Supplementary Information

Multifaceted Catalysis Approach to Nitrile Activation: Direct Synthesis of Halogenated Allyl Amides from Allylic Alcohols

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Contents

I. General Remarks

Unless otherwise indicated, all commercially available reagents and solvents were used directly from the supplier without further purification. All other reagents were prepared according to previously reported literature procedures, *vide infra*. Analytical grade dichloromethane was dried over calcium hydride and purified by distillation prior to use. Solvents for column chromatography were of technical grade and used without further purification. Column chromatography was performed on silica gel (60-120) mesh. Visualization was accomplished with UV light and/or potassium permanganate solution. NMR spectra were obtained on JEOL 270, Bruker DPX300, Bruker AV3400 or Bruker DPX400 spectrometers. The chemical shifts are reported as dimensionless δ values and are frequency referenced relative to TMS for ^{1}H and ^{13}C{^{1}H}. Coupling constants *J* are reported in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as “s”, “d”, “t” “q” or “m” for singlet, doublet, triplet, quartet or multiplet, respectively. IR spectra were recorded on a Perkin Elmer 1600 series FTIR-spectrophotometer. Mass spectra were recorded on a Bruker MicroTOF spectrometer ionised by electrospray ionisation (ESI). The melting points reported are uncorrected. Gas chromatographic data was obtained on a Hewlett Packard HP4890A gas chromatograph equipped with a Hewlett Packard HP3395 integrator system, employing a HP-5 (crosslinked 5% PH ME siloxane) column of dimensions 15 m × 0.53 mm × 1.5 μm.

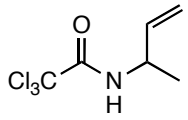
II. General procedure for the synthesis of allyl amides 3a-l

General Procedure A: A flame dried 5 mL microwave vial was charged with $PtCl_2$ (10 mol %), under a cone of nitrogen and the reaction vessel evacuated under vacuum for *ca.* 10 minutes prior to the addition of dichloromethane (1M solution). To the resulting suspension were added trichloroacetonitrile (2.2 equiv.) and the desired allylic alcohol (1 equiv.), the reaction vessel sealed and the mixture allowed to stir at ambient temperature or 60 ºC for 20 h. The reaction mixture was filtered through Celite® with dichloromethane as the eluent prior to removal of the solvent *in vaccuo*. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether, with 1% triethylamine) on silica gel to afford the corresponding allylic amide.

General Procedure B: A flame dried 5 mL microwave vial was charged with $PtCl_2$ (10 mol %), under a cone of nitrogen and the reaction vessel evacuated under vacuum for *ca.* 10 minutes prior to the addition of dichloromethane (1M solution). To the resulting suspension were added trichloroacetonitrile (2.2 equiv.) and the desired allylic alcohol (1 equiv.), the reaction vessel sealed and the mixture allowed to stir at ambient temperature for 40 h. The reaction mixture was filtered through Celite® with dichloromethane as the eluent prior to removal of the solvent *in vaccuo*. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether, with 1% triethylamine) on silica gel to afford the corresponding allylic amide.

General Procedure C: A flame dried 5 mL microwave vial was charged with $PtCl_2$ (10 mol %), under a cone of nitrogen and the reaction vessel evacuated under vacuum for *ca.* 10 minutes prior to the addition of dichloromethane (1M solution). To the resulting suspension were added trichloroacetonitrile (2.2 equiv.) and the desired allylic alcohol (1 equiv.), the reaction vessel sealed and the mixture allowed to stir at 80 °C for 20 h. The reaction mixture was filtered through Celite® with dichloromethane as the eluent prior to removal of the solvent *in vaccuo*. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether, with 1% triethylamine) on silica gel to afford the corresponding allylic amide.

N-(But-3-en-2-yl)-2,2,2-trichloroacetamide (3a)[1]



3a

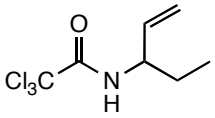
General Procedure A: $PtCl_2$ (11.6 mg, 0.043 mmol), dichloromethane (0.4 mL), (*E*)-2-buten-1-ol (37 µL, 0.43 mmol) and trichloroacetonitrile (94 µL, 0.94 mmol) were stirred at 60 ºC for 20 h. Purification by flash column chromatography (ethyl acetate/petroleum ether (1:9), with 1% triethylamine) afforded *N*-(but-3-en-2-yl)-2,2,2-trichloroacetamide (**3a**, 74 mg, 86%) as a clear oil.

General Procedure B: $PtCl_2$ (9.6 mg, 0.036 mmol), dichloromethane (0.4 mL), (*E*)-2-buten-1-ol (31 µL, 0.36 mmol) and trichloroacetonitrile (79 µL, 0.79 mmol) were stirred at ambient temperature for 40 h. Purification by flash column chromatography (ethyl acetate/petroleum ether (1:9), with 1% triethylamine) afforded *N*-(but-3-en-2-yl)-2,2,2-trichloroacetamide (**3a**, 77 mg, 99%) as a clear oil.

IR ($CHCl_3$) ν 3428, 3028, 1714, 1510 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 6.74-6.49 (1H, bs), 5.88 (1H, ddd, J = 17.2, 10.5, 5.1 Hz), 5.26 (1H, ddd, J = 17.2, 1.6, 0.8 Hz), 5.20 (1H, ddd, J = 10.5, 1.6, 0.8 Hz), 4.61-4.47

(1H, m), 1.36 (3H, d, J = 6.8 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 161.0, 137.6, 115.6, 92.7, 49.1, 19.7; HRMS (ESI) *m/z*: calculated for $[M+Na]^+$, $C_6H_8Cl_3NONa^+$, 237.9569, found: 237.9558.

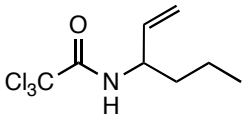
_N_-(Pent-3-en-2-yl)-2,2,2-trichloroacetamide (3b)[2]



3b

General Procedure A: $PtCl_2$ (10 mg, 0.038 mmol), dichloromethane (0.4 mL), (*Z*)-2-penten-1-ol (38 µL, 0.38 mmol) and trichloroacetonitrile (84 µL, 0.84 mmol) were stirred at 60 ºC for 20 h. Purification by flash column chromatography (ethyl acetate/petroleum ether (1:19), with 1% triethylamine) afforded *N*-(pent-3-en-2-yl)-2,2,2-trichloroacetamide (**3b**, 77 mg, 88%) as a clear oil. IR ($CHCl_3$) ν 3427, 3028, 1714, 1510 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 6.67-6.42 (1H, bs), 5.81 (1H, ddd, J = 15.4, 8.6, 5.6 Hz), 5.26 (1H, dt, J = 15.4, 1.1 Hz), 5.21 (1H, dt, J = 8.6, 1.1 Hz), 4.45-4.32 (1H, m), 1.81-1.57 (2H, m), 0.98 (3H, t, J = 7.4 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 161.3, 136.4, 116.2, 92.9, 54.8, 27.5, 10.0; HRMS (ESI) *m/z*: calculated for $[M+Na]^+$, $C_7H_{10}Cl_3NONa^+$, 251.9726, found: 251.9718.

_N_-(Hex-3-en-2-yl)-2,2,2-trichloroacetamide (3c)[3]



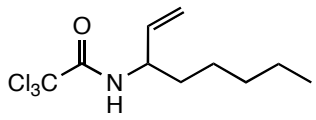
3c

General Procedure A [(*Z*)-2-hexen-1-ol]*:* $PtCl_2$ (10 mg, 0.038 mmol), dichloromethane (0.4 mL), (*Z*)-2-hexen-1-ol (47 µL, 0.39 mmol) and trichloroacetonitrile (88 µL, 0.88 mmol) were stirred at ambient temperature for 20 h. Purification by flash column chromatography (ethyl acetate/petroleum ether (1:9), with 1% triethylamine) afforded *N*-(hex-3-en-2-yl)-2,2,2-trichloroacetamide (**3c**, 66 mg, 69%) as a clear oil.

General Procedure A [(*E*)-2-hexen-1-ol]*:* $PtCl_2$ (10 mg, 0.038 mmol), dichloromethane (0.4 mL), (*E*)-2-hexen-1-ol (47 µL, 0.39 mmol) and trichloroacetonitrile (88 µL, 0.88 mmol) were stirred at ambient temperature for 20 h. Purification by flash column chromatography (ethyl acetate/petroleum ether (1:9), with 1% triethylamine) afforded *N*-(hex-3-en-2-yl)-2,2,2-trichloroacetamide (**3c**, 72 mg, 74%) as a clear oil.

IR ($CHCl_3$) ν 3425, 2963, 2254, 1795, 1510 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 6.67-6.44 (1H, bs), 5.80 (1H, ddd, J = 17.2, 10.5, 5.7 Hz), 5.25 (1H, dt, J = 17.2, 1.0 Hz), 5.20 (1H, dt, J = 10.5, 1.0 Hz), 4.49-4.36 (1H, m), 1.73-1.53 (2H, m), 1.48-1.33 (2H, m), 0.97 (3H, t, J = 7.3 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 161.2, 136.7, 116.0, 92.9, 53.4, 36.6, 18.9, 13.8; HRMS (ESI) *m/z*: calculated for $[M+H]^+$, $C_8H_{13}Cl_3NO^+$, 244.0058, found: 244.0046.

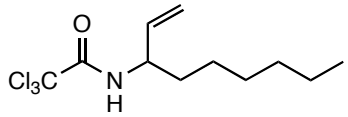
_N_-(Oct-3-en-2-yl)-2,2,2-trichloroacetamide (3d)[4]



3d

General Procedure A: $PtCl_2$ (10 mg, 0.038 mmol), dichloromethane (0.4 mL), (*E*)-2-octen-1-ol (60 µL, 0.38 mmol) and trichloroacetonitrile (84 µL, 0.84 mmol) were stirred at 60 ºC for 20 h. Purification by flash column chromatography (ethyl acetate/petroleum ether (1:9), with 1% triethylamine) afforded *N*-(oct-3-en-2-yl)-2,2,2-trichloroacetamide (**3d**, 94 mg, 71%) as a clear oil. IR ($CHCl_3$) ν 3425, 2933, 2861, 1715, 1510 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 6.61-6.41 (1H bs), 5.82 (1H, ddd, *J* = 17.2, 10.5, 5.7 Hz), 5.29-5.19 (2H, m), 4.48-4.36 (1H, m), 1.75-1.52 (2H, m), 1.45-1.24 (6H, m), 0.89 (3H, t, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 161.2, 136.7, 116.0, 92.9, 53.5, 34.4, 31.4, 25.2, 22.5, 13.9; HRMS (ESI) *m/z:* calculated for $[M+Na]^+$, $C_{10}H_{16}Cl_3NONa^+$, 294.0195, found: 294.0187.

_N_-(Non-3-en-2-yl)-2,2,2-trichloroacetamide (3e)

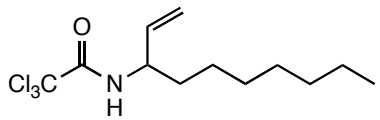


3e

General Procedure A: $PtCl_2$ (10 mg, 0.038 mmol), dichloromethane (0.4 mL), (*Z*)-2-nonen-1-ol (64 µL, 0.38 mmol) and trichloroacetonitrile (84 µL, 0.84 mmol) were stirred at 60 ºC for 20 h. Purification by column chromatography (ethyl acetate/petroleum ether (1:99), with 1% triethylamine) afforded *N*-(non-3-en-2-yl)-2,2,2-trichloroacetamide (**2e**, 52 mg, 46 %) as a clear oil.

