Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for:

Triple Copper Catalysis for the *one-pot* Synthesis of Vinyl Triazoles

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SUPPORTING INFORMATION

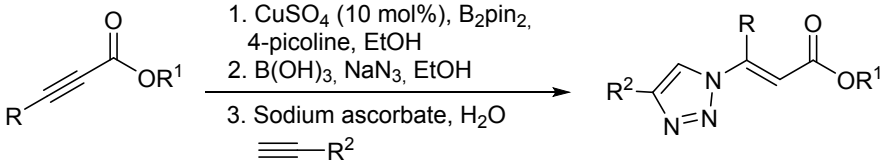
CONTENTS

1. General Information.

For the synthesis of the starting materials, all solvents were distilled from appropriate drying agents prior to use. For the synthesis of vinyl triazoles, ethanol HPLC grade was used. All reagents were used as received from commercial suppliers unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with silica gel F254 with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using vanillin solution. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.). ESI-QTOF-MS measurements were performed in the positive ion mode (m/z 50-2000 range). IR spectra were obtained on a FTIR-ATR instrument. All ^{1}H NMR and ^{13}C NMR spectra were recorded using a 400 MHz, spectrometer at 298K (frequencies for ^{1}H). Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of TMS, defined at δ = 0.00 ppm (^{1}H NMR) and δ = 77.0 (^{13}C NMR). Coupling constants are quoted in Hz (*J*). ^{1}H NMR splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), sextet (sext) and septet (sept). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m).
All acetylenic ester were synthetized following the same procedure reported by Santos.[1]

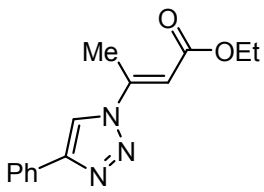
[1] Peck, C. L.; Calderoni, J. A.; Santos, W. L. Synthesis **2015**, *47*, 2242–2248.

2. General procedure for the synthesis of vinyl triazoles from alkynes



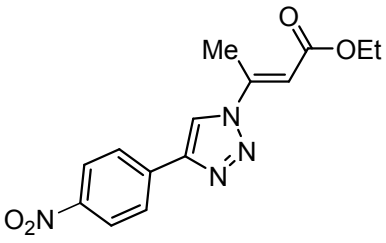
STEP 1: In a open air flask were added $CuSO_4.5H_2O$ (0.05 mmol, 12.5 mg, 10 mol%), bis(pinacolato)diboron (0.325 mmol, 82.5 mg, 0.65 equiv.), 4-picoline (0.25 mmol, 25 µL, 0.5 equiv.), ethanol (1 mL, HPLC grade), and alkyne (0.5 mmol, 1.0 equiv.). The solution was heated to 45 °C (oil bath temperature) and after 10 minutes additional amount of bis(pinacolato)diboron (0.325 mmol, 82.5 mg, 0.65 equiv.) was added. The reaction kept stirring for 20 hours at 45 °C. **STEP 2:** Next, $B(OH)_3$ (1.1 mmol, 68 mg, 2.2 equiv.), sodium azide (0.75 mmol, 49 mg, 1.5 equiv.) and ethanol (1 mL, HPLC grade) were added and the reaction kept stirring for 20 hours at 45 °C. **STEP 3:** Then, sodium ascorbate (0.015 mmol, 3 mg), deionized water (1 mL) and alkyne (0.75 mmol, 1.5 equiv.) were added to the reaction that remained stirring for another 20 hours at 45 °C. The aqueous layer was extracted with AcOEt (3x). The combined organic layers were dried on $MgSO_4$, filtered and concentrated in vacuo. The product was purified on column chromatography using hexane and ethyl acetate as eluent.

Ethyl (*E*)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4a**)



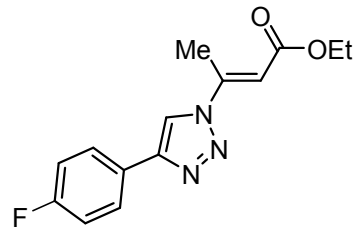
White solid. **Yield**: 70 mg, 52%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.88 - 7.84 (m, 2H), 7.47 - 7.42 (m, 2H), 7.40 - 7.34 (m, 1H), 6.55 (q, *J* = 1.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.87 (d, *J* = 1.0 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.6, 148.2, 147.3, 129.6, 128.9, 128.6, 125.8, 116.8, 109.2, 60.6, 15.6, 14.2. **IR** (ν_{max}, cm^{-1}): 3132, 2989, 1706, 1652, 1365, 1207, 1149, 1008, 763, 692. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{14}H_{16}N_3O_2$) requires *m*/*z* 258.1242, found: *m*/*z* 258.1224.

Ethyl (*E*)-3-(4-(4-nitrophenyl)-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4b**)



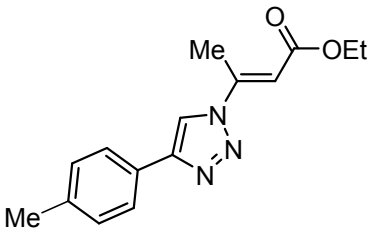
White Solid. **Yield**: 39 mg, 26%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 - 8.29 (m, 2H), 8.25 (s, 1H), 8.08 - 8.03 (m, 2H), 6.61 (q, *J* = 1.1 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.89 (d, *J* = 1.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 147.6, 146.9, 146.1, 135.9, 126.3, 124.4, 118.4, 110.2, 60.9, 15.7, 14.2. **IR** (ν_{max}, cm^{-1}): 3144, 2989, 1703, 1634, 1602, 1502, 1348, 1284, 1030, 852, 751. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{14}H_{15}N_4O_4$) requires *m*/*z* 303.1093, found: *m*/*z* 303.1093.

Ethyl (*E*)-3-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4c**)



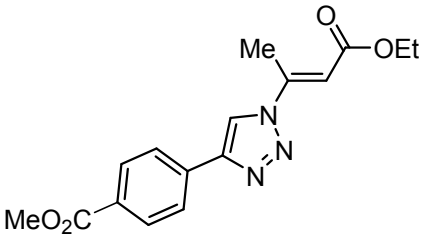
White solid. **Yield**: 34 mg, 25%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.88 – 7.80 (m, 2H), 7.18 – 7.10 (m, 2H), 6.54 (q, *J* = 0.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.88 (d, *J* = 0.9 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 162.9 (d, *J* = 248.3 Hz), 147.4, 147.3, 127.6 (d, *J* = 8.3 Hz), 125.8 (d, *J* = 3.3 Hz), 116.6, 116.0 (d, *J* = 21.8 Hz), 109.3, 60.7, 15.7, 14.2. **IR** (ν_{max}, cm^{-1}): 3111, 2978, 2920, 1714, 1657, 1230, 1150, 1014, 817, 692. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{14}H_{16}N_3O_2F$) requires *m*/*z* 276.1148, found: *m*/*z* 276.1147.

Ethyl (*E*)-3-(4-(p-tolyl)-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4d**)



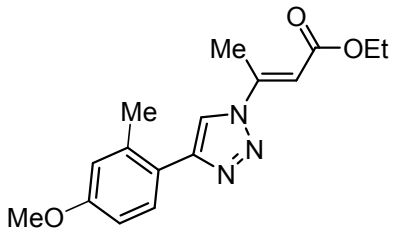
White solid. **Yield**: 44 mg, 33%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.80 - 7.70 (m, 2H), 7.27 – 7.24 (m, 2H), 6.53 (q, *J* = 1.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.88 (d, *J* = 1.0 Hz, 3H), 2.39 (s, 3H), 1.34 (t, *J* = 7,1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 148.4, 147.5, 138.7, 129.6, 126.8, 125.8, 116.4, 109.0, 60.7, 21.3, 15.7, 14.2. **IR** (ν_{max}, cm^{-1}): 3150, 2980, 2937, 1711, 1654, 1236, 1202, 1148, 1010, 797. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{15}H_{18}N_3O_2$) requires *m*/*z* 272.1399, found: *m*/*z* 272.1400.

Methyl (*E*)-4-(1-(4-ethoxy-4-oxobut-2-en-2-yl)-1*H*-1,2,3-triazol-4-yl)benzoate (**4e**)



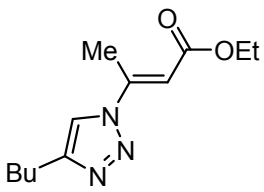
White solid. **Yield**: 32 mg, 20%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 3H), 7.98 - 7.92 (m, 2H), 6.58 (q, *J* = 0.7 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 2.89 (d, *J* = 0.7 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 165.6, 147.3, 147.2, 133.9, 130.3, 130.1, 125.7, 117.7, 109.7, 60.8, 52.2, 15.7, 14.2. **IR** (ν_{max}, cm^{-1}): 3151, 2984, 2924, 1713, 1658, 1633, 1237, 1181, 1020, 761, 686. **HRMS** (ESI+): exact mass calculated for $[M+Na]^+$ ($C_{16}H_{17}N_3O_4Na$) requires *m*/*z* 338.1117, found: *m*/*z* 338.1116.

Ethyl (*E*)-3-(4-(4-methoxy-2-methylphenyl)-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4f**)



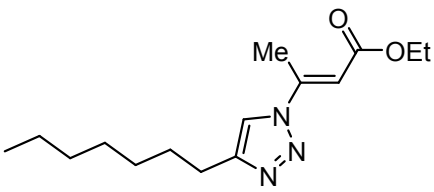
White solid. **Yield**: 31 mg, 20%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.73 – 7,66 (m, 1H), 6.86 – 6.81 (m, 2H), 6.51 (q, *J* = 1.1 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.89 (d, *J* = 1.1 Hz, 3H), 2.47 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 159.7, 147.6, 137.4, 130.3, 121.7, 118.3, 116.4 (2C), 111.5, 108.9, 60.7, 55.3, 21.6, 15.7, 14.2. **IR** (ν_{max}, cm^{-1}): 3185, 2977, 2901, 1715, 1643, 1200, 1145, 1045, 1017, 874, 783. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{16}H_{20}N_3O_3$) requires *m*/*z* 302.1505, found: *m*/*z* 302.1505.

Ethyl (*E*)-3-(4-butyl-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4g**)



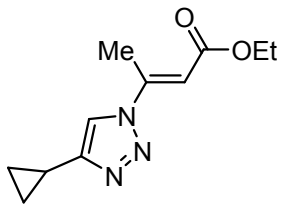
Yellow solid. **Yield**: 40.3 mg, 37%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 6.43, (q, *J* = 1.1 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.20 (d, *J* = 1.1 Hz, 3H), 2.75 (t, *J* = 7.6 Hz, 2H), 1.68 (quint, *J* = 7.6 Hz, 2H), 1.38 (sext, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 149.1, 147.6, 118.1, 108.5, 60.5, 32.2, 25.2, 22.2, 15.6, 14.2, 13.7. **IR** (ν_{max}, cm^{-1}): 3149, 2957, 2834, 1714, 1650, 1211, 1145, 1038, 985. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{12}H_{20}N_3O_2$) requires *m*/*z* 238.1555, found: *m*/*z* 238.1554.

Ethyl (*E*)-3-(4-heptyl-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4h**)



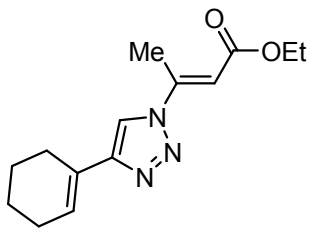
Yellow solid. **Yield**: 35.7 mg, 27%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 6.43 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.83 (s, 3H), 2.74 (t, *J* = 7.6 Hz, 2H), 1.69 (quint, *J* = 7.6 Hz, 2H), 1.40 – 1.23 (m, 11H), 0.88 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 149.2, 147.6, 118.1, 108.1, 60.6, 31.7, 29.2, 29.1, 29.0, 25.5, 22.6, 15.6, 14.2, 14.0. **IR** (ν_{max}, cm^{-1}): 3149, 2928, 2856, 1715, 1651, 1210, 1145, 1039, 984. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{15}H_{26}N_3O_2$) requires *m*/*z* 280.2025, found: *m*/*z* 280.2024.

Ethyl (*E*)-3-(4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4i**)



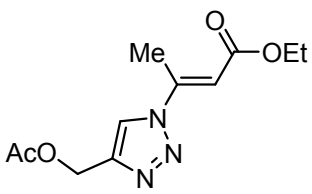
Yellow solid. **Yield**: 54 mg, 50%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 6.42 – 6.40 (m, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.80 (d, *J* = 1.0 Hz, 3H), 2.02 – 1.93 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.03 - 0.97 (m, 2H), 0.92 – 0.87 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 150.9, 147.5, 117.4, 108.4, 60.5, 15.5, 14.2, 7.8, 6.5. **IR** (ν_{max}, cm^{-1}): 3096, 2980, 1712, 1652, 1208, 1148, 1026, 873. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{11}H_{16}N_3O_2$) requires *m*/*z* 222.1243, found: *m*/*z* 222.1242.

Ethyl (*E*)-3-(4-(cyclohex-1-en-1-yl)-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4j**)



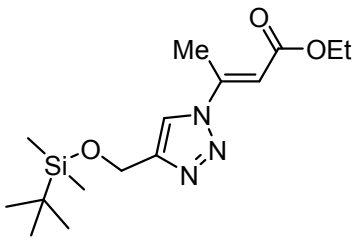
Yellow solid. **Yield**: 37.6 mg, 30%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 6.66 – 6.63 (m, 1H), 6.46 – 6.44 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.83 (d, *J* = 0.9 Hz, 3H), 2.40 – 2.35 (m, 2H), 2.25 - 2.20 (m, 2H), 1.82 – 1.75 (m, 2H), 1.72 – 1.65 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 150.0, 147.6, 126.6, 126.4, 115.3, 108.5, 60.6, 26.9, 25.3, 22.3, 22.1, 15.6, 14.2. **IR** (ν_{max}, cm^{-1}): 3124, 2927, 2834, 1711, 1652, 1208, 1151, 1004, 800. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{14}H_{20}N_3O_2$) requires *m*/*z* 262.1555, found: *m*/*z* 262.1552.

Ethyl (*E*)-3-(4-(acetoxymethyl)-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4k**)



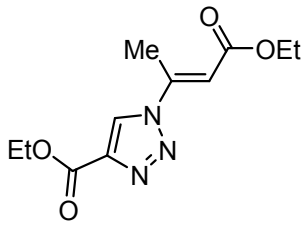
Pale Yellow solid. **Yield**: 38 mg, 30%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 6.50 (q, *J* = 1.1 Hz, 1H), 5.24 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.81 (d, *J* = 1.1 Hz, 3H), 2.09 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H) . **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 165.6, 147.2, 143.6, 121.6, 109.9, 60.3, 57.8, 20.8, 15.7, 14.2. **IR** (ν_{max}, cm^{-1}): 3138, 2984, 1719, 1646, 1149, 1027, 977, 868. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{11}H_{16}N_3O_4$) requires *m*/*z* 254.1141, found: *m*/*z* 254.1141.

Ethyl (*E*)-3-(4-(((tert-butyldimethylsilyl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4l**)



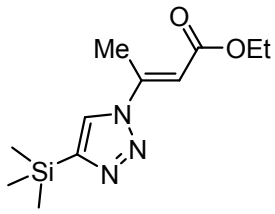
Yellow Oil. **Yield**: 74.6 mg, 45%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 0.7 Hz, 1H), 6.45 (q, *J* = 1.0 Hz, 1H), 4.85 (d, *J* = 0.7 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.81 (d, *J* = 1.0 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.91 (s, 9H), 0.11 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 149.4, 147.5, 119.1, 109.0, 60.6, 57.7, 25.8, 18.3, 15.7, 14.2, 5.3. **IR** (ν_{max}, cm^{-1}): 3150, 2954, 2858, 1715, 1652, 1146, 1036, 834, 776. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{17}H_{28}N_3O_3Si$) requires *m*/*z* 326.1900, found: *m*/*z* 326.1900.

Ethyl (*E*)-1-(4-ethoxy-4-oxobut-2-en-2-yl)-1*H*-1,2,3-triazole-4-carboxylate (**4m**)



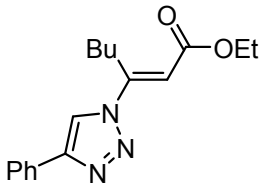
Pale Yellow solid. **Yield**: 46.2 mg, 37%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 6.65 (q, *J* = 1.1 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.83 (d, *J* = 1.1 Hz, 3H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 160.3, 146.5, 140.7, 125.1, 111.3, 61.7, 61.0, 15.7, 14.3, 14.2. **IR** (ν_{max}, cm^{-1}): 3139, 2985, 1722, 1706, 1650, 1264, 1181, 1037, 856, 773. **HRMS** (ESI+): exact mass calculated for $[M+Na]^+$ ($C_{11}H_{15}N_3O_4Na$) requires *m*/*z* 276.0960, found: *m*/*z* 276.0960.

Ethyl (*E*)-3-(4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl)but-2-enoate (**4n**)



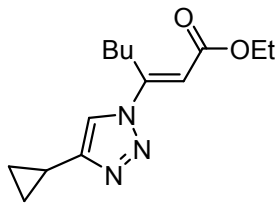
Yellow solid. **Yield**: 34.0 mg, 27%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 6.50 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.84 (d, *J* = 0.8 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 0.35 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 147.4, 126.5, 109.1, 60.6, 16.0, 14.2, 1.3. **IR** (ν_{max}, cm^{-1}): 3134, 2958, 2900, 1716, 1652, 1172, 1136, 841. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{11}H_{20}N_3O_2Si$) requires *m*/*z* 254.1325, found: *m*/*z* 254.1323.

Ethyl (*E*)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)hept-2-enoate (**4o**)



Yellow solid. **Yield**: 32.9 mg, 22%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.91 – 7.82 (m, 2H), 7.48 – 7.41 (m, 2H), 7.39 – 7.34 (m, 1H), 6.39 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.35 (m, 2H), 1.60 (quint, *J* = 7.2 Hz, 2H), 1.44 (sext, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 152.3, 148.2, 129.7, 129.0, 128.7, 125.85, 117.0, 109.35, 60.65, 30.4, 28.7, 22.5, 14.2, 13.7. **IR** (ν_{max}, cm^{-1}): 2941, 2930, 1703, 1645, 1378, 1239, 1191, 1148, 1007. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{17}H_{22}N_3O_2$) requires *m*/*z* 300.1712, found: *m*/*z* 300.1711.

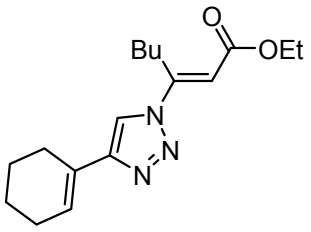
Ethyl (*E*)-3-cyclopropyl-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)acrylate (**4p**)



Yellow solid. **Yield**: 30.3 mg, 23%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 6.27 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.36 – 3.26 (m, 2H), 1.97 (tt, *J* = 8.4, 5.1 Hz, 1H), 1.55 (quint, *J* = 7.2 Hz, 2H), 1.42 (sext, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.03 – 0.97 (m, 2H), 0.95 – 0.88 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 152.4, 150.8, 117.4, 108.55, 60.5, 30.4, 28.6, 22.55, 14.2, 13.7, 7.9, 6.6. **IR** (ν_{max}, cm^{-1}): 2958, 2931, 1715, 1644, 1437, 1377, 1182, 1144, 1029,

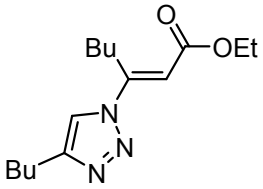
984. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{14}H_{22}N_3O_2$) requires *m*/*z* 264.1712, found: *m*/*z* 264.1702.

Ethyl (*E*)-3-(4-(cyclohex-1-en-1-yl)-1*H*-1,2,3-triazol-1-yl)hept-2-enoate (**4q**)



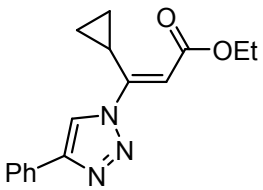
Yellow solid. **Yield**: 30.5 mg, 20%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 6.67 – 6.64 (m, 1H), 6.30 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.38 – 3.32 (m, 2H), 2.41 – 2.35 (m, 2H), 2.28 – 2.20 (m, 2H), 1.83 – 1.75 (m, 2H), 1.73 – 1.65 (m, 2H), 1.59 – 1.51 (m, 2H), 1.42 (sext, *J* = 7.4 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 152.5, 149.8, 126.5, 126.46, 115.5, 108.5, 60.5, 30.4, 28.6, 26.3, 25.3, 22.5, 22.3, 22.1, 14.2, 13.7. **IR** (ν_{max}, cm^{-1}): 2932, 2864, 1716, 1645, 1438, 1375, 1235, 1190, 1148, 1042. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{17}H_{26}N_3O_2$) requires *m*/*z* 304.2025, found: *m*/*z* 304.2016.

