Nickel-Catalyzed Synthesis of Acrylamides from Alpha Olefins and Isocyanates

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Supporting Information

Experimental Procedures and Spectroscopic Data for Compounds **1a** through **19**.
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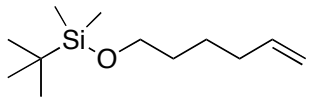
General Information.

Unless otherwise noted, all reactions were performed under an oxygen-free atmosphere of argon or nitrogen with rigid exclusion of moisture from reagents and glassware. Toluene and dichloromethane were distilled from calcium hydride. Bis(1,5-cyclooctadienyl)nickel(0) ($Ni(cod)_2$) and *N*,*N*'-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) were purchased from Strem Chemicals, Inc., stored under nitrogen atmosphere and used without further purification. All isocyanates were purchased from Aldrich Chemical Co. They were filtered to remove solid material and degassed with argon before use. Oct-1-ene, imidazole, and trifluoroacetic acid were purchased from Avocado Organics and used without further purification. Allylbenzene, vinylcyclohexane, 4-methylpent-1-ene, hex-5-en-2-one, hex-5-en-1-ol, and benzoyl chloride were purchased from Aldrich Chemical Co. and used without further purification. (*R*)-β-citronellene and triethylamine were purchased from Fluka and used without further purification. *Tert*-butyldimethylsilyl chloride was purchased from Alfa Aesar and used without further purification.

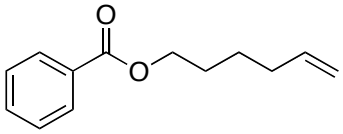
Analytical thin-layer chromatography (TLC) was performed using EM Science silica gel 60 F_{254} plates. The developed chromatogram was visualized by UV lamp (254 nm) or stained with aqueous potassium permanganate ($KMnO_4$). Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on Silicycle silica gel (230-400 mesh). ^1H and ^{13}C NMR spectra were recorded on Varian 500 MHz spectrometers in $CDCl_3$. Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), coupling constant in hertz (Hz), and integration. Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of $CDCl_3$ (77.23 ppm) on the δ scale. Infrared (IR) spectra were recorded on a Perkin-Elmer 2000 FT-IR. High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXII 3 Fourier Transform Mass Spectrometer by Ms. Li Li of the Massachusetts Institute of Technology, Department of Chemistry Instrumentation Facility. Specific rotations ($[\alpha]_D$) were measured on a Perkin-Elmer 241 polarimeter at 589 nm where applicable.

Preparation of Alkene Reagents.



***Tert*-butyl(hex-5-enyloxy)dimethylsilane.**
In a 250 mL flask equipped with stir bar, hex-5-en-1-ol (1.89 mL, 15.8 mmol, 1.05 equiv) was dissolved in 150 mL dichloromethane. Imidazole (2.04 g, 30.0 mmol, 2.0 equiv) was added, followed by *tert*-butyldimethylsilyl chloride (2.26 g, 15.0 mmol, 1.0 equiv). The cloudy white solution was stirred at room temperature under argon for 72 h. The reaction was quenched with saturated aqueous ammonium chloride and extracted with dichloromethane. The combined organics were washed with brine, dried with magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting colorless liquid was purified via column chromatography, using 90:10 hexane:ethyl acetate as the eluent, to afford the title compound as a colorless liquid (2.84 g, 88% yield). Spectral data were in agreement with literature values.[1]

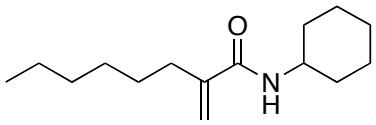
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.82 (ddt, J_d = 10, 17 Hz, J_t = 6.5 Hz, 1H), 5.01 (dq, J_d = 17 Hz, J_q = 1.5 Hz, 1H); 4.94 (dq, J_d = 10 Hz, J_q = 1 Hz, 1H); 3.62 (t, J = 6.5 Hz, 2H); 2.07 (q, J = 7 Hz, 2H); 1.54 (m, 2H); 1.44 (m, 2H); 0.90 (s, 9H); 0.06 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 139.2, 114.6, 63.3, 33.8, 32.5, 26.2, 25.4, 18.6, -5.1.
IR (NaCl, thin film, cm^{-1}): 3079, 2955, 2930, 2859, 1472, 1255, 1103, 910, 836, 775.



Hex-5-enyl benzoate.
In a 100 mL flask equipped with stir bar, triethylamine (5.0 mL, 36.0 mmol, 3.6 equiv) was added to a solution of hex-5-en-1-ol (1.2 mL, 10.0 mmol, 1 equiv) in 40 mL dichloromethane. Benzoyl chloride (1.4 mL, 12.0 mmol, 1.2 equiv) was added slowly via syringe. The solution became cloudy and the reaction flask became warm to the touch. The reaction was left to stir at room temperature under argon for 18 hours, after which it was quenched with saturated aqueous ammonium chloride and extracted with dichloromethane. The combined organics were washed with brine, dried with sodium sulfate, and concentrated under reduced pressure. The residue was purified via column chromatography, using 80:20 hexane:ethyl acetate as the eluent, to afford the title compound as a colorless liquid (1.86 g, 91% yield).
^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.06 (m, 2H); 7.57 (t, J = 1.5, 7.5 Hz, 1H); 7.45 (t, J = 8 Hz, 2H); (ddt, J_d = 10, 17 Hz, J_t = 6.5 Hz, 1H); 5.05 (dq, J_d = 17 Hz, J_q = 1.5 Hz, 1H); 4.99 (d, J = 10 Hz, 1H); 4.34 (t, J = 6.5 Hz, 2H); 2.14 (qt, J_q = 7 Hz, J_t = 1.5 Hz, 2H); 1.80 (m, 2H); 1.57 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 166.9, 138.6, 133.0, 130.7, 129.7, 128.5, 115.1, 65.1, 33.5, 28.4, 25.5.
IR (NaCl, thin film, cm^{-1}): 3074, 2938, 2861, 1721, 1452, 1315, 1274, 1176, 1114, 1070, 1027, 913, 711.

Alkene-Isocyanate Coupling Reactions.

General Procedure for Alkene–Isocyanate Coupling Reactions.
A 5 mL, side-necked sealable tube equipped with stir bar was brought into the glove box, along with a screw-cap and a rubber septum. In the box, $Ni(cod)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv) and IPr (19.5 mg, 0.05 mmol, 0.1 equiv) were added. The tube was capped and fitted with the rubber septum over the side neck. Outside the box, the reaction tube was put on an argon line, and 0.25 mL freshly distilled toluene was added via syringe, followed by alkene (0.5 mmol, 1 equiv), then isocyanate (1.0 mmol, 2 equiv), then 0.25 mL more toluene to wash the reagents into the bottom of the tube. The reaction tube was sealed, the argon line removed, and the reaction set to stir at 60ºC for 18-24 h. After this time, the reaction was opened to air and let stir for 15 min. It was diluted with ether and filtered through a plug of silica. The crude product was concentrated under reduced pressure and purified by column chromatography on silica, using 2:1 hexane:ethyl acetate as the eluent unless otherwise noted.



1a

***N*-cyclohexyl-2-methyleneoctanamide.**

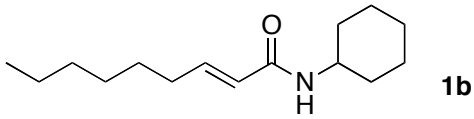
The reaction of $Ni(cod)_2$, IPr, 1-octene (78 μL, 0.5 mmol, 1 equiv), and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above afforded **1a** in 79% isolated yield as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.63 (br d, J = 6.5 Hz, 1H); 5.52 (d, J = 0.5 Hz, 1H); 5.22 (q, J = 1.5 Hz, 1H); 3.82 (m, 1H); 2.29 (td, J_t = 8 Hz, J_d = 0.5 Hz, 2H); 1.95 (m, 2H); 1.72 (dt, J_d = 14 Hz, J_t = 4 Hz, 2H); 1.63 (dt, J_d = 13 Hz, J_t = 4 Hz, 1H); 1.47-1.25 (m, 10H); 1.17 (m, 3H); 0.88 (t, J = 7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 168.4, 146.5, 116.7, 48.3, 33.3, 32.6, 31.8, 29.1, 28.2, 25.7, 25.0, 22.8, 14.3.

IR (NaCl, thin film, cm^{-1}): 3300, 2937, 2854, 1647, 1609, 1531, 1451, 1345, 1250, 1216, 1152, 1106, 929, 892, 727, 699.

HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{15}H_{27}NO$, 238.2165; found, 238.2165.



1b

(*E*)-*N*-cyclohexylnon-2-enamide.

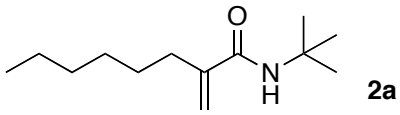
The reaction of $Ni(cod)_2$, IPr, 1-octene (78 μL, 0.5 mmol, 1 equiv), and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above afforded **1b** in 14% isolated yield as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.82 (dt, J_d = 15 Hz, J_t = 7 Hz, 1H); 5.72 (dt, J_d = 15 Hz, J_t = 1.5 Hz, 1H); 5.29 (br d, J = 7.5 Hz, 1H); 3.84 (m, 1H); 2.16 (m, 2H); 1.95 (m, 2H); 1.71 (dt, J_d = 14 Hz, J_t = 4 Hz, 2H); 1.63 (dm, J_d = 14 Hz, J_m = 4 Hz, 1H); 1.47-1.23 (m, 10H); 1.15 (m, 3H); 0.89 (t, J = 7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 165.3, 144.8, 124.0, 48.2, 33.5, 32.2, 31.9, 29.1, 28.5, 25.8, 25.1, 22.8, 14.3.

IR (NaCl, thin film, cm^{-1}): 3291, 3074, 2926, 2853, 1667, 1626, 1548, 1447, 1372, 1349, 1250, 1153, 985, 892, 726, 674.

HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{15}H_{27}NO$, 238.2165; found, 238.2166.



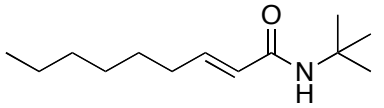
2a

***N-tert*-butyl-2-methyleneoctanamide.**

The reaction of $Ni(cod)_2$, IPr, 1-octene (78 μL, 0.5 mmol, 1 equiv), and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that 80:20 hexane:ethyl acetate was used as the eluent for chromatographic purification. Two successive rounds of column chromatography were needed for optimal purity, affording **2a** in 71% isolated yield as a pale yellow oil.

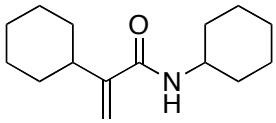
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.61 (br, 1H); 5.45 (d, J = 0.5 Hz, 1H); 5.16 (q, J = 1 Hz, 1H); 2.26 (t, J = 8 Hz, 2H); 1.42 (m, 2H); 1.37 (s, 9H); 1.34-1.24 (m, 6H); 0.87 (t, J = 7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 168.9, 147.5, 116.1, 51.4, 32.7, 31.9, 29.2, 29.0, 28.3, 22.8, 14.3.
IR (NaCl, thin film, cm$^{=1}$): 3323, 2960, 2928, 2859, 1655, 1623, 1531, 1452, 1392, 1364, 1240, 1225, 916.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{13}H_{25}NO$, 212.2009; found, 212.2015.



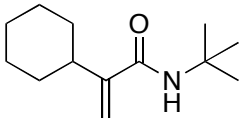
2b

(*E*)-*N*-*tert*-butylnon-2-enamide.
The reaction of $Ni(cod)_2$, IPr, 1-octene (78 μL, 0.5 mmol, 1 equiv), and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) was carried out in toluene following the general procedure above, with the exception that 80:20 hexane:ethyl acetate was used as the eluent for chromatographic purification. Two successive rounds of column chromatography were needed for optimal purity, affording **2b** in 17% isolated yield as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.78 (dt, J_d = 15 Hz, J_t = 7 Hz, 1H); 5.69 (dt, J_d = 15 Hz, J_t = 1.5 Hz, 1H); 5.29 (br, 1H); 2.15 (qd, J_q = 7.5 Hz, J_d = 1.5 Hz, 2H); 1.42 (m, J = 7.5 Hz, 2H); 1.38 (s, 9H); 1.34-1.22 (m, 6H); 0.88 (t, J = 7 Hz).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 165.6, 144.3, 124.7, 51.4, 32.1, 31.9, 29.1, 28.5, 22.8, 14.3.
IR (NaCl, thin film, cm^{-1}): 3274, 3075, 2959, 2928, 2857, 1666, 1629, 1553, 1453, 1364, 1227, 981.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{13}H_{25}NO$, 212.2009; found, 212.2006.



3a

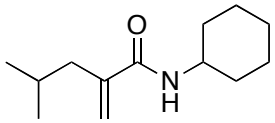
***N*,2-dicyclohexylprop-2-enamide.**
The reaction of $Ni(cod)_2$, IPr, vinylcyclohexane (68 μL, 0.5 mmol, 1 equiv) and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that two 1 mL portions of toluene were used for the reaction, afforded **3a** in 72% isolated yield as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.60 (br d, J = 6.5 Hz, 1H); 5.35 (s, 1H); 5.10 (d, J = 1.5 Hz, 1H); 3.82 (m, 1H); 2.44 (t, J = 11.5 Hz, 1H); 1.95 (m, 2H); 1.84-1.67 (m, 7H); 1.62 (dm, J_d = 13 Hz, J_m = 4 Hz, 1H); 1.37 (m, 4H); 1.14 (m, 6H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 169.5, 152.8, 113.1, 48.3, 39.8, 33.4, 32.0, 26.6, 26.4, 25.8, 25.1.
IR (NaCl, thin film, cm^{-1}): 3292, 2920, 2852, 1649, 1610, 1534, 1447, 1244, 1200, 1152, 1093, 916, 892.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{15}H_{25}NO$, 236.2009; found, 236.2011.



4a

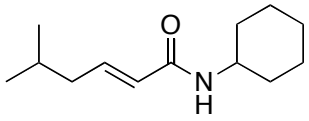
***N*-*tert*-butyl-2-cyclohexylprop-2-enamide.**

The reaction of $Ni(cod)_2$, IPr, vinylcyclohexane (68 μL, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that 90:10 hexane:ethyl acetate was used as the eluent for chromatographic purification, afforded **4a** in 91% isolated yield as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.59 (br, 1H); 5.29 (s, 1H); 5.05 (d, J = 1.5 Hz, 1H); 2.41 (t, J = 11.5 Hz, 1H); 1.77 (m, 4H); 1.68 (m, 1H); 1.37 (s, 9H); 1.31 (tt, J = 3.5, 13 Hz, 2H); 1.15 (tt, J = 3.5, 13 Hz, 1H); 1.08 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 170.0, 153.5, 112.7, 51.4, 39.7, 32.0, 28.9, 26.6, 26.4.
IR (NaCl, thin film, cm^{-1}): 3305, 2934, 2855, 1652, 1613, 1531, 1448, 1359, 1230, 914, 892.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{13}H_{23}NO$, 210.1852; found, 210.1850.



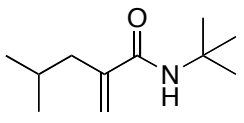
5a

***N*-cyclohexyl-4-methyl-2-methylenepentanamide.**
The reaction of $Ni(cod)_2$, IPr, 4-methylpent-1-ene (63 μL, 0.5 mmol, 1 equiv) and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that two 1 mL portions of toluene were used for the reaction, afforded **5a** in 74% isolated yield as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.63 (br, 1H); 5.53 (s, 1H); 5.18 (d, J = 1 Hz, 1H); 3.81 (m, 1H); 2.18 (dd, J = 1, 7 Hz, 2H); 1.94 (m, 2H); 1.75 (m, J = 7 Hz, 1H); 1.70 (m, 2H); 1.62 (m, 1H); 1.38 (qt, J_q = 12.5 Hz, J_t = 3.5 Hz, 2H); 1.16 (m, 3H); 0.89 (d, J = 6.5 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 168.5, 145.6, 117.9, 48.3, 42.2, 33.3, 27.3, 25.7, 25.0, 22.5.
IR (NaCl, thin film, cm^{-1}): 3293, 3086, 2935, 2855, 1648, 1612, 1536, 1449, 1247, 1152, 918, 727, 688.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{13}H_{23}NO$, 210.1852; found, 210.1851.



5b

(*E*)-*N*-cyclohexyl-5-methylhex-2-enamide.
The reaction of $Ni(cod)_2$, IPr, 4-methylpent-1-ene (63 μL, 0.5 mmol, 1 equiv) and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that two 1 mL portions of toluene were used for the reaction, afforded **5b** in 5% isolated yield as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ):
^{13}C NMR (125 MHz, $CDCl_3$, δ): 165.1, 143.6, 125.1, 48.3, 41.6, 33.5, 28.1, 25.8, 25.1, 22.6.
IR (NaCl, thin film, cm^{-1}): 3293, 2925, 2853, 1666, 1624, 1550, 1444, 1366, 1246, 1207, 985.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{13}H_{23}NO$, 210.1852; found, 210.1853.



6a

***N*-*tert*-butyl-4-methyl-2-methylenepentanamide.**

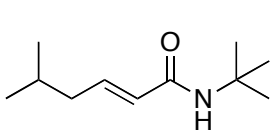
The reaction of $Ni(cod)_2$, IPr, 4-methylpent-1-ene (63 μL, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene was carried out following the general procedure above, with the exception that 80:20 hexane:ethyl acetate was used as the eluent for chromatographic purification. Mixed fractions were subjected to a second round of chromatographic purification using 90:10 hexane:ethyl acetate as the eluent, affording **6a** in 71% isolated yield as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.60 (br, 1H); 5.47 (d, J = 1 Hz, 1H); 5.15 (d, J = 1 Hz, 1H); 2.17 (dd, J = 1, 7 Hz, 2H); 1.76 (m, J = 7 Hz, 1H); 1.38 (s, 9H); 0.89 (d, J = 6.5 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 169.0, 146.5, 117.3, 51.4, 42.2, 28.9, 27.3, 22.6.

IR (NaCl, thin film, cm^{-1}): 3299, 2959, 2921, 2870, 1650, 1618, 1537, 1450, 1364, 1253, 1229, 921, 676.

HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{11}H_{21}NO$, 184.1696; found, 184.1702.



6b

(*E*)-*N*-*tert*-butyl-5-methylhex-2-enamide.

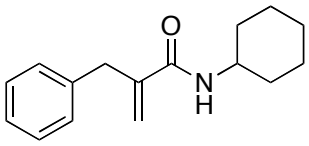
The reaction of $Ni(cod)_2$, IPr, 4-methylpent-1-ene (63 μL, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that 80:20 hexane:ethyl acetate was used as the eluent for chromatographic purification, afforded **6b** in 10% isolated yield as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.77 (dt, J_d = 15 Hz, J_t = 7.5 Hz, 1H); 5.68 (dt, J_d = 15 Hz, J_t = 1.5 Hz, 1H); 5.26 (br, 1H); 2.04 (td, J_t = 7 Hz, J_d = 1.5 Hz, 2H); 1.73 (m, J = 6.5 Hz, 1H); 1.39 (s, 9H); 0.92 (d, J = 6.5 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 165.5, 143.0, 125.8, 51.4, 41.5, 29.1, 28.1, 22.6.

IR (NaCl, thin film, cm^{-1}): 3266, 3078, 2953, 2924, 1666, 1626, 1556, 1449, 1389, 1359, 1337, 1270, 1252, 1229, 986, 891, 669.

HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{11}H_{21}NO$, 184.1696; found, 184.1697.



7a

2-benzyl-*N*-cyclohexylprop-2-enamide.

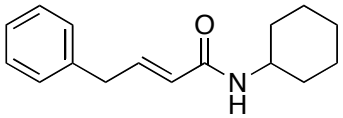
The reaction of $Ni(cod)_2$, IPr, allylbenzene (66 μL, 0.5 mmol, 1 equiv) and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that two 1 mL portions of toluene were used for the reaction, afforded **7a** in 65% isolated yield as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.31 (t, J = 7.5 Hz, 2H); 7.22 (m, 3H); 5.72 (s, 1H); 5.56 (br d, J = 4.5 Hz, 1H); 5.22 (d, J = 1 Hz, 1H); 3.77 (m, 1H); 3.66 (s, 2H); 1.82 (m, 2H); 1.59 (m, 3H); 1.33 (m, 2H); 1.13 (m, 1H); 1.04 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 167.4, 144.9, 138.6, 129.1, 128.8, 126.7, 119.5, 48.3, 39.0, 33.0, 25.7, 24.8.

IR (NaCl, thin film, cm^{-1}): 3303, 3062, 2926, 2851, 1648, 1611, 1537, 1449, 1343, 1241, 1150, 1088, 925, 891, 742, 700.

HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{16}H_{21}NO$, 244.1696; found, 244.1697.



7b

The reaction of $Ni(cod)_2$, IPr, allylbenzene (66 μL, 0.5 mmol, 1 equiv) and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that two 1 mL portions of toluene were used for the reaction, afforded **7b** in 8% isolated yield as a white solid.

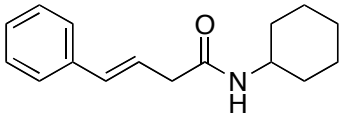
(*E*)-*N*-cyclohexyl-4-phenylbut-2-enamide.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.32 (t, J = 7.5 Hz, 2H); 7.24 (m, 1H); 7.19 (d, J = 7.5 Hz, 2H); 6.99 (dt, J_d = 15 Hz, J_t = 6.5 Hz, 1H); 5.66 (dt, J_d = 15 Hz, J_t = 1.5 Hz, 1H); 5.26 (br d, J = 7 Hz, 1H); 3.83 (m, 1H); 3.50 (dd, J = 1.5, 6.5 Hz, 2H); 1.93 (m, 2H); 1.70 (dt, J_d = 14 Hz, J_t = 4 Hz, 2H); 1.62 (m, 1H); 1.38 (m, 2H); 1.14 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 164.9, 142.9, 138.4, 129.1, 128.8, 126.7, 125.2, 48.3, 38.4, 33.4, 25.8, 25.1.

IR (NaCl, thin film, cm^{-1}): 3289, 2934, 2853, 1665, 1624, 1547, 1446, 1351, 980, 697.

HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{16}H_{21}NO$, 244.1696; found, 244.1694.



7c

(*E*)-*N*-cyclohexyl-4-phenylbut-3-enamide.

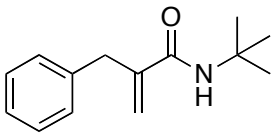
The reaction of $Ni(cod)_2$, IPr, allylbenzene (66 μL, 0.5 mmol, 1 equiv) and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that two 1 mL portions of toluene were used for the reaction, afforded **7c** in 22% isolated yield as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.40 (m, 2H); 7.34 (m, 2H); 7.27 (m, 1H); 6.54 (d, J = 16 Hz, 1H); 6.30 (dt, J_d = 16 Hz, J_t = 7.5 Hz, 1H); 5.47 (br, 1H); 3.79 (m, 1H); 3.14 (dd, J = 1.5, 7.5 Hz, 2H); 1.92 (m, 2H); 1.70 (dt, J_d = 14 Hz, J_t = 3.5 Hz, 2H); 1.61 (m, 1H); 1.37 (m, 2H); 1.12 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 169.8, 136.9, 134.7, 128.8, 128.0, 126.5, 122.8, 48.5, 41.3, 33.4, 25.7, 25.1.

IR (NaCl, thin film, cm^{-1}): 3290, 3064, 2933, 2853, 1636, 1545, 1447, 1347, 1248, 1180, 962, 690.

HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{16}H_{21}NO$, 244.1696; found, 244.1696.

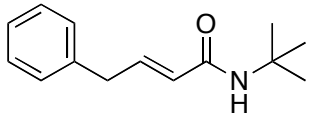


8a

2-benzyl-*N*-*tert*-butylprop2-enamide.

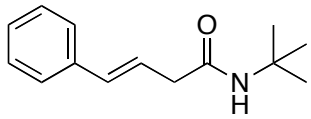
The reaction of $Ni(cod)_2$, IPr, allylbenzene (66 μL, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that two 1 mL portions of toluene were used for the reaction, afforded **8a** in 83% isolated yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.31 (m, 2H); 7.22 (m, 3H); 5.66 (d, J = 1 Hz, 1H); 5.52 (br, 1H); 5.17 (q, J = 1.5 Hz, 1H); 3.64 (s, 1H); 1.29 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 167.9, 145.8, 138.7, 129.1, 128.8, 118.9, 51.4, 39.1, 28.8.
IR (NaCl, thin film, cm^{-1}): 3325, 3063, 3029, 2969, 2925, 1655, 1622, 1530, 1453, 1392, 1365, 1299, 1224, 1075, 1031, 922, 743, 701.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{14}H_{19}NO$, 218.1539; found, 218.1539.



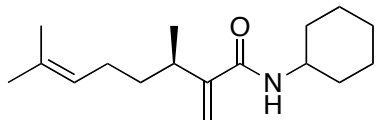
8b

(*E*)-*N*-*tert*-butyl-4-phenylbut-2-enamide.
The reaction of $Ni(cod)_2$, IPr, allylbenzene (66 μL, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that two 1 mL portions of toluene were used for the reaction, afforded **8b** and **8c** as a mixture in 6% combined yield. The yield of **8b** was determined to be 1% by integration of the ^{1}H NMR spectrum.
^{1}H NMR (500 MHz, $CDCl_3$, δ) identifying peaks: 6.96 (dt, J_d = 15 Hz, J_t = 6.5 Hz, 1H); 5.61 (dt, J_d = 15 Hz, J_t = 1.5 Hz, 1H); 3.49 (dd, J = 1.5 Hz, 6.5 Hz, 2H).



8c

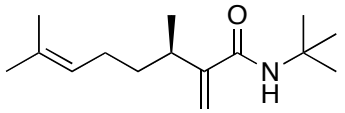
(*E*)-*N*-*tert*-butyl-4-phenylbut-3-enamide.
The reaction of $Ni(cod)_2$, IPr, allylbenzene (66 μL, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that two 1 mL portions of toluene were used for the reaction, afforded **8b** and **8c** as a mixture in 6% combined yield. The yield of **8c** was determined to be 5% by integration of the ^{1}H NMR spectrum.
^{1}H NMR (500 MHz, $CDCl_3$, δ) identifying peaks: 6.51 (d, J = 16 Hz, 1H); 6.30 (dt, J_d = 16 Hz, J_t = 7.5 Hz, 1H); 3.09 (dd, J = 1.5, 7.5 Hz, 2H).



