SUPPORTING INFORMATION FOR *CHEM. COMMUN.*

Diastereoselective allylation and crotylation of *N*-unsubstituted imines derived from ketones

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EXPERIMENTAL PROCEDURES and CHARACTERIZATION DATA

General. All ketones in liquid form were distilled prior to use. All ketones in solid form were used as received. All other reagents were used as received (Aldrich, Acros, Strem). MeOH was dried over magnesium methoxide and distilled prior to use. 2 M solutions of allyl, (*E*)- and (*Z*)-crotylboronic acid in anhydrous MeOH were prepared just prior to use (exact molarities were confirmed by titration with benzaldehyde).[1] Melting points are uncorrected and were measured on a Fisher-Johns melting point apparatus. ^{1}H and ^{13}C NMR were recorded at 300 or 500 MHz and 75 or 125 MHz respectively on a Bruker Spectrospin 300 or 500 MHz spectrometer. Proton chemical shifts were internally referenced to the residual proton resonance in $CDCl_3$ (δ 7.26). Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.00). Infrared spectra were obtained on a Bruker VECTOR22 FT-IR spectrometer. HRMS-CI and HRMS-ESI were performed on a Waters/Micromass GCT time-of-flight mass spectrometer and a Waters/Micromass Q-TOF Global quadrupole time-of-flight mass spectrometer respectively.

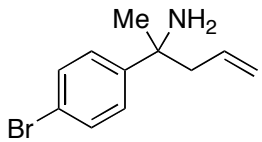
General procedure for allylation of *N*-unsubstituted imines derived from ketones (Table 2, equations 1-4)

To the ketone (0.5 mmol) was added a solution of ammonia in methanol (*ca*. 7M in MeOH, 0.75 mL, *ca*. 10 equiv.). The resulting solution was stirred for 15 min at rt. A freshly prepared solution of allylboronic acid (**5e**) (2M in MeOH, 0.4 ml, 0.8 mmol) was then added dropwise over 5 min. The reaction mixture was subsequently stirred for 16 h at rt. All volatiles were removed *in vacuo* and the residue re-dissolved in Et_2O (15 mL). The desired amine was then extracted with 1N HCl (15 ml). The acidic aqueous extract was washed with Et_2O (3 x 15 mL). The aqueous extract was next made alkaline by addition of solid NaOH (ca. 5 g). The alkaline aqueous layer was then extracted with dichloromethane (3 x 15 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford the desired amine.

General procedure for crotylation of *N*-unsubstituted imines derived from ketones (Table 3)

As above, except a freshly prepared solution of either (*E*)- or (*Z*)-crotylboronic acid (**7a** or **7b**) (2M in MeOH, 0.5 mL, 1.00 mmol) was used.

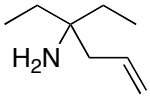
1-(4-Bromophenyl)-1-methylbut-3-enylamine (6a)



6a

6a isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 7.44 (2H, d, *J* = 8.5 Hz), 7.35 (2H, d, *J* = 8.5 Hz), 5.55 (1H, dddd, *J* = 18.0, 9.5, 8.0, 7.0 Hz), 5.09 – 5.04 (2H, m), 2.53 (1H, dd, *J* = 13.5, 7.0 Hz), 2.38 (1H, dd, *J* = 13.5, 8.0 Hz), 1.49 (2H, br s), 1.44 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) 147.79, 133.89, 131.14, 127.26, 120.12, 118.81, 54.45, 49.64, 30.93; IR (film) 3423, 1638 cm^{-1}; HRMS (CI) *m*/*z* calcd. for $C_{11}H_{15}BrN$ (MH^+) 240.0388, found 240.0395.

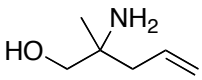
1,1-Diethylbut-3-enylamine (6b)



6b

6b isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) 5.77 (1H, ddt, *J* = 16.0, 11.0, 7.5 Hz)), 5.04 (1H, d, *J* = 11.0 Hz), 5.03 (1H, d, *J* = 16.0 Hz), 2.03 (2H, d, *J* = 7.5 Hz), 1.32 (4H, q, *J* = 7.5 Hz), 1.18 (2H, br s), 0.81 (6H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) 134.44, 117.69, 53.36, 43.85, 31.66, 7.70; IR (film) 3420, 1636 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_8H_{18}N$ (MH^+) 128.1439, found 128.1444.

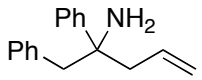
2-Amino-2-methylpent-4-en-1-ol (6c)



6c

6c isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) 5.79 (1H, ddt, *J* = 16.5, 10.5, 7.5 Hz), 5.12 – 5.01 (2H, m), 3.30 (1H, d, *J* = 10.5 Hz), 3.25 (1H, d, *J* = 10.5 Hz), 2.45 (3H, br s), 2.11 (2H, d, *J* = 7.5 Hz), 1.01 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) 133.77, 118.51, 68.07, 52.70, 44.28, 24.53; IR (film) 3345, 3157, 1639 cm^{-1}; HRMS (CI) *m*/*z* calcd. for $C_6H_{14}NO$ (MH^+) 116.1075, found 116.1072.

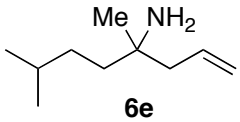
1-Benzyl-1-phenylbut-3-enylamine (6d)



6d

6d isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38 – 7.08 (8H, m), 6.90 – 6.84 (2H, m), 5.53 (1H, dddd, *J* = 17.0, 10.0, 8.5, 5.5 Hz), 5.15 – 5.00 (2H, m), 3.12 (1H, d, *J* = 13.0 Hz), 2.97 (1H, d, *J* = 13.0 Hz), 2.86 (1H, dd, *J* = 13.5, 5.5 Hz), 2.44 (1H, dd, *J* = 13.5, 8.5 Hz), 1.50 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.52, 137.09, 134.08, 130.68, 128.07, 127.86, 126.46, 126.30, 126.19, 118.81, 57.97, 50.54, 47.62; IR (film) ν 3401, 1677 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{20}N$ (MH^+) 238.1596, found 238.1585.

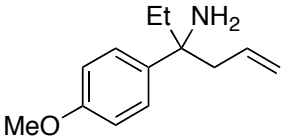
1-Methyl-1-(3-methylbutyl)but-3-enylamine (6e)



6e

6e isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.74 (1H, ddt, *J* = 17.0, 10.0, 7.5 Hz), 5.05 – 4.93 (2H, m), 2.00 (2H, d, *J* = 7.5 Hz), 1.40 (1H, septet, *J* = 6.5 Hz), 1.29 – 1.20 (2H, m), 1.19 – 1.03 (4H, m), 0.95 (3H, s), 0.80 (6H, d, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.50, 117.77, 51.14, 47.15, 40.36, 32.82, 28.45, 27.71, 22.53; IR (film) ν 3385, 1636 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{10}H_{22}N$ (MH^+) 156.1752, found 156.1745.

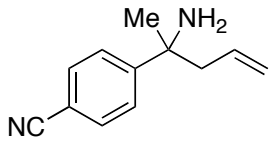
1-Ethyl-1-(4-Methoxyphenyl)but-3-enylamine (6f)



6f

6f isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (2H, d, *J* = 9.0 Hz), 6.86 (2H, d, *J* = 9.0 Hz), 5.53 (1H, dddd, *J* = 17.5, 10.0, 8.5, 6.0 Hz), 5.06 (1H, d, *J* = 17.5 Hz), 5.03 (1H, d, *J* = 10.0 Hz), 3.80 (3H, s), 2.59 (1H, dd, *J* = 13.5, 6.0 Hz), 2.36 (1H, dd, *J* = 13.5, 8.5 Hz), 1.85 (1H, dq, *J* = 14.0, 7.5 Hz), 1.66 (1H, dq, *J* = 14.0, 7.5 Hz), 1.52 (2H, br s), 0.71 (3H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.72, 138.66, 134.32, 126.93, 118.34, 113.27, 57.06, 55.16, 48.37, 36.05, 8.04; IR (film) ν 3420, 1638, 1610, 1511, 1248 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{13}H_{20}NO$ (MH^+) 206.1545, found 206.1565.

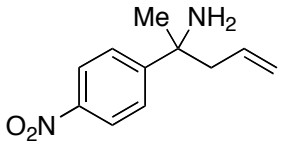
4-(1-Amino-1-methylbut-3-enyl)benzonitrile (6g)



6g

6g isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) 7.57 (4H, apparent s), 5.55 – 5.40 (1H, m), 5.07 – 4.97 (2H, m), 2.51 (1H, dd, *J* = 13.5, 6.5 Hz), 2.36 (1H, dd, *J* = 13.5, 8.0 Hz), 1.46 (2H, br s), 1.43 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) 154.26, 133.32, 131.99, 126.36, 119.37, 119.03, 110.05, 54.94, 49.50, 30.85; IR (film) 3499, 2228, 1639 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{12}H_{15}N_2$ (MH^+) 187.1235, found 187.1235.

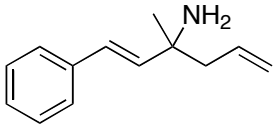
1-Methyl-1-(4-nitrophenyl)but-3-enylamine (6h)



6h

6h isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 8.16 (2H, d, *J* = 9.0 Hz), 7.66 (2H, d, *J* = 9.0 Hz), 5.53 (1H, dddd, *J* = 17.0, 10.5, 8.0, 7.0 Hz), 5.07 (1H, d, *J* = 10.5 Hz), 5.06 (1H, d, *J* = 17.0 Hz), 2.57 (1H, dd, *J* = 13.5, 7.0 Hz), 2.42 (1H, dd, *J* = 13.5, 8.0 Hz), 1.54 (2H, br s), 1.50 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) 156.28, 146.47, 133.13, 126.45, 123.30, 119.43, 55.01, 49.55, 30.92; IR (film) 3375, 1639, 1526, 1351 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{11}H_{15}N_2O_2$ (MH^+) 207.1134, found 207.1132.

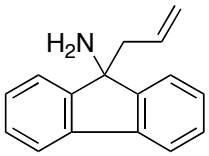
1-Methyl-1*E*-styrylbut-3-enylamine (6i)



6i

6i isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) 7.45 – 7.15 (5H, m), 6.46 (1H, d, *J* = 16.0 Hz), 6.28 (1H, d, *J* = 16.0 Hz), 5.87 – 5.72 (1H, m), 5.18 – 5.05 (2H, m), 2.31 (1H, dd, *J* = 16.5. 7.5 Hz), 2.23 (1H, dd, *J* = 16.5, 8.0 Hz), 1.41 (2H, br s), 1.27 (3H, s);); ^{13}C NMR ($CDCl_3$, 75 MHz) 138.42, 137.22, 133.95, 128.39, 128.27, 127.06, 126.14, 118.45, 52.96, 48.00, 28.57; IR (film) 3545, 1638 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{13}H_{18}N$ (MH^+) 118.1439, found 118.1449.

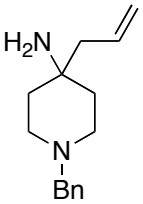
9-Allyl-9*H*-fluoren-9-ylamine (6j)



6j

6j isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 7.66 (2H, d, *J* = 7.5 Hz), 7.51 (2H, d, *J* = 7.0 Hz), 7.38 – 7.30 (4H, m), 5.57 (1H, ddt, *J* = 17.0, 10.0, 7.5 Hz), 5.01 (1H, dd, *J* = 17.0, 1.5 Hz), 4.96 (1H, d, *J* = 10.0 Hz), 2.70 (2H, d, *J* = 7.5 Hz), 1.81 (2H, br s); ^{13}C NMR ($CDCl_3$, 125 MHz) 150.86, 139.28, 133.22, 128.00, 127.53, 123.26, 119.85, 118.60, 64.71, 45.46; IR (film) 3360, 1640 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}N$ (MH^+) 222.1283, found 222.1278.

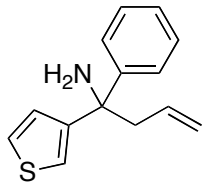
4-Allyl-1-benzylpiperidin-4-ylamine (6k)



6k

6k isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) 7.32 – 7.15 (5H, m), 5.81 (1H, ddt, *J* = 17.0, 10.0, 7.5 Hz), 5.12 – 5.01 (2H, m), 3.48 (2H, s), 2.58 – 2.48 (2H, dq, *J* = 12.0, 4.0 Hz), 2.30 (2H, dt, *J* = 11.0, 3.0 Hz), 2.09 (2H, d, *J* = 7.5 Hz), 1.61 (2H, ddd, *J* = 13.0, 10.5, 4.0 Hz), 1.41 – 1.31 (2H, m), 1.08 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) 138.43, 133.51, 128.88, 127.95, 126.69, 118.29, 63.08, 49.39, 48.67, 47.60, 37.83; IR (film) 3422, 1639 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{23}N_2$ (MH^+) 231.1861, found 231.1862.

1-Phenyl-1-thiophen-2-ylbut-3-enylamine (6l)

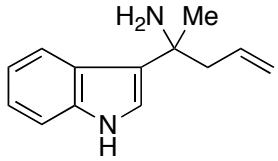


6l

6l isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 7.49 (2H, dt, *J* = 7.5, 1.0 Hz), 7.33 (2H, t, *J* = 8.0 Hz), 7.27 – 7.17 (2H, m), 6.94 (1H, dd, *J* = 5.0, 3.5 Hz), 6.90 (1H, dd, *J* = 3.5, 1.0 Hz), 5.62 (1H, ddt, *J* = 17.0, 10.0, 7.0 Hz), 5.19 (1H, d, *J* = 17.0, 1.5 Hz), 5.13 (1H, ddd, *J* = 10.0, 1.5, 1.0 Hz), 3.08 (1H, dd, *J* = 14.0, 7.0 Hz), 3.01 (1H, dd, *J* = 14.0, 7.5 Hz), 2.09 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) 154.78, 147.10, 133.63, 128.15, 126.77, 126.50, 126.01,

124.22, 123.64, 119.55, 59.32, 49.15; IR (film) 3410, 1639 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{14}H_{16}NS$ (MH^+) 230.1003, found 230.1017.

