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Enantioselective Construction of Quaternary *N*-Heterocycles by Palladium-Catalysed Decarboxylative Allylic Alkylation of Lactams

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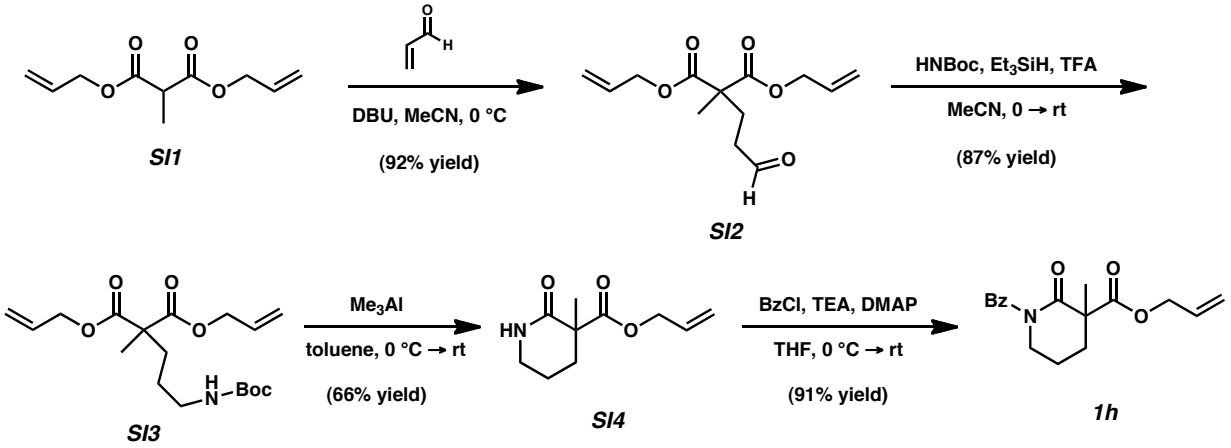
Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Brine solutions are saturated aqueous sodium chloride solutions. Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) was purchased from Strem and stored in a glove box. Lithium bis(trimethylsilyl)amide was purchased from Aldrich and stored in a glove box. Tris[bis(*p*-methoxybenzylidene)-acetone]dipalladium(0) ($Pd_2(pmdba)_3$) was prepared by known methods and stored in a glovebox.[1] (*S*)-*t*-BuPHOX, (*S*)-$(CF_3)_3$-*t*-BuPHOX, and allyl cyanoformate were prepared by known methods.[2,3,4] Selectfluor, methyl iodide, and ethyl iodide were purchased from Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Sodium hydride (NaH) was purchased as a 60% dispersion in mineral oil from Acros and used as such unless otherwise stated. Triethylamine was distilled from CaH_2 prior to use. Acrolein, acrylonitrile, methyl acrylate, and benzoyl chloride were distilled prior to use. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, anisaldehyde, $KMnO_4$, or CAM staining. ICN Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralpak (AD-H or AS) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. with visualization at 220 or 254 nm. Analytical chiral SFC was performed with a JACSO 2000 series instrument utilizing Chiralpak (AD-H or AS-H) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm), or a Chiralpak IC column (4.6 mm x 10 cm) obtained from Daicel Chemical Industries, Ltd with visualization at 210 or 254 nm. Optical rotations were measured with a Jasco P-2000 polarimeter at 589 nm. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 500 (at 500 MHz and 126 MHz, respectively) or a Mercury 300 (at 300 MHz and 75 MHz, respectively), and are reported relative to residual protio solvent ($CDCl_3$ = 7.26 and 77.0 ppm and C_6D_6 = 7.16 and 128.0 ppm, respectively). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra were obtained using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) or mixed (MM) ionization mode or from the Caltech Mass Spectral Facility.

Synthesis of Lactam Substrates

Representative Method 1: Diallyl Malonate Method

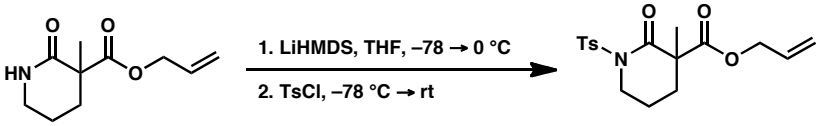


Aldehyde SI2: To a cooled (0 °C) solution of diallyl 2-methylmalonate (**SI1**)[5] (17.0 g, 84.7 mmol, 1.00 equiv) and acrolein (6.23 mL, 93.2 mmol, 1.10 equiv) in MeCN (282 mL) was added DBU (253 μL, 1.70 mmol, 0.02 equiv). After 15 min, the reaction mixture was diluted with saturated aqueous NH_4Cl (200 mL) and EtOAc (100 mL) and the phases were separated. The aqueous phase was extracted with EtOAc (3 x 200 mL) and the combined organic phases were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (8 x 16 cm SiO_2, 10 to 20% EtOAc in hexanes) to afford aldehyde **SI2** as a colorless oil (19.7 g, 92% yield). R_f = 0.32 (20% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.71 (t, J = 1.2 Hz, 1H), 5.83 (ddt, J = 17.2, 10.5, 5.7 Hz, 2H), 5.26 (dq, J = 17.2, 1.5 Hz, 2H), 5.19 (dq, J = 10.4, 1.3 Hz, 2H), 4.57 (dt, J = 5.6, 1.4 Hz, 4H), 2.55–2.45 (m, 2H), 2.20–2.10 (m, 2H), 1.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 171.2, 131.3, 118.5, 65.9, 52.8, 39.2, 27.7, 20.3; IR (Neat Film NaCl) 2988, 2945, 1732, 1230, 1186, 1116, 984, 935 cm^{-1}; HRMS (MM: ESI-APCI) m/z calc'd for $C_{13}H_{19}O_5$ $[M+H]^+$: 255.1227, found 255.1223.

Carbamate SI3: To a cooled (0 °C) solution of aldehyde **SI2** (19.7 g, 77.5 mmol, 1.00 equiv), $BocNH_2$[6] (22.7 g, 194 mmol, 2.50 equiv), and Et_3SiH (31.0 mL, 194 mmol, 2.50 equiv) in MeCN (310 mL) was added trifluoroacetic acid (12.1 mL, 163 mmol, 2.10 equiv) dropwise over 5 min. The reaction mixture was stirred at 0° C for 2 h and at ambient temperature for an additional 18 h, at which point the reaction mixture was cooled (0 °C), treated with saturated aqueous $NaHCO_3$ (150 mL), stirred for 40 min, and concentrated under reduced pressure to remove MeCN (~250 mL). The remaining material was diluted with Et_2O (200 mL) and the phases were separated. The aqueous phase was extracted with Et_2O (4 x 100 mL) and EtOAc (1 x 150 mL), and the combined organic phases were washed with brine (2 x 150 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (8 x 25 cm SiO_2, 5 to 15% EtOAc in hexanes) to afford carbamate **SI3** as a colorless oil (23.0 g, 87% yield). R_f = 0.32 (20% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (ddt, J = 17.3, 10.4, 5.7 Hz, 2H), 5.30 (dq, J = 17.2, 1.6, 1.5 Hz, 2H), 5.23 (dq, J = 10.4, 1.3, 1.3 Hz, 2H), 4.61 (dt, J = 5.6, 1.4 Hz, 4H), 4.55 (br s, 1H), 3.12 (q, J = 6.7 Hz, 2H), 2.00–1.75 (m, 2H), 1.44 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 155.8, 131.5, 118.4, 79.0, 65.7, 53.4, 40.4, 32.7, 28.3, 24.9, 19.9; IR (Neat Film NaCl) 3403, 2977, 2939, 1734, 1517, 1366, 1250, 1173, 985, 934 cm^{-1}; HRMS (MM: ESI-APCI) m/z calc'd for $C_{18}H_{29}NO_6Na$ $[M+Na]^+$: 378.1887, found 378.1892.

Lactam SI4: To a cooled (0 °C) solution of carbamate **SI3** (10.4 g, 30.6 mmol, 1.00 equiv) in toluene (306 mL) was added trimethylaluminum (11.7 mL, 61.1 mmol, 2.00 equiv) dropwise over 10 min. After 5 h the reaction was allowed to warm to ambient temperature and stirred for an additional 17 h. The reaction was cooled (0 °C), treated with brine (100 mL, *CAUTION: Gas evolution and exotherm*) in a dropwise manner over 30 min, and stirred until gas evolution ceased. The reaction mixture was then treated with saturated aqueous sodium potassium tartrate (200 mL) and stirred for 4 h. The phases were separated and the aqueous phase was extracted with EtOAc (5 x 150 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (5 x 16 cm SiO_2, 45 to 65% EtOAc in hexanes) to afford lactam **SI4** as a colorless oil (3.99 g, 66% yield). R_f = 0.41 (100% EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 (s, 1H), 6.00–5.75 (m, 1H), 5.30 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.70–4.50 (m, 2H), 3.40–3.20 (m, 2H), 2.30–2.15 (m, 1H), 1.94–1.59 (m, 3H), 1.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 172.0, 131.7, 118.1, 65.7, 50.1, 42.3, 33.0, 22.4, 19.3; IR (Neat Film NaCl) 3207, 3083, 2942, 2873, 1737, 1668, 1254, 1194, 1132 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{10}H_{16}NO_3$ $[M+H]^+$: 198.1125, found 198.1117.

Benzoyl Lactam 1h: To a cooled (0 °C) solution of lactam **SI4** (394 mg, 2.00 mmol, 1.00 equiv), triethylamine (840 µL, 6.00 mmol, 3.00 equiv), and DMAP (25.0 mg, 205 µmol, 0.102 equiv) in THF (8.00 mL) was added benzoyl chloride (470 µL, 4.00 mmol, 2.00 equiv) dropwise over 5 min. The reaction mixture was allowed to warm to ambient temperature and stirred for 14 h. The reaction mixture was then diluted with brine (10 mL) and EtOAc (10 mL), and the phases were separated. The aqueous phase was extracted with EtOAc (3 x 15 mL), and the combined organic phases were washed with brine (2 x 30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (3 x 25 cm SiO_2, 15 to 25% Et_2O in hexanes) to afford benzoyl lactam **1h** as an amorphous solid (550 mg, 91% yield). R_f = 0.38 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.63 (m, 2H), 7.52–7.42 (m, 1H), 7.42–7.32 (m, 2H), 5.98 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.40 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.33 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.72 (dt, *J* = 6.0, 1.3 Hz, 2H), 3.93–3.82 (m, 1H), 3.83–3.73 (m, 1H), 2.56–2.43 (m, 1H), 2.13–1.90 (m, 2H), 1.87–1.76 (m, 1H), 1.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 172.8, 172.4, 135.9, 131.6, 131.4, 128.0, 127.9, 119.5, 66.5, 52.9, 46.8, 33.8, 22.5, 20.2; IR (Neat Film NaCl) 3063, 2941, 2873, 1735, 1681, 1449, 1276, 1040, 942, 724 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{20}NO_4$ $[M+H]^+$: 302.1387, found 302.1388.

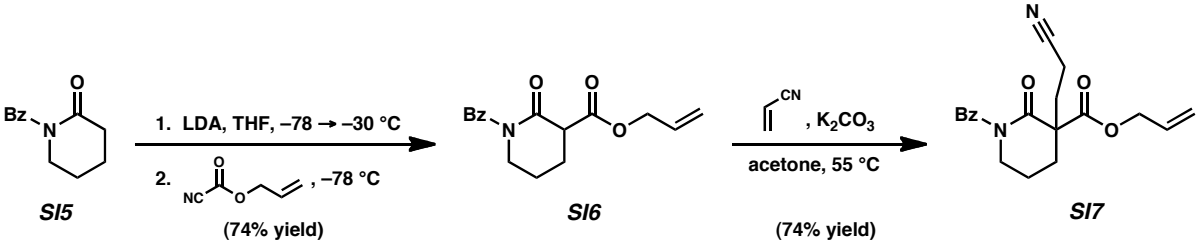


SI4 *1a*

Tosyl Lactam 1a: To a cooled (–78 °C) solution of LiHMDS (385 mg, 2.30 mmol, 1.15 equiv) in THF (8.0 mL) was added lactam **SI4** (394 mg, 2.00 mmol, 1.00 equiv). The reaction mixture warmed to 0 °C and stirred for 30 min, then cooled to –78 °C and treated with TsCl (572 mg, 3.00 mmol, 1.50 equiv). After 5 min, the reaction mixture was allowed to warm to ambient temperature for 30 min and treated with saturated aqueous NH_4Cl (10 mL). The phases were separated, and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (3 x 30 cm SiO_2, 4:1:1 hexanes-EtOAc-DCM) to afford tosyl lactam **1a** as a colorless oil (571 mg, 81% yield). R_f = 0.58 (33% EtOAc in hexanes); ^{1}H

NMR (500 MHz, $CDCl_3$) δ 7.93–7.83 (m, 2H), 7.35–7.27 (m, 2H), 5.68 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.17 (dq, *J* = 9.1, 1.4 Hz, 1H), 5.14 (q, *J* = 1.4 Hz, 1H), 4.47 (qdt, *J* = 13.2, 5.6, 1.4 Hz, 2H), 3.98 (ddd, *J* = 12.8, 6.9, 6.1 Hz, 1H), 3.90 (ddt, J = 12.4, 6.0, 0.8 Hz, 1H), 2.42 (s, 3H), 2.34–2.26 (m, 1H), 1.95 (tt, *J* = 6.5, 5.5 Hz, 2H), 1.71 (ddd, *J* = 14.2, 8.1, 6.6 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 169.9, 144.6, 135.7, 131.1, 129.2, 128.6, 118.7, 66.1, 52.8, 46.4, 32.4, 22.3, 21.6, 20.4; IR (Neat Film NaCl) 2942, 1740, 1691, 1353, 1284, 1167, 1090 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{21}NO_5SNa$ $[M+Na]^+$: 374.1033, found 374.1042.

Representative Method 2: Acylation and Alkylation Method

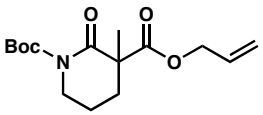


Acyl Lactam SI6: To a cooled (0 °C) solution of di*iso*propylamine (3.33 mL, 23.6 mmol, 1.20 equiv) in THF (131 mL) was added a solution of *n*-BuLi (8.84 mL, 21.7 mmol, 2.45 M in hexanes, 1.10 equiv) dropwise over 10 min. After 30 min at 0 °C, the reaction mixture was cooled to –78 °C. A solution of benzoyl lactam **SI5**[7] (4.00 g, 19.7 mmol, 1.00 equiv) in THF (25 mL) was added dropwise over 10 min. After an additional 2 h, the reaction mixture was warmed to –30 °C for 1 h, cooled to –78 °C, and treated with allyl cyanoformate (2.41 g, 21.7 mmol, 1.10 equiv). The reaction mixture was maintained at –78 °C for 2 h, allowed to warm to ambient temperature with stirring over 14 h, and diluted with half-saturated brine (100 mL) and EtOAc (100 mL). The phases were separated, and the aqueous phase was extracted with EtOAc (4 x 100 mL). The combined organic phases were washed with brine (2 x 100 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (5 x 30 cm SiO_2, 15 to 30% EtOAc in hexanes) to afford acyl lactam **SI6** as a colorless oil (4.18 g, 74% yield). R_f = 0.43 (35% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.75–7.62 (m, 2H), 7.52–7.43 (m, 1H), 7.42–7.33 (m, 2H), 5.95 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.29 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.75–4.60 (m, 2H), 3.95–3.72 (m, 2H), 3.59 (t, *J* = 6.4 Hz, 1H), 2.42–2.25 (m, 1H), 2.26–2.14 (m, 1H), 2.12–2.03 (m, 1H), 2.01–1.89 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 169.5, 169.2, 135.4, 131.9, 131.4, 128.2, 128.1, 119.3, 66.4, 51.1, 46.3, 25.5, 20.7; IR (Neat Film NaCl) 3063, 2952, 1738, 1682, 1449, 1284, 1152, 730, 700 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{18}NO_4$ $[M+H]^+$: 288.1230, found 288.1221.

Benzoyl Lactam SI7: To a mixture of acyl lactam **SI6** (750 mg, 2.61 mmol, 1.00 equiv) K_2CO_3 (1.80 g, 13.1 mmol, 5.00 equiv) in acetone (10.5 mL) was added acrylonitrile (344 μL, 5.22 mmol, 2.00 equiv). The reaction mixture was heated (55 °C) for 6 h, then cooled to ambient temperature and filtered. The retentate was washed with acetone (2 x 10 mL). The combined organic phases were concentrated under reduced pressure. The resulting oil was purified by flash chromatography (3 x 30 cm SiO_2, 5 to 30% EtOAc in hexanes) to afford benzoyl lactam **SI7** as a colorless oil (654 mg, 74% yield). R_f = 0.23 (20% EtOAc in hexanes developed twice); ^1H NMR (500 MHz, $CDCl_3$) δ 7.77–7.66 (m, 2H), 7.56–7.45 (m, 1H), 7.43–7.34 (m, 2H), 6.00 (ddt, *J* = 17.2, 10.3, 6.2 Hz, 1H), 5.44 (dq, *J* = 17.1, 1.3 Hz, 1H), 5.38 (dq, *J* = 10.3, 1.1 Hz, 1H), 4.77 (ddt, *J* = 6.1, 3.1, 1.2 Hz, 2H), 3.85 (ddd, *J* = 13.0, 9.6, 5.4 Hz, 1H), 3.76 (ddt, *J* = 13.0, 4.9, 1.4 Hz, 1H), 2.61 (ddd, *J* = 17.0, 8.4, 6.9 Hz, 1H), 2.53–2.35 (m, 2H), 2.22 (ddd, *J* = 8.8, 6.7,

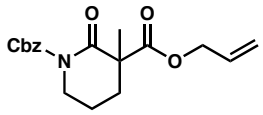
1.6 Hz, 2H), 2.12–1.95 (m, 2H), 1.89 (ddd, J = 13.6, 10.1, 5.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 171.2, 170.6, 135.4, 132.0, 130.8, 128.2, 128.1, 120.5, 119.1, 67.0, 55.4, 46.4, 31.7, 31.5, 20.0, 13.5; IR (Neat Film NaCl) 3067, 2952, 2248, 1733, 1683, 1449, 1271, 1196, 1175, 1152, 943, 725 cm^{-1}; HRMS (MM: ESI-APCI) m/z calc'd for $C_{19}H_{21}N_2O_4$ $[M+H]^+$: 341.1496, found 341.1492.

Preparation of Lactam Substrates Used in Figure 2



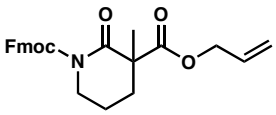
1b

Boc Lactam 1b: Prepared in a manner analogous to tosyl lactam **1a** using lactam **SI4** (394 mg, 2.00 mmol, 1.00 equiv) and Boc_2O (873 mg, 4.00 mmol, 2.00 equiv). Boc lactam **1b** (407 mg, 68% yield) was isolated as an amorphous solid by flash chromatography (SiO_2, 9 to 11% Et_2O in hexanes). R_f = 0.54 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.95–5.81 (m, 1H), 5.33 (dq, J = 17.2, 1.5 Hz, 1H), 5.22 (dq, J = 10.5, 1.5 Hz, 1H), 4.64 (m, 2H), 3.80–3.70 (m, 1H), 3.63–3.49 (m, 1H), 2.43–2.33 (m, 1H), 1.98–1.77 (m, 2H), 1.75–1.66 (m, 1H), 1.52 (s, 9H), 1.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 170.9, 153.1, 131.5, 118.4, 83.0, 65.9, 53.1, 46.0, 32.6, 28.0, 22.9, 20.1; IR (Neat Film NaCl) 2981, 2939, 1772, 1719, 1457, 1393, 1294, 1282, 1254, 1152, 988, 945, 852 cm^{-1}; HRMS (MM: ESI-APCI) m/z calc'd for $C_{15}H_{23}NO_5Na$ $[M+Na]^+$: 320.1468, found 320.1470.



1c

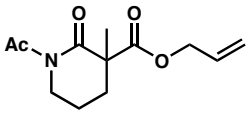
Cbz Lactam 1c: Prepared in a manner analogous to tosyl lactam **1a** using lactam **SI4** (394 mg, 2.00 mmol, 1.00 equiv) and CbzCl (682 mg, 4.00 mmol, 2.00 equiv). Cbz lactam **1c** (325 mg, 49% yield) was isolated as a colorless oil by flash chromatography (SiO_2, 14 to 17% Et_2O in hexanes). R_f = 0.34 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.40 (m, 2H), 7.39–7.28 (m, 3H), 5.85 (ddt, J = 17.1, 10.5, 5.6 Hz, 1H), 5.30 (dq, J = 10.5, 1.3 Hz, 1H), 5.29 (s, 2H), 5.19 (dq, J = 10.5, 1.3 Hz, 1H), 4.69–4.54 (m, 2H), 3.86–3.79 (m, 1H), 3.71–3.60 (m, 1H), 2.44–2.37 (m, 1H), 1.98–1.78 (m, 2H), 1.73 (ddd, J = 14.0, 9.1, 5.1 Hz, 1H), 1.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 170.9, 154.4, 135.4, 131.3, 128.5, 128.2, 128.0, 118.7, 68.6, 66.1, 53.3, 46.4, 32.5, 22.8, 20.0; IR (Neat Film NaCl) 2943, 2876, 1776, 1721, 1456, 1378, 1270, 1191, 1167, 1125, 1002, 941, 739, 698 cm^{-1}; HRMS (MM: ESI-APCI) m/z calc'd for $C_{18}H_{21}NO_5Na$ $[M+Na]^+$: 354.1312, found 354.1310.



1d

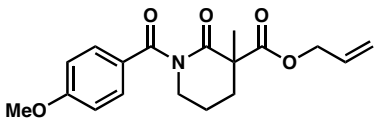
Fmoc Lactam 1d: Prepared in a manner analogous to tosyl lactam **1a** using lactam **SI4** (394 mg, 2.00 mmol, 1.00 equiv) and FmocCl (621 mg, 2.40 mmol, 1.20 equiv). Fmoc lactam **1c** (352 mg, 42% yield) was isolated as a colorless oil by flash chromatography (SiO_2, 2 to 12% Et_2O in hexanes). R_f = 0.28 (25%

EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.73 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 2H), 7.43–7.38 (m, 2H), 7.32 (tdd, *J* = 7.4, 4.8, 1.2 Hz, 2H), 5.91 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.36 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.25 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.69 (ddt, *J* = 5.6, 2.8, 1.4 Hz, 2H), 4.56–4.43 (m, 2H), 4.33 (t, *J* = 7.5 Hz, 1H), 3.86–3.79 (m, 1H), 3.73–3.61 (m, 1H), 2.44 (dddd, *J* = 13.8, 6.8, 5.0, 0.9 Hz, 1H), 2.00–1.83 (m, 2H), 1.78 (ddd, *J* = 14.0, 9.1, 5.0 Hz, 1H), 1.59 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 170.9, 154.5, 143.6, 141.2, 131.4, 127.8, 127.1, 125.4, 119.9, 118.7, 69.3, 66.1, 53.4, 46.6, 46.4, 32.6, 22.9, 20.0; IR (Neat Film NaCl) 2948, 2892, 1776, 1721, 1451, 1378, 1269, 1191, 997, 759, 742 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{25}H_{25}NO_5Na$ $[M+Na]^+$: 442.1625, found 442.1610.



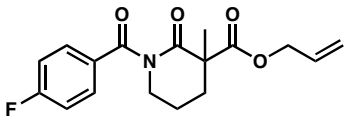
1e

Acetyl Lactam 1e: Prepared in a manner analogous to benzoyl lactam **1h** using lactam **SI4** (394 mg, 2.00 mmol, 1.00 equiv), acetic anhydride (940 μL, 10.0 mmol, 5.00 equiv), and triethylamine (2.80 mL, 20.0 mmol, 10.0 equiv). Acetyl lactam **1e** (347 mg, 72% yield) was isolated as a colorless oil by flash chromatography (SiO_2, 12 to 25% Et_2O in hexanes). R_f = 0.44 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 17.1, 10.4, 5.7 Hz, 1H), 5.31 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.25 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.66–4.60 (m, 2H), 3.78 (ddd, *J* = 13.1, 7.6, 5.3 Hz, 1H), 3.71–3.62 (m, 1H), 2.49 (s, 3H), 2.44–2.37 (m, 1H), 1.93–1.77 (m, 2H), 1.78–1.70 (m, 1H), 1.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 173.5, 172.4, 131.3, 119.1, 66.2, 53.2, 44.0, 32.9, 27.0, 22.7, 19.9; IR (Neat Film NaCl) 2985, 2942, 1739, 1699, 1457, 1368, 1301, 1261, 1190, 1132, 1048, 990, 959, 936 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{12}H_{18}NO_4$ $[M+H]^+$: 240.1230, found 240.1237.



1f

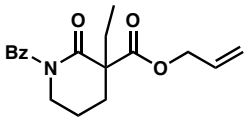
4-Methoxybenzoyl Lactam 1f: Prepared in a manner analogous to benzoyl lactam **1h** using lactam **SI4** (394 mg, 2.00 mmol, 1.00 equiv), 4-methoxybenzoyl chloride (682 mg, 4.00 mmol, 2.00 equiv), and triethylamine (840 μL, 6.00 mmol, 3.00 equiv). 4-Methoxybenzoyl lactam **1f** (425 mg, 64% yield) was isolated as a colorless oil by flash chromatography (SiO_2, $CHCl_3$-hexanes-Et_2O 6.5:5:1). R_f = 0.76 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81–7.67 (m, 2H), 6.93–6.79 (m, 2H), 6.05–5.88 (m, 1H), 5.39 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.31 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.71 (dt, *J* = 6.0, 1.3 Hz, 2H), 3.90–3.77 (m, 1H), 3.82 (s, 3H), 3.76–3.63 (m, 1H), 2.48 (ddd, *J* = 13.7, 5.7, 4.3 Hz, 1H), 2.06–1.89 (m, 2H), 1.80 (ddd, *J* = 13.5, 10.0, 5.0 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 172.6 (2C), 162.7, 131.4, 130.7, 127.7, 119.3, 113.3, 66.3, 55.3, 52.8, 46.9, 33.7, 22.5, 20.2; IR (Neat Film NaCl) 3080, 2941, 1732, 1682, 1604, 1512, 1456, 1390, 1257, 1173, 1139, 1029, 939, 844, 770 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{22}NO_5$ $[M+H]^+$: 332.1492, found 332.1501.



1g

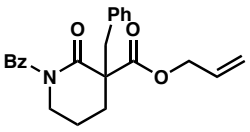
4-Fluorobenzoyl Lactam 1g: Prepared in a manner analogous to benzoyl lactam **1h** using lactam **SI4** (394 mg, 2.00 mmol, 1.00 equiv), 4-fluorobenzoyl chloride (470 μL, 4.00 mmol, 2.00 equiv), and triethylamine (840 μL, 6.00 mmol, 3.00 equiv). 4-Fluorobenzoyl lactam **1g** (557 mg, 87% yield) was isolated as an amorphous white solid by flash chromatography (SiO_2, 15 to 25% Et_2O in hexanes). R_f = 0.37 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84–7.72 (m, 2H), 7.12–6.97 (m, 2H), 5.99 (ddt, J = 17.2, 10.4, 5.9 Hz, 1H), 5.41 (dq, J = 17.2, 1.4 Hz, 1H), 5.35 (dq, J = 10.4, 1.2 Hz, 1H), 4.73 (dt, J = 6.0, 1.3 Hz, 2H), 3.89–3.82 (m, 1H), 3.81–3.75 (m, 1H), 2.57–2.42 (m, 1H), 2.09–1.91 (m, 2H), 1.89–1.75 (m, 1H), 1.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 172.9, 172.5, 164.8 (d, $J_{C\text{-}F}$ = 252.5 Hz), 131.8 (d, $J_{C\text{-}F}$ = 3.3 Hz), 131.3, 130.7 (d, $J_{C\text{-}F}$ = 9.0 Hz), 119.5, 115.2 (d, $J_{C\text{-}F}$ = 22.0 Hz), 66.5, 52.9, 47.0, 33.8, 22.4, 20.2; IR (Neat Film NaCl) 3079, 2943, 2874, 1734, 1684, 1602, 1508, 1277, 1240, 1193, 1140, 939, 849, 770 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{19}NO_4F$ $[M+H]^+$: 320.1293, found 320.1297.

Preparation of Lactam Substrates Used in Figure 3



SI8

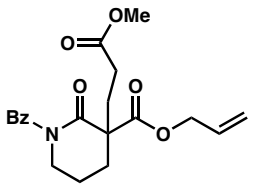
Benzoyl Lactam SI8: Prepared by representative method 1 using diallyl 2-ethylmalonate as a starting material. Benzoyl lactam **SI8** was isolated by flash chromatography (SiO_2, 15 to 25% Et_2O in hexanes) as a colorless oil. R_f = 0.38 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72–7.67 (m, 2H), 7.51–7.43 (m, 1H), 7.37 (dd, J = 8.3, 7.1 Hz, 2H), 5.99 (ddt, J = 17.3, 10.4, 5.9 Hz, 1H), 5.40 (dq, J = 17.2, 1.4 Hz, 1H), 5.33 (dq, J = 10.4, 1.2 Hz, 1H), 4.73 (dt, J = 6.0, 1.3 Hz, 2H), 3.93–3.63 (m, 2H), 2.43 (ddt, J = 13.7, 4.4, 1.4 Hz, 1H), 2.17–1.65 (m, 5H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 172.0, 171.8, 135.9, 131.6, 131.4, 128.0 (2C), 119.5, 66.4, 56.9, 46.4, 29.8, 28.6, 20.3, 9.0; IR (Neat Film NaCl) 3062, 2943, 2882, 1732, 1678, 1449, 1385, 1268, 1188, 1137, 980, 937, 723, 693, 660 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{22}NO_4$ $[M+H]^+$: 316.1543, found 316.1545.



SI9

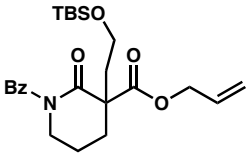
Benzoyl Lactam SI9: Prepared by representative method 1 using diallyl 2-benzylmalonate as a starting material. Benzoyl lactam **SI9** was isolated by flash chromatography (SiO_2, 15 to 35% Et_2O in hexanes) as a colorless oil. R_f = 0.32 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dt, J = 8.2, 0.9 Hz, 2H), 7.56–7.45 (m, 1H), 7.45–7.35 (m, 2H), 7.30–7.18 (m, 3H), 7.17–7.10 (m, 2H), 6.00 (ddt, J = 17.2, 10.4, 6.0 Hz, 1H), 5.43 (dq, J = 17.2, 1.4 Hz, 1H), 5.36 (dq, J = 10.4, 1.1 Hz, 1H), 4.75 (dq, J = 6.1, 1.1 Hz, 2H), 3.70 (dddd, J = 12.9, 5.0, 4.3, 1.7 Hz, 1H), 3.59 (ddd, J = 12.9, 10.5, 4.6 Hz, 1H), 3.47 (d, J = 13.7 Hz, 1H), 3.14 (d, J = 13.7 Hz, 1H), 2.36 (ddt, J = 13.7, 4.3, 1.7 Hz, 1H), 2.07–1.92 (m, 1H), 1.91–

1.75 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 171.5, 171.3, 135.9, 135.7, 131.8, 131.2, 130.9, 128.3, 128.2, 128.0, 127.0, 119.8, 66.7, 57.8, 46.2, 40.6, 29.8, 20.1; IR (Neat Film NaCl) 3062, 3029, 2941, 2890, 1731, 1701, 1682, 1449, 1273, 1190, 1147, 934, 723, 702, 661 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{24}NO_4$ $[M+H]^+$: 378.1700, found 378.1706.



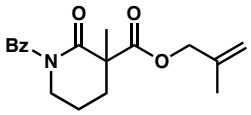
SI10

Benzoyl Lactam SI10: Prepared by representative method 2 using methyl acrylate as an alkylating reagent. Benzoyl lactam **SI10** was isolated by flash chromatography (SiO_2, 40 to 50% Et_2O in hexanes) as a colorless oil. R_f = 0.28 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.66 (m, 2H), 7.52–7.42 (m, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 6.04–5.93 (m, 1H), 5.41 (dq, *J* = 17.1, 1.1 Hz, 1H), 5.35 (dt, *J* = 10.4, 1.0 Hz, 1H), 4.79–4.68 (m, 2H), 3.88–3.79 (m, 1H), 3.79–3.72 (m, 1H), 3.63 (s, 3H), 2.56–2.41 (m, 2H), 2.40–2.28 (m, 1H), 2.27–2.18 (m, 2H), 2.08–1.92 (m, 2H), 1.85 (ddd, *J* = 15.2, 9.8, 5.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 173.1, 171.6, 171.3, 135.7, 131.7, 131.1, 128.0 (2C), 119.9, 66.6, 55.8, 51.7, 46.4, 31.0, 30.5, 29.7, 20.1; IR (Neat Film NaCl) 2952, 1735, 1685, 1449, 1273, 1194, 1174, 726 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{24}NO_6$ $[M+H]^+$: 374.1598, found 374.1592.



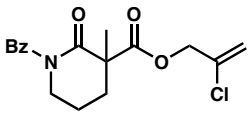
SI11

Benzoyl Lactam SI11: Prepared by representative method 2 using (2-bromoethoxy)-*tert*-butyldimethylsilane as an alkylating reagent. Benzoyl lactam **SI11** was isolated by flash chromatography (SiO_2, 10 to 40% Et_2O in hexanes) as a colorless oil. R_f = 0.18 (10% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74–7.62 (m, 2H), 7.52–7.42 (m, 1H), 7.40–7.30 (m, 2H), 5.98 (ddt, *J* = 17.1, 10.4, 6.0 Hz, 1H), 5.40 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.33 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.72 (dt, *J* = 6.0, 1.3 Hz, 2H), 3.80 (ddt, *J* = 6.4, 4.8, 2.4 Hz, 2H), 3.72 (td, *J* = 6.4, 0.8 Hz, 2H), 2.55–2.31 (m, 1H), 2.23 (dt, *J* = 14.1, 6.6 Hz, 1H), 2.16–2.03 (m, 2H), 2.02–1.92 (m, 2H), 0.86 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 171.7 (2C), 136.0, 131.6, 131.4, 128.0 (2C), 119.6, 66.5, 59.5, 55.3, 46.4, 37.8, 30.6, 25.9, 20.3, 18.2, –5.45, –5.47; IR (Neat Film NaCl) 2954, 2929, 2884, 2856, 1735, 1703, 1683, 1276, 1255, 1143, 1092, 836 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{24}H_{36}NO_5Si$ $[M+H]^+$: 446.2357, found 446.2361.



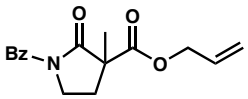
SI12

Benzoyl Lactam SI12: Prepared by representative method 1 using dimethallyl malonate as a starting material. Benzoyl lactam **SI12** was isolated by flash chromatography (SiO_2, 14 to 20% Et_2O in hexanes) as an amorphous white solid. R_f = 0.47 (25% EtOAc in hexanes); ^{1}H NMR δ 7.73–7.68 (m, 2H), 7.49–7.44 (m, 1H), 7.37 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 2H), 5.05 (s, 1H), 5.01 (s, 1H), 4.65 (dd, *J* = 17.5, 10.0 Hz, 2H), 3.87 (ddd, *J* = 12.9, 8.8, 5.6 Hz, 1H), 3.80 (ddt, *J* = 12.9, 5.2, 1.4 Hz, 1H), 2.55–2.46 (m, 1H), 2.08–1.95 (m, 2H), 1.86–1.79 (m, 1H), 1.79 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 172.8, 172.5, 139.3, 135.9, 131.6, 128.0 (2C), 114.2, 69.1, 53.0, 46.8, 33.8, 22.5, 20.3, 19.6; IR (Neat Film NaCl) 2941, 2873, 1735, 1682, 1449, 1276, 1192, 1140, 940, 724, 694, 659 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{21}NO_4Na$ $[M+Na]^+$: 338.1363, found 338.1373.



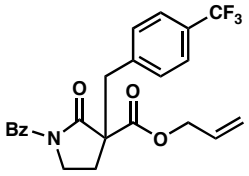
SI13

Benzoyl Lactam SI13: Prepared by representative method 1 using di-2-chloroallyl malonate as a starting material. Benzoyl lactam **SI13** was isolated by flash chromatography (SiO_2, 14 to 20% Et_2O in hexanes) as a colorless oil. R_f = 0.47 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76–7.64 (m, 2H), 7.56–7.41 (m, 1H), 7.43–7.31 (m, 2H), 5.54 (dt, *J* = 2.0, 1.1 Hz, 1H), 5.48 (d, *J* = 1.8 Hz, 1H), 4.80 (qd, *J* = 13.4, 1.0 Hz, 2H), 3.89 (ddd, *J* = 12.9, 8.9, 5.1 Hz, 1H), 3.80 (ddt, *J* = 13.0, 5.3, 1.3 Hz, 1H), 2.52 (dddd, *J* = 13.8, 5.6, 4.1, 1.3 Hz, 1H), 2.11–1.94 (m, 2H), 1.85 (ddd, *J* = 13.8, 10.2, 4.5 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 172.5, 172.1, 135.8, 135.3, 131.7, 128.1, 128.0, 116.4, 67.1, 52.9, 46.7, 33.7, 22.5, 20.1; IR (Neat Film NaCl) 2943, 2873, 1740, 1682, 1449, 1390, 1276, 1192, 1124, 1061, 943, 724, 695 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{18}NO_4ClNa$ $[M+Na]^+$: 358.0817 found 358.0819.



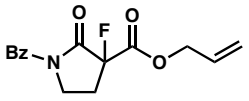
SI14

Benzoyl Lactam SI14: Prepared by representative method 2 using *N*-benzoyl pyrrolidinone[8] as a starting material and methyl iodide as an alkylating reagent. Benzoyl lactam **SI14** was isolated by flash chromatography (SiO_2, 5 to 20% EtOAc in hexanes) as a colorless oil. R_f = 0.45 (35% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64–7.55 (m, 2H), 7.56–7.46 (m, 1H), 7.45–7.35 (m, 2H), 5.92 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.34 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.67 (dt, *J* = 5.7, 1.4 Hz, 2H), 4.02 (ddd, *J* = 11.3, 8.4, 4.6 Hz, 1H), 3.95 (dt, *J* = 11.3, 7.7 Hz, 1H), 2.64 (ddd, *J* = 13.2, 7.7, 4.5 Hz, 1H), 2.06 (ddd, *J* = 13.2, 8.5, 7.6 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 170.9, 170.5, 133.9, 132.0, 131.2, 128.8, 127.8, 119.0, 66.4, 53.8, 43.3, 30.5, 20.0; IR (Neat Film NaCl) 2985, 2938, 1750, 1738, 1733, 1683, 1449, 1362, 1307, 1247, 1196, 1136, 972, 937, 860, 730, 699, 656 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{18}NO_4$ $[M+H]^+$: 288.1230, found 288.1228.



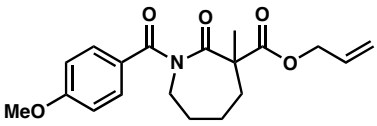
SI15

Benzoyl Lactam SI15: Prepared by representative method 2 using *N*-benzoyl pyrrolidinone[7] as a starting material and 4-(trifluoromethyl)benzyl bromide as an alkylating reagent. Benzoyl lactam **SI15** was isolated by flash chromatography (SiO_2, 10 to 20% EtOAc in hexanes) as a colorless oil. R_f = 0.28 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.56–7.49 (m, 3H), 7.44–7.38 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 5.92 (ddt, *J* = 17.3, 10.4, 5.8 Hz, 1H), 5.36 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.30 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.70 (dq, *J* = 5.8, 1.2 Hz, 2H), 3.84 (ddd, *J* = 11.2, 8.6, 7.6 Hz, 1H), 3.66 (ddd, *J* = 11.2, 8.8, 3.2 Hz, 1H), 3.39 (d, *J* = 14.0 Hz, 1H), 3.31 (d, *J* = 13.9 Hz, 1H), 2.51 (ddd, *J* = 13.3, 7.6, 3.3 Hz, 1H), 2.15 (dt, *J* = 13.3, 8.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 170.2, 169.8, 139.7 (d, $J_{C\text{-}F}$ = 1.5 Hz), 133.7, 132.3, 131.0, 130.9, 129.8 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.9, 127.9, 125.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.0 (q, $J_{C\text{-}F}$ = 272.0 Hz), 119.5, 66.8, 59.0, 43.6, 38.4, 26.2; IR (Neat Film NaCl) 3062, 2938, 2913, 1751, 1733, 1683, 1449, 1366, 1326, 1294, 1250, 1193, 1165, 1116, 1068, 861, 728 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{21}NO_4F_3$ $[M+H]^+$: 432.1417, found 432.1425.



SI16

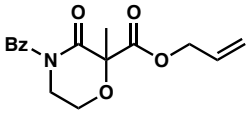
Benzoyl Lactam SI16: Prepared by representative method 2 using *N*-benzoyl pyrrolidinone[7] as a starting material and using Selectfluor as a fluorinating agent.[9] Benzoyl lactam **SI16** was isolated by flash chromatography (SiO_2, 10 to 20% EtOAc in hexanes) as a colorless oil. R_f = 0.28 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66–7.59 (m, 2H), 7.59–7.50 (m, 1H), 7.46–7.37 (m, 2H), 5.92 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.32 (dq, *J* = 10.4, 1.1 Hz, 1H), 4.77 (dt, *J* = 5.9, 1.3 Hz, 2H), 4.15 (ddd, *J* = 11.2, 8.8, 4.2 Hz, 1H), 4.01 (dddd, *J* = 11.3, 7.7, 7.0, 2.0 Hz, 1H), 2.80 (dddd, *J* = 14.1, 13.4, 7.8, 4.2 Hz, 1H), 2.53 (dddd, *J* = 23.0, 14.2, 8.8, 7.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 166.0 (d, *J* = 10.2 Hz), 165.8 (d, *J* = 5.5 Hz), 132.9, 132.7, 130.4, 129.0, 128.0, 120.0, 94.4 (d, *J* = 203.6 Hz), 67.2, 42.3 (d, *J* = 2.9 Hz), 29.0 (d, *J* = 21.7 Hz); IR (Neat Film NaCl) 3062, 2987, 2917, 1773, 1690, 1449, 1373, 1290, 1257, 1198, 1161, 1118, 1076, 983, 942, 859, 796, 731 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{19}NO_5F$ $[M+MeOH+H]^+$: 324.1242, found 324.1244.



SI17

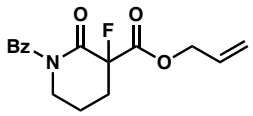
4-Methoxybenzoyl Lactam SI17: Prepared by combination of known methods[10] and representative method 1. Benzoyl lactam **SI17** was isolated by flash chromatography (SiO_2, 15 to 25% Et_2O in hexanes) as a colorless oil. R_f = 0.38 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79–7.68 (m, 2H), 6.94–6.80 (m, 2H), 5.99 (ddt, *J* = 17.1, 10.4, 6.1 Hz, 1H), 5.43 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.34 (dq, *J* =

10.4, 1.1 Hz, 1H), 4.76 (dt, *J* = 6.1, 1.2 Hz, 2H), 4.28–4.16 (m, 1H), 3.84 (s, 3H), 3.15 (ddd, *J* = 15.6, 11.1, 1.2 Hz, 1H), 2.28–2.17 (m, 1H), 2.01–1.87 (m, 2H), 1.87–1.76 (m, 1H), 1.63 (ddd, *J* = 14.8, 11.8, 3.7 Hz, 2H), 1.48 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 174.6, 172.8, 162.6, 131.3, 130.7, 128.2, 119.9, 113.5, 66.2, 55.3, 54.9, 44.6, 34.3, 28.1, 26.9, 24.9; IR (Neat Film NaCl) 2939, 1679, 1604, 1512, 1456, 1281, 1256, 1169, 1139, 1054, 961 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{19}H_{24}NO_5$ $[M+H]^+$: 346.1649, found 346.1642.



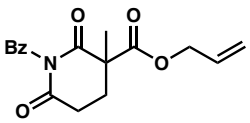
SI18

Benzoyl Lactam SI18: Prepared by representative method 2 using 3-morpholinone[11] as a starting material and methyl iodide as an alkylating reagent Benzoyl lactam **SI18** was isolated by flash chromatography (SiO_2, 5 to 15% EtOAc in hexanes) as a colorless oil. R_f = 0.40 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70–7.61 (m, 2H), 7.56–7.44 (m, 1H), 7.46–7.33 (m, 2H), 5.98 (ddt, *J* = 17.1, 10.4, 5.9 Hz, 1H), 5.41 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.34 (dq, *J* = 10.4, 1.1 Hz, 1H), 4.76 (dt, *J* = 6.0, 1.3 Hz, 2H), 4.24 (ddd, *J* = 12.4, 10.1, 3.2 Hz, 1H), 4.12 (ddd, *J* = 12.4, 4.1, 3.3 Hz, 1H), 4.02 (ddd, *J* = 13.2, 10.1, 4.1 Hz, 1H), 3.91 (dt, *J* = 13.2, 3.3 Hz, 1H), 1.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 169.0 (2C), 134.9, 132.2, 131.0, 128.3, 128.1, 119.8, 81.5, 66.8, 61.6, 45.3, 22.2; IR (Neat Film NaCl) 2943, 2892, 1749, 1689, 1149, 1375, 1311, 1281, 1246, 1124, 1080, 938, 727 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{18}NO_5$ $[M+H]^+$: 304.1179, found 304.1171.



SI19

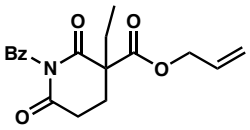
Benzoyl Lactam SI19: Prepared by representative method 2 using Selectfluor as a fluorinating agent.[8] Benzoyl lactam **SI19** was isolated by flash chromatography (SiO_2, 20 to 35% Et_2O in hexanes) as a colorless oil. R_f = 0.57 (35% Et_2O in hexanes developed three times); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.61 (m, 2H), 7.53–7.45 (m, 1H), 7.42–7.34 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.39 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.31 (dq, *J* = 10.4, 1.1 Hz, 1H), 4.76 (dt, *J* = 6.0, 1.3 Hz, 2H), 3.98 (dddd, *J* = 12.9, 6.0, 4.7, 1.1 Hz, 1H), 3.80 (dddd, *J* = 14.8, 8.8, 4.4, 1.7 Hz, 1H), 2.62–2.45 (m, 1H), 2.45–2.30 (m, 1H), 2.25–2.05 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 166.7 (d, *J* = 26.0 Hz), 166.3 (d, *J* = 23.5 Hz), 134.3, 132.3, 130.6, 128.3, 128.2, 119.9, 92.4 (d, *J* = 194.8 Hz), 67.1, 46.2, 31.9 (d, *J* = 22.4 Hz), 18.6 (d, *J* = 4.0 Hz); IR (Neat Film NaCl) 3064, 2956, 1768, 1711, 1691, 1450, 1396, 1304, 1271, 1190, 1137, 1102, 994, 944, 912, 726, 694, 658 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{17}NO_4F$ $[M+H]^+$: 306.1136, found 306.1131.



SI20

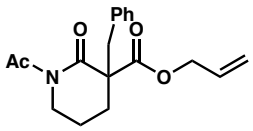
Benzoyl Glutarimide SI20: Prepared from glutarimide by combination of known methods[10] and representative method 1. Benzoyl glutarimide **SI20** (32 mg, 72% yield) was isolated as a colorless oil by

flash chromatography (SiO_2, 17 to 25% EtOAc in hexanes). R_f = 0.18 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.22 Hz, 2H), 7.62 (t, *J* = 7.46 Hz, 1H), 7.46 (dd, *J* = 8.22, 7.46 Hz, 2H), 5.93 (ddt, *J* = 17.2, 10.4, 6.0 Hz, 1H), 5.39 (dq, *J* = 17.2, 1.20 Hz, 1H), 5.32 (dq, *J* = 10.4, 1.20 Hz, 1H), 4.75 (ddt, *J* = 12.9, 6.0, 1.20 Hz, 1H), 4.71 (ddt, *J* = 12.9, 6.0, 1.20 Hz, 1H), 2.81–2.70 (m, 2H), 2.40 (ddd, *J* = 14.2, 5.13, 3.56 Hz, 1H), 2.10 (ddd, *J* = 14.2, 11.7, 6.36 Hz, 1H), 1.59 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 170.8, 170.7, 170.4, 134.9, 131.6, 130.8, 130.3, 129.0, 120.0, 66.9, 51.0, 30.0, 29.1, 20.8; IR (Neat Film NaCl) 3070, 2943, 2878, 1755, 1716, 1689, 1450, 1240, 1179, 975, 781 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{18}NO_5$ $[M+H]^+$: 316.1179, found 316.1192.



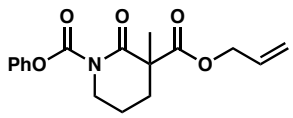
SI21

Benzoyl Glutarimide SI21: Prepared from glutarimide by combination of known methods[10] and representative method 1. Benzoyl glutarimide **SI21** (67 mg, 85% yield) was isolated as a colorless oil by flash chromatography (SiO_2, 17 to 25% EtOAc in hexanes). R_f = 0.24 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.28 Hz, 2H), 7.62 (t, *J* = 7.46 Hz, 1H), 7.46 (dd, *J* = 8.28, 7.46 Hz, 2H), 5.93 (ddt, *J* = 17.0, 10.4, 6.0 Hz, 1H), 5.39 (dq, *J* = 17.0, 1.2 Hz, 1H), 5.32 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.77 (ddt, *J* = 12.9, 6.0, 1.2 Hz, 1H), 4.74 (ddt, *J* = 12.9, 6.0, 1.2 Hz, 1H), 2.84–2.72 (m, 2H), 2.34 (ddd, *J* = 14.1, 5.2, 3.28 Hz, 1H), 2.19 (ddd, *J* = 14.1, 12.2, 5.88 Hz, 1H), 2.15–2.02 (m, 2H), 1.01 (t, *J* = 7.44 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 170.4, 170.2, 170.1, 134.9, 131.6, 130.8, 130.3, 129.0, 120.0, 66.8, 55.1, 29.9, 27.6, 25.6, 8.9; IR (Neat Film NaCl) 3068, 2975, 2884, 1755, 1716, 1694, 1450, 1270, 1180, 950, 779 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{20}NO_5$ $[M+H]^+$: 330.1336, found 330.1334.



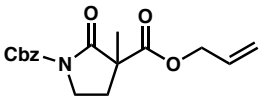
SI22

Acetyl Lactam SI22: Prepared by representative method 1 using dially 2-benzylmalonate as a starting material and acetic anhydride as an acetylating reagent. Acetyl lactam **SI22** was isolated by flash chromatography (SiO_2, 5 to 20% EtOAc in hexanes) as a colorless oil. R_f = 0.46 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.20 (m, 3H), 7.20–7.14 (m, 2H), 5.88 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.33 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.65 (dq, *J* = 5.8, 1.4 Hz, 2H), 3.73–3.62 (m, 1H), 3.53 (d, *J* = 13.6 Hz, 1H), 3.35 (ddd, *J* = 13.8, 9.1, 4.8 Hz, 1H), 3.16 (d, *J* = 13.6 Hz, 1H), 2.52 (s, 3H), 2.29–2.19 (m, 1H), 1.89–1.71 (m, 2H), 1.70–1.56 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 172.3, 171.6, 135.8, 131.2, 130.6, 128.3, 127.1, 119.3, 66.4, 58.1, 43.6, 41.2, 29.4, 27.2, 19.8; IR (Neat Film NaCl) 3063, 3029, 2942, 1733, 1699, 1496, 1455, 1368, 1296, 1234, 1177, 1116, 1034, 992, 975, 934, 746, 703 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{22}NO_4$ $[M+H]^+$: 316.1543, found 316.1541.



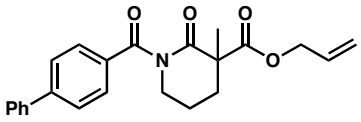
SI23

Phenyl Carbamate Lactam SI23: Prepared in a manner analogous to tosyl lactam **1a** using lactam **SI4** and phenyl chloroformate. Phenyl carbamate lactam **SI23** was isolated by flash chromatography (SiO_2, 5 to 20% EtOAc in hexanes) as a colorless oil. R_f = 0.42 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.26–7.21 (m, 1H), 7.20–7.16 (m, 2H), 5.91 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.36 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.77–4.59 (m, 2H), 3.90 (ddd, *J* = 12.9, 7.6, 5.3 Hz, 1H), 3.85–3.74 (m, 1H), 2.47 (dddd, *J* = 13.8, 6.2, 5.0, 1.0 Hz, 1H), 2.06–1.86 (m, 2H), 1.80 (ddd, *J* = 14.2, 9.3, 5.0 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 171.2, 153.3, 150.8, 131.3, 129.4, 126.0, 121.4, 118.8, 66.2, 53.4, 46.8, 32.7, 22.7, 20.1; IR (Neat Film NaCl) 2943, 1786, 1732, 1494, 1457, 1297, 1267, 1204, 1161, 1134, 982, 943, 752, 689, 665 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{20}NO_5$ $[M+H]^+$: 318.1336, found 318.1332.



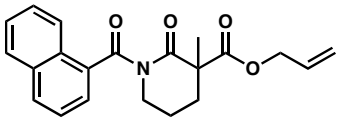
SI24

Benzyl Carbamate Lactam SI24: Prepared by representative method 2 using *N*-benzyloxycarbonylpyrrolidin-2-one[12] as a starting material and methyl iodide as an alkylating reagent. Cbz lactam **SI24** was isolated by flash chromatography (SiO_2, 5 to 15% EtOAc in hexanes) as a colorless oil. R_f = 0.40 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.40–7.28 (m, 3H), 5.87 (ddt, *J* = 17.1, 10.4, 5.6 Hz, 1H), 5.30 (dq, *J* = 17.2, 1.5 Hz, 1H) 5.30 (s, 2H), 5.23 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.69–4.55 (m, 2H), 3.82 (ddq, *J* = 10.7, 8.4, 5.8 Hz, 2H), 2.54 (ddd, *J* = 13.1, 7.4, 4.2 Hz, 1H), 1.93 (dt, *J* = 13.2, 8.3 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 170.7, 151.4, 135.1, 131.3, 128.6, 128.4, 128.1, 118.8, 68.3, 66.3, 53.3, 43.7, 30.5, 20.2; IR (Neat Film NaCl) 2984, 2939, 1793, 1758, 1725, 1456, 1383, 1300, 1202, 1138, 1009, 983, 774, 739, 698 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{20}NO_5$ $[M+H]^+$: 318.1336, found 318.1136.



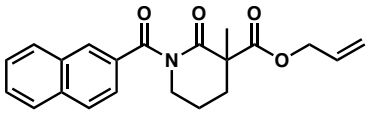
SI25

4-Phenylbenzoyl Lactam SI25: Prepared by representative method 1 using lactam **SI4** and 4-phenylbenzoyl chloride. 4-Phenylbenzoyl lactam **SI25** was isolated by flash chromatography (SiO_2, 5 to 15% EtOAc in hexanes) as an off-white solid. R_f = 0.27 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84–7.77 (m, 2H), 7.65–7.54 (m, 4H), 7.49–7.40 (m, 2H), 7.40–7.34 (m, 1H), 6.00 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.41 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.34 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.75 (dt, *J* = 5.9, 1.3 Hz, 2H), 3.95–3.84 (m, 1H), 3.81 (ddt, *J* = 12.9, 5.1, 1.4 Hz, 1H), 2.52 (dddd, *J* = 13.8, 5.7, 4.3, 1.4 Hz, 1H), 2.10–1.94 (m, 2H), 1.90–1.76 (m, 1H), 1.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 172.9, 172.5, 144.5, 140.3, 134.5, 131.4, 128.8, 128.7, 127.8, 127.3, 126.8, 119.5, 66.5, 52.9, 46.89, 33.8, 22.5, 20.3; IR (Neat Film NaCl) 3030, 2942, 2874, 1733, 1679, 1607, 1486, 1449, 1389, 1278, 1191, 1139, 939, 749, 698 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{24}NO_4$ $[M+H]^+$: 378.1700, found 378.1708.



SI26

1-Naphthoyl Lactam SI26: Prepared by representative method 1 using lactam **SI4** and 1-naphthoyl chloride. 1-Naphthoyl lactam **SI26** was isolated by flash chromatography (SiO_2, 10 to 20% EtOAc in hexanes) as a colorless oil. R_f = 0.50 (35% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07–8.01 (m, 1H), 7.90 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.88–7.83 (m, 1H), 7.57–7.47 (m, 3H), 7.42 (td, *J* = 7.6, 7.0, 1.2 Hz, 1H), 5.99–5.86 (m, 1H), 5.35 (dq, *J* = 17.3, 1.3 Hz, 1H), 5.30 (dq, *J* = 10.6, 1.0 Hz, 1H), 4.66 (ddt, *J* = 5.4, 4.2, 1.3 Hz, 2H), 4.13–3.91 (m, 2H), 2.49 (ddd, *J* = 13.6, 6.1, 4.5 Hz, 1H), 2.14–1.97 (m, 2H), 1.83 (ddd, *J* = 14.3, 9.9, 4.6 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 172.4, 172.1, 134.9, 133.6, 131.3, 130.3, 129.8, 128.4, 127.0, 126.1, 124.9, 124.4, 123.9, 119.3, 66.3, 52.9, 45.7, 33.4, 22.4, 20.1; IR (Neat Film NaCl) 3050, 2984, 2942, 1737, 1704, 1682, 1509, 1456, 1387, 1290, 1254, 1194, 1144, 1130, 935, 806, 783 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{22}NO_4$ $[M+H]^+$: 352.1543, found 352.1542.



SI27

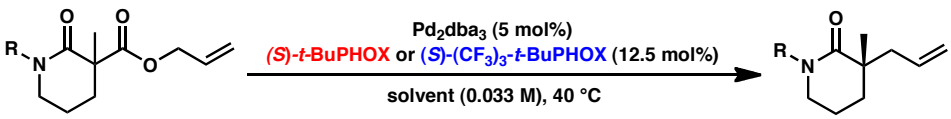
2-Naphthoyl Lactam SI27: Prepared by representative method 1 using lactam **SI4** and 2-naphthoyl chloride. 2-Naphthoyl lactam **SI27** was isolated by flash chromatography (SiO_2, 20 to 33% Et_2O in hexanes) as a colorless oil. R_f = 0.25 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (t, *J* = 1.2 Hz, 1H), 7.90 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.85–7.79 (m, 2H), 7.76 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.1, 6.9, 1.4 Hz, 1H), 6.01 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.42 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.34 (dq, *J* = 10.4, 1.1 Hz, 1H), 4.77 (dt, *J* = 5.9, 1.3 Hz, 2H), 3.93 (ddd, *J* = 12.8, 8.9, 5.3 Hz, 1H), 3.85 (ddt, *J* = 12.9, 5.1, 1.3 Hz, 1H), 2.52 (dddd, *J* = 13.8, 5.6, 4.2, 1.3 Hz, 1H), 2.12–1.93 (m, 2H), 1.84 (ddd, *J* = 13.7, 10.2, 4.7 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 172.8, 172.5, 134.8, 133.2, 132.5, 131.4, 129.2, 129.0, 127.7 (2C), 127.6, 126.3, 124.4, 119.4, 66.4, 52.9, 46.8, 33.7, 22.4, 20.2; IR (Neat Film NaCl) 3059, 2941, 2873, 1730, 1680, 1456, 1385, 1285, 1234, 1186, 1131, 936, 778, 762 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{22}NO_4$ $[M+H]^+$: 352.1543, found 352.1530.

General Procedure for Allylic Alkylation Screening Reactions

All reagents were dispensed as solutions using a Symyx Core Module within a nitrogen-filled glovebox. Oven-dried half-dram vials were charged with a solution of the palladium source (Pd_2dba_3 or Pd_2pmdba_3, 1.68 μmol, 0.05 equiv) in THF (368 μL). The palladium solutions were evaporated to dryness under reduced pressure using a Genevac centrifugal evaporator within the glovebox, and stirbars were added to the vials. The reaction vials were then charged with the desired reaction solvent (500 μL) and a solution of the PHOX ligand (4.20 μmol, 0.125 equiv) in the reaction solvent (250 μL) and stirred at ambient glovebox temperature (~28 °C). After 30 min, solutions of the lactam substrate (33.6 μmol, 1.0 equiv) in

the reaction solvent (250 μL) were added. The reaction vials were tightly capped and heated to the desired temperature. When complete consumption of the starting material was observed by colorimetric change (from light green to red-orange) and confirmed by thin layer chromatography on SiO_2 (typically less than 72 h), the reaction mixtures were removed from the glovebox, concentrated under reduced pressure, resuspended in an appropriate solvent for analysis (e.g., hexanes), filtered, and analyzed for enantiomeric excess (see Methods for the Determination of Enantiomeric Excess).

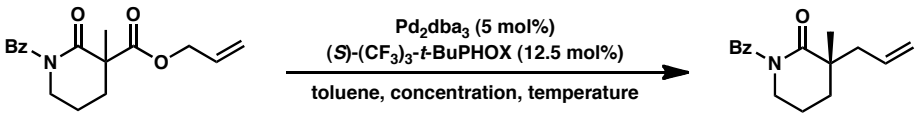
Results of Screening Various Reaction Parameters



%ee

	THF	MTBE	Toluene	Hex:Tol 2:1
R = Ts[a]	4.1 35.2	25.9 57.2	6.5 37.2	31.4 44.2
R = Boc[a]	57.3 70.3	74.5 72.1	73.6 73.0	76.7 71.0
R = Cbz	36.3 79.9	75.2 83.5	75.1 87.3	71.5 83.2
R = Fmoc	45.7 78.9	64.9 84.6	38.3 87.1	44.9 84.6
R = Ac	20.0 75.1	64.1 90.6[b]	61.6 90.2[b]	83.2 90.9[b]
R = 4-MeO-Bz	59.5 97.1	90.7 98.3	87.4 99.0	96.8 98.5
R = 4-F-Bz	42.3 95.3	85.8 99.0	83.2 99.3	96.4 99.4
R = Bz	52.2 96.2	88.3 99.2	85.8 99.0	96.4 98.8

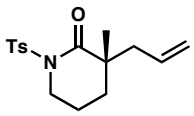
[a] Reactions for these substrates run at 50 °C. [b] Reaction performed at 60 °C



0.1 mmol

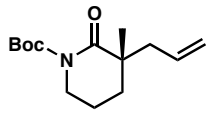
entry	temperature (°C)	concentration (M)	time (h)	% ee
1	40	0.033	43	99.2
2	45	0.033	22	98.9
3	50	0.033	12	98.7
4	55	0.033	6	98.2
5	40	0.10	43	98.9
6	40	0.20	43	97.4

Characterization Data for New Product Compounds in Figure 2



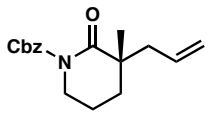
2a

Tosyl Lactam 2a: Reaction performed in MTBE at 40 °C. Tosyl lactam **2a** was isolated by flash chromatography (SiO_2, 3 to 15% Et_2O in hexanes) as a light yellow solid. 90.0% yield. R_f = 0.29 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89–7.84 (m, 2H), 7.33–7.27 (m, 2H), 5.41 (dddd, *J* = 16.9, 10.2, 8.1, 6.7 Hz, 1H), 4.99–4.86 (m, 2H), 3.99 (dddd, *J* = 11.9, 5.9, 4.9, 1.3 Hz, 1H), 3.82–3.71 (m, 1H), 2.42 (s, 3H), 2.41–2.34 (m, 1H), 2.07 (ddt, *J* = 13.6, 8.1, 1.0 Hz, 1H), 1.98–1.83 (m, 2H), 1.83–1.75 (m, 1H), 1.55–1.48 (m, 1H), 1.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 144.4, 136.2, 132.9, 129.2, 128.5, 118.9, 47.6, 44.2, 44.0, 32.1, 25.5, 21.6, 20.1; IR (Neat Film NaCl) 3074, 2938, 1689, 1597, 1454, 1351, 1283, 1171, 1103, 1089, 1039, 921, 814, 748 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{21}NO_3SNa$ $[M+Na]^+$: 330.1134, found 330.1141; $[\alpha]_D^{25}$ –69.2° (c 1.16, $CHCl_3$, 75% ee).



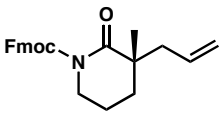
2b

Boc Lactam 2b: Reaction performed in toluene at 40 °C. Boc lactam **2b** was isolated by flash chromatography (SiO_2, 8 to 9% Et_2O in hexanes) as a colorless oil. 87.1% yield. R_f = 0.57 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (dddd, *J* = 17.1, 10.4, 7.8, 7.0 Hz, 1H), 5.14–5.02 (m, 2H), 3.71–3.61 (m, 1H), 3.58–3.48 (m, 1H), 2.48 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.26 (dd, *J* = 13.6, 7.9 Hz, 1H), 1.87–1.76 (m, 3H), 1.61–1.52 (m, 1H), 1.50 (s, 9H), 1.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.1, 153.7, 133.7, 118.5, 82.5, 47.4, 44.5, 44.2, 33.0, 28.0, 25.4, 19.7; IR (Neat Film NaCl) 3076, 2978, 2936, 1768, 1715, 1457, 1392, 1368, 1298, 1280, 1252, 1149, 999, 917, 854 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{14}H_{23}NO_3Na$ $[M+Na]^+$: 276.1570, found 276.1574; $[\alpha]_D^{25}$ –73.6° (c 1.025, $CHCl_3$, 81% ee).



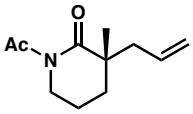
2c

Cbz Lactam 2c: Reaction performed in toluene at 40 °C. Cbz lactam **2c** was isolated by flash chromatography (SiO_2, 8 to 10% Et_2O in hexanes) as a colorless oil. 84.6% yield. R_f = 0.49 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2H), 7.36 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 2H), 7.33–7.29 (m, 1H), 5.74 (dddd, *J* = 16.6, 10.5, 7.8, 6.9 Hz, 1H), 5.26 (s, 2H), 5.13–5.02 (m, 2H), 3.80–3.72 (m, 1H), 3.67–3.58 (m, 1H), 2.51 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.26 (dd, *J* = 13.6, 7.9 Hz, 1H), 1.90–1.77 (m, 3H), 1.62–1.53 (m, 1H), 1.25 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.0, 154.8, 135.6, 133.4, 128.5, 128.2, 128.0, 118.8, 68.3, 47.8, 44.8, 44.2, 32.8, 25.5, 19.6; IR (Neat Film NaCl) 2940, 1772, 1712, 1456, 1377, 1296, 1270, 1218, 1161, 1001, 918 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{20}NO_3Na$ $[M+Na]^+$: 310.1414, found 310.1414; $[\alpha]_D^{25}$ –65.8° (c 1.48, $CHCl_3$, 86% ee).



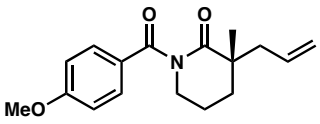
2d

Fmoc Lactam 2d: Reaction performed in toluene at 40 °C. Fmoc lactam **2d** was isolated by flash chromatography (SiO_2, 6 to 8% Et_2O in hexanes) as a colorless oil. 82.4% yield. R_f = 0.45 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 7.6, 1.0 Hz, 2H), 7.71 (ddd, *J* = 7.5, 3.6, 1.0 Hz, 2H), 7.41 (tt, *J* = 7.5, 0.9 Hz, 2H), 7.33 (ddt, *J* = 7.5, 2.0, 1.2 Hz, 2H), 5.80 (dddd, *J* = 17.9, 8.7, 7.9, 6.9 Hz, 1H), 5.18–5.10 (m, 2H), 4.53–4.42 (m, 2H), 4.33 (t, *J* = 7.4 Hz, 1H), 3.80–3.71 (m, 1H), 3.65–3.57 (m, 1H), 2.58 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.32 (ddt, *J* = 13.6, 7.8, 1.1 Hz, 1H), 1.93–1.79 (m, 3H), 1.64–1.57 (m, 1H), 1.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.0, 154.9, 143.7, 141.2, 133.5, 127.7, 127.1, 125.4, 119.9, 118.8, 68.9, 47.7, 46.7, 44.8, 44.2, 32.8, 25.5, 19.6; IR (Neat Film NaCl) 3067, 2945, 1770, 1712, 1478, 1451, 1377, 1297, 1269, 1161, 1000, 759, 740 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{24}H_{26}NO_3$ $[M+H]^+$: 376.1907, found 376.1914; $[\alpha]_D^{25}$ –38.5° (c 2.17, $CHCl_3$, 89% ee).



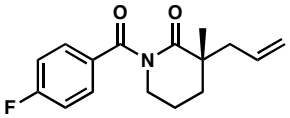
2e

Acetyl Lactam 2e: Reaction performed in toluene at 40 °C. Acetyl lactam **2e** was isolated by flash chromatography (SiO_2, 8 to 10% Et_2O in hexanes) as a colorless oil. 47.2% yield. R_f = 0.38 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (dddd, *J* = 16.6, 10.4, 7.8, 7.0 Hz, 1H), 5.14–5.04 (m, 2H), 3.82–3.72 (m, 1H), 3.60–3.49 (m, 1H), 2.50 (ddt, *J* = 13.6, 7.0, 1.2 Hz, 1H), 2.44 (s, 3H), 2.25 (ddt, *J* = 13.6, 7.7, 1.1 Hz, 1H), 1.91–1.71 (m, 3H), 1.64–1.52 (m, 1H), 1.25 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.3, 174.4, 133.3, 118.9, 45.4, 44.8, 44.4, 32.8, 27.2, 25.7, 19.4; IR (Neat Film NaCl) 2941, 1694, 1387, 1367, 1293, 1248, 1177, 1114, 1046, 920 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{11}H_{18}NO_2$ $[M+H]^+$: 196.1332, found 196.1329; $[\alpha]_D^{25}$ –100.9° (c 0.99, $CHCl_3$, 91% ee).



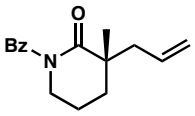
2f

4-Methoxybenzoyl Lactam 2f: Reaction performed in toluene at 40 °C. 4-Methoxybenzoyl lactam **2f** was isolated by flash chromatography (SiO_2, 15% EtOAc in hexanes) as a colorless oil. 92.7% yield. R_f = 0.36 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.48 (m, 2H), 6.92–6.82 (m, 2H), 5.76 (dddd, *J* = 17.2, 10.3, 7.7, 7.0 Hz, 1H), 5.19–5.03 (m, 2H), 3.83 (s, 3H), 3.80 (ddd, *J* = 12.1, 5.3, 1.4 Hz, 1H), 3.73–3.64 (m, 1H), 2.57 (ddt, *J* = 13.6, 7.1, 1.2 Hz, 1H), 2.29 (ddt, *J* = 13.7, 7.6, 1.1 Hz, 1H), 2.05–1.91 (m, 3H), 1.72–1.63 (m, 1H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.0, 174.9, 162.4, 133.4, 130.1, 128.4, 118.9, 113.5, 55.4, 47.3, 43.9, 43.4, 33.3, 25.3, 19.6; IR (Neat Film NaCl) 2937, 1675, 1604, 1511, 1254, 1164, 1029, 922, 840, 770 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{22}NO_3$ $[M+H]^+$: 288.1594, found 288.1595; $[\alpha]_D^{25}$ –94.2° (c 1.00, $CHCl_3$, 99% ee).



2g

4-Fluorobenzoyl Lactam 2g: Reaction performed in toluene at 40 °C. 4-Fluorobenzoyl lactam **2g** was isolated by flash chromatography (SiO_2, 9% Et_2O in hexanes) as a colorless oil. 89.4% yield. R_f = 0.41 (17% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59–7.47 (m, 2H), 7.12–6.99 (m, 2H), 5.74 (ddt, *J* = 17.0, 10.4, 7.3 Hz, 1H), 5.18–5.05 (m, 2H), 3.89–3.77 (m, 1H), 3.77–3.63 (m, 1H), 2.55 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.28 (dd, *J* = 13.7, 7.6 Hz, 1H), 2.07–1.88 (m, 3H), 1.76–1.62 (m, 1H), 1.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1, 174.2, 164.6 (d, $J_{C\text{-}F}$ = 252.4 Hz), 133.2, 132.5 (d, $J_{C\text{-}F}$ = 3.4 Hz), 123.0 (d, $J_{C\text{-}F}$ = 8.9 Hz), 119.1, 115.3 (d, $J_{C\text{-}F}$ = 22.1 Hz), 47.3, 44.0, 43.3, 33.3, 25.2, 19.5; IR (Neat Film NaCl) 3076, 2940, 1679, 1602, 1507, 1384, 1280, 1145, 922, 844, 769 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{19}NO_2F$ $[M+H]^+$: 276.1394, found 276.1392; $[\alpha]_D^{25}$ –85.5° (c 1.02, $CHCl_3$, 99% ee).



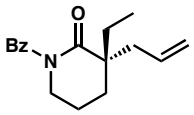
2h

Benzoyl Lactam 2h: Reaction performed in toluene at 40 °C. Benzoyl lactam **2h** was isolated by flash chromatography (SiO_2, 5 to 9% Et_2O in pentane) as a colorless oil. 84.7% yield. R_f = 0.55 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.50 (m, 2H), 7.49–7.43 (m, 1H), 7.40–7.35 (m, 2H), 5.75 (dddd, *J* = 17.1, 10.2, 7.7, 7.0 Hz, 1H), 5.19–5.03 (m, 2H), 3.92–3.78 (m, 1H), 3.72 (ddt, *J* = 12.6, 6.4, 6.0, 1.2 Hz, 1H), 2.55 (ddt, *J* = 13.7, 7.0, 1.2 Hz, 1H), 2.29 (ddt, *J* = 13.7, 7.7, 1.1 Hz, 1H), 2.07–1.87 (m, 3H), 1.75–1.60 (m, 1H), 1.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.0, 175.3, 136.5, 133.3, 131.3, 128.1, 127.4, 118.9, 47.1, 44.0, 43.3, 33.3, 25.1, 19.5; IR (Neat Film NaCl) 3074, 2939, 2870, 1683, 1478, 1449, 1386, 1282, 1151, 919, 726, 695 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1489, found 258.1491; $[\alpha]_D^{25}$ –91.2° (c 1.07, $CHCl_3$, 99% ee).

General Procedure for Preparative Allylic Alkylation Reactions

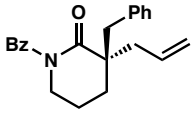
In a nitrogen-filled glovebox, an oven-dried 20 mL vial was charged with Pd_2pmdba_3 (27.4 mg, 0.025 mmol, 0.05 equiv) or Pd_2dba_3 (22.9 mg, 0.025 mmol, 0.05 equiv),[13] (*S*)-$(CF_3)_3$-*t*-BuPHOX (37.0 mg, 0.0625 mmol, 0.125 equiv), toluene (15 mL or 13 mL if the substrate is an oil), and a magnetic stir bar. The vial was stirred at ambient glovebox temperature (~28 °C) for 30 min and the substrate (0.50 mmol, 1.00 equiv) was added either as a solid or as a solution of an oil dissolved in toluene (2 mL). The vial was sealed and heated to 40 °C. When complete consumption of the starting material was observed by colorimetric change (from light green to red-orange) and confirmed by thin layer chromatography on SiO_2, the reaction mixtures were removed from the glovebox, concentrated under reduced pressure, and purified by flash chromatography to afford the desired alkylated product.

Characterization Data for New Product Compounds in Figure 3



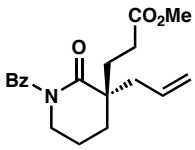
3

Benzoyl Lactam 3:[14] Benzoyl lactam **3** was isolated by flash chromatography (SiO_2, 15 to 20% Et_2O in hexanes) as a colorless oil. 97.2% yield. R_f = 0.39 (20% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.48–7.43 (m, 1H), 7.41–7.34 (m, 2H), 5.74 (dddd, *J* = 16.7, 10.4, 7.6, 7.0 Hz, 1H), 5.19–5.02 (m, 2H), 3.84–3.70 (m, 2H), 2.51 (ddt, *J* = 13.8, 7.0, 1.3 Hz, 1H), 2.28 (ddt, *J* = 13.8, 7.6, 1.2 Hz, 1H), 2.06–1.91 (m, 2H), 1.91–1.74 (m, 3H), 1.74–1.63 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 175.6, 136.7, 133.6, 131.2, 128.1, 127.4, 118.6, 47.4, 46.9, 41.3, 30.3 (2C), 19.6, 8.3; IR (Neat Film NaCl) 3072, 2970, 2941, 2880, 1678, 1448, 1384, 1283, 1147, 916, 725, 694 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1645, found 272.1649; $[\alpha]_D^{25}$ –28.6° (c 1.15, $CHCl_3$, 99% ee).



4

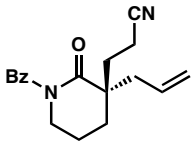
Benzoyl Lactam 4:[14] Benzoyl lactam **4** was isolated by flash chromatography (SiO_2, 10% Et_2O in hexanes) as a white solid. 84.8% yield. R_f = 0.48 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.52–7.46 (m, 1H), 7.43–7.37 (m, 2H), 7.32–7.22 (m, 3H), 7.18–7.11 (m, 2H), 5.80 (dddd, *J* = 16.8, 10.1, 7.6, 6.8 Hz, 1H), 5.21–5.06 (m, 2H), 3.70 (ddd, *J* = 12.2, 7.0, 4.8 Hz, 1H), 3.63 (ddd, *J* = 12.5, 7.7, 4.4 Hz, 1H), 3.34 (d, *J* = 13.4 Hz, 1H), 2.73–2.64 (m, 1H), 2.68 (d, *J* = 13.3 Hz, 1H), 2.25 (ddt, *J* = 13.8, 7.7, 1.1 Hz, 1H), 2.03–1.91 (m, 1H), 1.91–1.83 (m, 1H), 1.81 (dd, *J* = 6.7, 5.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.4, 175.5, 136.9, 136.6, 133.2, 131.4, 130.8, 128.2, 128.1, 127.6, 126.7, 119.3, 48.8, 46.8, 43.0, 42.9, 28.9, 19.6; IR (Neat Film NaCl) 3061, 3028, 2942, 1679, 1449, 1286, 1149, 919, 724, 704, 695 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{22}H_{24}NO_2$ $[M+H]^+$: 334.1802, found 334.1800; $[\alpha]_D^{25}$ +48.1° (c 0.825, $CHCl_3$, 99% ee).



5

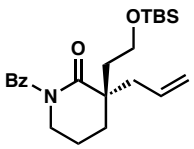
Benzoyl Lactam 5: Benzoyl lactam **5** was isolated by flash chromatography (SiO_2, 25% Et_2O in hexanes) as a light yellow oil. 91.8% yield. R_f = 0.39 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.49–7.44 (m, 1H), 7.41–7.31 (m, 2H), 5.72 (ddt, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.23–5.05 (m, 2H), 3.78 (t, *J* = 6.0 Hz, 2H), 3.67 (s, 3H), 2.58–2.47 (m, 1H), 2.42–2.24 (m, 3H), 2.08–1.97 (m, 4H), 1.93 (ddd, *J* = 14.0, 7.8, 4.6 Hz, 1H), 1.78 (ddd, *J* = 13.9, 7.1, 4.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.4, 175.5, 173.7, 136.5, 132.6, 131.4, 128.2, 127.4, 119.4, 51.7, 47.0, 46.6, 41.2, 32.2, 31.2, 29.0, 19.4; IR (Neat Film NaCl) 3073, 2950, 2874, 1736, 1679, 1448, 1281, 1150, 920, 727, 696, 665

cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{19}H_{24}NO_4$ $[M+H]^+$: 330.1700, found 330.1704; $[\alpha]_D^{25}$ +14.0° (c 0.72, $CHCl_3$, 99% ee).



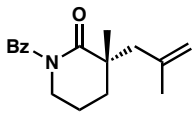
6

Benzoyl Lactam 6: Benzoyl lactam **6** was isolated by flash chromatography (SiO_2, 15 to 25% EtOAc in hexanes) as a colorless oil. 88.2% yield. R_f = 0.43 (35% EtOAc in hexanes); ^{1}H NMR (500 MHz, CDCl3) δ 7.52–7.47 (m, 3H), 7.41 (ddt, *J* = 8.7, 6.6, 1.0 Hz, 2H), 5.71 (ddt, *J* = 17.4, 10.1, 7.3 Hz, 1H), 5.28–5.15 (m, 2H), 3.88–3.79 (m, 1H), 3.76 (ddd, *J* = 12.9, 8.7, 4.2 Hz, 1H), 2.57 (ddt, *J* = 14.1, 7.3, 1.2 Hz, 1H), 2.44–2.29 (m, 3H), 2.13–2.04 (m, 2H), 2.03–1.89 (m, 3H), 1.87–1.78 (m, 1H); ^{13}C NMR (126 MHz, CDCl3) δ 176.8, 175.2, 136.2, 131.7, 131.5, 128.3, 127.3, 120.3, 119.5, 47.0, 46.5, 41.1, 32.7, 30.8, 19.2, 12.5; IR (Neat Film NaCl) 3074, 2945, 2876, 1678, 1448, 1389, 1282, 1151, 922, 727, 696 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{21}N_2O_2$ $[M+H]^+$: 297.1598, found 297.1603; $[\alpha]_D^{25}$ +46.9° (c 0.83, $CHCl_3$, 99% ee).



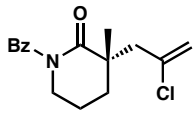
7

Benzoyl Lactam 7: Benzoyl lactam **7** was isolated by flash chromatography (SiO_2, 5 to 15% Et_2O in hexanes) as a colorless oil. 85.4% yield. R_f = 0.32 (10% Et_2O in hexanes); ^{1}H NMR (500 MHz, CDCl3) δ 7.54–7.48 (m, 2H), 7.48–7.42 (m, 1H), 7.41–7.33 (m, 2H), 5.76 (ddt, *J* = 17.3, 10.2, 7.3 Hz, 1H), 5.18–5.06 (m, 2H), 3.81–3.75 (m, 2H), 3.75–3.64 (m, 2H), 2.55 (ddt, *J* = 13.8, 7.1, 1.2 Hz, 1H), 2.33 (ddt, *J* = 13.8, 7.5, 1.1 Hz, 1H), 2.10–1.94 (m, 4H), 1.94–1.85 (m, 1H), 1.81 (ddd, *J* = 13.9, 7.3, 5.6 Hz, 1H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (126 MHz, CDCl3) δ 177.6, 175.5, 136.8, 133.4, 131.2, 128.1, 127.4, 118.9, 59.2, 46.9, 46.3, 42.2, 39.7, 30.8, 25.9, 19.6, 18.2, –5.4; IR (Neat Film NaCl) 2953, 2928, 2884, 2856, 1681, 1280, 1257, 1151, 1093, 836, 776, 725, 694 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{36}NO_3Si$ $[M+H]^+$: 402.2459, found 402.2467; $[\alpha]_D^{25}$ –3.71° (c 1.40, $CHCl_3$, 96% ee).



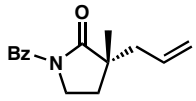
8

Benzoyl Lactam 8: Benzoyl lactam **8** was isolated by flash chromatography (SiO_2, 5 to 9% EtOAc in hexanes) as a colorless oil. 78.0% yield. R_f = 0.54 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, CDCl3) δ 7.54–7.50 (m, 2H), 7.48–7.43 (m, 1H), 7.41–7.35 (m, 2H), 4.89 (t, *J* = 1.8 Hz, 1H), 4.70 (dt, *J* = 2.1, 1.0 Hz, 1H), 3.94–3.84 (m, 1H), 3.74–3.63 (m, 1H), 2.75 (dd, *J* = 13.8, 1.3 Hz, 1H), 2.13 (dd, *J* = 13.8, 0.8 Hz, 1H), 2.08–1.94 (m, 3H), 1.69 (s, 3H), 1.68–1.61 (m, 1H), 1.37 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 178.8, 175.5, 141.9, 136.5, 131.3, 128.1, 127.4, 115.5, 47.2, 46.2, 44.0, 32.9, 26.9, 24.7, 19.8; IR (Neat Film NaCl) 3070, 2940, 1678, 1448, 1274, 1144, 726 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1645, found 272.1655; $[\alpha]_D^{25}$ –105.6° (c 0.99, $CHCl_3$, 97% ee).



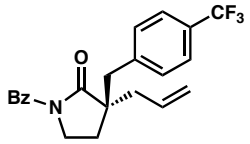
9

Benzoyl Lactam 9: Benzoyl lactam **9** was isolated by flash chromatography (SiO_2, 8 to 10% Et_2O in hexanes) as a colorless oil. 60.3% yield. R_f = 0.39 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.49 (m, 2H), 7.49–7.43 (m, 1H), 7.42–7.34 (m, 2H), 5.32 (d, *J* = 1.7 Hz, 1H), 5.18 (s, 1H), 3.92 (ddt, *J* = 12.7, 4.8, 1.7 Hz, 1H), 3.75–3.66 (m, 1H), 3.04 (dd, *J* = 14.5, 1.0 Hz, 1H), 2.50 (d, *J* = 14.5 Hz, 1H), 2.16 (ddd, *J* = 13.4, 10.2, 4.4 Hz, 1H), 2.12–1.98 (m, 2H), 1.86–1.77 (m, 1H), 1.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.9, 175.3, 138.3, 136.4, 131.4, 128.1, 127.4, 117.1, 47.0 (2C), 44.2, 32.8, 26.3, 19.7; IR (Neat Film NaCl) 2944, 2872, 1679, 1628, 1448, 1386, 1277, 1151, 894, 726 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{19}NO_2Cl$ $[M+H]^+$: 292.1099, found 292.1102; $[\alpha]_D^{25}$ –91.4° (c 0.94, $CHCl_3$, 95% ee).



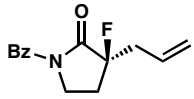
10

Benzoyl Lactam 10: Benzoyl lactam **10** was isolated by flash chromatography (SiO_2, 5 to 10% Et_2O in hexanes) as a colorless oil. 90.3% yield. R_f = 0.35 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58–7.54 (m, 2H), 7.53–7.48 (m, 1H), 7.43–7.38 (m, 2H), 5.78 (dddd, *J* = 17.1, 10.2, 7.8, 7.0 Hz, 1H), 5.22–5.09 (m, 2H), 3.87 (dd, *J* = 7.7, 6.7 Hz, 2H), 2.36 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.24 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.15 (dt, *J* = 12.9, 7.6 Hz, 1H), 1.85 (dt, *J* = 13.1, 6.7 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 170.8, 134.4, 133.0, 131.8, 128.8, 127.7, 119.3, 46.2, 42.8, 41.8, 29.3, 22.8; IR (Neat Film NaCl) 3075, 2974, 2902, 1742, 1674, 1448, 1377, 1357, 1306, 1243, 1156, 921, 860, 731, 694, 656 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{15}H_{18}NO_2$ $[M+H]^+$: 244.1332, found 244.1336; $[\alpha]_D^{25}$ –31.6° (c 1.04, $CHCl_3$, 98% ee).



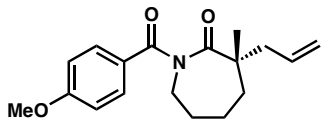
11

Benzoyl Lactam 11: Benzoyl lactam **11** was isolated by flash chromatography (SiO_2, 10 to 20% Et_2O in hexanes) as a colorless oil. 89.3% yield. R_f = 0.24 (20% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.56 (m, 2H), 7.56–7.51 (m, 1H), 7.49–7.45 (m, 2H), 7.42 (ddt, *J* = 7.8, 6.7, 1.0 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 5.83 (dddd, *J* = 17.1, 10.1, 7.8, 6.9 Hz, 1H), 5.28–5.10 (m, 2H), 3.70 (dt, *J* = 11.4, 7.5 Hz, 1H), 3.39 (dt, *J* = 11.4, 6.9 Hz, 1H), 3.10 (d, *J* = 13.4 Hz, 1H), 2.76 (d, *J* = 13.5 Hz, 1H), 2.48 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.32 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.05 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.1, 170.5, 140.9, 134.2, 132.3, 131.9, 130.7, 129.4 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.7, 127.7, 125.3 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.1 (q, $J_{C\text{-}F}$ = 272.2 Hz), 120.1, 51.3, 43.0, 41.9 (2C), 25.2; IR (Neat Film NaCl) 3080, 2977, 2913, 1738, 1677, 1325, 1294, 1244, 1164, 1121, 1067, 859, 728, 701, 665 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{22}H_{21}NO_2F_3$ $[M+H]^+$: 388.1524, found 388.1525; $[\alpha]_D^{25}$ +78.3° (c 1.90, $CHCl_3$, 93% ee).



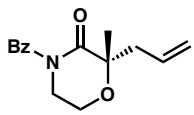
12

Benzoyl Lactam 12: Benzoyl lactam **12** was isolated by flash chromatography (SiO_2, 10 to 20% Et_2O in hexanes) as a white solid. 85.7% yield. R_f = 0.35 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63–7.58 (m, 2H), 7.58–7.52 (m, 1H), 7.49–7.40 (m, 2H), 5.87–5.73 (m, 1H), 5.32–5.20 (m, 2H), 4.00 (ddd, *J* = 11.5, 7.7, 6.5 Hz, 1H), 3.90–3.80 (m, 1H), 2.81–2.70 (m, 1H), 2.62–2.48 (m, 1H), 2.46–2.27 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 169.7 (d, $J_{C\text{-}F}$ = 23.1 Hz), 133.4, 132.4, 129.7 (d, $J_{C\text{-}F}$ = 7.1 Hz), 129.0, 127.9, 121.0, 97.0 (d, $J_{C\text{-}F}$ = 185.4 Hz), 42.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 38.4 (d, $J_{C\text{-}F}$ = 25.2 Hz), 28.5 (d, $J_{C\text{-}F}$ = 22.6 Hz); IR (Neat Film NaCl) 3076, 1760, 1676, 1365, 1314, 1253, 1132, 1058, 1008, 980, 920, 863, 791, 729 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{14}H_{15}NO_2F$ $[M+H]^+$: 248.1081, found 248.1092; $[\alpha]_D^{25}$ –120.5° (c 1.11, $CHCl_3$, 98% ee).



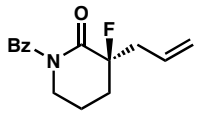
13

4-Methoxybenzoyl Lactam 13: Reaction performed in MTBE at 40 °C. 4-Methoxybenzoyl lactam **13** was isolated by flash chromatography (SiO_2, 8% Et_2O in hexanes) as a colorless oil. 83.2% yield. R_f = 0.48 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.48 (m, 2H), 6.91–6.82 (m, 2H), 5.86–5.66 (m, 1H), 5.18–5.02 (m, 2H), 4.03 (ddd, *J* = 15.0, 8.0, 2.4 Hz, 1H), 3.88 (ddd, *J* = 15.1, 8.5, 2.1 Hz, 1H), 3.83 (s, 3H), 2.50 (ddt, *J* = 13.6, 7.0, 1.2 Hz, 1H), 2.35 (ddt, *J* = 13.7, 7.6, 1.1 Hz, 1H), 1.92–1.77 (m, 4H), 1.77–1.62 (m, 2H), 1.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.3, 174.7, 162.2, 133.9, 130.0, 128.9, 118.6, 113.5, 55.4, 47.7, 44.7, 43.0, 35.1, 28.2, 25.0, 23.4; IR (Neat Film NaCl) 3074, 2932, 1673, 1605, 1511, 1279, 1255, 1168, 1112, 1025, 837 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{24}NO_3$ $[M+H]^+$: 302.1751, found 302.1744; $[\alpha]_D^{25}$ –34.7° (c 0.75, $CHCl_3$, 93% ee).



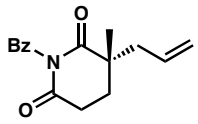
14

Benzoyl Lactam 14: Benzoyl lactam **14** was isolated by flash chromatography (SiO_2, 10 to 20% Et_2O in hexanes) as a colorless oil. 91.4% yield. R_f = 0.36 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.52–7.47 (m, 1H), 7.42–7.37 (m, 2H), 5.90 (ddt, *J* = 17.3, 10.3, 7.2 Hz, 1H), 5.26–5.10 (m, 2H), 4.12–3.95 (m, 3H), 3.94–3.81 (m, 1H), 2.71 (ddt, *J* = 14.1, 7.3, 1.2 Hz, 1H), 2.47 (ddt, *J* = 14.1, 7.0, 1.3 Hz, 1H), 1.48 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 173.1, 135.7, 132.1, 131.7, 128.1, 127.7, 119.3, 80.3, 59.4, 45.7, 43.1, 23.3; IR (Neat Film NaCl) 3075, 2978, 2894, 1685, 1448, 1373, 1283, 1227, 1111, 1092, 921, 726, 694 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{15}H_{18}NO_3$ $[M+H]^+$: 260.1287, found 260.1277; $[\alpha]_D^{25}$ –72.1° (c 0.97, $CHCl_3$, 99% ee).



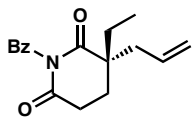
15

Benzoyl Lactam 15: Benzoyl lactam **15** was isolated by flash chromatography (SiO_2, 5 to 10% EtOAc in hexanes) as a colorless oil. 88.8% yield. R_f = 0.35 (35% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.57 (m, 2H), 7.53–7.47 (m, 1H), 7.44–7.37 (m, 2H), 5.87–5.70 (m, 1H), 5.28–5.15 (m, 2H), 3.91 (dddd, *J* = 12.8, 6.0, 4.7, 1.4 Hz, 1H), 3.74 (dddd, *J* = 13.6, 9.2, 4.5, 2.4 Hz, 1H), 2.86–2.60 (m, 2H), 2.33–2.14 (m, 2H), 2.13–1.89 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 170.8 (d, $J_{C\text{-}F}$ = 23.5 Hz), 135.0, 132.0, 130.6 (d, $J_{C\text{-}F}$ = 6.5 Hz), 128.3, 128.0, 120.4, 93.9 (d, $J_{C\text{-}F}$ = 179.3 Hz), 46.4, 40.0 (d, $J_{C\text{-}F}$ = 23.6 Hz), 32.1 (d, $J_{C\text{-}F}$ = 22.5 Hz), 19.1 (d, $J_{C\text{-}F}$ = 4.6 Hz); IR (Neat Film NaCl) 3078, 2956, 1715, 1687, 1478, 1449, 1435, 1390, 1288, 1273, 1175, 1152, 1000, 930, 725, 694, 662 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{15}H_{16}NO_2F$ $[M+H]^+$: 262.1238, found 262.1244; $[\alpha]_D^{25}$ –120.6° (c 1.09, $CHCl_3$, 99% ee).



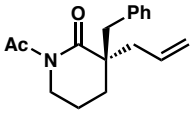
16

Benzoyl Glutarimide 16: Benzoyl glutarimide **16** was isolated by flash chromatography (SiO_2, 17 to 25% EtOAc in hexanes) as a colorless oil. 81% yield. R_f = 0.21 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.29 Hz, 2H), 7.63 (t, *J* = 7.45 Hz, 1H), 7.48 (dd, *J* = 8.29, 7.45 Hz, 2H), 5.77 (dddd, *J* = 17.4, 10.2, 7.4, 7.0 Hz, 1H), 5.22–5.16 (m, 2H), 2.87–2.77 (m, 2H), 2.59 (ddt, *J* = 13.8, 7.0, 1.0 Hz, 1H), 2.40 (ddt, *J* = 13.8, 7.4, 1.0 Hz, 1H), 2.12 (ddd, *J* = 14.2, 7.73, 6.81 Hz, 1H), 1.85 (ddd, *J* = 14.2, 6.5, 6.1 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.6, 171.6, 170.9, 134.8, 132.0, 131.9, 130.0, 129.1, 120.0, 41.9, 41.7, 29.2, 28.2, 22.8; IR (Neat Film NaCl) 3077, 2975, 2935, 1750, 1713, 1683, 1450, 1340, 1239, 1198, 981, 776 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{18}NO_3$ $[M+H]^+$: 272.1281, found 272.1281; $[\alpha]_D^{25}$ –31.3° (c 1.00, $CHCl_3$, 94% ee).



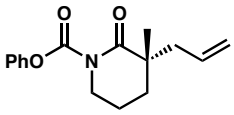
17

Benzoyl Glutarimide 17: Benzoyl glutarimide **17** was isolated by flash chromatography (SiO_2, 17 to 25% EtOAc in hexanes) as a colorless oil. 86% yield. R_f = 0.24 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.38 Hz, 2H), 7.64 (t, *J* = 7.46 Hz, 1H), 7.48 (dd, *J* = 8.38, 7.46 Hz, 2H), 5.75 (dddd, *J* = 17.2, 10.2, 7.7, 7.0 Hz, 1H), 5.20–5.15 (m, 2H), 2.86–2.76 (m, 2H), 2.60 (ddt, *J* = 14.0, 7.0, 1.1 Hz, 1H), 2.37 (ddt, *J* = 14.0, 7.7, 1.1 Hz, 1H), 2.05 (ddd, *J* = 14.3, 7.85, 6.81 Hz, 1H), 1.97 (ddd, *J* = 14.3, 6.56, 6.24 Hz, 1H), 1.87–1.75 (m, 2H), 0.97 (t, *J* = 7.46, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 171.6, 171.0, 134.8, 132.4, 131.9, 130.0, 129.0, 119.8, 45.4, 39.3, 29.0, 28.1, 25.4, 8.1; IR (Neat Film NaCl) 3076, 2974, 2940, 2882, 1750, 1713, 1683, 1450, 1340, 1239, 1195, 1001, 923, 778 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{20}NO_3$ $[M+H]^+$: 286.1438, found 286.1432; $[\alpha]_D^{25}$ –16.2° (c 1.00, $CHCl_3$, 96% ee).



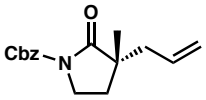
18

Acyl Lactam 18: Acyl lactam **18** was isolated by flash chromatography (SiO_2, 10 to 20% Et_2O in hexanes) as a colorless oil. 88.4% yield. R_f = 0.40 (35% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.17 (m, 3H), 7.17–7.09 (m, 2H), 5.77 (dddd, *J* = 17.0, 10.3, 7.9, 6.8 Hz, 1H), 5.19–5.05 (m, 2H), 3.60–3.48 (m, 1H), 3.44 (dddd, *J* = 13.0, 7.0, 4.6, 1.0 Hz, 1H), 3.27 (d, *J* = 13.3 Hz, 1H), 2.68 (d, *J* = 13.2 Hz, 1H), 2.66–2.62 (m, 1H), 2.51 (s, 3H), 2.23 (ddt, *J* = 13.5, 7.9, 1.1 Hz, 1H), 1.90–1.61 (m, 3H), 1.57–1.38 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 174.2, 137.1, 133.2, 130.4, 128.3, 126.8, 119.2, 49.7, 45.1, 44.8, 44.5, 29.0, 27.6, 19.6; IR (Neat Film NaCl) 3028, 2941, 1691, 1367, 1291, 1247, 111178, 1131, 1031, 923 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1645, found 272.1646; $[\alpha]_D^{25}$ +11.4° (c 1.03, $CHCl_3$, 88% ee).



