Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 651–652

Synthesis of oxazolines and oxazoles by the reaction of propynals with tosylmethyl isocyanide

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The ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded in $CDCl_3$ using Bruker DPX-400 and Bruker AV-400 instruments at 400.13, 100.61 and 40.56 MHz, respectively. The chemical shifts of ^{1}H and ^{13}C NMR signals were measured relative to TMS and those of ^{15}N NMR signals were determined relative to nitromethane. Chromato mass spectrometry was performed using an Agilent Technologies 5975C instrument with mass selective detector in EI mode at 70 eV, an AT-6890N chromatograph, an Ultra-2 column with 5% phenylmethylsilicone at evaporator temperature 250 °C, thermostat temperature 70–280 °C and the temperature rise rate 20 °C min^{-1}. The IR spectra were recorded using a Bruker IFC-25 instrument. Elemental analysis was performed on a Thermo Finning 1112ser automatic analyzer. Column chromatography was carried out using silica gel 60, 70–200 mesh (Merck). The starting aldehydes **1a**,**b** were synthesized according to the known protocol.[1] The aldehyde **1c** was also synthesized according to the known method.[2]

Synthesis of oxazolines 3a–c: a general procedure

An appropriate base (1 mmol) was added to a solution of aldehyde (1 mmol) and tosylmethyl isocyanide (1 mmol) in a solvent (6 ml) (see Table 1). The reaction mixture was stirred at room temperature for 24 h or at 55 °C for 2 h. Then the solvent was removed *in vacuo* and the residue was purified by column chromatography on SiO_2 with chloroform as eluent.

4-Tosyl-5-(trimethylsilylethynyl)-2-oxazoline **3a**. Yellow oil, yield 67%. IR (ν/cm^{-1}): 2961, 2355, 1617, 1494, 1149. ^{1}H NMR ($CDCl_3$) δ: 0.19 (s, 9H, Me_3Si), 2.47 (s, 3H, Me), 5.18 (dd, 1H, CH, *J* 1.5, 5.5 Hz), 5.61 (dd, 1H, CH, *J* 1.5, 5.5 Hz), 7.01 (s, 1H, CH=N), 7.38 (d, 2H, *m*-H, *J* 8.0 Hz), 7.84 (d, 2H, *o*-H, *J* 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: -0.4, 21.9, 68.4, 91.5, 95.2, 98.7, 129.7, 130.0, 132.95, 146.0, 159.0. GC–MS, *m*/*z* (%): 321 $[M]^+$ (0.2), 278 (4), 250 (14), 229 (18), 184 (6), 180 (13), 155 $[Tosyl]^+$ (41), 149 (36), 139 (44), 123 (11), 107 (11), 91 $[MePh]^+$ (100), 73 (47), 65 (54), 45 (23), 39 (22). Found (%): C, 56.42; H, 5.36; N, 4.35; S, 10.07; Si, 8.81. Calc. for $C_{15}H_{19}SNO_3Si$ (%): C, 56.39; H, 5.36; N, 4.39; S, 10.04; Si, 8.79.

4-Tosyl-5-(triethylgermylethynyl)-2-oxazoline **3b**. Yellow oil, yield 53%. IR (ν/cm^{-1}): 2955, 2873, 2205, 1687, 1496, 1147. ^{1}H NMR ($CDCl_3$) δ: 0.87 (q, 6H, CH_2^{Et}, J 7.8 Hz), 1.07 (t, 9H, Me^{Et}, J 7.8 Hz), 2.47 (s, 3H, Me^{Tos}), 5.17 (dd, 1H, CH, J 1.5, 5.5 Hz), 5.61 (d, 1H, CH, J 1.5, 5.5 Hz), 7.02 (s, 1H, CH=N), 7.38 (d, 2H, *m*-H, J 8.2 Hz), 7.82 (d, 2H, *o*-H, J 8.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 5.7, 9.05, 22.0, 68.7, 92.0, 93.75, 100.0, 129.7, 130.05, 133.1, 146.0, 159.1. ^{15}N NMR ($CDCl_3$) δ: -162.36. GC–MS, *m*/*z* (%): 407 $[M\text{-}1]^+$ (0.5), 373 (11), 349 $[M\text{-}1\text{-}Et_2]^+$ (0.8), 329 (5), 315 (8), 287 (3), 255 (20), 224 $[M\text{-}1\text{-}Et_3GeC{\equiv}C]^+$ (15), 218 (20), 195 (12), 166 (28), 149 (28), 139 (67), 121 (12), 99 (15), 91 $[MePh]^+$ (37), 71 (51), 57 (100), 43 (65), 41 (29). Found (%): C, 52.82; H, 6.26; N, 3.35; S, 7.57; Ge, 18.00. Calc. for $C_{18}H_{25}SNO_3Ge$ (%): C, 52.98; H, 6.18; N, 3.43; S, 7.86; Ge, 17.79.

4-Tosyl-5-(phenylethynyl)-2-oxazoline **3c**. Yellow oil, yield 56%. IR (ν/cm^{-1}): 2236, 1615, 1491, 1148. ^{1}H NMR ($CDCl_3$) δ: 2.48 (s, 3H, Me), 5.30 (dd, 1H, CH, J 1.5, 5.5 Hz), 5.88 (dd, 1H, CH, J 1.5, 5.5 Hz), 7.08 (s, 1H, CH=N), 7.32 (d, 2H, *o*-H^{Tos}, J 8.0 Hz), 7.35 (m, 3H, *m*-H^{Tos}, *p*-H^{Ph}), 7.46 (d, 2H, *m*-H^{Ph}, J 7.0 Hz), 7.87 (d, 2H, *o*-H^{Tos}, J 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.8, 68.7, 83.1, 88.9, 92.3, 121.0, 129.5, 129.6, 129.7, 130.0, 132.1, 132.9, 146.0, 159. GC–MS, *m*/*z* (%): 325 $[M]^+$ (2), 285 (17), 259 (3), 216 (4), 188 (8), 172 (14), 155 $[Tosyl]^+$ (11), 143 (9), 139 (18), 115 (27), 105 (31), 91 $[MePh]^+$ (100), 77 (35), 65 (48), 51 (17), 39 (20). Found (%): C, 66.42; H, 4.36; N, 4.34; S, 9.79. Calc. for $C_{18}H_{15}SNO_3$ (%): C, 66.44; H, 4.65; N, 4.31; S, 9.85.

5-(triethylgermylethynyl)-1,3-oxazole **4b**. Yellow oil, yield 58%. IR (ν/cm^{-1}): 2956, 2875, 2160, 1566, 1487, 1309, 1202. ^{1}H NMR ($CDCl_3$) δ: 0.93 (q, 6H, CH_2^{Et}, J 7.8 Hz), 1.11 (t, 9H, Me^{Et}, J 7.8 Hz), 7.22 (s, 1H, C=CH), 7.79 (s, 1H, CH=N). ^{13}C NMR ($CDCl_3$) δ: 5.7 (CH_2^{Et}), 9.0 (Me^{Et}), 91.0, 103.8, 130.4, 135.4, 150.65. GC–MS, *m*/*z* (%): 251 $[M]^+$ (2), 222 $[M\text{-}Et_3]^+$ (25), 207 (7), 196 (20), 177 (24), 168 (25), 149 (100), 139 (15), 121 (12), 105 (25), 97 (24), 71 (48), 57 (81), 44 (99), 41 (82). Found (%): C, 52.62; H, 6.86; N, 5.35; Ge, 28.58. Calc. for $C_{11}H_{17}NOGe$ (%): C, 52.46; H, 6.80; N, 5.56; Ge, 28.82.

