SUPPORTING INFORMATION

Stereoselective Piperidine Synthesis through Oxidative Carbon–Hydrogen Bond Functionalizations of Enamides

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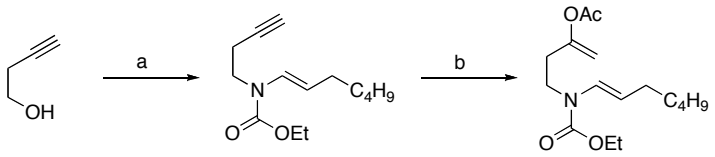
General

Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz and 75 MHz, respectively, a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz, respectively, or a Bruker Avance 500 spectrometer at 500 MHz and 125 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.26 ppm, C_6D_6 = 7.16 ppm, for ^{13}C NMR: $CDCl_3$ = 77.23 ppm, C_6D_6 = 128.06 ppm. Data are reported as follows: (s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; dt = doublet of triplets; td = triplet of doublets; tt = triplet of triplets; ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets; dtd = doublet of triplet of doublets; br = broad). High resolution mass spectra were recorded on a Micromass UK Limited Q-Tof Ultima API or a Fissions VG Autospec spectrometer. Infrared (IR) spectra were collected on a Mattson Cygnus 100 spectrometer. Samples for IR were prepared as a thin film on NaCl plate by dissolving the compound in CH_2Cl_2 and then evaporating the solvent. Methylene chloride was distilled under N_2 from CaH_2. Nitromethane was purchased from Sigma Aldrich, stored over 4 Å molecular sieves, and used without further purification. DDQ was purchased from Sigma Aldrich and used without further purification. Analytical TLC was performed on E. Merck pre-coated (25 mm) silica gel 60F-254 plates. Visualization was done under UV light (254 nm). Flash chromatography was done using ICN SiliTech 32-63 60 Å silica gel. Reagent grade ethyl acetate, diethyl ether, pentane, and hexanes (commercial mixture) were puchrased from EM Science and used for chromatography without further purification. All reactions were performed in oven or flame-dried glassware under a positive pressure of N_2 with magnetic stirring unless otherwise noted.

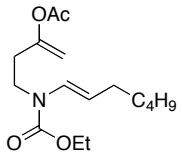
General procedure for the cyclization reactions:
To the substrate (1 equiv) in nitromethane (~0.1 M substrate concentration) was added activated, powdered 4 Å molecular sieves (1 mass equiv). Lithium perchlorate (1 eq) was added if indicated. The reaction mixture was stirred at rt for 5 min, then DDQ (1.2 or 1.5 equiv) was added in one portion. The reaction was monitored by TLC and usually showed complete consumption of starting material within 3 min. Upon completion, the reaction mixture was quenched with a few drops of NEt_3, concentrated on a rotary evaporator, and purified by flash chromatography to give the desired cyclized product.

General procedure for the construction of *N*-vinyl carbamates or *N*-vinyl sulfonamides (A)
To a primary alcohol (1 equiv) in Et_2O was added MsCl (1.5 equiv) followed by Et_3N (2.0 equiv) dropwise at 0 ˚C. The reaction mixture was stirred at rt for 30 min. The resulting salts were filtered, and the reaction mixture was concentrated on a rotary evaporator. The crude mesylate was dissolved in DMF, then NaN_3 (1.2 equiv) was added and the reaction mixture was stirred at 70 °C for 2 h. The reaction mixture was quenched with water and extracted with Et_2O (4x). The combined organic layers were washed with water and brine, dried over $MgSO_4$, then were concentrated to ~0.1 M based on starting alcohol. To the crude azide in Et_2O was added $LiAlH_4$ (1.0 M in Et_2O, 1.0 equiv) dropwise at 0˚C. The reaction mixture was stirred at 0˚C for 30 min, then was quenched with H_2O dropwise until gas evolution ceased. The reaction mixture was filtered through a plug of Celite. To the crude amine in Et_2O was added the appropriate chloroformate or sulfonyl chloride (1.2 equiv) followed by NEt_3 (1.2 equiv) dropwise at 0˚C. The reaction mixture was stirred at room temperature until complete consumption of starting material was observed by TLC, then was filtered, concentrated, and purified by flash chromatography (hexanes/EtOAc eluent). The purified carbamate was dissolved in benzene, then heptanal and catalytic PPTS or PTSA added. The reaction mixture was stirred at reflux overnight in a Dean-Stark apparatus. The reaction mixture was quenched with a few drops of NEt_3, concentrated, and purified by flash chromatography (hexanes/EtOAc eluent) to yield the *N*-vinyl carbamate or sulfonamide. For some compounds, it was necessary to stir the product with $NaBH_4$ (1 equiv) in EtOH to reduce an inseparable impurity that presumably arises from the aldehyde. The impurity was then removed by flash chromatography.

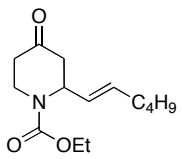


Reagents and conditions
a) General procedure (A), 43% (5 steps). b) HOAc, $[(p\text{-cymene})RuCl_2]_2$, Fur_3P, Na_2CO_3, 1-decyne, PhMe, 80 °C, 83%.

Scheme 1. Synthesis of substrate **5b**.



(*E*)-4-((Ethoxycarbonyl)(hept-1-en-1-yl)amino)but-1-en-2-yl acetate (5b)
^{1}H NMR (300 MHz, $CDCl_3$, two rotamers) δ 6.84 (d, *J* = 14.7 Hz, 0.5H), 6.69 (d, *J* = 14.0 Hz, 0.5H), 4.93-4.70 (m, 3H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.67 (br s, 2H), 2.45 (br s, 2H), 2.15 (s, 3H), 2.03 (dt, *J* = 6.9, 6.6 Hz, 2H), 1.44-1.22 (m, 6H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, two rotamers) δ 169.2, 154.4, 153.9, 153.5, 126.6, 126.1, 109.9, 109.7, 103.2, 62.3, 62.1, 41.8, 41.5, 31.5, 31.2, 30.5, 30.3, 22.7, 21.3, 14.7, 14.3; IR (neat) 2958, 2927, 2856, 1760, 1710, 1663, 1465, 1260, 1323, 1202, 1108, 1044, 1019, 949, 881 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{27}NO_4Na$ $[M+Na]^+$ 320.1838, found 320.1837.

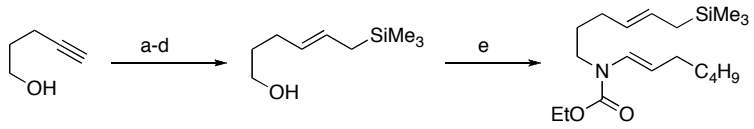


(*E*)-Ethyl 2-(hex-1-en-1-yl)-4-oxopiperidine-1-carboxylate (7b)

The general cyclization reaction procedure was followed with **5b** (38 mg, 0.13 mmol), 4 Å molecular sieves (38 mg), and DDQ (43 mg, 0.19 mmol) in nitromethane (1.2 mL). The reaction was stirred for 3 min then was purified by flash chromatography (1:1 hexanes:DCM) to yield the desired product (26 mg, 82%) as a faint yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58 (tdt, *J* = 15.7, 6.8, 1.4 Hz, 1H), 5.36 (dd, *J* = 15.6, 4.7 Hz, 1H), 5.16 (br s, 1H), 4.28-4.15 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.33 (ddd, *J* = 13.7, 11.0, 4.2 Hz, 1H), 2.67 (dd, *J* = 14.9, 6.7 Hz, 1H), 2.52 (d, *J* = 5.0 Hz, 1H), 2.50-2.39 (m, 1H), 2.38-2.27 (m, 1H), 2.02 (td, *J* = 7.1, 6.7 Hz, 2H), 1.38-1.22 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 155.7, 134.7, 127.8, 62.1, 52.9, 44.4, 40.8, 39.0, 32.2, 31.4, 22.4, 14.9, 14.1; IR (neat) 2959, 2928, 2872, 1719, 1700, 1465, 1420, 1311, 1239, 1173, 1107, 1033, 977 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{24}NO_3$ $[M+H]^+$ 254.1756, found 254.1751.

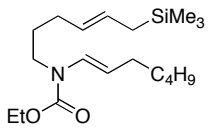
Catalytic method

To **1** (38 mg, 0.13 mmol) in $MeNO_2$ (1.5 mL) were added activated 4 Å molecular sieves (40 mg) and $Mn(OAc)_3$ (205 mg, 0.765 mmol). DDQ (4 mg, 0.02 mmol) was added in one portion, and the reaction mixture was stirred at rt for 24 h. The reaction was quenched with a drop of NEt_3 then was purified by flash chromatography (3:1 to 2:1 hexanes:EtOAc) to yield the desired product (24 mg, 75%) as a faint yellow oil.



Reagents and conditions
a) TBDMSCl, imidazole, DMF, 90%. b) Cp_2ZrCl_2, DIBAL-H, THF, 0 °C, then I_2, –78 °C to rt, 80%. c) Me_3SiCH_2MgCl, $Pd(PPh_3)_4$, THF, MeOH, CSA, 76% (two steps). e) General procedure (A), 28%, five steps.

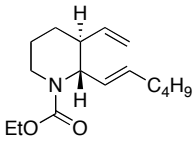
Scheme 2. Synthesis of substrate **8**.[1]



Ethyl (*E*)-hept-1-en-1-yl((*E*)-6-(trimethylsilyl)hex-4-en-1-yl)carbamate (8)

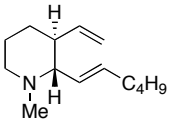
^{1}H NMR (300 MHz, $CDCl_3$, two rotamers) δ 6.85 (d, *J* = 15.1 Hz, 0.5H), 6.72 (d, *J* = 13.5 Hz, 0.5H), 5.42 (dt, *J* = 15.1, 7.9 Hz, 1H), 5.24 (dt, *J* = 15.1, 6.6 Hz, 1H), 4.84 (dt, *J* = 14.2, 7.1 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.47 (br s, 2H), 2.08-1.93 (m, 4H), 1.65-1.52 (m, 2H), 1.44-1.21 (m, 8H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 6.6 Hz, 3H), –0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 305K) δ 154.2, 127.9, 127.1, 126.7, 109.6, 61.9, 43.9, 31.5, 30.5, 30.4, 30.3, 27.3, 22.8, 22.7, 14.8, 14.2, -1.8; IR (neat) 2955, 2928, 2856, 1711, 1661, 1411, 1324, 1249, 1192, 1154, 1105, 1048, 1023, 947, 850 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{19}H_{37}NO_2Si$ $[M^+]$ 339.2594, found 339.2590.

[1] Vinyl iodide formation: Z. Huang, E-i. Negishi, *Org. Lett.* 2006, **8**, 3675.



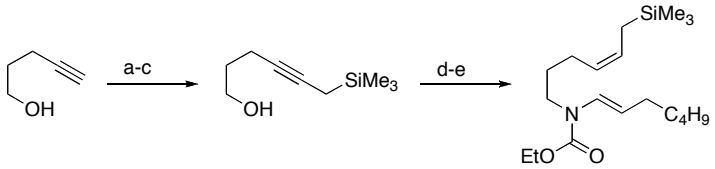
Ethyl *trans*-2-((*E*)-hex-1-en-1-yl)-3-vinylpiperidine-1-carboxylate (9)

The general cyclization reaction procedure was followed with **8** (100 mg, 0.29 mmol), 4 Å molecular sieves (100 mg), and DDQ (100 mg, 0.44 mmol) in nitromethane (3.0 mL). The reaction was stirred for 3 min then was purified by flash chromatography (10:1 to 2:1 hexanes:EtOAc) to yield the desired product (dr > 20:1, 50 mg, 65%) as a faint yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (ddd, J = 17.3, 10.5, 6.6 Hz, 1H), 5.59-5.40 (m, 2H), 5.13 (ddd, J = 17.3, 1.5, 1.5 Hz, 1H), 5.08 (ddd, J = 10.5, 1.5, 1.5 Hz, 1H), 4.72 (br s, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.99 (dd, J = 13.2, 3.6 Hz, 1H), 2.90 (td, J = 12.9, 3.4 Hz, 1H), 2.39 (br s, 1H), 2.04 (dt, J = 6.8, 5.9 Hz, 2H), 1.87-1.62 (m, 2H), 1.60-1.50 (m, 2H), 1.44-1.25 (m, 4H), 1.24 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 140.4, 132.7, 127.8, 115.1, 61.3, 55.9, 41.2, 39.6, 32.3, 31.6, 24.8, 22.4, 20.6, 14.9, 14.1; IR (neat) 2931, 2859, 1698, 1424, 1256, 1164, 1104 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{16}H_{27}NO_2$ [M^+] 265.2042, found 265.2034.



***trans*-2-((*E*)-Hex-1-en-1-yl)-3-vinyl-*N*-methylpiperidine**

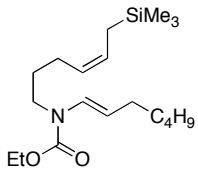
To **9** (12 mg, 0.046 mmol) in anhydrous THF under argon was added 1M $LiAlH_4$ in Et_2O (0.093 mL, 0.093 mmol). The reaction mixture was stirred at 80 °C for 2 h then was quenched with water. The crude mixture was filtered through a plug of Celite, concentrated, and purified twice by flash chromatography (100:5:1 EtOAc:MeOH:NH_4OH then 10:1 DCM:MeOH) to yield the product (7.8 mg, 81%) as a faint yellow oil. ^{1}H NMR (500 MHz, C_6D_6) δ 5.72 (ddd, J = 17.2, 10.6, 7.7 Hz, 1H), 5.44 (dt, J = 15.4, 6.5 Hz, 1H), 5.35 (dd, J = 15.5, 8.6 Hz, 1H), 5.00-4.93 (m, 2H), 2.84-2.77 (m, 1H), 2.24 (s, 3H), 2.19-2.09 (m, 1H), 2.05-2.00 (m, 1H), 1.96 (dt, J = 6.7, 6.7 Hz, 2H), 1.86 (td, J = 11.7, 2.6 Hz, 1H), 1.76-1.65 (m, 2H), 1.50-1.44 (m, 1H), 1.33-1.22 (m, 4H), 1.12 (ddd, J = 15.6, 13.2, 4.4 Hz, 1H), 0.85 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 142.3, 133.6, 133.0, 114.0, 72.8, 56.5, 46.2, 44.6, 32.3, 31.9, 31.1, 25.5, 22.5, 14.1; IR (neat) 2928, 2853, 2776, 1459, 1373, 1110, 972 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{14}H_{26}N$ [M+H]$^+$ 208.2065, found 208.2068.



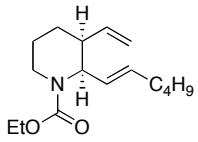
Reagents and conditions
a) Dihydropyran, *p*-TsOH, CH_2Cl_2, 99%. b) *n*BuLi, THF, then Me_3SiCH_2I, –78 to 65 °C. c) MeOH, *p*-TsOH, 74% (two steps). d) General procedure (A), 27%, five steps. e) $NiCl_2$, $NaBH_4$, EtOH, 84%.

Scheme 3. Synthesis of substrate **10**.[2]

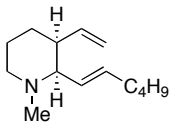
[2] P2-Ni reduction: C. A. Brown, V. K. Ahuja, *J. Org. Chem.* 1973, **38**, 2226.



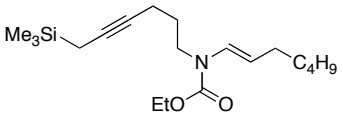
Ethyl (E)-hept-1-en-1-yl((Z)-6-(trimethylsilyl)hex-4-en-1-yl)carbamate (10)
^{1}H NMR (300 MHz, $CDCl_3$, two rotamers) δ 6.85 (d, *J* = 13.4 Hz, 0.5H), 6.72 (d, *J* = 12.2 Hz, 0.5H), 5.43 (dt, *J* = 10.4, 8.5 Hz, 1H), 5.33-5.20 (m, 1H), 4.86 (dt, *J* = 14.6, 7.2 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.49 (br s, 2H), 2.09-1.91 (m, 4H), 1.68-1.55 (m, 2H), 1.46 (d, *J* = 8.5 Hz, 2H), 1.42-1.20 (m, 6H), 1.29 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 6.6 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 305K, two rotamers) δ 154.5, 154.0, 127.1, 126.5, 126.4, 109.5, 61.9, 43.9, 31.5, 30.5, 30.3, 27.7, 27.0, 24.6, 22.7, 18.7, 14.8, 14.2, –1.63; IR (neat) 2955, 2927, 2856, 1711, 1661, 1412, 1325, 1250, 1191, 1106, 1018, 947, 855 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{19}H_{37}NO_2Si$ [M^+] 339.2594, found 339.2584.



Ethyl *cis*-2-((*E*)-hex-1-en-1-yl)-3-vinylpiperidine-1-carboxylate (11)
The general cyclization reaction procedure was followed with **10** (50 mg, 0.15 mmol), 4 Å molecular sieves (50 mg), and DDQ (50 mg, 0.22 mmol) in nitromethane (2.0 mL). The reaction was stirred for 3 min then was purified by flash chromatography (10:1 to 2:1 hexanes:EtOAc) to yield the desired product (dr = 3.3:1, 35 mg total, 91%) as a faint yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (ddd, *J* = 17.2, 10.1, 6.7 Hz, 1H), 5.59-5.41 (m, 2H), 5.11-4.98 (m, 2H), 4.72 (br s, 1H), 4.21-4.06 (m, 2H), 3.98 (d, *J* = 10.7 Hz, 1H), 2.87 (t, *J* = 11.1 Hz, 1H), 2.41-2.29 (m, 1H), 2.02 (dt, *J* = 6.3, 6.2 Hz, 2H), 1.76-1.60 (m, 2H), 1.55-1.40 (m, 2H), 1.39-1.20 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 140.4, 135.1, 123.3, 114.9, 61.4, 56.7, 43.8, 39.3, 32.5, 31.6, 25.5, 24.9, 22.3, 14.9, 14.1; IR (neat) 2931, 2859, 1698, 1423, 1257, 1166 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{16}H_{28}NO_2$ $[M+H]^+$ 266.2120, found 266.2144.

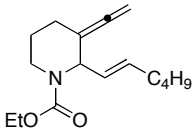


***cis*-2-((*E*)-Hex-1-en-1-yl)-3-vinyl-*N*-methylpiperidine**
To **11** (18 mg, 0.069 mmol) in anhydrous THF under argon was added 1M $LiAlH_4$ in Et_2O (0.14 mL, 0.14 mmol). The reaction mixture was stirred at 60 °C for 4 h then was quenched with water. The crude mixture was filtered through a plug of Celite, concentrated, and purified twice by flash chromatography (100:5:1 EtOAc:MeOH:NH_4OH then 10:1 DCM:MeOH) to yield the product (12 mg, 85%) as a faint yellow oil. ^{1}H NMR (500 MHz, C_6D_6) δ 6.25-6.11 (m, 1H), 5.54 (dd, *J* = 15.3, 9.4 Hz, 1H), 5.43 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.09-5.00 (m, 2H), 2.75 (d, *J* = 6.4 Hz, 1H), 2.61-2.52 (m, 1H), 2.49 (br s, 1H), 2.19 (s, 3H), 2.11 (t, *J* = 9.7 Hz, 1H), 1.96 (dt, *J* = 6.9, 6.5 Hz, 2H), 1.76-1.65 (m, 1H), 1.50 (br s, 2H), 1.33-1.19 (m, 5H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 135.4, 126.3, 114.8, 68.9, 52.7, 45.2, 44.1, 32.4, 31.8, 27.5, 23.8, 22.3, 14.1; IR (neat) 2928, 2854, 2776, 1553, 1444, 1370, 1112, 971, 910 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{14}H_{26}N$ $[M+H]^+$ 208.2065, found 208.2064.



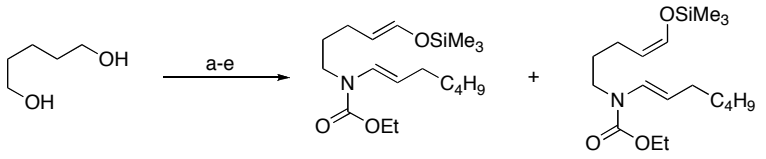
(*E*)-Ethyl hept-1-en-1-yl(6-(trimethylsilyl)hex-4-yn-1-yl)carbamate (12)

^{1}H NMR (300 MHz, $CDCl_3$, two rotamers) δ 6.86 (d, *J* = 14.1 Hz, 0.5H), 6.72 (d, *J* = 15.1 Hz, 0.5H), 4.93 (dt, *J* = 14.4, 7.1 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.57 (br s, 2H), 2.23-2.13 (m, 2H), 2.03 (td, *J* = 7.1, 6.8 Hz, 2H), 1.79-1.65 (m, 2H), 1.43 (t, *J* = 2.6 Hz, 2H), 1.40-1.24 (m, 6H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 6.7 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, two rotamers) δ 154.6, 154.0, 127.1, 126.5, 109.5, 78.2, 77.8, 61.9, 43.5, 43.3, 31.5, 30.5, 30.3, 27.1, 26.7, 22.7, 16.8, 14.8, 14.2, 7.1, –1.9; IR (neat) 3087, 2956, 2856, 2221, 1946, 1709, 1661, 1412, 1324, 1250, 1188, 1108, 1020, 949, 850 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{19}H_{36}NO_2Si$ $[M+H]^+$ 338.2515, found 338.2548.



(*E*)-Ethyl 2-(hex-1-en-1-yl)-3-vinylidenepiperidine-1-carboxylate (13)

The general cyclization reaction procedure was followed with **12** (35 mg, 0.10 mmol), 4 Å molecular sieves (35 mg), and DDQ (35 mg, 0.16 mmol) in nitromethane (1.0 mL). The reaction was stirred for 3 min then was purified by flash chromatography (6:1 hexanes:EtOAc) to yield the desired product (20 mg, 73%) as a faint yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 (dtd, *J* = 15.4, 6.6, 1.7 Hz 1H), 5.39 (ddt, *J* = 15.4, 4.1, 1.2 Hz, 1H), 5.26 (br s, 1H), 4.76-4.62 (m, 2H), 4.15 (m, 2H), 4.05 (d, *J* = 13.7 Hz, 1H), 2.91 (td, *J* = 13.0, 3.2 Hz, 1H), 2.30-2.21 (m, 2H), 2.05 (dt, *J* = 6.9, 6.9 Hz, 2H), 1.75-1.64 (m, 1H), 1.63-1.50 (m, 1H), 1.42-1.29 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 155.8, 133.2, 127.6, 98.1, 74.9, 61.5, 56.3, 39.9, 32.1, 31.5, 25.9, 25.8, 22.4, 14.9, 14.1; IR (neat) 2928, 2856, 1963, 1701, 1420, 1345, 1264, 1178, 1148, 1101, 1056, 966, 889, 845, 768 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{16}H_{26}NO_2$ $[M+H]^+$ 264.1946, found 264.1991.



Reagents and conditions
a) *n*BuLi, THF, then TBDMSCl, 89%. b) General reaction scheme (A), 23% for five steps.
c) Bu_4NF, THF, 99%. d) SO_3•Pyr, Et_3N, DMSO, CH_2Cl_2, 87%. e) TESCl, NaBr, Et_3N, DMF, 61%, 1:2.4 mixture of isomers.

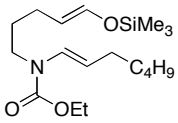
Scheme 4. Synthesis of substrates **14** and **16**.

Procedure for enolsilane formation:[3]

To NaBr (1.6 equiv) in DMF was added TESCl, and the mixture was stirred for 20 min. To the solution was added the aldehyde (1 equiv) in DMF (~0.1 M final substrate concentration), followed by NEt_3 (1.6 equiv). After stirring at rt overnight, an addition 1 equiv of both TESCl and NEt_3 were added. The reaction mixture was stirred at rt for an additional 24 h, then was

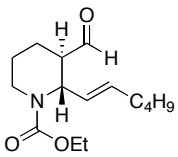
[3] Enolsilane formation: A. Saeed, M. A. Kahn, J. Iqbal, *Synth. Commun*. 1988, **18**, 1679.

concentrated and purified by flash chromatography (4:1 hexanes:EtOAc) to give the enolsilane as a clear oil in 61% yield and as a 2.4:1 mixture of *Z* and *E* isomers. The isomers were separated with an AnaLogix IntelliFlash 280 MPLC. 174.2 mg of the mixture was loaded onto a Varian SF-40g column. A gradient of 20% to 60% DCM in hexanes was used over 40 min followed by an EtOAc flush of the column. 4 mL fractions were collected.



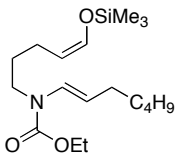
Ethyl (*E*)-hept-1-en-1-yl((*E*)-5-((triethylsilyl)oxy)pent-4-en-1-yl)carbamate (14)

^{1}H NMR (400 MHz, $CDCl_3$, two rotamers) δ 6.85 (d, *J* = 14.0 Hz, 0.5H), 6.71 (d, *J* = 13.7 Hz, 0.5H), 6.26 (dt, *J* = 11.9, 1.2 Hz, 1H), 4.98 (dt, *J* = 11.9, 7.4 Hz, 1H), 4.83 (dt, *J* = 14.2, 7.0 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.55-3.38 (m, 2H), 2.07-1.97 (m, 2H), 1.90 (dt, *J* = 7.2, 7.2 Hz, 2H), 1.63-1.50 (m, 2H), 1.41-1.24 (m, 6H), 1.28 (t, *J* = 6.9 Hz, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.66 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, two rotamers) δ 155.0, 153.8, 140.7, 127.0, 126.4, 110.6, 109.6, 62.1, 62.0, 43.9, 43.3, 31.5, 30.6, 30.3, 28.0, 27.5, 25.0, 22.7, 14.8, 14.3, 6.7, 4.6; IR (neat) 2956, 2927, 2877, 1710, 1662, 1463, 1412, 1324, 1258, 1165, 1013, 946 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{21}H_{42}NO_3Si$ $[M+H]^+$ 384.2934, found 384.2943.



Ethyl *trans*-3-formyl-2-((*E*)-hex-1-en-1-yl)piperidine-1-carboxylate (15)

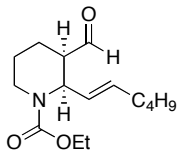
The general cyclization reaction procedure was followed with **14** (8.1 mg, 0.021 mmol), 4 Å molecular sieves (10 mg), and DDQ (5.8 mg, 0.025 mmol) in nitromethane (0.2 mL). The reaction was stirred for 3 min then was purified by flash chromatography (10:1 to 4:1 hexanes:EtOAc) to yield the desired product (dr = 6.7:1, 5.1 mg total, 90%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 5.60 (dt, *J* = 15.3, 6.8 Hz , 1H), 5.46 (dd, *J* = 15.5, 4.9 Hz, 1H), 5.37 (br s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.96 (d, *J* = 12.7 Hz, 1H), 2.89 (td, *J* = 13.0, 3.7 Hz, 1H), 2.44 (br s, 1H), 2.14 (d, *J* = 13.6 Hz, 1H), 2.07 (dt, *J* = 6.7, 6.7 Hz, 2H), 1.74 (tt, *J* = 13.5, 4.7 Hz, 1H), 1.53-1.49 (m, 1H), 1.45 (dt, *J* = 13.2, 4.3 Hz, 1H), 1.39-1.22 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 156.1, 133.9, 126.4, 61.7, 51.6, 50.5, 39.3, 32.3, 31.5, 22.4, 22.0, 19.6, 14.8, 14.1; IR (neat) 2955, 2930, 2862, 1728, 1695, 1424, 1316, 1253, 1191, 1122, 1101, 1047, 971 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{25}NO_3Na$ $[M+Na]^+$ 290.1732, found 290.1734.



Ethyl (*E*)-hept-1-en-1-yl((*Z*)-5-((triethylsilyl)oxy)pent-4-en-1-yl)carbamate (16)

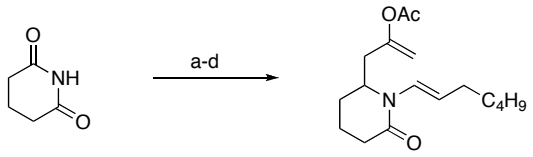
^{1}H NMR (400 MHz, $CDCl_3$, two rotamers) δ 6.84 (d, *J* = 14.3 Hz, 0.5H), 6.71 (d, *J* = 13.9 Hz, 0.5H), 6.21 (d, *J* = 5.8 Hz, 1H), 4.85 (dt, *J* = 14.1, 6.9 Hz, 1H), 4.45 (td, *J* = 6.7, 6.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.55-3.39 (m, 2H), 2.10 (td, *J* = 7.1, 6.8 Hz, 2H), 2.05-1.95 (m, 2H), 1.58 (br s, 2H), 1.40-1.23 (m, 6H), 1.27 (t, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.87 (t, *J* = 6.7 Hz, 3H), 0.64 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

154.7, 154.0, 139.1, 127.1, 126.5, 109.6, 109.4, 61.9, 61.8, 43.9, 43.8, 31.5, 30.5, 30.3, 27.4, 26.9, 22.7, 21.2, 14.8, 14.2, 6.7, 4.6; IR (neat) 3030, 2957, 2928, 2877, 1711, 1659, 1463, 1412, 1326, 1277, 1187, 1104, 1068, 1014, 948 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{21}H_{42}NO_3Si$ $[M+H]^+$ 384.2934, found 384.2967.



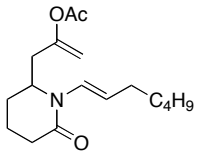
Ethyl *cis*-3-formyl-2-((*E*)-hex-1-en-1-yl)piperidine-1-carboxylate (17)

The general cyclization reaction procedure was followed with **16** (40.1 mg, 0.105 mmol), 4 Å molecular sieves (40 mg), and DDQ (28 mg, 0.12 mmol) in nitromethane (1.0 mL). The reaction was stirred for 3 min then purified by flash chromatography (10:1 to 4:1 hexanes:EtOAc) to yield the desired product (dr = 2.7:1, 25.7 mg, 93%) as a faint yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 1H), 5.74 – 5.56 (m, 1H), 5.41 (dd, *J* = 15.2, 7.0 Hz, 1H), 5.30 (br s, 1H), 4.23 – 4.09 (m, 2H), 4.02 (d, *J* = 11.9 Hz, 1H), 2.89 (td, *J* = 13.2, 2.8 Hz, 1H), 2.56 (dt, *J* = 12.3, 4.0 Hz, 1H), 1.98 (m, 3H), 1.78 (d, *J* = 13.1 Hz, 1H), 1.62 (m, 1H), 1.54 – 1.41 (m, 1H), 1.36 – 1.22 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.05, 155.82, 136.49, 122.91, 61.71, 52.65, 52.17, 39.66, 32.34, 31.33, 24.66, 22.34, 19.83, 14.90, 14.08; IR (neat) 2930, 2859, 1724, 1696, 1423, 1256, 1165, 1094, 971 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{25}NO_3Na$ (M^+ + Na) 290.1732, found 290.1730.



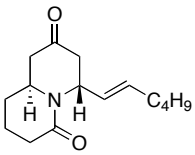
Reagents and conditions
a) $NaBH_4$, EtOH, then HCl, 23%. b) Allenyltributyl tin, BF_3•OEt_2, CH_2Cl_2, 66%.
c) Heptanal, *p*-TsOH, benzene, reflux, 77%. d) HOAc, $[(p\text{-cymene})RuCl_2]_2$, Fur_3P, Na_2CO_3, 1-decyne, PhMe, 80 °C.

Scheme 5. Synthesis of compound **19**.



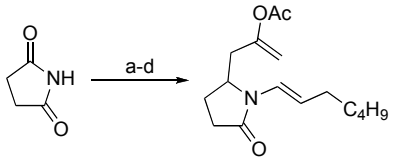
(*E*)-3-(1-(hept-1-en-1-yl)-6-oxopiperidin-2-yl)prop-1-en-2-yl acetate (19)

^{1}H NMR (300 MHz, $CDCl_3$, major regioisomer) δ 7.21 (d, *J* = 15.0 Hz, 1H), 5.03 (dt, *J* = 14.7, 7.1 Hz, 1H), 4.90 (d, *J* = 1.7 Hz, 1H), 4.83-4.80 (m, 1H), 3.96 (d, *J* = 8.7 Hz, 1H), 2.73 (dd, *J* = 14.7, 2.5 Hz, 1H), 2.53-2.43 (m, 2H), 2.36 (dd, *J* = 14.9, 10.7 Hz, 1H), 2.17 (s, 3H), 2.14-2.03 (m, 3H), 1.97-1.72 (m, 2H), 1.43-1.22 (m, 7H), 0.89 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, major regioisomer) δ 168.9, 168.3, 152.8, 125.1, 112.5, 104.6, 51.1, 35.5, 32.1, 31.5, 30.6, 30.1, 24.8, 22.6, 21.2, 16.0, 14.2; IR (neat) 3075, 2927, 2856, 1759, 1649, 1428, 1408, 1369, 1332, 1188, 1092, 1021, 960 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{17}H_{27}NO_3$ [M^+] 293.1991, found 293.1989.



(*E*)-4-(hex-1-en-1-yl)hexahydro-1H-quinolizine-2,6-dione (20)

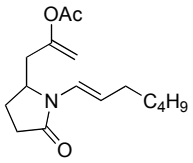
The general cyclization reaction procedure was followed with **19** (46 mg (39 mg desired regioisomer), 0.15 mmol), 4 Å molecular sieves (50 mg), and DDQ (52 mg, 0.230 mmol) in nitromethane (1.5 mL). The reaction was stirred for 3 min then was purified by flash chromatography (4:1 to 1:1 hexanes:EtOAc) to yield the desired product (23 mg, 70% based on amount of desired starting regioisomer) as a faint yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88-5.80 (m, 1H), 5.58 (dtd, *J* = 15.3, 6.7, 1.7 Hz, 1H), 5.30 (ddt, *J* = 15.7, 4.6, 1.4 Hz, 1H), 3.81 (dt, *J* = 12.7, 6.3 Hz, 1H), 2.59 (d, *J* = 4.7 Hz, 2H), 2.46 (t, *J* = 6.4 Hz, 2H), 2.36-2.31 (m, 2H), 2.11-1.95 (m, 3H), 1.93-1.81 (m, 1H), 1.81-1.68 (m, 1H), 1.67-1.54 (m, 1H), 1.37-1.18 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.25, 169.7, 135.4, 127.4, 50.5, 50.0, 48.2, 43.8, 33.2, 32.3, 31.3, 29.9, 22.3, 18.8, 14.1; IR (neat) 2955, 2929, 2870, 1719, 1643, 1440, 1414, 1336, 1181, 1089, 978 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{15}H_{23}NO_2$ [M^+] 249.1729, found 249.1728.



Reagents and conditions

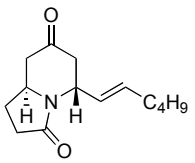
a) $NaBH_4$, EtOH, then HCl, 23%. b) Allenyltributyl tin, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C to rt, 66%. c) Heptanal, *p*-TsOH, benzene, reflux, 77%. d) HOAc, [(*p*-cymene)$RuCl_2]_2$, Fur_3P, Na_2CO_3, 1-decyne, PhMe, 80 °C, 76%.

Scheme 6. Synthesis of compound **21**.



(*E*)-3-(1-(Hept-1-en-1-yl)-5-oxopyrrolidin-2-yl)prop-1-en-2-yl acetate (21)

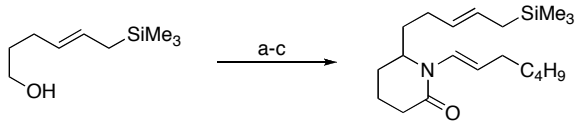
^{1}H NMR (400 MHz, $CDCl_3$, major regioisomer) δ 6.69 (d, *J* = 14.7 Hz, 1H), 4.92 (dt, *J* = 14.5, 7.1 Hz, 1H), 4.87-4.84 (m, 1H), 4.78 (br s, 1H), 4.01 (t, *J* = 8.5 Hz, 1H), 2.64 (dd, *J* = 14.9, 2.3 Hz, 1H), 2.57-2.46 (m, 1H), 2.39-2.26 (m, 2H), 2.11 (s, 3H), 2.07-1.94 (m, 3H), 1.38-1.30 (m, 2H), 1.29-1.19 (m, 5H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major regioisomer) δ 172.6, 169.0, 152.5, 122.0, 113.4, 104.8, 54.4, 35.0, 31.4, 30.4, 29.9, 29.8, 23.0, 22.6, 21.1, 14.1; IR (neat) 2955, 2923, 2854, 1755, 1694, 1660, 1403, 1368, 1204, 1178, 1018, 953 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{25}NO_3Na$ [M+Na]$^+$ 302.1732, found 302.1754.



(*E*)-5-(Hex-1-en-1-yl)hexahydroindolizine-3,7-dione (22)

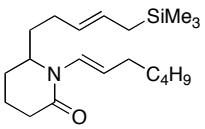
The general cyclization reaction procedure was followed with **21** (5.6:1 ratio of desired regioisomer to undesired) (76 mg (64 mg desired regioisomer), 0.27 mmol), 4 Å molecular sieves (75 mg), and DDQ (92 mg, 0.41 mmol) in nitromethane (2.7 mL). The reaction was stirred for 3 min then was purified by flash chromatography (4:1 to 1:1 hexanes:EtOAc) to yield the desired product (412 mg, 77% based on amount of desired starting regioisomer) as a faint yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61 (dtd, *J* = 15.2, 6.8, 1.5 Hz, 1H), 5.31 (dd, *J* = 15.5, 5.1 Hz, 1H), 5.16 (t, *J* = 5.2

Hz, 1H), 4.01-3.87 (m, 1H), 2.66-2.44 (m, 5H), 2.40-2.29 (m, 1H), 2.23 (dd, *J* = 13.8, 11.5 Hz, 1H), 2.00 (td, *J* = 6.8, 6.7 Hz, 2H), 1.81-1.66 (m, 1H), 1.37-1.19 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.5, 173.6, 135.0, 126.2, 53.0, 49.3, 48.5, 43.9, 32.1, 31.2, 30.1, 25.1, 22.3, 14.0; IR (neat) 2957, 2925, 2871, 2856, 1716, 1690, 1412, 1360, 1287, 1255, 1230, 1202 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{22}NO_2$ $[M+H]^+$ 236.1651, found 236.1632.



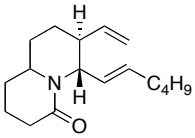
Reagents and conditions
a) Br_2, Ph_3P, pyridine, CH_2Cl_2, 0 °C, 69%. b) Mg, THF, then glutaramide, then $NaCNBH_3$, HOAc, 41%. g) (*E*)-1-Iodo-1-hexene, CuI, N,N'-dimethylethylenediamine,Cs_2CO_3, THF, 110 °C, 11%.