Ethyl (*E*)-3-(4-butyl-1*H*-1,2,3-triazol-1-yl)hept-2-enoate (**4r**)



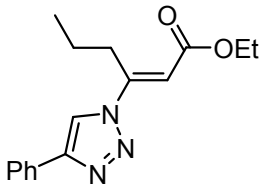
Yellow solid. **Yield**: 39 mg, 28%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 0.7 Hz, 1H), 6.30 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.38 – 3.29 (m, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 1.73 – 1.64 (m, 2H), 1.60 – 1.52 (m, 2H), 1.48 – 1.37 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.98 – 0.90 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 152.5, 149.1, 118.3, 108.6, 60.5, 31.2, 30.4, 28.7, 25.2, 22.5, 22.3, 14.2, 13.8, 13.7. **IR** (ν_{max}, cm^{-1}): 2957, 2930, 1716, 1644, 1441, 1376, 1186, 1145, 1039, 985. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{15}H_{26}N_3O_2$) requires *m*/*z* 280.2025, found: *m*/*z* 280.2023 .

Ethyl (*E*)-3-cyclopropyl-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)acrylate (**4s**)



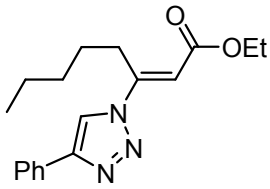
Yellow solid. **Yield**: 65 mg, 46%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.90 – 7.80 (m, 2H), 7.46 – 7.40 (m, 2H), 7.37 – 7.32 (m, 1H), 6.40 (d, *J* = 0.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.84 (ttd, *J* = 8.5, 5.4, 0.9 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.14 – 1.07 (m, 2H), 0.89 – 0.83 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2, 151.8, 147.4, 129.7, 128.9, 128.5, 125.7, 119.5, 115.8, 60.7, 14.2, 12.3, 8.5. **IR** (ν_{max}, cm^{-1}): 3138, 3083, 2982, 1719, 1708, 1633, 1245, 1156, 1037, 765, 694. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{16}H_{18}N_3O_2$) requires *m*/*z* 284.1399, found: *m*/*z* 284.1392.

Ethyl (*E*)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)hex-2-enoate (**4t**)



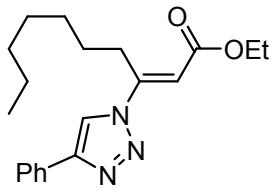
Yellow solid. **Yield**: 34.2 mg, 24%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.90 – 7.85 (m, 2H), 7.49 – 7.42 (m, 2H), 7.45 – 7.35 (m, 1H), 6.42 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.40 – 3.34 (m, 2H), 1.73 – 1.62 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 152.0, 148.2, 129.7, 128.9, 128.7, 125.9, 117.0, 109.6, 60.7, 30.6, 21.7, 14.2, 13.7. **IR** (ν_{max}, cm^{-1}): 3040, 2927, 1717, 1649, 1264, 1202, 1155. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{16}H_{20}N_3O_2$) requires *m*/*z* 286.1556, found: *m*/*z* 286.1553.

Ethyl (*E*)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)oct-2-enoate (**4u**)



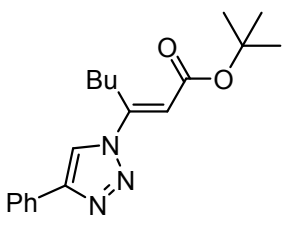
Yellow solid. **Yield**: 39 mg, 25%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.90 – 7.84 (m, 2H), 7.49 – 7.42 (m, 2H), 7.41 – 7.34 (m, 1H), 6.40 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.35 (m, 2H), 1.70 – 1.57 (m, 2H), 1.47 – 1.34 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 152.3, 148.2, 129.7, 128.9, 128.7, 125.9, 117.0, 109.3, 60.7, 31.5, 28.9, 28.0, 22.3, 14.2, 13.9. **IR** (ν_{max}, cm^{-1}): 3115, 2923, 1710, 1649, 1455, 1378, 1193, 1148, 1042, 1007, 871, 762, 692. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{18}H_{24}N_3O_2$) requires *m*/*z* 314.1869, found: *m*/*z* 314.1868.

Ethyl (*E*)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)dec-2-enoate (**4v**)



Yellow solid. **Yield**: 54.6 mg, 32%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.89 – 7.85 (m, 2H), 7.49 – 7.43 (m, 2H), 7.40 – 7.35 (m, 1H), 6.40 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.44 – 3.31 (m, 2H), 1.66 – 1.58 (m, 2H), 1.45 – 1.38 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.30 - 1.22 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 152.3, 148.2, 129.7, 128.9, 128.7, 125.9, 117.0, 109.4, 60.7, 31.7, 29.4, 29.0, 28.9, 28.4, 22.6, 14.2, 14.1. **IR** (ν_{max}, cm^{-1}): 3143, 2928, 2856, 1715, 1644, 1377, 1203, 1174, 1147, 1046, 1006, 761, 693. **HRMS** (ESI+): exact mass calculated for $[M+Na]^+$ ($C_{20}H_{28}N_3O_2$) requires *m*/*z* 342.2182, found: *m*/*z* 342.2180.

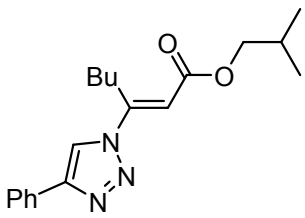
Tert-butyl (*E*)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)hept-2-enoate (**4w**)



White solid. **Yield**: 45.8 mg, 28%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.90 – 7.82 (m, 2H), 7.49 – 7.42 (m, 2H), 7.40 – 7.34 (m, 1H), 6.30 (s, 1H), 3.41 – 3.31 (m, 2H), 1.62 – 1.55 (m, 2H), 1.54 (s, 9H), 1.50 – 1.41 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 151.0, 148.0, 129.7, 128.9, 128.6, 125.8, 117.1, 111.6, 81.3, 30.2, 28.6, 28.1, 22.5, 13.8. **IR** (ν_{max}, cm^{-1}): 2945, 2927, 2878, 1710, 1650, 1456, 1141, 1016, 764, 692. **HRMS**

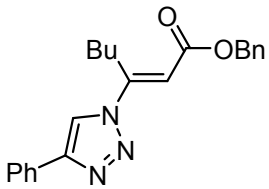
(ESI+): exact mass calculated for $[M+H]^+$ ($C_{19}H_{26}N_3O_2$) requires *m*/*z* 328.2025, found: *m*/*z* 328.2021.

Isobutyl (*E*)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)hept-2-enoate (**4x**)



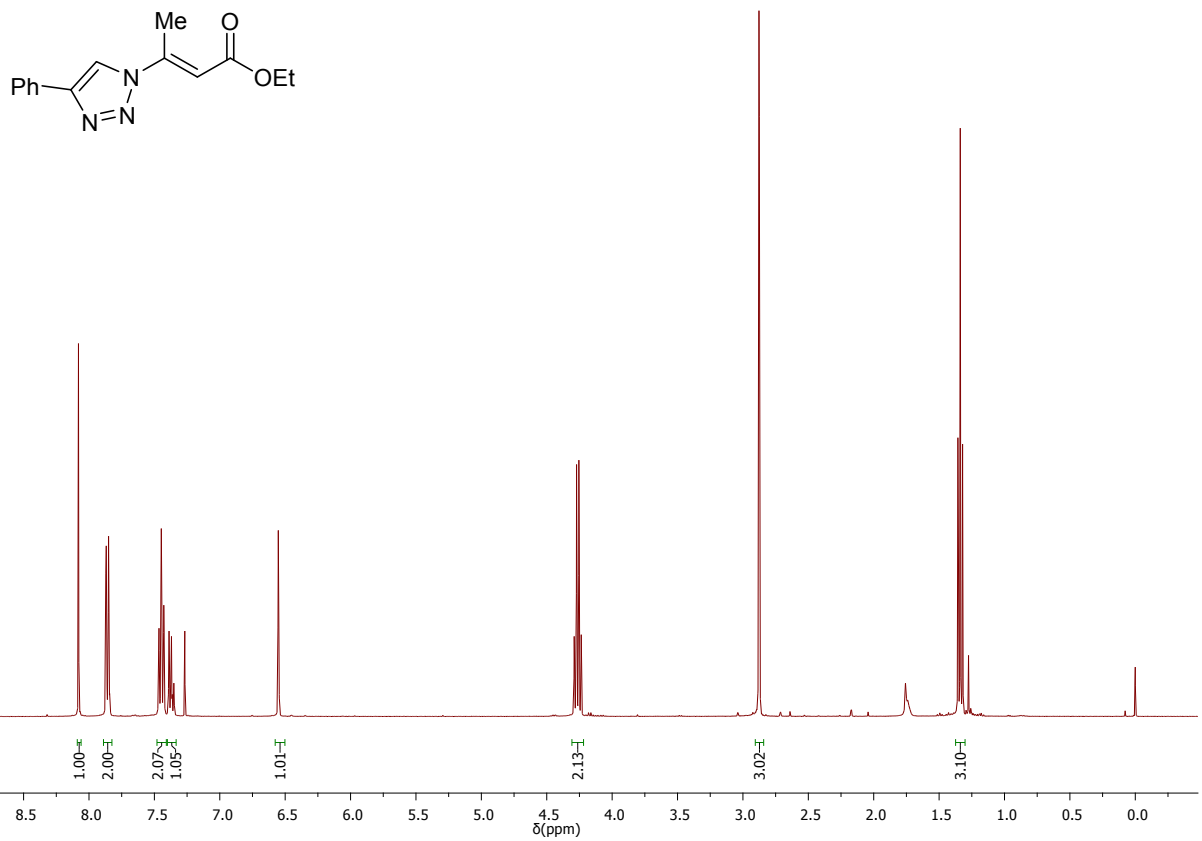
White solid. **Yield**: 55.6 mg, 34%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.92 – 7.83 (m, 2H), 7.48 – 7.39 (m, 2H), 7.40 – 7.32 (m, 1H), 6.42 (s, 1H), 3.98 (d, *J* = 6.6 Hz, 2H), 3.42 – 3.34 (m, 2H), 2.08 – 1.92 (m, 1H), 1.58 (quint, *J* = 7.3 Hz, 2H), 1.44 (sext, *J* = 7.3 Hz, 2H), 0.98 (d, *J* = 6.7 Hz, 6H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 152.2, 148.1, 129.6, 128.9, 128.6, 125.8, 117.1, 109.3, 70.8, 30.3, 28.7, 27.7, 22.5, 19.1, 13.7. **IR** (ν_{max}, cm^{-1}): 3128, 2956, 2928, 2872, 1714, 1648, 1484, 1195, 1152, 1050, 1015, 982, 860, 764, 691. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{19}H_{26}N_3O_2$) requires *m*/*z* 328.2025, found: *m*/*z* 328.2034.

Benzyl (*E*)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)hept-2-enoate (**4y**)

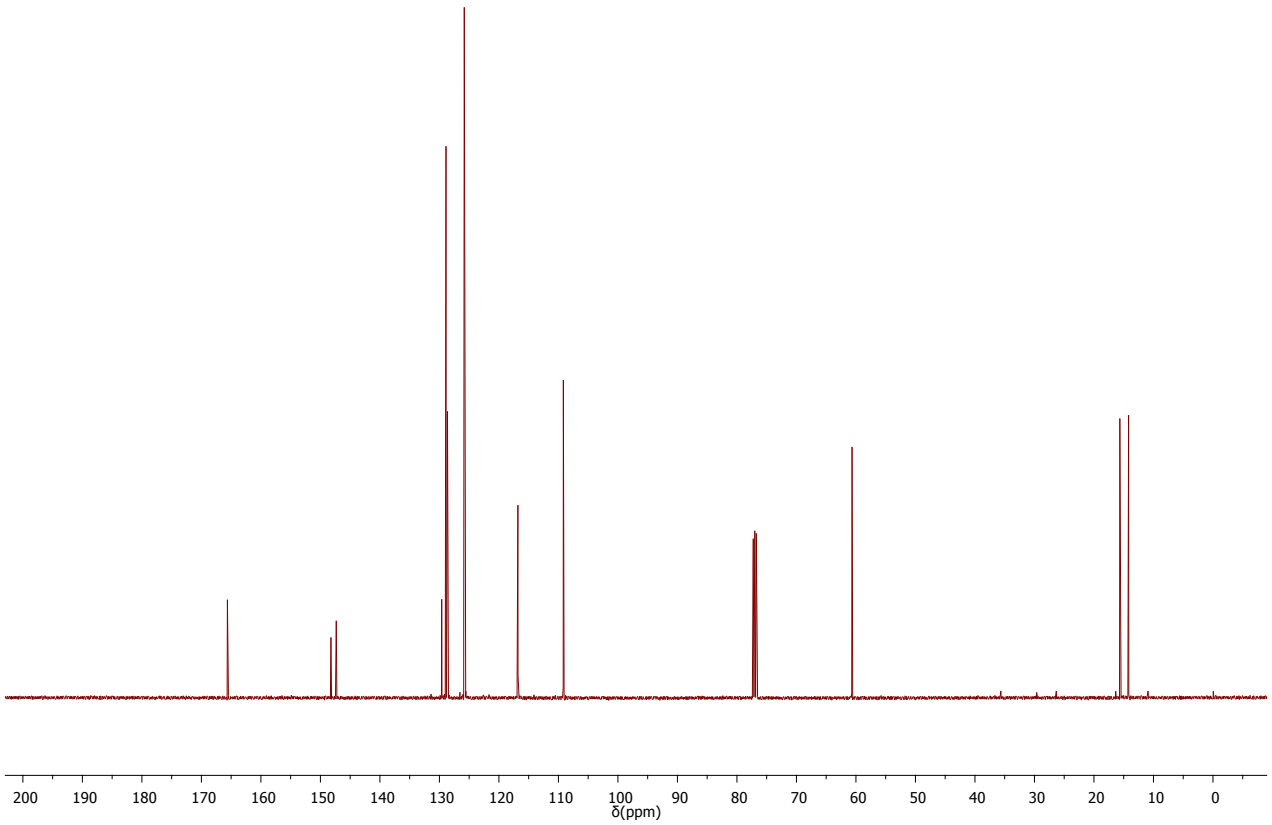


White solid. **Yield**: 63.2 mg, 35%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.88 – 7.83 (m, 2H), 7.50 – 7.31 (m, 8H), 6.45 (s, 1H), 5.24 (s, 2H), 3.45 – 3.36 (m, 2H), 1.64 – 1.55 (m, 2H), 1.43 (sext, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 152.8, 148.2, 135.6, 129.6, 129.9, 128.7, 128.6, 128.4, 128.3, 125.9, 117.0, 108.8, 66.5, 30.4, 28.8, 22.6, 13.7. **IR** (ν_{max}, cm^{-1}): 3132, 2959, 2928, 2858, 1712, 1653, 1389, 1187, 1141, 1017, 869, 763, 693, 593. **HRMS** (ESI+): exact mass calculated for $[M+H]^+$ ($C_{22}H_{24}N_3O_2$) requires *m*/*z* 362.1869, found: *m*/*z* 362.1860.

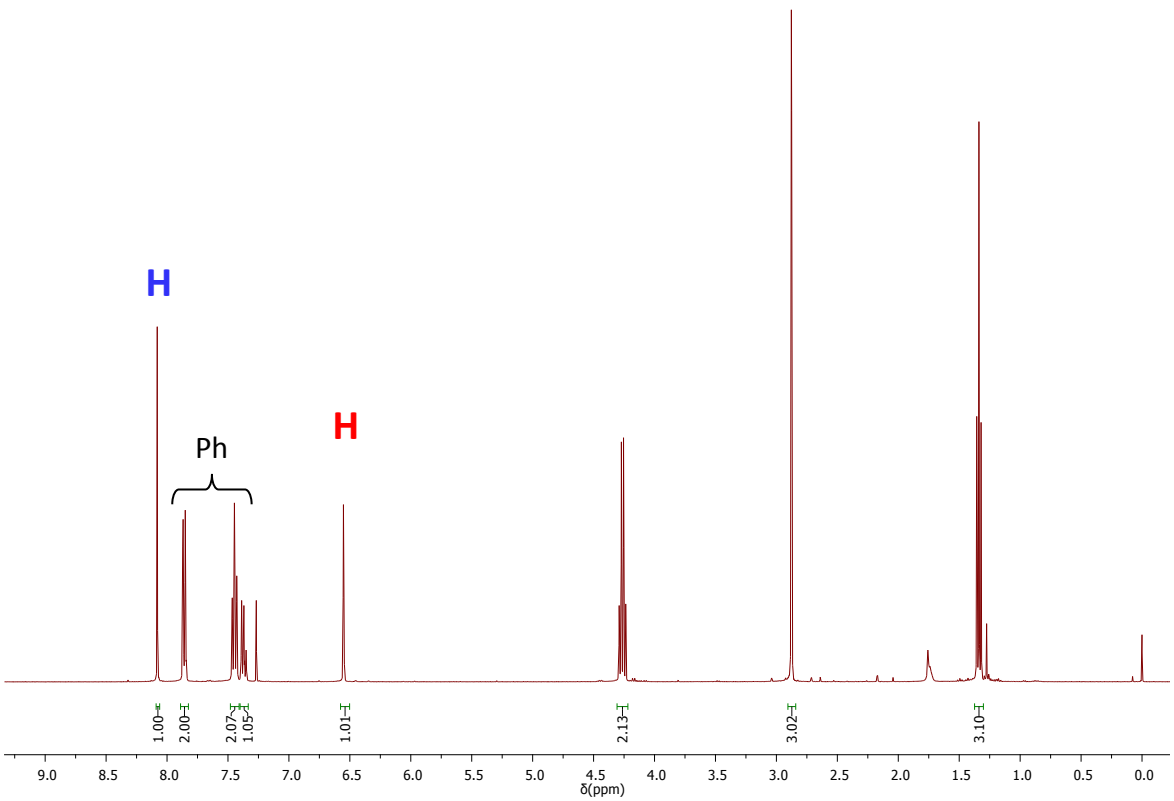
NMR Spectra



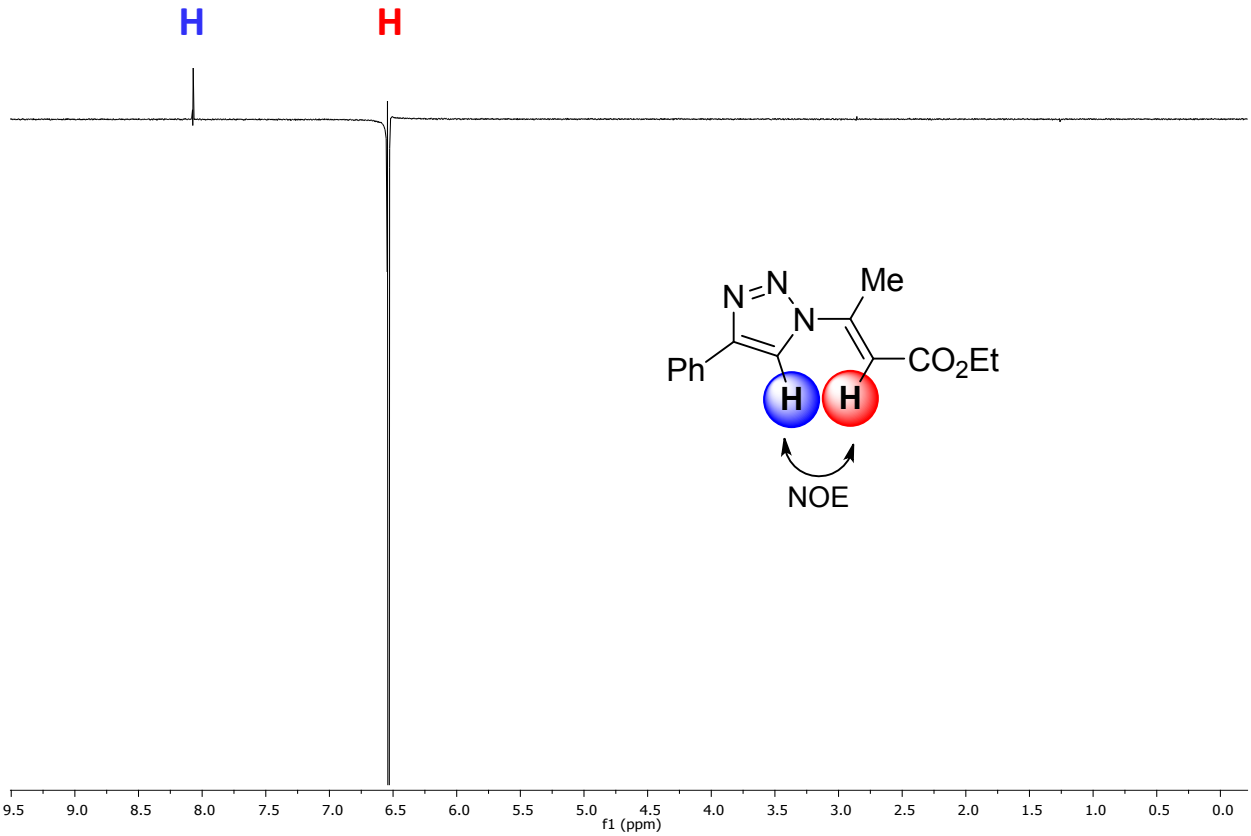
^{1}H NMR spectrum for compound **4a** in $CDCl_3$, 400 MHz



