1.91
1.90
1.90
1.30
1.29
1.27
MeO
O
NHCO2Et
0.92
2.00
2.01
3.01
1.96
2.00
3.03
f1 (ppm)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71.6
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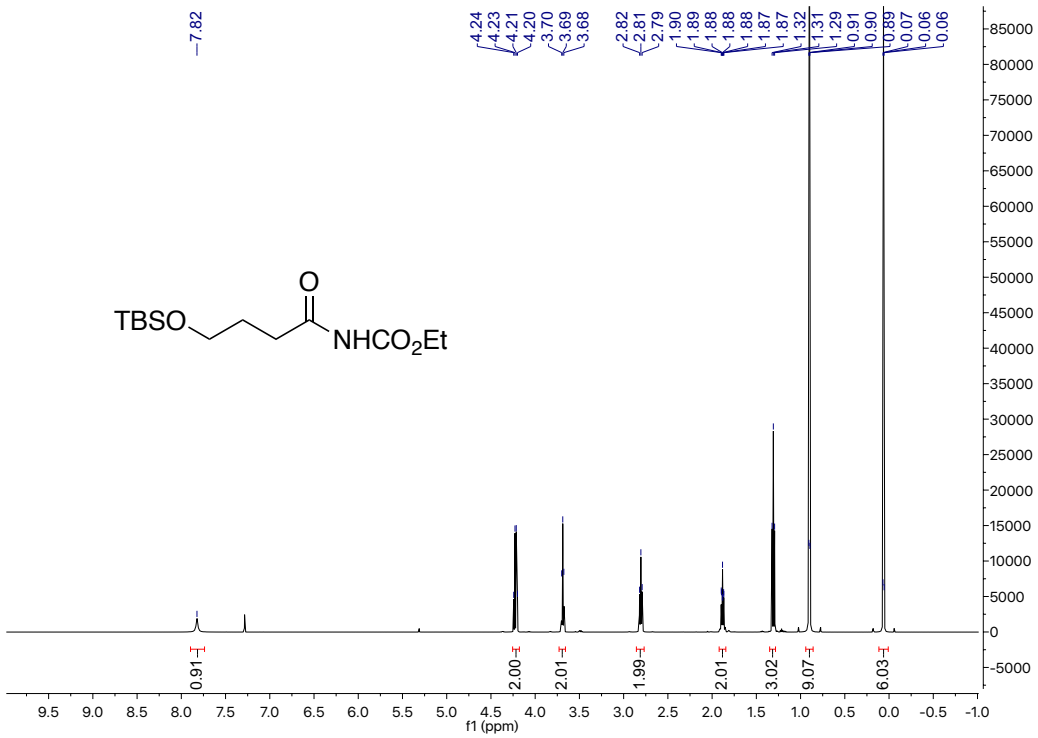
24.1
14.2
MeO
O
NHCO2Et
f1 (ppm)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4.23
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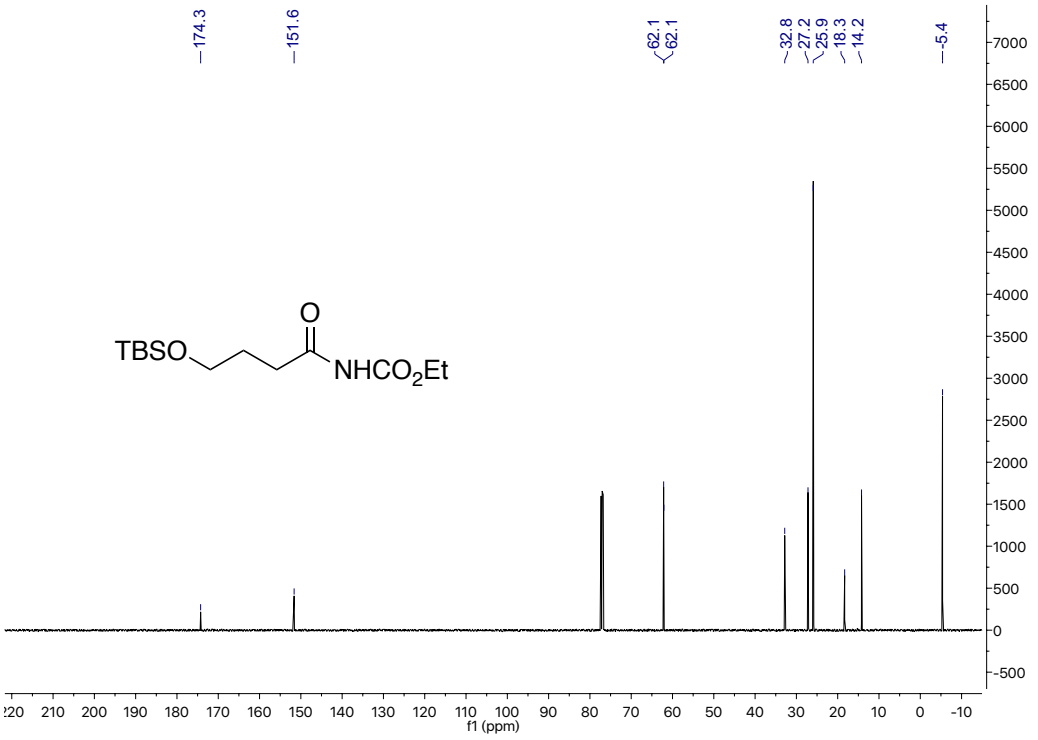
4.20
3.70
3.69
3.68
2.82
2.81
2.79
1.90
1.89
1.88
1.88
1.88
1.87
1.87
1.32
1.31
1.29
0.91
0.90
0.89
0.07
0.06
0.06
TBSO
O
NHCO2Et
0.91
2.00
2.01
1.99
2.01
3.02
9.07
6.03
f1 (ppm)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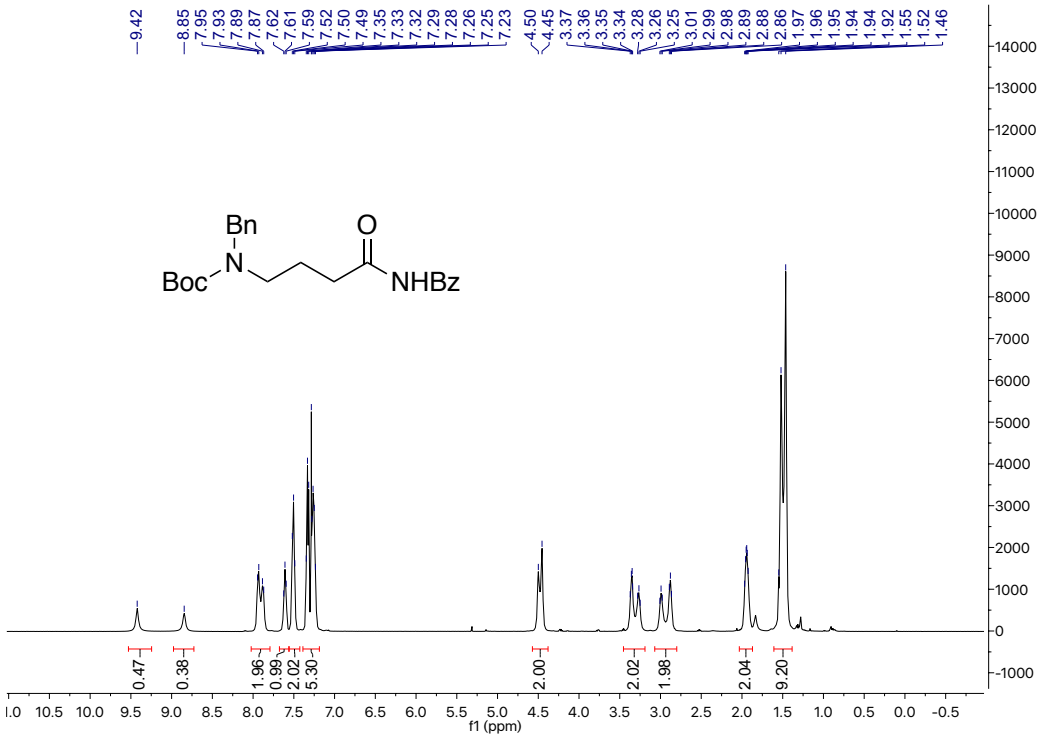
62.1
62.1
32.8
27.2
25.9
18.3
14.2
-5.4
TBSO
O
NHCO2Et
f1 (ppm)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7.89
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7.50
7.49
7.35
7.33
7.32
7.29
7.28
7.26
7.25
7.23
4.50
4.45
3.37
3.36
3.35
3.34
3.28
3.26
3.25
3.01
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2.89
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2.86
1.97
1.96
1.95
1.94
1.94
1.92
1.55
1.52
1.46
Bn
O
N
Boc
NHBz
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0.38
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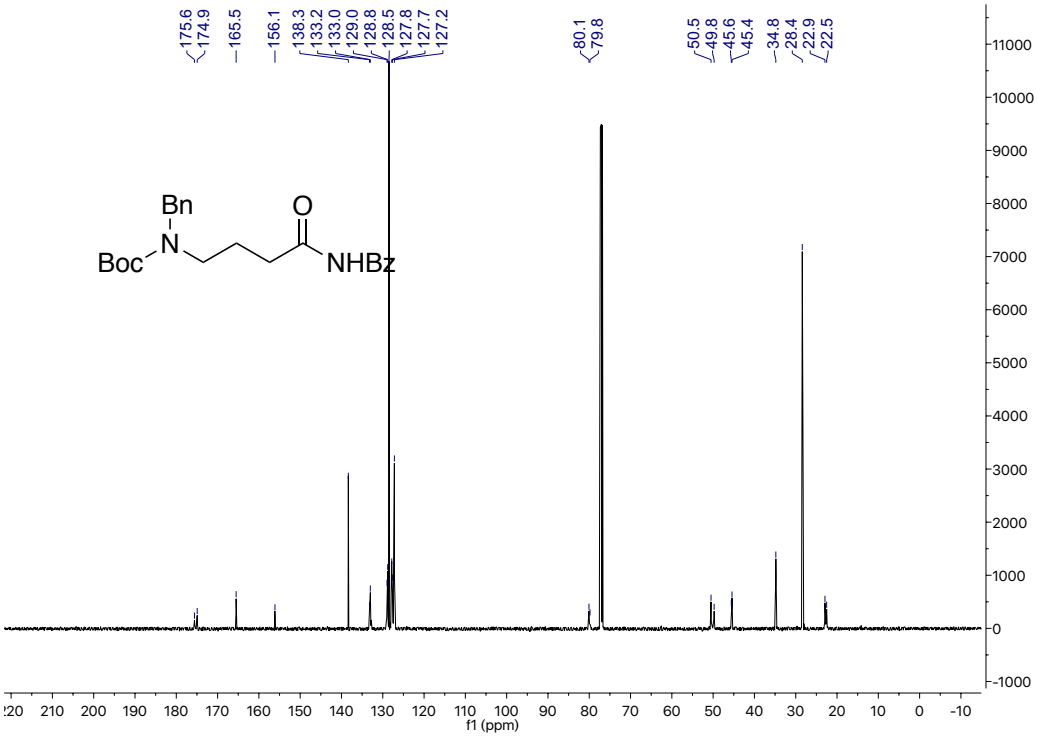
0.99
2.02
5.30
2.00
2.02
1.98
2.04
9.20
f1 (ppm)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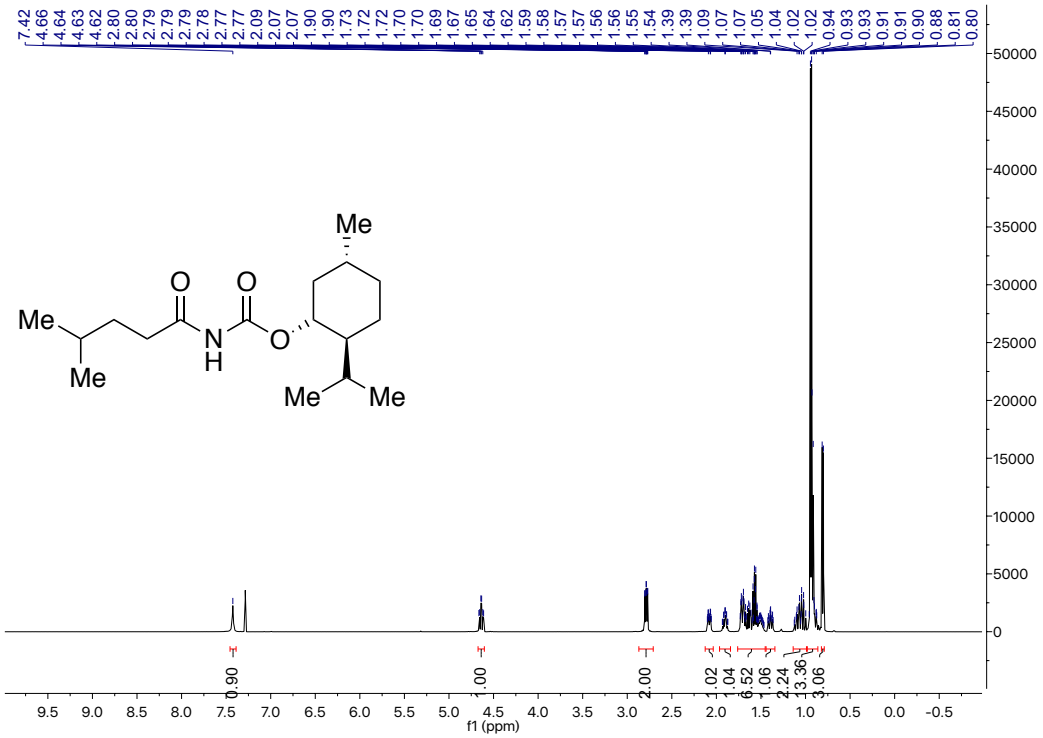
138.3
133.2
133.0
129.0
128.8
128.5
127.8
127.7
127.2
80.1
79.8
50.5
49.8
45.6
45.4
34.8
28.4
22.9
22.5
Bn
O
N
Boc
NHBz
f1 (ppm)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4.63
4.62
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2.80
2.79
2.79
2.79
2.78
2.77
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2.09
2.07
2.07
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1.90
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1.72
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1.64
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1.59
1.58
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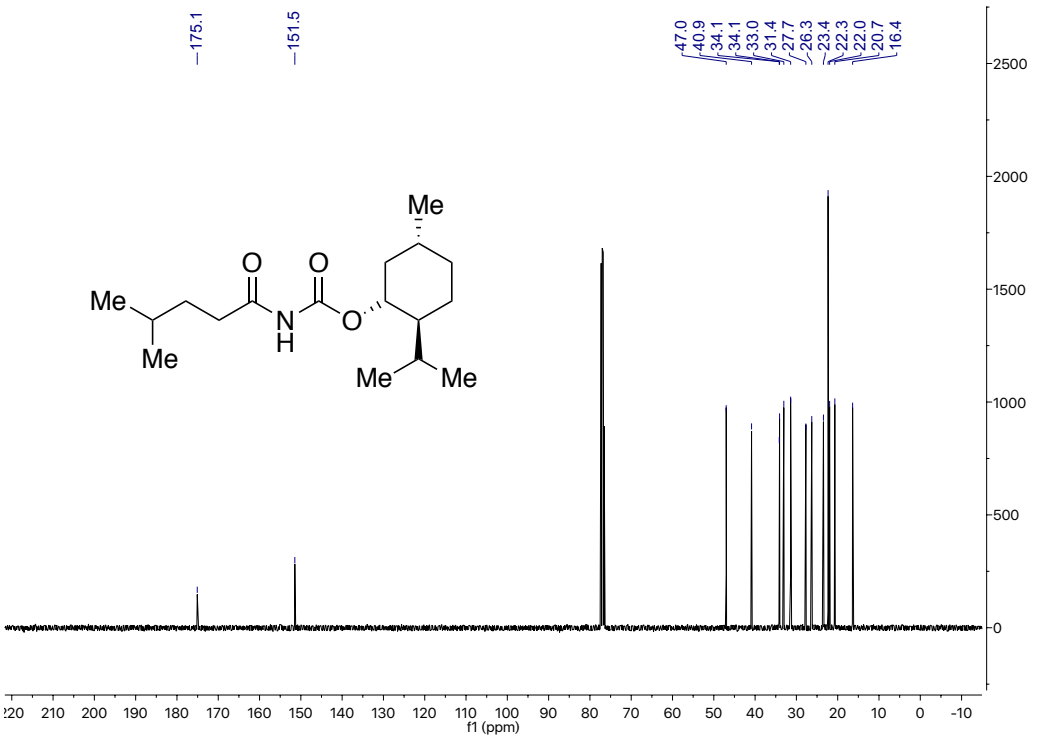
1.54
1.39
1.39
1.09
1.07
1.07
1.05
1.04
1.02
1.02
0.94
0.93
0.93
0.91
0.91
0.90
0.88
0.81
0.80
Me
O
O
Me
N
H
O
Me
Me
Me
Me
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0.90
1.00
2.00
1.02
1.04
6.52
1.06
2.24
13.36
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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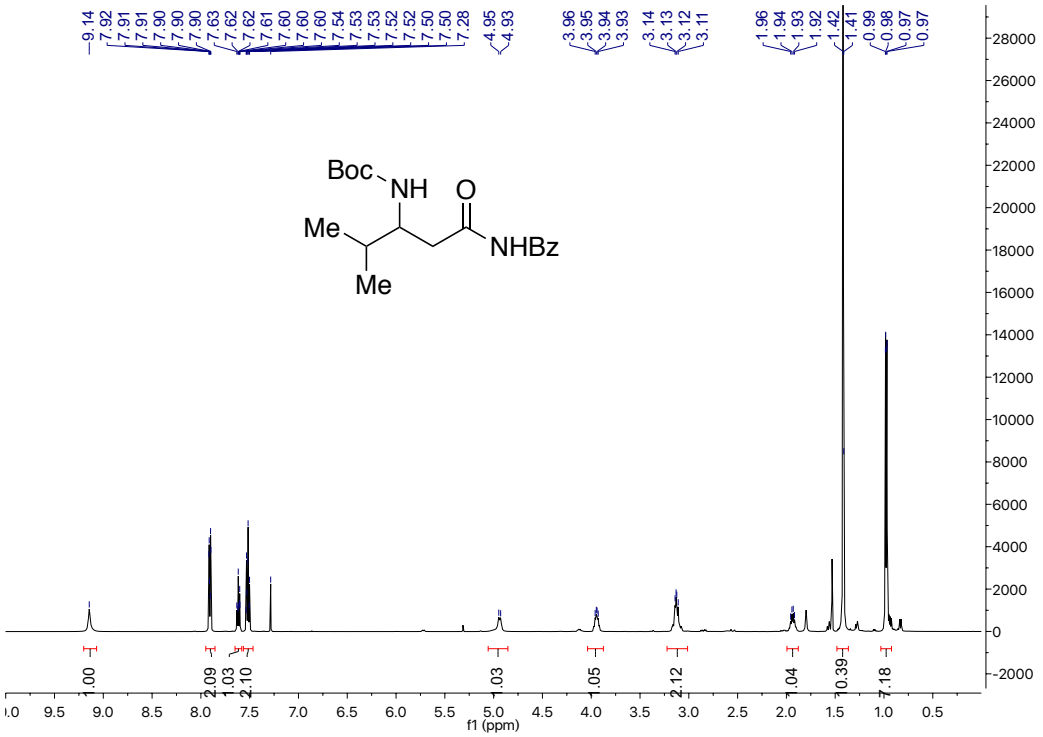
47.0
40.9
34.1
34.1
33.0
31.4
27.7
26.3
23.4
22.3
22.0
20.7
16.4
Me
O
O
Me
N
H
O
Me
Me
Me
Me
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.60
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7.60
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7.53
7.52
7.52
7.50
7.50
7.28
4.95
4.93
3.96
3.95
3.94
3.93
3.14
3.13
3.12
3.11
1.96
1.94
1.93
1.92
1.42
1.41
0.99
0.98
0.97
0.97
Boc
NH
O
Me
NHBz
Me
1.00
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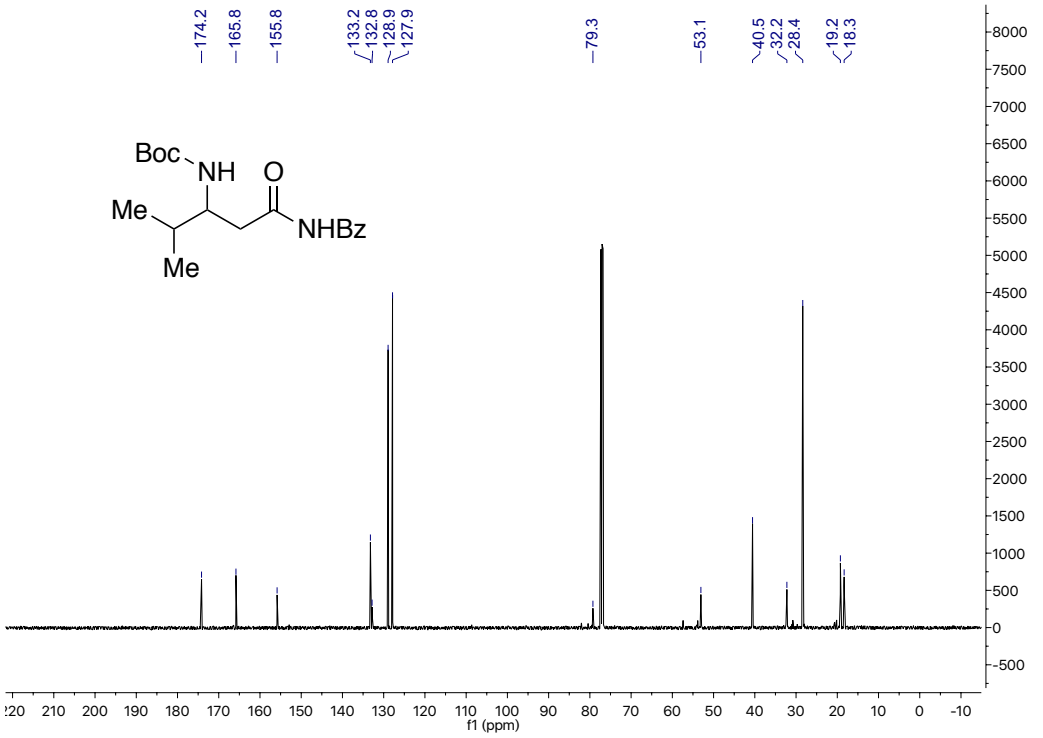
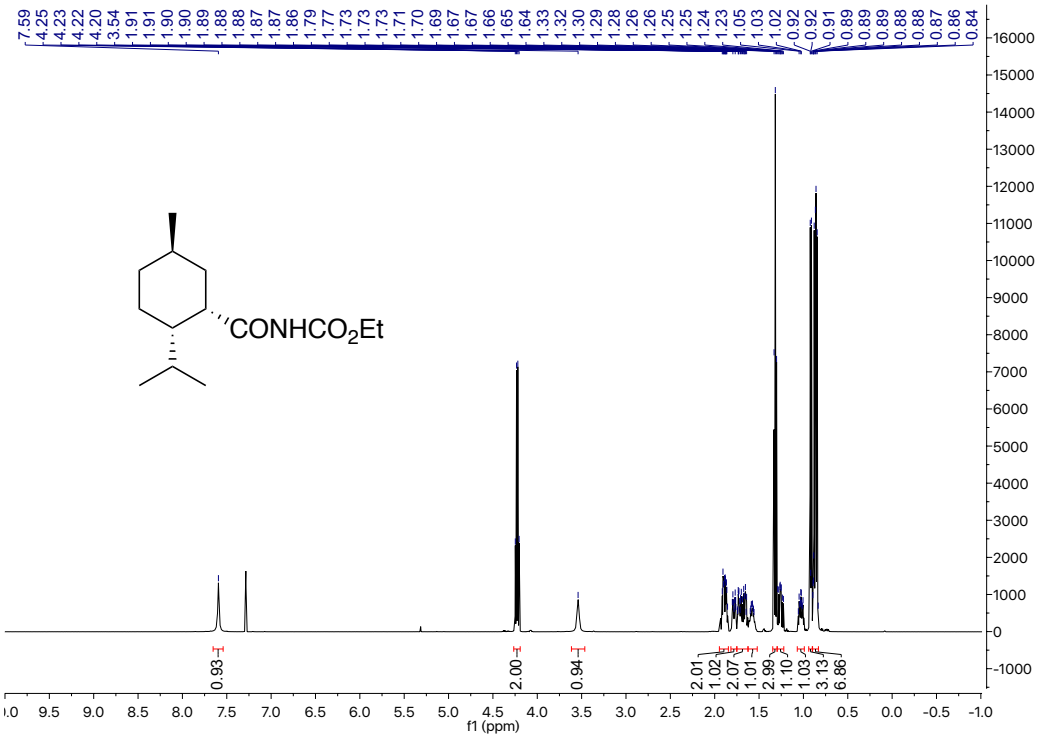
1.03
2.10
1.03
1.05
2.12
1.04
10.39
7.18
f1 (ppm)


174.2
165.8
155.8
133.2
132.8
128.9
127.9
79.3
53.1
40.5
32.2
28.4
19.2
18.3
Boc
NH
O
Me
NHBz
Me
f1 (ppm)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4.23
4.22
4.20
3.54
1.91
1.91
1.90
1.90
1.89
1.88
1.88
1.87
1.87
1.86
1.79
1.77
1.73
1.73
1.73
1.71
1.70
1.69
1.67
1.67
1.66
1.65
1.64
1.33
1.32
1.30
1.29
1.28
1.26
1.26
1.25
1.25
1.24
1.23
1.05
1.03
1.02
0.92
0.92
0.91
0.89
0.89
0.89
0.88
0.88
0.87
0.86
0.84
CONHCO2Et
0.93
2.00
0.94
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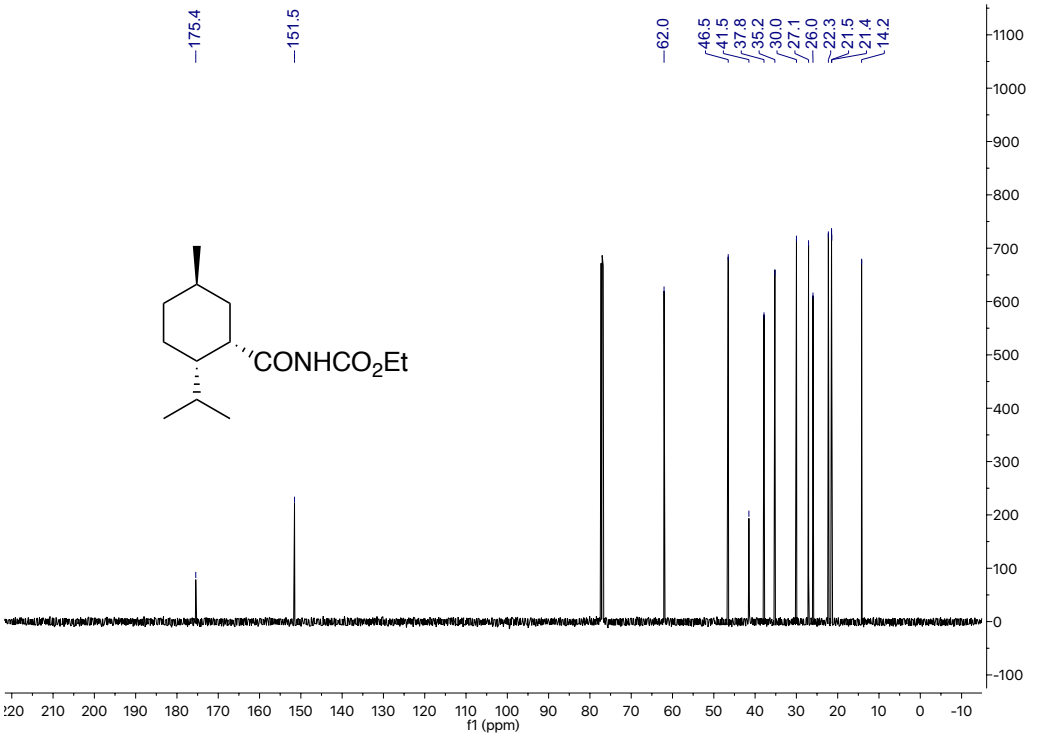
1.02
2.07
1.01
2.99
1.10
1.03
3.13
6.86
f1 (ppm)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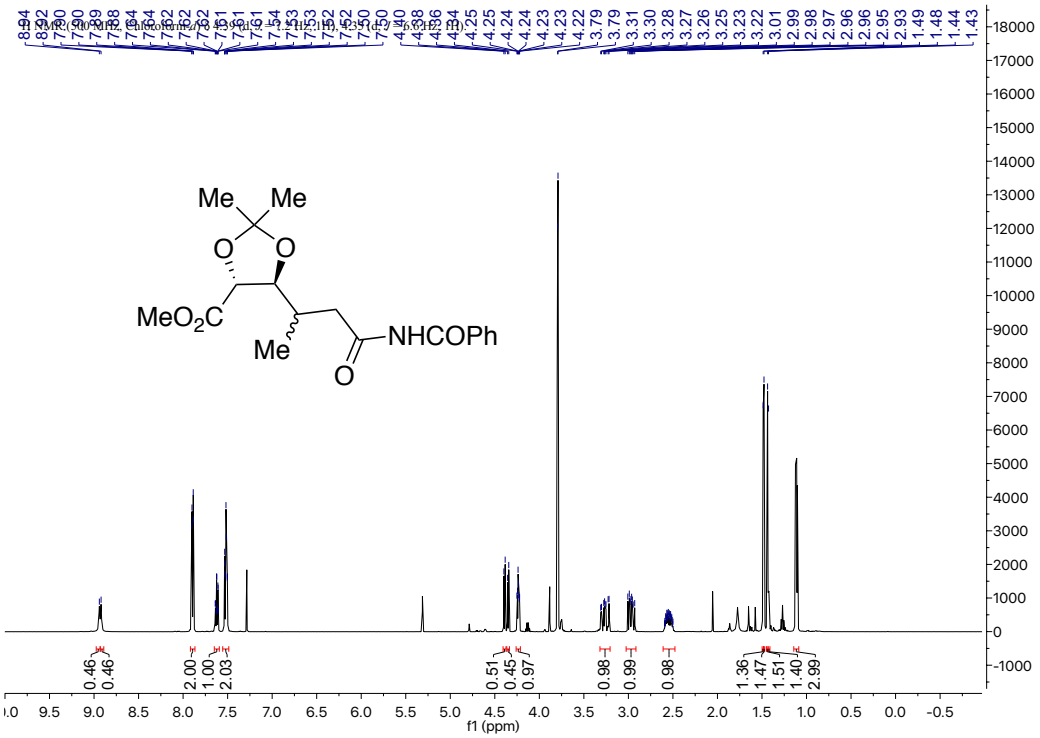
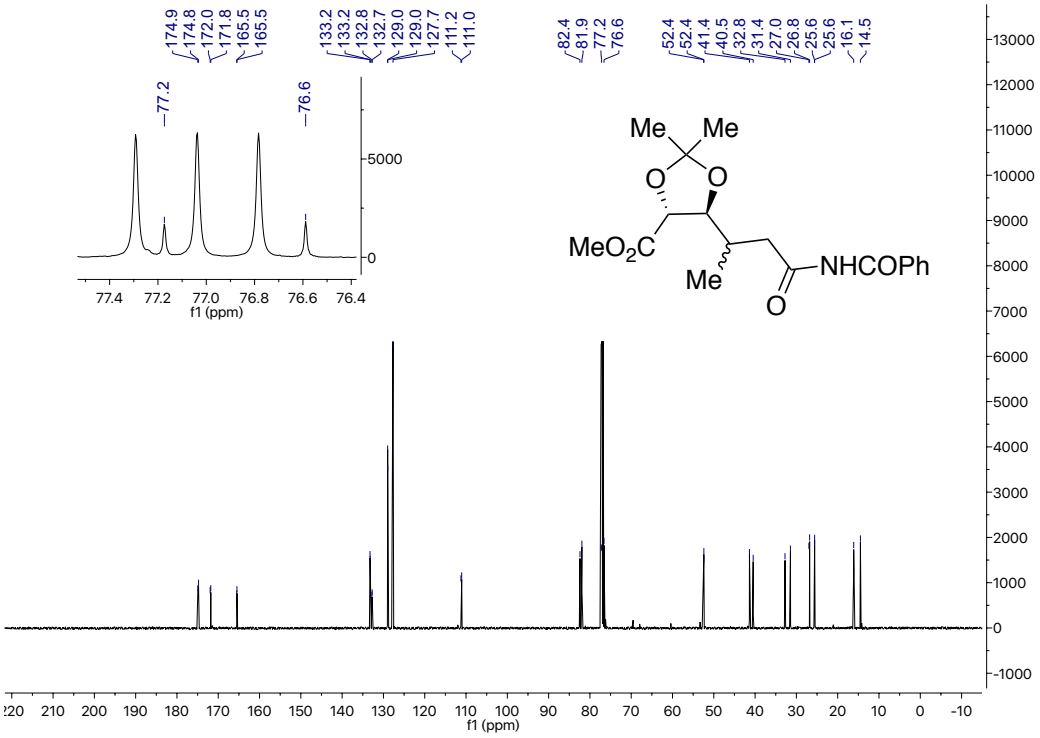
151.5
62.0
46.5
41.5
37.8
35.2
30.0
27.1
26.0
22.3
21.5
21.4
14.2
CONHCO2Et
f1 (ppm)