5-(Phenylethynyl)-1,3-oxazole **4c**. Yellow oil, yield 54%. IR (ν/cm^{-1}): 2220 (C≡C), 1571, 1491, 1445, 1311. ^{1}H NMR ($CDCl_3$) δ: 7.33 (s, 1H, C=CH), 7.38-7.40 (m, 3H, *m*-H, *p*-H), 7.54 (d, 2H, *o*-H, J 7.6 Hz), 7.89 (s, 1H, CH=N). ^{13}C NMR ($CDCl_3$) δ: 97.6, 121.6, 128.6, 129.5, 130.0, 130.1, 130.6, 135.4, 151.3. GC–MS, *m*/*z* (%): 169 $[M]^+$ (71), 140 $[M\text{-}Et_3]^+$ (2), 129 (6), 114

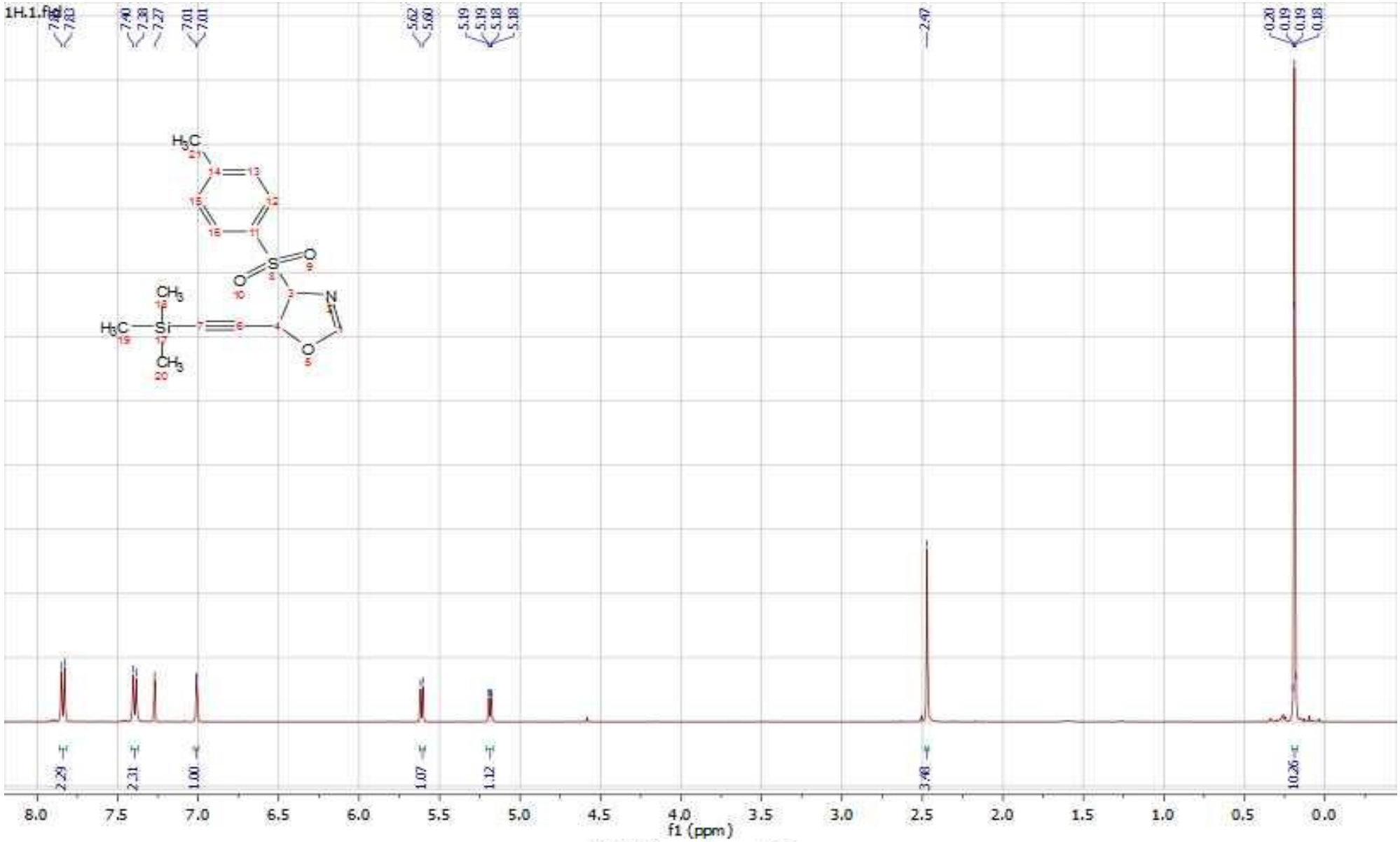
(100), 101 (2), 88 (11), 75 (7), 63 (12), 51 (5), 39 (5). Found (%): C, 65.57; H, 3.56; N, 7.00. Calc. for $C_{11}H_7NO$ (%): C, 65.65; H, 3.51; N, 6.96.

5-Ethynyl-1,3-oxazole **5**. Orange oil, yield 43%. IR (ν/cm^{-1}): 3130, 2360, 1310, 1084. ^{1}H NMR ($CDCl_3$) δ: 3.58 (s, 1H, HC≡C), 7.33 (s, 1H, CH=C), 7.85 (s, 1H, CH=N). ^{13}C NMR ($CDCl_3$) δ: 70.7, 86.4, 129.8, 134.45, 151.4. GC–MS, *m*/*z* (%): 93 $[M]^+$ (64), 65 (65), 53 (13), 38 (100). Found (%): C, 64.42; H, 3.23; N, 15.15. Calc. for C_5H_3NO (%): C, 64.52; H, 3.22; N, 15.05.

References

1 I. A. Novokshonova, V. V. Novokshonov and A. S. Medvedeva, *Synthesis*, 2008, 3797.

2 L. Brandsma, *Preparative Acetylenic Chemistry*, 2nd edn., *Studies in Organic Chemistry*, Elsevier, Amsterdam, 1988, vol. 34.



