Polysaccharide-based superporous hydrogel embedded with copper nanoparticles: A green and versatile catalyst for the synthesis of 1,2,3-triazoles

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Contents

1. Thermal analysis

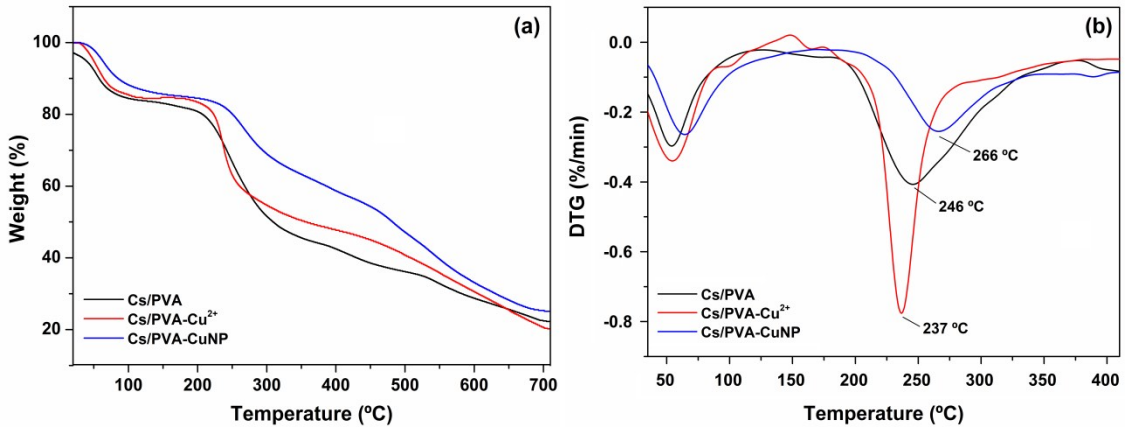


Figure S1. TGA (a) and DTG (b) curves recorded for Cs/PVA, Cs/PVA-Cu^{2+} and Cs/PVA-CuNP hydrogels.

2. Visual characterization

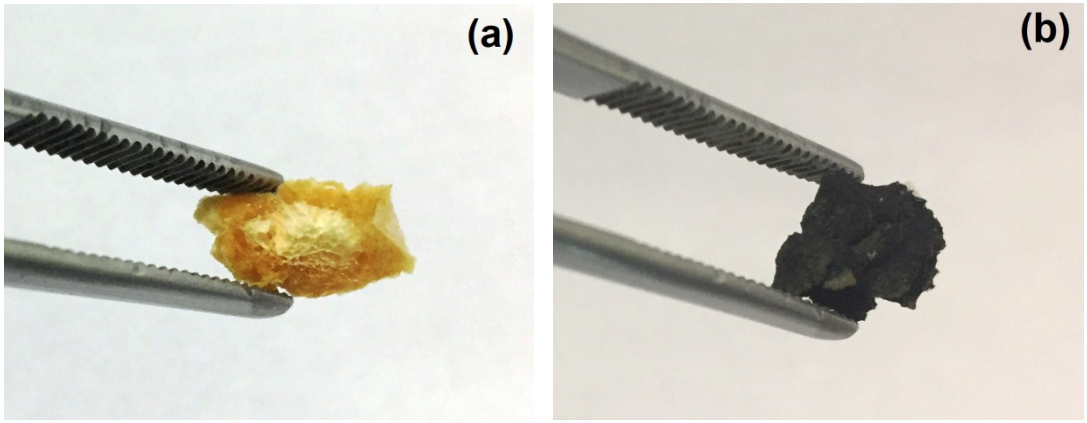


Figure S2. Photographic images of Cs/PVA (a) and Cs/PVA-CuNP hydrogels at dry state.

3. EDS analyses

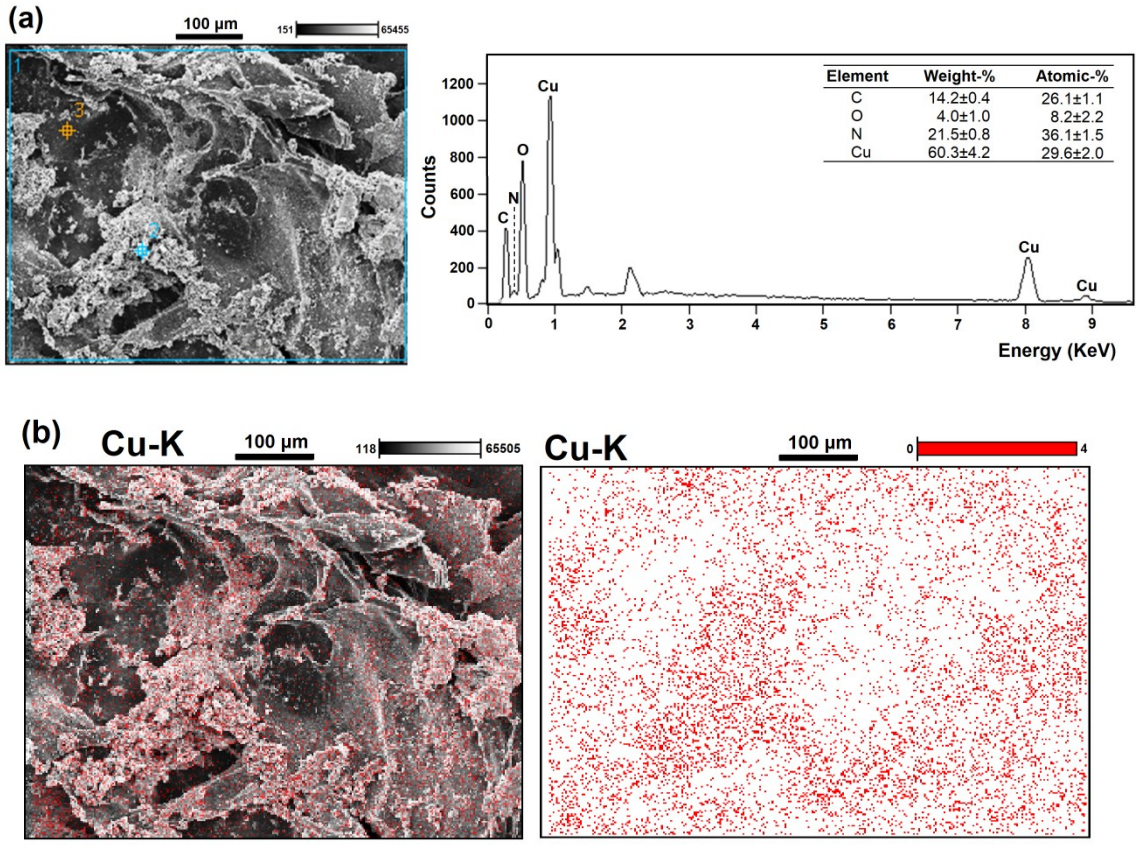


Figure S3. EDS spectrum (a) and EDS mapping analysis (b) recorded from the Cs/PVA-CuNP surface.

4. Swelling experiments at different pH and temperature conditions

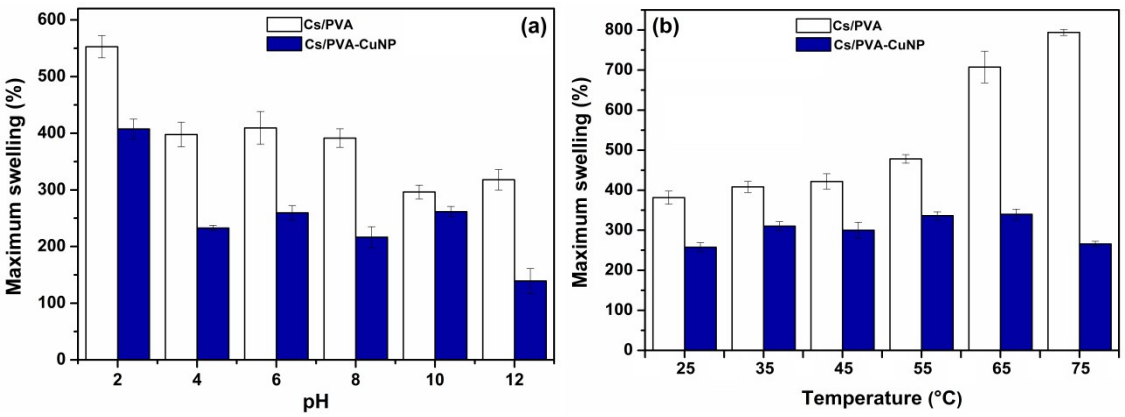
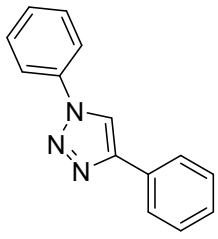


Figure S4. Maximum swelling of Cs/PVA and Cs/PVA-CuNP hydrogels calculated for samples immersed at different pH (a) and temperature conditions (b) for 24 h.