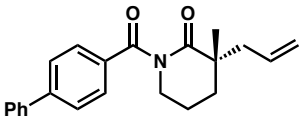
19

Phenyl Carbamate Lactam 19: Phenyl Carbamate lactam **19** was isolated by flash chromatography (SiO_2, 10 to 20% Et_2O in hexanes) as a colorless oil. 82.2% yield. R_f = 0.39 (35% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.25–7.21 (m, 1H), 7.20–7.15 (m, 2H), 5.79 (dddd, *J* = 16.7, 10.4, 7.8, 7.0 Hz, 1H), 5.18–5.08 (m, 2H), 3.89–3.82 (m, 1H), 3.78–3.70 (m, 1H), 2.55 (ddt, *J* = 13.6, 7.0, 1.2 Hz, 1H), 2.33 (ddt, *J* = 13.6, 7.8, 1.1 Hz, 1H), 2.00–1.85 (m, 3H), 1.70–1.59 (m, 1H), 1.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.3, 153.8, 150.8, 133.3, 129.3, 125.9, 121.5, 118.9, 48.2, 45.0, 44.1, 33.0, 25.3, 19.6; IR (Neat Film NaCl) 3074, 2939, 2870, 1783, 1733, 1718, 1494, 1299, 1265, 1203, 1153, 991, 920 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{20}NO_3$ $[M+H]^+$: 274.1438, found 274.1444; $[\alpha]_D^{25}$ –81.6° (c 1.11, $CHCl_3$, 94% ee).



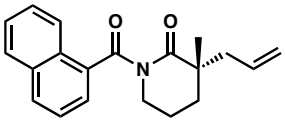
20

Benzyl Carbamate Lactam 20: Benzyl carbamate lactam **20** was isolated by flash chromatography (SiO_2, 10 to 30% Et_2O in hexanes) as a colorless oil. 85.9% yield. R_f = 0.41 (35% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.46–7.42 (m, 2H), 7.37 (ddd, *J* = 7.4, 6.3, 1.5 Hz, 2H), 7.35–7.30 (m, 1H), 5.74 (dddd, *J* = 15.9, 11.0, 7.9, 6.9 Hz, 1H), 5.28 (s, 2H), 5.18–5.06 (m, 2H), 3.77–3.63 (m, 2H), 2.33 (ddt, *J* = 13.8, 6.9, 1.2 Hz, 1H), 2.24 (ddt, *J* = 13.8, 7.9, 1.0 Hz, 1H), 2.03 (ddd, *J* = 12.9, 8.1, 6.9 Hz, 1H), 1.74 (ddd, *J* = 13.2, 7.7, 5.9 Hz, 1H), 1.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 151.7, 135.3, 133.0, 128.6, 128.3, 128.1, 119.1, 68.0, 45.5, 42.9, 41.7, 29.5, 22.6; IR (Neat Film NaCl) 3066, 2973, 2930, 2903, 1789, 1750, 1719, 1456, 1380, 1363, 1301, 1217, 1001, 919, 776, 736 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{20}NO_3$ $[M+H]^+$: 274.1438, found 274.1438; $[\alpha]_D^{25}$ –41.4° (c 1.02, $CHCl_3$, 91% ee).



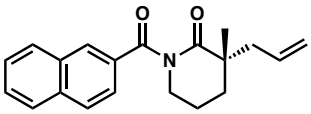
21

4-Phenylbenzoyl Lactam 21: 4-Phenylbenzoyl lactam **21** was isolated by flash chromatography (SiO_2, 10 to 15% Et_2O in pentane) as a colorless oil. 84.6% yield. R_f = 0.43 (35% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.64–7.57 (m, 6H), 7.45 (ddd, *J* = 7.8, 6.7, 1.1 Hz, 2H), 7.40–7.34 (m, 1H), 5.84–5.70 (m, 1H), 5.20–5.09 (m, 2H), 3.91–3.82 (m, 1H), 3.74 (ddd, *J* = 12.1, 7.4, 5.7 Hz, 1H), 2.59 (ddd, *J* = 13.7, 7.0, 1.3 Hz, 1H), 2.32 (ddt, *J* = 13.7, 7.7, 1.2 Hz, 1H), 2.10–1.91 (m, 3H), 1.77–1.64 (m, 1H), 1.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1, 175.1, 144.2, 140.2, 135.1, 133.3, 128.8, 128.1, 127.8, 127.2, 126.9, 119.0, 47.2, 44.0, 43.3, 33.3, 25.2, 19.5; IR (Neat Film NaCl) 3073, 2938, 2869, 1677, 1607, 1478, 1383, 1295, 1279, 1145, 922, 849, 743, 698 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{22}H_{24}NO_2$ $[M+H]^+$: 334.1802, found 334.1812; $[\alpha]_D^{25}$ –82.6° (c 0.75, $CHCl_3$, 99% ee).



22

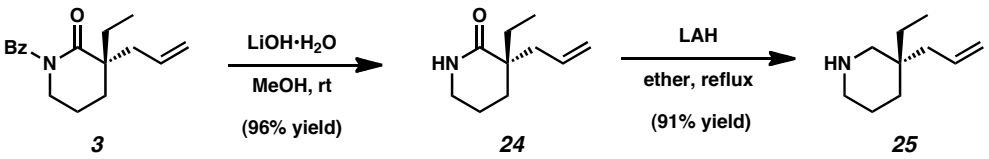
1-Naphthoyl Lactam 22: 1-Naphthoyl lactam **22** was isolated by flash chromatography (SiO_2, 10 to 20% Et_2O in hexanes) as a white solid. 86.3% yield. R_f = 0.42 (35% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.03–7.97 (m, 1H), 7.90–7.83 (m, 2H), 7.55–7.46 (m, 2H), 7.42 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.37 (dd, *J* = 7.1, 1.3 Hz, 1H), 5.64 (dddd, *J* = 17.2, 10.2, 7.6, 7.1 Hz, 1H), 5.16–4.97 (m, 2H), 4.05 (dddd, *J* = 12.8, 6.3, 5.2, 1.3 Hz, 1H), 3.95–3.82 (m, 1H), 2.43 (ddt, *J* = 13.7, 7.1, 1.2 Hz, 1H), 2.19 (ddt, *J* = 13.7, 7.6, 1.1 Hz, 1H), 2.11–1.99 (m, 2H), 1.99–1.91 (m, 1H), 1.73–1.64 (m, 1H), 1.18 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 174.3, 135.8, 133.6, 133.1, 130.0, 129.8, 128.4, 126.9, 126.2, 124.9, 124.5, 123.3, 118.9, 46.4, 44.1, 43.3, 33.2, 24.8, 19.5; IR (Neat Film NaCl) 3062, 2937, 2869, 1702, 1677, 1381, 1295, 1251, 1147, 923, 781 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{22}NO_2$ $[M+H]^+$: 308.1645, found 308.1648; $[\alpha]_D^{25}$ –102.3° (c 1.12, $CHCl_3$, 99% ee).



23

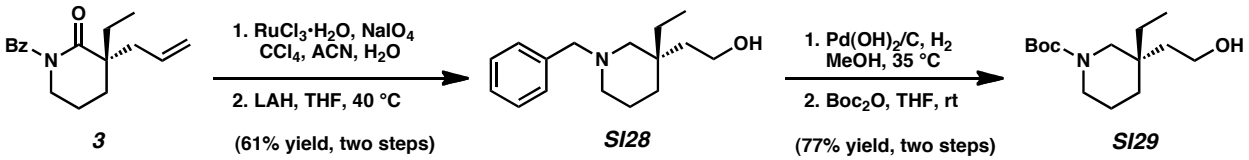
2-Naphthoyl Lactam 23: 2-Naphthoyl lactam **23** was isolated by flash chromatography (SiO_2, 10 to 20% Et_2O in hexames) as a colorless oil. 82.1% yield. R_f = 0.42 (35% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.93–7.76 (m, 3H), 7.63–7.43 (m, 3H), 5.87–5.67 (m, 1H), 5.21–5.06 (m, 2H), 3.95–3.84 (m, 1H), 3.84–3.72 (m, 1H), 2.58 (ddt, *J* = 13.8, 7.1, 1.2 Hz, 1H), 2.33 (ddt, *J* = 13.7, 7.6, 1.1 Hz, 1H), 2.12–1.89 (m, 3H), 1.71 (ddt, *J* = 10.9, 4.9, 4.3, 2.4 Hz, 1H), 1.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.0, 175.3, 134.6, 133.7, 133.3, 132.5, 128.9, 128.1, 127.7 (2C), 127.5, 126.4, 124.1, 118.9, 47.2, 44.0, 43.3, 33.3, 25.1, 19.5; IR (Neat Film NaCl) 3059, 2938, 2869, 1677, 1467, 1383, 1293, 1234, 1165, 1139, 923, 862, 822, 780, 762 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{20}H_{22}NO_2$ $[M+H]^+$: 308.1650, found 308.1638; $[\alpha]_D^{25}$ –257.4° (c 0.92, $CHCl_3$, 97% ee).

Procedures for the Conversion of Benzoyl Lactam 3 to Various Derivatives



Piperidin-2-one 24: To a solution of lactam **3** (2.00 g, 7.37 mmol, 1.00 equiv) in MeOH (188 mL) was added a solution of LiOH•H_2O (464 mg, 11.1 mmol, 1.50 equiv) in H_2O (75 mL). After 20 h, the reaction mixture was concentrated under reduced pressure and diluted with saturated aqueous $NaHCO_3$ (100 mL) and EtOAc (75 mL). The phases were separated, and the aqueous phase was extracted with EtOAc (4 x 75 mL). The combined organic phases were washed with brine (2 x 30 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (3 x 25 cm SiO_2, 40 to 60% EtOAc in hexanes) to afford known[14] lactam **24** as a colorless oil (1.18 g, 96% yield). R_f = 0.21 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.05 (br s, 1H), 5.88–5.66 (m, 1H), 5.12–4.95 (m, 2H), 3.25 (td, *J* = 5.8, 1.9 Hz, 2H), 2.48 (ddt, *J* = 13.6, 6.7, 1.3 Hz, 1H), 2.18 (ddt, *J* = 13.6, 8.1, 1.0 Hz, 1H), 1.87–1.62 (m, 5H), 1.49 (dq, *J* = 13.5, 7.4 Hz, 1H), 0.89 (t, *J* = 7.5 Hz, 3H); $[\alpha]_D^{25}$ –13.7° (c 0.57, $CHCl_3$, 99% ee).

Piperidine 25: To a solution of piperidin-2-one **24** (250 mg, 1.49 mmol, 1.00 equiv) in ether (14.9 mL) was added lithium aluminum hydride (170 mg, 4.48 mmol, 3.0 equiv) (*Caution: Gas evolution and exotherm*). After stirring at ambient temperature for 5 min, the reaction mixture was heated to reflux for 36 h, cooled (0 °C), and quenched with saturated aqueous K_2CO_3 (20 mL, *Caution: Gas evolution and exotherm*). The phases were separated, and the aqueous phase was extracted with Et_2O (4 x 75 mL). The combined organic phases were washed with brine (2 x 30 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure to provide piperidine **23** (206 mg, 90% yield) as a colorless oil. R_f = 0.29 (20% MeOH in DCM); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 16.4, 10.6, 7.5 Hz, 1H), 5.10–4.96 (m, 2H), 2.81–2.68 (m, 2H), 2.53 (dd, *J* = 13.0, 20.0 Hz, 2H), 2.06 (d, *J* = 7.5 Hz, 2H), 2.02 (br s, 1H), 1.55–1.42 (m, 2H), 1.40–1.30 (m, 2H), 1.32 (q, *J* = 7.5 Hz, 2H), 0.80 (t, J = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.6, 116.9, 55.1, 47.0, 39.2, 34.9, 33.6, 27.7, 22.4, 7.1; IR (Neat Film NaCl) 3298, 3073, 2963, 2931, 2853, 2799, 1638, 1462, 1125, 996, 911 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{10}H_{20}N$ $[M+H]^+$: 154.1590, found 154.1590; $[\alpha]_D^{25}$ –7.5° (c 0.80, MeOH, 96% ee).



Alcohol SI28:[15] To a vigorously stirred mixture of benzoyl lactam **3** (291 mg, 1.07 mmol, 1.00 equiv) and $NaIO_4$ (915 mg, 4.28 mmol, 4.00 equiv) in CCl_4 (4.3 mL), MeCN (4.3 mL), and H_2O (6.5 mL) was added $RuCl_3$•H_2O (11.0 mg, 0.053 mmol, 0.05 equiv). After 28 h, the reaction mixture was diluted with half-saturated brine (30 mL) and extracted with DCM (5 x 25 mL). The combined organics were washed with half-saturated brine, dried (Na_2SO_4), and concentrated under reduced pressure. The resulting residue was suspended in Et_2O (30 mL) and filtered through a pad of celite. The celite pad was washed with Et_2O

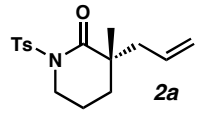
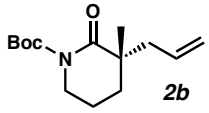
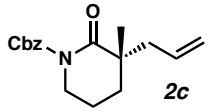
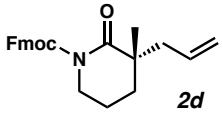
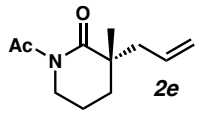
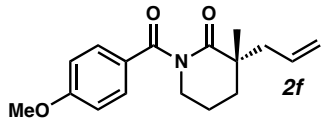
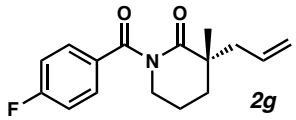
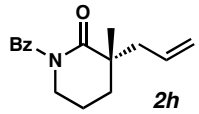
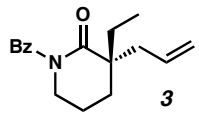
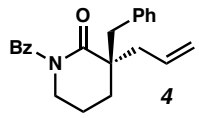
(2 x 15 mL), and the combined filtrate was concentrated under reduced pressure. This crude residue was used in the next step without further purification.

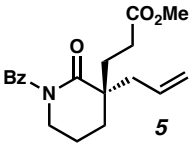
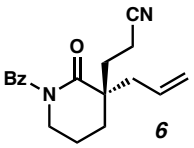
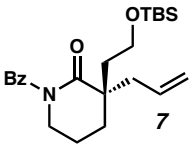
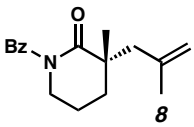
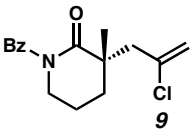
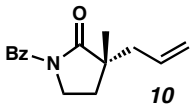
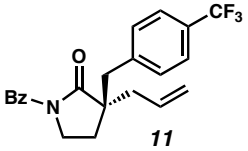
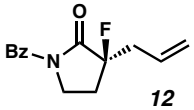
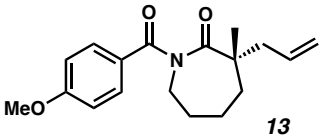
With cooling from a room temperature bath, the above residue was dissolved in THF (19 mL) and then treated with lithium aluminum hydride (487 mg, 12.9 mmol, 12.0 equiv) *(Caution: Gas evolution and exotherm)*. The reaction mixture was stirred at ambient temperature for 12 h and then warmed to 40 °C for an addition 12 h. The reaction mixture was then cooled (0 °C) and dropwise treated with brine (20 mL, *Caution: Gas evolution and exotherm*). Once gas evolution had ceased the reaction mixture was diluted with half-saturated brine (20 mL) and EtOAc (20 mL). The phases were separated and the aqueous phase was extracted with EtOAc (5 x 50 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (3 x 12 cm SiO_2, 35 to 70% EtOAc in hexanes) to afford alcohol **SI28** as a colorless oil (162 mg, 61% yield for two steps). R_f = 0.36 (75% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.24 (m, 5H), 3.80–3.72 (m, 1H), 3.71–3.60 (m, 2H), 3.31 (br s, 1H), 2.85–2.70 (br s, 2H), 2.00–1.70 (br s, 4H), 1.66–1.45 (m, 3H), 1.35–1.10 (m, 3H), 0.81 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.5, 128.4, 127.4, 63.9, 63.4, 59.4, 52.9, 39.9, 35.9, 35.1, 33.4, 22.4, 7.5; IR (Neat Film NaCl) 3345 (br), 2933, 2793, 1453, 1350, 1115, 1040, 1028, 739 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{26}NO$ $[M+H]^+$: 248.2009, found 248.2016.

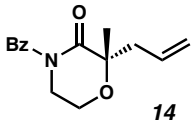
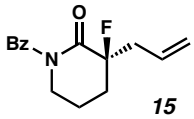
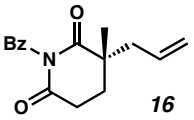
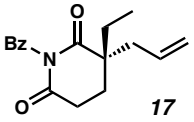
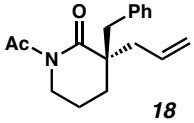
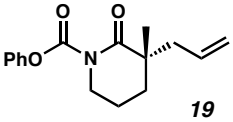
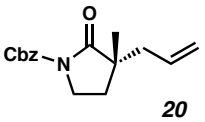
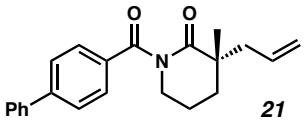
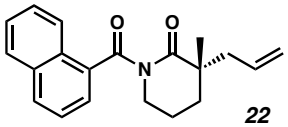
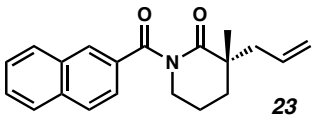
Alcohol SI29: A mixture of alcohol **SI28** (162.3 mg, 0.656 mmol, 1.00 equiv) and 20% $Pd(OH)_2/C$ (50 mg) in MeOH (15 mL) was stirred under an H_2 atmosphere for 3.5 h. The reaction mixture was filtered through a pad of celite. The celite pad was washed with MeOH (2 x 15 mL), and the combined filtrate was concentrated under reduced pressure. This crude residue was used in the next step without further purification.

To a solution of the above residue in THF (10 mL) was added Boc_2O (150 mg, 0.689 mmol, 1.05 equiv). After stirring for 24 h, the reaction mixture was concentrated under reduced pressure and partitioned between DCM (20 mL) and saturated aqueous $NaHCO_3$ (20 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (2 x 20 cm SiO_2, 15 to 35% EtOAc in hexanes) to afford alcohol **SI29** as a colorless oil (130 mg, 77% yield for two steps). R_f = 0.34 (35% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.74–3.60 (m, 2H), 3.48 (br s, 1H), 3.31 (br s, 1H), 3.20 (br s, 1H), 2.96 (br s, 1H), 2.16 (br s, 1H), 1.66–1.55 (m, 1H), 1.55–1.42 (m, 3H), 1.44 (s, 9H), 1.40–1.27 (m, 2H), 1.25–1.15 (m, 1H), 0.83 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 79.4, 58.7, 52.5, 44.5, 36.1, 35.3, 34.6, 28.4, 27.6, 21.2, 7.4 ; IR (Neat Film NaCl) 3439 (br), 2967, 2934, 2861, 1693, 1670, 1429, 1365, 1275, 1248, 1162, 1045, 865, 767 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{14}H_{28}NO_3$ $[M+H]^+$: 258.2064, found 258.2069; $[\alpha]_D^{25}$ –7.0° (c 1.13, $CHCl_3$, 96% ee).

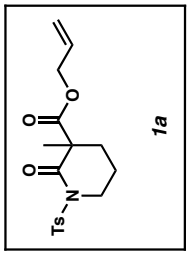
Methods for the Determination of Enantiomeric Excess

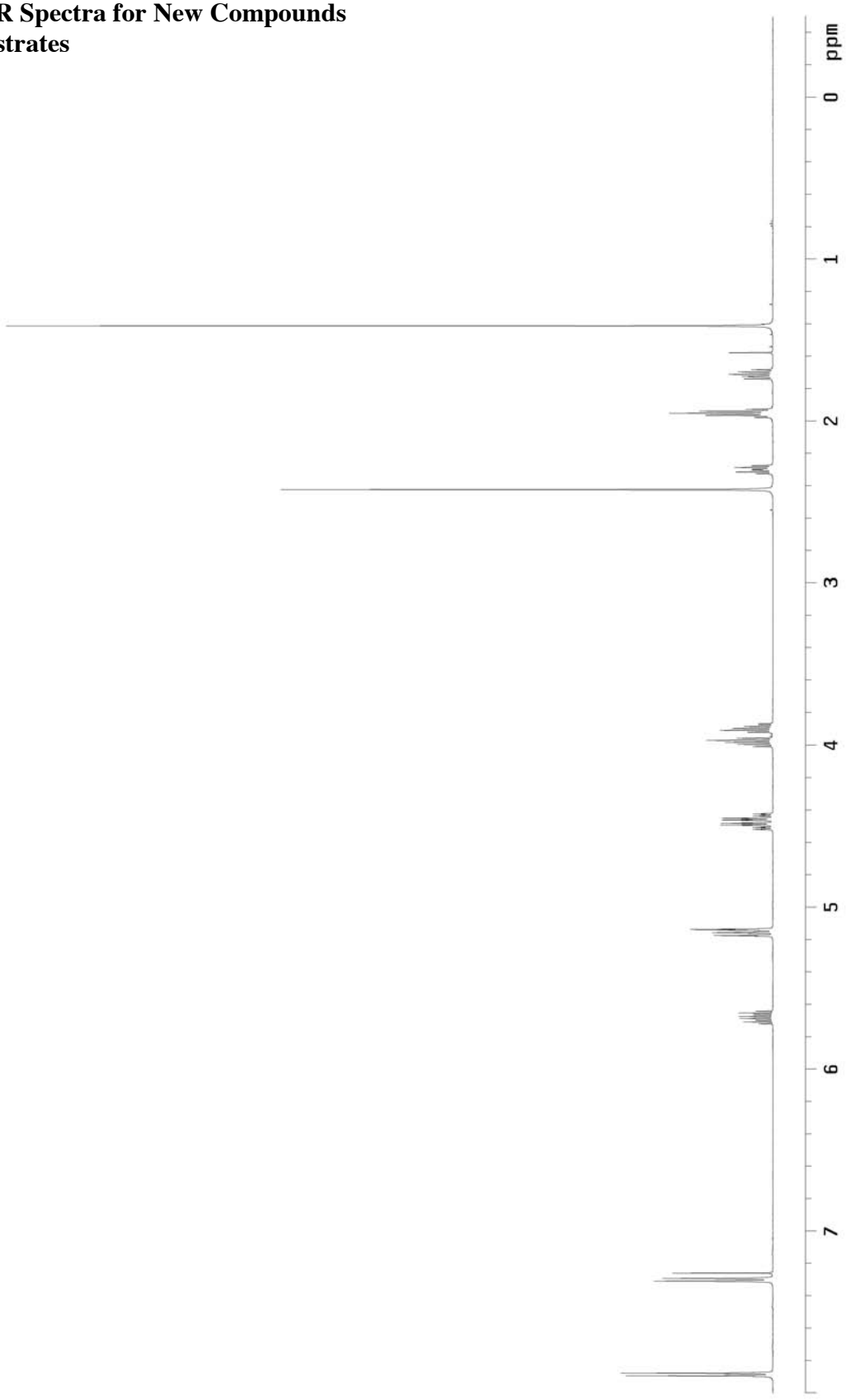
entry	product	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
1	 *2a*	HPLC Chiralpak AD-H 5% EtOH in hexanes isocratic, 1.0 mL/min 254 nm	19.10	15.77	75
2	 *2b*	HPLC Chiralcel OJ-H 0.1% IPA in hexanes isocratic, 1.0 mL/min 220 nm	15.22	18.10	81
3	 *2c*	HPLC Chiralcel OJ-H 3% EtOH in hexanes isocratic, 1.0 mL/min 220 nm	18.68	17.60	86
4	 *2d*	HPLC Chiralcel OD 3% EtOH in hexanes isocratic, 1.0 mL/min 254 nm	28.89	21.47	89
5	 *2e*	HPLC Chiralcel OJ 1% IPA in hexanes isocratic, 1.0 mL/min 254 nm	10.15	9.71	91
6	 *2f*	HPLC Chiralcel OD-H 3% IPA in hexanes isocratic, 1.0 mL/min 254 nm	15.73	18.12	99
7	 *2g*	HPLC Chiralcel OJ-H 2% IPA in hexanes isocratic, 1.0 mL/min 254 nm	29.12	19.74	99
8	 *2h*	HPLC Chiralcel OJ-H 5% IPA in hexanes isocratic, 1.0 mL/min 254 nm	32.97	31.16	99
9	 *3*	SFC Chiralcel OJ-H 3% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	3.85	2.49	99
10	 *4*	SFC Chiralcel OD-H 10% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	3.84	3.20	99

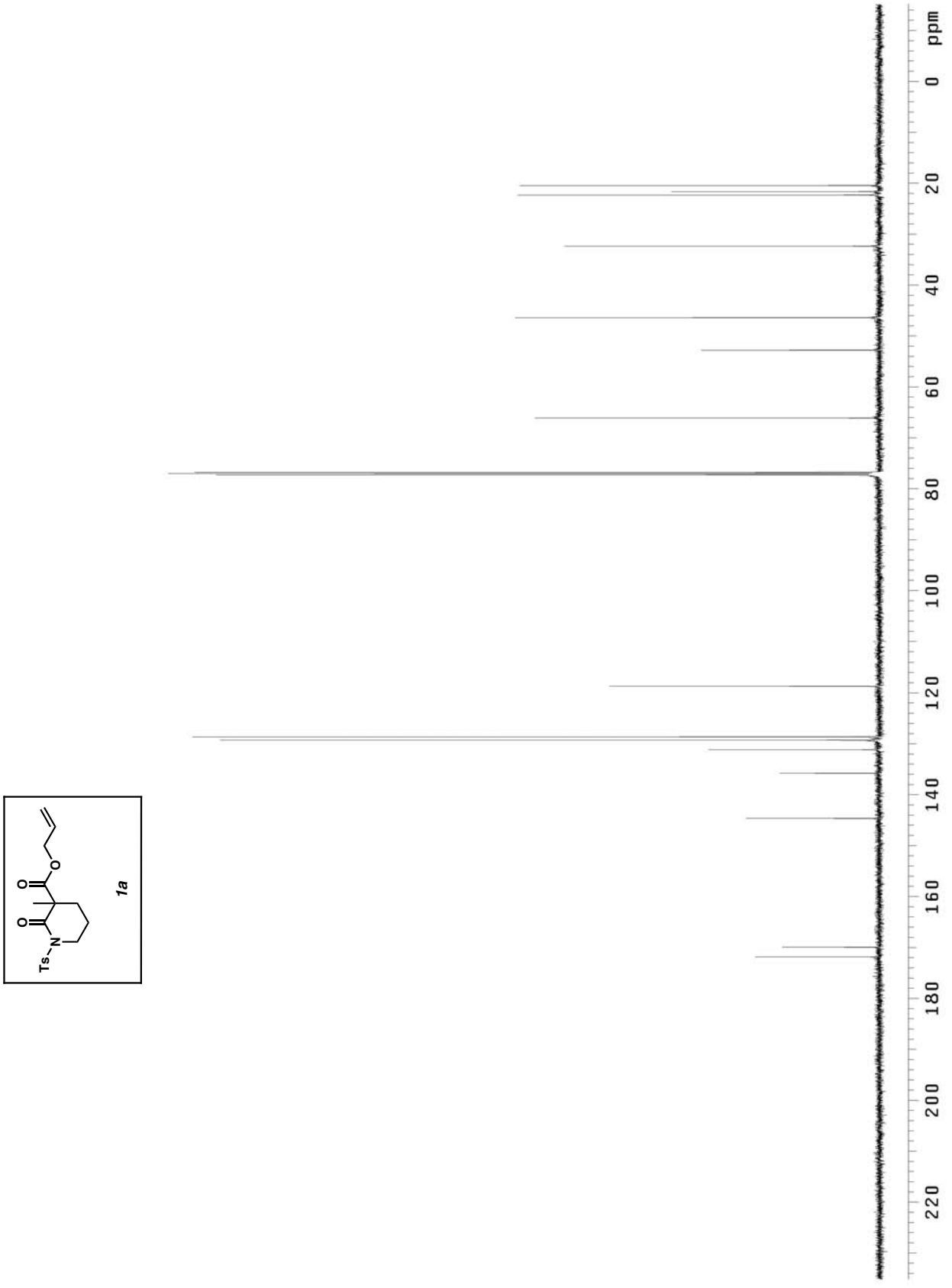
entry	product	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
11	 5	HPLC Chiralpak AD-H 3% EtOH in hexane isocratic, 1.0 mL/min 254 nm	32.69	27.83	99
12	 6	SFC Chiralpak IC 10% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	2.67	3.84	99
13	 7	HPLC Chiralcel OJ-H 3% IPA in hexane isocratic, 1.0 mL/min 254 nm	7.75	5.95	96
14	 8	HPLC Chiralcel OJ-H 8% IPA in hexane isocratic, 1.0 mL/min 254 nm	25.94	19.12	97
15	 9	HPLC Chiralpak AD 2% IPA in hexane isocratic, 1.0 mL/min 254 nm	18.72	27.05	95
16	 10	SFC Chiralcel OJ-H 10% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	2.93	1.84	98
17	 11	SFC Chiralcel OJ-H 5% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	2.31	3.73	93
18	 12	SFC Chiralpak AD-H 15% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	4.16	5.05	99
19	 13	HPLC Chiralcel OJ-H 5% IPA in hexane isocratic, 1.0 mL/min 254 nm	29.16	24.82	93

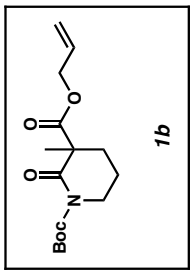
entry	product	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
20	 *14*	SFC Chiralpak AD-H 10% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	1.96	1.41	99
21	 *15*	SFC Chiralcel OJ-H 5% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	2.55	2.25	99
22	 *16*	SFC Chiralcel OJ-H 3% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	3.05	2.72	94
23	 *17*	SFC Chiralpak OJ-H 3% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	3.28	2.87	96
24	 *18*	SFC Chiralpak AD-H 3% MeOH in CO_2 isocratic, 3.0 mL/min 235 nm	4.03	4.69	88
25	 *19*	SFC Chiralcel OB-H 10% MeOH in CO_2 isocratic, 5.0 mL/min 210 nm	2.65	2.39	94
26	 *20*	SFC Chiralpak AD-H 15% MeOH in CO_2 isocratic, 5.0 mL/min 210 nm	4.23	2.51	91
27	 *21*	SFC Chiralcel OJ-H 10% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	4.53	3.80	99
28	 *22*	SFC Chiralcel OB-H 10% MeOH in CO_2 isocratic, 5.0 mL/min 210 nm	4.05	4.60	99
29	 *23*	SFC Chiralpak AD-H 20% MeOH in CO_2 isocratic, 5.0 mL/min 254 nm	3.73	2.93	97

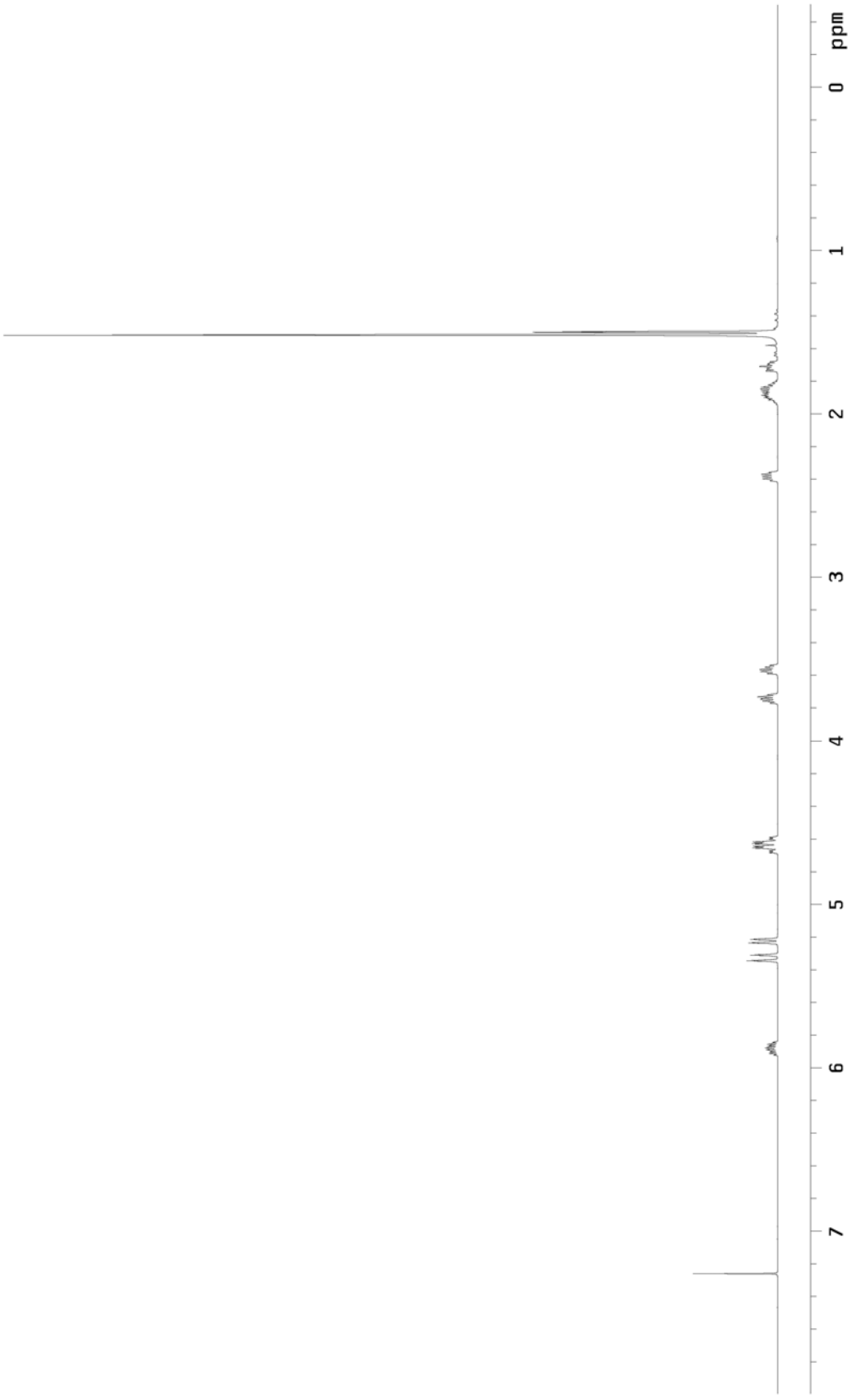
^{1}H and ^{13}C NMR Spectra for New Compounds
Alkylation Substrates

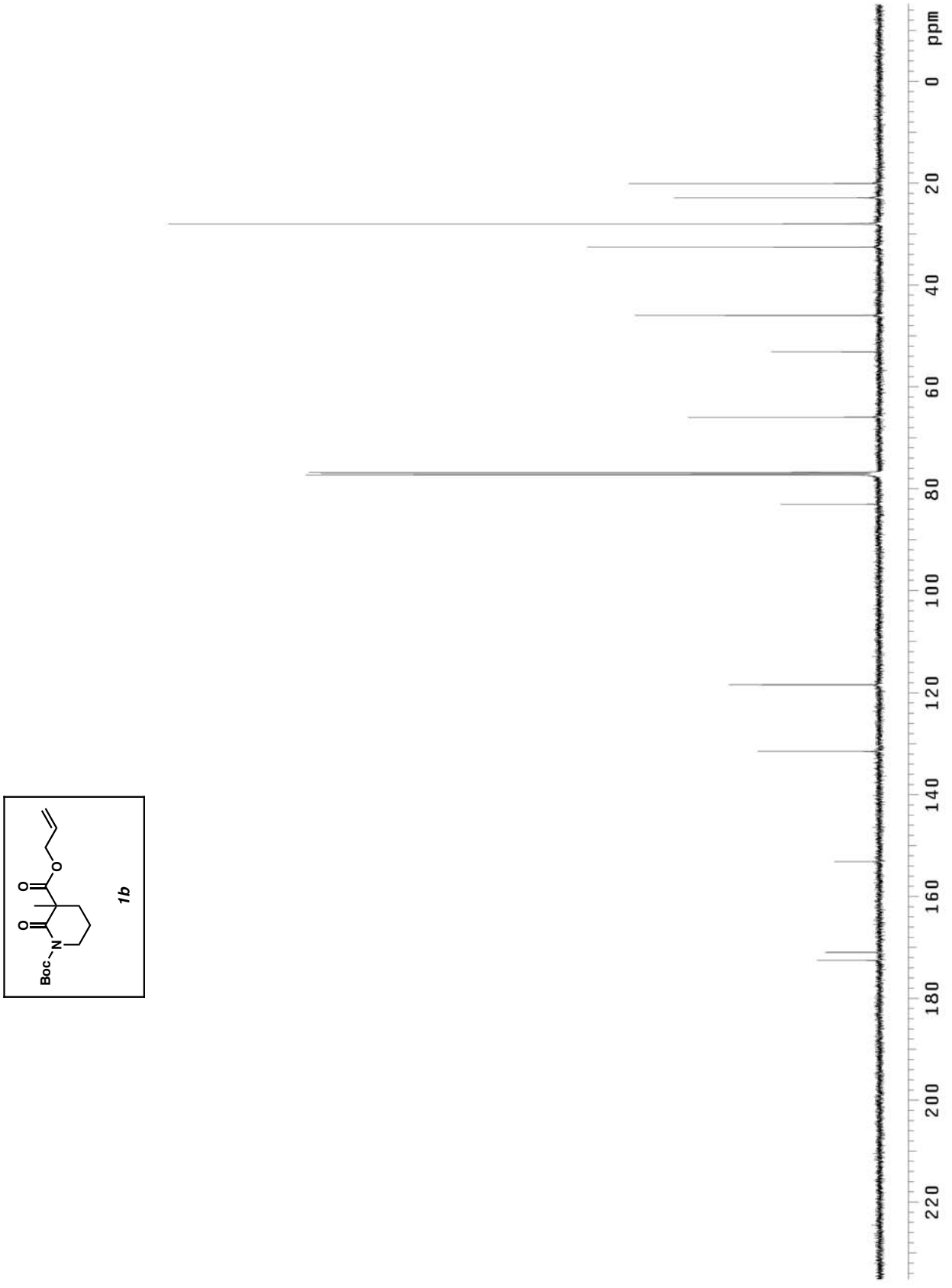


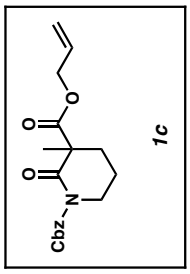


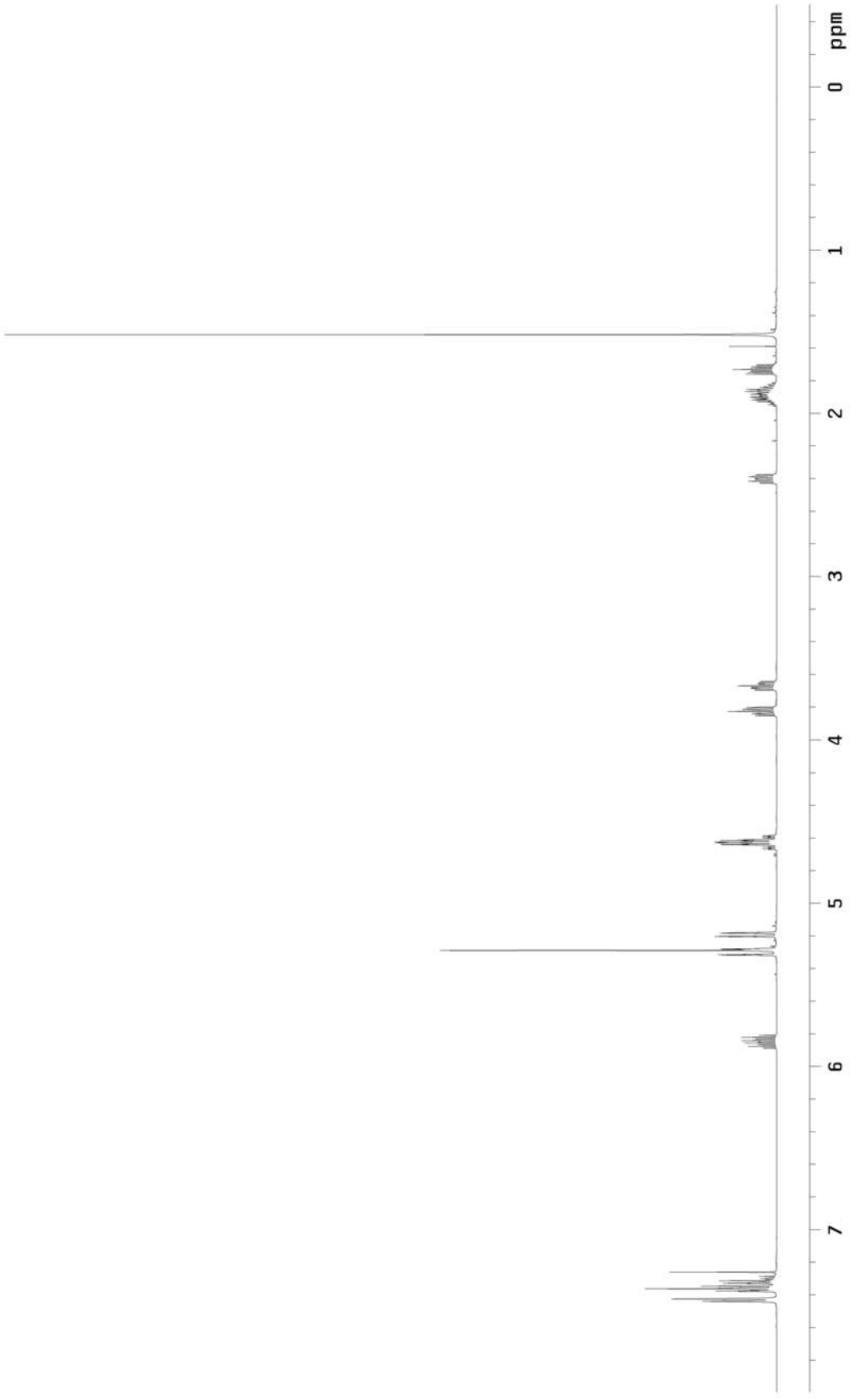


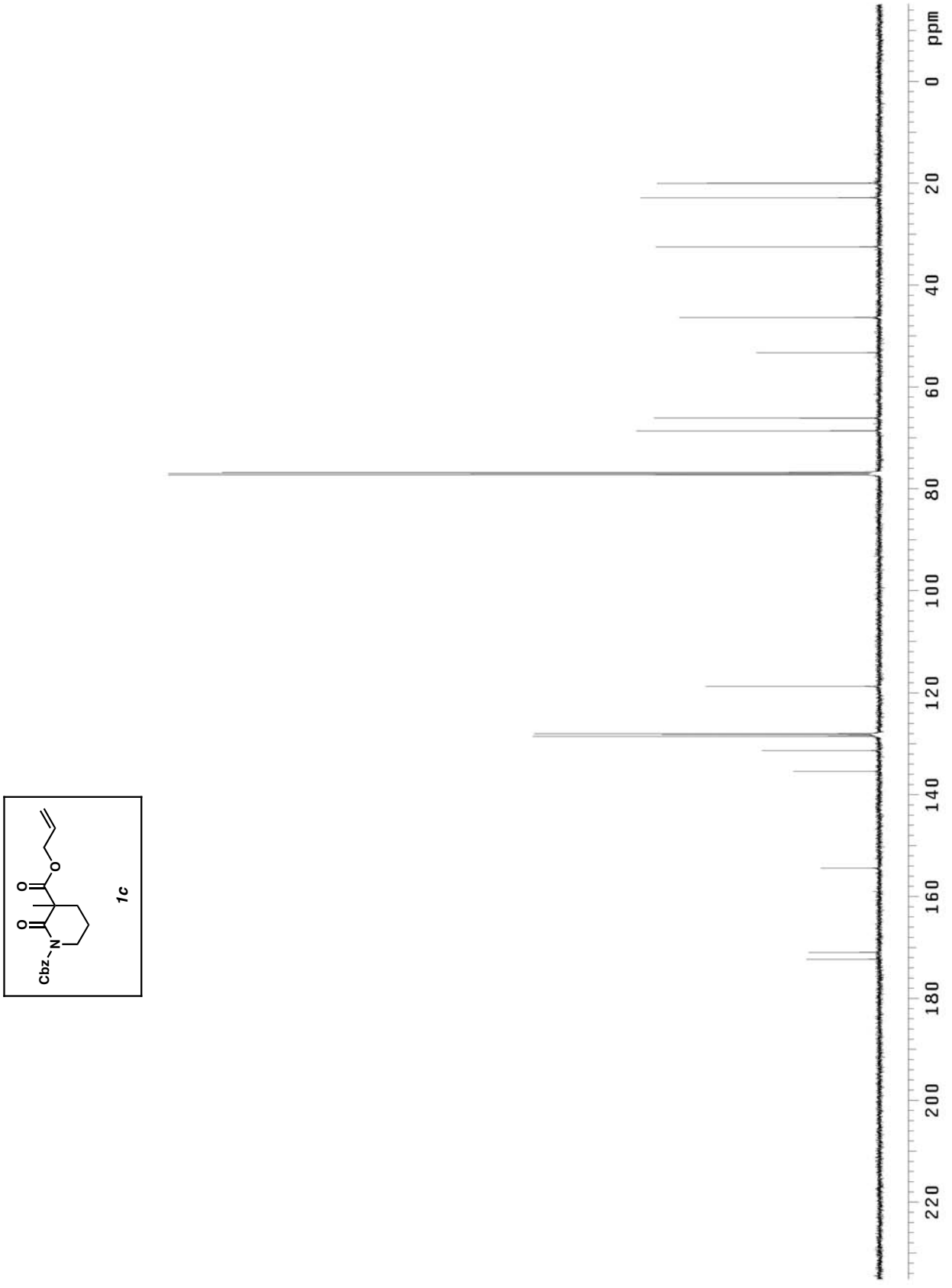


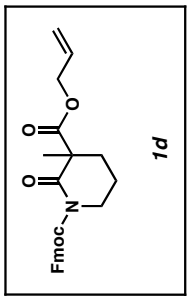


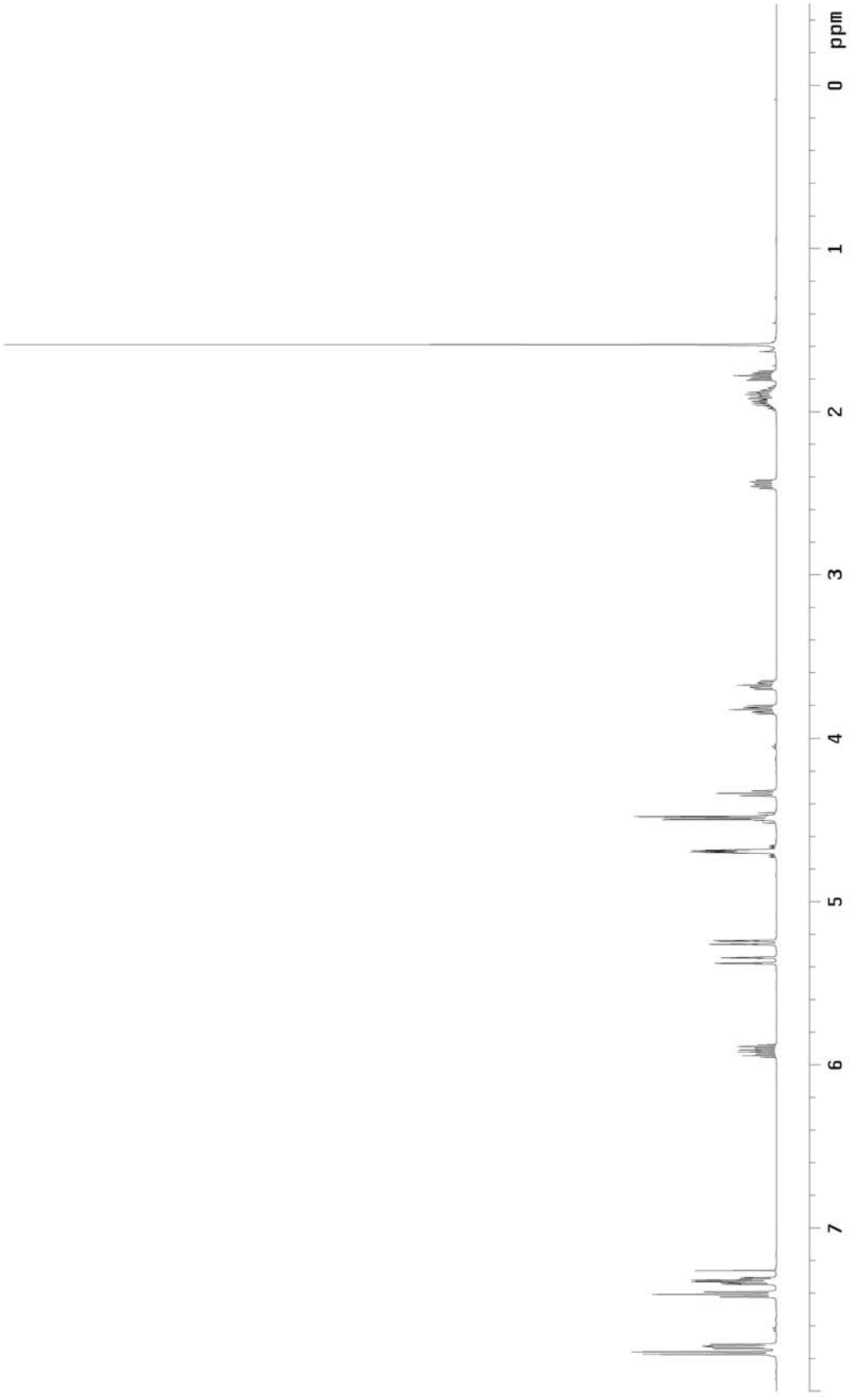


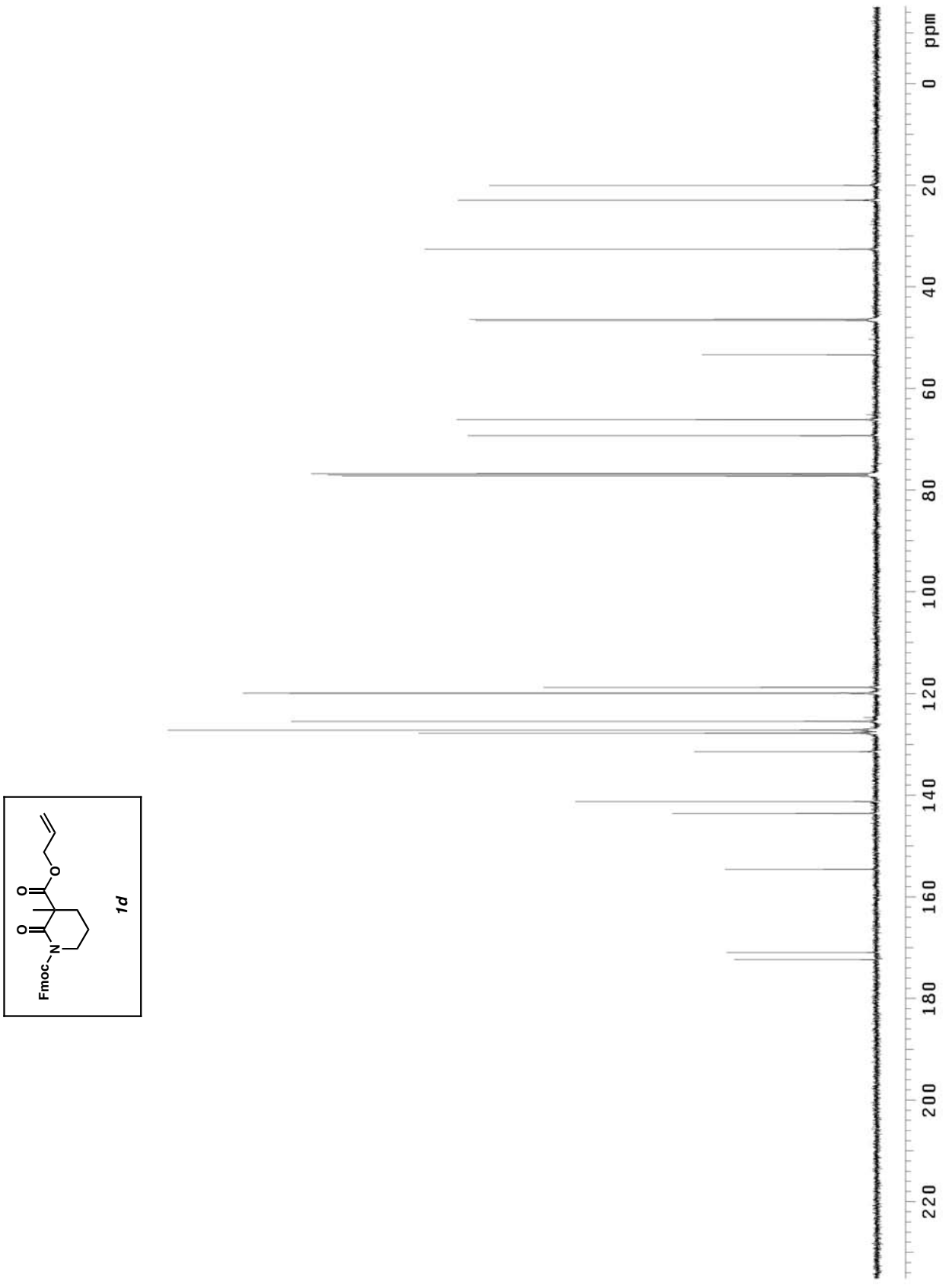


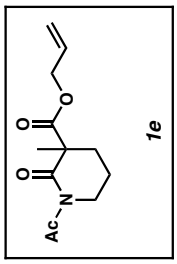


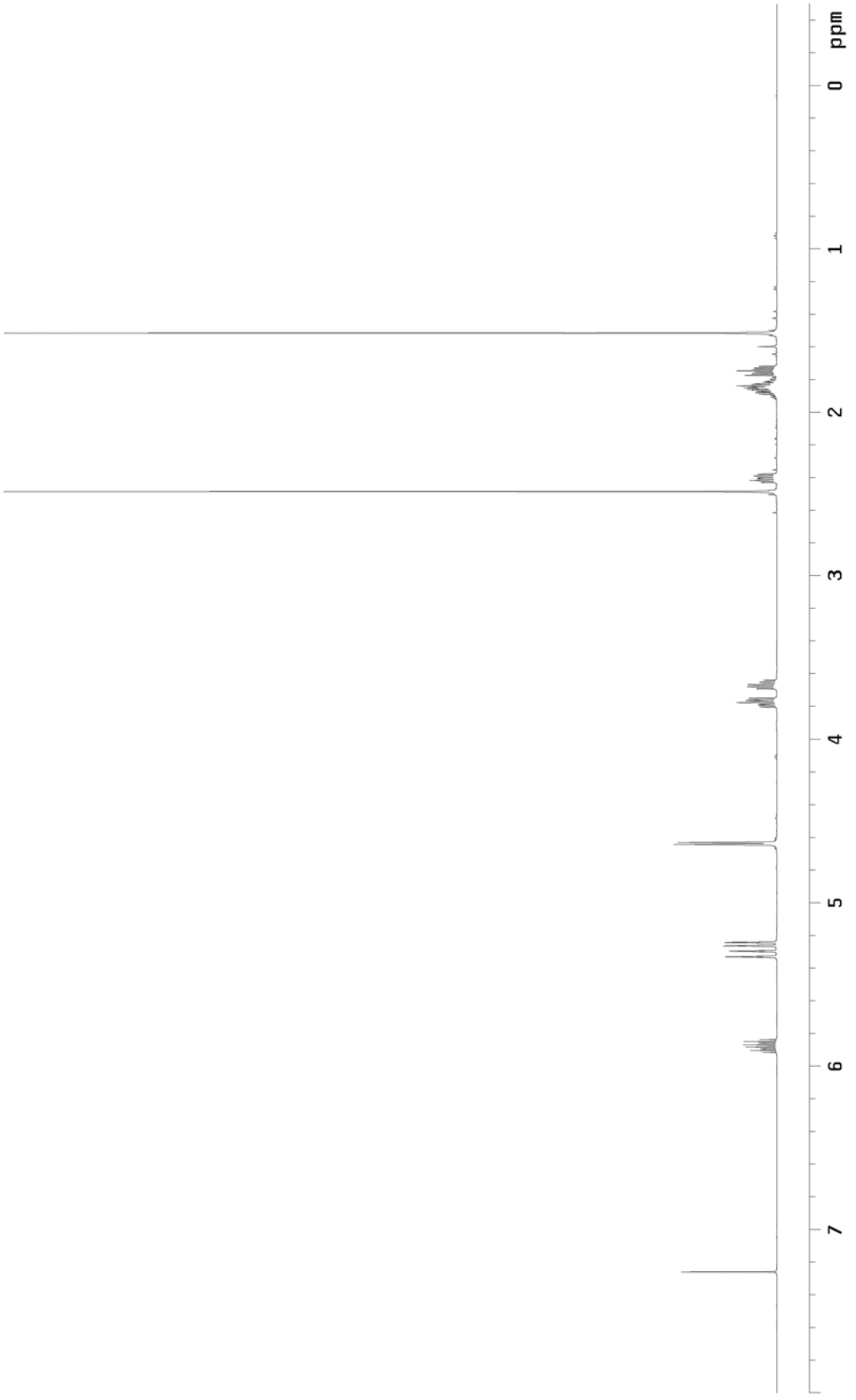


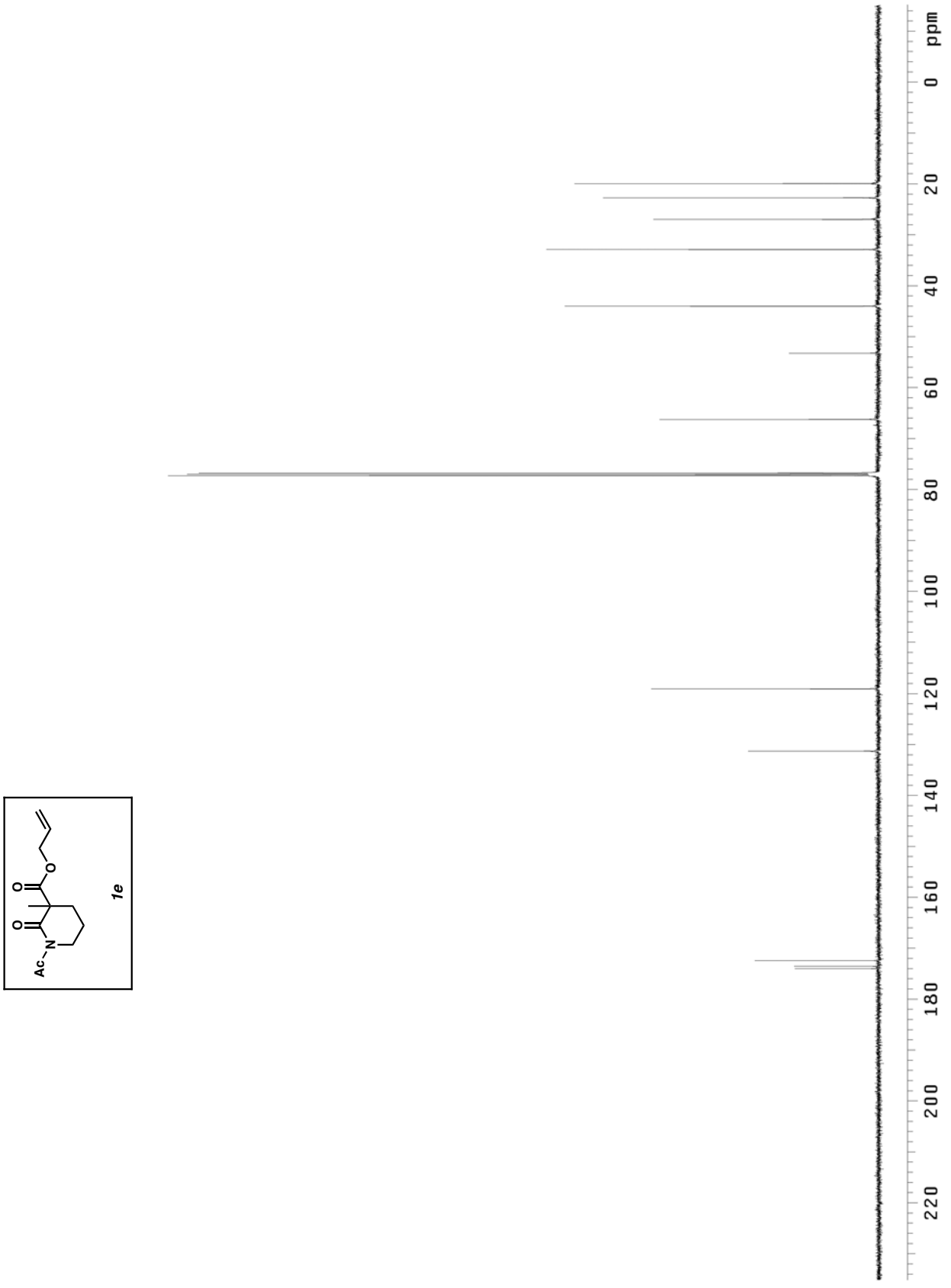


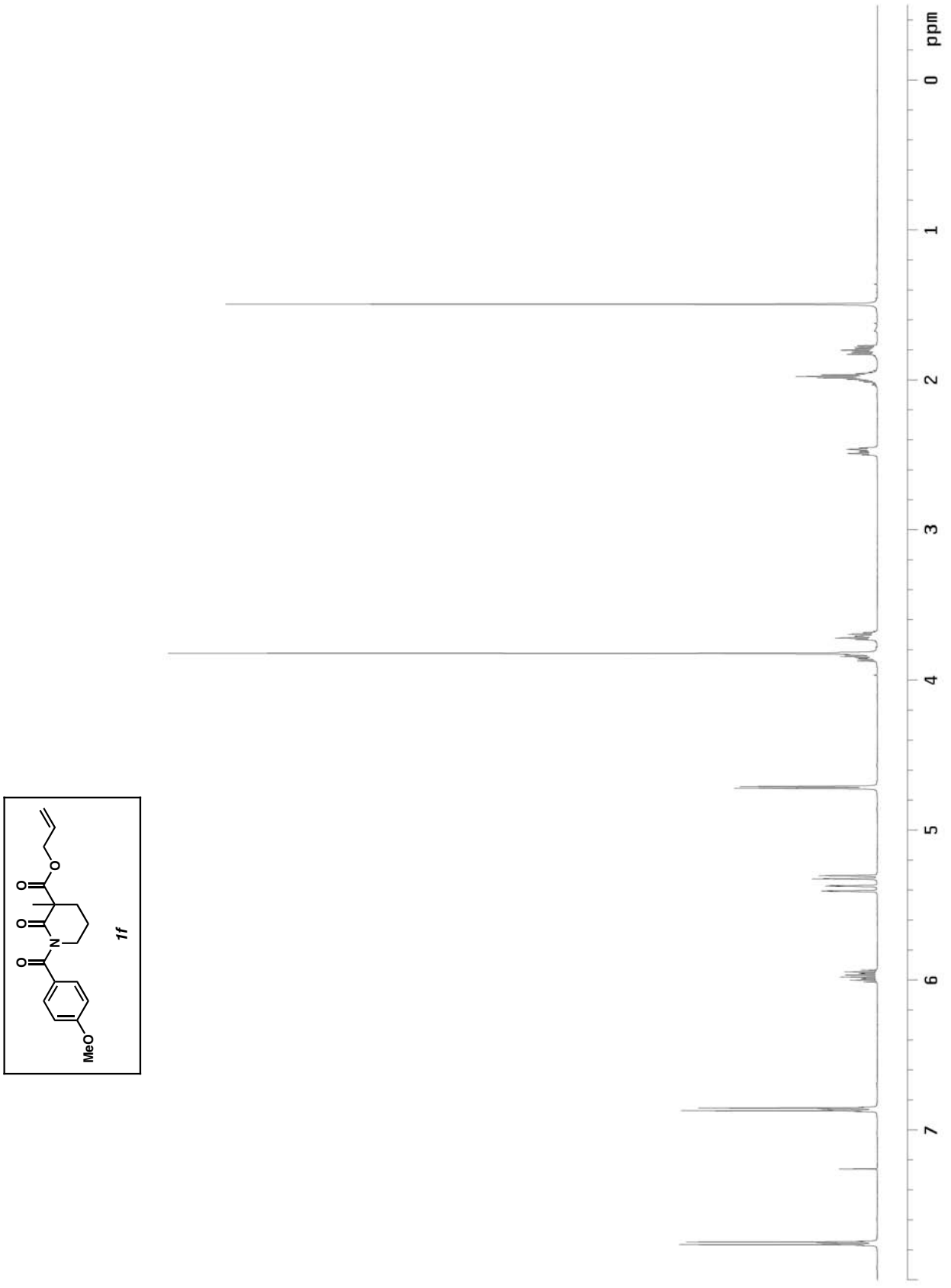


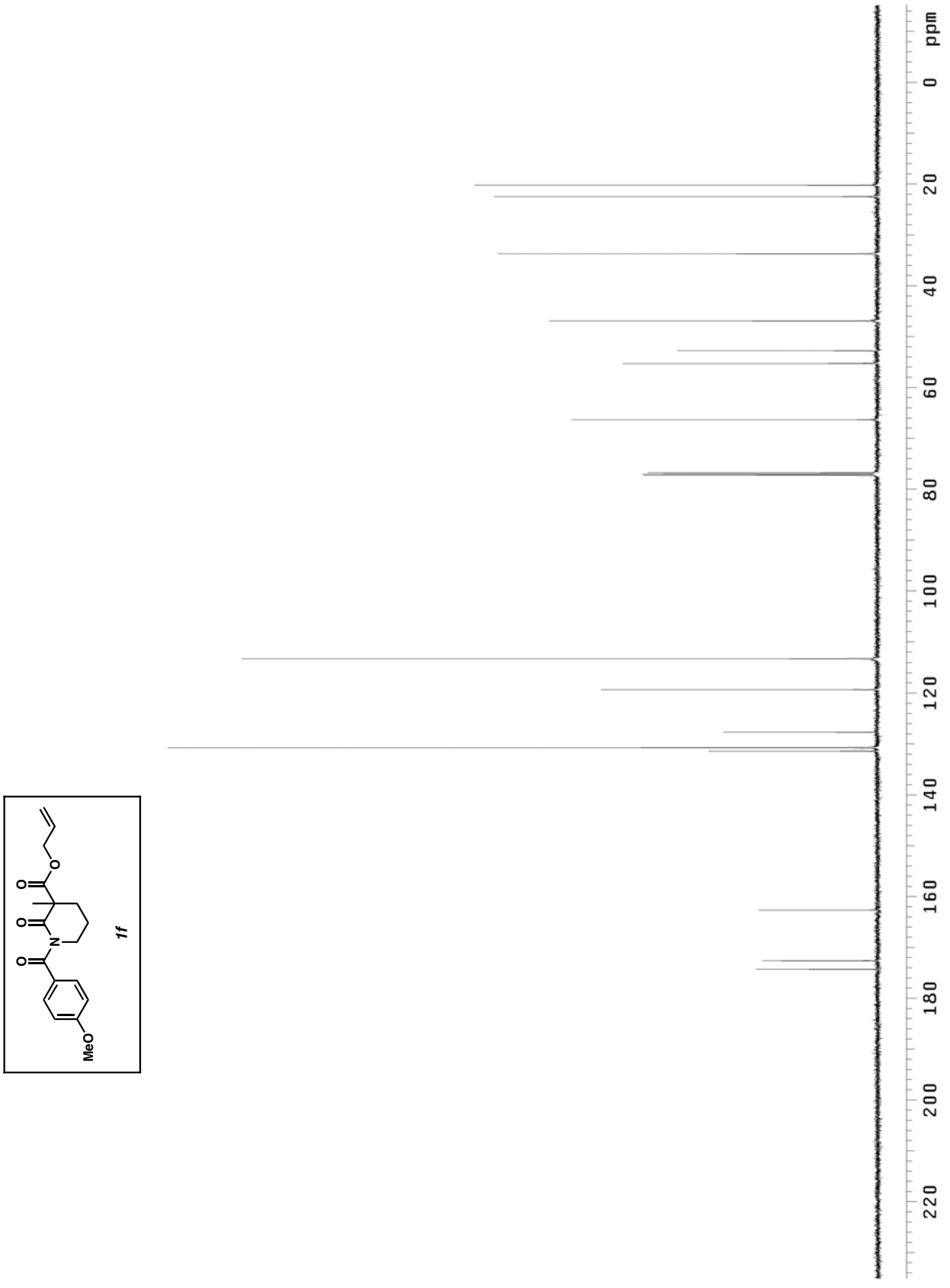


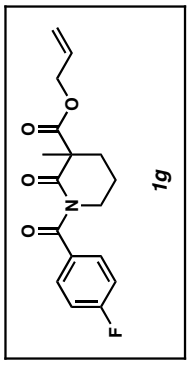


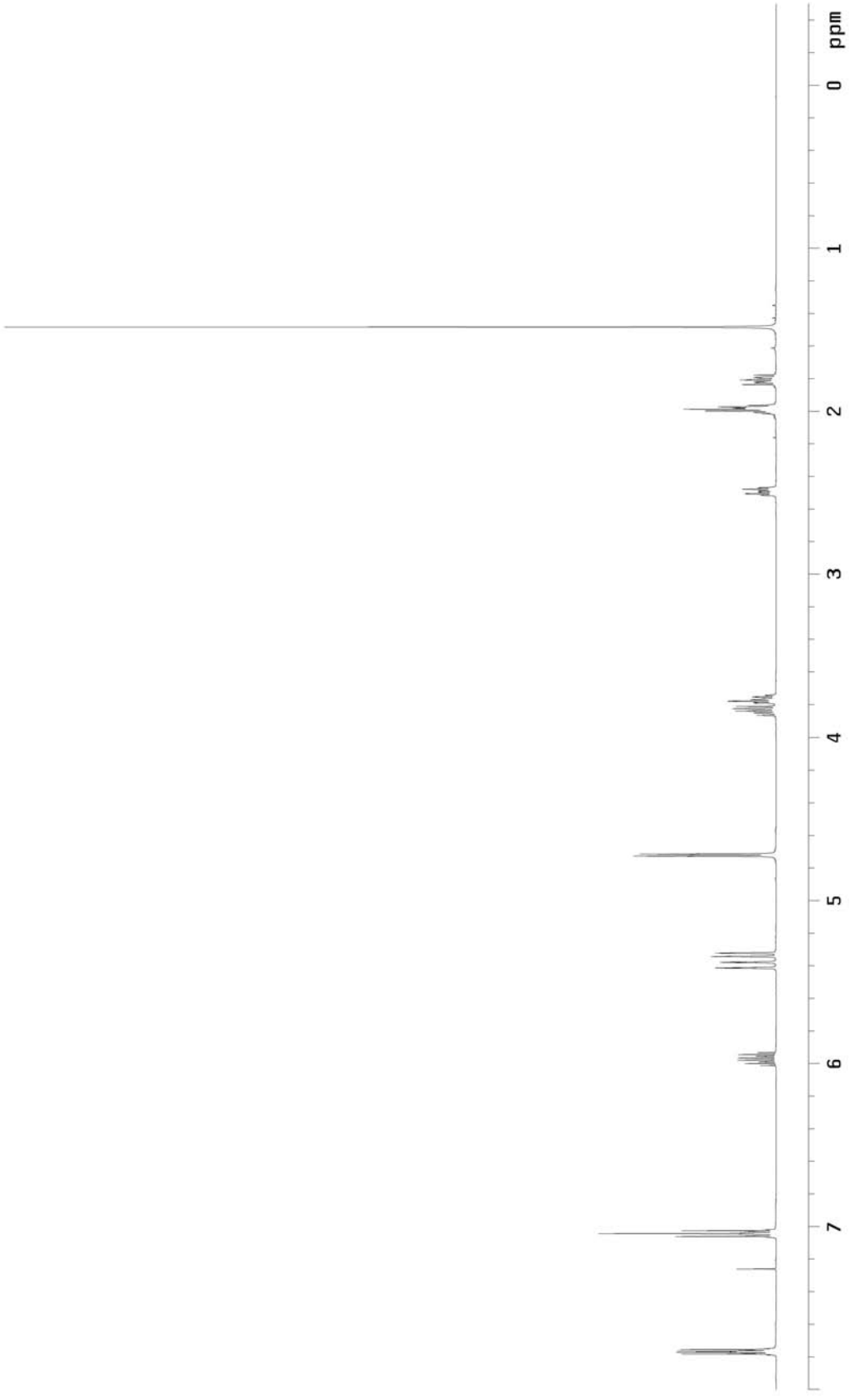


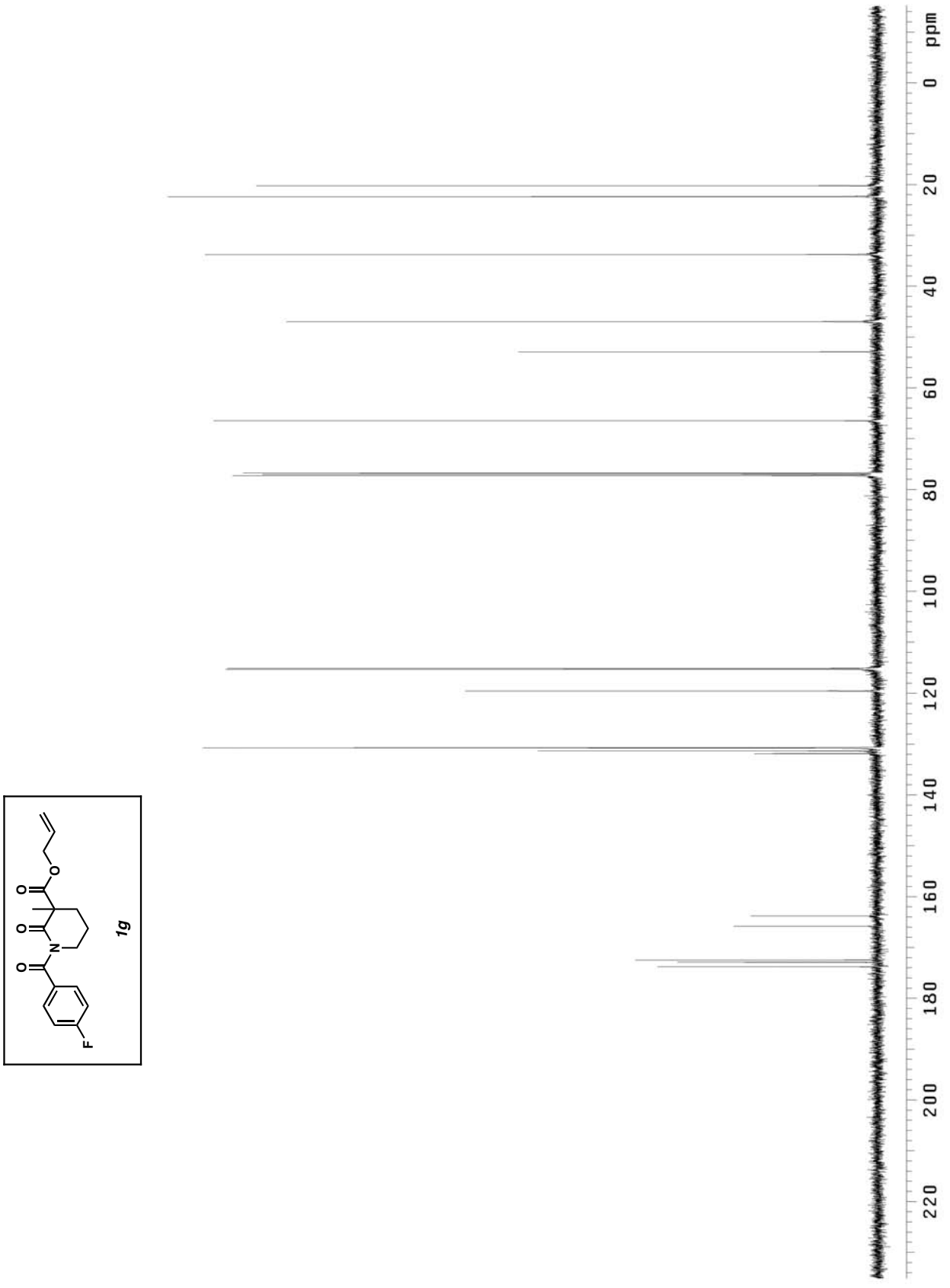


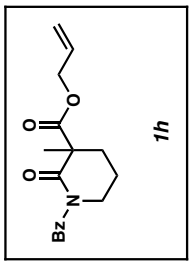


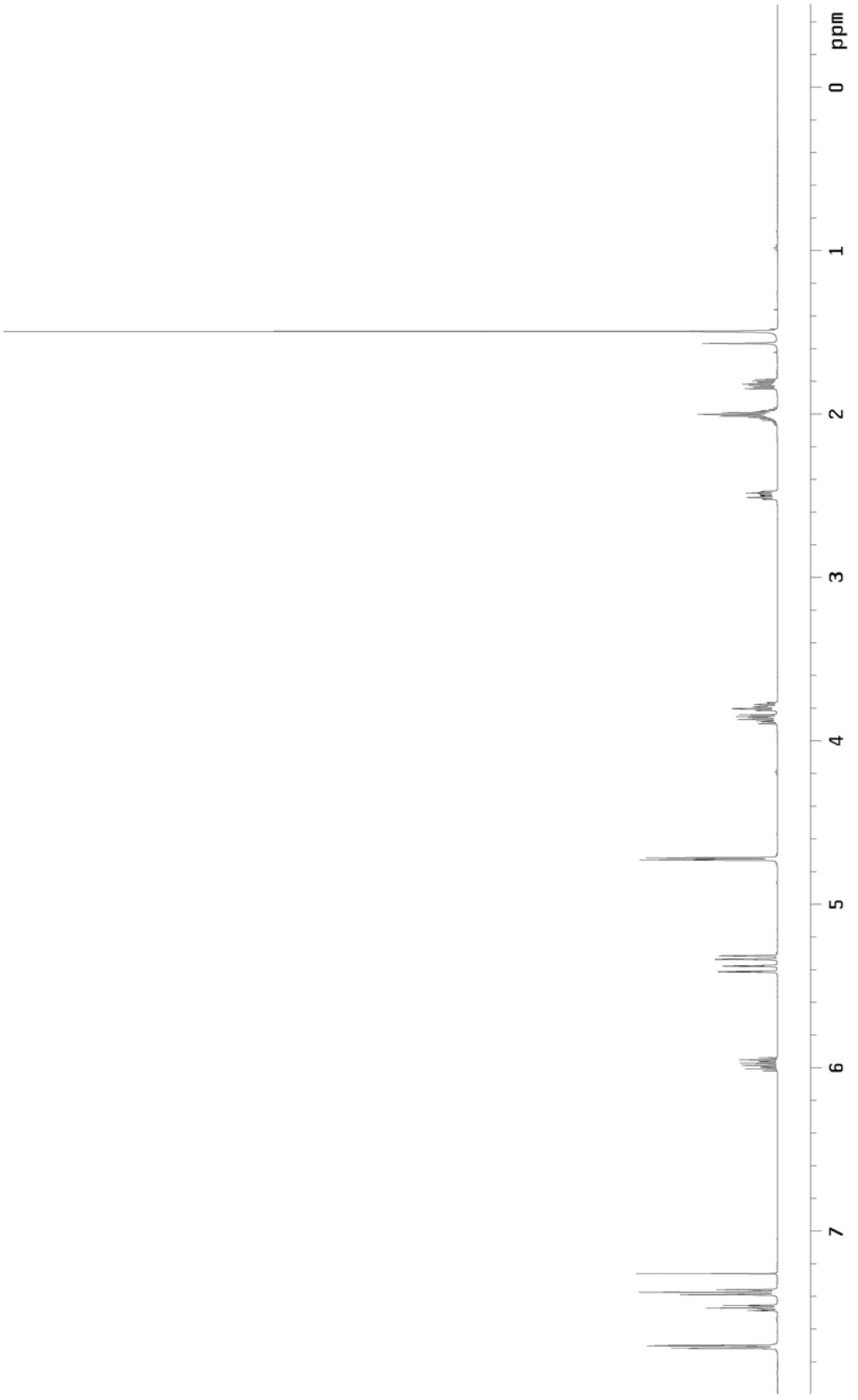


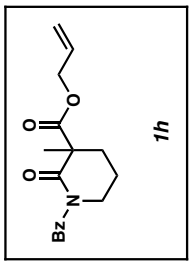


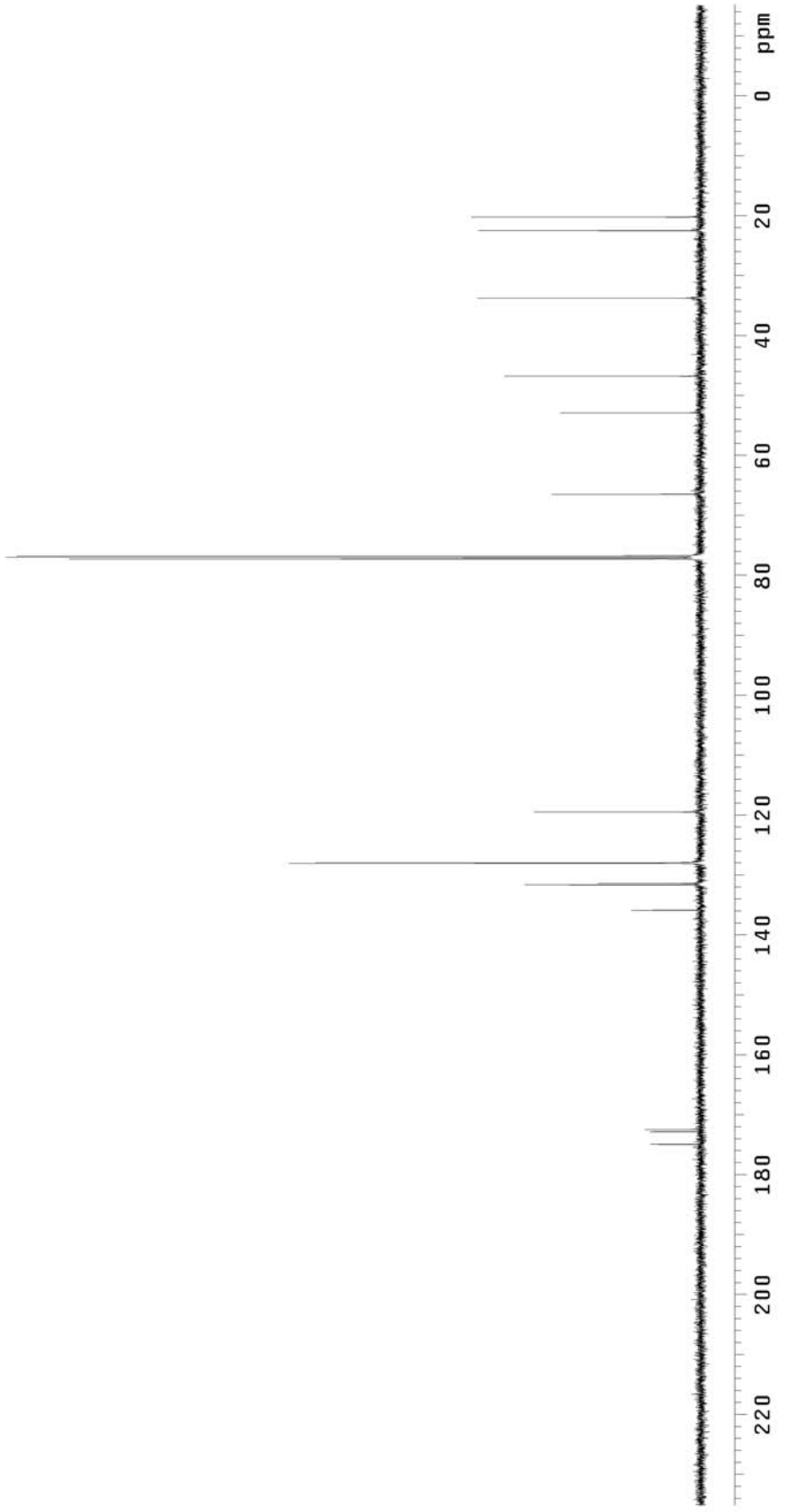


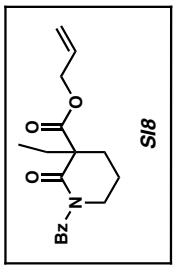












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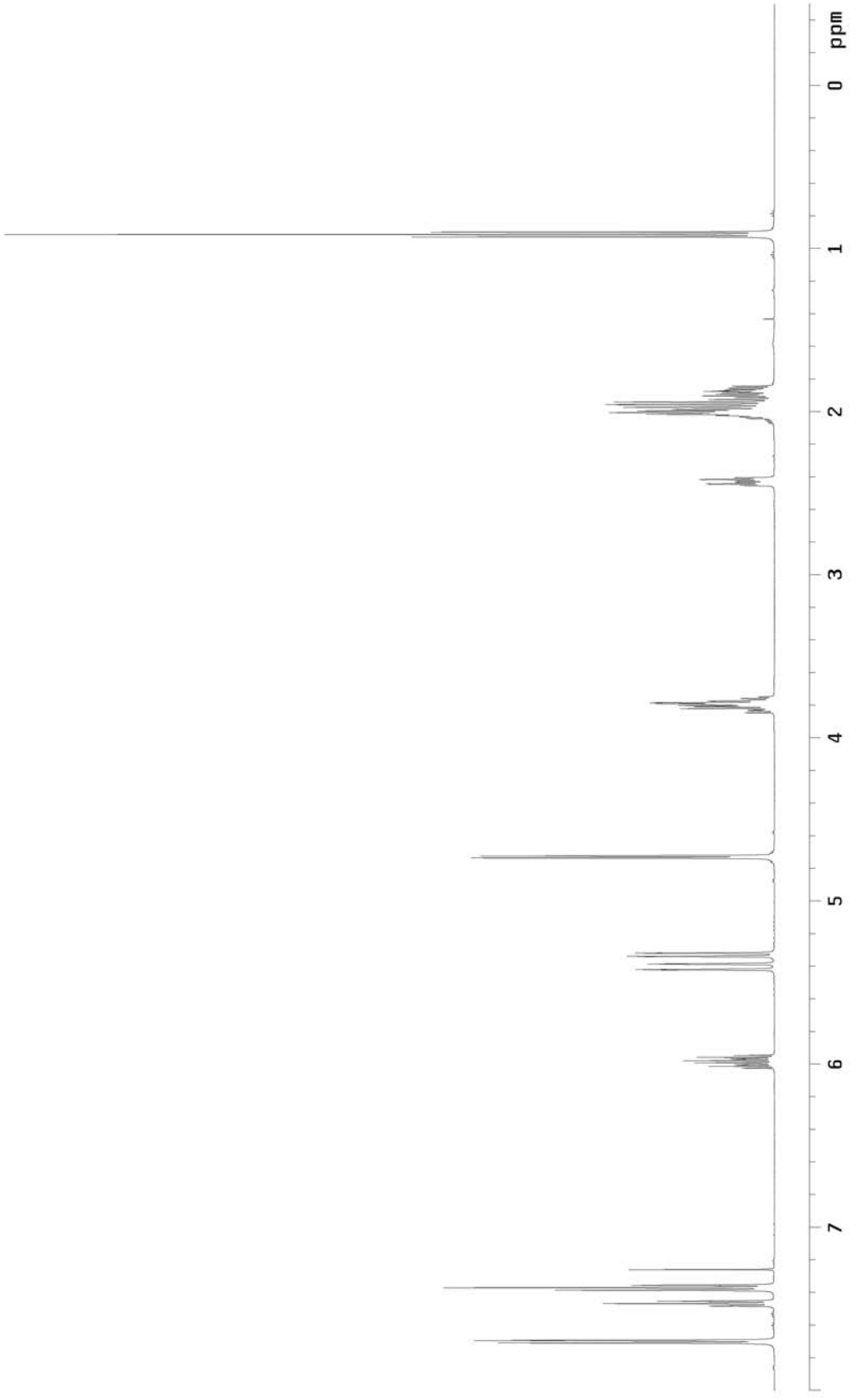