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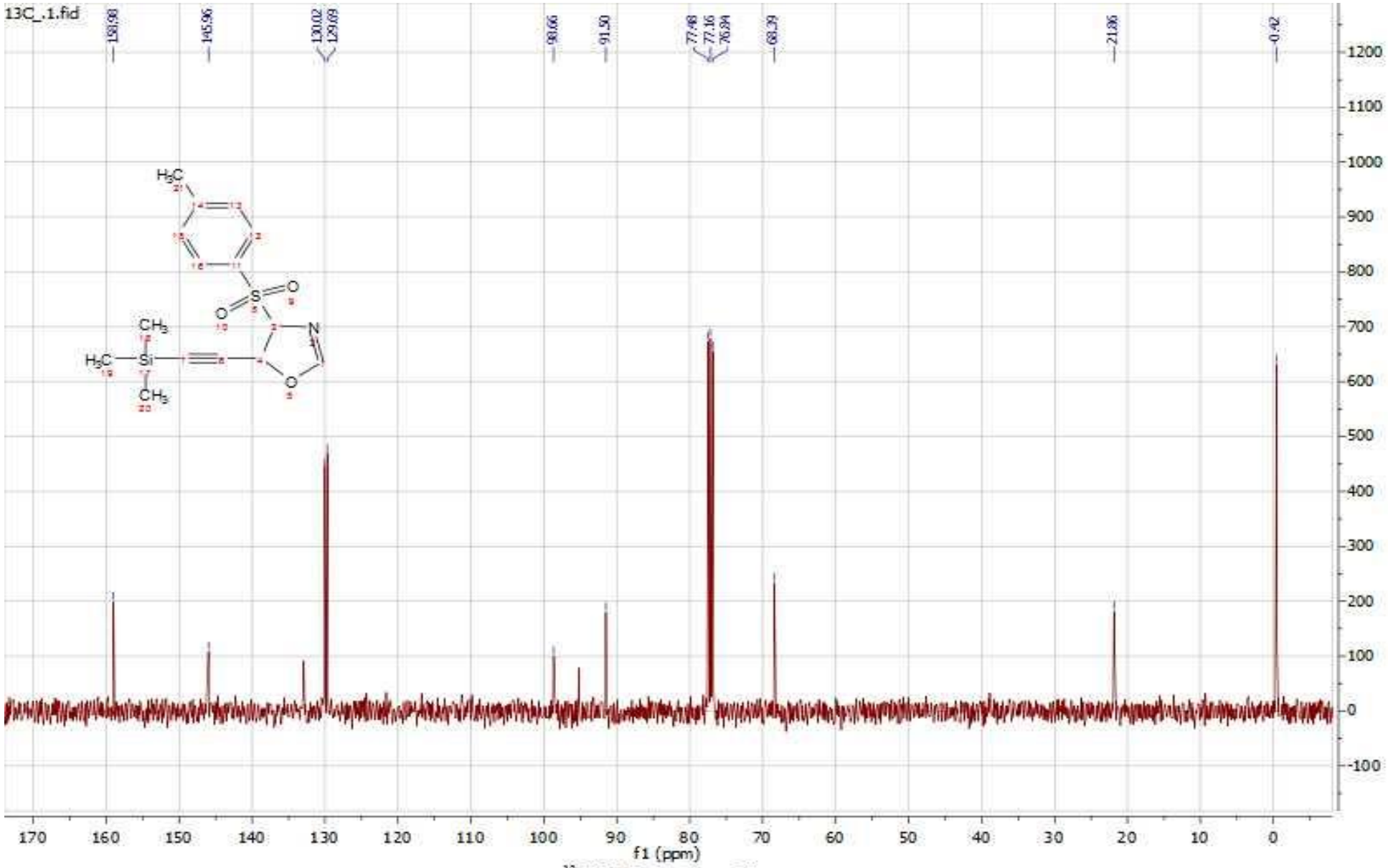

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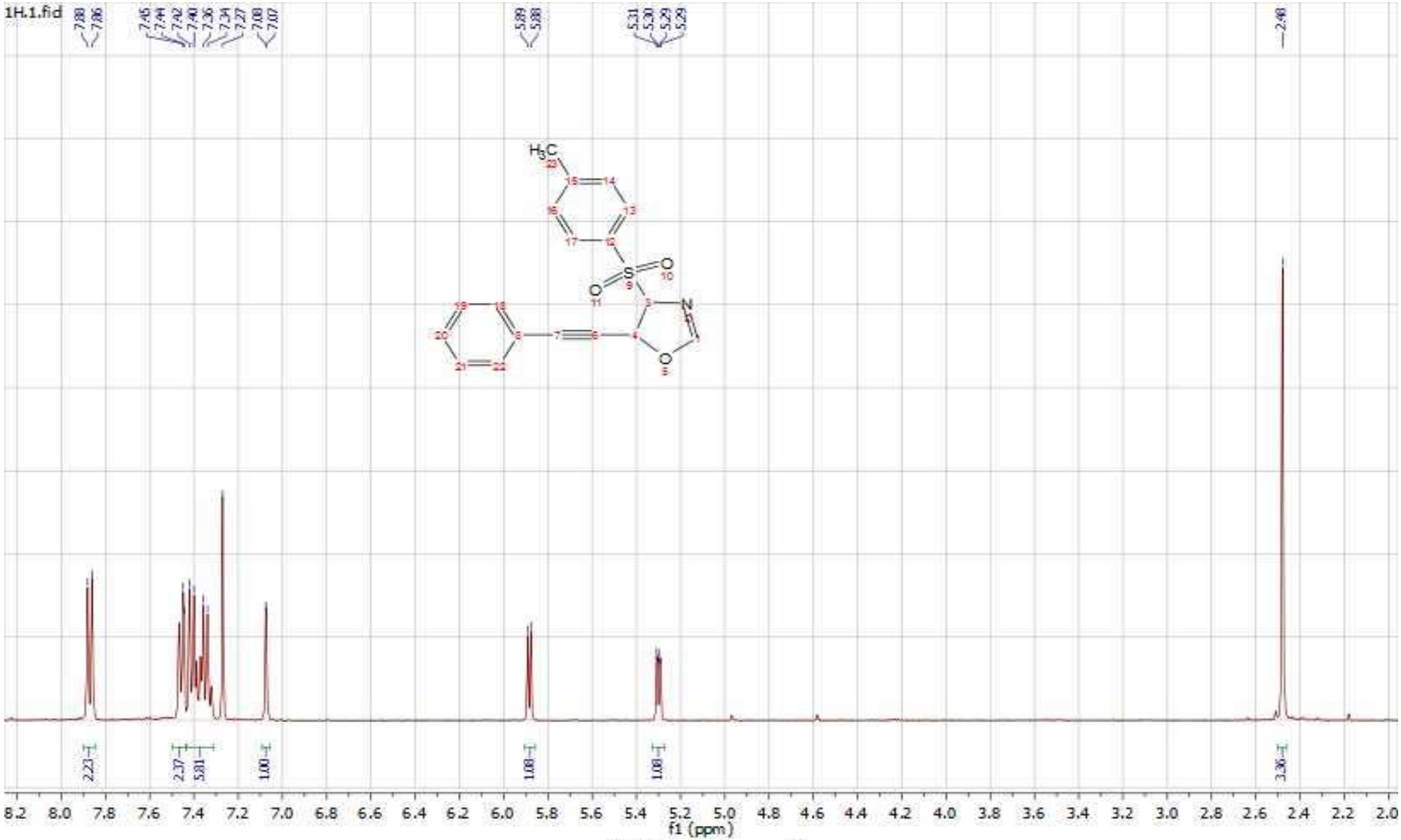