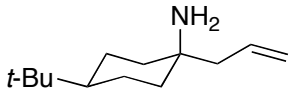
1-(1*H*-Indol-3-yl)-1-methylbut-3-enylamine (6m)



6m

6m isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 8.03 (1H, br s), 7.84 (1H, d, *J* = 8.0 Hz), 7.37 (1H, d, *J* = 8.0 Hz), 7.19 (1H, dt, *J* = 7.5, 1.0 Hz), 7.12 (1H, dt, *J* = 7.5, 1.0 Hz), 7.07 (1H, d, *J* = 2.5 Hz), 5.65 (1H, ddt, *J* = 17.5, 10.0, 7.5 Hz), 5.06 (1H, d, *J* = 17.5 Hz), 5.03 (1H, d, *J* = 10.0 Hz), 2.79 (1H, dd, *J* = 13.5, 7.5 Hz), 2.63 (1H, dd, *J* = 13.5, 7.5 Hz), 1.85 (2H, br s), 1.61 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) 137.30, 134.93, 125.20, 124.74, 121.77, 120.91, 120.51, 119.21, 117.92, 111.35, 52.39, 48.20, 30.00; IR (film) 3205, 1639 cm^{-1}.

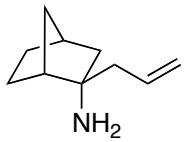
1-Allyl-4-*tert*-butylcyclohexylamine (6n)



6n

6n isolated as a clear, colorless oil (d.r. = 87:13). The diastereomeric ratio was determined by ^{1}H NMR of the crude sample. Main diastereomer: ^{1}H NMR ($CDCl_3$, 300 MHz) 5.83 (1H, ddt, *J* = 17.0, 10.5, 7.5 Hz), 5.08 – 4.98 (2H, m), 2.02 (2H, d, *J* = 7.5 Hz), 1.60 – 1.40 (4H, m), 1.34 – 1.00 (6H, m), 0.90 – 0.83 (1H, m), 0.83 (9H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) 134.26, 117.87, 50.16, 49.94, 48.11, 38.43, 32.30, 27.50, 22.42; IR (film) 3368, 1638 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{13}H_{26}N$ (MH^+) 196.2065, found 196.2068.
The stereochemistry of **6n** (axial NH_2) was confirmed by converting it (allylbromide, $^iPr_2NEt$, CH_2Cl_2; 49%) to the previously known compound *N*-Allyl-1-Allyl-4-*tert*-butylcyclohexylamine (axial $NHCH_2CH{=}CH$).[2]

2-Allyl-bicyclo[2.2.1]hept-2-ylamine (6o)

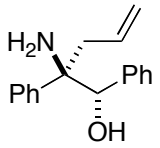


6o

6o isolated as a clear, colorless oil (d.r. = 94:6). The diastereomeric ratio was determined by ^{1}H NMR of the crude sample. Main diastereomer: ^{1}H NMR ($CDCl_3$, 300 MHz) 5.78 (1H, ddt, *J* =

17.0, 10.5, 7.5 Hz), 5.08 – 4.97 (2H, m), 2.10 (2H, d, *J* = 7.5 Hz), 1.88 (1H, d, *J* = 3.5 Hz), 1.78 (1H, ddt, *J* = 12.5, 9.0, 3.0 Hz), 1.60 – 1.42 (3H, m), 1.24 – 1.08 (6H, m), 0.82 (1H, dd, *J* = 12.5, 3.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) 134.57, 117.95, 57.99, 47.41, 46.69, 46.48, 38.30, 37.54, 28.43, 22.92; IR (film) 3400, 1638 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{10}H_{18}N$ (MH^+) 152.1439, found 152.1435.

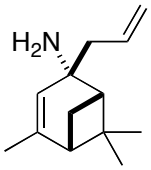
2-Amino-1,2-diphenylpent-4-en-1-ol (6p)



6p

6p isolated as a clear, colorless crystalline solid. The diastereomeric ratio (d.r. = 88:12) was determined by ^{1}H NMR of the crude sample. Main diastereomer: m.p. = 85–86 °C (CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) 7.30 – 7.06 (8H, m), 6.90 – 6.85 (2H, m), 5.56 – 5.40 (1H, m), 5.12 (1H, d, *J* = 17.0 Hz), 5.00 (1H, d, *J* = 10.0 Hz), 4.74 (1H, s), 2.95 (1H, dd, *J* = 14.0, 5.5 Hz), 2.65 (1H, dd, *J* = 14.0, 9.0 Hz), 2.08 (3H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) 142.54, 140.02, 133.74, 127.62, 127.42, 127.24, 127.10, 126.71, 126.50, 118.96, 79.91, 61.70, 43.45; IR (film) 3422, 1638 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{17}H_{20}NO$ (MH^+) 254.1545, found 254.1543.
The stereochemistry of **6p** was confirmed by X-ray crystallography (see page 33).

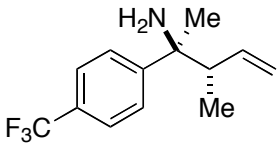
(1*S,2*R**,5*R**)-2-Allyl-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ylamine (6q)**



6q

6q isolated as a clear, colorless oil (d.r. = 97:3). The diastereomeric ratio was determined by ^{1}H NMR of the crude sample. ^{1}H NMR ($CDCl_3$, 300 MHz) 5.85 (1H, ddt, *J* = 17.5, 10.5, 7.5 Hz), 5.13 – 5.02 (3H, m), 2.36 (1H, dt, *J* = 9.0, 5.5 Hz), 2.20 (1H, dd, *J* = 13.5, 7.0 Hz), 2.13 (1H, dd, *J* = 13.5, 8.0 Hz), 1.98 – 1.88 (2H, m), 1.68 (3H, d, *J* = 1.5 Hz), 1.60 – 1.35 (3H, m), 1.33 (3H, s), 1.05 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) 143.51, 133.89, 124.42, 118.23, 57.24, 52.84, 47.64, 45.88, 41.87, 33.78, 27.36, 23.85, 22.77; IR (film) 3410, 1713, 1681, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_{22}N$ (MH^+) 192.1752, found 192.1756.

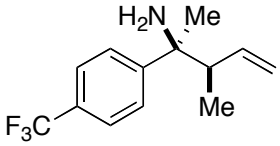
(1*S,2*S**)-1,2-Dimethyl-1-(4-trifluoromethylphenyl)but-3-enylamine (4a)**



4a

4a isolated as a clear, colorless oil (d.r. = 97:3). The diastereomeric ratio was determined by ^{1}H NMR of the crude sample. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60 (2H, d, *J* = 9.0 Hz), 7.56 (2H, d, *J* = 9.0 Hz), 5.66 – 5.53 (1H, m), 5.10 – 5.00 (2H, m), 2.53 (1H, pentet, *J* = 7.0 Hz), 1.49 (2H, br s), 1.46 (3H, s), 0.91 (3H, d, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.45, 139.63, 128.52 (q, *J* = 30 Hz), 126.37, 124.79 (q, *J* = 3.5 Hz), 124.64 (q, *J* = 270 Hz), 116.45, 55.96, 48.82, 27.13, 14.30; IR (film) ν 3378, 1636 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}F_3N$ (MH^+) 244.1313, found 244.1305.

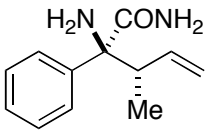
(1*S,2*R**)-1,2-Dimethyl-1-(4-trifluoromethylphenyl)but-3-enylamine (4b)**



4b

4b isolated as a clear, colorless oil (d.r. = 96:4). The diastereomeric ratio was determined by ^{1}H NMR of the crude sample. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (4H, apparent s), 5.75 (1H, ddd, *J* = 18.5, 10.5, 8.0 Hz), 5.13 – 5.03 (2H, m), 2.53 (1H, pentet, *J* = 7.5 Hz), 1.58 (2H, br s), 1.43 (3H, s), 0.78 (3H, d, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.10, 139.46, 128.02 (q, J = 30 Hz), 126.23, 125.83 (q, *J* = 270 Hz), 124.73 (q, *J* = 3.5 Hz), 116.34, 55.56, 48.65, 29.51, 14.51; IR (film) ν 3390, 1637 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}F_3N$ (MH^+) 244.1313, found 244.1304.

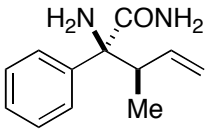
(2*S,3*S**)-2-Amino-3-methyl-2-phenylpent-4-enoic acid amide (4c)**



4c

4c isolated as a clear, colorless, crystalline solid (d.r. = 97:3): m.p = 90 °C (CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65 – 7.58 (2H, m), 7.35 – 7.18 (4H, m), 6.20 (1H, br s), 5.46 (1H, ddd, *J* = 17.5, 10.0, 6.5 Hz), 5.05 – 4.95 (2H, m), 3.59 (1H, pentet, *J* = 6.5 Hz), 1.59 (2H, br s), 1.08 (3H, d, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.99, 141.60, 138.23, 128.16, 127.04, 125.64, 116.69, 65.54, 42.58, 12.27; IR (film) ν 3441, 3207, 1710, 1620, 1637 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{11}H_{17}N_2O$ (MH^+) 205.1341, found 205.1332.

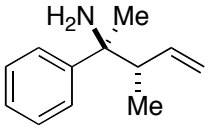
(2*S,3*R**)-2-Amino-3-methyl-2-phenylpent-4-enoic acid amide (4d)**



4d

4d isolated as a clear, colorless, crystalline solid (d.r. = 96:4): m.p = 136 °C (CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz) 7.64 – 7.60 (2H, m), 7.35 – 7.24 (4H, m), 6.02 (1H, ddd, *J* = 17.5, 10.5, 5.0 Hz), 5.59 (1H, br s), 5.26 (1H, dt, *J* = 10.5, 1.5 Hz), 5.17 (1H, dt, *J* = 17.5, 1.5 Hz), 3.76 – 3.69 (1H, m), 1.63 (2H, br s), 0.73 (3H, d, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) 177.15, 141.16, 139.07, 128.24, 127.06, 125.54, 117.21, 65.47, 41.87, 10.97; IR (film) 3432, 3170, 1715, 1633 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{11}H_{17}N_2O$ (MH^+) 205.1341, found 205.1337.

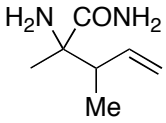
(1*S,2*S**)-1,2-Dimethyl-1-phenylbut-3-enylamine (4e)**[3]



4e

4e isolated as a clear, colorless oil (d.r. = 97:3). The diastereomeric ratio was determined by ^{1}H NMR of the crude sample. ^{1}H NMR ($CDCl_3$, 300 MHz) 7.42 – 7.10 (4H, m), 5.65 –5.55 (1H, m), 4.96 – 5.02 (2H, m), 2.45 (1H, dq, *J* = 7.0 Hz), 1.50 (2H, br s), 1.38 (3H, s), 0.83 (3H, d, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) 148.22, 140.30, 127.87, 126.13, 125.79, 115.90, 56.81, 49.02, 26.68, 14.49.

2-Amino-2,3-dimethylpent-4-enoicacid amide (4f)



4f

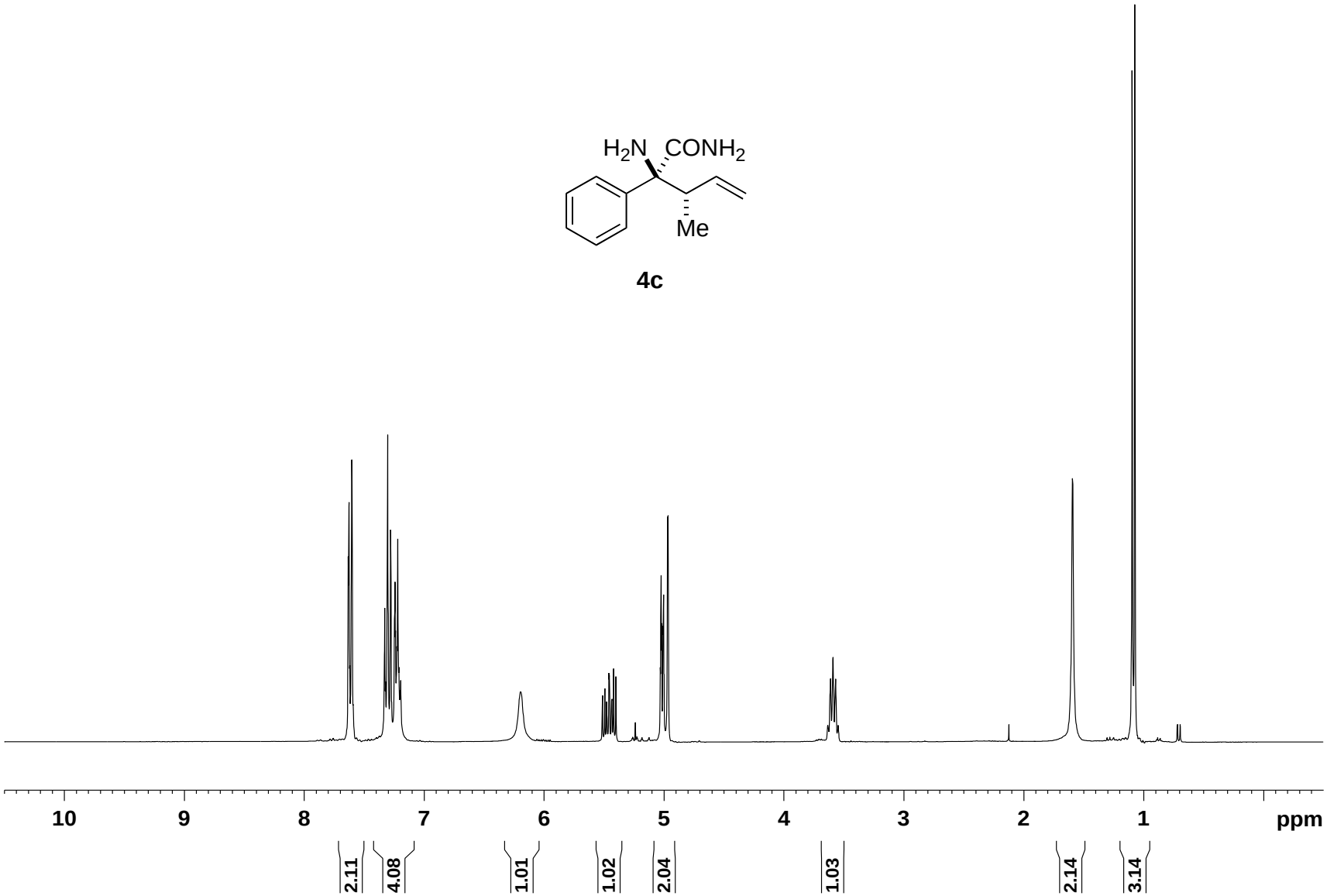
4f isolated as a clear, colorless oil (d.r. = 60:40). The diastereomeric ratio was determined by ^{1}H NMR of the crude sample. Main diastereomer: ^{1}H NMR ($CDCl_3$, 300 MHz) 7.41 (1H, br s), 5.95 – 5.60 (2H, m), 5.15 – 5.05 (2H, m), 2.81 (1H, pentet, *J* = 6.5 Hz), 1.28 (3H, s), 1.26 (2H, br s), 0.99 (3H, d, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) 180.06, 139.33, 116.28, 59.62, 43.29, 25.10, 11.88; IR (film) 3444, 3250, 1691, 1654, 1557 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_7H_{14}N_2O$ (MH^+) 143.1184, found 143.1186.