Scheme 7. Synthesis of compound **23**.[4]



1-((E)-hex-1-en-1-yl)-6-((E)-5-(trimethylsilyl)pent-3-en-1-yl)piperidin-2-one (21)

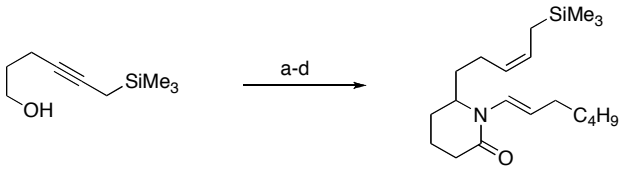
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 14.8 Hz, 1H), 5.43 (dtt, *J* = 15.1, 7.9, 1.2 Hz, 1H), 5.21 (dt, *J* = 15.0, 6.8 Hz, 1H), 5.01 (dt, *J* = 14.5, 7.2 Hz, 1H), 3.81-3.70 (m, 1H), 2.56-2.34 (m, 2H), 2.16-2.01 (m, 3H), 1.99-1.87 (m, 2H), 1.85-1.67 (m, 4H), 1.59-1.45 (m, 1H), 1.42 (d, *J* = 8.0 Hz, 2H), 1.39-1.26 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H), –0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 127.9, 127.2, 125.5, 112.6, 53.1, 32.8, 32.2, 31.1, 30.5, 30.0, 24.9, 23.0, 22.4, 16.2, 14.2, –1.7; IR (neat) 2953, 2927, 2872, 1665, 1650, 1408, 1330, 1272, 1247, 961, 851; HRMS (ESI) *m/z* calcd for $C_{19}H_{35}NONaSi$ $[M+Na]^+$ 344.2386, found 344.2387.



***trans*-6-((*E*)-Pent-1-en-1-yl)-7-vinylhexahydro-1H-quinolizin-4(6H)-one (24)**

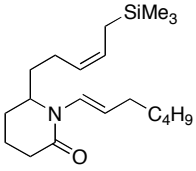
The general cyclization reaction procedure was followed with **23** (13 mg, 0.040 mmol), 4 Å molecular sieves (15 mg), and DDQ (14 mg, 0.061 mmol) in nitromethane (0.5 mL). The reaction was stirred for 3 min then was purified by flash chromatography (6:1 to 2:1 hexanes:EtOAc) to yield the desired product (dr > 20:1, 10 mg, 97%) as a faint yellow oil. ^{1}H NMR (300 MHz, C_6D_6) δ 5.95-5.79 (m, 2H), 5.57 (dtd, *J* = 15.5, 6.8, 1.6 Hz, 1H), 5.38 (dd, *J* = 15.6, 5.0 Hz, 1H), 5.28 (ddd, *J* = 17.4, 1.4, 1.4 Hz, 1H), 5.10 (ddd, *J* = 10.7, 1.4, 1.4 Hz, 1H), 3.16-3.03 (m, 1H), 2.42-2.28 (m, 2H), 2.22-2.09 (m, 1H), 1.94 (dt, *J* = 7.1, 6.0 Hz, 2H), 1.73-1.58 (m, 1H), 1.40-1.21 (m, 6H), 1.20-1.08 (m, 1H), 1.05-0.89 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 140.0, 132.6, 128.1, 115.3, 52.5, 51.8, 40.7, 34.7, 33.5, 30.9, 29.3, 24.8, 22.6, 19.2, 13.9; IR (neat) 2930, 2870, 1639, 1454, 1416, 1344, 1329, 1296, 1182, 966 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{26}NO$ $[M+H]^+$ 248.2014, found 248.1998.

[4] Addition of Grignard reagents to glutarimide and subsequent deoxygenation: W. F. J. Karstens, M. Stole, F. P. J. T. Rutjes, H. Kooijman, A. L. Spek, H. Hiemstra, *J. Organomet. Chem.* 2001, **624**, 244.



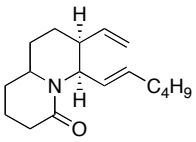
Reagents and conditions
a) Br_2, Ph_3P, pyridine, CH_2Cl_2, 0 °C, 69%. b) Mg, THF, reflux, then glutarimide, 0 °C, then $NaCNBH_3$, HOAc, 13%. c) (*E*)-1-Iodo-1-hexene, CuI, N,N-dimethylethylenediamine, Cs_2CO_3, THF, 110 °C, 10%. d) $NiCl_2$, $NaBH_4$, EtOH, 87%.

Scheme 8. Synthesis of compound **25**.



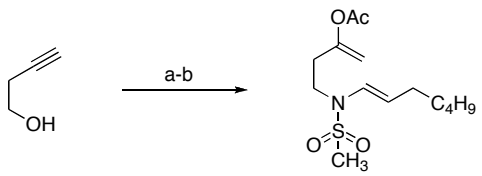
1-((*E*)-Hex-1-en-1-yl)-6-((*Z*)-5-(trimethylsilyl)pent-3-en-1-yl)piperidin-2-one (25)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 14.8 Hz, 1H), 5.46 (dt, *J* = 10.4, 8.7 Hz, 1H), 5.24 (dt, *J* = 10.7, 7.1 Hz, 1H), 5.04 (dt, *J* = 14.5, 7.1 Hz, 1H), 3.79-3.72 (m, 1H), 2.55-2.38 (m, 2H), 2.08 (dt, *J* = 6.9, 6.9 Hz, 2H), 2.05-1.84 (m, 4H), 1.83-1.71 (m, 3H), 1.60-1.50 (m, 1H), 1.47 (dd, *J* = 8.5, 3.4 Hz, 2H), 1.40-1.27 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 127.0, 125.8, 125.5, 112.5, 53.3, 32.7, 32.2, 31.0, 30.4, 25.1, 24.1, 22.4, 18.8, 16.2, 14.2, –1.56; IR (neat) 3006, 2953, 2926, 2872, 1664, 1648, 1407, 1330, 1272, 1247, 1178, 852 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{35}NONaSi$ $[M+Na]^+$ 344.2386, found 344.2395.



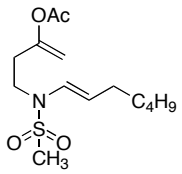
***cis*-6-((E)-pent-1-en-1-yl)-7-vinylhexahydro-1H-quinolizin-4(6H)-one (26)**

The general cyclization reaction procedure was followed with **25** (30 mg, 0.093 mmol), 4 Å molecular sieves (30 mg), and DDQ (32 mg, 0.14 mmol) in nitromethane (1 mL). The reaction was stirred for 3 min then was purified by flash chromatography (6:1 to 2:1 hexanes:EtOAc) to yield the desired product (dr = 3.3:1, 23 mg total, 99%) as a faint yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ 5.83 (t, *J* = 5.8 Hz, 1H), 5.75 (ddd, *J* = 15.0, 8.1, 6.8 Hz, 1H), 5.69 (ddd, *J* = 17.1, 10.6, 6.3 Hz, 1H), 5.50 (dd, *J* = 15.3, 6.8 Hz, 1H), 4.99 (ddd, *J* = 10.3, 1.6, 1.6 Hz, 1H), 4.96 (ddd, *J* = 17.3, 1.7, 1.7 Hz, 1H), 3.11-2.99 (m, 1H), 2.36 (dtd, *J* = 17.1, 4.8, 1.9 Hz, 1H), 2.22-2.11 (m, 2H), 1.93 (td, *J* = 7.6, 6.9 Hz, 2H), 1.47-1.20 (m, 7H), 1.20-1.08 (m, 1H), 1.01-0.89 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 140.0, 135.0, 123.5, 115.0, 53.3, 51.5, 43.2, 34.8, 34.1, 33.5, 30.8, 24.7, 22.5, 19.3, 13.8; IR (neat) 2930, 2870, 1640, 1439, 1416, 1331, 1278, 1183, 969, 912 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{16}H_{26}NO$ $[M+H]^+$ 248.2014, found 248.1014.

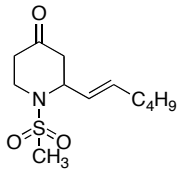


Reagents and conditions
a) General procedure (A), 18% for five steps. b) HOAc, [(*p*-cymene)$RuCl_2$]$_2$, Fur_3P, Na_2CO_3, 1-decyne, PhMe, 80 °C, 75%.

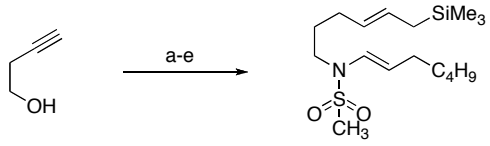
Scheme 9. Synthesis of compound **27**.



(*E*)-4-(*N*-(Hept-1-en-1-yl)methylsulfonamido)but-1-en-2-yl acetate (27)
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.35 (d, *J* = 14.2 Hz, 1H), 4.95 (dt, *J* = 14.3, 7.1 Hz, 1H), 4.85 (d, *J* = 1.8 Hz, 1H), 4.82-4.78 (m, 1H), 3.64-3.55 (m, 2H), 2.86 (s, 3H), 2.58-2.50 (m, 2H), 2.16 (s, 3H), 2.03 (dt, 7.1, 6.9 Hz, 2H), 1.43-1.22 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 152.8, 125.0, 113.4, 103.8, 43.3, 38.8, 32.1, 31.4, 30.3, 30.0, 22.6, 21.3, 14.2; IR (neat) 3018, 2929, 2856, 1757, 1658, 1458, 1348, 1154, 1080, 1021, 962, 882, 756 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{25}NO_4NaS$ $[M+Na]^+$ 326.1402, found 326.1382.

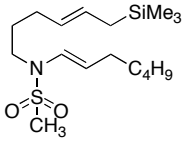


(*E*)-2-(Hex-1-en-1-yl)-1-(methylsulfonyl)piperidin-4-one (28)
The general cyclization reaction procedure was followed with **27** (60 mg, 0.20 mmol), 4 Å molecular sieves (60 mg), and DDQ (67 mg, 0.30 mmol) in nitromethane (2.0 mL). The reaction was stirred for 3 min then was purified by flash chromatography (2:1 to 1:2 hexanes:EtOAc) to yield the desired product (35 mg, 69%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (dtd, *J* = 15.0, 6.8, 1.2 Hz, 1H), 5.44 (ddt, *J* = 15.5, 6.7, 1.4 Hz, 1H), 4.90 (t, *J* = 6.2 Hz, 1H), 3.98 (ddt, *J* = 13.0, 7.2, 1.9 Hz, 1H), 3.32 (ddd, *J* = 13.0, 12.2, 3.5 Hz, 1H), 2.91 (s, 3H), 2.85 (ddd, *J* = 14.5, 6.6, 0.6 Hz, 1H), 2.70-2.60 (m, 1H), 2.53 (dt, *J* = 14.6, 2.0 Hz, 1H), 2.39 (ddt, *J* = 14.9, 3.7, 2.0 Hz, 1H), 2.04 (dt, *J* = 7.0, 7.0 Hz, 2H), 1.37-1.22 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 137.2, 125.6, 56.1, 46.1, 41.3, 40.6, 40.1, 32.3, 31.2, 22.4, 14.0; IR (neat) 2958, 2929, 2872, 1720, 1334, 1225, 1151, 1049, 962 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{21}NO_3SK$ $[M+K]^+$ 298.0879, found 298.0905.



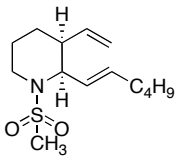
Reagents and conditions
a) TBDMSCl, imidazole, DMF, 90%. b) Cp_2ZrCl_2, DIBAL-H, THF, then I_2, –78 °C. c) Me_3SiCH_2MgCl, $Pd(PPh_3)_4$, THF. d) CSA, MeOH, 76%, two steps. e) General procedure (A), 32% for five steps.

Scheme 10. Synthesis of compound **34**.



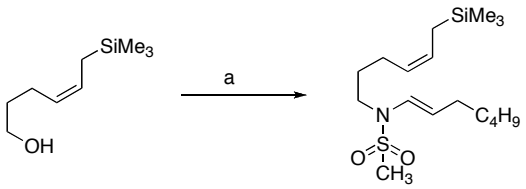
***N*-((*E*)-Hept-1-en-1-yl)-*N*-((*E*)-6-(trimethylsilyl)hex-4-en-1-yl)methanesulfonamide (34)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (d, *J* = 14.2 Hz, 1H), 5.43 (dtt, *J* = 15.1, 8.0, 1.1 Hz, 1H), 5.22 (dt, *J* = 15.0, 6.8 Hz, 1H), 4.92 (dt, *J* = 14.2, 7.2 Hz, 1H), 3.40 (dd, *J* = 7.6, 7.5 Hz, 2H), 2.83 (s, 3H), 2.02 (dt, *J* = 7.2, 7.2 Hz, 4H), 1.73-1.61 (m, 2H), 1.40 (dd, *J* = 8.0, 0.7 Hz, 2H), 1.38-1.22 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H), –0.02 (s, 9H); ^{13}C NMR (109 MHz, $CDCl_3$) δ 127.7, 127.3, 125.5, 113.0, 45.5, 38.5, 31.5, 30.4, 30.1, 30.0, 27.6, 22.9, 22.7, 14.3, –1.8; IR (neat) 3017, 2928, 2856, 1657, 1462, 1350, 1247, 1155, 962, 850 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{35}NO_2NaSSi$ $[M+Na]^+$ 368.2055, found 368.2093.



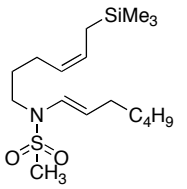
***cis*-2-((E)-hex-1-en-1-yl)-3-vinyl-N-(methylsulfonyl)piperidine (35)**

The general cyclization reaction procedure was followed with **34** (50 mg, 0.15 mmol), 4 Å molecular sieves (50 mg), $LiClO_4$ (15 mg, 0.145 mmol) and DDQ (49 mg, 0.22 mmol) in nitromethane (1.5 mL). The reaction was stirred for 3 min then was purified by flash chromatography (8:1 to 2:1 hexanes:EtOAc) to yield the desired product (dr = 3.7:1, 32 mg total, 82%) as a faint yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.06 (ddd, *J* = 17.4, 10.5, 6.8 Hz, 1H), 5.81-5.71 (m, 2H), 5.18 (ddd, *J* = 17.4, 1.4, 1.4 Hz, 1H), 5.14 (ddd, *J* = 10.5, 1.4, 1.4 Hz, 1H), 4.36 (d, *J* = 4.5 Hz, 1H), 3.60 (dd, *J* = 13.8, 3.9 Hz, 1H), 3.03 (td, *J* = 12.2, 3.1 Hz, 1H), 2.76 (s, 3H), 2.36 (br s, 1H), 2.11-2.05 (m, 2H), 1.89-1.79 (m, 2H), 1.67-1.60 (m, 1H), 1.56-1.51 (m, 1H), 1.41-1.28 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 135.7, 125.5, 115.8, 59.4, 42.5, 41.5, 38.8, 32.4, 31.5, 24.6, 22.5, 21.0, 14.1; IR (neat) 2954, 2927, 2857, 1455, 1334, 1157, 962, 923 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{14}H_{26}NO_2S$ $[M+H]^+$ 272.1684, found 272.1694.



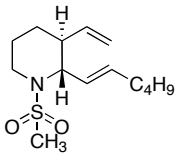
Reagents and conditions
a) General procedure (A), 24% for five steps.

Scheme 11. Synthesis of compound **36**.



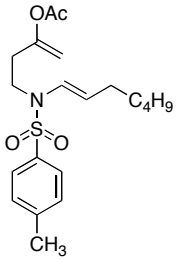
***N*-((*E*)-Hept-1-en-1-yl)-*N*-((*Z*)-6-(trimethylsilyl)hex-4-en-1-yl)methanesulfonamide (36)**

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.37 (d, *J* = 14.2 Hz, 1H), 5.45 (dt, *J* = 10.7, 8.6 Hz, 1H), 5.25 (dt, *J* = 10.9, 7.2 Hz, 1H), 4.95 (dt, *J* = 14.1, 7.1 Hz, 1H), 3.23 (dd, *J* = 7.8, 7.4 Hz, 2H), 2.84 (s, 3H), 2.03 (dt, *J* = 7.5, 6.8 Hz, 4H), 1.76-1.62 (m, 2H), 1.47 (d, *J* = 8.6 Hz, 2H), 1.43-1.22 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.0, 125.9, 125.5, 113.0, 45.7, 38.6, 31.5, 30.4, 30.1, 27.5, 24.4, 22.7, 18.8, 14.3, –1.56; IR (neat) 3007, 2954, 2927, 2856, 1656, 1349, 1322, 1247, 1154, 961, 854 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{17}H_{36}NO_2SSi$ $[M+H]^+$ 346.2236, found 346.2251.



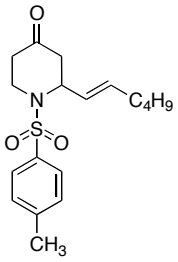
***trans*-2-((E)-hex-1-en-1-yl)-3-vinyl-N-(methylsulfonyl)piperidine (37)**

The general cyclization reaction procedure was followed with **36** (50 mg, 0.15 mmol), 4 Å molecular sieves (50 mg), $LiClO_4$ (15 mg, 0.15 mmol) and DDQ (49 mg, 0.22 mmol) in nitromethane (1.5 mL). The reaction was stirred for 3 min then was purified by flash chromatography (8:1 to 2:1 hexanes:EtOAc) to yield the desired product (dr = 2.7:1, 37 mg total, 93%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.61 (ddt, *J* = 15.2, 9.1, 1.2 Hz, 1H), 5.56 (ddd, *J* = 17.4, 10.5, 7.1 Hz, 1H), 5.04 (ddd, *J* = 11.7, 1.5, 1.5 Hz, 1H), 5.01 (ddd, *J* = 4.9, 1.6, 1.6 Hz, 1H), 4.40 (dd, *J* = 9.0, 4.9 Hz, 1H), 3.69-3.63 (m, 1H), 2.90 (td, *J* = 12.5, 3.3 Hz, 1H), 2.75 (s, 3H), 2.56-2.46 (m, 1H), 2.07 (td, *J* = 7.0, 6.9 Hz, 2H), 1.86-1.78 (m, 1H), 1.77-1.63 (m, 2H), 1.53-1.41 (m, 1H), 1.40-1.23 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 138.1, 121.3, 115.5, 59.5, 44.5, 40.8, 38.6, 32.5, 31.5, 25.5, 24.6, 22.5, 14.1; IR (neat) 2930, 2858, 1332, 1153, 993, 968, 992 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{14}H_{26}NO_2S$ $[M+H]^+$ 272.1684, found 272.1678.



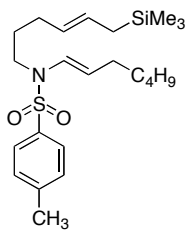
(*E*)-4-(*N*-(Hept-1-en-1-yl)-4-toluenesulfonamido)but-1-en-2-yl acetate (38)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.32-7.24 (m, 2H), 6.45 (d, *J* = 14.2 Hz, 1H), 4.88-4.78 (m, 2H), 4.76-4.73 (m, 1H), 3.42 (dd, *J* = 7.7, 7.5 Hz, 2H), 2.46 (dd, *J* = 7.8, 7.5 Hz, 2H), 2.40 (s, 3H), 2.13 (s, 3H), 2.01 (dt, *J* = 7.2, 7.1 Hz, 2H), 1.37-1.17 (m, 6H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 152.9, 143.8, 136.2, 129.9, 127.1, 125.5, 113.8, 103.5, 43.4, 31.7, 31.3, 30.3, 29.8, 22.6, 21.7, 21.2, 14.2; IR (neat) 3069, 3030, 2956, 2927, 2856, 1757, 1656, 1598, 1458, 1354, 1162, 1092, 1020, 948, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{29}NO_4NaS$ $[M+Na]^+$ 402.1715, found 402.1740.



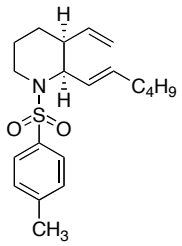
(*E*)-2-(Hex-1-en-1-yl)-1-tosylpiperidin-4-one (39)

The general cyclization reaction procedure was followed with **38** (30 mg, 0.079 mmol), 4 Å molecular sieves (30 mg), and DDQ (27 mg, 0.12 mmol) in nitromethane (0.7 mL). The reaction was stirred for 3 min then was purified by flash chromatography (8:1 to 4:1 hexanes:EtOAc) to yield the desired product (17 mg, 64%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.53 (dtd, *J* = 15.2, 6.7, 1.5 Hz, 1H), 5.16 (dd, *J* = 15.6, 5.3 Hz, 1H), 4.94 (t, *J* = 5.0 Hz, 1H), 4.02 (ddt, *J* = 13.4, 7.1, 2.0 Hz, 1H), 3.28 (ddd, *J* = 13.4, 12.1, 3.6 Hz, 1H), 2.66 (dd, *J* = 14.7, 6.6 Hz, 1H), 2.54-2.45 (m, 2H), 2.43 (s, 3H), 2.33-2.24 (m, 1H), 1.90 (td, *J* = 7.0, 6.8 Hz, 2H), 1.24-1.16 (m, 4H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 143.9, 137.5, 136.3, 130.0, 127.4, 126.0, 55.4, 45.1, 40.8, 40.6, 32.1, 31.1, 22.3, 21.7, 14.0; IR (neat) 2957, 2928, 2872, 1721, 1598, 1458, 1343, 1225, 1343, 1225, 1159, 1095, 1047, 980, 927 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{25}NO_3NaS$ $[M+Na]^+$ 358.1453, found 358.1437.



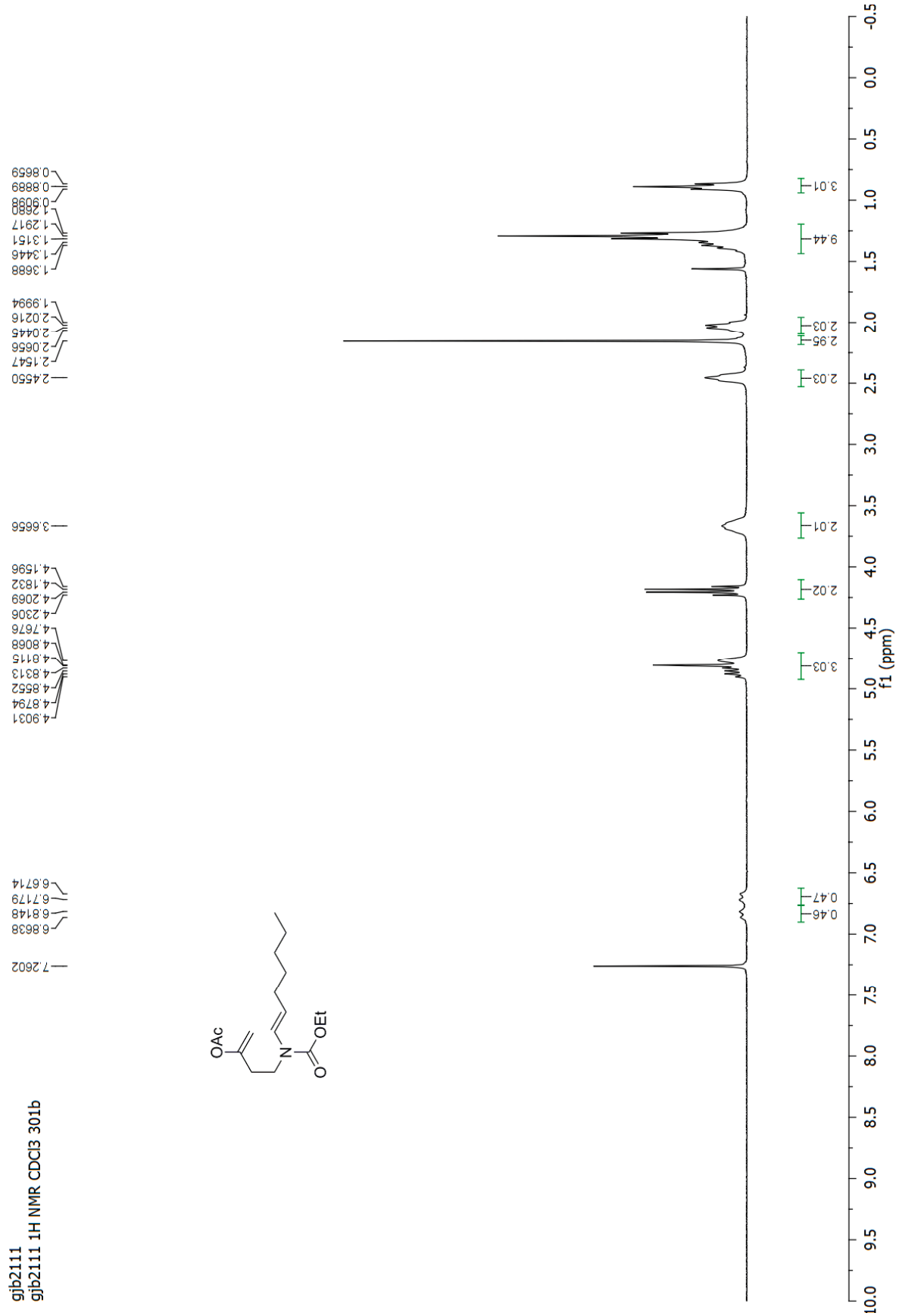
_N_-((_E_)-Hept-1-en-1-yl)-_N_-((_E_)-6-(trimethylsilyl)hex-4-en-1-yl)toluenesulfonamide (40)

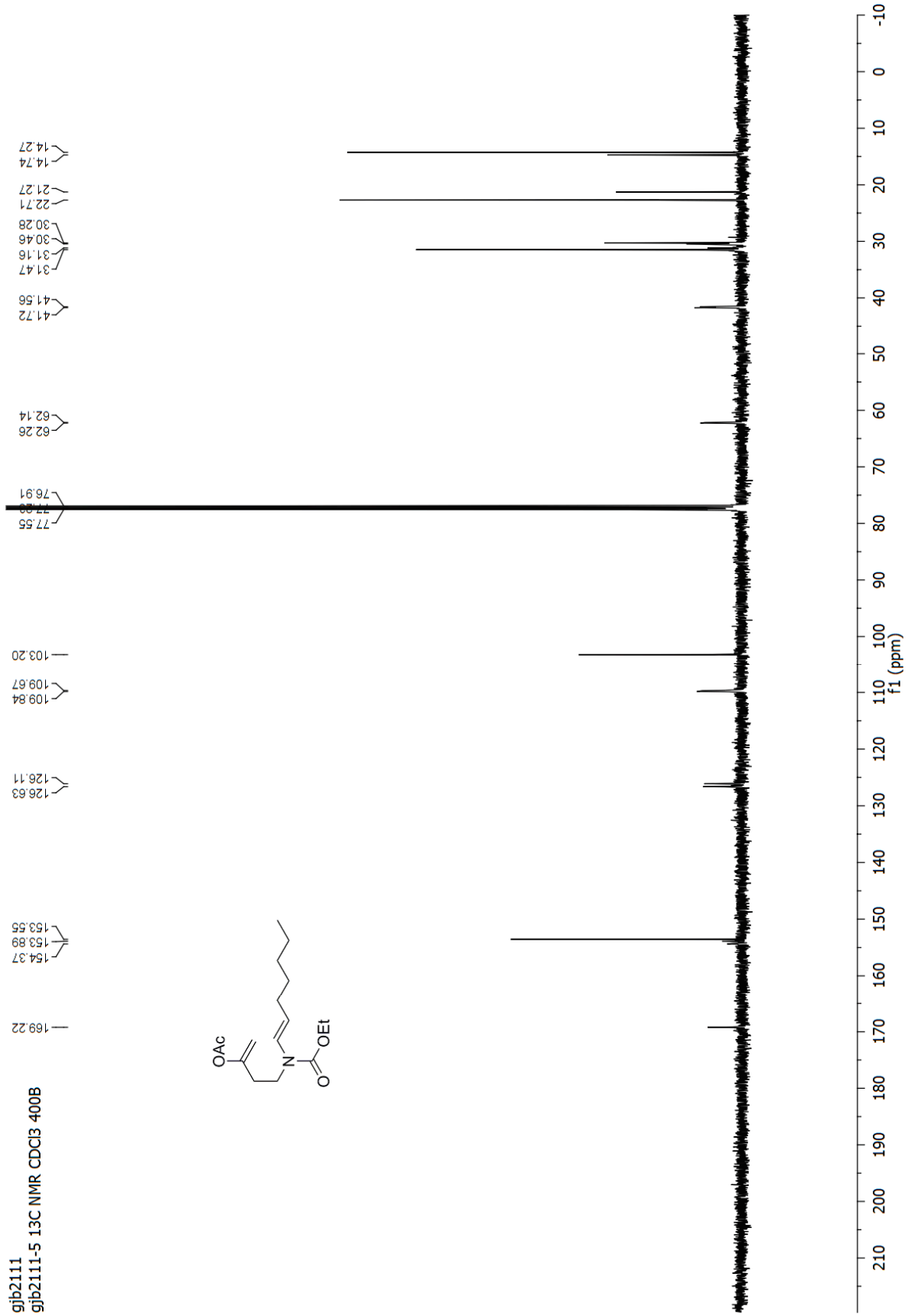
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 6.47 (d, J = 14.2 Hz, 1H), 5.39 (dt, J = 15.6, 7.9 Hz, 1H), 5.19 (dt, J = 14.8, 6.6 Hz, 1H), 4.81 (dt, J = 14.2, 7.2 Hz, 1H), 3.23 (m, J = 7.6, 7.4 Hz, 2H), 2.41 (s, 3H), 2.08-1.93 (m, 4H), 1.65-1.54 (m, 2H), 1.39 (d, J = 7.8 Hz, 2H), 1.37-1.18 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H), –0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 136.4, 129.8, 127.5, 127.5, 127.1, 125.9, 113.4, 45.5, 31.4, 30.4, 30.2, 30.0, 27.3, 22.8, 22.7, 21.7, 14.3, –1.8; IR (neat) 3017, 2953, 2928, 2857, 1656, 1598, 1458, 1404, 1354, 1247, 1163, 1093, 965, 850 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{23}H_{40}NO_2SSi$ $[M+H]^+$ 422.2549, found 422.2545.

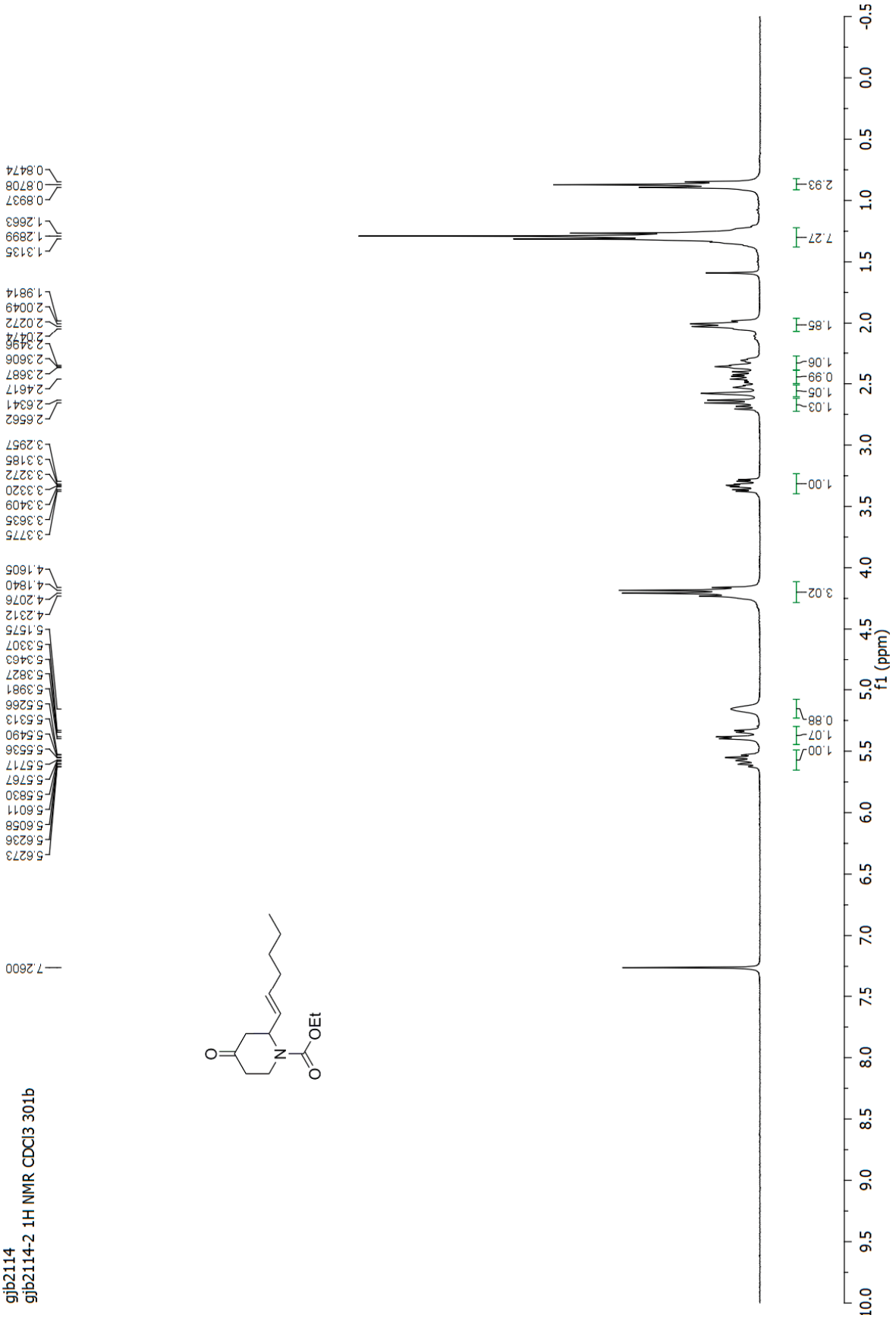


(_E_)-2-(Hex-1-en-1-yl)-1-tosyl-3-vinylpiperidine (41)

The general cyclization reaction procedure was followed with **40** (50 mg, 0.12 mmol), 4 Å molecular sieves (50 mg), $LiClO_4$ (13 mg, 0.12 mmol) and DDQ (40 mg, 0.18 mmol) in nitromethane (1.2 mL). The reaction was stirred for 3 min then was purified by flash chromatography (8:1 to 2:1 hexanes:EtOAc) to yield the desired product (dr = 4.0:1 cis:trans, 31 mg total, 75%) as a faint yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, two diastereomers 1:0.25 ratio) δ 7.65-7.61 (m, 2.5H), 7.23 (d, J = 8.0 Hz, 2.5H), 6.02 (ddd, J = 17.5, 10.5, 7.1 Hz, 1H), 5.56 (ddd, J = 10.3, 8.4, 5.0 Hz, 0.25H), 5.53-5.46 (m, 1H), 5.33 (ddt, J = 15.4, 7.2, 1.4 Hz, 1H), 5.23 (ddt, J = 15.3, 8.1, 1.4 Hz, 0.25H), 5.16 (ddd, J = 17.3, 1.5, 1.5 Hz, 1H), 5.09 (ddd, J = 10.5, 1.4, 1.4 Hz, 1H), 5.02-4.99 (m, 0.25H), 4.99-4.97 (m, 0.25H), 4.50 (dd, J = 8.0, 4.8 Hz, 0.25H), 4.41 (d, J = 7.0 Hz, 1H), 3.76-3.71 (m, 0.25H), 3.65-3.60 (m, 1H), 2.92 (td, J = 12.2, 3.2 Hz, 1H), 2.84 (td, J = 12.7, 3.0 Hz, 0.25H), 2.40 (s, 3.75H), 2.33-2.28 (m, 1H), 1.89-1.81 (m, 2.5H), 1.79-1.67 (m, 2.5H), 1.63-1.44 (m, 2.5H), 1.41-1.32 (m, 0.5H), 1.28-1.14 (m, 5H), 0.87 (t, J = 7.0 Hz, 2.25H), 0.86 (t, J = 6.9 Hz, 0.75H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 139.9, 139.9, 137.9, 137.8, 136.8, 134.3, 129.4, 129.4, 127.8, 127.7, 125.6, 120.9, 115.5, 115.3, 59.3, 59.2, 44.4, 42.9, 41.7, 40.9, 32.2, 32.1, 31.2, 25.3, 24.7, 24.6, 22.4, 22.4, 21.6, 21.0, 14.1, 14.1; IR (neat) 2953, 2929, 2859, 1454, 1339, 1162, 1092, 968, 924, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{29}NO_2NaS$ $[M+Na]^+$ 370.1817, found 370.1830.