Me
Me
O
O
MeO2C
Me
NHCOPh
O
f1 (ppm)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76.6
5000
0
77.4
77.2
77.0
76.8
76.6
76.4
f1 (ppm)
Me
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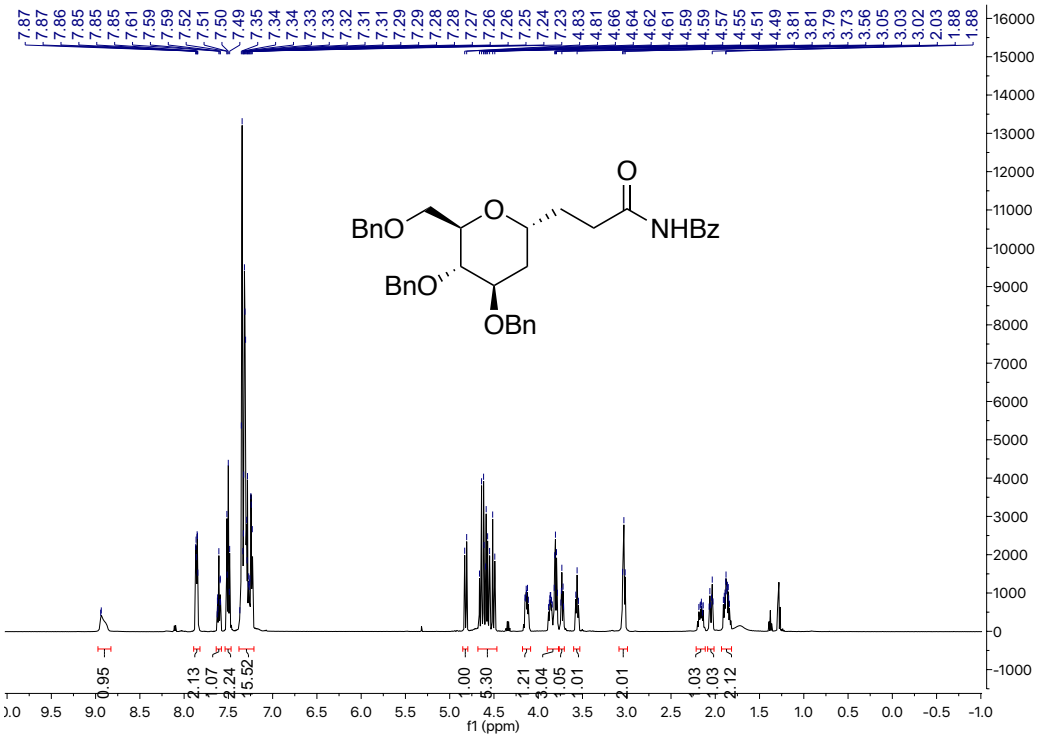
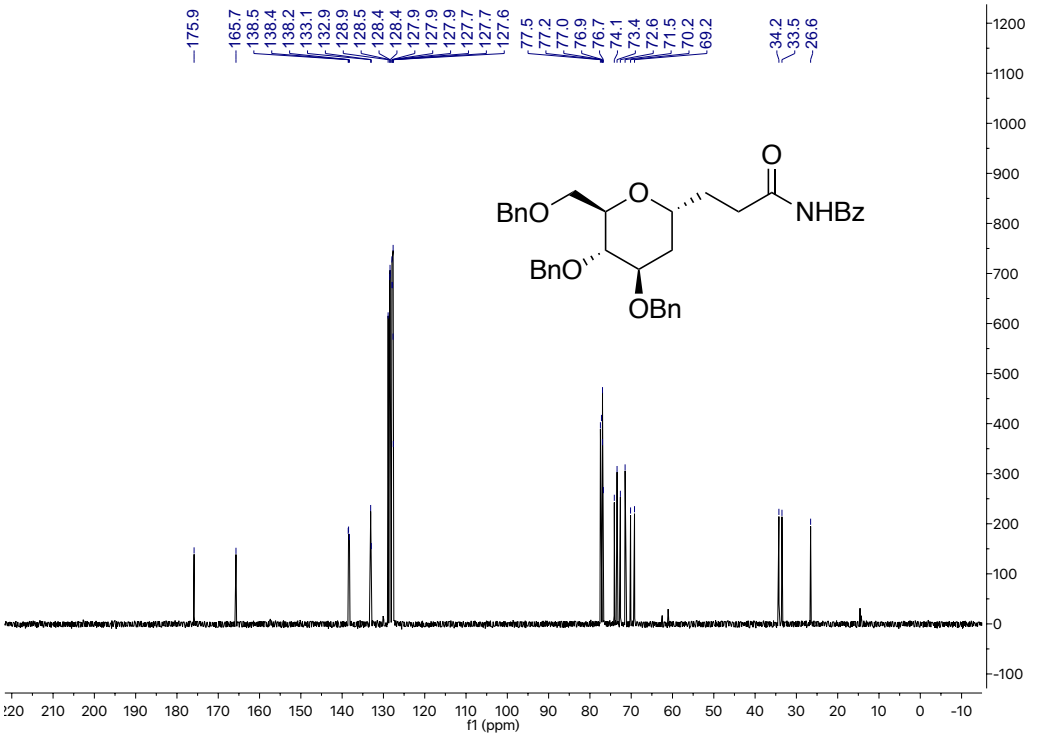
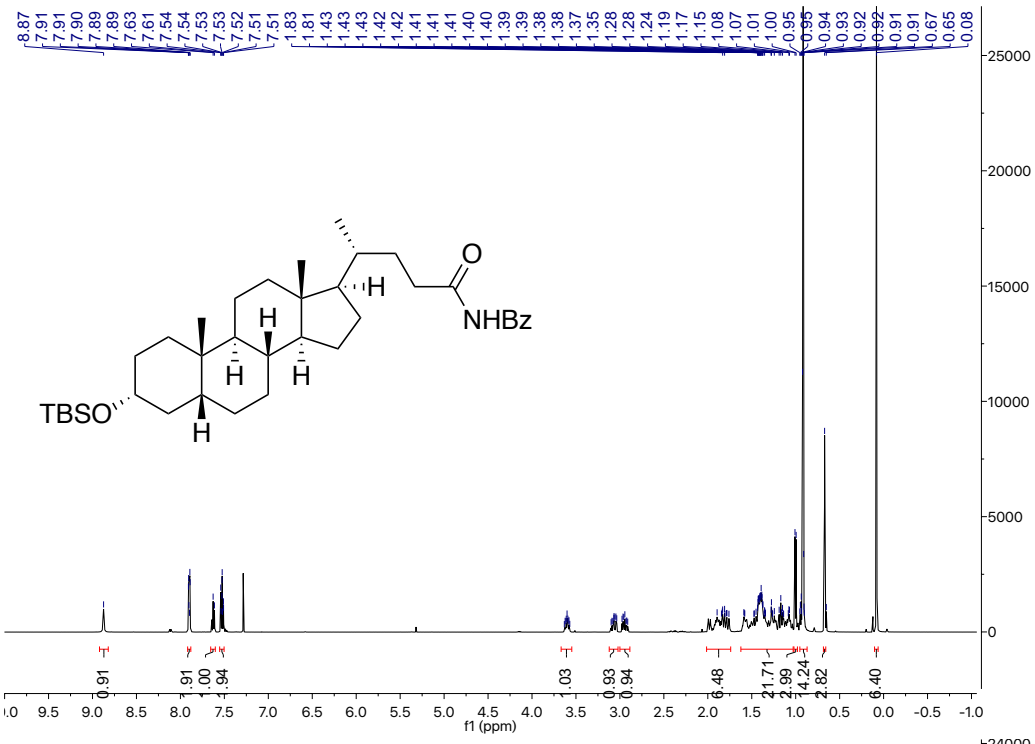
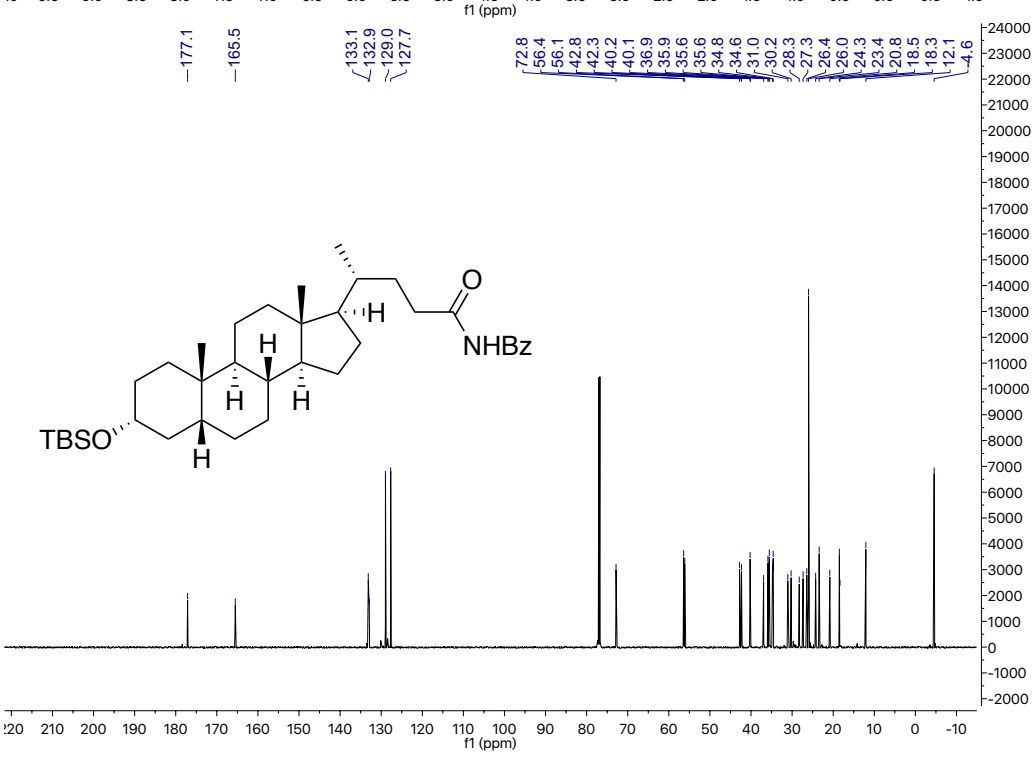
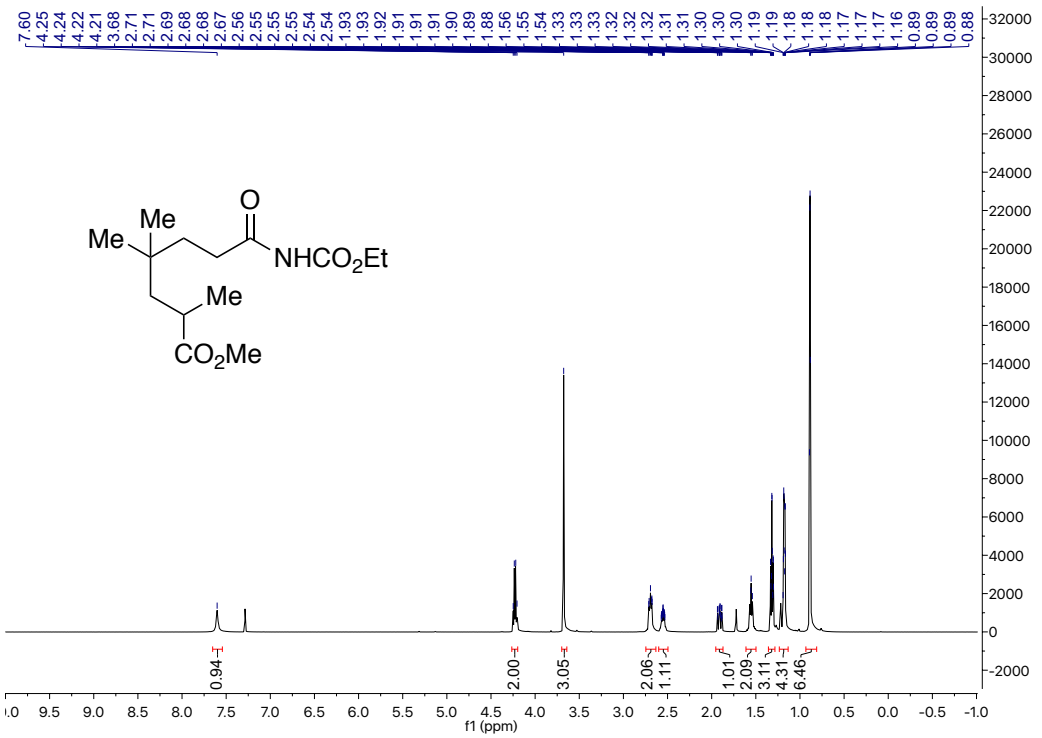
O
O
MeO2C
Me
NHCOPh
O
f1 (ppm)


BnO
BnO
OBn
O
NHBz
f1 (ppm)


BnO
BnO
OBn
O
NHBz
f1 (ppm)


TBSO
H
O
NHBz
f1 (ppm)


TBSO
H
O
NHBz
f1 (ppm)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4.24
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2.68
2.68
2.67
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2.55
2.55
2.54
2.54
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1.93
1.92
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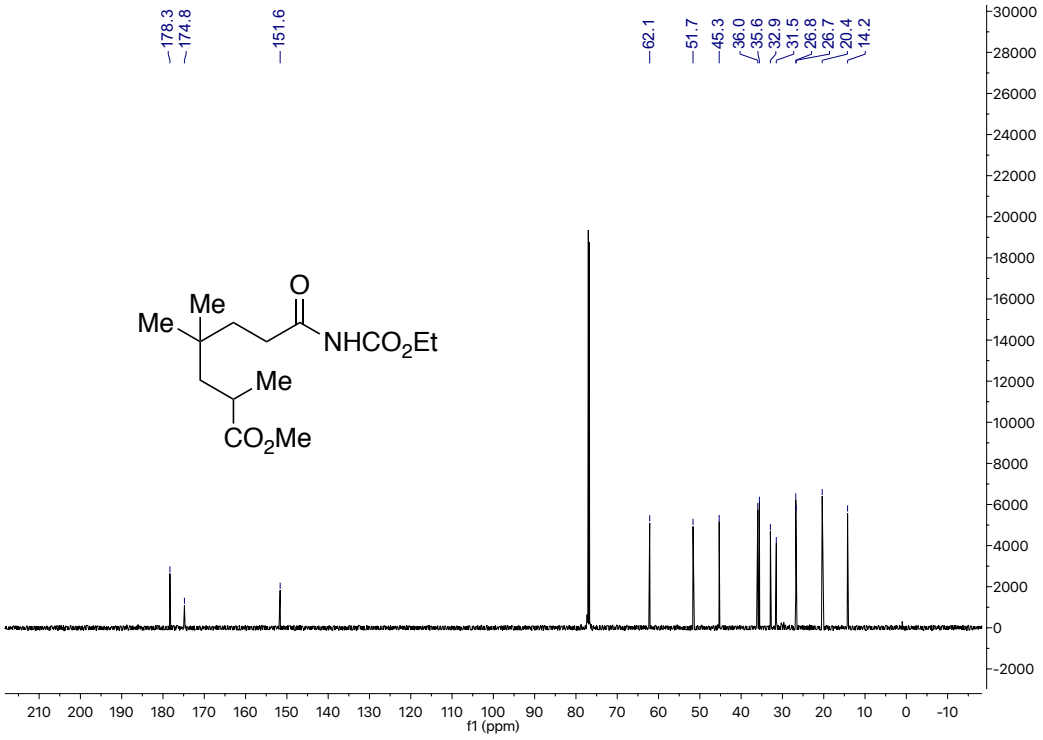
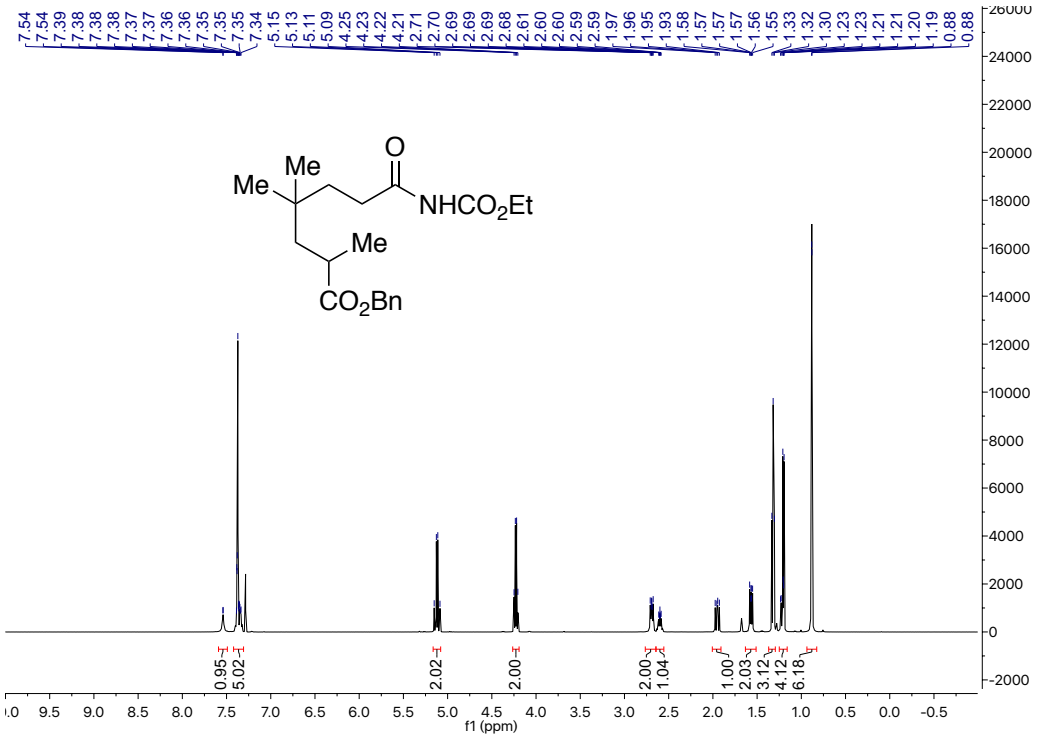
1.33
1.33
1.32
1.32
1.32
1.31
1.31
1.30
1.30
1.30
1.19
1.19
1.18
1.18
1.18
1.17
1.17
1.17
1.16
0.89
0.89
0.88
Me
Me
O
NHCO2Et
Me
CO2Me
0.94
2.00
3.05
2.06
1.11
1.01
2.09
3.11
4.31
6.46
f1 (ppm)


178.3
174.8
151.6
62.1
51.7
45.3
36.0
35.6
32.9
31.5
26.8
26.7
20.4
14.2
Me
Me
O
NHCO2Et
Me
CO2Me
f1 (ppm)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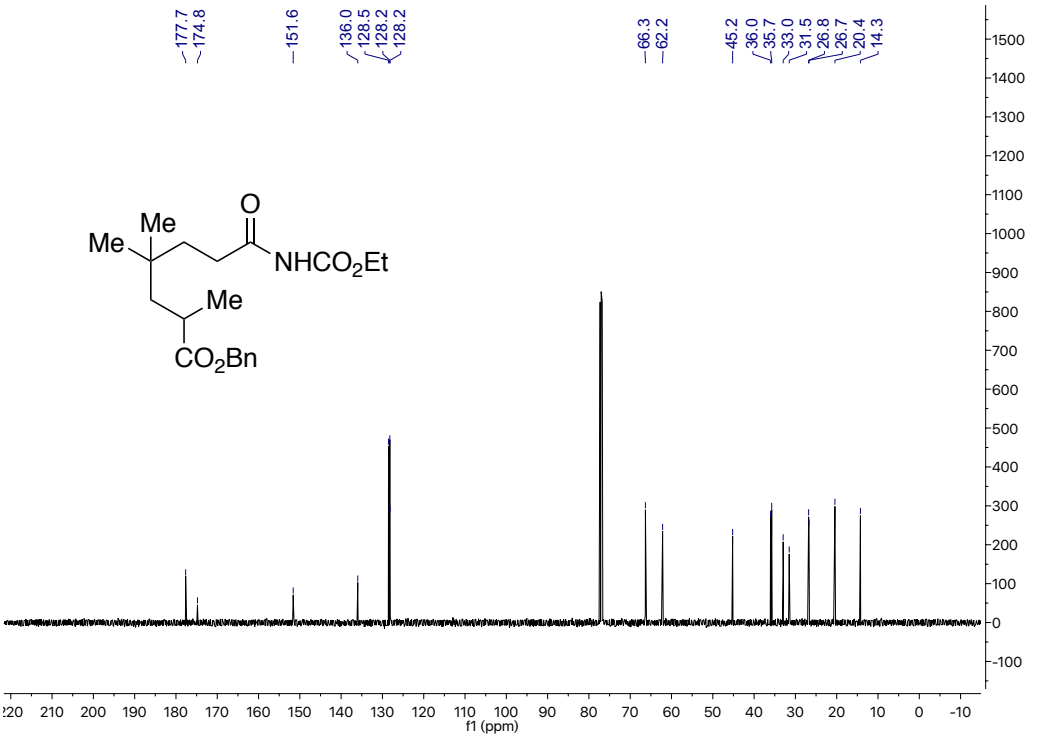
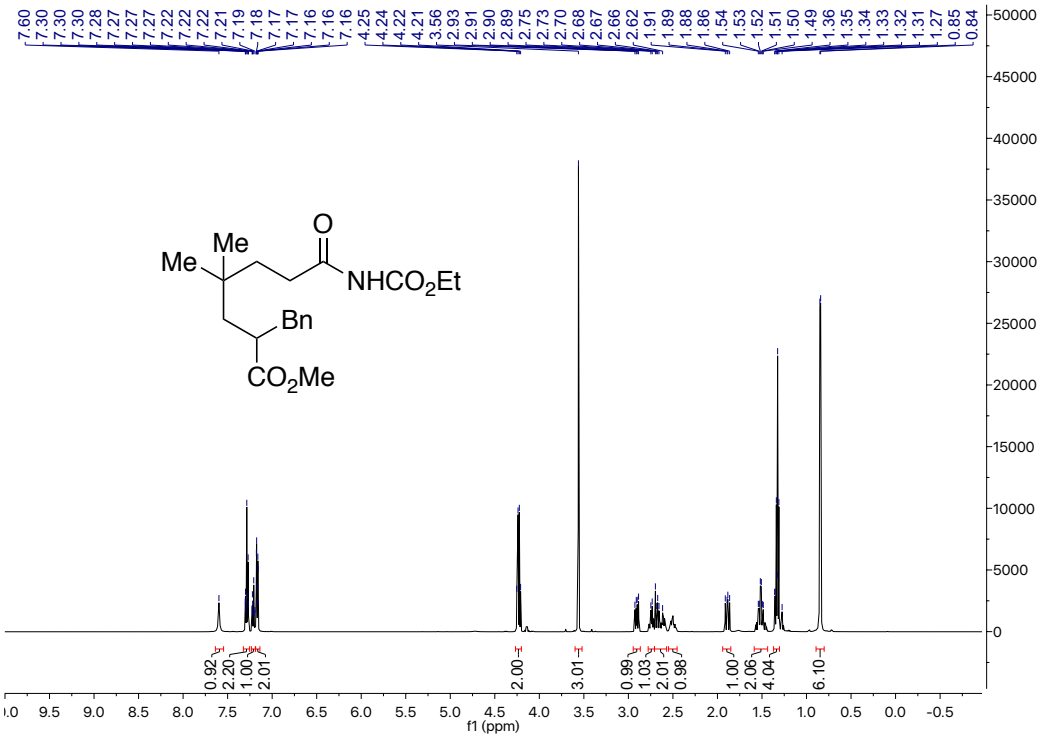
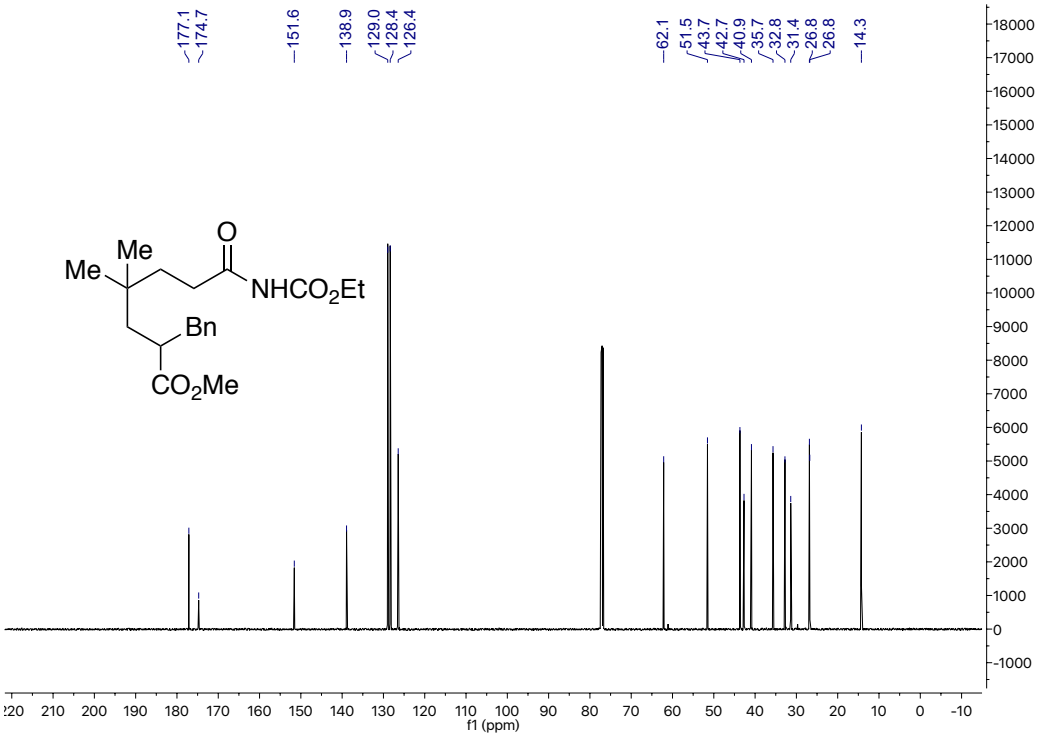
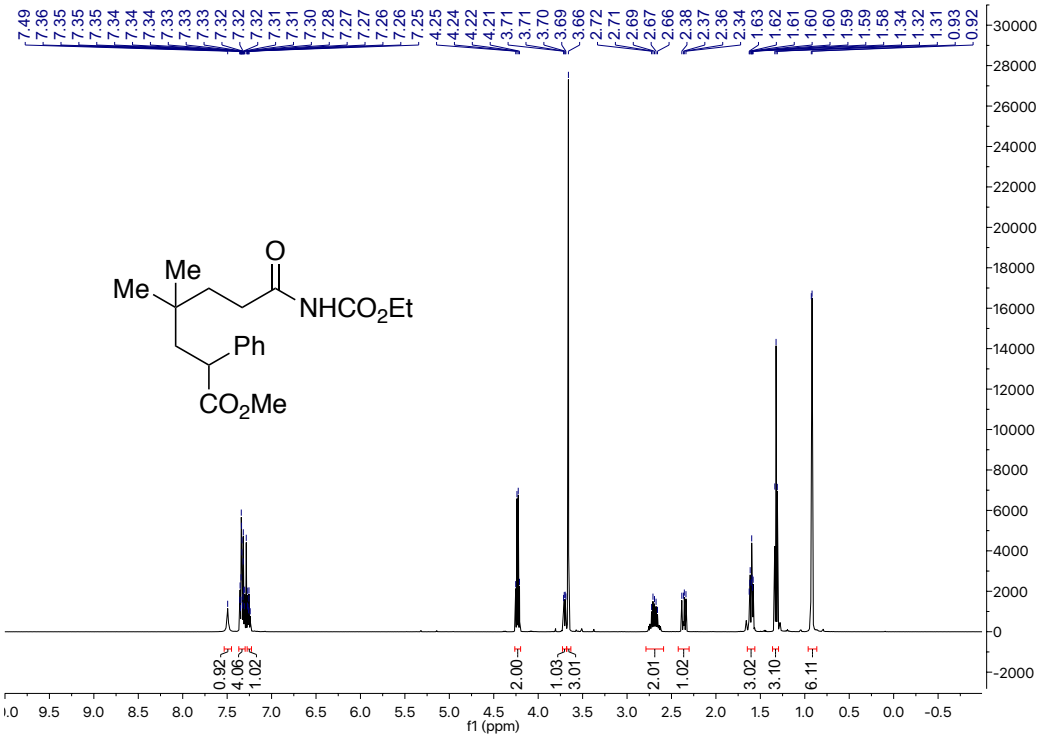
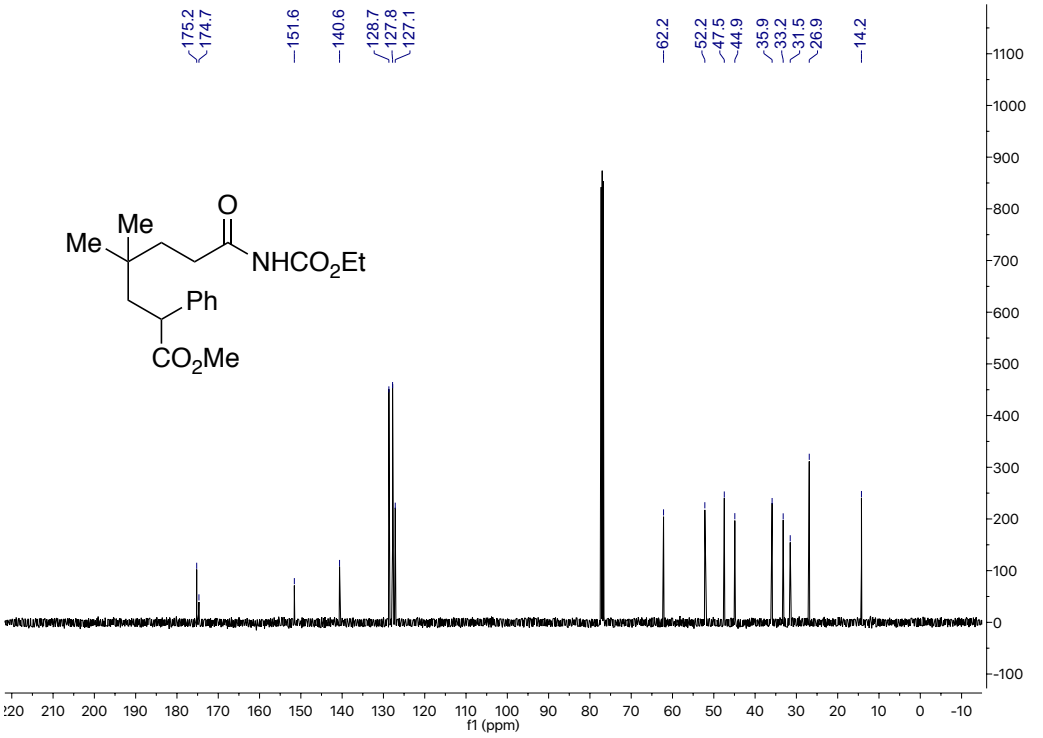
Me
O
NHCO2Et
Me
CO2Bn
f1 (ppm)