5. General experimental procedure for the synthesis of 1,4-disubstituted 1,2,3-triazoles

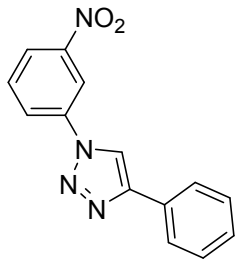
Aryl azides **1** (0.157 mmol), terminal alkynes **2** (0.157 mmol), Cs/PVA-CuNP hydrogel (10 mol-%, 1 mg of Cu per hydrogel sample) and a mixture of EtOH/H_2O (1:1) (1.5 mL) were added to a glass vial. Then, the heterogeneous reaction mixture was sonicated for 6 h at room temperature in an ultrasonic bath. After the total disappearance of starting materials, DCM (3 mL) was added and the reaction mixture was sonicated for additional 5 min. The reaction mixture was then separated by the Cs/PVA-CuNP using a Pasteur pipette. This procedure was then repeated for four times and the combined extracts were dried over $MgSO_4$ and concentrated under vacuum. The crude products obtained were subsequently purified by column chromatography on silica gel using a mixture of hexane/ethyl acetate as eluent to afford the desired products **3a-h**. All products were characterized by Nuclear Magnetic Resonance (NMR) spectroscopy in a Bruker Avance DPX 400 spectrometer at 400 MHz (^{1}H) and at 100 MHz (^{13}C). All NMR spectra were acquired using $CDCl_3$ or DMSO-d_6 as deuterated solvents and tetramethylsilane (TMS) was used as internal standard. The recovered Cs/PVA-CuNP sample was dried under vacuum and could be reused directly in subsequent reactions. The data of obtained compounds **3a-h** are in agreement with the already published data.[1,2]

6. Spectral data of the products

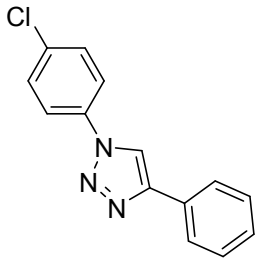


1,4-diphenyl-1*H*-1,2,3-triazole[1] (3a). Yield: 0.032 g (92%); white solid; m.p = 181-183 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 9.30 (s, 1H), 7.96 (d, *J*=8.0 Hz, 4H), 7.64 (d, *J*=7.8 Hz, 2H), 7.54-7.48 (m, 3H), 7.39 (t, *J*=7.4 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ = 147.32, 136.65, 130.26, 129.93, 129.00, 128.72, 128.24, 125.35, 120.01, 119.62.

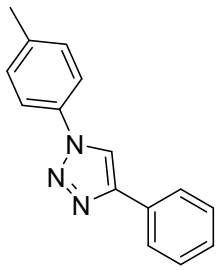
[1] Kaboudin, B.; Mostafalu, R.; Yokomatsu, T. *Green Chem*. **2013**, *15*, 2266-2274.
[2] Chen, Z.; Yan, Q.; Liu, Z.; Zhang, Y. *Chem. Eur. J.* **2014**, *20*, 17635-17639.



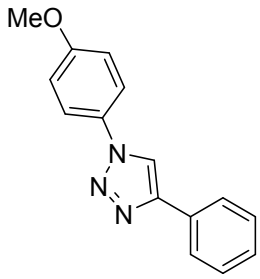
4-(3-nitrophenyl)-1-phenyl-1*H*-1,2,3-triazole[2] (3b). Yield: 0.035 g (84%); brown yellow solid; m.p = 93-94 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 9.54 (s, 1H), 8.78 (t, J = 21 Hz, 1H), 8.45 (ddd, J = 8.1, 2.1, 0.8 Hz, 1H), 8.34 (ddd, J = 8.1, 2.1, 0.8 Hz, 1H)., 7.97-7.93 (m, 3H), 7.51 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ = 148.60, 147.72, 137.24, 131.66, 129.92, 129.11, 128.52, 125.93, 125.43, 123.16, 120.06, 114.60.



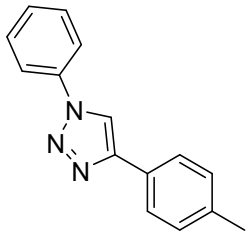
1-(4-chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole[1] (3c). Yield: 0.026 g (65%); light yellow solid; m.p = 222-224 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 9.32 (s, 1H), 8.00 (d, J=8.8 Hz, 2H), 7.94 (d, J=7.8 Hz, 2H), 7.72 (d, J=8.8 Hz, 2H), 7.51 (t, J=7.6 Hz, 2H), 7.39 (t, J=7.4 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ = 147.53, 135.49, 133.05, 130.13, 130.00, 129.11, 128.43, 125.42, 121.75, 119.77.



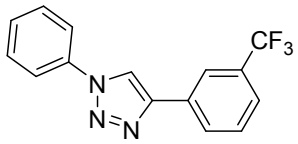
4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole[1] (3d). Yield: 0.032 g (86%); light yellow solid; m.p = 169-171 °C;^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.06 (s, 1H), 7.81 (d, J=7.2 Hz, 2H), 7.57 (d, J=8.4 Hz, 2H), 7.35 (t, J=7.5 Hz, 2H), 7.28-7.21 (m, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 148.33, 138.96, 134.85, 130.44, 130.34, 128.98, 128.43, 125.92, 120.49, 117.75, 21.19.



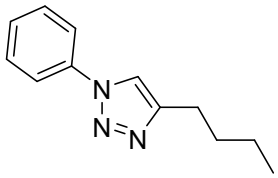
1-(4-methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole[1] (3e). Yield: 0.034 g (85%); light yellow solid; m.p = 162-164 °C;^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.02 (s, 1H), 7.80 (d, *J*=7.3 Hz, 2H), 7.57 (d, *J*=8.8 Hz, 2H), 7.34 (t, *J*=7.5 Hz, 2H),), 7.25 (t, *J*=7.3 Hz, 1H), 6.91 (t, *J*=8.8 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 159.89, 148.26, 130.57, 130.46, 128.97, 128.39, 125.88, 122.20, 117.96, 114.85, 55.70.



1-phenyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole[1] (3f). Yield: 0.030 g (82%);light yellow solid; m.p = 152-154 °C.^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.05 (s, 1H), 7.71-7.66 (m, 4H), 7.42 (t, *J*=7.7 Hz, 2H), 7.33 (t, *J*=7.4 Hz, 1H), 7.15 (t, *J*=7.7 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 148.54, 138.36, 137.16, 129.81, 129.67, 128.74, 127.50, 125.83, 120.52, 117.36, 21.39.



1-phenyl-4-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole[2] (3g). Yield: 0.025 g (54%); yellow solid; m.p. = 113-115 °C;. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.19 (s, 1H), 8.05 (s, 1H), 7.98 (d, *J*=7.3, 1H), 7.67 (d, *J*=7.7 Hz, 2H), 7.50-7.32 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 147.11, 136.90, 131.39 (q, *J*=32 Hz), 131.18, 129.91, 129.53, 129.07 (d, *J*=2.8 Hz), 125.02 (q, *J*=3.7 Hz), 124.11 (q, *J*=272 Hz), 122.65 (q, *J*=3.7 Hz), 120.58, 118.32.



4-butyl-1-phenyl-1*H*-1,2,3-triazole[2] (3h). Yield: 0.017 g (55%); White solid; m.p = 58-59 °C ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.65 (m, 3H), 7.41 (t, *J*=7.8, 2H), 7.32 (t, *J*= 7.4 Hz, 1H), 2.71 (t, *J*=7.7 Hz, 2H), 1.64 (quint., *J*=7.7 Hz, 2H), 1.34 (sext., *J*=7.4 Hz, 2H), 0.87 (t, *J*=7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 149.22, 137.34, 129.72, 128.45, 120.43, 118.88, 31.57, 25.41, 22.38, 13.89.

7. Selected Spectra

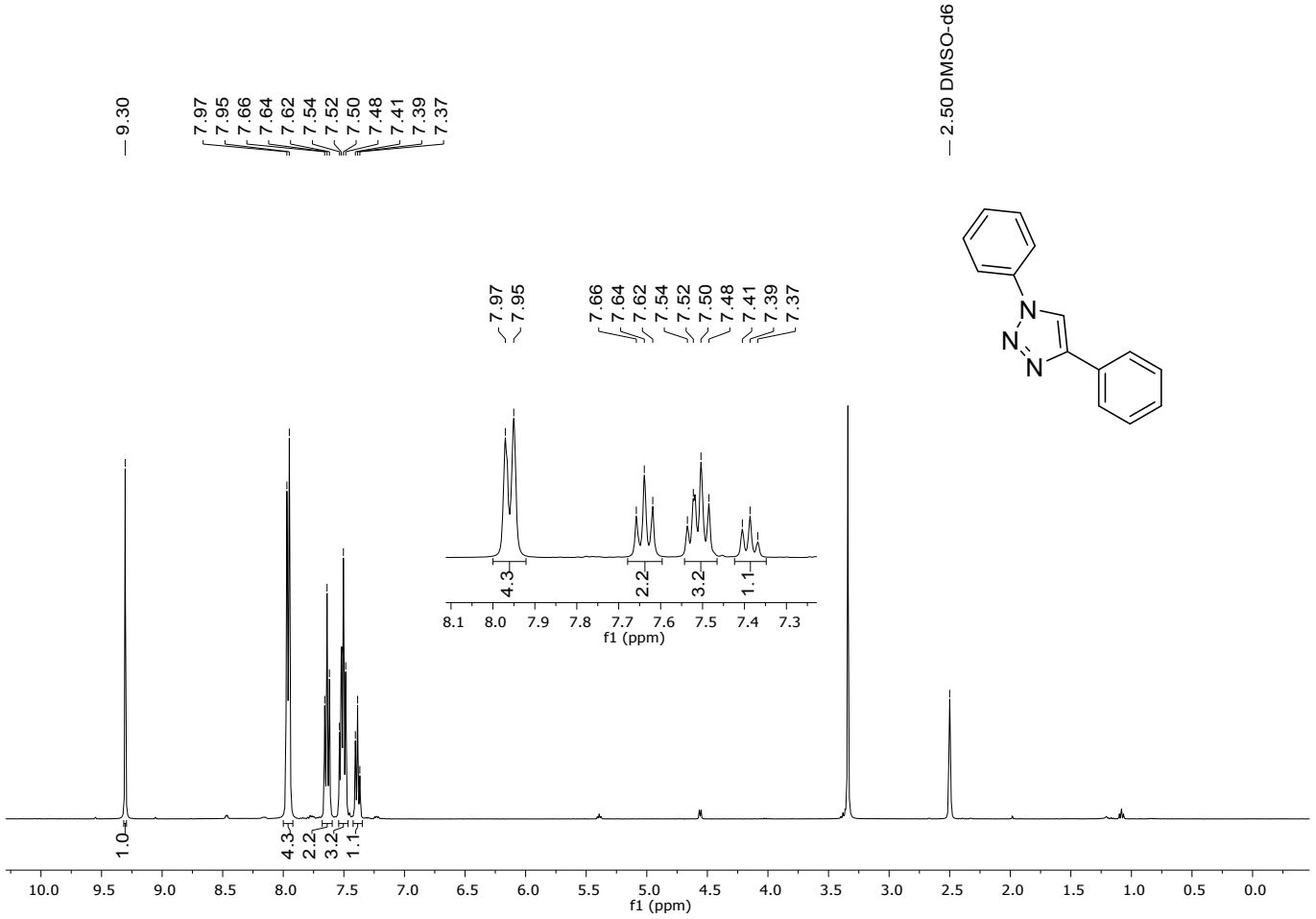


Figure 1. ^{1}H NMR (400 MHz) spectrum for compound **3a** in DMSO-d_6.