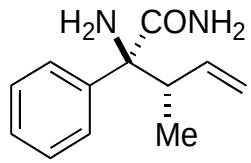
References

1) H. C. Brown, U. S. Racherla and P. J. Pellechia, *J. Org. Chem.*, 1990, **55**, 1868.
2) D. L. Wright, J. P. Schulte, II and M. A. Page, *Org. Lett.*, 2000, **2**, 1847.
3) C. Ogawa, M. Sugiura and S. Kobayashi, *J. Org. Chem.*, 2002, **67**, 5359.

Selected ^{1}H and ^{13}C NMR Spectra

4c

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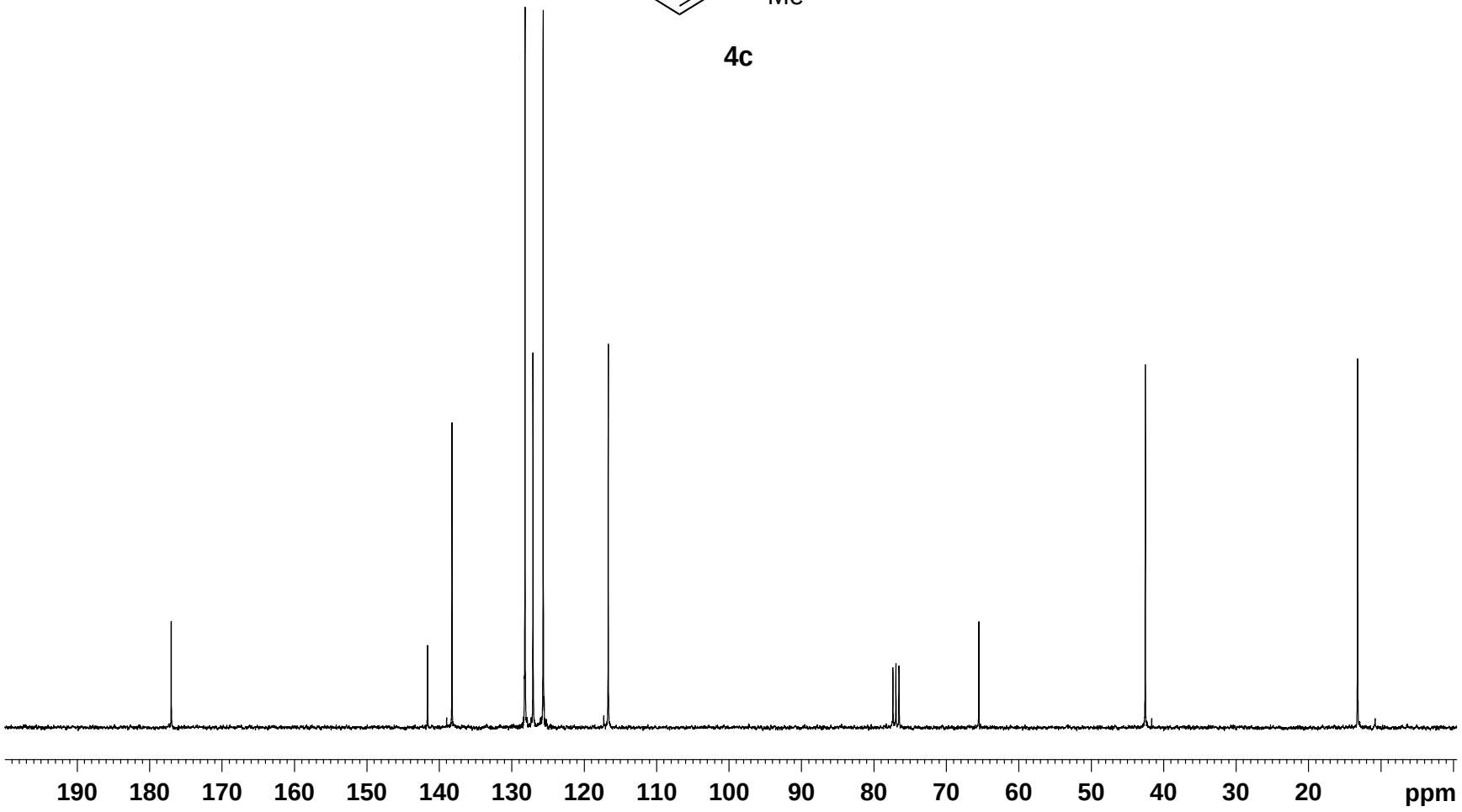
CONH2
Me

4c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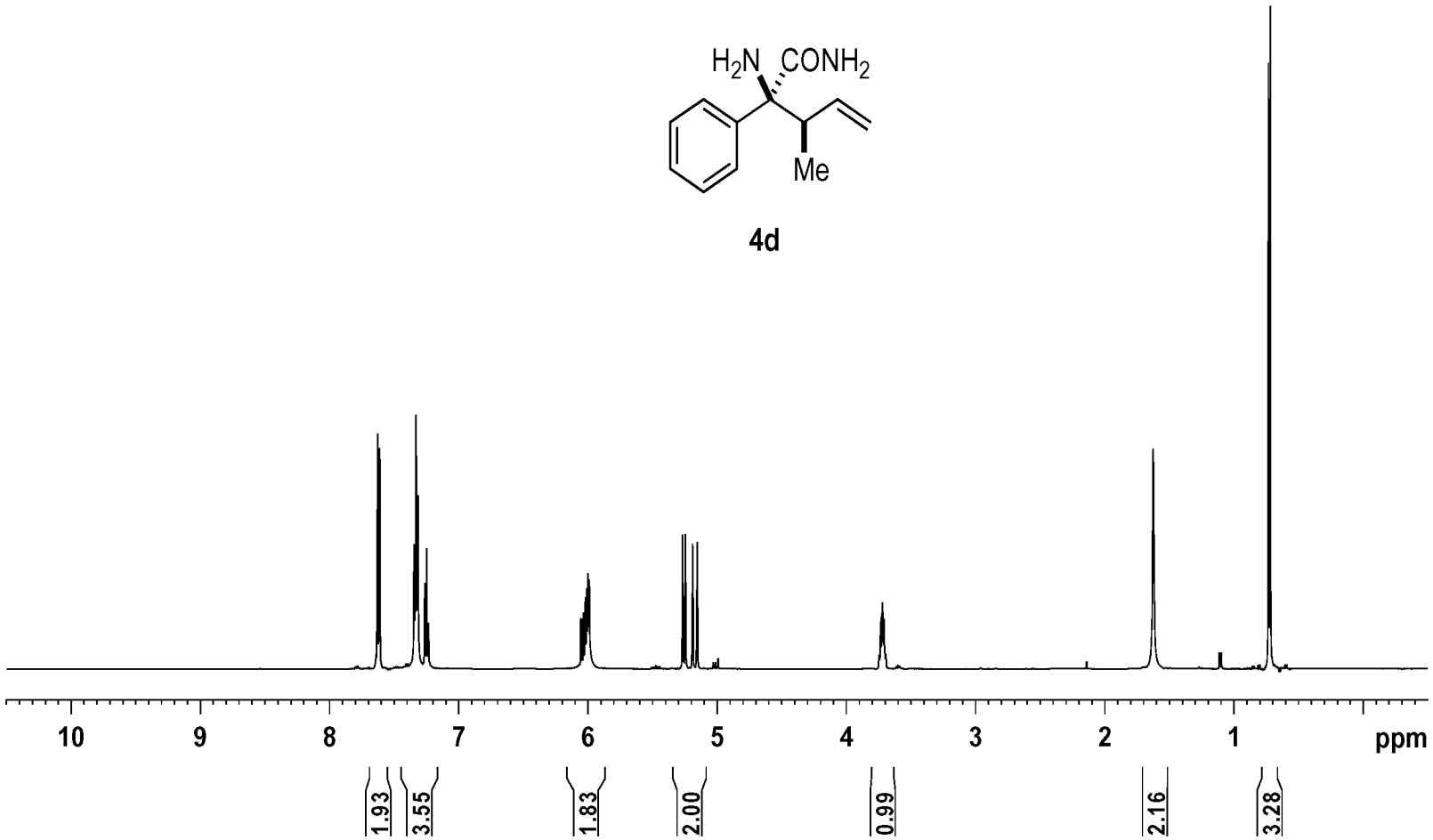
H2N
CONH2
Me
4d
10
9
8
7
6
5
4
3
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1
ppm
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1.83
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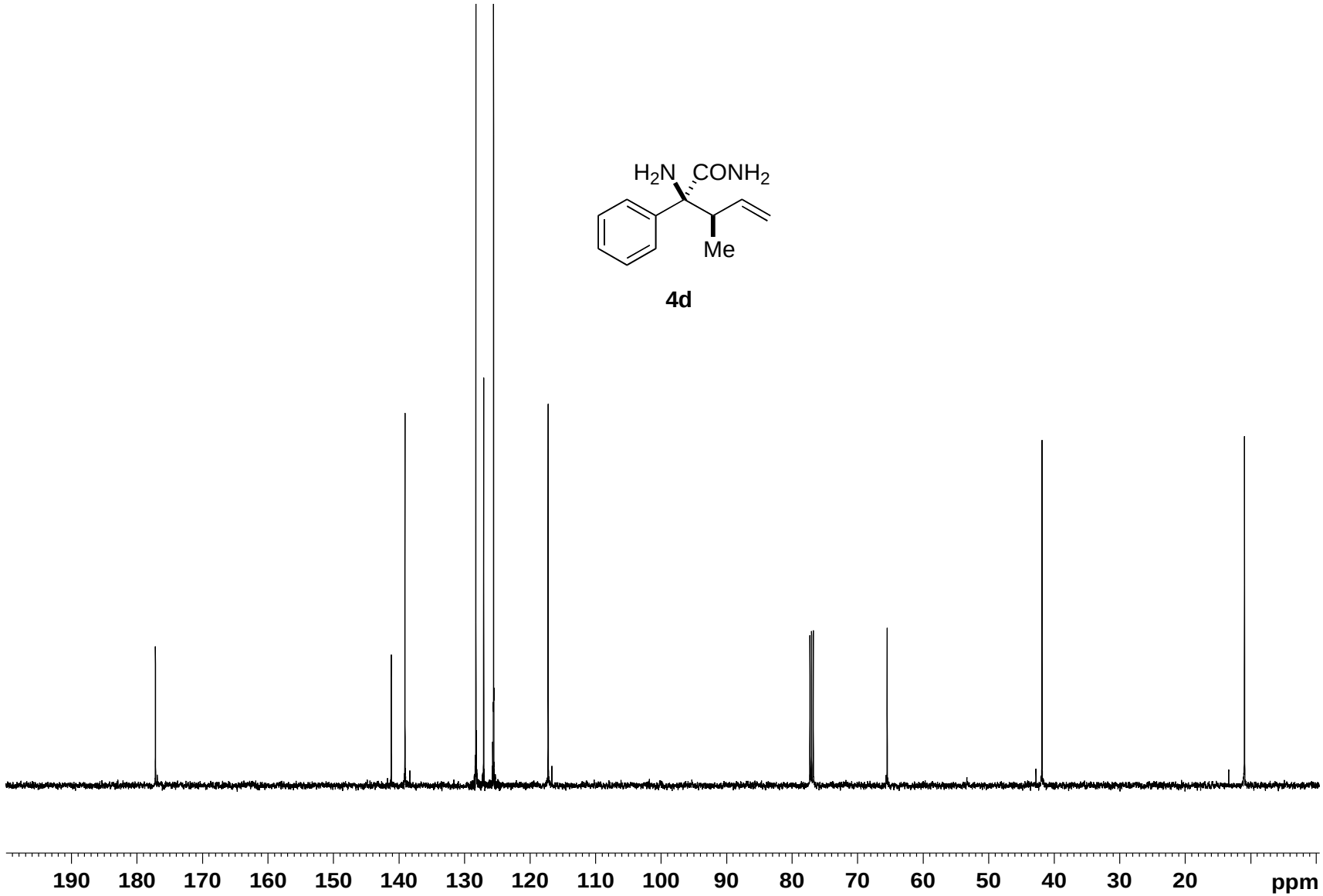
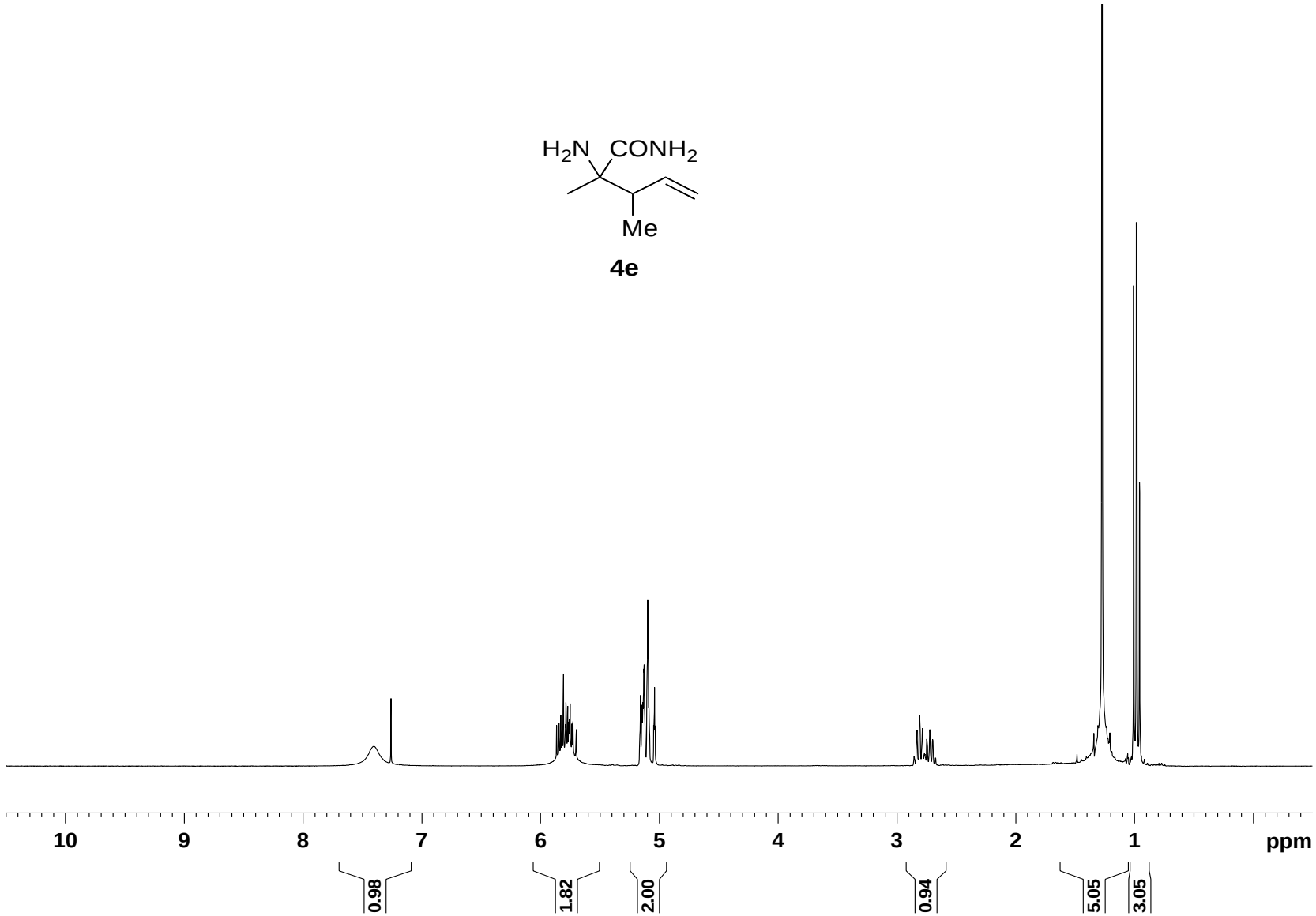
0.99
2.16
3.28