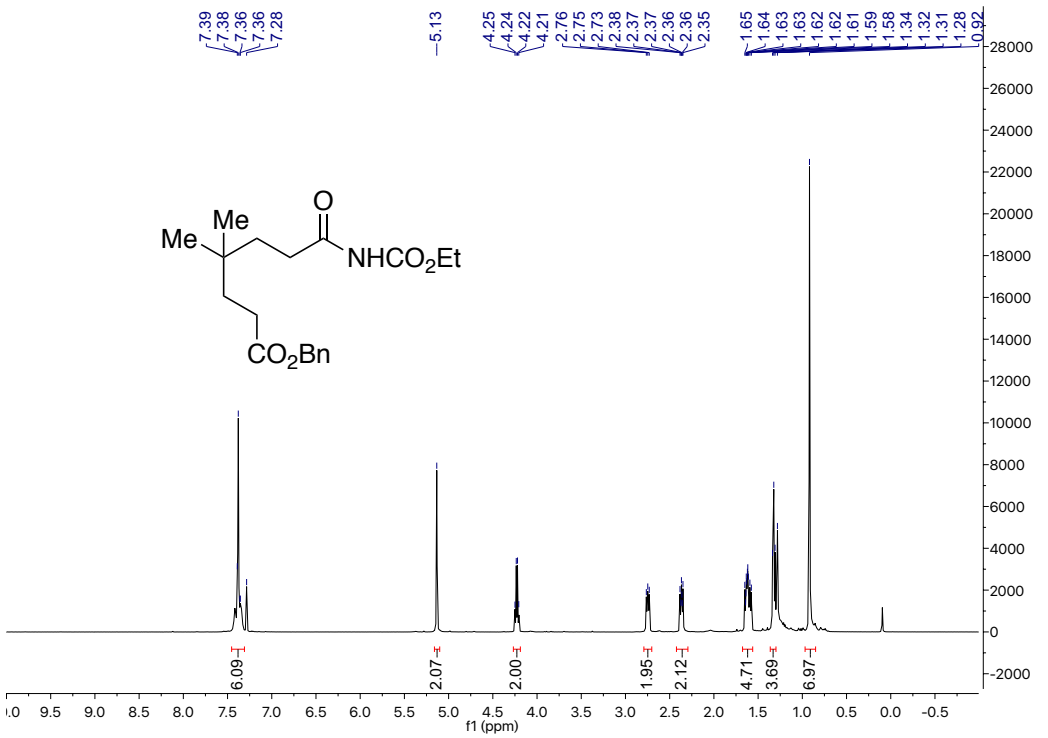

Me
Me
O
NHCO2Et
Me
CO2Bn
f1 (ppm)


Me
Me
O
NHCO2Et
Bn
CO2Me
f1 (ppm)


Me
Me
O
NHCO2Et
Bn
CO2Me
f1 (ppm)


7.49 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.28 7.27 7.27 7.26 7.26 7.25 4.25 4.24 4.22 4.21 3.71 3.71 3.70 3.69 3.66 2.72 2.71 2.69 2.67 2.66 2.38 2.37 2.36 2.34 1.63 1.62 1.61 1.60 1.60 1.59 1.59 1.58 1.34 1.32 1.31 0.93 0.92
Me
Me
O
NHCO2Et
Ph
CO2Me
0.92 4.06 1.02 2.00 1.03 3.01 2.01 1.02 3.02 3.10 6.11
f1 (ppm)


175.2 174.7 151.6 140.6 128.7 127.8 127.1 62.2 52.2 47.5 44.9 35.9 33.2 31.5 26.9 14.2
Me
Me
O
NHCO2Et
Ph
CO2Me
f1 (ppm)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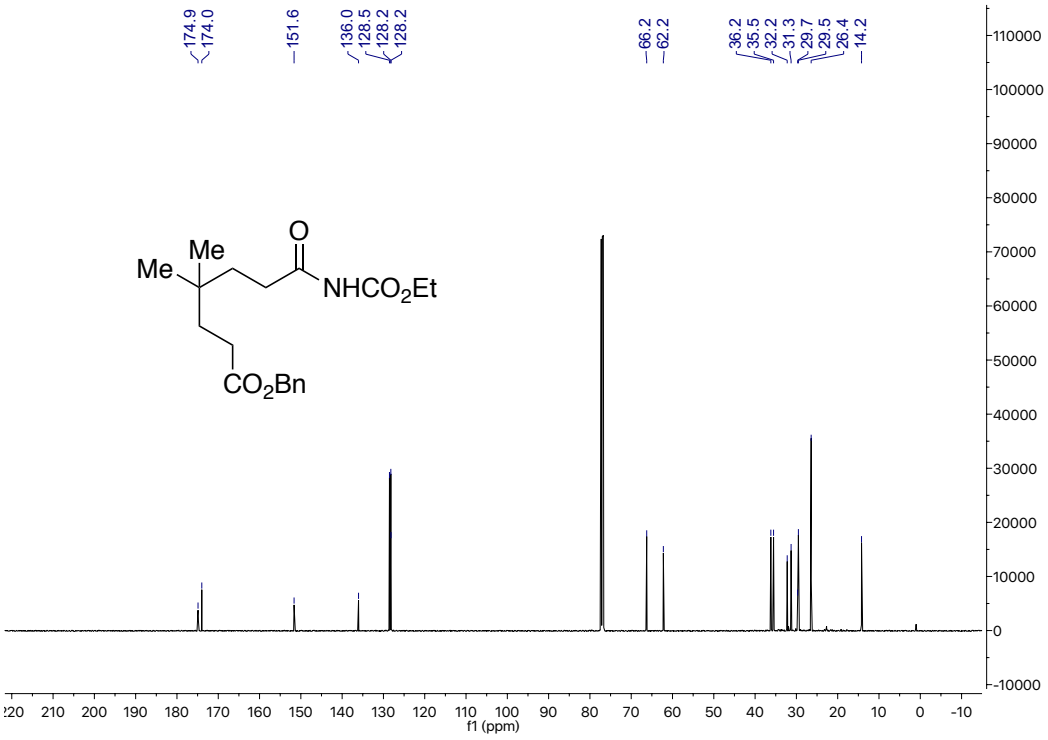
7.28
5.13
4.25
4.24
4.22
4.21
2.76
2.75
2.73
2.38
2.37
2.37
2.36
2.36
2.35
1.65
1.64
1.63
1.63
1.62
1.62
1.61
1.59
1.58
1.34
1.32
1.31
1.28
0.92
Me
Me
O
NHCO2Et
CO2Bn
6.09
2.07
2.00
1.95
2.12
4.71
3.69
6.97
f1 (ppm)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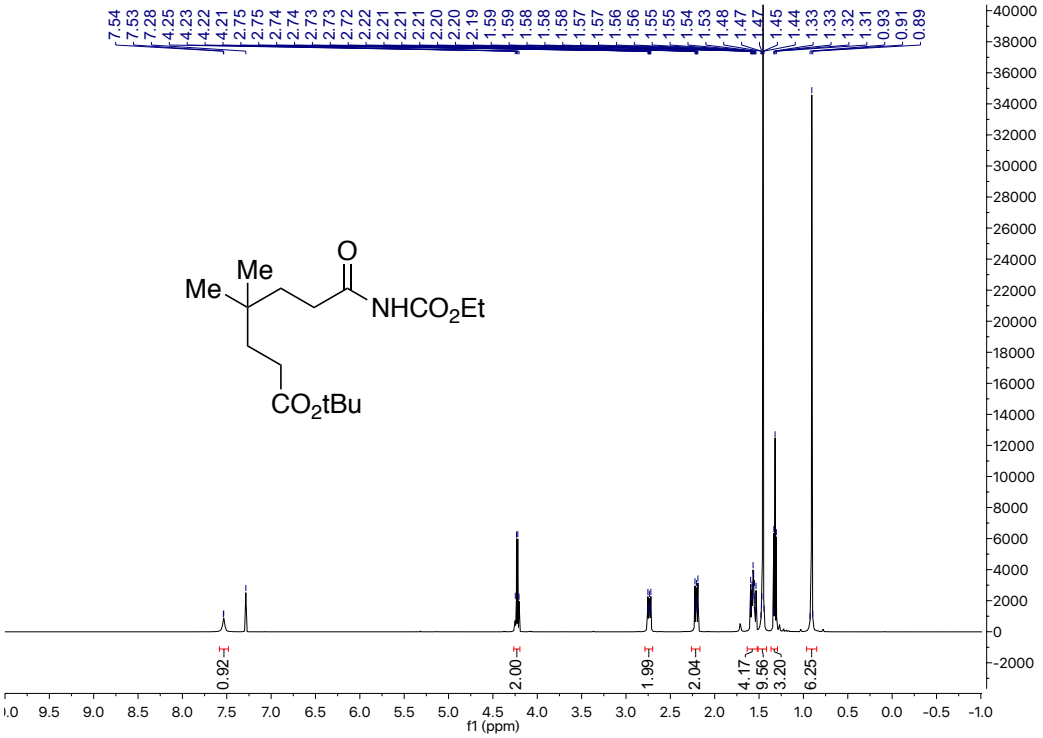
174.0
151.6
136.0
128.5
128.2
128.2
66.2
62.2
36.2
35.5
32.2
31.3
29.7
29.5
26.4
14.2
Me
Me
O
NHCO2Et
CO2Bn
f1 (ppm)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7.28
4.25
4.23
4.22
4.21
2.75
2.75
2.74
2.74
2.73
2.73
2.72
2.22
2.21
2.21
2.21
2.20
2.20
2.19
1.59
1.59
1.58
1.58
1.58
1.57
1.57
1.56
1.56
1.55
1.55
1.54
1.53
1.48
1.47
1.47
1.45
1.44
1.33
1.33
1.32
1.31
0.93
0.91
0.89
Me
Me
O
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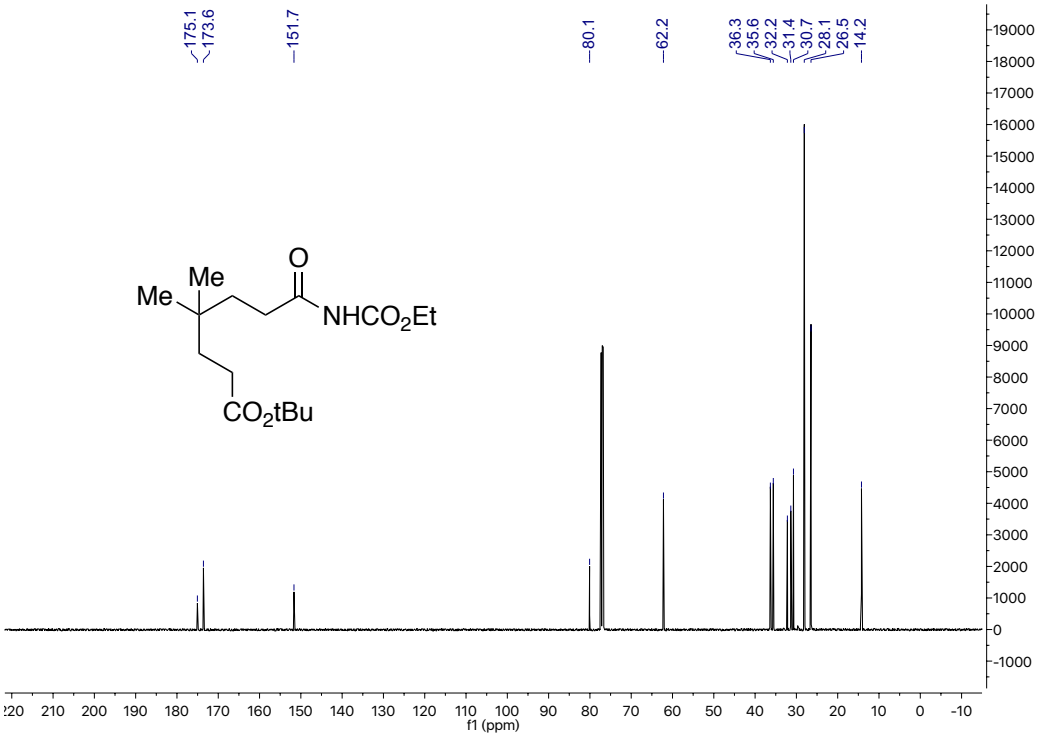
CO2tBu
0.92
2.00
1.99
2.04
4.17
9.56
3.20
6.25
f1 (ppm)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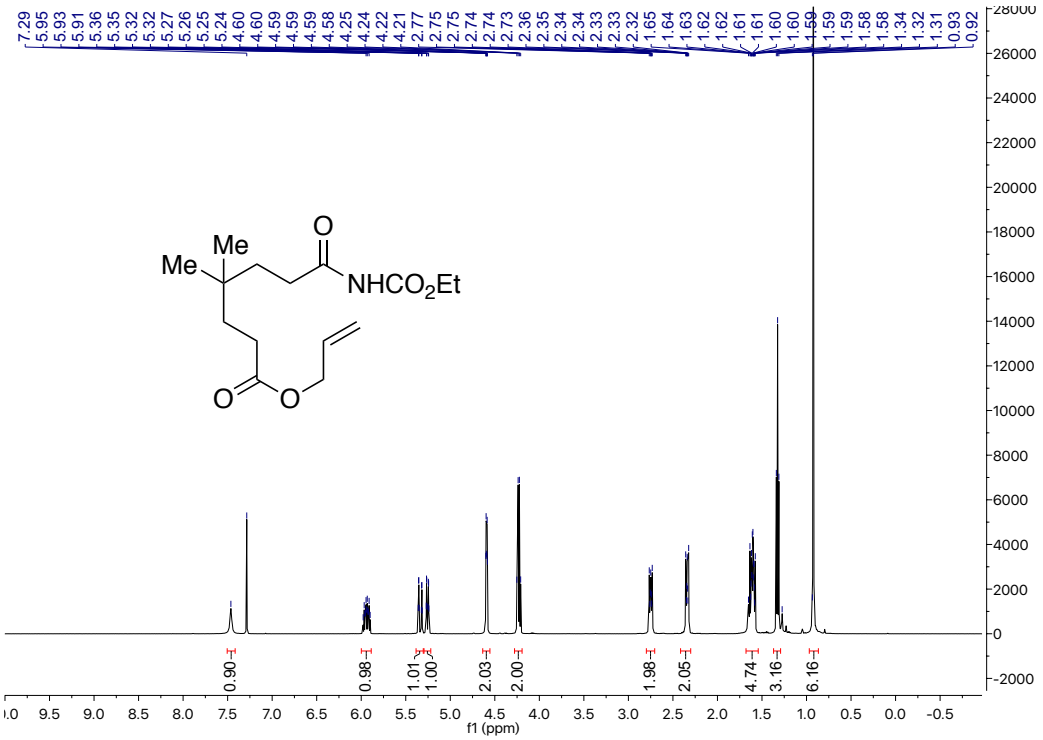
151.7
80.1
62.2
36.3
35.6
32.2
31.4
30.7
28.1
26.5
14.2
Me
Me
O
NHCO2Et
CO2tBu
f1 (ppm)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5.91
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5.35
5.32
5.32
5.27
5.26
5.25
5.24
4.60
4.59
4.59
4.59
4.58
4.25
4.24
4.22
4.21
2.77
2.75
2.74
2.74
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2.34
2.34
2.33
2.33
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1.62
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1.61
1.61
1.60
1.60
1.59
1.59
1.59
1.58
1.58
1.34
1.32
1.31
0.93
0.92
Me
Me
O
NHCO2Et
O
O
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1.00
2.03
2.00
1.98
2.05
4.74
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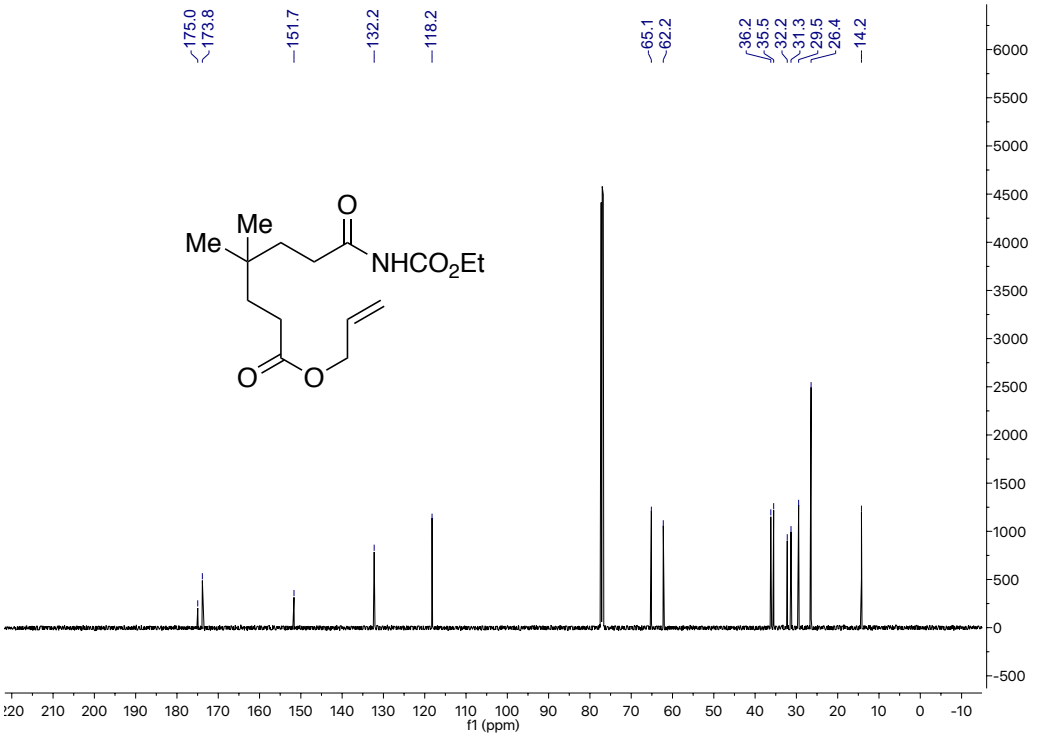
6.16
f1 (ppm)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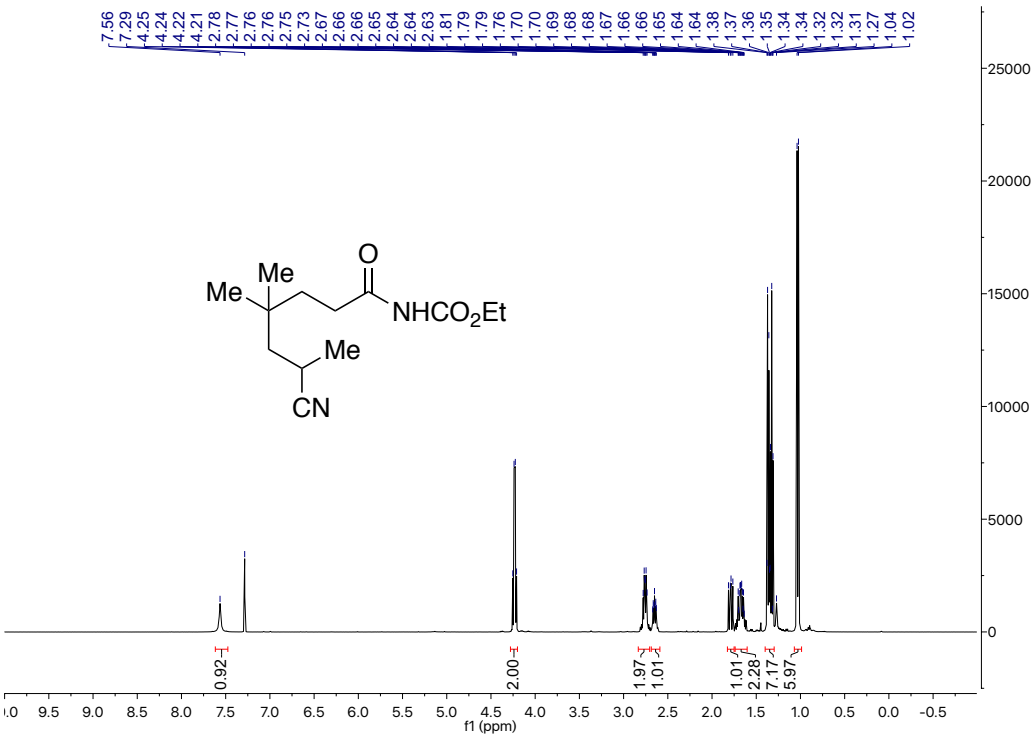
173.8
151.7
132.2
118.2
65.1
62.2
36.2
35.5
32.2
31.3
29.5
26.4
14.2
Me
Me
O
NHCO2Et
O
O
f1 (ppm)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2.75
2.73
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2.65
2.64
2.64
2.63
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1.76
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1.69
1.68
1.68
1.67
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1.66
1.65
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1.64
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1.36
1.35
1.34
1.34
1.32
1.32
1.31
1.27
1.04
1.02
Me
Me
O
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Me
CN
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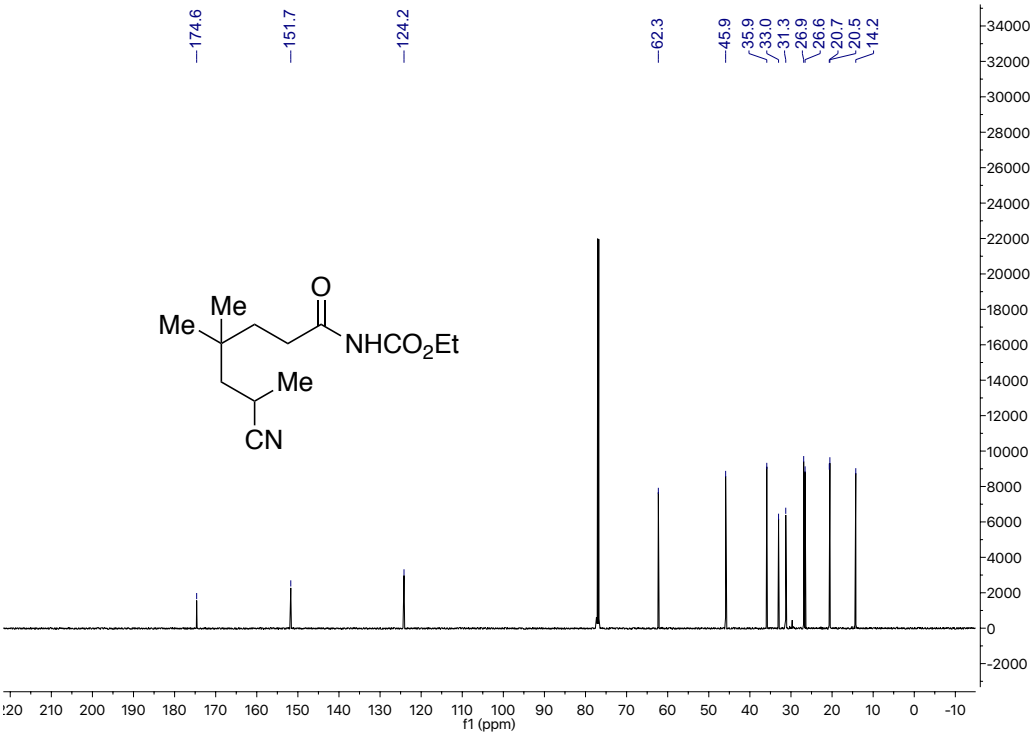
2.00
1.97
1.01
1.01
2.28
7.17
5.97
f1 (ppm)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124.2
62.3
45.9
35.9
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31.3
26.9
26.6
20.7
20.5
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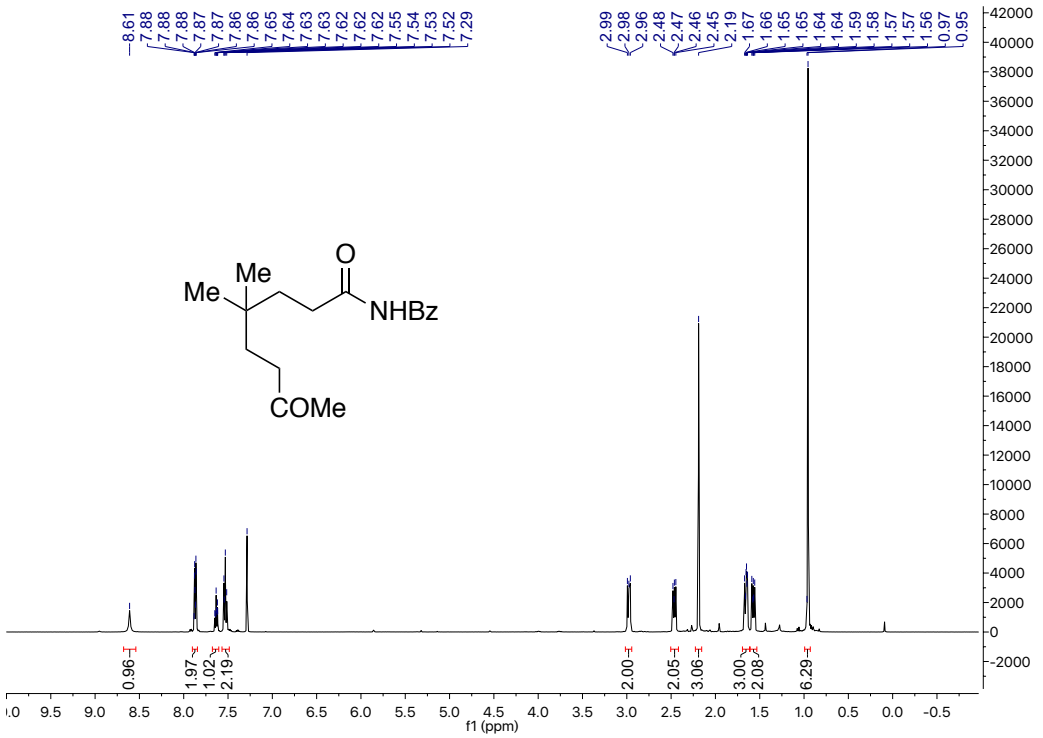
Me
Me
O
NHCO2Et
Me
CN
f1 (ppm)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7.88
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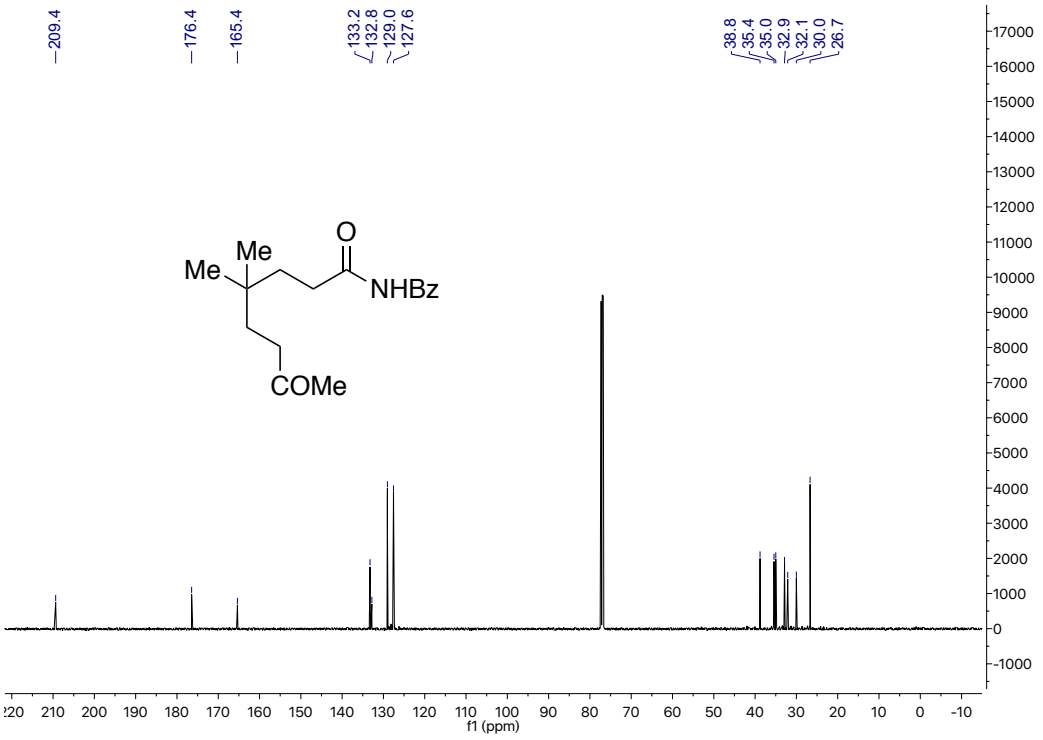
7.86
7.65
7.64
7.63
7.63
7.62
7.62
7.62
7.55
7.54
7.53
7.52
7.29
2.99
2.98
2.96
2.48
2.47
2.46
2.45
2.19
1.67
1.66
1.65
1.65
1.64
1.64
1.59
1.58
1.57
1.57
1.56
0.97
0.95
O
Me
Me
NHBz
COMe
0.96
1.97
1.02
2.19
2.00
2.05
3.06
3.00
2.08
6.29
f1 (ppm)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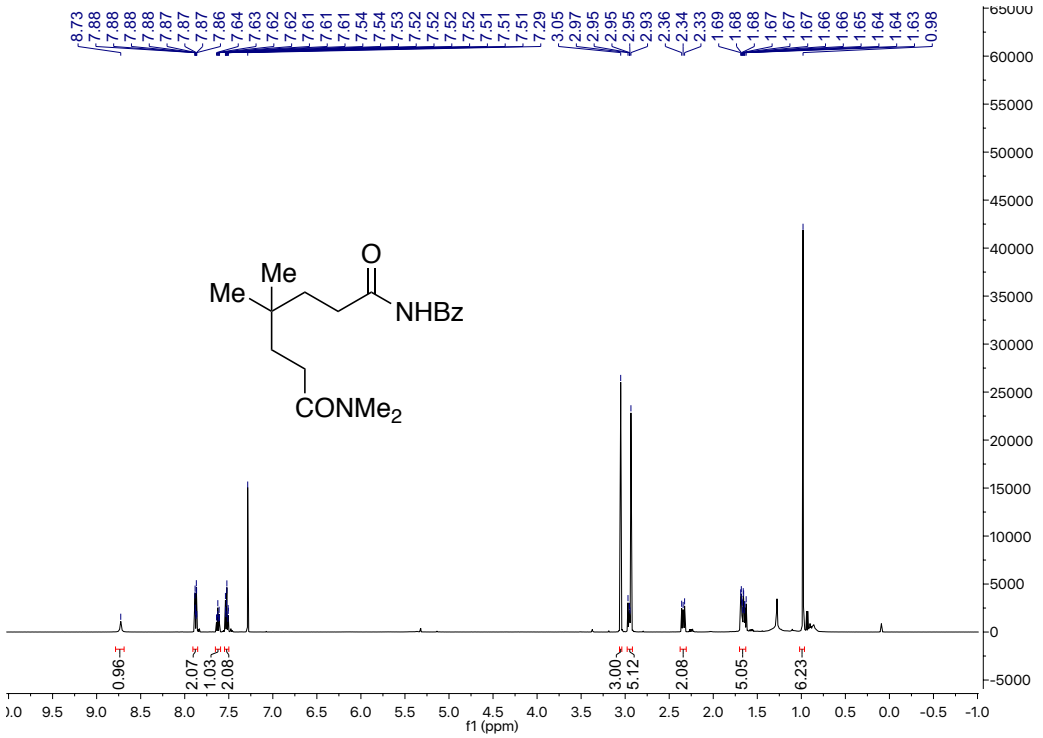
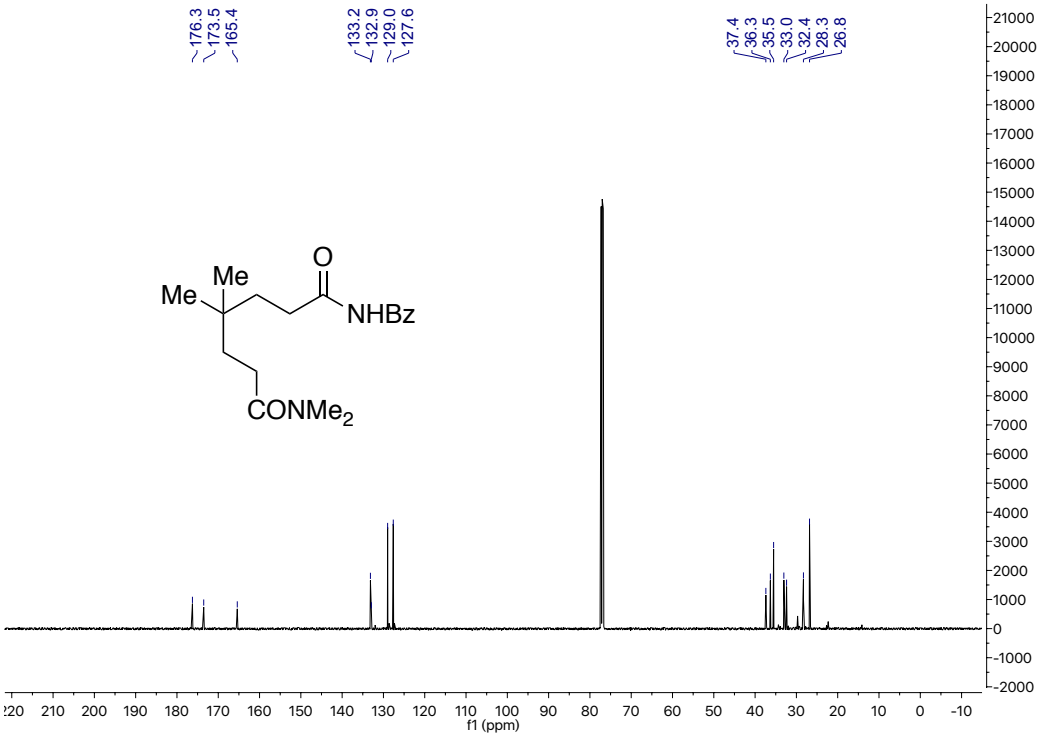
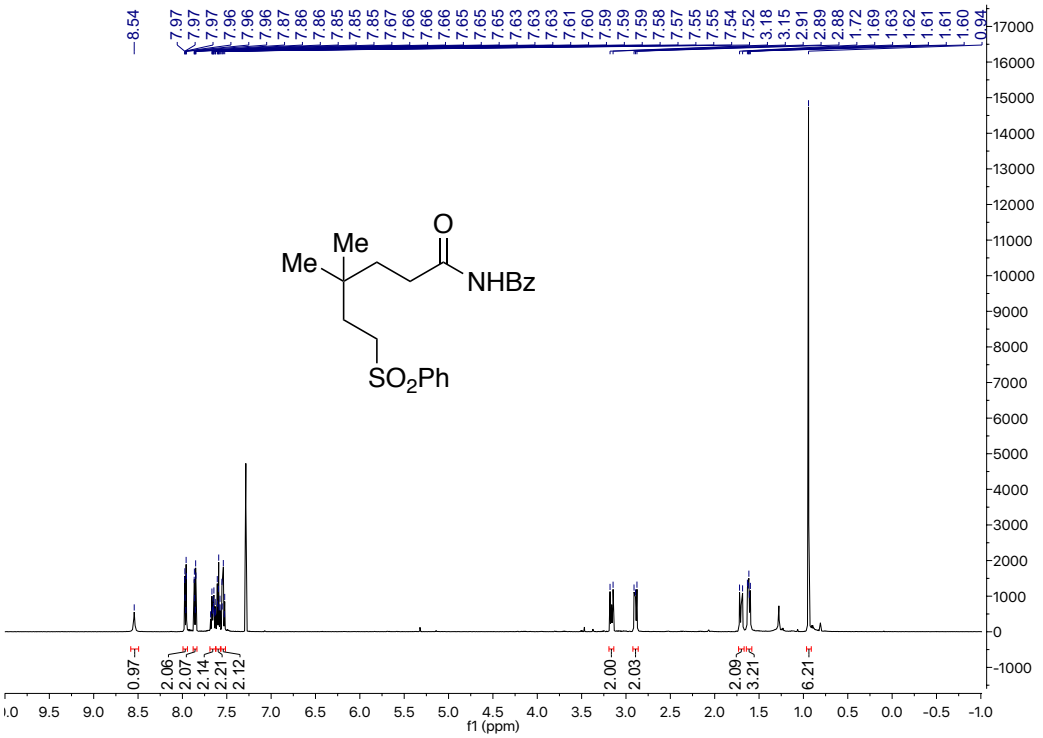
176.4
165.4
133.2
132.8
129.0
127.6
38.8
35.4
35.0
32.9
32.1
30.0
26.7
O
Me
Me
NHBz
COMe
f1 (ppm)