General Procedure B: $PtCl_2$ (12.6 mg, 0.047 mmol), dichloromethane (0.5 mL), (*Z*)-2-nonen-1-ol (79 µL, 0.47 mmol) and trichloroacetonitrile (103 µL, 1.03 mmol) were stirred at ambient temperature 40 h. Purification by column chromatography (ethyl acetate/petroleum ether (1:9), with 1% triethylamine) afforded *N*-(non-3-en-2-yl)-2,2,2-trichloroacetamide (**3e**, 85 mg, 63%) as a clear oil. IR ($CHCl_3$) ν 3425, 2931, 1715, 1510 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 6.58 (1H, d, *J* = 6.9 Hz), 5.65 (1H, ddd, *J* = 17.2, 10.4, 5.7 Hz), 5.33-5.26 (2H, m), 4.38-4.48 (1H, m), 1.75-1.51 (2H, m), 1.46-1.22 (8H, m), 0.98-0.83 (3H, m); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 161.2, 136.7, 116.0, 92.9, 53.6, 34.4, 31.4, 28.9, 25.5, 22.5, 14.0; HRMS (ESI) *m/z:* calculated for $[M+Na^+]$, $C_{11}H_{18}Cl_3NONa^+$, 308.0347, found: 308.0334.

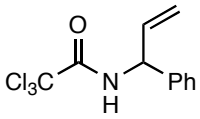
_N_-(Dec-3-en-2-yl)-2,2,2-trichloroacetamide (3f)[4]



3f

General Procedure A: $PtCl_2$ (10 mg, 0.038 mmol), dichloromethane (0.4 mL), (*E*)-2-decen-1-ol (73 µL, 0.38 mmol) and trichloroacetonitrile (84 µL, 0.84 mmol) were stirred at 60 ºC for 20 h. Purification by column chromatography (ethyl acetate/petroleum ether (1:19), with 1% triethylamine) afforded *N*-(dec-3-en-2-yl)-2,2,2-trichloroacetamide (**3f**, 59 mg, 50%) as a clear oil. IR ($CHCl_3$) ν 3424, 2929, 1711, 1503 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 6.53 (1H, d, *J* = 7.5 Hz), 5.82 (1H, ddd, *J* = 17.2, 10.4, 5.7 Hz), 5.33-5.17 (2H, m), 4.48-4.38 (1H, m), 1.75-1.51 (2H, m), 1.46-1.22 (10H, m), 0.88 (3H, t, *J* = 6.8 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 161.2, 136.7, 116.0, 92.9, 53.6, 34.5, 31.7, 29.2, 29.18, 29.13, 25.5, 22.6, 14.1; HRMS (ESI) *m/z:* calculated for $[M+Na]^+$, $C_{12}H_{20}Cl_3NONa^+$, 322.0508, found: 322.0506.

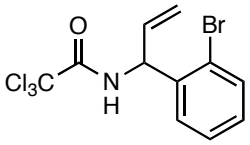
2,2,2-Trichloro-*N*-(1-phenylallyl)acetamide (3g)[5]



3g

General Procedure A: $PtCl_2$ (8.2 mg, 0.03 mmol), dichloromethane (0.3 mL), (*E*)-cinnamyl alcohol (41 mg, 0.30 mmol) and trichloroacetonitrile (66 µL, 0.66 mmol) were stirred at 60 ºC for 20 h. Purification by column chromatography (diethyl ether/petroleum ether (1:9), with 1% triethylamine) afforded 2,2,2-trichloro-*N*-(1-phenylallyl)acetamide (**3g**, 45 mg, 54 %) as a clear oil. IR ($CHCl_3$) ν 3426, 3033, 3015, 2928, 1716, 1506 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 7.43-7.34 (5H, m), 6.91 (1H, br.s), 6.07 (1H, ddd, *J* = 17.1, 10.5, 5.5 Hz), 5.59 (1H, dd, *J* = 7.7, 5.5 Hz), 5.41-5.30 (2H, m); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 160.9, 138.8, 135.5, 129.1, 128.4, 127.7, 117.2, 92.6, 57.1; HRMS (ESI) *m/z:* calculated for $[M+H]^+$, $C_{13}H_{10}Cl_3NO^+$, 299.9726, found: 299.9719.

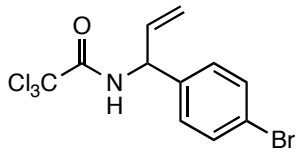
***N*-(1-(2-Bromophenyl)allyl)-2,2,2-trichloroacetamide (3h)[6]**



3h

General Procedure A: $PtCl_2$ (14 mg, 0.054 mmol), dichloromethane (0.5 mL), (*E*)-3-(2-bromophenyl)-2-propen-1-ol (115 mg, 0.54 mmol) and trichloroacetonitrile (118 µL, 1.18 mmol) were stirred at 60 ºC for 20 h. Purification by flash column chromatography (diethyl ether/petroleum ether (1:9), with 1% triethylamine) afforded *N*-(1-(2-bromophenyl)allyl)-2,2,2-trichloroacetamide (**3h**, 91 mg, 47 %) as a clear oil. IR ($CHCl_3$) ν 3427, 2927, 1717, 1498 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 7.62 (1H, d, *J* = 7.9 Hz), 7.35 (2H, d, *J* = 4.1 Hz), 7.24-7.19 (1H, m), 7.10 (1H, d, *J* = 6.2 Hz), 6.07 (1H, ddd, *J* = 17.2, 10.4, 4.8 Hz), 5.91-5.83 (1H, m), 5.38 (1H, dd, *J* = 10.4, 1.4 Hz), 5.29 (1H, dd, *J* = 17.2, 1.4 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 160.8, 137.7, 134.5, 133.8, 129.9, 129.1, 128.0, 123.8, 117.6, 92.5, 57.0; HRMS (ESI) *m/z:* calculated for $[M+Na]^+$, $C_{11}H_{10}Cl_3NONa^+$, 377.8831, found: 377.8811.

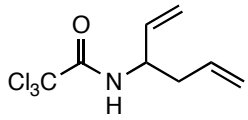
***N*-(1-(4-Bromophenyl)allyl)-2,2,2-trichloroacetamide (3i)[6]**



3i

General Procedure A: $PtCl_2$ (8 mg, 0.03 mmol), dichloromethane (0.3 mL), (*E*)-3-(4-bromophenyl)-2-propen-1-ol (64 mg, 0.3 mmol) and trichloroacetonitrile (66 µL, 0.66 mmol) were stirred at 60 ºC for 20 h. Purification by flash column chromatography (ethyl acetate/petroleum ether (1:19), with 1% triethylamine) afforded *N*-(1-(4-bromophenyl)allyl)-2,2,2-trichloroacetamide (**3i**, 48 mg, 45 %) as a clear oil. IR ($CHCl_3$) ν 3425, 2929, 1716, 1490 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 7.53 (2H, d, J = 8.4 Hz), 7.22 (2H, d, J = 8.4 Hz), 6.90 (1H, d, J = 6.8 Hz), 6.05 (1H, ddd, J = 17.1, 10.4, 5.6 Hz), 5.55 (1H, dd, 6.8, 5.6 Hz), 5.40 (1H, dd, J = 10.4, 1.1 Hz), 5.33 (1H, dd, J = 17.1, 1.1 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_c 161.0, 137.8, 135.1, 132.2, 128.8, 122.4, 117.9, 92.5, 56.5; HRMS (ESI) *m/z:* calculated for $[M+Na]^+$, $C_{11}H_9Cl_3NONa^+$, 377.8826, found: 377.8826.

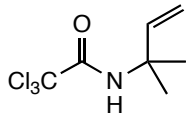
***N*-(Hexa-1,5-dien-3-yl)-2,2,2-trichloroacetamide (3j)[7]**



3j

General Procedure A: $PtCl_2$ (12 mg, 0.04 mmol), dichloromethane (0.4 mL), (*E*)-2,5-hexadien-1-ol (44 µL, 0.40 mmol) and trichloroacetonitrile (88 µL, 0.88 mmol) were stirred at 60 ºC for 20 h. Purification by flash column chromatography (ethyl acetate/petroleum ether (1:19), with 1% triethylamine) afforded *N*-(hexa-1,5-dien-3-yl)-2,2,2-trichloroacetamide (**3j**, 30 mg, 31 %) as a clear oil. IR ($CHCl_3$) ν 3423, 2985, 1715, 1508 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 6.79-6.56 (1H, bs), 5.98-5.69 (2H, m), 5.38-5.04 (4H, m), 4.61-4.46 (1H, m), 2.58-2.29 (2H, m); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 161.1, 135.9, 132.6, 119.5, 116.2, 92.8, 52.2, 38.5; HRMS (ESI) *m/z:* calculated for $[M+Na]^+$, $C_8H_{10}Cl_3NONa^+$, 263.9721, found: 263.9716.

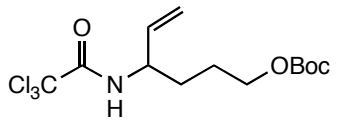
***N*-(2-Methylbut-3-en-2-yl)-2,2,2-trichloroacetamide (3k)[8]**



3k

General Procedure A: $PtCl_2$ (11.5 mg, 0.043 mmol) dichloromethane (0.4 mL), (*E*)-3-methyl-2-buten-1-ol (44 µL, 0.43 mmol) and trichloroacetonitrile (95 µL, 0.95 mmol) were stirred at 60 ºC for 20 h. Purification by column chromatography (diethyl ether/petroleum ether (1:25), with 1% triethylamine) afforded *N*-(2-methylbut-3-en-2-yl)-2,2,2-trichloroacetamide (**3k**, 58 mg, 59%) as a clear oil. IR ($CHCl_3$) ν 3428, 3028, 1714, 1510 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$, 298 K) δ_H 6.61 (1H, br.s) 6.03 (1H, dd, J = 17.4, 10.7 Hz) 5.23 (1H, d, J = 17.4) 5.17 (1H, d, J = 10.67) 1.54 (6H, s); $^{13}C\{^1H\}$ NMR (75 MHz $CDCl_3$, 298 K) δ_c 161.7, 137.6, 115.6, 98.5, 49.0, 19.7; HRMS (ESI) m/z: calculated for $[M+Na]^+$, $C_7H_{10}Cl_3NONa^+$, 251.9726, found: 251.9731.

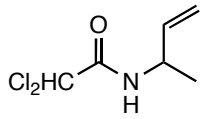
tert-Butyl (5-(2,2,2-Trichloroacetamido)hept-6-en-1-yl) carbonate (3l)



3l

General Procedure A: $PtCl_2$ (4.5 mg, 0.017 mmol), dichloromethane (0.2 mL), (*E*)-*tert*-butyl (7-hydroxyhept-5-en-1-yl) carbonate (39 mg, 0.17 mmol) and trichloroacetonitrile (37 µL, 0.37 mmol) were stirred at 60 ºC for 20 h. Purification by column chromatography (ethyl acetate/petroleum ether (1:25), with 1% triethylamine) afforded *tert*-butyl (5-(2,2,2-trichloroacetamido)hept-6-en-1-yl) carbonate (**3l**, 35 mg, 55%) as a clear oil. IR ($CHCl_3$) ν 3422, 2932, 1735, 1580 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 6.55 (1H, d, *J* = 7.9 Hz), 5.80 (1H, ddd, *J* = 17.1, 10.5, 5.7 Hz), 5.28 - 5.19 (2H, m), 4.47 - 4.37 (1H, m), 4.06 (4H, t, 6.5 Hz), 1.77 - 1.60 (6H, m), 1.48 (9H, s); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 161.2, 153.5, 136.3, 116.4, 92.7, 81.9, 66.5, 53.4, 34.0 28.3, 27.7, 21.9; HRMS (ESI) *m/z:* calculated for $[M+Na^+]$, $C_{14}H_{22}Cl_3NO_4Na^+$, 396.0507, found: 396.0522.