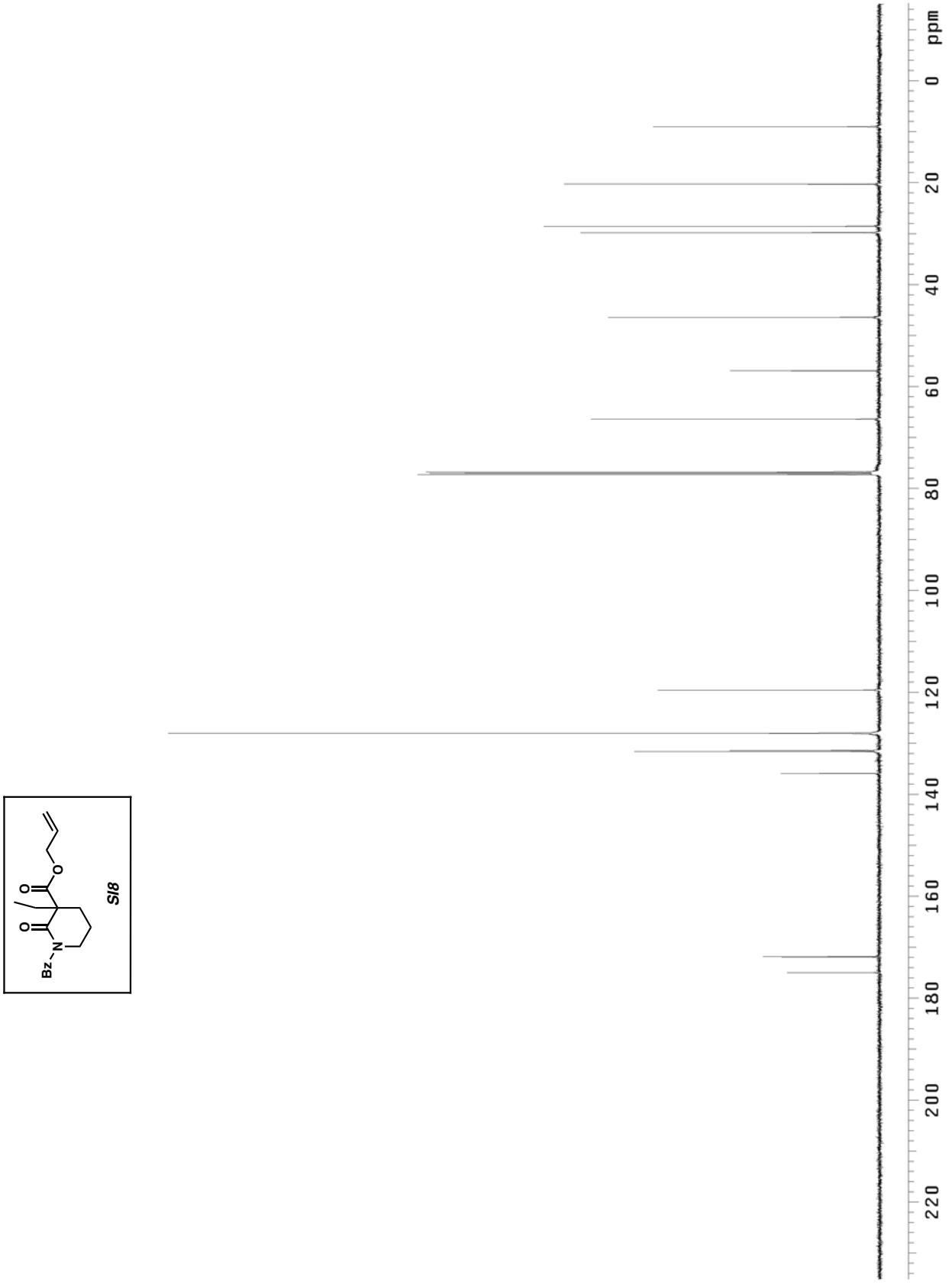

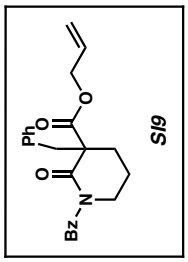

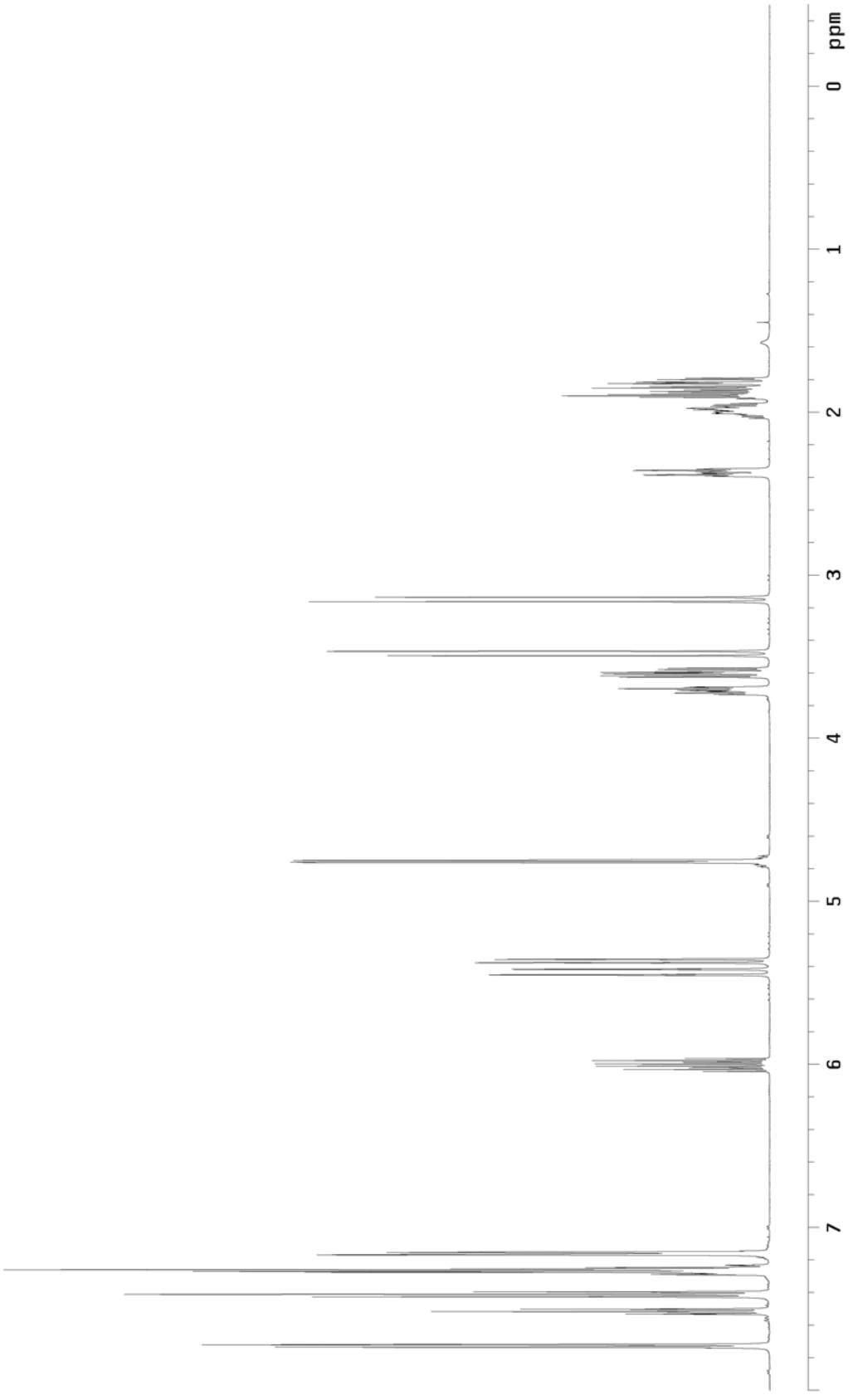

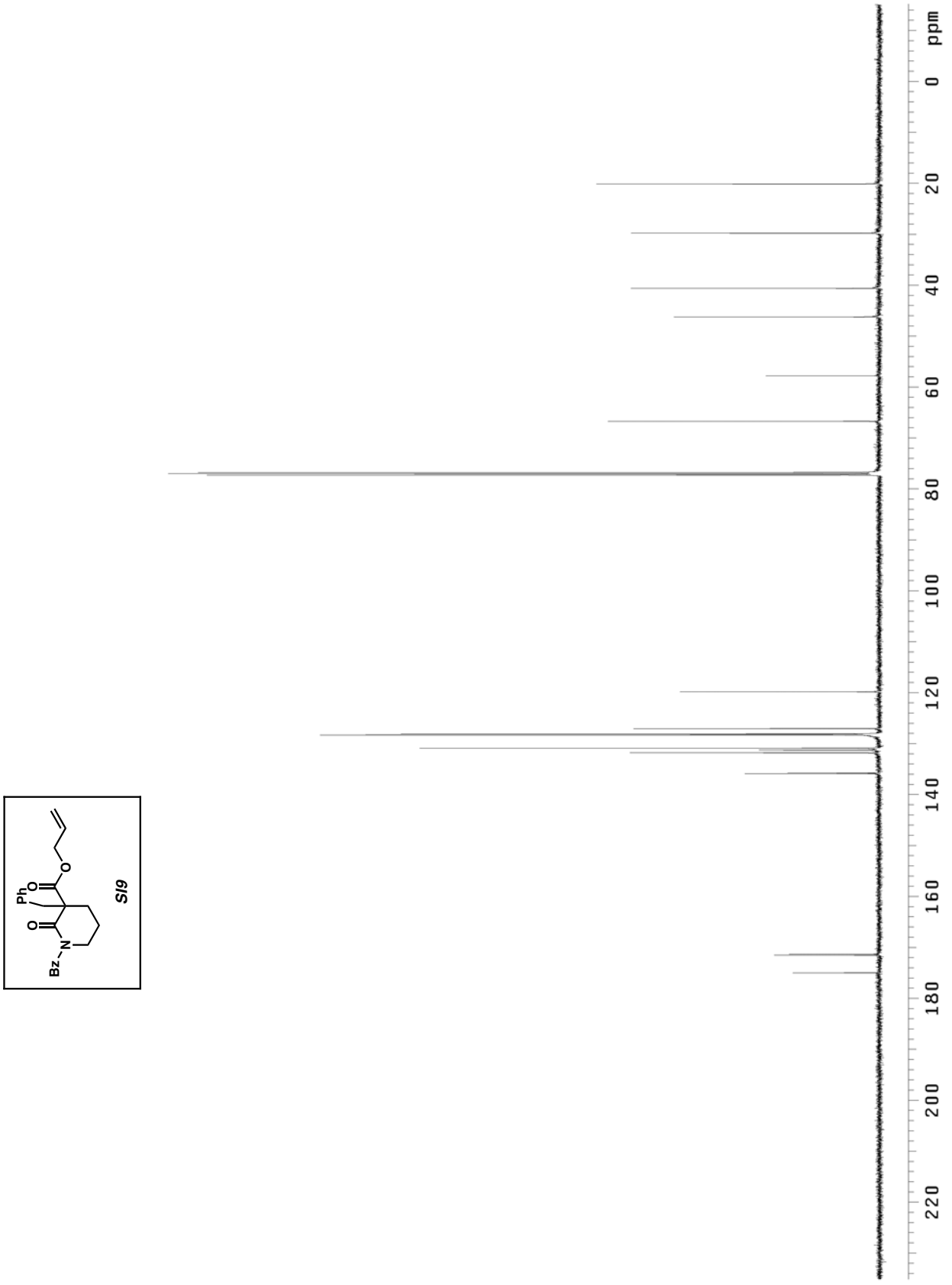

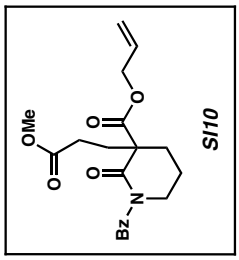

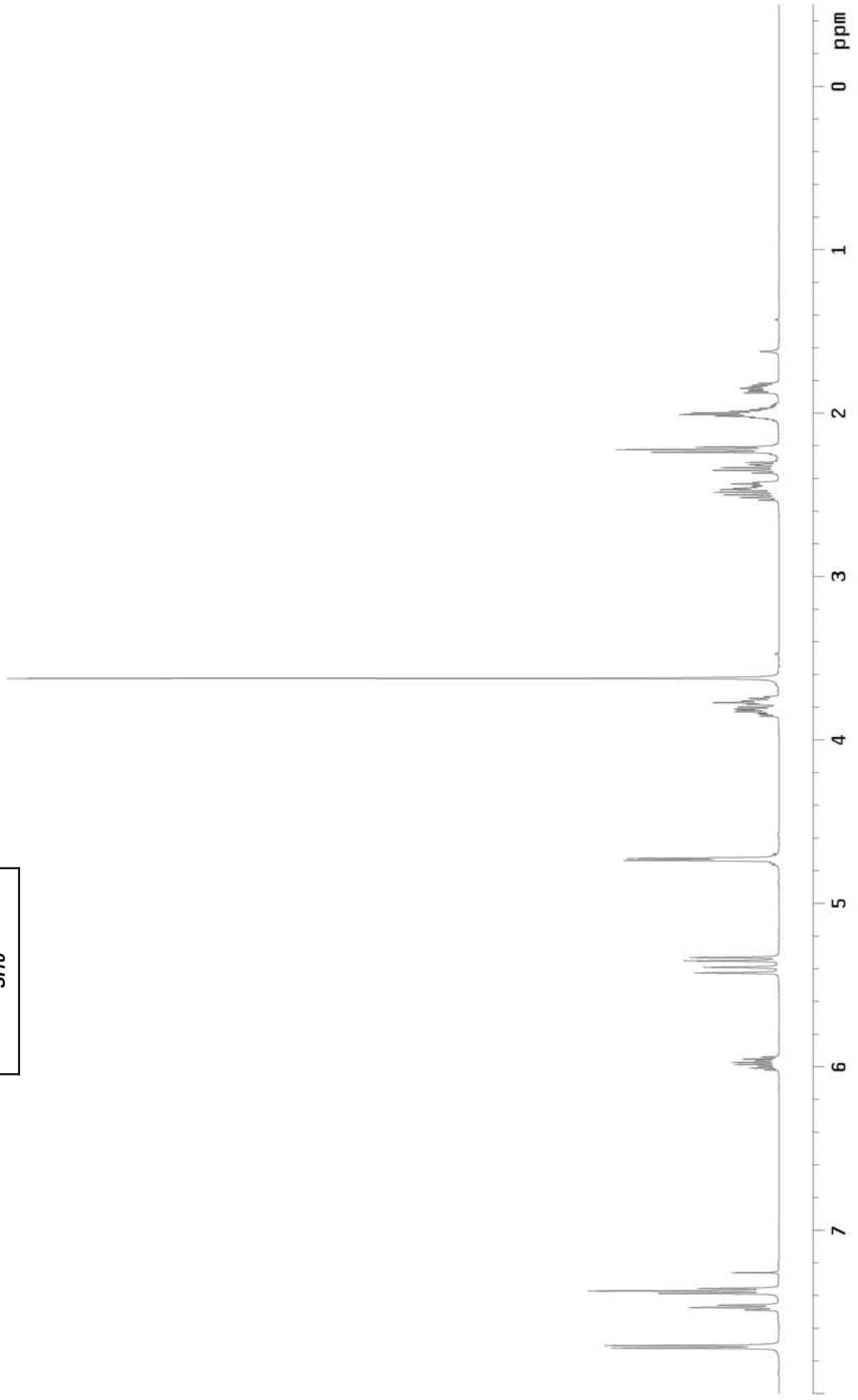

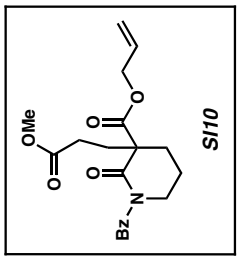

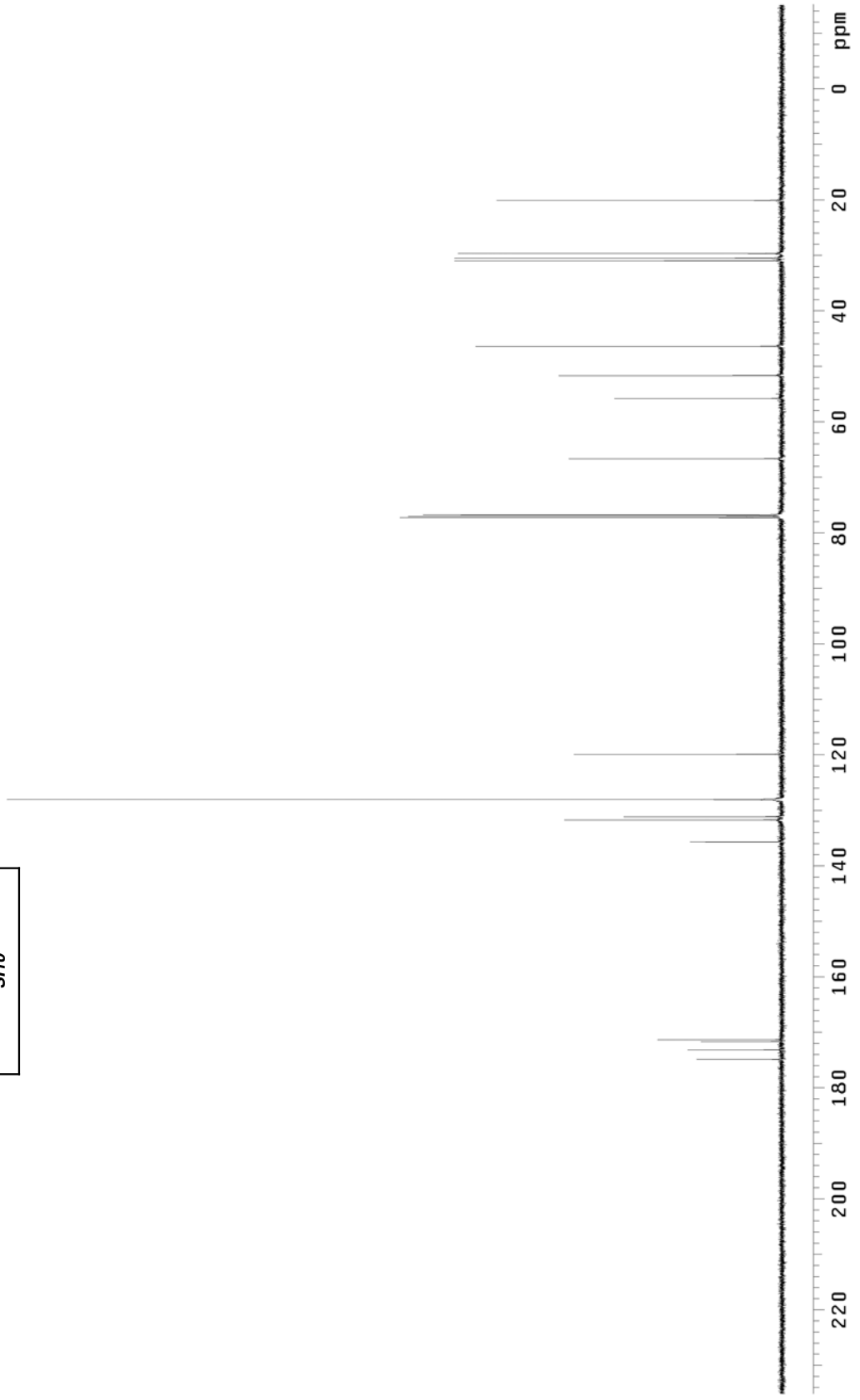

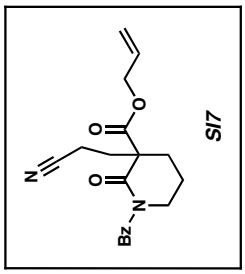

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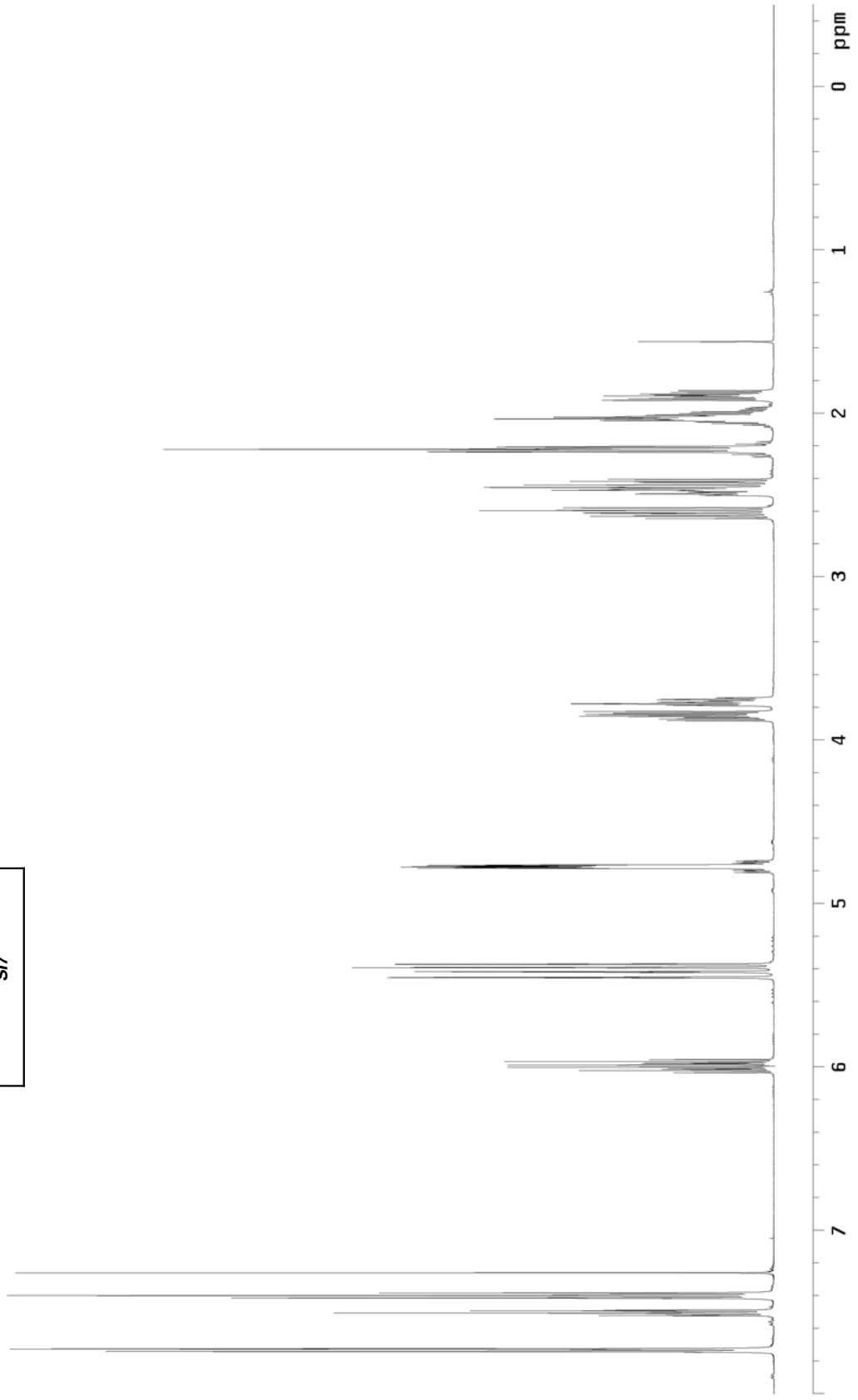

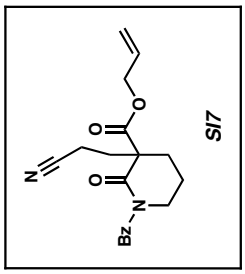

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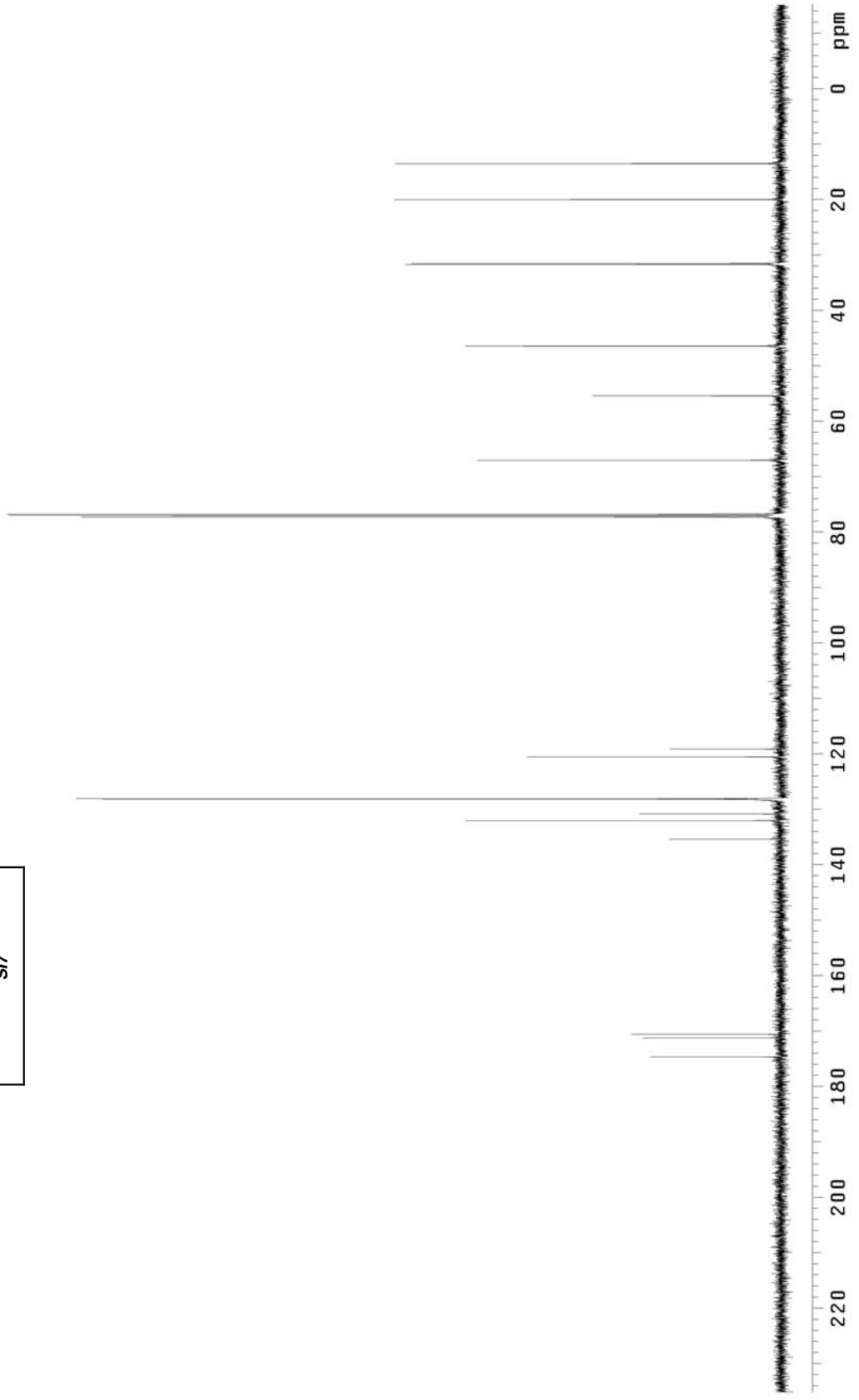

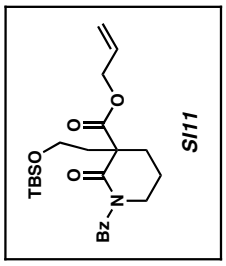

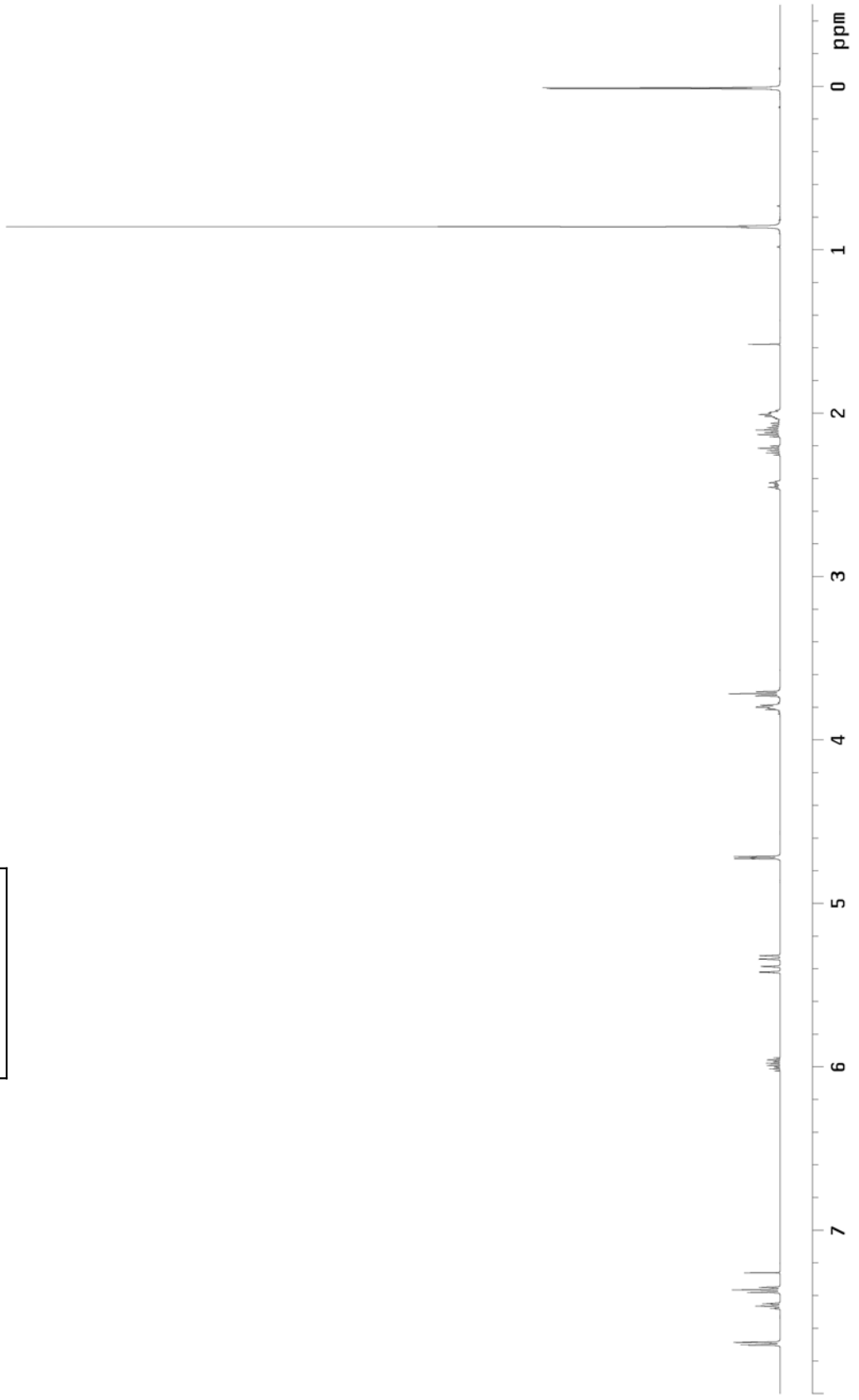

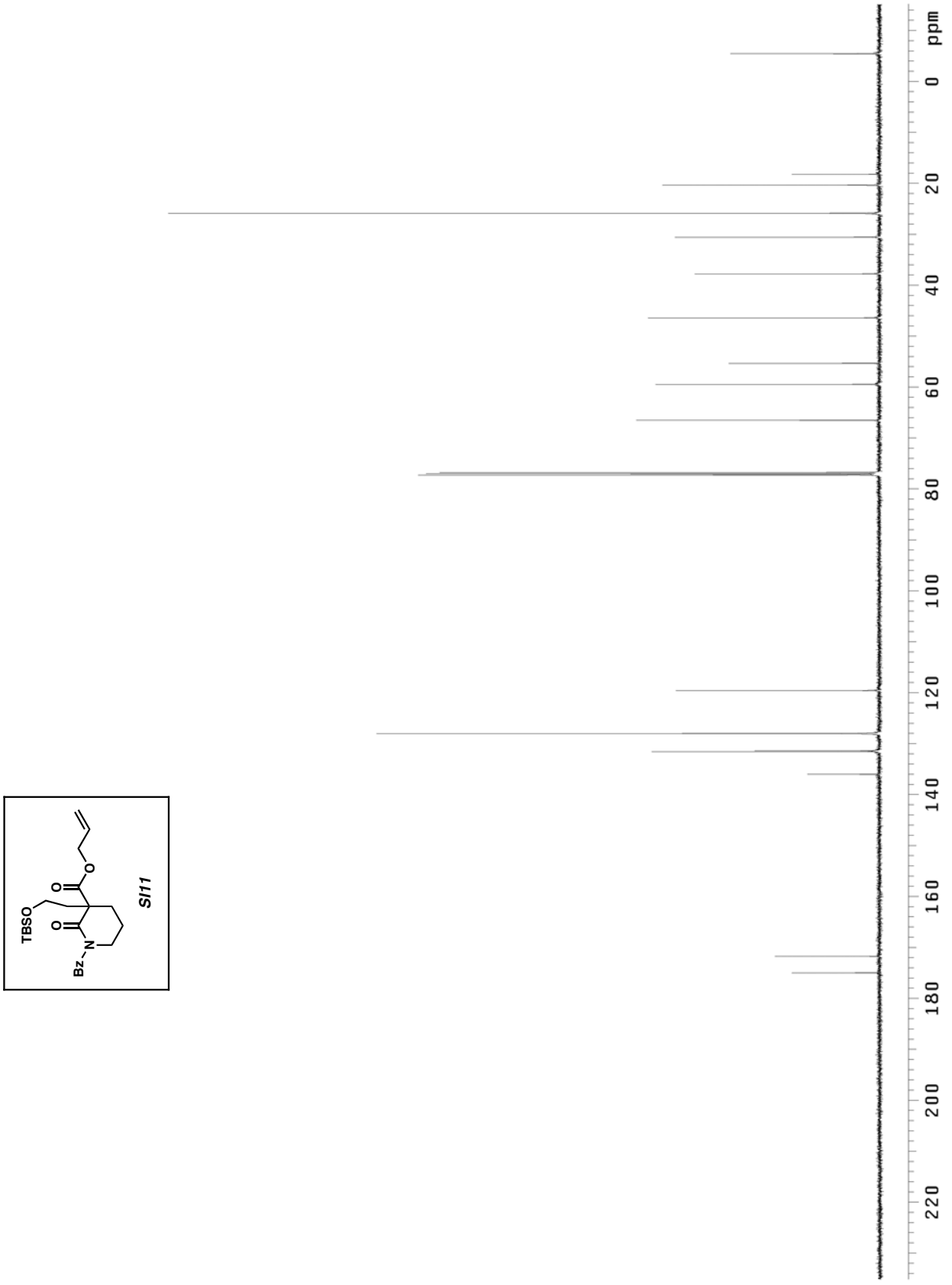

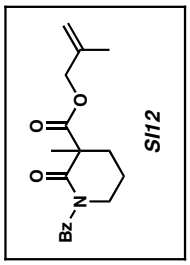

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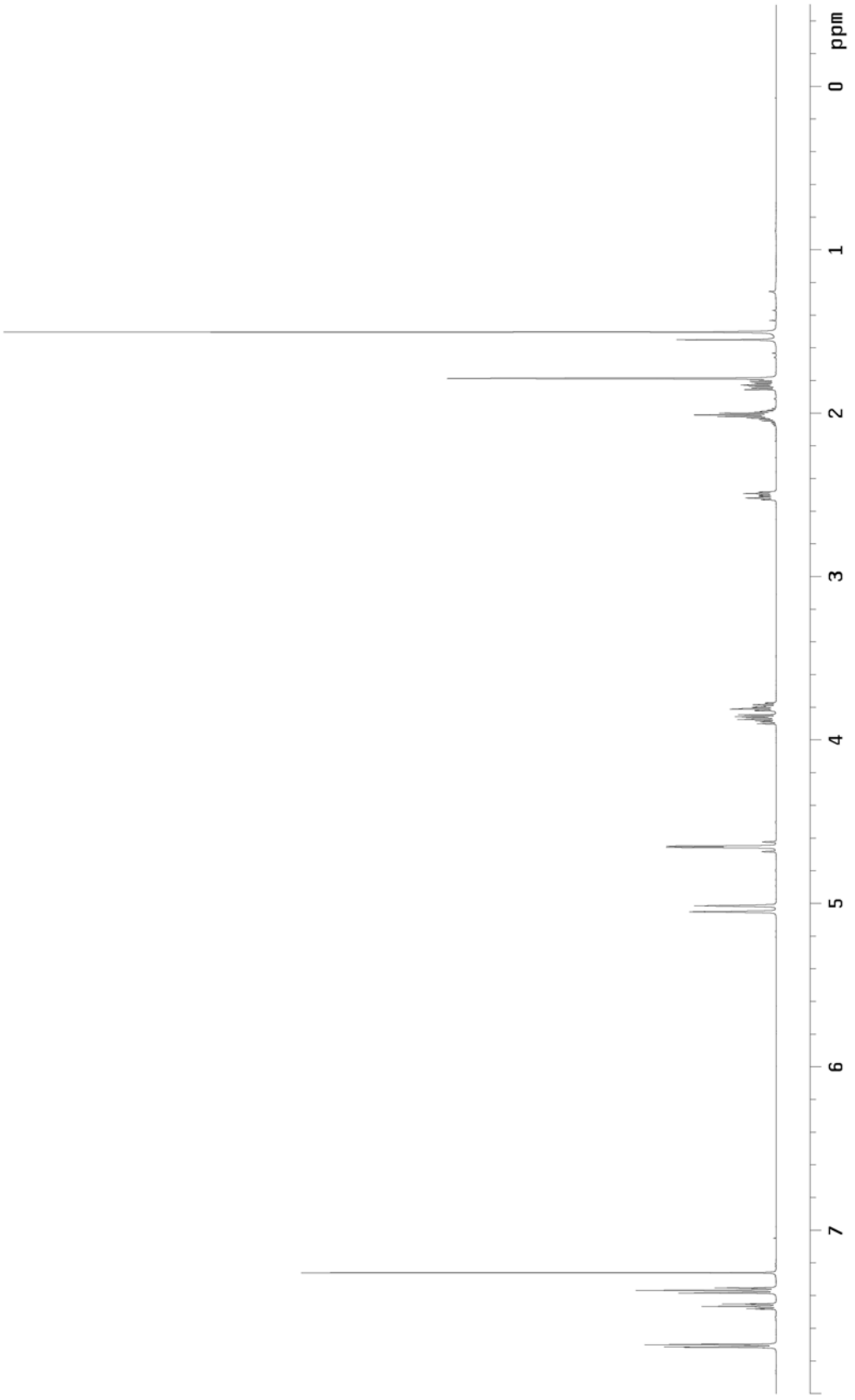

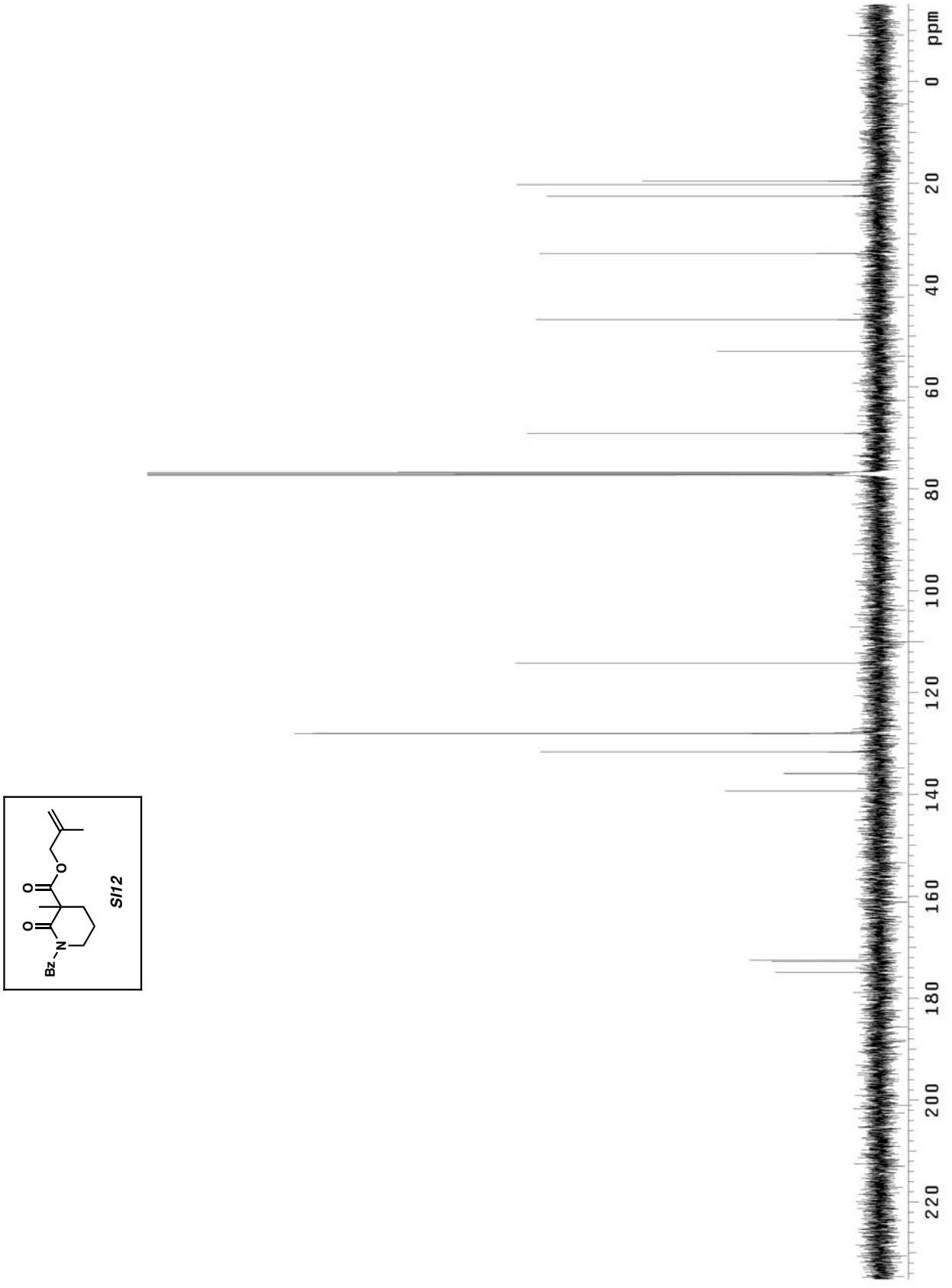

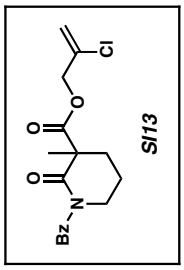

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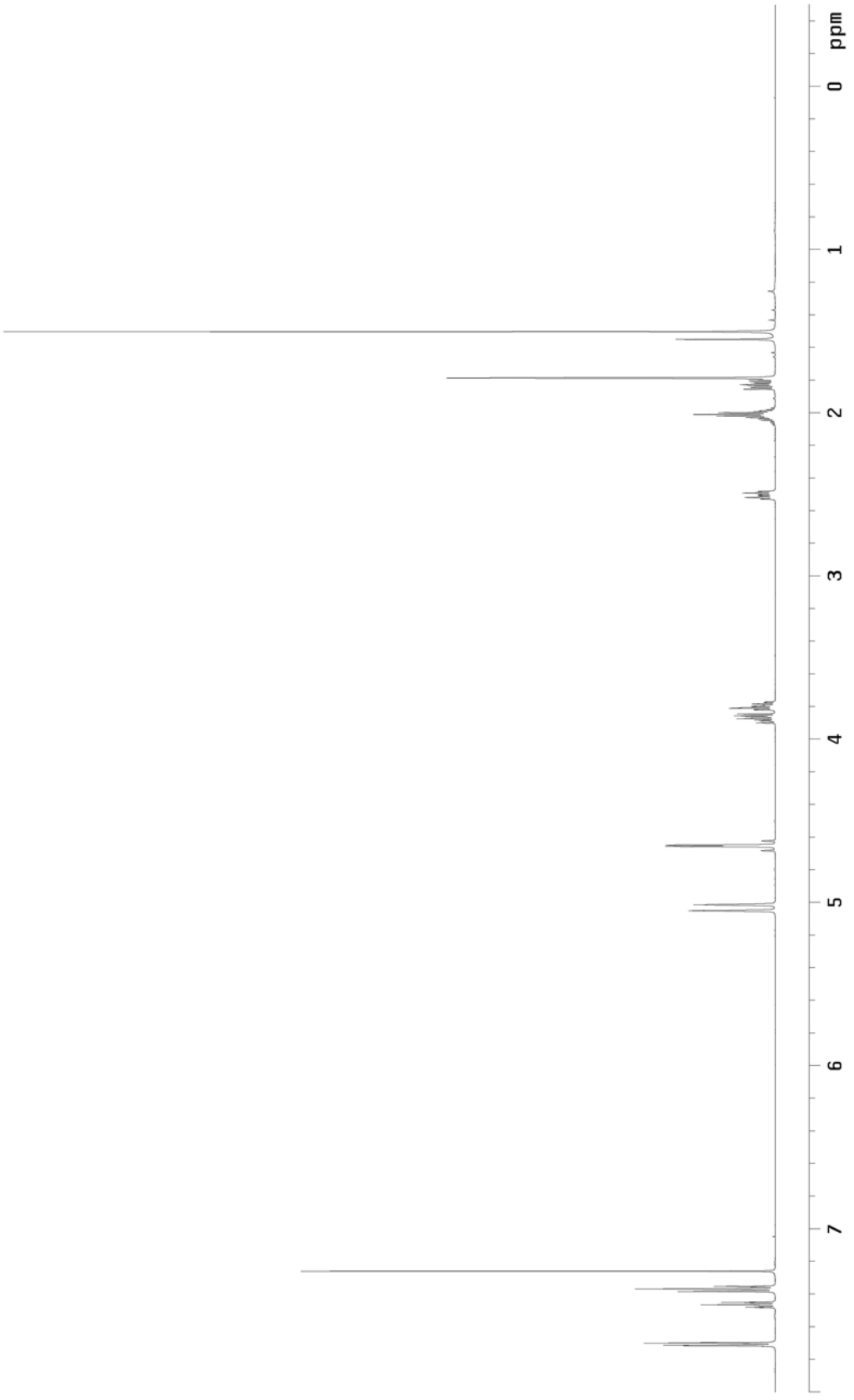

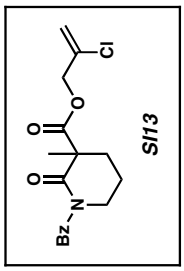

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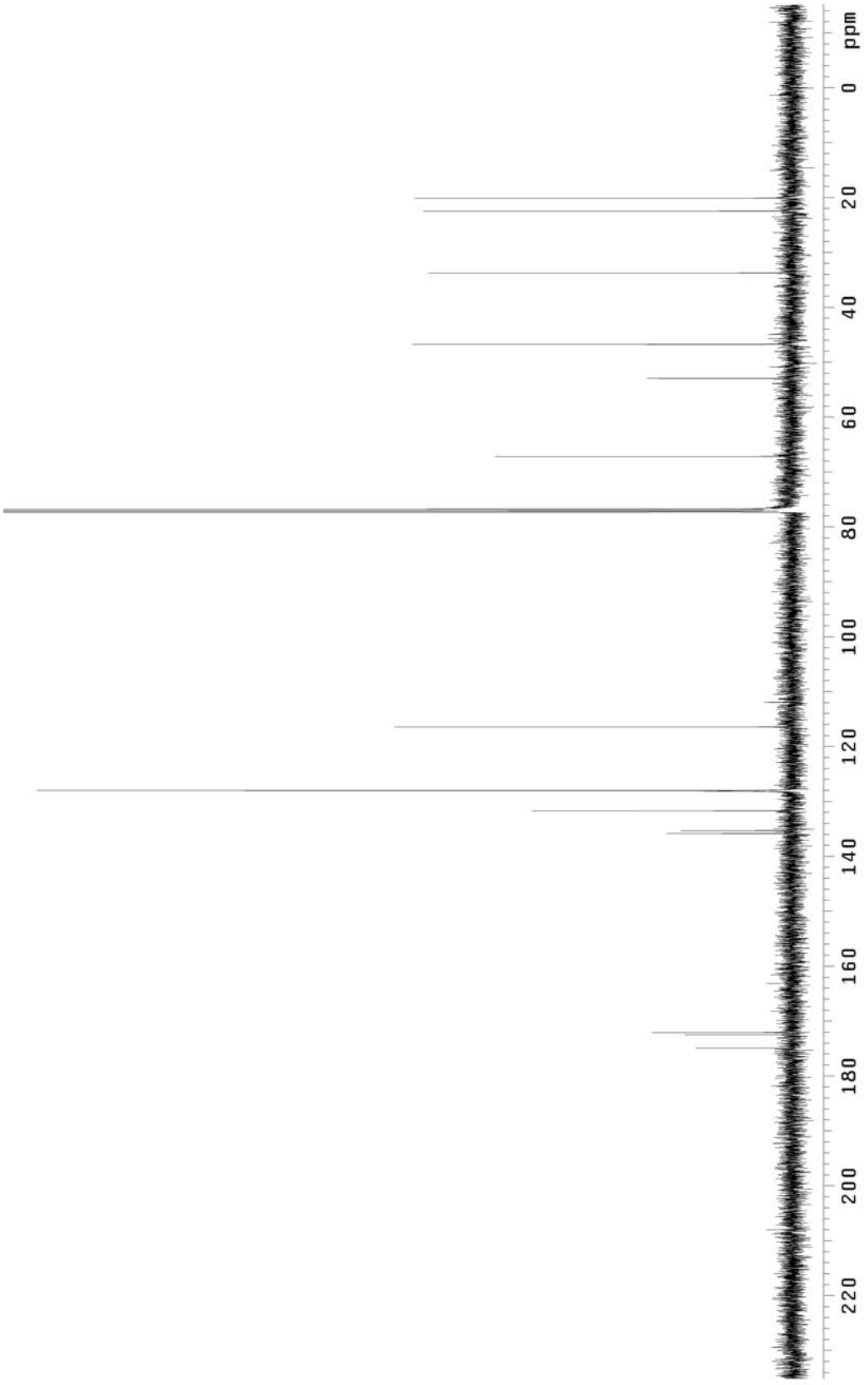

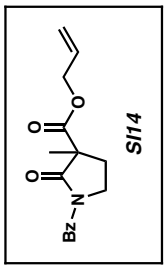

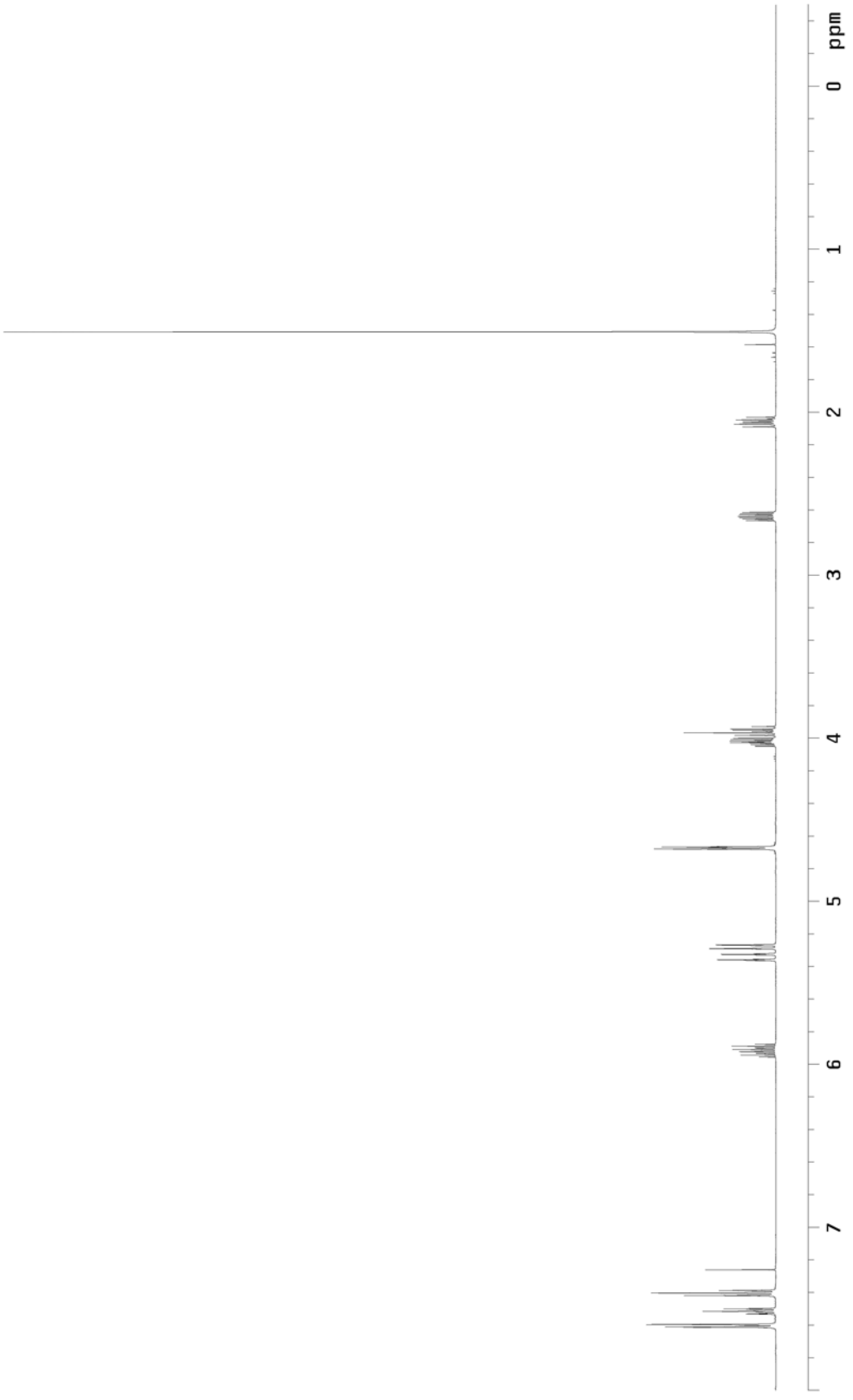

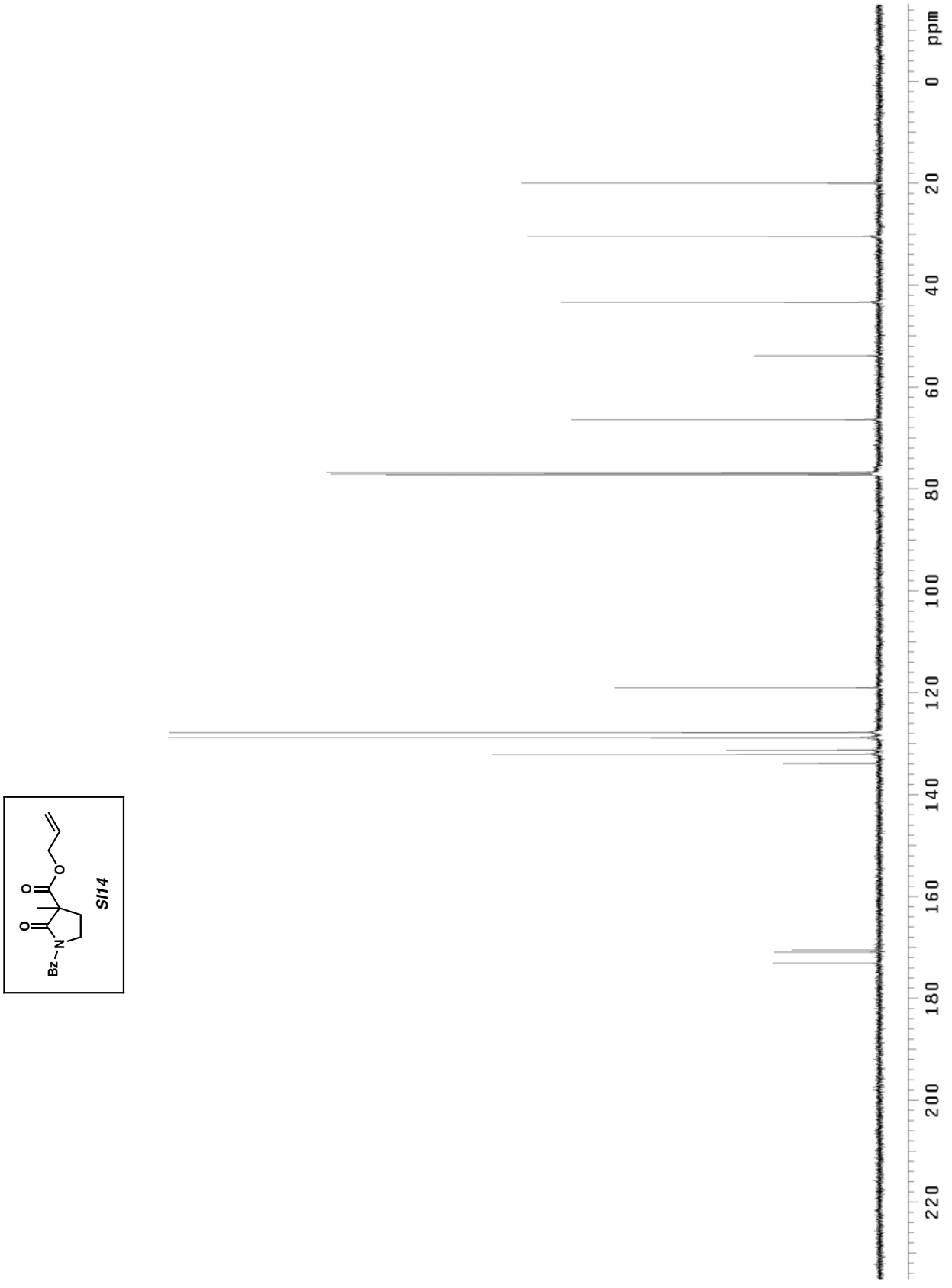

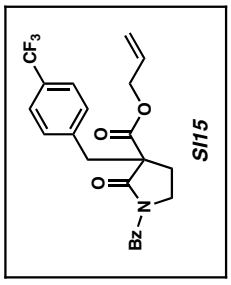

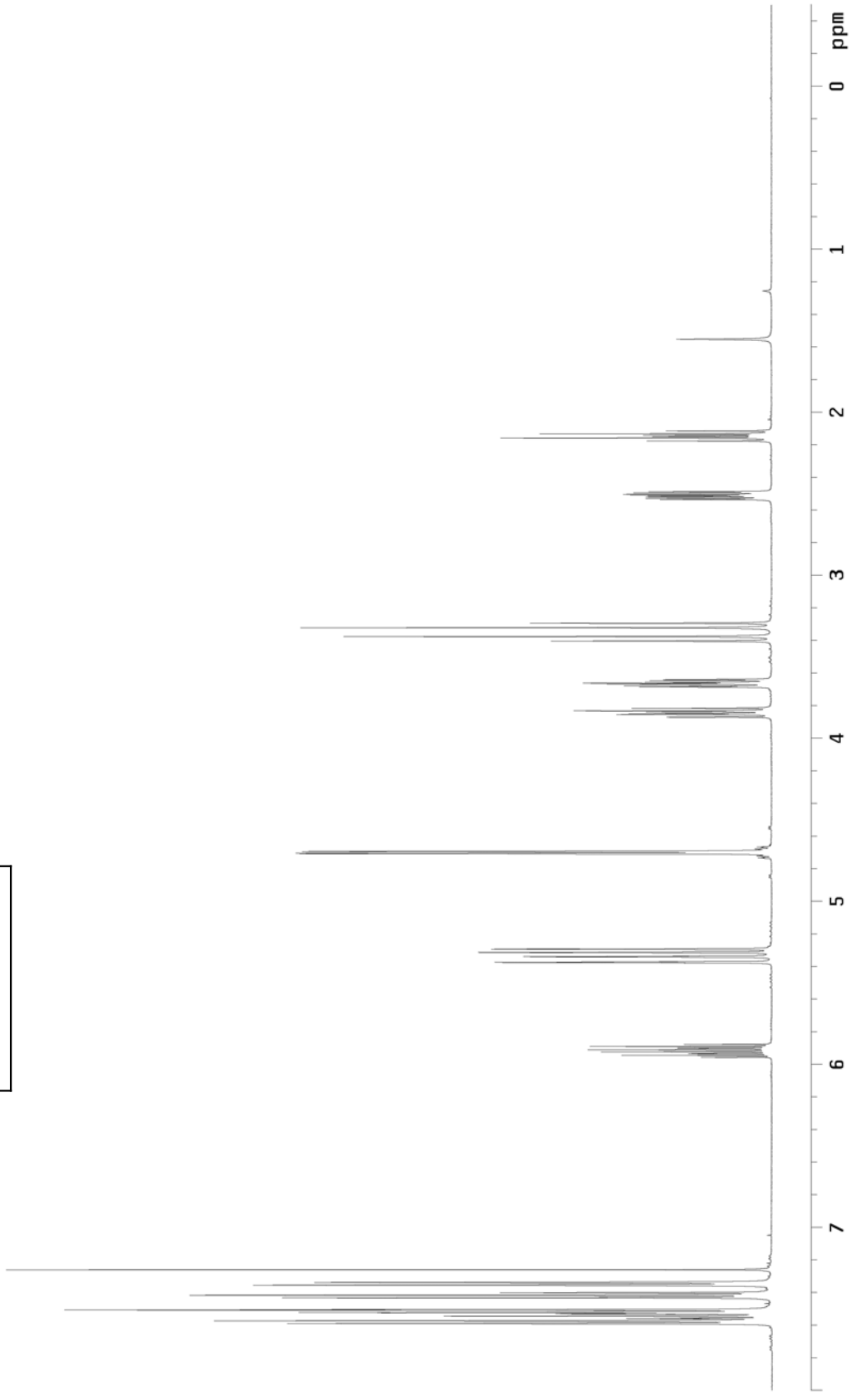

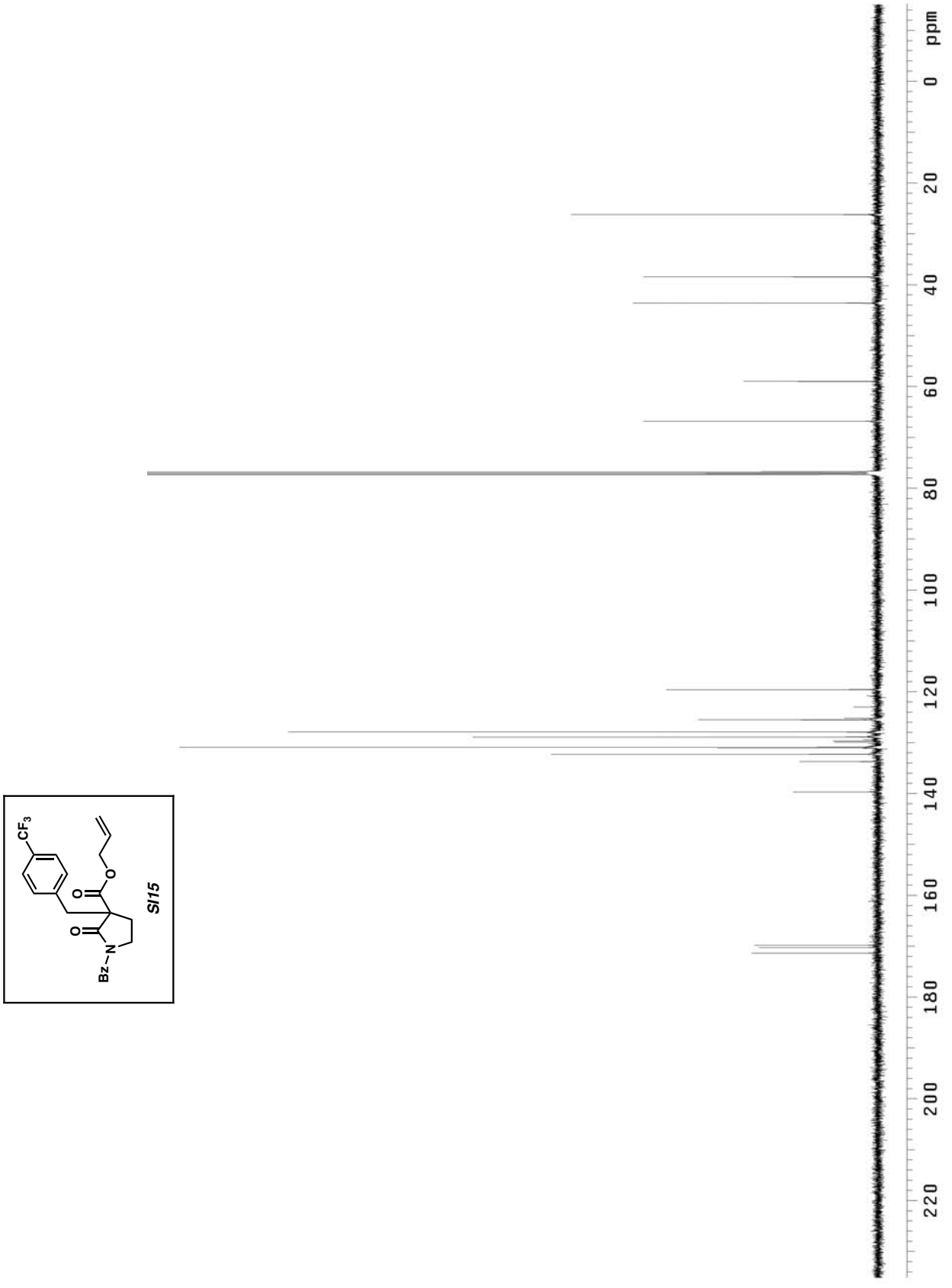

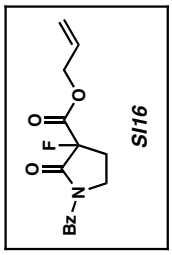

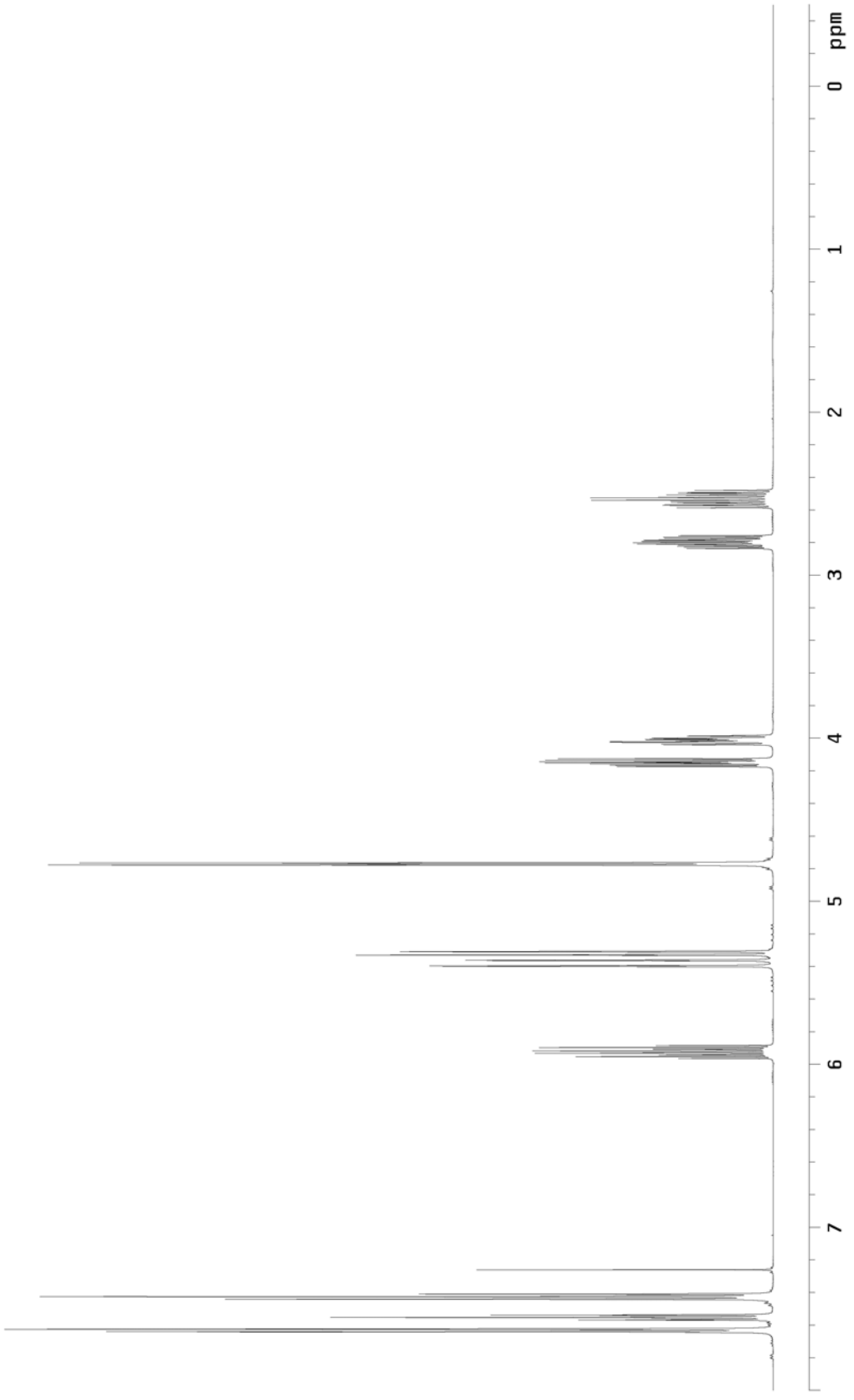

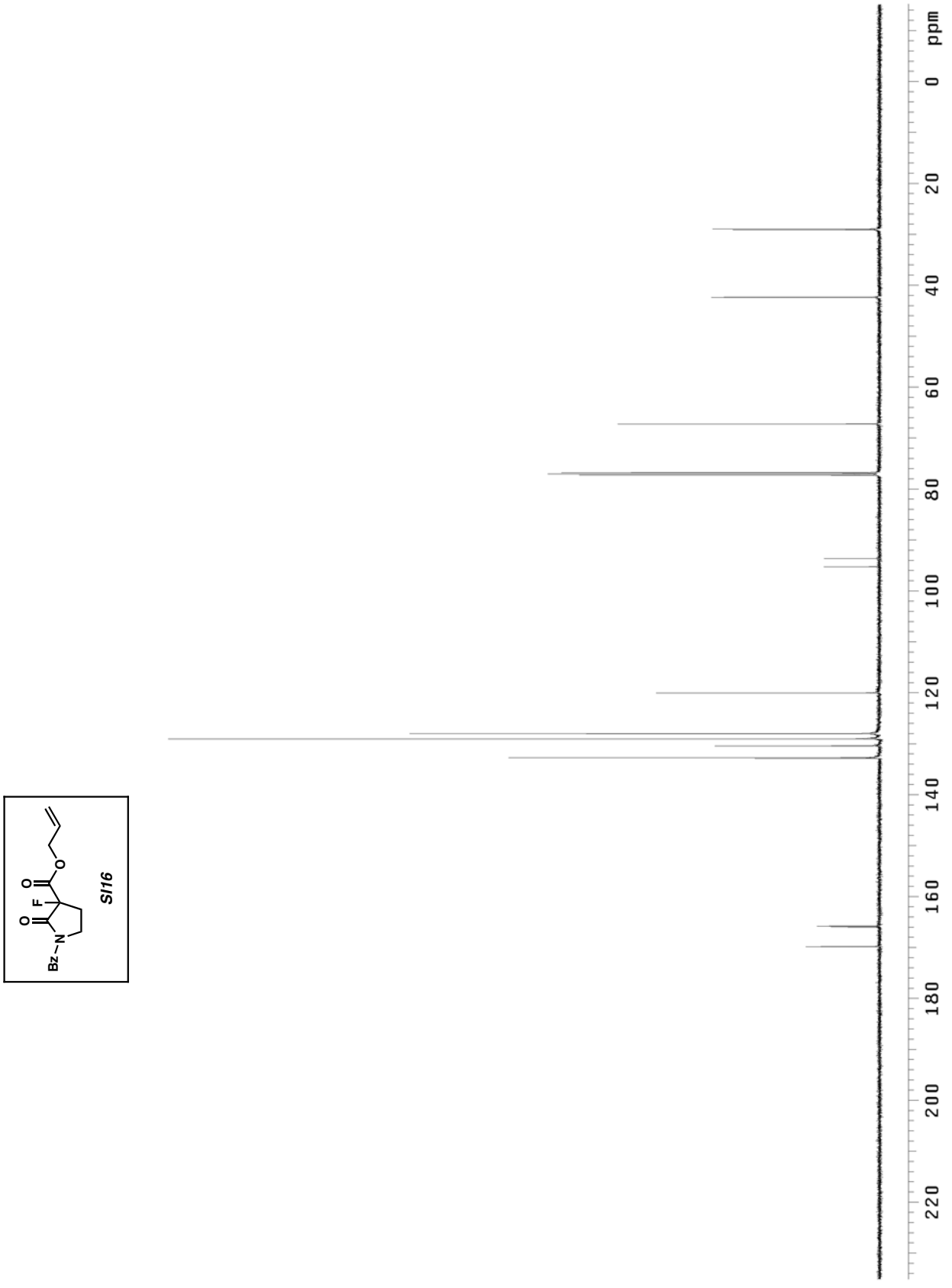

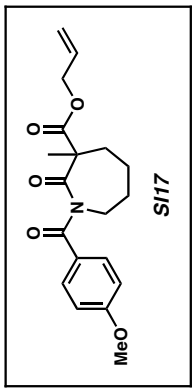

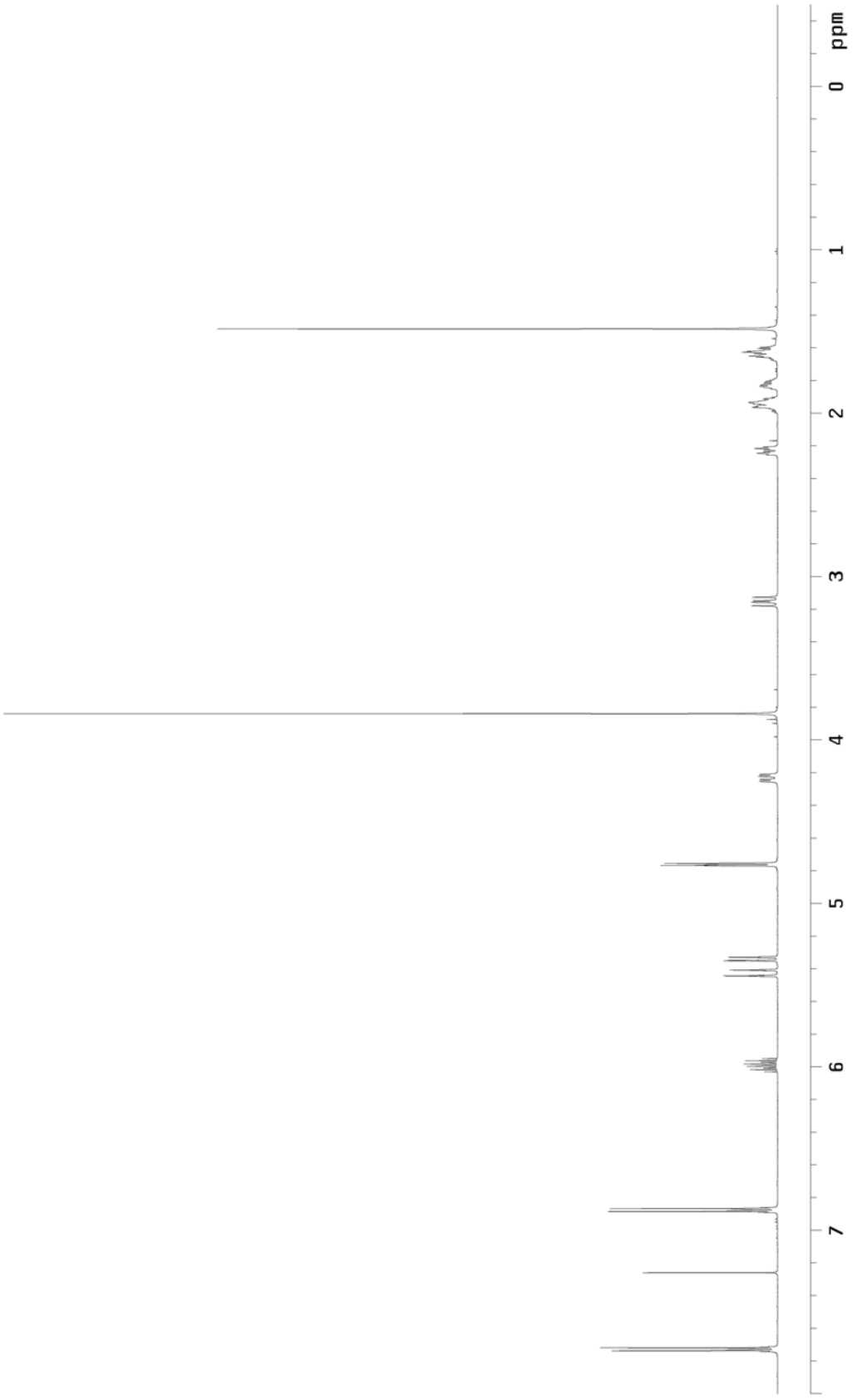

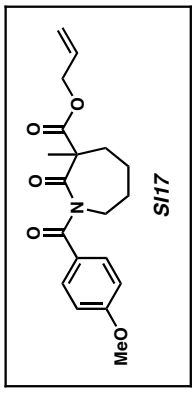

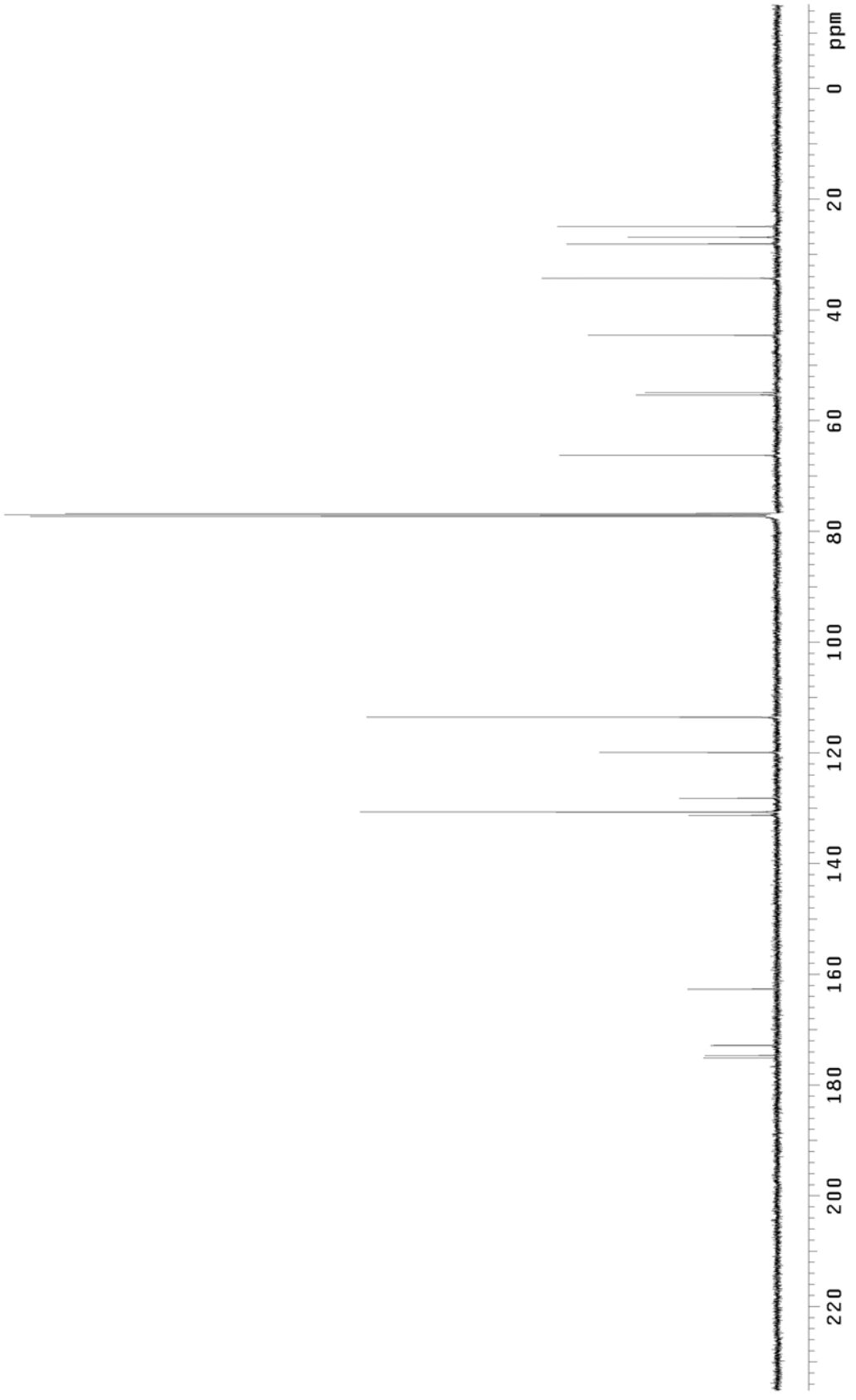

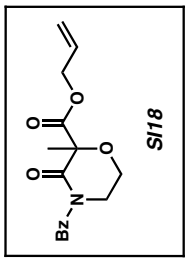

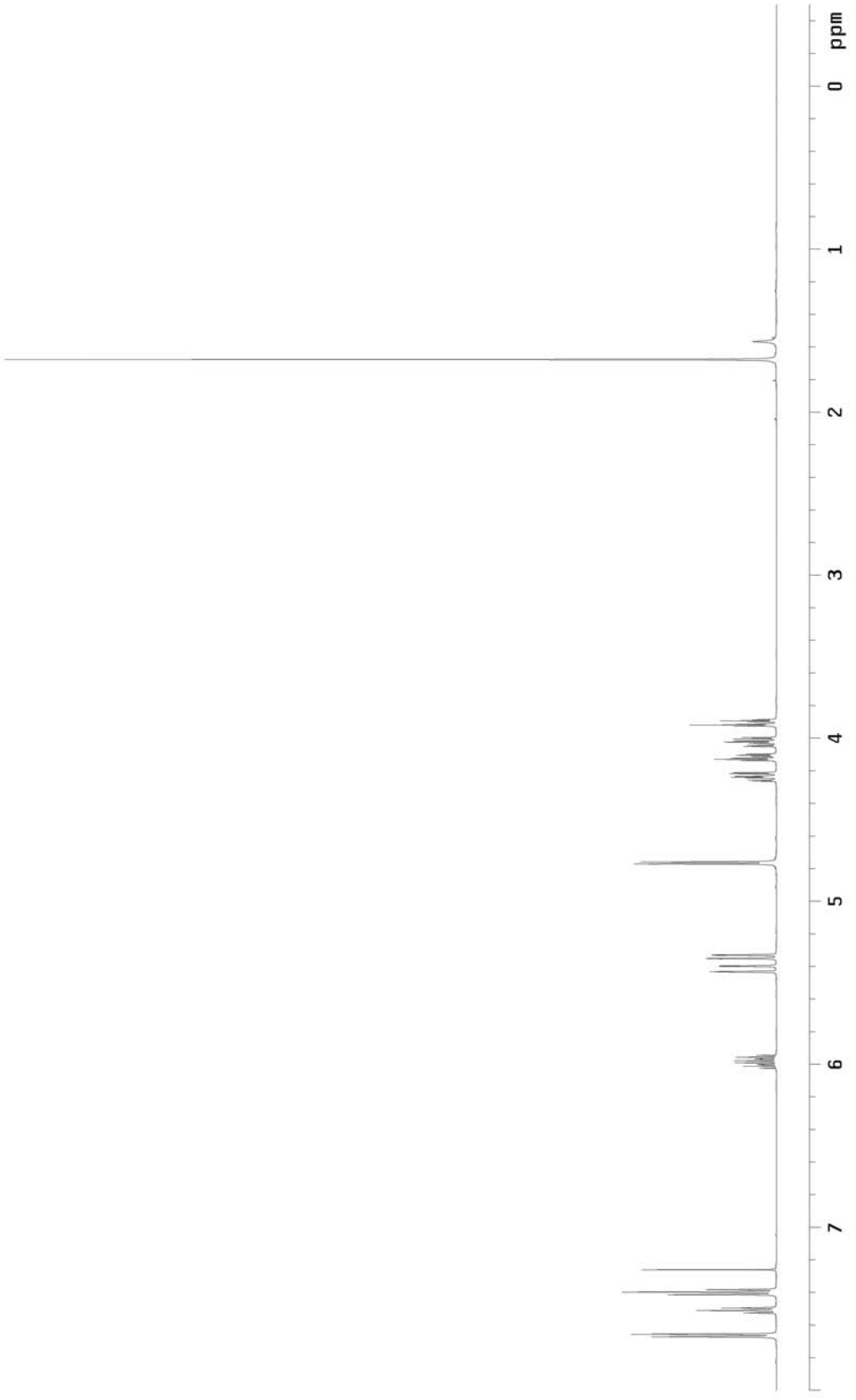

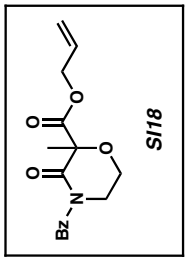

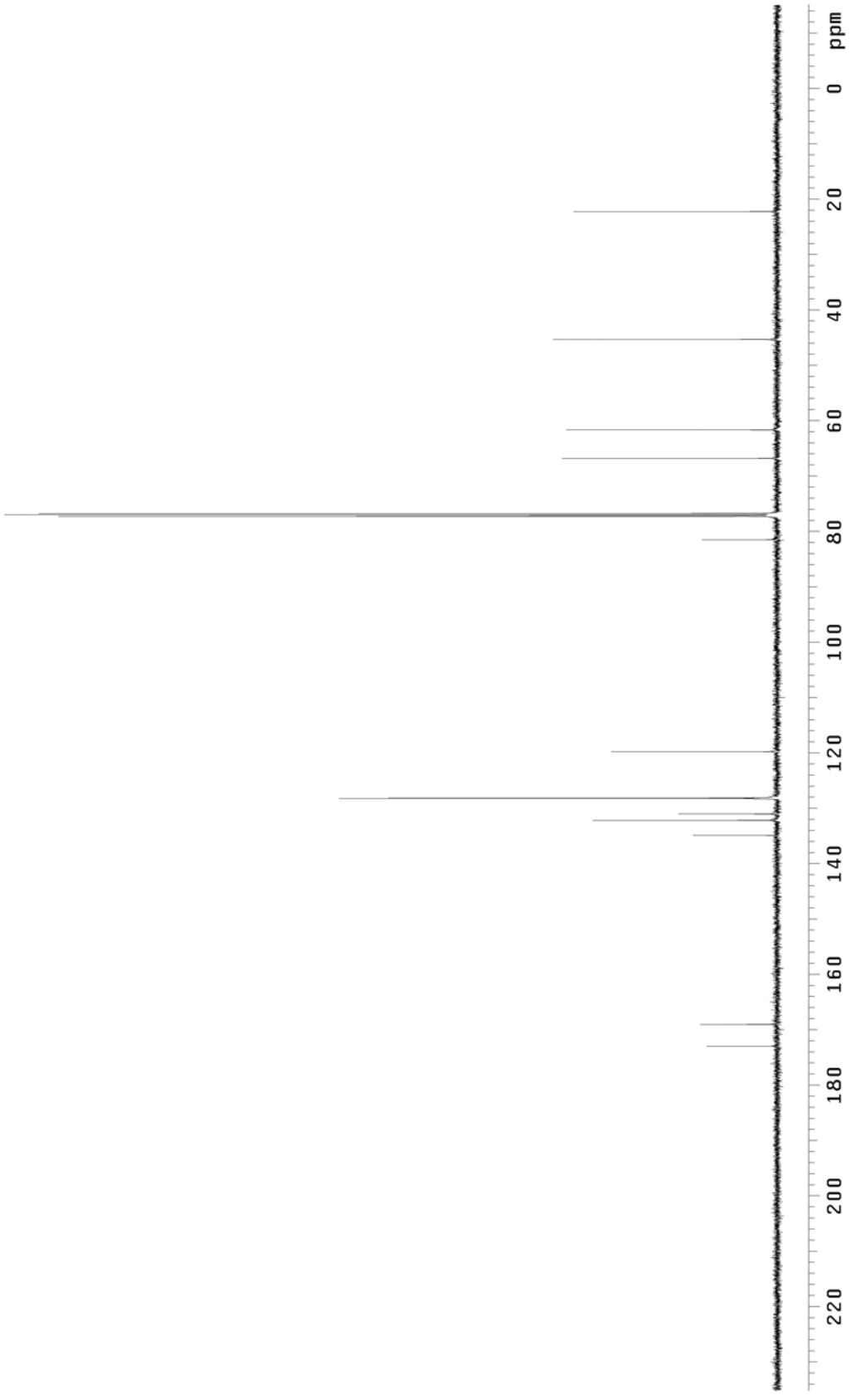

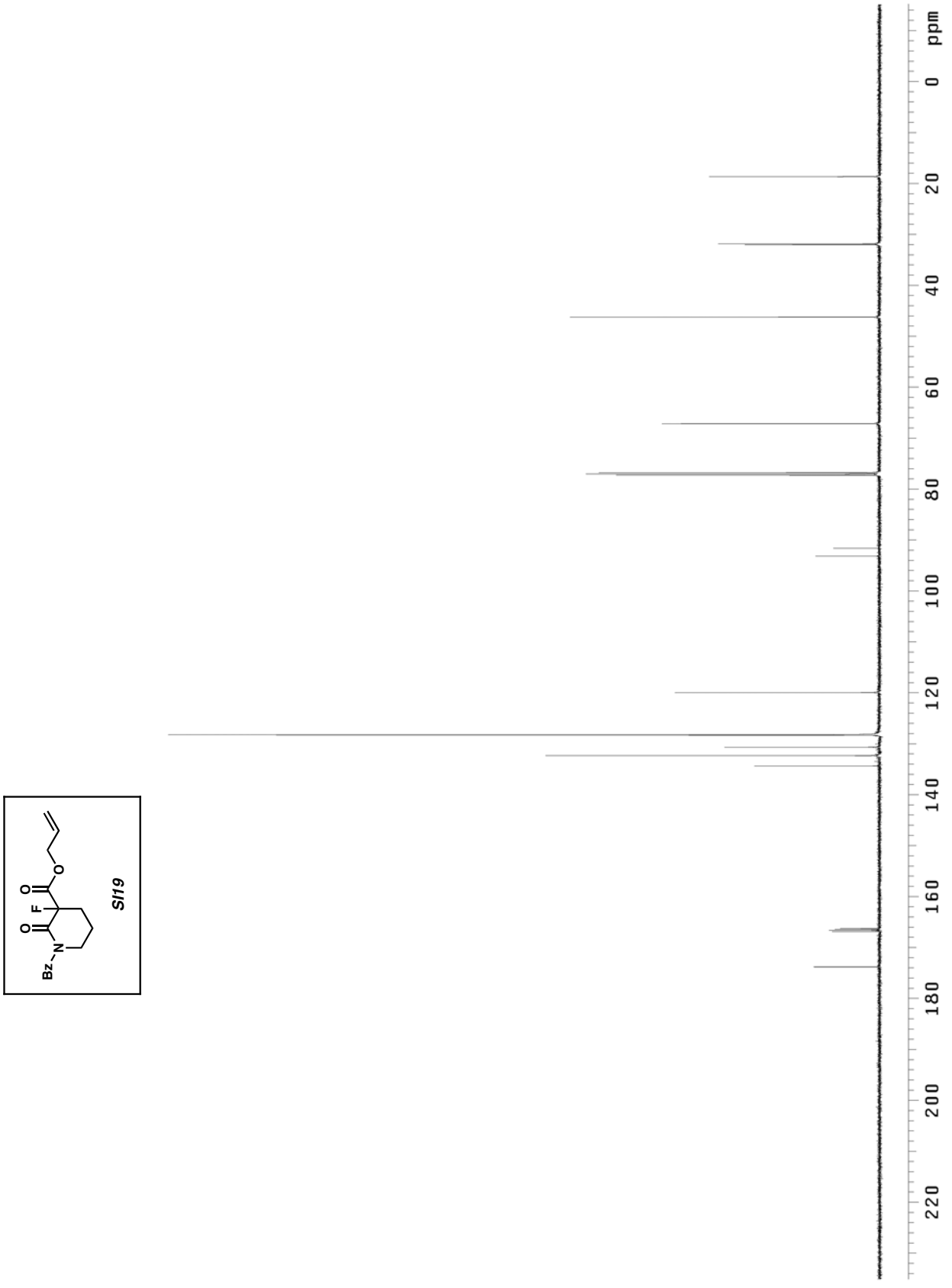

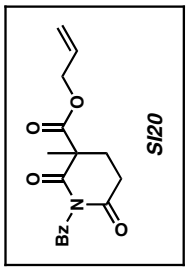

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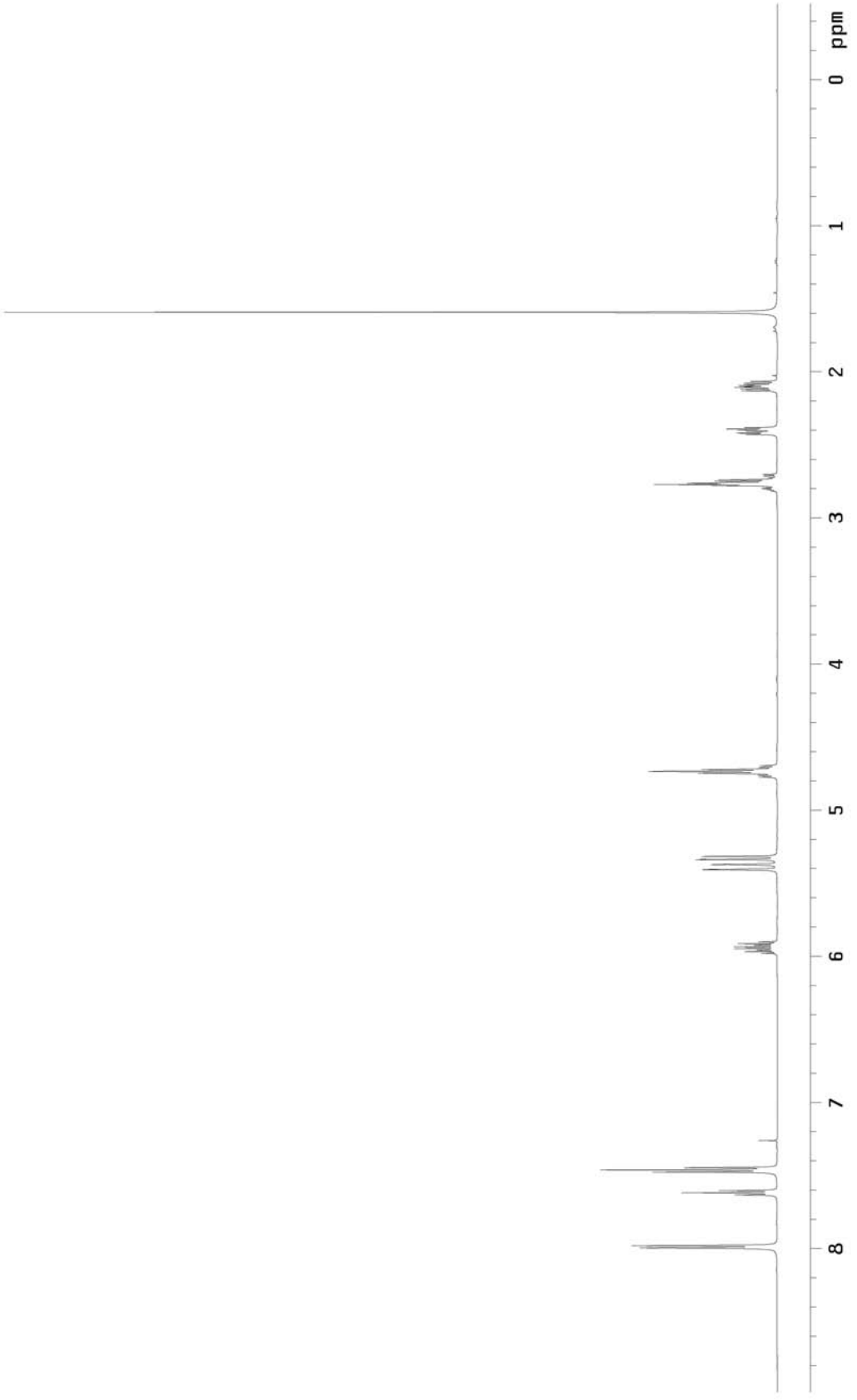

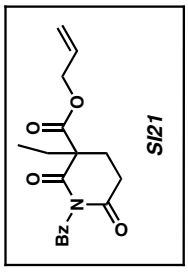

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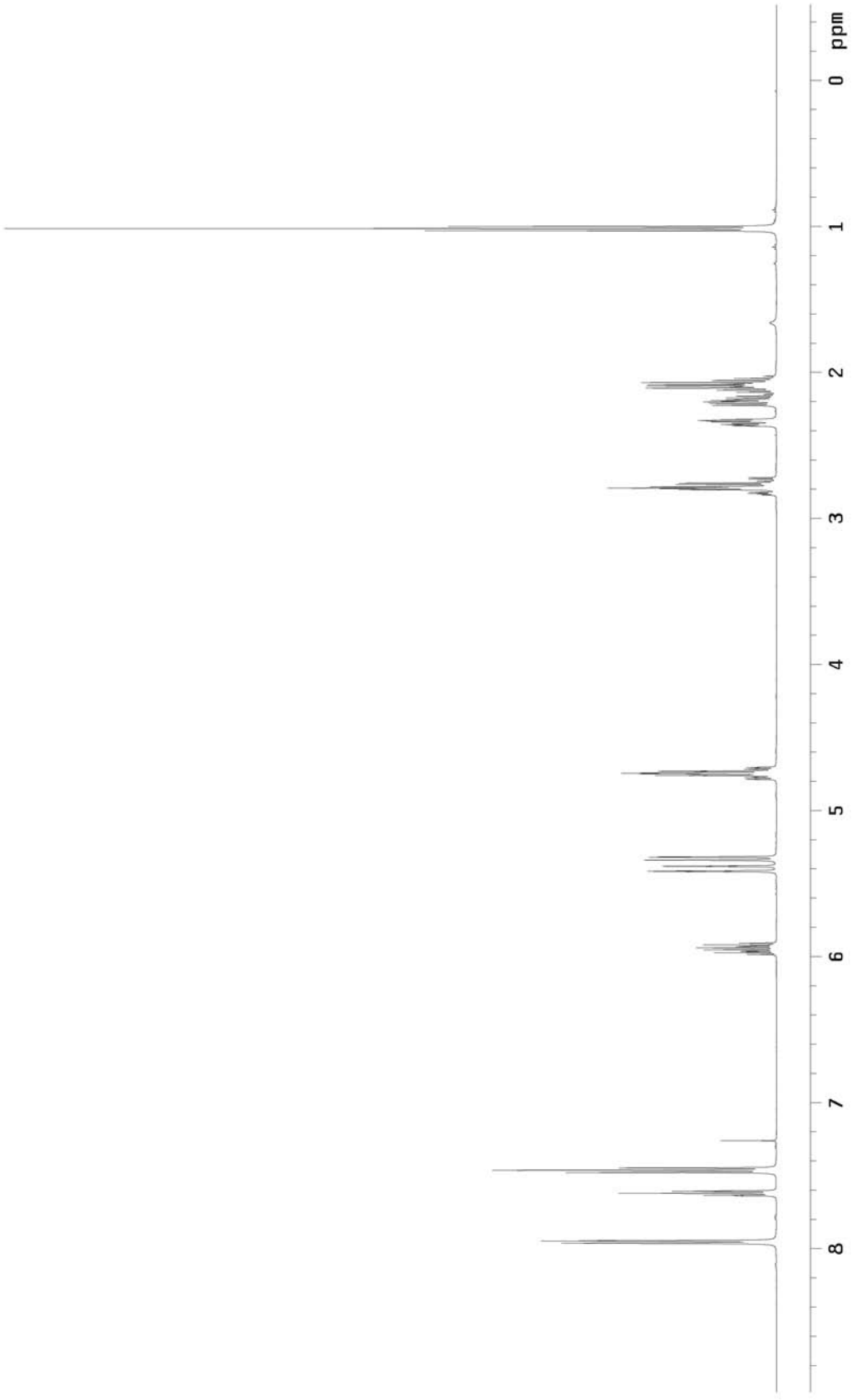