9a

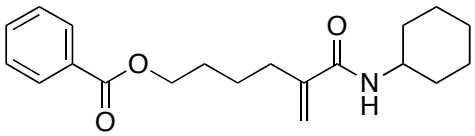
(*R*)-*N*-cyclohexyl-3,7-dimethyl-2-methyleneoct-6-enamide.
The reaction of $Ni(cod)_2$, IPr, *R*)-(-)-β-citronellene (91 μL, 0.5 mmol, 1 equiv) and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene was carried out following the general procedure above, with the exception that 75:25 hexane:ethyl acetate was used as the eluent for chromatographic purification, affording **9a** in 86% isolated yield as a colorless oil that slowly crashed out to a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ):5.62 (br d, J = 7 Hz, 1H); 5.45 (s, 1H); 5.15 (d, J = 0.5 Hz, 1H); 5.10 (tm, J_t = 7 Hz, J_m = 1.5 Hz, 1H); 3.82 (m, 1H); 2.64 (m, J = 7 Hz, 1H); 1.96 (m, 4H); 1.72 (dt, J_d = 14 Hz, J_t = 4 Hz, 2H); 1.68 (d, J = 1 Hz, 3H); 1.63 (dt, J_d = 14 Hz, J_t = 4 Hz, 1H); 1.59 (s, 3H); 1.55 (m, 1H); 1.38 (m, 2H); 2.33 (m, 1H); 1.16 (m, 3H); 1.08 (d, J = 7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 169.2, 152.3, 131.9, 124.5, 114.3, 48.3, 35.8, 35.1, 33.4, 26.0, 25.9, 25.8, 25.1, 19.4, 17.9.
IR (NaCl, thin film, cm^{-1}): 3289, 2931, 2854, 1647, 1609, 1534, 1449, 1377, 1242, 1151, 917, 892.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{17}H_{29}NO$, 264.2322; found, 264.2315.
$[\alpha]_D$ (*c* 0.019, 22°C, $CHCl_3$): -5.6°



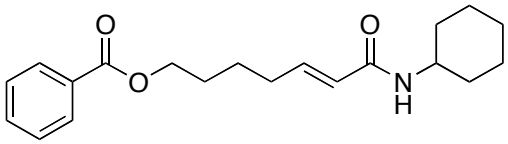
10a

(*R*)-*N*-*tert*-butyl-3,7-dimethyl-2-methyleneoct-6-enamide.
The reaction of $Ni(cod)_2$, IPr, (*R*)-(-)-β-citronellene (91 μL, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene was carried out following the general procedure above, with the exception that 80:20 hexane:ethyl acetate was used as the eluent for chromatographic purification. Two successive rounds of column chromatography were needed for optimal purity, affording **10a** in 82% isolated yield as a pale yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.59 (br, 1H); 5.38 (s, 1H); 5.10 (d, J = 0.5 Hz, 1H); 5.09 (tm, J_t = 7 Hz, J_m = 1.5 Hz, 1H); 2.62 (sextet, J = 7 Hz, 1H); 1.97 (m, J = 7 Hz, 2H); 1.67 (d, J = 1 Hz, 3H); 1.59 (s, 3H); 1.54 (m, 1H); 1.38 (s, 9H); 1.31 (m, 1H); 1.07 (d, J = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 169.8, 153.1, 131.8, 124.6, 113.7, 51.4, 35.7, 35.1, 28.9, 25.9, 19.4, 17.9.
IR (NaCl, thin film, cm^{-1}): 3325, 2966, 2927, 1653, 1620, 1528, 1452, 1392, 1365, 1296, 1223, 920.
HRMS-ESI (m / z): $[M + Na]^+$ calculated for $C_{15}H_{17}NO$, 260.1985; found, 260.1985.
$[\alpha]_D$ (*c* 0.010, 22°C, $CHCl_3$): -4.7°



11a

5-(cyclohexylcarbamoyl)hex-5-enyl benzoate.
The reaction of $Ni(cod)_2$, IPr, hex-5-enyl benzoate (102 mg, 0.5 mmol, 1 equiv) and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene was carried out following the general procedure above, with the exception that 1:1 hexane:ethyl acetate was used as the eluent for chromatographic purification. Two successive rounds of column chromatography were needed for optimal purity, affording **11a** in 74% isolated yield as a colorless oil that slowly crystallized to a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.04 (dd, J = 1.5, 8 Hz, 2H); 7.56 (tt, J = 1.5, 7.5 Hz, 1H); 7.44 (t, J = 8 Hz, 2H); 5.66 (br d, J = 7.5 Hz, 1H); 5.54 (s, 1H); 5.26 (s, 1H); 4.34 (t, J = 6.5 Hz, 2H); 3.81 (m, 1H); 2.40 (t, J = 7.5 Hz, 2H); 1.93 (m, 2H); 1.81 (m, 2H); 1.70 (m, 2H); 1.63 (m, 3H); 1.38 (qt, J_q = 12.5 Hz, J_t = 3.5 Hz, 2H); 1.16 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 168.1, 166.8, 146.0, 133.1, 130.5, 129.7, 128.5, 117.0, 64.9, 48.4, 33.3, 32.3, 28.5, 25.7, 25.0, 24.8.
IR (NaCl, thin film, cm^{-1}): 3309, 3063, 2932, 2855, 1720, 1653, 1611, 1530, 1451, 1315, 1275, 1117, 925, 712.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{20}H_{27}NO_3$, 330.2064; found, 330.2065.



11b

(*E*)-7-(cyclohexylamino)-7-oxohept-5-enyl benzoate.

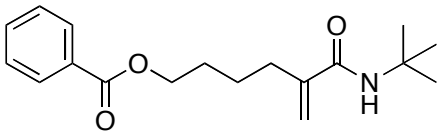
The reaction of $Ni(cod)_2$, IPr, hex-5-enyl benzoate (102 mg, 0.5 mmol, 1 equiv) and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene was carried out following the general procedure above, with the exception that 1:1 hexane:ethyl acetate was used as the eluent for chromatographic purification. Two successive rounds of column chromatography were needed for optimal purity, affording **11b** in 13% isolated yield as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.05 (dd, J = 1.5, 8.5 Hz, 2H); 7.57 (tt, J = 1.5, 7.5 Hz, 1H); 7.45 (t, J = 8 Hz, 2H); 6.83 (dt, J_d = 15 Hz, Jt = 7 Hz, 1H); 5.76 (dt, J_d = 15 Hz, J_t = 1.5 Hz, 1H); 5.27 (br d, J = 7.5 Hz, 1H); 4.34 (t, J = 6.5 Hz, 2H); 3.84 (m, 1H); 2.26 (qd, J_q = 7.5 Hz, J_d = 1.5 Hz, 2H); 1.95 (m, 2H); 1.81 (m, 2H); 1.72 (dt, J_d = 14 Hz, J_t = 3.5 Hz, 2H); 1.63 (m, 3H); 1.39 (qt, J_q = 13 Hz, J_t = 3.5 Hz, 2H); 1.15 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 166.8, 165.0, 143.7, 133.1, 130.5, 129.8, 128.6, 124.6, 64.8, 48.3, 33.4, 31.7, 28.4, 25.8, 25.1, 25.0.

IR (NaCl, thin film, cm^{-1}): 3288, 3069, 2927, 2853, 1720, 1667, 1625, 1545, 1449, 1349, 1315, 1276, 1111, 1070, 982, 708.

HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{20}H_{27}NO_3$, 330.2064; found, 330.2061.



12a

5-(*tert*-butylcarbamoyl)hex-5-enyl benzoate.

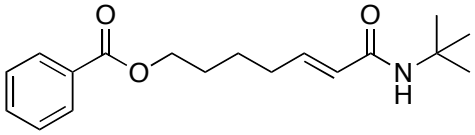
The reaction of $Ni(cod)_2$, IPr, hex-5-enyl benzoate (102 mg, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene was carried out following the general procedure above, with the exception that a gradient from 2:1 hexane:ethyl acetate to 1:1 hexane:ethyl acetate was used as the eluent for chromatographic purification. Two successive rounds of column chromatography were needed for optimal purity, affording **12a** in 72% isolated yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.04 (d, J = 8 Hz, 2H); 7.56 (tt, J = 1.5, 7.5 Hz, 1H); 7.44 (t, J = 8 Hz, 2H); 5.63 (br, 1H); 5.47 (s, 1H); 5.22 (d, J = 0.5 Hz, 1H); 4.34 (t, J = 6.5 Hz, 2H); 2.37 (t, J = 7.5 Hz, 2H); 1.81 (m, 2H); 1.62 (m, 2H); 1.38 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 168.7, 166.8, 147.0, 133.1, 130.6, 129.7, 128.5, 116.4, 65.0, 51.5, 32.4, 28.9, 28.6, 24.8.

IR (NaCl, thin film, cm^{-1}): 3328, 2964, 1719, 1659, 1623, 1525, 1452, 1275, 1117, 712.

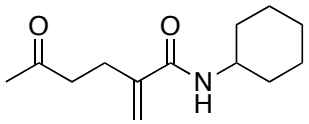
HRMS-ESI (m / z): $[M + Na]^+$ calculated for $C_{18}H_{25}NO_3$, 326.1727; found, 326.1723.



12b

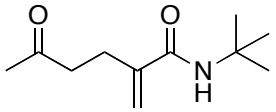
(*E*)-7-(*tert*-butylamino)-7-oxohept-5-enyl benzoate.

The reaction of $Ni(cod)_2$, IPr, hex-5-enyl benzoate (102 mg, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene was carried out following the general procedure above, with the exception that a gradient from 2:1 hexane:ethyl acetate to 1:1 hexane:ethyl acetate was used as the eluent for chromatographic purification. A second round of column chromatography using 2:1 benzene:ethyl acetate as the eluent was needed for optimal purity, affording **12b** in 12% isolated yield as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.05 (m, 2H); 7.57 (m, 1H); 7.46 (m, 2H); 6.79 (dt, J_d = 15 Hz, J_t = 7 Hz, 1H); 5.72 (dt, J_d = 15 Hz, J_t = 1.5 Hz, 1H); 5.25 (br, 1H); 4.33 (t, J = 6.5 Hz, 2H); 2.25 (qd, J_q = 7 Hz, J_d = 1.5 Hz, 2H); 1.81 (m, 2H); 1.62 (m, 2H); 1.39 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 166.9, 165.4, 143.3, 133.1, 130.6, 129.8, 128.6, 125.4, 64.8, 51.5, 31.6, 29.1, 28.4, 25.0.
IR (NaCl, thin film, cm^{-1}): 3296, 3070, 2964, 2929, 1719, 1669, 1631, 1545, 1452, 1274, 1115, 712.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{18}H_{25}NO_3$, 304.1907; found, 304.1911.



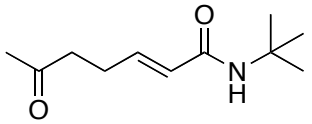
13a

***N*-cyclohexyl-2-methylene-5-oxohexanamide.**
The reaction of $Ni(cod)_2$, IPr, hex-5-en-2-one (58 μL, 0.5 mmol, 1 equiv), and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that 2:1 ethyl acetate:hexane was used as the eluent for chromatographic purification, afforded **13a** in 24% isolated yield as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.85 (br, 1H); 5.58 (s, 1H); 5.28 (s, 1H); 3.81 (m, 1H); 2.68 (t, J = 7 Hz, 2H); 2.58 (t, J = 7 Hz, 2H); 2.16 (s, 3H); 1.94 (m, 2H); 1.73 (dt, J_d = 14 Hz, J_t = 4 Hz, 2H); 1.63 (dt, J_d = 13 Hz, J_t = 4 Hz, 1H); 1.39 (qt, J_q = 13.5 Hz, J_t = 3.5 Hz, 2H); 1.18 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 208.4, 167.7, 144.8, 118.2, 48.5, 42.6, 33.3, 30.2, 26.7, 25.7, 25.1.
IR (NaCl, thin film, cm^{-1}): 3296, 2933, 2856, 1711, 1648, 1611, 1529, 926.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{13}H_{21}NO_2$, 224.1645; found, 224.1639.



14a

***N-tert*-butyl-2-methylene-5-oxohexanamide.**
The reaction of $Ni(cod)_2$, IPr, hex-5-en-2-one (58 μL, 0.5 mmol, 1 equiv), and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that 2:1 ethyl acetate:hexane was used as the eluent for chromatographic purification, afforded **14a** in 70% isolated yield as a pale yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.81 (br, 1H); 5.50 (s, 1H); 5.22 (s, 1H); 2.65 (t, J = 7 Hz, 2H); 2.53 (t, J = 7 Hz, 2H); 2.14 (s, 3H); 1.37 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 208.3, 168.3, 145.7, 117.5, 51.5, 42.5, 30.1, 28.9, 26.8.
IR (NaCl, thin film, cm^{-1}): 3337, 2969, 2929, 1715, 1662, 1625, 1527, 1453, 1364, 1225, 1162, 928, 733.
HRMS-ESI (m / z): $[M + Na]^+$ calculated for $C_{11}H_{19}NO_2$, 220.1308; found, 220.1308.



14b

(*E*)-*N*-*tert*-butyl-6-oxohept-2-enamide.

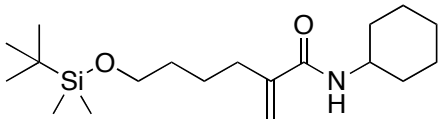
The reaction of $Ni(cod)_2$, IPr, hex-5-en-2-one (58 μL, 0.5 mmol, 1 equiv), and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above, with the exception that 2:1 ethyl acetate:hexane was used as the eluent for chromatographic purification, afforded **14b** in 2% isolated yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.72 (dt, J_d = 15 Hz, J_t = 7Hz, 1H); 5.72 (dt, J_d = 15 Hz, J_t = 1.5 Hz, 1H); 5.26 (br, 1H); 2.58 (t, J = 7 Hz, 2H); 2.44 (qd, J_q = 7 Hz, J_d = 1.5 Hz, 2H); 2.16 (s, 3H); 1.38 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 207.5, 165.2, 141.8, 125.9, 51.5, 42.1, 30.2, 29.0, 25.9.

IR (NaCl, thin film, cm^{-1}): 3297, 2966, 2922, 1717, 1670, 1631, 1542, 1455, 1363, 1225, 1161, 979.

HRMS-ESI (m / z): $[M + Na]^+$ calculated for $C_{11}H_{19}NO_2$, 220.1308; found, 220.1306.



15a

6-(*tert*-butyldimethylsilyloxy)-*N*-cyclohexyl-2-methylenehexanamide.

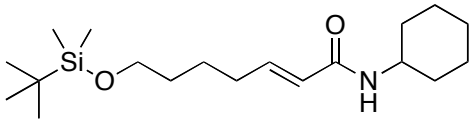
The reaction of $Ni(cod)_2$, IPr, *tert*-butyl(hex-5-enyloxy)dimethylsilane (107 mg, 0.5 mmol, 1 equiv), and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above afforded **15a** in 68% isolated yield as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.64 (br d, J = 7 Hz, 1H); 5.54 (s, 1H); 5.23 (d, J = 1 Hz, 1H); 3.82 (m, 1H); 3.62 (t, J = 6 Hz, 2H); 2.32 (t, J = 7 Hz, 2H); 1.95 (m, 2H); 1.72 (dt, J_d = 14 Hz, J_t = 3.5 Hz, 2H); 1.63 (m, 1H); 1.53 (m, 4H); 1.39 (qt, J_q = 12 Hz, J_t = 3.5 Hz, 2H); 1.17 (m, 3H), 0.89 (s, 9H); 0.05 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 168.3, 146.2, 116.9, 63.2, 48.3, 33.3, 32.5, 32.3, 26.2, 25.7, 25.0, 24.6, 18.5, -5.1.

IR (NaCl, thin film, cm^{-1}): 3306, 2932, 2857, 1651, 1612, 1531, 1256, 1105, 836, 776, 734.

HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{19}H_{37}NO_2Si$, 340.2666; found, 340.2674.



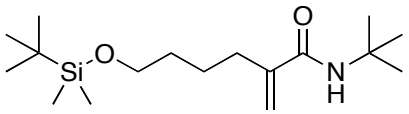
15b

***(E)*-7-(*tert*-butyldimethylsilyloxy)-*N*-cyclohexylhept-2-enamide.**

The reaction of $Ni(cod)_2$, IPr, *tert*-butyl(hex-5-enyloxy)dimethylsilane (107 mg, 0.5 mmol, 1 equiv), and cyclohexyl isocyanate (128 μL, 1.0 mmol, 2 equiv) in toluene following the general procedure above afforded **15b** in 17% isolated yield as a white solid.

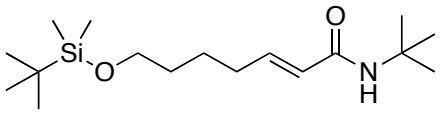
^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.81 (dt, J_d = 15 Hz, J_t = 7 Hz, 1H); 5.73 (dt, J_d = 15 Hz, J_t = 1.5 Hz, 1H); 5.35 (br d, J = 8 Hz, 1H); 3.83 (m, 1H); 3.61 (t, J = 6 Hz, 2H); 2.19 (qd, J_q = 7 Hz, J_d = 1.5 Hz, 2H); 1.71 (dt, J_d = 14, 3.5 Hz, 2H); 1.63 (m, 1H); 1.52 (m, 4H); 1.38 (qt, J_q = 12 Hz, J_t = 3.5, 2H); 1.15 (m, 3H); 0.89 (s, 9H); 0.05 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 165.2, 144.4, 124.2, 63.0, 48.2, 33.4, 32.5, 32.0, 26.2, 25.8, 25.1, 24.8, 18.6, -5.1.
IR (NaCl, thin film): 3288, 3246, 3068, 2929, 2855, 1667, 1625, 1550, 1255, 1102, 835, 774.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{19}H_{37}NO_2Si$, 340.2666; found, 340.2677.



16a

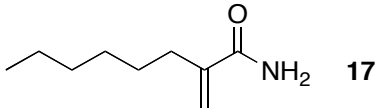
***N-tert*-butyl-6-(*tert*-butyldimethylsilyloxy)-2-methylenehexanamide.**
The reaction of $Ni(cod)_2$, IPr, *tert*-butyl(hex-5-enyloxy)dimethylsilane (107 mg, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene was carried out following the general procedure above, with the exception that 80:20 hexane:ethyl acetate was used as the eluent for chromatographic purification. Two successive rounds of column chromatography were needed for optimal purity, affording **16a** in 65% isolated yield as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.61 (br, 1H); 5.46 (s, 1H); 5.18 (d, J = 1 Hz, 1H); 3.61 (t, J = 6 Hz, 2H); 2.29 (t, J = 7 Hz, 2H); 1.51 (m, 4H); 1.38 (s, 9H); 0.88 (s, 9H); 0.04 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 168.8, 147.2, 116.3, 63.2, 51.4, 32.6, 32.4, 28.9, 26.1, 24.6, 18.6, -5.1.
IR (NaCl, thin film, cm^{-1}): 3324, 2957, 2930, 2859, 1656, 1624, 1530, 1255, 1105, 836, 775.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{17}H_{35}NO_2Si$, 314.2510; found, 314.2519.



16b

***(E)*-*N*-*tert*-butyl-7-(*tert*-butyldimethylsilyloxy)hept-2-enamide.**
The reaction of $Ni(cod)_2$, IPr, *tert*-butyl(hex-5-enyloxy)dimethylsilane (107 mg, 0.5 mmol, 1 equiv) and *tert*-butyl isocyanate (117 μL, 1.0 mmol, 2 equiv) in toluene was carried out following the general procedure above, with the exception that 80:20 hexane:ethyl acetate was used as the eluent for chromatographic purification. Two successive rounds of column chromatography were needed for optimal purity, affording **16b** in 9% isolated yield as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.77 (dt, J_d = 15 Hz, J_t = 7 Hz, 1H); 5.69 (dt, J_d = 15 Hz, J_t = 1.5 Hz, 1H); 5.27 (br, 1H); 3.60 (t, J = 6 Hz, 2H); 2.17 (qd, J_q = 8.5 Hz, J_d = 1.5 Hz, 2H); 1.51 (m, 4H); 1.38 (s, 9H); 0.89 (s, 9H); 0.04 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 165.6, 143.9, 124.9, 63.1, 51.4, 32.5, 31.9, 29.1, 26.2, 24.8, 18.6, -5.1.
IR (NaCl, thin film, cm^{-1}): 3263, 3070, 2927, 2856, 1665, 1628, 1555, 1361, 1250, 1099, 833, 773.
HRMS-ESI (m / z): $[M + H]^+$ calculated for $C_{17}H_{35}NO_2Si$, 314.2510; found, 314.2518.

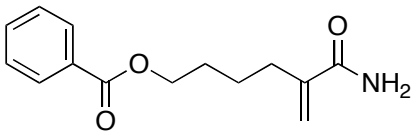
Deprotection of Selected *N*-*tert*-butyl Amides.



17

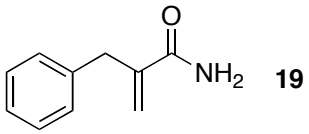
2-methyleneoctanamide.

Compound **2a** (42.5 mg, 0.20 mmol) was dissolved in approximately 2 mL neat trifluoroacetic acid and was transferred to a 5 mL, side-necked sealable tube equipped with stir bar. The reaction was sealed and heated at reflux for 18 hours. The reaction was allowed to cool to room temperature, and the trifluoroacetic acid was carefully removed under reduced pressure. The yellow residue was purified via column chromatography, using 1:1 hexane: ethyl acetate as the eluent, to afford **17** in 69% yield as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.82 (br, 2H); 5.69 (d, *J* = 0.5 Hz, 1H); 5.35 (m, 1H); 2.30 (t, *J* = 7 Hz, 2H); 1.47 (m, 2H); 1.36-1.25 (m, 6H); 0.88 (t, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 171.1, 144.8, 118.9, 32.4, 31.8, 29.1, 28.2, 22.8, 14.3.
IR (NaCl, thin film, cm^{-1}): 3358, 3184, 2956, 2928, 2857, 1665, 1628, 1602, 1468, 1435, 1265, 1115, 926, 740.
HRMS-ESI (m / z): $[M+H]^+$ calculated for $C_9H_{17}NO$, 156.1383; found, 156.1386.



18

5-carbamoylhex-5-enyl benzoate.
Compound **12a** (25.9 mg, 0.085 mmol) was dissolved in approximately 2 mL neat trifluoroacetic acid and was transferred to a 5 mL, side-necked sealable tube equipped with stir bar. The reaction was sealed and heated at reflux for 24 hours. The reaction tube was allowed to cool to room temperature. Its contents were dropped slowly into 40 mL saturated aqueous sodium bicarbonate. The product was extracted in 6 x 30 mL diethyl ether. The combined organics were dried with sodium sulfate, filtered, and concentrated under reduced pressure. Column chromatography was performed, eluting first with 2:1 ethyl acetate:hexane, and then neat ethyl acetate, to afford **18** in 81% yield as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.05 (m, 2H); 7.57 (tt, *J* = 1.5, 7.5 Hz, 1H); 7.45 (t, *J* = 8 Hz, 2H); 5.9-5.4 (br, 2H); 5.71 (s, 1H); 5.40 (t, *J* = 1.5 Hz, 1H); 4.35 (t, *J* = 6.5 Hz, 2H); 2.42 (t, *J* = 7.5 Hz, 2H); 1.83 (m, 2H); 1.66 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 170.6, 166.9, 144.2, 133.1, 130.5, 129.7, 128.6, 119.3, 64.9, 32.1, 28.5, 24.8.
IR (NaCl, thin film, cm^{-1}): 3367, 3182, 2944, 2920, 2869, 1716, 1663, 1603, 1471, 1450, 1436, 1410, 1318, 1279, 1120, 1072, 931, 824, 710.
HRMS-ESI (m / z): $[M+H]^+$ calculated for $C_{14}H_{17}NO_3$, 248.1281; found, 248.1278.



19

2-benzylprop-2-enamide.
Compound **8a** (25.3 mg, 0.116 mmol) was dissolved in approximately 2 mL neat trifluoroacetic acid and was transferred to a 5 mL, side-necked sealable tube equipped with stir bar. The reaction was sealed and heated at reflux for 16 hours. The reaction tube was allowed to cool to room temperature. Its contents were dropped slowly into 40 mL saturated aqueous sodium bicarbonate. The product was extracted in 6 x 25 mL diethyl ether. The combined organics were dried with sodium sulfate, filtered, and concentrated under reduced pressure. Column

chromatography was performed with ethyl acetate as the eluent, affording **19** in 70% yield as a white solid. Spectral data were in agreement with literature values.[2]

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.35-7.2 (m, 5H); 5.87 (d, J = 0.5 Hz, 1H); 5.64 (br, 2H); 5.34 (d, J = 0.5 Hz, 1H); 3.67 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 170.1, 143.4, 138.4, 129.1, 128.9, 126.9, 121.6, 38.7.

IR (NaCl, thin film, cm^{-1}): 3362, 3192, 3029, 1666, 1592, 1455, 1409, 1345, 1183, 1107, 950, 742, 699.

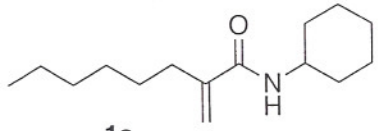
HRMS-ESI (m / z): $[M+H]^+$ calculated for $C_{10}H_{11}NO$, 162.0913; found, 162.0920.

References:

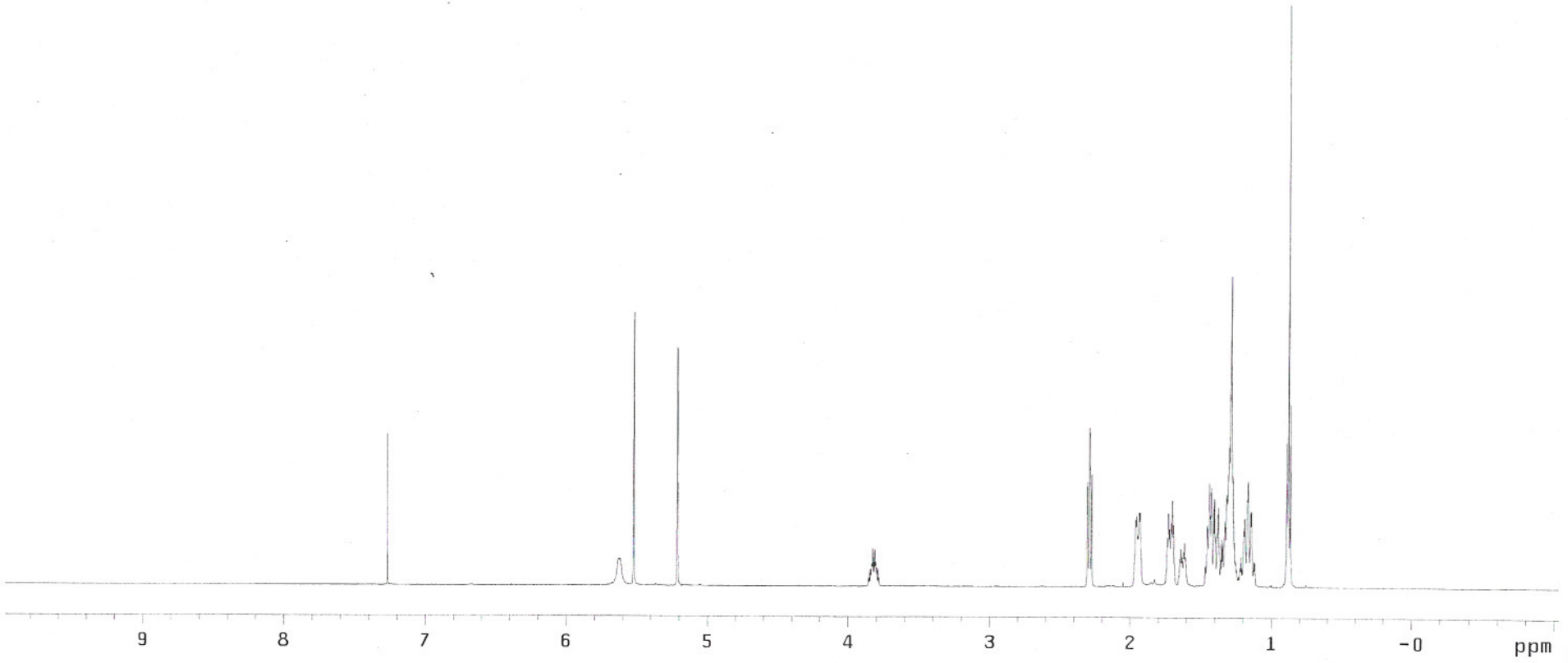
(1) Myers, A. G.; Lanman, B. A. *J. Am. Chem. Soc.* **2002**, *124*, 12969.