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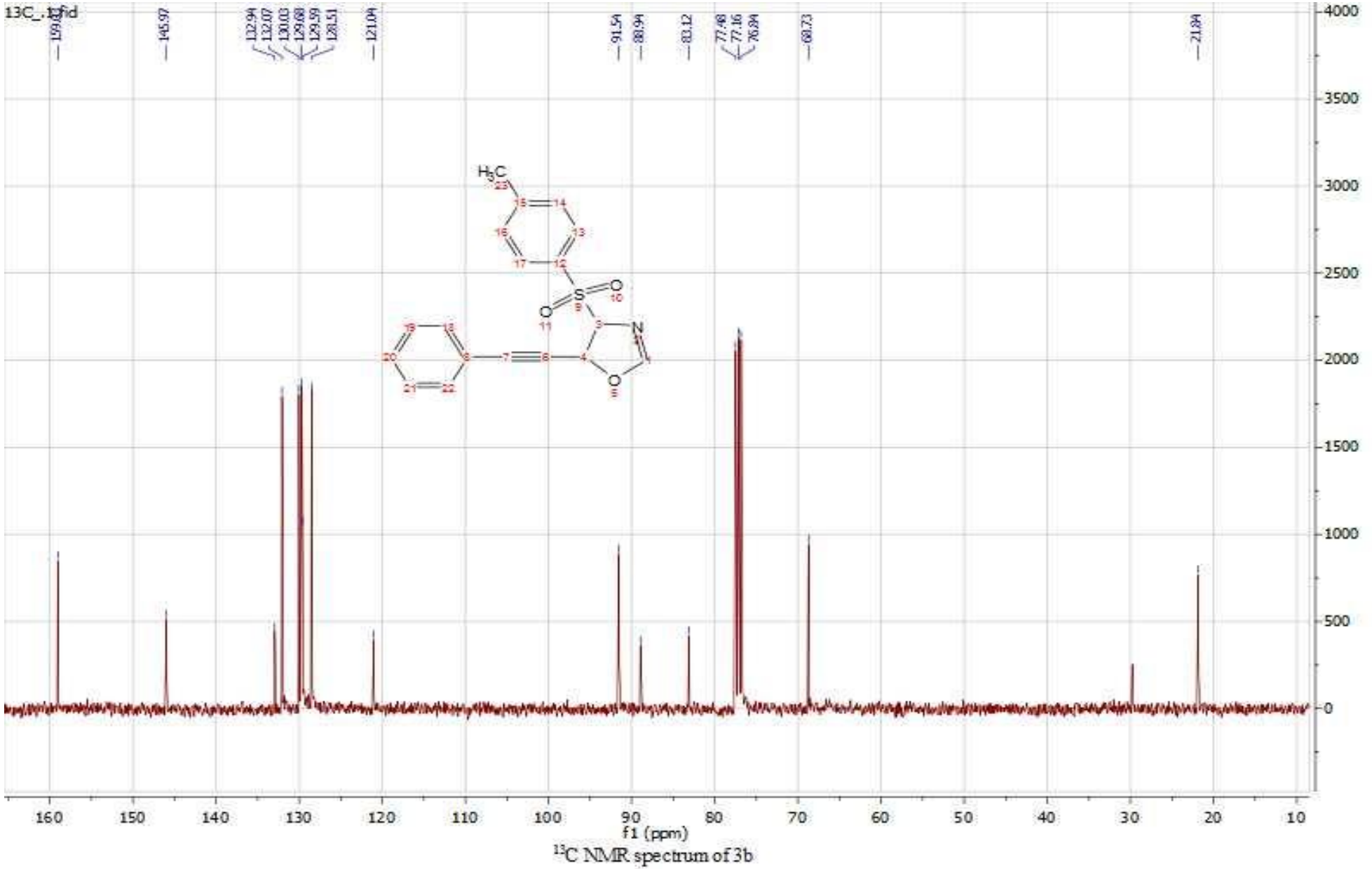

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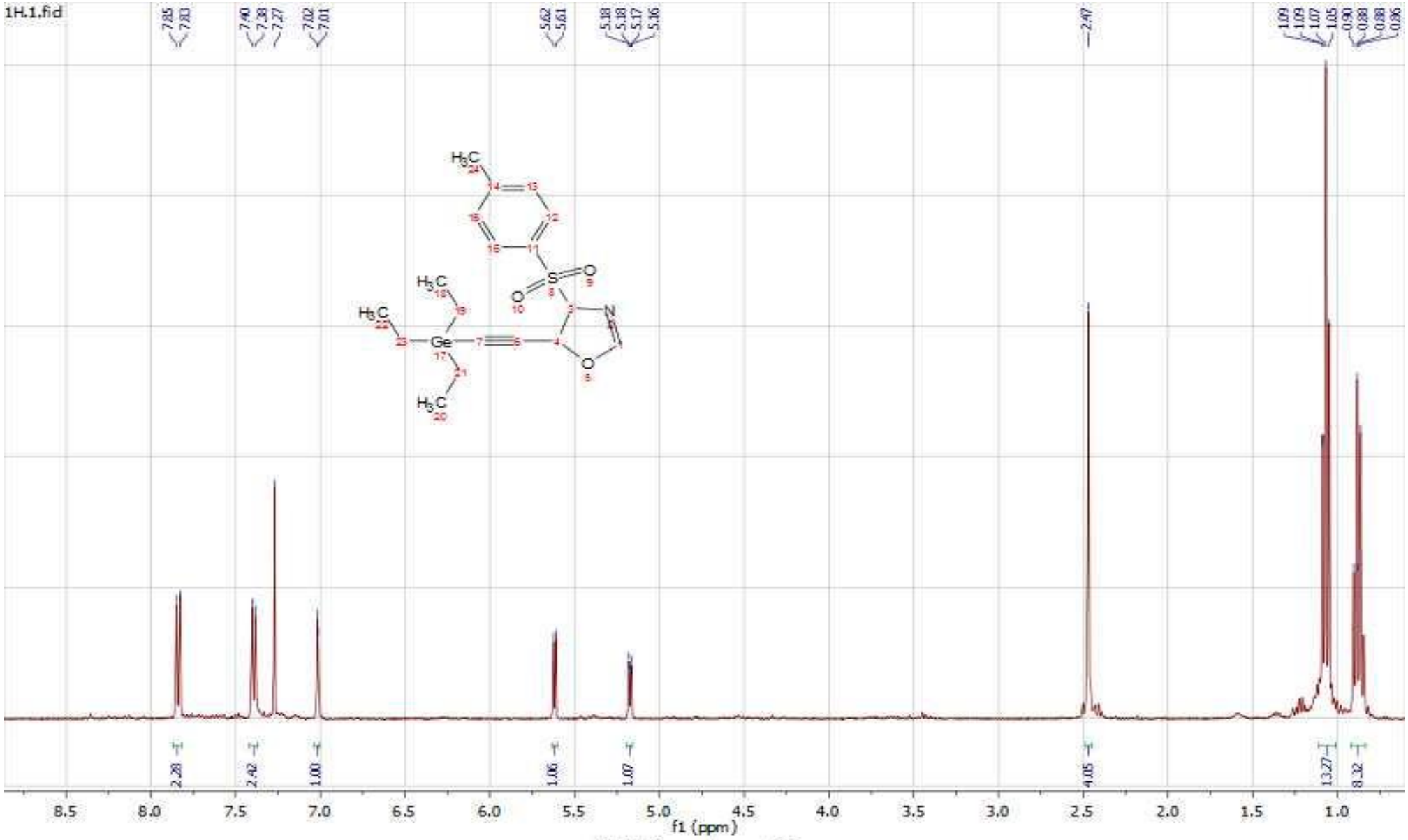