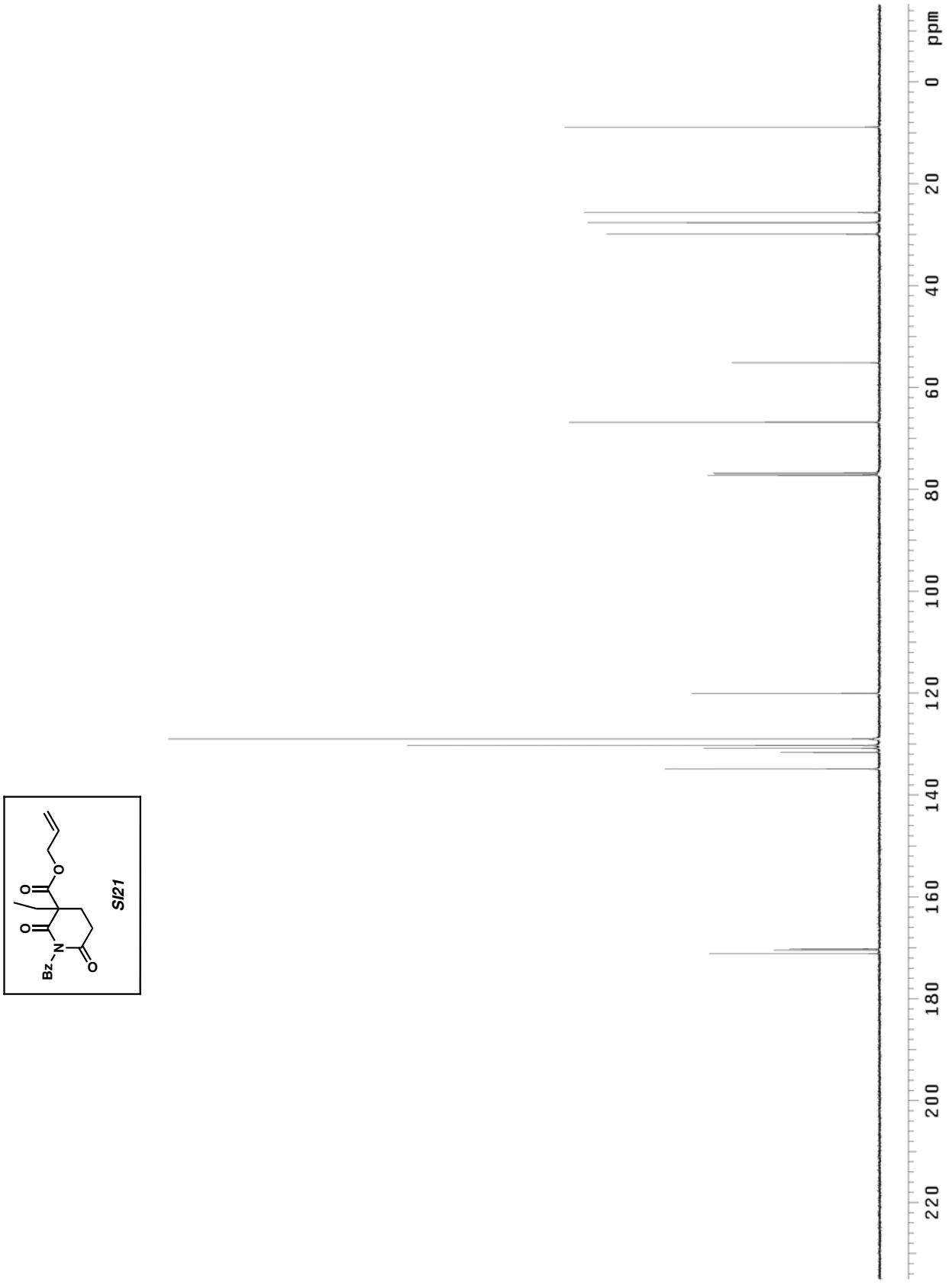

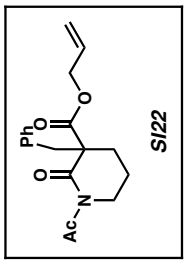

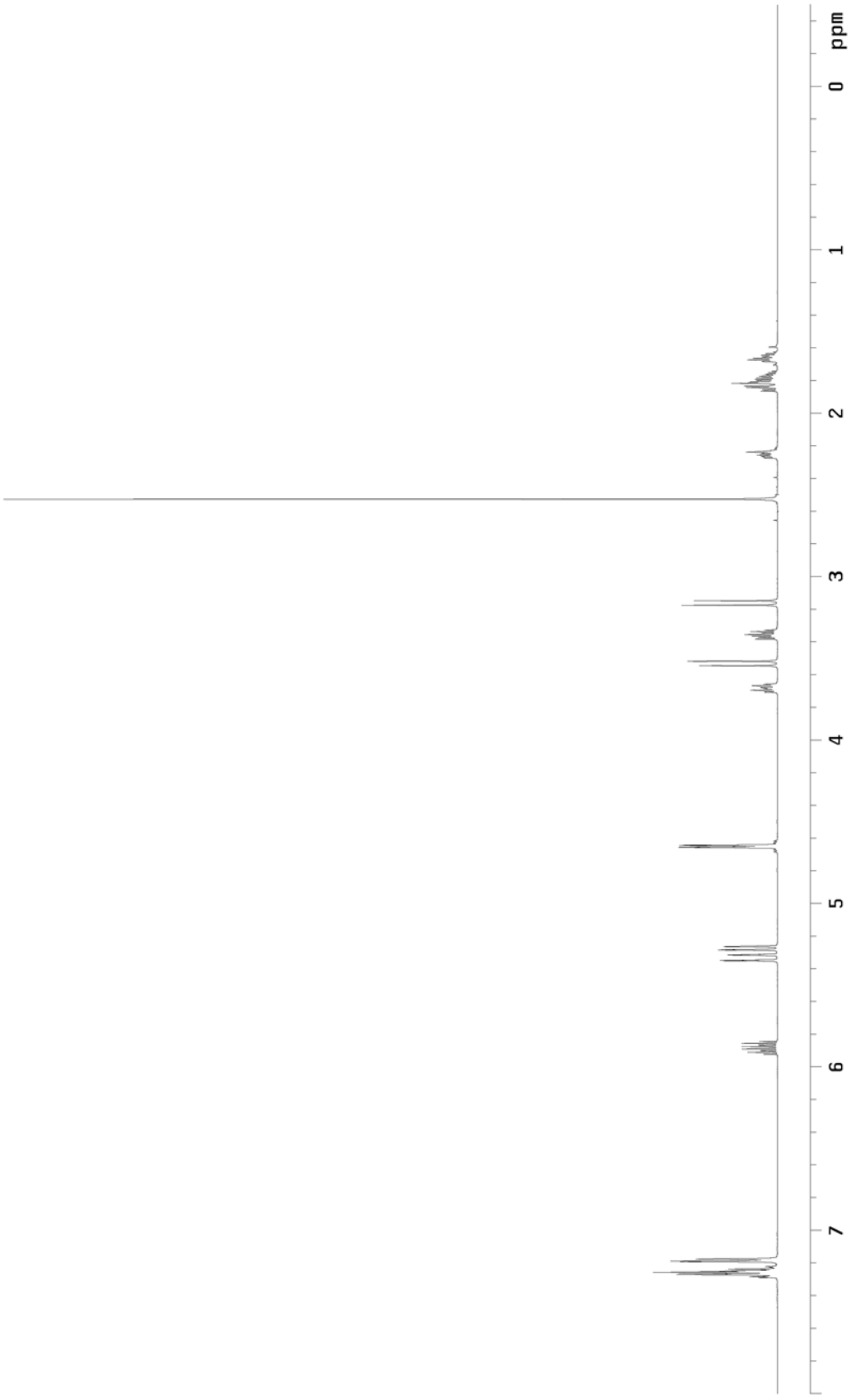

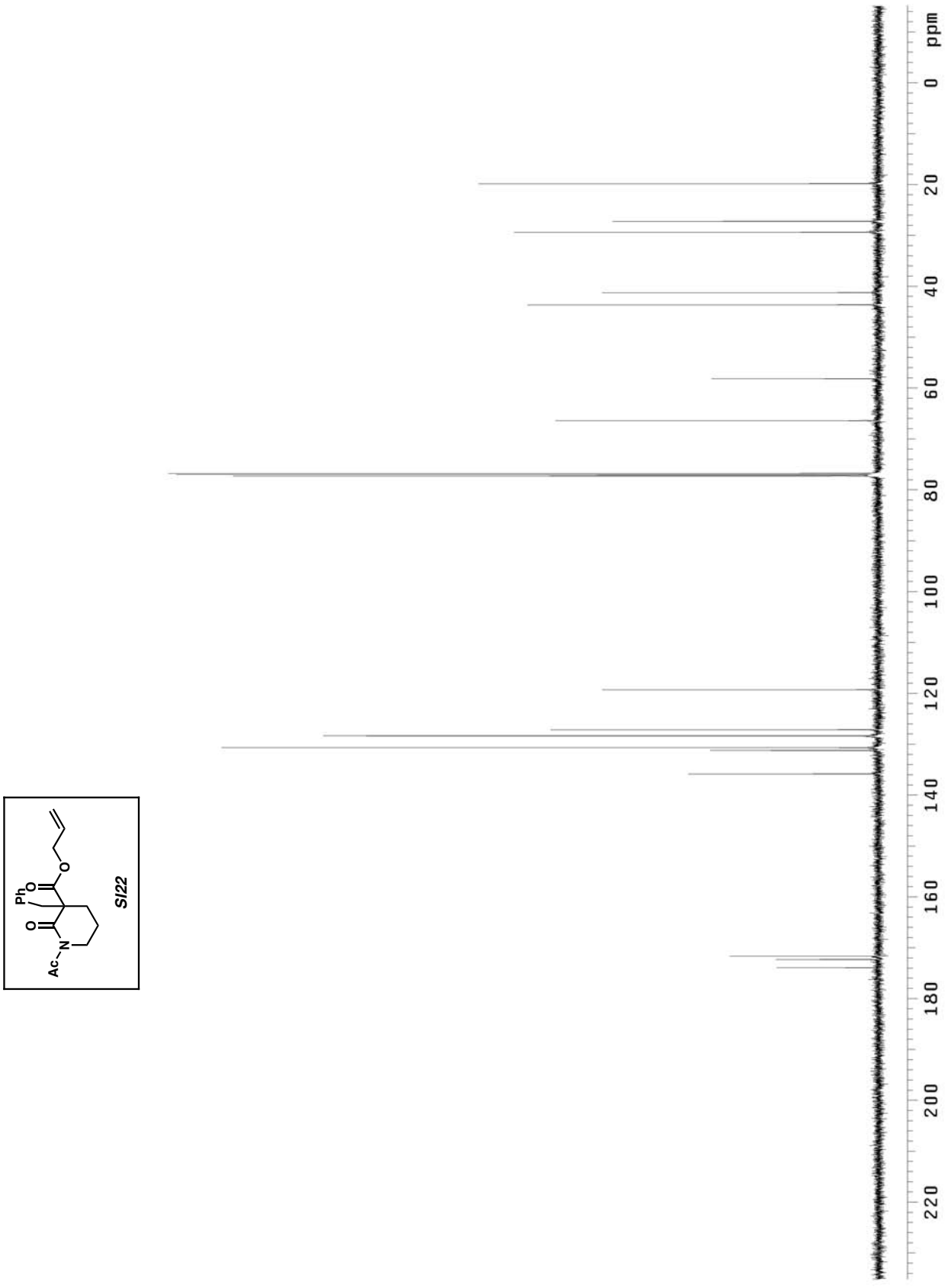

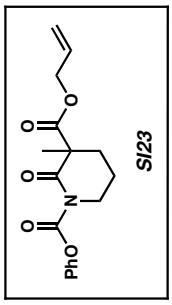

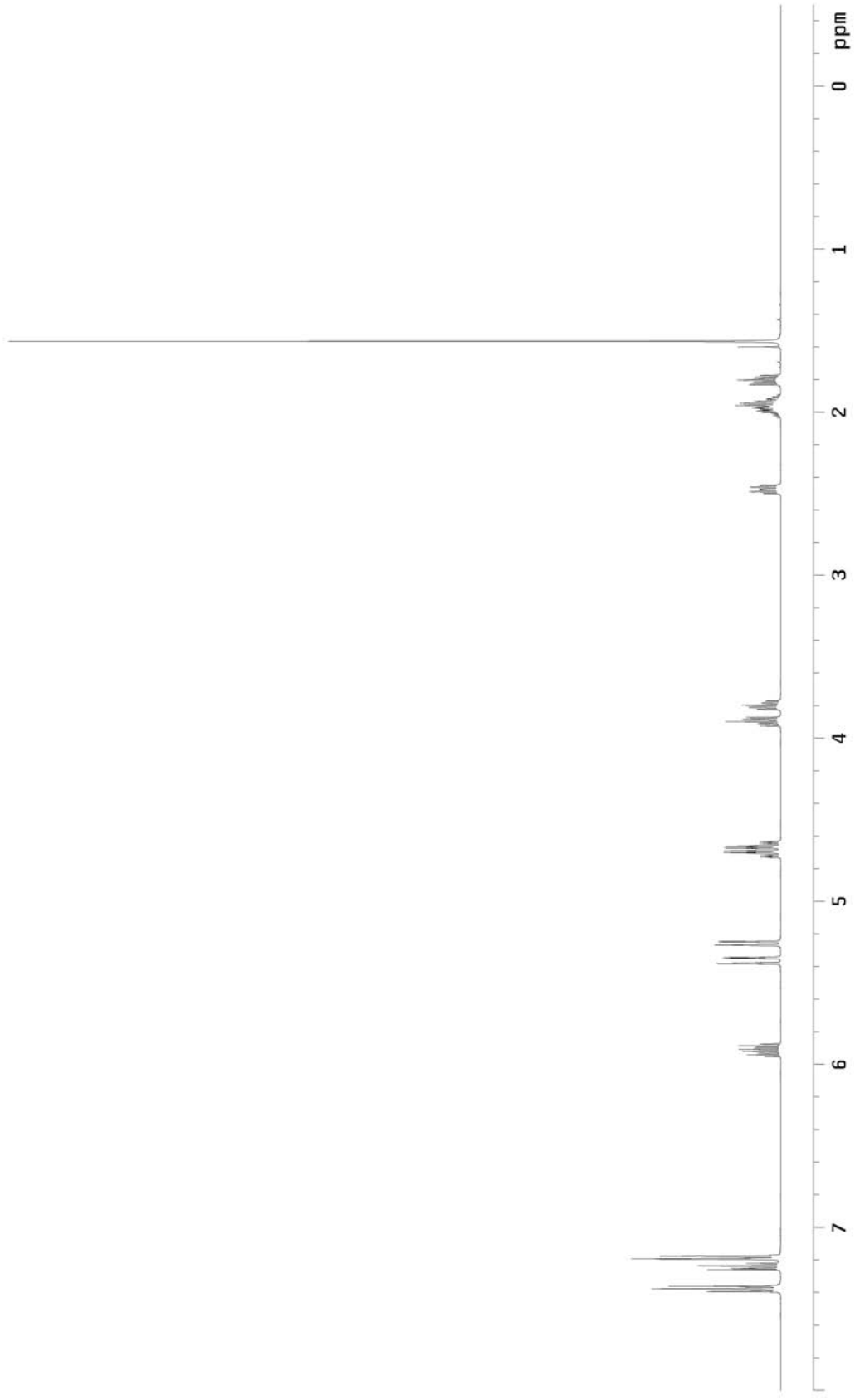

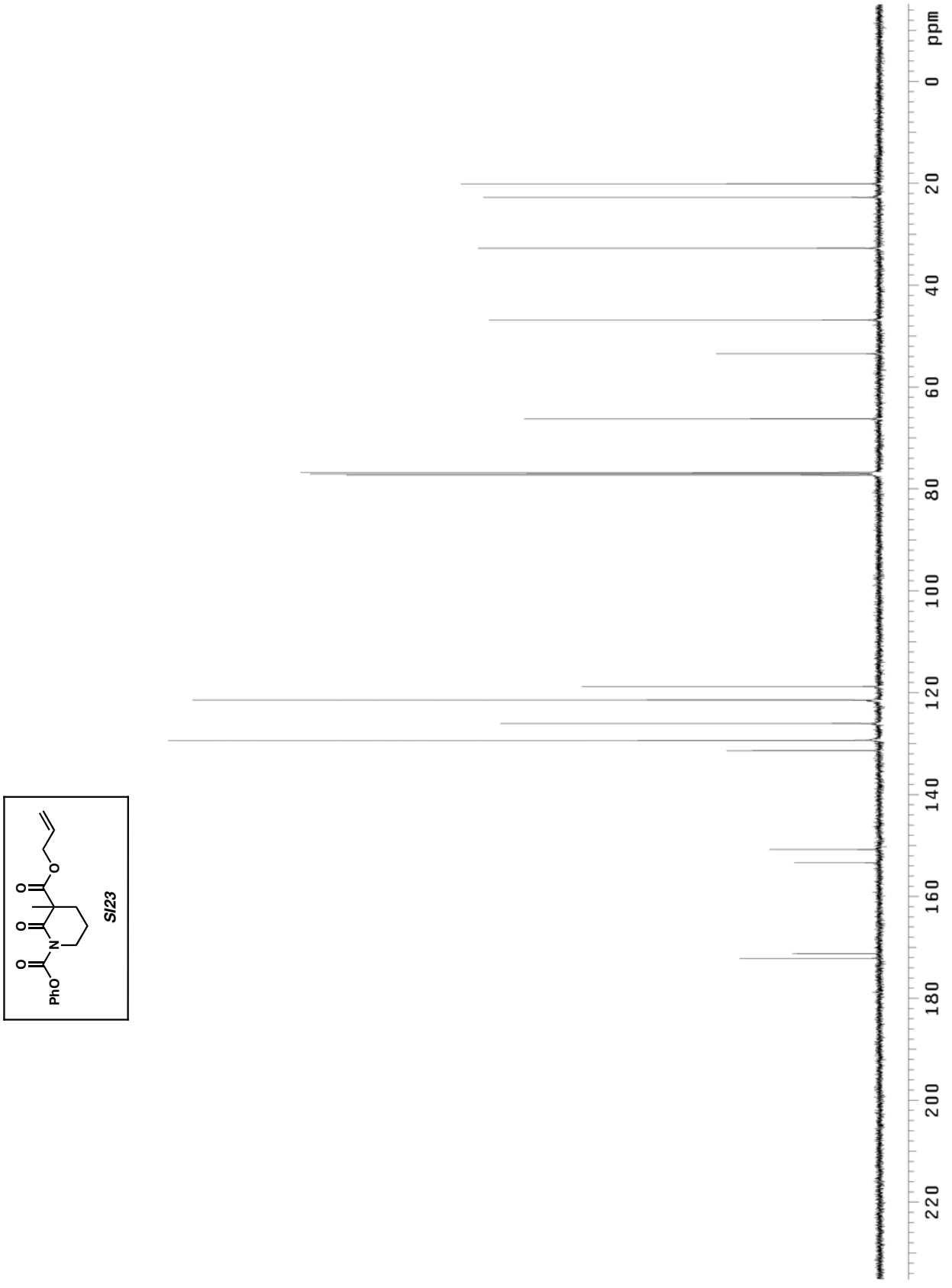

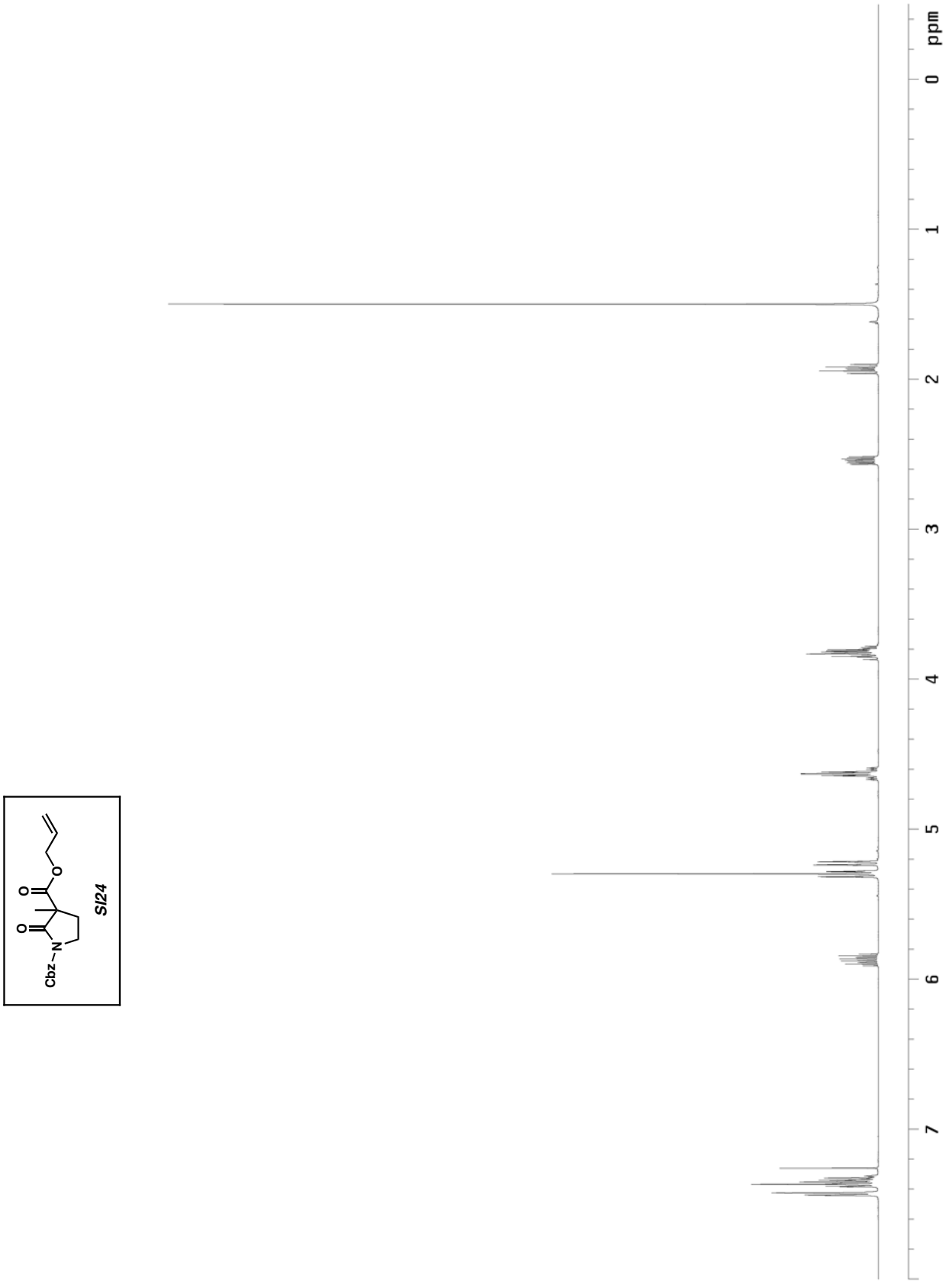

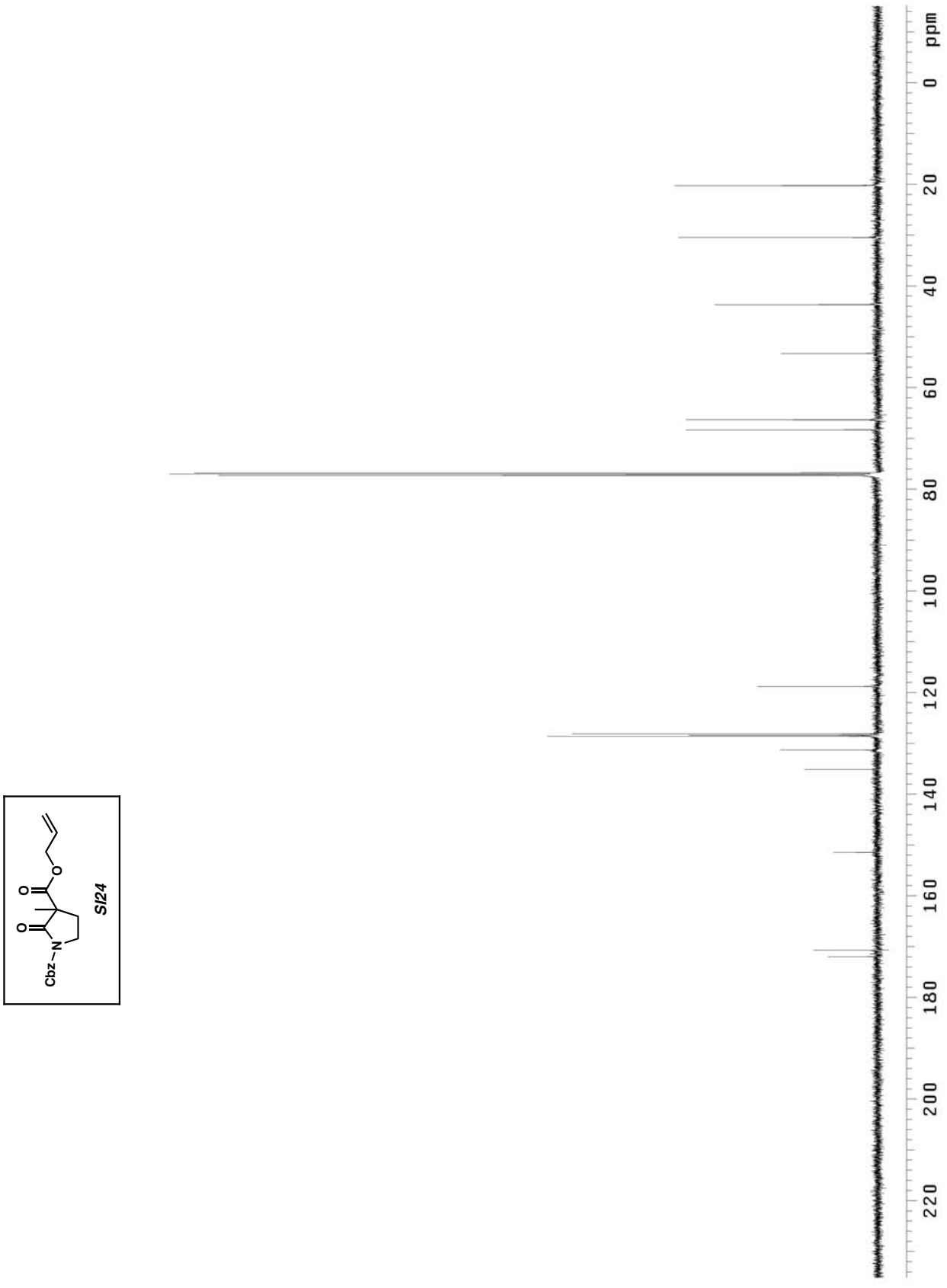

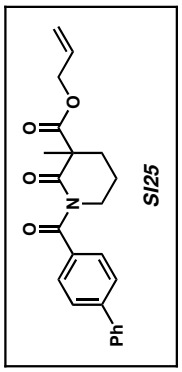

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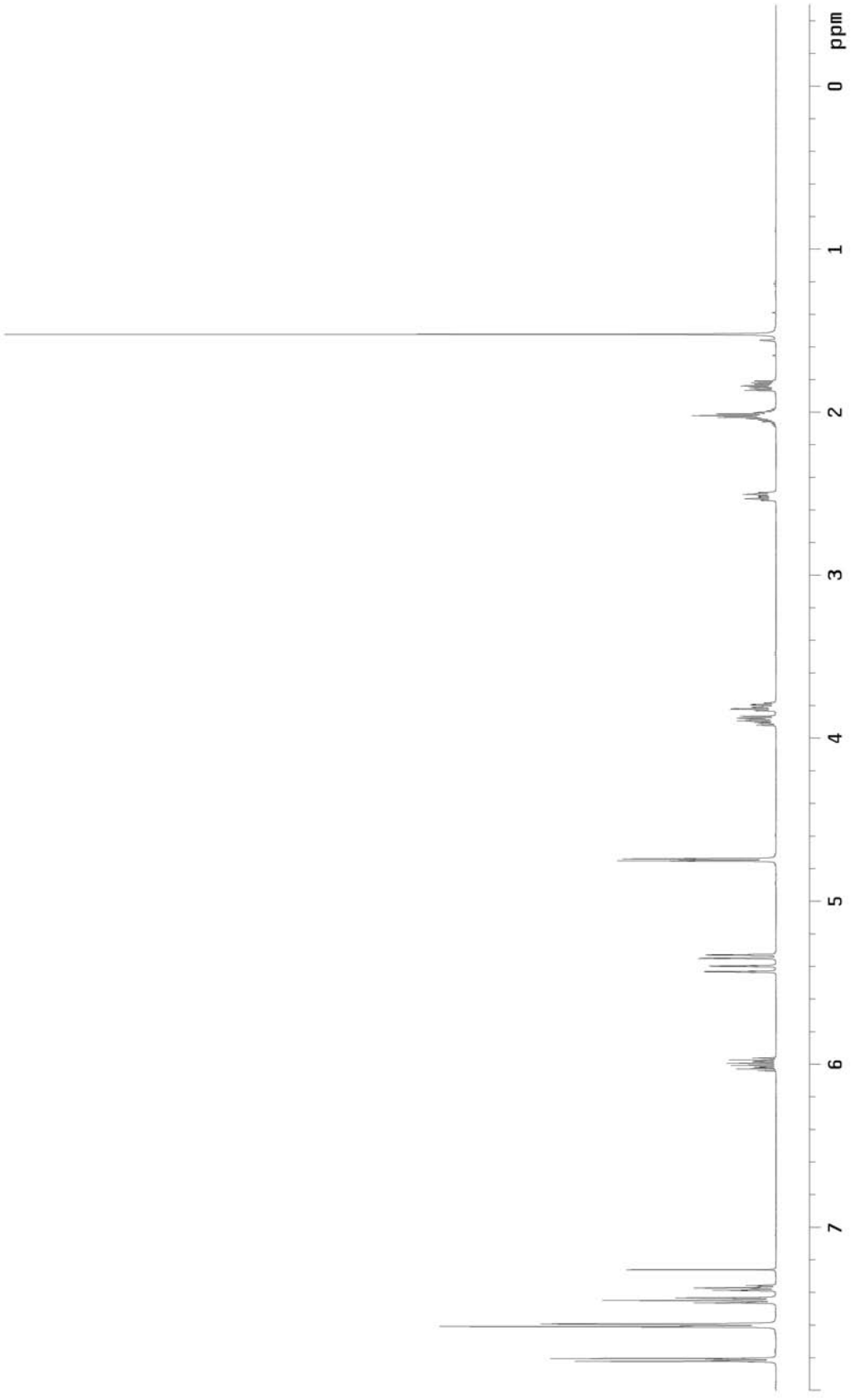
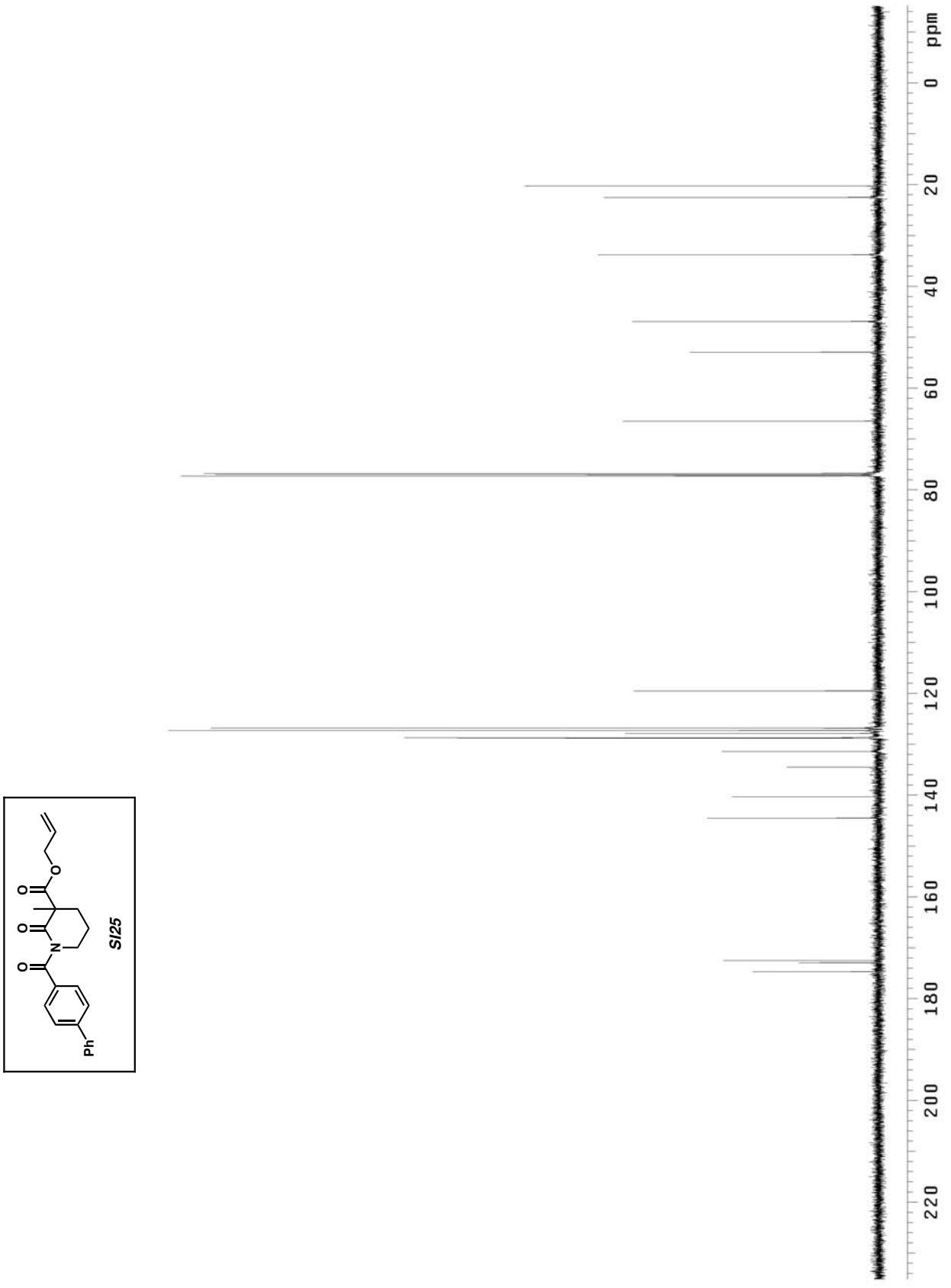
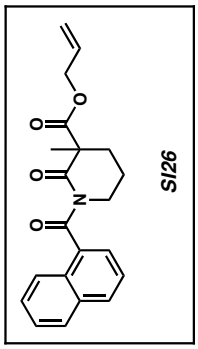
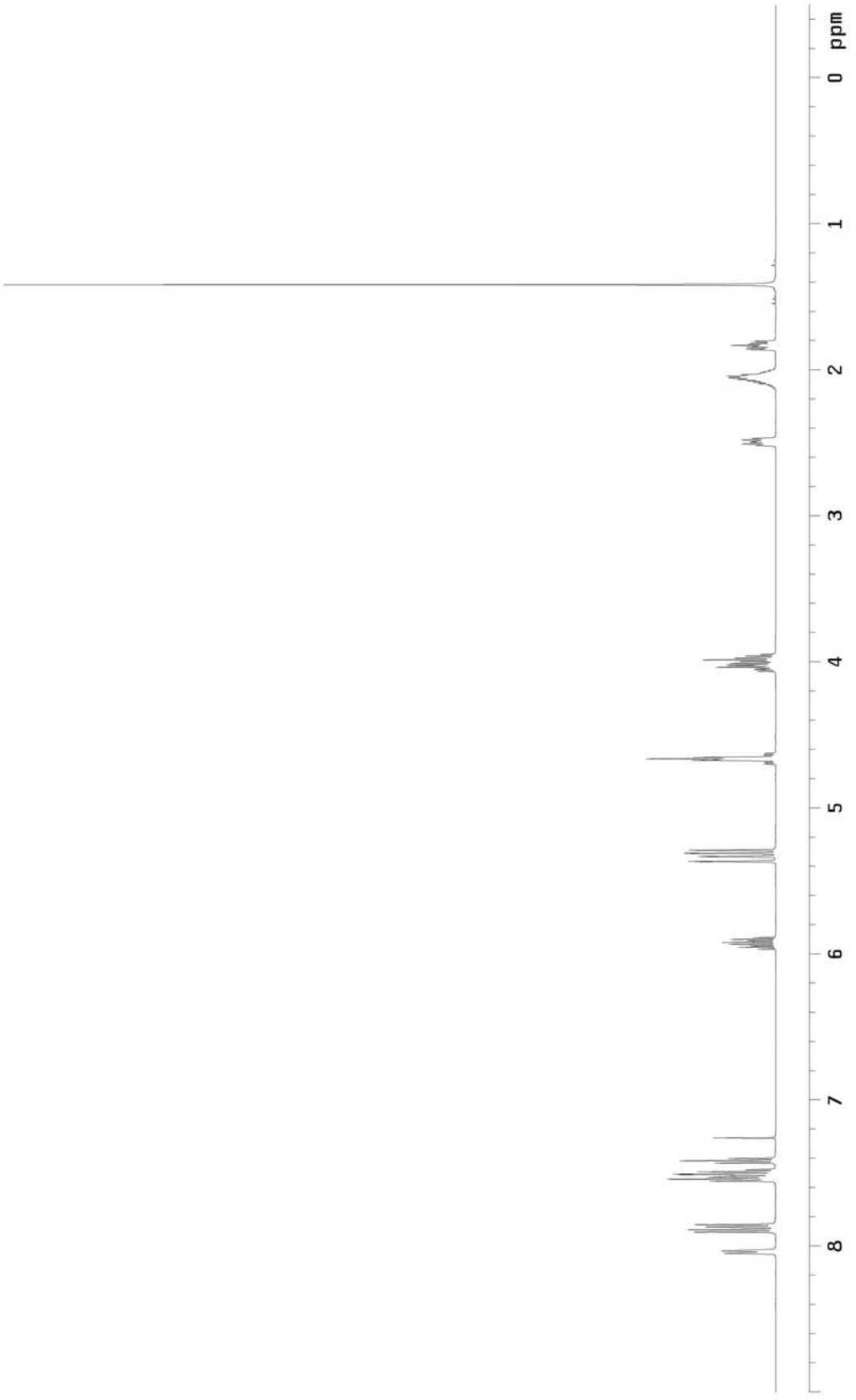
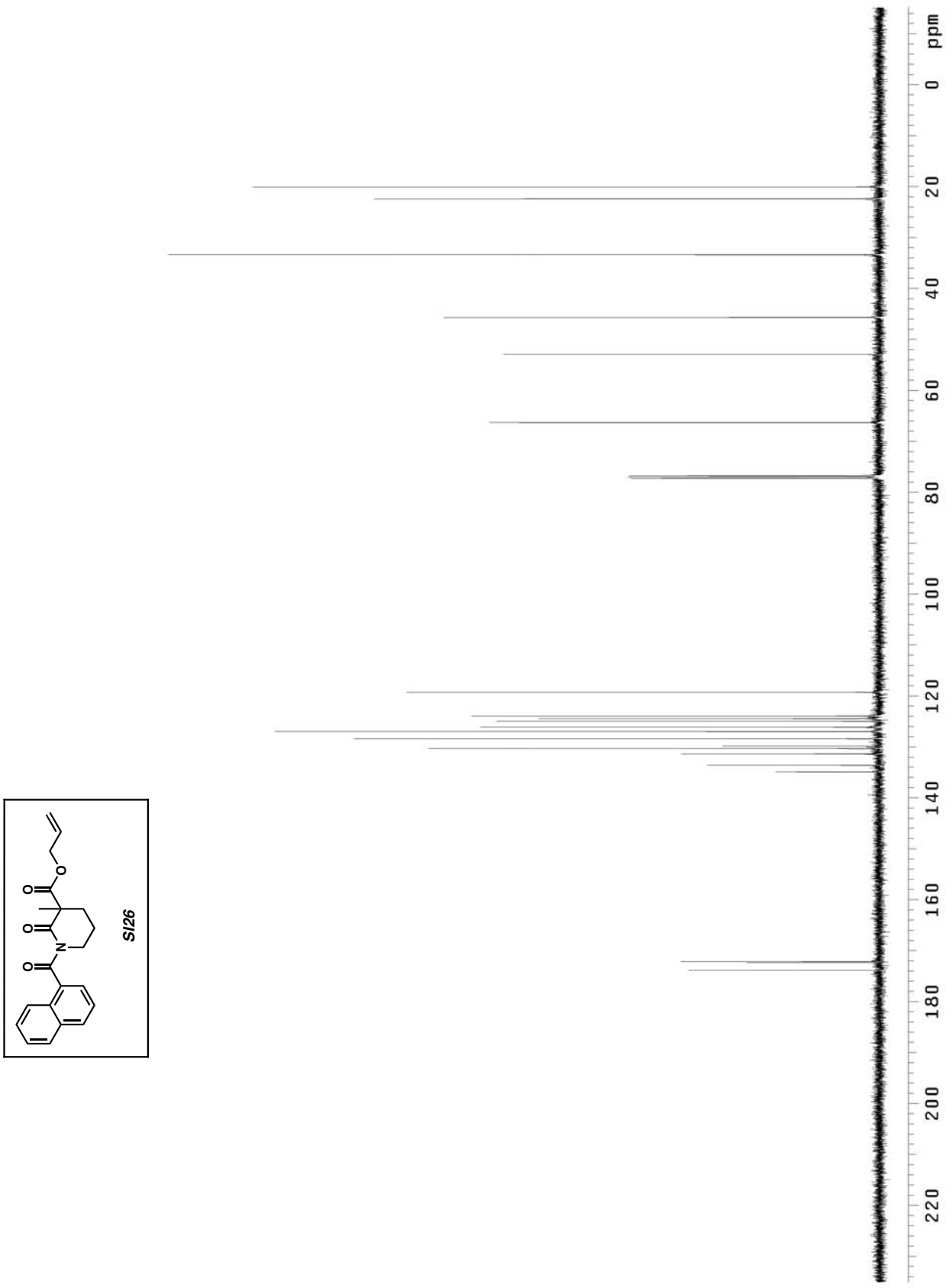
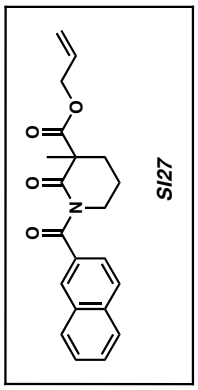


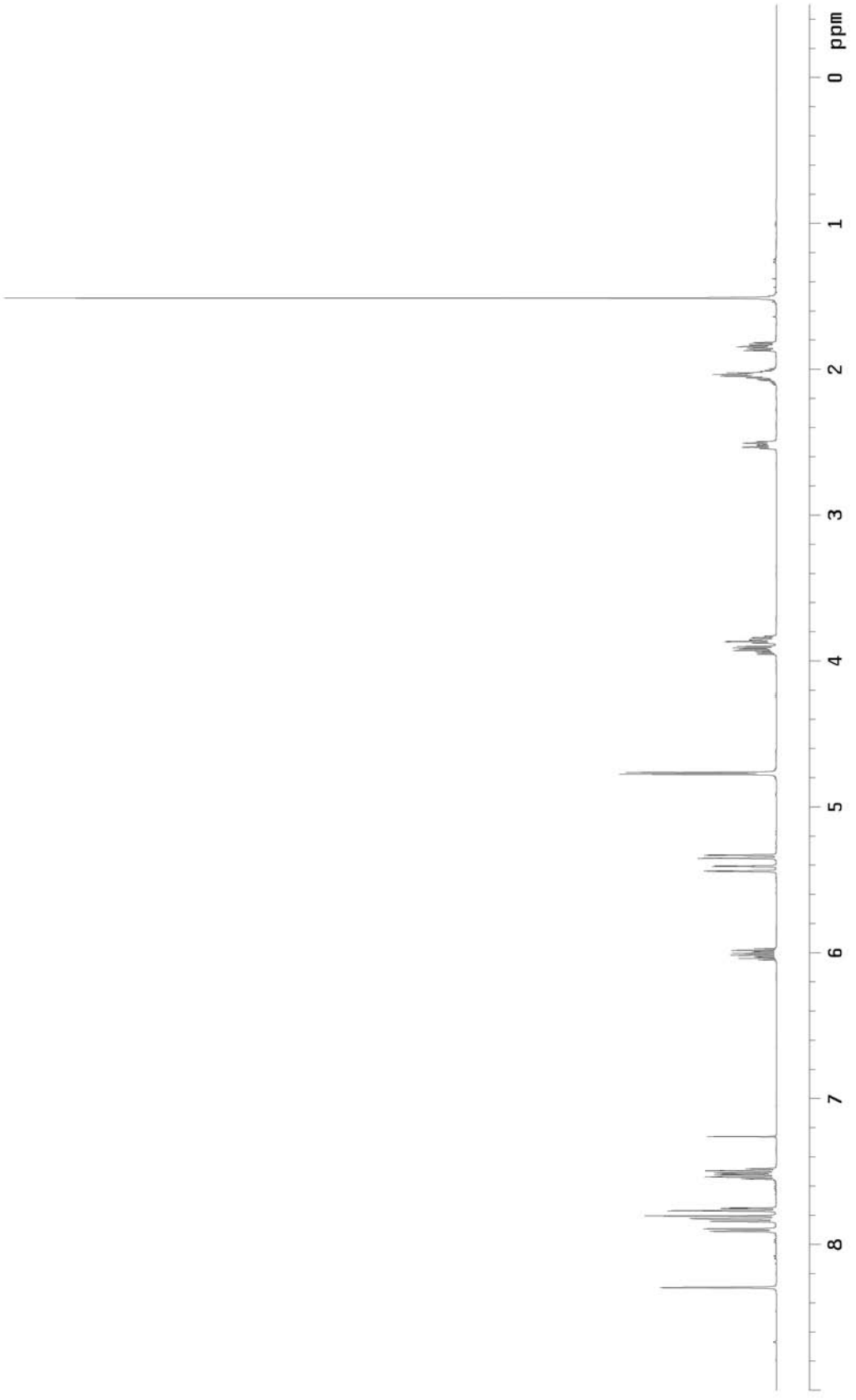


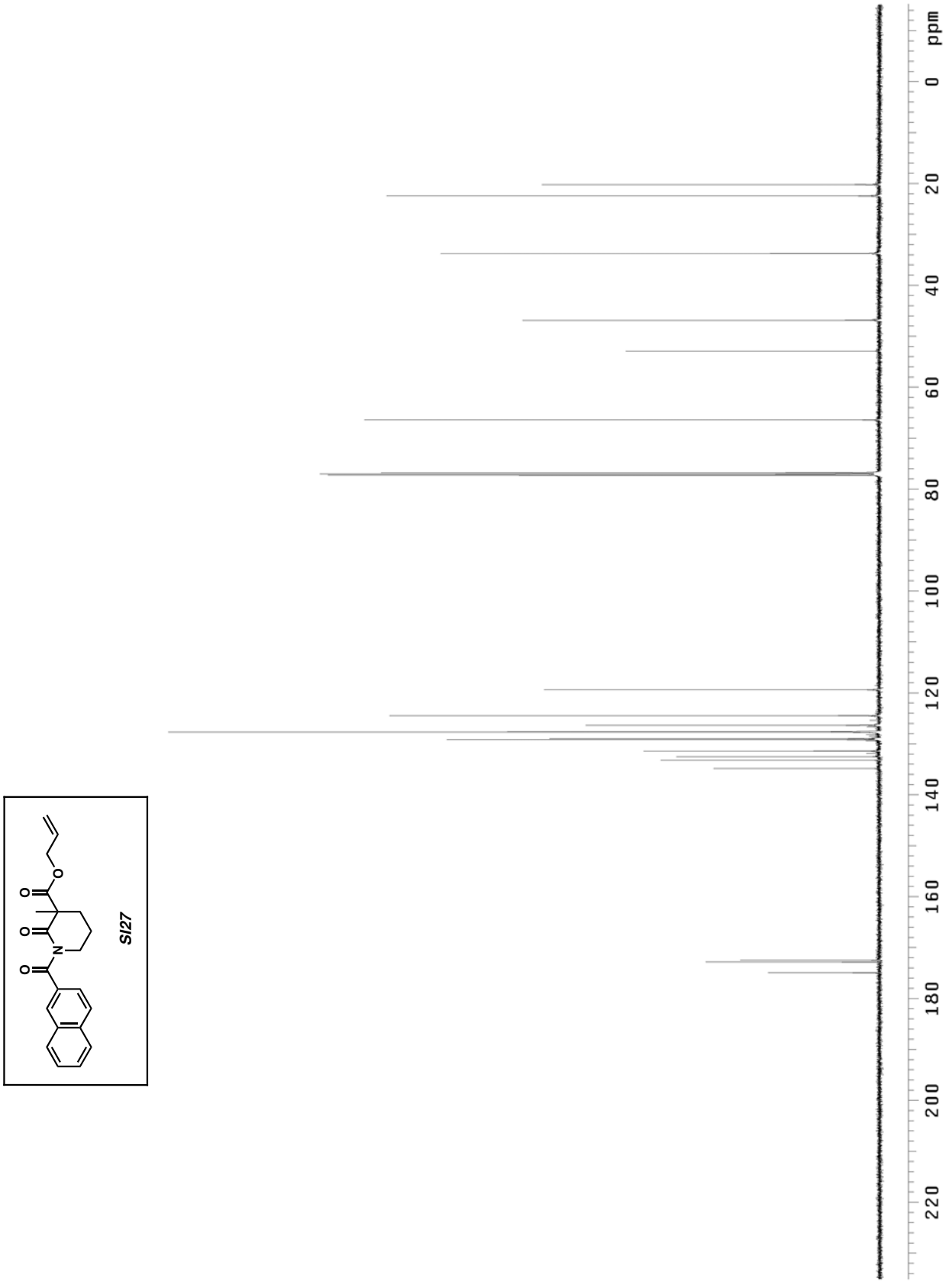




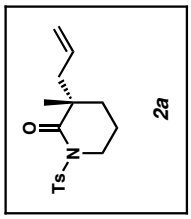


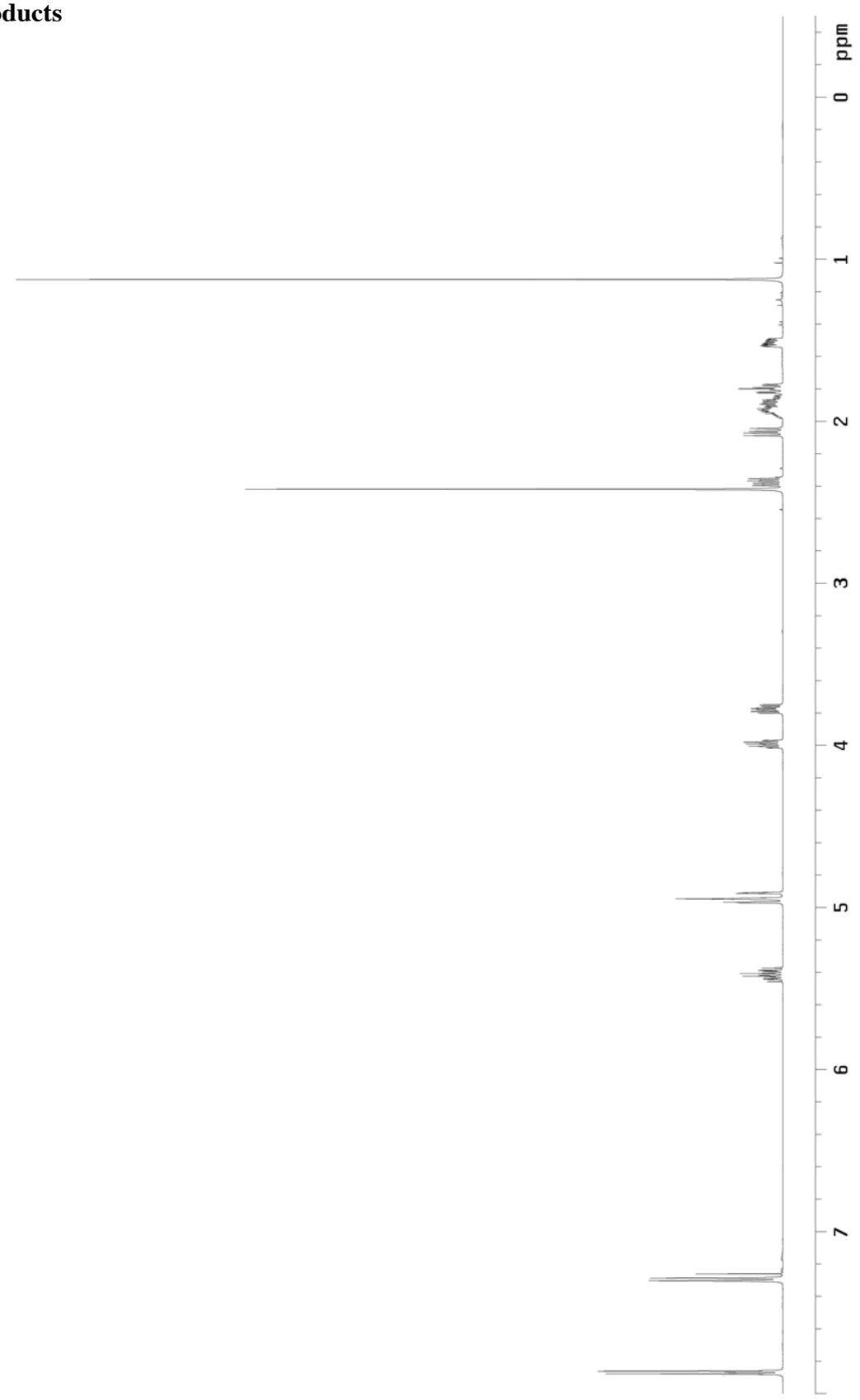


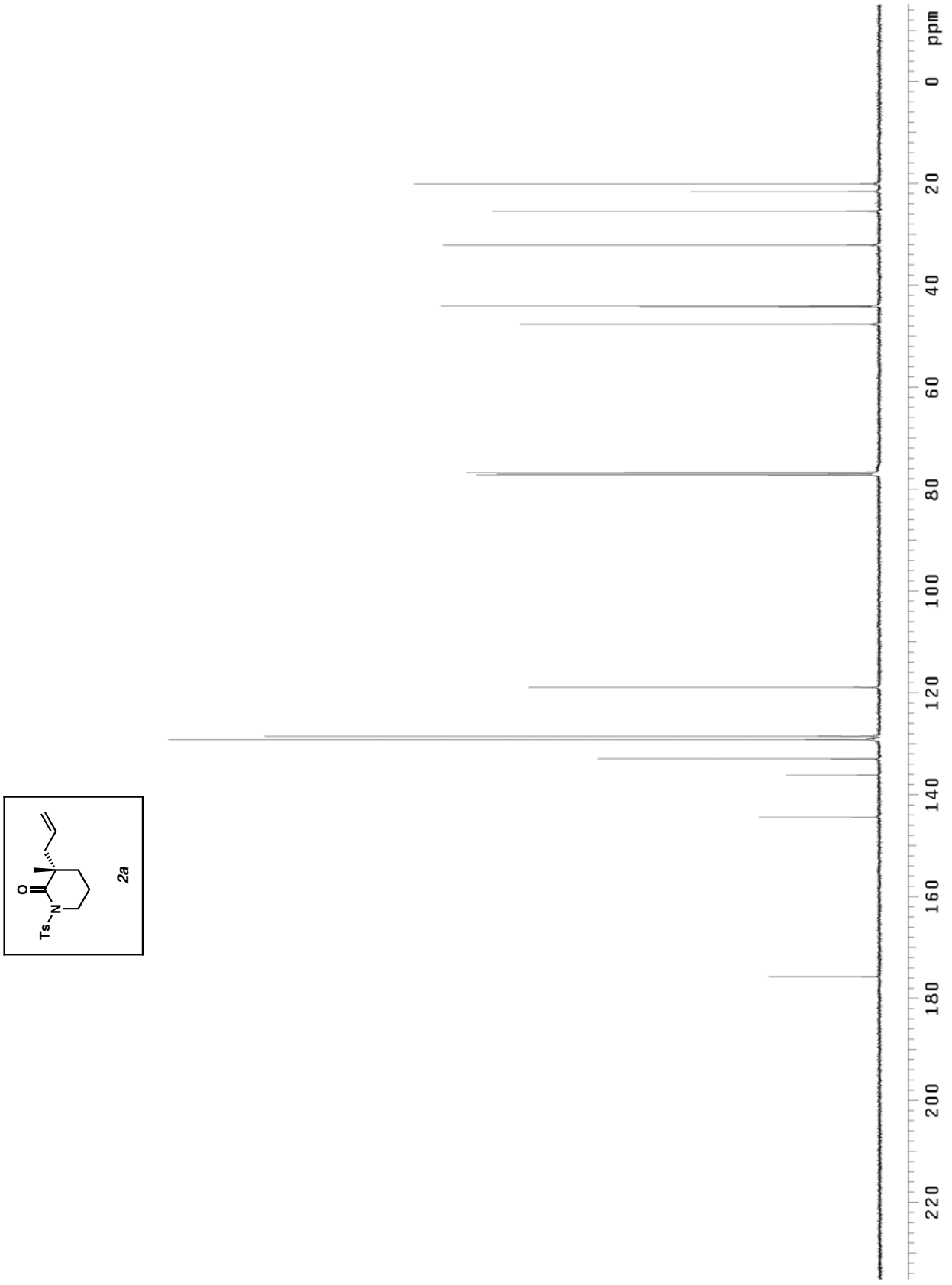


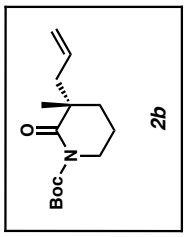


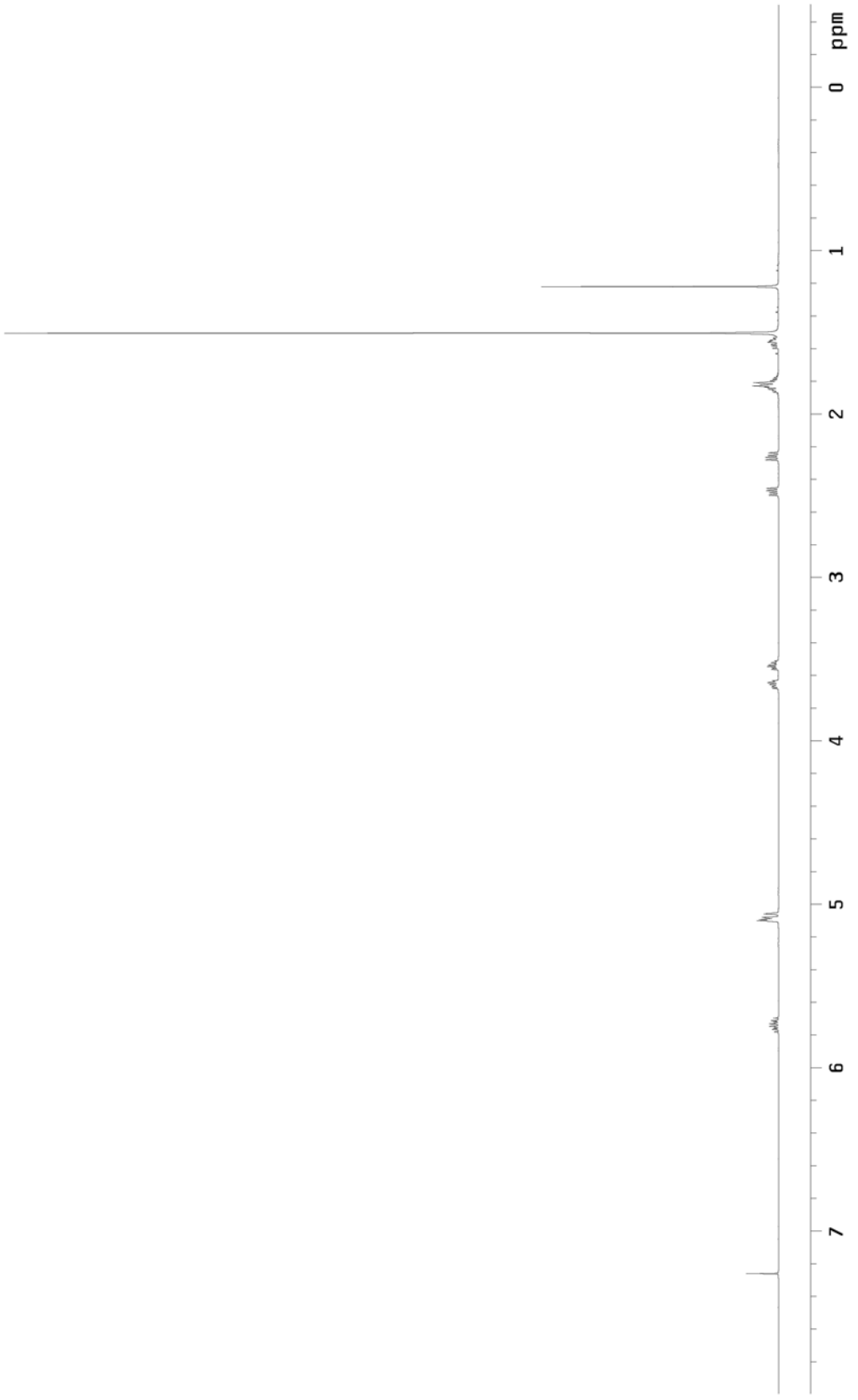
Alkylation Products

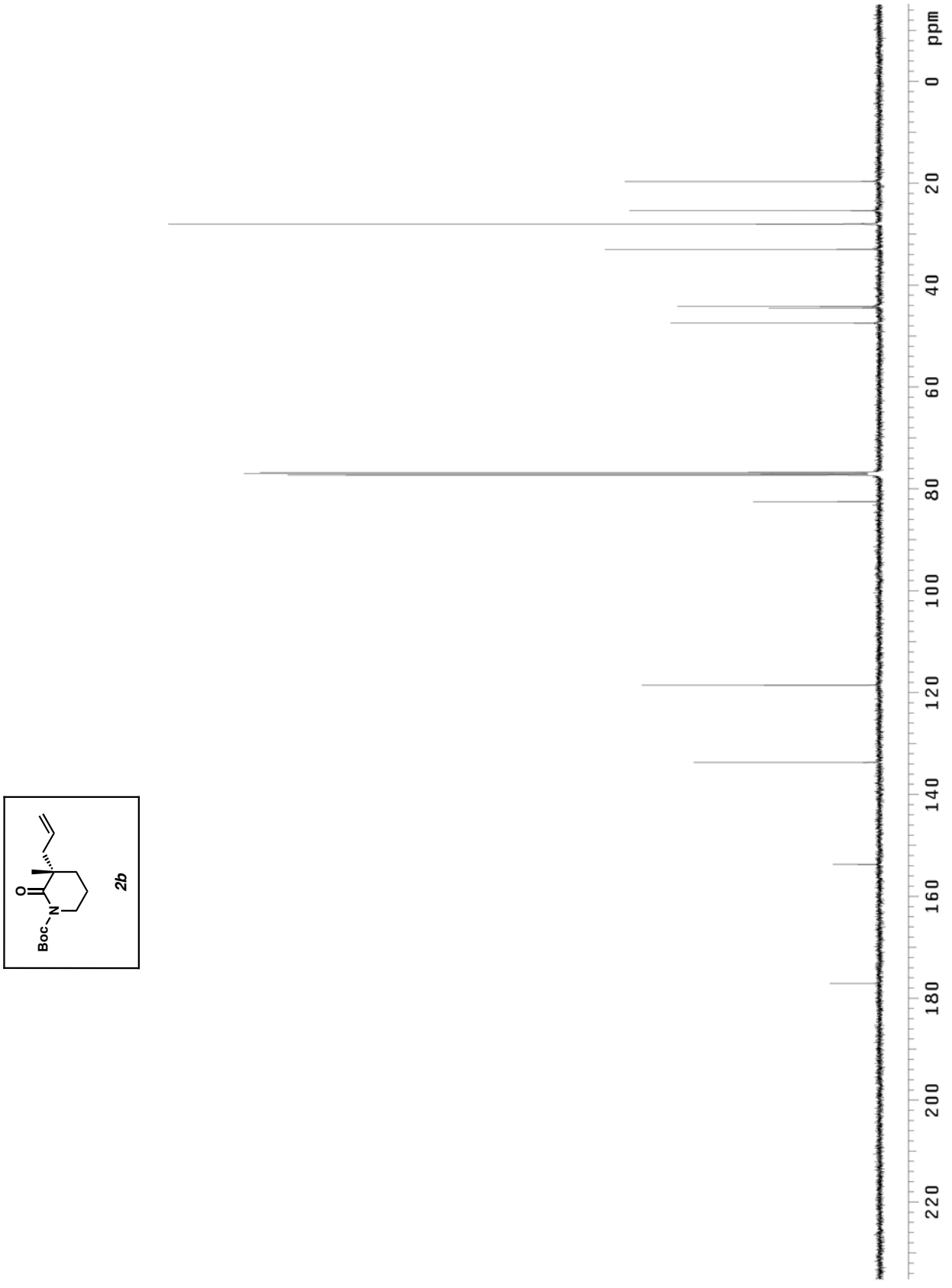


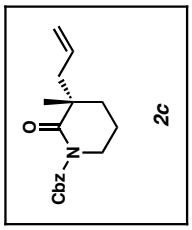












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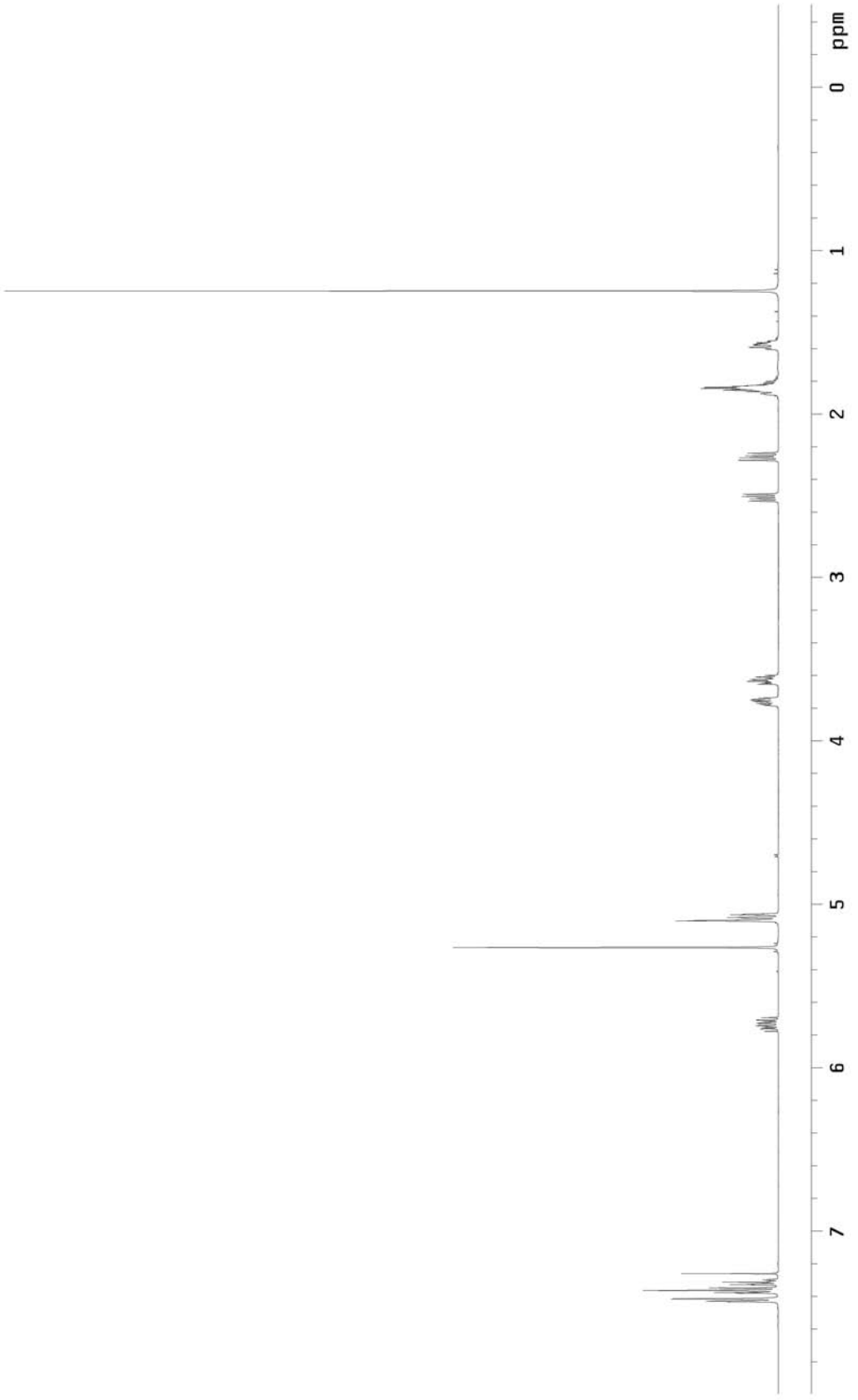