8.73 7.88 7.88 7.88 7.88 7.87 7.87 7.87 7.86 7.64 7.63 7.62 7.62 7.61 7.61 7.61 7.54 7.54 7.53 7.52 7.52 7.52 7.52 7.51 7.51 7.51 7.29 3.05 2.97 2.95 2.95 2.95 2.93 2.36 2.34 2.33 1.69 1.68 1.68 1.67 1.67 1.67 1.66 1.66 1.65 1.64 1.64 1.63 0.98
O
Me
Me
NHBz
CONMe2
0.96 2.07 1.03 2.08 3.00 5.12 2.08 5.05 6.23
f1 (ppm)


176.3 173.5 165.4 133.2 132.9 129.0 127.6 37.4 36.3 35.5 33.0 32.4 28.3 26.8
O
Me
Me
NHBz
CONMe2
f1 (ppm)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7.96
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7.85
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7.67
7.66
7.66
7.65
7.65
7.65
7.63
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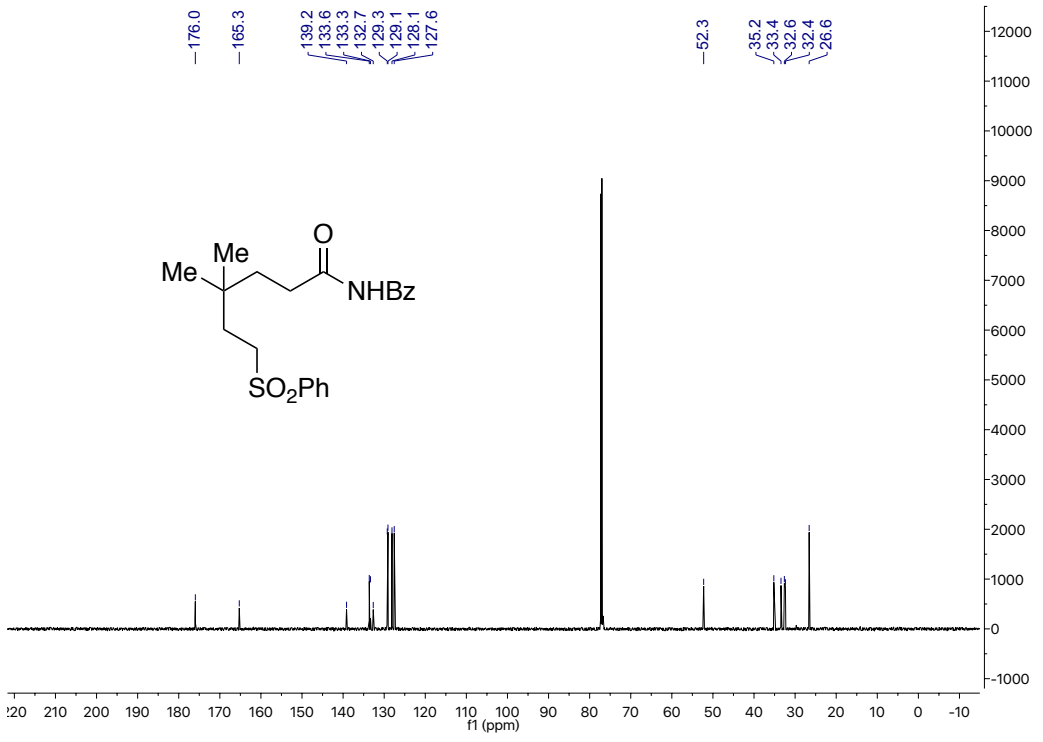
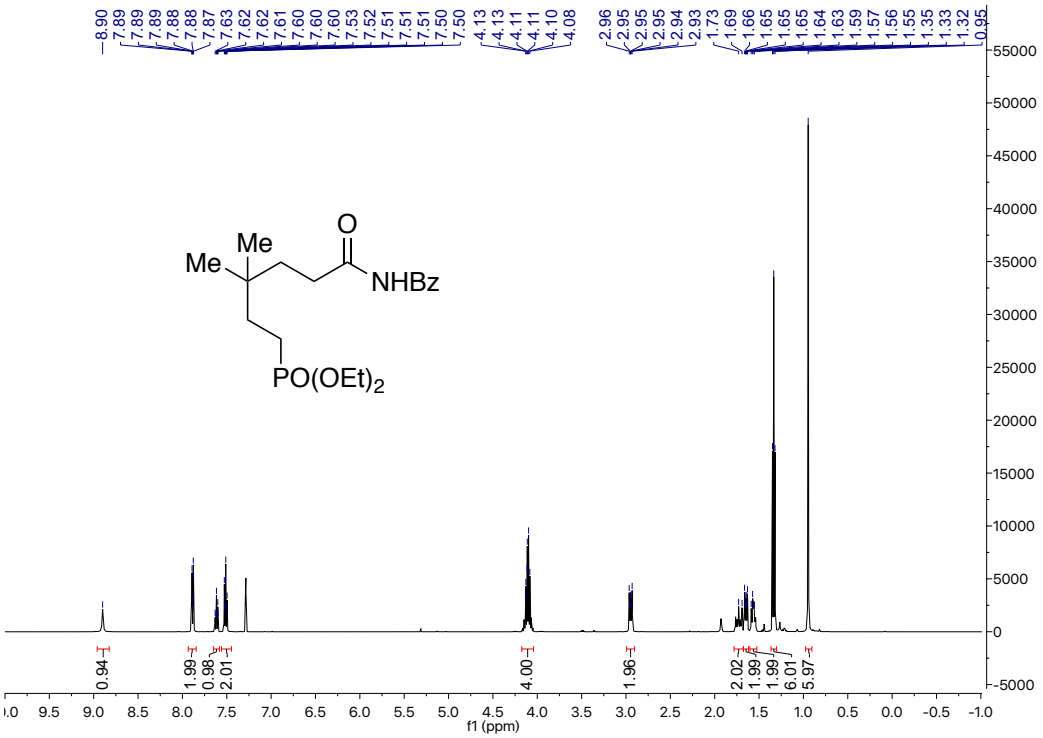
7.63
7.61
7.60
7.59
7.59
7.59
7.58
7.57
7.55
7.55
7.54
7.52
3.18
3.15
2.91
2.89
2.88
1.72
1.69
1.63
1.62
1.61
1.61
1.60
0.94
Me
Me
O
NHBz
SO2Ph
0.97
2.06
2.07
2.14
2.21
2.12
2.00
2.03
2.09
3.21
6.21
f1 (ppm)


176.0
165.3
139.2
133.6
133.3
132.7
129.3
129.1
128.1
127.6
52.3
35.2
33.4
32.6
32.4
26.6
Me
Me
O
NHBz
SO2Ph
f1 (ppm)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7.89
7.89
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7.87
7.63
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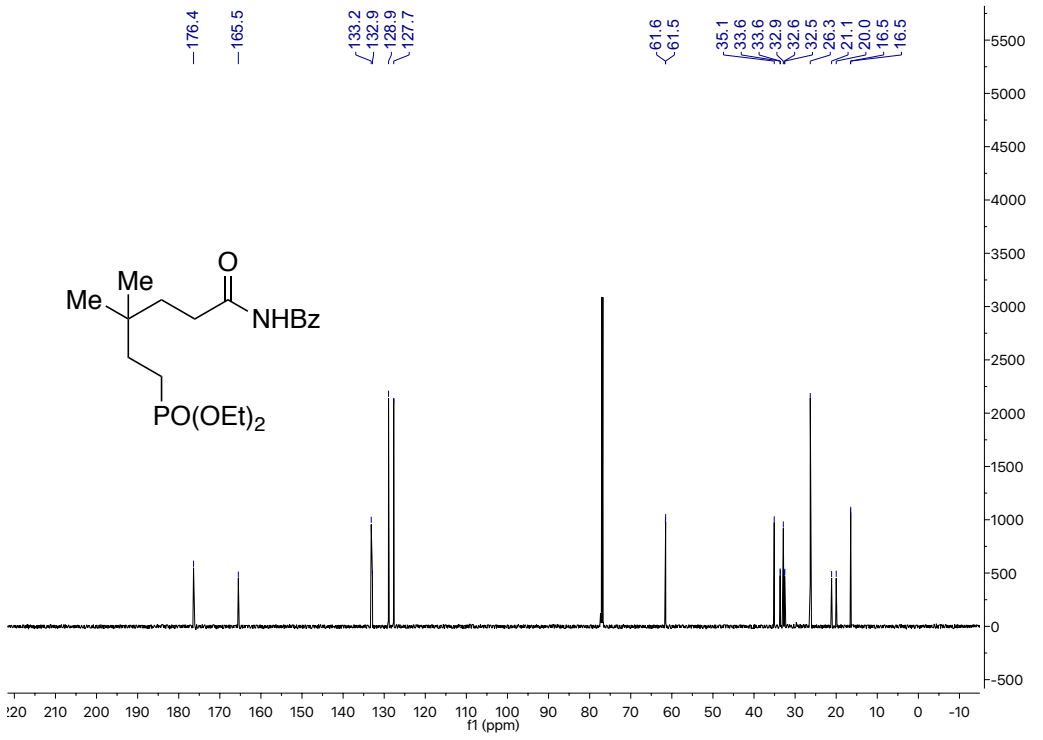
7.62
7.61
7.60
7.60
7.60
7.53
7.52
7.51
7.51
7.51
7.50
7.50
4.13
4.13
4.11
4.11
4.10
4.08
2.96
2.95
2.95
2.95
2.94
2.93
1.73
1.69
1.66
1.65
1.65
1.65
1.64
1.63
1.59
1.57
1.56
1.55
1.35
1.33
1.32
0.95
O
Me
Me
NHBz
PO(OEt)2
0.94
1.99
0.98
2.01
4.00
1.96
2.02
1.99
1.99
6.01
5.97
f1 (ppm)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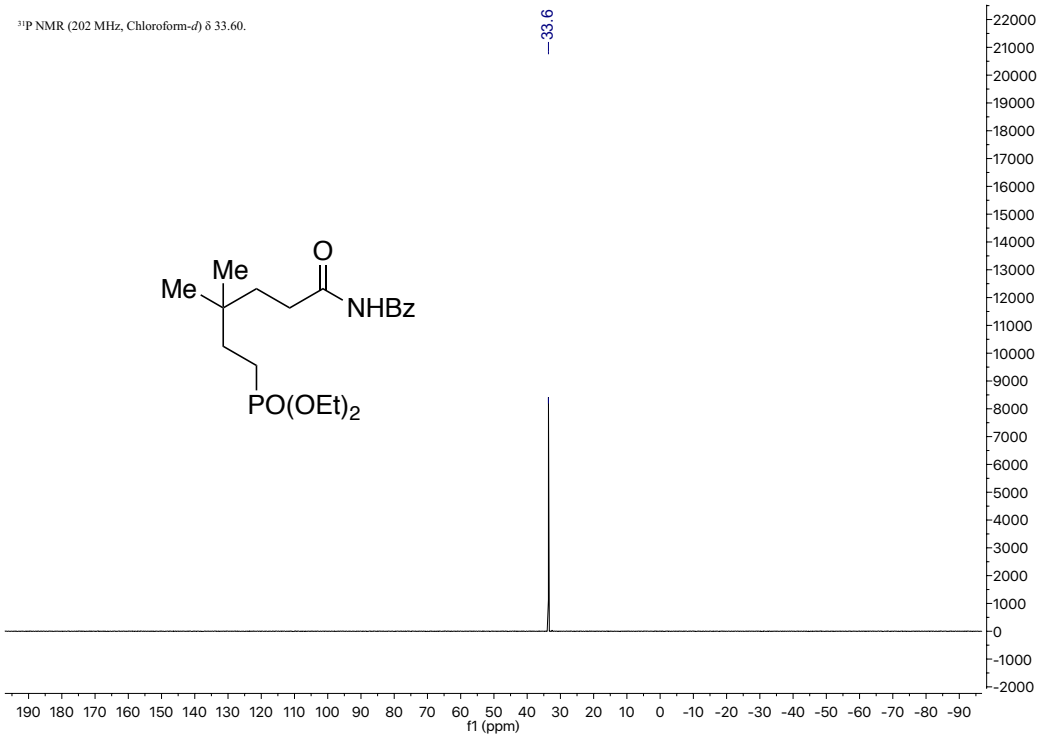
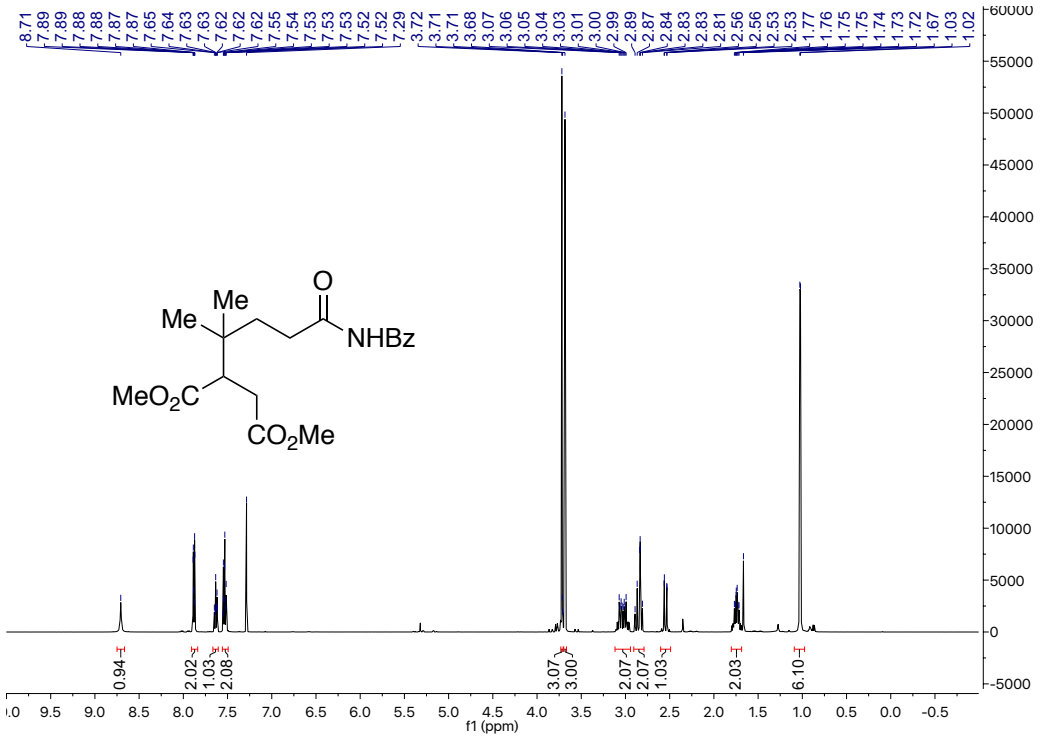
165.5
133.2
132.9
128.9
127.7
61.6
61.5
35.1
33.6
33.6
32.9
32.6
32.5
26.3
21.1
20.0
16.5
16.5
O
Me
Me
NHBz
PO(OEt)2
f1 (ppm)

^{31}P NMR (202 MHz, Chloroform-*d*) δ 33.60.

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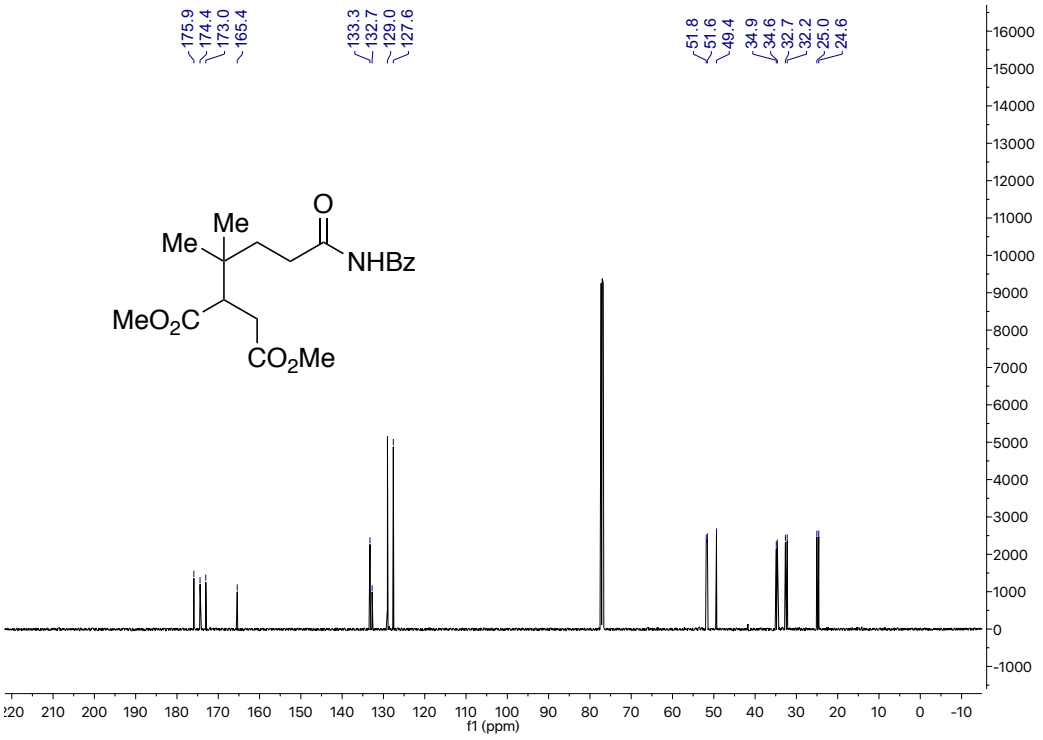
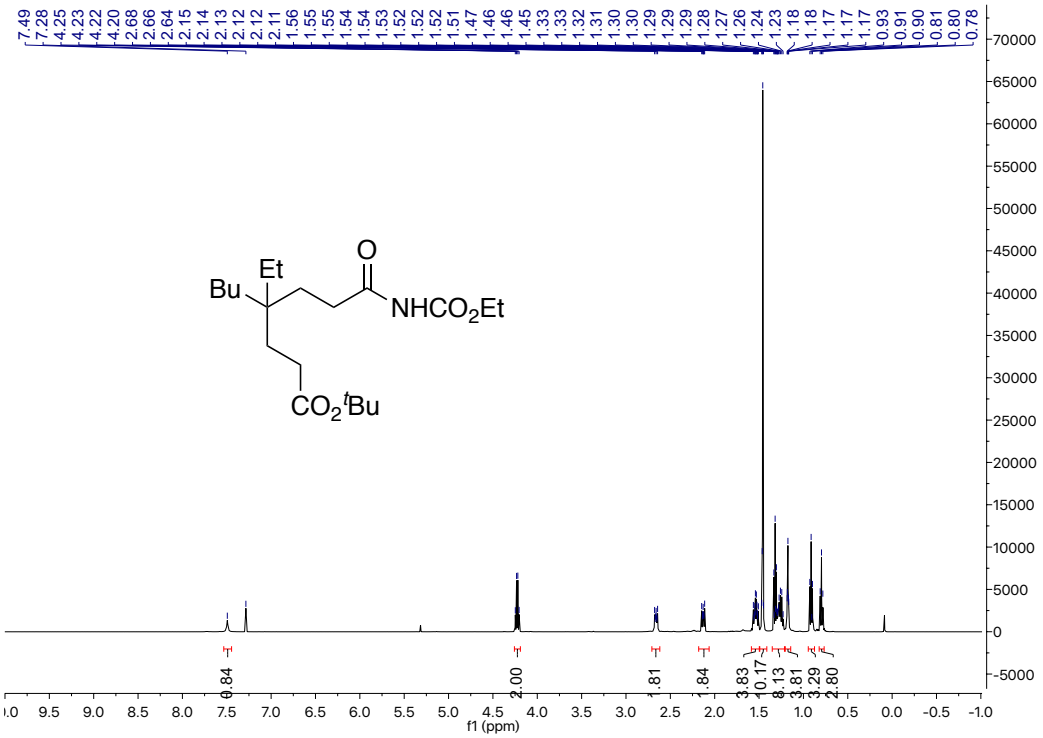
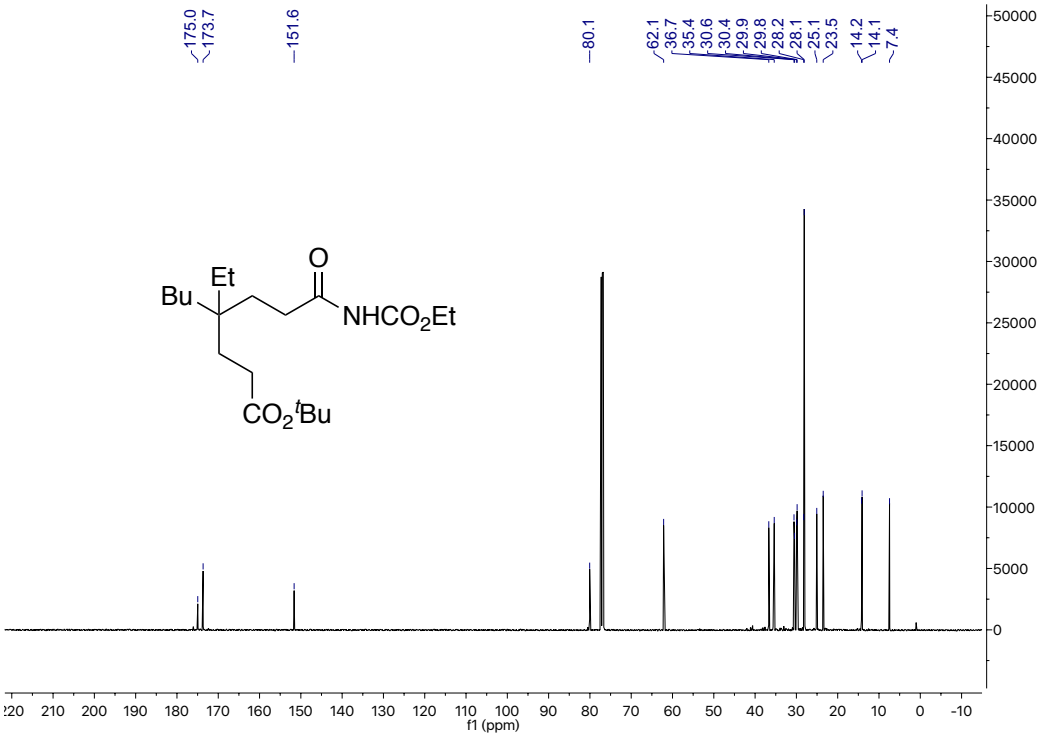
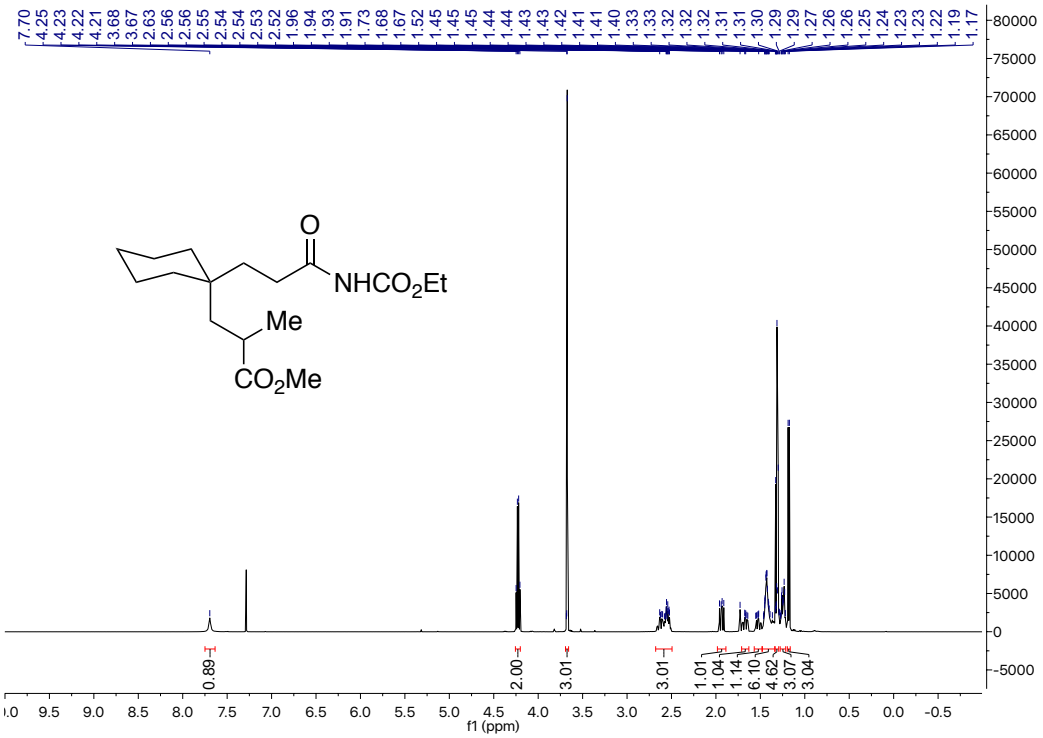
7.62
7.55
7.54
7.53
7.53
7.53
7.52
7.52
7.29
3.72
3.71
3.71
3.68
3.07
3.06
3.05
3.04
3.03
3.01
3.00
2.99
2.89
2.87
2.84
2.83
2.83
2.81
2.56
2.56
2.53
2.53
1.77
1.76
1.75
1.75
1.74
1.73
1.72
1.67
1.03
1.02
Me
Me
O
NHBz
MeO2C
CO2Me
0.94
2.02
1.03
2.08
3.07
3.00
2.07
2.07
1.03
2.03
6.10
f1 (ppm)