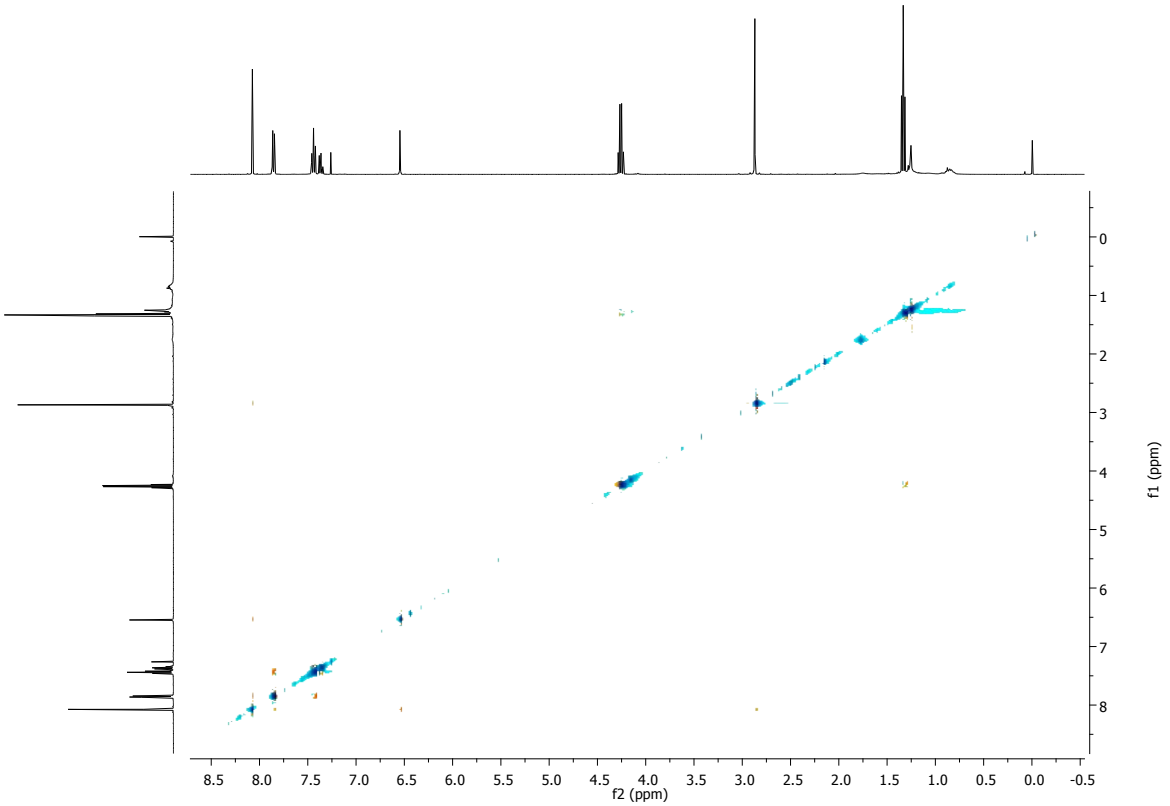
^{13}C NMR spectrum for compound **4a** in $CDCl_3$, 100 MHz



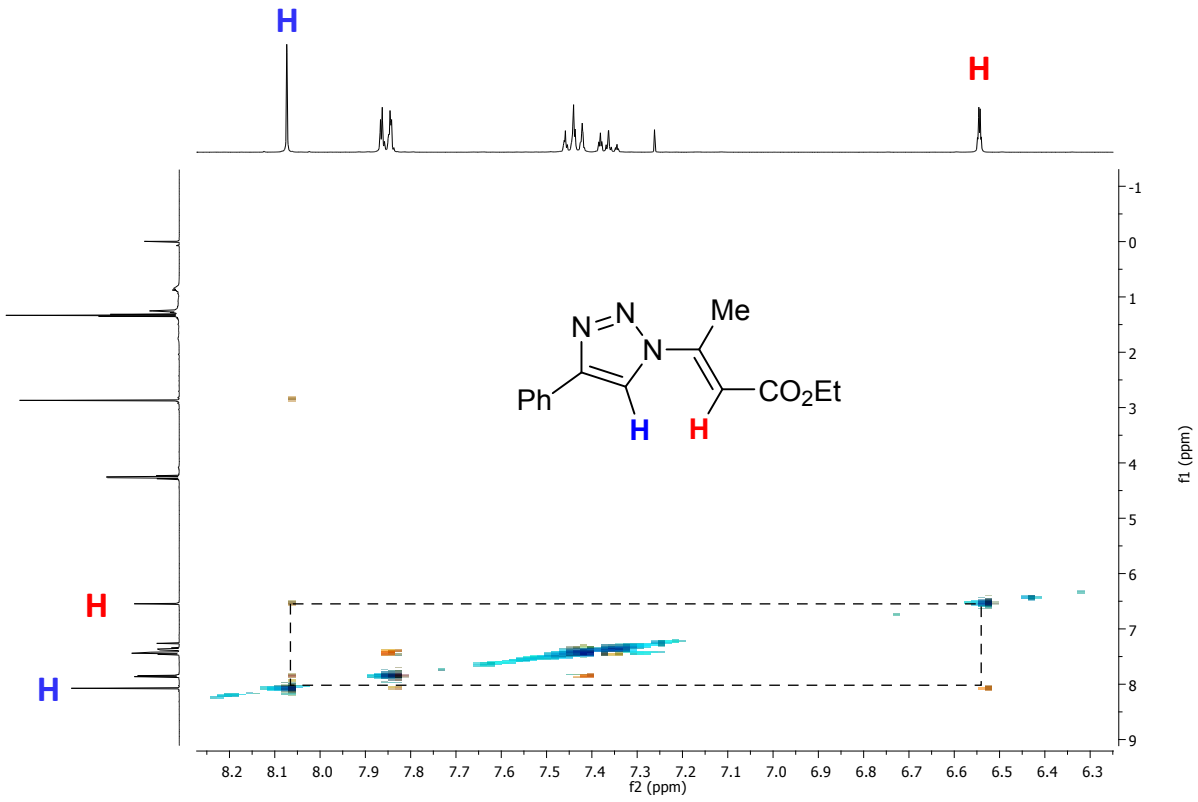
^{1}H NMR spectrum for compound **4a** in $CDCl_3$, 400 MHz



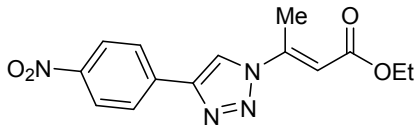
NOESY-1D NMR spectrum for compound **4a** in $CDCl_3$ (400 MHz), showing the interaction between vinyl hydrogen and triazole hydrogen.

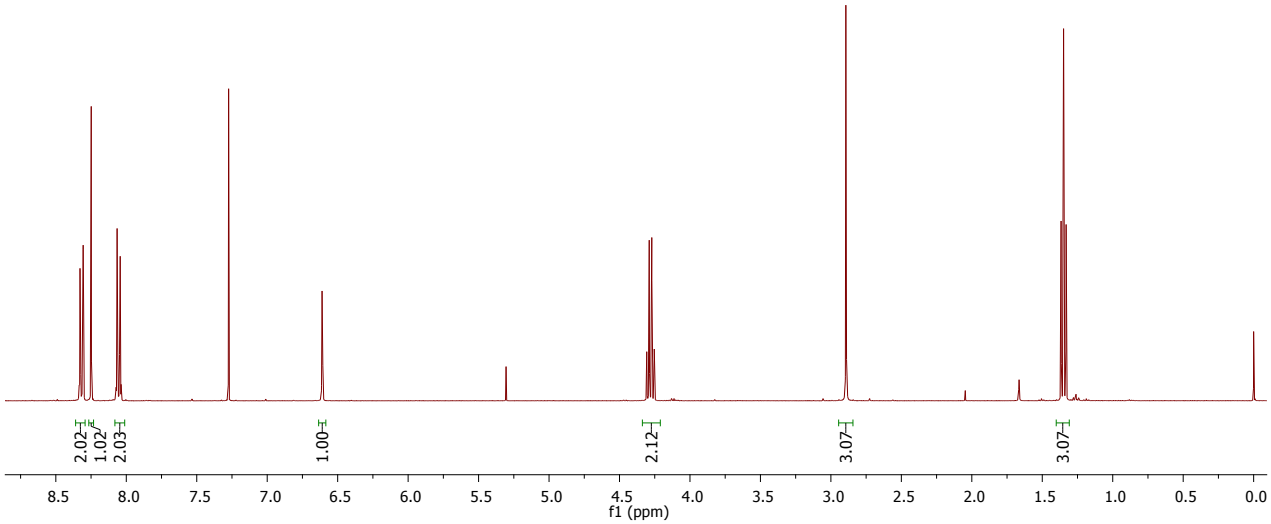


NOESY-2D NMR spectrum for compound **4a** in $CDCl_3$ (400 MHz).

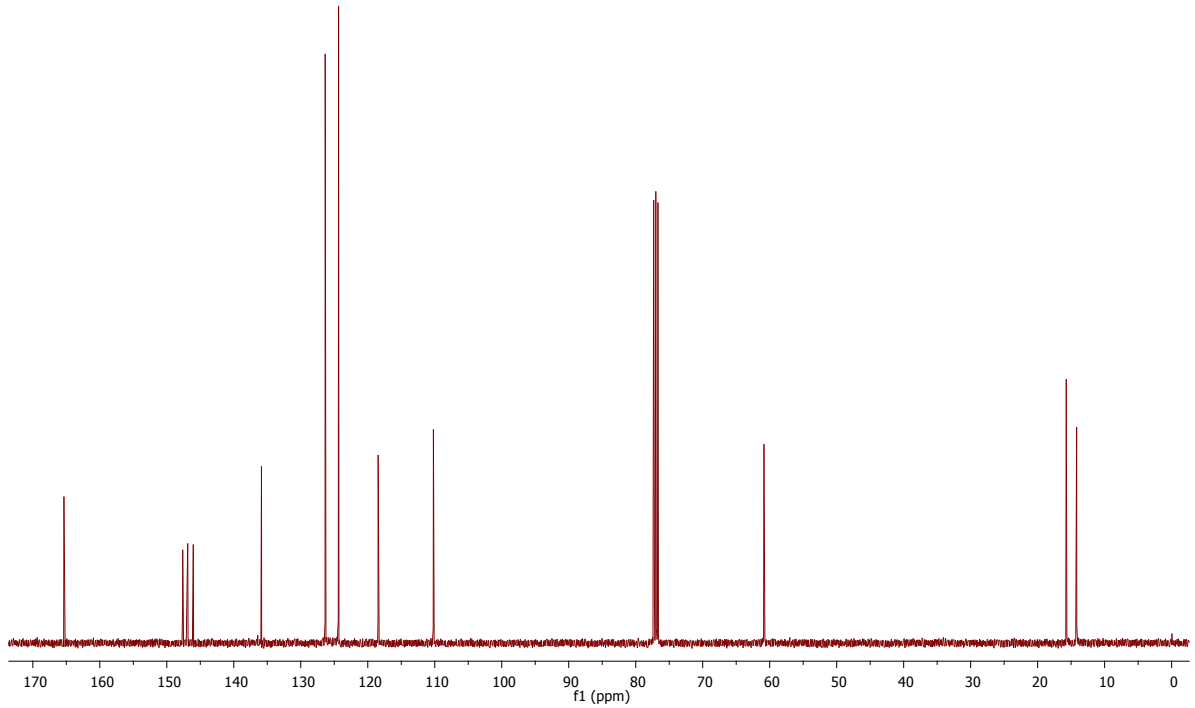


Expansion of NOESY-2D NMR spectrum for compound **4a** in $CDCl_3$ (400 MHz).

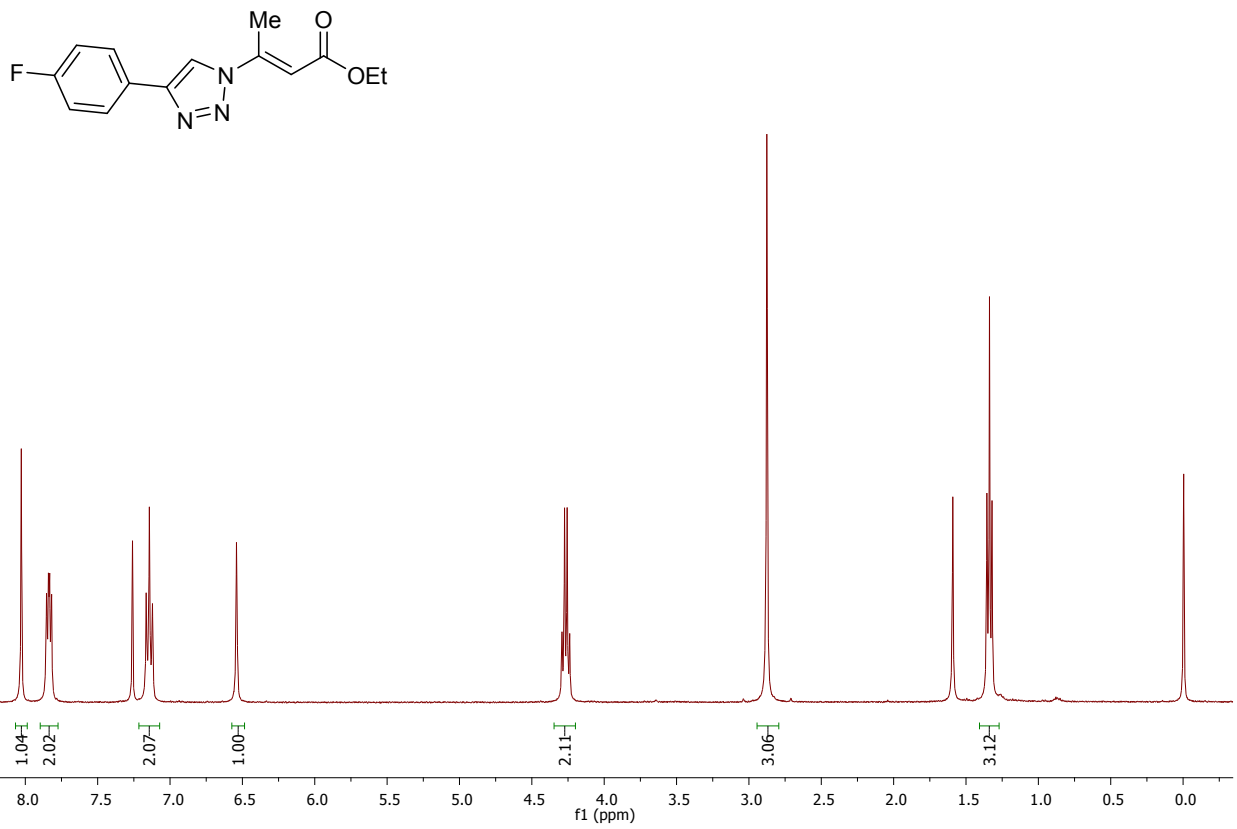




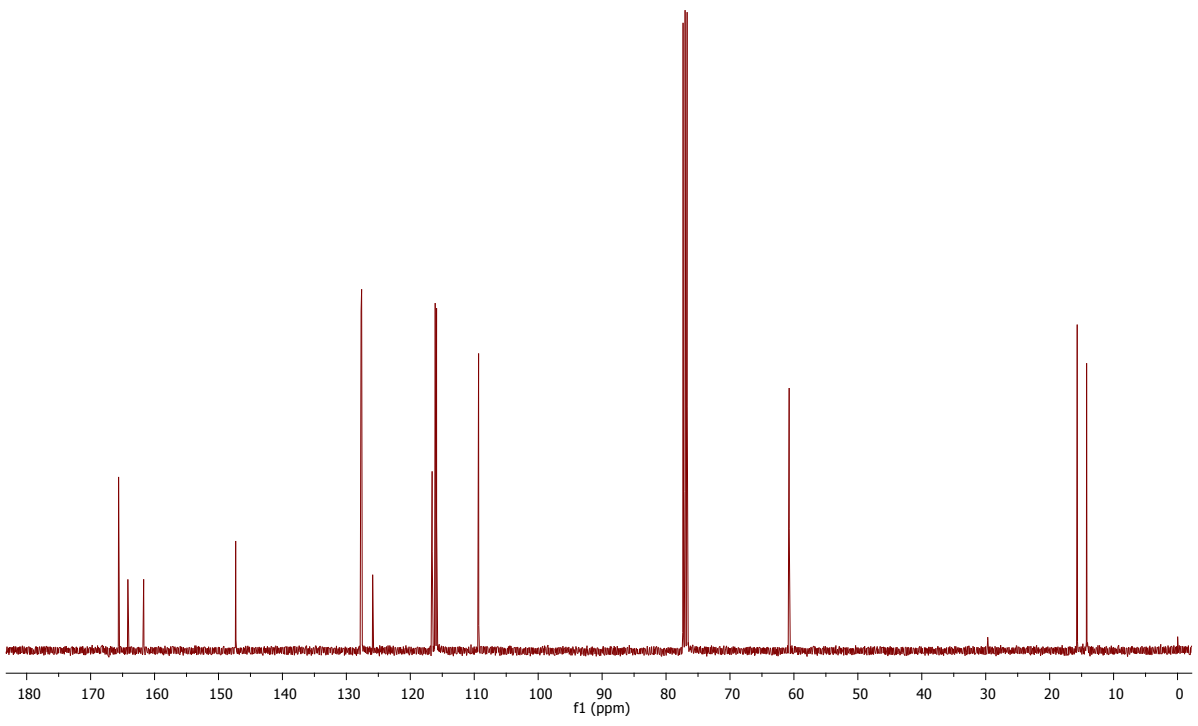
^{1}H NMR spectrum for compound **4b** in $CDCl_3$, 400 MHz



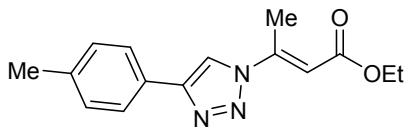
^{13}C NMR spectrum for compound **4b** in $CDCl_3$, 100 MHz

