N-Heterocycles from Chromium Aminocarbenes.

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Supporting information

GENERAL CONSIDERATIONS

All reactions were performed under an inert atmosphere of argon in glassware that had been flame-dried. Solvents were distilled from potassium/benzophenone ketyl (THF, Et_2O), from calcium hydride (CH_2Cl_2, toluene, benzene, *m*-xylene, DMF, Et_3N).

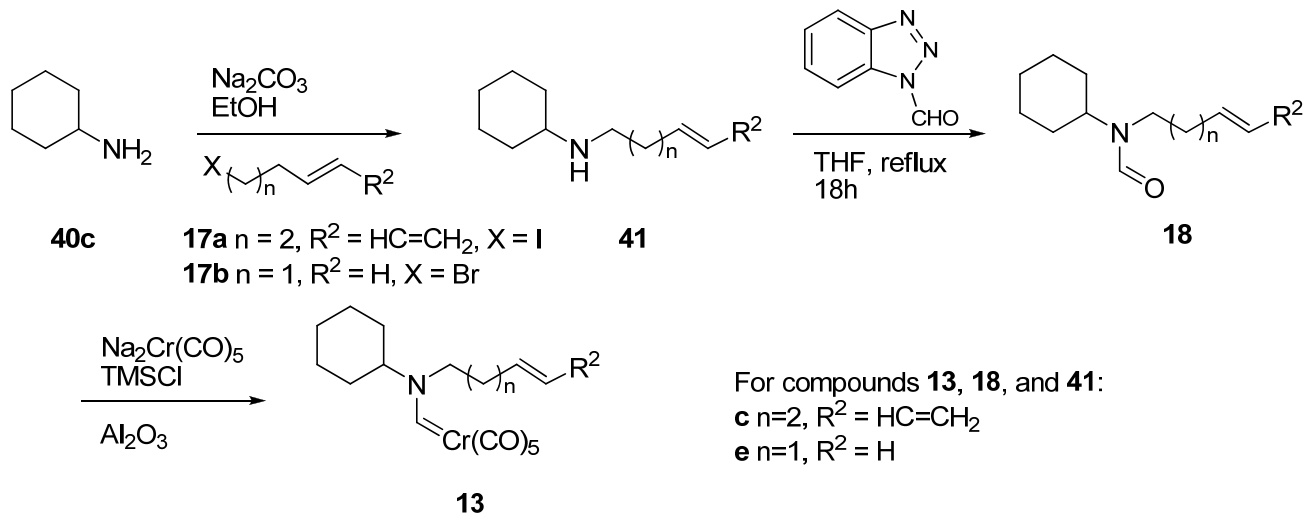
- ✓ $Cr(CO)_6$ (Aldrich or Strem) was reduced in a thin power and washed with anhydrous ethanol and ether. Naphtalene was recristallyzed in anhydrous ethanol.
- ✓ TMSCl was distilled from calcium hydride. Isobutylamine was distilled prior to use.

Aluminum oxide (Brockmann 1) came from Aldrich. Proton nuclear magnetic resonance (**^{1}H NMR**) spectra were recorded on a 300 MHz or 400 MHz spectrometer. NMR samples were dissolved in chloroform-*d* (unless specified otherwise) and chemical shifts are reported in ppm relative to the residual undeuterated solvent. Carbon nuclear magnetic resonance (**^{13}C NMR**) spectra were recorded on a 75.5 MHz or 100.7 MHz spectrometer. NMR samples were dissolved in chloroform-d (unless specified otherwise) and chemical shifts are reported in ppm relative to the solvent. LRMS analyses were performed on a GC system spectrometer (30 m length, 25µ OD, DB-5 ms column) coupled with a mass spectrometer. High-resolution spectrometry was performed by electrospray time-of-flight. Reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm silica gel coated glass plate UV 254, vanillin, $KMnO_4$, PMA, Dragen Dorff, or by **^{1}H NMR**. Silica gel (particule size: 230-400 mesh) was used for flash chromatography. Melting points are uncorrected.

SYNTHESIS OF CHROMIUM AMINOCARBENES

Synthesis of chromium aminocarbene 13a-b (see after the synthesis of 13c and 13e)

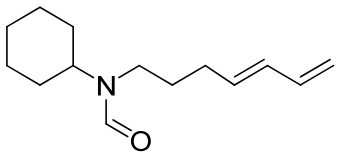
Synthesis of chromium aminocarbene 13c and 13e



40c **17a** n = 2, R^2 = HC=CH_2, X = I **41** **18**
17b n = 1, R^2 = H, X = Br

13

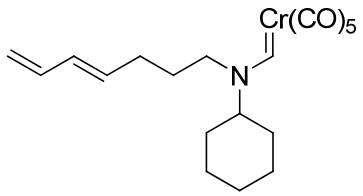
*(E)-N-cyclohexyl-N-(hepta-4,6-dien-1-yl)formamide (**18c**)*



Cyclohexylamine **40c** (6.24 mL, 54.5 mmol) was added to a solution of the iodide **17a** (4.04g, 18.2 mmol) and sodium carbonate (3.86 g, 36.4 mmol) in ethanol (226 mL). The reaction was refluxed for 20 h, cooled to rt and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel using a solution of methanol in DCM (10 to 30%). The secondary amine was isolated as a salt so it was dissolved in DCM, washed with 1N NaOH, dried over magnesium sulfate, filtered and evaporated under reduced pressure to afford amine **41c** (3.55 g, 92%), which was used directly in the next step without further characterisation. *N*-Formylbenzotriazole (3.51 g, 23.9 mmol) was added to a solution of the amine **41c** (3.55 g, 18.4 mmol) in THF (155 mL). The reaction mixture was heated to reflux temperature for 18 h. Then, 2 N NaOH (200 mL) was added at rt and the reaction mixture was stirred for 30 min. The mixture was extracted with dichloromethane (3 x 250mL). The combined organic layers were separated and dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by flash

chromatography on silica gel using a solution of ethyl acetate in hexanes (10:90 to 30:70) as eluent. The product (3.26 g, 80%) was obtained as pale yellow oil and as a mixture of rotamers (ratio = 73:27). **^{1}H NMR** (major rotamer) (300 MHz, $CDCl_3$) δ (ppm) 8.15 (s, 1H), 6.30 (dt, 1H, *J* = 16.9, 10.2 Hz), 6.07 (dd, 1H, *J* = 15.1, 10.2 Hz), 5.69 (dt, 1H, *J* = 15.1, 7.1 Hz), 5.09 (d, 1H, *J* = 16.9 Hz), 4.97 (d, 1H, *J* = 10.2 Hz), 3.24-3.17 (m, 3H), 2.10 (q, 2H, *J* = 7.2 Hz), 1.90-1.74 (m, 3H), 1.74-1.60 (m, 3H), 1.56-1.40 (m, 3H), 1.31 (qt, 2H, *J* = 12.5, 3.3 Hz), 1.11 (qt, 1H, *J* = 12.7, 3.3 Hz). **^{1}H NMR** (minor rotamer) (300 MHz, $CDCl_3$) δ (ppm) 8.04 (s, 1H), 6.30 (dt, 1H, *J* = 16.9, 10.2 Hz), 6.07 (dd, 1H, *J* = 15.1, 10.2 Hz), 5.64 (dt, 1H, *J* = 15.1, 6.8 Hz), 5.12 (d, 1H, *J* = 16.9 Hz), 5.00 (d, 1H, *J* = 10.2 Hz), 3.99 (tt, 1H, *J* = 11.8, 3.5 Hz), 3.18-3.13 (m, 2H), 2.10 (q, 2H, *J* = 7.2 Hz), 1.90-1.74 (m, 3H), 1.74-1.60 (m, 3H), 1.56-1.40 (m, 3H), 1.31 (qt, 2H, *J* = 12.5, 3.3 Hz), 1.11 (qt, 1H, *J* = 12.7, 3.3 Hz). **^{13}C NMR** (major rotamer) (100.7 MHz, $CDCl_3$) δ (ppm) 162.5 (d), 137.2 (d), 134.1 (d), 131.7 (d), 115.3 (t), 58.7 (d), 41.6 (t), 33.0 (t), 30.9 (t), 30.4 (t), 28.7 (t), 26.0 (t), 25.4 (t). **^{13}C NMR** (minor rotamer) (100.7 MHz, $CDCl_3$) δ (ppm) 163.2 (d), 136.9 (d), 133.2 (d), 132.3 (d), 115.8 (t), 52.9 (d), 44.7 (t), 33.0 (t), 31.2 (t), 29.7 (t), 28.7 (t), 26.0 (t), 25.6 (t). **IR** (neat) ν (cm^{-1}) 3010, 2932, 2856, 1670, 1004. **LRMS** (*m/z*, relative intensity) 244 (MNa^+, 100). **Exact Mass** calcd for $C_{14}H_{23}NNaO$: 244.1672, found: 244.1670.

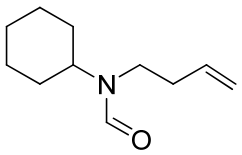
*(E)-Pentacarbonyl[(N-cyclohexyl-N-(hepta-4,6-dien-1-yl)amino)methylene]chromium(0) (**13c**)*



Naphtalene (4.63 g, 36.1 mmol) was added to small pieces of sodium (830 mg, 36.1 mmol) in a round-bottomed flask. Anhydrous THF (72 mL) was added and the reaction mixture was stirred at rt for 4 h. The dark green solution was added over 1.5 h, using a syringe pump, to a solution of purified (see general consideration above) $Cr(CO)_6$ (3.98 g, 18.1 mmol) in THF (217 mL) at -78 ºC. The CO_2/acetone cooling bath was removed and the reaction mixture was stirred at rt for 18 h. The dark orange solution was cooled back to -78 ºC and a solution of the formamide **18c** (2.00 g, 9.04 mmol) in THF (6 mL) was added over 3 min. The reaction mixture was stirred at -78 ºC for 30 min. The CO_2/acetone cooling bath was removed and the reaction mixture was warmed up to 0 ºC and maintained at that temperature while stirring for 1 h. The reaction mixture was cooled down again to -78 ºC and TMSCl (3.44 mL, 27.1 mmol) was rapidly added. The reaction mixture was stirred at -78 ºC

for an additional 30 min., neutral Al_2O_3 (29 g) was added and the reaction mixture was warmed up to rt. The solvent was evaporated under reduced pressure and the residue was charged on top of a silica gel column for chromatographic purification using a solution of ethyl acetate in hexanes (100% hexanes first to remove the residual naphthalene and then 5:95) as eluent. The product **13c** (3.23 g, 90%) was obtained as a pale yellow solid and as a mixture of rotamers (ratio = 66:34). **^{1}H NMR** (major rotamer) (400 MHz, $CDCl_3$) δ (ppm) 11.01 (s, 1H), 6.33 (dt, 1H, *J* = 17.0, 10.4 Hz), 6.12 (dd, 1H, *J* = 15.2, 10.4 Hz), 5.71 (dt, 1H, *J* = 15.2, 7.1 Hz), 5.15 (d, 1H, *J* = 17.0 Hz), 5.03 (d, 1H, *J* = 10.0 Hz), 3.99-3.94 (m, 2H), 3.39-3.33 (m, 1H), 2.25 (q, 2H, *J* = 7.2 Hz), 1.95-1.81 (m, 4H), 1.80-1.44 (m, 4H), 1.42-1.12 (m, 4H). **^{1}H NMR** (minor rotamer) (400 MHz, $CDCl_3$) δ (ppm) 10.86 (s, 1H), 6.31 (dt, 1H, *J* = 17.1, 10.3 Hz), 6.08 (dd, 1H, *J* = 15.3, 10.3 Hz), 5.63 (dt, 1H, *J* = 15.3, 6.9 Hz), 5.15 (d, 1H, *J* = 17.0 Hz), 5.03 (d, 1H, *J* = 10.0 Hz), 4.64 (tt, 1H, *J* = 11.8, 2.9 Hz), 3.41-3.36 (m, 2H), 2.10 (q, 2H, *J* = 7.2 Hz), 1.95-1.81 (m, 4H), 1.80-1.44 (m, 4H), 1.42-1.12 (m, 4H). **^{13}C NMR** (both rotamers) (100.7 MHz, $CDCl_3$) δ (ppm) 259.5 (d), 254.2 (d), 224.6 (s), 224.5 (s), 217.9 (s), 217.8 (s), 137.0 (d), 136.8 (d), 132.9 (d), 132.9 (d), 132.6 (d), 132.4 (d), 116.4 (t), 116.1 (t), 69.9 (d), 69.7 (d), 59.6 (t), 56.1 (t), 33.5 (t), 31.7 (t), 31.2 (t), 29.9 (t), 29.8 (t), 29.2 (t), 25.8 (t), 25.3 (t), 25.3 (t), 25.2 (t). note : some signals are missing because some signals of the two rotamers overlap. **IR** (neat) ν (cm^{-1}) 3037, 3009, 2939, 2861, 2054 2096-1760 (br), 1535, 1004. **LRMS** (*m/z*, relative intensity) 420 ($(MNa)^+$, 20), 392 ($(M+Na-CO)^+$, 10), 364 ($(M+Na-2CO)^+$, 100). **Exact Mass** calcd for $C_{19}H_{23}CrNNaO_5$: 420.0874, found: 420.0869.

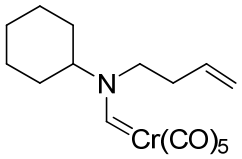
*N-cyclohexyl-N-(3-buten-1-yl)formamide (**18e**)*



Same procedure as per compound **18c** with *N*-cyclohexyl-*N*-(4-butenyl)amine **41e** (0.463 g, 3.02 mmol) in THF (25 mL), *N*-formylbenzotriazole (0.747 g, 5.08 mmol) giving formamide **18e** (0.423 g, 77%) as colorless oil and as a 3 : 1 mixture of rotamers. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.15 (s) and 8.03 (s) (1H, rotamers), 5.75 (m, 1H), 5.05 (app. m, 2H), 4.01 (m) and 3.24 (m) (2H, rotamers), 3.24 (app. m) and 2.31 (app. m) (4H, rotamers) 1.75 (complex m, 5H), 1.47 (m, 2H), 1.31 (m, 2H), 1.10 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) as a mixture of rotamers *δ* 163.2 (CH), 162.3 (CH),135.4 (CH), 134.3 (CH), 117.8 (CH_2), 116.6 (CH_2), 58.6 (CH), 52.5 (CH), 44.6 (CH_2), 41.4 (CH_2), 36.1 (CH_2), 33.5 (CH_2), 32.9 (CH_2), 30.8 (CH), 25.9 (CH), 25.5 (CH_2), 25.3 (CH_2); **IR** (NaCl) *v* 3076, 2931, 2856, 1668, 1451, 1416.

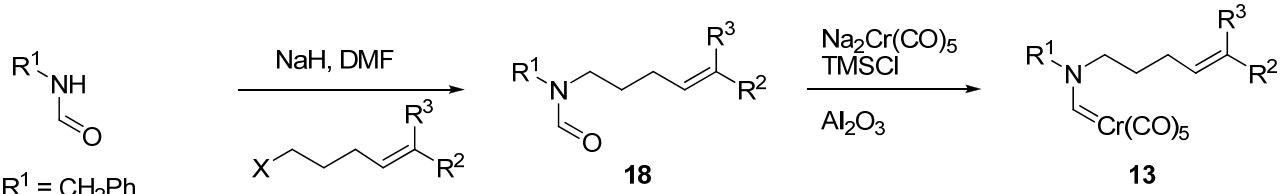
LRMS (*m/z*, relative intensity) 204 (MNa^+). **Exact Mass** calcd for $C_{11}H_{19}NONa$: 204.1359, found : 204.1361.

*Pentacarbonyl[(N-cyclohexyl-N-(3-buten-1-yl)amino)methylene]chromium(0) (**13e**)*



Following the same procedure described above as per the preparation of complex **13c**, the formamide **18e** (0.223 g, 0.625 mmol) was converted into the corresponding carbene **13e** (0.067 g, 30%), obtained as bright-yellow oil and as a 1:1 mixture of rotamers. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.03 (s) and 10.72 (s) (1H, rotamers), 5.88 (m) and 5.69 (m) (1H, rotamers), 5.15 (m, 2H), 4.66 (m) and 3.50 (m) (1H, rotamers), 4.06 (m) and 3.50 (m) (2H, rotamers), 2.57 (m) and 2.38 (m) (2H, rotamers) 2.00 - 1.85 (complex m) and 1.78 - 1.45 (6H, rotamers), 1.40 - 1.20 (m), 1.01 (m) and 0.95 - 0.85 (4H, rotamers); **^{13}C NMR** (100 MHz, $CDCl_3$) as a mixture of rotamers δ 260.0 (CH), 254.8 (CH), 224.3 (C), 224.2 (C), 217.6 (C), 217.6 (C), 133.4 (CH), 133.3 (CH), 119.1 (CH_2), 118.1 (CH_2), 69.8 (CH), 69.6 (CH), 59.0 (CH_2), 55.8 (CH_2), 35.5 (CH_2), 33.8 (CH_2), 33.3 (CH_2), 31.5 (CH_2), 25.7 (CH_2), 25.3 (CH_2); **IR** (NaCl) *v* 3085, 2935, 2856, 2056, 1991 to 1875, 1526. **LRMS** (*m/z*, relative intensity) 324 $(M\text{-}2CO)^+$. **Exact Mass** calcd for $C_{14}H_{19}CrNO_3Na$: 324.0662, found 324.0670.

Synthesis of chromium aminocarbene 13a, 13b, 13d and 13f-i

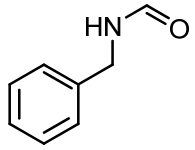


16a $R^1 = CH_2Ph$
16b $R^1 = CH_2$-*c*-C_6H_{11}
16c $R^1 = c$-C_6H_{11}
16d $R^1 = i$-Bu

17a $R^2 = HC{=}CH_2$, $R^3 = H$, X = I
17c $R^2 = H$, $R^3 = H$, X = Br
17d $R^2 = Me$, $R^3 = H$, X = I
17l $R^2 = R^3 = Me$, X = I

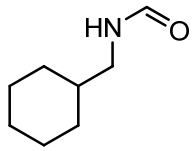
For compounds **13** and **18**:
a $R^1 = CH_2Ph$, $R^2 = HC{=}CH_2$, $R^3 = H$
b $R^1 = CH_2$-*c*-C_6H_{11}, $R^2 = HC{=}CH_2$, $R^3 = H$
d $R^1 = c$-C_6H_{11}, $R^2 = H$, $R^3 = H$
f $R^1 = i$-Bu , $R^2 = H$, $R^3 = H$
g $R^1 = t$-Bu , $R^2 = H$, $R^3 = H$
h $R^1 = t$-Bu , $R^2 = Me$, $R^3 = H$
l $R^1 = c$-C_6H_{11}, $R^2 = R^3 = Me$

*N-Benzylformamide (**16a**)*



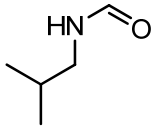
Synthesized following the procedure from Freudenreich and al.[1] ^{1}H NMR spectra identical to published data.[2] **M.P.** 56-58 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) as a mixture of rotamers δ (ppm) 8.28 (s) and 8.21 (d, *J* = 12.0 Hz) (1H, rotamers), 7.41-7.24 (m, 5H), 5.92-6.64 (br s, 1H), 4.50 (d, *J* = 6.0 Hz) and 4.43 (d, *J* = 6.5 Hz) (2H, rotamers).

*N-(Cyclohexylmethyl)formamide (**16b**)*



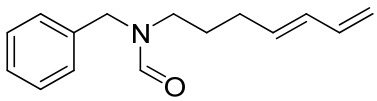
Formic acid (17.0 mL, 451 mmol) was slowly added to cyclohexanemethylamine (10.0 mL, 76.9 mmol) at 0 °C. The solution was refluxed for 7 h and then cooled to room temperature. The solution was concentrated under reduced pressure to produce an orange oil. The oil was dissolved in an aqueous saturated ammonium chloride solution and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed twice with saturated aqueous sodium bicarbonate and once with brine. It was dried over anhydrous magnesium sulphate, filtered and concentrated under reduced pressure to produce an orange oil. The crude product was purified by flash chromatography on a silica gel column eluting with 10% to 60% of ethyl acetate in hexanes to yield **81** (6.07 g, 56%) as a colorless oil. ^{1}H NMR spectra identical to published data.[3] **^{1}H NMR** (300 MHz, $CDCl_3$) as a 3.4 : 1.0 mixture of rotamers δ (ppm) 8.19 (s) and 7.99 (d, *J* = 11.6 Hz) (1H, rotamers), 5.60 (br s, 1H), 3.14 (t, *J* = 6.6 Hz) and 3.04 (t, *J* = 6.6 Hz) (2H, rotamers), 1.79-1.65 (m, 5H), 1.55-1.32 (m, 1H), 1.31-1.06 (m, 3H), 1.02-0.83 (m, 2H).

*N-Isobutylformamide (**16d**)*



N-Isobutylamine (12.0 mL, 119 mmol) and ethyl formate (184 mL, 2.29 mol) were heated to reflux for 12 h. The solution was cooled to rt and concentrated under reduced pressure to yield (12.1 g, 100%) of product **16d** as colorless oil and as a 2.9 : 1.0 mixture of rotamers. It was used crude in the next step without further purification. It's proton NMR spectra was identical to published data.[4] **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 8.20 (s) and 8.01 (d, J = 21.1 Hz) (1H, rotamers), 5.59 (br s, 1H), 3.14 (t, J = 6.6 Hz) and 3.03 (t, J = 6.6 Hz) (2H, rotamers), 1.80 (m, J = 6.6 Hz) and 1.75 (m, J = 6.6 Hz) (1H, rotamers), 0.93 (d, 6H, J = 6.6 Hz).

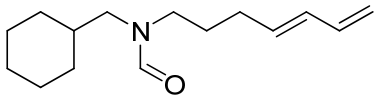
*(E)-N-(Benzyl)-N-(hepta-4,6-dienyl)formamide (**18a**)*



Sodium hydride (2.76 g, 60% in mineral oil, 69.0 mmol) was added to a solution of *N*-benzylformamide (9.09 g, 67.3 mmol) in tetrahydrofuran (155 mL) and dimethylformamide (80 mL) at 0 °C. The reaction was warmed to room temperature and stirred for 40 min. A solution of iodide **17a** (11.9 g, 53.8 mmol) in tetrahydrofuran (26 mL) was then added via cannula. The resulting mixture was heated at 35 °C for 150 min. The reaction mixture was cooled to room temperature and water (350 mL) was added. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried over anhydrous magnesium sulphate, filtered and concentrated under reduced pressure. The resulting yellowish oil was dissolved in diethyl ether and the organic layer was washed with brine three times, dried over anhydrous magnesium sulphate, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on a silica gel column eluting with 10% to 50% of diethyl ether in hexanes to yield **18a** (10.3 g, 84%) as colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) as a 1.2 : 1.0 mixture of rotamers δ (ppm) 8.28 (s) and 8.18 (s) (1H, rotamers), 7.40-7.19 (m, 5H), 6.28 (ddd, 1H, J = 16.8, 9.8, 9.8 Hz), 6.03 (dd, 1H, J = 14.8, 9.8 Hz), 5.68-5.53 (m, 1H), 5.11 (d, J = 16.8 Hz) and 5.08 (d, J = 16.8 Hz) (1H, rotamers), 5.00 (d, J = 9.9 Hz) and 4.97 (d, J = 9.9) (1H, rotamers), 4.54 (s) and 4.39 (s) (2H, rotamers), 3.23 (t, J = 7.3 Hz) and 3.14 (t, J = 7.3 Hz) (2H, rotamers), 2.05 (q, 2H, J = 7.3 Hz), 1.61 (quint, 2H, J = 7.3 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) as a mixture of rotamers δ (ppm)162.9 (d), 137.0 (d), 136.7 (d), 136.4 (s), 136.1 (s),

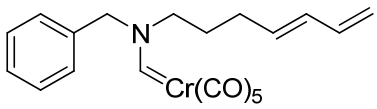
133.6 (d), 132.8 (d), 132.2 (d), 131.6 (d), 128.9 (d), 128.6 (d), 128.1 (d), 128.1 (d), 127.6 (d), 127.5 (d), 115.8 (t), 115.2 (t), 51.3 (t), 46.0 (t), 45.1 (t), 41.6 (t), 29.7 (t), 29.1 (t), 27.3 (t), 26.3 (t). **IR** (neat) ν (cm^{-1}) 3086, 3063, 3030, 3006, 2930, 2864, 1672, 1428, 1005. **LRMS** (*m/z*, relative intensity): 229 (M^+, 96), 148 (58), 90 (100). **HRMS** calcd for $C_{15}H_{19}NO$: 229.1467, found: 229.1469.

*(E)-N-(Cyclohexylmethyl)-N-(hepta-4,6-dienyl)formamide (**18b**)*



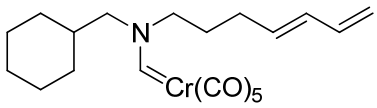
Sodium hydride (441 mg, 60% in mineral oil, 11.0 mmol) was added to a solution of *N*-(cyclohexylmethyl)formamide **16a** (1.07 g, 7.57 mmol) in tetrahydrofuran (18 mL) and dimethylformamide (10 mL) at 0 ºC. The reaction mixture was warmed to rt and stirred for 40 min. A solution of iodide **17a** (1.52 g, 6.84 mmol) in tetrahydrofuran (3 mL) was then added *via* cannula. The resulting mixture was heated to 45-50 °C for 2.5 h. The reaction mixture was cooled to rt and a saturated aqueous ammonium chloride solution was added. The mixture was diluted with a 1 : 1 solution of water and saturated aqueous ammonium chloride. The aqueous layer was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The resulting yellowish oil was dissolved in diethyl ether and the organic layer was washed twice with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on a silica gel column eluting with 15% to 30% of ethyl acetate in hexanes to yield **18b** (1.12 g, 69%) as colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) as a 1.5 : 1.0 mixture of rotamers δ (ppm) 8.08 (s) and 7.98 (s) (1H, rotamers), 6.31 (dt, 1H, *J* = 16.9, 9.0 Hz), 6.07 (dd, 1H, *J* = 15.1, 9.0 Hz), 5.69 (dt, *J* = 15.1, 7.1 Hz) and 5.64 (dt, *J* = 15.1, 7.1 Hz) (1H, rotamers), 5.12 (d, *J* = 16.9 Hz) and 5.10 (d, *J* = 16.9 Hz) (1H, rotamers), 5.01 (d, *J* = 9.0 Hz) and 4.98 (d, *J* = 9.0 Hz) (1H, rotamers), 3.28 (t, *J* = 7.4 Hz) and 3.20 (t, *J* = 7.2 Hz) (2H, rotamers), 3.15 (d, *J* = 7.2 Hz) and 3.00 (d, *J* = 7.7 Hz) (2H, rotamers), 2.10 (q, *J* = 7.1 Hz) and 2.09 (q, *J* = 7.1 Hz) (2H, rotamers), 1.79-1.45 (m, 8H), 1.30-1.11 (m, 3H), 1.01-0.77 (m, 2H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) (mixture of rotamers unresolvable) δ (ppm) 163.3 (d), 163.2 (d), 137.2 (d), 137.0 (d), 134.0 (d), 133.2 (d), 132.4 (d), 131.8 (d), 116.0 (t), 115.5 (t), 54.3 (t), 48.1 (t), 47.3 (t), 42.6 (t), 36.2 (d), 35.8 (d), 31.0 (t), 30.8 (t), 30.2 (t), 29.5 (t), 28.0 (t), 26.9 (t), 26.6 (t), 26.6 (t), 26.0 (t), 25.9 (t). **IR** (neat) ν (cm^{-1}) 2926, 2852, 1674, 1430. **LRMS** (*m/z*, relative intensity): 235 (M^+, 32), 152 ($(M-C_6H_{11})^+$, 100), 94 (55), 79 (63). **Exact Mass** calcd for $C_{15}H_{25}NO$: 235.1936, found: 235.1933.

*(E)-Pentacarbonyl[(N-(benzyl)-N-(hepta-4,6-dienyl)amino)methylene]chromium(0) (**13a**)*



Same procedure as per the preparation of complex **13c**, $Cr(CO)_6$ (3.85 g, 17.5 mmol), formamide **18a** (2.05 g, 8.98 mmol) yielded **13a** (2.32 g, 64%), as yellowish oil and as a 1.07 : 1.00 (*Z* : *E*) mixture of rotamers. **^{1}H NMR** (300 MHz, CDCl3) as a 1.07 : 1.00 (*Z* : *E*) mixture of rotamers δ (ppm) 11.11 (s) and 11.07 (s) (1H, rotamers), 7.46-7.36 (m, 3H), 7.30 (dd, *J* = 7.1, 1.1 Hz) and 7.13 (dd, *J* = 6.9, 1.7 Hz) (2H, rotamers), 6.30 (dt, *J* = 16.8, 10.3 Hz) and 6.28 (dt, *J* = 16.8, 10.3 Hz) (1H, rotamers), 6.06 (dt, 1H, *J* = 14.8, 10.3 Hz), 5.66 (dt, *J* = 14.8, 7.2 Hz) and 5.54 (dt, *J* = 14.8, 7.1 Hz) (1H, rotamers), 5.24 (s) and 4.76 (s) (2H, rotamers), 5.13 (dd, 1H, *J* = 16.8, 3.3 Hz), 5.02 (dd, 1H, *J* = 10.3, 3.3 Hz), 3.92-3.85 (m) and 3.42 (t, *J* = 7.1 Hz) (2H, rotamers), 2.20 (q, *J* = 7.2 Hz) and 2.02 (q, *J* = 7.1 Hz) (2H, rotamers), 1.97-1.86 (m) and 1.71 (quint, *J* = 7.1 Hz) (2H, rotamers). **^{13}C NMR** (75.5 MHz, $CDCl_3$) as a mixture of rotamers δ (ppm) 265.4 (d), 265.1 (d), 223.8 (s), 223.7 (s), 217.4 (s), 217.3 (s), 136.6 (d), 136.4 (d), 133.6 (s), 133.5 (s), 132.7 (d), 132.3 (d), 131.7 (d), 129.3 (d), 129.2 (d), 128.9 (d), 128.7 (d), 127.7 (d), 127.3 (d), 116.3 (t), 115.9 (t), 68.7 (t), 62.6 (t), 60.7 (t), 56.1 (t), 29.4 (t), 28.8 (t), 27.9 (t), 27.5 (t). **IR** (neat) ν (cm^{-1}) 2055, 1973, 1910, 1516, 1453. **LRMS** (*m/z*, relative intensity): 405 (M^+, 3), 349 ($[M-(CO)_2]^+$, 5), 321 ($[M-(CO)_3]^+$, 7), 265 ($[M-(CO)_5]^+$, 34), 213 ($[M-Cr(CO)_5]^+$, 74), 173 (64), 91 (100). **HRMS** calcd for $C_{20}H_{19}CrNO_5$: 405.0668, found: 405.0659.

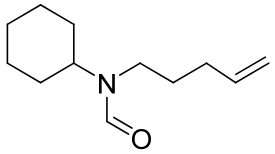
*(E)-Pentacarbonyl[(N-(cyclohexylmethyl)-N-(hepta-4,6-dienyl)amino)methylene]chromium(0) (**13b**)*



Same procedure as per the preparation of complex **13c**, $Cr(CO)_6$ (2.07 g, 9.41 mmol) in tetrahydrofuran (120 mL), formamide **18b** (1.11 g, 4.72 mmol) yielded carbene **13b** (1.78 g, 92%) obtained as yellowish oil and as a 3.6 : 1.0 (*E* : *Z*) mixture of rotamers. **^{1}H NMR** (300 MHz, $CDCl_3$) as a 3.6 : 1.0 (*E* : *Z*) mixture of rotamers δ (ppm) 10.93 (s) and 10.72 (s) (1H, rotamers), 6.33 (dt, *J* = 17.0, 10.1 Hz) and 6.31 (dt, 17.0, 10.1 Hz) (1H, rotamers), 6.12 (dd, *J* = 14.9, 10.1 Hz) and 6.08 (dd, *J* = 14.9, 10.1 Hz) (1H, rotamers), 5.70 (dt, *J* = 14.9, 7.2 Hz) and 5.61 (dt, *J* = 14.9, 7.2 Hz) (1H, rotamers), 5.14 (d, 1H, *J* = 17.0 Hz), 5.03 (d, 1H, *J* = 10.1 Hz), 3.93-3.87 (m) and 3.55 (t, *J* = 7.2 Hz) (2H, rotamers), 3.82

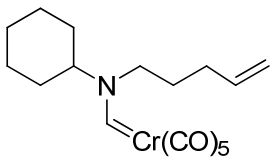
(d, *J* = 7.7 Hz) and 3.39 (d, *J* = 7.0 Hz) (2H, rotamers), 2.24 (q, *J* = 7.2 Hz) and 2.06 (q, *J* = 7.2 Hz) (2H, rotamers), 1.93-1.54 (m, 8H), 1.33-0.79 (m, 5H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) (mixture of rotamers unresolvable) δ (ppm) 263.2 (d), 262.4 (d), 224.2 (s), 224.2 (s), 218.0 (s), 217.8 (s), 136.9 (d), 136.7 (d), 133.1 (d), 132.7 (d), 132.6 (d), 132.1 (d), 116.6 (t), 116.2 (t), 70.9 (t), 64.0 (t), 62.2 (t), 57.1 (t), 36.8 (d), 36.4 (d), 30.5 (t), 30.4 (t), 29.8 (t), 29.1 (t), 28.4 (t), 28.0 (t), 26.3 (t), 26.3 (t), 26.1 (t), 25.8 (t). **IR** (neat) ν (cm^{-1}) 2930, 2854, 2055, 1973, 1910, 1522. **LRMS** (*m/z*, relative intensity): 411 (M^+, 1), 271 ($(M-(CO)_5)^+$, 8), 219 ($(M-Cr(CO)_5)^+$, 69), 136 ($(M-C_6H_{11}Cr(CO)_5)^+$, 100). **Exact Mass** calcd for $C_{20}H_{25}NO_5Cr$: 411.1138, found: 411.1130.

*N-Cyclohexyl-N(4-penten-1-yl)formamide (**18d**)*



Following the same procedure as per **18b**, NaH (17.16 mmol, 60% in mineral oil) in THF and DMF (57 mL 2:1 ratio, 0.3 M), *N*-cyclohexylformamide **16c** (1.74 mL, 13.2 mmol), alkyl iodide **17c** (2.59 g, 13.2 mmol) gave the desired formamide **18d** (1.26 g, 70%) as colourless oil and as a 2:1 mixture of two rotamers. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.13 (s) and 8.03 (s) (1H, rotamers), 5.78 (m, 1H), 5.07-4.92 (m, 2H), 3.97 (m) and 4.23-3.11 (m) (4H, rotamers), 2.05 (m, 2H), 1.87-1.57 (m, 6H), 1.46 (m, 2H), 1.31 (m, 2H), 1.11 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) as a mixture of rotamers *δ* 163.0 (d), 162.3 (d),137.7 (d), 137.0 (d), 115.6 (t), 114.9 (t), 58.5 (d), 52.6 (d), 44.4 (t), 41.4 (t), 32.8 (t), 31.3 (t), 30.6 (t), 28.0 (t), 25.8 (t), 25.4 (t), 25.1 (t); **IR** (NaCl) *v* 3474, 3076, 2930, 1663. **LRMS** (*m/z*, relative intensity) 218 (MNa^+). **Exact Mass** calcd for $C_{12}H_{21}NONa$: 218.1521, found : 218.1524.

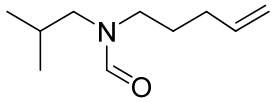
*Pentacarbonyl[(N-cyclohexyl-N-(4-penten-1-yl)amino)methylene]chromium(0) (**13d**)*



Following the same procedure described above as per the preparation of complex **13c**, the formamide **18d** (0.488 g, 2.50 mmol) was converted into the corresponding carbene **13d** (0.784 g, 84%), as a bright-yellow solid and as a 3:1 mixture of rotamers. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 10.99 (s) and 10.85

(s) (rotamers, 1H), 5.84 (m, 1H), 5.10 (d, 1H), 5.06 (d, J = 10.8 Hz, 1H), 4.63 (t, J = 11.5 Hz) and 3.38 (t, J = 8.5 Hz) (rotamers, 2H), 3.96 (m, 2H), 2.21 (m, 2H), 2.06 (m, 1H), 1.95-1.80 (complex m, 4H), 1.70 (m, 2H), 1.66-1.46 (complex m, 1H), 1.33 (m, 3H), 1.17 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) as a mixture of rotamers δ 224.2 (CO), 217.7 (CO), 136.7 (CH), 116.1 (CH_2), 69.7 (CH), 59.3 (CH_2), 55.7 (CH_2), 33.3 (CH_2), 31.5 (CH_2), 30.8 (CH_2), 28.6 (CH_2), 25.5 (CH_2), 24.9 (CH_2); **IR** (NaCl) ν 3085, 2938, 2860, 2054, 1915, 1532. **Exact Mass** calcd for $C_{15}H_{21}CrNO_3Na$ (MNa^+ - 2CO) : 338.0819, found : 338.0827.

*N-Isobutyl-N(4-penten-1-yl) formamide (**18f**)*

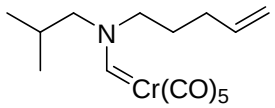


KHMDS (0.5 M in Toluene, 33.6 ml, 16.8 mmol) was added to a solution of isobutylformamide **16d** (1.7 g, 16.5 mmol) and 18-C-6 (886.8 mg, 3.4 mmol) at rt. After stirring 1.5 h at rt, 1-bromo-4-pentene (2 g, 1.6 ml, 13.4 mmol) was added and the resulting mixture was stirred at that temperature and monitored by TLC. When the reaction was complete, the solvent was removed under reduced pressure and water was added. The resulting aqueous phase was extracted with DCM (3 times). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography (60% Et_2O in hexanes) yielded (2.01 g, 90%) of amide **18f** as colorless oil and as a 1.5 : 1.0 mixture of rotamers.

Rotamer A : **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 8.10 (s, 1H), 5.88–5.69 (m, 1H), 5.08–5.04 (m, 2H), 3.25–3.18 (m, 2H), 3.14 (d, J = 7.6Hz, 2H), 2.07 (dd, J = 13.2, 6.3 Hz, 2H), 1.99–1.80 (m, 1H), 1.71–1.57 (m, 2H), 0.90 (d, J = 6.81Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm) 163.26 (d), 137.13 (d), 115.92 (t), 49.07 (t), 46.96 (t), 30.50 (t), 27.49 (t), 26.33 (d), 20.15 (q). **IR** (KBr) υ (cm^{-1}) 3077, 1674, 1468. **LRMS** (*m/z*, relative intensity) 192 ($M+Na^+$, 100). **Exact Mass** calcd for $C_{10}H_{19}NNaO$ 192.1364, found : 192.1358.

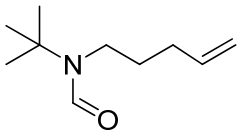
Rotamer B : **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 8.01 (s, 1H), 5.88–5.69 (m, 1H), 5.02–4.96 (m, 2H), 3.32–3.25 (m, 2H), 2.98 (d, J = 7.4 Hz, 2H), 2.07 (dd, J = 13.2, 6.3 Hz, 2H), 1.99–1.80 (m, 1H), 1.71–1.57 (m, 2H), 0.89 (d, J = 6.81Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm) 163.13 (d), 137.73 (d), 115.26 (t), 55.40 (t), 42.30 (t), 31.20 (t), 26.75 (t), 26.41 (d), 19.86 (q).

*Pentacarbonyl[(N-isobutyl-N-(4-penten-1-yl)amino)methylene]chromium(0) (**13f**)*



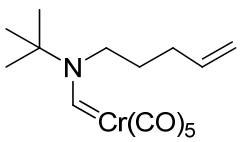
Following the same procedure described above as per the preparation of complex **13c**, the formamide **18f** (400 mg, 2.36 mmol) was converted into the corresponding carbene **13f** (662.9 mg, 81%), as colorless oil and as a 1 : 3 mixture of rotamers. Rotamer A : **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 10.95 (s, 1H), 5.92–5.66 (m, 1H), 5.15–5.01 (m, 2H), 3.99–3.87 (m, 2H), 3.37 (d, *J* = 7.7 Hz, 2H), 2.08–1.94 (m, 2H), 1.88 (ddd, *J* = 15.2, 10.2, 6.2 Hz, 2H), 1.75 (dd, *J* = 14.3, 7.3 Hz, 1H), 1.02 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 263.31 (d), 224.15 (s), 217.88 (s), 217.75 (s), 136.30 (d), 116.77 (t), 63.38 (t), 63.07 (t), 30.20 (t), 27.47 (t), 26.91 (d), 19.52 (q). **IR** (KBr) υ (cm^{-1}) : 2964, 1973, 1909. Rotamer B : **^{1}H NMR** (300 MHz, CDCl3) δ (ppm) 10.78 (s, 1H), 5.92–5.66 (m, 1H), 5.15–5.01 (m, 2H), 3.83 (d, *J* = 8.0 Hz, 2H), 3.56 (t, *J* = 7.1 Hz, 2H), 2.20 (dd, *J* = 14.2, 7.3 Hz, 2H), 2.08–1.94 (m, 2H), 1.88 (ddd, *J* = 15.2, 10.2, 6.2 Hz, 2H), 1.75 (dd, *J* = 14.3, 7.3 Hz, 1H), 0.89 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (75 MHz, CDCl3) δ 262.54 (d), 224.15 (s), 217.88 (s), 217.75 (s), 136.80 (d), 116.24 (t), 71.91 (d), 56.94 (t), 30.85 (t), 27.93 (t), 27.31 (d), 19.58 (q).

*N-t-Butyl-N(4-penten-1-yl) formamide (**18g**)*



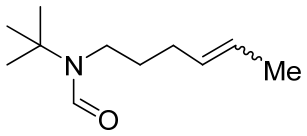
Following the procedure as per formamide **18b**, *N*-(*t*-butyl)formamide (0.47 mL, 4.19 mmol) was alkylated with iodide **17c** (1.50 g, 7.65 mmol) to give formamide **18g** as colorless oil (0.729 g, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.38 (s, 1H), 5.78 (m, 1H), 5.01 (d, *J* = 16.6 Hz, 1H), 4.94 (d, *J* = 9.5 Hz, 1H), 3.23 (m, 2H), 2.05 (q, *J* = 7.1 Hz, 2H), 1.63 (m, 2H), 1.33 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 161.4 (d), 137.7 (d), 115.0 (t), 55.3 (s), 41.0 (t), 31.5 (t), 29.6 (q), 28.3 (t); **IR** (NaCl) *v* 2970, 2931, 1659, 1372. **LRMS** (*m/z*, relative intensity) 192 (MNa^+). **Exact Mass** calcd for $C_{10}H_{19}NONa$ 192.1364, found 192.1358.

*Pentacarbonyl[(N-tert-butyl-N-(4-penten-1-yl)amino)methylene]chromium(0) (**13g**)*



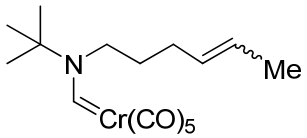
Following the same procedure described above as per the preparation of complex **13c**, the formamide **18g** (1.60 g, 9.45 mmol) was converted into the corresponding carbene **13g** (2.79 g, 86%) obtained as air-sensitive bright-yellow oil and a single rotamer. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 11.38 (s, 1H), 5.84 (m, 1H), 5.10 (dm, J = 17.2 Hz, 1H), 5.05 (dm, J = 10.2 Hz, 1H), 4.02 (m, 2H), 2.21 (q, J = 7.0 Hz, 2H), 1.91 (m, 2H), 1.34 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 256.0 (d), 224.3 (s), 217.7 (s), 136.7 (d), 116.0 (t), 67.6 (s), 54.9 (t), 31.0 (t), 30.5 (t), 30.0 (q); **IR** (NaCl) v 3081, 2988, 2052, 1977, 1919. **Exact Mass** calcd for $C_{13}H_{19}CrNO_3Na$ (MNa^+ -2CO) : 312.0668, found: 312.0672.

*(E)- and (Z)-N-Isobutyl-N(4-hexen-1-yl) formamide (**18h**)*



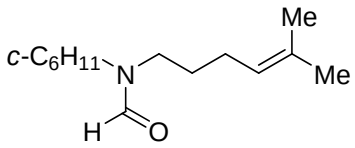
Following the procedure as per formamide **18b**, *N*-(*t*-butyl)formamide (0.47 mL, 4.19 mmol) was alkylated with iodide **17d** (800 mg, 3.81 mmol) to give formamide **18h** (0.320 g, 46%) as colorless oil and as a single rotamer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 5.41 (m, 2H), 3.22 (m, 2H), 1.97 (m, 2H), 1.65-1.53 (covered, complex m, 5H), 1.34 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.4 (d), 130.3 (d), 125.4 (d), 55.3 (s), 41.1 (t), 30.4 (t), 29.6 (q), 29.1 (t), 17.8 (q); **IR** (NaCl) v 2979, 2922, 1655. **LRMS** (*m/z*, relative intensity) 206 (MNa^+). **Exact Mass** calcd for $C_{11}H_{21}NONa$: 206.1515, found : 206.1518.

*(E)- and (Z)-Pentacarbonyl[(N-isobutyl-N-(4-hexen-1-yl)amino)methylene]chromium(0) (**13h**)*



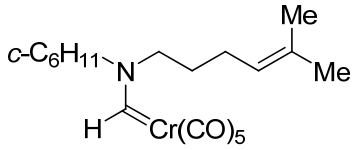
Following the same procedure as per the preparation of complex **13c**, the formamide **18h** (0.550 g, 3.00 mmol) was converted into the corresponding carbene **13h** (0.852 g, 79%) obtained as air-sensitive bright-yellow oil and as a single rotamer. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 11.36 (s, 1H), 5.48 (m, 2H), 4.00 (m, 2H), 2.12 (app. m, 2H), 1.88 (m, 2H), 1.67 (d, J = 5.3 Hz, 3H), 1.34 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 255.4 (d), 224.3 (s), 217.7 (s), 129.2 (d), 126.6 (d), 67.5 (s), 55.0 (t), 31.2 (t), 30.0 (q), 29.8 (t), 17.8 (q); **IR** (NaCl) v 2988, 2948, 2054, 1915. **LRMS** (*m/z*, relative intensity) 326 (MNa^+). **Exact Mass** calcd for $C_{14}H_{21}CrNO_3Na$: 326.0819, found : 326.0823.

N-cyclohexyl-N-(5-methyl-4-hexen-1-yl)formamide ***(18l)***



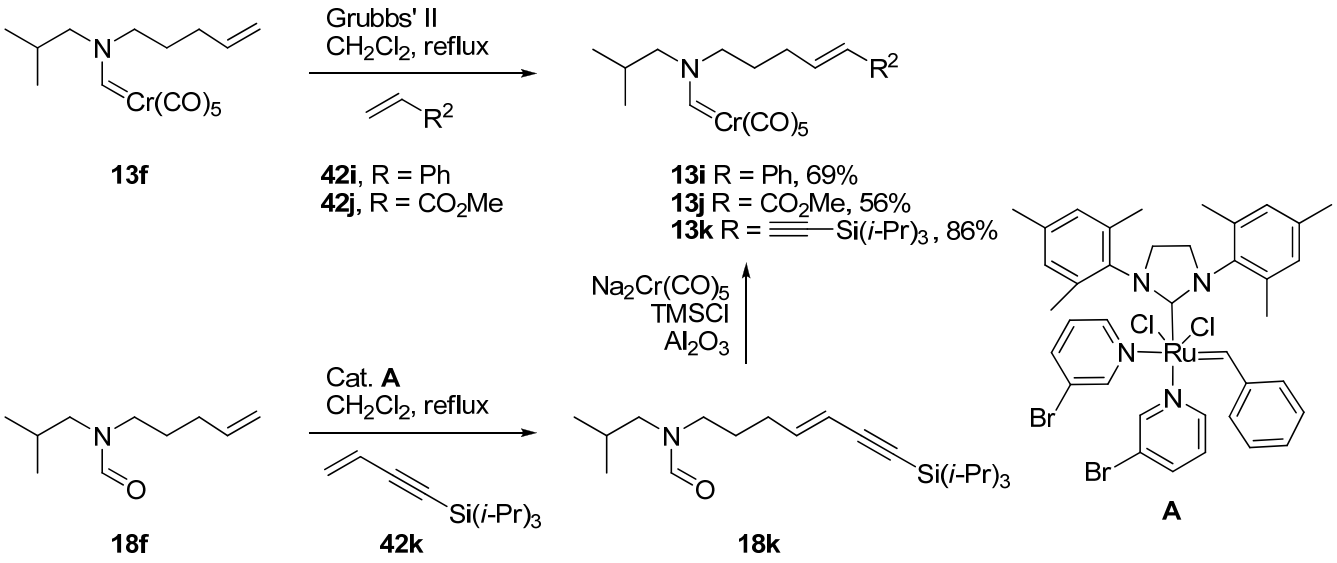
Following the procedure as per formamide **18b**, *N*-(cyclohexyl)formamide (0.590 mL, 4.45 mmol) was alkylated with iodide **17l** (1.00 g, 4.76 mmol) to give formamide **18l** (508 mg, 51%) as colorless oil and as a single rotamer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s) and 7.94 (s) (1H, rotamers), 5.00 (m, 1H), 3.89 (m) and 3.09 (m) (1H, rotamers), 3.09 (m) and 1.90 (m) (4H, rotamers), 1.80-1.35 (complex m, 8H), 1.59 (s, 3H), 1.51 (s, 3H), 1.24 (m, 2H), 1.05 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5 (d), 162.7 (d), 132.9 (s), 132.1 (s), 124.0 (d), 123.4 (d), 58.9 (d), 53.2 (d), 45.2 (t), 42.1 (t), 33.4 (t), 32.2 (t), 31.2 (t), 29.6 (t), 26.3 (t), 26.2 (t), 25.9 (t), 25.7 (t), 25.5 (t), 18.2 (q), 18.2 (q); **IR** (NaCl) *v* 3327, 2928, 2852, 1676; **HRMS** (ESI, 70 eV) [MNa^+] $C_{14}H_{25}NONa$, calcd. 246.1828, found 246.1833.

Pentacarbonyl[(N-cyclohexyl-N-(5-methyl-4-hexen-1-yl)amino)methylene]chromium(0) ***(13l)***

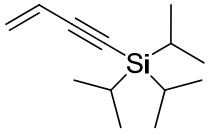


Following the same procedure described above as per the preparation of complex **13c**, the formamide **18l** (0.447 g, 2.00 mmol) was converted into the corresponding carbene to give 569 mg (71%) of product **13l** as yellow oil and as a 2:1 mixture of rotamers. Rotamer A : **^{1}H NMR** (300 MHz, $CDCl_3$) 10.97 (s) and 10.82 (s) (1H, rotamers), 5.16 (m) and 5.07 (m) (1H, rotamers), 4.64 (m) and 3.37 (m) (1H, rotamers), 3.95 (m) and 3.37 (m) (2H, rotamers), 2.15 (dd, J = 7.4 and 7.4 Hz) and 1.97 (dd, J = 14.5 and 7.2 Hz) (2H, rotamers), 1.90 - 1.75 (complex m, 6H), 1.72 (d, J = 4.7 Hz, 3H), 1.62 (d, J = 8.5 Hz, 3H), 1.33 (m, 5H), 1.19 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 258.8 (d), 253.5 (d), 224.3 (s), 224.2 (s), 217.7 (s), 217.6 (s), 133.3 (s) 129.4 (d), 129.2 (d), 69.4 (d), 69.4 (d), 59.6 (t), 55.9 (t), 33.3 (t), 33.0 (t), 25.7 (t), 25.2 (t), 25.1 (t), 24.9 (t), 17.7 (q), 17.6 (q); **IR** (NaCl) *v* 2935, 2856, 2052, 1972 to 1880, 1535; **HRMS** (ESI, 70 eV) [MNa^+-2CO] $C_{17}H_{26}CrNO_3Na$, calcd. 366.1132, found 366.1132.

Synthesis of chromium aminocarbene 13i-k

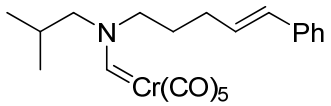


But-3-en-1-ynyltriisopropylsilane ***42k***



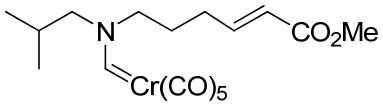
Vinylbromide (1.0 M in THF, 6.68 mL, 6.68 mmol) in THF was added to a solution triisopropylsilylacetylene (1 mL, 4.46 mmol), $PdCl_2(PPh_3)_2$ (62.58 mg, 0.09 mmol) and CuI (33.96 mg, 0.18 mmol) in Et_3N (4.5 mL) at 25 °C. After stirring for 3 h at 25 °C, 1 N HCl (aq) was added to the solution. A saturated aqueous NH_4Cl solution was added, and the product was extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate, and concentrated under vacuum. Purification by column chromatography with hexane yielded enyne **42k** (801 mg, 86%) as colorless oil. The ^{1}H NMR spectra was identical to published data.[5] **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 5.84 (dd, J = 17.6, 10.9 Hz, 1H), 5.68 (dd, J = 17.6, 2.5 Hz, 1H), 5.49 (dd, J = 10.9, 2.5 Hz, 1H), 1.08 (d, J = 3.1 Hz, 21H).

*(E)-Pentacarbonyl[(N-isobutyl-N-(5-phenyl-4-penten-1-yl)methylene]chromium(0) (**13i**)*



Styrene **42i** (603.2 mg, 5.79 mmol) and chromium aminocarbene **13f** (200 mg, 0.58 mmol) were added sequencially via syringe in a stirred solution of DCM and Grubbs 2nd generation catalyst (24.6 mg, 0.03 mmol). The mixture was heated to reflux for 24h. The reaction mixture was then reduced in volume and purified directly on a silica gel column to give 168.9 mg (69%) of product **13i** as yellow oil and as a 1 : 3 mixture of rotamers. Rotamer A : **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.92 (s, 1H), 7.36–7.22 (m, 5H), 6.39 (m, 1H), 6.17–6.02 (m, 1H), 3.78 (d, *J* = 8.1 Hz, 2H), 3.54 (t, *J* = 7.8 Hz, 2H), 2.13 (dd, *J* = 13.8, 6.8 Hz, 2H), 1.81–1.72 (m, 2H), 1.60–1.35 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 263.68 (d) ,224.11 (s), 217.91 (s), 217.78 (s), 137.11 (s), 132.06 (d), 129.97 (d), 128.76 (d), 127.80 (d), 127.58 (d), 126.20 (d), 71.97 (t), 63.09 (t), 57.05 (t), 30.23 (t), 29.52 (d), 28.06 (t), 26.98 (d), 22.80 (t), 19.56 (q). **IR** (KBr) υ (cm^{-1}) : 2963, 2054, 1972, 1910, 1673. Rotamer B : **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 7.36–7.22 (m, 5H), 6.39 (m, 1H), 6.17–6.02 (m, 1H), 3.95–3.86 (m, 2H), 3.32 (d, *J* = 7.7 Hz, 2H), 2.30 (dd, *J* = 14.5, 7.1 Hz, 2H), 1.91 (td, *J* = 15.2, 7.5 Hz, 2H), 1.60–1.35 (m, 1H), 0.83 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 262.93 (d), 224.11 (s), 217.91 (s), 217.78 (s), 137.35 (s), 131.59 (d), 129.97 (d), 128.72 (d), 128.42 (d), 127.42 (d), 126.20 (d), 71.97 (t), 63.43 (t), 57.05 (t), 31.74 (t), 29.52 (d), 28.56 (t), 27.33 (d), 22.80 (t), 19.62 (q).

*(E)-Pentacarbonyl[(N-isobutyl-N-(5-methylcarboxy-4-penten-1-yl)methylene]chromium(0) (**13j**)*

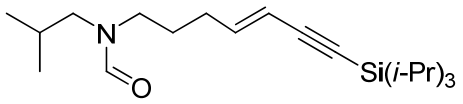


Same procedure as per **13i** using methyl metacrylate **42j** (546 mg, 6.34 mmol) and chromium aminocarbene **13f** (219 mg, 0.63 mmol) The reaction mixture was then reduced in volume and purified directly on a silica gel colomn to give 122.6 mg (48%) of product **13j** as yellow oil and as 1 : 4 mixture of rotamers.

Rotamer A : **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.82 (s, 1H), 7.05–6.83 (m, 1H), 5.9 (d, *J* = 7.5 Hz, 1H), 3.97–3.89 (m, 2H), 3.73 (d, *J* = 4.9 Hz, 3H), 3.37 (d, *J* = 7.7 Hz, 2H), 2.35 (dd, *J* = 14.1, 7.0 Hz, 2H), 2.05–1.88 (m, 2H), 1.83 (dd, *J* = 14.6, 7.4 Hz, 1H), 0.89 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (75 MHz, CDCl3) δ 264.8 (d), 233.9 (s), 217.8 (s), 217.7 (s), 166.8 (s), 146.2 (d), 122.9 (d), 71.9 (t), 56.7 (t), 51.7

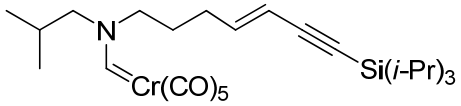
(q), 29.8 (t), 29.2 (d), 27.4 (t), 27.3 (d), 19.5 (q). **IR** (KBr) υ (cm^{-1}) : 2954, 2054, 2039, 1971, 1923, 1727, 1672. Rotamer B : **^{1}H NMR** (300 MHz, $CDCl_3$) δ 11.00 (s, 1H), 7.05–6.83 (m, 1H), 5,88 (d, *J* = 7.5 Hz, 1H), 3.83 (d, *J* = 8.0 Hz, 2H), 3.73 (d, *J* = 4.9 Hz, 3H), 3.58 (t, *J* = 7.2 Hz, 2H), 2.18 (dd, *J* = 14.5, 7.6 Hz, 2H), 2.05–1.88 (m, 2H), 1.83 (dd, *J* = 14.6, 7.4 Hz, 1H), 1.03 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (75 MHz, CDCl3) δ 264.0 (d), 233.9 (s), 217.8 (s), 217.7 (s), 166.8 (s), 146.8 (d), 122.5 (d), 71.9 (t), 56.7 (t), 51.7 (q), 29.8 (t), 29.2 (d), 27.4 (t), 27.3 (d), 19.6 (q).

*(E)-N-isobutyl-N-(7-(triisopropylsilyl)hept-4-en-6-ynyl)formamide (**18k**)*



To a solution of enyne **42k** (101 mg, 0.49 mmol) in benzene (2,43 mL) catalyst **A** was added (41 mg, 0.05 mmol) followed by terminal alkene **18f** (246 mg, 1.46 mmol). The reaction mixture was stirred for 39 h at 70° C under a nitrogen atmosphere. After removal of the organic solvent under reduced pressure, the residue was purified by column chromatography on silica gel with 40/60 hexane/ether to yield 146,4 mg (86%) of the formamide **18k** as a colorless oil and as a 1 : 1.76 mixture of rotamers. Rotamer A : **^{1}H NMR** (300 MHz, $CDCl_3$) 8.03–7.98 (m, 1H), 5.67–5.44 (m, 1H), 5.35 (tdd, *J* = 9.9, 9.3, 2.4 Hz, 1H), 3.30 (ddd, *J* = 11.5, 7.1, 3.2 Hz, 2H), 2.29–2.18 (m, 1H), 2.05–1.83 (m, 2H) , 1.73–1.57 (m, 1H), 1.73–1.57 (m, 3H), 1.07 (d, *J* = 5.1 Hz, 18H), 0.89 (d, *J* = 6.5 Hz, 6H). Rotamer B : **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.11–8.06 (m, 1H), 6.23–6.07 (m, 1H), 5.94 (ddt, *J* = 12.5, 11.0, 7.5 Hz, 1H), 3.22 (dd, *J* = 9.4, 4.4 Hz, 2H), 3.16–3.08 (m, 2H), 2.37 (ddd, J = 15.8, 11.6, 7.3 Hz, 2H), 2.17–2.05 (m, 2H), 1.73–1.57 (m, 1H), 1.73–1.57 (m, 3H), 1.07 (d, *J* = 5.1 Hz, 18H), 0.89 (d, *J* = 6.5 Hz, 6H). Both rotamers : **^{13}C NMR** (76 MHz, $CDCl_3$) δ 163.3 (d), 163.1 (d), 163.1 (d), 162.8 (d), 144.1 (d), 143.5 (d), 143.3 (d), 142.6 (d), 128.9 (d), 127.6 (d), 127.6 (d), 126.6 (d), 126.3 (d), 125.6 (d), 125.3 (d), 111.6 (d), 111.3 (d), 111.0 (d), 110.7 (d), 103.6 (s), 103.3 (s), 96.1 (s), 95.6 (s), 55.6 (t), 55.6 (t), 55.5 (t), 54.7 (t), 49.4 (t), 49.2 (t), 47.9 (t), 47.5 (t), 44.4 (t), 42.8 (t), 42.5 (t), 32.0 (t), 30.6 (t), 29.9 (t), 28.2 (t), 28.0 (t), 27.6 (t), 26.9 (d), 26.8 (d), 26.6 (d), 26.4 (t), 26.4 (t), 25.1 (t), 20.2 (d), 19.9 (q), 18.8 (q), 18.1 (q), 17.8 (q), 13.0 (q), 11.4 (q). **IR** (KBr) υ (cm^{-1}) : 3021, 2145, 1937, 1676. **LRMS** (*m/z*, relative intensity) 372 (MNa^+). **Exact Mass** calcd for $C_{21}H_{39}NOSiNa$ 372.2699, found: 372.2709.

Pentacarbonyl[(N-isobutyl-N-(7-triisopropylsilyl-4-hepten-6-yn-1-yl)methylene]chromium(0) ***(13k)***

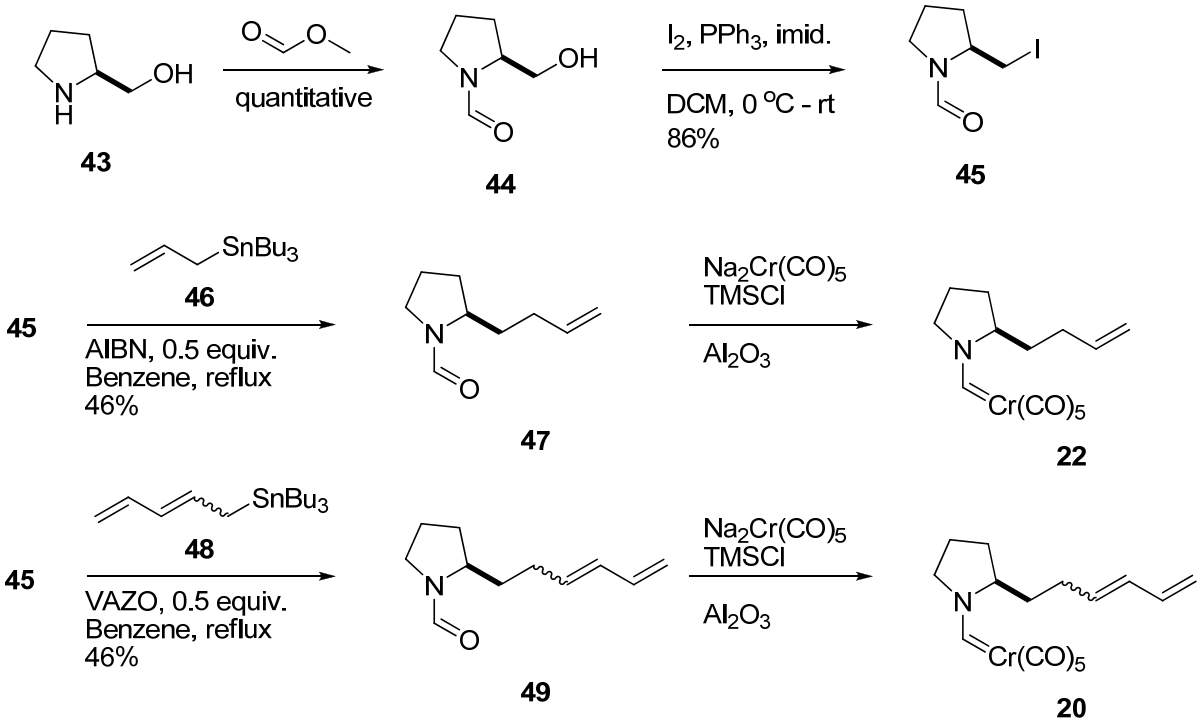


Following the same procedure described above as per the preparation of complex **13c**, the formamide **18k** (301.9 mg, 0.86 mmol) was converted into the corresponding carbene to give 270 mg (59%) of product **13k** as yellow oil and as a mixture 1 : 3 : 6 : 0.5 of rotamers and geometrical isomers, A, B, C, and D). Rotamer A : **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.81 (s, 1H), 6.26–6.12 (m, 1H), 5.58–5.47 (m, 1H), 3.94 (m, 2H), 3.81 (dd, *J* = 8.1, 2H), 3.59-3.51 (m, 2H), 3.40 (d, *J* = 8.1 Hz, 2H), 2.37–2.23 (m, 2H), 2.06–1.86 (m, 3H), 1.04–1.02 (d, *J* = 6.9 Hz, 18H), 0.91-0.89 (d, *J* = 7.2 Hz, 6H). Rotamer B : **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.79 (s, 3H), 6.03–5.88 (m, 1H), 5.47–5.36 (m, 1H), 3.94 (m, 2H), 3.81 (d , *J* = 7.8 Hz, 2H), 3.59-3.51 (m, 2H), 3.36 (d, *J* = 7.5 Hz, 2H), 2.61–2.38 (m, 2H), 1.79 (d, *J* = 5.1 Hz, 3H), 1.03-1.01 (d, *J* = 6.9 Hz, 18H), 0.90-0.87 (d, *J* = 6.6 Hz, 6H). Rotamer C : **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.78 (s, 6H), 6.03–5.88 (m, 1H), 5.71–5.58 (m, 1H), 3.94 (m, 2H), 3.77 (d, *J* = 8.0 Hz, 2H), 3.59-3.51 (m, 2H), 3.36 (d, *J* = 7.5 Hz, 2H), 2.61–2.38 (m, 2H), 1.67 (ddd, *J* = 13.2, 9.0, 6.0 Hz, 3H), 1.12–1.05 (d, *J* = 5.7 18H), 0.90-0.88 (d, *J* = 6.6 Hz, 6H). Rotamer D : **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.76 (s, 1H), 6.26–6.12 (m, 1H), 5.29–5.15 (m, 1H), 3.94 (m, 2H), 3.81 (d , *J* = 7.8 Hz, 2H), 3.59-3.51 (m, 2H), 3.34 (d, *J* = 6.9 Hz, 2H), 2.37–2.23 (m, 2H), 2.23–2.08 (m, 3H), 1.03-1.01 (d, *J* = 6.9 Hz, 18H) , 0.89-0.87 (d, *J* = 7.5 Hz, 6H).

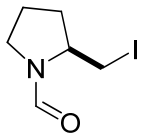
All rotamers : **^{13}C NMR** (75 MHz, $CDCl_3$) δ 262.74 (d), 262.39 (d), 224.20 (s), 217.91 (s), 217.75 (s), 217.69 (s), 142.10 (s), 130.46 (d) , 129.17 (d), 127.74 (d), 125.57 (d), 125.21 (d), 124.66 (d), 111.56 (s), 103.21 (s), 72.00 (t), 63.93 (t), 63.22 (t), 56.96 (t), 56.81 (t), 31.93 (t), 31.71 (t), 27.85 (t), 27.51 (t), 27.32 (d), 27.28 (d), 26.97 (d), 26.85 (d), 26.50 (t), 19.54 (q), 18.74 (q), 18.06 (q), 17.98 (q), 11.39 (q).

IR (KBr) υ (cm^{-1}) : 2964, 2055, 1974, 1916, 1674.

Synthesis of chromium aminocarbenes 20 and 22.



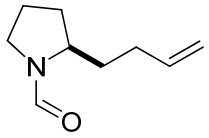
*(S)-2-(Iodomethyl)pyrrolidine-1-carbaldehyde (**45**)*



Iodine (982 mg, 3.87 mmol) was added to a solution of triphenylphosphine (1.02 g, 3.87 mmol) and imidazole (290 mg, 4.26 mmol) in 15 mL of anhydrous dichloromethane at 0 ºC. The reaction mixture was stirred at 0 ºC for 45 min. A solution of the alcohol **44**[6] (500 mg, 3.87 mmol) in 3 mL of anhydrous dichloromethane was added at 0 ºC. The reaction mixture was stirred at rt for 18 h. Then, a 1 N aqueous solution of $Na_2S_2O_3$ (20 mL) was added and the phases were separated. The aqueous layer was extracted with dichloromethane (2 x 15 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by flash chromatography on a silica gel column using solutions of acetone in hexanes (20:80 to 40:60) as eluent. The iodide **45** (791 mg, 86 %) was obtained as a colorless solid and as a 56 : 44 mixture of rotamers. Note: an impurity forms rapidly upon storing the product, even in the refregirator, turning the solid to a pale brown color. **^{1}H NMR** (both rotamers) (300 MHz, $CDCl_3$) δ (ppm) 8.35 (s, 1H), 8.29 (s,

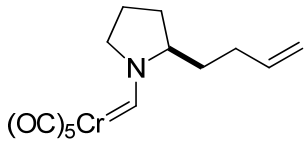
1H), 4.08-3.93 (m, 2H), 3.67-3.55 (m, 2H), 3.54-3.49 (m, 3H), 3.48-3.37 (m, 1H), 3.26 (dd, 1H, *J* = 10.3, 5.3 Hz), 3.19 (dd, 1H, *J* = 10.2, 8.2 Hz), 2.25-2.06 (m, 2H), 2.04-1.78 (m, 6H). **^{13}C NMR** (both rotamers) (75.5 MHz, $CDCl_3$) δ (ppm) 161.1 (d), 161.0 (d), 58.2 (d), 55.6 (d), 47.3 (t), 44.0 (t), 31.5 (t), 31.4 (t), 23.8 (t), 22.1 (t), 10.6 (t), 10.4 (t). **IR** (neat) ν (cm^{-1}) 3068, 2970, 2876, 1666, 1383, 1158. **LRMS** (*m/z*, relative intensity) 238 (M^+, 10), 112 (40), 98 (100). **Exact Mass** calcd for $C_6H_{10}INO$: 238.9807, found: 238.9814. **$[\alpha]_D$** = -77.4.

*(R)-2-(but-3-enyl)pyrrolidine-1-carbaldehyde (**47**)*



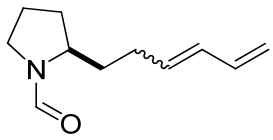
Allyltributylstannane **46** (0.55 mL, 1.8 mmol) and AIBN (73 mg, 0.446 mmol) were added to a solution of the iodide **45** (213 mg, 0.891 mmol) in anhydrous benzene (0.9 mL, 1M). The reaction mixture was heated to reflux temperature for 5.5 h and cooled down before the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on a silica gel column using solutions of acetone in hexanes (0:100-30:70-50:50) as eluent. The product **47** (60 mg, 44 %) was obtained as colorless oil and as a 71 : 29 mixture of rotamers. **^{1}H NMR** (major rotamer) (300 MHz, $CDCl_3$) δ (ppm) 5.70-5.54 (m, 1H), 4.91-4.73 (m, 2H), 3.67-3.58 (m, 1H), 3.44-3.32 (m, 1H), 3.28-3.10 (m, 1H), 1.97-1.60 (m, 5H), 1.60-1.45 (m, 2H), 1.45-1.13 (m, 2H). **^{1}H NMR** (minor rotamer) (300 MHz, $CDCl_3$) δ (ppm) 5.70-5.54 (m, 1H), 4.91-4.73 (m, 2H), 3.87-3.77 (m, 1H), 3.44-3.32 (m, 1H), 3.28-3.10 (m, 1H), 1.97-1.60 (m, 5H), 1.60-1.45 (m, 2H), 1.45-1.13 (m, 2H). **^{13}C NMR** (major rotamer) (75.5 MHz, $CDCl_3$) δ (ppm) 160.8 (d), 137.1 (d), 115.3 (t), 56.9 (d), 43.1 (t), 34.8 (t), 30.3 (t), 30.1 (t), 22.3 (t). **^{13}C NMR** (minor rotamer) (75.5 MHz, $CDCl_3$) δ (ppm) 160.8 (d), 137.8 (d), 114.5 (t), 54.8 (d), 46.2 (t), 32.6 (t), 29.9 (t), 29.9 (t), 23.6 (t). **IR** (neat) ν (cm^{-1}) 3676-3346 (br), 3075, 2972, 2931, 2876, 1663, 1649, 1415, 1384. **LRMS** (*m/z*, relative intensity) 154 (MH^+, 5), 153 (M^+, 5), 111 (40), 98 (100). **Exact Mass** calcd for $C_9H_{15}NO$: 153.1154, found: 153.1158. **$[\alpha]_D$** = -44.1.

*(R)-Pentacarbonyl[(3-buten-1-yl)pyrrolidine)methylene]chromium(0) (**22**)*



Following the same procedure described above as per the preparation of complex **13c**, the formamide **47** (245 mg, 1.60 mmol) was converted into the corresponding carbene **22** (422 mg, 80%) obtained as air-sensitive yellow oil and as single rotamer. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 11.0 (s, 1H), 5.77 (dddd, 1H, *J* = 16.8, 10.2, 6.4, 6.4 Hz), 5.11-5.02 (m, 2H), 4.16-3.97 (m, 2H), 3.73-3.63 (m, 1H), 2.31-2.11 (m, 3H), 2.11-2.00 (m, 2H), 1.90-1.70 (m, 2H), 1.66-1.53 (m, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ (ppm) 255.2 (d), 224.1 (s), 217.9 (s), 136.6 (d), 116.4 (t), 71.1 (d), 56.1 (t), 34.2 (t), 30.4 (t), 29.9 (t), 23.6 (t). **IR** (neat) ν (cm^{-1}) 3081, 2980, 2932, 2055, 2021-1773, 1515. **LRMS** (*m/z*, relative intensity) 296 ($(M-2CO+Na)^+$, 100). **Exact mass** calcd for $C_{12}H_{15}CrNNaO_3$: 296.0349, found: 296.0359.

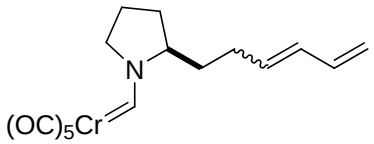
*Mixture of E and Z (R)-2-(hexa-3,5-dienyl)pyrrolidine-1-carbaldehyde (**49**)*



Tributyl(penta-2,4-dienyl)stannane **48** (ratio E:Z = 86:14, 2.44 g, 6.83 mmol) and 1,1-azobis(cyclohexanecarbonitrile) (VAZO) (334 mg, 1.37 mmol) were added to a solution of the iodide **45** (817 mg, 3.42 mmol) in anhydrous benzene (3.4 mL, 1M). The reaction mixture was heated to reflux temperature for 5 h and cooled down before the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on a silica gel column using solutions of acetone in hexanes (0:100 to 50:50) as eluent. Diene **49** (282 mg, 46 %) was obtained as colorless oil and as a 80 : 20 mixture of *E* and *Z* double bonds, each geometrical isomer itself existing as a mixture of rotamers. **^{1}H NMR** (*E* double bond, major rotamer) (400 MHz, $CDCl_3$) δ (ppm) 8.22 (s, 1H), 6.27 (dt, 1H, *J* = 17.0, 10.3 Hz), 6.05 (dd, 1H, *J* = 15.2, 10.3 Hz), 5.63 (dt, 1H, *J* = 15.2, 6.8 Hz), 5.09 (d, 1H, *J* = 17.0 Hz), 4.97 (d, 1H, *J* = 10.3 Hz), 3.80-3.73 (m, 1H), 3.59-3.48 (m, 1H), 3.41-3.27 (m, 1H), 2.14-2.06 (m, 2H), 2.05-1.60 (m, 5H), 1.60-1.48 (m, 1H). **^{1}H NMR** (*E* double bond, minor rotamer) (400 MHz, $CDCl_3$) δ (ppm) 8.22 (s, 1H), 6.27 (dt, 1H, *J* = 17.0, 10.3 Hz), 6.05 (dd, 1H, *J* = 15.2, 10.3 Hz), 5.68 (dt, 1H, *J* = 15.2, 6.8 Hz), 5.05 (d, 1H, *J* = 17.0 Hz), 4.93 (d, 1H, *J* = 10.3 Hz), 4.02-3.95 (m, 1H), 3.59-

3.48 (m, 1H), 3.41-3.27 (m, 1H), 2.25-2.15 (m, 2H), 2.05-1.60 (m, 5H), 1.44-1.34 (m, 1H). **^{1}H NMR** (*Z* double bond, major rotamer) (400 MHz, $CDCl_3$) δ (ppm) 8.22 (s, 1H), 6.56 (dt, 1H, *J* = 16.8, 11.7 Hz), 6.10-5.93 (m, 1H), 5.38 (dt, 1H, *J* = 10.6, 7.5 Hz), 5.19 (d, 1H, *J* = 17.0 Hz), 5.12 (d, 1H, *J* = 10.3 Hz), 3.80-3.73 (m, 1H), 3.59-3.48 (m, 1H), 3.41-3.27 (m, 1H), 2.14-2.06 (m, 2H), 2.05-1.60 (m, 5H), 1.60-1.48 (m, 1H). **^{1}H NMR** (*Z* double bond, minor rotamer) (400 MHz, $CDCl_3$) δ (ppm) 8.22 (s, 1H), 6.59 (dt, 1H, *J* = 16.8, 11.7 Hz), 6.10-5.93 (m, 1H), 5.43 (dt, 1H, *J* = 10.6, 7.5 Hz), 5.12 (d, 1H, *J* = 16.8 Hz), 5.09 (d, 1H, *J* = 11.7 Hz), 4.02-3.95 (m, 1H), 3.59-3.48 (m, 1H), 3.41-3.27 (m, 1H), 2.25-2.15 (m, 2H), 2.05-1.60 (m, 5H), 1.44-1.34 (m, 1H). **^{13}C NMR** (*E* double bond, major rotamer) (100 MHz, $CDCl_3$) δ (ppm) 161.1 (d), 136.9 (d), 133.3 (d), 132.1 (d), 115.8 (t), 57.3 (d), 43.5 (t), 35.5 (t), 30.6 (t), 29.1 (t), 22.7 (t). **^{13}C NMR** (*E* double bond, minor rotamer) (100 MHz, $CDCl_3$) δ (ppm) 161.2 (d), 137.3 (d), 134.3 (d), 131.4 (d), 115.1 (t), 55.1 (d), 46.6 (t), 33.2 (t), 30.4 (t), 29.2 (t), 23.9 (t). **^{13}C NMR** (*Z* double bond, major rotamer) (100 MHz, $CDCl_3$) δ (ppm) 161.1 (d), 131.8 (d), 130.7 (d), 130.4 (d), 118.1 (t), 57.3 (d), 43.5 (t), 35.9 (t), 30.6 (t), 29.1 (t), 24.4 (t). **^{13}C NMR** (*Z* double bond, minor rotamer) (100 MHz, $CDCl_3$) δ (ppm) 161.2 (d), 132.19 (d), 131.8 (d), 129.7 (d), 117.3 (t), 55.1 (d), 46.6 (t), 33.6 (t), 30.4 (t), 29.2 (t), 24.6 (t). **IR** (neat) ν (cm^{-1}) 3080, 2926, 2864, 1668, 1643, 1385. **LRMS** (*m/z*, relative intensity) 202 ($(M + Na)^+$, 100), 185 (5). **Exact Mass** calcd for $C_{11}H_{17}NONa$: 202.1208, found: 202.1199. **$[\alpha]_D$** = -36.2.