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OEt
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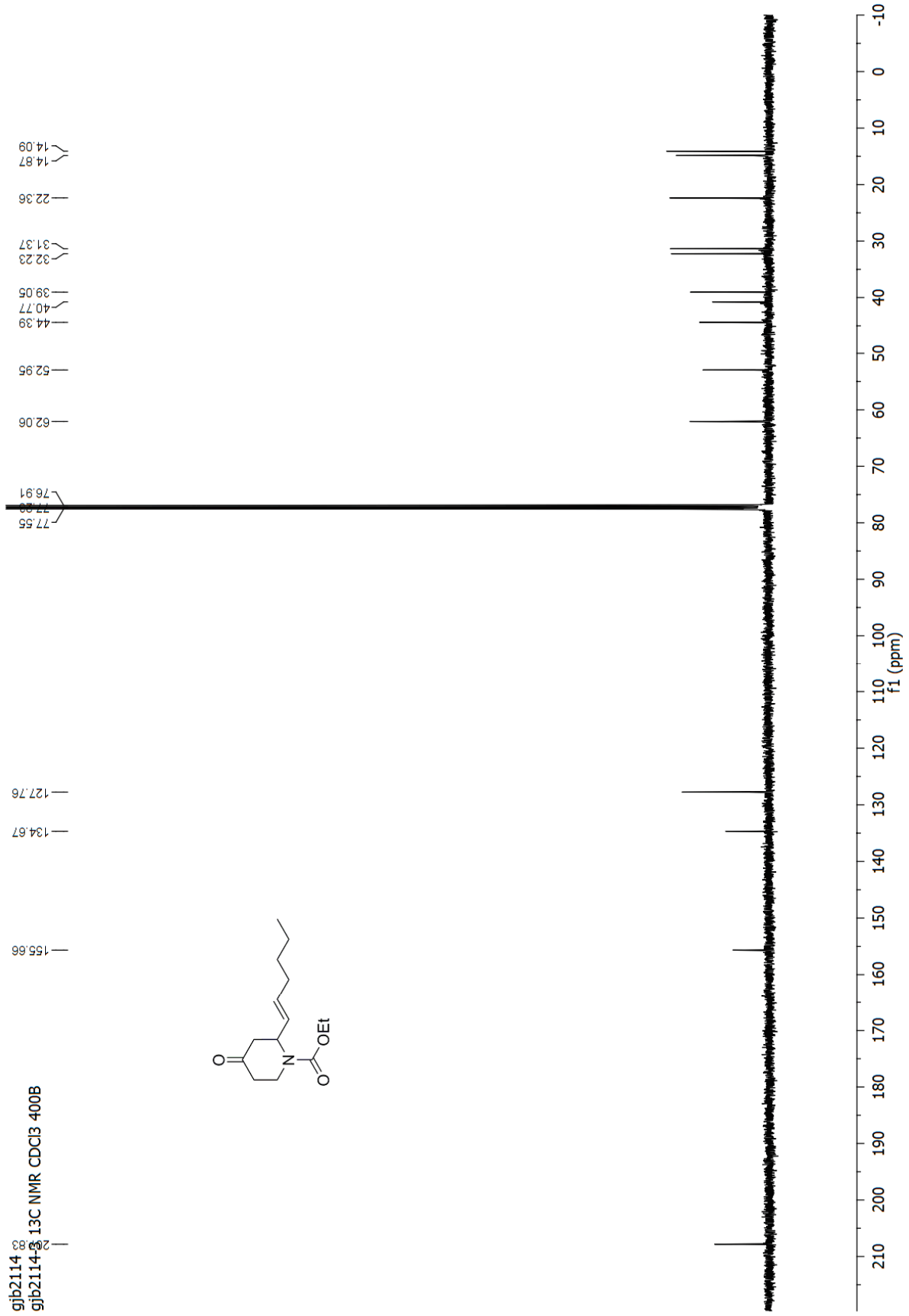
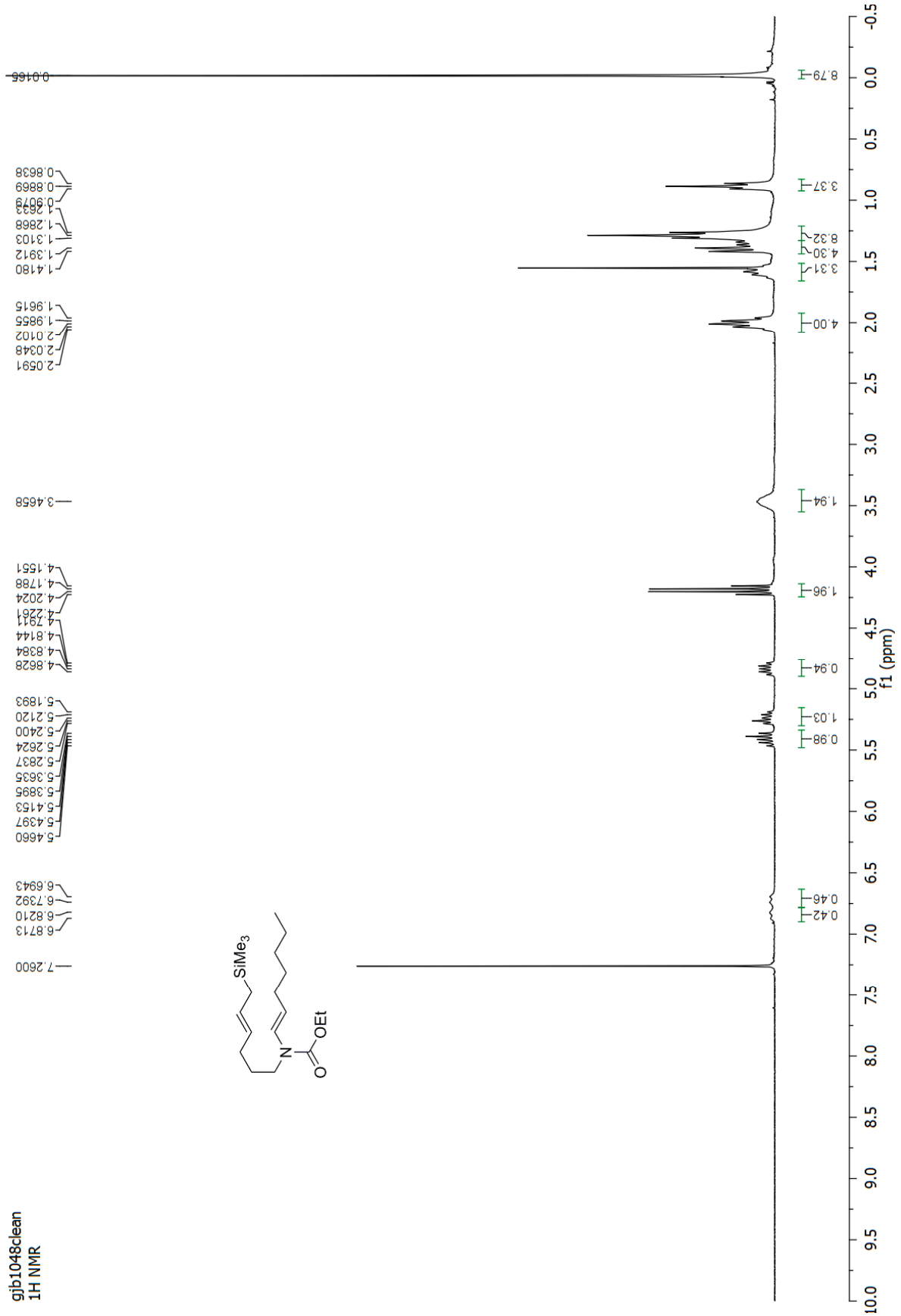
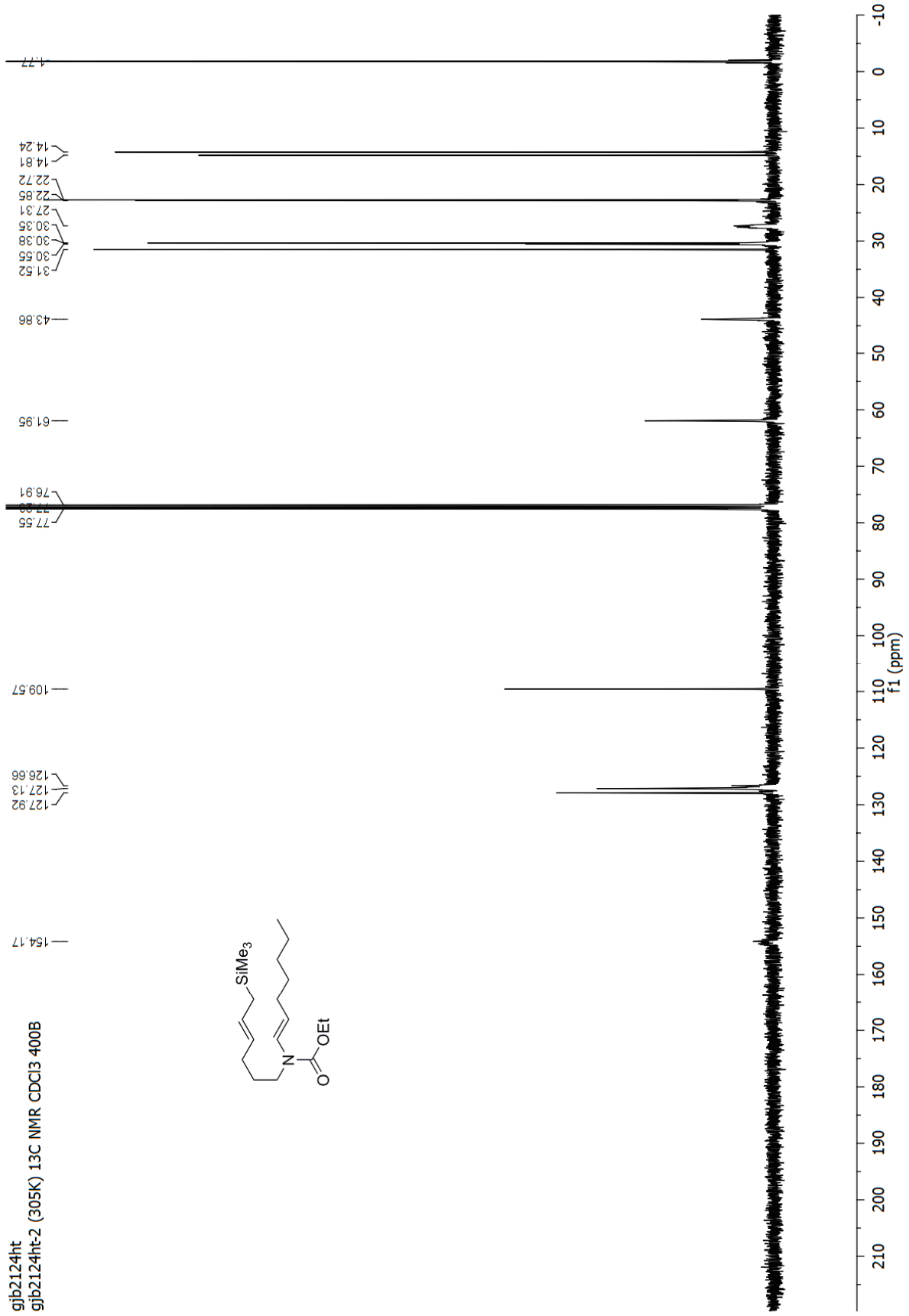
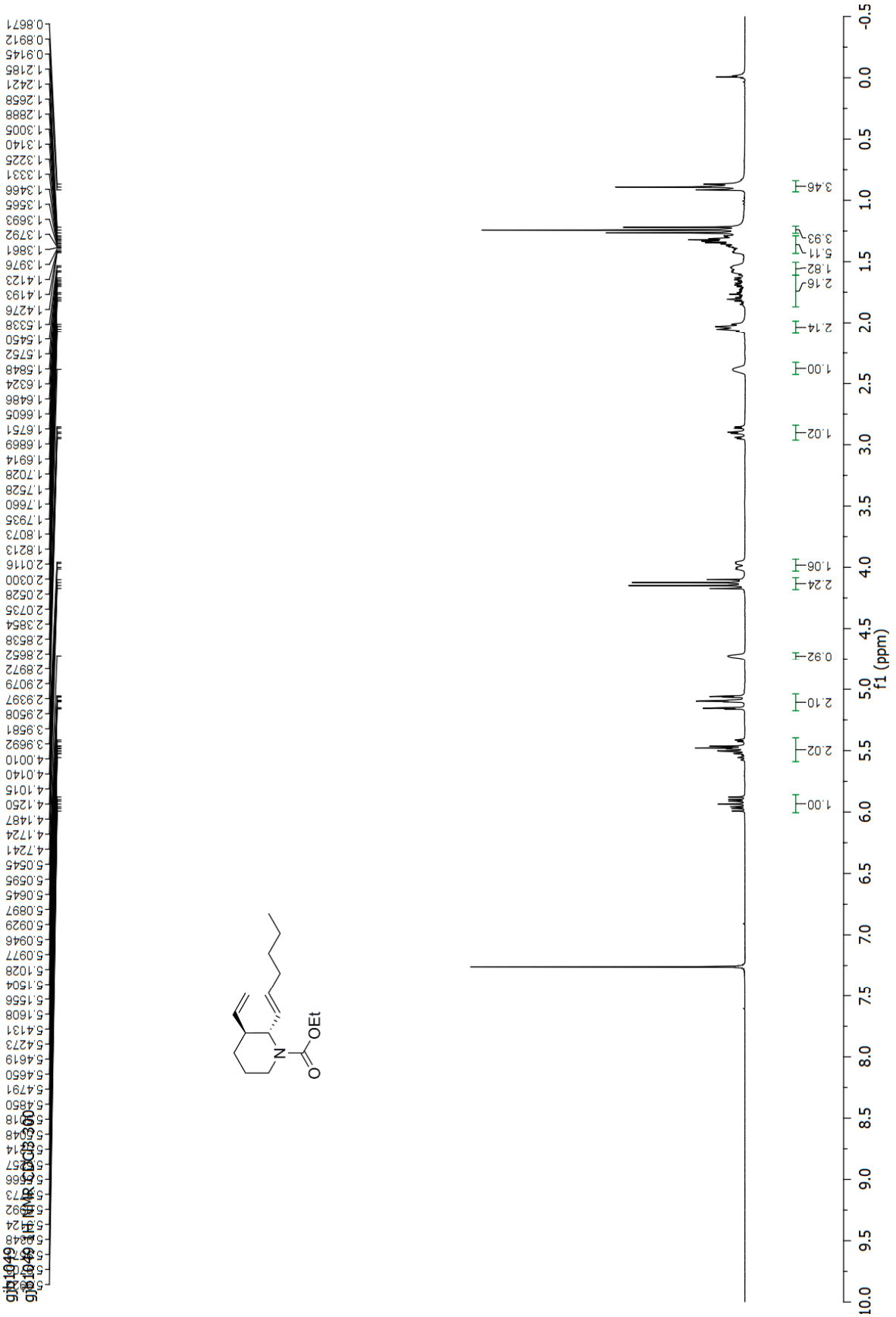
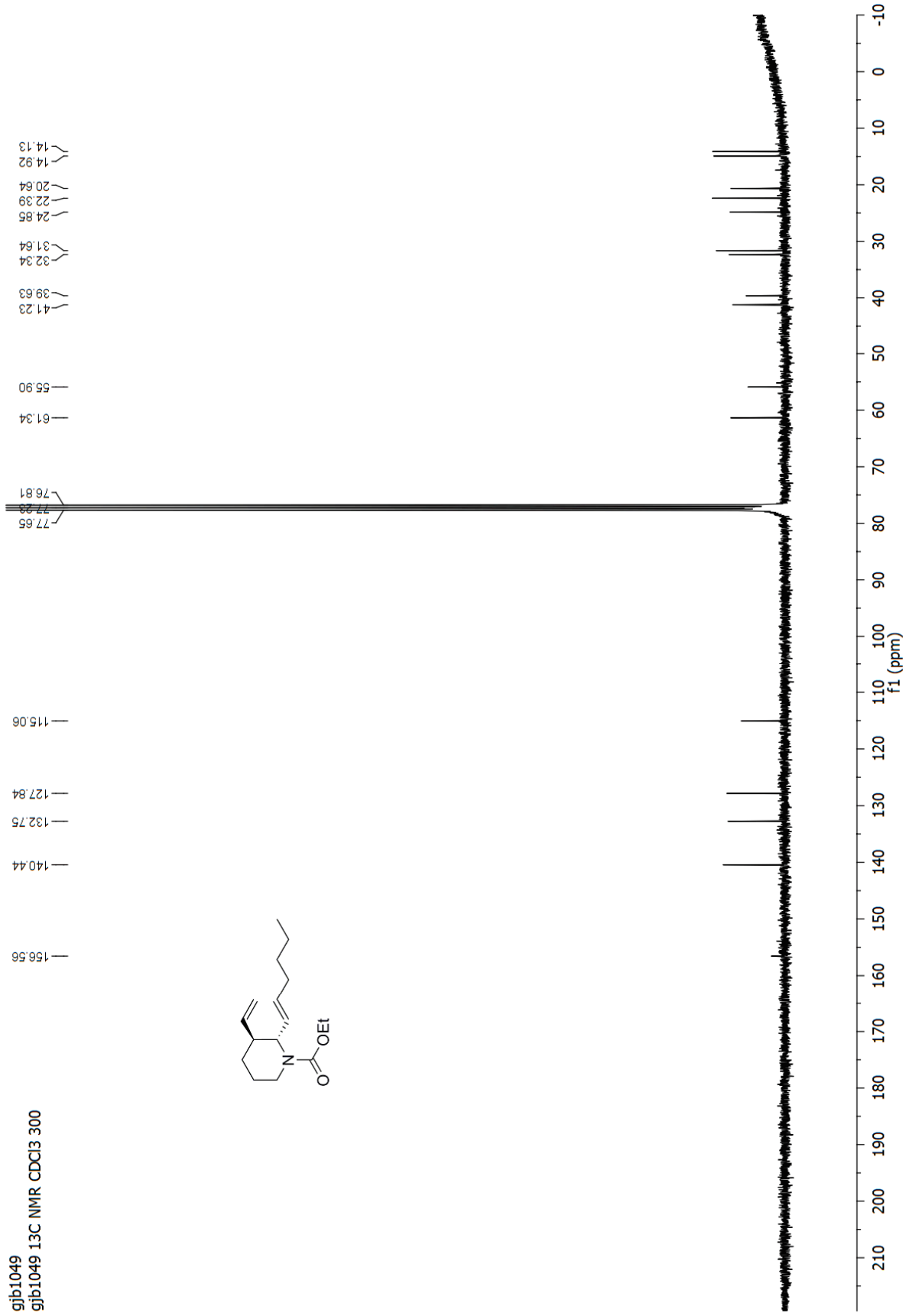
N
O
f1 (ppm)

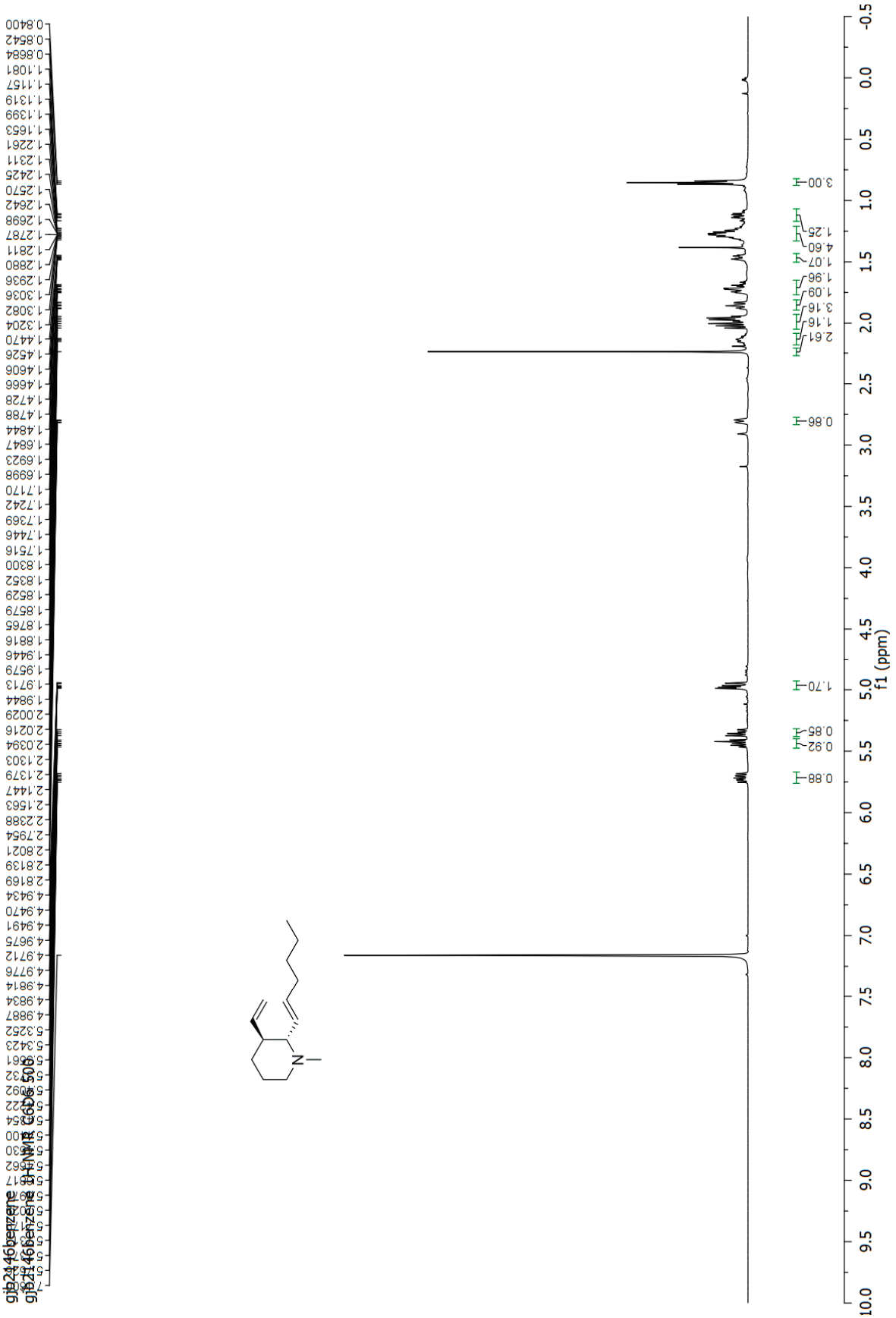


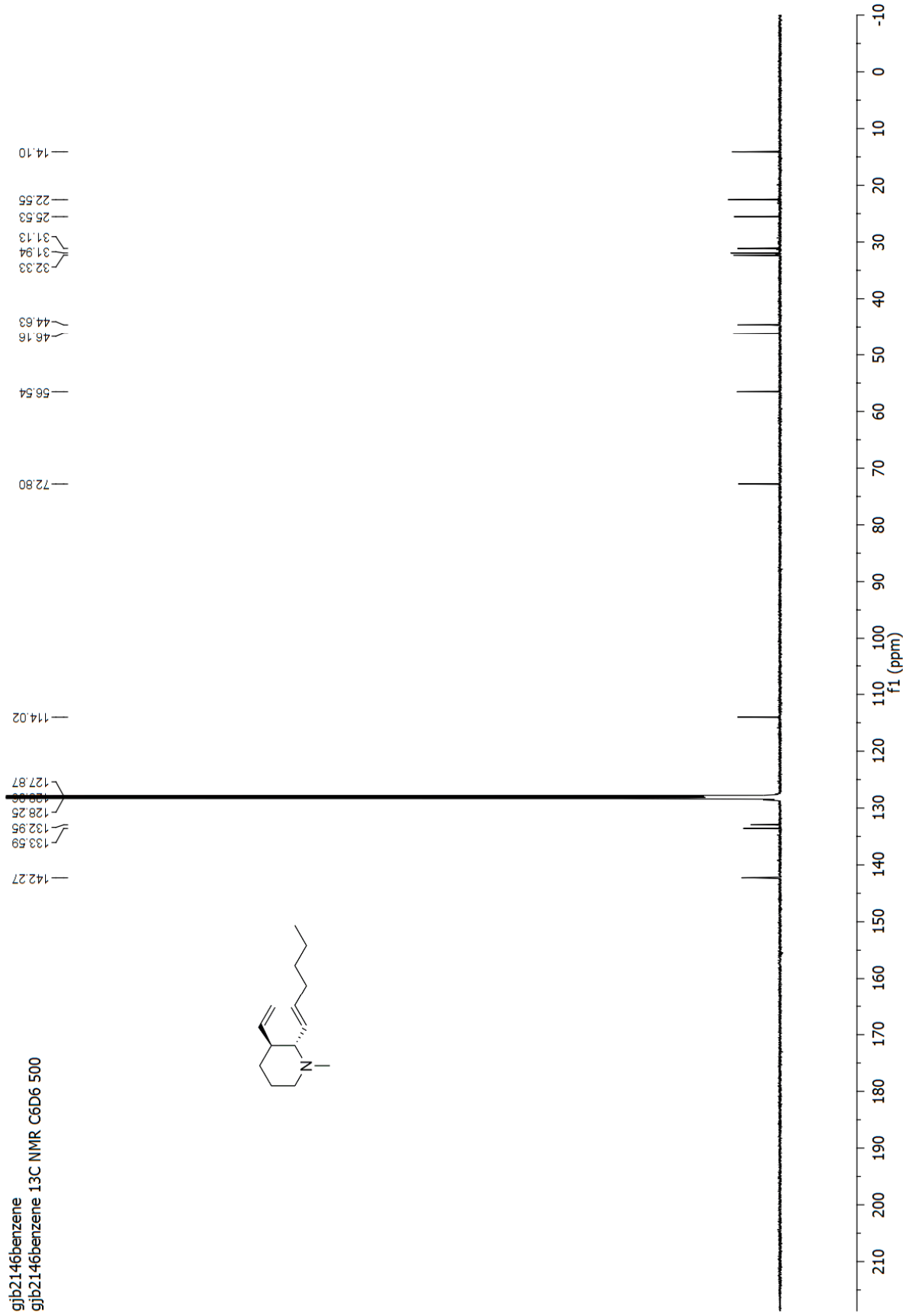








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gjb2146benzene 13C NMR C6D6 500
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25.53
31.13
31.94
32.33
44.63
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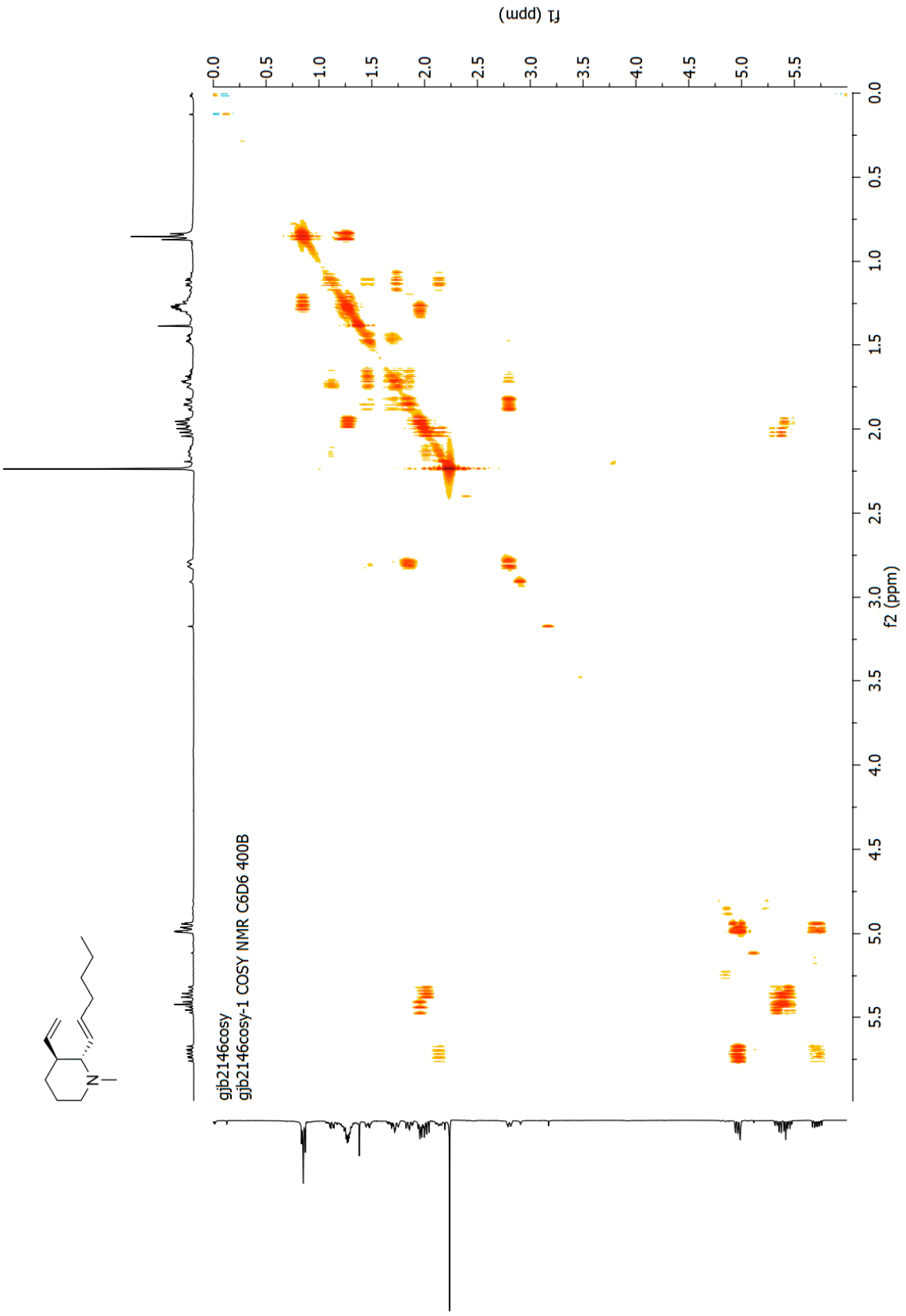
128.25
132.95
133.59
142.27
f1 (ppm)


f1 (ppm)
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0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f2 (ppm)
gjb2146cosy
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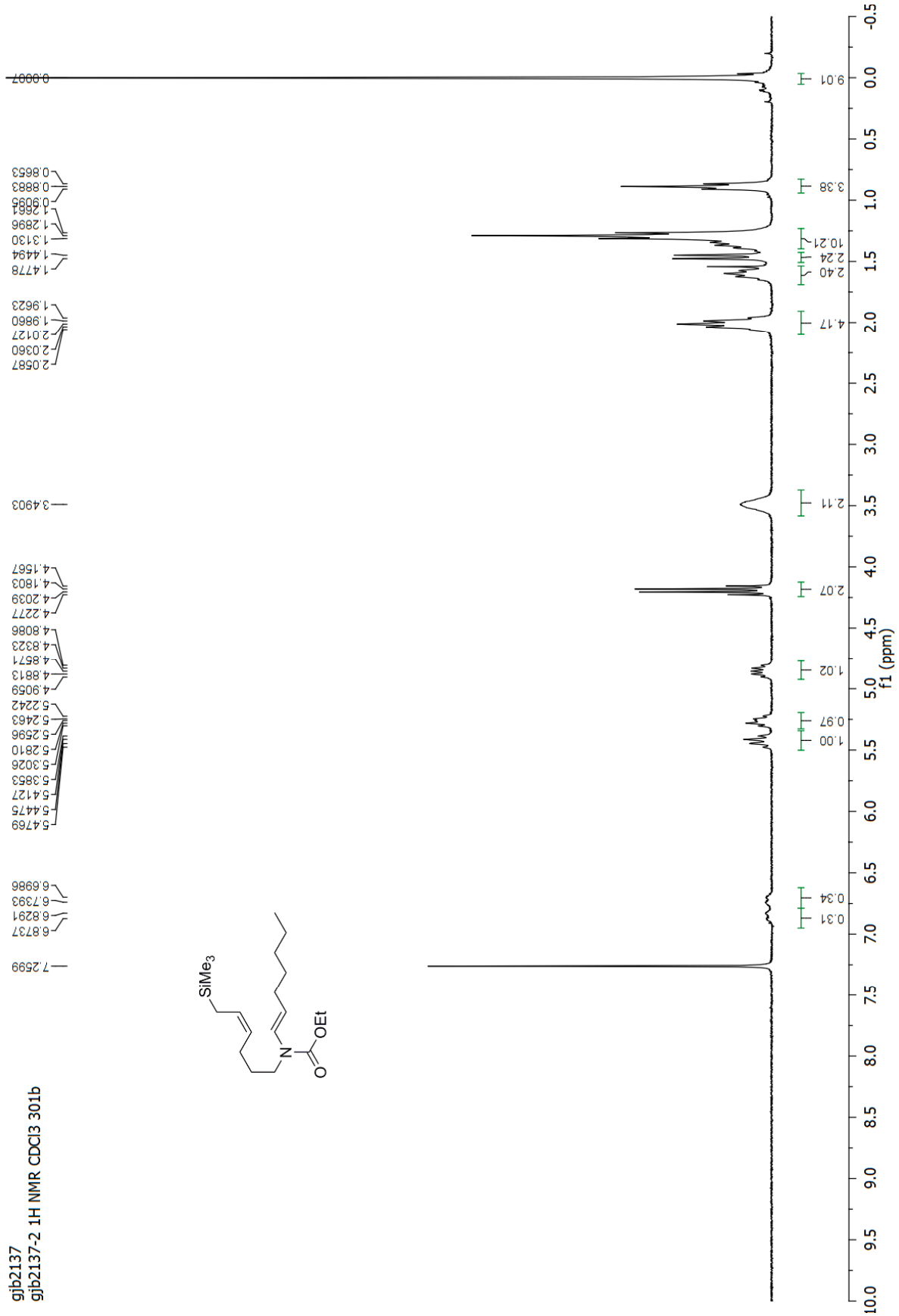
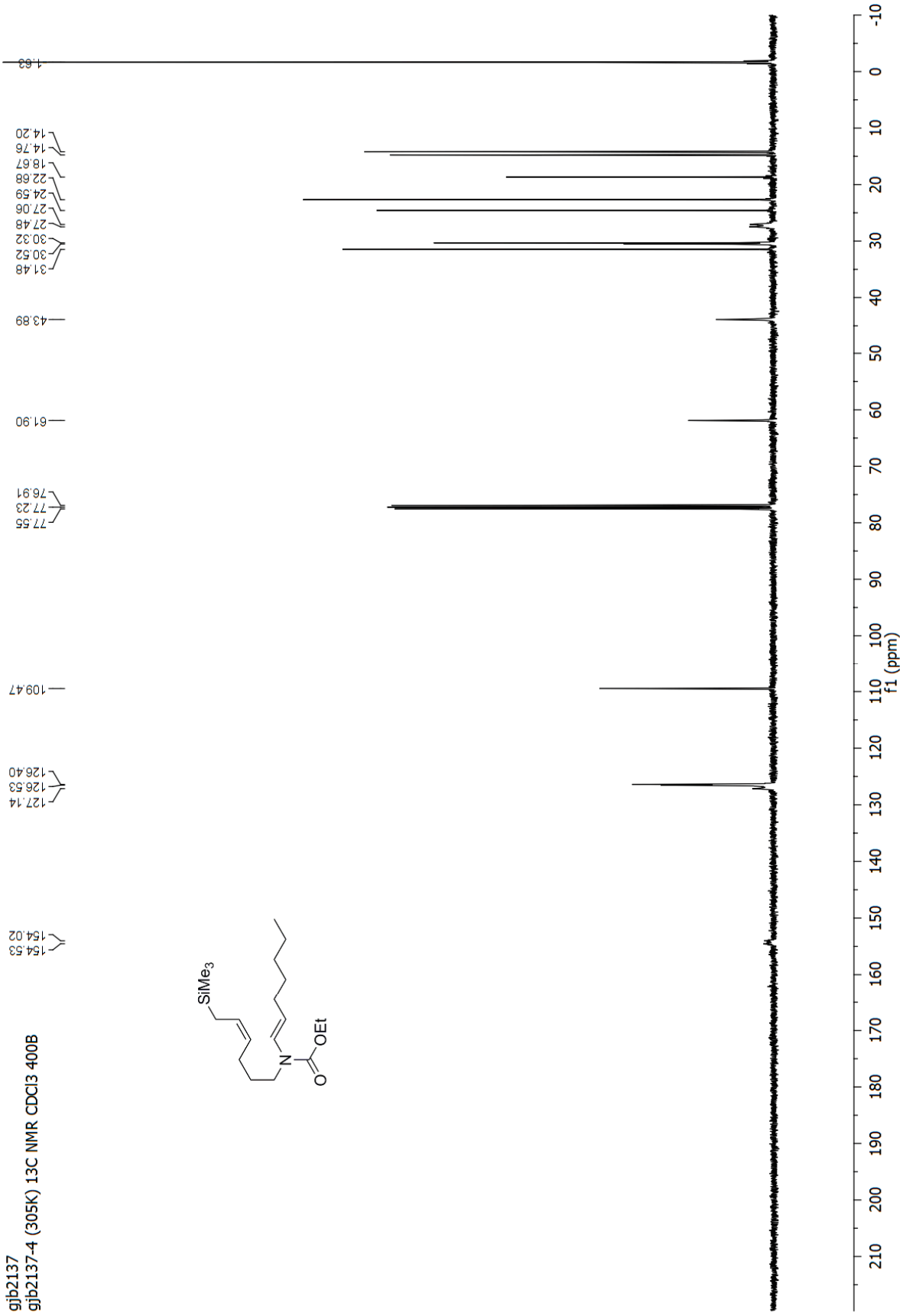
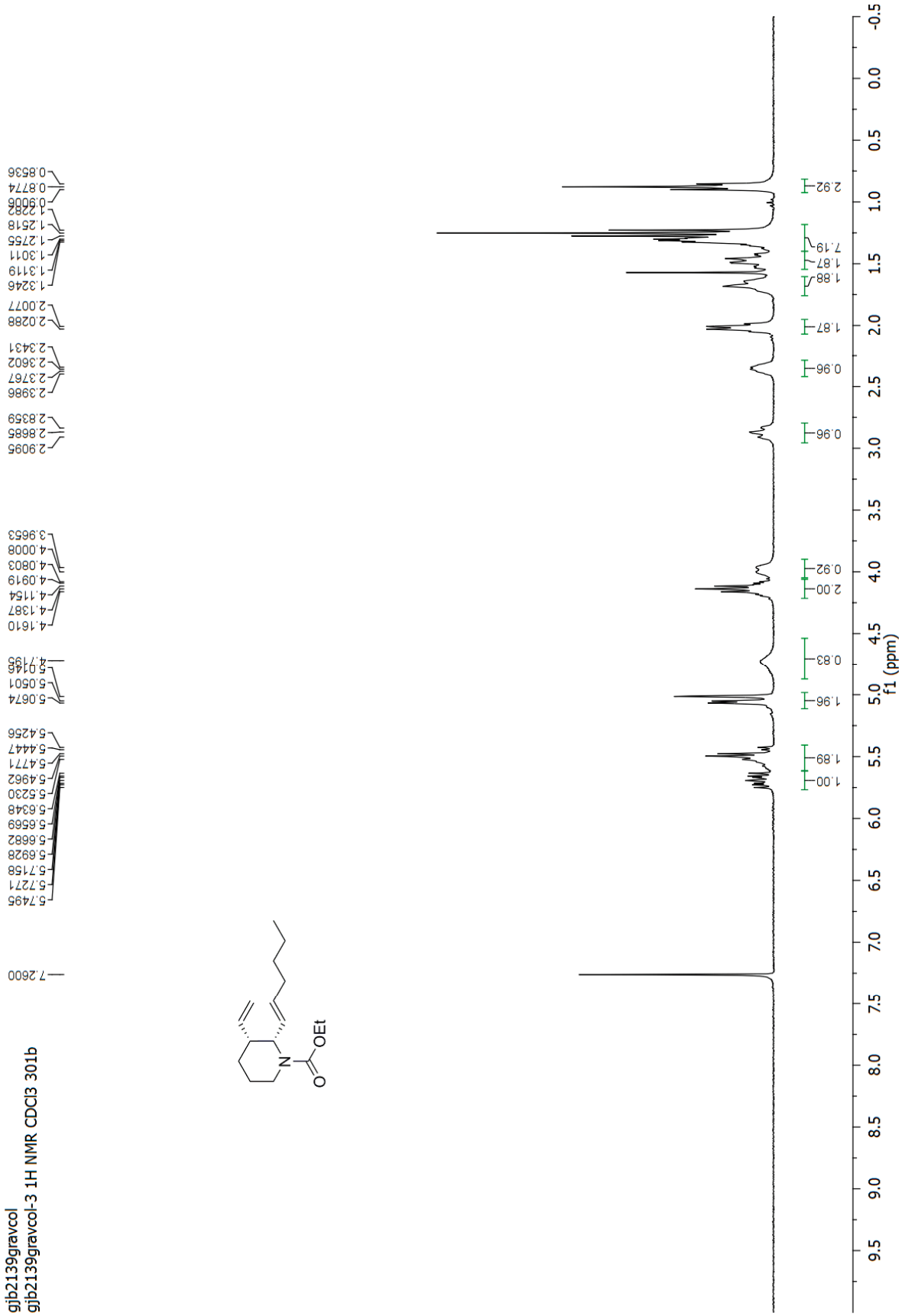
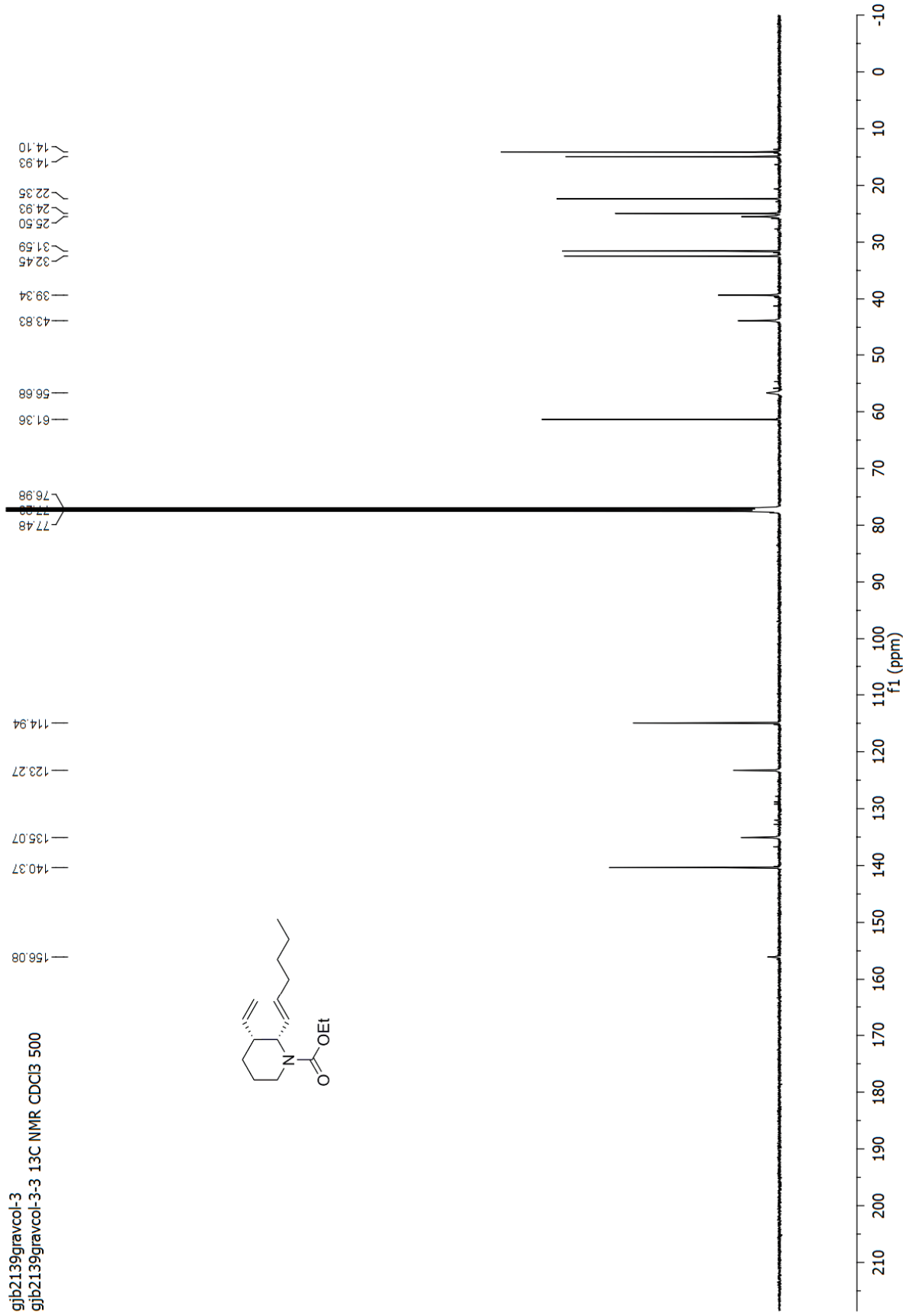
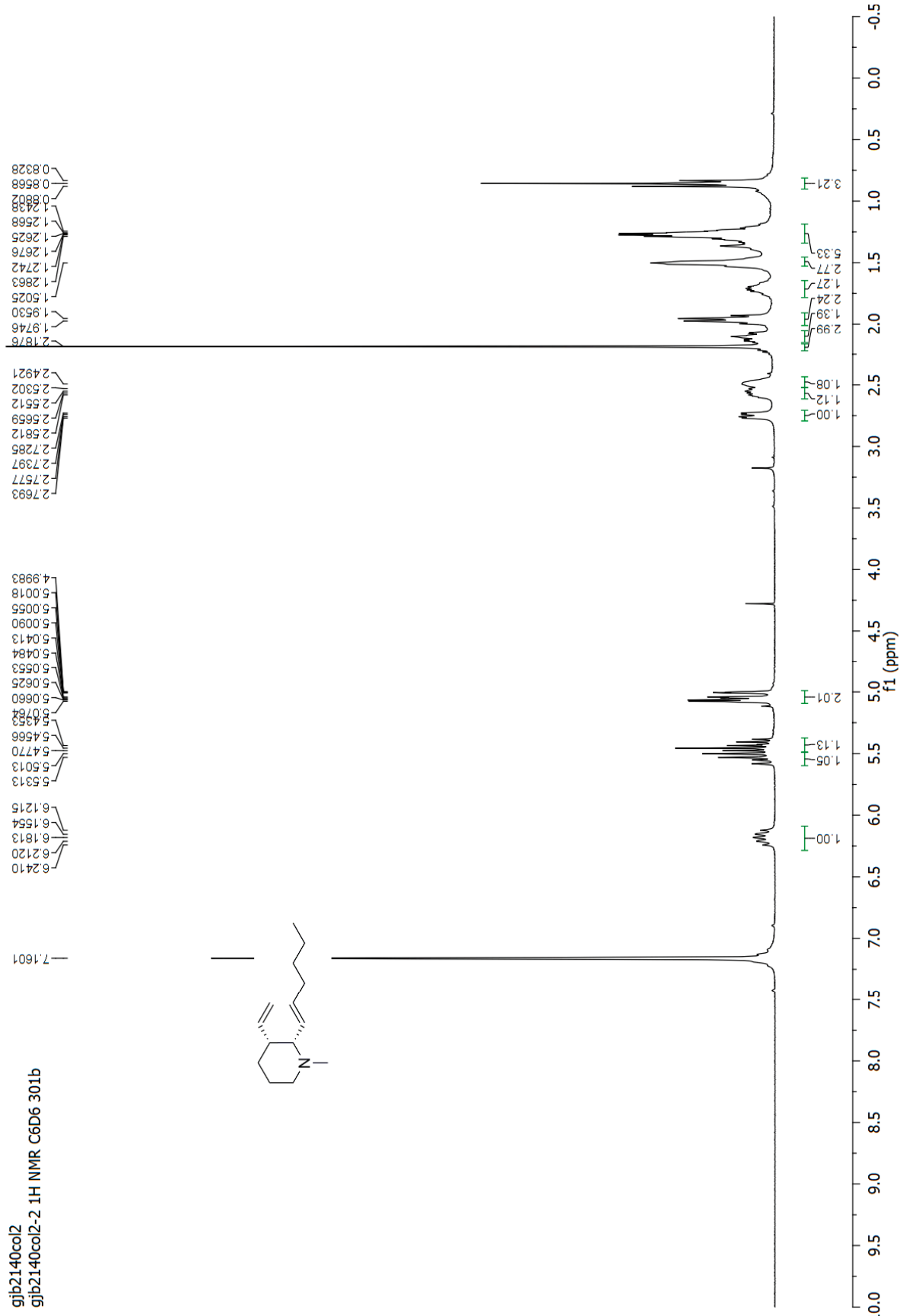
N