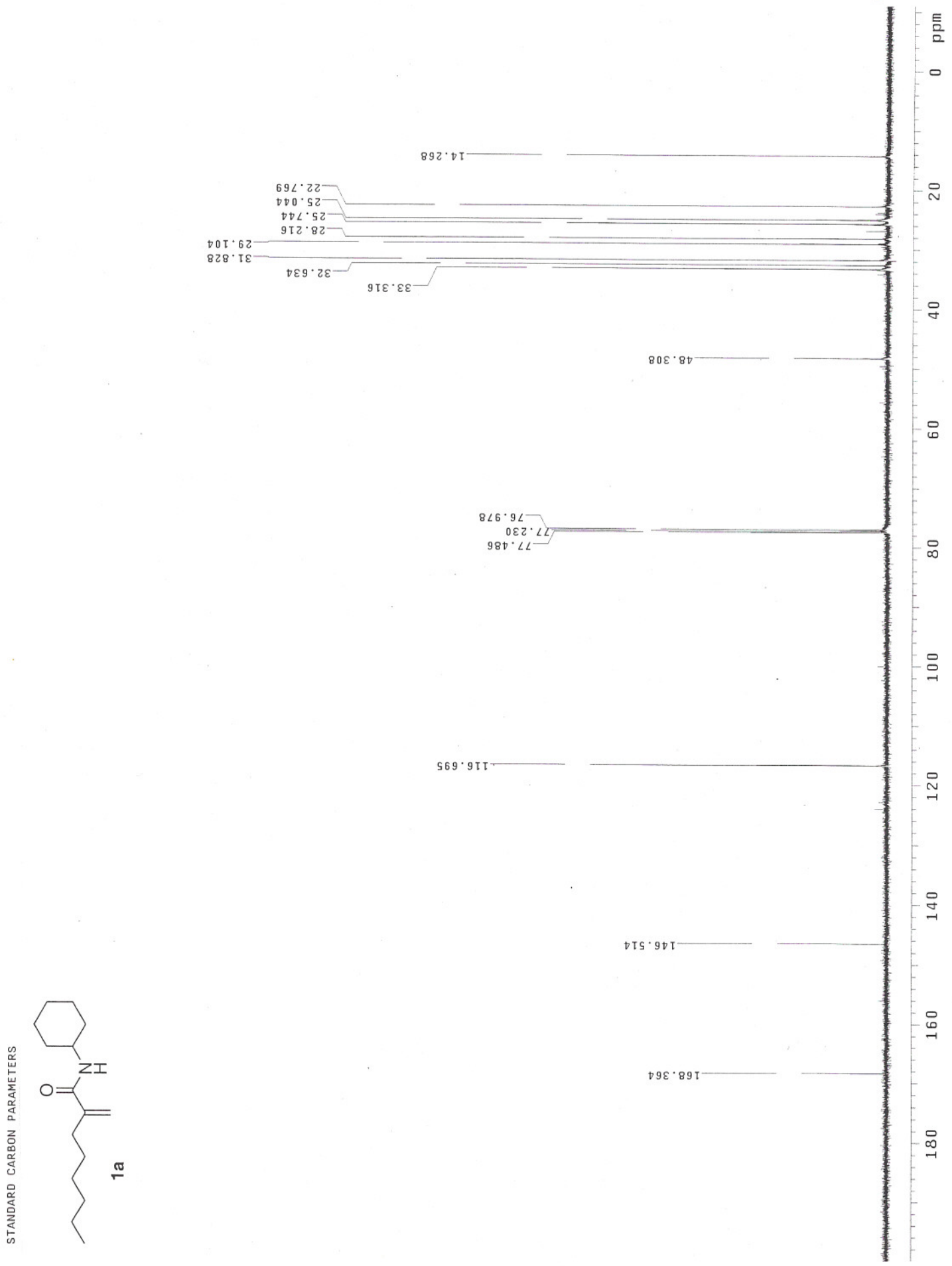
(2) Muller, J.-C.; Fleury, J.-P. *Bull. Soc. Chim. Fr.* **1970**, *2*, 738.

STANDARD PROTON PARAMETERS



1a

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29.104
28.216
25.744
25.044
22.769
14.268
ppm
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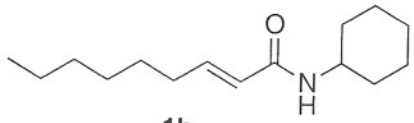
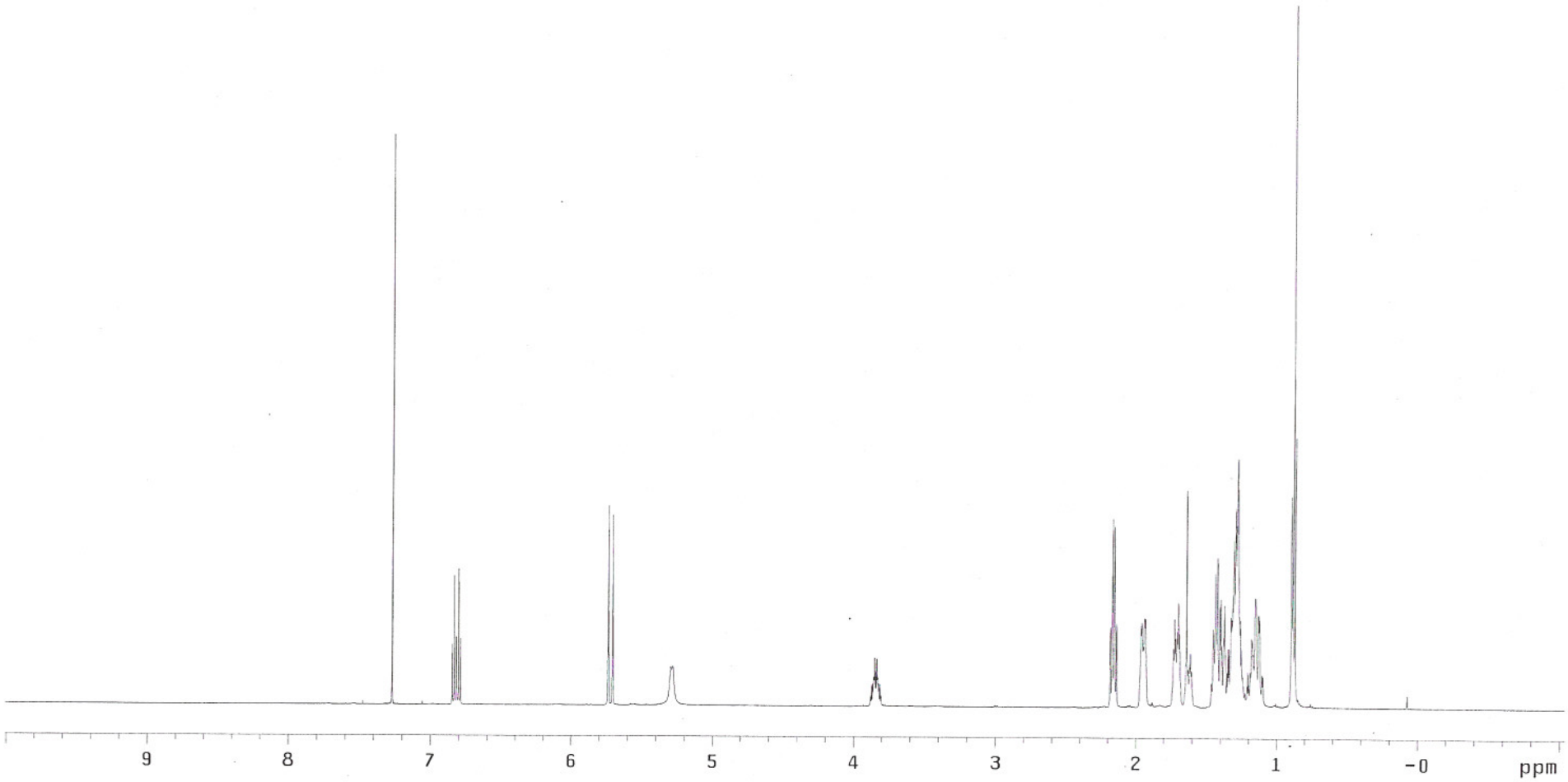
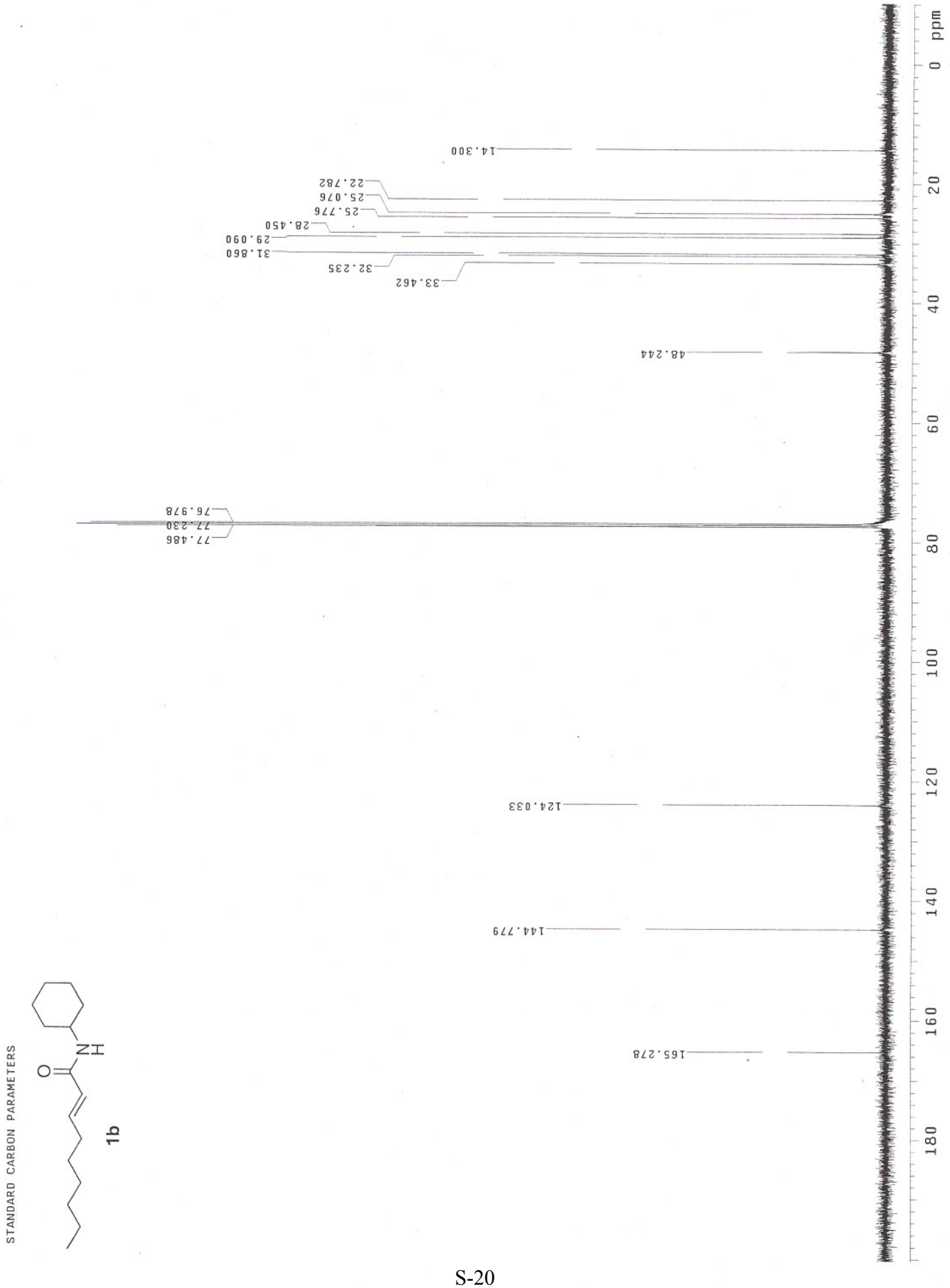
20
40
60
80
100
120
140
160
180

STANDARD PROTON PARAMETERS



1b




STANDARD CARBON PARAMETERS
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20
40
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80
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120
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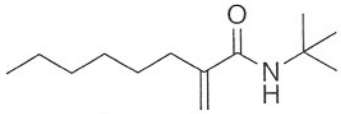
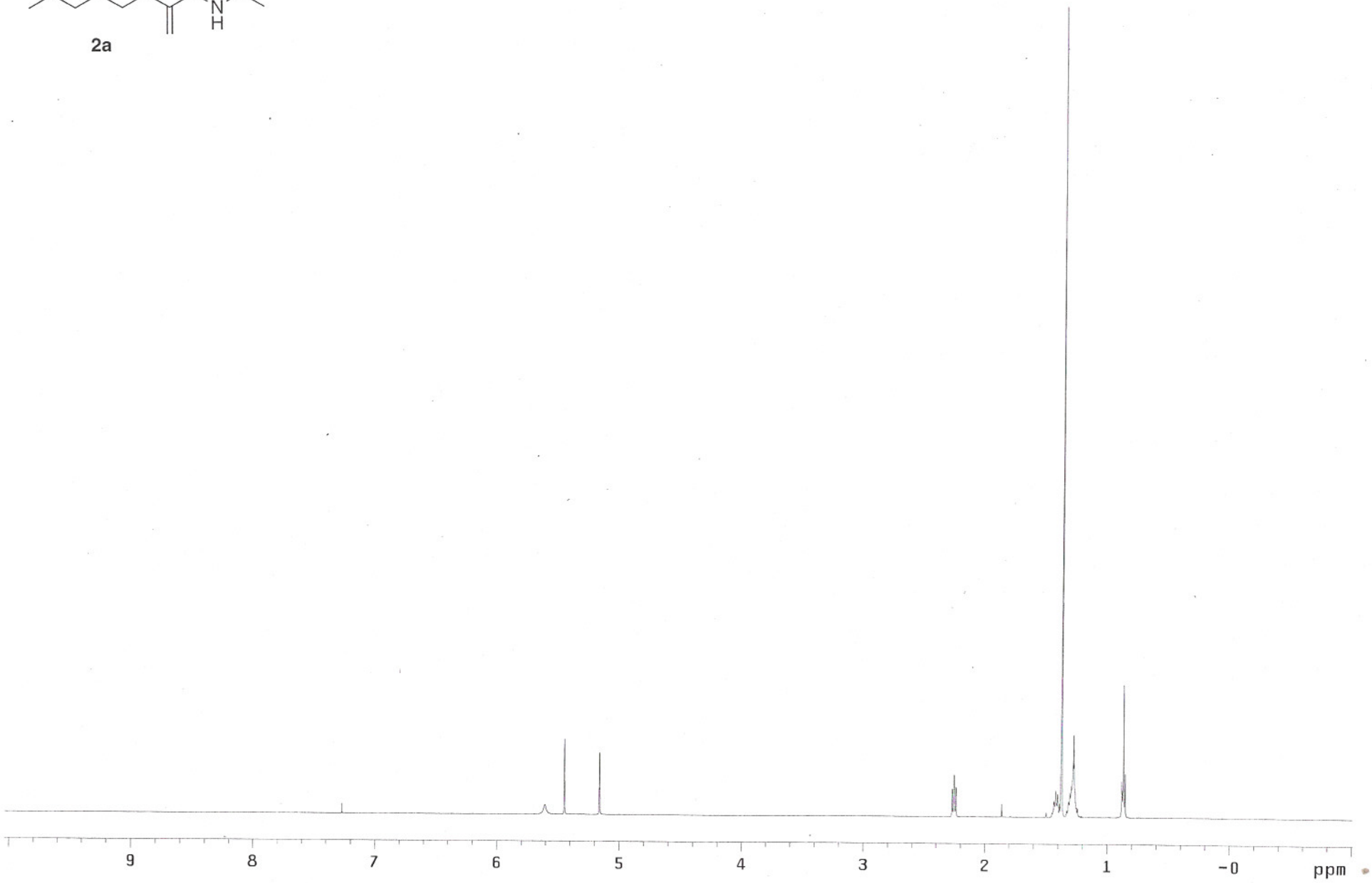
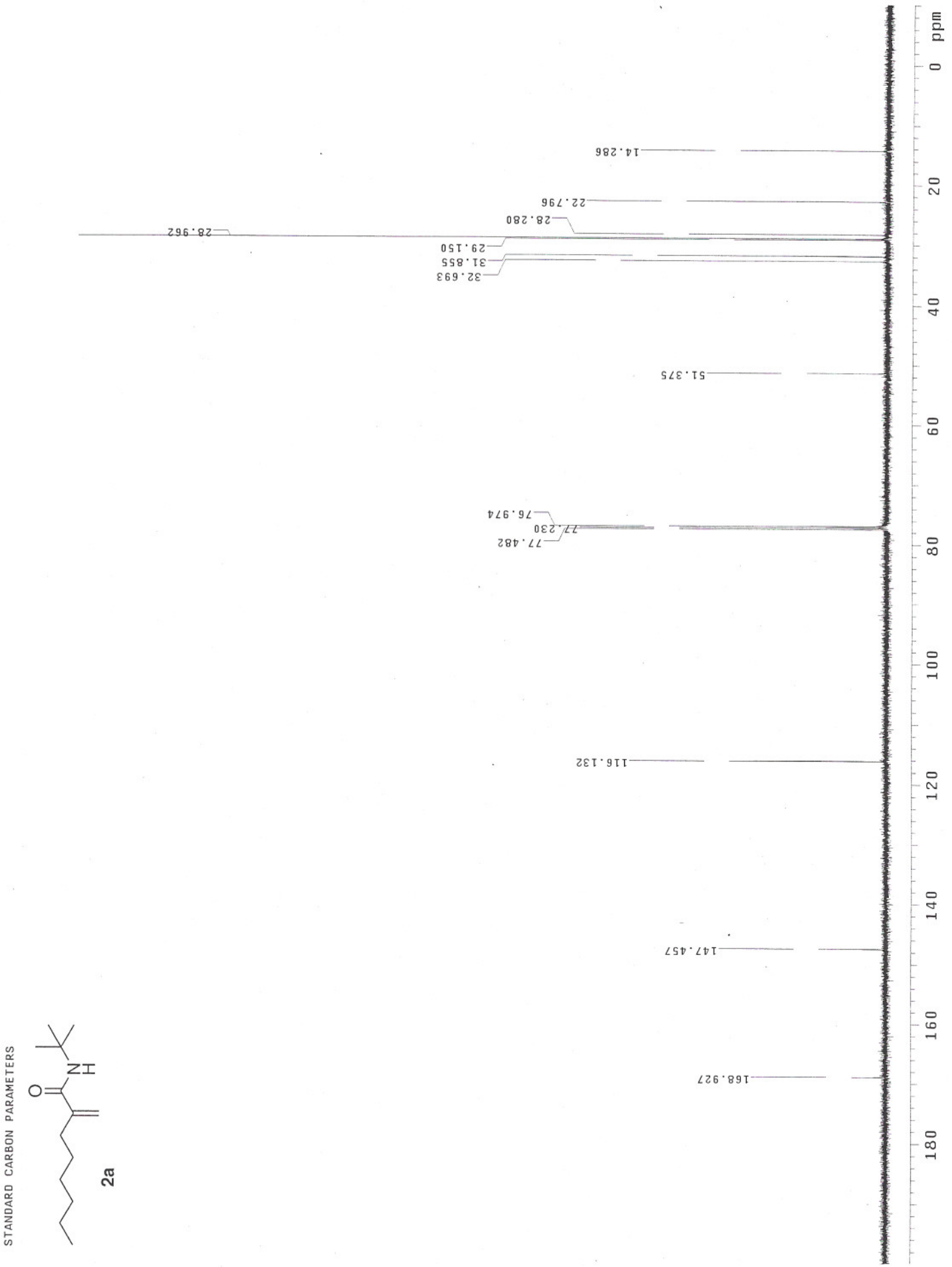
180

STANDARD PROTON PARAMETERS



2a




STANDARD CARBON PARAMETERS
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28.962
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14.286
ppm
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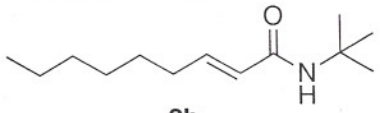
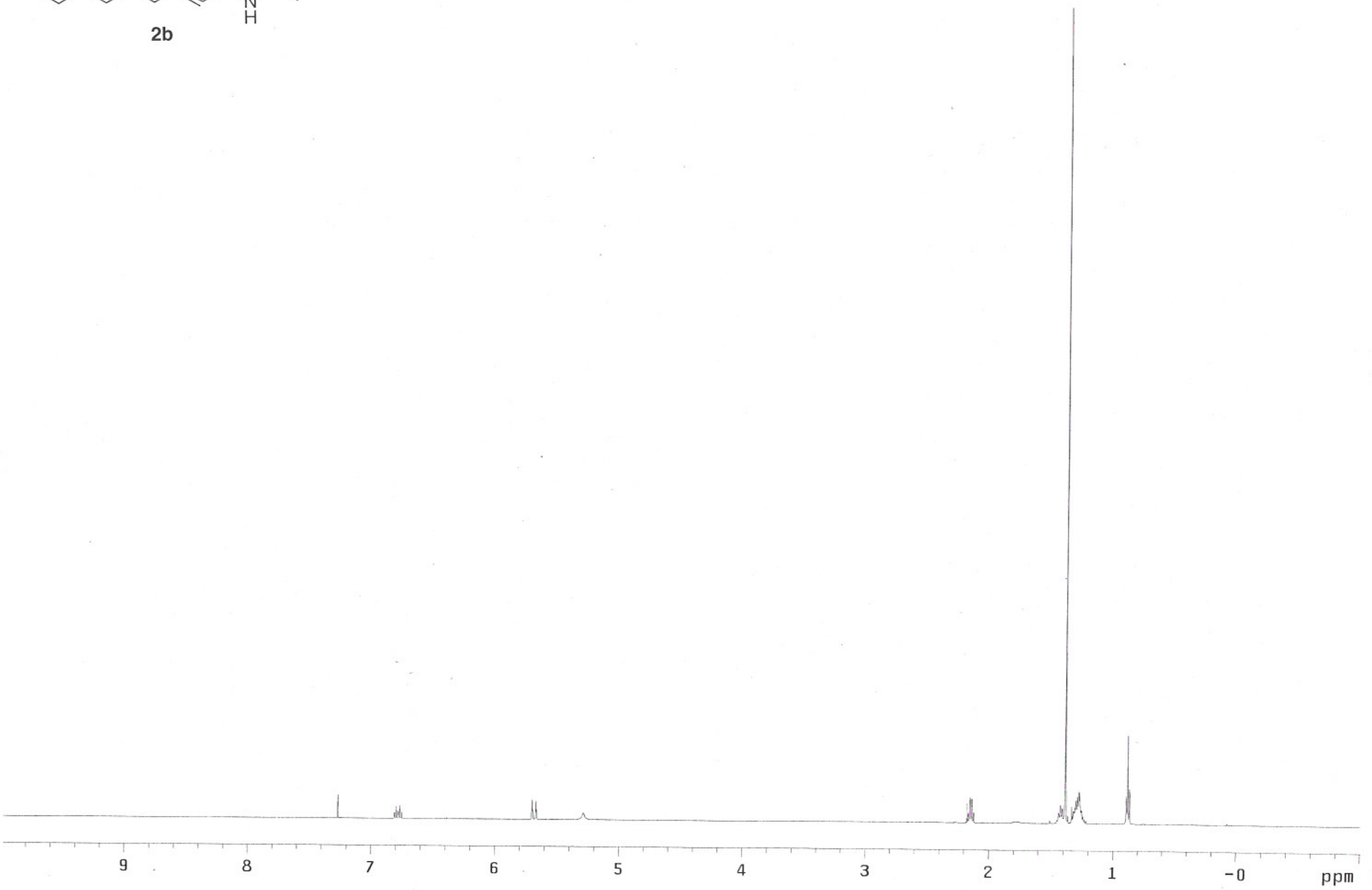
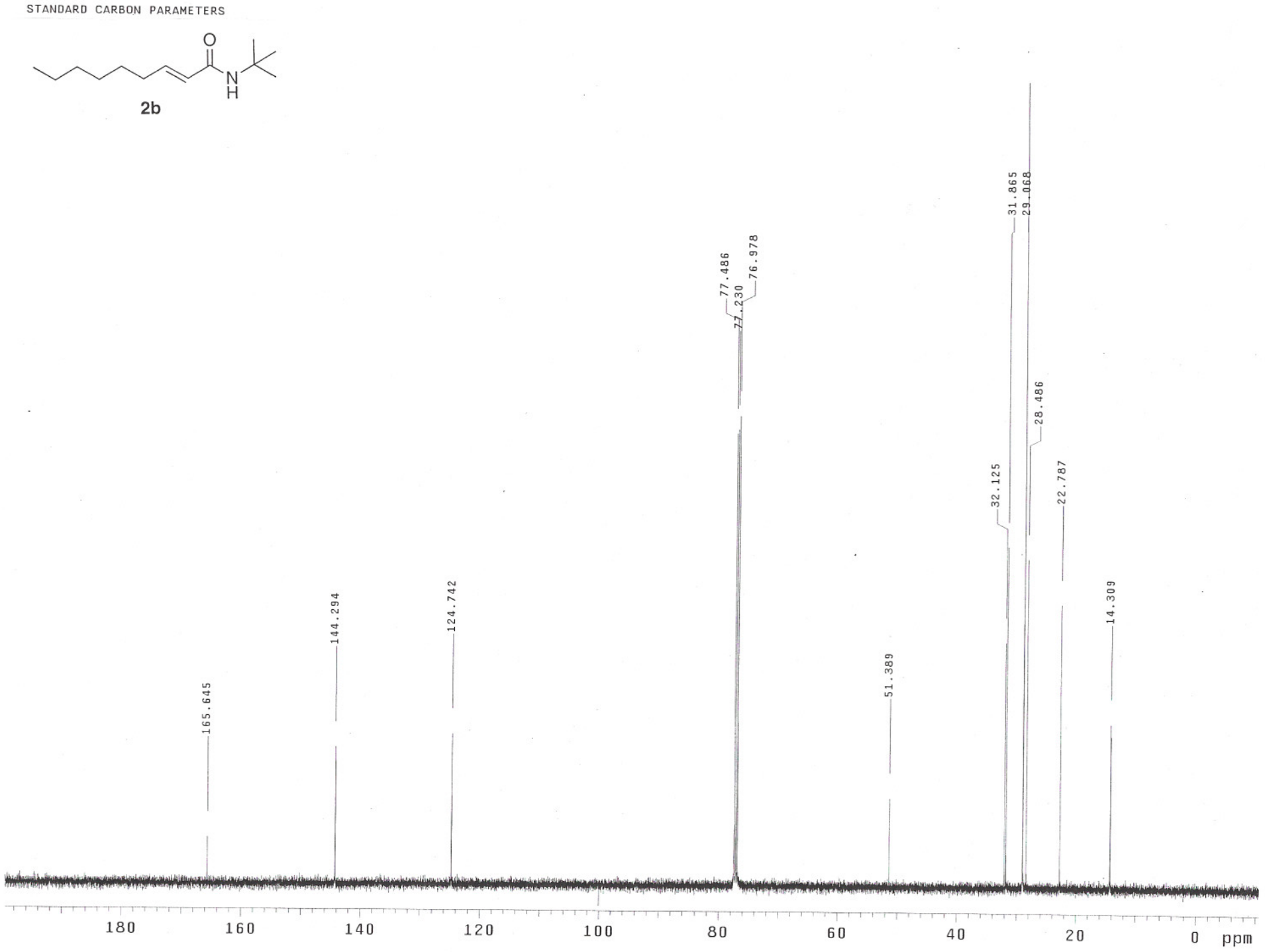
40
60
80
100
120
140
160
180