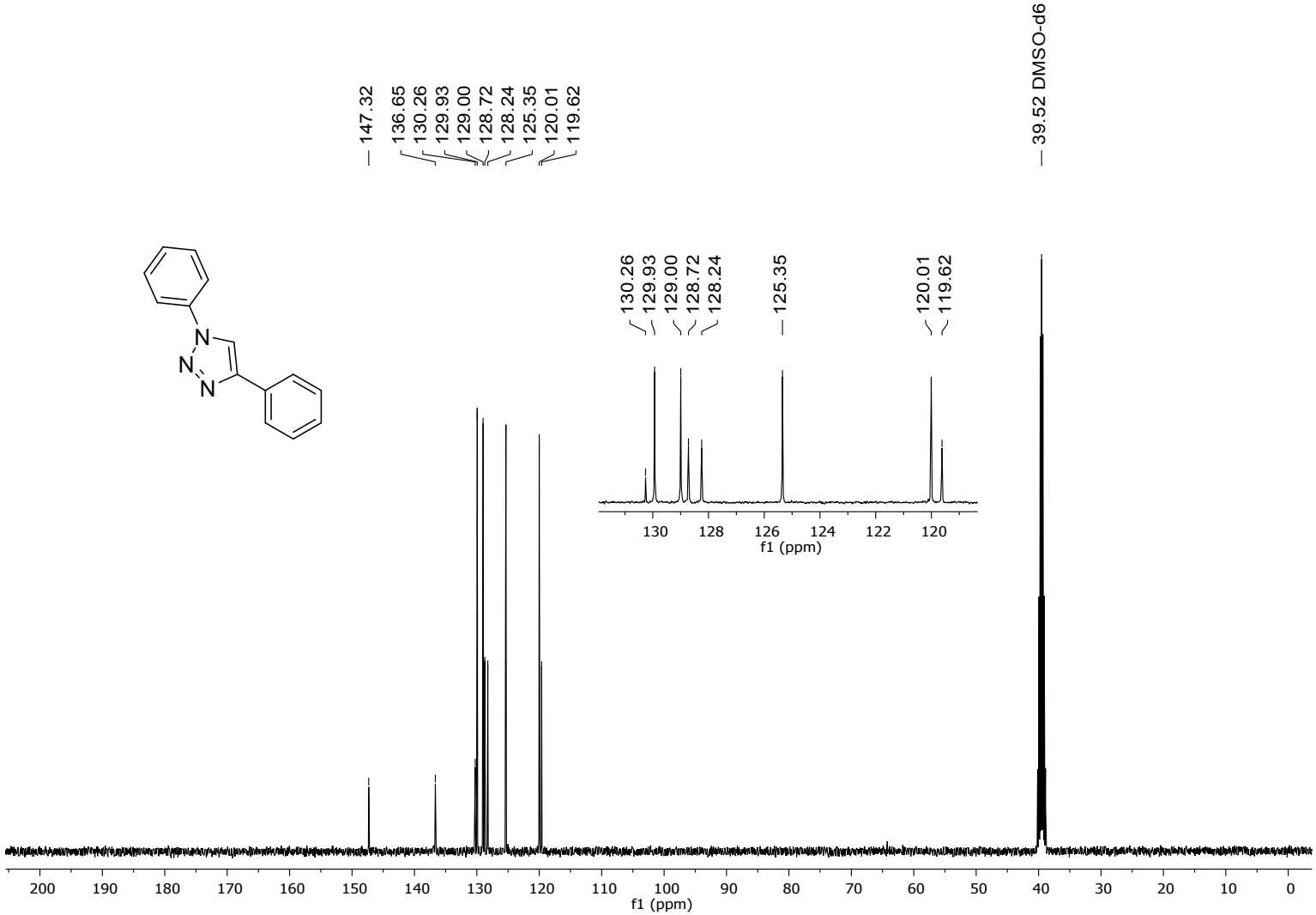


Figure 2. ^{13}C NMR (100 MHz) spectrum for compound **3a** in DMSO-d_6.

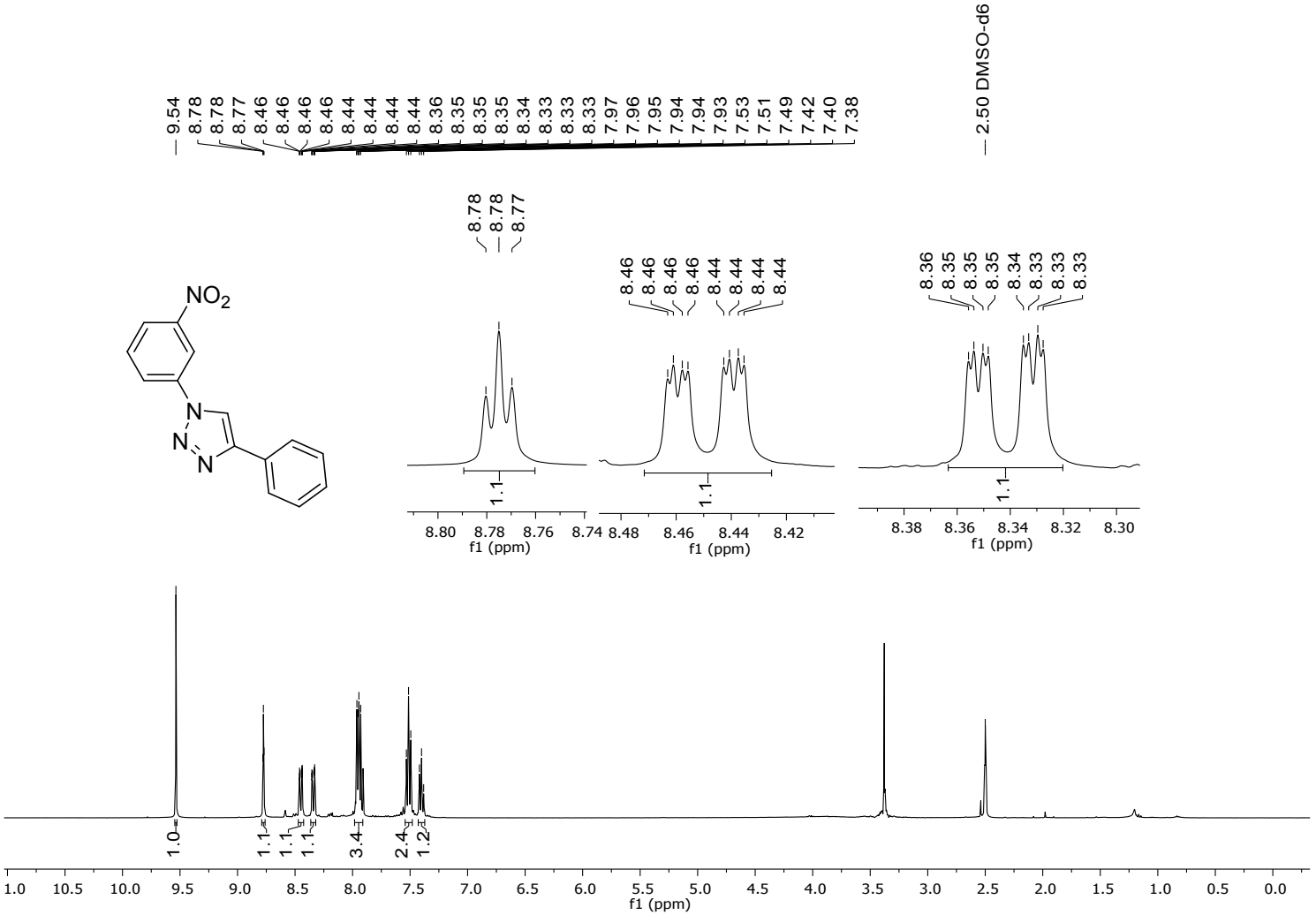


Figure 3. ^{1}H NMR (400 MHz) spectrum for compound **3b** in DMSO-d_6.