***N*-(But-3-en-2-yl)-2,2-dichloroacetamide (4a):**

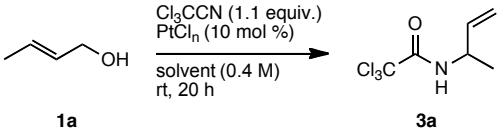


4a

General Procedure C: $PtCl_2$ (12 mg, 0.045 mmol), dichloromethane (0.4 mL), (*E*)-2-buten-1-ol (37 µL, 0.44 mmol) and dichloroacetonitrile (78 µL, 0.97 mmol) were stirred at 80 ºC for 20 h. Purification by flash column chromatography (ethyl acetate/petroleum ether (1:15), with 1% triethylamine) afforded *N*-(but-3-en-2-yl)-2,2-dichloroacetamide (**4a**, 20 mg, 25 %) as a clear oil. IR ($CHCl_3$) ν 3419, 3089, 2986, 1696, 1538 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ_H 6.74-6.55 (1H, bs), 5.96 (1H, s), 5.83 (1H, ddd, *J* =17.3, 10.5, 6.0 Hz), 5.23-5.12 (2H, m), 4.57-4.47 (1H, m), 1.30 (3H, d, *J* = 6.0 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ_C 163.4, 137.9, 115.0, 66.4, 47.8, 19.7; HRMS (ESI) *m/z*: calculated for $[M+Na]^+$, $C_6H_9Cl_2NONa^+$, 203.9954, found: 203.9956.

IV. Optimisation of the multifaceted catalysis approach to allylamide synthesis

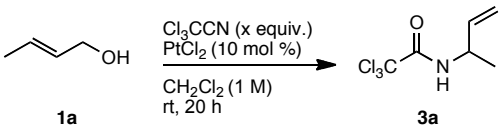
Table SI 1. Catalyst and solvent screen



1a **3a**

Entry	Solvent	Catalyst	Yield (%)	Catalyst	Yield (%)
1	*n*-hexane	$PtCl_2$	41	$PtCl_4$	34
2	Toluene	$PtCl_2$	48	$PtCl_4$	41
3	Diethyl ether	$PtCl_2$	35	$PtCl_4$	18
4	Dichloromethane	$PtCl_2$	53	$PtCl_4$	0
5	Tetrahydrofuran	$PtCl_2$	30	$PtCl_4$	22
6	Methanol	$PtCl_2$	0	$PtCl_4$	0
7	Acetonitrile	$PtCl_2$	0	$PtCl_4$	0
8	Dimethylacetamide	$PtCl_2$	5	$PtCl_4$	15
9	Dimethyl sulfoxide	$PtCl_2$	0	$PtCl_4$	0
10	Water-d_2	$PtCl_2$	0	$PtCl_4$	0
11	Dichloromethane	$FeCl_2$	0		
12	Dichloromethane	$MnCl_2$	0		
13	Dichloromethane	$Er(OTf)_3$	0		
14	Dichloromethane	$Yb(OTf)_3$	0		
15	Dichloromethane	$WOCl_4$	0		
16	Dichloromethane	$PdCl_2$	0		
17	Dichloromethane	$Pd(OAc)_2$ / xanthphos	0		
18	Dichloromethane	$Pd(OAc)_2$ / dppf	0		
19	Dichloromethane	$[Pt(COD)Cl_2]$	0		
20	Dichloromethane	$[Pt(bpy)Cl_2]$	0		
21	Dichloromethane	[Cu(IMes)Cl] / $AgBF_4$ (10 mol %)	0		

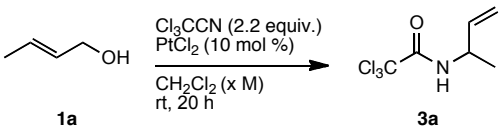
Table SI 2. Equivalents of trichloroacetonitrile screen



1a **3a**

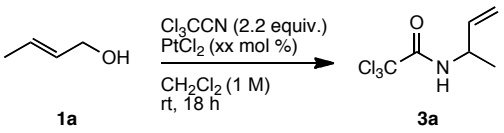
Entry	Equiv.	Yield (%)
1	0.5	66 (based on Cl_3CCN)
2	1.1	56
3	2.2	80
4	5.0	80

Table SI 3. Molarity of reaction screen



Entry	Molarity (M)	Yield (%)
1	0.1	13
2	0.4	53
3	1	56
4	2	53

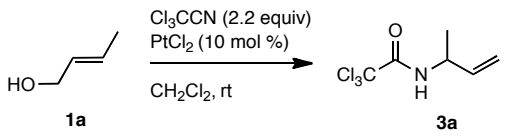
Table SI 4. Catalyst loading



Entry	Catalyst loading (mol %) [notes]	Yield (%)
1	20	73
2	10	75
3	5	34
4	5 [75 h]	49
5	1	12
6	0.1 [toluene, 160 °C]	0 - decomposition

Table SI 5. Catalyst poisoning experiment

A catalyst poisoning experiment was conducted by adding various amounts of acetonitrile to the reaction of allyl alcohol **1a** and trichloracetonitrile after 6 h (Table SI 5). It was found that excess acetonitrile effectively quenched the reaction due to its increased affinity for the platinum catalyst in comparison to trichloroacetonitrile. Acetonitrileis not sufficiently activated to allow nucleophilic addition of allyl alcohol **1a** under these conditions. Whereas the addition of 0.1 equivalents of acetonitrile gave almost the same yield of product **3a** as the control reaction (compare entries 3 and 4), indicating that the nitrile bound platinum species is capable of catalysing the formation and rearrangement of imidate **2**. Importantly, no imidate **2**/**6** was observed in this study, further supporting the supposition that the formation of **2**/**6** is the rate-limiting step of the overall sequence.

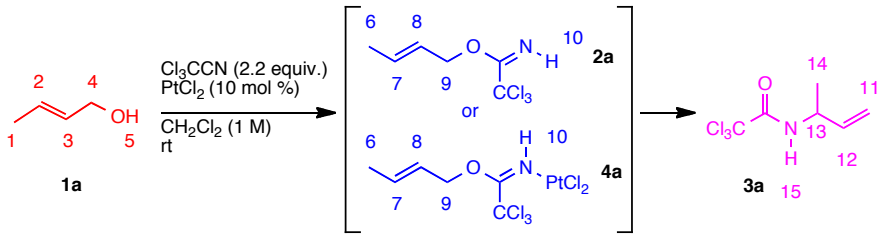


entry	conditions /additives	yield (%)
1	no additives, work-up at 6 h	30
2	MeCN (5.0 equiv.) at 6 h, work-up at 12 h	38
3	MeCN (0.1 equiv.) at 6 h, work-up at 12 h	49
4	no additives, work-up at 12 h	54

VII. NMR Kinetic Measurements

Whilst, it was impossible to ascertain whether the platinum was bound to the nitrogen during the rearrangement or if it forms a π-adduct to promote the [3,3]-sigmatropic rearrangement, several intriguing and unassignable peaks are found in the NMR that indicate platinum coordination.

An oven dried J. Youngs NMR tube was loaded with $PtCl_2$ (10.6 mg) under a blanket of nitrogen and CD_2Cl_2 (0.4 mL) was added followed by the addition of 2-buten-1-ol (**1a**, 34 µL) and trichloroacetonitrile (88 µL). The tube was sealed and subjected to hourly ^1H and $^{13}C\{^1H\}$ NMR analysis for 19 hours (Figure SI 1 and Figure SI 2).



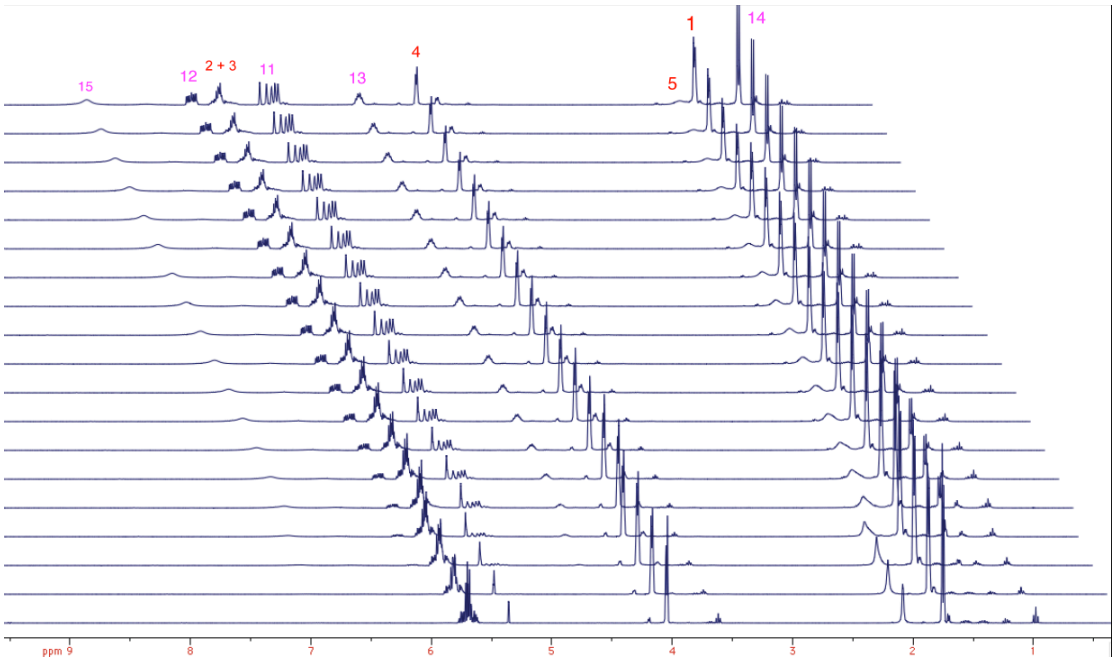
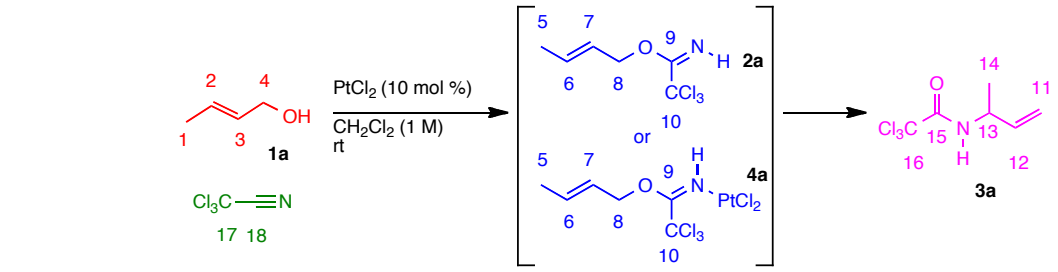


Figure SI 1. *In situ* ^1H NMR monitoring of the Pt-MFC synthesis of allyl amides