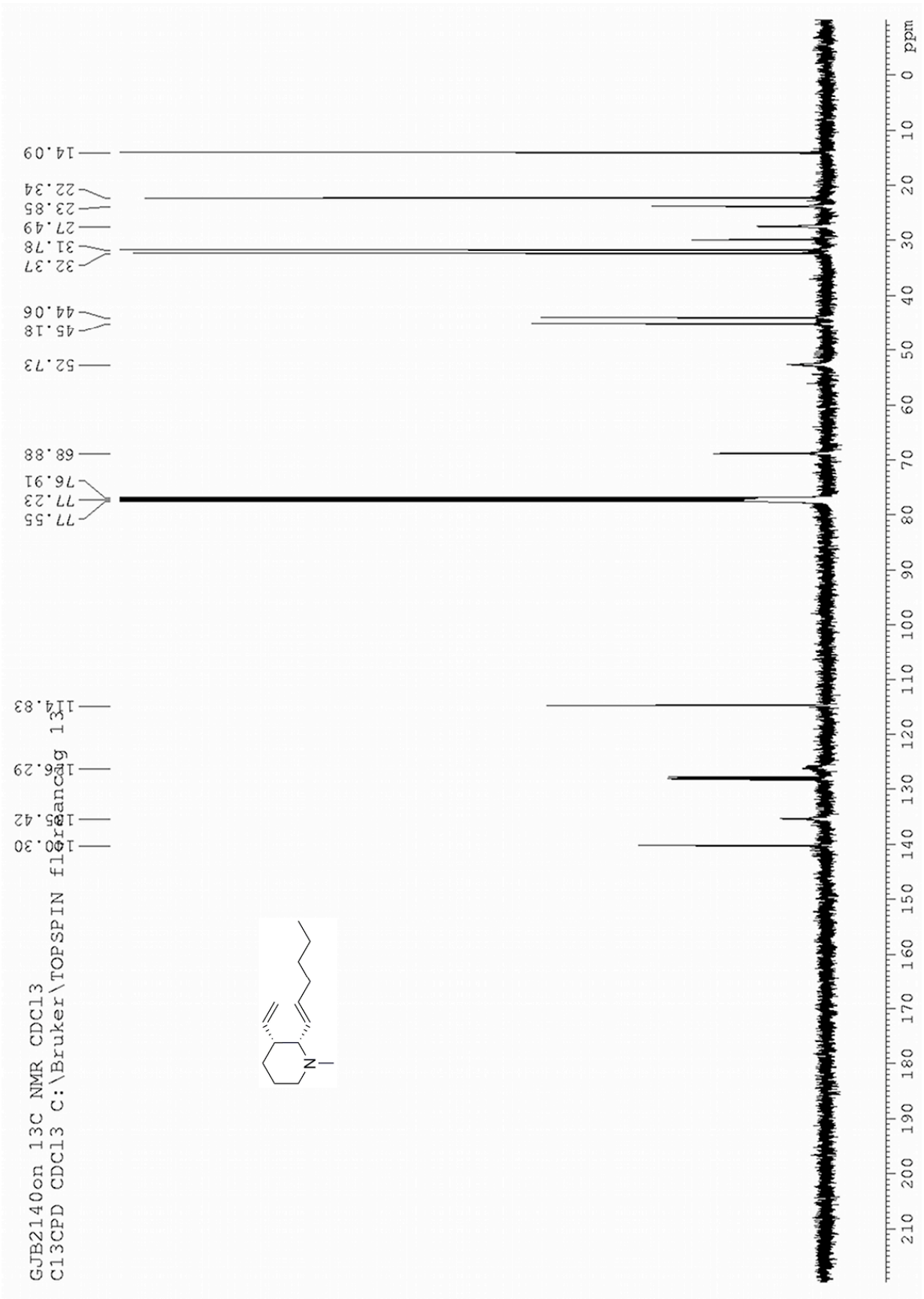


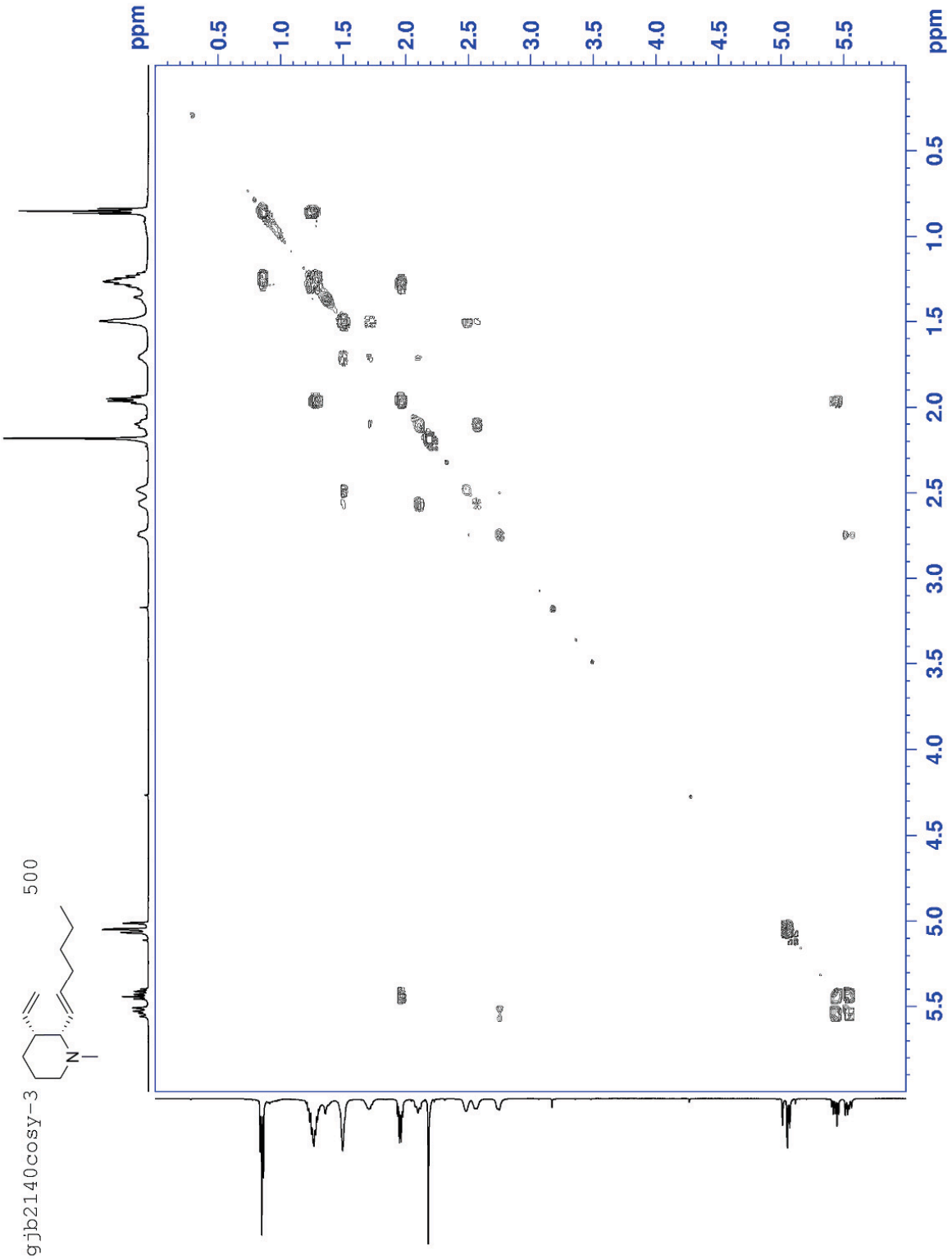








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2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
ppm
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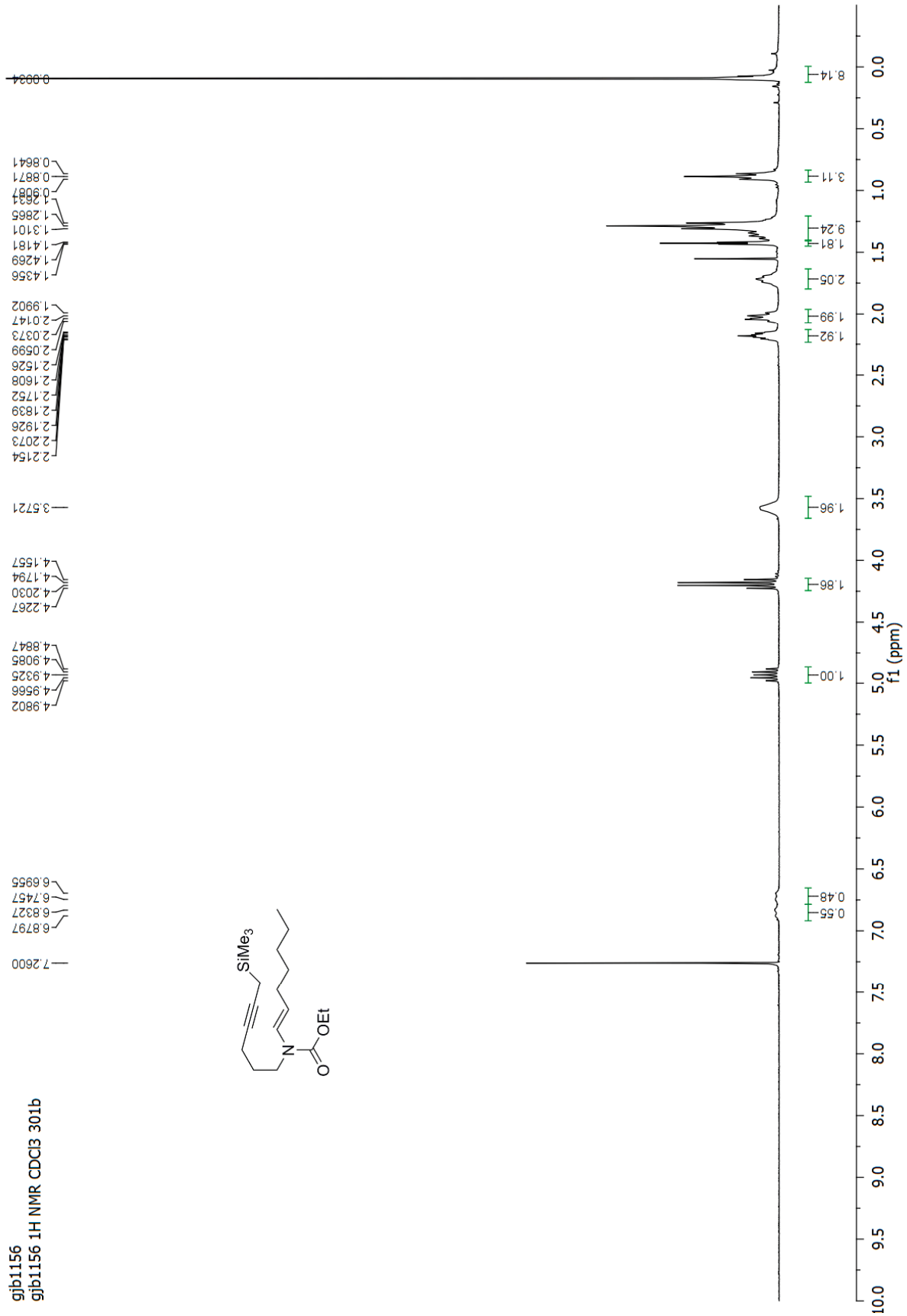
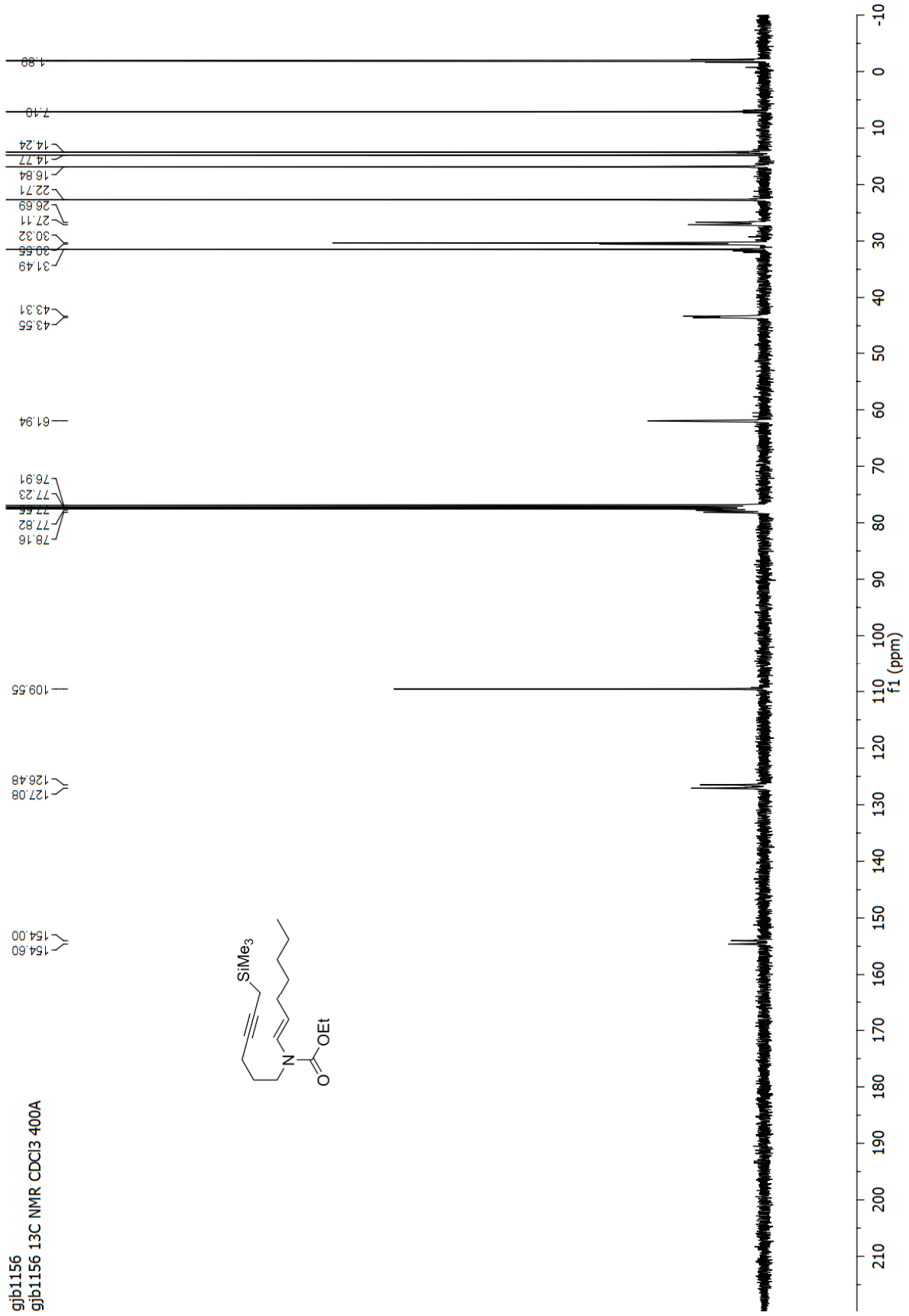
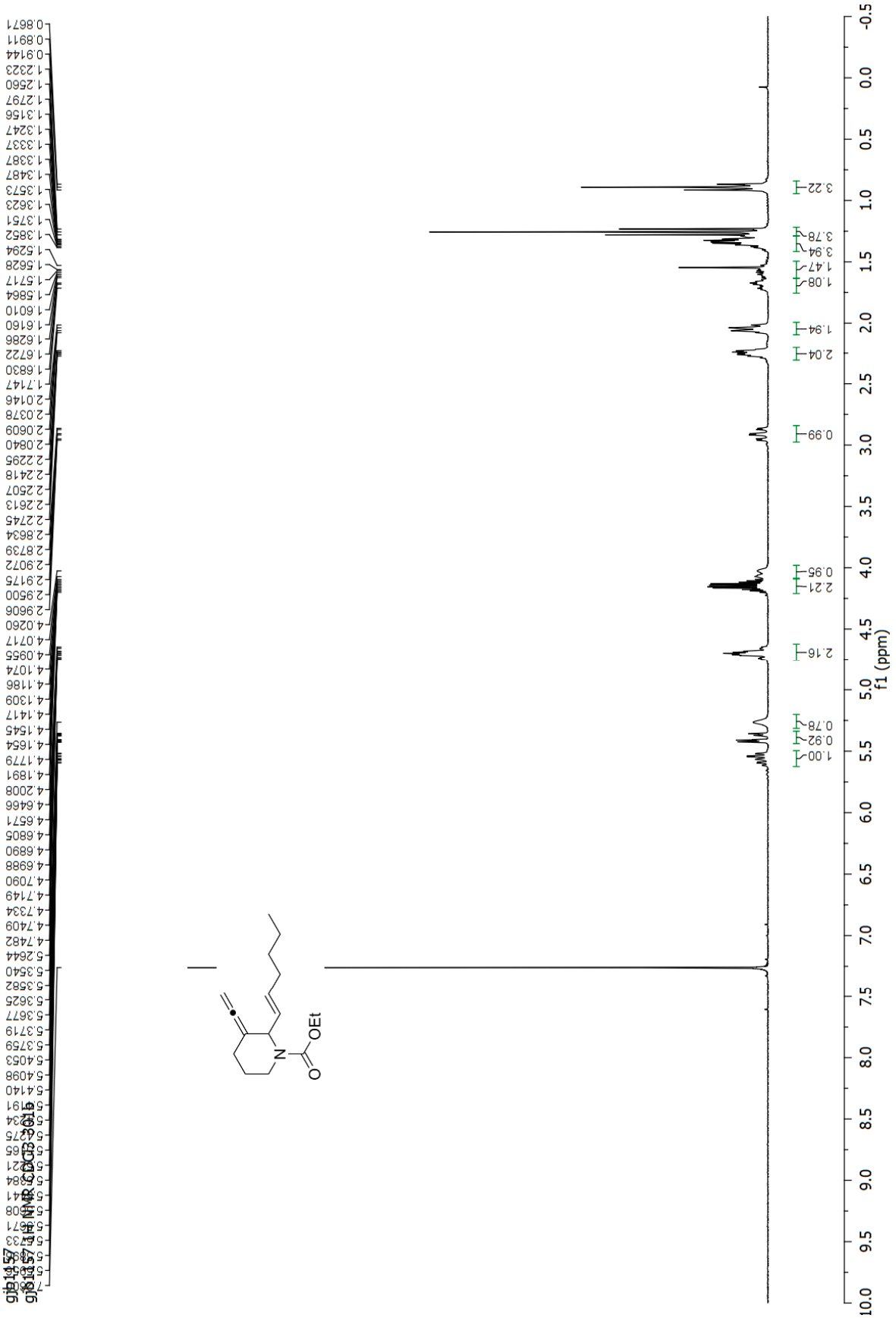
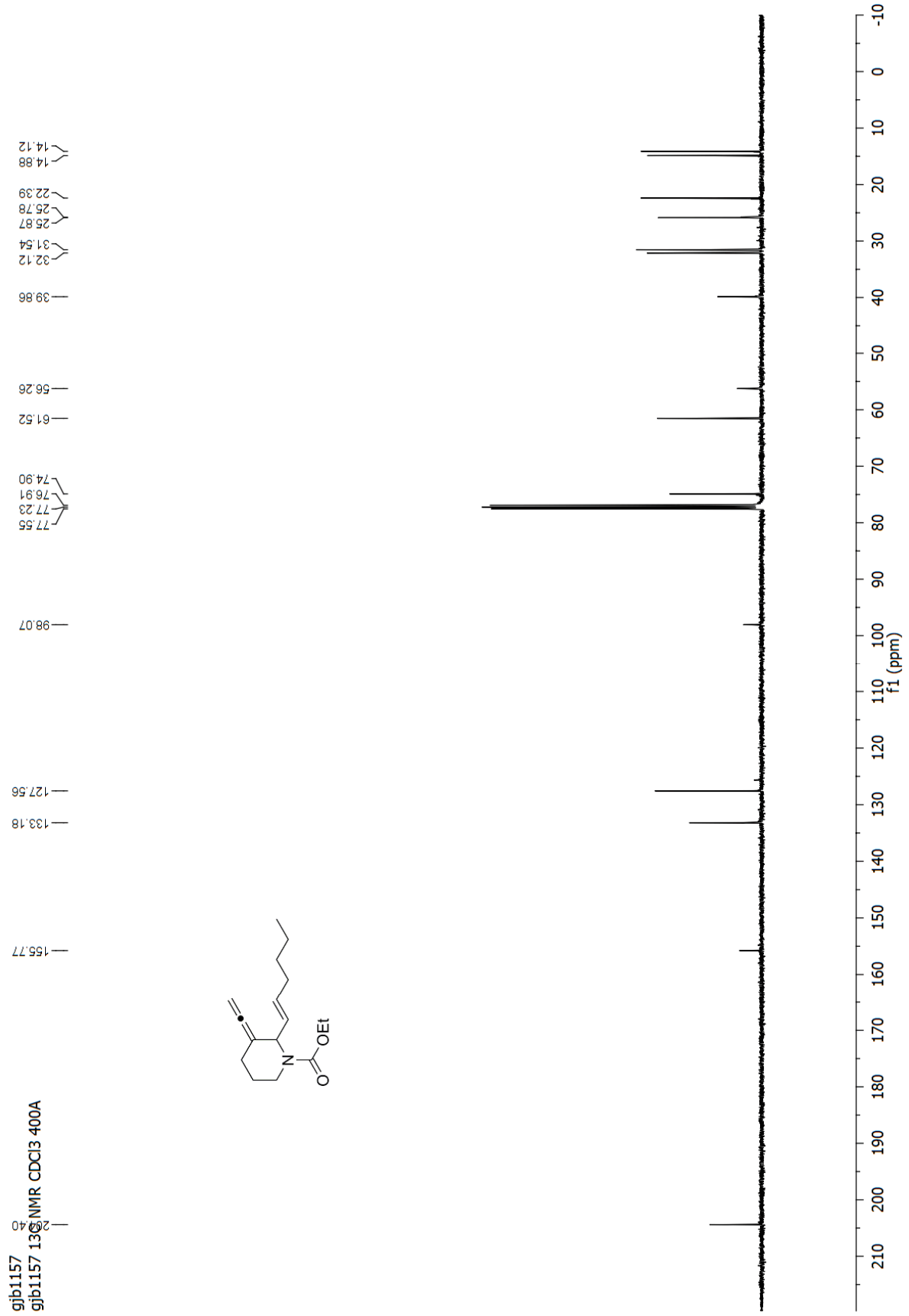
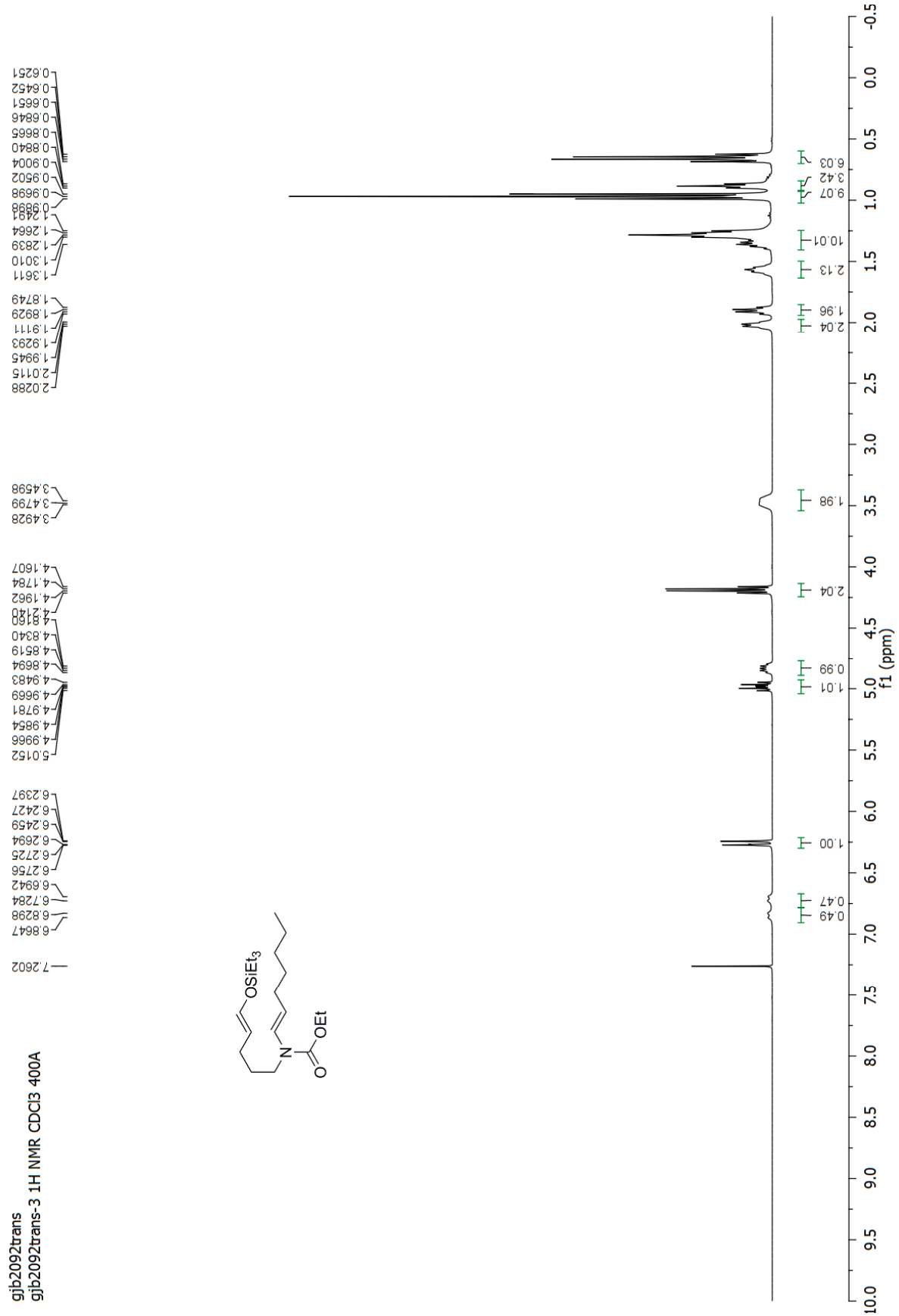
gjb2140cosy-3

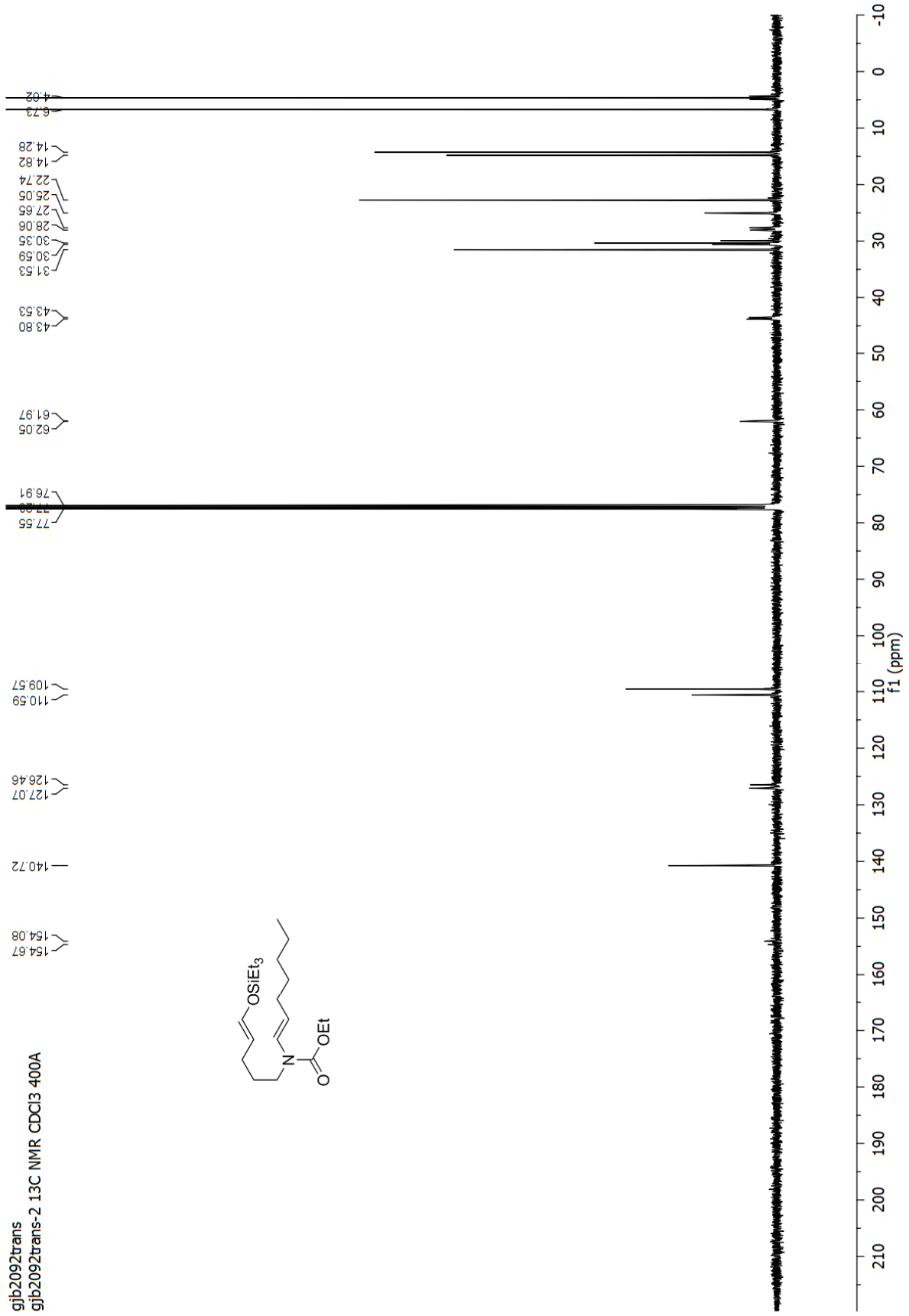


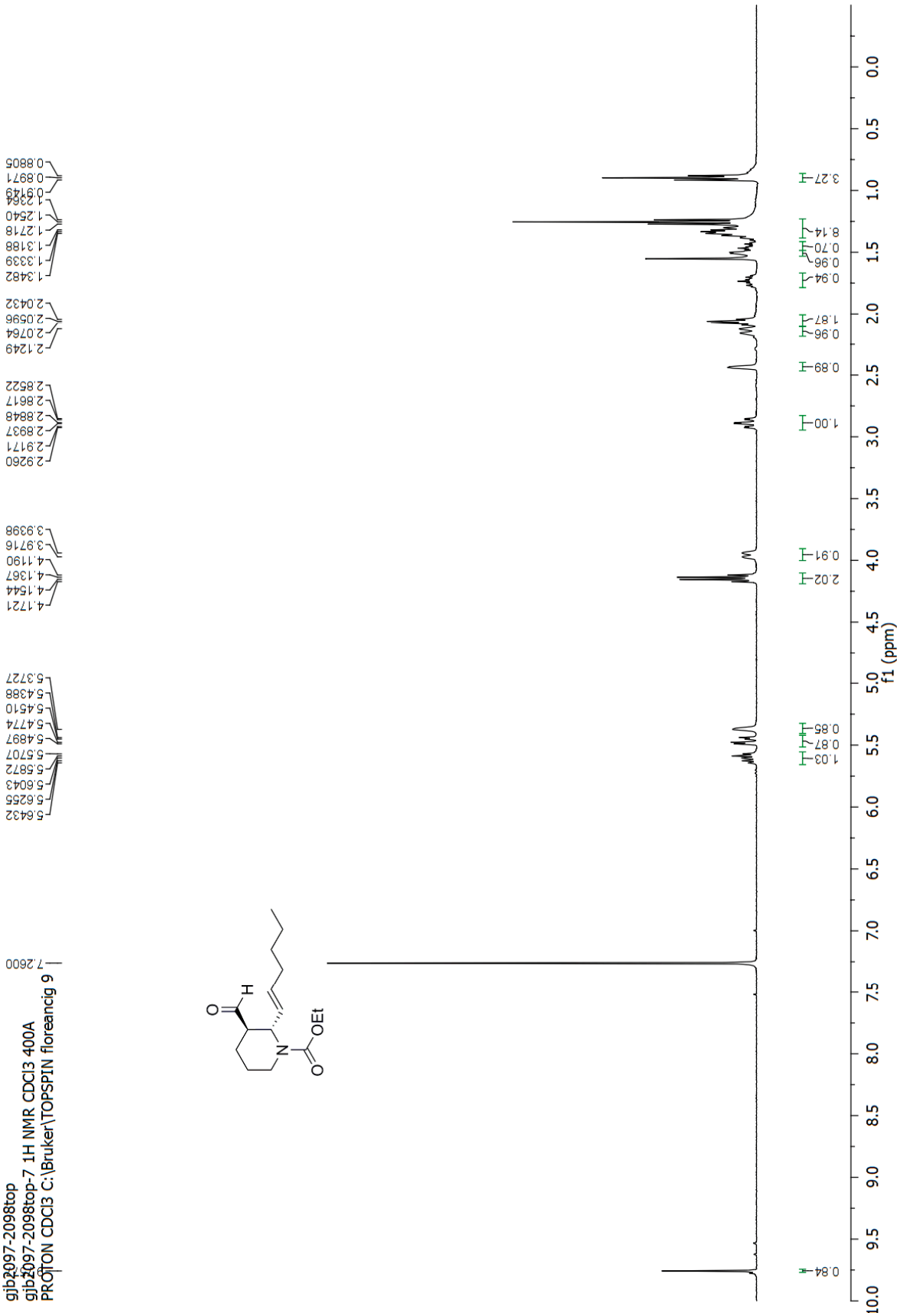


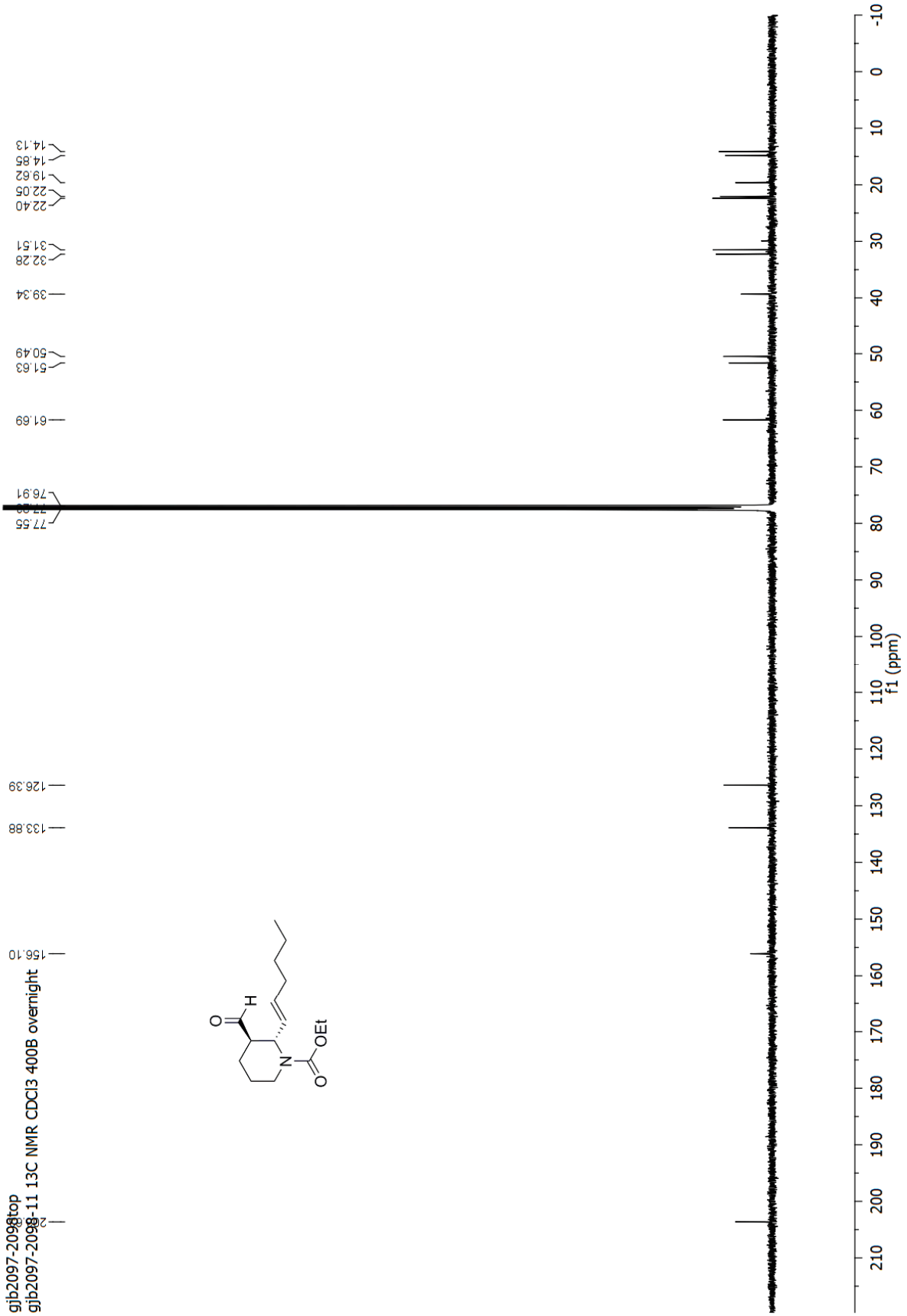

OEt
O
N
f1 (ppm)