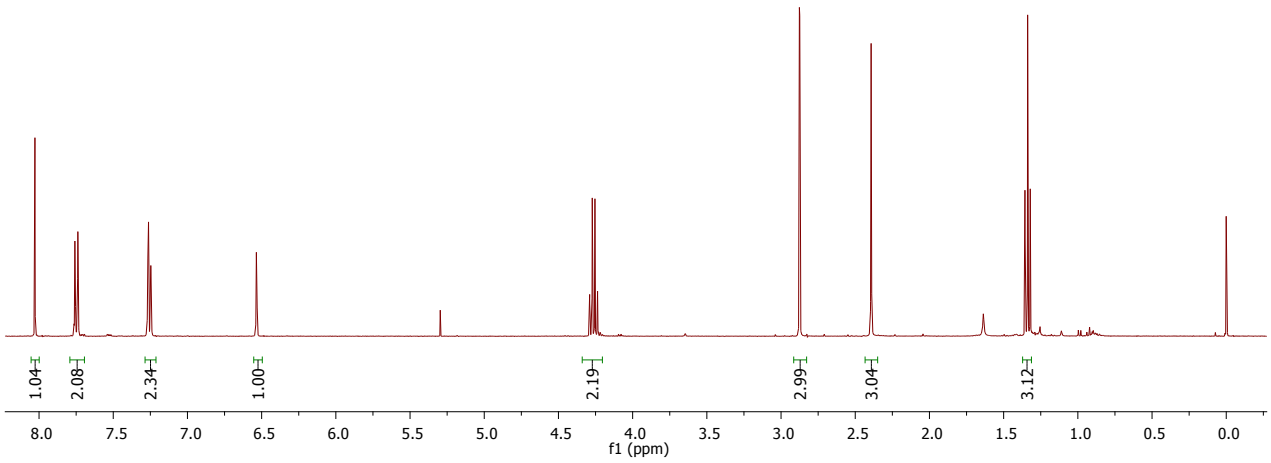


^{1}H NMR spectrum for compound **4c** in $CDCl_3$, 400 MHz

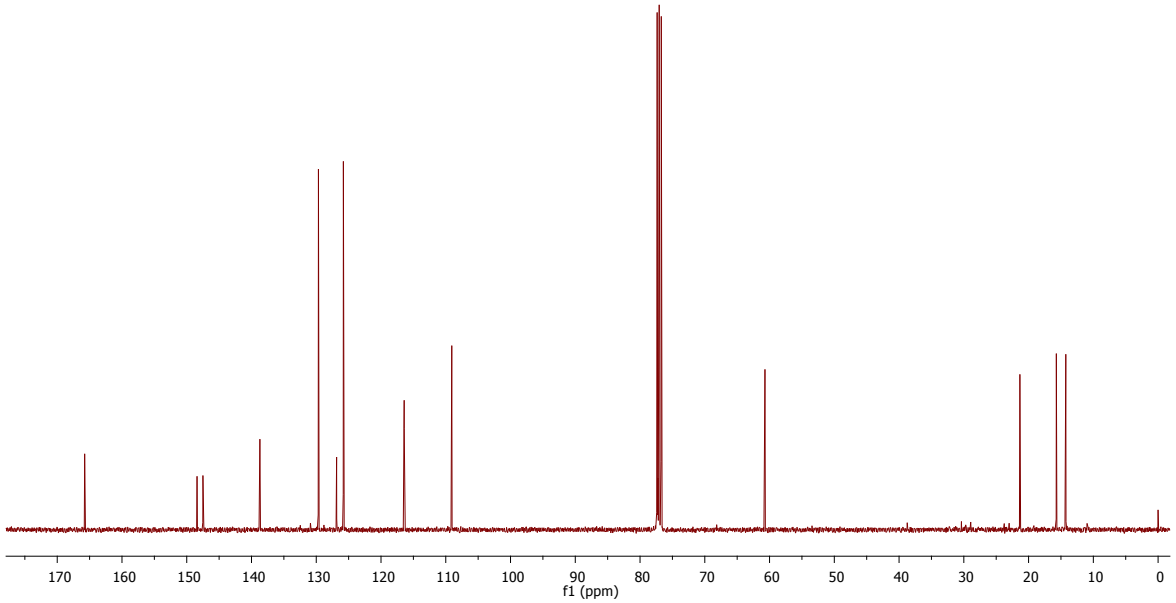


^{13}C NMR spectrum for compound **4c** in $CDCl_3$, 100 MHz

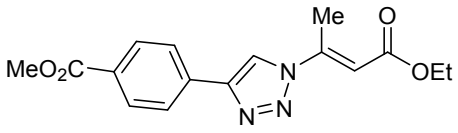


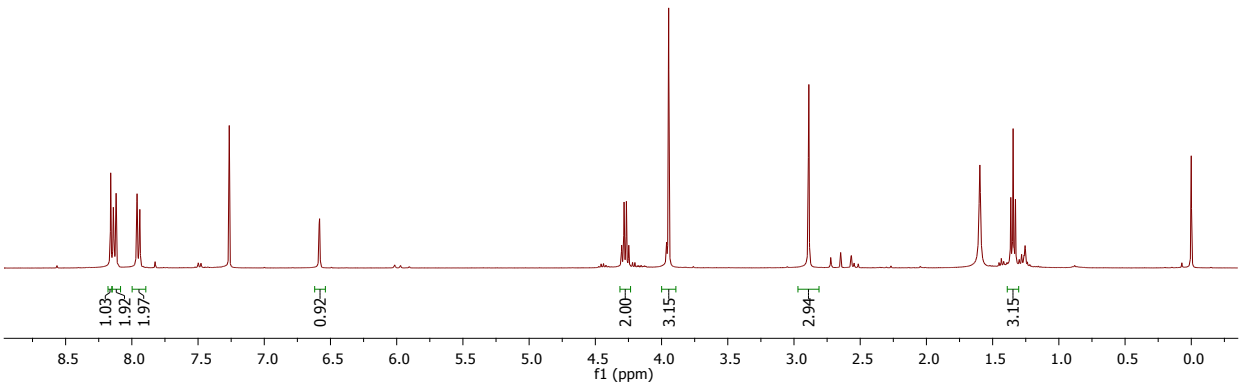


^{1}H NMR spectrum for compound **4d** in $CDCl_3$, 400 MHz

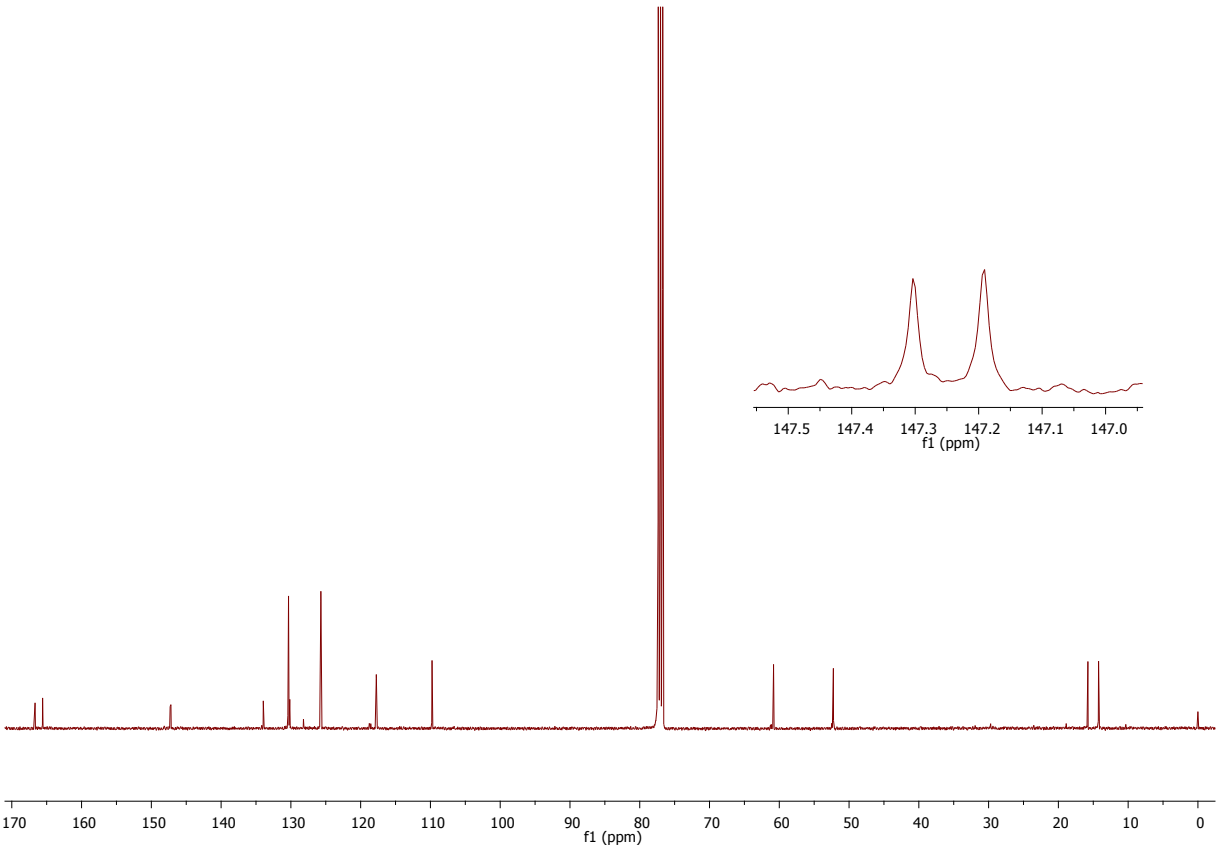


^{13}C NMR spectrum for compound **4d** in $CDCl_3$, 100 MHz

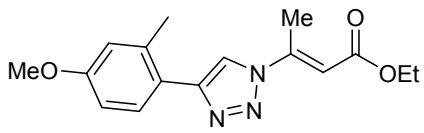


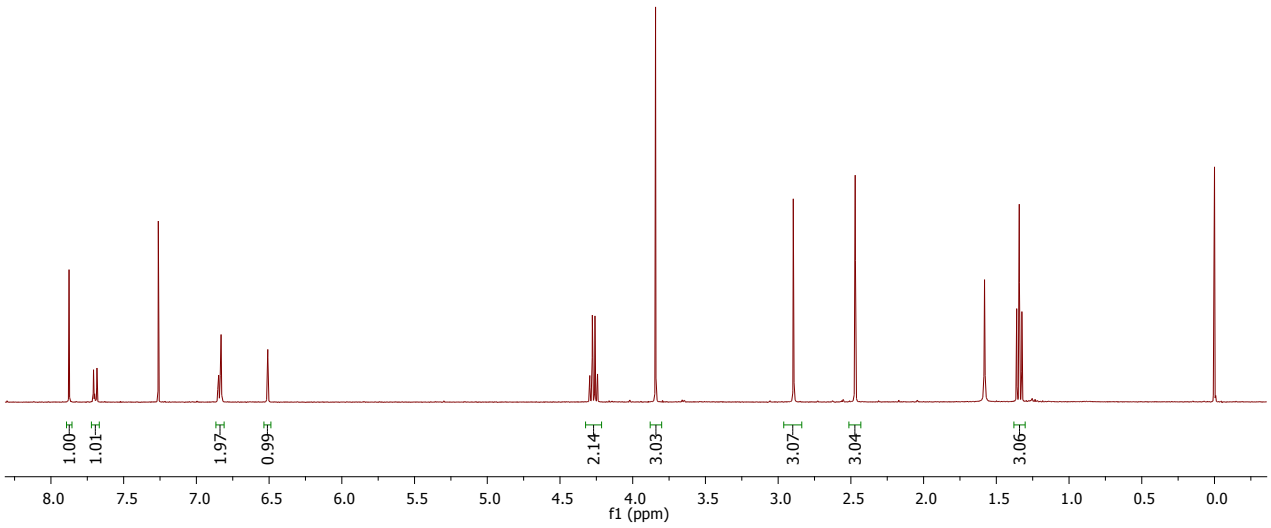


^{1}H NMR spectrum for compound **4e** in $CDCl_3$, 400 MHz

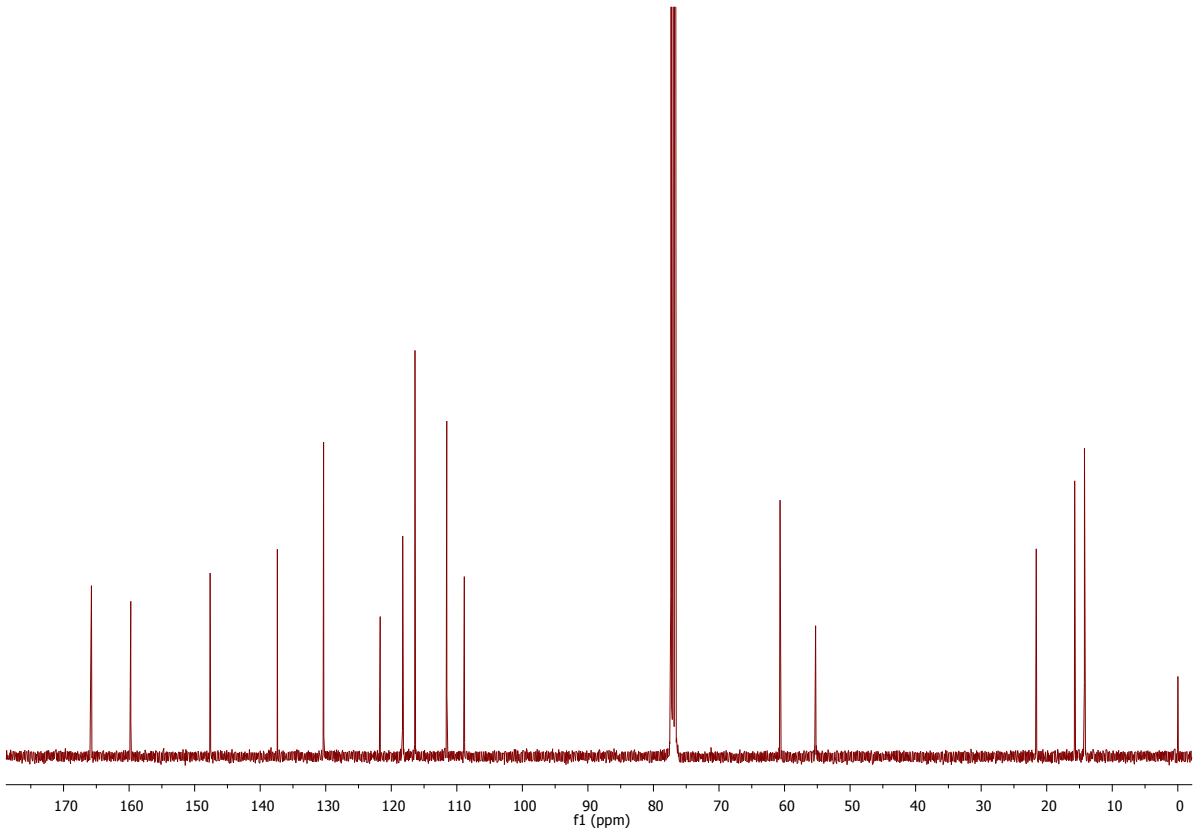


^{13}C NMR spectrum for compound **4e** in $CDCl_3$, 100 MHz

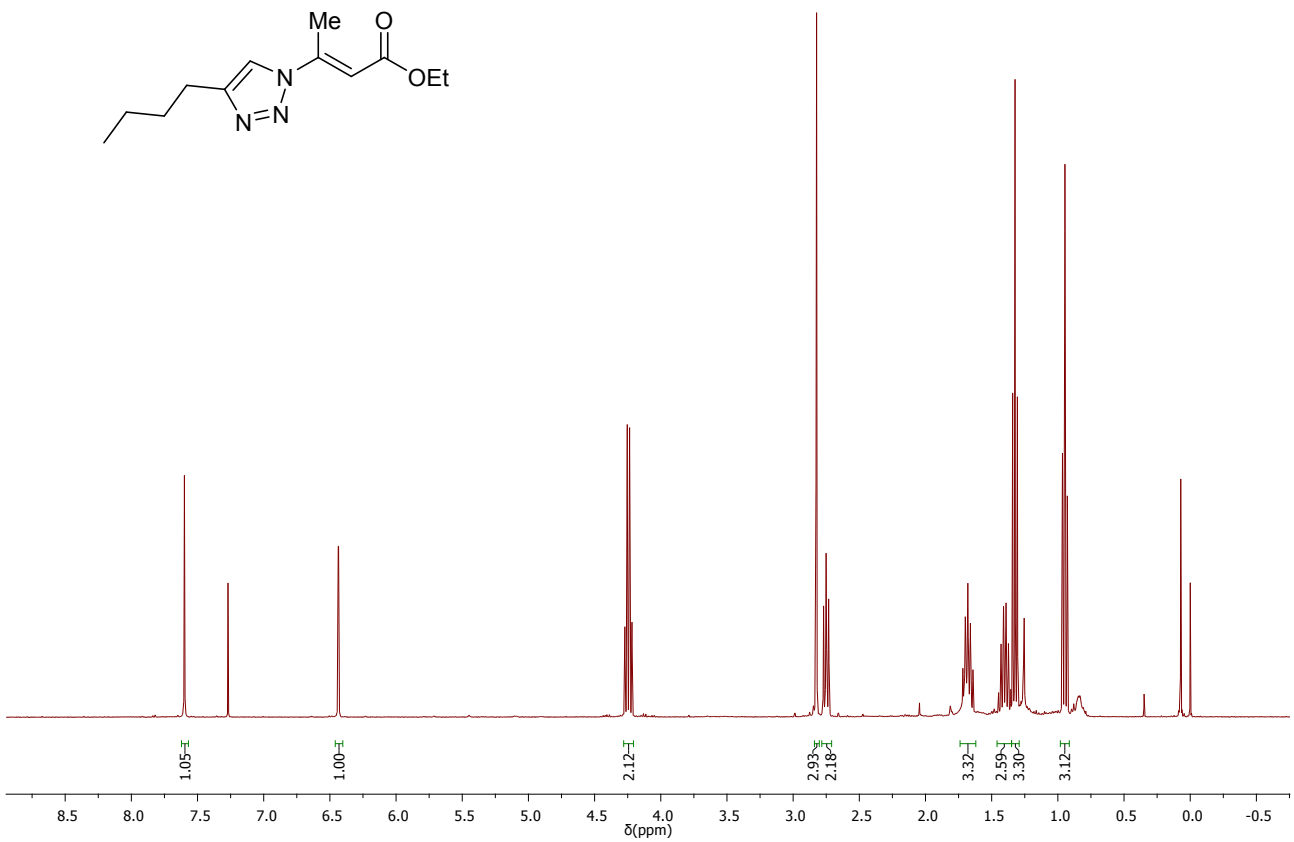




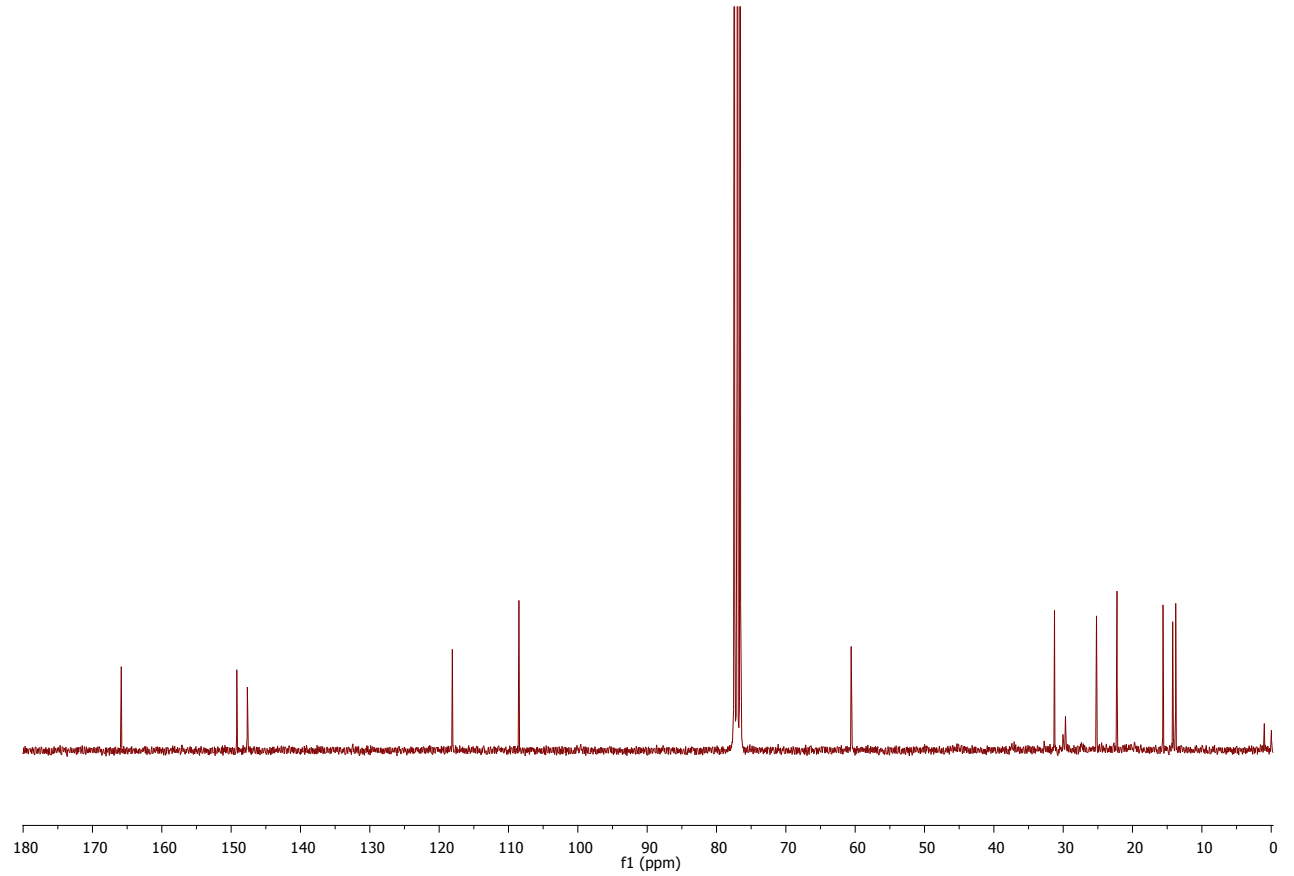
^{1}H NMR spectrum for compound **4f** in $CDCl_3$, 400 MHz