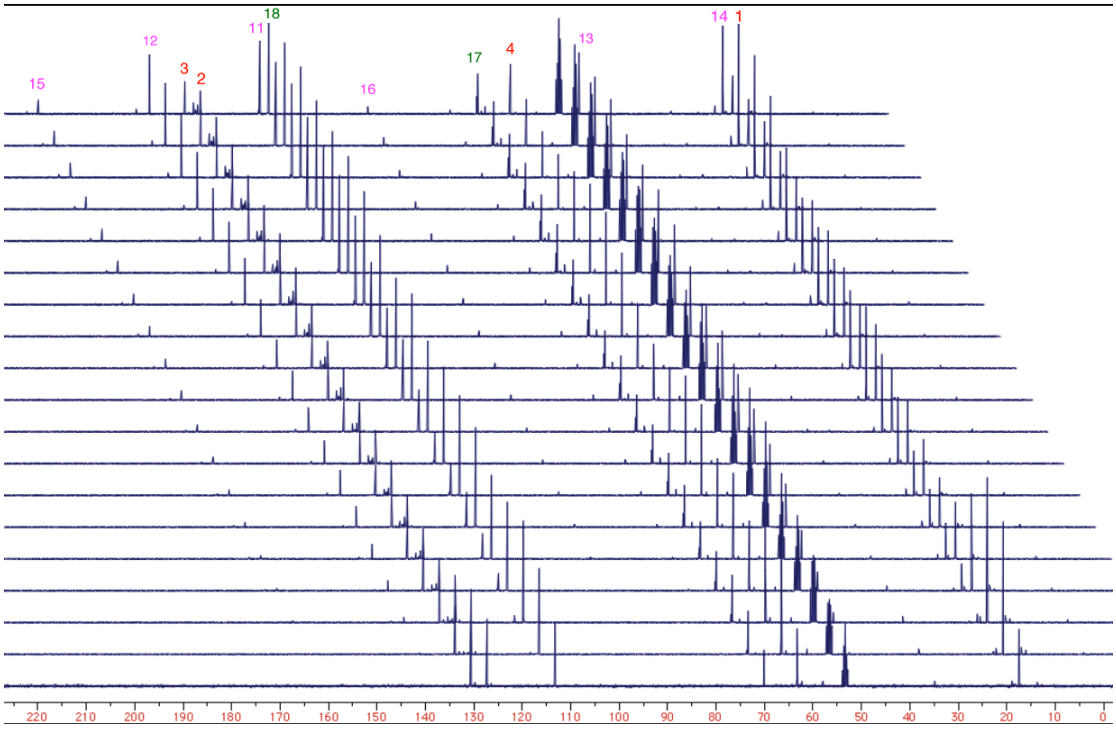


Figure SI 2. *In situ* $^{13}C\{^{1}H\}$ NMR monitoring of the Pt-MFC synthesis of allyl amides

VIII. GC Kinetic Measurements

General Procedure B was followed with the addition of an internal standard (*n*-decane, 1 equiv.) for GC analysis via an internal standard method of quantification. Samples (0.1 mL) were taken periodically over the course of the reaction and diluted up to 2 mL with HPLC dichloromethane prior to elution through a small Celite® plug for GC analysis. Program for analysis: initial temperature at 32 °C, held for 2.5 minutes, ramp 5 °C/minute next 150 °C, held for 10 minutes. The temperature of the injector and detector were maintained at 250 °C. Retention times of analytes: 2-buten-1-ol, 1.125 min; trichloroacetonitrile 1.181 min; decane, 9.445 min; trichloroimidate, 15.763; trichloroamide, 17.336. The data is summarised in Figures SI 3 and SI4.

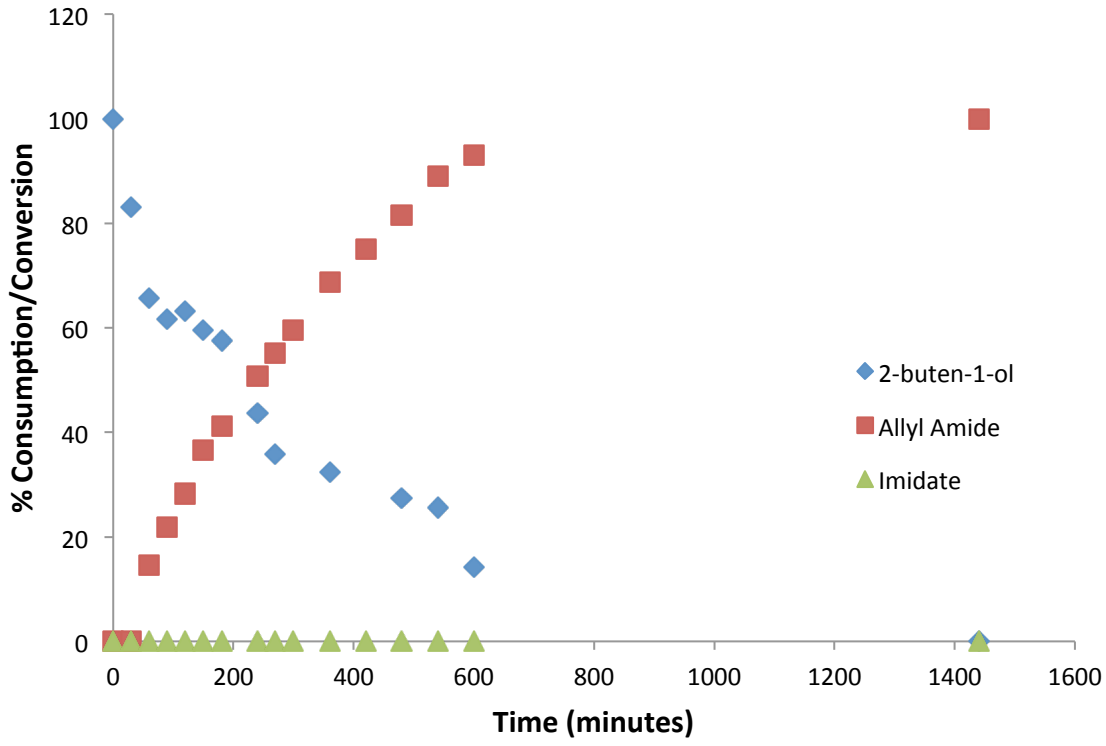


Figure SI 3. GC analysis of the reaction progress as a function of time.

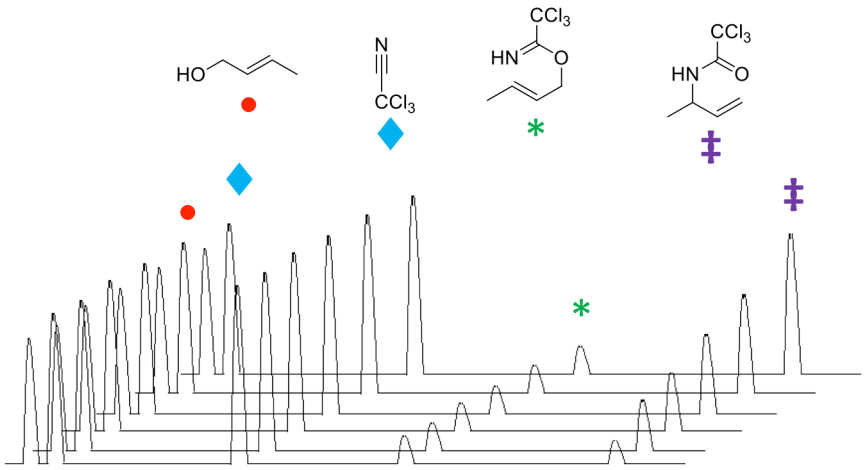


Figure SI 4. GC analysis of the reaction at various time points showing that at any given point in time only a minimal amount of imidate * is present (pictorial representation of the collected GC traces).

IX. References

1. H. Nagashima, N. Ozaki, M. Ishii, K. Seki, M. Washiyama and K. Itoh, *J. Org. Chem.*, 1993, **58**, 464–470.
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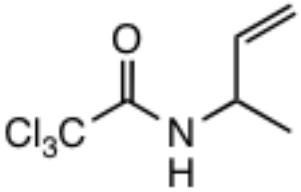

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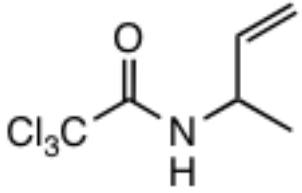

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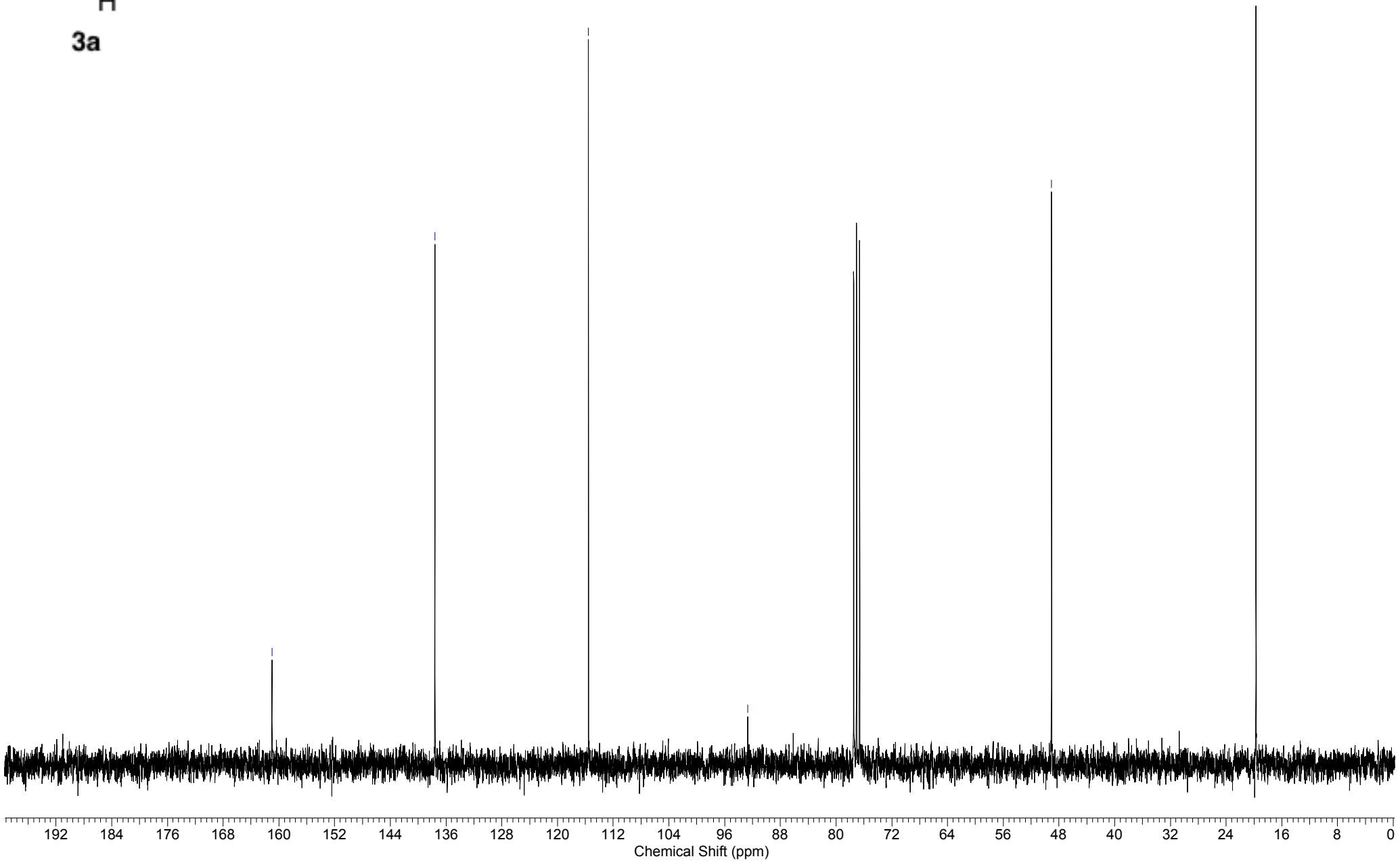