STANDARD PROTON PARAMETERS



2b




STANDARD CARBON PARAMETERS
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H
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76.978
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32.125
31.865
29.068
28.486
22.787
14.309
180
160
140
120
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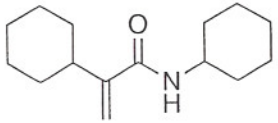
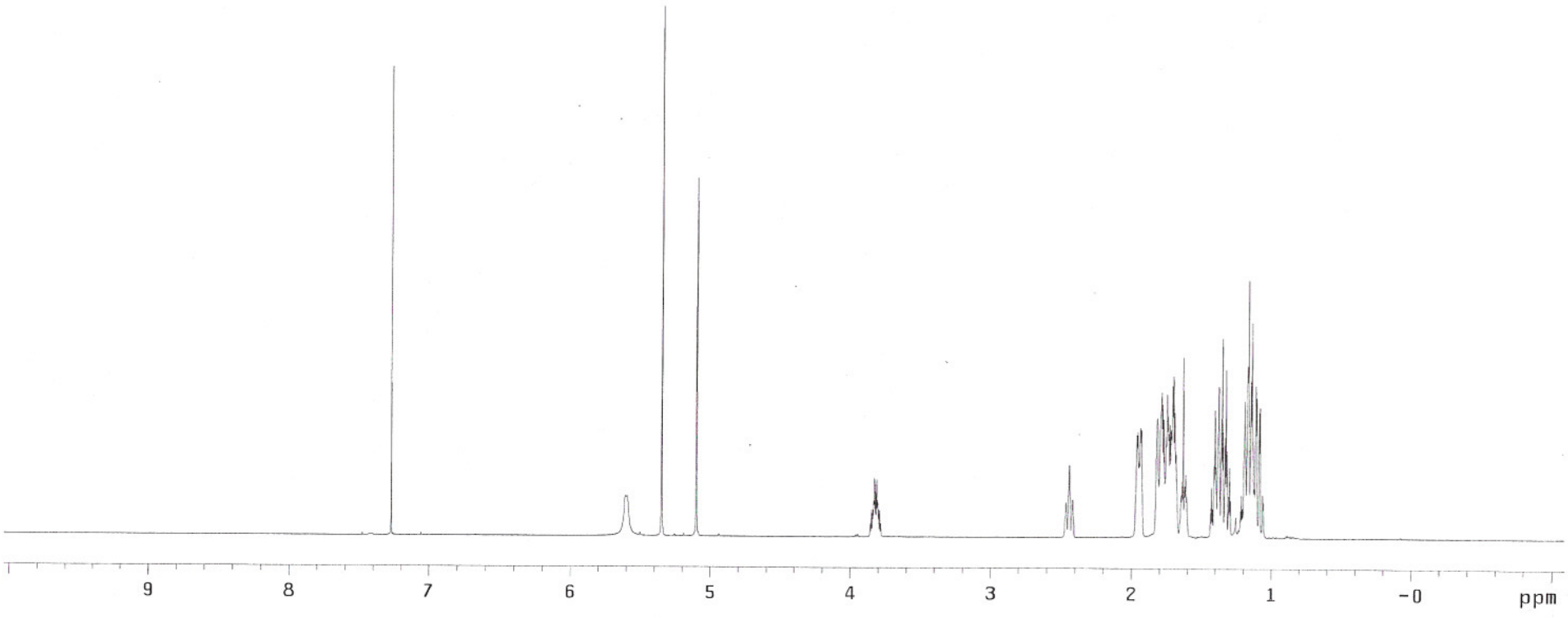
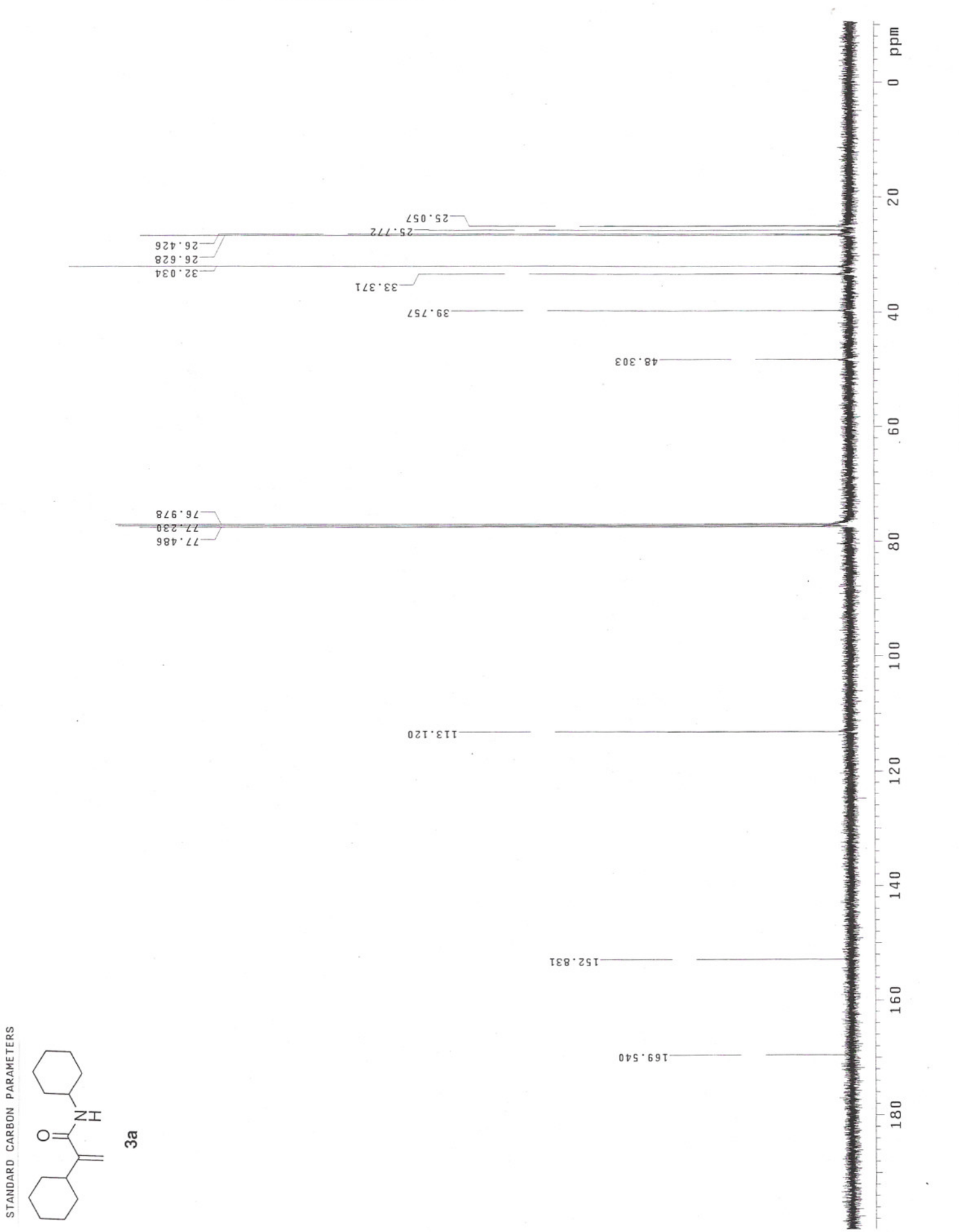
80
60
40
20
0
ppm

STANDARD PROTON PARAMETERS



3a




STANDARD CARBON PARAMETERS
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39.757
33.371
32.034
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25.057
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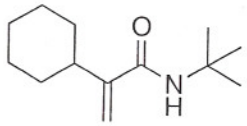
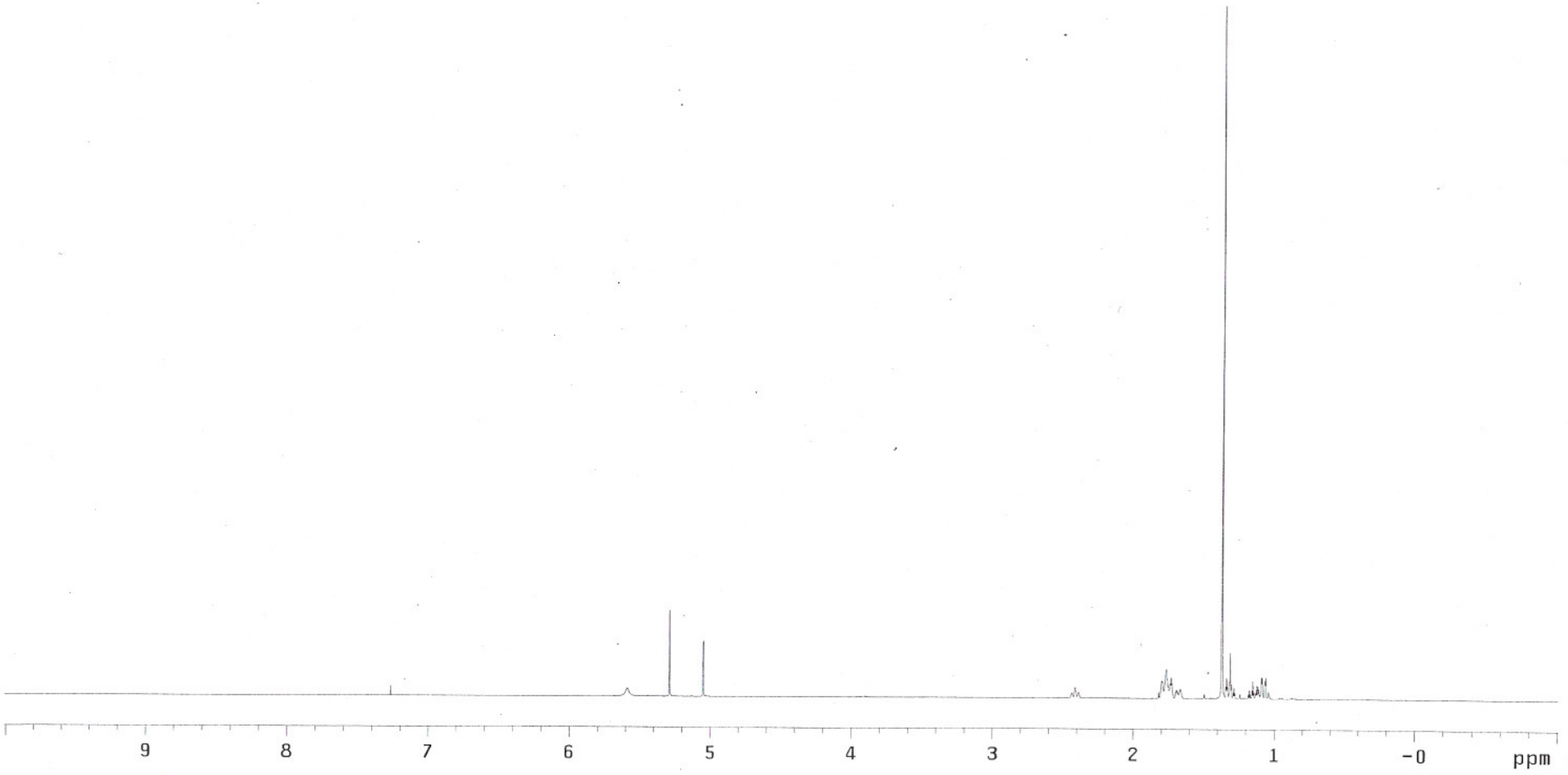
20
40
60
80
100
120
140
160
180

STANDARD PROTON PARAMETERS



4a



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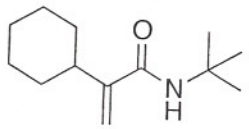
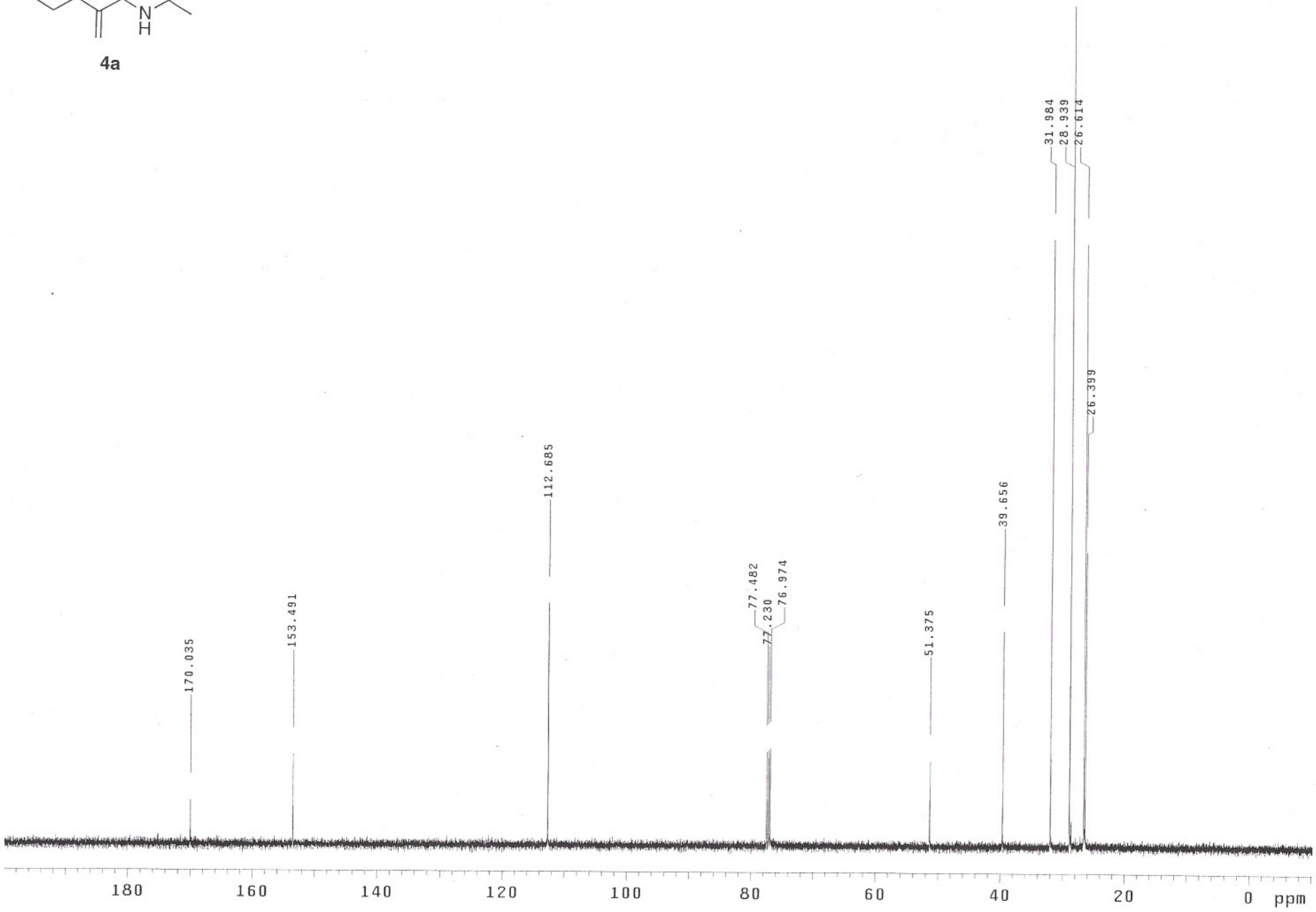
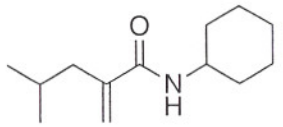