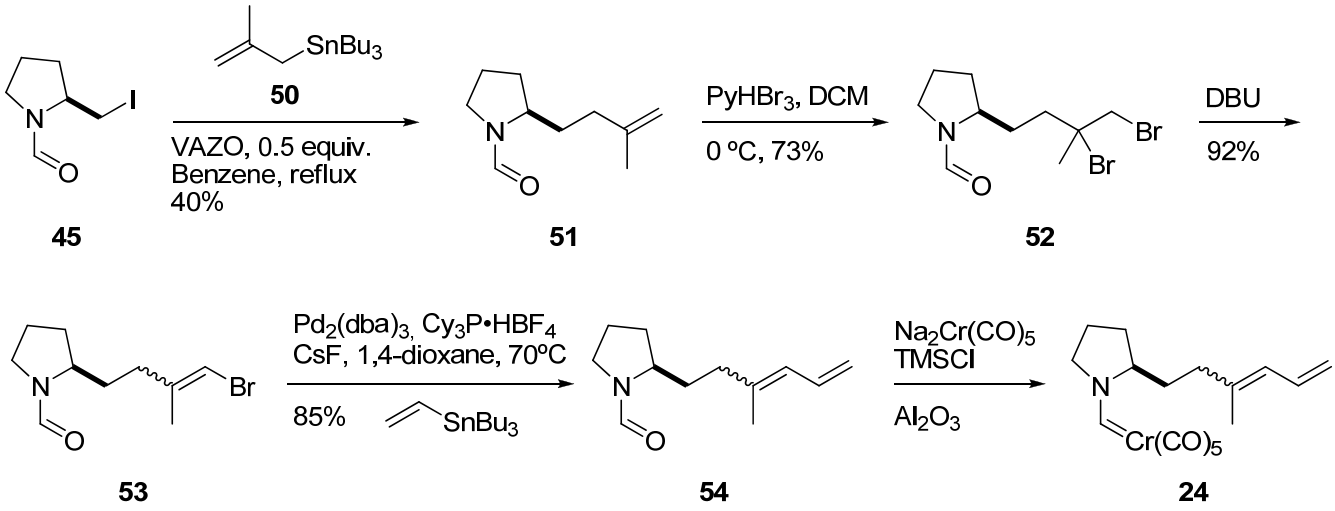
*Mixture of E and Z (R)-Pentacarbonyl[(3-buten-1-yl)pyrrolidine)methylene]chromium(0) (**20**)*



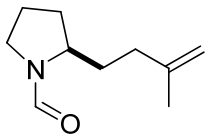
Following the same procedure as per the preparation of complex **13c**, the formamide **49** (537 mg, 3.00 mmol) was converted into the corresponding carbene **20** (808 mg, 76%) obtained as air-sensitive yellow oil and as a single rotamer. **^{1}H** (*E* double bound) (400 MHz, $CDCl_3$) δ (ppm) 10.99 (s, 1H), 6.30 (dt, 1H, *J* = 16.9, 10.2 Hz), 6.08 (dd, 1H, *J* = 15.3, 10.2 Hz), 5.63 (dt, 1H, *J* = 15.3, 7.6 Hz), 5.14 (d, 1H, *J* = 16.9 Hz), 5.03 (d, 1H, *J* = 10.2 Hz), 4.14-3.99 (m, 2H), 3.71-3.64 (m, 1H), 2.29-2.02 (m, 4H), 1.88-1.71 (m, 2H), 1.65-1.52 (m, 2H). **^{1}H** (*Z* double bound) (400 MHz, $CDCl_3$) δ (ppm) 6.57 (dt, 1H, *J* = 16.4, 11.1 Hz), 6.12-6.04 (m, 1H), 5.37 (dt, 1H, *J* = 10.6, 7.5 Hz), 5.25 (d, 1H, *J* = 16.4 Hz), 4.14-3.99 (m, 2H), 3.71-3.64 (m, 1H), 2.29-2.02 (m, 4H), 1.88-1.71 (m, 2H), 1.65-1.52 (m, 2H). **^{13}C** (*E* double

bound) (100 MHz, $CDCl_3$) δ (ppm) 255.0 (d), 224.3 (s), 218.0 (s), 136.8 (d), 132.7 (d), 132.4 (d), 116.4 (t), 71.3 (d), 56.2 (t), 34.6 (t), 30.5 (t), 28.9 (t), 23.7 (t). **^{13}C** (*Z* double bound) (100 MHz, $CDCl_3$) δ (ppm) 255.0 (d), 224.3 (s), 218.0 (s), 131.6 (d), 131.0 (d), 129.9 (d), 118.7 (t), 71.3 (d), 56.2 (t), 34.9 (t), 30.6 (t), 28.9 (t), 24.0 (t). **IR** (neat) ν (cm^{-1}) 3088, 2975, 2944, 2882, 2359, 2340, 2054, 1972, 1937, 1902, 1516, 1506, 1453, 1005, 679, 655. **LRMS** (*m/z*, relative intensity) 378 ($(M+Na)^+$, 35), 350 (15), 322 (99), 292 (20), 224 (35), 194 (100). **Exact Mass** calcd for $C_{16}H_{17}CrNO_5Na$: 378.0404, found: 378.0410. **$[\alpha]_D$** = +69.821.

Synthesis of chromium aminocarbene (24)



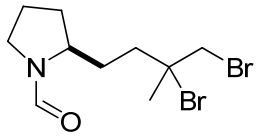
*(R)-2-(3-methylbut-3-enyl)pyrrolidine-1-carbaldehyde (**51**)*



Tributyl(2-methylallyl)stannane **50** (5.07 g, 14.7 mmol) and 1,1-azobis(cyclohexanecarbonitrile) (VAZO) (717 mg, 2.94 mmol) were added to a solution of the iodide **45** (1.75 g, 7.34 mmol) in anhydrous benzene (7.3 mL, 1M). The reaction mixture was heated to reflux temperature for 5 h and cooled down before the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on a silica gel column using solutions of acetone in hexanes (0:100 to 30:70) as eluent. The product **51** (491 mg, 40 %) was obtained as colorless oil and as a mixture of rotamers

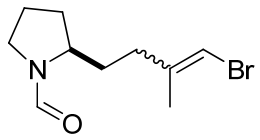
(ratio = 76:24, ^{1}H NMR). **^{1}H NMR** (major rotamer) (300 MHz, $CDCl_3$) δ (ppm) 8.25 (s, 1H), 4.69 (s, 2H), 3.82-3.72 (m, 1H), 3.63-3.49 (m, 1H), 3.47-3.30 (m, 1H), 2.14-1.52 (m, 8H), 1.72 (s, 3H). **^{1}H NMR** (minor rotamer) (300 MHz, $CDCl_3$) δ (ppm) 8.24 (s, 1H), 4.75 (s, 2H), 4.05-3.94 (m, 1H), 3.63-3.49 (m, 1H), 3.47-3.30 (m, 1H), 2.14-1.52 (m, 7H), 1.72 (s, 3H), 1.48-1.37 (m, 1H). **^{13}C NMR** (major rotamer) (100 MHz, $CDCl_3$) δ (ppm) 161.2 (d), 144.5 (s), 110.8 (d), 57.5 (d), 43.5 (t), 34.2 (t), 34.0 (t), 30.7 (t), 22.7 (t), 22.7 (q). **^{13}C NMR** (minor rotamer) (100 MHz, $CDCl_3$) δ (ppm) 161.2 (d), 145.4 (s), 110.2 (d), 55.2 (d), 46.6 (t), 34.3 (t), 31.7 (t), 30.4 (t), 24.0 (t), 22.7 (q). **IR** (neat) ν (cm^{-1}) 3074, 2967, 2935, 2876, 1654, 1452, 1419, 1385, 1176, 887. **LRMS** (*m/z*, relative intensity) 190 ($(M + Na)^+$, 100). **Exact Mass** calcd for $C_{10}H_{17}NONa$: 190.1202, found: 190.1202. **$[\alpha]_D$** = -59.23.

*(2S)-2-(3,4-Dibromo-3-methylbutyl)pyrrolidine-1-carbaldehyde (**52**)*



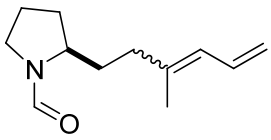
Pyridinium tribromide (1.63 g, 5.09 mmol) was added to a solution of the alkene **51** (740 mg, 4.42 mmol) in dichloromethane (12.5 mL) at 0 ºC. The reaction mixture was stirred at 0 ºC for 1.5 h. A saturated aqueous solution of sodium bicarbonate (15 mL) and a 1 N solution of $Na_2S_2O_3$ (15 mL) were added. The mixture was extracted with dichloromethane (3 x 30 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by flash chromatography on a silica gel column using a solution of acetone in hexanes (20:80) as eluent. The dibromide **52** (1.05 g, 73 %) was obtained as colorless oil and as a 65 : 35 mixture of rotamers, each as a mixture of diastereomers. **^{1}H NMR** (major rotamer) (300 MHz, $CDCl_3$) δ (ppm) 8.29 (s, 1H), 3.88-3.76 (m, 3H), 3.66-3.52 (m, 1H), 3.41-3.31 (m, 1H), 2.10-1.55 (m, 8H), 1.86 (s, 3H). **^{1}H NMR** (minor rotamer) (300 MHz, $CDCl_3$) δ (ppm) 8.25 (s, 1H), 4.14-4.00 (m, 1H), 3.88-3.76 (m, 2H), 3.66-3.52 (m, 1H), 3.49-3.41 (m, 1H), 2.10-1.55 (m, 8H), 1.83 (s, 3H). **^{13}C NMR** (mixture of rotamers and diastereomers) (75.5 MHz, $CDCl_3$) δ (ppm) 161.2 (d), 160.8 (d), 67.3 (s), 66.5 (s), 57.1 (d), 54.5 (d), 54.4 (d), 46.3 (t), 43.2 (t), 42.5 (t), 42.1 (t), 41.8 (t), 38.3 (t), 31.8 (t), 31.7 (t), 30.6 (q), 30.3 (t), 29.8 (t), 23.6 (t), 22.5 (t). **IR** (neat) ν (cm^{-1}) 2969, 2875, 1666, 1383. **LRMS** (*m/z*, relative intensity) 350 ($(M+Na)^+$, 100), 270 ($(M+Na)^+$-HBr, 40). **Exact Mass** calcd for $C_{10}H_{17}Br_2NONa$: 349.9549, found: 349.9556. **$[\alpha]_D$** = -40.18.

*(R)-2-(4-bromo-3-methylbut-3-enyl)pyrrolidine-1-carbaldehyde (**53**)*



DBU (4.49 mL, 30.1 mmol) was added to the dibromide **52** (983 mg, 3.01 mmol) and the reaction mixture was stirred at rt for 18 h. A 1 N aqueous HCl solution (30 mL) was added and the mixture was extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure to yield 679 mg (92%) of pure vinylbromide **53** as a mixture of rotamers and *E* and *Z* double bond isomers. **^{1}H NMR** (mixture of rotamers and *E* and *Z* isomers) (300 MHz, $CDCl_3$) δ (ppm) 8.29 (s) and 8.25 (s) (1H, rotamers and isomers), 5.96-5.93 (m), 5.91 (s) and 5.86 (s) (1H, rotamers and isomers), 4.02-3.92 (m) and 3.82-3.70 (m) (1H, rotamers), 3.65-3.50 (m, 1H), 3.48-3.29 (m, 1H), 2.31-1.53 (m) and 1.48-1.37 (m) (8H, rotamers and isomers), 1.80 (s (br), 3H). **^{13}C NMR** (mixture of rotamers and isomers, some signals are missing because of overlapping) (75.5 MHz, $CDCl_3$) δ (ppm) 161.0 (d), 160.8 (d), 141.0 (s), 140.3 (s), 140.2 (s), 101.9 (d), 101.5 (d), 101.3 (d), 100.8 (d), 57.3 (d), 57.0 (d), 54.8 (d), 54.6 (d), 46.3 (t), 43.2 (t), 34.6 (t), 33.7 (t), 32.8 (t), 31.4 (t), 30.8 (t), 30.6 (t), 30.3 (t), 30.2 (t), 30.1 (t), 23.7 (t), 22.4 (t), 22.0 (q), 21.9 (q), 19.0 (q). **IR** (neat) ν (cm^{-1}) 3070, 2975, 2947, 2876, 1666, 1416, 1384, 1161. **LRMS** (*m/z*, relative intensity) 286 ($(M+K)^+$, 5), 268 ($(M+Na)^+$, 100) 246 ($(M+H)^+$, 2). **Exact Mass** calcd for $C_{10}H_{16}BrNONa$: 268.0307, found: 268.0305. **$[\alpha]_D$** = -48.83.

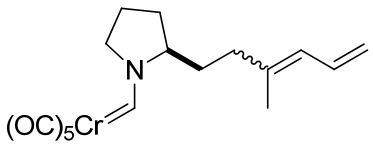
*(R)-2-(3-methylhexa-3,5-dienyl)pyrrolidine-1-carbaldehyde (**54**)*



Vinylbromides **53** (1.34 g, 5.45 mmol), $Pd_2(dba)_3$ (100 mg, 0.109 mmol) and PCy_3HBF_4 (161 mg, 0.436 mmol) were mixed in anhydrous dioxane (5.5 mL) and charged in a seal-type screw-cap vial. Tributyl(vinyl)stannane (1.91 mL, 6.54 mmol) and CsF (1.82 g, 12.0 mmol) were added. Argon was bubbled in the solution for 3 min., the vial was shut sealed, and the reaction mixture was heated to 70 ºC for 18 h. Then, the vial was opened and another portion of $Pd_2(dba)_3$ (100 mg, 0.109 mmol) was

added, the vial was sealed again and the reaction mixture was heated to 70 ºC for an additional 18 h. The solvent was then evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel using solutions of ethyl acetate in hexanes (30:70 to 70:30). A pale yellow oil (897 mg, 85%) was obtained as a mixture of rotamers and *E* and *Z* double bonds. **^{1}H NMR** (mixture of rotamers and E/Z double bonds) (300 MHz, $CDCl_3$) δ (ppm) 8.25 (s, 1H), (6.56 (dt, *J* = 16.9, 10.4 Hz) and 6.50 (dt, *J* = 16.9, 10.4 Hz), 1H), 5.91-5.81 (m, 1H), (5.12 (d, *J* = 16.9 Hz) and 5.08 (d, *J* = 16.9 Hz), 1H), (5.02 (d, *J* = 10.4 Hz) and 4.98 (d, *J* = 10.4 Hz), 1H), (4.04-3.92 (m) and 3.82-3.69 (m), 1H), (3.65-3.47 (m) and 3.46-3.28 (m), 2H), (2.30-1.50 (m) and 1.48-1.33 (m), 8H), (2.08, 1.78, 1.76 and 1.62 (s, 3H)). **^{13}C NMR** (mixture of rotamers and isomers, some signals are missing because or overlaping) (75.5 MHz, $CDCl_3$) δ (ppm) 160.7 (d), 160.6 (d), 138.6 (s), 138.3 (s), 137.5 (s), 137.3 (s), 132.9 (d), 132.6 (d), 132.5 (d), 132.1 (d), 126.6 (d), 126.1 (d), 125.8 (d), 125.3 (d), 115.2 (t), 115.0 (t), 114.4 (t), 57.2 (d), 57.0 (d), 54.8 (d), 54.7 (d), 46.1 (t), 43.0 (t), 35.7 (t), 35.7 (t), 34.0 (t), 33.7 (t), 31.5 (t), 31.3 (t), 30.2 (t), 30.1 (t), 29.9 (t), 28.4 (t), 28.3 (t), 23.5 (t), 23.5 (t), 23.2 (q), 22.2 (t), 22.2 (t), 16.3 (q). **IR** (neat) ν (cm^{-1}) 3081, 3040, 2968, 2875, 1663, 1383. **LRMS** (*m/z*, relative intensity) 216 ($(M+Na)^+$, 100). **Exact Mass** calcd for $C_{12}H_{19}NNaO$: 216.1364, found: 216.1363.

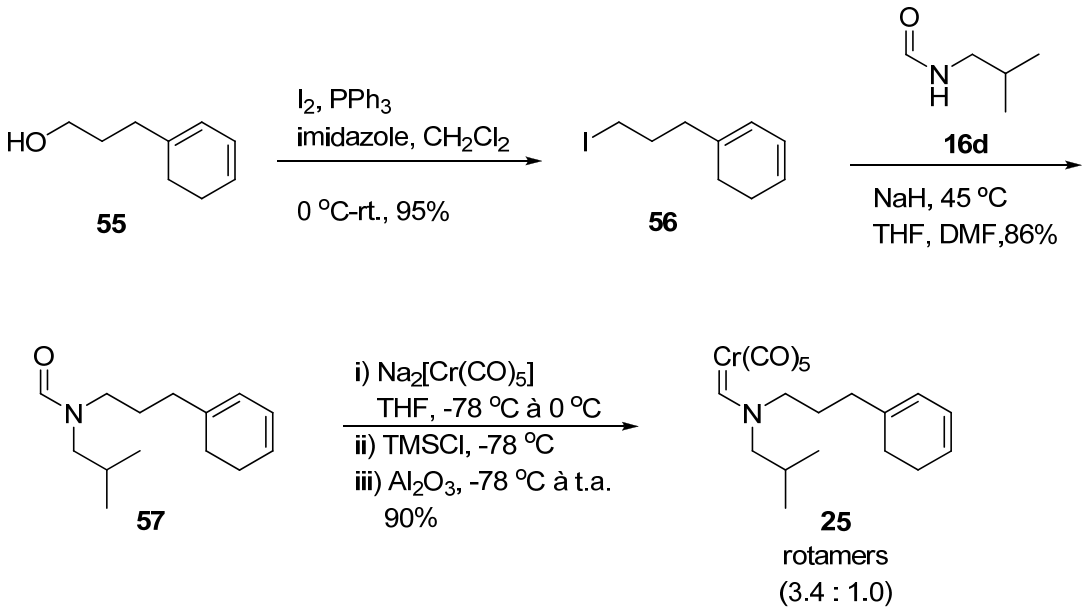
*Mixture of E and Z (R)-pentacarbonyl[(2-(3-methylhexa-3,5-dienyl)pyrrolidine)methylene]chromium(0) (**24**)*



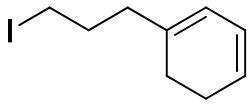
Following the same procedure as per the preparation of complex **13c**, the formamide **54** (318 mg, 1.65 mmol) was converted into the corresponding carbene **24** (425 mg, 70%) obtained as air-sensitive yellow oil and as a single rotamer but as a mixture of *E* and *Z* isomers 67:33). **^{1}H NMR** (*E* double bound) (400 MHz, $CDCl_3$) δ (ppm) 10.98 (s, 1H), 6.55 (dt, 1H, *J* = 16.9, 10.4 Hz), 5.86 (d, 1H, *J* = 11.0 Hz), 5.14 (d, 1H, *J* = 16.9 Hz), 5.04 (d, 1H, *J* = 9.9 Hz), 4.16-3.99 (m, 2H), 3.70-3.60 (m, 1H), 2.30-2.09 (m, 4H), 2.06-1.96 (m, 1H), 1.90-1.74 (m, 2H), 1.77 (s, 3H), 1.68-1.59 (m, 1H). **^{1}H NMR** (*Z* double bound) (400 MHz, $CDCl_3$) δ (ppm) 10.98 (s, 1H), 6.46 (dt, 1H, *J* = 16.6, 10.4 Hz), 5.90 (d, 1H, *J* = 11.4 Hz), 5.14 (d, 1H, *J* = 16.9 Hz), 5.04 (d, 1H, *J* = 9.9 Hz), 4.16-3.99 (m, 2H), 3.70-3.60 (m, 1H), 2.30-2.09 (m, 4H), 2.06-1.96 (m, 1H), 1.90-1.74 (m, 2H), 1.79 (s, 3H), 1.68-1.59 (m, 1H). **^{13}C NMR** (*E* double bound)

(75.5 MHz, $CDCl_3$) δ (ppm) 254.8 (d), 223.9 (s), 217.7 (s), 136.8 (s), 132.7 (d), 126.6 (d), 115.8 (t), 71.1 (d), 55.9 (t), 35.5 (t), 32.8 (t), 30.2 (t), 23.4 (t), 16.4 (q). **IR** (neat) ν (cm^{-1}) 3085, 2976, 2939, 2880, 2054, 2030-1769 (br), 1519, 1453, 903. **LRMS** (*m/z*, relative intensity) 392 ($(M+Na)^+$, 70), 336 (100), 306 (65). **Exact Mass** calcd for $C_{17}H_{19}CrNO_5Na$: 392.0561, found: 392.0560.

Synthesis of chromium aminocarbene (25)



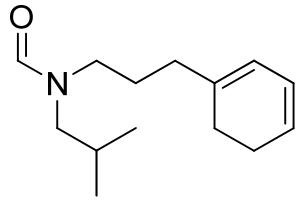
*3-(Cyclohexa-1, 3-dienyl)-1-iodopropane (**56**)*



Iodine (7.32 g, 28.8 mmol) was added to a solution of triphenylphosphine (7.93 g, 30.2 mmol) and imidazole (2.43 g, 35.7 mmol) in dichloromethane (250 mL) at 0 °C. After 15 min, a solution of alcohol **55**[7] (3.80 g, 27.5 mmol) in dichloromethane (10 mL) was added and the solution was warmed to rt. After 1 h, the solution was treated with a 1.0 M aqueous solution of sodium thiosulfate. The organic layer was separated and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on a silica gel column eluting with 0% to 1% of diethyl ether in hexanes to yield **56** (6.46 g, 95%) as colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 5.91-5.83 (m, 1H), 5.73-5.65 (m, 2H), 3.19 (t, 2H, *J*

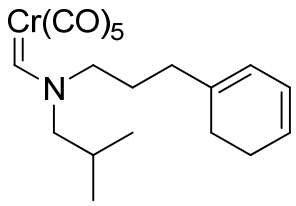
= 6.9 Hz), 2.23-2.12 (m, 4H), 2.11-2.02 (m, 2H), 1.96 (quint, 2H, *J* = 6.9 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ (ppm) 137.2 (s), 124.6 (d), 124.0 (d), 119.8 (d), 37.9 (t), 31.3 (t), 26.3 (t), 23.0 (t), 6.7 (t). **IR** (neat) ν (cm^{-1}) 3035, 2926, 2870, 2820, 1422, 1213, 1167. **LRMS** (*m/z*, relative intensity): 246 (M^+, 30), 119 (10), 91 (100). **Exact Mass** calcd for $C_9H_{11}I$: 245.9905, found: 245.9909.

*N-(3-(Cyclohexa-1, 3-dienyl)propyl)-N-(2-methylpropyl)formamide (**57**)*



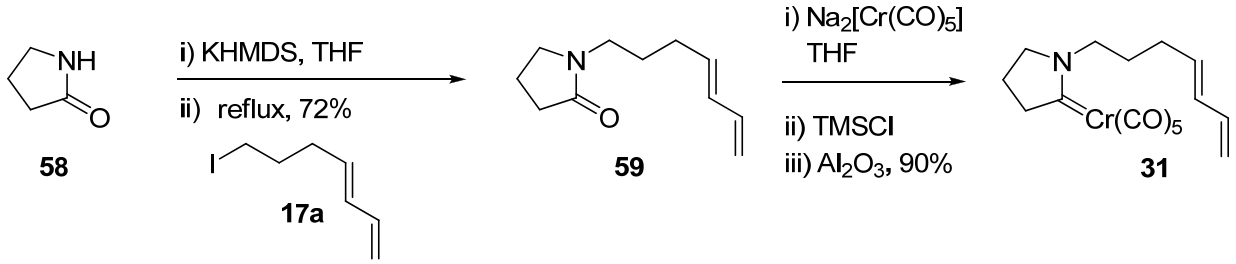
Sodium hydride (1.30 g, 60% in mineral oil, 32.5 mmol) was added to a solution of *N*-isobutylformamide **16d** (2.91 g, 28.8 mmol) in tetrahydrofuran (56 mL) and *N*,*N*-dimethylformamide (42 mL) at 0 °C. The reaction mixture was warmed to rt and stirred for 30 min. A solution of iodide **56** (6.40 g, 25.8 mmol) in tetrahydrofuran (11 mL) was then added *via* cannula. The resulting mixture was heated to 45 °C for 1 h. The reaction mixture was cooled to rt and saturated aqueous ammonium chloride (150 mL) was added. The mixture was further diluted with a 1 : 1 solution of water and saturated aqueous ammonium chloride. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The resulting yellowish oil was dissolved in diethyl ether and the combined organic layers was washed three times with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on a silica gel column eluting with 10% to 30% of ethyl acetate in hexanes to yield **57** (4.91 g, 86%) as colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) as a 1.4 : 1.0 mixture of rotamers δ (ppm) 8.10 (s) and 8.00 (s) (1H, rotamers), 5.91-5.82 (m, 1H), 5.73-5.62 (m, 2H), 3.31-3.25 (m) and 3.21 (t, *J* = 7.1 Hz) (2H, rotamers), 3.14 (d, *J* = 7.7 Hz) and 2.98 (d, *J* = 7.2 Hz) (2H, rotamers), 2.23-1.79 (m, 7H), 1.75-1.62 (m, 2H), 0.89 (d, *J* = 6.6 Hz) and 0.88 (d, *J* = 6.6 Hz) (6H, rotamers). **^{13}C NMR** (75.5 MHz, $CDCl_3$) as a mixture of rotamers δ (ppm) 162.8 (d), 138.3 (s), 137.4 (s), 124.4 (d), 124.3 (d), 123.8 (d), 123.6 (d), 119.4 (d), 118.8 (d), 55.1 (t), 48.7 (t), 46.7 (t), 42.2 (t), 34.4 (t), 33.7 (t), 26.5 (d), 26.1 (t), 25.7 (d), 25.7 (t), 24.8 (t), 22.7 (t), 19.9 (q), 19.6 (q). **IR** (neat) ν (cm^{-1}) 3037, 2958, 2870, 2825, 1674, 1427. **LRMS** (*m/z*, relative intensity): 221 (M^+, 27), 220 (100), 178 ($(M-C_3H_7)^+$, 40), 164 ($(M-C_4H_9)^+$, 9), 91 (66). **Exact Mass** calcd for $C_{14}H_{22}NO$: 220.1701, found: 220.1706.

*Pentacarbonyl[(N-(3-(Cyclohexa-1, 3-dienyl)propyl)-N-(2-methylpropyl)amino)methylene]chromium(0) (**25**)*

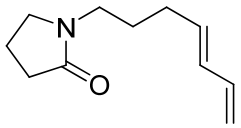


Following the procedure as per the preparation of complex **13c**, formamide **57** (2.00 g, 9.04 mmol) in tetrahydrofuran (6 mL) gave carbene **25** (3.24 g, 90%) obtained as yellowish oil and as a 3.4 : 1.0 mixture of rotamers. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 10.95 (s) and 10.79 (s) (1H, rotamers), 5.93-5.84 (m, 1H), 5.76-5.63 (m, 2H), 3.97-3.87 (m) and 3.56 (t, *J* = 7.2 Hz) (2H, rotamers), 3.83 (d, *J* = 8.3 Hz) and 3.37 (d, *J* = 7.7 Hz) (2H, rotamers), 2.25-1.72 (m, 9H), 1.03 (d, *J* = 6.6 Hz) and 0.90 (d, *J* = 6.6 Hz) (6H, rotamers). **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ (ppm) 263.4 (d), 262.6 (d), 224.2 (s), 218.0 (s), 217.8 (s), 137.7 (s), 136.9 (s), 124.7 (d), 124.6 (d), 124.5 (d), 120.3 (d), 119.8 (d), 72.0 (t), 63.7 (t), 63.1 (t), 57.2 (t), 34.4 (t), 33.7 (t), 27.4 (d), 27.0 (t), 26.5 (t), 26.3 (t), 26.0 (t), 23.1 (t), 23.0 (t), 19.7 (q), 19.6 (q). **IR** (neat) ν (cm^{-1}) 2963, 2934, 2873, 2055, 1973, 1908. **LRMS** (*m/z*, relative intensity): 397 (M^+, 8), 341 ($(M-(CO)_2)^+$, 8), 285 ($(M-(CO)_4)^+$, 12), 257 ($(M-(CO)_5)^+$, 100), 162 (60), 84 (98). **Exact Mass** calcd for $C_{19}H_{23}NO_5Cr$: 397.0981, found: 397.0988.

Synthesis of chromium aminocarbene (31)

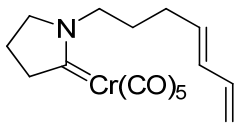


*(E)-1-(hepta-4,6-dienyl)pyrrolidin-2-one (**59**)*



KHMDS (4.92 mL, 2.46 mmol, 0.5M in toluene) was slowly added to a solution of pyrrolidin-2-one **58** in THF (9 mL) at rt. The reaction mixture was stirred for 1 h. A solution of the iodide **17a** (546 mg, 2.46 mmol) in THF (3 mL) was added slowly. The reaction mixture was heated to reflux temperature for 6 h. Water (20 mL) was then added and the mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on a silica gel column using a solution of acetone in hexanes (40:60) as eluent. Amide **59** (319 mg, 72%) was obtained as colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 6.29 (dt, 1H, *J* = 16.8, 10.2 Hz), 6.06 (dd, 1H, *J* = 15.2, 10.3 Hz), 5.68 (dt, 1H, *J* = 15.2, 7.1 Hz), 5.09 (d, 1H, *J* = 16.8 Hz), 4.97 (d, 1H, *J* = 10.3 Hz), 3.37 (t, 2H, *J* = 7.3 Hz), 3.28 (t, 2H, *J* = 7.4 Hz), 2.38 (t, 2H, *J* = 7.3 Hz), 2.09 (q, 2H, *J* = 7.1 Hz), 2.01 (quint, 2H, *J* = 7.3 Hz), 1.62 (quint, 2H, *J* = 7.4 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ (ppm) 174.8 (s), 136.9 (d), 133.7 (d), 131.4 (d), 115.1 (t), 47.0 (t), 42.0 (t), 30.9 (t), 29.7 (t), 26.6 (t), 17.8 (t). **IR** (neat) ν (cm^{-1}) 3084, 2928, 2864, 1680, 1428, 1287, 1006. **LRMS** (*m/z*, relative intensity) 202 ($(M+Na)^+$, 100). **Exact Mass** calcd for $C_{11}H_{17}NNaO$: 202.1202, found: 202.1207.

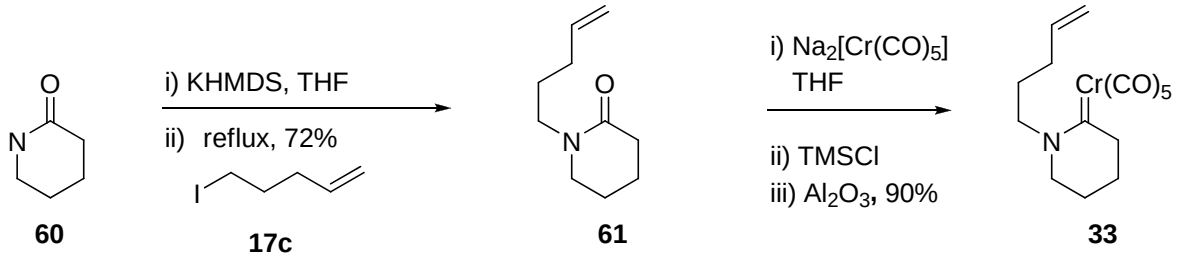
*Chromium aminocarbene (**31**)*



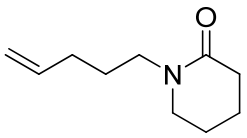
Following the procedure as per the preparation of complex **13c**, amide **59** (308 mg, 1.72 mmol) in tetrahydrofuran (6 mL) gave carbene **31** (550 mg, 90%) obtained as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 6.32 (dt, 1H, *J* = 16.9, 10.3 Hz), 6.12 (dd, 1H, *J* = 15.0, 10.3 Hz), 5.70 (dt, 1H, *J* = 15.0, 7.0 Hz), 5.14 (d, 1H, *J* = 16.9 Hz), 5.02 (d, 1H, *J* = 10.3 Hz), 4.01 (t, 2H, *J* = 8.1 Hz), 3.74 (t, 2H, *J* = 7.5 Hz), 3.33 (t, 2H, *J* = 7.5 Hz), 2.24 (q, 2H, *J* = 7.2 Hz), 1.94-1.86 (m, 4H). **^{13}C NMR** (100.7 MHz, C_6D_6) δ (ppm) 264.0 (s), 223.4 (s), 218.6 (s), 137.0 (d), 132.6 (d), 132.6 (d), 115.8 (t), 58.2 (t), 56.2 (t), 54.8 (t), 29.6 (t), 27.4 (t), 20.4 (t). **IR** (neat) ν (cm^{-1}) 3085, 3037, 2949, 2882, 2053, 2012-1774

(br), 1526, 1005. **LRMS** (*m/z*, relative intensity) 378 ($(M+Na)^+$, 20), 322 ($(M+Na-2CO)^+$, 100). **Exact Mass** calcd for $C_{16}H_{17}CrNNaO_5$: 378.0410, found: 378.0407.

Synthesis of chromium aminocarbene (33)

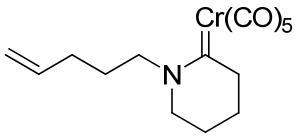


*1-(Pent-4-enyl)piperidin-2-one (**61**)*



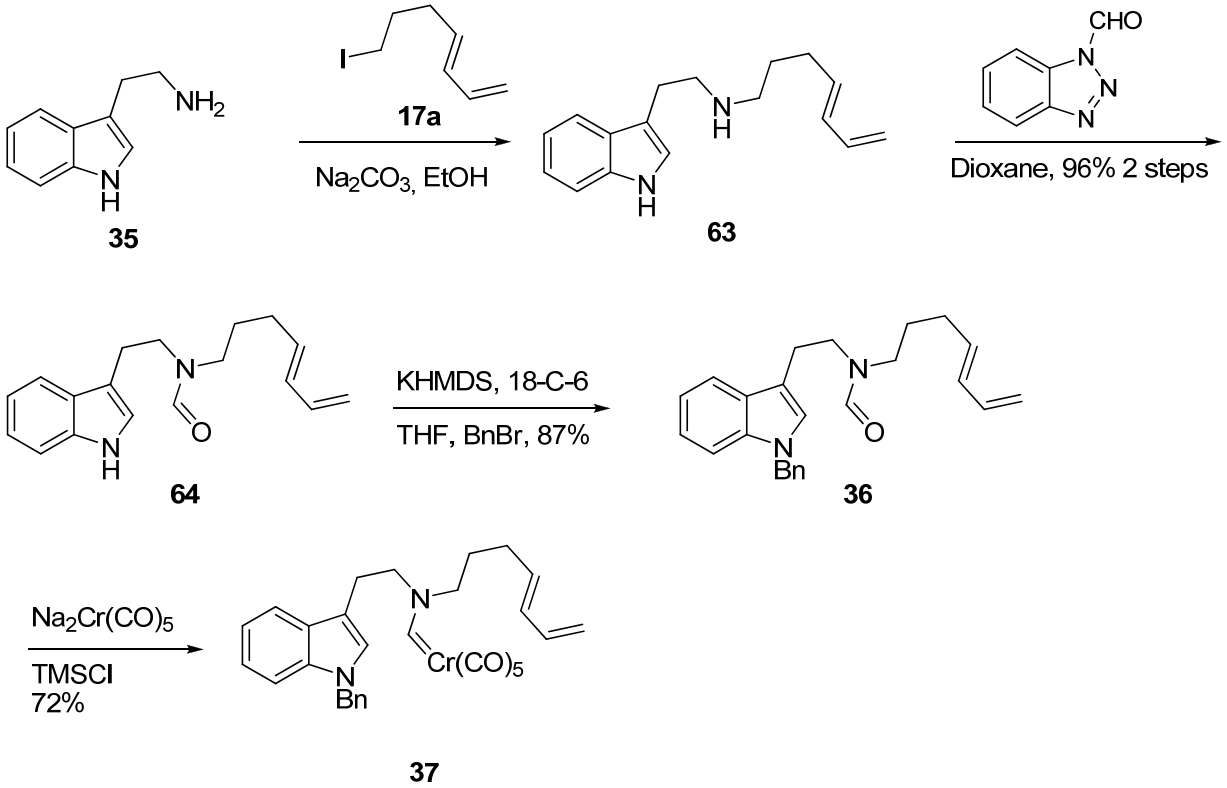
To a magnetically stirred suspension of NaH (0.177 g, 1.1 eq.) in THF (13 mL) and DMF (7 mL) was added valerolactam **60** (0.397 g, 4.00 mmol), resulting in a thick white sludge. The reaction mixture was stirred at rt for 0.5 h and then treated with a solution of 5-iodopent-1-ene **17c** (0.941 g, 4.80 mmol). The resulting mixture was heated to 60 °C for 2.5 h and then allowed to cool to rt. NH_4Cl (sat. aq. solution) was added and the separated aqueous layer extracted with EtOAc (2x). The combined organic layers were washed with water (3x) and brine, then dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product as a pale-yellow liquid. The crude material was subjected to flash column chromatography (silica gel, EtOAc elution) to give the title formamide **61** (0.365 g, 55%) as colourless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.80 (m, 1H), 5.01 (dq, J = 17.1 and 1.7 Hz, 1H), 4.95 (dq, J = 10.2 and 1.7 Hz, 1H), 3.34 (app t, J = 7.5 Hz, 2H), 3.25 (m, 2H), 2.36 (m, 2H), 2.05 (q, J = 6.9 Hz, 2H), 1.82 - 1.73 (complex m, 4H), 1.63 (quintet, J = 7.6 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.6 (CO), 137.9 (CH), 114.8 (CH_2), 47.9 (CH_2), 46.8 (CH_2), 32.3 (CH_2), 31.0 (CH_2), 26.2 (CH_2), 23.2 (CH_2), 21.3 (CH_2); **IR** (NaCl) *v* 3531, 3072, 2935, 2863, 1650, 1494, 1466, 1352. **HRMS** (*m/z*, relative intensity) 190 (MNa^+). **Exact Mass** calcd for $C_{10}H_{17}NONa$: 190.1208, found : 190.1209.

*Chromium aminocarbene (**33**)*

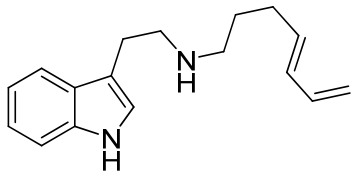


Following the procedure as per the preparation of complex **13c**, amide **61** (0.350 g, 2.09 mmol) in tetrahydrofuran (6 mL) gave carbene **33** (0.547 g, 76%) obtained as air-sensitive yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.82 (m, 1H), 5.06 (app. m, 2H), 4.07 (app. s, 2H), 3.45 (app. s, 2H), 3.16 (app. s, 2H), 2.20 (app. s, 2H), 1.87 (app. s, 2H), 1.78 (app. s, 2H), 1.55 (app. s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 269.9 (CCr), 223.4 (CO), 218.0 (CO), 136.8 (CH), 116.0 (CH_2), 64.2 (CH_2), 50.9 (CH_2), 49.6 (CH_2), 30.6 (CH_2), 27.8 (CH_2), 21.6 (CH_2), 17.1 (CH_2); **IR** (NaCl) ν 3076, 2948, 2878, 2051, 1902, 1521, 674, 657. **HRMS** (*m/z*, relative intensity) 366 (MNa^+). **Exact Mass** calcd for $C_{15}H_{17}CrNO_5Na$: 366.0410, found : 366.0413.

Synthesis of chromium aminocarbene (37)

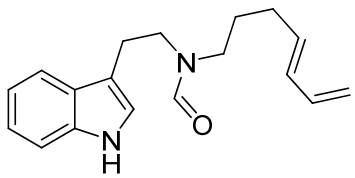


*(E)-N-(2-(1H-indol-3-yl)ethyl)hepta-4,6-dien-1-amine (**63**)*



Tryptamine (3.00 g, 18.7 mmol) was charged in a dry sealed screw-cap vial followed by anhydrous ethanol (50 mL), Na_2CO_3 (1.99 g, 18.7 mmol) and iodide **17a** (2.08 g, 9.37 mmol). The vial was shut sealed and the mixture was heated to 110 °C for 18 h. The vial was opened, and the solvent was evaporated, the product was solubilised in dichloromethane (30 mL), and water was added (30 mL). The aqueous phase was then washed with dichloromethane (3 x 20 mL). The organic fractions were combined and the solvent was evaporated to obtain the crude product (3.09 g). The product **63** is difficult to purify and the crude mixture was used directly for the next reaction. However, for characterisation purposes, 250 mg were transferred on a silica gel column (2% solution of **A** in dichloromethane; **A** = 5% NH_4OH in MeOH) to afford pure amine **63** as colorless oil (47.0 mg, 21%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 7.97 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.24–7.06 (m, 2H), 7.02 (d, *J* = 2.1 Hz, 1H), 6.32 (dt, *J* = 16.9, 10.2 Hz, 1H), 6.05 (dd, *J* = 22.2, 11.1 Hz, 1H), 5.71 (dt, *J* = 22.2, 7.5, 1H), 5.10 (d, *J* = 16.8 Hz, 1H), 4.97 (d, *J* = 10.2 Hz, 1H), 2.95–2.74 (m, 4H), 2.55 (t, *J* = 7.3, 2H), 2.12 (q, *J* = 7.5 Hz, 2H), 1.59 (quint, *J* = 7.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) 137.2 (d), 136.2 (s), 135.0 (d), 131.2 (d), 127.5 (s), 121.8 (d), 121.6 (d), 119.1 (d), 118.8 (d), 114.9 (t), 114.4 (s), 111.2 (d), 54.7 (t), 53.6 (t), 30.5 (t), 26.6 (t), 22.9 (t). **IR** (NaCl) ν (cm^{-1}) 3419, 3140 - 2859 (br), 1650. **LRMS** (*m/z*, relative intensity) 255 (MH^+, 100), 144 (5). **Exact Mass** cacld for $C_{17}H_{22}N_2$: 255.1856 (MH^+), found: 255.1866 (MH^+)

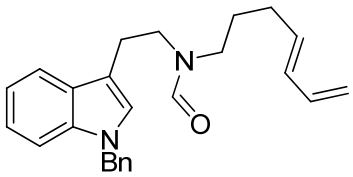
*(E)-N-(2-(1H-indol-3-yl)ethyl)-N-(hepta-4,6-dienyl)formamide (**64**)*



1H-Benzo[d][1,2,3]triazole-1-carbaldehyde (120 mg, 1.33 mmol) in dry 1,4-dioxane (5.0 mL) was added to the crude *N*-alkyltryptamine **63** (260 mg, 1.02 mmol) in dry 1,4-dioxane (5.0 mL). The solution was heated in a sealed screw-cap vial at 110 °C for 18 h. A solution of NaOH 1N (10 mL) was then added and the reaction mixture was agitated for 30 min. Water was added and the aqueous solution

was extracted with dichloromethane (3 x 20 mL). Organic fractions were combined and dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure to afford crue oil. The crude product was subjected to silica gel column chromatography (A 2.5% solution of **A** in dichloromethane; **A** = 5% NH_4OH in MeOH) to afford the pure product **64** as colorless oil (135 mg, 96 %) and as a mixture of rotamers. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.58 (s, 1H), 8.10 (s, 1H), 7.78 (s, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 17.1 Hz, 2H), 7.31–7.08 (m, 4H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.92 (d, *J* = 2.3 Hz, 1H), 6.43–6.23 (m, 2H), 6.16– 5.99 (m, 2H), 5.84–5.49 (m, 2H), 5.14 (d, *J* = 16.9 Hz, 2H), 5.02 (dd, *J* = 10.1, 4.6 Hz, 2H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.52 (t, *J* = 6.8 Hz, 2H), 3.40 (t, *J* = 7.1 Hz, 2H), 3.17 (t, *J* = 7.1 Hz, 2H), 3.10–2.93 (m, 4H), 2.20–1.99 (m, 4H), 1.81–1.51 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.3 (d), 163.2 (d), 137.2 (d), 137.0 (d), 136.6 (s), 136.5 (s), 134.0 (d), 133.2 (d), 132.4 (d), 132.0 (d), 127.5 (s), 127.1 (s), 122.8 (d), 122.4 (d), 122.3 (d), 122.2 (d), 119.8 (d), 119.6 (d), 118.8 (d), 118.4 (d), 116.0 (t), 115.6 (t), 112.9 (s), 111.8 (d), 111.5 (d), 48.2 (t), 47.4 (t), 43.3 (t), 42.2 (t), 30.7 (t), 30.2 (t), 29.4 (t), 28.1 (t), 27.2 (t), 25.3 (t), 23.5 (t). **IR** (NaCl disk) ν (cm^{-1}) 3288 (br), 2935, 1663. **Exact Mass** *m/z* (relative intensity) 283 (5) $(MH)^+$, 305 (100) $(MNa)^+$. **Exact Mass** calcd for $C_{18}H_{22}N_2O$: 305.1624 $(MNa)^+$, found : 305.1634 $(MNa)^+$

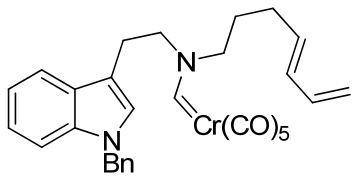
*(E)-N-(2-(1-benzyl-1H-indol-3-yl)ethyl)-N-(hepta-4,6-dienyl)formamide (**36**)*



KHMDS (0.5 M in toluene, 1.43 mL, 0.708 mmol) was added to a solution of formamide **64** (102 mg, 0.375 mmol) and 18-C-6 (49.0 mg, 0.188 mmol) in THF (1.00 mL) at rt. After stirring 1.5 h at rt, benzylbromide (0.09 mL, 0.7 mmol) was added. The resulting mixture was heated to reflux for 18h. Solvent was removed under reduced pressure and water was added. The resulting aqueous phase was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford crude (235 mg, 175%). The crude product was chromatographed on silica gel (A 1% solution of **A** in dichloromethane; **A** = 5% NH_4OH in MeOH) to give pure product **36** as yellow wax (118 mg, 87%). For the mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.06 (s, 1H), 7.83 (s, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.39–7.03 (m, 16H), 6.98 (s, 1H), 6.90 (s, 1H), 6.30 (dt, J =

18.6, 10.0 Hz, 2H), 6.06 (dd, J = 14.6, 10.0 Hz, 2H), 5.75–5.53 (m, 2H), 5.25 (s, 4H), 5.12 (d, J = 18.6 Hz, 2H), 5.05–4.95 (m, 2H), 3.67–3.57 (m, 2H), 3.51 (t, J = 7.0 Hz, 2H), 3.41–3.31 (m, 2H), 3.13 (t, J = 7.0 Hz, 2H), 3.08–2.93 (m, 4H), 2.16–1.99 (m, 4H), 1.76–1.54 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) 163.2 (d), 163.1 (d), 137.9 (s), 137.7 (s), 137.3 (s), 137.0 (d), 136.9 (s), 134.0 (d), 133.2 (d), 132.5 (d), 132.0 (d), 129.1 (d), 129.0 (d), 128.3(s), 127.9 (d), 127.9 (d), 127.1 (d), 127.0 (d), 126.8 (d), 126.4 (d), 122.4 (d), 122.2 (d), 119.6 (d), 119.5 (d), 119.2 (d), 118.8 (d), 116.0 (t), 115.6 (t), 112.4 (s), 111.2 (s), 110.3 (d), 110.0 (d), 50.1 (t), 48.2 (t), 47.5 (t), 43.5 (t), 42.3 (t), 30.2 (t), 29.4 (t), 28.2 (t), 27.2 (t), 25.5 (t), 23.6 (t). **IR** (NaCl disk) ν (cm^{-1}) 3029, 2929, 2860, 1669. **Exact Mass** *m/z* (relative intensity) 395 (70) (MNa^+), 373 (10) (MH^+). **Exact Mass** calcd for $C_{25}H_{28}N_2O$: 395.2094 (MNa^+), found : 395.2108 (MNa^+).

*Chromium aminocarbene (**37**)*



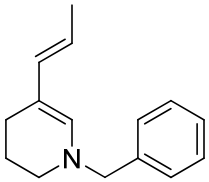
Following the procedure as per the preparation of complex **13c**, formamide **36** (1.14 g, 2.60 mmol) in tetrahydrofuran (10 mL) gave carbene **33** (1.20 g, 72 %) obtained as air-sensitive yellow oil. **^{1}H NMR** (300 MHz, CDCl3) δ (ppm) 10.96 (s, 1H), 10.35 (s, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.36 –7.02 (m, 17H), 6.88 (s, 1H), 6.39–6.22 (m, 2H), 6.17–6.01 (m, 2H), 5.73–5.51 (m, 2H), 5.41 (t, *J* = 6.4 Hz, 2H), 5.31 (s, 2H), 5.26 (s, 2H), 5.15 (dd, J = 10.1, 4.0 Hz, 2H), 5.05 (dd, J = 10.1, 4.0 Hz, 2H), 4.31–4.21 (m, 2H), 3.93–3.82 (m, 2H), 3.57 (t, *J* = 8.6 Hz, 2H), 3.34–3.22 (m, 2H), 3.08 (t, *J* = 6.4 Hz, 2H), 2.27–2.15 (m, 2H), 2.06 (q, *J* = 6.4 Hz, 2H), 1.94–1.70 (m, 4H).**^{13}C NMR** (75 MHz, CDCl3) δ (ppm) 263.0 (s), 262.0 (s), 233.4 (s), 224.1 (s), 217.8 (d), 217.7 (d), 137.5 (s), 137.0 (d), 136.9 (s), 136.8 (s), 136.6 (d), 133.1 (d), 132.6 (d), 132.6 (d), 131.9 (d), 128.9 (d), 128.9 (d), 127.8 (d), 127.8 (d), 127.0 (d), 126.9 (d), 126.9 (d), 126.8 (d), 122.4 (d), 122.3 (d), 119.8 (d), 119.7 (d), 118.5 (d), 118.2 (d), 116.5 (t), 116.1 (t), 110.5 (d), 110.5 (s), 110.3 (d), 109.6 (s), 94.5 (s), 92.9 (s), 89.7 (s), 63.9 (t), 63.8 (t), 57.5 (t), 56.9 (t), 50.2 (t), 50.1 (t), 29.6 (t), 29.0 (t), 28.4 (t), 28.3 (t), 25.4 (t), 25.1 (t). **IR** (NaCl disk) ν (cm^{-1}) 3965, 3031, 2939, 2054 (sharp), 1938 (broad). **Exact Mass** *m/z* (relative intensity) 435 (50, MH^+-4CO), 408 (50). **Exact Mass** calcd for $C_{30}H_{28}N_2CrO_5$: 408.1658, found : 408.1669.

Cycloadducts

General procedure for the thermolysis of chromium aminocarbenes

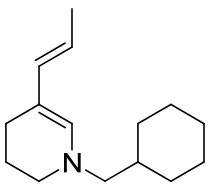
The chromium carbene and PPh_3 (1.2 equiv.) were diluted in dry toluene (0.01M) and the solution was degassed three times by freeze-thaw cycles under reduced pressure for 2 minutes and put back under argon at -78 °C. After the reaction was warmed up to rt, it was heated to reflux temperature for several hours (the reaction was monitored by NMR). The reaction mixture was cooled, filtered on celite and the filtrate was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel.

*(E)-1-Benzyl-5-(prop-1-enyl)-1,2,3,4-tetrahydropyridine **15a***



Same as per the general procedure with aminocarbene **18a** (85 mg, 0.21 mmol) and triphenylphosphine (64 mg, 0.25 mmol). Quantitative conversion by NMR, the product could not be purified. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 7.35-7.20 (m, 5H), 6.07 (s, 1H), 5.98 (d, 1H, *J* = 14.9 Hz), 5.16 (dq, 1H, *J* = 14.9, 5.9 Hz), 4.02 (s, 2H), 2.86 (t, 2H, *J* = 5.5 Hz), 2.12 (t, 2H, *J* = 6.1 Hz), 1.95-1.75 (m, 2H), 1.54 (d, 3H, *J* = 5.9 Hz). **LRMS** (*m/z*, relative intensity) 213 ($(MH)^+$, 100), 198 (15), 91 (100). **Exact mass** calcd for $C_{15}H_{19}N$: 213.1517, found: 213.1515.

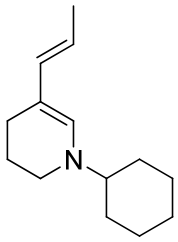
*(E)-1-Cyclopropylmethyl-5-(prop-1-enyl)-1,2,3,4-tetrahydropyridine **15b***



Same as per the general procedure with aminocarbene **18b** (83 mg, 0.20 mmol) and triphenylphosphine (64 mg, 0.25 mmol). Quantitative conversion by NMR, the product could not be purified. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 5.97 (d, 1H, *J* = 15.4 Hz), 5.95 (s, 1H), 5.08 (dq, 1H, *J* = 15.4, 6.7 Hz), 2.95

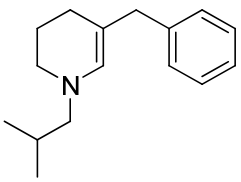
(t, 2H, *J* = 5.6 Hz), 2.68 (d, 2H, *J* = 6.0 Hz), 2.12 (t, 2H, *J* = 5.1 Hz), 1.89 (quint, 2H, *J* = 6.0 Hz) , 1.70 (d, 3H, *J* = 6.7 Hz), 1.70-1.59 (m, 5H), 1.35-1.05 (m, 4H), 0.90-0.77 (m, 2H). **LRMS** (*m/z*, relative intensity) 219 ($(MH)^+$, 25), 136 (100). **Exact mass** calcd for $C_{15}H_{25}N$: 219.1987, found: 219.1982.

(E)-1-Cyclohexyl-5-(prop-1-enyl)-1,2,3,4-tetrahydropyridine ***15c***



To chromium aminocarbene **18c** (81 mg, 0.20 mmol) and triphenylphosphine (64 mg, 0.25 mmol) was added toluene (20 mL). The solution was put under vacuum for 5 minutes at -78 ^oC and put back under argon to degass solvent. This procedure was done 3 times. The solution was then refluxed for 3 h and the solvent was evaporated. NMR analysis of the crude product indicated the presence of the dienamine **15c** as the major product which proved unstable to purification. Tricarbonyl(η^6-toluene)chromium and phosphine derivatives were also found as other major components. The dienamine was characterized as the crude product. **^{1}H NMR** (300 MHz, C_6D_6) δ (ppm) 6.27 (d, 1H, *J* = 15.2 Hz), 6.08 (s, 1H), 5.33 (dq, 1H, *J* = 15.2, 6.6 Hz), 2.78 (t, 2H, *J* = 5.5 Hz), 2.47 (tt, 1H, *J* = 11.3, 3.2 Hz), 2.26 (t, 2H, *J* = 6.4 Hz), 1.95 (dd, 1H, *J* = 6.6, 1.3 Hz), 1.78 (quint, 2H, *J* = 6.0 Hz), 1.70-1.59 (m, 4H), 1.55-1.46 (m, 2H), 1.26-0.86 (m, 6H). **^{13}C NMR** (75.5 MHz, C_6D_6) note : two sp^2 carbons are not reported since they can not be recognized from phosphine derivatives carbons. δ (ppm) 112.0 (d), 108.0 (s), 63.0 (d), 44.2 (t), 31.1 (t), 26.3 (t), 26.1 (t), 23.1 (t), 22.5 (t), 18.7 (q). **LRMS** (*m/z*, relative intensity) 206 ($(MH)^+$, 100). **Exact mass** calcd for $C_{14}H_{24}N$: 206.1903, found: 206.1914.

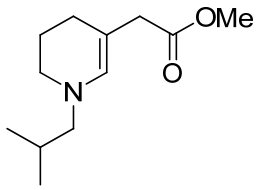
5-Benzyl-1-isobutyl-1,2,3,4-tetrahydropyridine ***15i***



A solution of chromium carbene **13i** (161.3 mg, 0.38 mmol) in dried and degassed toluene (0.03 M solution) was treated with polymer-bound triphenylphosphine, (100-200 mesh, extent of labeling: ~3.0

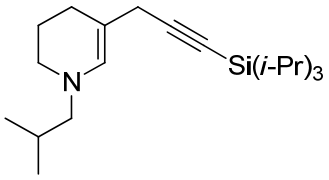
mmol/g loading, 2 % cross-linked with divinylbenzene, 2 eq) and was heated to 110 °C while monitoring by TLC. The mixture was filtered and concentrated under reduced pressure. The ^{1}H NMR of the crude showed a complete conversion to a fairly clean product. Purification by flash chromatography (100 % hexane with silica gel pretreated with Et_3N) yielded 29.1 mg of adduct **15i** (33%) as yellow oil. The low yield is due to the instability of the enamine to silica. **^{1}H NMR** (300 MHz, C_6D_6) δ (ppm) 7.18 (m, 5H), 5.74 (s, 1H), 3.26 (s, 2H), 2.67–2.56 (m, 2H), 2.37 (d, *J* = 7.3 Hz, 2H), 1.86 (t, *J* = 6.3 Hz, 2H), 1.67 (dt, *J* = 10.1, 6.6 Hz, 2H), 1.39 - 1.26 (m, 1H), 0.79 (d, *J* = 8.8 Hz, 6H). **^{13}C NMR** (75 MHz, C_6D_6) δ (ppm) 142.13 (s), 134.12 (d), 129.08 (d), 128.51 (d), 126.07 (d), 106.35 (s), 63.84 (t), 47.58 (t), 42.60 (t), 27.23 (d), 24.94 (t), 23.25 (t), 20.42 (q). **IR** (KBr) υ (cm^{-1}) : 3025, 2952, 1663. **LRMS** (*m/z*, relative intensity) 230 (MNa^+, 100). **Exact Mass** calcd for $C_{16}H_{23}NNa$ 230.1903, found: 230.1913.

methyl 2-(1-isobutyl-1,4,5,6-tetrahydropyridin-3-yl)acetate ***15j***



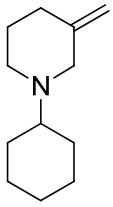
Same procedure as per compound **15i** using chromium aminocarbene **13j** (110.6 mg, 0.27 mmol). The mixture was filtered and concentrated under reduced pressure. The ^{1}H NMR of the crude showed a complete conversion to a fairly clean product. Purification by flash chromatography (100 % hexane with silica gel pre-treated with Et_3N) gave 14 mg of product **15j** in an isolated yield of 24% as yellow oil. The low yield is due to the instability of the enamine to silica. **^{1}H NMR** (300 MHz, C_6D_6) δ 5.70 (s, 1H), 3.36 (s, 3H), 2.89 (d, *J* = 0.6 Hz, 2H), 2.62 (dd, *J* = 7.1, 3.9 Hz, 2H), 2.31 (d, *J* = 7.3 Hz, 2H), 2.11 (t, *J* = 6.4 Hz, 2H), 1.77–1.64 (m, 2H), 1.63–1.52 (m, 1H), 0.75 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (75 MHz, C_6D_6) δ (ppm) 172.64 (s), 135.63 (d), 99.35 (s), 63.58 (t), 51.03 (q), 47.14 (t), 41.15 (t), 27.28 (d), 25.44 (t), 23.08 (t), 20.33 (q). **IR** (KBr) υ (cm^{-1}) : 2951, 1738, 1663. **LRMS** (m/z, relative intensity) 212 (MNa^+,100). **Exact Mass** calcd for $C_{12}H_{21}NO_2Na$ 212.1645, found: 212.1650.

1-isobutyl-5-(3-(triisopropylsilyl)prop-2-ynyl)-1,2,3,4-tetrahydropyridine ***15k***



Same procedure as per compound **15i** using chromium aminocarbene **13k** (94.2 mg, 0.18 mmol). The mixture was filtered and concentrated under reduced pressure. The ^{1}H NMR of the crude showed a complete conversion to a fairly clean product. Purification by flash chromatography (100 % hexane with silica gel pretreated with Et_3N) isolated yield (20.6 mg, 34%) of product **15k** as colorless oil. The low yield is due to the instability of the enamine to silica. **^{1}H NMR** (300 MHz, C_6D_6) δ 6.02 (m, 1H), 2.89 (d, *J* = 1.5 Hz, 2H), 2.68 – 2.60 (m, 2H), 2.40 (d, *J* = 4.5 Hz, 2H), 1.97 (dd, *J* = 14.2, 6.5 Hz, 2H), 1.72 (td, *J* = 11.3, 6.3 Hz, 3H), 1.64 (d, *J* = 6.9 Hz, 1H), 1.27-1.05 (m, 2H), 1.22 (d, *J* = 6 Hz, 18H), 0.81 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (75 MHz, C_6D_6) δ 133.62 (d), 108.19 (s), 101.20 (s), 81.43 (s), 63.83 (t), 47.68 (t), 27.36 (d), 26.40 (t), 25.30 (t), 23.20 (t), 20.41 (d), 19.00 (q), 11.81 (q). **IR** (KBr) υ (cm^{-1}) : 2953, 2170, 2062, 1940, 1669. **LRMS** (m/z, relative intensity) 334 (MH^+). **Exact Mass** calculated for $C_{21}H_{39}NSi$ 334.2925 $[MH]^+$, found: 334.2937 $[MH]^+$.

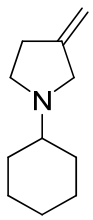
(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine ***19d***



Following the general procedure for the thermolysis of chromium aminocarbenes, chromium carbene **13d** (200 mg, 0.539 mmol) and PPh_3 (170 mg, 0.647 mmol) were reacted to give adduct **19d**. Flash column chromatography (silica gel, DCM–DCM/MeOH v/v 4:1 gradient elution) of the crude material yielded the title amine **19d** (67 mg, 69%) as a colourless oil that quickly turns dark-orange. **^{1}H NMR** (300 MHz, $CDCl_3$) *δ* 4.74 (d, *J* = 8.4 Hz, 2H), 3.04 (s, 2H), 2.60 (t, *J* = 5.5 Hz, 2H), 2.38-2.18 (complex m, 1H), 2.14 (t, *J* = 6.5 Hz, 2H), 1.89 (m, 2H), 1.79 (m, 2H), 1.32-1.15 (complex m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 144.8 (C), 109.3 (CH_2), 63.6 (CH), 56.3 (CH_2), 49.2 (CH_2), 44.6 (CH_2), 33.0 (CH_2), 32.2 (CH_2), 28.6 (CH_2), 26.3 (CH_2), 26.0 (CH_2); **IR** (NaCl) *ν* 3072, 2929, 2853, 2789, 1659,

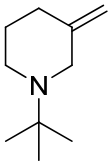
1451, 886. **LRMS** (m/z, relative intensity) 180 (MH^+). **Exact Mass** $C_{12}H_{22}N$, calc. 180.1752, found 180.1750.

*(E)-8-(Prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine **19e***



Following the general procedure for the thermolysis of chromium aminocarbenes, chromium carbene **13e** (330 mg, 0.924 mmol) and PPh_3 (288 mg, 1.10 mmol) were reacted to give adduct **19e**. Flash column chromatography (silica gel, DCM–DCM/MeOH v/v 4:1 gradient elution) of the crude material yielded the title amine **19e** (64 mg, 42%) as a colourless oil that quickly turns dark-orange. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.39 (bs, 2H), 3.38 (s, 2H), 2.85 (bs, 2H), 2.56 (app. s, 2H), 2.21 (m, 1H), 1.89 (m, 2H), 1.77 (m, 2H), 1.62 (m, 1H), 1.42-1.12 (complex m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 106.1 (CH_2), 64.1 (CH), 56.6 (CH_2), 51.6 (CH_2), 31.1 (CH_2), 31.0 (CH_2), 25.7 (CH_2), 24.9 (CH_2), the quaternary carbon signal is obscured; **IR** (NaCl) ν 3068, 2929, 2853, 2781, 1659, 1451, 886. **LRMS** (m/z, relative intensity) 166 (MH^+). **Exact Mass** calcd for $C_{11}H_{20}N$: 166.1590, found : 166.1586.

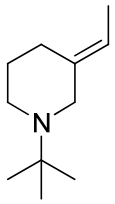
*(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine **19g***



A solution of chromium aminocarbene **13g** (0.050 g, 0.145 mmol) in toluene without additive was heated at 100 °C for 2.5 h. Flash column chromatography (NEt_3-treated silica gel, pentane–pentane/ether 95:5 gradient elution) of the crude material yielded the title amine **19g** (20 mg, 90%) as a colourless oil that quickly turned bright-red. A trace of enamine **15g** was visible in the ^{1}H NMR spectrum of the product (signal at 5.95 ppm). Characterization for **19g** : **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.73 (d, J = 11.1 Hz, 2H), 3.02 (s, 2H), 2.59 (t, J = 5.4 Hz, 2H), 2.13 (t, J = 6.2 Hz, 2H), 1.65 (m, 1H), 1.09 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.8 (C), 108.8 (CH_2), 53.4 (CH_2), 46.3 (CH_2), 33.0 (CH_2), 27.2 (CH_2), 26.0 (CH_3), the signal due to the aliphatic quaternary carbon is covered or obscured;

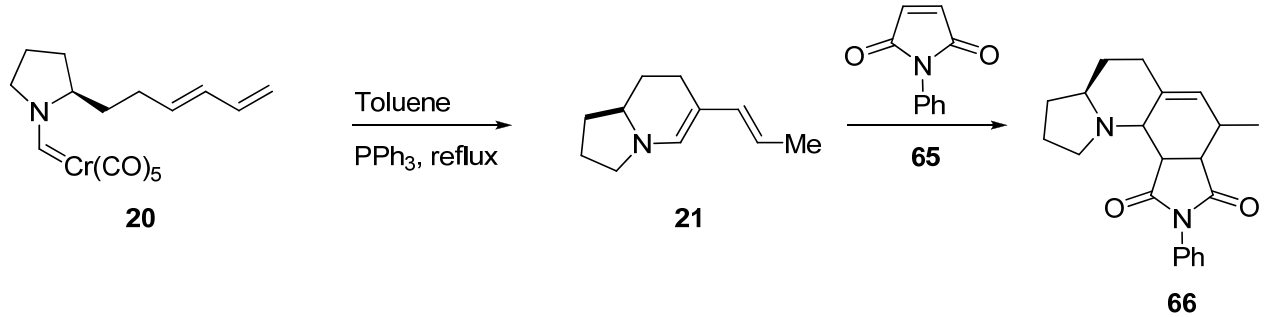
IR (NaCl) *v* 3072, 2975, 2931, 2860, 2785, 1654, 1359, 1204, 886. **LRMS** (m/z, relative intensity) 154 (MH^+). **Exact Mass** calcd for $C_{10}H_{20}N$: 154.1590, found : 154.1597.

*(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine **19h***



Following the general procedure for the thermolysis of chromium aminocarbenes, chromium carbene **13h** (0.200 g, 0.557 mmol) and PPh_3 (175 mg, 0.668 mmol) were reacted to give adduct **19h**. Flash column chromatography (silica gel, DCM–DCM/MeOH v/v 4:1 gradient elution) of the crude material yielded the title amine **19h** (67 mg, 72%) as a colourless oil that quickly turns dark-orange. A trace of the enamine **15h** could be seen in the ^1H NMR (signal at 5.96 ppm). Characterization for **19h** : **^1H NMR** (400 MHz, $CDCl_3$) δ 5.24 (m, 1H), 2.90 (s, 2H), 2.55 (m, 2H), 2.07 (t, J = 6.0 Hz, 2H), 1.56 (m, 2H), 1.51 (d, J = 6.7 Hz, 3H), 1.02 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.2 (C), 118.0 (CH), 55.1 (CH_2), 46.9 (CH_2), 26.6 (CH_2), 26.2 (CH_2), 25.9 (CH_3), 12.8 (CH_3), the signal due to the aliphatic quaternary carbon is obscured; **IR** (NaCl) *v* 2969, 2933, 2781, 1654, 1359, 1204. **LRMS** (m/z, relative intensity) 168 (MH^+). **Exact Mass** calcd for $C_{11}H_{22}N$: 168.1747, found : 168.1754.

*(E)-6-(prop-1-enyl)-1,2,3,7,8,8a-hexahydroindolizine **21***



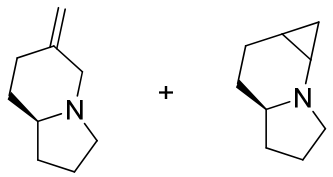
20 **21** **66**

Following the general procedure for the thermolysis of chromium aminocarbenes, chromium carbene **20** (113 mg, 0.319 mmol) and PPh_3 (101 mg, 0.383 mmol) were reacted to give dienamine **21**, which could not be purified because of its instability. It was characterized as the crude product as well as its Diels-Alder adduct **66** (see below)

Crude **21** : **^{1}H NMR** (400 MHz, C_6D_6) δ (ppm) 6.15 (d, 1H, *J* = 15.2 Hz), 6.06 (s, 1H), 5.26 (dq, 1H, *J* = 15.2, 6.6 Hz), 2.97-2.89 (m, 1H), 2.85 (ddd, 1H, *J* = 8.7, 7.0, 3.7 Hz), 2.71 (q, 1H, *J* = 8.7 Hz), 2.27 (ddd, 1H, *J* = 16.4, 5.2, 1.5 Hz), 2.16-2.08 (m, 1H), 1.83 (dd, 3H, *J* = 6.6, 1.4 Hz), 1.70-1.60 (m, 2H), 1.42-1.30 (m, 2H), 1.18-1.04 (m, 2H). **^{13}C NMR** (100 MHz, C_6D_6) δ (ppm) Note : two sp^2 carbons are missing because of overlaping signals with phosphine derivatives. 112.1 (d), 108.4 (s), 56.3 (d), 49.8 (t), 32.6 (t), 28.1 (t), 24.2 (t), 22.8 (t), 18.6 (q). **LRMS** (*m/z*, relative intensity) 196 (MNa^+, 15), 164 (MH^+, 100). **Exact Mass** calcd for $C_{11}H_{18}N$: 164.1434, found: 164.1440.

Adduct **66** was obtained as follows: After heating chromium carbene **20** in toluene at reflux for 6.5 h, a solution of *N*-phenylmaleimide (4 equiv.) in toluene (3 mL) was added and the reflux was maintained for 13 h. The reaction was cooled and the solvent evaporated. The crude product was purified by flash chromatography on silica gel column using a 5:95 solution of (NH_4OH:MeOH) in dichloromethane (2:98 to 5:95) as the eluent. The compound (10.2 mg, 15%) was obtained as a single diastereomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.49-7.28 (m, 3H), 7.19-7.15 (m, 2H), 5.48 (s, 1H), 5.74-5.69 (m, 1H), 3.43 (dd, 1H, *J* = 8.3, 7.3 Hz), 3.11 (dd, 1H, *J* = 8.3, 5.2 Hz), 2.92 (d, 1H, *J* = 7.3 Hz), 2.54-2.41 (m, 2H), 2.29-2.20 (m, 1H), 2.17-2.09 (m, 1H), 2.03-1.87 (m, 3H), 1.85-1.68 (m, 2H), 1.58-1.45 (m, 2H), 1.51 (d, 3H, *J* = 7.2 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 176.9 (s), 174.7 (s), 139.0 (s), 132.4 (s), 129.3 (d), 129.1 (d), 128.5 (d), 126.8 (d), 126.6 (d), 126.1 (d), 63.7 (d), 62.3 (d), 52.6 (t), 46.0 (d), 44.5 (d), 31.8 (t), 30.5 (d), 28.4 (t), 27.3 (t), 22.0 (t), 17.6 (q). **IR** (neat) ν (cm^{-1}) 3068, 3037, 2966, 2932, 2875, 1712, 1500, 1380, 1179. **LRMS** (*m/z*, relative intensity) 337 (MH^+, 100). **Exact Mass** calcd for $C_{21}H_{25}N_2O_2$: 337.1911, found: 337.1912.

(R)-6-methyleneoctahydroindolizine (**23a**) and (3aR)-octahydro-1H-cyclopropa[e]indolizine (**23b**)



23a **23b**

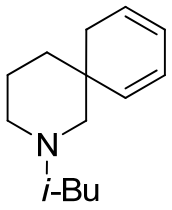
Degassed (freeze and thaw) benzene (11 mL) was added to chromium aminocarbene **22** (36.5 mg, 0.111 mmol) and PPh_3 (32.0 mg, 0.122 mmol) in a sealed tube. The reaction was heated at 111 ^oC for 18 hours. The reaction was evaporated under reduce pressure without heating (products are volatile). After evaporation of the solvent, alkene **23a** and cyclopropane **23b** (ratio **23a**:**23b** = 1:3) were the only

products present (along with phosphine derivatives). They were caracterised as a crude mixture du to their instability to purification.

Alkene **23a**: **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 4.85-4.82 (m, 1H), 4.81-4.79 (m, 1H), 3.51 (d, 1H, *J* = 11.4 Hz), 2.65 (d, 1H, *J* = 11.4 Hz), 2.45-1.11 (m, 11H) (this large multiplet was reported due to the incapacity to distinguish alkene **23a** signals from cyclopropane **23b** signals). **^{13}C NMR** (75.5 MHz, $CDCl_3$) note: The quaternary carbon is missing since it overlaps with triphenylphosphine derivatives. δ (ppm) 109.7 (t), 63.9 (d), 59.5 (t), 54.2 (t), 33.0 (t), 31.6 (t), 30.2 (t), 21.6 (t). **LRMS** (*m/z*, relative intensity) 138 (MH^+, 100). **Exact mass** calcd for $C_9H_{16}N$: 138.1283, found: 138.1279.

Cyclopropane **23b**: **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 3.18-3.05 (m, 1H), 2.55 (dddd, 1H, *J* = 6.9, 6.9, 6.9, 4.5 Hz), 2.45-1.11 (m, 9H) (this large multiplet was reported du to the incapacity to distinguish cyclopropane **23a** signals from alkene **23b** signals), 1.02-0.84 (m, 2H), 0.40 (q, 1H, *J* = 5.4 Hz), 0.30 (ddd, 1H, *J* = 12.3, 6.9, 5.4 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ (ppm) 55.4 (d), 52.3 (t), 35.8 (d), 30.0 (t), 27.5 (t), 23.3 (t), 20.5 (t), 6.8 (d), 5.9 (t). **LRMS** (*m/z*, relative intensity) 138 (MH^+, 100). **Exact mass** calcd for $C_9H_{16}N$: 138.1283, found: 138.1279.

*Piperidine **26***

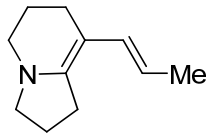


26

A solution of aminocarbene **25** (1.05 g, 2.64 mmol) in toluene was degassed by putting the flask under vacuum at -78 °C for 2 min and by subsequently purging the flask with argon. This procedure was repeated three times. Then, triphenylphosphine (728 mg, 2.77 mmol) the reaction mixture was heated to reflux. Upon completion of the reaction, the mixture was cooled to rt. The solution was concentrated under reduced pressure and the crude product was purified by flash chromatography on a silica gel column saturated with triethylamine eluting with 0% to 30% of diethyl ether in hexanes to yield 326 mg (60%) **26** as colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) 5.88-5.56 (m, 4H), 2.47-1.90 (m, 5H), 2.03 (dd, 1H, *J* = 17.6, 4.4 Hz), 1.97 (d, 2H, *J* = 7.0 Hz), 1.74 (sept, 1H, *J* = 7.0 Hz), 1.63-1.44 (m, 3H), 1.39-1.16 (m, 1H), 0.86 (d, 6H, *J* = 7.0 Hz). **^{1}H NMR** (300 MHz, C_6D_6) 5.91-5.80 (m, 3H), 5.72-5.62 (m, 1H), 2.56-1.86 (m, 5H), 2.01 (dd, 1H, *J* = 17.3, 3.6 Hz), 1.92 (d, 2H, *J* = 7.2 Hz), 1.67 (sept, 1H, *J* = 7.2 Hz), 1.63-1.39 (m, 3H), 1.34-1.16 (m, 1H), 0.92-0.88 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ (ppm)

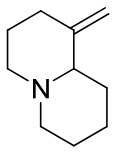
135.4 (d), 125.3 (d), 123.3 (d), 122.5 (d), 67.0 (t), 62.2 (t), 55.3 (t), 35.5 (t), 33.9 (t), 25.6 (d), 22.1 (t), 20.8 (q), 20.8 (q) (one aromatic quaternary carbon is missing). **IR** (neat) ν (cm^{-1}) 3037, 2951, 2933, 2868, 2802, 2773, 1465, 1377, 1101. **LRMS** (*m/z*, relative intensity): 205 (M^+, 5), 162 ($(M-C_3H_7)^+$, 100), 100 (57), 91 (61). **Exact Mass** calcd for $C_{14}H_{23}N$: 205.1830, found: 205.1828.

(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine ***32***



Following the general procedure for the thermolysis of chromium aminocarbenes, chromium carbene **31** (85 mg, 0.24 mmol) and PPh_3 (75 mg, 0.29 mmol) were reacted to give dienamine **32**, which could not be purified because of its instability. It was characterized as the crude product. **^{1}H NMR** (300 MHz, **$CDCl_3$**) δ (ppm) 6.19 (d, 1H, *J* = 15.3 Hz), 5.09 (dq, 1H, *J* = 15.3, 6.6 Hz), 2.99 (t, 2H, *J* = 6.6 Hz), 2.94 (t, 2H, *J* = 5.8 Hz), 2.57 (t, 2H, *J* = 7.5 Hz), 2.11 (t, 2H, *J* = 6.6 Hz), 1.93 (quint, 2H, *J* = 6.1 Hz), 1.84 (quint, 2H, *J* = 7.2 Hz), 1.77 (d, 3H, *J* = 6.6 Hz). **^{1}H NMR** (300 MHz, **C_6D_6**) δ (ppm) 6.40 (d, 1H, *J* = 15.1 Hz), 5.26 (dq, 1H, *J* = 15.1, 6.6 Hz), 2.67 (t, 2H, *J* = 5.5 Hz), 2.62 (t, 2H, *J* = 6.5 Hz), 2.36 (t, 2H, *J* = 7.6 Hz), 2.22 (t, 2H, *J* = 6.5 Hz), 1.99 (quint, 2H, *J* = 7.0 Hz), 1.92 (d, 3H, *J* = 6.6 Hz), 1.80 (quint, 2H, *J* = 6.5 Hz). **^{13}C NMR** (75.5 MHz, **C_6D_6**) δ (ppm) 143.9 (s), 112.2 (d), 110.4 (d), 100.0 (s), 53.2 (t), 46.3 (t), 30.8 (t), 27.8 (t), 22.9 (t), 22.2 (t), 21.8 (t), 19.0 (q). **LRMS** (*m/z*, relative intensity) 196 ($(M+Na)^+$, 95), 164 (MH^+, 100). **Exact mass** calcd for $C_{11}H_{18}N$: 164.1434, found: 164.1433.

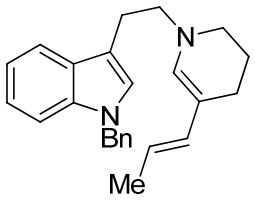
1-methyleneoctahydro-1H-quinolizine ***34***



Following the general procedure for the thermolysis of chromium aminocarbenes, chromium carbene **13i** (0.200 g, 0.580 mmol) but only 0.3 equiv. of PPh_3 (46 mg, 0.174 mmol) were reacted to give adduct **19i**. Flash column chromatography (NEt_3-treated silica gel, pentane–pentane/ether 95:5 gradient elution) of the crude material yielded the title amine **34** (61 mg, 69%) as a colourless oil that quickly turned dark-orange. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 4.76 (s, 2H), 2.88 (d, *J* = 11.8 Hz, 2H), 2.37 (d, *J* =

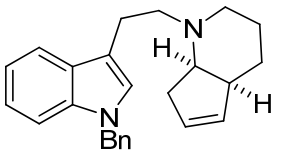
11.8 Hz, 1H), 2.18 (m, 2H), 2.04 (m, 2H), 1.80 (m, 2H), 1.73-1.40 (covered 5H), 1.28 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3 (C), 106.9 (CH_2), 64.6 (CH), 57.3 (CH_2), 56.8 (CH_2), 35.1 (CH_2), 28.5 (CH_2), 26.9 (CH_2), 25.7 (CH_2), 24.5 (CH_2); **IR** (NaCl) *v* 3085, 2935, 2851, 2745, 2679, 1647, 1438, 1281, 891. **LRMS** (m/z, relative intensity) 152 (MH^+). **Exact Mass** calcd for $C_{10}H_{18}N$: 152.1439, found : 152.1434.

*(E)-1-benzyl-3-(2-(5-(prop-1-enyl)-3,4-dihydropyridin-1(2H)-yl)ethyl)-1H-indole **38***



Following the general procedure for the thermolysis of chromium aminocarbenes, chromium carbene **37** (220 mg, 0.39 mmol) and PPh_3 (120 mg, 0.44 mmol) were reacted to give adduct **38**, which proved too unstable to purify. **^{1}H NMR** (300 MHz, C_6D_6) δ (ppm) 7.56 –7.30 (m, 9H), 6.56 (s, 1H), 6.12 (d, *J* = 15.3 Hz, 1H), 5.94 (s, 1H), 5.26 (dq, *J* = 15.3, 6.4 Hz 1H), 4.73 (s, 2H), 3.17–2.96 (m, 4H), 2.87–2.66 (m, 4H), 1.86 (d, *J* = 6.4 Hz, 3H), 1.78–1.61 (m, 4H). **IR** (NaCl disk) ν (cm^{-1}) 3055, 2927, 1923, 1886. **LRMS** *m/z* (relative intensity) 357 (MH^+, 100), 345 (30). **Exact Mass** calculated for $C_{25}H_{28}N_2$: 357.5106 (MH^+), found : 357.2340 (MH^+).