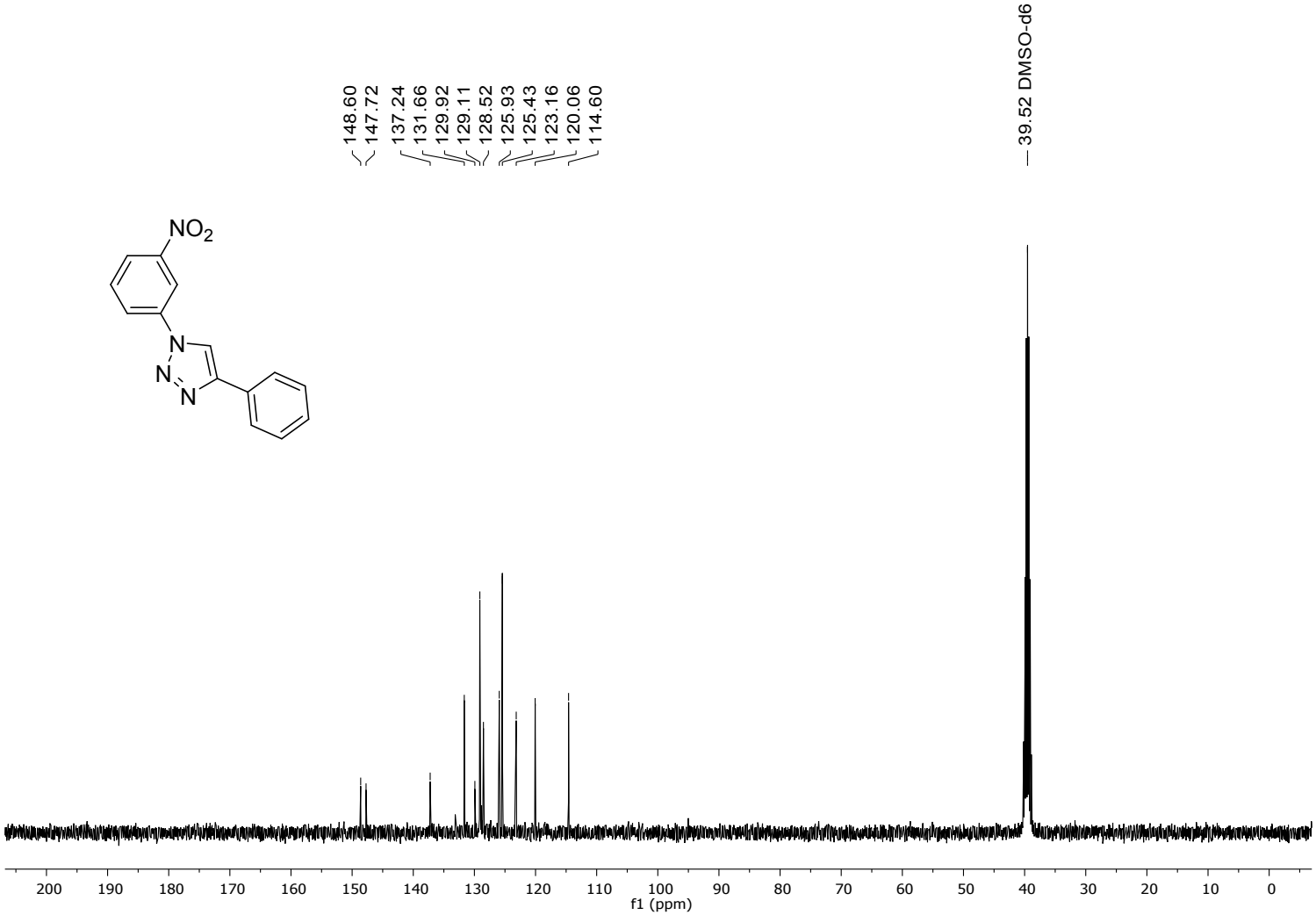


Figure 4. ^{13}C NMR (100 MHz) spectrum for compound **3b** in DMSO-d_6.

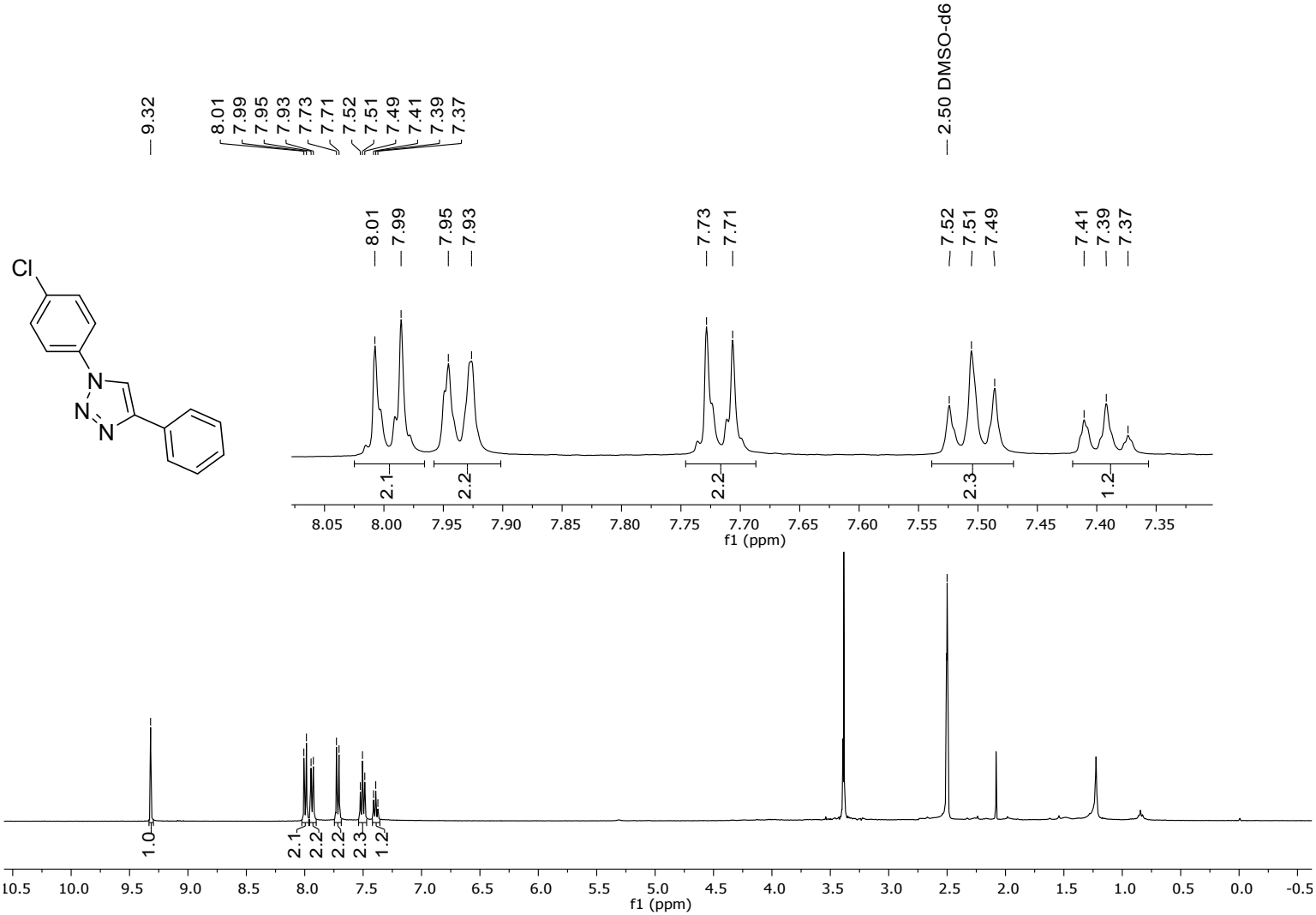


Figure 5. ^{1}H NMR (400 MHz) spectrum for compound **3c** in DMSO-d_6.

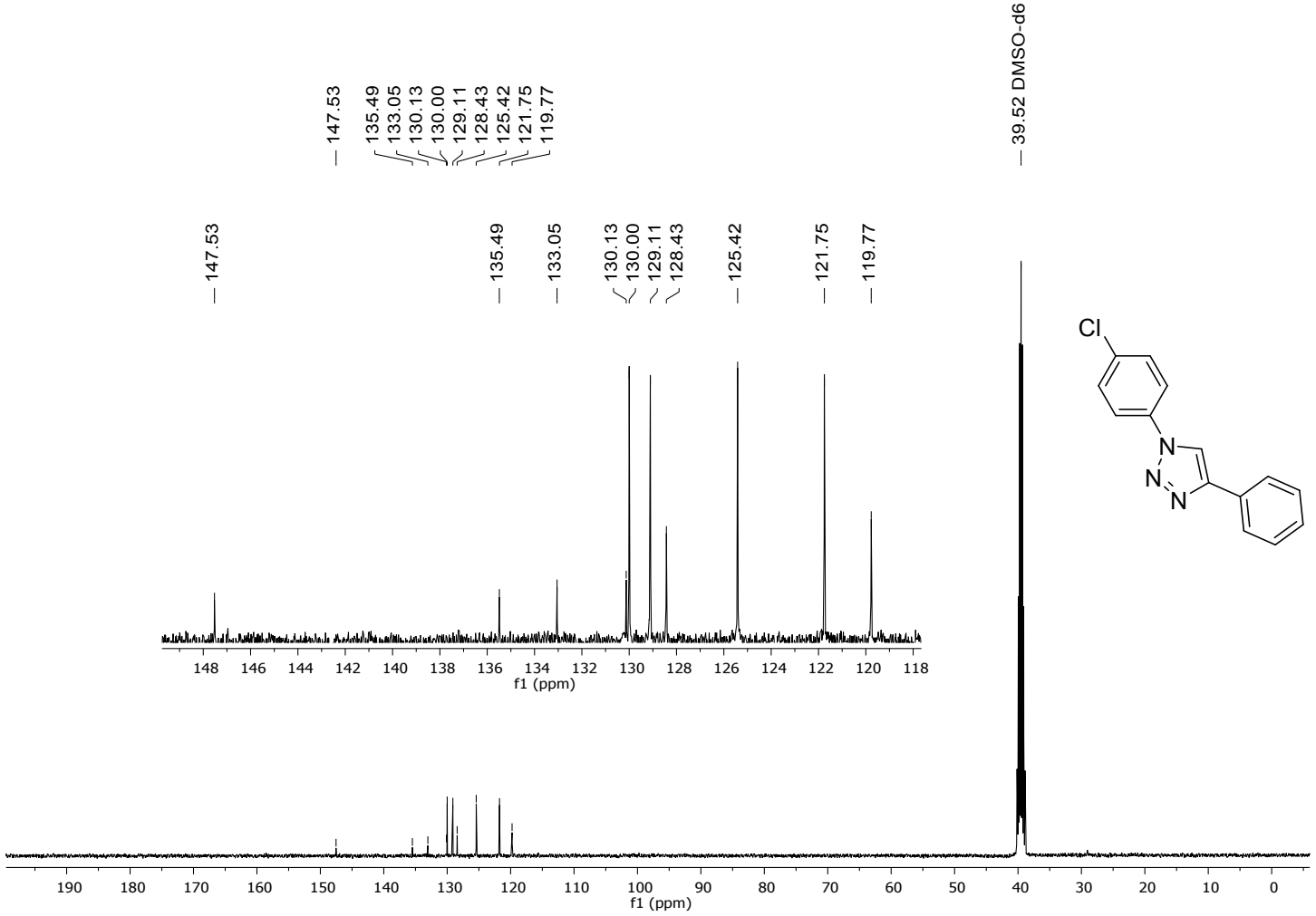


Figure 6. ^{13}C NMR (100 MHz) spectrum for compound **3c** in DMSO-d_6.