175.9
174.4
173.0
165.4
133.3
132.7
129.0
127.6
51.8
51.6
49.4
34.9
34.6
32.7
32.2
25.0
24.6
Me
Me
O
NHBz
MeO2C
CO2Me
f1 (ppm)


Bu
Et
O
NHCO2Et
CO2tBu
f1 (ppm)


Bu
Et
O
NHCO2Et
CO2tBu
f1 (ppm)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3.67
2.63
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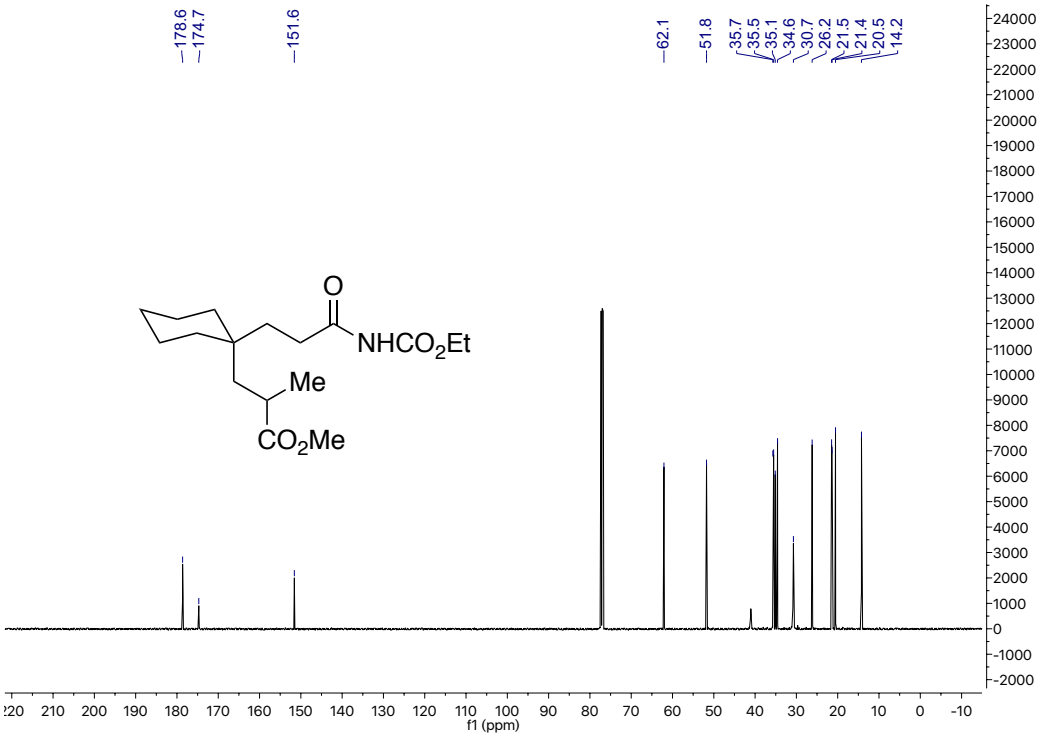
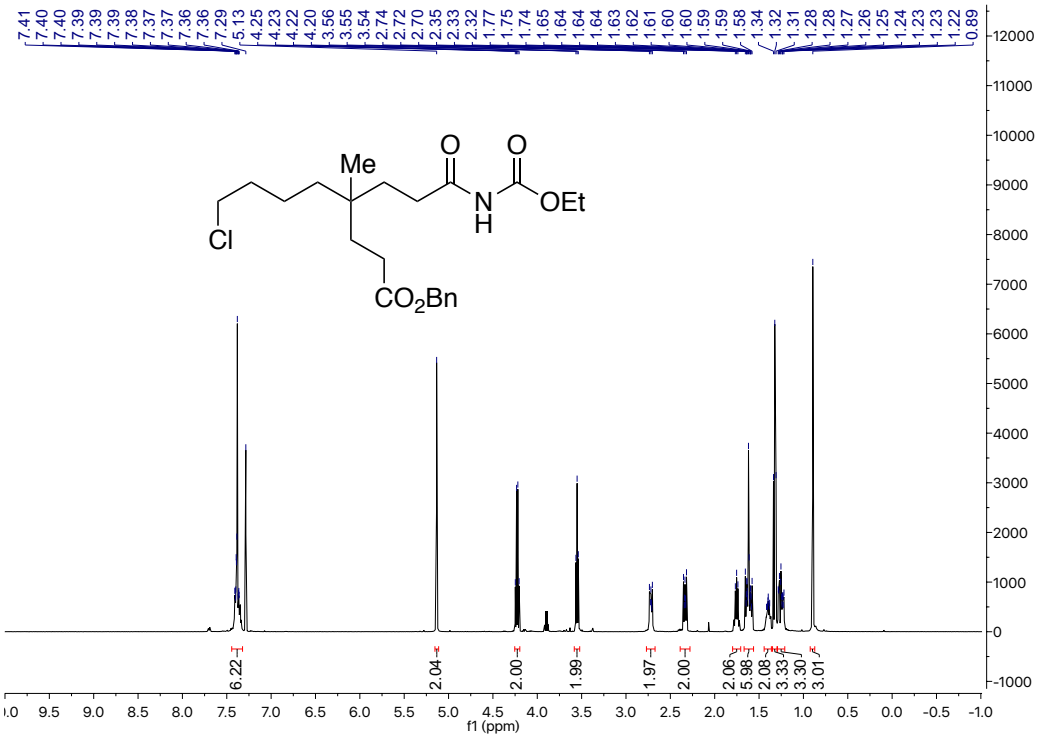
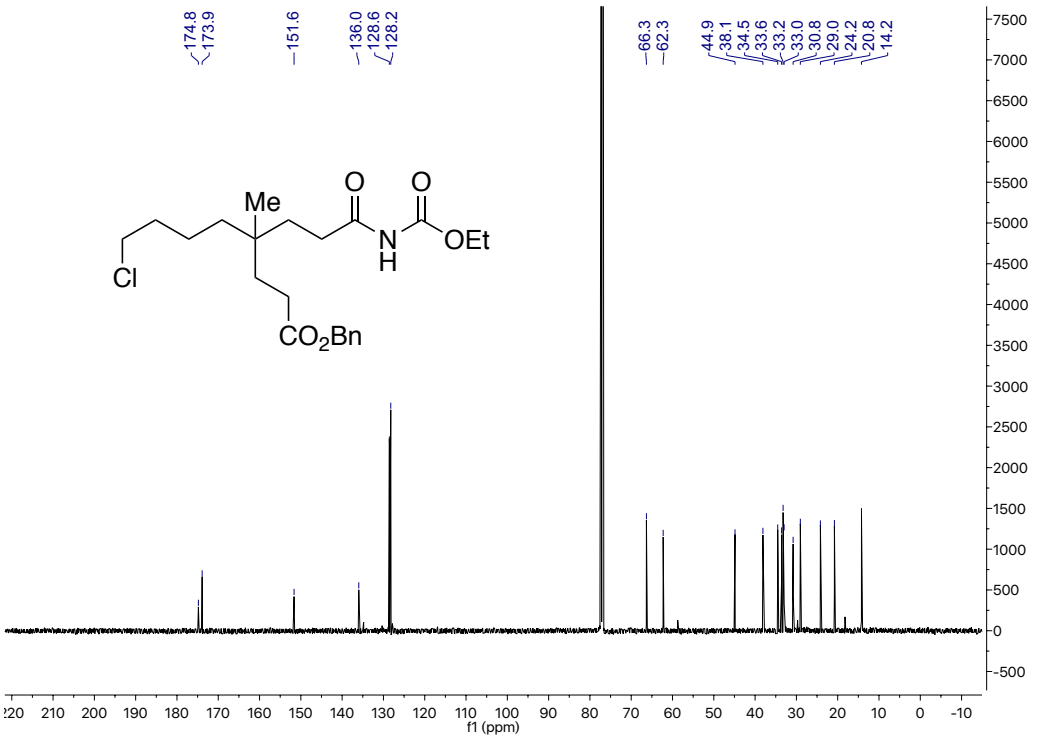
2.56
2.55
2.54
2.54
2.53
2.52
1.96
1.94
1.93
1.91
1.73
1.68
1.67
1.52
1.45
1.45
1.45
1.44
1.44
1.43
1.43
1.42
1.41
1.41
1.40
1.33
1.33
1.32
1.32
1.32
1.31
1.31
1.30
1.29
1.29
1.27
1.26
1.26
1.25
1.24
1.23
1.23
1.22
1.19
1.17
O
NHCO2Et
Me
CO2Me
0.89
2.00
3.01
3.01
1.01
1.04
1.14
6.10
4.62
3.07
3.04
f1 (ppm)


178.6
174.7
151.6
62.1
51.8
35.7
35.5
35.1
34.6
30.7
26.2
21.5
21.4
20.5
14.2
O
NHCO2Et
Me
CO2Me
f1 (ppm)


7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.29 5.13 4.25 4.23 4.22 4.20 3.56 3.55 3.54 2.74 2.72 2.70 2.35 2.33 2.32 1.77 1.75 1.74 1.65 1.64 1.64 1.64 1.63 1.62 1.61 1.60 1.60 1.59 1.59 1.58 1.34 1.32 1.31 1.28 1.28 1.27 1.26 1.25 1.24 1.23 1.23 1.22 0.89
Me
O
O
N
H
OEt
Cl
CO2Bn
6.22
2.04
2.00
1.99
1.97
2.00
2.06
5.98
2.08
3.33
3.30
3.01
f1 (ppm)


174.8 173.9 151.6 136.0 128.6 128.2 66.3 62.3 44.9 38.1 34.5 33.6 33.2 33.0 30.8 29.0 24.2 20.8 14.2
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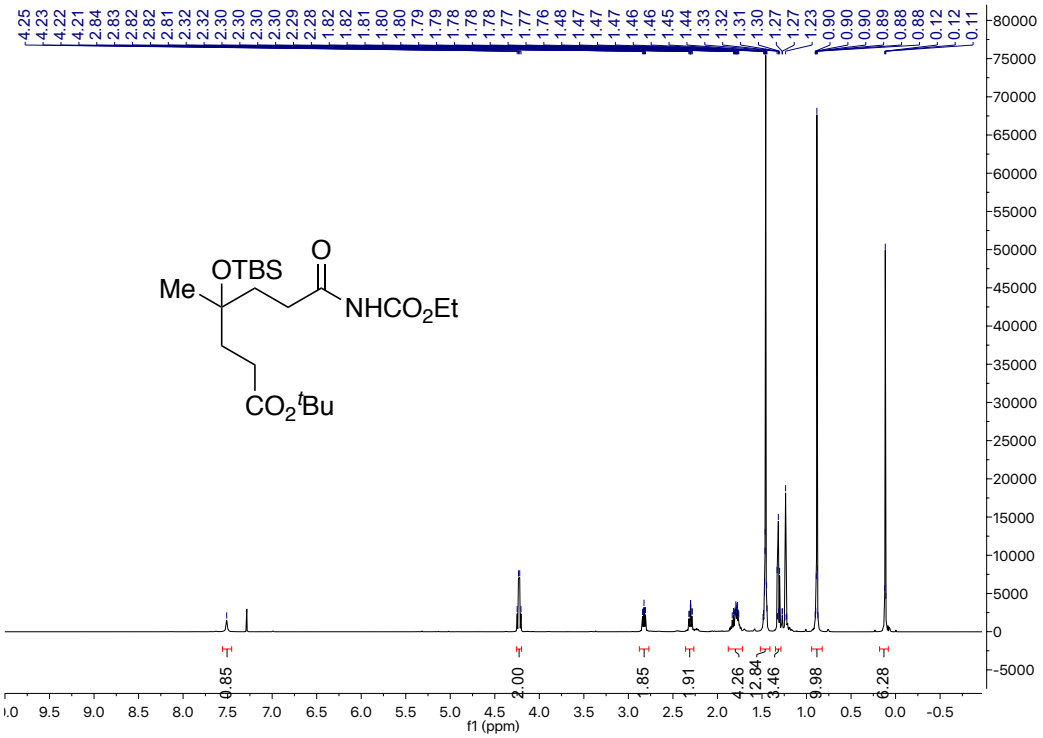
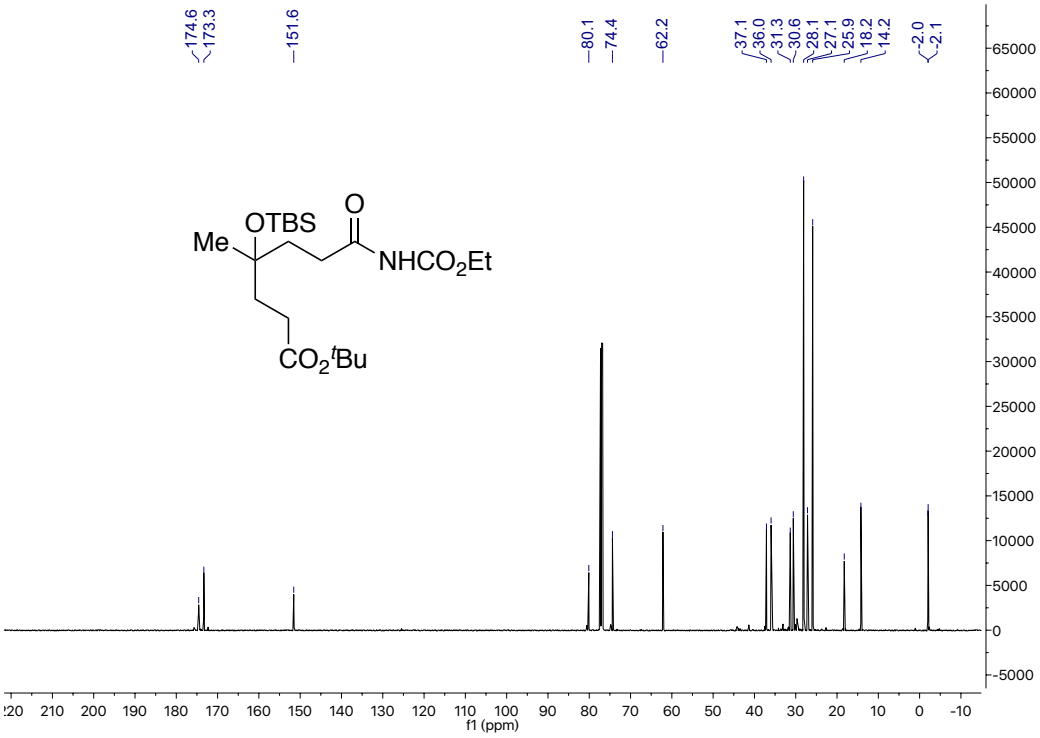
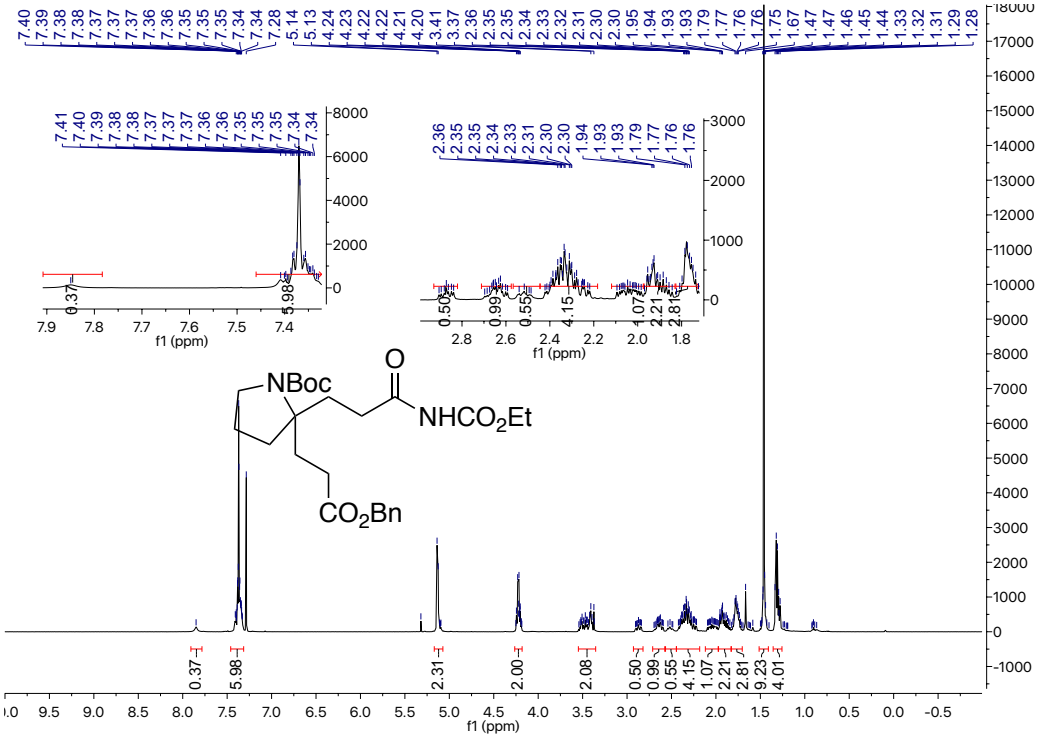
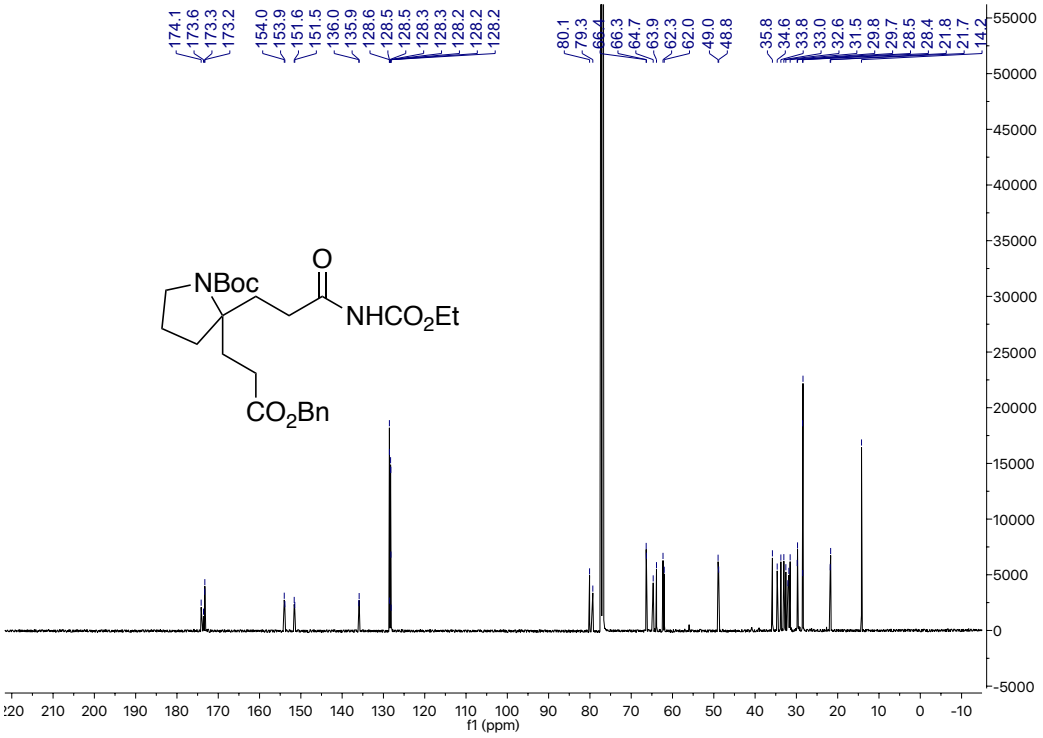
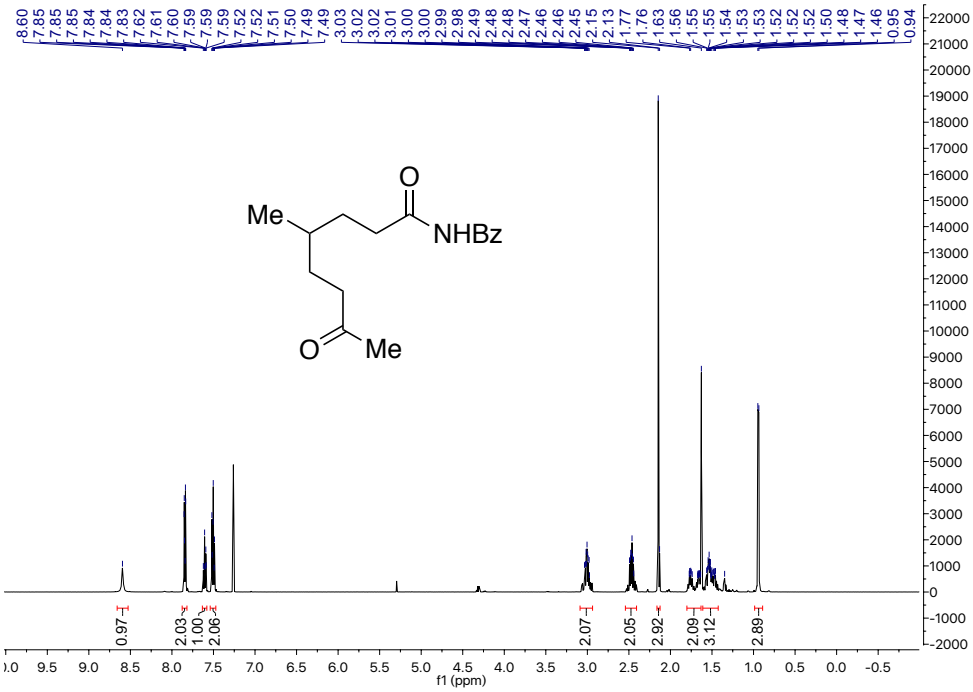
O
N
H
OEt
Cl
CO2Bn
f1 (ppm)

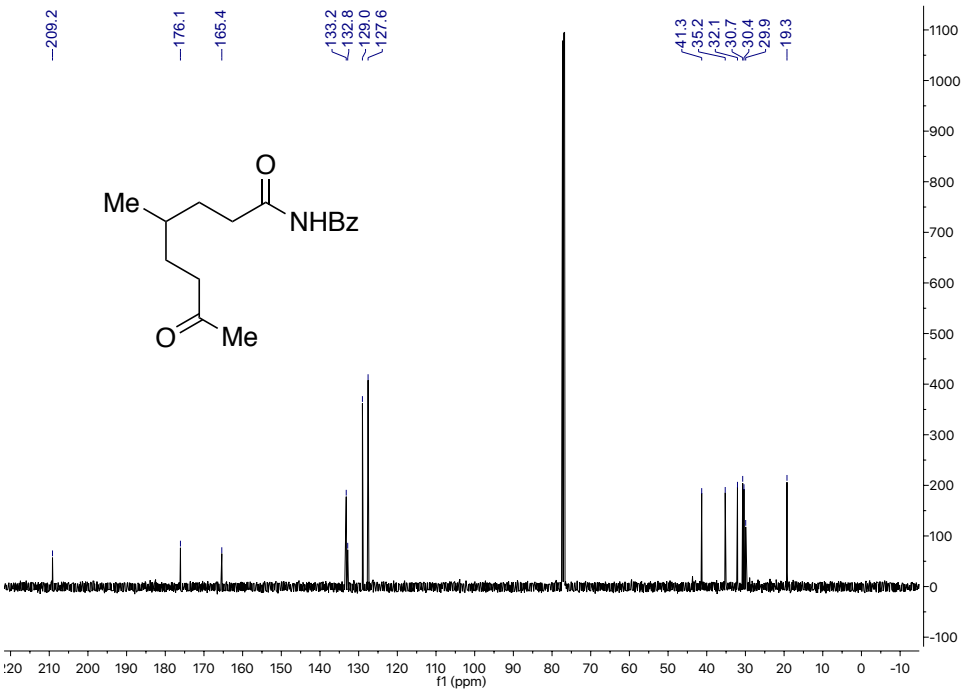

Me
OTBS
O
NHCO2Et
CO2tBu
f1 (ppm)


Me
OTBS
O
NHCO2Et
CO2tBu
f1 (ppm)


NBoc
O
NHCO2Et
CO2Bn
f1 (ppm)


NBoc
O
NHCO2Et
CO2Bn
f1 (ppm)