4a

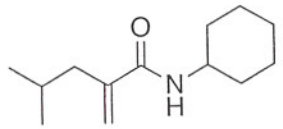


STANDARD PROTON PARAMETERS



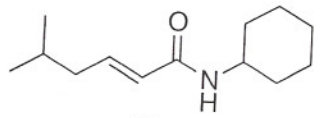
5a

STANDARD CARBON PARAMETERS

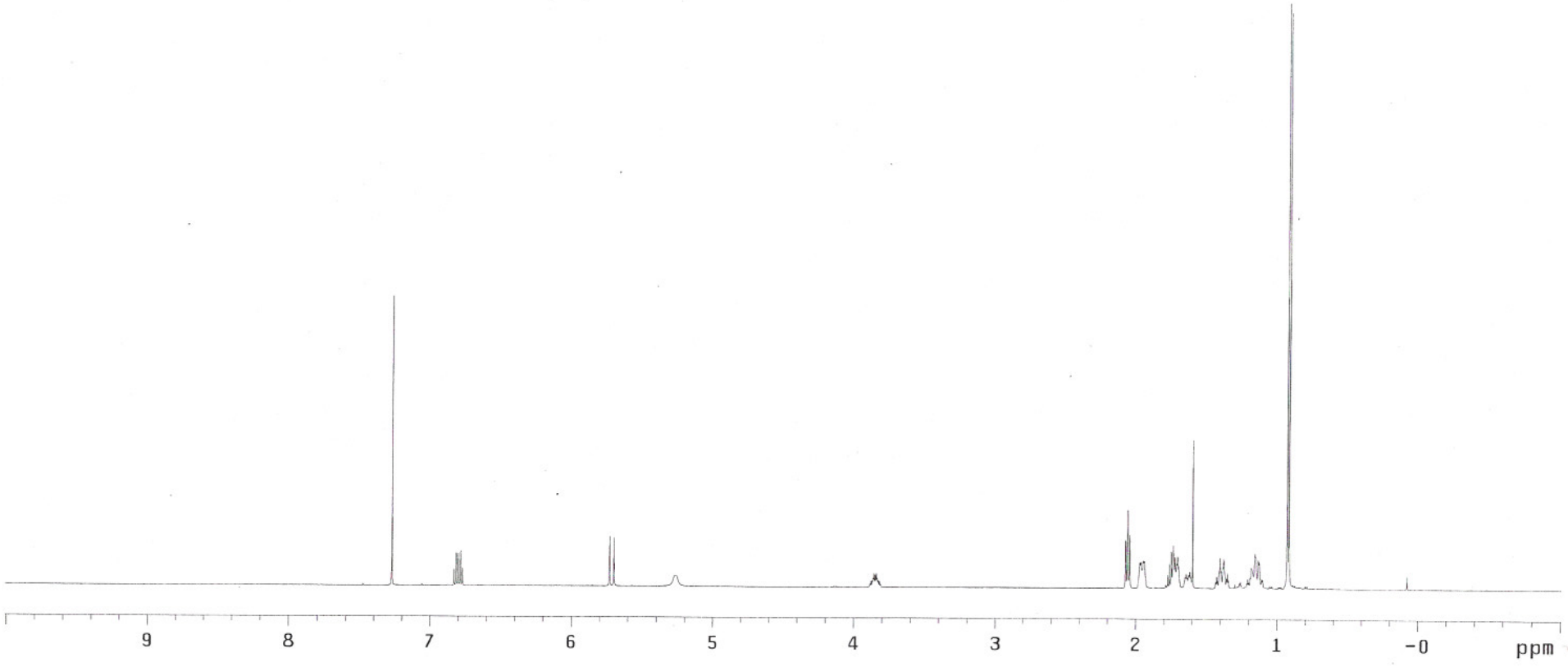


5a

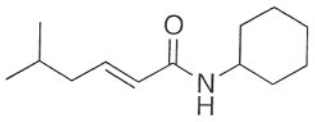
STANDARD PROTON PARAMETERS



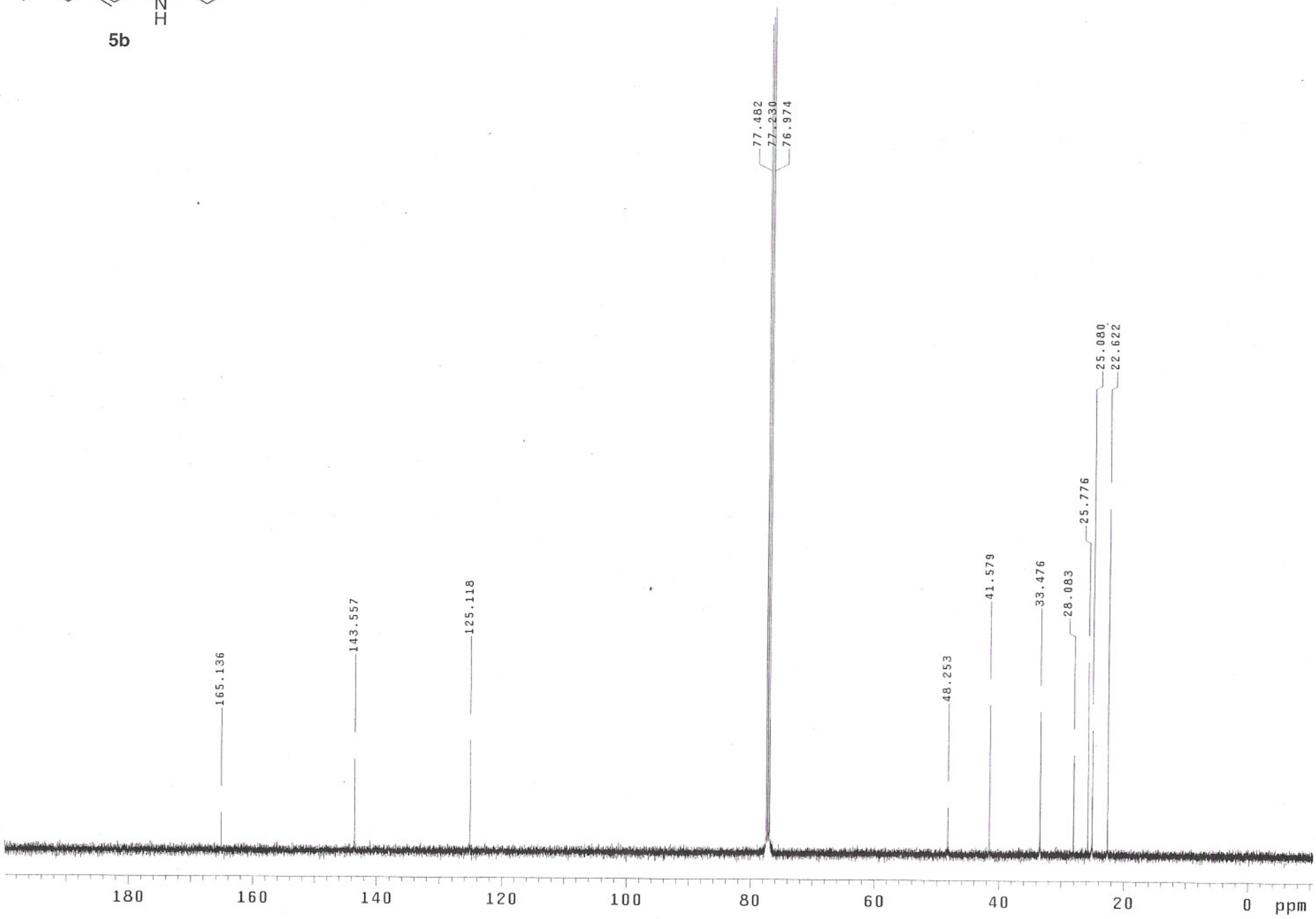
5b



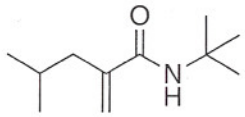
STANDARD CARBON PARAMETERS



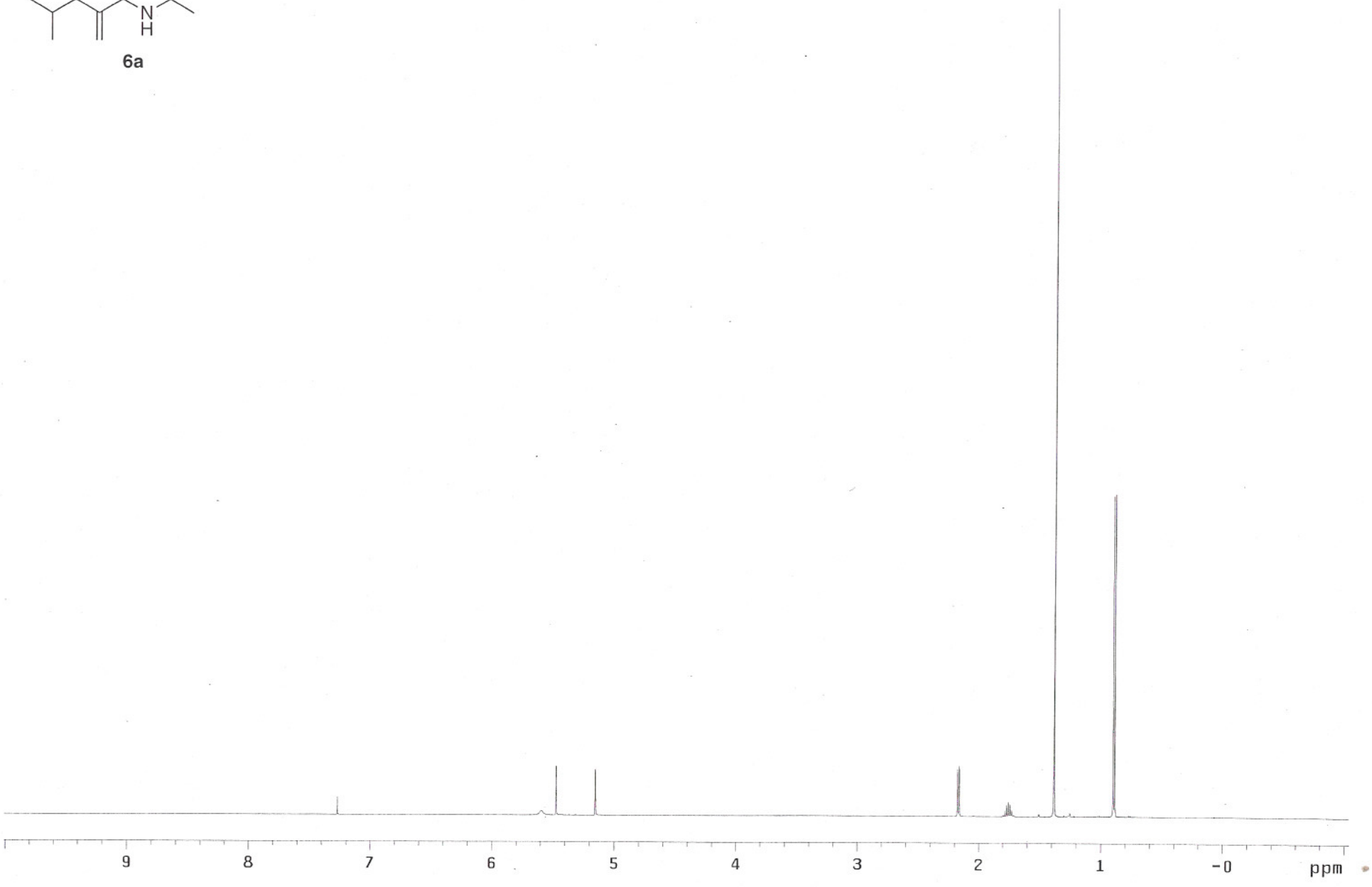
5b



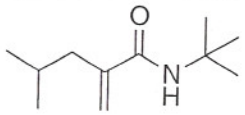
STANDARD PROTON PARAMETERS



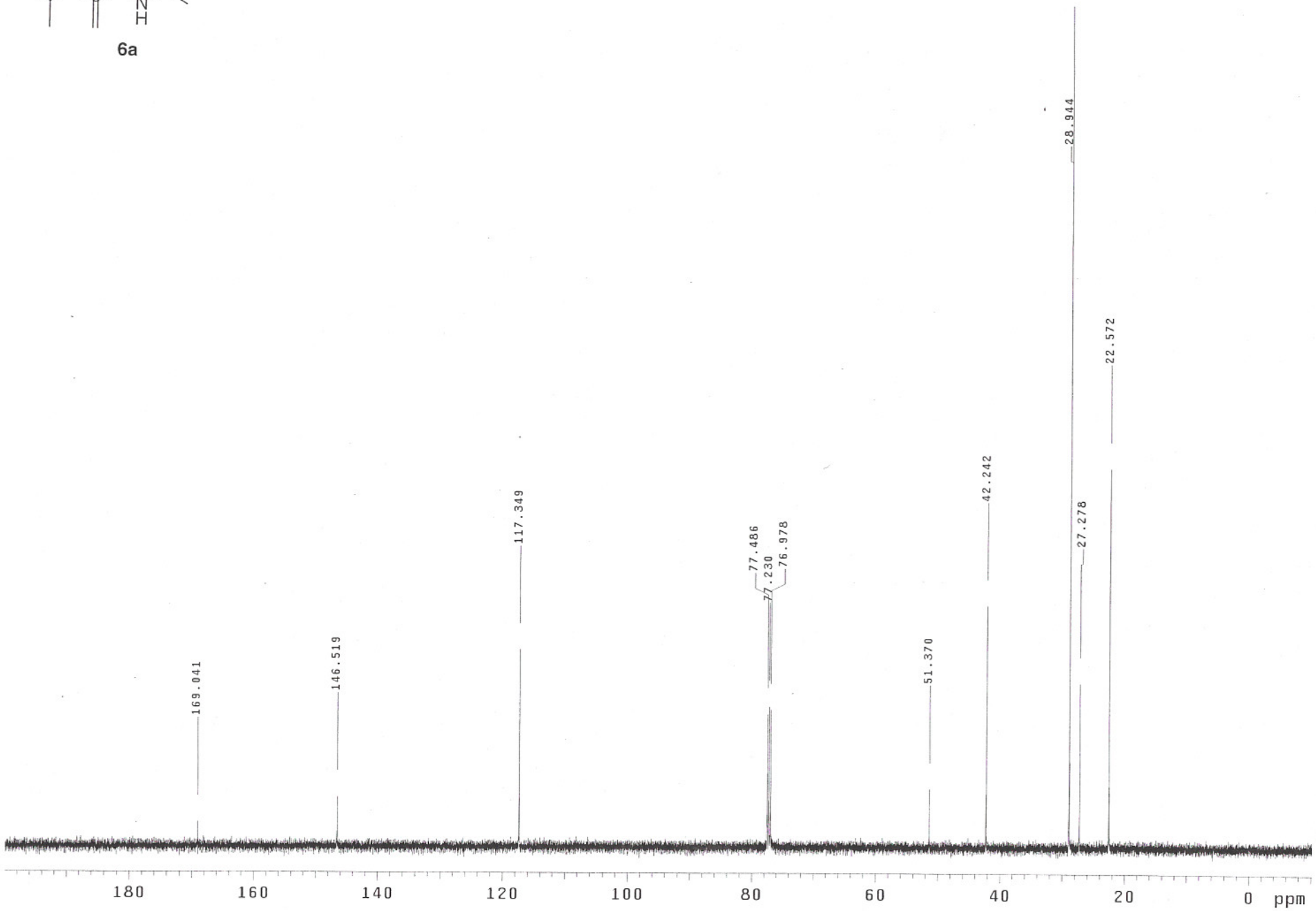
6a



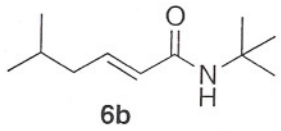
STANDARD CARBON PARAMETERS



6a

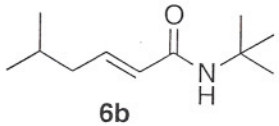


STANDARD PROTON PARAMETERS

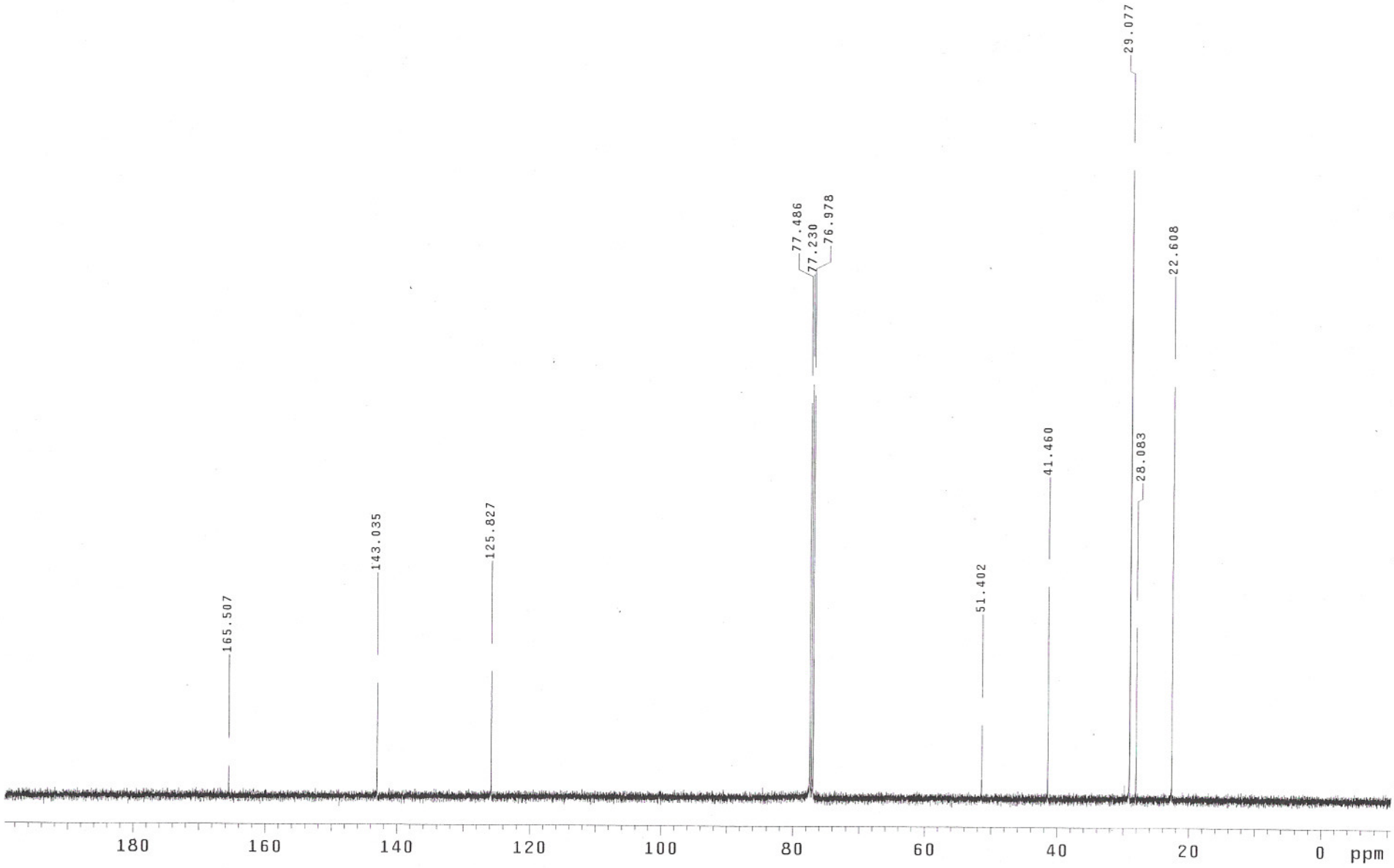


6b

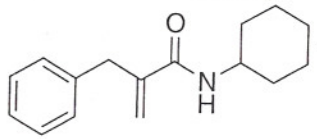
STANDARD CARBON PARAMETERS



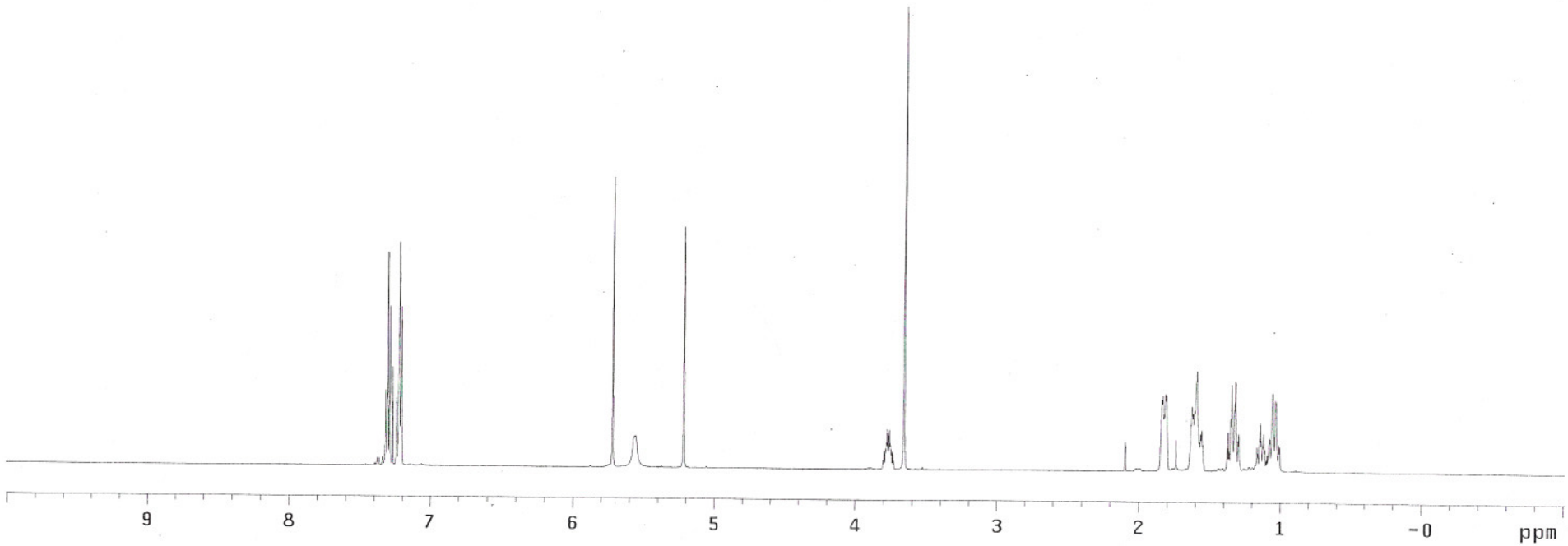
6b



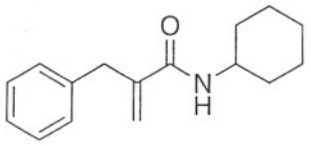
STANDARD PROTON PARAMETERS



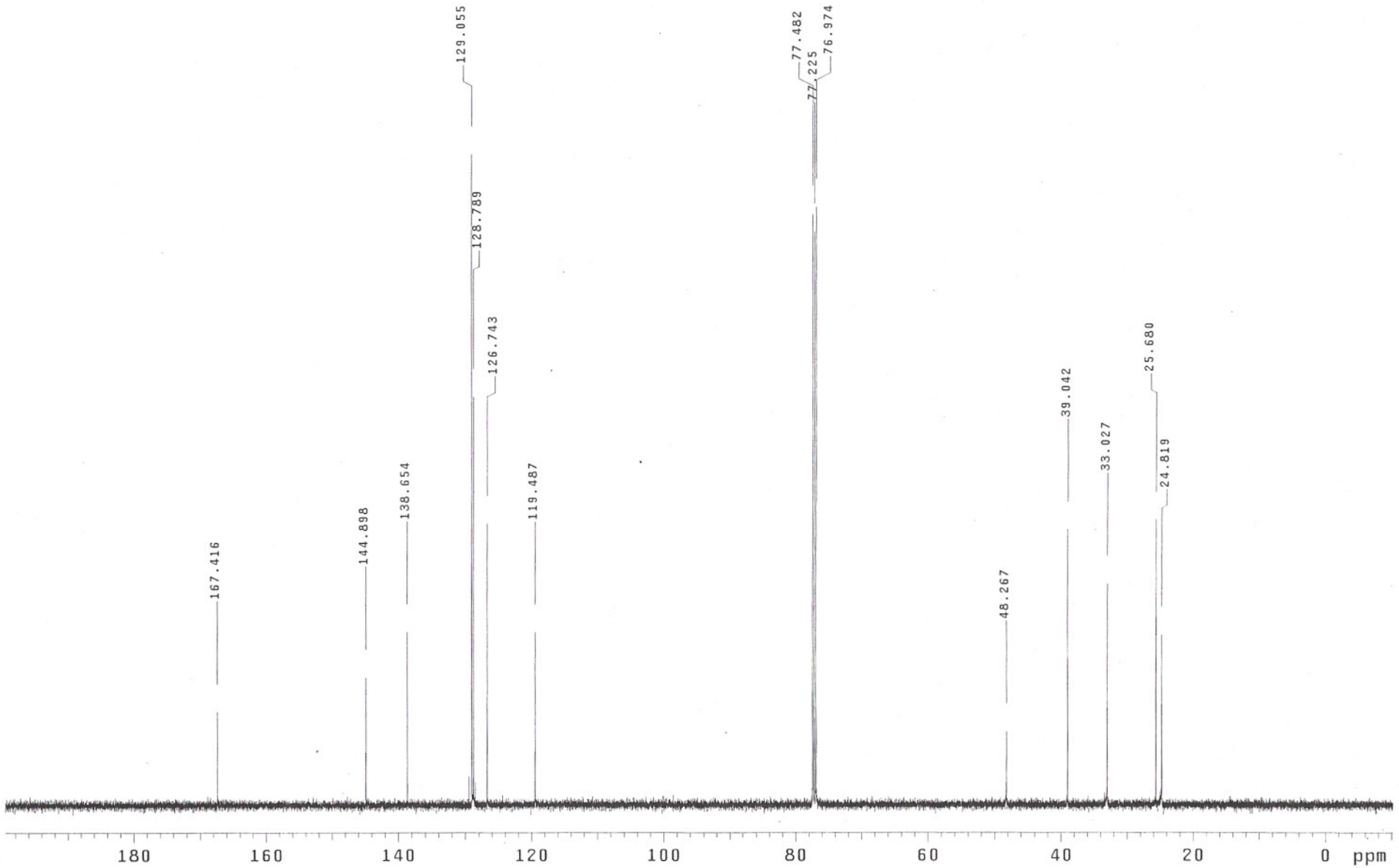
7a



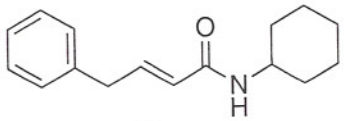
STANDARD CARBON PARAMETERS



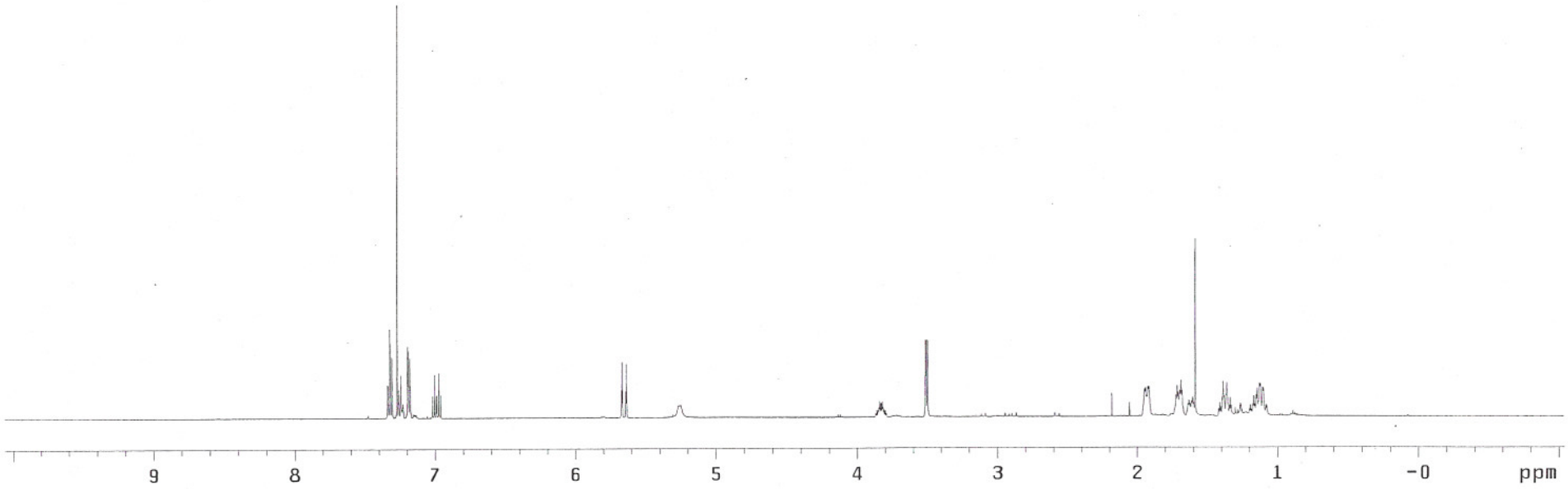
7a



STANDARD PROTON PARAMETERS



7b



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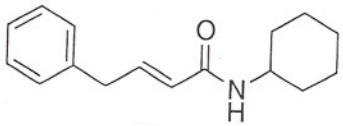
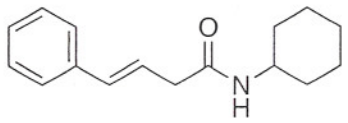
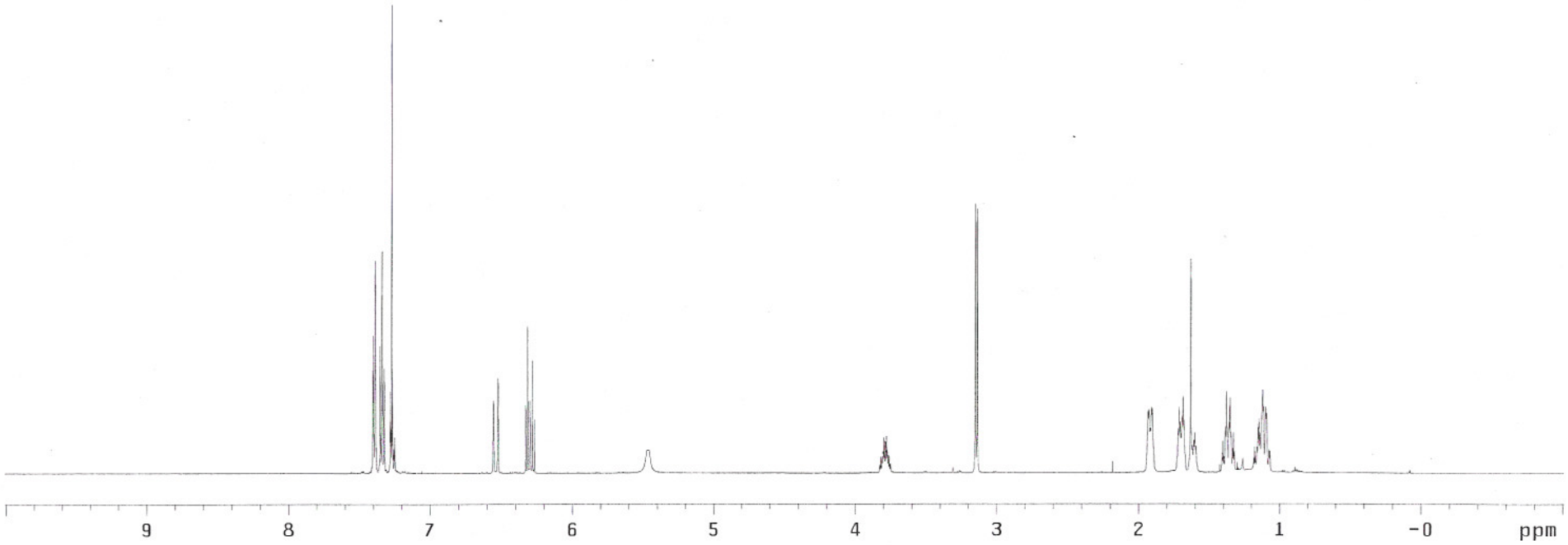