H2N
CONH2
Me
4d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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CONH2
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4e
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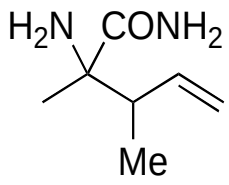
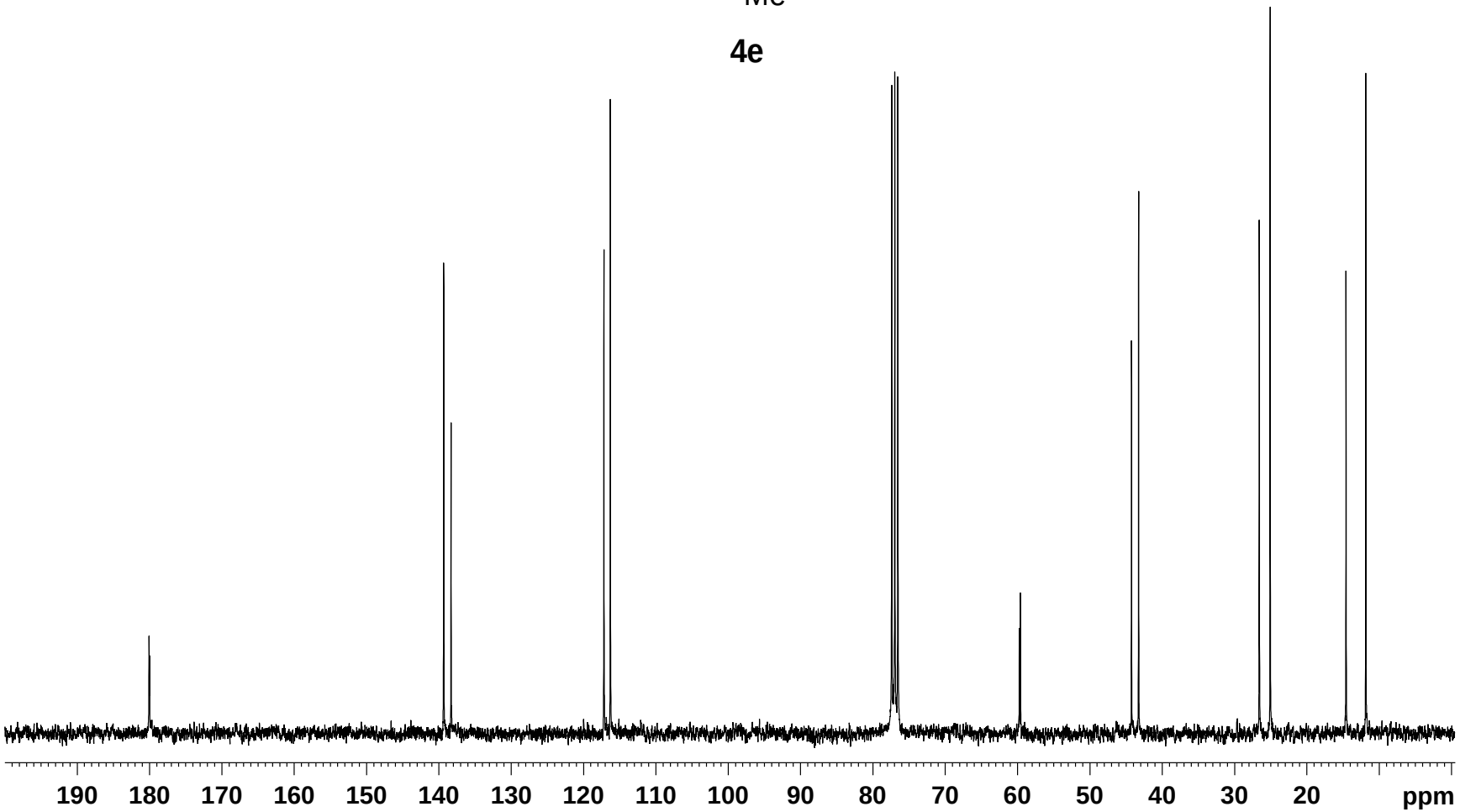
3.05


H2N
CONH2
Me

4e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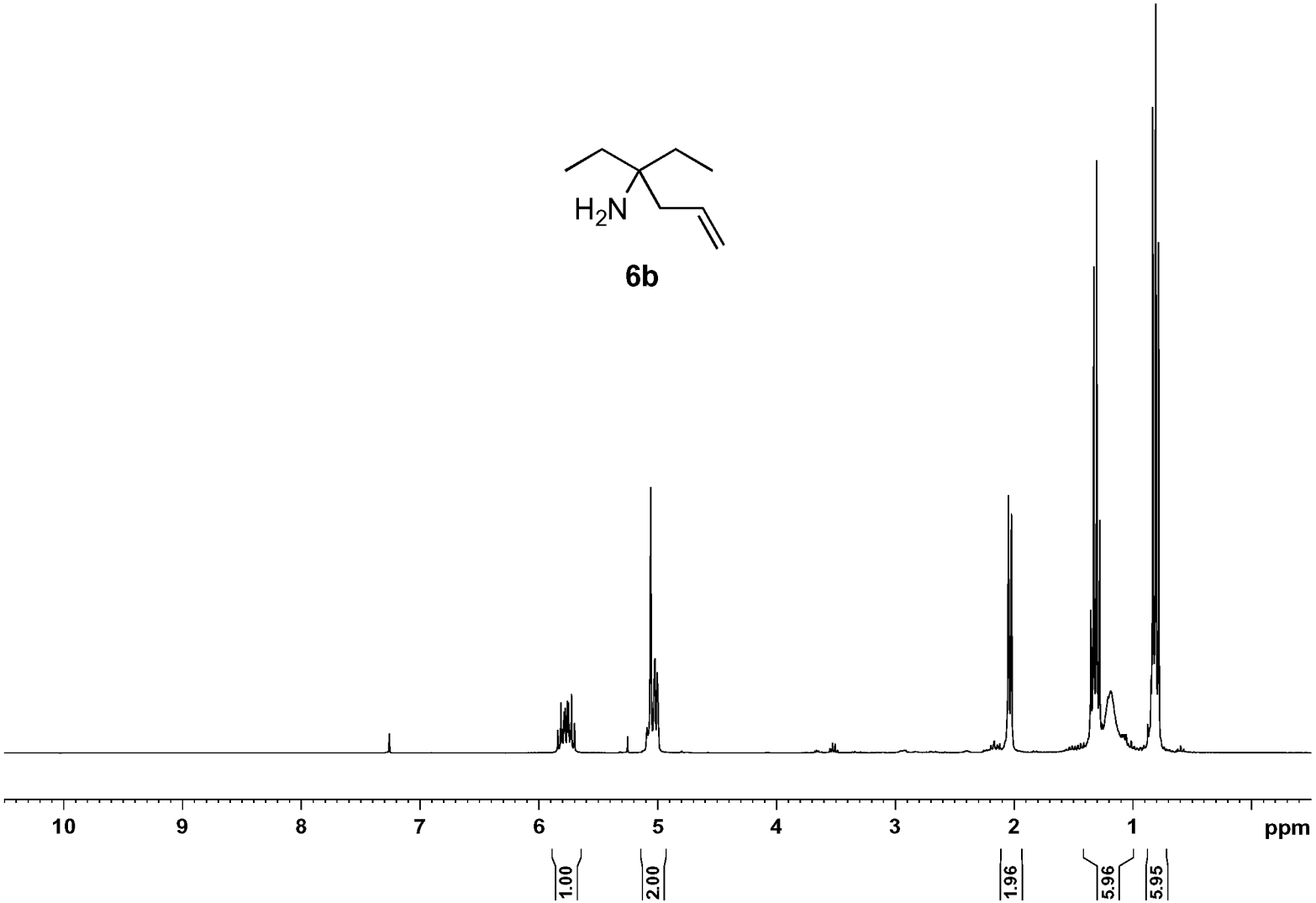
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2.00
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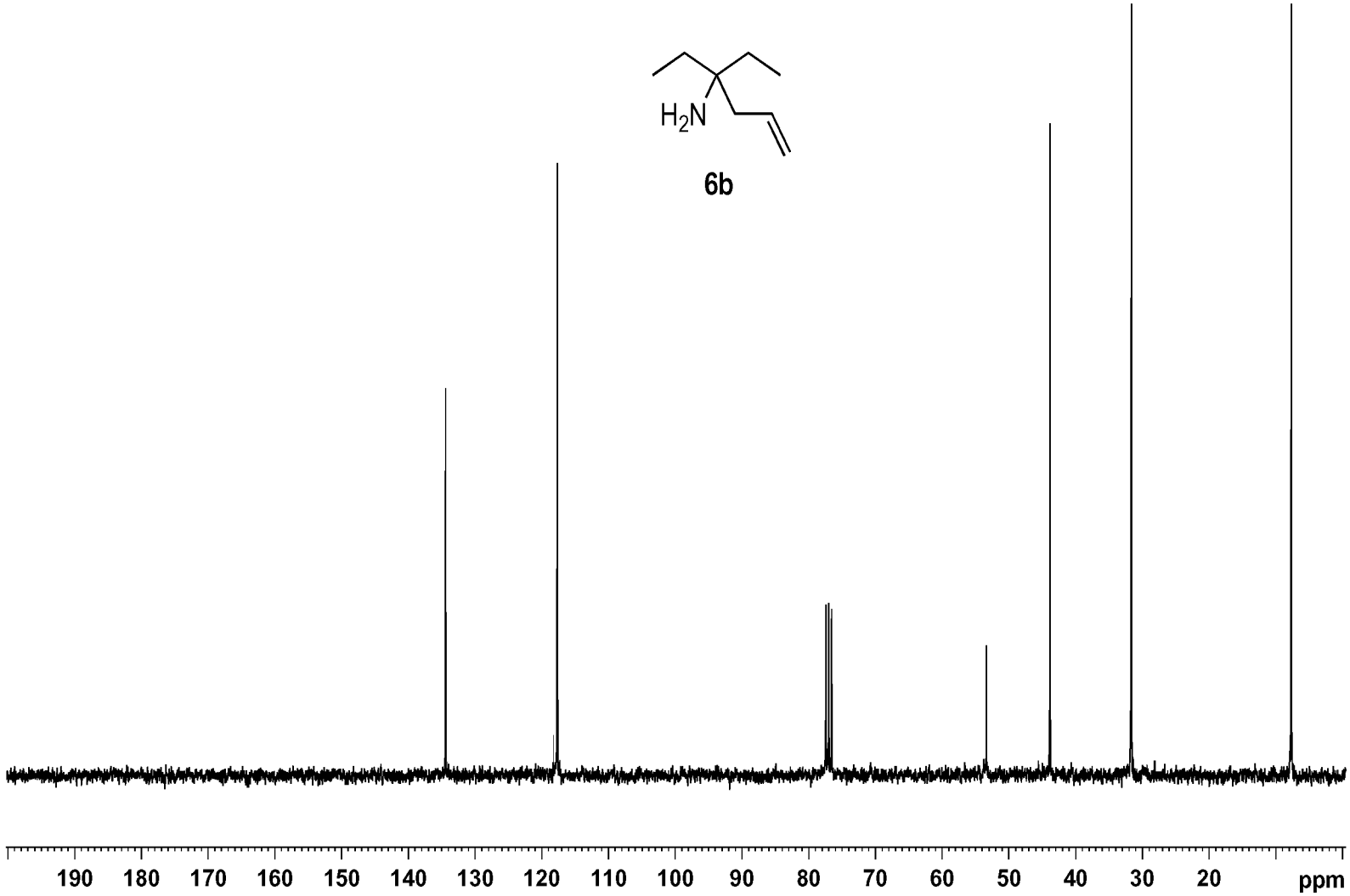
5.96
5.95