*1-Benzyl-3-(2-((4aS,7aR)-4,4a-dihydro-1H-cyclopenta[c]pyridin-2(3H,7H,7aH)-yl)ethyl)-1H-indole **39***



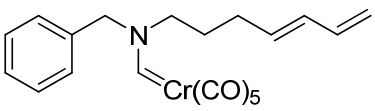
In a flask were added the chromium aminocarbene **37** (220 mg, 0.39 mmol) in dry toluene (40 mL). The mixture was degassed 3 times with freeze-thaw cycles under reduced pressure at -78 °C for 5 min. The mixture was heated to reflux until reaction was complete (24h). The mixture was cooled to rt and the solvent was evaporated under reduced pressure. The product was chromatographed on silica gel (A solution of **A** 2% in DCM; **A** = 5% NH_4OH in MeOH) to give pure product **39** as a colorless paste (50 mg, 58%). **^{1}H NMR** (300 MHz, CDCl3) δ (ppm) 7.64 (d, J = 7.1 Hz, 1H), 7.36–7.04 (m, 8H), 6.97 (s, 1H), 5.86 (d, J = 4.5 Hz, 1H), 5.78–5.71 (m, 1H), 5.27 (s, 2H), 3.45 (q, J = 7.0 Hz, 1H), 3.10–2.91 (m,

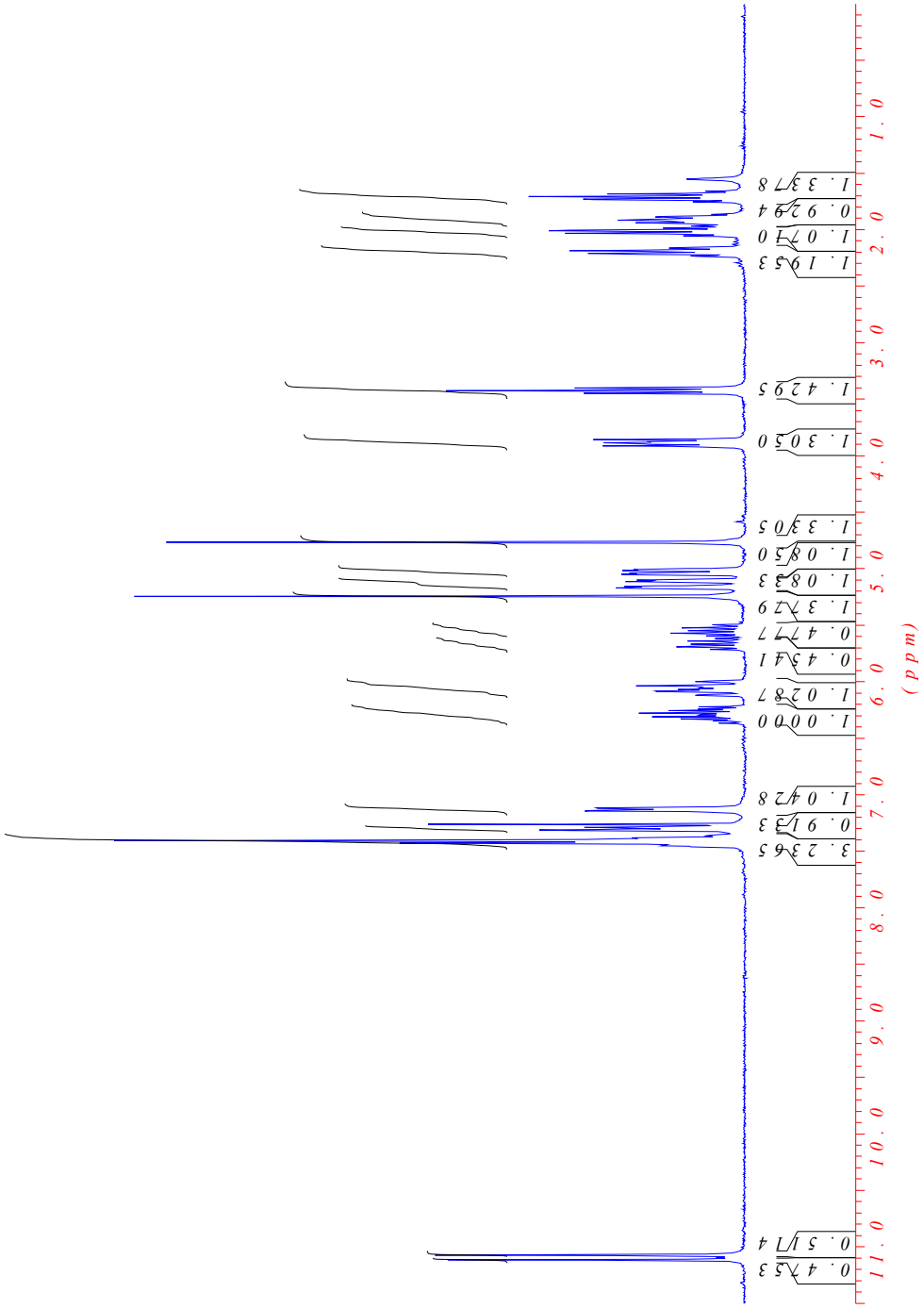
2H), 2.88–2.71 (m, 2H), 2.67–2.32 (m, 2H), 2.23–2.11 (m, 2H), 1.90–1.71 (m, 2H), 1.69–1.50 (m, 2H), 1.24–1.03 (m, 1H). **^{13}C NMR** (75 MHz, CDCl3) δ (ppm) 137.9 (s), 136.7 (s), 136.4 (d), 128.9 (s), 128.7 (d), 128.3 (s), 127.7 (d), 126.9 (d), 125.9 (d), 121.9 (d), 119.2 (d), 119.1(d), 109.8 (d), 62.6 (d), 57.1 (t), 50.0 (t), 48.2 (t), 42.2 (d), 29.1 (t), 27.4 (t), 23.2 (t). **IR** (NaCl disk) ν (cm^{-1}) 3051, 2927, 1926, 1668, 1466. **LRMS** *m/z* (relative intensity) 357 (100) (MH^+), 356 (10, M^+). **Exact Mass** calcd for $C_{25}H_{28}N_2$: 357.5106, found : 357.2335.

^{1}H NMR SPECTRA

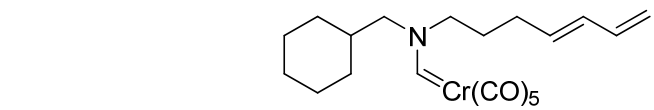
In numerical order

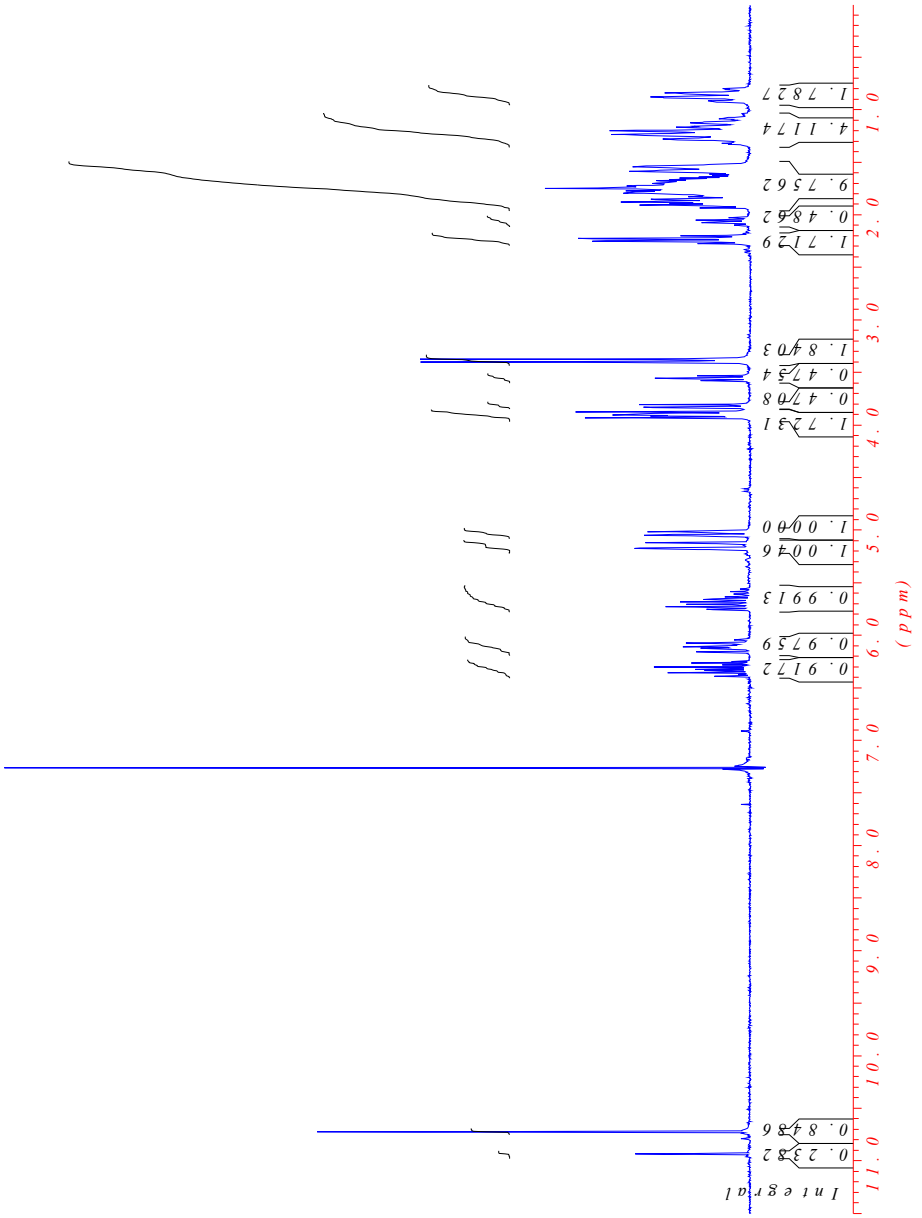
(E)-Pentacarbonyl[(N-(benzyl)-N-(hepta-4,6-dienyl)amino)methylene]chromium(0) ***(13a)***



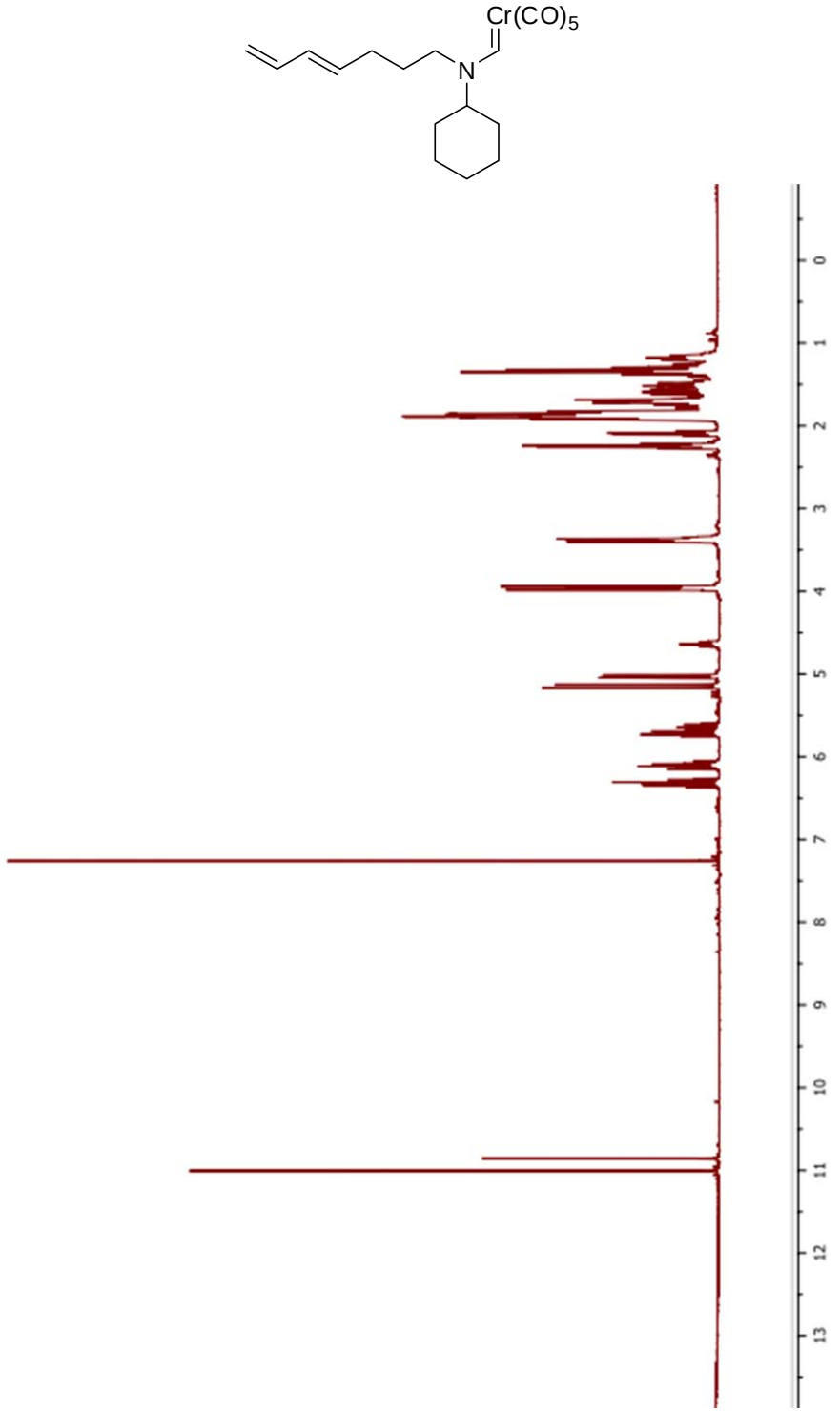


*(E)-Pentacarbonyl[(N-(cyclohexylmethyl)-N-(hepta-4, 6-dienyl)amino)methylene]chromium(0) (**13b**)*

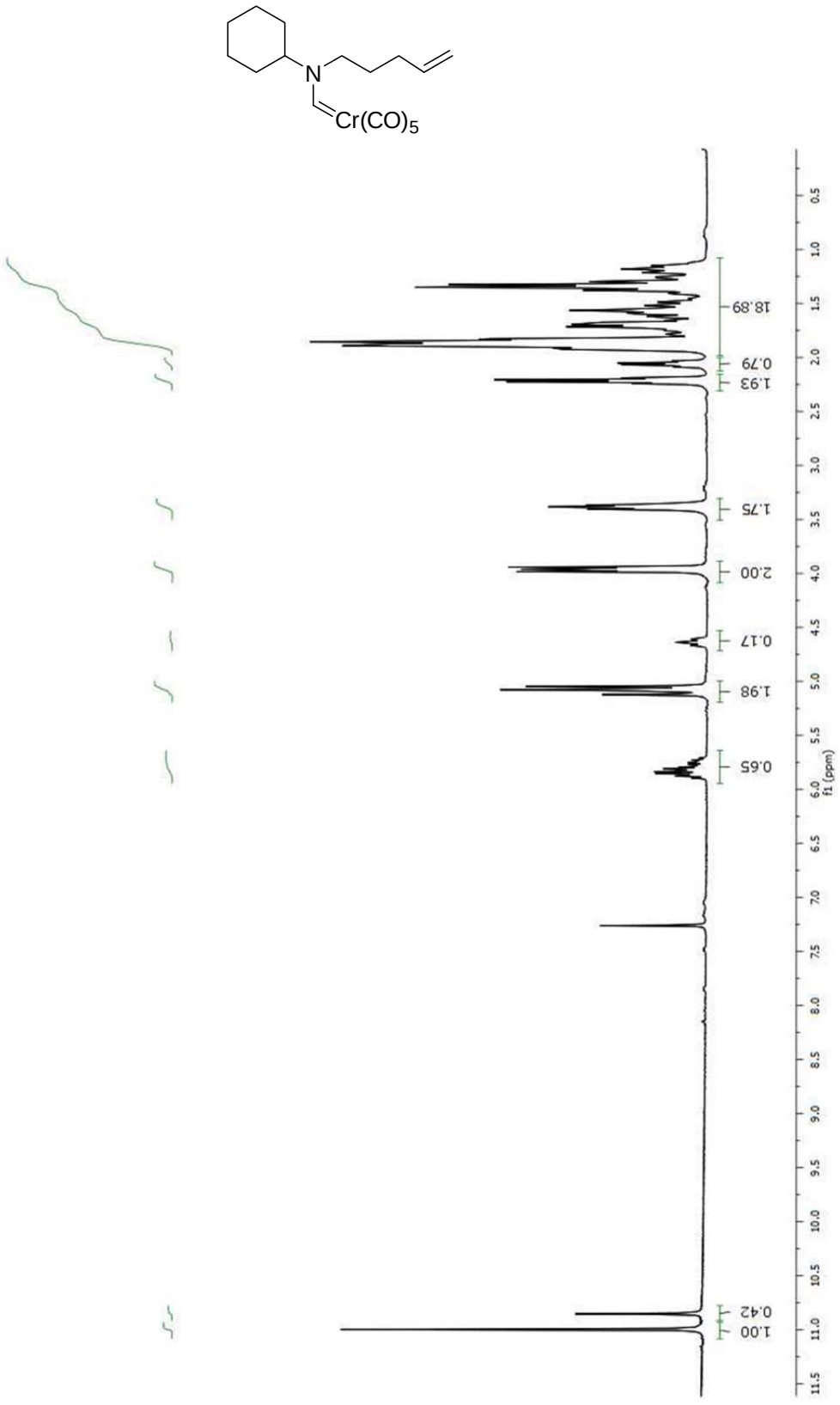




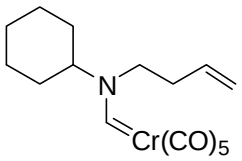
*(E)-Pentacarbonyl[(N-cyclohexyl-N-(hepta-4,6-dien-1-yl)amino)methylene]chromium(0) (**13c**)*

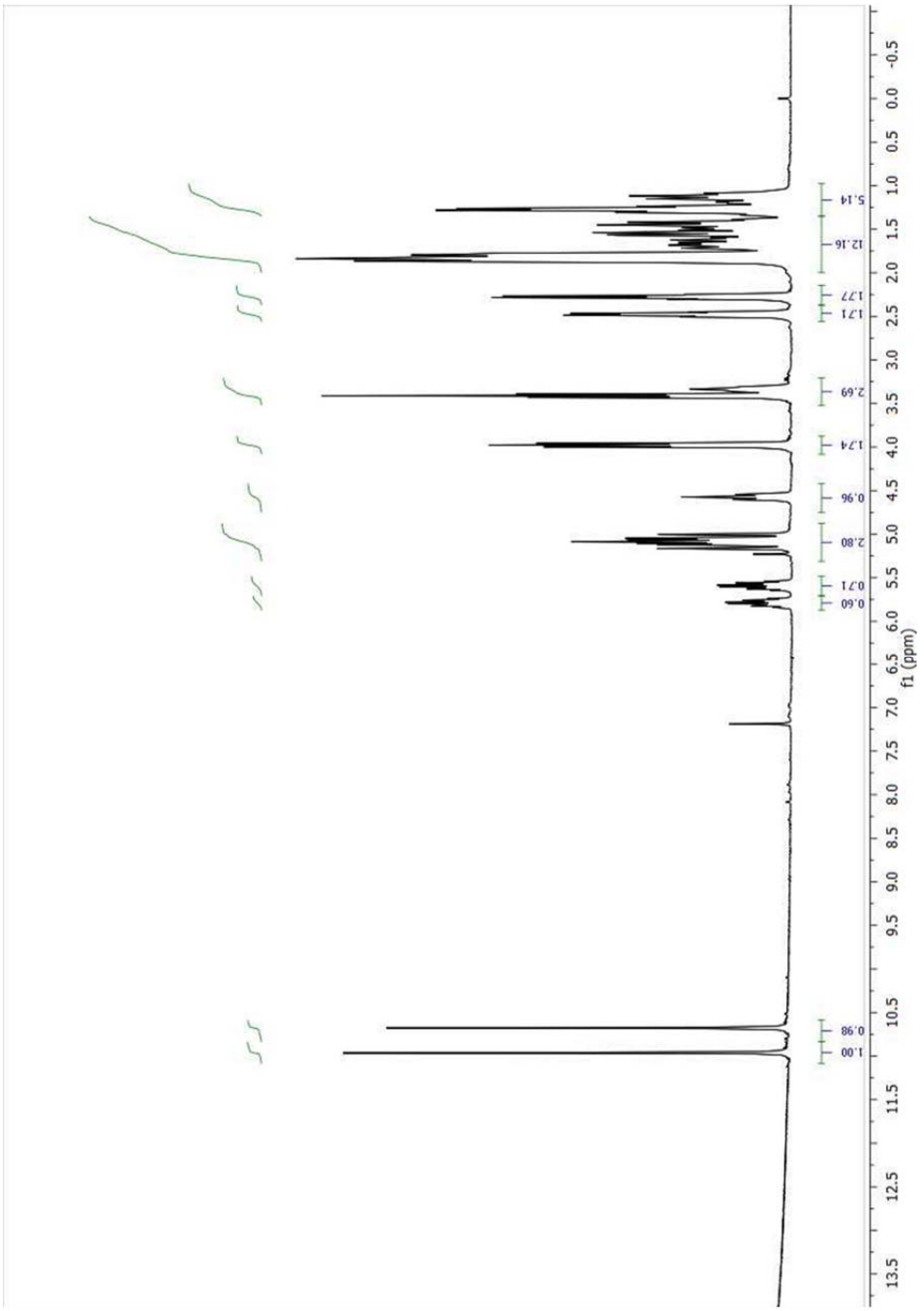


*(E)-Pentacarbonyl[(N-cyclohexyl-N-(4-penten-1-yl)amino)methylene]chromium(0) (**13d**)*

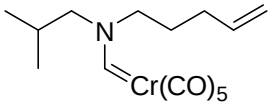


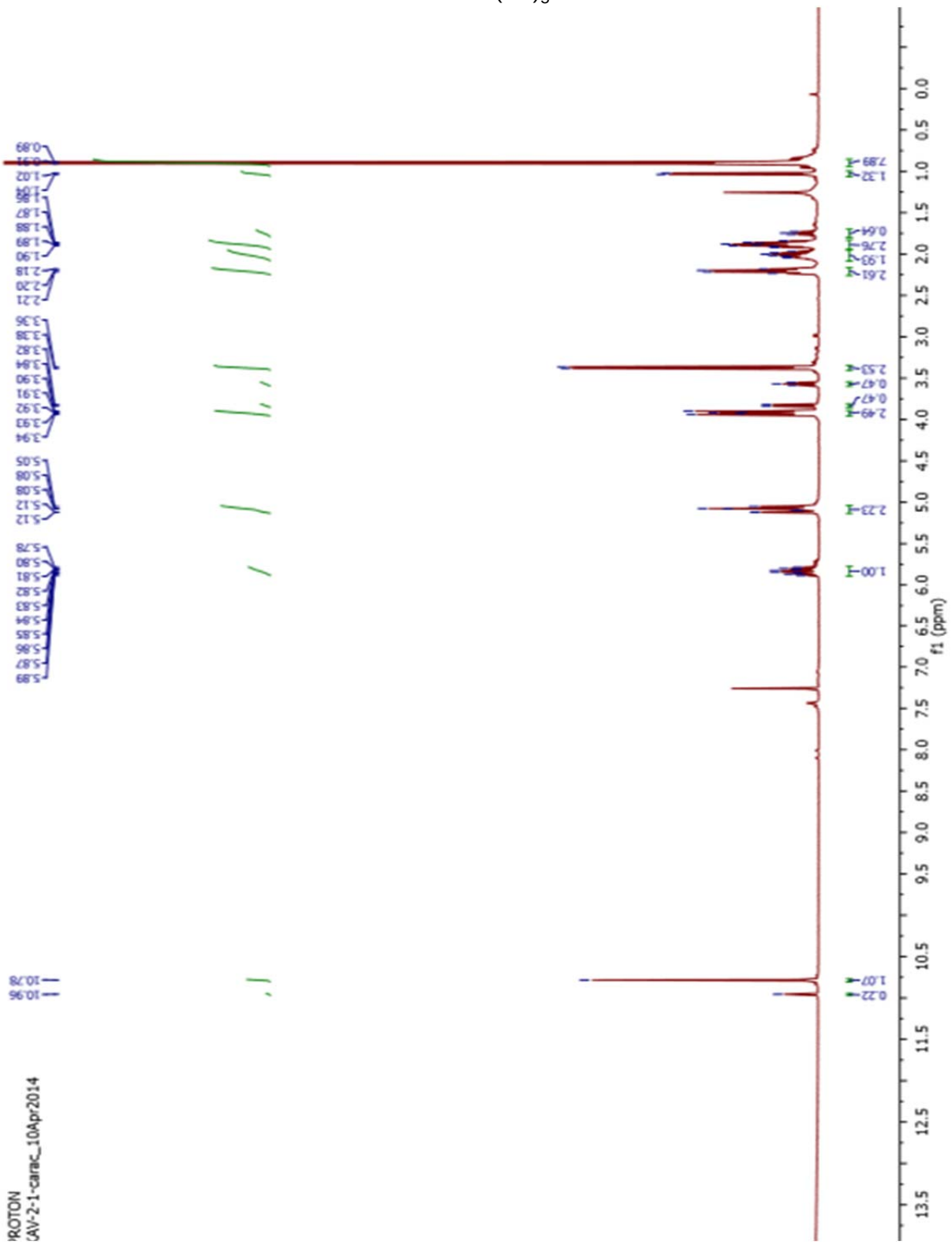
*(E)-Pentacarbonyl[(N-cyclohexyl-N-(3-buten-1-yl)amino)methylene]chromium(0) (**13e**)*



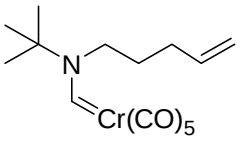


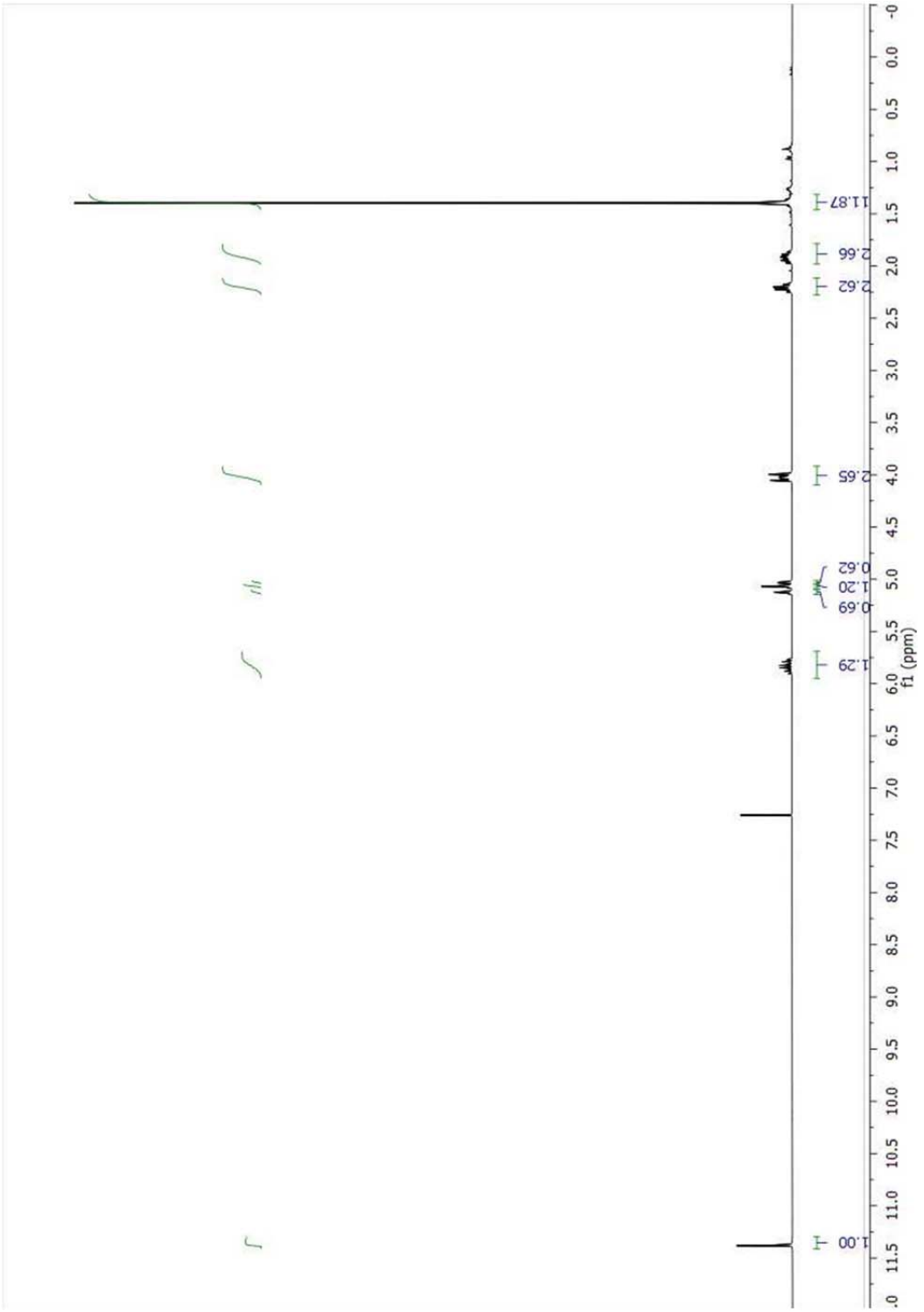
*(E)-Pentacarbonyl[(N-isobutyl-N-(4-penten-1-yl)amino)methylene]chromium(0) (**13f**)*



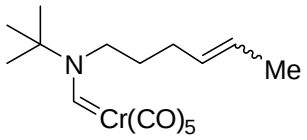


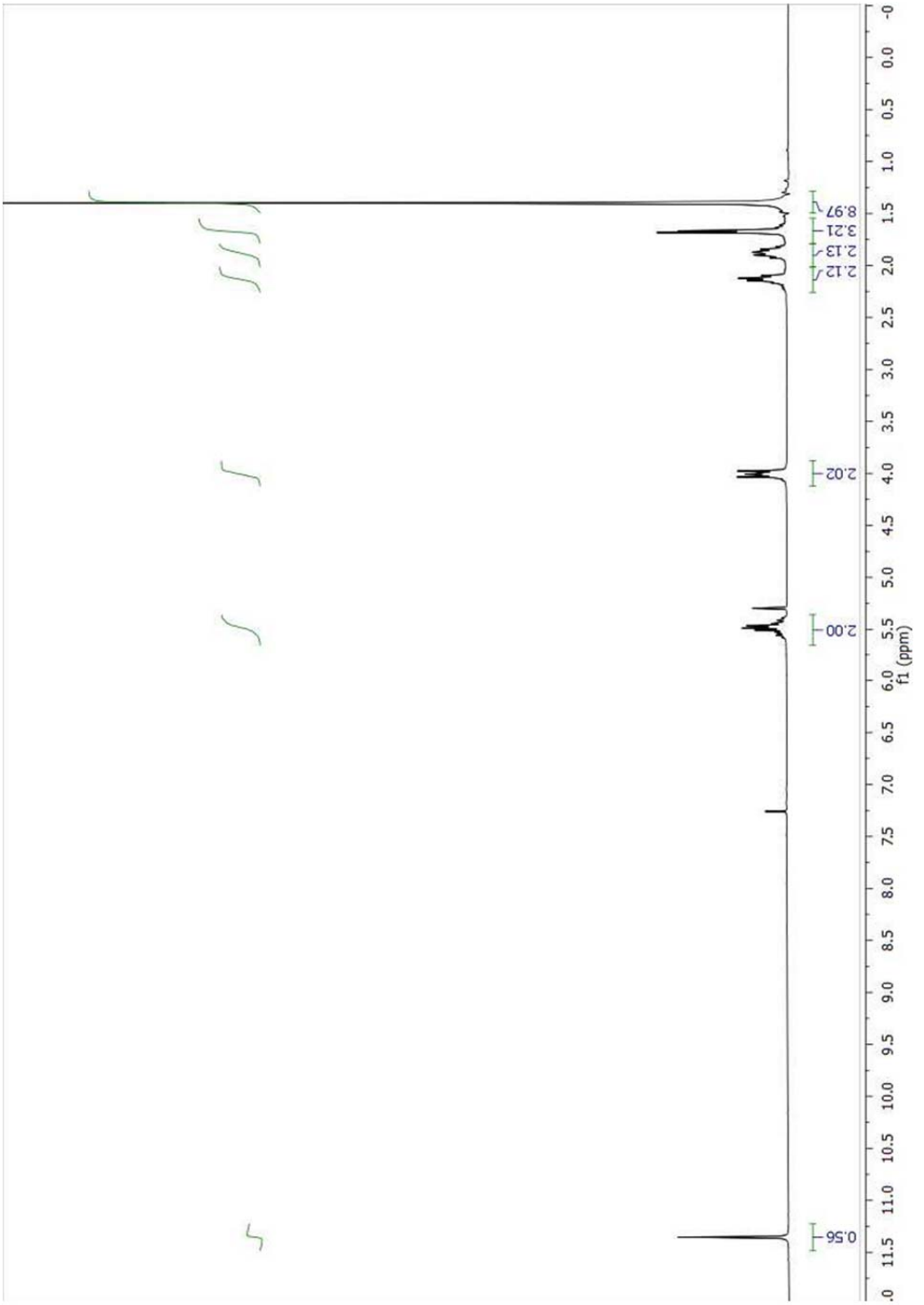
*(E)-Pentacarbonyl[(N-tert-butyl-N-(4-penten-1-yl)amino)methylene]chromium(0) (**13g**)*



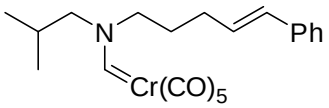


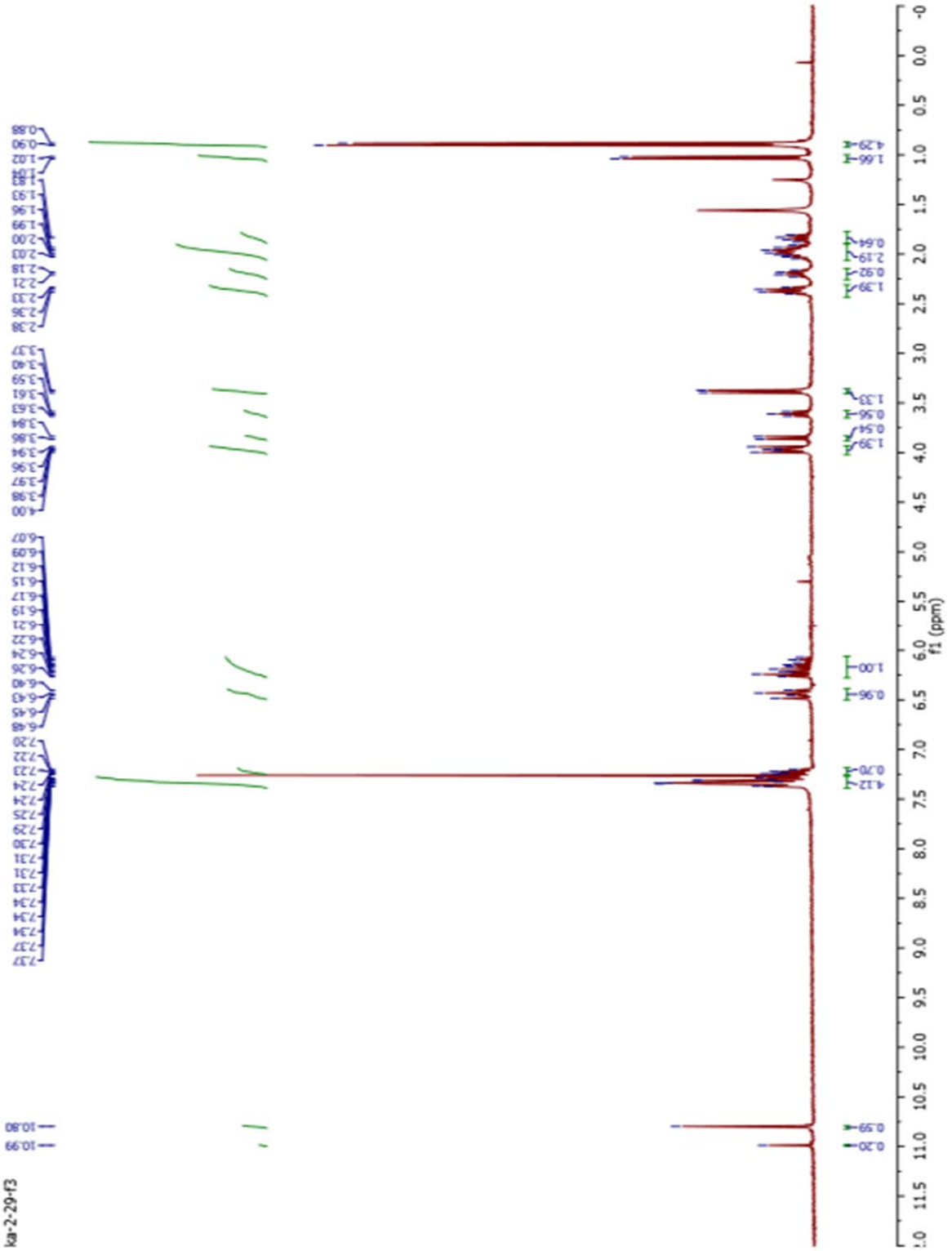
(E)-Pentacarbonyl[(N-isobutyl-N-(4-hexen-1-yl)amino)methylene]chromium(0) ***(13h)***



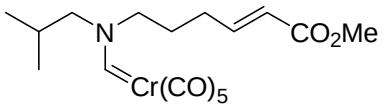


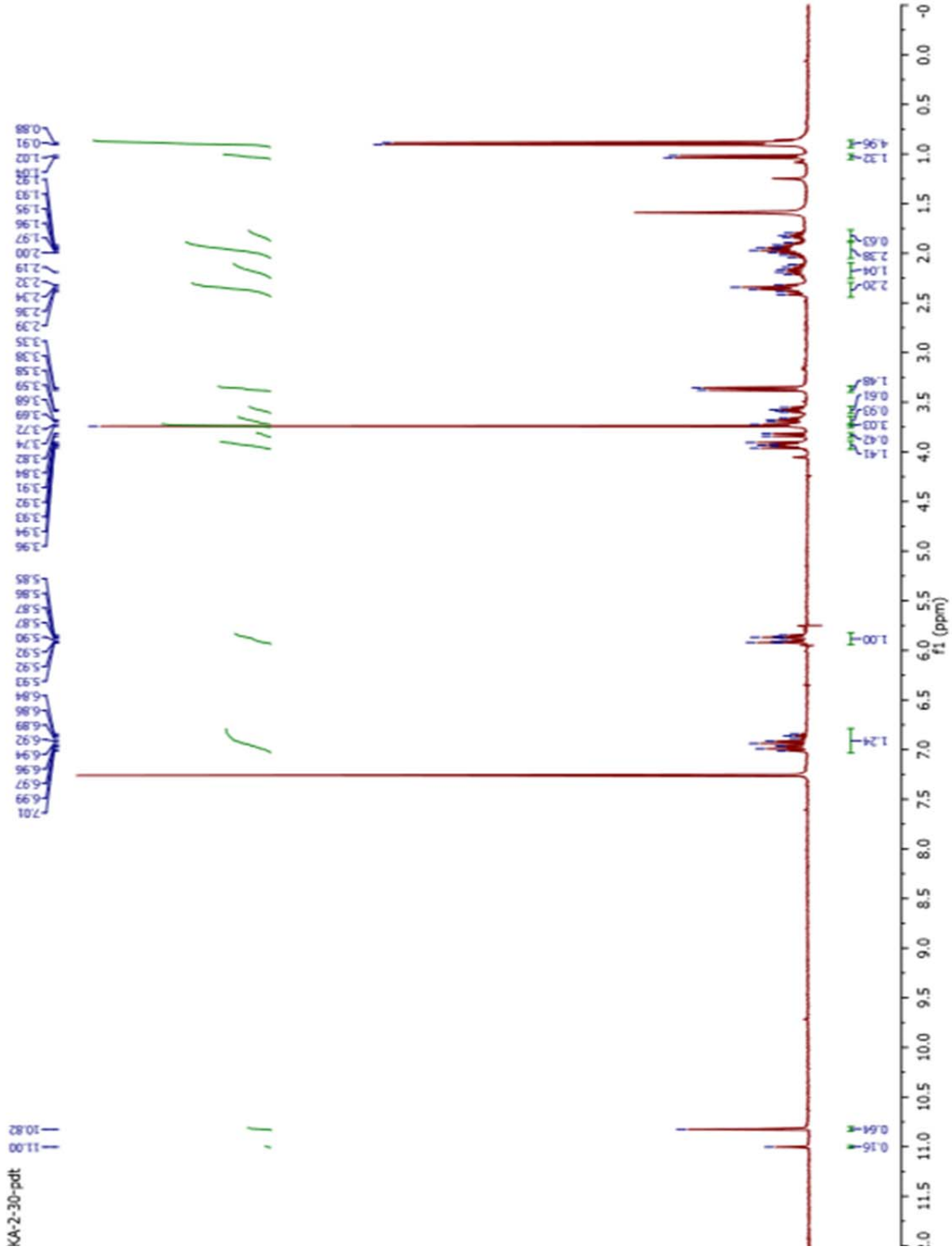
*Pentacarbonyl[(N-isobutyl-N-(5-phenyl-4-penten-1-yl amino)methylene]chromium(0) (**13i**)*



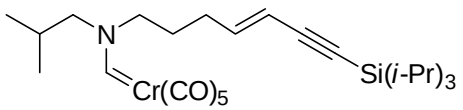


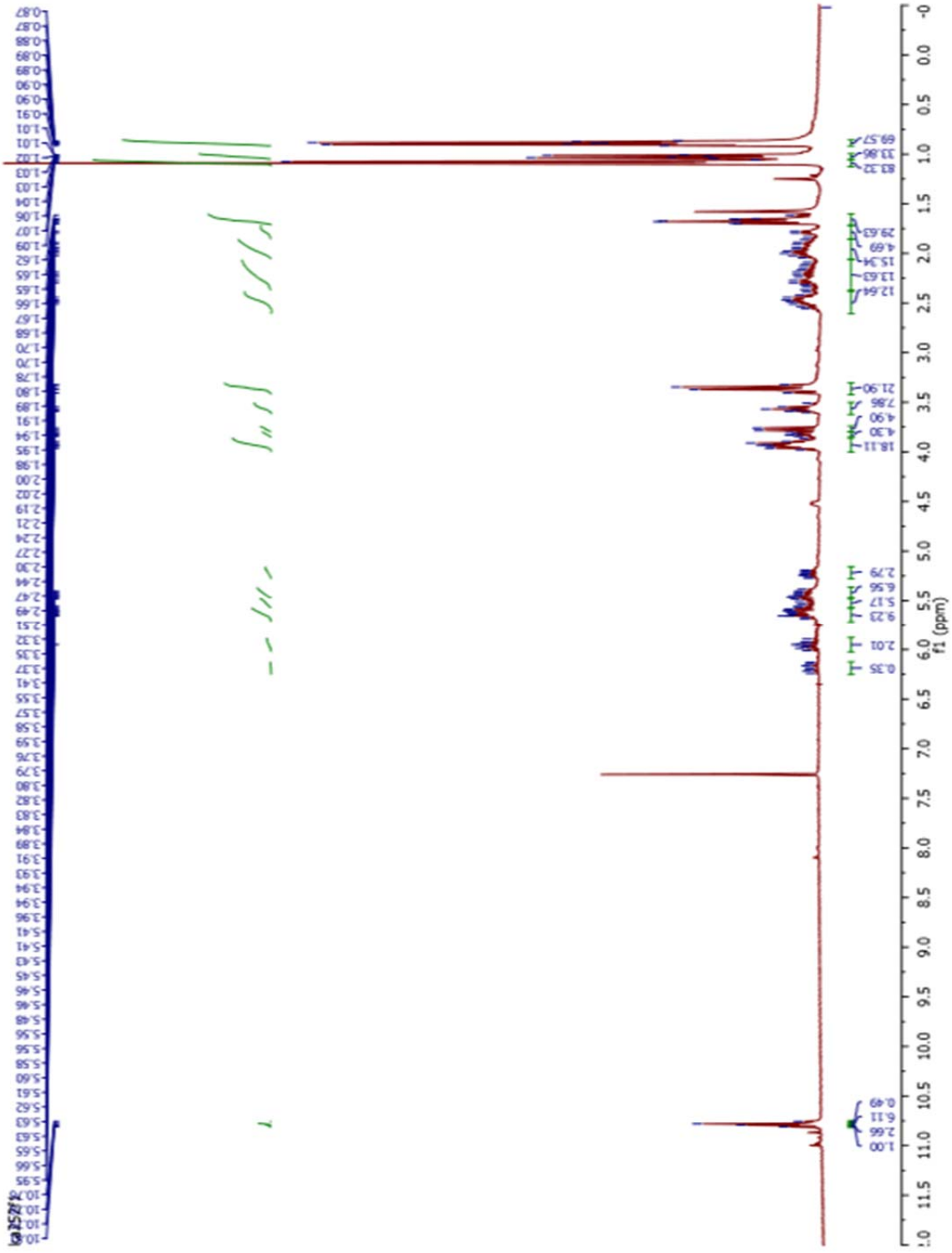
*Pentacarbonyl[(N-isobutyl-N-(5-methylcarboxy-4-penten-1-yl)amino)methylene]chromium(0) (**13j**)*



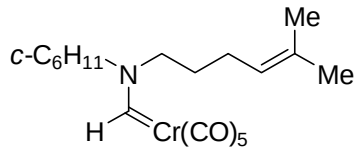


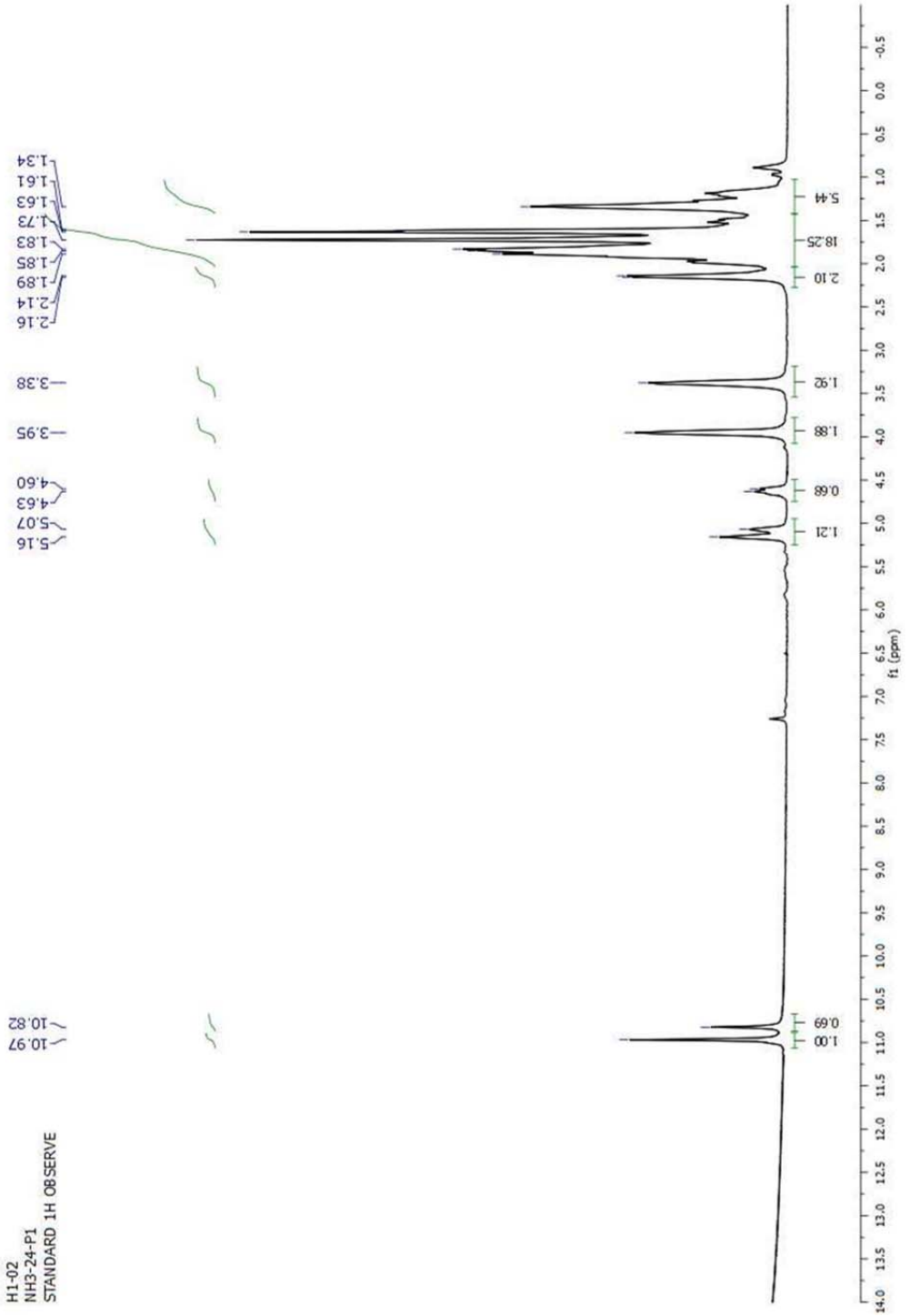
Pentacarbonyl[(N-isobutyl-N-(7-triisopropylsilyl-4-hepten-6-yn-1-yl) amino)methylene]chromium(0) ***(13k)***



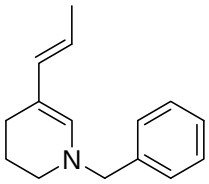


Pentacarbonyl[(N-cyclohexyl-N-(5-methyl-4-hexen-1-yl) amino)methylene]chromium(0) (**13l**)





(E)-1-Benzyl-5-(prop-1-enyl)-1,2,3,4-tetrahydropyridine ***15a***



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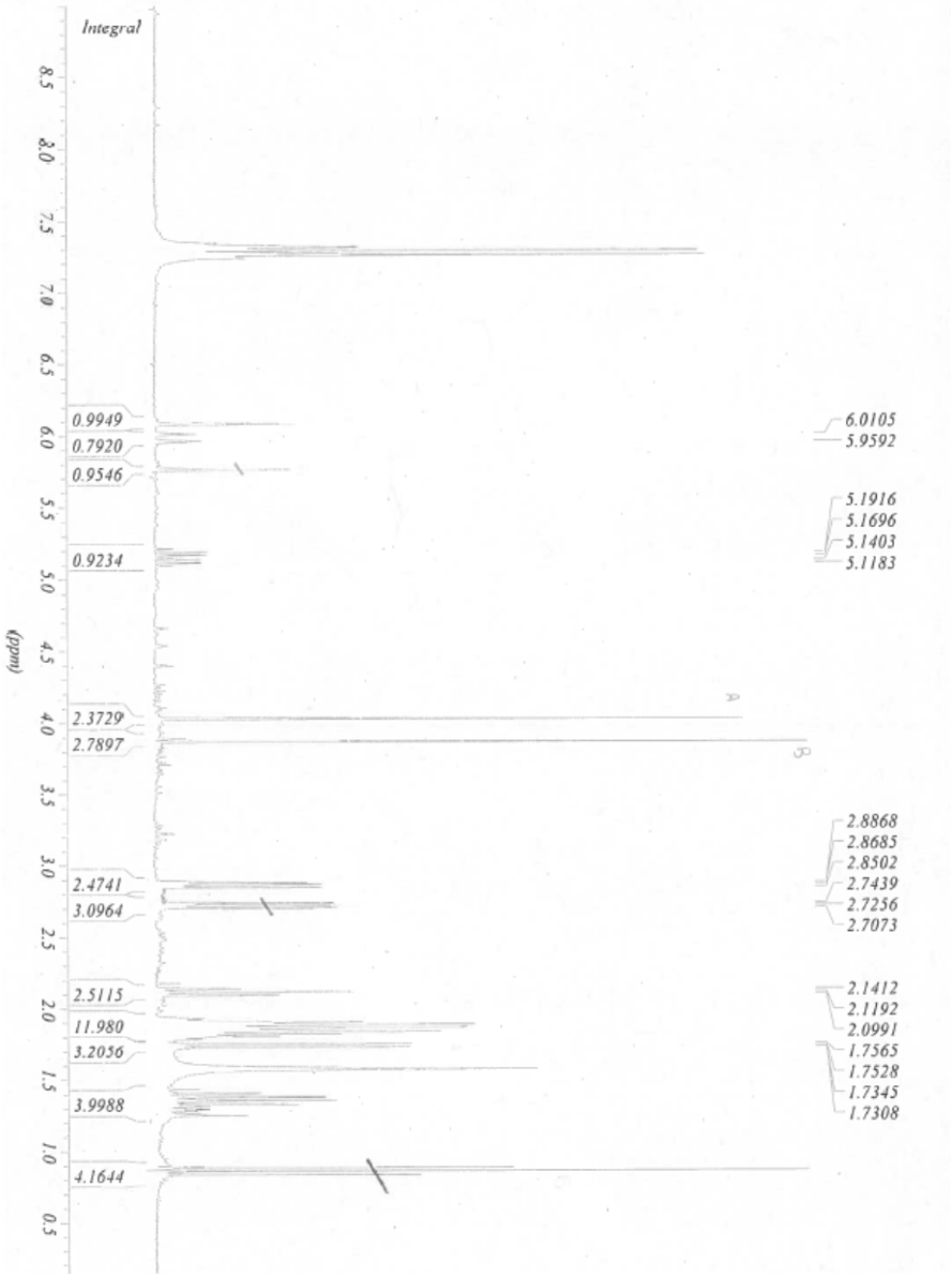
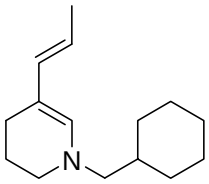


(E)-1-Cyclopropylmethyl-5-(prop-1-enyl)-1,2,3,4-tetrahydropyridine ***15b***



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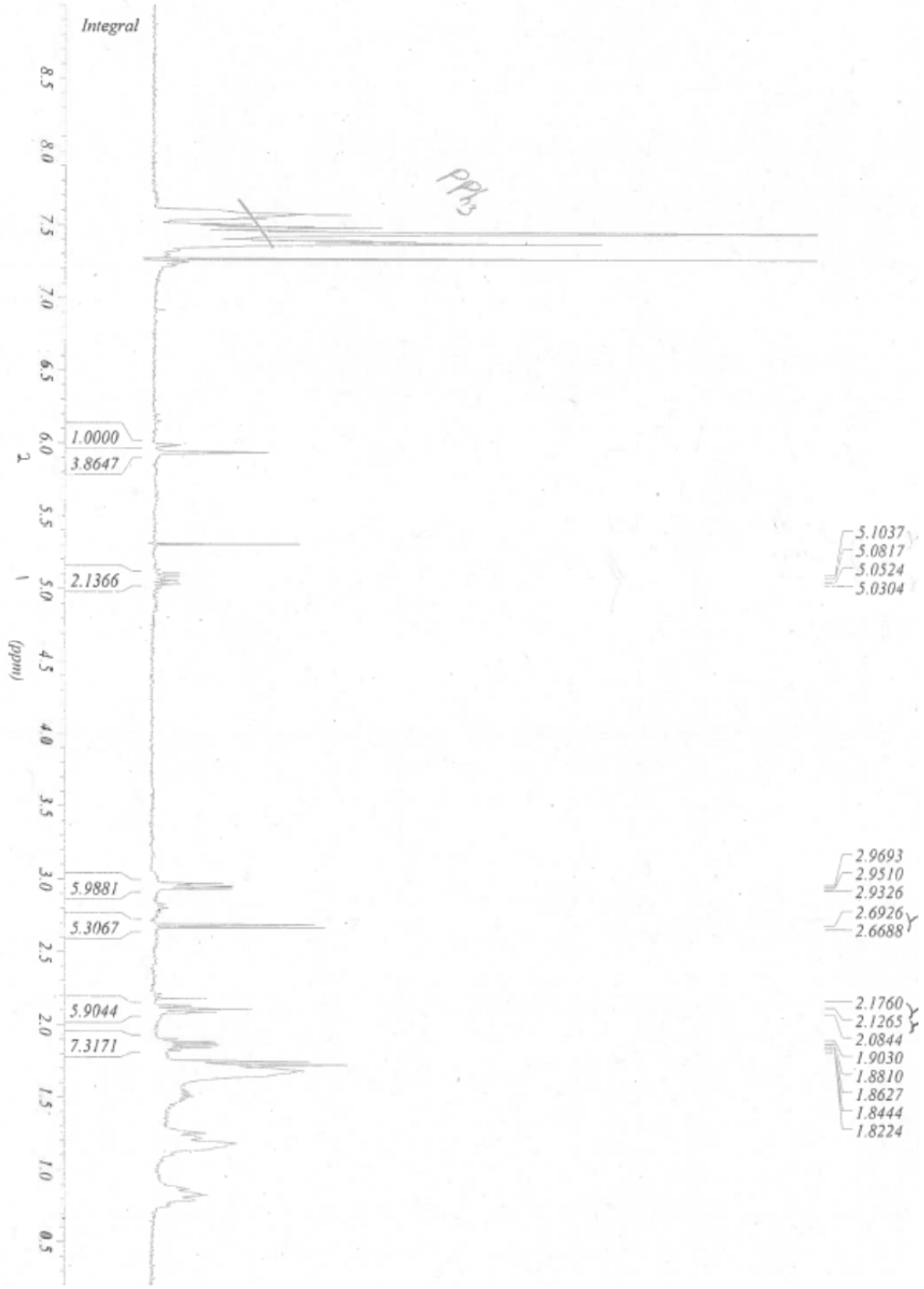
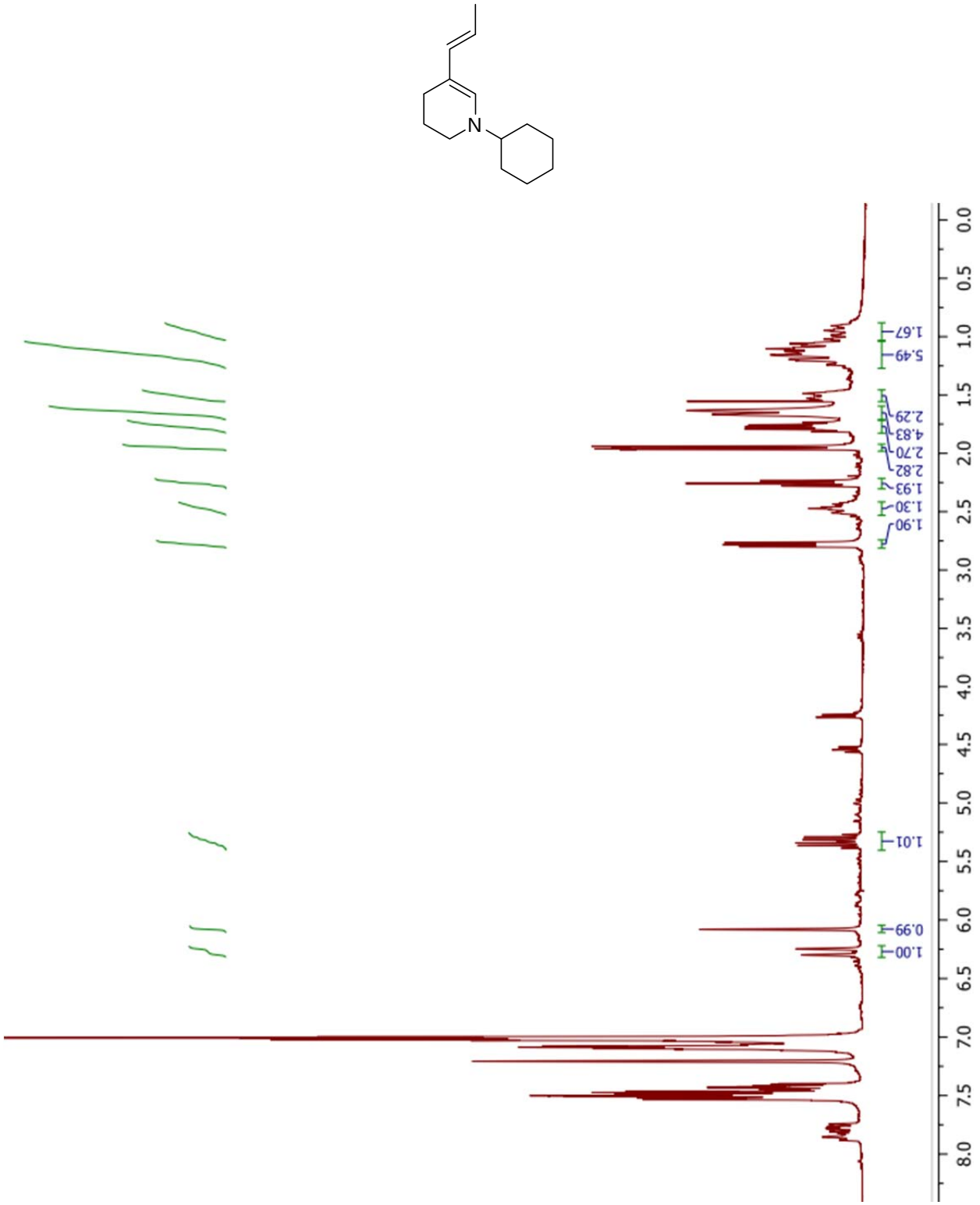
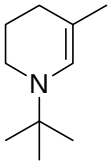
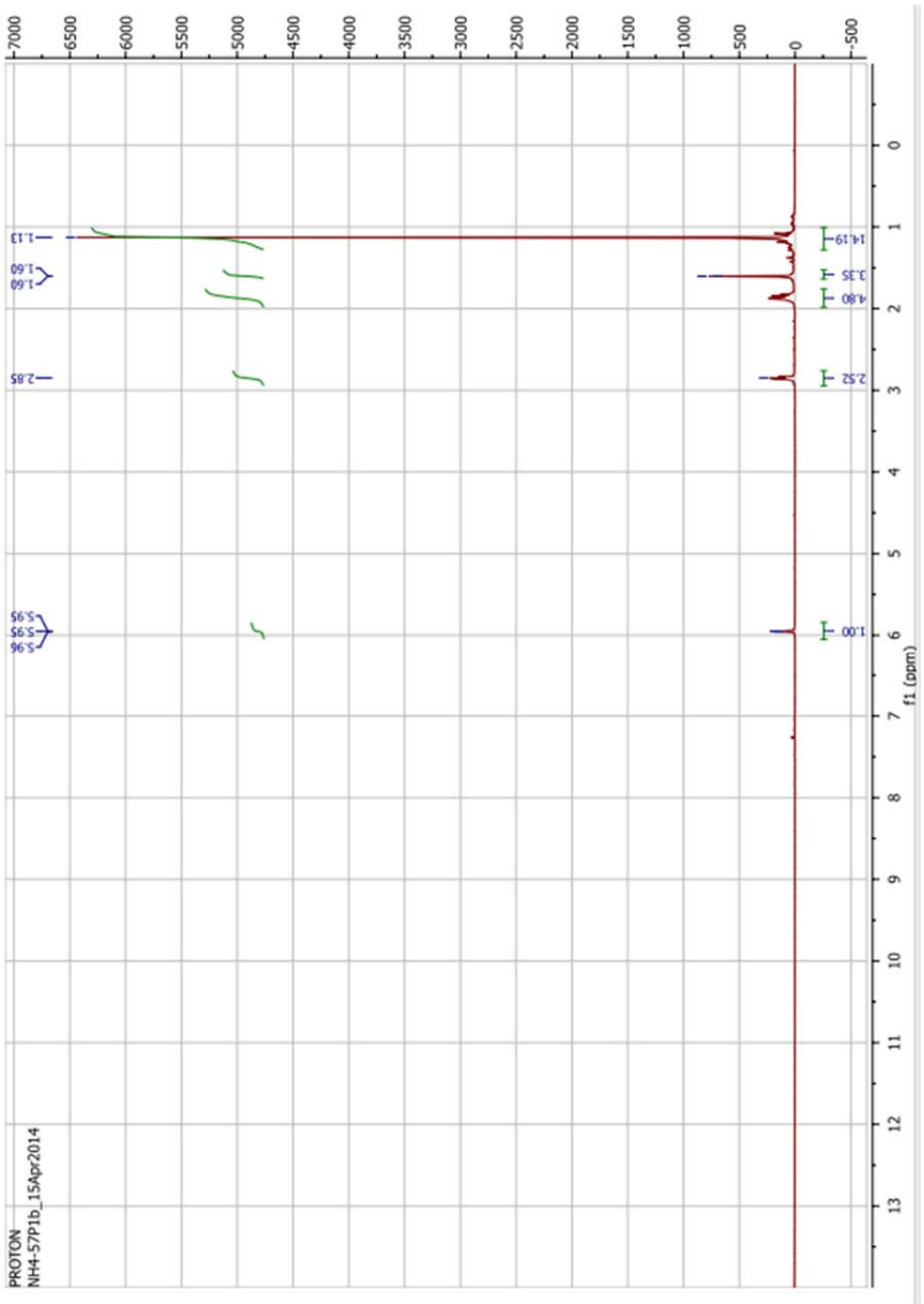


(E)-1-cyclohexyl-5-(prop-1-enyl)-1,2,3,4-tetrahydropyridine ***15c***

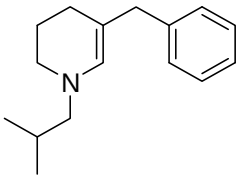


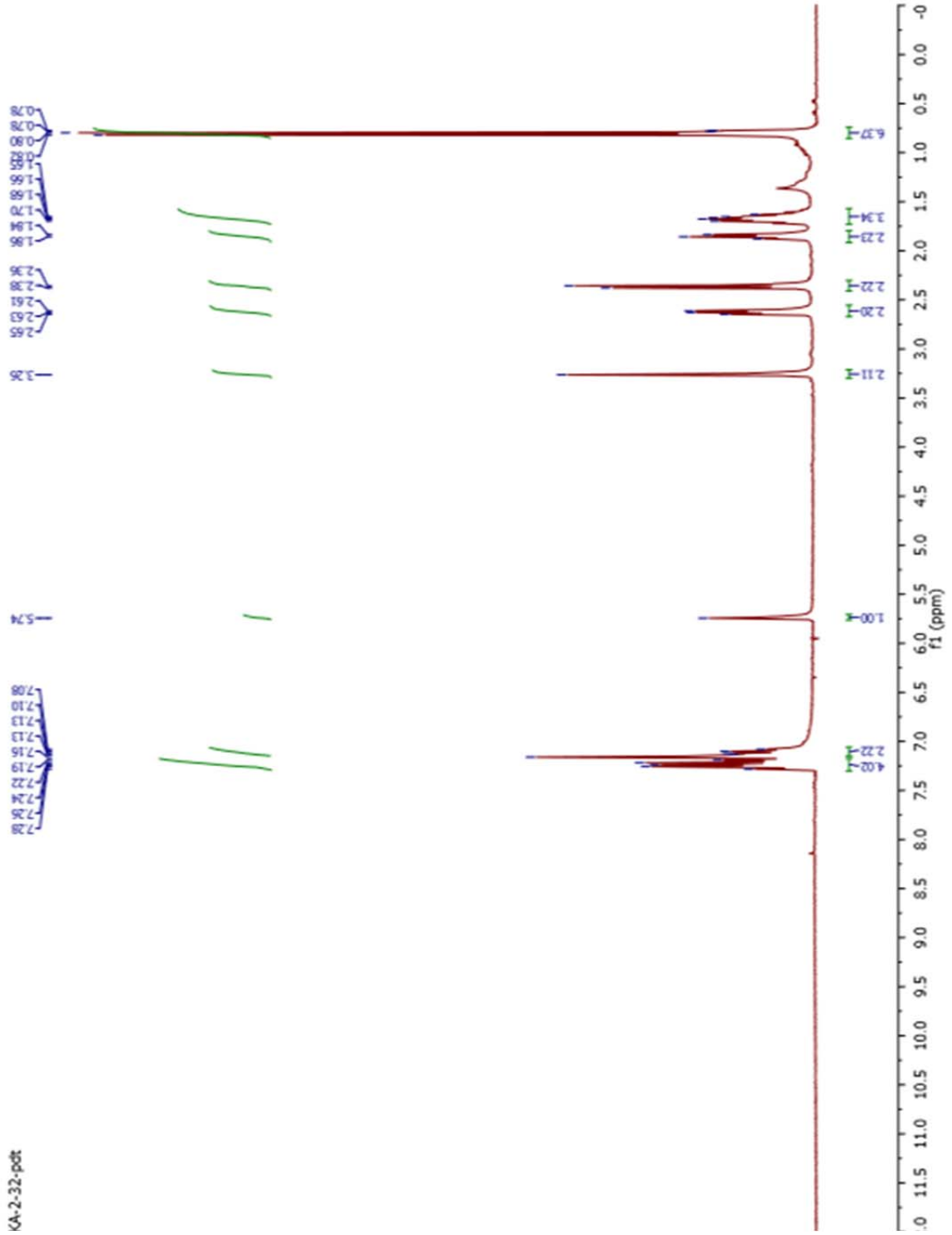
N-tert-Butyl-1,2,3,4-tetrahydropyridine ***15g***



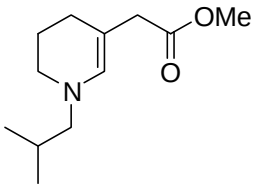


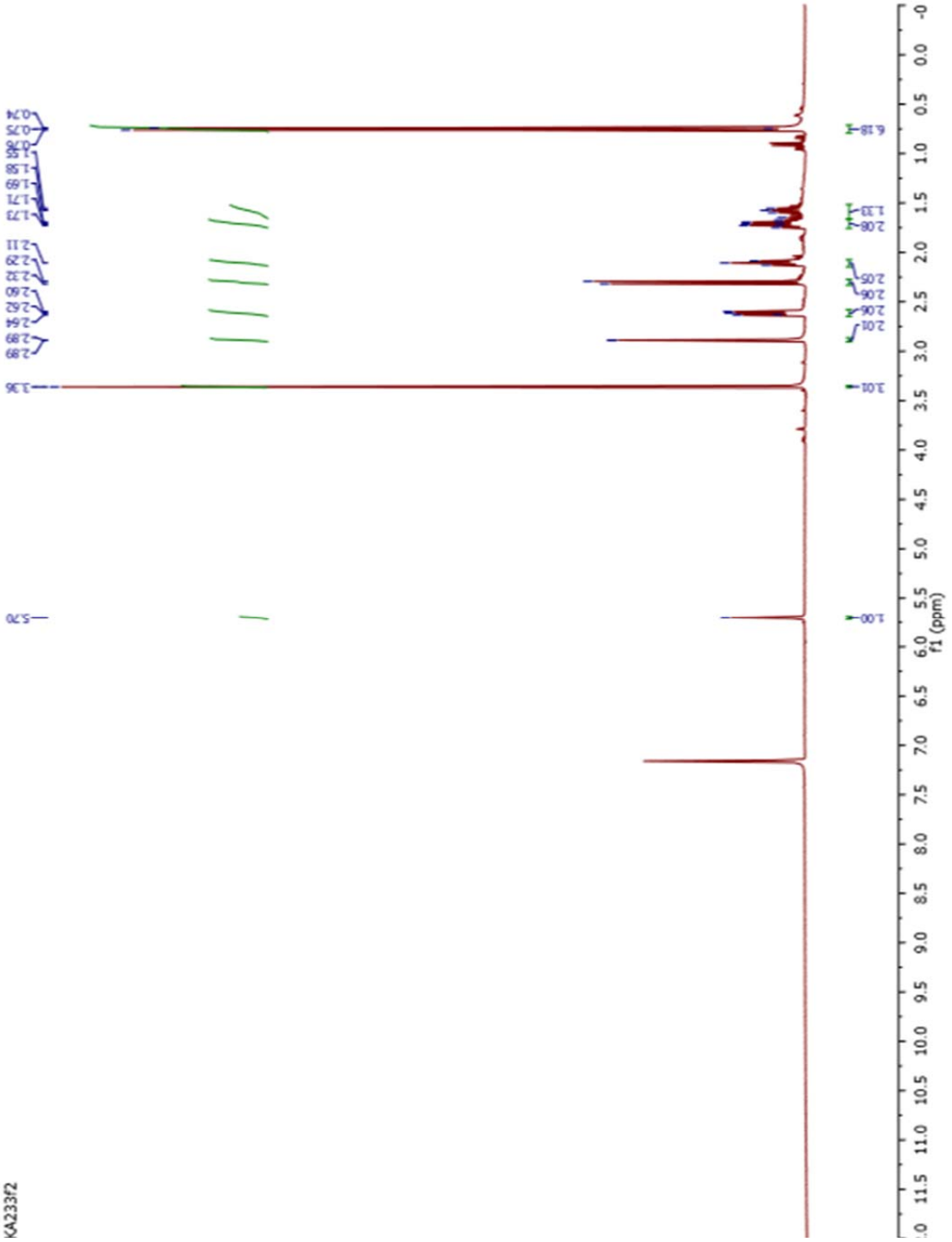
5-Benzyl-1-isobutyl-1,2,3,4-tetrahydropyridine ***15i***



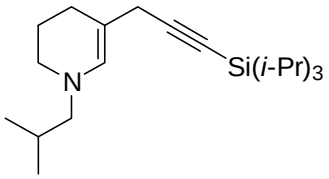


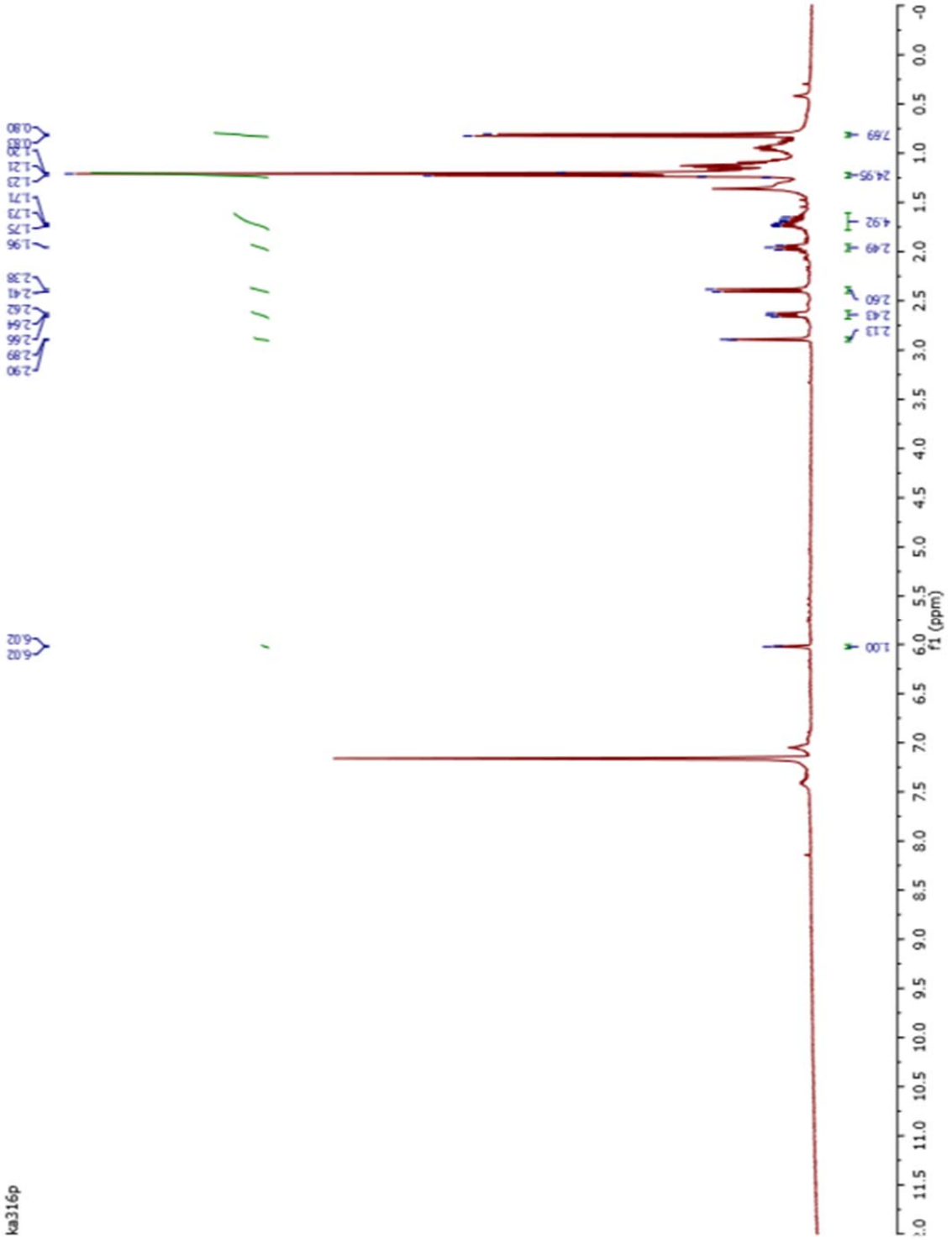
methyl 2-(1-isobutyl-1,4,5,6-tetrahydropyridin-3-yl)acetate ***15j***



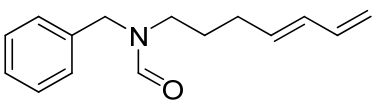


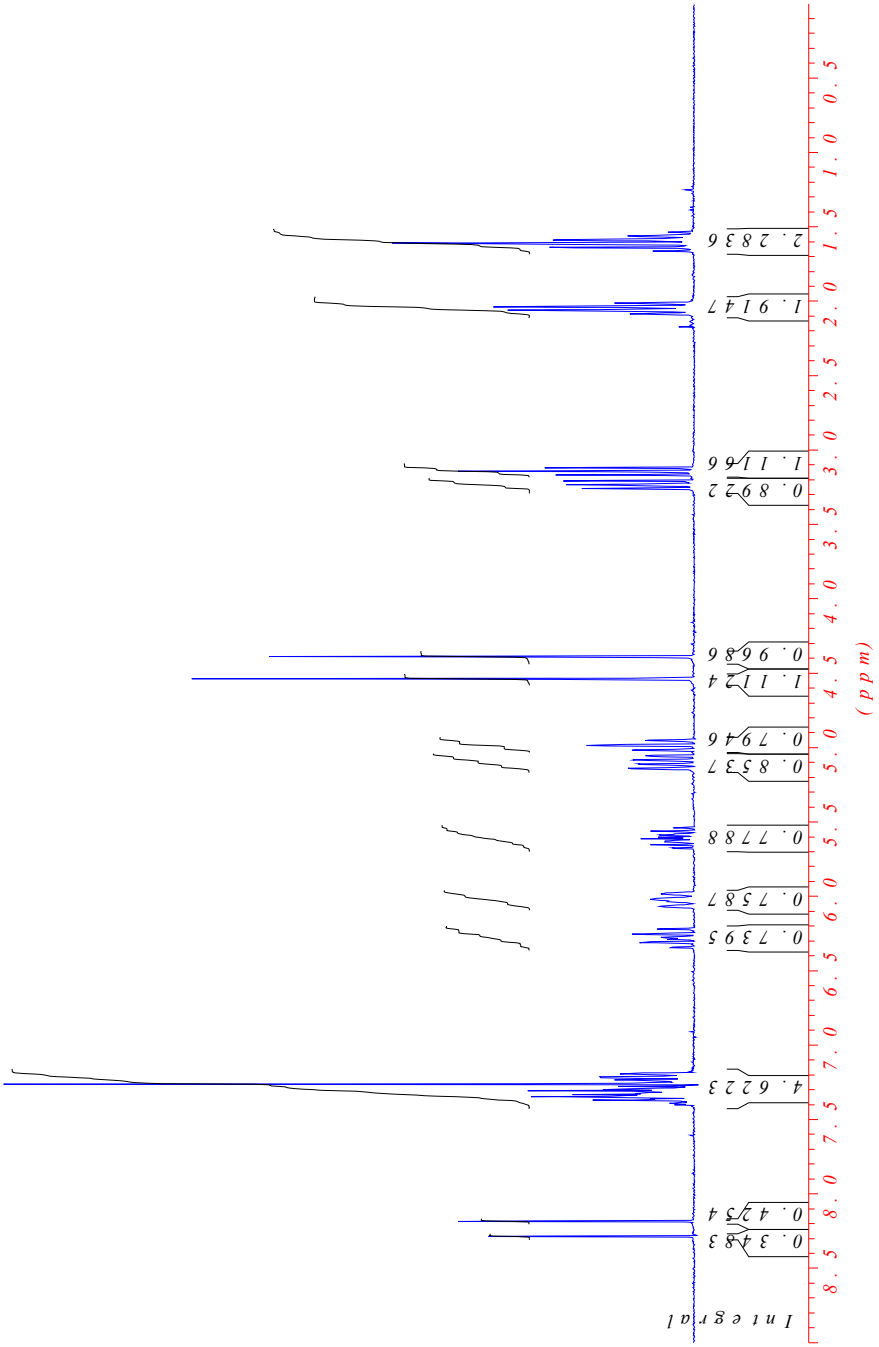
1-isobutyl-5-(3-(triisopropylsilyl)prop-2-ynyl)-1,2,3,4-tetrahydropyridine ***15k***