8.60 7.85 7.85 7.85 7.84 7.84 7.83 7.62 7.61 7.60 7.59 7.59 7.59 7.52 7.52 7.51 7.50 7.49 7.49
3.03 3.02 3.02 3.01 3.00 3.00 2.99 2.98 2.49 2.48 2.48 2.47 2.46 2.46 2.45 2.15 2.13 1.77 1.76 1.63 1.56 1.55 1.55 1.54 1.53 1.53 1.52 1.52 1.52 1.50 1.48 1.47 1.46 0.95 0.94
Me
O
NHBz
O
Me
0.97
2.03
1.00
2.06
2.07
2.05
2.92
2.09
3.12
2.89
f1 (ppm)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132.8
129.0
127.6
41.3
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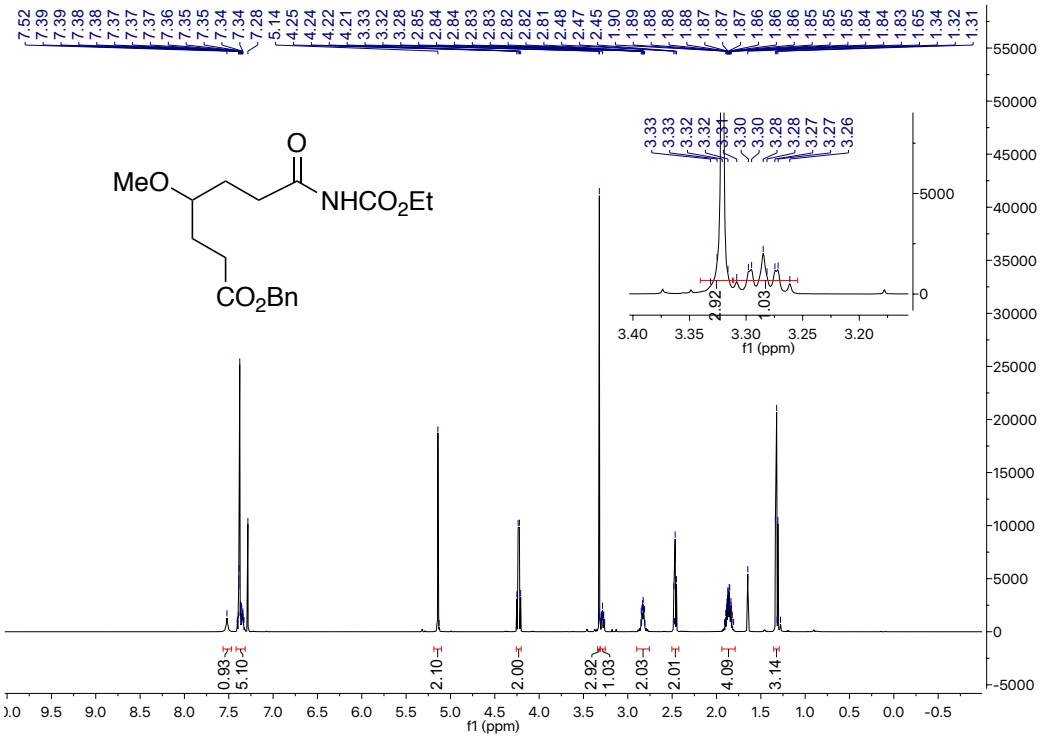
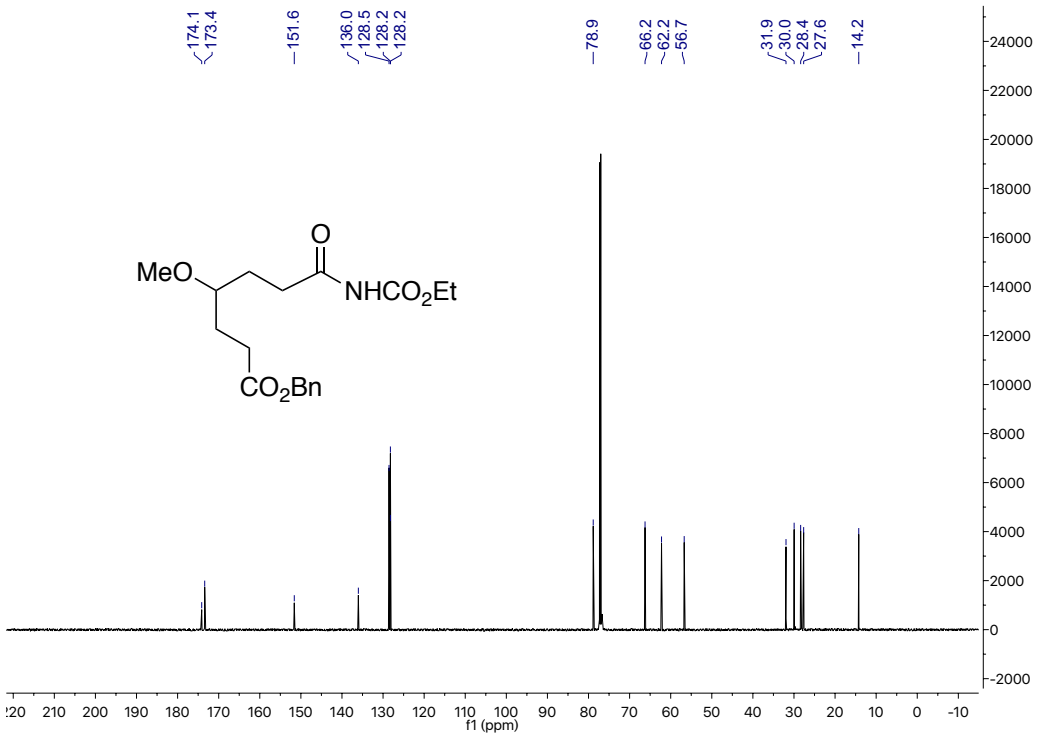
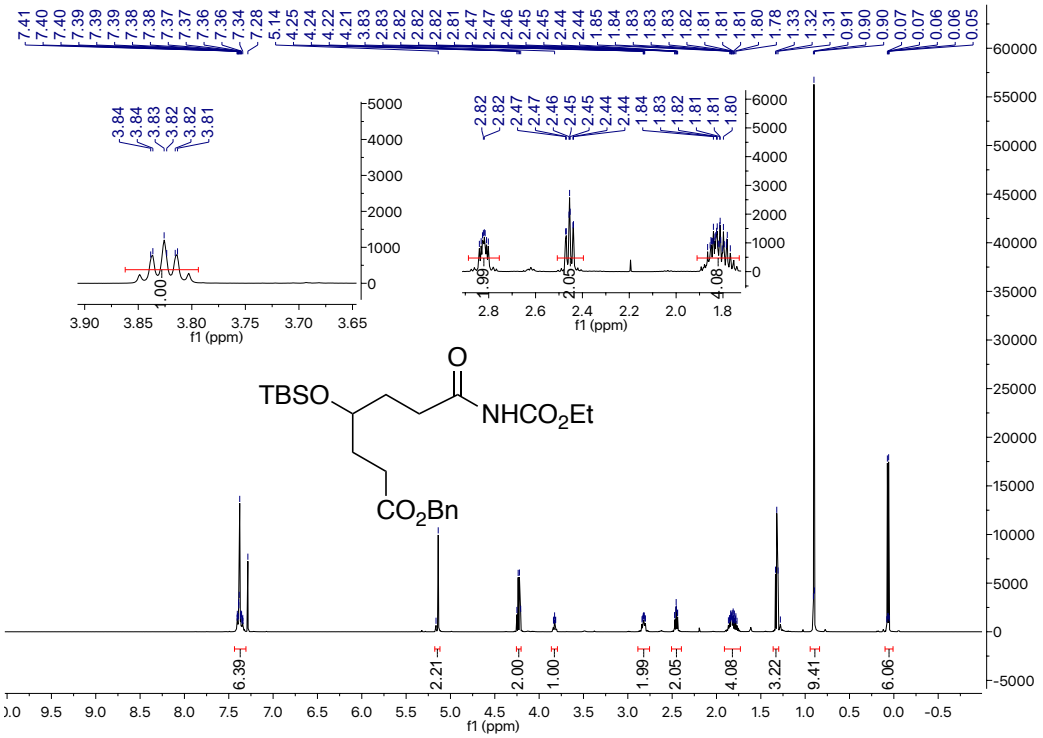
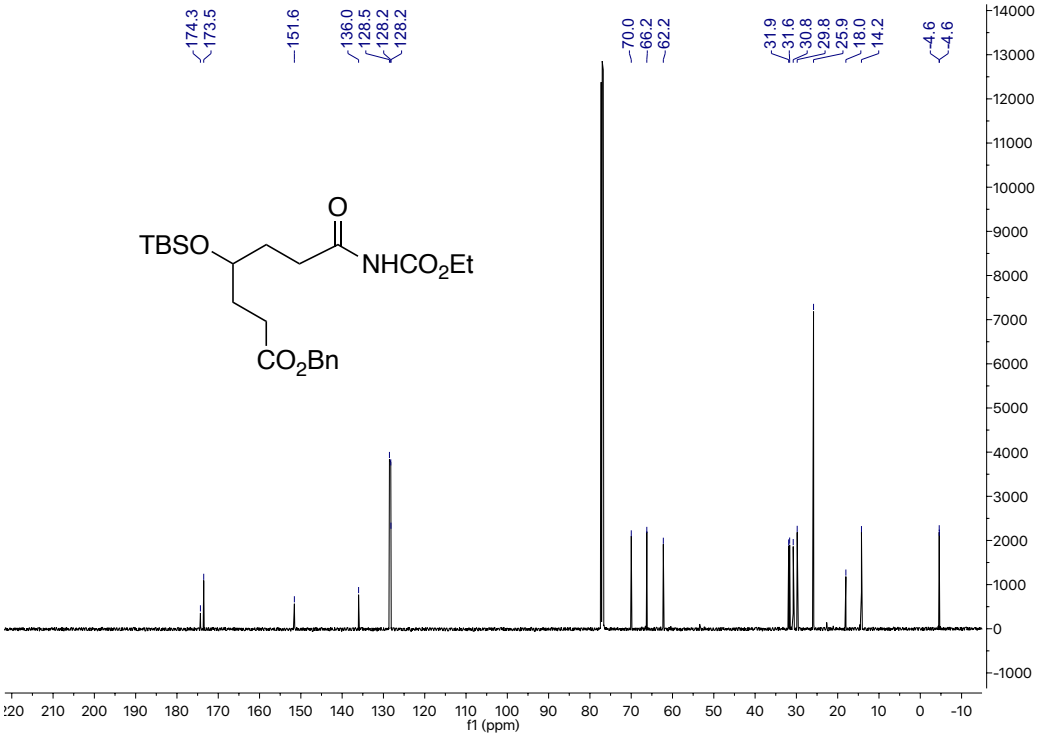
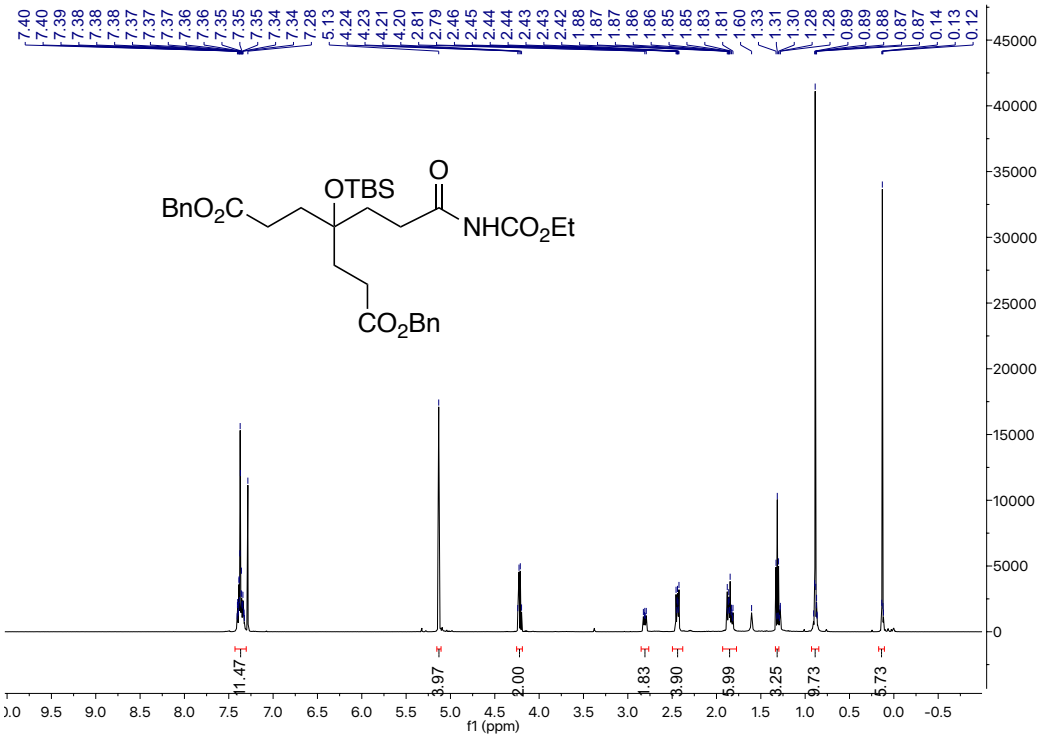
32.1
30.7
30.4
29.9
19.3
Me
O
NHBz
O
Me
f1 (ppm)

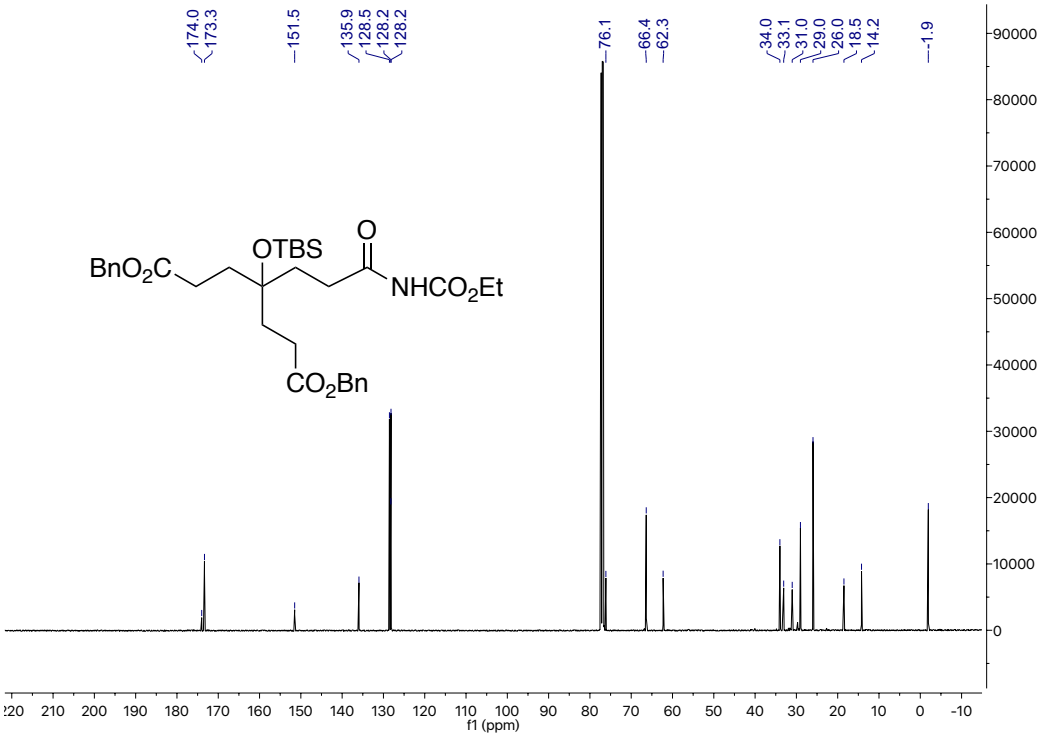

MeO
O
NHCO2Et
CO2Bn
f1 (ppm)


MeO
O
NHCO2Et
CO2Bn
f1 (ppm)


TBSO
O
NHCO2Et
CO2Bn
f1 (ppm)


TBSO
O
NHCO2Et
CO2Bn
f1 (ppm)


BnO2C
OTBS
O
NHCO2Et
CO2Bn
f1 (ppm)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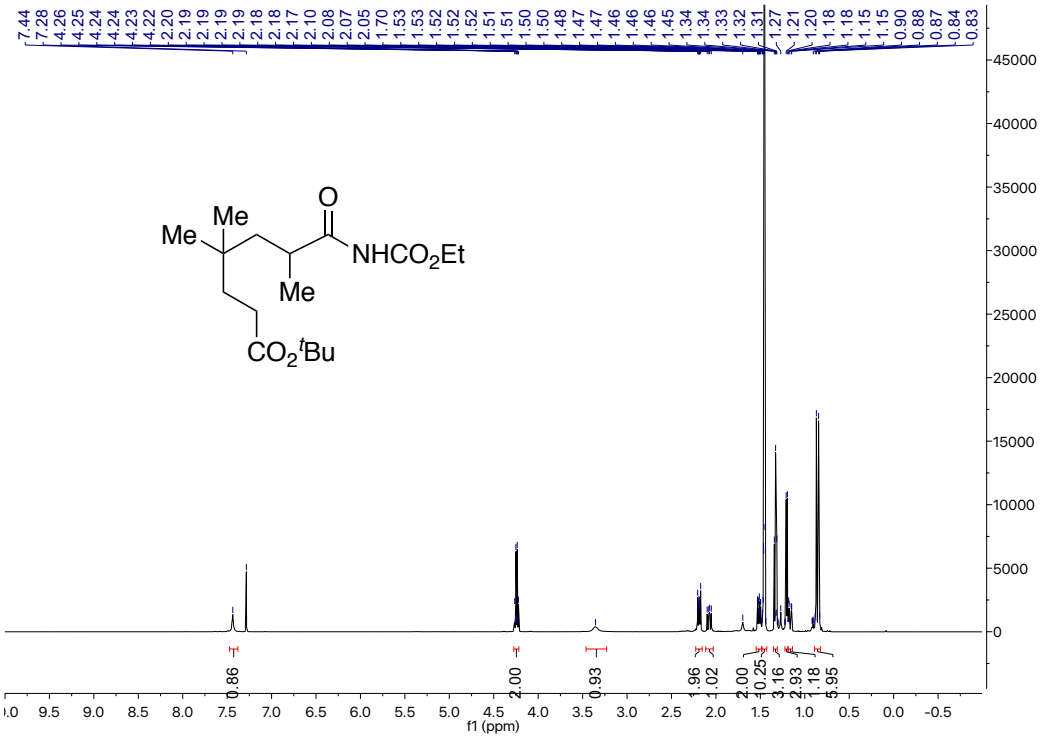
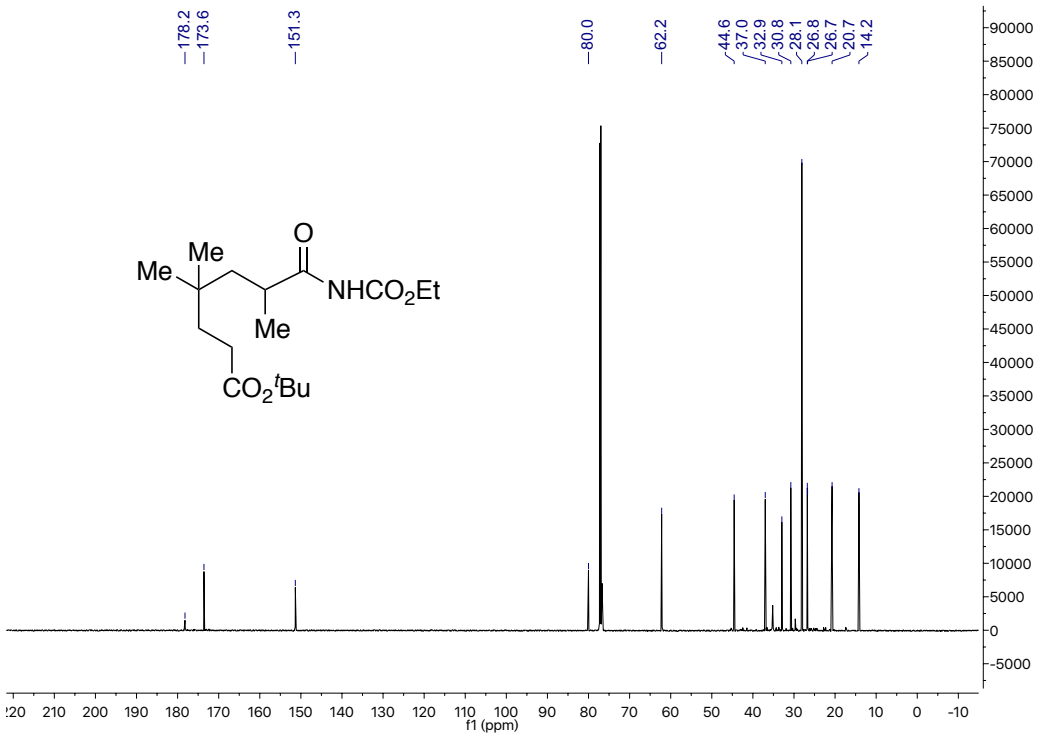
OTBS
O
NHCO2Et
CO2Bn
f1 (ppm)


Me
Me
O
NHCO2Et
Me
CO2tBu
f1 (ppm)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Me
O
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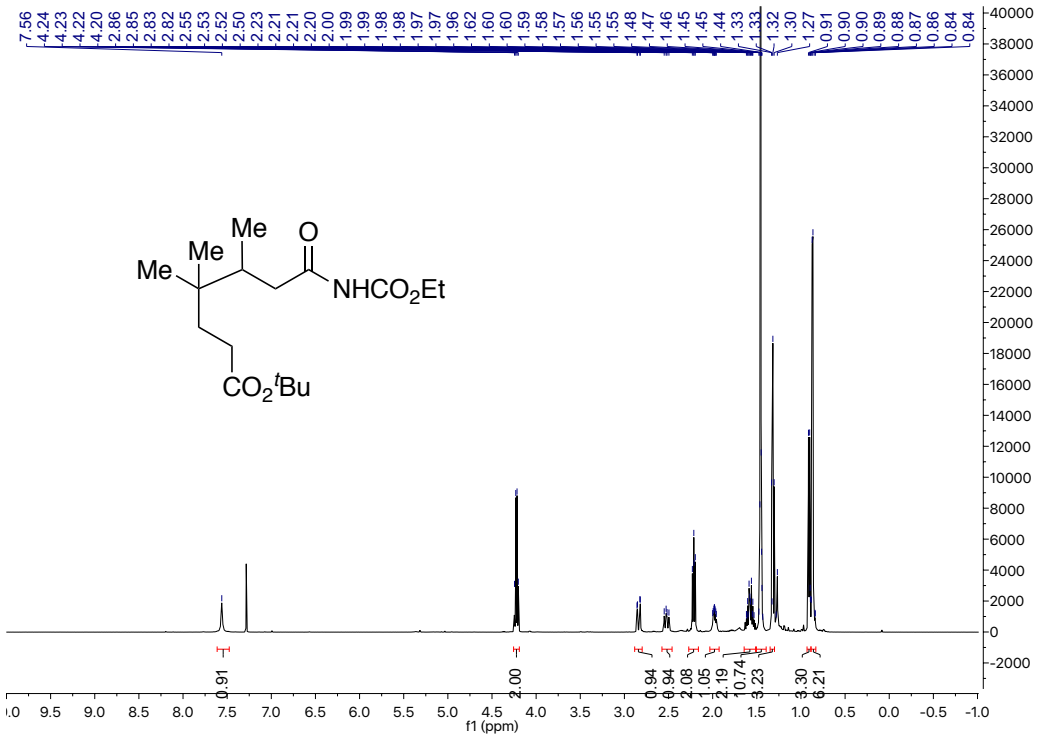
Me
CO2tBu
f1 (ppm)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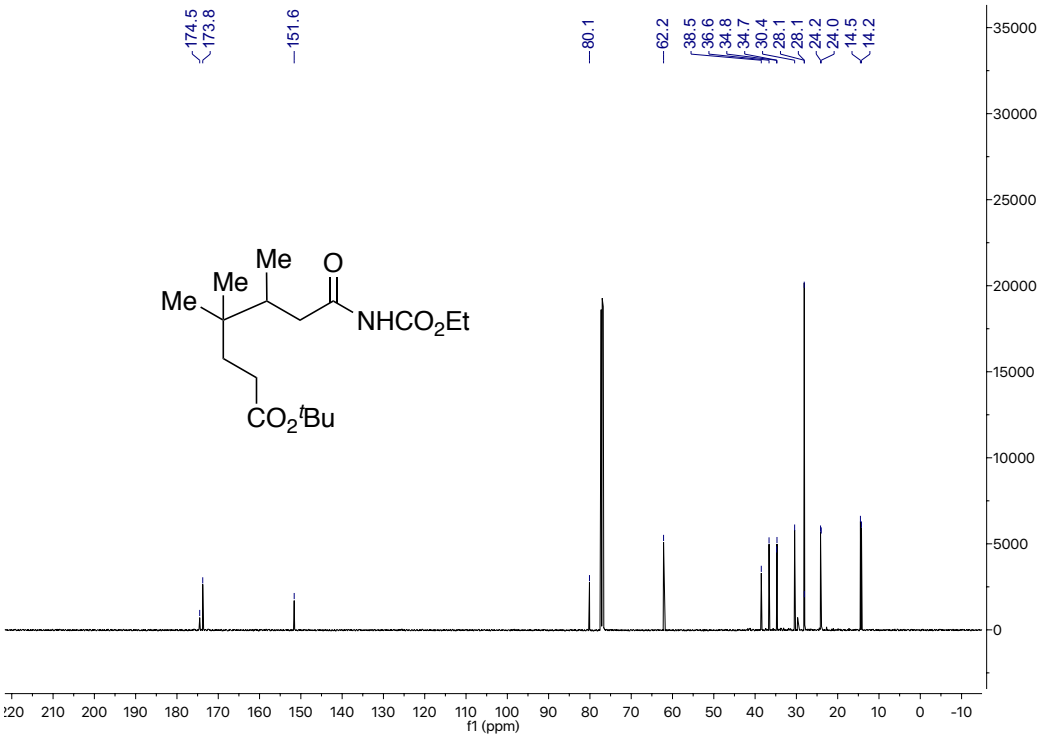
Me
Me
O
NHCO2Et
CO2tBu
f1 (ppm)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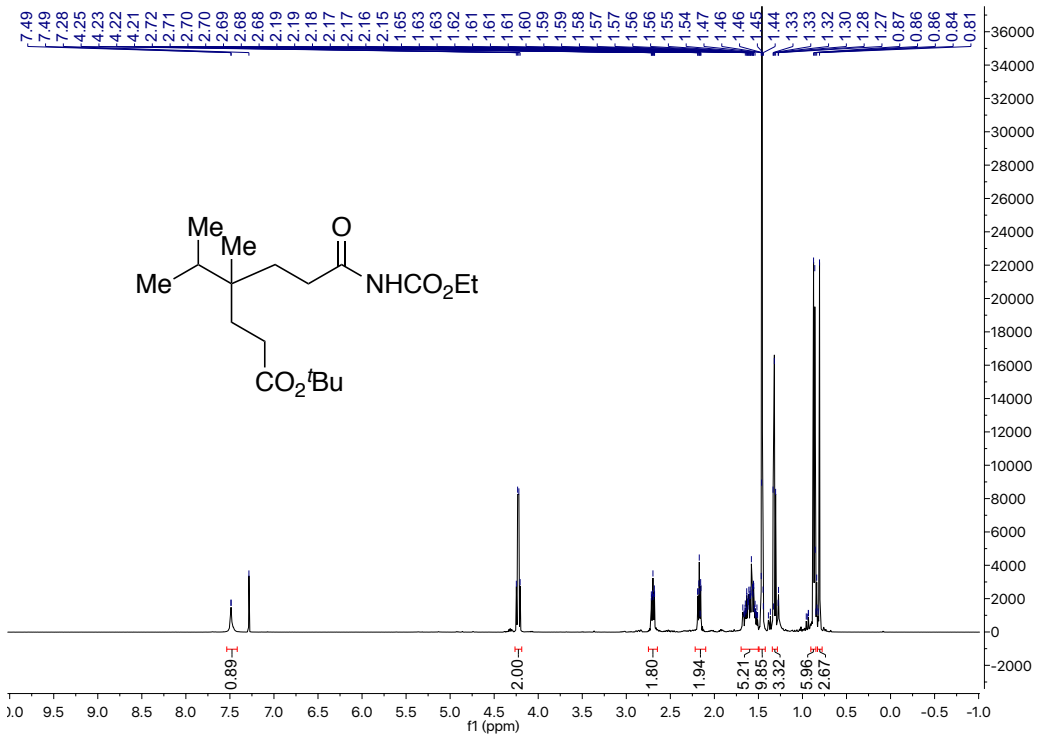
Me
Me
O
NHCO2Et
CO2tBu
f1 (ppm)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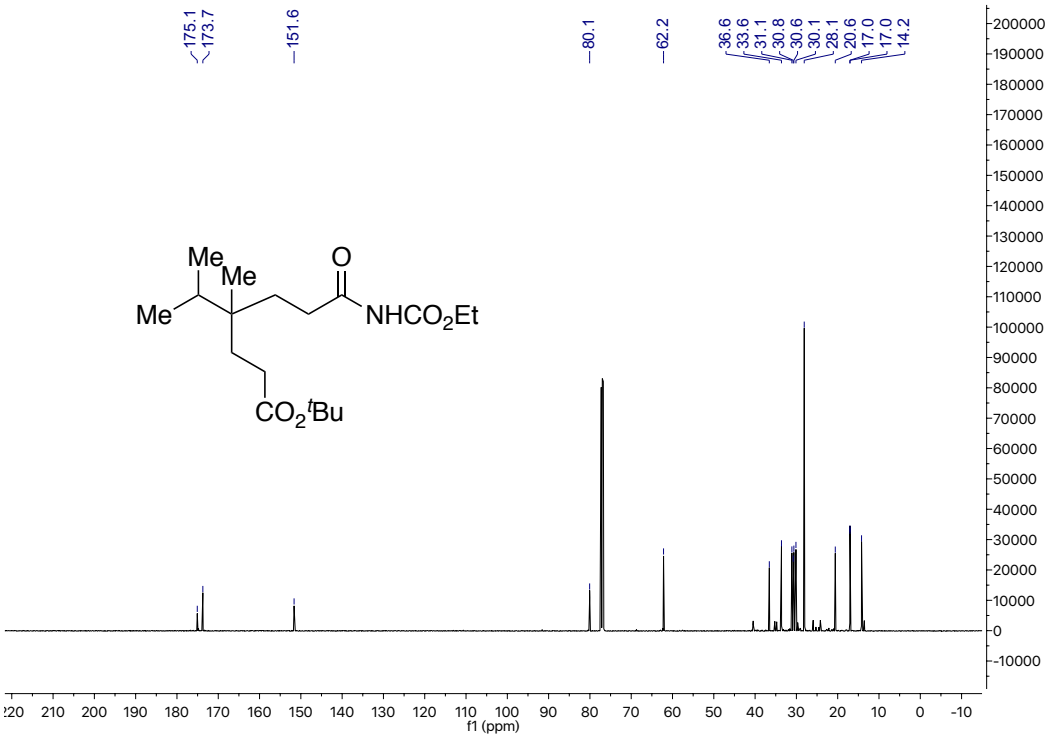
Me
Me
O
NHCO2Et
CO2tBu
f1 (ppm)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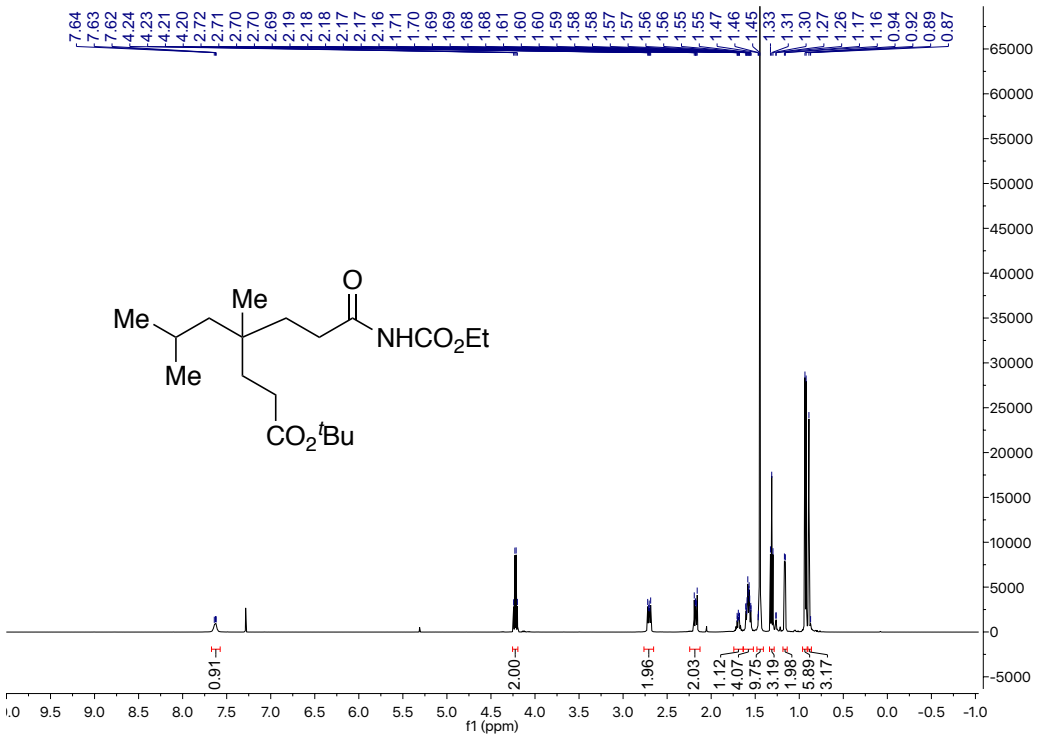
Me
Me
O
NHCO2Et
CO2tBu
f1 (ppm)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1.47
1.46
1.45
1.33
1.31
1.30
1.27
1.26
1.17
1.16
0.94
0.92
0.89
0.87
Me
Me
Me
O
NHCO2Et
CO2tBu
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9.75
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1.98
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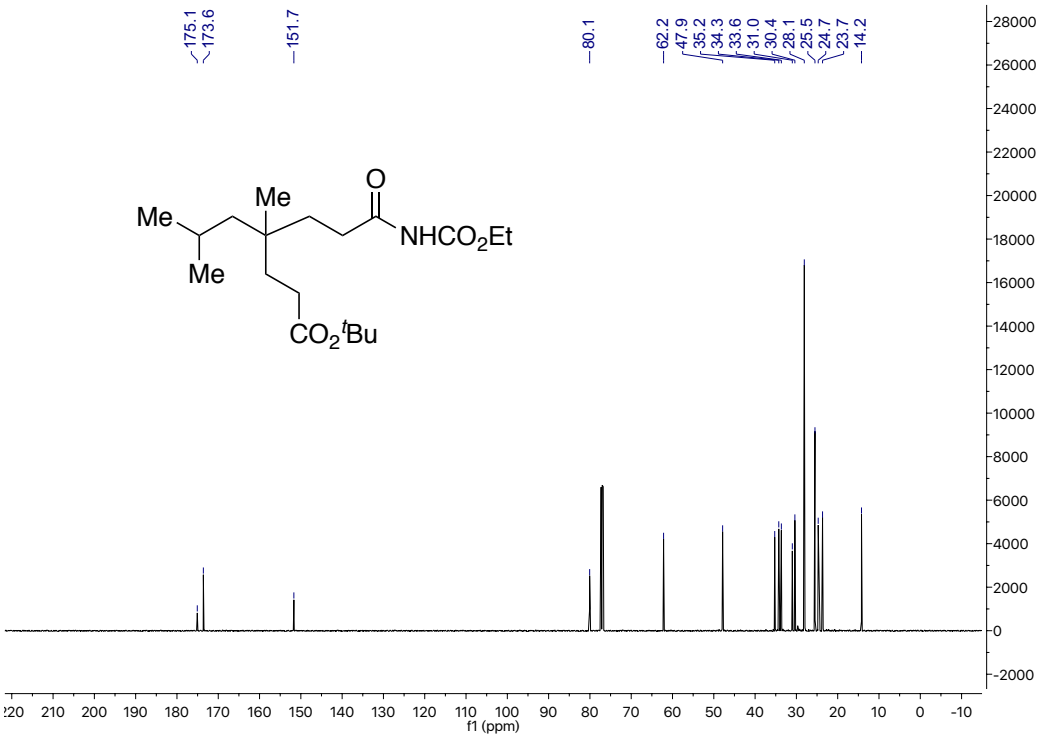
3.17
f1 (ppm)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80.1
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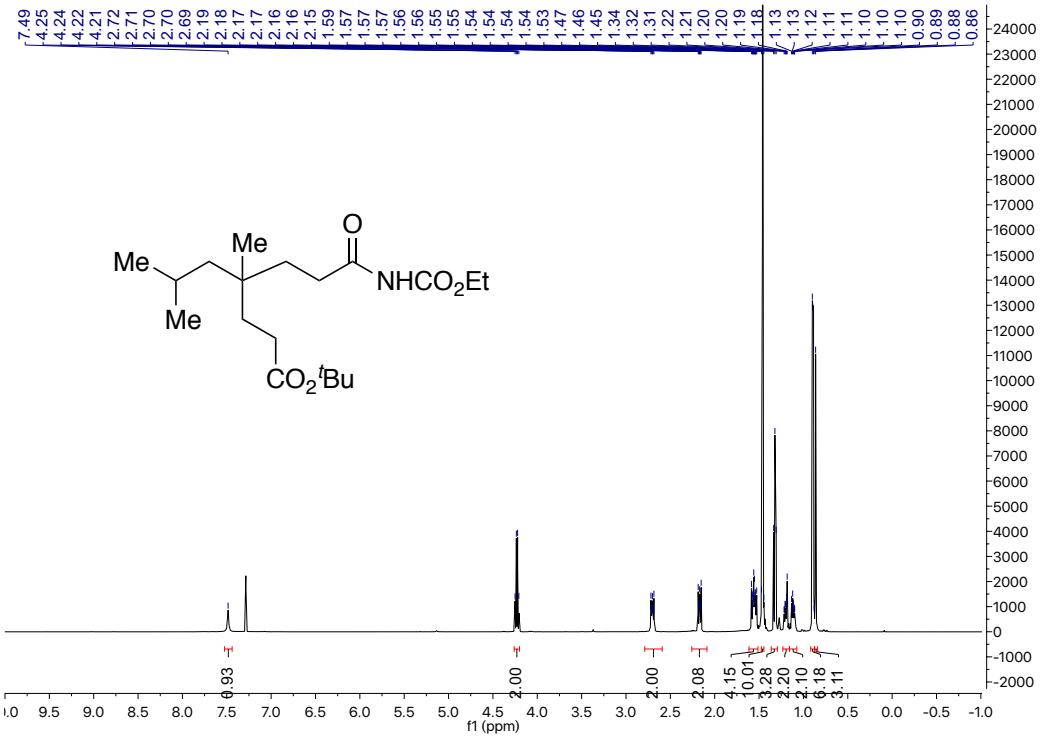
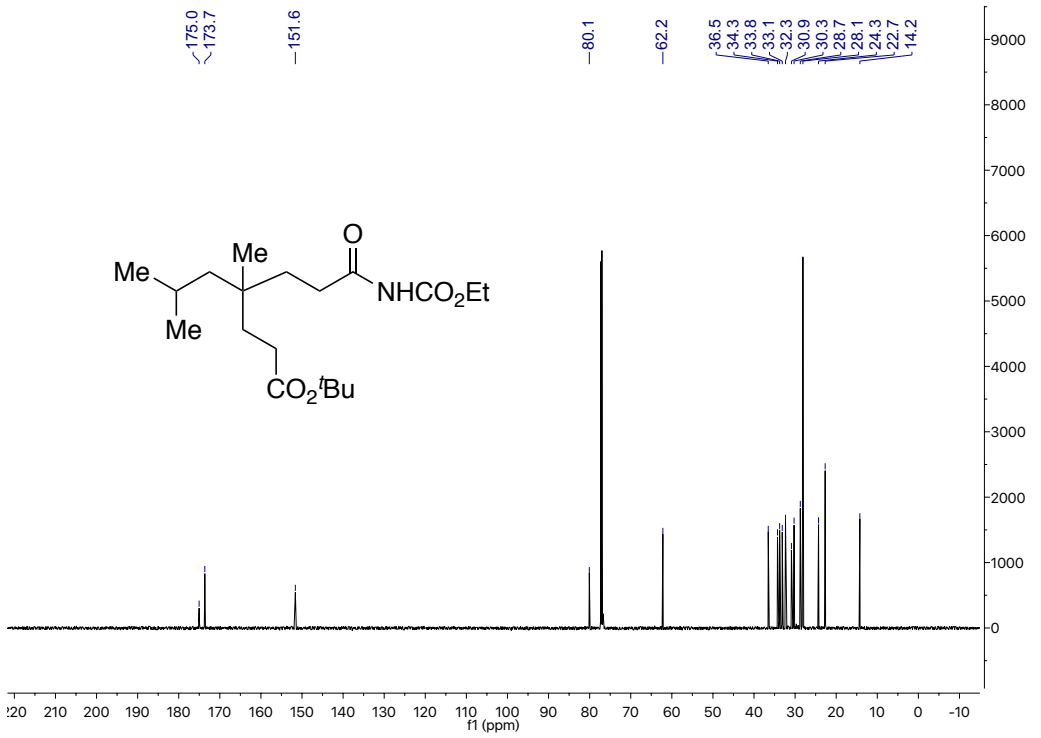
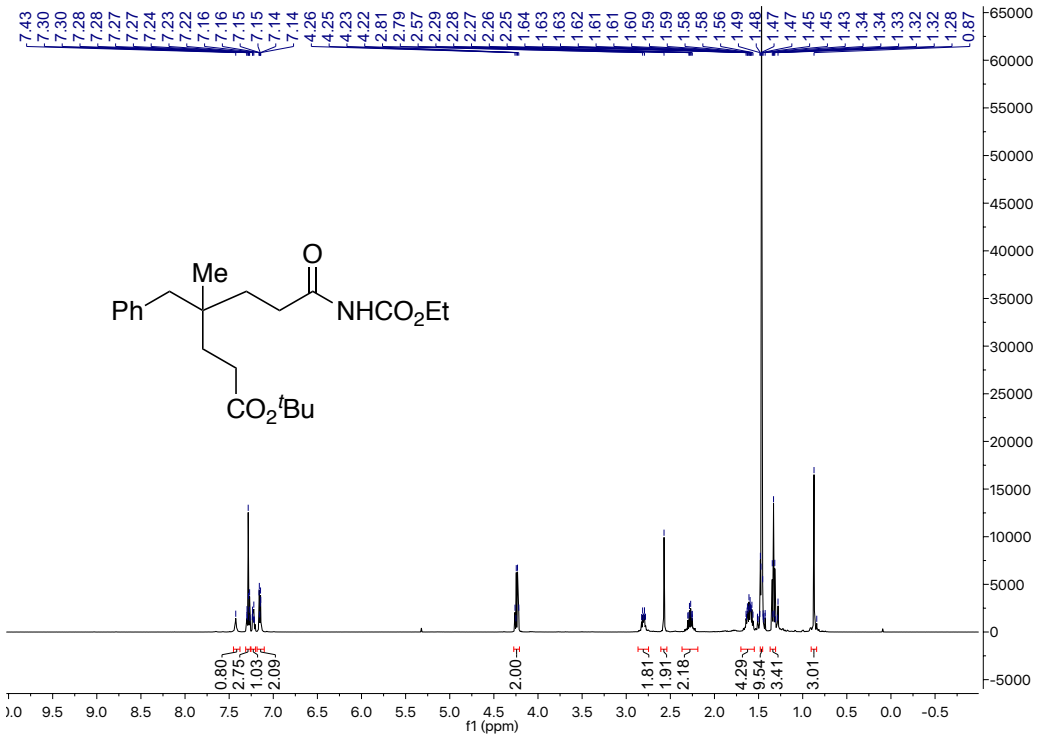
35.2
34.3
33.6
31.0
30.4
28.1
25.5
24.7
23.7
14.2
Me
Me
Me
O
NHCO2Et
CO2tBu
f1 (ppm)