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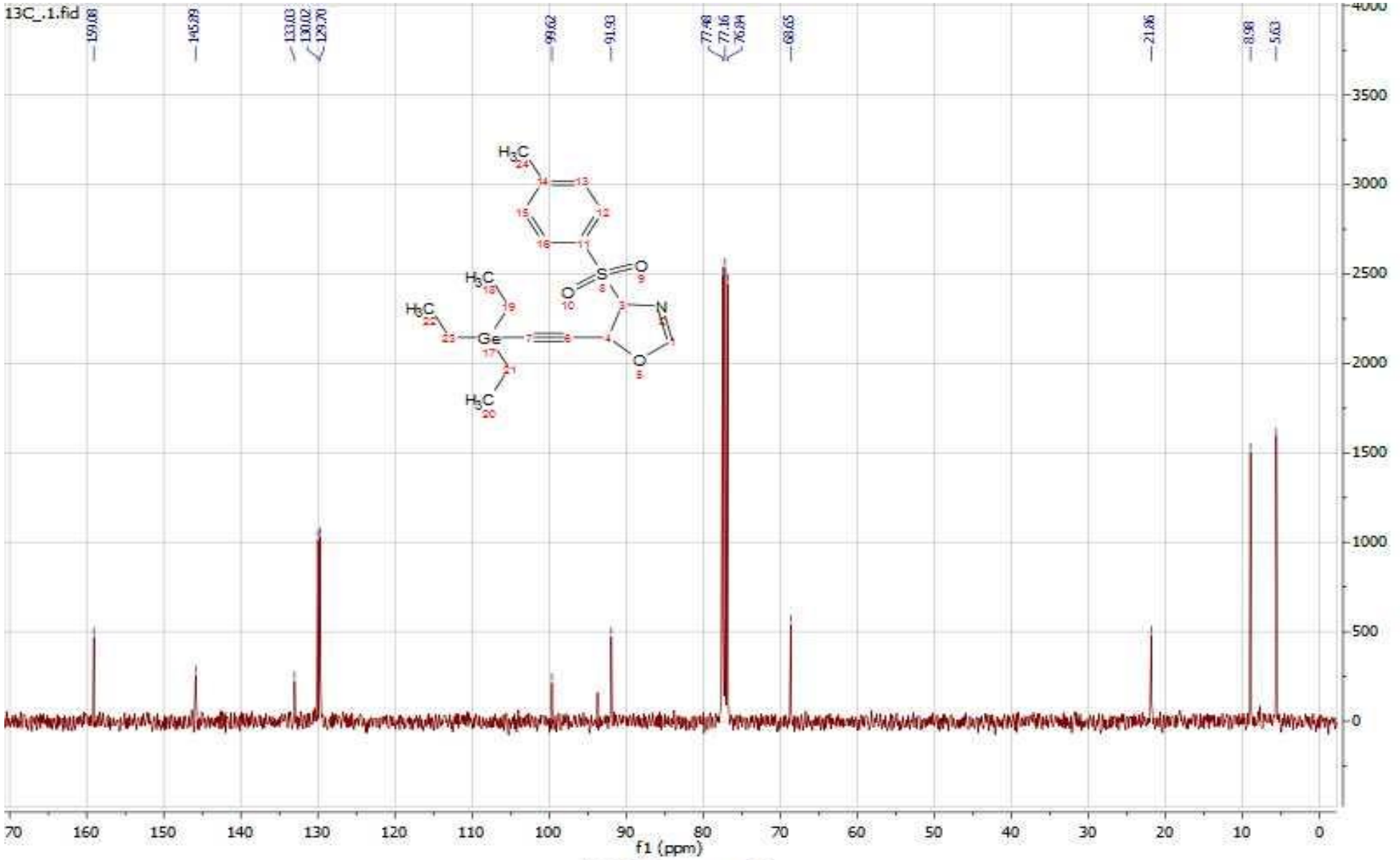

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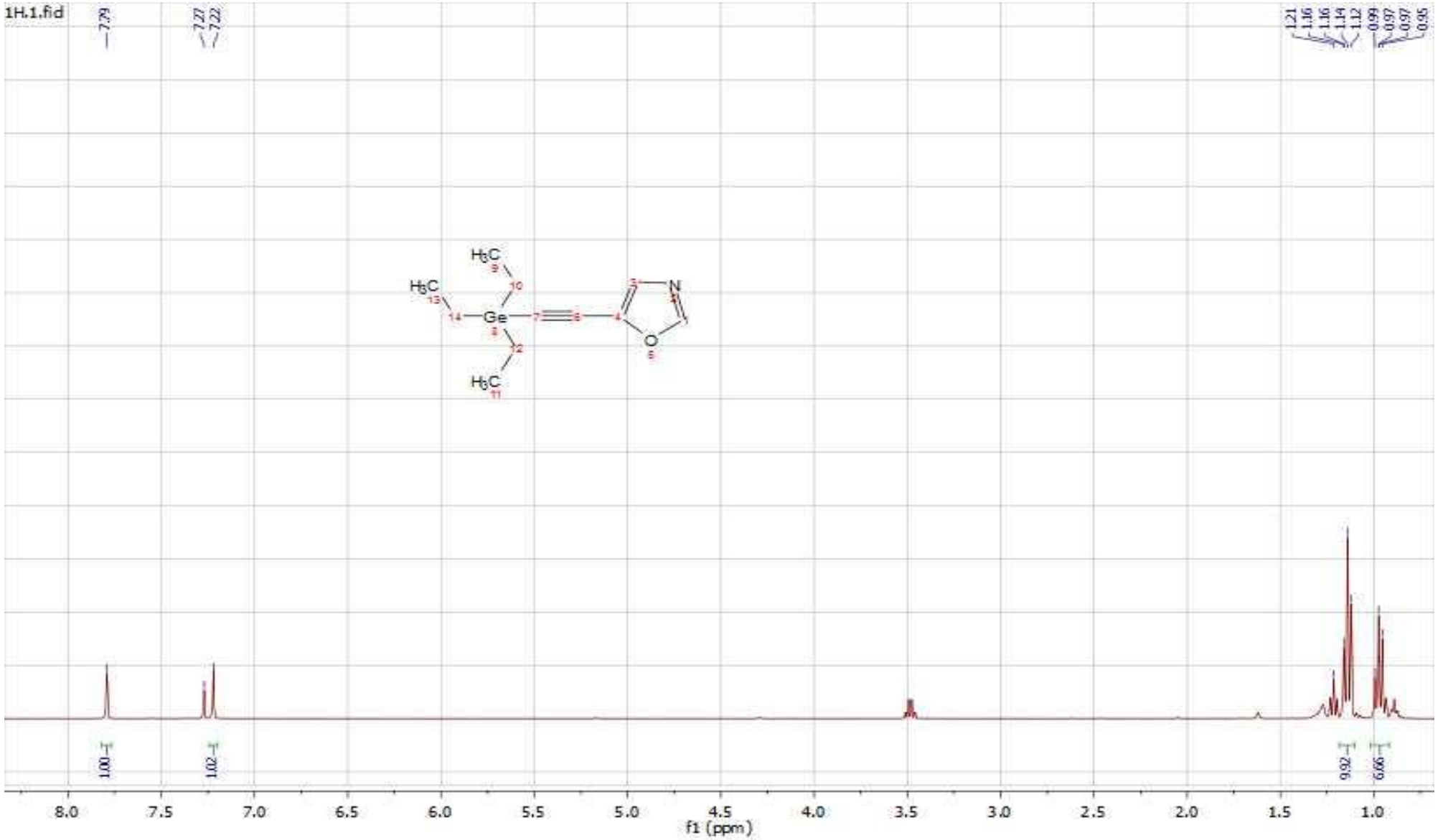

