**Supporting Information for**

# Dioxazoles, A New Mild Nitrene Transfer Reagent in Gold Catalysis: Highly Efficient Synthesis of Functionalized Oxazoles

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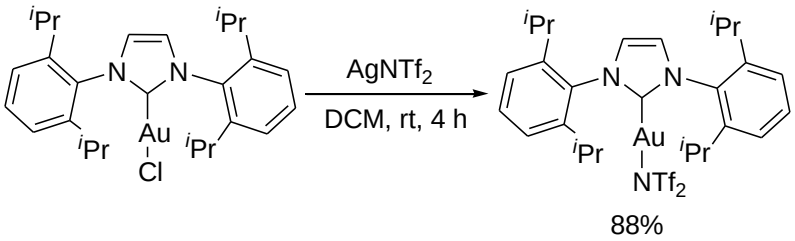
**Contents**:



**General Methods**. All reactions were carried out under Argon unless noted. DCM and DCE were distilled from $CaH_2$. Toluene was distilled from sodium and benzophenone. THF was distilled from sodium and benzophenone or purified using Innovative Technology Solvent Purifier (for the synthesis of substrates). MeCN was purified using Innovative Technology Solvent Purifier. Unless noted, all commercial reagents were used without further purification. $Ph_3PAuCl$,[1] $PPh_3AuNTf_2$,[2] $IPrAuNTf_2$,[3] and $IPrAu(MeCN)SbF_6$[4] were prepared according to the published methods. 1,3-Bis(2,6-di-isopropylphenyl)imidazole-2-ylidenegold(I) chloride

was purchased from Stream Chemical Company or synthesized by the published method.[5] (Acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate was purchased from Aldrich Chemical Company. $AgNTf_2$ was purchased from Aldrich Chemical Company or prepared by the published method.[6] Other silver salts were purchased from Stream or Acros Chemical Company. $^1H$ and $^{13}C$ NMR spectra were recorded at room temperature in $CDCl_3$ (containing 0.03% TMS), DMSO-$d_6$ (containing 0.03% TMS) or $CD_2Cl_2$ (containing 0.05% TMS) on Varian XL-400 MHz spectrometer, Agilent 400 MHz NMR spectrometer, or Agilent DDR 600 MHz spectrometer. $^1H$ NMR spectra was recorded at 400 MHz or 600 MHz, $^{13}C$ NMR spectra was recorded at 100 MHz or 150 MHz. $^1H$ NMR spectra was recorded with tetramethylsilane ($\delta$ = 0.00 ppm) as internal reference; $^{13}C$ NMR spectra was recorded with $CDCl_3$ ($\delta$ = 77.00 ppm), DMSO-$d_6$ ($\delta$ = 39.52 ppm) or $CD_2Cl_2$ ($\delta$ = 53.84 ppm) as internal reference. High-resolution mass spectra was obtained by using Waters Micromass GCT mass spectrometer or Agilent Technologies 6224 TOF LC/MS. IR spectra were obtained by using a Nicolet iS10 spectrometer. Melting points were measured using a SGW-4 microscopic melting point apparatus and were uncorrected. Single crystal X-ray diffraction data was collected on Bruker SMART diffractometer with graphite-monochromated Mo-K radiation ( = 0.71073 Å).

**Synthesis of IPrAuNTf$_2$.**[3]

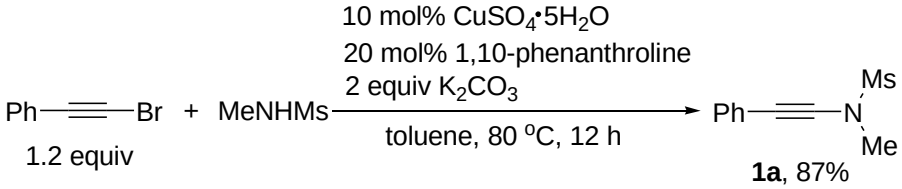



To a solution of $AgNTf_2$ (1.03 g, 2.65 mmol) in DCM (30 mL) was added IPrAuCl (1.65 g, 2.65 mmol). The resulting mixture was stirred at room temperature for 4 h and filtered through celite. The pad of celite was further washed with dichloromethane. Then the solvent was reduced under the reduced pressure, and pentane was added resulting in the immediate precipitation of a white solid. The solid was filtered and dried under high vacuum to give IPrAuNTf$_2$ as a white solid in 88% yield (2.03 g). $^1H$ NMR (400 MHz, $CD_2Cl_2$, $Me_4Si$) $\delta$ 7.53 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 4H), 7.31 (s, 2H), 2.49 (sept, *J* = 6.8 Hz, 4H), 1.29 (d, *J* = 6.8 Hz, 12H), 1.21 (d, *J* = 6.8 Hz, 12H); $^{13}C$ NMR (400 MHz, $CD_2Cl_2$, $Me_4Si$) $\delta$ 168.31, 146.15, 134.01, 131.18, 124.58, 124.39, 119.32 (q, *J* = 321.4 Hz), 29.29, 24.41, 24.07. Anal. Calcd for $C_{29}H_{36}AuF_6N_3O_4S_2$: C, 40.23; H, 4.19; N, 4.85. Found: C, 40.21; H, 4.18; N, 4.89.

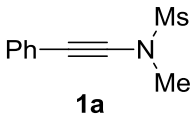
**General procedure for the synthesis of ynamides 1.**

**Method A : For *N*-alkyl substituted ynamides**

**Typical procedure for the synthesis of ynamide 1a.**




To a dry flask were added *N*-methylmethanesulfonamide (1.09 g, 10 mmol), $CuSO_4$•$5H_2O$ (249.7 mg, 1.0 mmol), 1,10-phenanthroline (360.4 mg, 2.0 mmol) and $K_2CO_3$ (2.764 g, 20 mmol). Then toluene (40 mL) and (bromoethynyl)benzene (2.172 g, 12 mmol) were added, and the resulting mixture was stirred at 80 $^oC$ for 12 h under an atmosphere of argon. When the reaction was complete, the crude mixture was cooled down to room temperature, filtered through celite and washed with ethyl acetate. After solvent evaporation, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford compound **1a** (1.82 g, 87%) as a yellow solid.

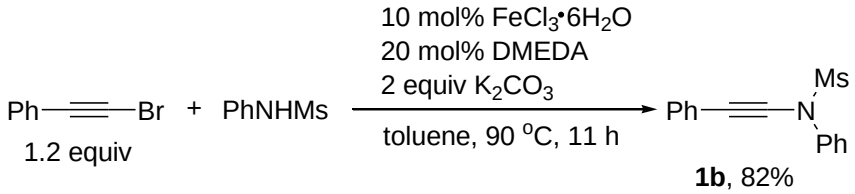



**1a**

***N*-Methyl-*N*-(phenylethynyl)methanesulfonamide (1a).** $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.42-7.39 (m, 2H), 7.33-7.28 (m, 3H), 3.29 (s, 3H), 3.11 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 131.43, 128.25, 128.02, 122.25, 82.94, 69.34, 39.13, 36.65. The spectroscopic data are in agreement with that previously reported.[7]

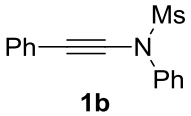
**Method B : For *N*-aryl substituted ynamides**

**Typical procedure for the synthesis of ynamide 1b.**[8]



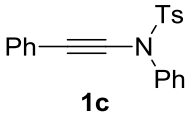

To a dry flask were added *N*-phenylmethanesulfonamide (856.1 mg, 5 mmol), $K_2CO_3$ (1.38 g, 10 mmol) and $FeCl_3$•$6H_2O$ (135.2 mg, 0.5 mmol). Then anhydrous toluene (20 mL), (bromoethynyl)benzene (1.09 g, 6 mmol) and *N*,*N*′-dimethylethane-1,2-diamine (DMEDA) (88 mg, 1 mmol) were added. The resulting mixture was stirred at 90 $^oC$ for 11 h under an

atmosphere of argon. When the reaction was complete, the crude mixture was cooled down to room temperature, filtered through celite and washed with ethyl acetate. After solvent evaporation, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford compound **1b** (1.11 g, 82%) as a white solid.



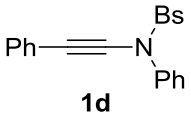

**1b**

***N*-Phenyl-*N*-(phenylethynyl)methanesulfonamide (1b).** $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.45-7.41 (m, 4H), 7.37-7.33 (m, 1H), 7.30-7.29 (m, 3H), 3.13 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 138.60, 131.48, 129.43, 128.29, 128.26, 128.15, 125.49, 122.15, 81.95, 70.86, 36.73. The spectroscopic data are in agreement with that previously reported.[9]



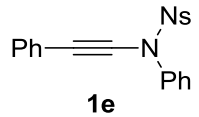

**1c**

**4-Methyl-*N*-phenyl-*N*-(phenylethynyl)benzenesulfonamide (1c).** Method B was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow solid in 51% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.40-7.27 (m, 12H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 144.98, 138.87, 132.82, 131.38, 129.47, 129.05, 128.24, 128.22, 127.93, 126.22, 122.53, 82.92, 70.43, 21.66. The spectroscopic data are in agreement with that previously reported.[9]



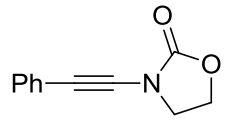

**1d**

**4-Bromo-*N*-phenyl-*N*-(phenylethynyl)benzenesulfonamide (1d).** Method B was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product as a yellow solid in 89% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.65-7.57 (m, 4H), 7.40-7.29 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 138.56, 134.65, 132.20, 131.51, 129.61, 129.26, 129.23, 128.52, 128.32, 128.21, 126.20, 122.20, 82.35, 70.73. HRMS (ESI) calcd for $C_{20}H_{15}BrNO_2S$ $[M+H]^+$: 412.0001, found 412.0001. The spectroscopic data are in agreement with that previously reported.[9]



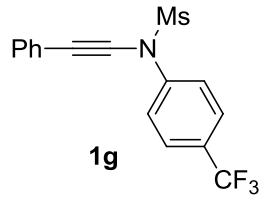

**1e**

**4-Nitro-*N*-phenyl-*N*-(phenylethynyl)benzenesulfonamide (1e).** Method B was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded the title product as a yellow solid in 66% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.36-8.33 (m, 2H), 7.93-7.90 (m, 2H), 7.40-7.36 (m, 5H), 7.33-7.29 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 150.73, 140.95, 138.14, 131.58, 129.43, 129.42, 128.87, 128.50, 128.39, 126.09, 124.08, 121.74, 81.62, 71.07. IR (neat): 3103, 3062, 2918, 2243, 1606, 1590, 1533, 1489, 1455, 1441, 1401, 1381, 1349, 1308, 1292, 1202, 1174, 1108, 1086, 1080, 1023, 1012, 968, 929, 902, 855, 787, 763, 738, 692, 683 $cm^{-1}$; HRMS (EI) calcd for $C_{20}H_{14}N_2O_4S$: 378.0674, found 378.0668.




**1f**

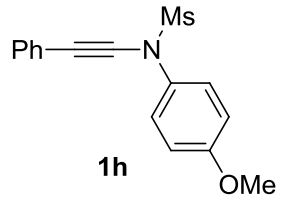
**3-(Phenylethynyl)oxazolidin-2-one (1f).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 4:1 to 2:1) afforded the title product as a white solid in 85% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.45-7.43 (m, 2H), 7.31-7.27 (m, 3H), 4.46 (t, $J$ = 8.8 Hz, 2H), 3.98 (t, $J$ = 8.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 155.89, 131.43, 128.22, 128.11, 122.03, 78.90, 71.02, 63.04, 46.91. The spectroscopic data are in agreement with that previously reported.[7]




**1g**

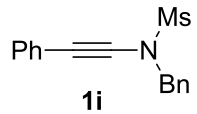
***N*-(Phenylethynyl)-*N*-(4-(trifluoromethyl)phenyl)methanesulfonamide (1g).** Method B was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow liquid in 31% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.74-7.67 (m, 4H), 7.47-7.46 (m, 2H), 7.33-7.32 (m, 3H), 3.18 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 141.65, 131.59, 129.74 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 128.54, 128.37, 126.54 (q, $^{3}J_{C\text{-}F}$ =

3.8 Hz), 124.88, 123.57 (q, $^{1}J_{C\text{-}F}$ = 271 Hz), 121.65, 80.72, 72.25, 37.28. IR (neat): 3018, 2930, 2241, 1615, 1511, 1415, 1370, 1320, 1211, 1167, 1111, 1066, 1017, 959, 907, 843, 788, 753, 730, 691, 683 $cm^{-1}$; HRMS (EI) calcd for $C_{16}H_{12}NO_2F_3S$: 339.0541, found 339.0536.



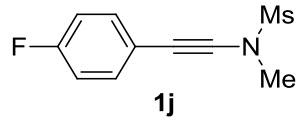
**1h**

***N*-(4-Methoxyphenyl)-*N*-(phenylethynyl)methanesulfonamide (1h).** Method B was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1 to 3:1) afforded the title product as a yellow solid in 33% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.49-7.41 (m, 4H), 7.30-7.28 (m, 3H), 6.95-6.92 (m, 2H), 3.81 (s, 3H), 3.12 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 159.55, 131.39, 131.13, 128.22, 128.02, 127.40, 122.24, 114.58, 82.39, 70.14, 55.46, 36.35. The spectroscopic data are in agreement with that previously reported.[10]



**1i**

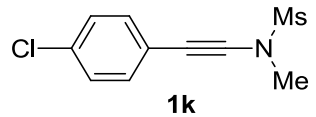
***N*-Benzyl-*N*-(phenylethynyl)methanesulfonamide (1i).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 98% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.50-7.47 (m, 2H), 7.42-7.33 (m, 5H), 7.29-7.26 (m, 3H), 4.70 (s, 2H), 2.92 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 134.41, 131.29, 128.92, 128.75, 128.69, 128.22, 127.94, 122.35, 81.90, 71.48, 55.80, 38.85. The spectroscopic data are in agreement with that previously reported.[7]



**1j**

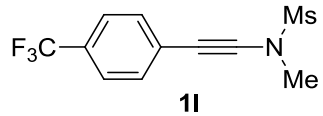
***N*-((4-Fluorophenyl)ethynyl)-*N*-methylmethanesulfonamide (1j).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow liquid in 89% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.42-7.37 (m, 2H), 7.03-6.97 (m, 2H), 3.29 (s, 3H), 3.12 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 162.32 (d, $^{1}J_{C\text{-}F}$ = 248.2 Hz), 133.56 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 118.29 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 115.51 (d,

$^{2}J_{C\text{-}F}$ = 22.0 Hz), 82.54, 68.24, 39.08, 36.68. The spectroscopic data are in agreement with that previously reported.[11]



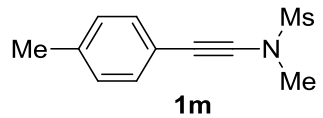

**1k**

***N*-((4-Chlorophenyl)ethynyl)-*N*-methylmethanesulfonamide (1k).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow solid in 88% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.34-7.31 (m, 2H), 7.29-7.26 (m, 2H), 3.29 (s, 3H), 3.12 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 133.96, 132.63, 128.59, 120.85, 83.80, 68.44, 39.09, 36.86. The spectroscopic data are in agreement with that previously reported.[7]



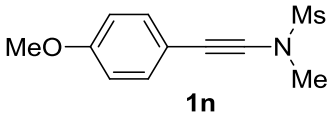

**1l**

***N*-Methyl-*N*-((4-(trifluoromethyl)phenyl)ethynyl)methanesulfonamide (1l).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow liquid in 86% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.56-7.54 (m, 2H), 7.49-7.47 (m, 2H), 3.32 (s, 3H), 3.14 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 131.06, 129.28 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 126.39, 125.12 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.85 (q, $^{1}J_{C\text{-}F}$ = 270.2 Hz), 85.41, 68.60, 39.01, 36.97. The spectroscopic data are in agreement with that previously reported.[7]



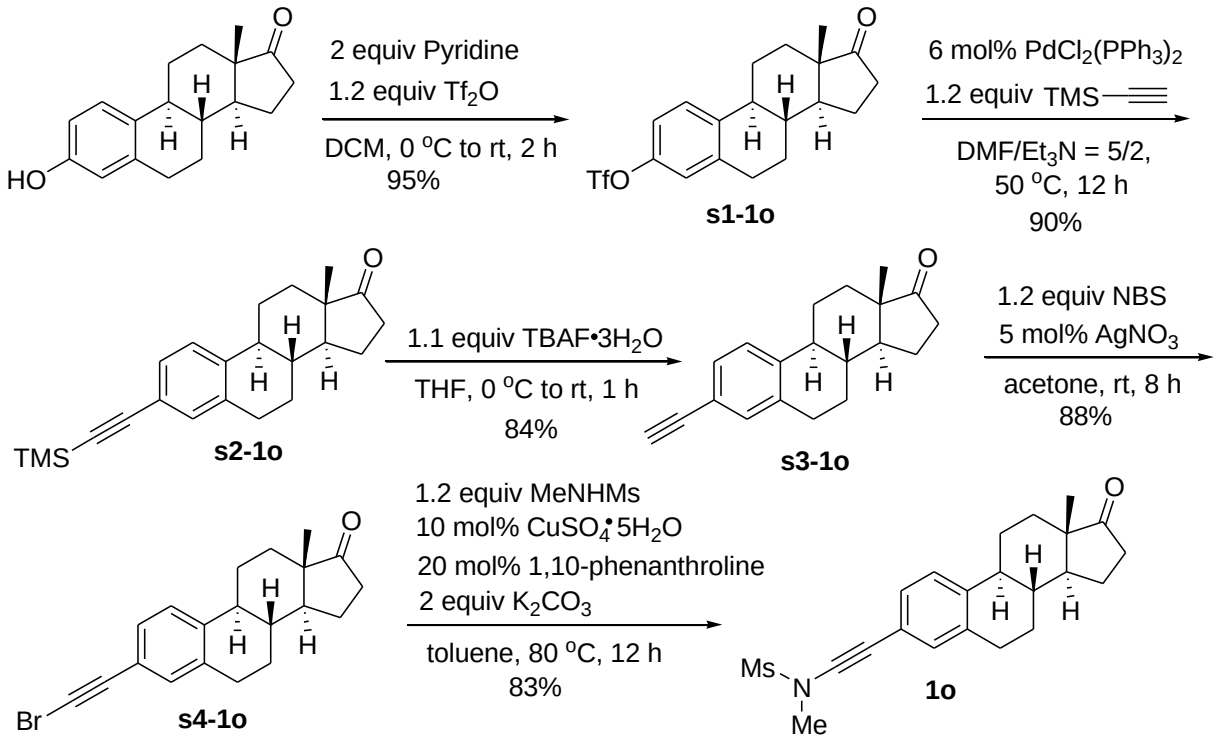

**1m**

***N*-Methyl-*N*-(*p*-tolylethynyl)methanesulfonamide (1m).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow solid in 92% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.30 (d, $J$ = 8.0 Hz, 2H), 7.10 (d, $J$ = 8.0 Hz, 2H), 3.27 (s, 3H), 3.10 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 138.21, 131.50, 128.99, 119.08, 82.24, 69.29, 39.13, 36.51, 21.33. The spectroscopic data are in agreement with that previously reported.[7]




**1n**

***N*-((4-Methoxyphenyl)ethynyl)-*N*-methylmethanesulfonamide (1n).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1 to 2:1) afforded the title product as a yellow solid in 88% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.38-7.34 (m, 2H), 6.85-6.81 (m, 2H), 3.80 (s, 3H), 3.27 (s, 3H), 3.11 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 159.58, 133.47, 114.12, 113.87, 81.55, 68.99, 55.21, 39.19, 36.47. The spectroscopic data are in agreement with that previously reported.[7]




To a solution of 1,3,5(10)-estratrien-3-ol-17-one (2.704 g, 10 mmol) in DCM (40 mL) was added pyridine (1.6 mL, 20 mmol). Then $Tf_2O$ (2 mL, 12 mmol, diluted with 20 mL DCM) was added dropwise to the mixture at 0 °C. The resulting solution was warmed up to room temperature and stirred for 2 h. Then the mixture was quenched with saturated ammonium chloride solution, extracted with dichloromethane, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford **s1-1o** in 95% isolated yield (3.823 g) as a white solid.

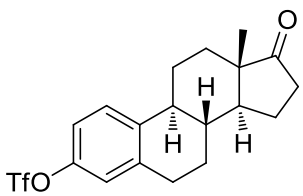
To a solution of the above **s1-1o** (2.012 g, 5.0 mmol) in triethylamine (4 mL) and DMF (10 mL) were added ethynyltrimethylsilane (589.3 mg, 6 mmol) and $Pd(PPh_3)_2Cl_2$ (210.6 mg,

0.3 mmol) at room temperature. Then the mixture was stirred at 50 $^{o}$C for 12 h. After the starting material was consumed, the reaction mixture was quenched with 3 N HCl solution, extracted with dichloromethane, washed with water and brine followed by drying over anhydrous $Na_2SO_4$. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 8:1 to 5:1) to afford compound **s2-1o** (1.576 g, 90%) as a light yellow solid.

To a solution of the above **s2-1o** (1.576 g, 4.5 mmol) in THF (20 mL) was added TBAF $3H_2O$ (1.562 g, 4.95 mmol) at 0 $^{o}$C. The resulting solution was warmed up to room temperature and stirred for 1 h. Then the mixture was quenched with water, extracted with dichloromethane, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:1) to afford **s3-1o** in 84% isolated yield (1.053 g) as a white solid.

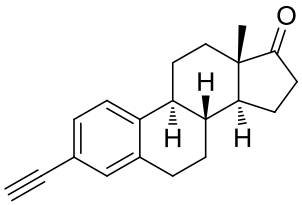
To a solution of **s3-1o** (1.053 g, 3.8 mmol) in acetone (20 mL) were added *N*-bromosuccinimide (811.6 mg, 4.56 mmol) and $AgNO_3$ (32.3 mg, 0.19 mmol) at room temperature. The mixture was stirred at the same temperature for 8 h. The reaction mixture was diluted with hexanes and filtered through a pad of celite using dichloromethane as an eluent. The filtrate was collected and evaporated under the reduced pressure, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 5:1:1) to afford compound **s4-1o** (1.196 g, 88%) as a white solid.

To a dry flask were added *N*-methylmethanesulfonamide (432.2 mg, 3.96 mmol), $CuSO_4$ $5H_2O$ (82.4 mg, 0.33 mmol), 1,10-phenanthroline (118.9 mg, 0.66 mmol) and $K_2CO_3$ (912.2 mg, 6.6 mmol). Then anhydrous toluene (15 mL) and **s4-1o** (1.182 g, 3.3 mmol) were added, and the resulting mixture was stirred at 80 $^{o}$C for 12 h under an atmosphere of argon. When the reaction was complete, the crude mixture was cooled down to room temperature, filtered through celite and washed with ethyl acetate. After solvent evaporation, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 3:1:1) to afford compound **1o** (1.057 g, 83%) as a light yellow solid.



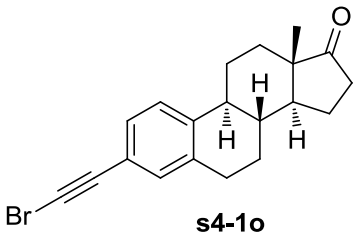

**s1-1o**

**(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate (s1-1o).** $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.35 (d, *J* = 8.8 Hz, 1H), 7.05-7.02 (m, 1H), 7.00 (s, 1H), 2.97-2.93 (m, 2H), 2.52 (dd, *J* = 18.6, 8.4 Hz, 1H), 2.42-2.39 (m, 1H), 2.33-2.27 (m, 1H), 2.20-1.97 (m, 4H), 1.70-1.42 (m, 6H), 0.92 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 220.38, 147.50, 140.21, 139.24, 127.13, 121.15, 118.66 (q, *J* = 319 Hz), 118.21, 50.27, 47.77, 44.00, 37.64, 35.72, 31.39, 29.30, 25.99, 25.59, 21.47, 13.69. The spectroscopic data are in agreement with that previously reported.[12]




**s3-1o**

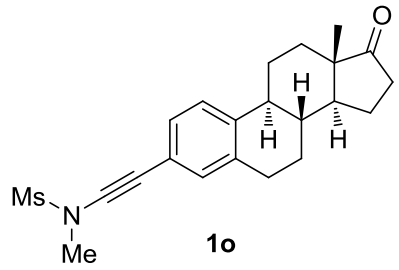
**(8*R*,9*S*,13*S*,14*S*)-3-Ethynyl-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[a]phenanthren-17(14*H*)-one (s3-1o).** M.p. 173-175 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.27-7.23 (m, 3H), 3.02 (s, 1H), 2.88-2.86 (m, 2H), 2.51 (dd, *J* = 18.8, 9.2 Hz, 1H), 2.40-2.38 (m, 1H), 2.28-2.24 (m, 1H), 2.18-1.94 (m, 4H), 1.67-1.36 (m, 6H), 0.90 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 220.58, 140.68, 136.50, 132.45, 129.27, 125.25, 119.24, 83.63, 76.46, 50.28, 47.77, 44.24, 37.74, 35.69, 31.37, 28.92, 26.13, 25.41, 21.43, 13.69. IR (neat): 3304, 2967, 2932, 2869, 2101, 1733, 1492, 1453, 1430, 1407, 1370, 1253, 1212, 1139, 1080, 1051, 1037, 1008, 944, 921, 904, 884, 824, 781, 737, 708, 652 cm$^{-1}$; HRMS (ESI) calcd for $C_{20}H_{23}O$ $[M+H]^+$: 279.1743, found 279.1740.




**s4-1o**

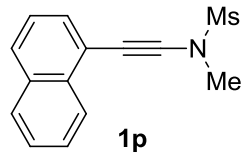
**(8*R*,9*S*,13*S*,14*S*)-3-(Bromoethynyl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (s-1l).** M.p. 201-203 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.22-7.19 (m, 3H), 2.89-2.86 (m, 2H), 2.51 (dd, *J* = 18.8, 8.8 Hz, 1H), 2.41-2.38 (m, 1H), 2.30-2.25 (m, 1H), 2.19-1.95 (m, 4H), 1.68-1.38 (m, 6H), 0.91 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 220.70, 140.69, 136.63, 132.40, 129.22, 125.36, 119.92, 80.01, 50.40,

48.76, 47.87, 44.38, 37.83, 35.79, 31.47, 29.01, 26.23, 25.48, 21.53, 13.78. IR (neat): 2976, 2933, 2873, 2190, 1732, 1496, 1469, 1453, 1426, 1404, 1372, 1339, 1258, 1215, 1139, 1083, 1051, 1005, 968, 913, 834, 824, 788, 750, 707 $cm^{-1}$; HRMS (EI) calcd for $C_{20}H_{21}OBr$: 356.0776, found 356.0779.



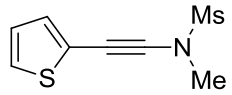

**1o**

***N*-Methyl-*N*-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl)ethynyl)methanesulfonamide (1o).** M.p. 145-147 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.27-7.17 (m, 3H), 3.29 (s, 3H), 3.12 (s, 3H), 2.89-2.86 (m, 2H), 2.51 (dd, *J* = 19.0, 8.8 Hz, 1H), 2.41-2.39 (m, 1H), 2.30-2.25 (m, 1H), 2.19-1.95 (m, 4H), 1.68-1.38 (m, 6H), 0.91 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 220.73, 140.05, 136.56, 132.01, 128.79, 125.31, 119.48, 82.29, 69.31, 50.36, 47.85, 44.30, 39.17, 37.85, 36.56, 35.76, 31.43, 28.98, 26.23, 25.49, 21.48, 13.75. IR (neat): 3017, 2928, 2858, 2236, 1731, 1452, 1407, 1357, 1259, 1203, 1157, 1120, 1085, 1053, 1008, 963, 889, 869, 823, 784, 772, 713, 657 $cm^{-1}$; HRMS (ESI) calcd for $C_{22}H_{28}NO_3S$ $[M+H]^+$: 386.1784, found 386.1785.



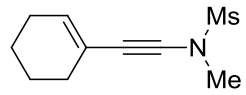

**1p**

***N*-Methyl-*N*-(naphthalen-1-ylethynyl)methanesulfonamide (1p).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a brown liquid in 85% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.61-7.53 (m, 1H), 7.50-7.46 (m, 1H), 7.51-7.45 (m, 1H), 7.39-7.36 (m, 1H), 3.33 (s, 3H), 3.11 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 133.02, 132.94, 129.51, 128.24, 128.16, 126.74, 126.31, 125.82, 125.06, 119.95, 87.64, 67.76, 39.15, 36.69. IR (neat): 3057, 3006, 2931, 2232, 1586, 1507, 1456, 1409, 1353, 1323, 1256, 1208, 1157, 1072, 1039, 1015, 944, 838, 799, 769, 700 $cm^{-1}$; HRMS (ESI) calcd for $C_{14}H_{14}NO_2S$ $[M+H]^+$: 260.0740, found 260.0740.



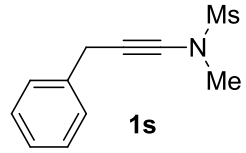

**1q**

***N*-Methyl-*N*-(thiophen-2-ylethynyl)methanesulfonamide (1q).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow liquid in 86% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.28 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.22 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.97 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.28 (s, 3H), 3.11 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 133.29, 128.01, 126.97, 122.21, 86.36, 62.72, 39.12, 36.96. The spectroscopic data are in agreement with that previously reported.[7]



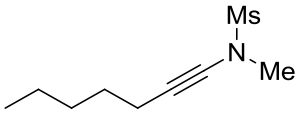

**1r**

***N*-(Cyclohex-1-en-1-ylethynyl)-*N*-methylmethanesulfonamide (1r).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow liquid in 93% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 6.09-6.07 (m, 1H), 3.20 (s, 3H), 3.06 (s, 3H), 2.11-2.07 (m, 4H), 1.65-1.56 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 134.83, 119.54, 80.53, 70.87, 39.19, 36.22, 29.41, 25.59, 22.22, 21.37. The spectroscopic data are in agreement with that previously reported.[13]



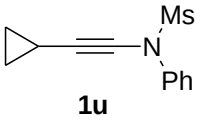

**1s**

***N*-Methyl-*N*-(3-phenylprop-1-yn-1-yl)methanesulfonamide (1s).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow liquid in 81% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.32-7.23 (m, 5H), 3.70 (s, 2H), 3.17 (s, 3H), 3.02 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 136.63, 128.40, 127.59, 126.51, 76.09, 66.78, 38.97, 36.03, 24.52. IR (neat): 3028, 2933, 2256, 1679, 1495, 1454, 1351, 1154, 1075, 1034, 959, 850, 768, 733, 697 $cm^{-1}$; HRMS (ESI) calcd for $C_{11}H_{14}NO_2S$ $[M+H]^+$: 224.0740, found 224.0741.




**1t**

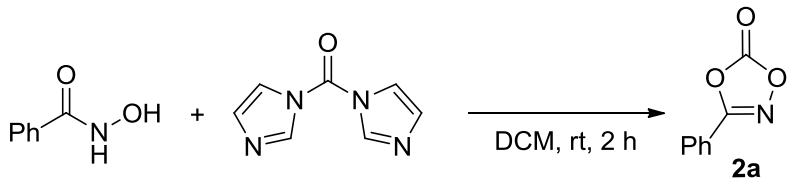
***N*-(Hept-1-yn-1-yl)-*N*-methylmethanesulfonamide (1t).** Method A was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow liquid in 91% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 3.16 (s, 3H), 3.03 (s, 3H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.54-1.50 (m, 2H), 1.38-1.31 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 74.10, 69.14, 39.12, 35.77, 30.93, 28.49, 22.06, 18.22, 13.89. IR (neat): 2956, 2933, 2860, 2254, 1459, 1353, 1324, 1278, 1156, 1042, 1021, 960, 932, 816, 782, 765 cm$^{-1}$; HRMS (ESI) calcd for $C_9H_{18}NO_2S$ $[M+H]^+$: 204.1053, found 204.1055.




**1u**

***N*-(Cyclopropylethynyl)-*N*-phenylmethanesulfonamide (1u).** Method B was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solide in 82% yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.50-7.47 (m, 2H), 7.42-7.38 (m, 2H), 7.34-7.31 (m, 1H), 3.07 (s, 3H), 1.42-1.35 (m, 1H), 0.86-0.72 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 139.07, 129.28, 127.99, 125.40, 75.13, 68.57, 36.24, 8.83, -0.76. The spectroscopic data are in agreement with that previously reported.[14]

**Synthesis of dioxazole 3-phenyl-1,4,2-dioxazol-5-one (2a).**[15]

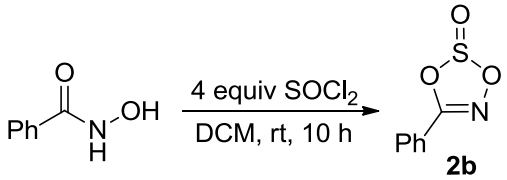



**2a**

To a solution of *N*-hydroxybenzamide (1.37 g, 10 mmol) in DCM (100 mL) was added CDI (1,1'-carbonyldiimidazole) (1.62 g, 10 mmol). The resulting solution was stirred at room temperature and for 2 h. Then the mixture was quenched with 1 M HCl, extracted with dichloromethane, washed by water and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under the reduced pressure to afford the title product as a white solid in 85% (1.38 g) isolated yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.86-7.84 (m, 2H), 7.68-7.64 (m, 1H),

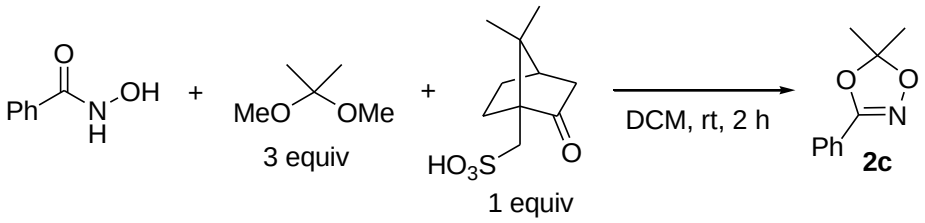
7.58-7.53 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 163.45, 153.78, 133.74, 129.32, 126.52, 120.00. The spectroscopic data are in agreement with that previously reported.[15]

**Synthesis of 5-phenyl-1,3,2,4-dioxathiazole 2-oxide (2b).**[15]




To a solution of thionyl chloride (1.5 mL, 20 mmol) in DCM (20 mL) was added *N*-hydroxybenzamide (685.7 mg, 5 mmol). The resulting solution was stirred at room temperature and for 10 h. Excessive thionyl chloride and solvent were removed under the reduced pressure to afford the title product as a light yellow oil in 89% (818.3 mg) yield. $^1$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.59-7.55 (m, 1H), 7.50-7.46 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.07, 132.91, 129.06, 127.89, 120.52. The spectroscopic data are in agreement with that previously reported.[15]

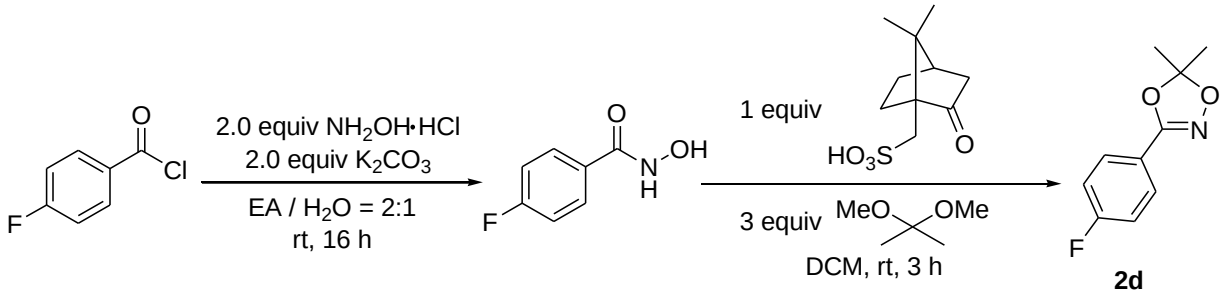
**Synthesis of 5,5-dimethyl-3-phenyl-1,4,2-dioxazole (2c).**[15]




To a solution of *N*-hydroxybenzamide (6.857 g, 50 mmol) in DCM (150 mL) were added 2,2-dimethoxypropane (15.623 g, 150 mmol), L(-)-camphorsulfonic acid (11.615 g, 50 mmol). The resulting solution was stirred at room temperature and for 2 h. Then the mixture was quenched with saturated $NaHCO_3$ solution, extracted with dichloromethane, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford the title product as a colorless oil in 86% (7.628 g) isolated yield. $^1$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.79-7.77 (m, 2H), 7.48-7.39 (m, 3H), 1.68 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.09, 131.14, 128.46, 126.50, 123.52, 115.39, 24.72. The spectroscopic data are in agreement with that previously reported.[15]

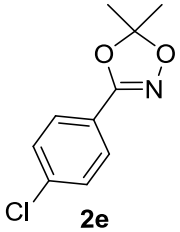
**Synthesis of dioxazoles 2d-2p from acyl chloride.**

**Typical procedure for the synthesis of 3-(4-Fluorophenyl)-5,5-dimethyl-1,4,2-dioxazole (2d).**

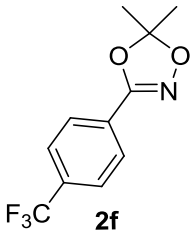



To a flask were added $NH_2OH$•HCl (694.9 mg, 10.0 mmol), ethyl acetate (30 mL), $H_2O$ (20 mL) and $K_2CO_3$ (1.38 g, 10.0 mmol) at 0 $^oC$. After that, 4-fluorobenzoyl chloride (793 mg, 5.0 mmol) dissolved in 10 mL ethyl acetate was added dropwise.[16] The resulting solution was warmed up to room temperature and stirred for 16 h. The resulting mixture was extracted with ethyl acetate, washed with water and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under the reduced pressure and the residue was used directly for the next step without further purification.

To a solution of above 4-fluoro-*N*-hydroxybenzamide in DCM (30 mL) were added 2,2-dimethoxypropane (1.56 g, 15 mmol) and L(-)-camphorsulfonic acid (1.16 g, 5.0 mmol). The resulting solution was stirred at room temperature for 3 h. Then the mixture was quenched with saturated $NaHCO_3$ solution, extracted with dichloromethane, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a yellow oil in 92% (897.1 mg) yield. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.79-7.76 (m, 2H), 7.12-7.08 (m, 2H), 1.68 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 164.24 (d, $^1J_{C\text{-}F}$ = 250.9 Hz), 157.25, 128.66 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 119.73 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 115.64 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 115.55, 24.56. IR (neat): 3078, 2993, 2938, 1623, 1605, 1513, 1455, 1414, 1375, 1359, 1294, 1220, 1169, 1156, 1099, 1074, 1014, 979, 947, 888, 841, 815, 721, 662 $cm^{-1}$; HRMS (ESI) calcd for $C_{10}H_{11}FNO_2$ $[M+H]^+$: 196.0768, found 196.0769.

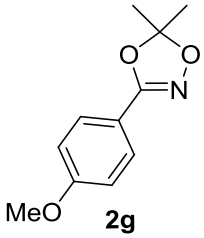


**3-(4-Chlorophenyl)-5,5-dimethyl-1,4,2-dioxazole (2e).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a colorless oil in 88% overall yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.72-7.70 (m, 2H), 7.40-7.38 (m, 2H), 1.68 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.44, 137.28, 128.86, 127.86, 122.08, 115.89, 24.78. IR (neat): 2991, 2938, 1723, 1620, 1600, 1495, 1453, 1405, 1375, 1360, 1277, 1216, 1168, 1092, 1075, 1015, 978, 946, 890, 834, 815, 762, 737, 716 $cm^{-1}$; HRMS (ESI) calcd for $C_{10}H_{11}ClNO_2$ $[M+H]^+$: 212.0473, found 212.0474.



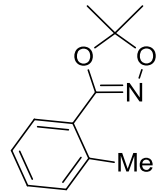
**2f**

**5,5-Dimethyl-3-(4-(trifluoromethyl)phenyl)-1,4,2-dioxazole (2f).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a colorless oil in 89% overall yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.90 (d, $J$ = 8.0 Hz, 2H), 7.67 (d, $J$ = 8.4 Hz, 2H), 1.71 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.08, 132.68 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 127.10 (q, $^{5}J_{C\text{-}F}$ = 1.1 Hz), 126.81, 125.43 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.57 (q, $^{1}J_{C\text{-}F}$ = 271.0 Hz), 116.35, 24.62. IR (neat): 2995, 2938, 1730, 1619, 1575, 1517, 1456, 1415, 1377, 1321, 1219, 1166, 1125, 1109, 1080, 1063, 1018, 979, 948, 894, 848, 814, 776, 700, 652 $cm^{-1}$; HRMS (ESI) calcd for $C_{11}H_{11}F_3NO_2$ $[M+H]^+$: 240.0736, found 246.0738.



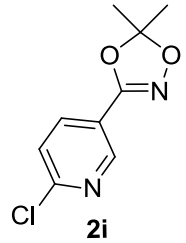
**2g**

**3-(4-Methoxyphenyl)-5,5-dimethyl-1,4,2-dioxazole (2g).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a colorless oil in 86% overall yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.73-7.69 (m, 2H), 6.93-6.89 (m, 2H), 3.82 (s, 3H), 1.66 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 161.78, 157.94, 128.16, 114.87, 113.85, 55.15, 24.57. IR (neat): 2990, 2938, 2840, 1715, 1607, 1572, 1515, 1457, 1423, 1362, 1307, 1281, 1252, 1215, 1166, 1112, 1078, 1026, 1010, 978, 945, 884, 836, 817, 793, 771, 728, 697, 655 $cm^{-1}$; HRMS (ESI) calcd for $C_{11}H_{14}NO_3$ $[M+H]^+$: 208.0968, found 208.0970.



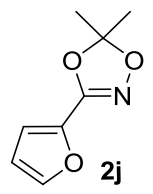

**2h**

**5,5-Dimethyl-3-(*o*-tolyl)-1,4,2-dioxazole (2h).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a colorless oil in 90% overall yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.70-7.68 (m, 1H), 7.38-7.34 (m, 1H), 7.28-7.23 (m, 2H), 2.57 (s, 3H), 1.68 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.54, 138.49, 131.27, 130.71, 128.58, 125.71, 122.61, 114.09, 24.76, 22.23. IR (neat): 2990, 2926, 2866, 1723, 1611, 1597, 1496, 1455, 1375, 1342, 1286, 1253, 1217, 1170, 1130, 1062, 1050, 978, 946, 886, 823, 764, 741, 720, 679, 659 $cm^{-1}$; HRMS (ESI) calcd for $C_{11}H_{14}NO_2$ $[M+H]^+$: 192.1019, found 192.1019.



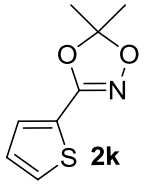

**2i**

**3-(6-Chloropyridin-3-yl)-5,5-dimethyl-1,4,2-dioxazole (2i).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a light yellow solid in 52% overall yield. M.p. 95-96 $^{o}$C $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.76 (d, *J* = 2.0 Hz, 1H), 8.03 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 1.71 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 155.62, 153.87, 147.58, 136.34, 124.29, 119.09, 116.75, 24.82. IR (neat): 3059, 2993, 1727, 1621, 1587, 1553, 1458, 1387, 1375, 1345, 1288, 1219, 1171, 1136, 1108, 1078, 1015, 979, 947, 904, 837, 827, 807, 758, 736, 703, 656 $cm^{-1}$; HRMS (ESI) calcd for $C_9H_{10}ClN_2O_2$ $[M+H]^+$: 213.0425, found 213.0427.



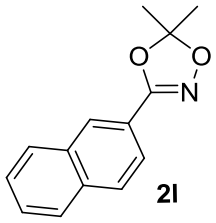

**2j**

**3-(Furan-2-yl)-5,5-dimethyl-1,4,2-dioxazole (2j).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a yellow oil in 59% overall yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.56 (d, *J* = 0.4 Hz, 1H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.52 (dd, *J* = 3.2, 1.6 Hz, 1H), 1.68 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 151.75, 145.19, 138.68, 115.95, 113.61, 111.51, 24.50. IR (neat): 2993, 1660, 1621, 1589, 1498, 1465, 1376, 1343, 1305, 1218, 1170, 1141, 1110, 1083, 1019, 979, 948, 895, 852, 813, 758, 739, 656 cm$^{-1}$; HRMS (ESI) calcd for $C_8H_{10}NO_3$ [M+H]$^+$: 168.0655, found 168.0655.



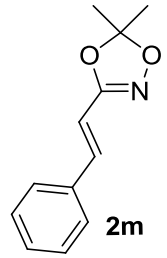
**2k**

**5,5-Dimethyl-3-(thiophen-2-yl)-1,4,2-dioxazole (2k).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a light yellow oil in 67% overall yield. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.50 (dd, *J* = 4.0, 0.8 Hz, 1H), 7.46 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.08 (dd, *J* = 4.8, 4.0 Hz, 1H), 1.68 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 154.84, 129.32, 129.23, 127.45, 124.42, 115.86, 24.58. IR (neat): 2993, 1651, 1620, 1589, 1553, 1528, 1460, 1417, 1375, 1345, 1418, 1170, 1136, 1109, 1080, 1059, 1016, 978, 948, 904, 837, 808, 758, 737, 697, 656 cm$^{-1}$; HRMS (ESI) calcd for $C_8H_{10}NO_2S$ [M+H]$^+$: 184.0427, found 184.0427.



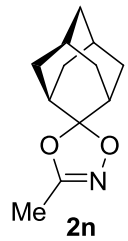
**2l**

**5,5-Dimethyl-3-(naphthalen-2-yl)-1,4,2-dioxazole (2l).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a white solid in 96% overall yield. M.p. 90-92 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.22 (d, *J* = 0.4 Hz, 1H), 7.89-7.80 (m, 4H), 7.54-7.47 (m, 2H), 1.72 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.32, 134.41, 132.54, 128.54, 128.38, 127.76, 127.52, 126.84, 126.74, 123.02, 120.83, 115.60, 24.82. IR (neat): 3059, 2989, 2936, 1713, 1615, 1592, 1569, 1510, 1474, 1453, 1393, 1373, 1355, 1253, 1215, 1197, 1166, 1129, 1069, 981, 962, 937, 927, 897, 864, 852, 823, 815, 780, 746, 680, 663 cm$^{-1}$; HRMS (ESI) calcd for $C_{14}H_{14}NO_2$ [M+H]$^+$: 228.1019, found 228.1020.



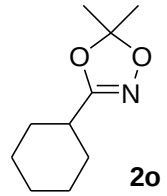
**2m**

**(*E*)-5,5-Dimethyl-3-styryl-1,4,2-dioxazole (2m).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a white solid in 81% overall yield. M.p. 68-70 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.47-7.44 (m, 2H), 7.38-7.31 (m, 3H), 7.17 (d, *J* = 16.4 Hz, 1H), 6.60 (d, *J* = 16.4 Hz, 1H), 1.65 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.33, 137.55, 134.82, 129.39, 128.76, 127.17, 115.26, 109.31, 24.71. IR (neat): 3062, 3030, 2990, 2937, 1717, 1641, 1583, 1571, 1496, 1450, 1372, 1216, 1155, 1074, 1002, 964, 894, 868, 837, 815, 751, 691 cm$^{-1}$; HRMS (ESI) calcd for $C_{12}H_{14}NO_2$ $[M+H]^+$: 204.1019, found 204.1021.



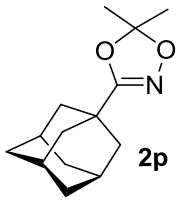
**2n**

**(*1r,3r,5r,7r*)-3'-Methylspiro[adamantane-2,5'-[1,4,2]dioxazole] (2n).** The reaction was carried out using *N*-hydroxyacetamide, (1*r*,3*r*,5*r*,7*r*)-2,2-dimethoxyadamantane (1.0 equiv) and L(-)-Camphorsulfonic acid in DCM. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a white solid in 76% (785 mg) yield. M.p. 77-79 $^{o}$C $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 2.09 (s, 2H), 2.04-1.94 (m, 7H), 1.85-1.83 (m, 2H), 1.79-1.72 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.54, 118.05, 36.66, 36.04, 34.58, 34.24, 26.56, 26.31, 9.65. IR (neat): 2908, 2855, 1719, 1697, 1673, 1652, 1452, 1392, 1352, 1311, 1290, 1299, 1276, 1233, 1113, 1086, 1057, 1021, 997, 953, 918, 874, 795, 701, 676, 656 cm$^{-1}$; HRMS (ESI) calcd for $C_{12}H_{18}NO_2$ $[M+H]^+$: 208.1332, found 208.1332.



**2o**

**3-Cyclohexyl-5,5-dimethyl-1,4,2-dioxazole (2o).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a colorless oil in 47% overall yield. $^1$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 2.40-2.33 (m, 1H), 1.93-1.89 (m, 2H), 1.80-1.76 (m, 2H), 1.69-1.65 (m, 1H), 1.54 (s, 6H), 1.49-1.40 (m, 2H), 1.36-1.23 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 163.14, 113.70, 33.60, 28.81, 25.47, 25.09, 24.35. IR (neat): 2989, 2932, 2856, 1633, 1452, 1452, 1373, 1337, 1216, 1155, 1021, 1007, 989, 955, 895, 872, 859, 819, 754, 733 cm$^{-1}$; HRMS (ESI) calcd for $C_{10}H_{18}NO_2$ $[M+H]^+$: 184.1332, found 184.1333.

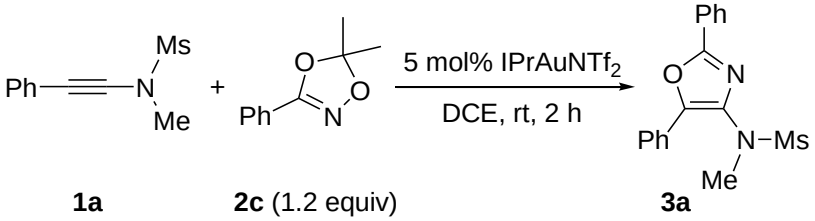



**2p**

**3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-5,5-dimethyl-1,4,2-dioxazole (2p).** Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product as a light yellow solid in 84% overall yield. M.p. 73-75 $^o$C. $^1$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 2.03 (m, 3H), 1.89 (d, *J* = 2.8 Hz, 6H), 1.78-1.70 (m, 6H), 1.54 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 166.05, 113.82, 38.72, 36.36, 32.91, 27.57, 24.44. IR (neat): 2989, 2904, 2851, 1728, 1626, 1453, 1372, 1342, 1301, 1217, 1187, 1164, 1103, 1079, 1059, 995, 974, 951, 865, 821, 737, 685 cm$^{-1}$; HRMS (ESI) calcd for $C_{14}H_{22}NO_2$ $[M+H]^+$: 236.1645, found 236.1650.

**Synthesis of oxazoles 3.**

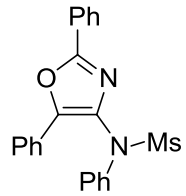
**Typical procedure for the synthesis of *N*-(2,5-Diphenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3a).**




**1a** **2c** (1.2 equiv) **3a**

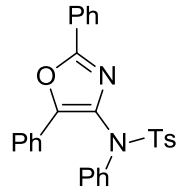
To a solution of 5,5-dimethyl-3-phenyl-1,4,2-dioxazole **2c** (63.8 mg, 0.36 mmol) and ynamide **1a** (62.8 mg, 0.3 mmol) in DCE (3 mL) was added $IPrAuNTf_2$ (13.0 mg, 0.015 mmol). After the reaction mixture was stirred at room temperature for 2 h, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to afford **3a** (93.7 mg, 95%) as a white solid. M.p. 175-177 $^o$C. $^1$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.08-8.06 (m, 2H), 8.02 (d, *J* = 8.0 Hz, 2H),

7.50-7.45 (m, 5H), 7.39-7.36 (m, 1H), 3.33 (s, 3H), 3.21 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.32, 145.29, 134.68, 130.79, 128.97, 128.81, 128.79, 126.84, 126.78, 126.23, 125.24, 37.92, 36.86. IR (neat): 3018, 2934, 1616, 1600, 1556, 1494, 1447, 1412, 1364, 1339, 1328, 1283, 1237, 1189, 1154, 1145, 1075, 1065, 1033, 1024, 1003, 994, 972, 965, 948, 928, 848, 783, 764, 732, 703, 694, 676 cm$^{-1}$; HRMS (ESI) calcd for $C_{17}H_{17}N_2O_3S$ $[M+H]^+$: 329.0954, found 329.0956.




**3b**

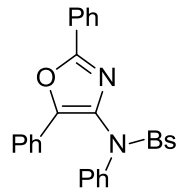
***N*-(2,5-Diphenyloxazol-4-yl)-*N*-phenylmethanesulfonamide (3b).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 81.4 mg **1b**, 3 mL DCE, 13.0 mg IPrAuNTf$_2$ were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:1) afforded the title product as a white solid in 96% (112.6 mg) isolated yield. M.p. 195-197 $^o$C. $^1$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.12-8.11 (m, 2H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.49 (m, 3H), 7.45-7.41 (m, 2H), 7.38-7.33 (m, 3H), 7.31-7.26 (m, 1H), 3.33 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.19, 145.86, 139.99, 134.13, 130.82, 129.31, 128.99, 128.80, 128.75, 127.75, 126.85, 126.60, 126.32, 125.31, 38.58. IR (neat): 3027, 2924, 2850, 1616, 1596, 1554, 1487, 1448, 1405, 1365, 1350, 1239, 1204, 1163, 1152, 1141, 1092, 1068, 1026, 1015, 965, 951, 927, 910, 833, 784, 762, 726, 710, 693 cm$^{-1}$; HRMS (ESI) calcd for $C_{22}H_{19}N_2O_3S$ $[M+H]^+$: 391.1111, found 391.1111.




**3c**

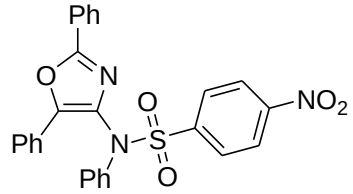
***N*-(2,5-Diphenyloxazol-4-yl)-4-methyl-*N*-phenylbenzenesulfonamide (3c).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 104.2 mg **1c**, 3 mL DCE, 13.0 mg IPrAuNTf$_2$ were stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 15:1) afforded the title product as a white solid in 72% (101.1 mg) isolated yield. M.p. 188-190 $^o$C. $^1$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.09 (d, *J* = 7.6 Hz,

2H), 8.05-8.03 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.53-7.46 (m, 7H), 7.38-7.34 (m, 1H), 7.27-7.20 (m, 5H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.85, 146.45, 143.89, 139.83, 135.35, 134.38, 130.61, 129.14, 128.97, 128.93, 128.79, 127.52, 127.40, 127.19, 126.93, 126.25, 125.42, 21.64. IR (neat): 3055, 2928, 2854, 1614, 1596, 1553, 1495, 1484, 1447, 1371, 1342, 1248, 1211, 1186, 1159, 1092, 1069, 1024, 1016, 954, 912, 847, 812, 777, 756, 726, 715, 701, 686, 666 cm$^{-1}$; HRMS (ESI) calcd for $C_{28}H_{23}N_2O_3S$ $[M+H]^+$: 467.1424, found 467.1424.




**3d**

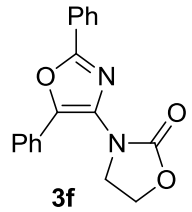
**4-Bromo-*N*-(2,5-diphenyloxazol-4-yl)-*N*-phenylbenzenesulfonamide (3d).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 123.7 mg **1d**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:1) afforded the title product as a white solid in 86% (137.3 mg) isolated yield. M.p. 226-228 $^{o}$C. $^1$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.07-8.02 (m, 4H), 7.69-7.46 (m, 10H), 7.36-7.26 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.93, 146.43, 139.43, 137.19, 134.01, 131.56, 130.72, 130.62, 129.06, 128.80, 128.25, 127.85, 127.41, 126.92, 126.69, 126.17, 125.36. IR (neat): 3082, 2966, 1615, 1596, 1575, 1553, 1485, 1447, 1391, 1371, 1360, 1346, 1326, 1281, 1246, 1210, 1183, 1169, 1159, 1147, 1089, 1067, 1010, 947, 915, 833, 821, 777, 764, 741, 700, 688, 676, 651 cm$^{-1}$; HRMS (ESI) calcd for $C_{27}H_{20}BrN_2O_3S$ $[M+H]^+$: 531.0373, found 531.0370.




**3e**

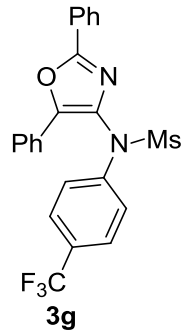
***N*-(2,5-Diphenyloxazol-4-yl)-4-nitro-*N*-phenylbenzenesulfonamide (3e).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 113.5 mg **1e**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:1) afforded the title product as a yellow

solid in 77% (115.3 mg) isolated yield. M.p. 248-250 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.34-8.31 (m, 2H), 8.06-8.04 (m, 2H), 8.02-7.99 (m, 4H), 7.52-7.48 (m, 7H), 7.42-7.38 (m, 1H), 7.32-7.26 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.18, 150.36, 146.62, 143.82, 139.10, 133.67, 130.98, 130.48, 129.32, 129.30, 128.96, 128.93, 128.28, 127.40, 126.82, 126.55, 126.22, 125.45, 123.50. IR (neat): 3110, 3066, 3034, 1611, 1588, 1551, 1526, 1486, 1448, 1404, 1370, 1349, 1325, 1310, 1244, 1209, 1170, 1144, 1089, 1071, 1015, 950, 916, 857, 778, 765, 747, 739, 701, 690, 683, 652 cm$^{-1}$; HRMS (ESI) calcd for $C_{27}H_{20}N_3O_5S$ $[M+H]^+$: 498.1118, found 498.1116.



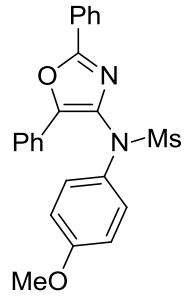
**3f**

**3-(2,5-Diphenyloxazol-4-yl)oxazolidin-2-one (3f).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 56.2 mg **1f**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 89% (82.1 mg) isolated yield. M.p. 206-208 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.07-8.05 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.47-7.43 (m, 5H), 7.37-7.34 (m, 1H), 4.57 (t, *J* = 7.6 Hz, 2H), 4.10 (t, *J* = 8.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.62, 156.23, 143.44, 131.26, 130.73, 128.77, 128.69, 127.01, 126.76, 126.23, 125.19, 62.87, 46.02. IR (neat): 3058, 2924, 2850, 1753, 1619, 1598, 1557, 1485, 1452, 1445, 1406, 1330, 1242, 1212, 1160, 1123, 1094, 1071, 1042, 1027, 977, 953, 934, 920, 839, 776, 765, 749, 704, 696, 688, 676 cm$^{-1}$; HRMS (ESI) calcd for $C_{18}H_{15}N_2O_3$ $[M+H]^+$: 307.1077, found 307.1079.



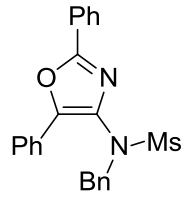
**3g**

***N*-(2,5-Diphenyloxazol-4-yl)-*N*-(4-(trifluoromethyl)phenyl)methanesulfonamide (3g).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 101.8 mg **1g**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 96% (131.6 mg) isolated yield. M.p. 175-177 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.14-8.12 (m, 2H), 7.96-7.94 (m, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.51-7.50 (m, 3H), 7.46-7.42 (m, 2H), 7.37-7.33 (m, 1H), 3.34 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.57, 146.34, 143.12, 133.24, 131.05, 129.30, 129.27 (q, $^2J_{C-F}$ = 32.7 Hz), 128.88, 126.65, 126.47 (q, $^3J_{C-F}$ = 3.8 Hz), 126.37, 126.29, 126.14, 125.26, 123.68 (q, $^1J_{C-F}$ = 271 Hz), 39.00. IR (neat): 3078, 3030, 2930, 1613, 1554, 1513, 1488, 1447, 1419, 1365, 1352, 1325, 1249, 1213, 1186, 1162, 1144, 1121, 1113, 1092, 1069, 1026, 1015, 980, 968, 926, 895, 858, 843, 835, 782, 768, 760, 723, 709, 700, 688, 669 $cm^{-1}$; HRMS (ESI) calcd for $C_{23}H_{18}F_3N_2O_3S$ $[M+H]^+$: 459.0985, found 459.0986.



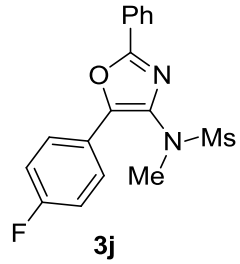
**3h**

***N*-(2,5-Diphenyloxazol-4-yl)-*N*-(4-methoxyphenyl)methanesulfonamide (3h).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 90.4 mg **1h**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1 to 3:1) afforded the title product as a white solid in 99% (125.1 mg) isolated yield. M.p. 191-193 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.12-8.09 (m, 2H), 8.02-8.00 (m, 2H), 7.67 (d, *J* = 9.6 Hz, 2H), 7.50-7.41 (m, 5H), 7.34-7.31 (m, 1H), 6.88 (d, *J* = 9.2 Hz, 2H), 3.74 (s, 3H), 3.32 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 159.06, 158.07, 145.49, 134.44, 132.57, 130.74, 128.90, 128.75, 128.69, 128.63, 126.83, 126.64, 126.24, 125.26, 114.40, 55.33, 38.20. IR (neat): 3014, 2924, 2850, 1616, 1604, 1556, 1505, 1486, 1468, 1448, 1366, 1346, 1323, 1293, 1243, 1211, 1164, 1154, 1108, 1071, 1030, 1015, 978, 953, 928, 839, 831, 794, 780, 757, 717, 698, 688 $cm^{-1}$; HRMS (ESI) calcd for $C_{23}H_{21}N_2O_4S$ $[M+H]^+$: 421.1217, found 421.1218.




**3i**

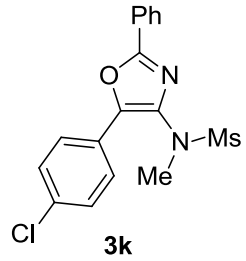
***N*-Benzyl-*N*-(2,5-diphenyloxazol-4-yl)methanesulfonamide (3i).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 85.6 mg **1i**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 6:1) afforded the title product as a white solid in 85% (103.1 mg) isolated yield. M.p. 154-156 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.06-8.03 (m, 2H), 7.76-7.74 (m, 2H), 7.48-7.45 (m, 3H), 7.32-7.22 (m, 5H), 7.12-7.08 (m, 3H), 4.81 (s, 2H), 3.19 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.24, 147.16, 134.53, 132.61, 130.71, 129.31, 128.81, 128.78, 128.27, 128.19, 128.00, 126.90, 126.41, 126.21, 125.45, 54.74, 38.38. IR (neat): 3002, 2926, 2850, 1620, 1556, 1496, 1487, 1460, 1448, 1391, 1356, 1346, 1320, 1221, 1156, 1089, 1069, 1054, 1037, 1024, 959, 925, 915, 856, 821, 774, 757, 730, 701, 687 $cm^{-1}$; HRMS (ESI) calcd for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$: 405.1267, found 405.1269.




**3j**

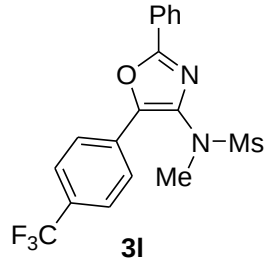
***N*-(5-(4-fluorophenyl)-2-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3j).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 68.2 mg **1j**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 6:1) afforded the title product as a white solid in 89% (92.1 mg) isolated yield. M.p. 182-184 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.06-7.99 (m, 4H), 7.49-7.47 (m, 3H), 7.17-7.12 (m, 2H), 3.32 (s, 3H), 3.19 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 162.86 (d, $^{1}J_{C\text{-}F}$ = 248.6 Hz), 158.28, 144.59, 134.29 (d, $^{5}J_{C\text{-}F}$ = 1.9 Hz), 130.84, 128.82, 127.33 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 126.71, 126.21, 123.10 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 115.92 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 37.89, 36.66. IR (neat): 3030, 3006, 2926, 2854, 1626, 1604, 1591, 1556, 1509, 1487, 1448, 1415, 1367, 1339, 1325, 1304, 1232, 1190, 1160, 1151, 1089, 1065, 1023,

1004, 973, 947, 930, 859, 839, 811, 776, 765, 739, 715, 694 $cm^{-1}$; HRMS (ESI) calcd for $C_{17}H_{16}FN_2O_3S$ $[M+H]^+$: 347.0860, found 347.0862.




**3k**

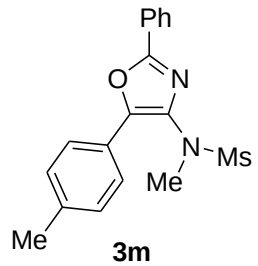
***N*-(5-(4-Chlorophenyl)-2-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3k).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 73.1 mg **1k**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 85% (92.5 mg) isolated yield. M.p. 184-186 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.06-8.03 (m, 2H), 7.95-7.93 (m, 2H), 7.49-7.47 (m, 3H), 7.42-7.40 (m, 2H), 3.32 (s, 3H), 3.19 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.51, 144.35, 134.96, 134.74, 130.93, 129.00, 128.82, 126.60, 126.47, 126.25, 125.25, 37.85, 36.65. IR (neat): 3006, 2925, 2850, 1622, 1563, 1491, 1452, 1405, 1365, 1341, 1320, 1288, 1245, 1183, 1155, 1094, 1067, 1013, 998, 974, 964, 950, 929, 854, 826, 780, 767, 735, 714, 692 $cm^{-1}$; HRMS (ESI) calcd for $C_{17}H_{16}ClN_2O_3S$ $[M+H]^+$: 363.0565, found 363.0566.




**3l**

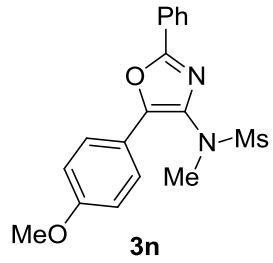
***N*-Methyl-*N*-(2-phenyl-5-(4-(trifluoromethyl)phenyl)oxazol-4-yl)methanesulfonamide (3l).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 83.2 mg **1l**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 9 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 83% (99.2 mg) isolated yield. M.p. 162-164 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.13 (d, $J$ = 8.4 Hz, 2H), 8.09-8.07 (m, 2H), 7.70 (d, $J$ = 8.4 Hz, 2H), 7.51-7.50 (m, 3H), 3.35 (s, 3H), 3.20 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 159.20, 143.88, 136.30, 131.21, 130.34 (q, $^2J_{C-F}$ = 32.6 Hz), 130.04 (q, $^5J_{C-F}$ = 1.5 Hz), 128.90, 126.43, 126.40, 125.73 (q, $^3J_{C-F}$ = 3.8 Hz),

125.32, 123.84 (q, $^1J_{C\text{-}F}$ = 271 Hz), 37.85, 36.63. IR (neat): 3074, 2934, 1620, 1552, 1485, 1449, 1413, 1369, 1346, 1322, 1254, 1163, 1146, 1006, 1066, 1013, 1002, 959, 928, 847, 779, 764, 747, 728, 702, 692, 684 $cm^{-1}$; HRMS (ESI) calcd for $C_{18}H_{16}F_3N_2O_3S$ $[M+H]^+$: 397.0828, found 397.0830.




**3m**

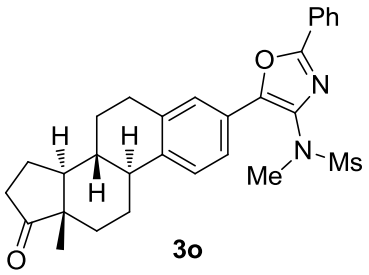
***N*-Methyl-*N*-(2-phenyl-5-(*p*-tolyl)oxazol-4-yl)methanesulfonamide (3m).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 67.0 mg **1m**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 88% (90.8 mg) isolated yield. M.p. 157-159 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.06-8.03 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.48-7.45 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.31 (s, 3H), 3.19 (s, 3H), 2.37 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.94, 145.50, 139.07, 134.00, 130.61, 129.44, 128.74, 126.89, 126.13, 125.17, 123.99, 37.85, 36.80, 21.36. IR (neat): 3026, 2932, 2850, 1606, 1555, 1509, 1486, 1451, 1409, 1367, 1338, 1241, 1202, 1184, 1153, 1098, 1063, 1025, 999, 972, 857, 840, 820, 784, 762, 735, 714, 704, 693 $cm^{-1}$; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_3S$ $[M+H]^+$: 343.1111, found 343.1113.




**3n**

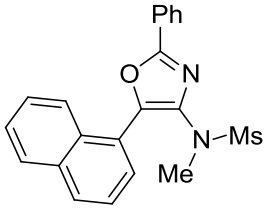
***N*-(5-(4-Methoxyphenyl)-2-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3n).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 71.8 mg **1n**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 50 $^oC$ for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 3:1) afforded the title product as a white solid in 71% (76.5 mg) isolated yield. M.p. 203-205 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.05-8.03 (m, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.48-7.46 (m, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.31 (s, 3H), 3.19

(s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 160.12, 157.68, 145.52, 133.17, 130.56, 128.78, 127.01, 126.91, 126.11, 119.55, 114.26, 55.29, 37.94, 36.78. IR (neat): 3078, 3013, 2922, 2847, 1621, 1607, 1573, 1556, 1510, 1487, 1449, 1429, 1370, 1343, 1332, 1298, 1283, 1254, 1188, 1175, 1166, 1146, 1117, 1093, 1067, 1029, 993, 953, 919, 853, 831, 796, 777, 764, 736, 717, 694, 686 cm$^{-1}$; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_4S$ $[M+H]^+$: 359.1060, found 359.1061.



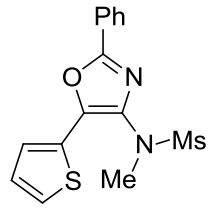

**3o**

***N*-Methyl-*N*-(5-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl)-2-phenyloxazol-4-yl)methanesulfonamide (3o).** 0.3 mmol scale. Following the typical procedure, 63.8 mg 5,5-dimethyl-3-phenyl-1,4,2-dioxazole **2c**, 115.7 mg **1o**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^{o}$C for 2 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: chloromethane = 2:1:1) afforded the title product as a white solid in 97% (146.7 mg) isolated yield. M.p. 214-216 $^{o}$C. $^1$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.07-8.05 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.48-7.47 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 1H), 3.32 (s, 3H), 3.20 (s, 3H), 3.00-2.96 (m, 2H), 2.50 (dd, *J* = 18.8, 8.8 Hz, 1H), 2.44-2.40 (m, 1H), 2.33-2.28 (m, 1H), 2.16-1.96 (m, 4H), 1.66-1.44 (m, 6H), 0.91 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 220.66, 157.95, 145.30, 140.82, 136.87, 134.15, 130.60, 128.71, 126.79, 126.08, 125.73, 125.50, 124.20, 122.70, 50.29, 47.77, 44.30, 37.81, 37.76, 36.73, 35.68, 31.38, 29.33, 26.20, 25.39, 21.41, 13.67. IR (neat): 3009, 2930, 2854, 2242, 1733, 1622, 1557, 1501, 1450, 1407, 1374, 1344, 1260, 1155, 1085, 1054, 1008, 963, 890, 869, 840, 822, 776, 762, 735, 713, 699, 688 cm$^{-1}$; HRMS (ESI) calcd for $C_{29}H_{33}N_2O_4S$ $[M+H]^+$: 505.2156, found 505.2153.



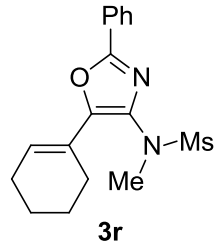

**3p**

***N*-Methyl-*N*-(5-(naphthalen-1-yl)-2-phenyloxazol-4-yl)methanesulfonamide (3p).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 77.8 mg **1p**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 88% (100.2 mg) isolated yield. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.13-8.07 (m, 3H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.94-7.88 (m, 2H), 7.58-7.50 (m, 3H), 7.47-7.45 (m, 3H), 3.194 (s, 3H), 3.188 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 159.24, 145.34, 137.05, 133.64, 131.00, 130.79, 130.41, 128.85, 128.82, 128.56, 126.95, 126.92, 126.22, 126.15, 125.32, 125.07, 123.62, 38.17, 37.45. IR (neat): 3050, 3006, 2930, 1701, 1612, 1591, 1558, 1508, 1487, 1449, 1401, 1343, 1324, 1270, 1241, 1152, 1050, 1024, 958, 859, 803, 775, 760, 733, 712, 690 $cm^{-1}$; HRMS (ESI) calcd for $C_{21}H_{19}N_2O_3S$ $[M+H]^+$: 379.1111, found 379.1113.



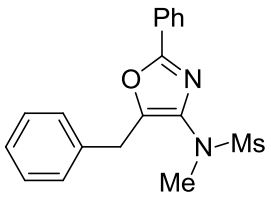

**3q**

***N*-Methyl-*N*-(2-phenyl-5-(thiophen-2-yl)oxazol-4-yl)methanesulfonamide (3q).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 64.6 mg **1q**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:0 to 3:1:1) afforded the title product as a yellow solid in 94% (94.4 mg) isolated yield. M.p. 198-200 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.04 (s, 2H), 7.64 (s, 1H), 7.47-7.40 (m, 4H), 7.11 (s, 1H), 3.32 (s, 3H), 3.18 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.97, 142.56, 133.19, 130.78, 128.80, 127.71, 127.64, 127.00, 126.64, 126.22, 125.90, 37.63, 36.81. IR (neat): 3018, 2926, 1625, 1552, 1489, 1452, 1435, 1363, 1342, 1317, 1243, 1227, 1178, 1156, 1142, 4087, 1072, 1059, 1038, 1020, 961, 856, 940, 781, 763, 701, 691 $cm^{-1}$; HRMS (ESI) calcd for $C_{15}H_{15}N_2O_3S_2$ $[M+H]^+$: 335.0519, found 335.0520.



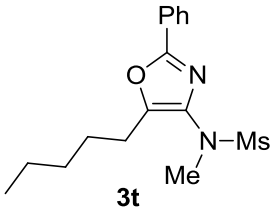

**3r**

***N*-(5-(Cyclohex-1-en-1-yl)-2-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3r).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 64.0 mg **1r**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 50 $^oC$ for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 50% (49.9 mg) isolated yield. M.p. 198-200 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.98-7.96 (m, 2H), 7.45-7.44 (m, 3H), 6.62-6.60 (m, 1H), 3.26 (s, 3H), 3.14 (s, 3H), 2.55-2.54 (m, 2H), 2.27-2.25 (m, 2H), 1.79-1.73 (m, 2H), 1.69-1.64 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.38, 147.02, 133.00, 130.45, 128.72, 128.55, 127.13, 126.07, 124.95, 38.27, 36.71, 25.52, 24.41, 22.14, 21.67. IR (neat): 3018, 2933, 2874, 2826, 1637, 1587, 1556, 1490, 1447, 1432, 1393, 1338, 1326, 1287, 1226, 1161, 1150, 1087, 1064, 1050, 1024, 984, 966, 929, 908, 853, 835, 809, 782, 764, 729, 705, 691 $cm^{-1}$; HRMS (ESI) calcd for $C_{17}H_{21}N_2O_3S$ $[M+H]^+$: 333.1267, found 333.1270.



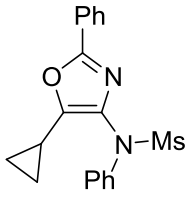

**3s**

***N*-(5-Benzyl-2-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3s).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 67.0 mg **1s**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a colorless liquid in 70% (72.0 mg) isolated yield. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.94-7.92 (m, 2H), 7.44-7.40 (m, 3H), 7.33-7.30 (m, 4H), 7.28-7.22 (m, 1H), 4.15 (s, 2H), 3.25 (s, 3H), 3.06 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.93, 147.38, 136.48, 135.26, 130.52, 128.79, 128.71, 128.63, 127.08, 126.82, 126.08, 37.92, 36.12, 30.54. IR (neat): 3058, 3017, 2918, 2846, 1640, 1601, 1557, 1496, 1488, 1472, 1449, 1426, 1360, 1335, 1236, 1182, 1148, 1122, 1074, 1065, 1045, 1026, 979, 966, 919, 898, 866, 789, 777, 760, 719, 696, 688, 669 $cm^{-1}$; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_3S$ $[M+H]^+$: 343.1111, found 343.1114.



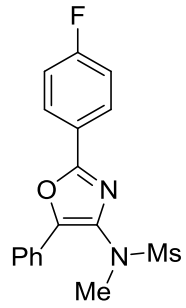

**3t**

***N*-Methyl-*N*-(5-pentyl-2-phenyloxazol-4-yl)methanesulfonamide (3t).** Following the typical procedure, 0.3 mmol scale, 63.8 mg **2c**, 61.0 mg **1t**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product as a colorless oil in 30% (29 mg) yield. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.98-7.95 (m, 2H), 7.45-7.43 (m, 3H), 3.27 (s, 3H), 3.03 (s, 3H), 2.78 (t, *J* = 7.2 Hz, 2H), 1.74-1.68 (m, 2H), 1.40-1.36 (m, 4H), 0.93-0.90 (m, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.32, 149.52, 134.60, 130.32, 128.72, 127.34, 125.96, 37.94, 36.02, 31.35, 27.10, 24.27, 22.27, 13.93. IR (neat): 2954, 2929, 2859, 1640, 1559, 1488, 1450, 1345, 1192, 1150, 1066, 1042, 1025, 962, 861, 775, 724, 691, 675 $cm^{-1}$; HRMS (ESI) calcd for $C_{16}H_{23}N_2O_3S[M+H]^+$: 323.1424, found 323.1427.



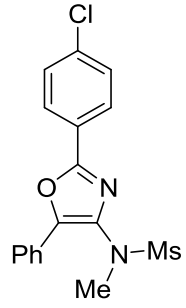

**3u**

***N*-(5-Cyclopropyl-2-phenyloxazol-4-yl)-*N*-phenylmethanesulfonamide (3u).** 0.3 mmol scale. Following the typical procedure, 63.8 mg **2c**, 70.6 mg **1u**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 2 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 89% (94.8 mg) isolated yield. M.p. 127-129 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.98-7.95 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.44-7.36 (m, 5H), 7.32-7.28 (m, 1H), 3.24 (s, 3H), 2.06-1.99 (m, 1H), 1.03-0.99 (m, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.05, 150.13, 140.59, 133.93, 130.24, 129.21, 128.63, 127.58, 127.17, 127.11, 125.89, 38.44, 6.90, 5.81. IR (neat): 3050, 3018, 2928, 2850, 1639, 1595, 1557, 1485, 1450, 1410, 1394, 1347, 1327, 1284, 1246, 1207, 1164, 1150, 1115, 1096, 1072, 1057, 1047, 1030, 1006, 964, 949, 912, 904, 870, 846, 816, 788, 771, 761, 724, 710, 699, 685 $cm^{-1}$; HRMS (ESI) calcd for $C_{19}H_{19}N_2O_3S$ $[M+H]^+$: 355.1111, found 355.1112.




**3v**

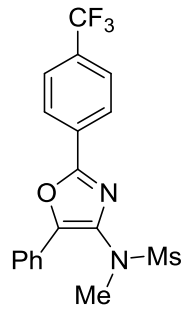
***N*-(2-(4-Fluorophenyl)-5-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3v).** 0.3 mmol scale. Following the typical procedure, 70.3 mg 3-(4-fluorophenyl)-5,5-dimethyl-1,4,2-dioxazole **2d**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:0 to 3:1:1) afforded the title product as a white solid in 90% (93.1 mg) isolated yield. M.p. 188-190 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.06-8.03 (m, 2H), 7.99 (d, $J$ = 7.6 Hz, 2H), 7.47-7.43 (m, 2H), 7.37-7.33 (m, 1H), 7.18-7.14 (m, 2H), 3.31 (s, 3H), 3.20 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 164.18 (d, $^1J_{C-F}$ = 250.9 Hz), 157.45, 145.31, 134.64, 128.98, 128.75, 128.37 (d, $^3J_{C-F}$ = 8.8 Hz), 126.62, 125.16, 123.18 (d, $^4J_{C-F}$ = 3.0 Hz), 116.02 (d, $^2J_{C-F}$ = 22.4 Hz), 37.83, 36.83. IR (neat): 3066, 3021, 2933, 1611, 1600, 1501, 1463, 1453, 1416, 1365, 1338, 1325, 1286, 1228, 1188, 1154, 1144, 1101, 1090, 1062, 1033, 1012, 994, 973, 961, 951, 927, 853, 815, 764, 746, 721, 696 $cm^{-1}$; HRMS (ESI) calcd for $C_{17}H_{16}FN_2O_3S$ $[M+H]^+$: 347.0860, found 347.0861.




**3w**

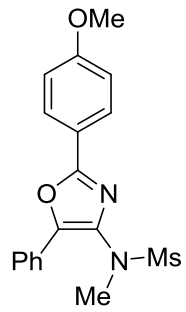
***N*-(2-(4-Chlorophenyl)-5-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3w).** 0.3 mmol scale. Following the typical procedure, 76.2 mg 3-(4-chlorophenyl)-5,5-dimethyl-1,4,2-dioxazole **2e**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:1) afforded the title product as a white solid in 93% (101.6 mg) isolated yield. M.p. 215-217 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.00 (m, 4H), 7.46-7.37 (m, 5H), 3.32 (s, 3H),

3.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.36, 145.57, 136.88, 134.76, 129.15, 128.81, 127.48, 126.57, 125.32, 125.26, 37.88, 36.89. IR (neat): 3070, 3022, 2933, 1611, 1600, 1501, 1463, 1453, 1416, 1365, 1338, 1325, 1286, 1228, 1188, 1154, 1144, 1101, 1090, 1062, 1033, 1012, 1003, 994, 973, 961, 951, 927, 853, 815, 764, 746, 721, 696 cm$^{-1}$; HRMS (ESI) calcd for $C_{17}H_{16}ClN_2O_3S$ $[M+H]^+$: 363.0565, found 363.0566.



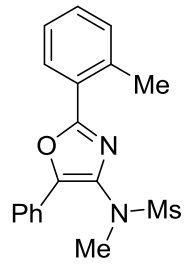

**3x**

***N*-Methyl-*N*-(5-phenyl-2-(4-(trifluoromethyl)phenyl)oxazol-4-yl)methanesulfonamide (3x).** 0.3 mmol scale. Following the typical procedure, 88.3 mg 5,5-dimethyl-3-(4-(trifluoromethyl)phenyl)-1,4,2-dioxazole **2f**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^o$C for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:0 to 3:1:1) afforded the title product as a white solid in 77% (92.1 mg) isolated yield. M.p. 190-192 $^o$C. $^1$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.17 (d, $J$ = 8.4 Hz, 2H), 8.03-8.01 (m, 2H), 7.74 (d, $J$ = 8.4 Hz, 2H), 7.49-7.45 (m, 2H), 7.40-7.37 (m, 1H), 3.33 (s, 3H), 3.21 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 156.82, 146.23, 134.99, 132.23 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 129.96 (q, $^5J_{C\text{-}F}$ = 1.1 Hz), 129.38, 128.87, 126.47, 126.41, 125.84 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.40, 123.71 (q, $^1J_{C\text{-}F}$ = 271.4 Hz), 37.87, 36.89. IR (neat): 3018, 2925, 2850, 1618, 1600, 1563, 1496, 1448, 1415, 1373, 1347, 1322, 1239, 1186, 1156, 1114, 1093, 1070, 1060, 1033, 1016, 1005, 993, 973, 950, 920, 859, 851, 779, 765, 730, 701, 690, 683 cm$^{-1}$; HRMS (ESI) calcd for $C_{18}H_{16}F_3N_2O_3S$ $[M+H]^+$: 397.0828, found 397.0830.



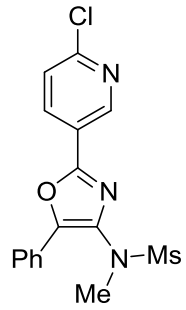

**3y**

***N*-(2-(4-Methoxyphenyl)-5-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3y).** 0.3 mmol scale. Following the typical procedure, 74.6 mg 3-(4-methoxyphenyl)-5,5-dimethyl-1,4,2-dioxazole **2g**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 4 h. Column chromatography on silica gel (wet loading, eluent: petroleum ether: ethyl acetate = 5:1 to petroleum ether: ethyl acetate: dichloromethane = 2:1:1) afforded the title product as a white solid in 92% (98.8 mg) isolated yield. M.p. 199-201 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.99 (d, *J* = 7.2 Hz, 4H), 7.45-7.44 (m, 2H), 7.37-7.35 (d, *J* = 6.8 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 3.87 (s, 3H), 3.32 (s, 3H), 3.21 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 161.68, 158.50, 144.66, 134.57, 128.76, 127.98, 126.96, 125.11, 119.64, 114.24, 55.39, 37.92, 36.90. IR (neat): 3023, 2950, 1615, 1596, 1583, 1500, 1464, 1453, 1439, 1421, 1367, 1342, 1322, 1306, 1284, 1256, 1196, 1175, 1152, 1118, 1100, 1064, 1028, 1004, 997, 972, 965, 909, 858, 834, 806, 798, 772, 762, 743, 721, 691 $cm^{-1}$; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_4S$ $[M+H]^+$: 359.1060, found 359.1062.