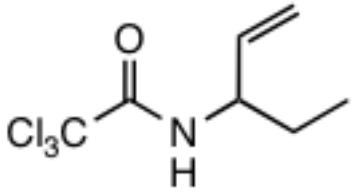

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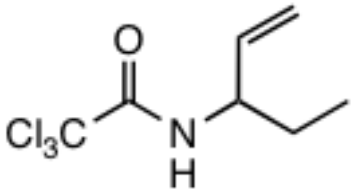
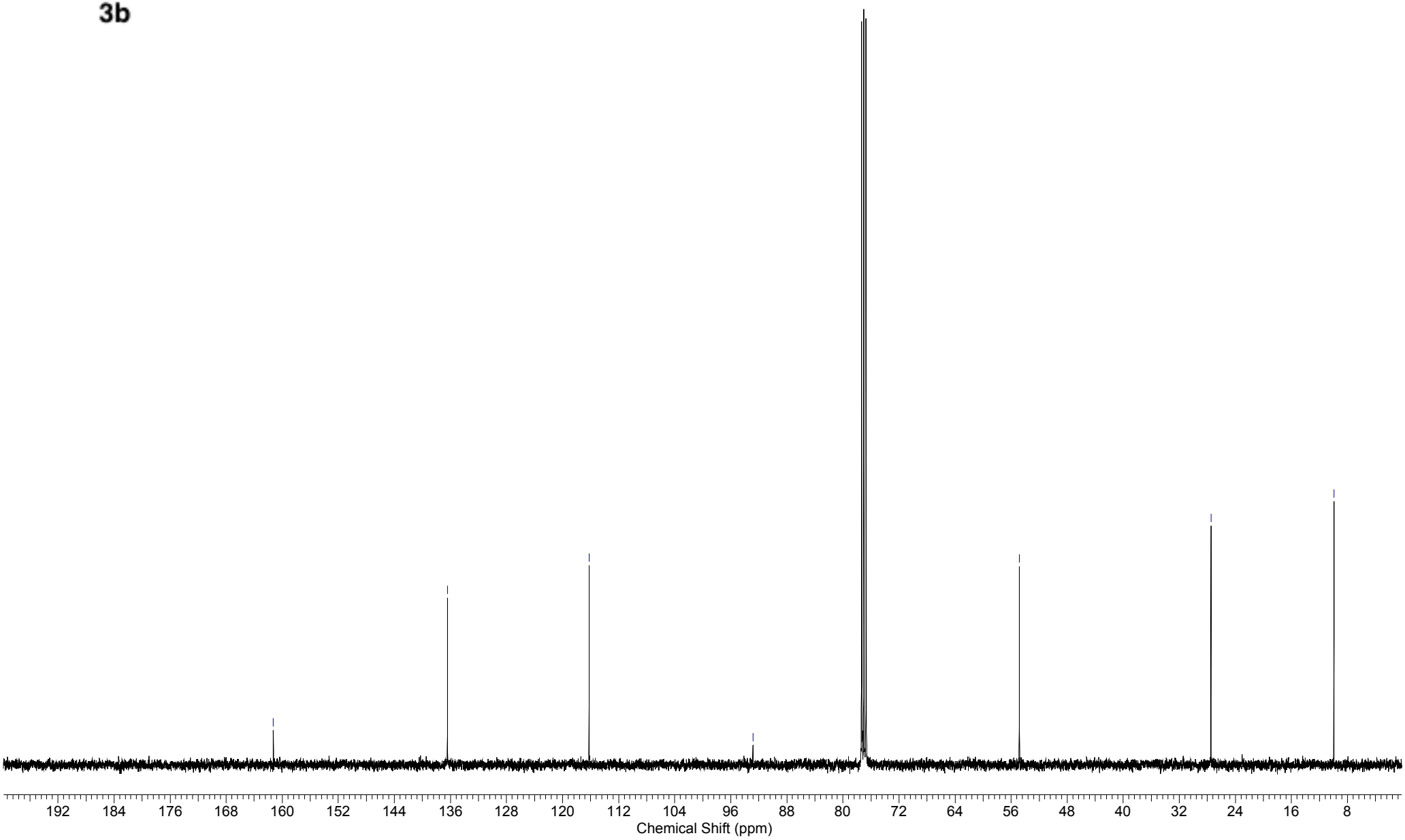

O
Cl3C
N
H

3b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184
176
168
160
152
144
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128
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96
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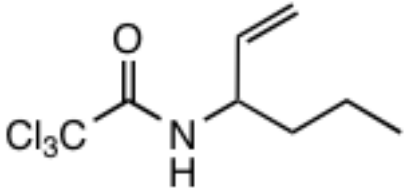
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


O
Cl3C
N
H

3c

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0
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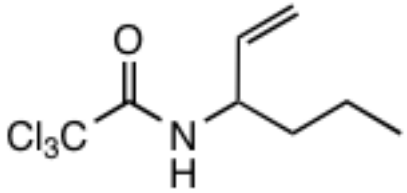

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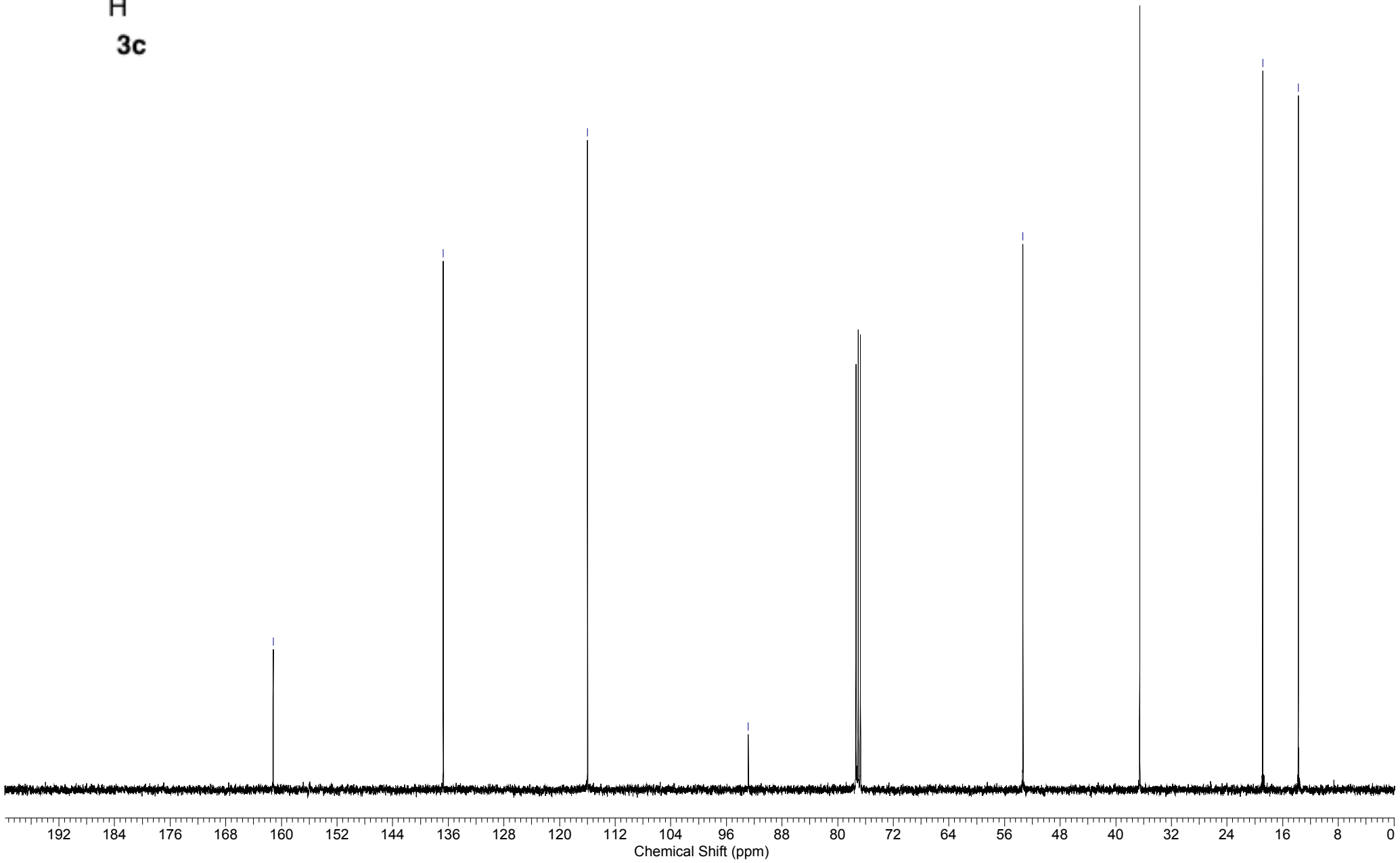

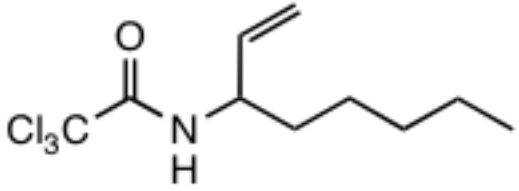

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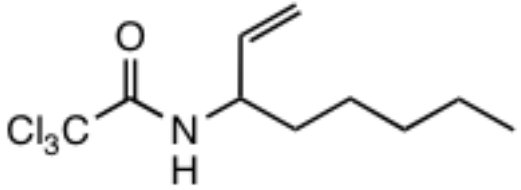