7b

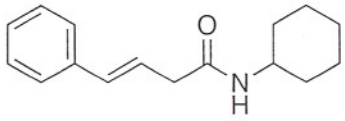
STANDARD PROTON PARAMETERS



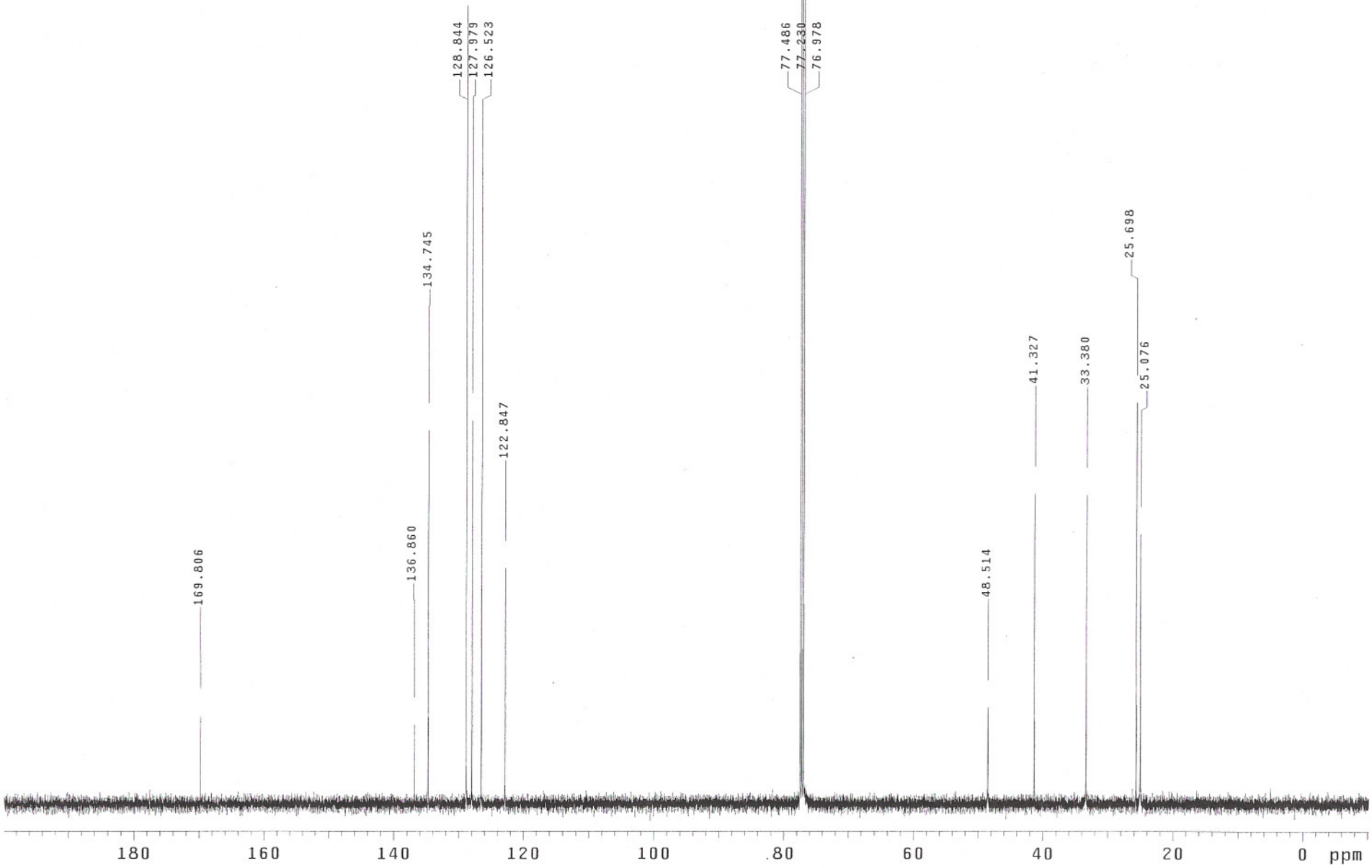
7c



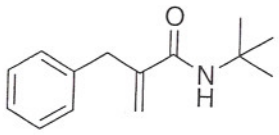
STANDARD CARBON PARAMETERS



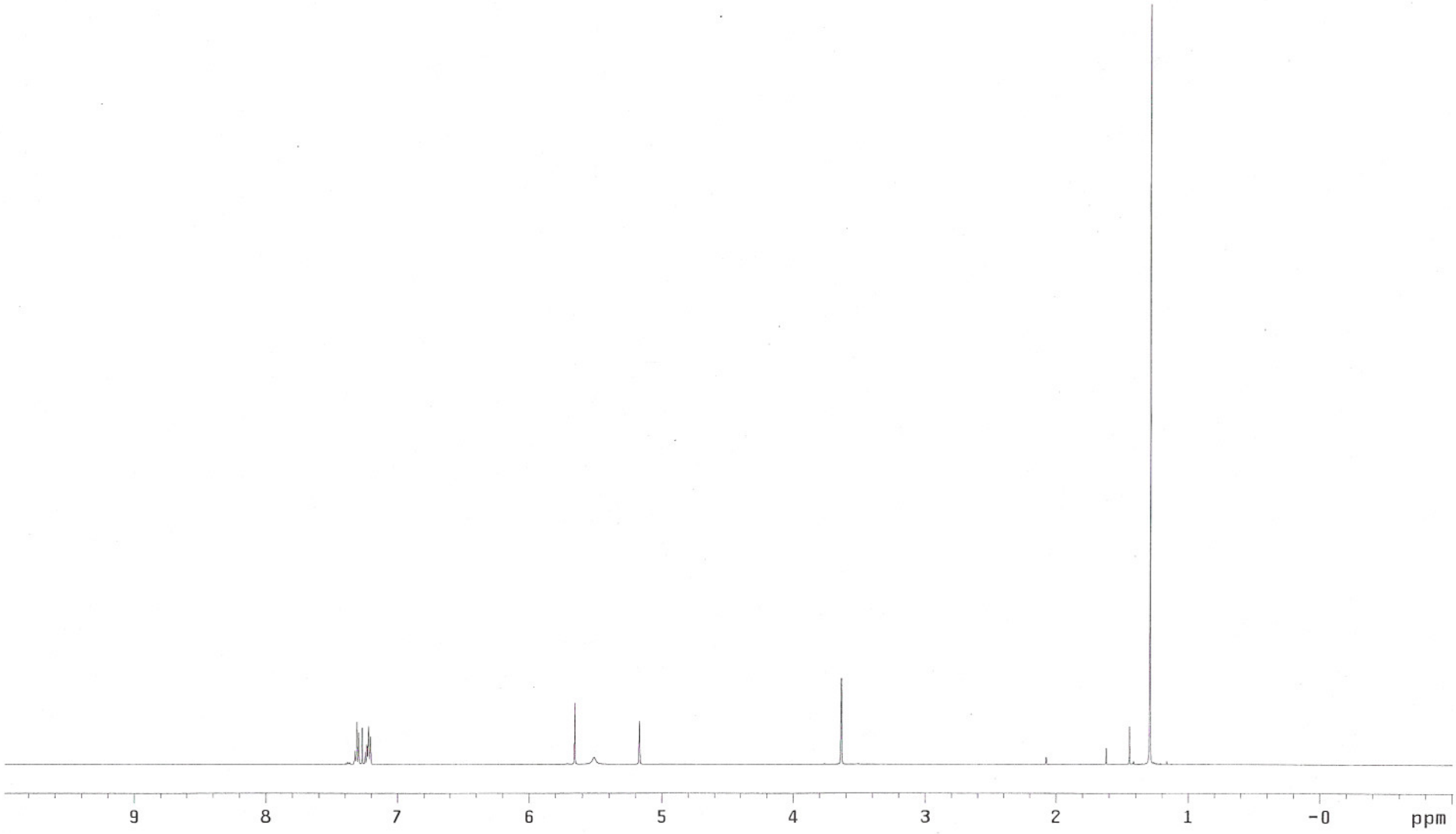
7c

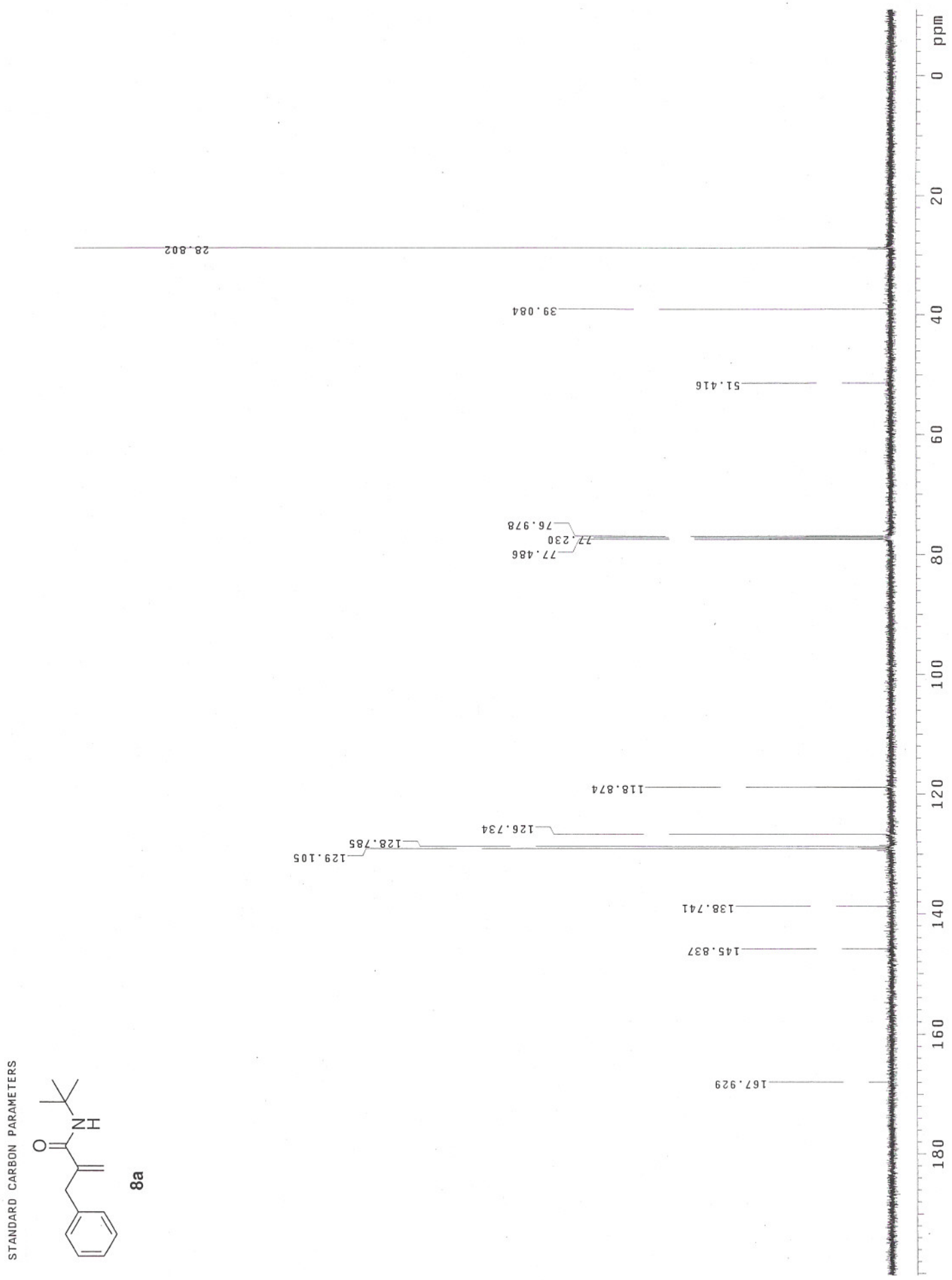


STANDARD PROTON PARAMETERS



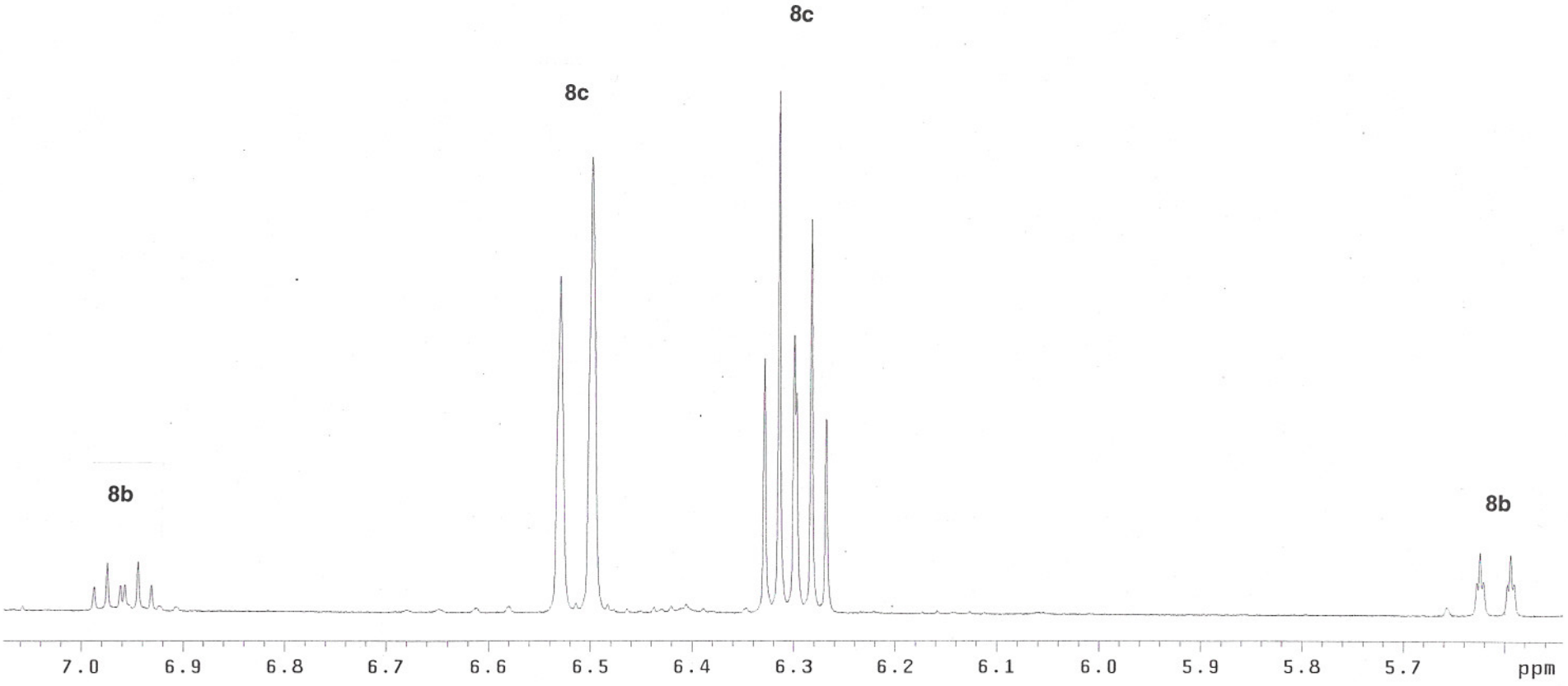
8a



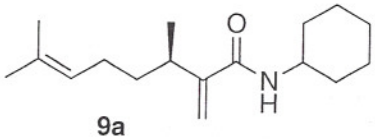

STANDARD CARBON PARAMETERS
8a
167.929
145.837
138.741
129.105
128.785
126.734
118.874
77.486
77.230
76.978
51.416
39.084
28.802
ppm
0
20
40
60
80
100
120
140
160
180

STANDARD PROTON PARAMETERS

8b & 8c

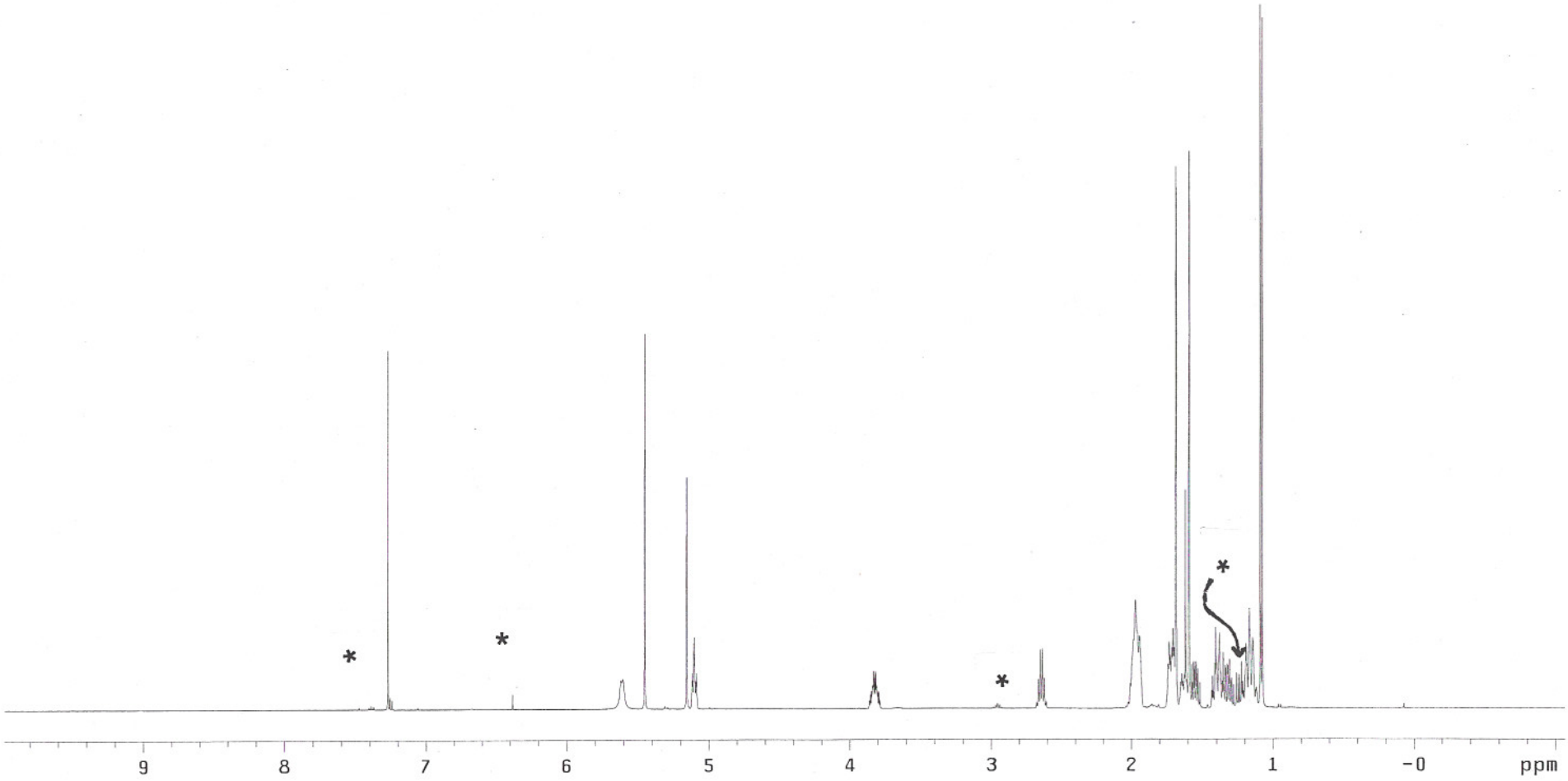


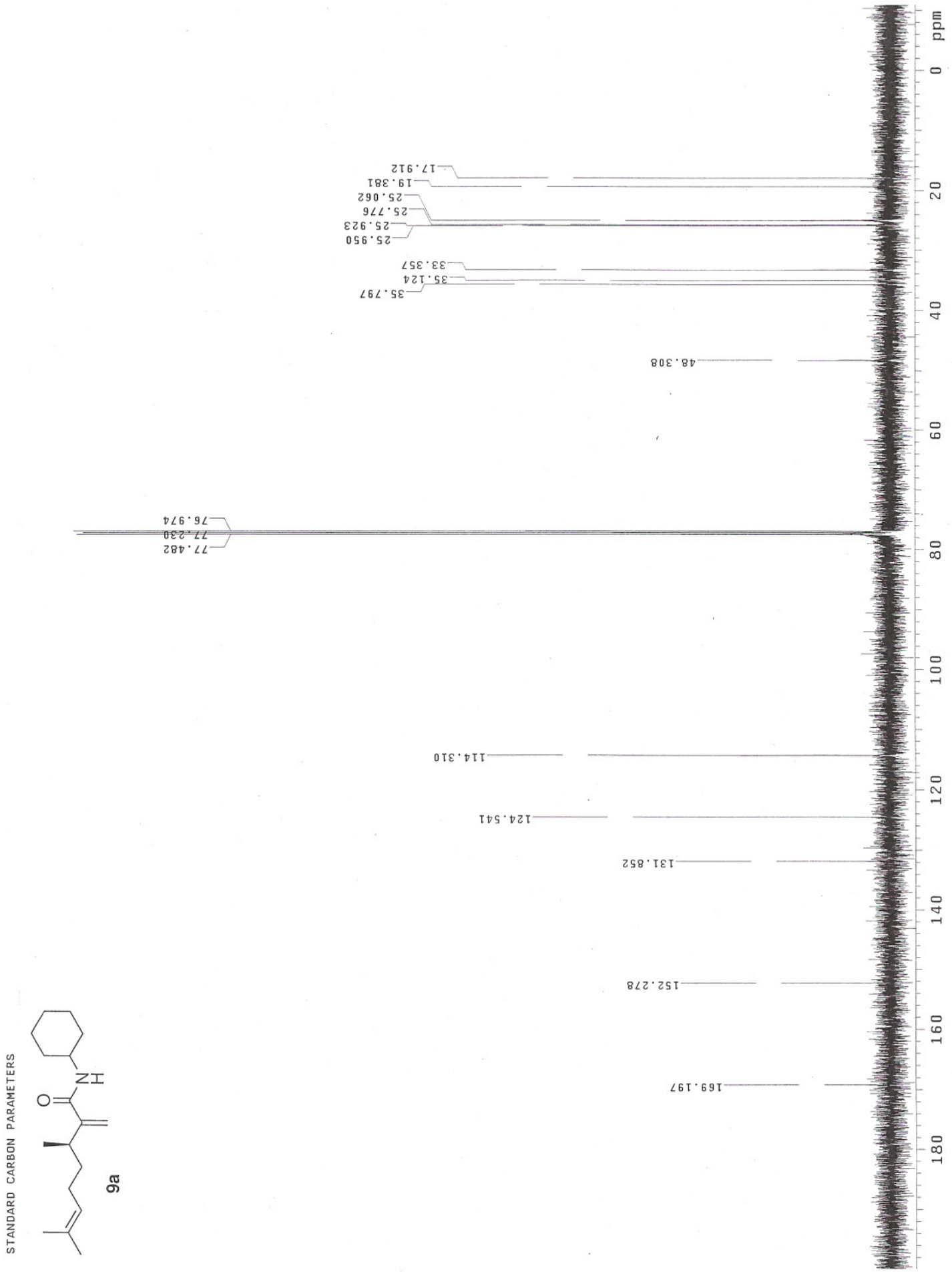
STANDARD PROTON PARAMETERS



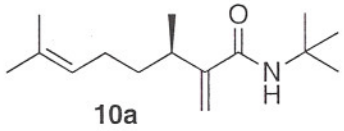
9a

* indicates ligand-derived impurity (approx. 2%)



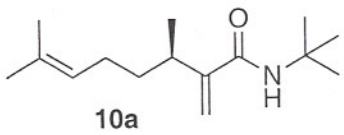

STANDARD CARBON PARAMETERS
9a
169.197
152.278
131.852
124.541
114.310
77.482
77.230
76.974
48.308
35.797
35.124
33.357
25.950
25.923
25.776
25.062
19.381
17.912
ppm