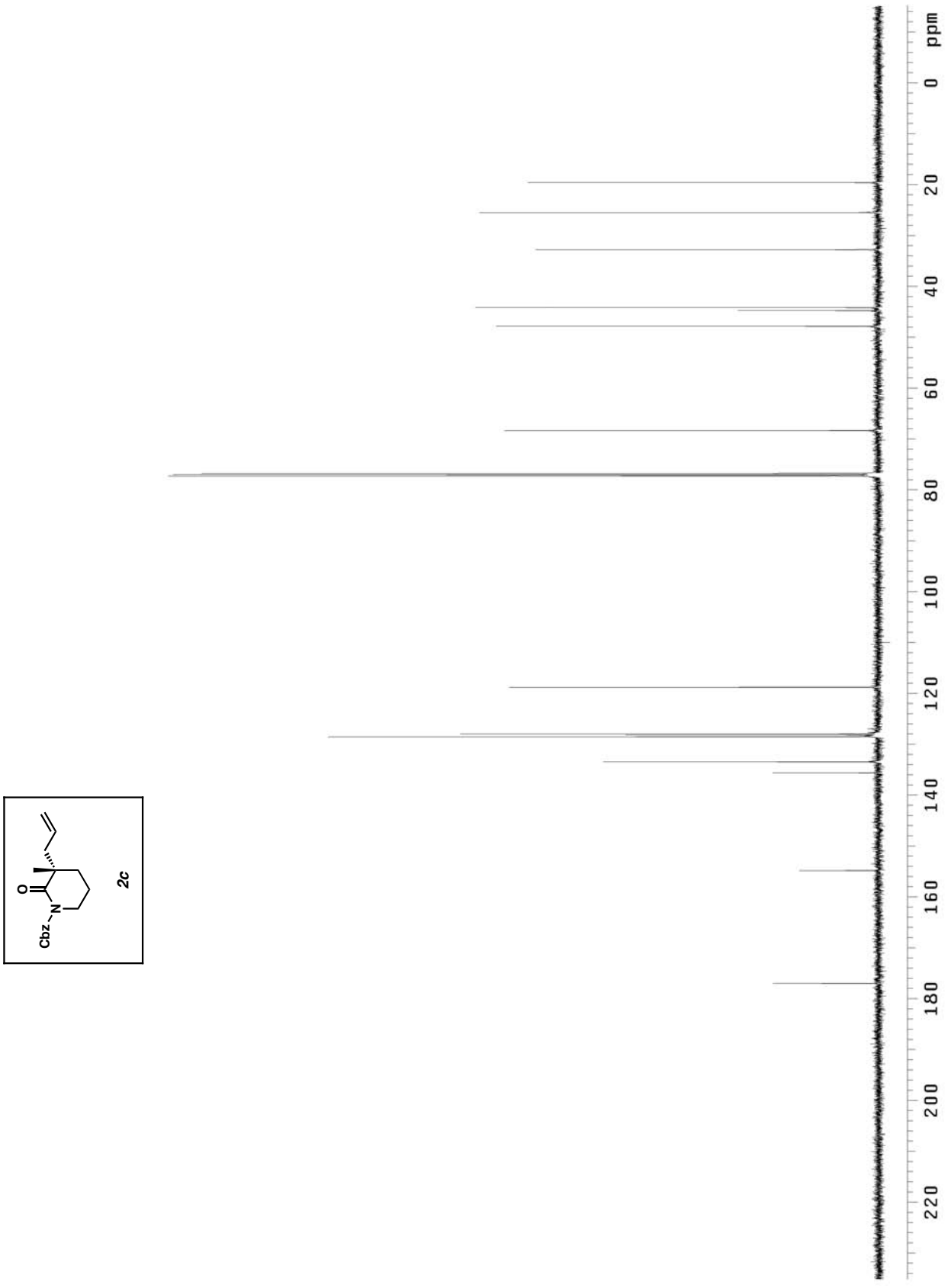

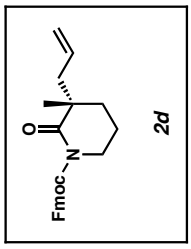

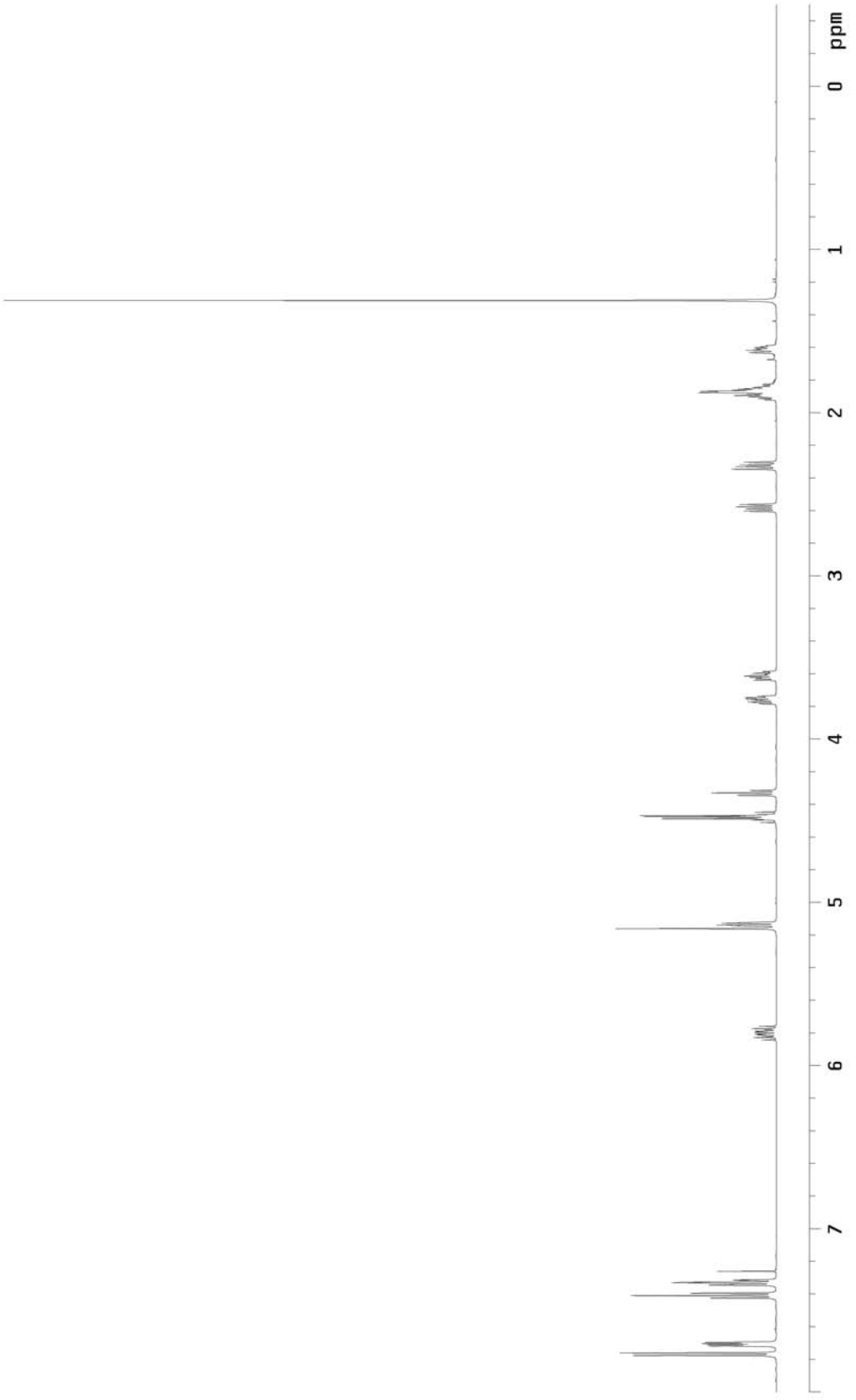

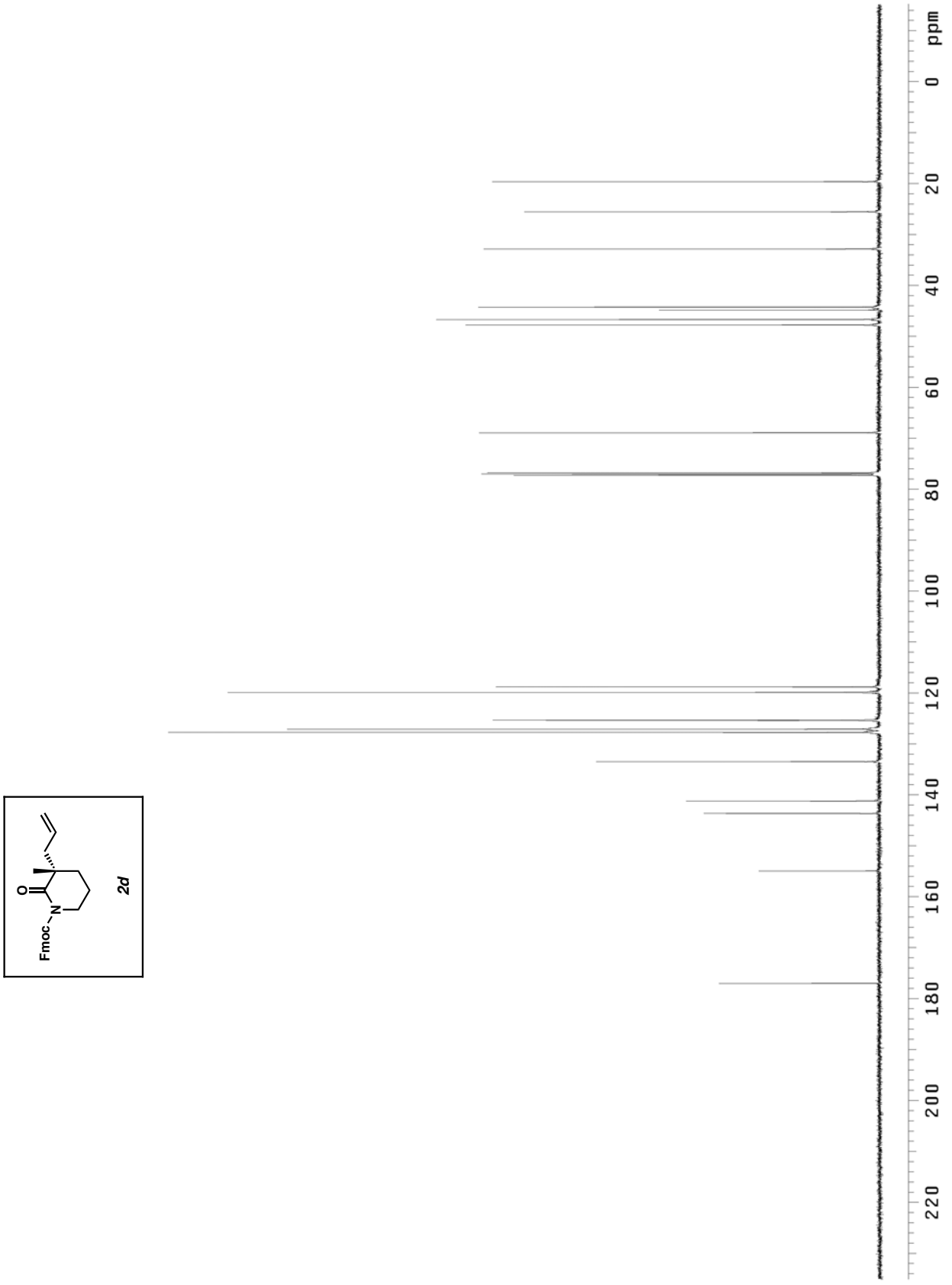

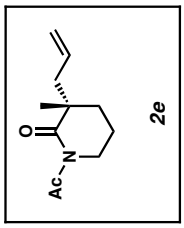

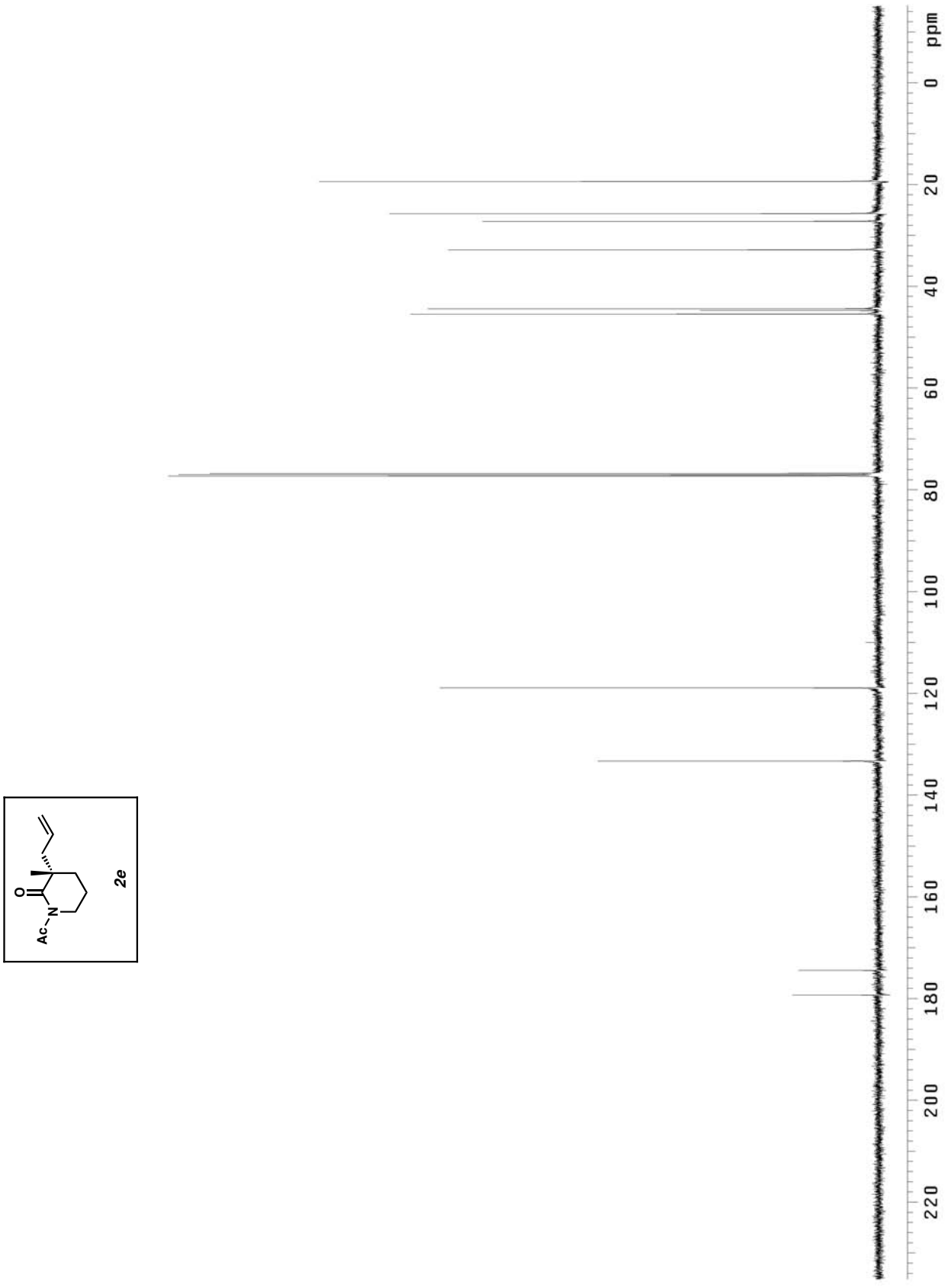

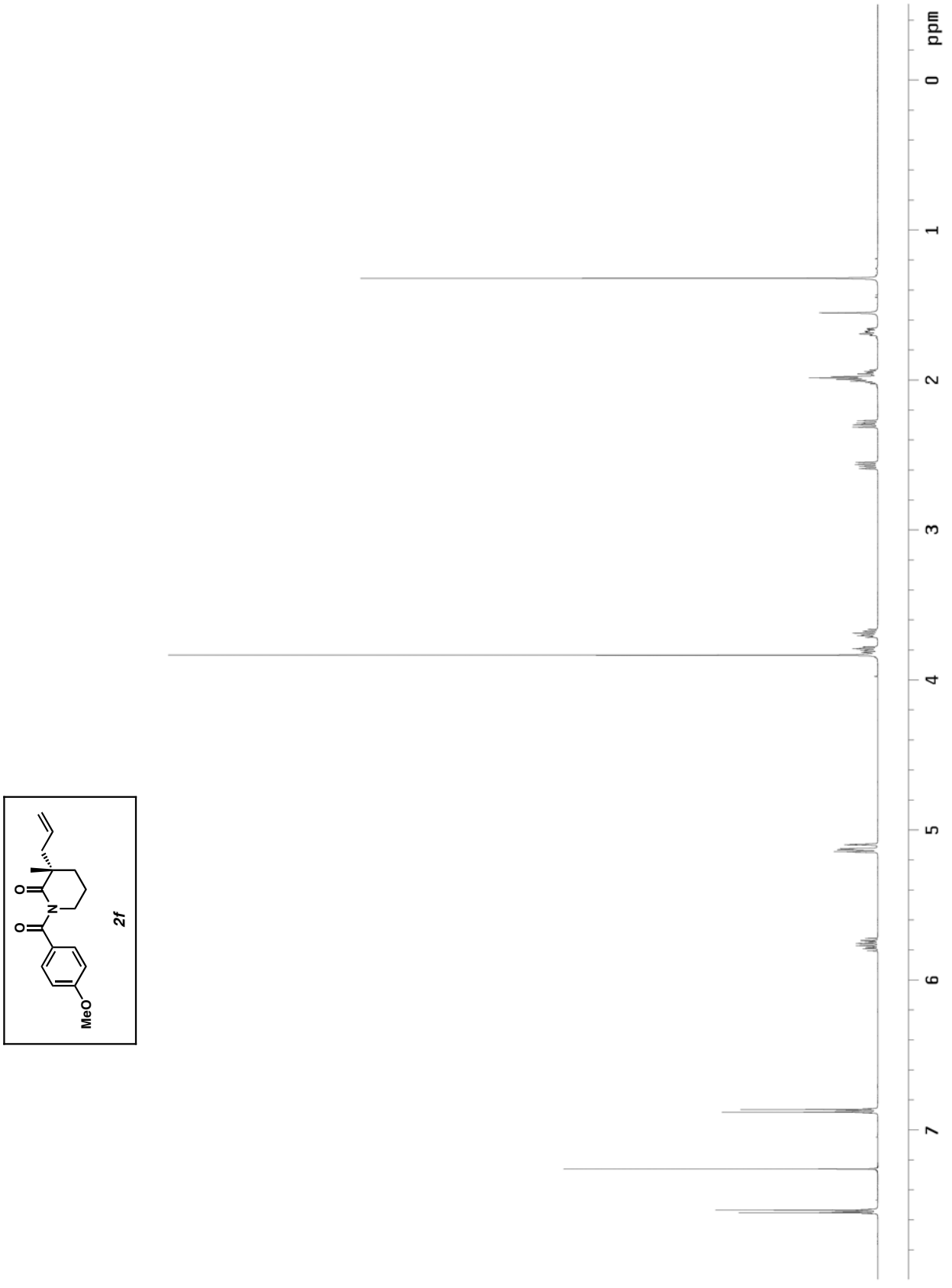

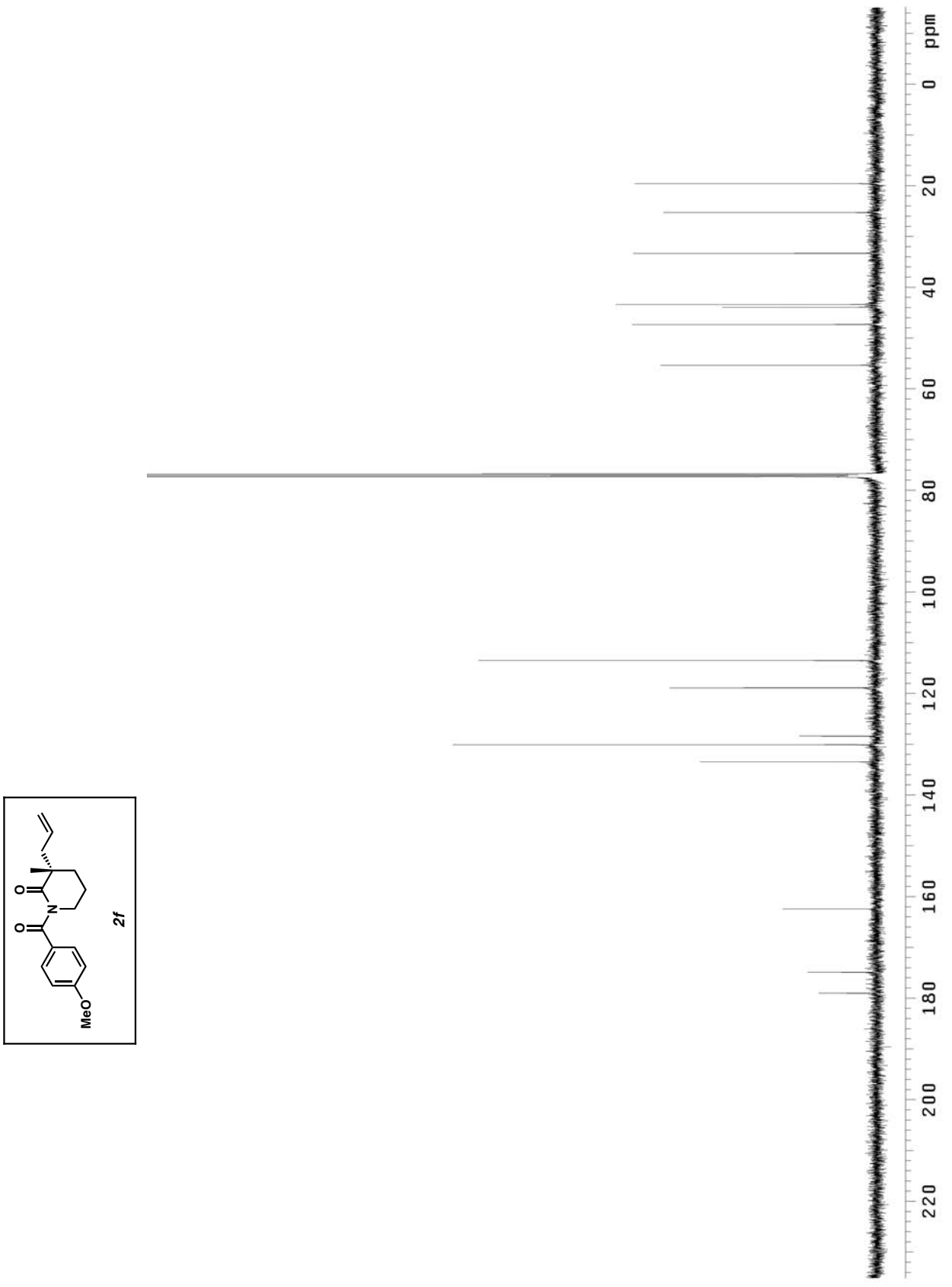

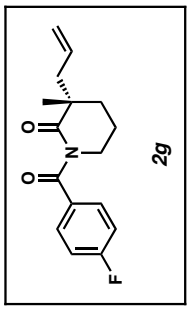

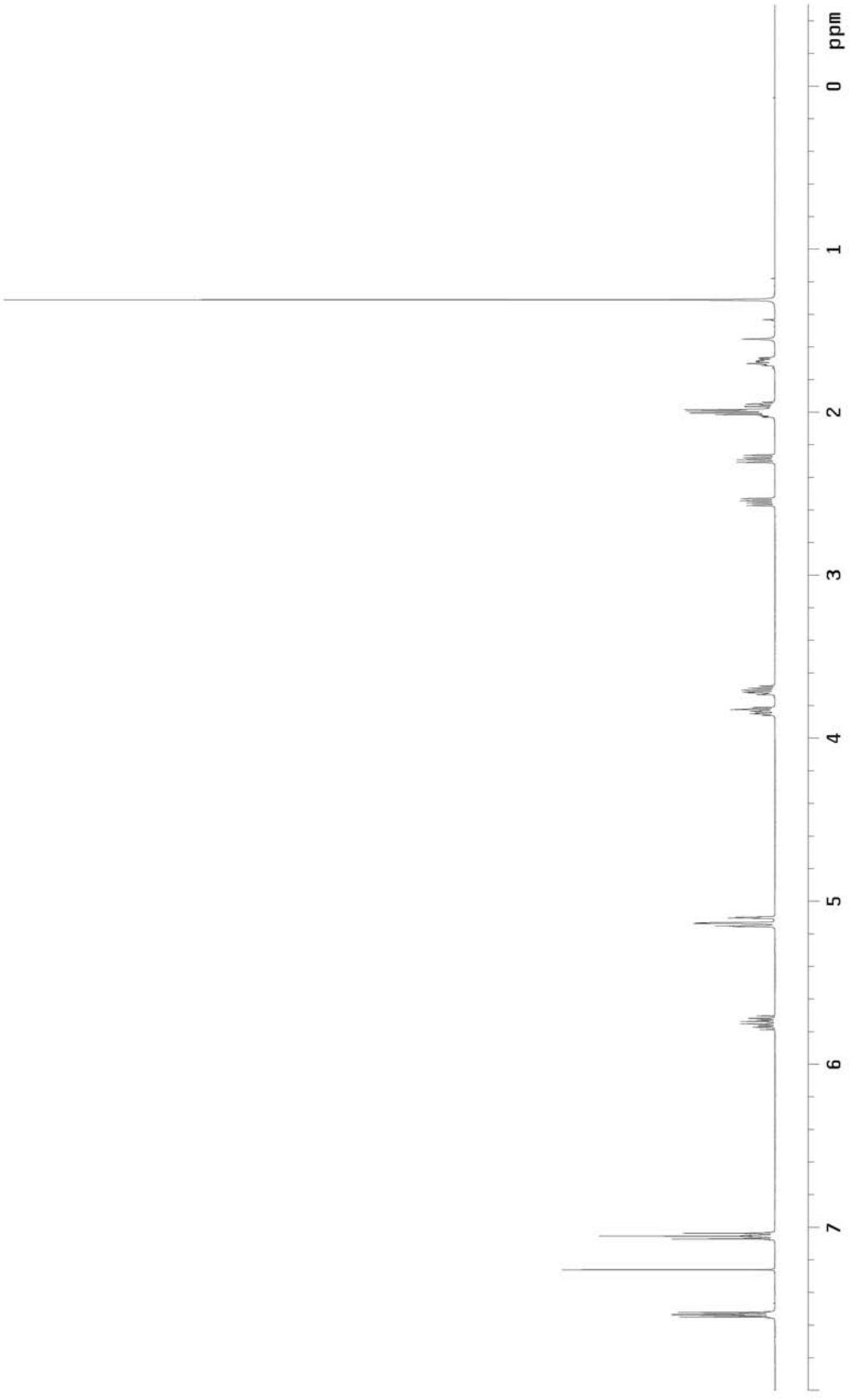

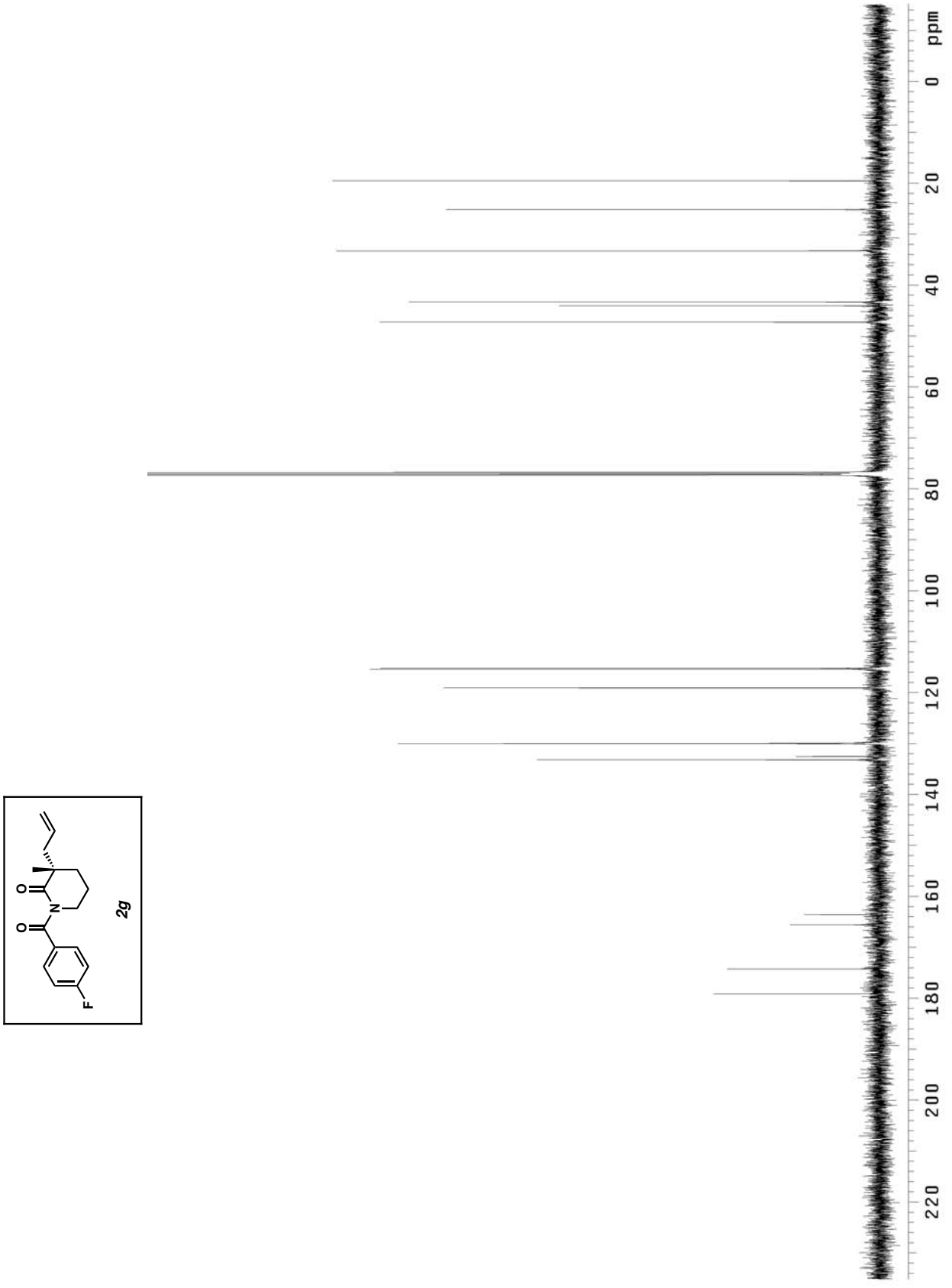

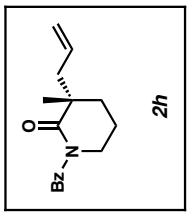

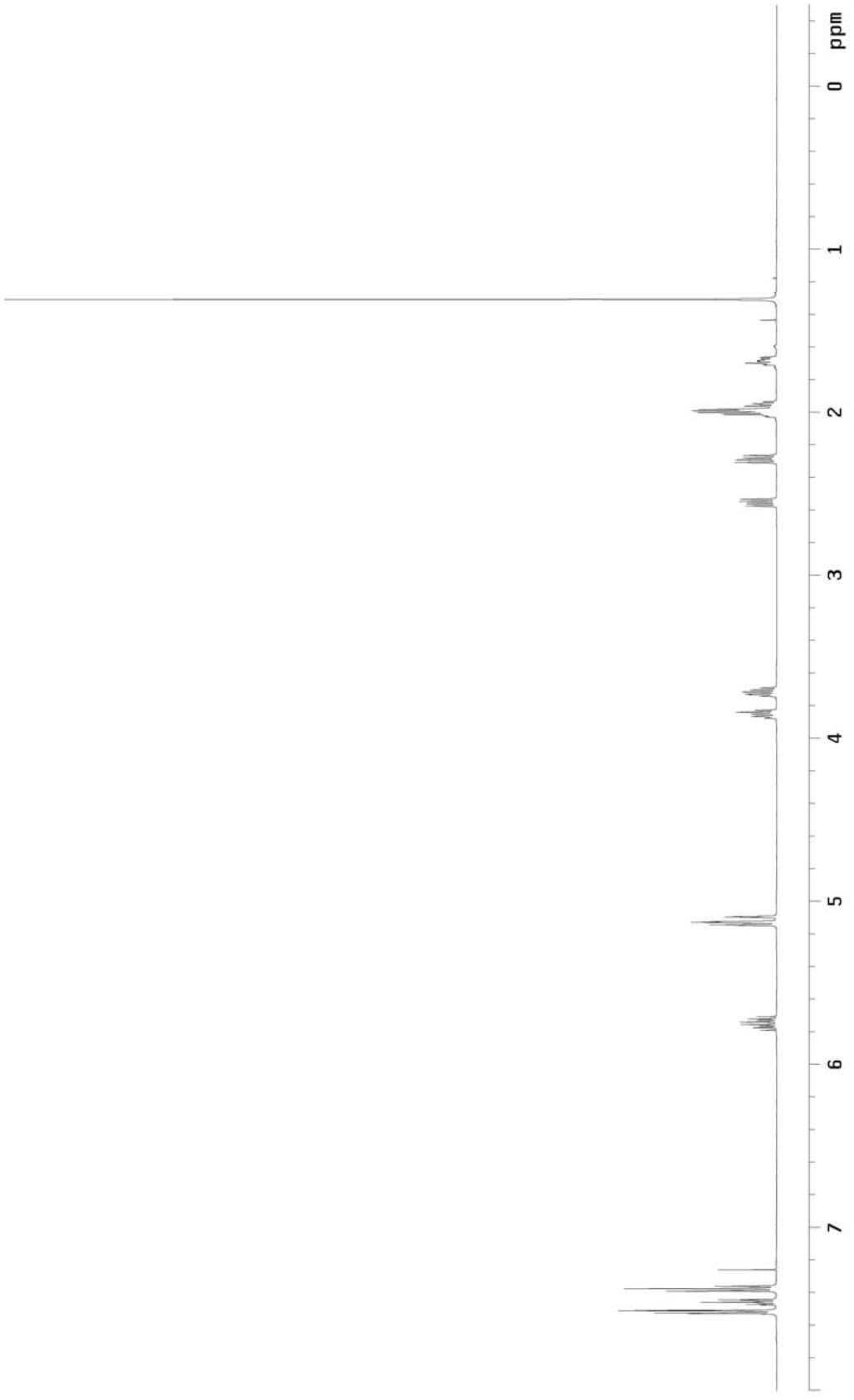

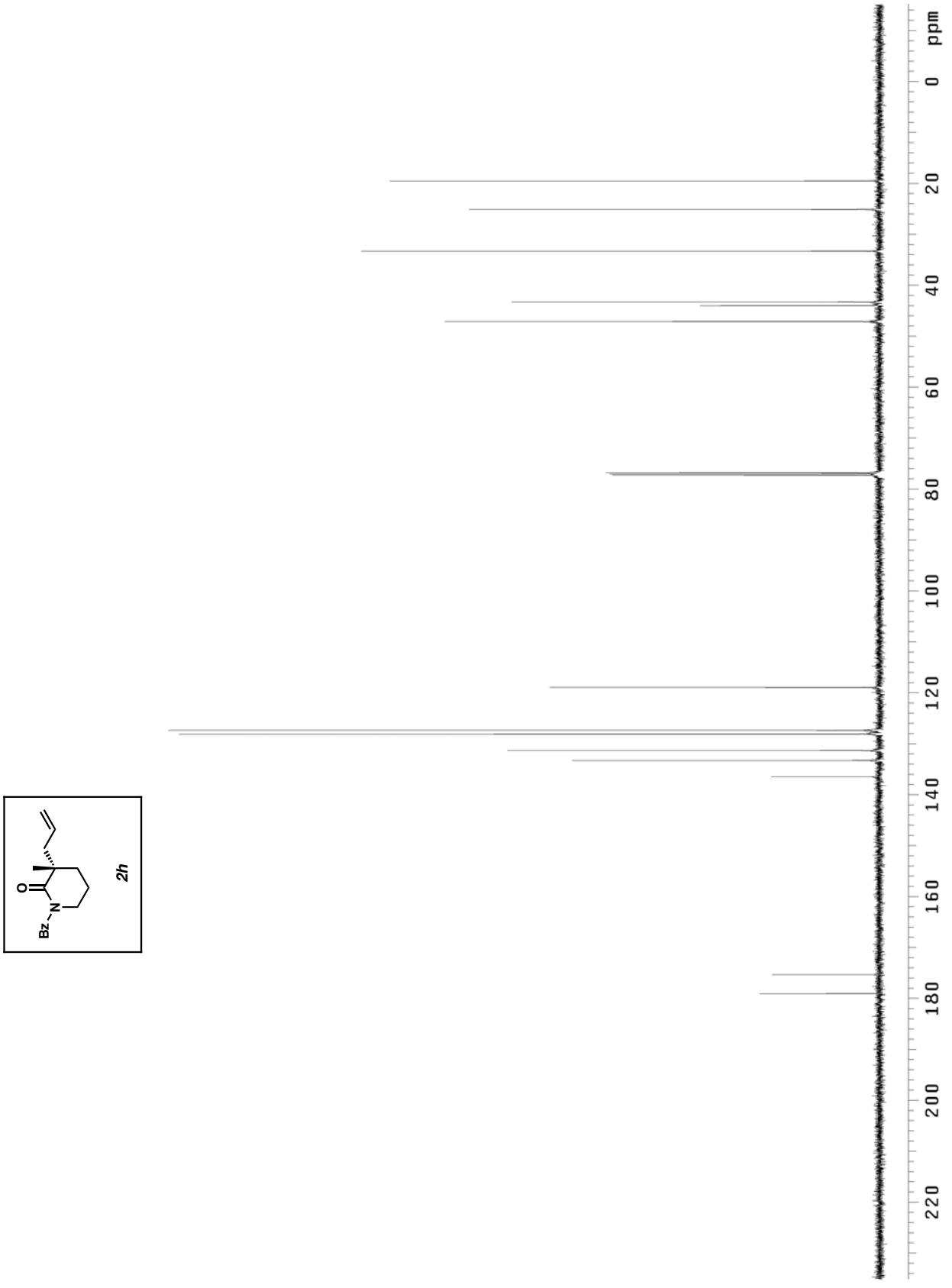

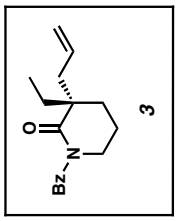

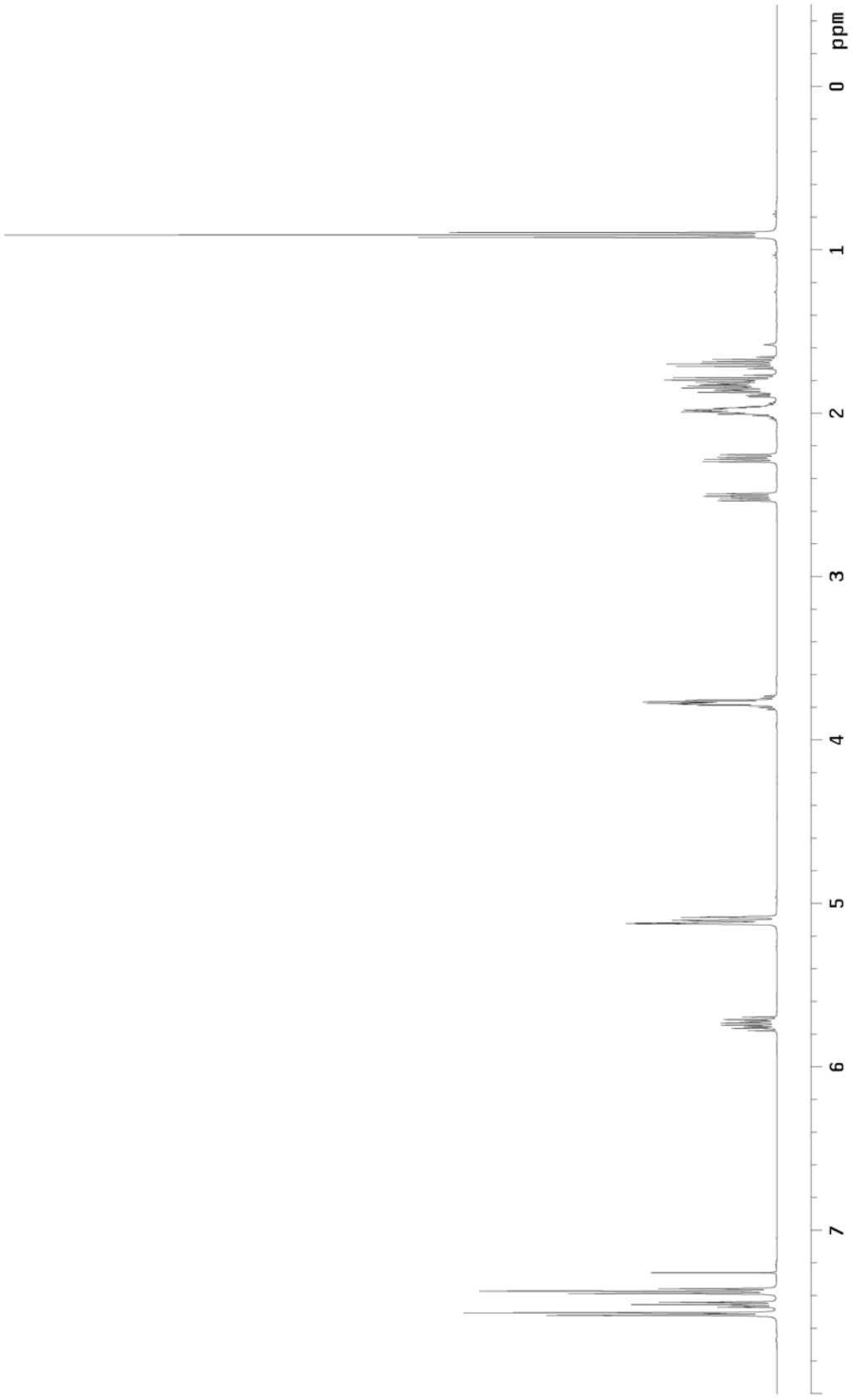

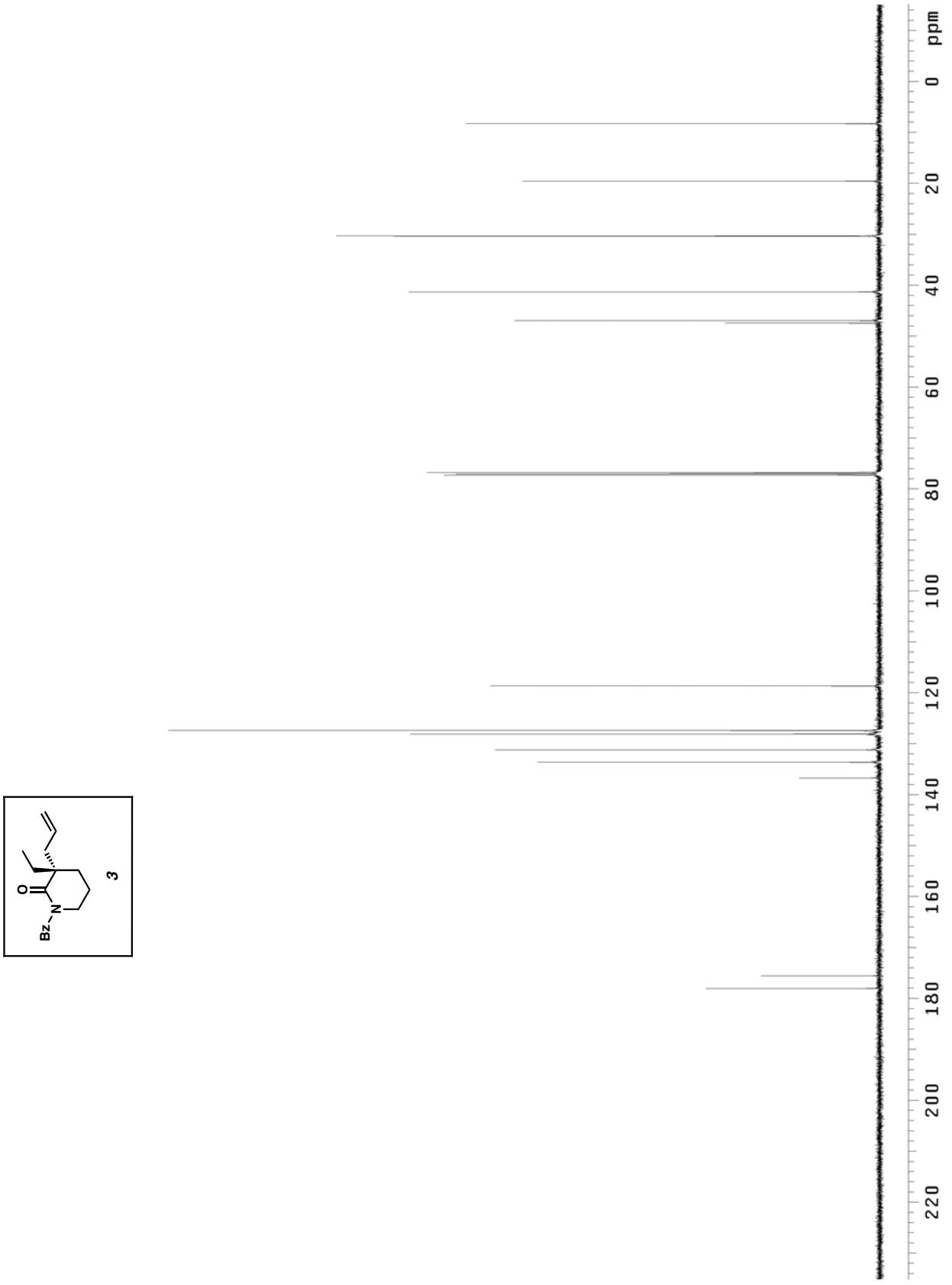

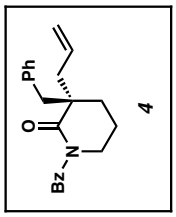

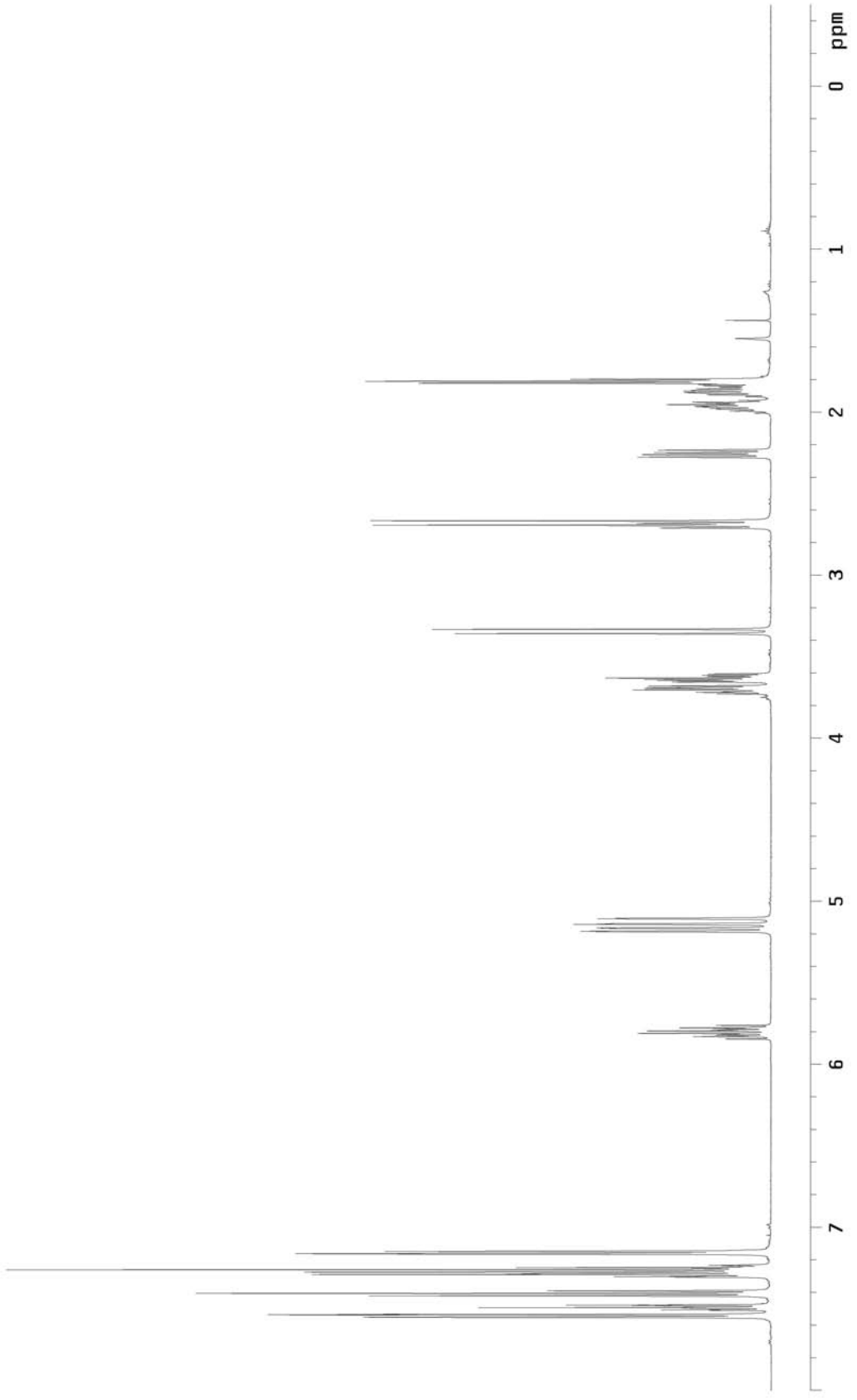

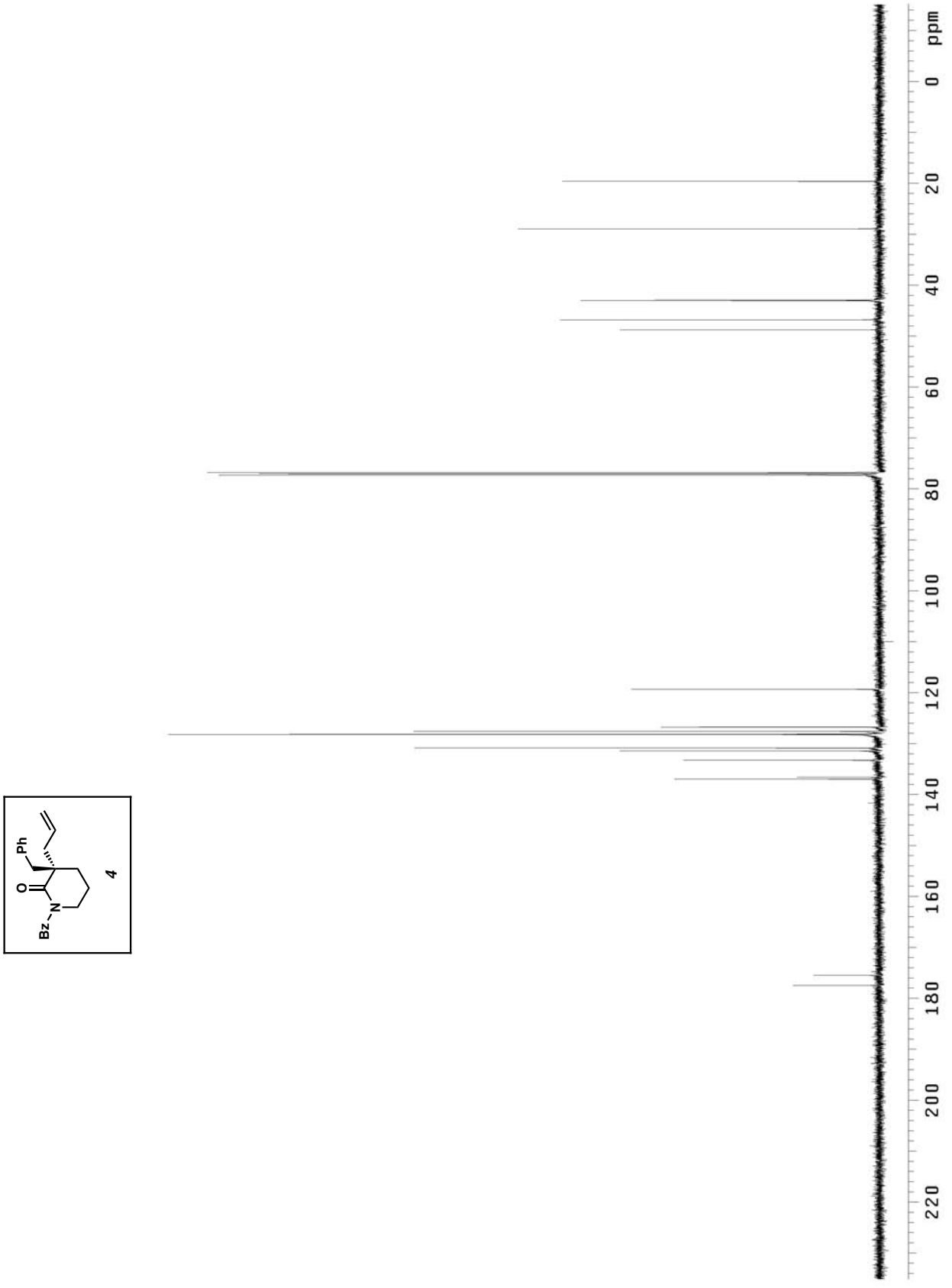

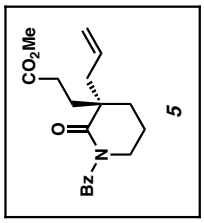

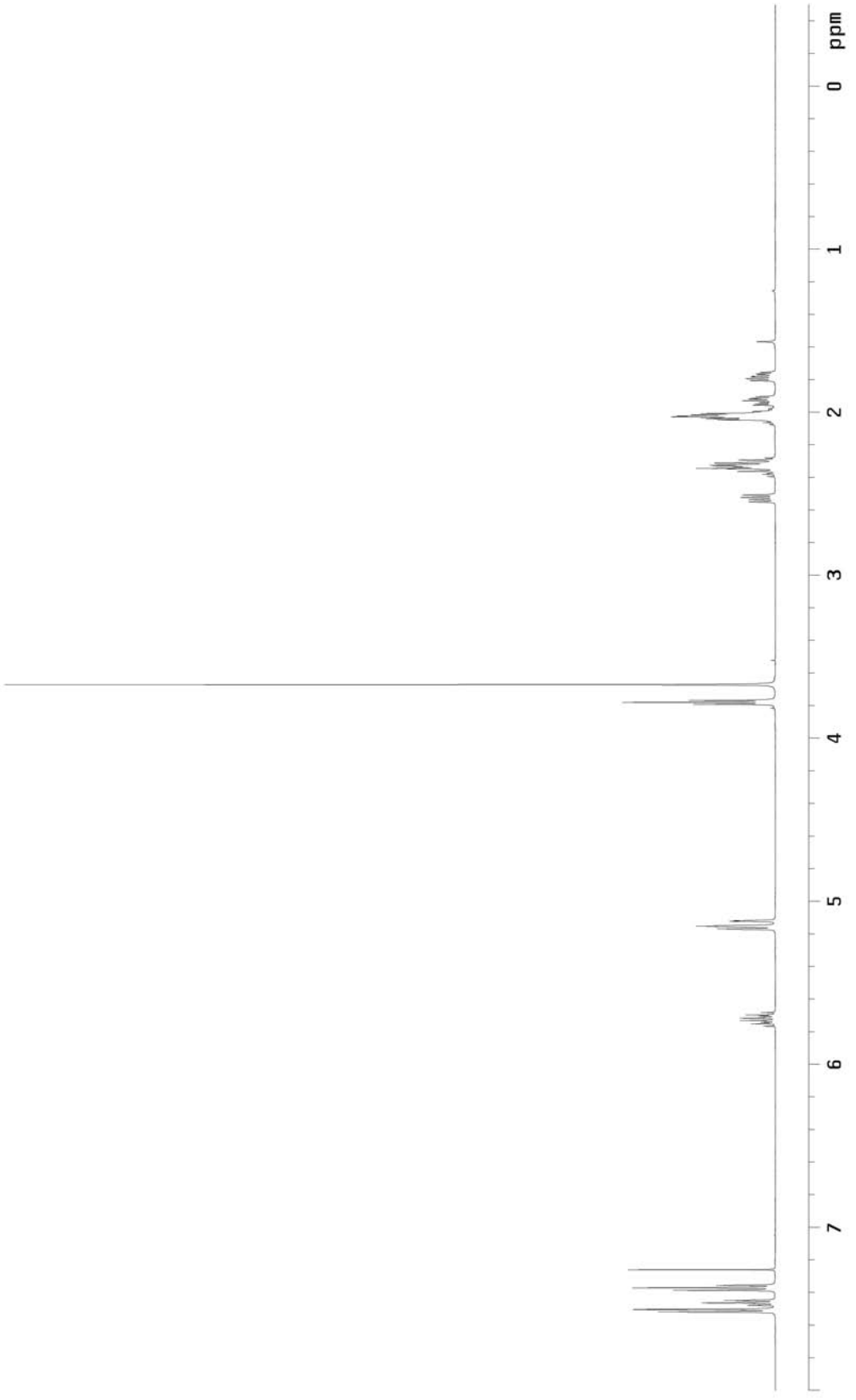

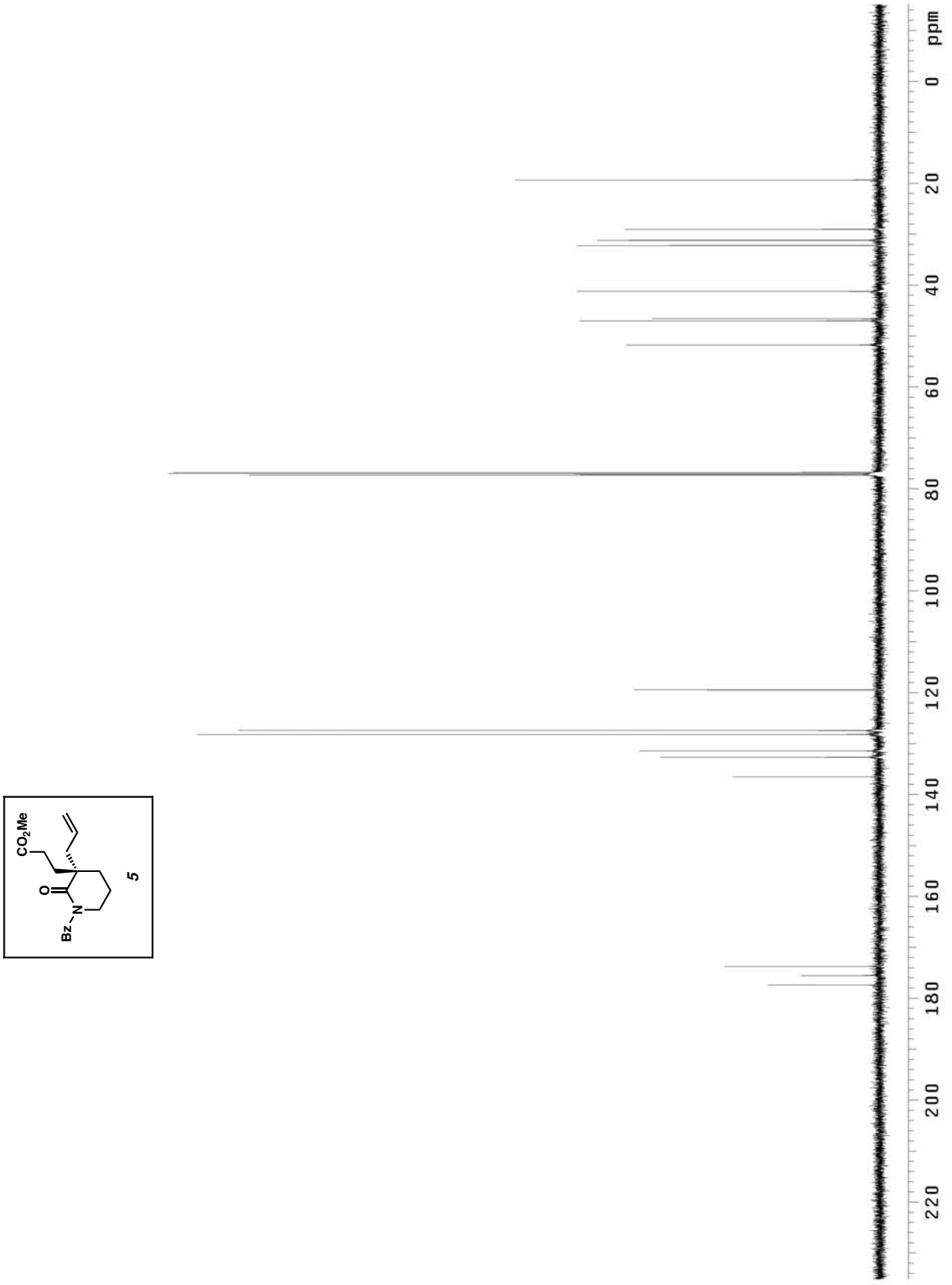

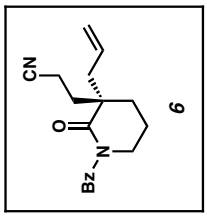

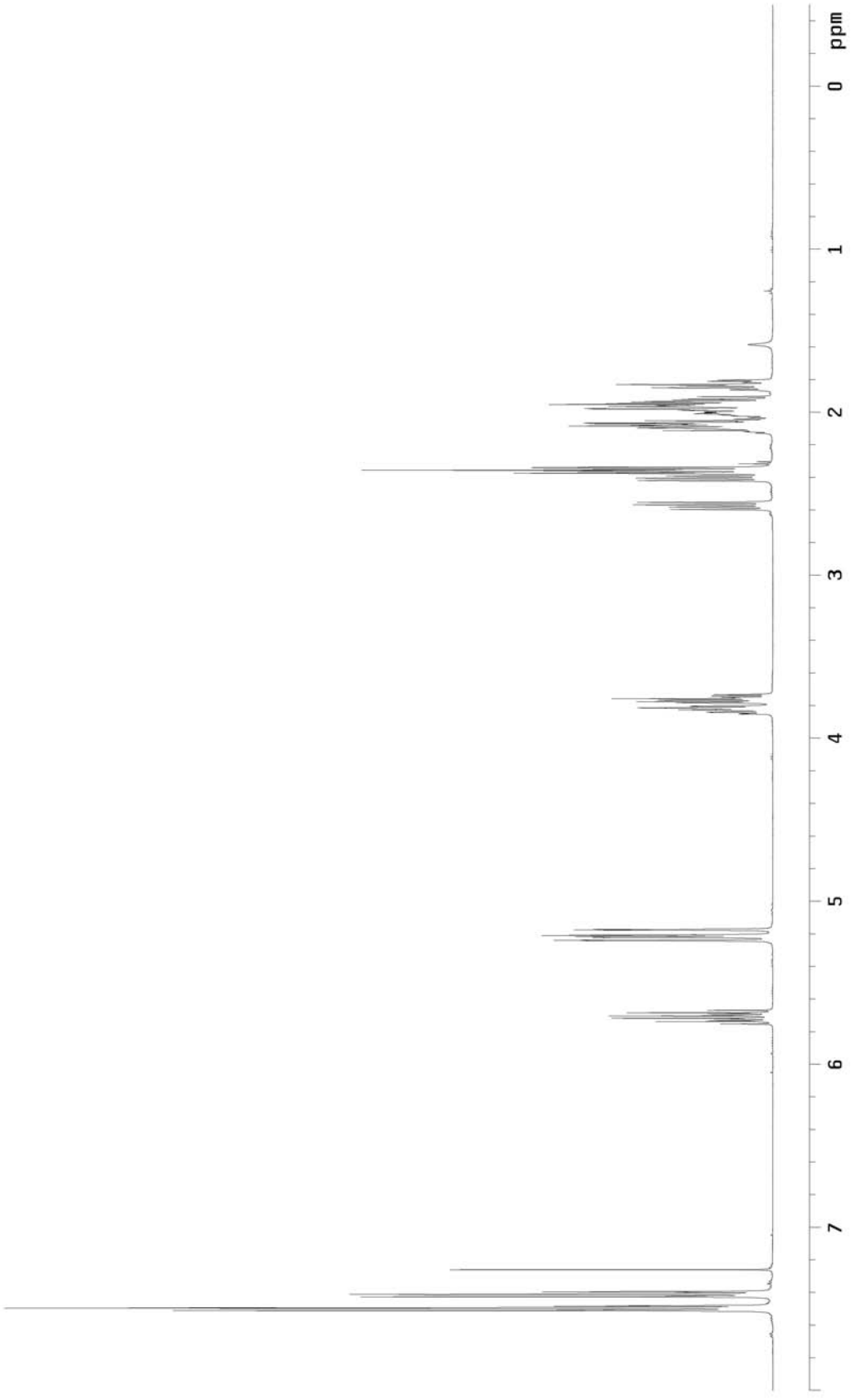

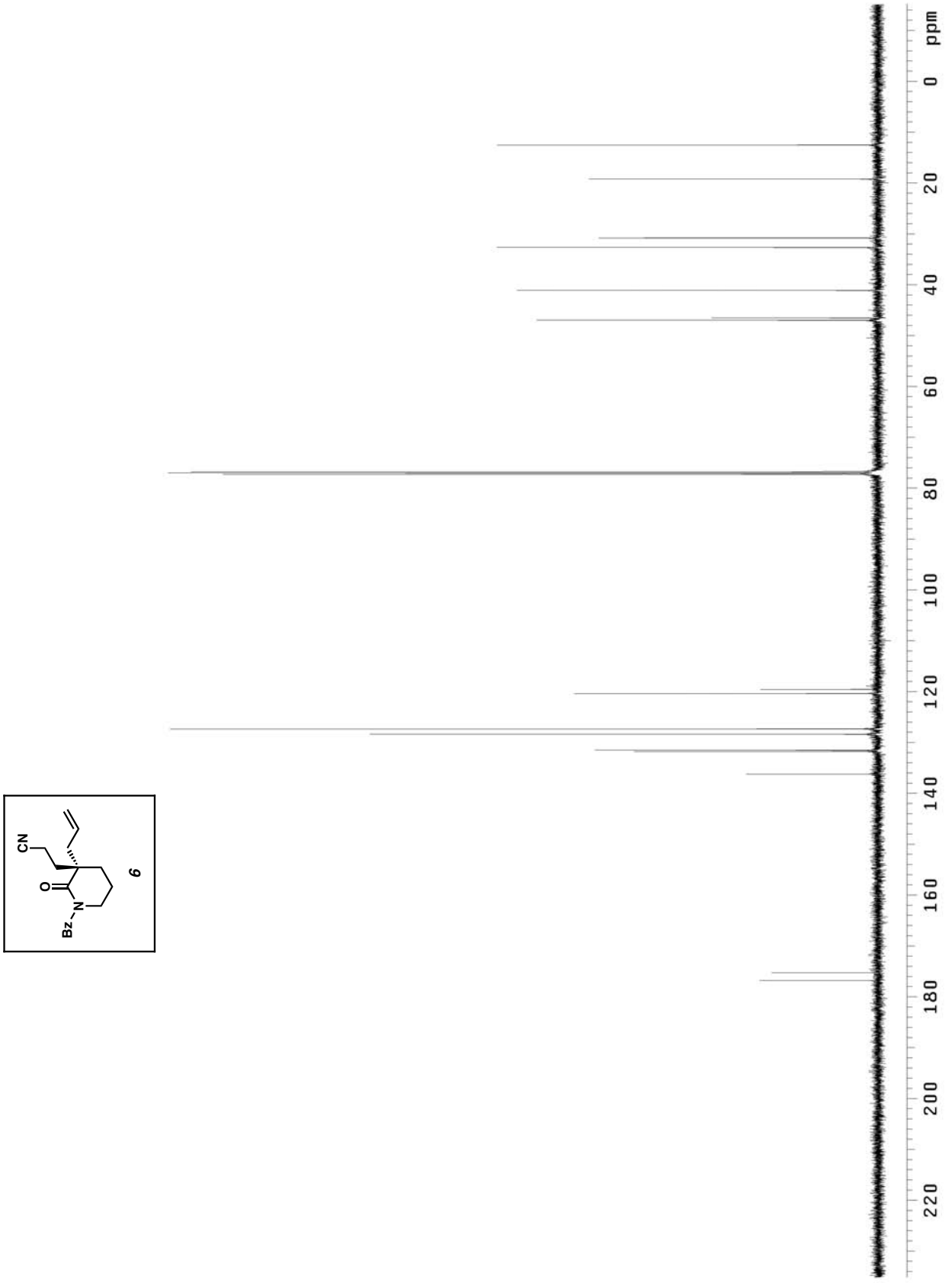

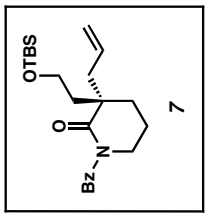

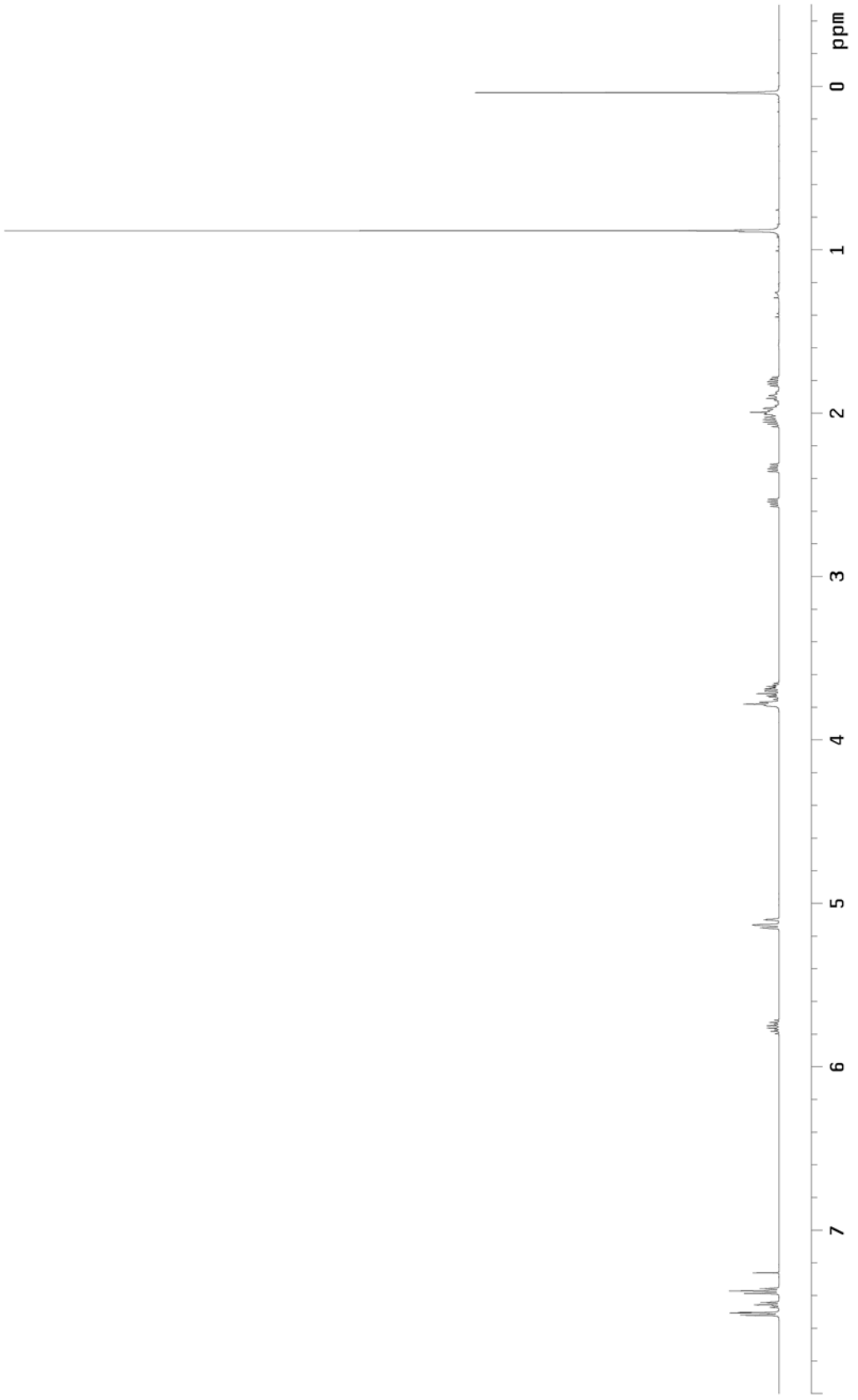

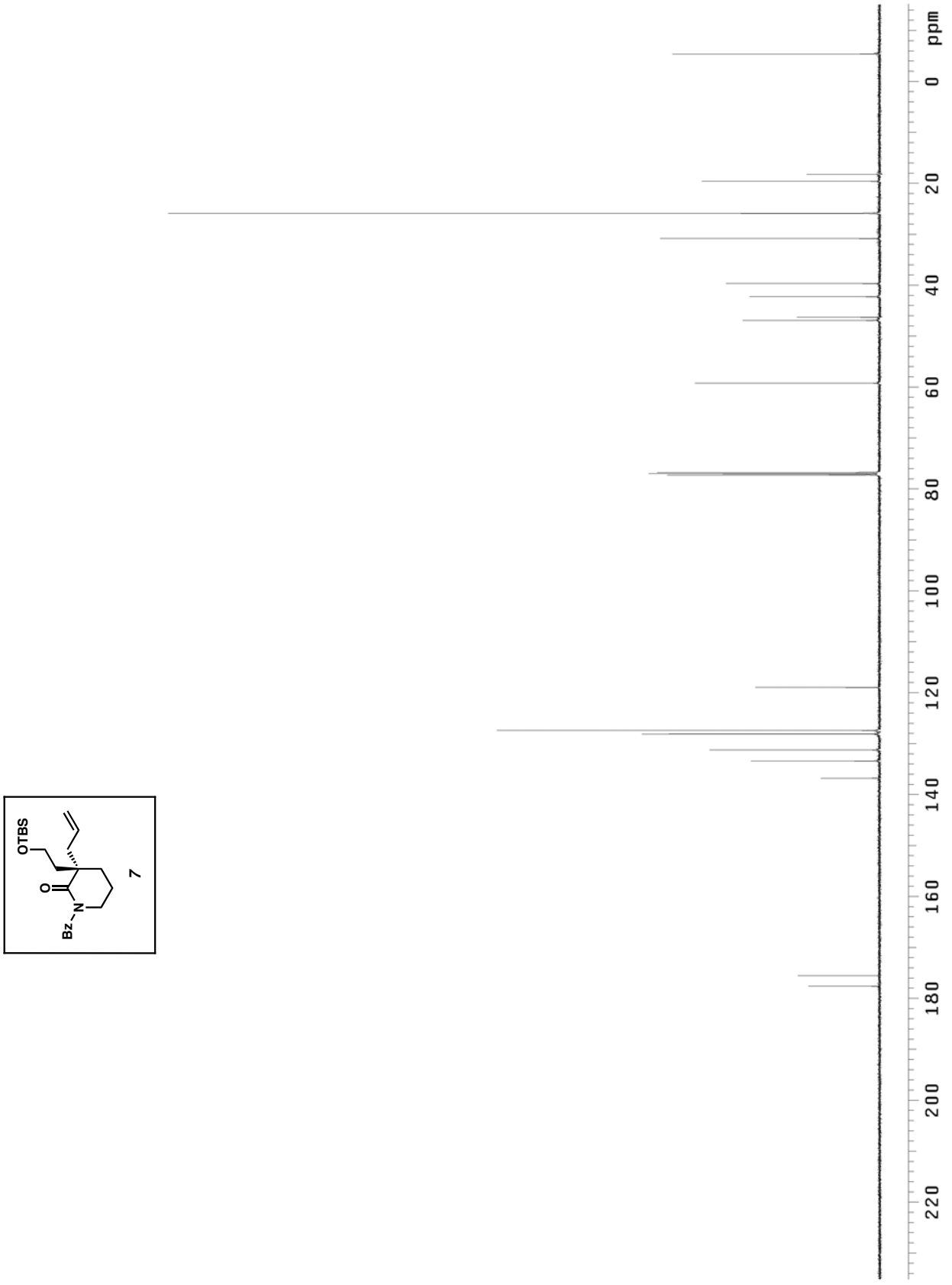

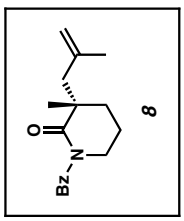

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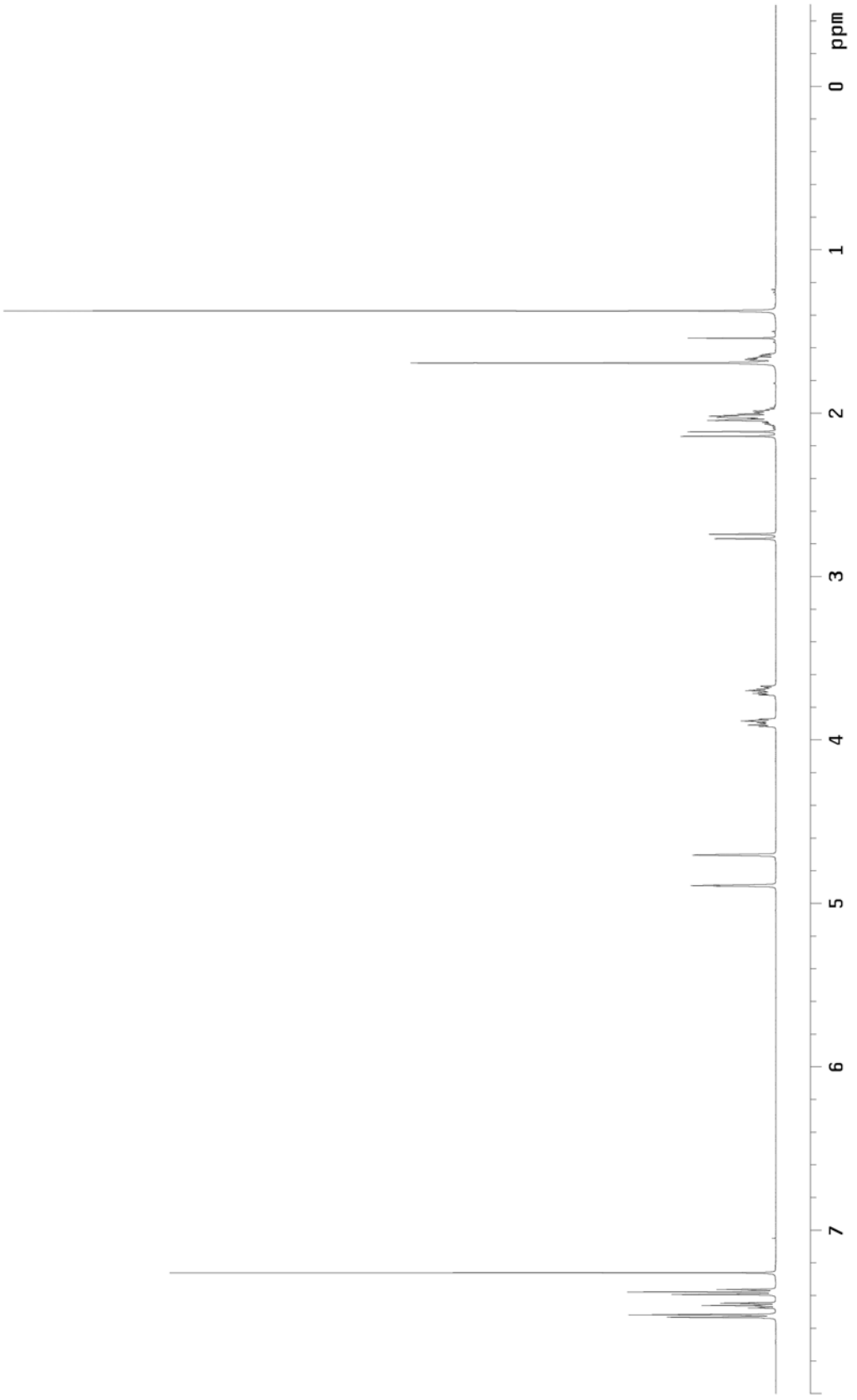
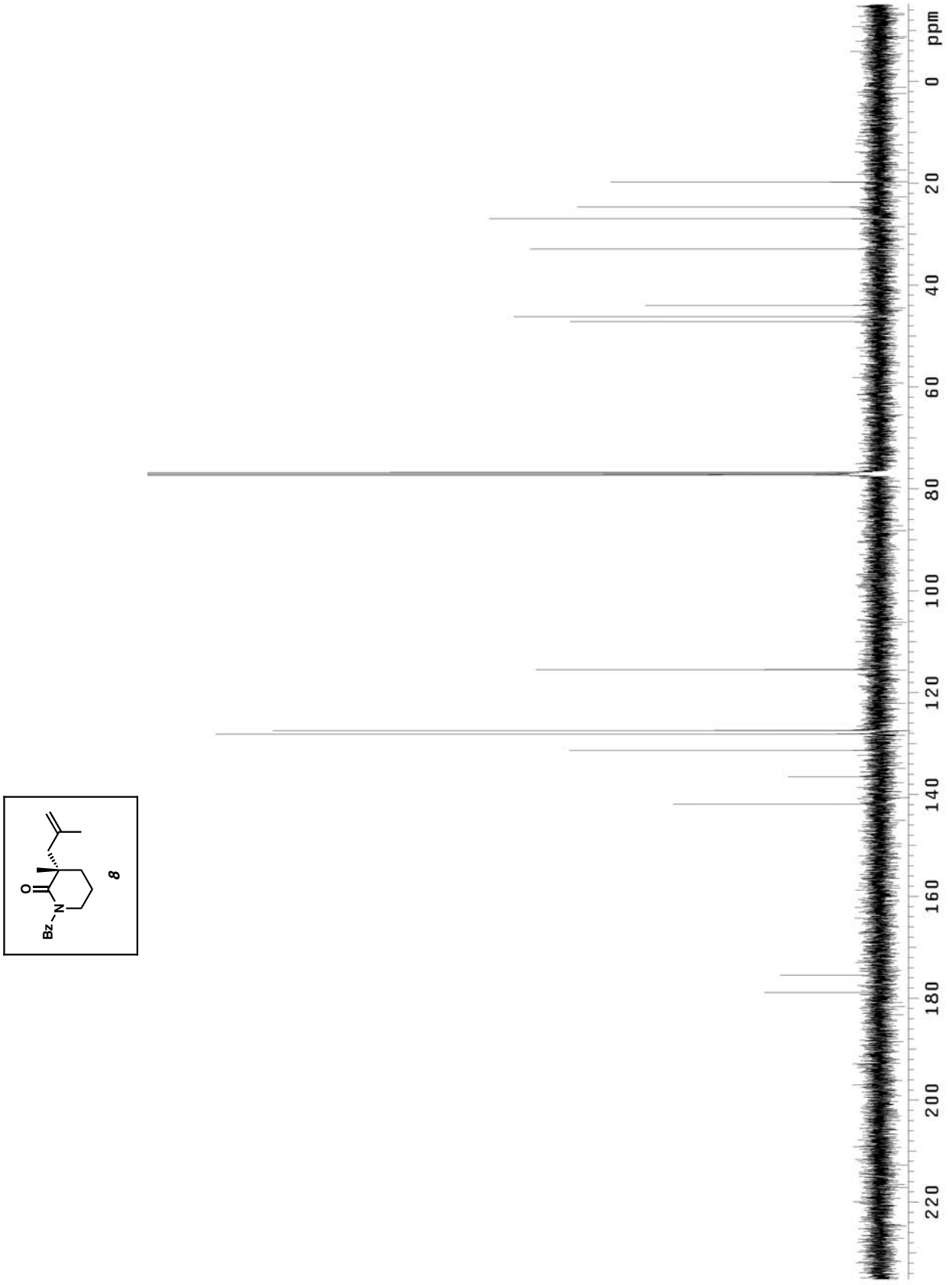
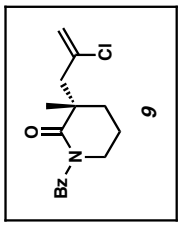
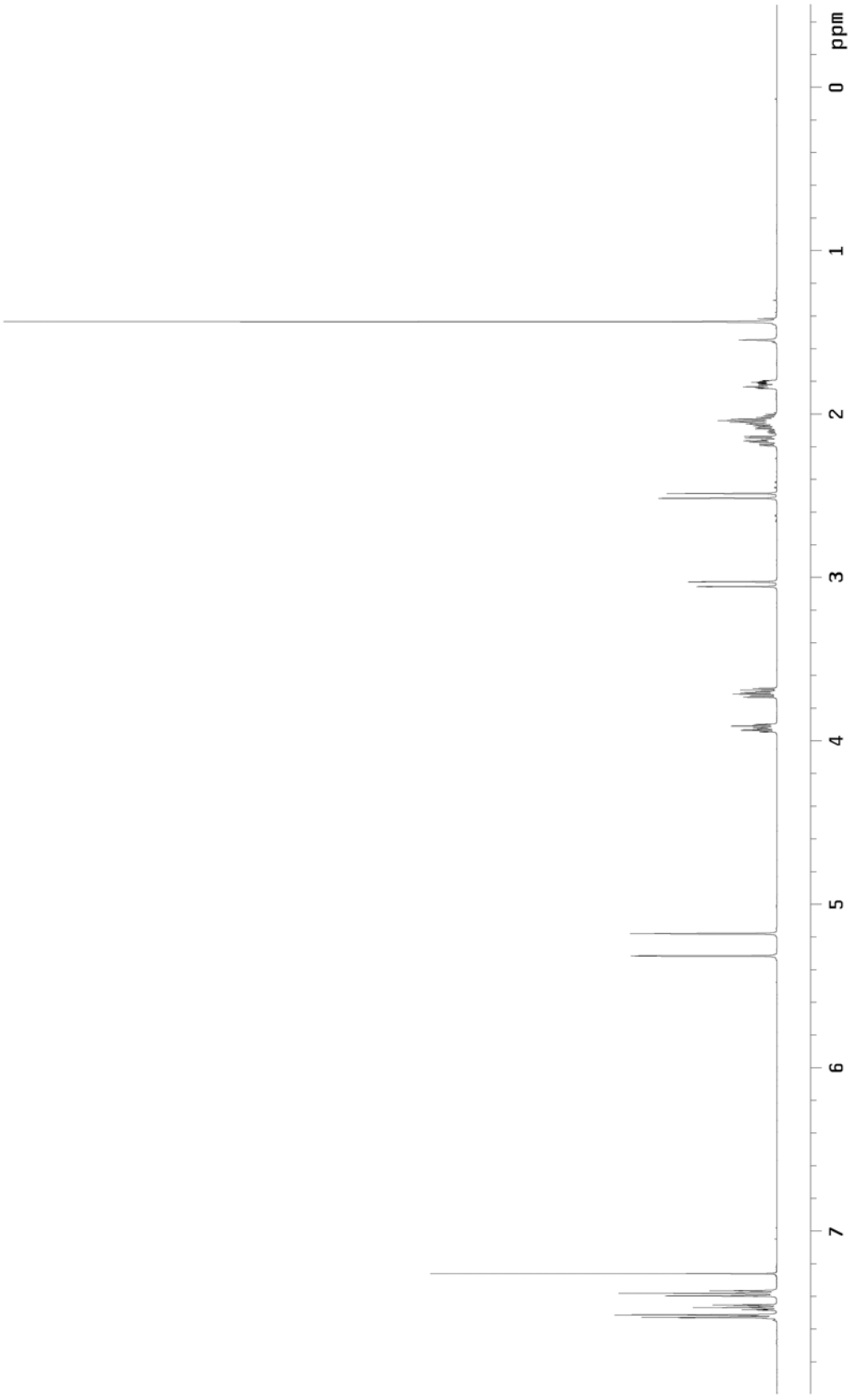
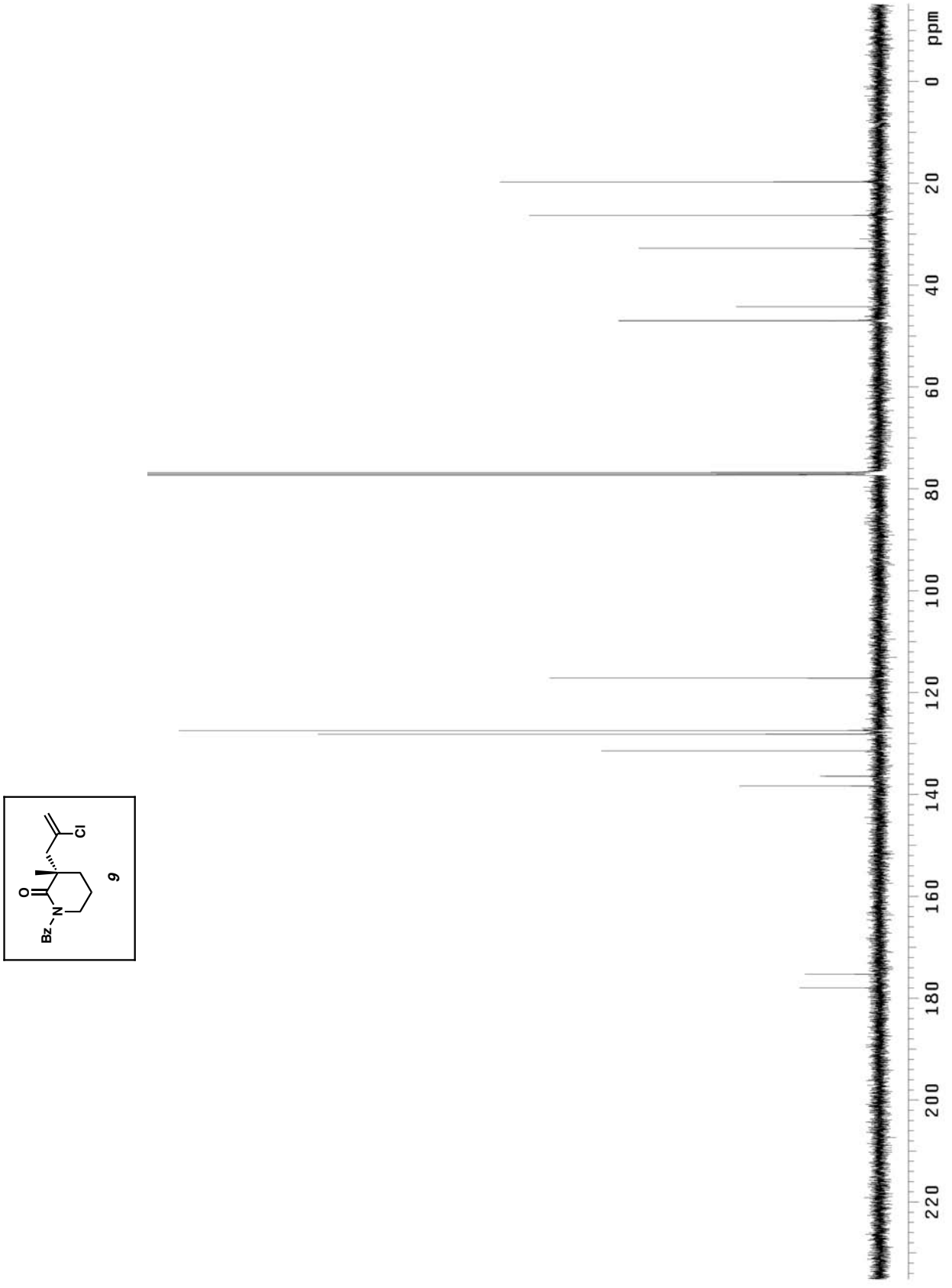
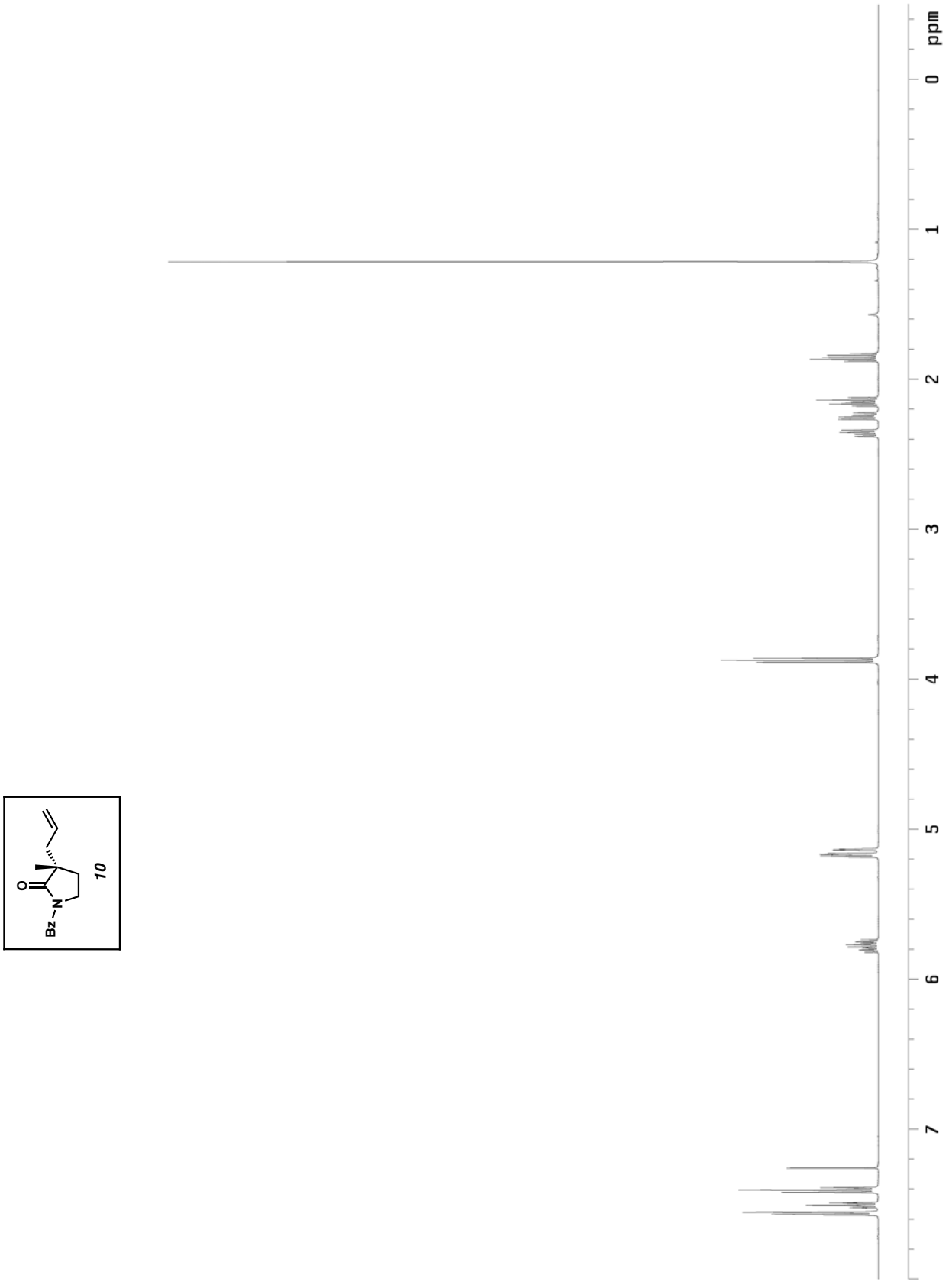