Me
Me
Me
O
NHCO2Et
CO2tBu
f1 (ppm)


Me
Me
Me
O
NHCO2Et
CO2tBu
f1 (ppm)


Me
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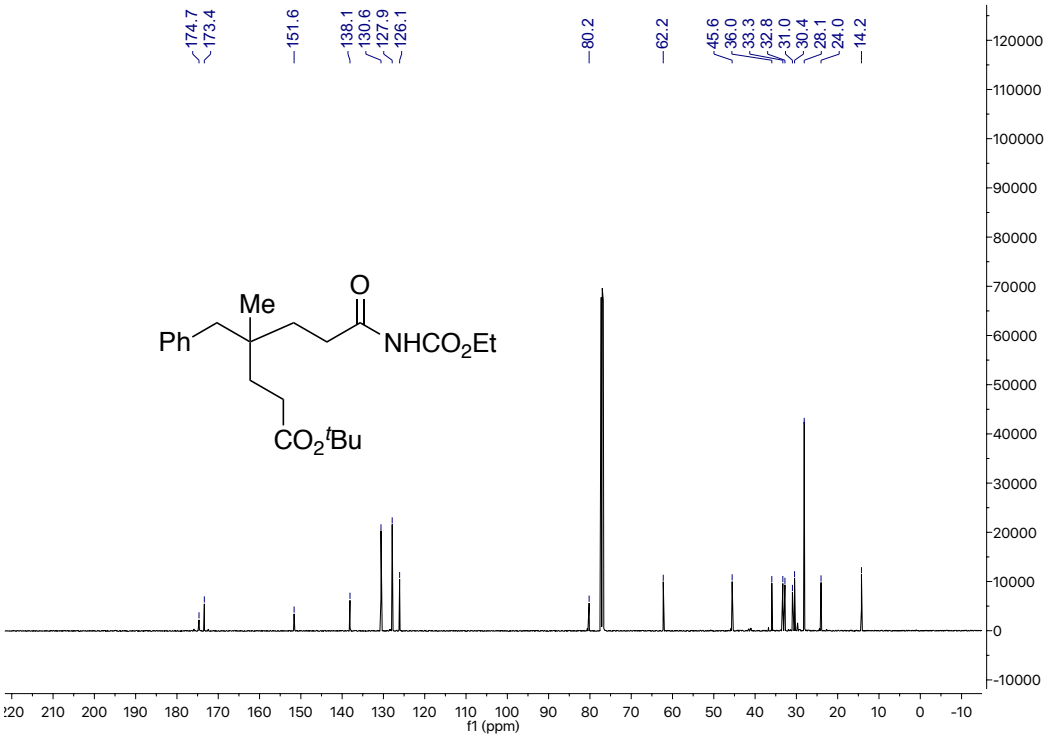
Ph
NHCO2Et
CO2tBu
f1 (ppm)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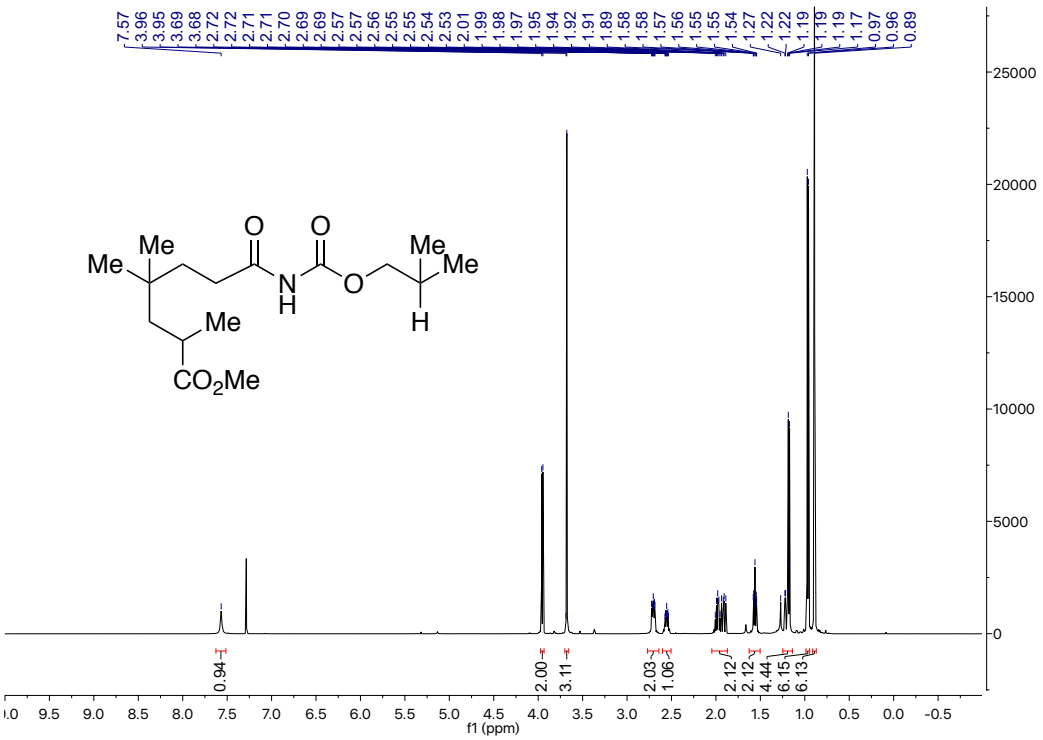
Ph
NHCO2Et
CO2tBu
f1 (ppm)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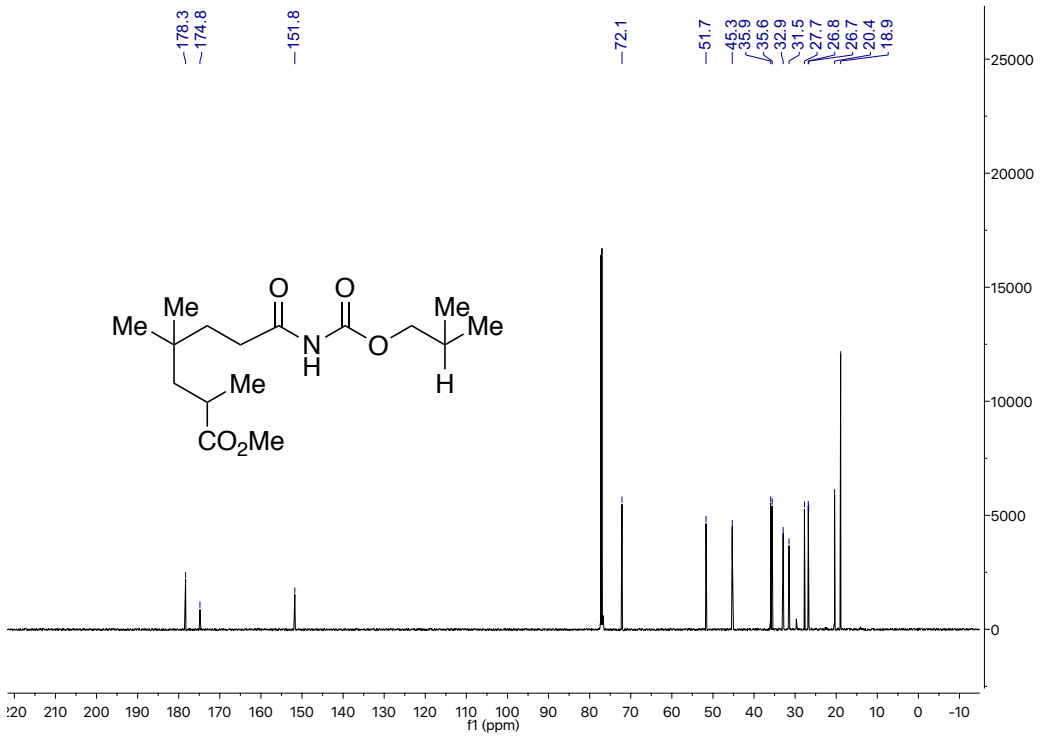
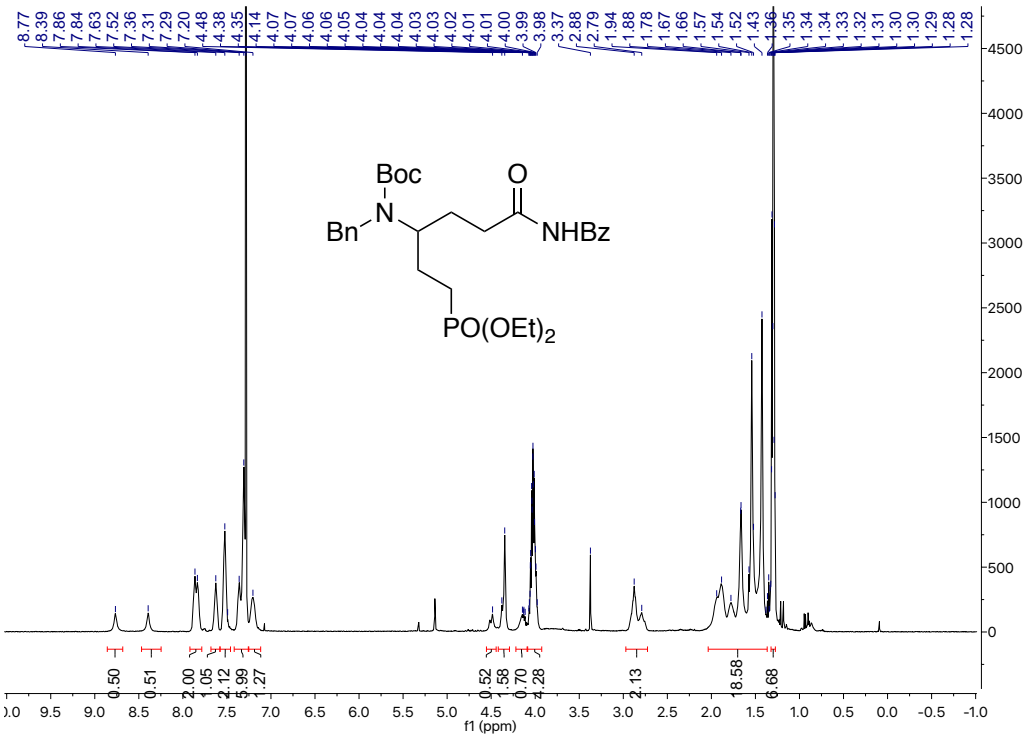
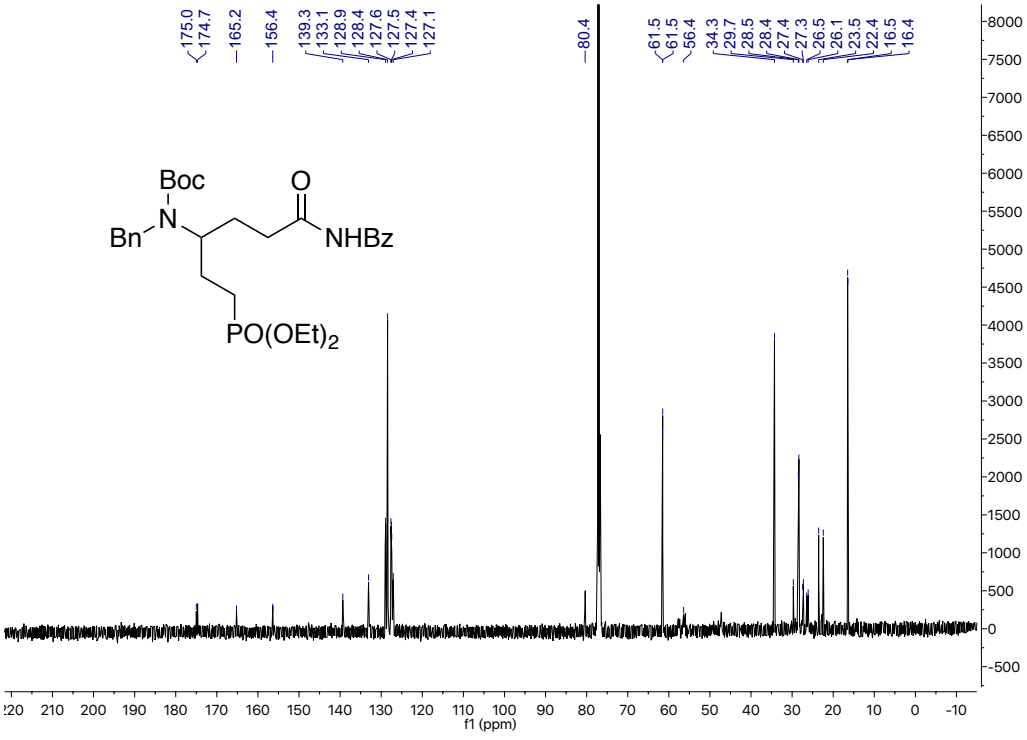
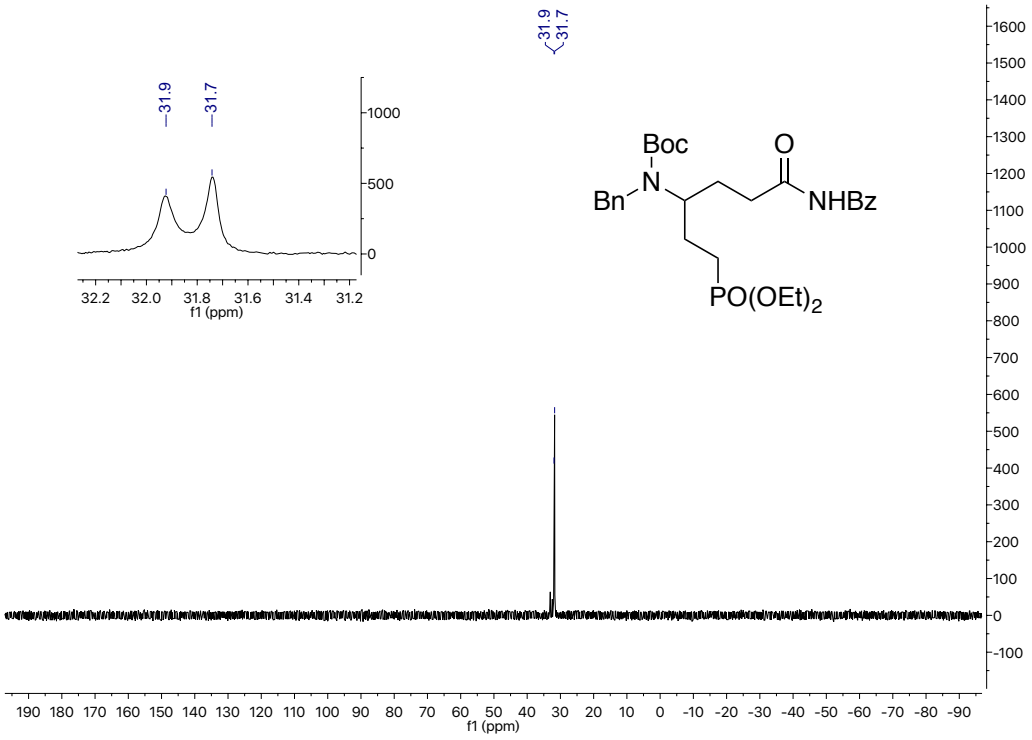
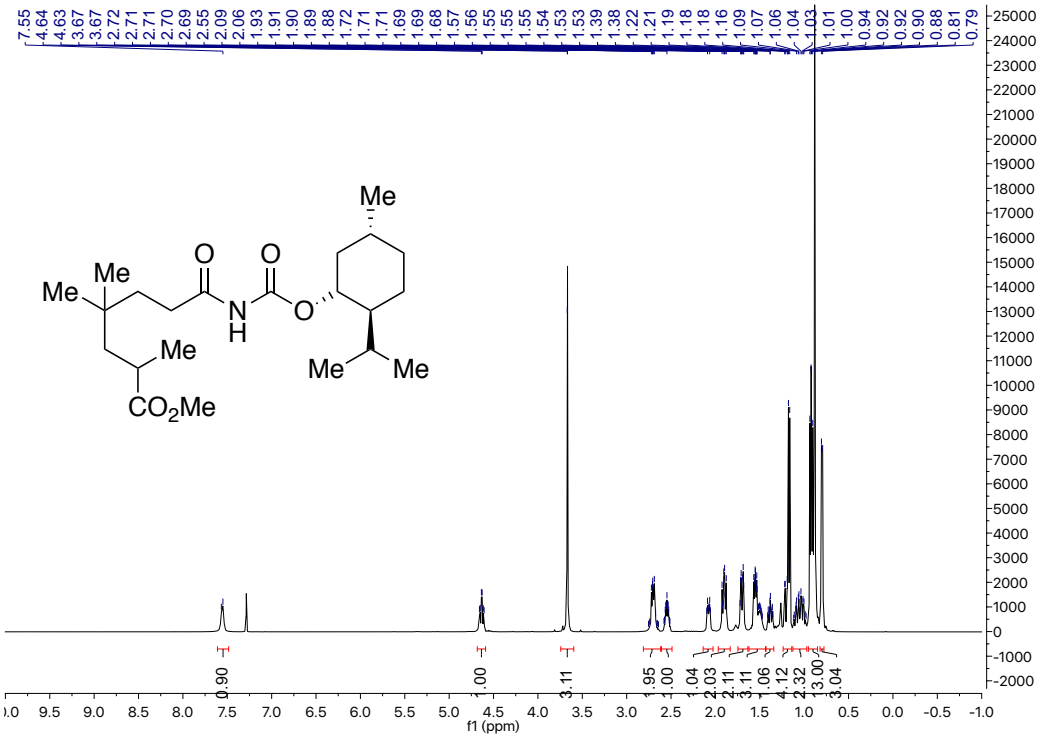
1.19
1.17
0.97
0.96
0.89
Me
Me
O
O
N
H
O
Me
Me
H
Me
CO2Me
0.94
2.00
3.11
2.03
1.06
2.12
2.12
4.44
6.15
6.13
f1 (ppm)

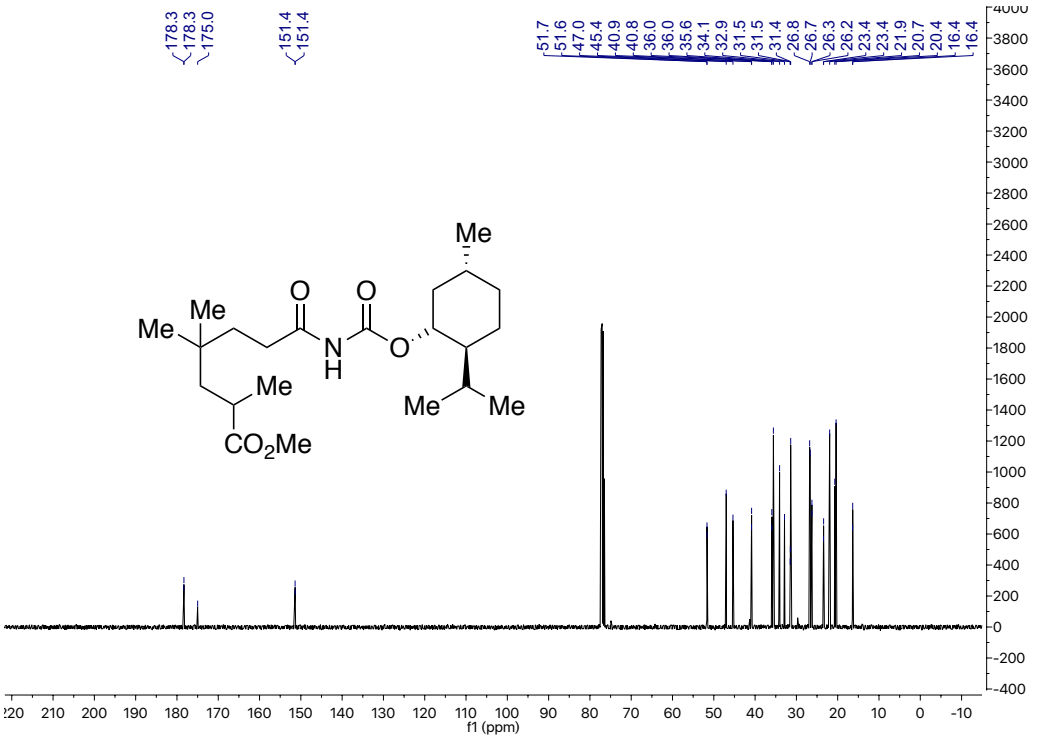

178.3
174.8
151.8
72.1
51.7
45.3
35.9
35.6
32.9
31.5
27.7
26.8
26.7
20.4
18.9
Me
Me
O
O
N
H
O
Me
Me
H
Me
CO2Me
f1 (ppm)