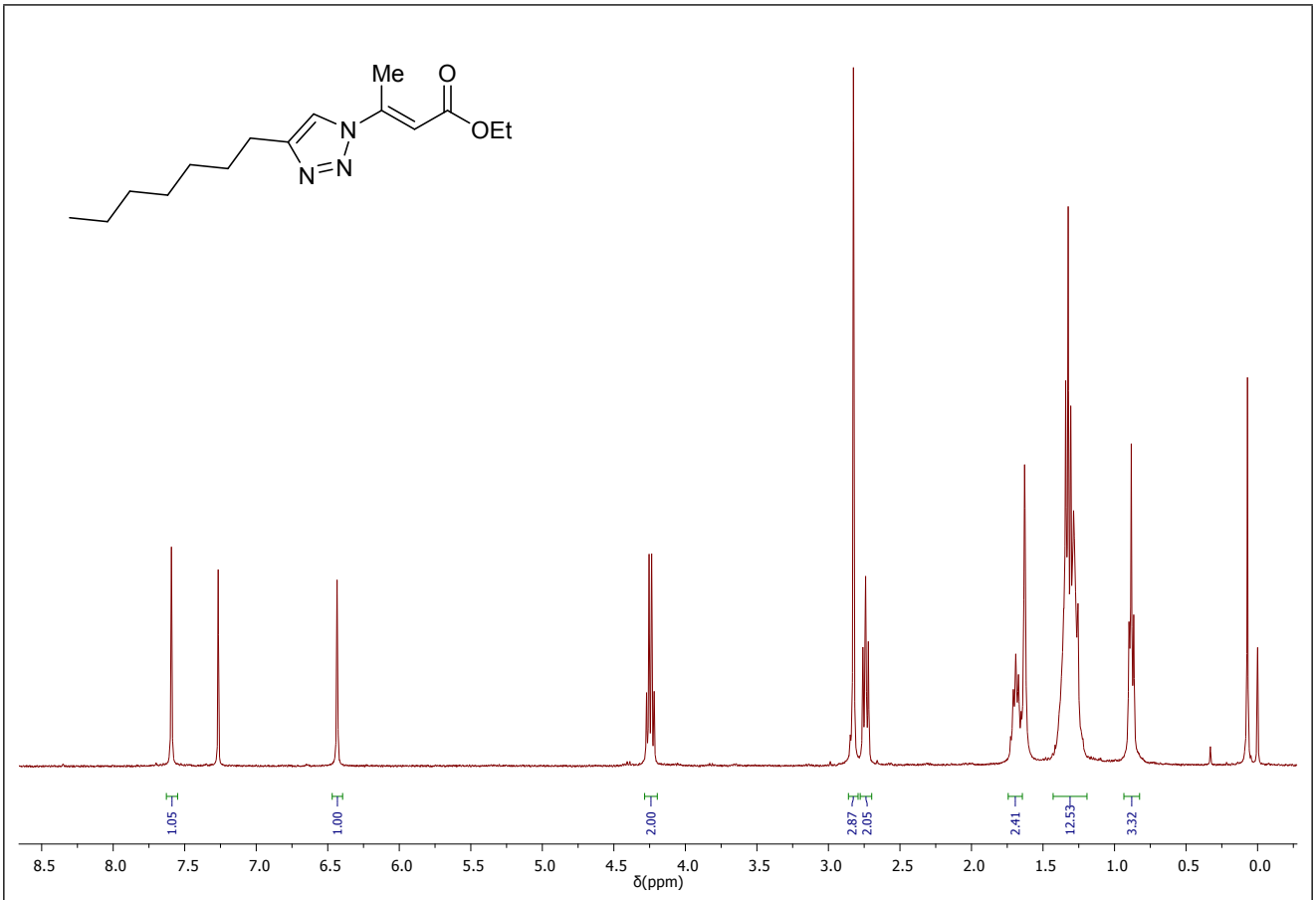
^{13}C NMR spectrum for compound **4f** in $CDCl_3$, 100 MHz



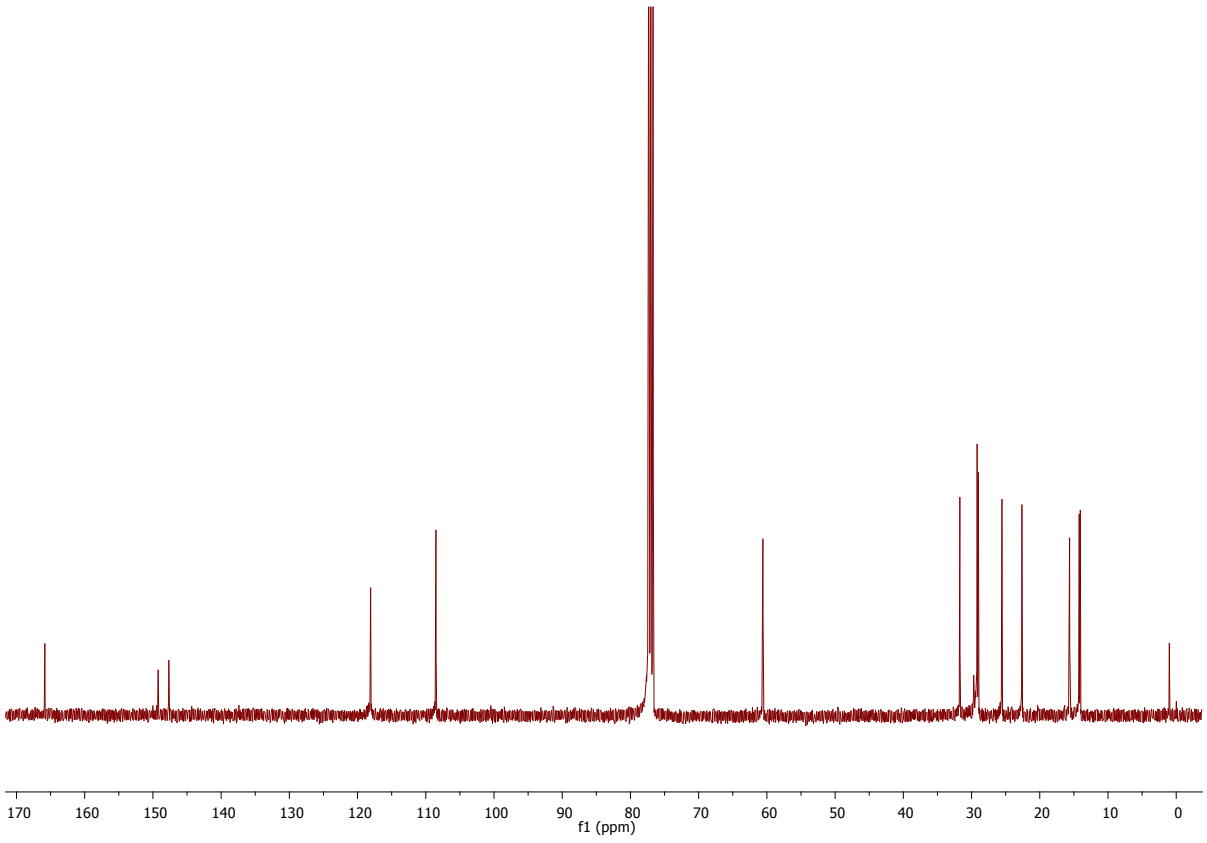
^{1}H NMR spectrum for compound **4g** in $CDCl_3$, 400 MHz



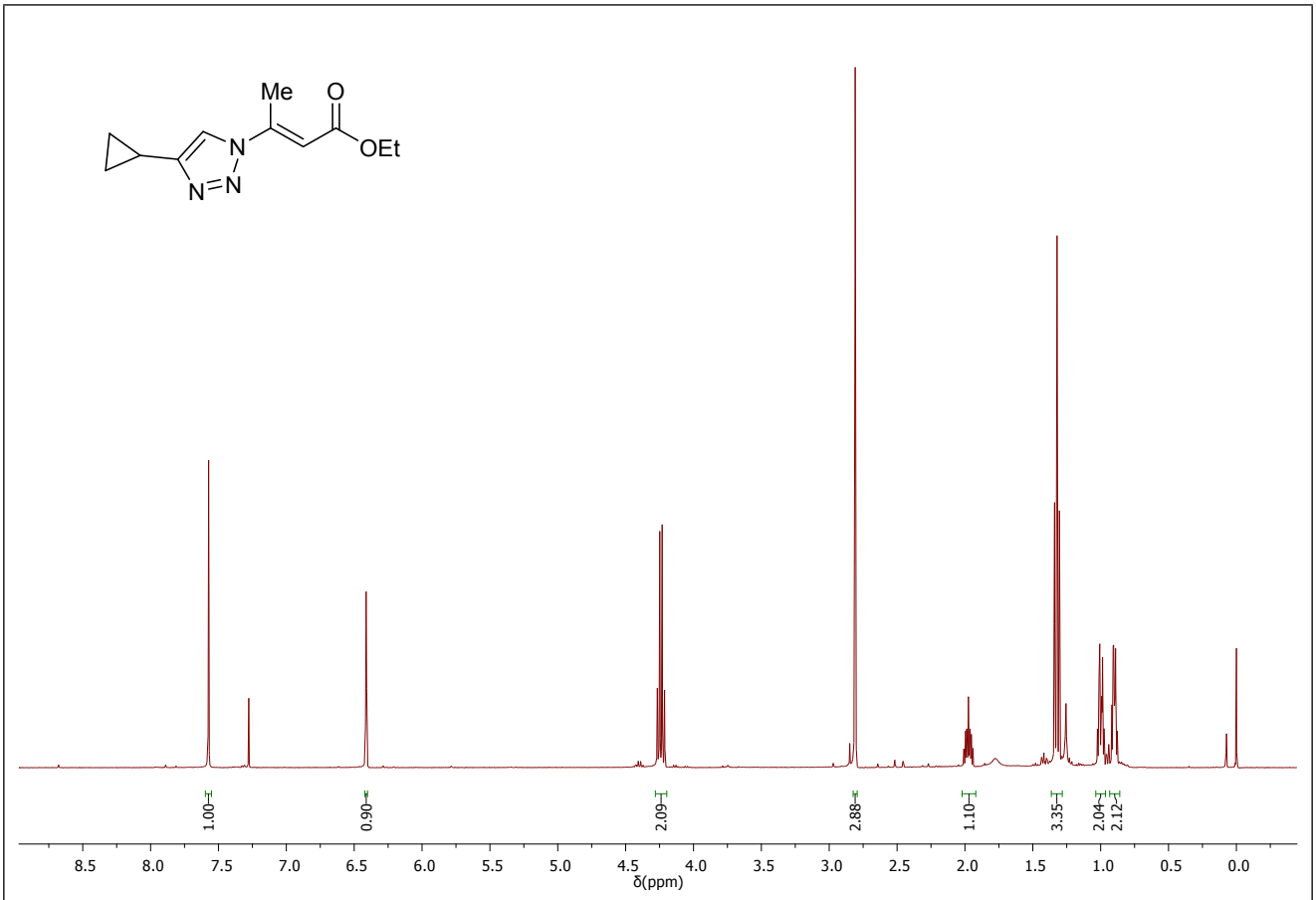
^{13}C NMR spectrum for compound **4g** in $CDCl_3$, 100 MHz



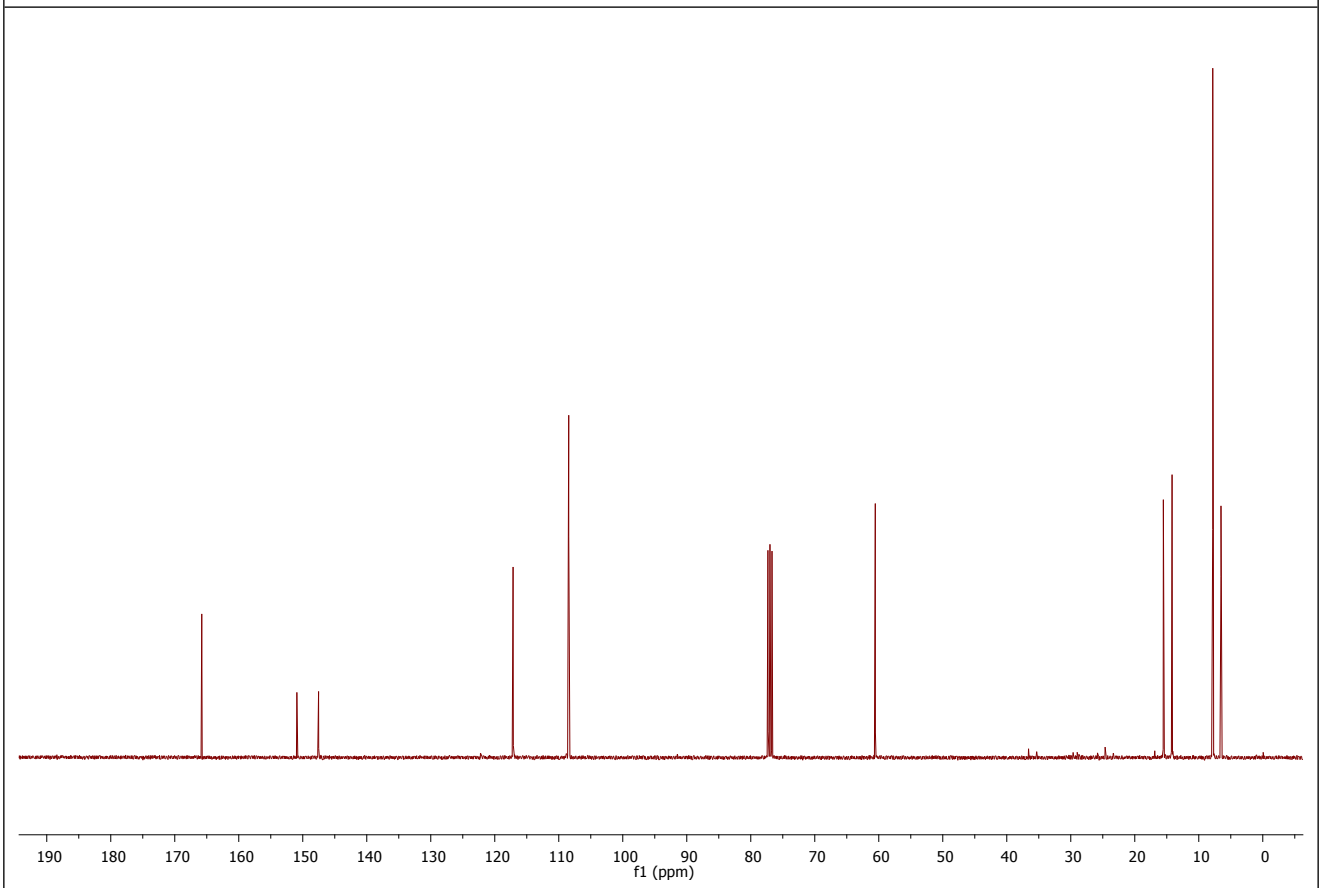
^{1}H NMR spectrum for compound **4h** in $CDCl_3$, 400 MHz



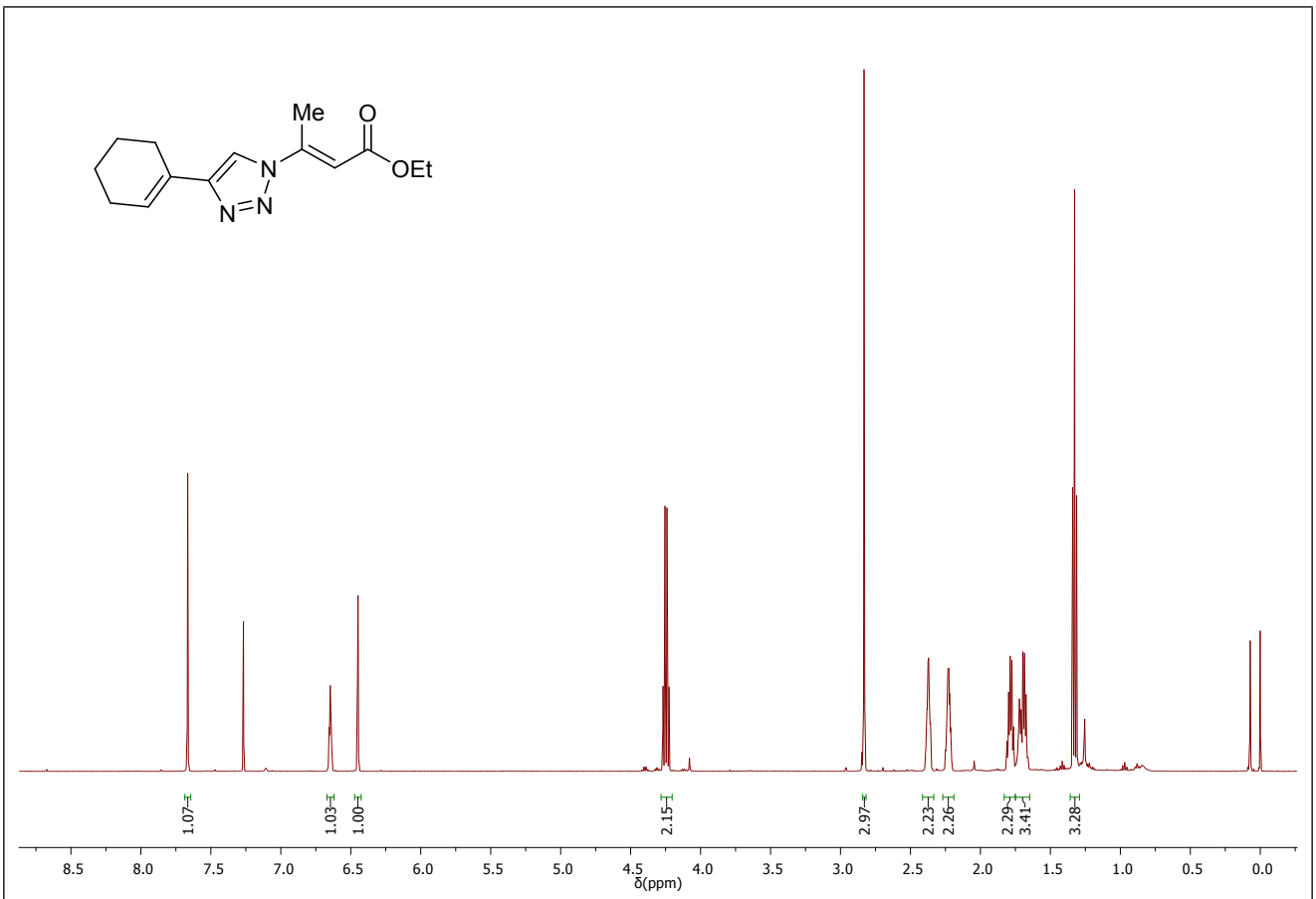
^{13}C NMR spectrum for compound **4h** in $CDCl_3$, 100 MHz