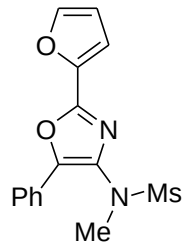

**3z**

***N*-Methyl-*N*-(5-phenyl-2-(*o*-tolyl)oxazol-4-yl)methanesulfonamide (3z).** 0.3 mmol scale. Following the typical procedure, 68.8 mg 5,5-dimethyl-3-(*o*-tolyl)-1,4,2-dioxazole **2h**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 3 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:0 to 3:1:1) afforded the title product as a white solid in 90% (92.0 mg) isolated yield. M.p. 154-156 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.47-7.43 (m, 2H), 7.37-7.29 (m, 4H), 3.32 (s, 3H), 3.20 (s, 3H), 2.72 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.59, 144.66, 137.35, 134.40, 131.74, 130.35, 128.89, 128.76, 128.43, 126.76, 126.04, 125.57, 125.19, 37.93, 36.62, 22.09. IR (neat): 3018, 2924, 2853, 1616, 1596, 1536, 1495, 1462, 1448, 1362, 1342, 1319, 1239, 1181, 1156, 1139, 1091, 1066, 1045, 1033, 1002, 995, 958, 916, 872, 847, 804, 773, 757, 734, 721, 697, 687, 668 $cm^{-1}$; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_3S$ $[M+H]^+$: 343.1111, found 343.1112.




**3za**

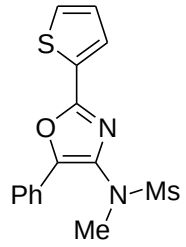
***N*-(2-(6-Chloropyridin-3-yl)-5-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3za).** 0.2 mmol scale. Following the typical procedure, 51.0 mg 3-(6-chloropyridin-3-yl)-5,5-dimethyl-1,4,2-dioxazole **2i**, 41.9 mg **1a**, 2 mL DCE, 8.7 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:1 to 3:1:1) afforded the title product as a white solid in 75% (54.4 mg) isolated yield. M.p. 214-216 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 9.05 (d, *J* = 2.0 Hz, 1H), 8.27 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.50-7.46 (m, 3H), 7.42-7.38 (m, 1H), 3.33 (s, 3H), 3.20 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 155.09, 153.27, 147.47, 146.42, 135.85, 134.95, 129.54, 128.93, 126.18, 125.42, 124.51, 122.10, 37.87, 36.98. IR (neat): 3062, 3006, 2933, 1612, 1600, 1567, 1495, 1463, 1450, 1372, 1343, 1322, 1288, 1236, 1157, 1147, 1130, 1109, 1062, 1032, 1022, 1003, 992, 961, 951, 857, 841, 771, 758, 743, 729, 705, 687 $cm^{-1}$; HRMS (ESI) calcd for $C_{16}H_{15}ClN_3O_3S$ $[M+H]^+$: 364.0517, found 364.0519.




**3zb**

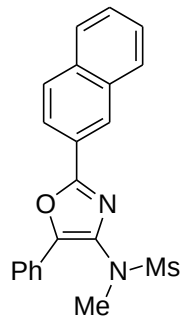
***N*-(2-(Furan-2-yl)-5-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3zb).** 0.3 mmol scale. Following the typical procedure, 60.2 mg 3-(furan-2-yl)-5,5-dimethyl-1,4,2-dioxazole **2j**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 3 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:0 to 3:1:1) afforded the title product as a white solid in 95% (91.0 mg) isolated yield. M.p. 150-152 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.00 (s, 2H), 7.59-7.37 (m, 4H), 7.09 (s, 1H), 6.57 (s, 1H), 3.32 (s, 3H), 3.18 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 151.10, 144.87, 144.84, 142.17, 134.20, 129.07, 128.71, 126.33, 125.21, 112.25, 111.96, 37.72, 36.84. IR (neat):

3118, 3024, 2937, 1638, 1618, 1598, 1528, 1495, 1450, 1410, 1360, 1337, 1234, 1184, 1173, 1153, 1139, 1112, 1072, 1063, 1035, 1014, 1004, 993, 966, 922, 898, 885, 871, 836, 822, 769, 750, 708, 690 $cm^{-1}$; HRMS (ESI) calcd for $C_{15}H_{15}N_2O_4S$ $[M+H]^+$: 319.0747, found 319.0750.




**3zc**

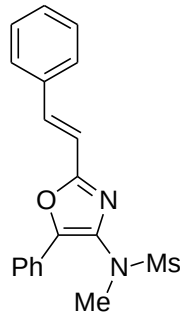
***N*-Methyl-*N*-(5-phenyl-2-(thiophen-2-yl)oxazol-4-yl)methanesulfonamide (3zc).** 0.3 mmol scale. Following the typical procedure, 66.0 mg 5,5-dimethyl-3-(thiophen-2-yl)-1,4,2-dioxazole **2k**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 2 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:1) afforded the title product as a white solid in 95% (95.5 mg) isolated yield. M.p. 156-158 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 2.8 Hz, 1H), 7.46-7.43 (m, 3H), 7.37-7.34 (m, 1H), 7.14-7.11 (m, 1H), 3.30 (s, 3H), 3.18 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 154.60, 144.75, 134.39, 129.27, 128.96, 128.89, 128.74, 128.19, 128.01, 126.52, 125.17, 37.84, 36.88. IR (neat): 3103, 3015, 2937, 2850, 1612, 1572, 1508, 1495, 1448, 1420, 1372, 1348, 1334, 1319, 1274, 1239, 1202, 1174, 1151, 1072, 1051, 1043, 1029, 1003, 990, 973, 955, 924, 851, 834, 773, 760, 730, 705, 686, 660 $cm^{-1}$; HRMS (ESI) calcd for $C_{15}H_{15}N_2O_3S_2$ $[M+H]^+$: 335.0519, found 335.0521.




**3zd**

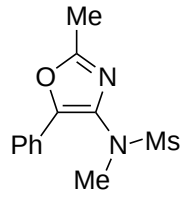
***N*-Methyl-*N*-(2-(naphthalen-2-yl)-5-phenyloxazol-4-yl)methanesulfonamide (3zd).** 0.3 mmol scale. Following the typical procedure, 81.8 mg 5,5-dimethyl-3-(naphthalen-2-yl)-1,4,2-dioxazole **2l**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 2 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane

= 5:1:0 to 2:1:1) afforded the title product as a white solid in 97% (110.3 mg) isolated yield. M.p. 197-199 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.50 (s, 1H), 8.10-8.04 (m, 3H), 7.93-7.88 (m, 2H), 7.84-7.82 (m, 1H), 7.53-7.44 (m, 4H), 7.38-7.34 (m, 1H), 3.34 (s, 3H), 3.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.37, 145.36, 134.79, 134.16, 132.80, 128.95, 128.75, 128.62, 128.59, 127.80, 127.42, 126.83, 126.73, 126.16, 125.23, 124.00, 122.89, 37.88, 36.88. IR (neat): 3052, 2934, 1695, 1614, 1547, 1509, 1494, 1447, 1340, 1327, 1320, 1234, 1178, 1155, 1085, 1072, 1058, 1030, 1005, 995, 966, 937, 916, 900, 892, 862, 835, 824, 766, 754, 732, 710, 687 cm$^{-1}$; HRMS (ESI) calcd for $C_{21}H_{19}N_2O_3S$ $[M+H]^+$: 379.1111, found 379.1112.



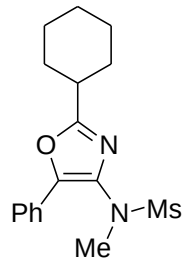

**3ze**

**(*E*)-*N*-Methyl-*N*-(5-phenyl-2-styryloxazol-4-yl)methanesulfonamide (3ze).** 0.3 mmol scale. Following the typical procedure, 73.2 mg (*E*)-5,5-dimethyl-3-styryl-1,4,2-dioxazole **2m**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^{o}$C for 2 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:0 to 2:1:1) afforded the title product as a white solid in 97% (103.2 mg) isolated yield. M.p. 192-194 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.56-7.53 (m, 3H), 7.45-7.32 (m, 6H), 6.87 (d, *J* = 16.4 Hz, 1H), 3.28 (s, 3H), 3.16 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.04, 144.83, 136.74, 135.00, 134.64, 129.37, 128.91, 128.80, 128.67, 127.13, 126.59, 125.17, 113.07, 37.71, 36.70. IR (neat): 3050, 3007, 2926, 2850, 1643, 1621, 1597, 1578, 1535, 1495, 1463, 1448, 1365, 1336, 1321, 1239, 1210, 1180, 1165, 1150, 1070, 1033, 1008, 975, 917, 861, 846, 785, 755, 729, 685 cm$^{-1}$; HRMS (ESI) calcd for $C_{19}H_{19}N_2O_3S$ $[M+H]^+$: 355.1111, found 355.1113.




**3zf**

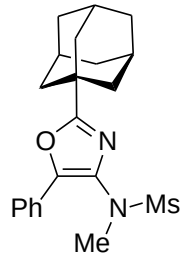
***N*-Methyl-*N*-(2-methyl-5-phenyloxazol-4-yl)methanesulfonamide (3zf).** 0.3 mmol scale. Following the typical procedure, 74.6 mg (1R,3S,5r,7r)-3'-methylspiro[adamantane-2,5'-[1,4,2]dioxazole] **2n**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at room temperature for 10 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 2:1) afforded the title product as a white solid in 71% (56.7 mg) isolated yield. M.p. 140-142 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.44-7.40 (m, 2H), 7.36-7.32 (m, 1H), 3.25 (s, 3H), 3.13 (s, 3H), 2.50 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 158.70, 145.27, 133.02, 128.76, 128.73, 126.80, 125.01, 37.79, 36.81, 14.30. IR (neat): 3004, 2925, 2853, 1627, 1583, 1494, 1450, 1387, 1358, 1336, 1321, 1297, 1275, 1239, 1176, 1149, 1133, 1102, 1067, 1035, 1003, 994, 976, 921, 853, 774, 725, 712, 691, 673, 666 $cm^{-1}$; HRMS (ESI) calcd for $C_{12}H_{15}N_2O_3S$ $[M+H]^+$: 267.0798, found 267.0801.




**3zg**

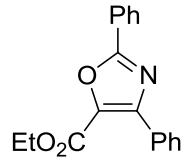
***N*-(2-Cyclohexyl-5-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3zg).** 0.3 mmol scale. Following the typical procedure, 66.0 mg 3-cyclohexyl-5,5-dimethyl-1,4,2-dioxazole **2o**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^{o}$C for 3 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 94% (94.4 mg) isolated yield. M.p. 110-112 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.91-7.89 (m, 2H), 7.43-7.39 (m, 2H), 7.33-7.30 (m, 1H), 3.25 (s, 3H), 3.13 (s, 3H), 2.84-2.76 (m, 1H), 2.12-2.08 (m, 2H), 1.86-1.82 (m, 2H), 1.74-1.71 (m, 1H), 1.66-1.56 (m, 2H), 1.45-1.25 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 165.16, 144.35, 132.76, 128.54, 128.46, 126.94, 124.88, 37.69, 37.53, 36.72, 30.27, 25.52, 25.34. IR (neat): 3010, 2936, 2857, 1626, 1565, 1496, 1470, 1448, 1358, 1341, 1325, 1241, 1201, 1179, 1149, 1077, 1028, 1003, 992,

972, 893, 866, 844, 718, 774, 756, 734, 715, 693 $cm^{-1}$; HRMS (ESI) calcd for $C_{17}H_{23}N_2O_3S$ $[M+H]^+$: 335.1424, found 335.1425.




**3zh**

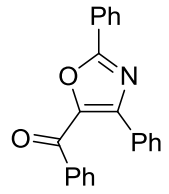
***N*-(2-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-5-phenyloxazol-4-yl)-*N*-methylmethanesulfonamide (3zh).** 0.3 mmol scale. Following the typical procedure, 84.7 mg 3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-5,5-dimethyl-1,4,2-dioxazole **2p**, 62.8 mg **1a**, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 3 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 96% (111.4 mg) isolated yield. M.p. 163-165 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.91-7.89 (m, 2H), 7.43-7.39 (m, 2H), 7.33-7.29 (m, 1H), 3.25 (s, 3H), 3.13 (s, 3H), 2.10 (bs, 3H), 2.07-2.06 (m, 6H), 1.83-1.76 (m, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 167.81, 144.05, 132.84, 128.56, 128.42, 127.14, 124.93, 40.14, 37.78, 36.85, 36.29, 35.75, 27.81. IR (neat): 3018, 2905, 2851, 1626, 1555, 1495, 1449, 1360, 1340, 1325, 1273, 1237, 1152, 1101, 1072, 1004, 994, 969, 954, 865, 834, 772, 760, 714, 690, 677 $cm^{-1}$; HRMS (ESI) calcd for $C_{21}H_{27}N_2O_3S$ $[M+H]^+$: 387.1737, found 387.1739.




**6**

**Ethyl 2,4-diphenyloxazole-5-carboxylate (6).** 0.3 mmol scale. Following the typical procedure, 63.8 mg 5,5-dimethyl-3-phenyl-1,4,2-dioxazole **2c**, 52.3 mg ethyl 3-phenylpropiolate, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 24 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 40:1) afforded the title product as a white solid in 51% (44.8 mg) isolated yield. M.p. 123-125 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.22-8.20 (m, 2H), 8.13-8.11 (m, 2H), 7.54-7.41 (m, 6H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 162.06, 158.63, 147.92, 136.31, 131.53, 130.40, 129.58, 129.40, 128.82, 128.03, 127.33, 126.32, 61.36, 14.19. IR (neat): 3050, 2978, 2924, 2850, 1706, 1608, 1591, 1583, 1566, 1545, 1492, 1481, 1448, 1397, 1375,

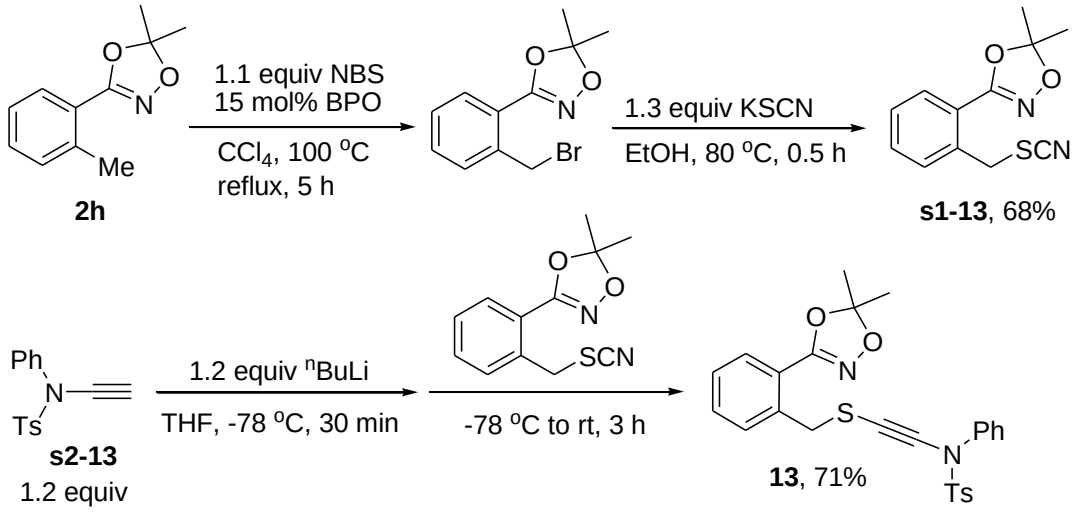
1355, 1317, 1304, 1289, 1244, 1184, 1160, 1138, 1113, 1091, 1072, 1037, 1024, 990, 954, 926, 870, 835, 783, 760, 720, 711, 686, 675 $cm^{-1}$; HRMS (ESI) calcd for $C_{18}H_{16}NO_3$ $[M+H]^+$: 294.1125, found 294.1126.



**7**

**(2,4-Diphenyloxazol-5-yl)(phenyl)methanone (7).** 0.3 mmol scale. Following the typical procedure, 63.8 mg 5,5-dimethyl-3-phenyl-1,4,2-dioxazole **2c**, 61.9 mg 1,3-diphenylprop-2-yn-1-one, 3 mL DCE, 13.0 mg $IPrAuNTf_2$ were stirred at 80 $^oC$ for 24 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded the title product as a white solid in 50% (48.8 mg) isolated yield. M.p. 147-149 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 8.19-8.17 (m, 2H), 8.10-8.08 (m, 2H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.60-7.41 (m, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 183.14, 161.91, 148.81, 143.43, 137.49, 132.85, 131.73, 130.56, 129.82, 129.55, 129.28, 128.96, 128.33, 128.19, 127.40, 126.26. IR (neat): 3057, 1649, 1598, 1576, 1549, 1529, 1488, 1476, 1451, 1444, 1359, 1321, 1292, 1302, 1232, 1162, 1072, 1027, 1013, 998, 976, 959, 935, 894, 796, 783, 730, 716, 696, 686, 673 $cm^{-1}$; HRMS (ESI) calcd for $C_{22}H_{16}NO_2$ $[M+H]^+$: 326.1176, found 326.1175.

**Synthesis of compound 13.**

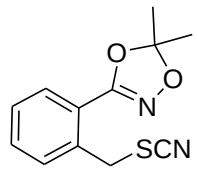



To a solution of 5,5-dimethyl-3-(*o*-tolyl)-1,4,2-dioxazole (1.91 g, 10 mmol) in $CCl_4$ (30 mL) were added NBS (1.96 g, 11 mmol) and BPO (75%, wetted with ca. 25% Water, 484.5 mg,

1.5 mmol). The resulting solution was refluxed at 100 $^{o}$C for 5 h. Then the mixture was quenched with saturated $NaHCO_3$ solution, extracted with dichloromethane, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under the reduced pressure and the residue was used directly for the next step.

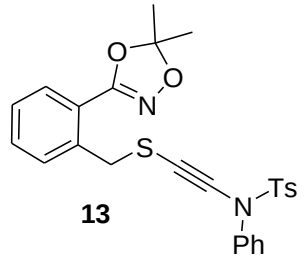
To a solution of the above substrate in EtOH (20 mL) was added KSCN (1.26 g, 13 mmol). The resulting solution was stirred at 80 $^{o}$C for 0.5 h. Then the reaction mixture was filtered through a pad of silica gel using ethyl acetate as an eluent. The filtrate was collected and evaporated under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: = 10:1) to afford compound **s1-13** (1.68 g, 68%) as a white solid.

To a solution of *N*-ethynyl-4-methyl-*N*-phenylbenzenesulfonamide **s2-13** (976.8 mg, 3.6 mmol) in THF (15 mL) was added *n*-BuLi (1.44 mL, 3.6 mmol, 2.5 M in hexanes) at -78 $^{o}$C. After stirring at the same temperature for 30 min, **s1-13** (744.9 mg, 3 mmol, dissolved in 5 mL THF) was added at -78 $^{o}$C. Then the dry-ice/ acetone bath was removed. The reaction mixture was warmed up to room temperature and stirred for 3 h. Then the resulting mixture was quenched with saturated ammonium chloride solution, extracted with ethyl acetate, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: = 10:1) to afford compound **13** (1.05 g, 71%) as a yellow oil.




**s1-13**

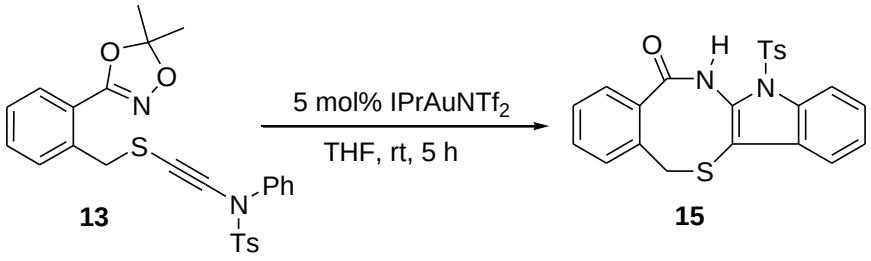
**5,5-Dimethyl-3-(2-(thiocyanatomethyl)phenyl)-1,4,2-dioxazole (s1-13).** M.p. 109-111 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.83 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.54-7.44 (m, 3H), 4.46 (s, 2H), 1.70 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.22, 134.97, 131.40, 131.03, 129.10, 128.93, 121.76, 114.93, 113.27, 38.20, 24.71. IR (neat): 3076, 2992, 2938, 2155, 1711, 1607, 1594, 1568, 1498, 1453, 1420, 1385, 1373, 1351, 1287, 1249, 1215, 1169, 1116, 1063, 1046, 976, 948, 893, 842, 819, 781, 768, 711, 680, 660 cm$^{-1}$; HRMS (ESI) calcd for $C_{12}H_{13}N_2O_2S$ $[M+H]^+$: 249.0692, found 249.0695.




**13**

***N*-(((2-(5,5-Dimethyl-1,4,2-dioxazol-3-yl)benzyl)thio)ethynyl)-4-methyl-*N*-phenylbenzenesulfonamide (13).** $^{1}$H NMR (400 MHz, $CDCl_3$, $Me_4Si$) δ 7.76 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.56-7.54 (m, 2H), 7.37-7.25 (m, 7H), 7.15 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.11-7.08 (m, 2H), 4.19 (s, 2H), 2.43 (s, 3H), 1.67 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, $Me_4Si$) δ 157.53, 144.93, 138.87, 136.67, 133.08, 131.19, 130.54, 129.44, 129.04, 128.87, 128.18, 127.99, 127.59, 125.97, 121.92, 114.58, 89.34, 65.19, 40.37, 24.72, 21.62. IR (neat): 3062, 2990, 2931, 2159, 1717, 1594, 1570, 1488, 1454, 1372, 1348, 1307, 1266, 1216, 1187, 1172, 1089, 1063, 1045, 979, 948, 922, 888, 814, 767, 735, 703, 691, 661 $cm^{-1}$; HRMS (ESI) calcd for $C_{26}H_{24}N_2NaO_4S_2$ $[M+Na]^+$: 515.1070, found 515.1069.

**Trapping of α-imino gold-carbene intermediate.**

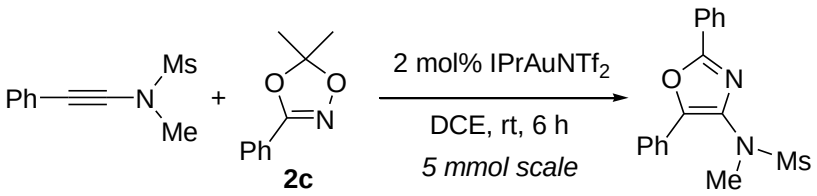



**13** **15**

To a solution of **13** (147.8 mg, 0.3 mmol) in THF (3 mL) was added $IPrAuNTf_2$ (13.0 mg, 0.015 mmol) at room temperature. After stirring for 5 h. The solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (eluent: petroleum ether: ethyl acetate: = 2:1) to afford compound **15** (90.9 mg, 70%) as a white solid. M.p. 268-270 $^{o}$C. $^{1}$H NMR (400 MHz, DMSO-$d_6$, $Me_4Si$, 80 $^{o}$C) δ 9.67 (bs, 1H), 7.83 (d, *J* = 5.6 Hz, 1H), 7.65 (d, *J* = 5.6 Hz, 2H), 7.34 (d, *J* = 5.6 Hz, 2H), 7.31-7.27 (m, 4H), 7.20-7.17 (m, 1H), 7.12 (td, *J* = 5.2, 1.2 Hz, 1H), 6.86 (d, *J* = 4.8 Hz, 1H), 4.32 (bs, 2H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, $Me_4Si$, 80 $^{o}$C) δ 171.17, 145.05, 136.29, 135.06, 132.88, 131.37, 130.07, 129.74, 129.13, 128.38, 127.05, 127.02, 126.35, 125.37, 125.33, 123.26, 118.57, 113.62, 109.44, 32.16, 20.55. IR (neat): 3197, 2923, 2848, 1690, 1663, 1589, 1494, 1448, 1371,

1335, 1314, 1294, 1245, 1215, 1189, 1172, 1123, 1098, 1027, 951, 815, 796, 775, 766, 753, 737, 702, 670 $cm^{-1}$; HRMS (ESI) calcd for $C_{23}H_{19}N_2O_3S_2$ $[M+H]^+$: 435.0832, found 435.0832.

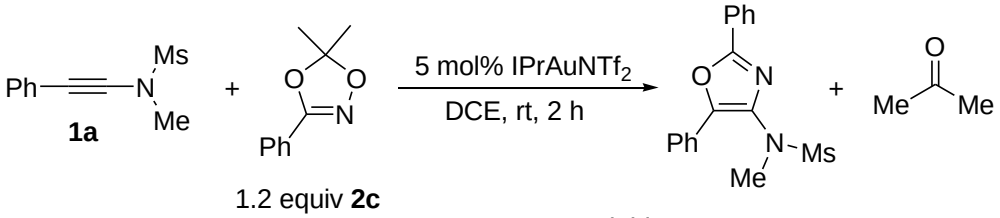
**Gram scale synthesis of oxazole 3a.**




**1a**, 1.05 g 1.2 equiv **3a**, 89%, 1.47 g

To a solution of 5,5-dimethyl-3-phenyl-1,4,2-dioxazole **2c** (1.06 g, 6 mmol) and ynamide **1a** (1.05 g, 5 mmol) in DCE (20 mL) was added $IPrAuNTf_2$ (86.6 mg, 0.1 mmol). After the reaction mixture was stirred at room temperature for 6 h, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to afford **3a** (1.47 g, 89%) as a white solid.

**Detection of the released acetone.**




NMR yield: **3a**, 98% 99%

To a solution of 5,5-dimethyl-3-phenyl-1,4,2-dioxazole **2c** (63.8 mg, 0.36 mmol) and ynamide **1a** (62.8 mg, 0.3 mmol) in DCE (1 mL) was added $IPrAuNTf_2$ (13.0 mg, 0.015 mmol). After the reaction mixture was stirred at room temperature for 2 h, 21 μL $CH_2Br_2$ was added. The $^1H$ NMR of the crude reaction mixture revealed that **3a** was formed in 98% NMR yield, and acetone was formed in 99% NMR yield.

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**X-ray crystal structure of compounds IPrAuNTf$_2$, 3b, 15.**

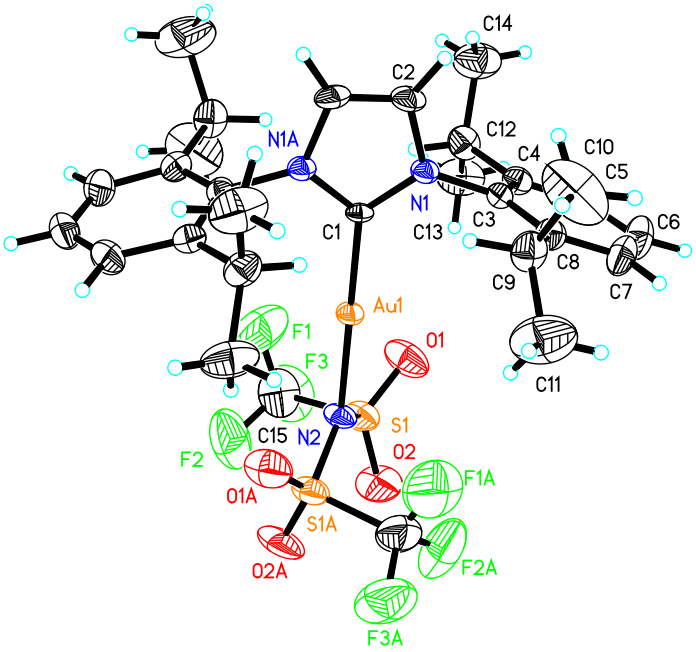



**Figure 1.** X-ray crystal structure of IPrAuNTf$_2$

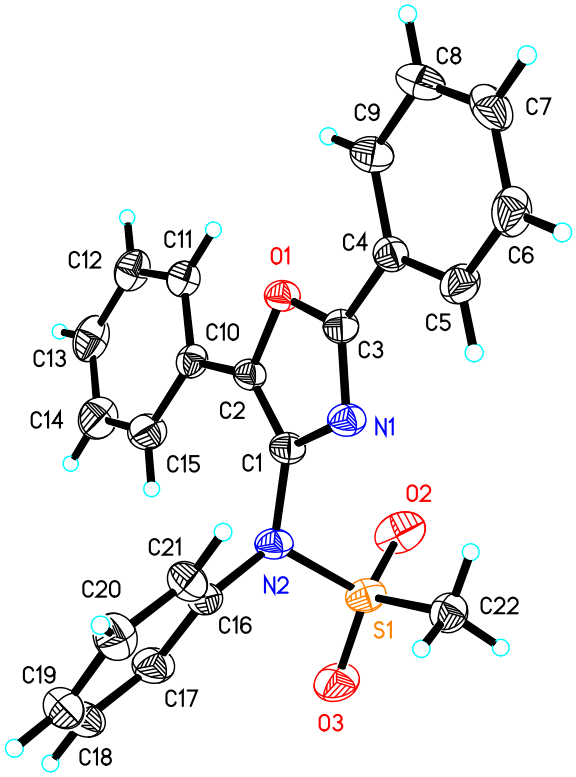



**Figure 2.** X-ray crystal structure of compound **3b**

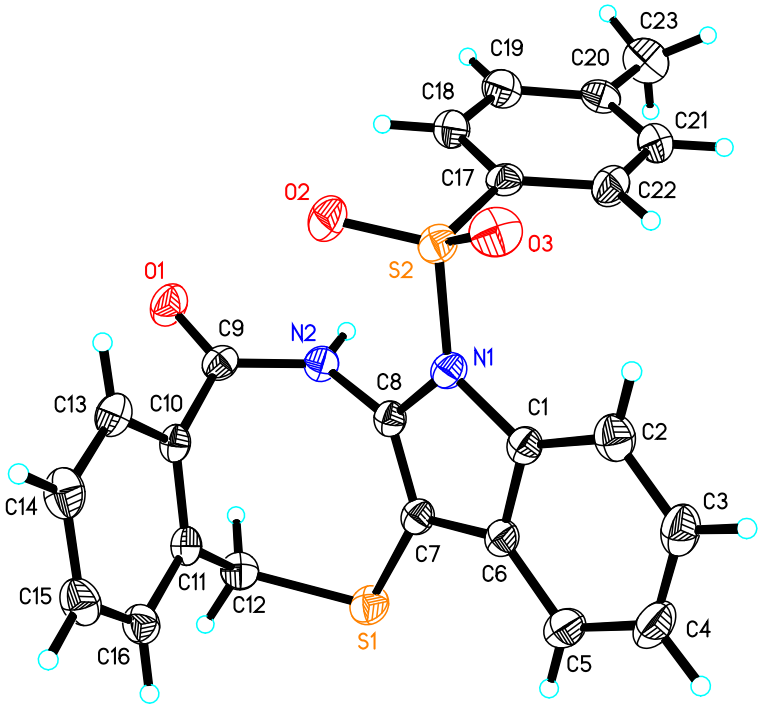
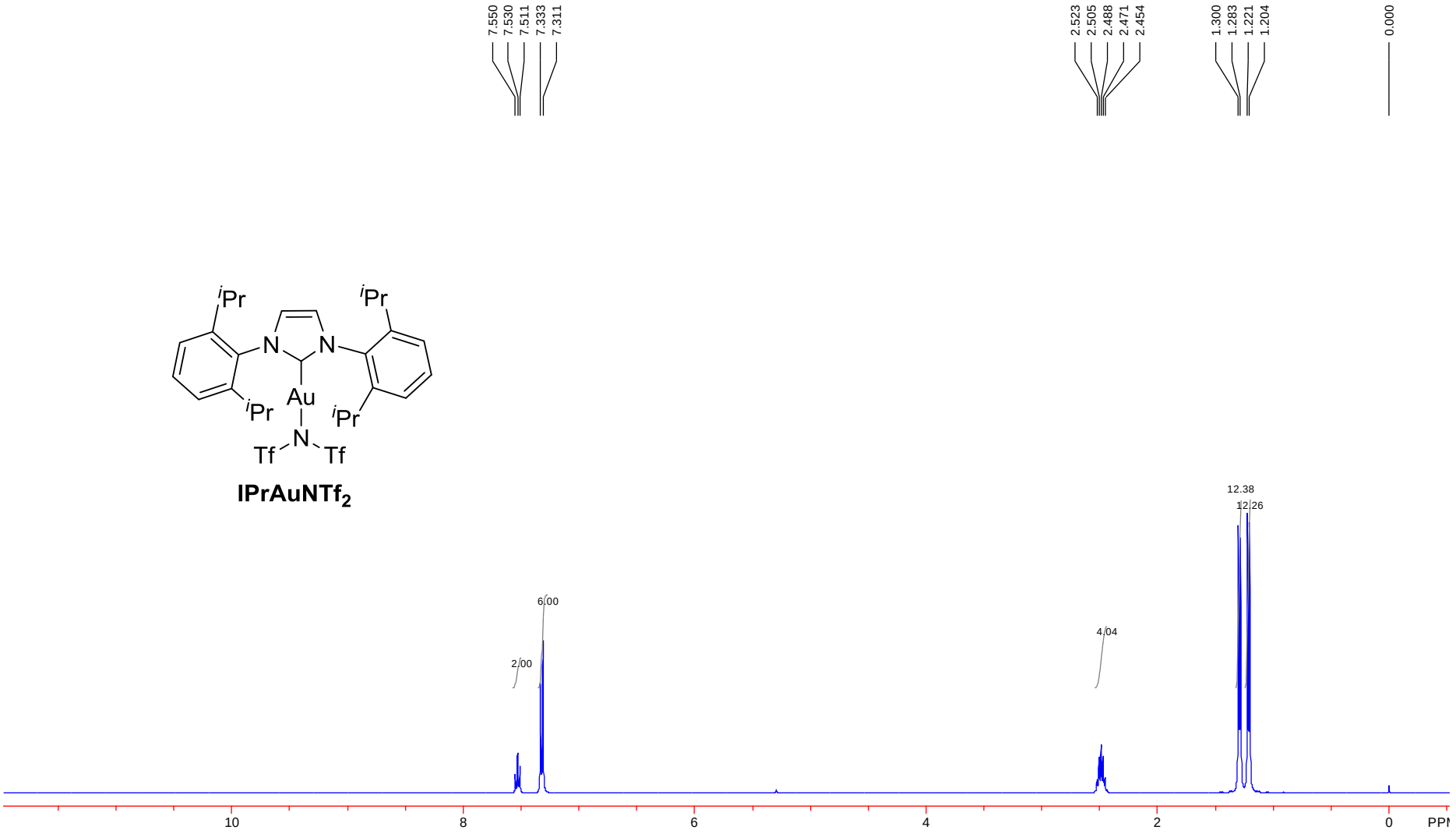
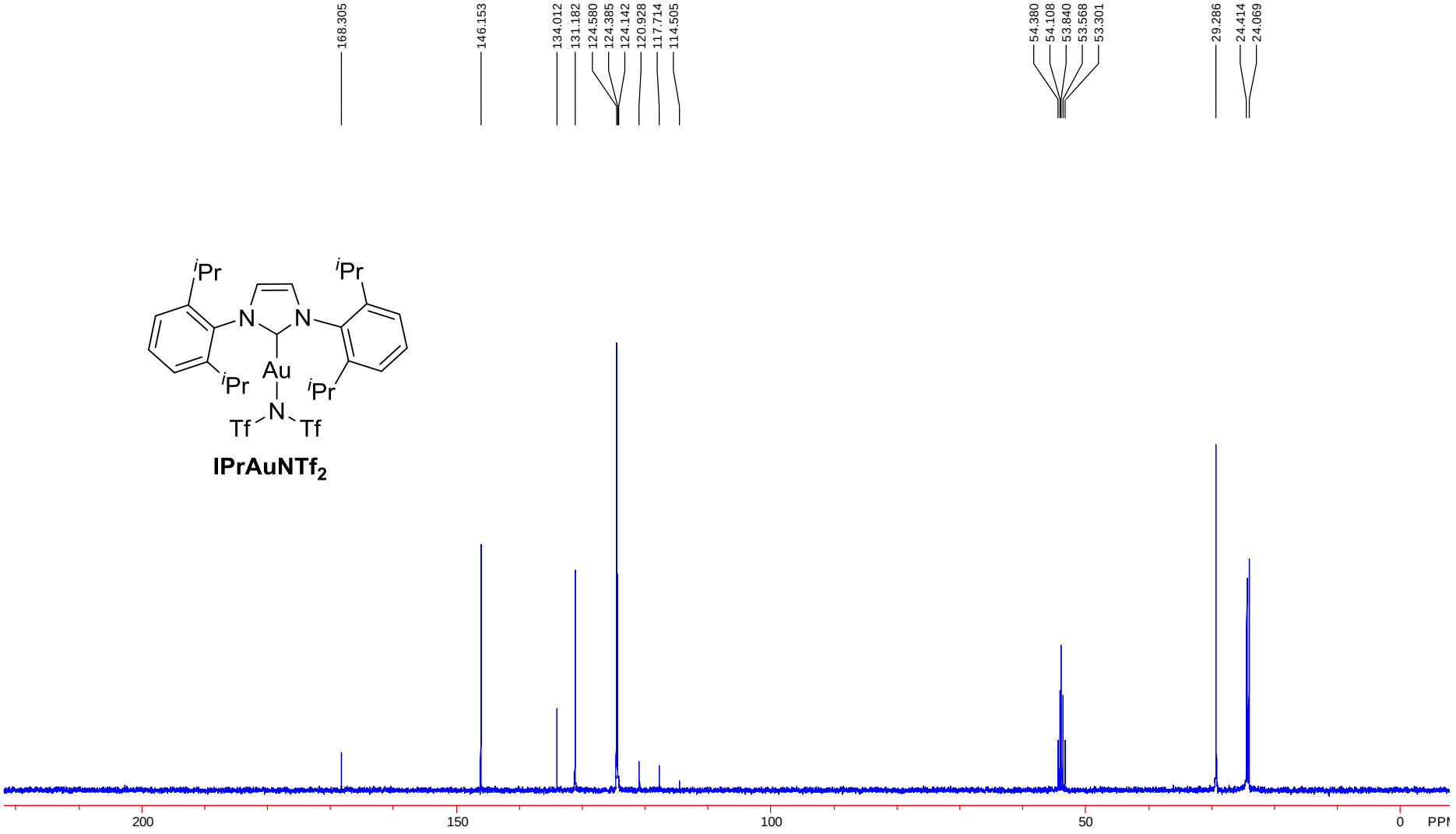



**Figure 3.** X-ray crystal structure of compound **15**

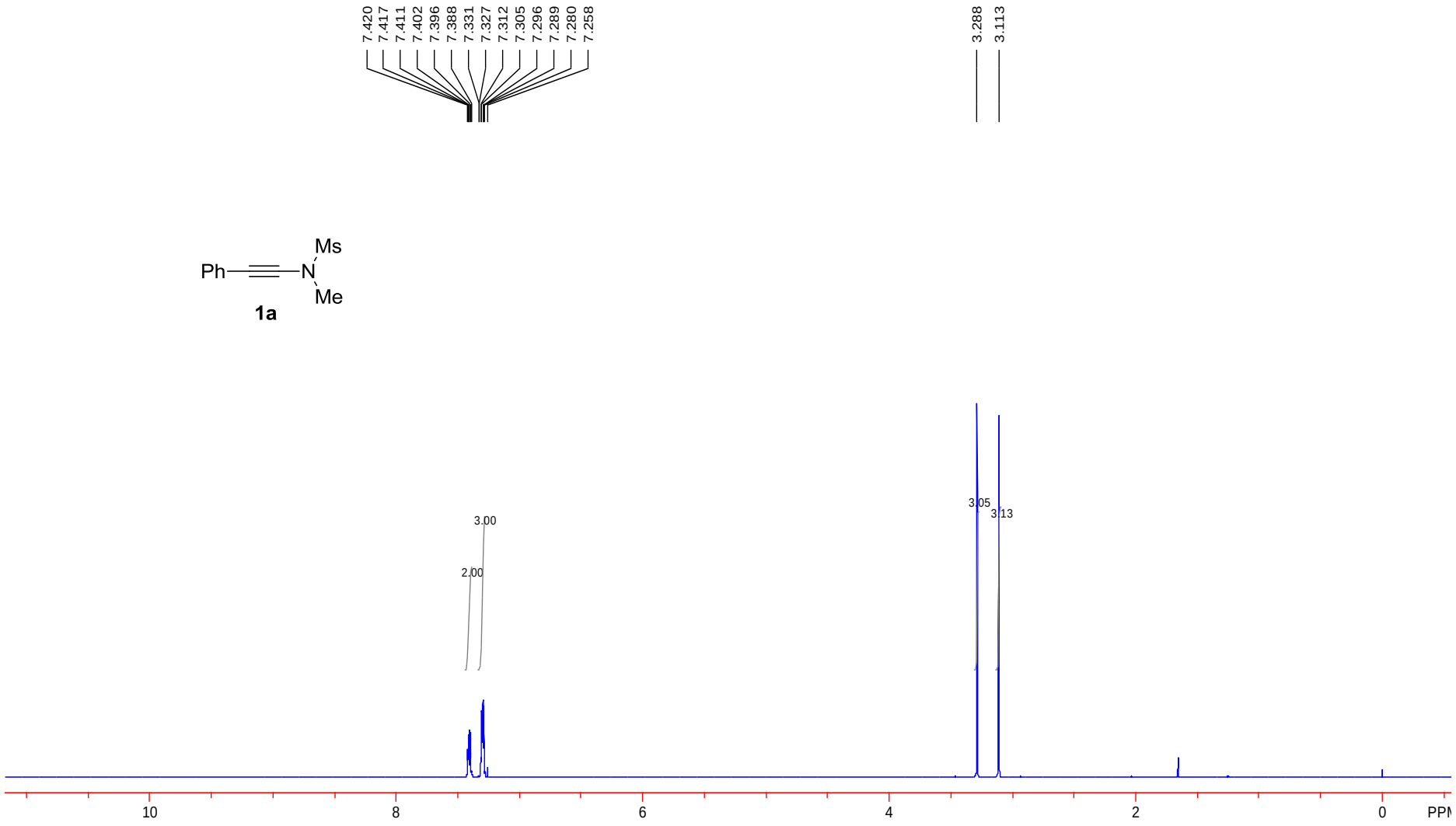
**$^{1}$H NMR (400 MHz, $CD_2Cl_2$)**



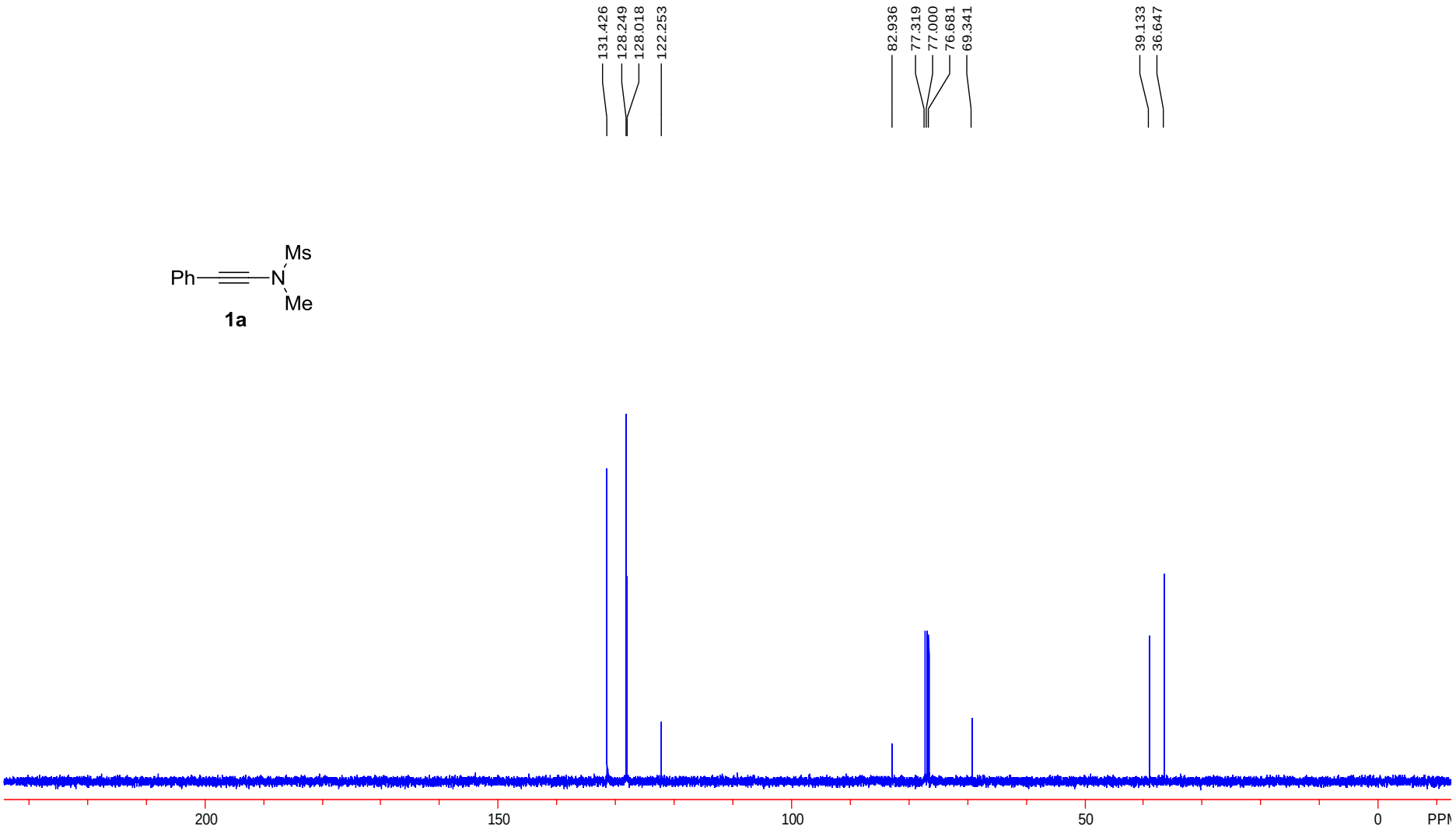
**$^{13}$C NMR (100 MHz, $CD_2Cl_2$)**



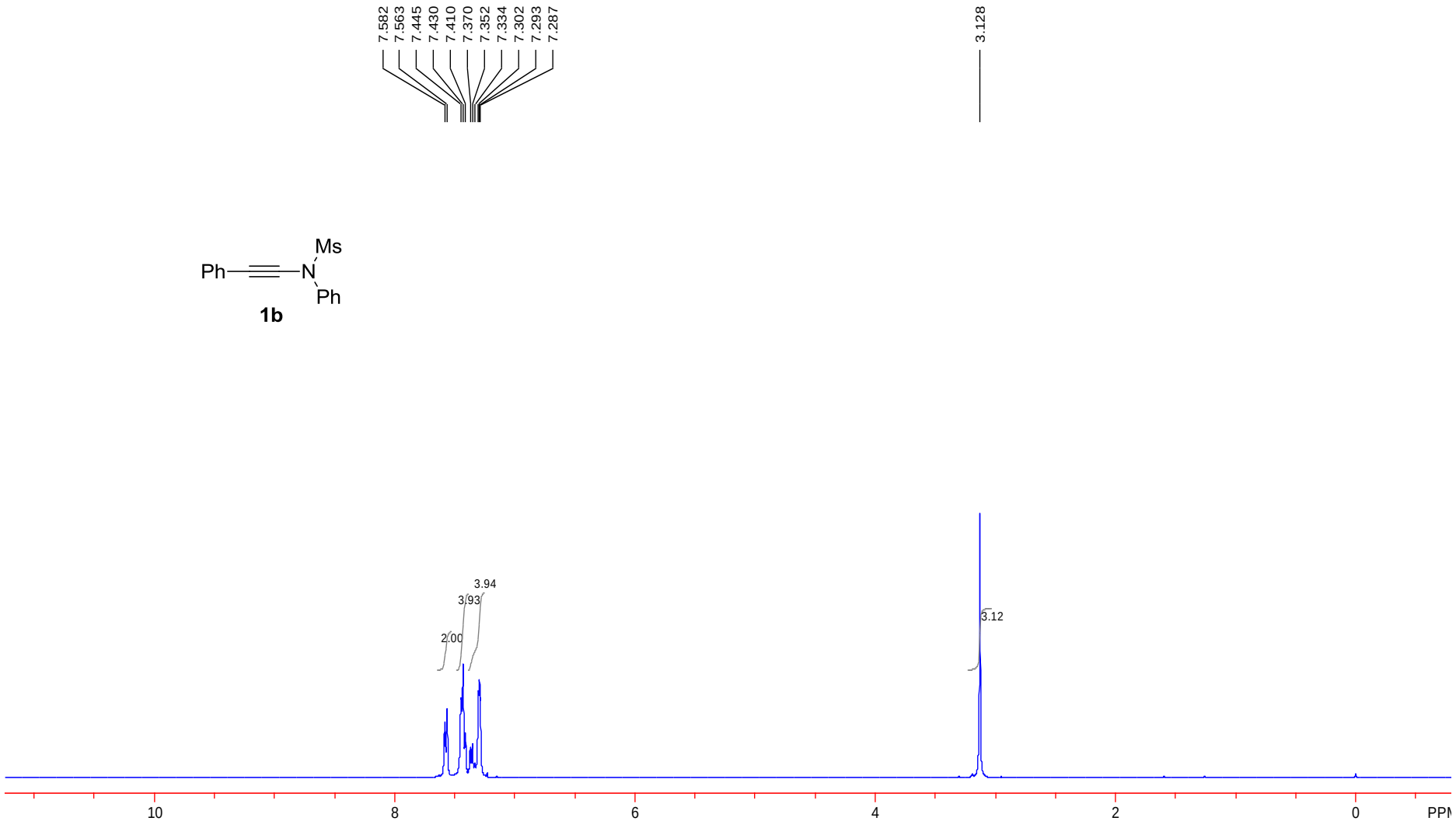
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**



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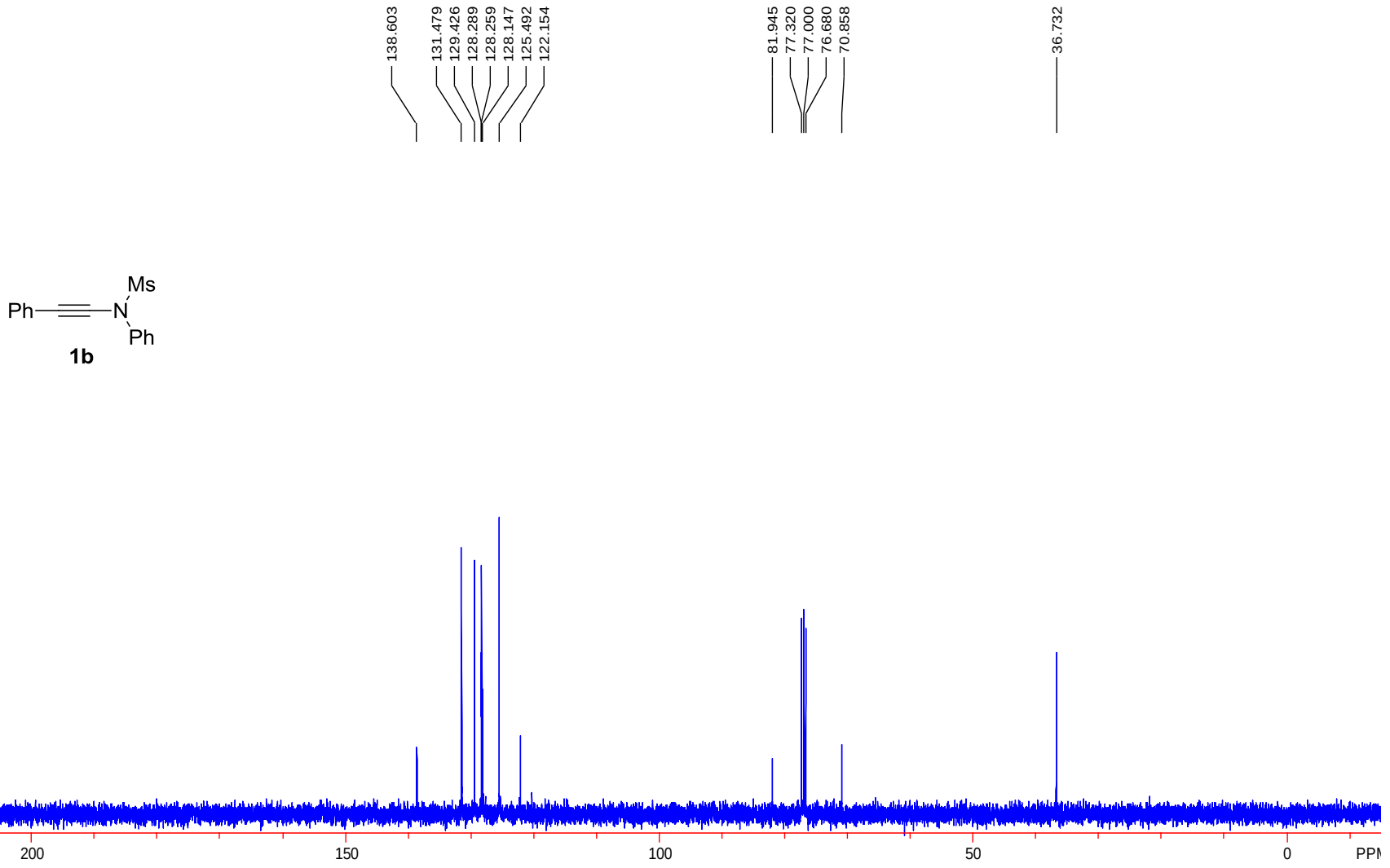
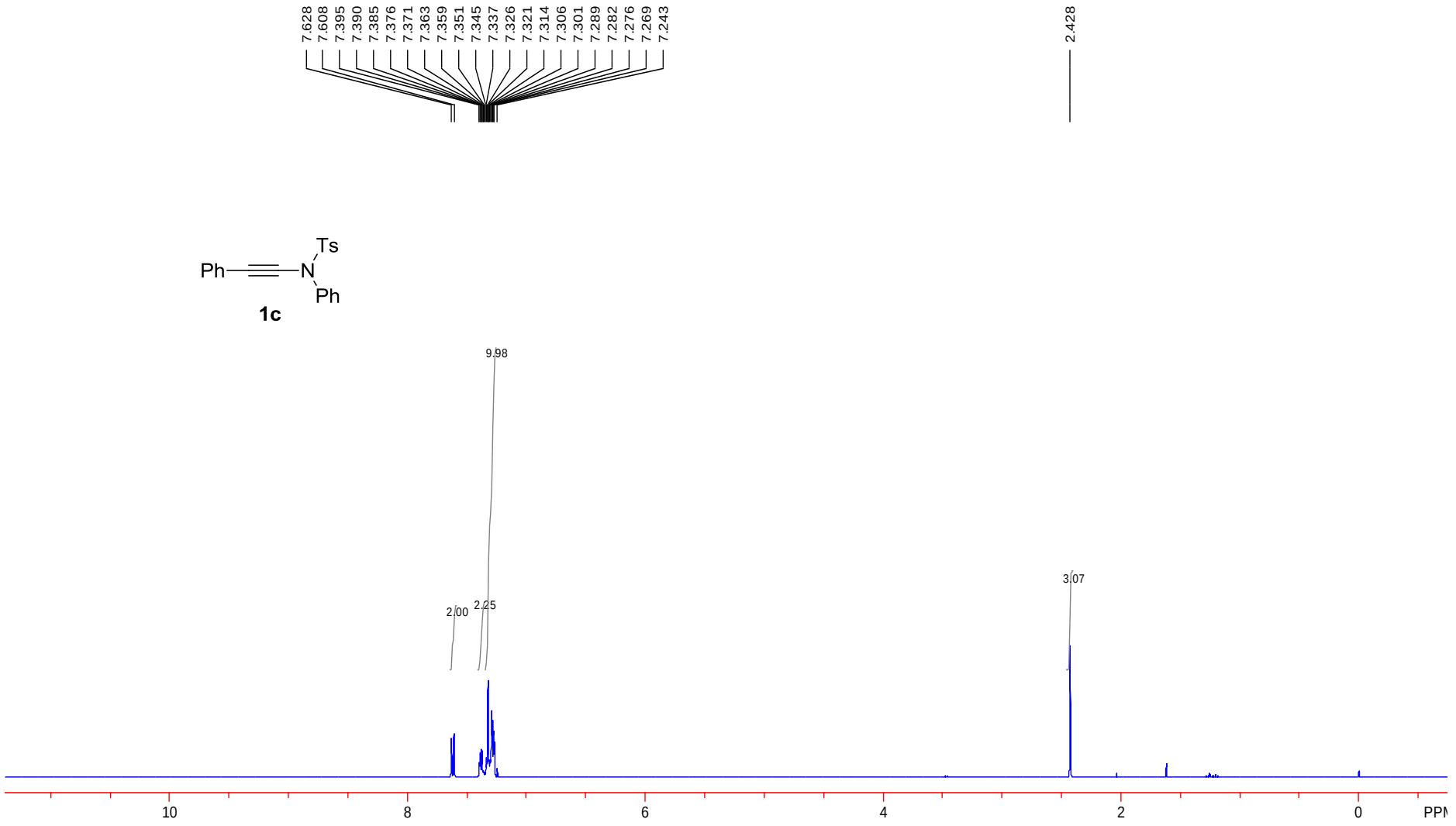



**1b**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**



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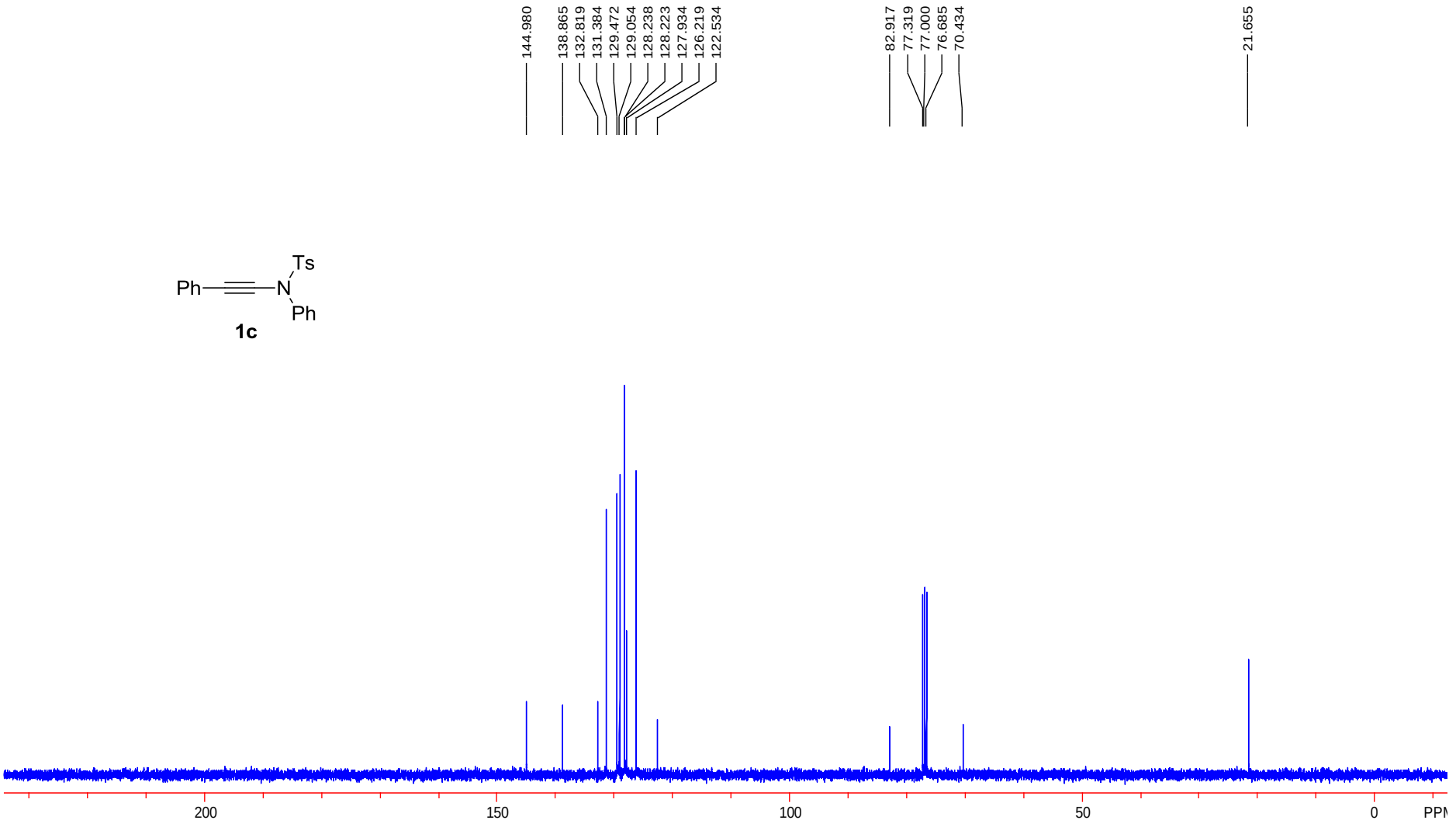

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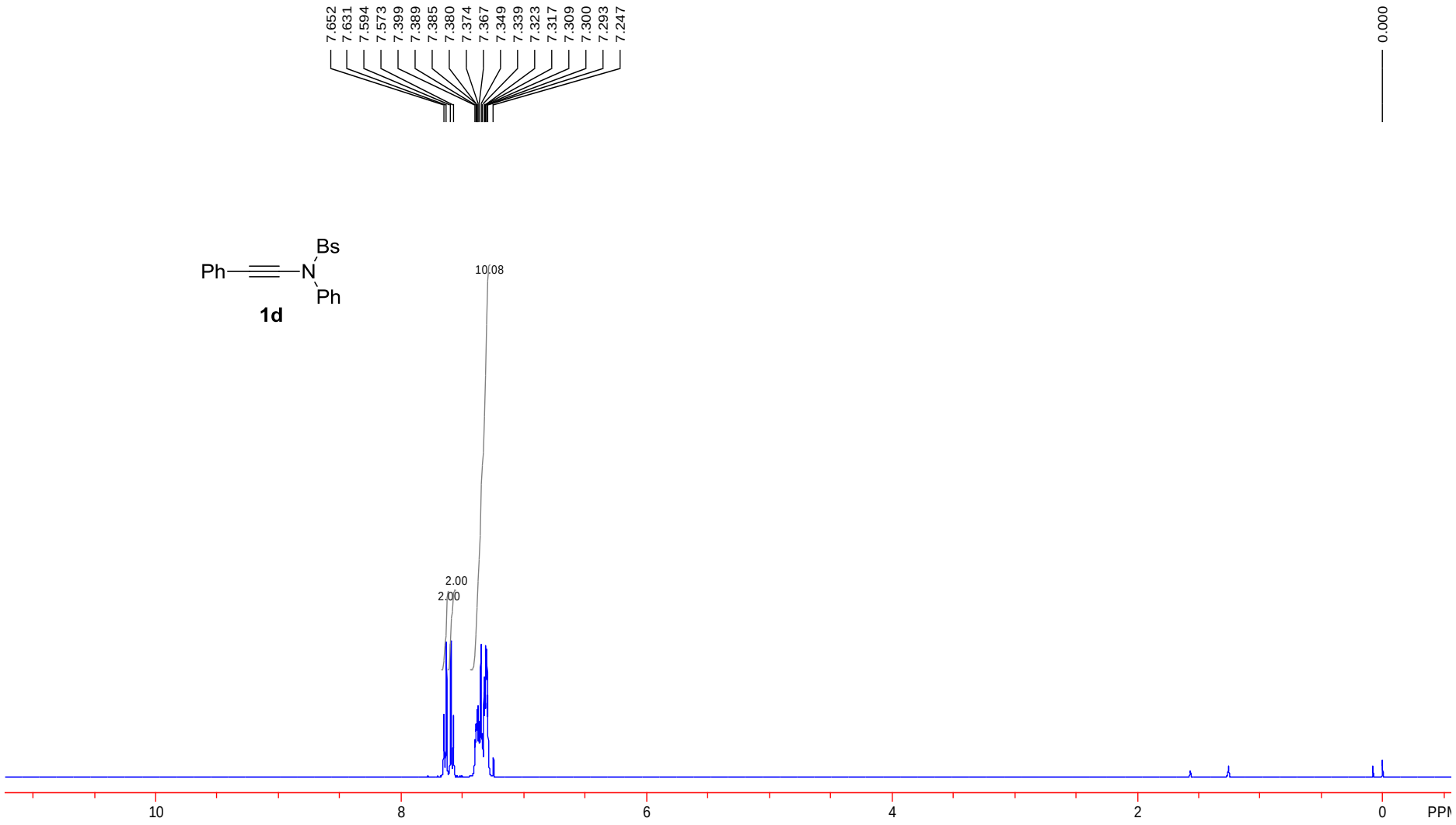

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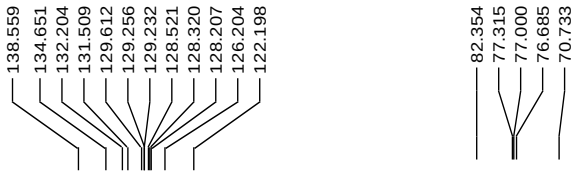


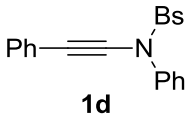


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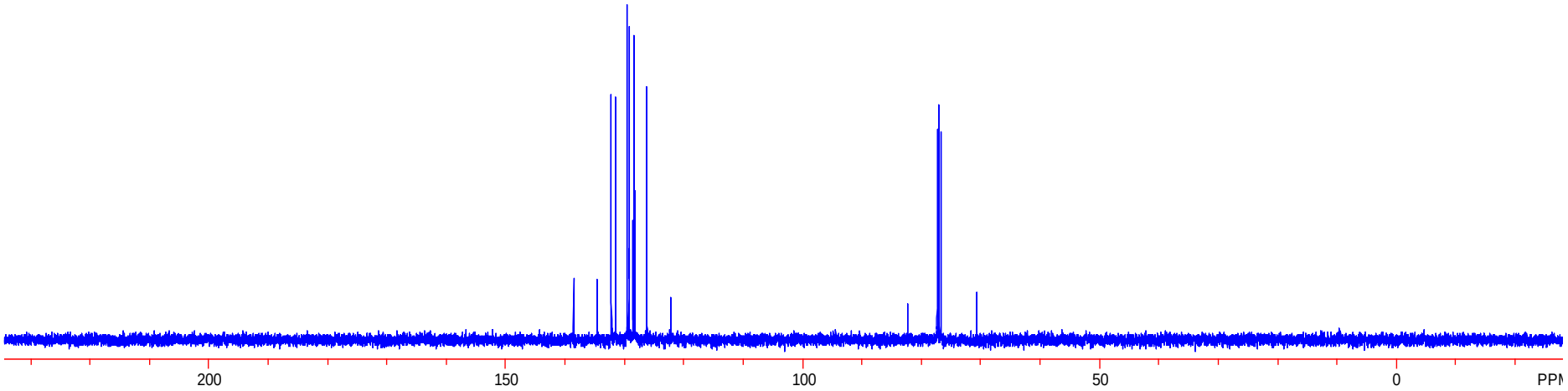
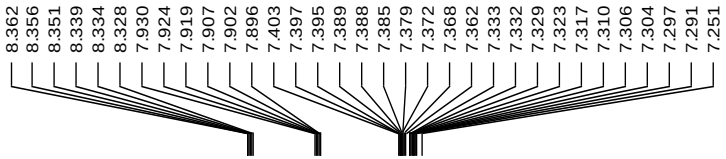
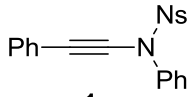


**$^1$H NMR (400 MHz, $CDCl_3$)**

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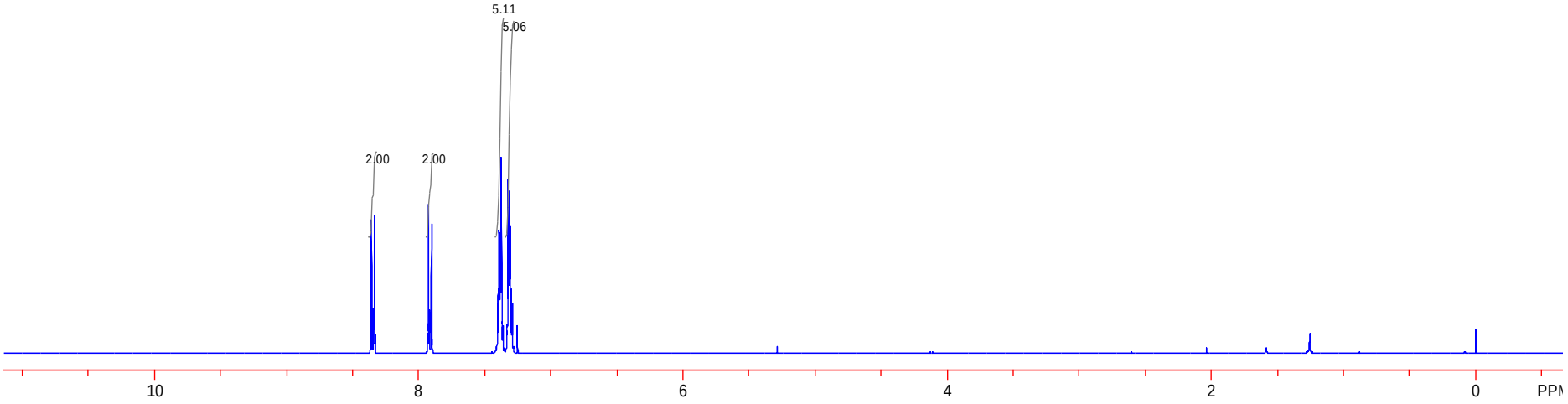
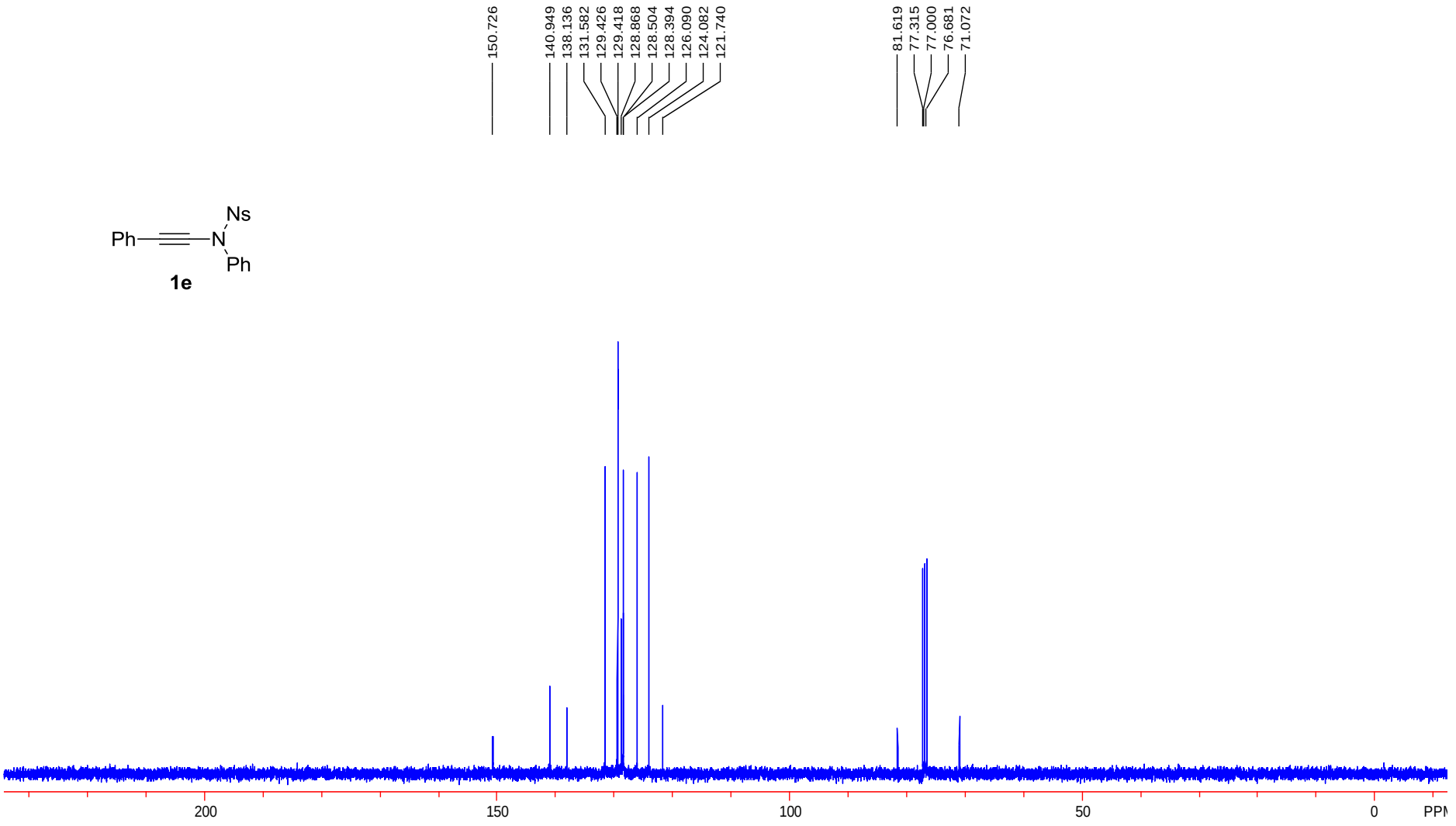


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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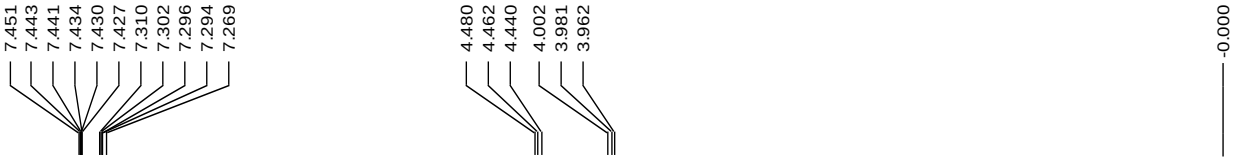


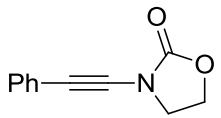


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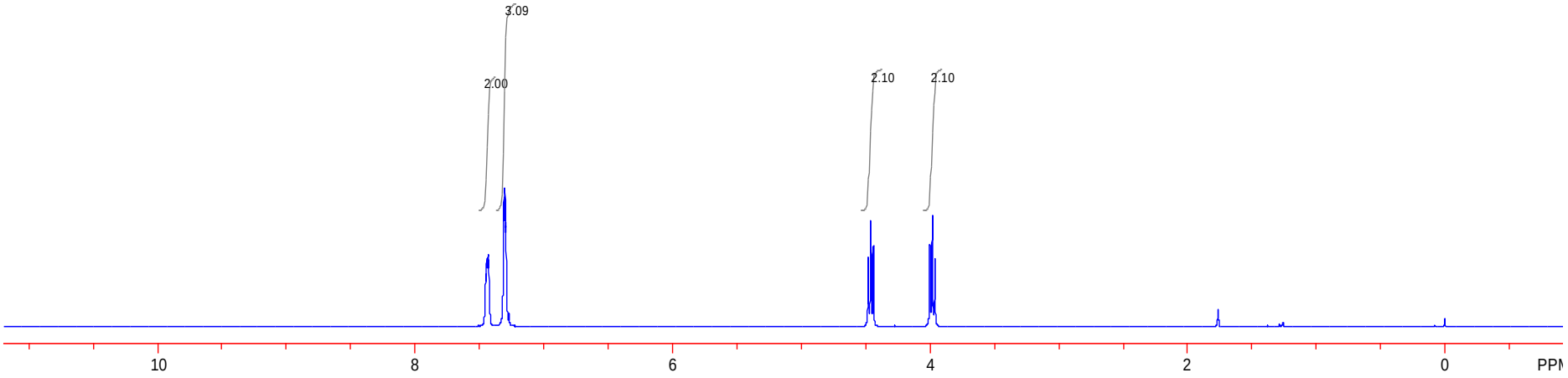
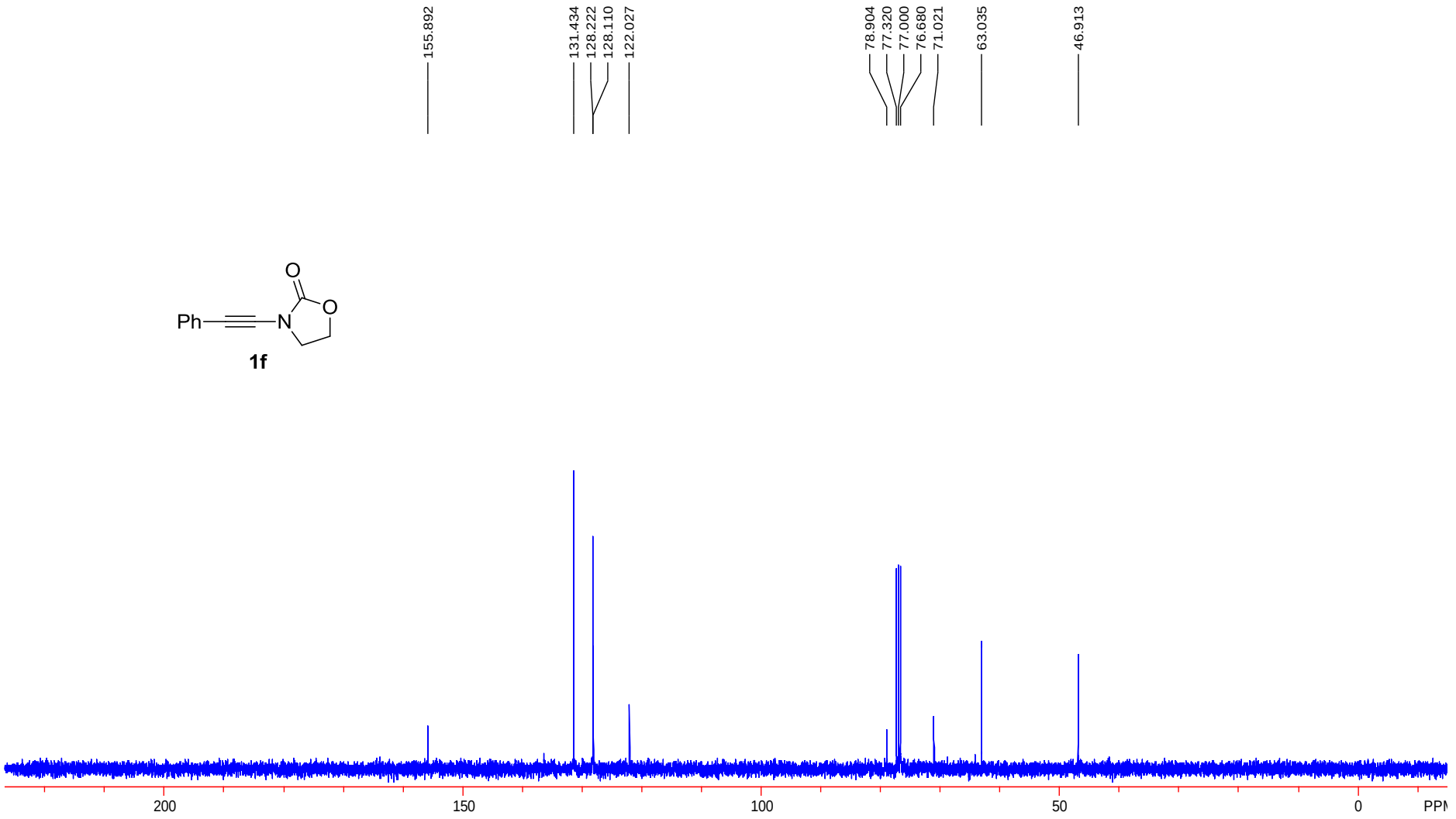


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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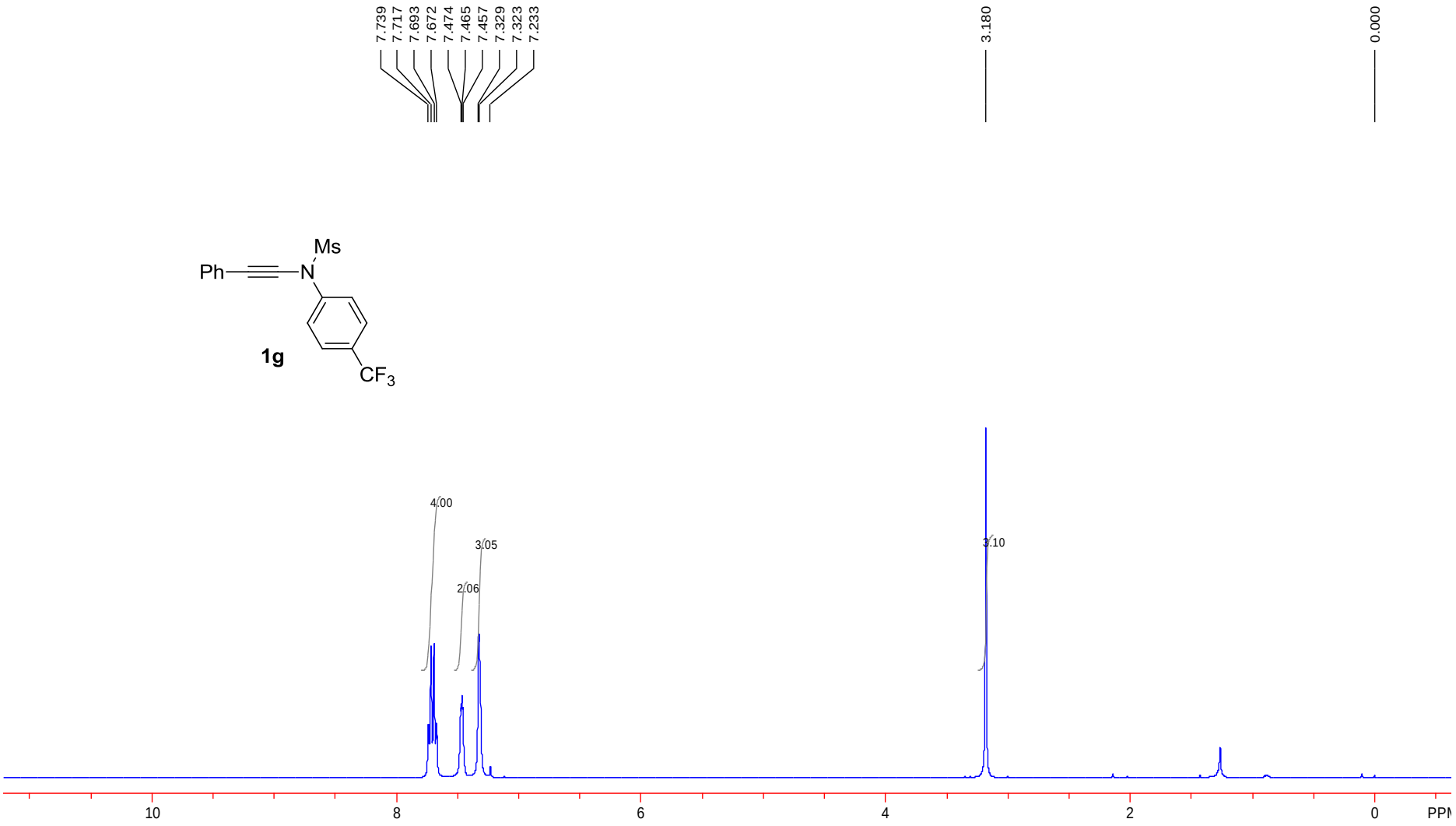

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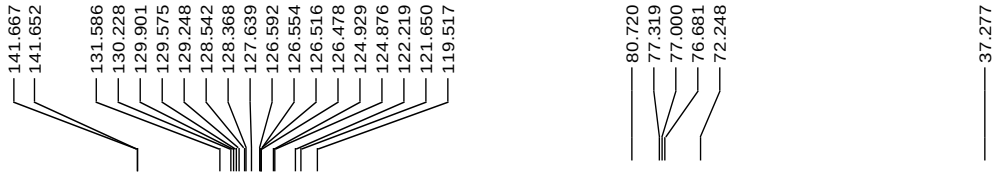