STANDARD PROTON PARAMETERS

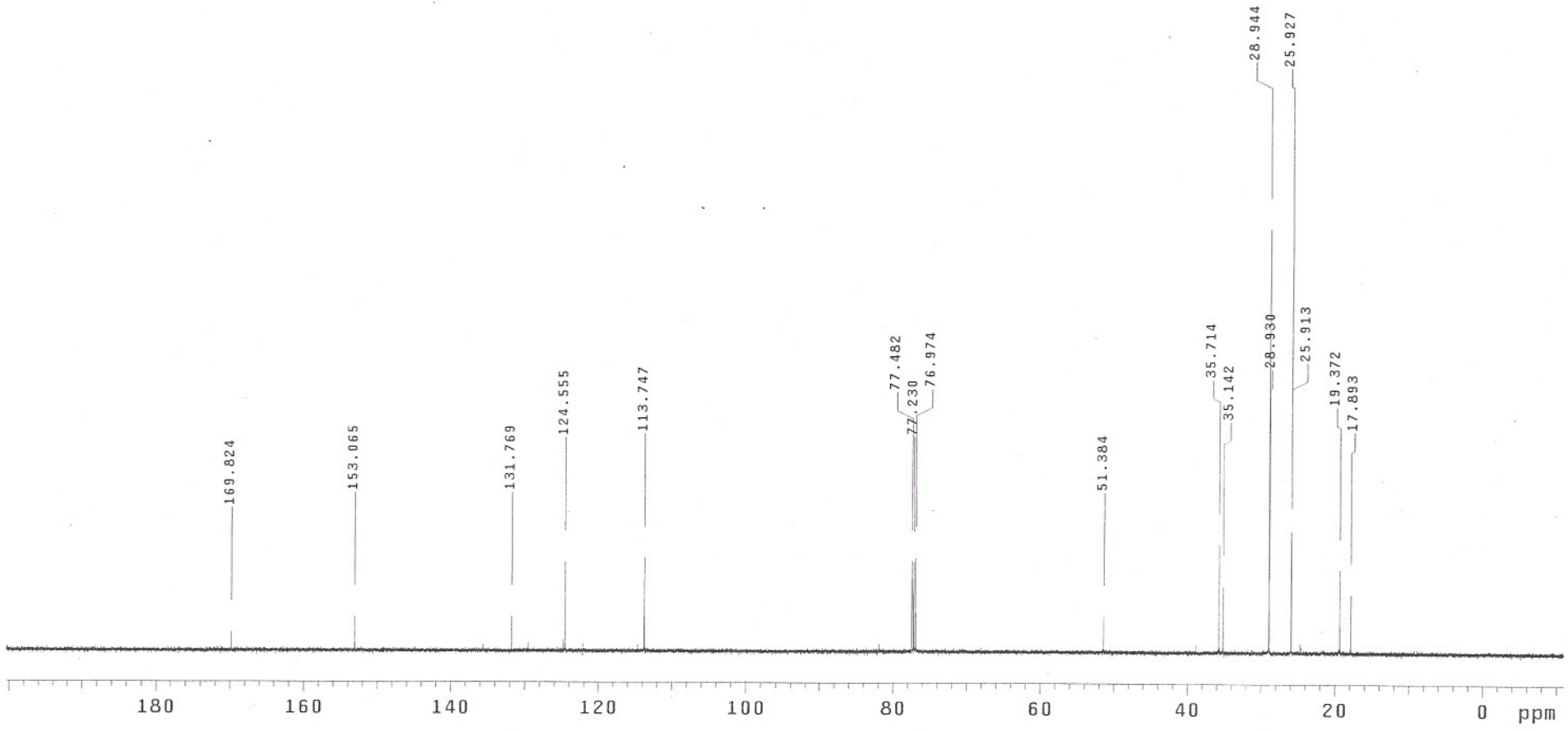


10a

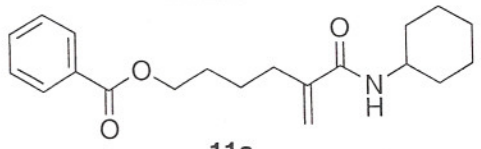
STANDARD CARBON PARAMETERS



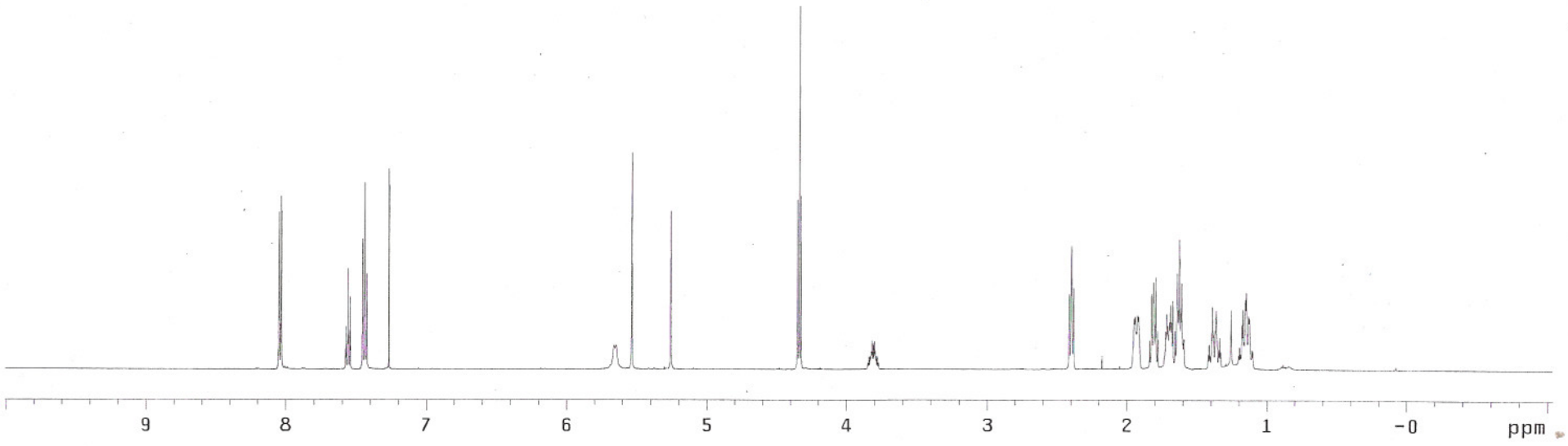
10a



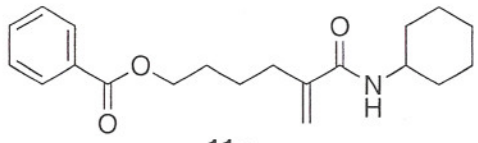
STANDARD PROTON PARAMETERS



11a

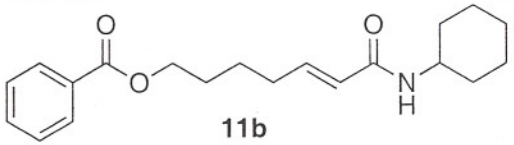


STANDARD CARBON PARAMETERS

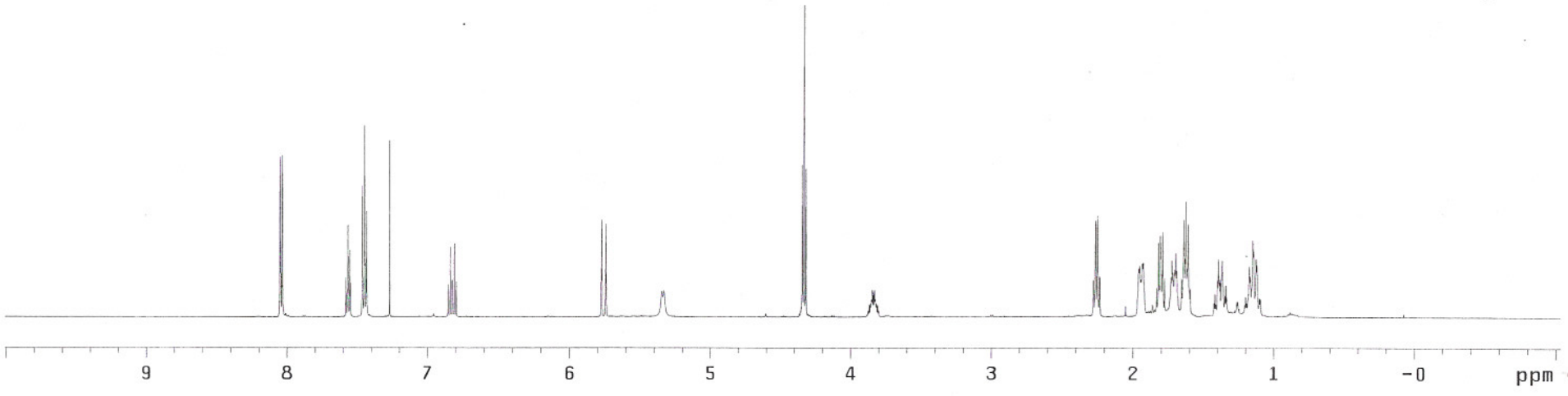


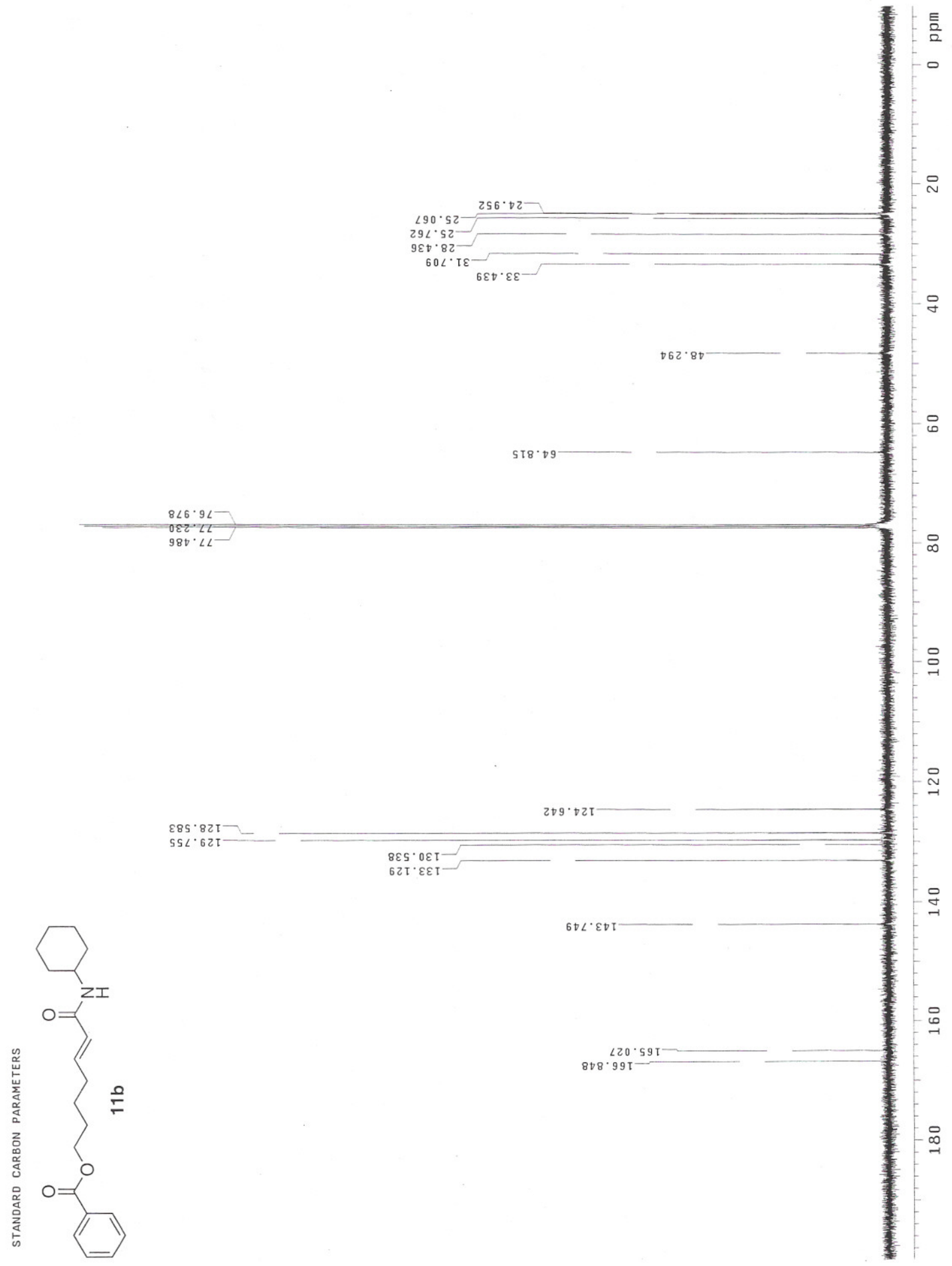
11a

STANDARD PROTON PARAMETERS

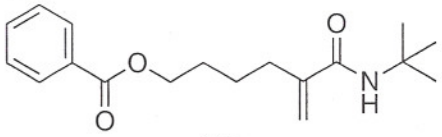


11b

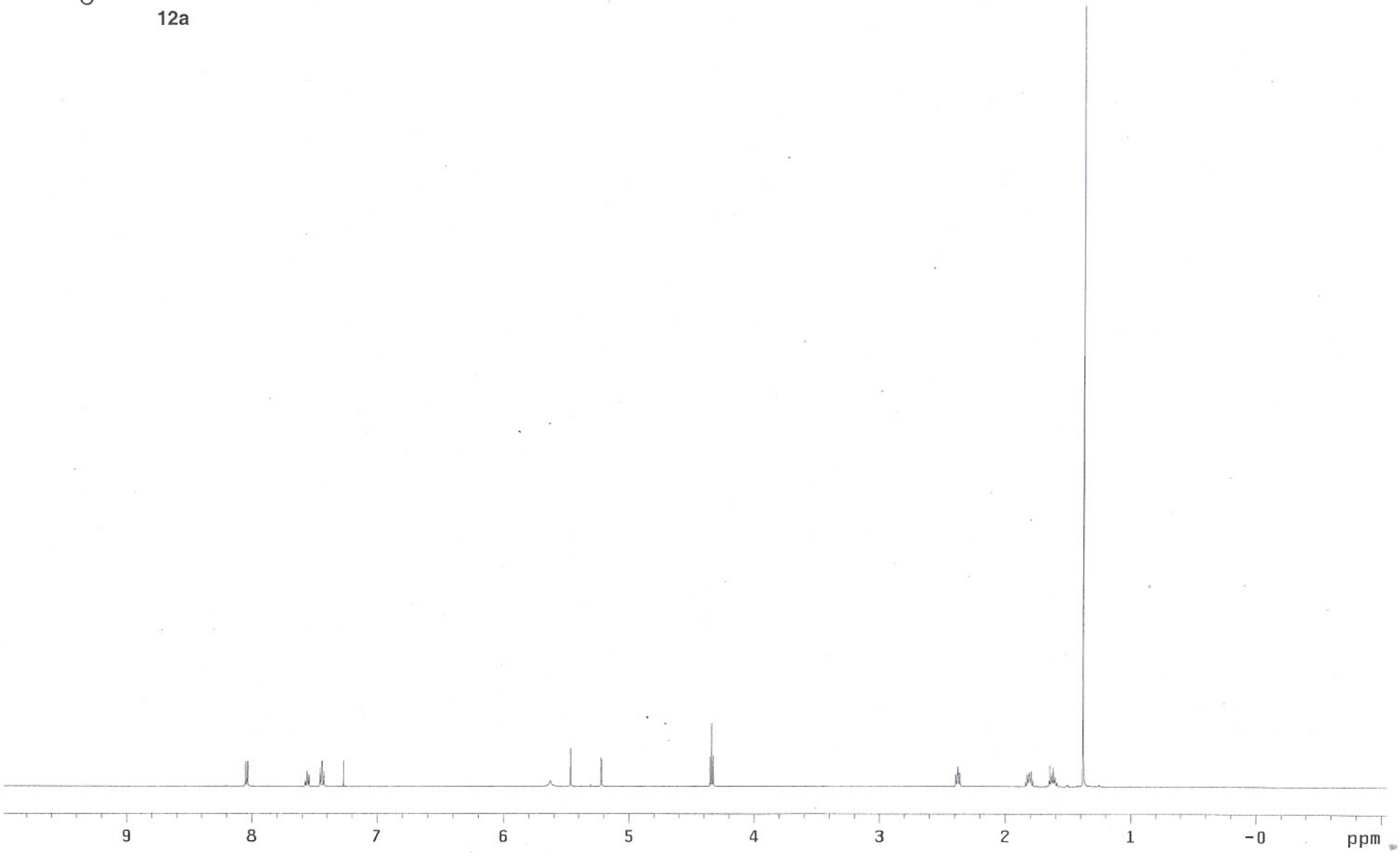



STANDARD CARBON PARAMETERS
11b
24.952
25.067
25.762
28.436
31.709
33.439
48.294
64.815
76.978
77.230
77.486
124.642
128.583
129.755
130.538
133.129
143.749
165.027
166.848
0 ppm
20
40
60
80
100
120
140
160
180

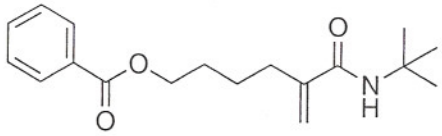
STANDARD PROTON PARAMETERS



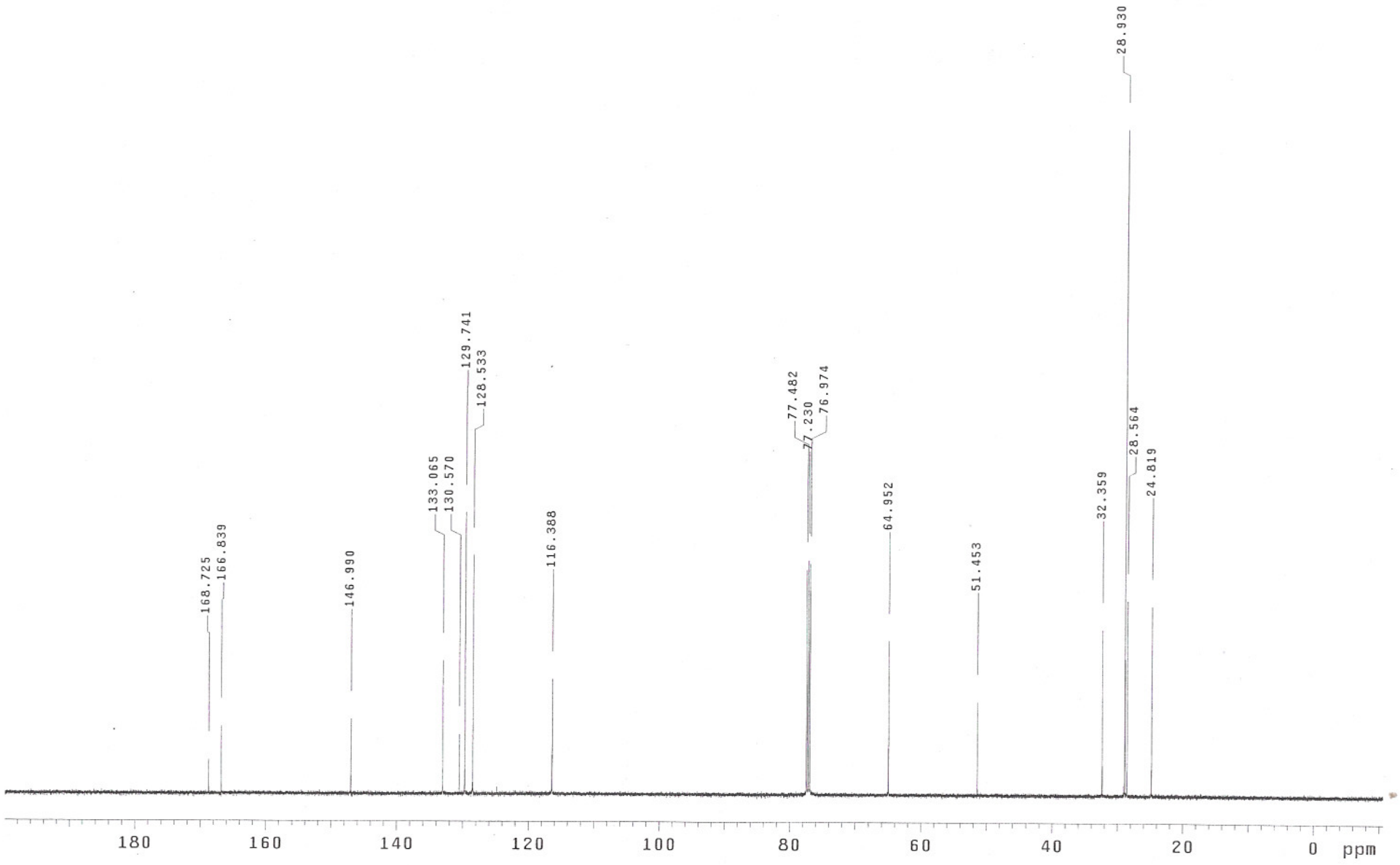
12a



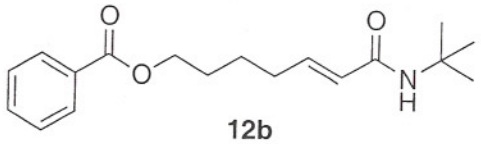
STANDARD CARBON PARAMETERS



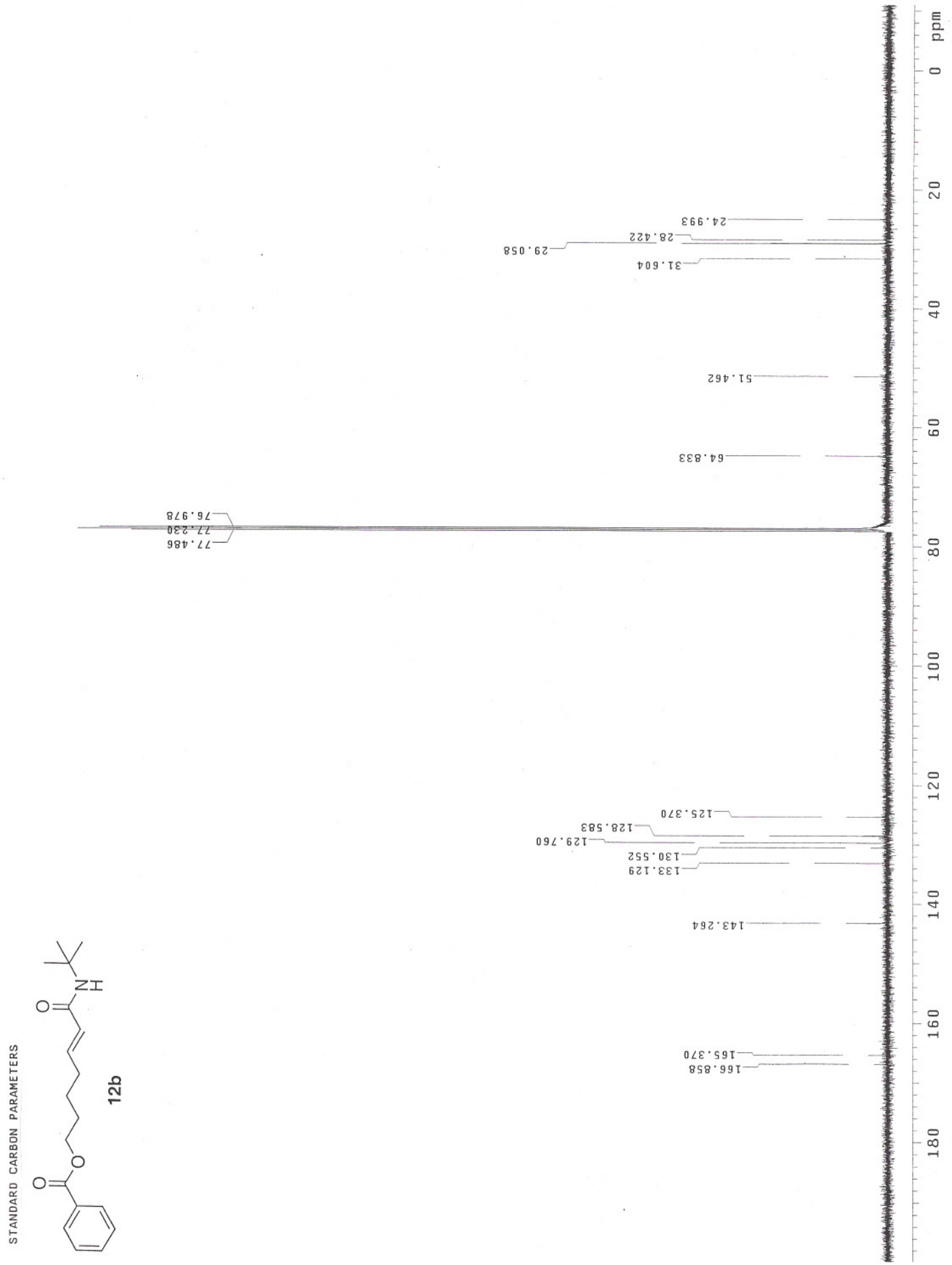
12a



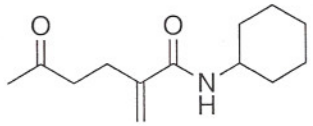
STANDARD PROTON PARAMETERS



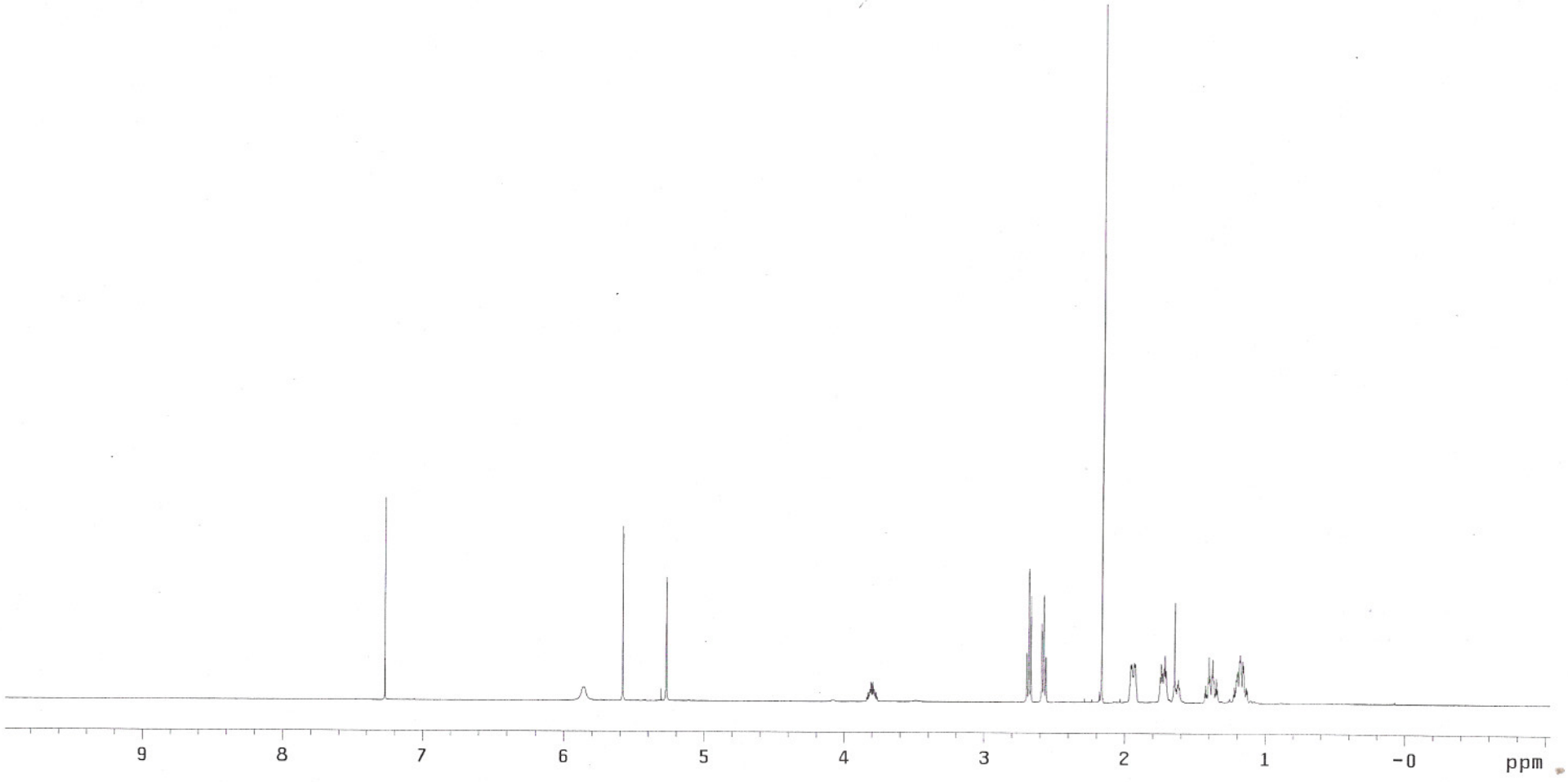
12b


STANDARD CARBON PARAMETERS
12b
166.858
165.370
143.264
133.129
130.552
129.760
128.583
125.370
77.486
77.230
76.978
64.833
51.462
31.604
29.058
28.422
24.993
ppm
0
20
40
60
80
100
120
140
160
180

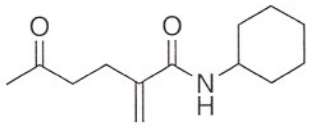
STANDARD PROTON PARAMETERS



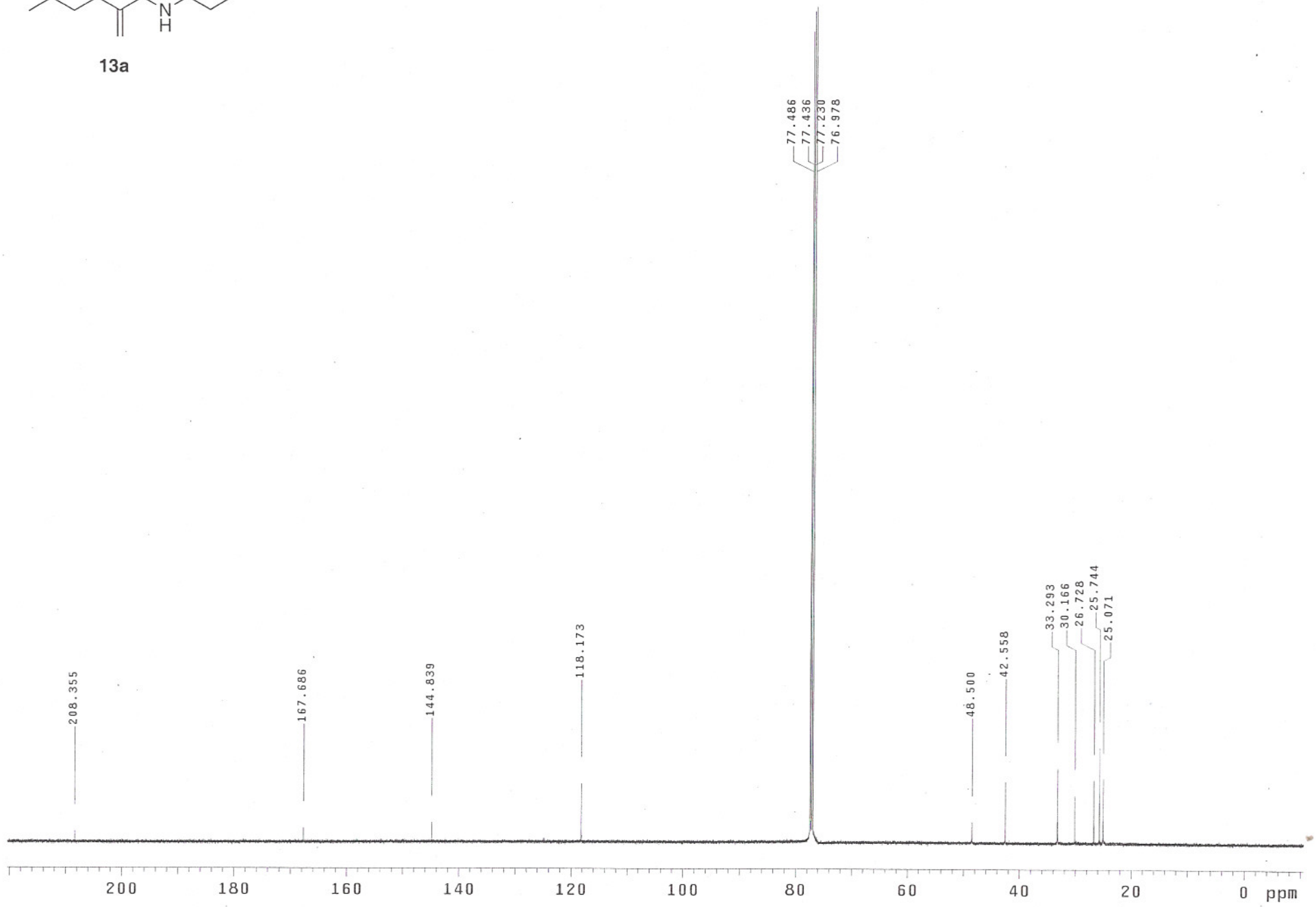
13a



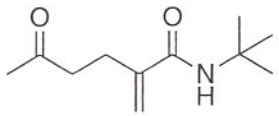
STANDARD CARBON PARAMETERS



13a

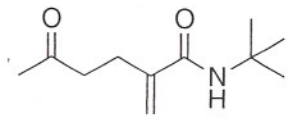


STANDARD PROTON PARAMETERS



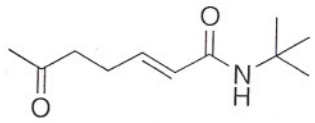
14a

STANDARD CARBON PARAMETERS



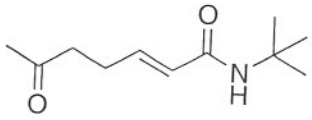
14a

STANDARD PROTON PARAMETERS



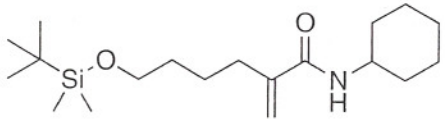
14b

STANDARD CARBON PARAMETERS



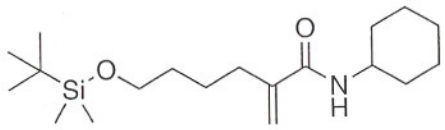
14b

STANDARD PROTON PARAMETERS

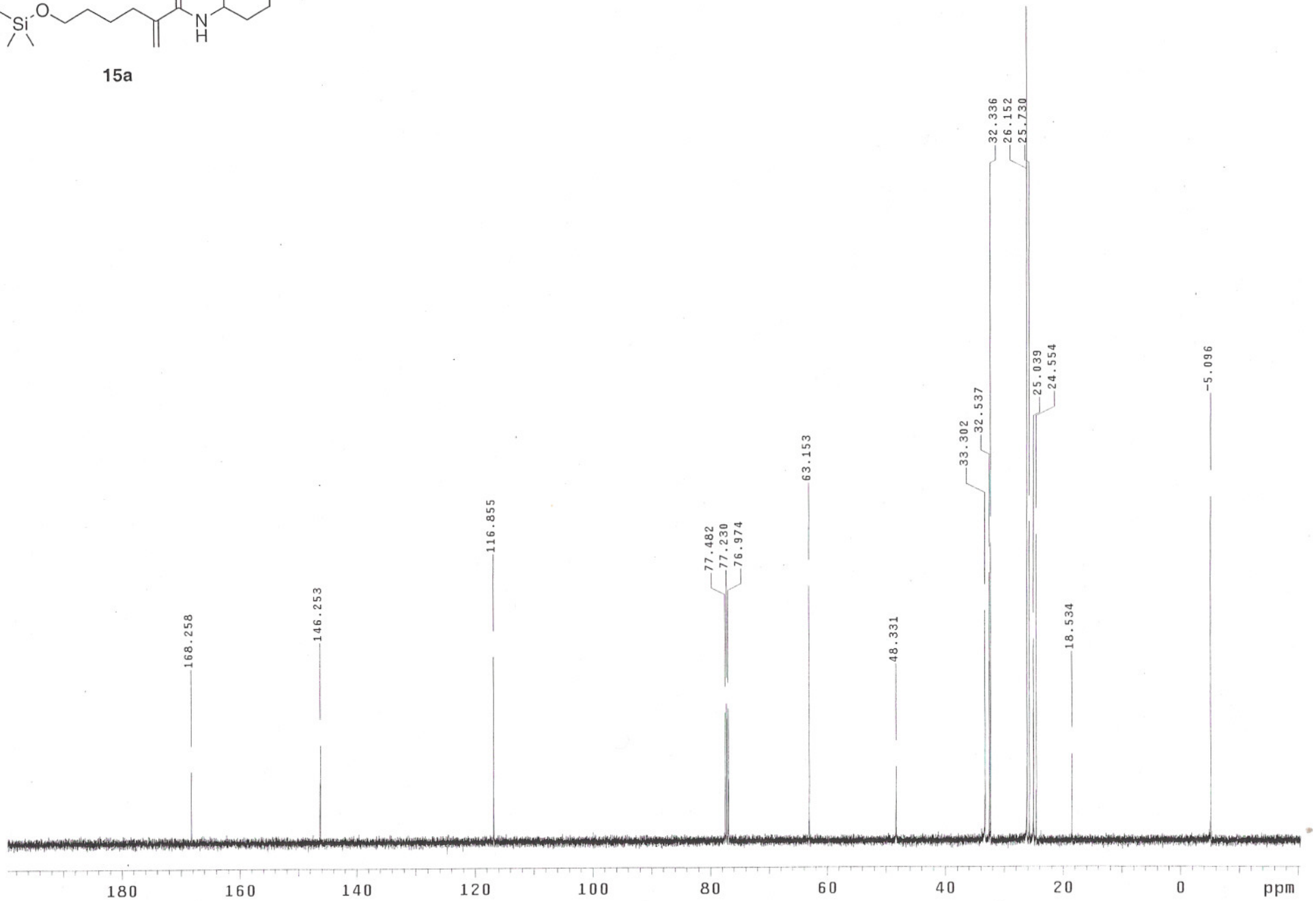


15a

STANDARD CARBON PARAMETERS



15a



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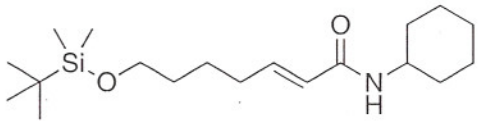

15b

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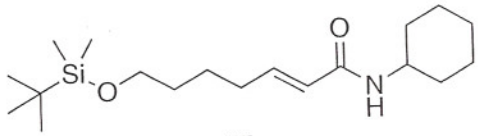