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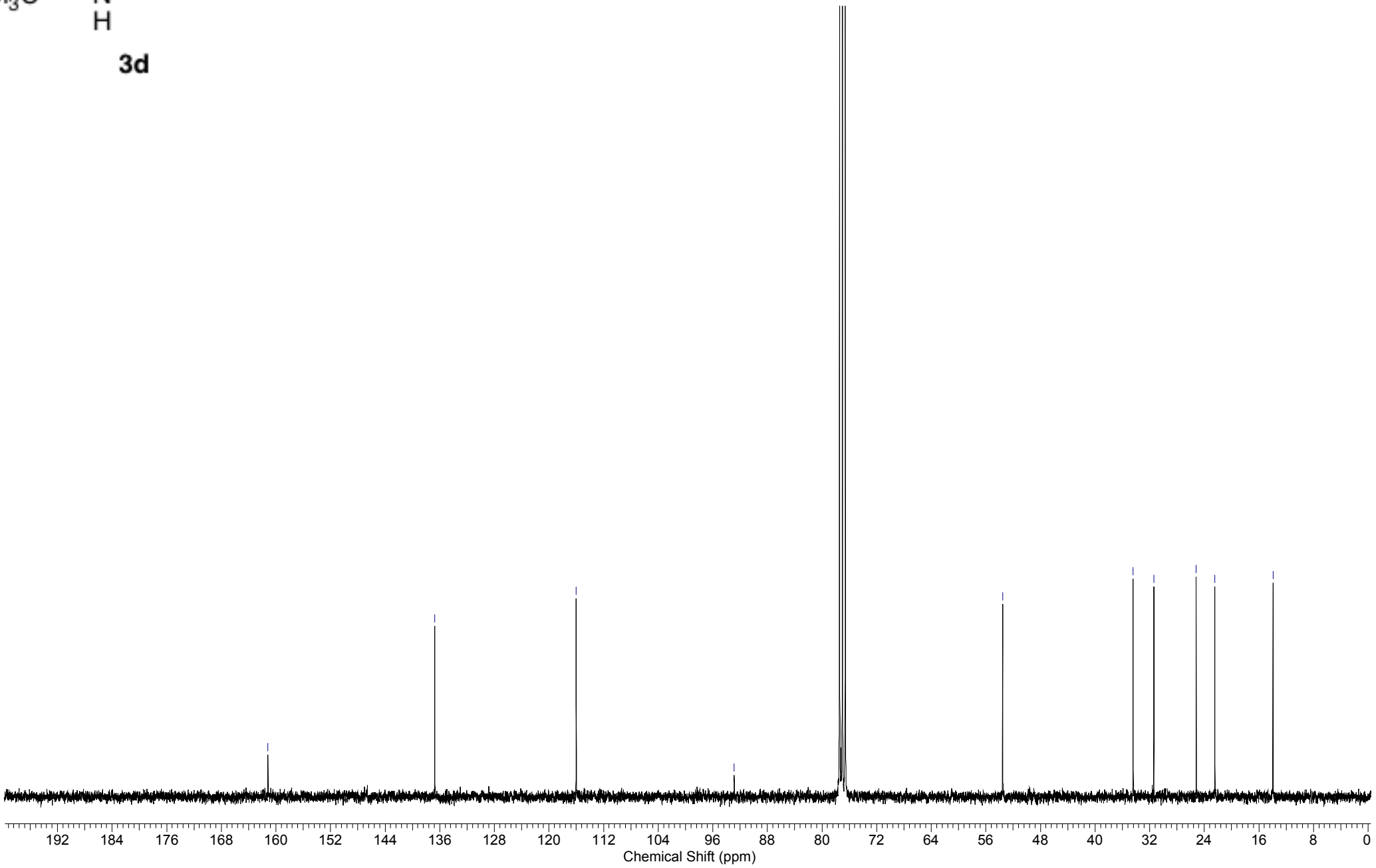

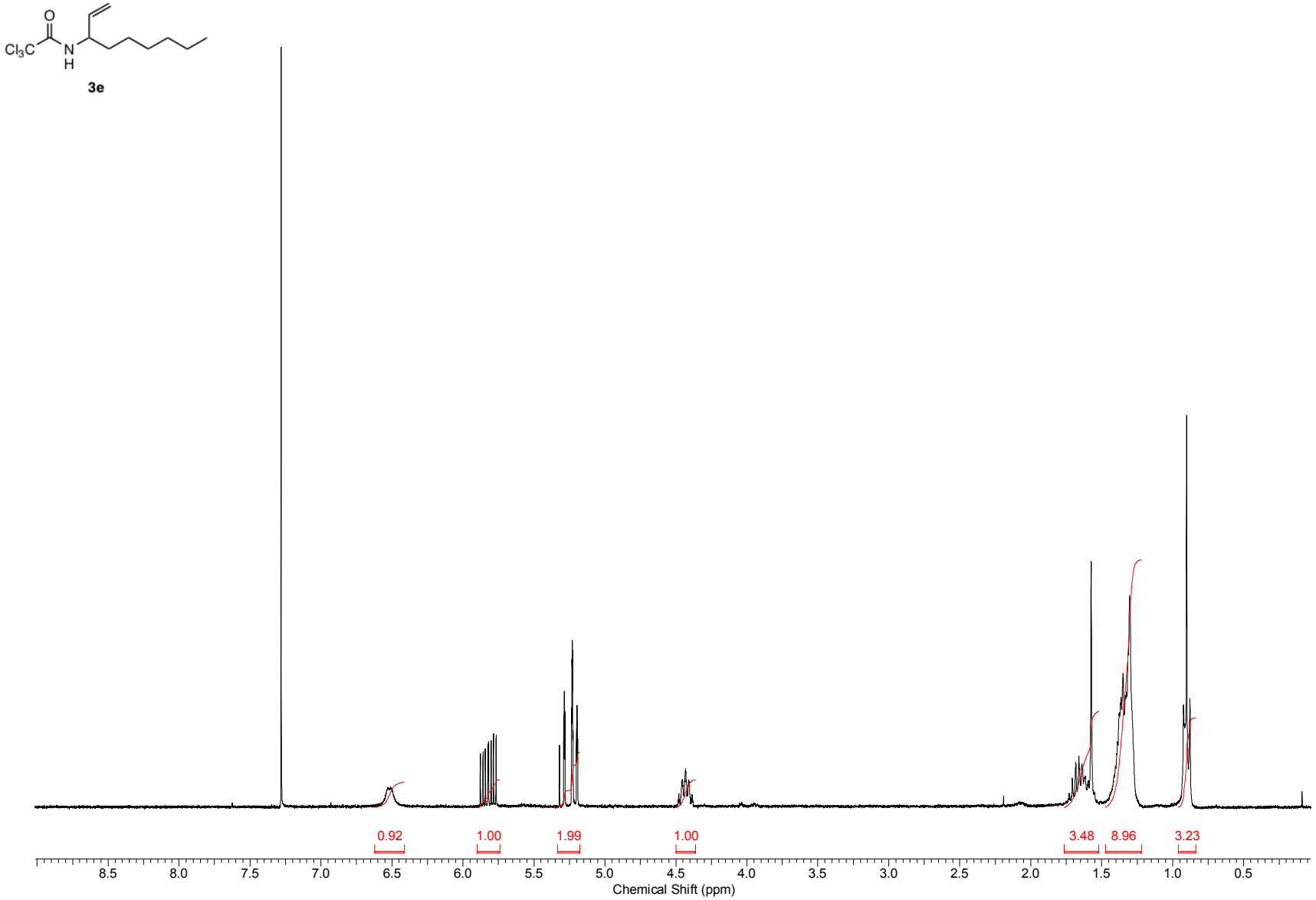

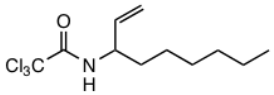

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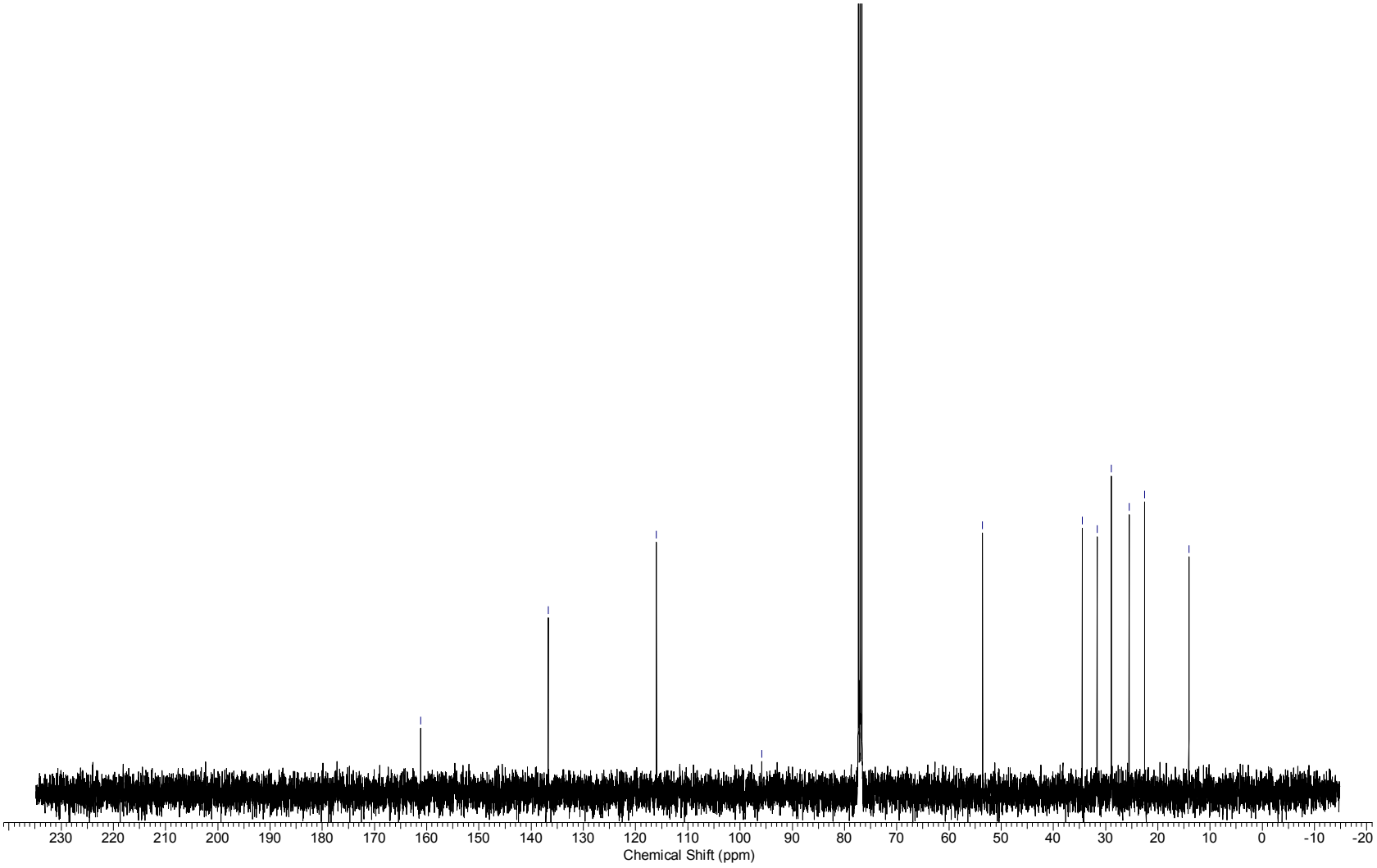