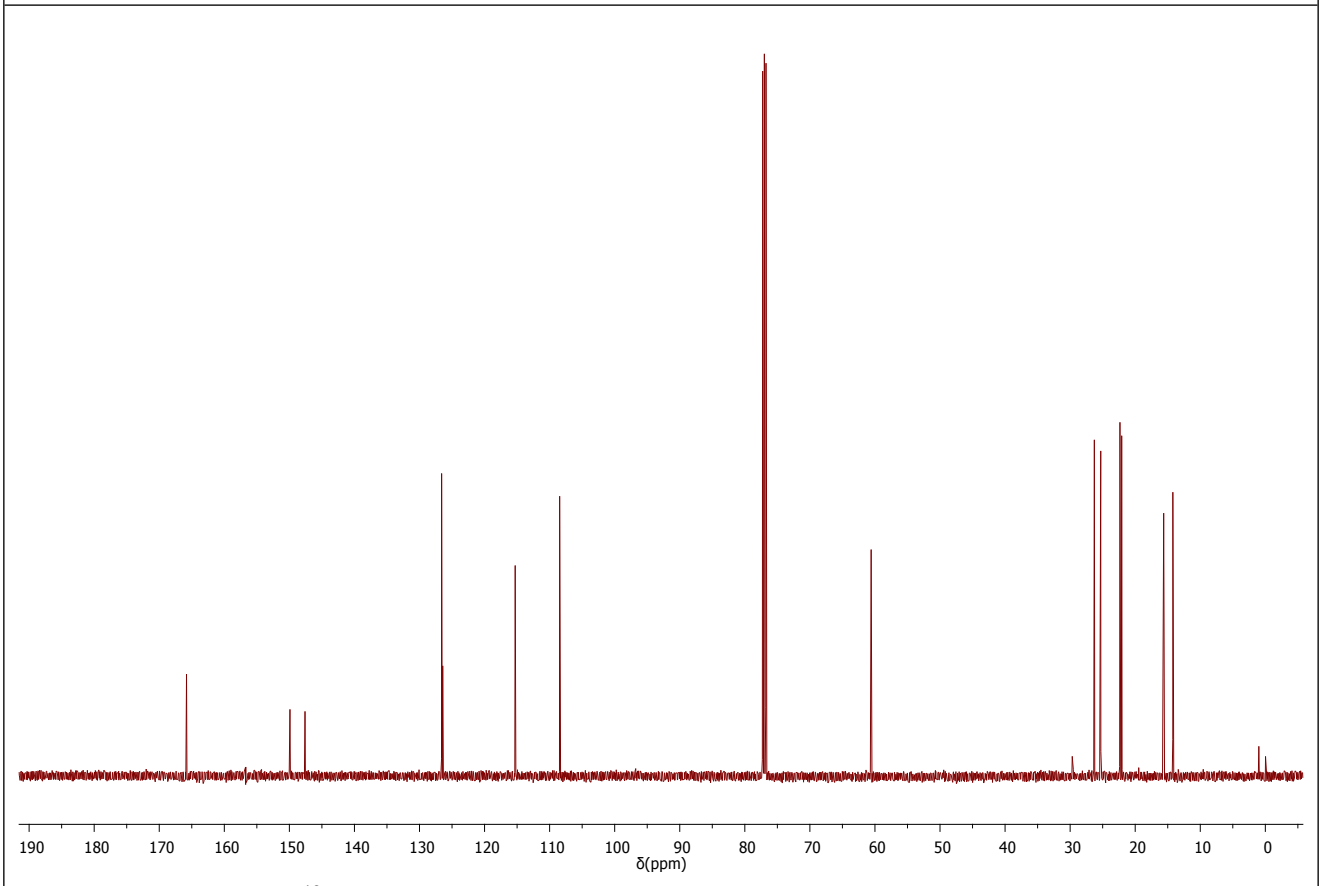
^{1}H NMR spectrum for compound **4i** in $CDCl_3$, 400 MHz



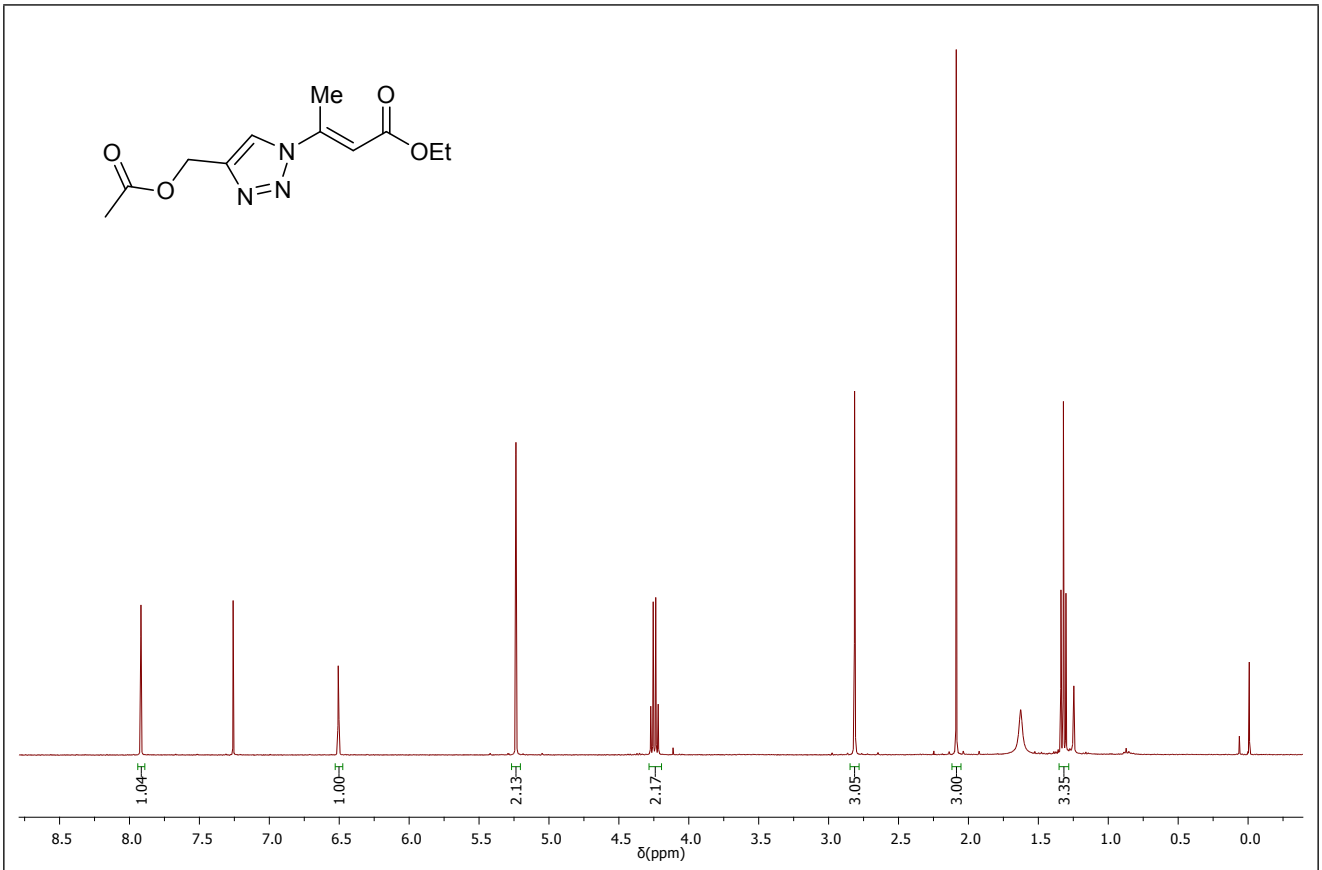
^{13}C NMR spectrum for compound **4i** in $CDCl_3$, 100 MHz



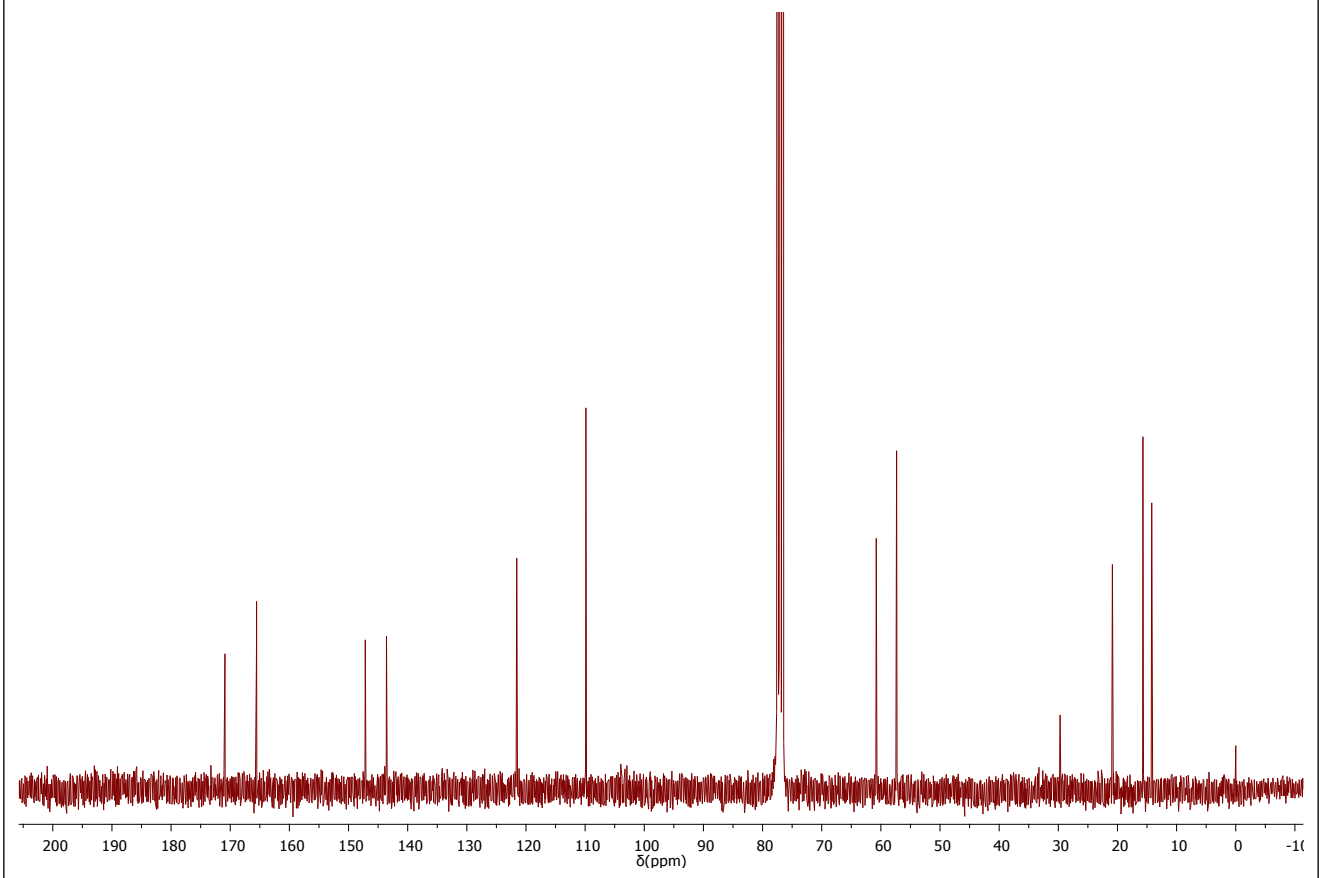
^{1}H NMR spectrum for compound **4j** in $CDCl_3$, 400 MHz



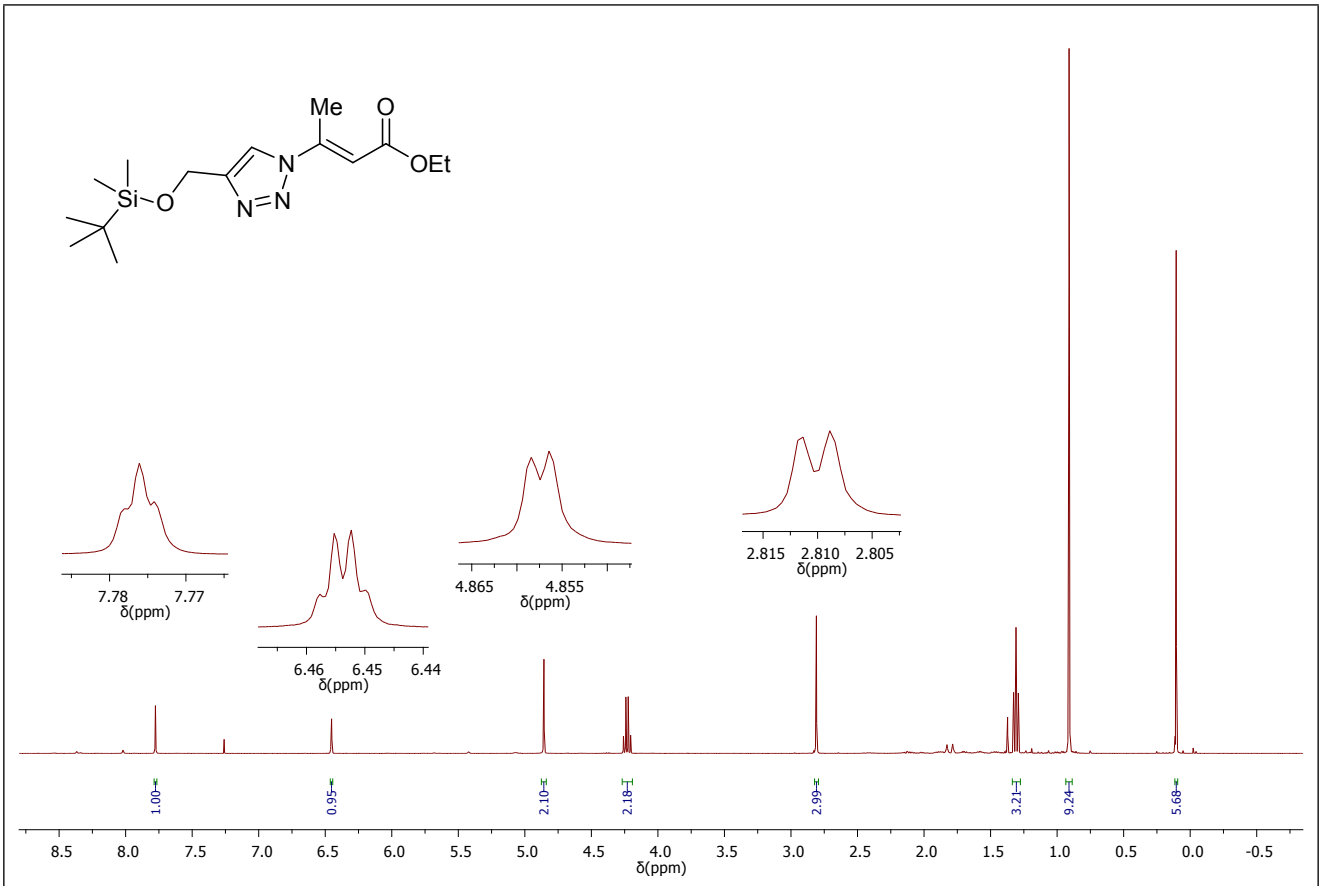
^{13}C NMR spectrum for compound **4j** in $CDCl_3$, 100 MHz



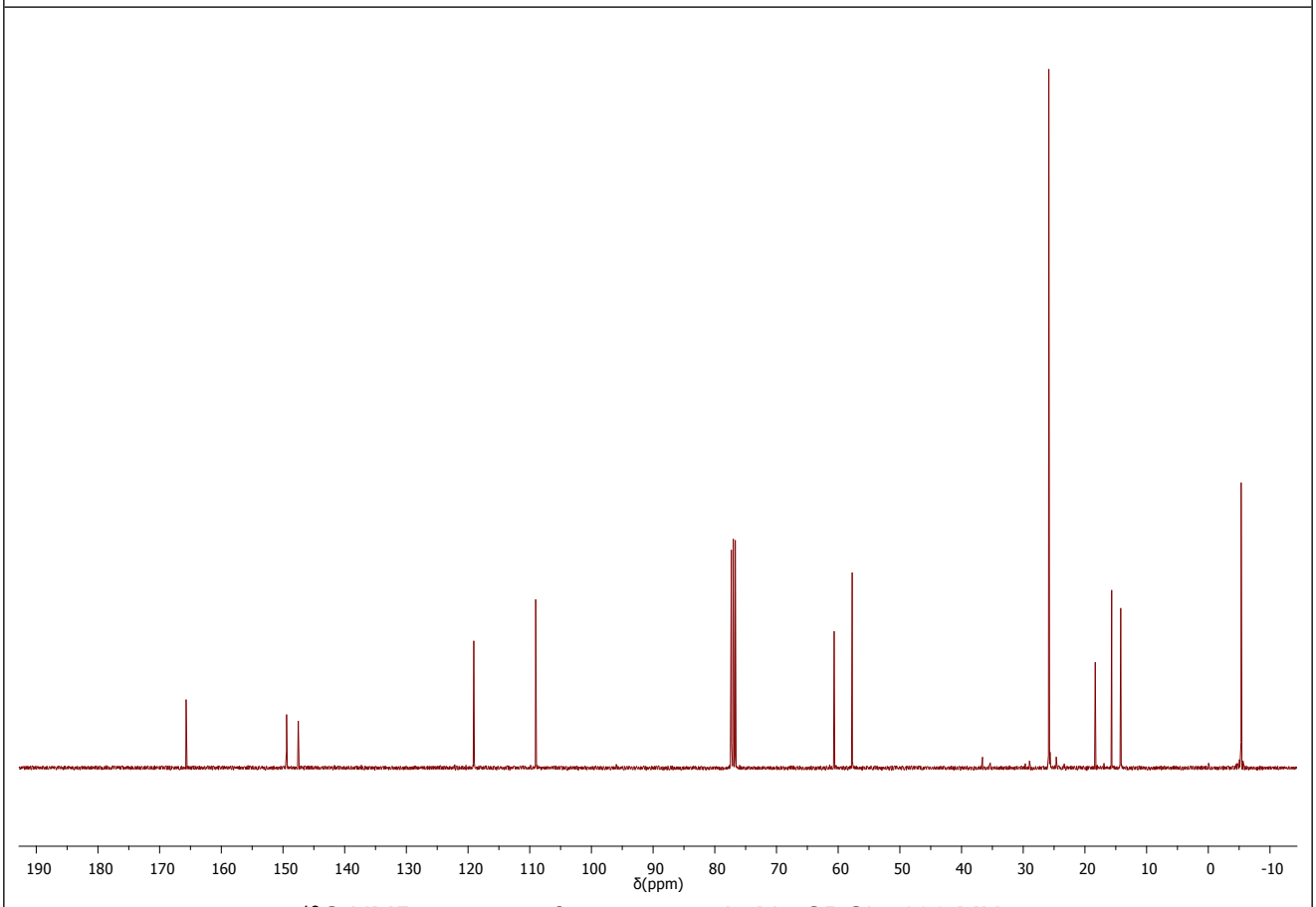
^{1}H NMR spectrum for compound **4k** in $CDCl_3$, 400 MHz



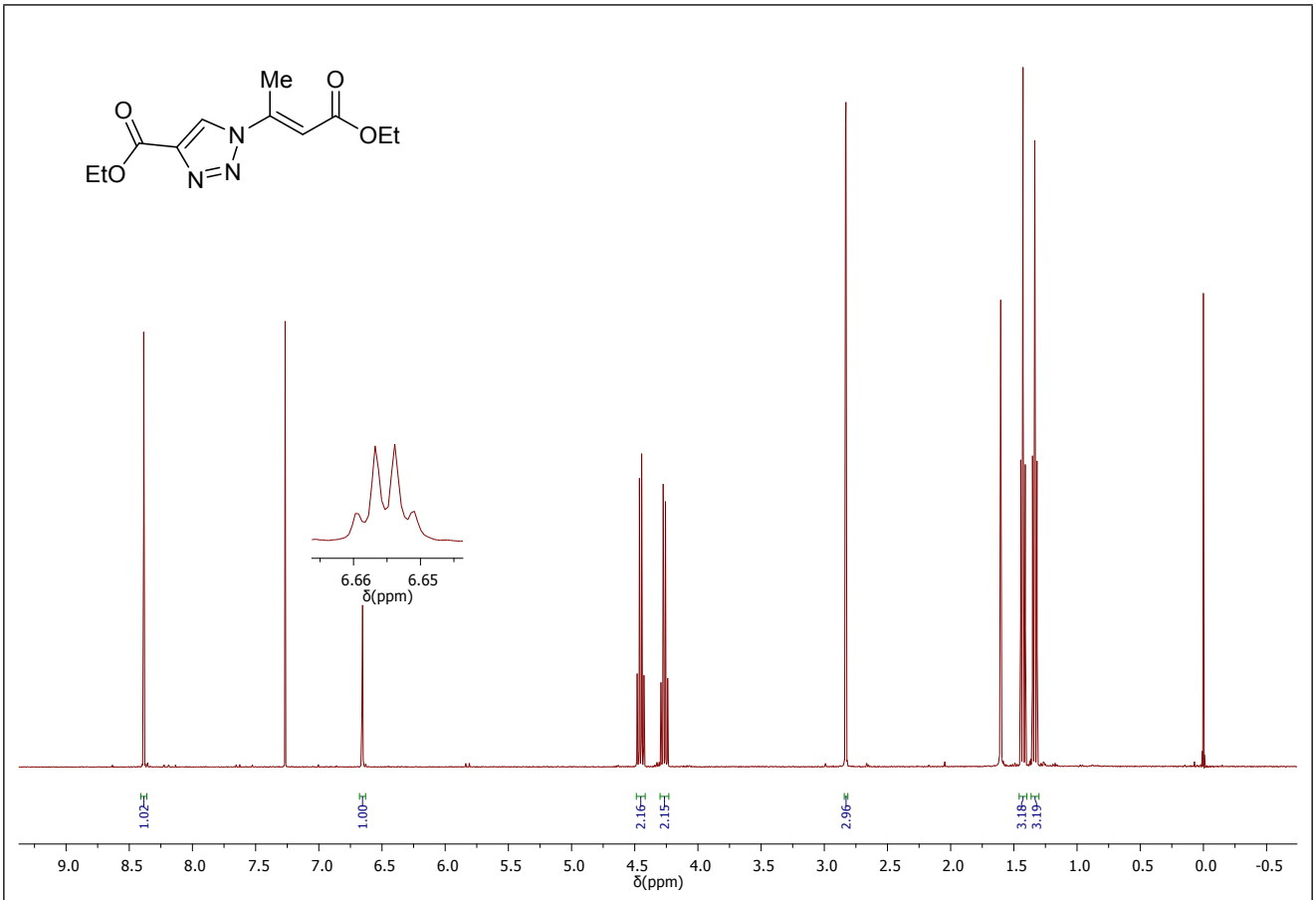
^{13}C NMR spectrum for compound **4k** in $CDCl_3$, 100 MHz