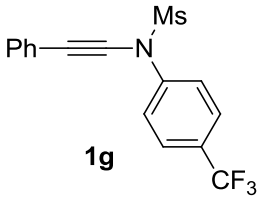


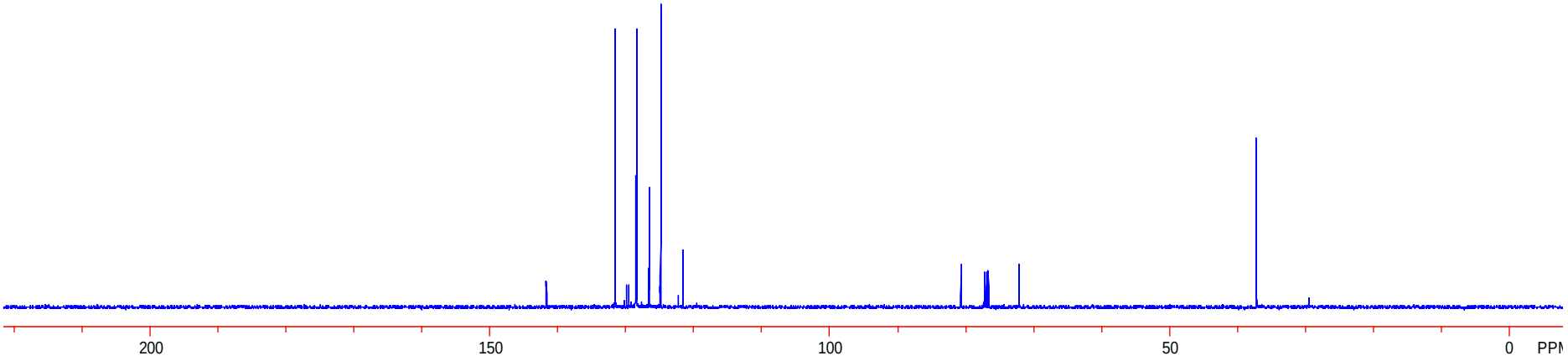

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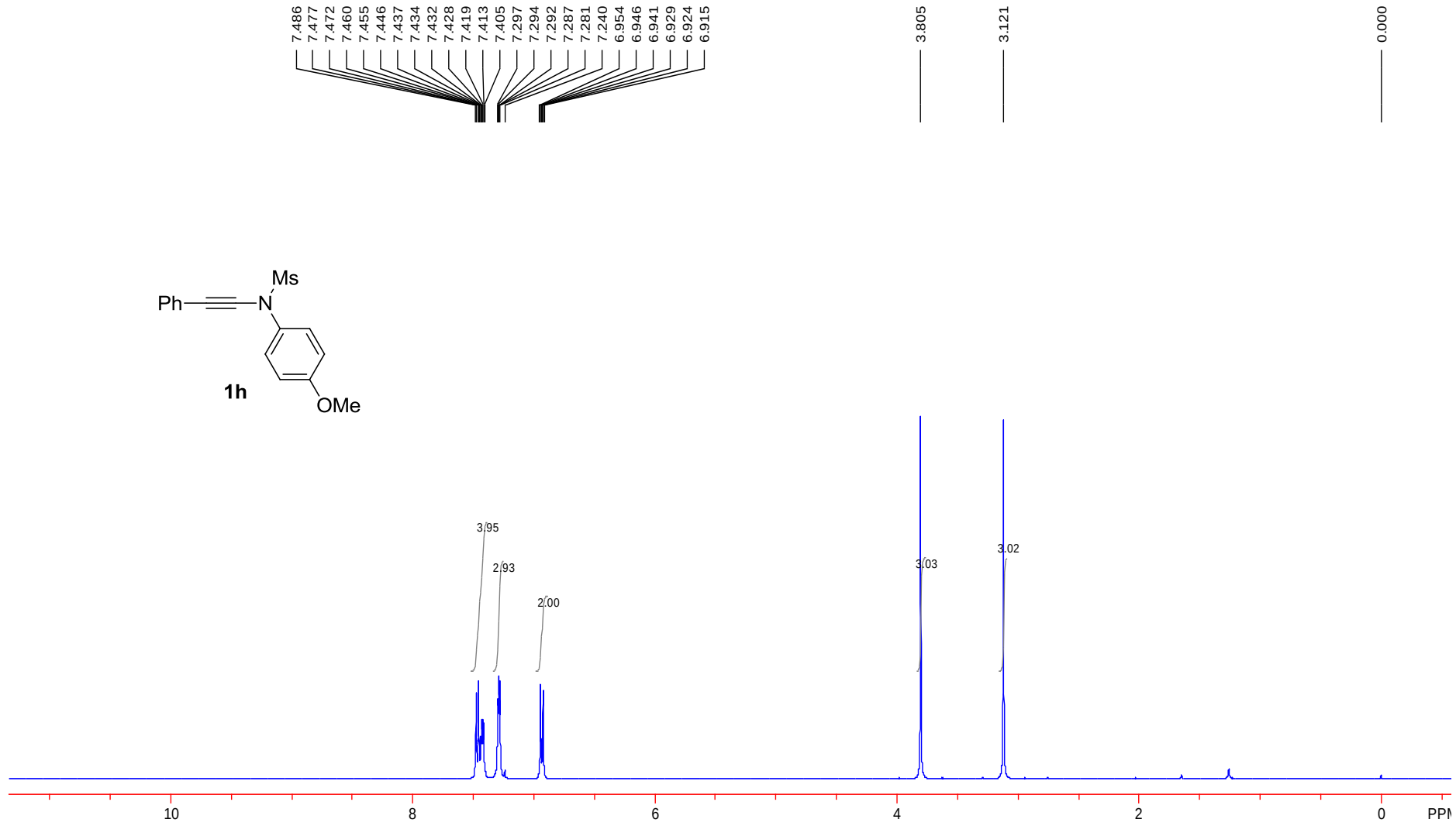

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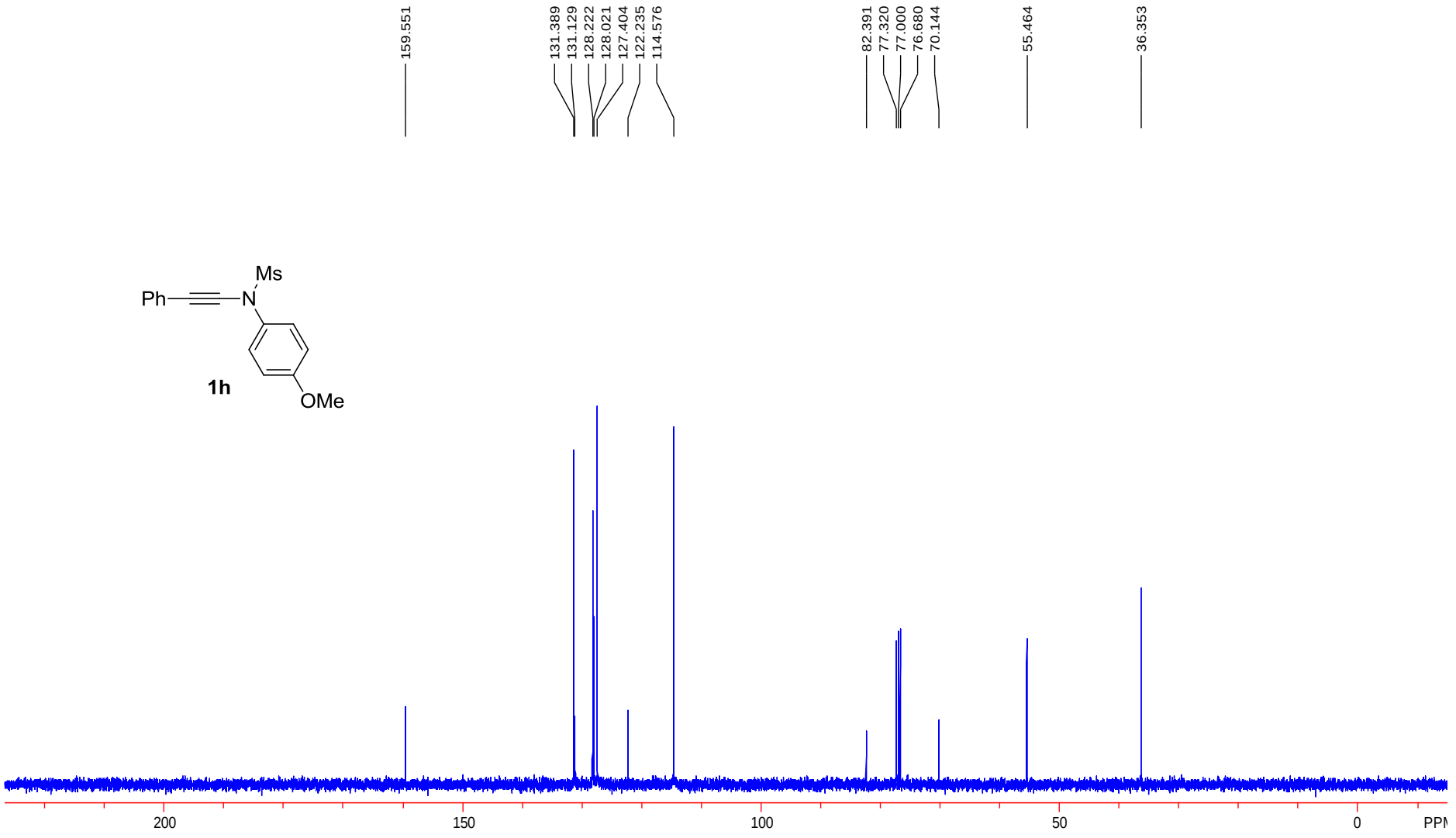

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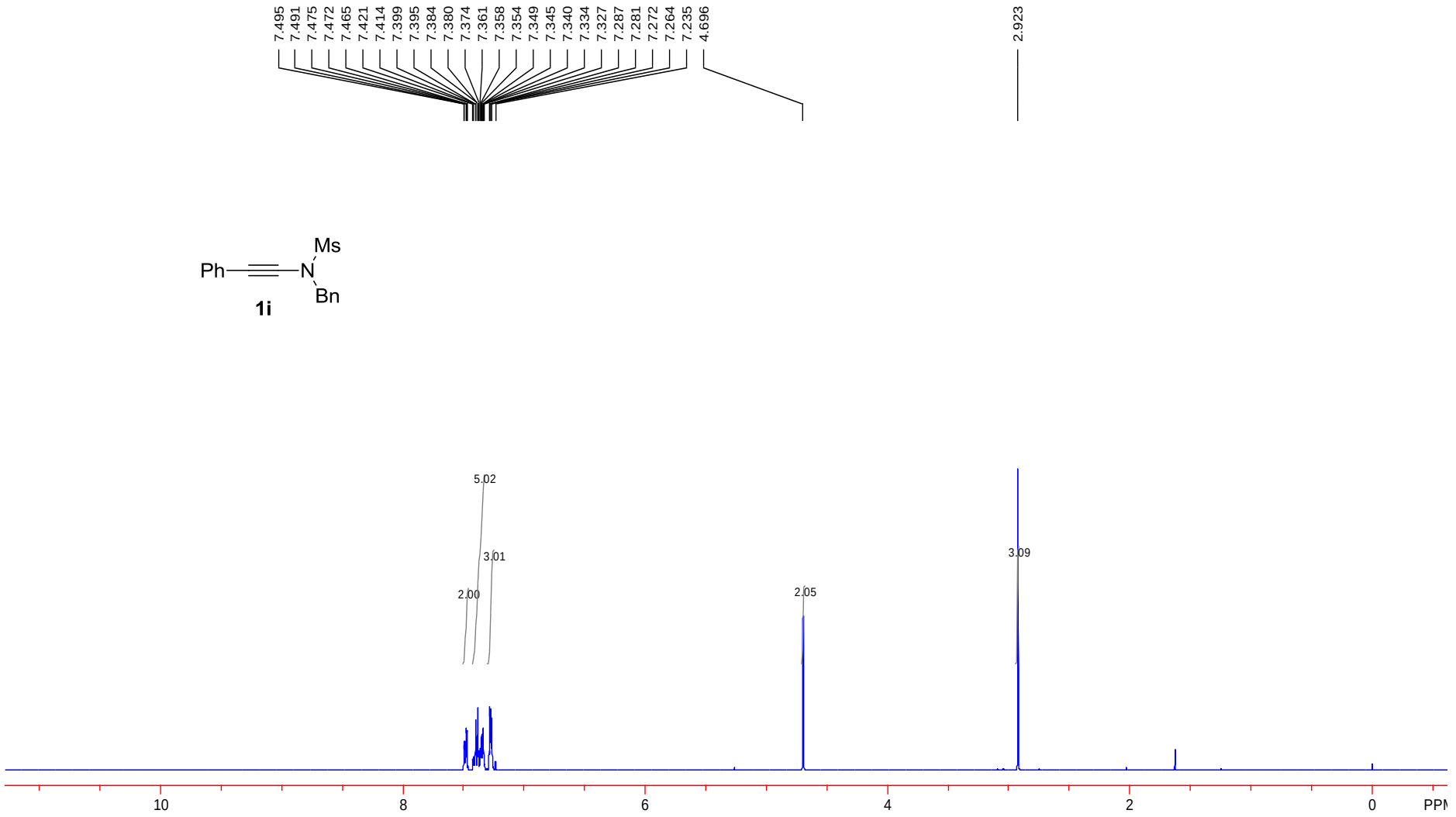

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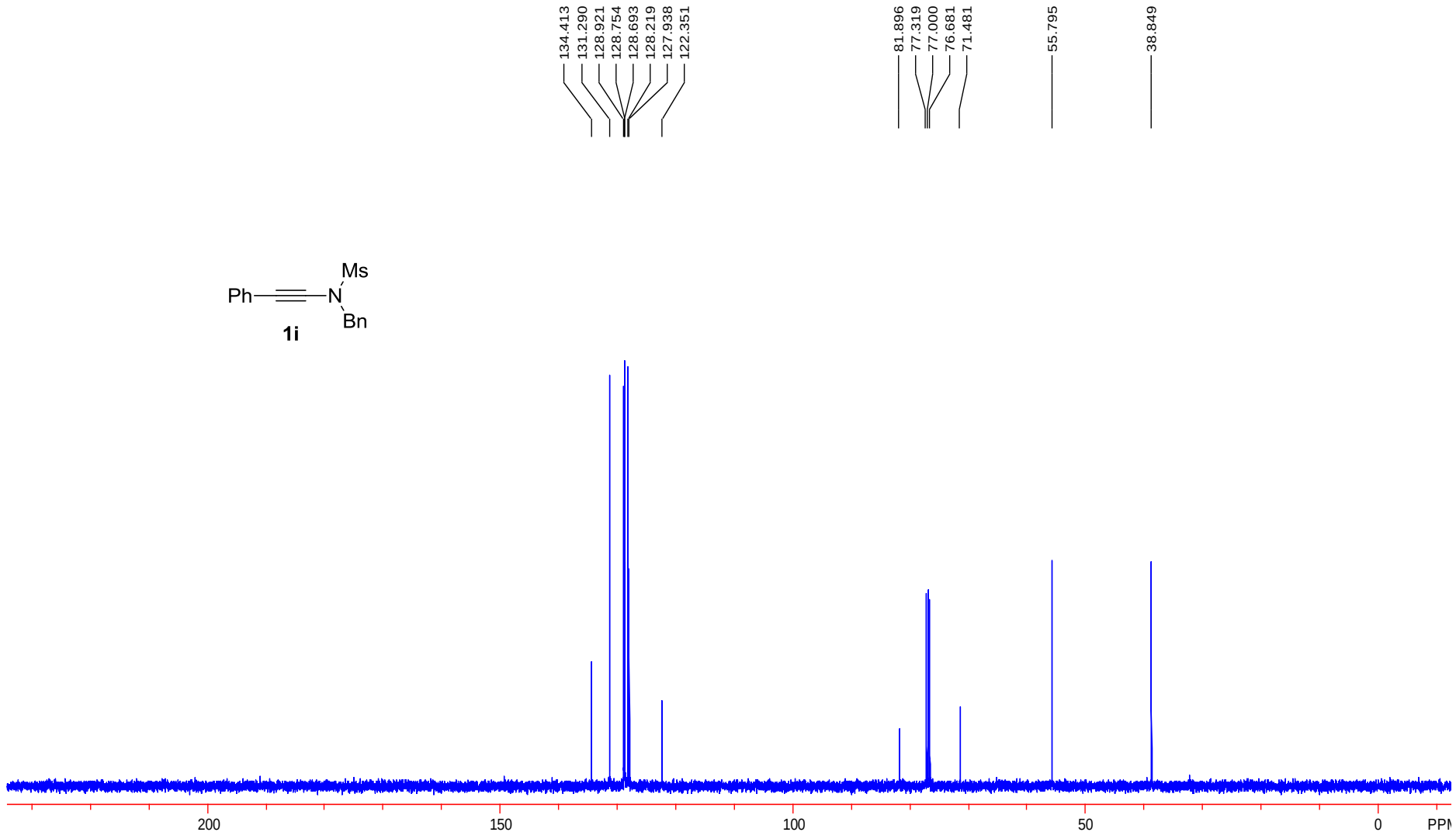

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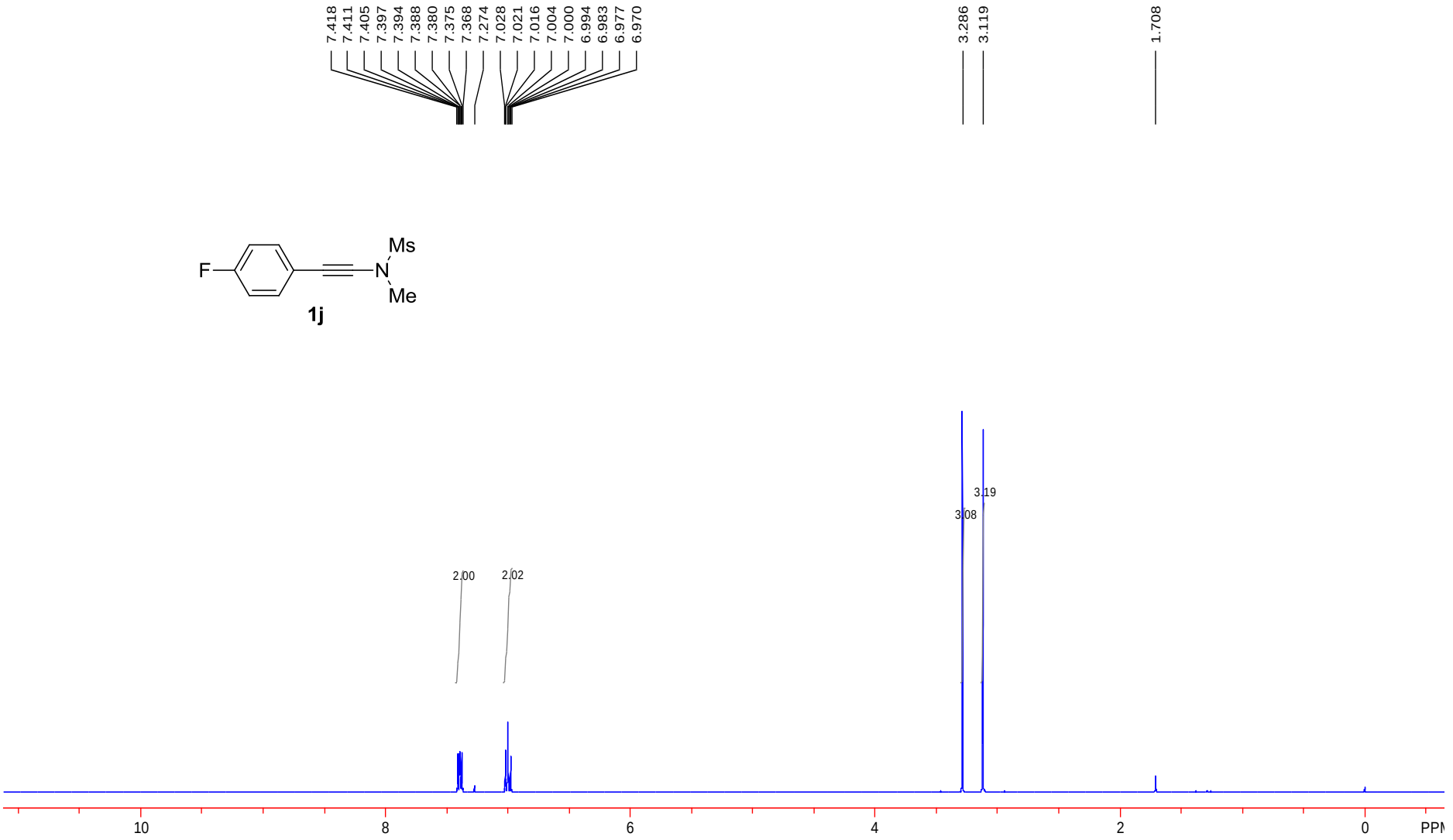
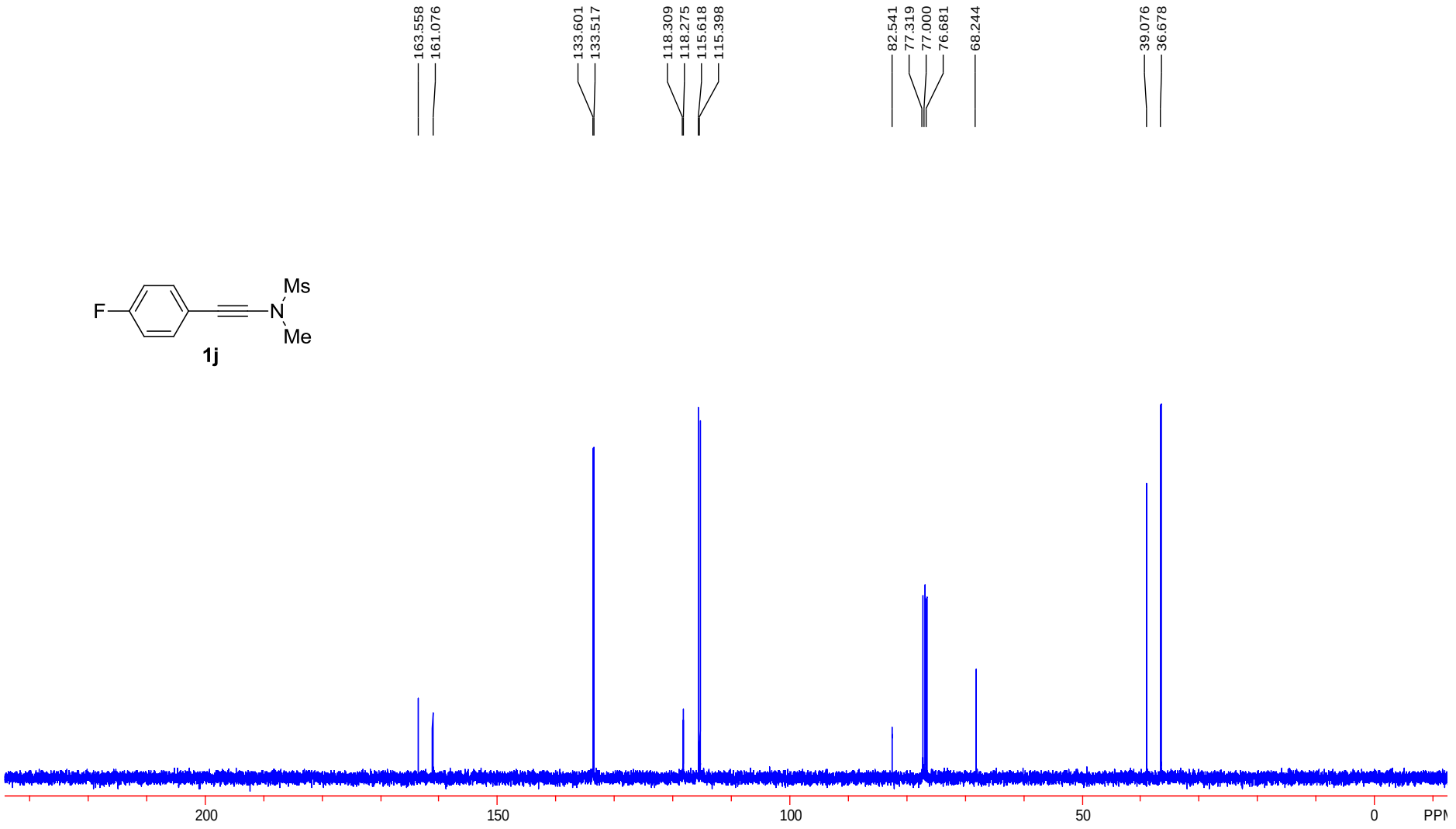


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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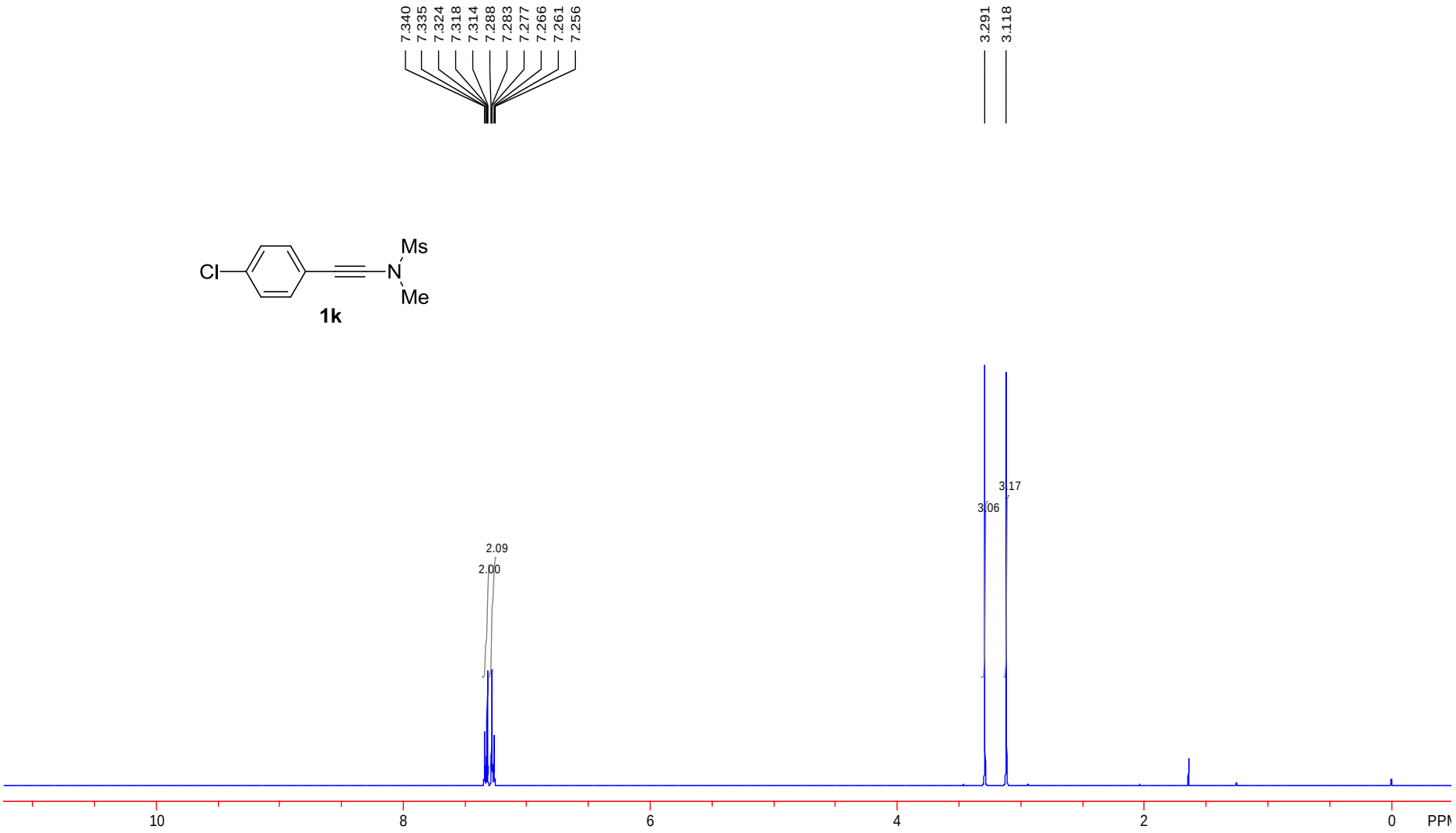

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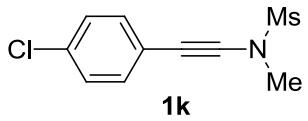


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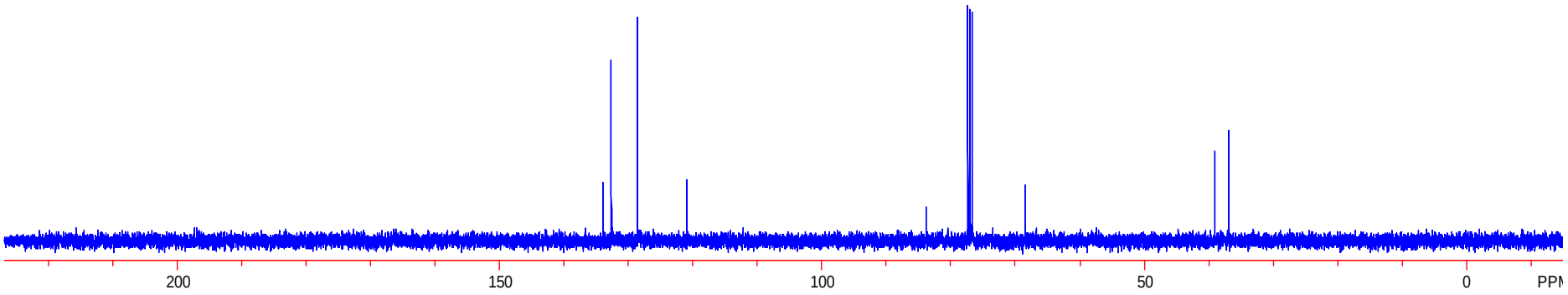
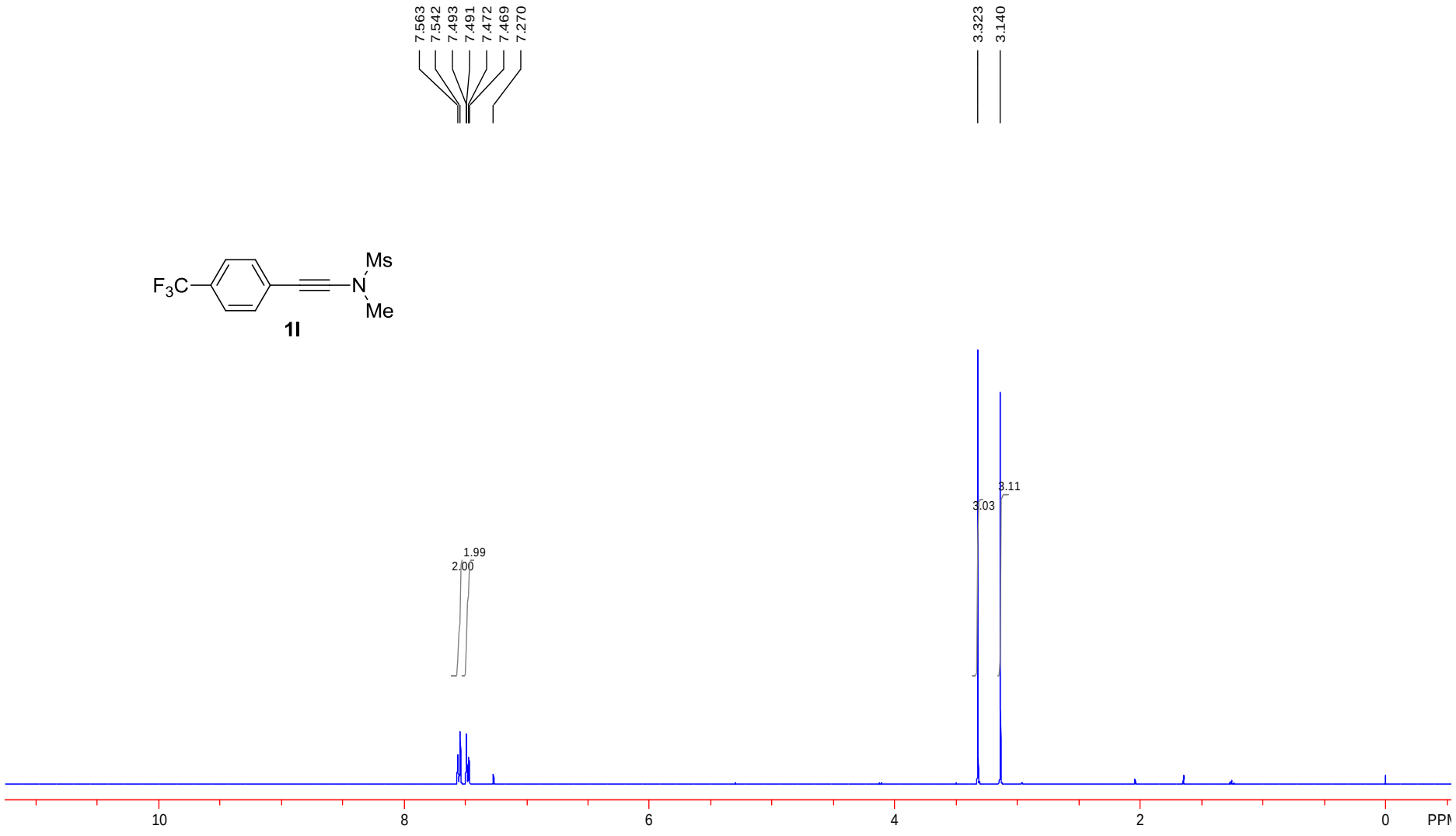
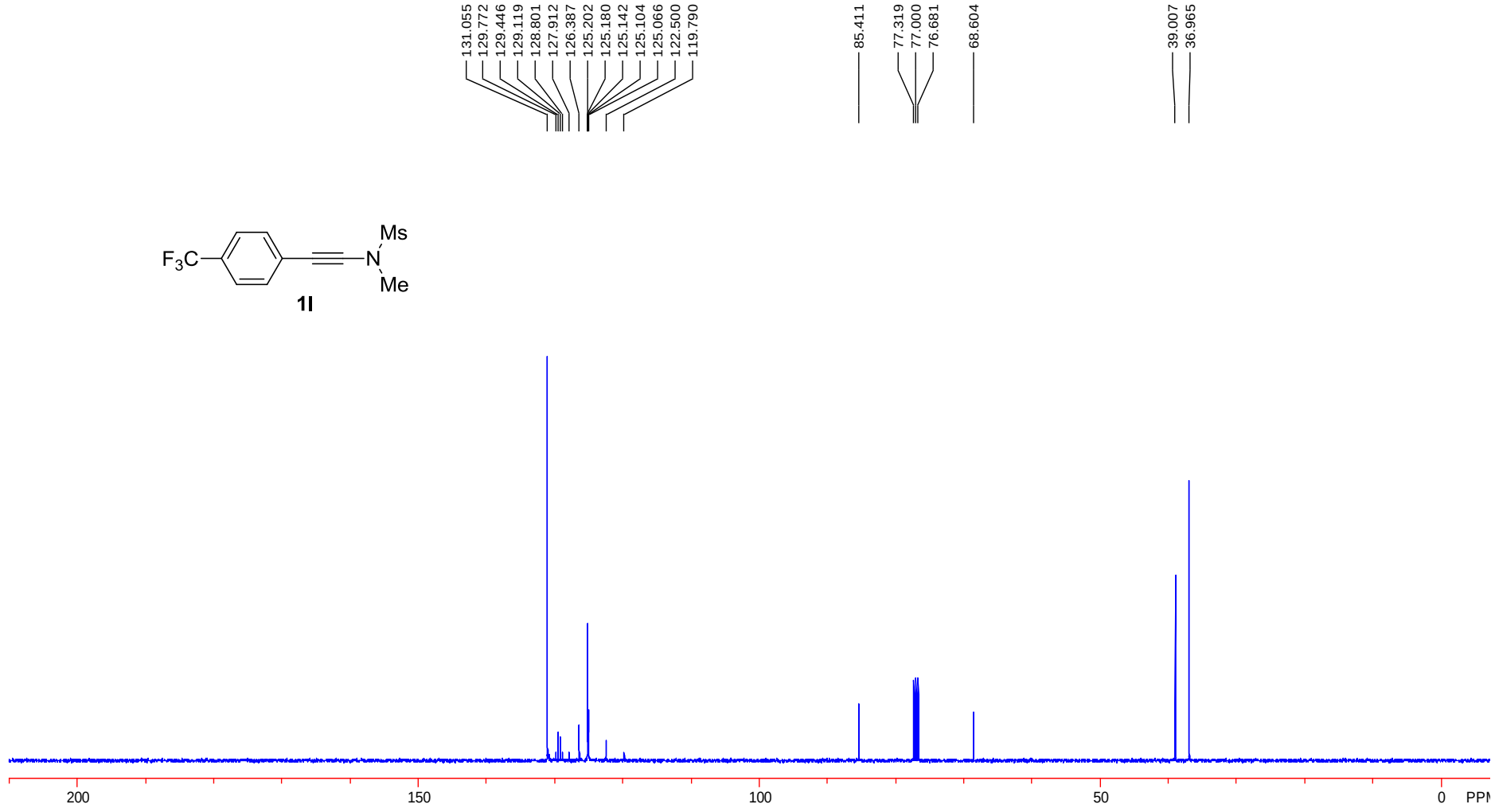


**$^{1}$H NMR (400 MHz, $CDCl_3$)**

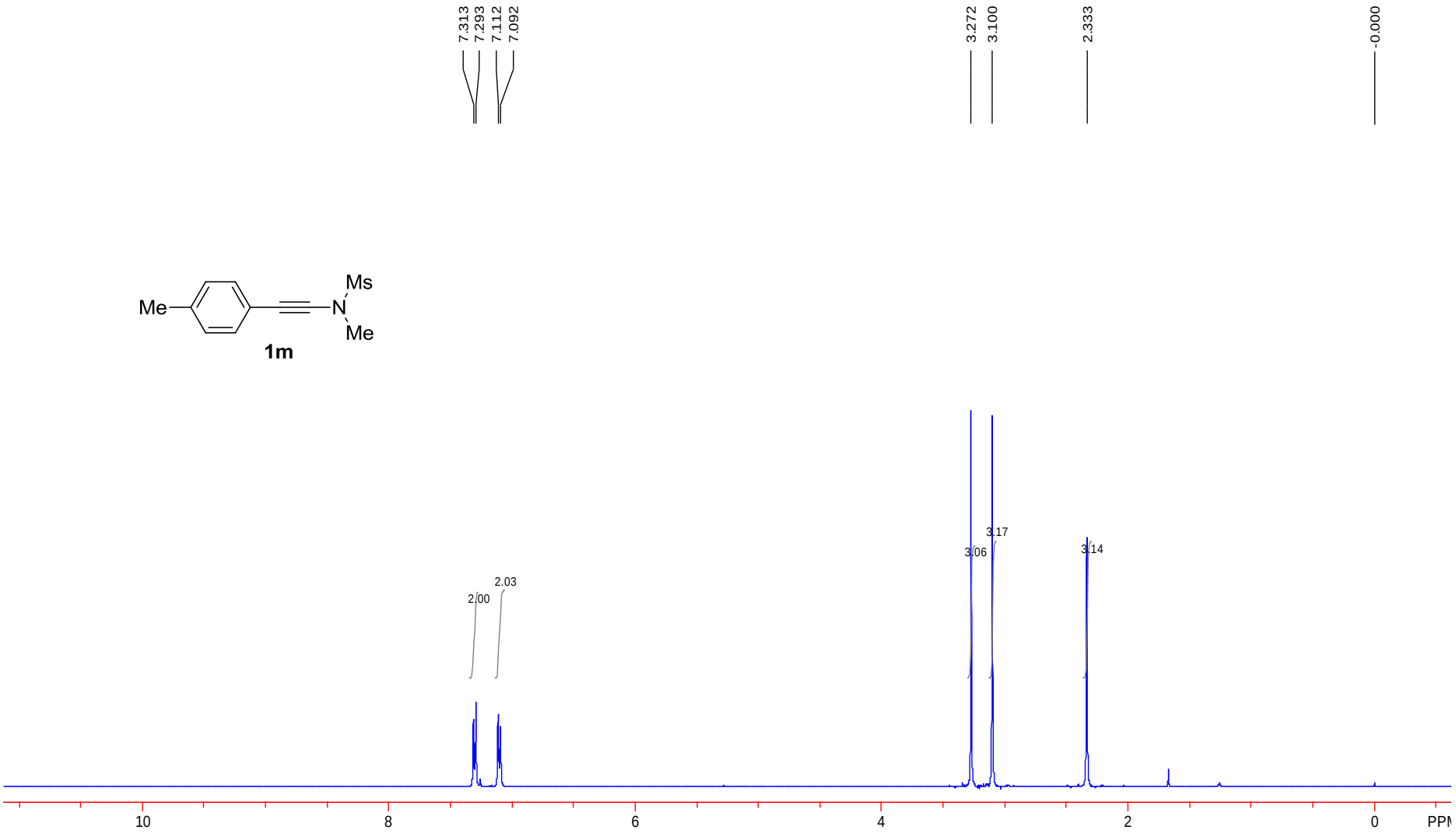


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

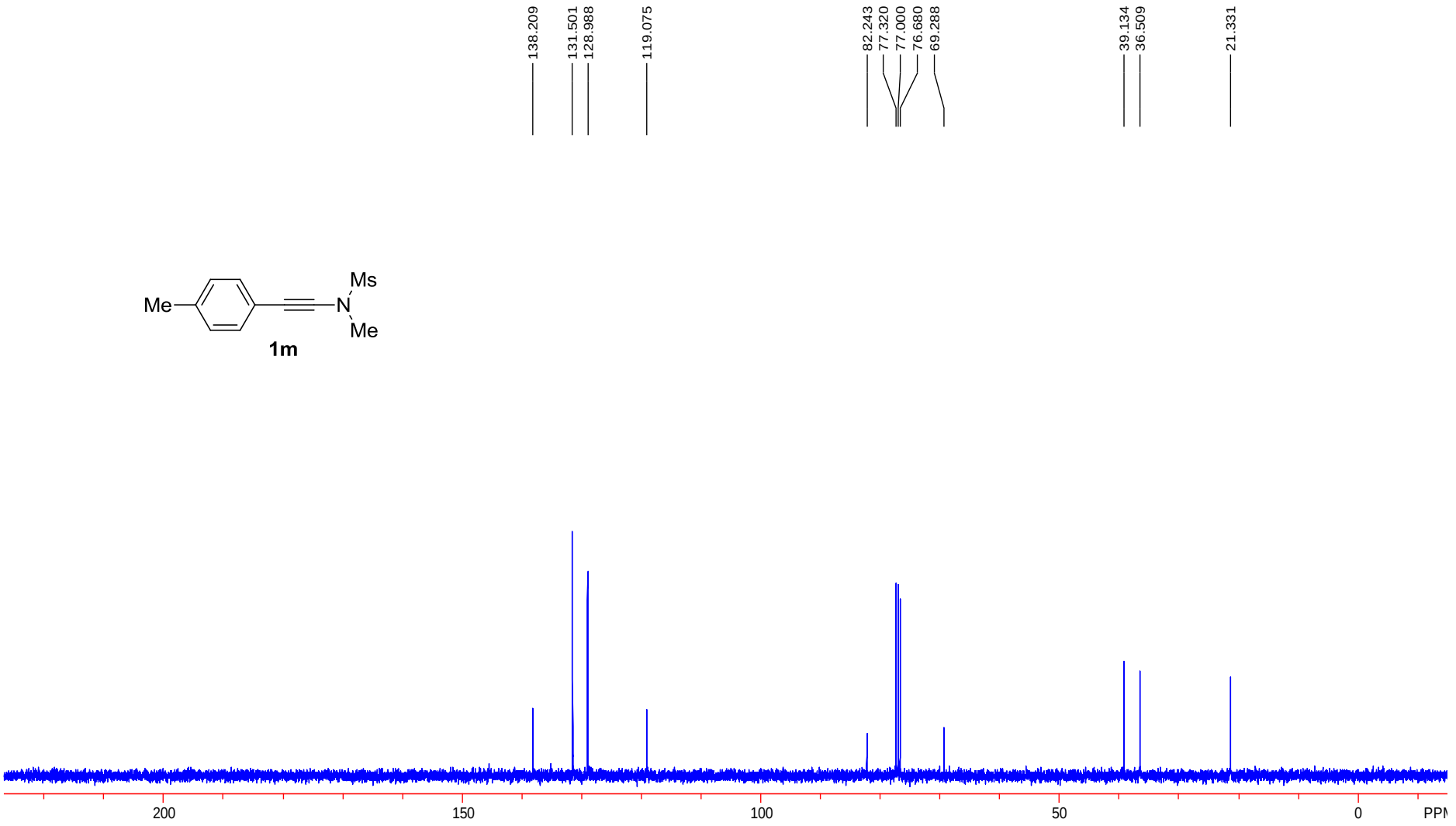



**1l**

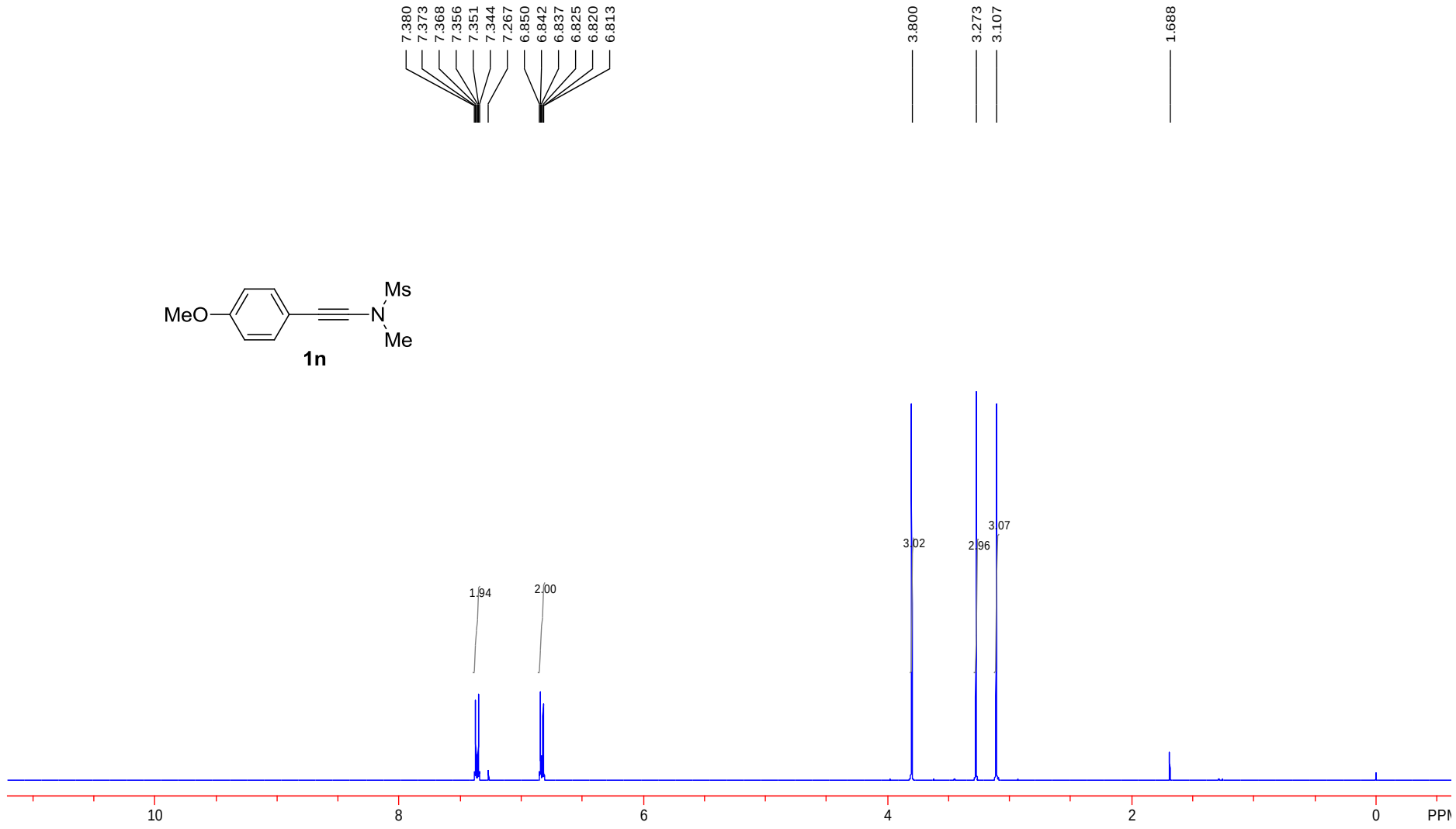
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



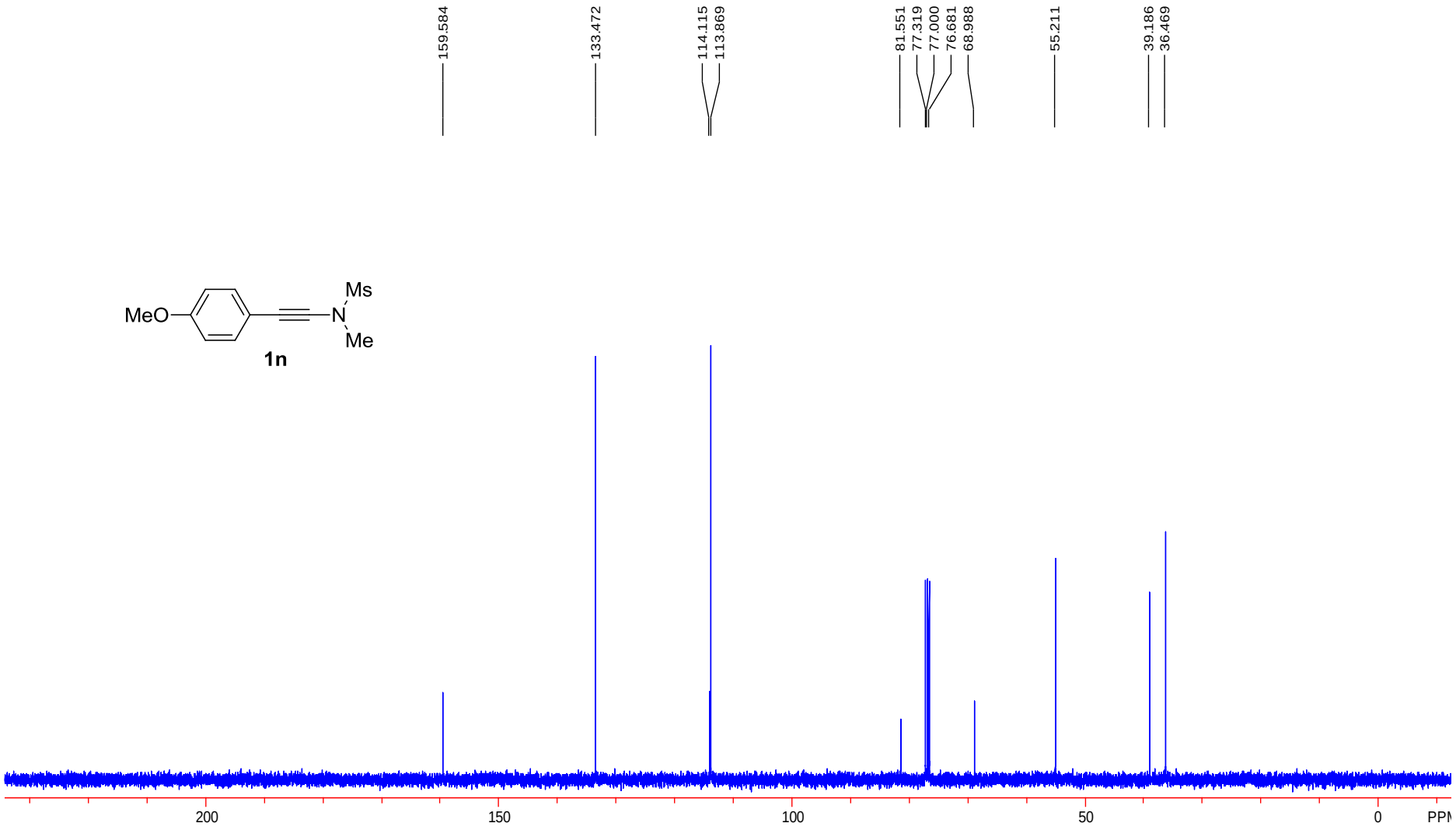
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



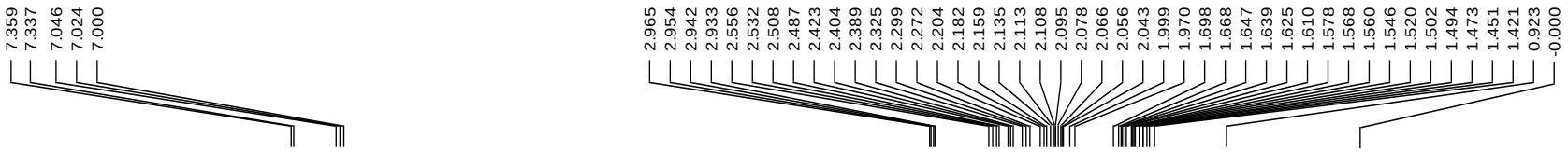
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

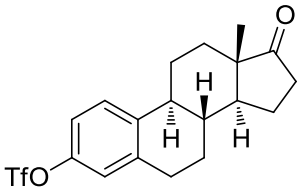


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

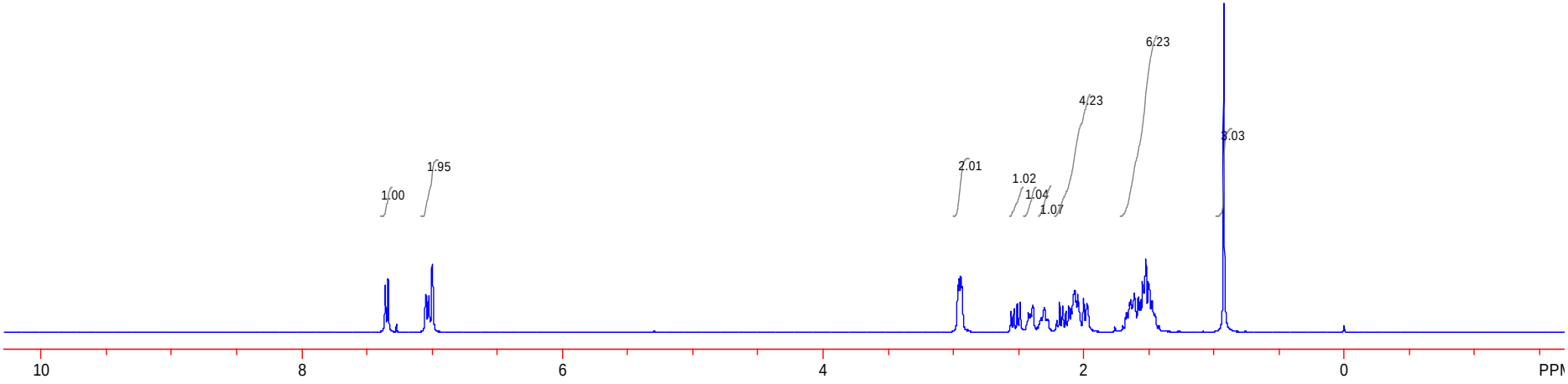


**$^{1}$H NMR (400 MHz, $CDCl_3$)**

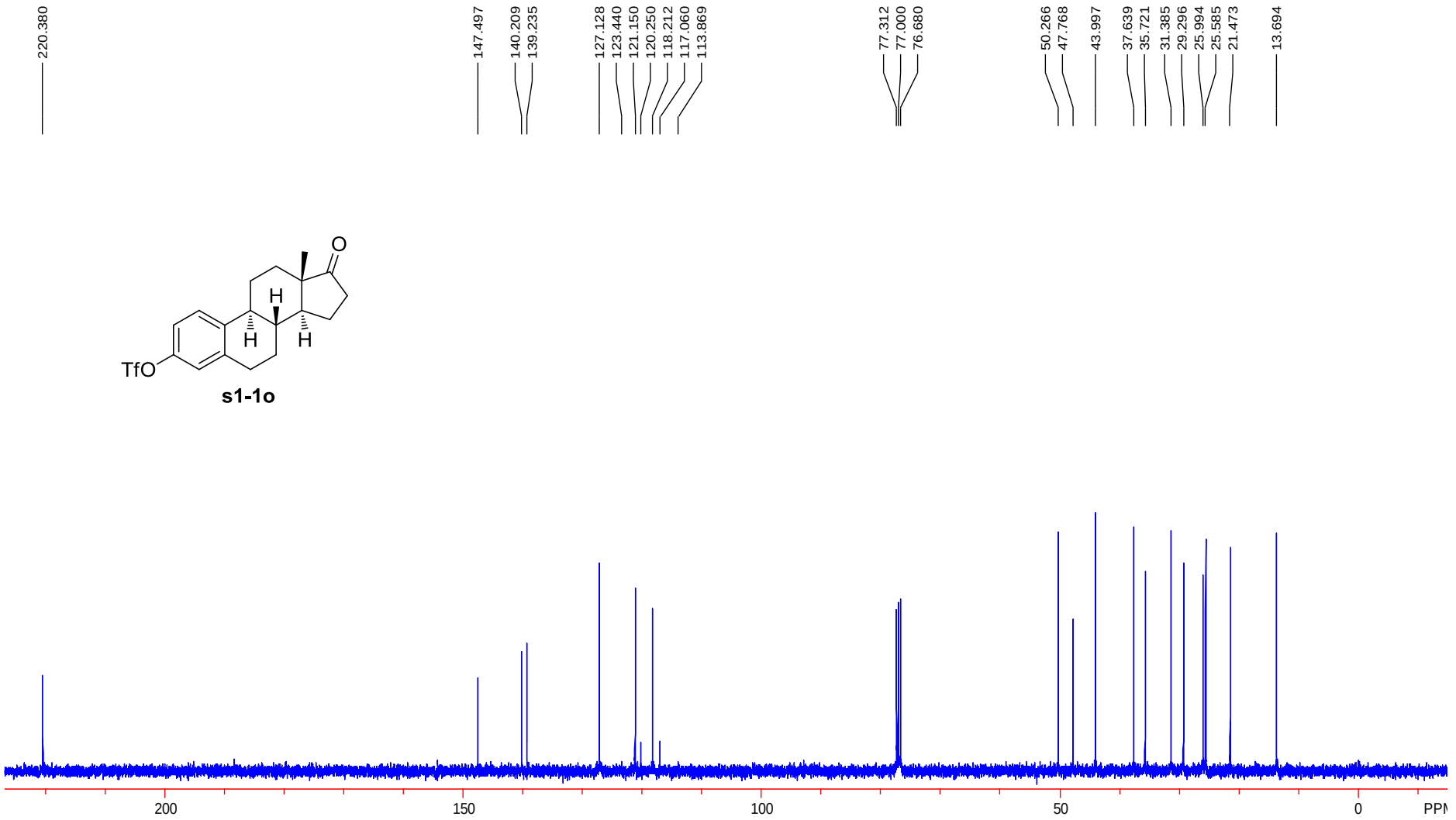



**s1-1o**

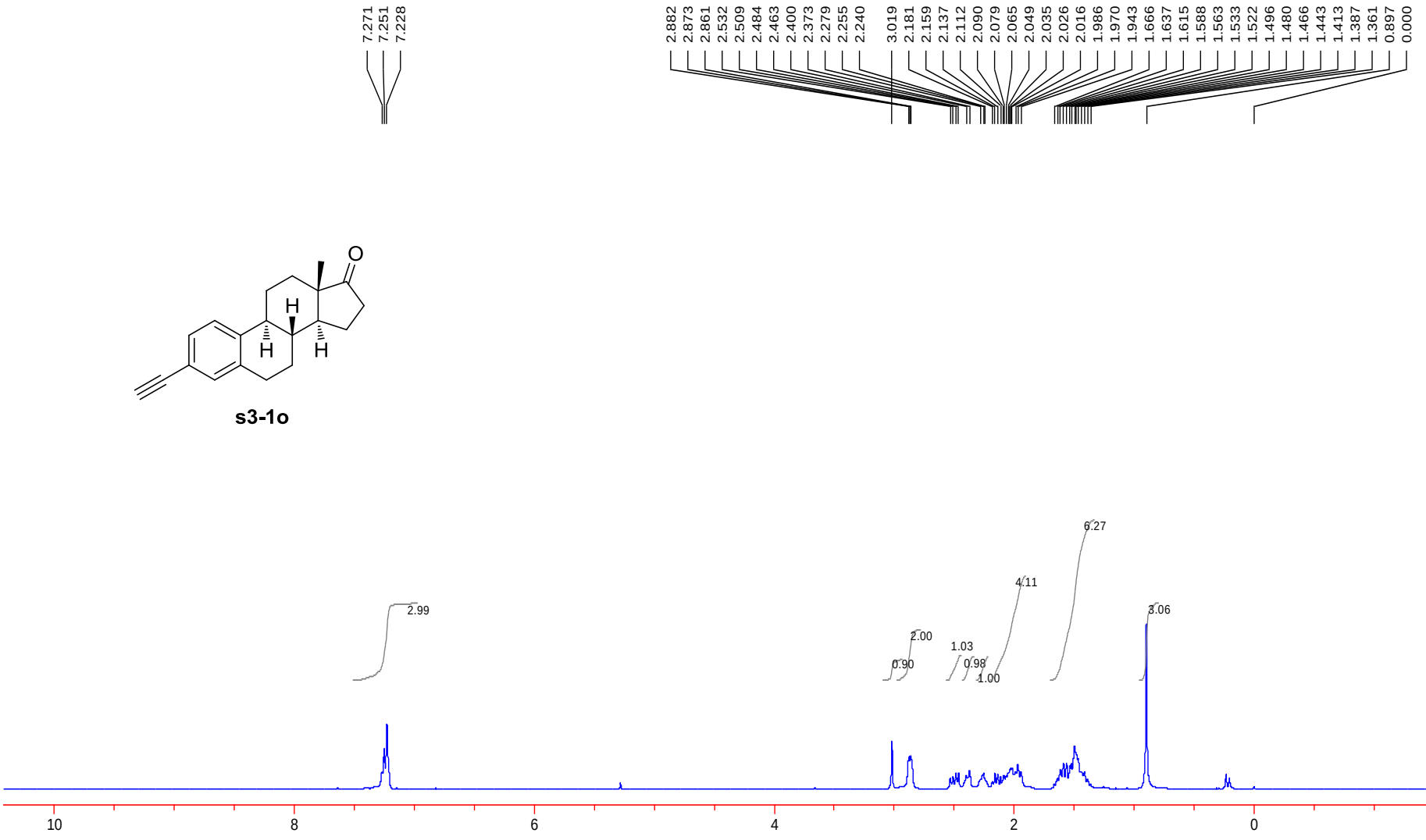


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

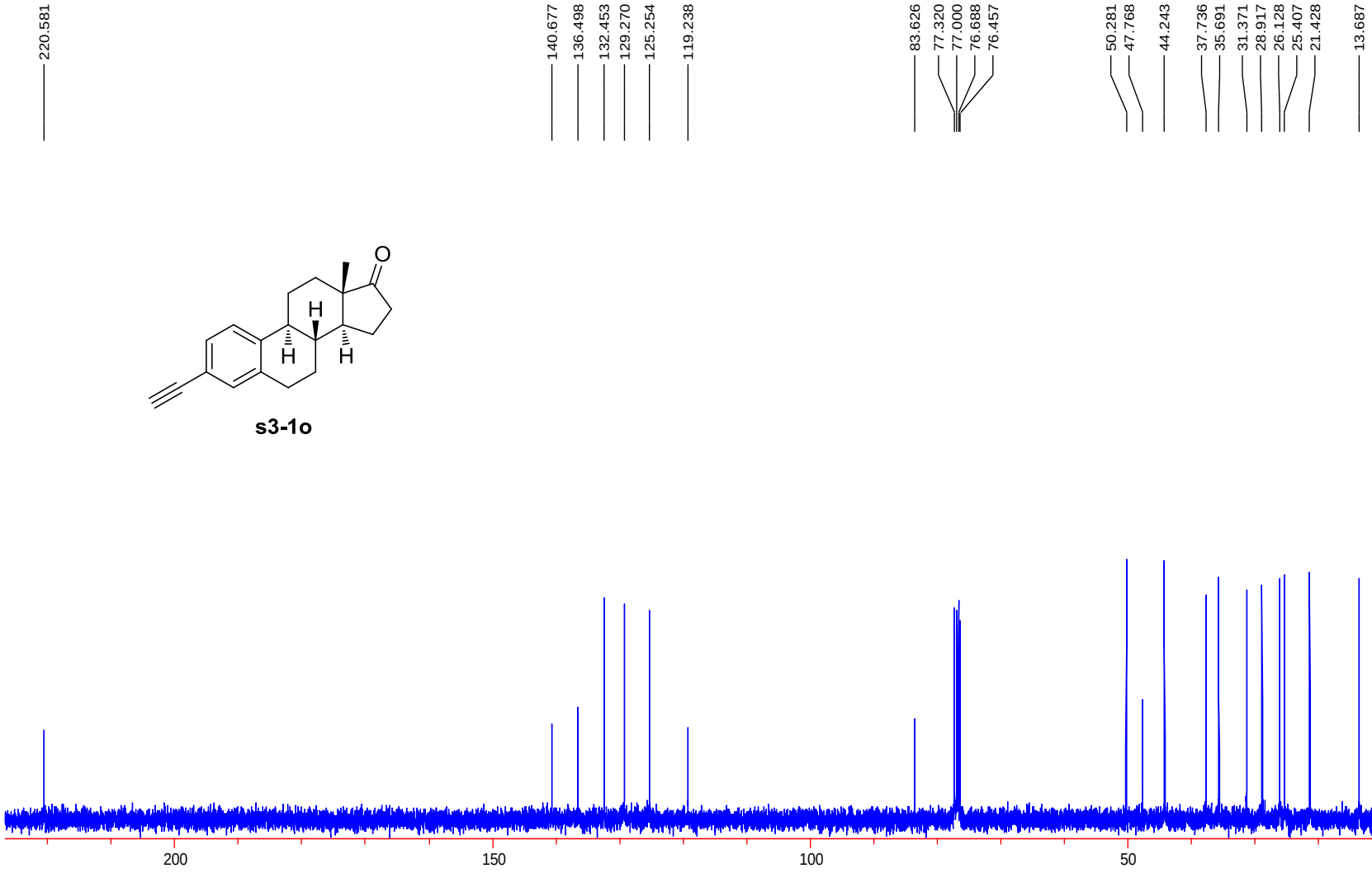



**s1-1o**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

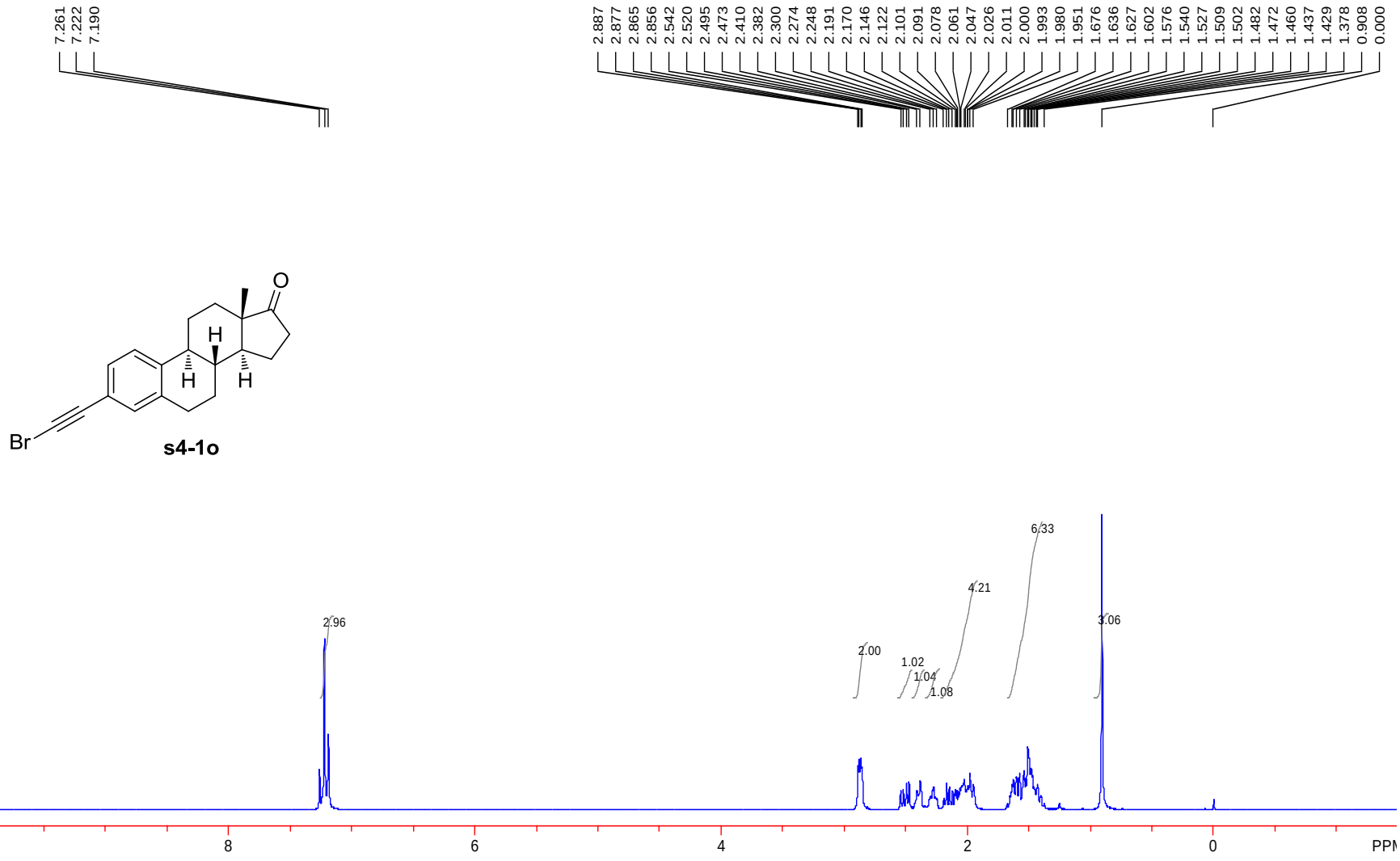


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

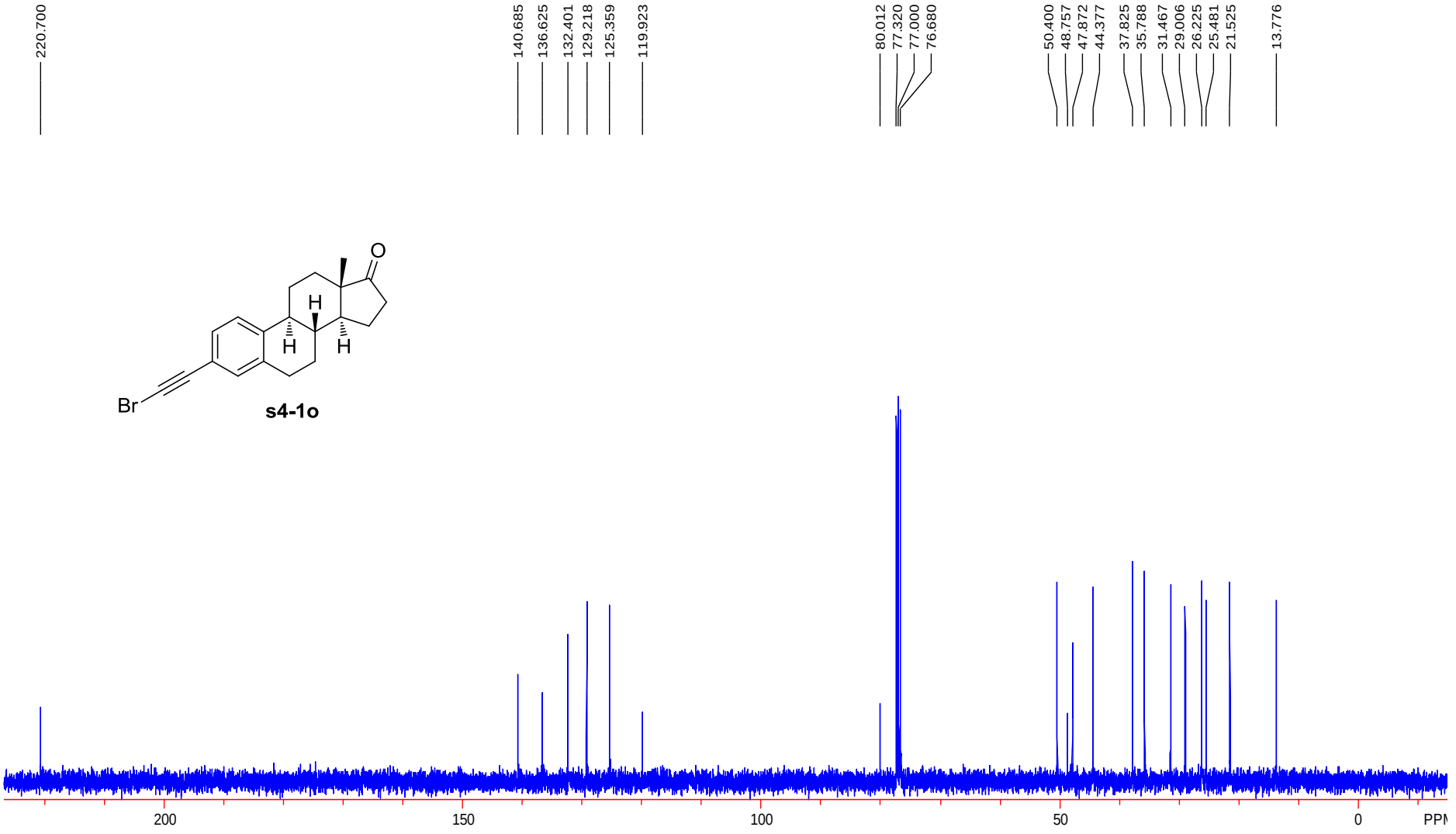



**s3-1o**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**



**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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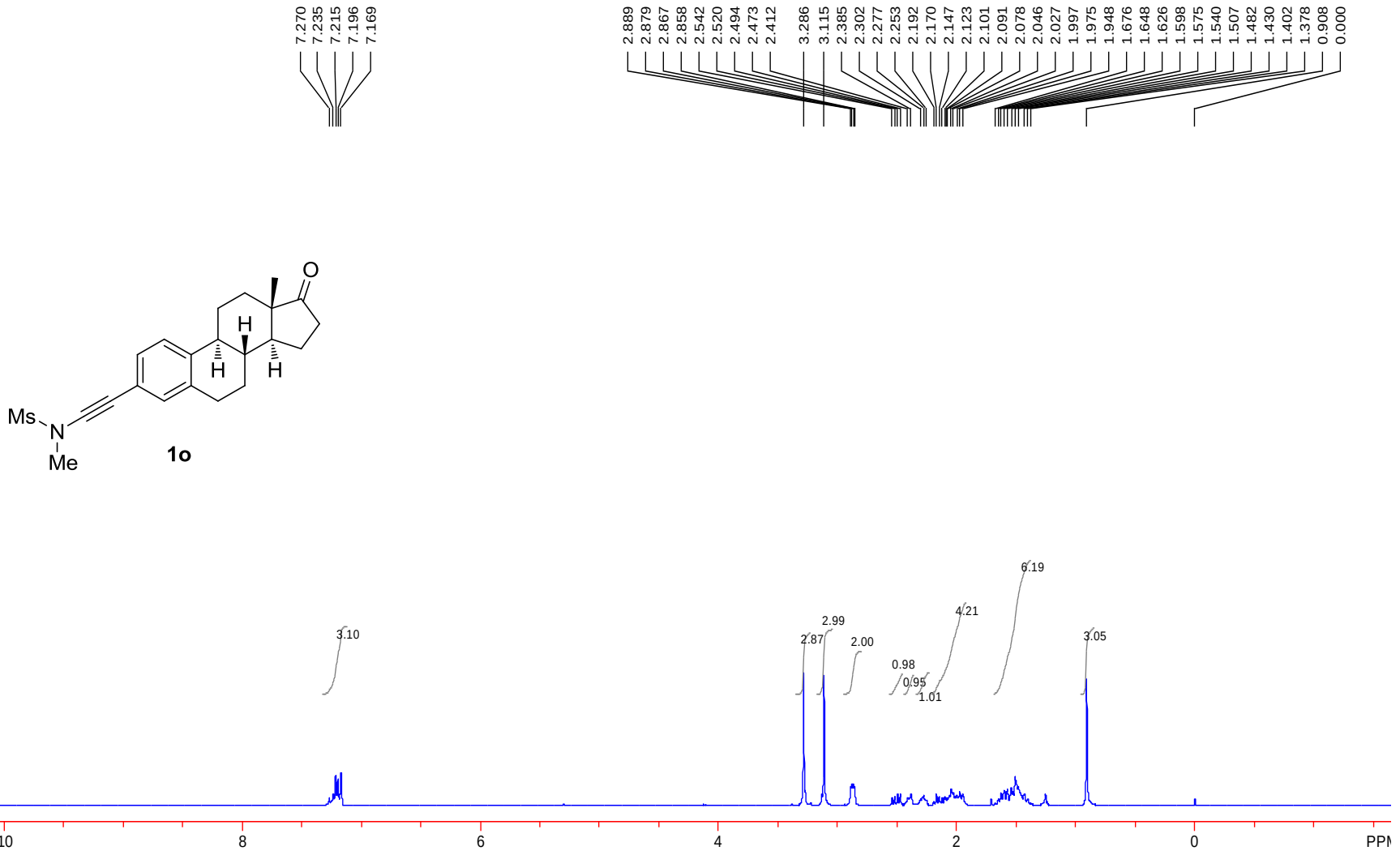
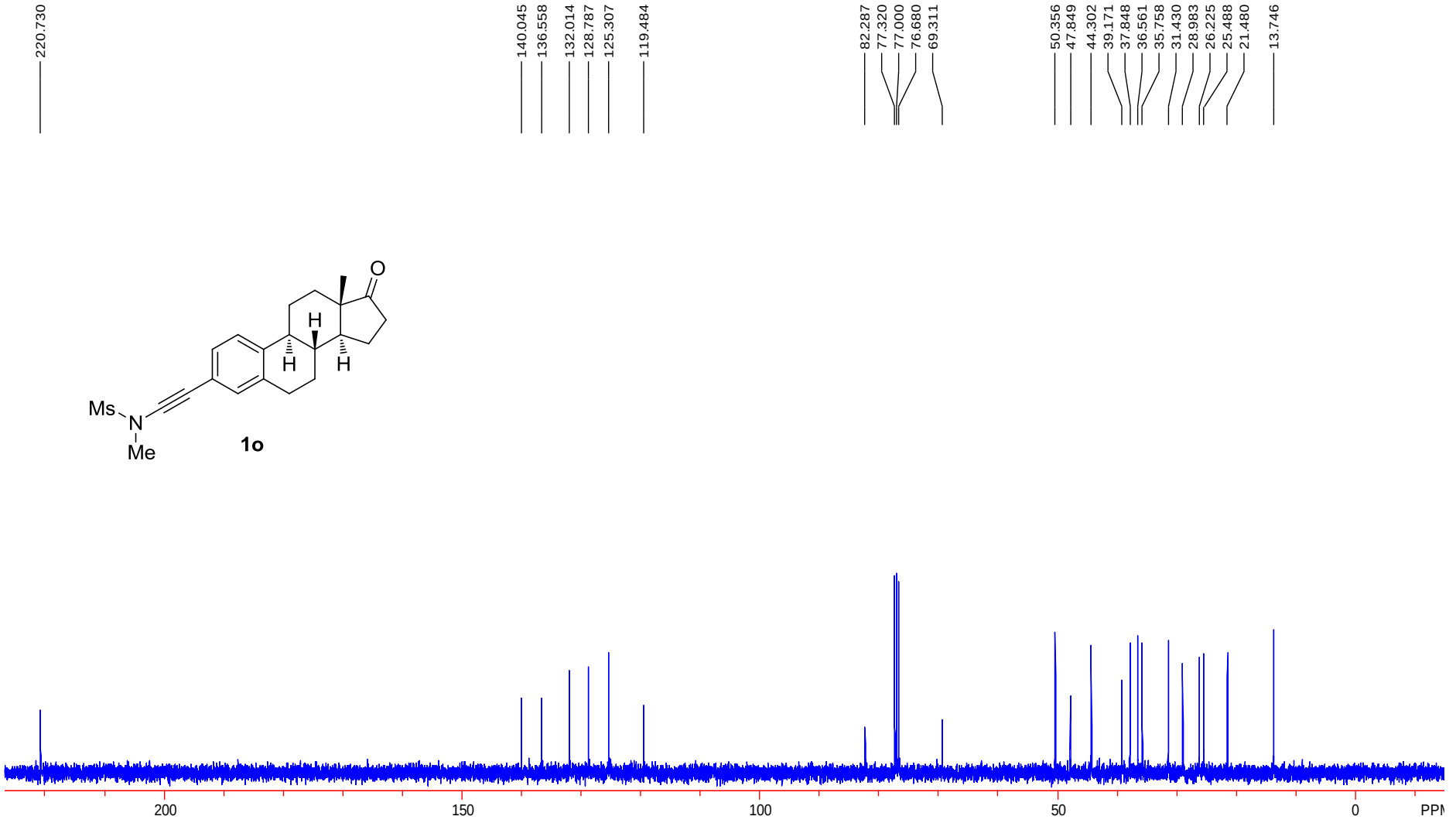


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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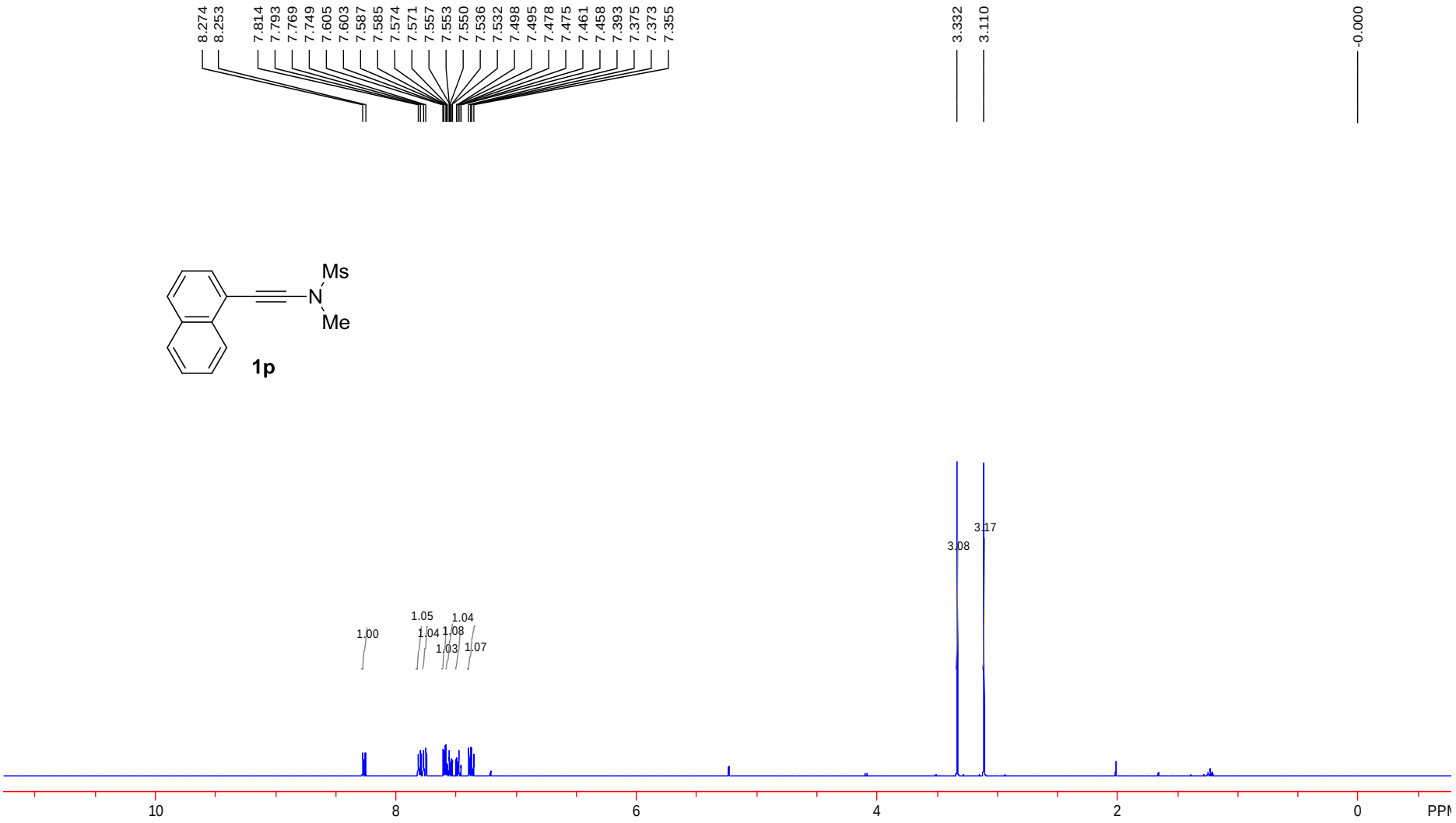

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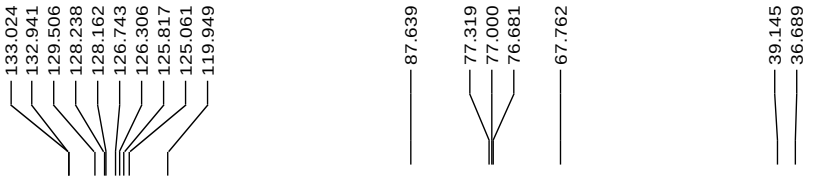