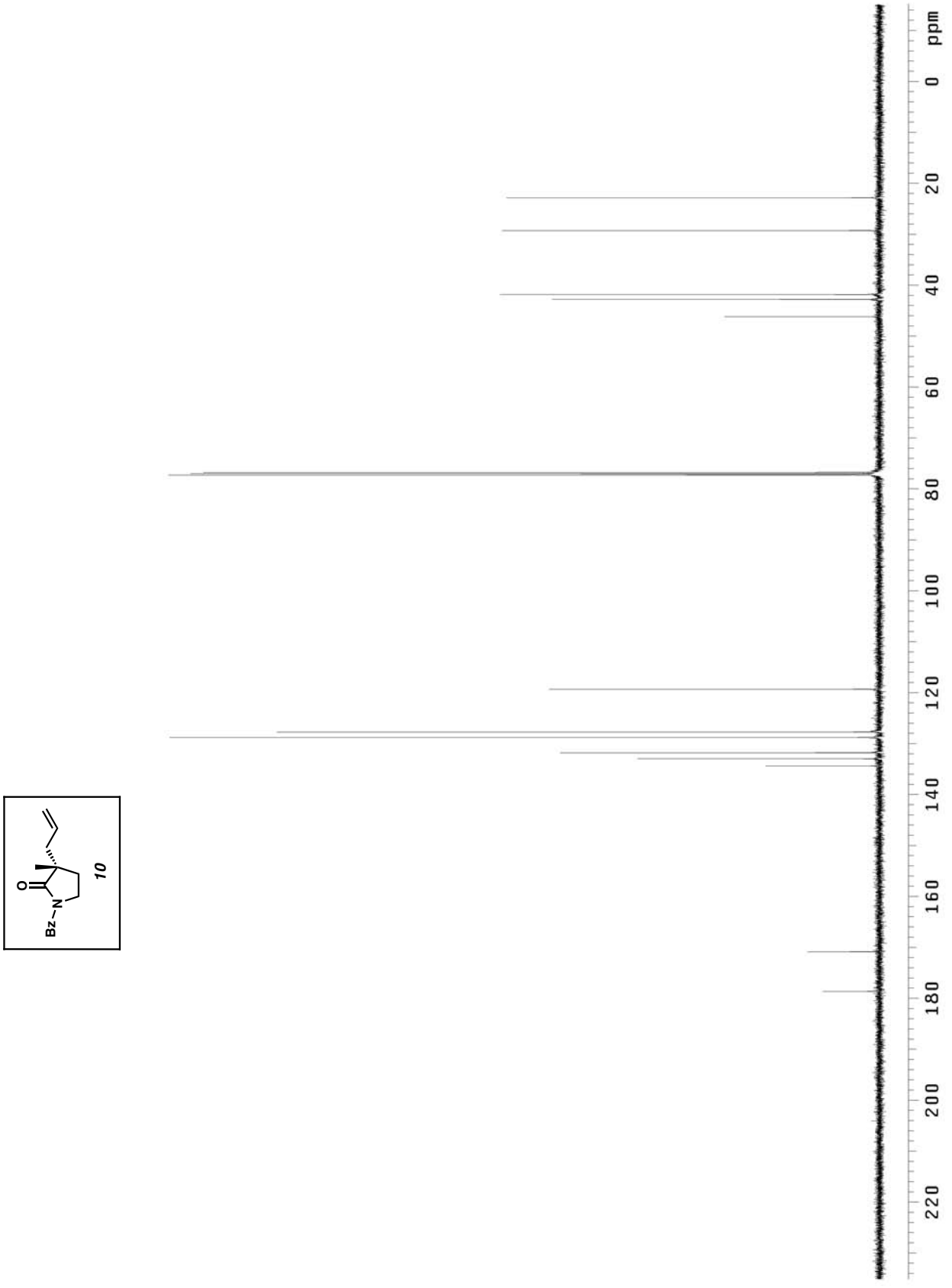


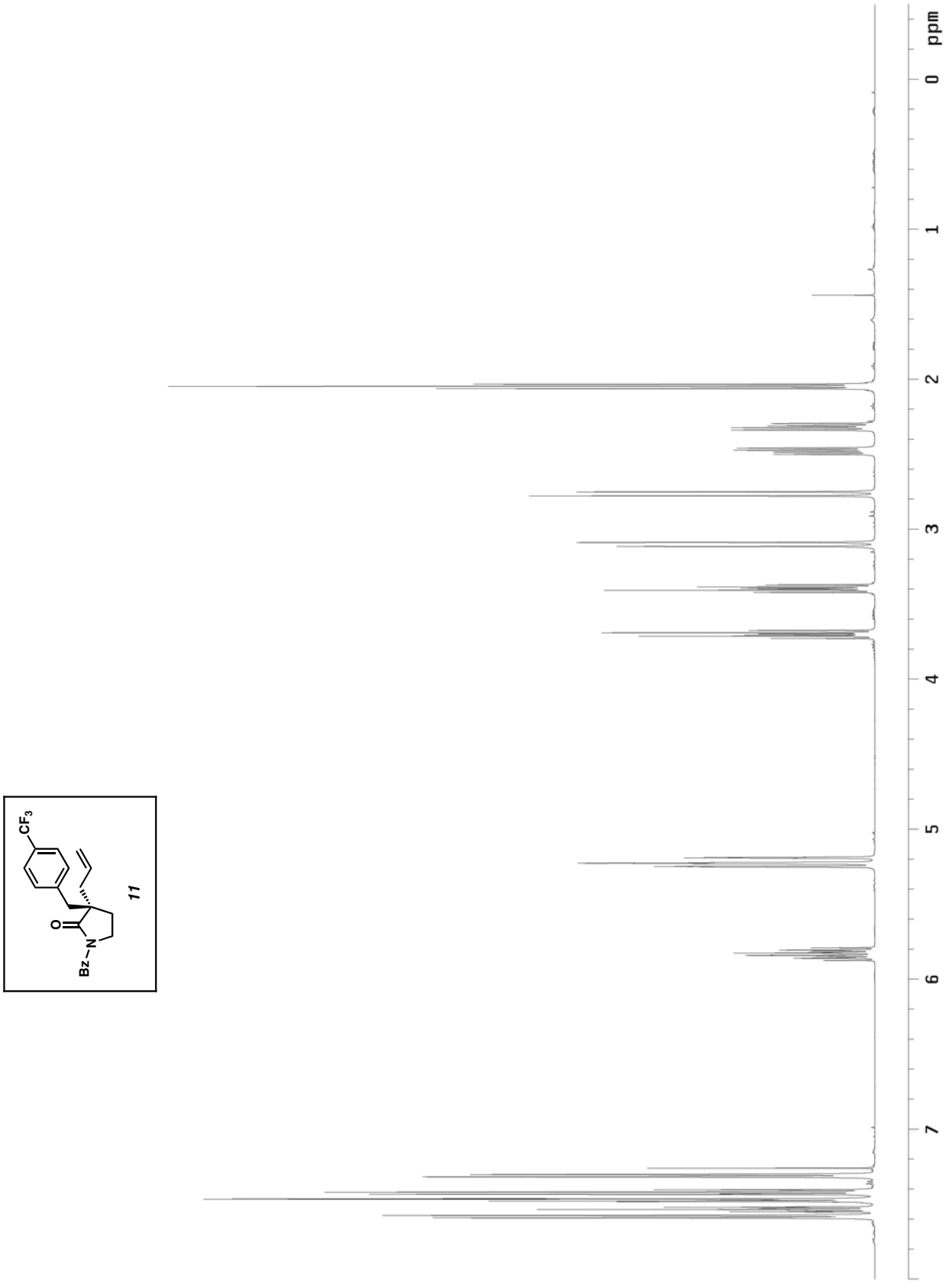


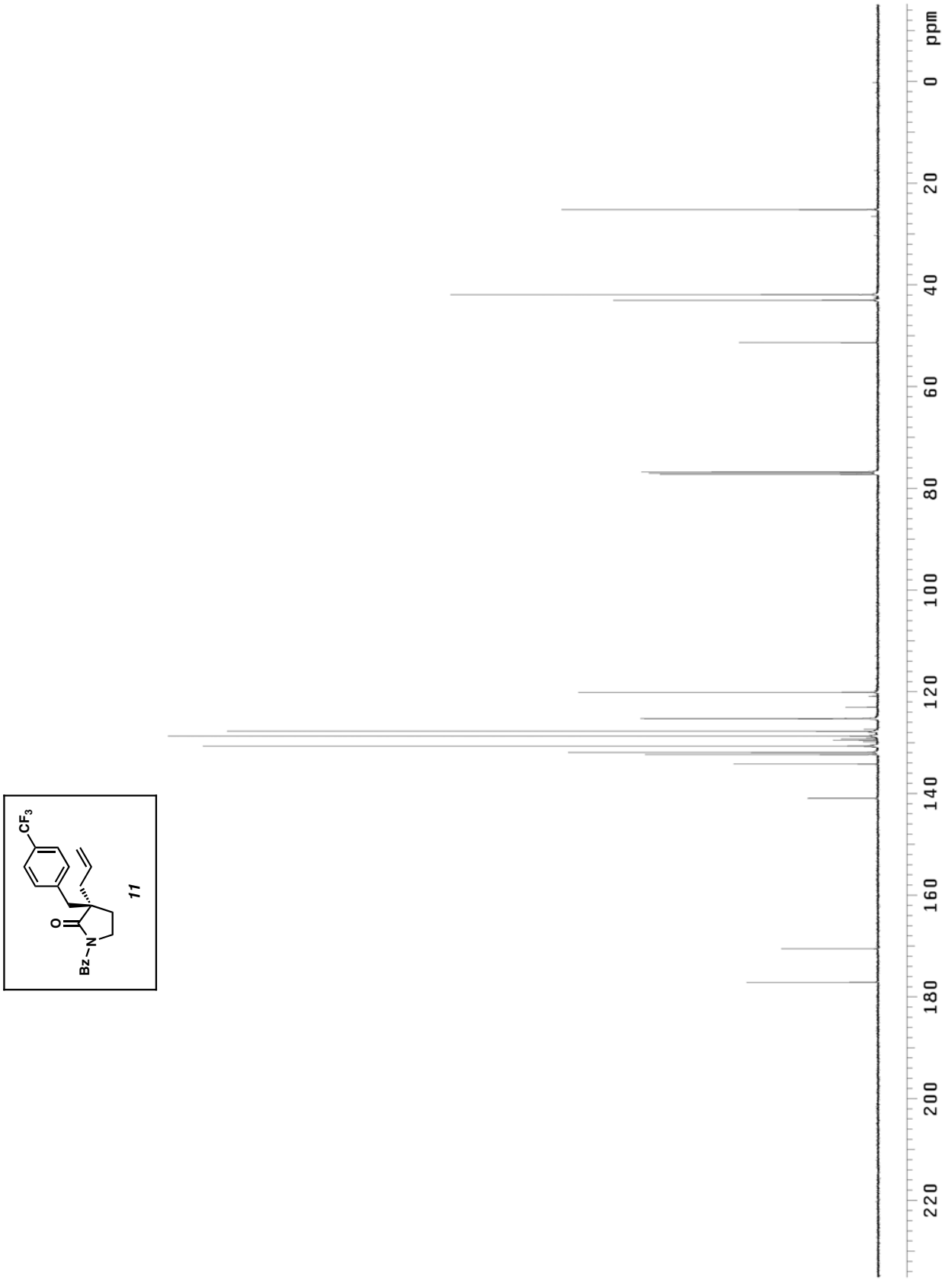


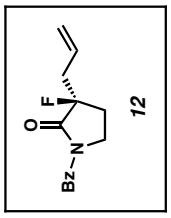


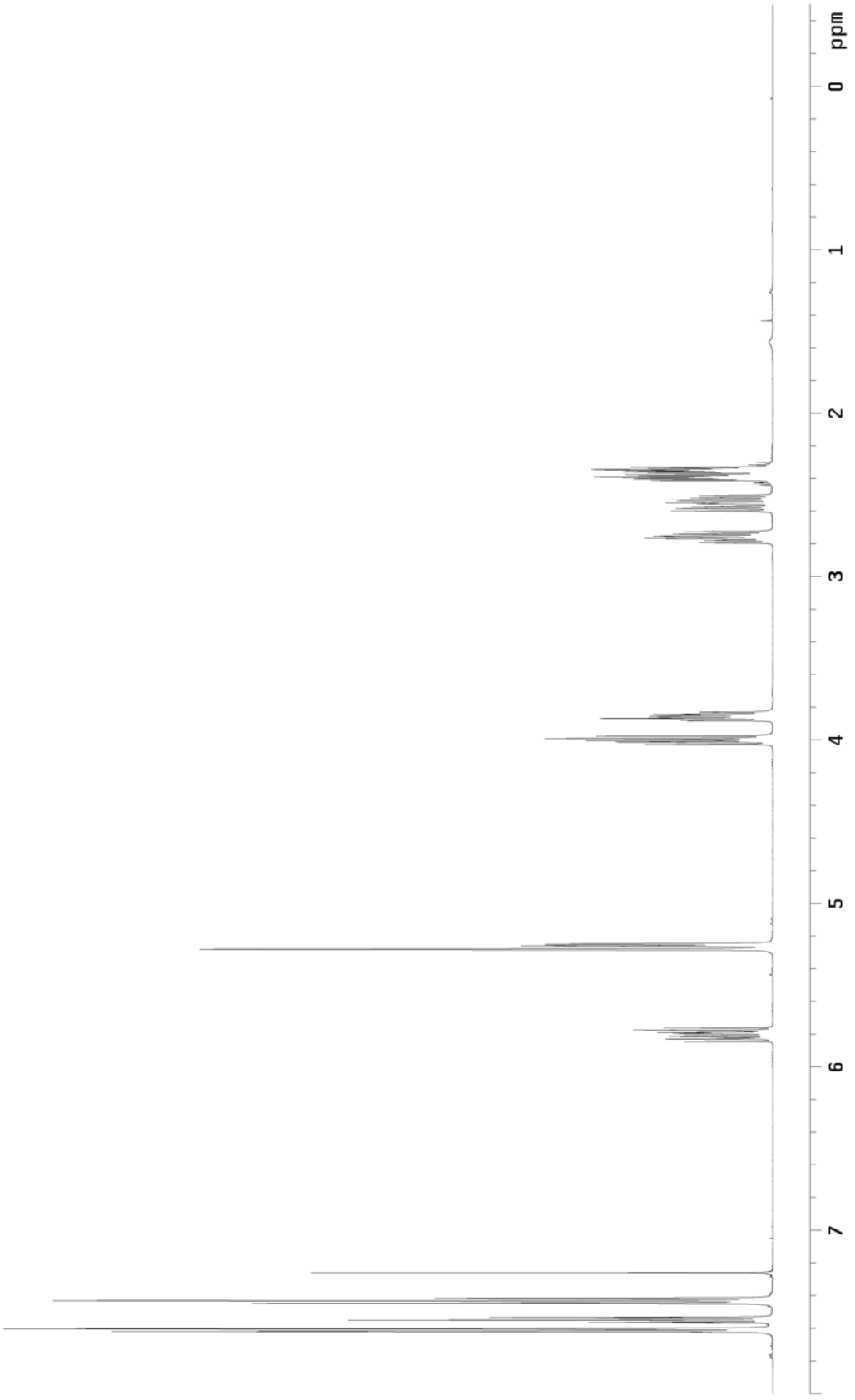


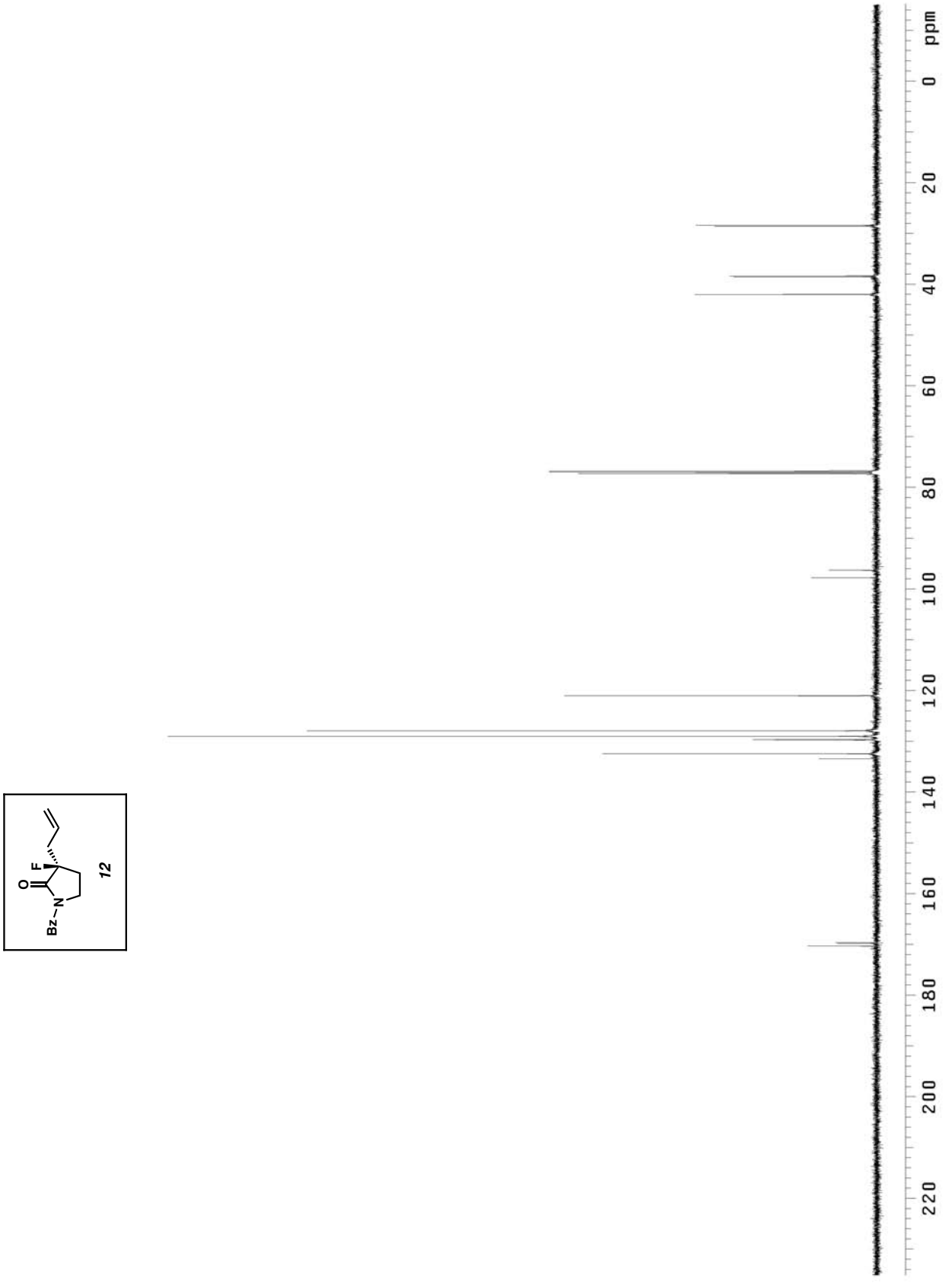


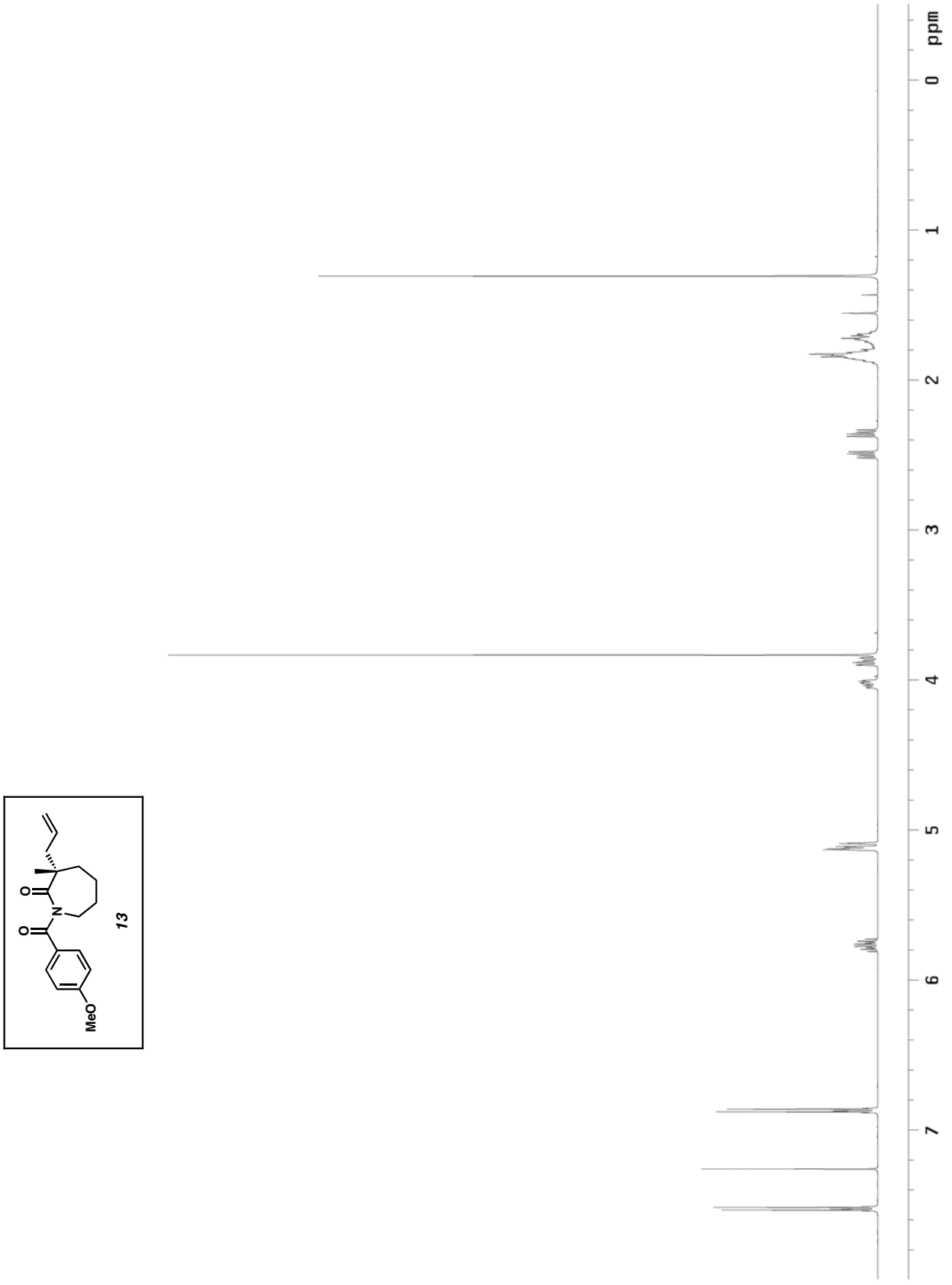


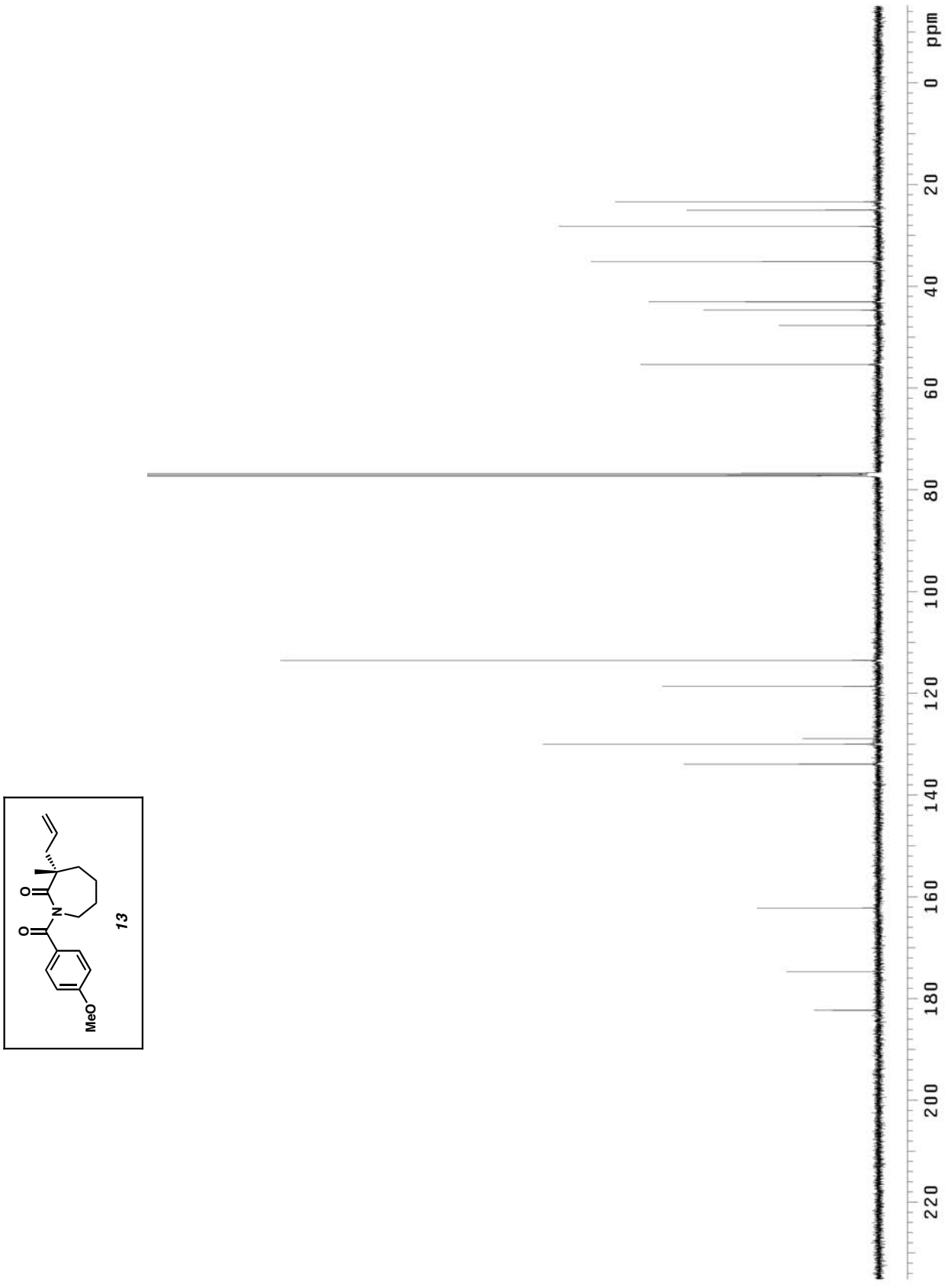


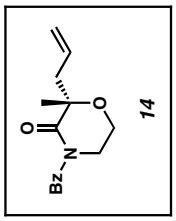


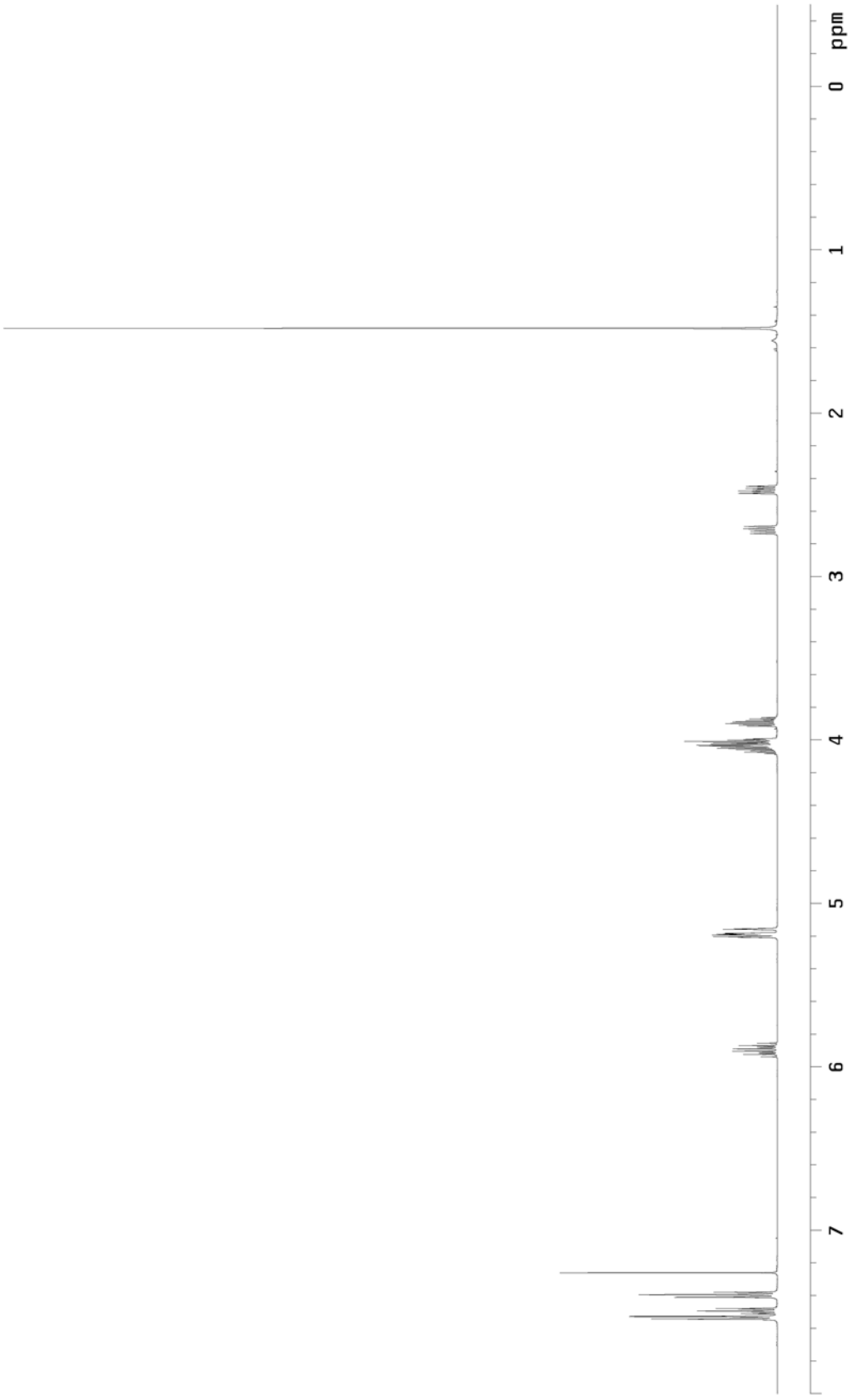


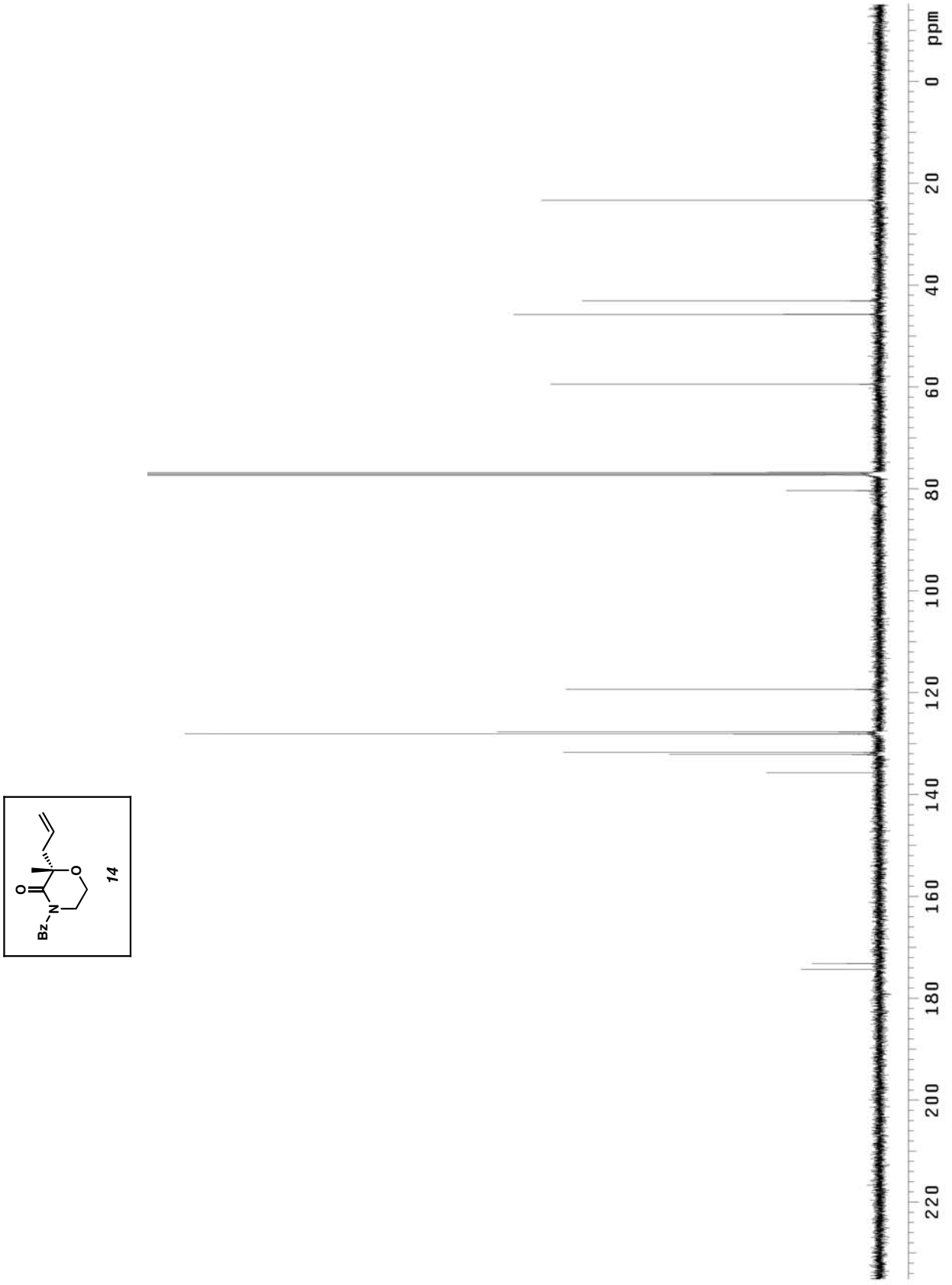


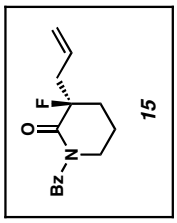


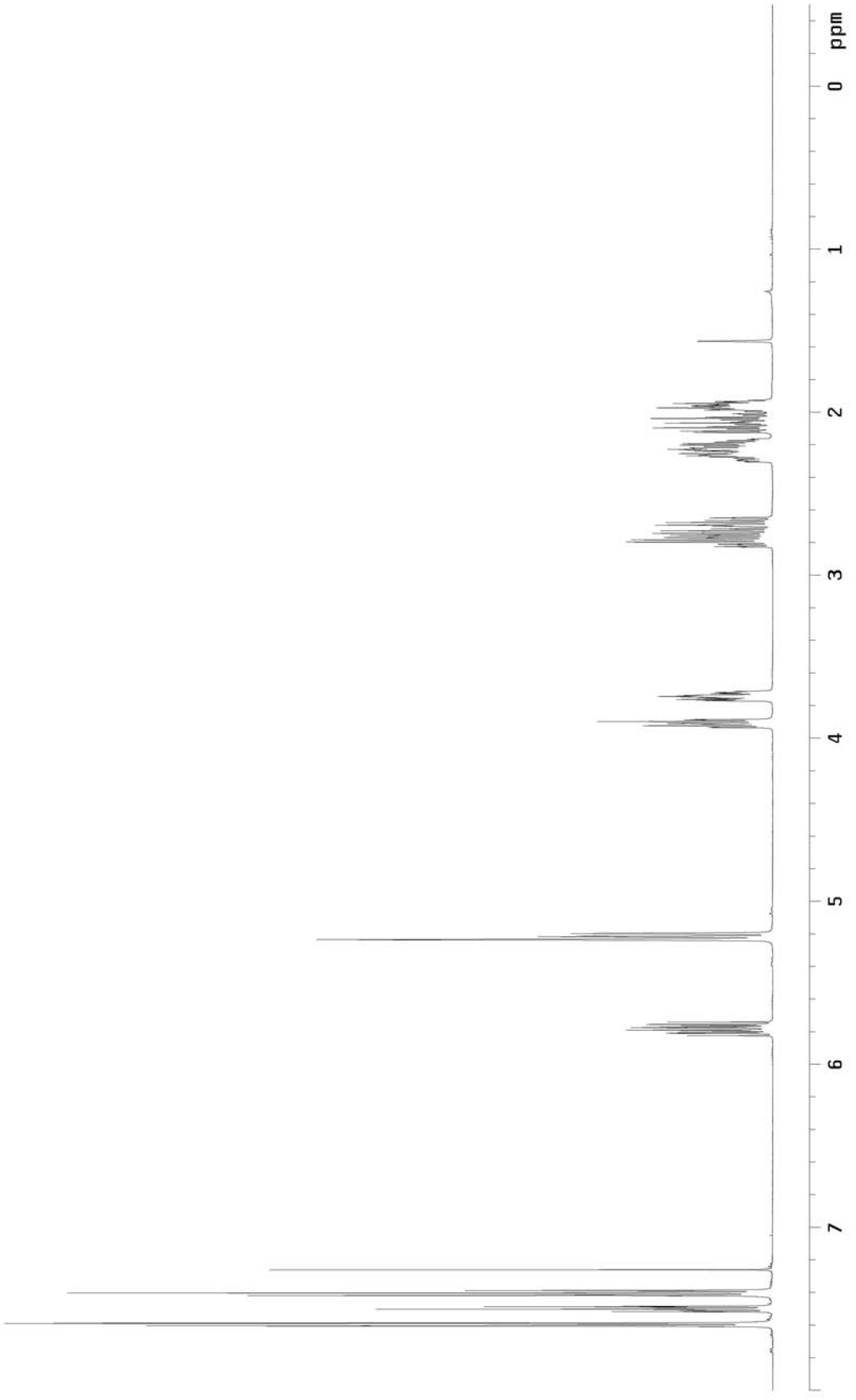


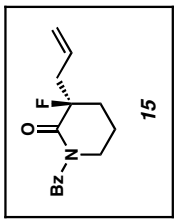


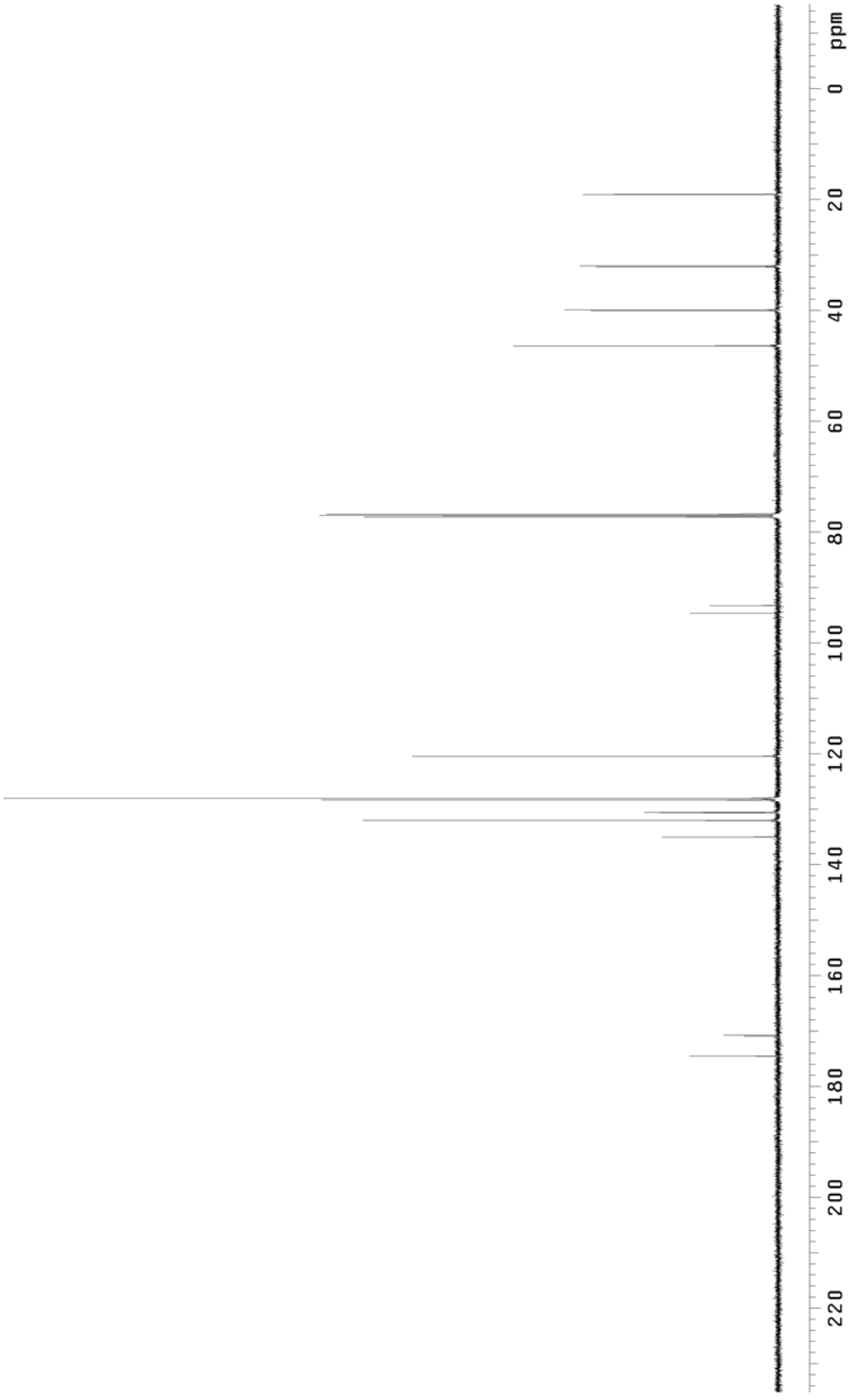


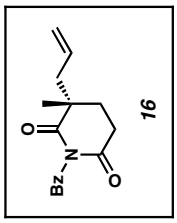


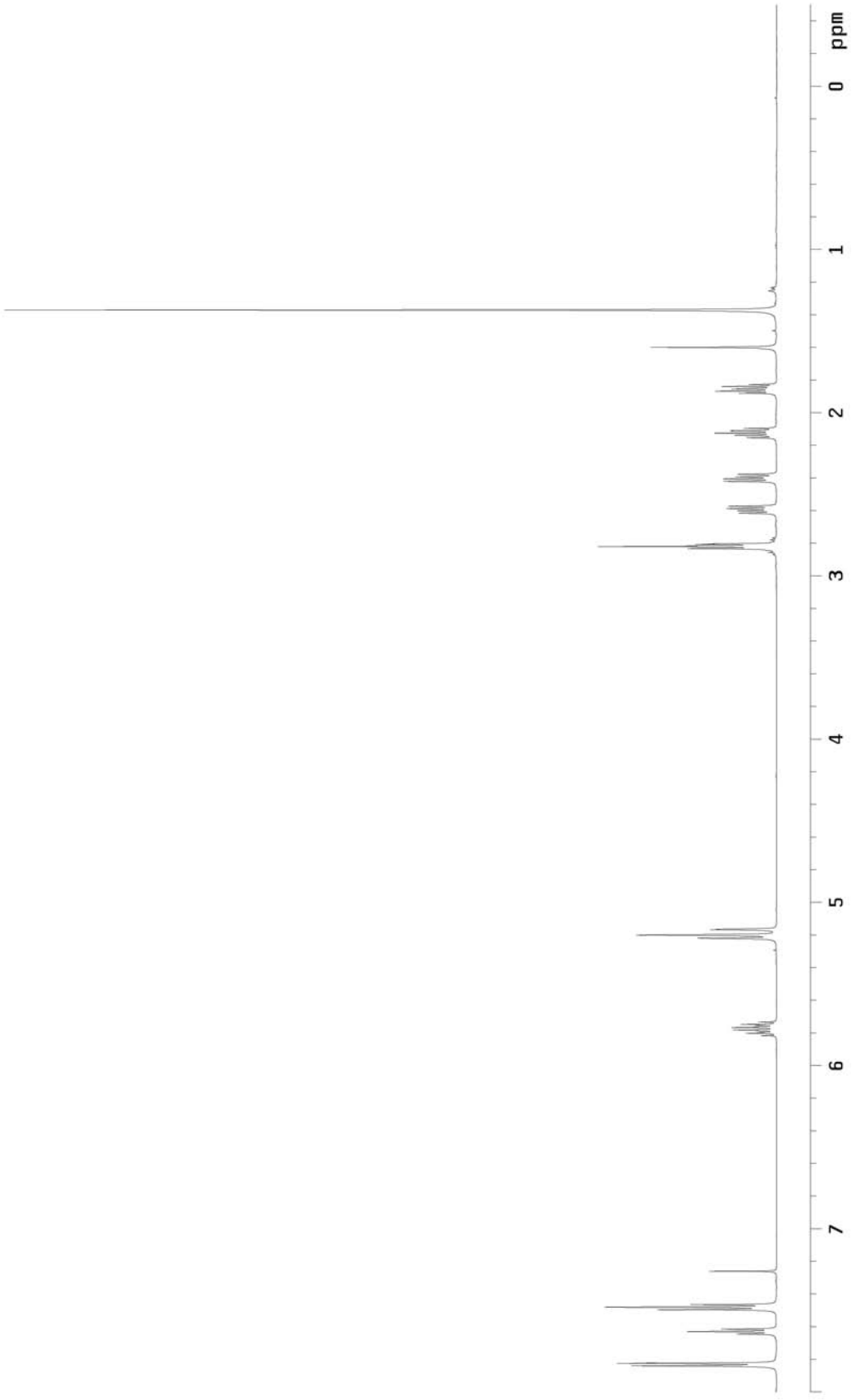


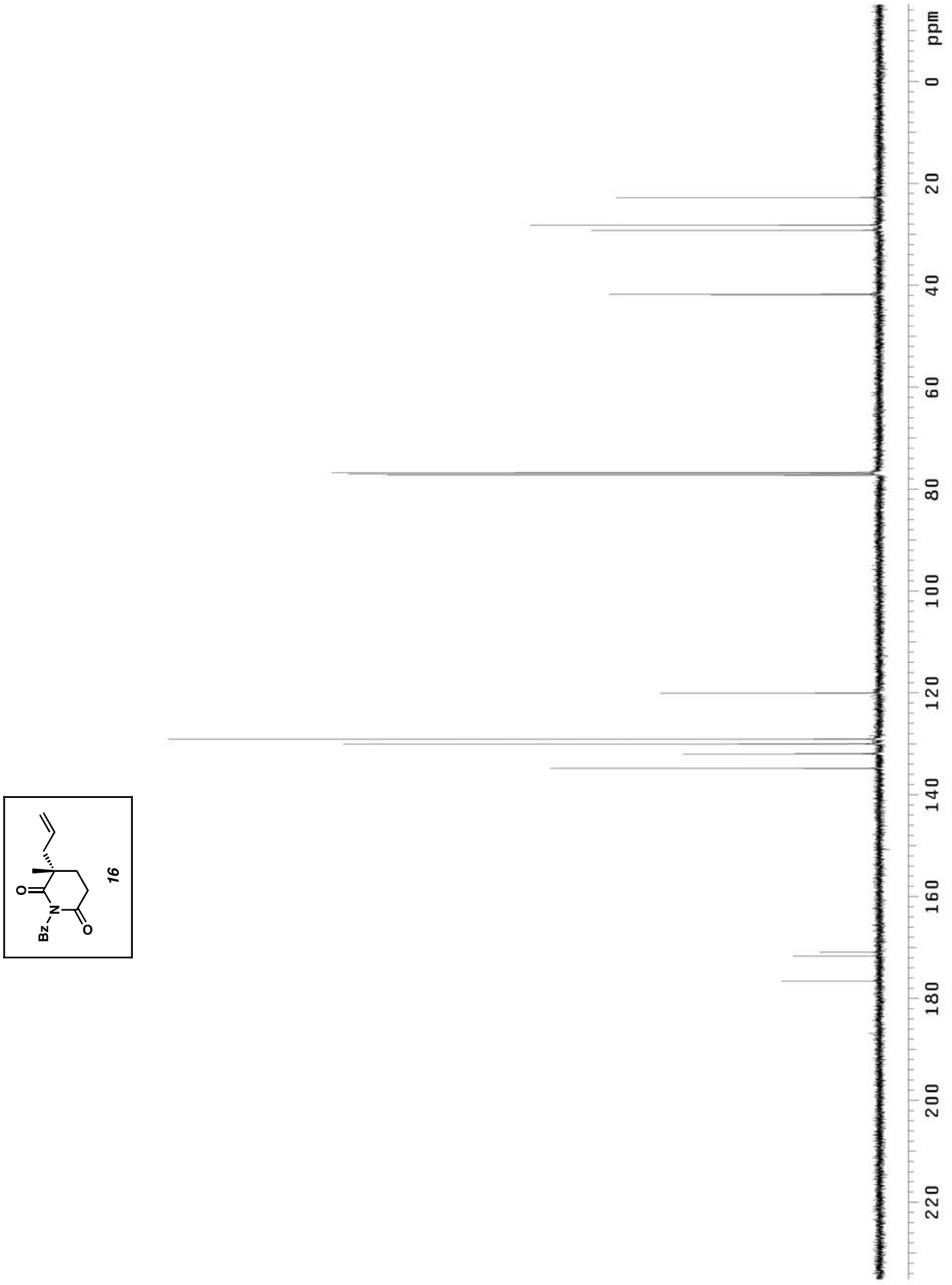


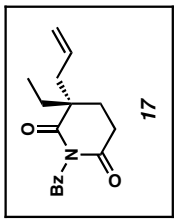


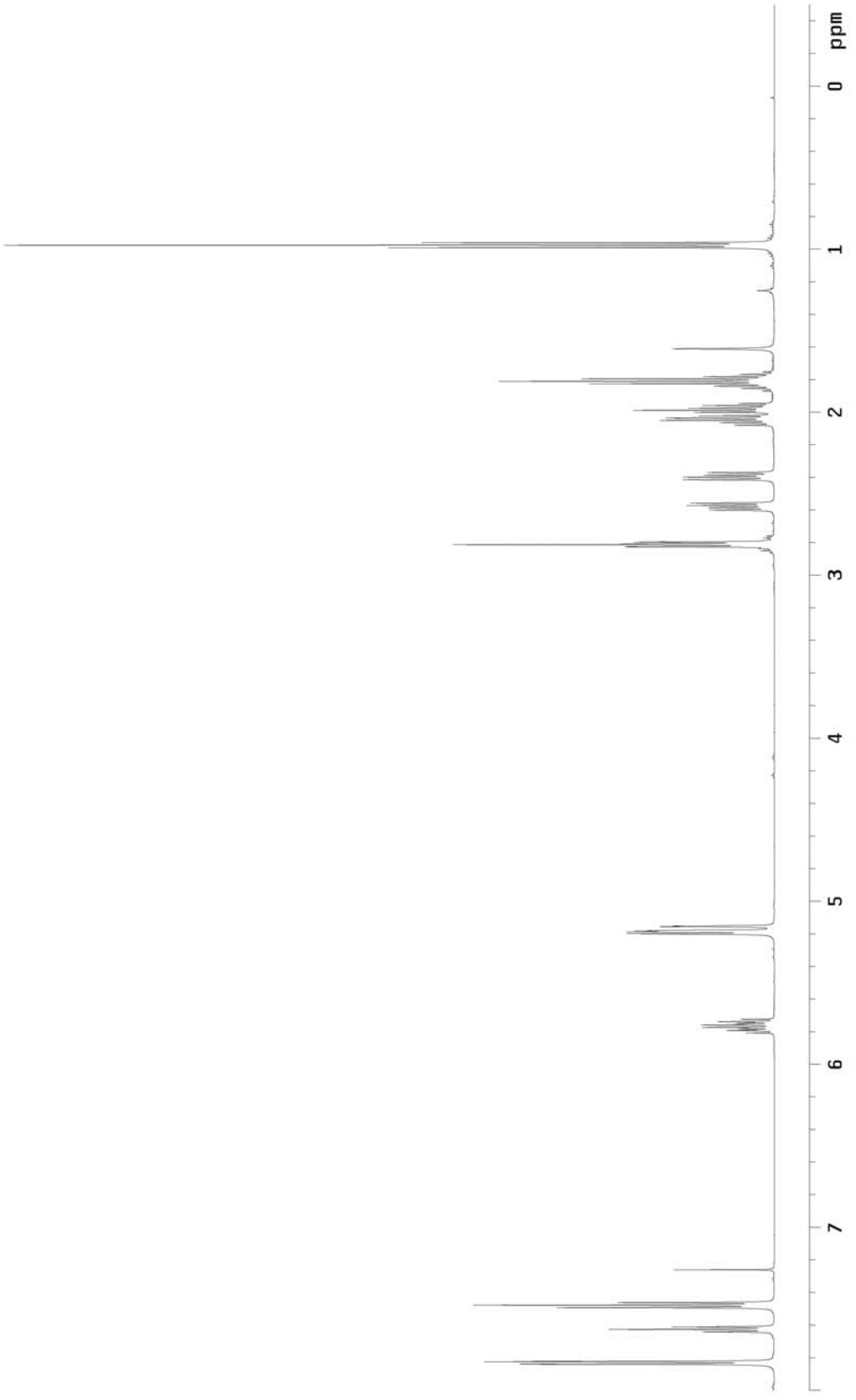


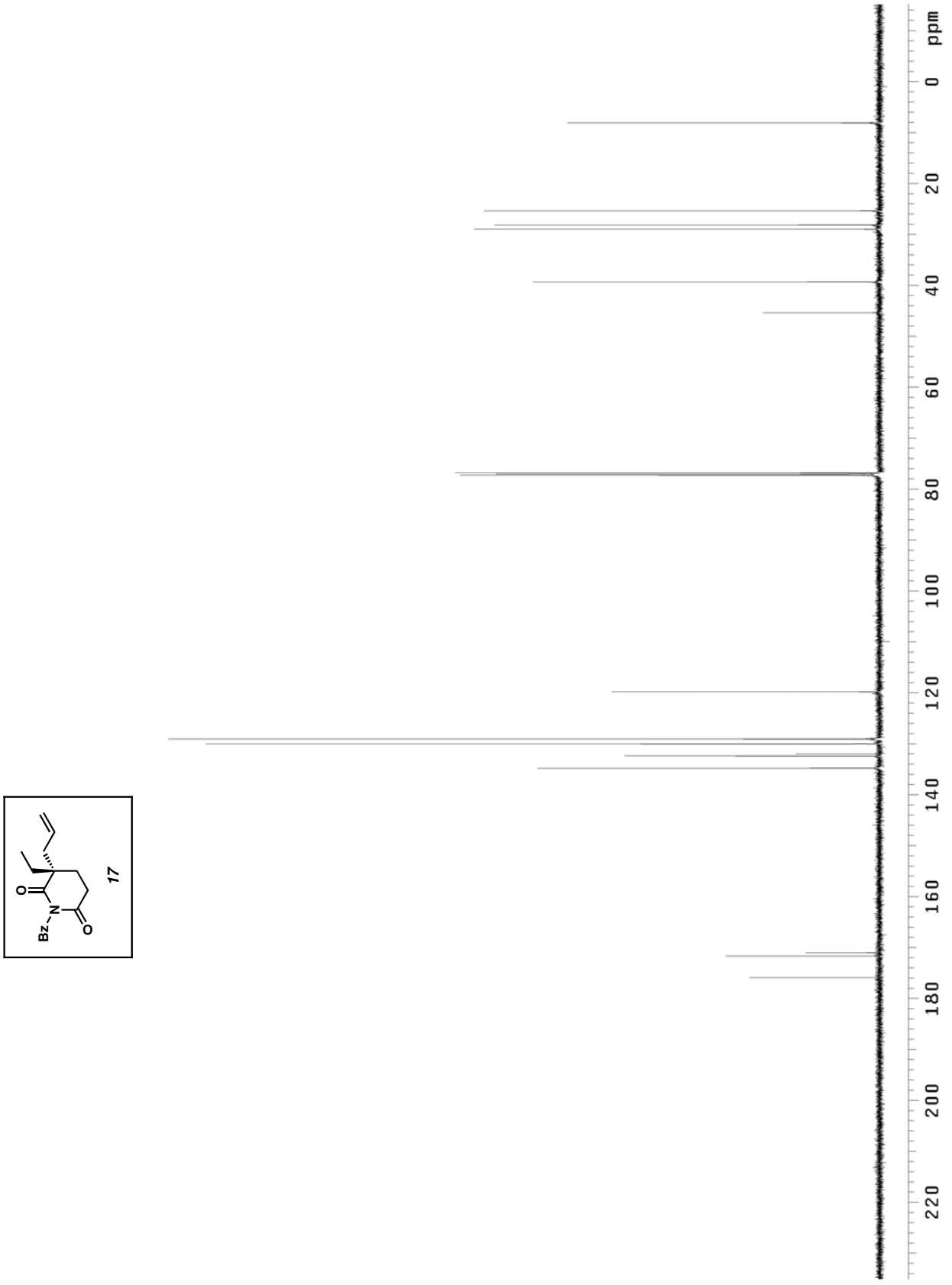


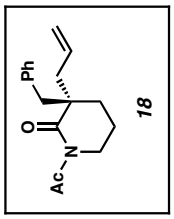


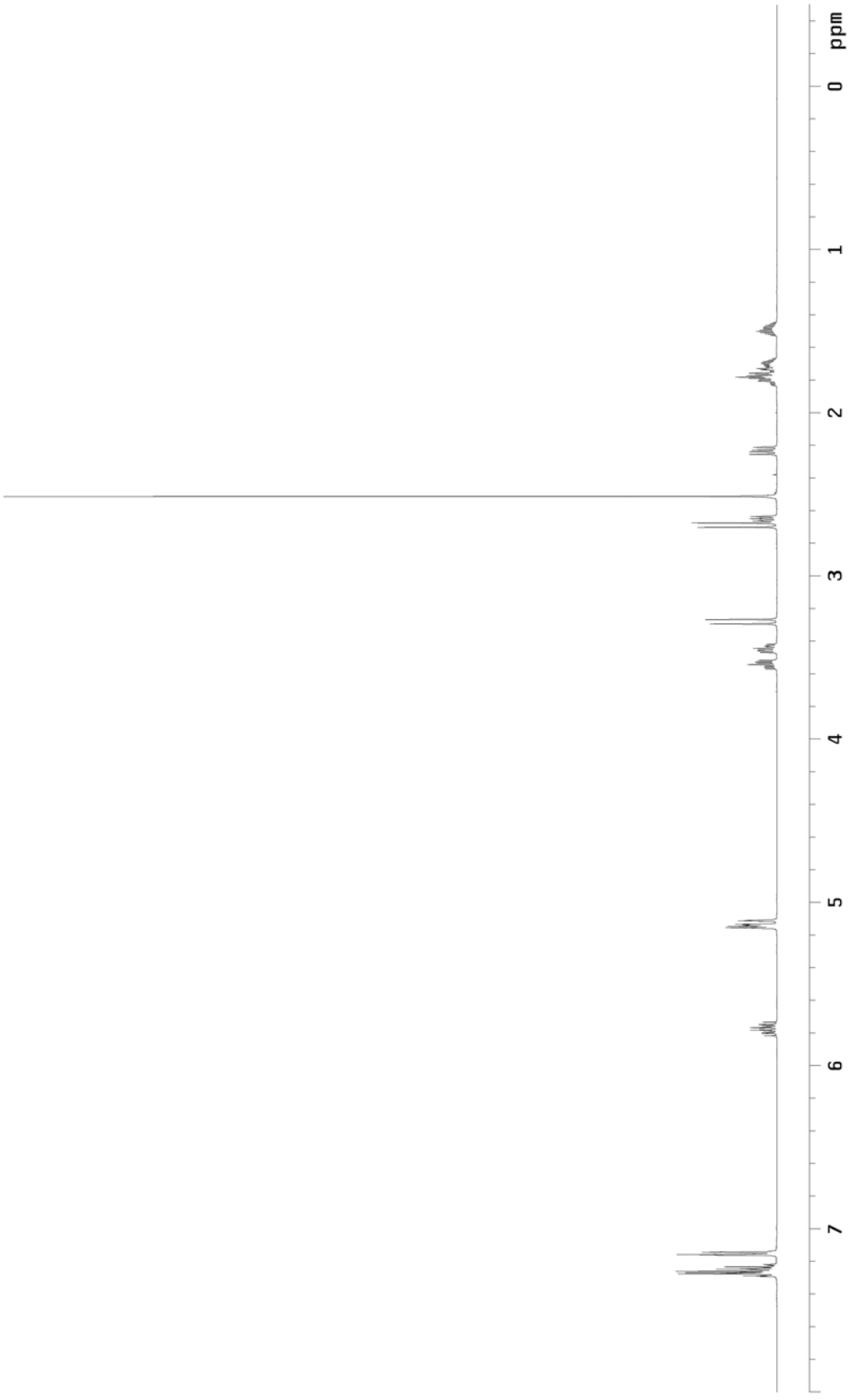


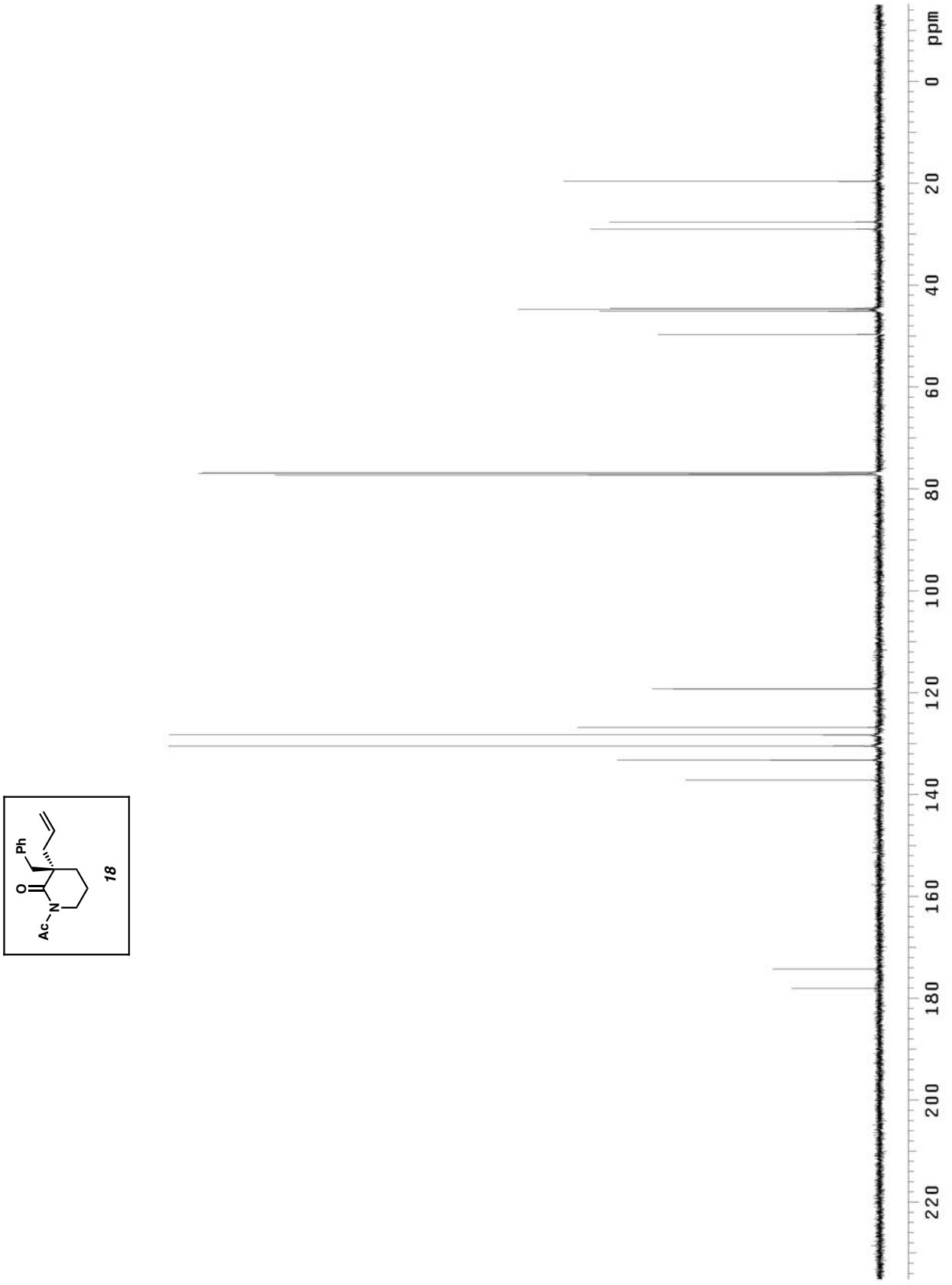


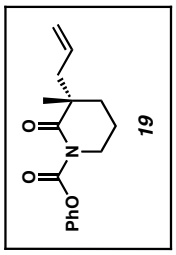


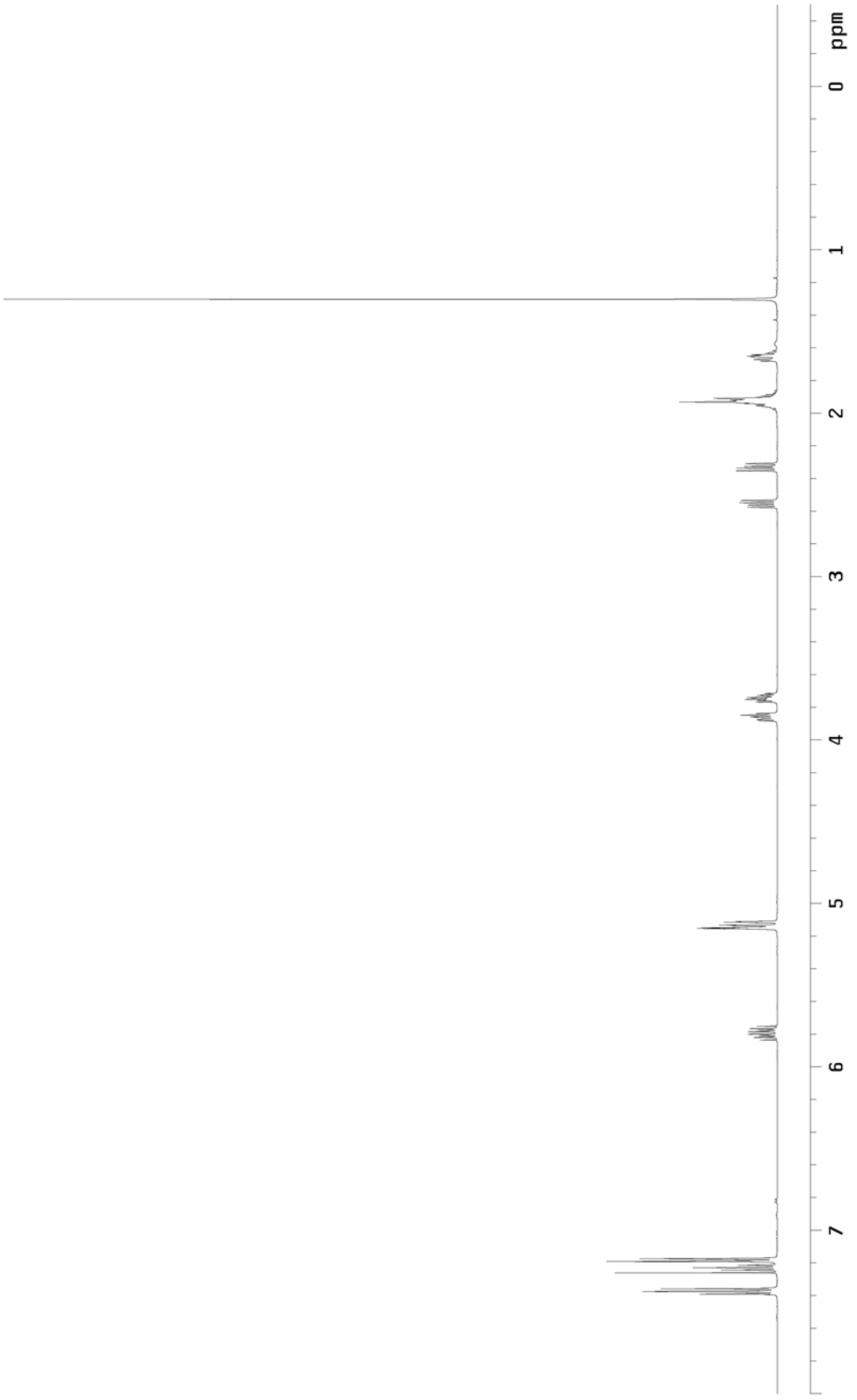


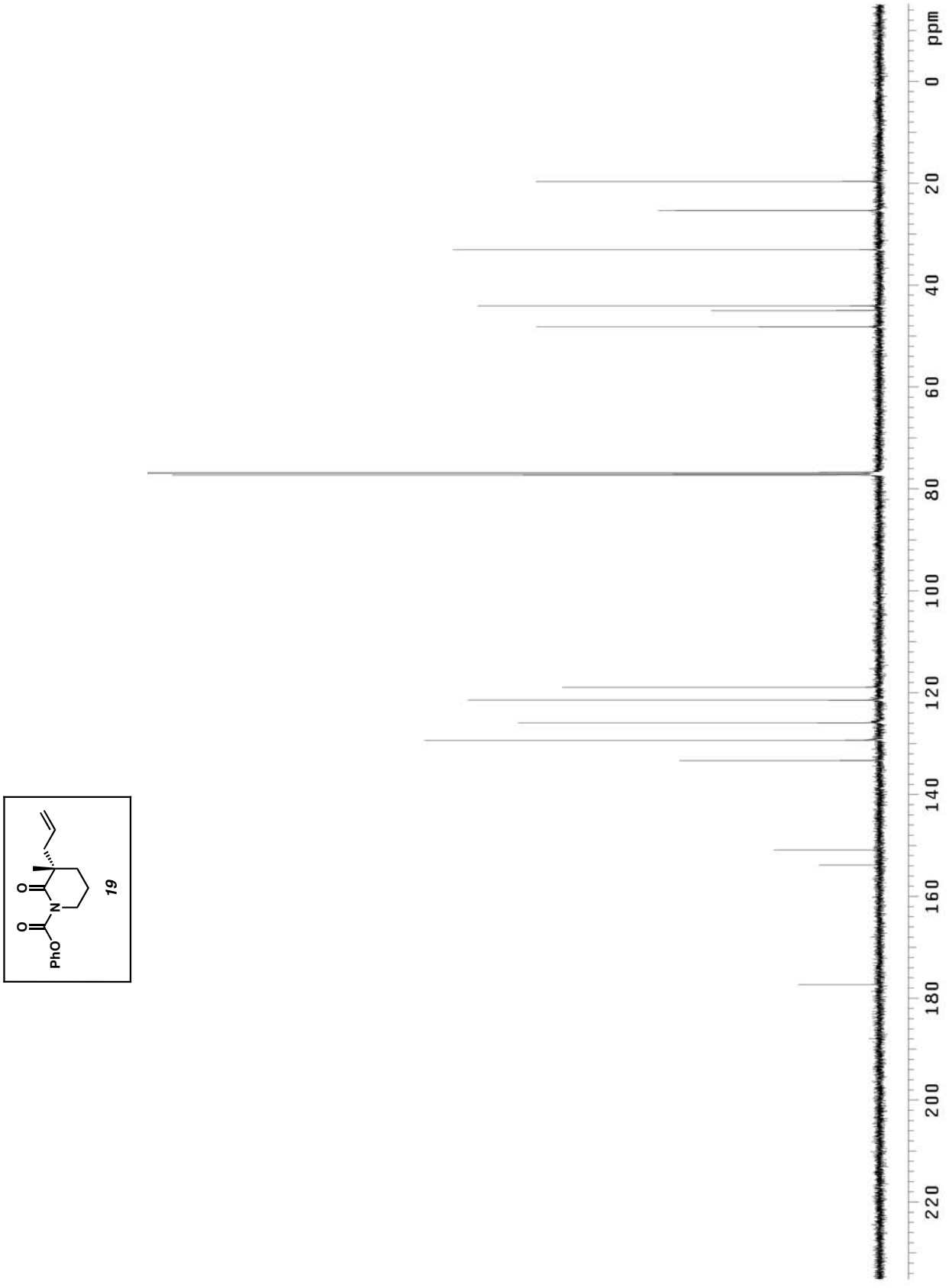


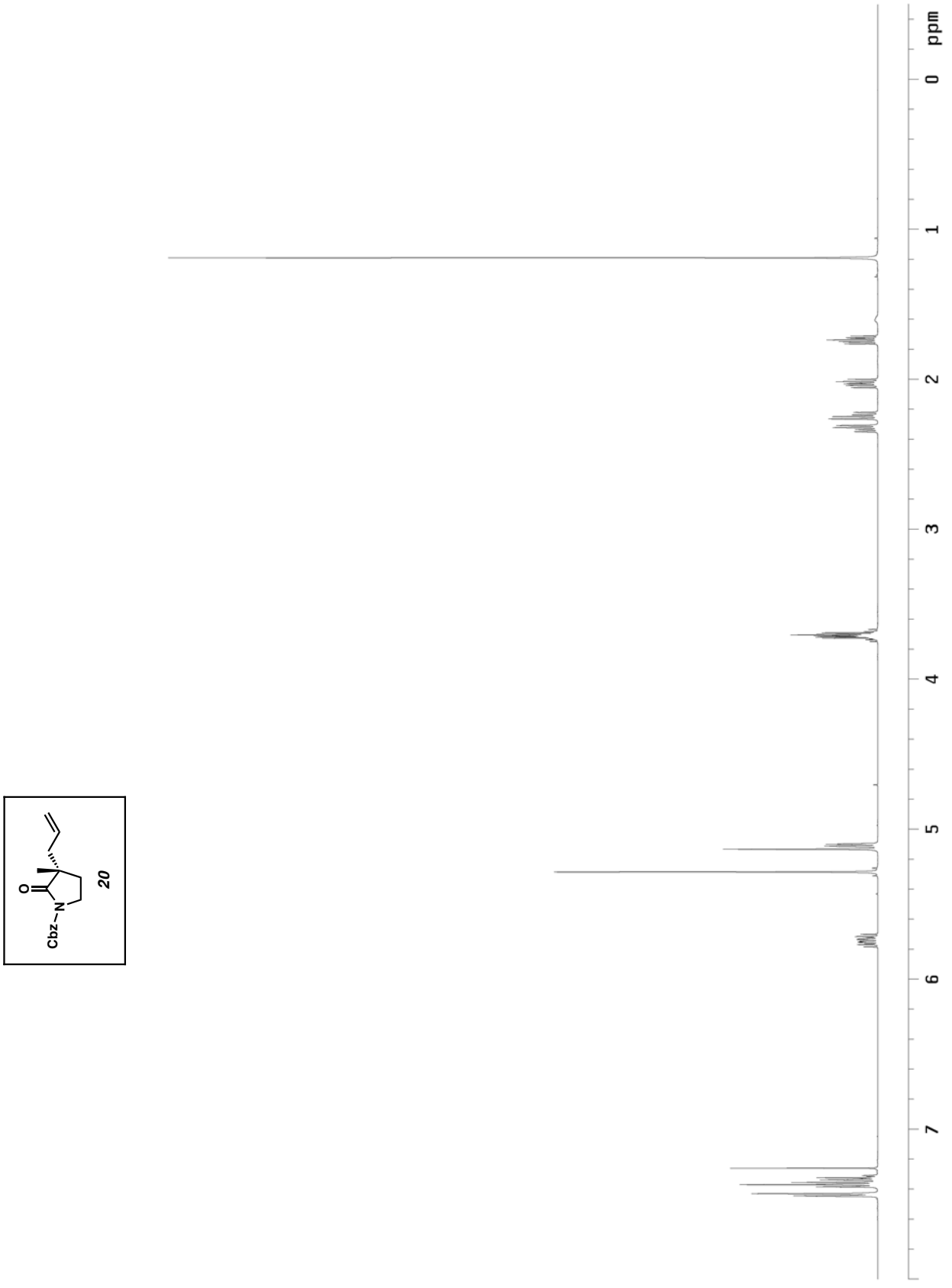


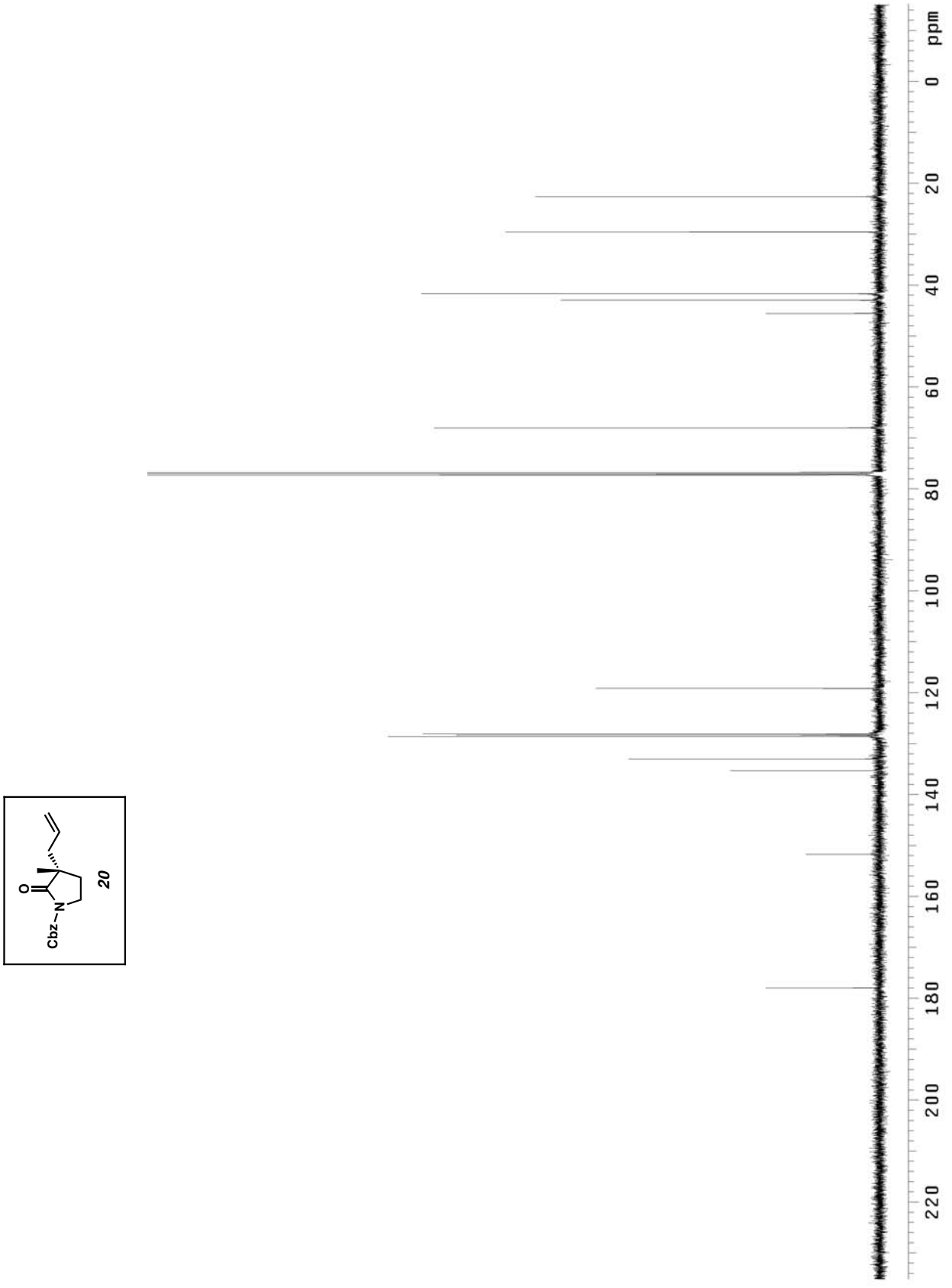


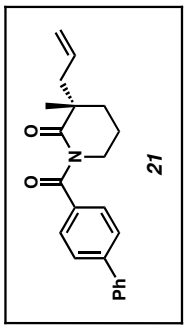


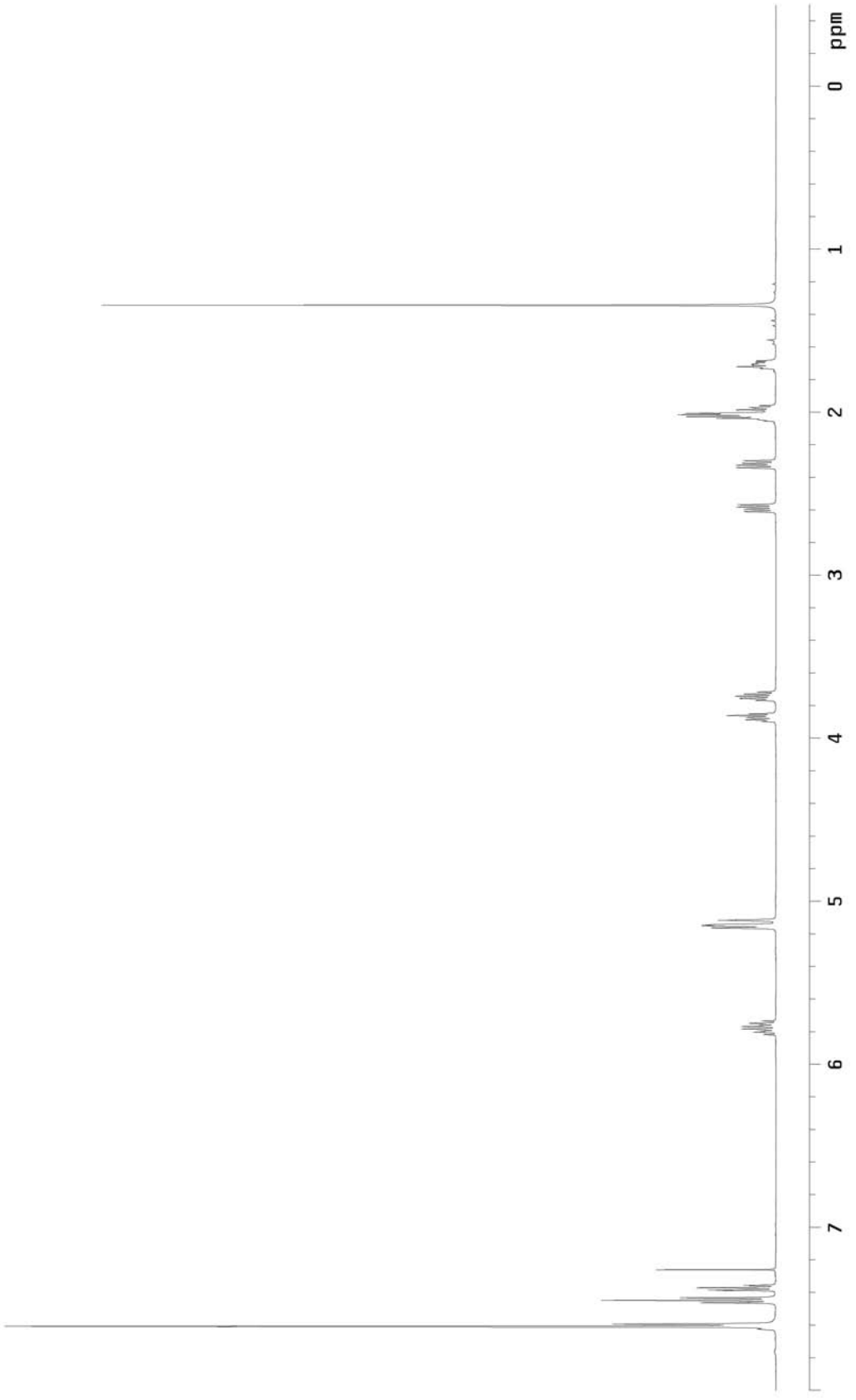


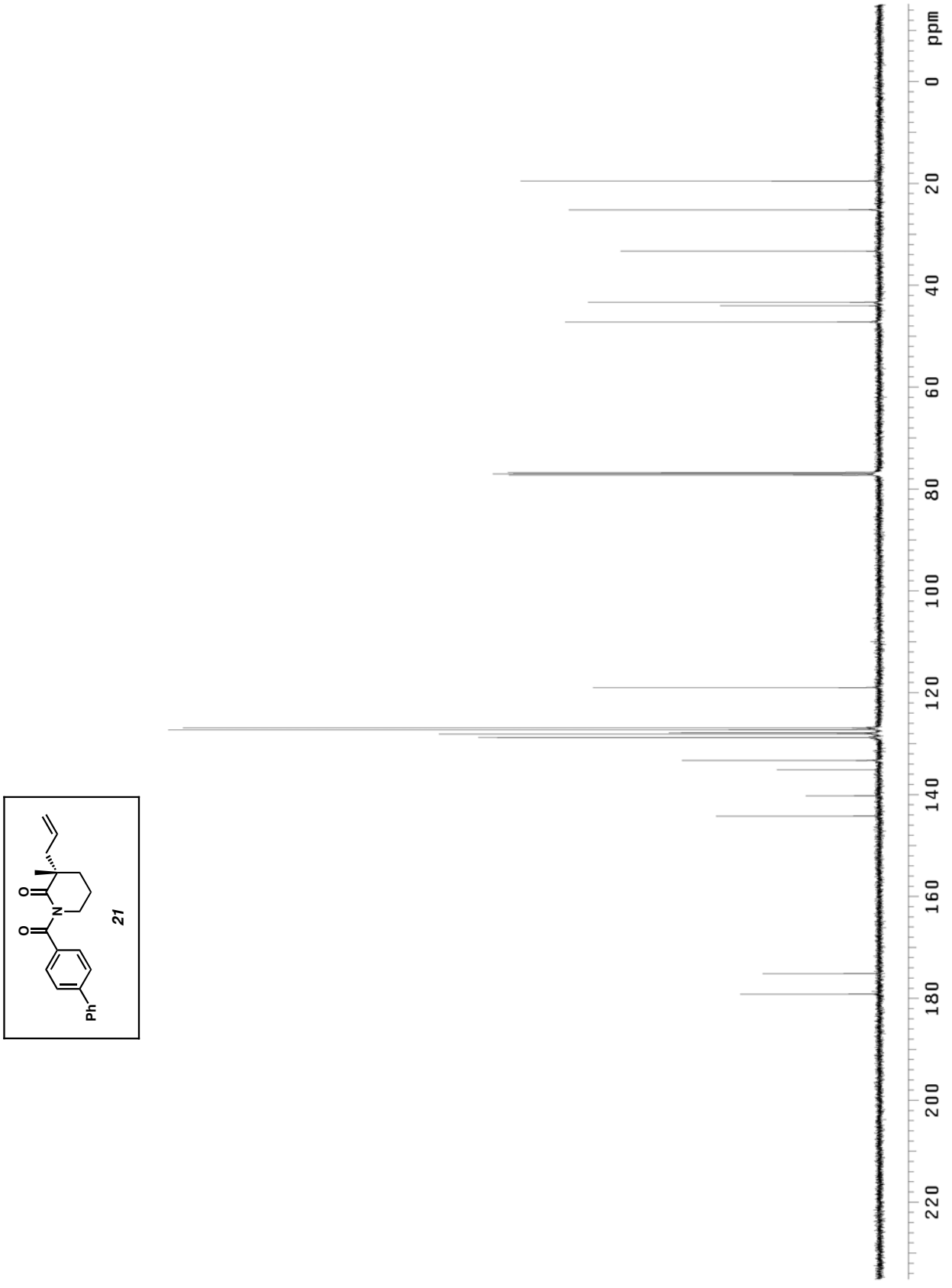


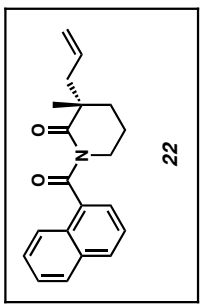


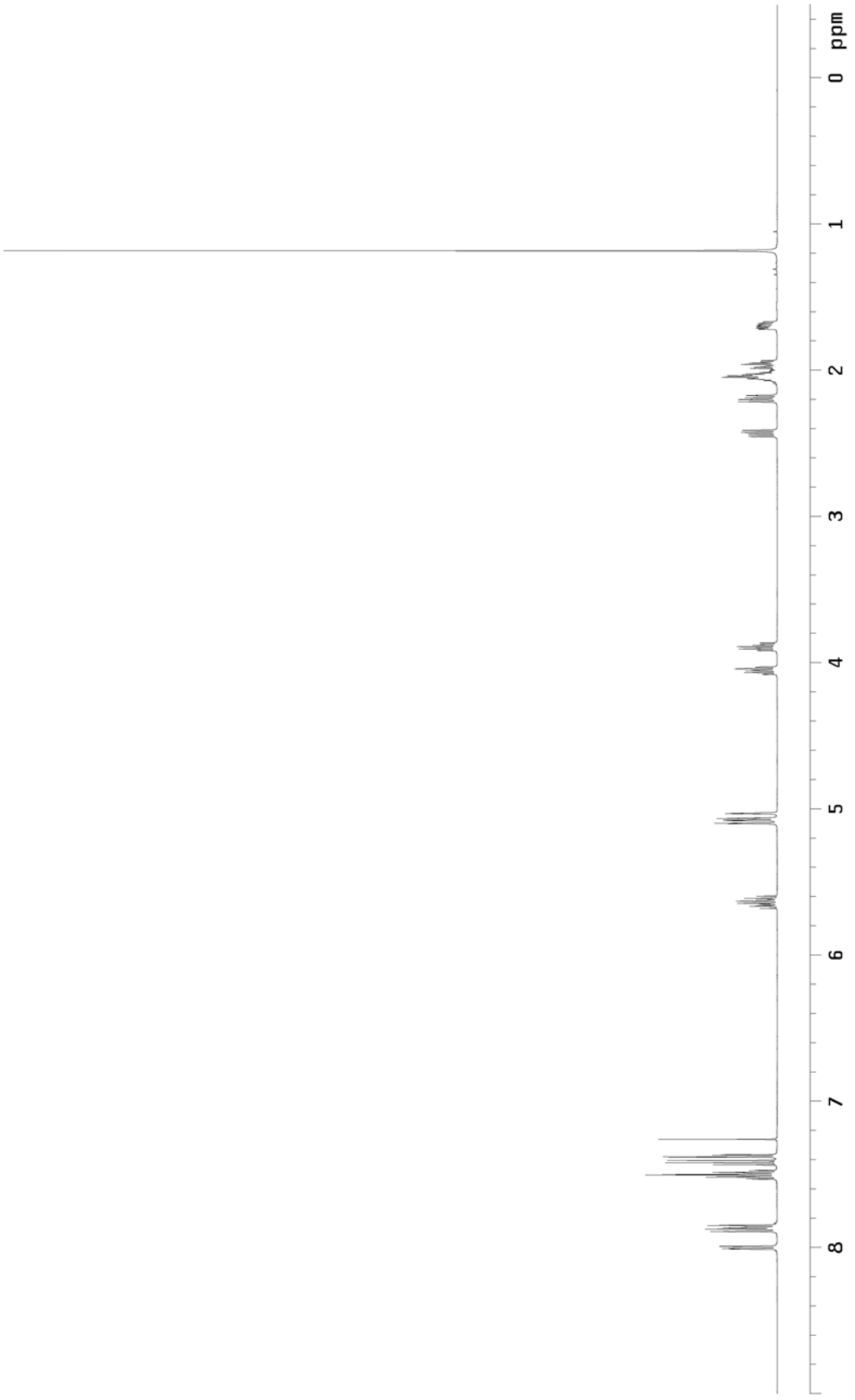


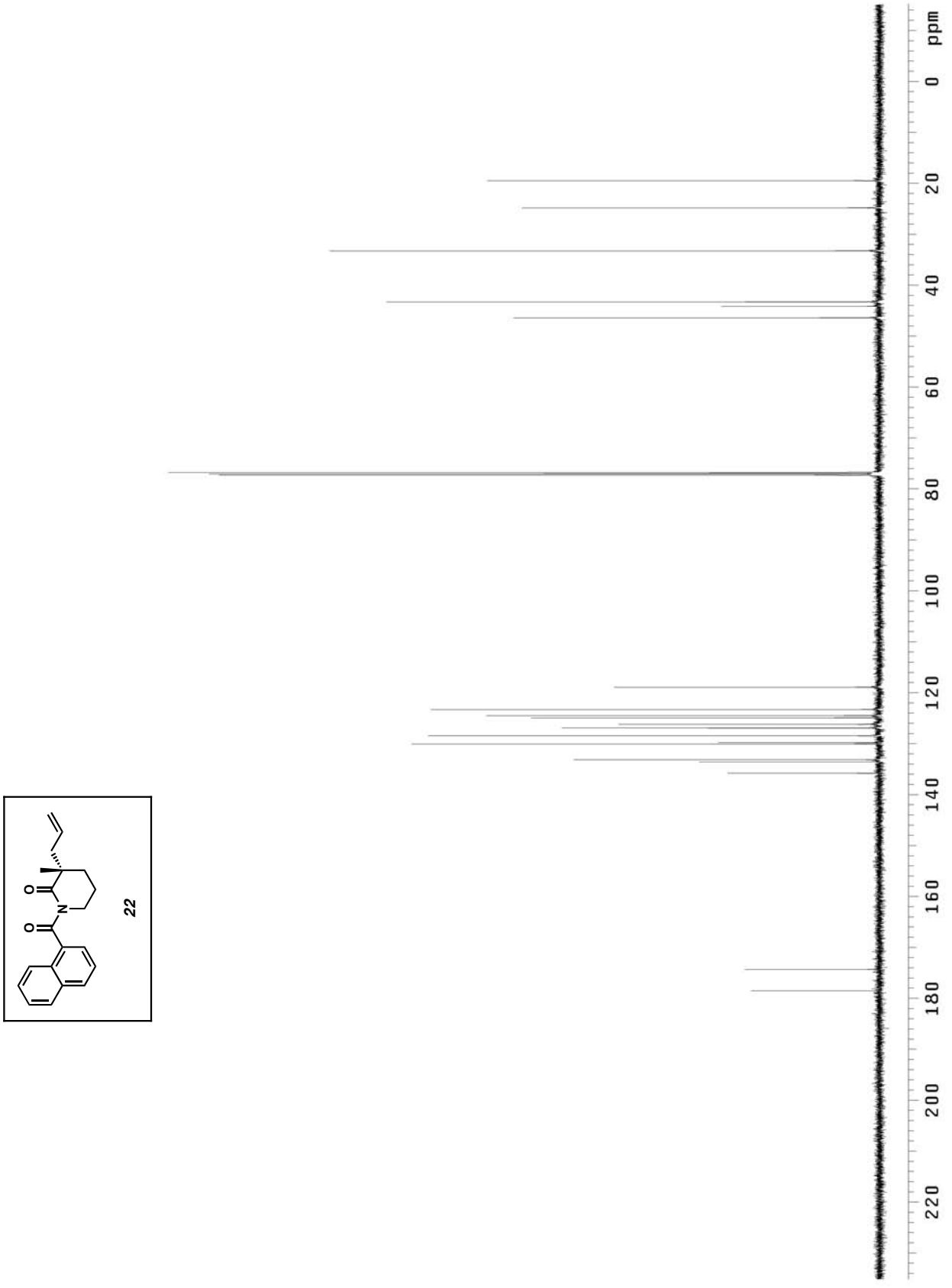


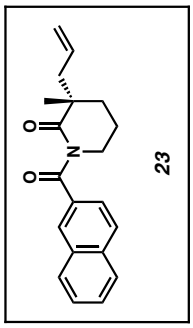


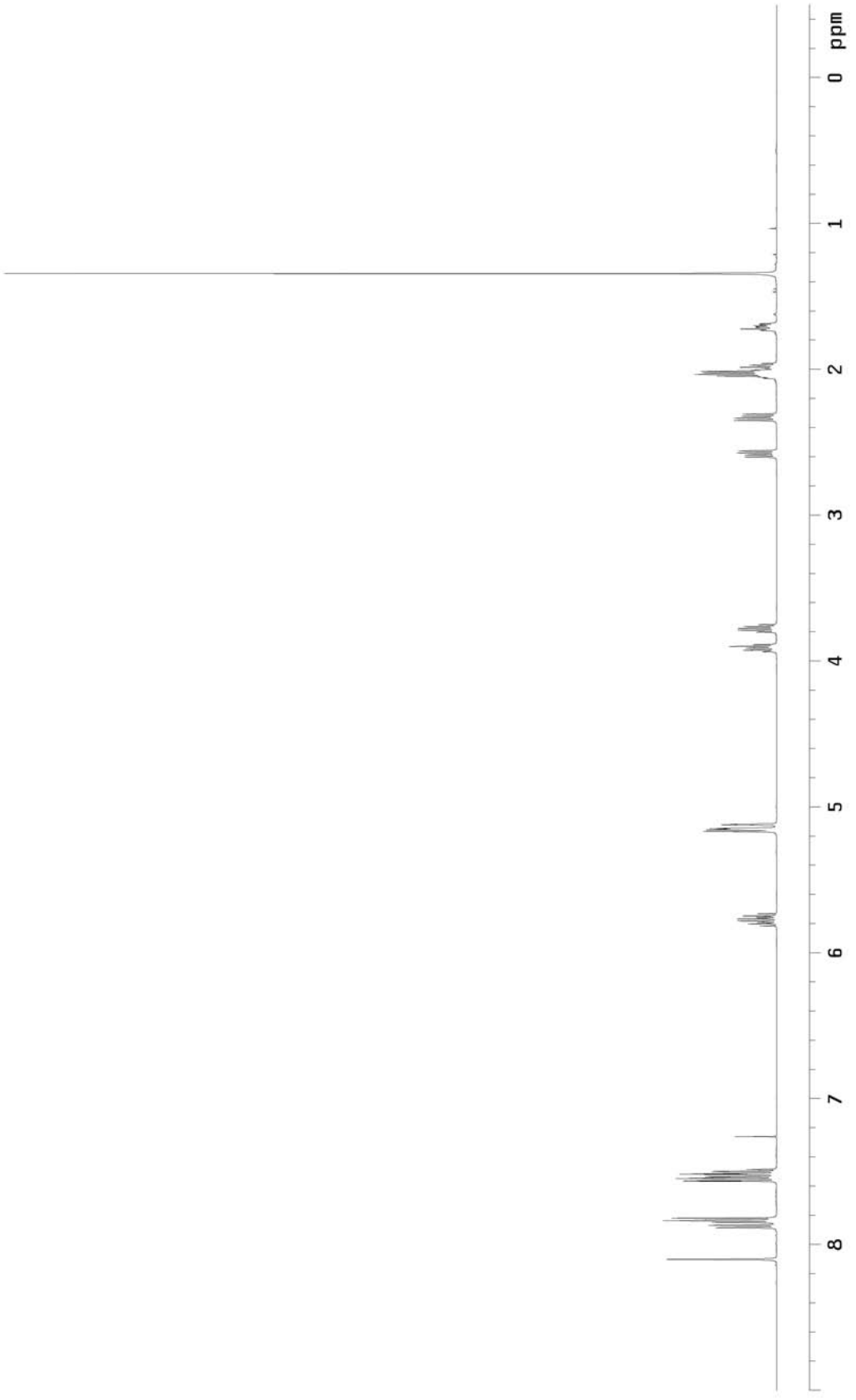


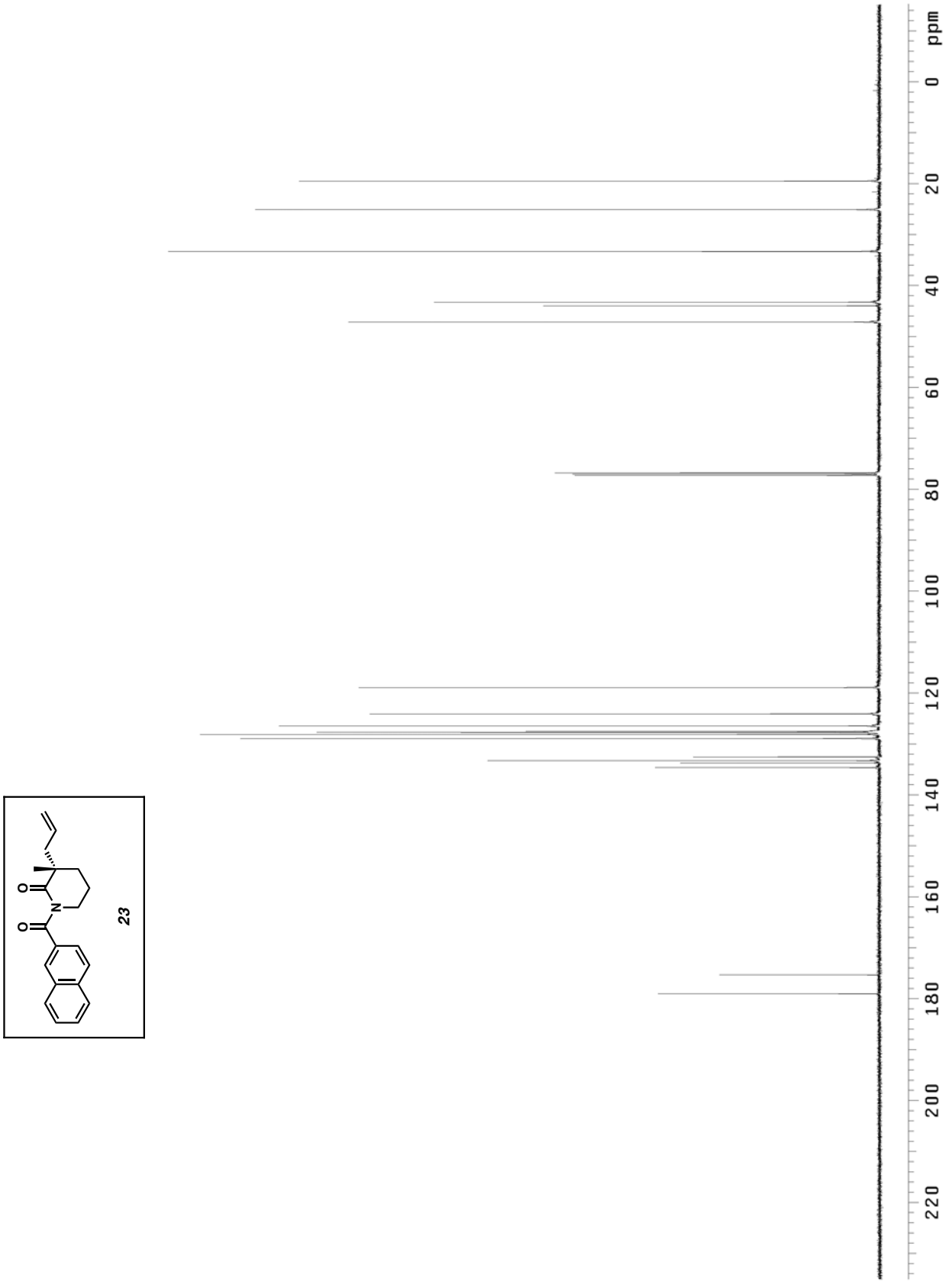




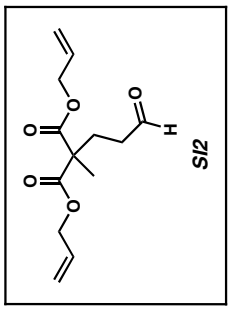


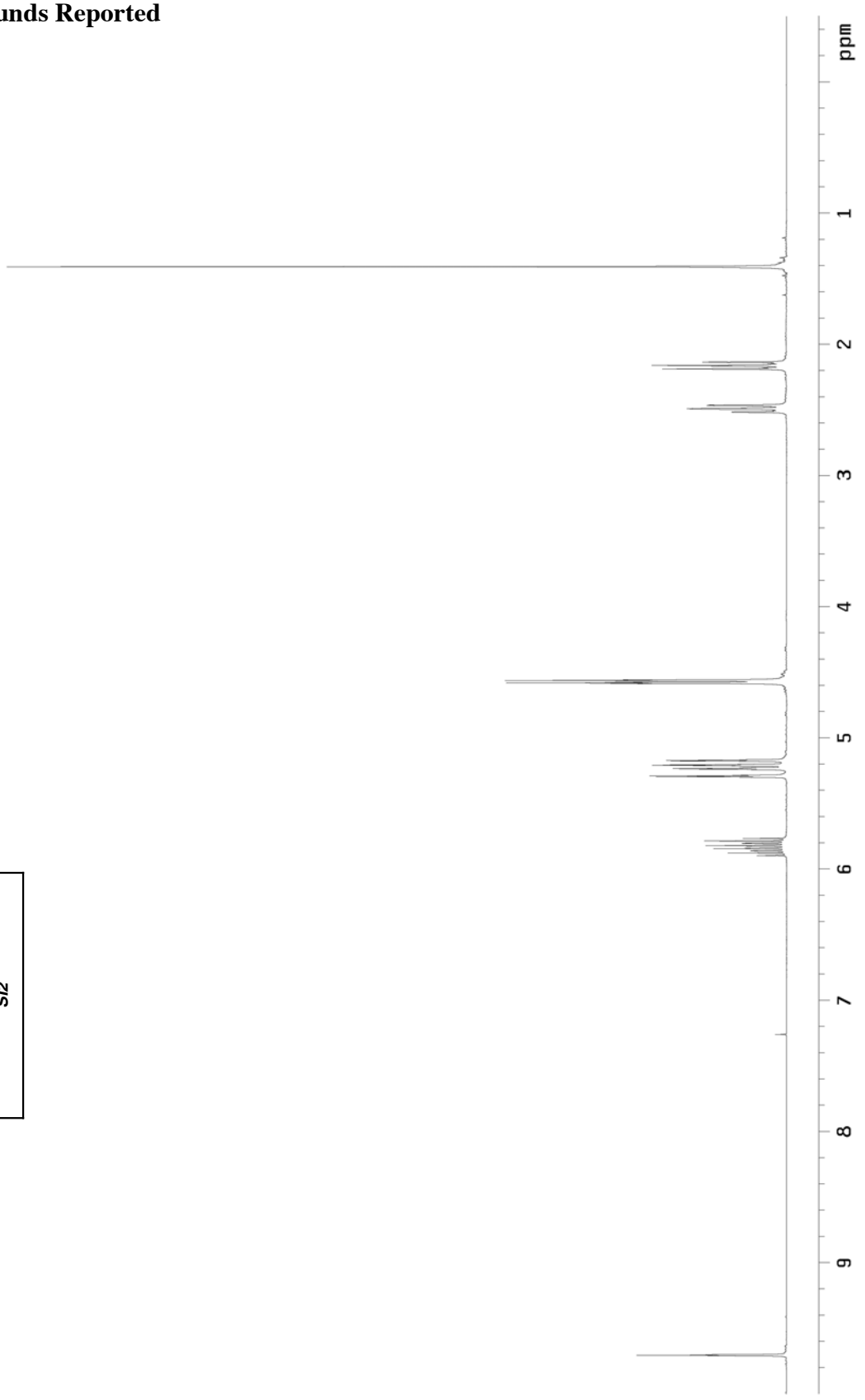


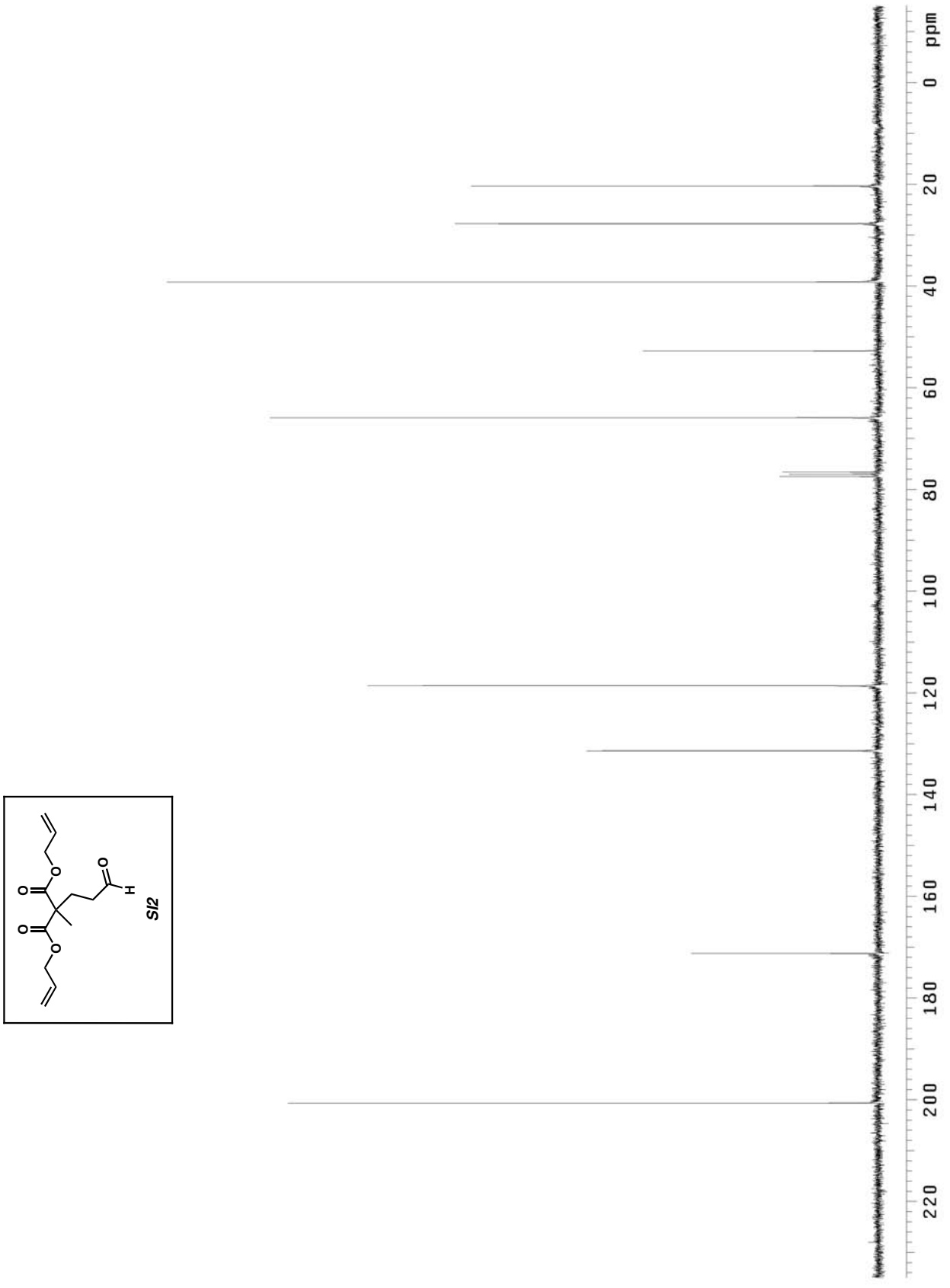


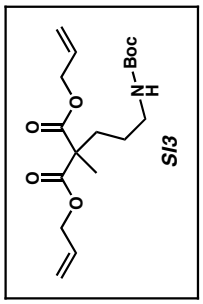


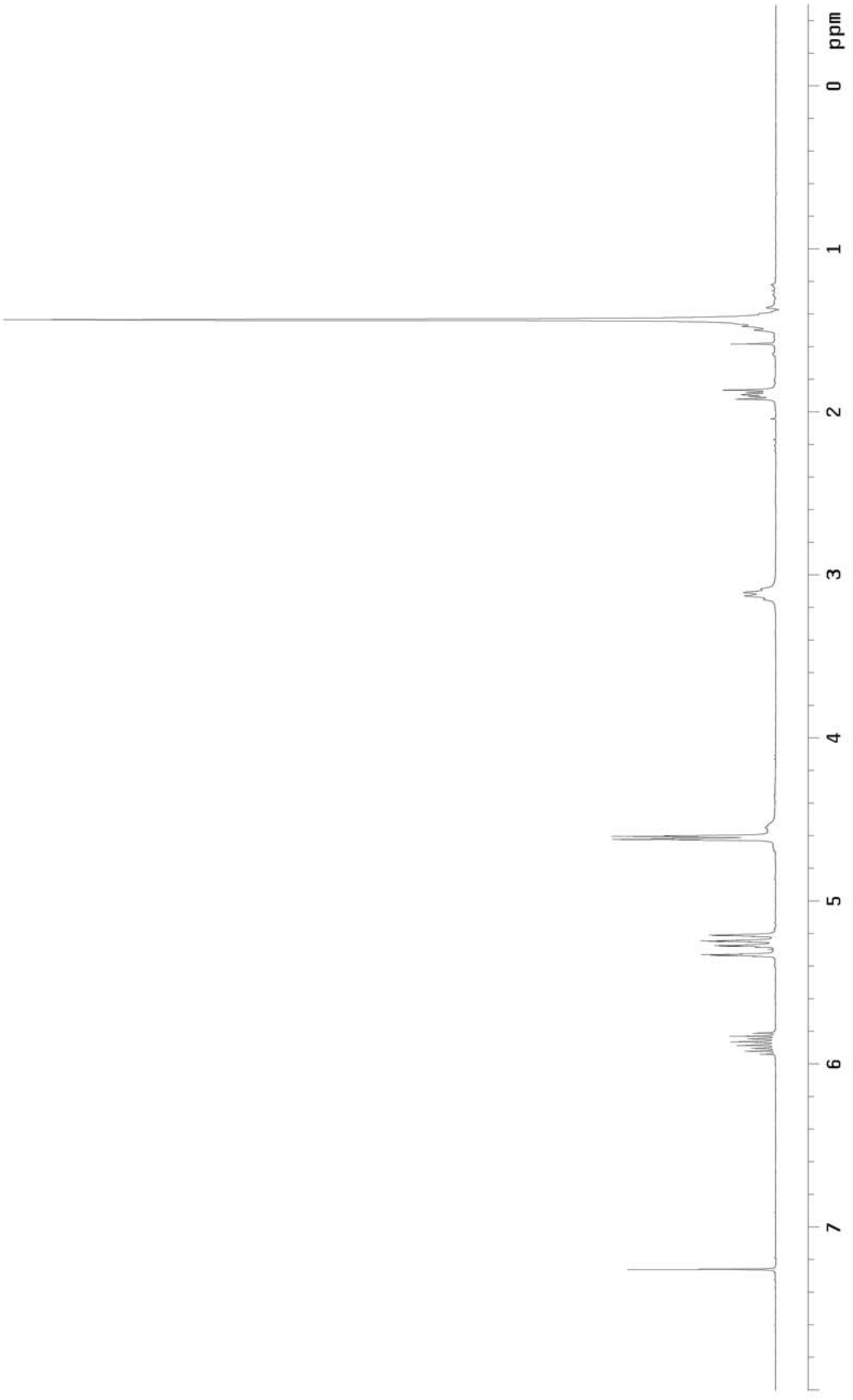
Other Compounds Reported

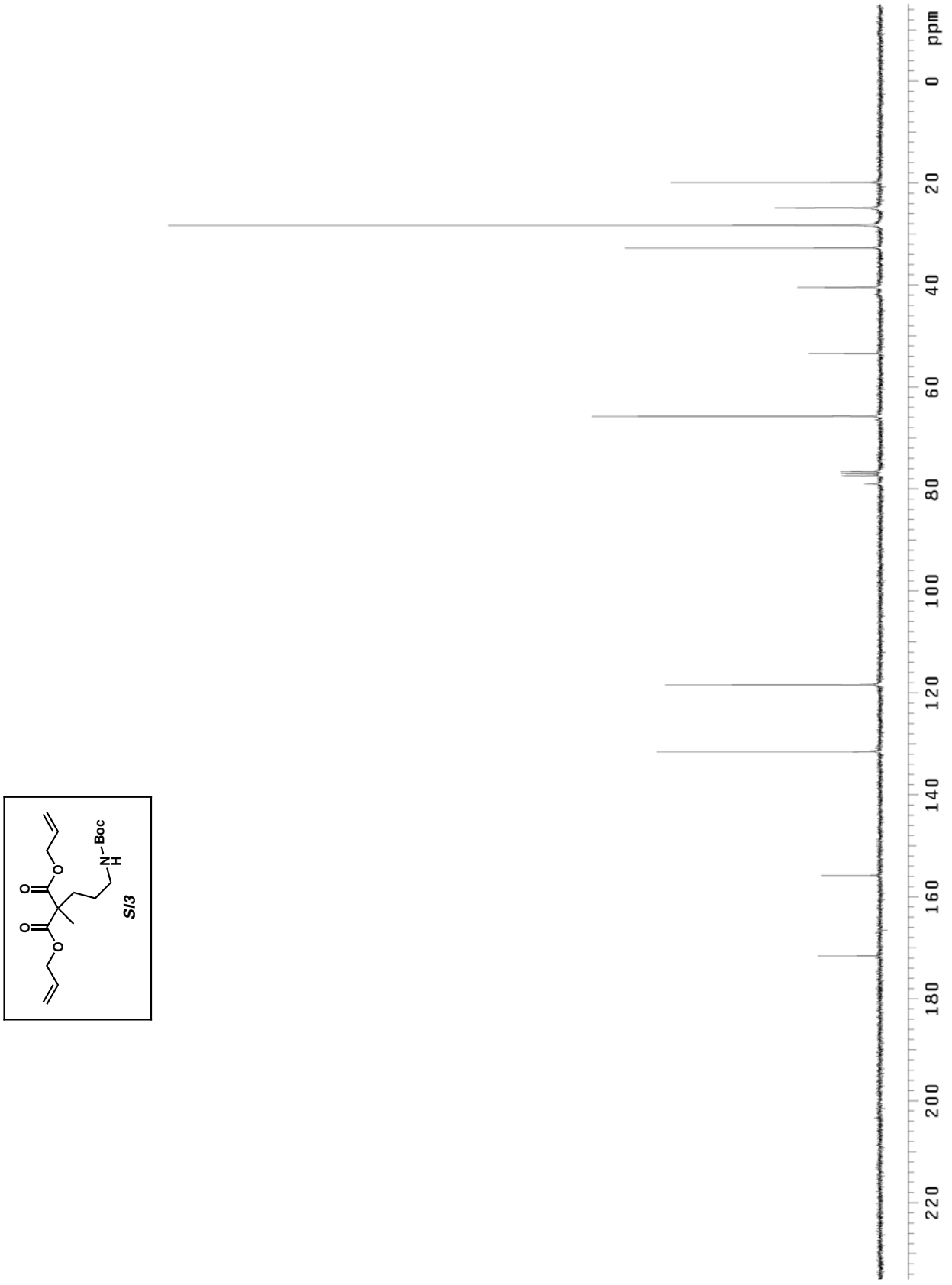


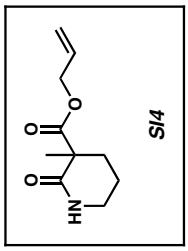












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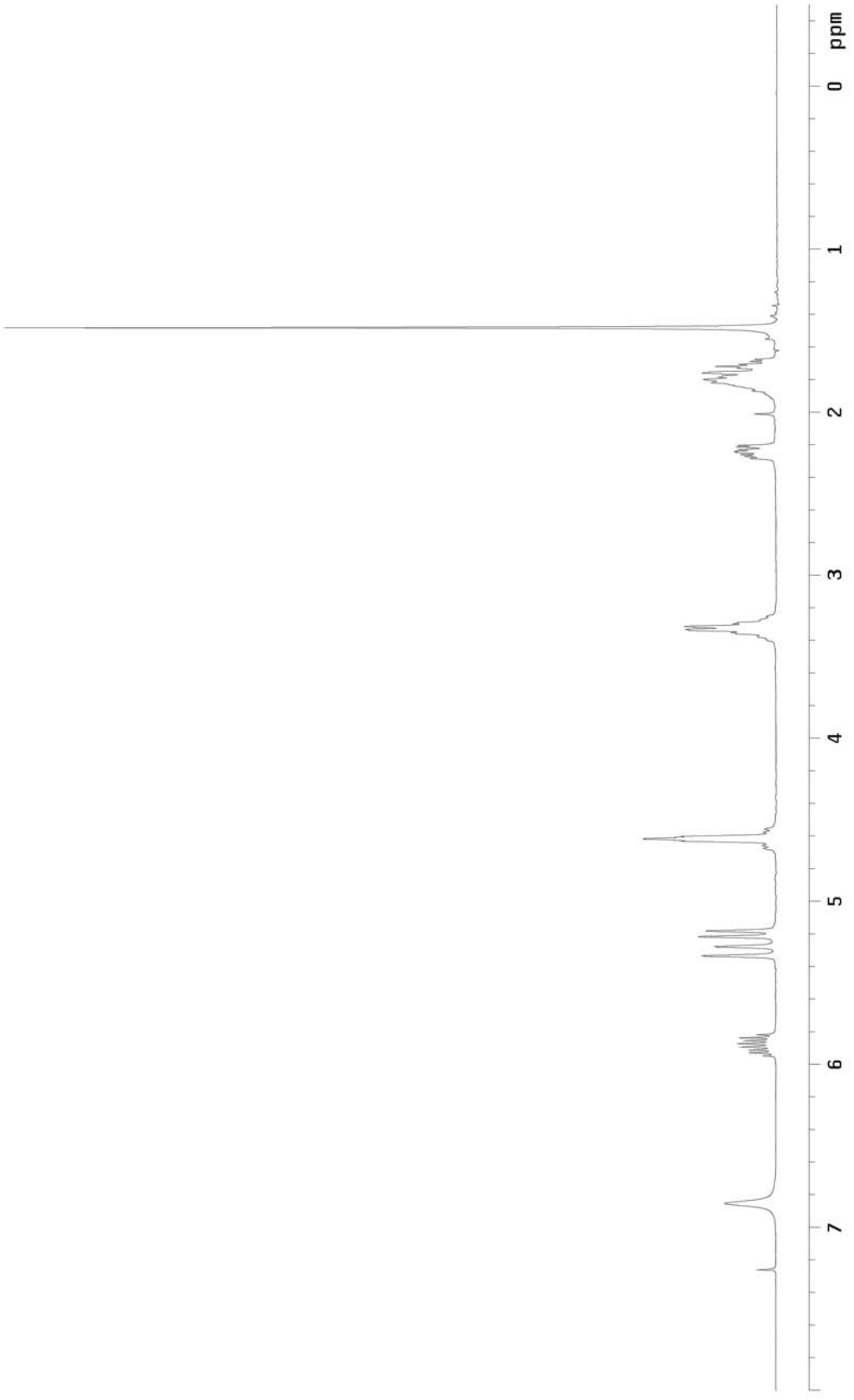

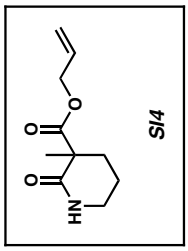

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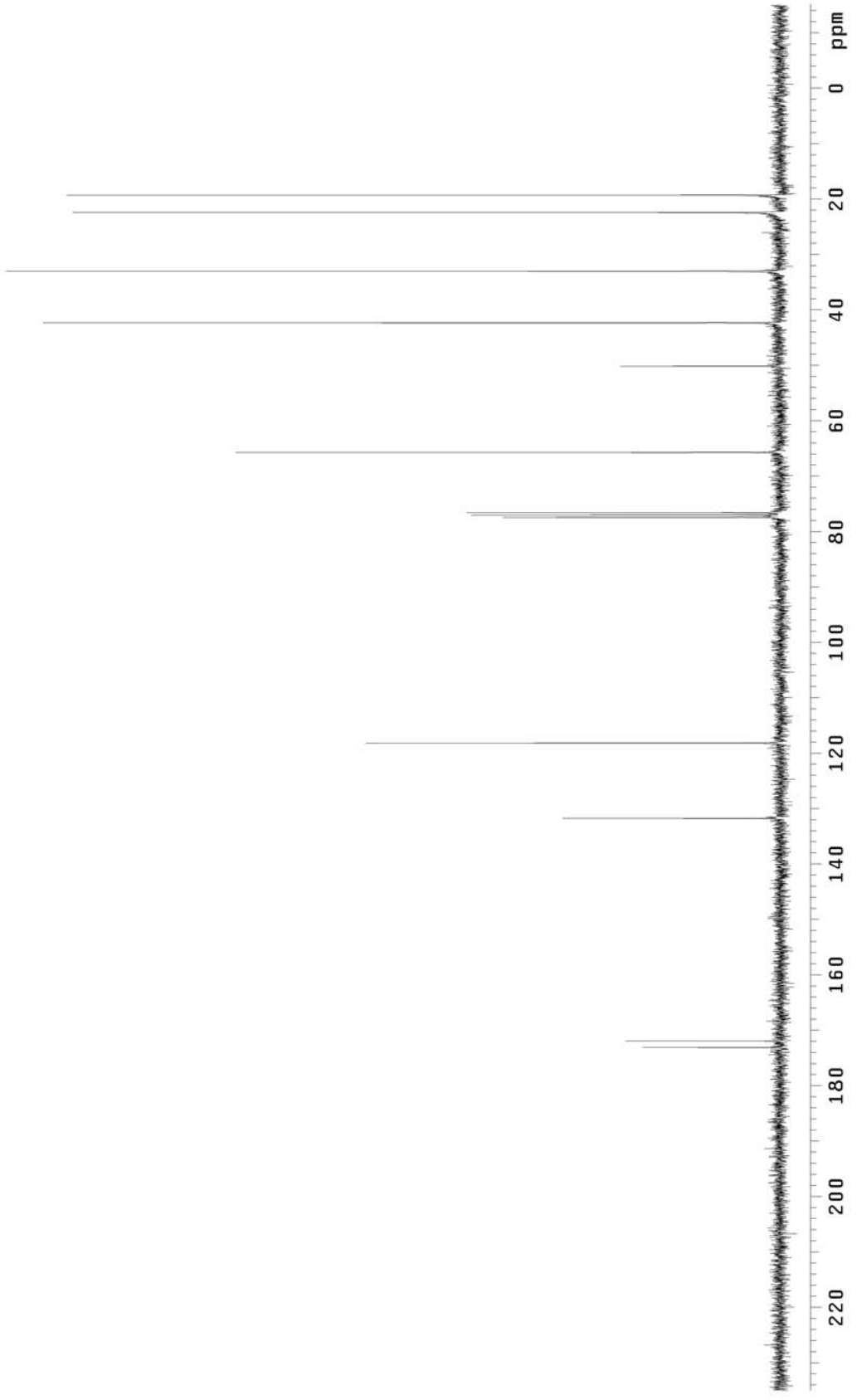

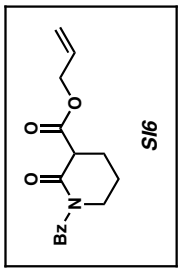

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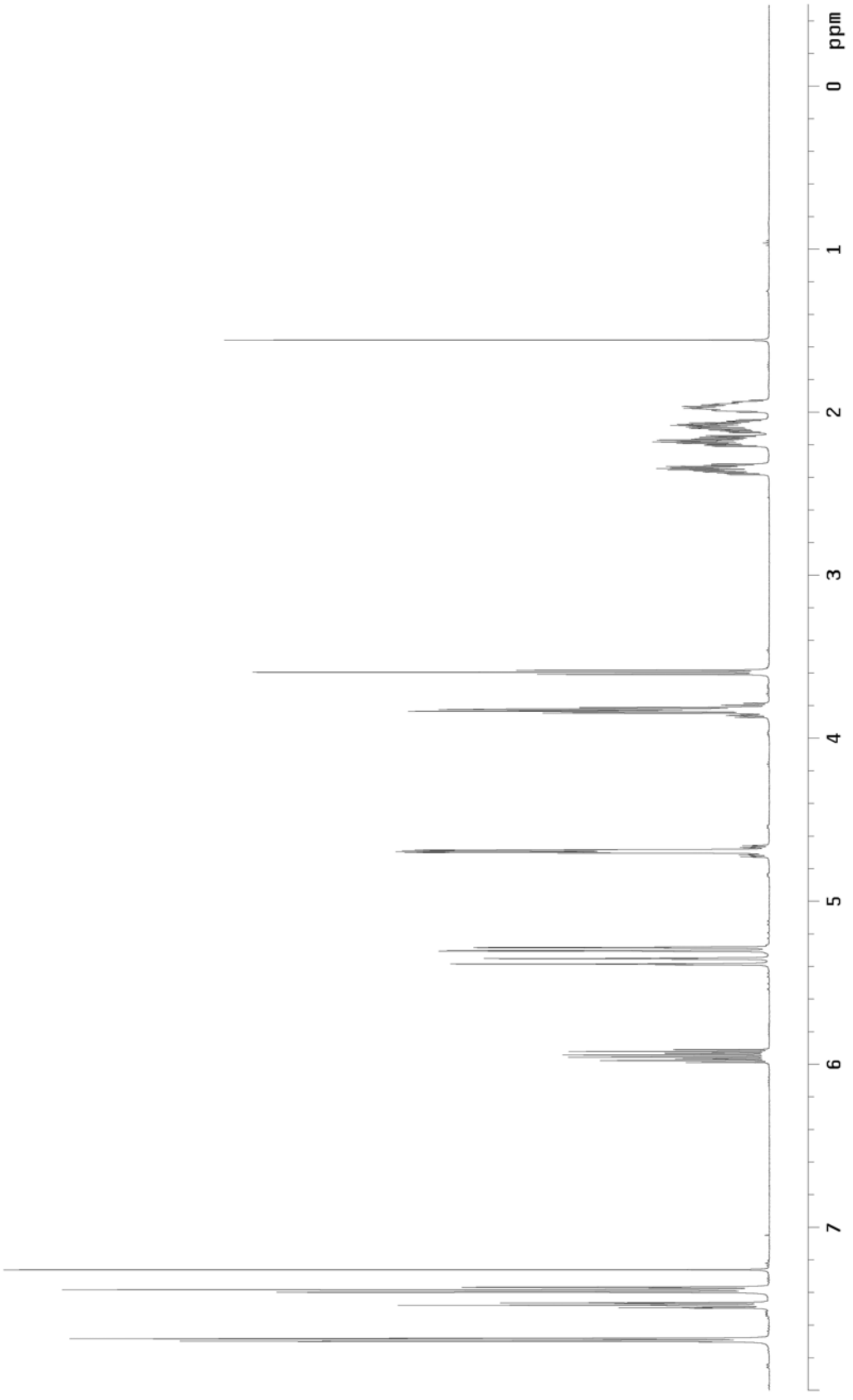
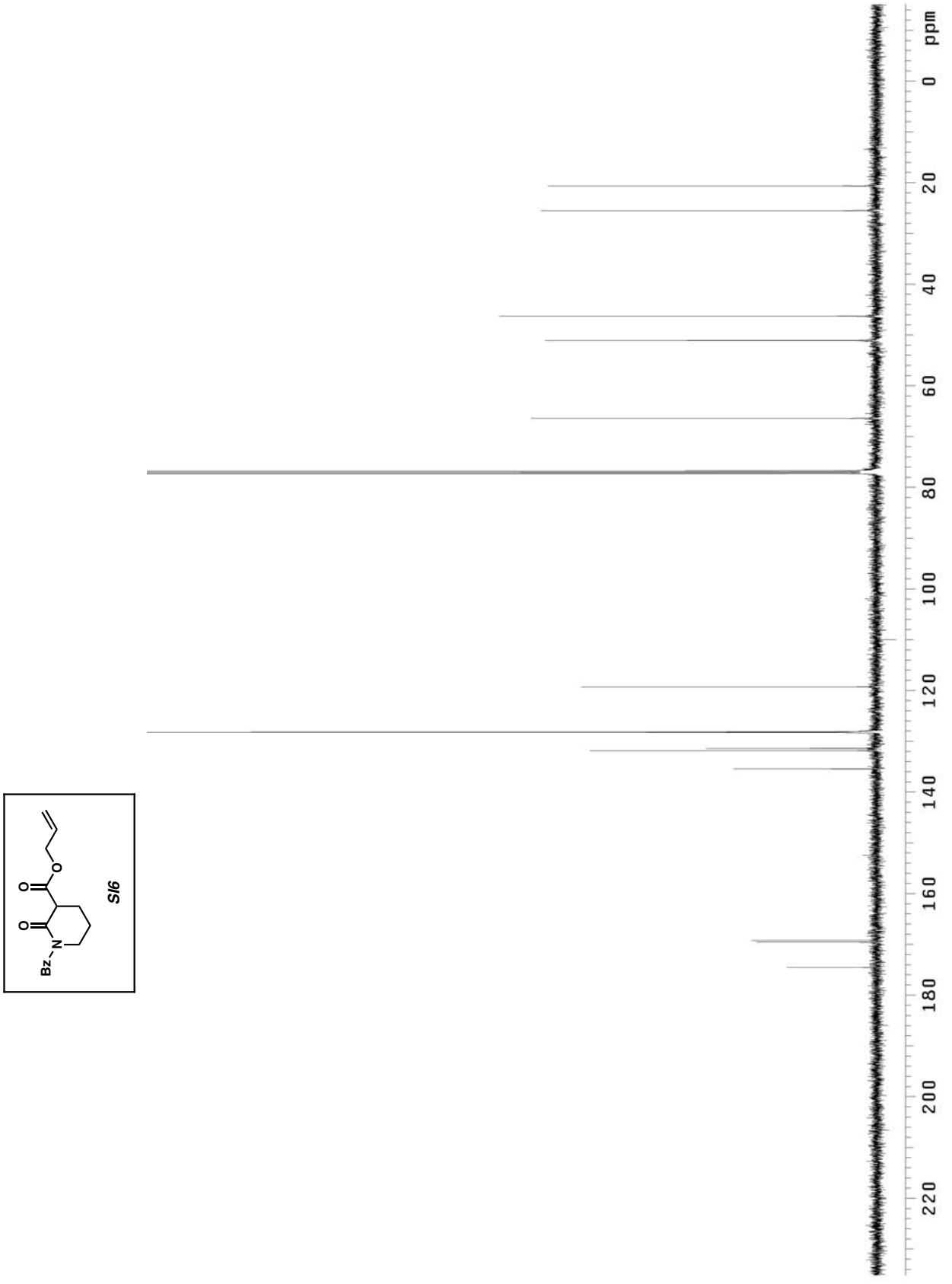
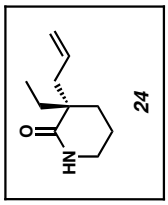
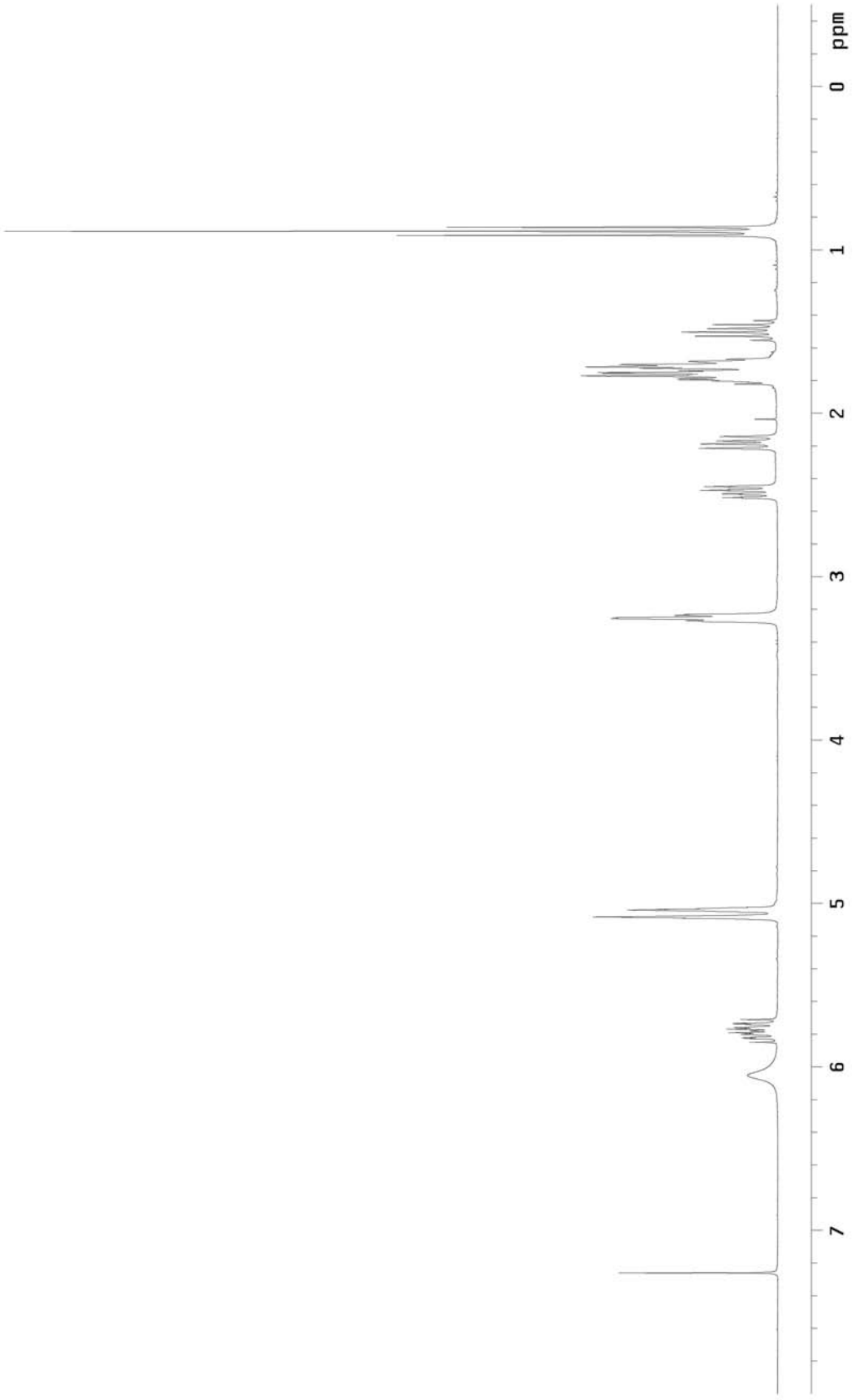
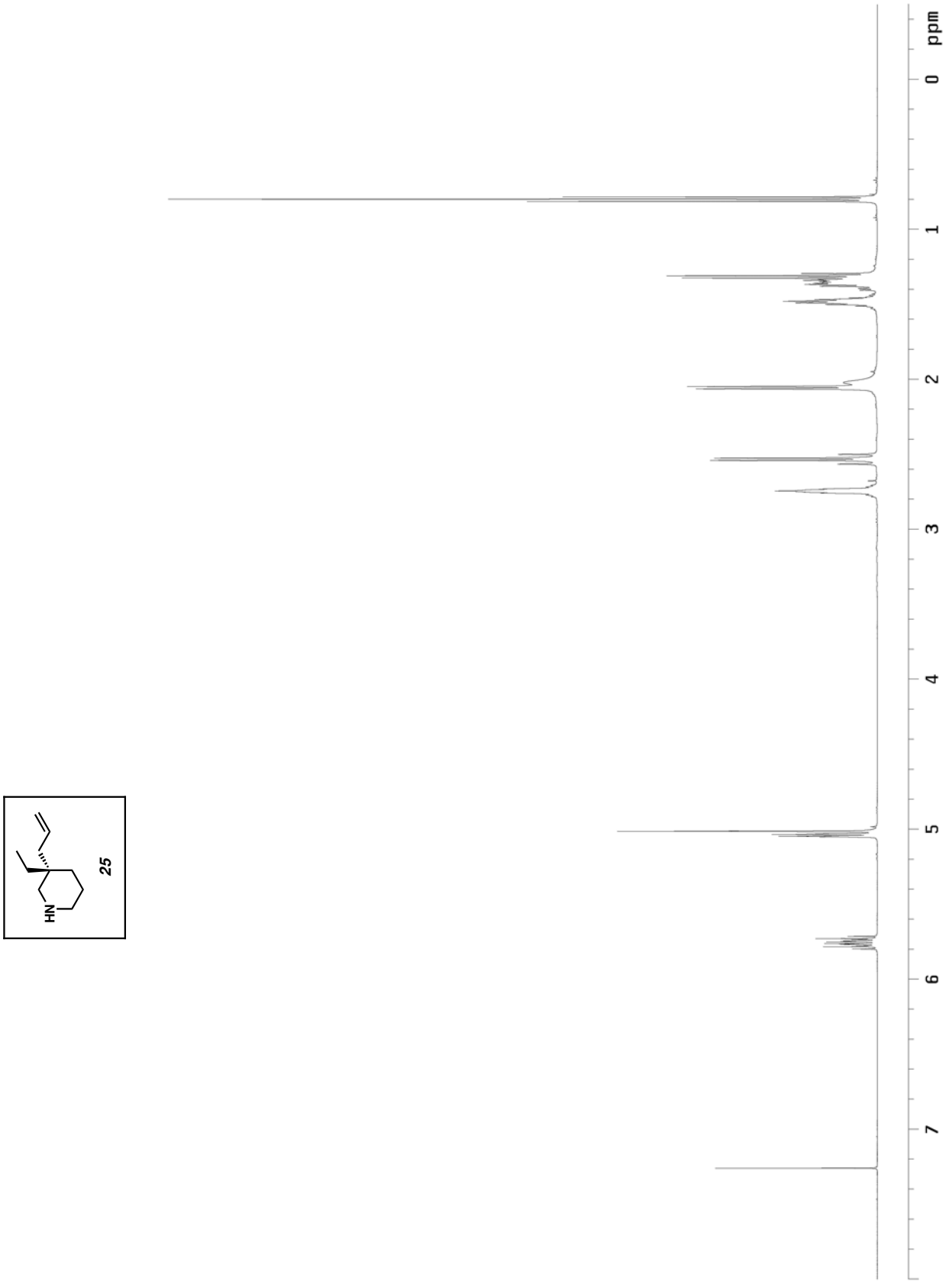
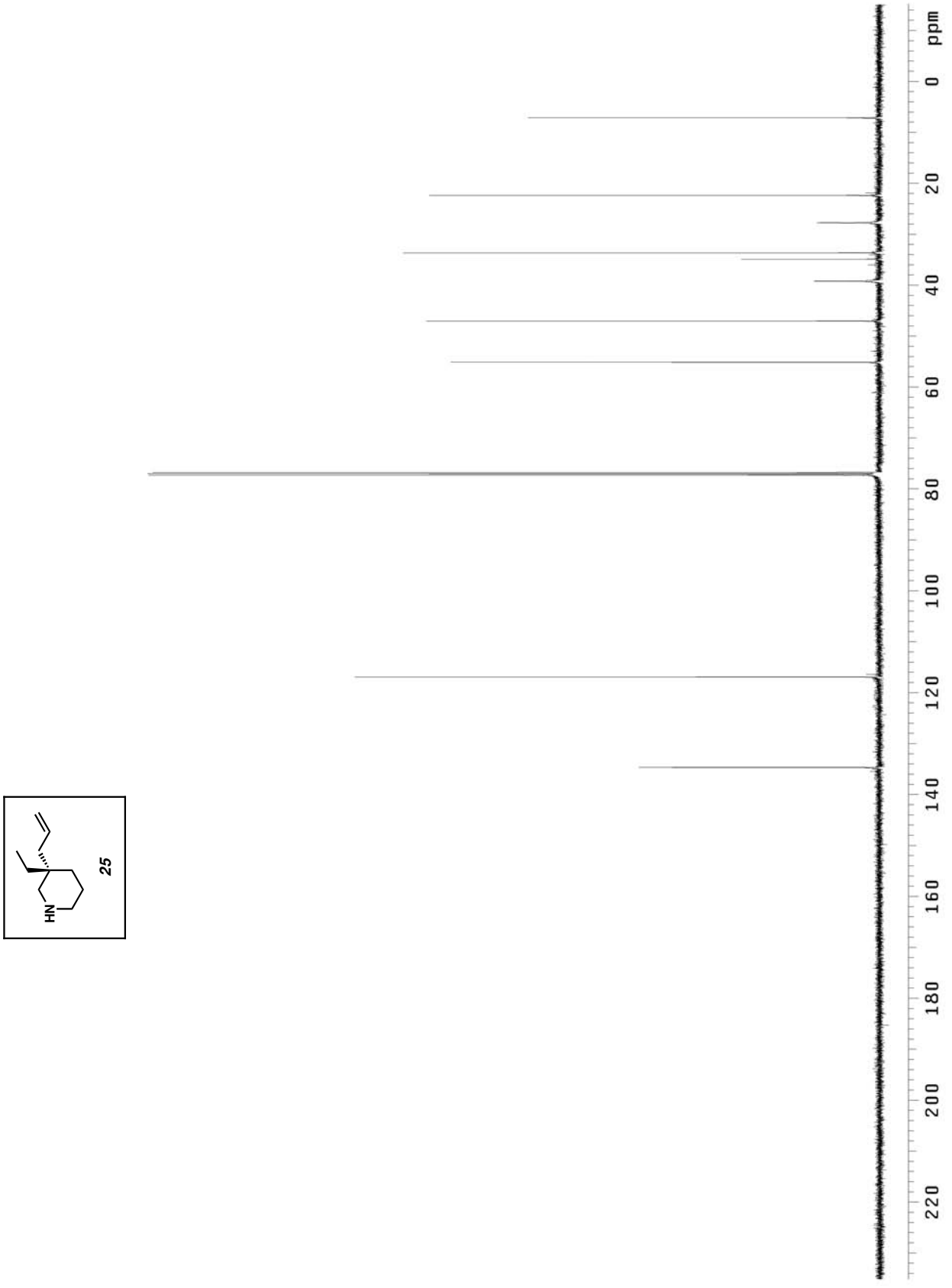