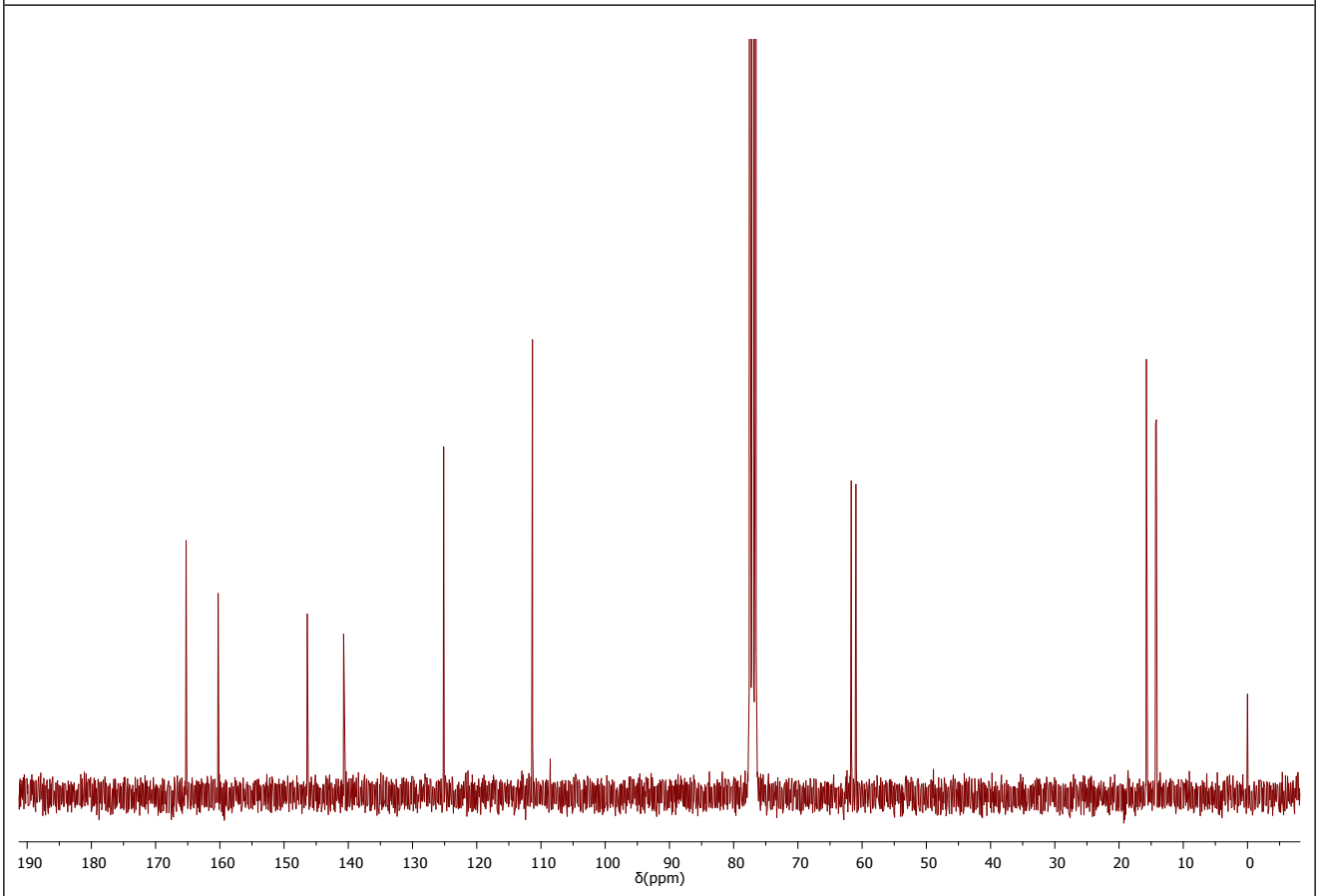
^{1}H NMR spectrum for compound **4l** in $CDCl_3$, 400 MHz



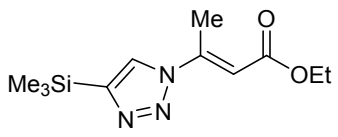
^{13}C NMR spectrum for compound **4l** in $CDCl_3$, 100 MHz



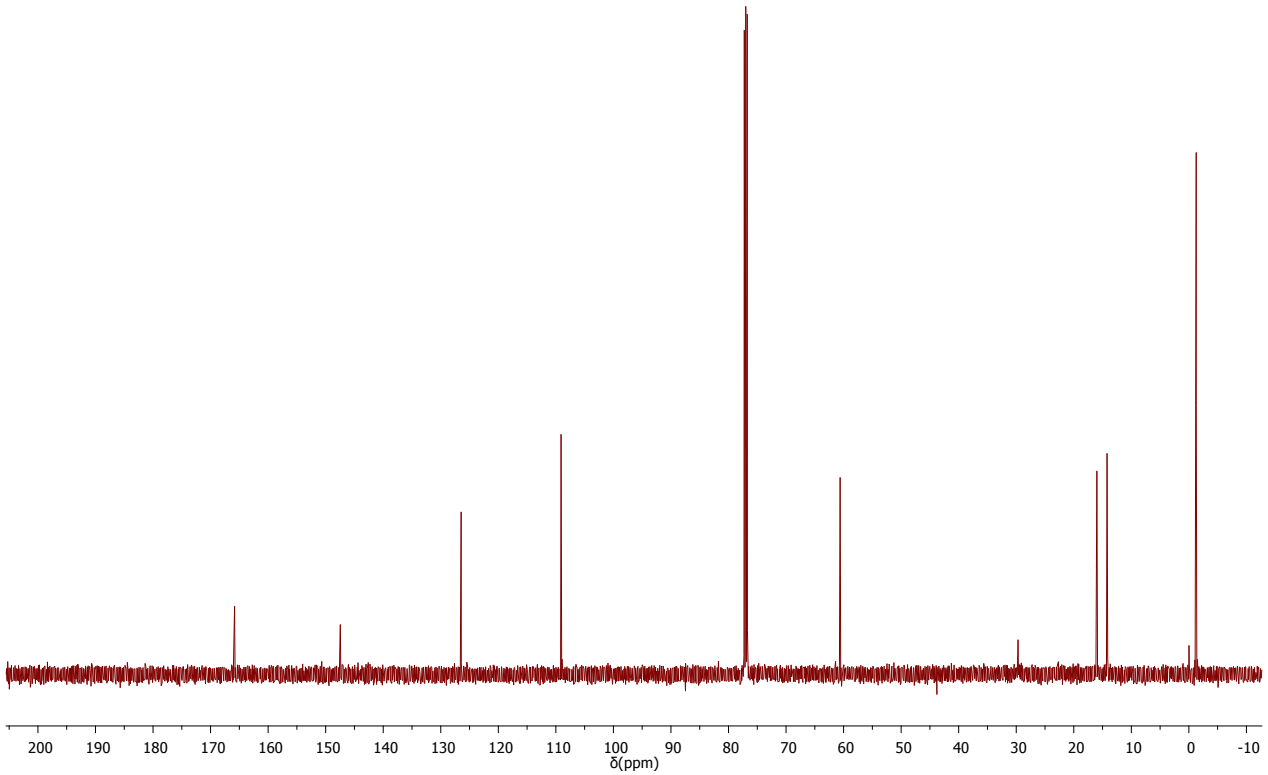
^{1}H NMR spectrum for compound **4m** in $CDCl_3$, 400 MHz



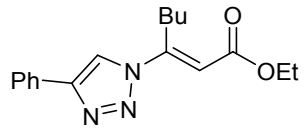
^{13}C NMR spectrum for compound **4m** in $CDCl_3$, 100 MHz

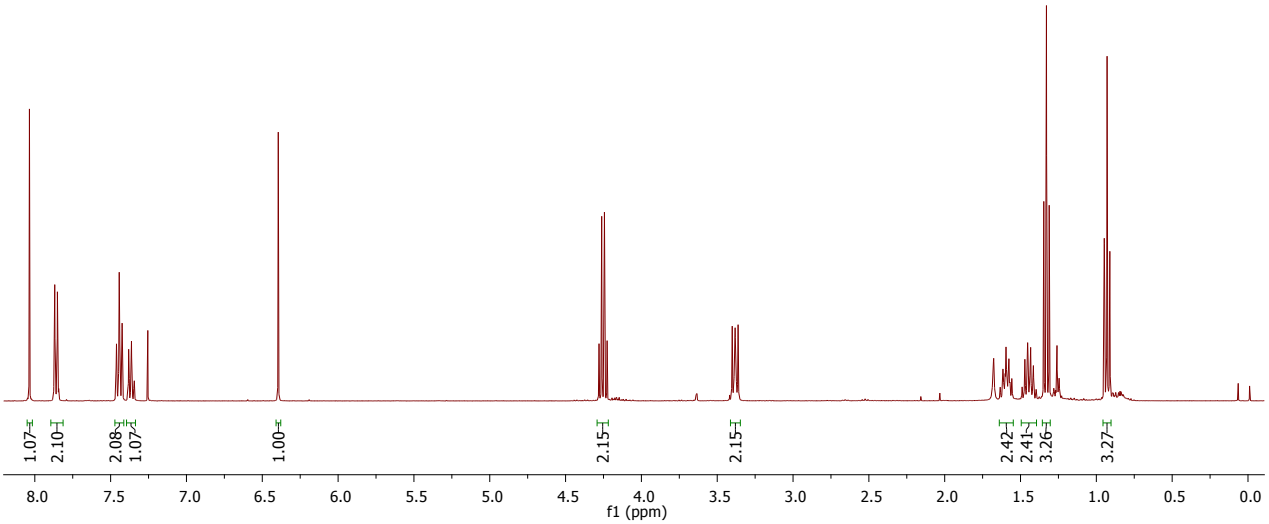


^{1}H NMR spectrum for compound **4n** in $CDCl_3$, 400 MHz

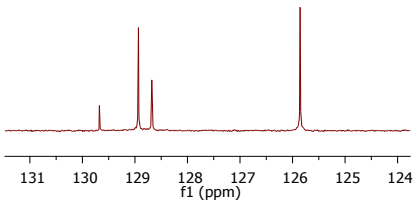


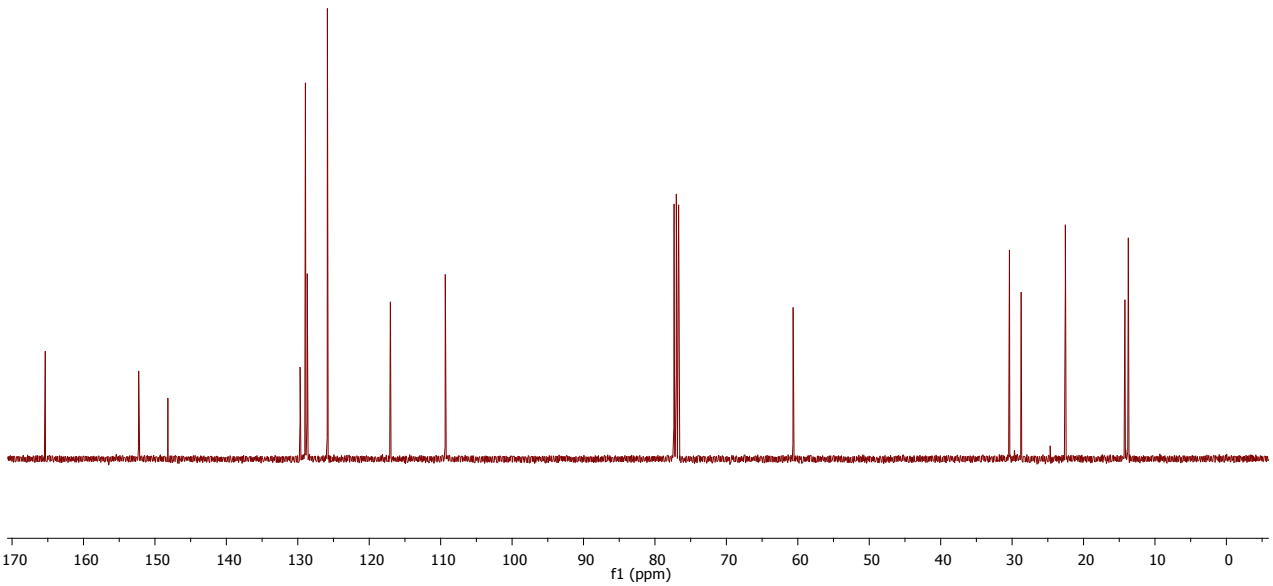
^{13}C NMR spectrum for compound **4n** in $CDCl_3$, 100 MHz



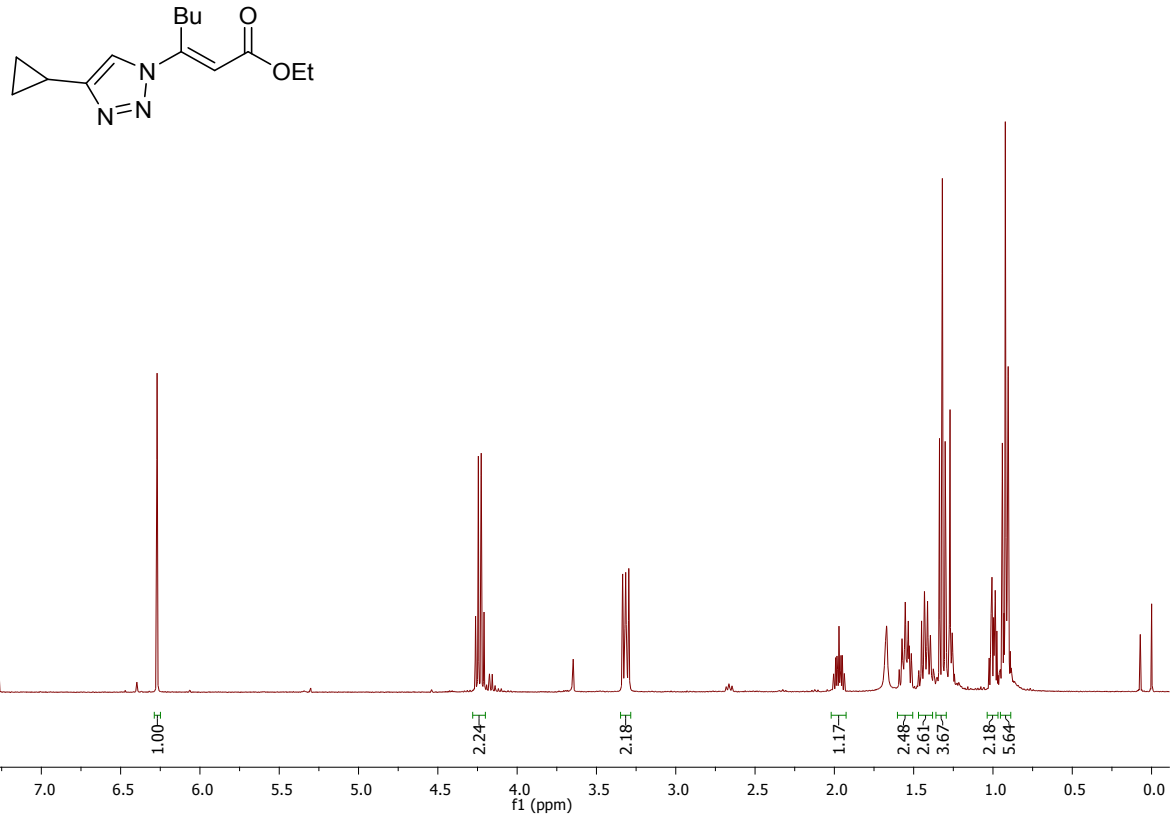


^{1}H NMR spectrum for compound **4o** in $CDCl_3$, 400 MHz

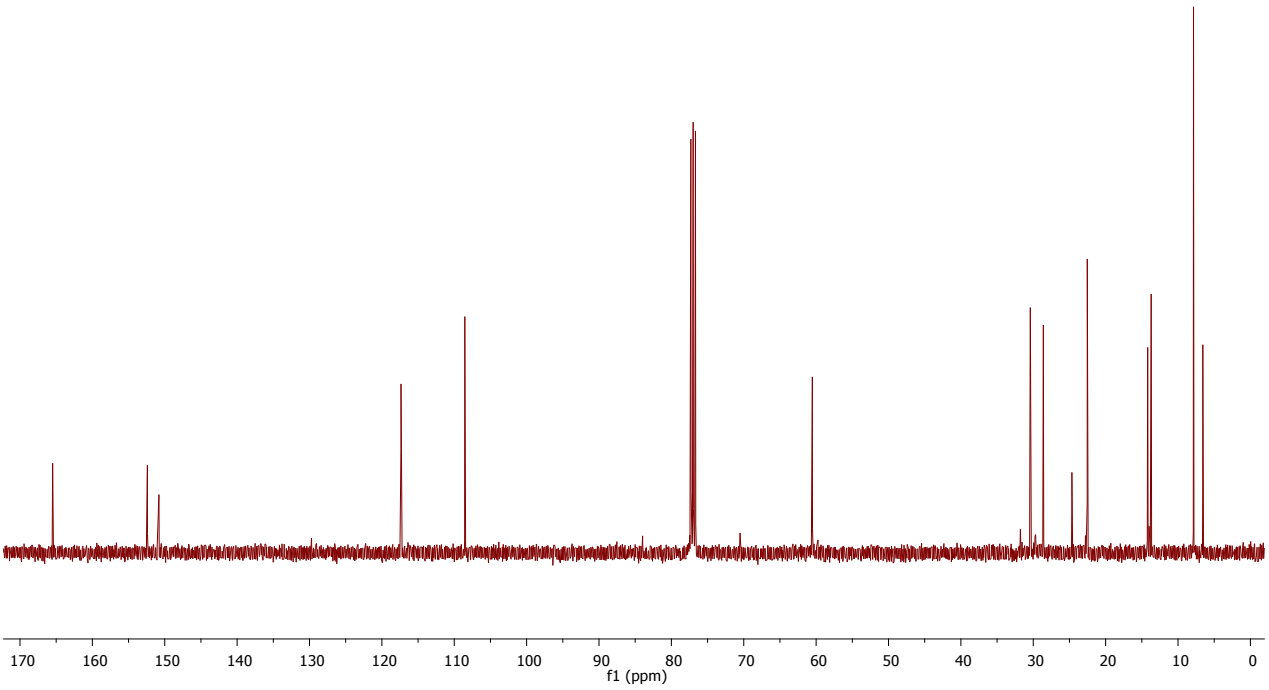




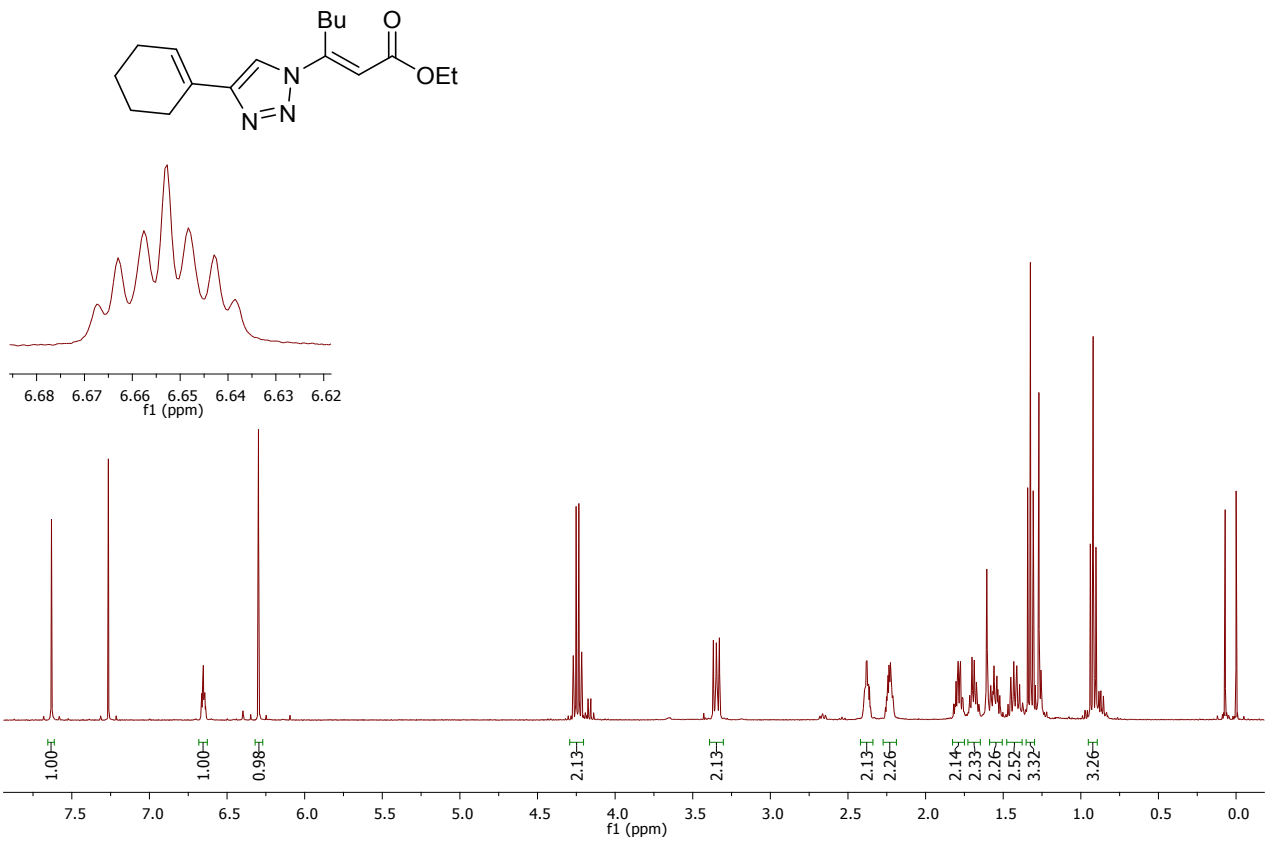
^{13}C NMR spectrum for compound **4o** in $CDCl_3$, 100 MHz