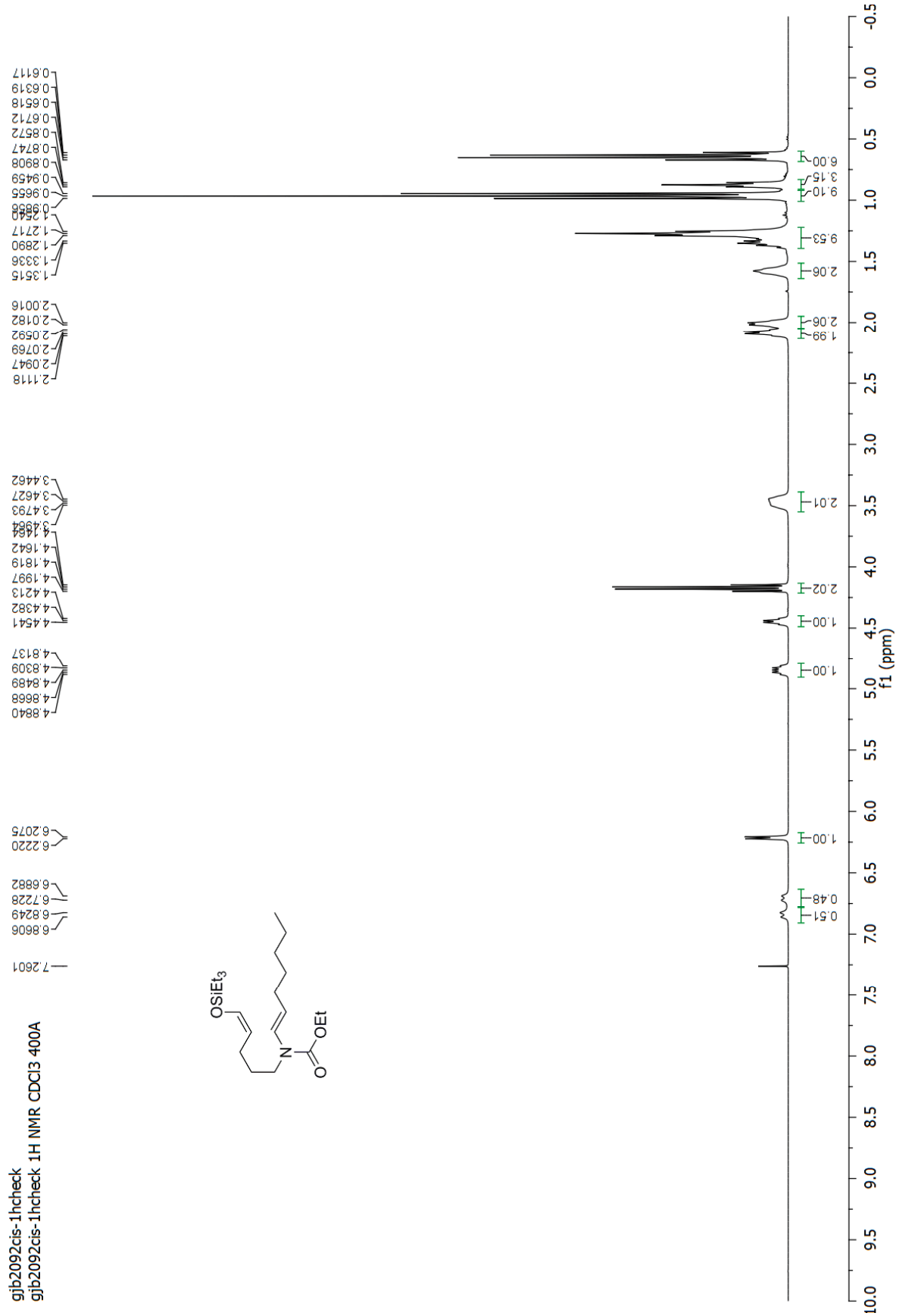


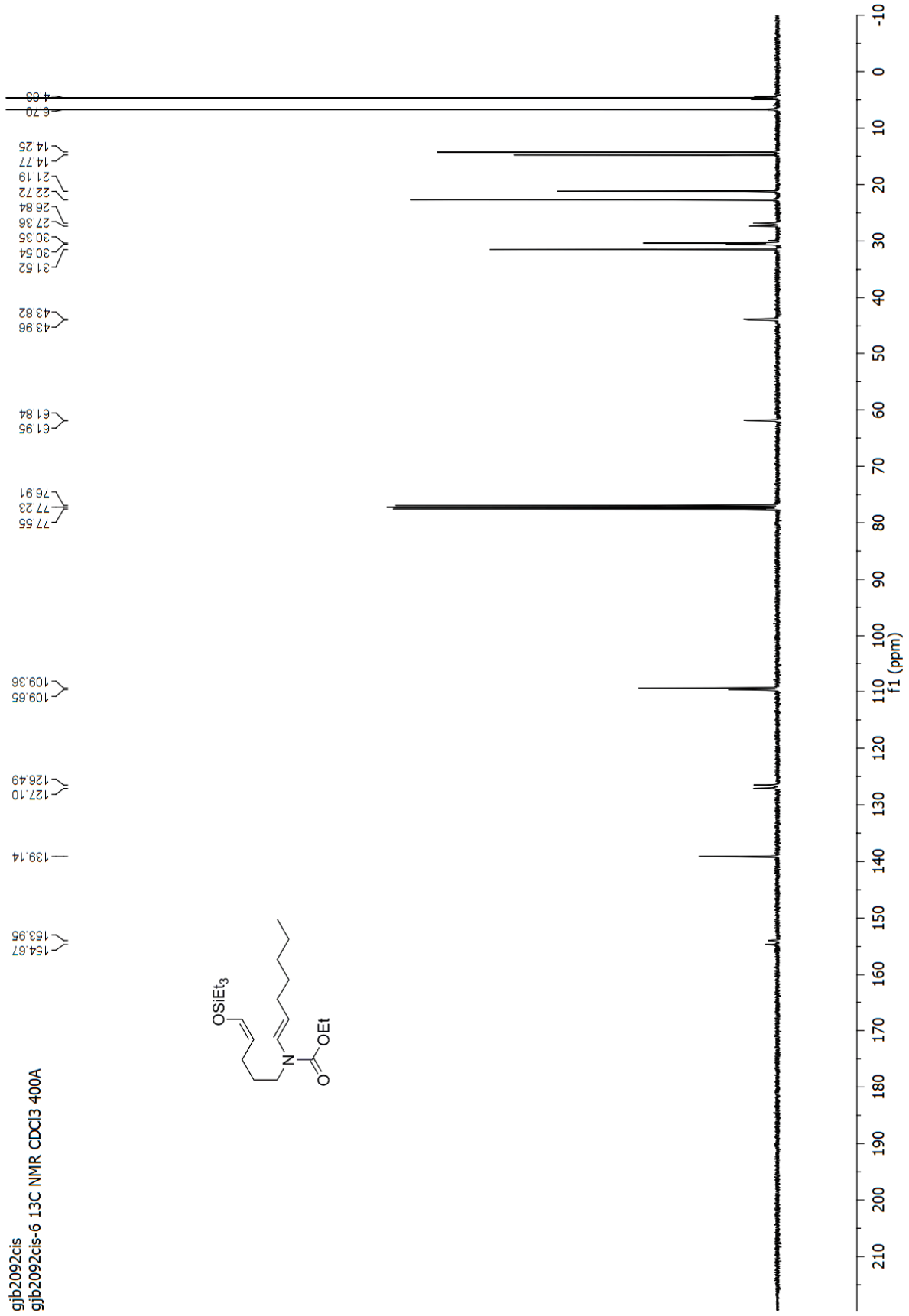


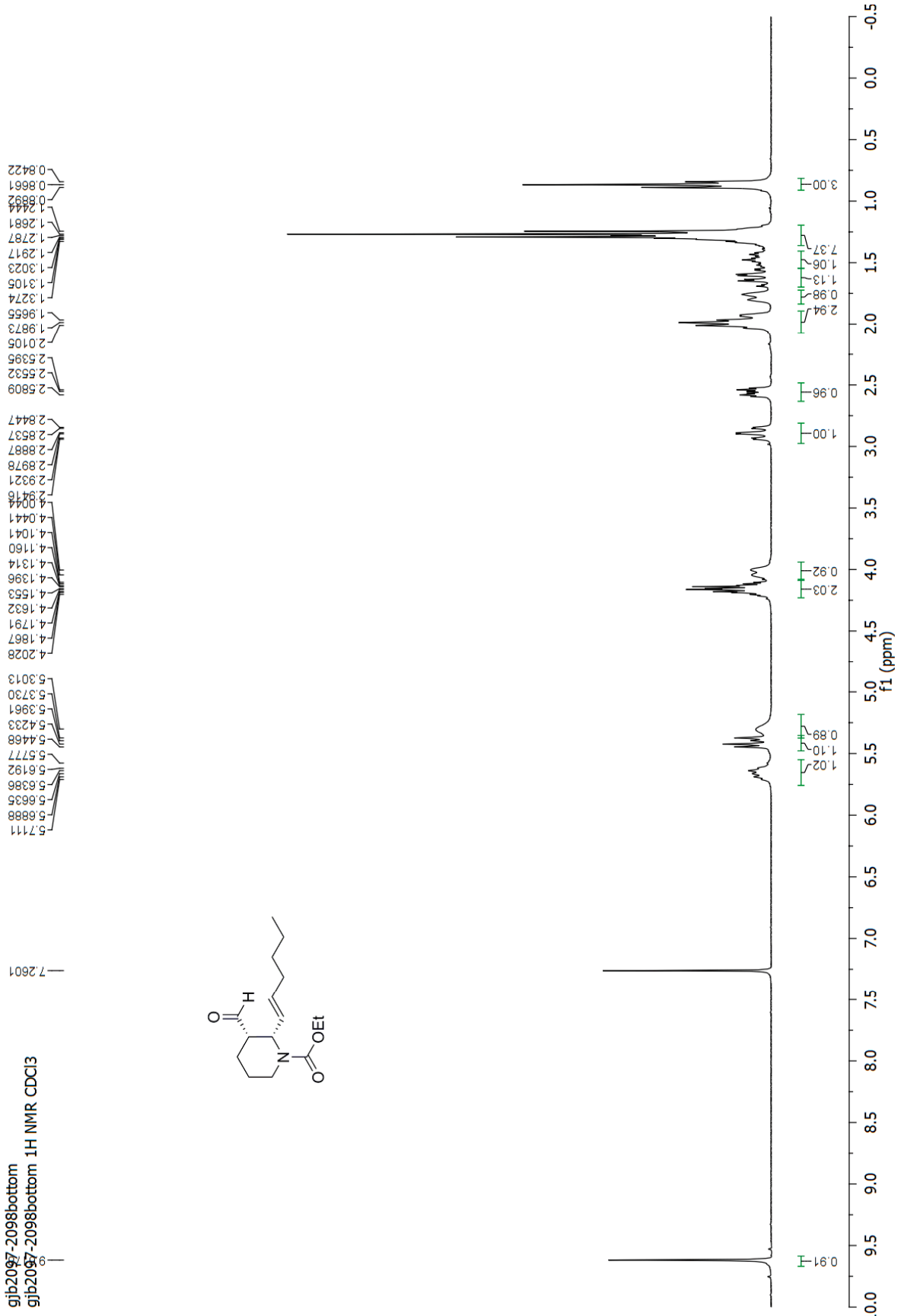


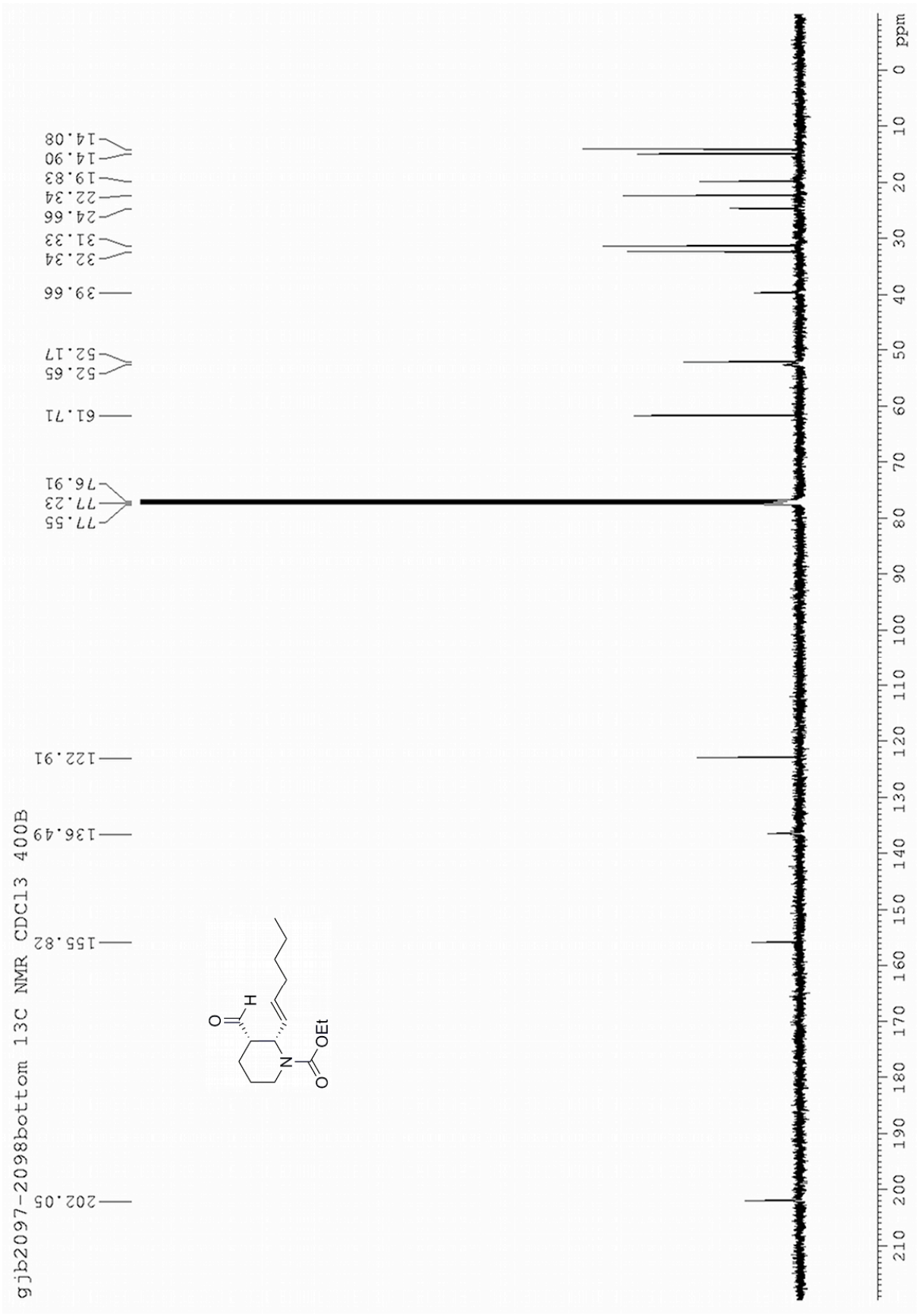


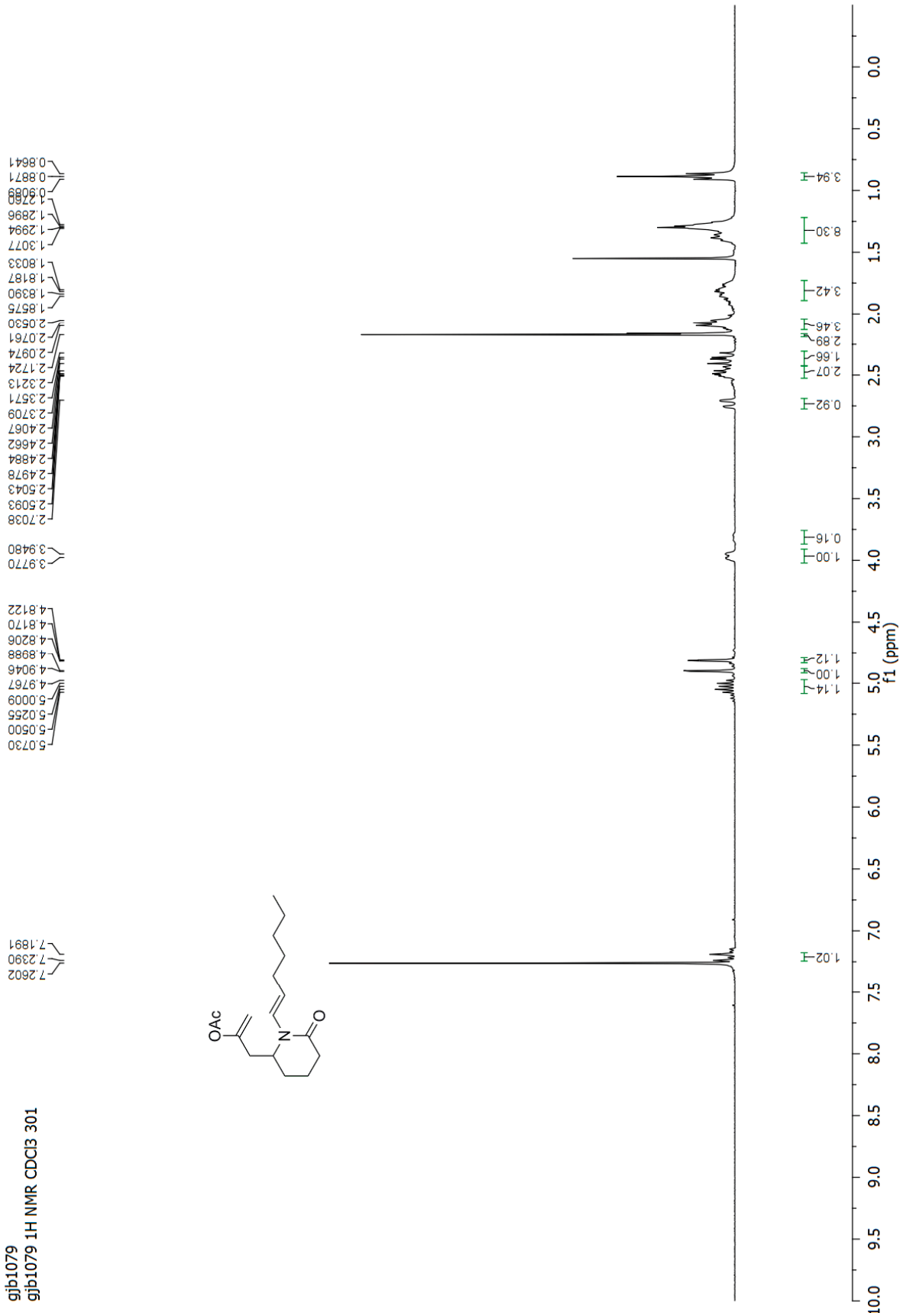


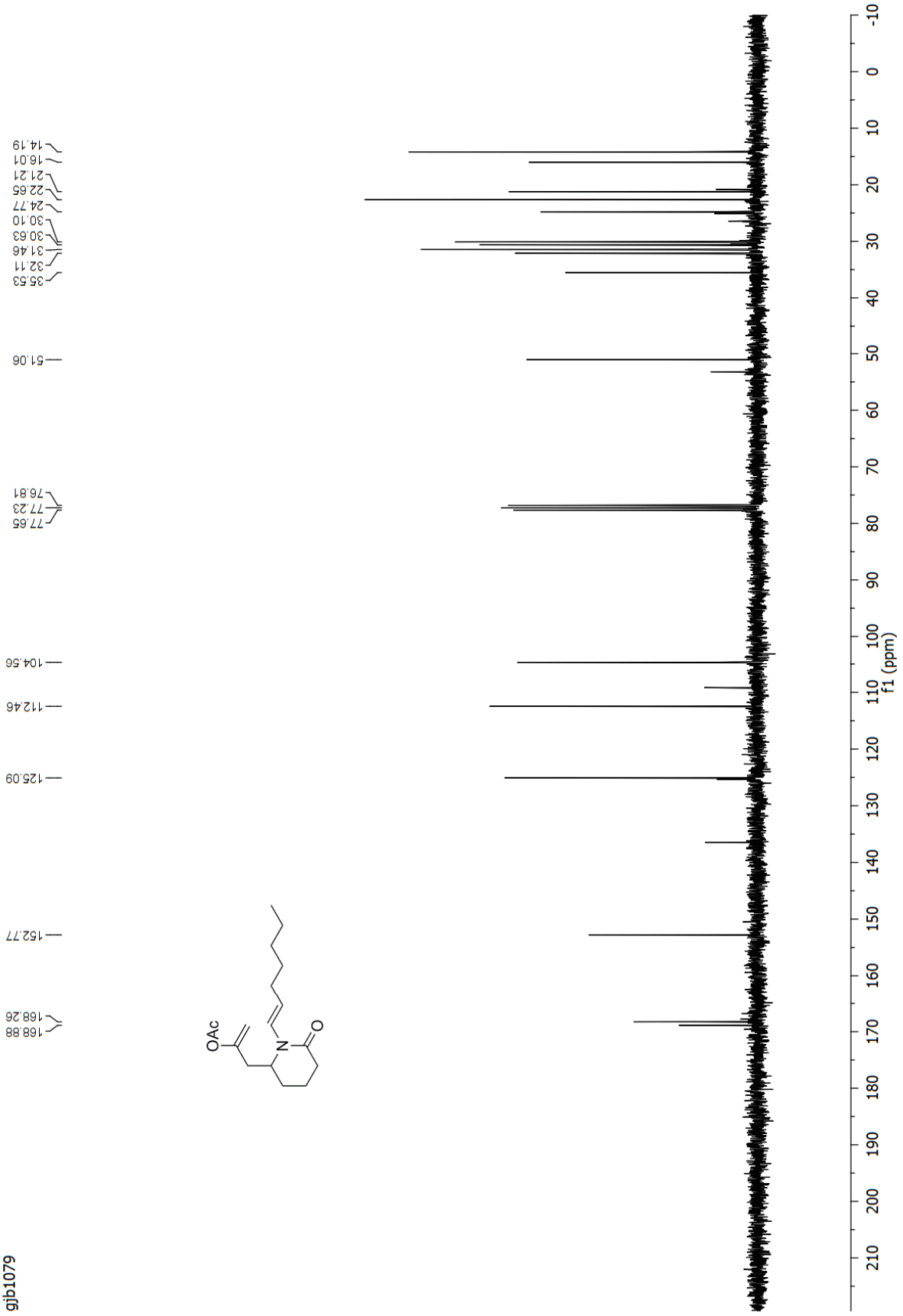


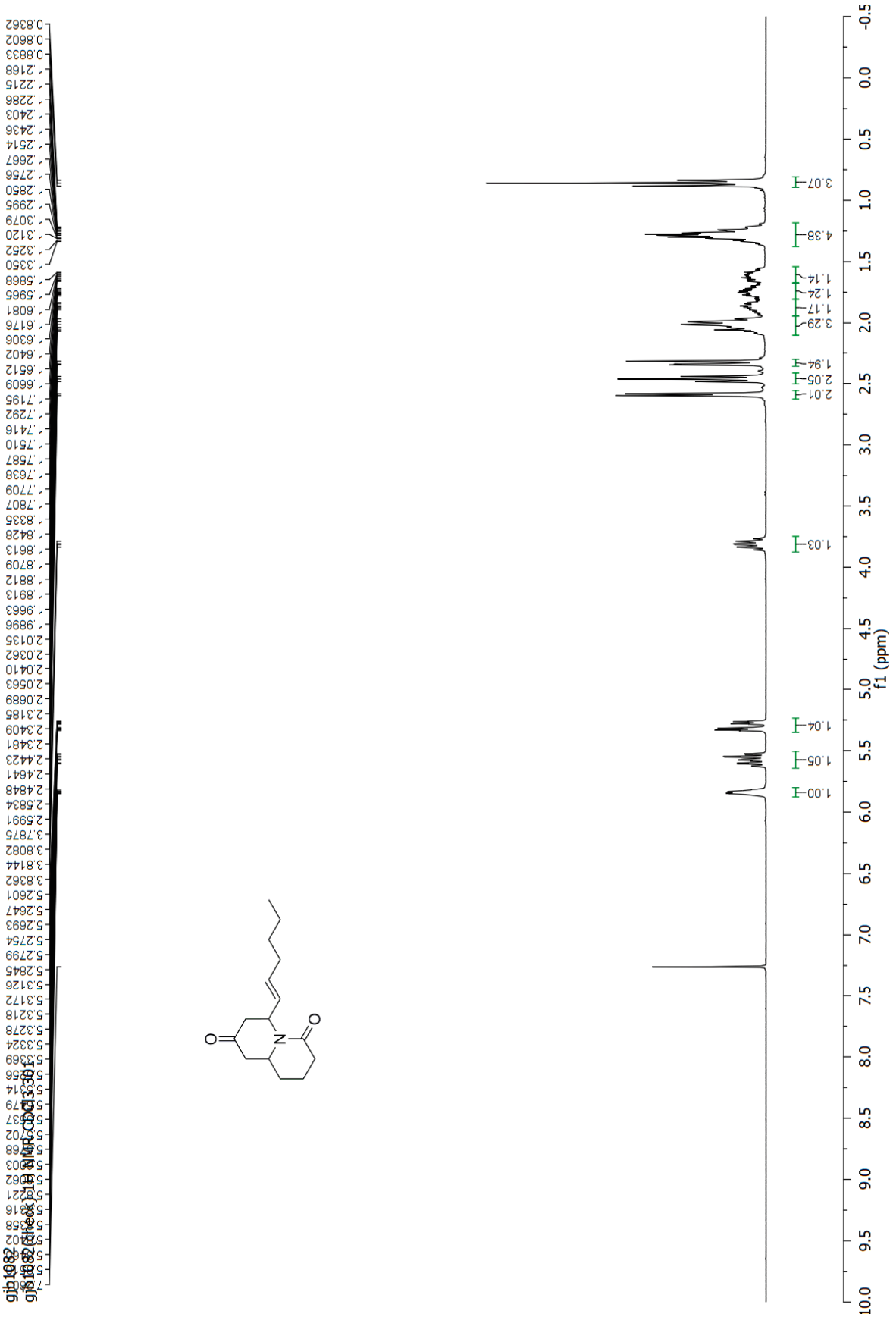


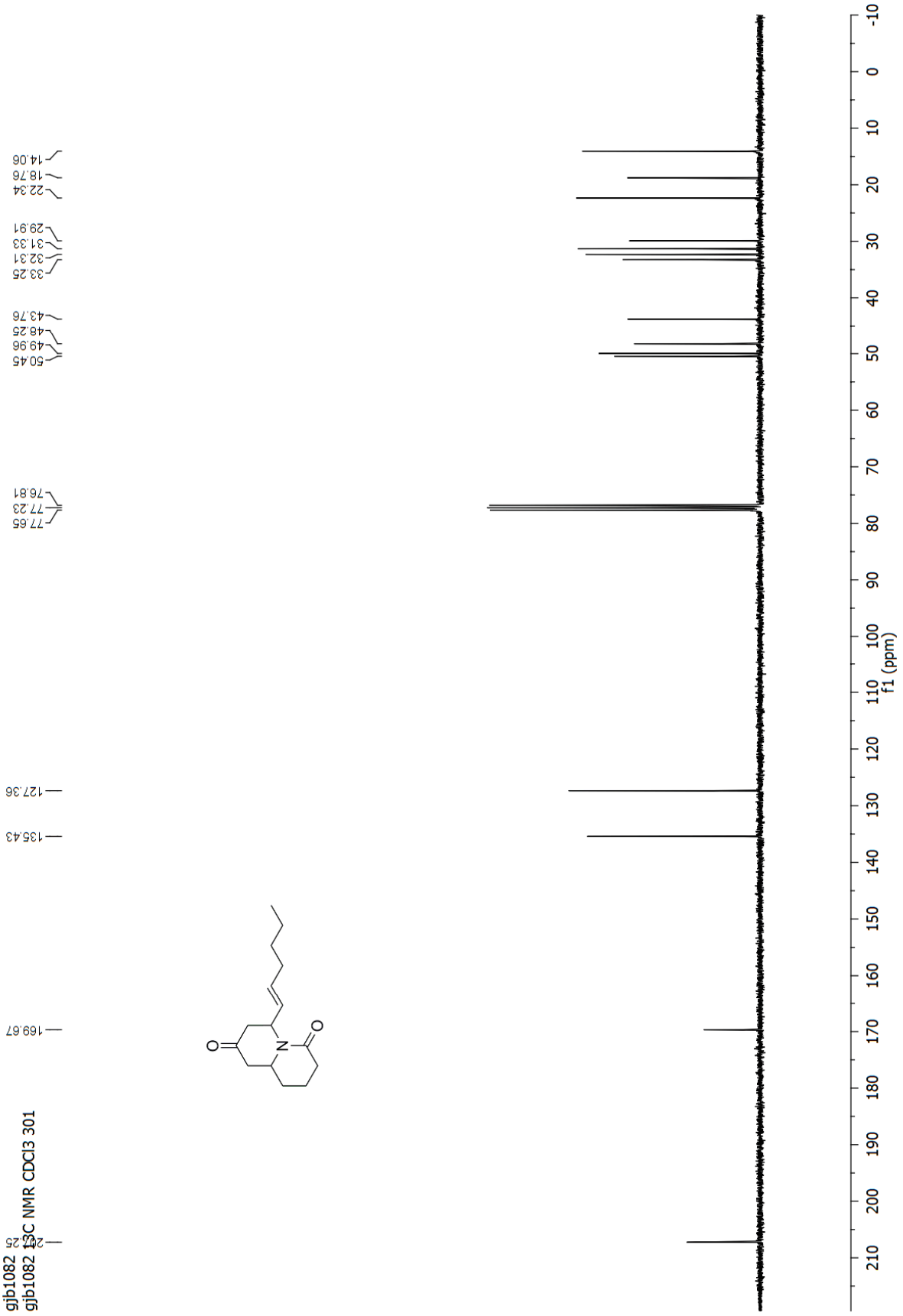


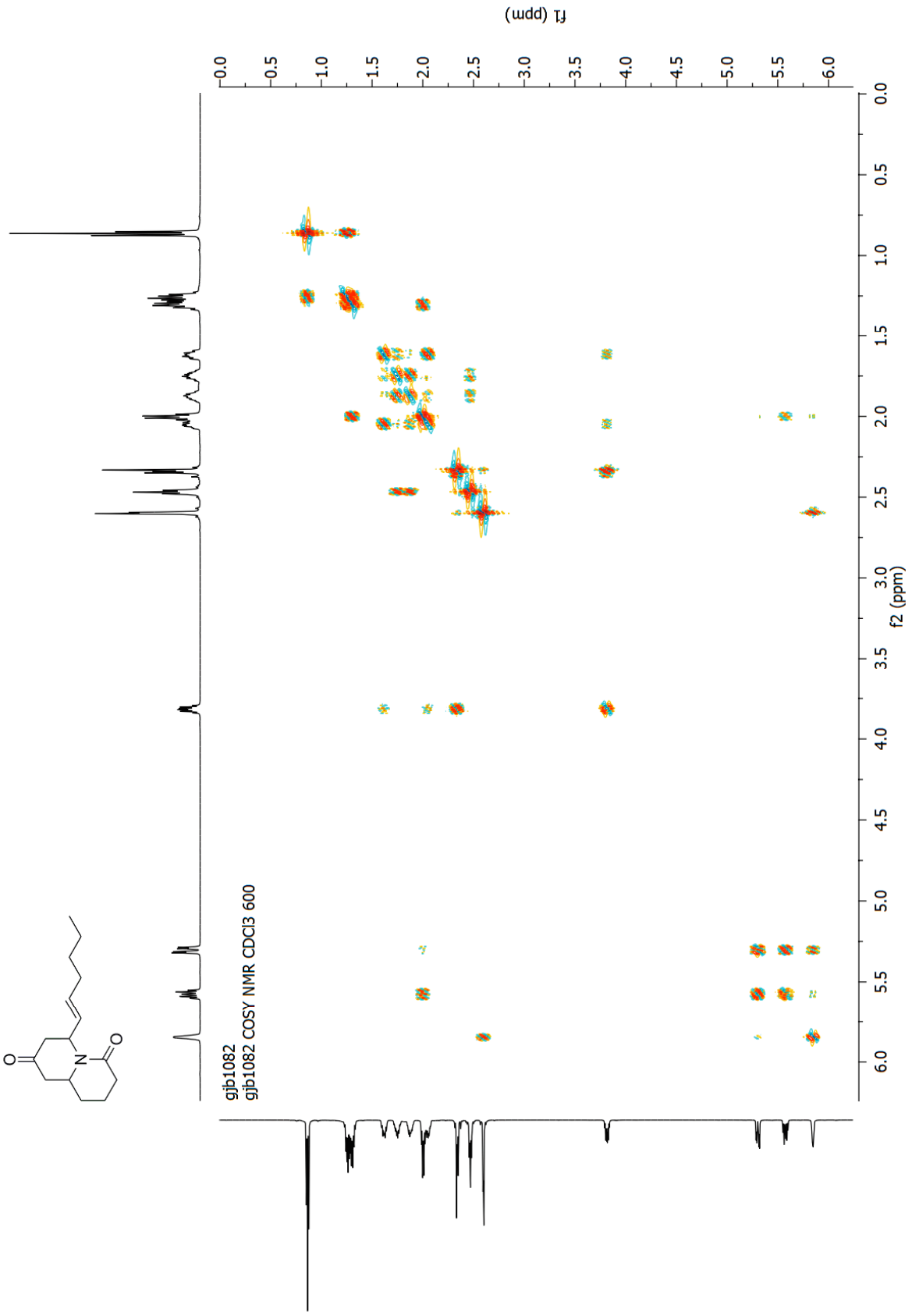








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f2 (ppm)