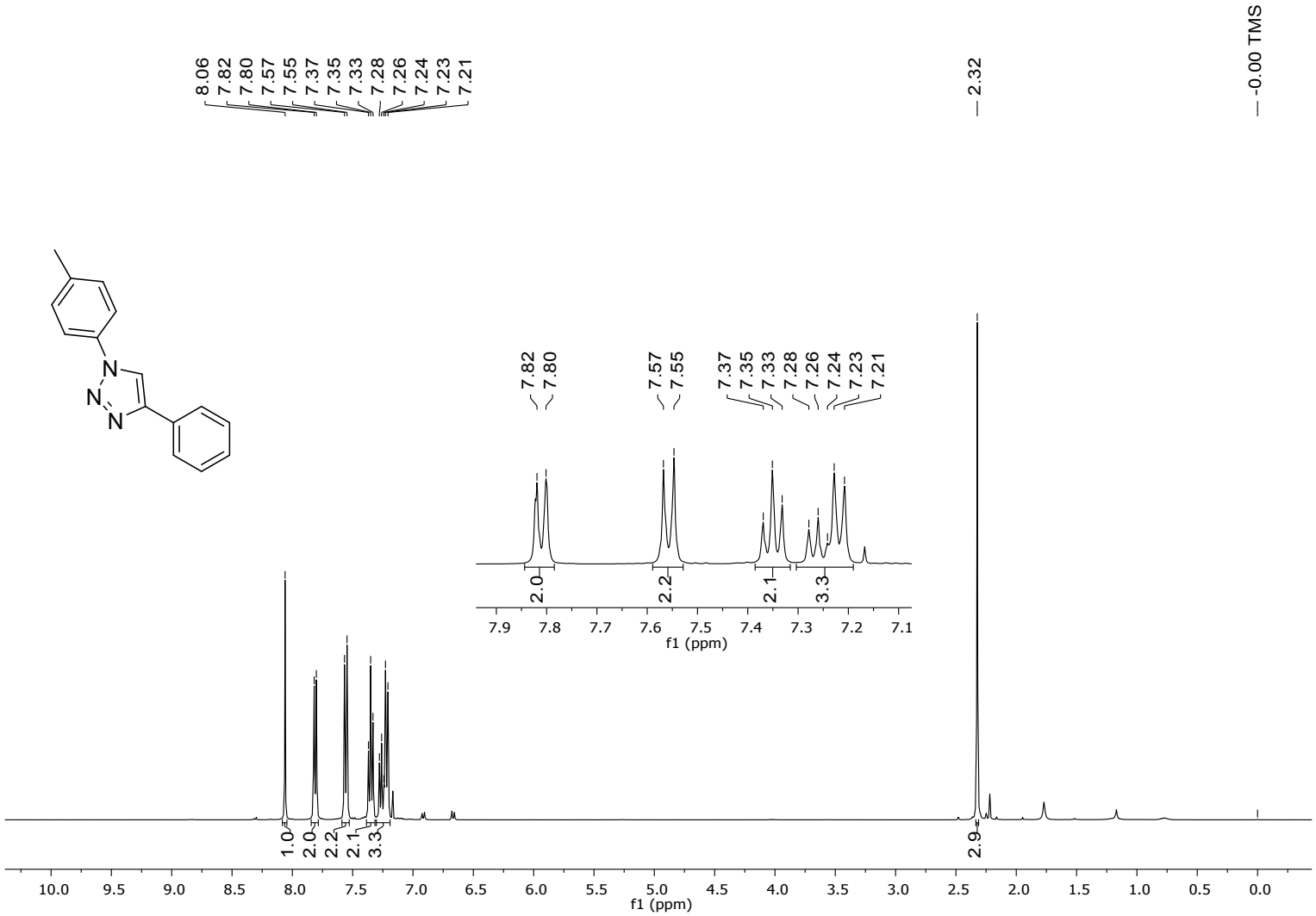


Figure 7. ^{1}H NMR (400 MHz) spectrum for compound **3d** in $CDCl_3$.

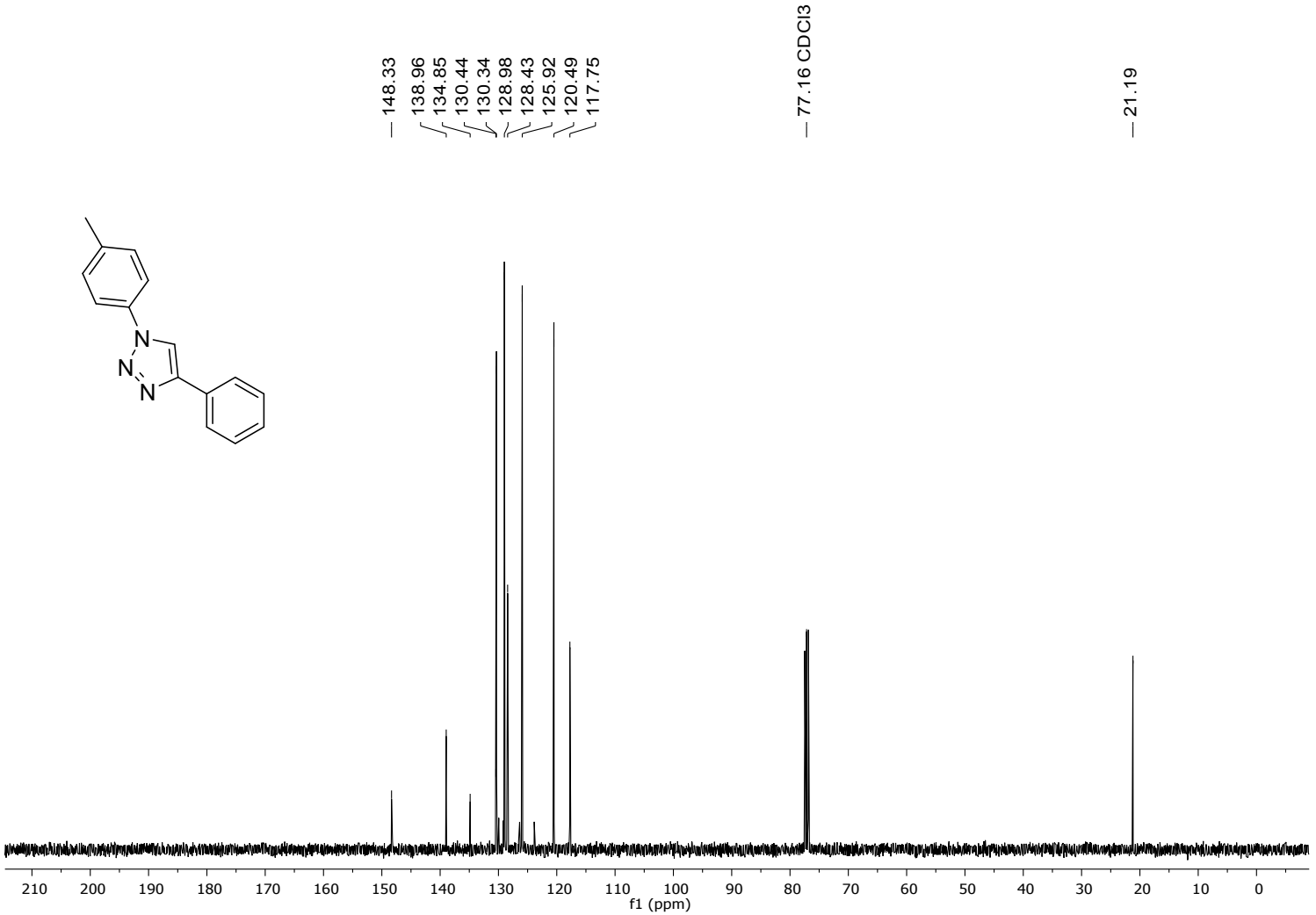


Figure 8. ^{13}C NMR (100 MHz) spectrum for compound **3d** in $CDCl_3$.