H2N
6b
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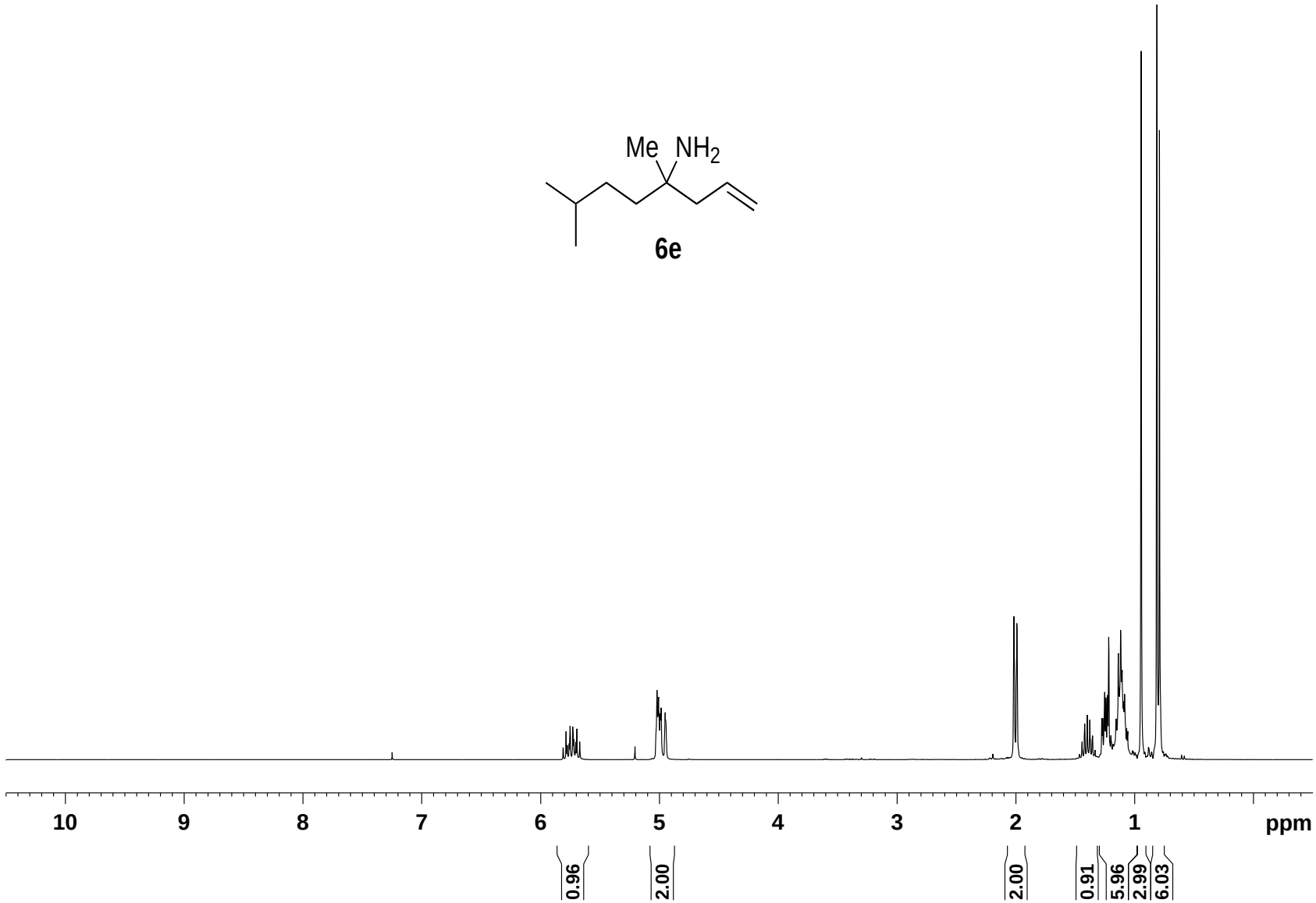
ppm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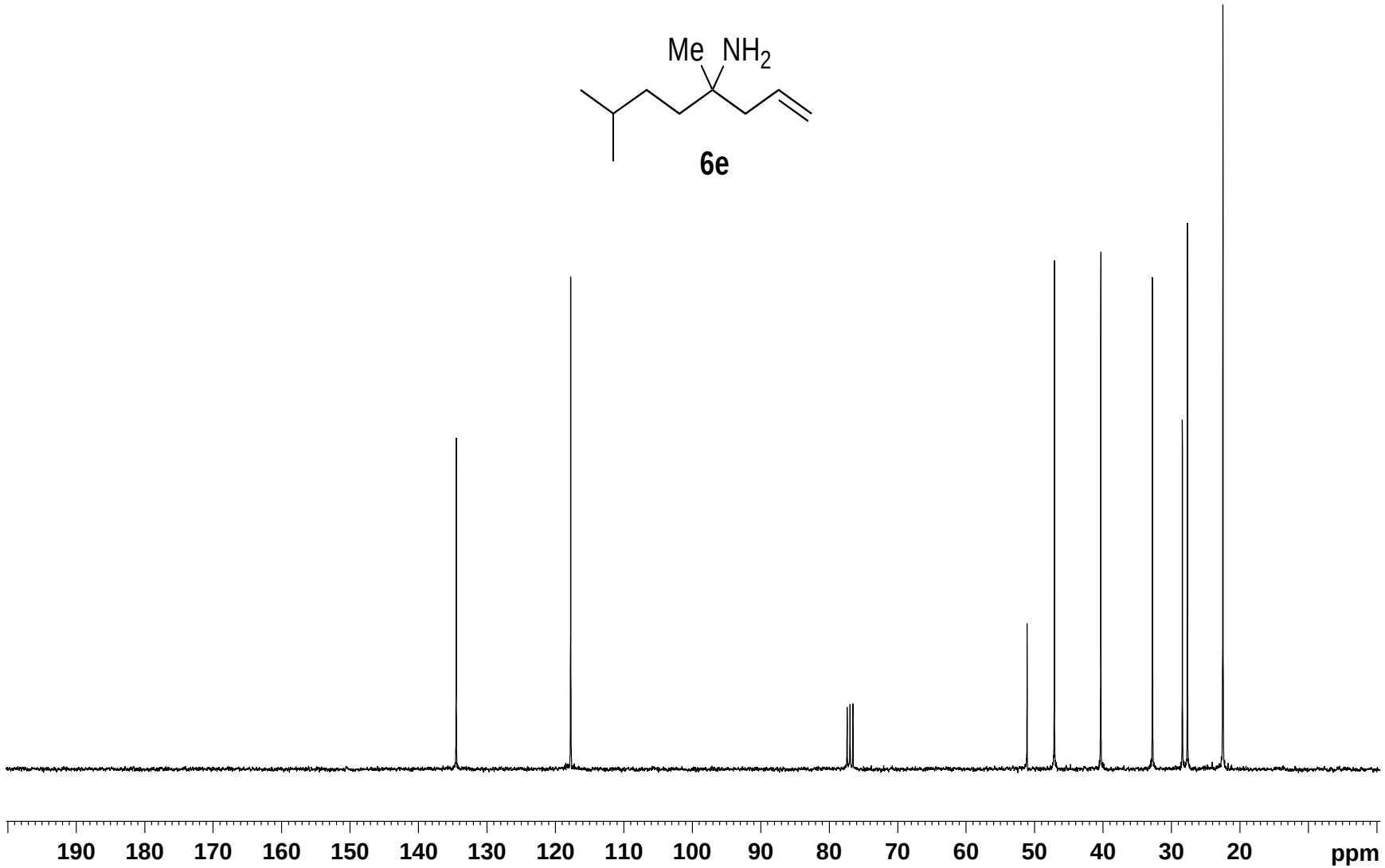
2.99
6.03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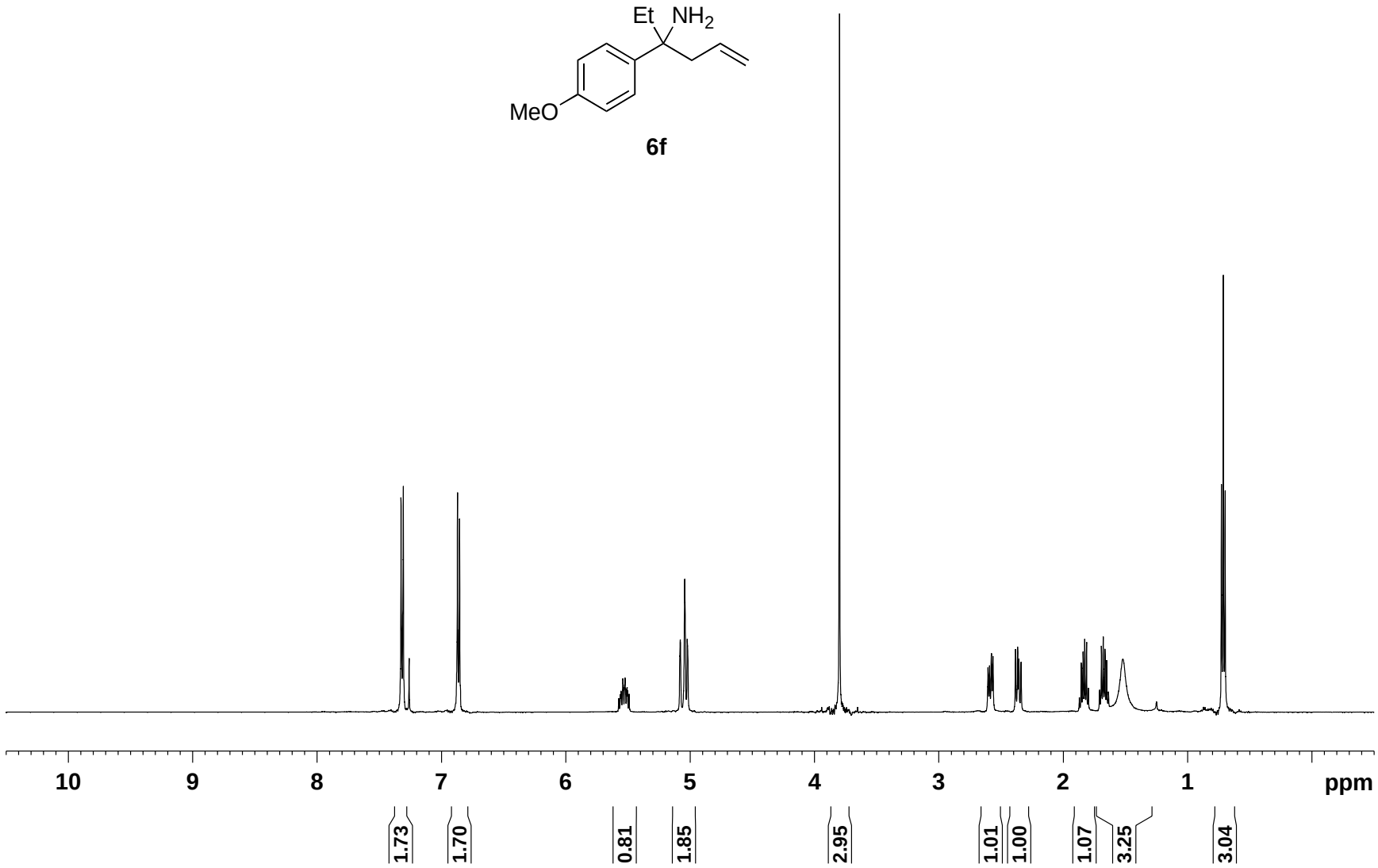
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1.01
1.00
1.07
3.25
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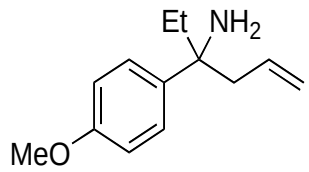
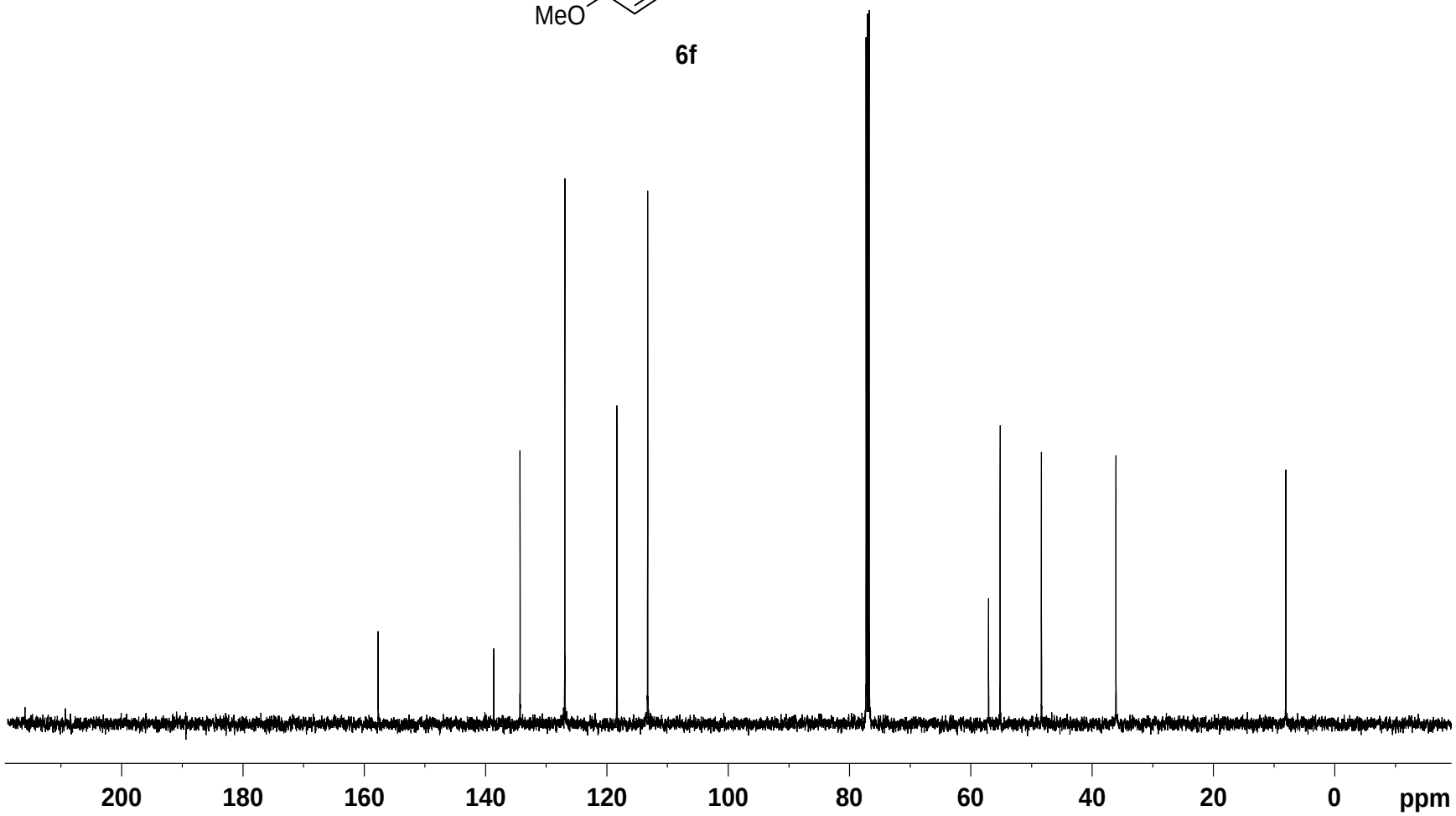
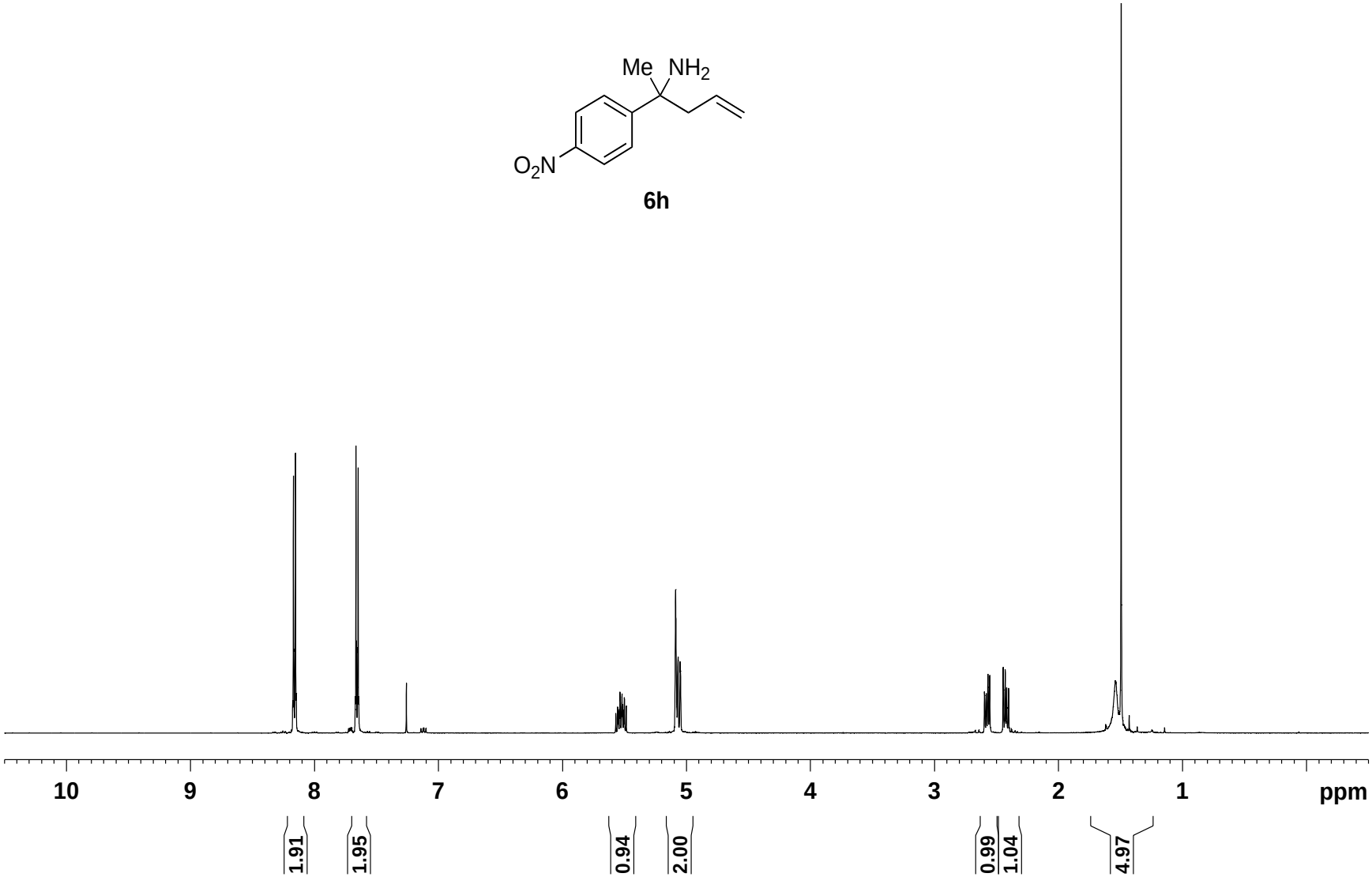