f1 (ppm)
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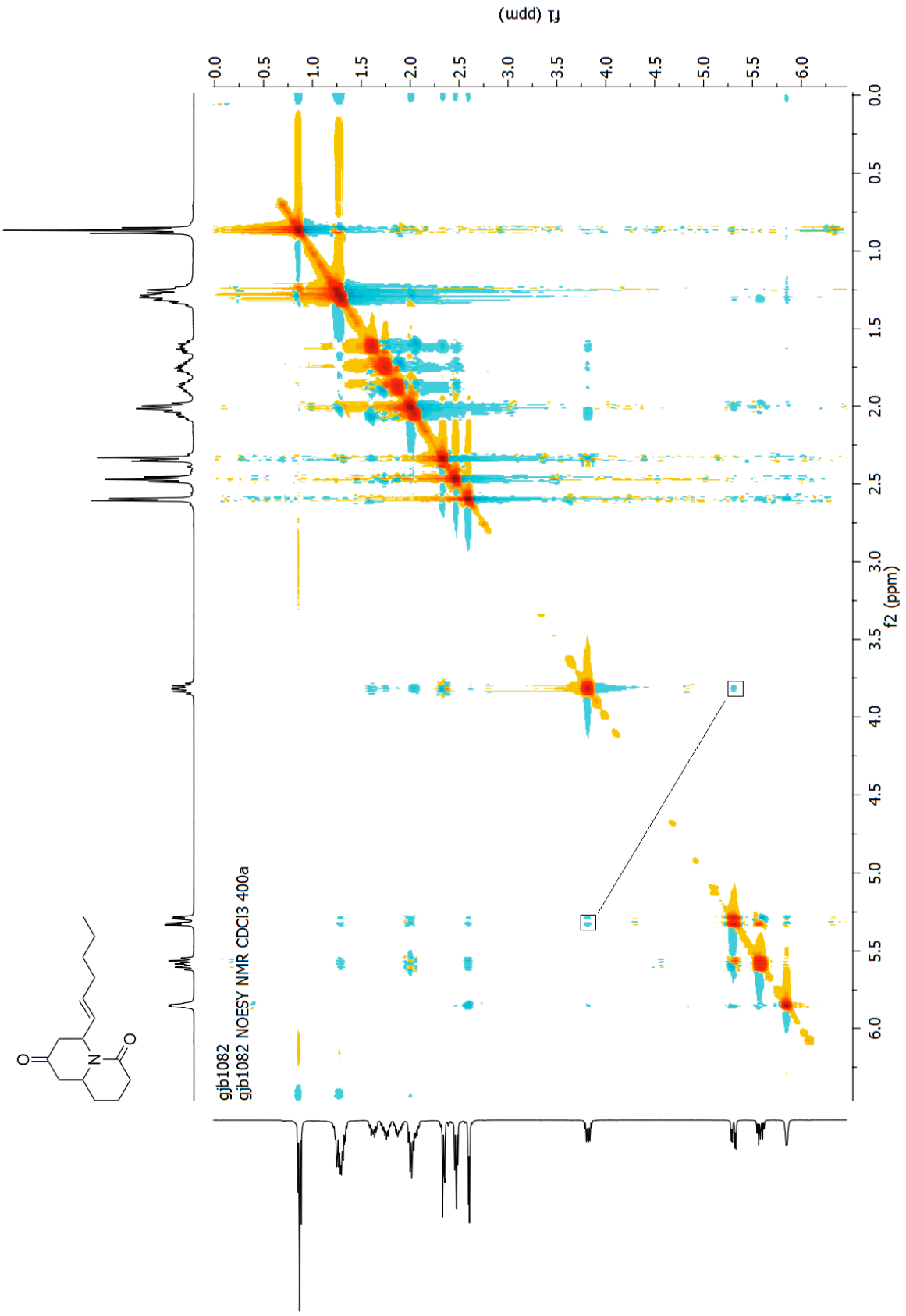
N
O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6.0
f2 (ppm)
gjb1082
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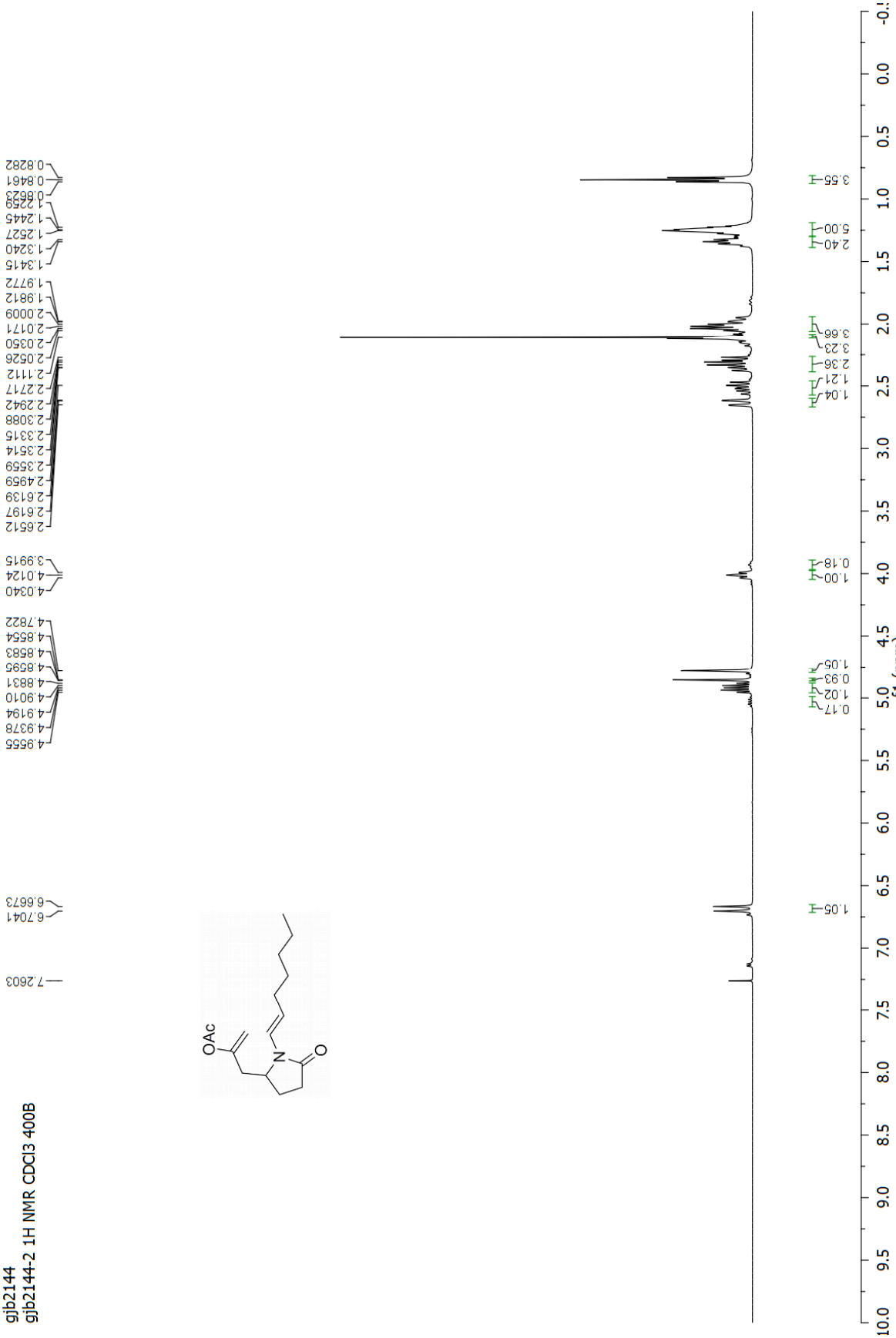
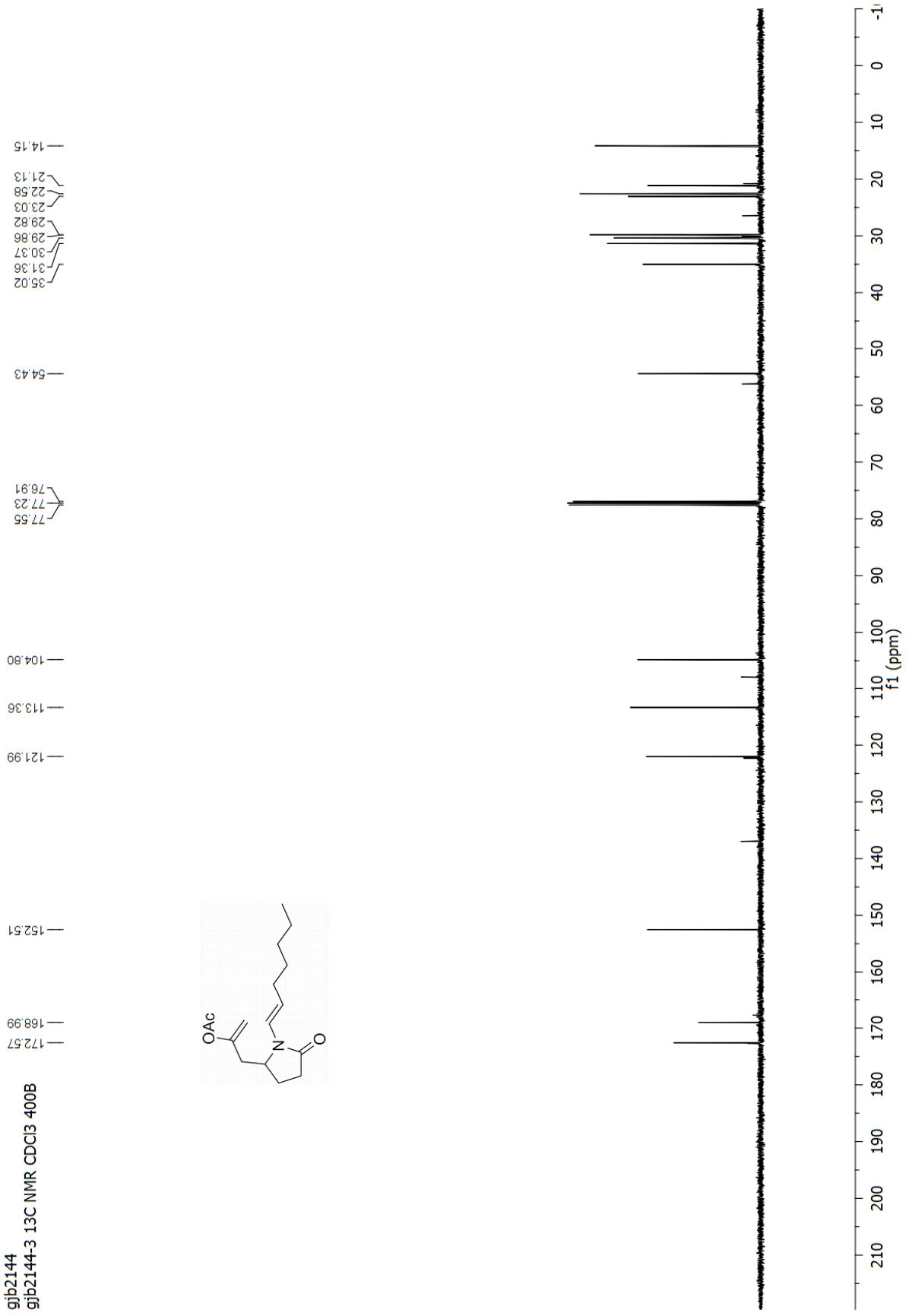
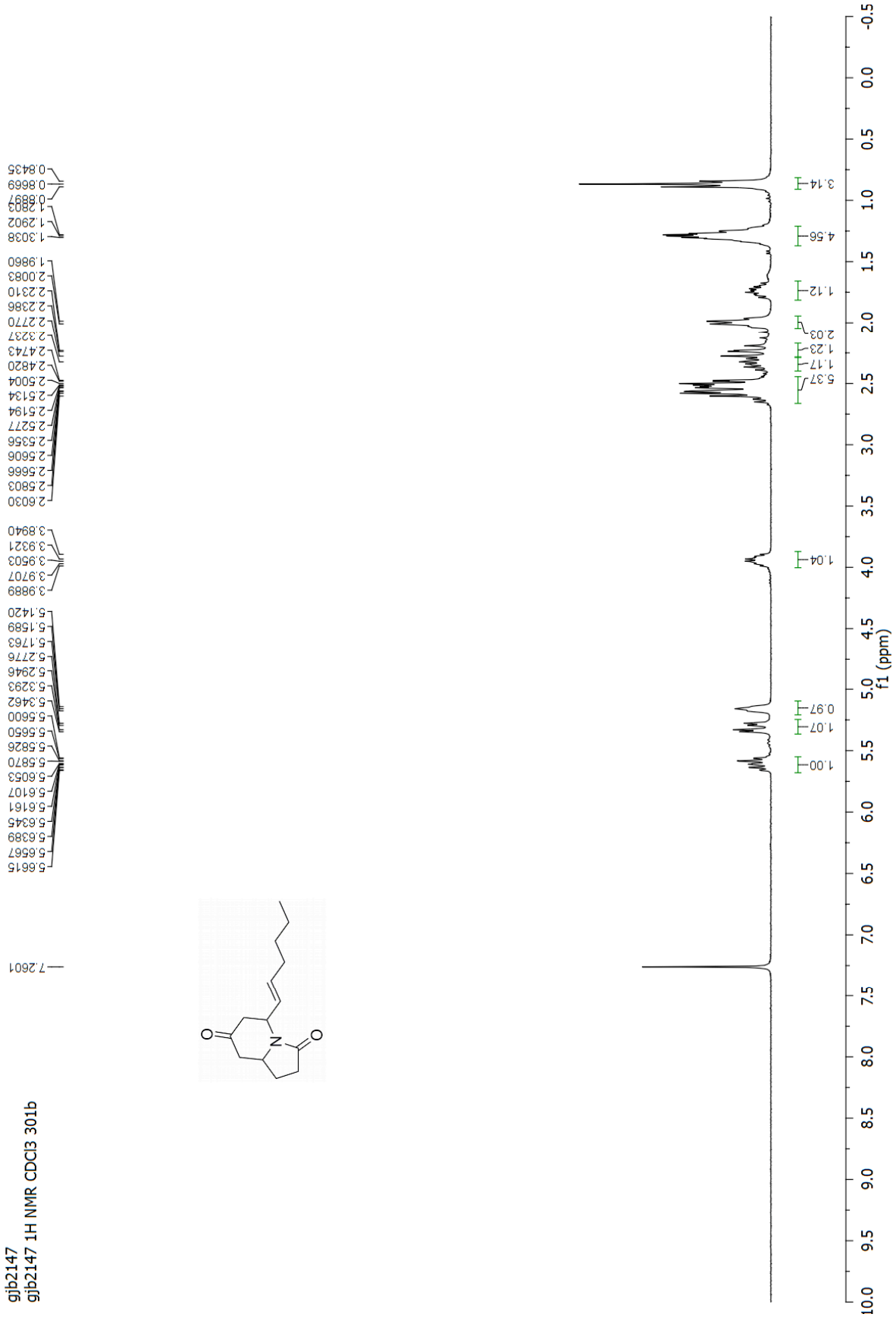
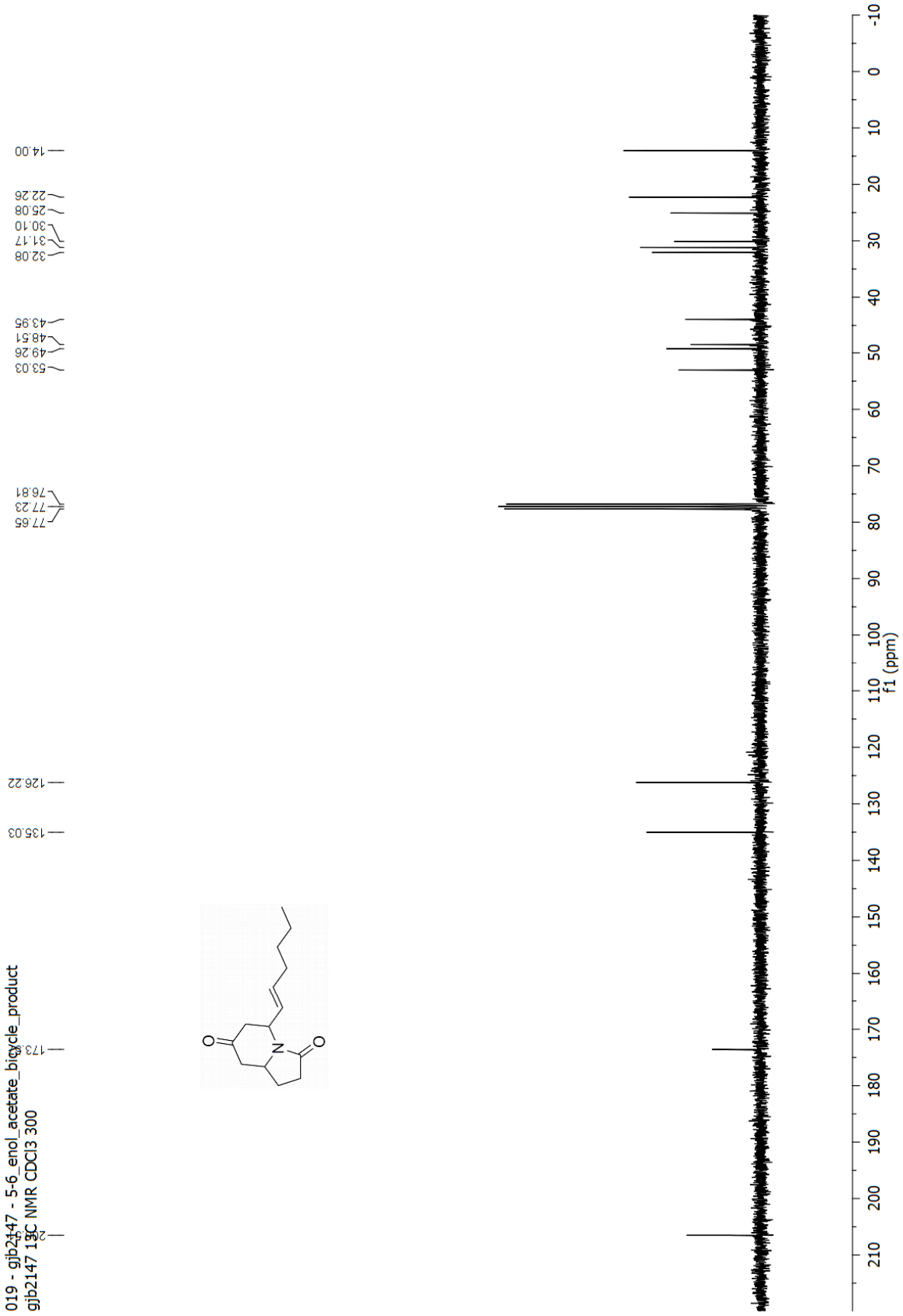
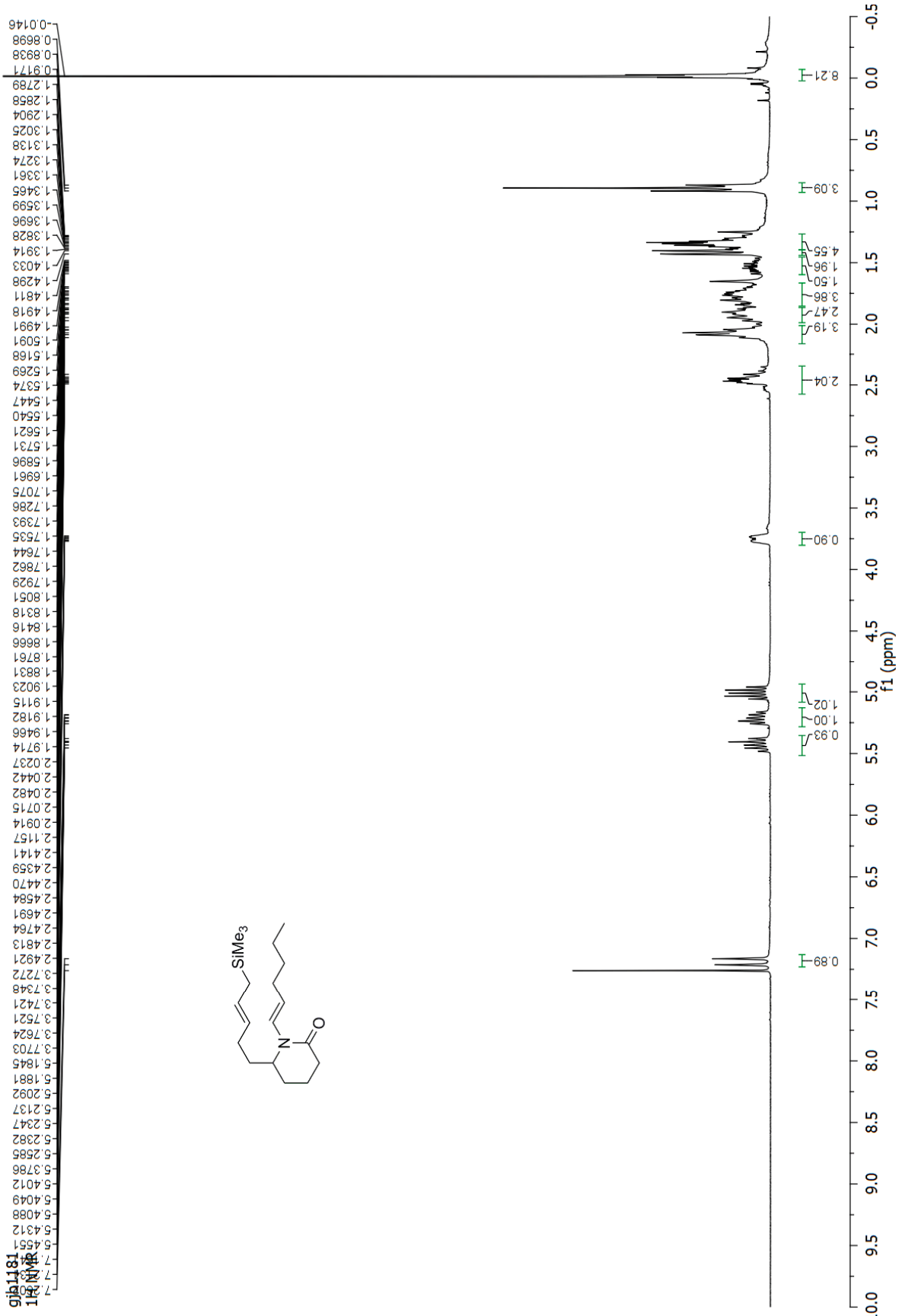
O
N
O