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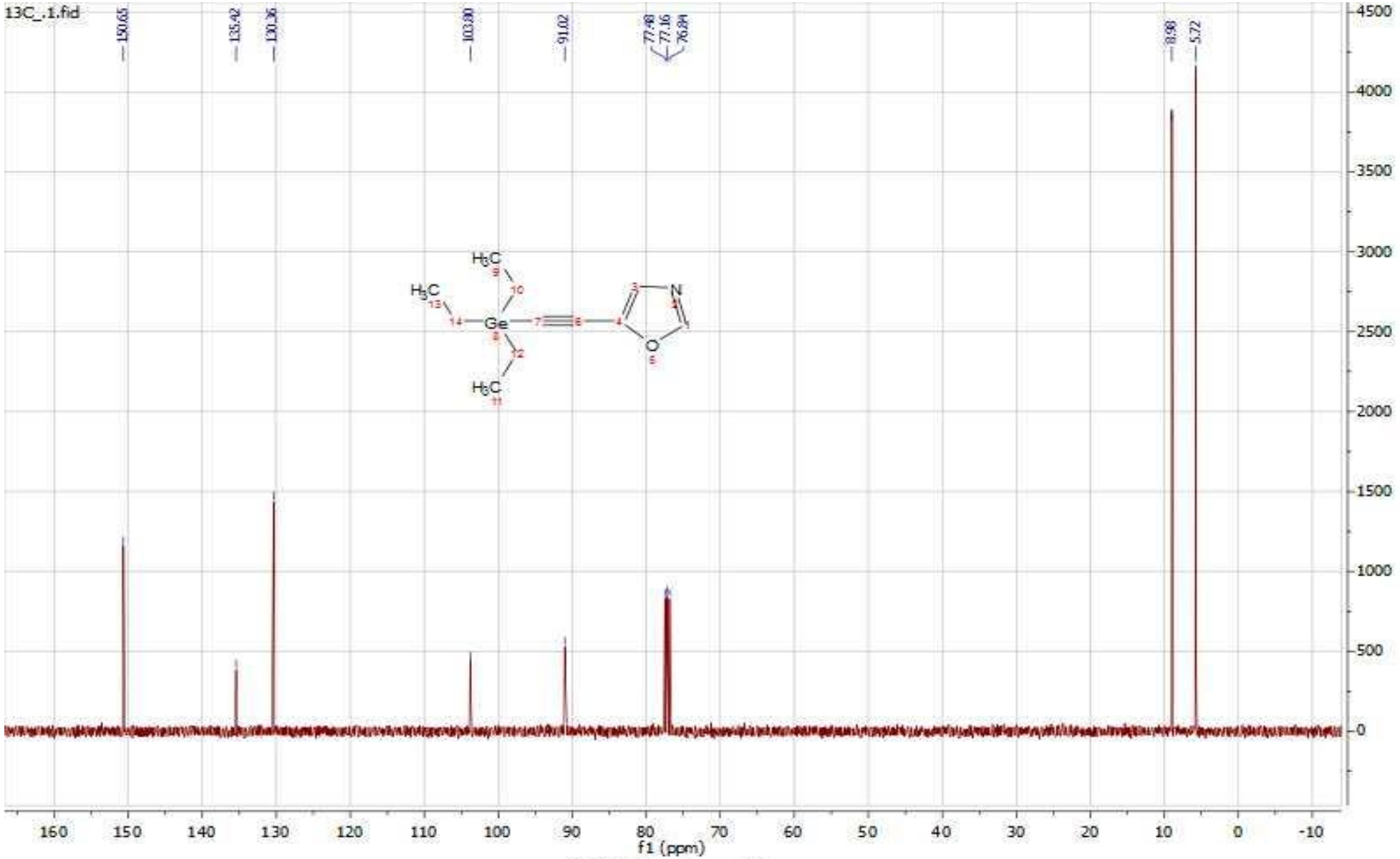