6f

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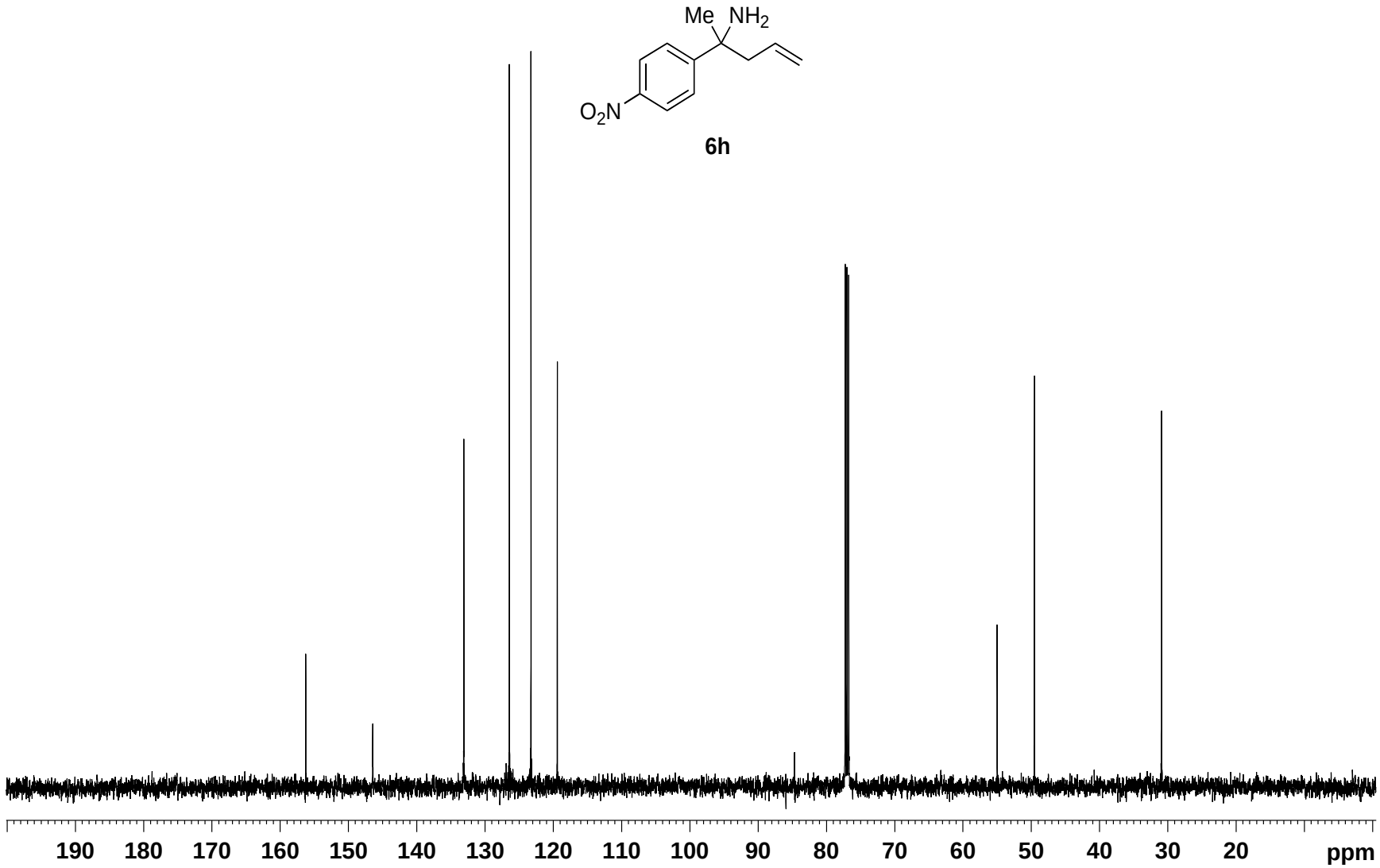
1.04
4.97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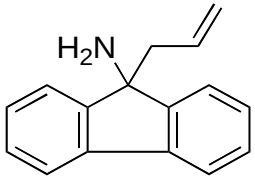
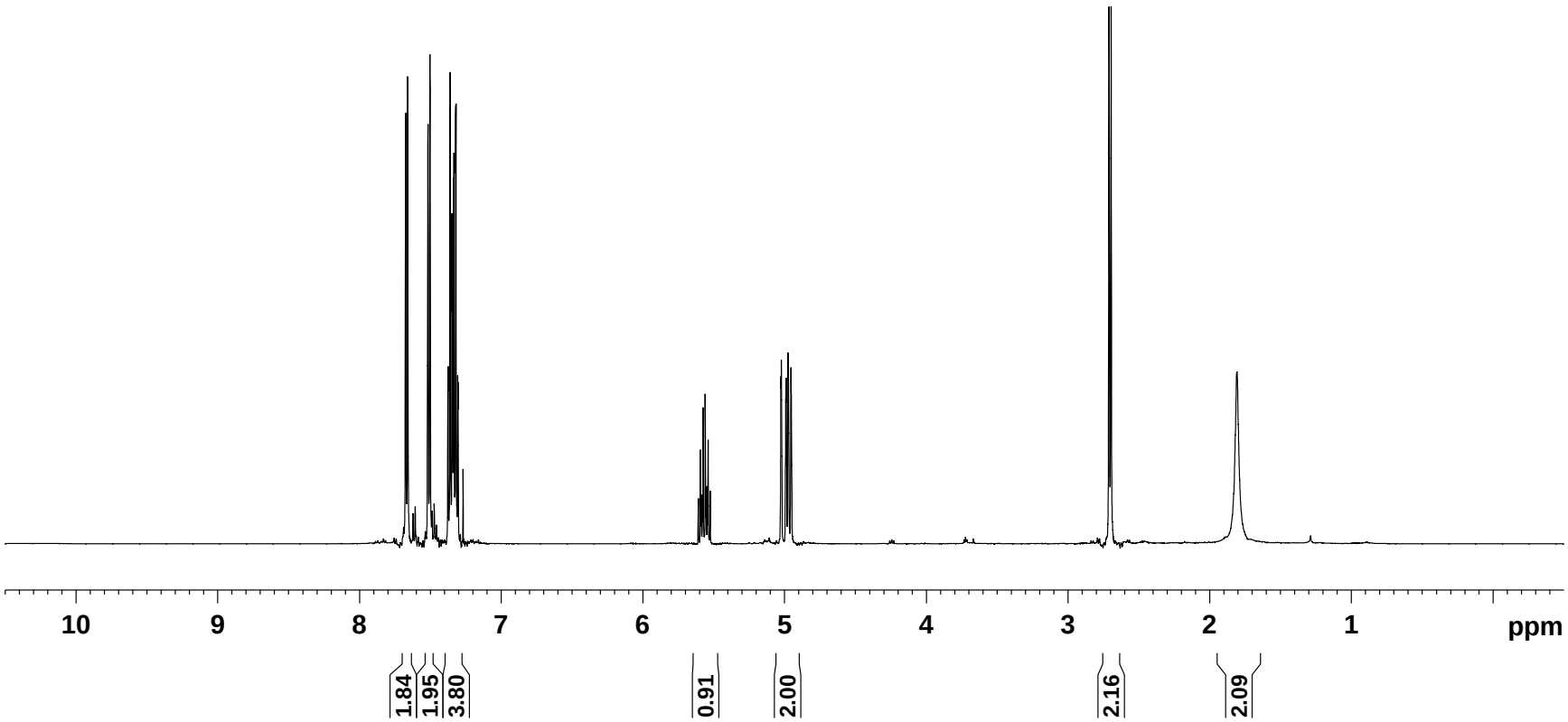
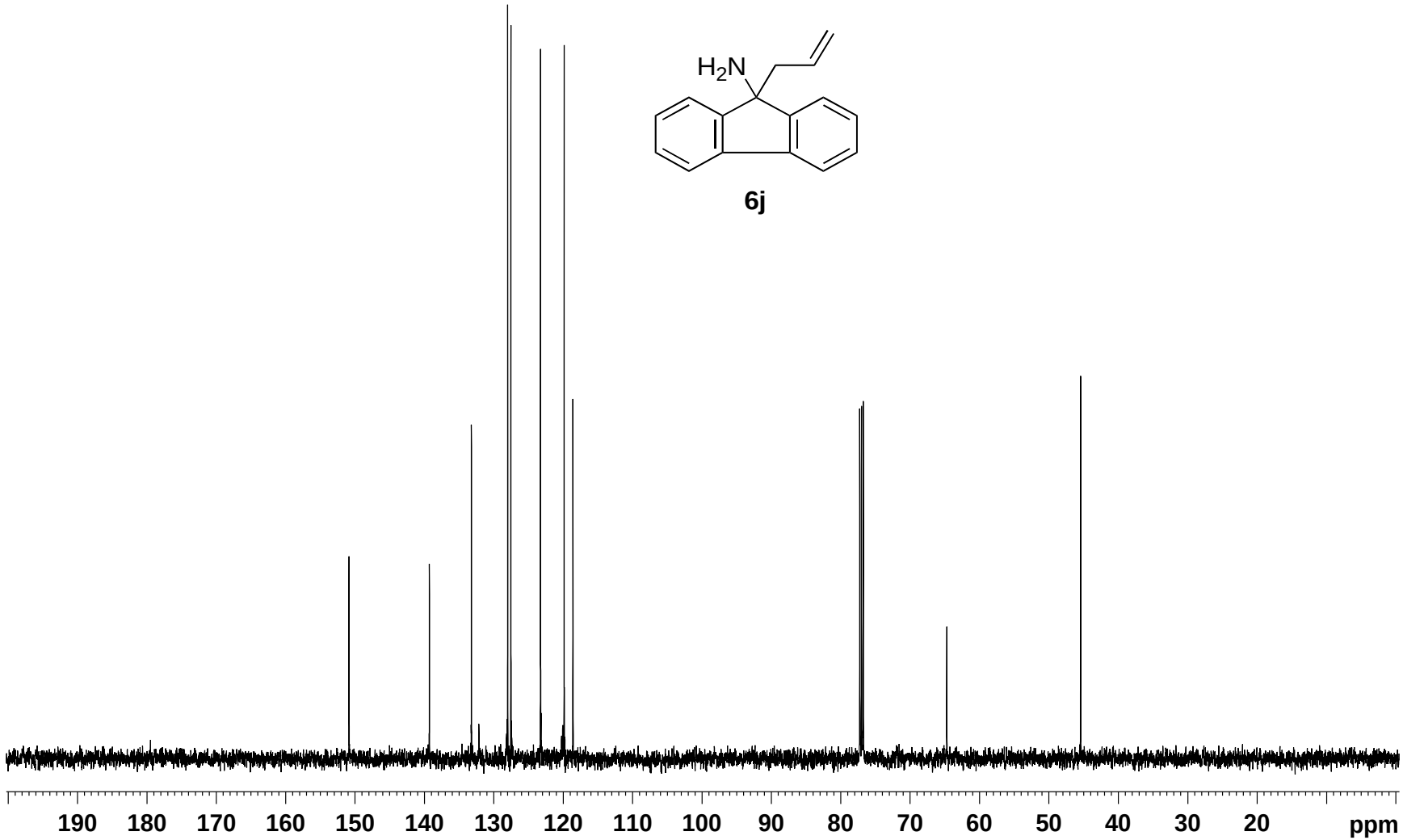
ppm