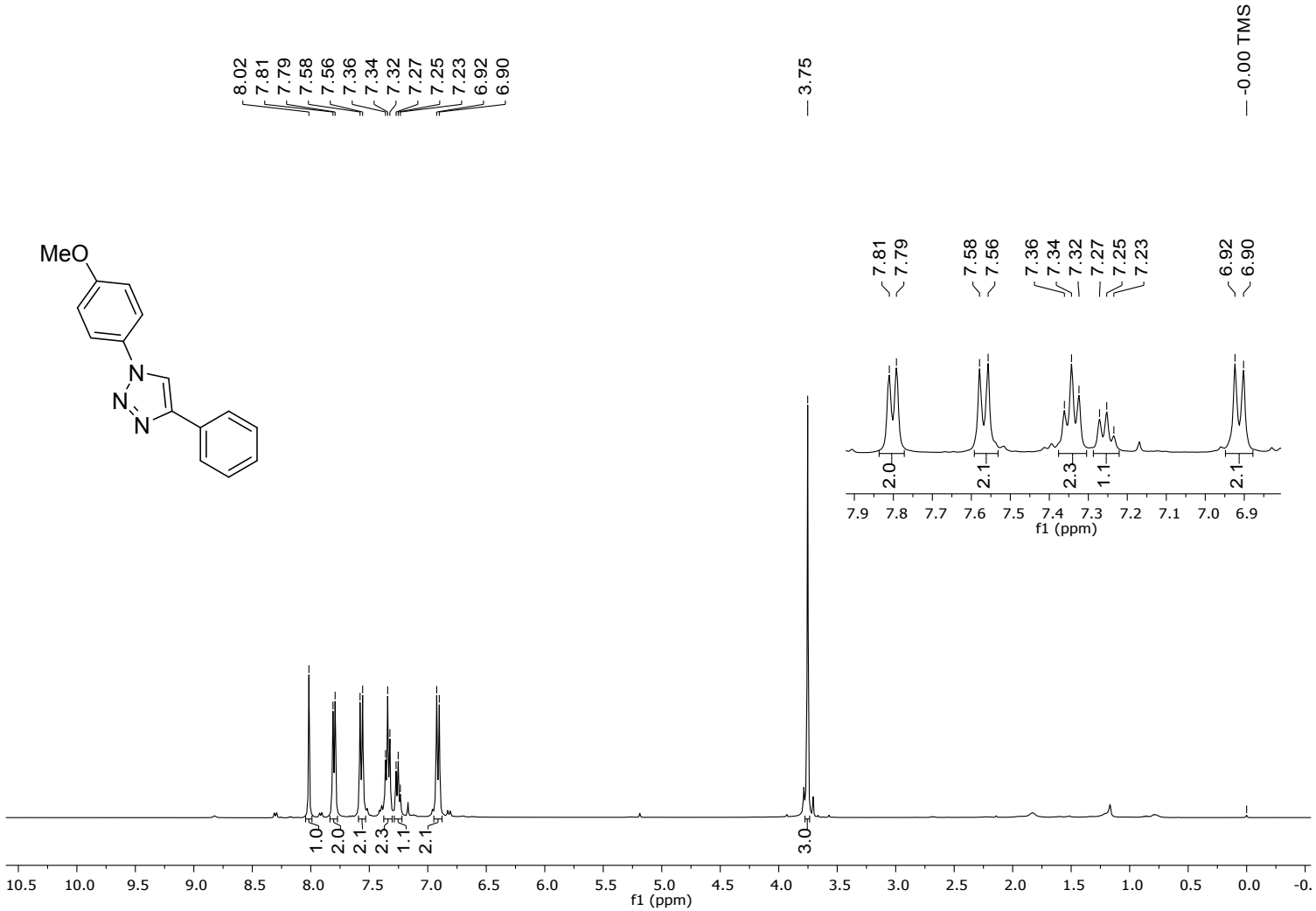


Figure 9. ^{1}H NMR (400 MHz) spectrum for compound **3e** in $CDCl_3$.

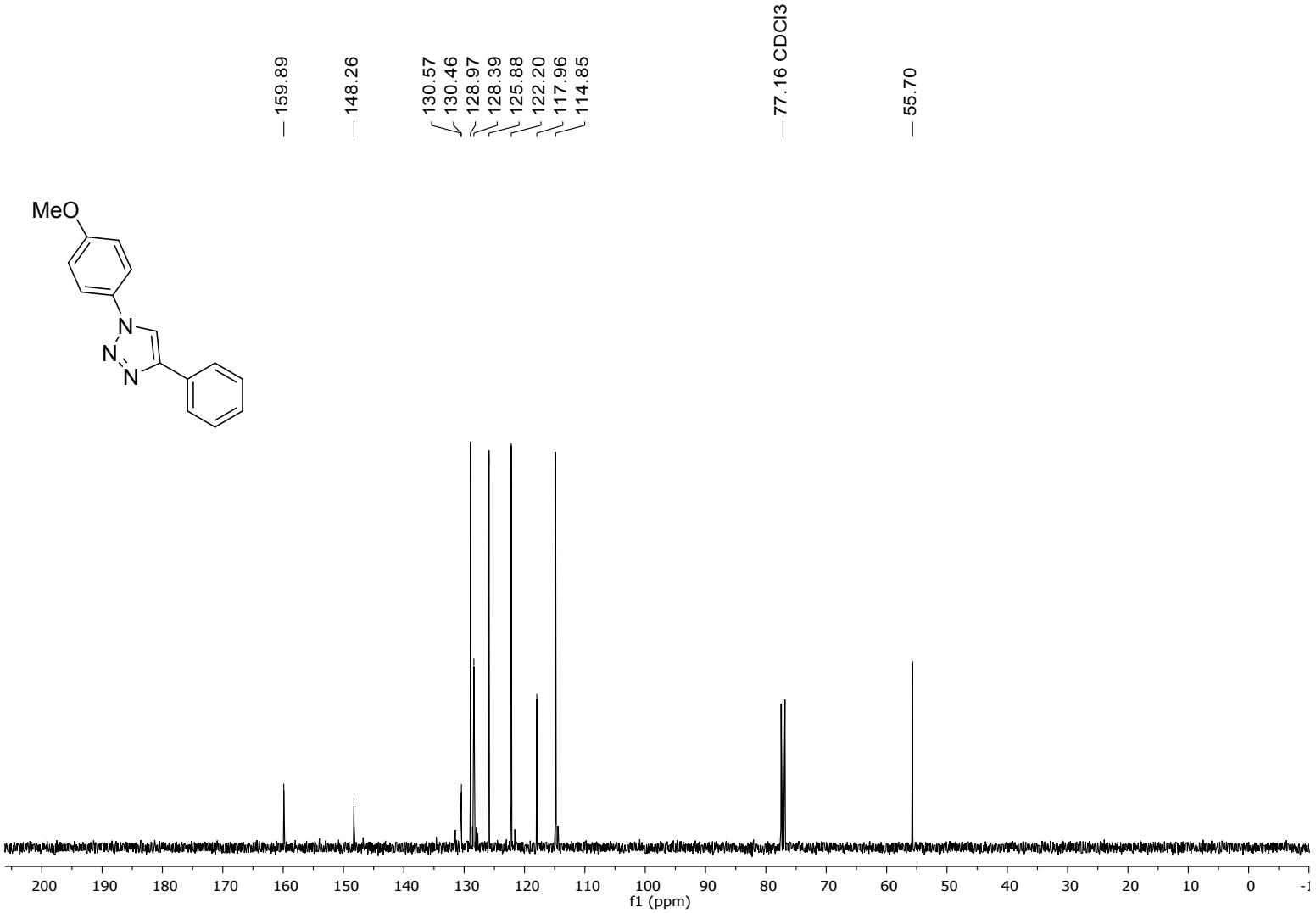


Figure 10. ^{13}C NMR (100 MHz) spectrum for compound **3e** in $CDCl_3$.

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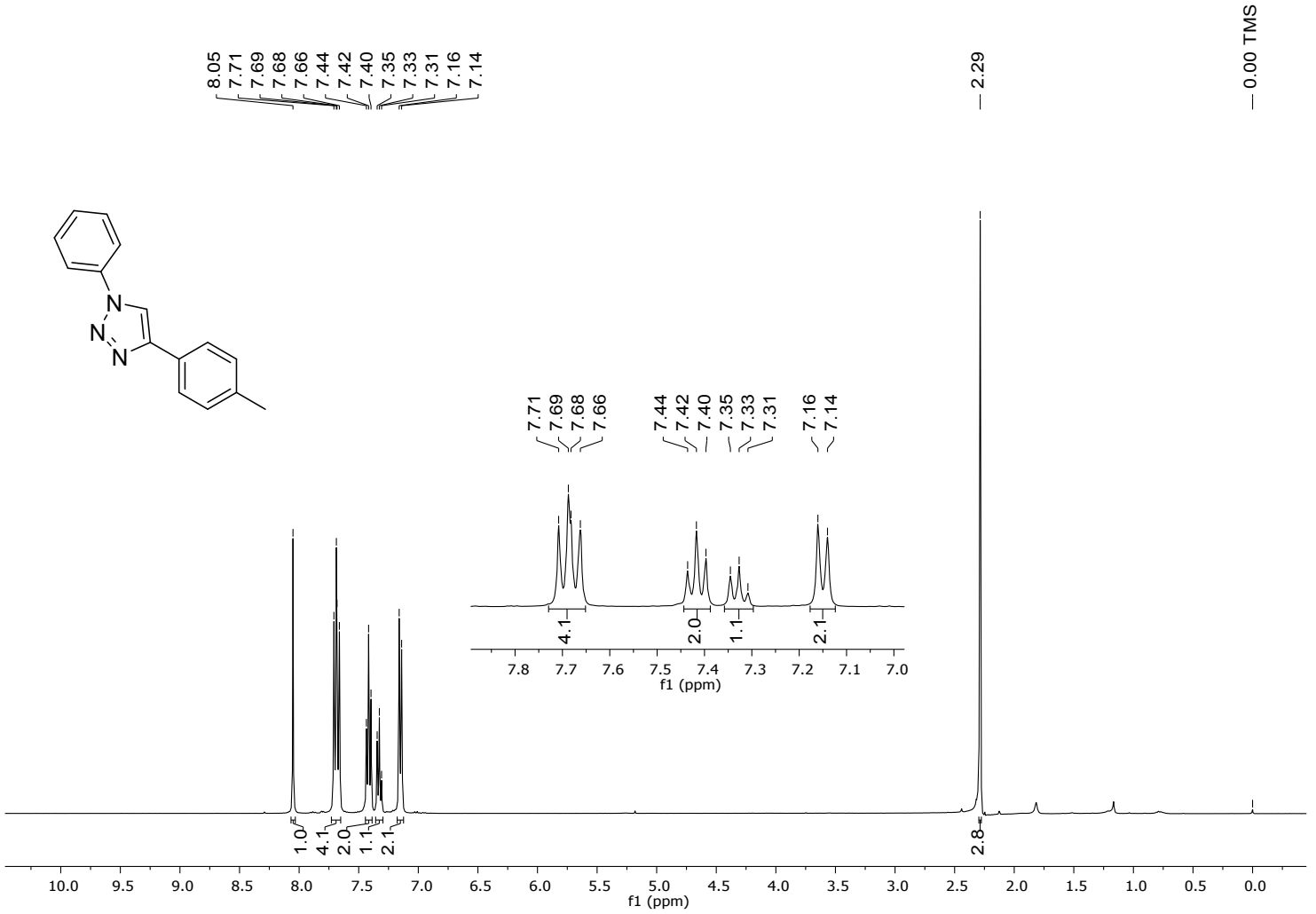

Figure 11. ^{1}H NMR (400 MHz) spectrum for compound **3f** in $CDCl_3$.