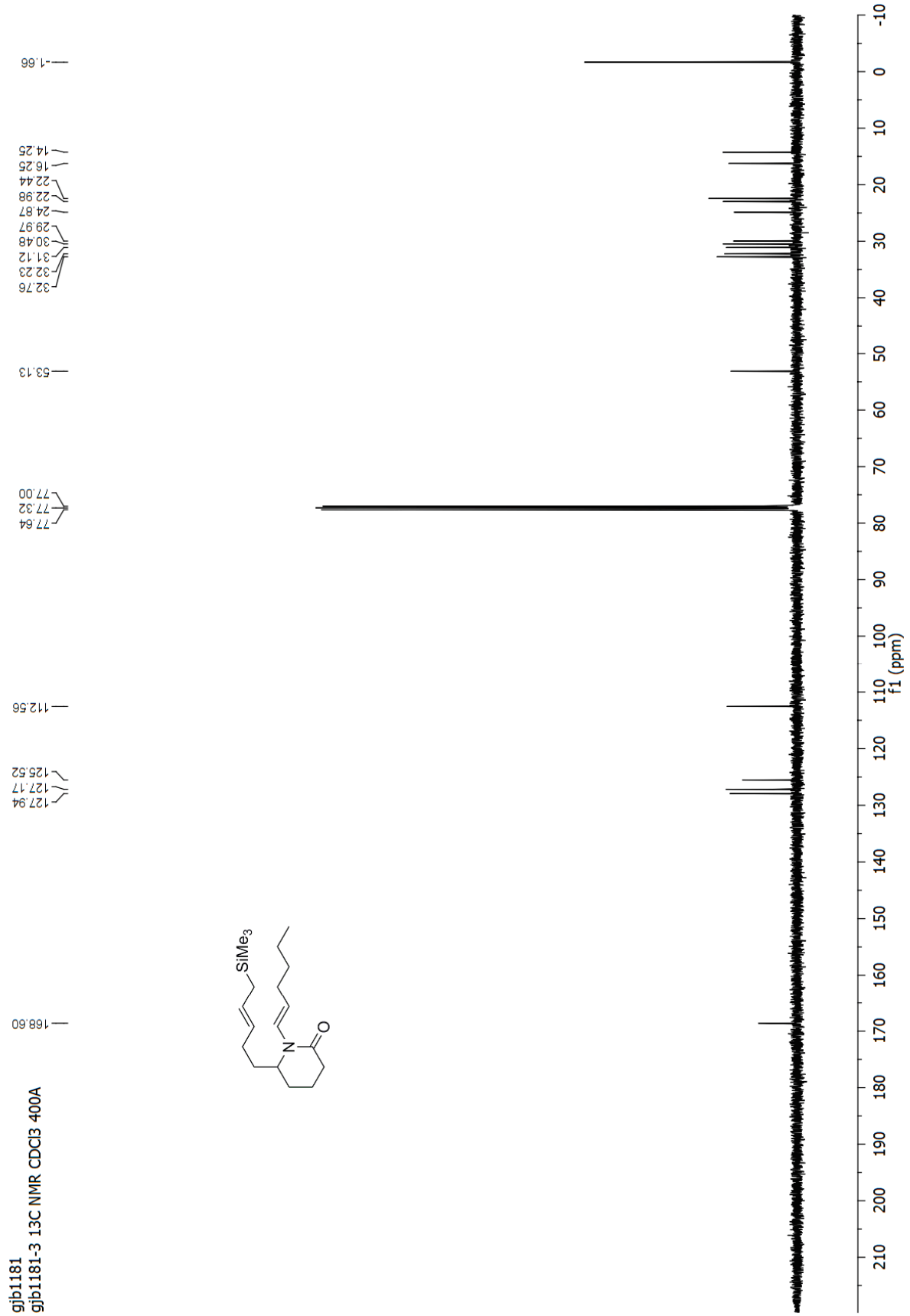


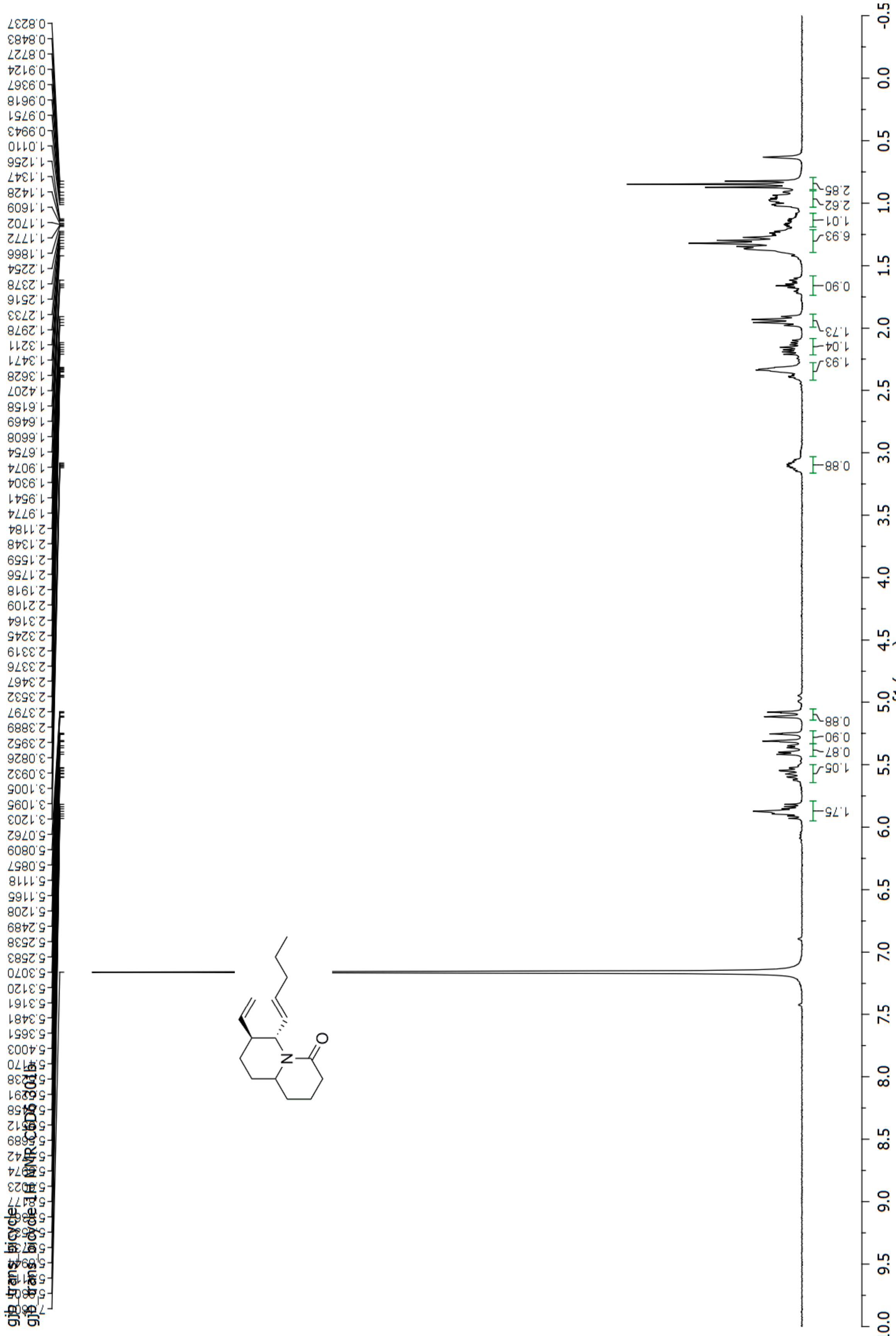


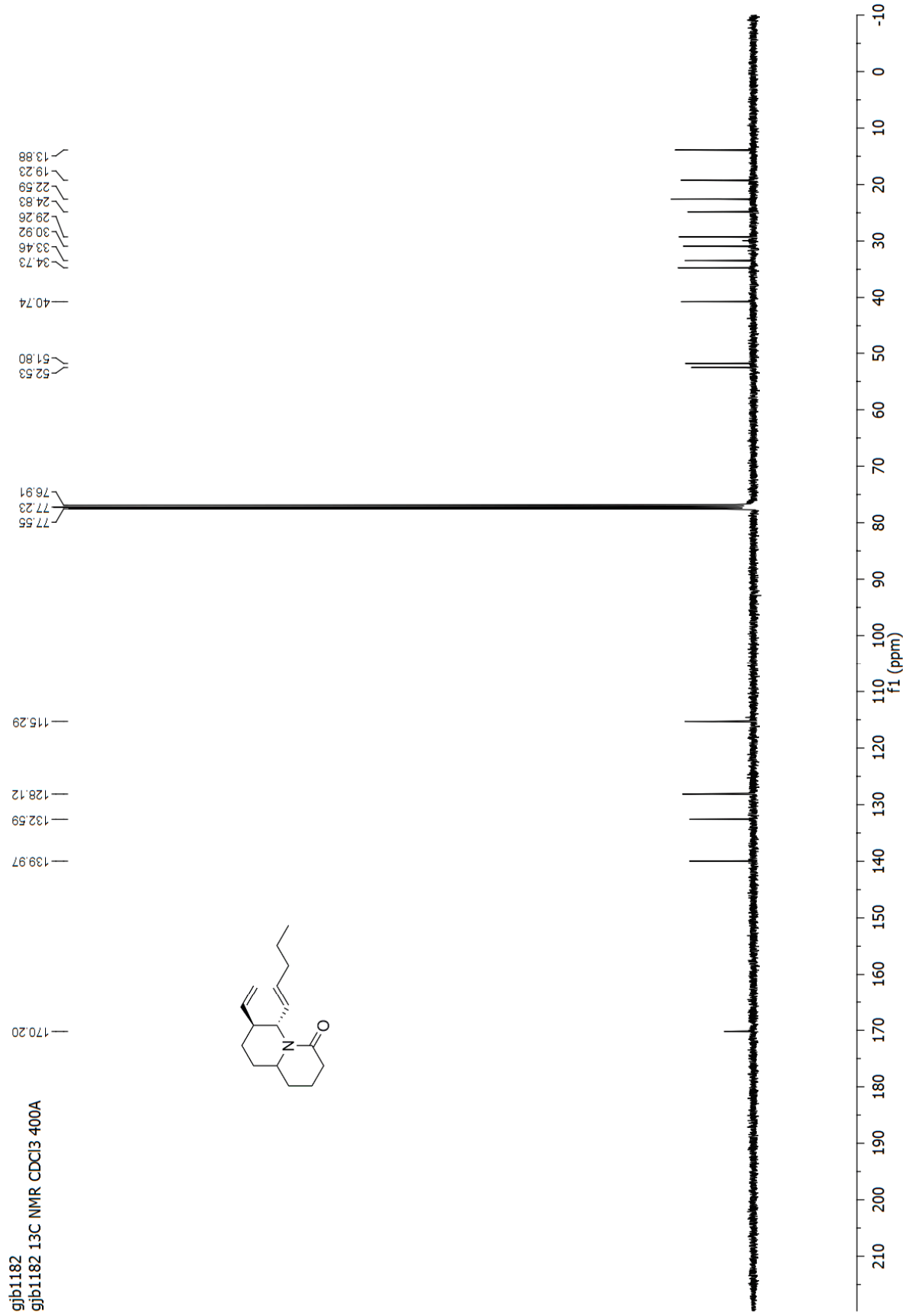


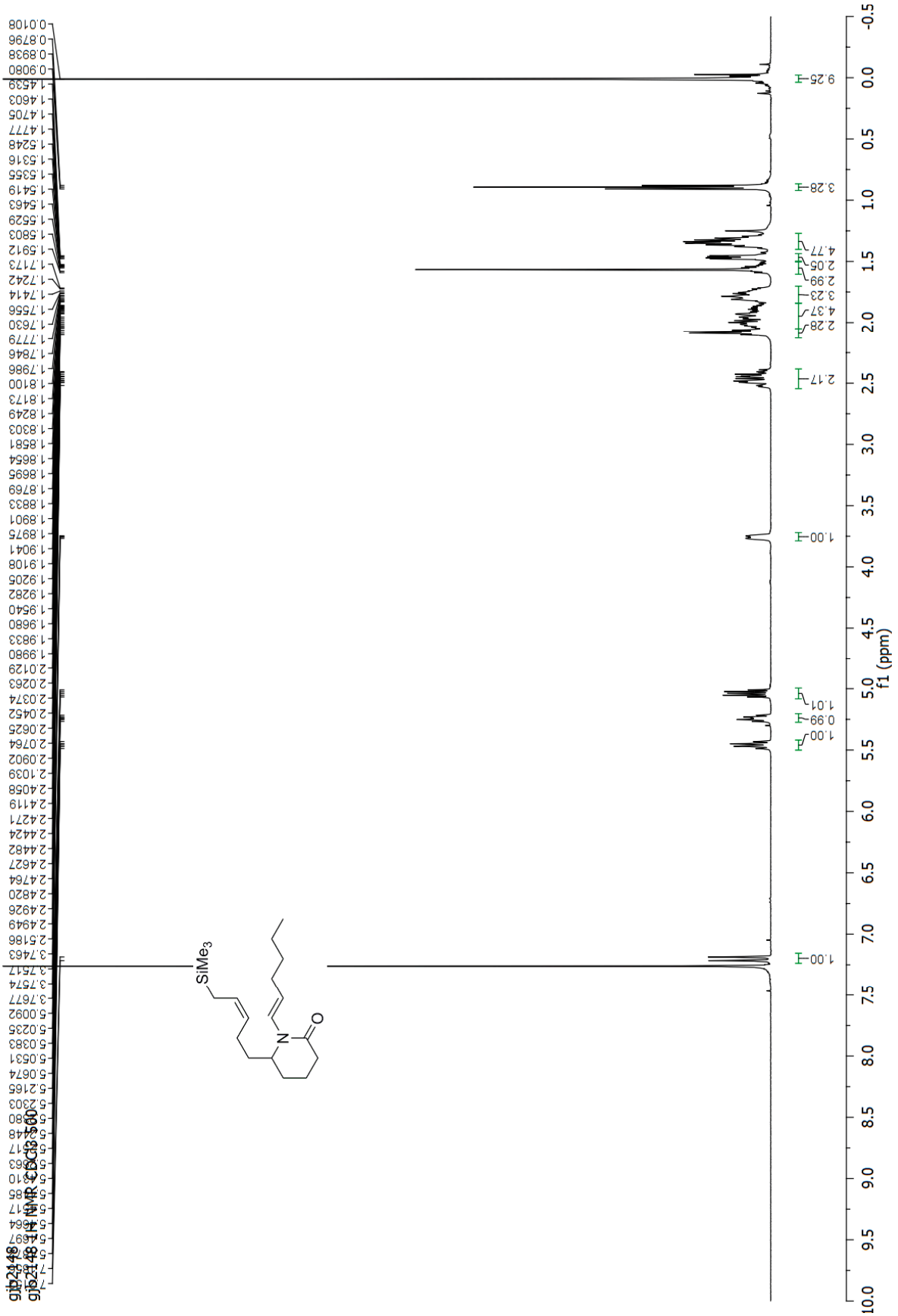


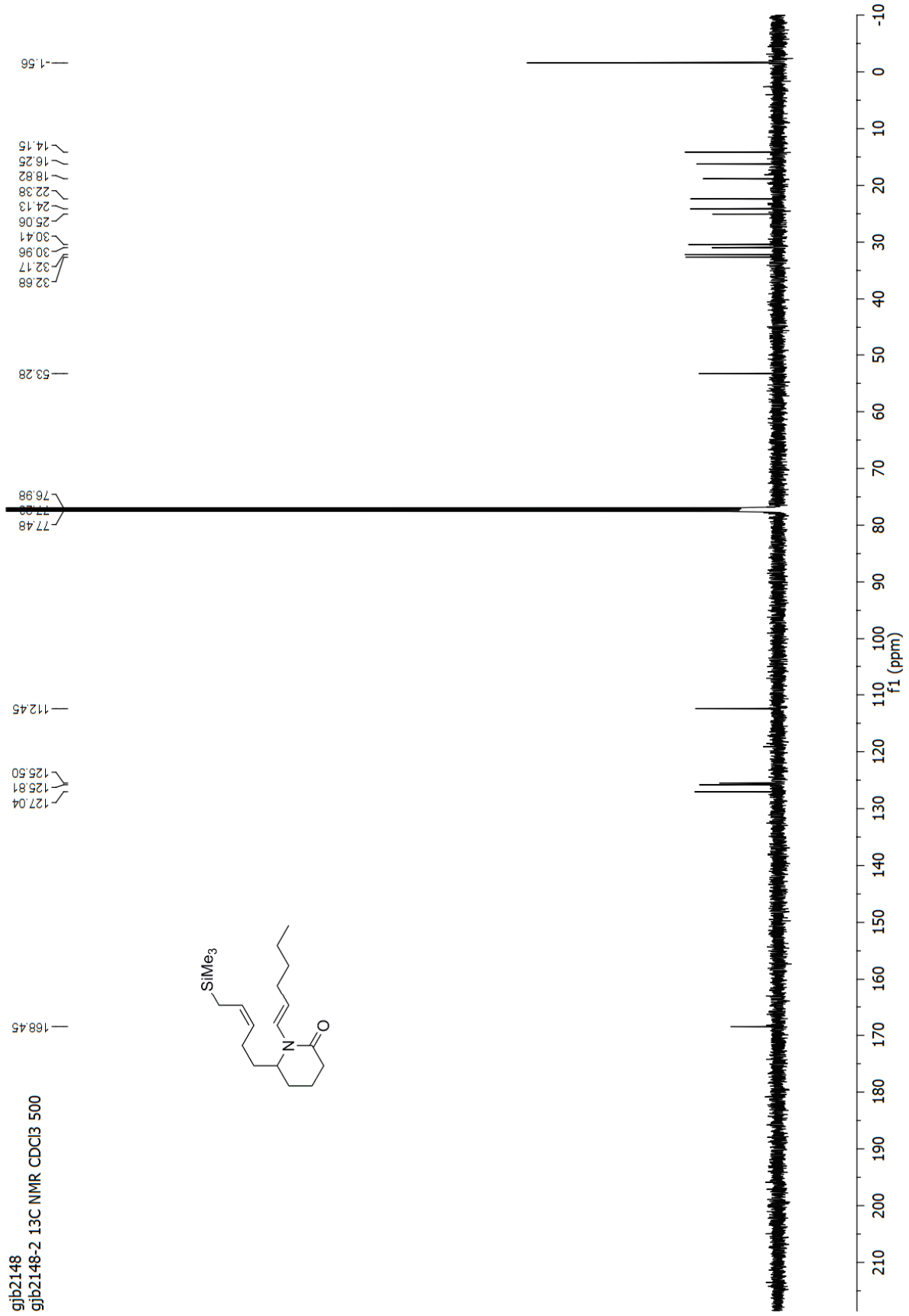


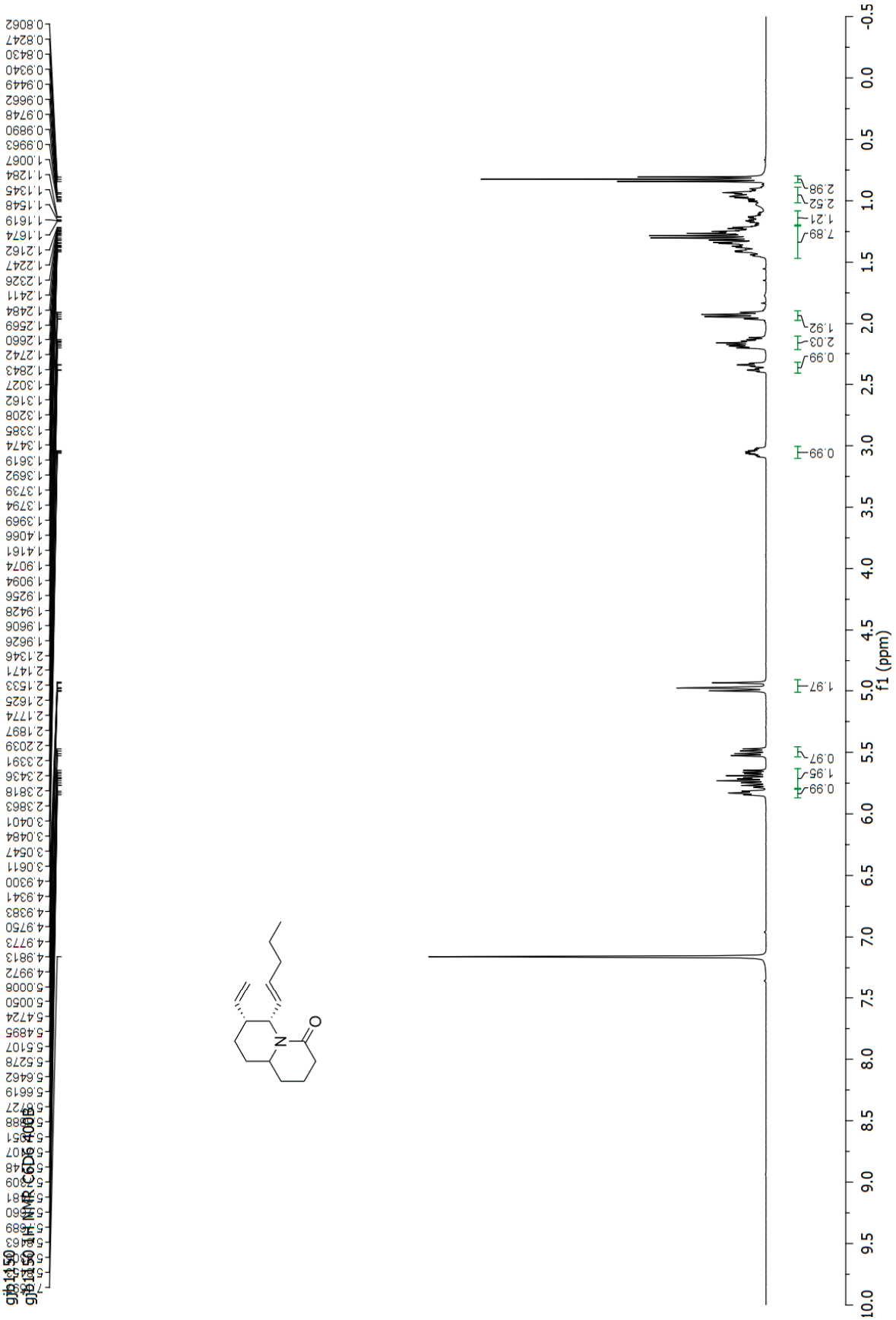


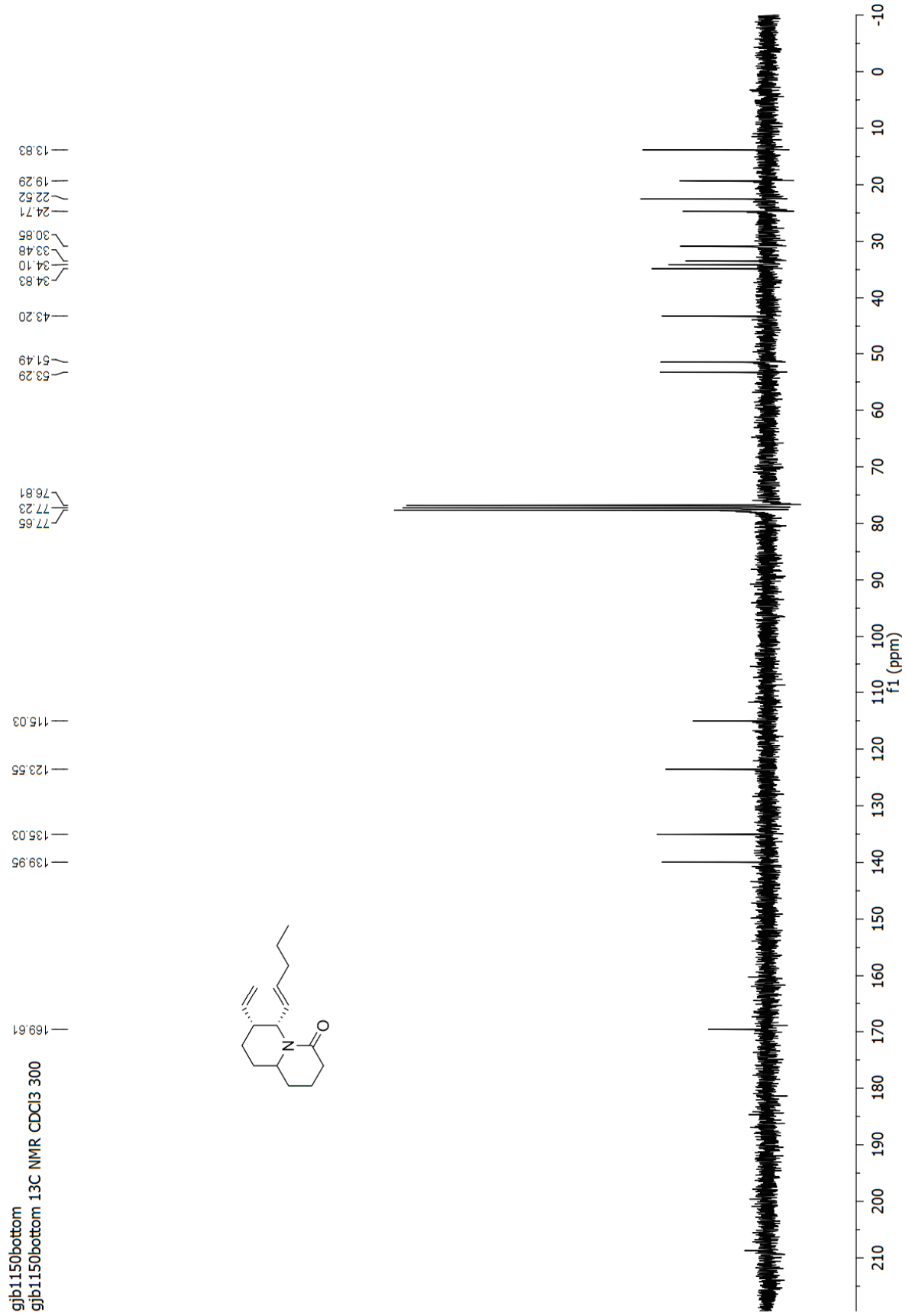

f1 (ppm)

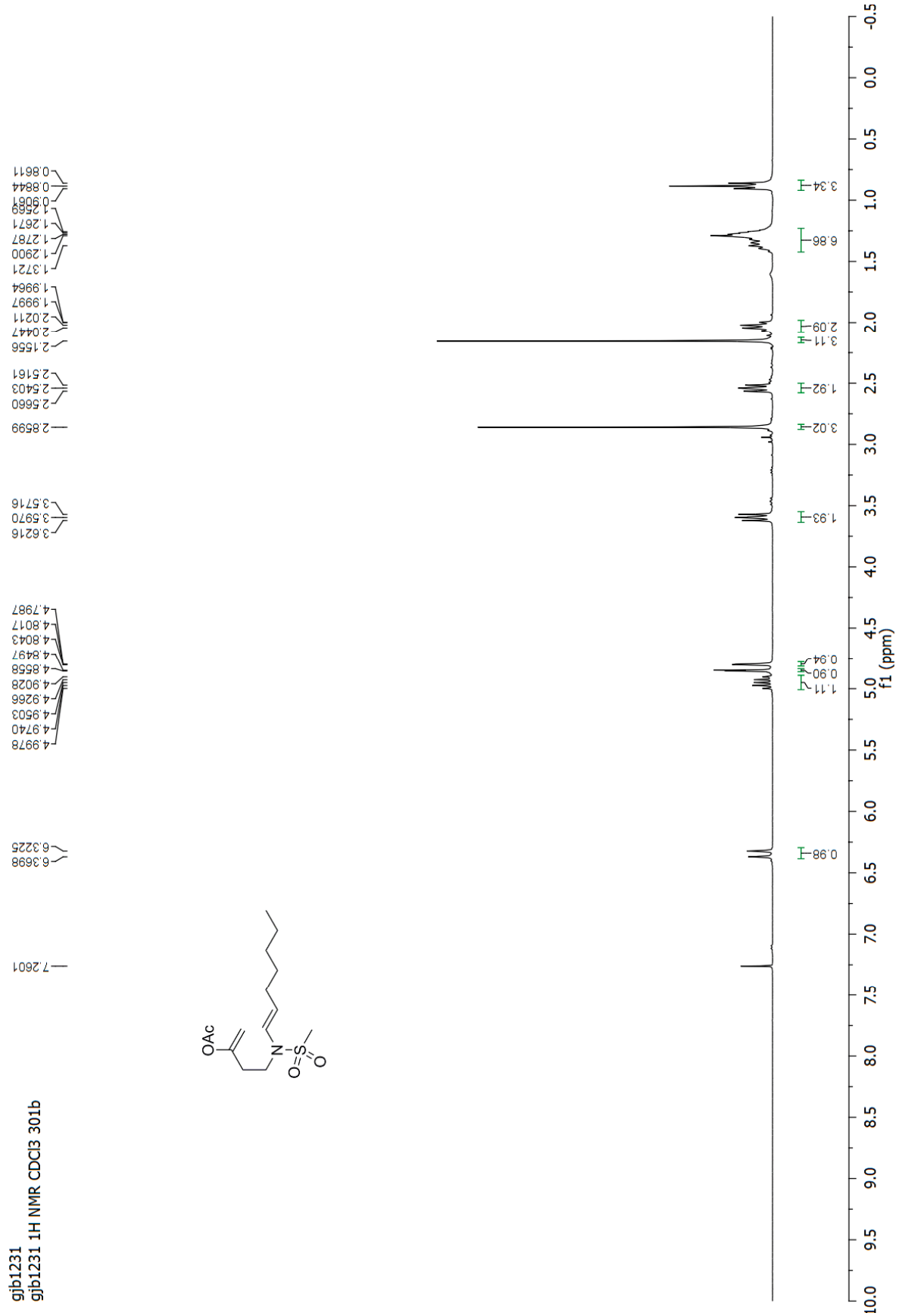


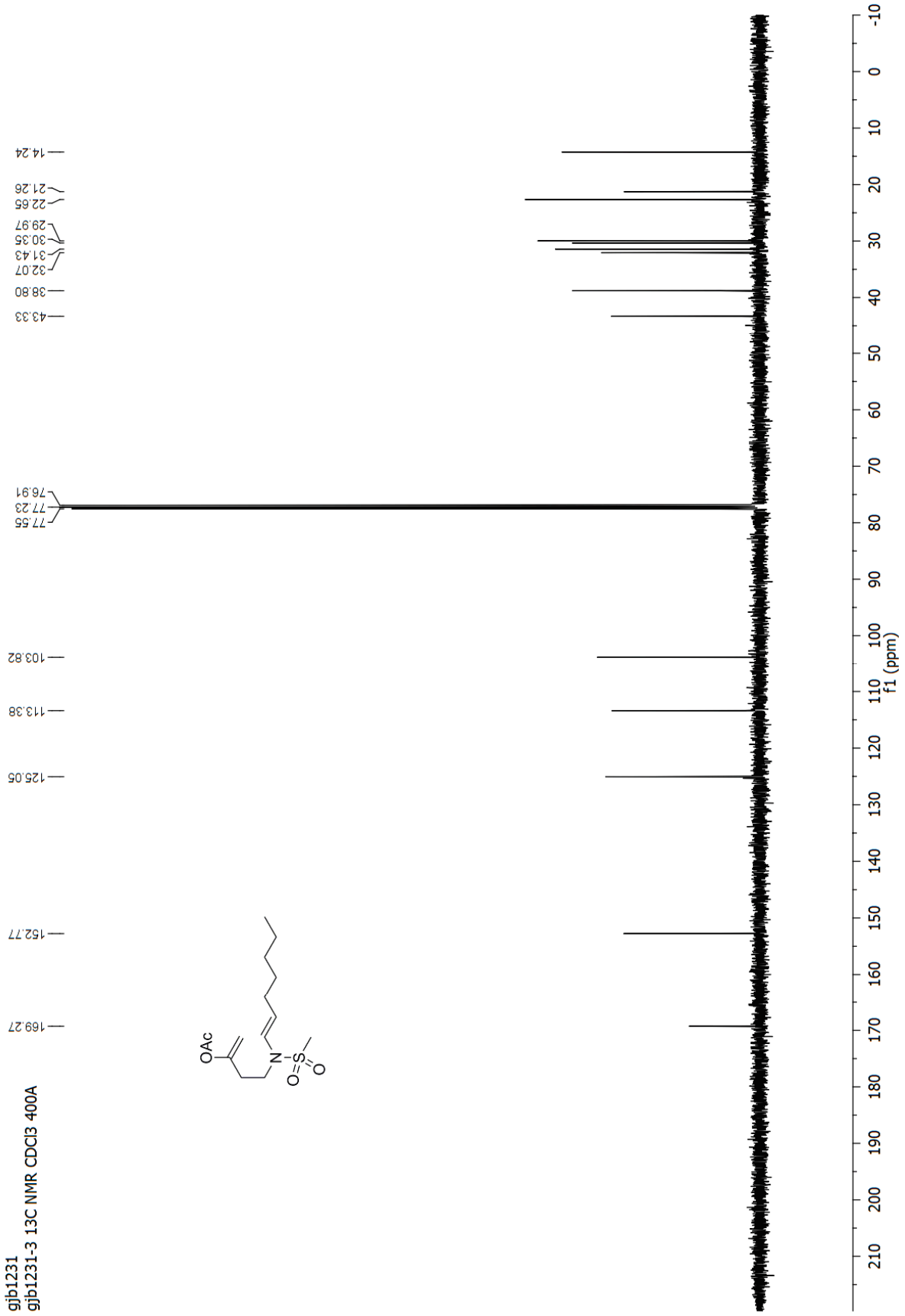


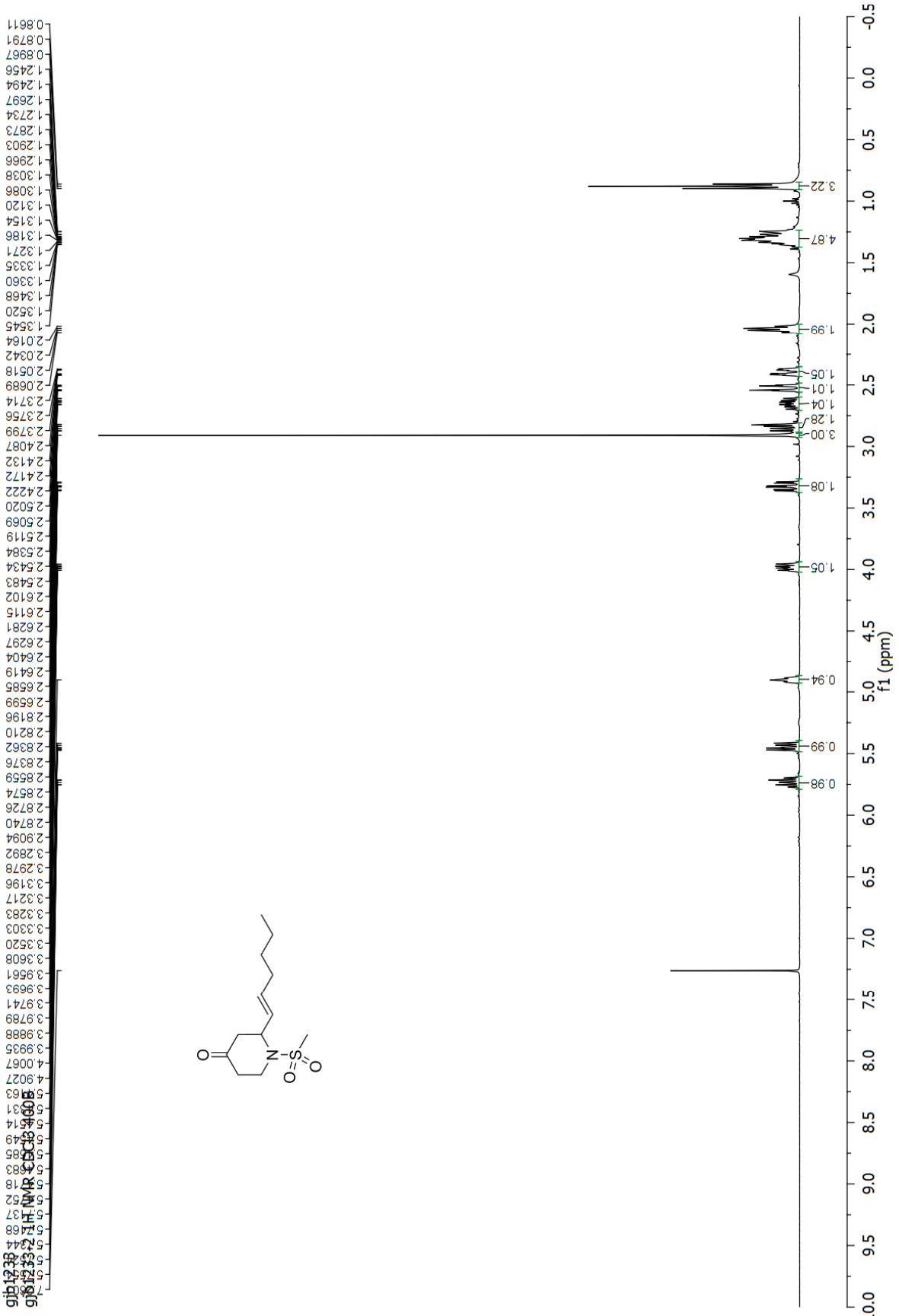


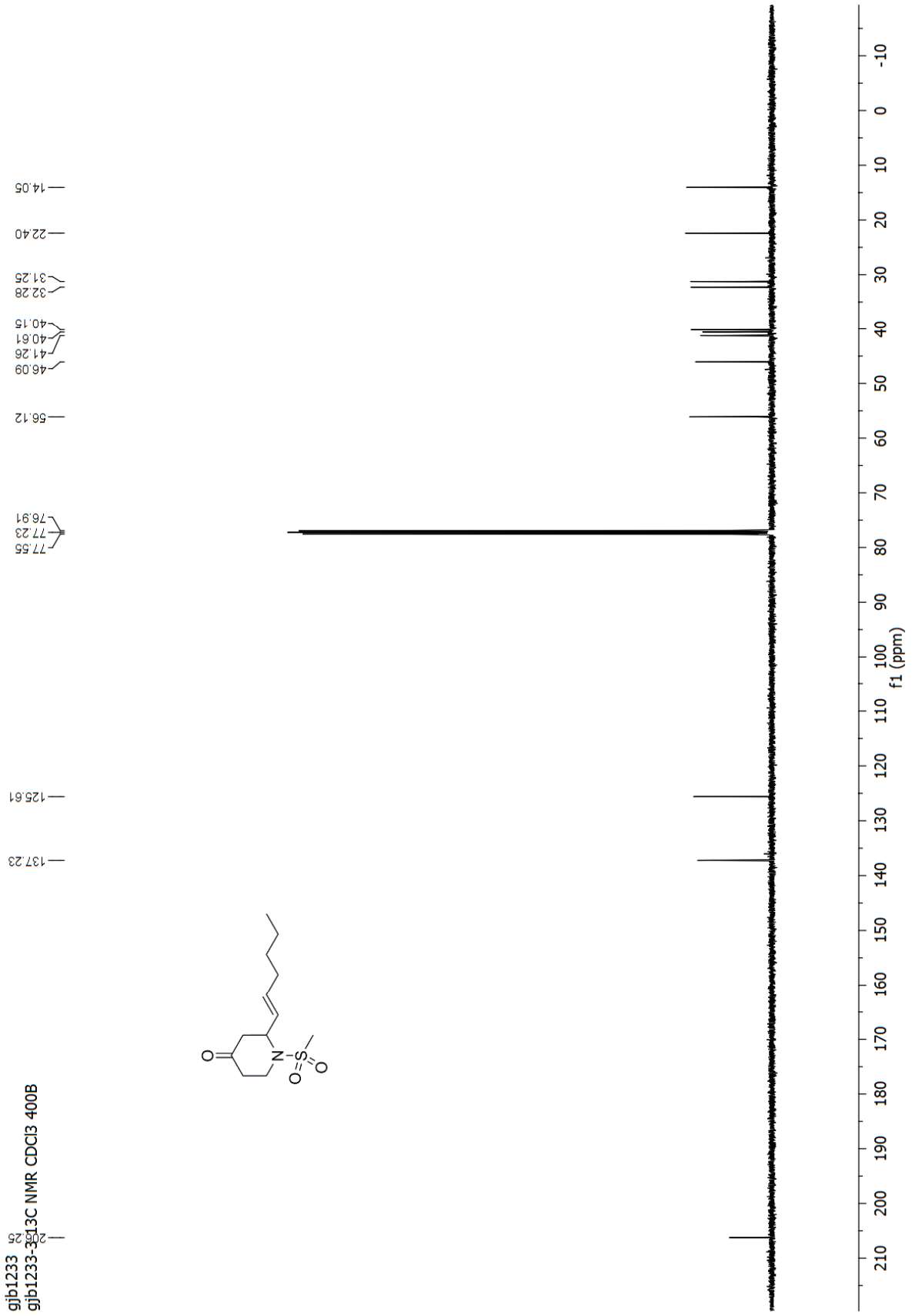


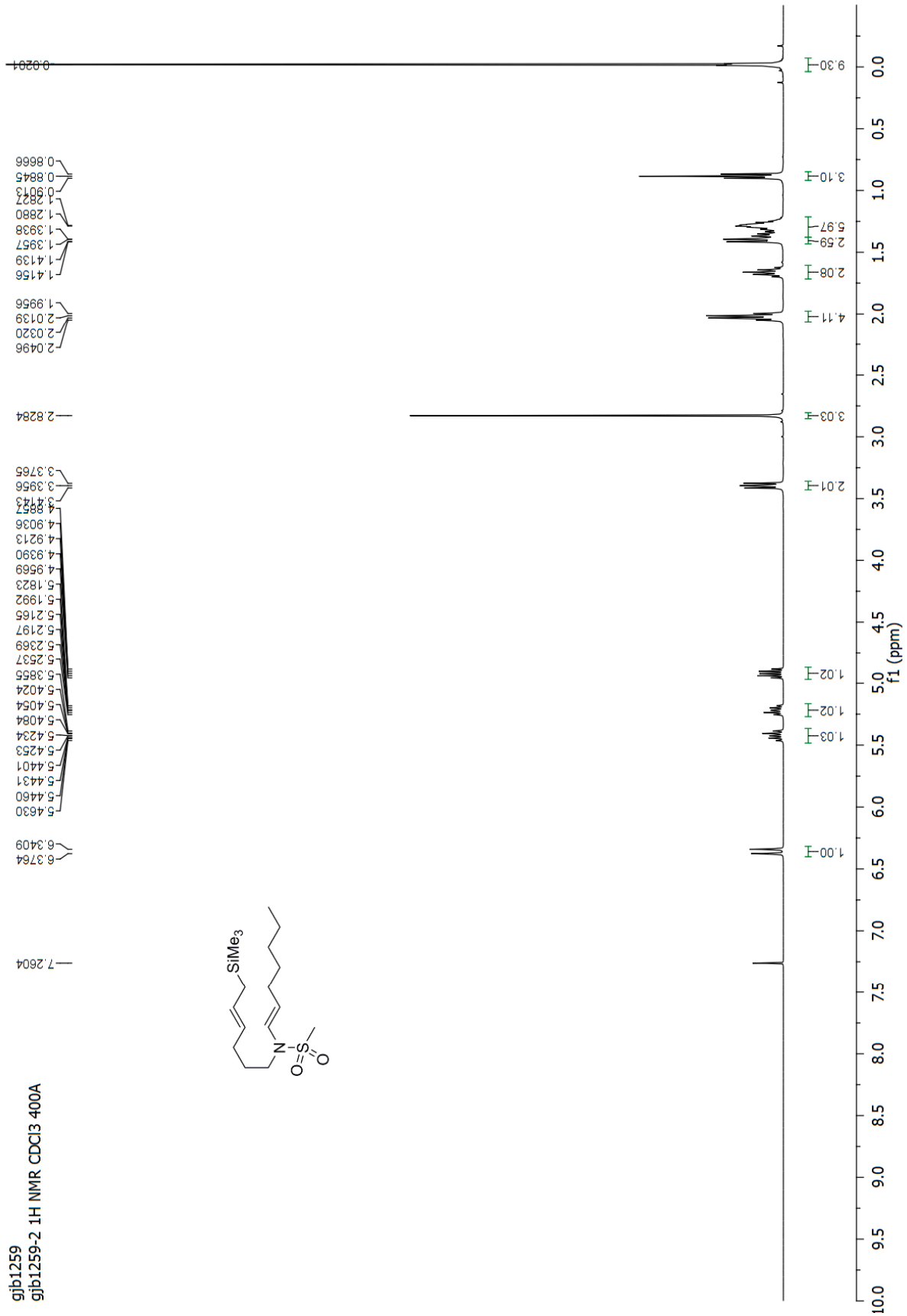


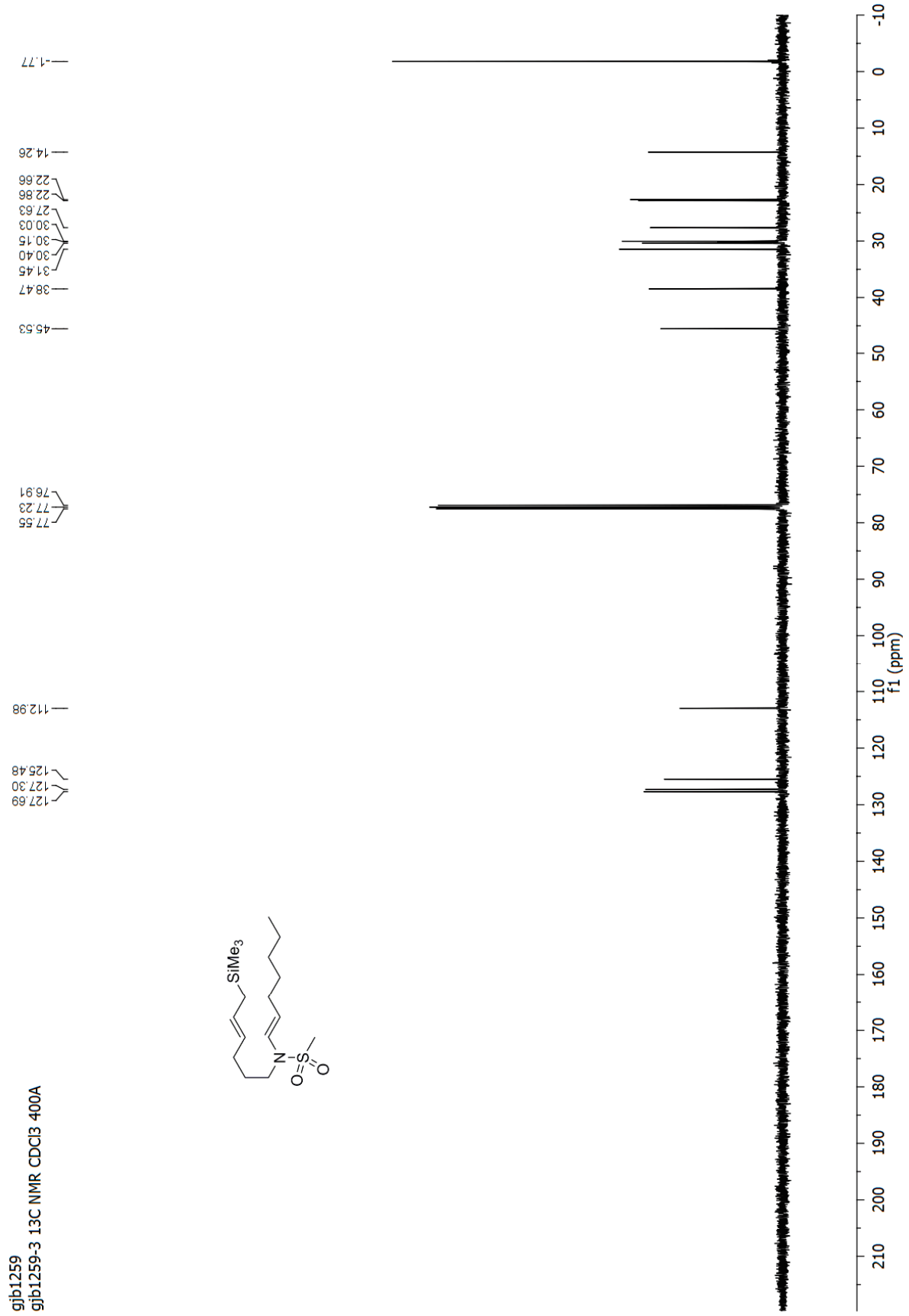

gjb1231
gjb1231 1H NMR CDCl3 301b
7.2601
6.3698
6.3225
4.9978
4.9740
4.9503
4.9266
4.9028
4.8558
4.8497
4.8043
4.8017
4.7987
3.6216
3.5970
3.5716
2.8599
2.5660
2.5403
2.5161
2.1556
2.0447
2.0211
1.9997
1.9964
1.3721
1.2900
1.2787
1.2671
1.2569
0.9067
0.8844
0.8611
OAc
N
S
O
O
0.98
1.11
0.90
0.94
1.93
3.02
1.92
2.09
3.11
6.86
3.34
f1 (ppm)

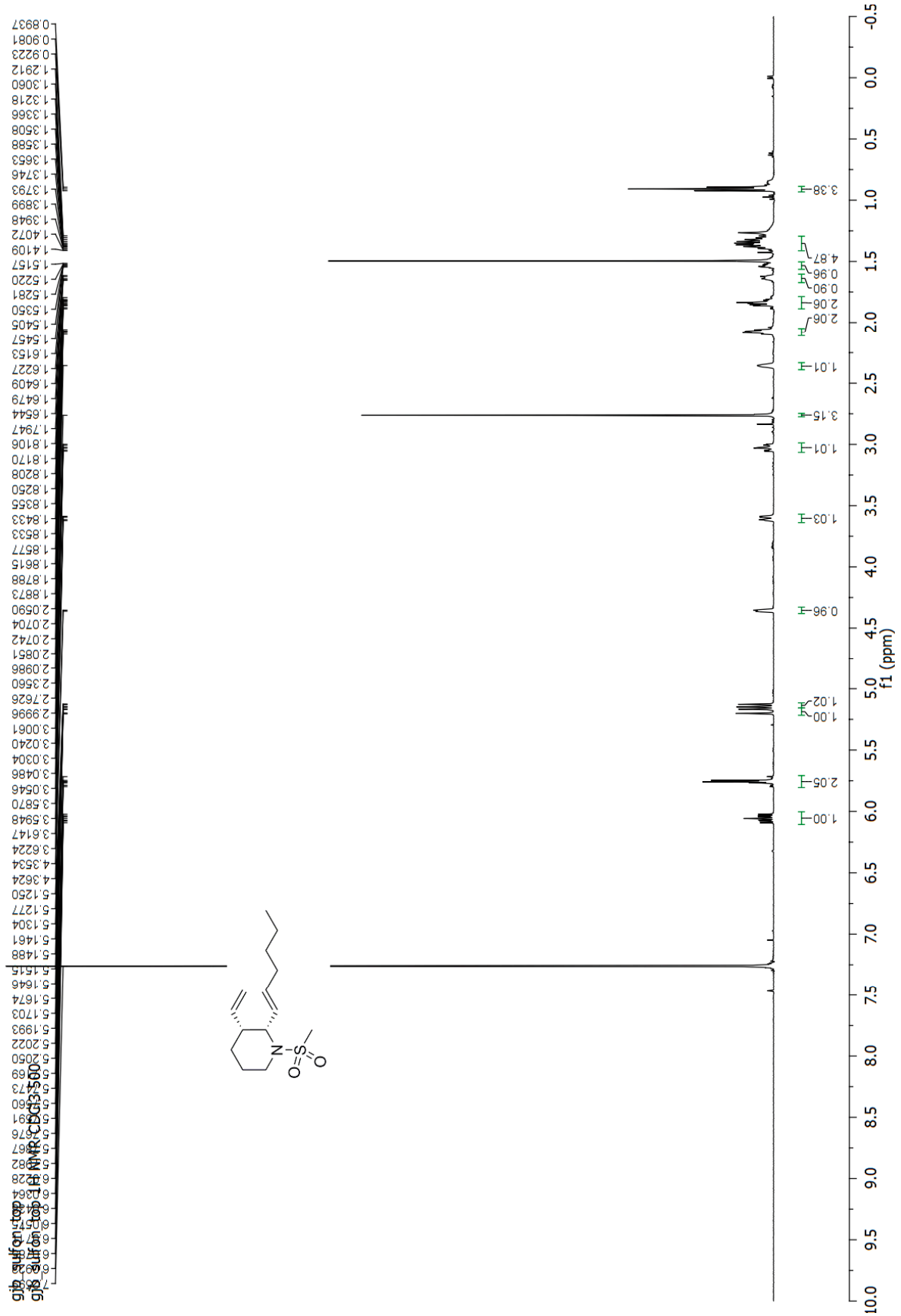

gjb1231
gjb1231-3 13C NMR CDCl3 400A
169.27
152.77
125.05
113.38
103.82
77.55
77.23
76.91
43.33
38.80
32.07
31.43
30.35
29.97
22.65
21.26
14.24
OAc
N
S
O
O
f1 (ppm)