6j

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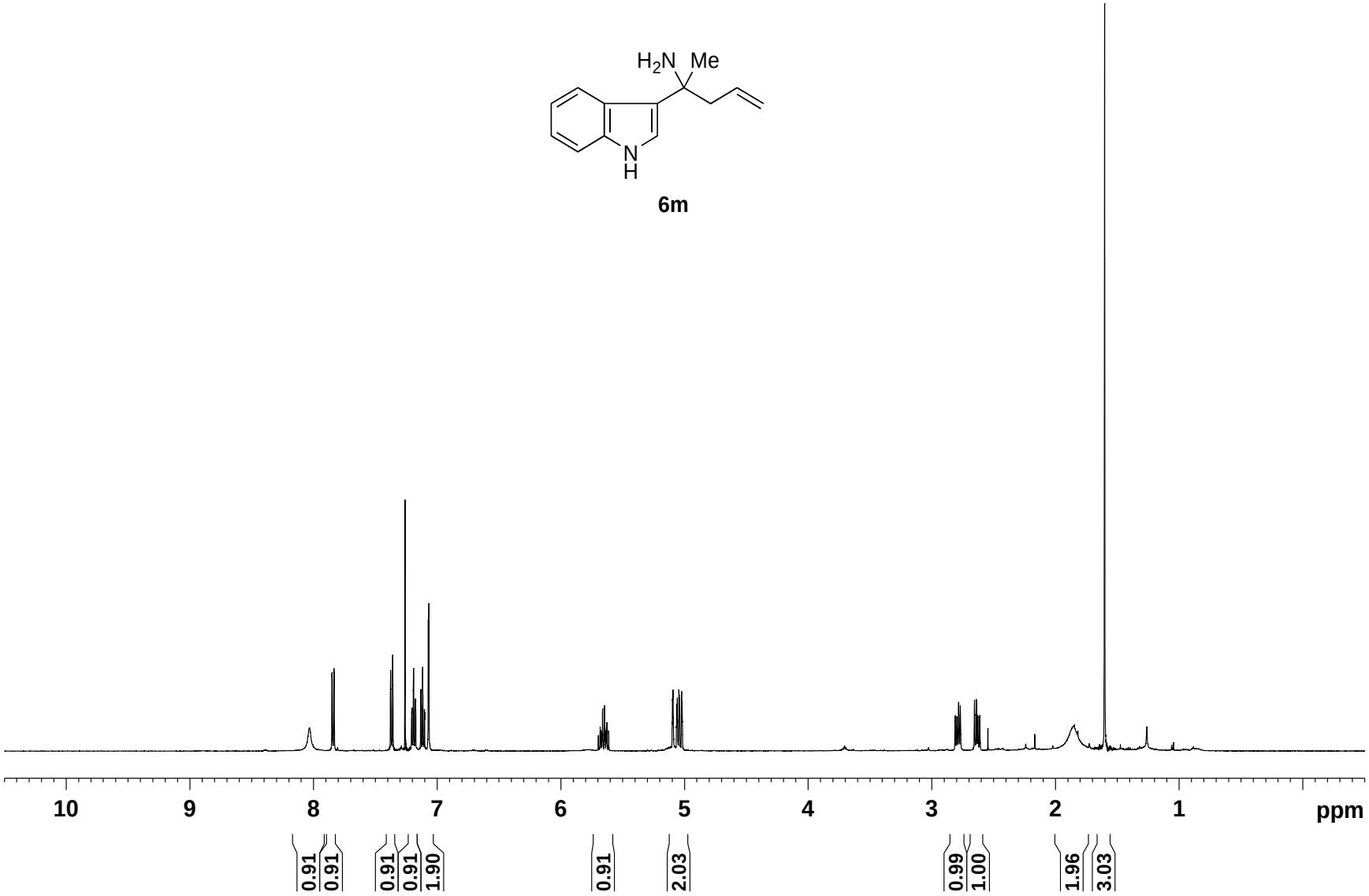
ppm

H2N
Me
N
H

6m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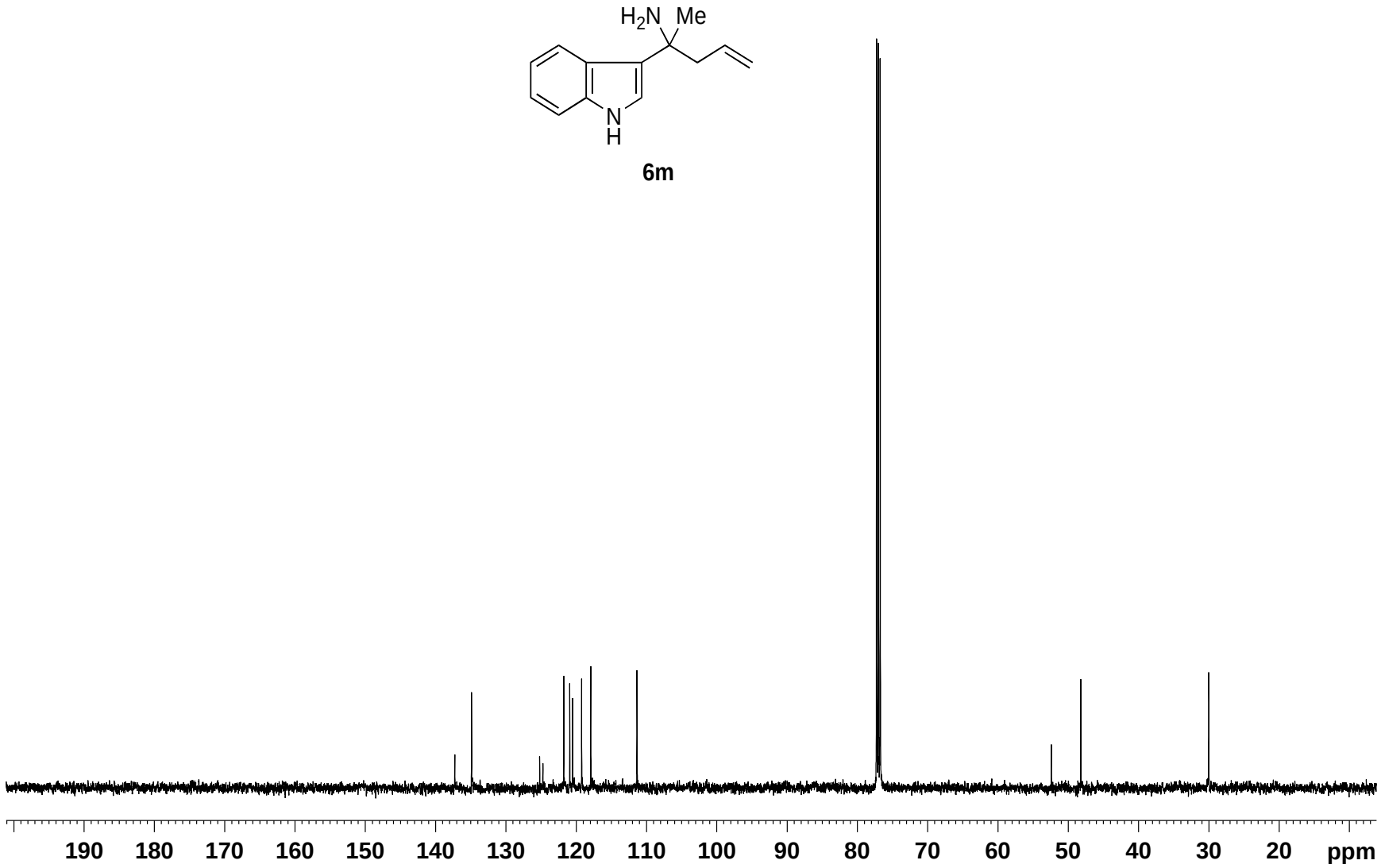
3.03