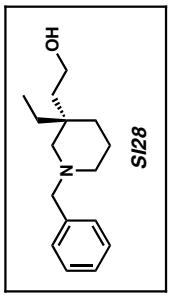


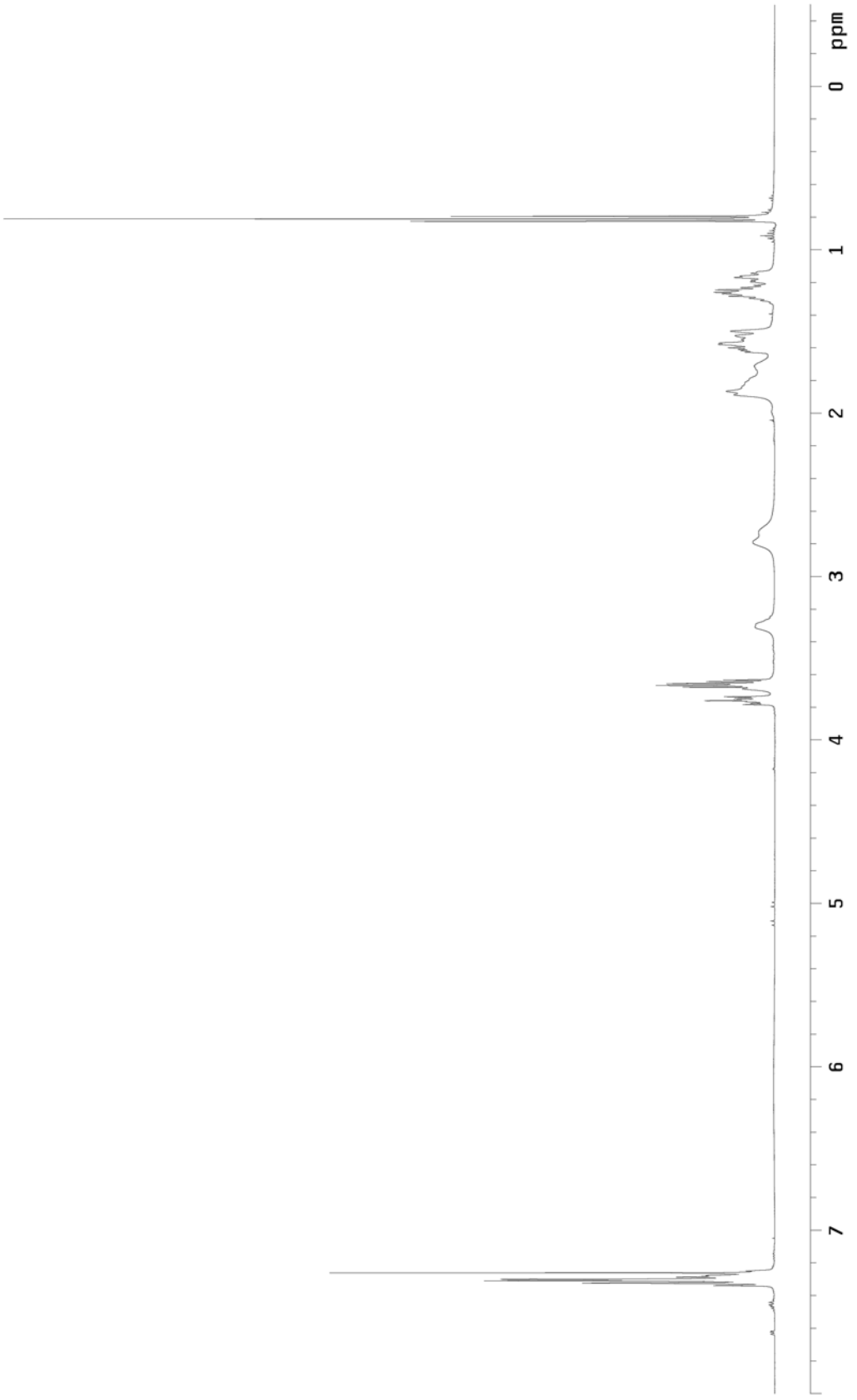


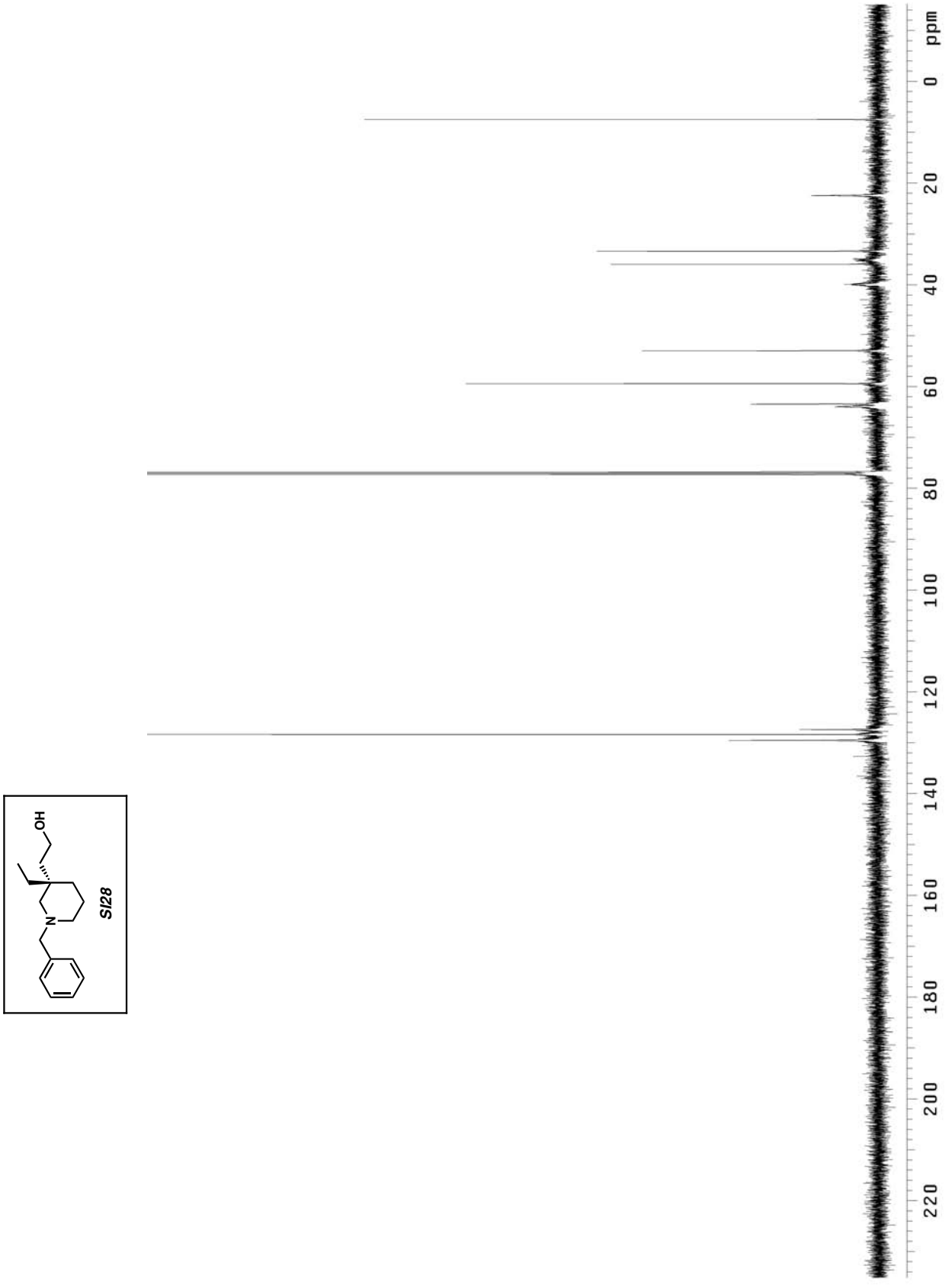


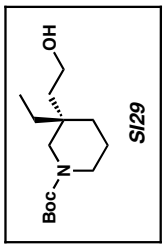


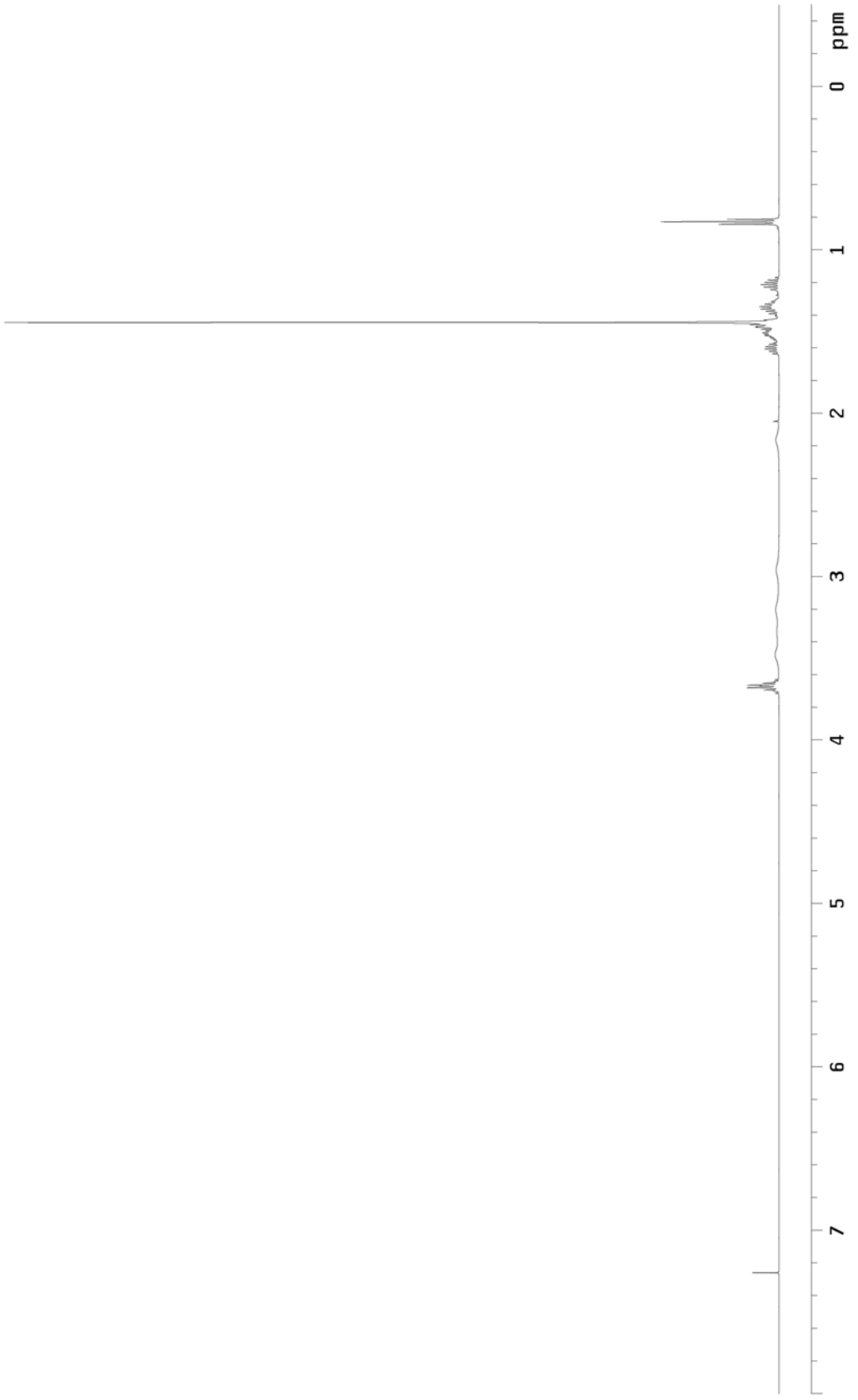


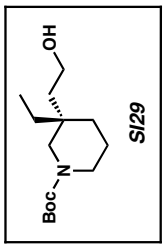


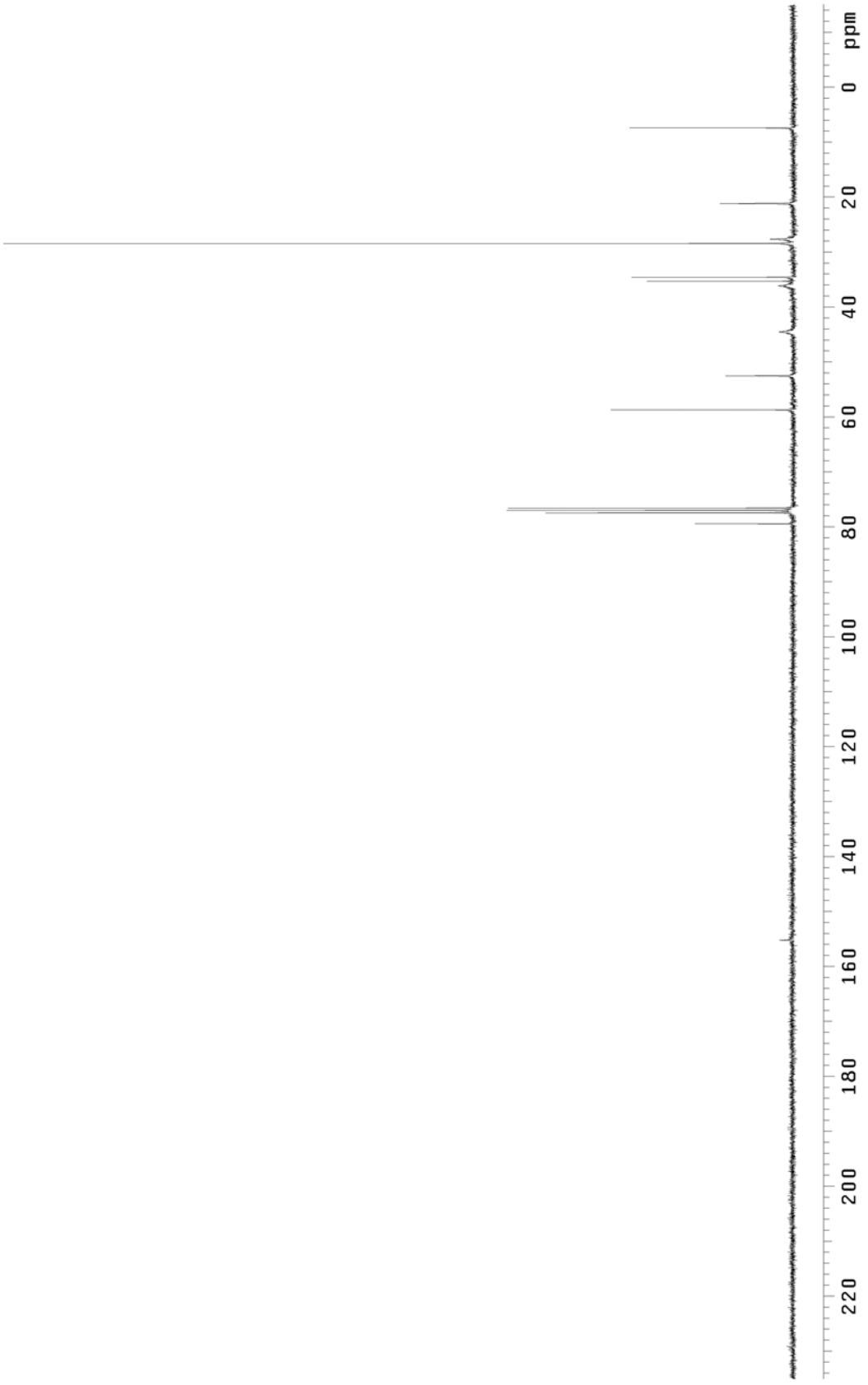




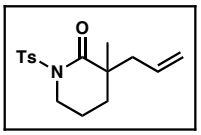








Representative Chiral HPLC and SFC Traces For Lactam Products

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Sample Name: DCBI_289
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Acq. Instrument : HPLC 1                               Location : Vial 21
Injection Date  : 8/19/2010 10:41:13 AM                    Inj :   1
                                                     Inj Volume : 5.0 µl
Acq. Method     : C:\CHEM32\2\METHODS\5ETOH30_254.M
Last changed    : 4/26/2010 8:48:08 PM
Analysis Method : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed    : 7/29/2011 10:14:35 AM by BM
                  (modified after loading)
Method Info     : 5% IPA    10 min  equil   1 mL/min

Sample Info     : DCBI_289 HPLC1 TS amide

================================================================================
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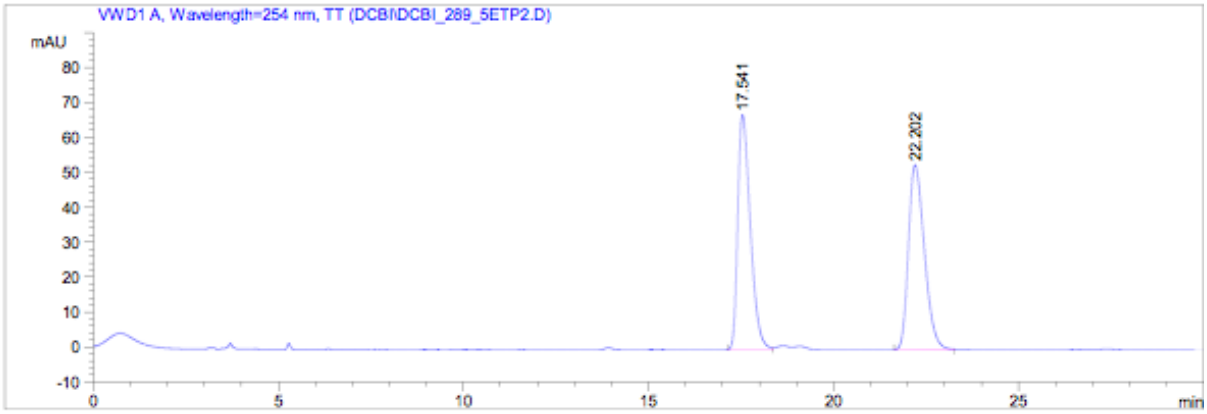


```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  17.541 BB    0.3618 1590.65735   67.25409  50.0177
   2  22.202 BB    0.4616 1589.53296   52.95609  49.9823

Totals :                  3180.19031  120.21018

HPLC 1 7/29/2011 10:20:19 AM BM                          Page   1 of 2
```

```
Data File C:\CHEM32\1\DATA\DCBIII\YLIII_89HPLC1_POS2_5ETOH_A.D
Sample Name: YLIII_89
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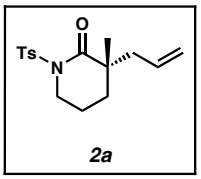

2a

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Acq. Instrument  : HPLC 1                                Location : Vial 61
Injection Date   : 7/4/2011 1:07:36 PM                       Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\2\METHODS\5ETOH30_254.M
Last changed     : 4/26/2010 8:48:08 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 10:14:35 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
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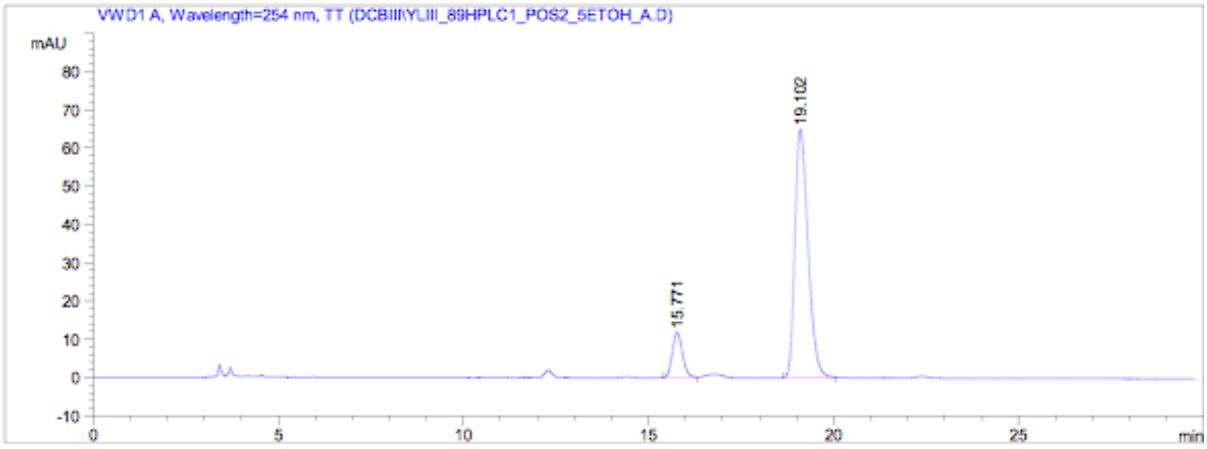


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                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  15.771 BB    0.2858  227.43112   11.88755  12.4167
   2  19.102 BB    0.3812 1604.22852   64.97955  87.5833

Totals :                  1831.65964   76.86711
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Sample Name: YLII_57-2_Boc_rac
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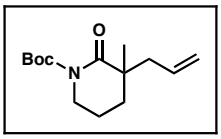


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Acq. Operator    : JCH                                  Seq. Line :   4
Acq. Instrument  : HPLC 1                                Location : Vial 8
Injection Date   : 5/19/2011 4:15:46 PM                      Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\2\METHODS\01IPA30_220_D.M
Last changed     : 9/7/2010 8:52:24 PM by DCB
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 10:25:04 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```
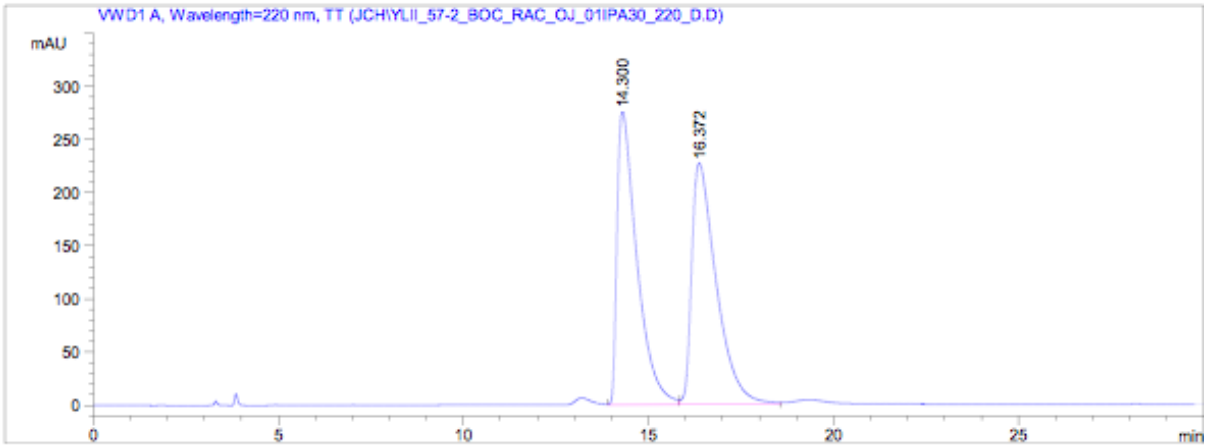
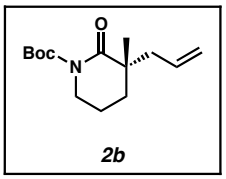



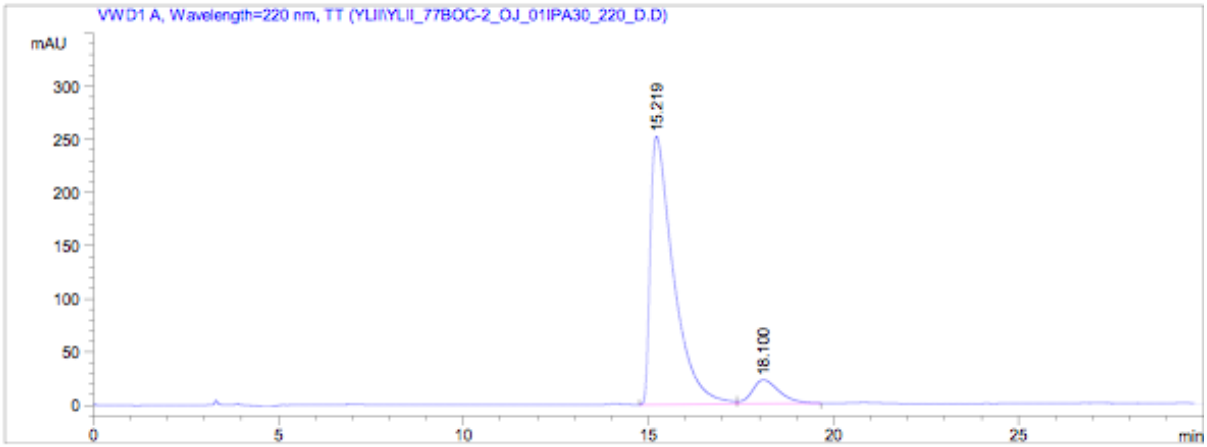

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  14.300 VV    0.5484 1.02753e4   275.66995  49.4172
   2  16.372 VB    0.6785 1.05177e4   226.86935  50.5828

Totals :                  2.07930e4   502.53931
```

```
Data File C:\CHEM32\1\DATA\YLII\YLII_77BOC-2_OJ_01IPA30_220_D.D
Sample Name: YLII_77Boc
```



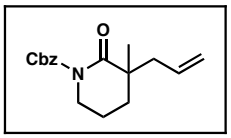
2b

```
Acq. Operator    : YL                                  Seq. Line :   8
Acq. Instrument  : HPLC 1                               Location : Vial 23
Injection Date   : 6/2/2011 1:58:01 PM                      Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\2\METHODS\01IPA30_220_D.M
Last changed     : 9/7/2010 8:52:24 PM by DCB
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 10:25:04 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```

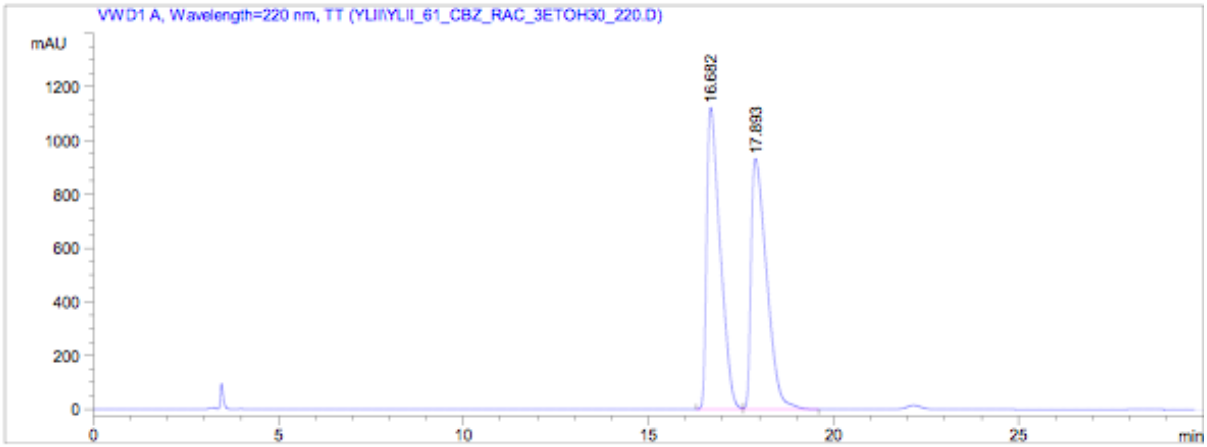



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  15.219 BV    0.6191 1.09821e4   252.37016  90.5780
   2  18.100 VB    0.6014 1142.37195   22.43169   9.4220

Totals :                  1.21245e4   274.80185
```

```
Data File C:\CHEM32\1\DATA\YLII\YLII_61_CBZ_RAC_3ETOH30_220.D
Sample Name: YLII_61_Cbz_rac
```

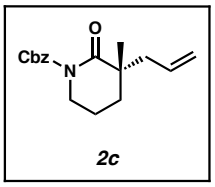



```
Acq. Operator    : YL                                  Seq. Line :   9
Acq. Instrument  : HPLC 1                               Location : Vial 10
Injection Date   : 5/20/2011 2:47:41 AM                      Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\2\METHODS\3ETOH30_220.M
Last changed     : 11/7/2010 11:44:02 AM by tkim
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 10:28:27 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```



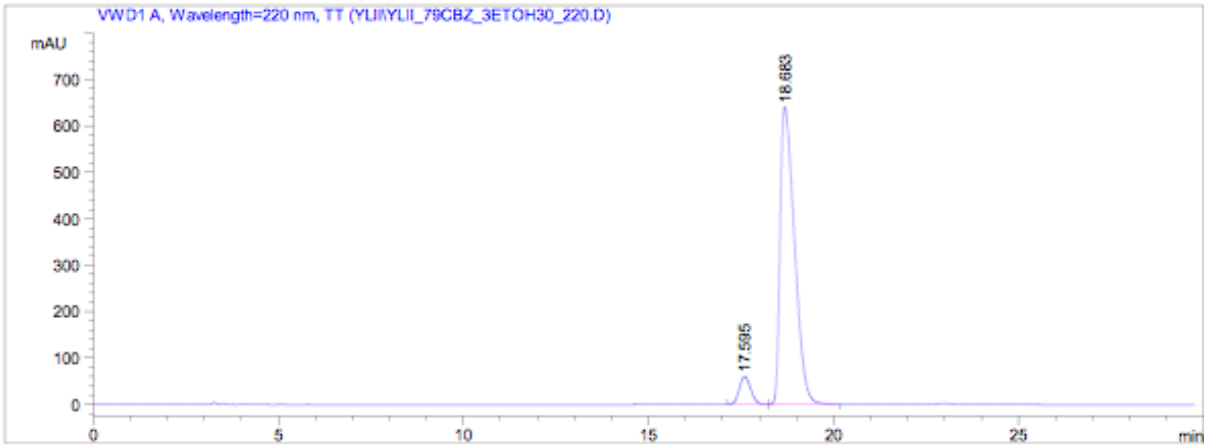

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  16.682 VV    0.3757 2.84287e4  1124.77881  51.0329
   2  17.893 VB    0.4539 2.72778e4   933.05023  48.9671

Totals :                 5.57065e4  2057.82904
```

```
Data File C:\CHEM32\1\DATA\YLII\YLII_79CBZ_3ETOH30_220.D
Sample Name: YLII_79Cbz
```



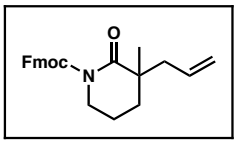
2c

```
Acq. Operator    : YL                                  Seq. Line :  12
Acq. Instrument  : HPLC 1                               Location : Vial 24
Injection Date   : 6/2/2011 3:00:38 PM                      Inj :   1
                                                     Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\2\METHODS\3ETOH30_220.M
Last changed     : 11/7/2010 11:44:02 AM by tkim
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 10:30:08 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```

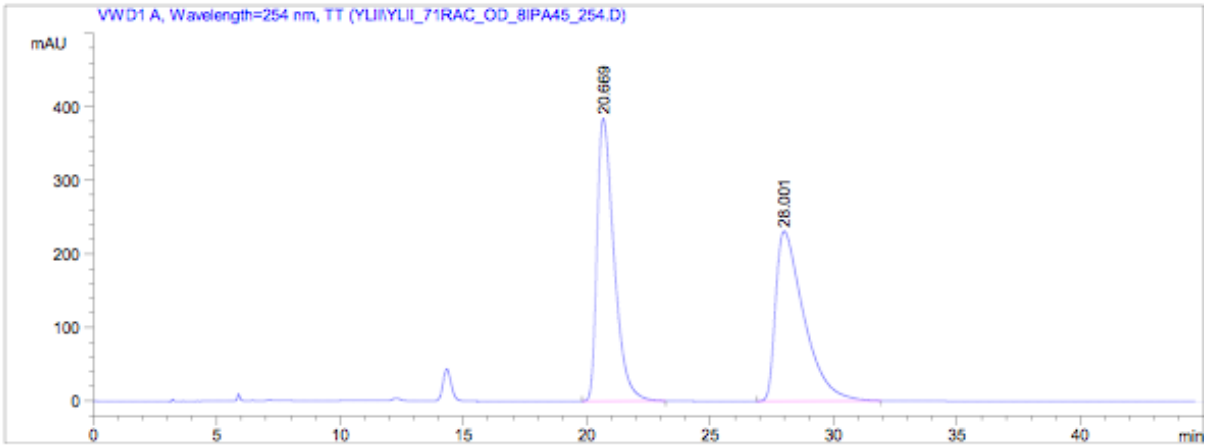



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  17.595 BV    0.3304 1283.26135   60.50865   6.9133
   2  18.683 VB    0.4244 1.72789e4   641.04041  93.0867

Totals :                  1.85622e4   701.54906
```

```
Data File C:\CHEM32\1\DATA\YLII\YLII_71RAC_OD_8IPA45_254.D
Sample Name: YLII_71rac
```

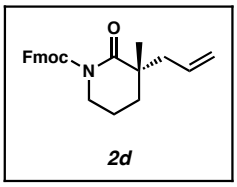



```
Acq. Operator    : YL                                  Seq. Line :   4
Acq. Instrument  : HPLC 1                               Location : Vial 17
Injection Date   : 5/26/2011 4:10:23 PM                     Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\2\METHODS\8IPA45_254.M
Last changed     : 4/26/2010 10:45:46 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 10:33:47 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```



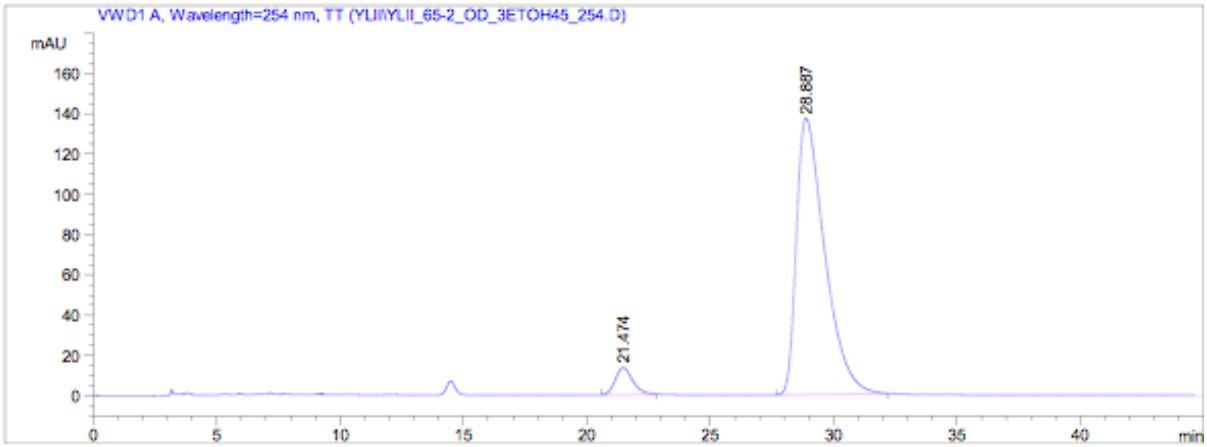

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  20.669 BB    0.7256 1.83637e4   383.83423  49.9785
   2  28.001 BB    1.1624 1.83795e4   230.88930  50.0215

Totals :                  3.67433e4   614.72353
```

```
Data File C:\CHEM32\1\DATA\YLII\YLII_65-2_OD_3ETOH45_254.D
Sample Name: YLII_65-2
```



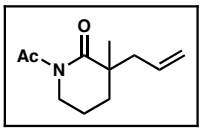
2d

```
Acq. Operator    : YL                                  Seq. Line :   4
Acq. Instrument  : HPLC 1                               Location : Vial 8
Injection Date   : 5/23/2011 9:38:54 AM                     Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\1\METHODS\8IPA45_254.M
Last changed     : 4/26/2010 10:45:46 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 10:31:43 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```

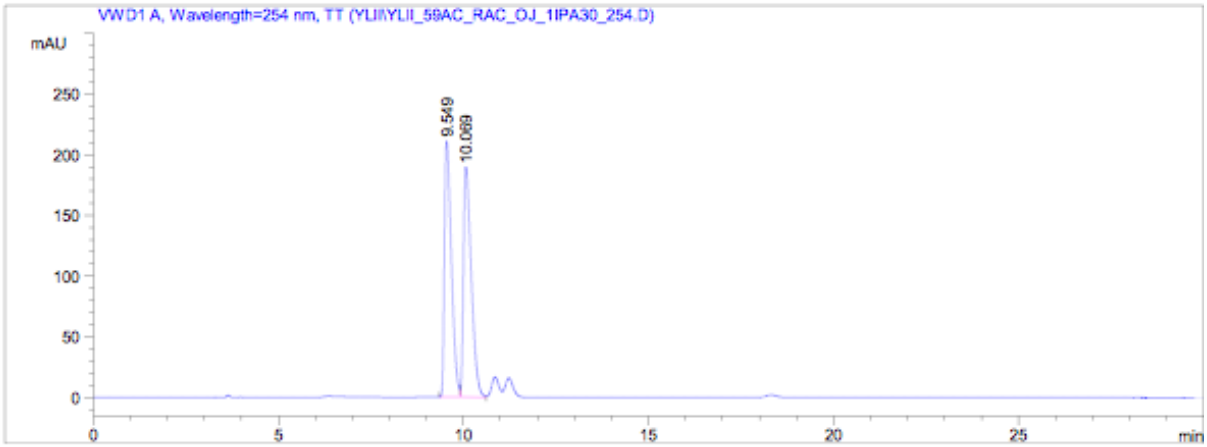



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  21.474 BB    0.6472  660.55054   13.38225   5.6849
   2  28.887 BB    1.1350 1.09588e4   137.30792  94.3151

Totals :                  1.16193e4   150.69018
```

```
Data File C:\CHEM32\1\DATA\YLII\YLII_59AC_RAC_OJ_1IPA30_254.D
Sample Name: YLII_59Ac_rac
```

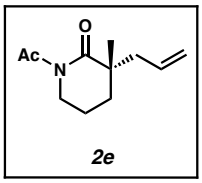



```
Acq. Operator   : YL                                  Seq. Line :   4
Acq. Instrument : HPLC 1                              Location : Vial 19
Injection Date  : 5/27/2011 12:25:33 PM                   Inj :   1
                                                     Inj Volume : 5.0 µl
Acq. Method     : C:\CHEM32\2\METHODS\1IPA30_254.M
Last changed    : 4/26/2010 8:33:09 PM
Analysis Method : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed    : 7/29/2011 10:35:37 AM by BM
                  (modified after loading)
Method Info     : 5% IPA    10 min  equil   1 mL/min
```



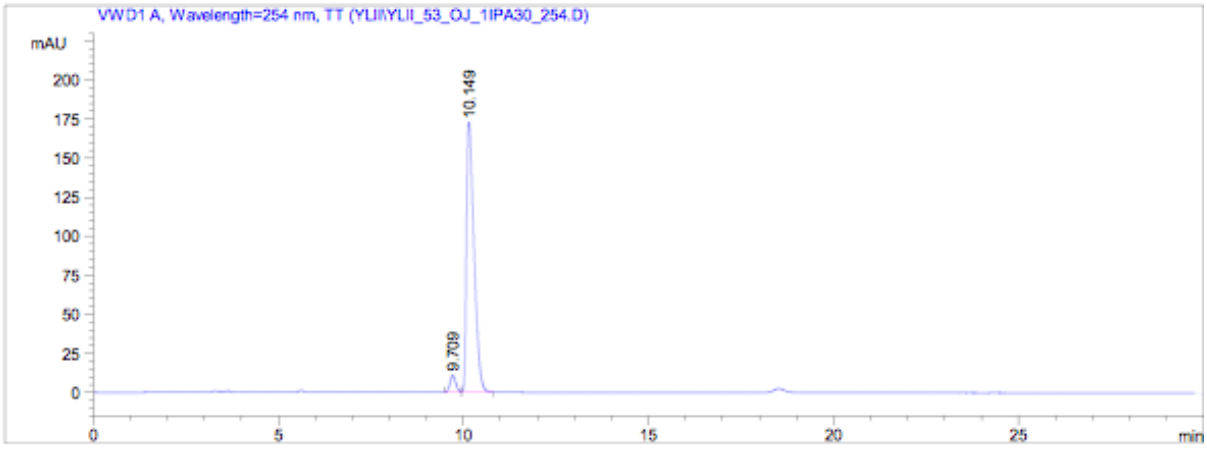

```
                        Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1   9.549 BV    0.1998 2742.82764  210.81544  49.6222
   2  10.069 VV    0.2239 2784.58911  189.43260  50.3778

Totals :                  5527.41675  400.24805
```

```
Data File C:\CHEM32\1\DATA\YLII\YLII_53_OJ_1IPA30_254.D
Sample Name: YLII_53
```



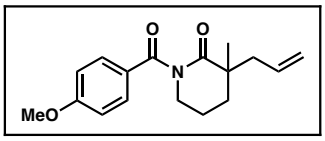
2e

```
Acq. Operator    : YL                                  Seq. Line :   4
Acq. Instrument  : HPLC 1                               Location : Vial 18
Injection Date   : 5/27/2011 11:13:11 AM                    Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\2\METHODS\1IPA30_254.M
Last changed     : 4/26/2010 8:33:09 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 10:36:36 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```

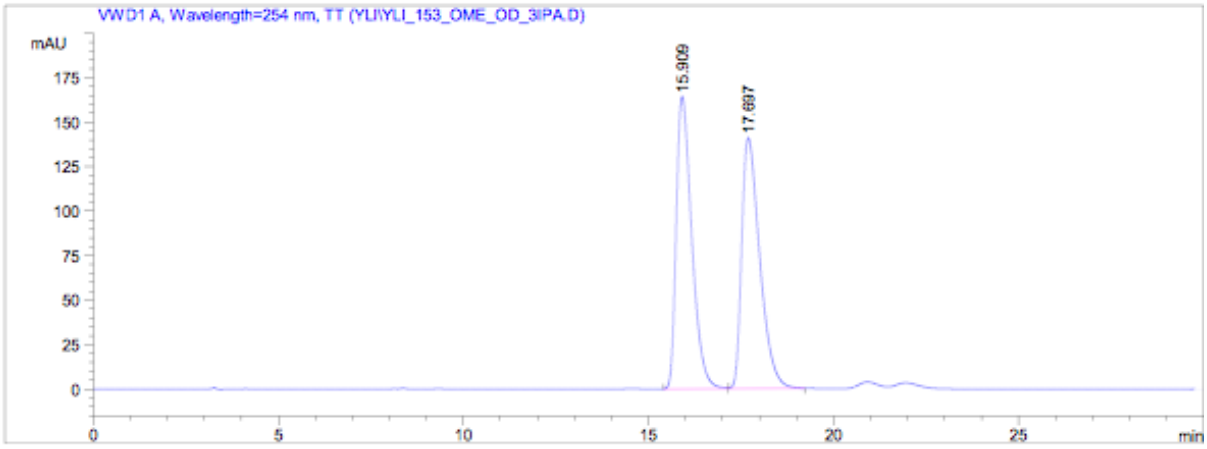



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1   9.709 BV    0.1726  118.91815   10.70099   4.6243
   2  10.149 VB    0.2166 2452.69287  172.73965  95.3757

Totals :                  2571.61102  183.44065
```

```
Data File C:\CHEM32\1\DATA\YLI\YLI_153_OME_OD_3IPA.D
Sample Name: YLI_153_
```

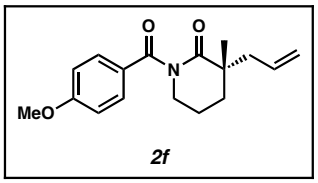



```
Acq. Operator    : YL                                Seq. Line :  29
Acq. Instrument  : HPLC 1                             Location : Vial 13
Injection Date   : 2/21/2011 6:57:45 AM                   Inj :   1
                                                    Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\2\METHODS\3IPA30_254.M
Last changed     : 4/26/2010 8:31:20 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 10:50:17 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```



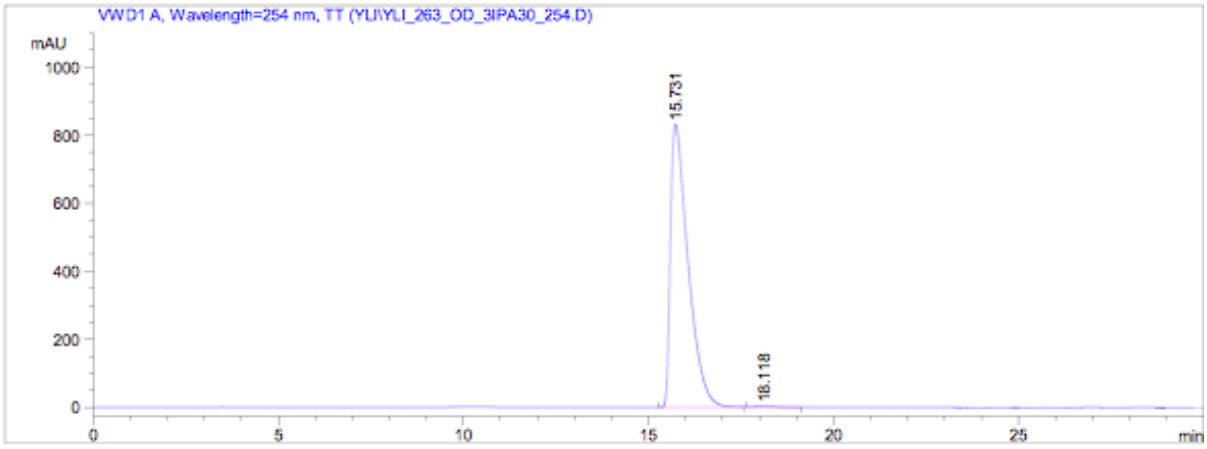

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  15.909 BB    0.4485 4780.88037  164.41164  50.0182
   2  17.697 BB    0.5172 4777.40430  140.88832  49.9818

Totals :                  9558.28467  305.29996
```

```
Data File C:\CHEM32\1\DATA\YLI\YLI_263_OD_3IPA30_254.D
Sample Name: YLI_263
```



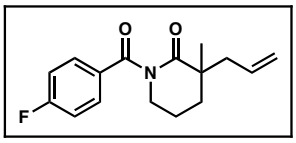
2f

```
Acq. Operator    : YL                                  Seq. Line :   4
Acq. Instrument  : HPLC 1                               Location : Vial 46
Injection Date   : 4/18/2011 11:50:03 AM                    Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\1\METHODS\3IPA30_254.M
Last changed     : 4/26/2010 8:31:20 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 10:47:21 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```

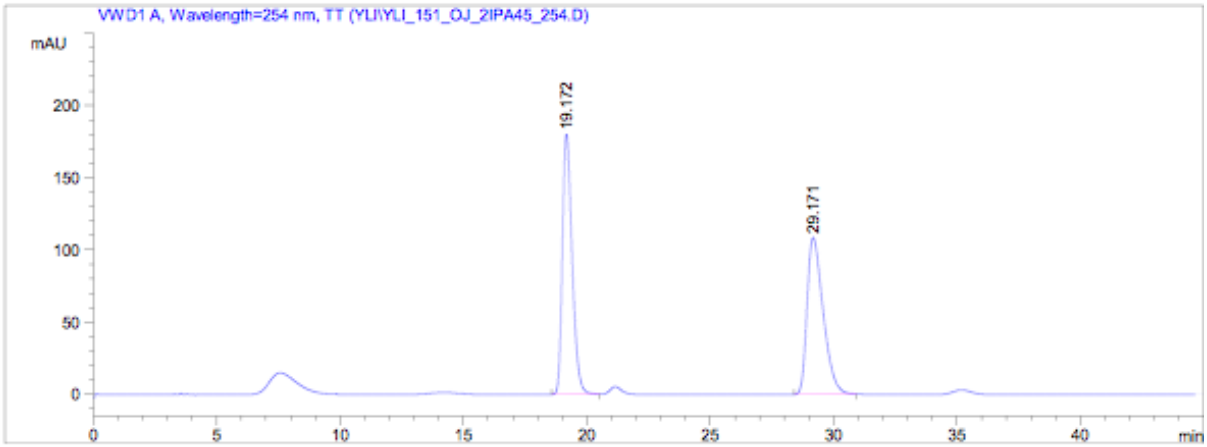



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  15.731 BB    0.4938 2.76283e4   831.88440  99.4584
   2  18.118 BB    0.4850  150.44589    3.79598   0.5416

Totals :                 2.77788e4   835.68038
```

```
Data File C:\CHEM32\1\DATA\YLI\YLI_151_OJ_2IPA45_254.D
Sample Name: YLI_151
```

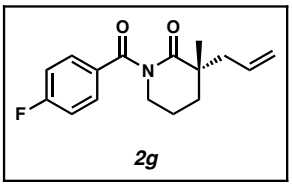



```
Acq. Operator   : YL                                Seq. Line :   8
Acq. Instrument : HPLC 1                            Location : Vial 12
Injection Date  : 3/9/2011 4:44:24 PM                  Inj :   1
                                                   Inj Volume : 5.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\2IPA45_254.M
Last changed    : 4/26/2010 10:42:22 PM
Analysis Method : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed    : 7/29/2011 10:58:11 AM by BM
                  (modified after loading)
Method Info     : 5% IPA    10 min  equil   1 mL/min
```



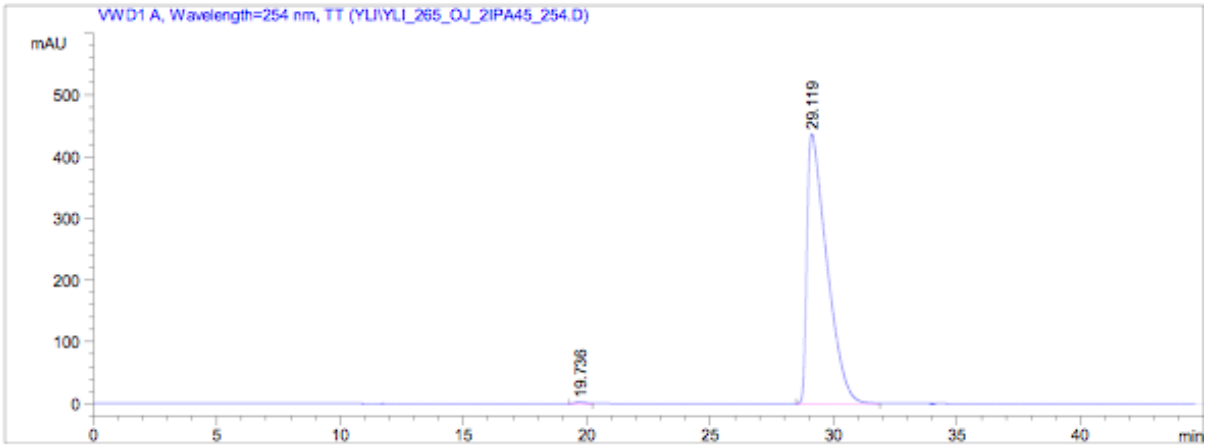

```
                        Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|---------|---------|--------|
   1  19.172 BB    0.4233 4942.04053  180.23906  50.1212
   2  29.171 BB    0.6854 4918.13232  108.64030  49.8788

Totals :                  9860.17285  288.87936
```

```
Data File C:\CHEM32\1\DATA\YLI\YLI_265_OJ_2IPA45_254.D
Sample Name: YLI_265
```



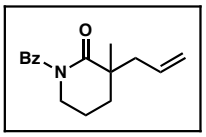
2g

```
Acq. Operator    : YL                                Seq. Line :   9
Acq. Instrument  : HPLC 1                             Location : Vial 47
Injection Date   : 4/18/2011 12:53:11 PM                  Inj :   1
                                                    Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\1\METHODS\2IPA45_254.M
Last changed     : 4/26/2010 10:42:22 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 11:01:34 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```

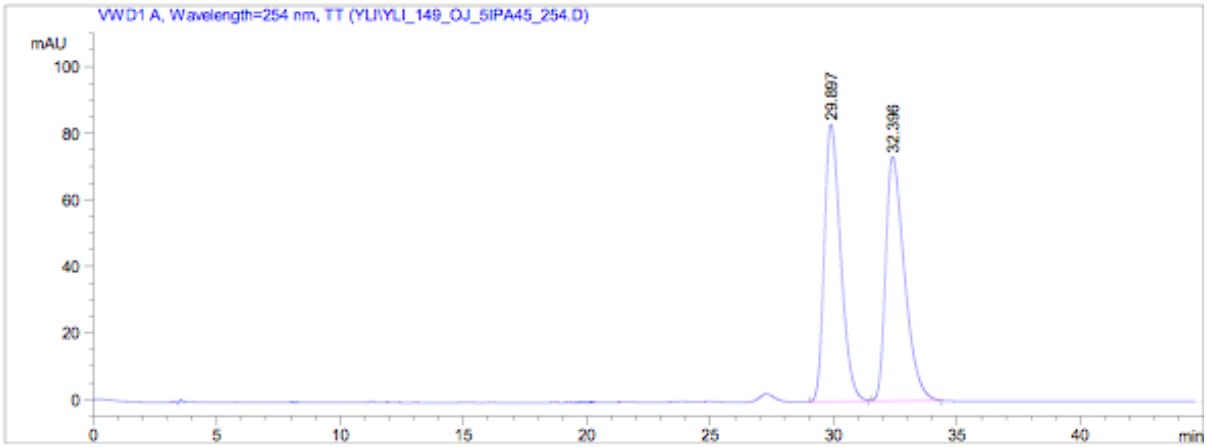



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  19.736 BV    0.3262   78.32276    2.89796   0.3201
   2  29.119 BB    0.7849 2.43899e4   437.12598  99.6799

Totals :                  2.44682e4   440.02394
```

```
Data File C:\CHEM32\1\DATA\YLI\YLI_149_OJ_5IPA45_254.D
Sample Name: YLI_149
```

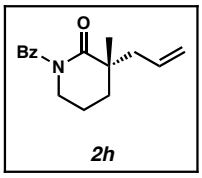



```
Acq. Operator    : YL                                  Seq. Line :  40
Acq. Instrument  : HPLC 1                               Location : Vial 13
Injection Date   : 3/10/2011 3:59:08 AM                     Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\1\METHODS\5IPA45_254.M
Last changed     : 4/26/2010 10:44:29 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 11:06:10 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```

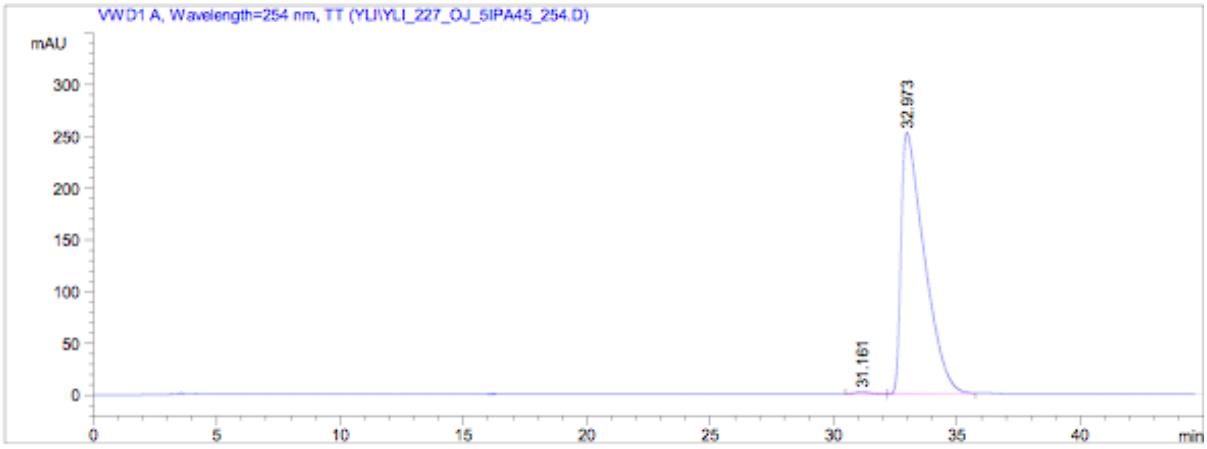



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  29.897 BB    0.7021 3840.42310   83.35200  49.6362
   2  32.396 BB    0.7817 3896.71704   73.40163  50.3638

Totals :                  7737.14014  156.75362
```

```
Data File C:\CHEM32\1\DATA\YLI\YLI_227_OJ_5IPA45_254.D
Sample Name: YLI_227
```

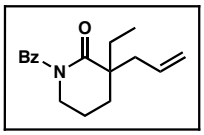



```
Acq. Operator    : YL                                  Seq. Line :   4
Acq. Instrument  : HPLC 1                               Location : Vial 26
Injection Date   : 3/27/2011 5:59:05 PM                      Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\1\METHODS\5IPA45_254.M
Last changed     : 4/26/2010 10:44:29 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 11:04:39 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```



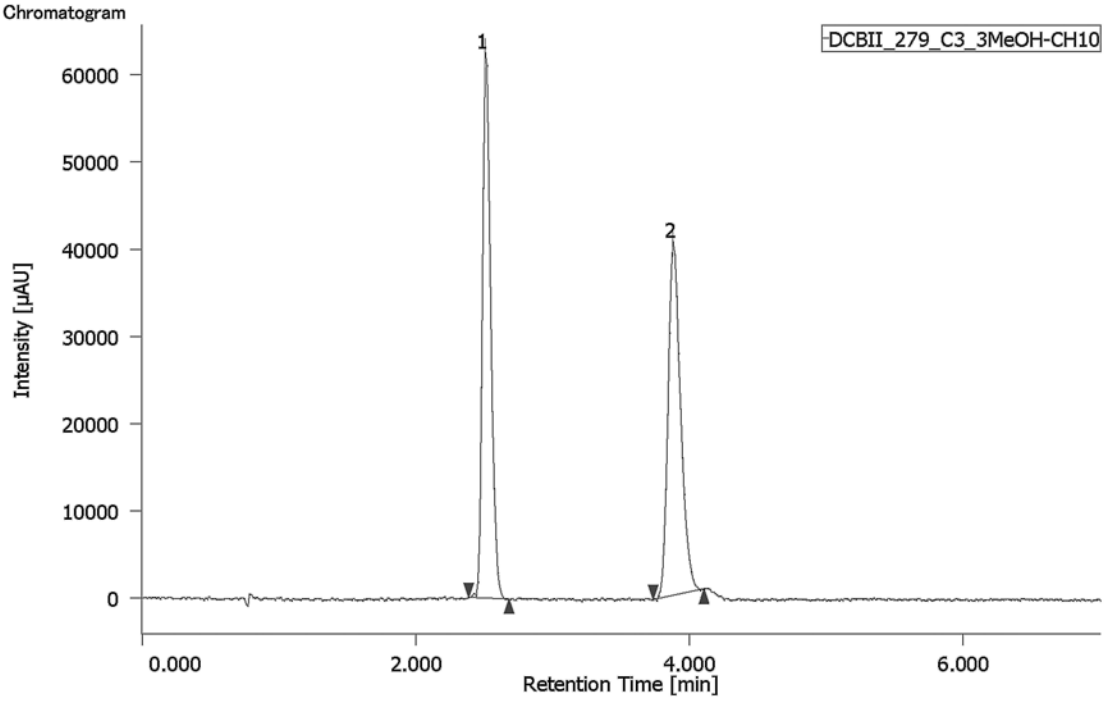

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  31.161 BV    0.5177   87.67049    2.00378   0.5279
   2  32.973 VB    0.9216 1.65184e4   252.59338  99.4721

Totals :                  1.66060e4   254.59716
```

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/11/2011 10:57:09 AM
Volume	5.00 [µL]
Sample #	4
Project Name	Cal Tech SFC
Executed Sequence	DCBII_279a
Chromatogram Name	DCBII_279_C3_3MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBII_279a
Control Method	Solv 1 Col 3 Isocratic 3B 5mL_min 10MPa 15 min

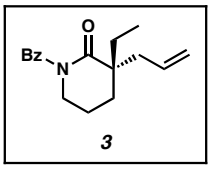
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.507	266268	62473	50.787	2.387	2.680	0.065	10.038	1.418
2	Unknown	10	3.880	258018	40569	49.213	3.733	4.107	0.097	N/A	1.309

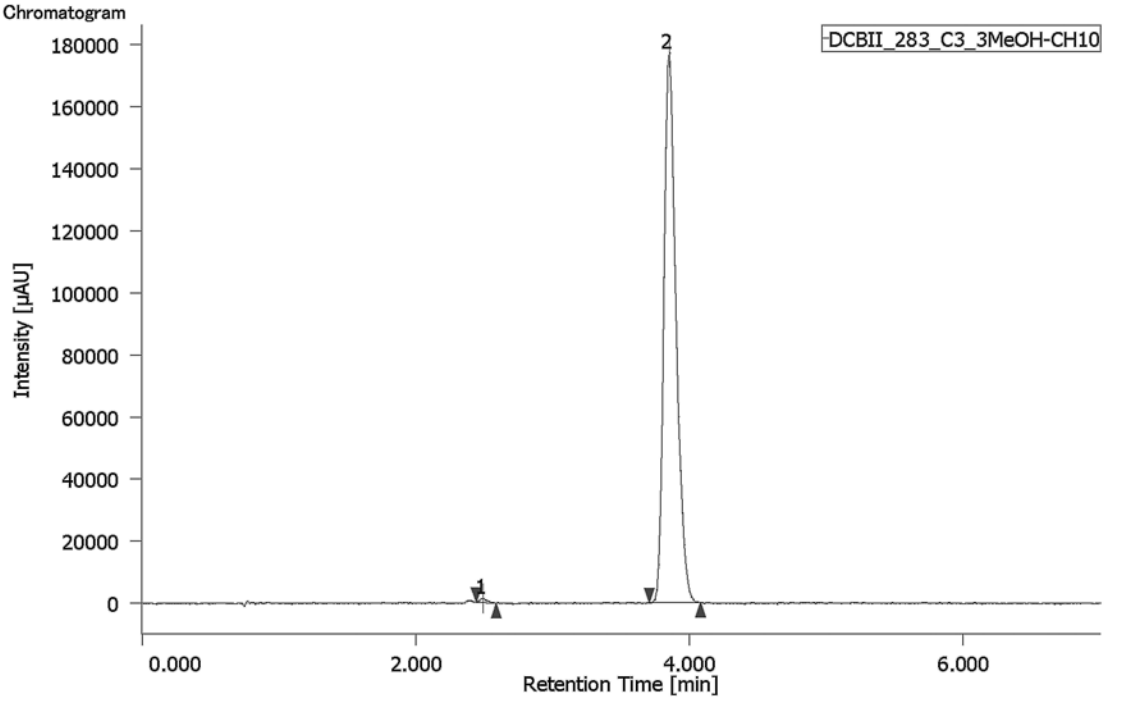
Analytical Report SFC



3

Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/11/2011 3:31:25 PM
Volume	5.00 [µL]
Sample #	1
Project Name	Cal Tech SFC
Executed Sequence	DCBII_283
Chromatogram Name	DCBII_283_C3_3MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBII_283
Control Method	Solv 1 Col 3 Isocratic 3B 5mL_min 10MPa 15 min

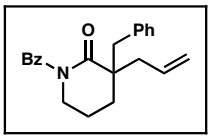
Chromatogram



Peak Information

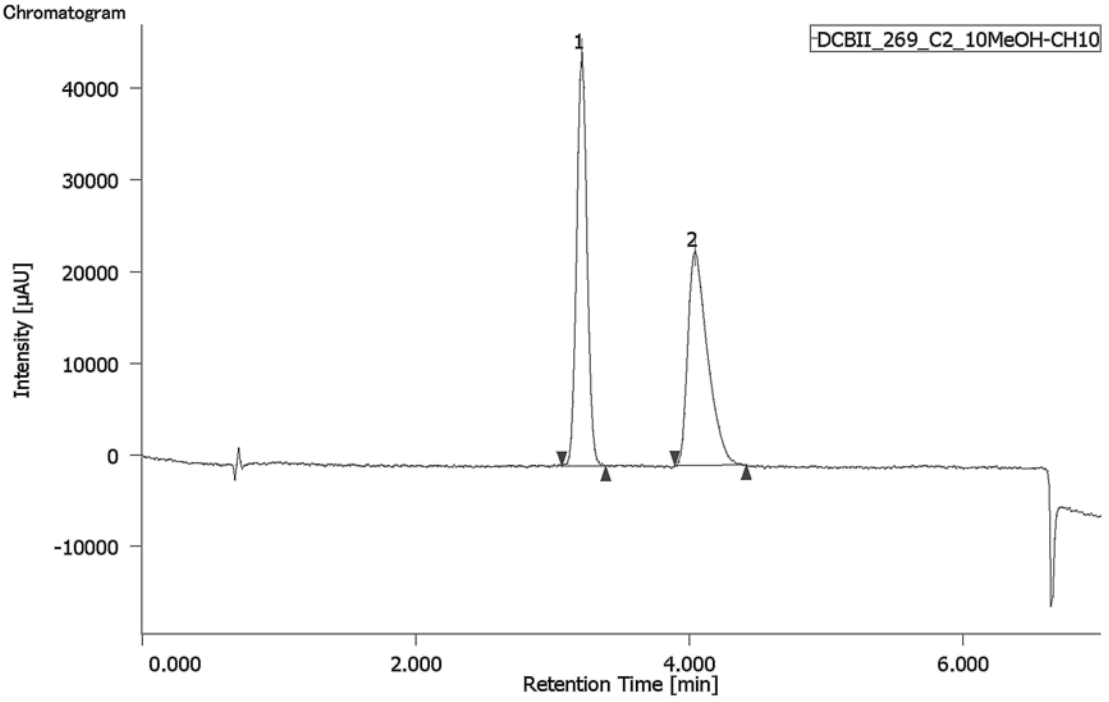
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.493	5222	1412	0.471	2.440	2.587	0.051	10.978	1.332
2	Unknown	10	3.853	1103548	177127	99.529	3.707	4.080	0.095	N/A	1.241

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/5/2011 11:21:25 PM
Volume	5.00 [µL]
Sample #	2
Project Name	Cal Tech SFC
Executed Sequence	DCBII_269
Chromatogram Name	DCBII_269_C2_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBII_269
Control Method	Solv 1 Col 2 Isocratic 10B 5mL_min 10MPa 10min

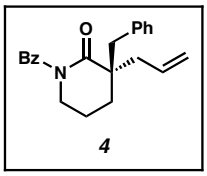
Chromatogram



Peak Information

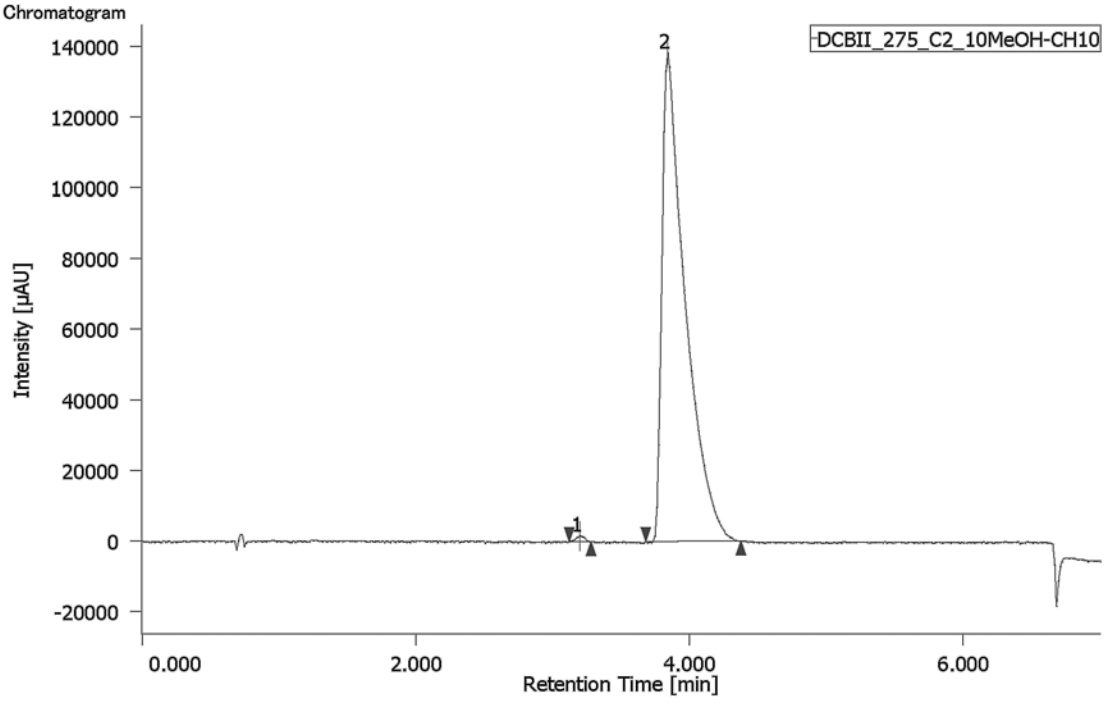
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	3.213	239364	45096	50.317	3.067	3.387	0.083	4.115	1.032
2	Unknown	10	4.040	236349	23425	49.683	3.893	4.413	0.154	N/A	1.591

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/6/2011 11:14:57 PM
Volume	5.00 [µL]
Sample #	3
Project Name	Cal Tech SFC
Executed Sequence	DCBII_275
Chromatogram Name	DCBII_275_C2_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBII_275
Control Method	Solv 1 Col 2 Isocratic 10B 5mL_min 10MPa 10min

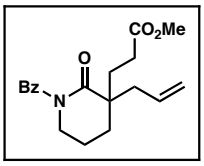
Chromatogram



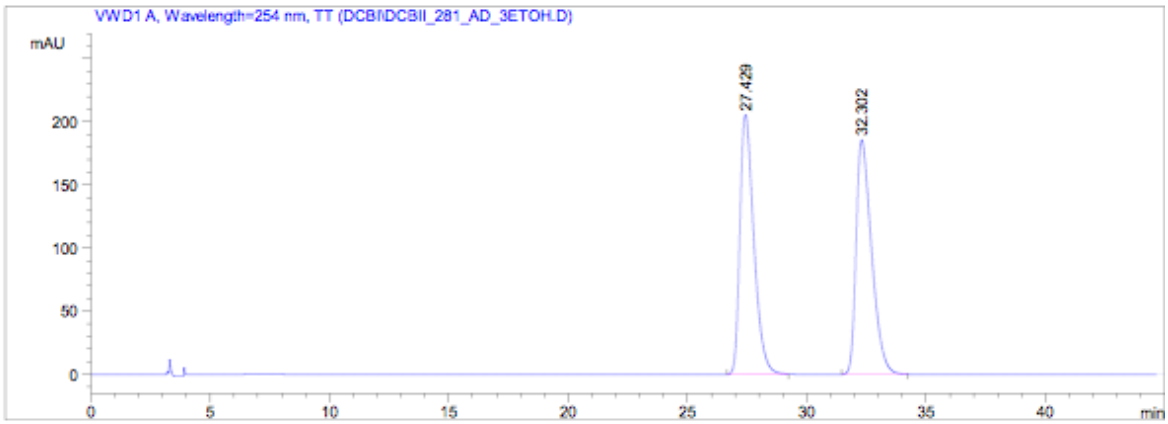
Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	3.200	7272	1719	0.444	3.120	3.280	0.073	3.096	0.955
2	Unknown	10	3.840	1632029	138312	99.556	3.680	4.373	0.171	N/A	2.617

```
Data File C:\CHEM32\1\DATA\DCBI\DCBII_281_AD_3ETOH.D
Sample Name: DCBII_281_esterRac
```

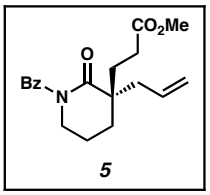



```
Acq. Operator   : DCB                                 Seq. Line :  25
Acq. Instrument : HPLC 1                               Location : Vial 41
Injection Date  : 4/9/2011 6:28:20 AM                      Inj :   1
                                                     Inj Volume : 5.0 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\3ETOH45_254.M
Last changed    : 4/26/2010 10:54:15 PM
Analysis Method : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed    : 7/29/2011 12:50:07 PM by BM
                  (modified after loading)
Method Info     : 5% IPA    10 min  equil   1 mL/min
```



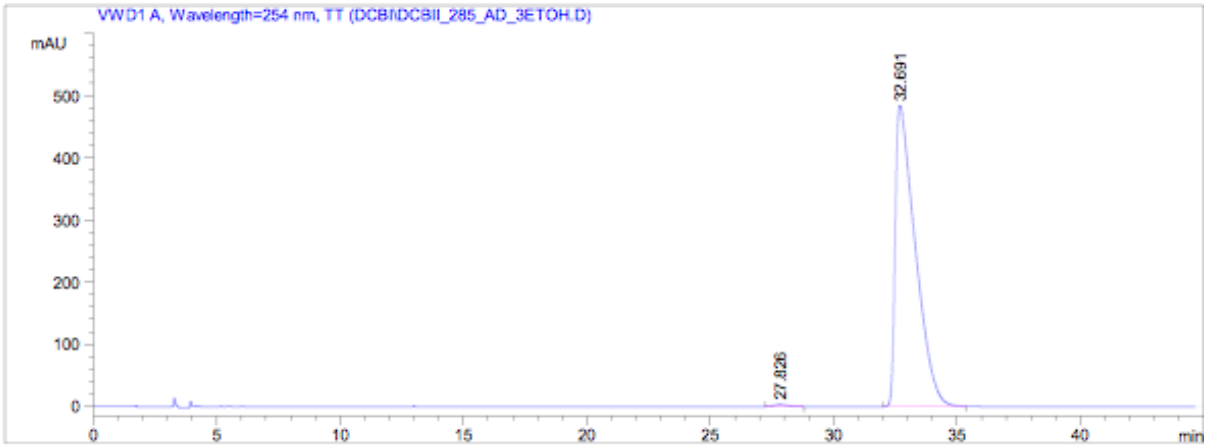

```
                        Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  27.429 BB    0.6174 8334.97266  205.80576  49.9521
   2  32.302 BB    0.6752 8350.95508  185.73674  50.0479

Totals :                  1.66859e4   391.54250
```

```
Data File C:\CHEM32\1\DATA\DCBI\DCBII_285_AD_3ETOH.D
Sample Name: DCBII_285
```



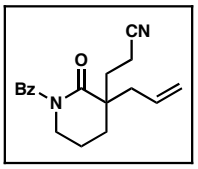
5

```
Acq. Operator    : DCB                                Seq. Line :   8
Acq. Instrument  : HPLC 1                              Location : Vial 42
Injection Date   : 4/10/2011 9:14:43 PM                    Inj :   1
                                                     Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\1\METHODS\3ETOH45_254.M
Last changed     : 4/26/2010 10:54:15 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 12:46:59 PM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```



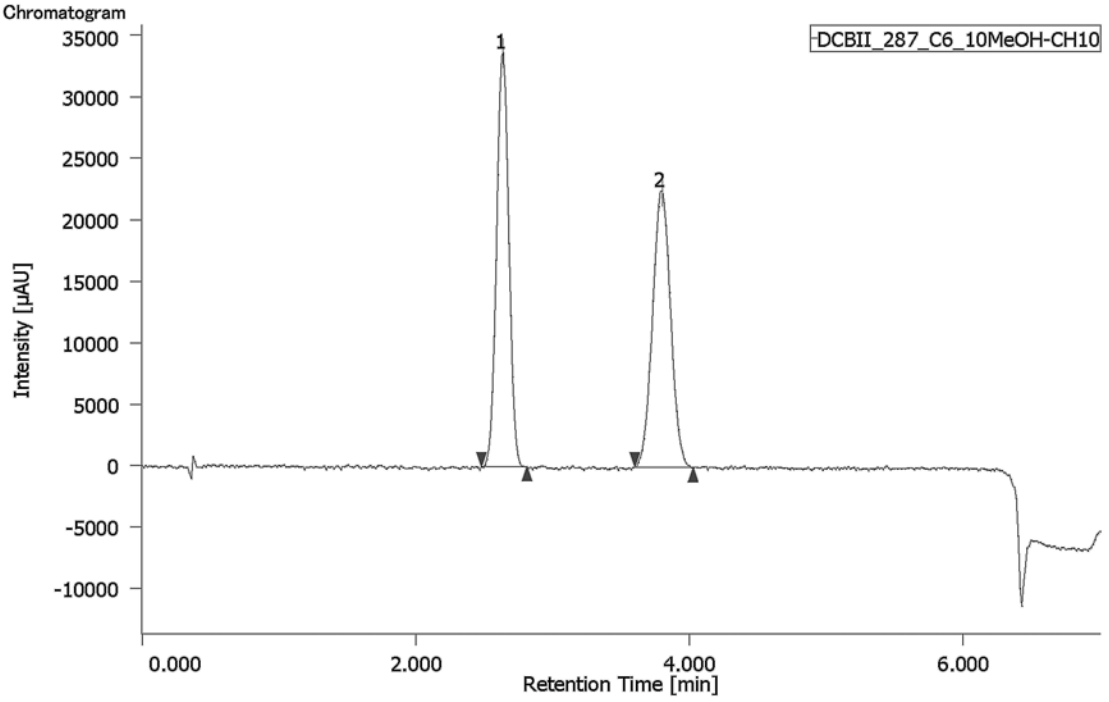

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  27.826 BB    0.4591  123.43498    3.25033   0.4504
   2  32.691 BB    0.7959 2.72792e4   483.95120  99.5496

Totals :                  2.74026e4   487.20153
```

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/12/2011 8:16:48 PM
Volume	5.00 [µL]
Sample #	1
Project Name	Cal Tech SFC
Executed Sequence	DCBII_287
Chromatogram Name	DCBII_287_C6_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBII_287
Control Method	Solv 1 Col 6 Isocratic 10B 5mL_min 10MPa 10min

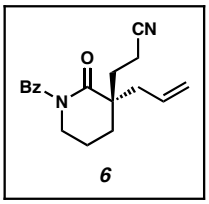
Chromatogram



Peak Information

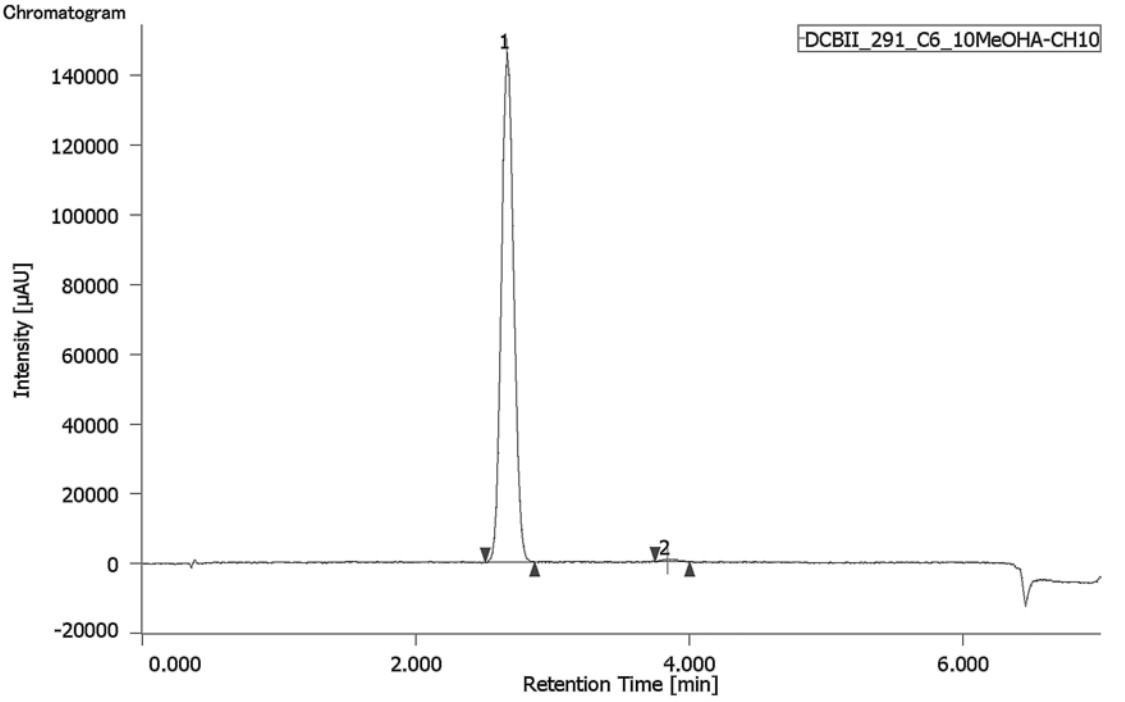
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.640	207981	33631	50.072	2.480	2.813	0.097	5.660	0.961
2	Unknown	10	3.800	207381	22440	49.928	3.600	4.027	0.145	N/A	0.992

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/17/2011 3:40:55 PM
Volume	5.00 [µL]
Sample #	4
Project Name	Cal Tech SFC
Executed Sequence	DCBII_291
Chromatogram Name	DCBII_291_C6_10MeOHA
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBII_291
Control Method	Solv 1 Col 6 Isocratic 10B 5mL_min 10MPa 10min

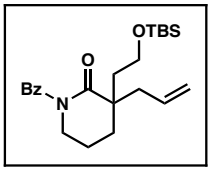
Chromatogram



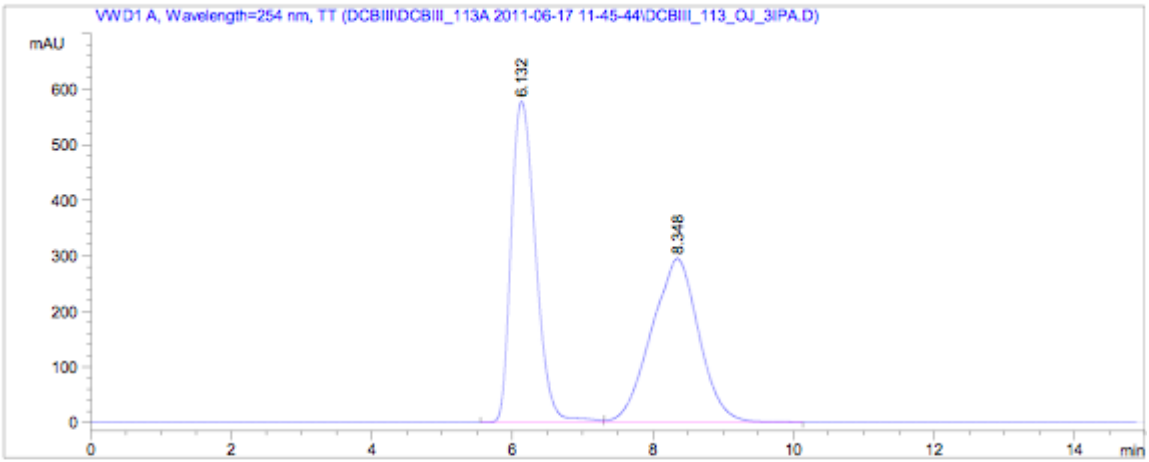
Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.667	912578	146016	99.360	2.507	2.867	0.098	5.971	1.106
2	Unknown	10	3.840	5880	746	0.640	3.747	4.000	0.134	N/A	1.280

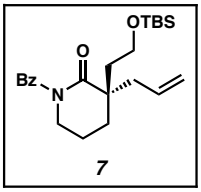
```
Data File C:\CHEM32\2\DATA\DCBIII\DCBIII_113A 2011-06-17 11-45-44\DCBIII_113_OJ_3IPA.D
Sample Name: DCBIII_113
```




```
================================================================================
    Acq. Operator    : DCB                              Seq. Line :   4
    Acq. Instrument  : HPLC 2                            Location : Vial 21
    Injection Date   : 6/17/2011 12:08:19 PM                 Inj :   1
                                                       Inj Volume : 5.0 µl
    Different Inj Volume from Sequence !     Actual Inj Volume : 3.0 µl
    Acq. Method      : C:\CHEM32\2\DATA\DCBIII\DCBIII_113A 2011-06-17 11-45-44\3IPA30_254.M
    Last changed     : 4/26/2010 8:31:20 PM
    Analysis Method  : C:\CHEM32\2\METHODS\POS1.M
    Last changed     : 7/29/2011 12:59:34 PM by DCB
                       (modified after loading)
    Method Info      : Position # 1 METHOD : (No Column) Valve to Position # 1 (By-Pass / Flush
                       Line).

================================================================================
```

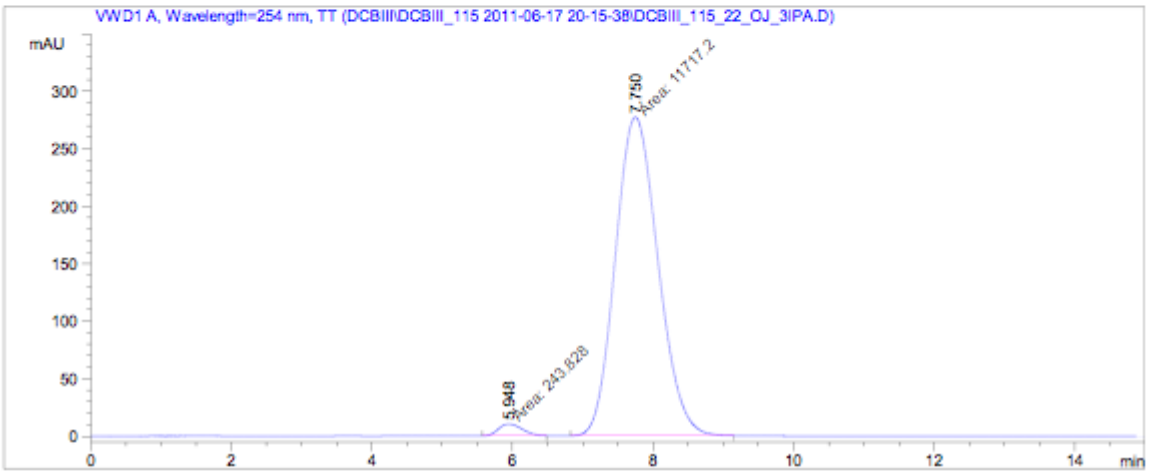



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.132 BV    0.3811 1.39639e4   577.44043  50.2375
   2   8.348 VB    0.6667 1.38318e4   294.82968  49.7625

Totals :                  2.77957e4   872.27011


================================================================================
                          Summed Peaks Report
================================================================================

HPLC 2 7/29/2011 1:00:11 PM DCB                              Page   1 of 2
```




```
Data File C:\CHEM32\2\DATA\DCBIII\DCBIII_115 2011-06-17 20-15-38\DCBIII_115_22_OJ_3IPA.D
Sample Name: DCBIII_115_22
```

Acq. Operator	: DCB	Seq. Line	: 11
Acq. Instrument	: HPLC 2	Location	: Vial 41
Injection Date	: 6/17/2011 10:13:45 PM	Inj	: 1
		Inj Volume	: 5.0 µl
Acq. Method	: C:\CHEM32\2\DATA\DCBIII\DCBIII_115 2011-06-17 20-15-38\3IPA15_254.M		
Last changed	: 6/23/2010 11:23:00 AM by LREPKA		
Analysis Method	: C:\CHEM32\2\METHODS\POS1.M		
Last changed	: 7/29/2011 12:56:33 PM by DCB (modified after loading)		
Method Info	: Position # 1 METHOD : (No Column) Valve to Position # 1 (By-Pass / Flush Line).		



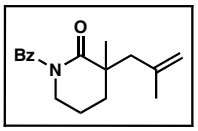
Area Percent Report

```
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT
```

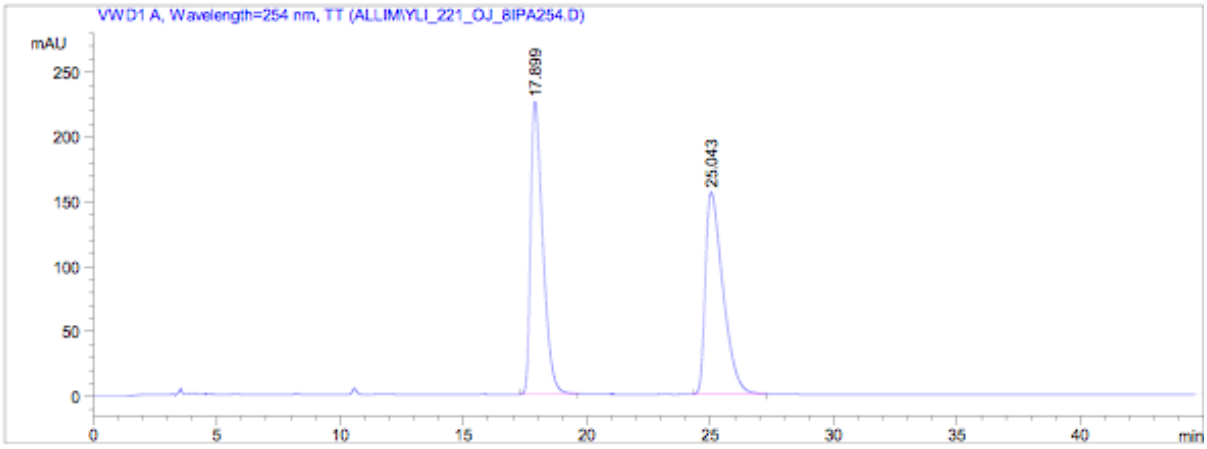
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.948	MM	0.3963	243.82837	10.25436	2.0385
2	7.750	MM	0.7041	1.17172e4	277.35931	97.9615
Totals :				1.19610e4	287.61367	

Summed Peaks Report

```
Data File C:\CHEM32\1\DATA\ALLIM\YLI_221_OJ_8IPA254.D
Sample Name: YLI_221
```

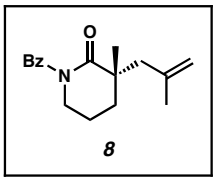



```
Acq. Operator    : ADL                                  Seq. Line :  24
Acq. Instrument  : HPLC 1                                Location : Vial 17
Injection Date   : 3/24/2011 3:55:13 AM                      Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\1\METHODS\8IPA45_254.M
Last changed     : 4/26/2010 10:45:46 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 11:12:34 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```



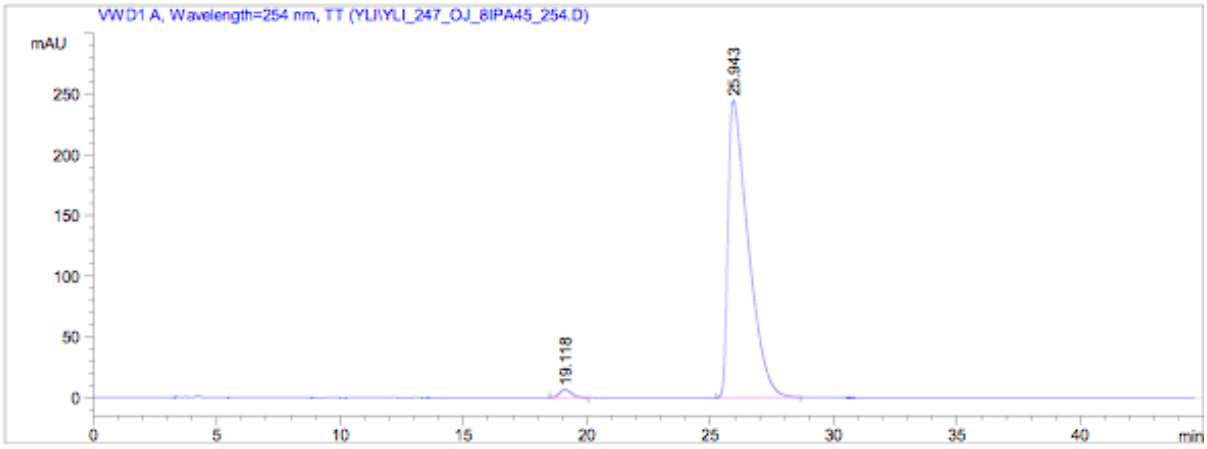

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  17.899 BB    0.5203 7701.64990  225.75133  50.0205
   2  25.043 BB    0.7410 7695.34424  155.73499  49.9795

Totals :                 1.53970e4   381.48631
```

```
Data File C:\CHEM32\1\DATA\YLI\YLI_247_OJ_8IPA45_254.D
Sample Name: YLI_247
```



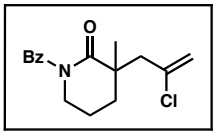
8

```
Acq. Operator    : YL                                Seq. Line :   4
Acq. Instrument  : HPLC 1                             Location : Vial 35
Injection Date   : 4/11/2011 10:58:08 AM                  Inj :   1
                                                    Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\1\METHODS\8IPA45_254.M
Last changed     : 4/26/2010 10:45:46 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 11:11:21 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```