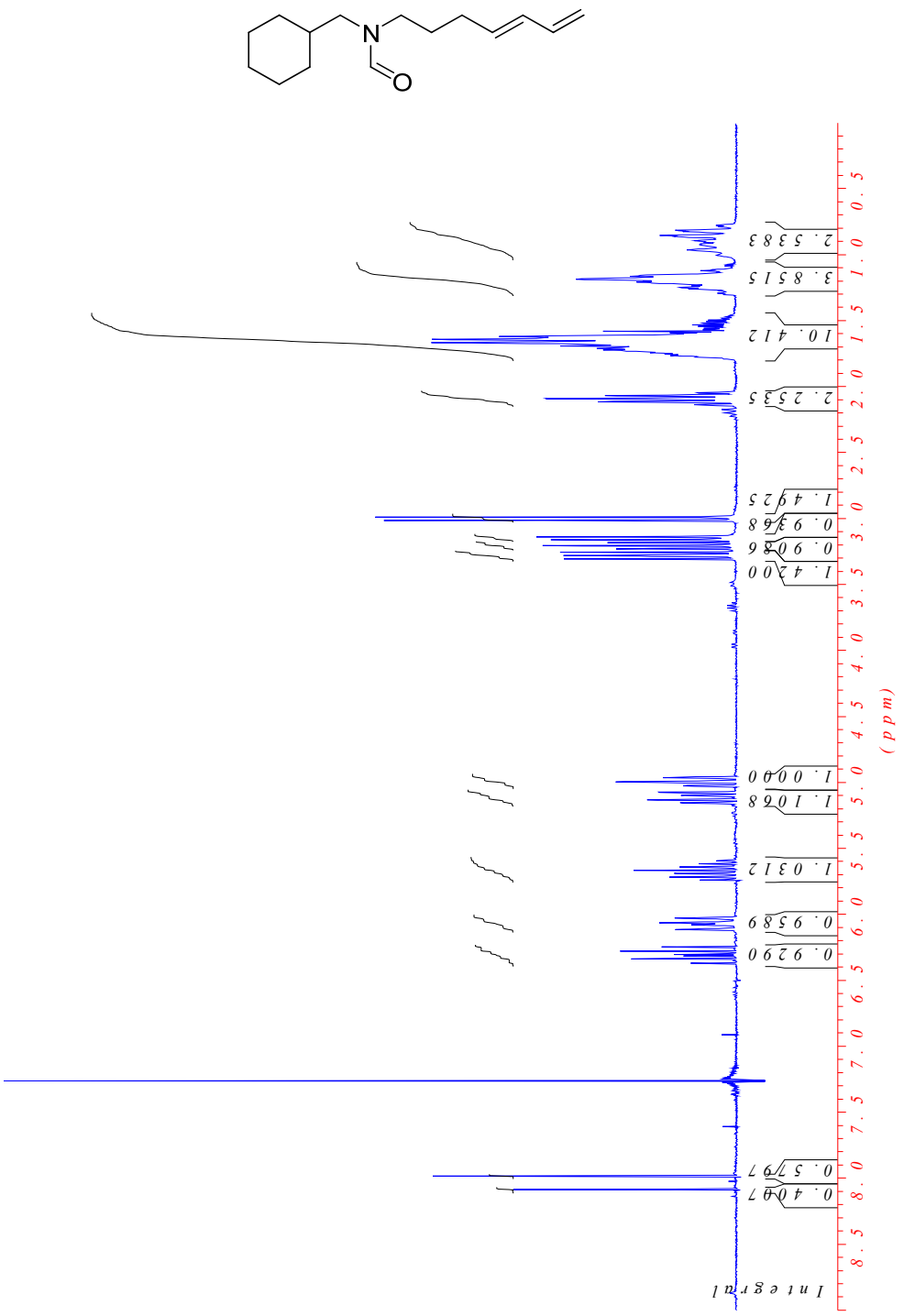


*(E)-N-(Benzyl)-N-(hepta-4,6-dienyl)formamide (**18a**)*

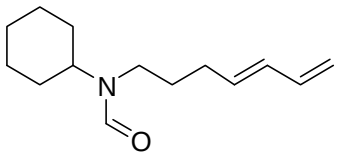


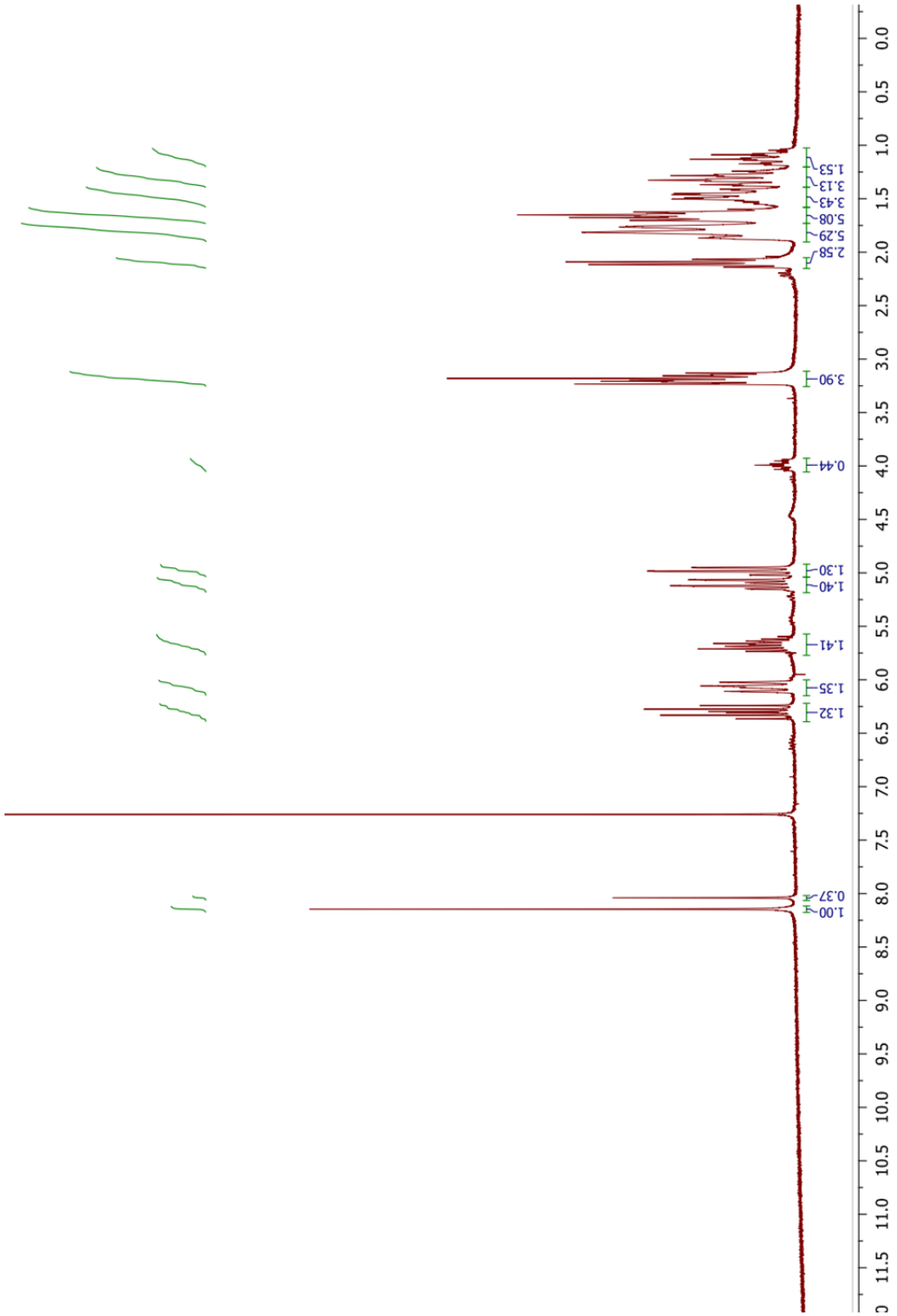


*(E)-N-(Cyclohexylmethyl)-N-(hepta-4, 6-dienyl)formamide (**18b**)*

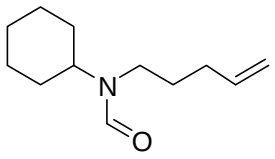


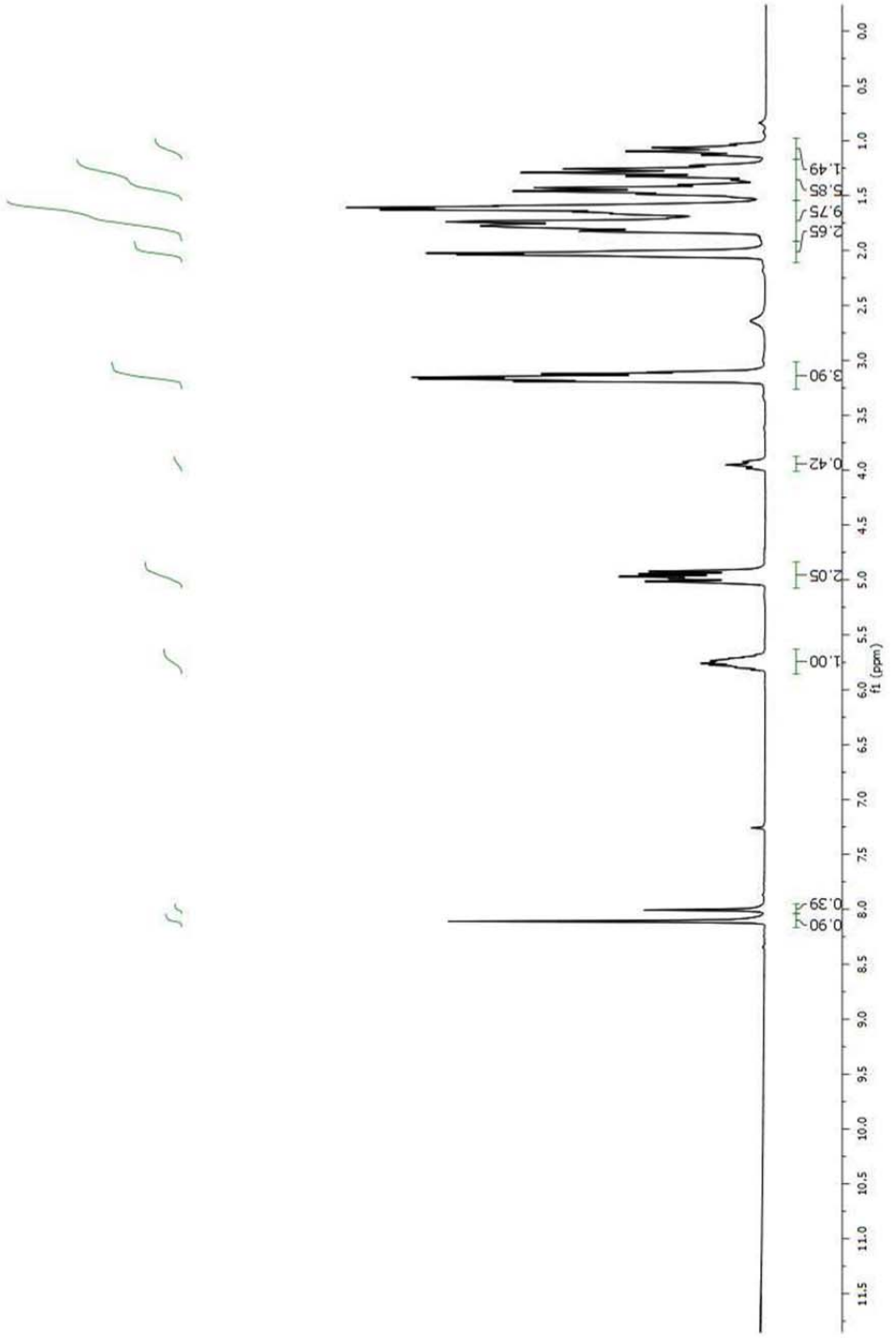
*(E)-N-cyclohexyl-N-(hepta-4,6-dien-1-yl)formamide (**18c**)*



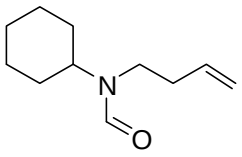


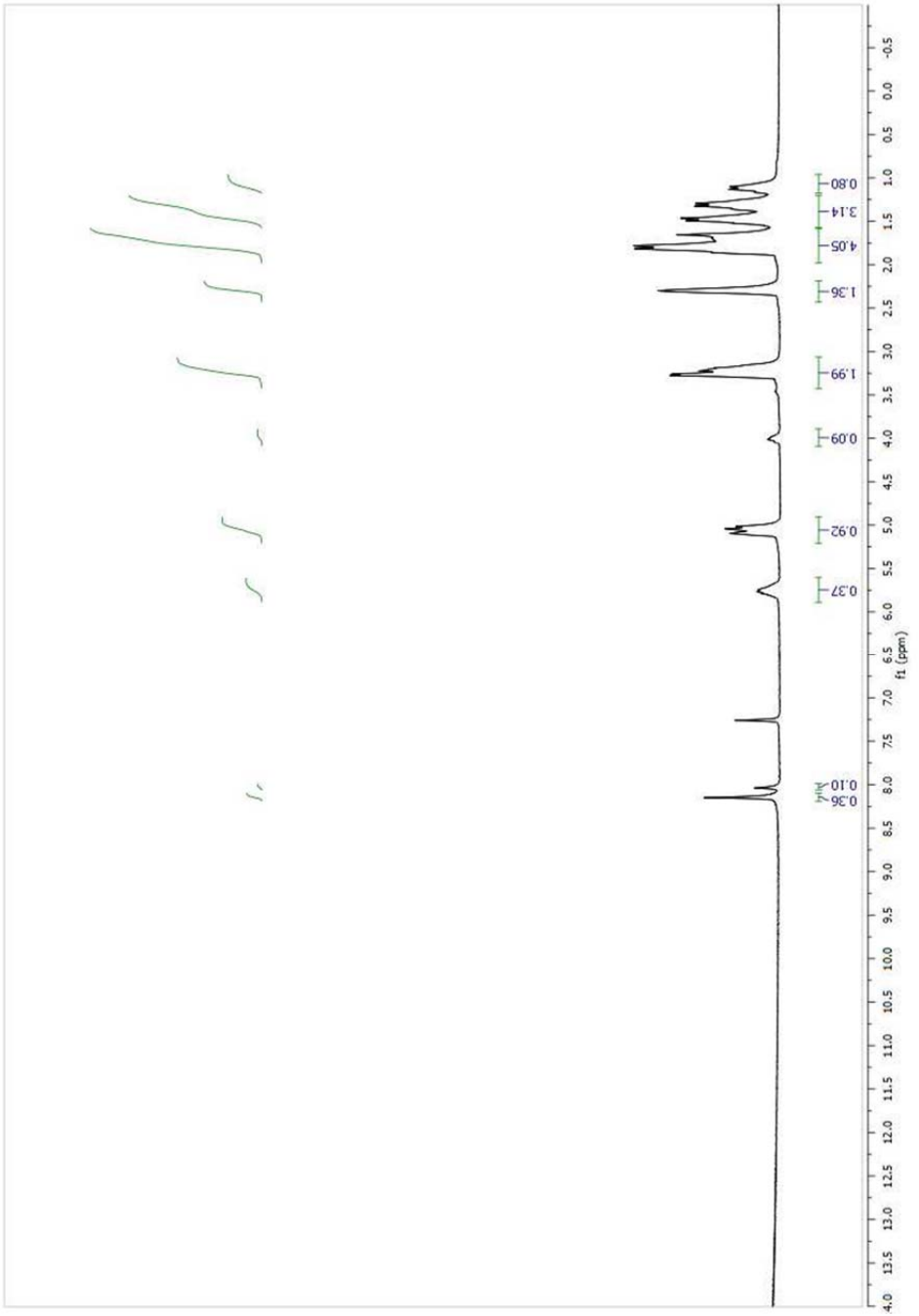
*N-Cyclohexyl-N(4-penten-1-yl) formamide (**18d**)*



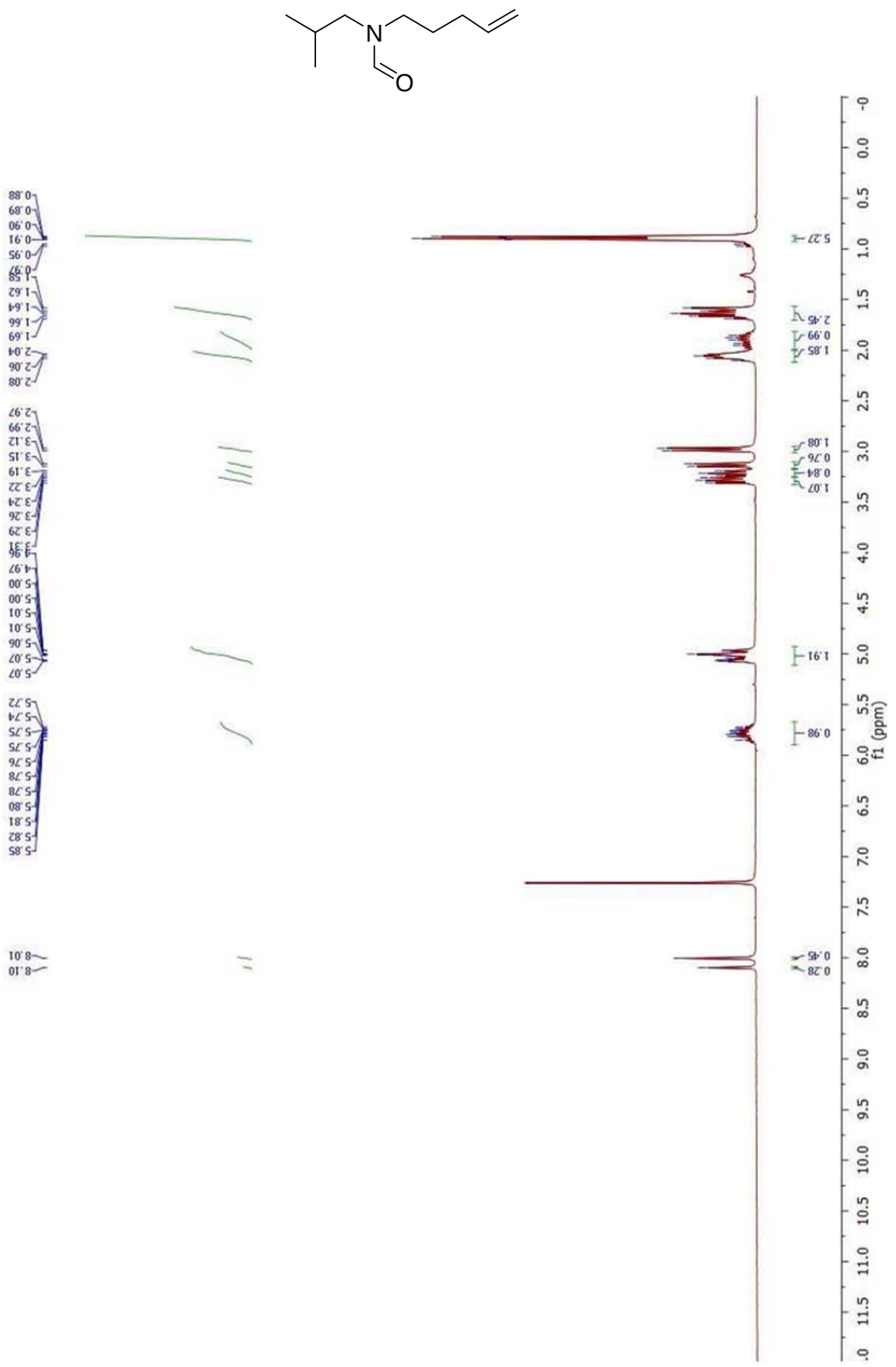


*N-cyclohexyl-N-(3-buten-1-yl)formamide (**18e**)*

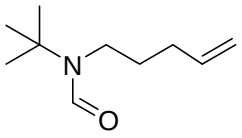


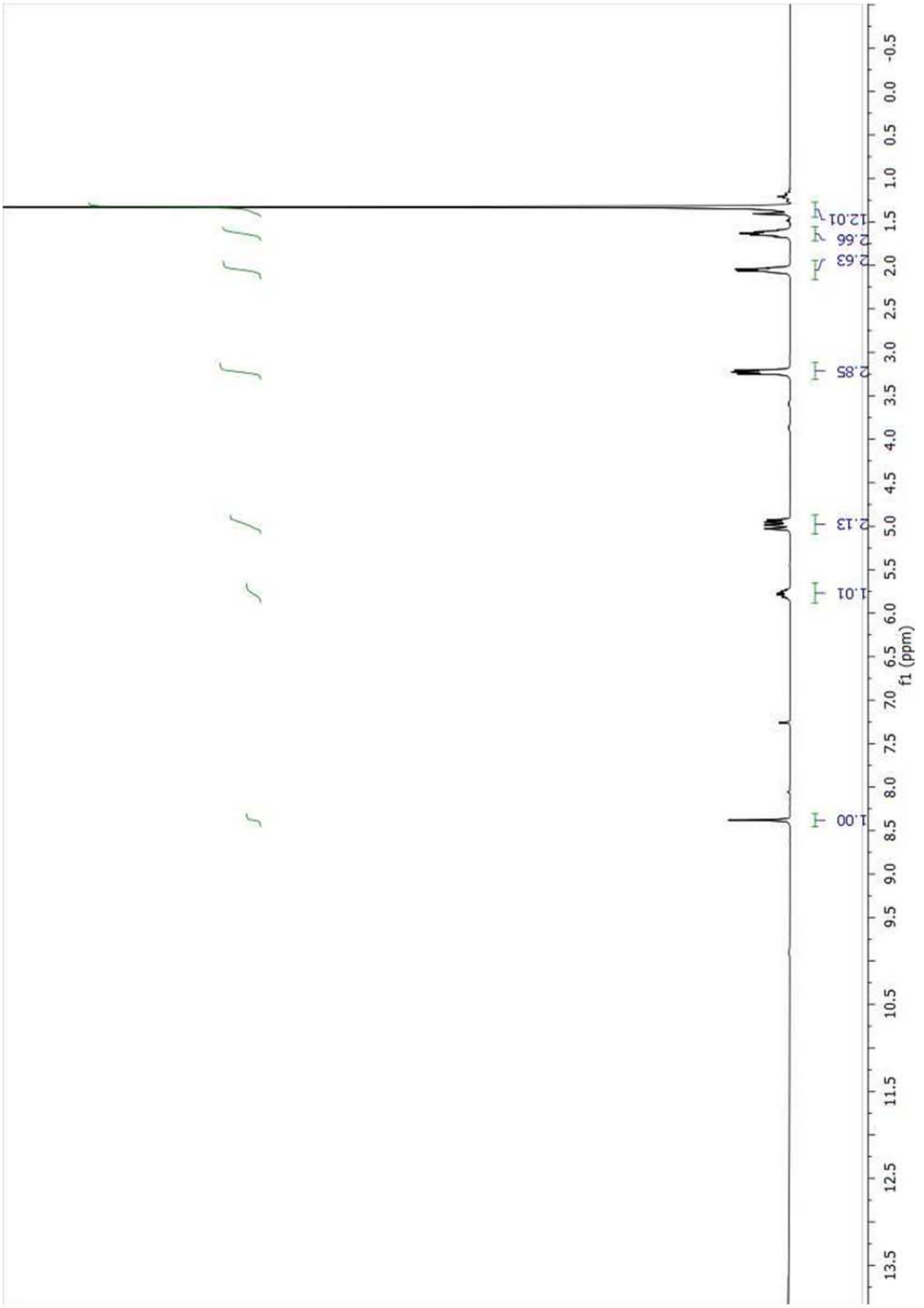


*N-Isobutyl-N(4-penten-1-yl) formamide (**18f**)*

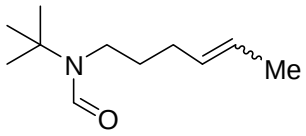


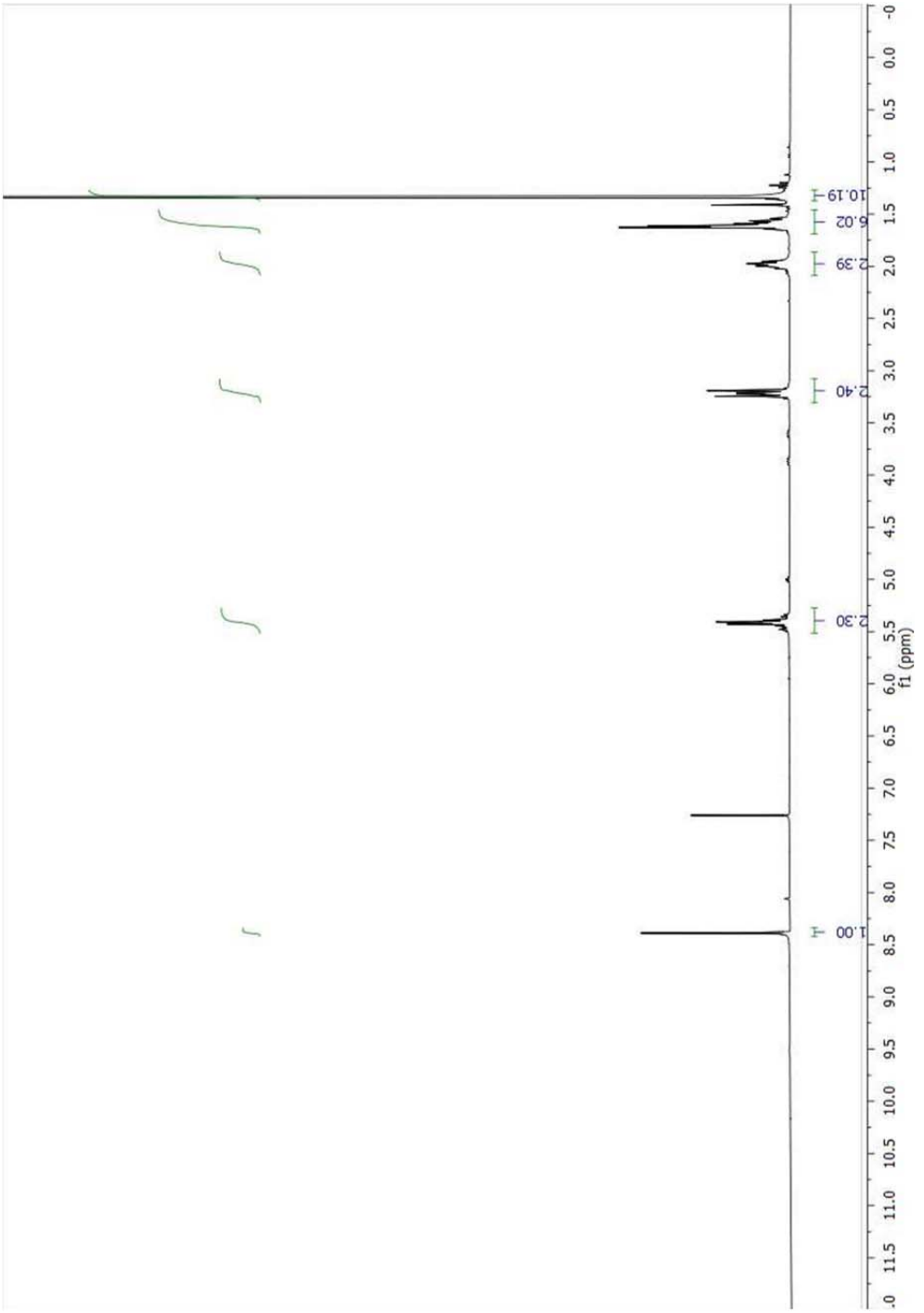
*N-tert-butyl-N(4-penten-1-yl) formamide (**18g**)*



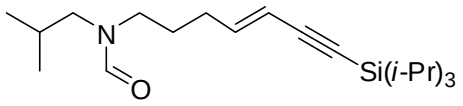


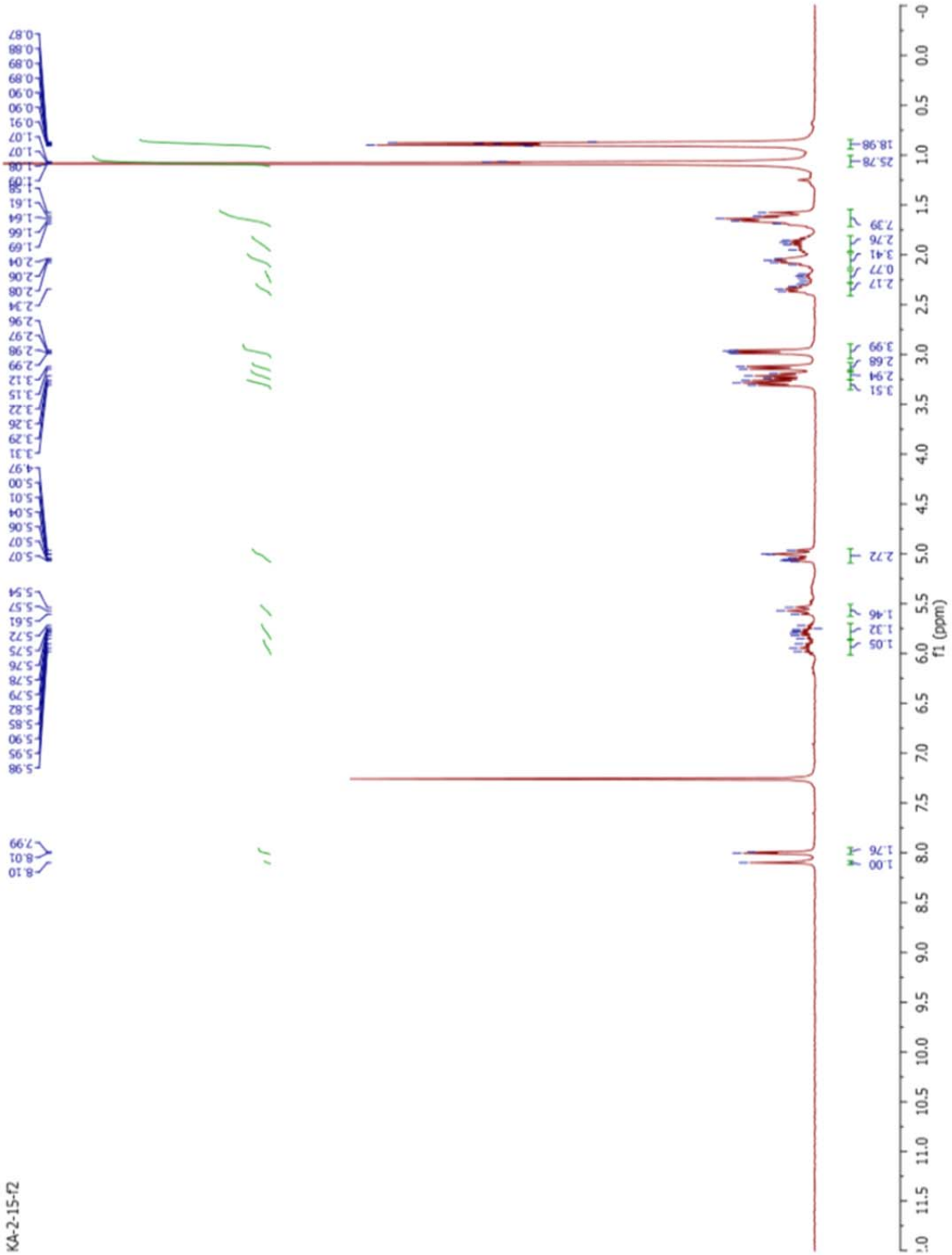
*N-Isobutyl-N(4-hexen-1-yl) formamide (**18h**)*



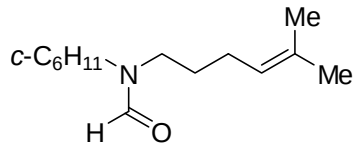


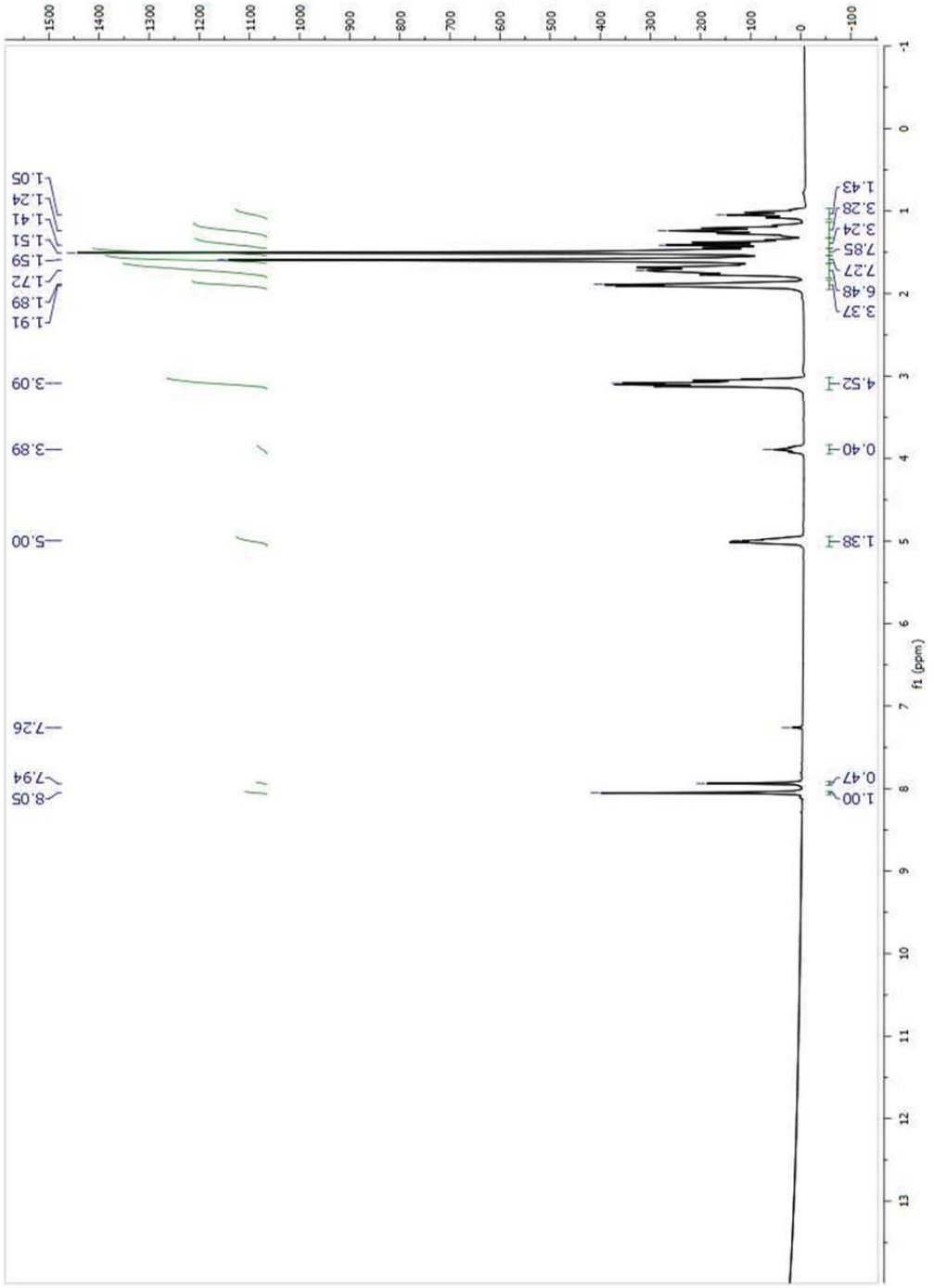
*(E)-N-isobutyl-N-(7-(triisopropylsilyl)hept-4-en-6-ynyl)formamide (**18k**)*



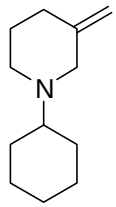


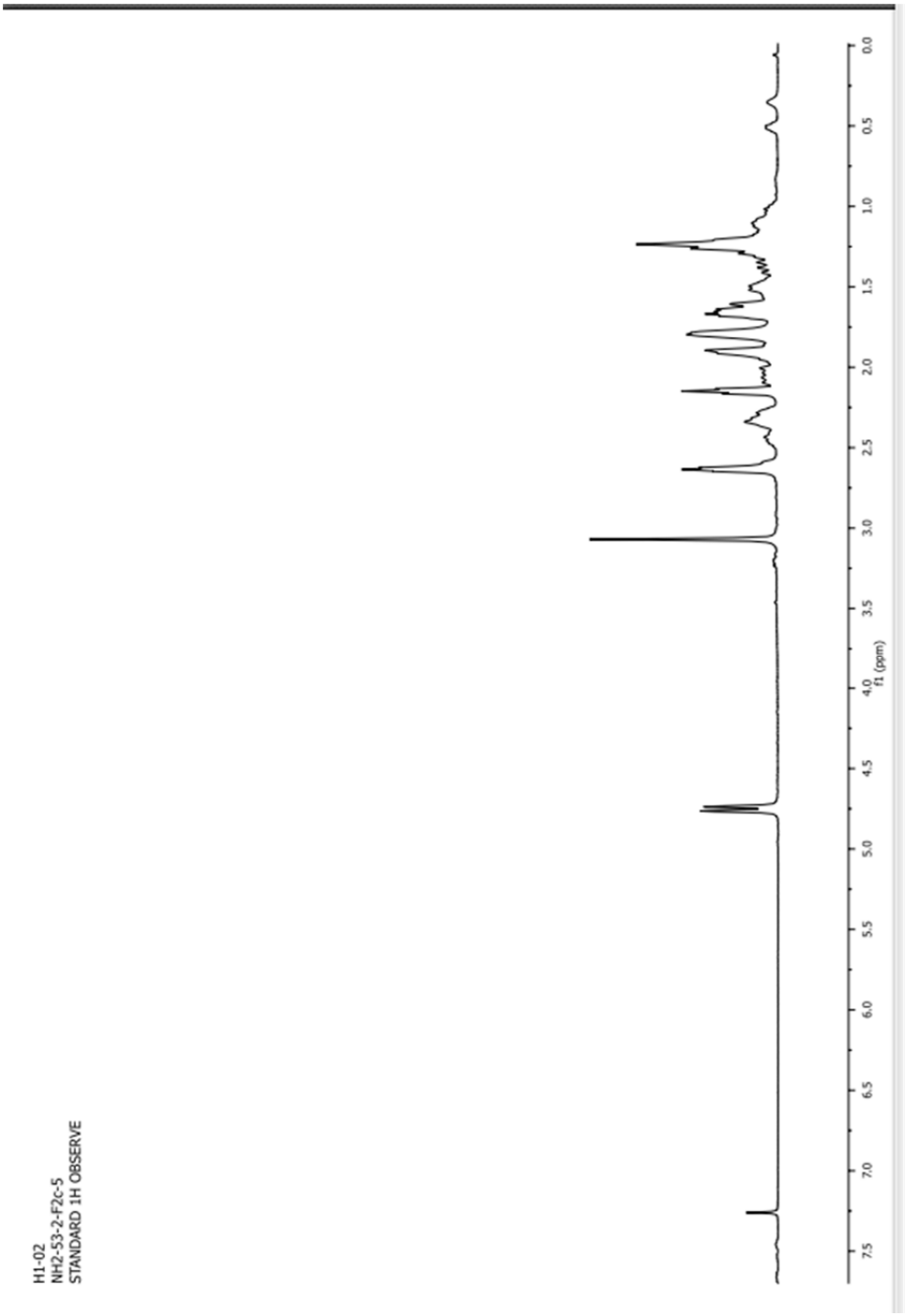
N-cyclohexyl-N-(5-methyl-4-hexen-1-yl)formamide (***18l***)



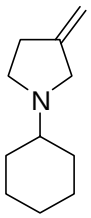


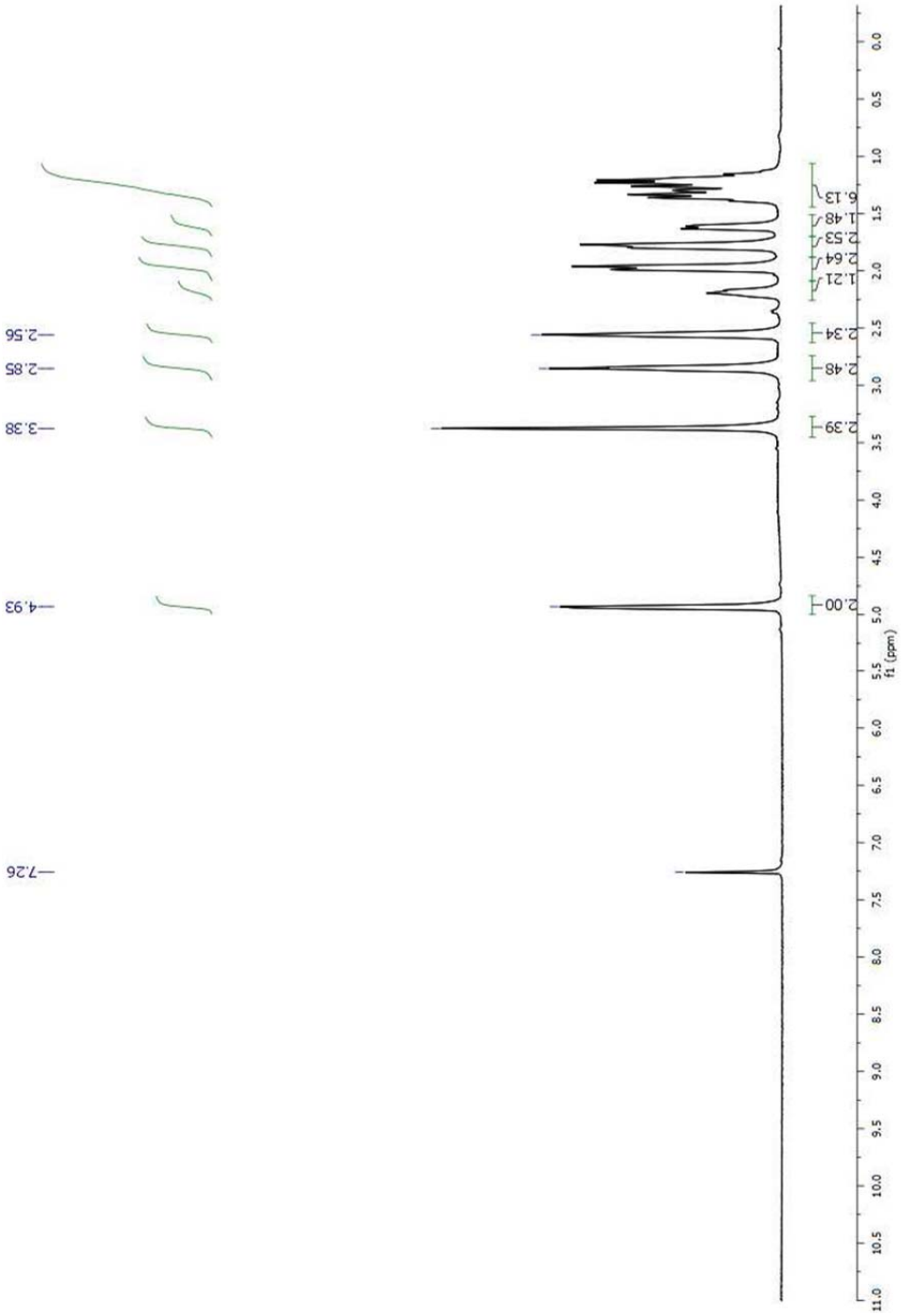
(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine ***19d***



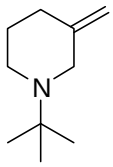


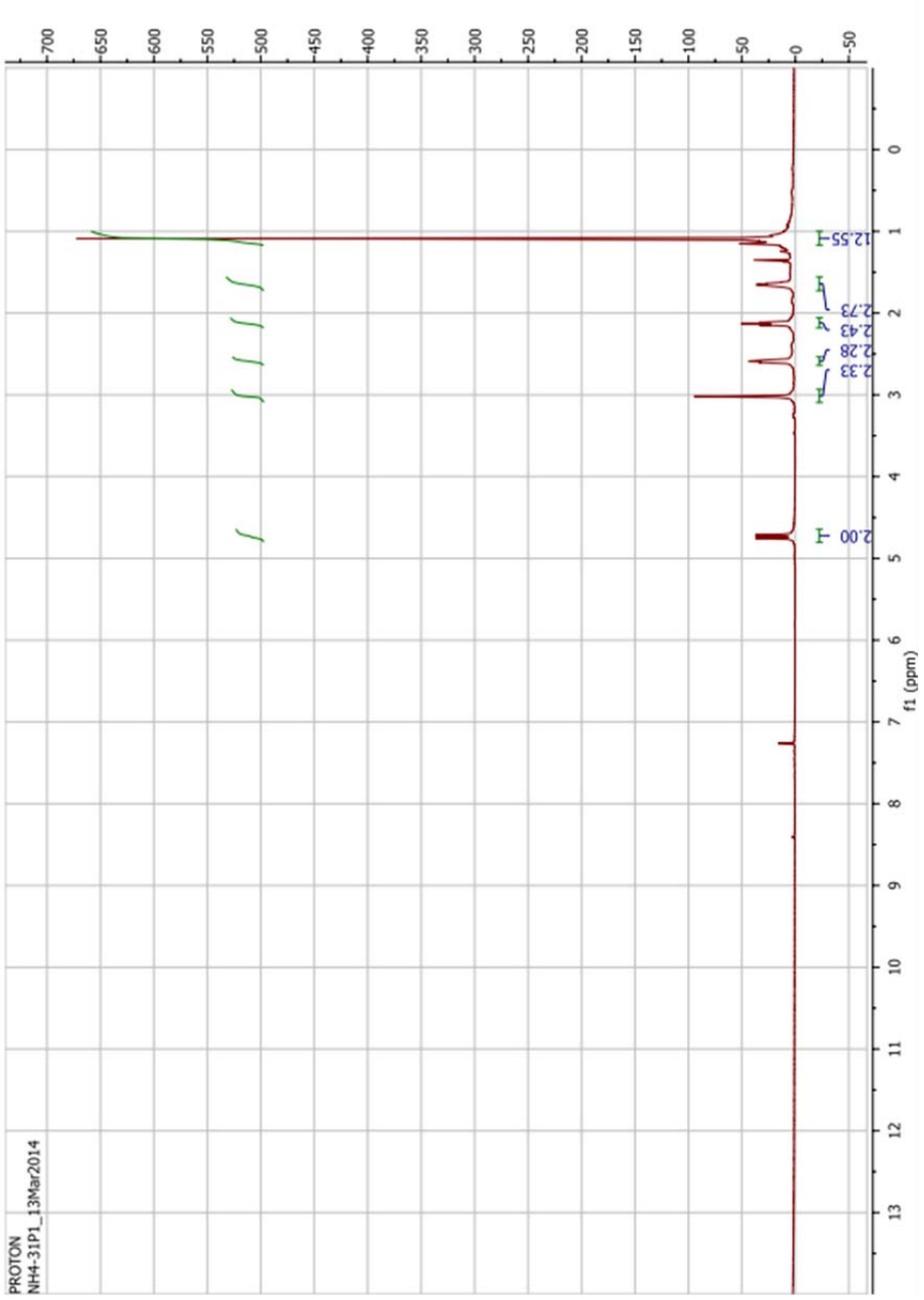
(E)-8-(Prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine ***19e***



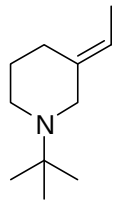


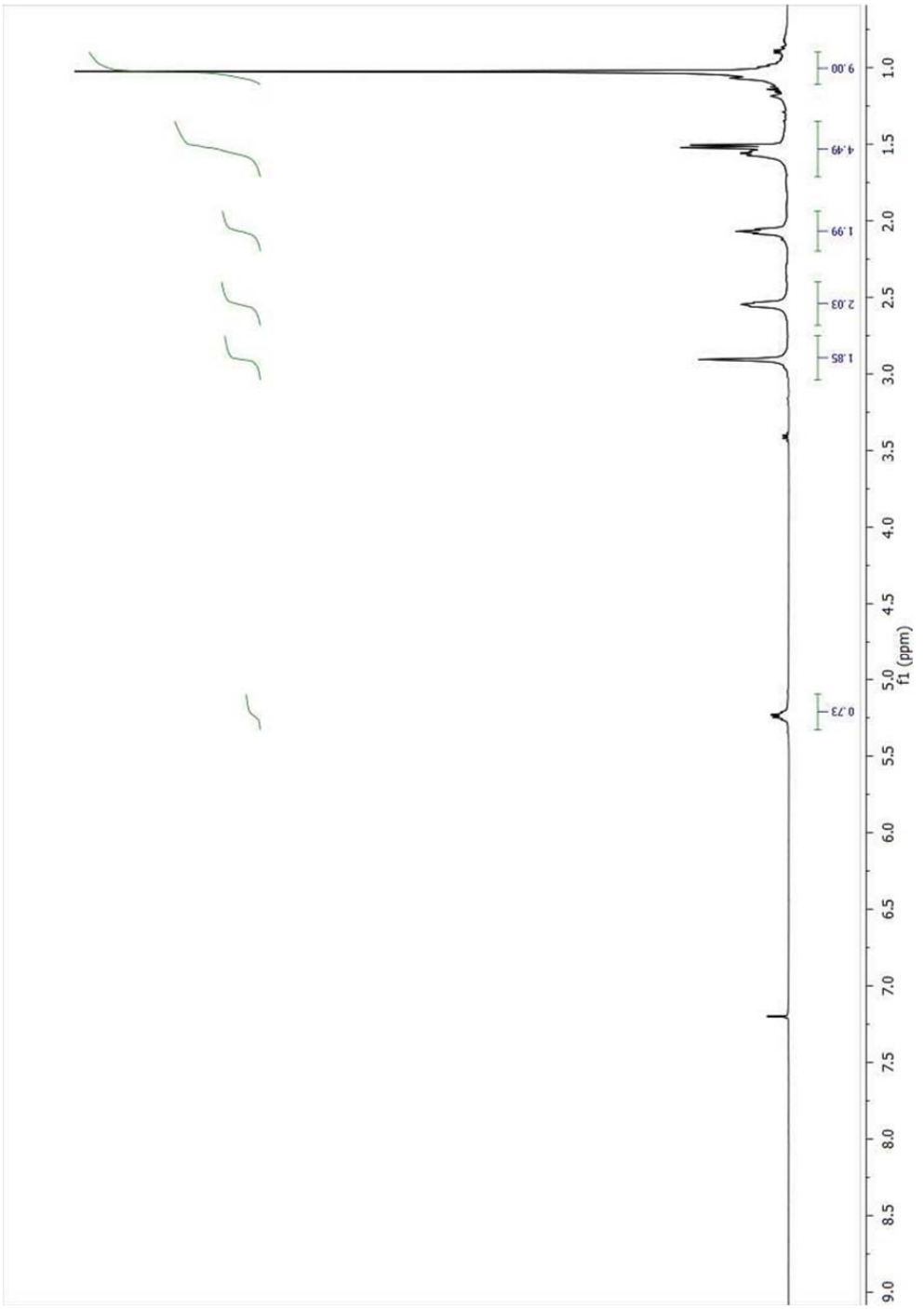
(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine ***19g***



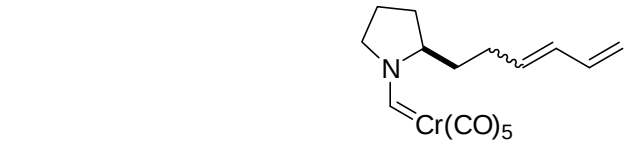


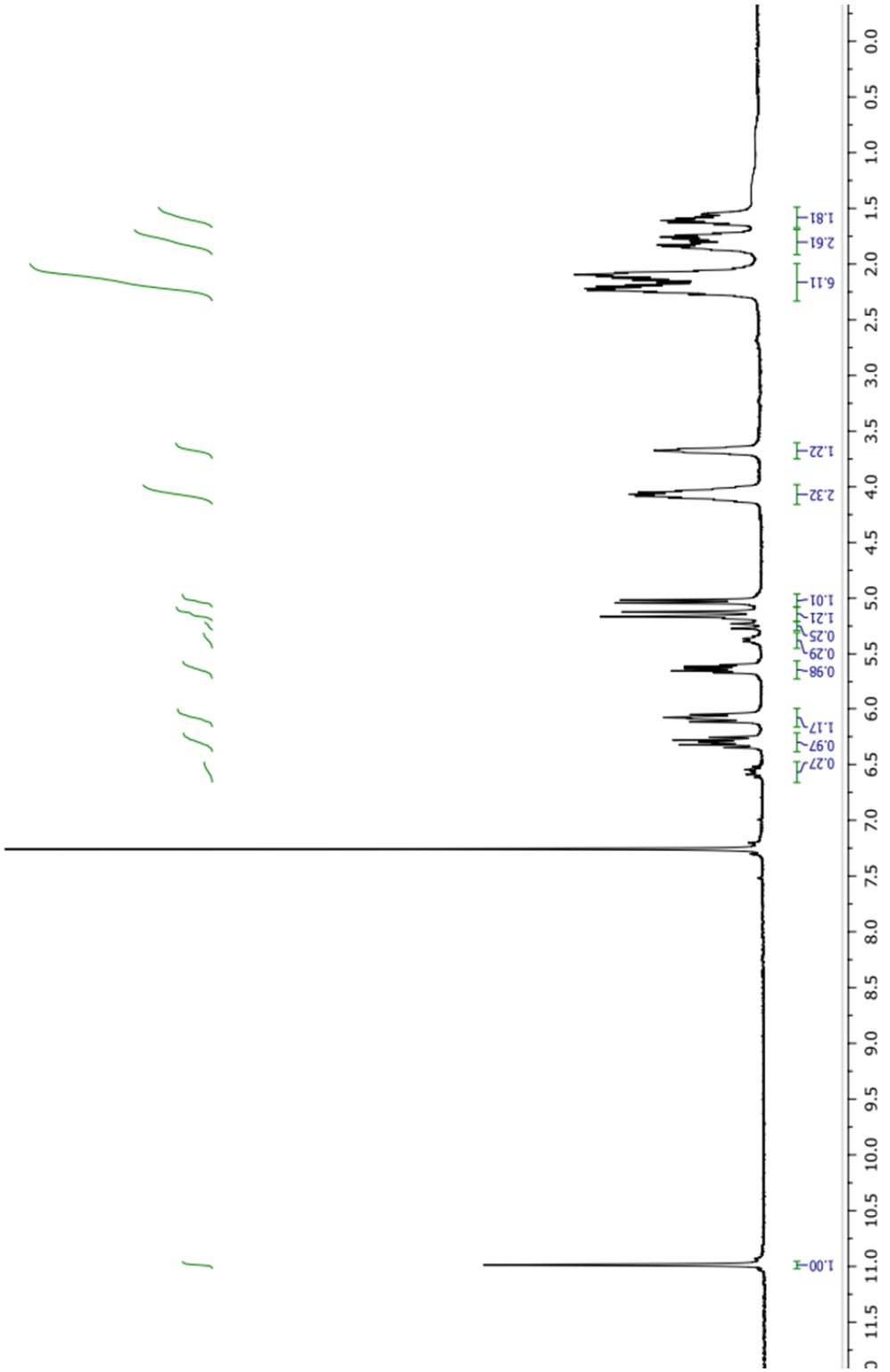
(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine ***19h***



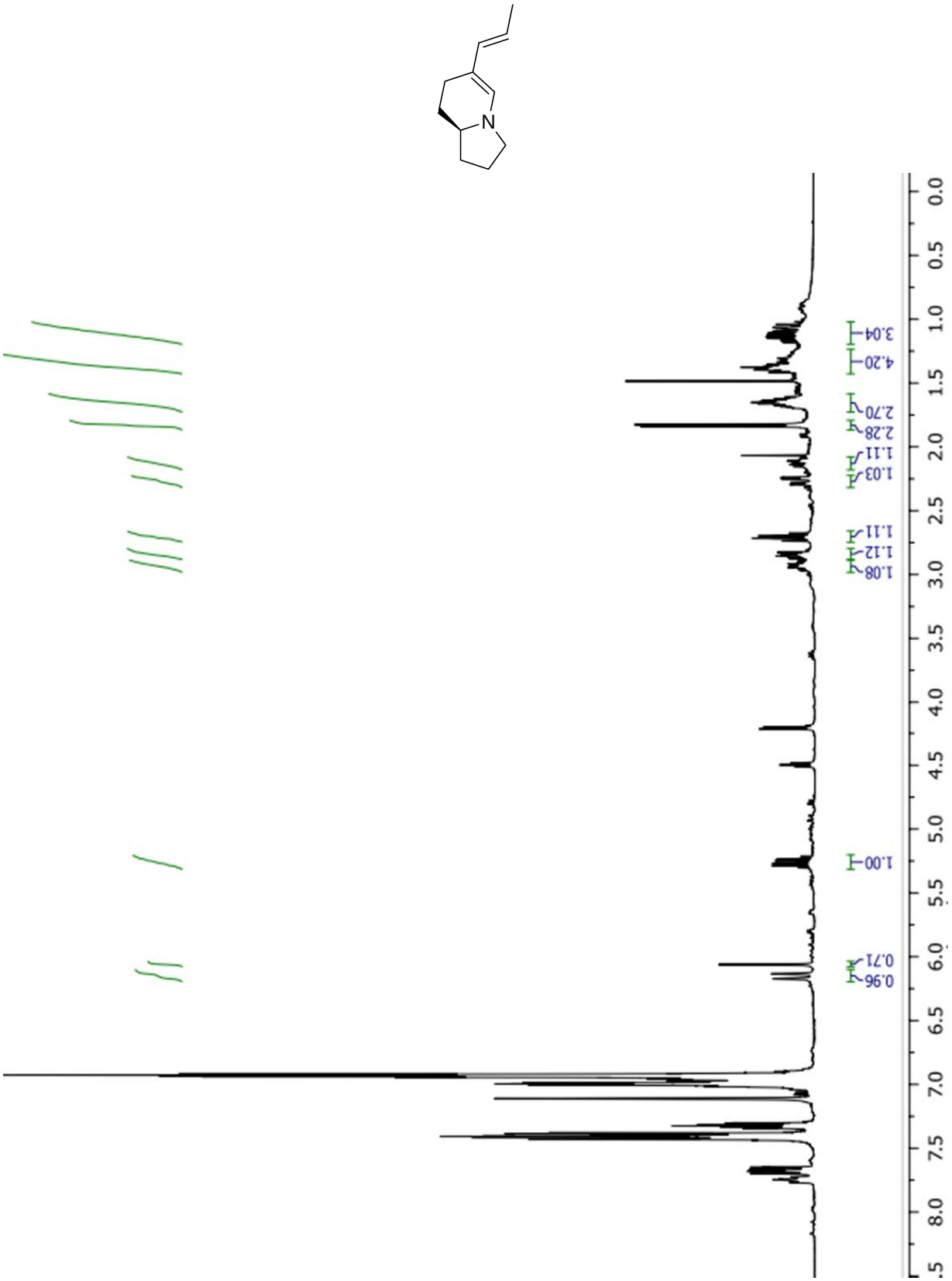


*Mixture of E and Z (R)-Pentacarbonyl[(3-buten-1-yl)pyrrolidine)methylene]chromium(0) (**20**)*

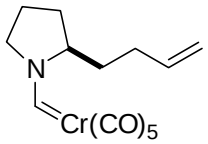


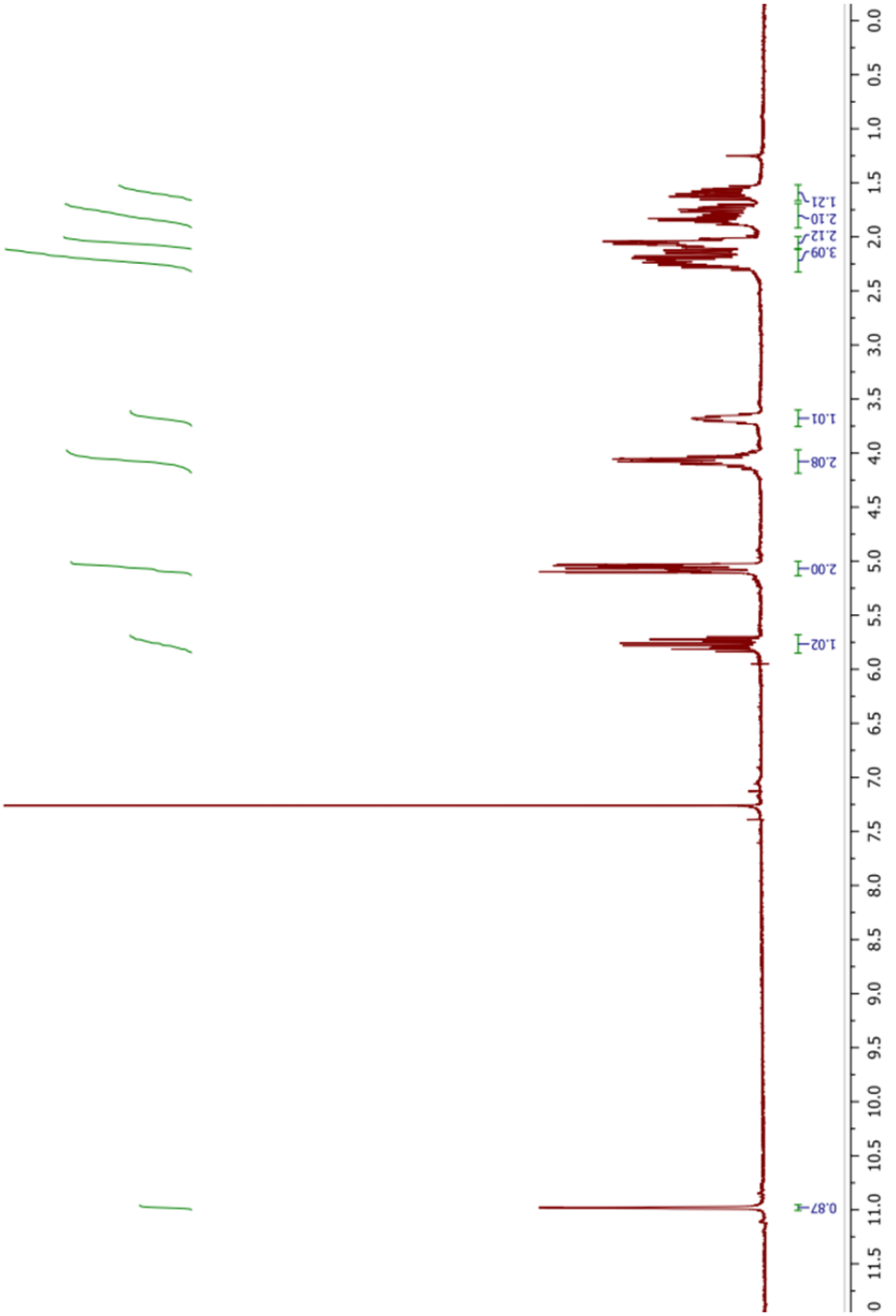


*(R,E)-6-(prop-1-enyl)-1,2,3,7,8,8a-hexahydroindolizine (**21**)*

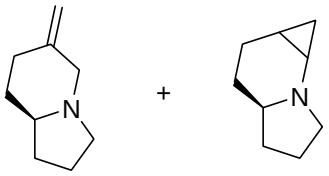


*(R)-Pentacarbonyl[(3-buten-1-yl)pyrrolidine)methylene]chromium(0) (**22**)*

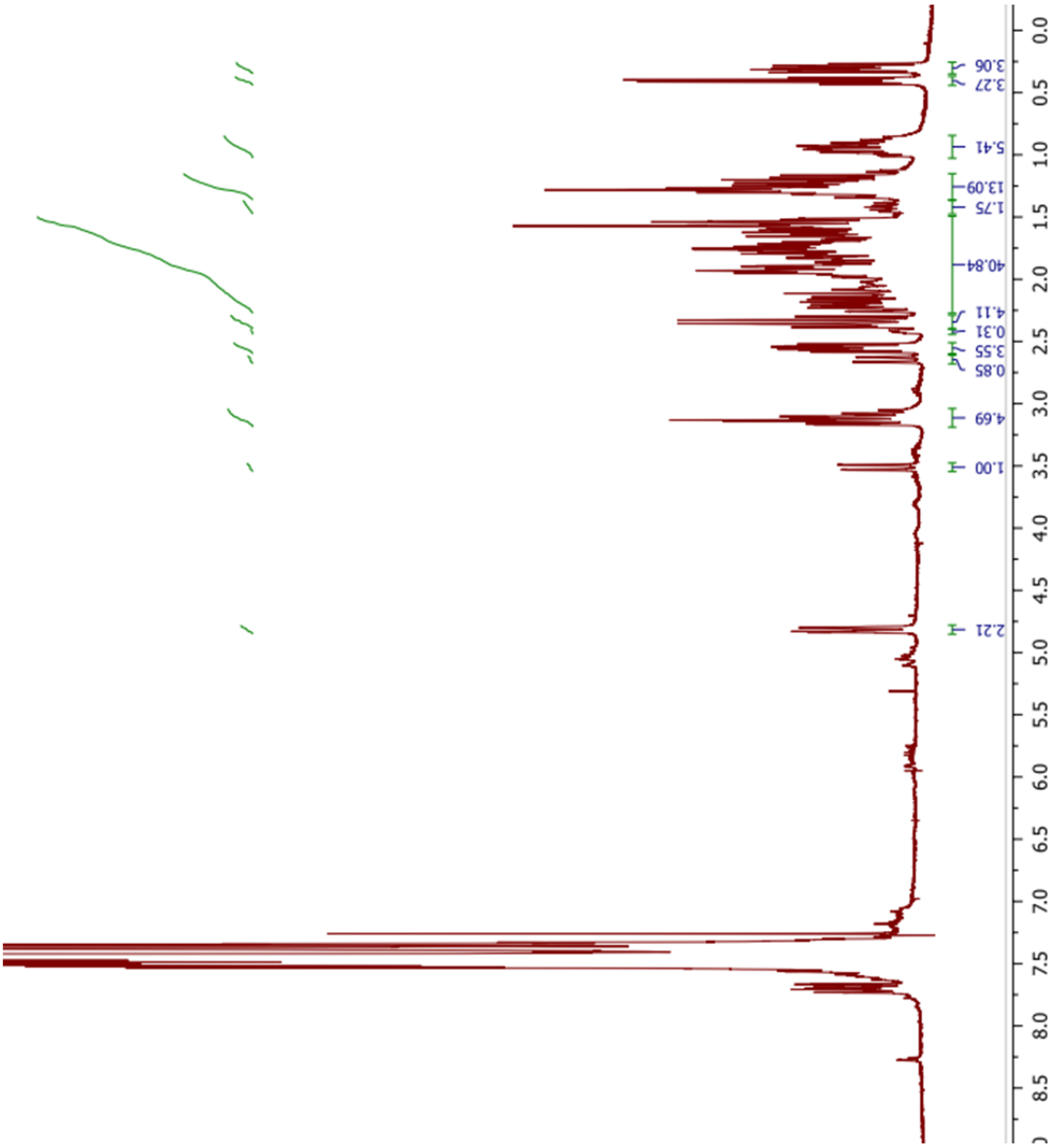




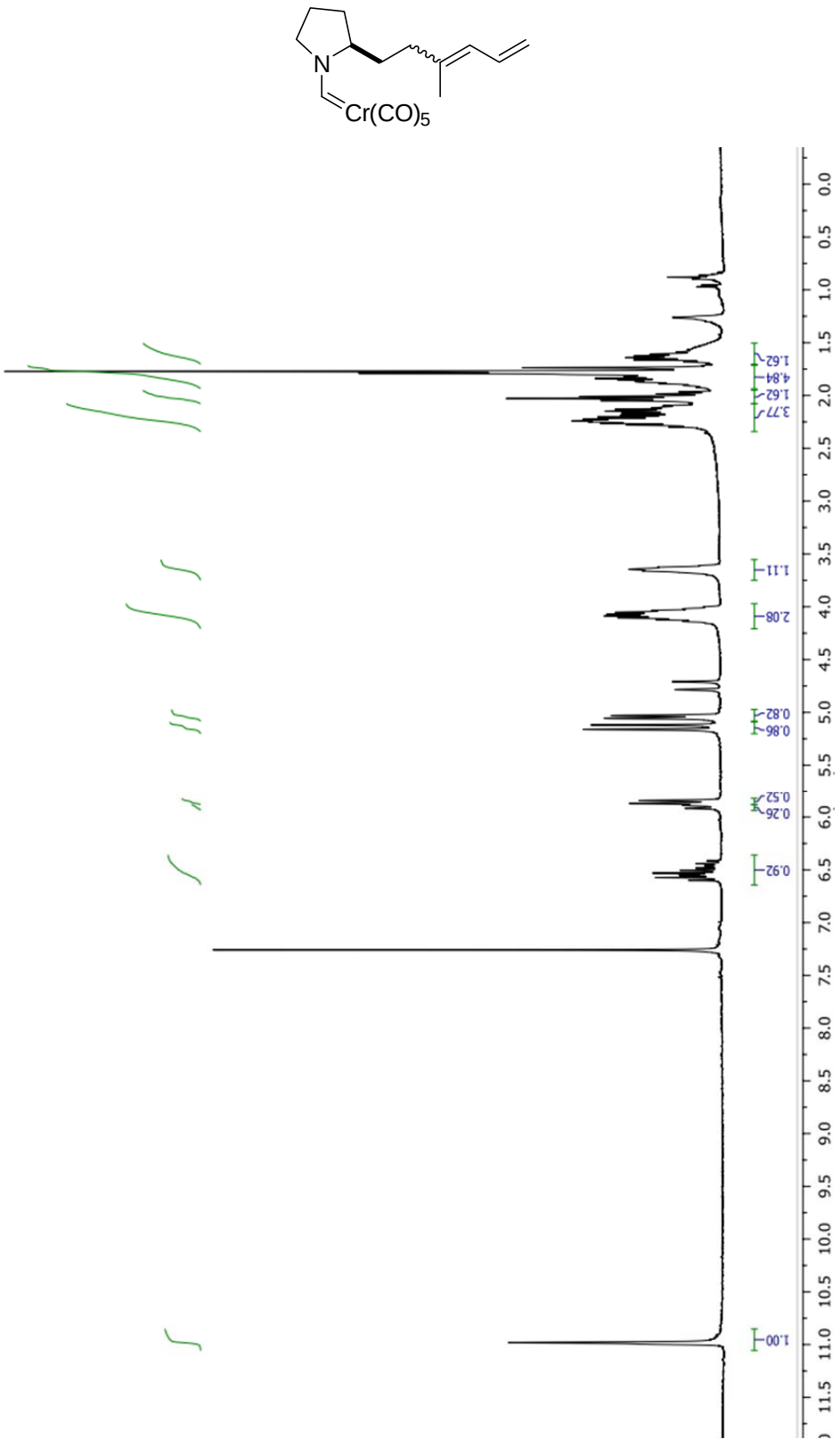
*(R)-6-methyleneoctahydroindolizine (**23a**) and (3aR)-octahydro-1H-cyclopropa[e]indolizine (**23b**)*



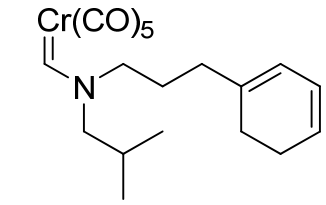
23a **23b**

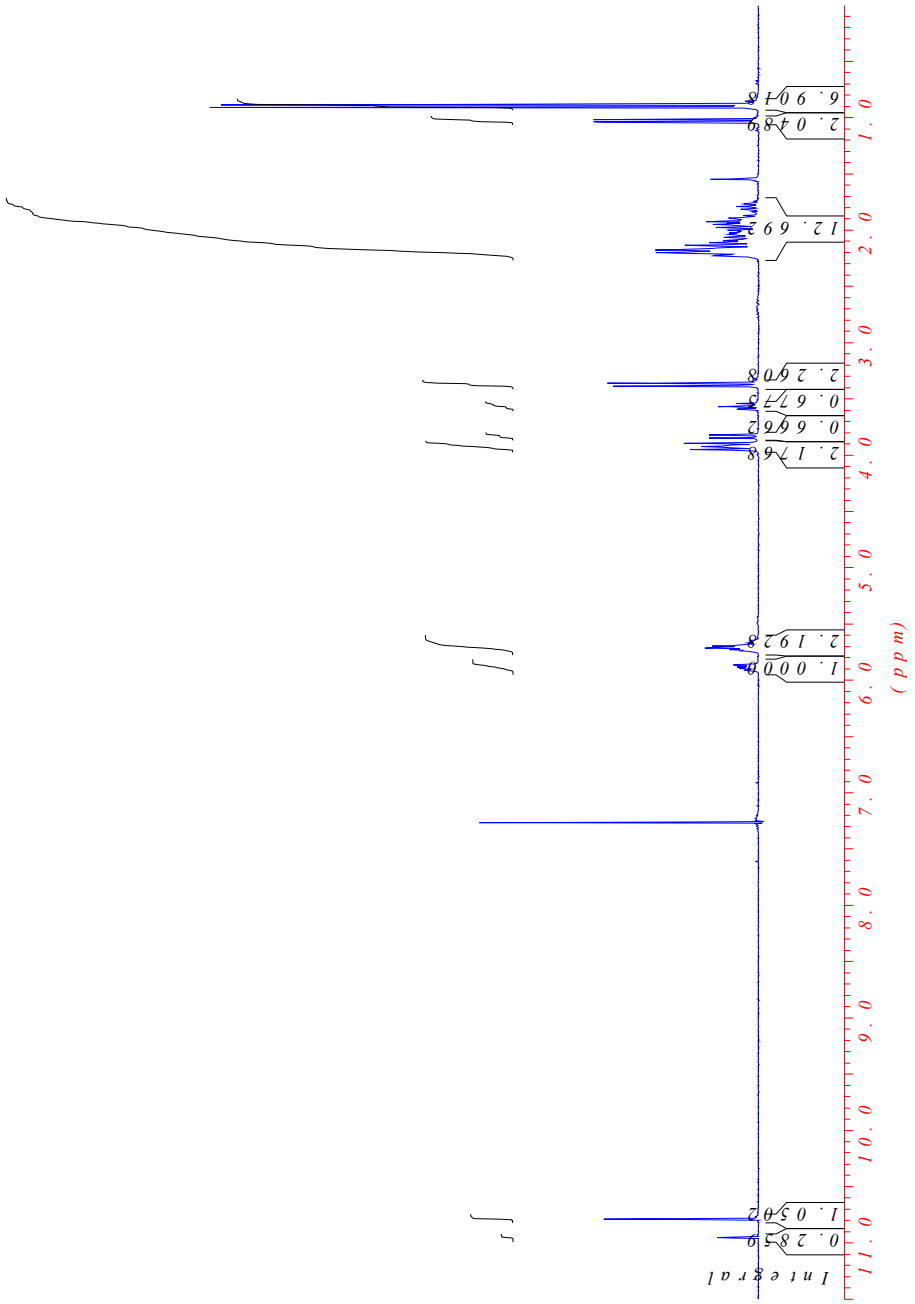


Mixture of E and Z (R)-pentacarbonyl[(2-(3-methylhexa-3,5-dienyl)pyrrolidine)methylene]chromium(0) ***(24)***

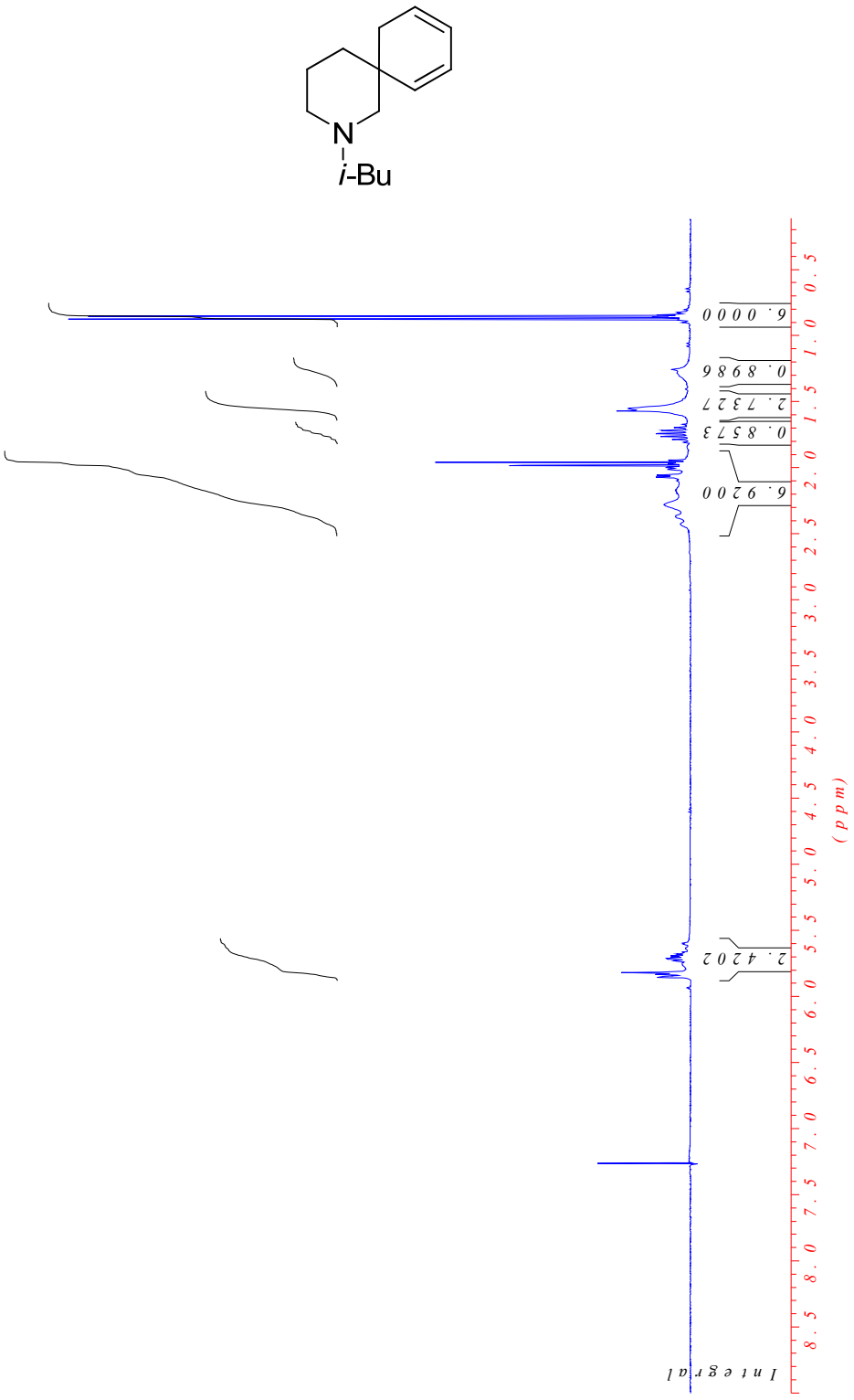


*Pentacarbonyl[(N-(3-(Cyclohexa-1, 3-dienyl)propyl)-N-(2-methylpropyl)amino)methylene]chromium(0) (**25**)*