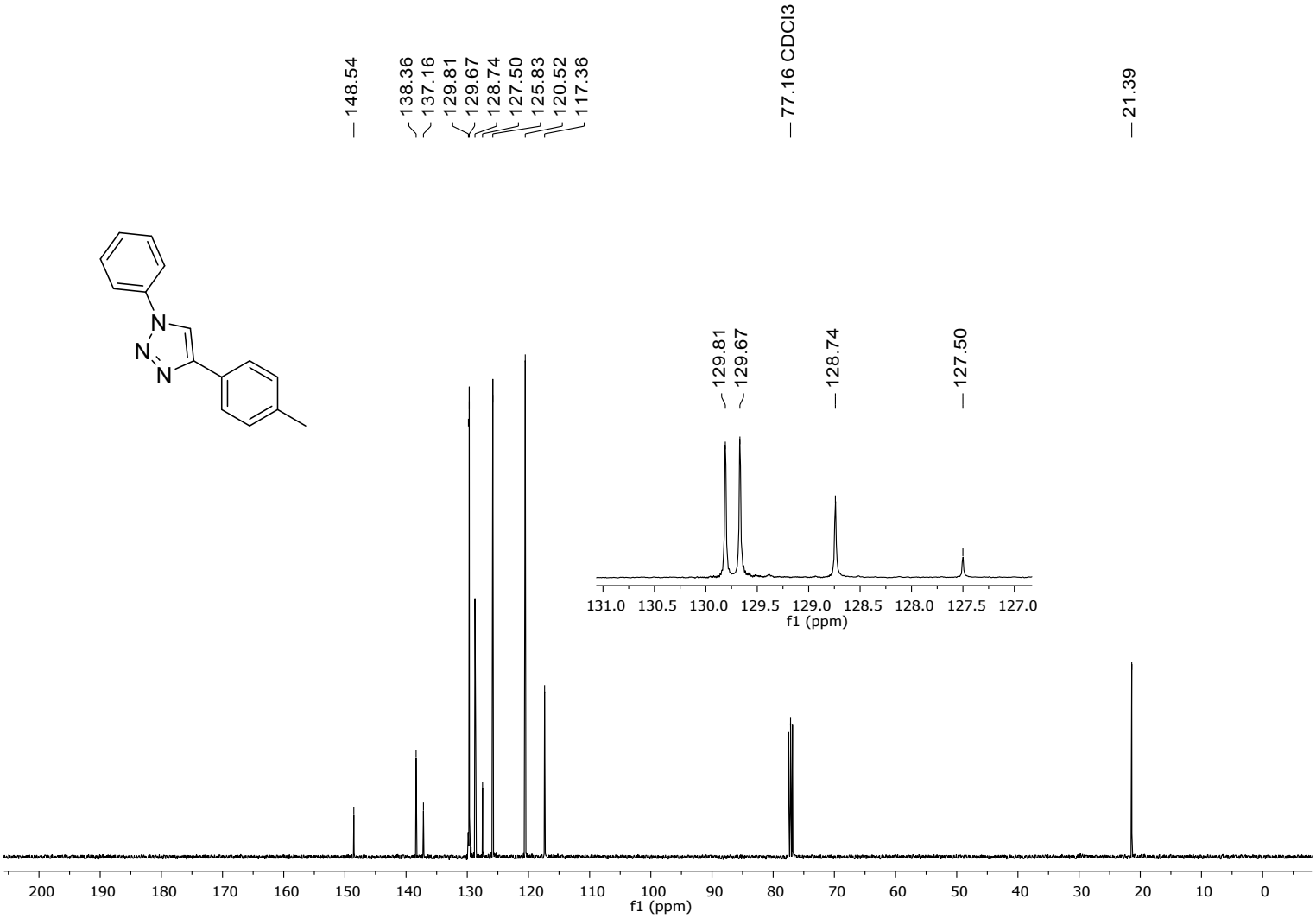

Figure 12. ^{13}C NMR (100 MHz) spectrum for compound **3f** in $CDCl_3$.

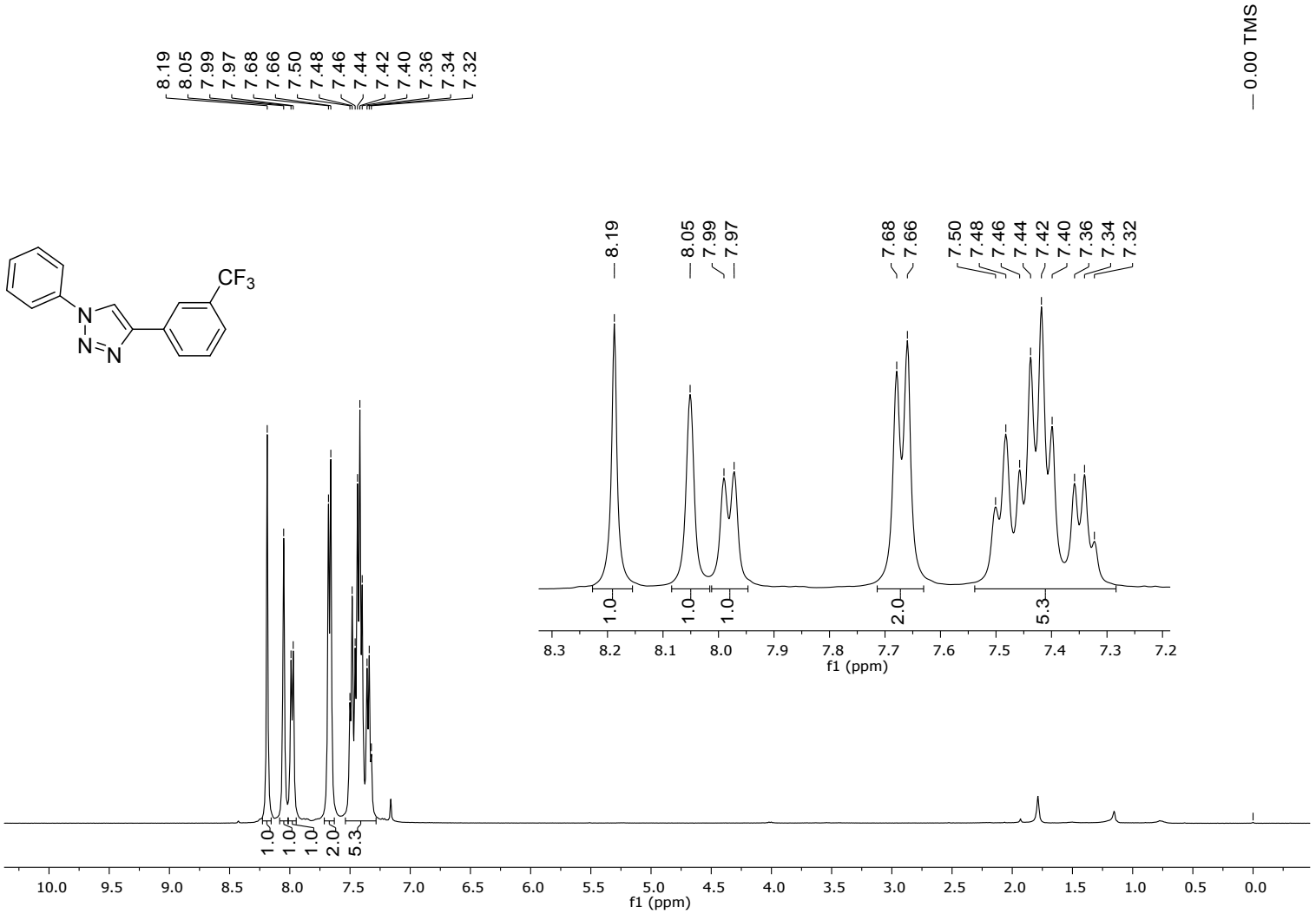

Figure 13. ^{1}H NMR (400 MHz) spectrum for compound **3g** in $CDCl_3$.