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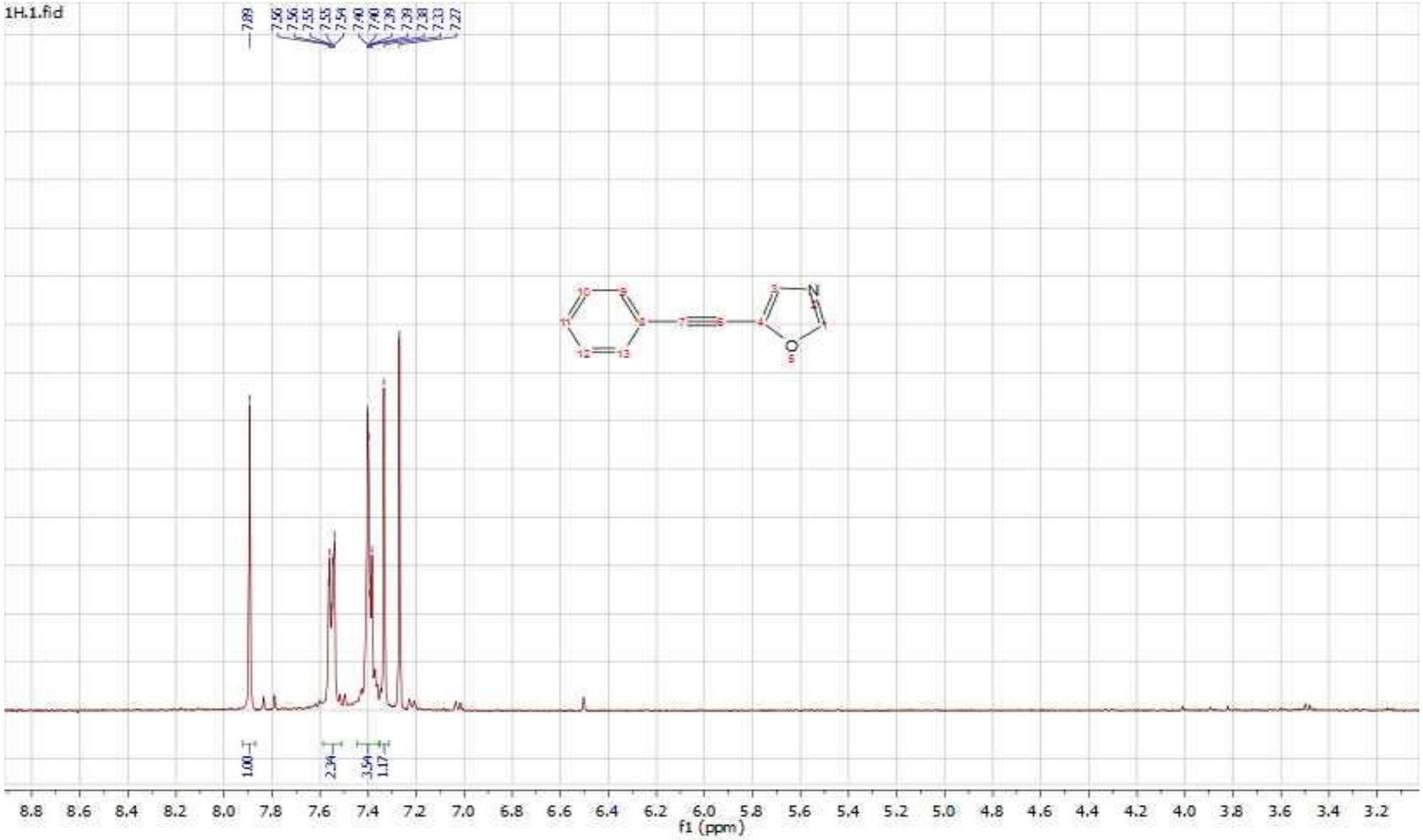

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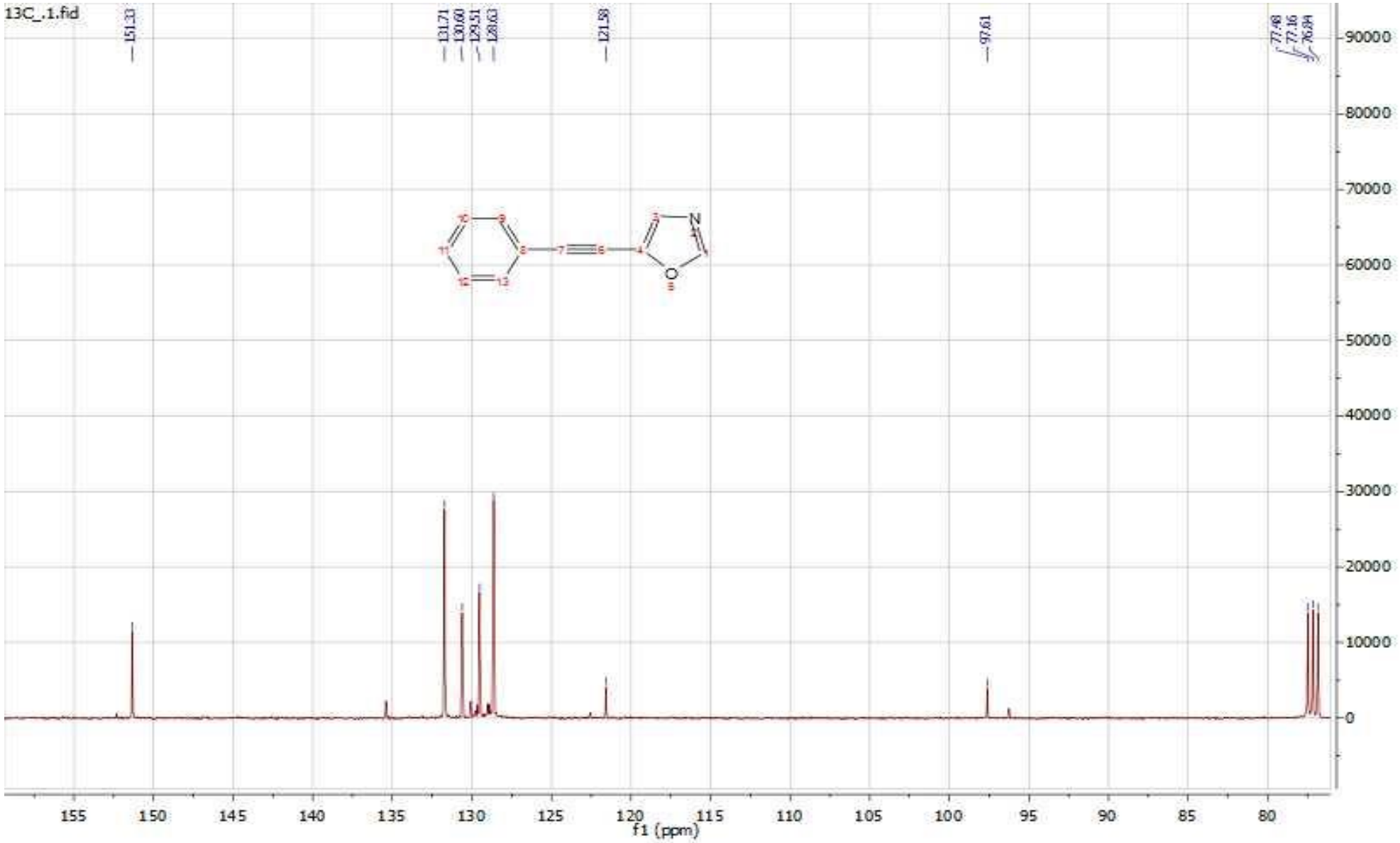