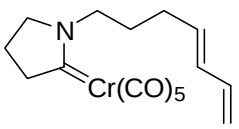


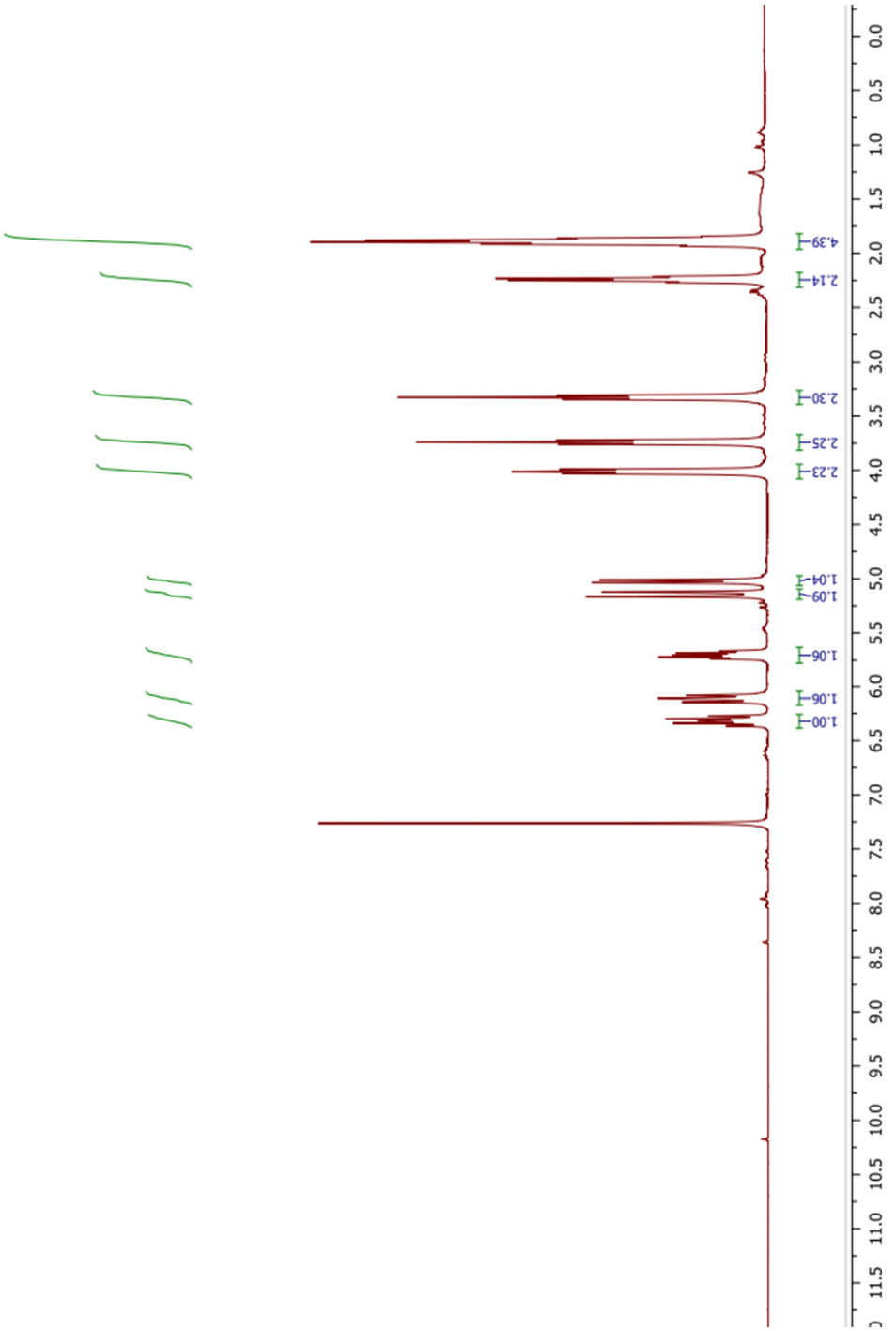


Piperidine ***26***

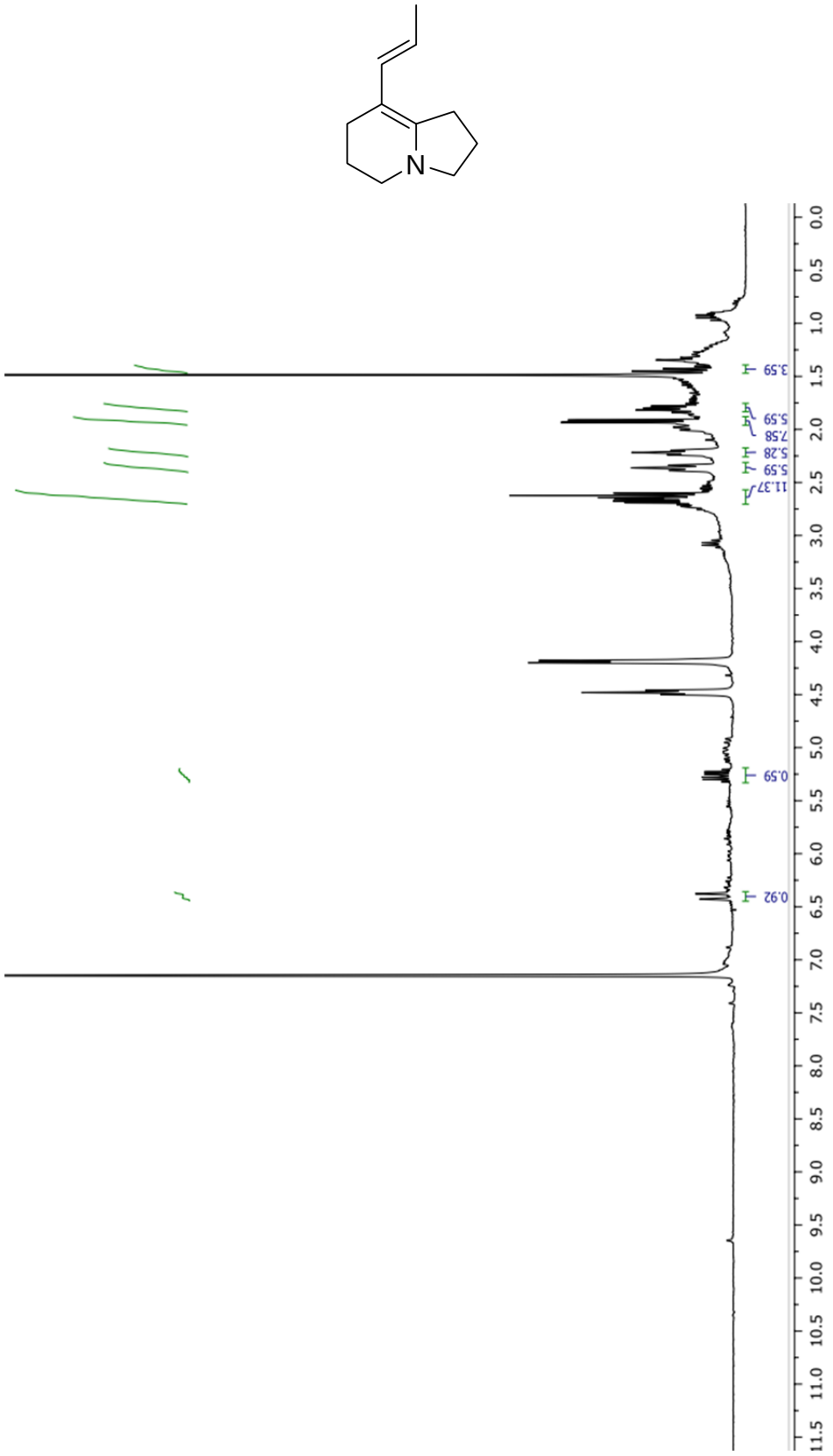


*Chromium aminocarbene (**31**)*

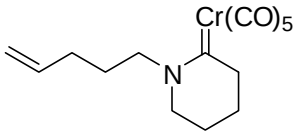


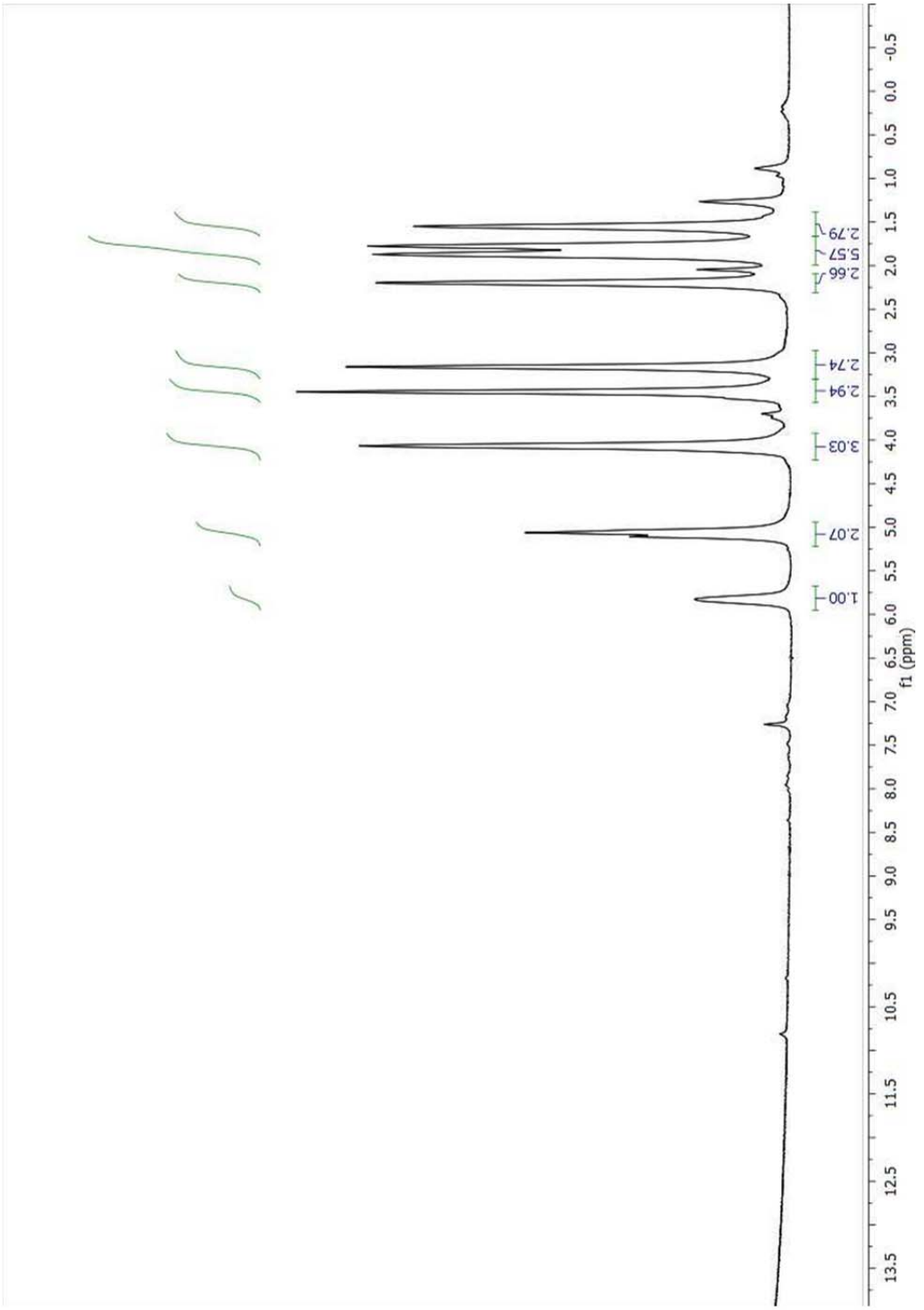


*(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine (**32**) in C_6D_6*

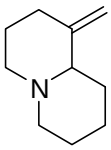


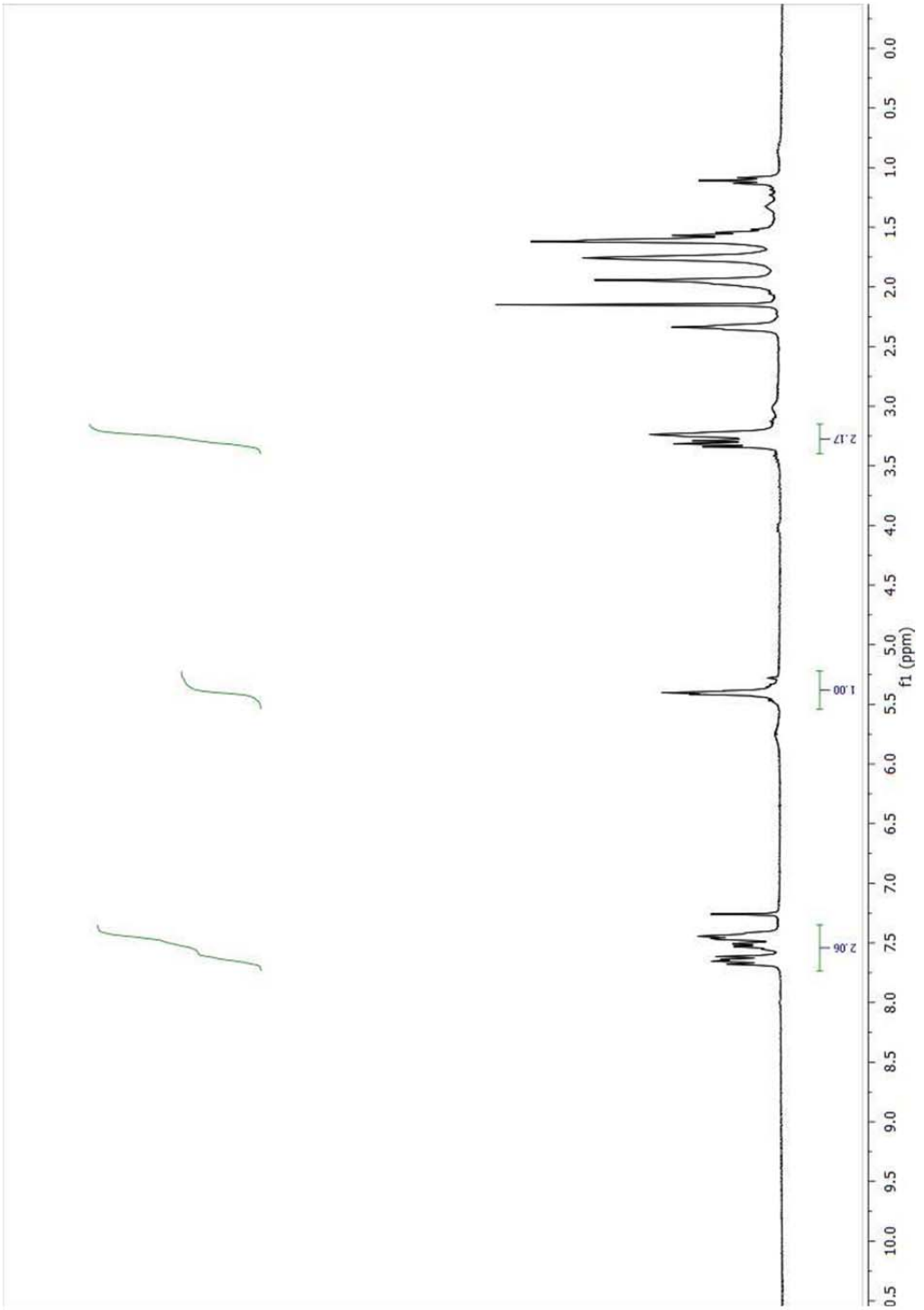
*Chromium aminocarbene (**33**)*



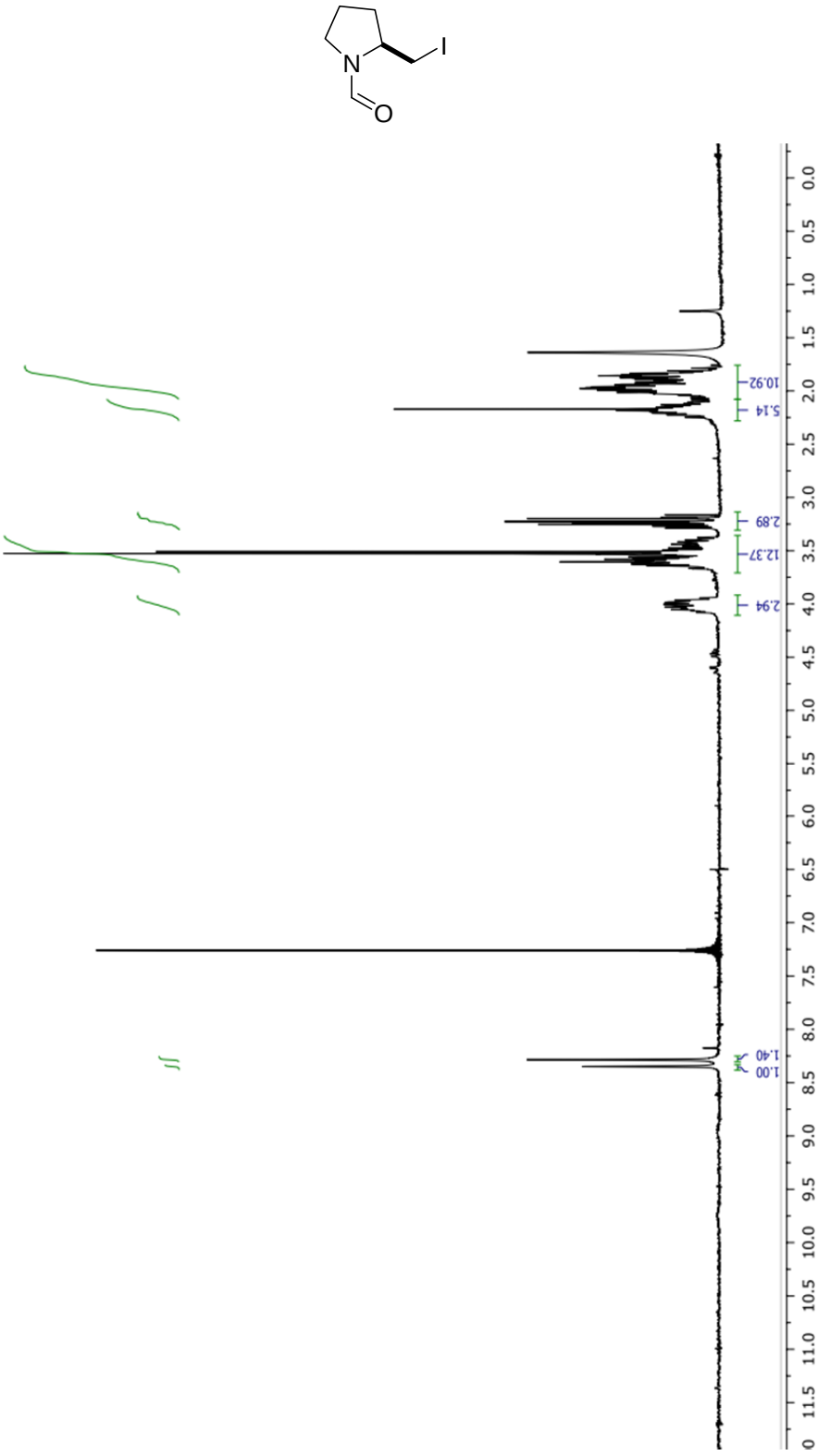


*1-Methyleneoctahydro-1H-quinolizine (**34**)*

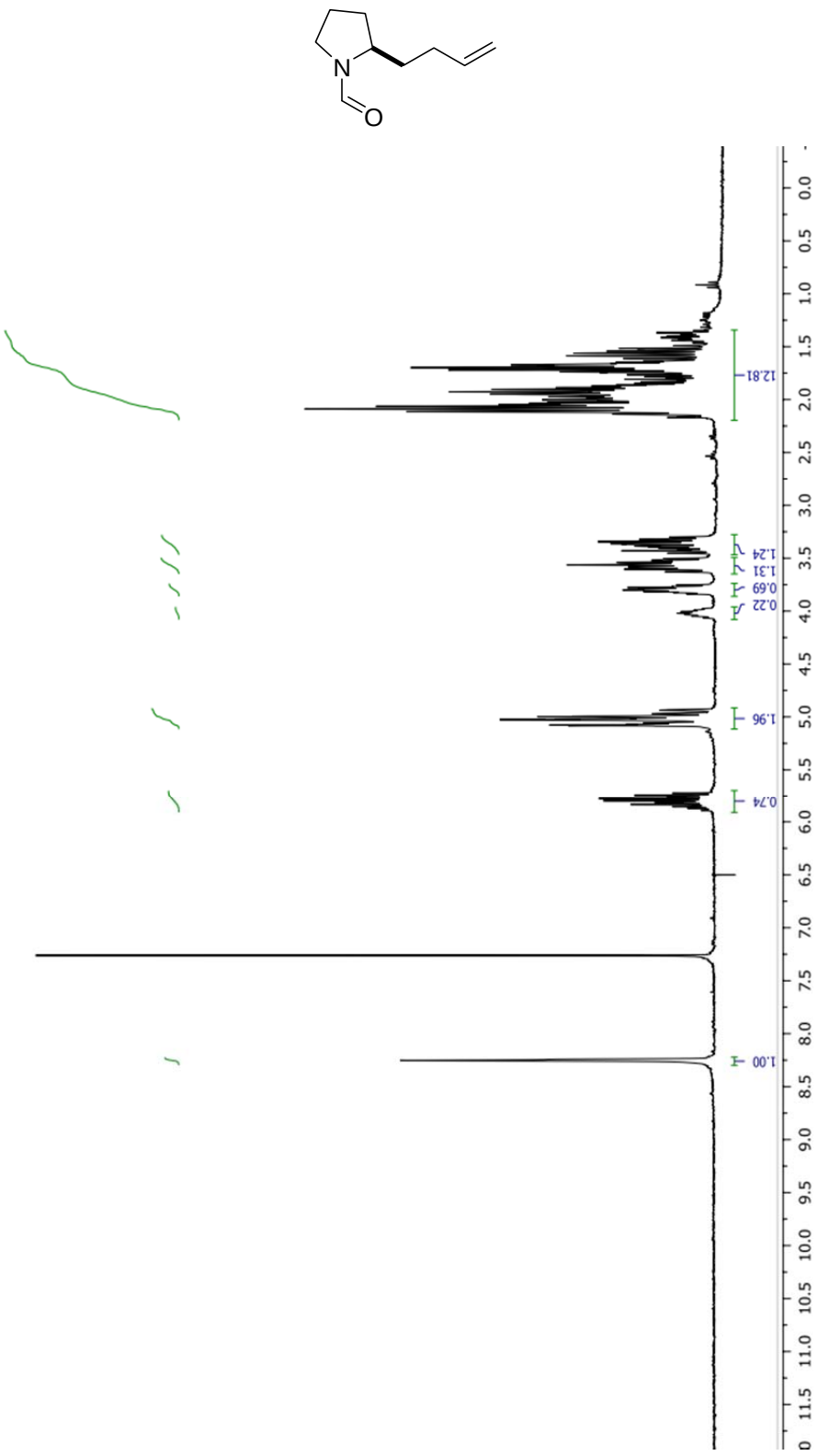




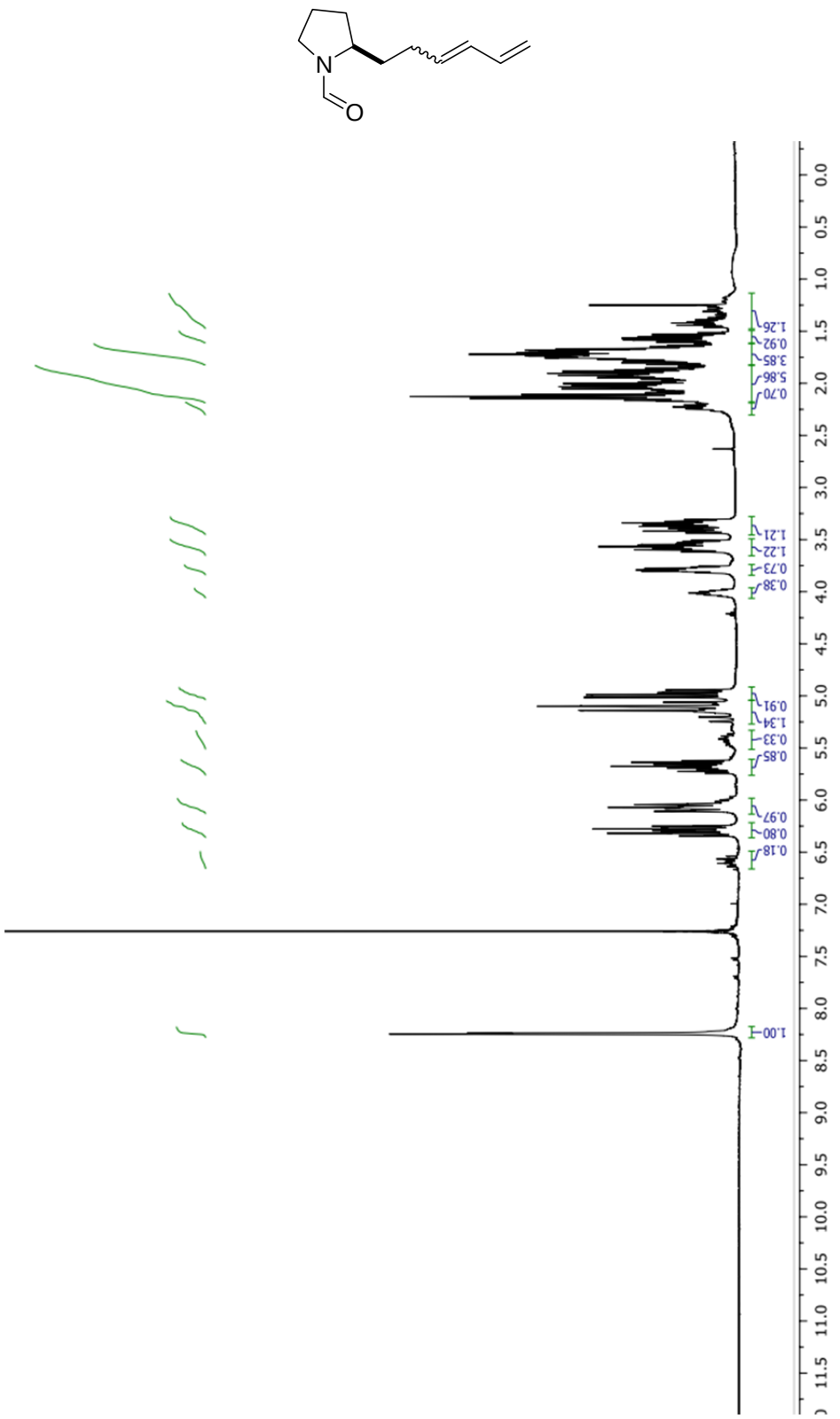
*(S)-2-(iodomethyl)pyrrolidine-1-carbaldehyde (**45**)*



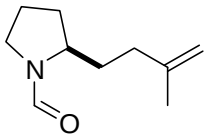
*(R)-2-(but-3-enyl)pyrrolidine-1-carbaldehyde (**47**)*

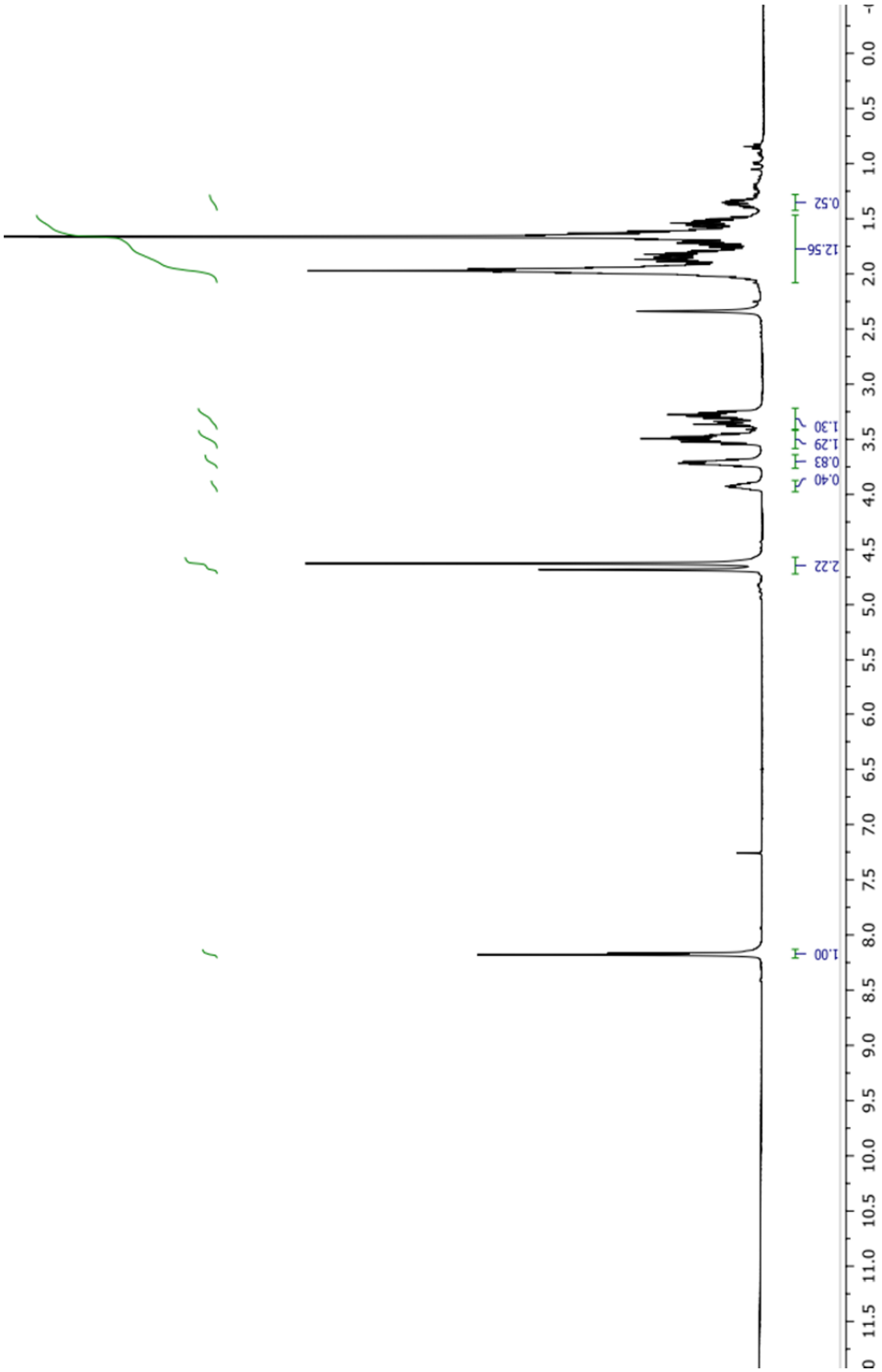


*Mixture of E and Z (R)-2-(hexa-3,5-dienyl)pyrrolidine-1-carbaldehyde (**49**)*

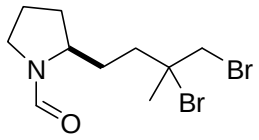


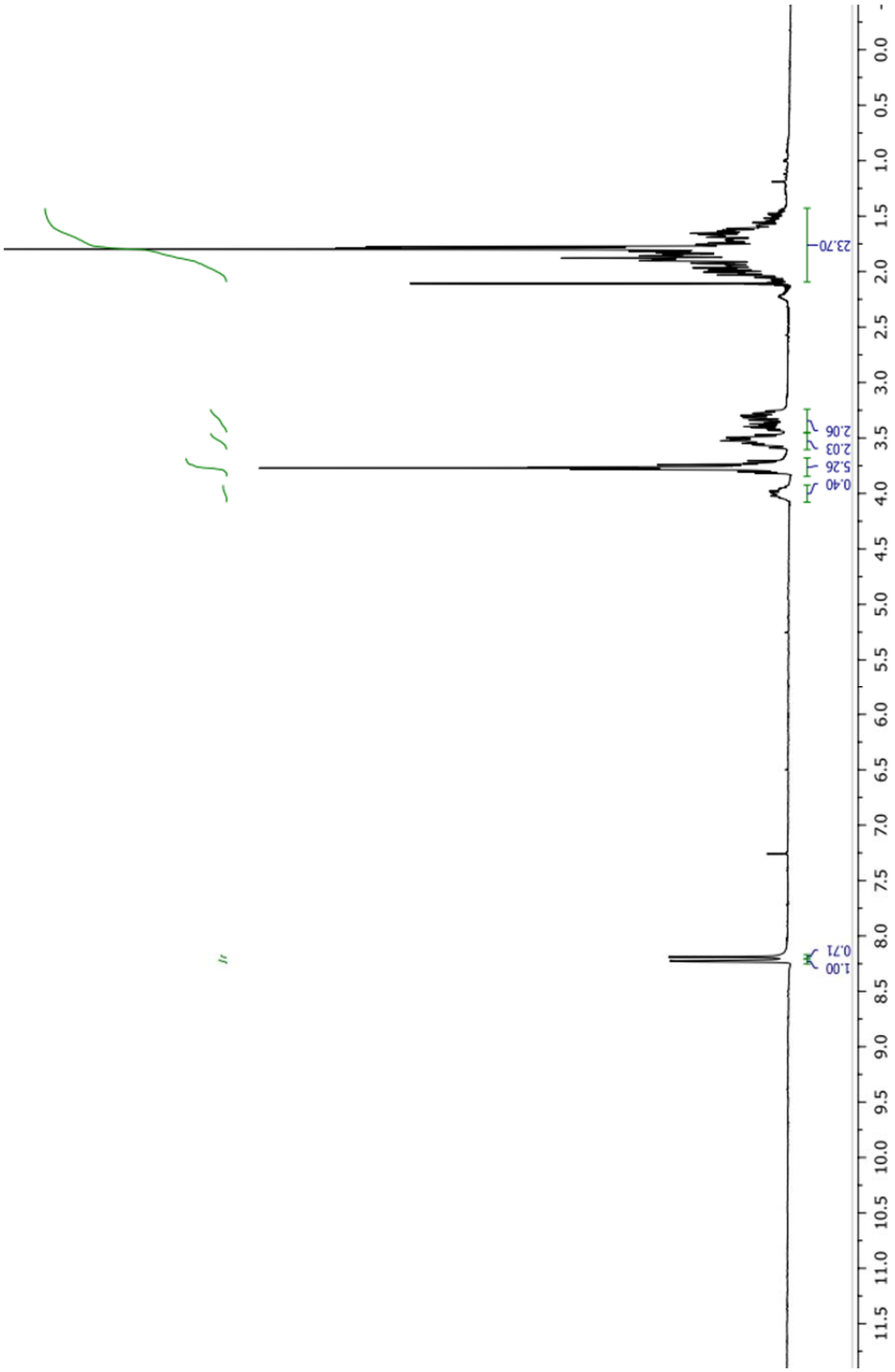
*(R)-2-(3-methylbut-3-enyl)pyrrolidine-1-carbaldehyde (**51**)*



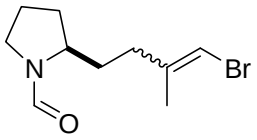


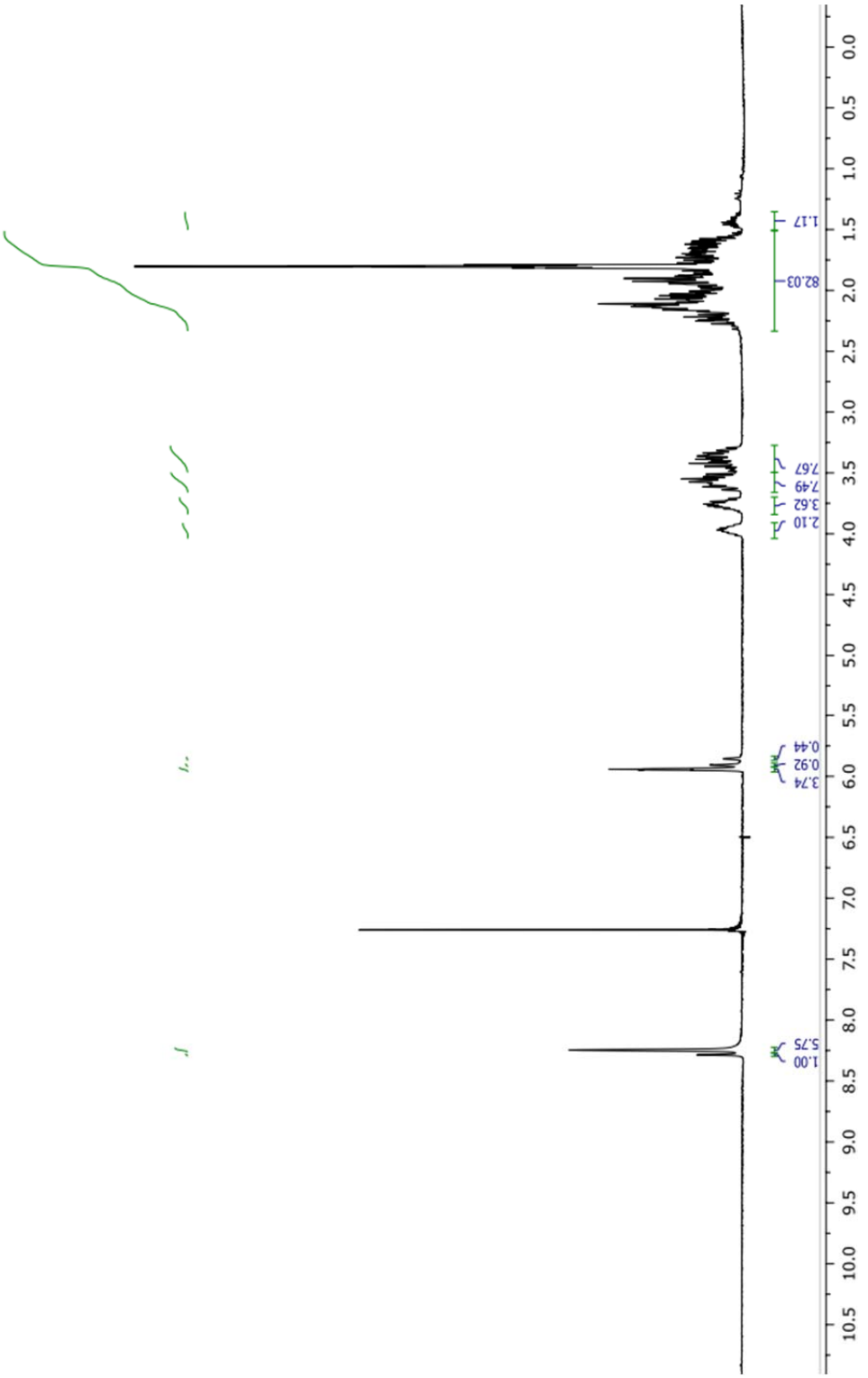
*(2S)-2-(3,4-Dibromo-3-methylbutyl)pyrrolidine-1-carbaldehyde (**52**)*



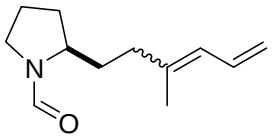


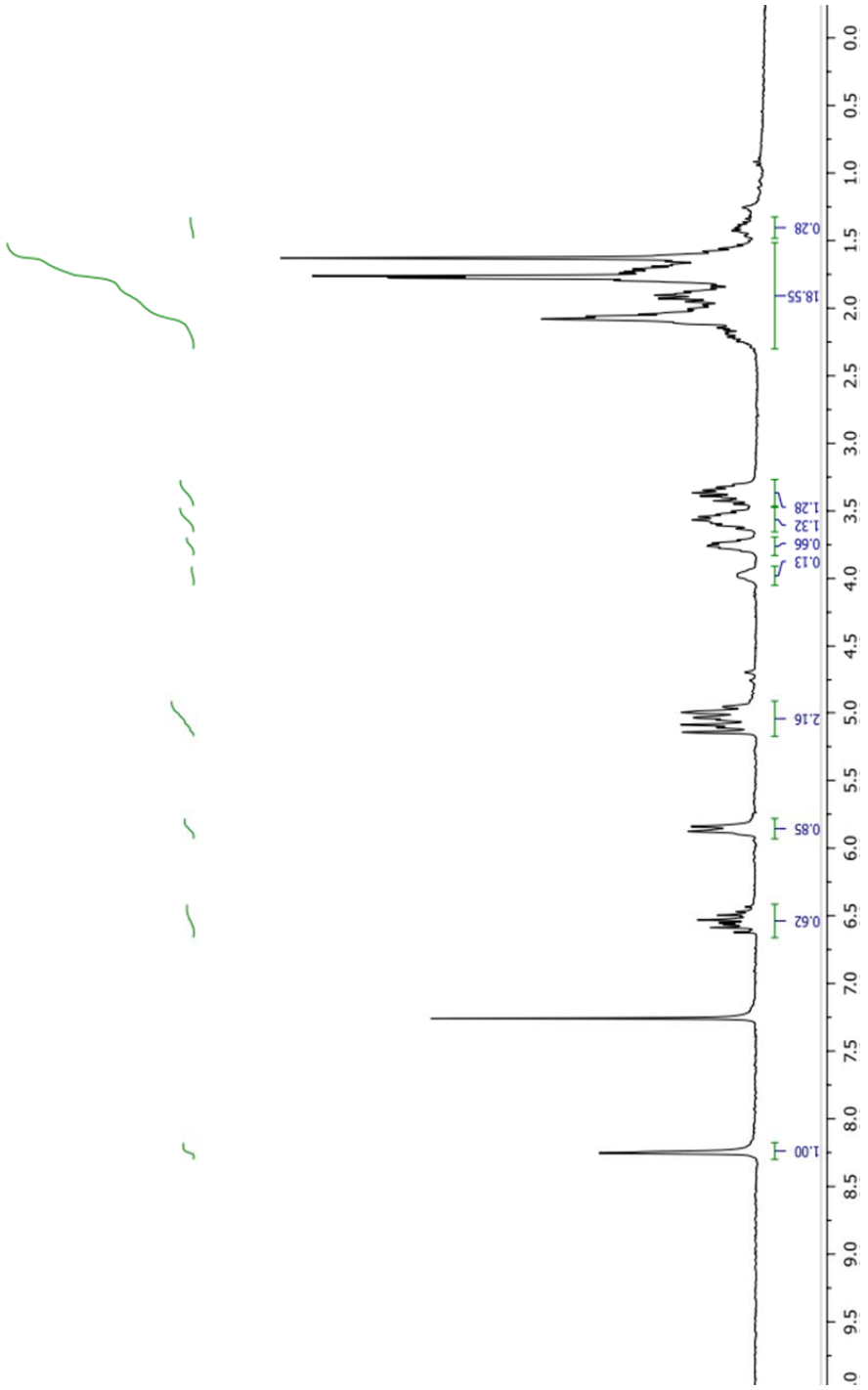
*(R)-2-(4-bromo-3-methylbut-3-enyl)pyrrolidine-1-carbaldehyde (**53**)*



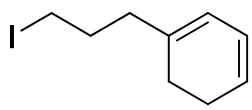


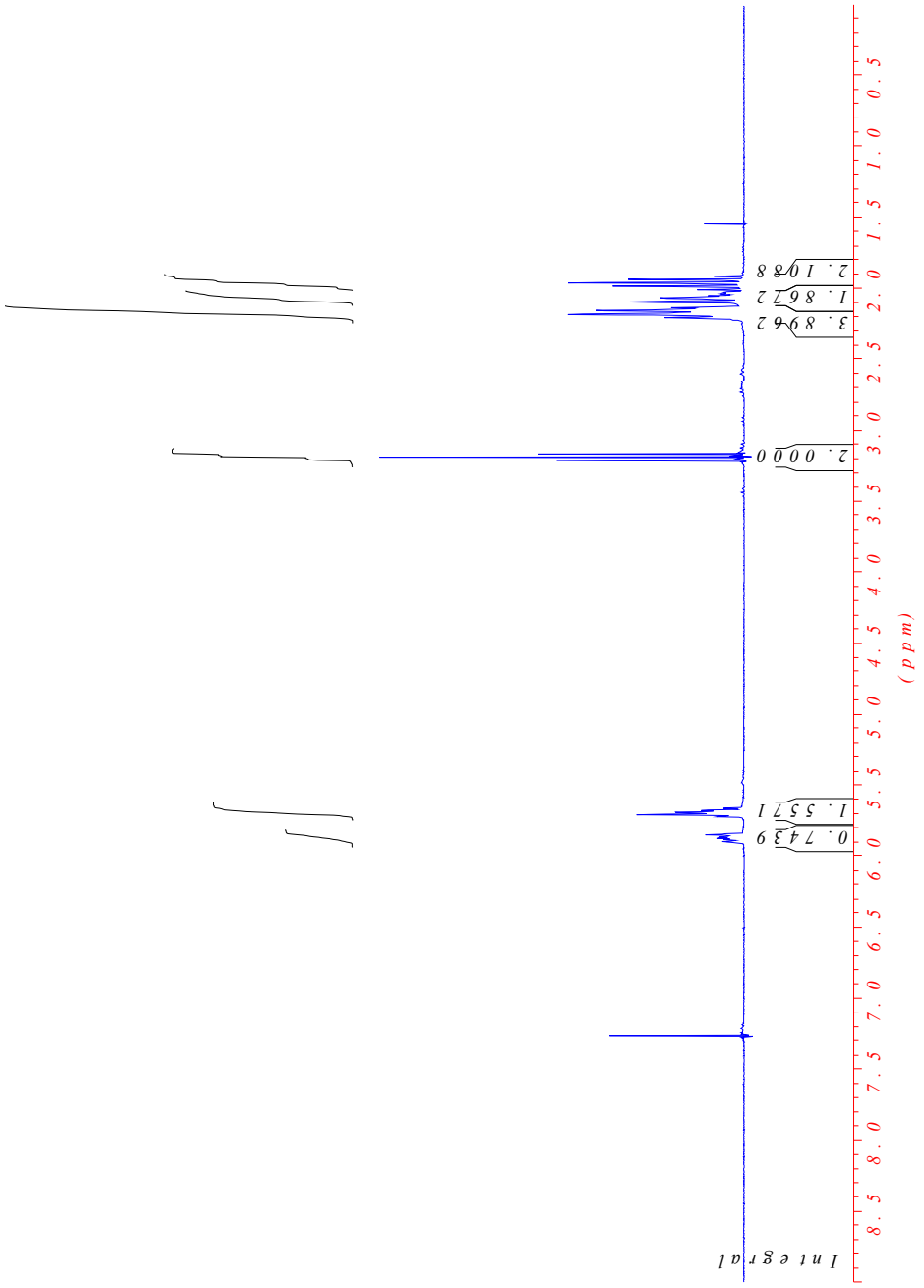
*(R)-2-(3-methylhexa-3,5-dienyl)pyrrolidine-1-carbaldehyde (**54**)*



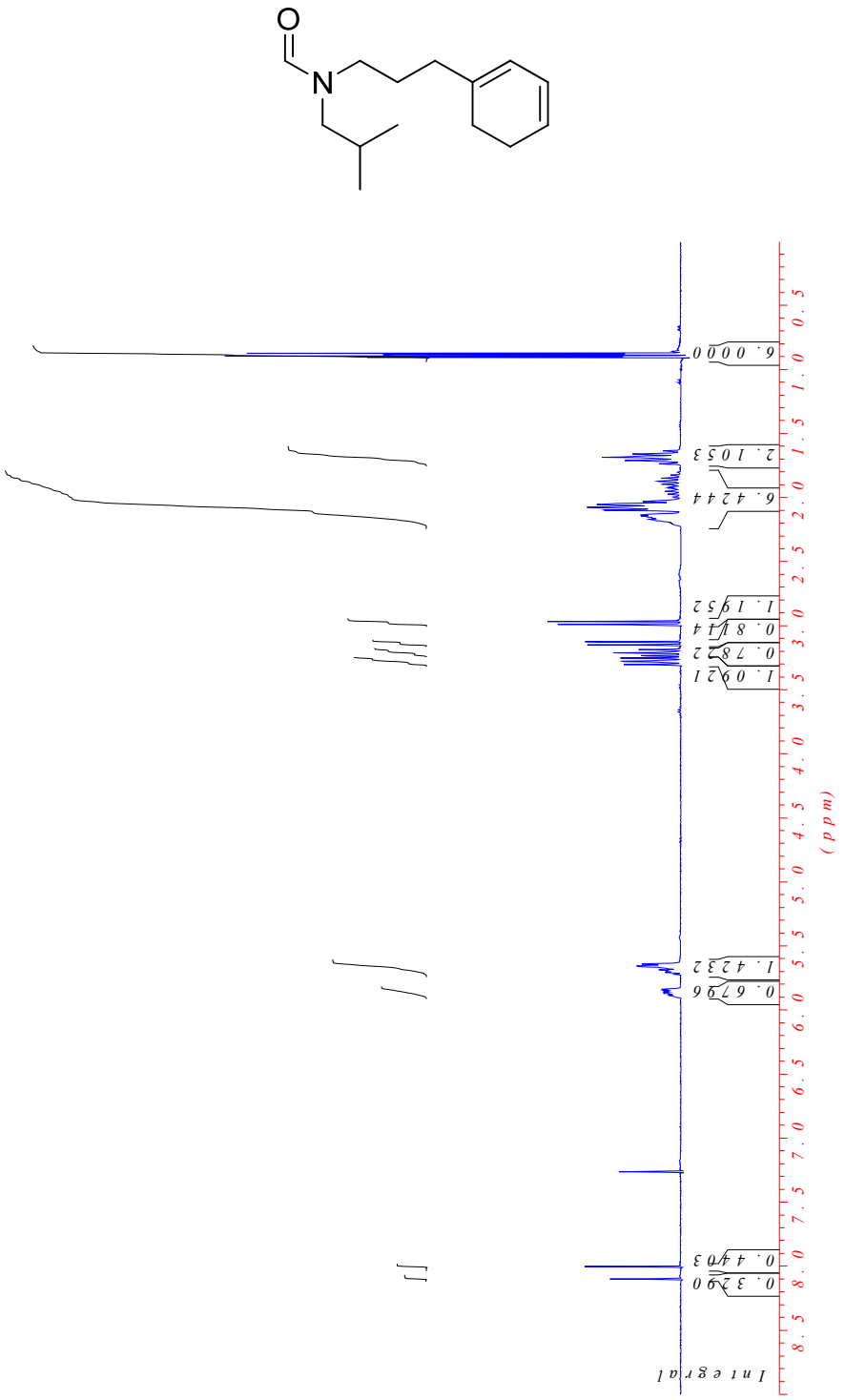


*3-(Cyclohexa-1, 3-dienyl)-1-iodopropane (**56**)*

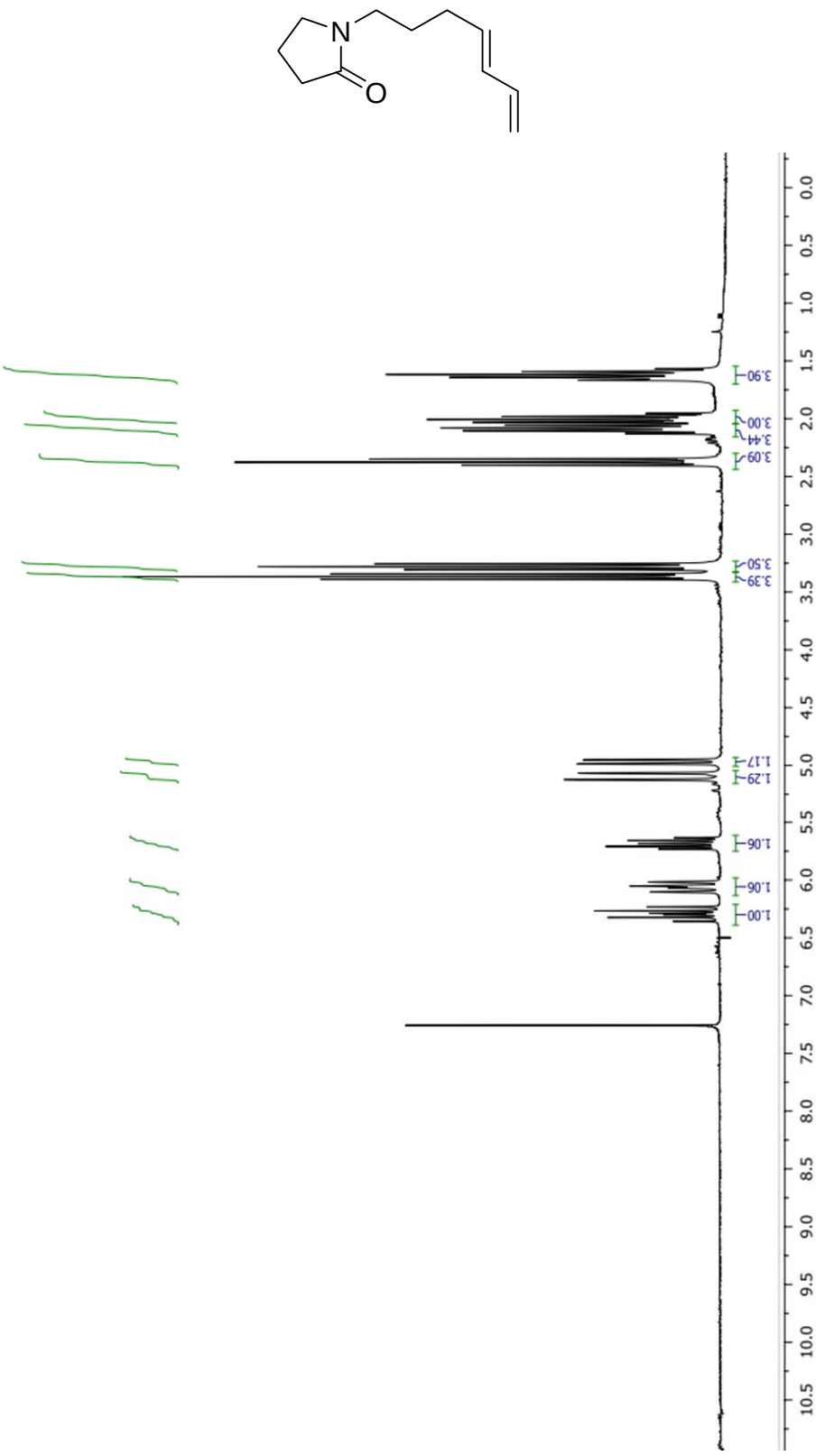




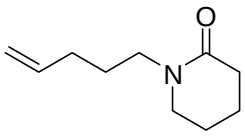
*N-(3-(Cyclohexa-1, 3-dienyl)propyl)-N-(2-methylpropyl)formamide (**57**)*

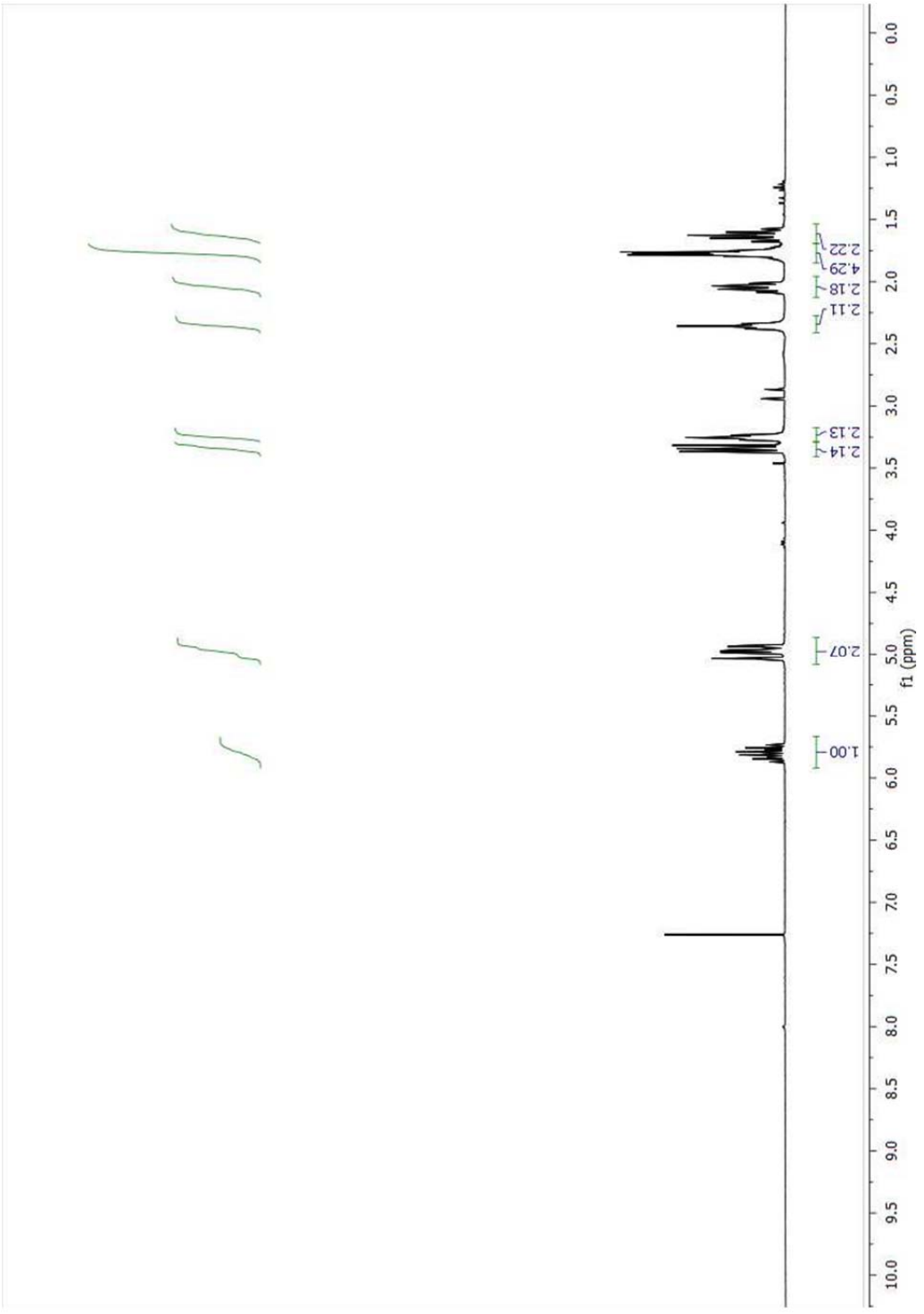


*(E)-1-(hepta-4,6-dienyl)pyrrolidin-2-one (**59**)*

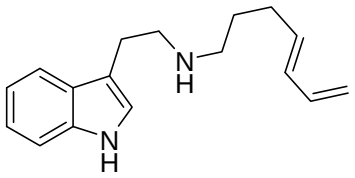


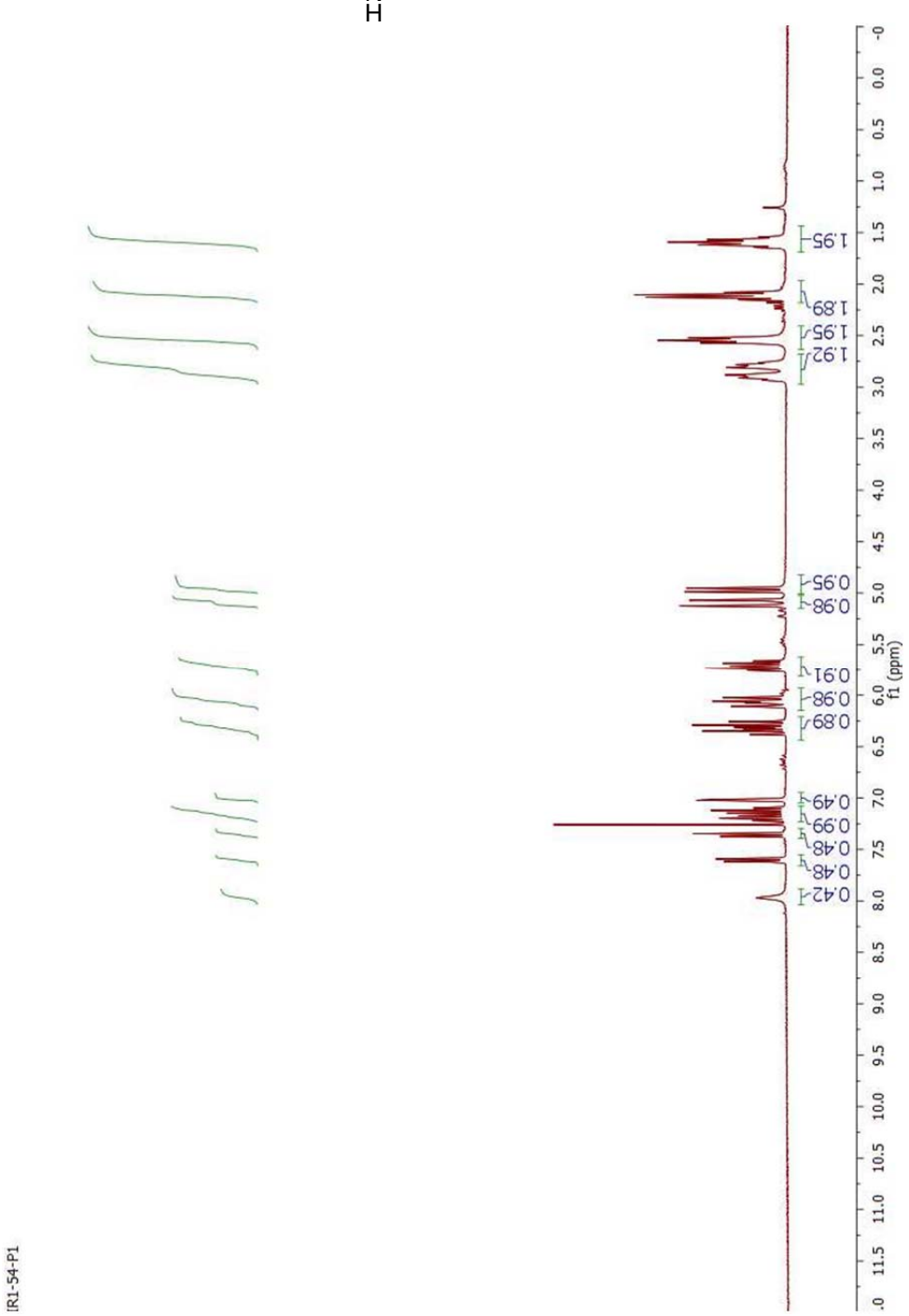
*1-(Pent-4-enyl)piperidin-2-one (**61**)*



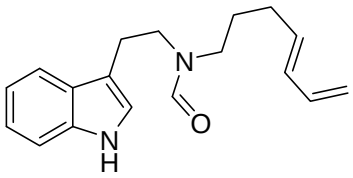


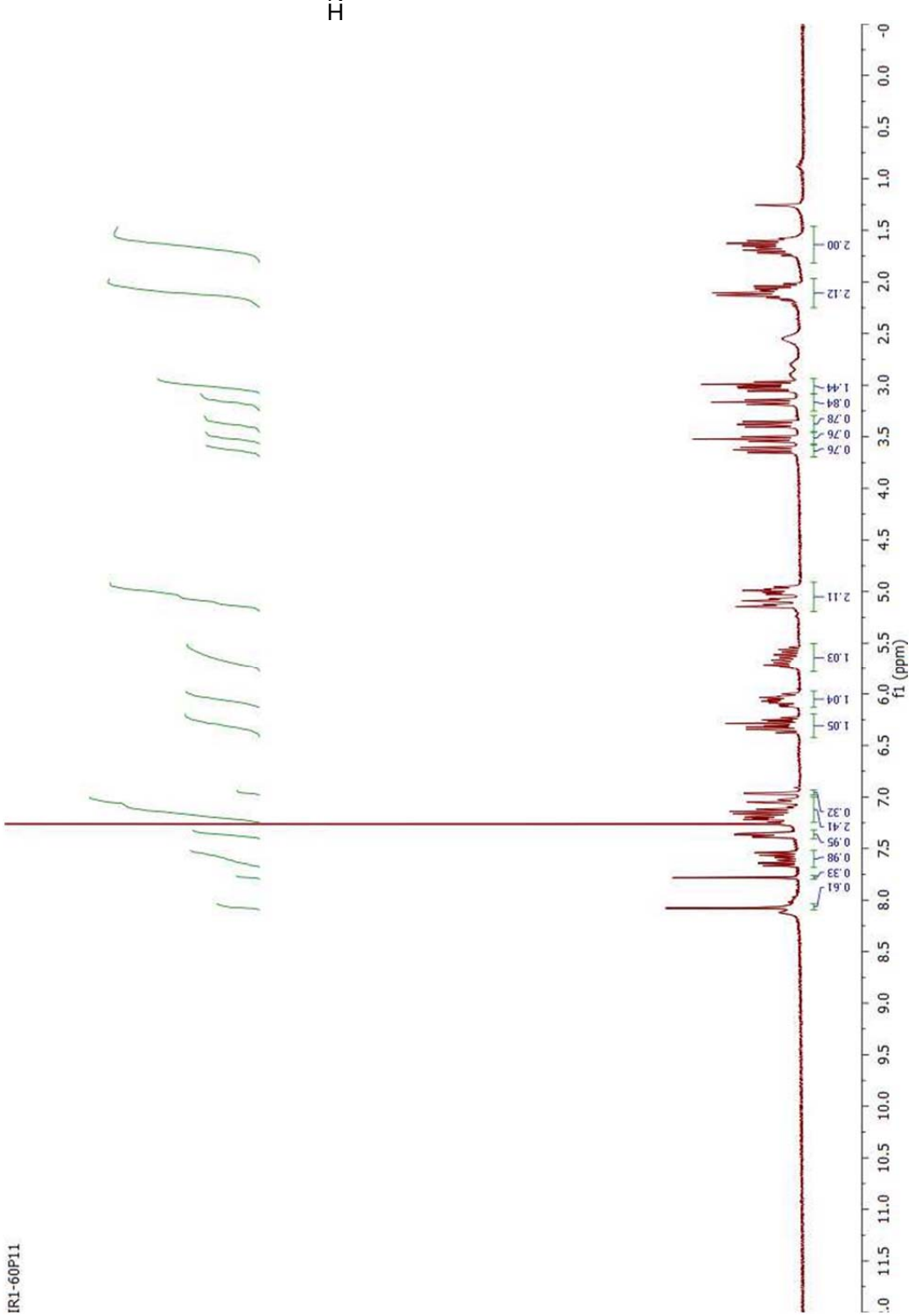
*(E)-N-(2-(1H-indol-3-yl)ethyl)hepta-4,6-dien-1-amine (**63**)*



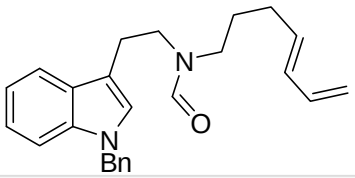


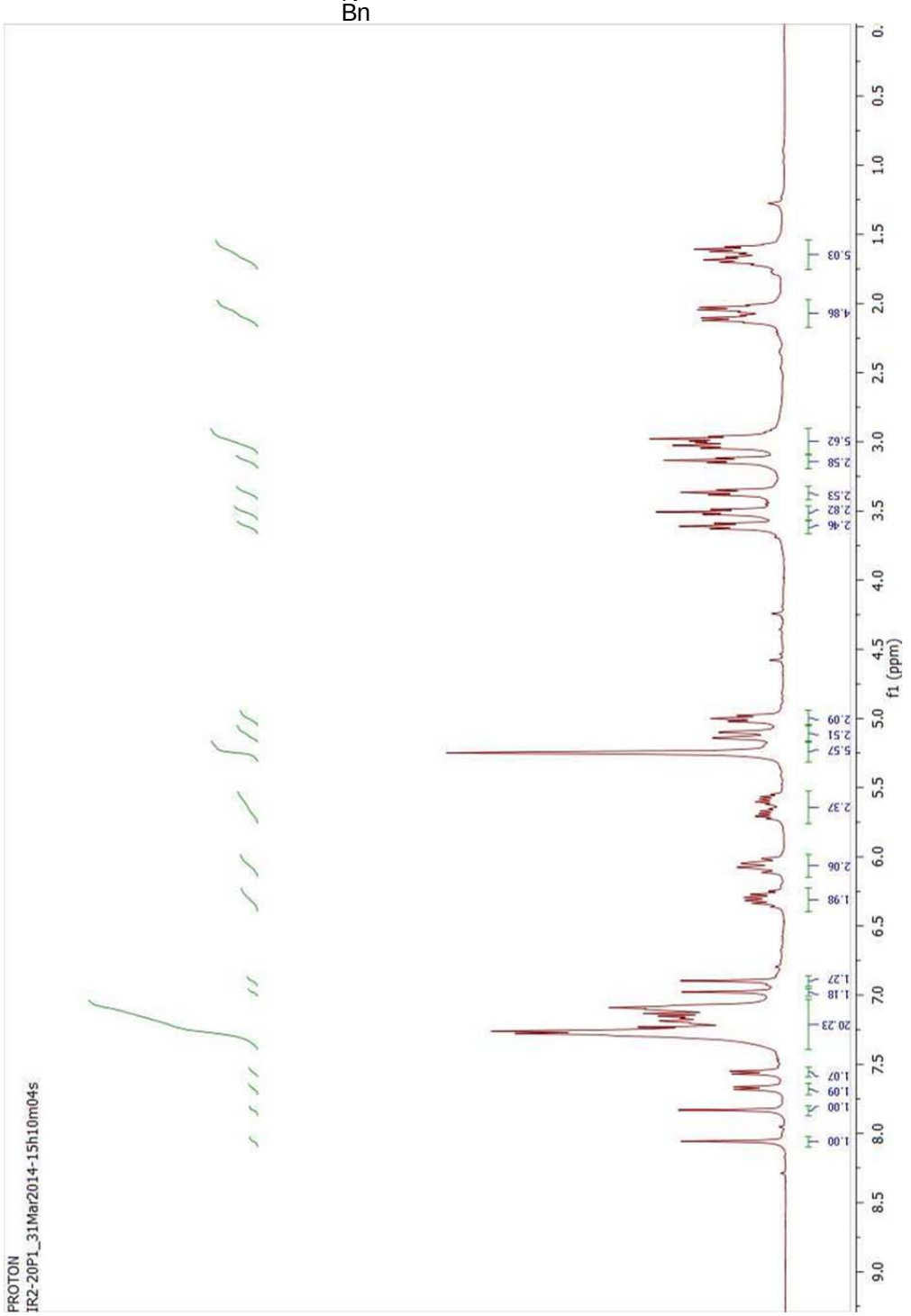
*(E)-N-(2-(1H-indol-3-yl)ethyl)-N-(hepta-4,6-dienyl)formamide (**64**)*



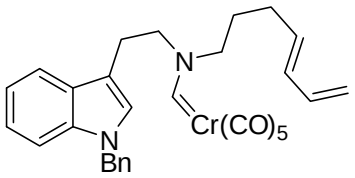


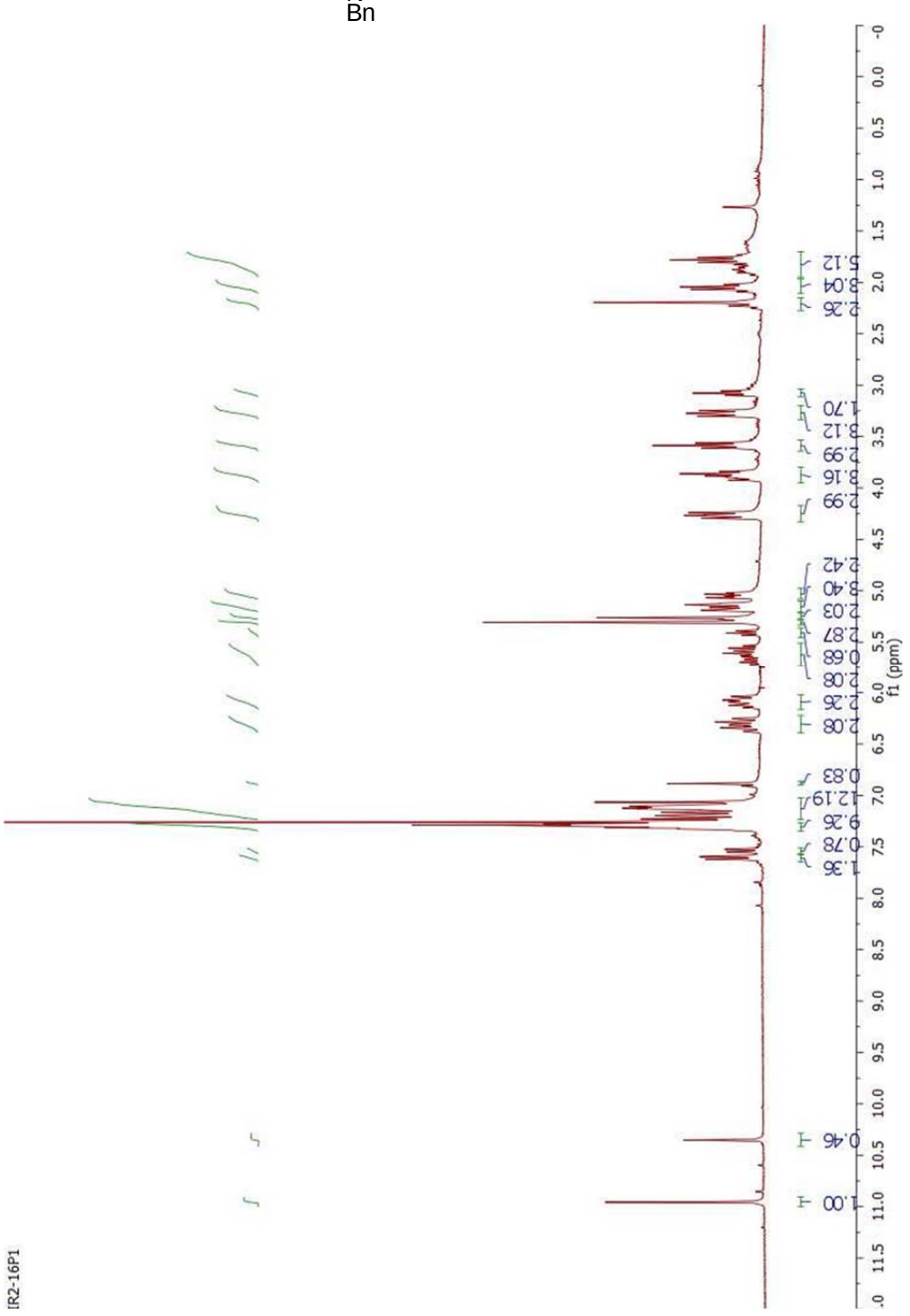
*(E)-N-(2-(1-benzyl-1H-indol-3-yl)ethyl)-N-(hepta-4,6-dienyl)formamide (**36**)*



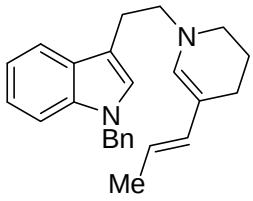


*Pentacarbonyl[((E)-N-(2-(1-benzyl-1H-indol-3-yl)ethyl)-N-(hepta-4,6-dienyl)amino)methylene]chromium(0) (**37**)*

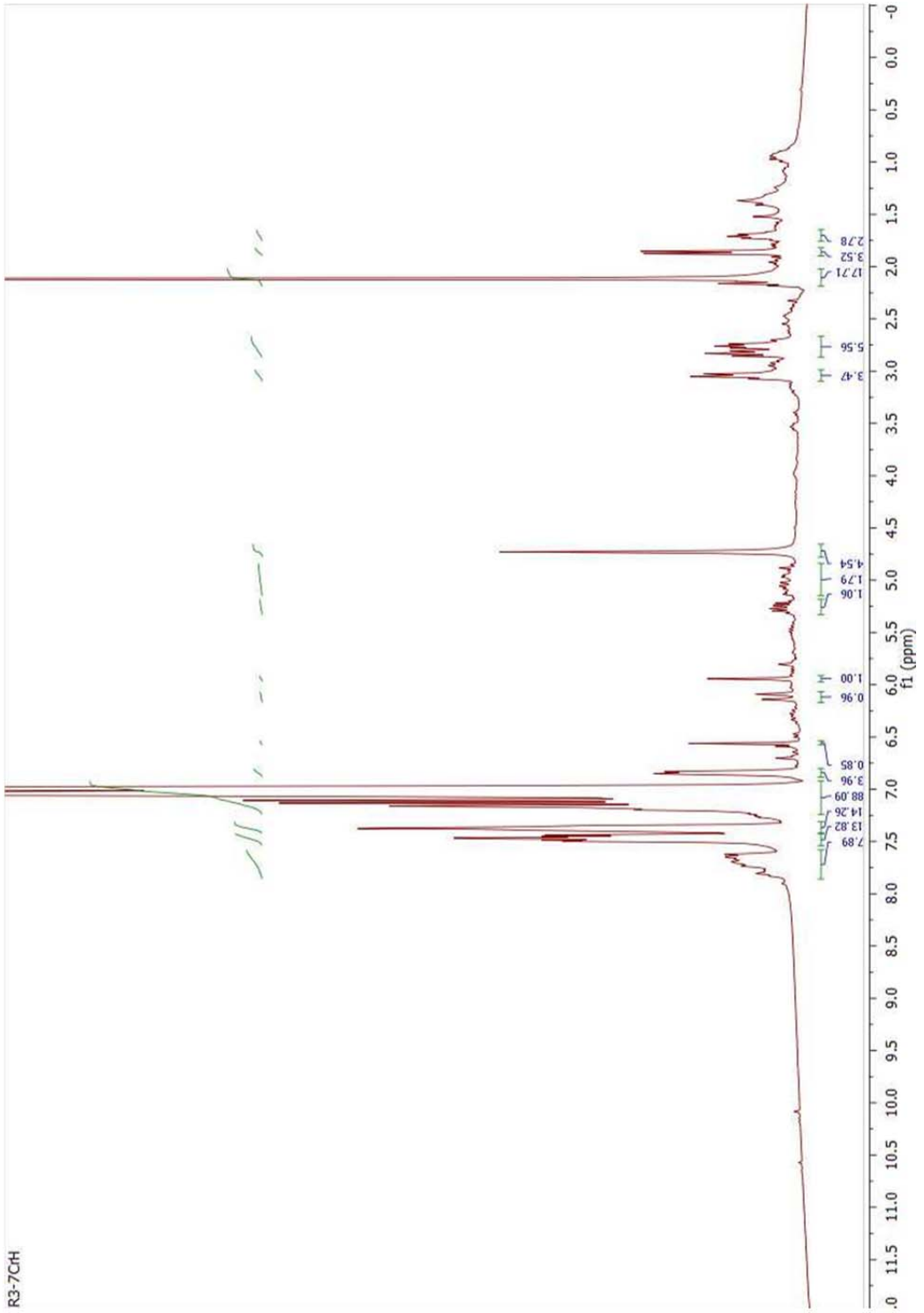




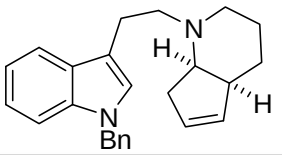
*(E)-1-benzyl-3-(2-(5-(prop-1-enyl)-3,4-dihydropyridin-1(2H)-yl)ethyl)-1H-indole (**38**)*

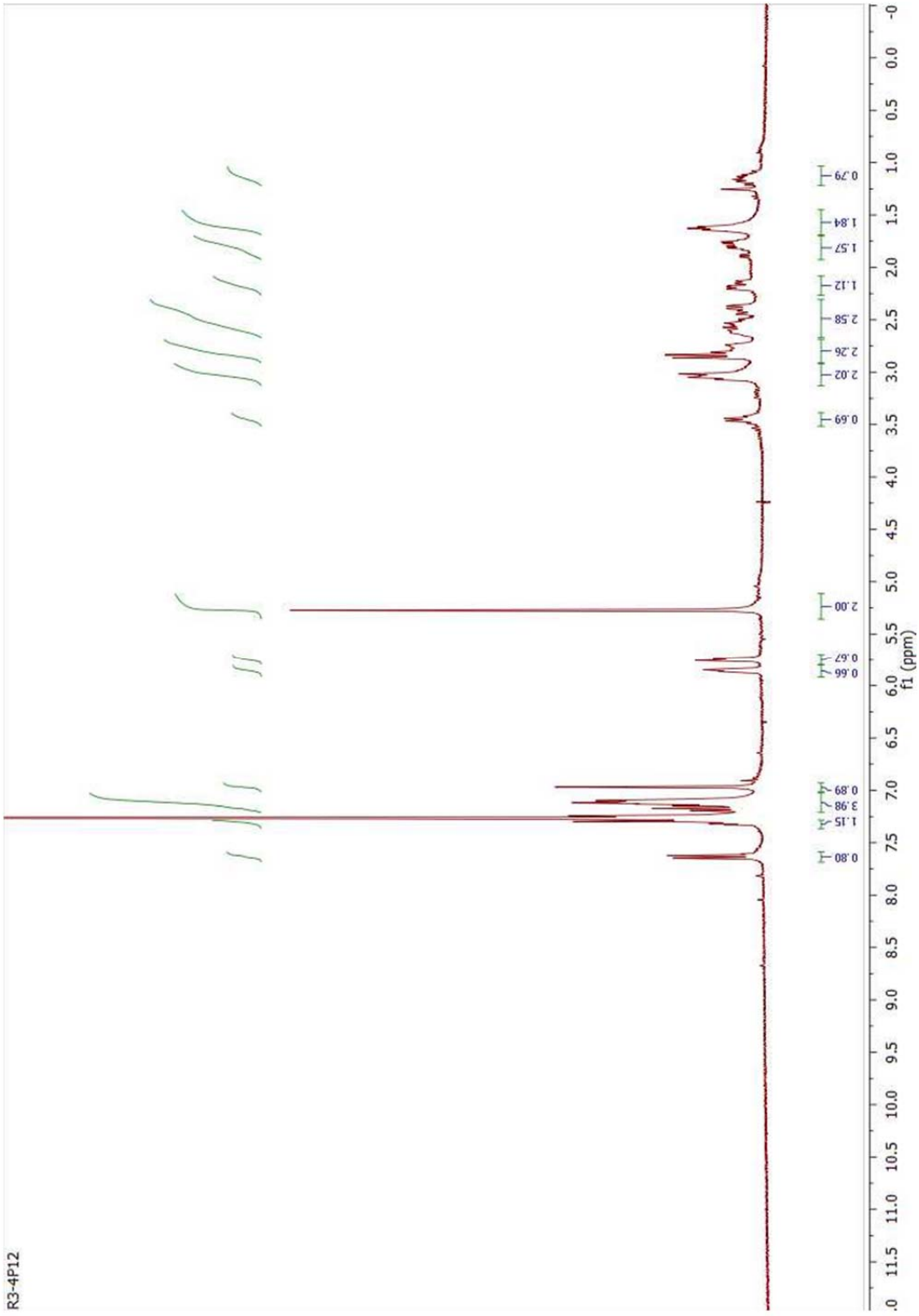


CRUDE

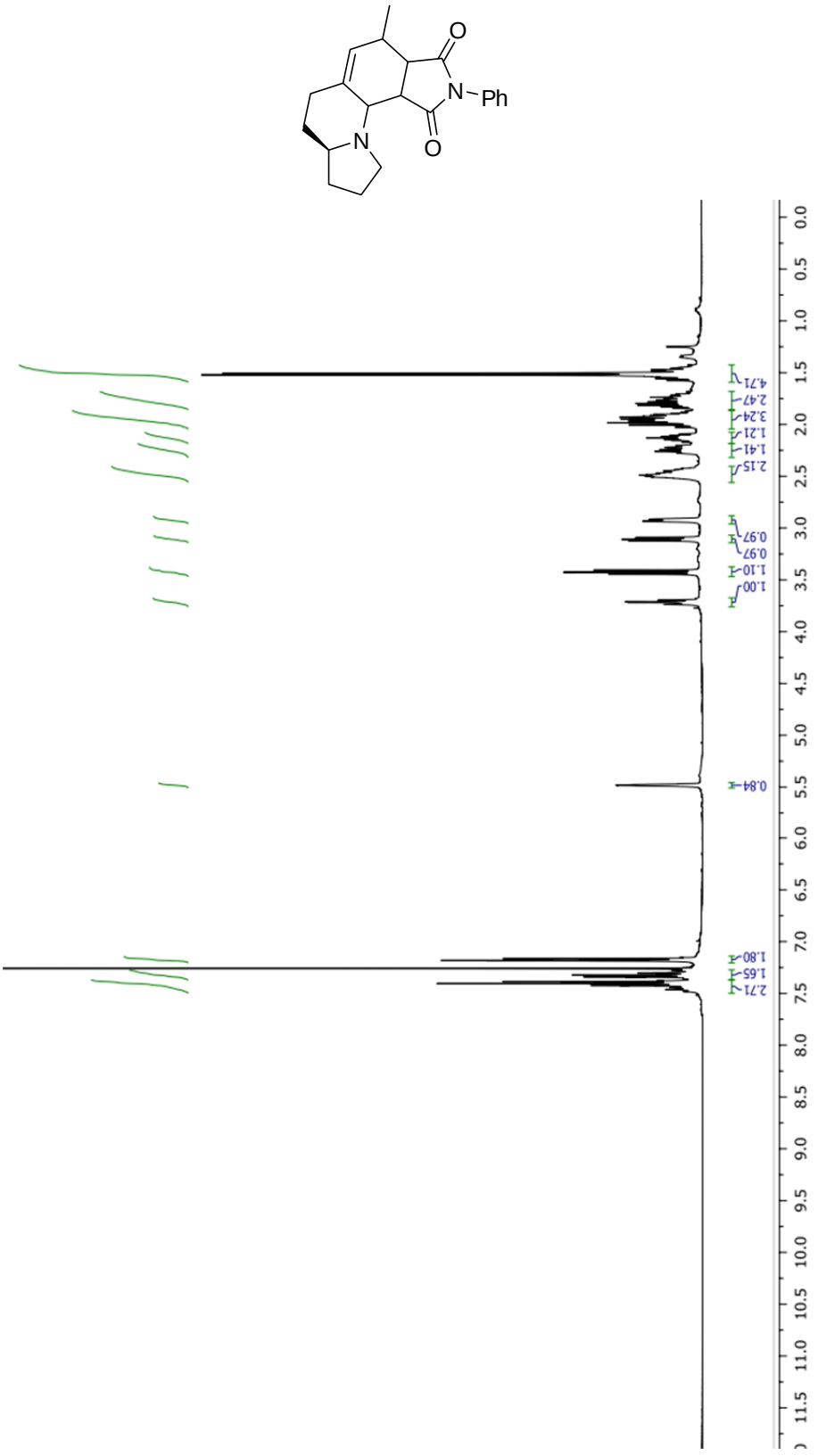


*1-benzyl-3-(2-(4,4a-dihydro-1H-cyclopenta[c]pyridin-2(3H,7H,7aH)-yl)ethyl)-1H-indole (**39**)*