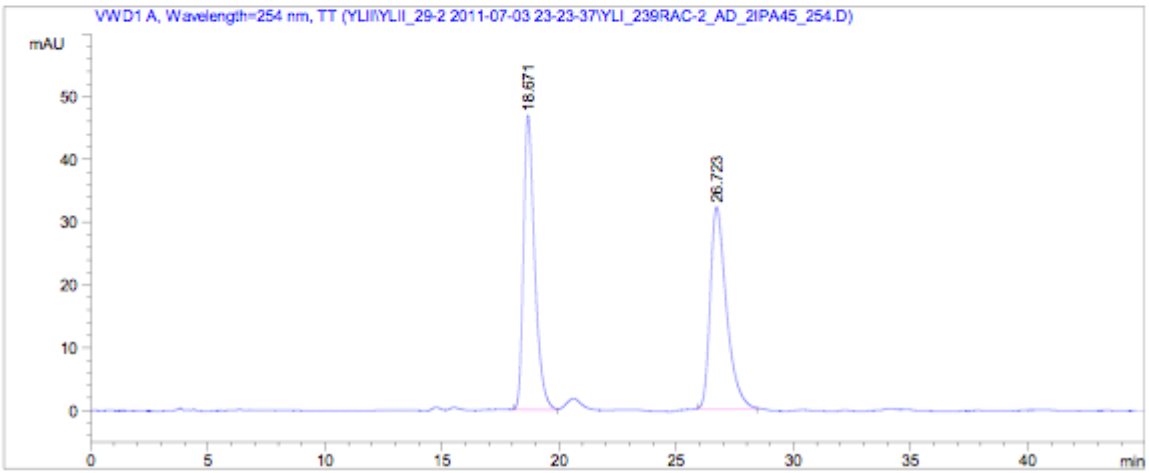



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  19.118 BB    0.4655  231.12241    6.51539   1.6361
   2  25.943 BB    0.8181 1.38954e4   244.75729  98.3639

Totals :                  1.41265e4   251.27269
```

```
Data File C:\CHEM32\2\DATA\YLII\YLII_29-2 2011-07-03 23-23-37\YLI_239RAC-2_AD_2IPA45_254.D
Sample Name: YLI_239rac
```

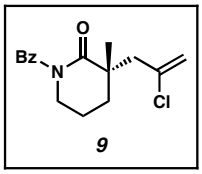



```
Acq. Operator    : YL                                  Seq. Line :   7
Acq. Instrument  : HPLC 2                               Location : Vial 13
Injection Date   : 7/4/2011 12:54:50 AM                    Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\2\DATA\YLII\YLII_29-2 2011-07-03 23-23-37\2IPA45_254.M
Last changed     : 4/26/2010 10:42:22 PM
Analysis Method  : C:\CHEM32\2\METHODS\POS1.M
Last changed     : 7/29/2011 11:27:02 AM by DCB
                   (modified after loading)
Method Info      : Position # 1 METHOD : (No Column) Valve to Position # 1 (By-Pass / Flush
                   Line).
```

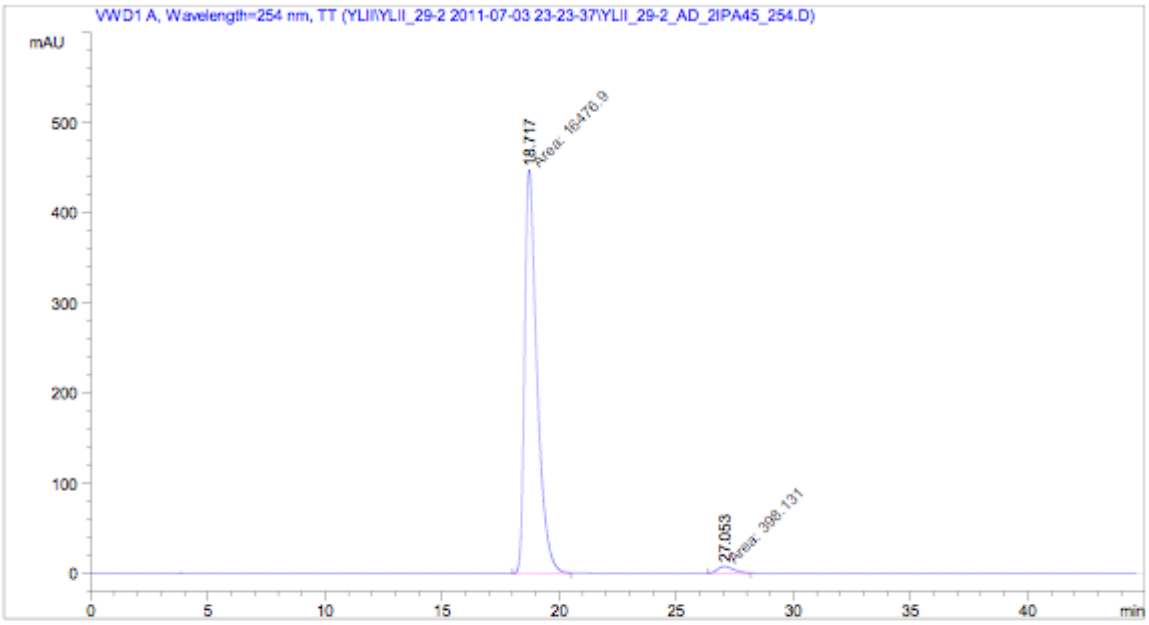



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.671 BB    0.5043 1559.92273   46.92644  49.9427
   2  26.723 BB    0.7288 1563.49976   32.24076  50.0573

Totals :                  3123.42249   79.16720


                          Summed Peaks Report

HPLC 2 7/29/2011 11:27:05 AM DCB                              Page   1 of 2
```

```
Data File C:\CHEM32\2\DATA\YLII\YLII_29-2 2011-07-03 23-23-37\YLII_29-2_AD_2IPA45_254.D
Sample Name: YLII_29

================================================================================
Acq. Operator   : YL                                Seq. Line :   4
Acq. Instrument : HPLC 2                           Location : Vial 12
Injection Date  : 7/3/2011 11:47:34 PM                 Inj :   1
                                                  Inj Volume : 5.0 µl
Acq. Method     : C:\CHEM32\2\DATA\YLII\YLII_29-2 2011-07-03 23-23-37\2IPA45_254.M
Last changed    : 4/26/2010 10:42:22 PM
Analysis Method : C:\CHEM32\2\METHODS\POS1.M
Last changed    : 7/29/2011 11:23:27 AM by DCB
                  (modified after loading)
Method Info     : Position # 1 METHOD : (No Column) Valve to Position # 1 (By-Pass / Flush
                  Line).
```

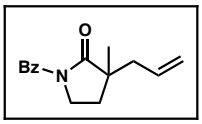


9



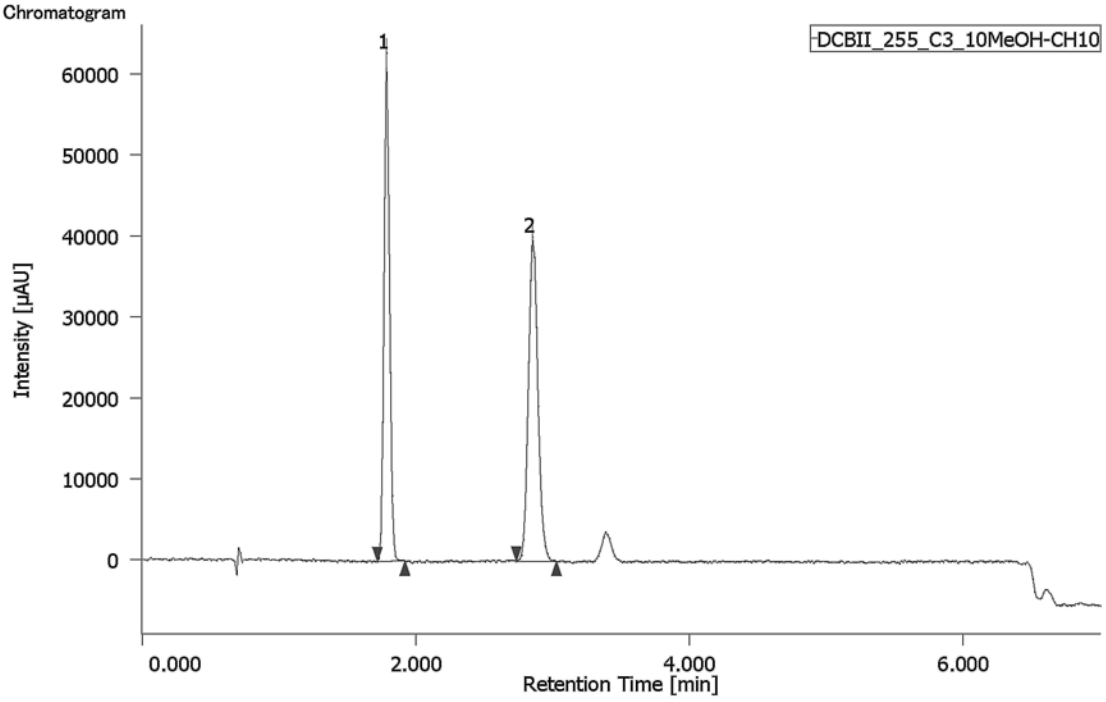

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  18.717 MM    0.6129 1.64769e4   448.08109  97.6407
   2  27.053 MM    0.8383  398.13113    7.91549   2.3593

Totals :                  1.68751e4   455.99658

HPLC 2 7/29/2011 11:23:39 AM DCB                          Page   1 of 2
```

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/4/2011 2:08:37 AM
Volume	5.00 [µL]
Sample #	1
Project Name	Cal Tech SFC
Executed Sequence	DCB_Screen2
Chromatogram Name	DCBII_255_C3_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCB_Screen2
Control Method	Solv 1 Col 3 Isocratic 10B 5mL_min 10MPa 10min

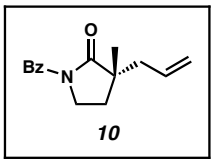
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	1.787	170030	62773	47.338	1.720	1.920	0.042	11.057	1.123
2	Unknown	10	2.853	189151	40089	52.662	2.733	3.027	0.072	N/A	1.146

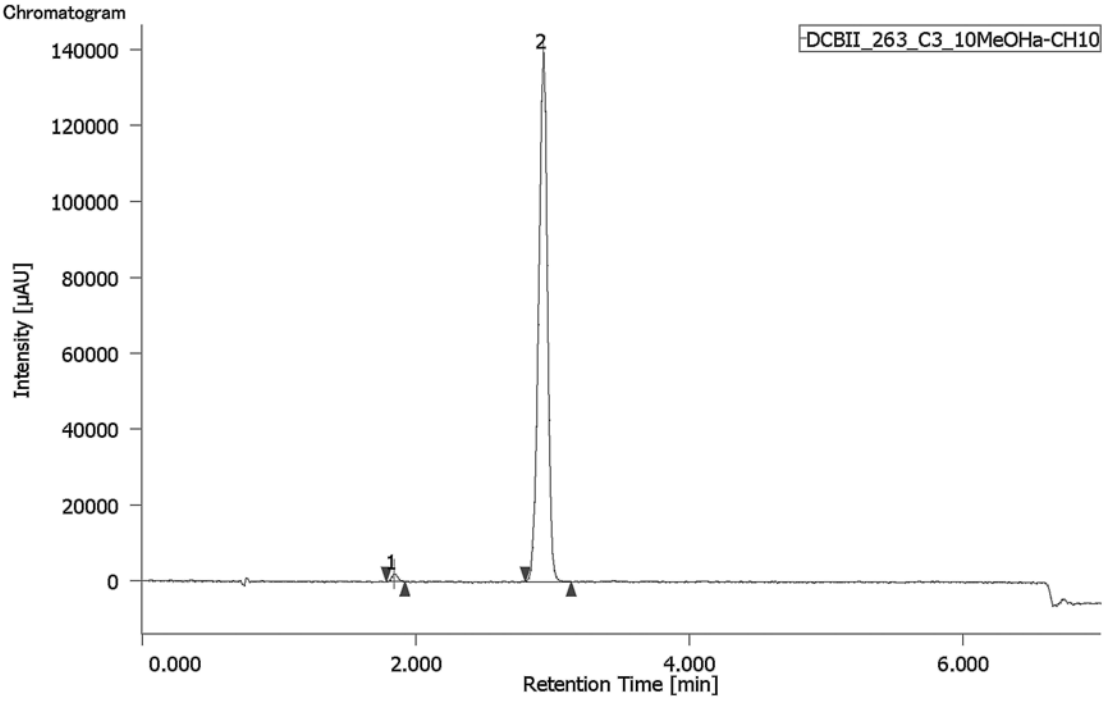
Analytical Report SFC



10

Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/12/2011 6:02:44 PM
Volume	5.00 [µL]
Sample #	5
Project Name	Cal Tech SFC
Executed Sequence	DCBII_265
Chromatogram Name	DCBII_263_C3_10MeOHa
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBII_265
Control Method	Solv 1 Col 3 Isocratic 10B 5mL_min 10MPa 10min

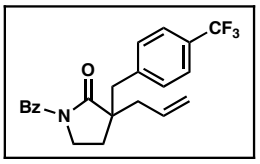
Chromatogram



Peak Information

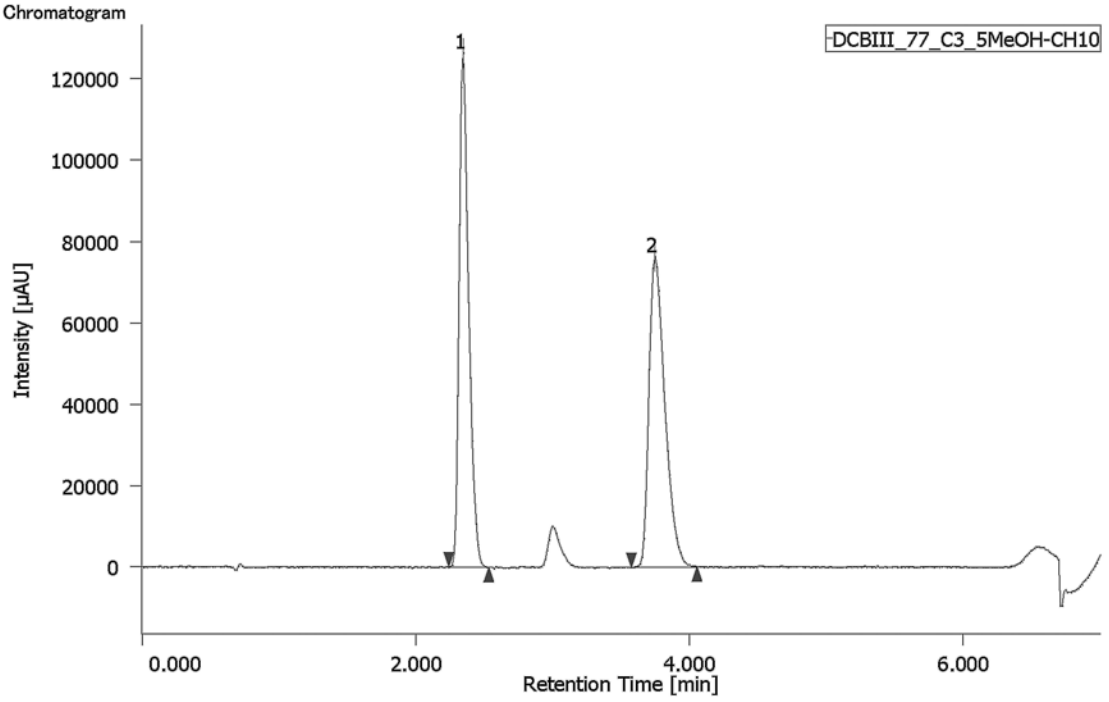
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	1.840	6425	2038	1.007	1.787	1.920	0.049	10.760	1.293
2	Unknown	10	2.933	631698	139373	98.993	2.800	3.133	0.070	N/A	0.901

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/26/2011 3:26:08 PM
Volume	5.00 [µL]
Sample #	31
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_77a
Chromatogram Name	DCBIII_77_C3_5MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_77a
Control Method	Solv 1 Col 3 Isocratic 5B 5mL_min 10MPa 10min

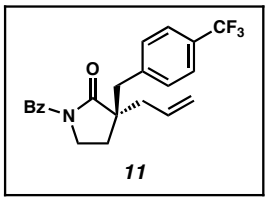
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.347	616849	126358	50.061	2.240	2.533	0.075	8.342	1.329
2	Unknown	10	3.747	615340	76449	49.939	3.573	4.053	0.123	N/A	1.525

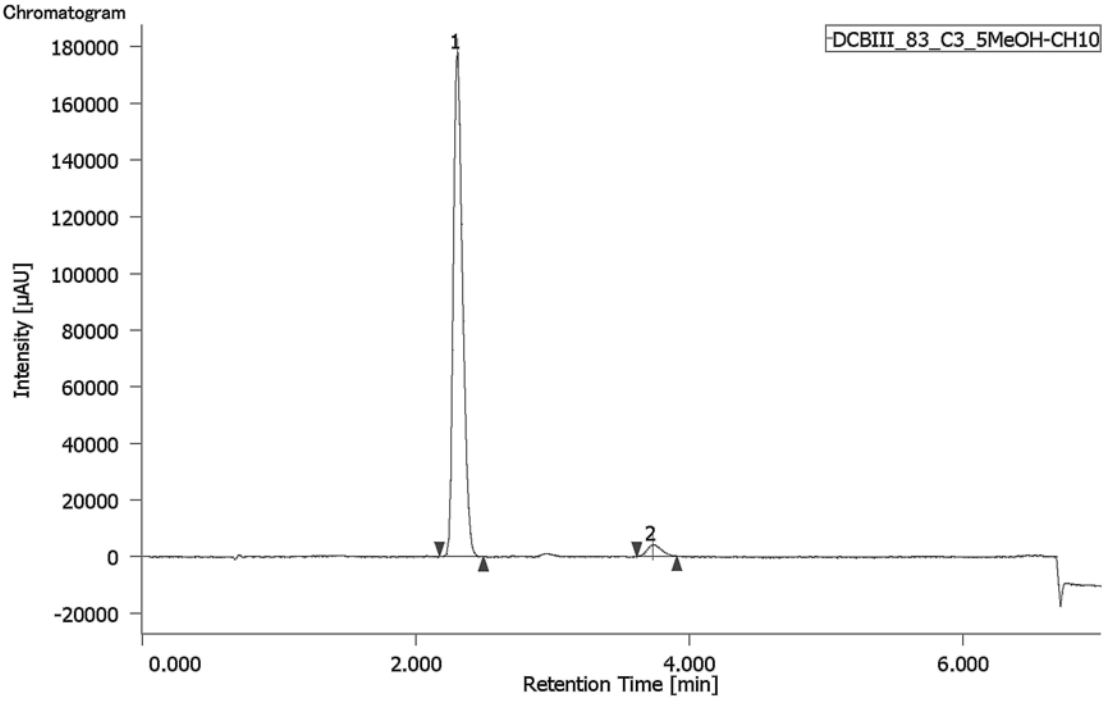
Analytical Report SFC



11

Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/27/2011 9:22:30 PM
Volume	5.00 [µL]
Sample #	2
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_83
Chromatogram Name	DCBIII_83_C3_5MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_83
Control Method	Solv 1 Col 3 Isocratic 5B 5mL_min 10MPa 10min

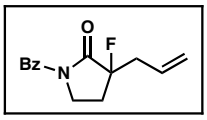
Chromatogram



Peak Information

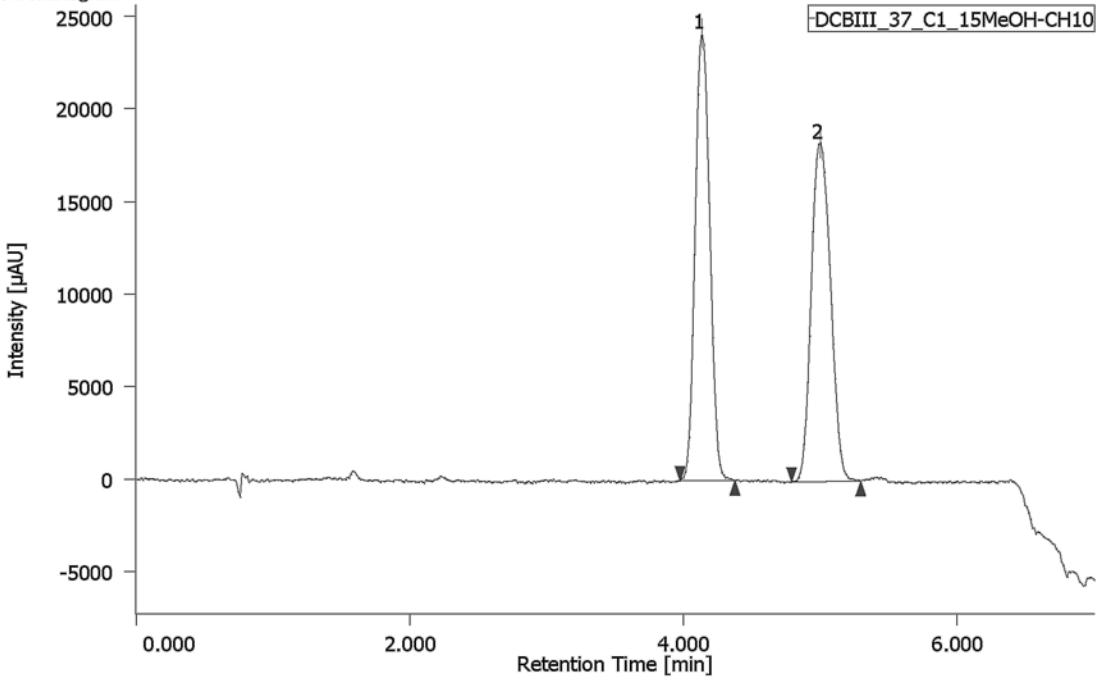
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.307	852148	177687	96.520	2.173	2.493	0.074	8.858	1.210
2	Unknown	10	3.733	30722	4115	3.480	3.613	3.907	0.116	N/A	1.214

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/22/2011 8:13:21 PM
Volume	5.00 [µL]
Sample #	4
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_37
Chromatogram Name	DCBIII_37_C1_15MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_37
Control Method	Solv 1 Col 1 Isocratic 15B 5mL_min 10MPa 10min

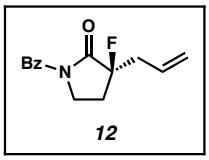
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	4.133	178884	24178	49.992	3.973	4.373	0.117	3.728	1.105
2	Unknown	10	5.000	178940	18270	50.008	4.787	5.293	0.157	N/A	1.096

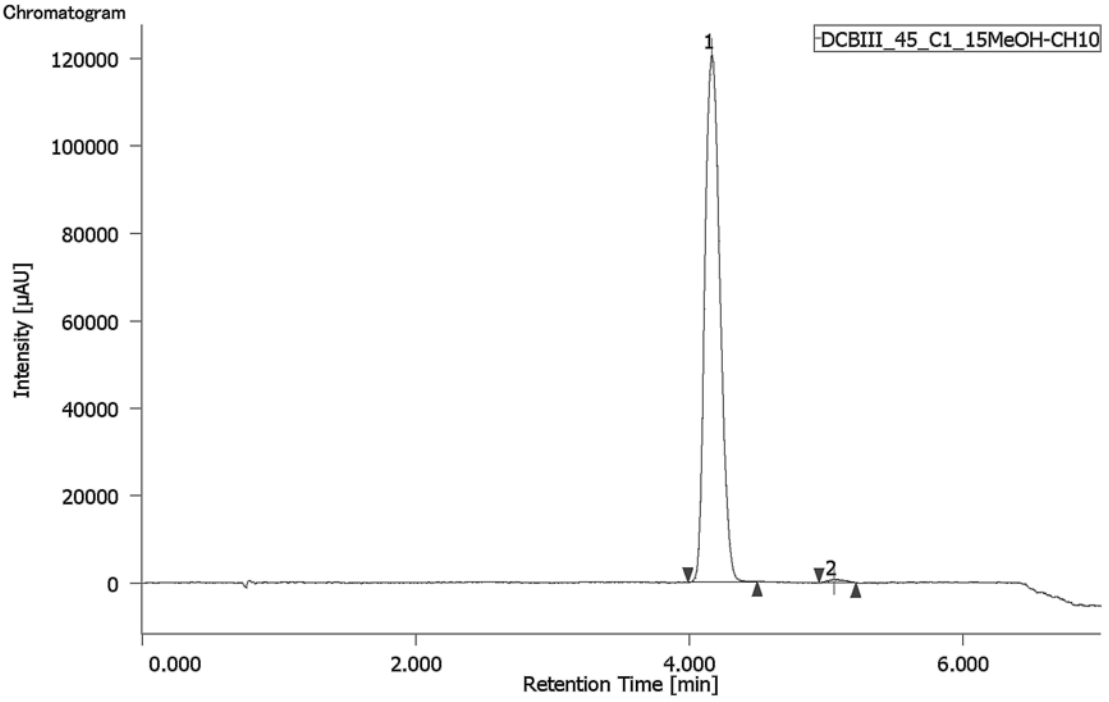
Analytical Report SFC



12

Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/23/2011 12:14:53 AM
Volume	5.00 [µL]
Sample #	5
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_45
Chromatogram Name	DCBIII_45_C1_15MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_45
Control Method	Solv 1 Col 1 Isocratic 15B 5mL_min 10MPa 10min

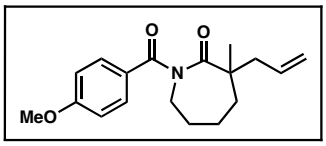
Chromatogram



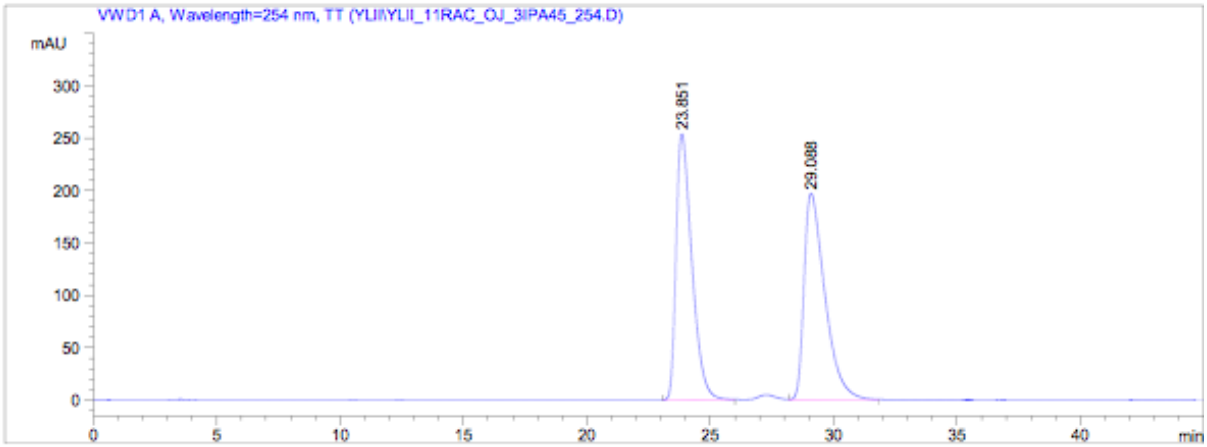
Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	4.160	927738	121116	99.348	3.987	4.493	0.122	3.778	1.231
2	Unknown	10	5.053	6089	701	0.652	4.947	5.213	0.157	N/A	1.322

```
Data File C:\CHEM32\1\DATA\YLII\YLII_11RAC_OJ_3IPA45_254.D
Sample Name: YLII_11rac
```

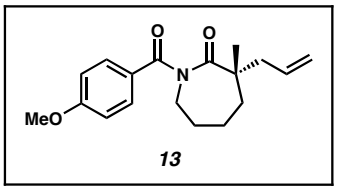



```
Acq. Operator    : YL                                  Seq. Line :   9
Acq. Instrument  : HPLC 1                               Location : Vial 4
Injection Date   : 5/3/2011 8:52:20 PM                      Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\1\METHODS\5IPA45_254.M
Last changed     : 4/26/2010 10:44:29 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 11:30:53 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```



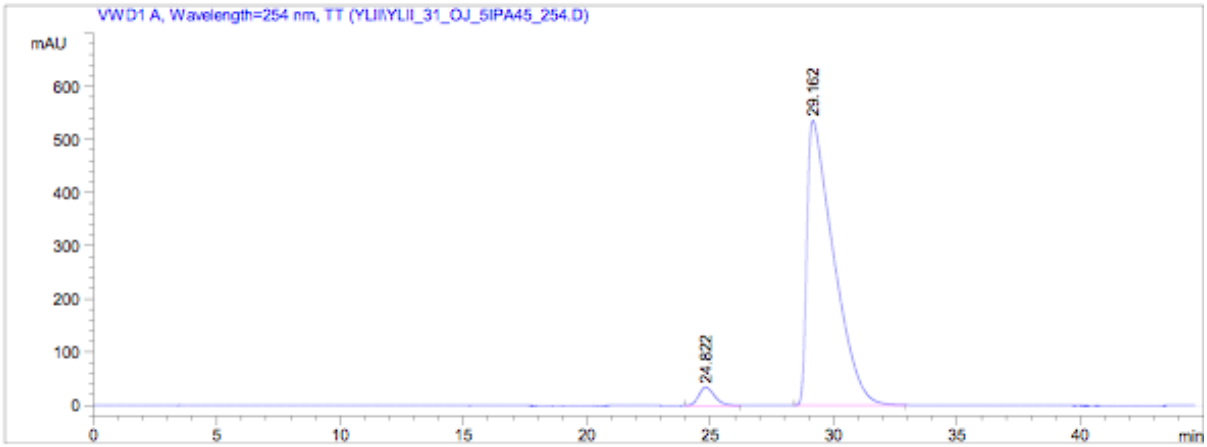

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  23.851 BB    0.6710 1.12818e4   254.06015  49.4580
   2  29.088 VB    0.8701 1.15291e4   196.94516  50.5420

Totals :                 2.28109e4   451.00531
```

```
Data File C:\CHEM32\1\DATA\YLII\YLII_31_OJ_5IPA45_254.D
Sample Name: YLII_31
```



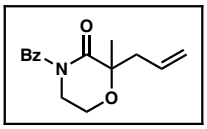
13

```
Acq. Operator    : YL                                  Seq. Line :   4
Acq. Instrument  : HPLC 1                               Location : Vial 7
Injection Date   : 5/9/2011 2:57:13 PM                      Inj :   1
                                                      Inj Volume : 5.0 µl
Acq. Method      : C:\CHEM32\1\METHODS\5IPA45_254.M
Last changed     : 4/26/2010 10:44:29 PM
Analysis Method  : C:\CHEM32\2\METHODS\5IPA_EQUIL.M
Last changed     : 7/29/2011 11:29:37 AM by BM
                   (modified after loading)
Method Info      : 5% IPA    10 min  equil   1 mL/min
```



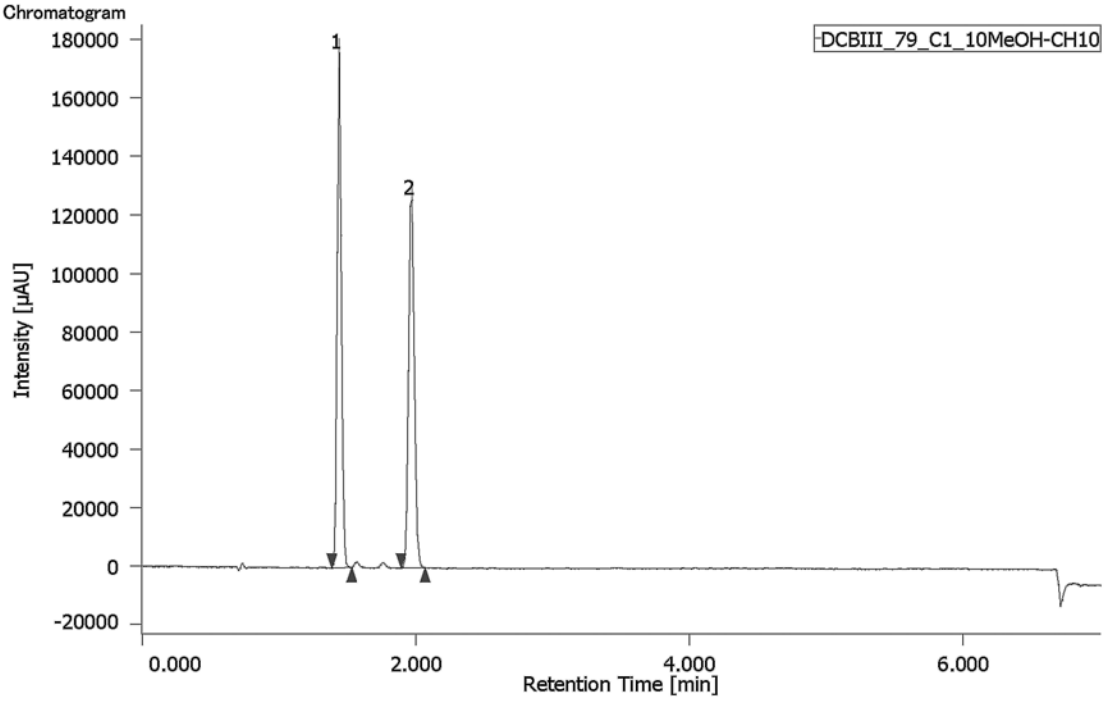

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  24.822 BB    0.6578 1514.60022   34.20794   3.6393
   2  29.162 BB    1.0397 4.01027e4   535.49139  96.3607

Totals :                  4.16173e4   569.69933
```

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/26/2011 3:57:24 PM
Volume	5.00 [µL]
Sample #	32
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_77a
Chromatogram Name	DCBIII_79_C1_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_77a
Control Method	Solv 1 Col 1 Isocratic 10B 5mL_min 10MPa 10min

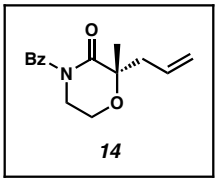
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	1.440	375493	175813	49.996	1.387	1.533	0.034	7.800	1.064
2	Unknown	10	1.973	375560	125767	50.004	1.893	2.067	0.046	N/A	0.973

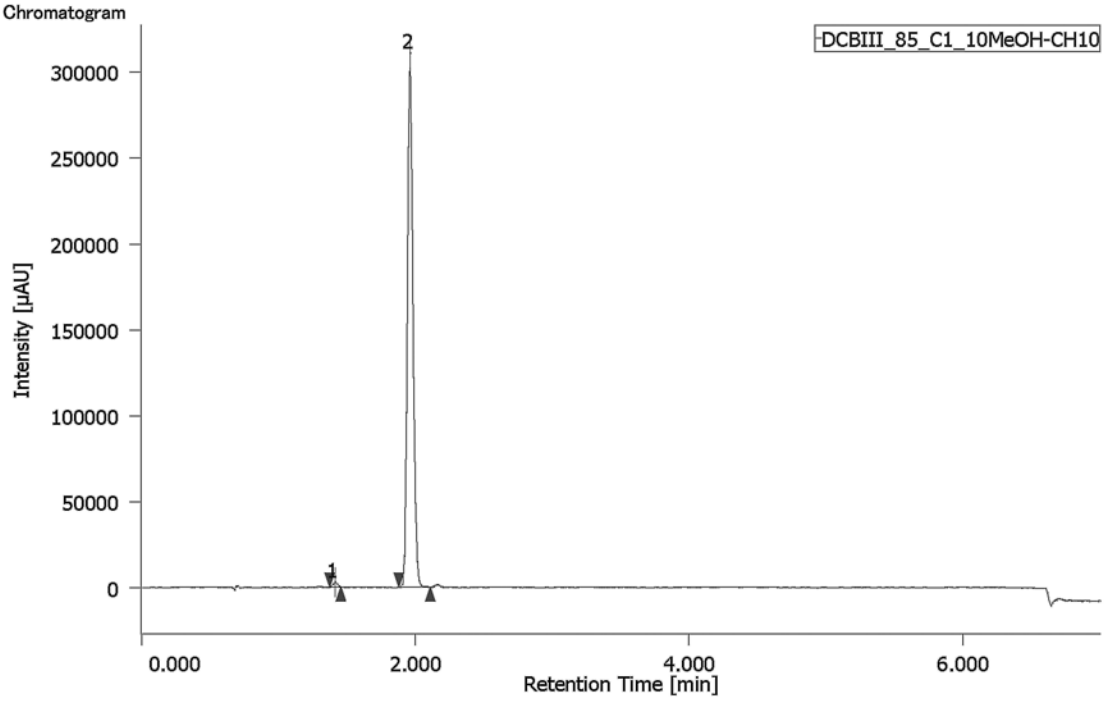
Analytical Report SFC



14

Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/27/2011 10:04:14 PM
Volume	5.00 [µL]
Sample #	3
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_83
Chromatogram Name	DCBIII_85_C1_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_83
Control Method	Solv 1 Col 1 Isocratic 10B 5mL_min 10MPa 10min

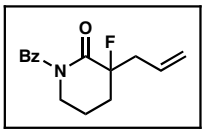
Chromatogram



Peak Information

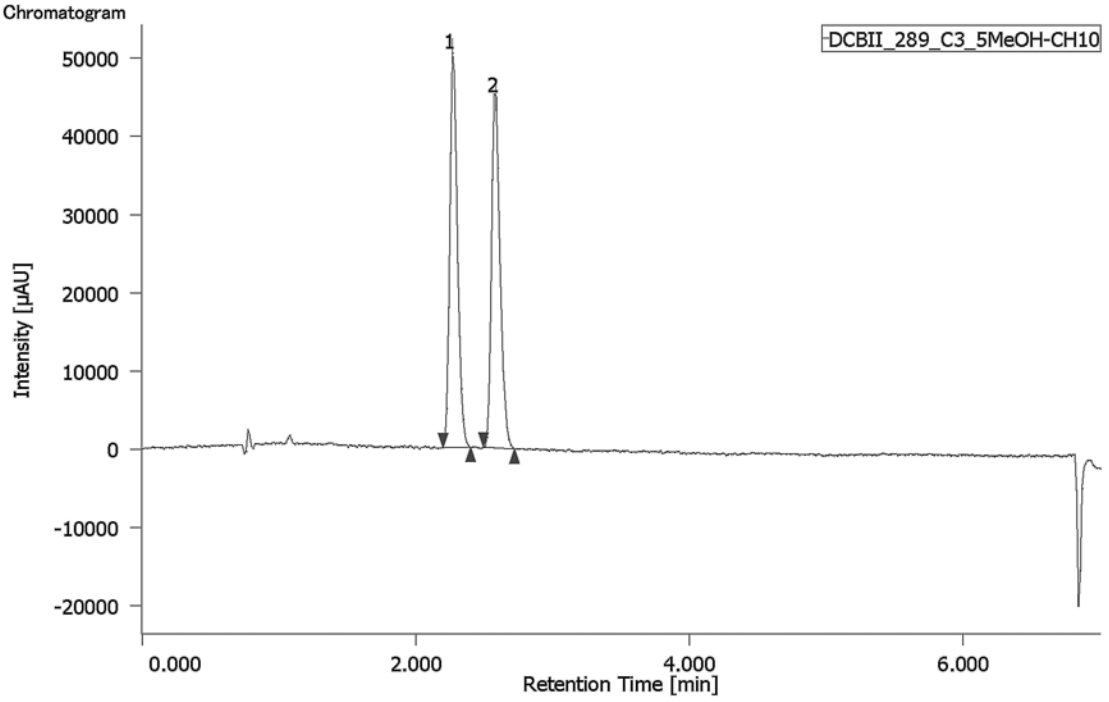
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	1.413	6067	2785	0.678	1.373	1.453	0.036	7.978	1.038
2	Unknown	10	1.960	888319	310582	99.322	1.880	2.107	0.045	N/A	1.129

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/15/2011 1:15:35 PM
Volume	5.00 [µL]
Sample #	2
Project Name	Cal Tech SFC
Executed Sequence	DCBII_289
Chromatogram Name	DCBII_289_C3_5MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBII_289
Control Method	Solv 1 Col 3 Isocratic 5B 5mL_min 10MPa 10min

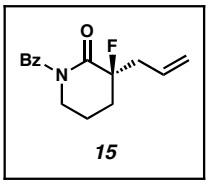
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.267	197348	50388	49.966	2.200	2.400	0.060	2.974	1.401
2	Unknown	10	2.587	197618	44842	50.034	2.493	2.720	0.067	N/A	1.157

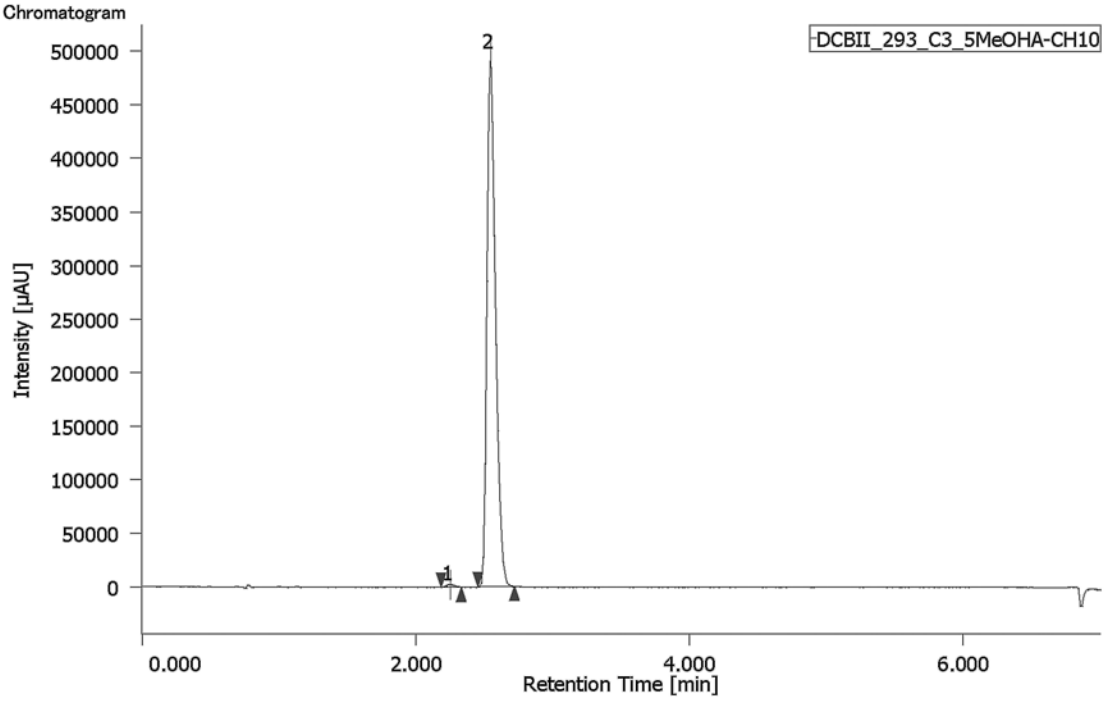
Analytical Report SFC



15

Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/17/2011 3:51:23 PM
Volume	5.00 [µL]
Sample #	5
Project Name	Cal Tech SFC
Executed Sequence	DCBII_291
Chromatogram Name	DCBII_293_C3_5MeOHA
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBII_291
Control Method	Solv 1 Col 3 Isocratic 5B 5mL_min 10MPa 10min

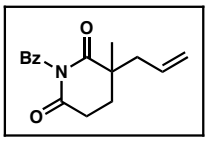
Chromatogram



Peak Information

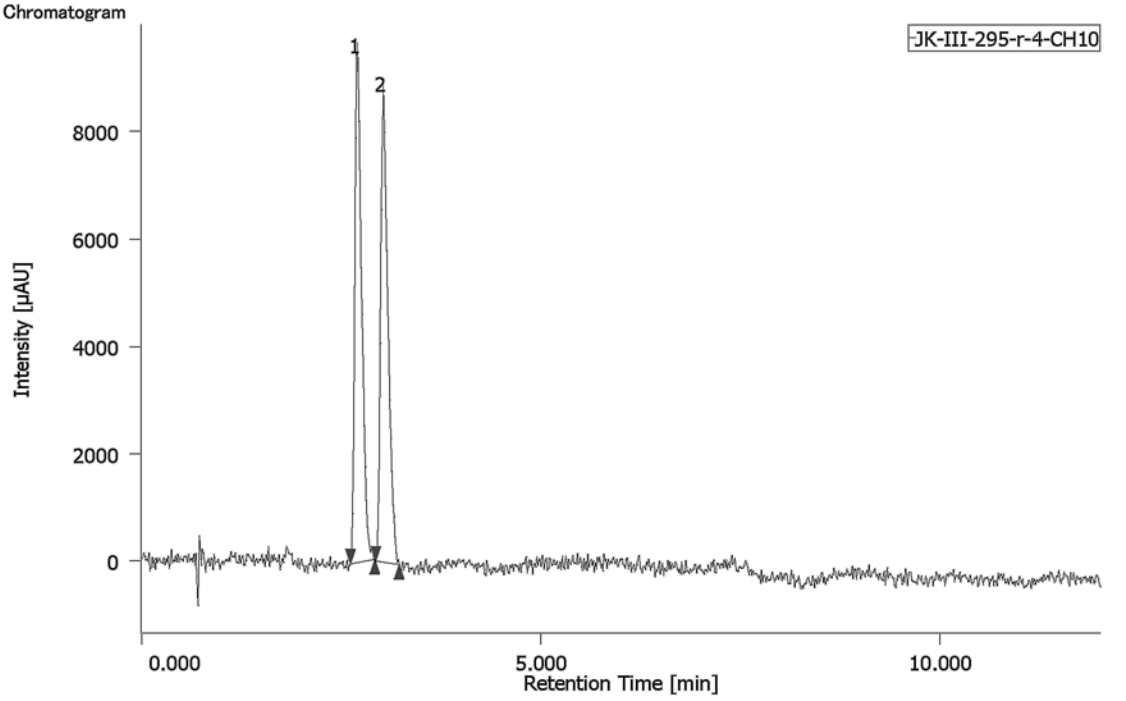
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.253	8809	2265	0.408	2.187	2.333	0.061	2.707	1.099
2	Unknown	10	2.547	2151227	498155	99.592	2.453	2.720	0.067	N/A	1.337

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	8/21/2011 11:44:55 AM
Volume	5.00 [µL]
Sample #	4
Project Name	Cal Tech SFC
Executed Sequence	JK-III-295-racemic
Chromatogram Name	JK-III-295-r-4
Sample Name	
Acquisition Time	12.0 [min]
Acquisition Sequence	JK-III-295-racemic
Control Method	Solv 1 Col 3 Isocratic 3B 5mL_min 10MPa 15 min

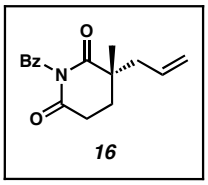
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.707	57252	9406	50.560	2.613	2.920	0.094	1.949	1.387
2	Unknown	10	3.027	55984	8685	49.440	2.933	3.227	0.099	N/A	1.511

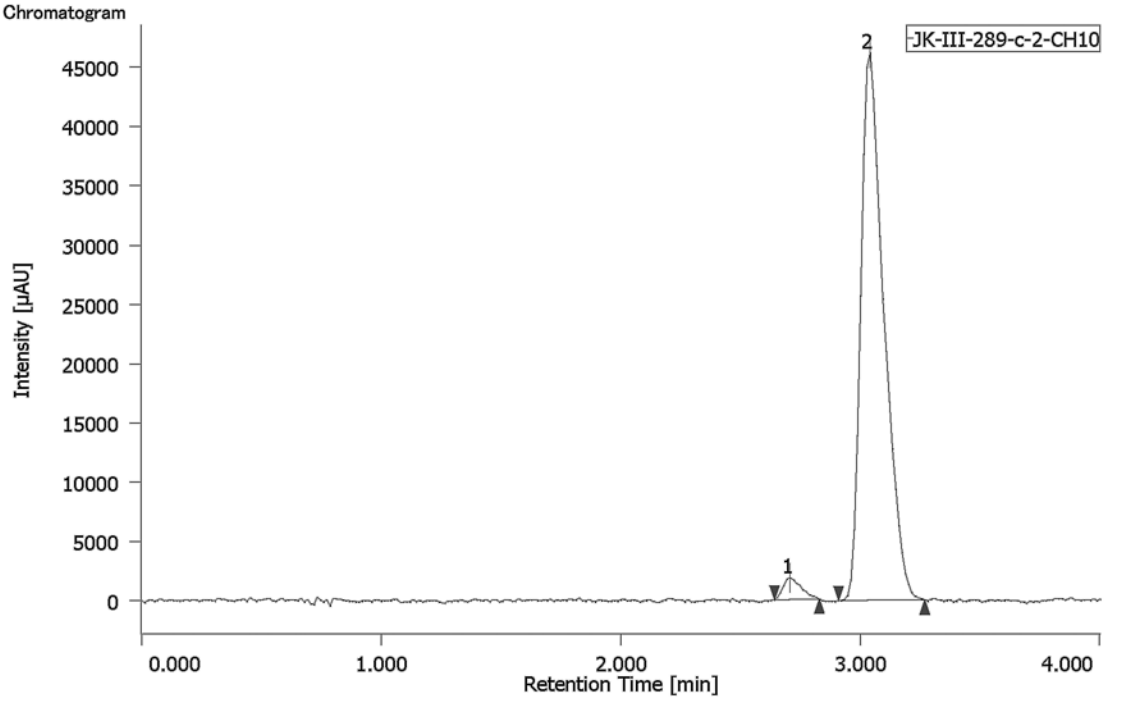
Analytical Report SFC



16

Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	8/21/2011 12:19:23 PM
Volume	2.00 [µL]
Sample #	5
Project Name	Cal Tech SFC
Executed Sequence	JK-III-289-c
Chromatogram Name	JK-III-289-c-2
Sample Name	
Acquisition Time	12.0 [min]
Acquisition Sequence	JK-III-289-c
Control Method	Solv 1 Col 3 Isocratic 3B 5mL_min 10MPa 15 min

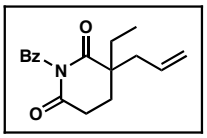
Chromatogram



Peak Information

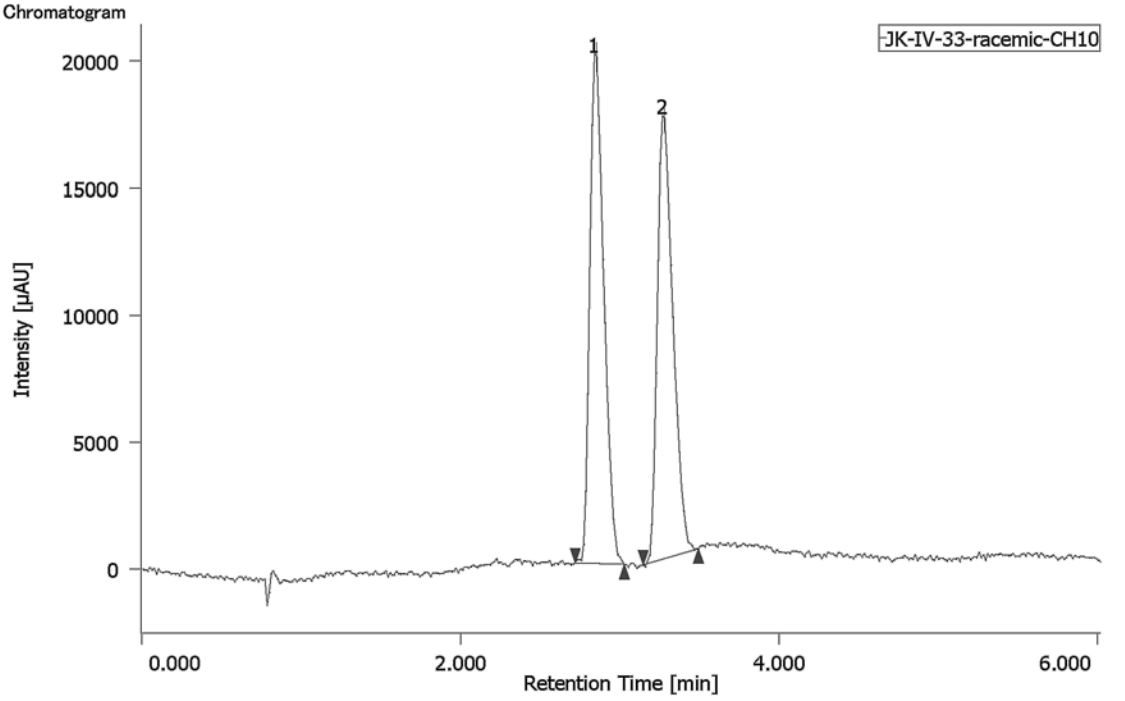
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.707	9653	1838	3.025	2.640	2.827	0.083	2.114	1.429
2	Unknown	10	3.040	309418	46150	96.975	2.907	3.267	0.103	N/A	1.435

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	8/24/2011 8:17:20 PM
Volume	5.00 [µL]
Sample #	4
Project Name	Cal Tech SFC
Executed Sequence	JK-IV-33-racemic
Chromatogram Name	JK-IV-33-racemic
Sample Name	
Acquisition Time	12.0 [min]
Acquisition Sequence	JK-IV-33-racemic
Control Method	Solv 1 Col 3 Isocratic 3B 5mL_min 10MPa 15 min

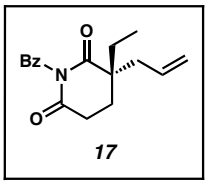
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.853	122589	19941	50.688	2.720	3.027	0.097	2.460	1.267
2	Unknown	10	3.280	119260	17340	49.312	3.147	3.493	0.108	N/A	1.281

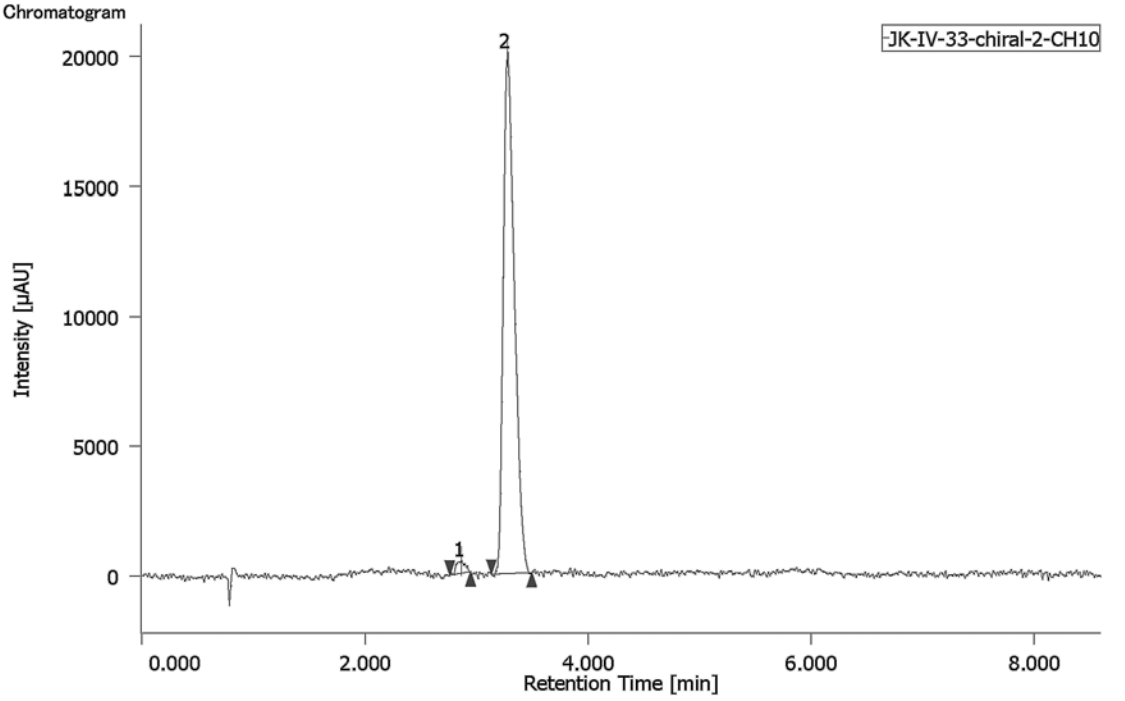
Analytical Report SFC



17

Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	8/24/2011 8:39:15 PM
Volume	5.00 [µL]
Sample #	5
Project Name	Cal Tech SFC
Executed Sequence	JK-IV-33-chiral
Chromatogram Name	JK-IV-33-chiral-2
Sample Name	
Acquisition Time	12.0 [min]
Acquisition Sequence	JK-IV-33-chiral
Control Method	Solv 1 Col 3 Isocratic 3B 5mL_min 10MPa 15 min

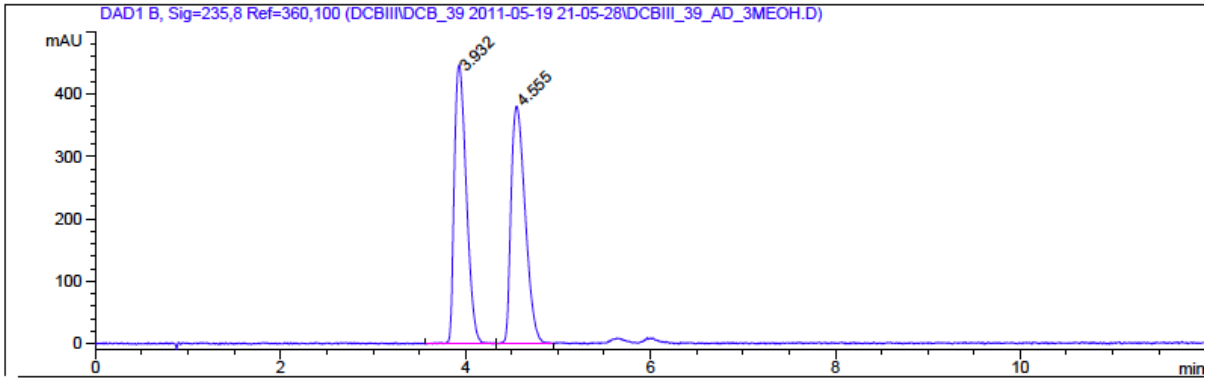
Chromatogram



Peak Information

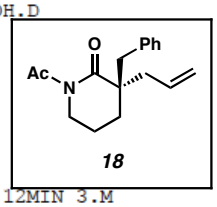
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.867	2710	478	1.921	2.760	2.947	0.112	2.217	0.822
2	Unknown	10	3.280	138383	20064	98.079	3.133	3.493	0.108	N/A	1.395

```
Data File C:\CHEM32\1\DATA\DCBIII\DCB_39 2011-05-19 21-05-28\DCBIII_39_AD_3MEOH.D
Sample Name: DCBIII_39

    ======================================================================
    Acq. Operator   : DCB                          Seq. Line :   2
    Acq. Instrument : Instrument 1                  Location : P4-A-01
    Injection Date  : 5/19/2011 9:09:14 PM               Inj :   1
                                                   Inj Volume : 5 µl
    Acq. Method     : C:\Chem32\1\DATA\DCBIII\DCB_39 2011-05-19 21-05-28\S1C2 12MIN 3.M
    Last changed    : 5/19/2011 9:00:10 PM by DCB
    Analysis Method : C:\CHEM32\1\DATA\DCBIII\DCB_39 2011-05-19 21-05-28\DCBIII_39_AD_3MEOH.D\DA.M (
                      S1C2 12MIN 3.M)
    Last changed    : 7/29/2011 1:05:27 PM by MEK
                      (modified after loading)
    Method Info     : S1C2 12min 3.M: 3% MeOH, AD-H 3 mL/min, 12 min
```



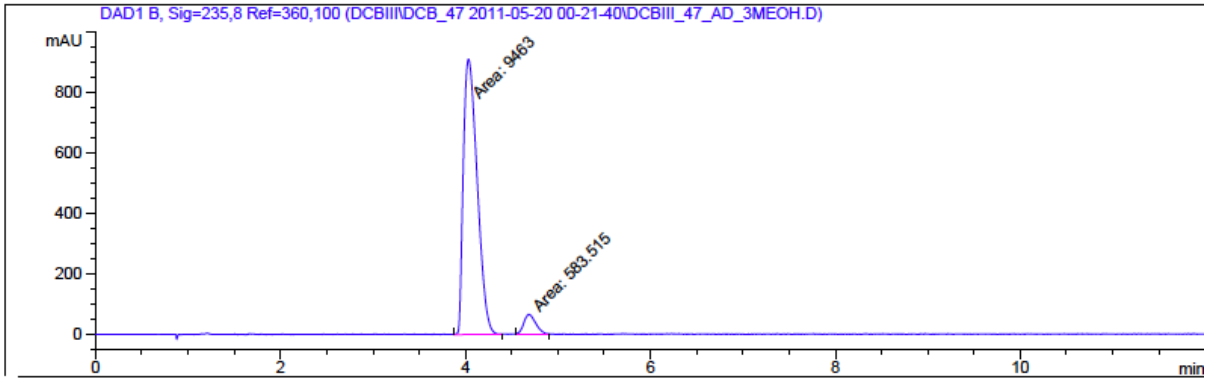

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=235,8 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   3.932 VV    0.1458 4057.47485  447.28833  49.9657
       2   4.555 VV    0.1724 4063.05298  381.06885  50.0343

    Totals :                   8120.52783  828.35718

    ======================================================================
                              *** End of Report ***
```

Data File C:\CHEM32\1\DATA\DCBIII\DCB_47 2011-05-20 00-21-40\DCBIII_47_AD_3MEOH.D
Sample Name: DCBIII_47



18

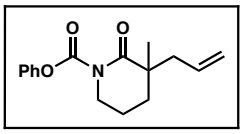
```
==========================================================================
Acq. Operator   : DCB                              Seq. Line :   1
Acq. Instrument : Instrument 1                     Location : P4-A-02
Injection Date  : 5/20/2011 12:22:07 AM               Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\DCBIII\DCB_47 2011-05-20 00-21-40\S1C2 12MIN 3.M
Last changed    : 5/19/2011 9:00:10 PM by DCB
Analysis Method : C:\CHEM32\1\DATA\DCBIII\DCB_39 2011-05-19 21-05-28\DCBIII_39_AD_3MEOH.D\DA.M (
                  S1C2 12MIN 3.M)
Last changed    : 7/29/2011 1:11:23 PM by MEK
                  (modified after loading)
Method Info     : S1C2 12min 3.M: 3% MeOH, AD-H 3 mL/min, 12 min
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=235,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.034 MM    0.1732 9463.00000  910.74158  94.1919
   2   4.688 MM    0.1498  583.51471   64.92155   5.8081

Totals :                  1.00465e4   975.66313

==========================================================================
                        *** End of Report ***
```

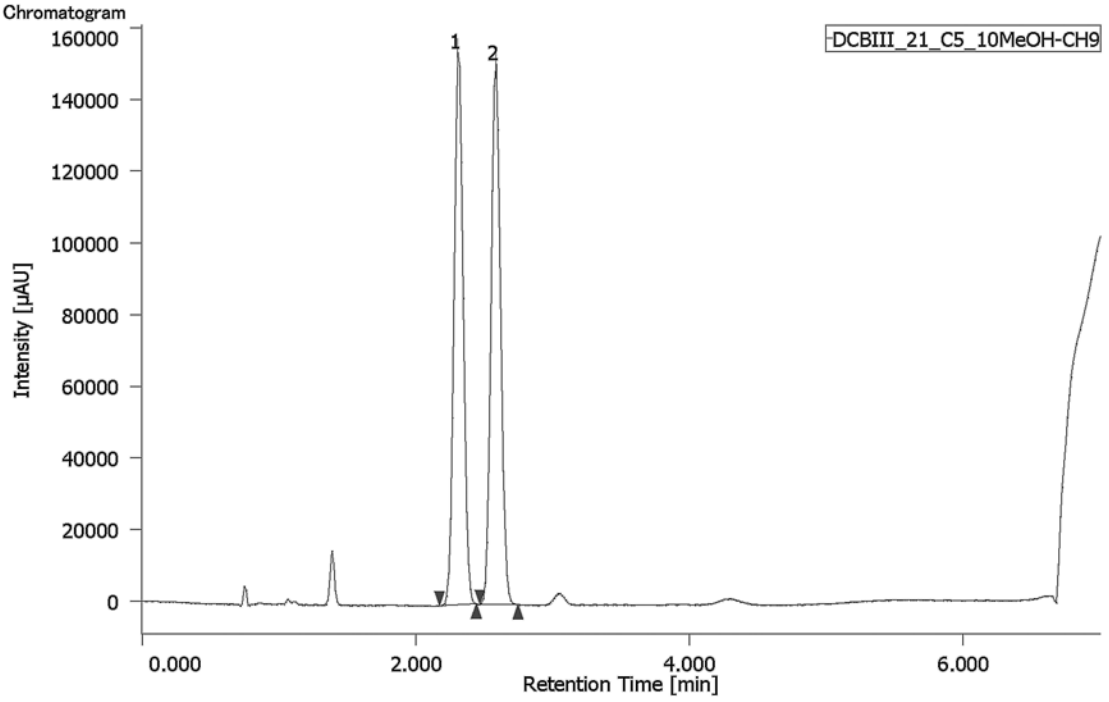
Instrument 1 7/29/2011 1:11:32 PM MEK Page 1 of 1

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/1/2011 1:35:19 PM
Volume	5.00 [µL]
Sample #	3
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_17
Chromatogram Name	DCBIII_21_C5_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_17
Control Method	Solv 1 Col 5 Isocratic 10B 5mL_min 10MPa 10min

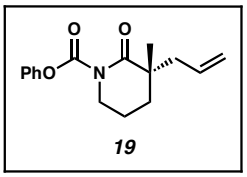
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	9	2.307	734302	153995	49.956	2.173	2.440	0.075	2.183	1.125
2	Unknown	9	2.587	735583	150637	50.044	2.467	2.747	0.076	N/A	1.021

Analytical Report SFC



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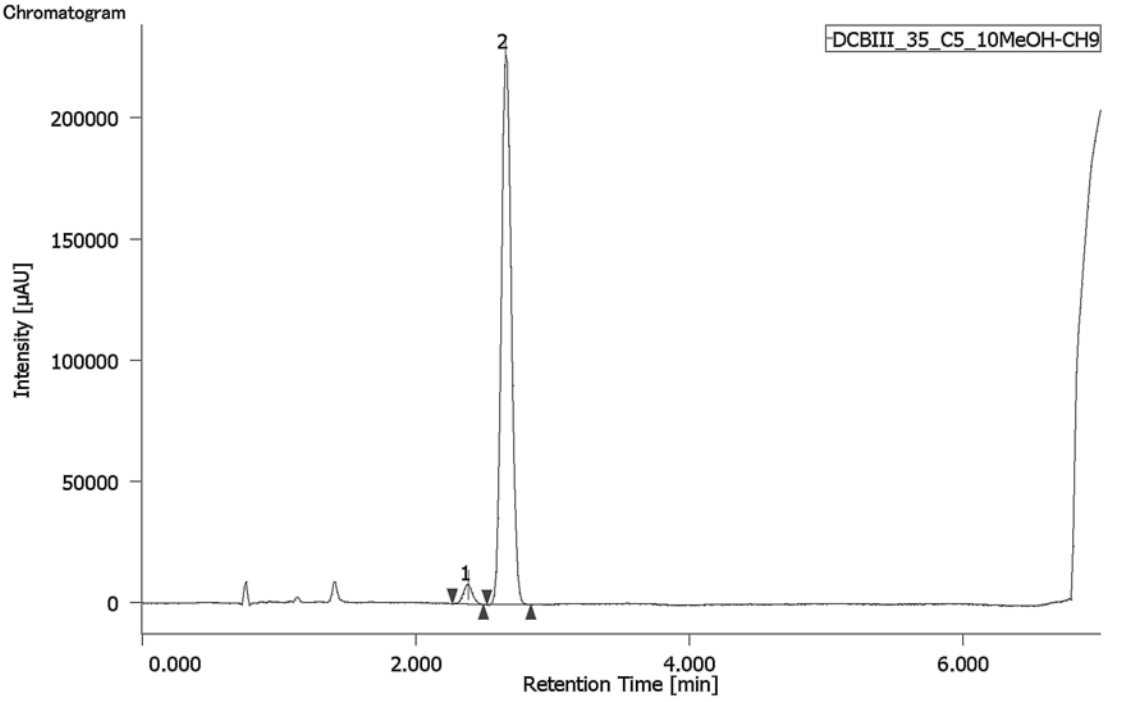
Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/5/2011 12:41:22 AM
Volume	5.00 [µL]
Sample #	6
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_35
Chromatogram Name	DCBIII_35_C5_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_35
Control Method	Solv 1 Col 5 Isocratic 10B 5mL_min 10MPa 10min

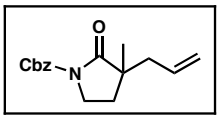
Chromatogram



Peak Information

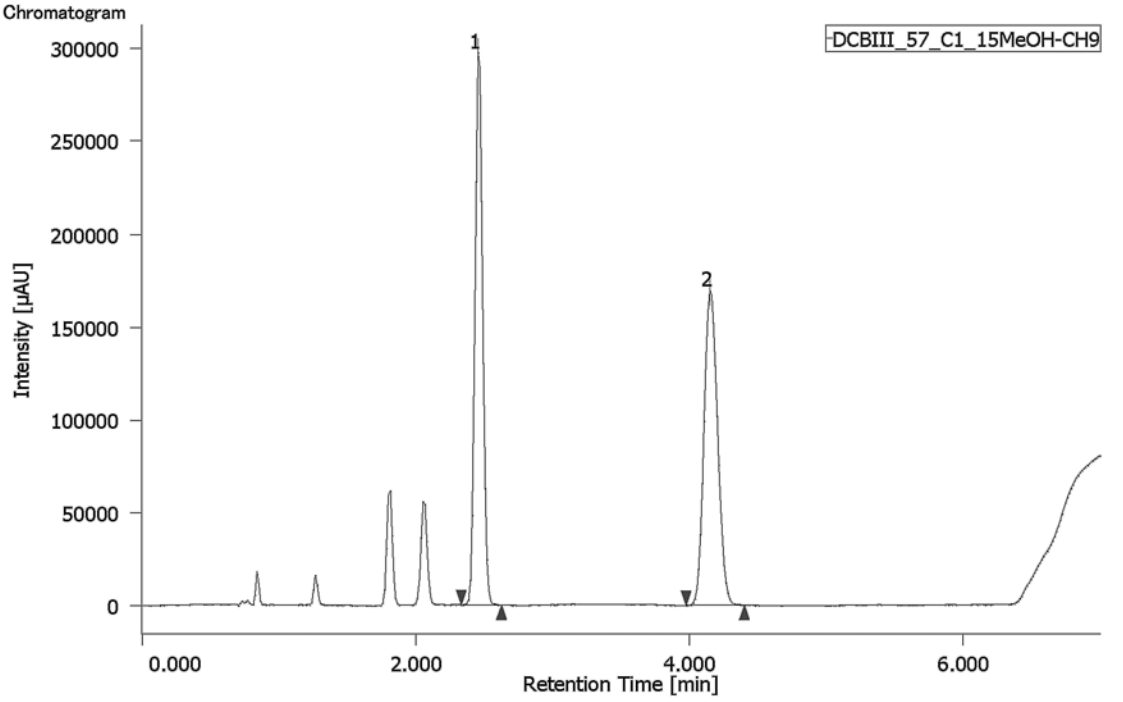
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	9	2.387	38548	7972	3.254	2.267	2.493	0.075	2.042	0.979
2	Unknown	9	2.653	1145994	227635	96.746	2.520	2.840	0.079	N/A	1.179

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/18/2011 12:33:33 AM
Volume	1.00 [µL]
Sample #	10
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_57
Chromatogram Name	DCBIII_57_C1_15MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_57
Control Method	Solv 1 Col 1 Isocratic 15B 5mL_min 10MPa 10min

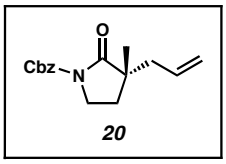
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	9	2.453	1159128	296771	49.907	2.333	2.627	0.061	11.847	1.206
2	Unknown	9	4.147	1163438	169323	50.093	3.973	4.400	0.108	N/A	1.184

Analytical Report SFC



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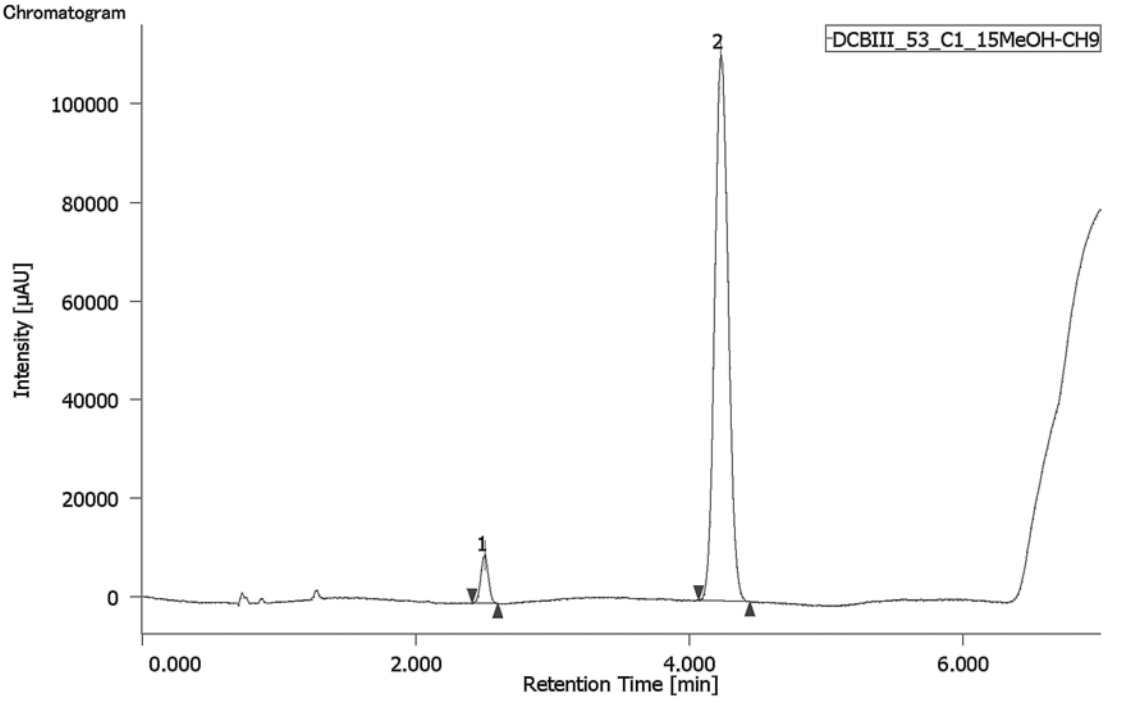
Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/18/2011 11:47:09 PM
Volume	4.00 [µL]
Sample #	2
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_53
Chromatogram Name	DCBIII_53_C1_15MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_53
Control Method	Solv 1 Col 1 Isocratic 15B 5mL_min 10MPa 10min

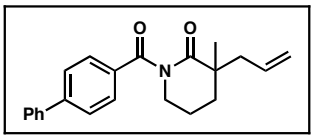
Chromatogram



Peak Information

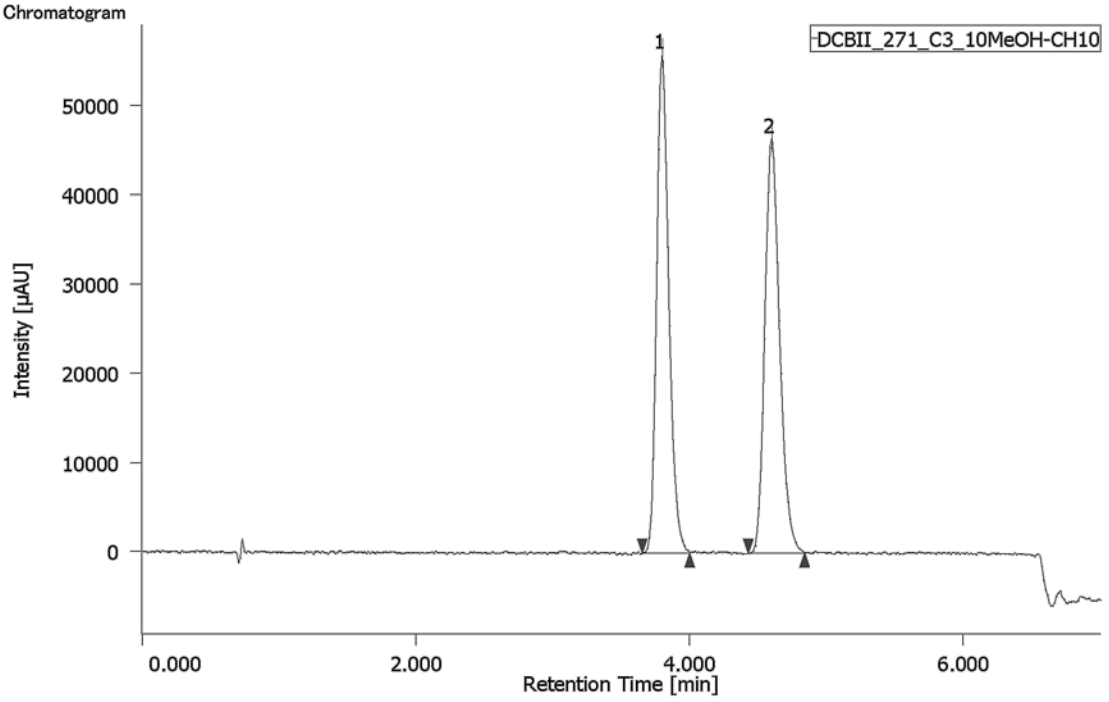
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	9	2.507	37665	9731	4.674	2.413	2.600	0.061	11.992	0.961
2	Unknown	9	4.227	768184	111202	95.326	4.067	4.440	0.108	N/A	1.126

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/6/2011 4:21:27 PM
Volume	5.00 [µL]
Sample #	2
Project Name	Cal Tech SFC
Executed Sequence	DCBII_271
Chromatogram Name	DCBII_271_C3_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBII_271
Control Method	Solv 1 Col 3 Isocratic 10B 5mL_min 10MPa 10min

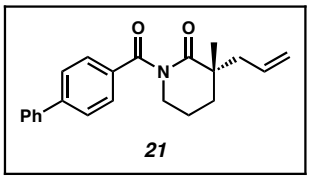
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	3.800	347849	56002	49.922	3.653	4.000	0.094	4.522	1.221
2	Unknown	10	4.600	348941	46525	50.078	4.427	4.840	0.114	N/A	1.202

Analytical Report SFC



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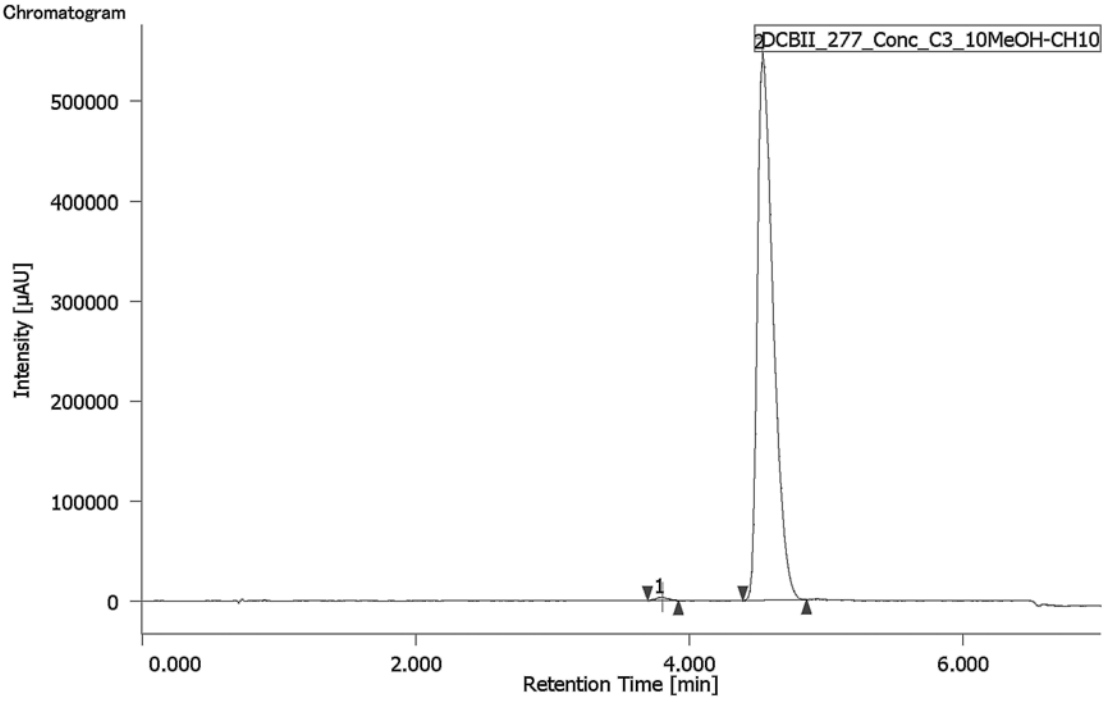
Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	4/8/2011 4:30:22 PM
Volume	5.00 [µL]
Sample #	3
Project Name	Cal Tech SFC
Executed Sequence	FV-III-289-105MeOH-5mL-ColumnScreen
Chromatogram Name	DCBII_277_Conc_C3_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	FV-III-289-105MeOH-5mL-ColumnScreen
Control Method	Solv 1 Col 3 Isocratic 10B 5mL_min 10MPa 10min

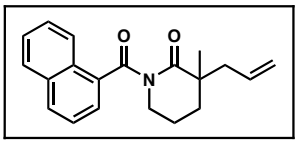
Chromatogram



Peak Information

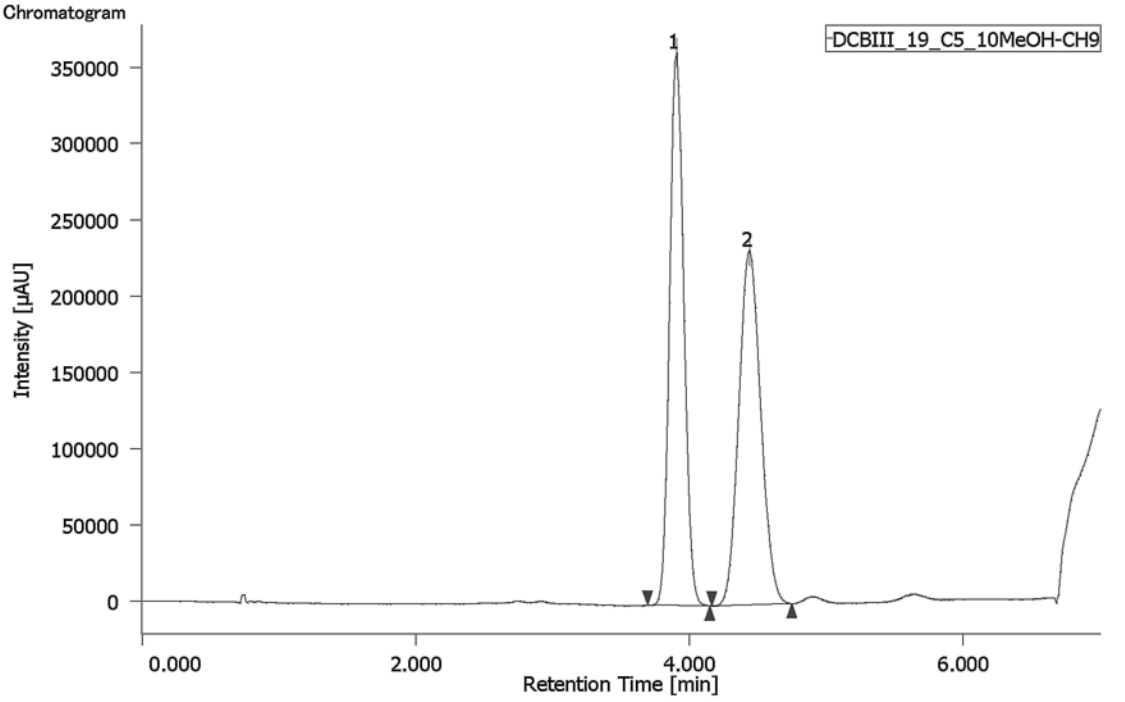
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	3.800	20118	3364	0.456	3.693	3.920	0.091	4.036	1.087
2	Unknown	10	4.533	4393654	546949	99.544	4.387	4.853	0.123	N/A	1.691

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/1/2011 12:32:48 PM
Volume	5.00 [µL]
Sample #	2
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_17
Chromatogram Name	DCBIII_19_C5_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_17
Control Method	Solv 1 Col 5 Isocratic 10B 5mL_min 10MPa 10min

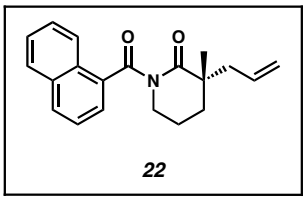
Chromatogram



Peak Information

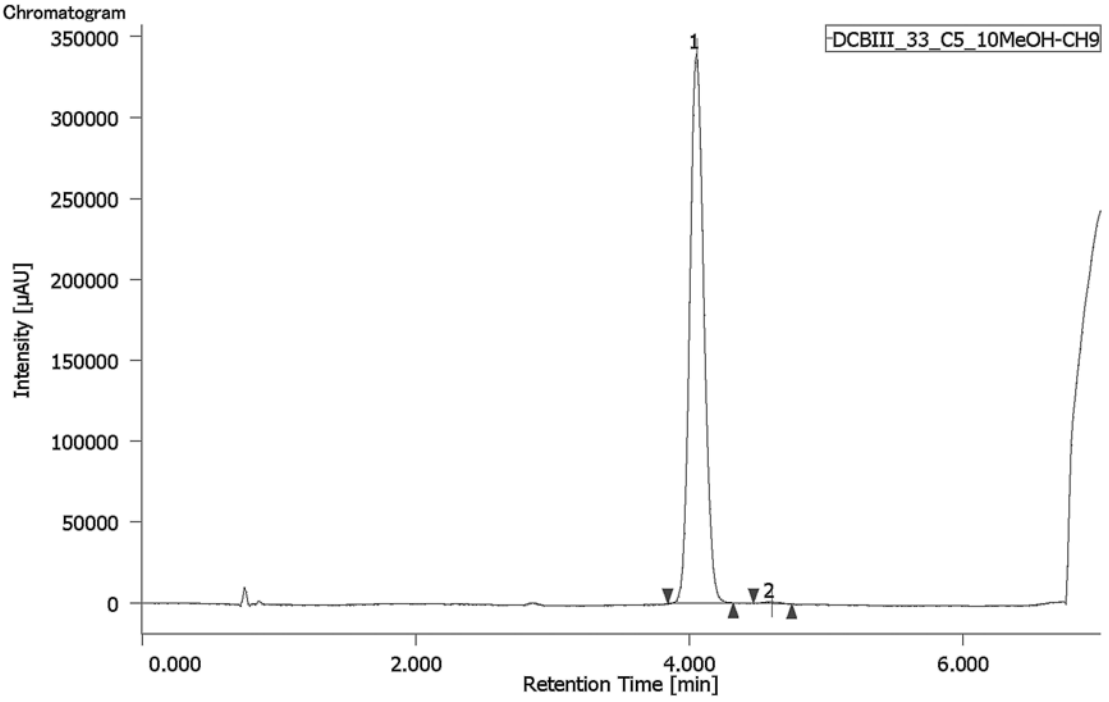
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	9	3.907	2599977	362239	50.068	3.693	4.147	0.112	2.197	1.058
2	Unknown	9	4.440	2592906	232330	49.932	4.160	4.747	0.175	N/A	1.073

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/4/2011 11:08:15 AM
Volume	5.00 [µL]
Sample #	9
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_33
Chromatogram Name	DCBIII_33_C5_10MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_33
Control Method	Solv 1 Col 5 Isocratic 10B 5mL_min 10MPa 10min

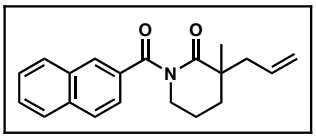
Chromatogram



Peak Information

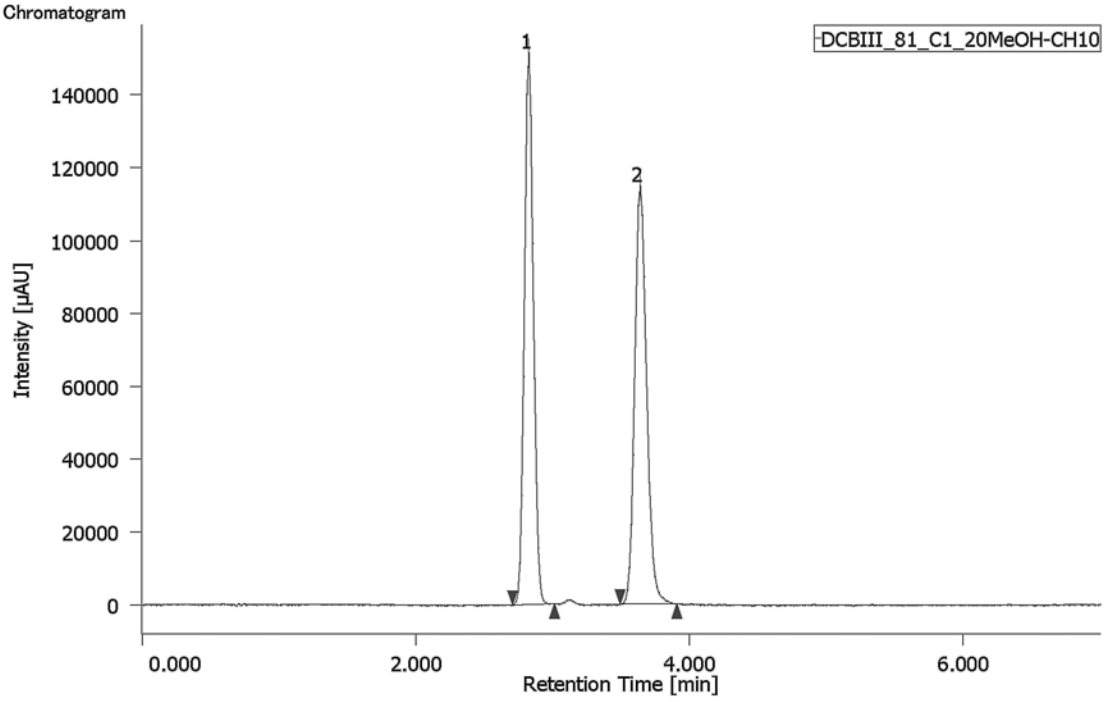
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	9	4.053	2459360	339918	99.639	3.840	4.320	0.113	2.425	1.064
2	Unknown	9	4.600	8904	1019	0.361	4.467	4.747	0.153	N/A	1.007

Analytical Report SFC



Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/26/2011 8:49:48 PM
Volume	5.00 [µL]
Sample #	33
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_81
Chromatogram Name	DCBIII_81_C1_20MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_81
Control Method	Solv 1 Col 1 Isocratic 20B 5mL_min 10MPa 10min

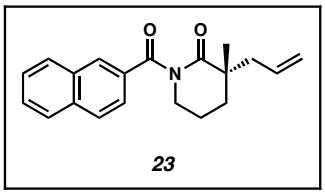
Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.827	689172	151401	49.792	2.707	3.013	0.071	5.853	1.034
2	Unknown	10	3.640	694927	114728	50.208	3.493	3.907	0.093	N/A	1.145

Analytical Report SFC



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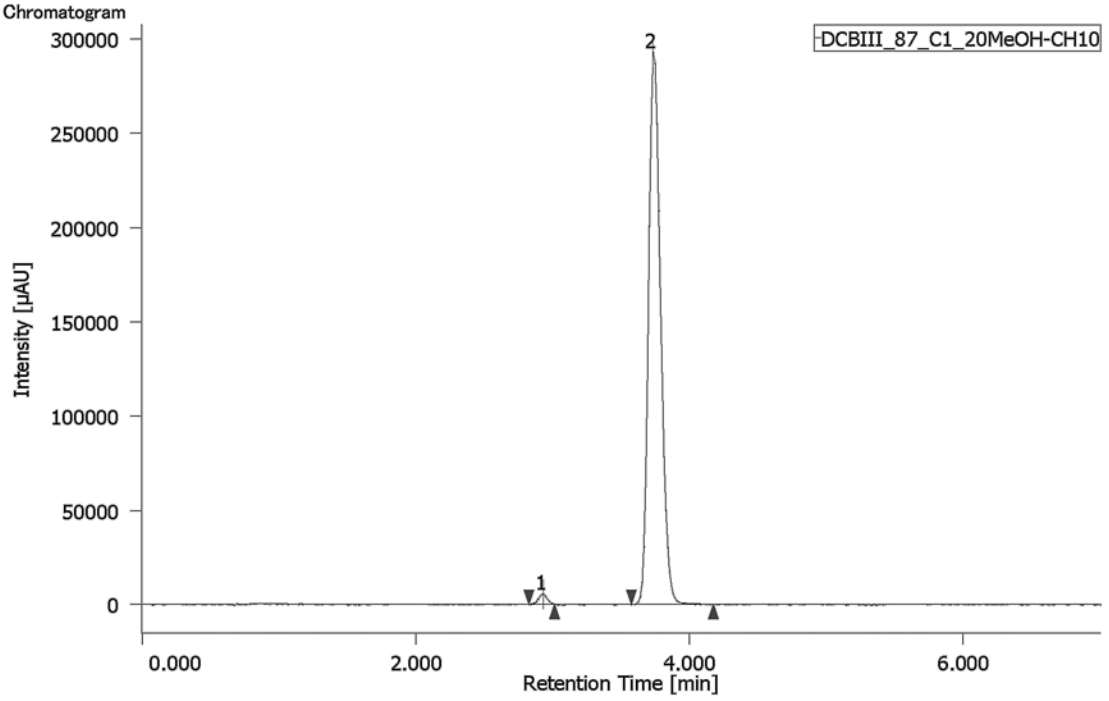
Chromatogram Information	
User Name	User
HPLC System Name	Jasco SFC w PDA
Injection Date	5/27/2011 9:53:48 PM
Volume	5.00 [µL]
Sample #	4
Project Name	Cal Tech SFC
Executed Sequence	DCBIII_83
Chromatogram Name	DCBIII_87_C1_20MeOH
Sample Name	
Acquisition Time	7.0 [min]
Acquisition Sequence	DCBIII_83
Control Method	Solv 1 Col 1 Isocratic 20B 5mL_min 10MPa 10min

Chromatogram



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Peak Start	Peak End	Peak Width	Resolution	Symmetry Factor
1	Unknown	10	2.933	23962	5302	1.324	2.827	3.013	0.072	5.688	0.933
2	Unknown	10	3.733	1785816	292661	98.676	3.573	4.173	0.094	N/A	1.303

References

(1) (a) Ukai, T.; Kawazure, H.; Ishii, Y.; Bonnet, J. J.; Ibbers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253. (b) Fairlamb, I. J. S.; Kapdi, A. R.; Lee, A. F. *Org. Lett.* **2004**, *6*, 4435.

(2) (a) Peer, M.; de Jong, J. C.; Kiefer, M.; Langer, T.; Rieck, H.; Schell, H.; Sennhenn, P.; Sprinz, J.; Steinhagen, H.; Wiese, B.; Helmchen, G. *Tetrahedron* **1996**, *52*, 7547. (b) Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 15044. (c) Krout, M. R.; Mohr, J. T.; Stoltz, B. M. *Org. Synth.* **2009**, *86*, 181.

(3) McDougal, N. T.; Streuff, J.; Mukherjee, H.; Virgil, S. C.; Stoltz, B. M. *Tetrahedron Lett.* **2010**, *51*, 5550.

(4) Donnelly, D. M. X.; Finet, J.-P.; Rattigan, B. A. *J. Chem. Soc. Perkin Trans. 1* **1993**, 1729.

(5) Compound SI1 can be prepared by methylation of diallyl malonate in a manner analogous to dimethyl 2-methylmalonate or by esterification of 2-methyl malonic acid, see: (a) Hosokawa, T.; Yamanaka, T.; Itotani, M.; Murahashi, S.-I. *J. Org. Chem.* **1995**, *60*, 6159. (b) Imao, D.; Itoi, A.; Yamazaki, A.; Shirakura, M.; Ohtoshi, R.; Ogata, K.; Ohmori, Y.; Ohta, T.; Ito, Y. *J. Org. Chem.* **2007**, *72*, 1652.

(6) Tsuzuki, Y.; Chiba, K.; Mizuno, K.; Tomita, K.; Suzuki, K. *Tetrahedron: Asymmetry* **2001**, *12*, 2989.

(7) (a) Filippis, A.; Pardo, D. G.; Cossy, J. *Synthesis* **2004**, *17*, 2930. (b) Foti, C. J.; Comins, D. L. *J. Org. Chem.* **1995**, *60*, 2656.

(8) (a) Sasaki, H.; Mori, Y.; Nakamura, J.; Shibasaki, J. *J. Med. Chem.* **1991**, *34*, 628. (b) Giovannini, A.; Savoia, D.; Umani-Ronchi, A. *J. Org. Chem.* **1989**, *54*, 228.

(9) The fluorination was performed in a manner analogous to β-ketoesters, see: Mohr, J. T.; Behenna, D. C.; Harned, A. M.; Stoltz, B. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 6924.

(10) Griera, R.; Hugnet, J.; Bosch, J. *Synth. Commun.* **2004**, *34*, 323.

(11) Song, Y.; Jia, Z. J.; Pandey, A.; Scarborough, R. M.; Scarborough, C. Factor XA Inhibitors. U.S. Patent Application 2007/259924A1, November 8, 2007.

(12) Peroche, S.; Remuson, R.; Gelas-Mialhe, Y.; Gramain, J.-C. *Tetrahedron Lett.* **2001**, *42*, 4617.

(13) The palladium source was chosen solely to simplify the chromatographic separation of the dba from the lactam product.

(14) Benzoyl lactam **3** and benzoyl lactam **4** were determined to be of the (*S*) configuration using anomalous scattering methods during single crystal X-ray studies of derivative compounds obtained by exchanging the benzoyl group with a 4-bromobenzoyl group and performing an olefin cross metathesis with 3-nitrostyrene. The absolute configurations of all other compounds were assigned by analogy. Crystallographic data for the derivative compounds of benzoyl lactam **3** and benzoyl lactam **4** have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers 845601 and 845602, respectively.

(15) Adapted from a related sequence, see: Amat, M.; Lozano, O.; Escolano, C.; Molins, E.; Bosch, J. *J. Org. Chem.* **2007**, *72*, 4431.