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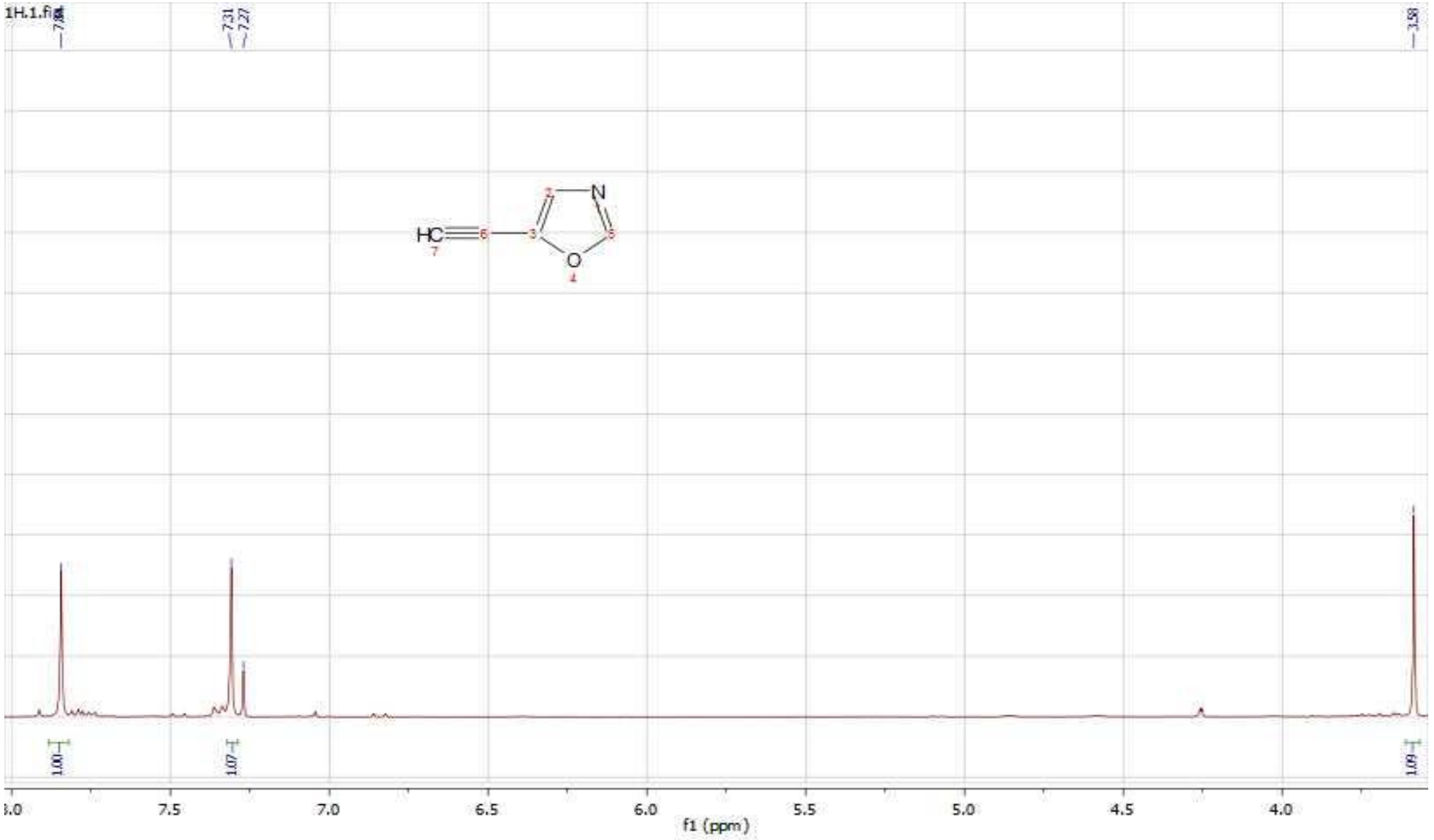
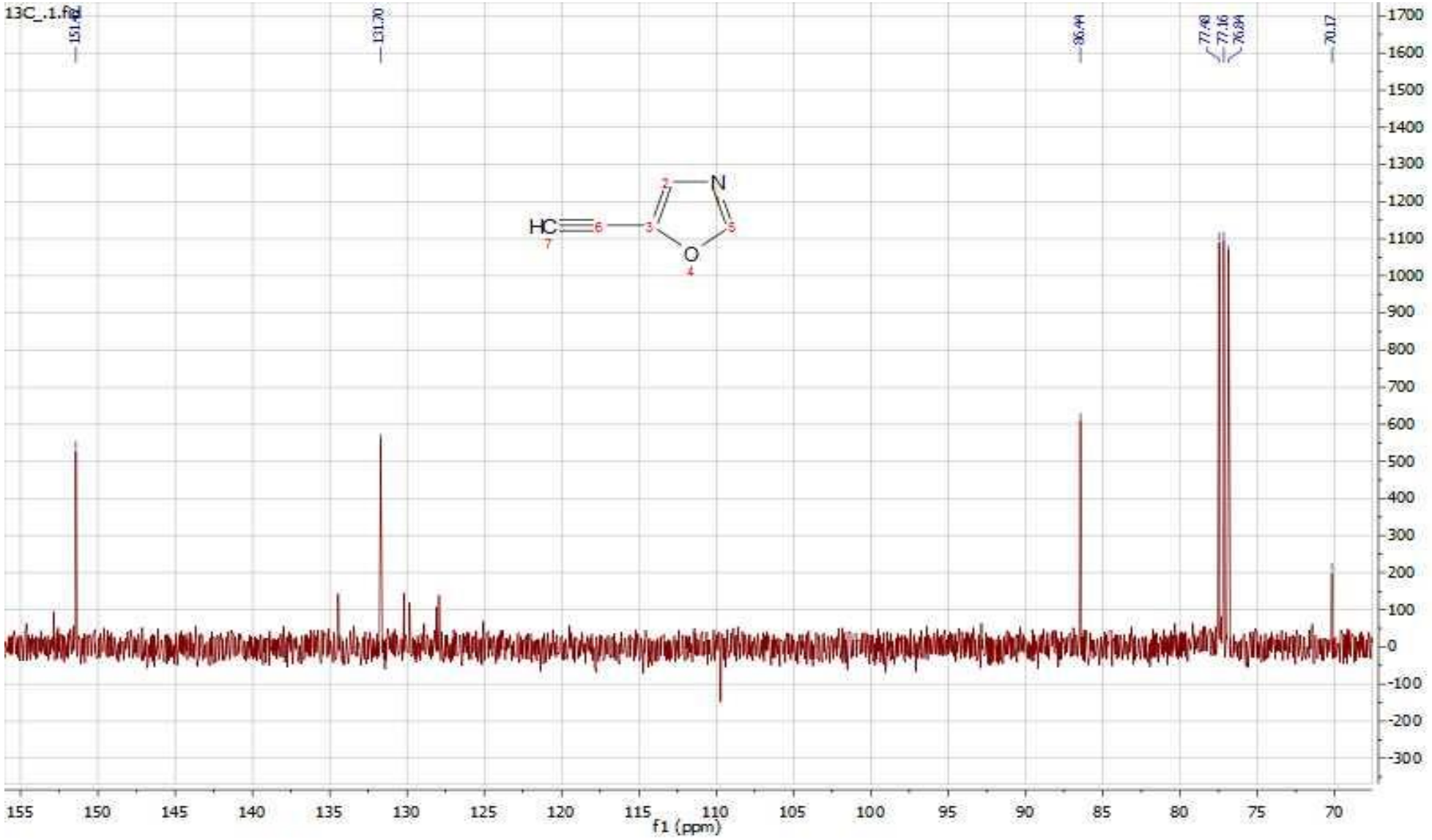


^{1}H NMR spectrum of 5



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