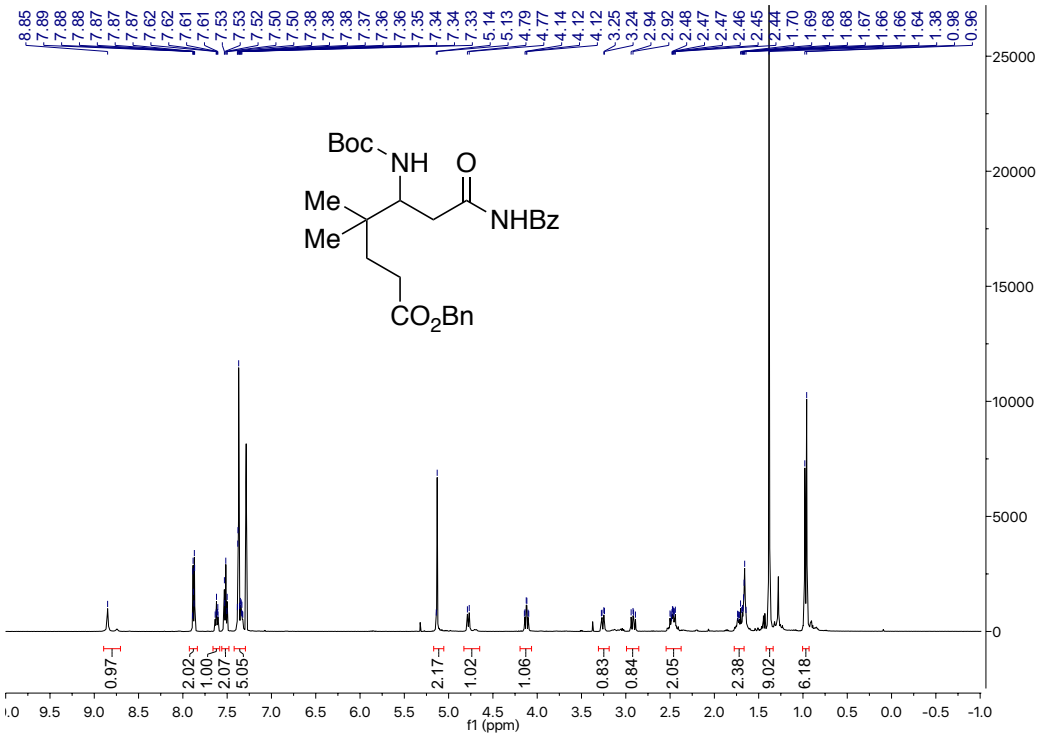

Boc
O
N
Bn
NHBz
PO(OEt)2
f1 (ppm)

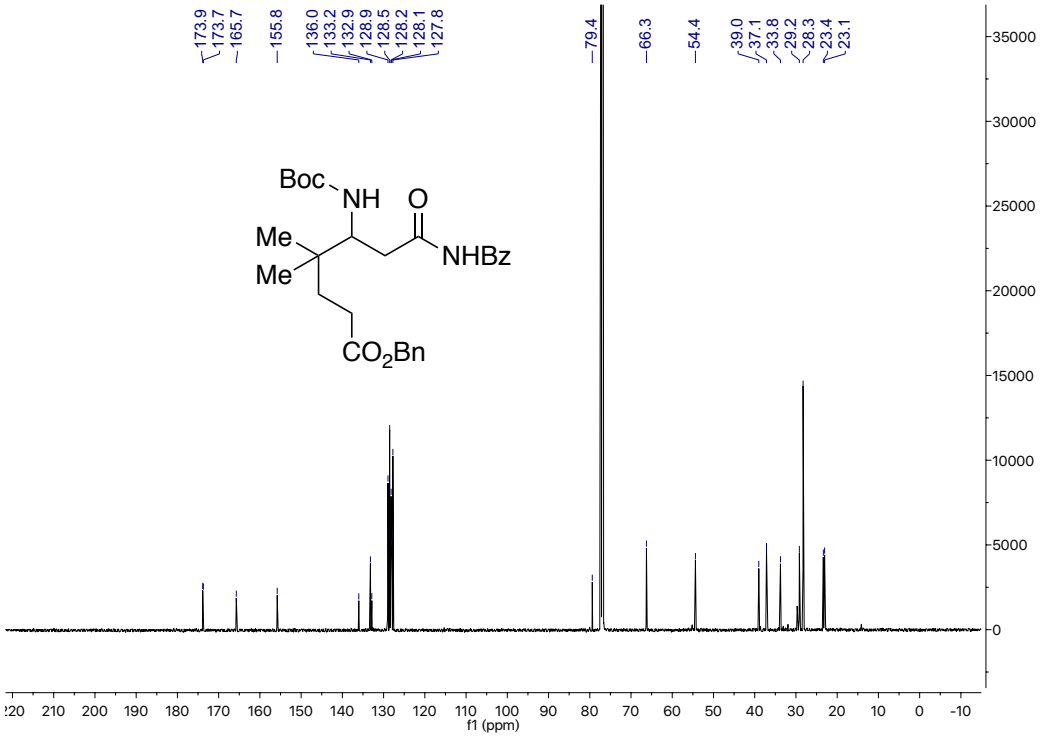

Boc
O
N
Bn
NHBz
PO(OEt)2
f1 (ppm)

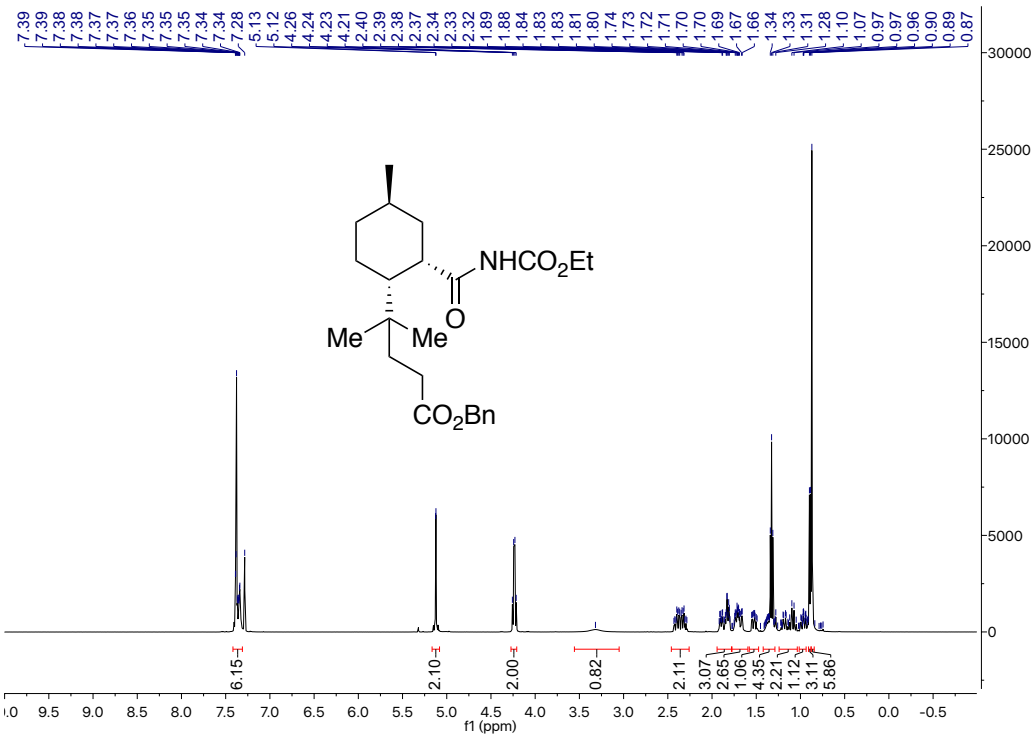

31.9
31.7
Boc
O
N
Bn
NHBz
PO(OEt)2
f1 (ppm)

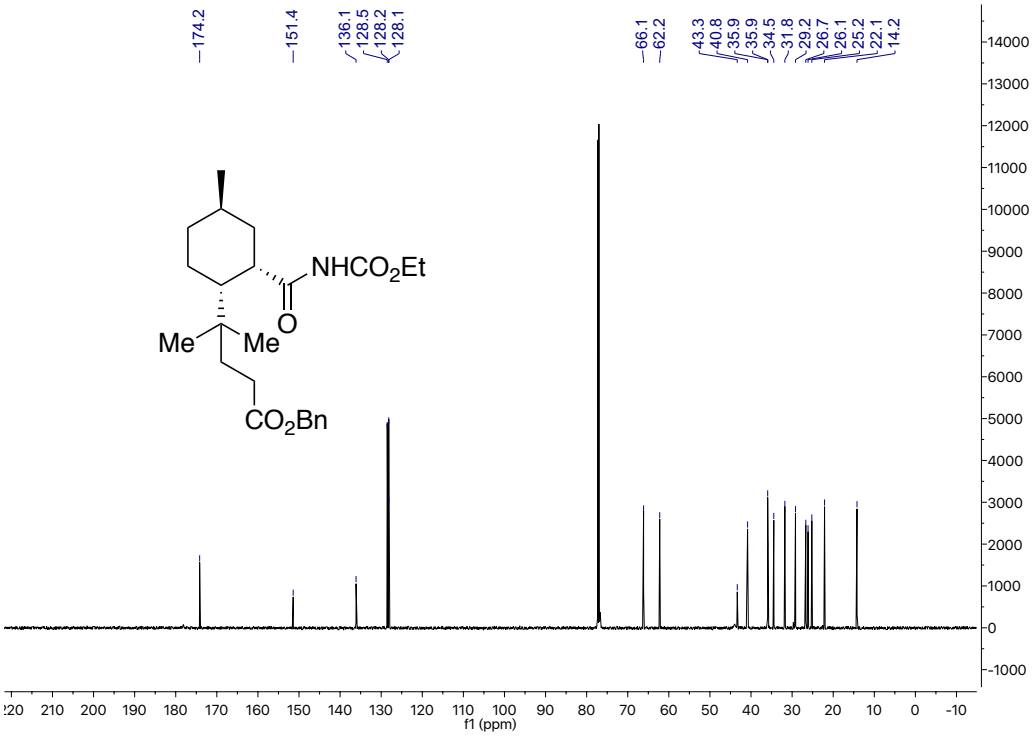

7.55
4.64
4.63
3.67
3.67
2.72
2.71
2.71
2.70
2.69
2.55
2.09
2.06
1.93
1.91
1.90
1.89
1.88
1.72
1.71
1.71
1.69
1.69
1.68
1.57
1.56
1.55
1.55
1.55
1.54
1.53
1.53
1.39
1.38
1.22
1.21
1.19
1.18
1.18
1.16
1.09
1.07
1.06
1.04
1.03
1.01
1.00
0.94
0.92
0.90
0.88
0.81
0.79
Me
O
O
Me
Me
N
H
O
Me
Me
Me
CO2Me
0.90
1.00
3.11
1.95
1.00
1.04
2.03
2.11
3.11
1.06
4.12
2.32
13.00
3.04
f1 (ppm)

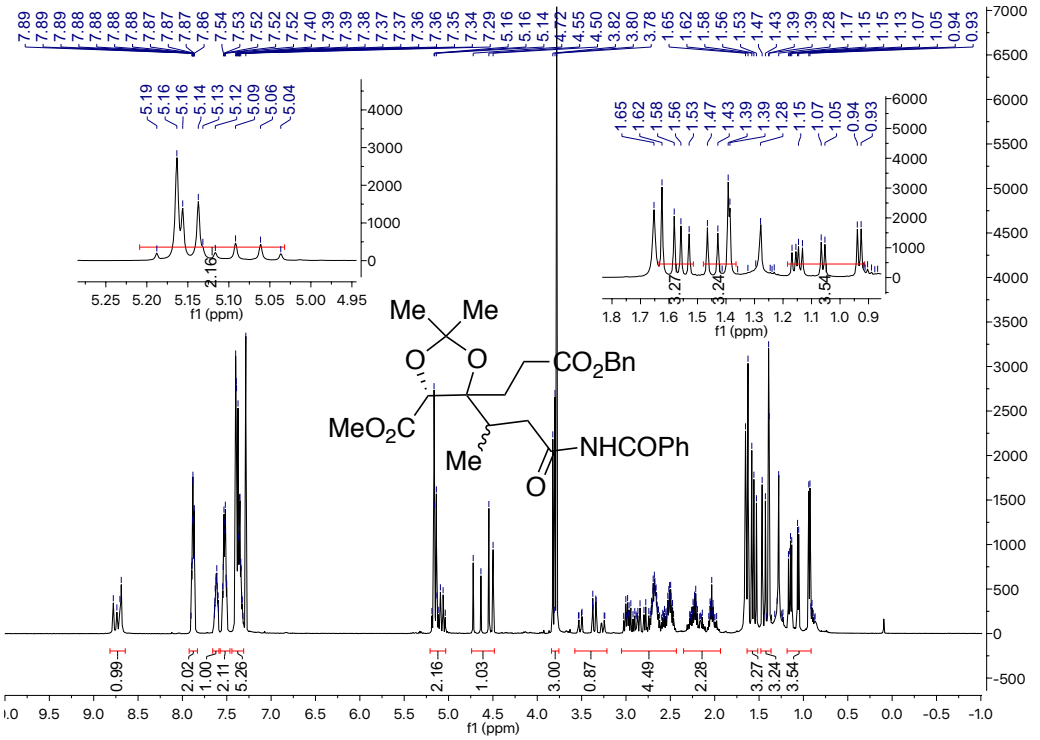

178.3
178.3
175.0
151.4
151.4
51.7
51.6
47.0
45.4
40.9
40.8
36.0
36.0
35.6
34.1
32.9
31.5
31.5
31.4
26.8
26.7
26.3
26.2
23.4
23.4
21.9
20.7
20.4
16.4
16.4
Me
O
O
Me
Me
N
H
O
Me
Me
Me
CO2Me
f1 (ppm)

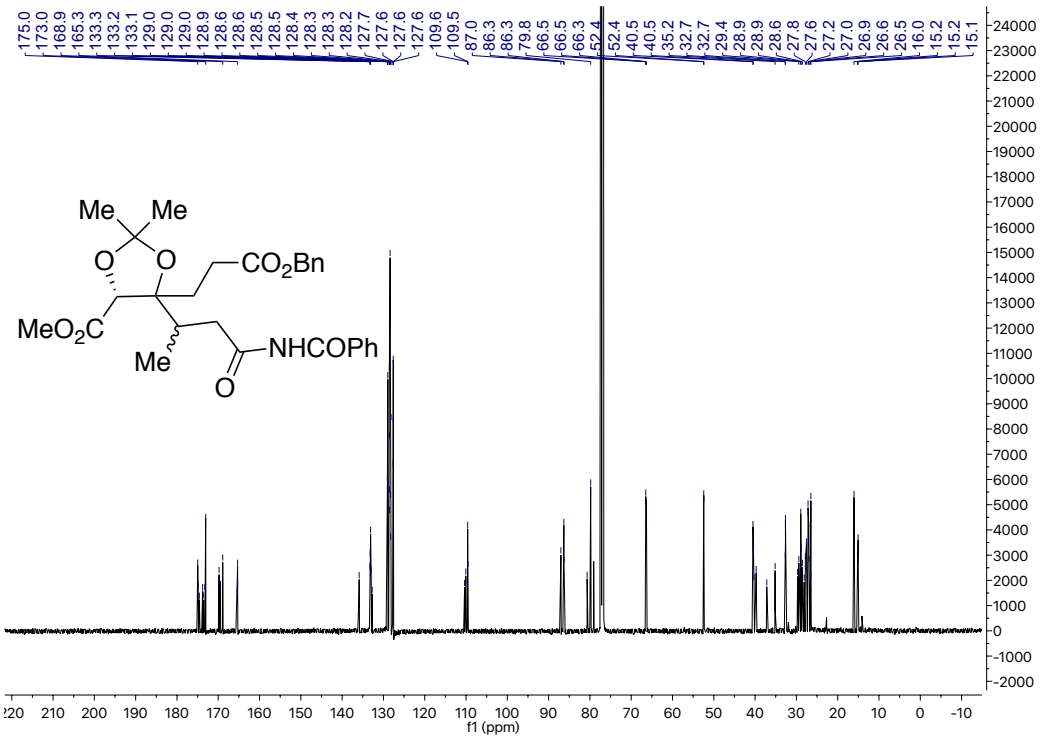

Boc
NH
O
Me
Me
NHBz
CO2Bn
f1 (ppm)

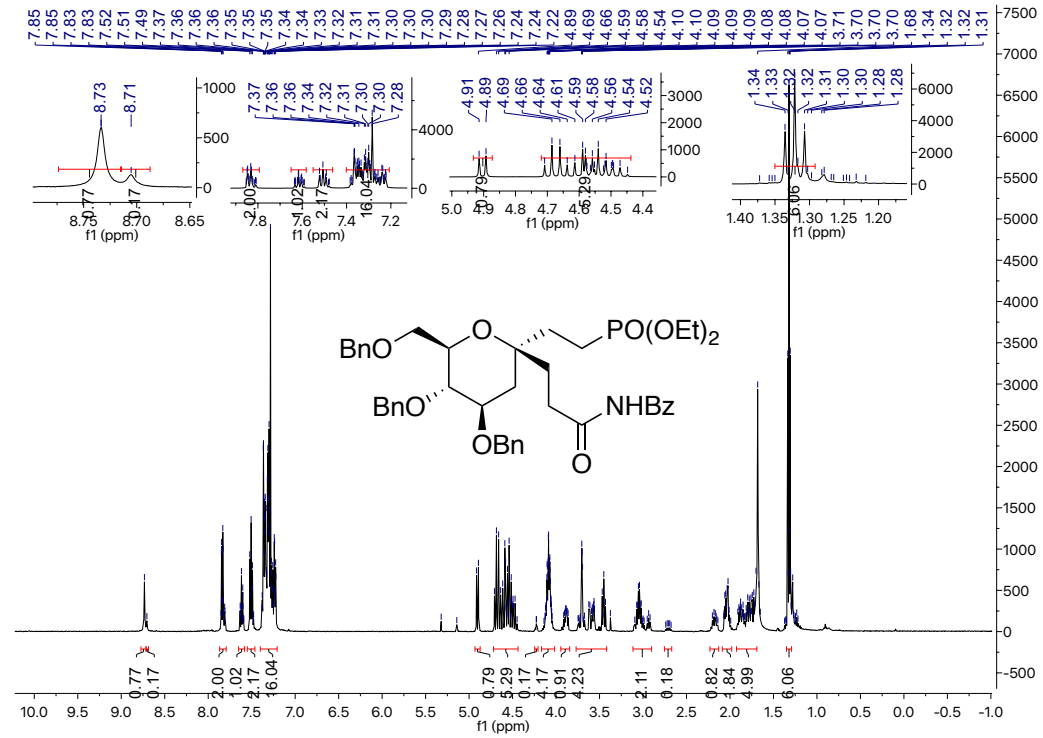

Boc
NH
O
Me
Me
NHBz
CO2Bn
f1 (ppm)

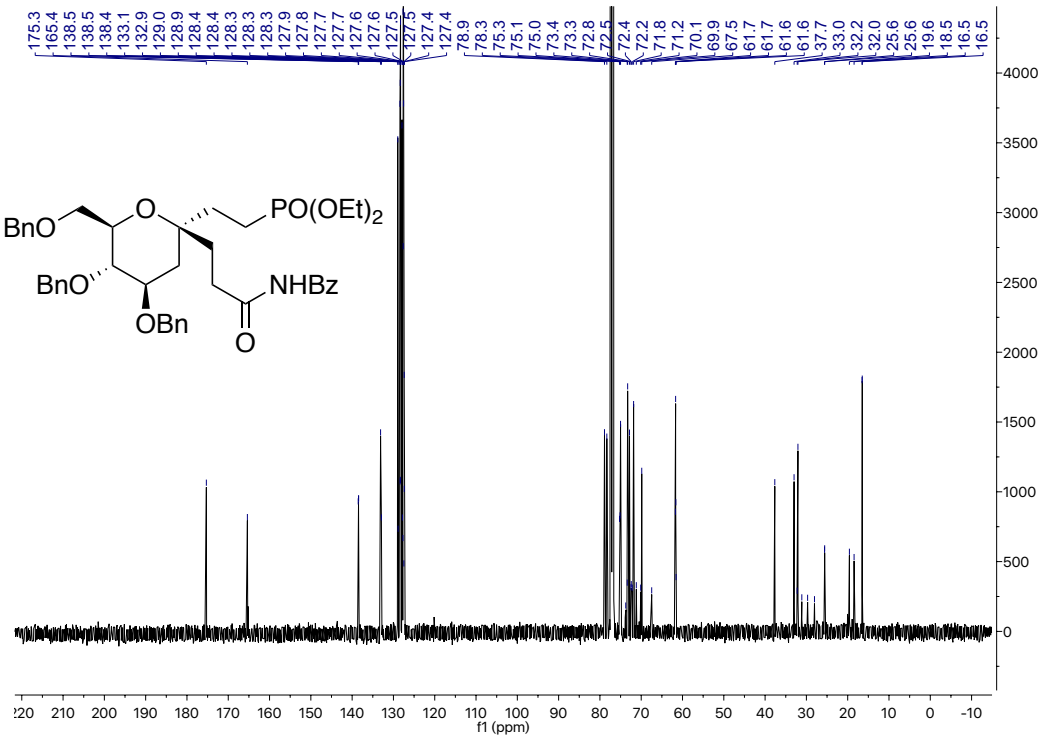

7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.28 5.13 5.12 4.26 4.24 4.23 4.21 2.40 2.39 2.38 2.37 2.34 2.33 2.32 1.89 1.88 1.84 1.83 1.83 1.81 1.80 1.74 1.73 1.72 1.71 1.70 1.70 1.69 1.67 1.66 1.34 1.33 1.31 1.28 1.10 1.07 0.97 0.97 0.96 0.90 0.89 0.87
NHCO2Et
O
Me
Me
CO2Bn
6.15
2.10
2.00
0.82
2.11
3.07
2.65
1.06
4.35
2.21
1.12
3.11
5.86
f1 (ppm)

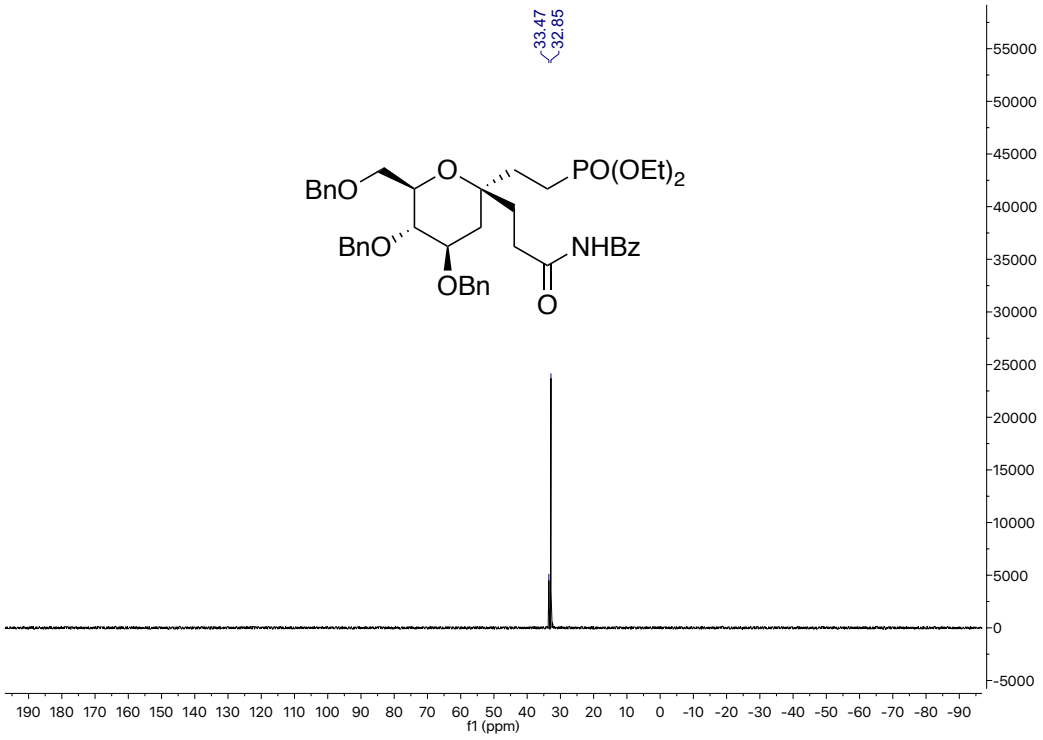

174.2
151.4
136.1
128.5
128.2
128.1
66.1
62.2
43.3
40.8
35.9
35.9
34.5
31.8
29.2
26.7
26.1
25.2
22.1
14.2
NHCO2Et
O
Me
Me
CO2Bn
f1 (ppm)

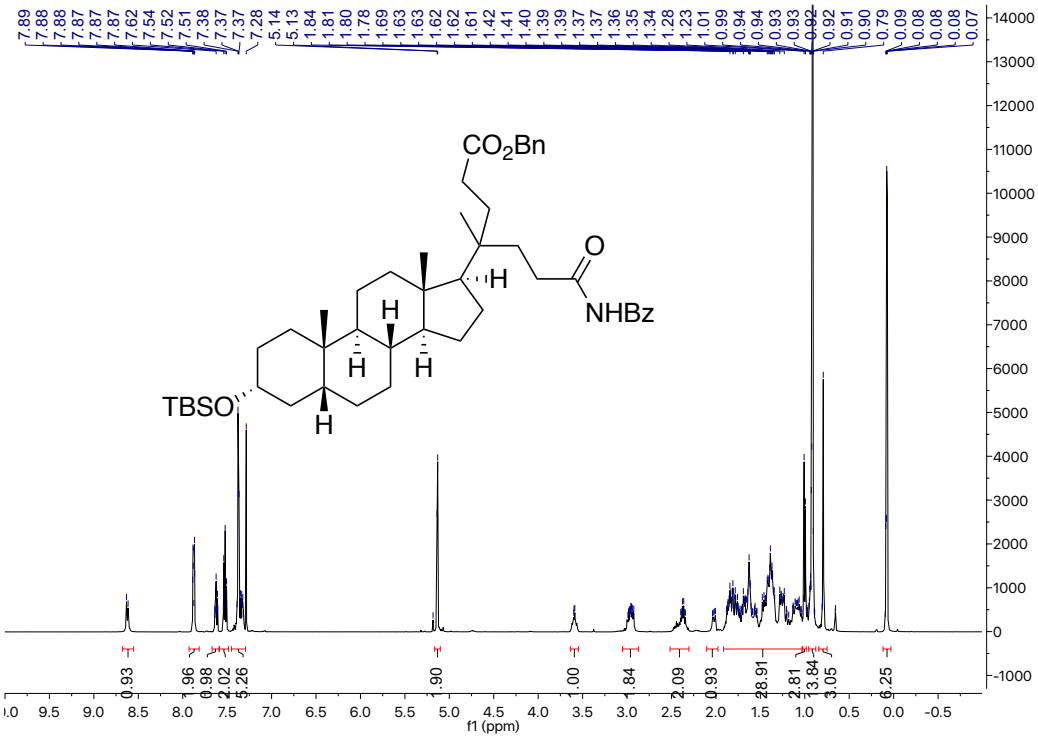

Me
Me
O
O
CO2Bn
MeO2C
Me
NHCOPh
O
f1 (ppm)

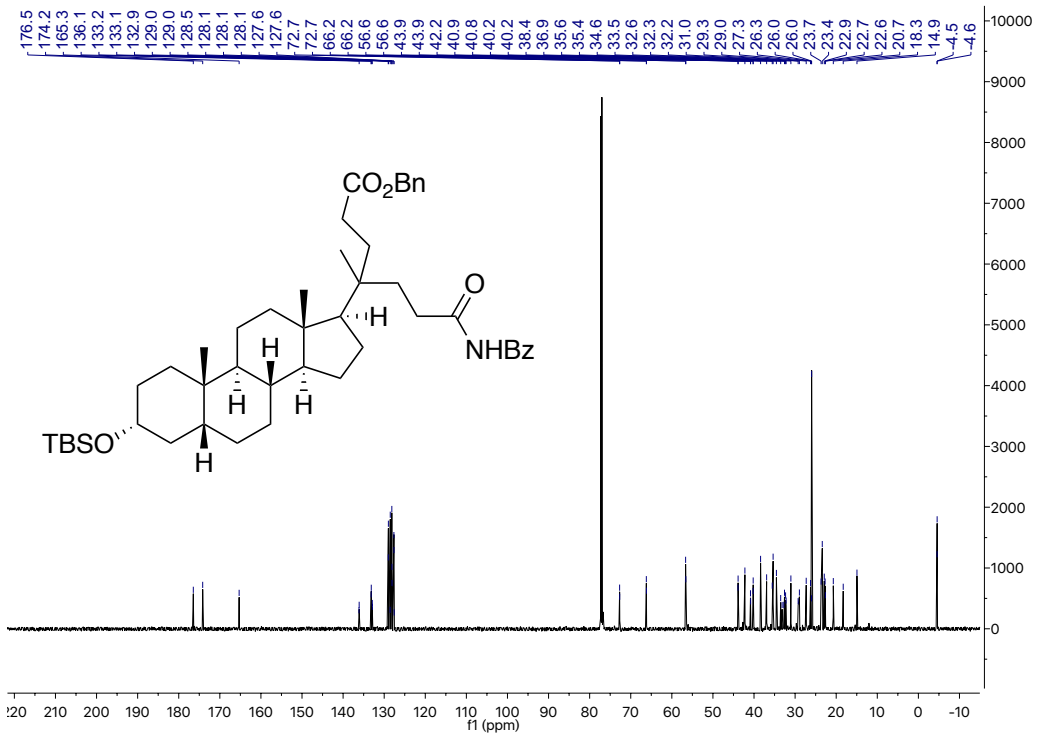

Me
Me
O
O
CO2Bn
MeO2C
Me
NHCOPh
O
f1 (ppm)


BnO
O
PO(OEt)2
BnO
NHBz
OBn
O
f1 (ppm)


BnO
O
PO(OEt)2
BnO
NHBz
OBn
O
f1 (ppm)


33.47
32.85
BnO
O
PO(OEt)2
BnO
NHBz
OBn
O
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


CO2Bn
O
NHBz
TBSO
H
f1 (ppm)


CO2Bn
O
NHBz
TBSO
H
f1 (ppm)