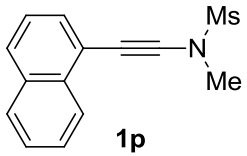


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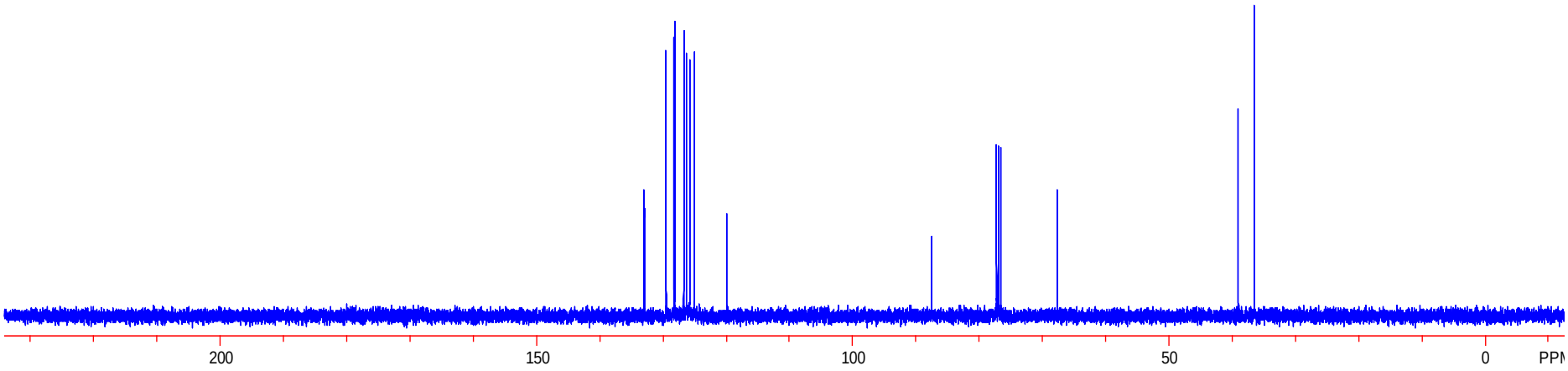
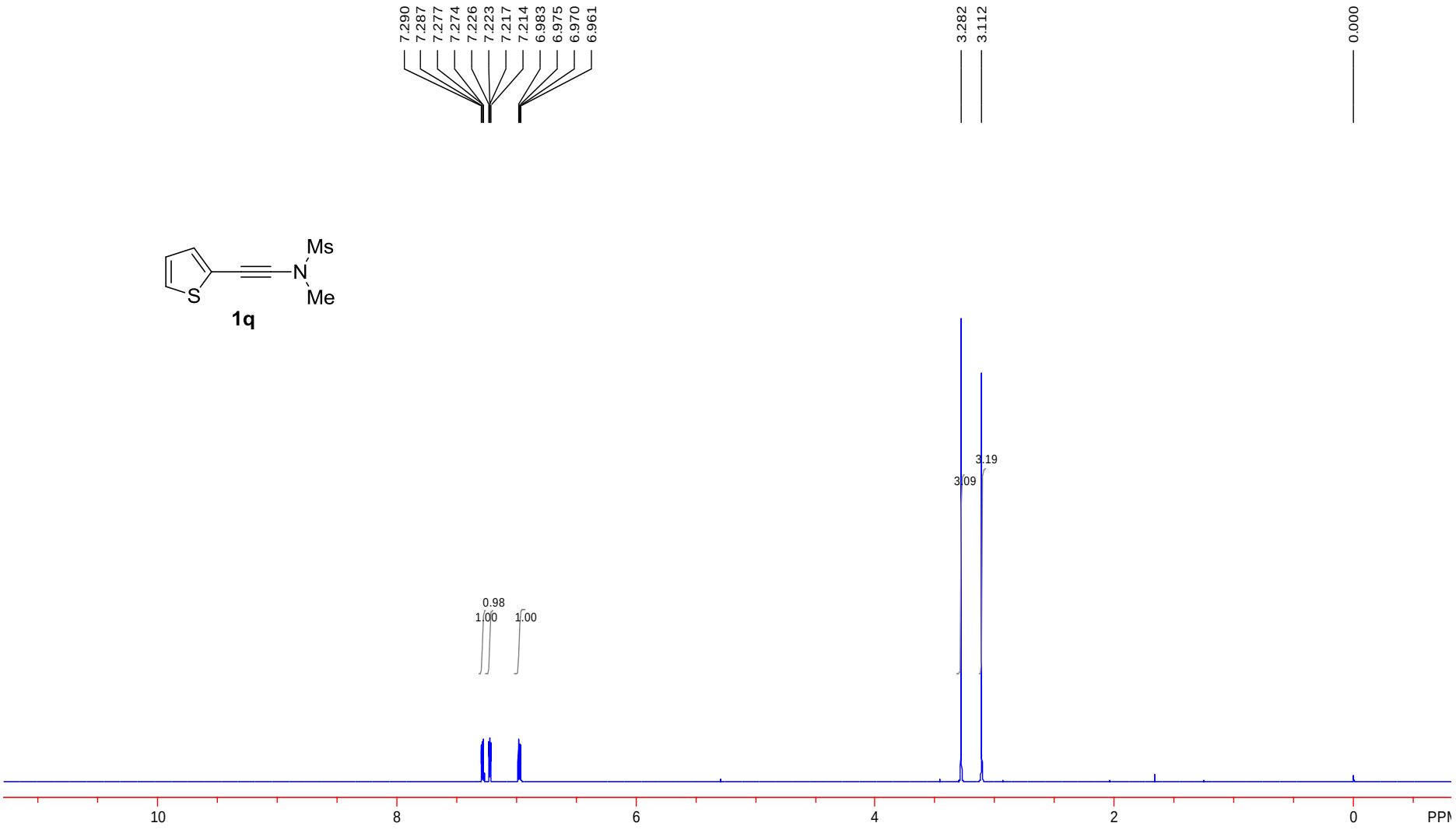
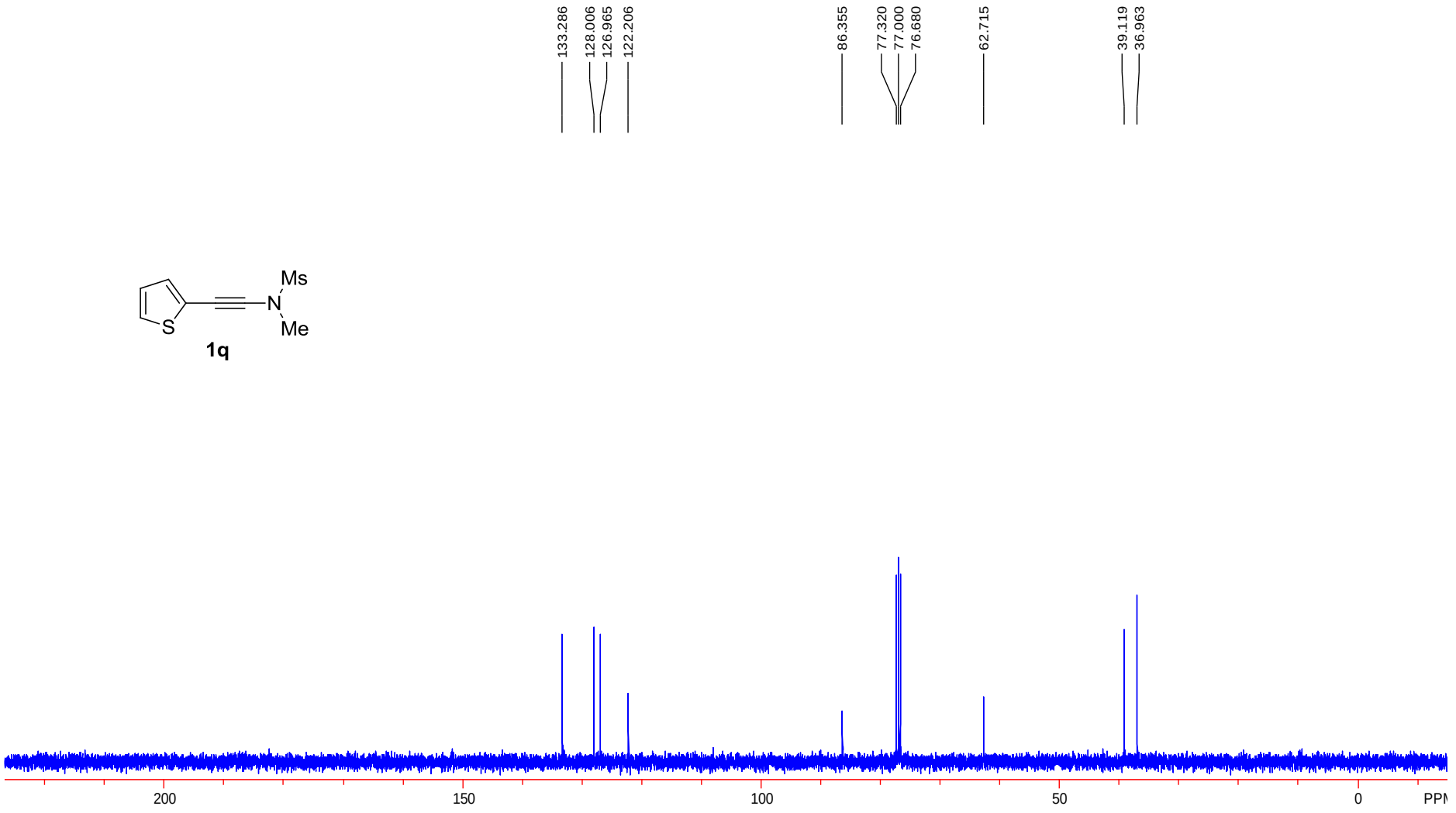


**$^{1}$H NMR (400 MHz, $CDCl_3$)**



**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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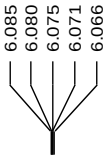


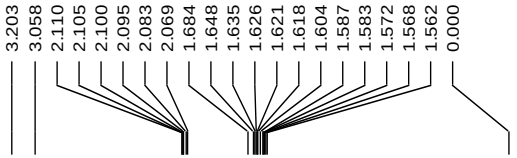


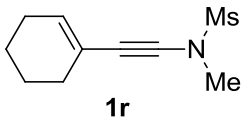


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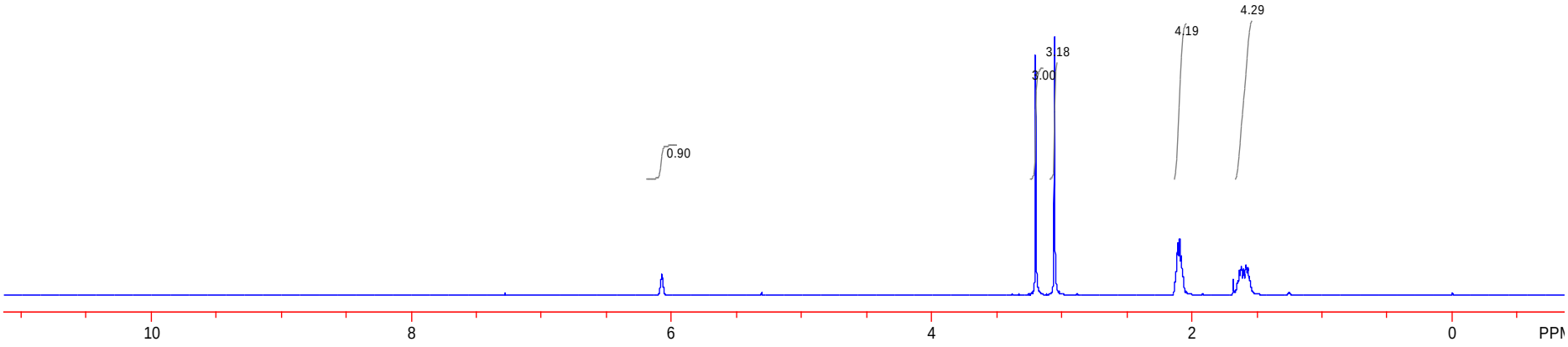
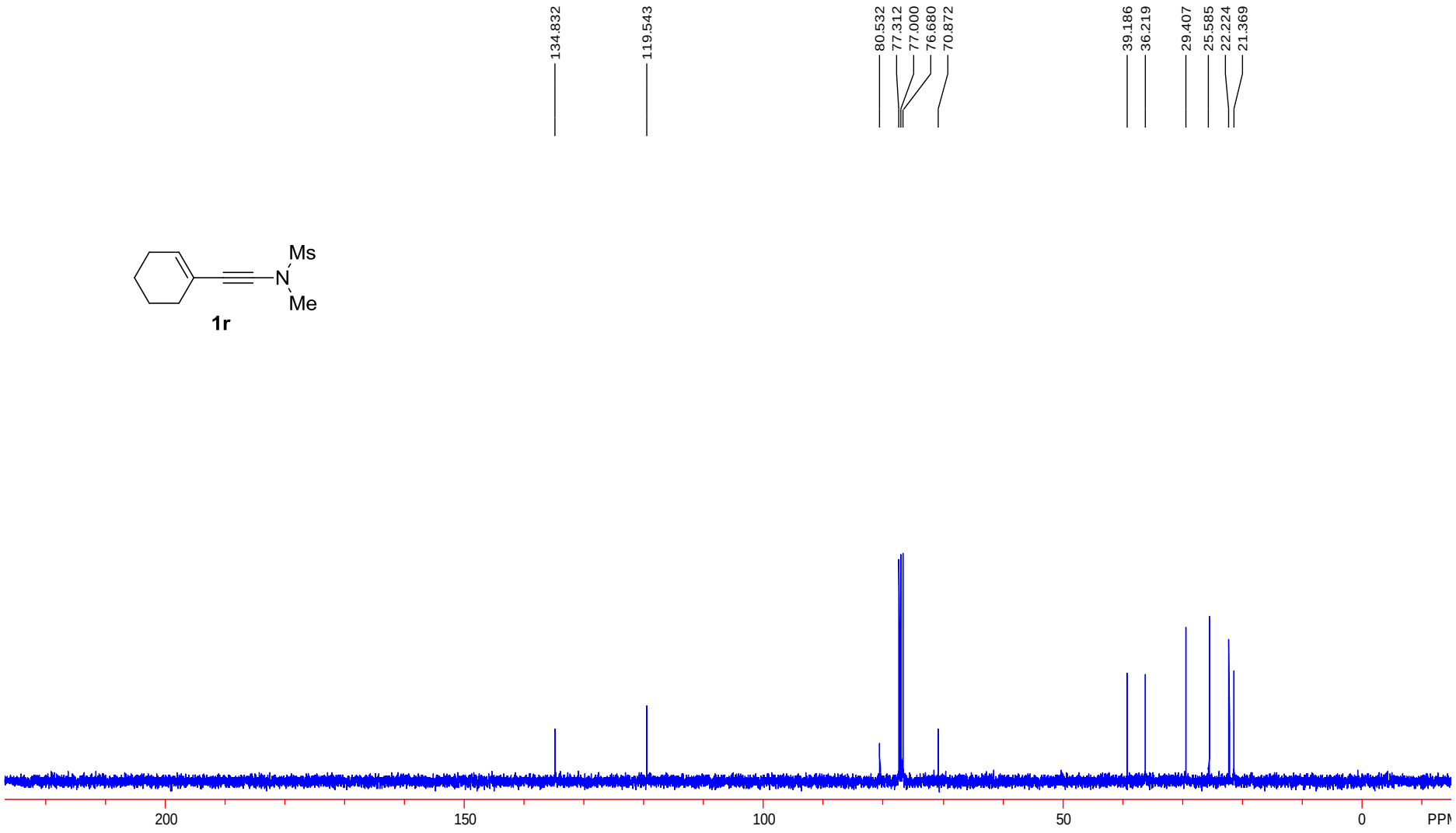
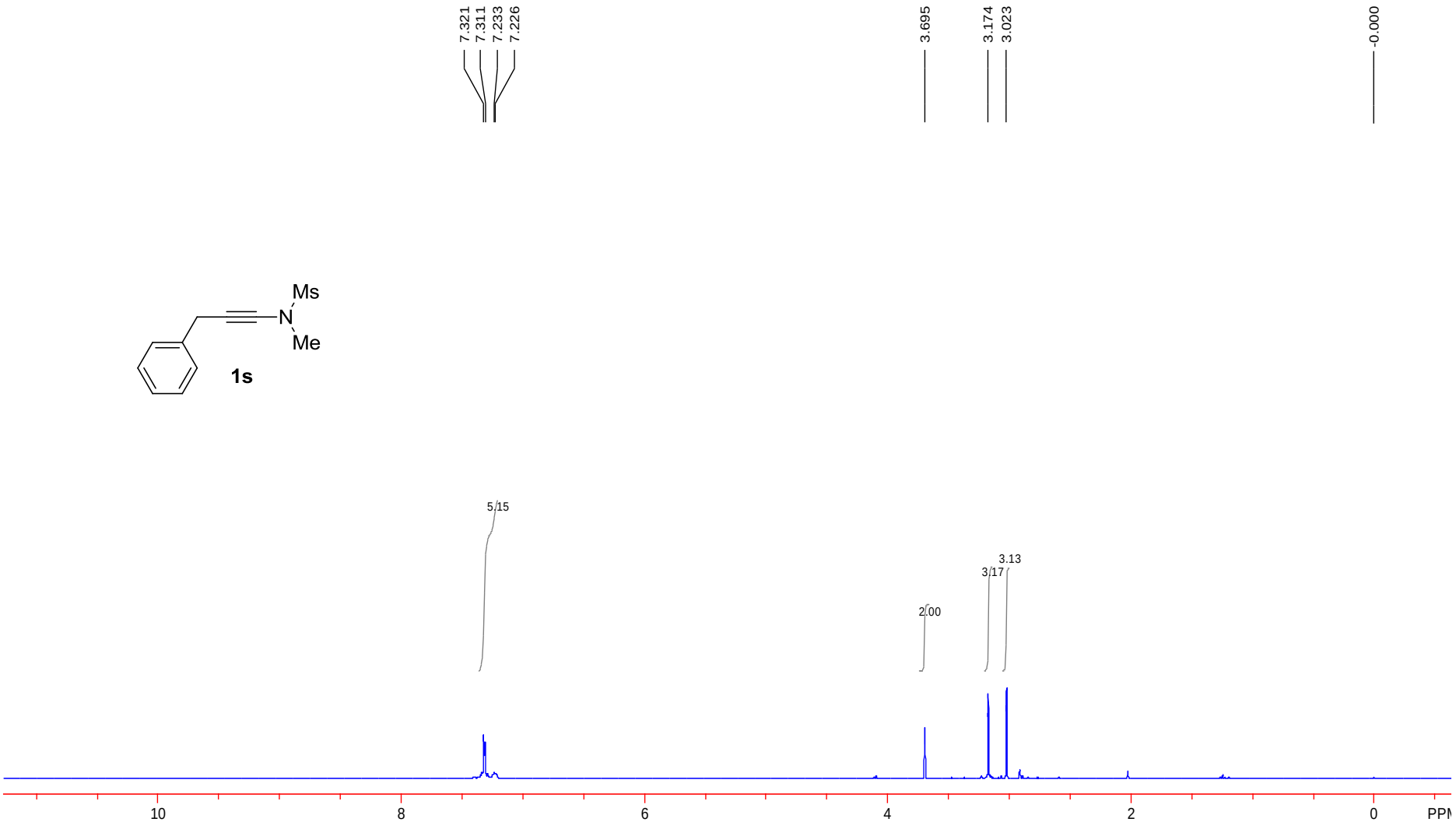


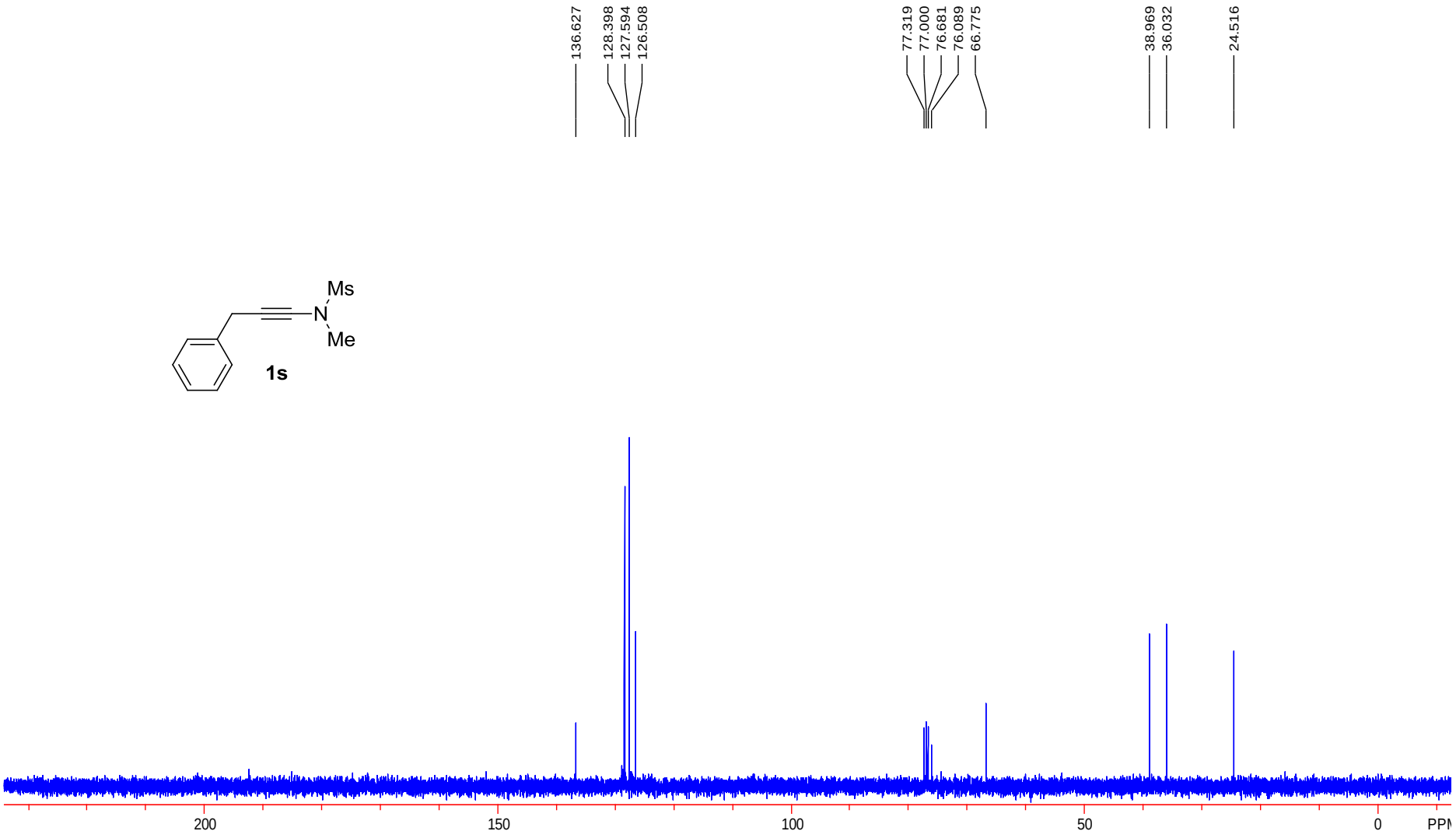
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



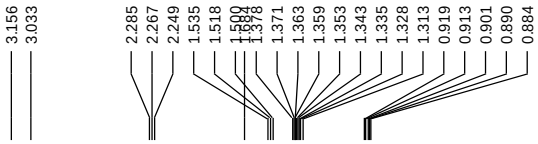
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

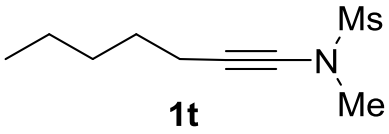


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^1$H NMR (400 MHz, $CDCl_3$)**

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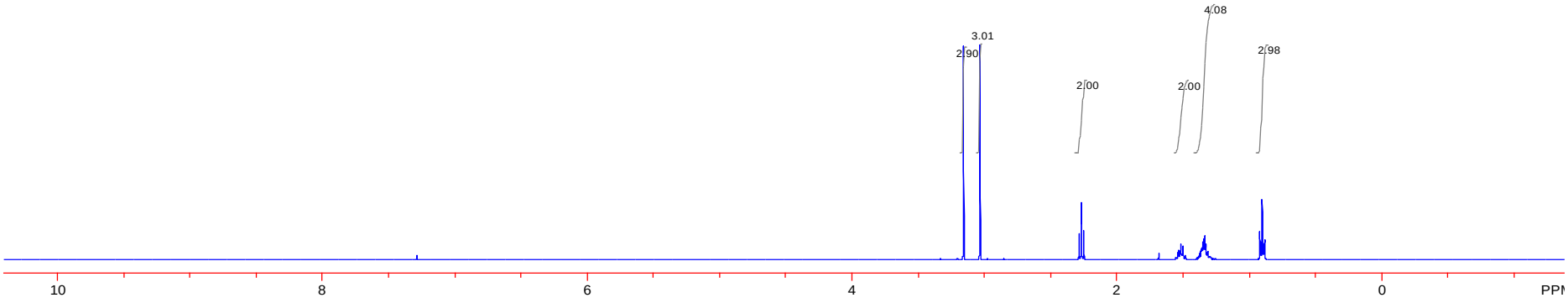
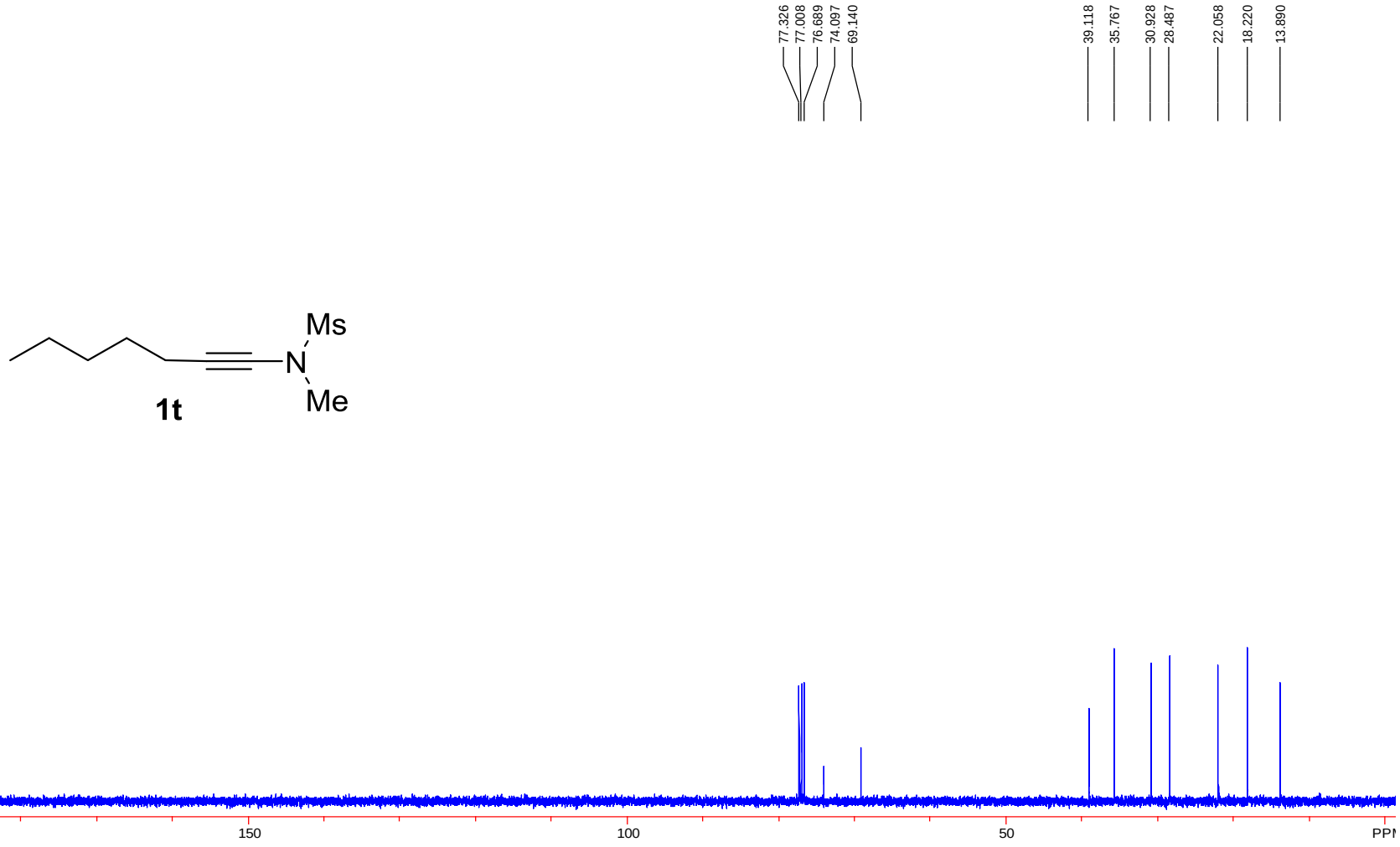


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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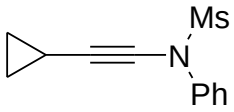


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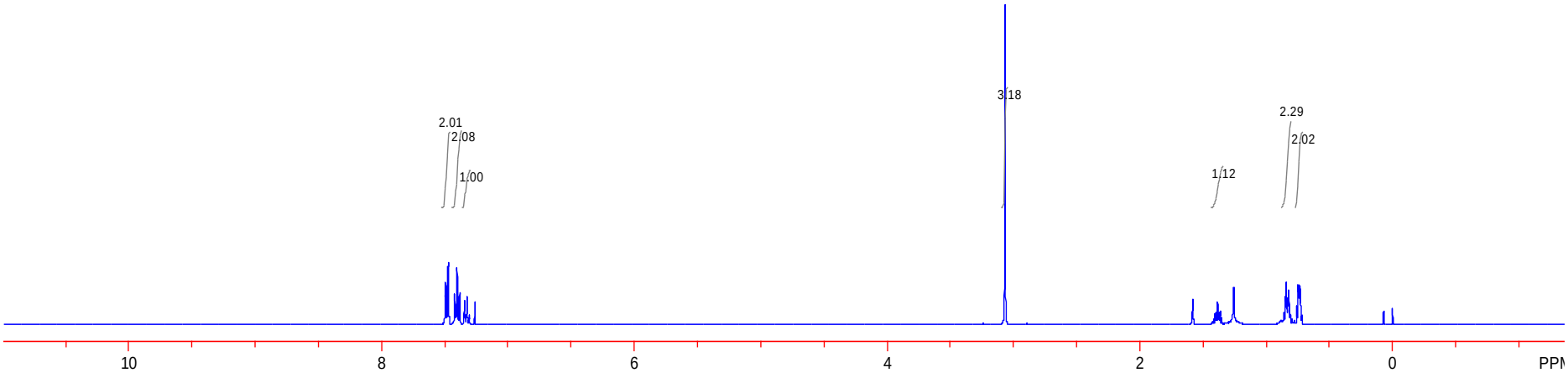
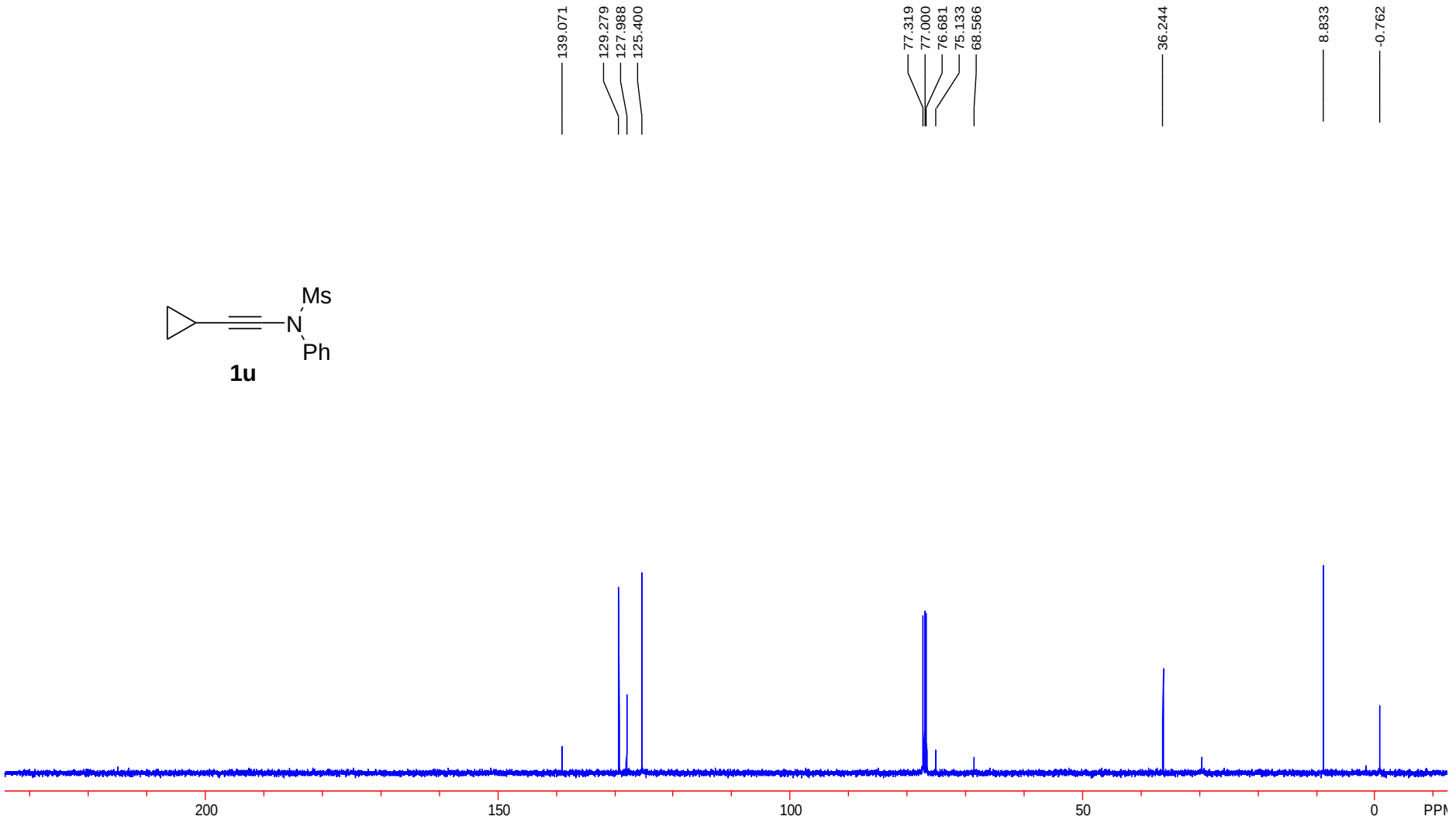
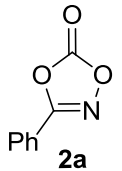


**$^{13}$C NMR (100 MHz, $CDCl_3$)**




**1u**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**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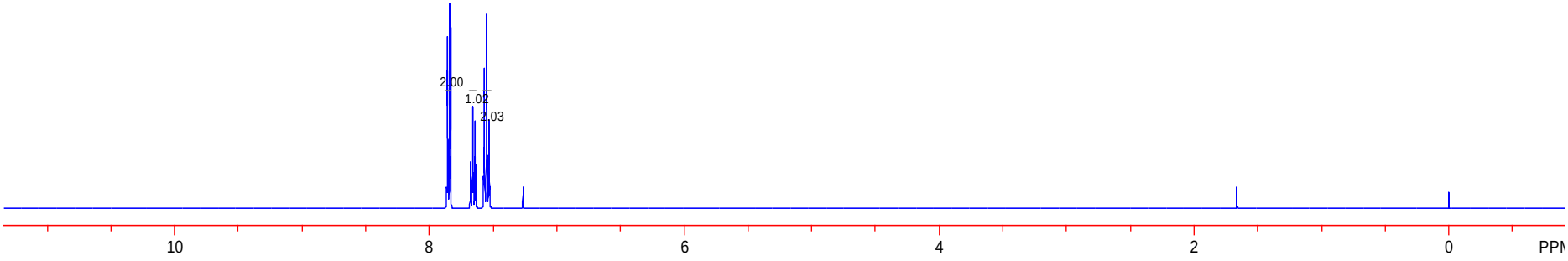
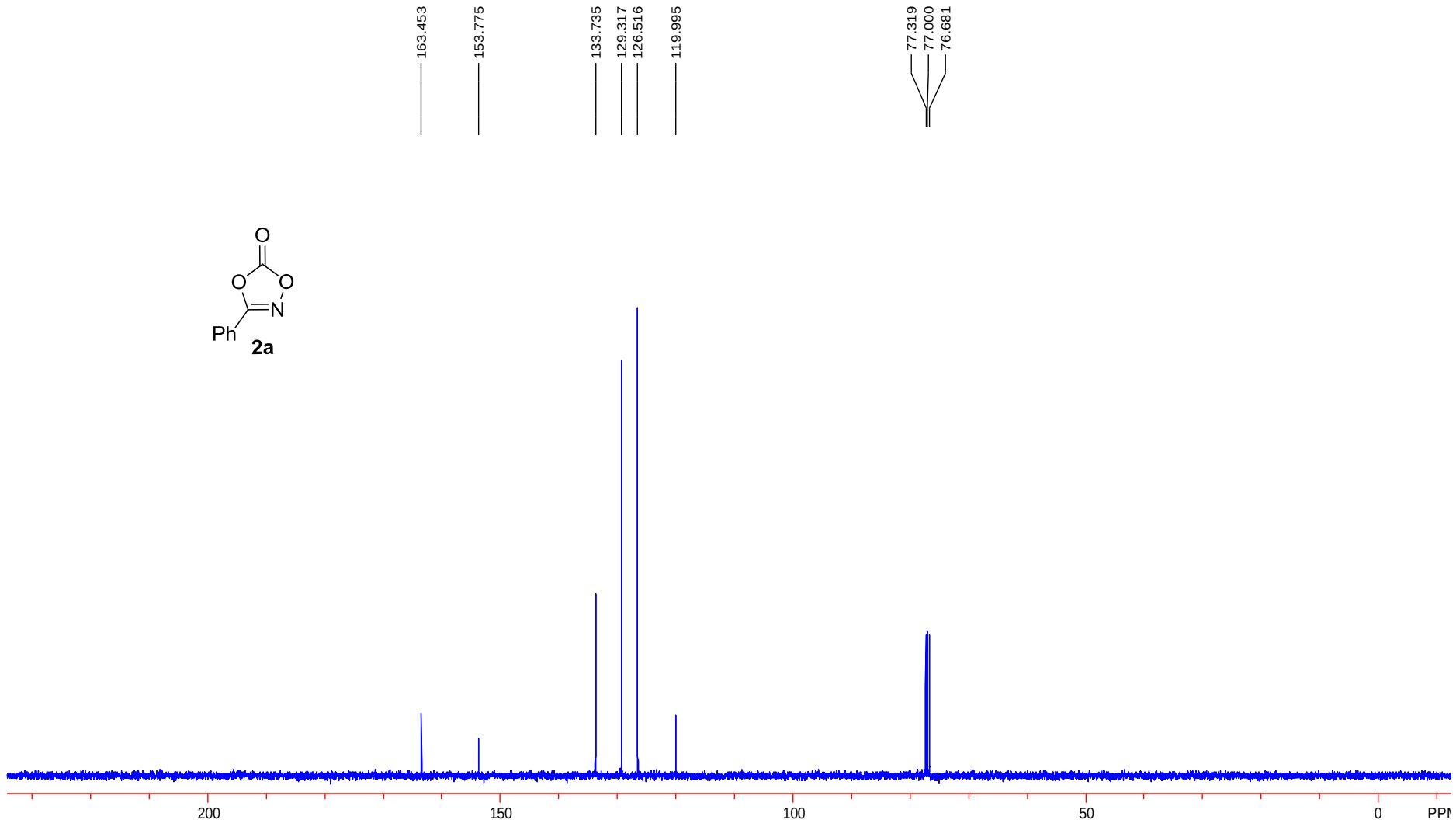
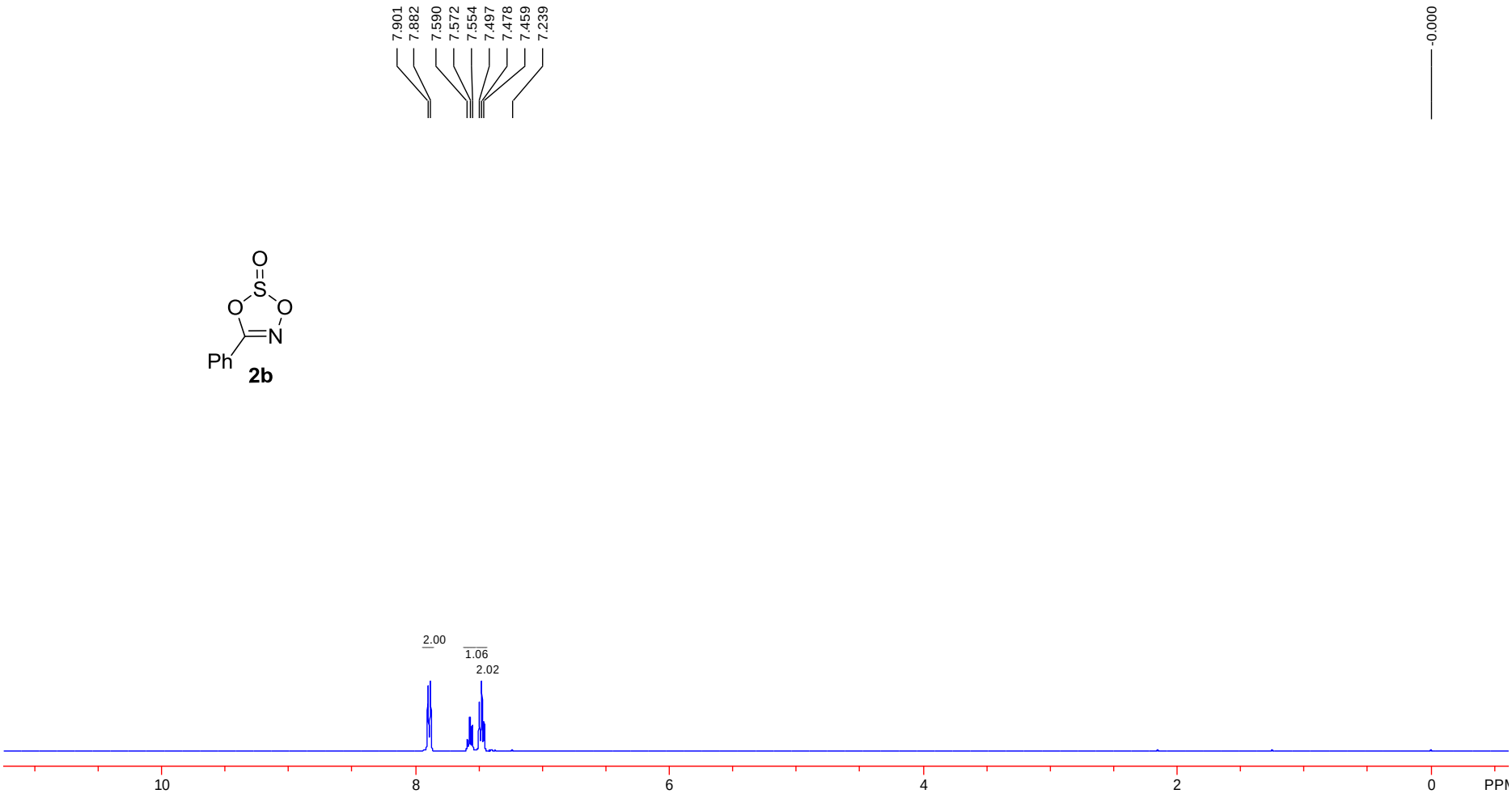


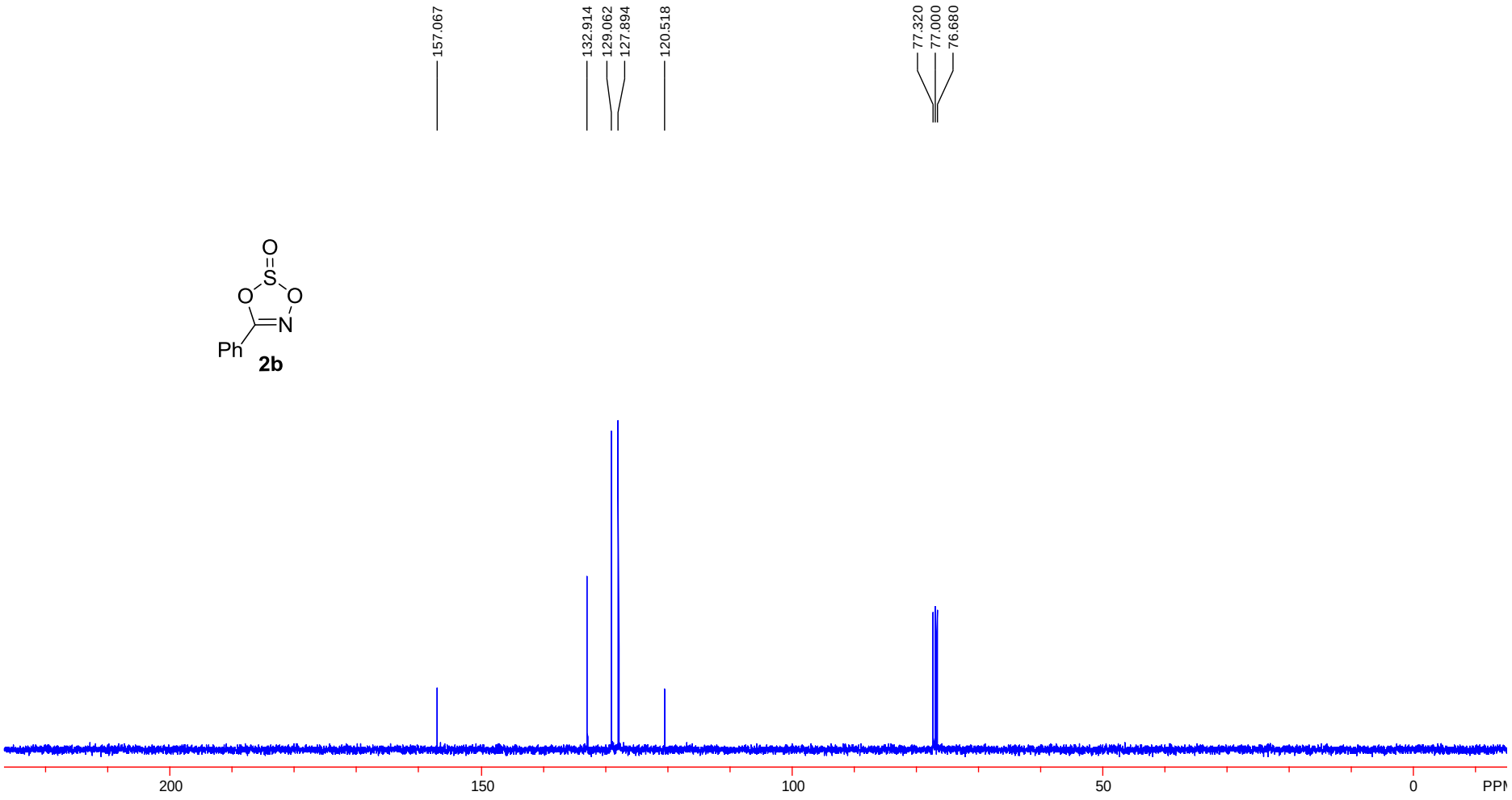
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**



**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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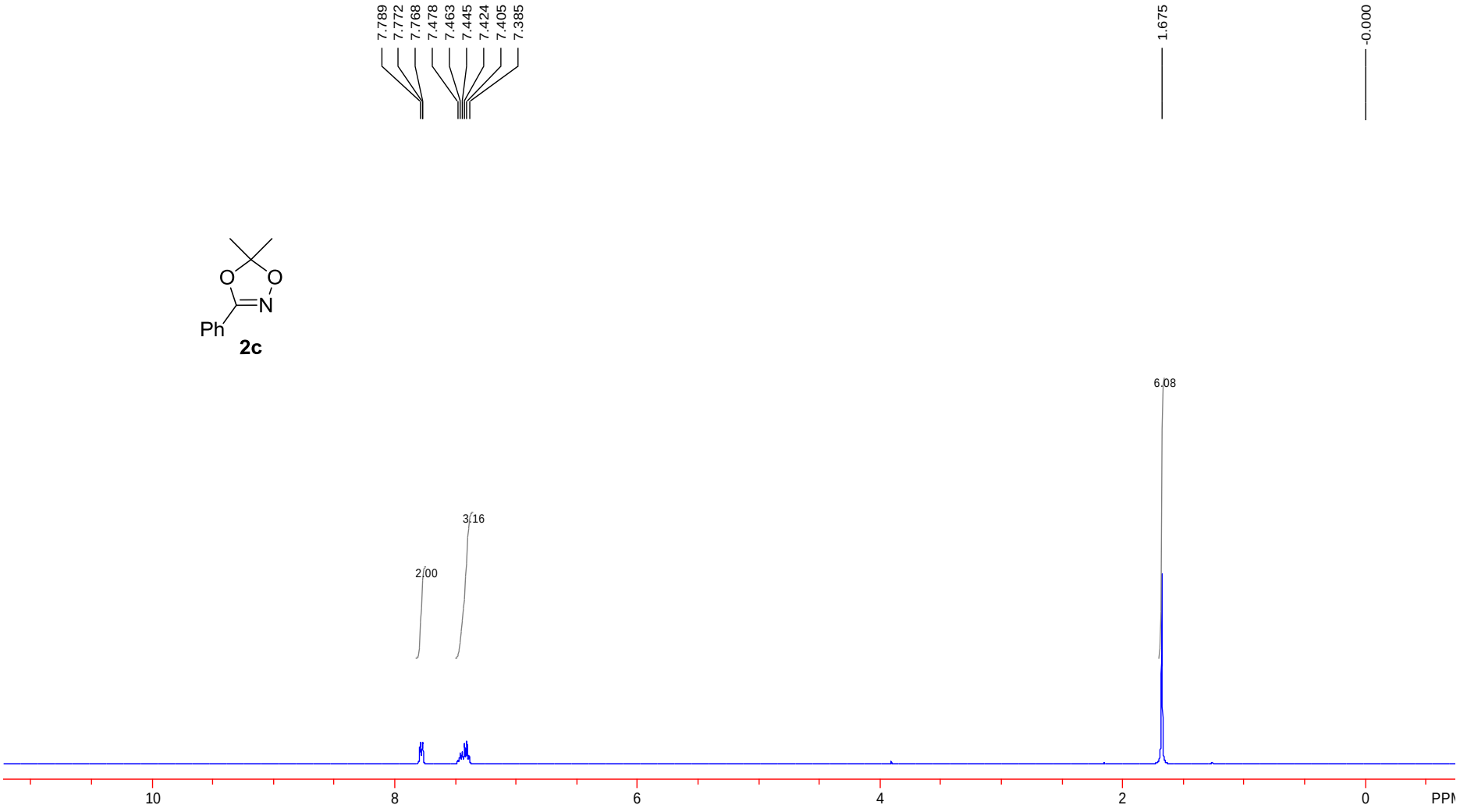
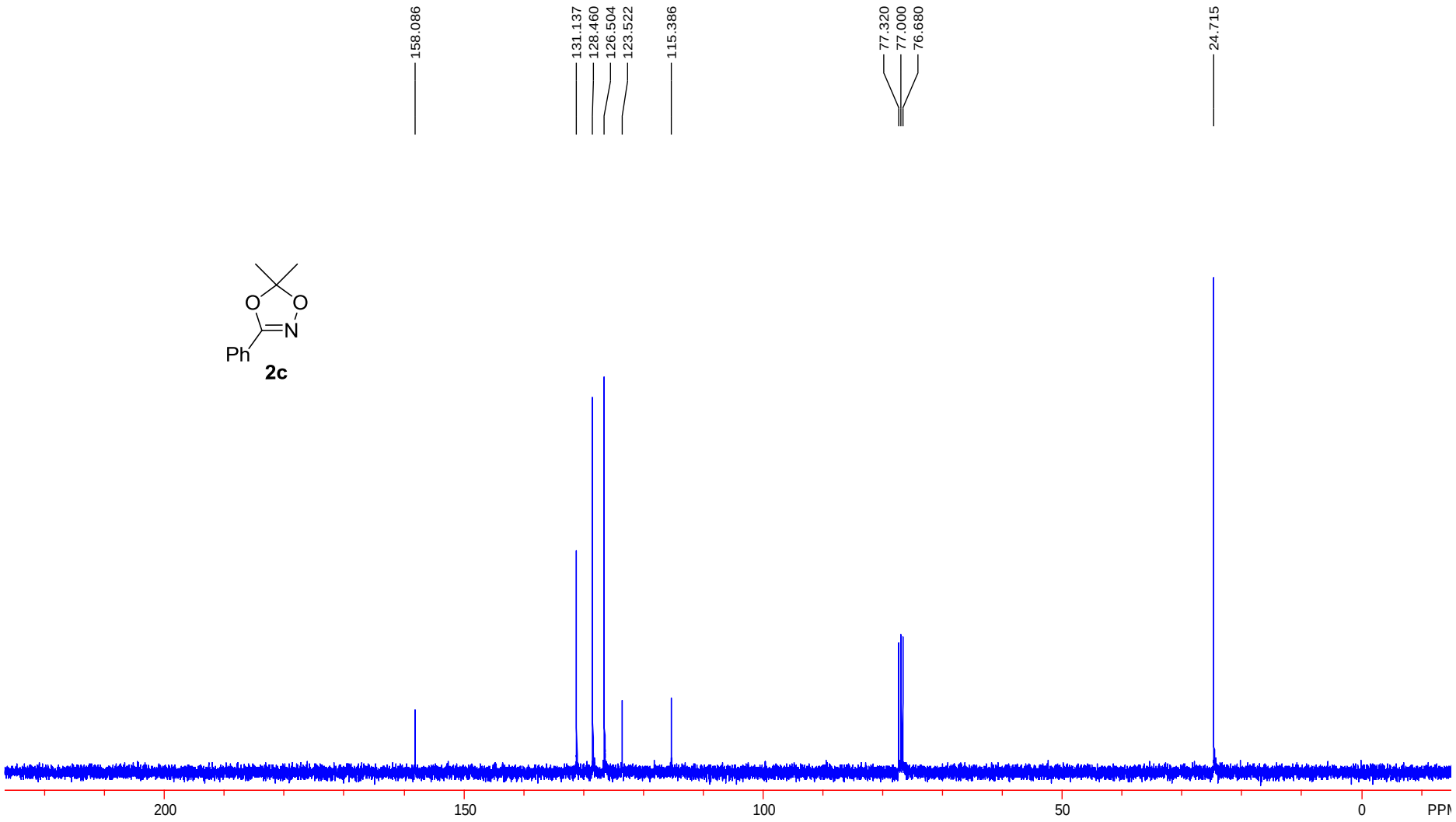
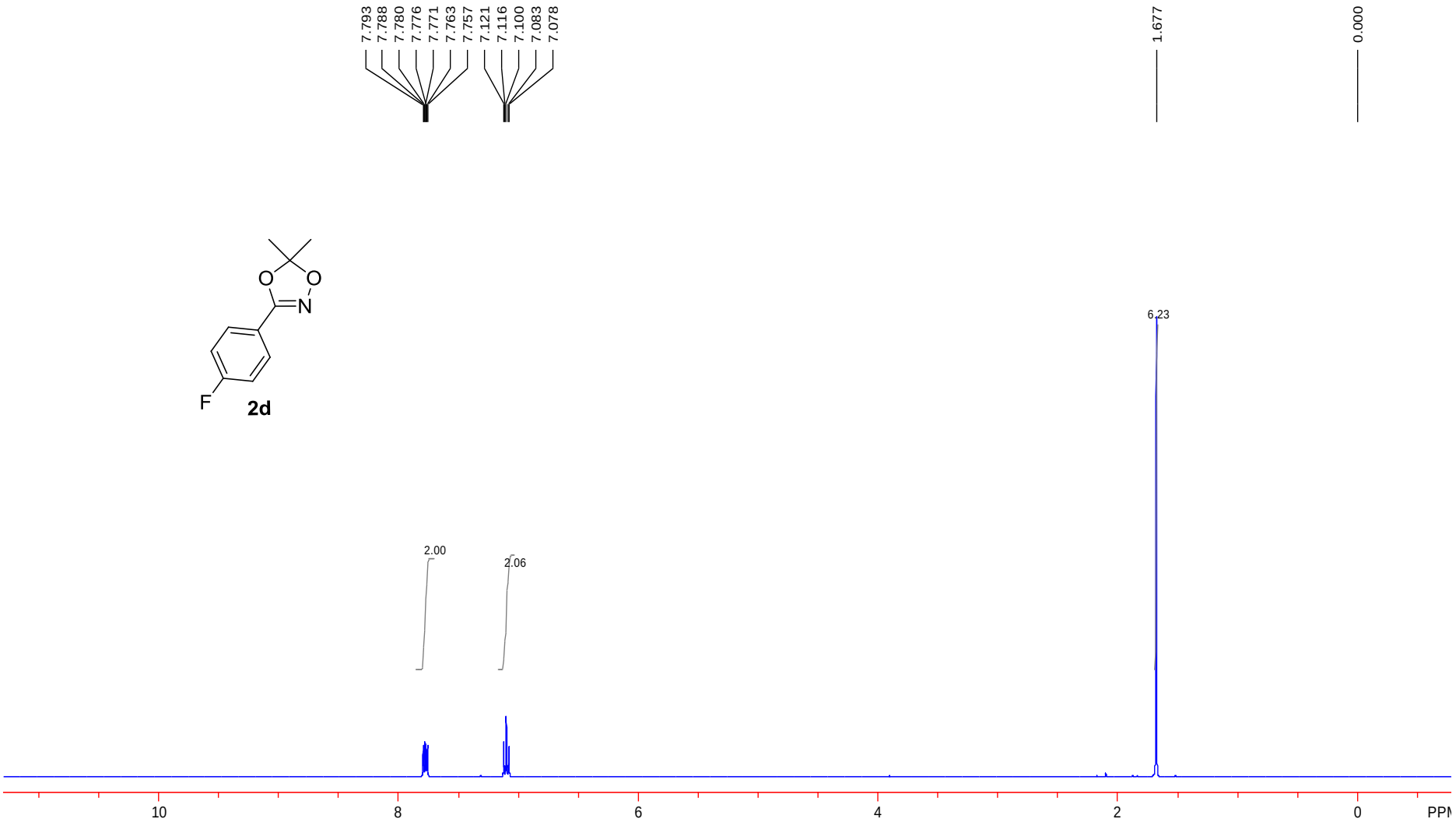


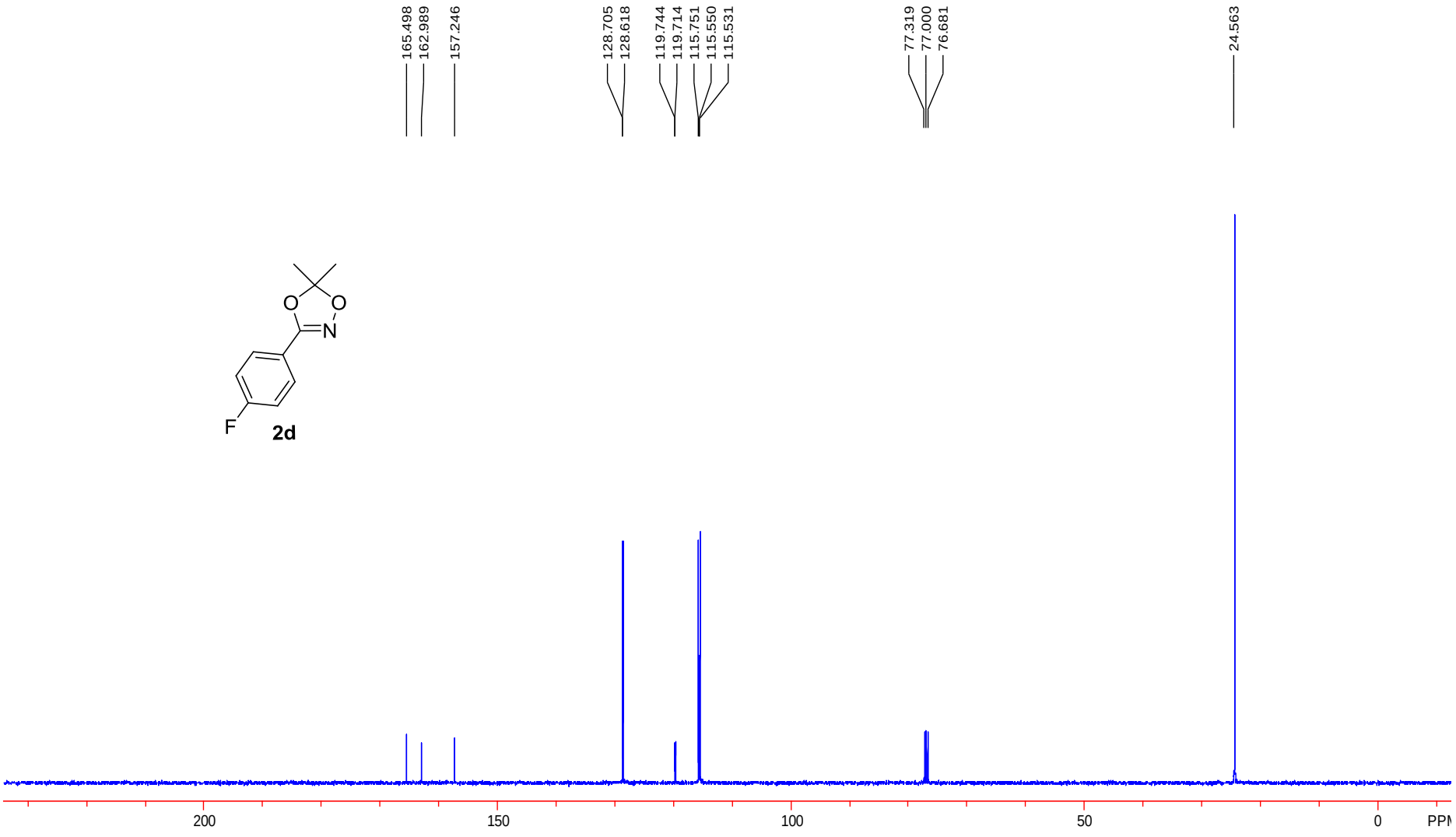
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**



**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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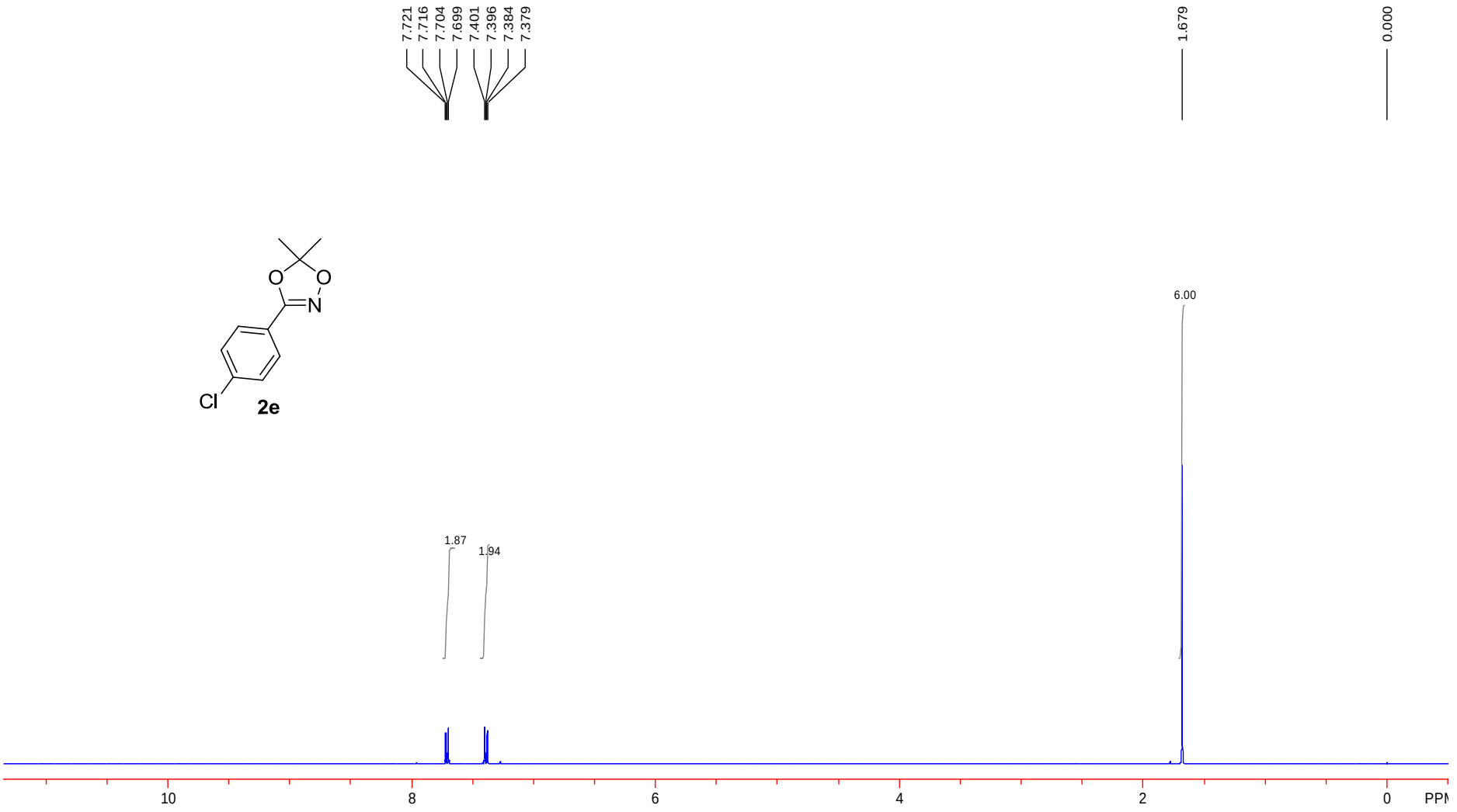
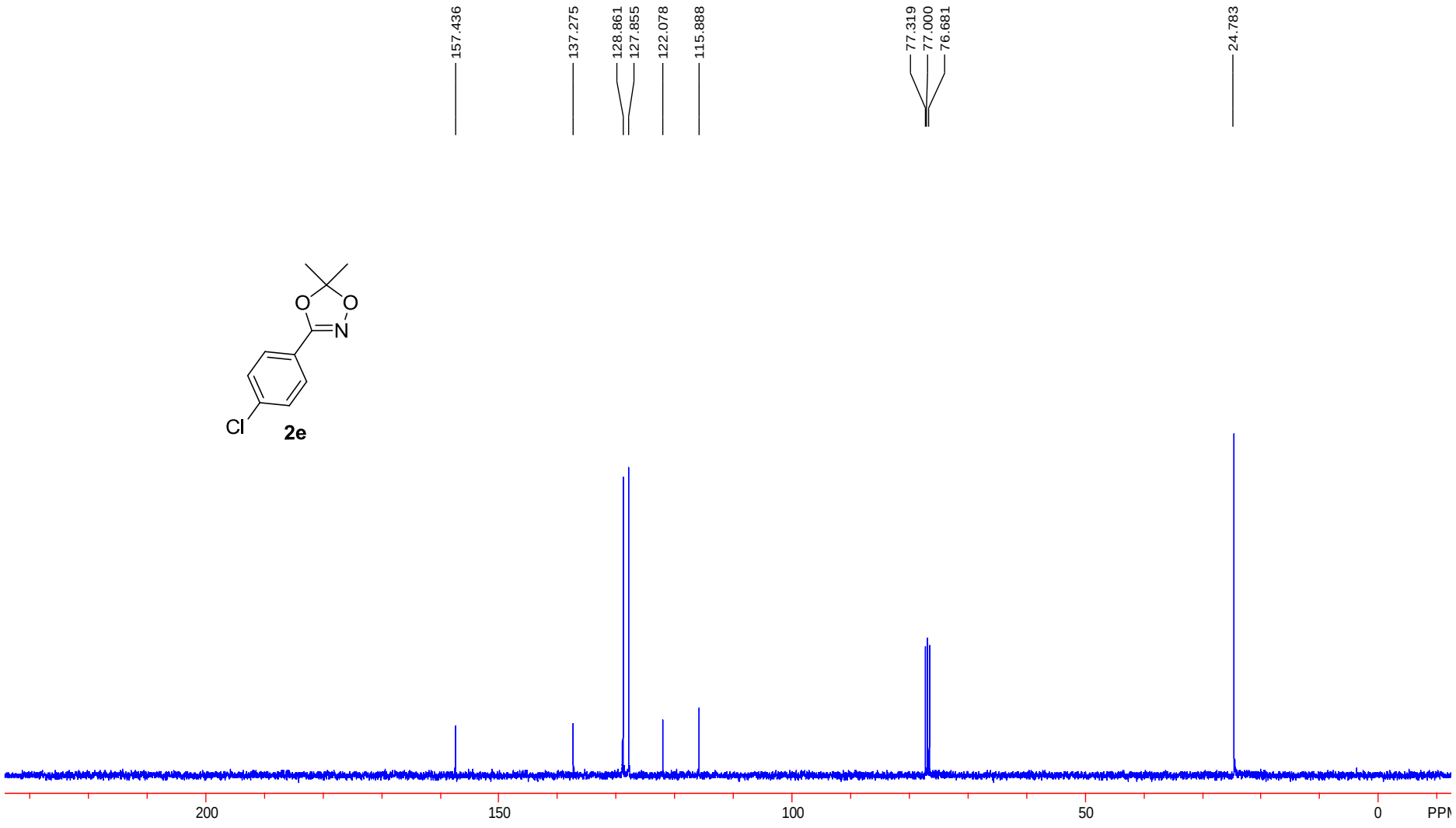


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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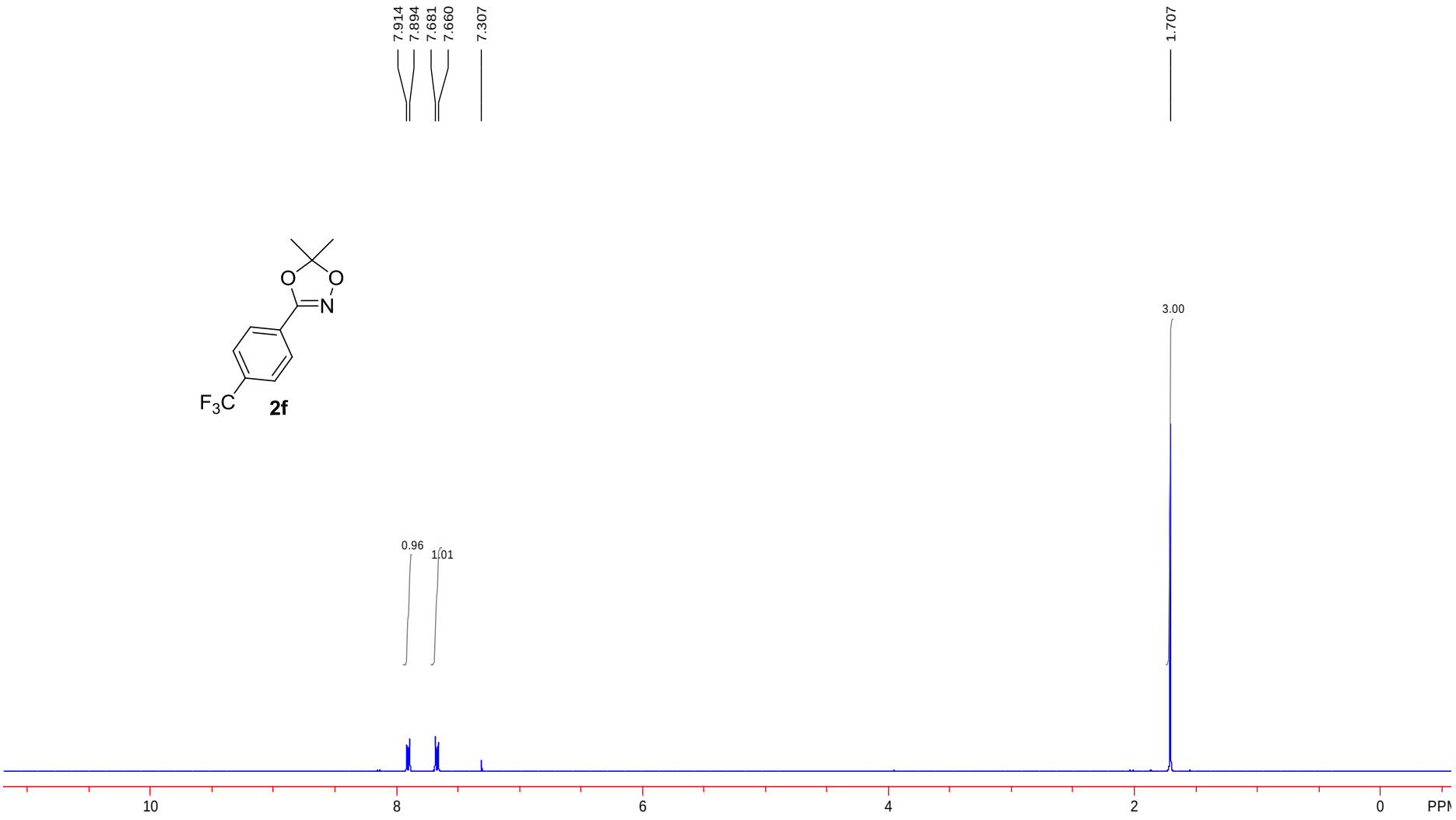

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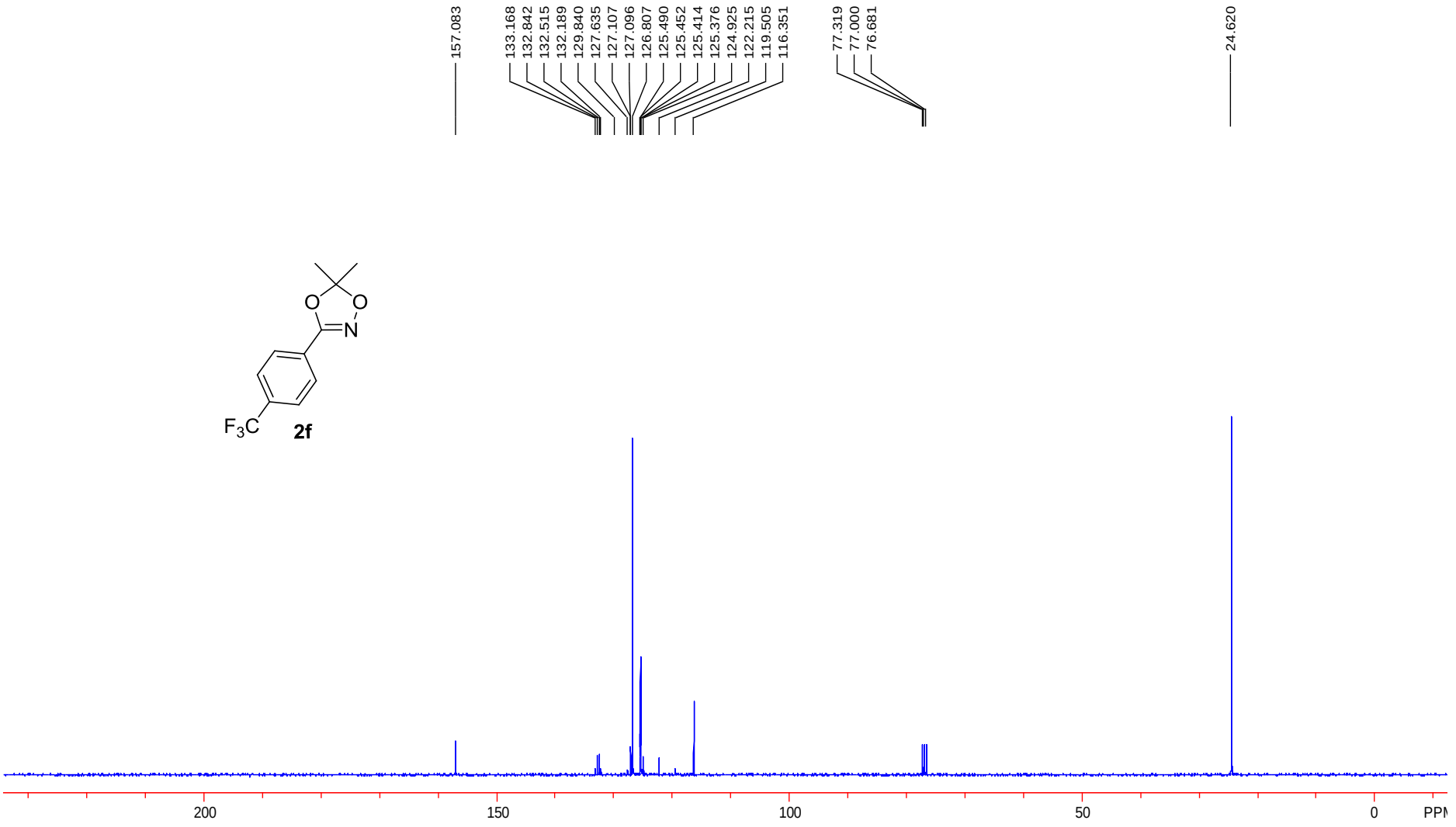

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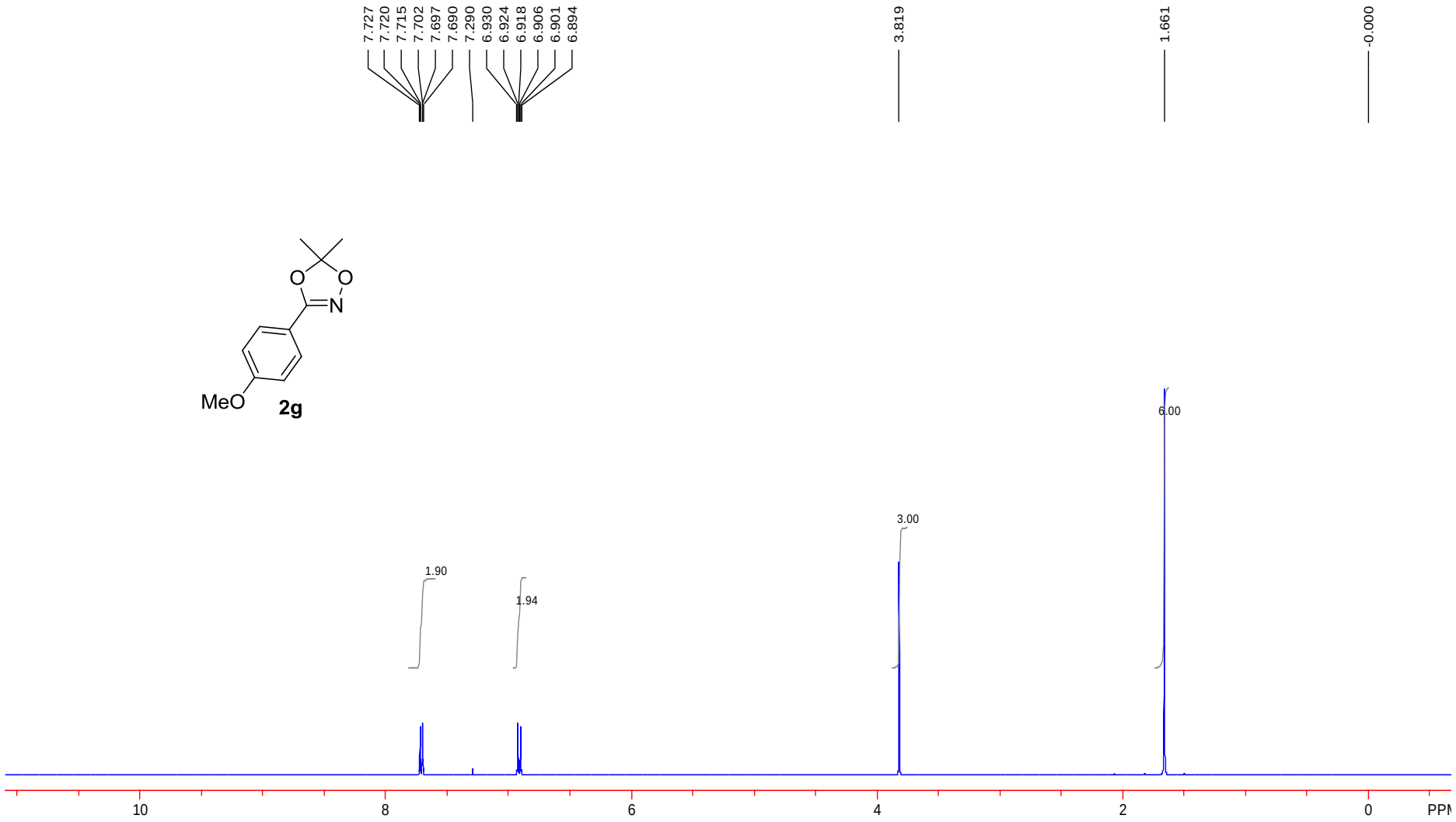

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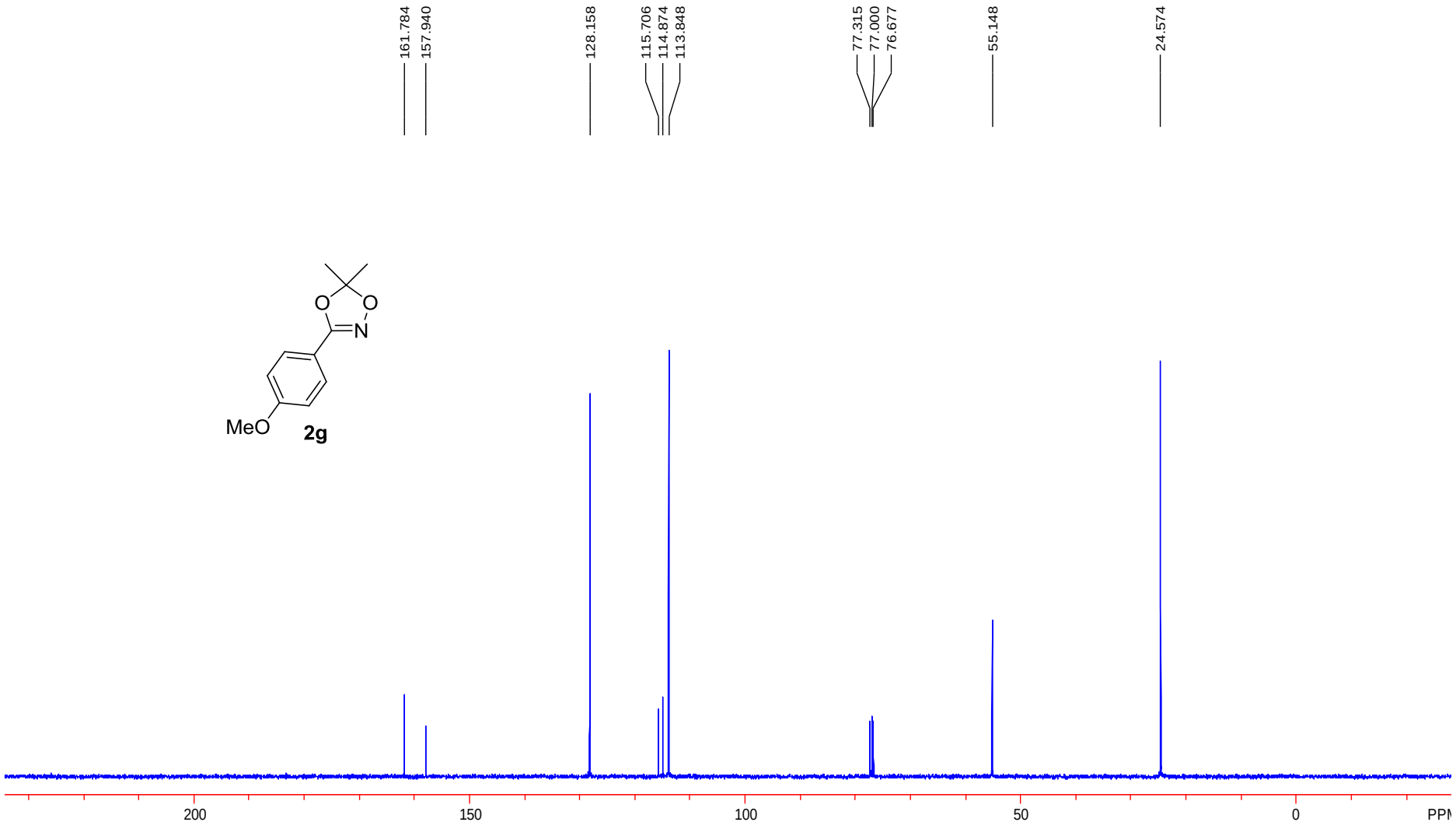

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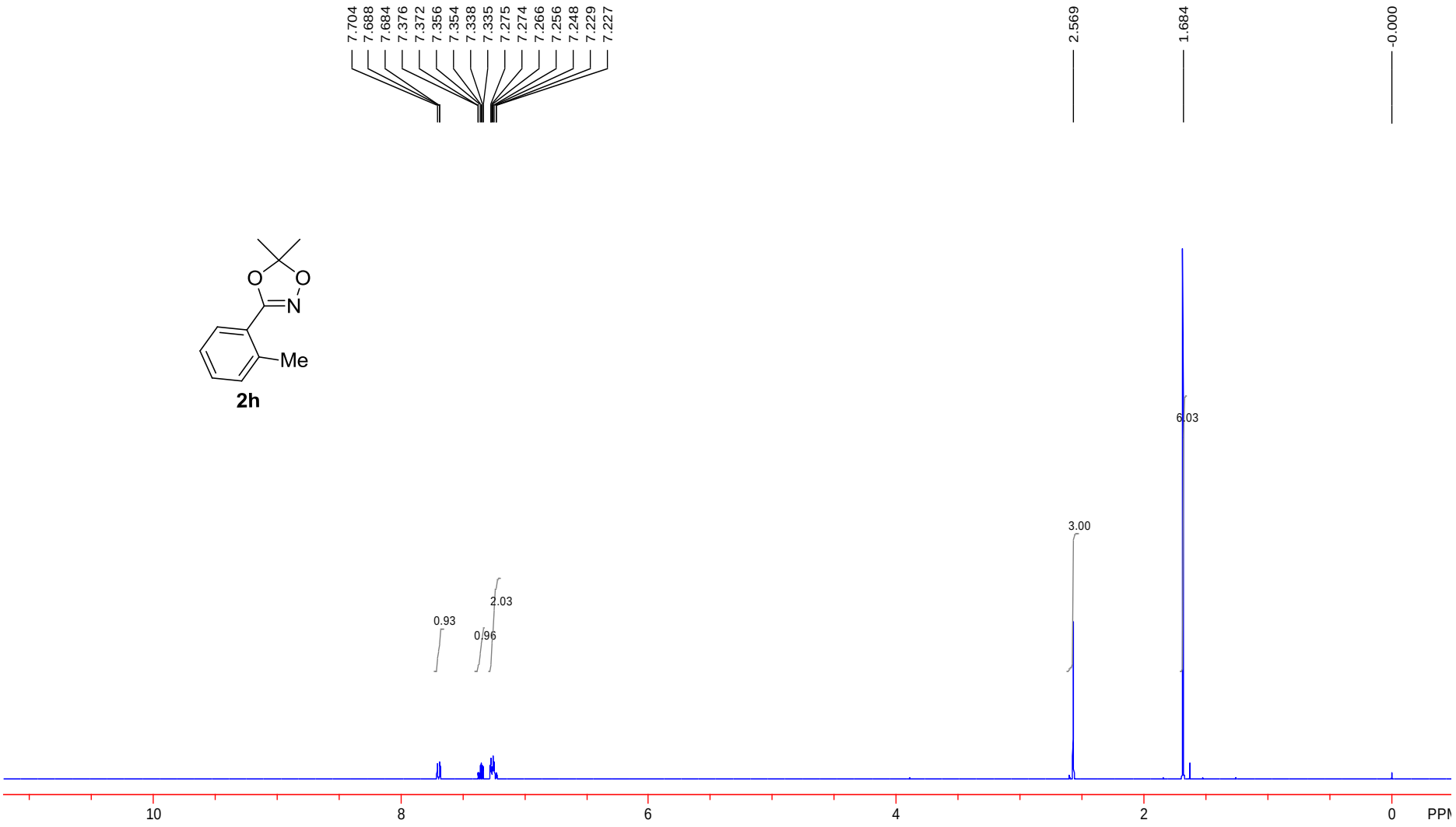