15b

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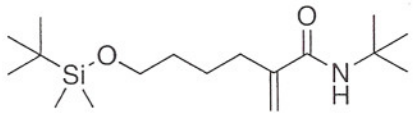
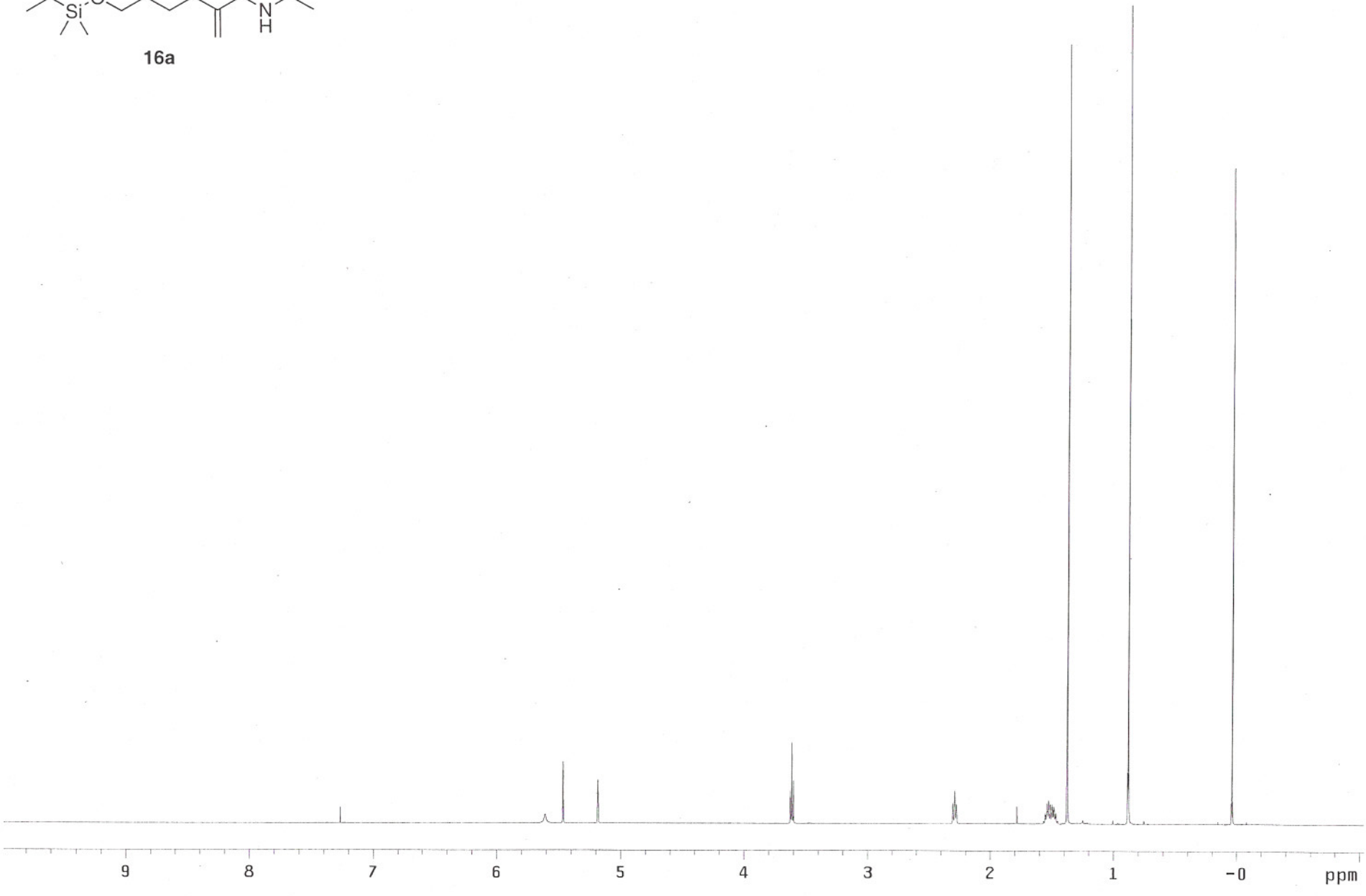


16a



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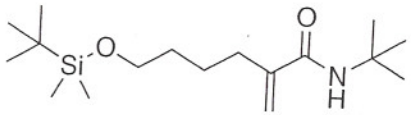

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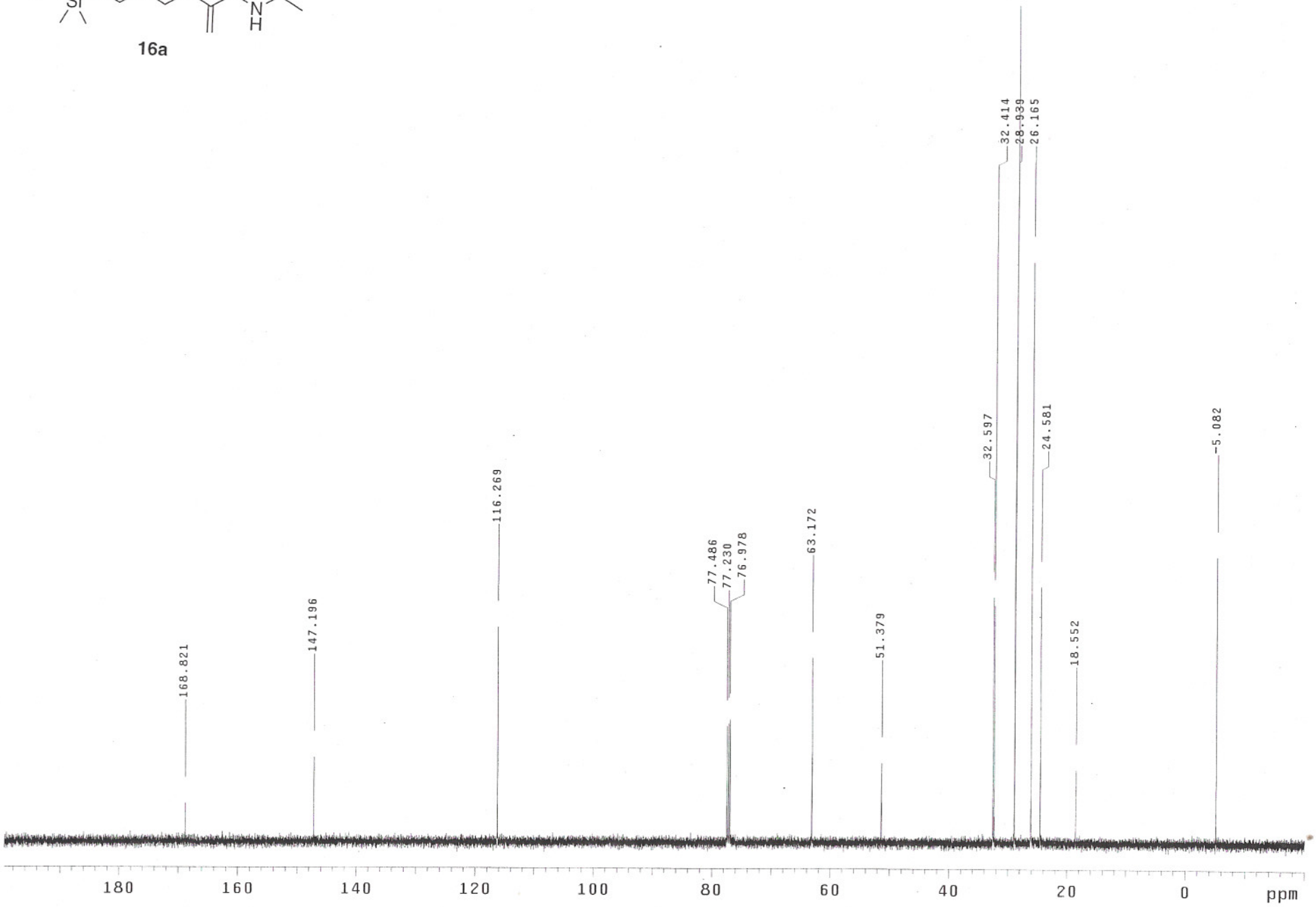

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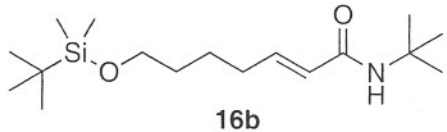

16b

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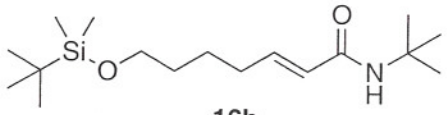

16b

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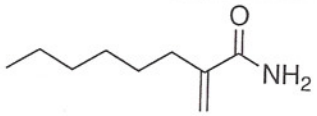
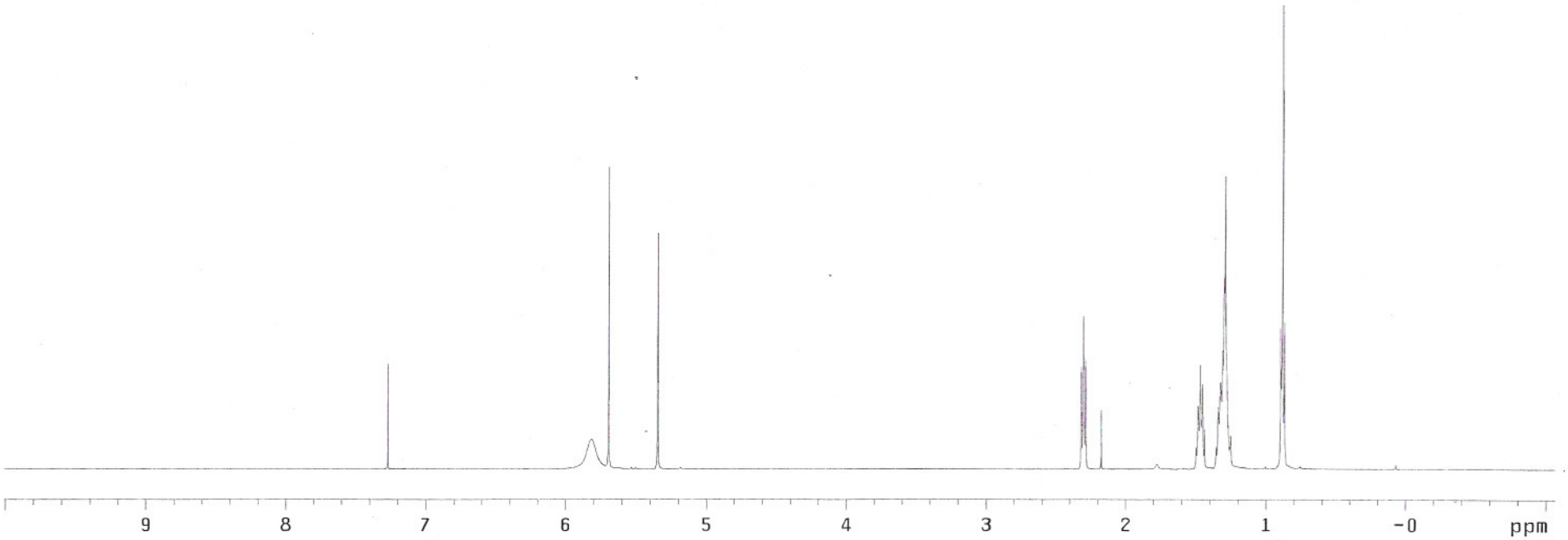
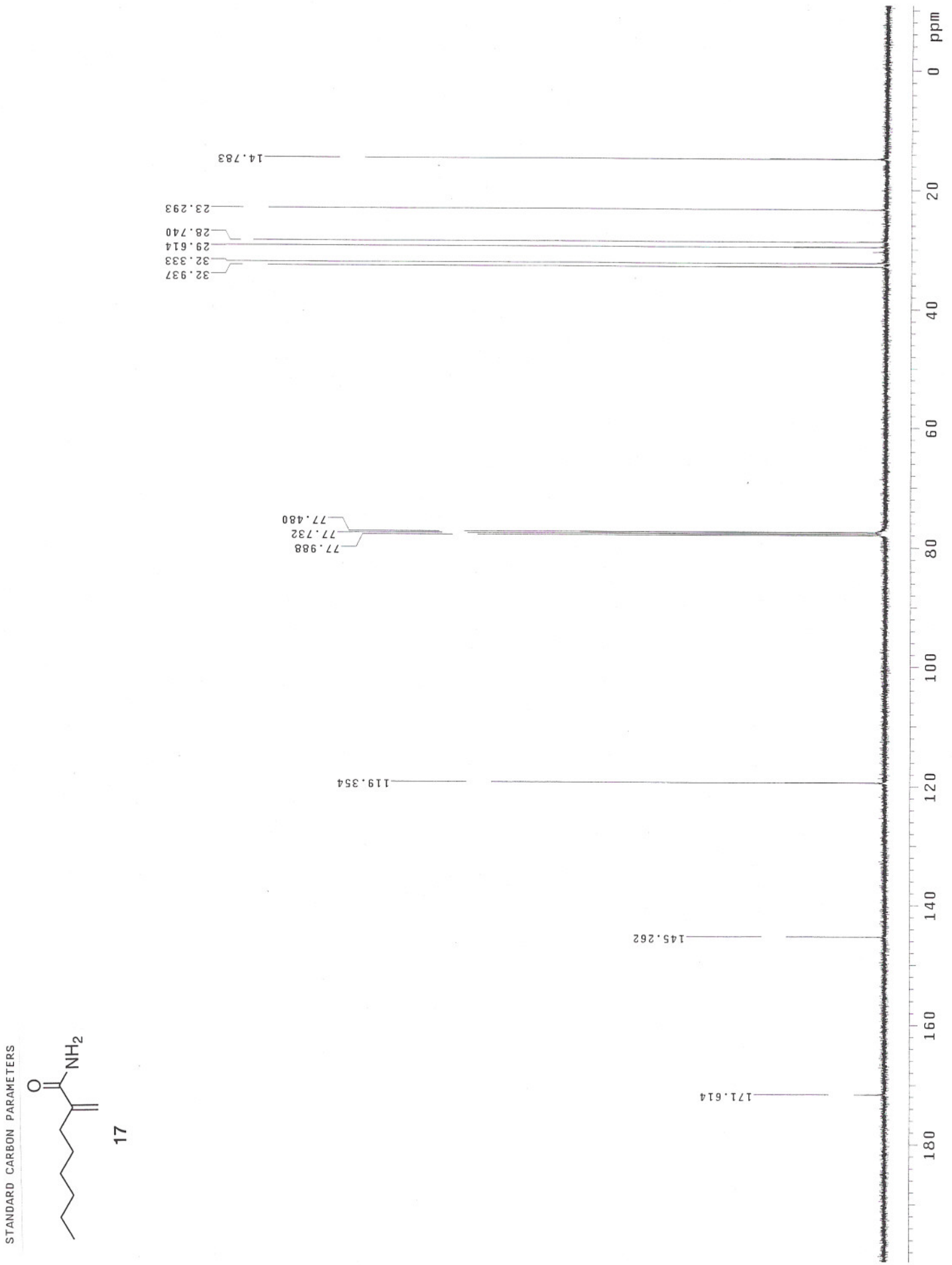
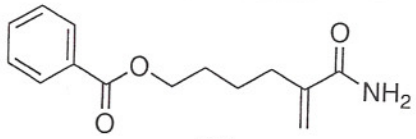


17

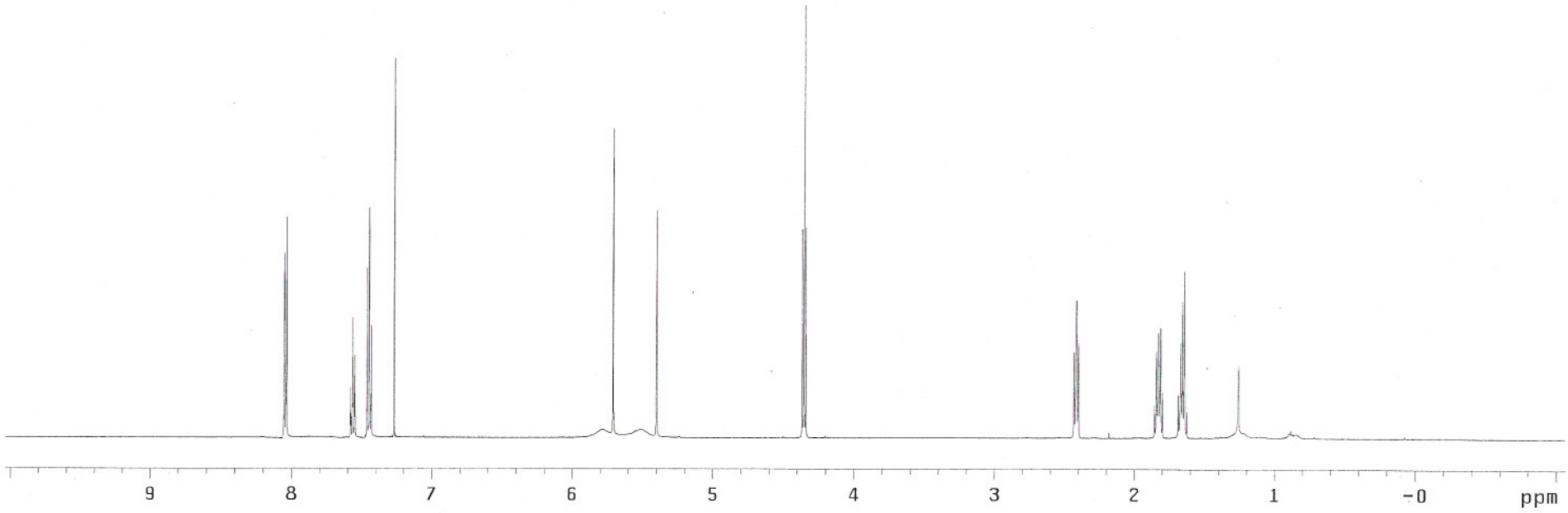



STANDARD CARBON PARAMETERS
O
NH2
17
14.783
23.293
28.740
29.614
32.333
32.937
77.480
77.732
77.988
119.354
145.262
171.614
ppm
0
20
40
60
80
100
120
140
160
180

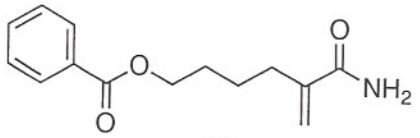
STANDARD PROTON PARAMETERS



18



STANDARD CARBON PARAMETERS



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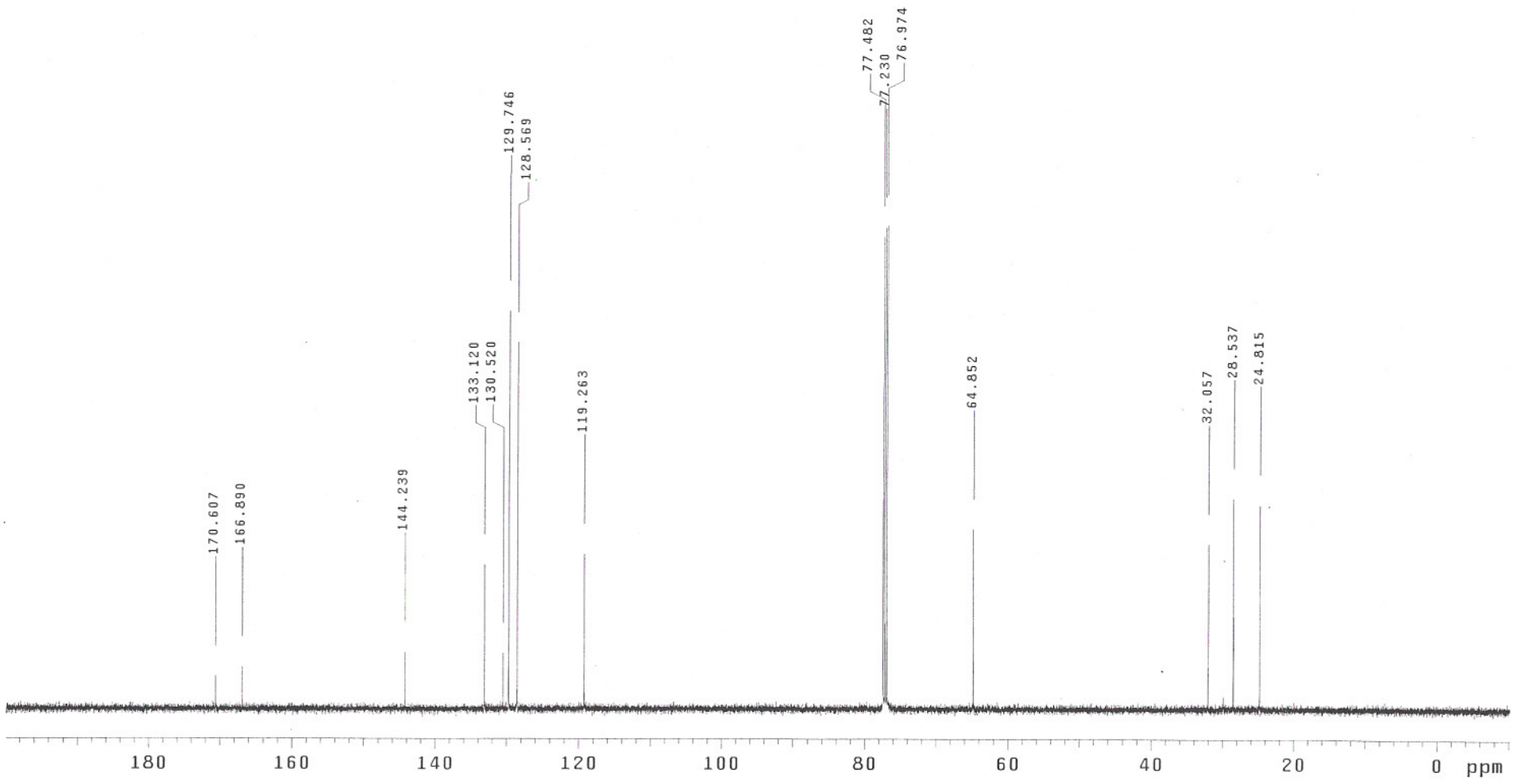

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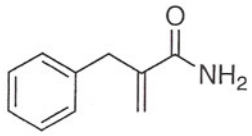
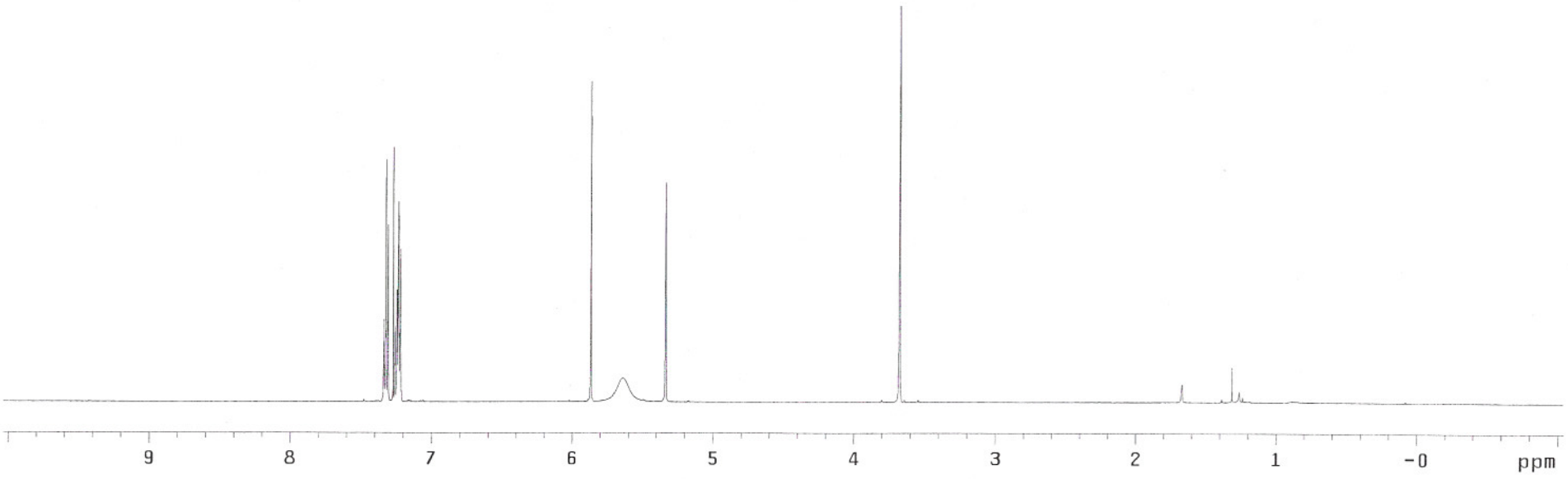
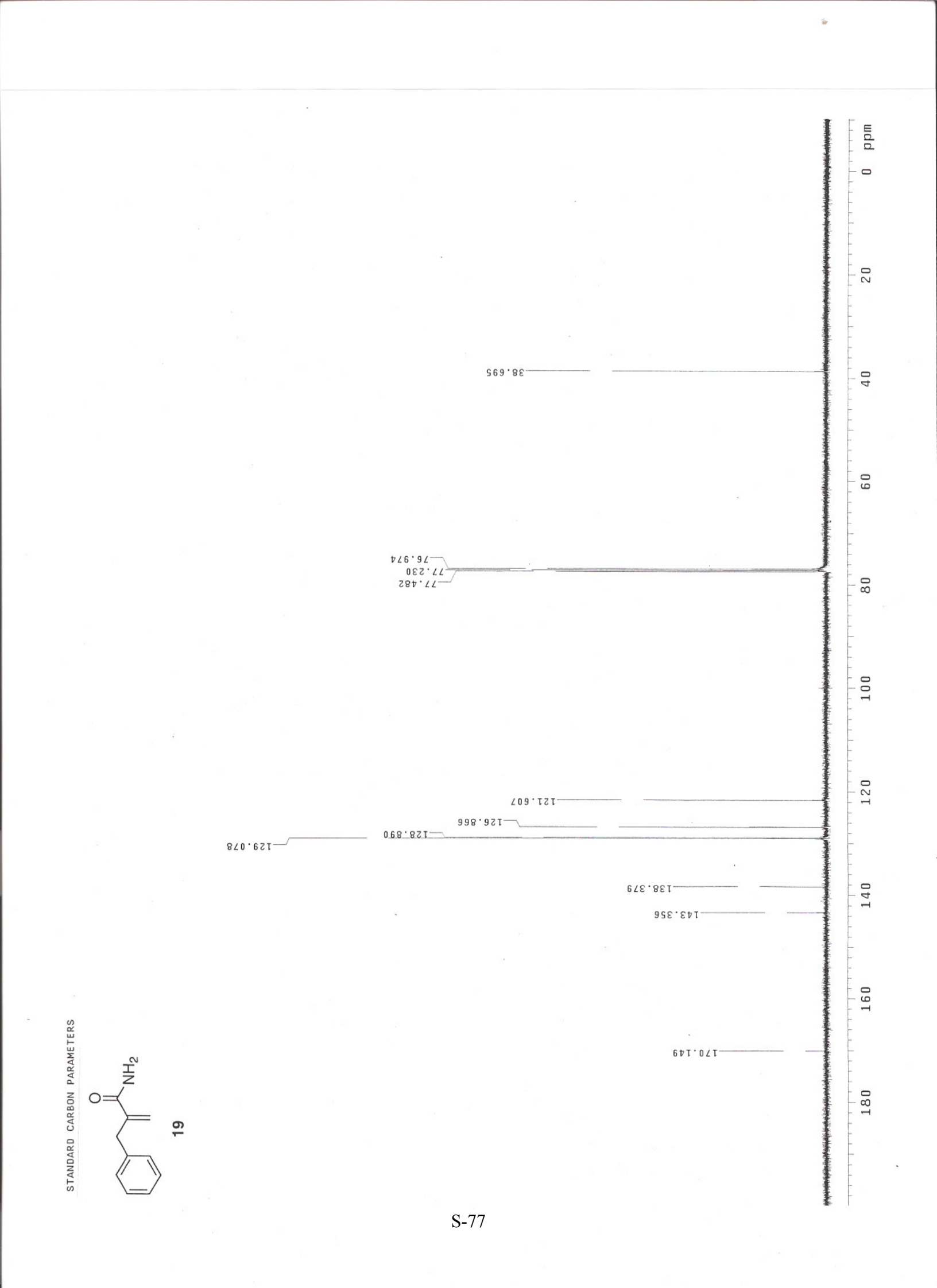


19




STANDARD CARBON PARAMETERS
19
170.149
143.356
138.379
129.078
128.890
126.866
121.607
77.482
77.230
76.974
38.695
ppm
0
20
40
60
80
100
120
140
160
180