H2N
Me
N
H
6m
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160
150
140
130
120
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90
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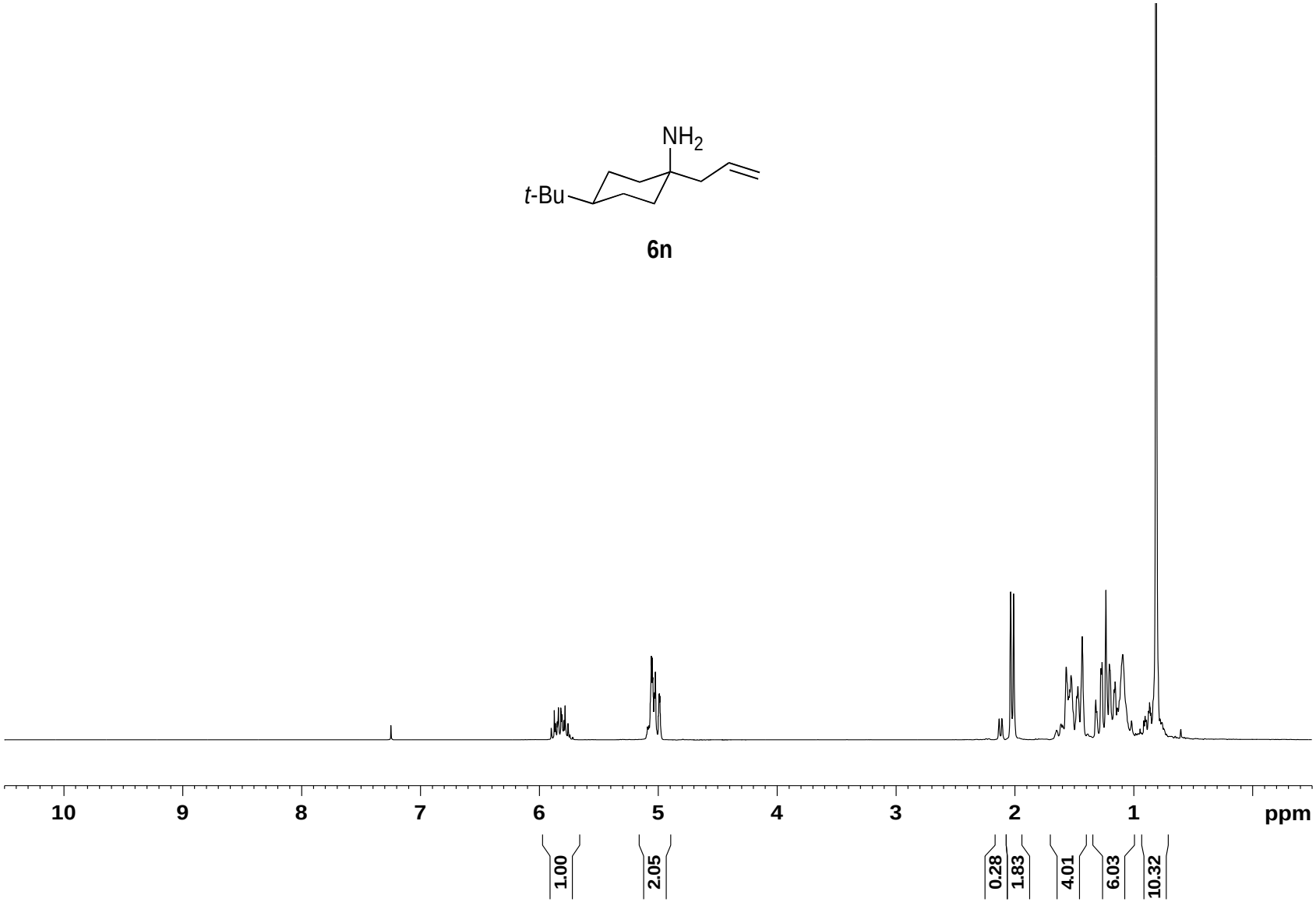
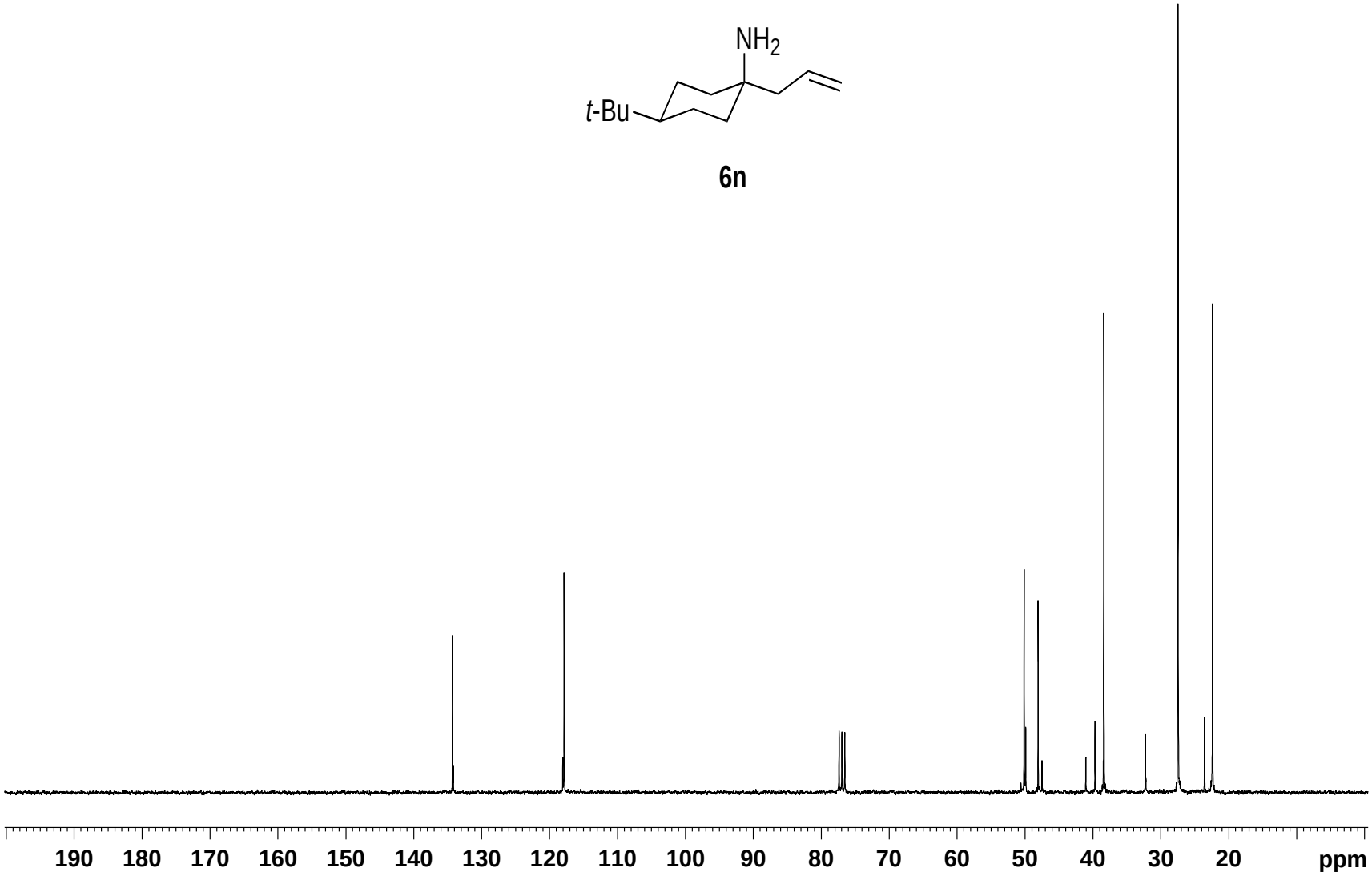
70
60
50
40
30
20
ppm

6n



NH2
t-Bu

6n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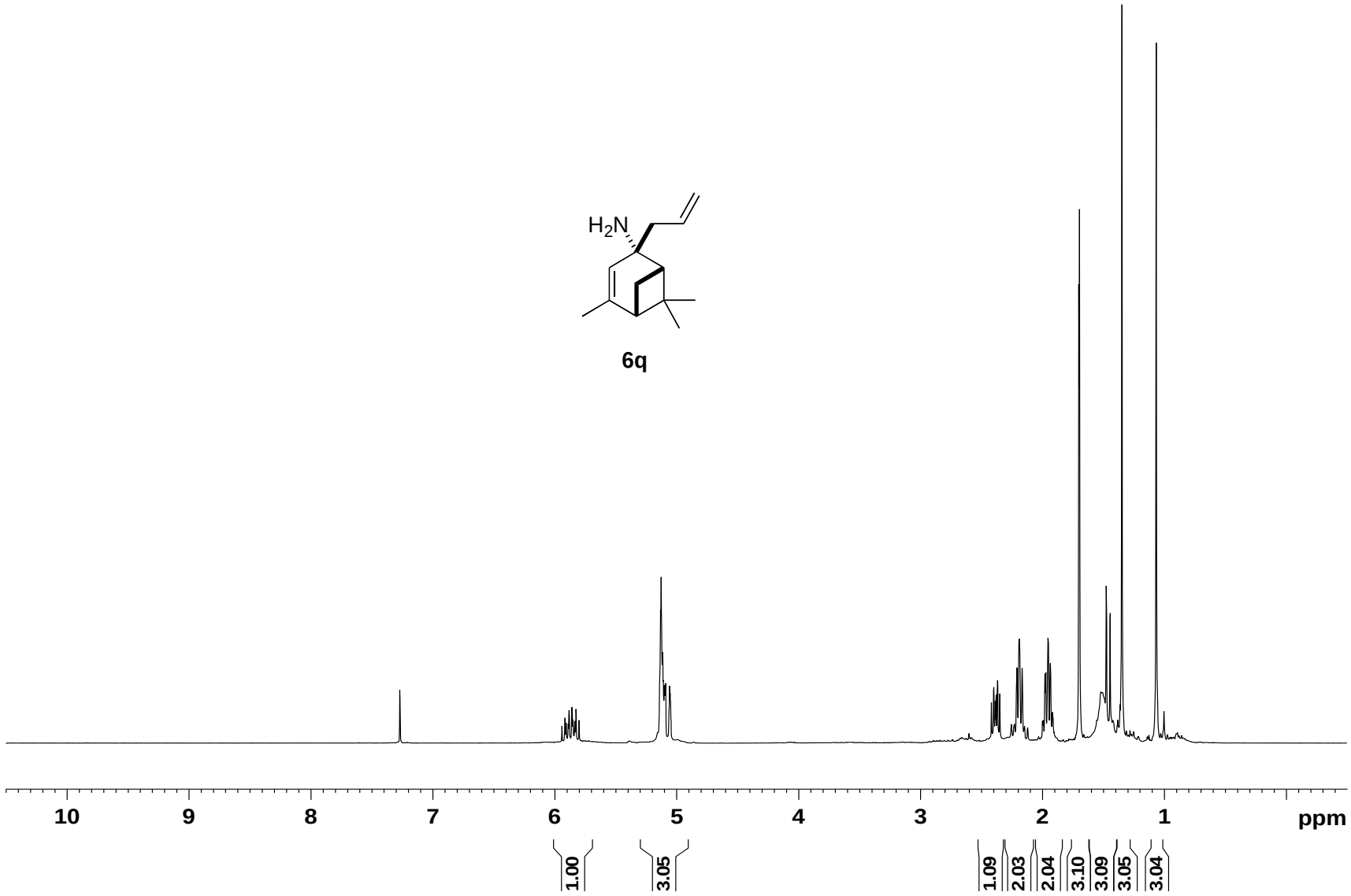
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6
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3
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ppm
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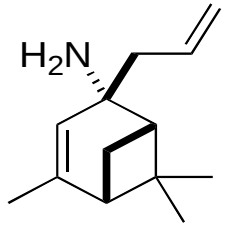
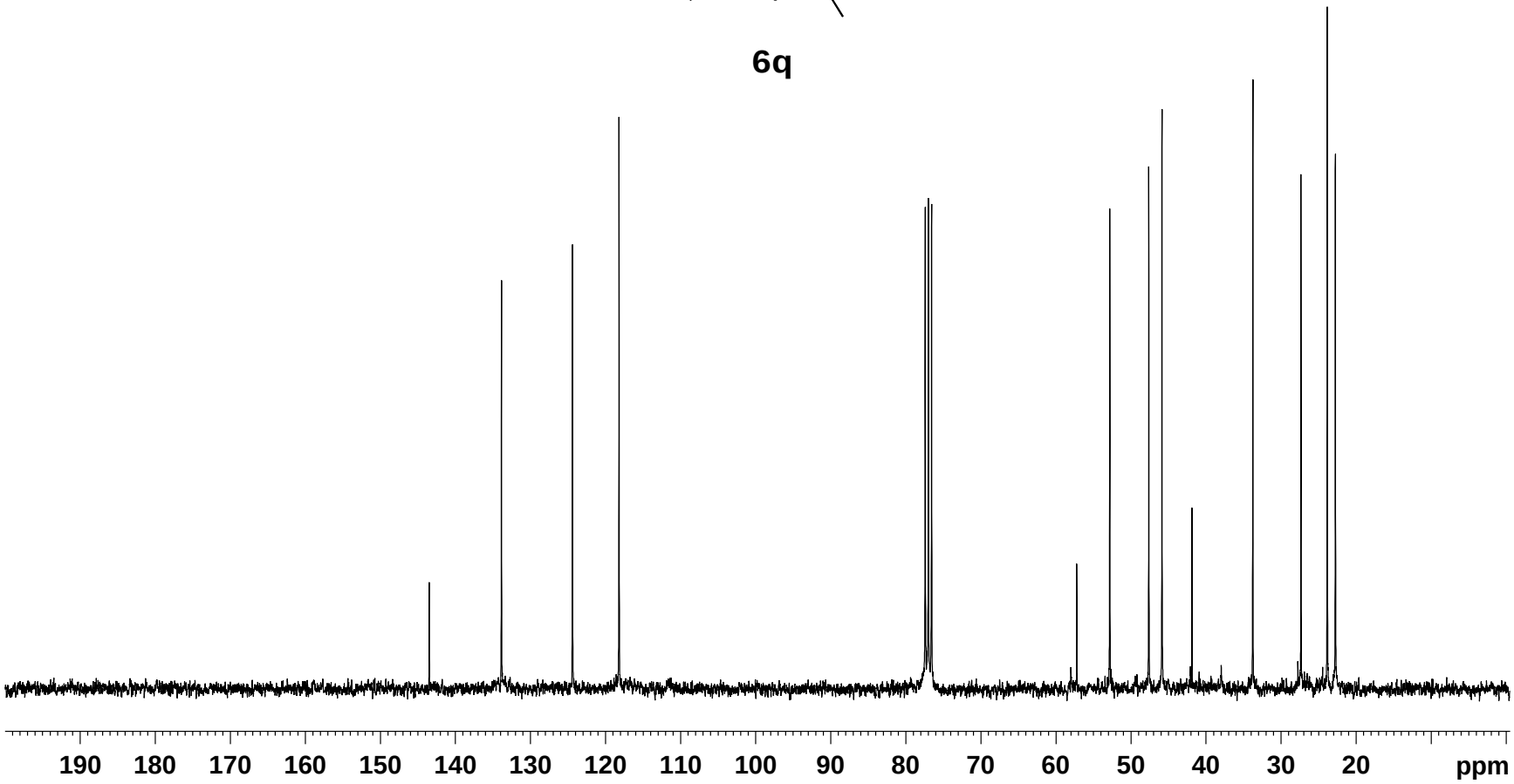
2.03
2.04
3.10
3.09
3.05
3.04


H2N

6q


190
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30
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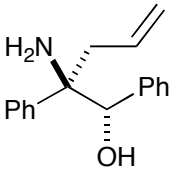
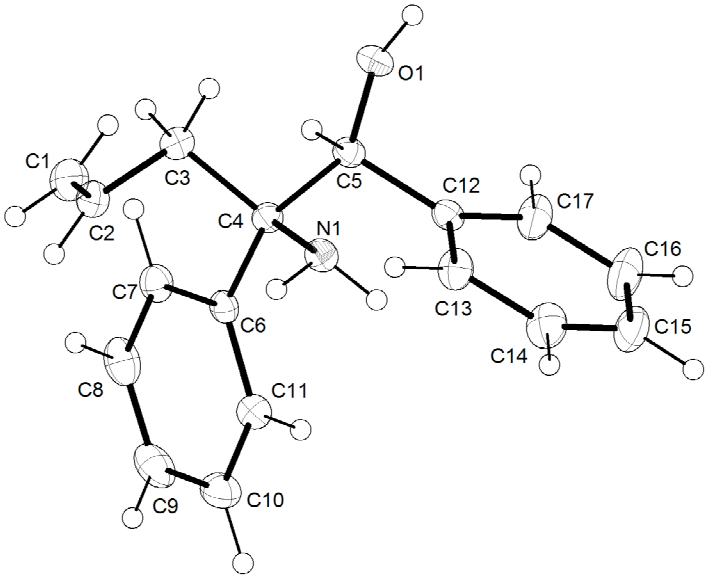
ppm

ORTEP Plot of 6p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