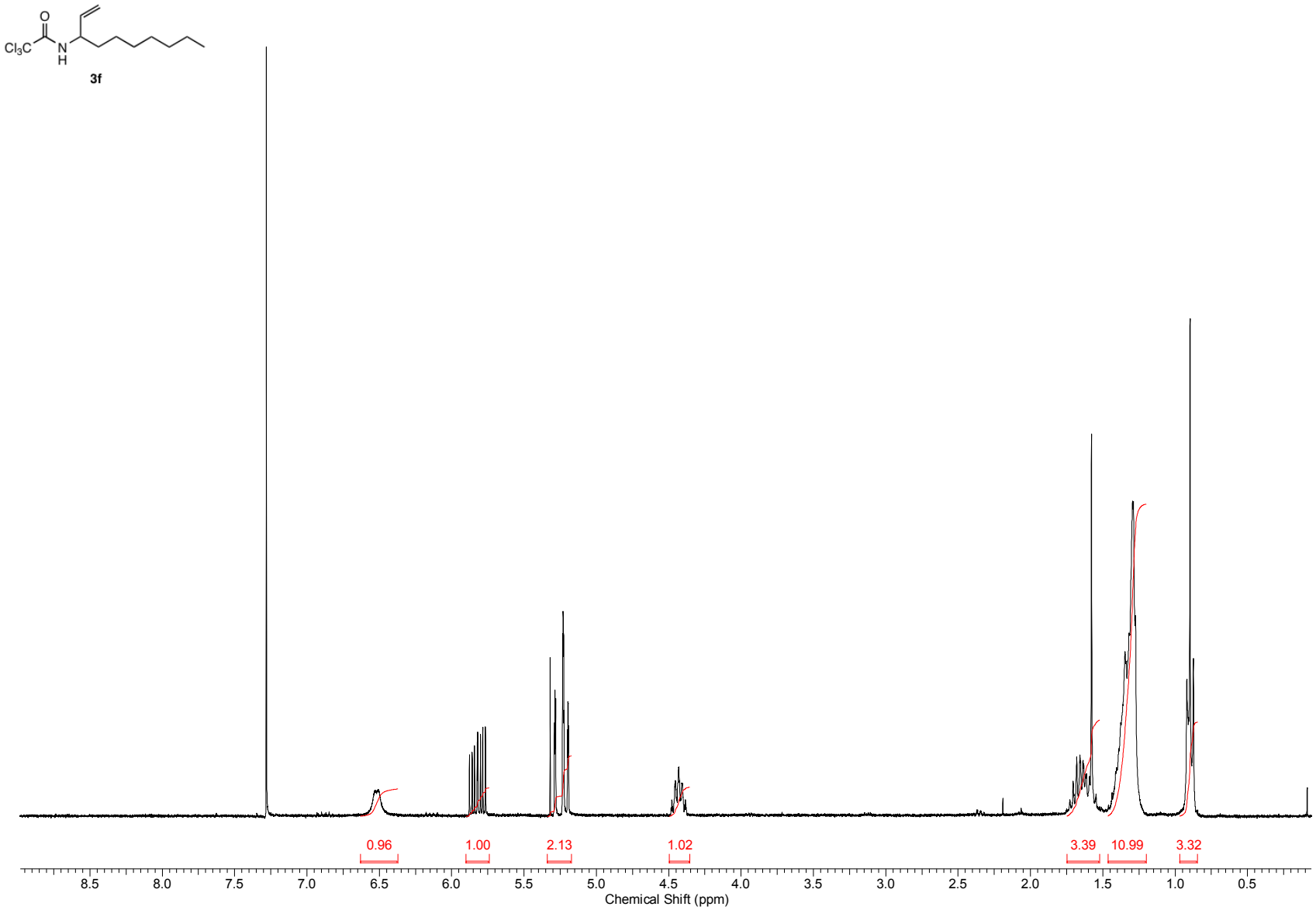

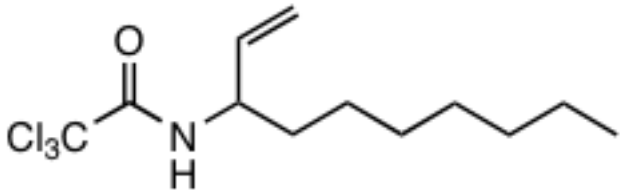

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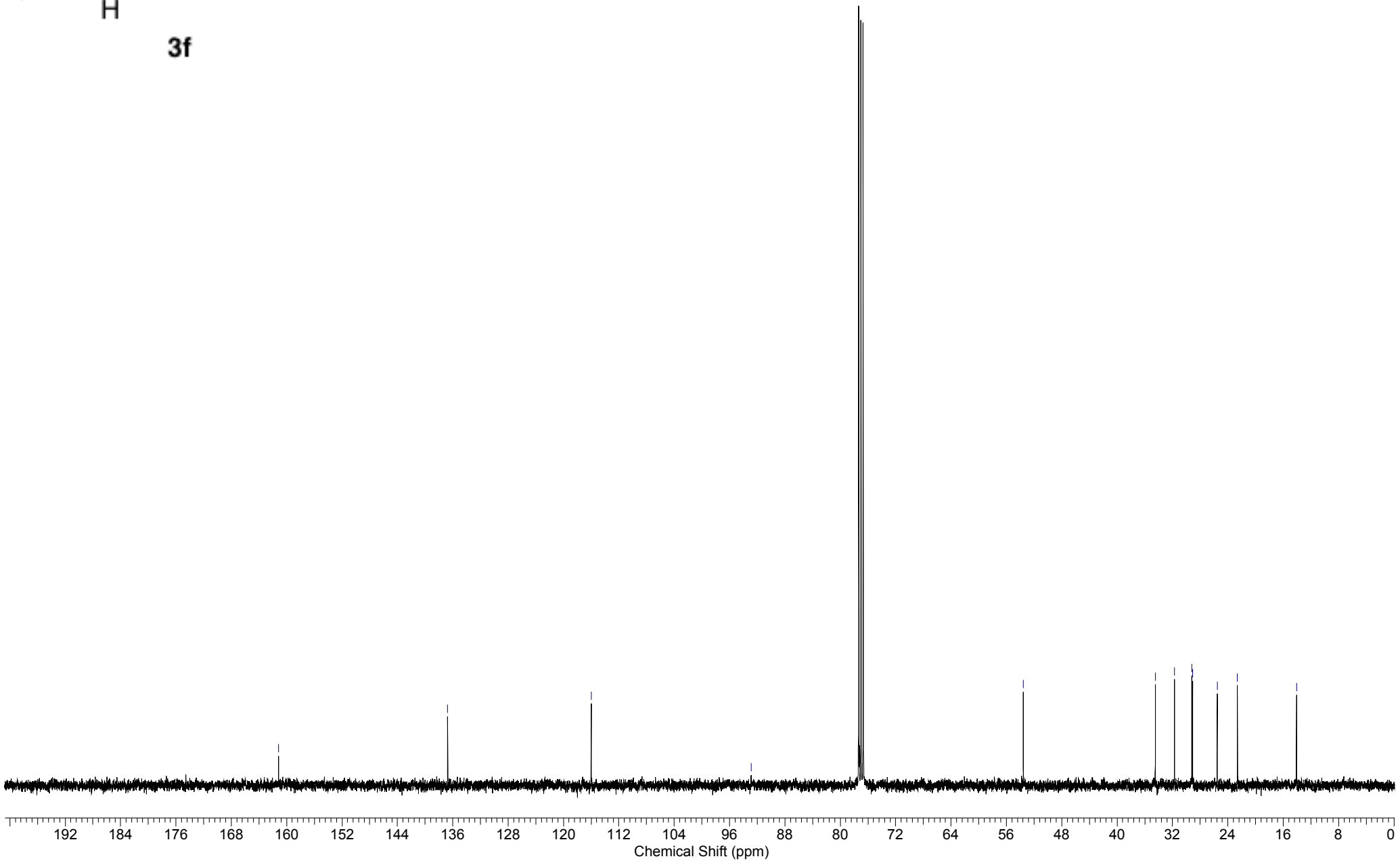

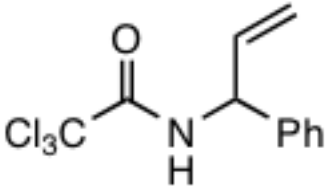

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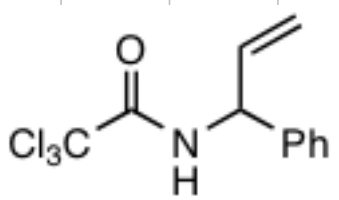

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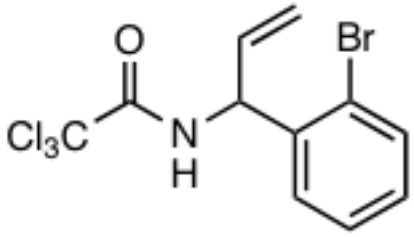

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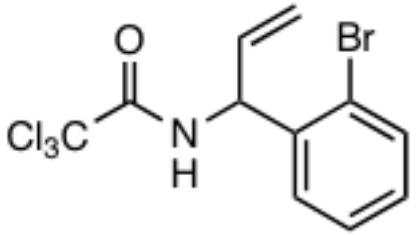

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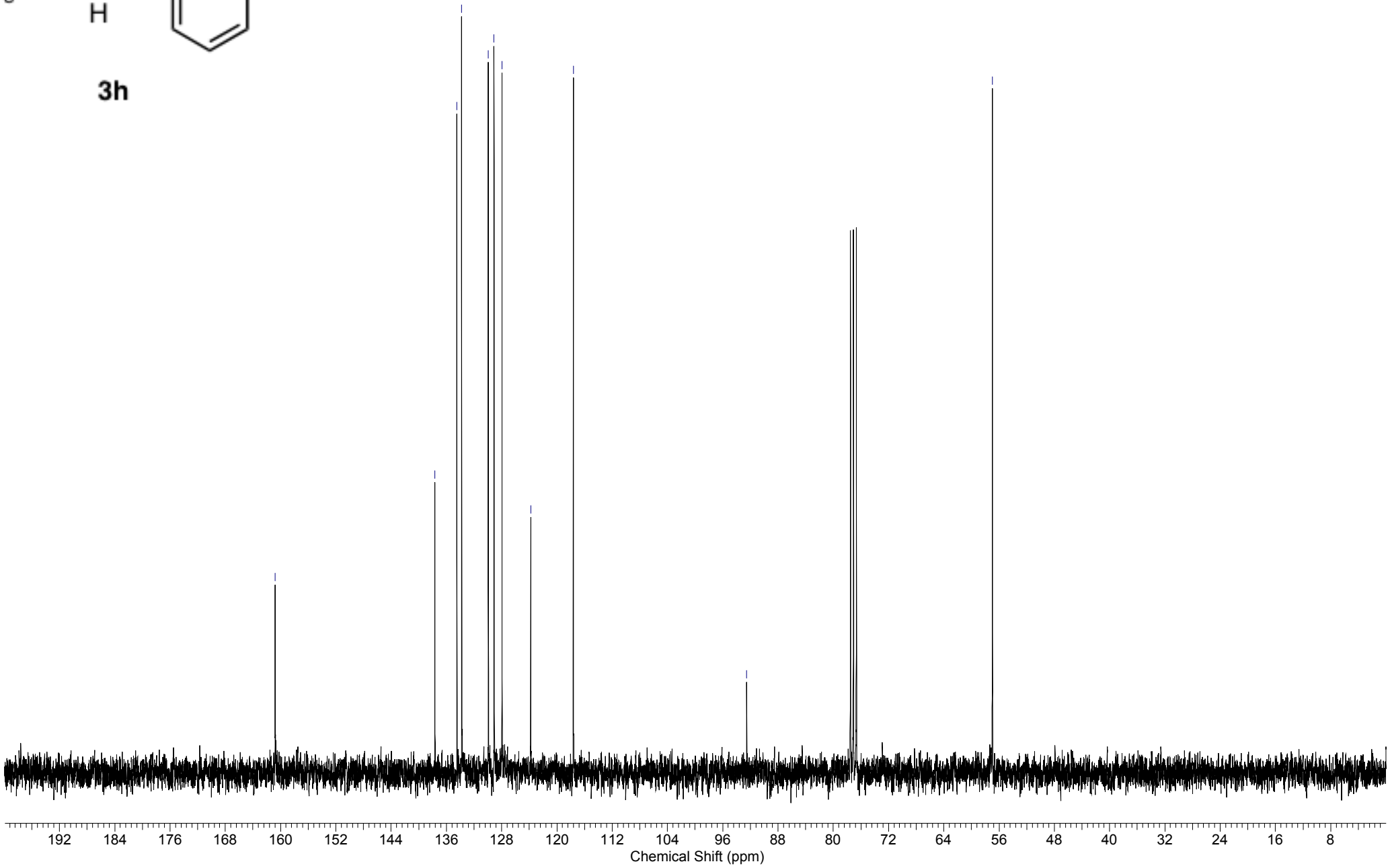