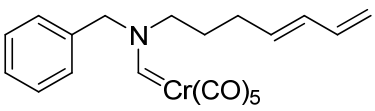
*(7aR)-4-methyl-2-phenyl-3a,4,6,7,7a,8,9,10,11a,11b-decahydro-1H-dipyrrolo[1,2-a:3',4'-h]quinoline-1,3(2H)-dione (**66**)*

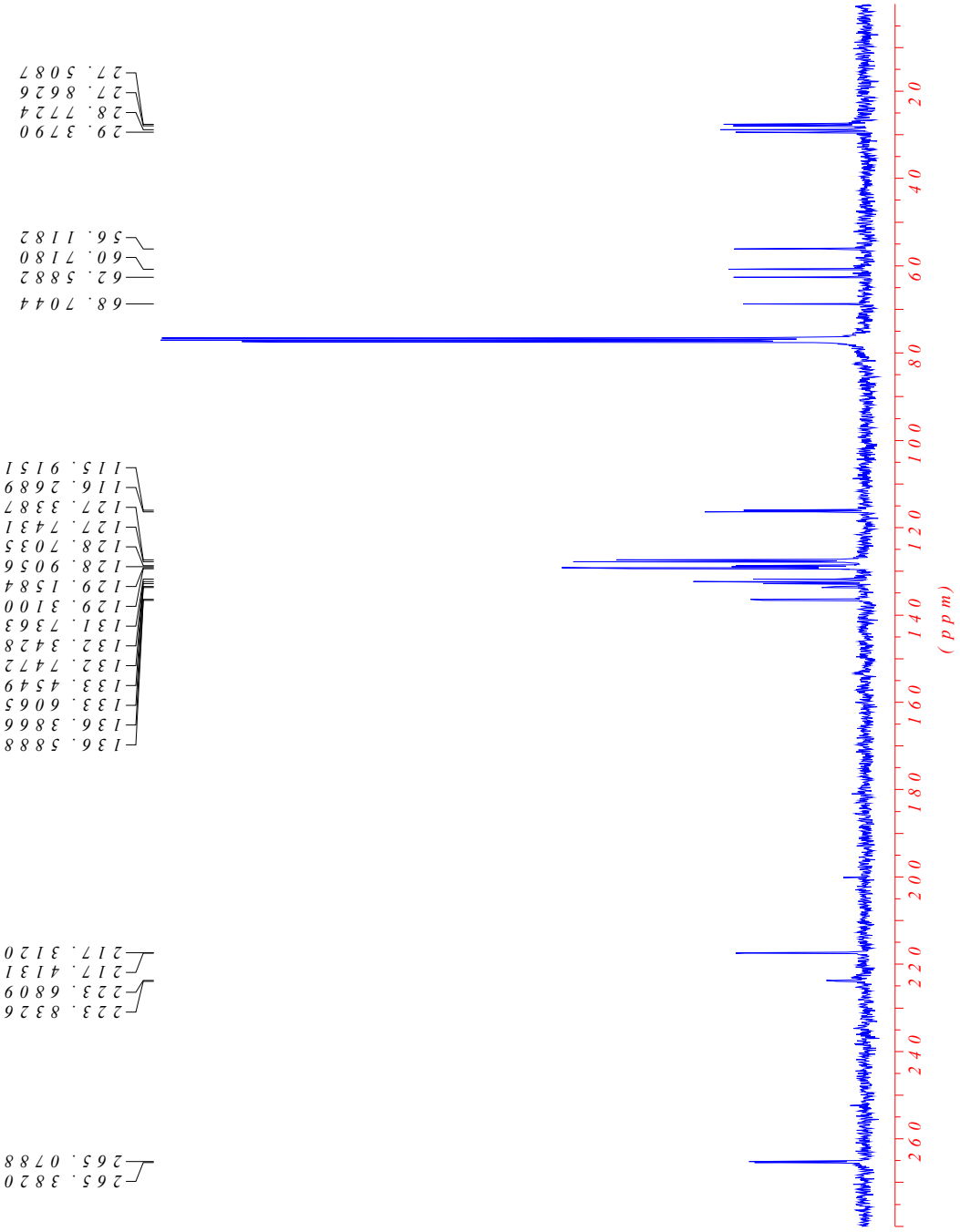


^{13}C NMR SPECTRA

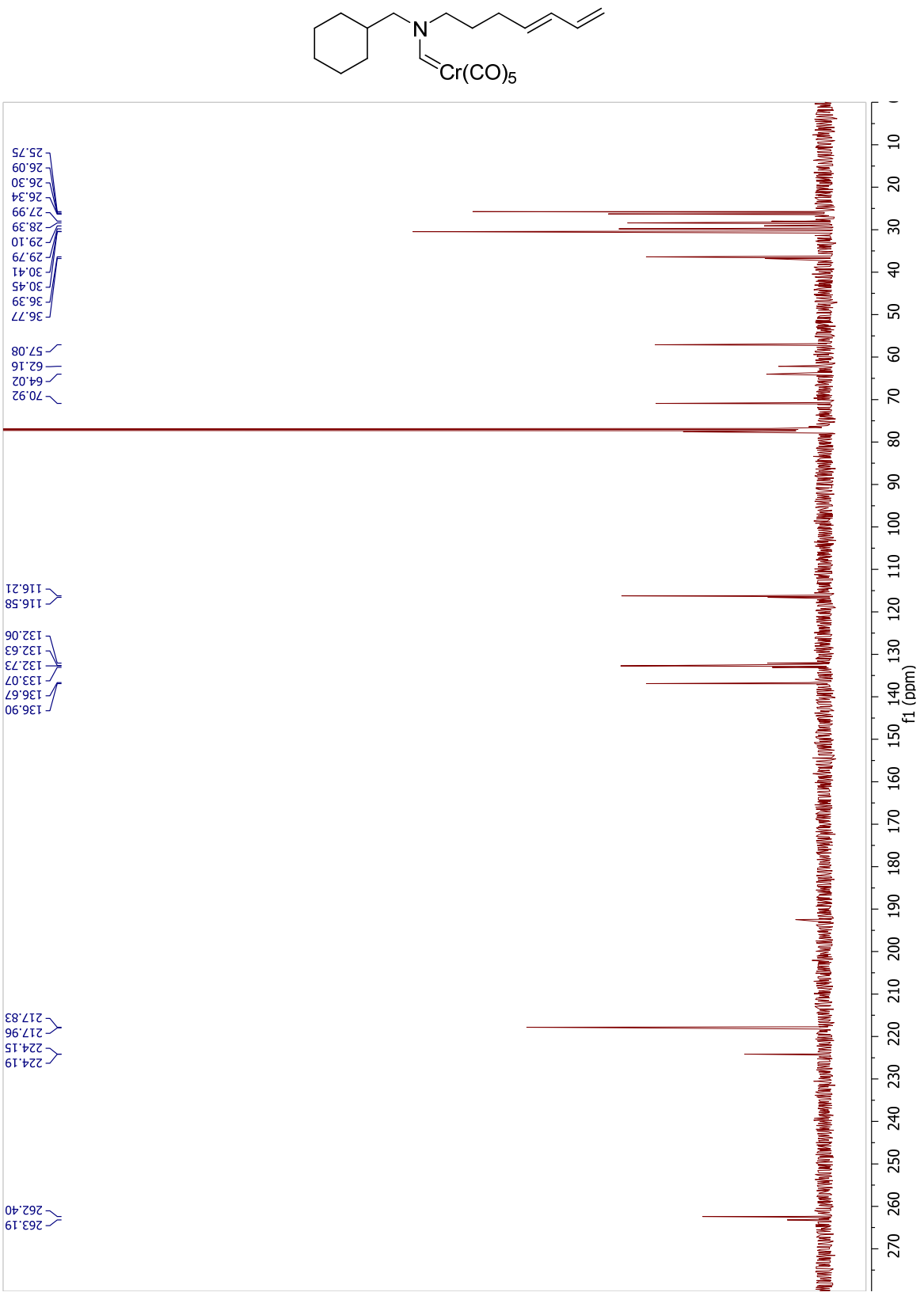
In numerical order

*(E)-Pentacarbonyl[(N-(benzyl)-N-(hepta-4,6-dienyl)amino)methylene]chromium(0) (**13a**)*

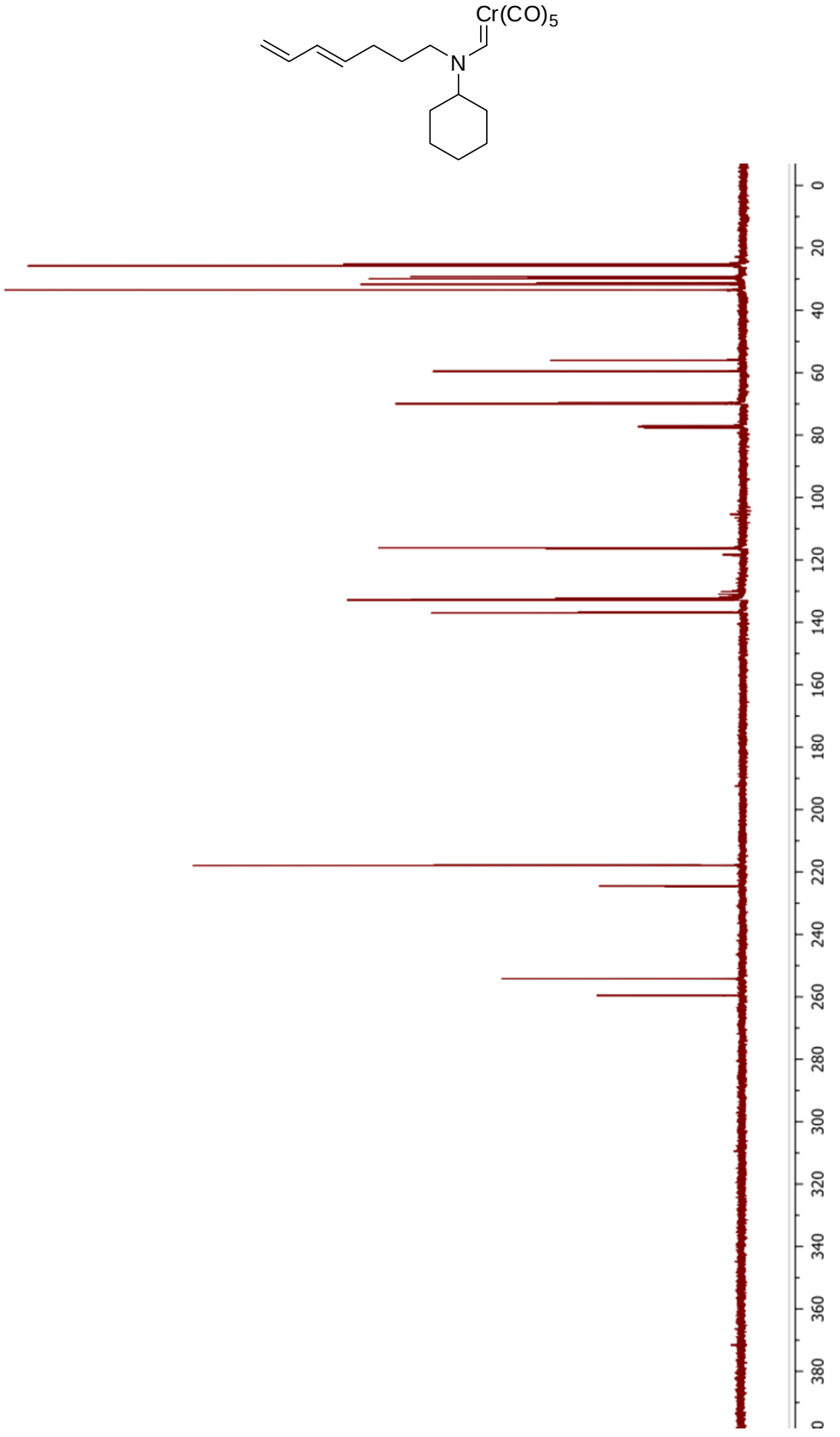




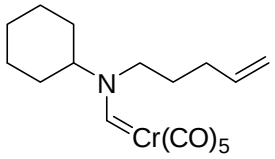
*(E)-Pentacarbonyl[(N-(cyclohexylmethyl)-N-(hepta-4, 6-dienyl)amino)methylene]chromium(0) (**13b**)*

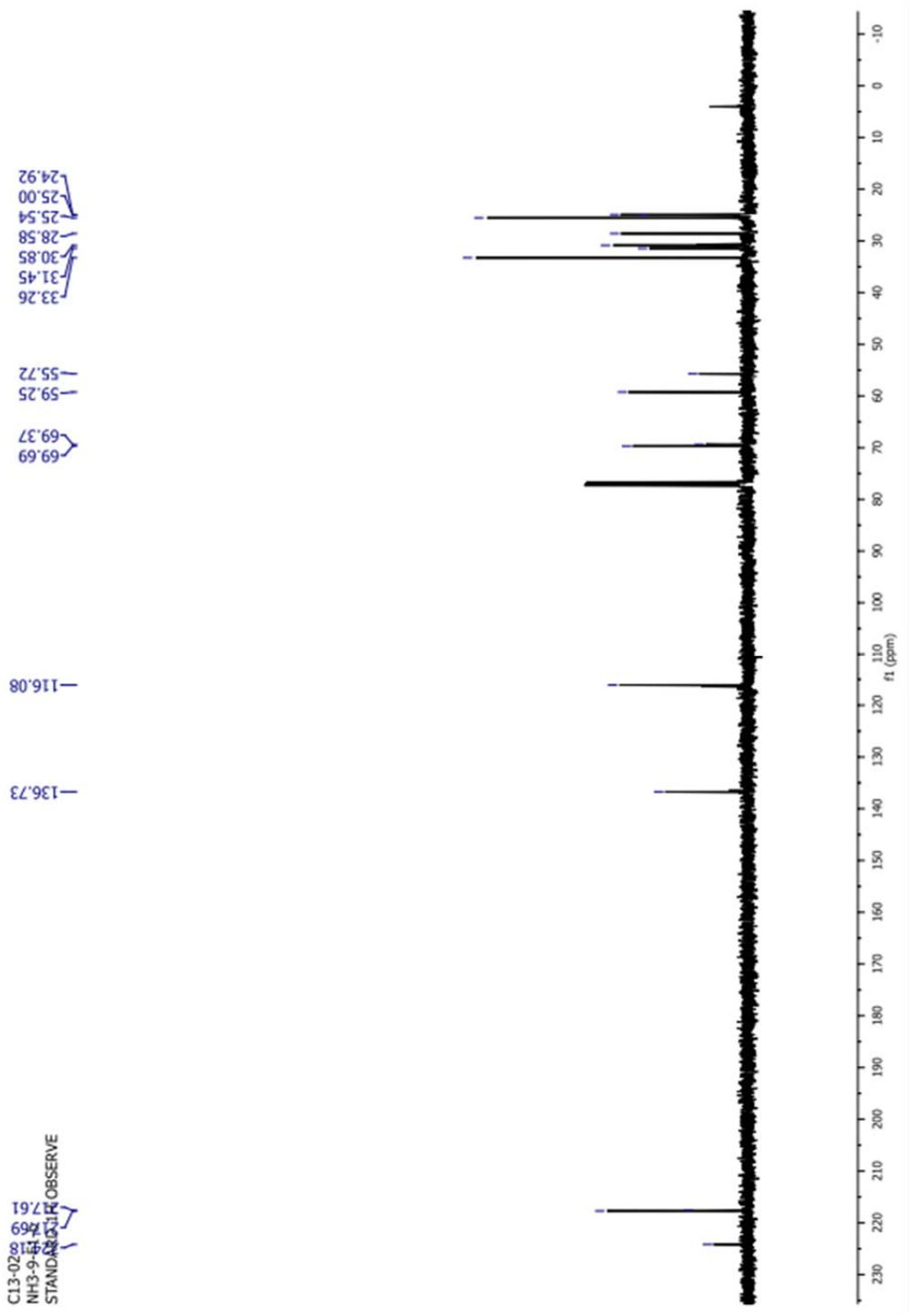


*(E)-Pentacarbonyl[(N-cyclohexyl-N-(hepta-4,6-dien-1-yl)amino)methylene]chromium(0) (**13c**)*

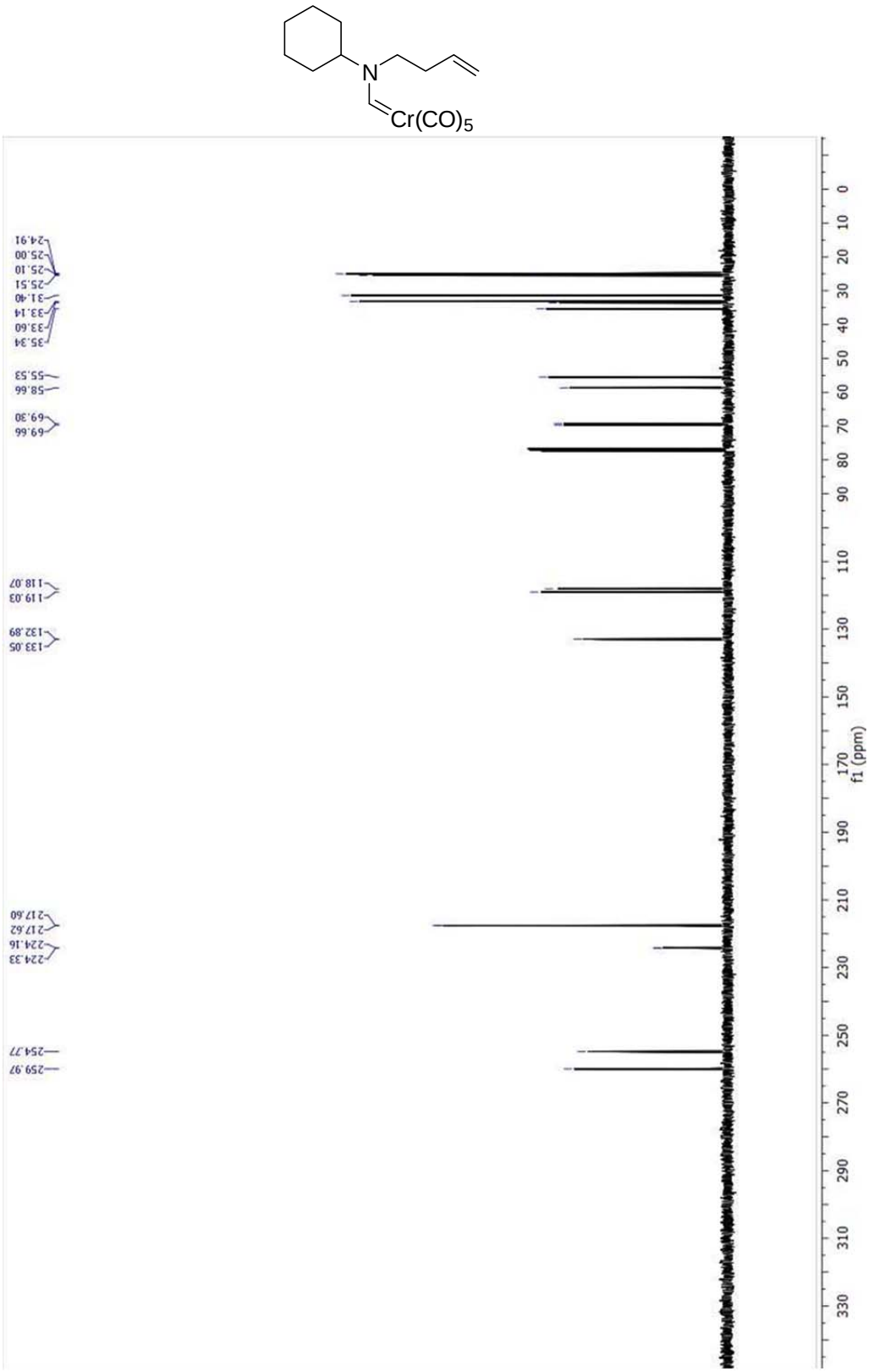


*(E)-Pentacarbonyl[(N-cyclohexyl-N-(4-penten-1-yl)amino)methylene]chromium(0) (**13d**)*

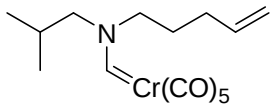


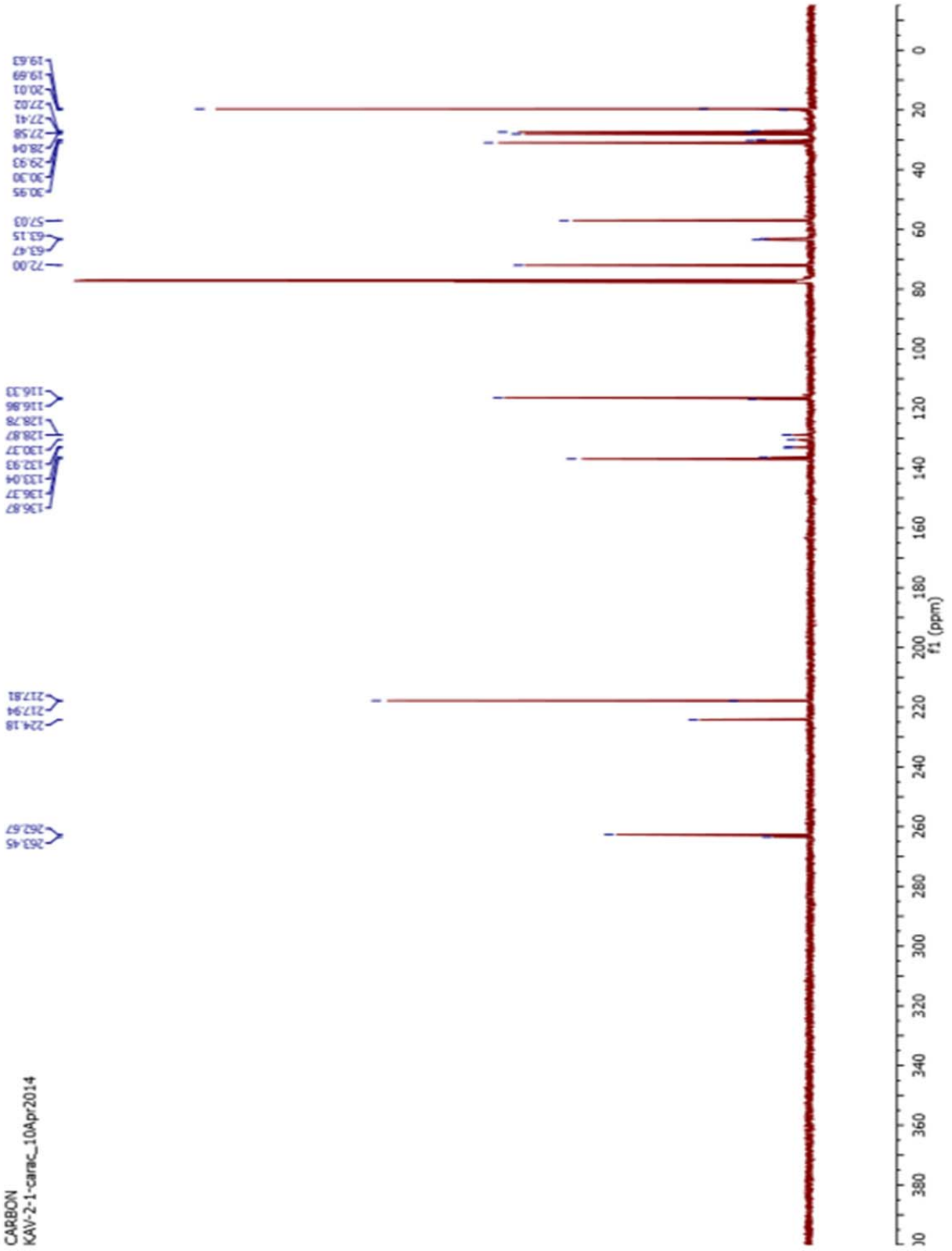


*(E)-Pentacarbonyl[(N-cyclohexyl-N-(3-buten-1-yl)amino)methylene]chromium(0) (**13e**)*

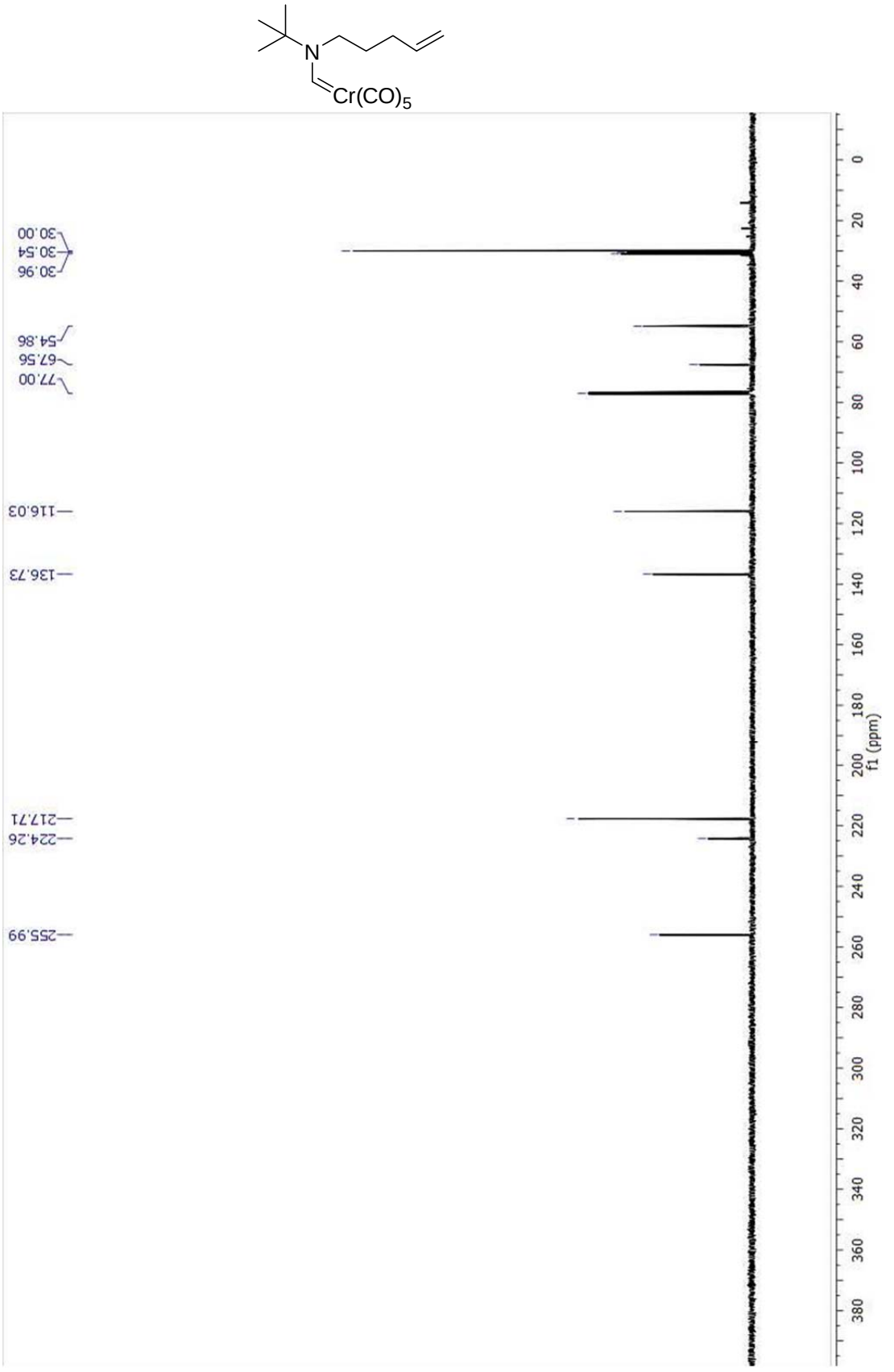


*(E)-Pentacarbonyl[(N-isobutyl-N-(4-penten-1-yl)amino)methylene]chromium(0) (**13f**)*

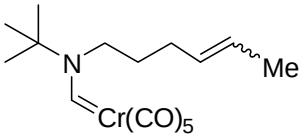


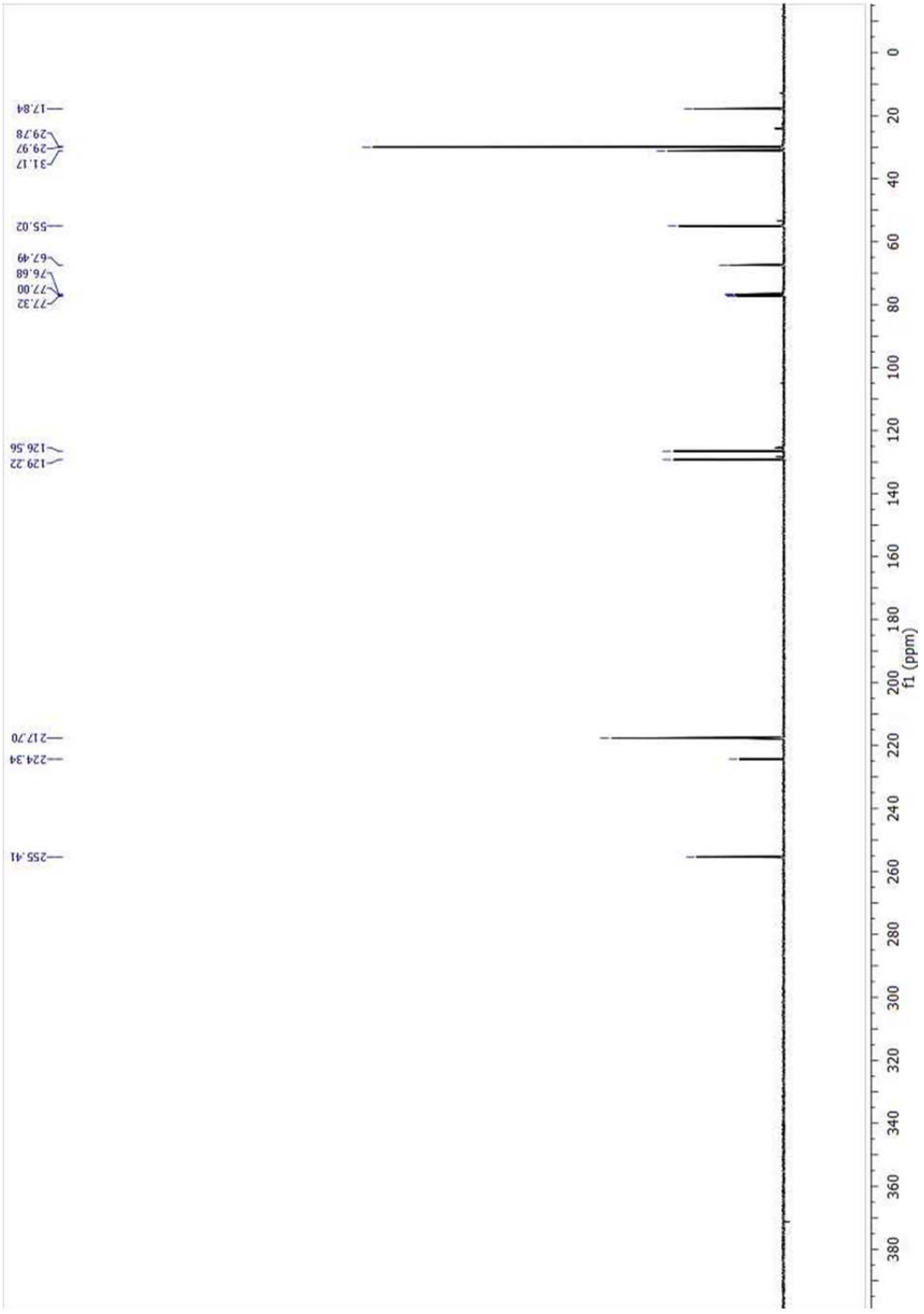


*(E)-Pentacarbonyl[(N-tert-butyl-N-(4-penten-1-yl)amino)methylene]chromium(0) (**13g**)*

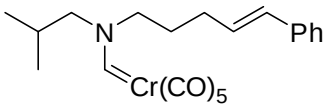


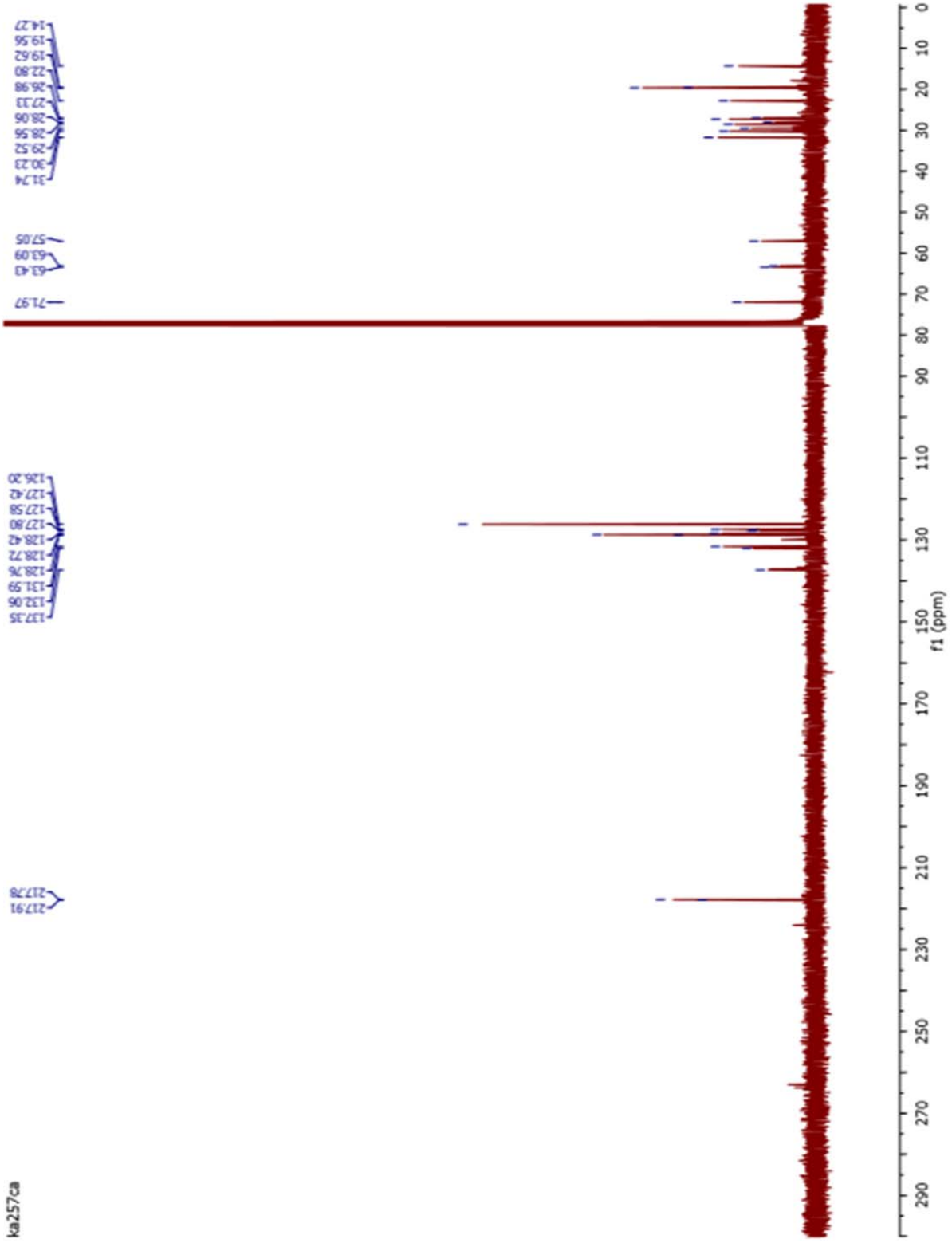
*(E)-Pentacarbonyl[(N-isobutyl-N-(4-hexen-1-yl)amino)methylene]chromium(0) (**13h**)*



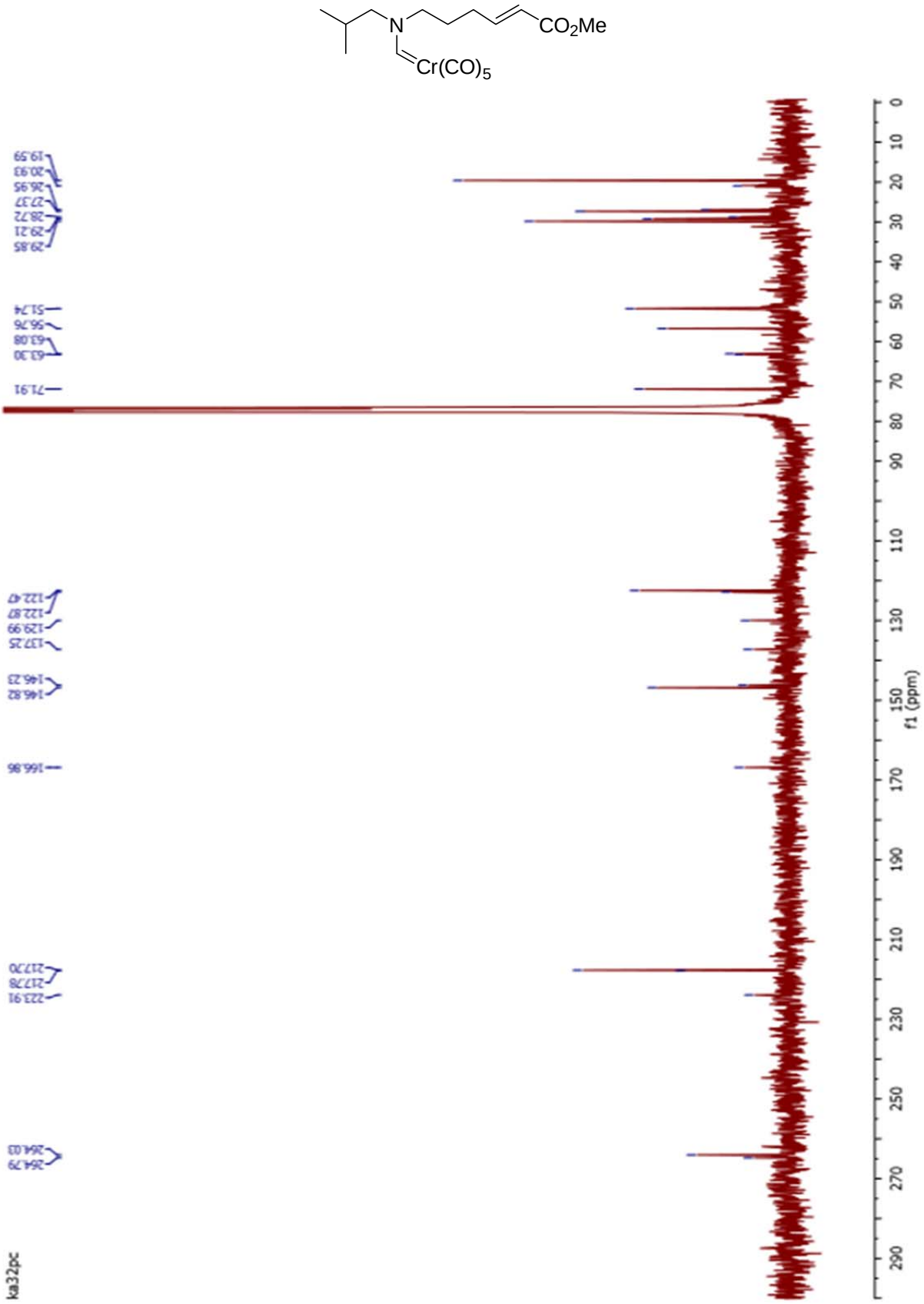


*Pentacarbonyl[(N-isobutyl-N-(5-phenyl-4-penten-1-yl)amino)methylene]chromium(0) (**13i**)*

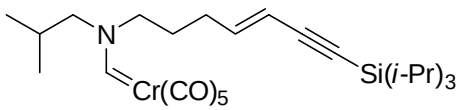


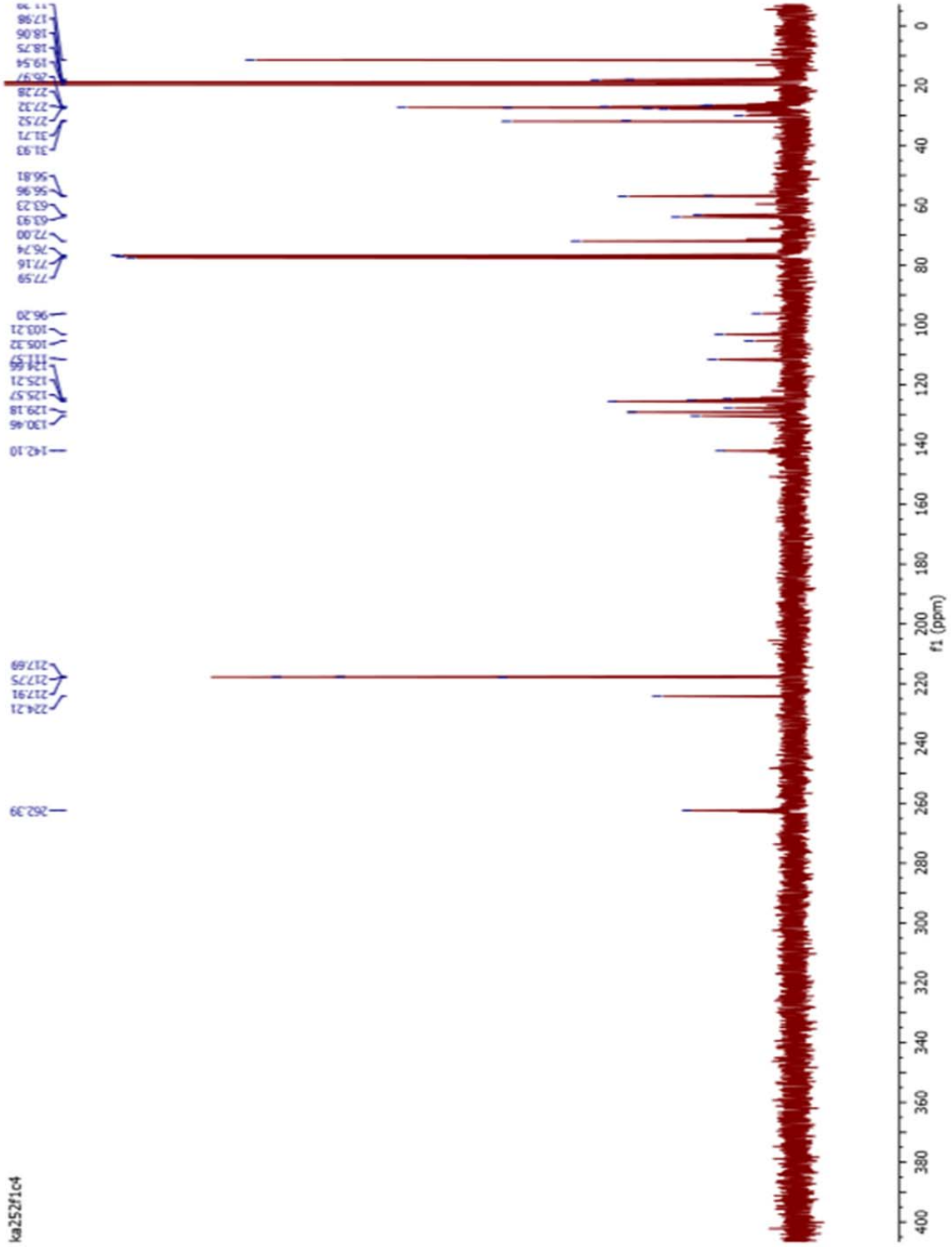


*Pentacarbonyl[(N-isobutyl-N-(5-methylcarboxy-4-penten-1-yl)amino)methylene]chromium(0) (**13j**)*

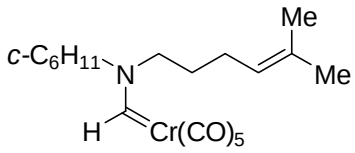


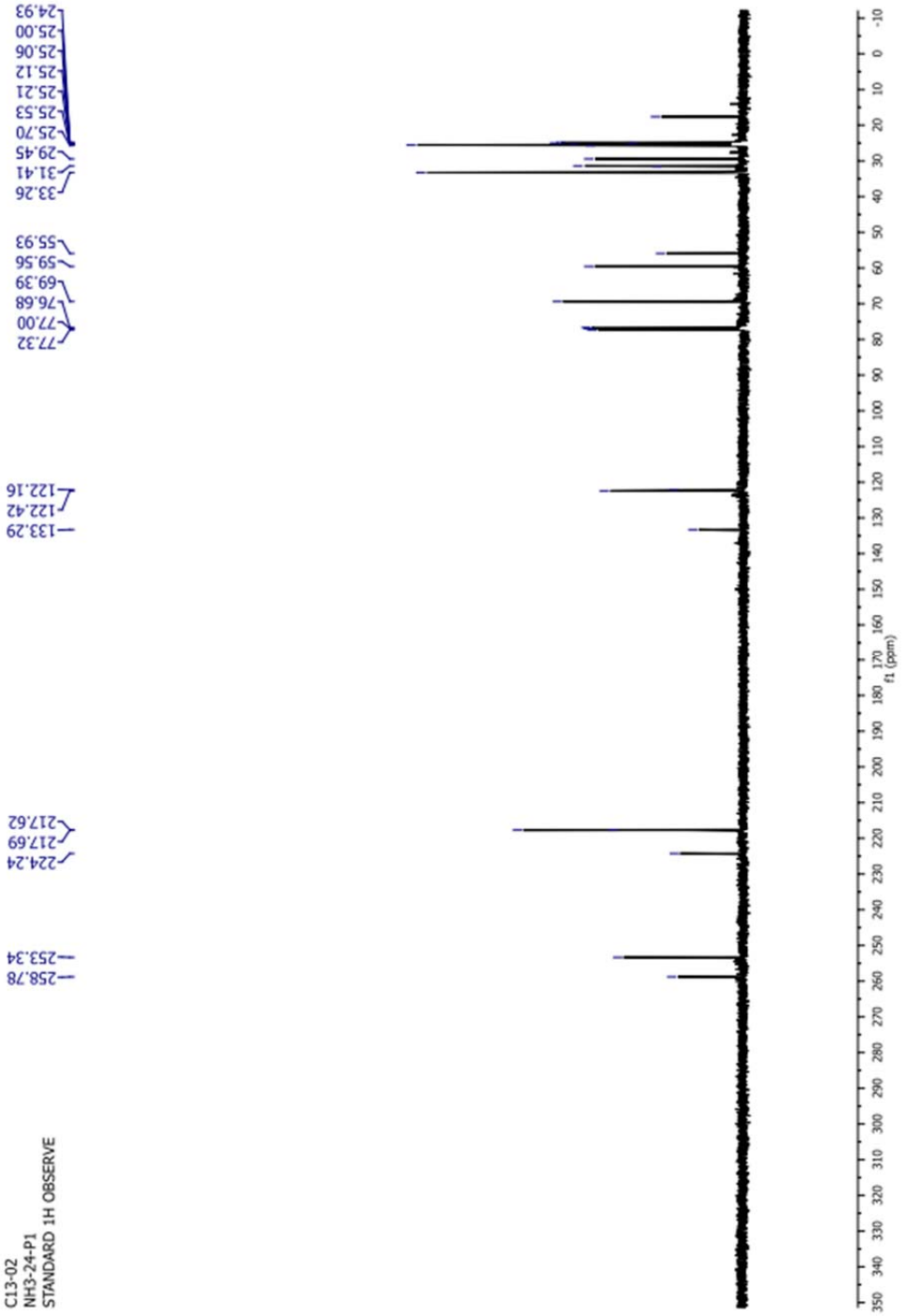
Pentacarbonyl[(N-isobutyl-N-(7-triisopropylsilyl-4-hepten-6-yn-1-yl)amino)methylene]chromium(0) ***(13k)***



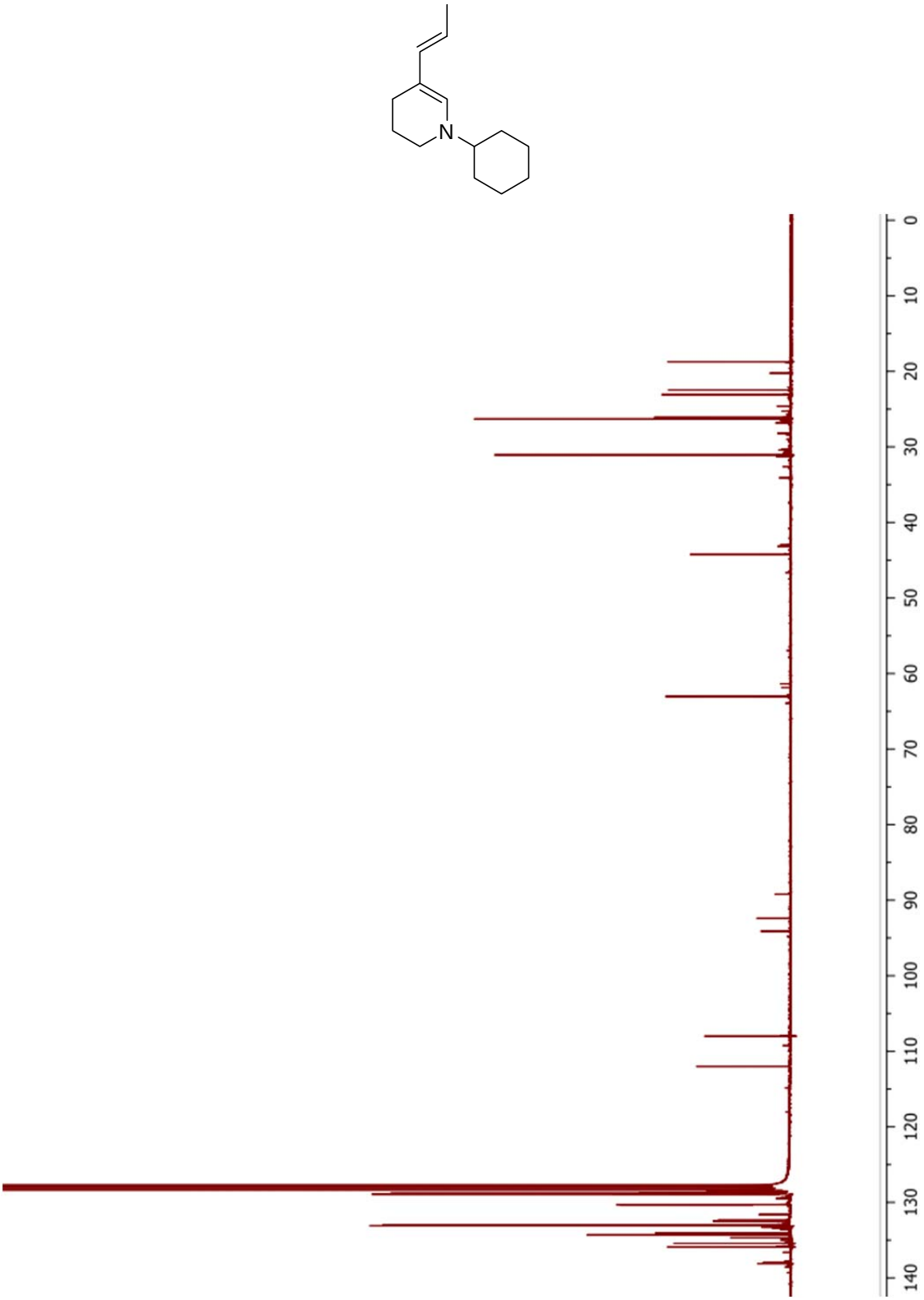


Pentacarbonyl[(N-cyclohexyl-N-(5-methyl-4-hexen-1-yl)amino)methylene]chromium(0) ***(13l)***

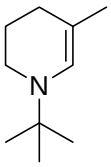


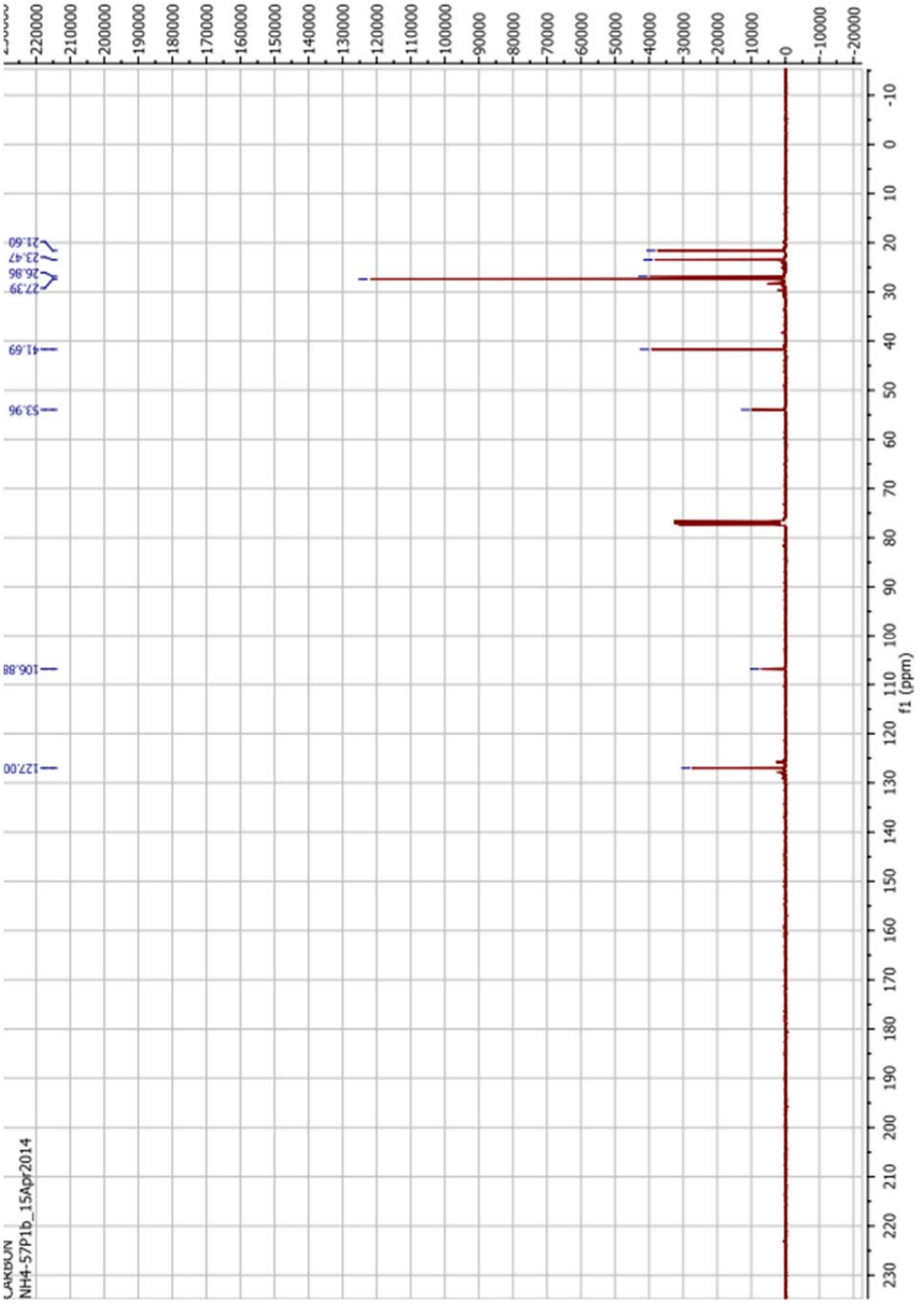


(E)-1-cyclohexyl-5-(prop-1-enyl)-1,2,3,4-tetrahydropyridine ***15c***

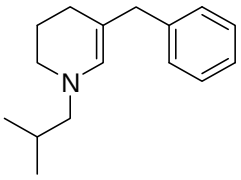


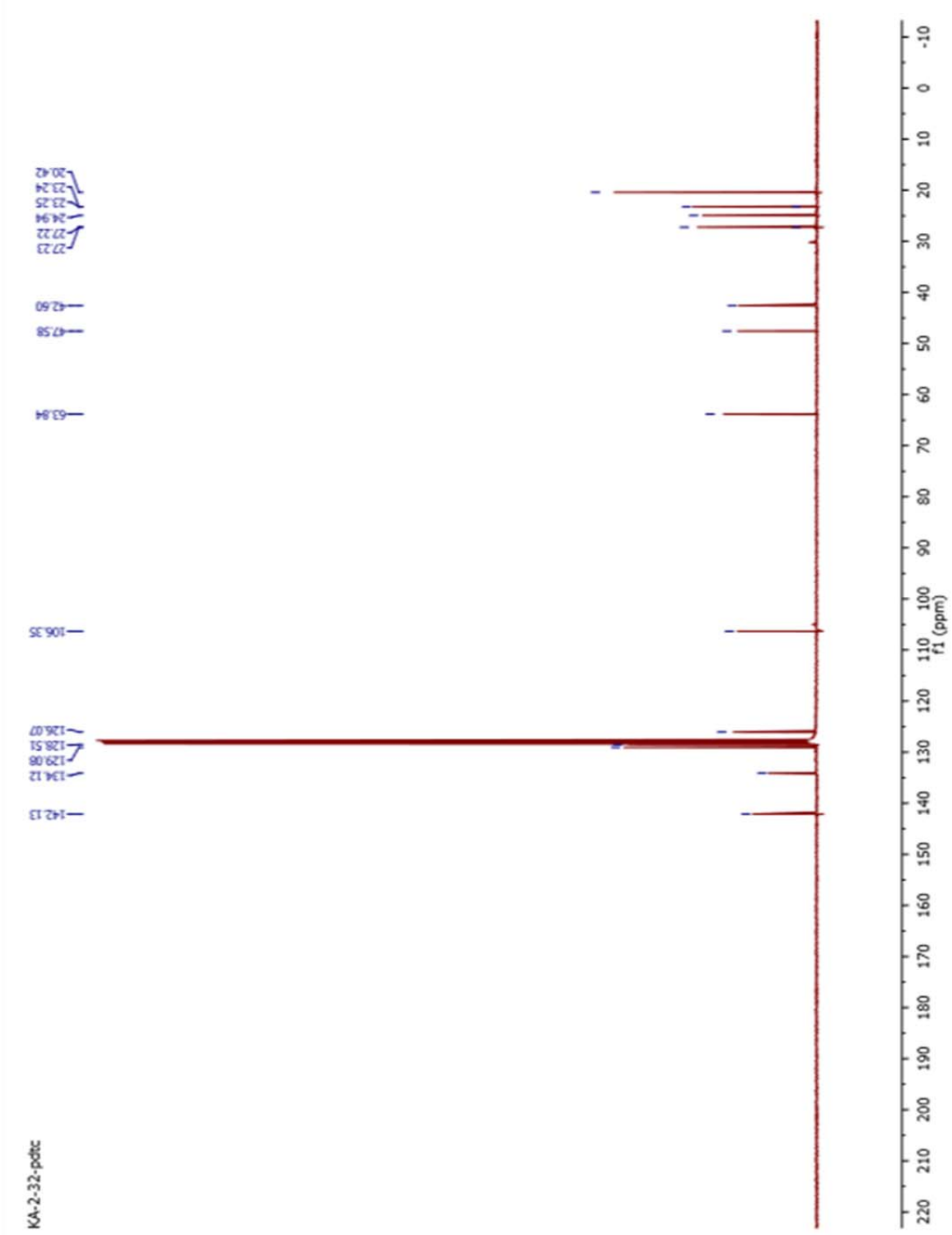
N-tert-Butyl-1,2,3,4-tetrahydropyridine ***15g***



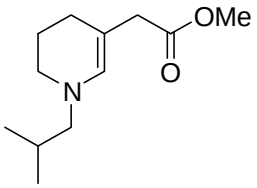


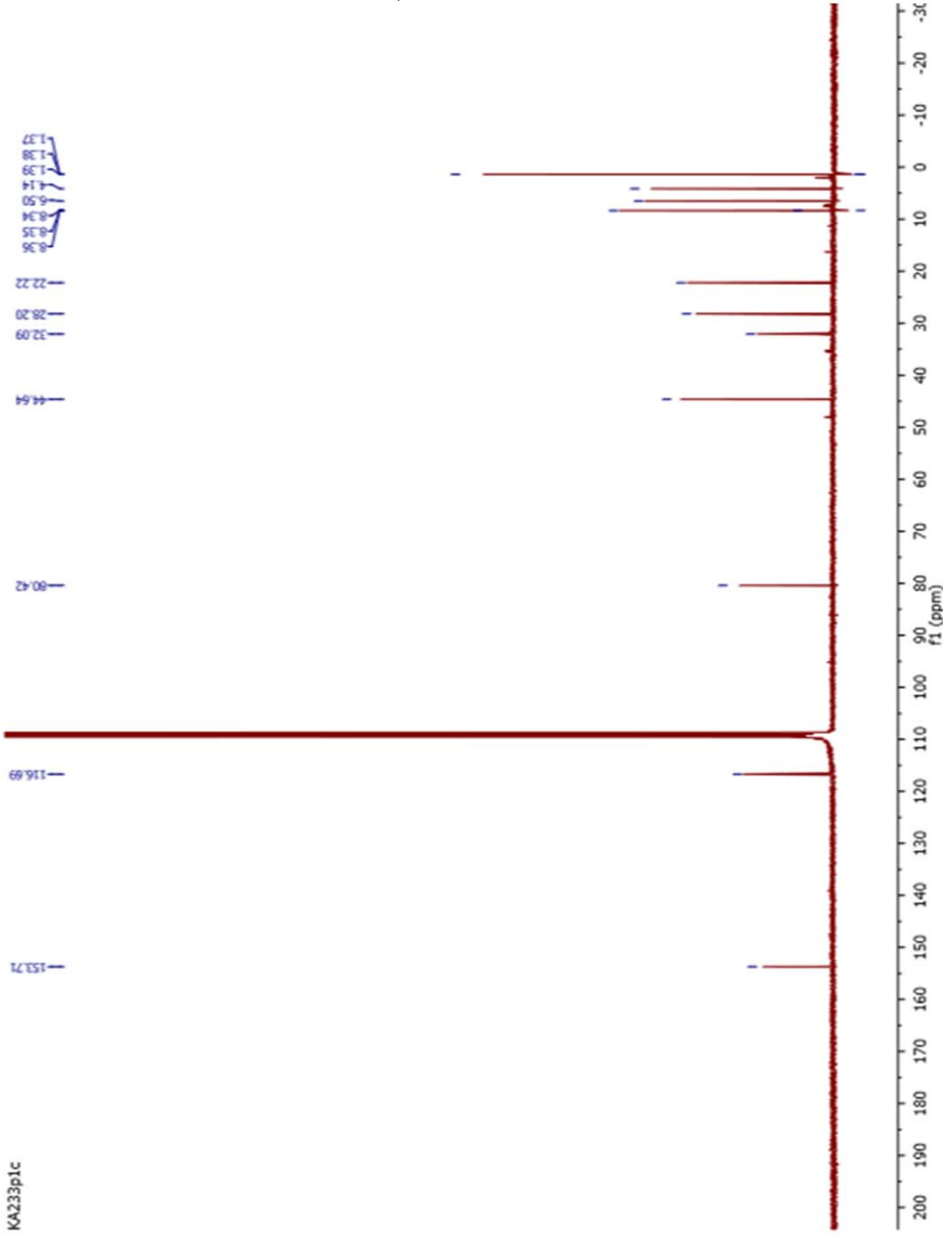
5-Benzyl-1-isobutyl-1,2,3,4-tetrahydropyridine ***15i***



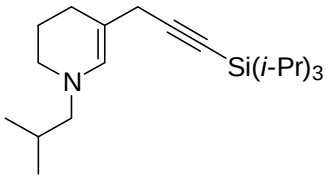


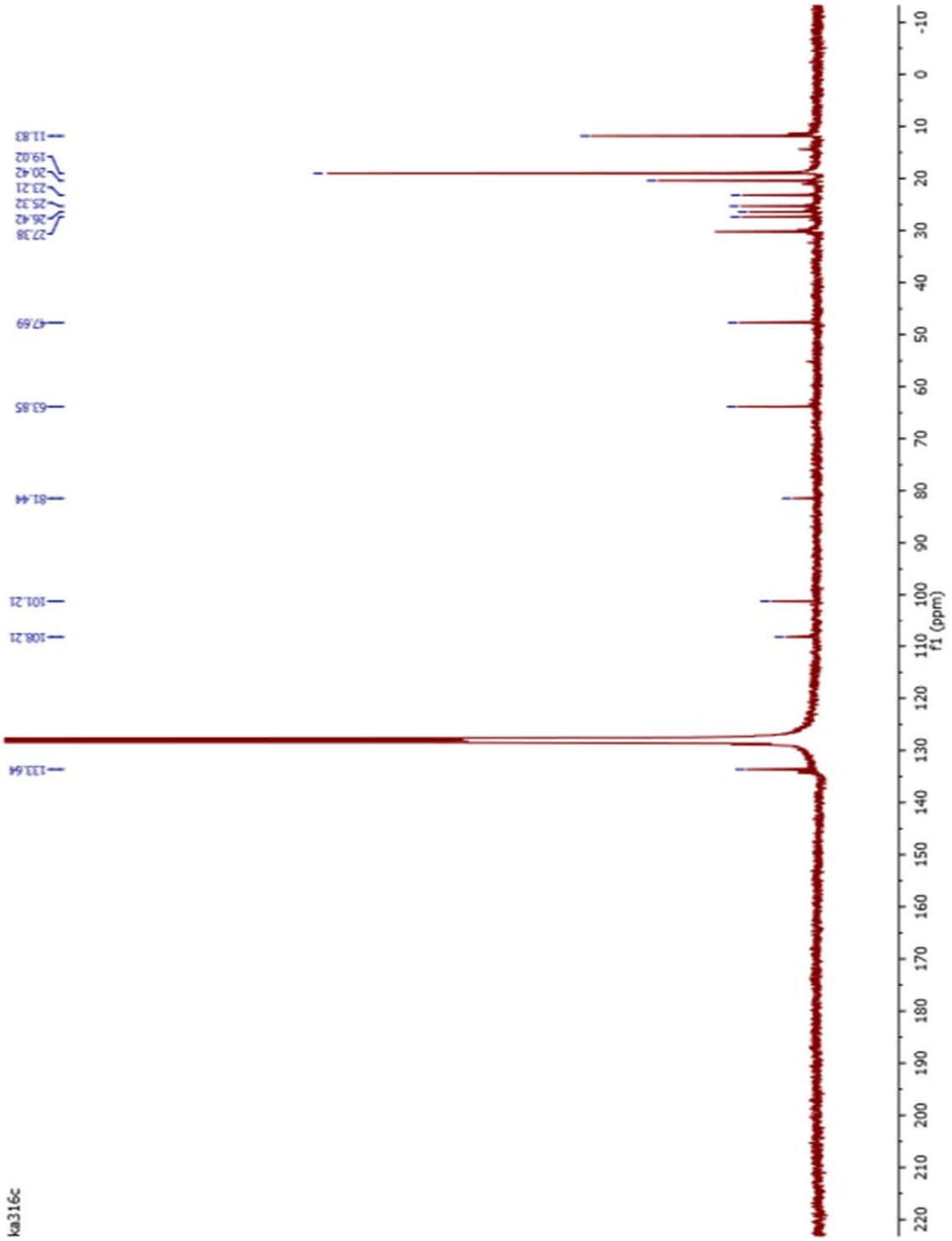
methyl 2-(1-isobutyl-1,4,5,6-tetrahydropyridin-3-yl)acetate ***15j***



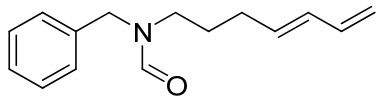


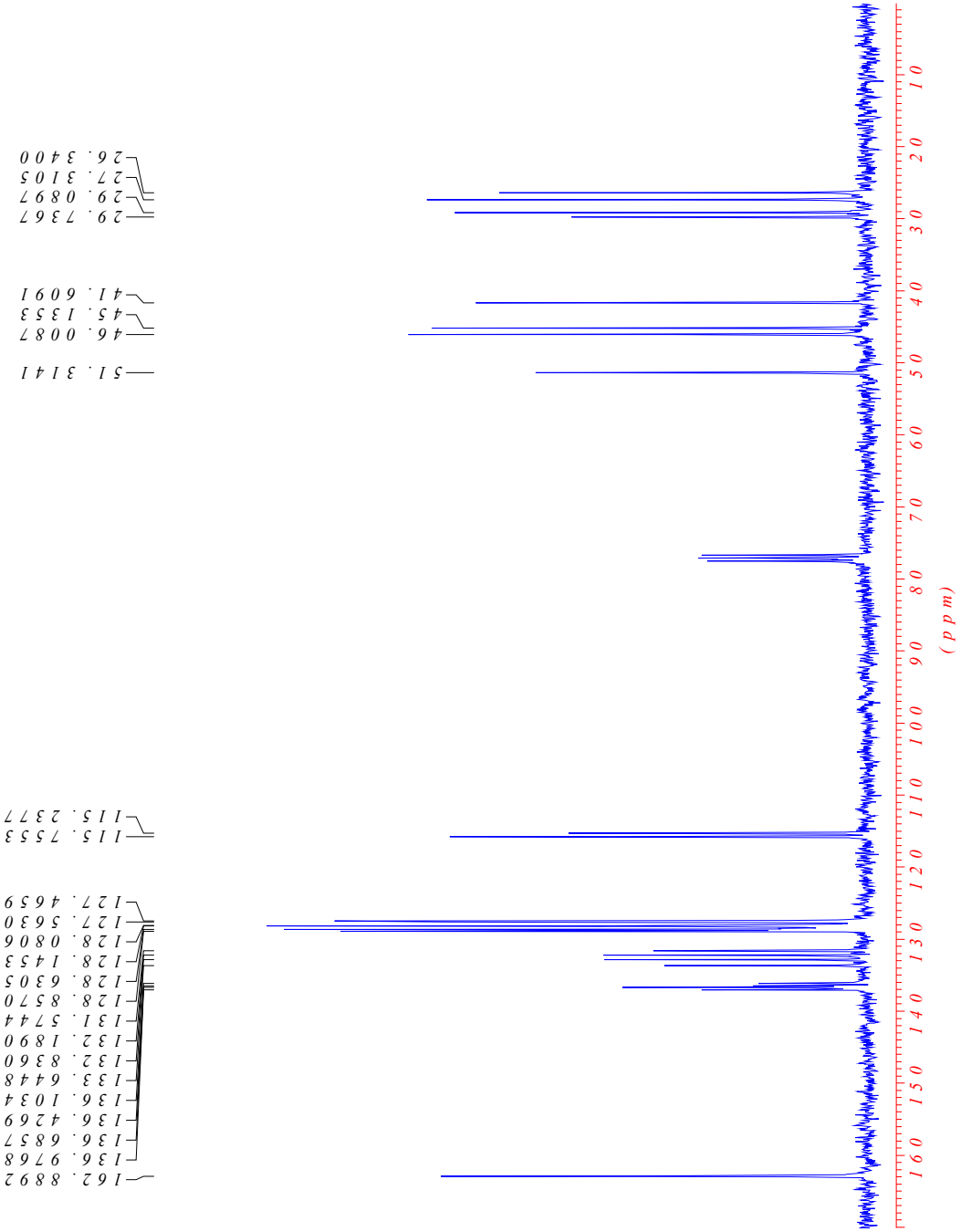
1-isobutyl-5-(3-(triisopropylsilyl)prop-2-ynyl)-1,2,3,4-tetrahydropyridine ***15k***



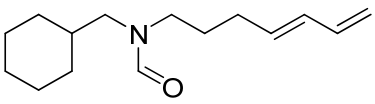


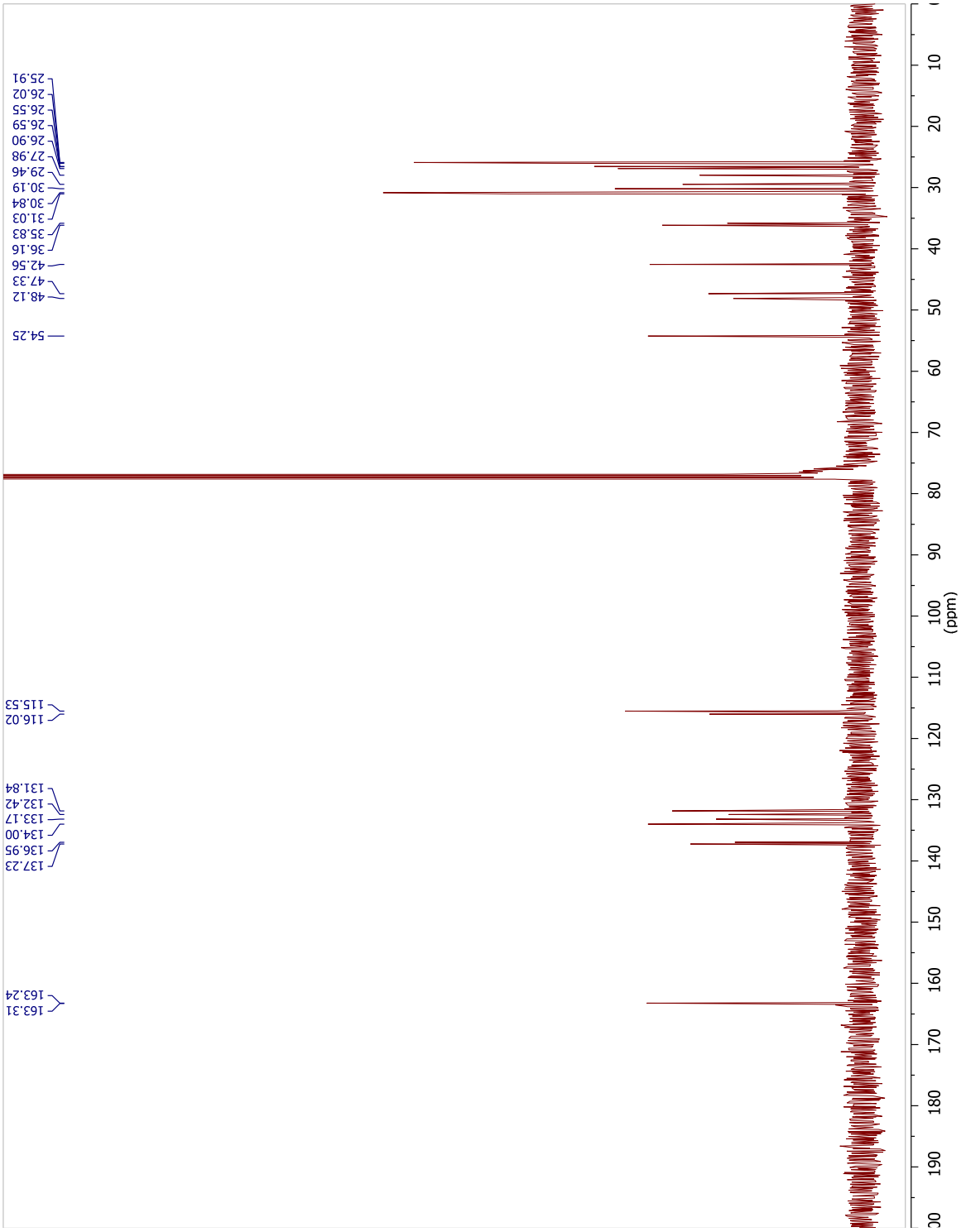
*(E)-N-(Benzyl)-N-(hepta-4,6-dienyl)formamide (**18a**)*



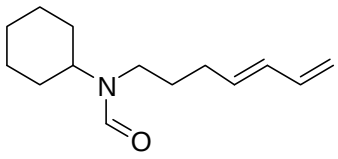


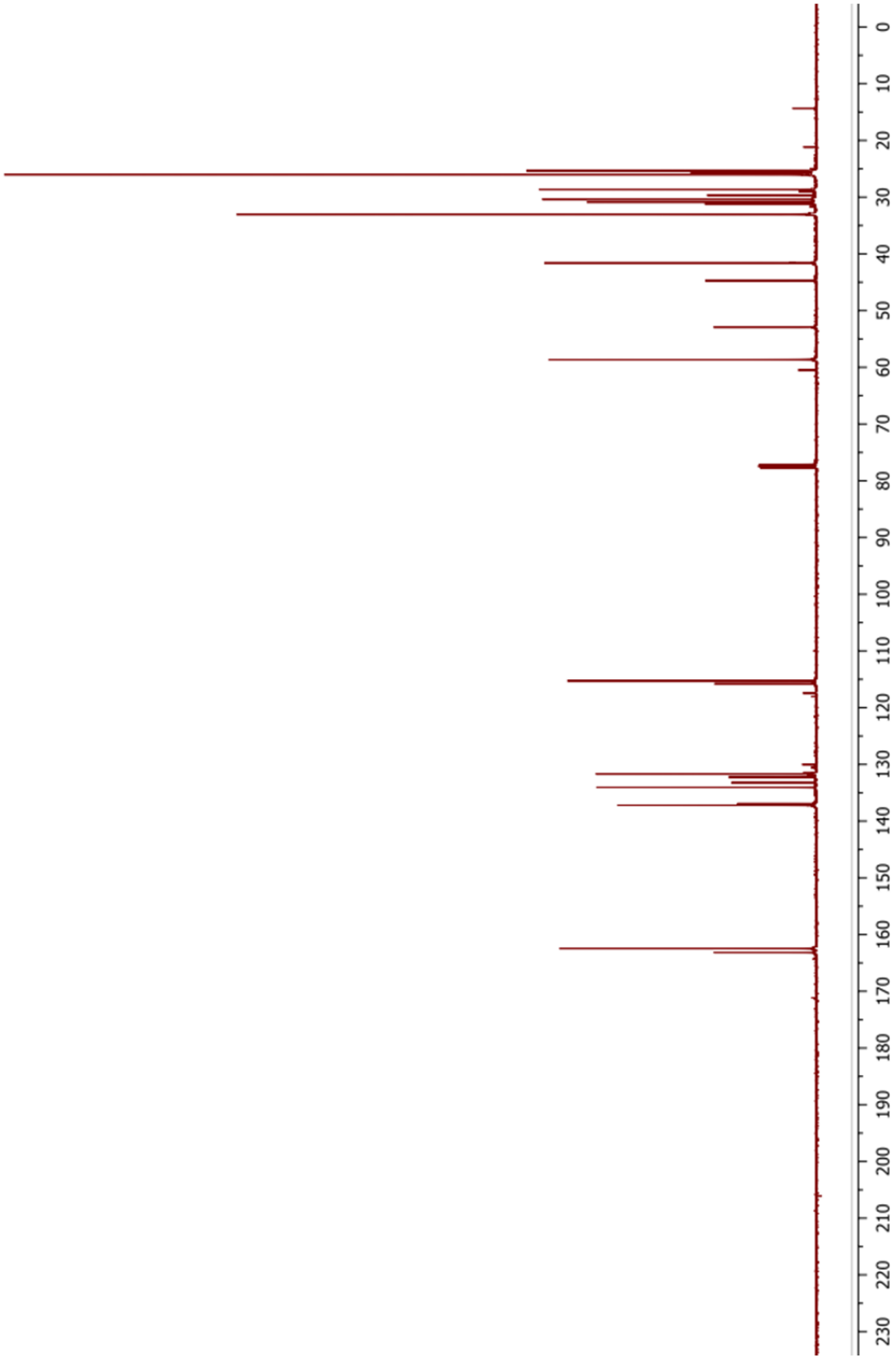
*(E)-N-(Cyclohexylmethyl)-N-(hepta-4, 6-dienyl)formamide (**18b**)*