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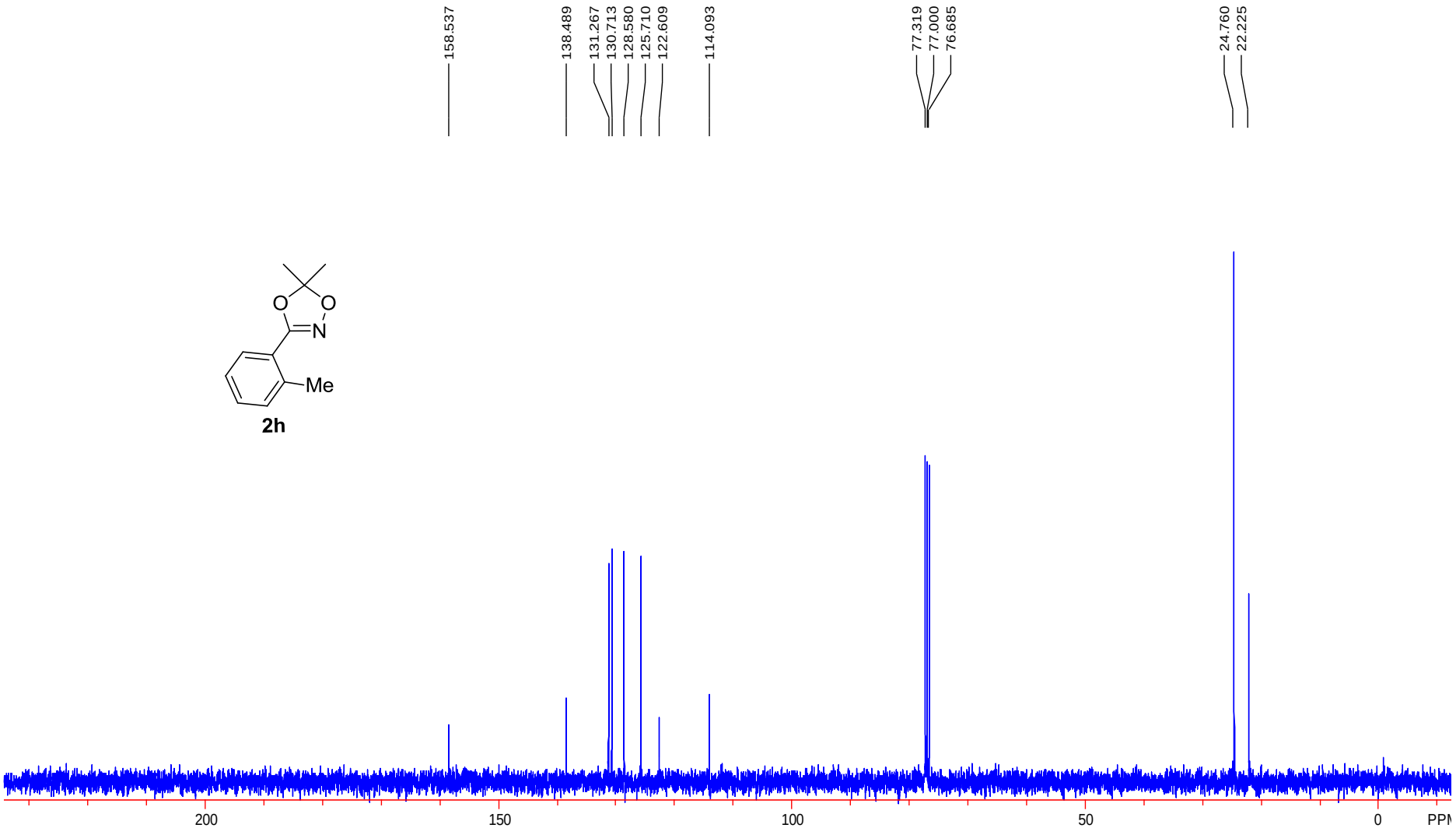

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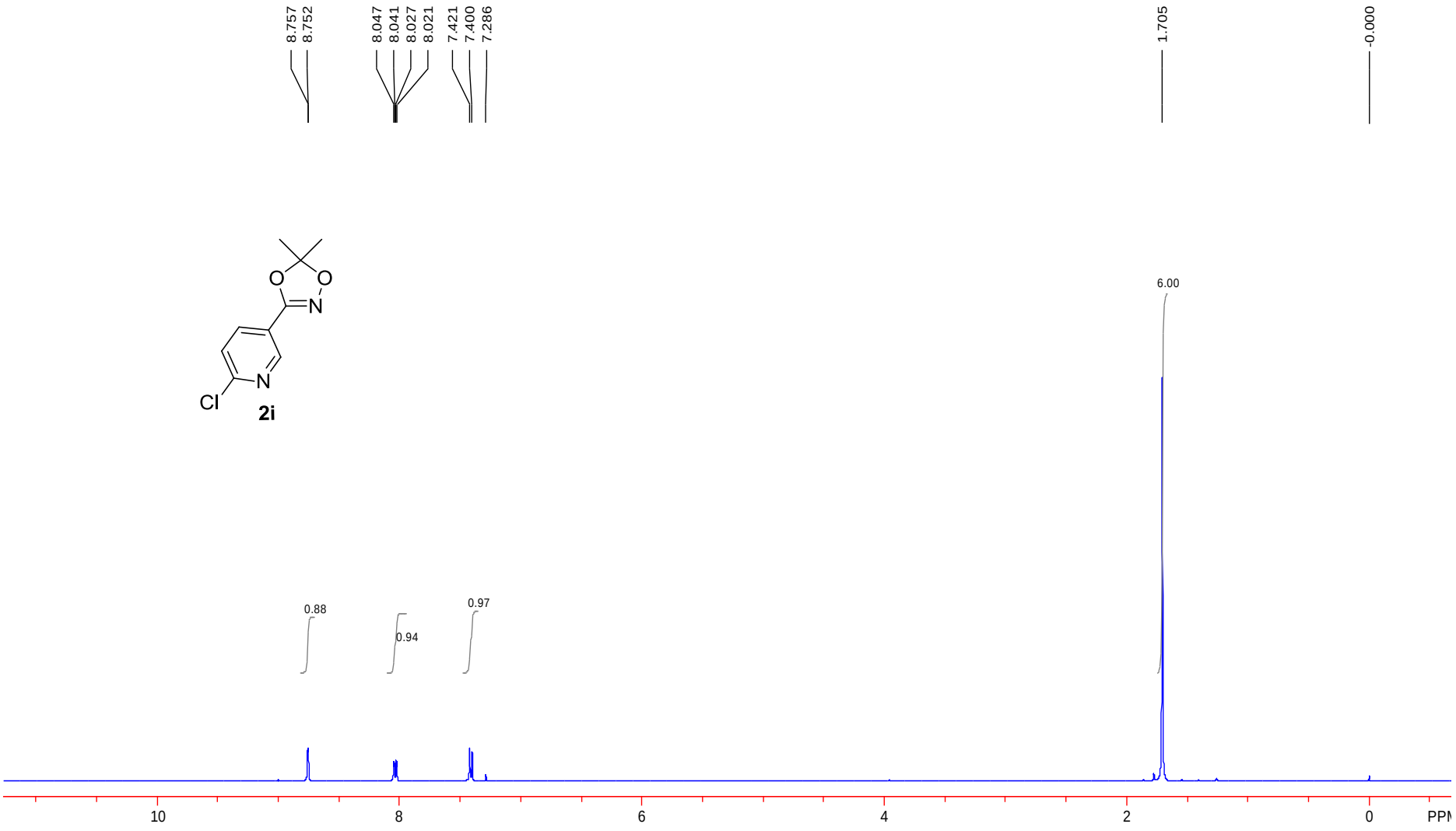
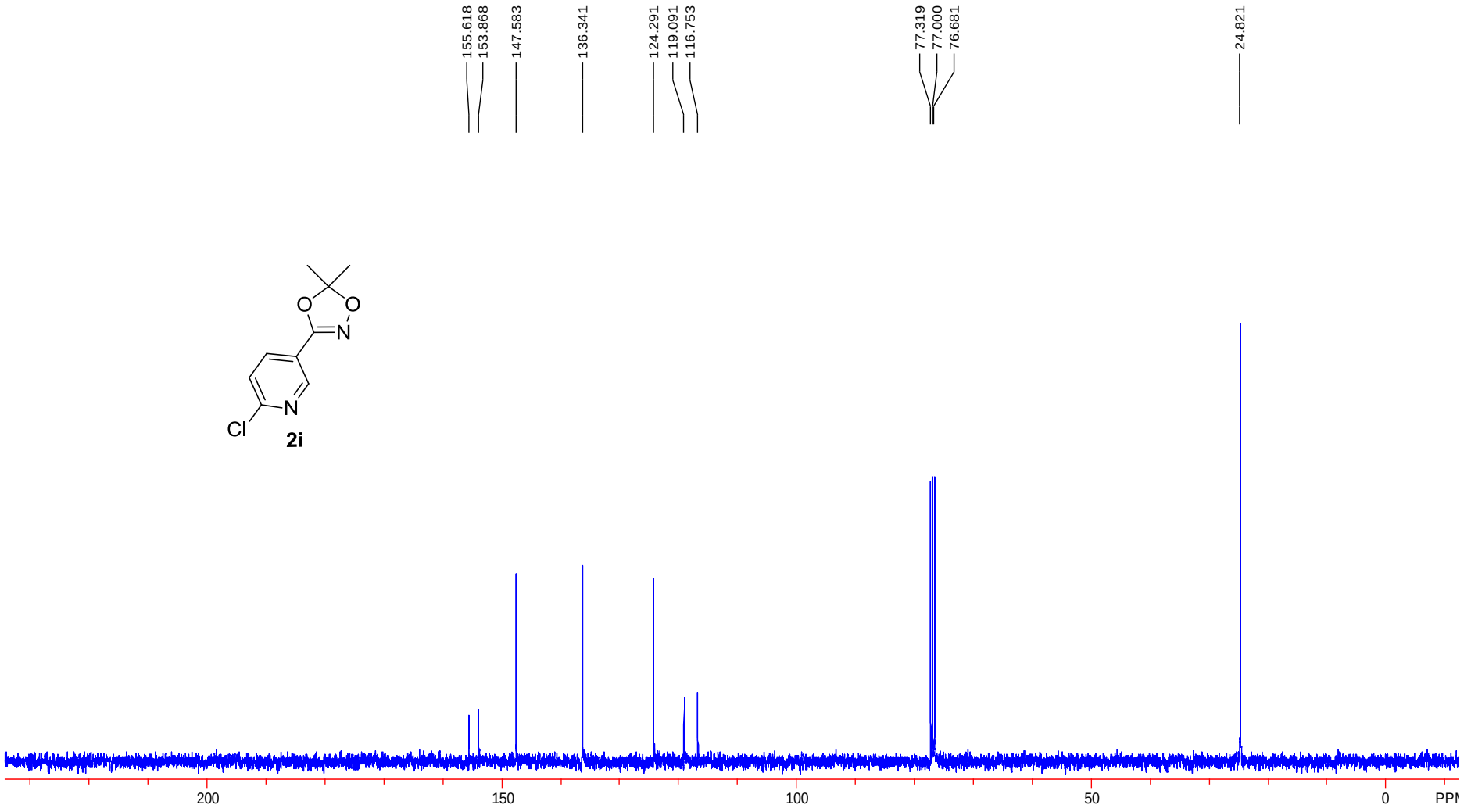


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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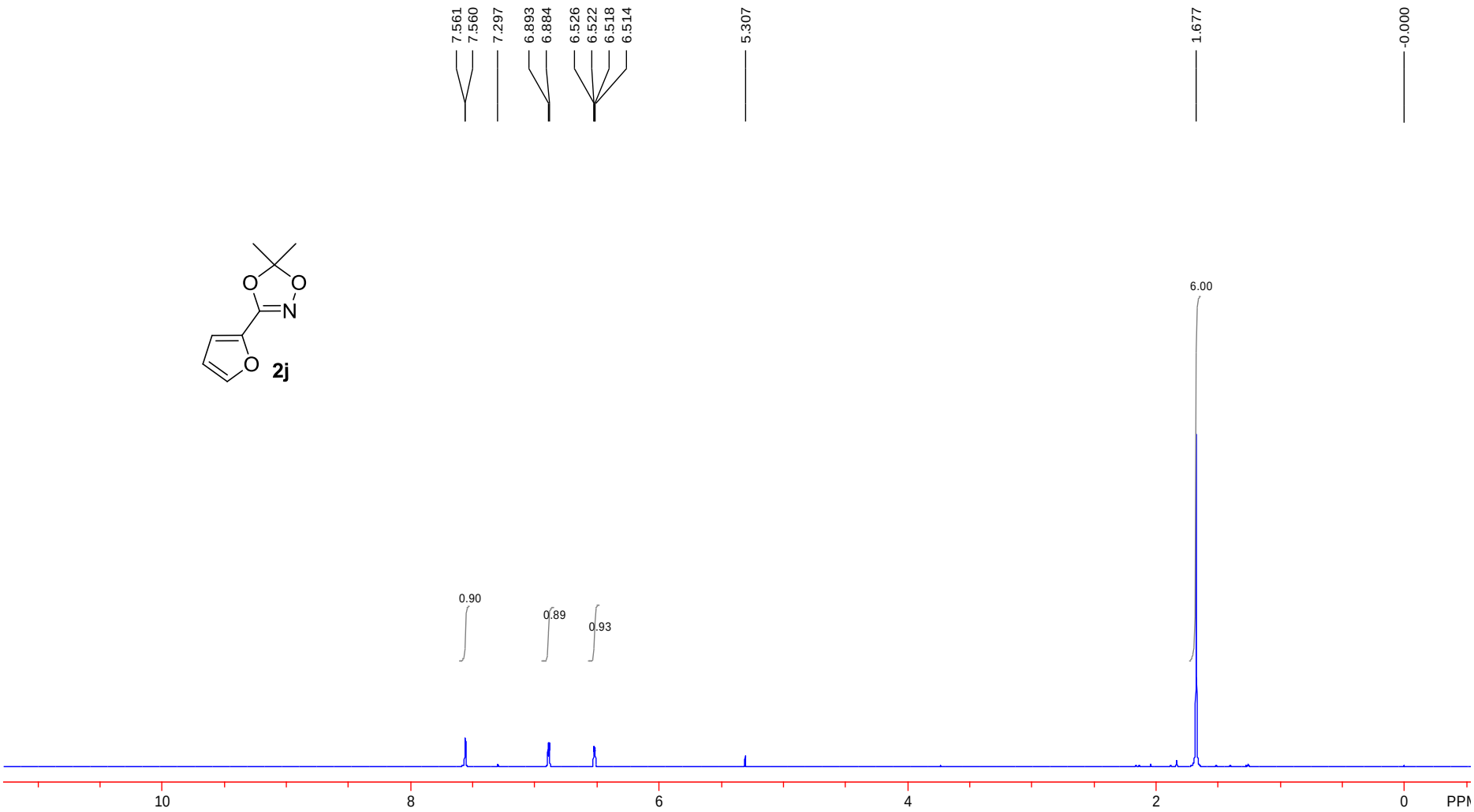

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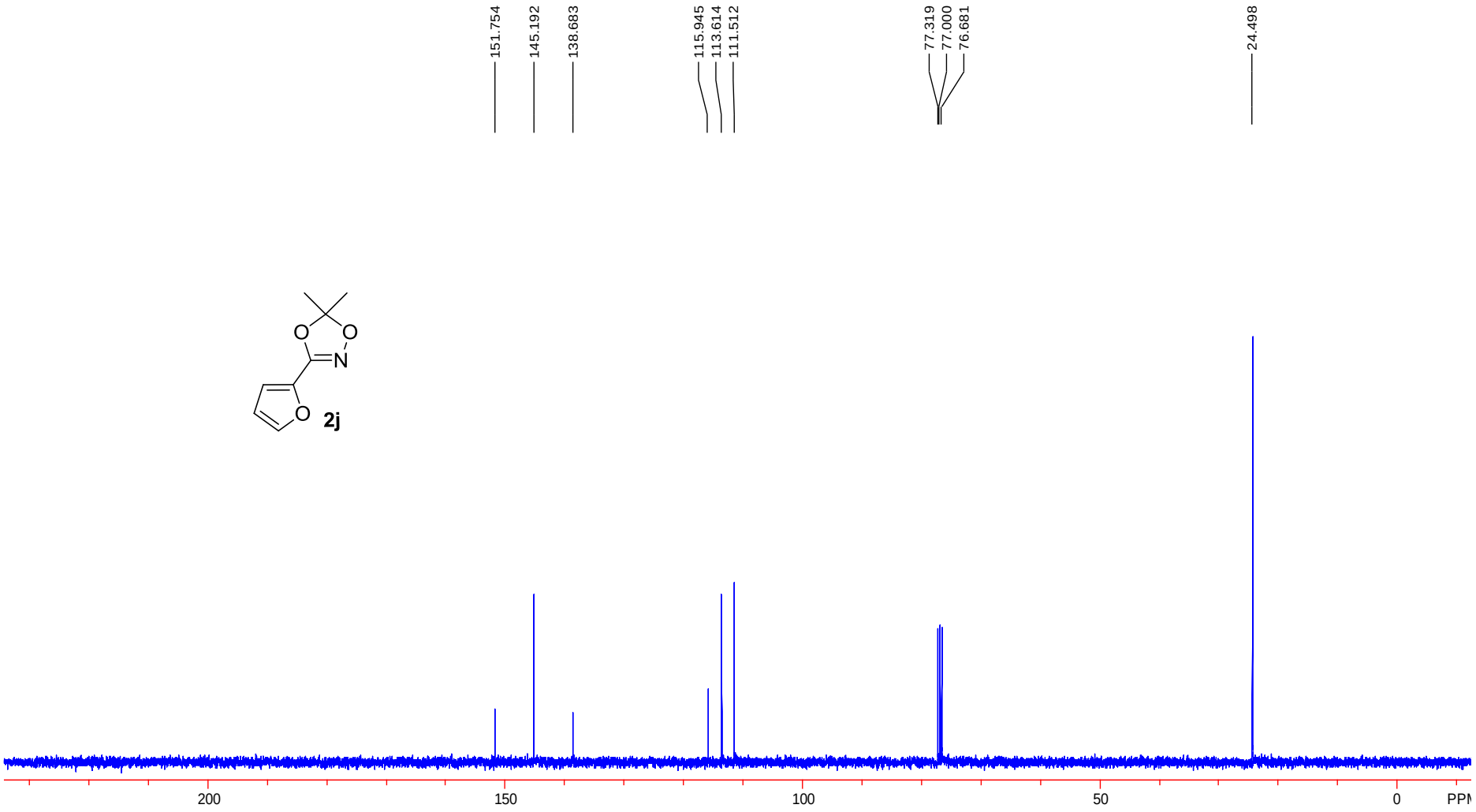

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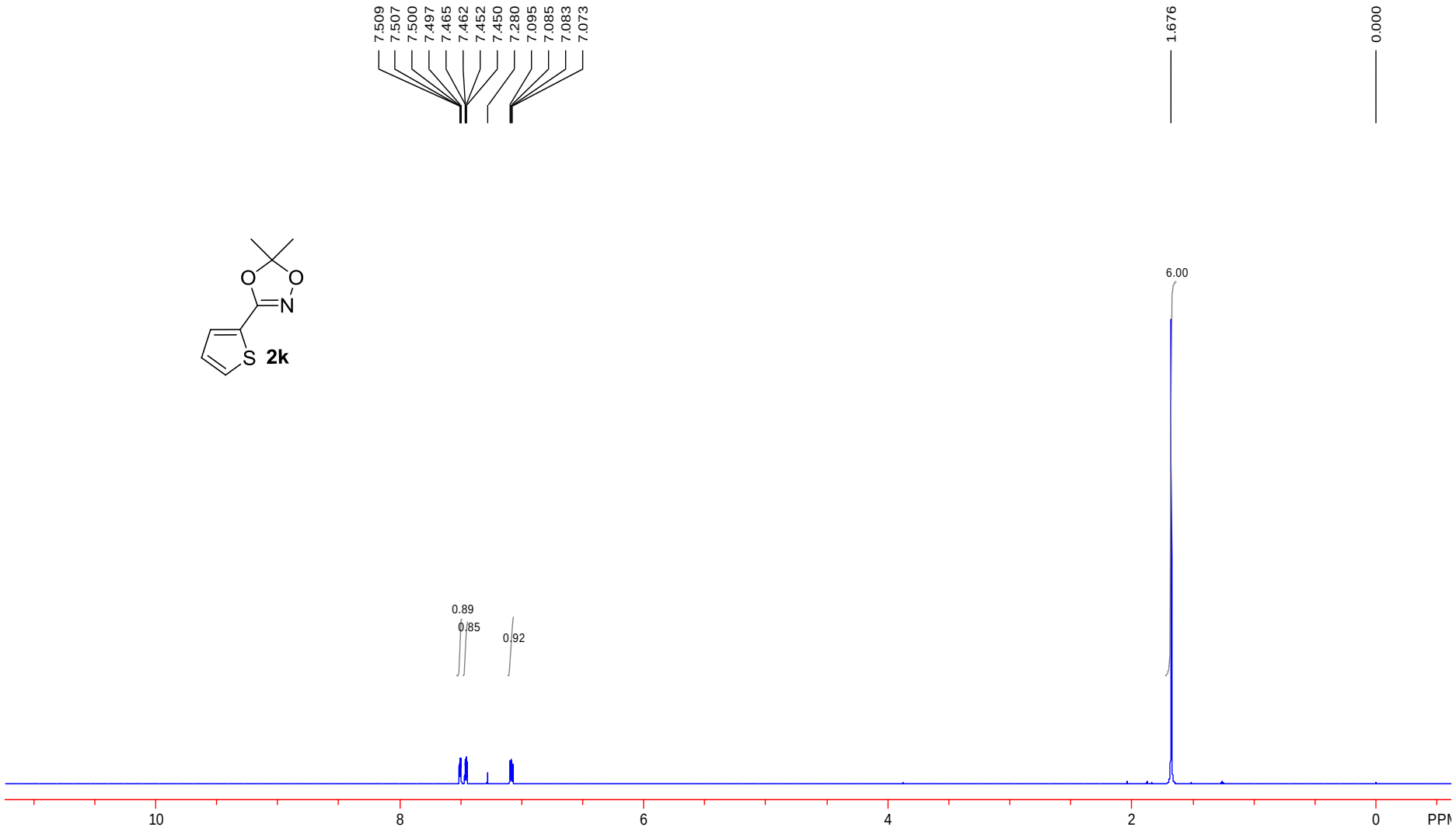

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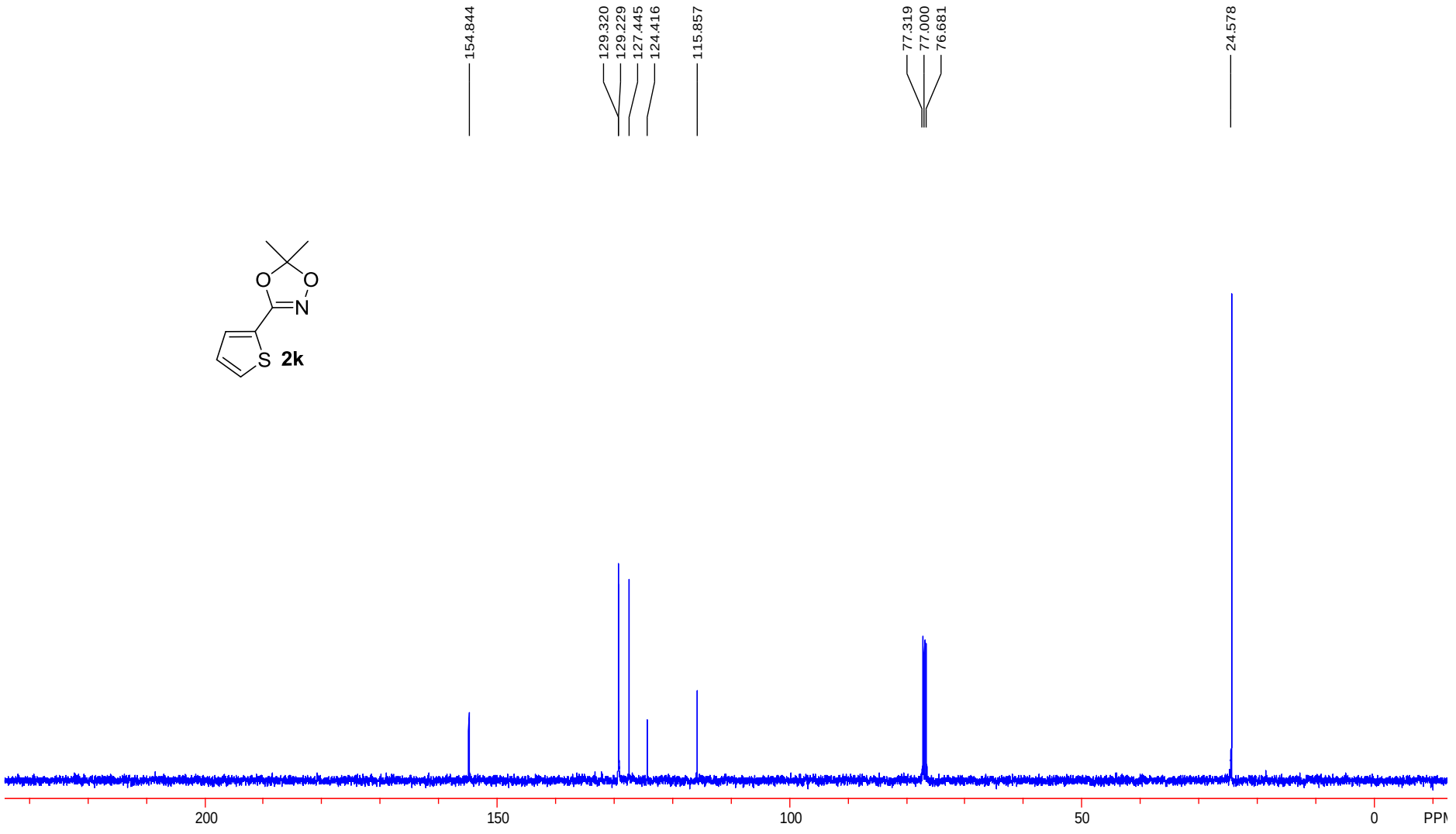

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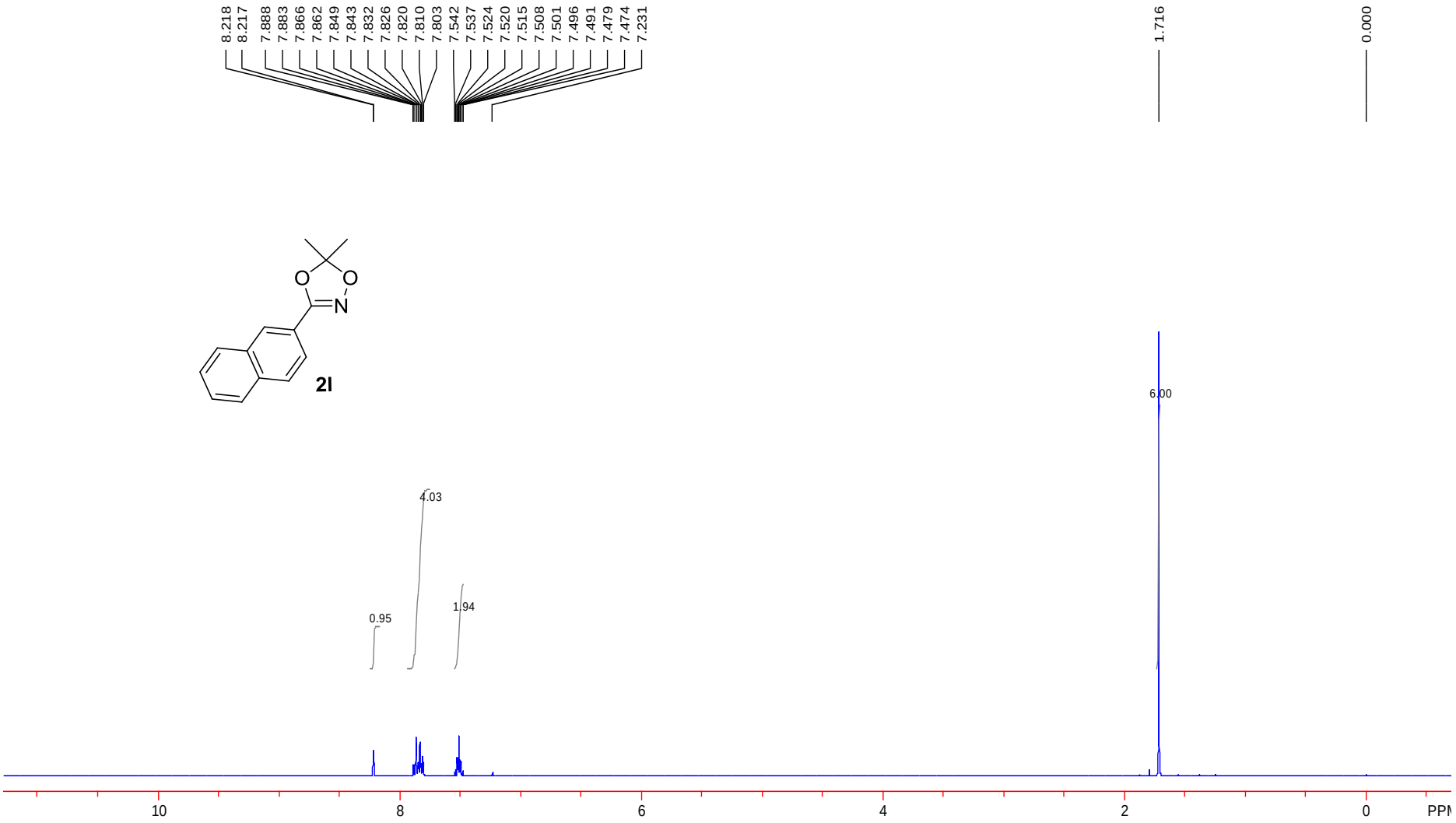
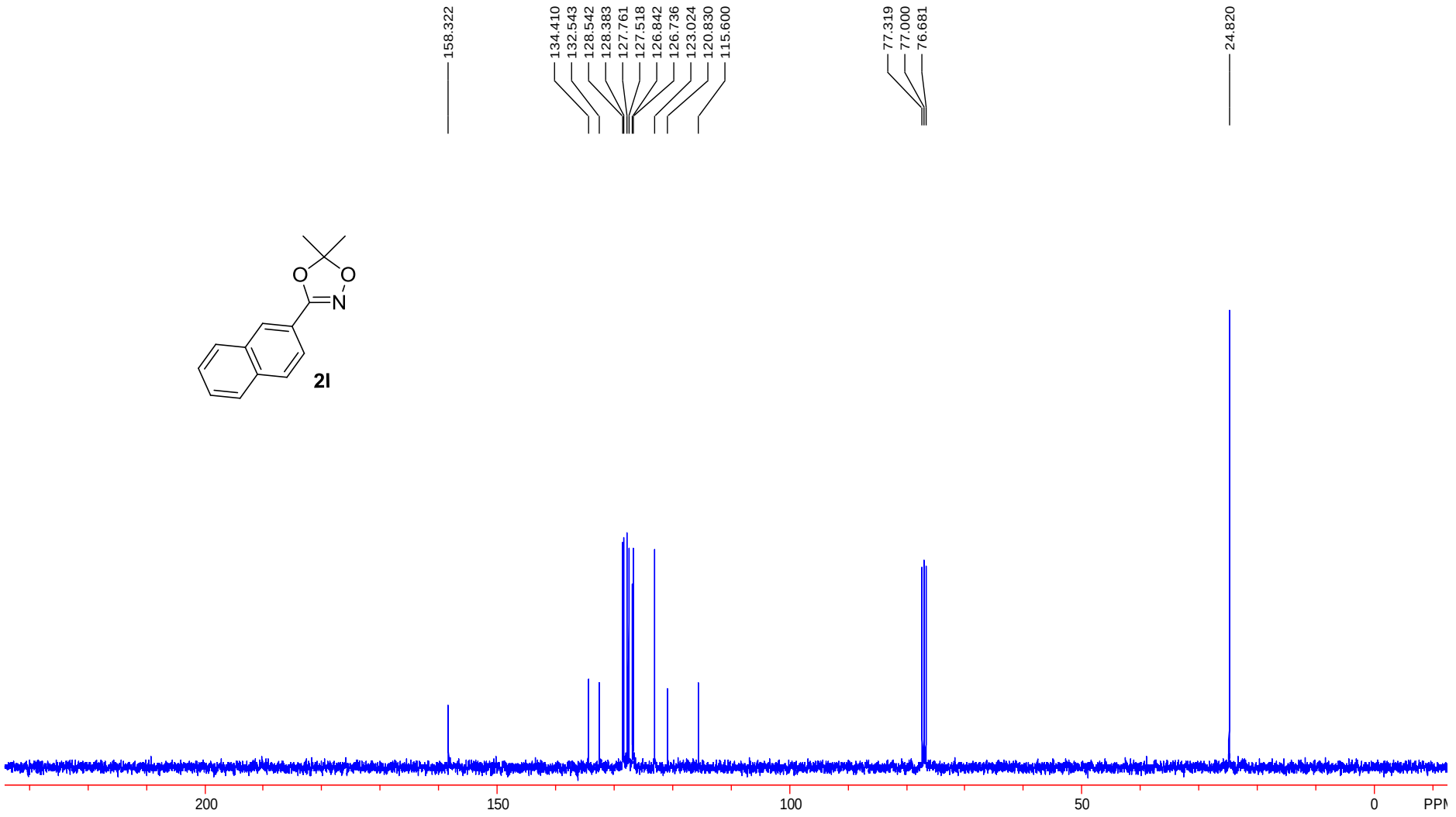
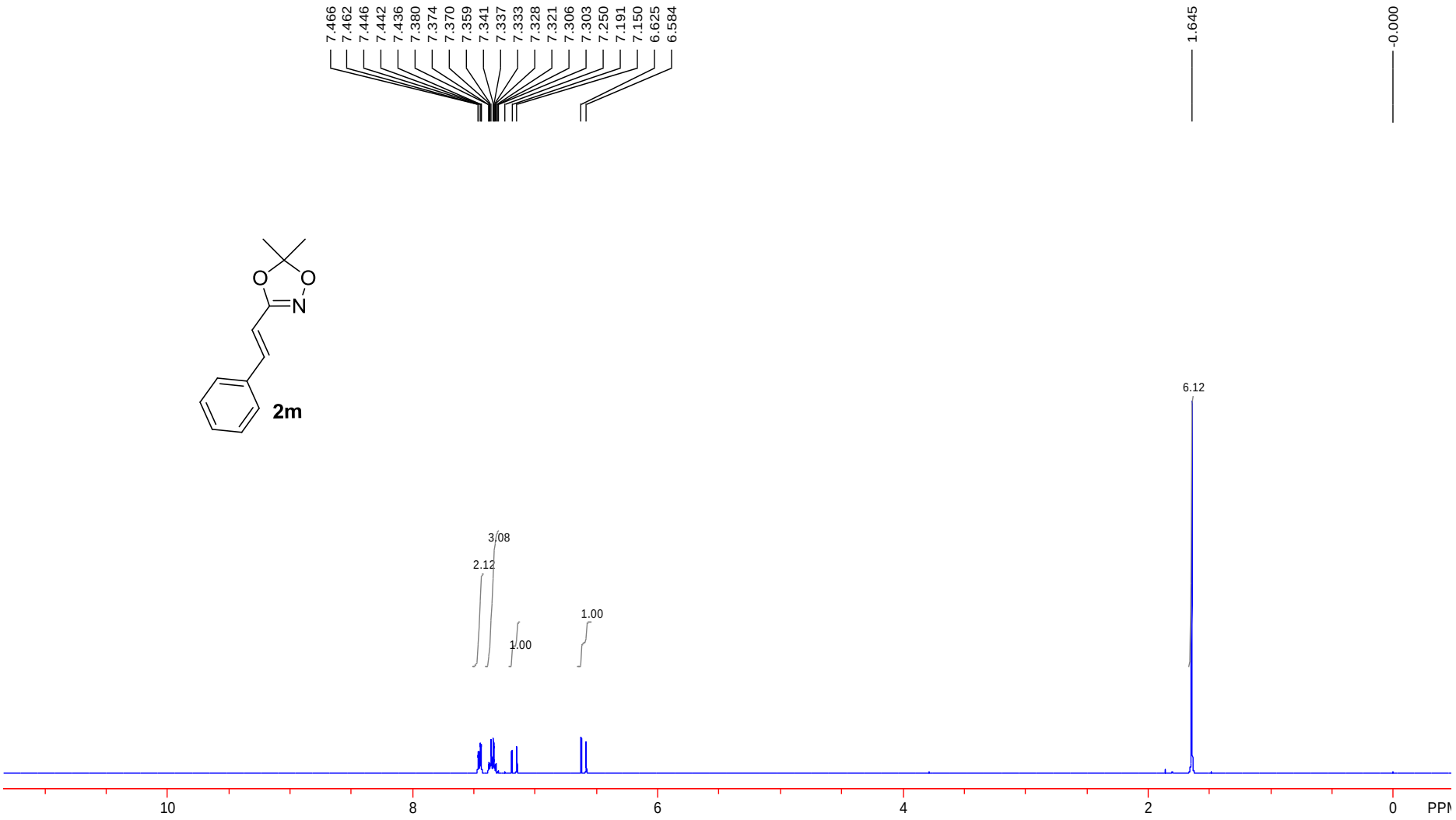


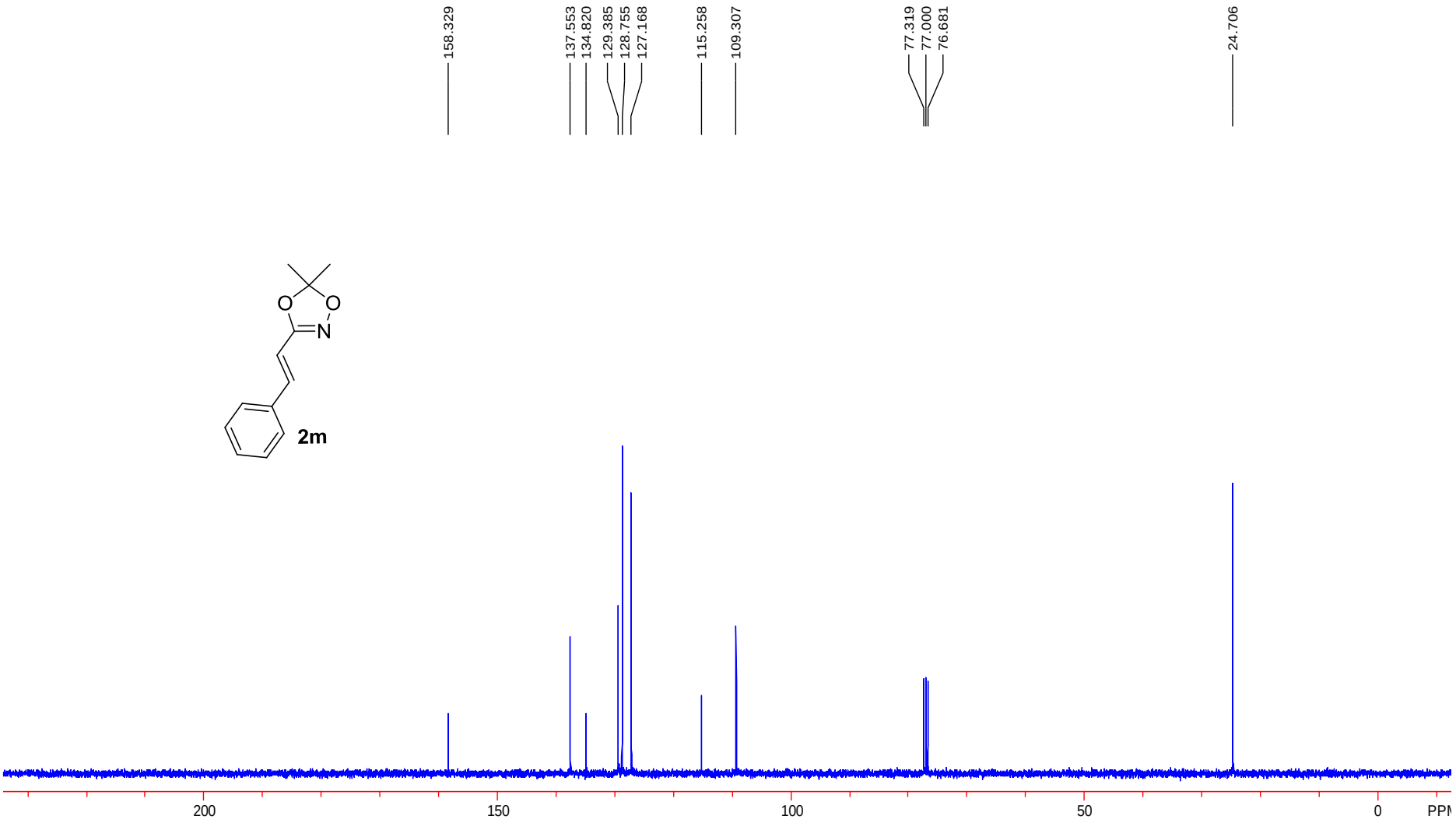
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



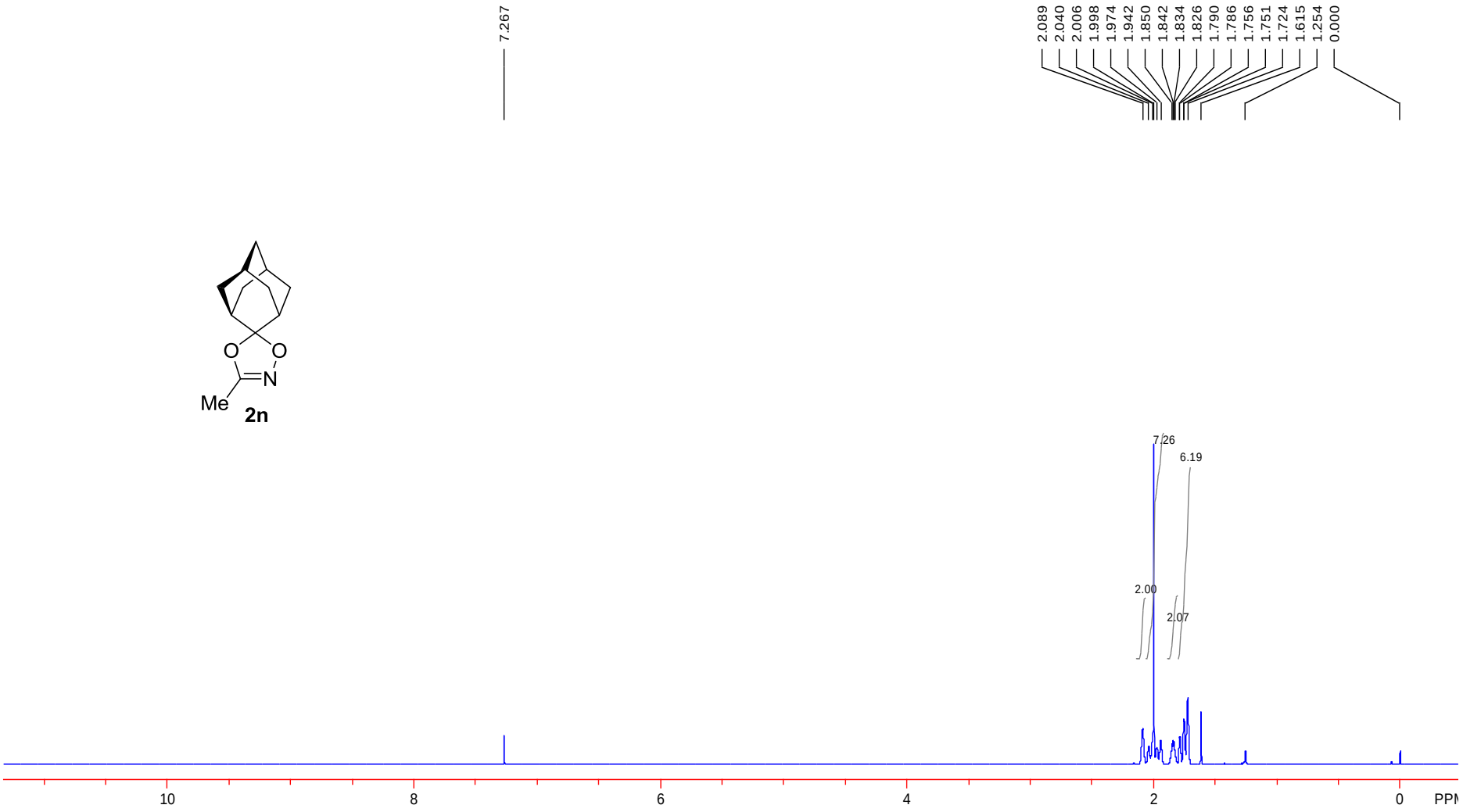
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



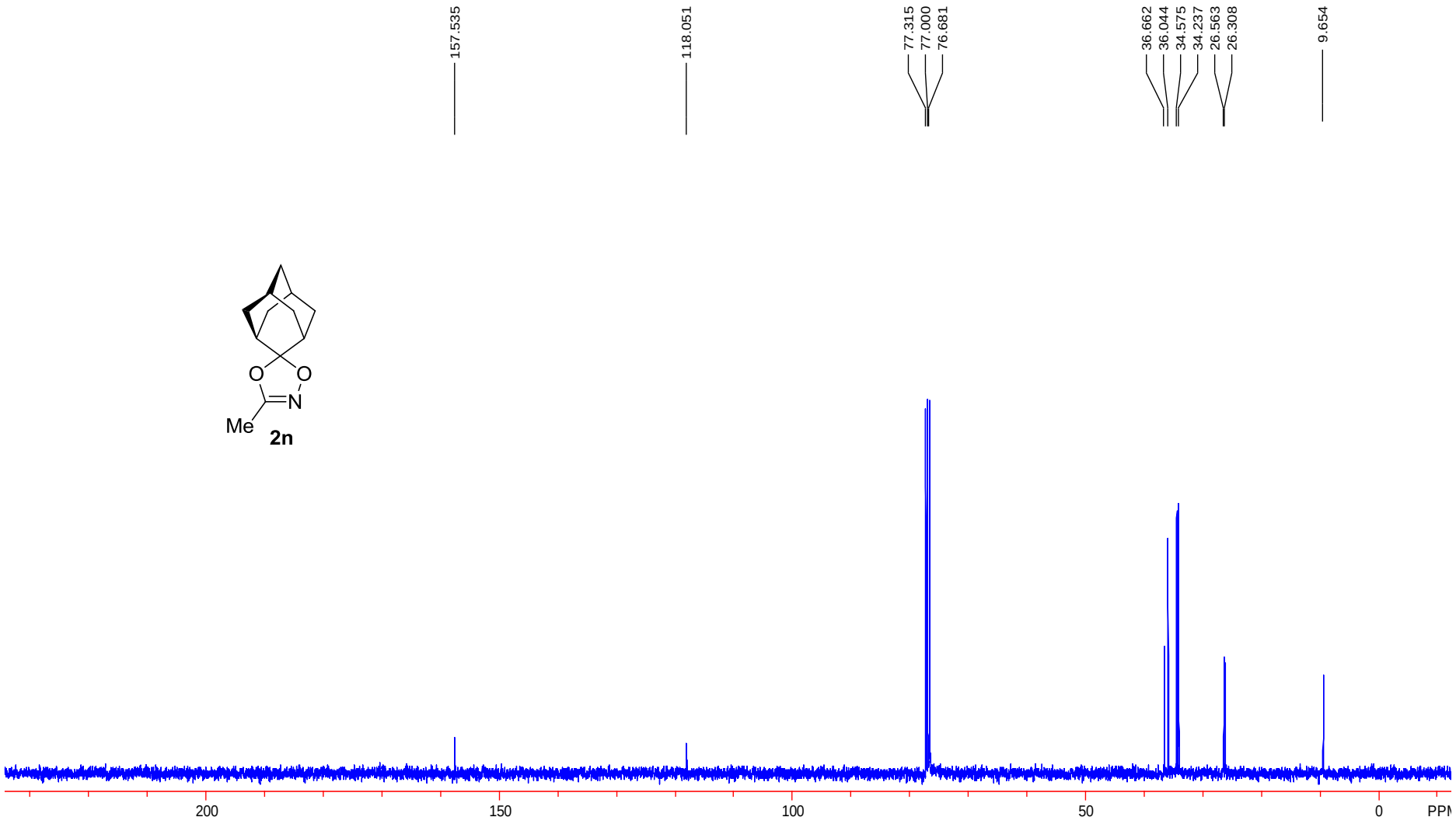
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



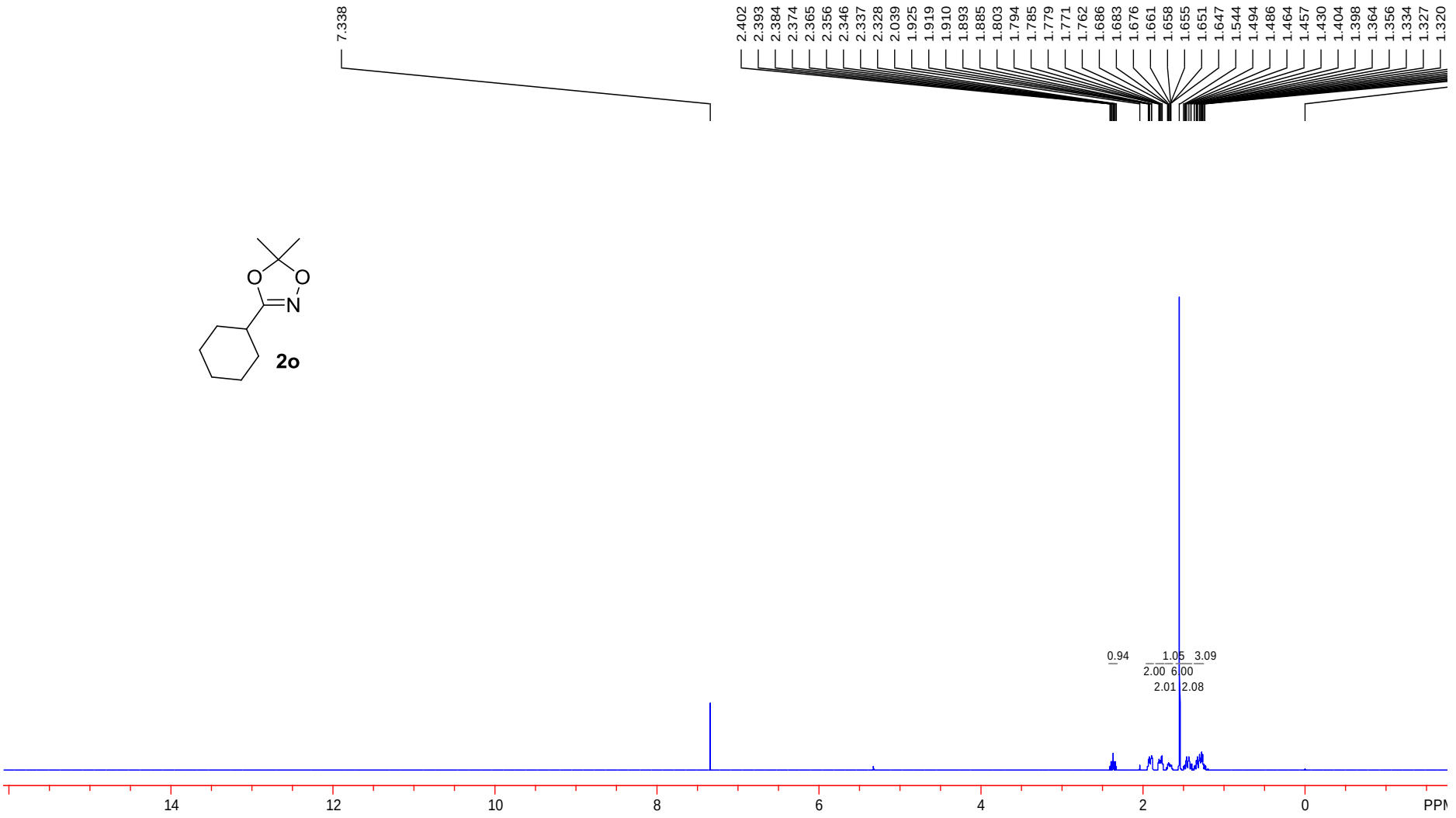
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



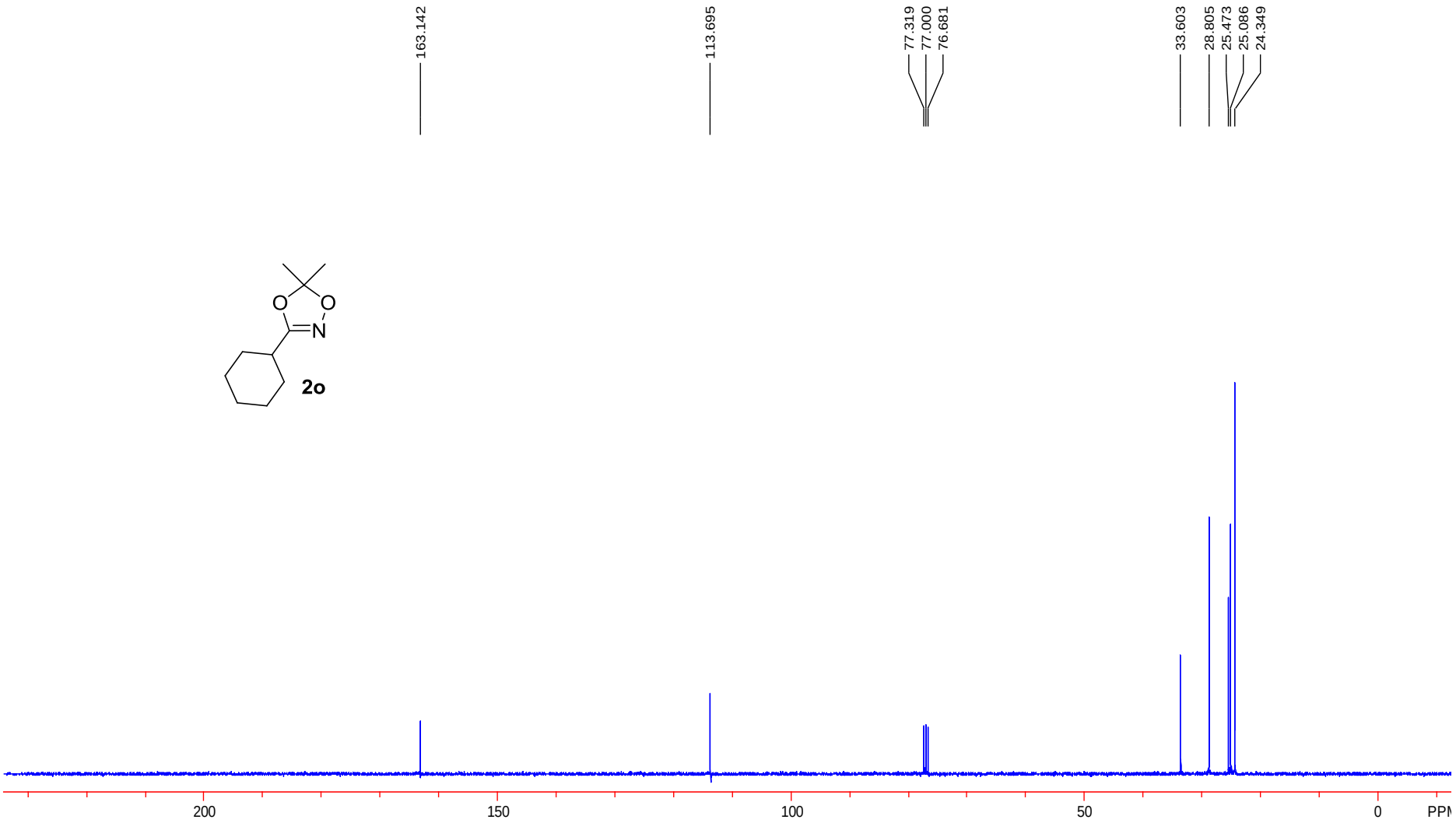
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**



**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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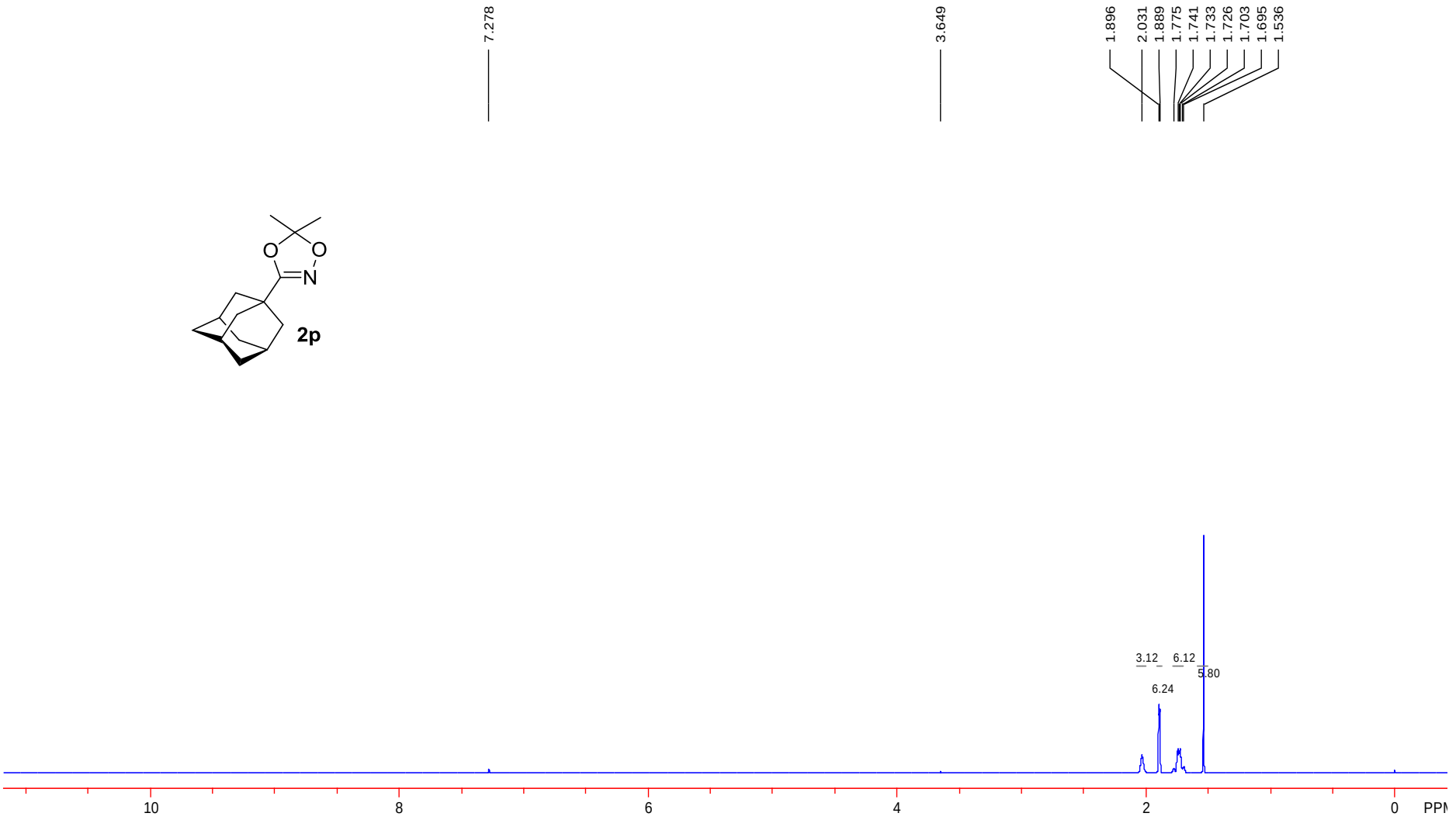
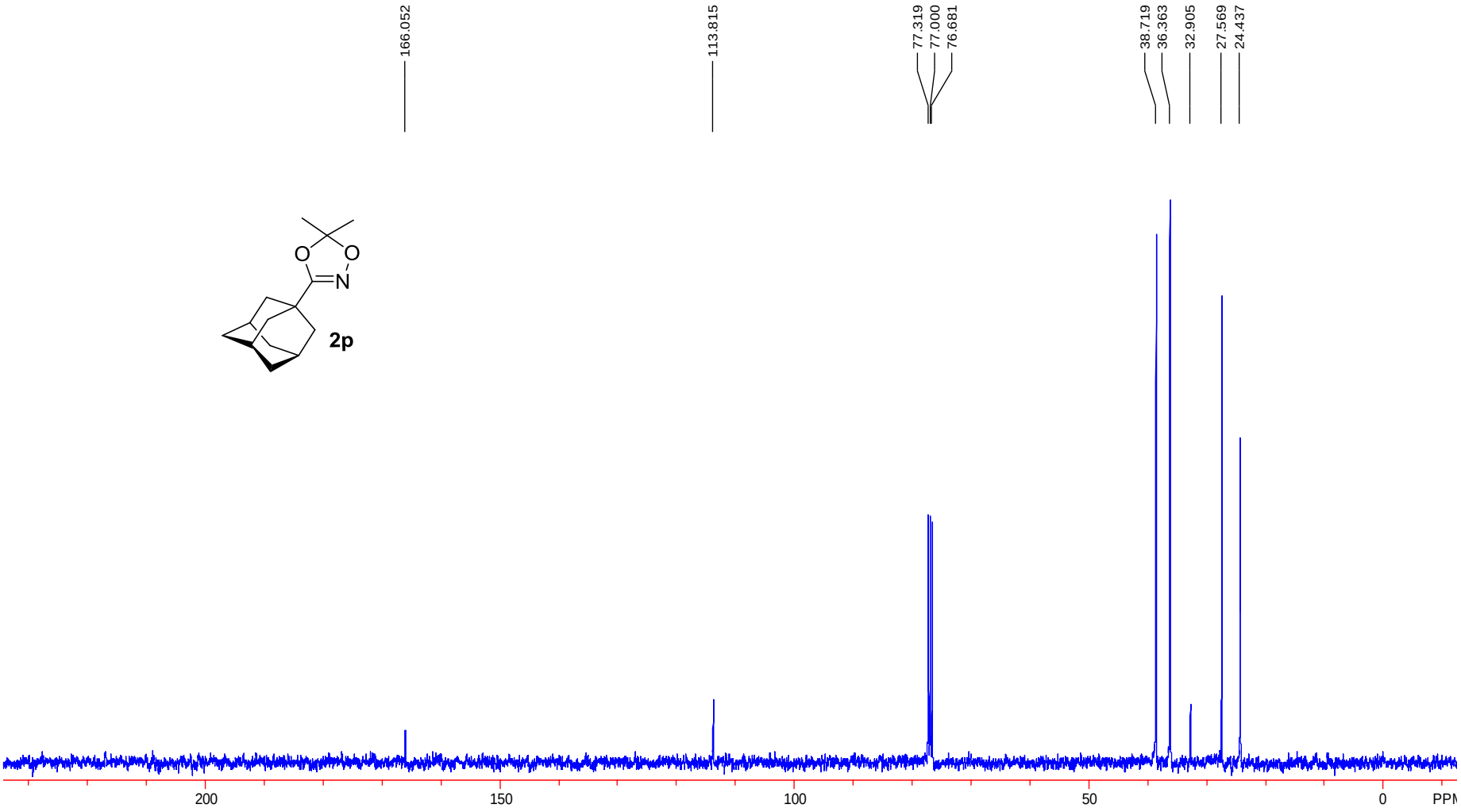
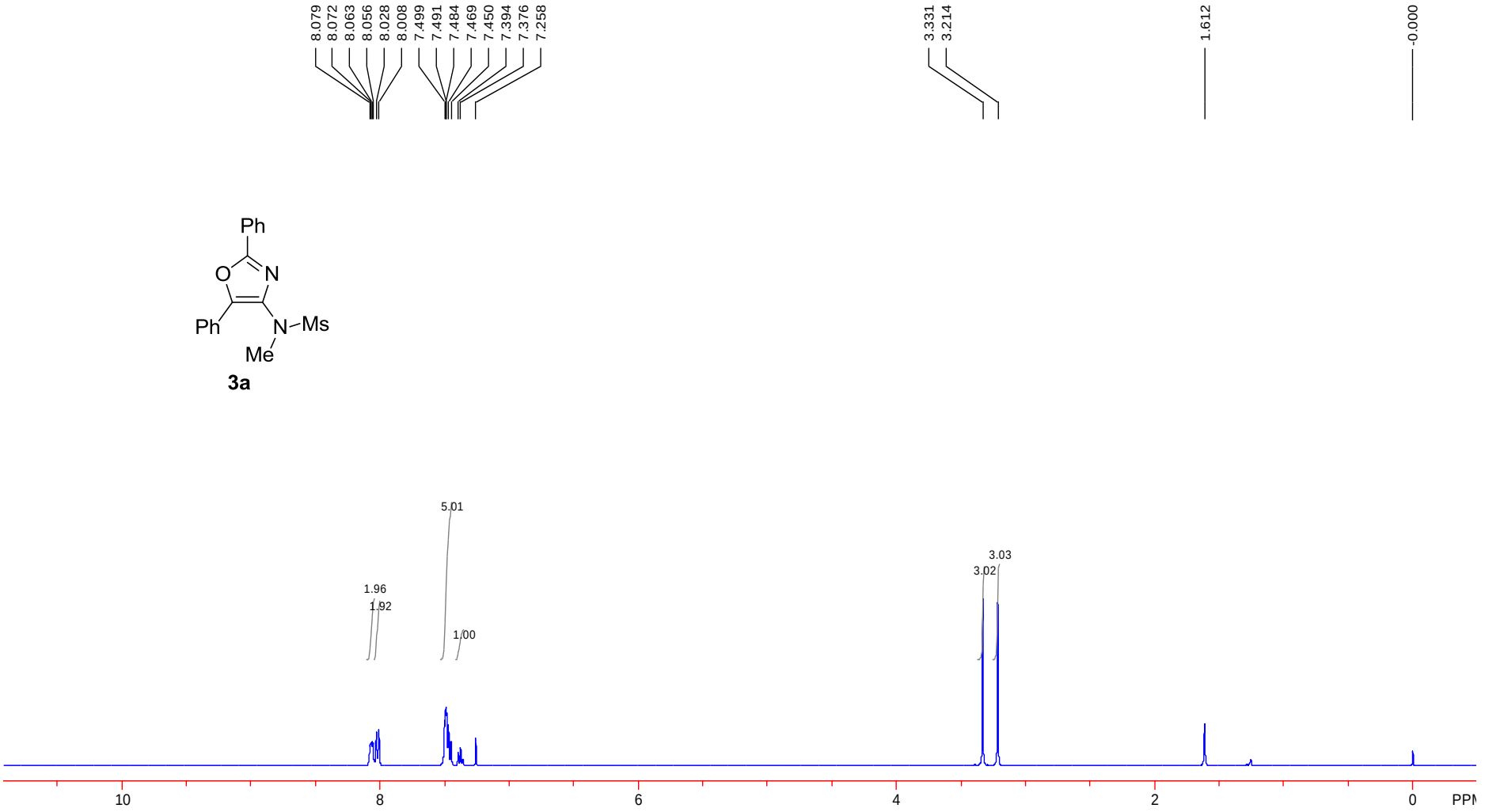


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^1$H NMR (400 MHz, $CDCl_3$)**



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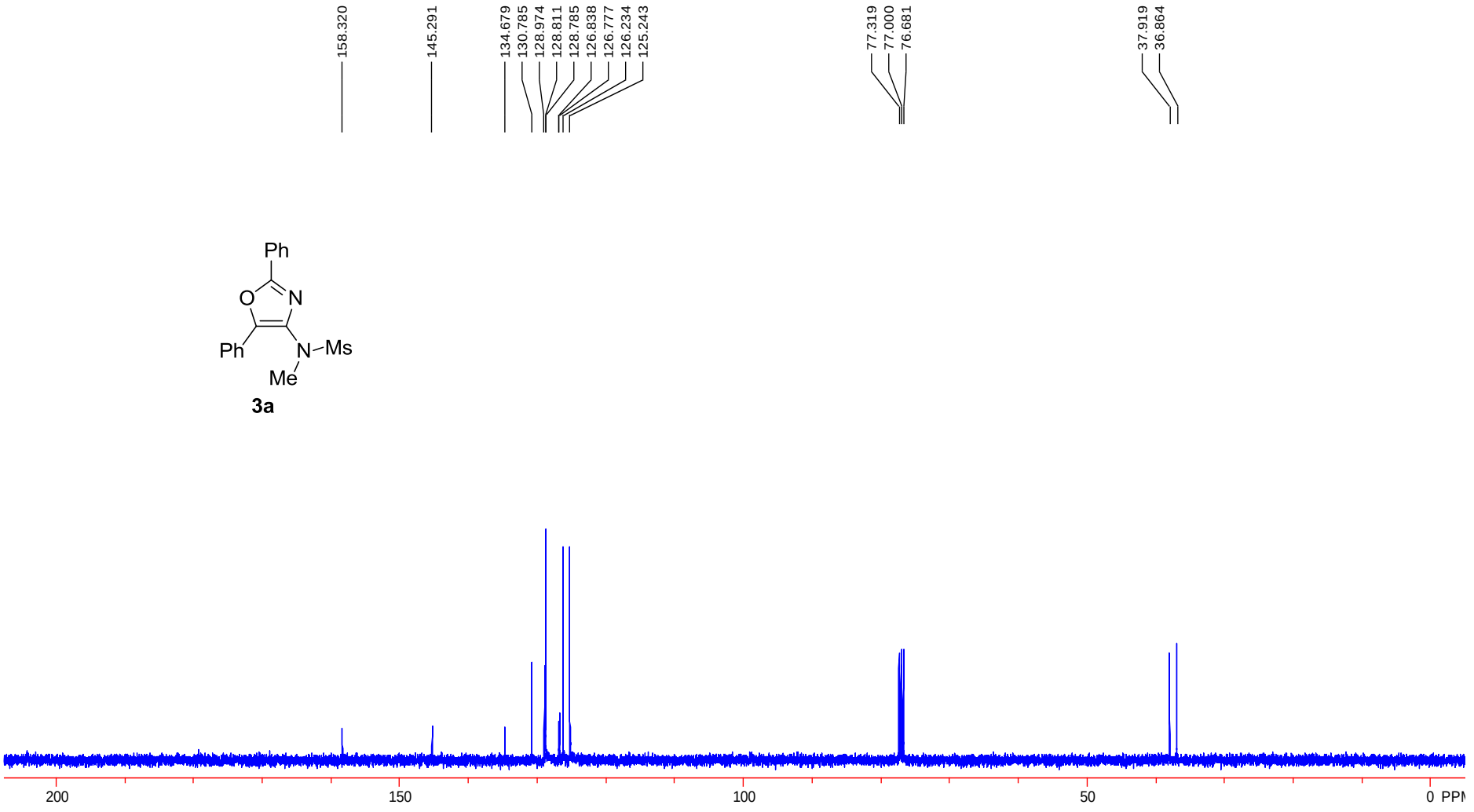
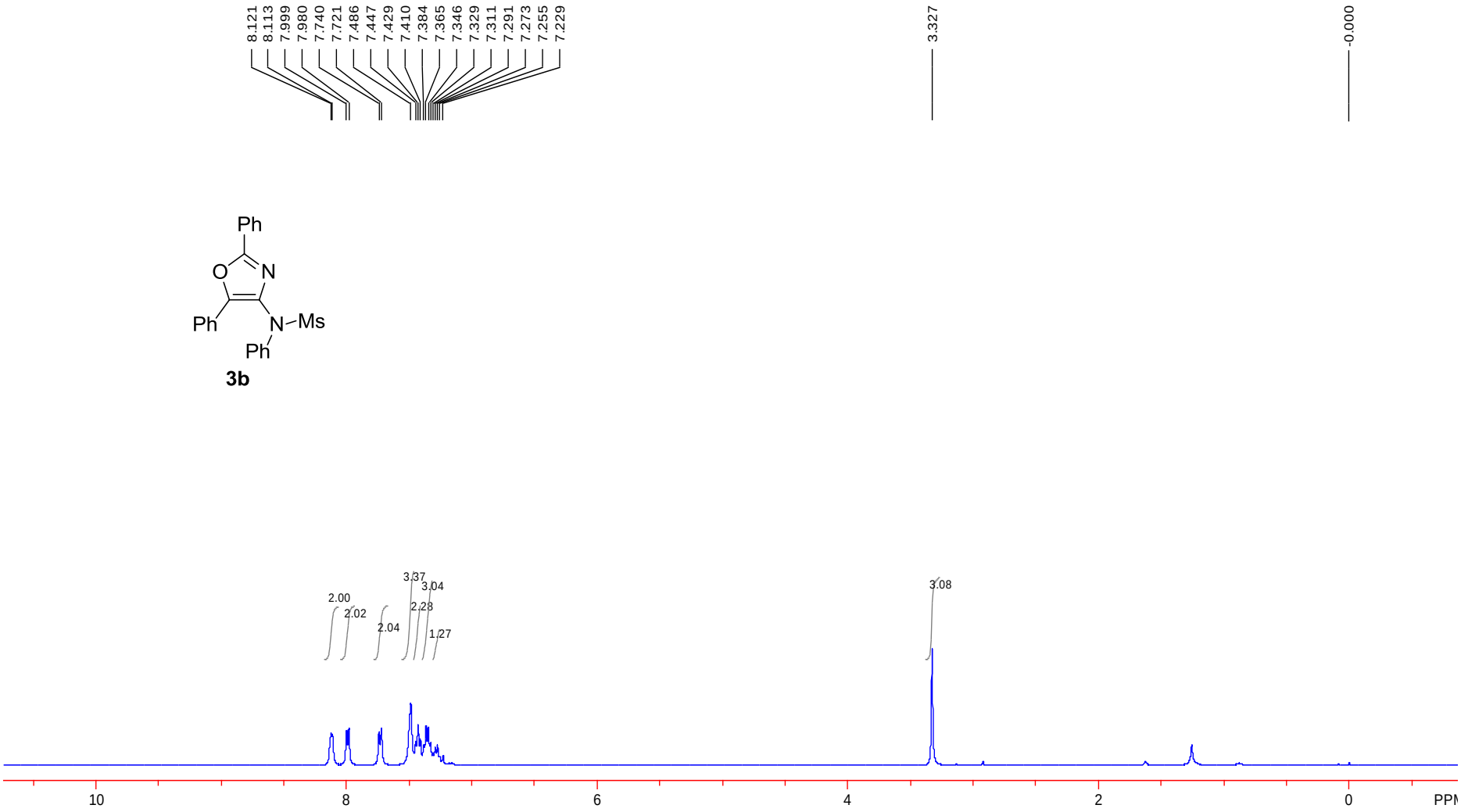
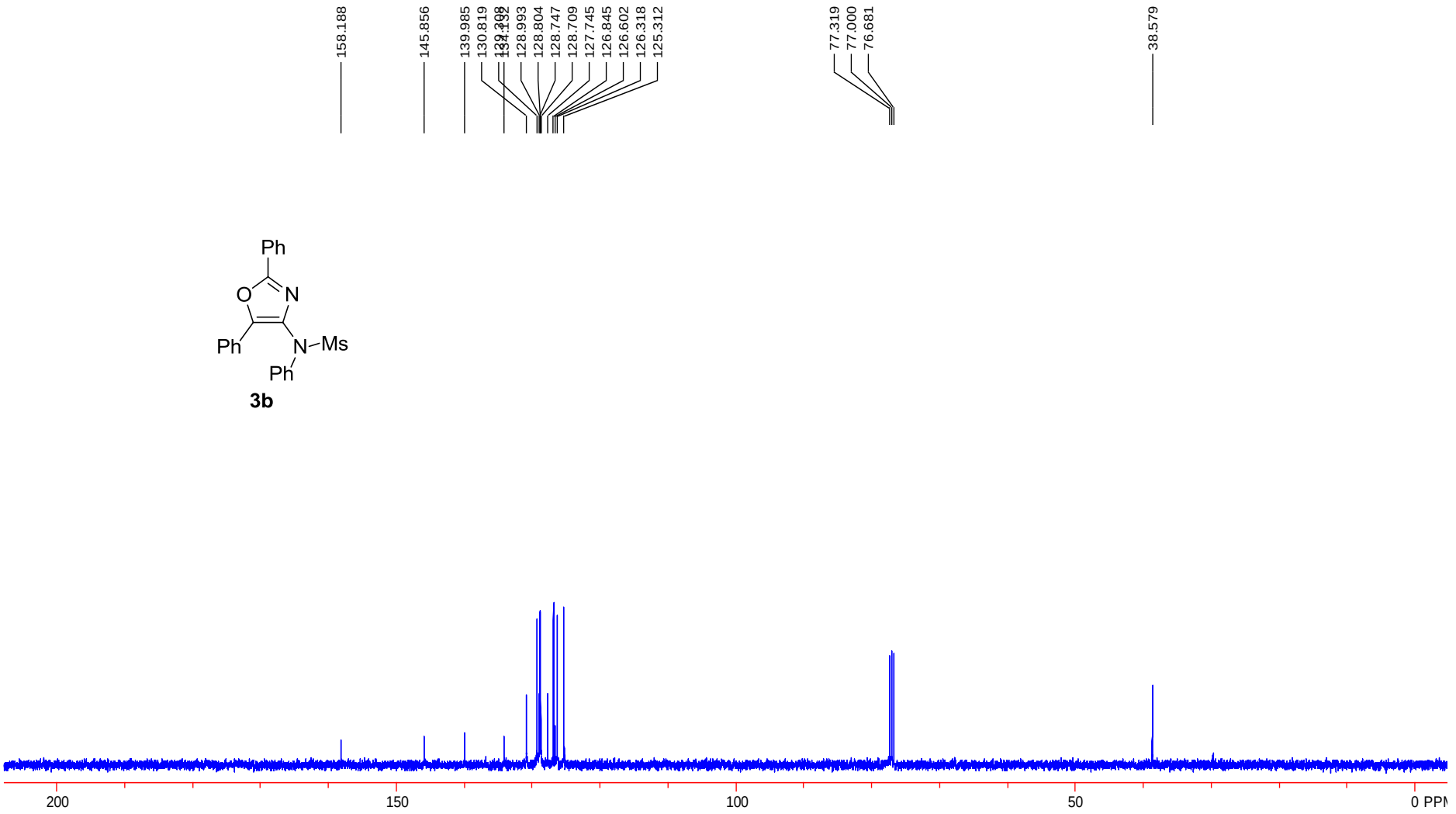