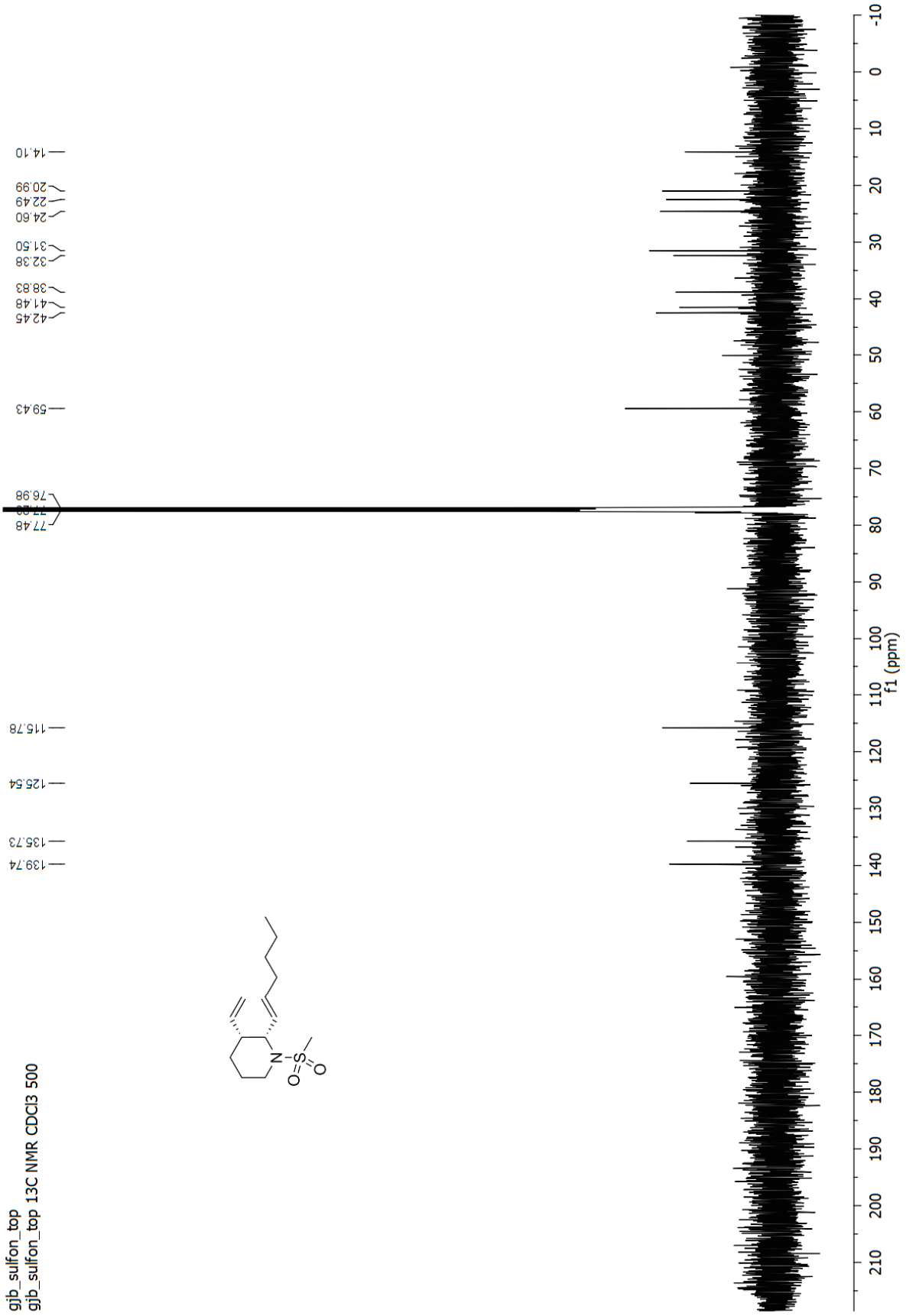


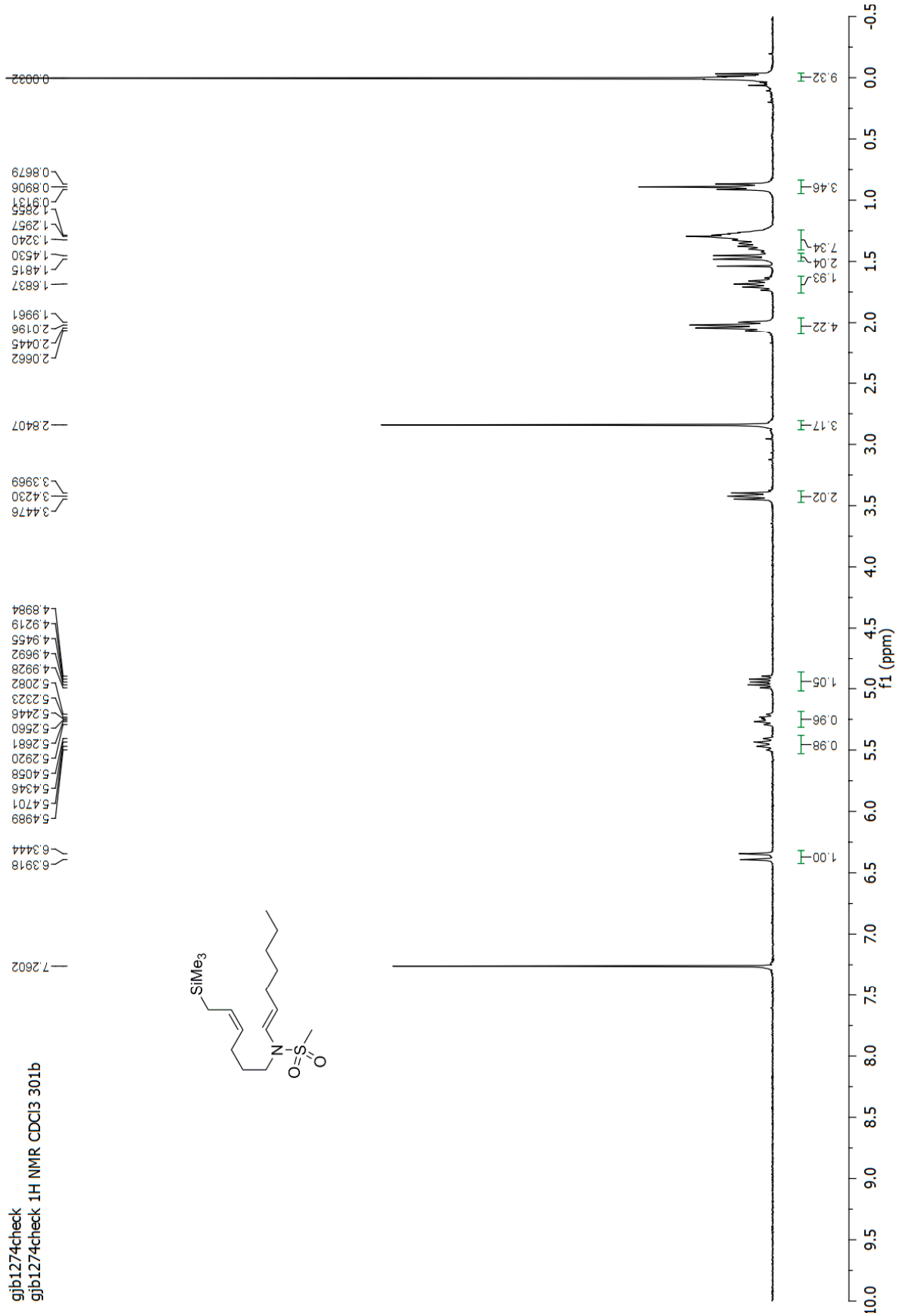

gjb1233
gjb1233-3 13C NMR CDCl3 400B
14.05
22.40
31.25
32.28
40.15
40.61
41.26
46.09
56.12
76.91
77.23
77.55
125.61
137.23
f1 (ppm)

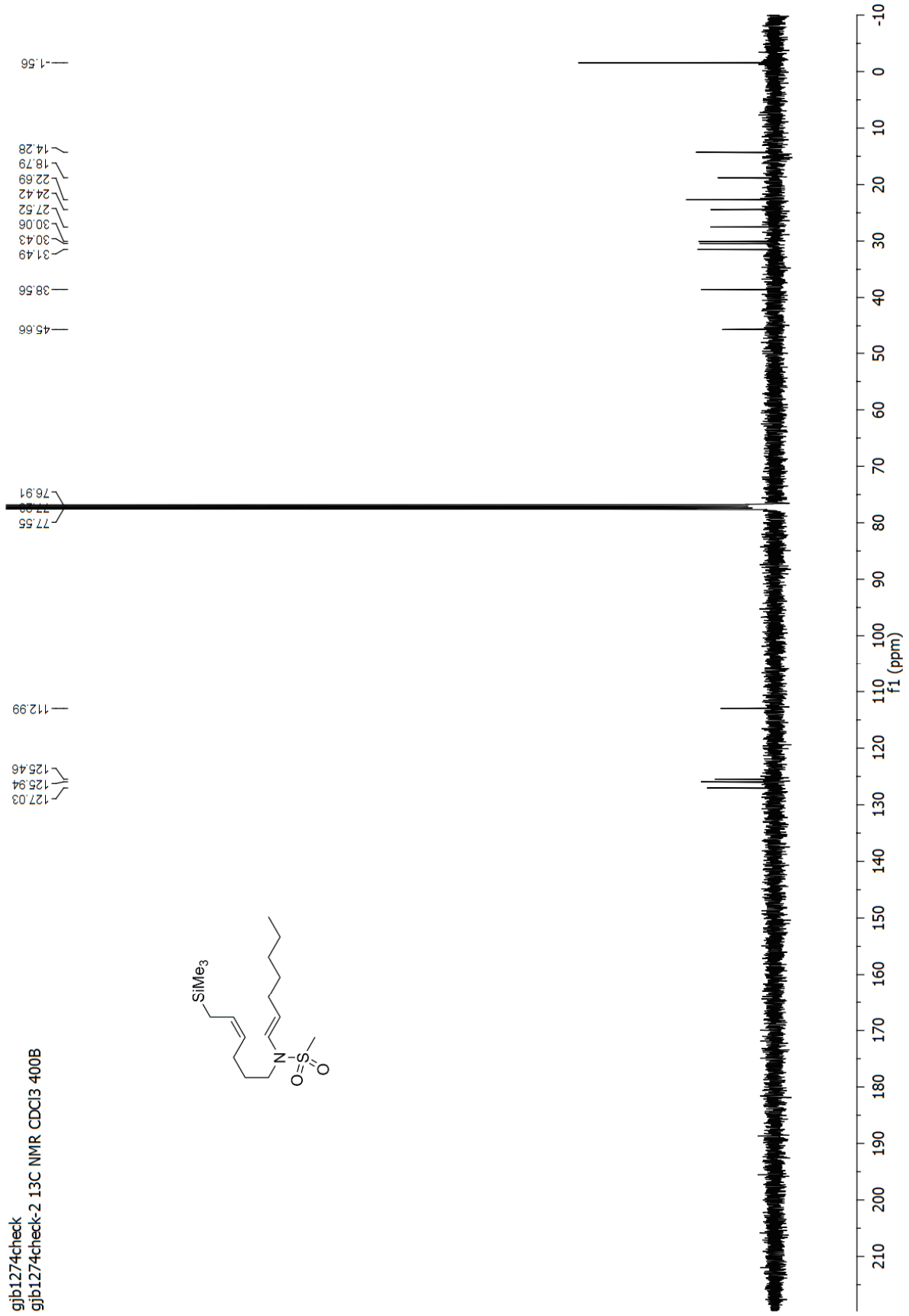


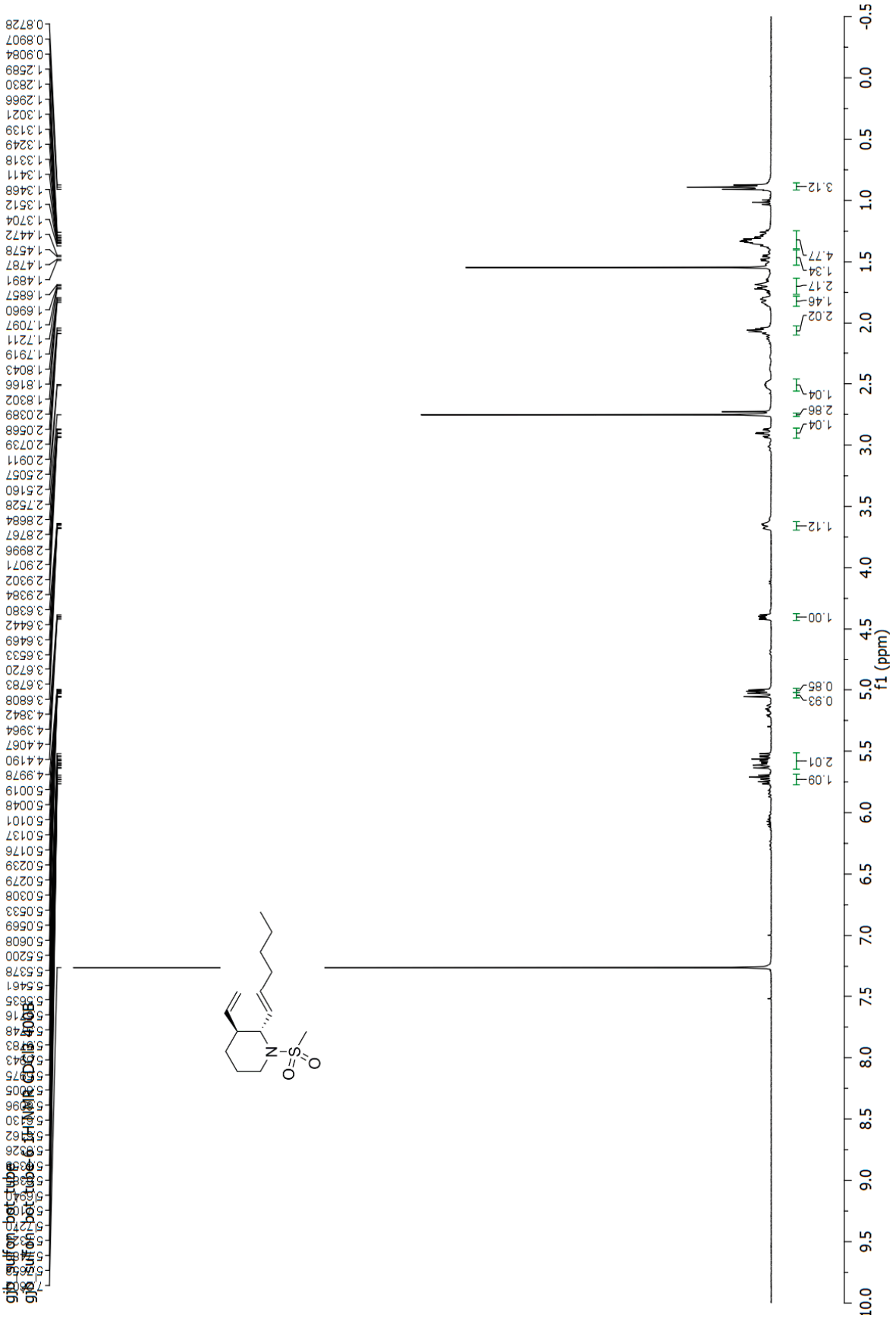

gjb1259
gjb1259-3 13C NMR CDCl3 400A
-1.77
14.26
22.66
22.86
27.63
30.03
30.15
30.40
31.45
38.47
45.53
76.91
77.23
77.55
112.98
125.48
127.30
127.69
SiMe3
N
S
O
O
f1 (ppm)

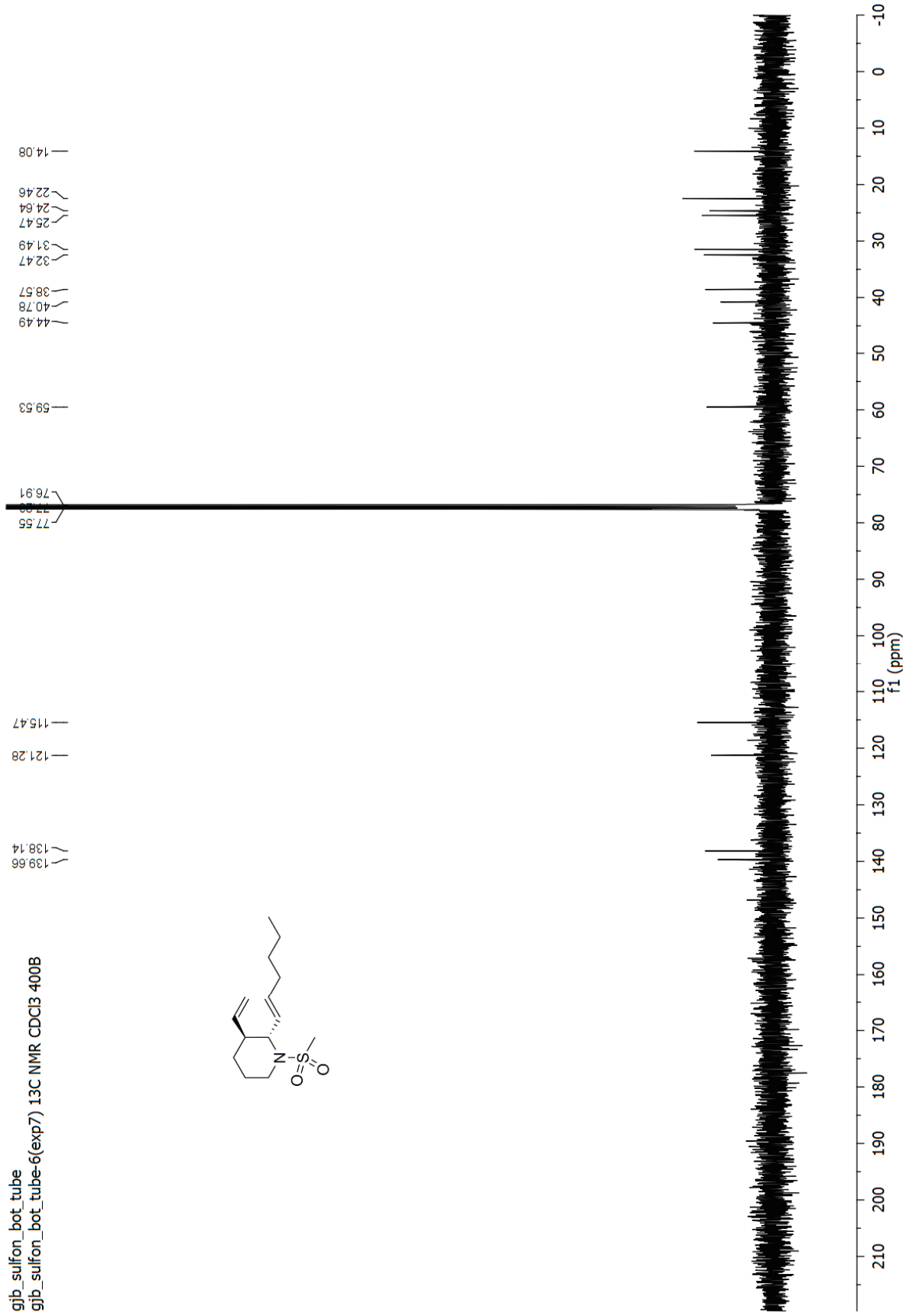


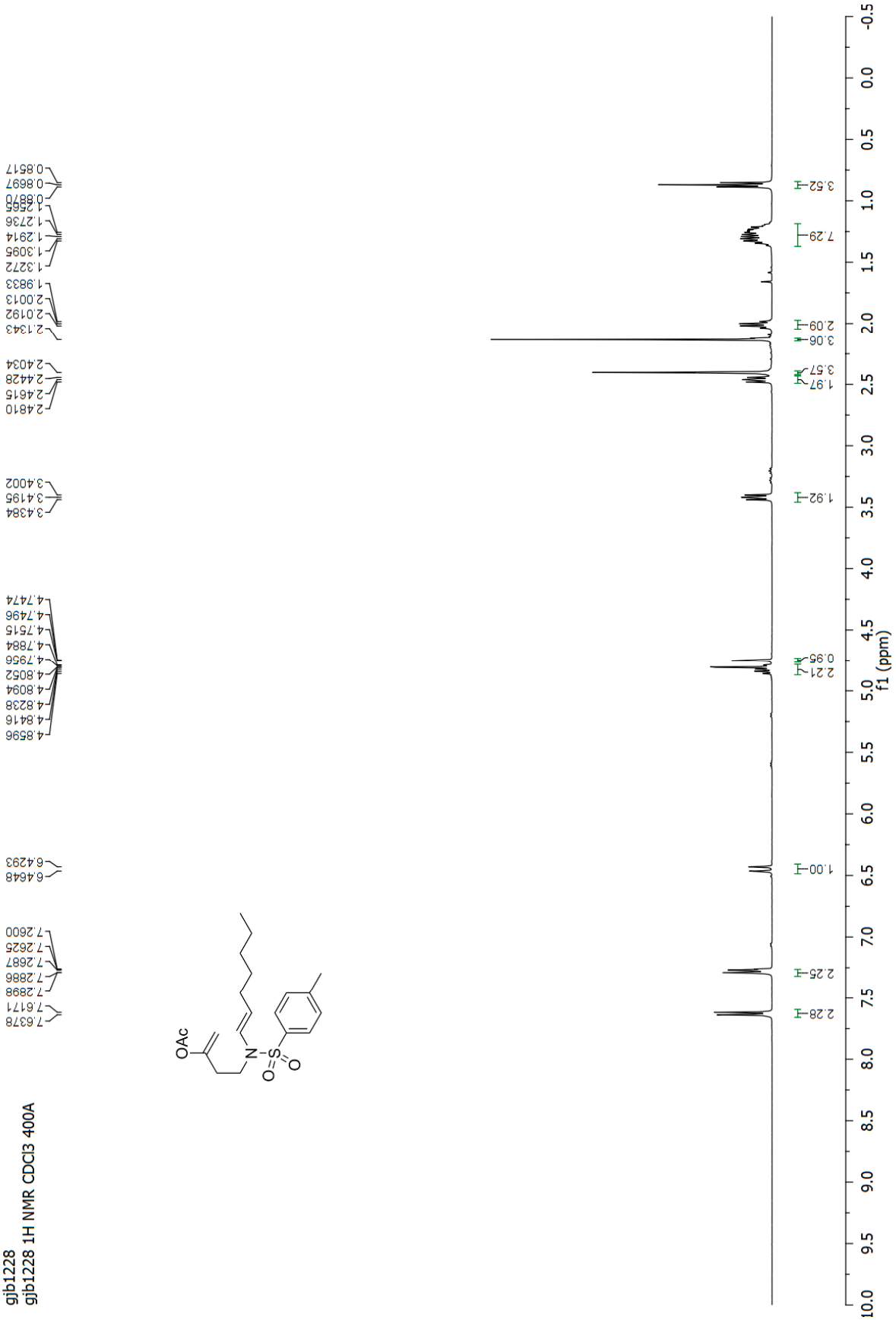


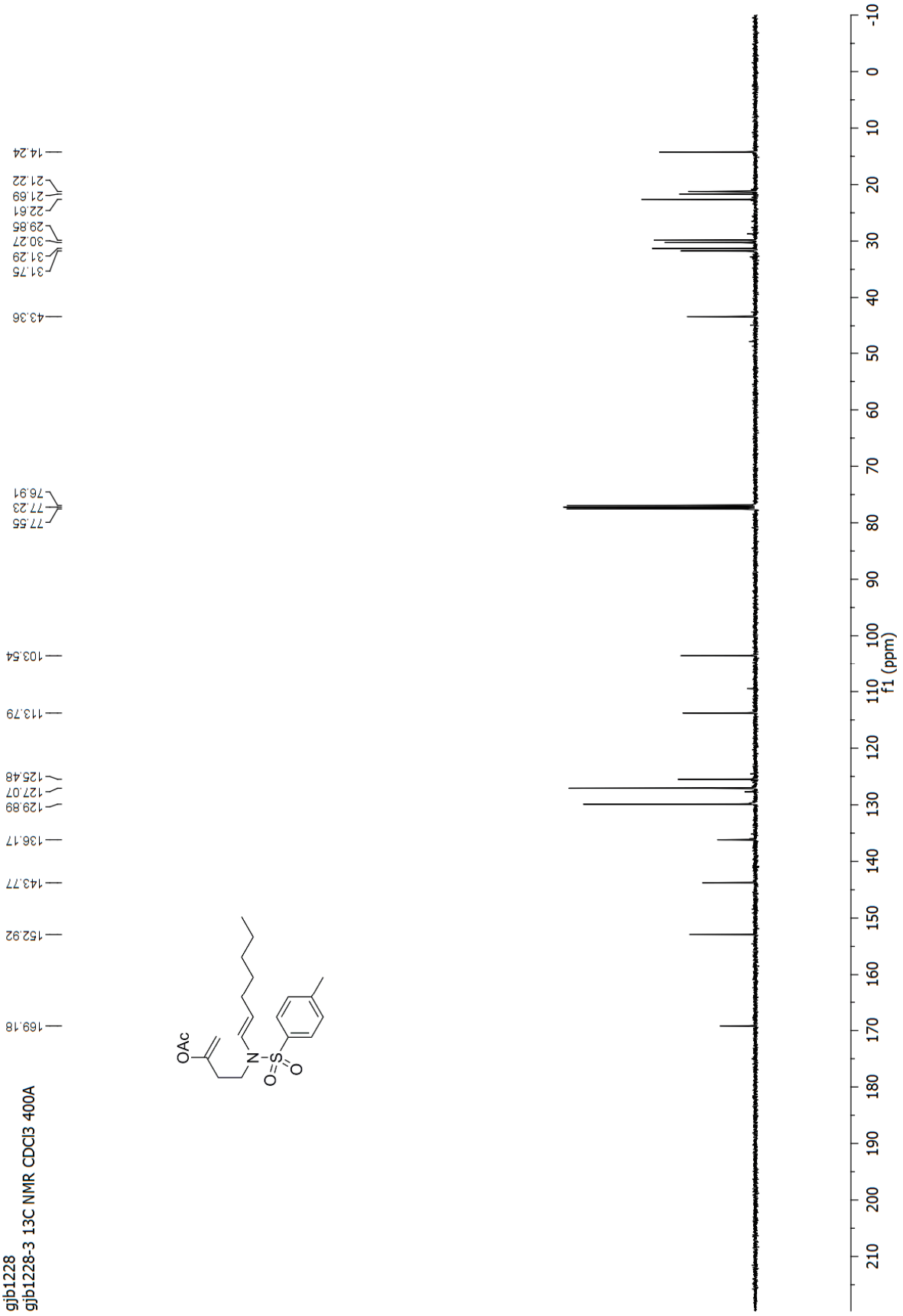


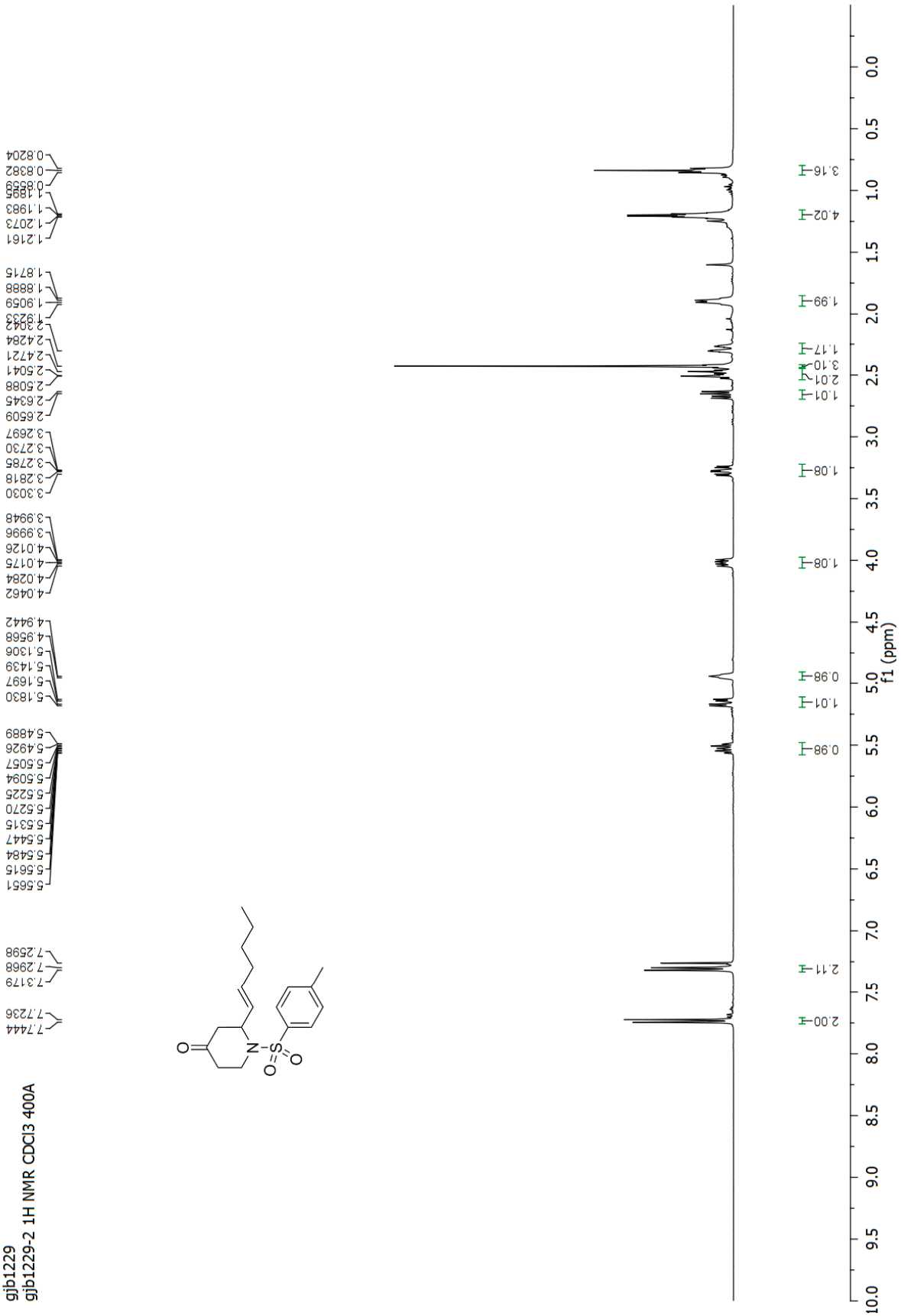


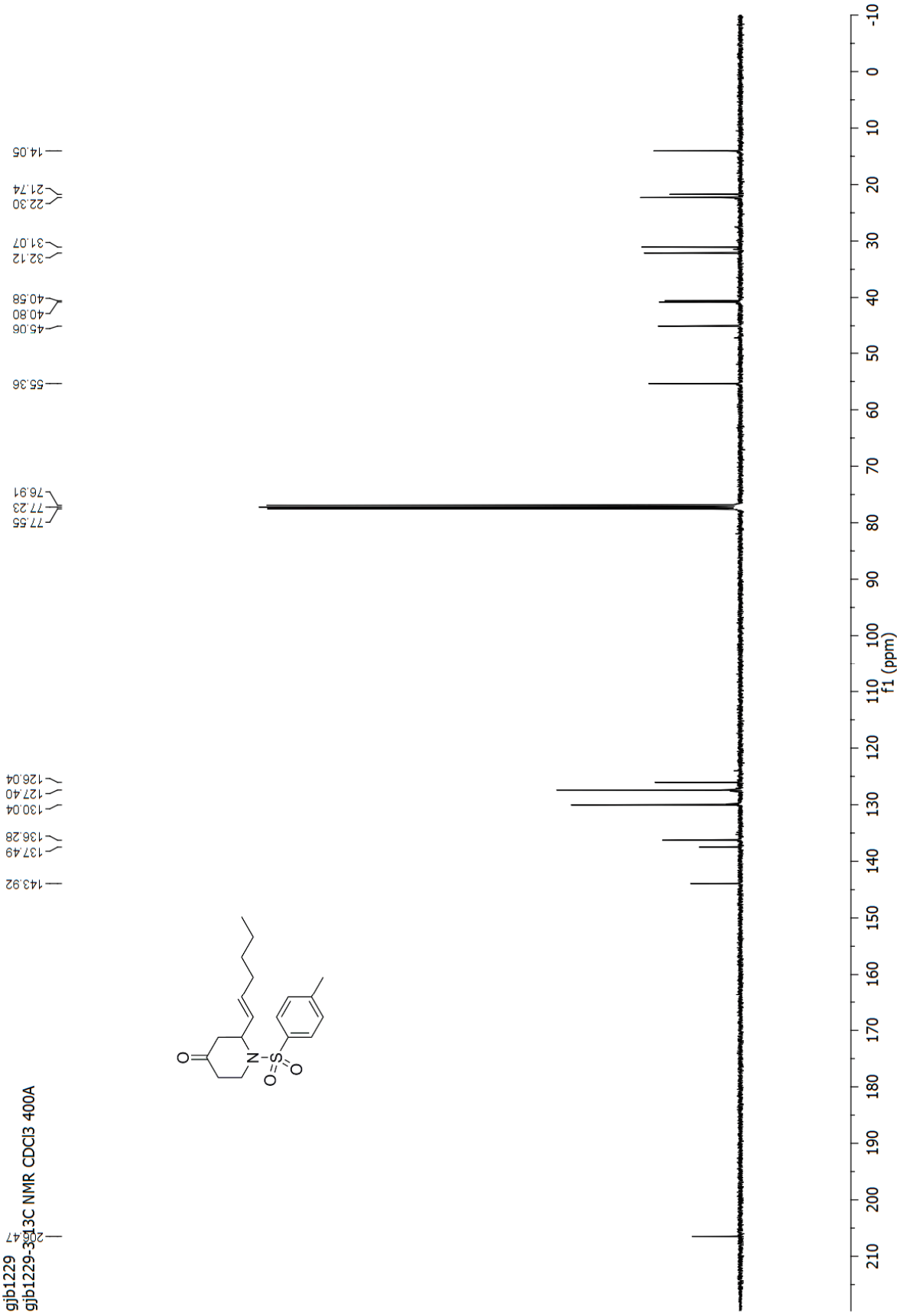


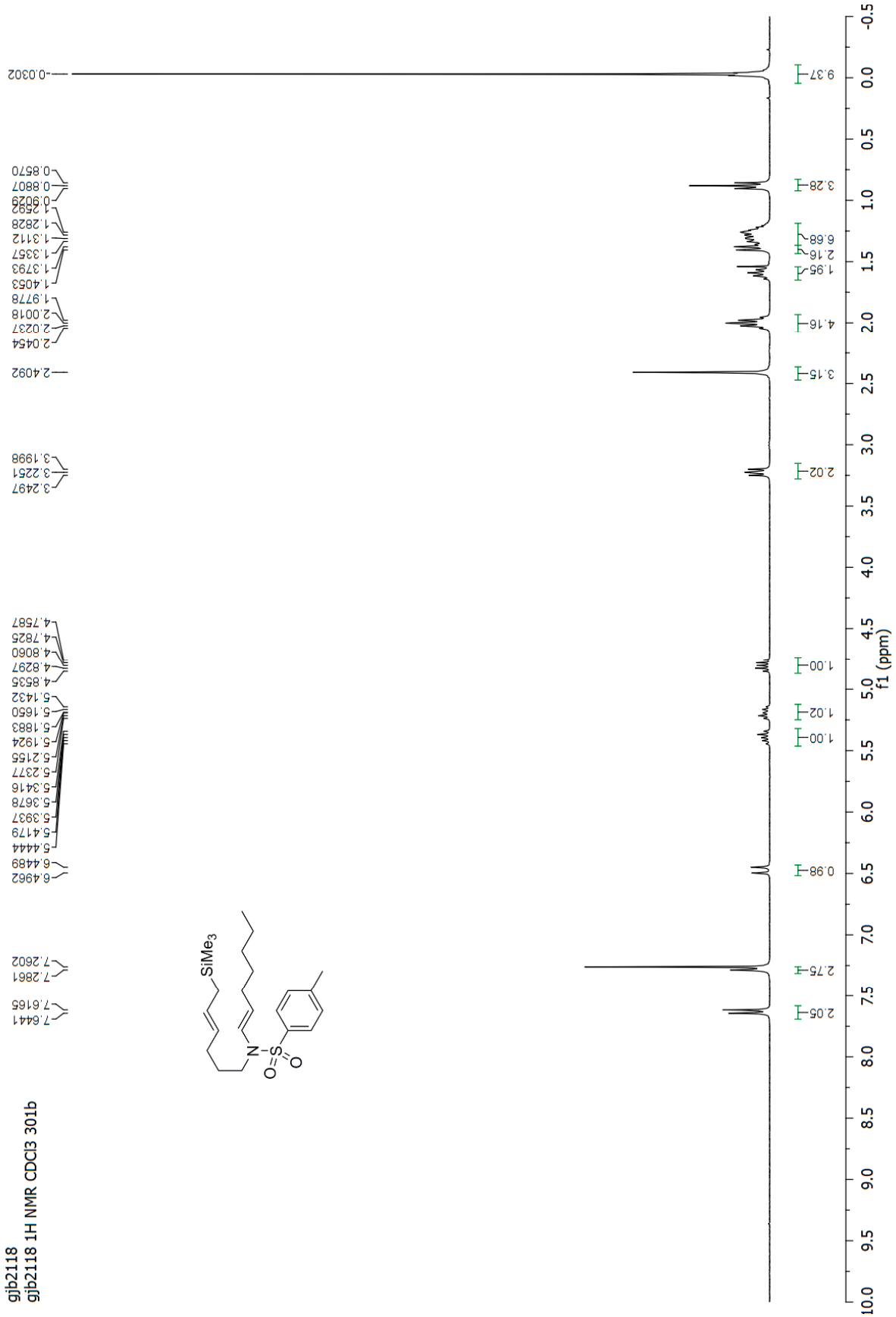

gjb_sulfon_bot_tube
gjb_sulfon_bot_tube-6(exp7) 13C NMR CDCl3 400B
139.66
138.14
121.28
115.47
77.55
76.91
59.53
44.49
40.78
38.57
32.47
31.49
25.47
24.64
22.46
14.08
f1 (ppm)

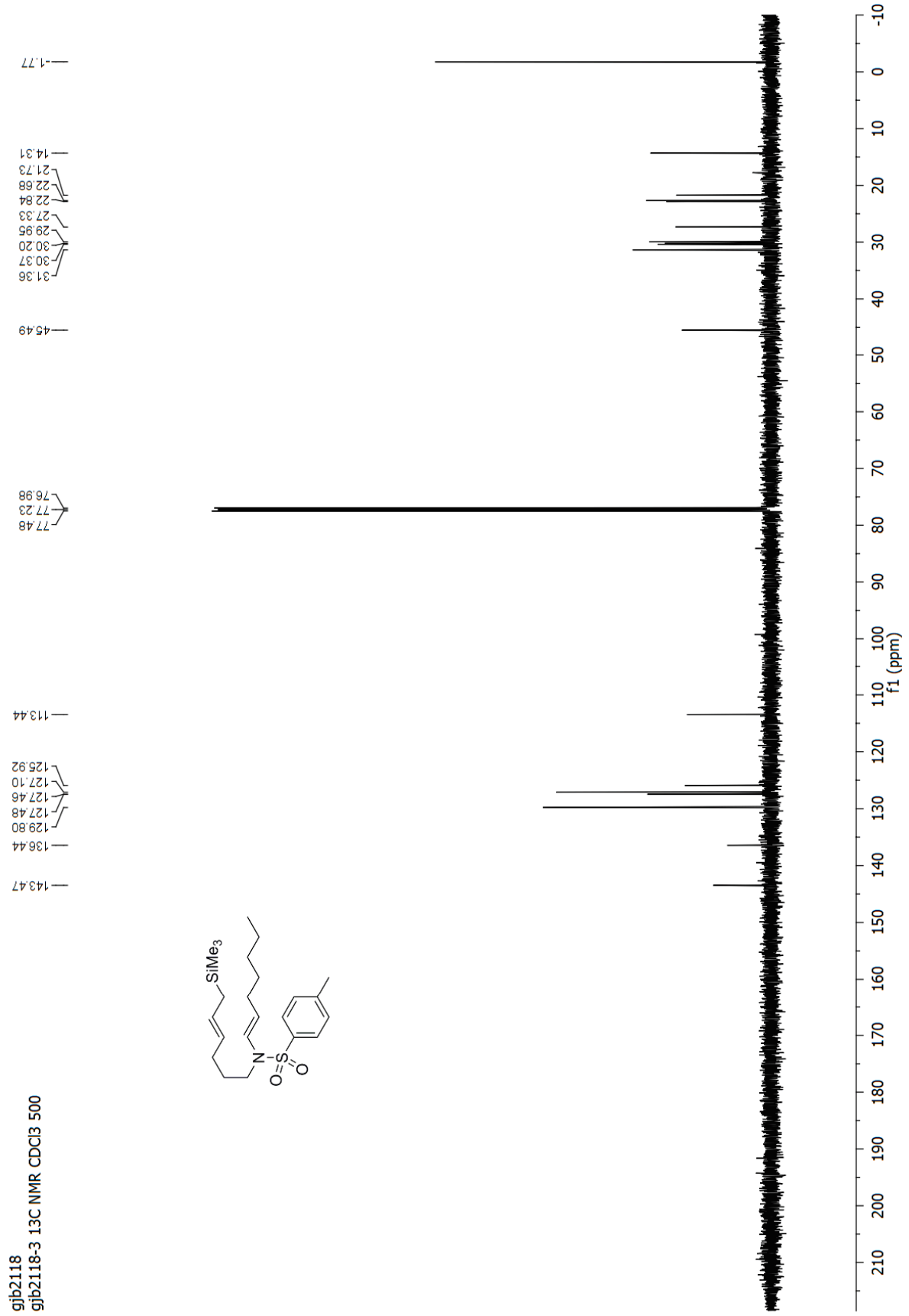

gjb1228
gjb1228 1H NMR CDCl3 400A
OAc
N
S
O
O
f1 (ppm)




gjb1229
gjb1229-2 1H NMR CDCl3 400A
f1 (ppm)


gjb1229
gjb1229-3C NMR CDCl3 400A
14.05
21.74
22.30
31.07
32.12
40.58
40.80
45.06
55.36
76.91
77.23
77.55
126.04
127.40
130.04
136.28
137.49
143.92
f1 (ppm)




gjb2118
gjb2118-3 13C NMR CDCl3 500
SiMe3
N
S
O
O
-1.77
14.31
21.73
22.68
22.84
27.33
29.95
30.20
30.37
31.36
45.49
76.98
77.23
77.48
113.44
125.92
127.10
127.46
127.48
129.80
136.44
143.47
f1 (ppm)