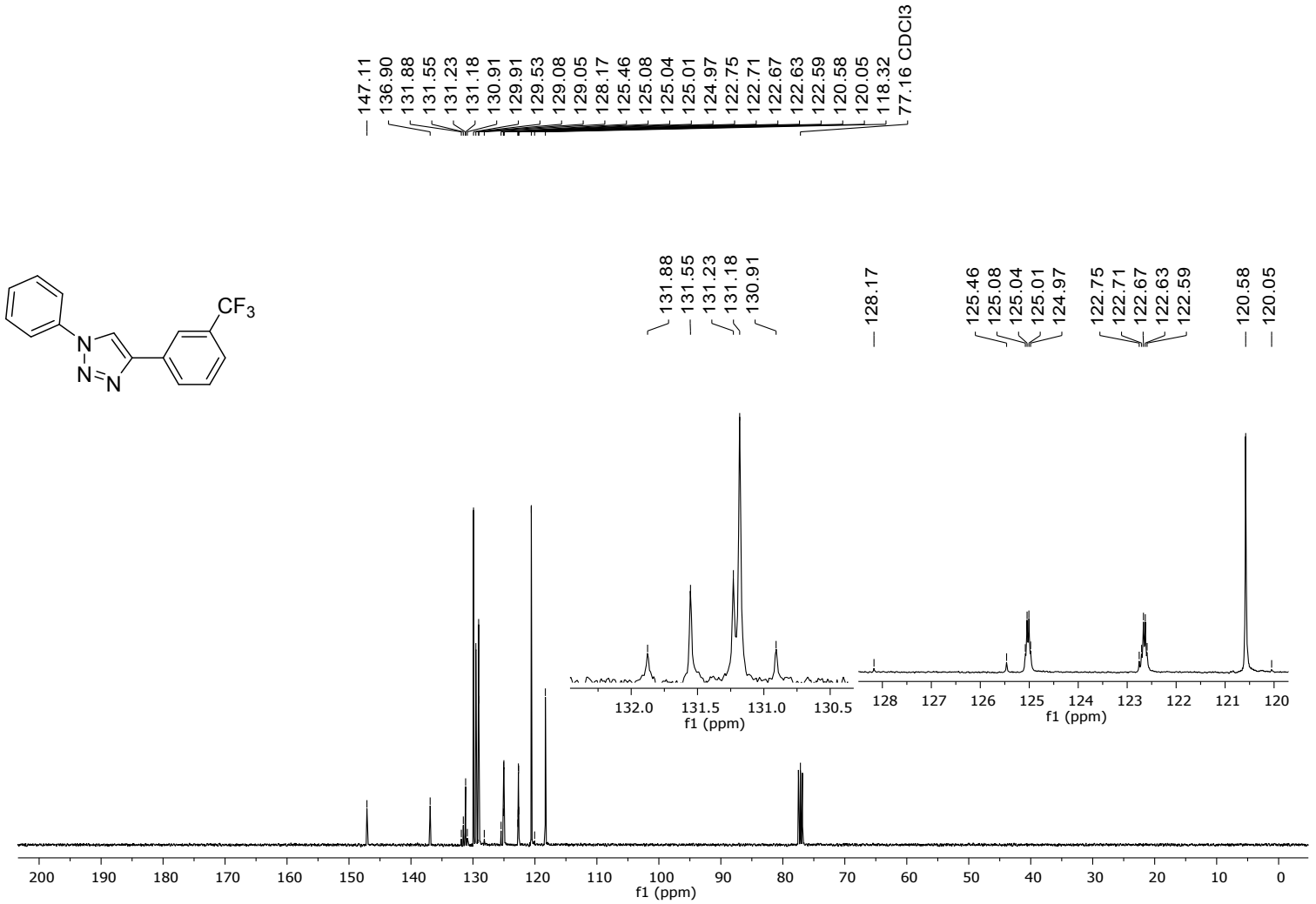

Figure 14. ^{13}C NMR (100 MHz) spectrum for compound **3g** in $CDCl_3$.

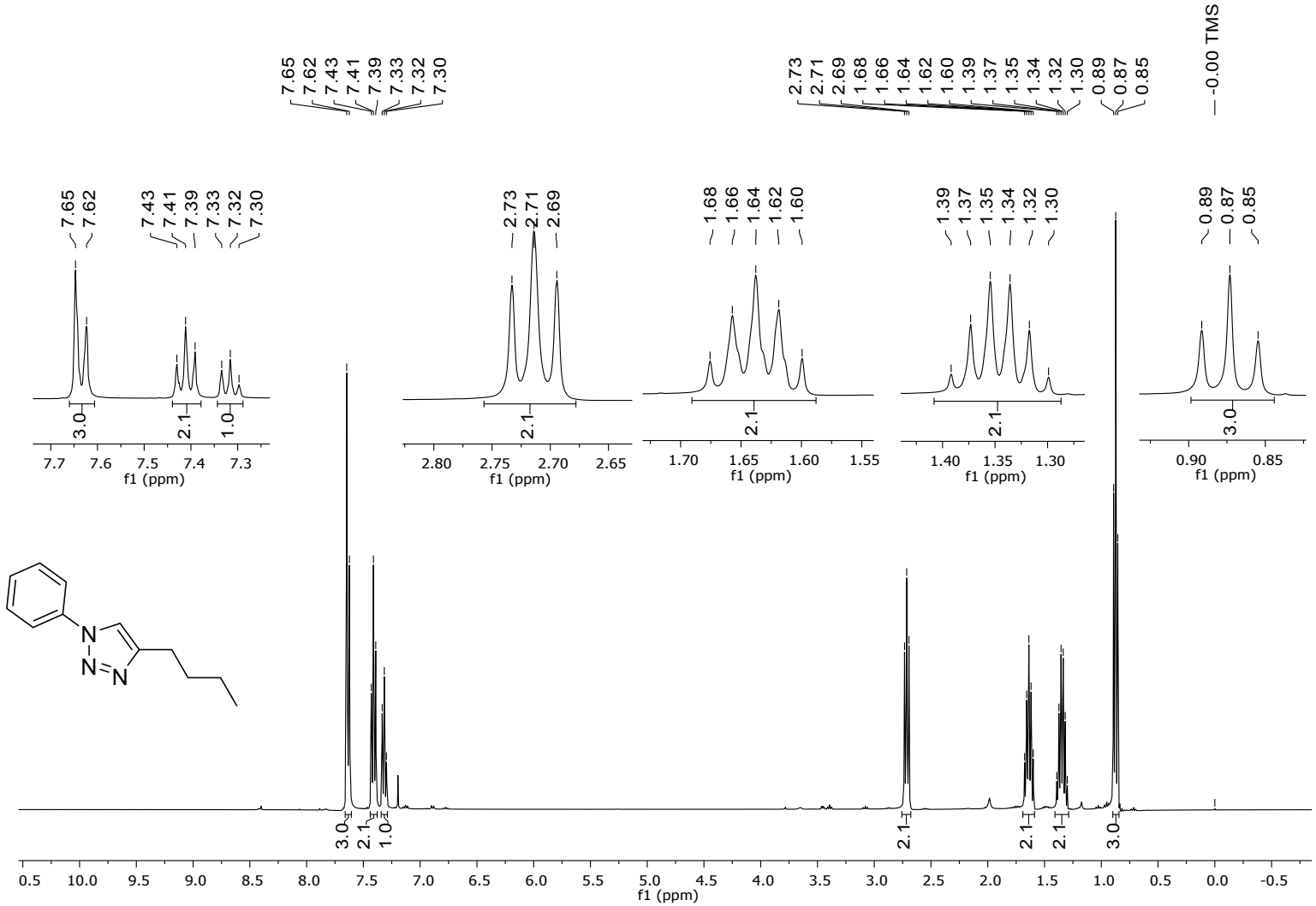

Figure 15. ^{1}H NMR (400 MHz) spectrum for compound **3h** in $CDCl_3$.

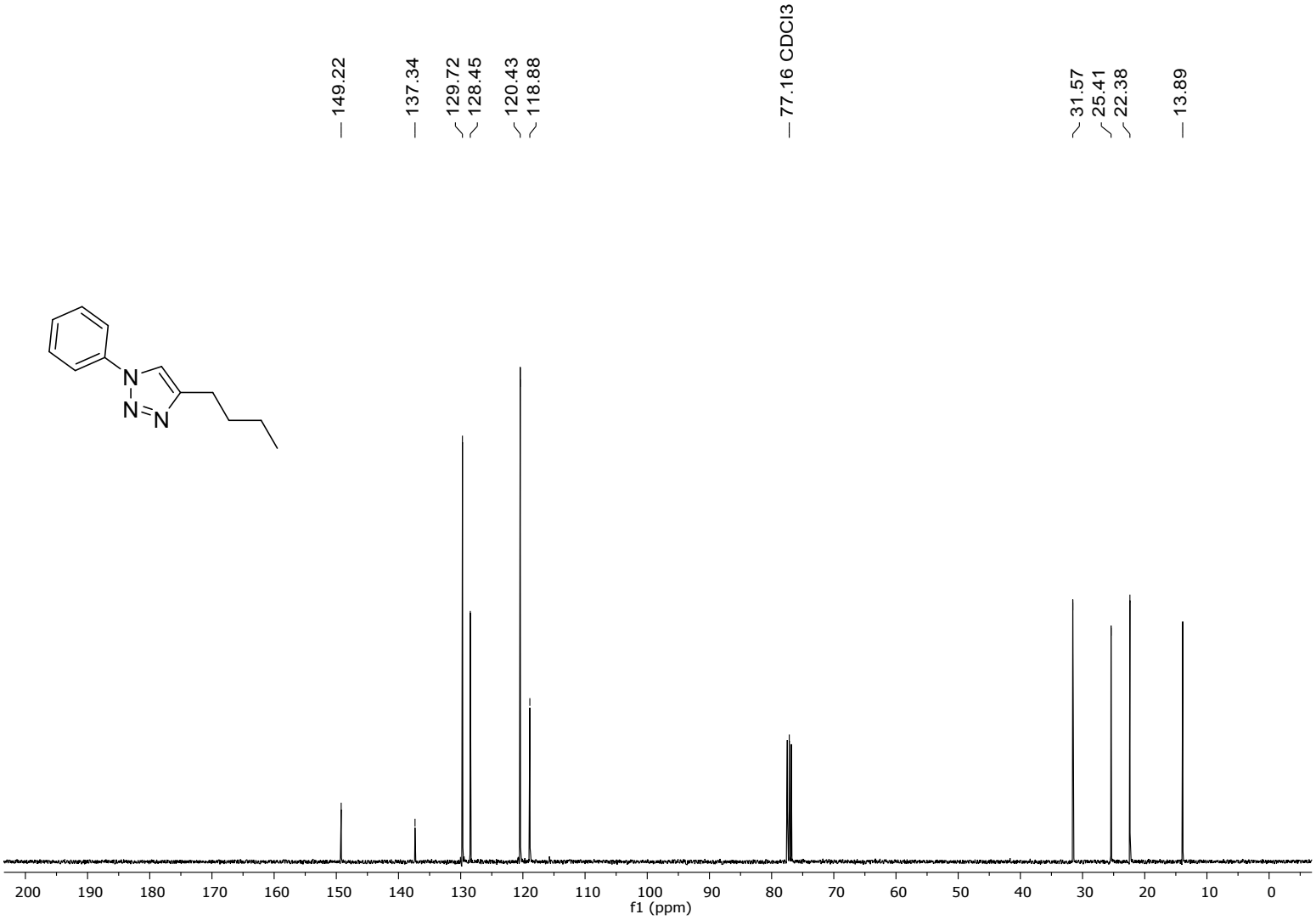

Figure 16. ^{13}C NMR (100 MHz) spectrum for compound **3h** in $CDCl_3$.