**$^{1}$H NMR (400 MHz, $CDCl_3$)**



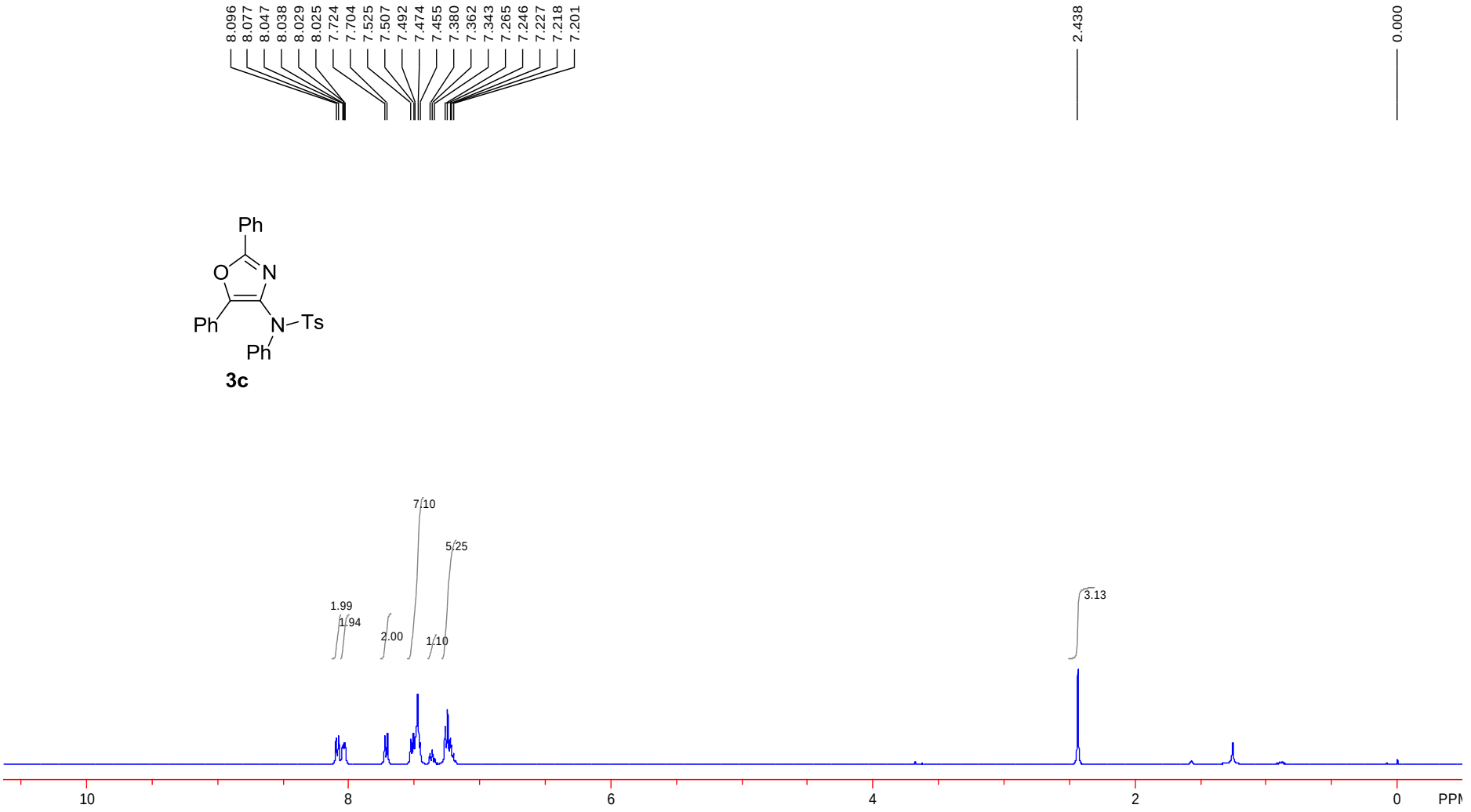

**3b**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

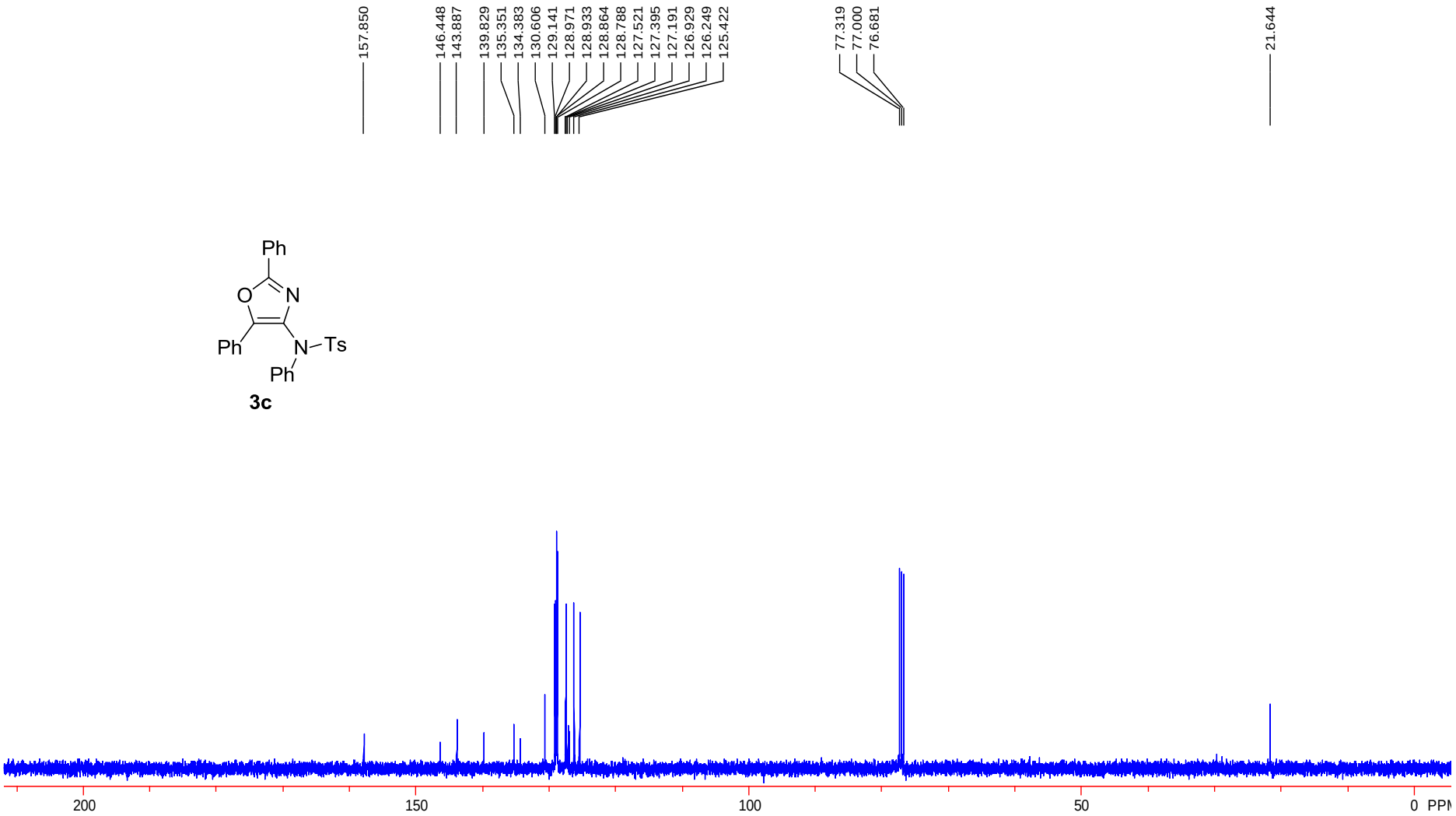



**3b**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

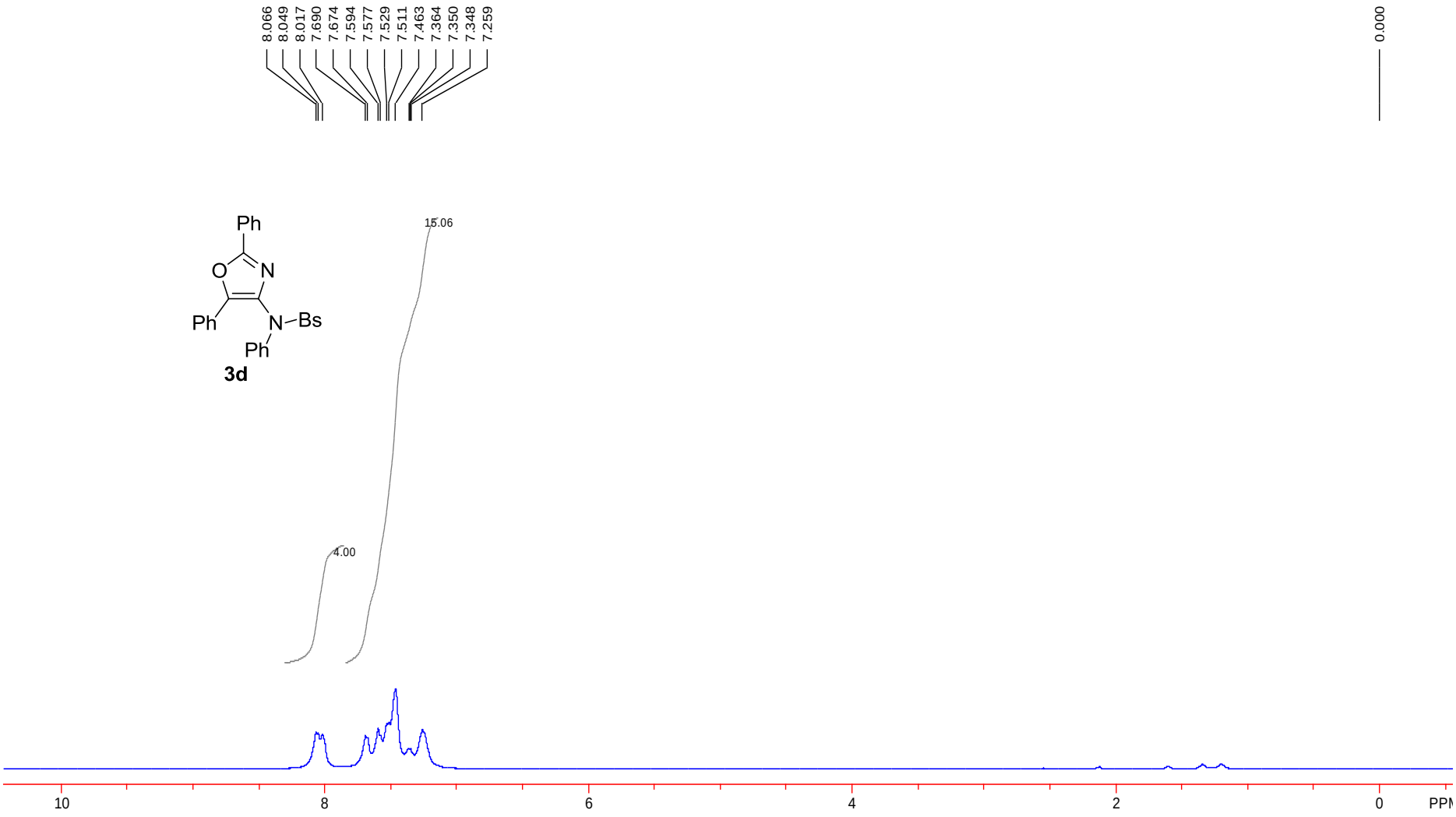


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

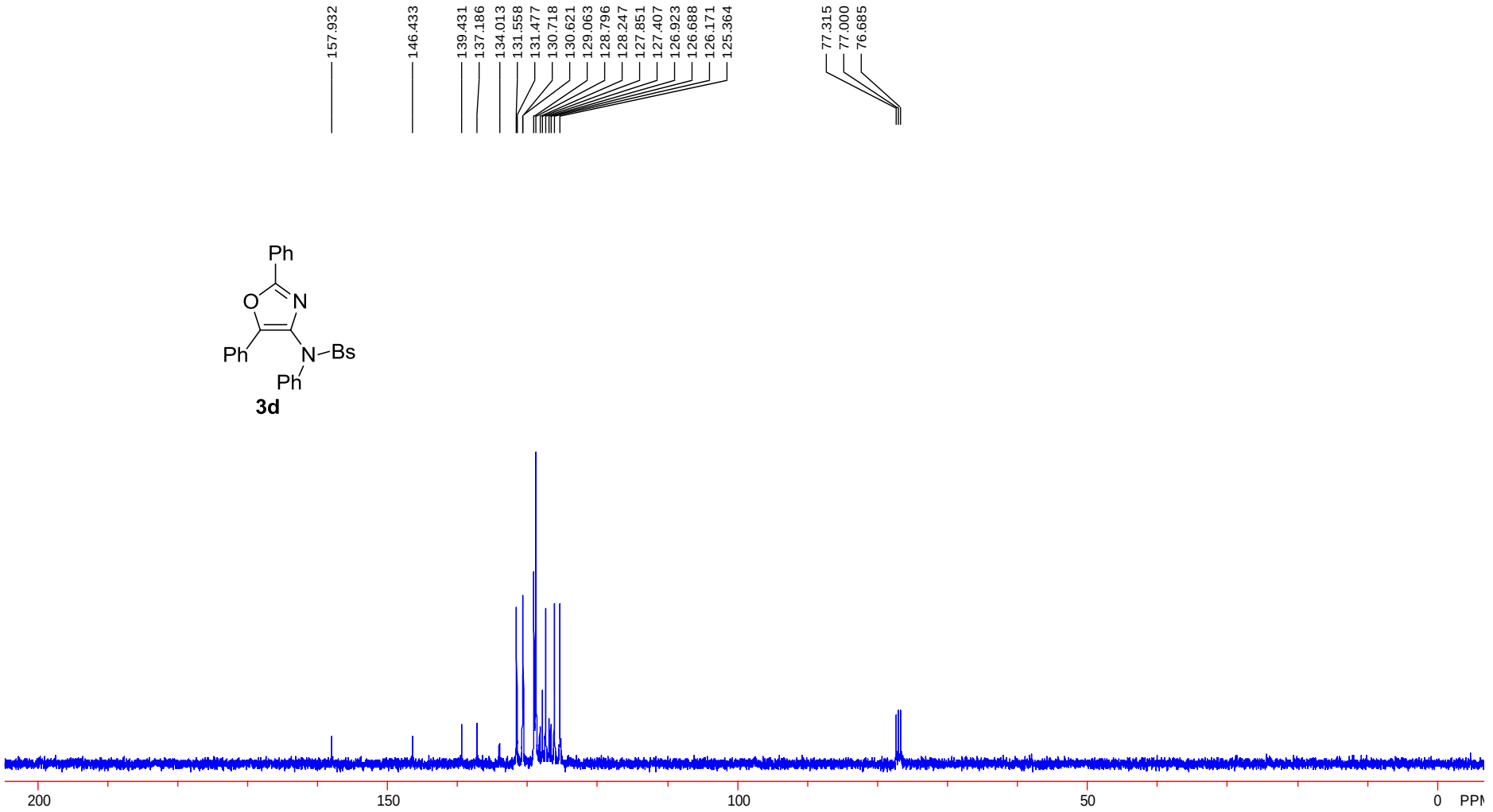



**3c**

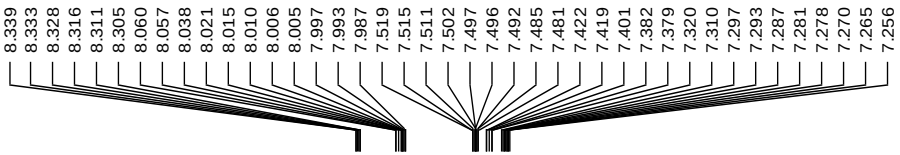
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

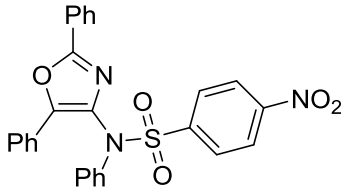


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

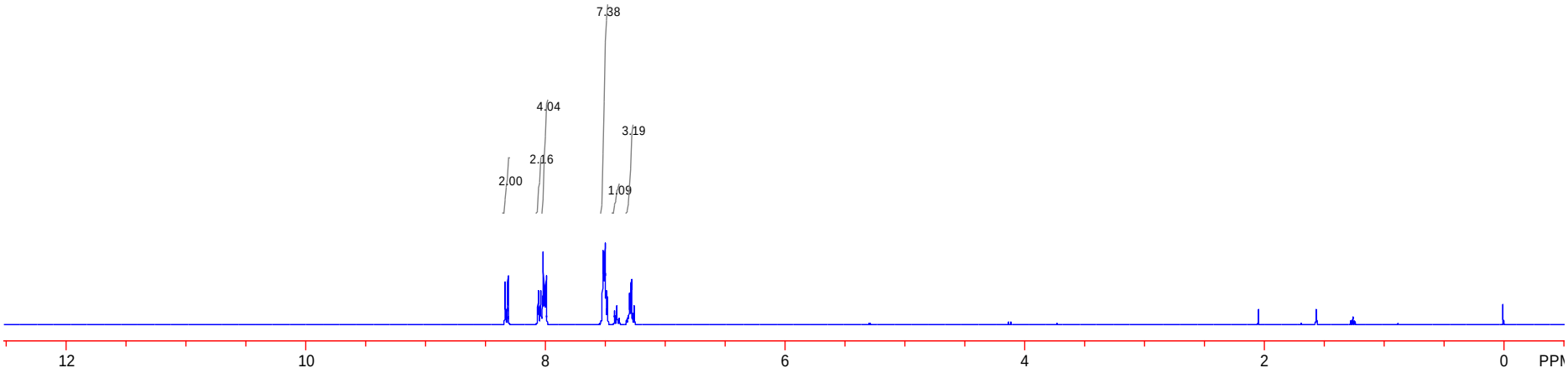


**$^{1}$H NMR (400 MHz, $CDCl_3$)**

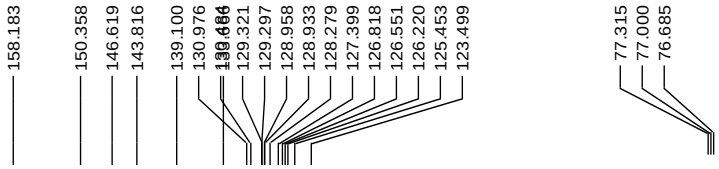


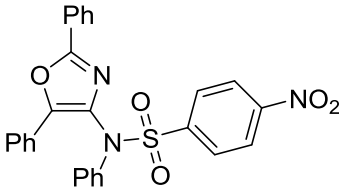




**3e**

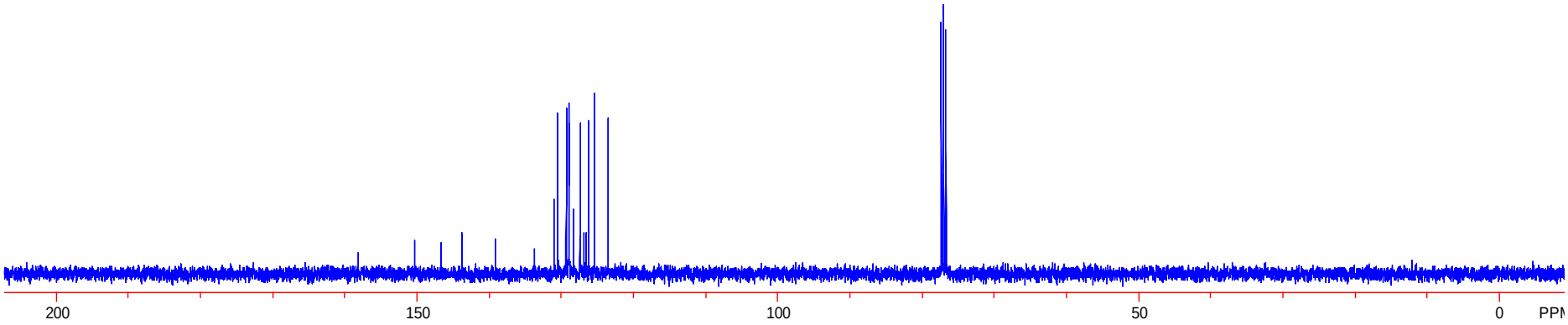


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

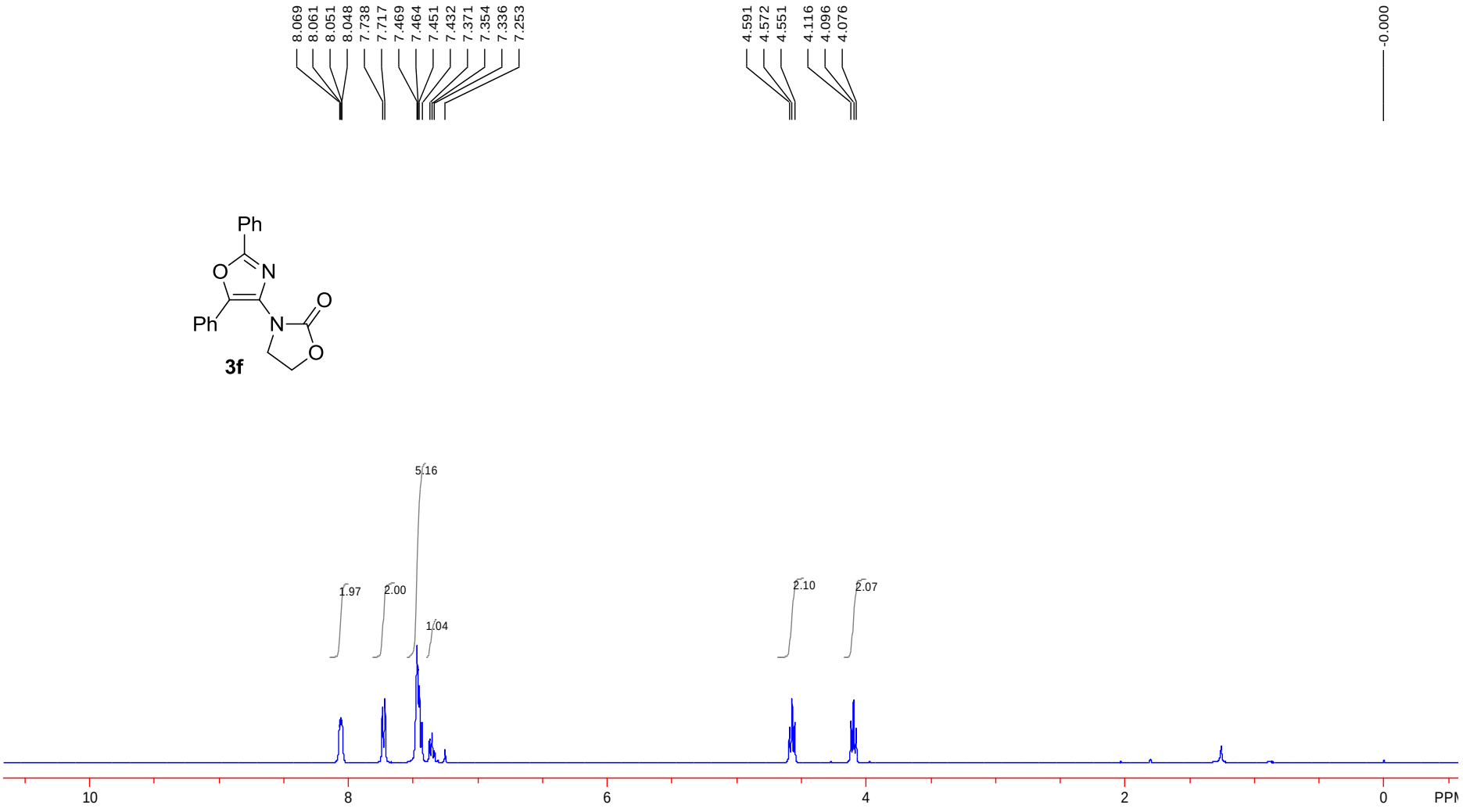


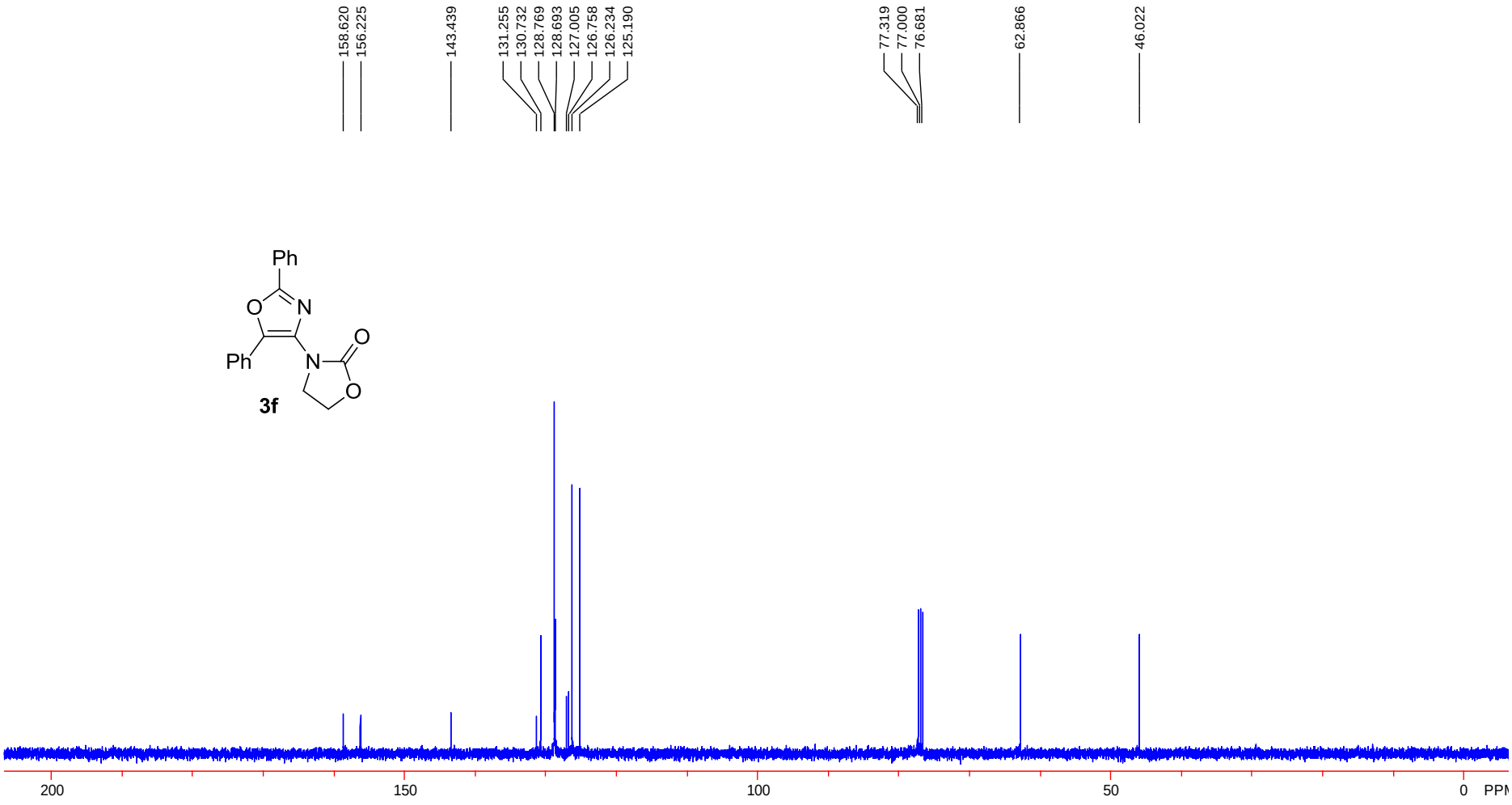

**3e**



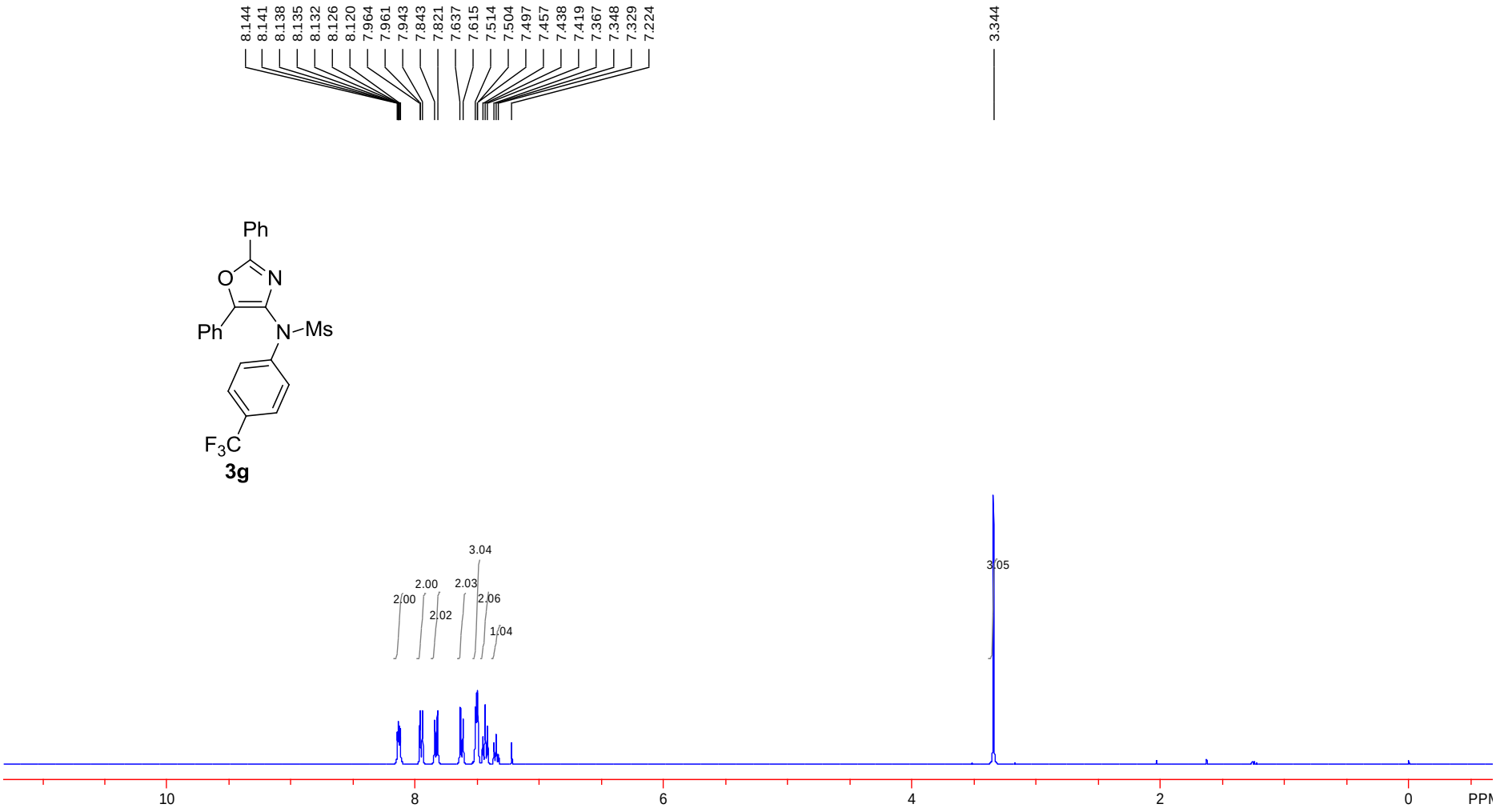
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



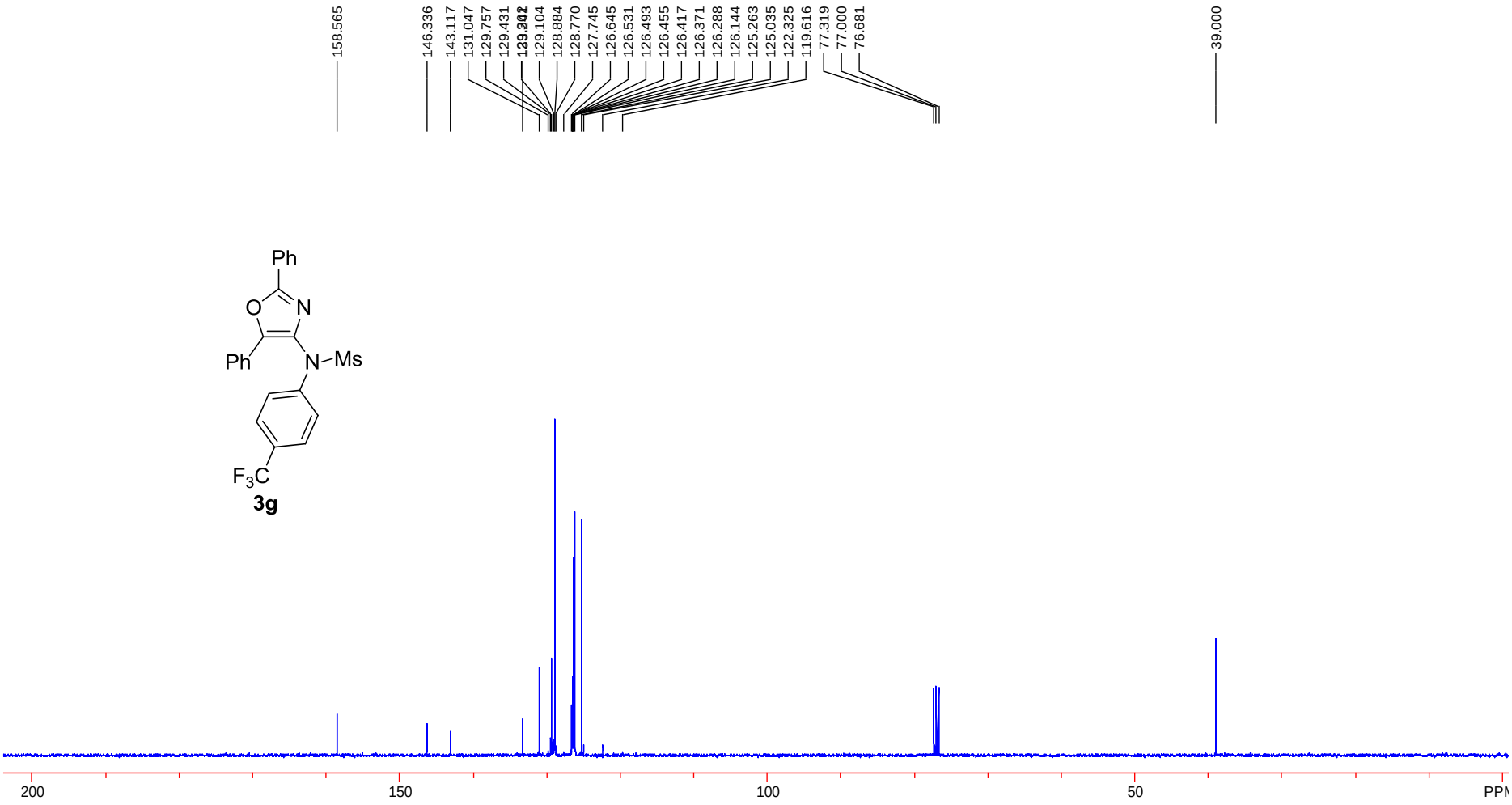
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



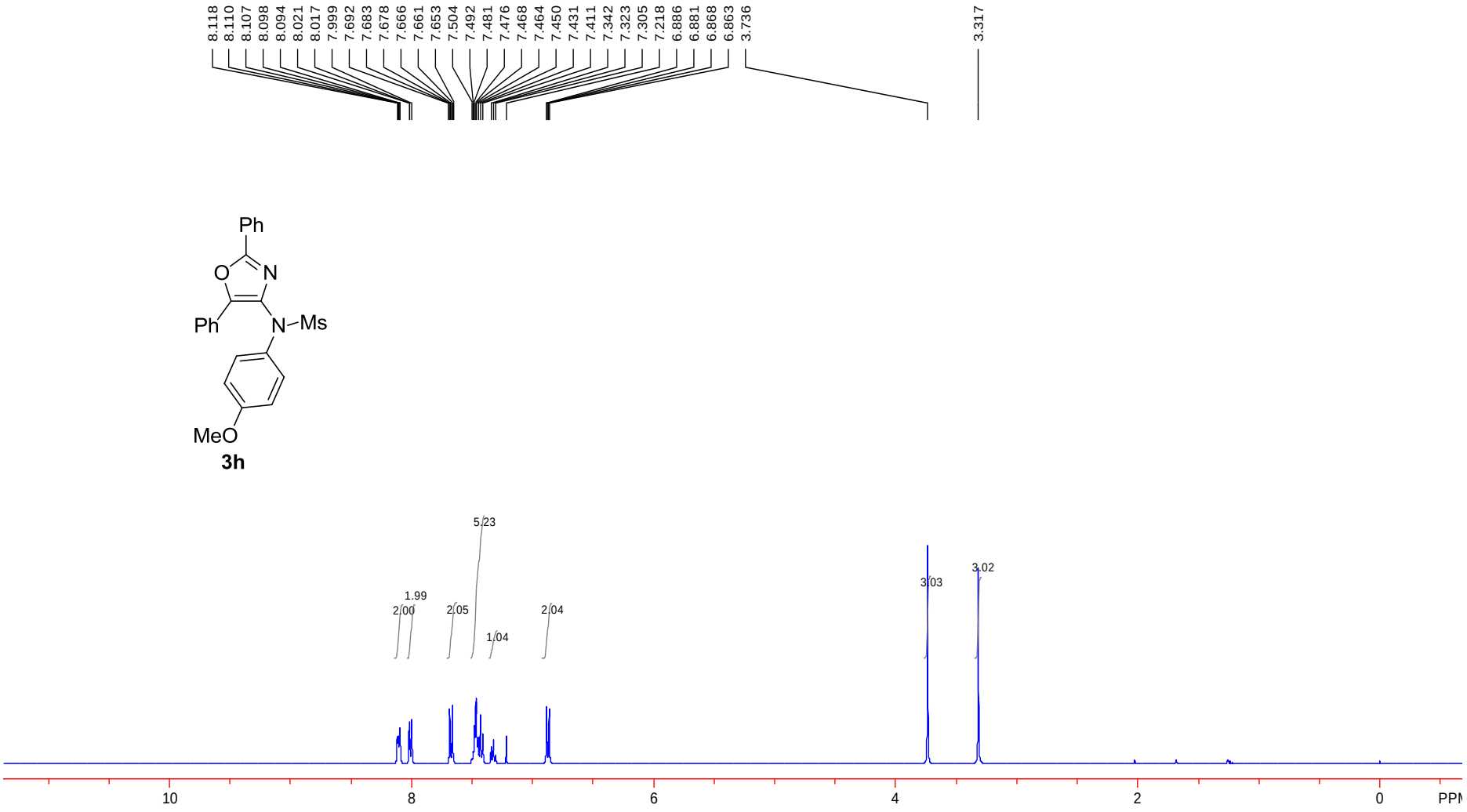
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



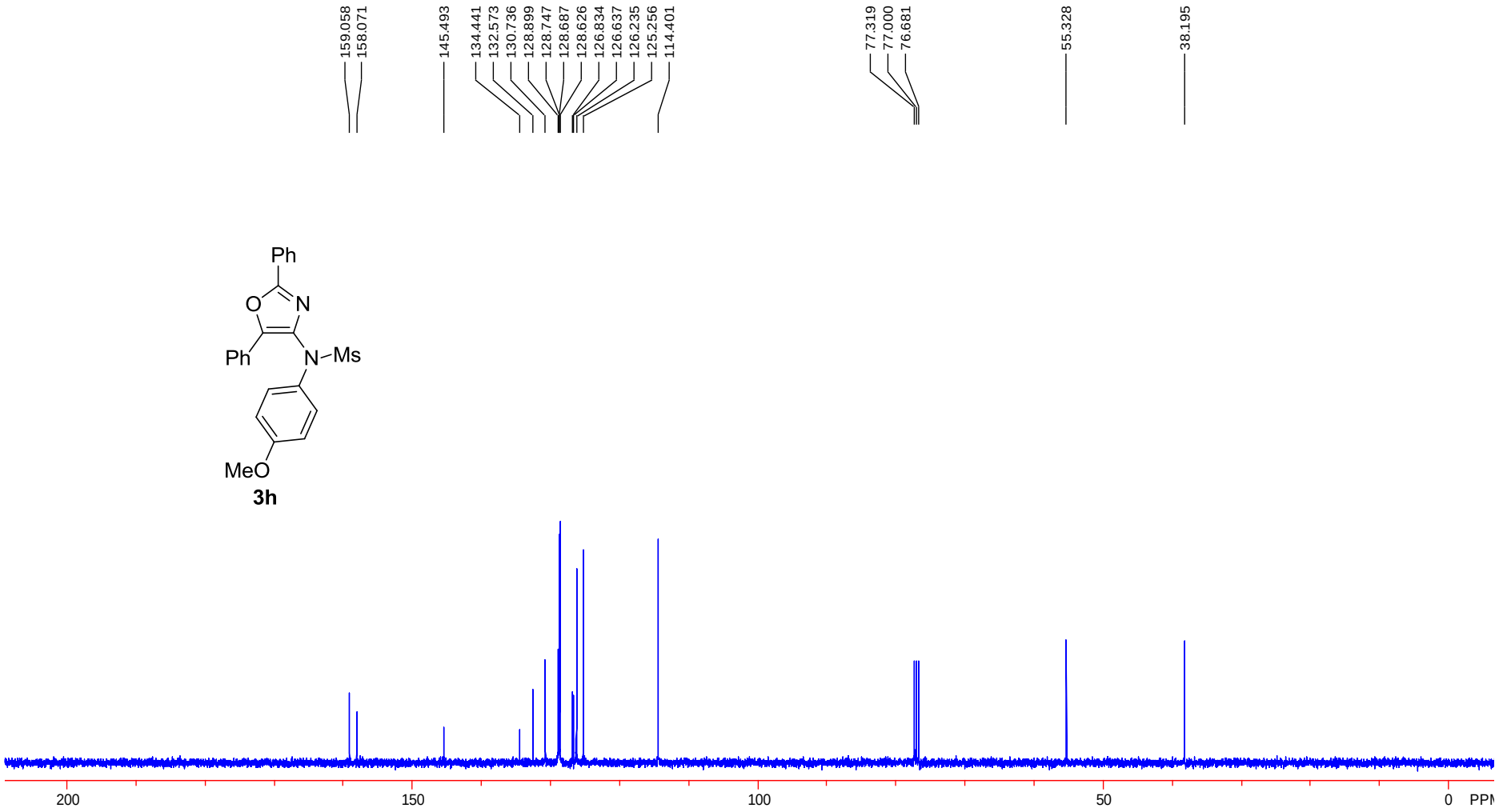
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



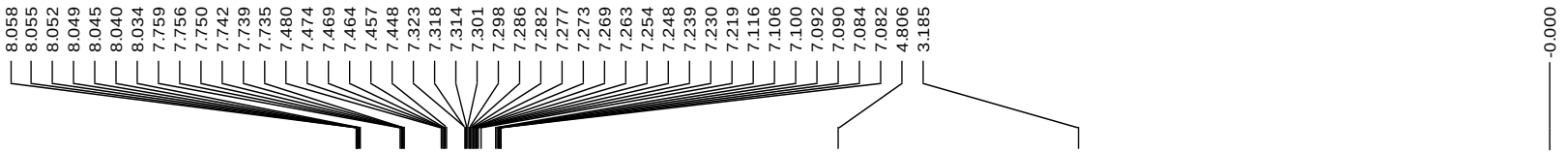
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

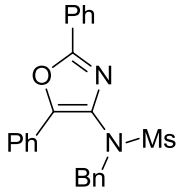


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

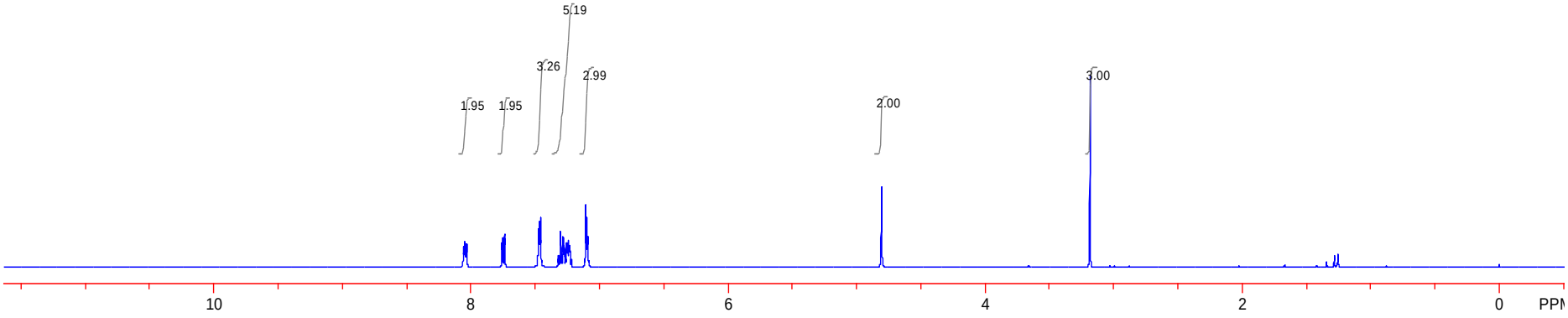


**$^{1}$H NMR (400 MHz, $CDCl_3$)**

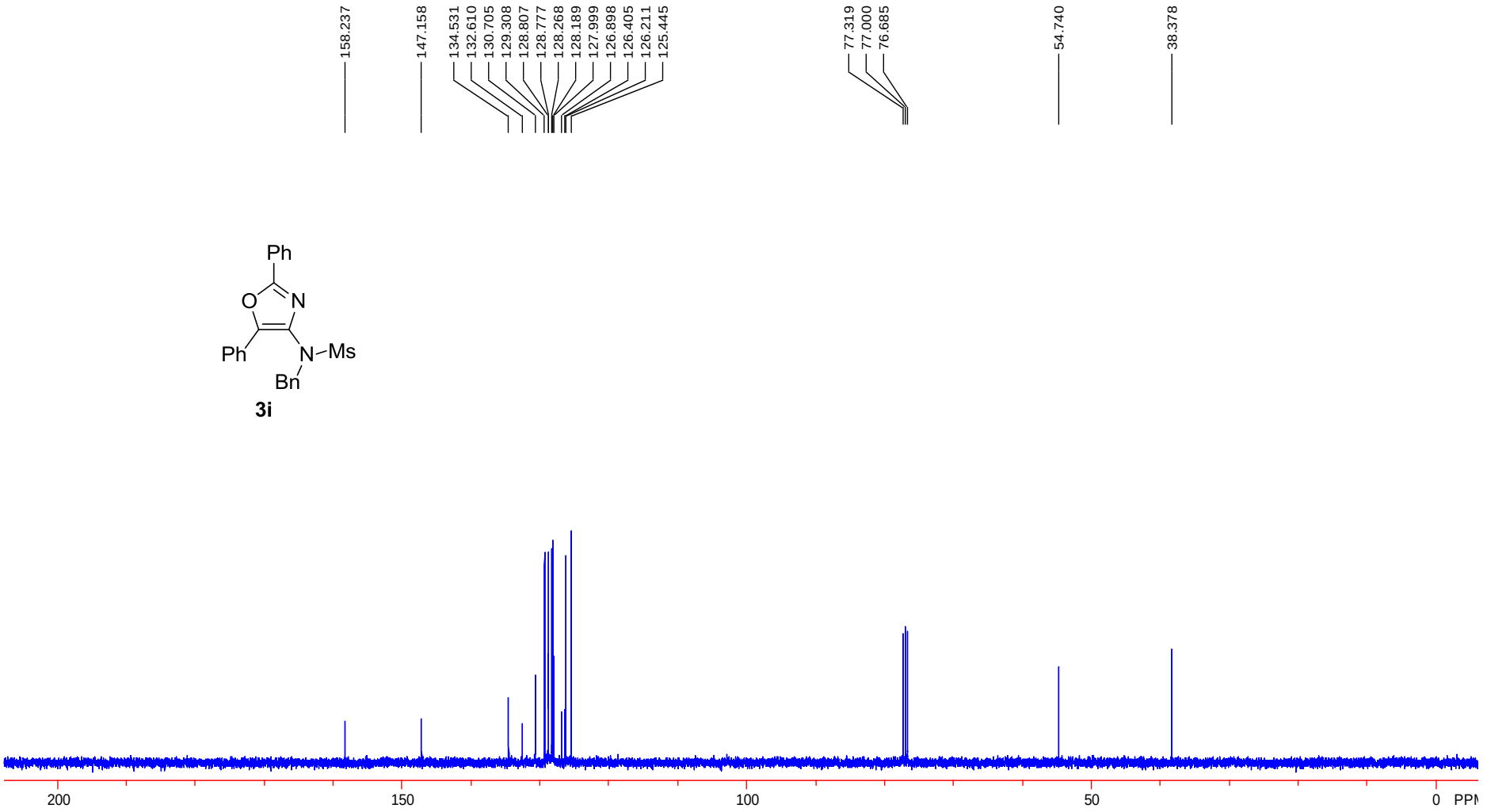



**3i**

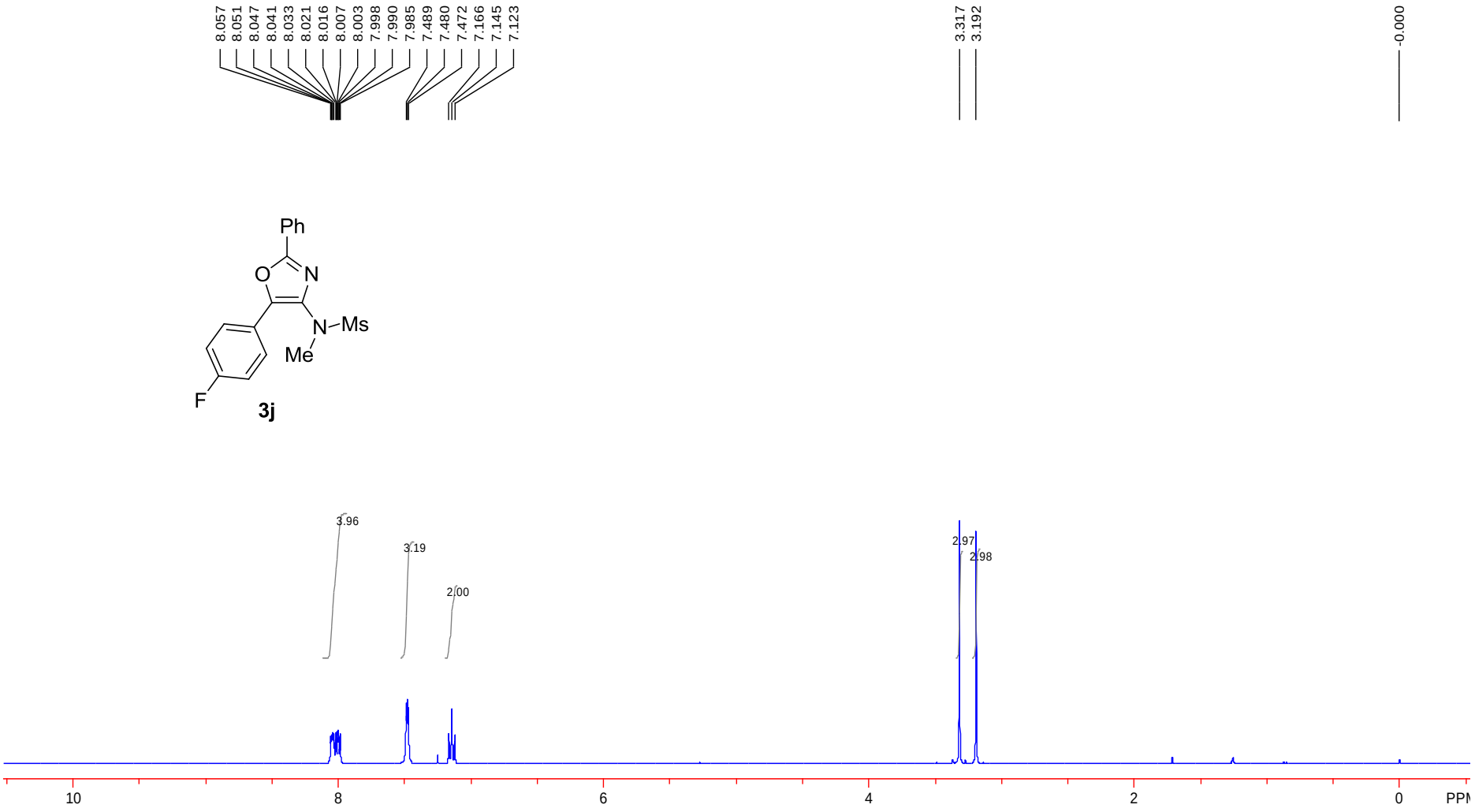


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

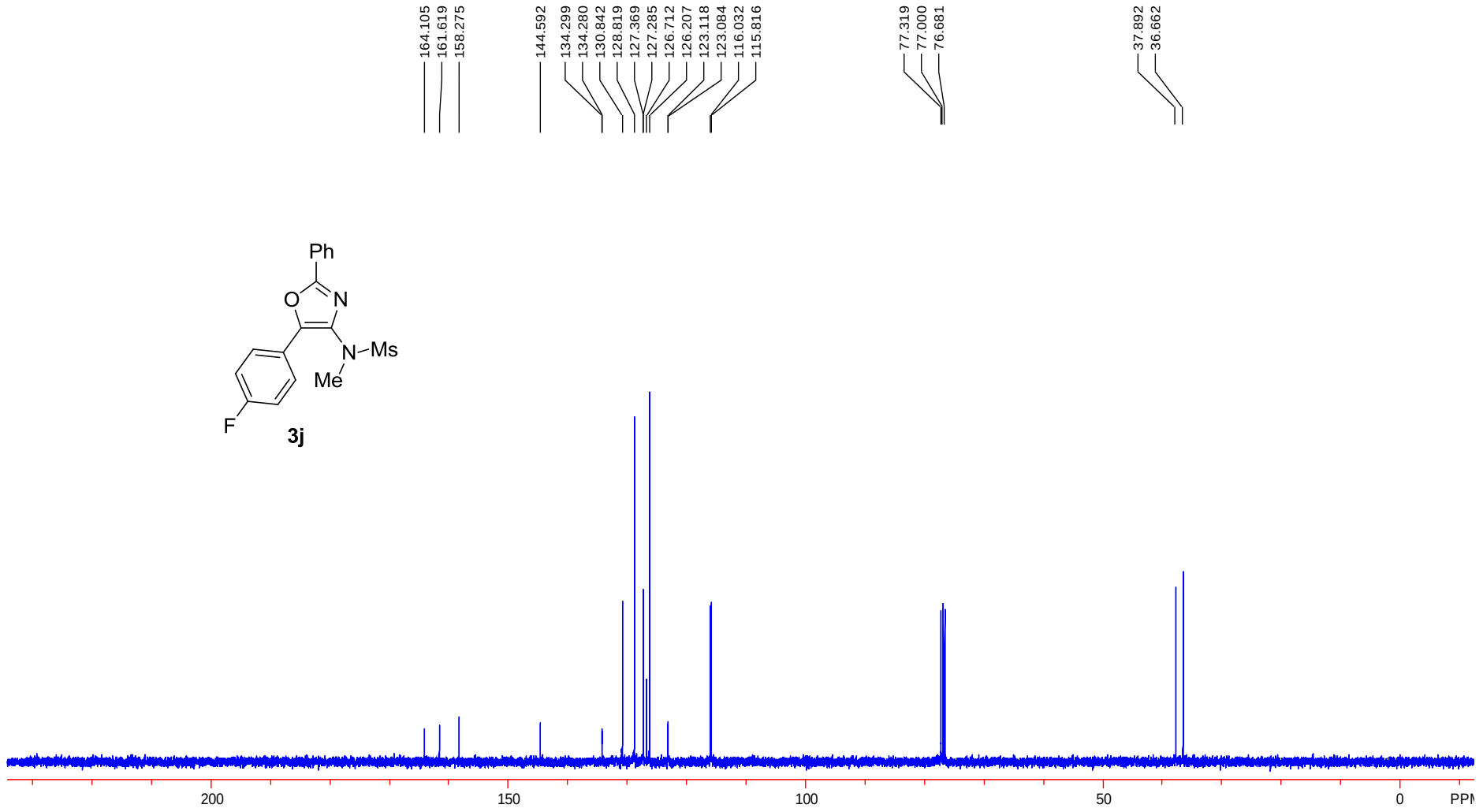



**3i**

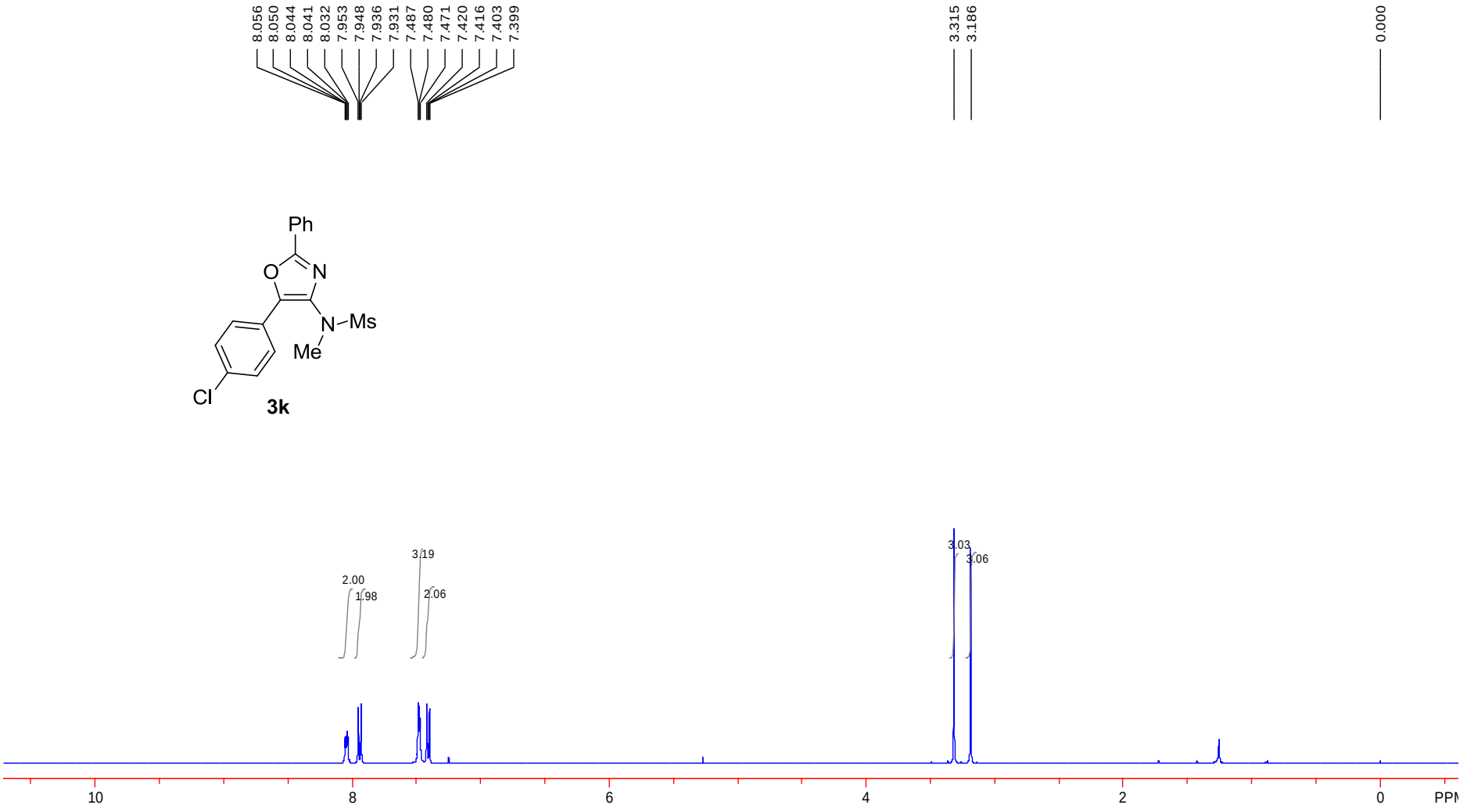
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



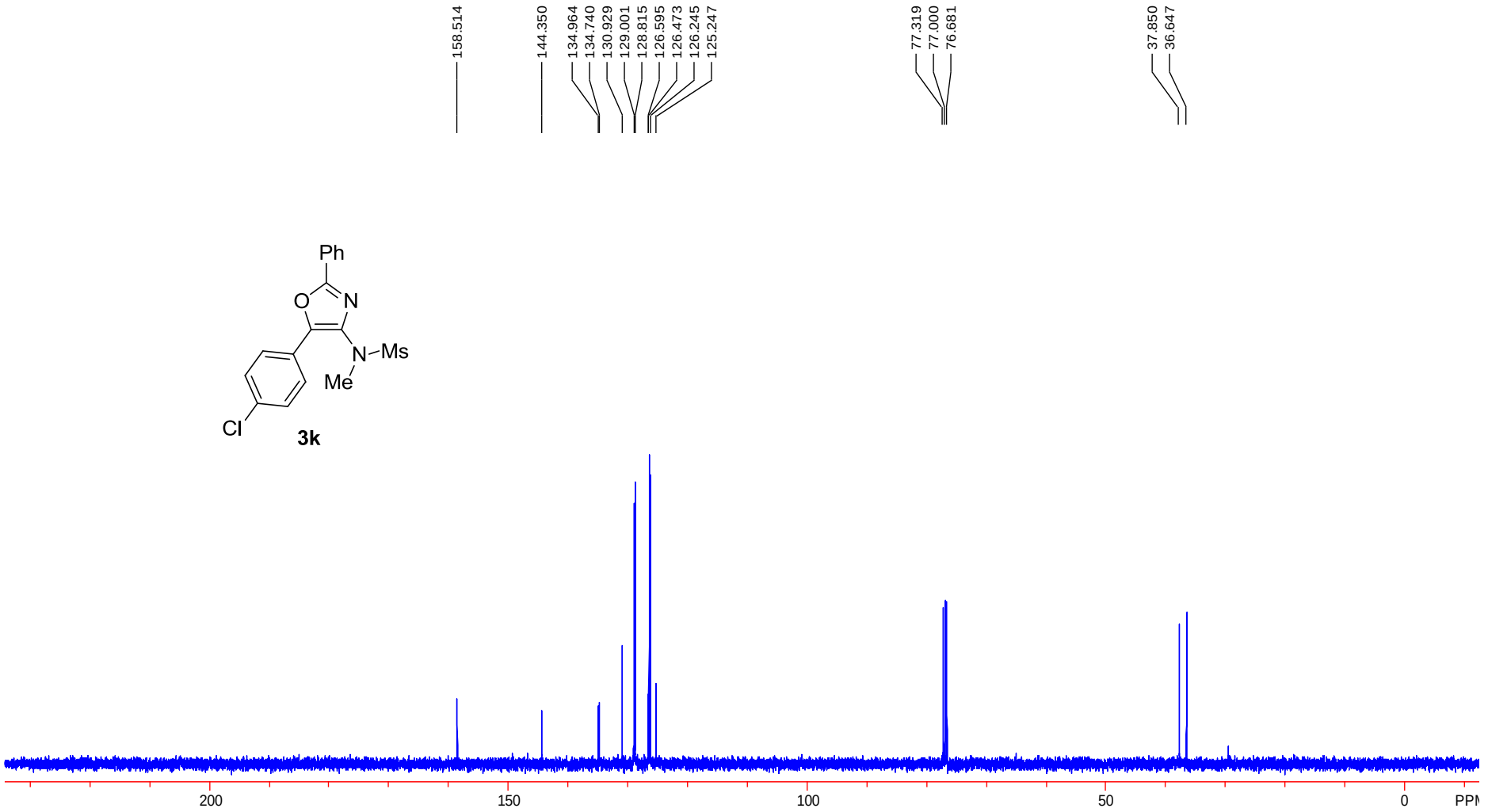
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



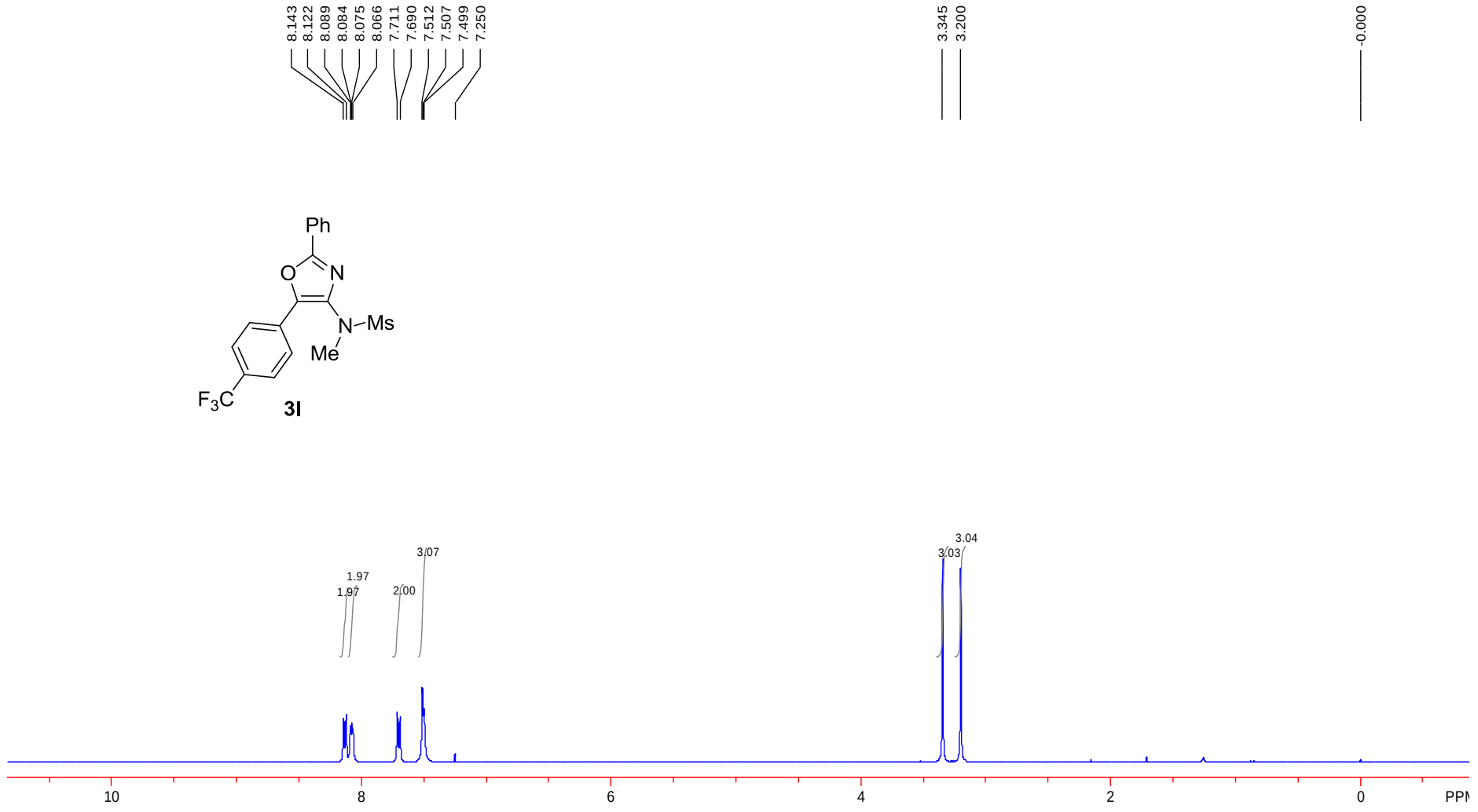
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



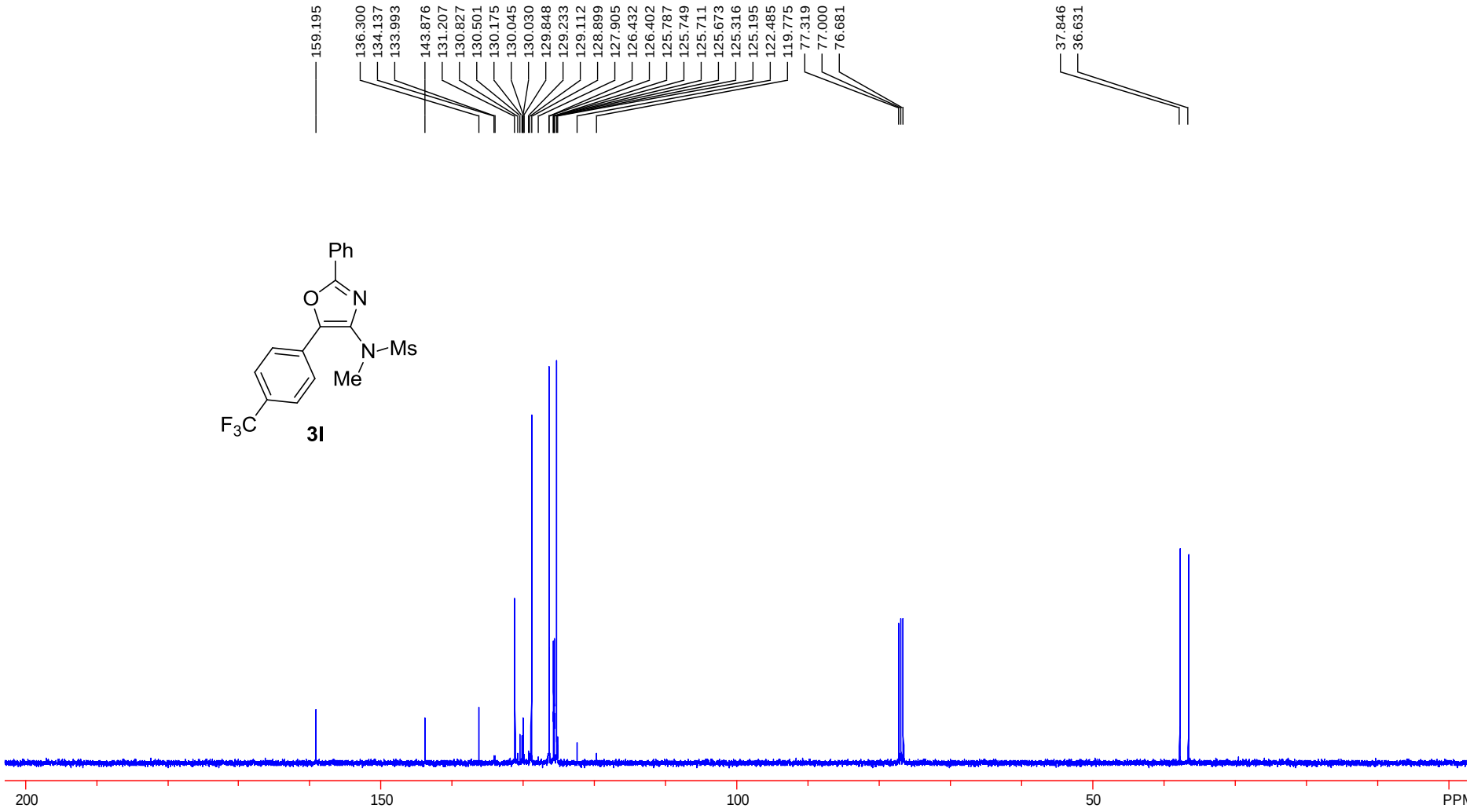
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



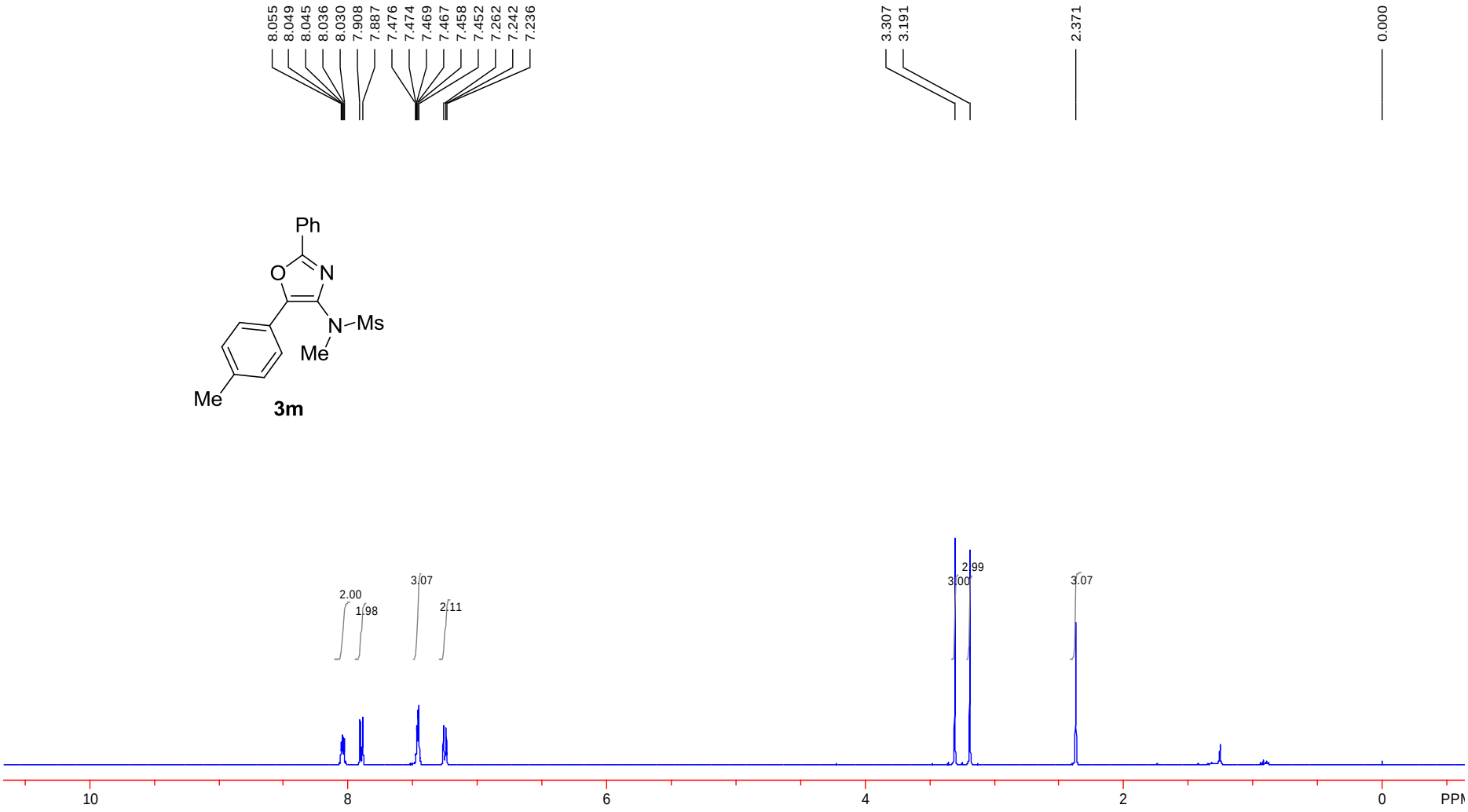
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



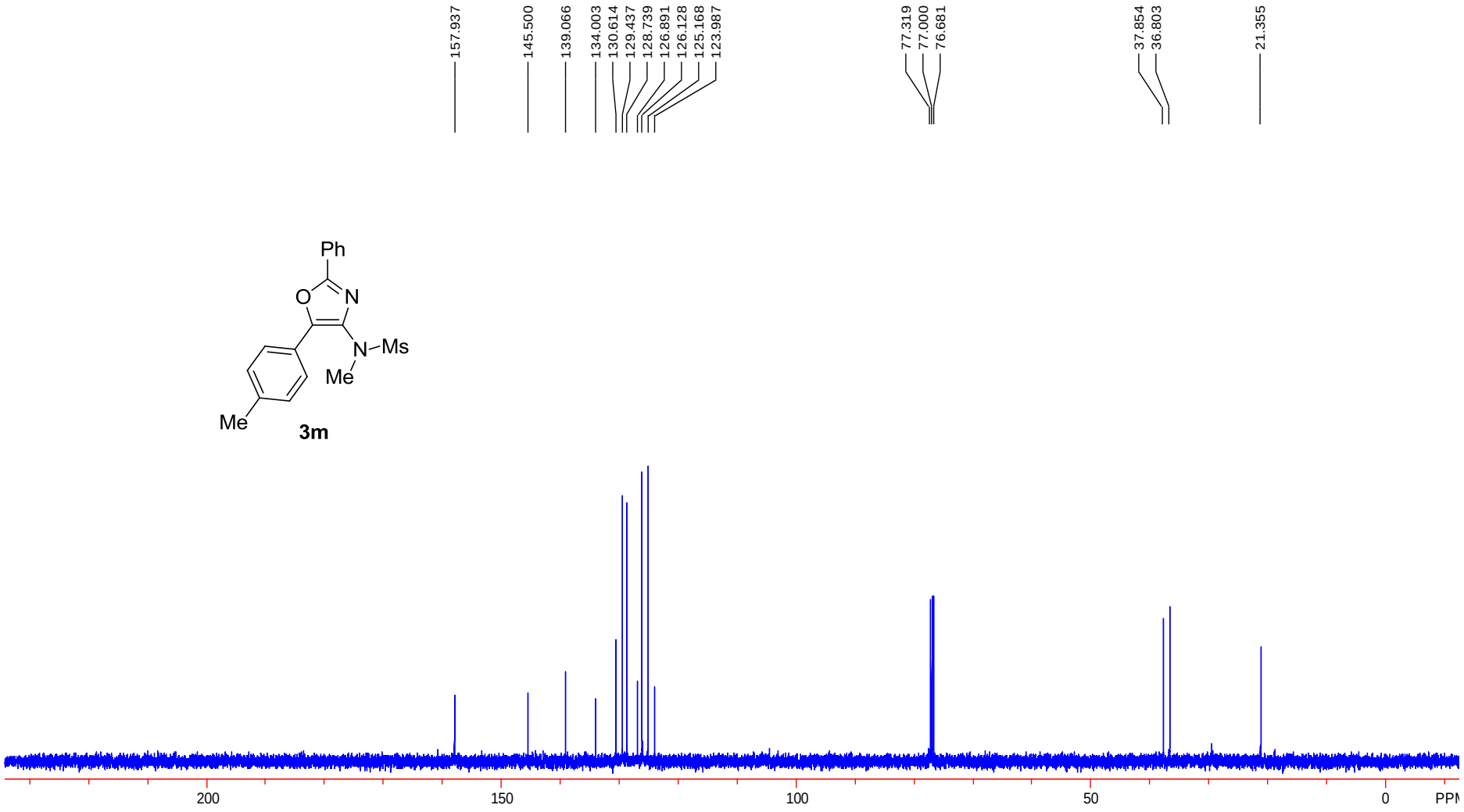
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



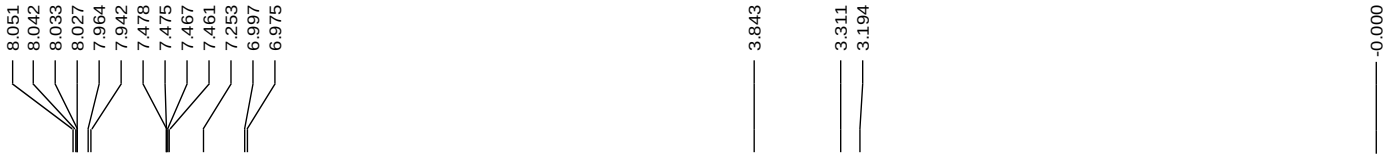
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

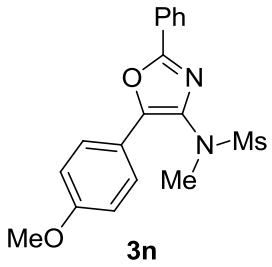


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

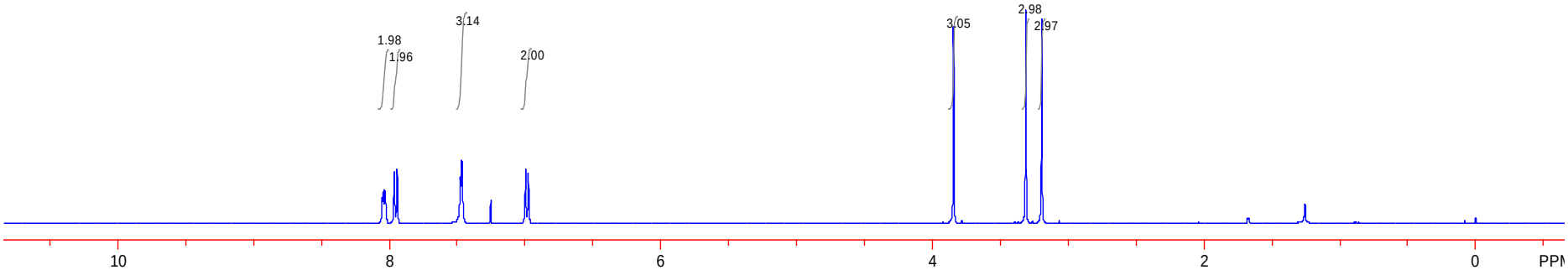


**$^1$H NMR (400 MHz, $CDCl_3$)**

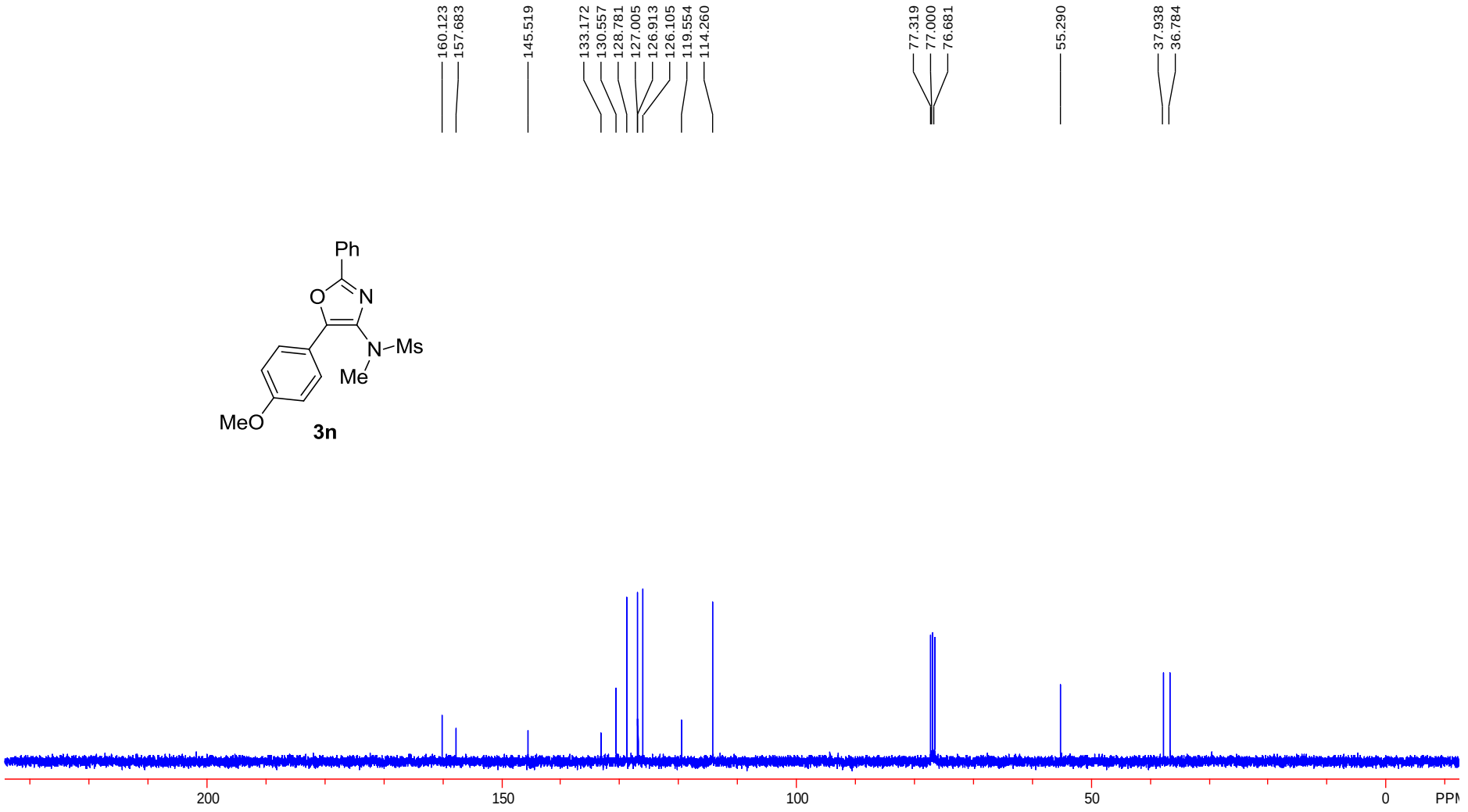


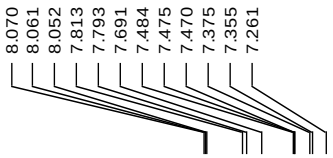

**3n**

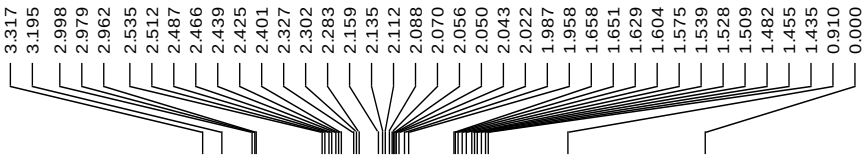


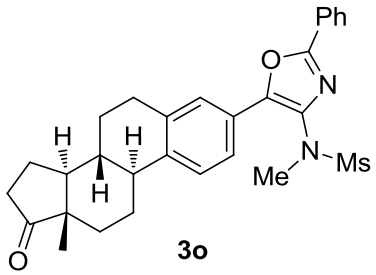
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



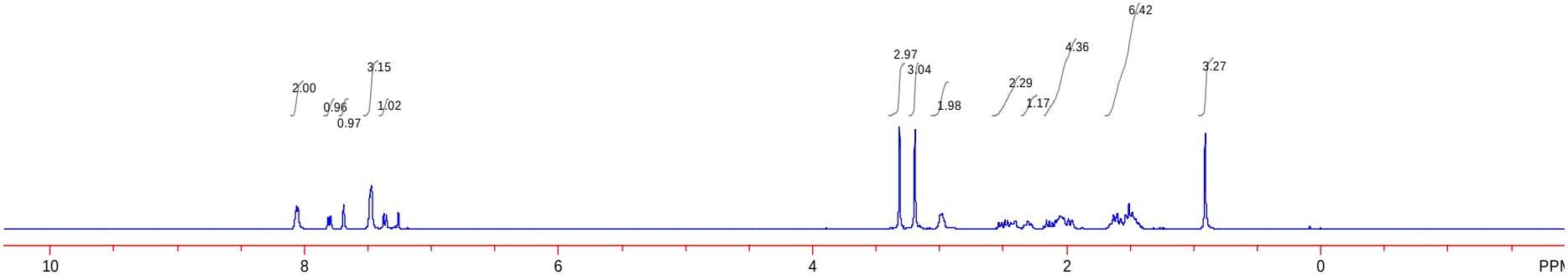
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