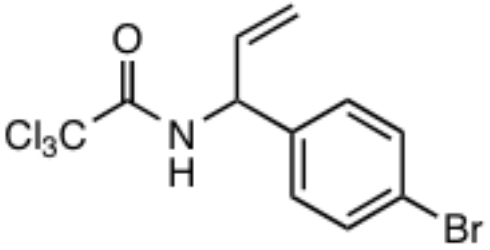

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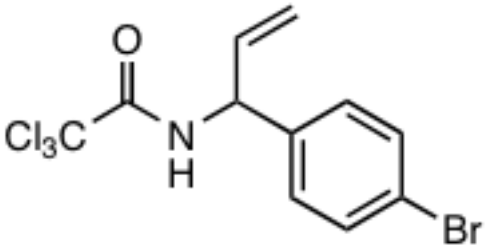

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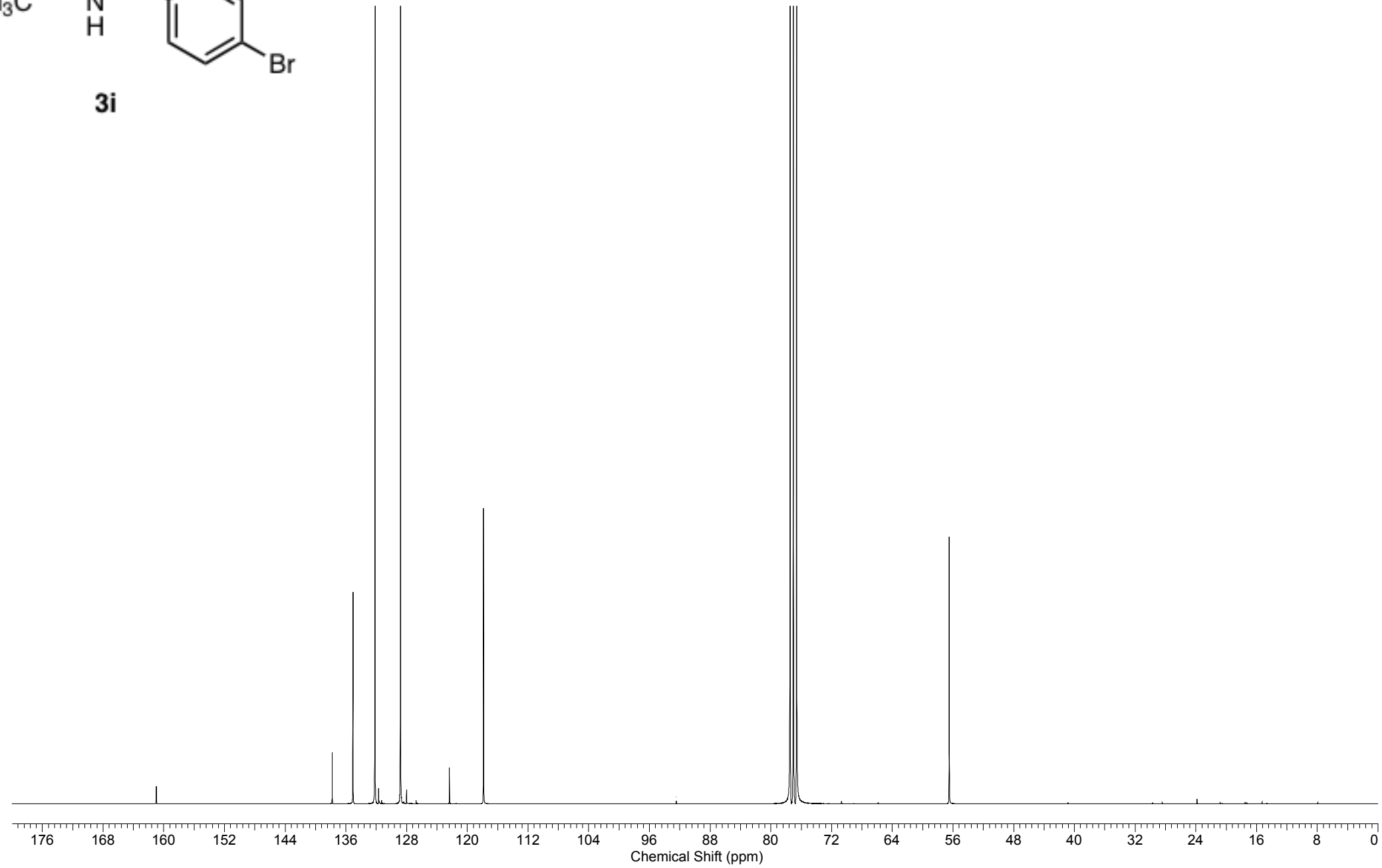

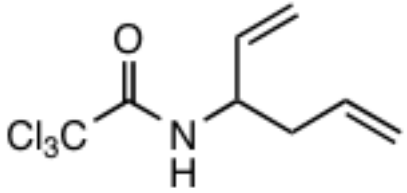

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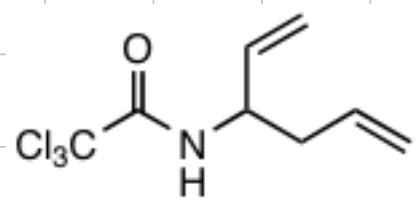

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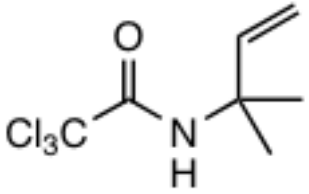

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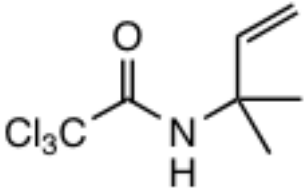

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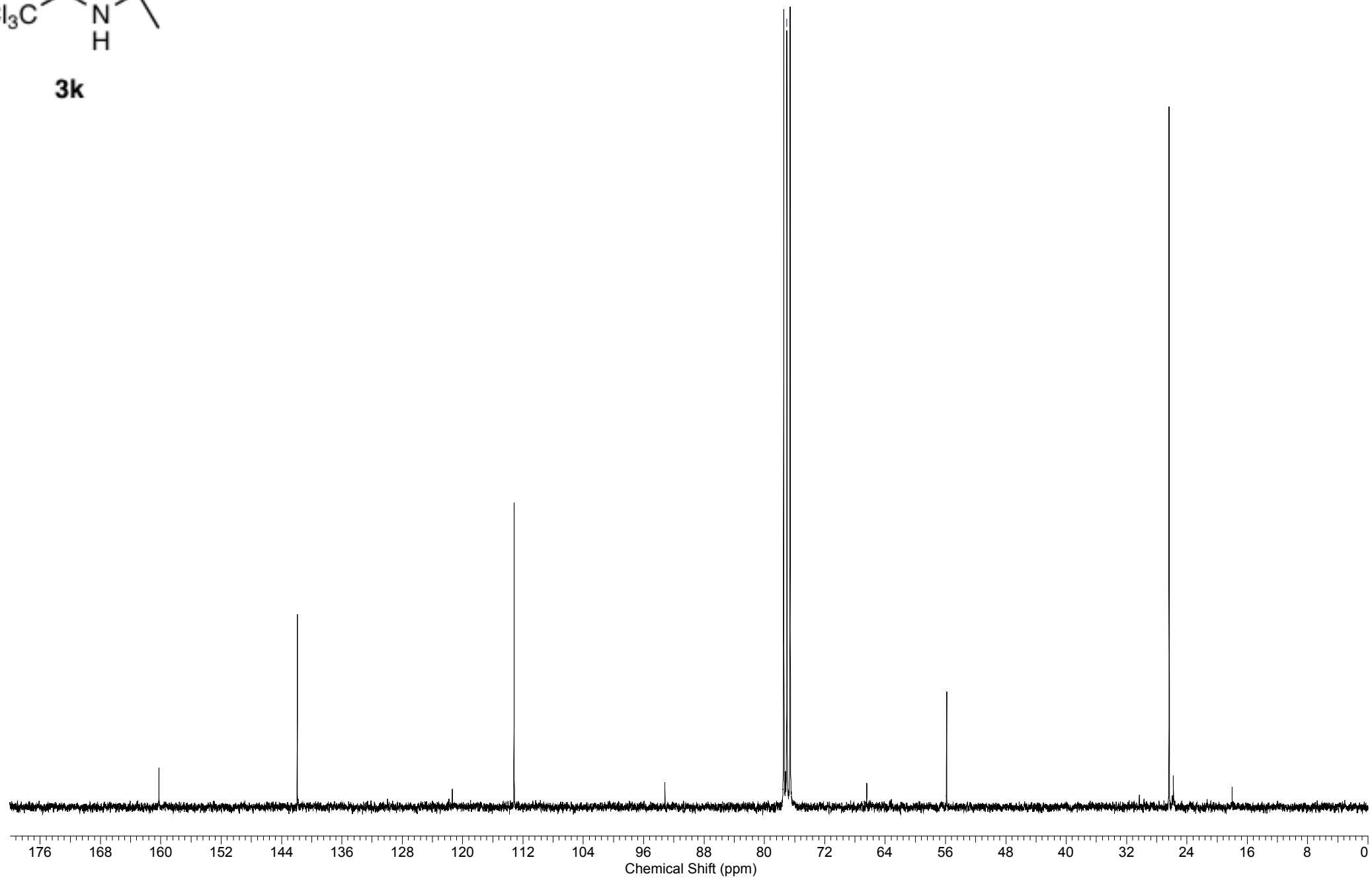
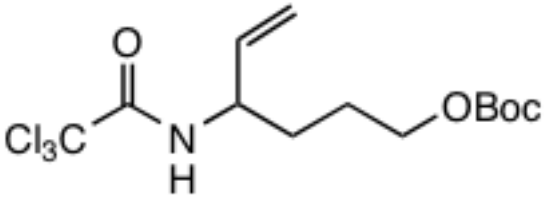
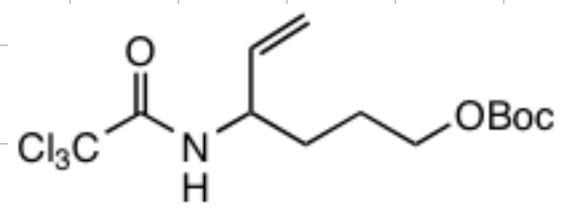



O
Cl3C
N
H
OBoc

3l

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



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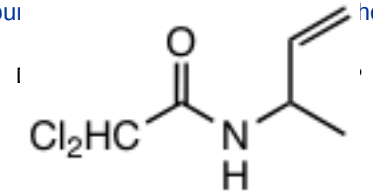
O
Cl2HC
N
H

4a

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.5
1.0
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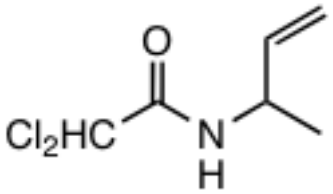
0
Chemical Shift (ppm)



4a