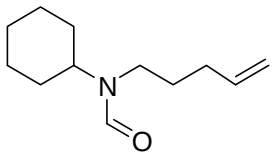


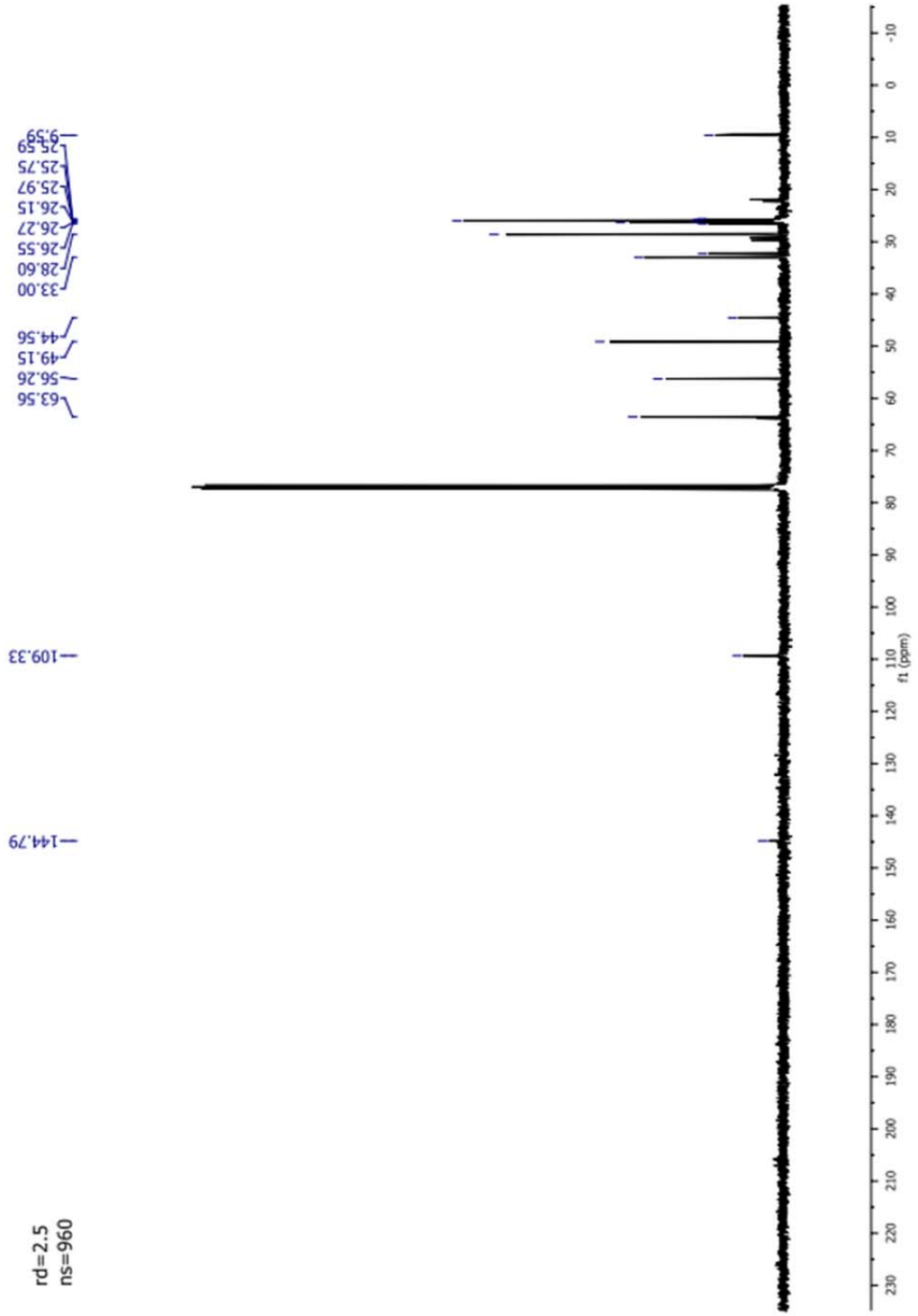
*(E)-N-cyclohexyl-N-(hepta-4,6-dien-1-yl)formamide (**18c**)*



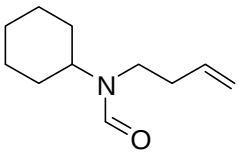


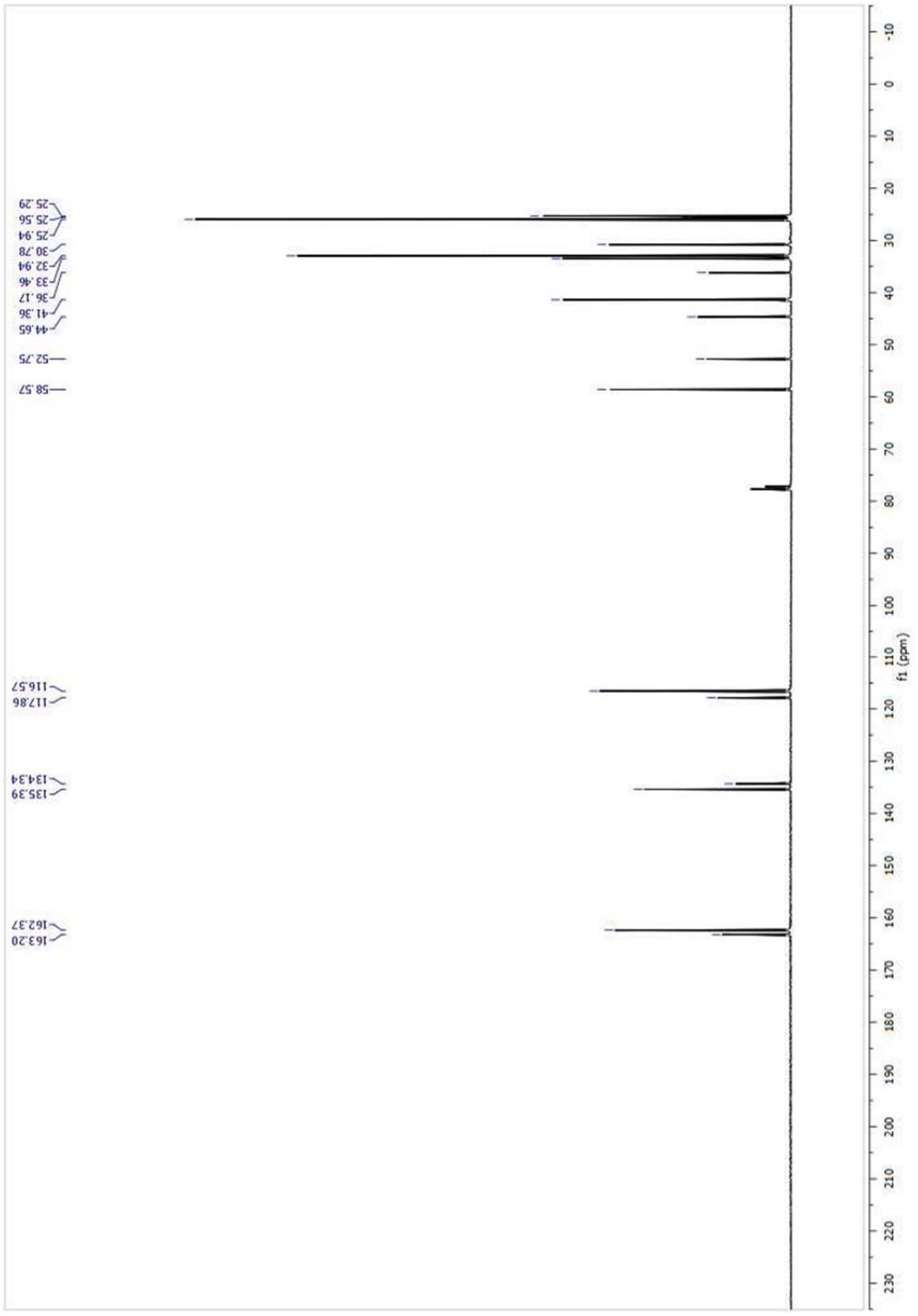
*N-Cyclohexyl-N(4-penten-1-yl) formamide (**18d**)*



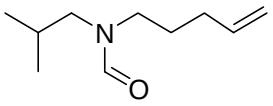


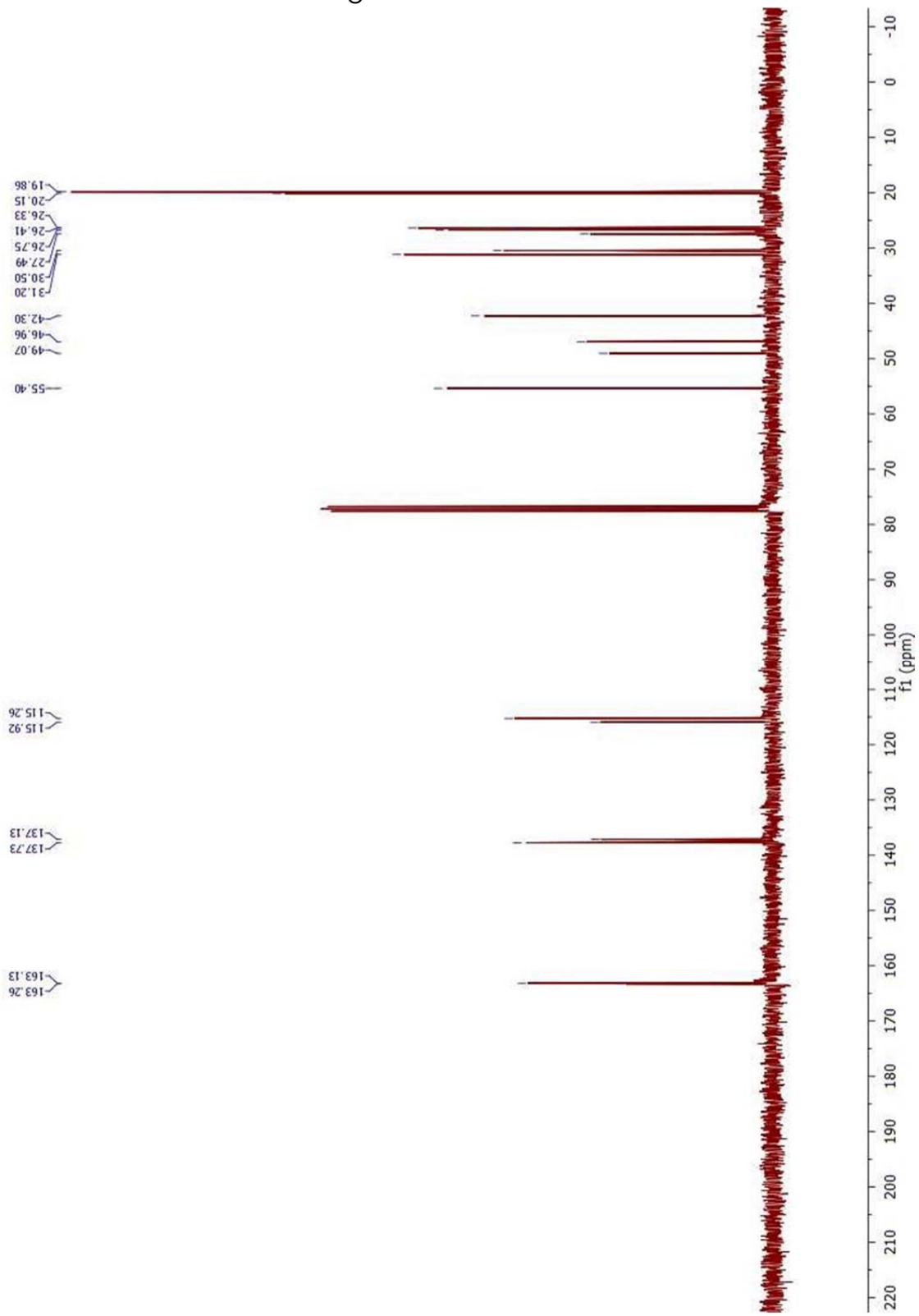
*(E)-N-cyclohexyl-N-(3-buten-1-yl)formamide (**18e**)*



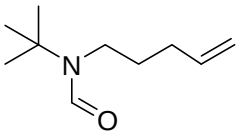


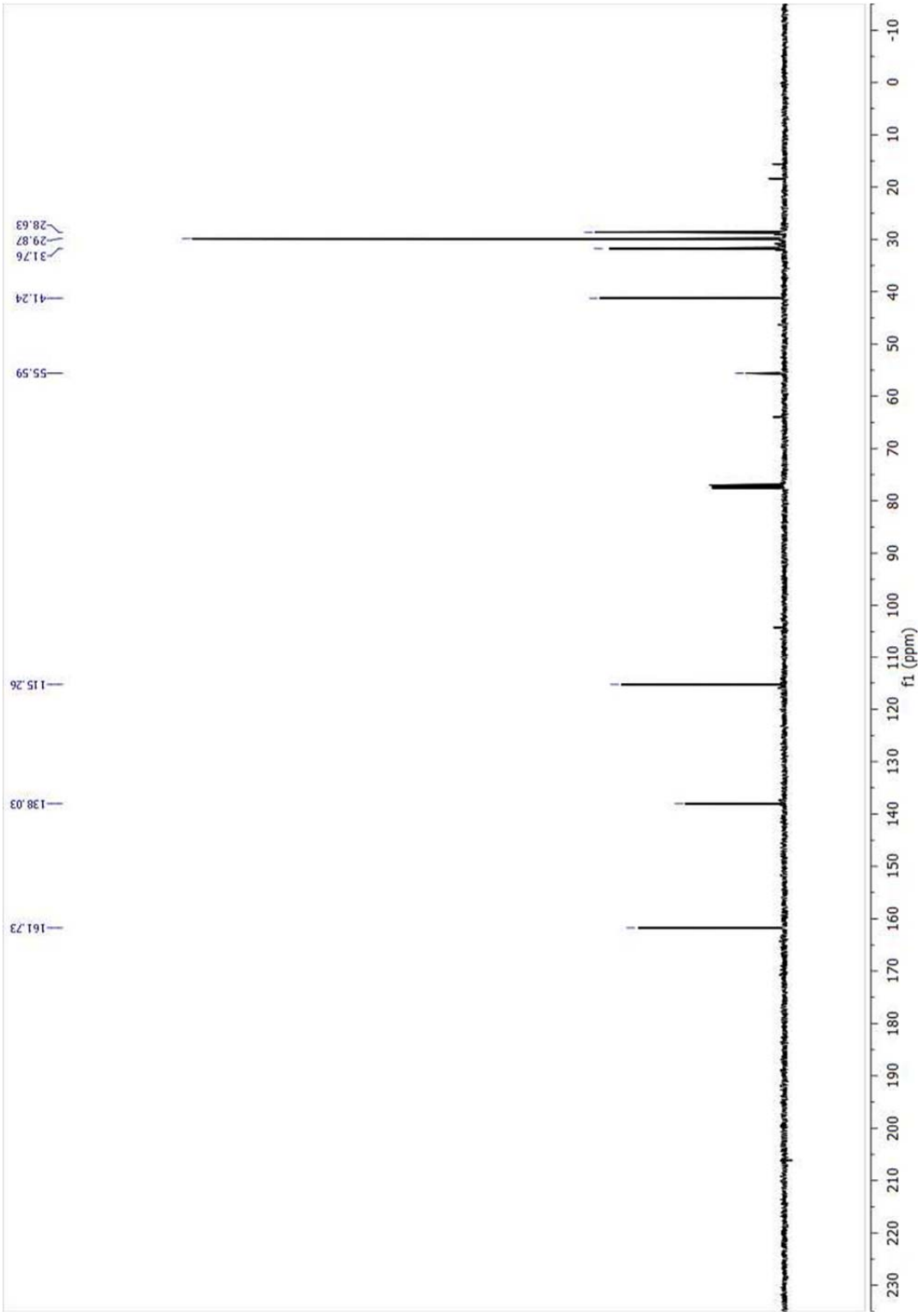
*N-Isobutyl-N(4-penten-1-yl) formamide (**18f**)*



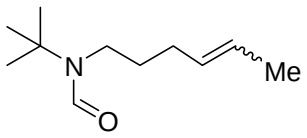


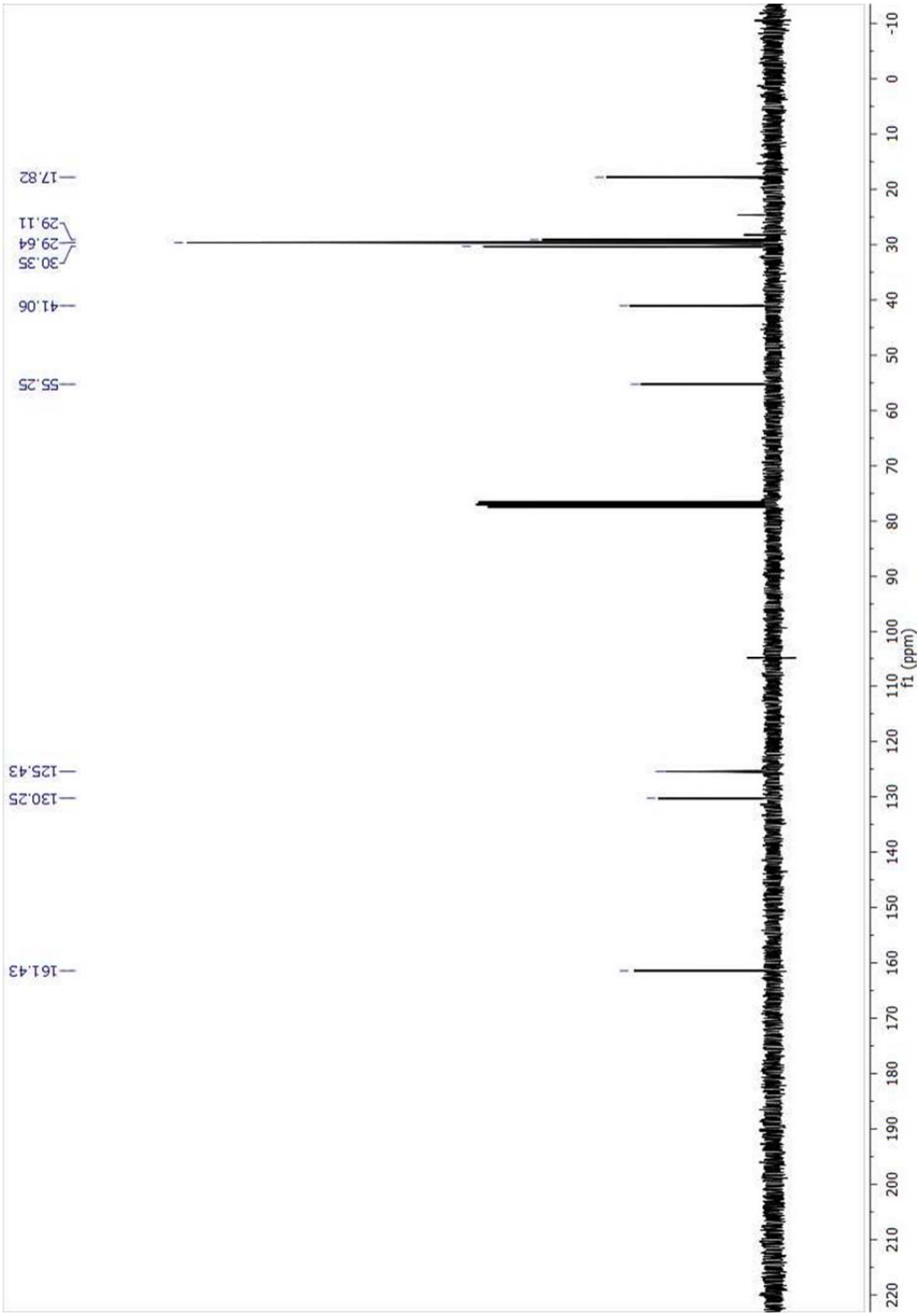
*N-tert-butyl-N(4-penten-1-yl) formamide (**18g**)*



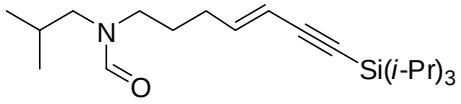


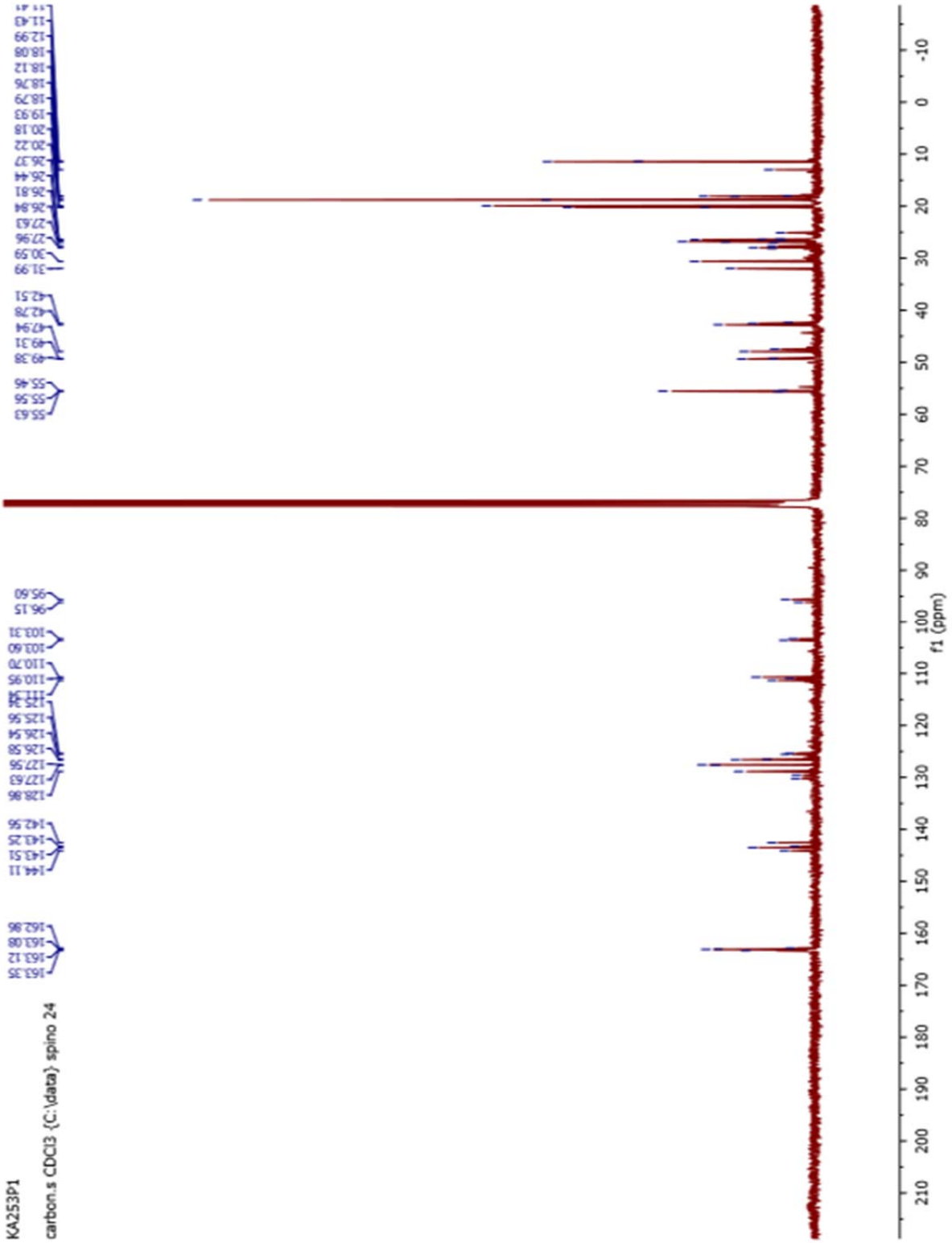
*N-Isobutyl-N(4-hexen-1-yl) formamide (**18h**)*



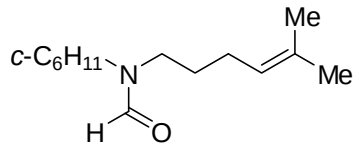


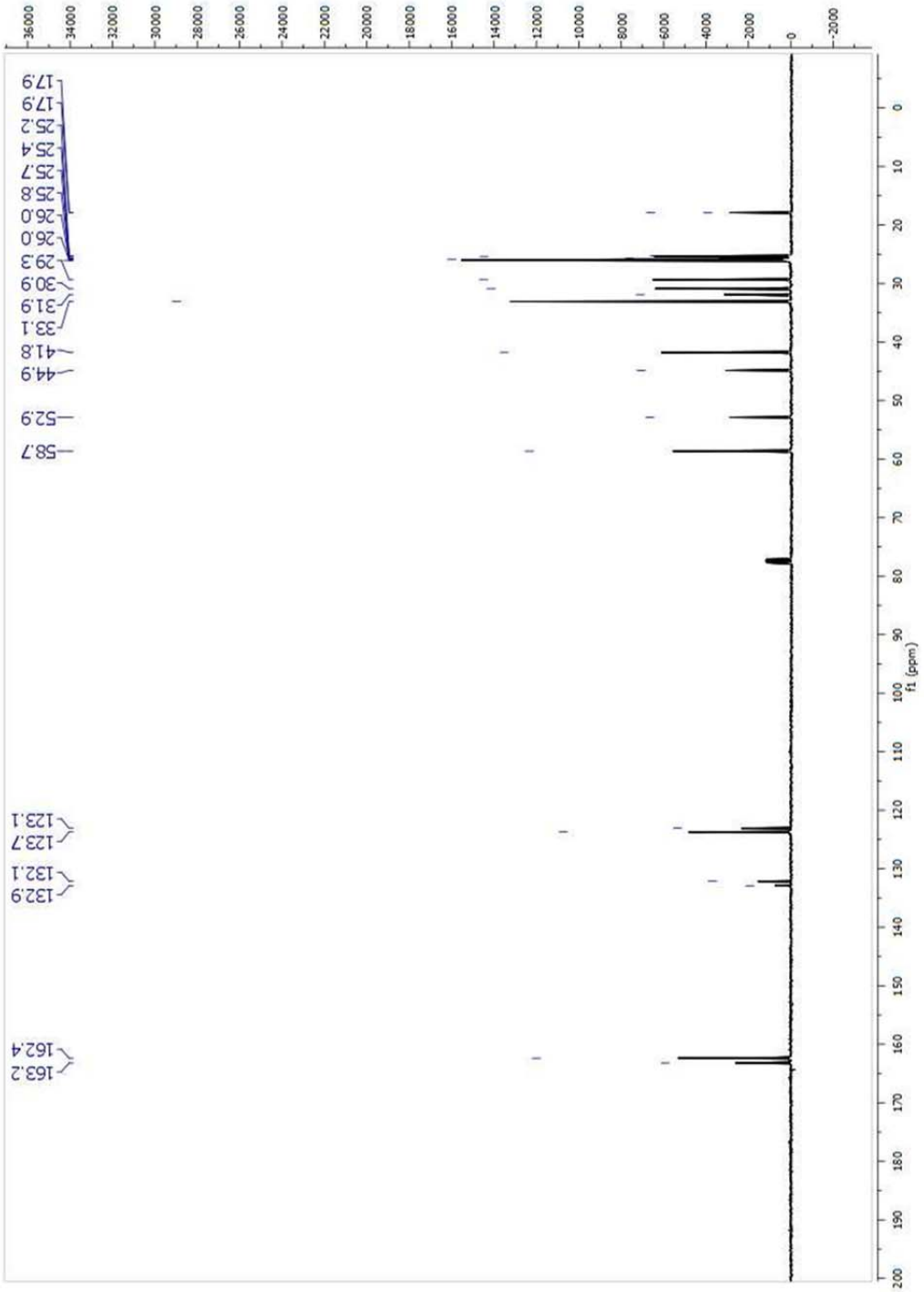
*(E)-N-isobutyl-N-(7-(triisopropylsilyl)hept-4-en-6-ynyl)formamide (**18k**)*



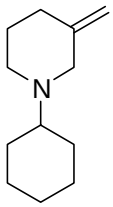


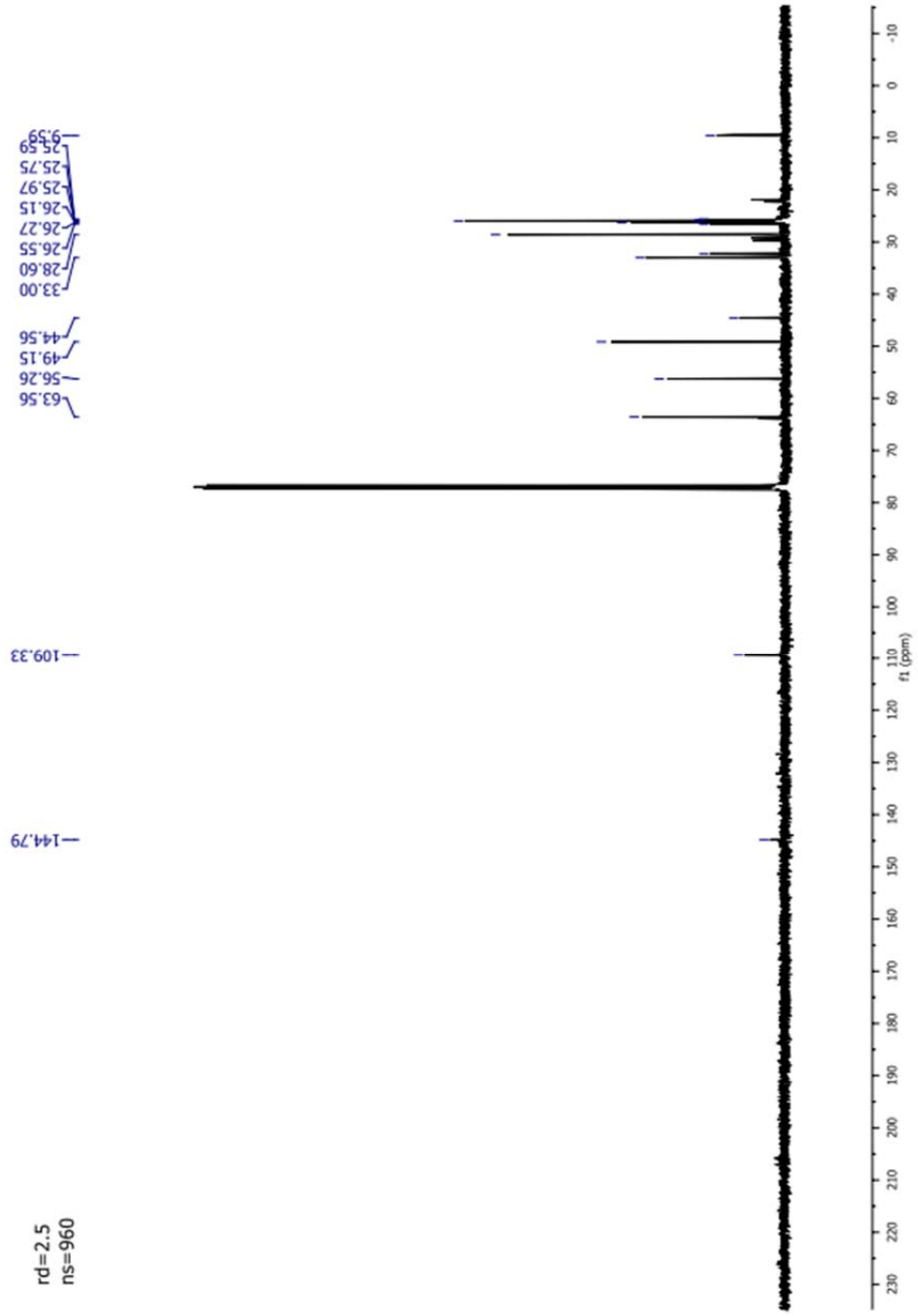
N-cyclohexyl-N-(5-methyl-4-hexen-1-yl)formamide (**18l**)



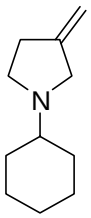


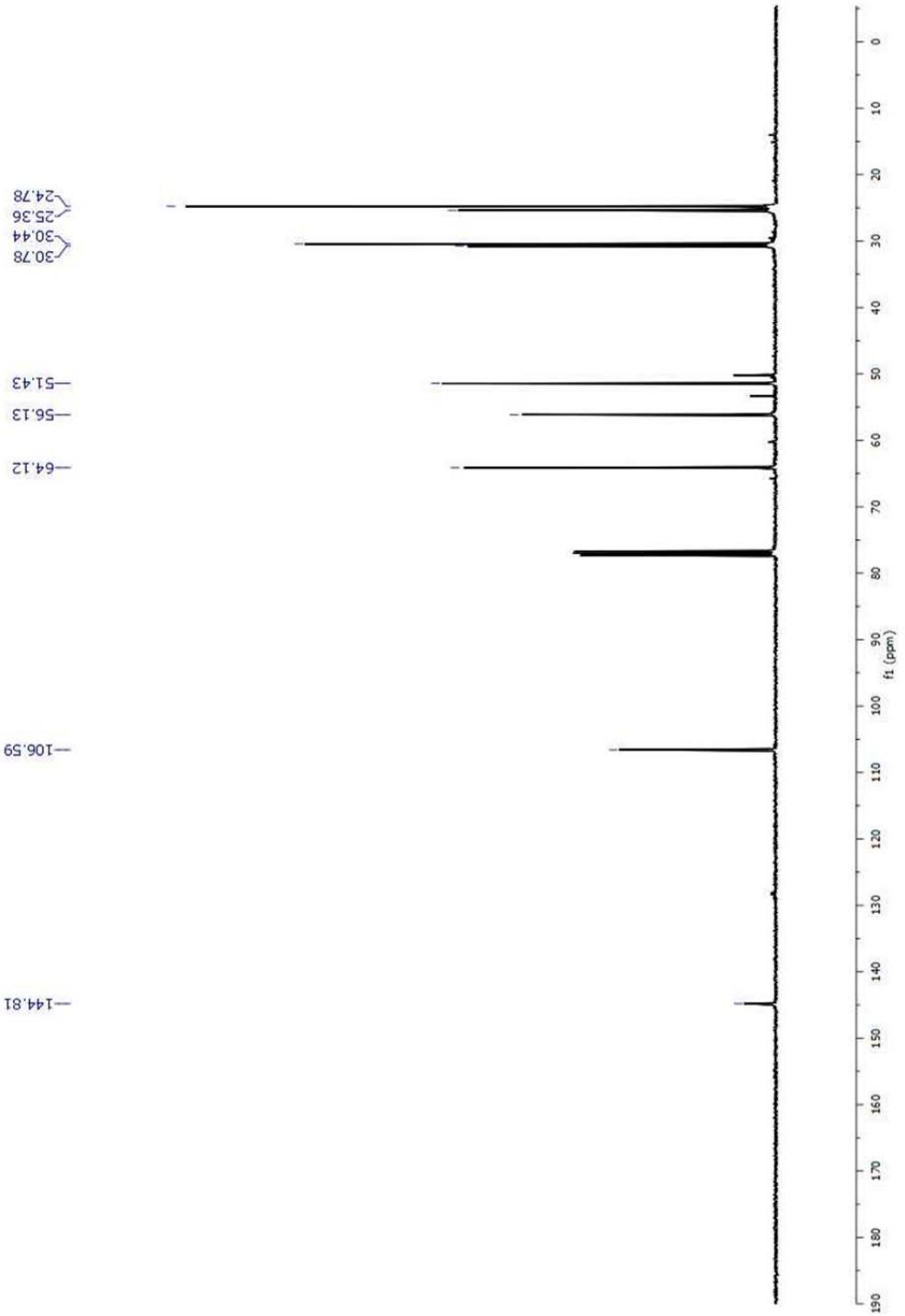
(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine ***19d***



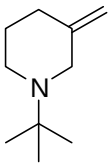


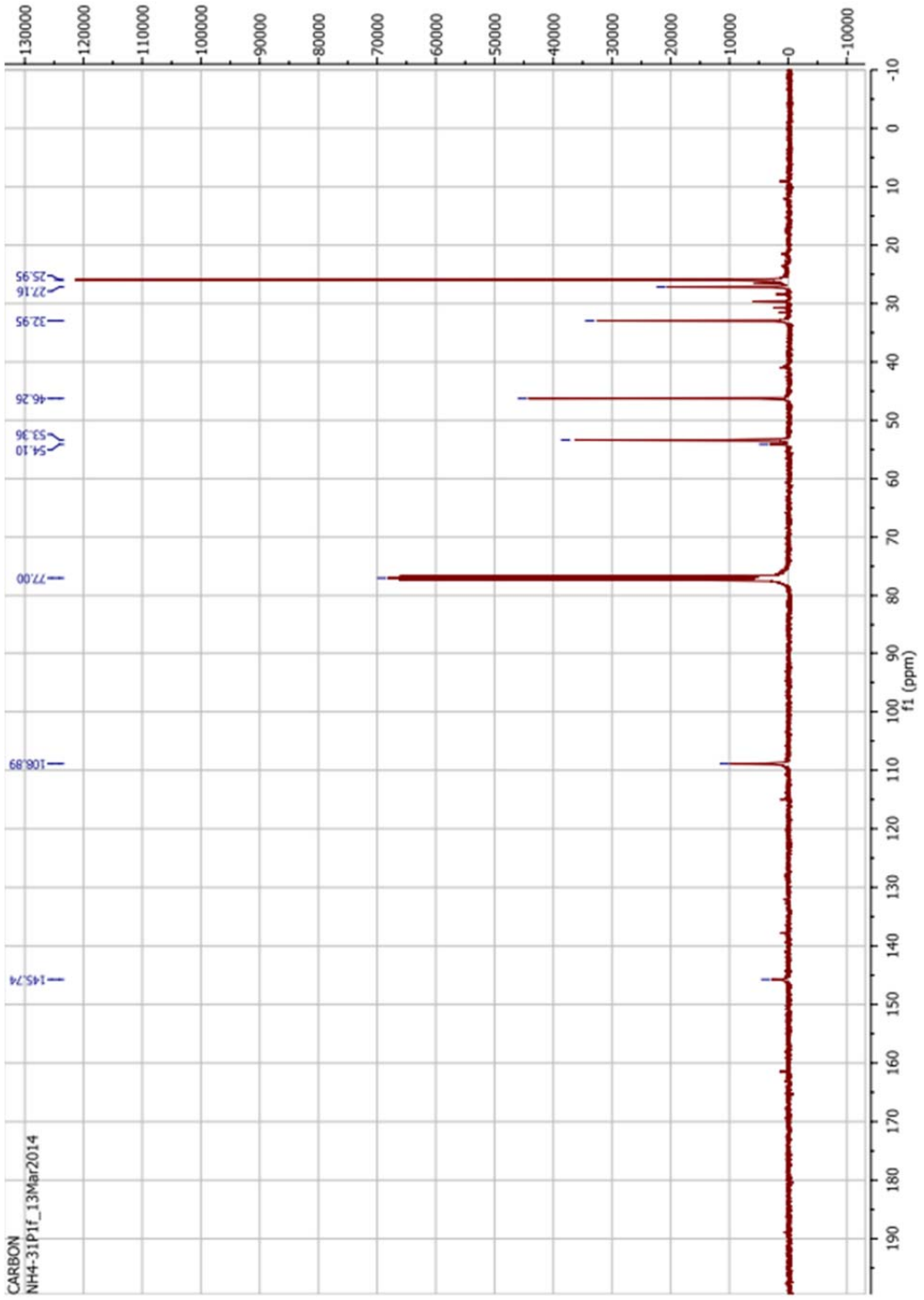
(E)-8-(Prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine ***19e***



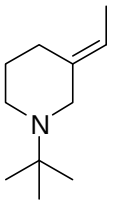


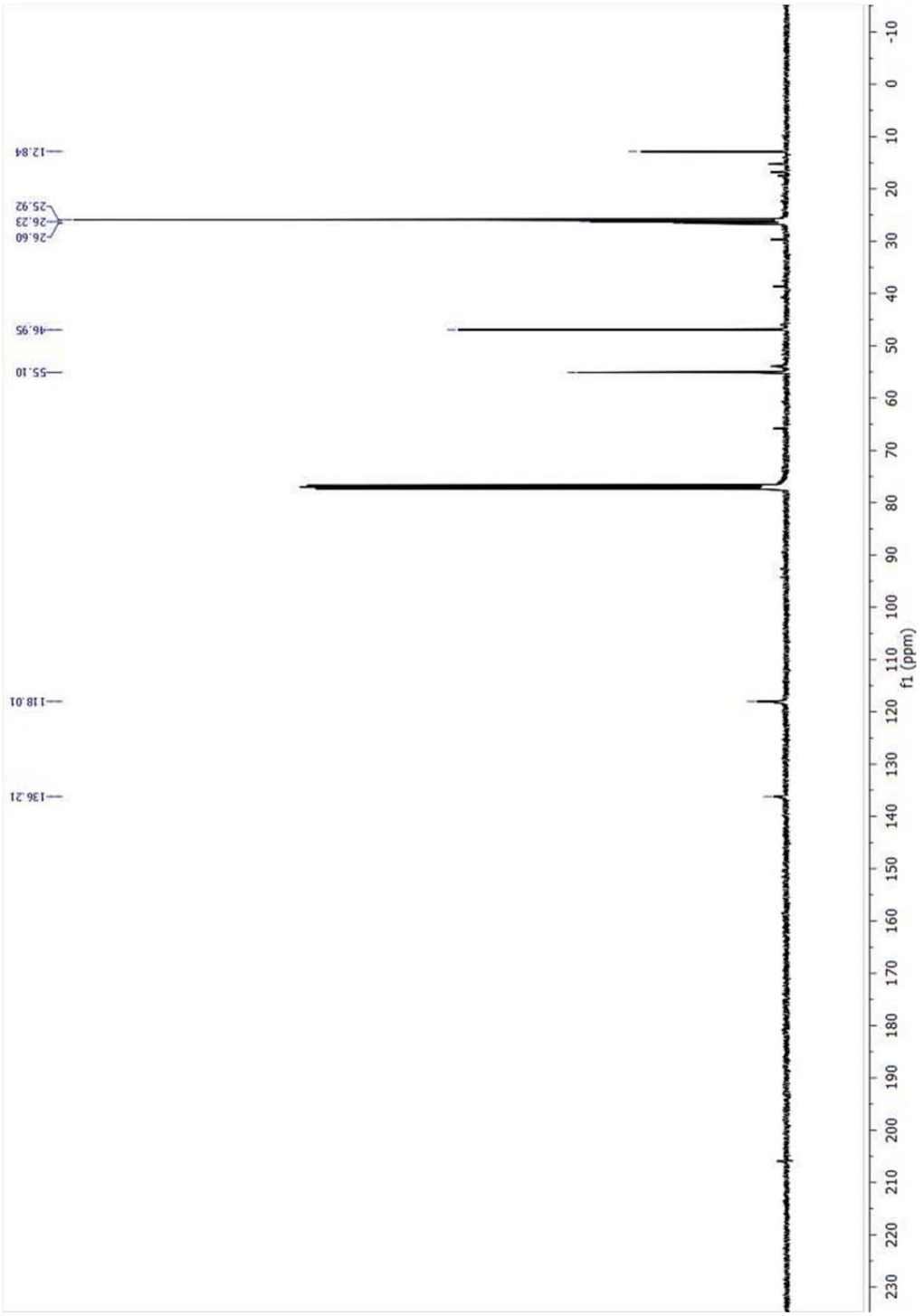
(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine ***19g***



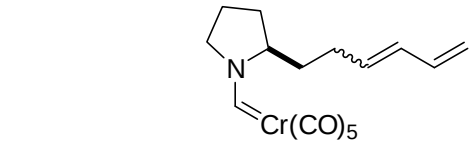


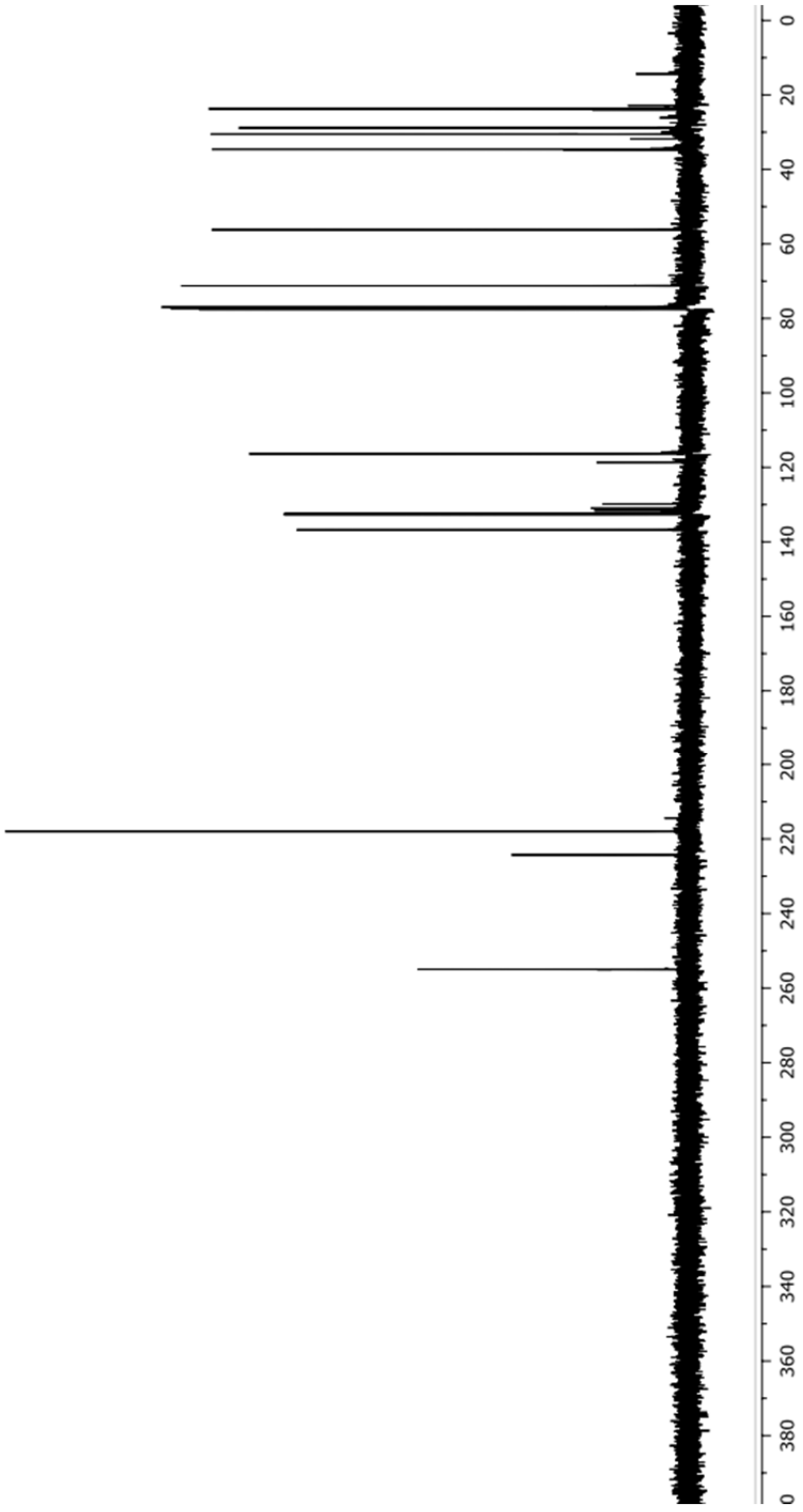
(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine ***19h***



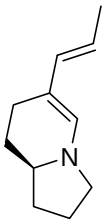


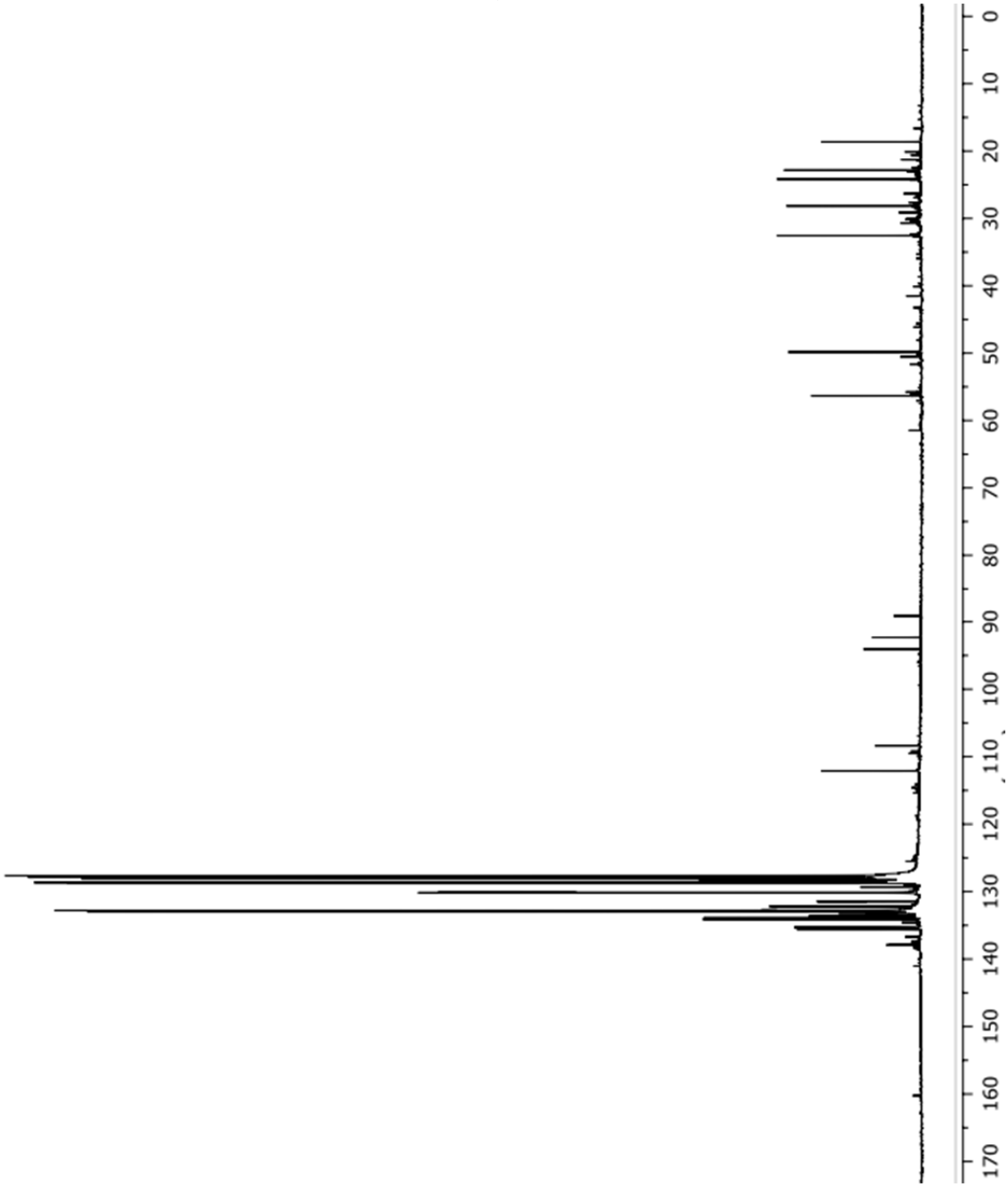
*Mixture of E and Z (R)-Pentacarbonyl[(3-buten-1-yl)pyrrolidine)methylene]chromium(0) (**20**)*



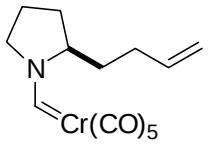


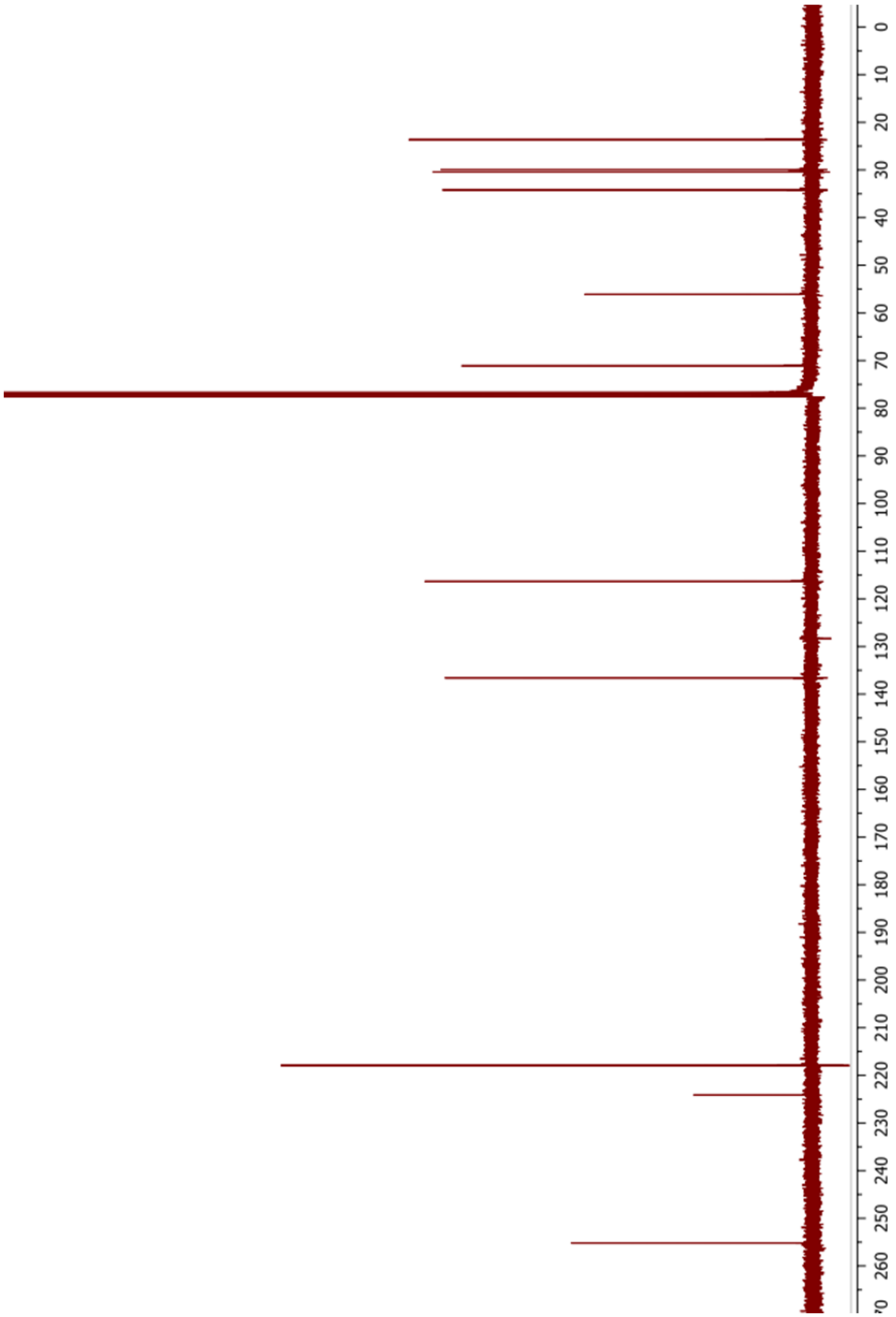
*(R,E)-6-(prop-1-enyl)-1,2,3,7,8,8a-hexahydroindolizine (**21**)*



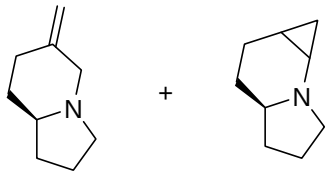


*(R)-Pentacarbonyl[(3-buten-1-yl)pyrrolidine)methylene]chromium(0) (**22**)*

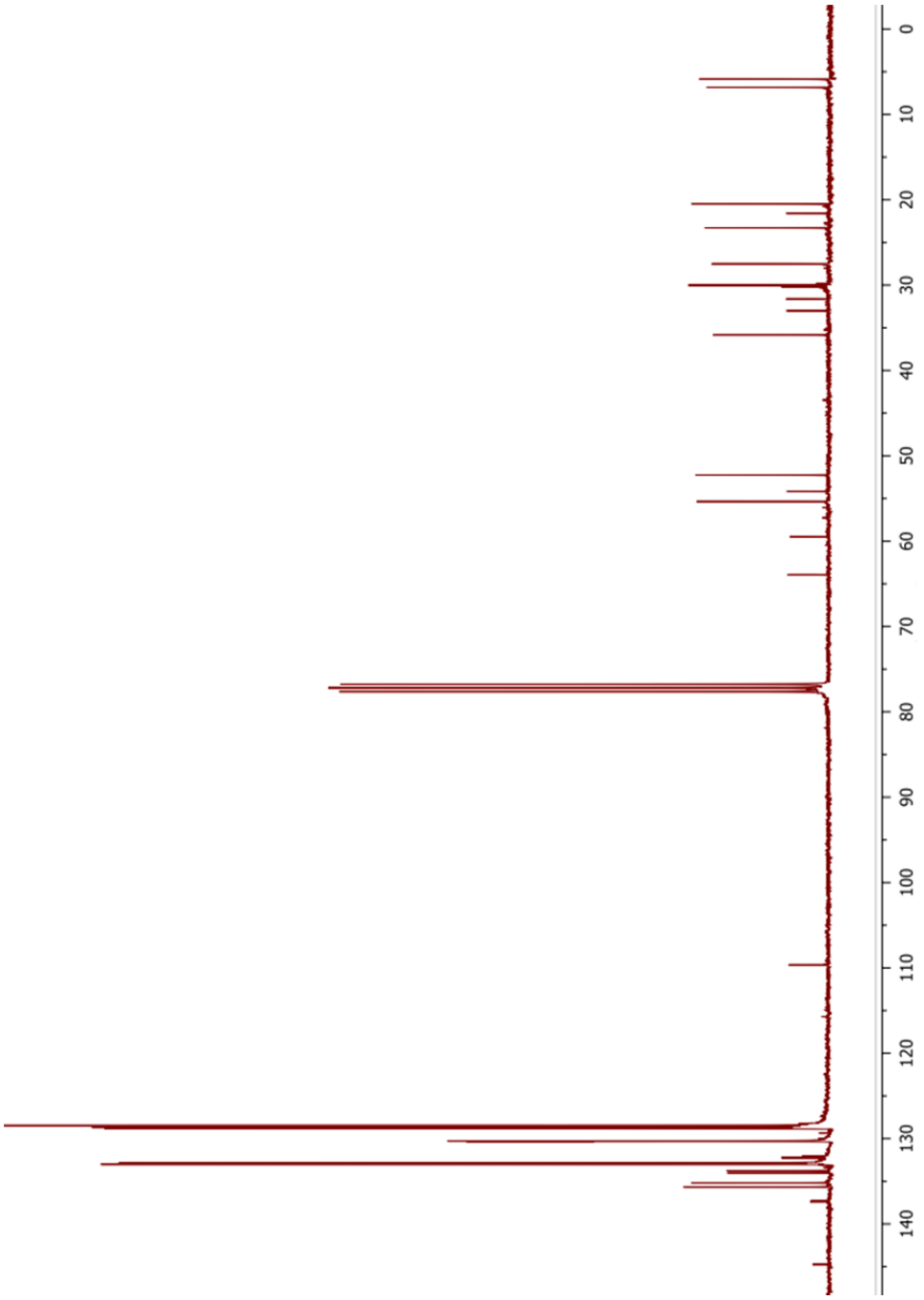




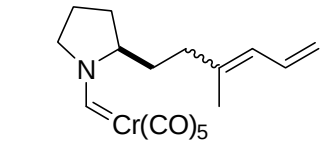
*(R)-6-methyleneoctahydroindolizine (**23a**) and (3aR)-octahydro-1H-cyclopropa[e]indolizine (**23b**)*

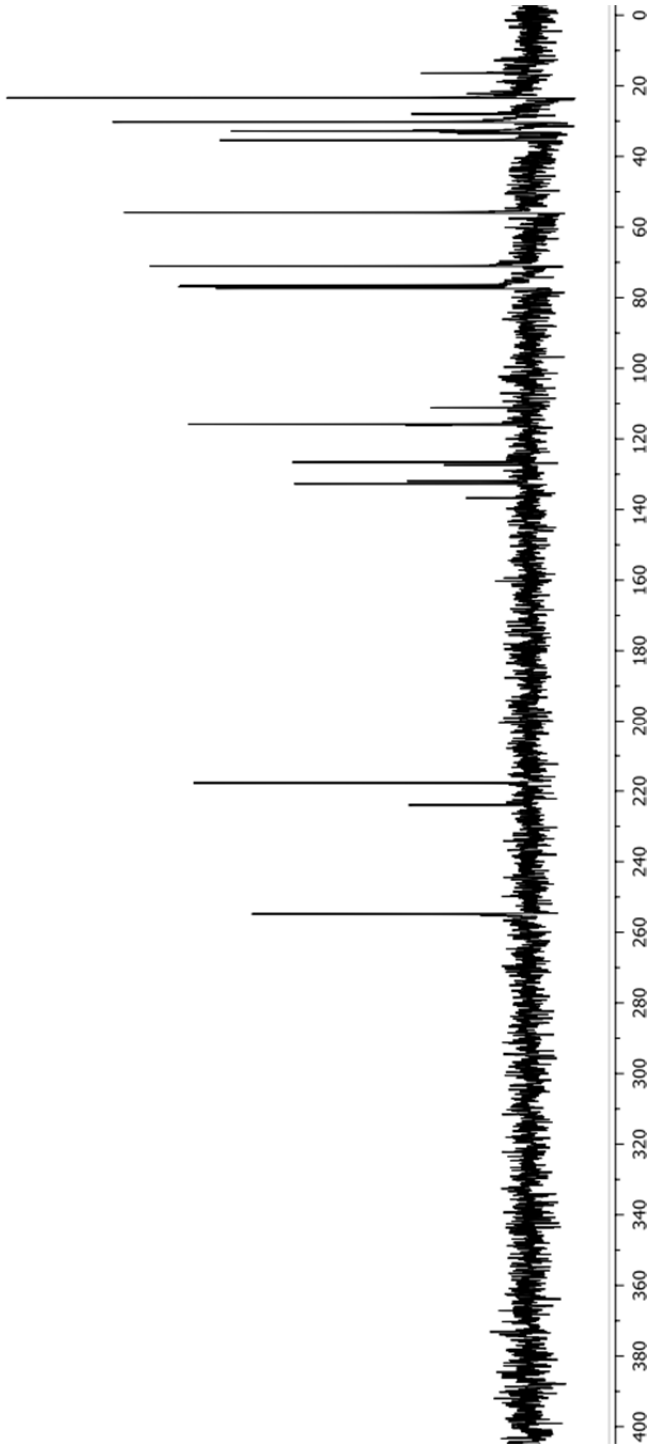


23a **23b**

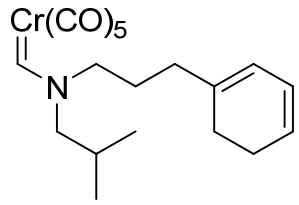


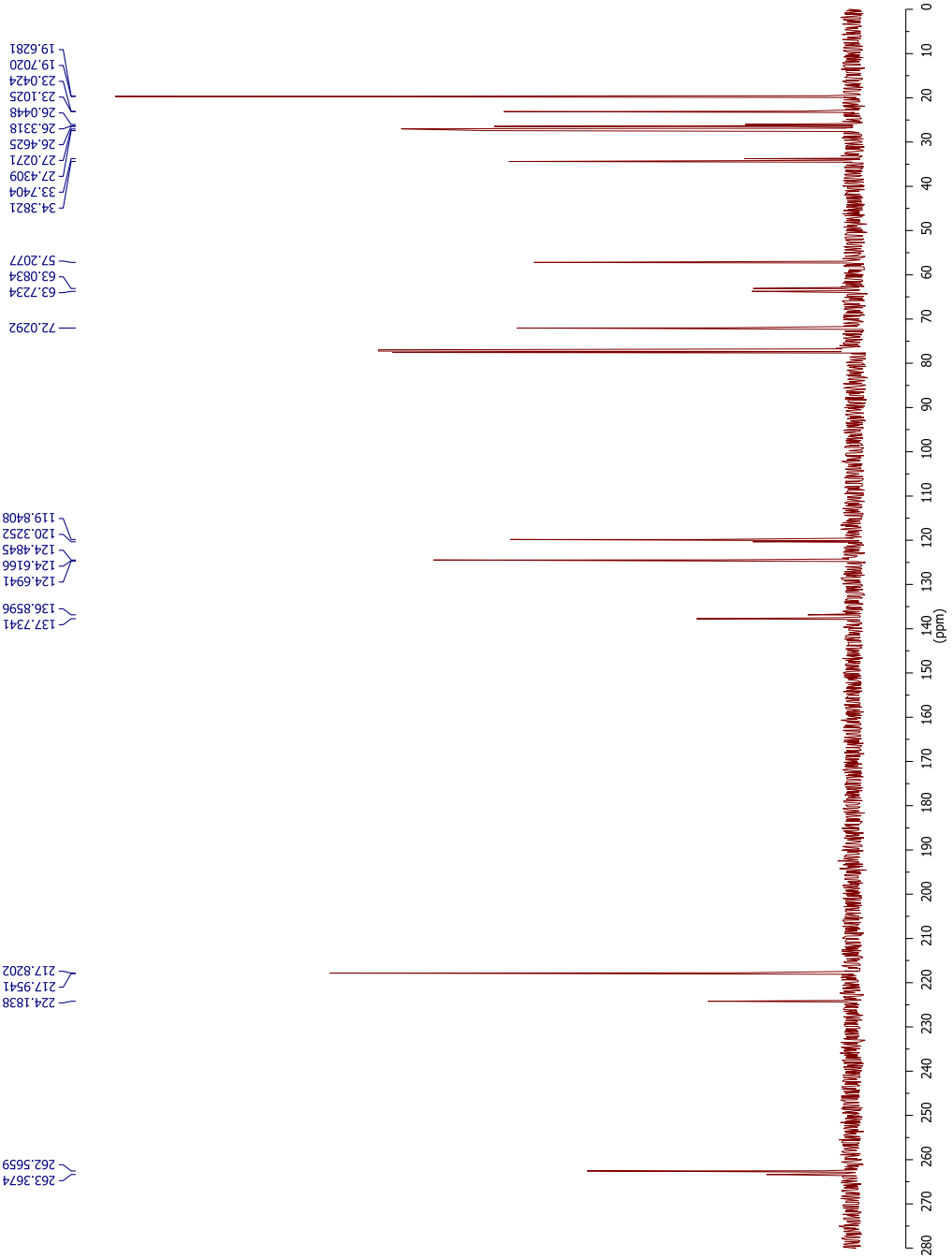
Mixture of E and Z (R)-pentacarbonyl[(2-(3-methylhexa-3,5-dienyl)pyrrolidine)methylene]chromium(0) ***(24)***



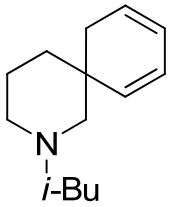


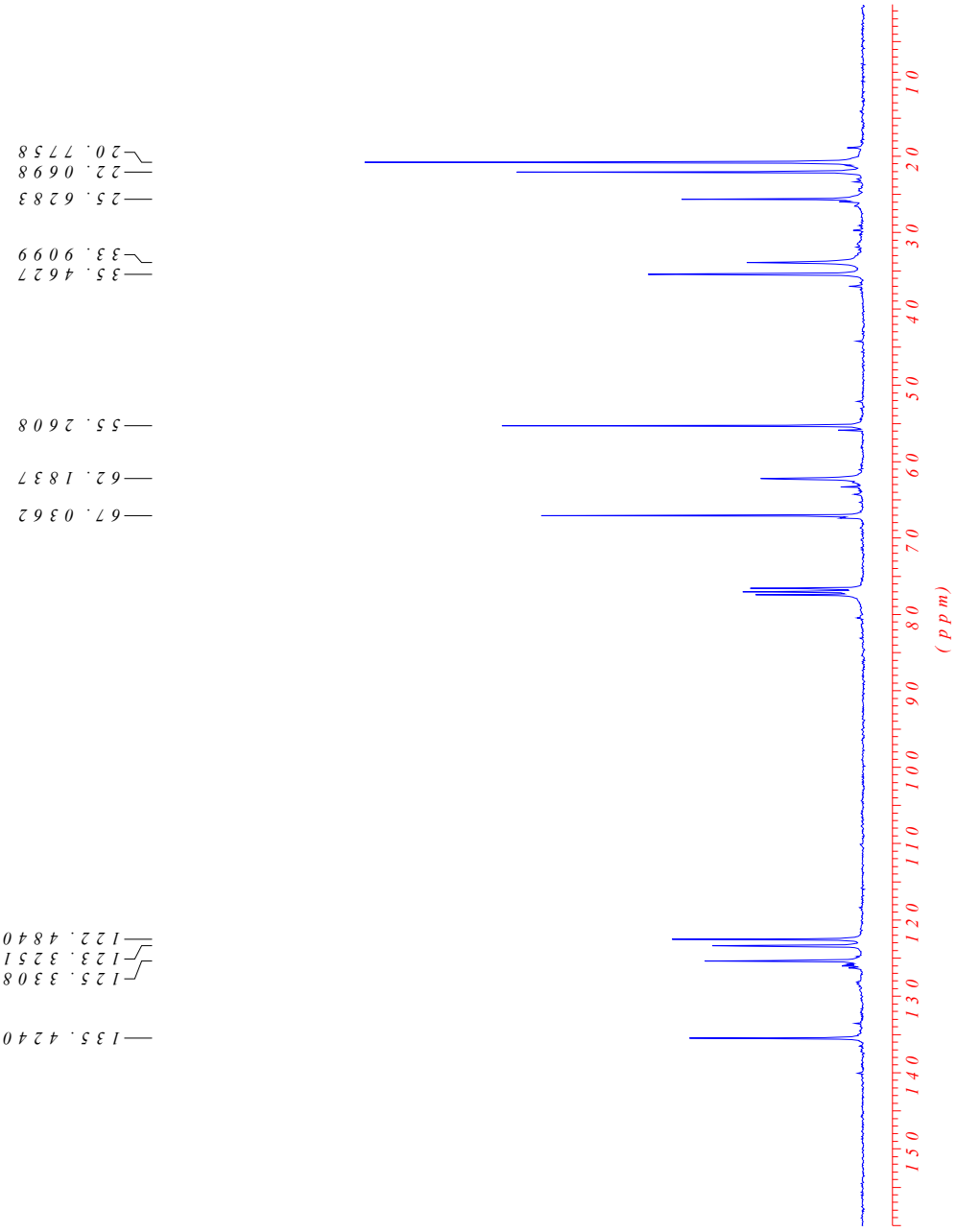
*Pentacarbonyl[(N-(3-(Cyclohexa-1, 3-dienyl)propyl)-N-(2-methylpropyl)amino)methylene]chromium(0) (**25**)*



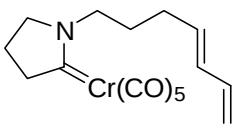


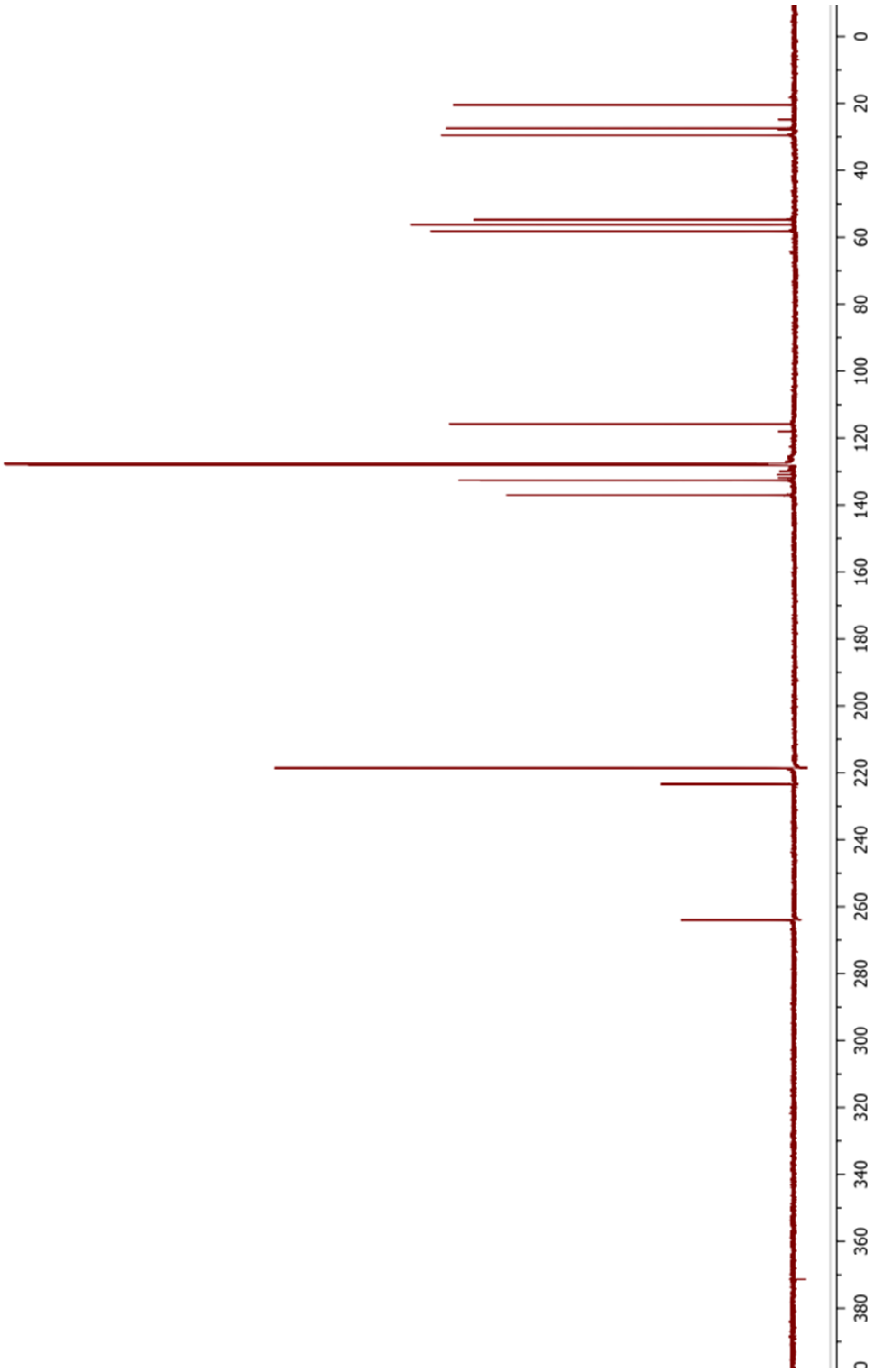
Piperidine ***26***



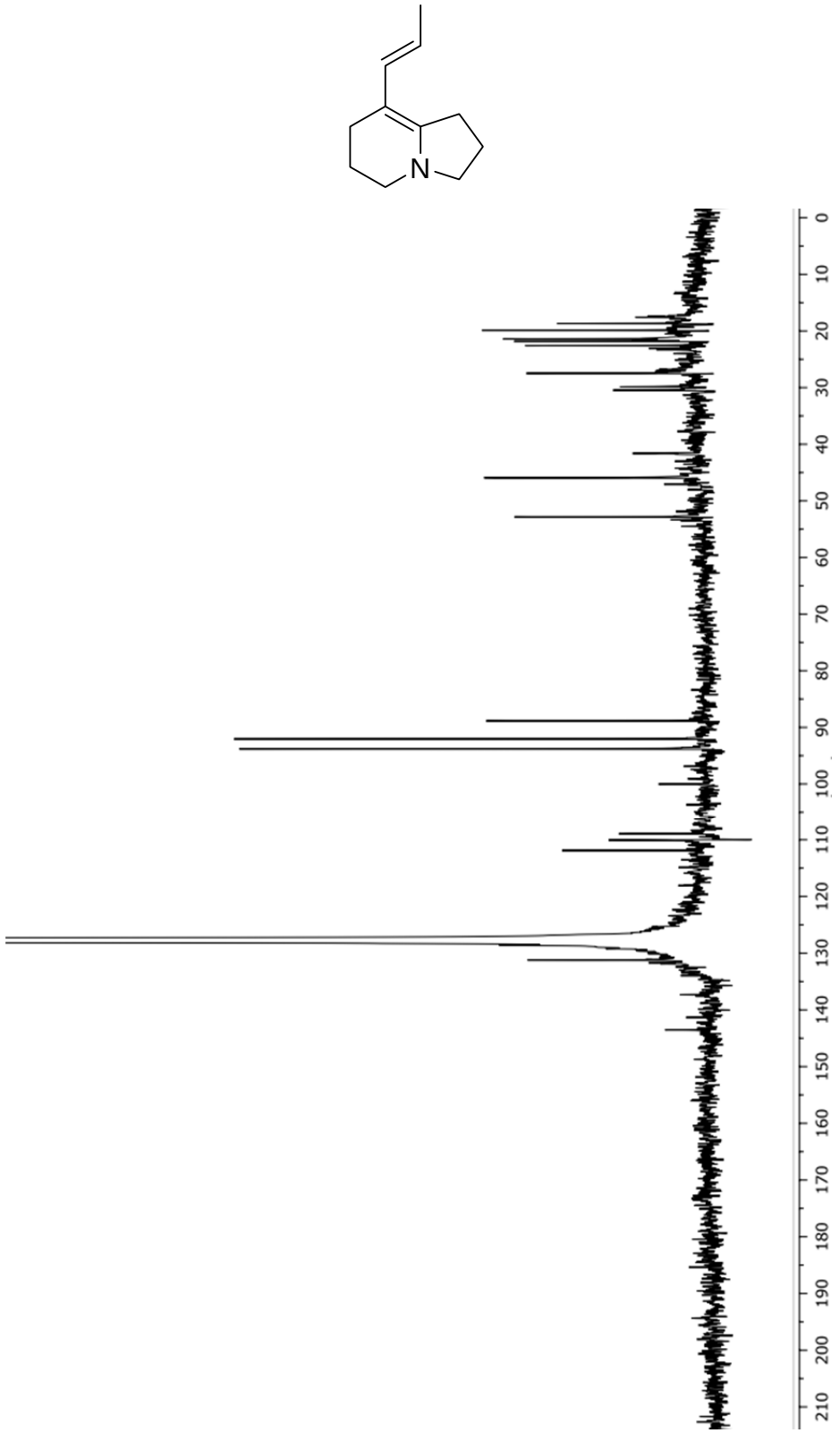


*Chromium aminocarbene (**31**)*

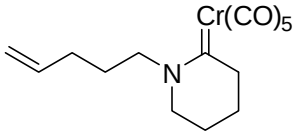


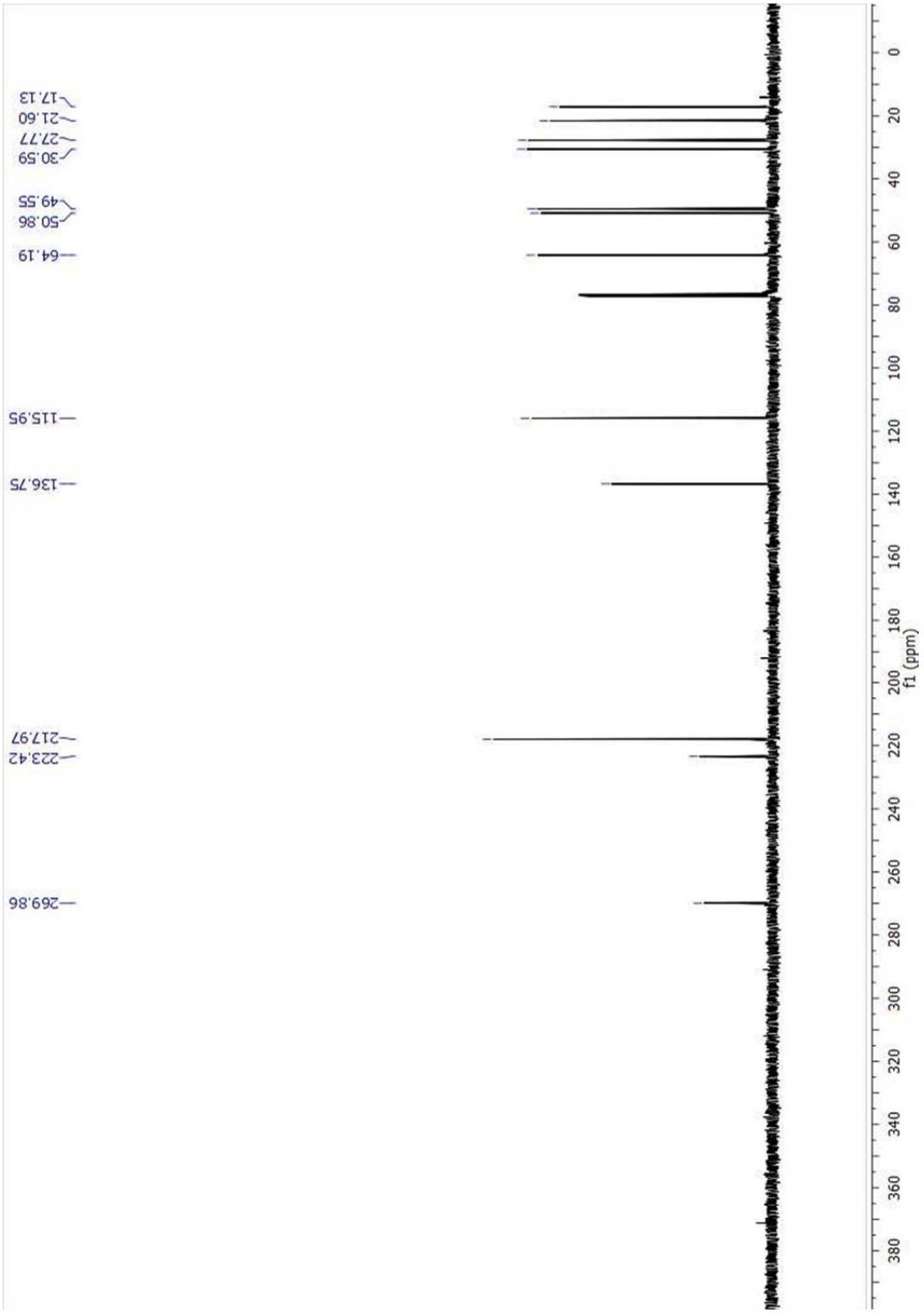


*(E)-8-(prop-1-enyl)-1,2,3,5,6,7-hexahydroindolizine (**32**)*

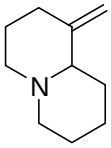


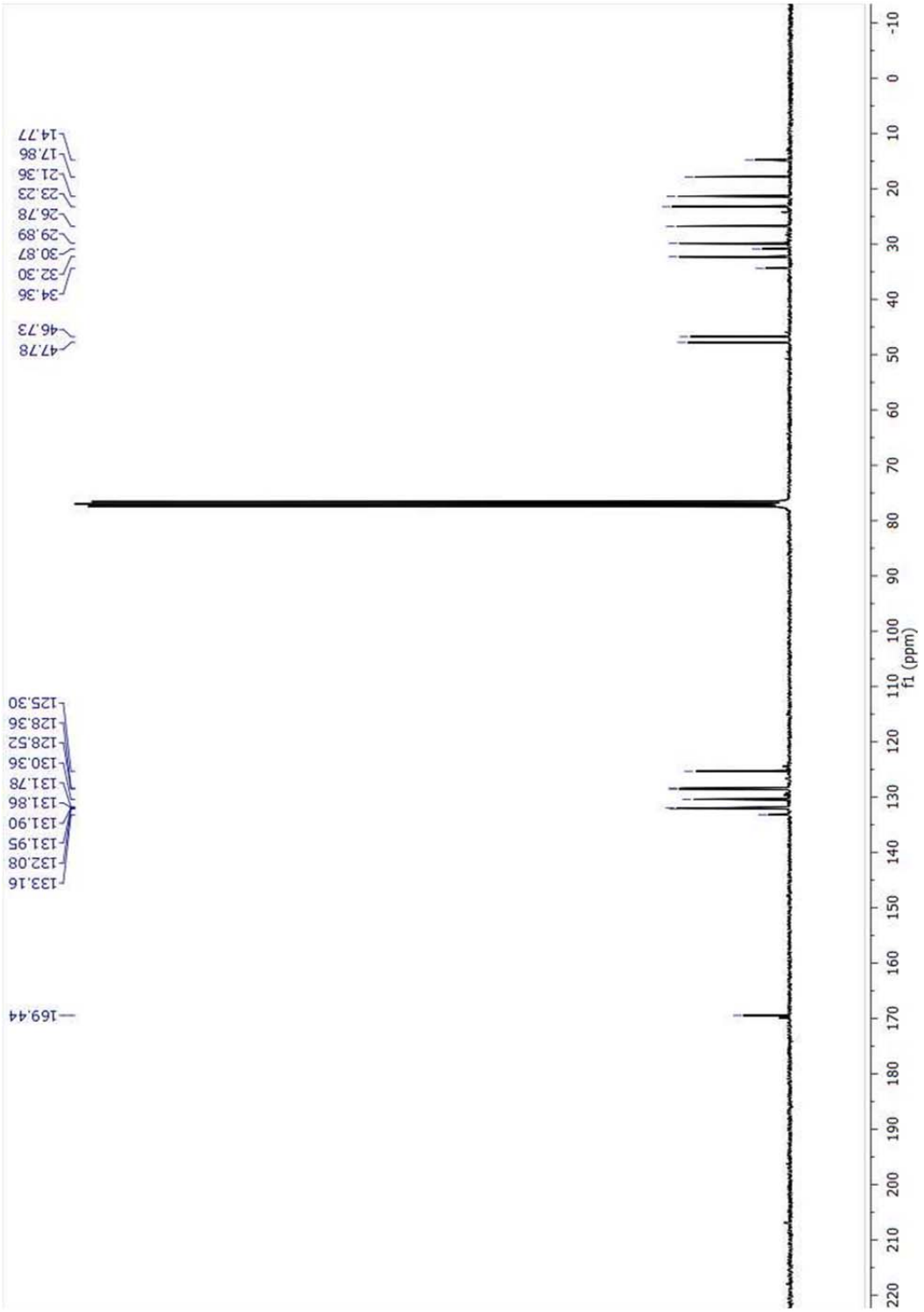
*Chromium aminocarbene (**33**)*



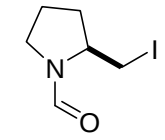


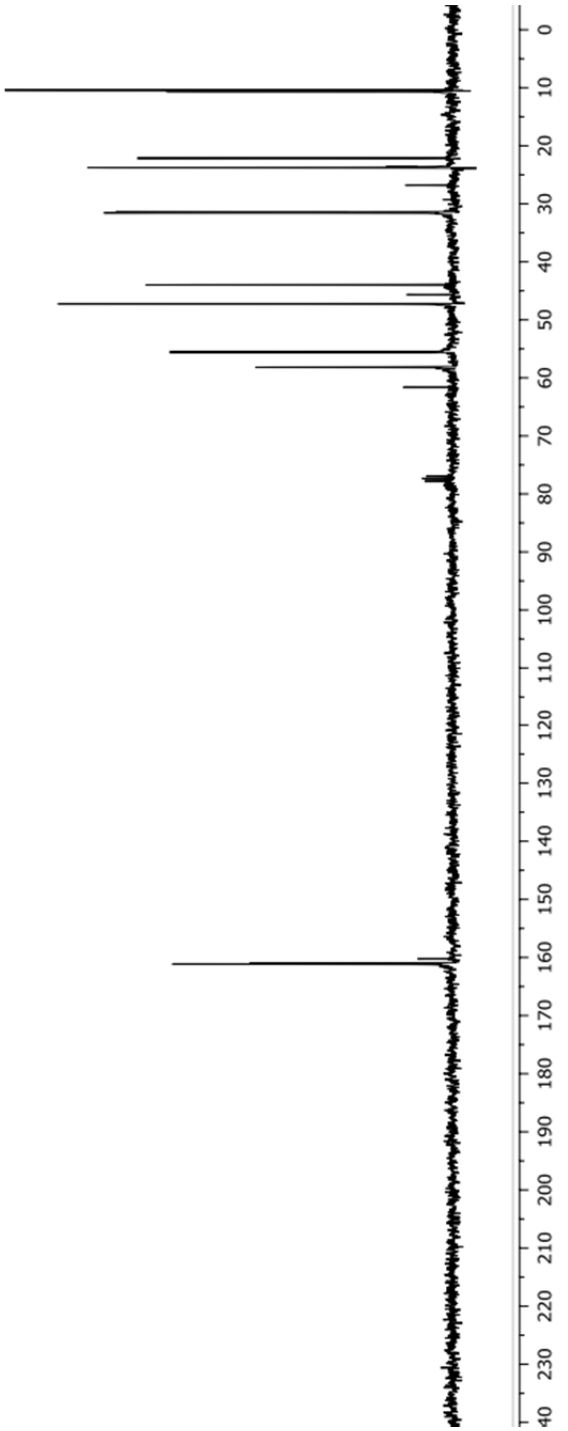
*1-methyleneoctahydro-1H-quinolizine (**34**)*