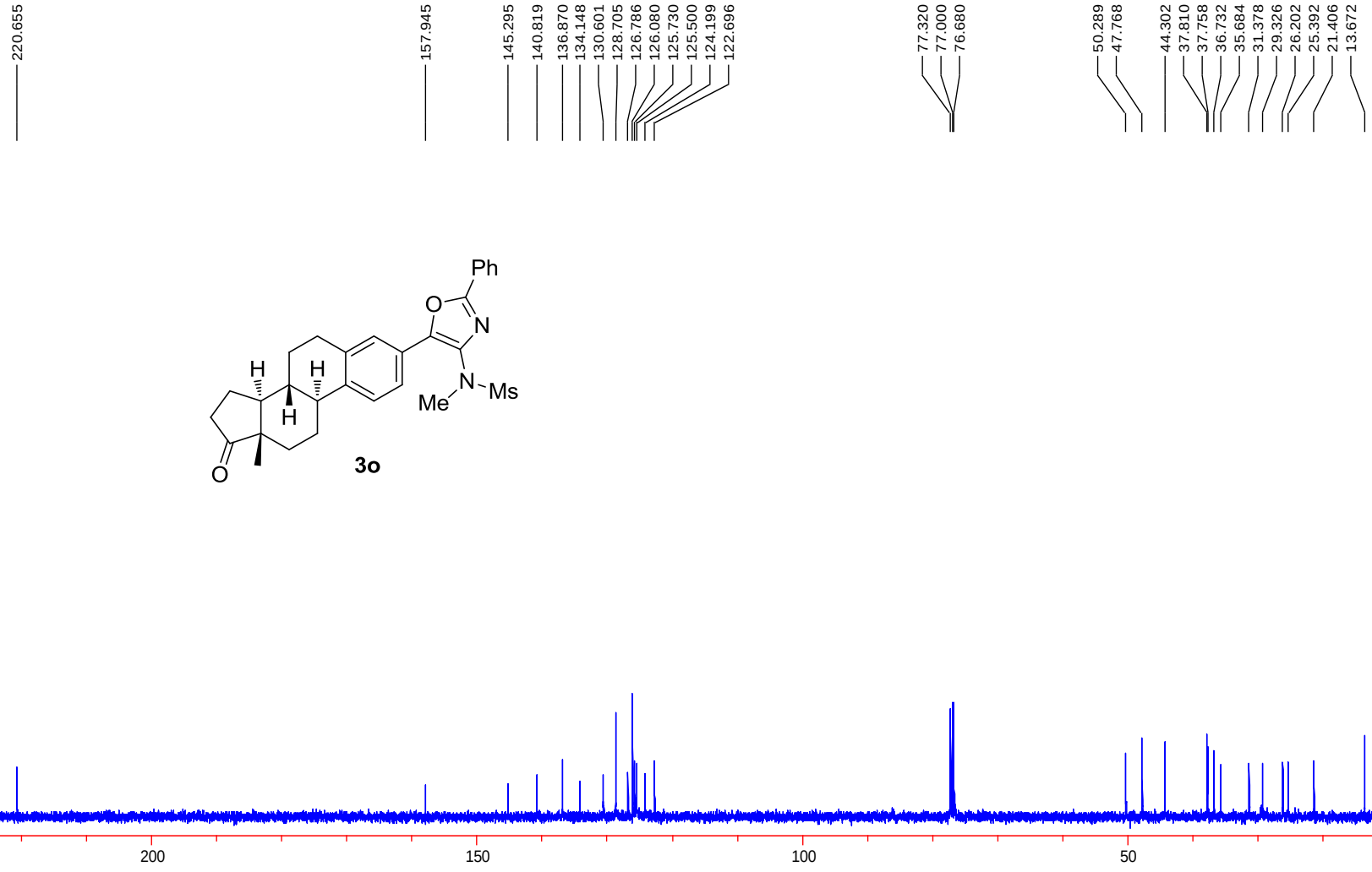



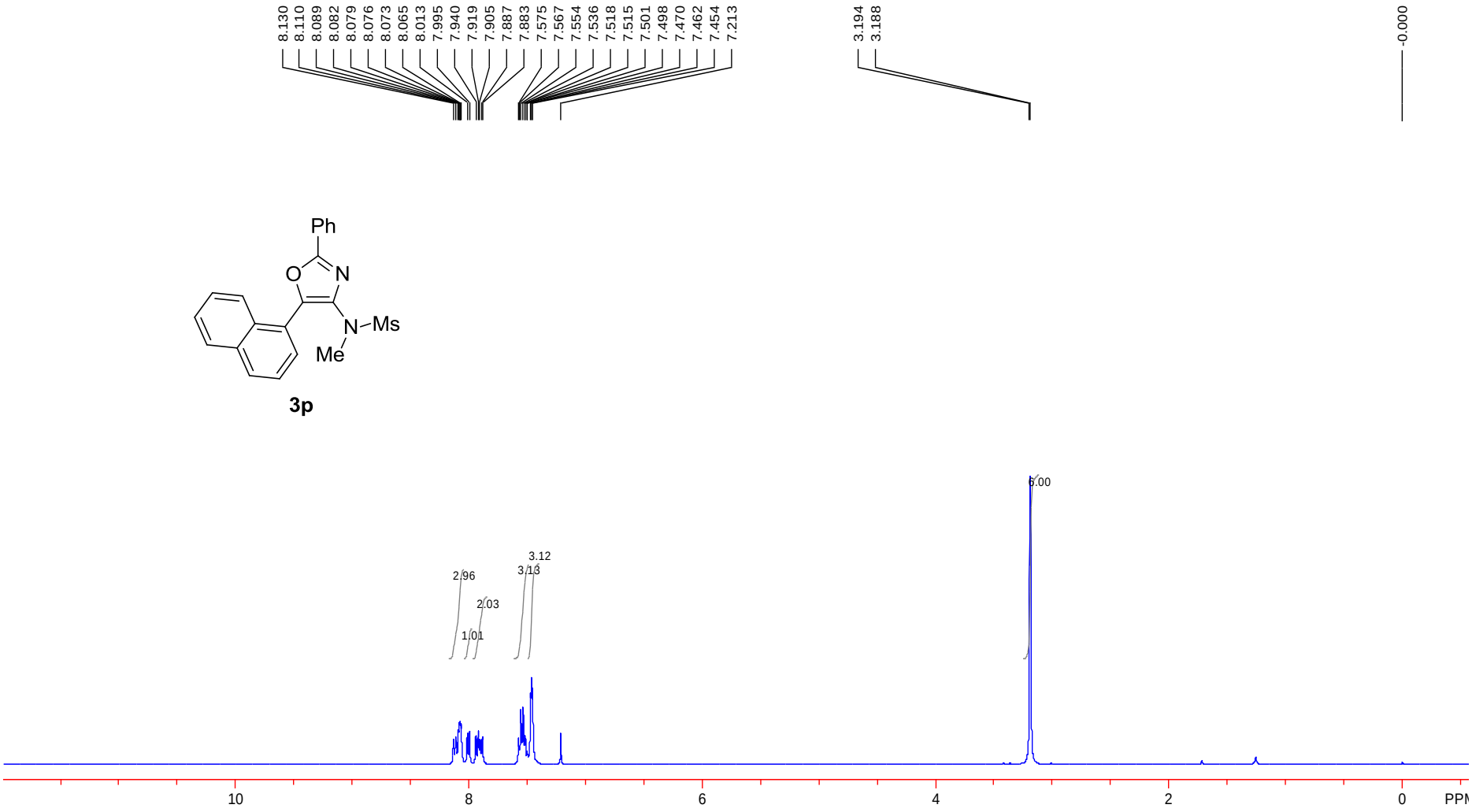

**3o**



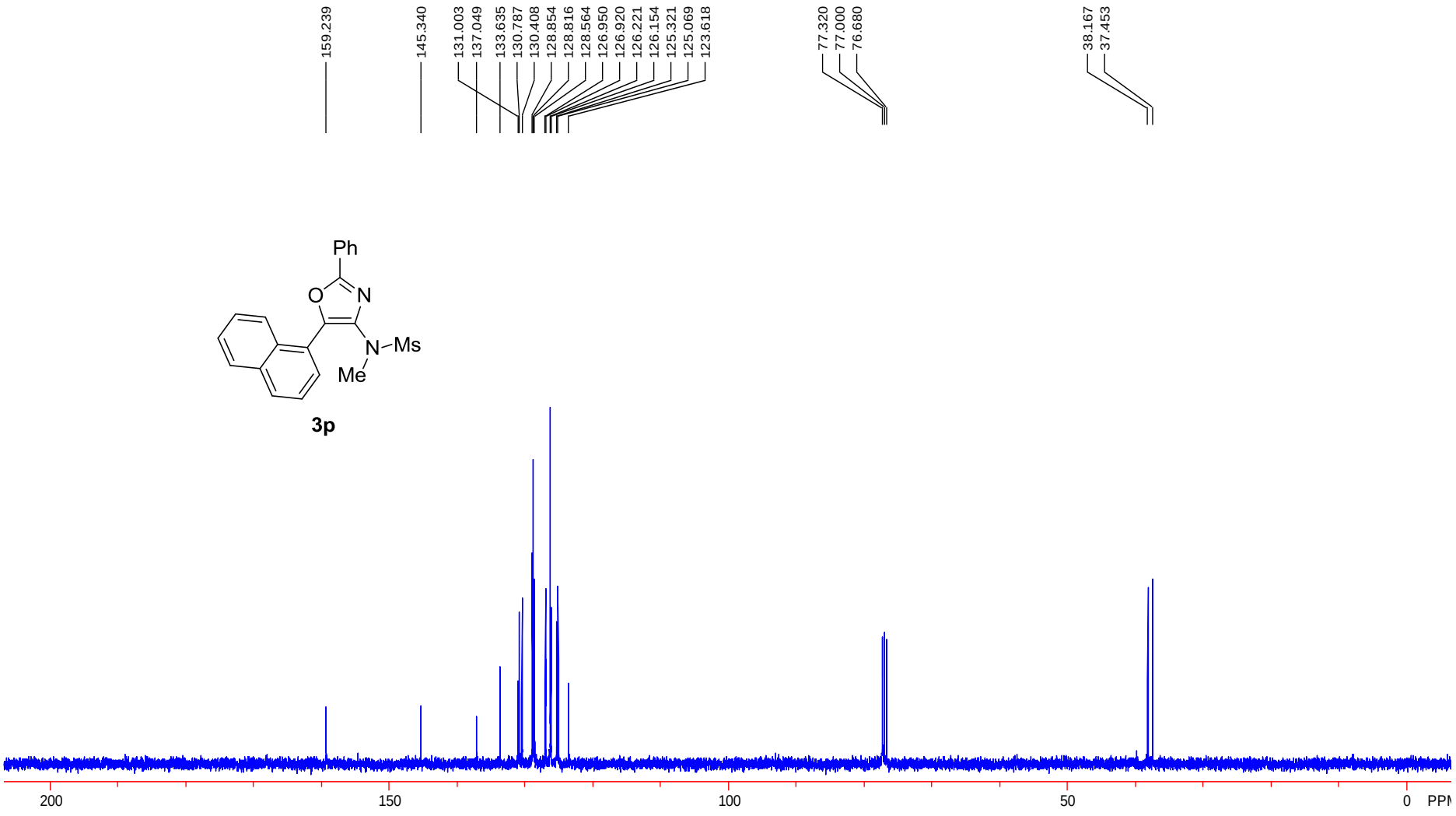
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



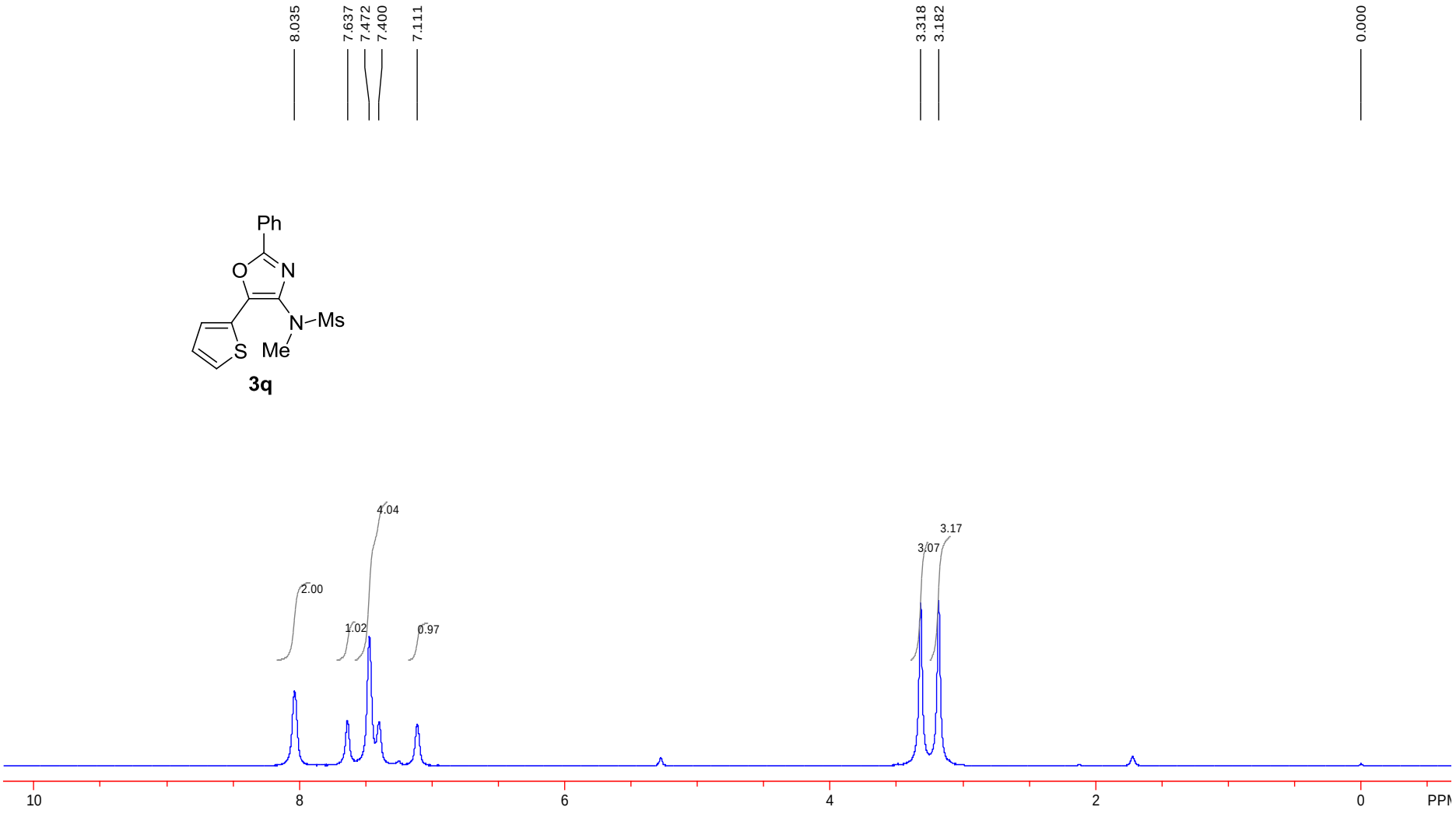
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



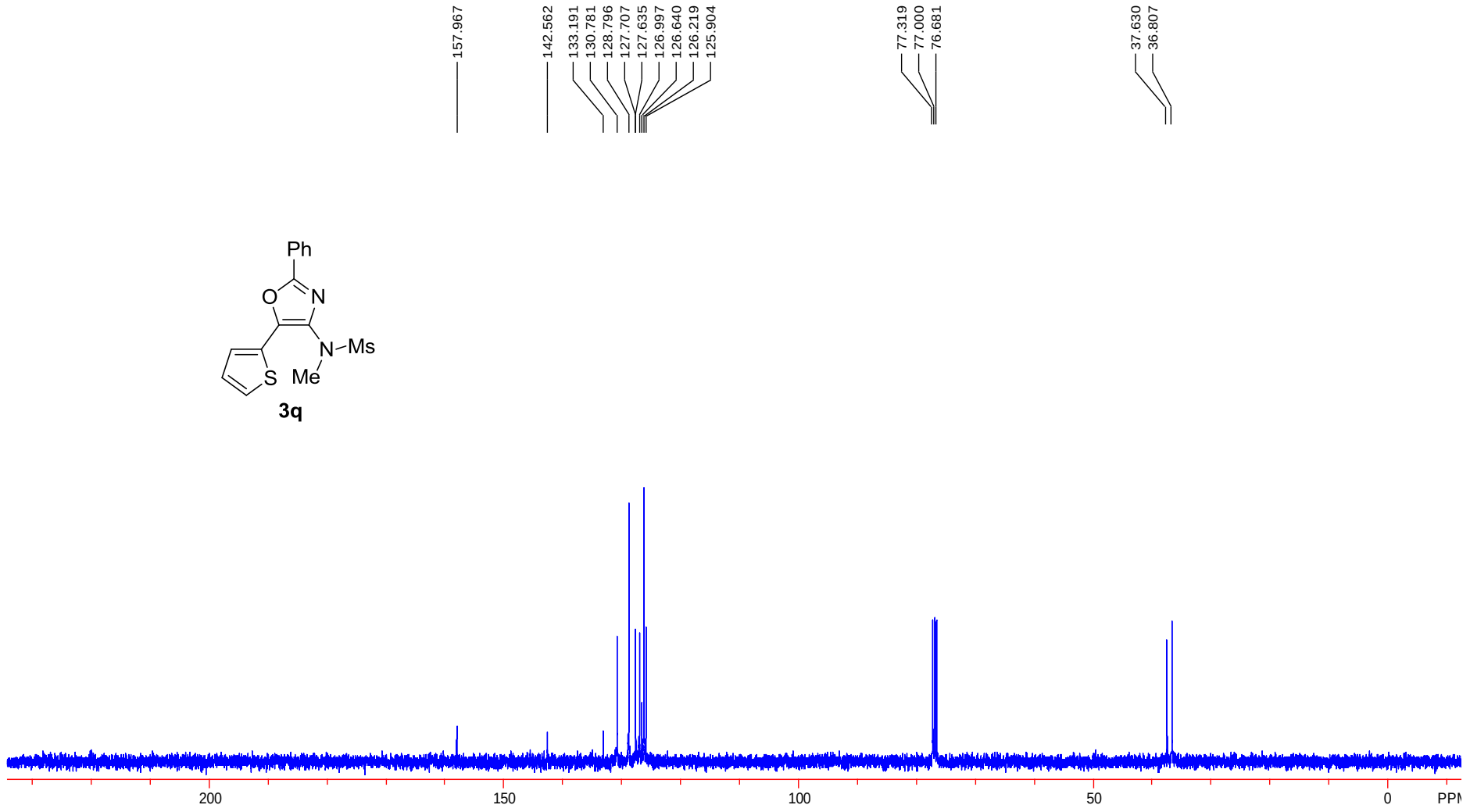
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



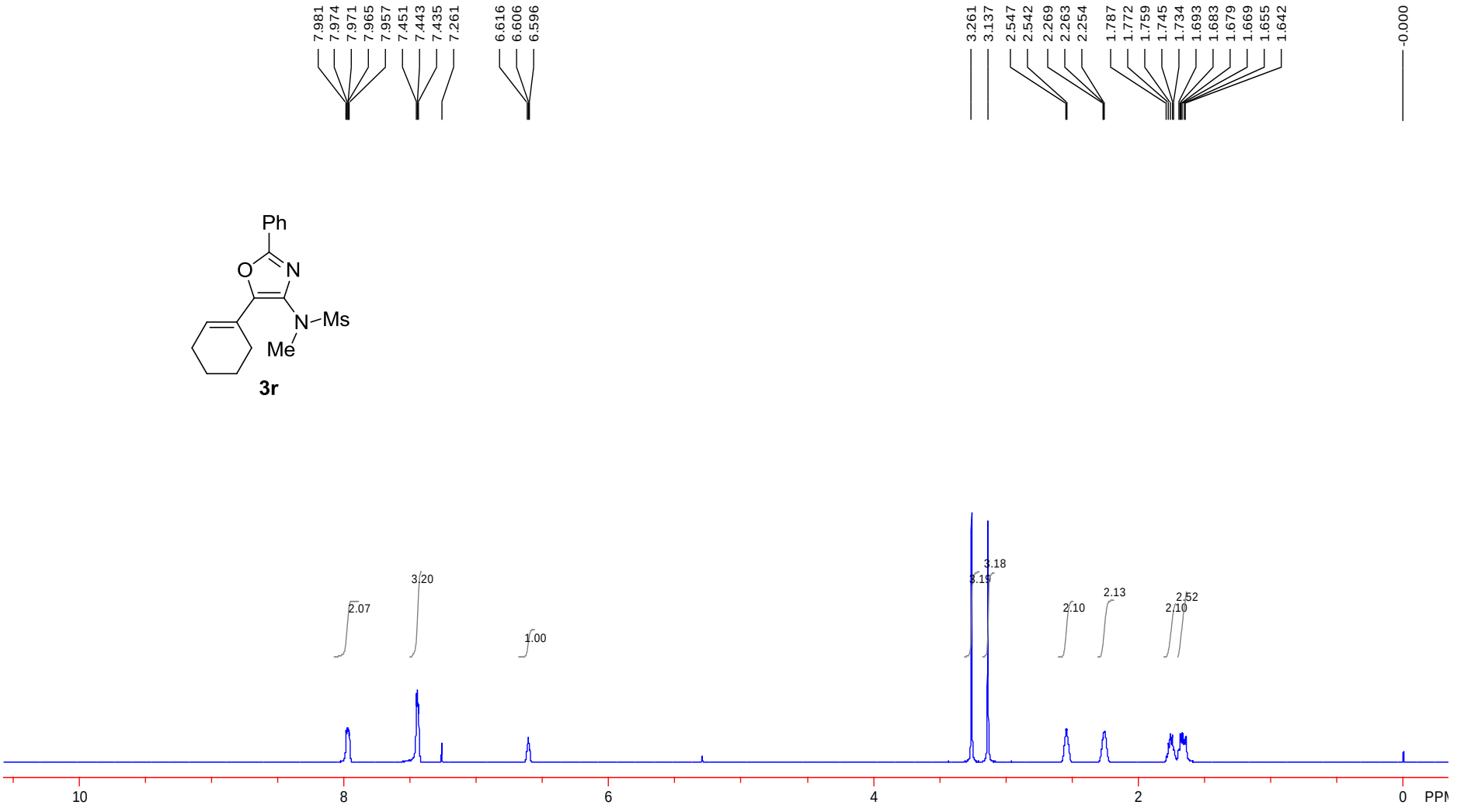
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



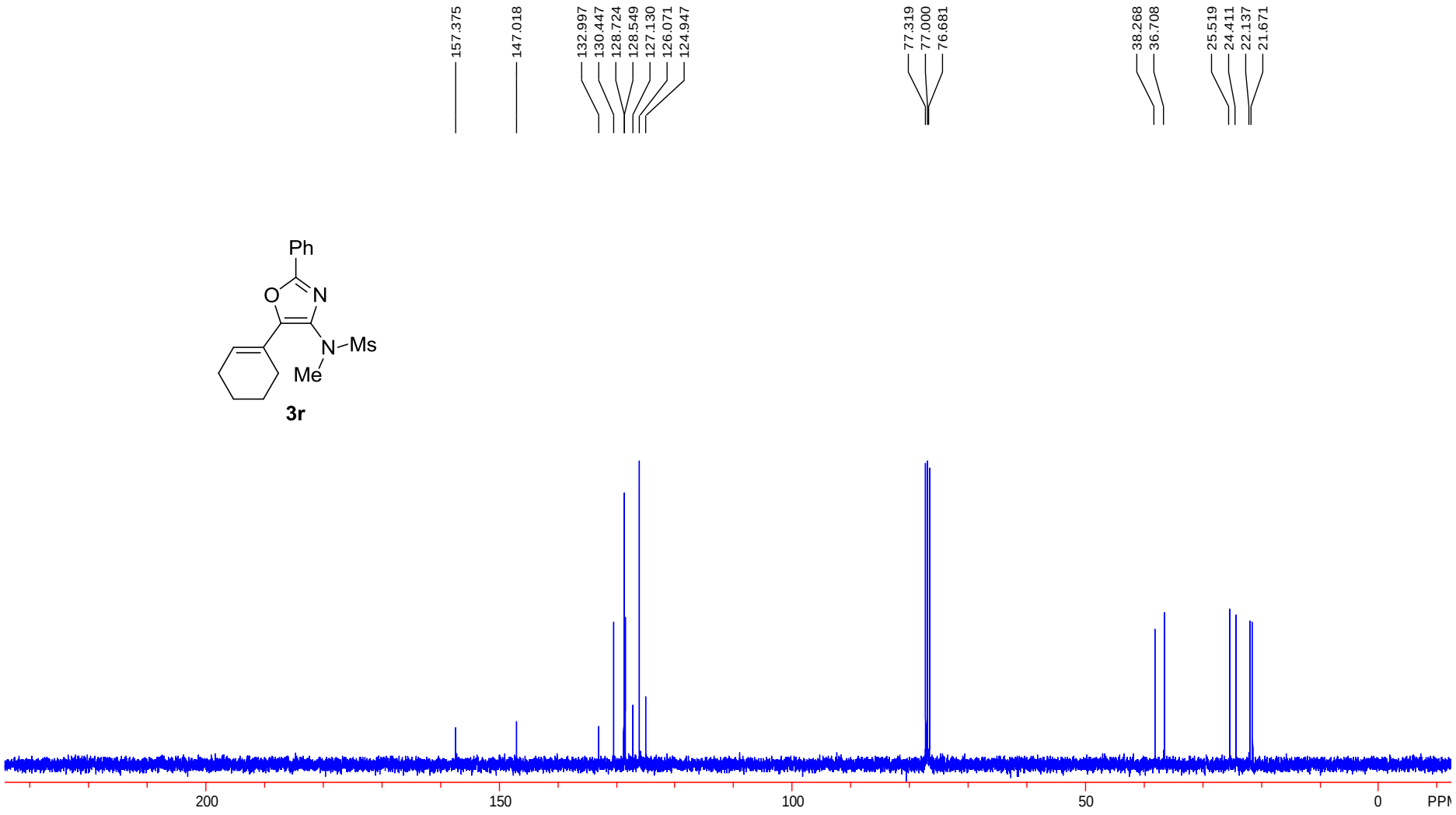
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



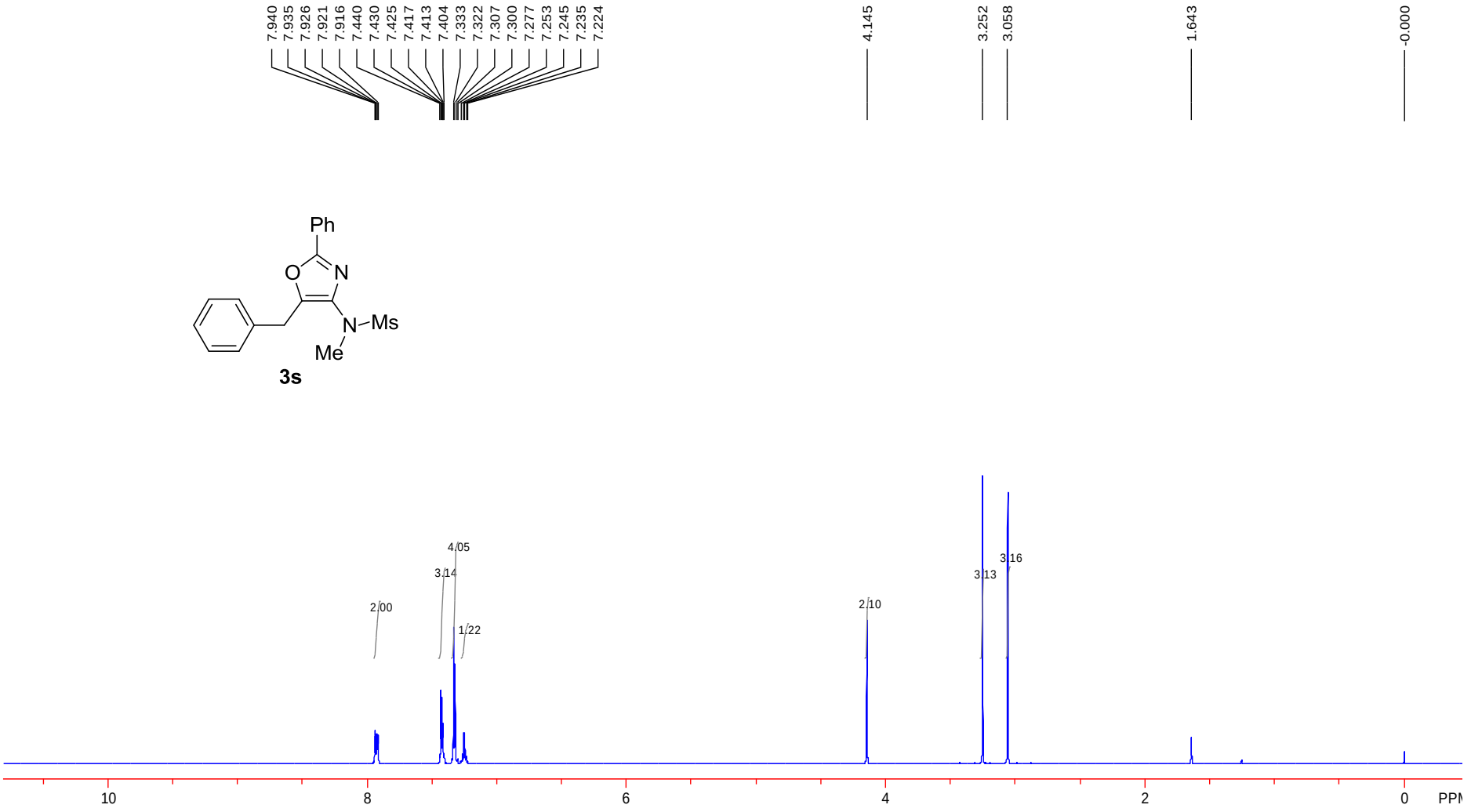
**$^1$H NMR (400 MHz, $CDCl_3$)**



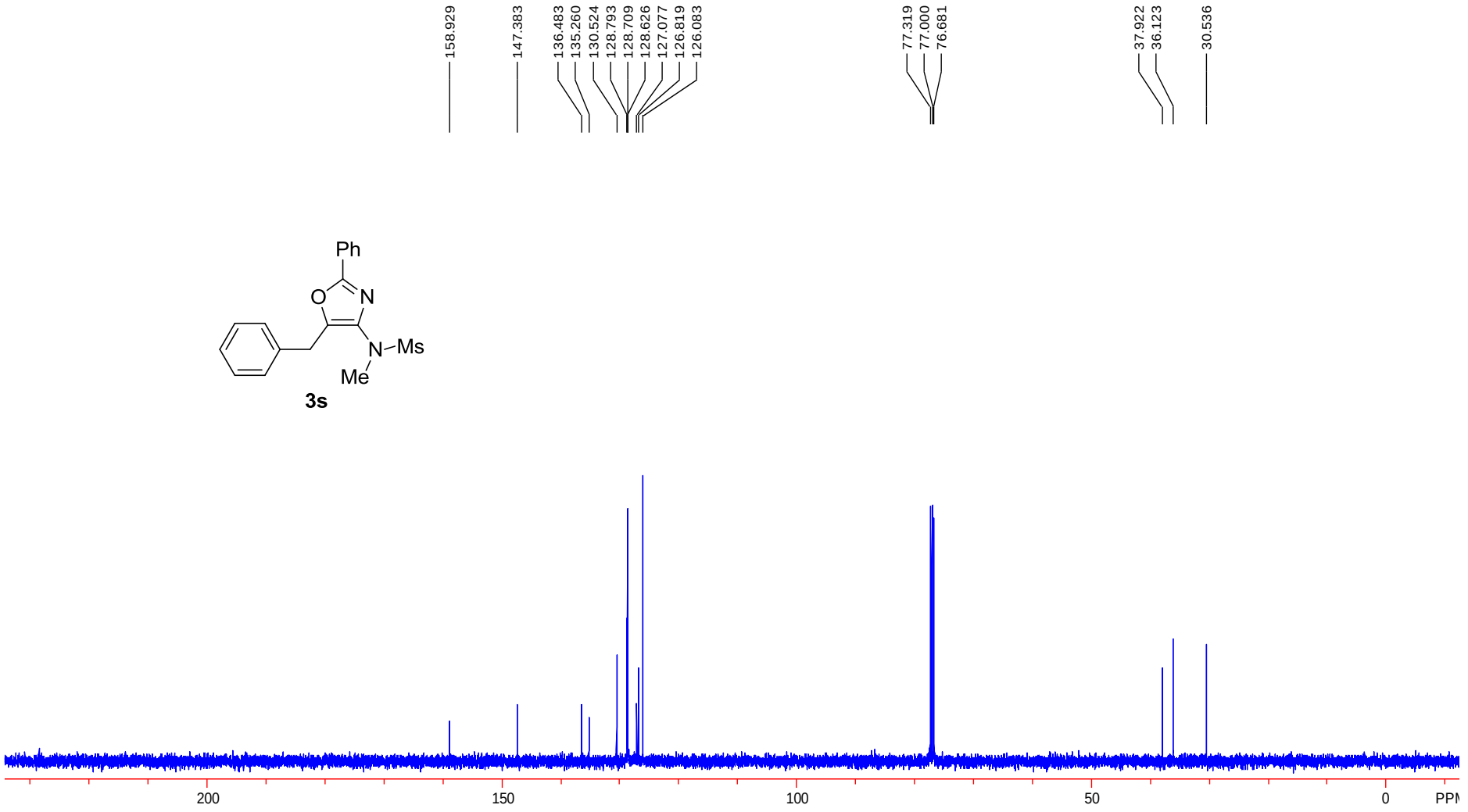
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



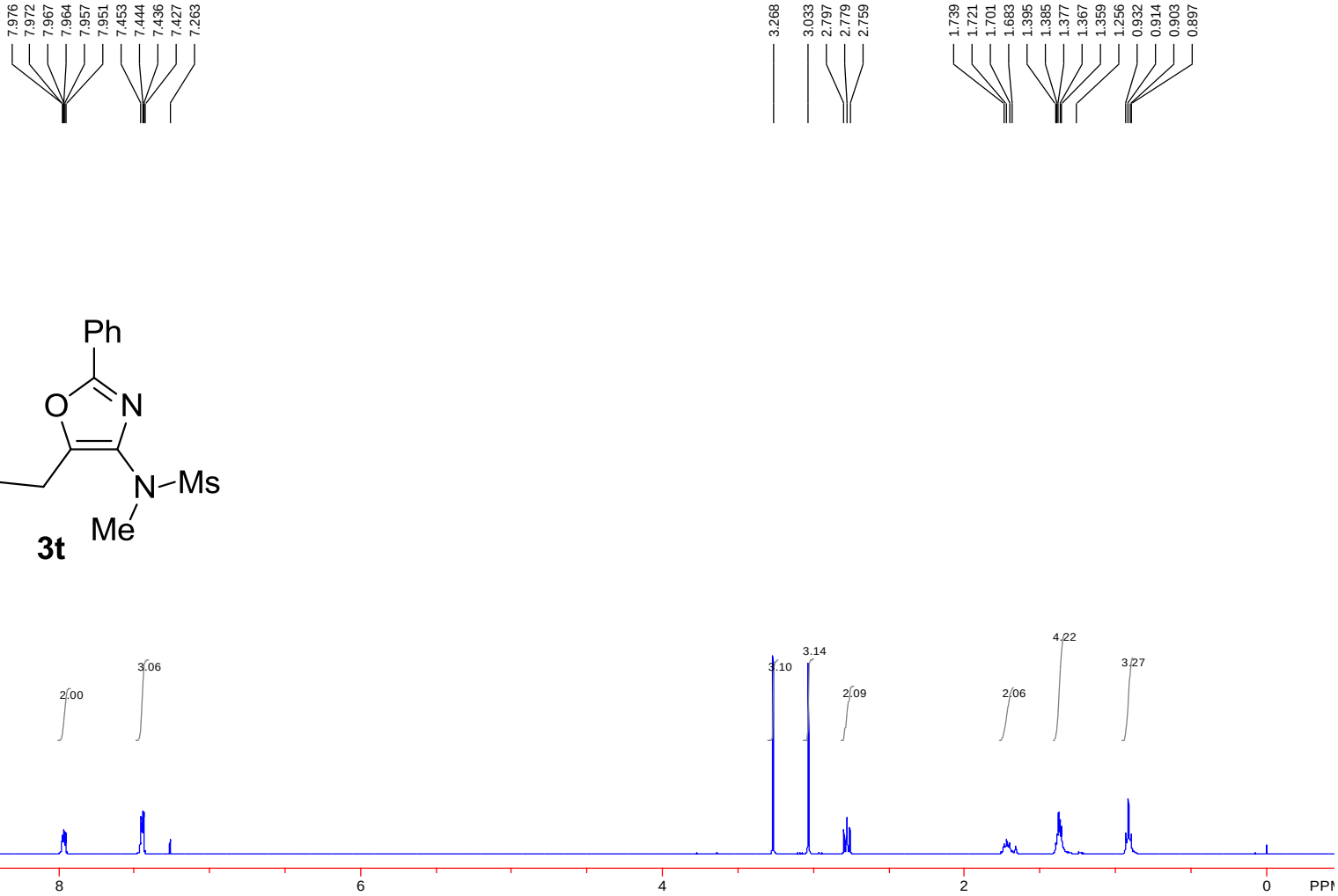
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



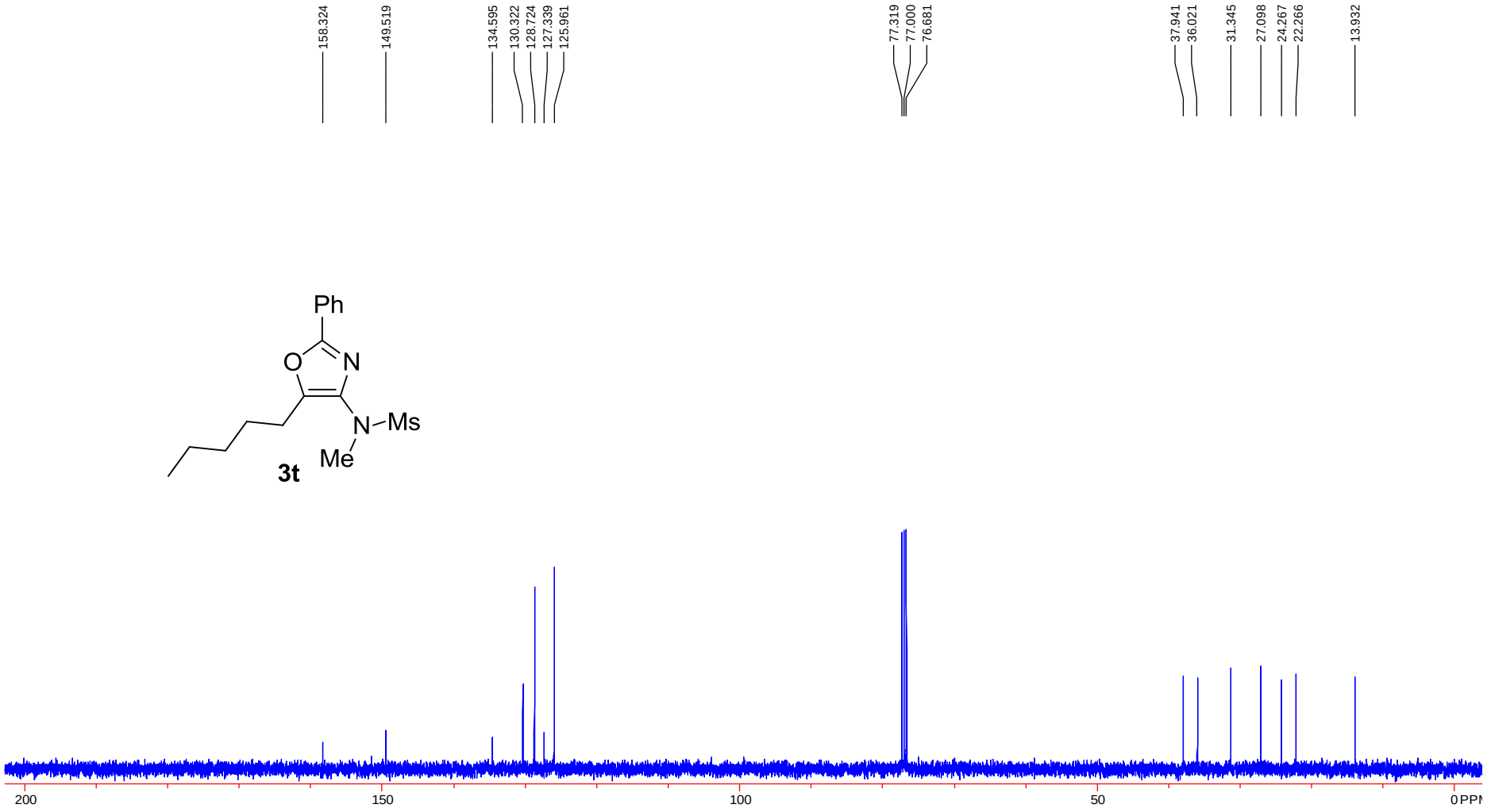
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



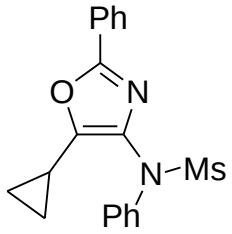
**$^1$H NMR (400 MHz, $CDCl_3$)**



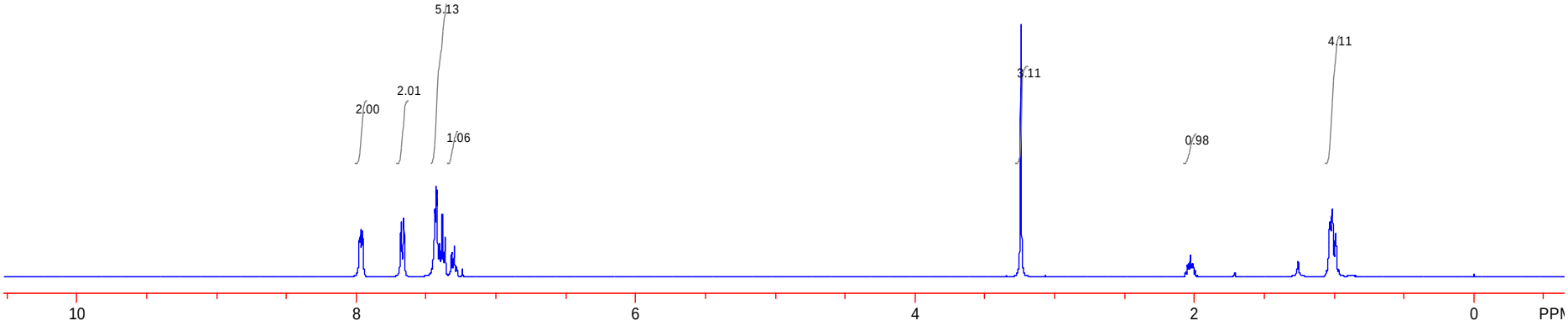
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



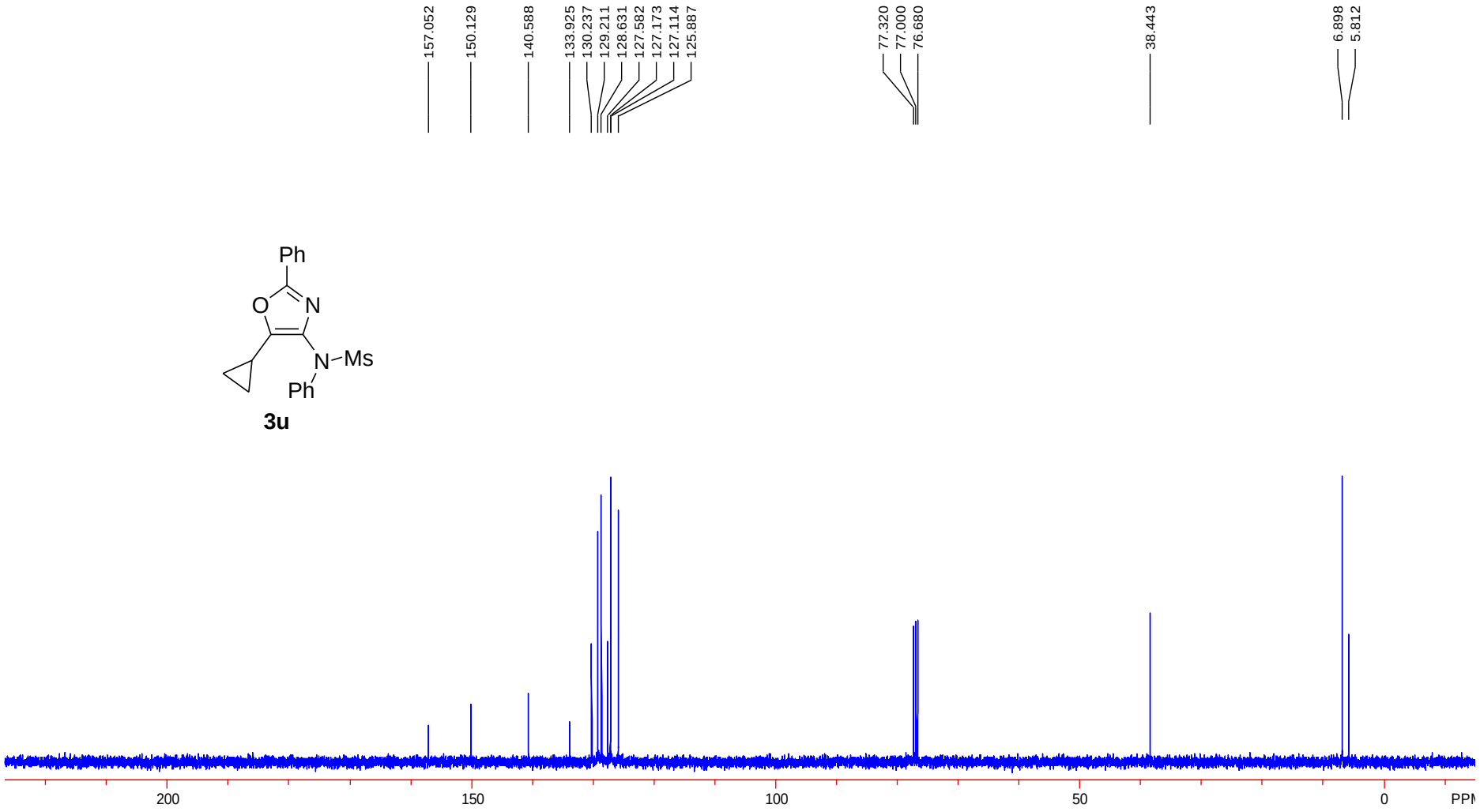
**$^1$H NMR (400 MHz, $CDCl_3$)**


**3u**



**$^{13}$C NMR (100 MHz, $CDCl_3$)**




**3u**

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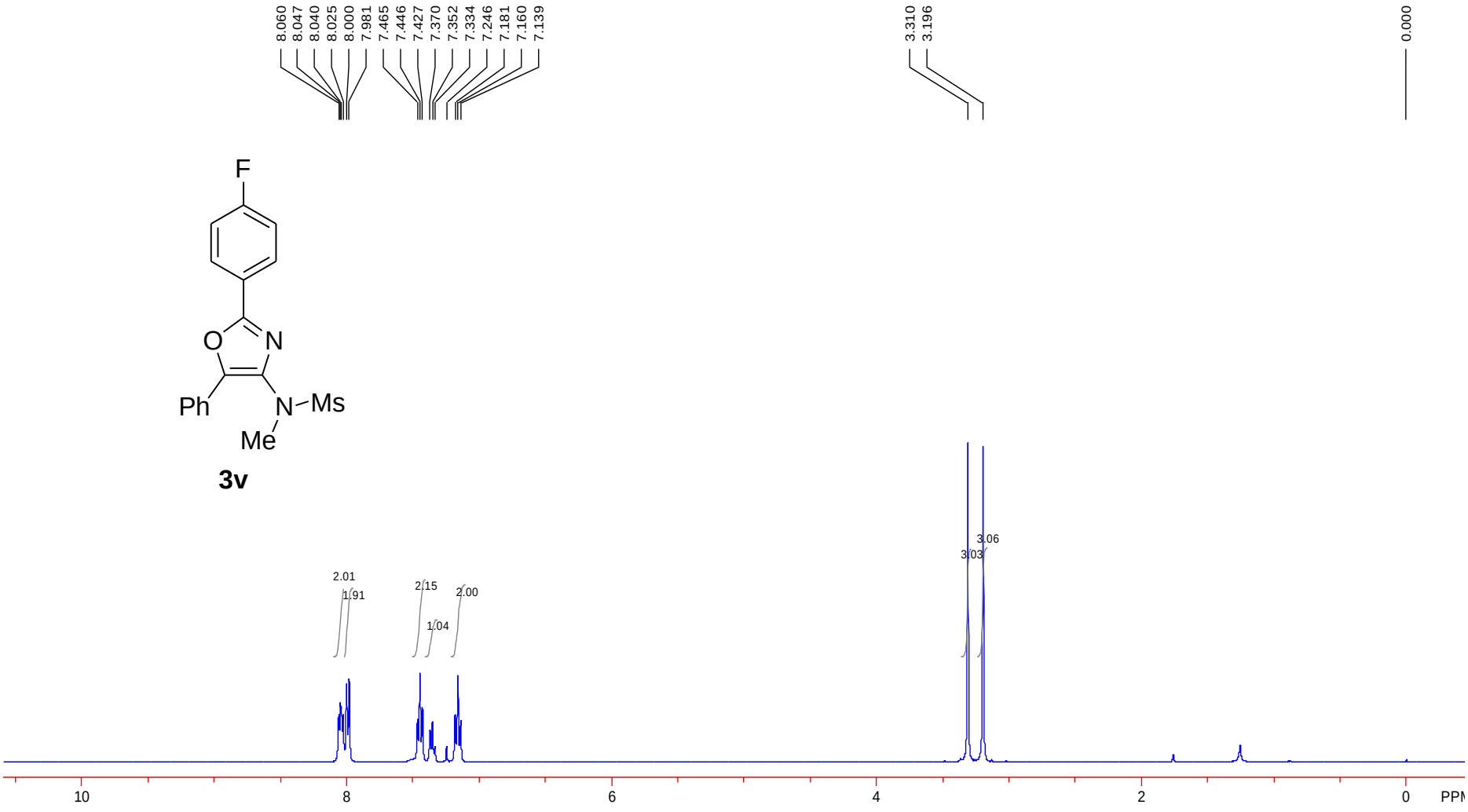
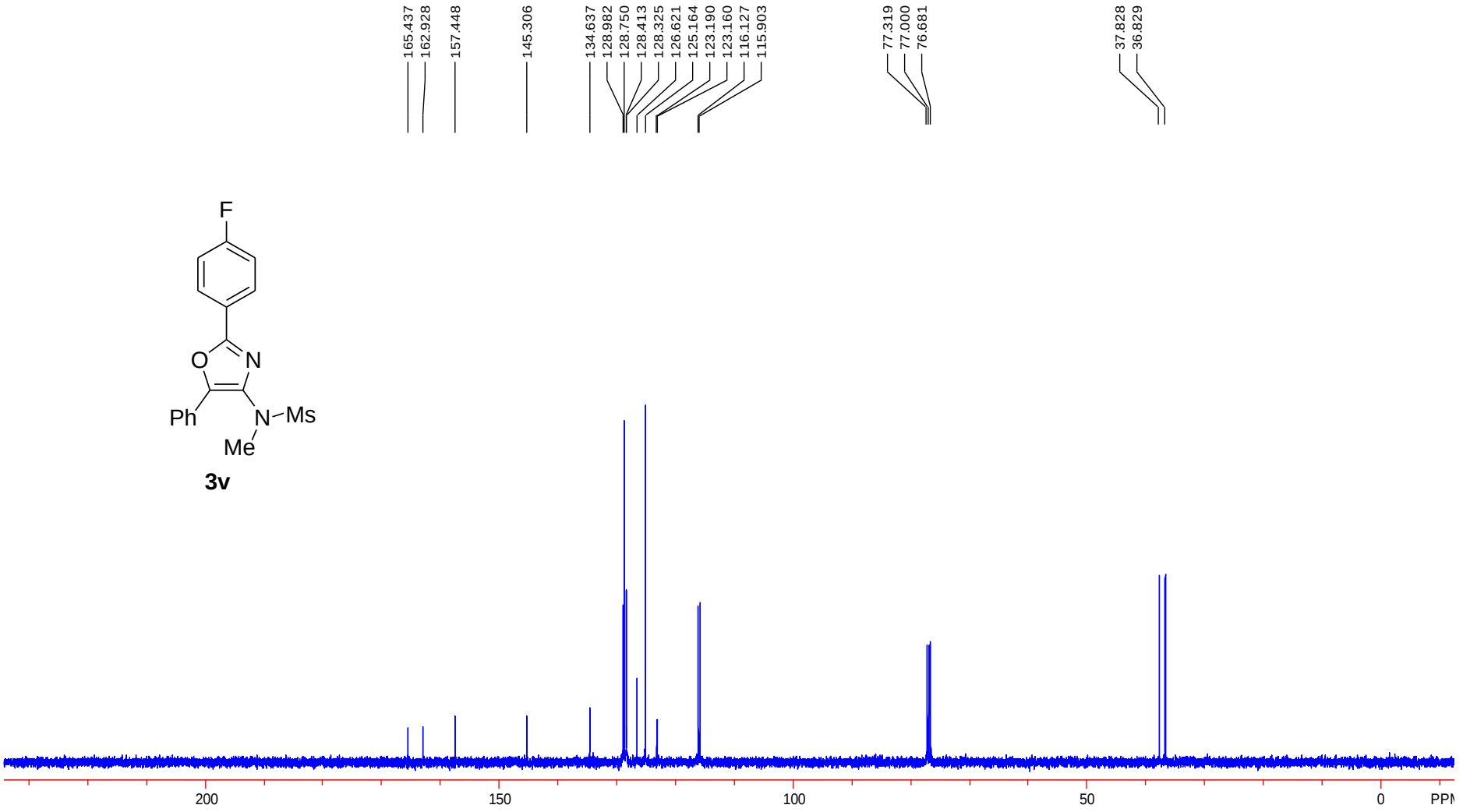
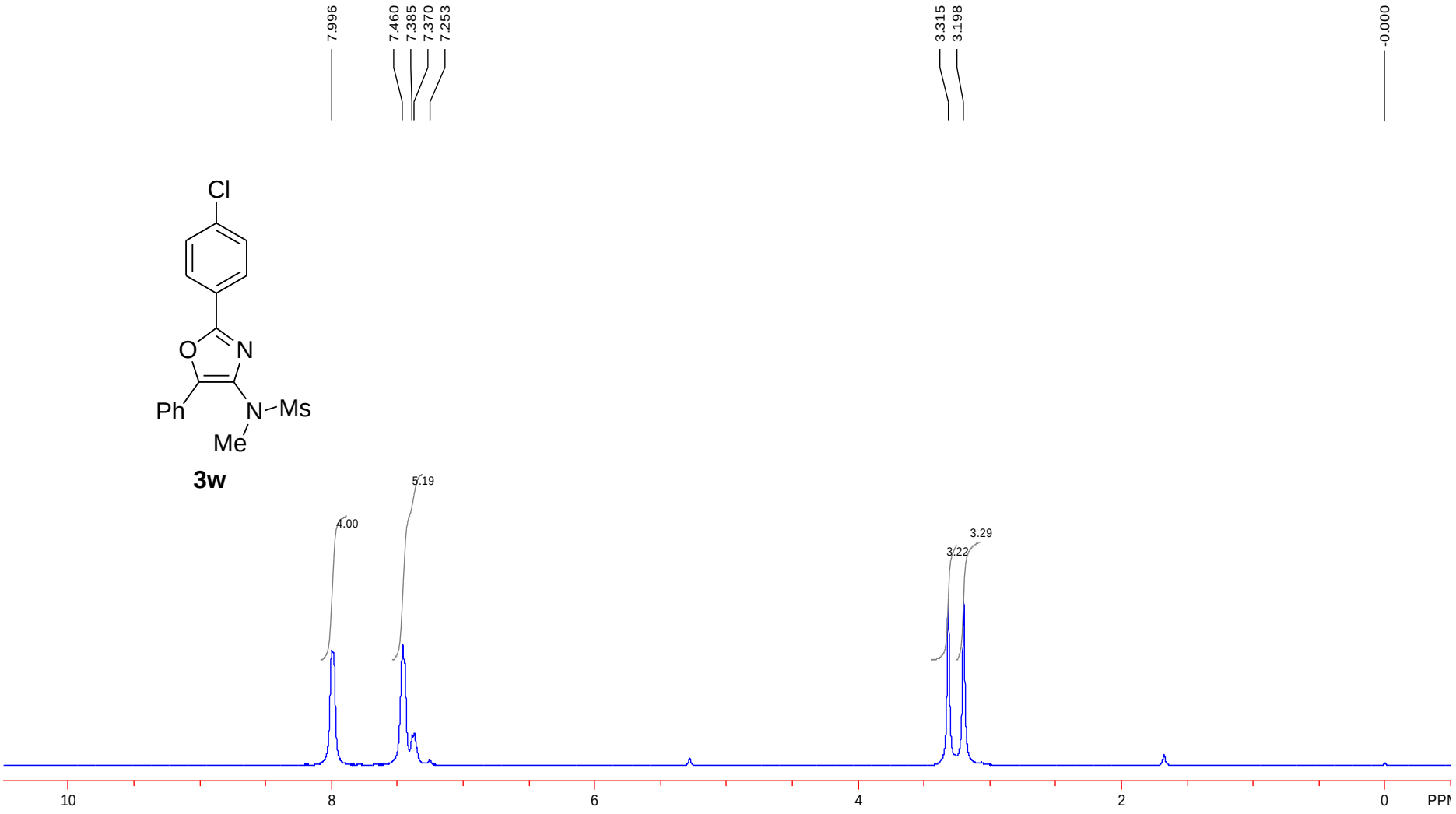


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**



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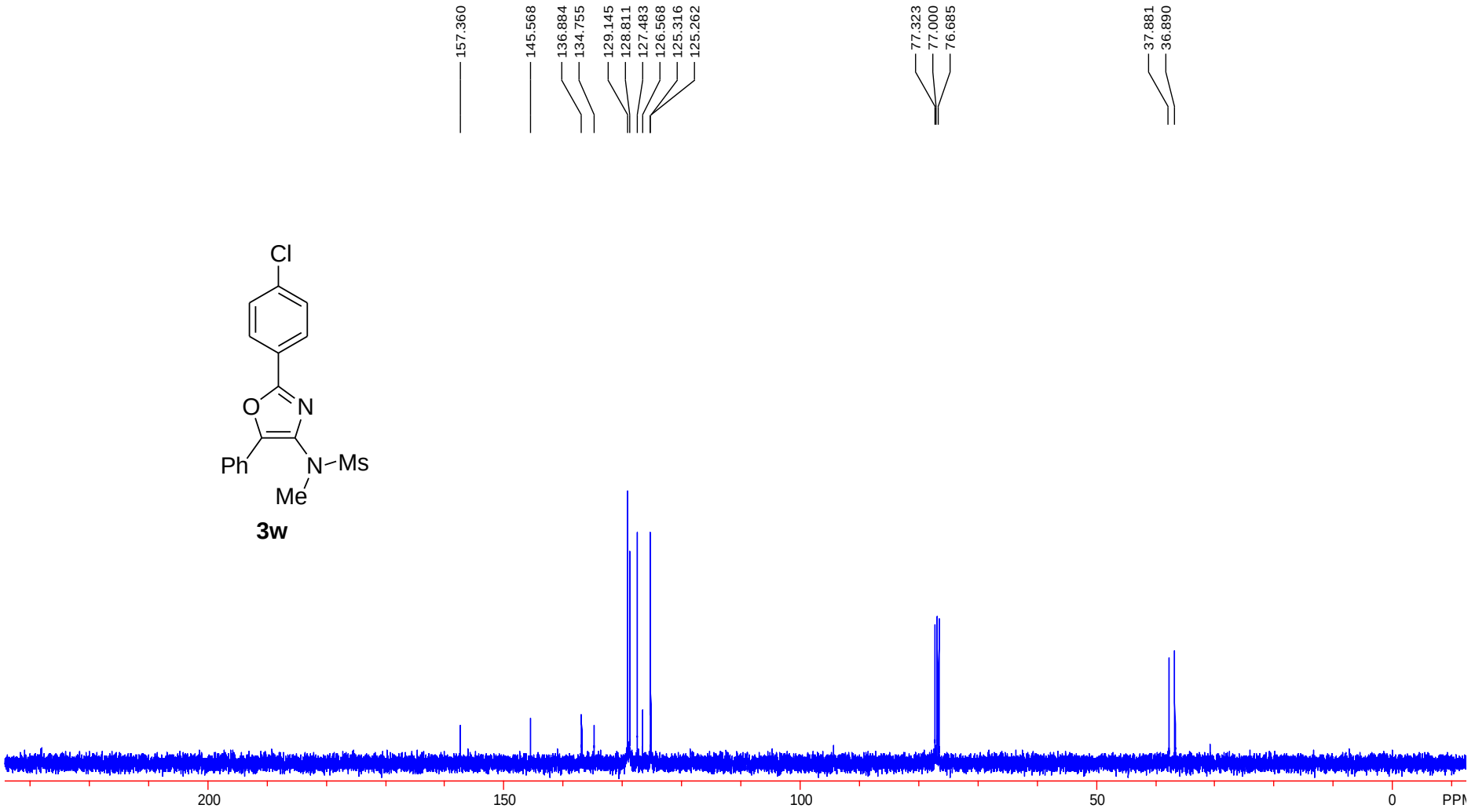

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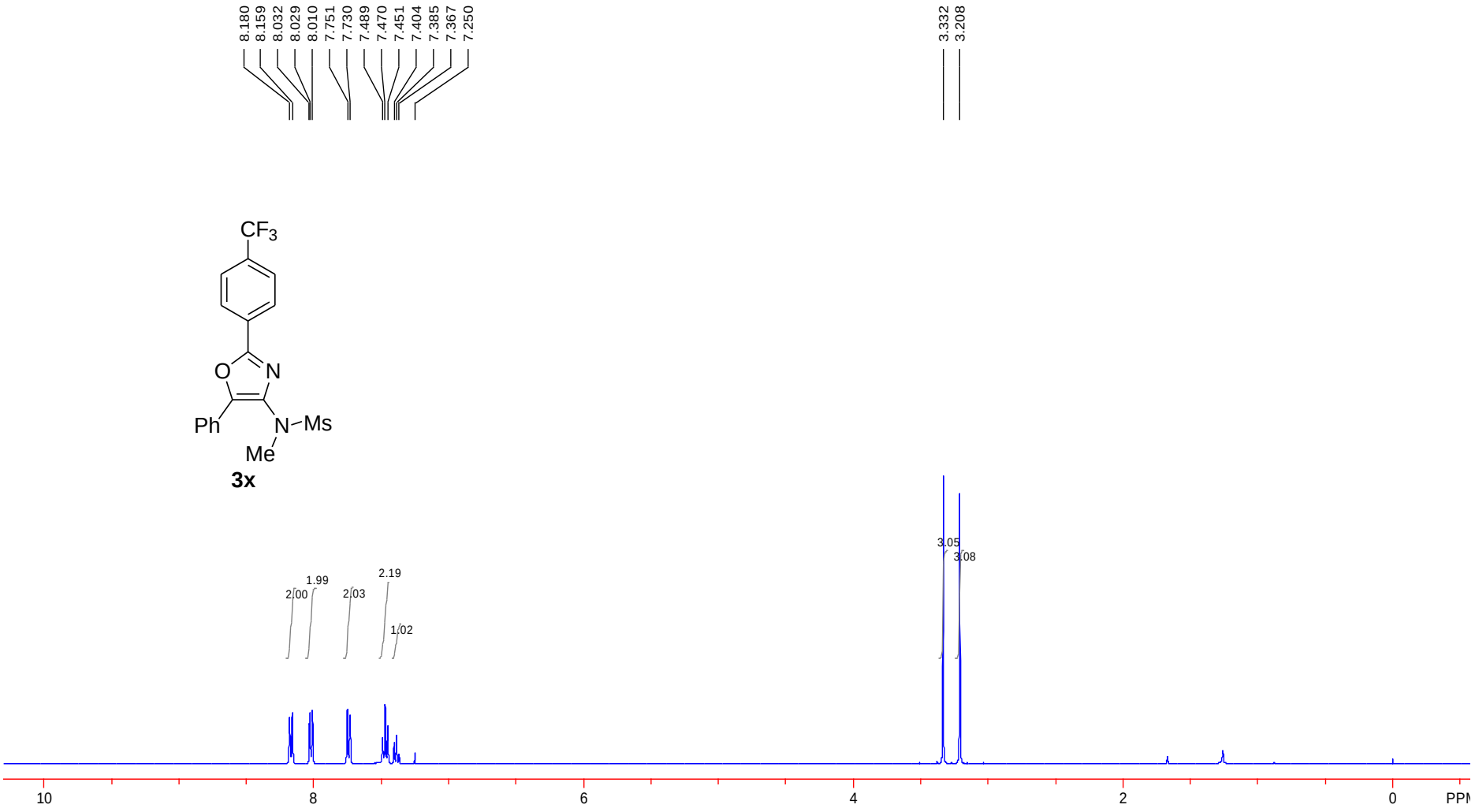

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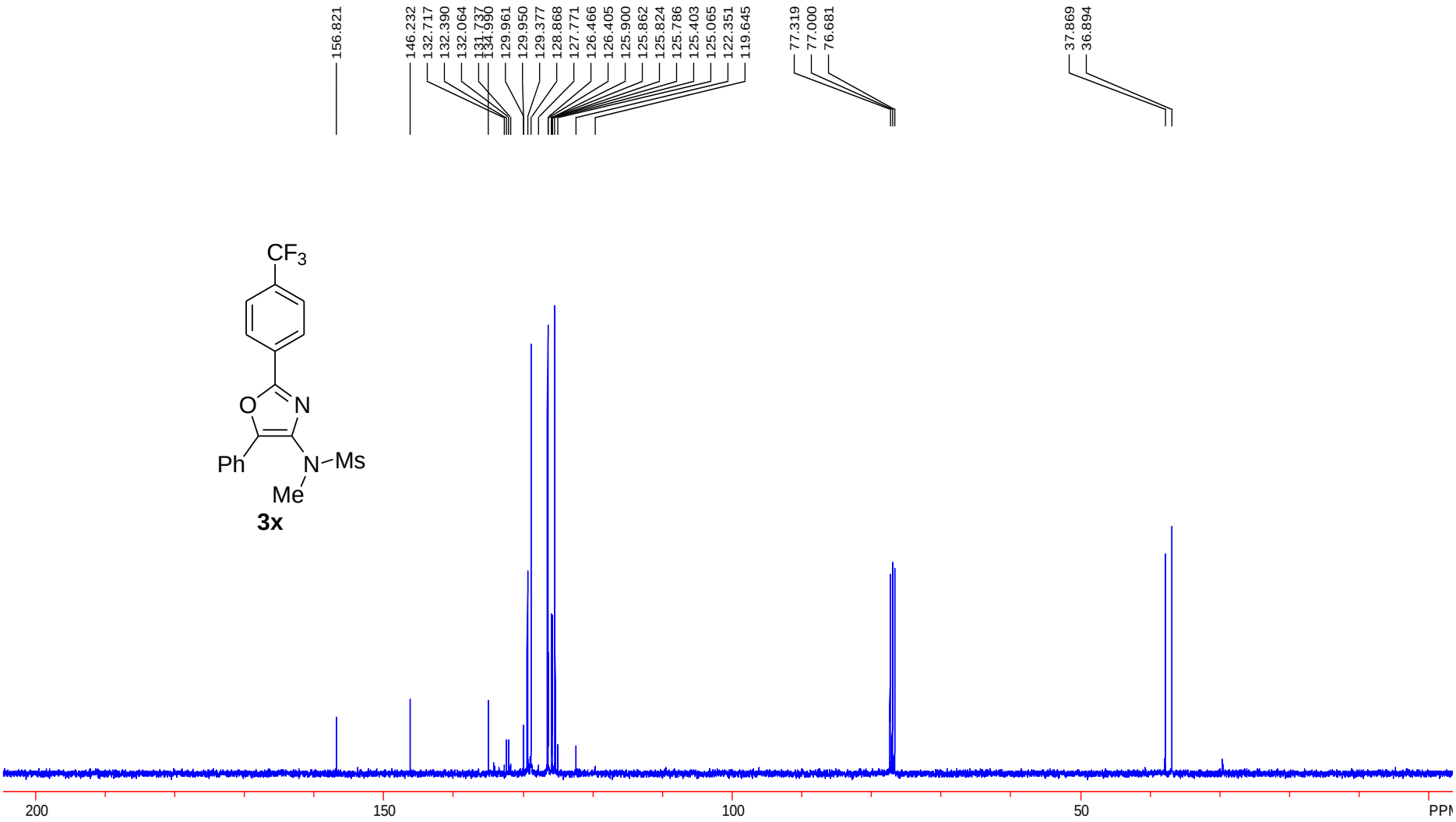

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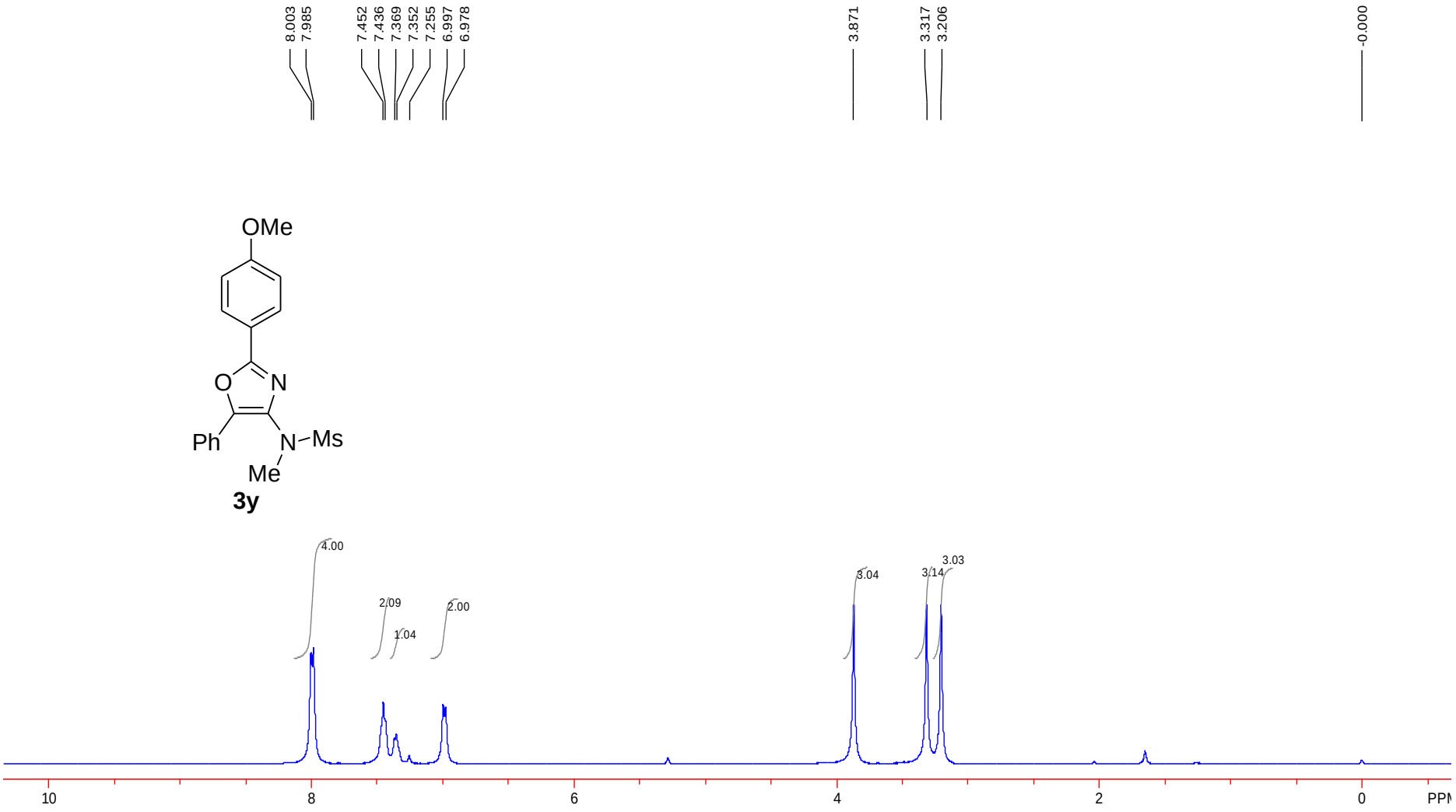
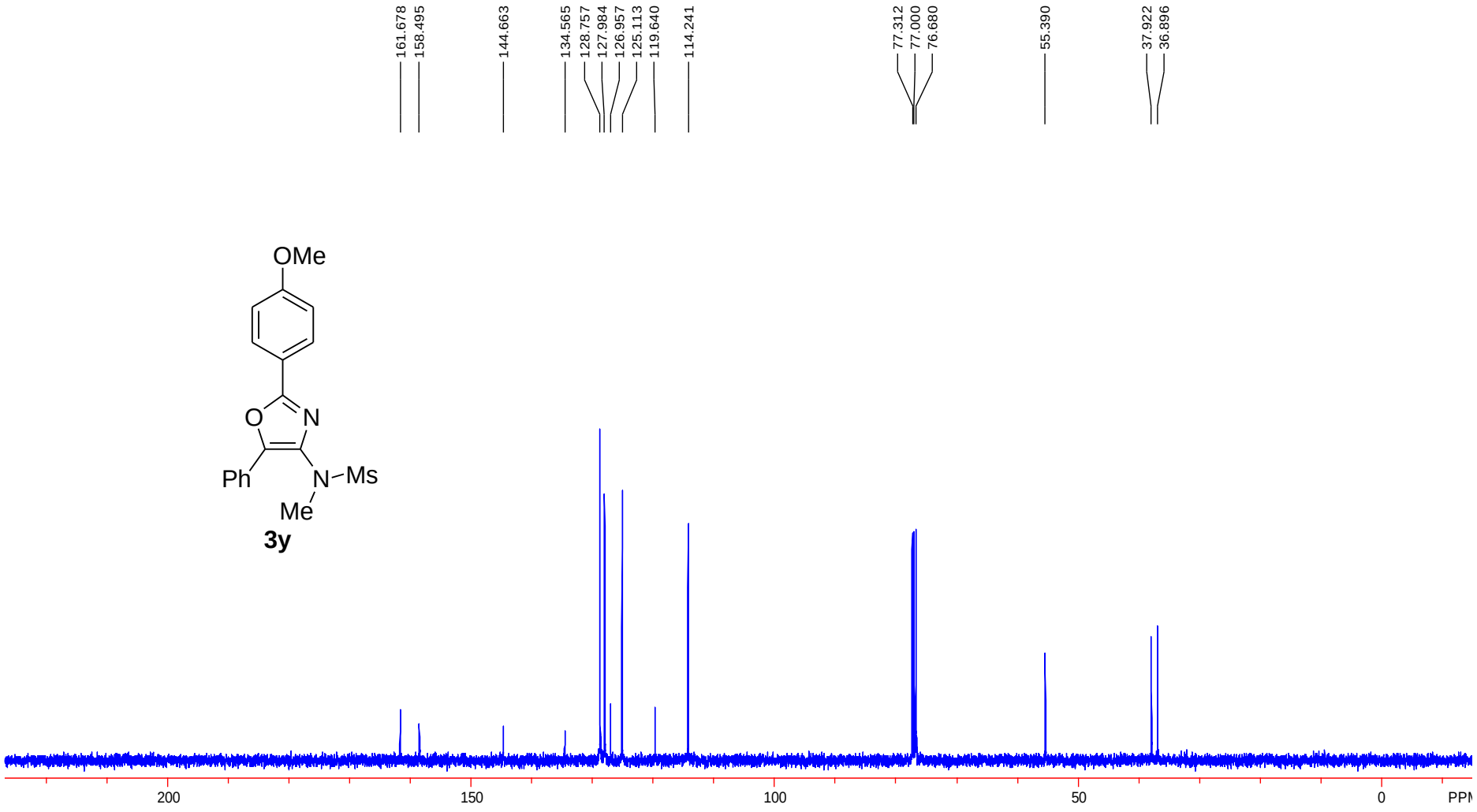


**$^{13}$C NMR (100 MHz, $CDCl_3$)**



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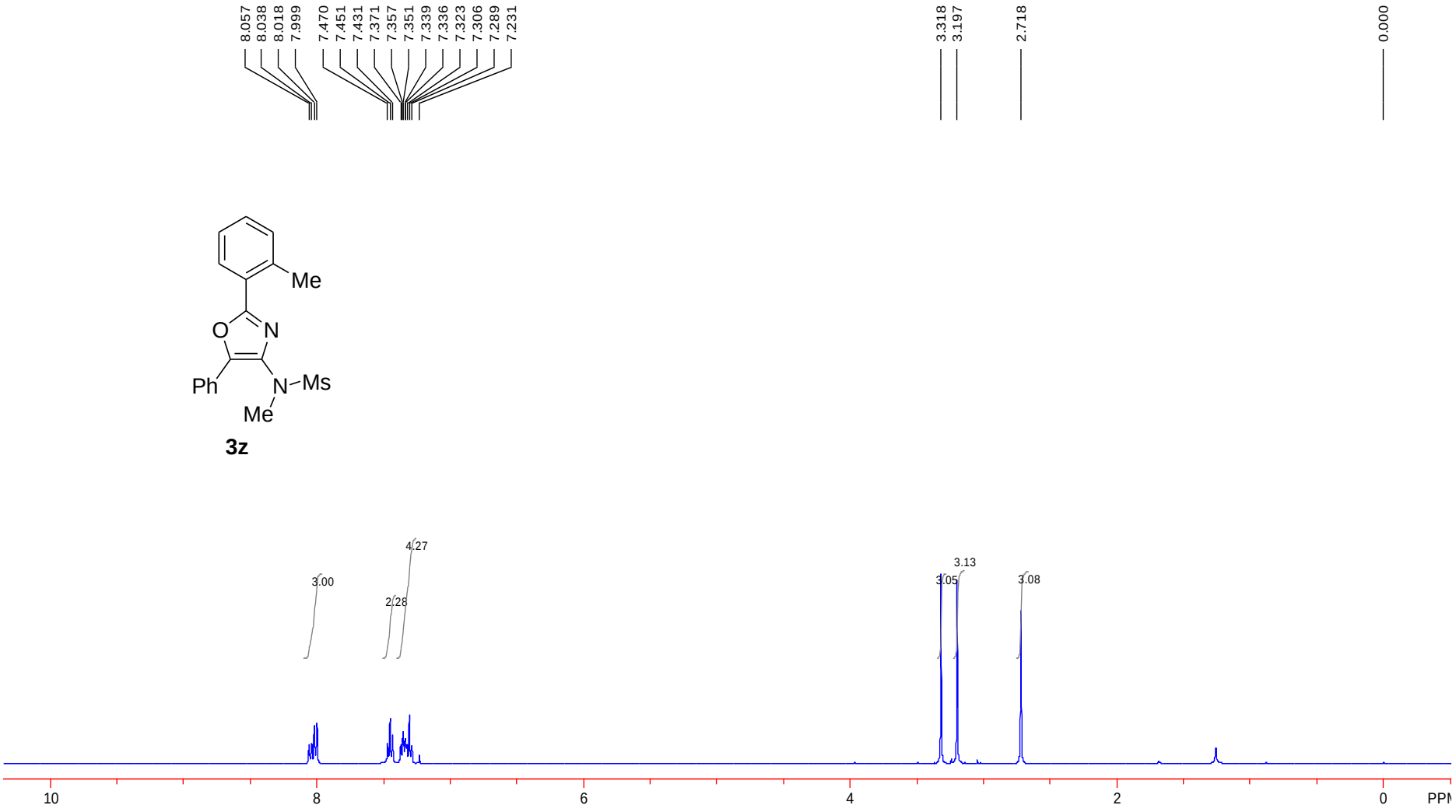
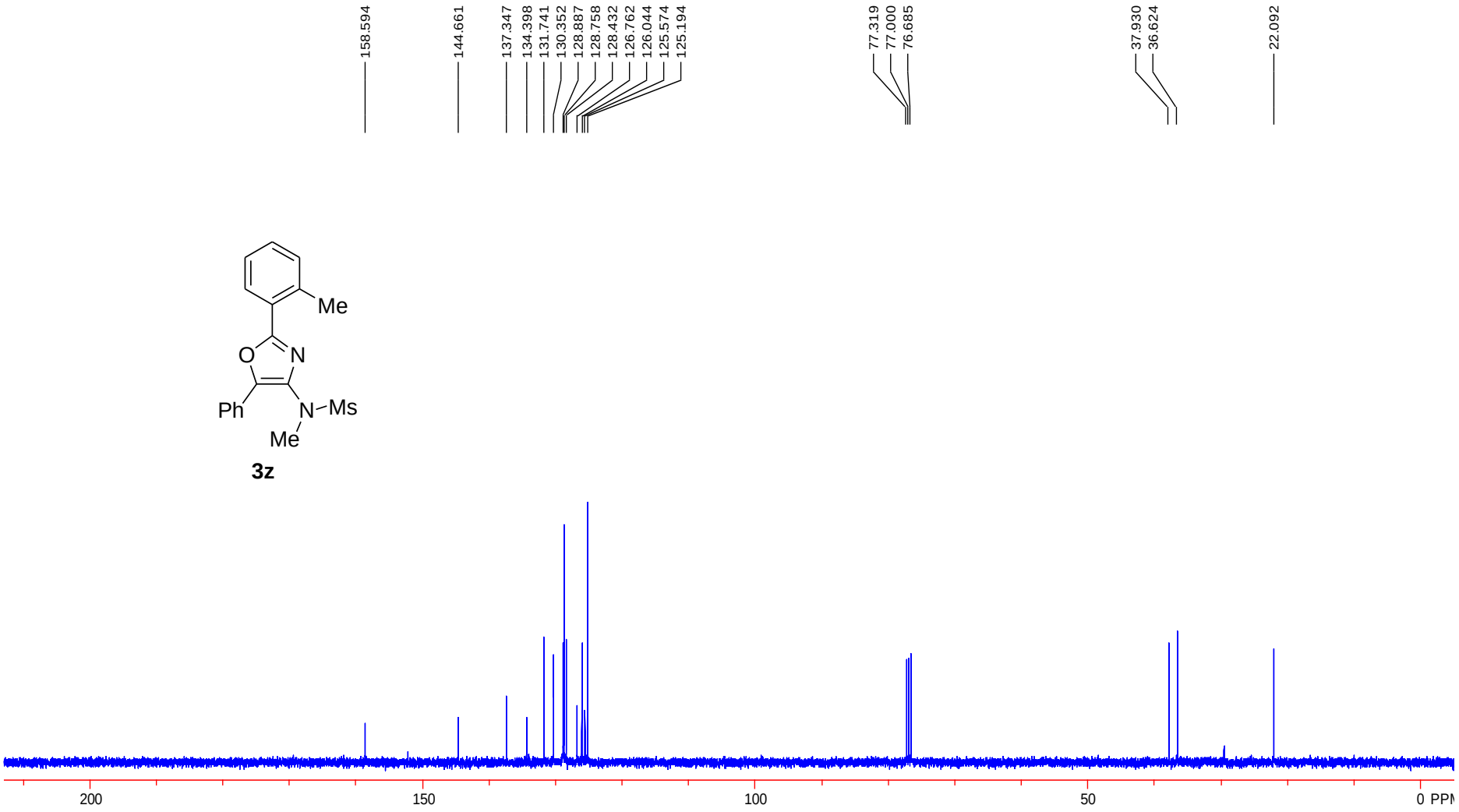
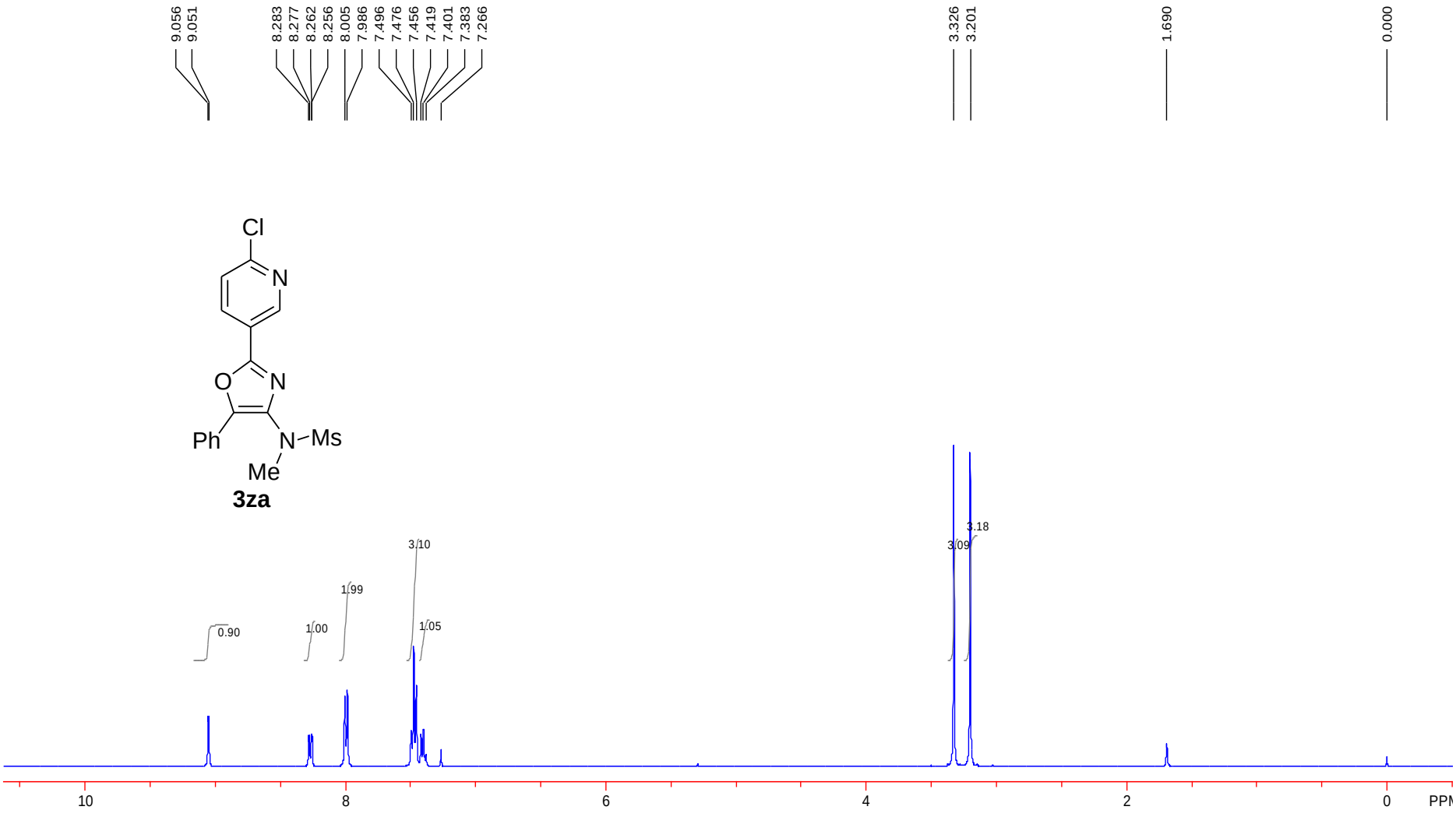


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

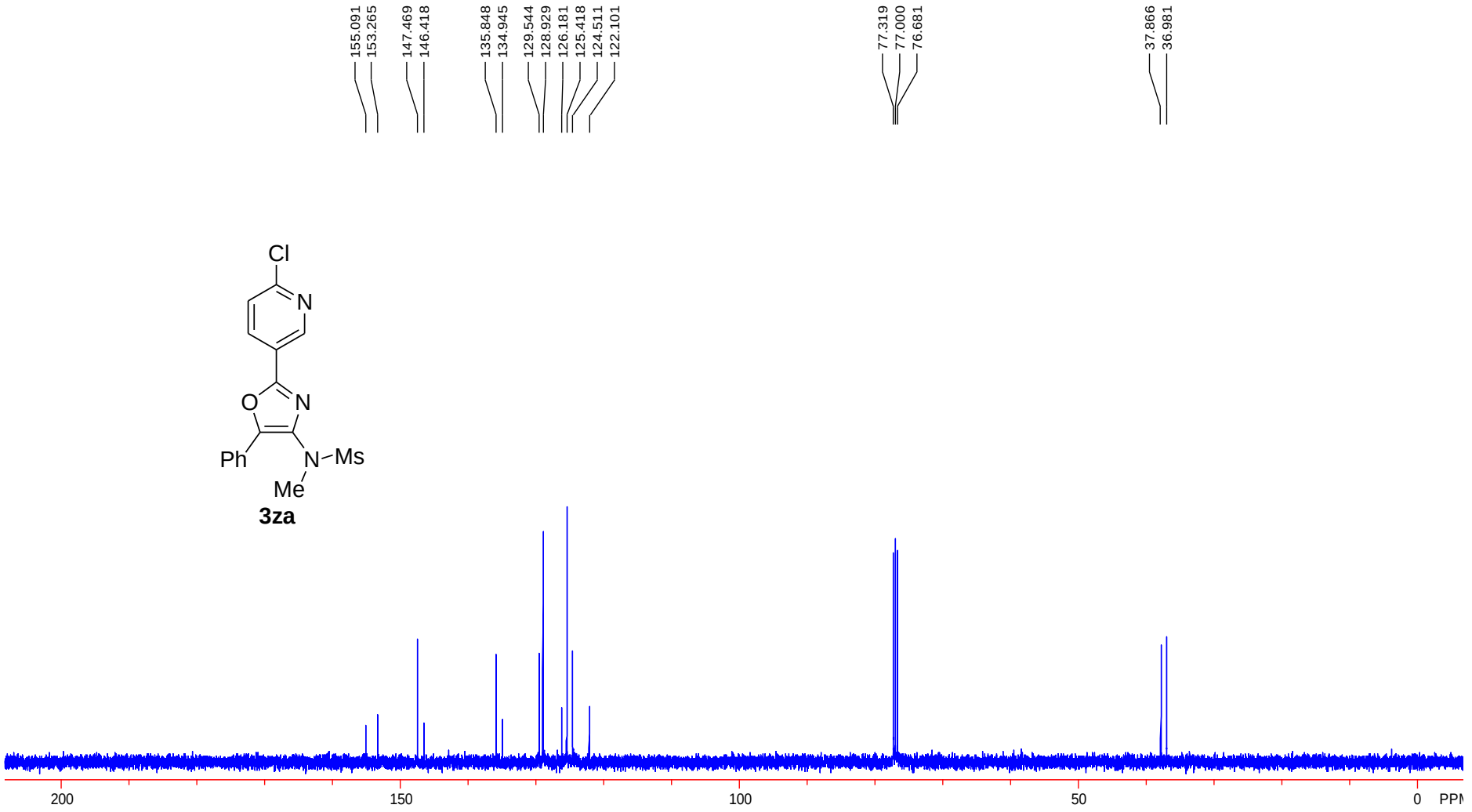



**3z**

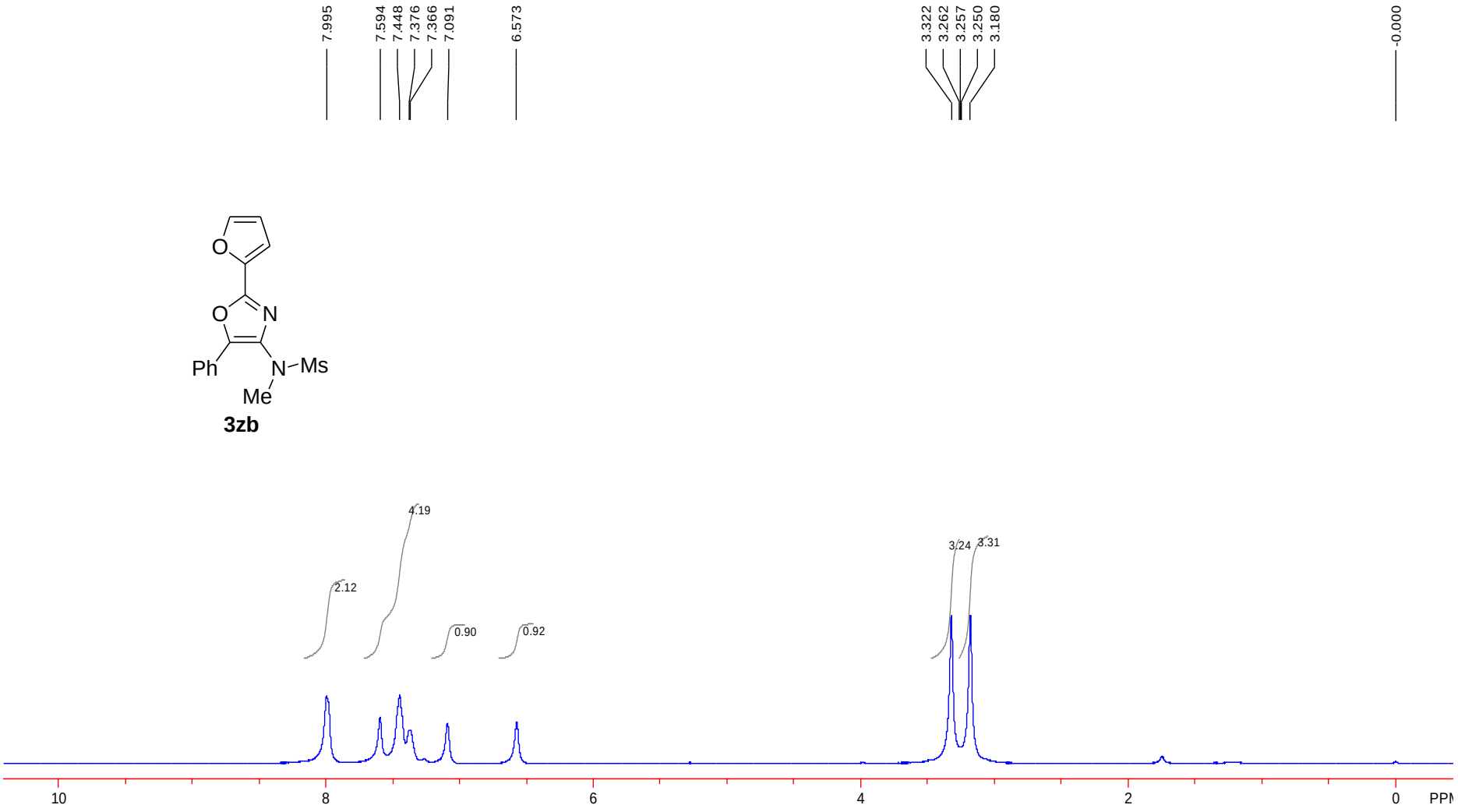
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



**$^{13}$C NMR (100 MHz, $CDCl_3$)**

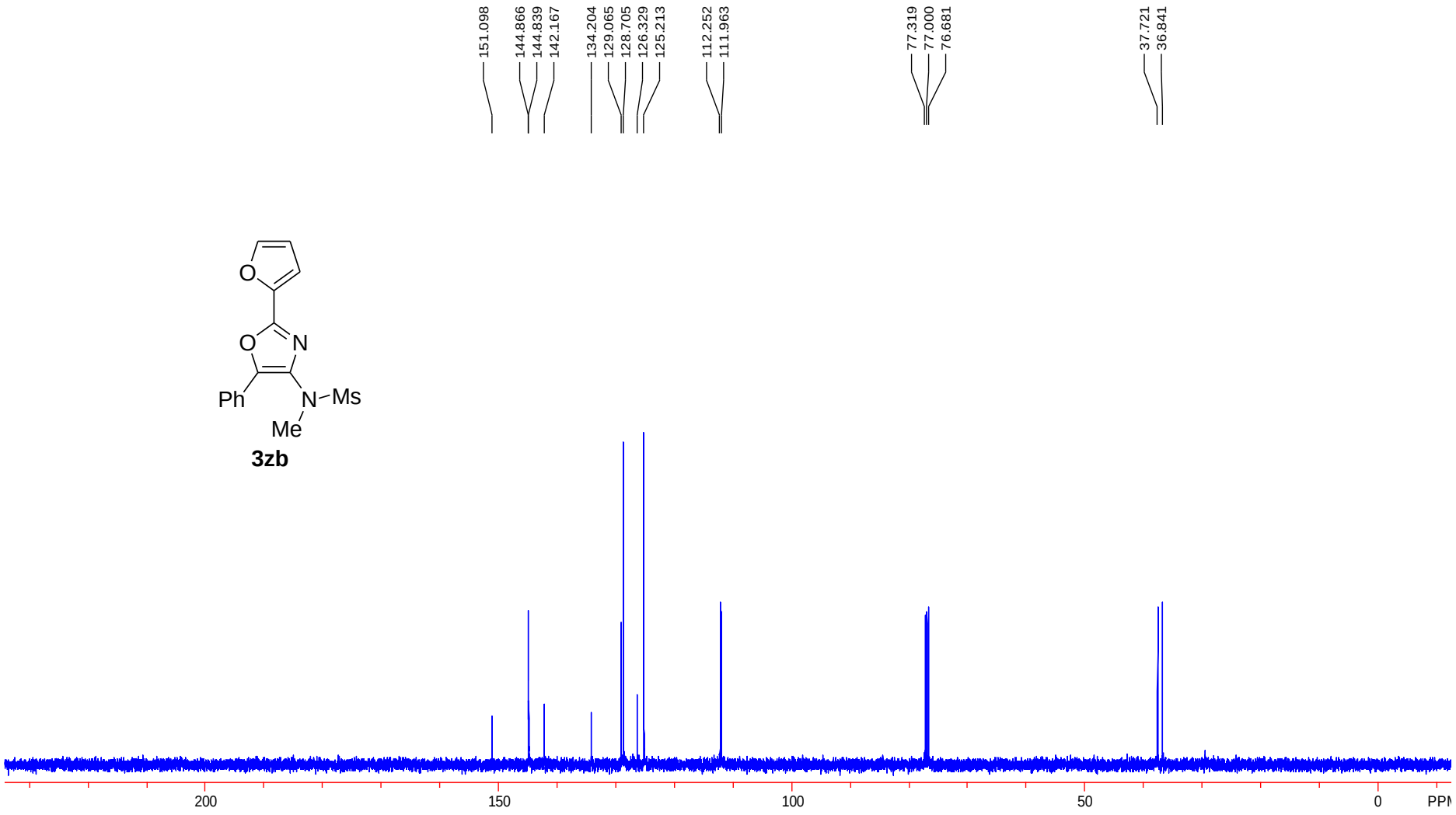


**$^{1}$H NMR (400 MHz, $CDCl_3$)**

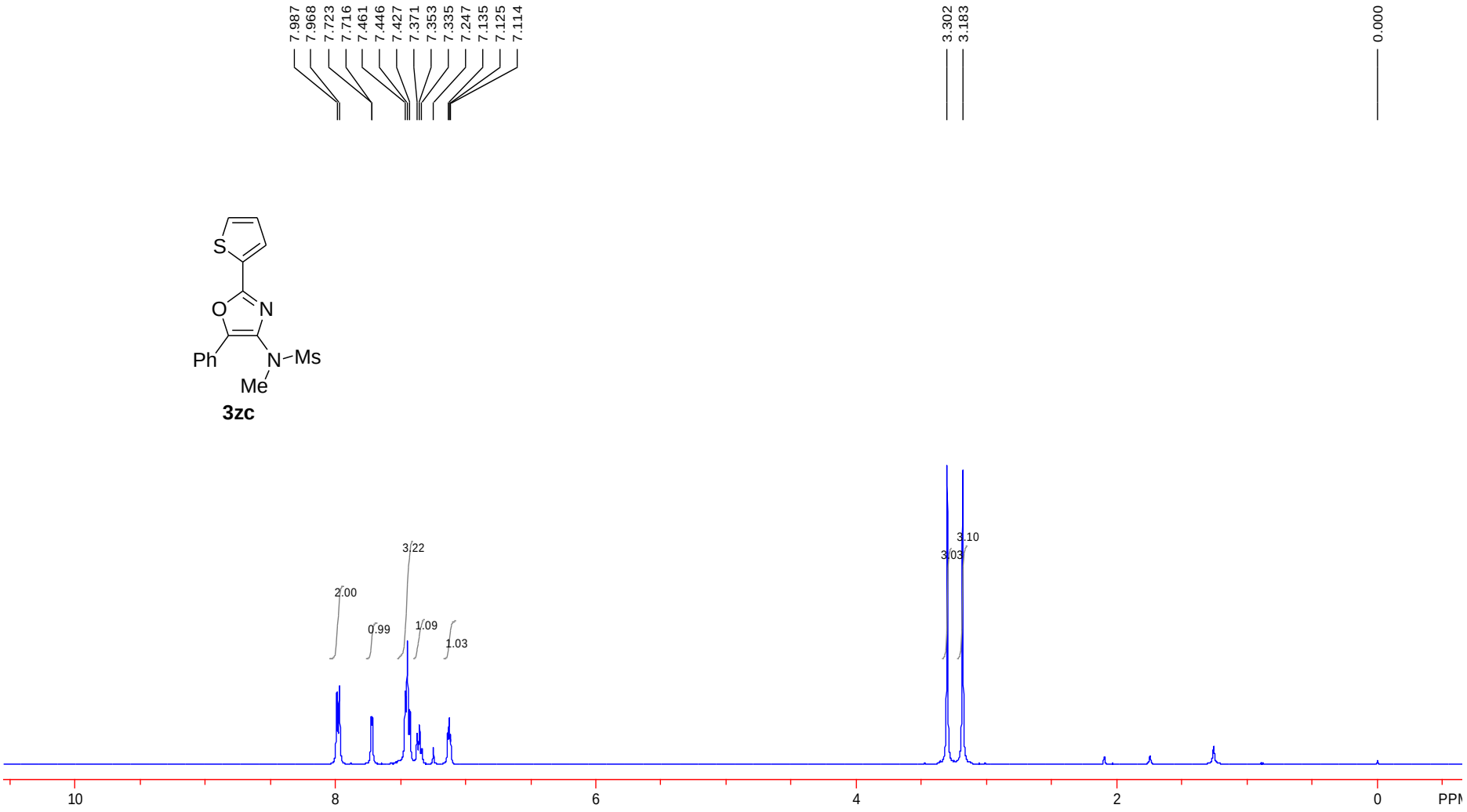



**3zb**

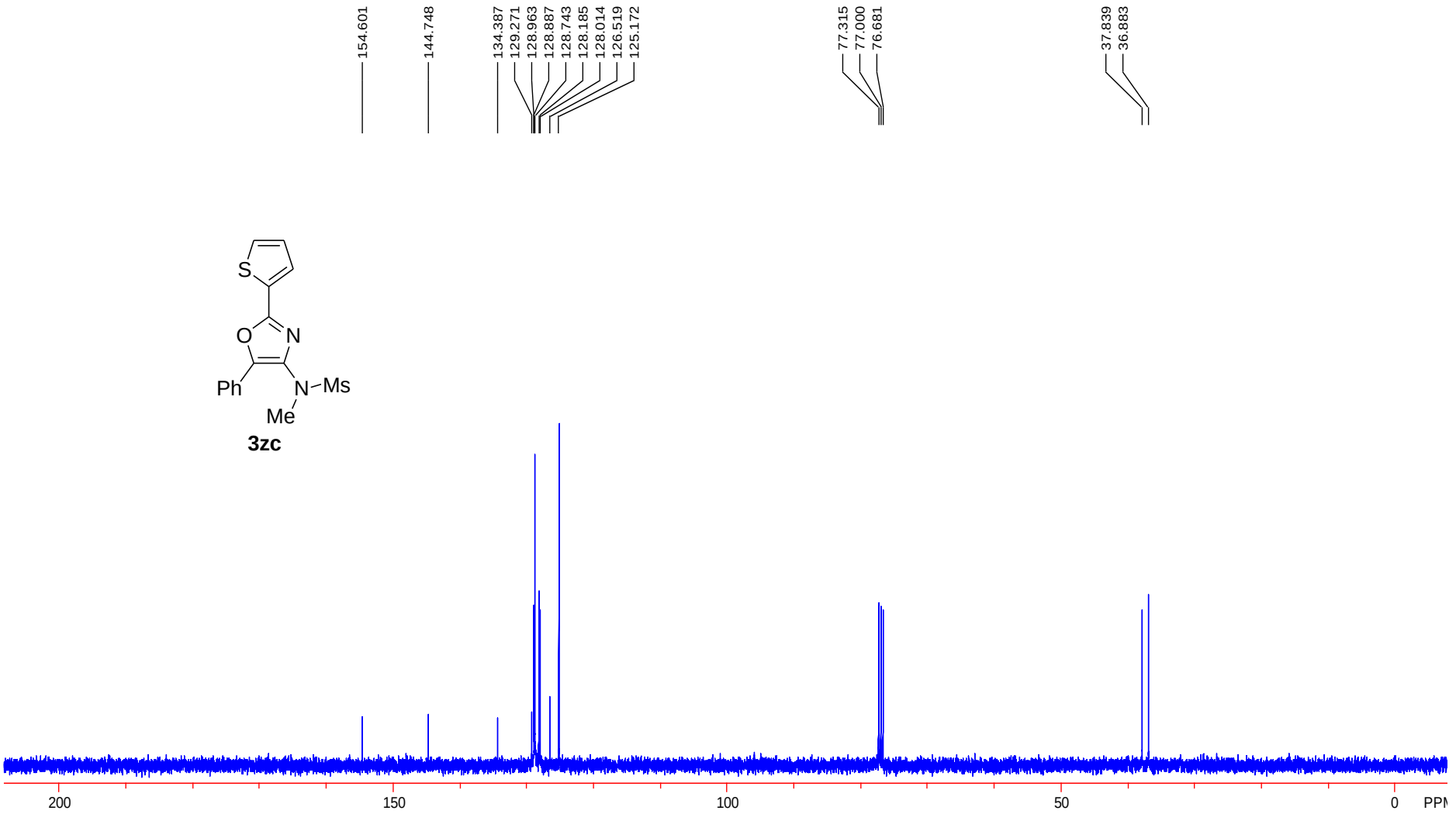
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



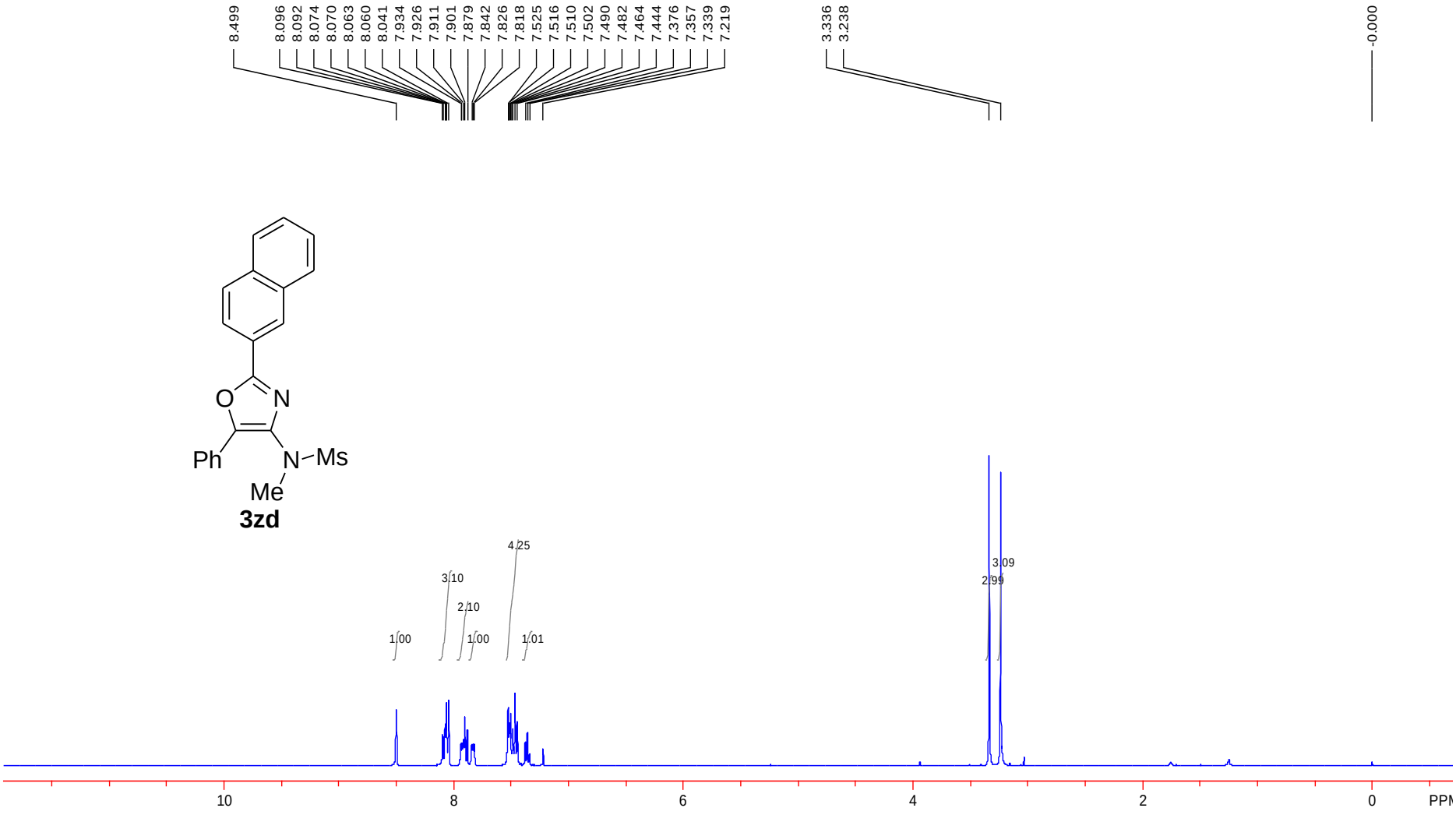
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



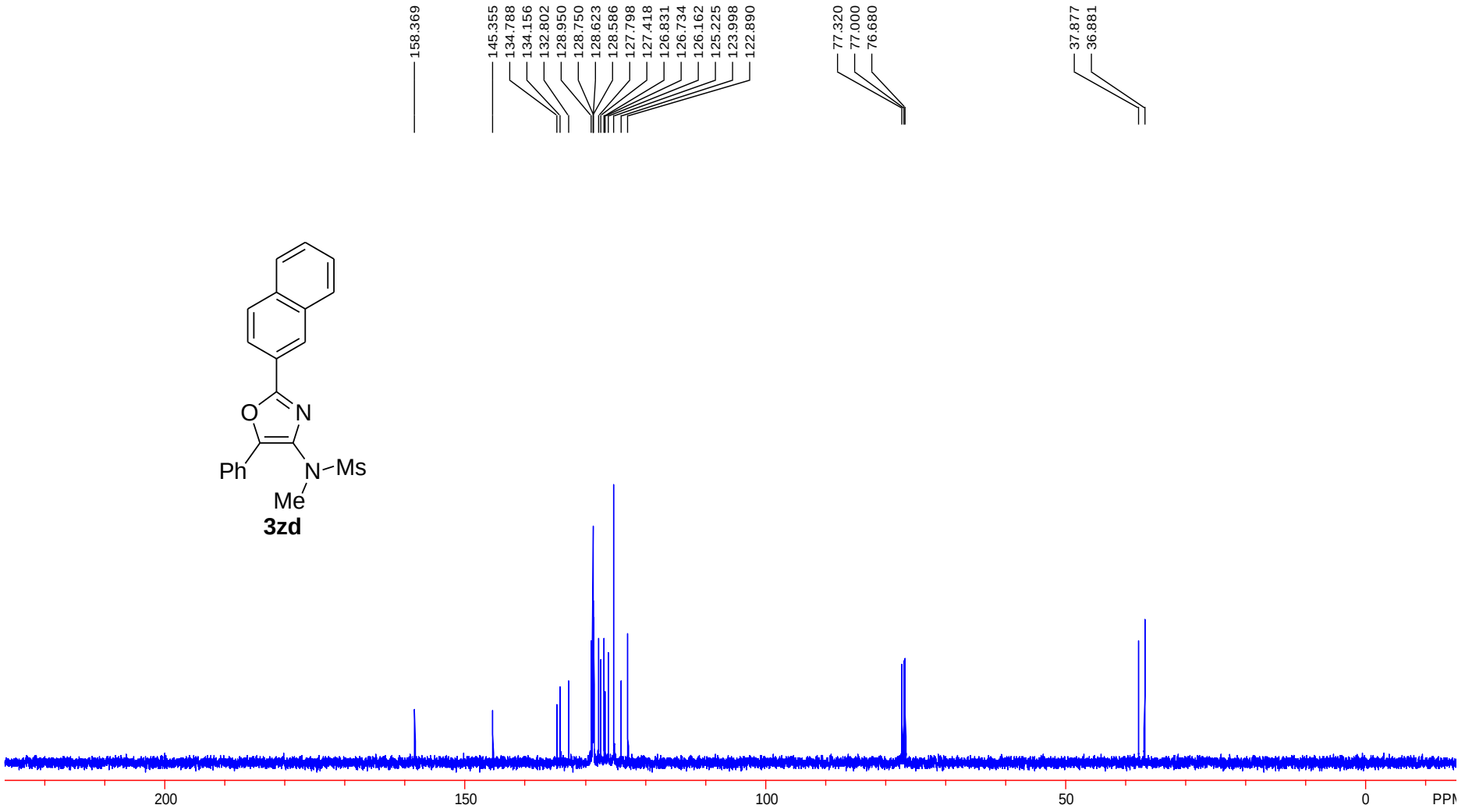
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**

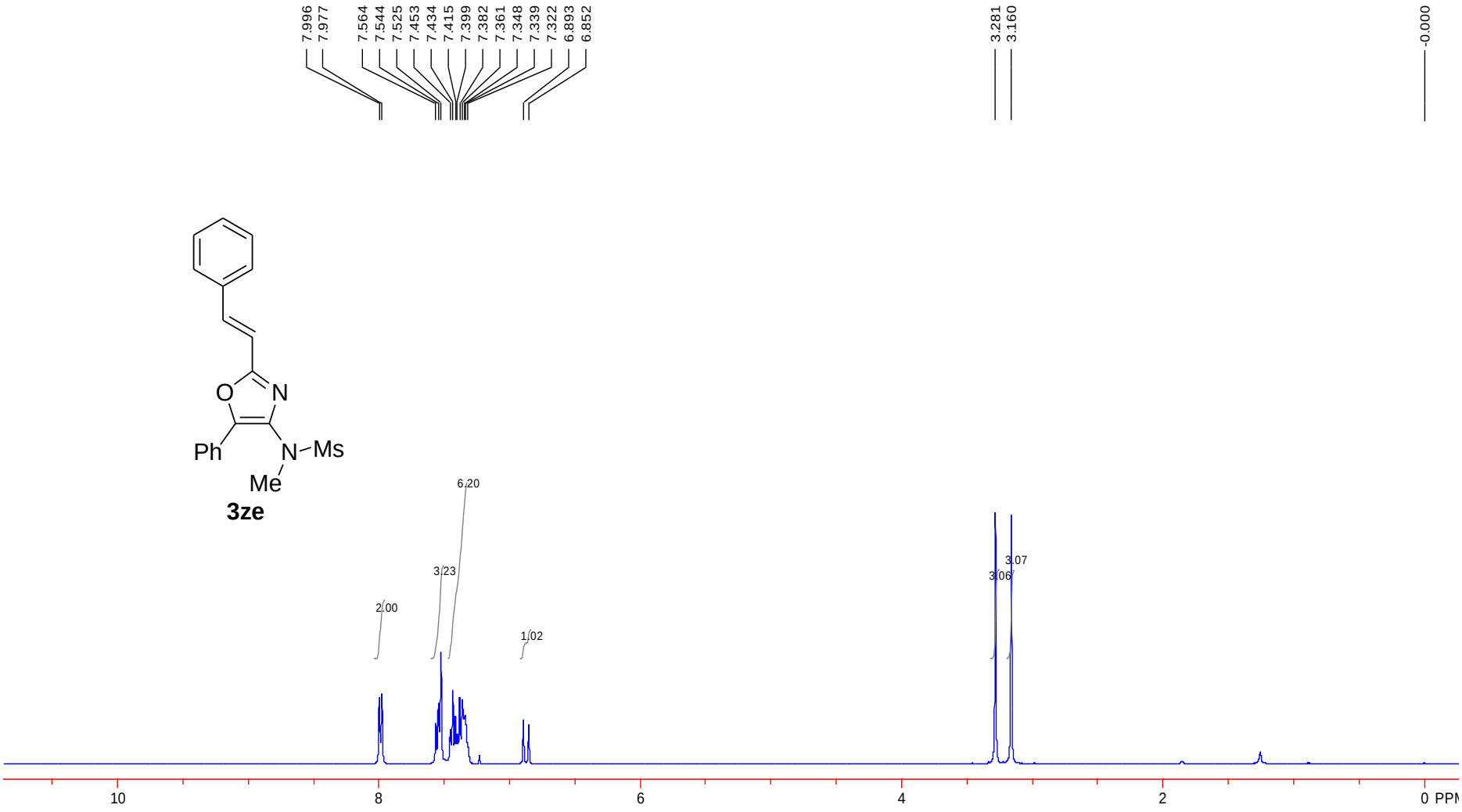


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

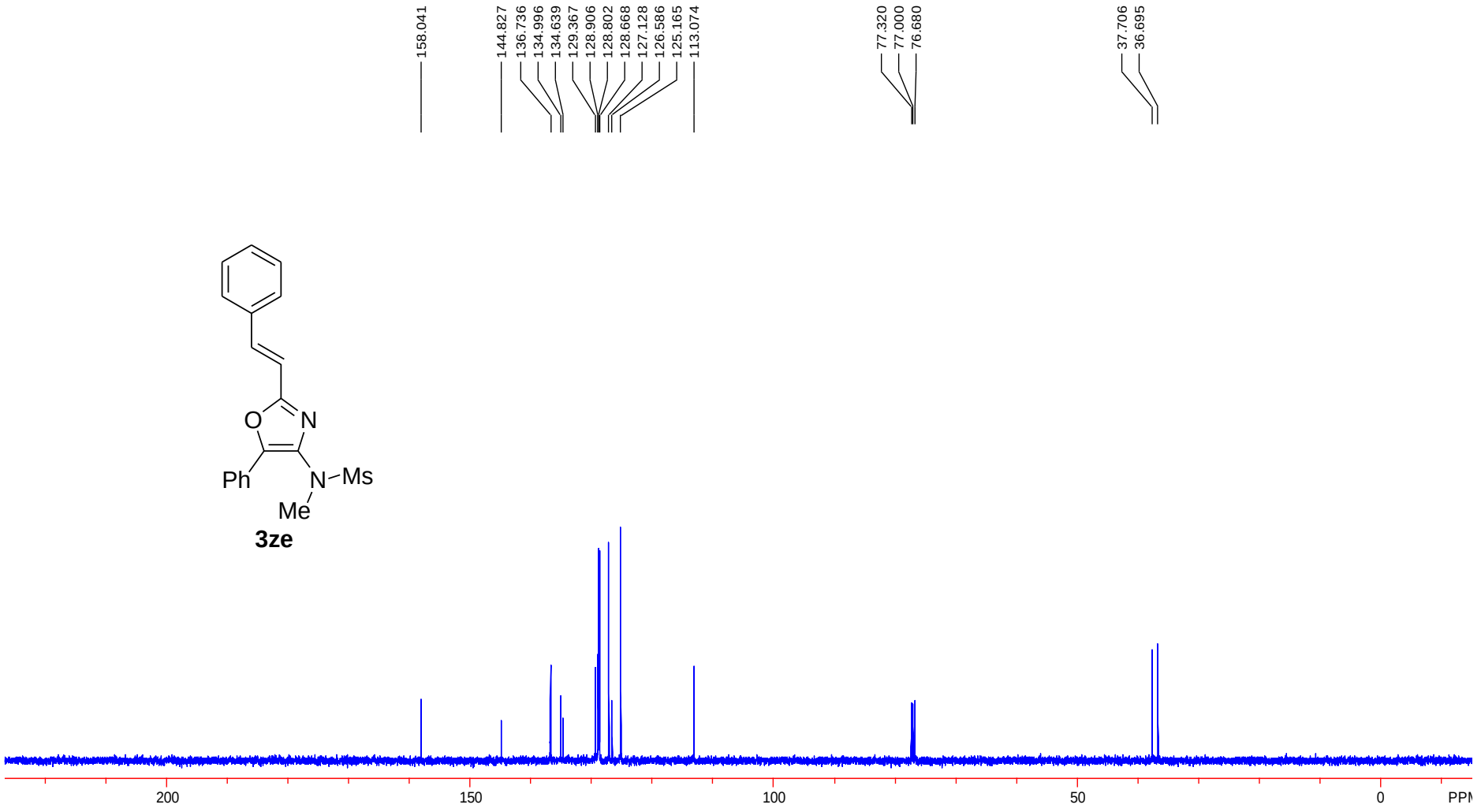



**3zd**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

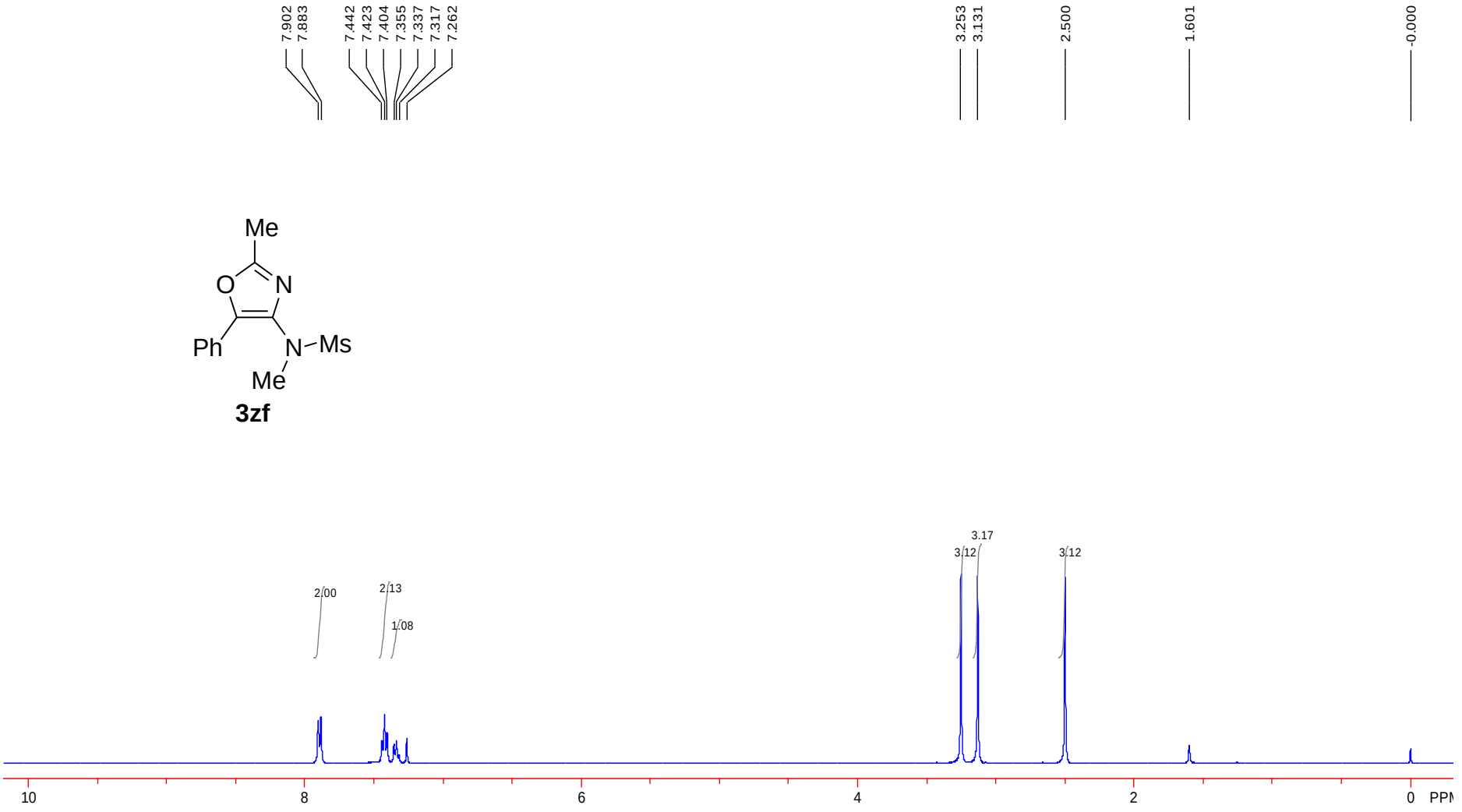


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

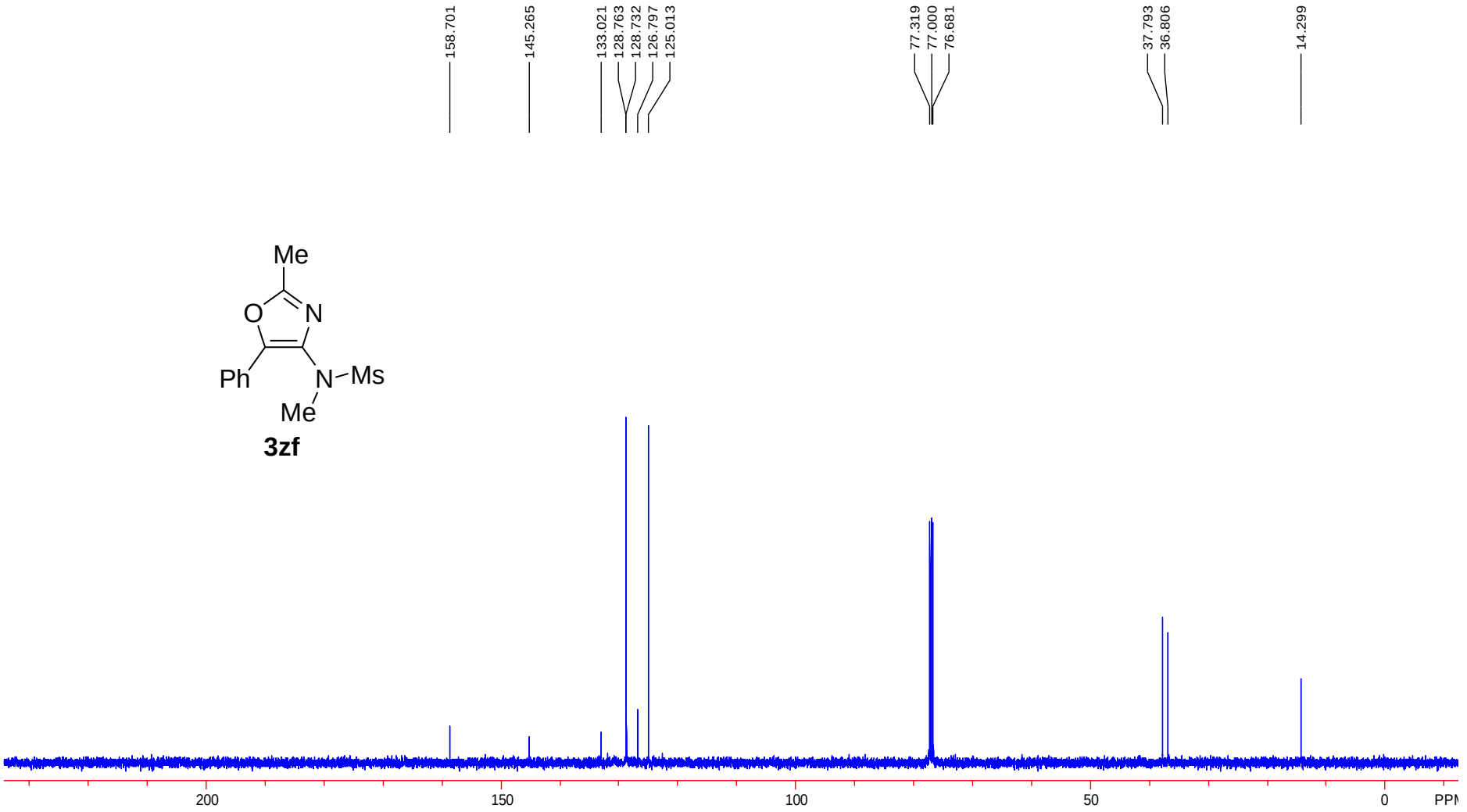



**3ze**

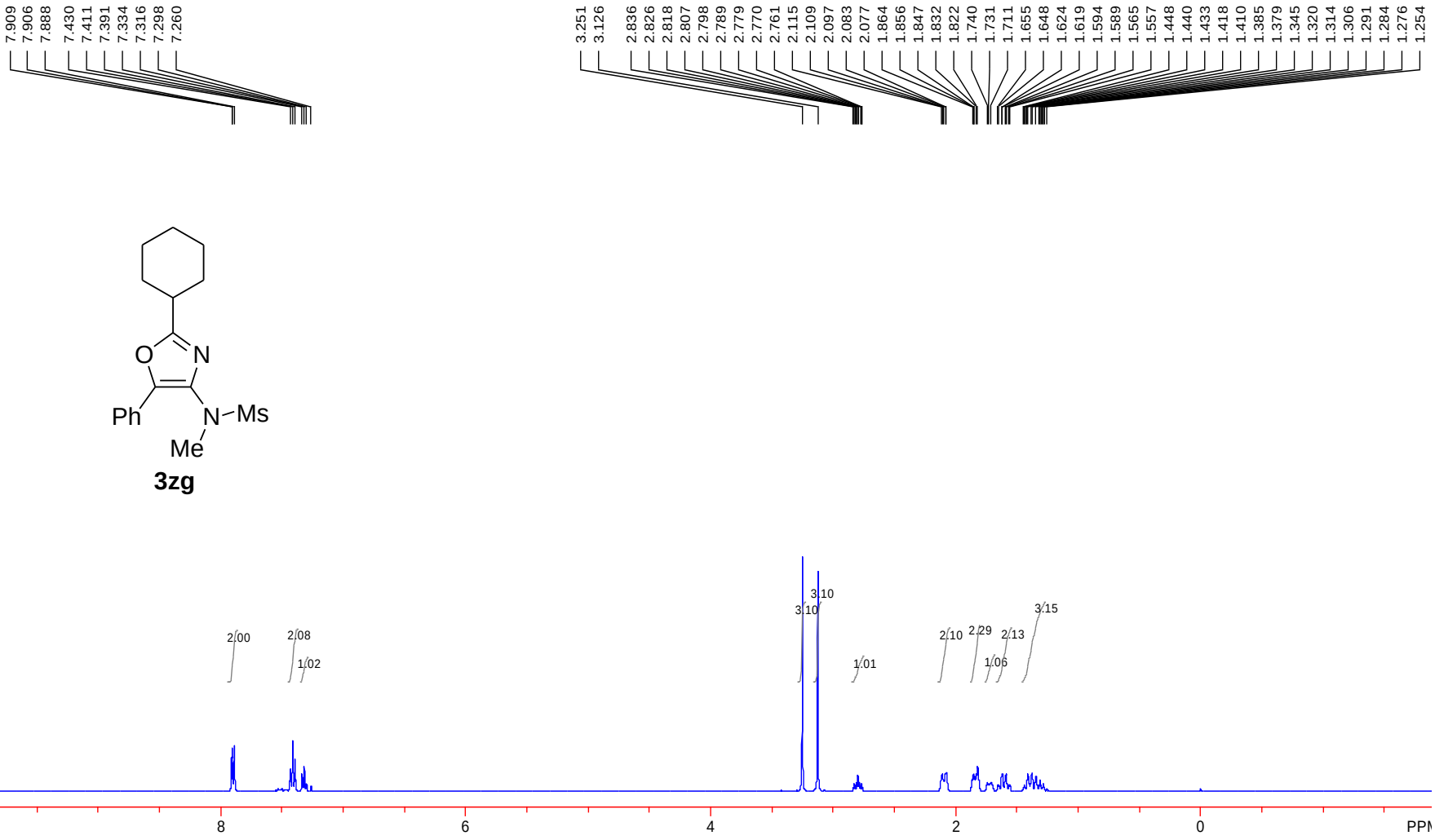
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



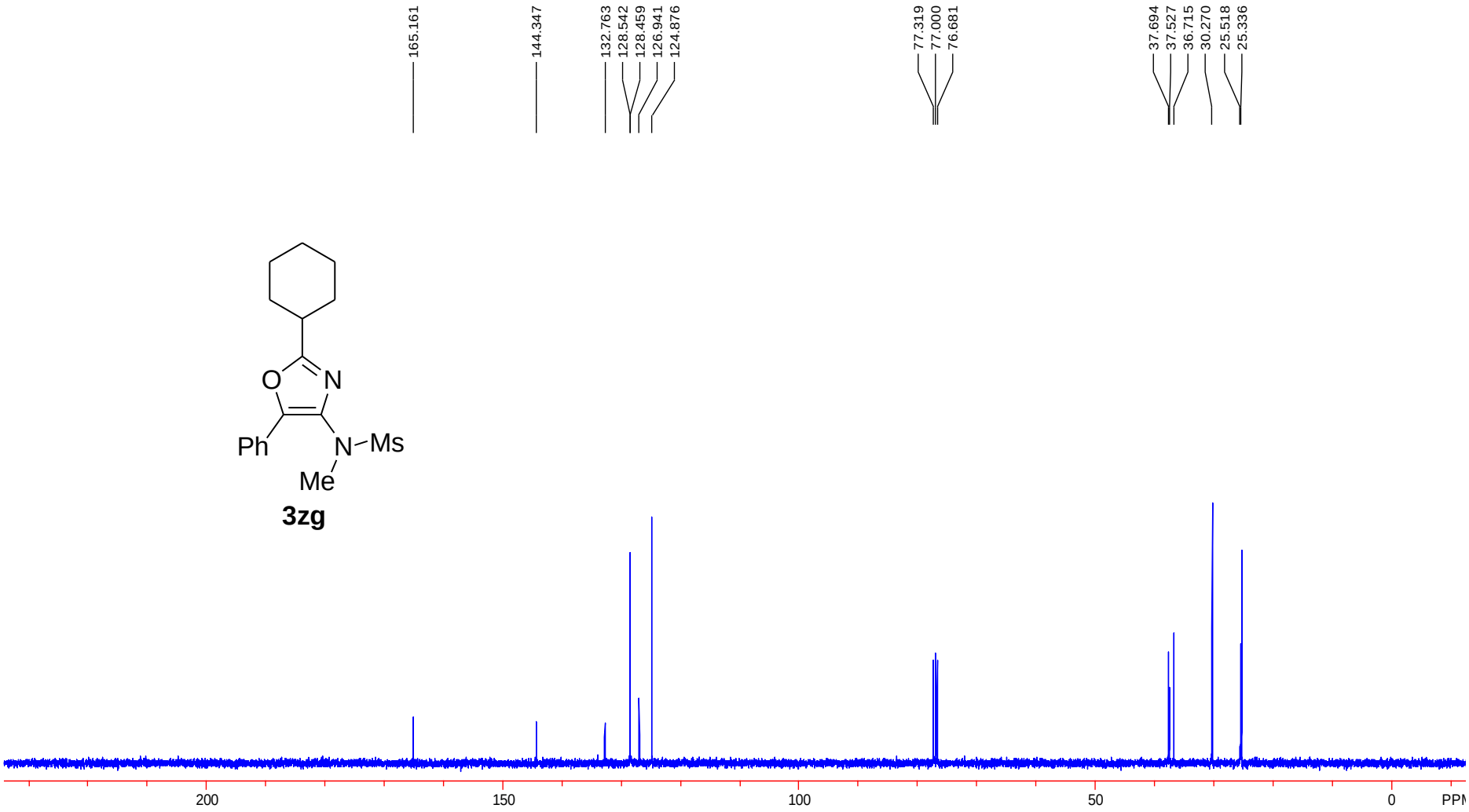
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



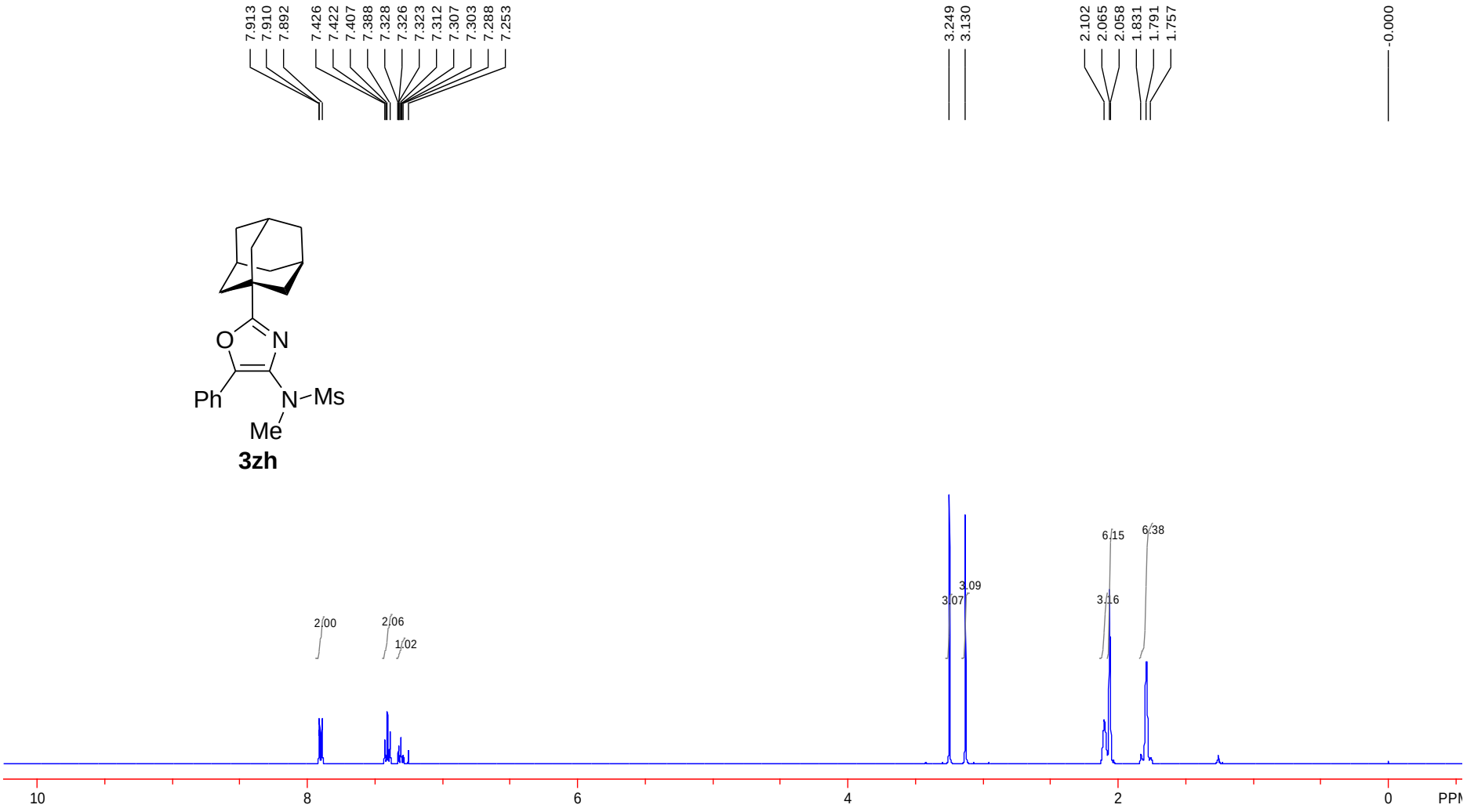
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



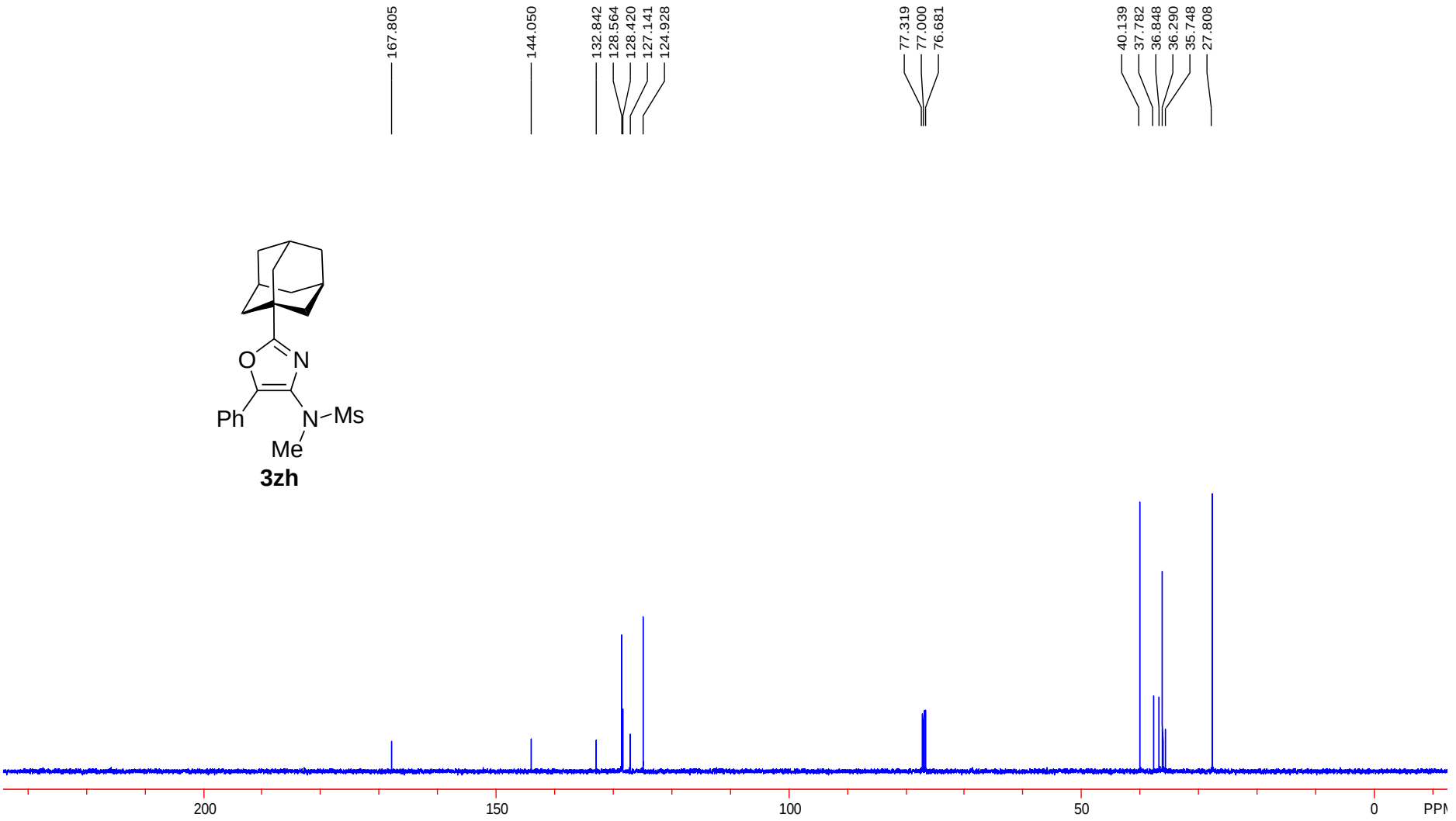
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**

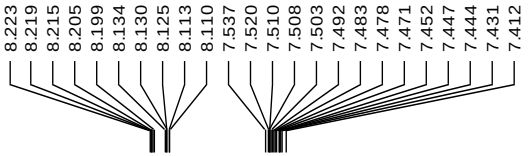


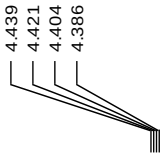
**$^{13}$C NMR (100 MHz, $CDCl_3$)**

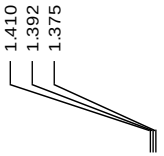



**3zh**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

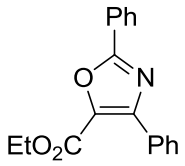


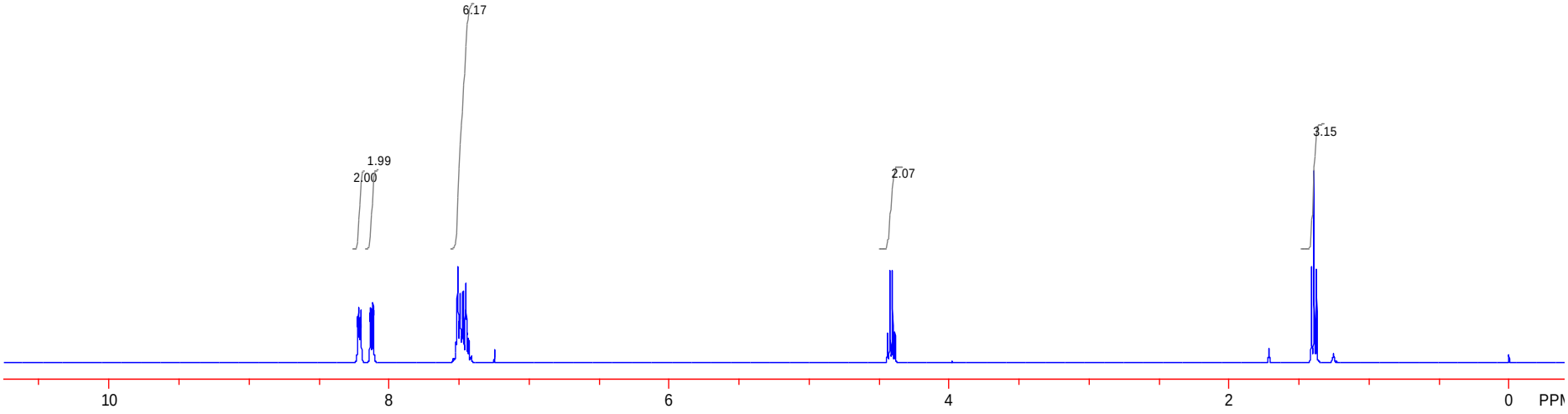





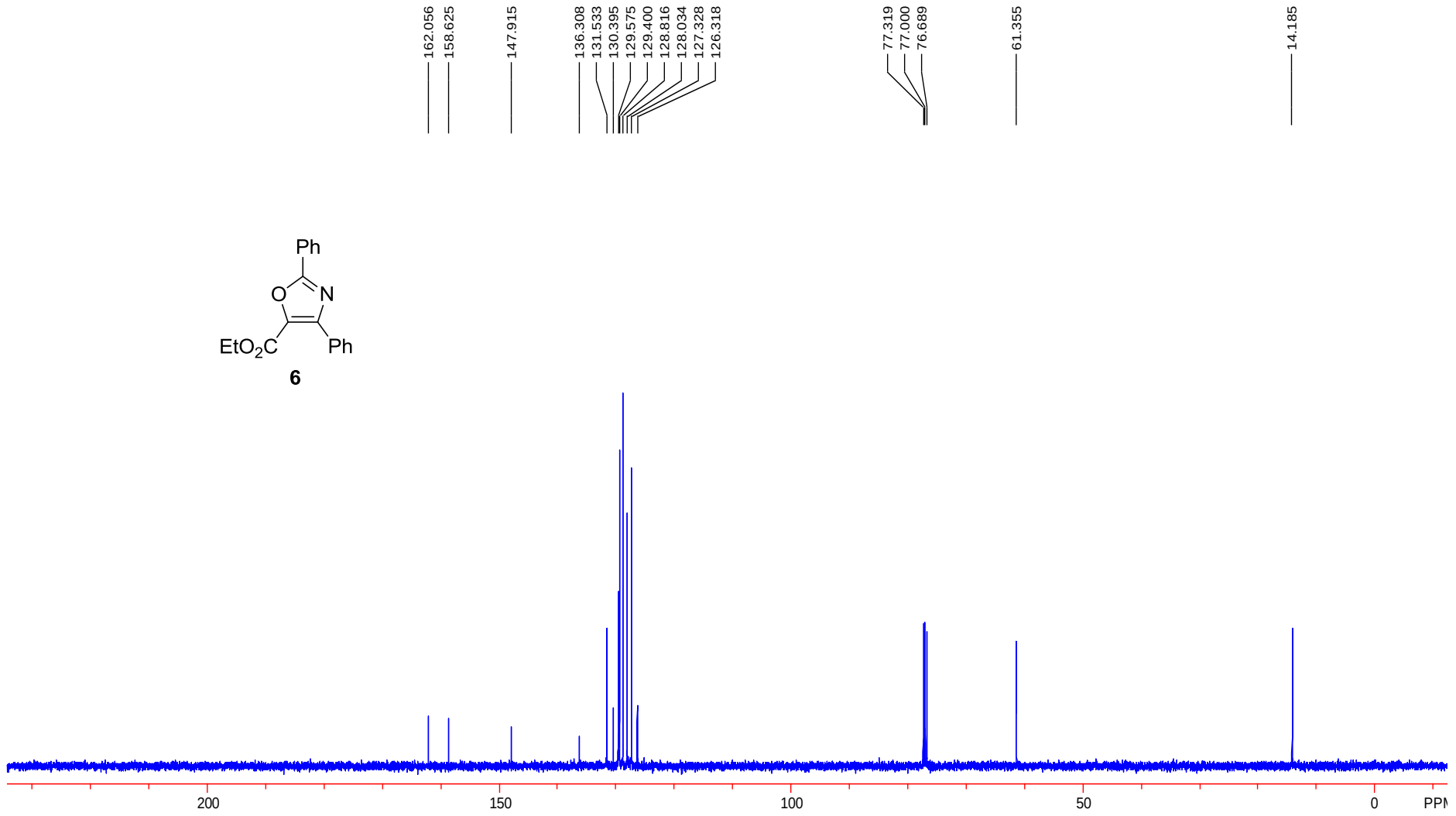




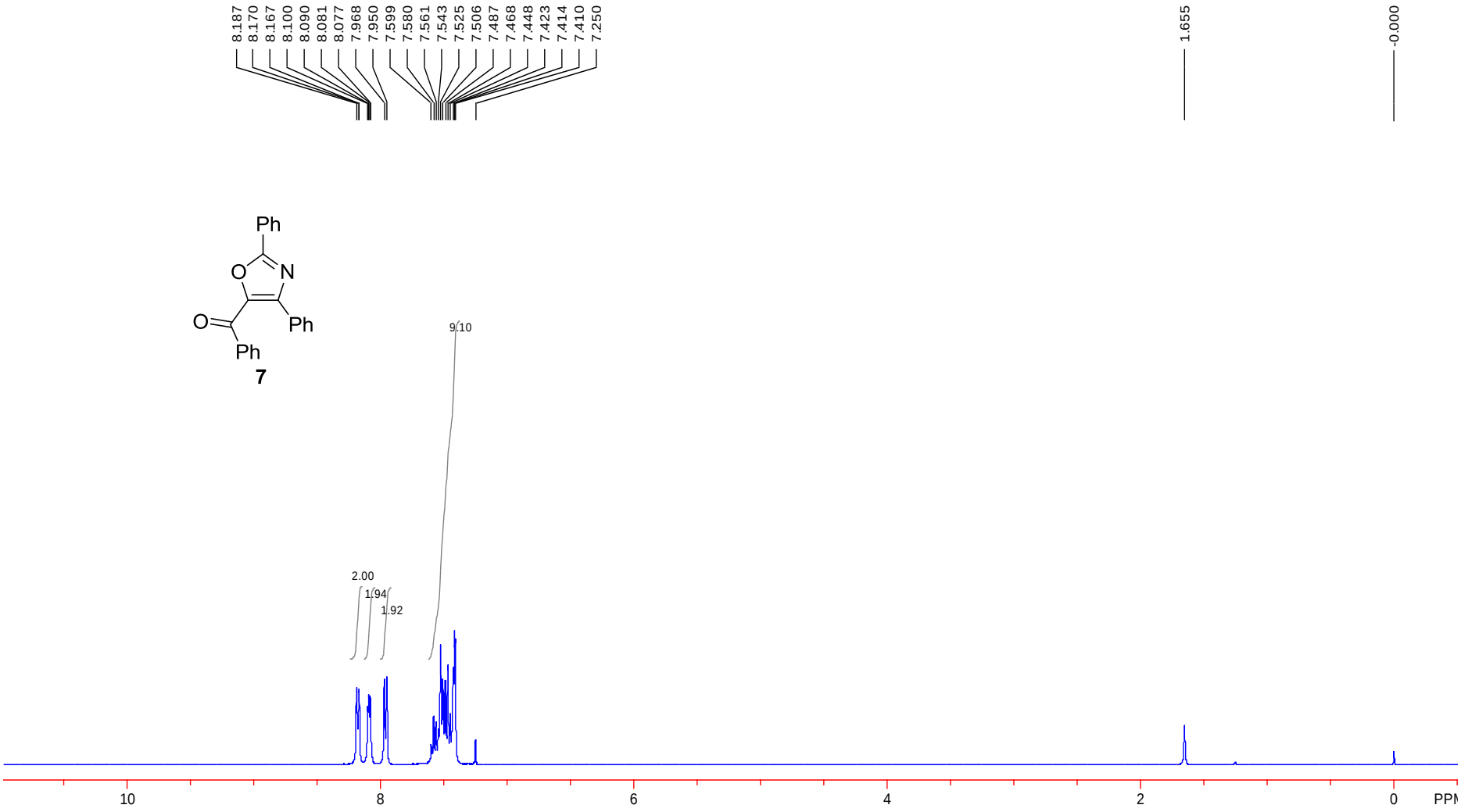

**6**



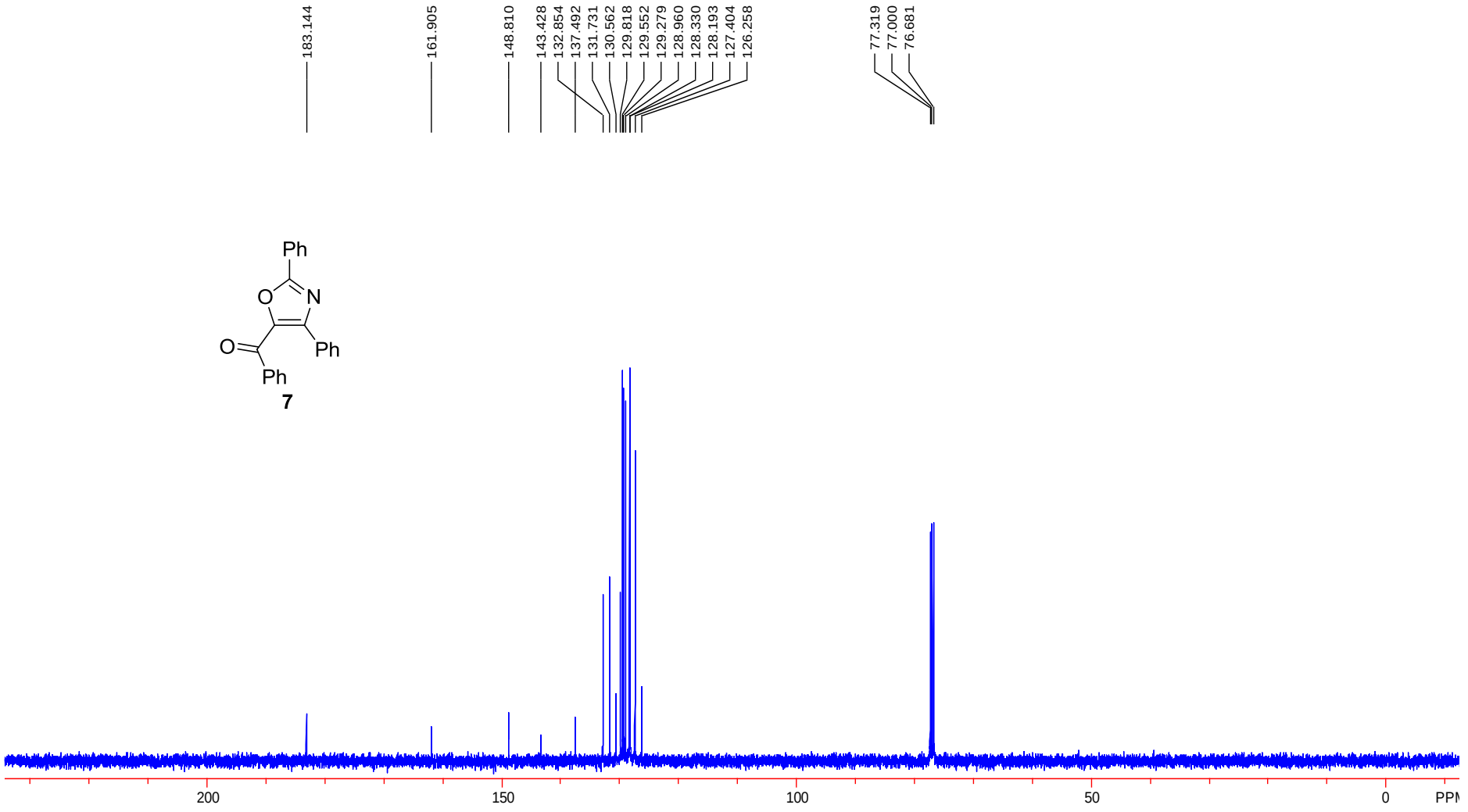
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



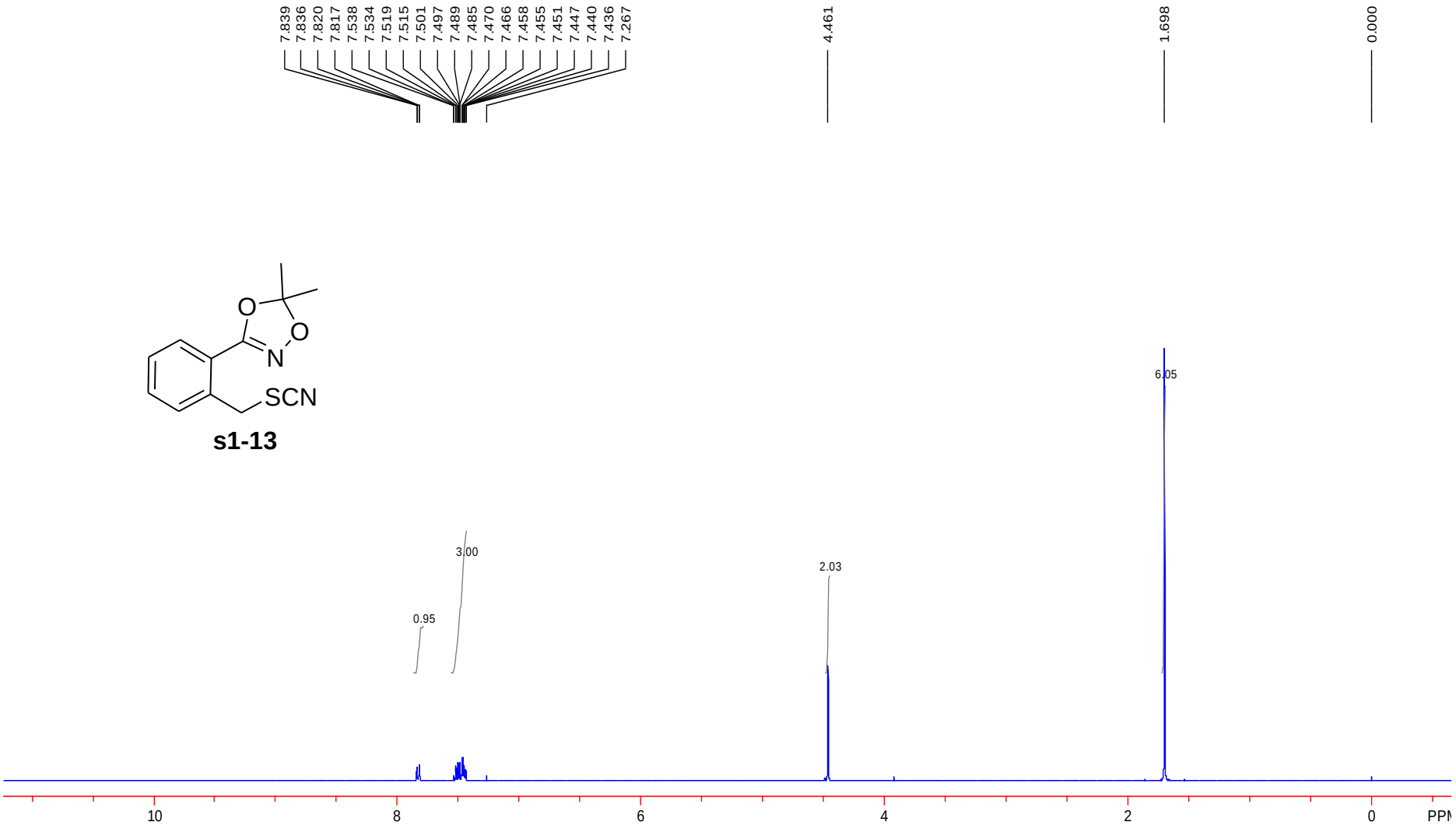
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



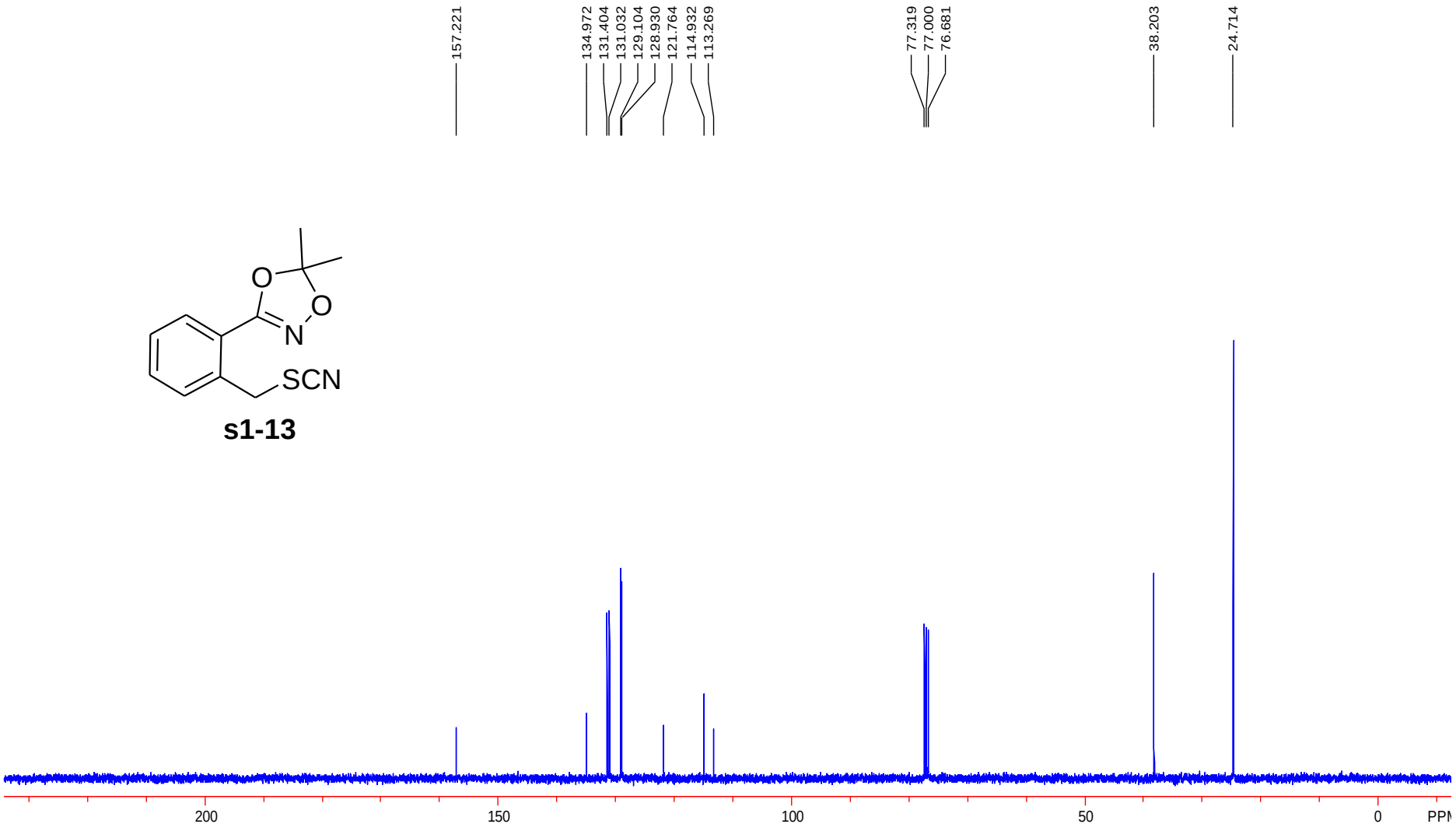
**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**

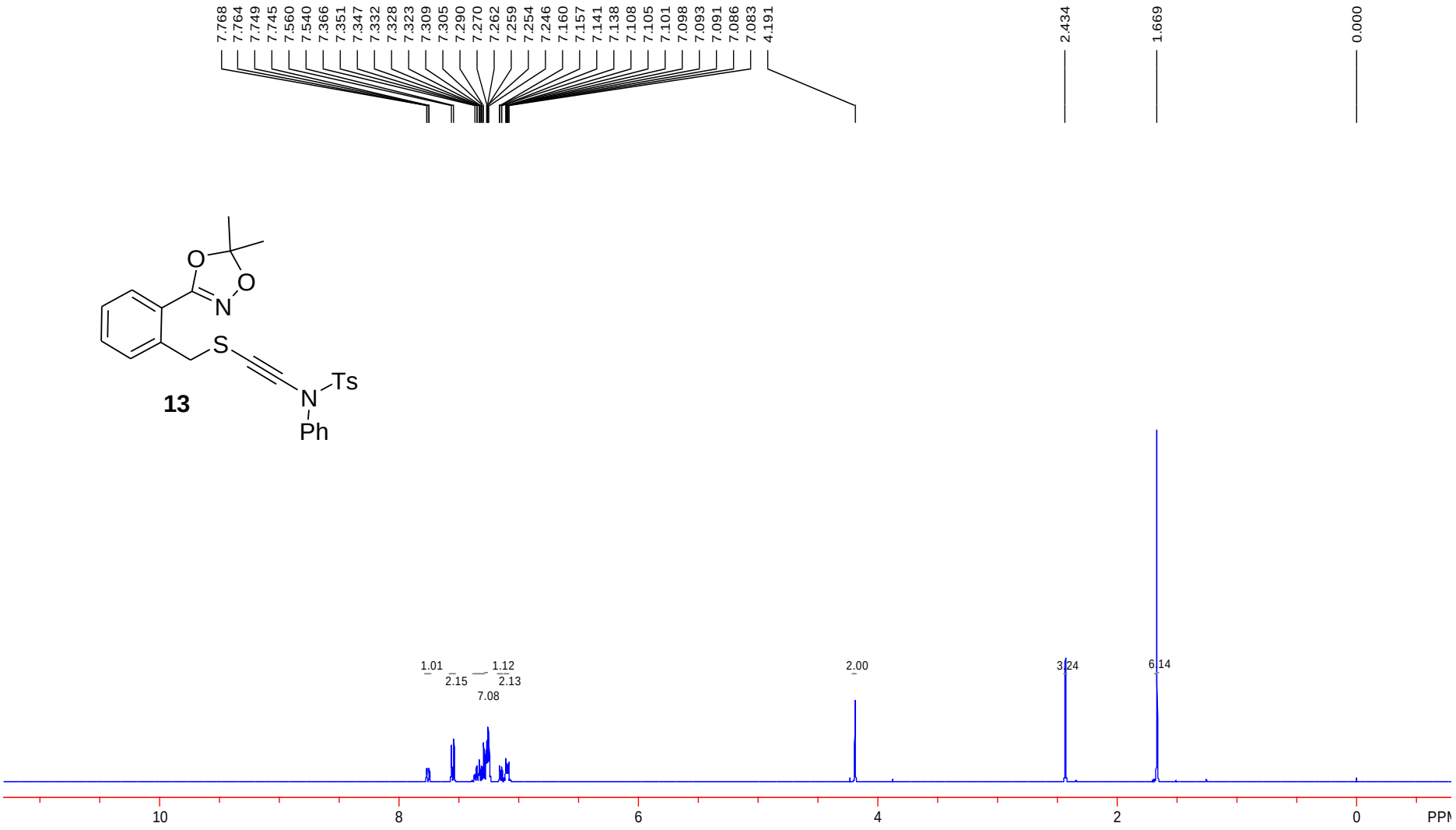


**$^{13}$C NMR (100 MHz, $CDCl_3$)**

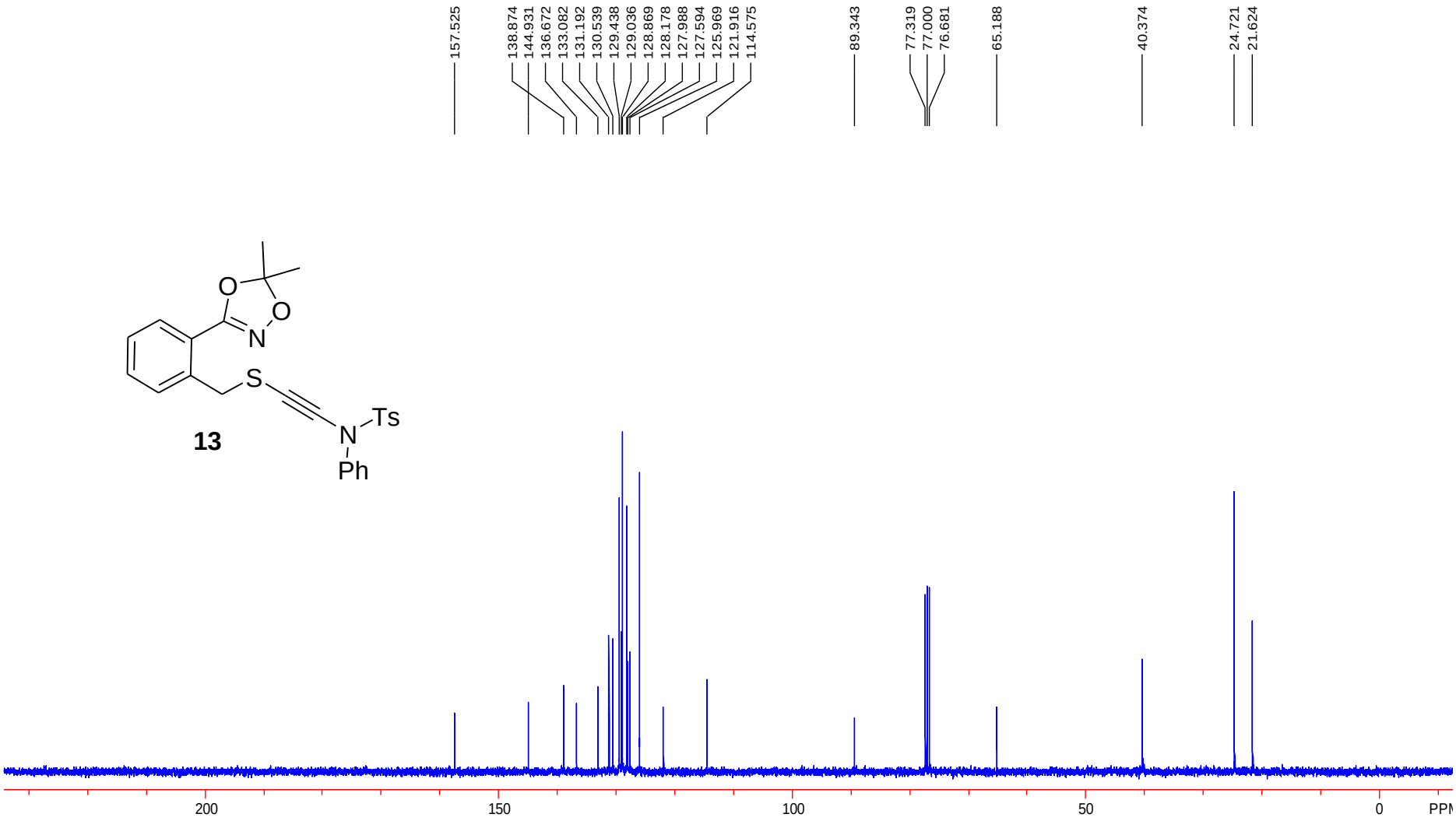



**s1-13**

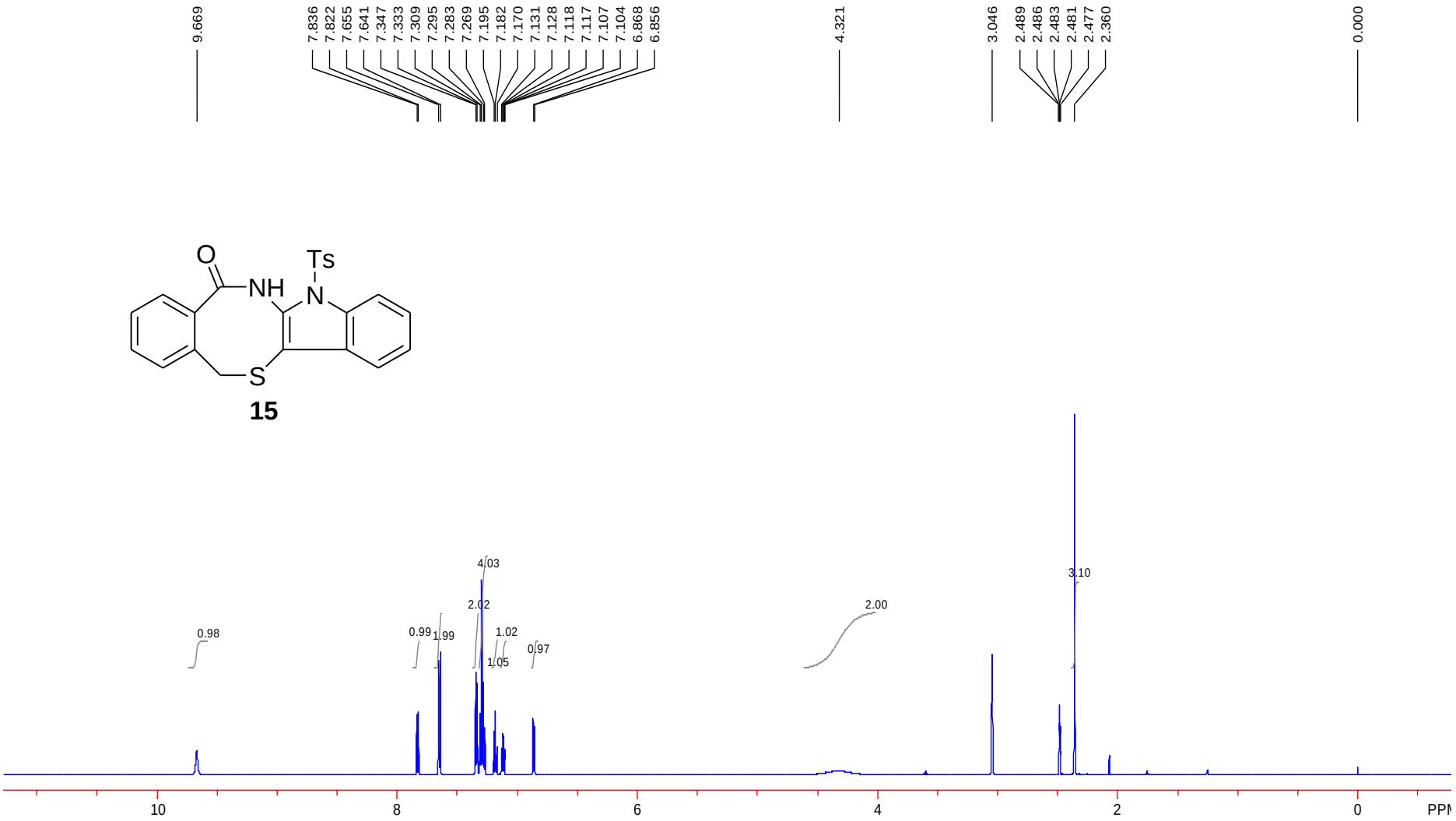
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



**$^{13}$C NMR (100 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, DMSO-$d_6$, $Me_4Si$, 80 $^{o}$C)**



**$^{13}$C NMR (400 MHz, DMSO-$d_6$, 80 $^{o}$C)**