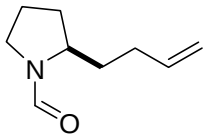


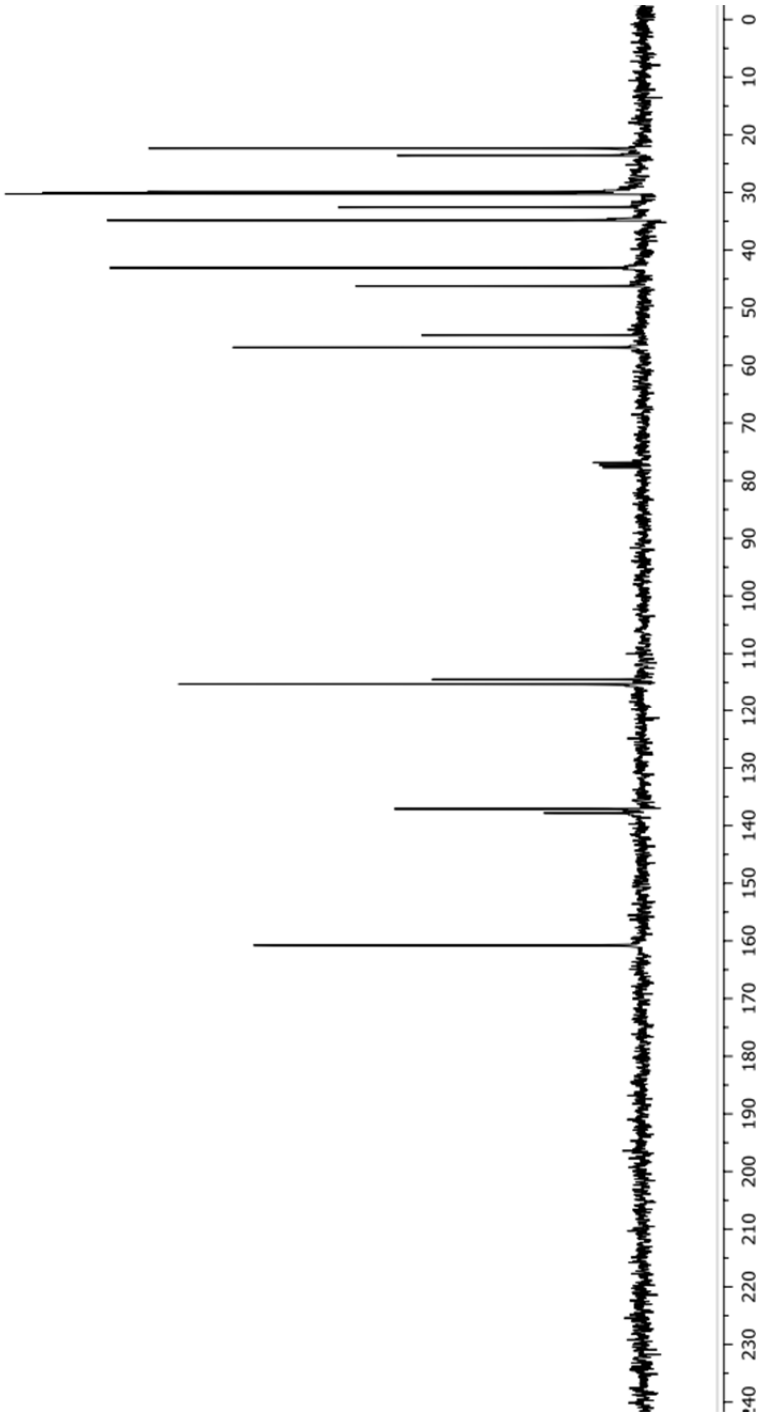
*(S)-2-(iodomethyl)pyrrolidine-1-carbaldehyde (**45**)*



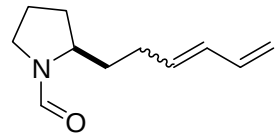


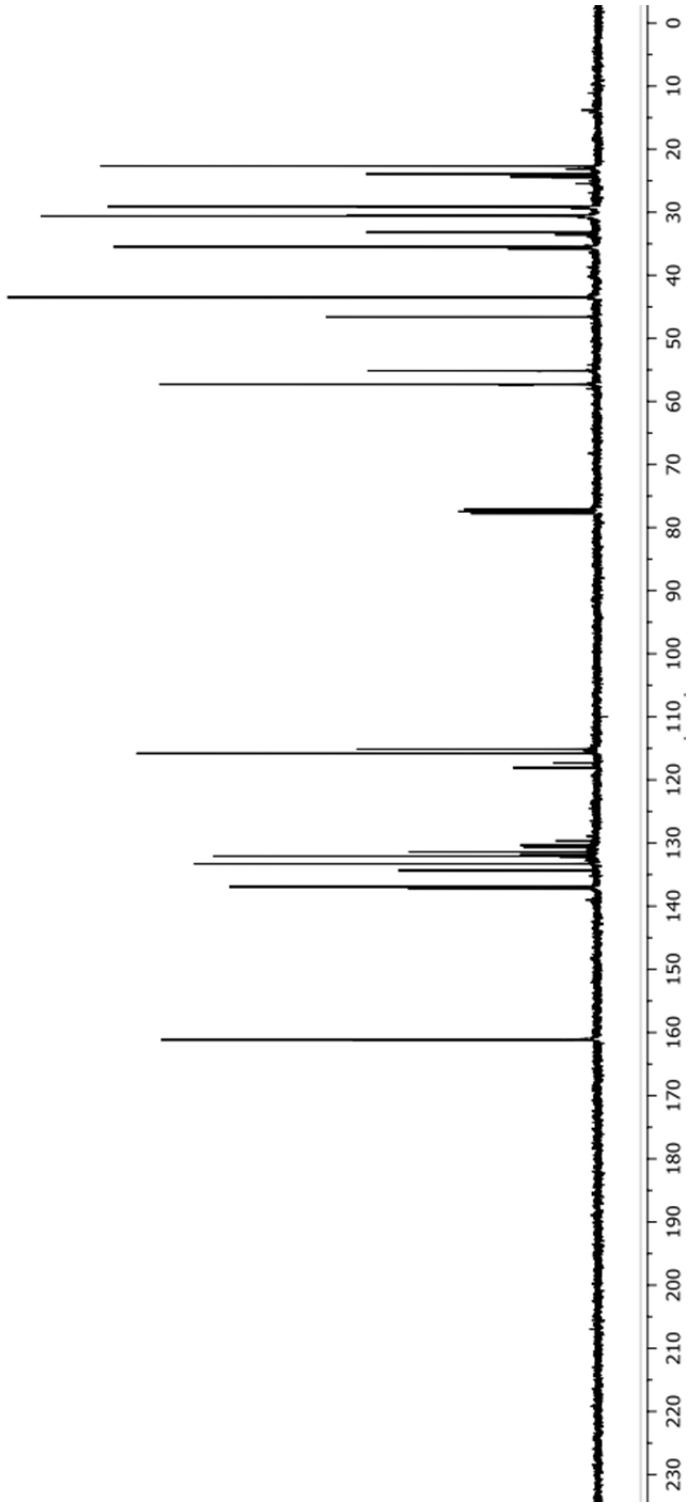
*(R)-2-(but-3-enyl)pyrrolidine-1-carbaldehyde (**47**)*



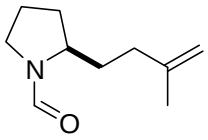


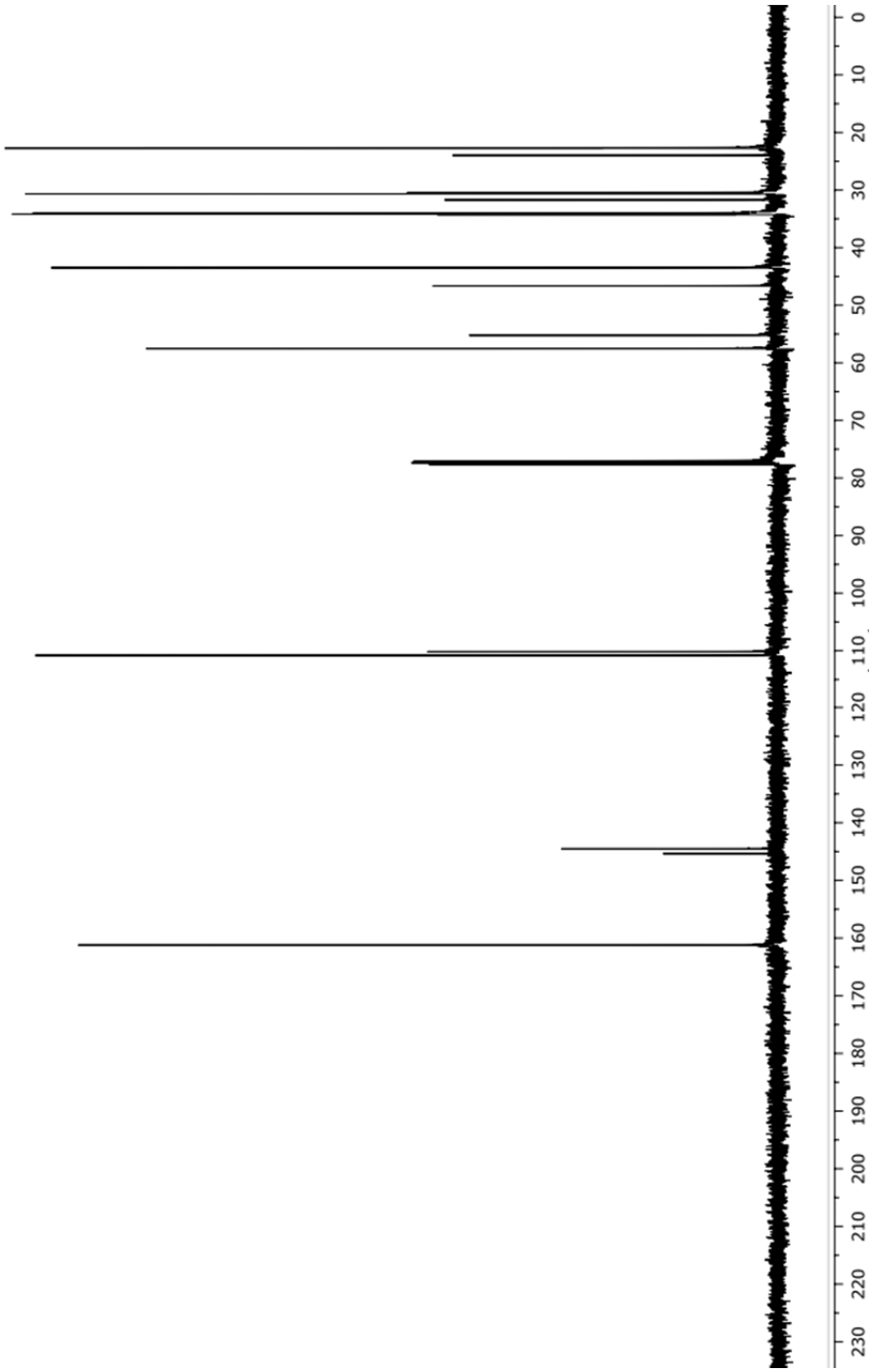
*Mixture of E and Z (R)-2-(hexa-3,5-dienyl)pyrrolidine-1-carbaldehyde (**49**)*



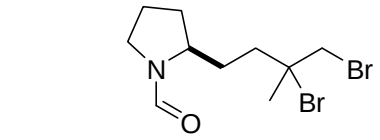


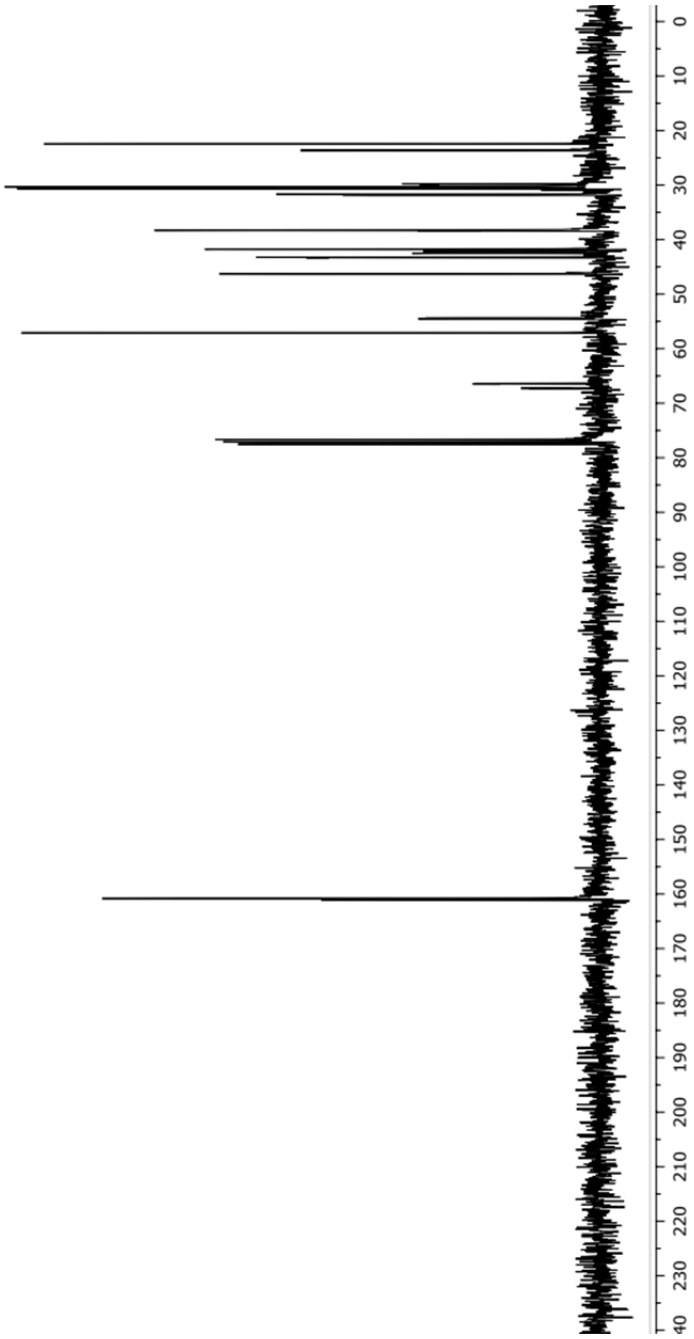
*(R)-2-(3-methylbut-3-enyl)pyrrolidine-1-carbaldehyde (**51**)*



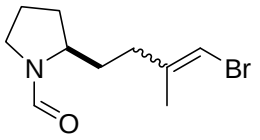


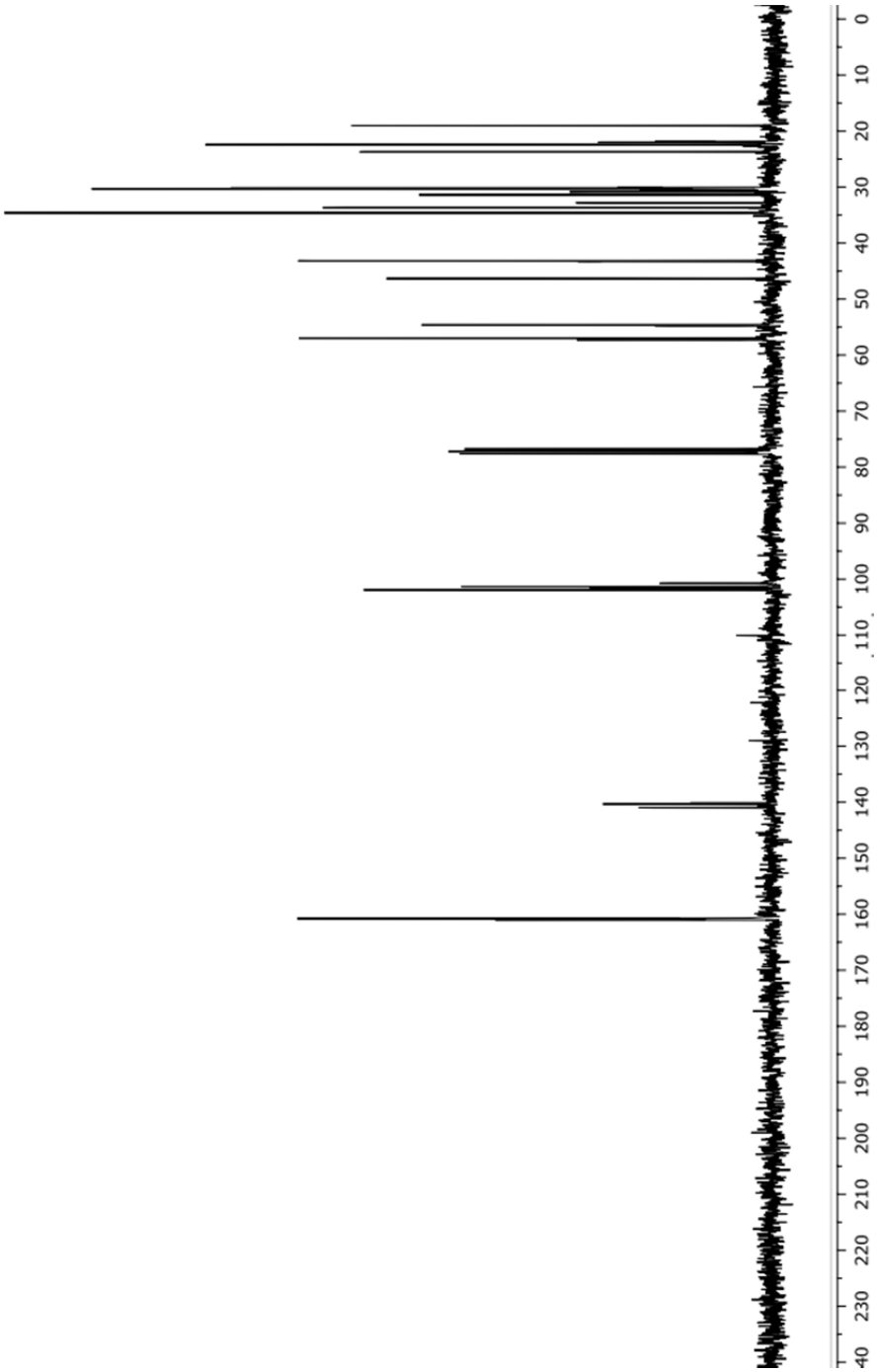
*(2S)-2-(3,4-Dibromo-3-methylbutyl)pyrrolidine-1-carbaldehyde (**52**)*



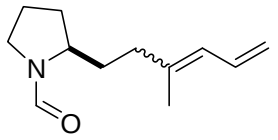


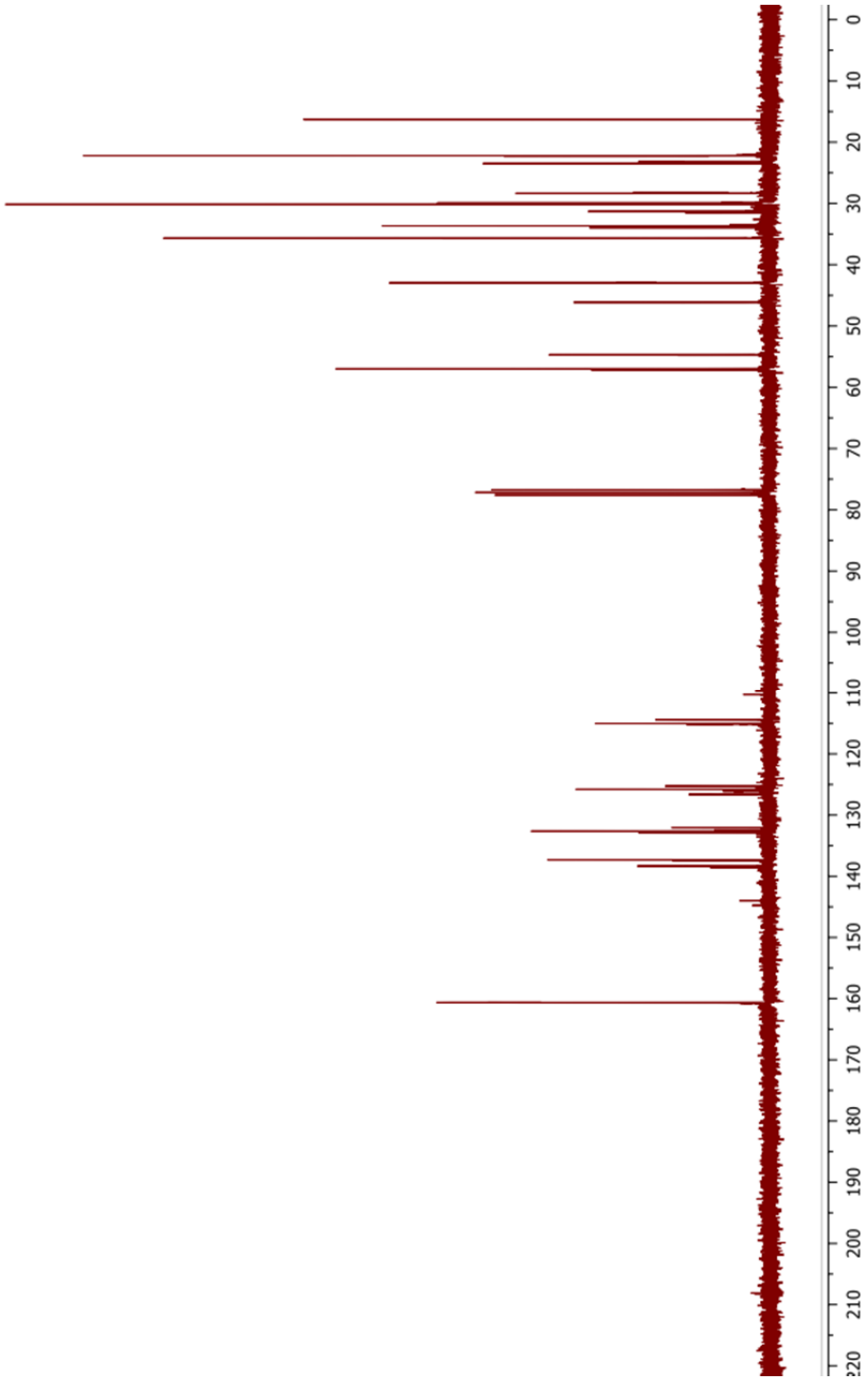
*(R)-2-(4-bromo-3-methylbut-3-enyl)pyrrolidine-1-carbaldehyde (**53**)*



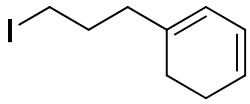


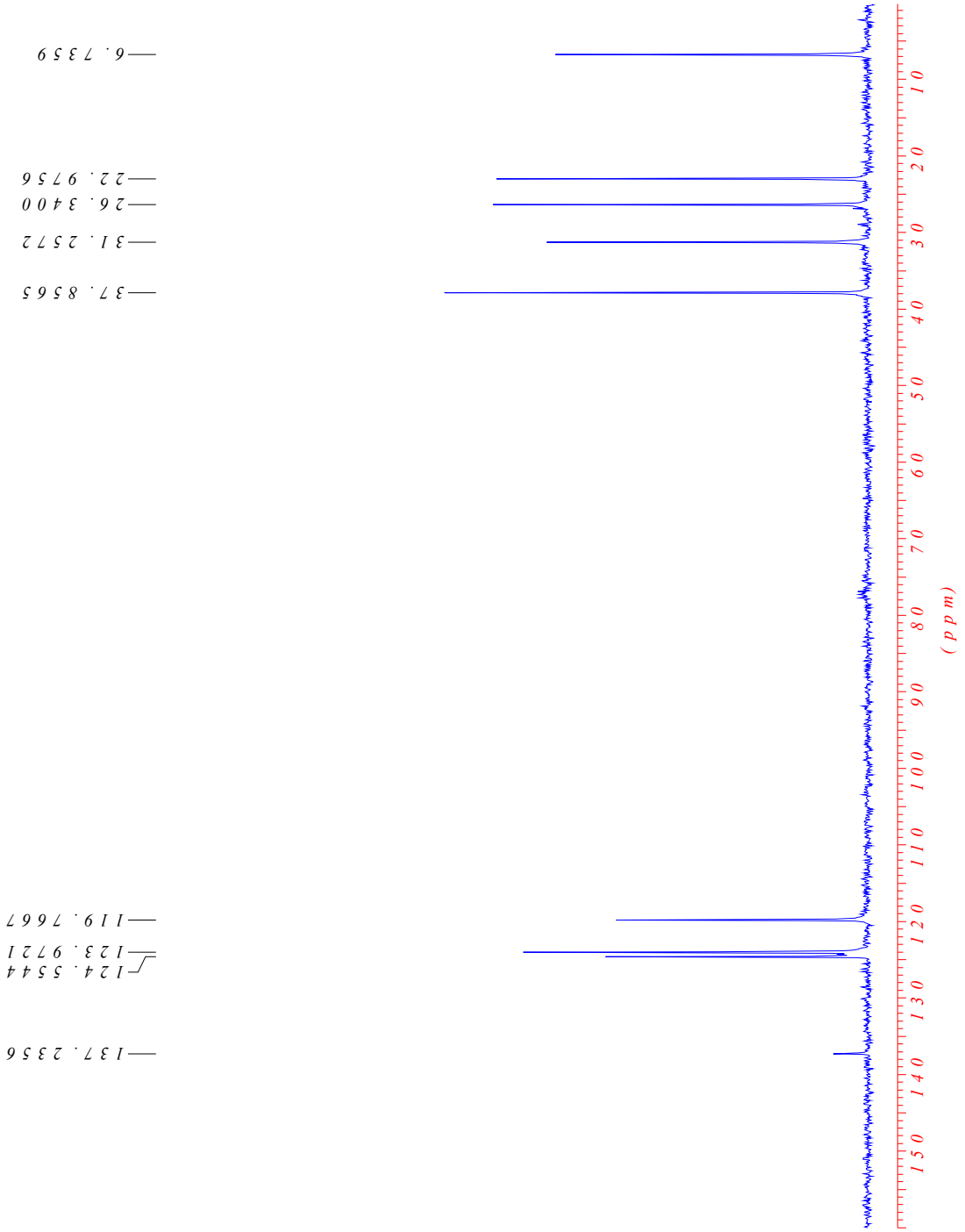
*(R)-2-(3-methylhexa-3,5-dienyl)pyrrolidine-1-carbaldehyde (**54**)*



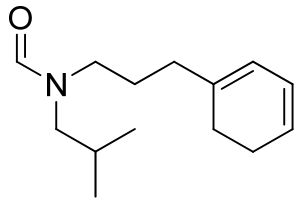


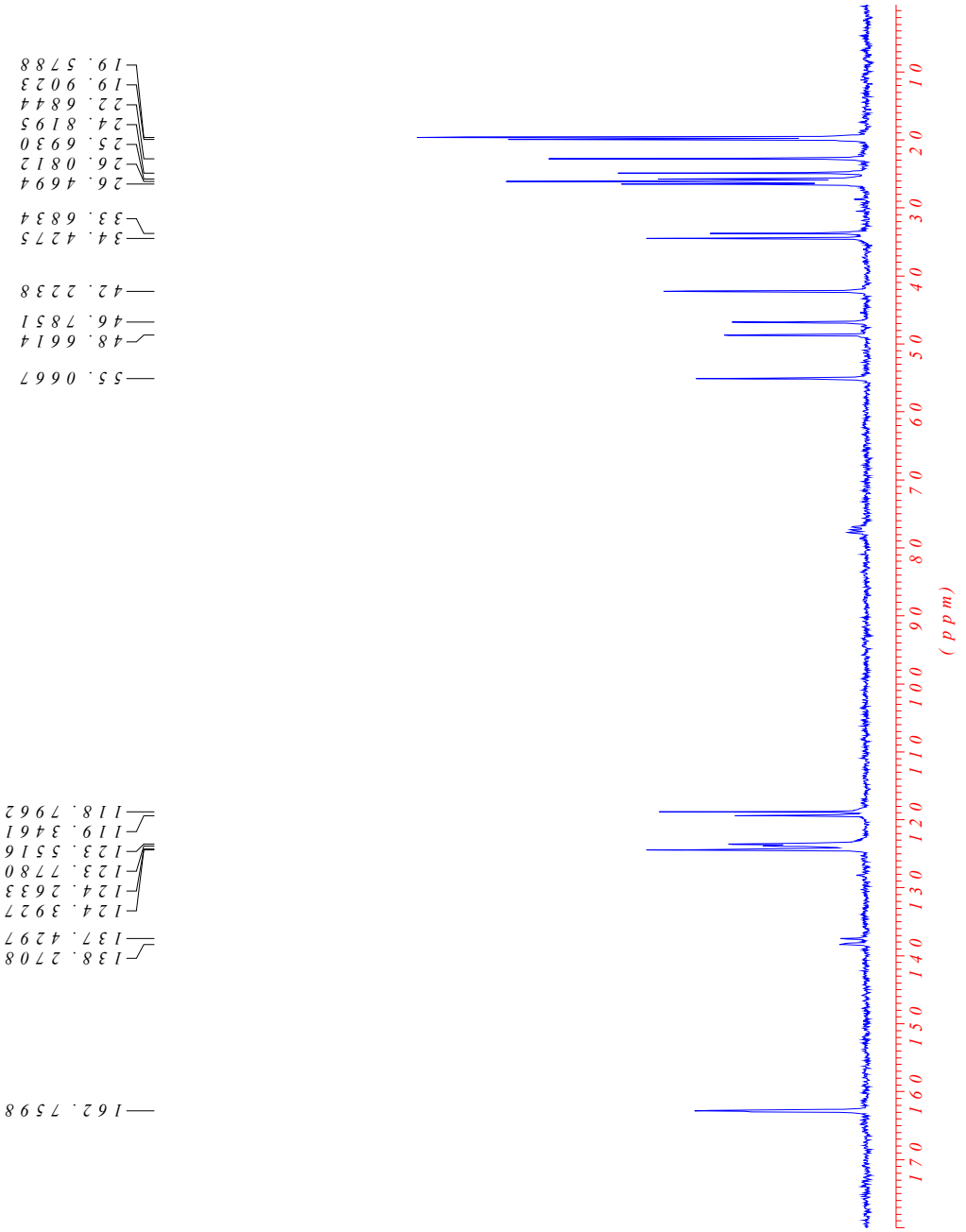
*3-(Cyclohexa-1, 3-dienyl)-1-iodopropane (**56**)*



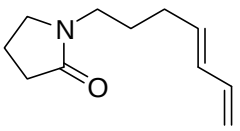


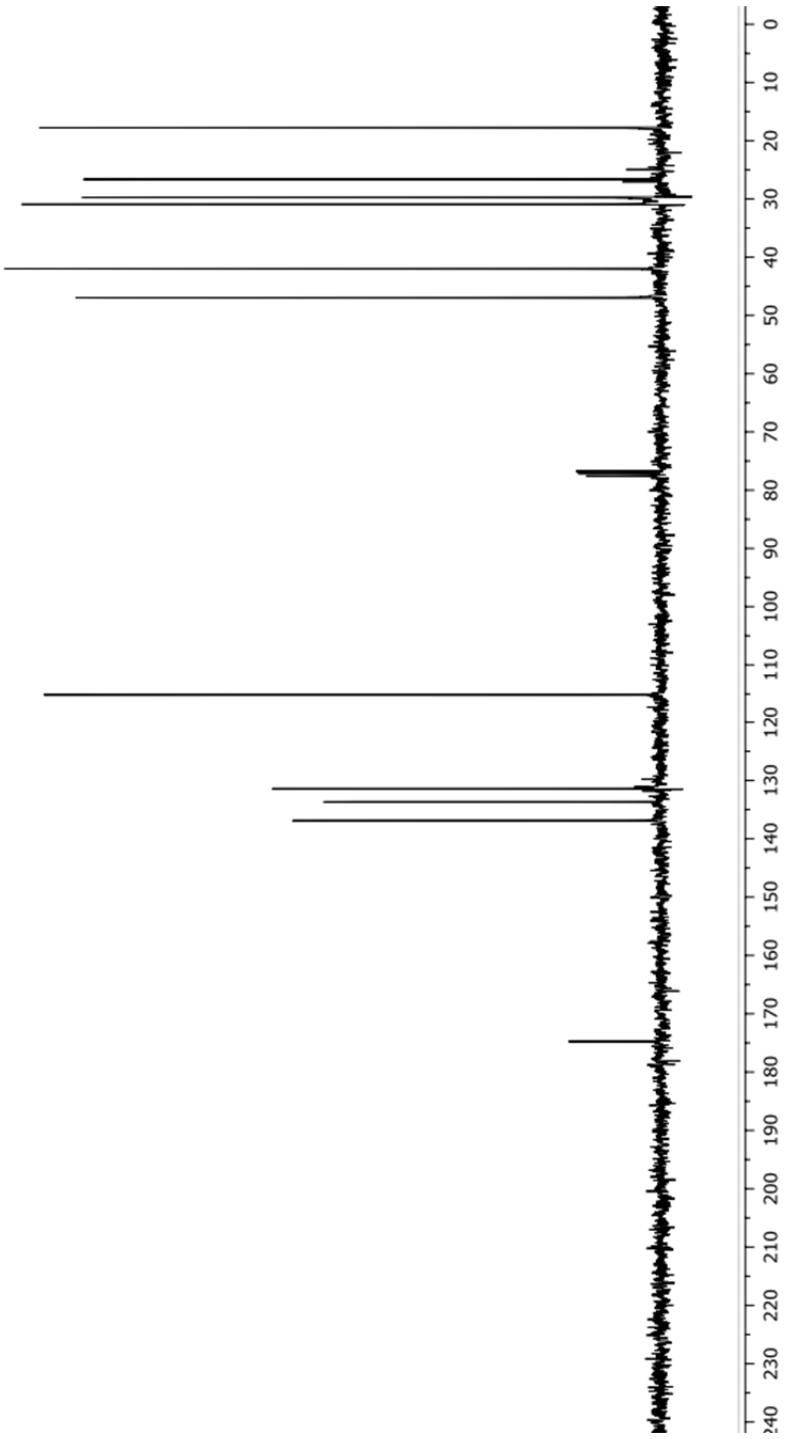
*N-(3-(Cyclohexa-1, 3-dienyl)propyl)-N-(2-methylpropyl)formamide (**57**)*



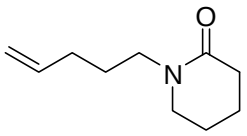


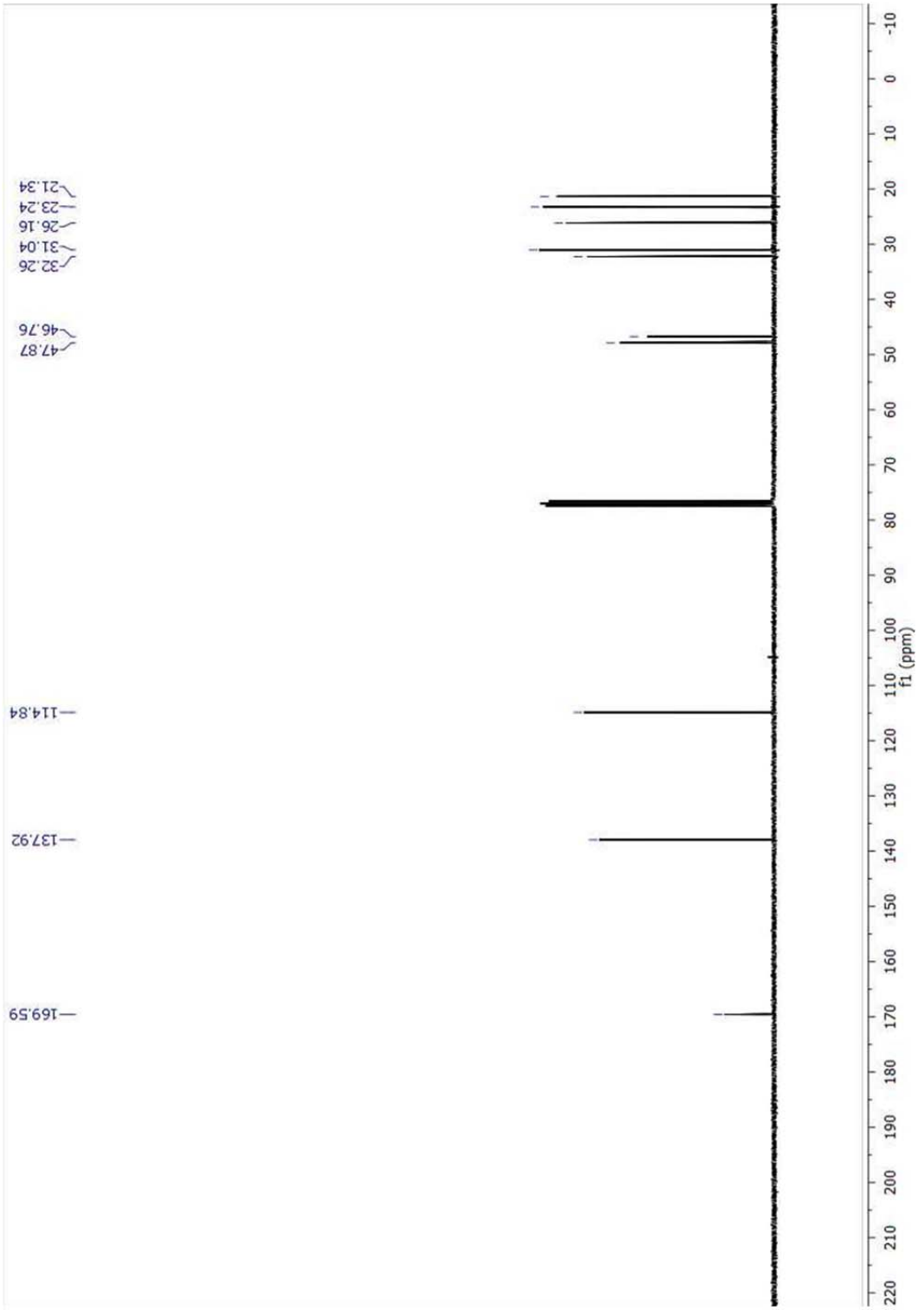
*(E)-1-(hepta-4,6-dienyl)pyrrolidin-2-one (**59**)*



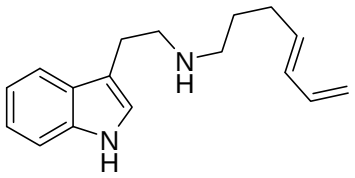


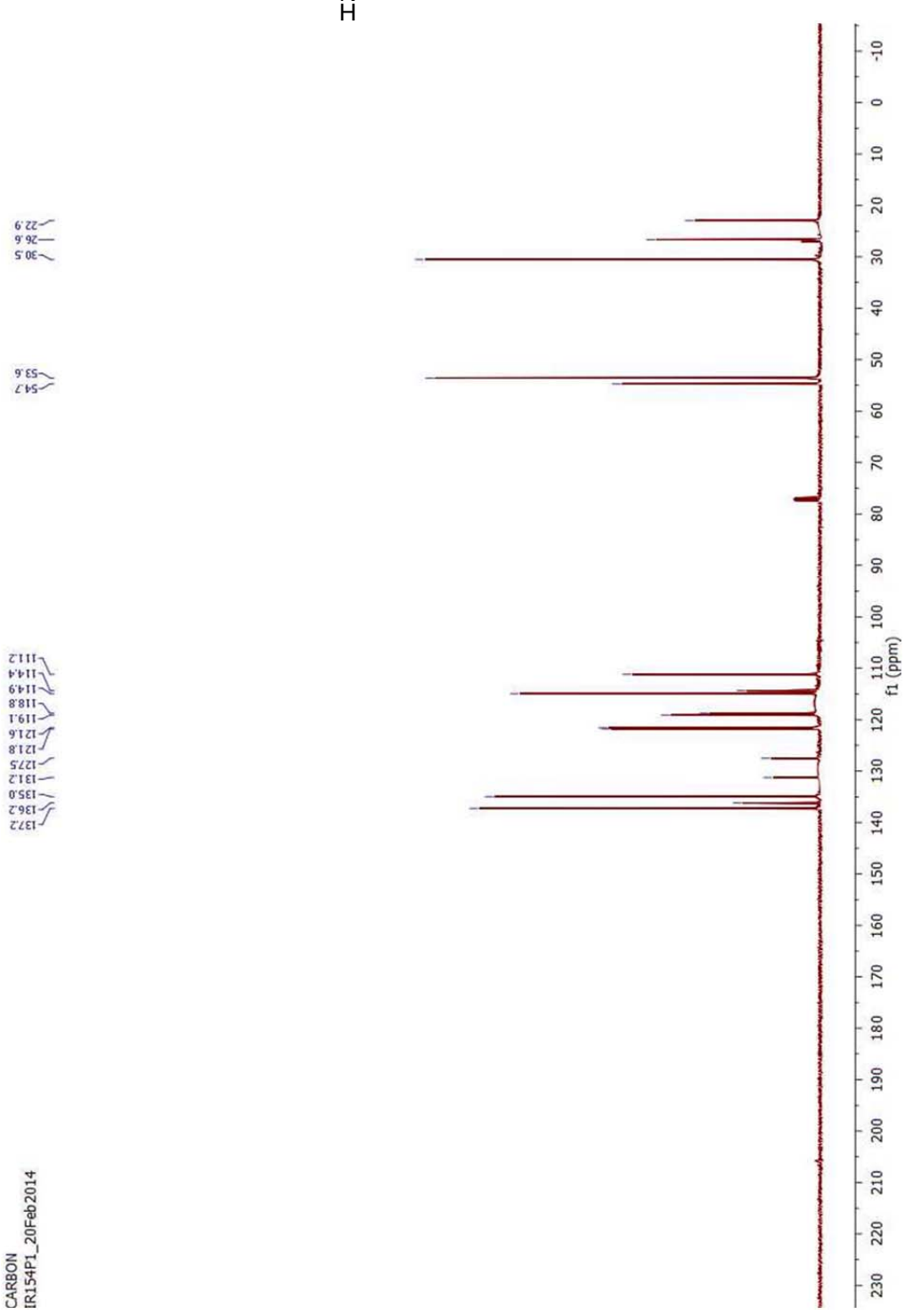
*1-(Pent-4-enyl)piperidin-2-one (**61**)*



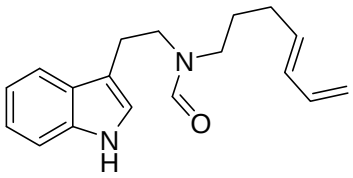


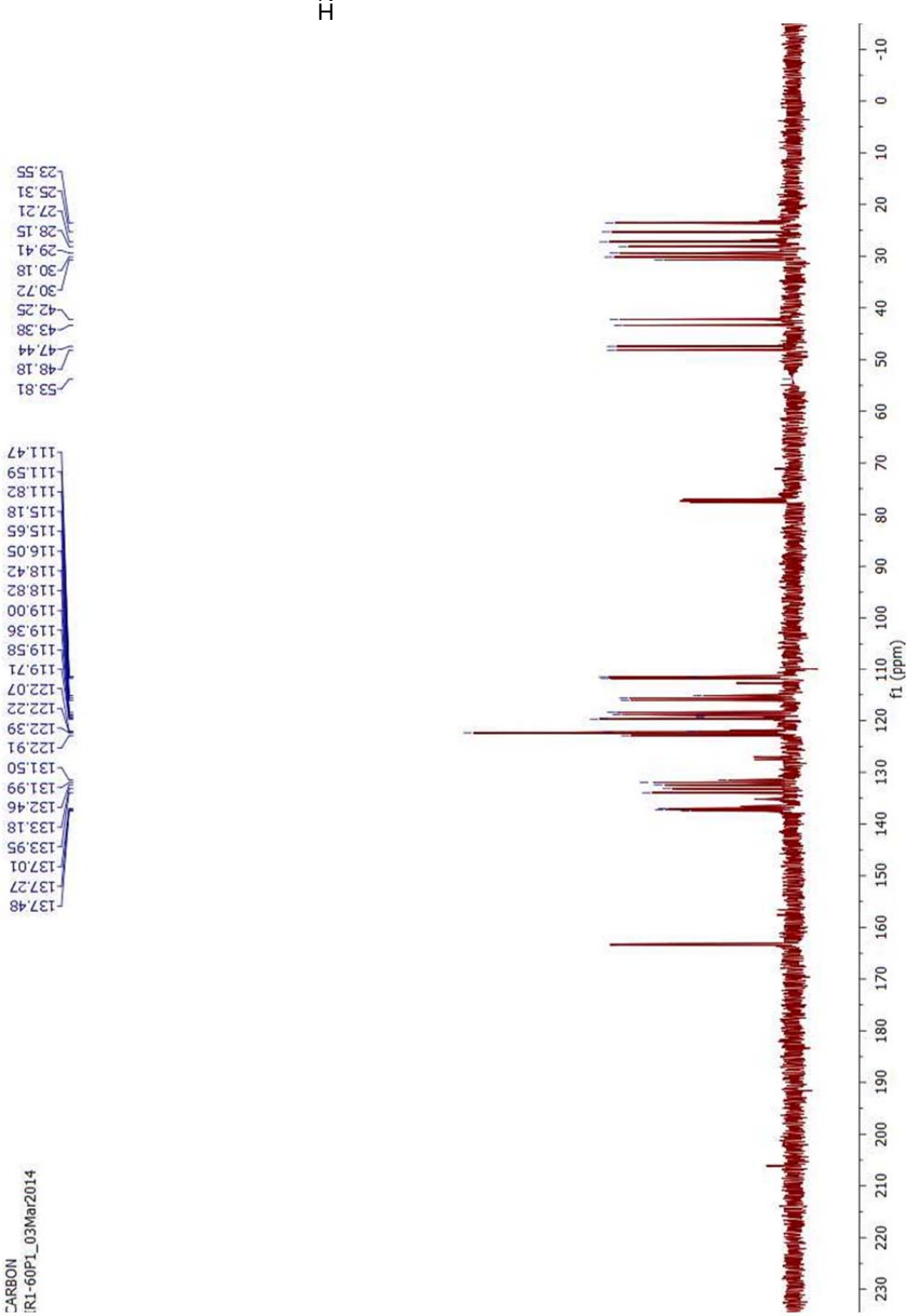
*(E)-N-(2-(1H-indol-3-yl)ethyl)hepta-4,6-dien-1-amine (**63**)*



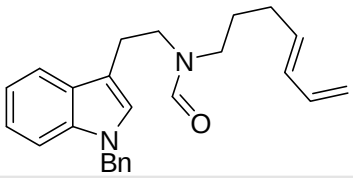


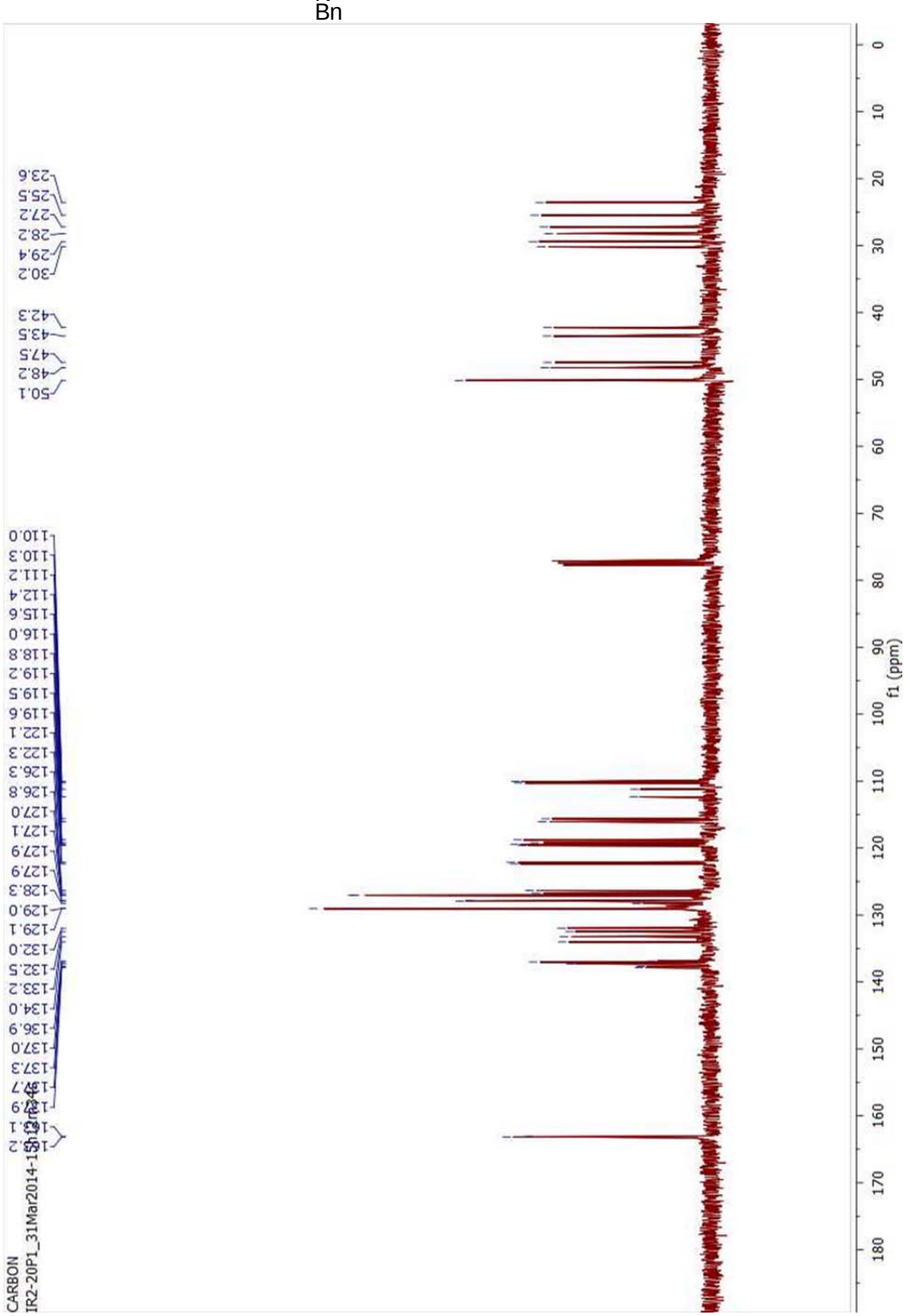
*(E)-N-(2-(1H-indol-3-yl)ethyl)-N-(hepta-4,6-dienyl)formamide (**64**)*



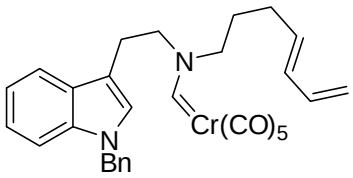


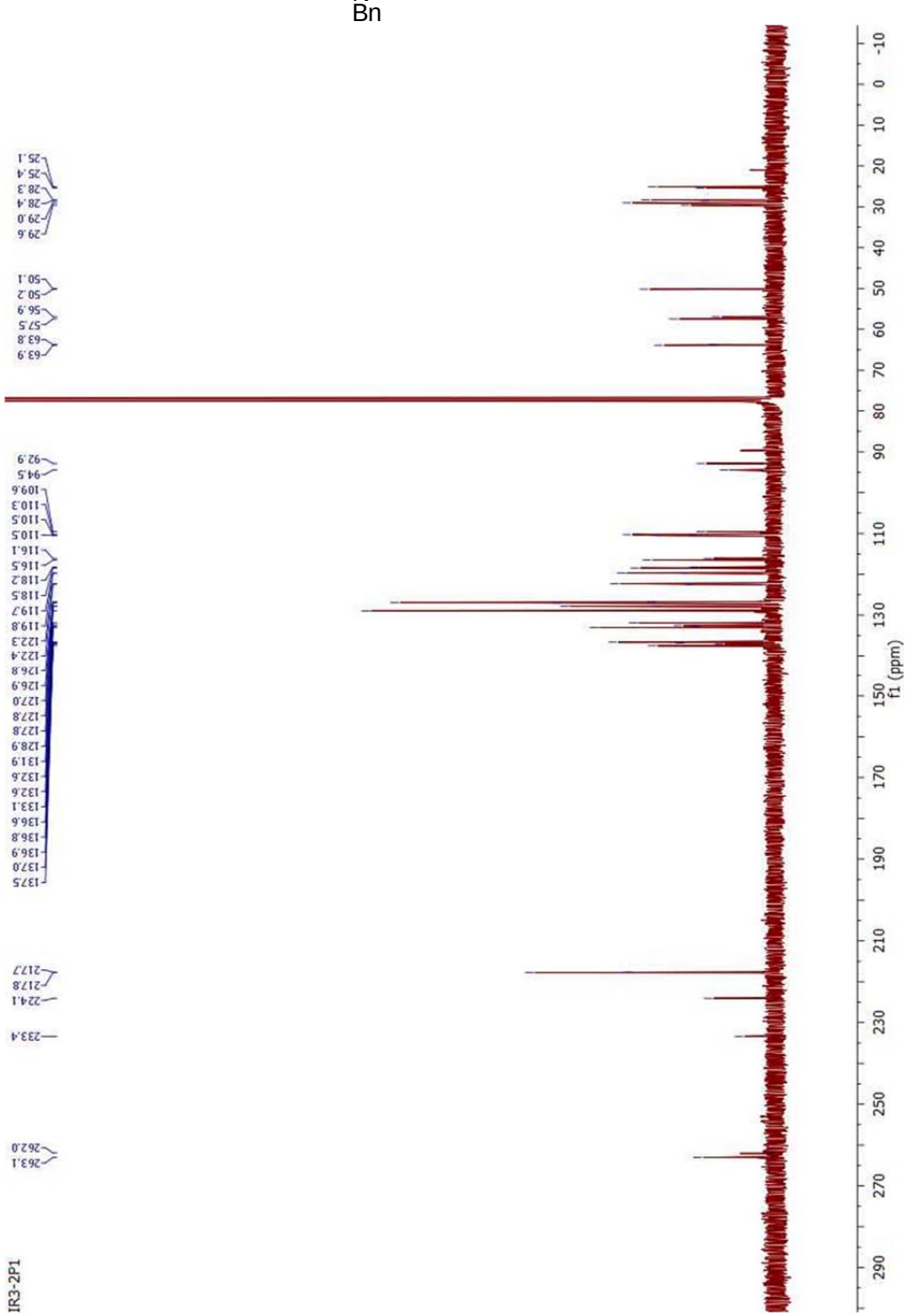
*(E)-N-(2-(1-benzyl-1H-indol-3-yl)ethyl)-N-(hepta-4,6-dienyl)formamide (**36**)*



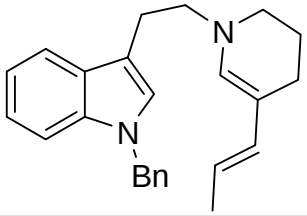


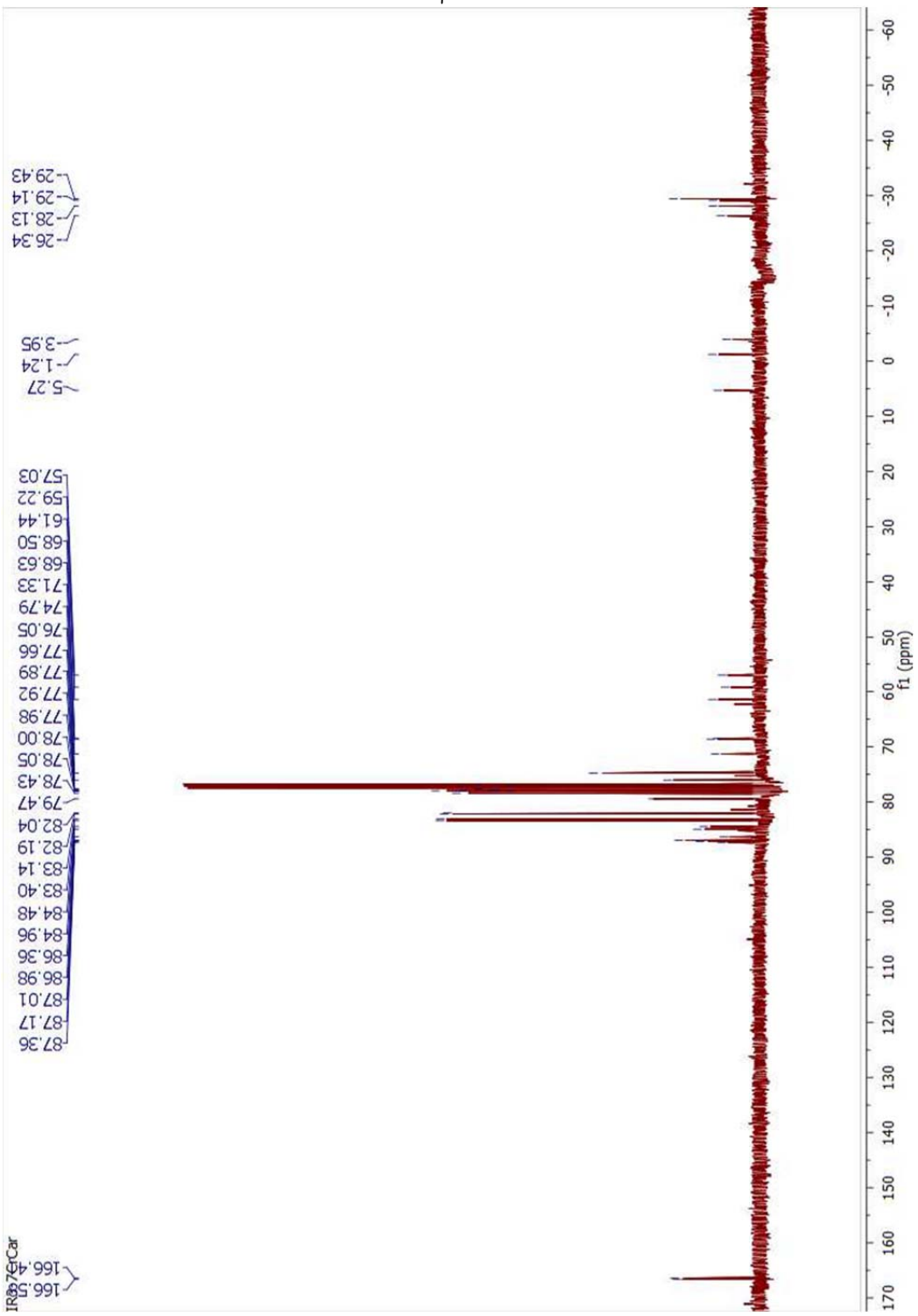
*Pentacarbonyl[((E)-N-(2-(1-benzyl-1H-indol-3-yl)ethyl)-N-(hepta-4,6-dienyl)amino)methylene]chromium(0) (**37**)*



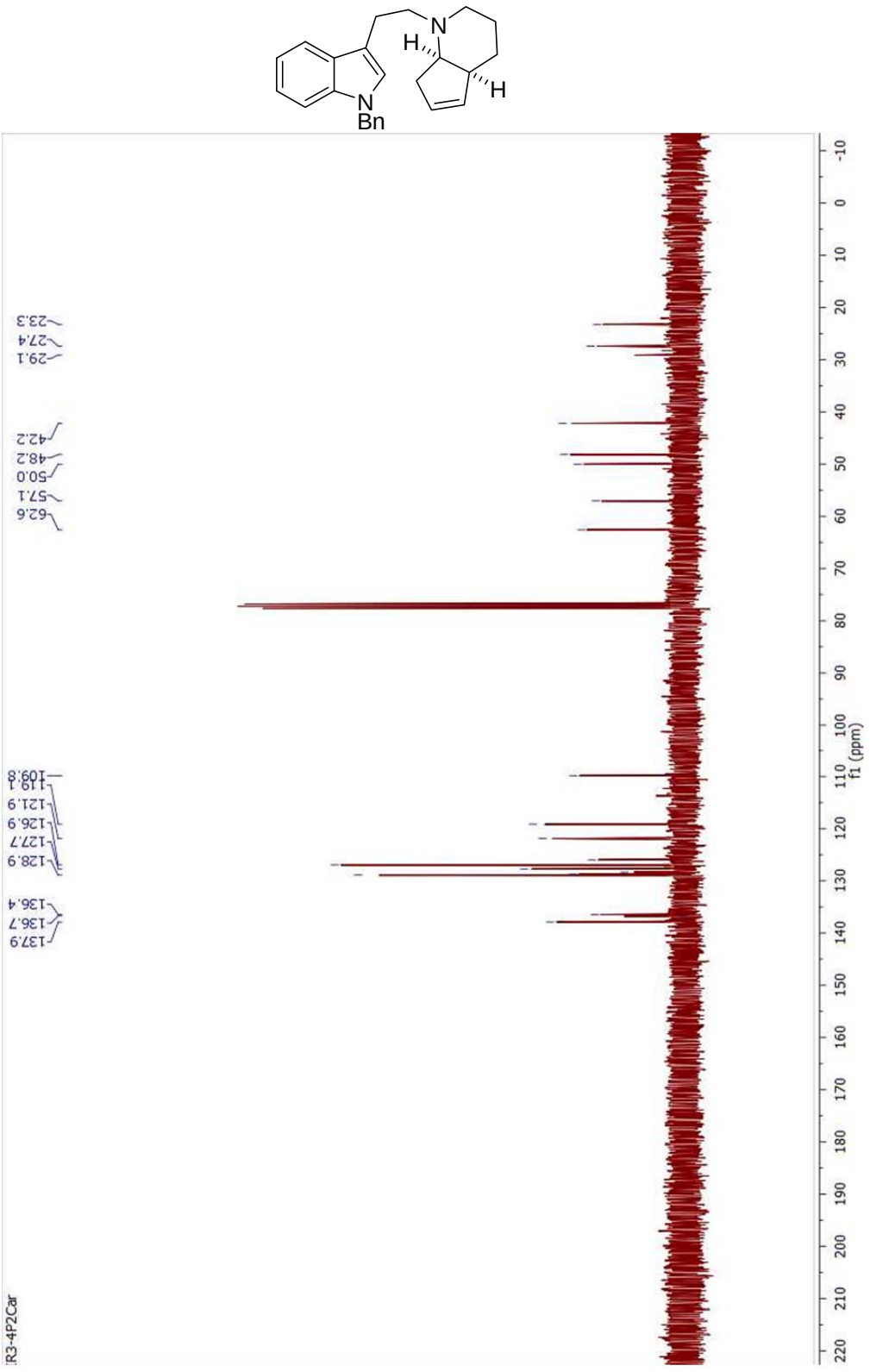


*(E)-1-benzyl-3-(2-(5-(prop-1-enyl)-3,4-dihydropyridin-1(2H)-yl)ethyl)-1H-indole (**38**)*

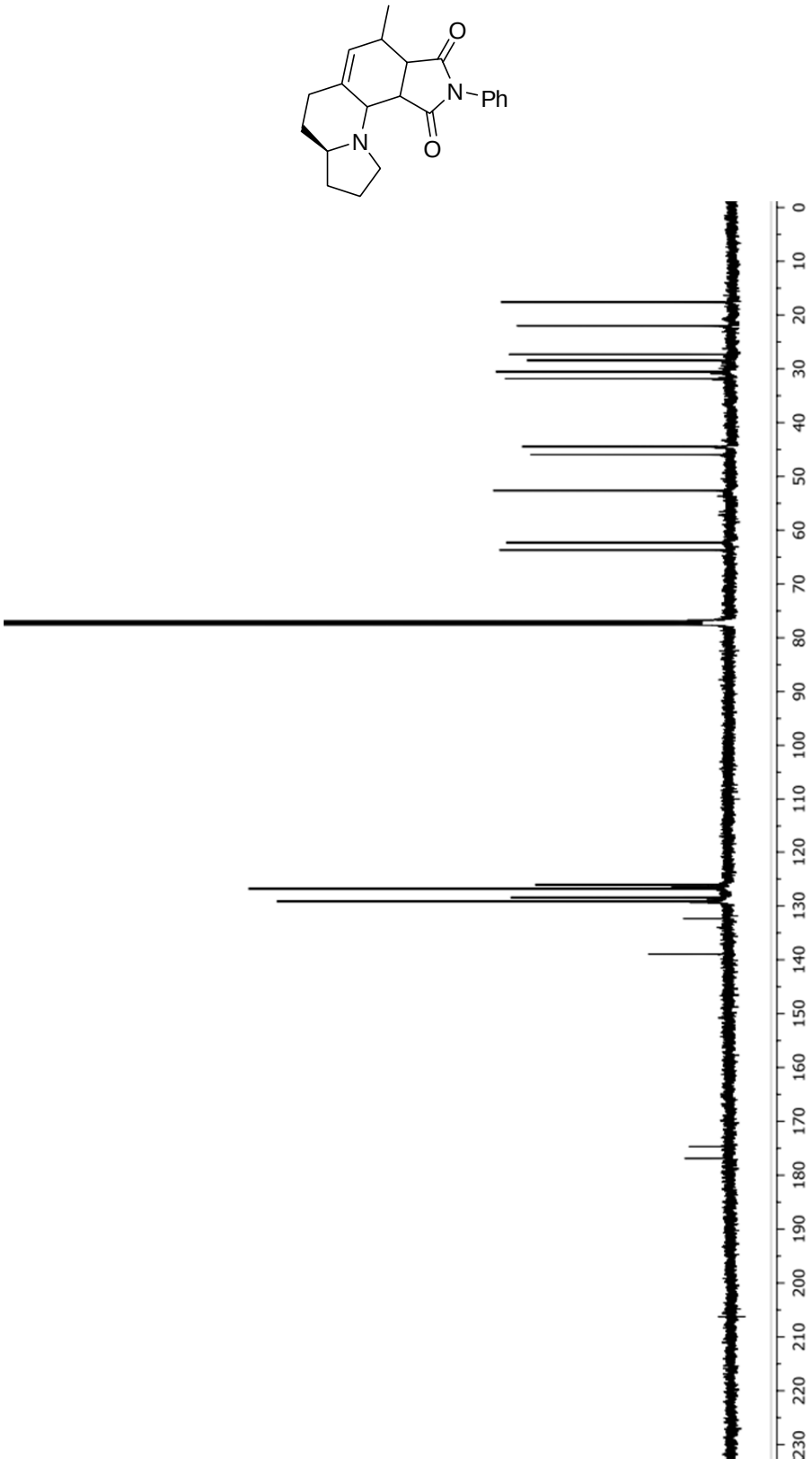




*1-benzyl-3-(2-(4,4a-dihydro-1H-cyclopenta[c]pyridin-2(3H,7H,7aH)-yl)ethyl)-1H-indole (**39**)*

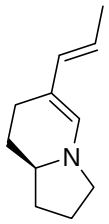


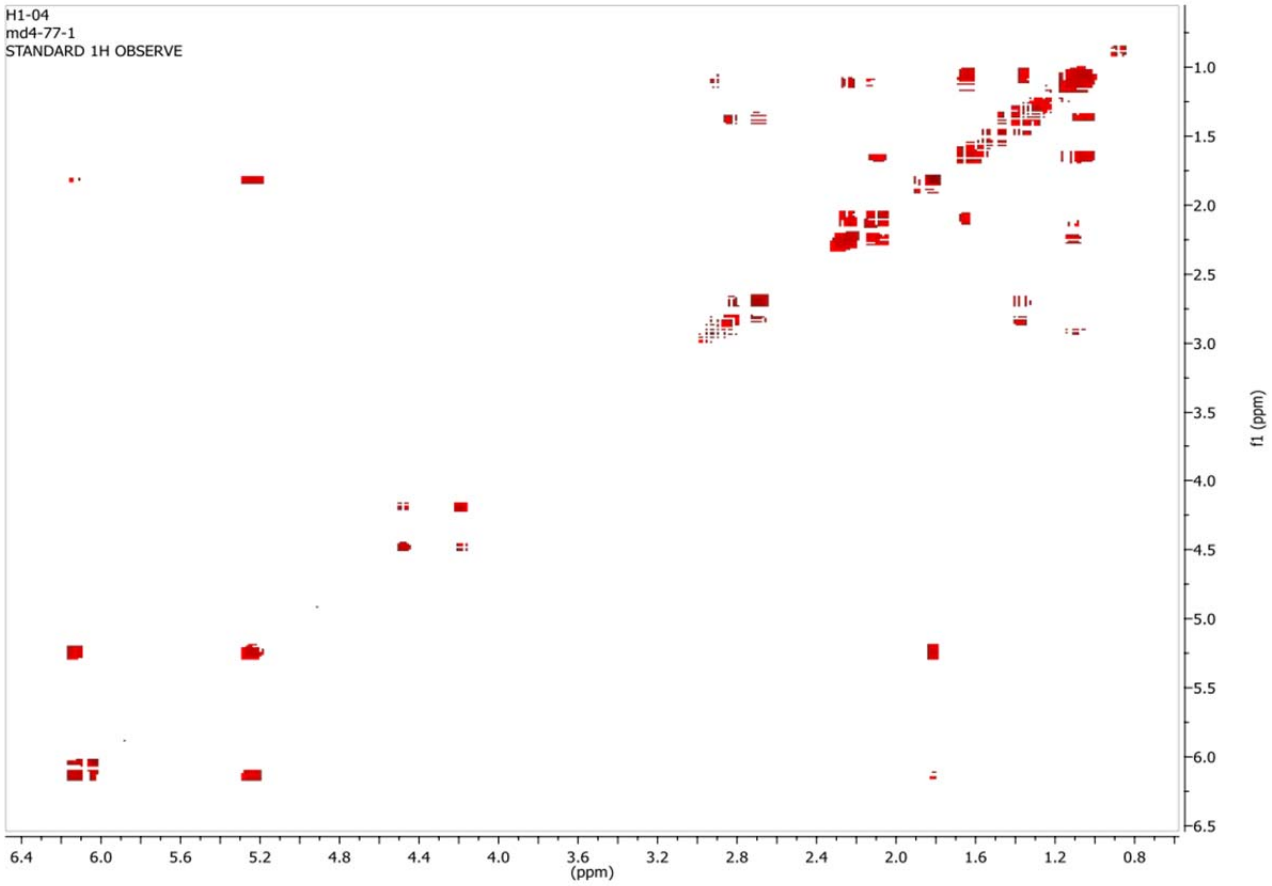
*(7aR)-4-methyl-2-phenyl-3a,4,6,7,7a,8,9,10,11a,11b-decahydro-1H-dipyrrolo[1,2-a:3',4'-h]quinoline-1,3(2H)-dione (**66**)*



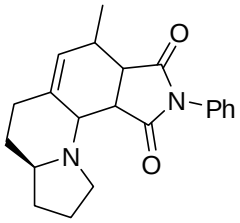
COSY SPECTRA

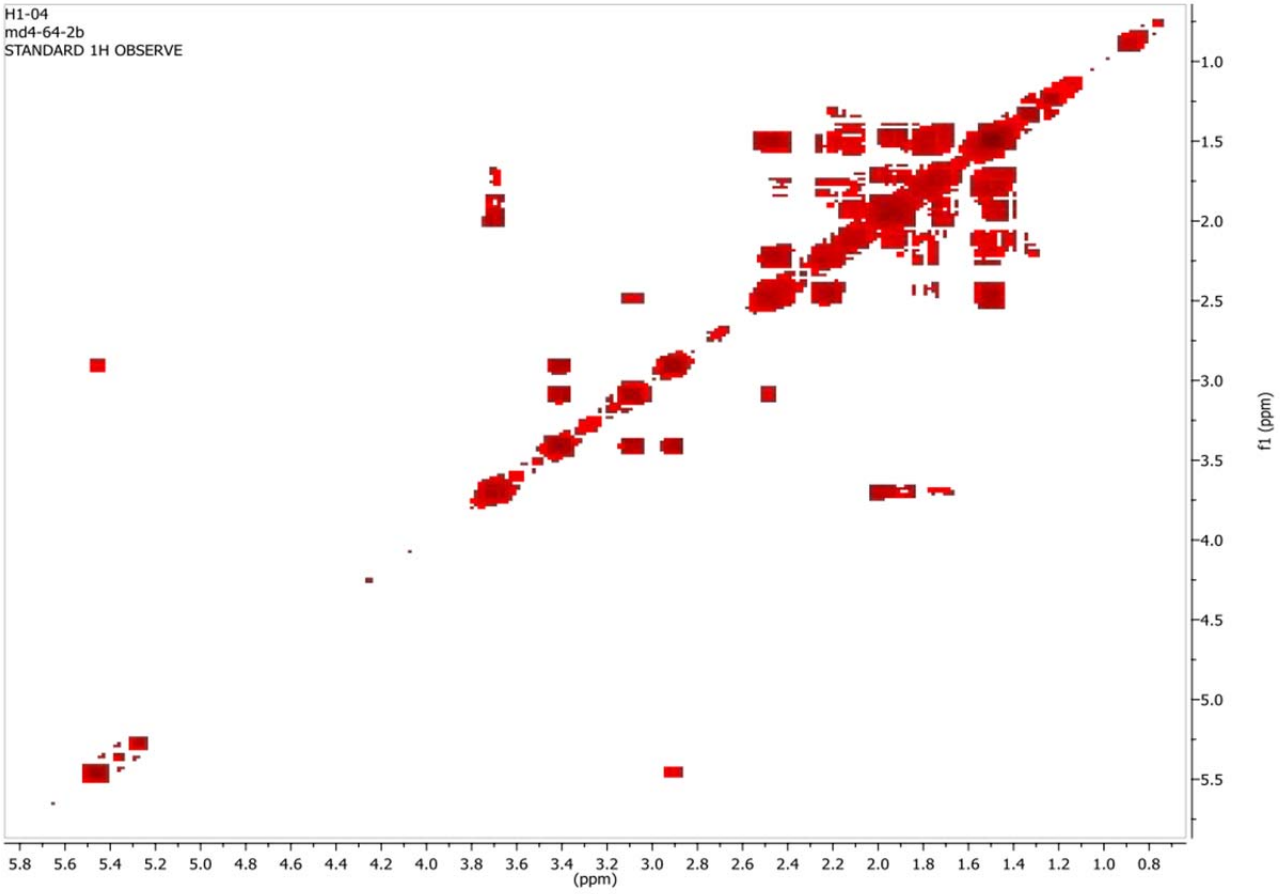
*(R,E)-6-(prop-1-enyl)-1,2,3,7,8,8a-hexahydroindolizine (**21**) in C_6D_6*





*(7aR)-4-methyl-2-phenyl-3a,4,6,7,7a,8,9,10,11a,11b-decahydro-1H-dipyrrolo[1,2-a:3',4'-h]quinoline-1,3(2H)-dione (**66**) in $CDCl_3$*





References and notes

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