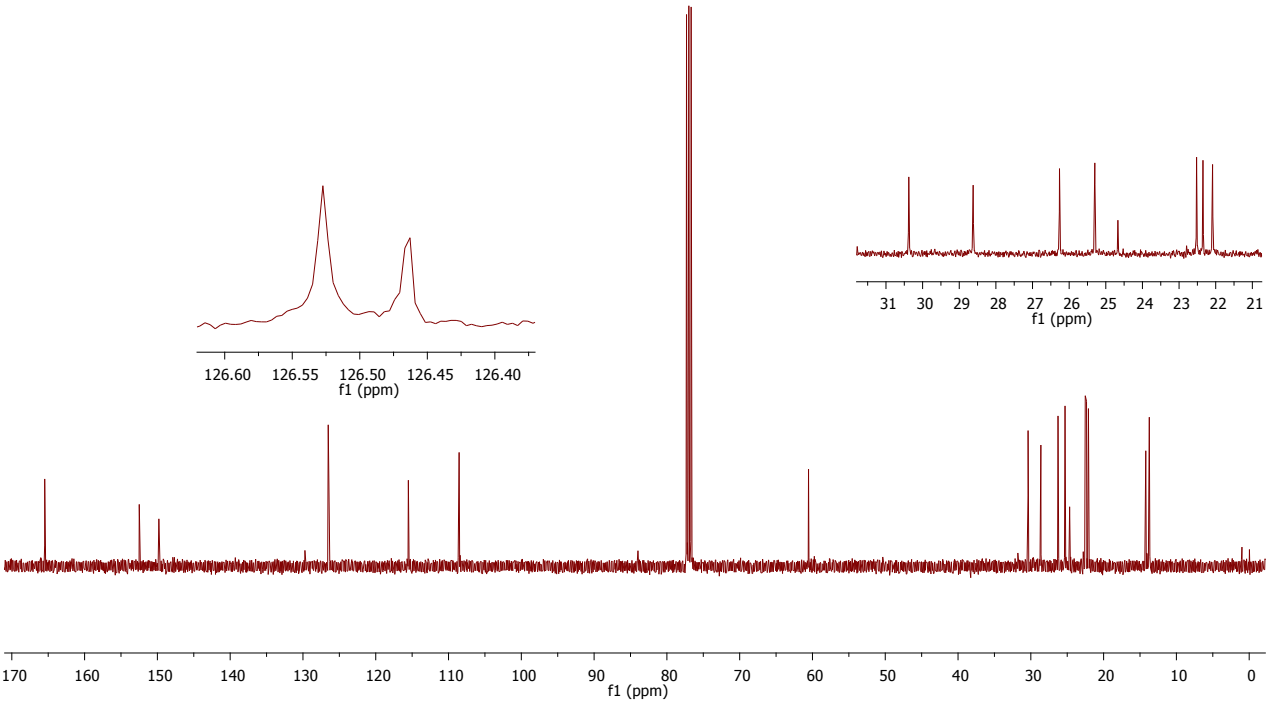
^{1}H NMR spectrum for compound **4p** in $CDCl_3$, 400 MHz



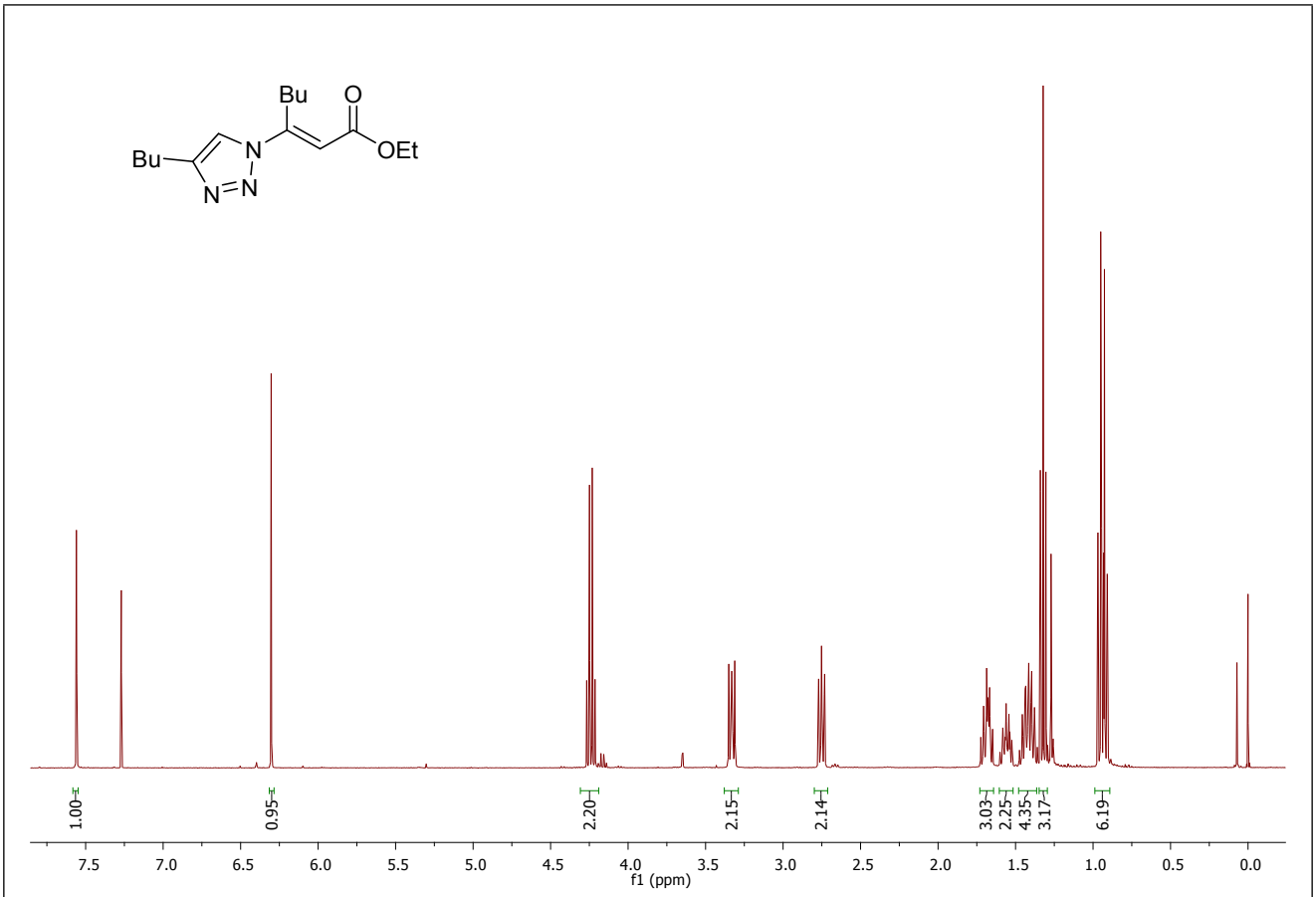
^{13}C NMR spectrum for compound **4p** in $CDCl_3$, 100 MHz



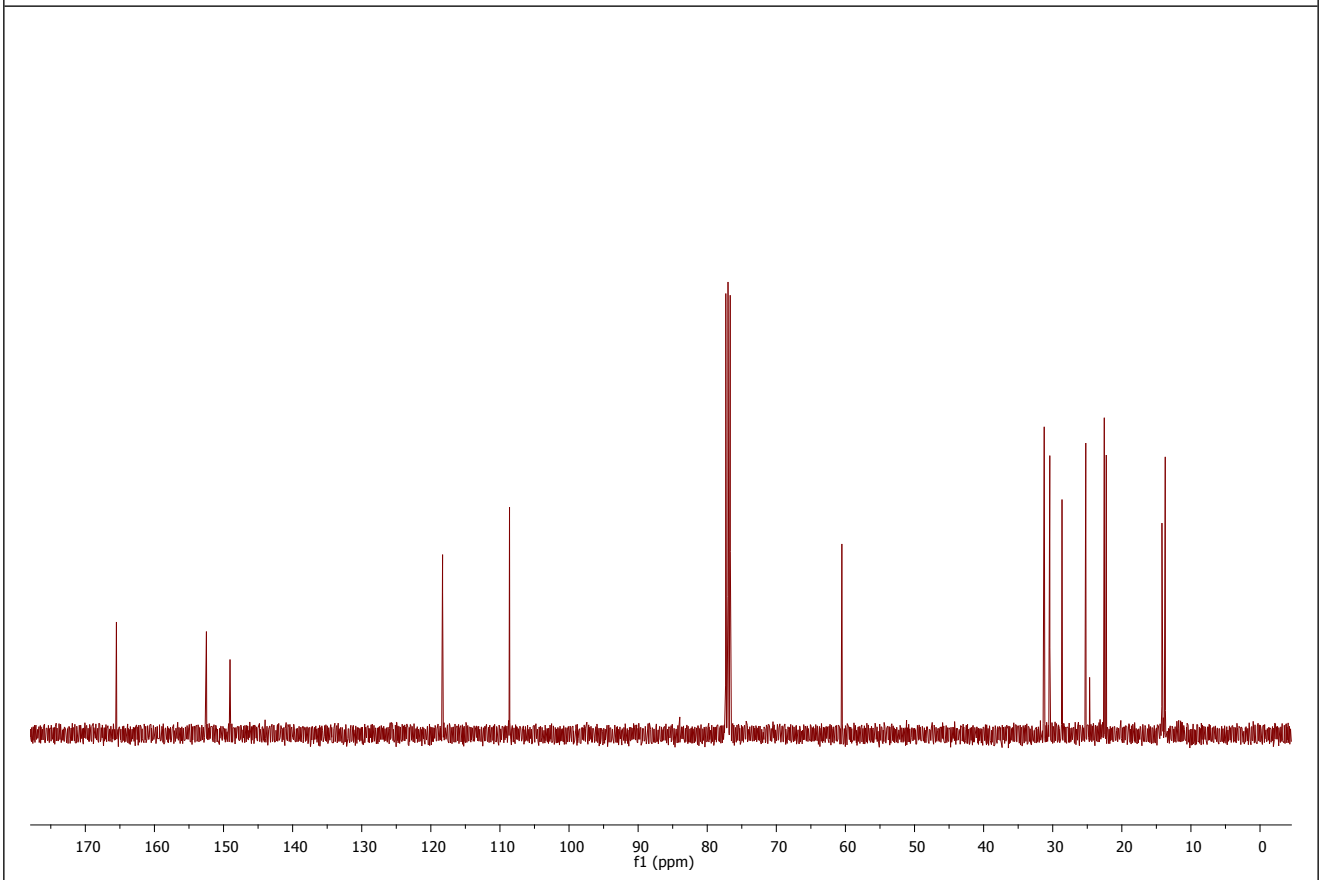
^{1}H NMR spectrum for compound **4q** in $CDCl_3$, 400 MHz



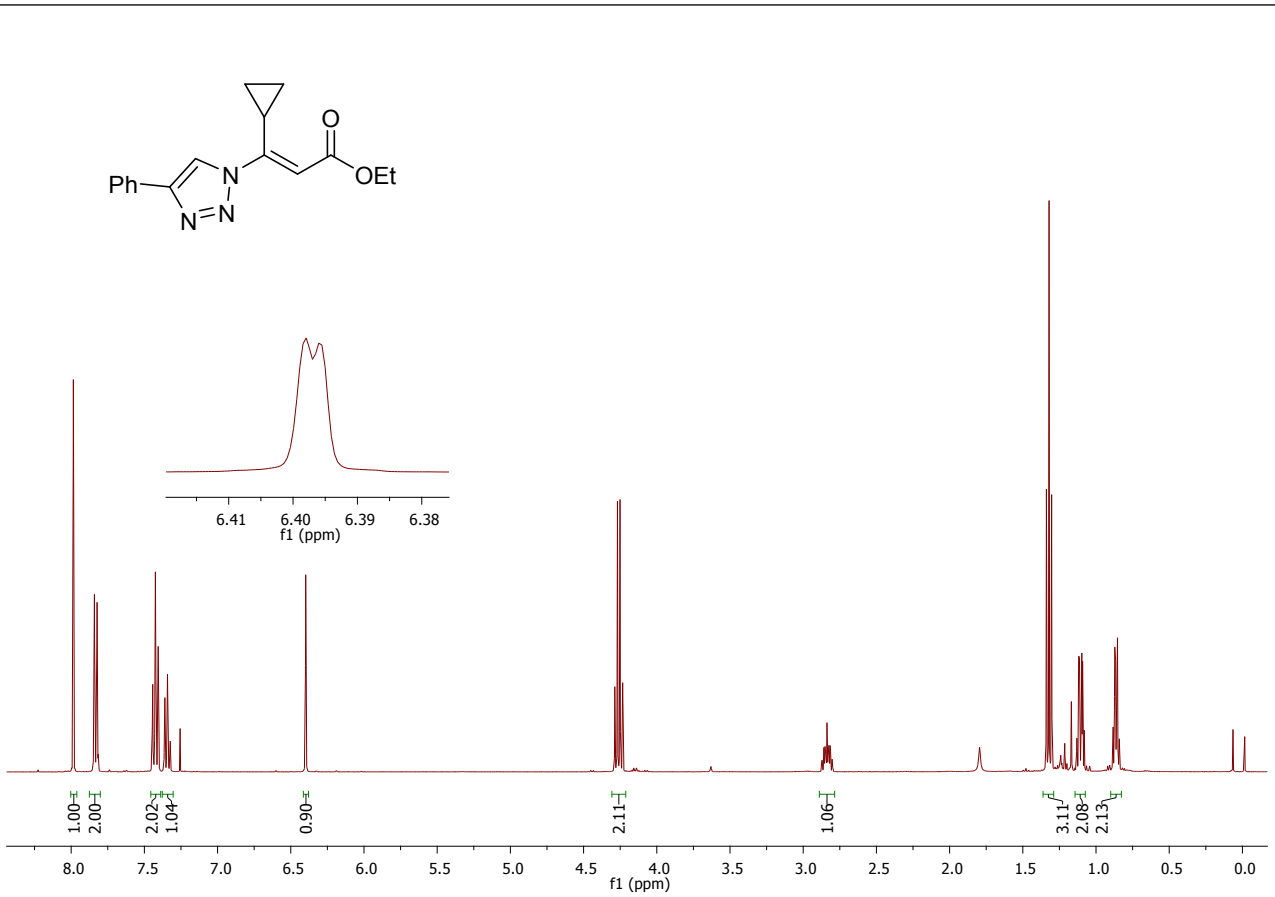
^{13}C NMR spectrum for compound **4q** in $CDCl_3$, 100 MHz



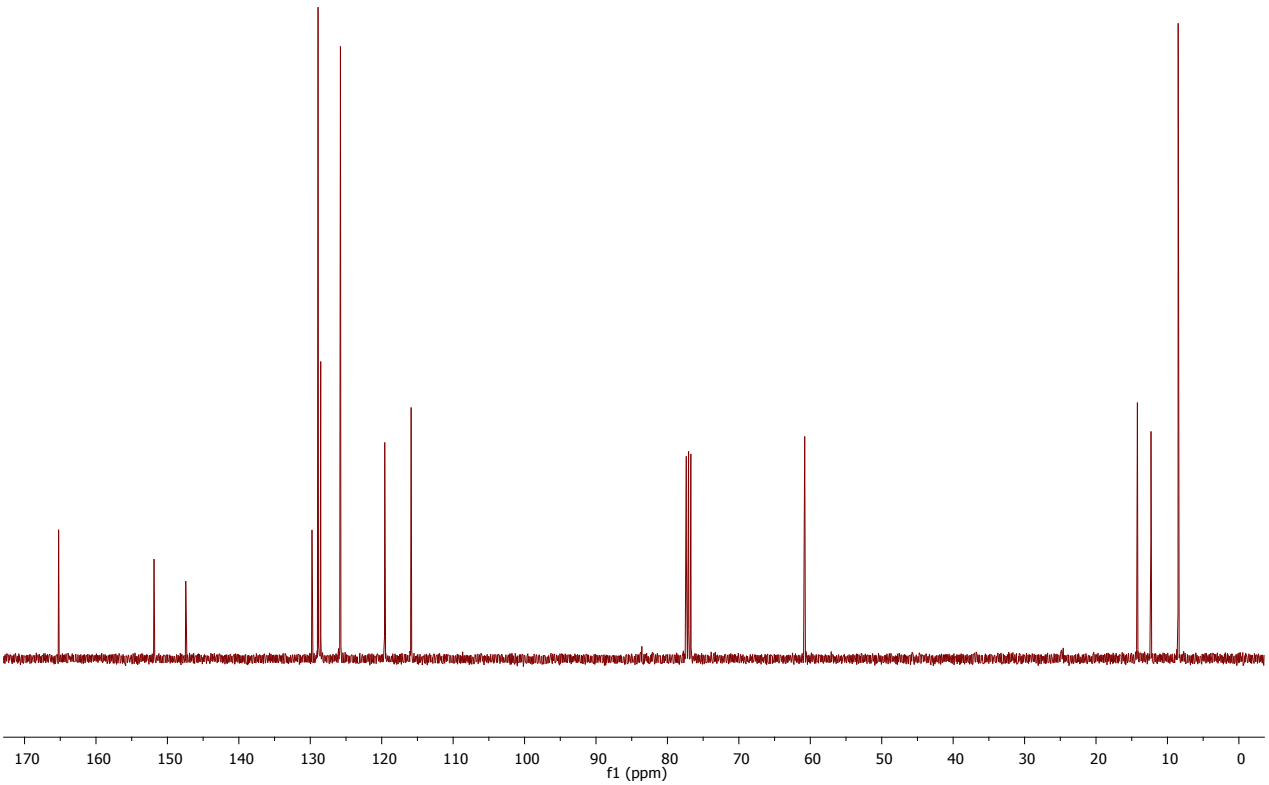
^{1}H NMR spectrum for compound **4r** in $CDCl_3$, 400 MHz



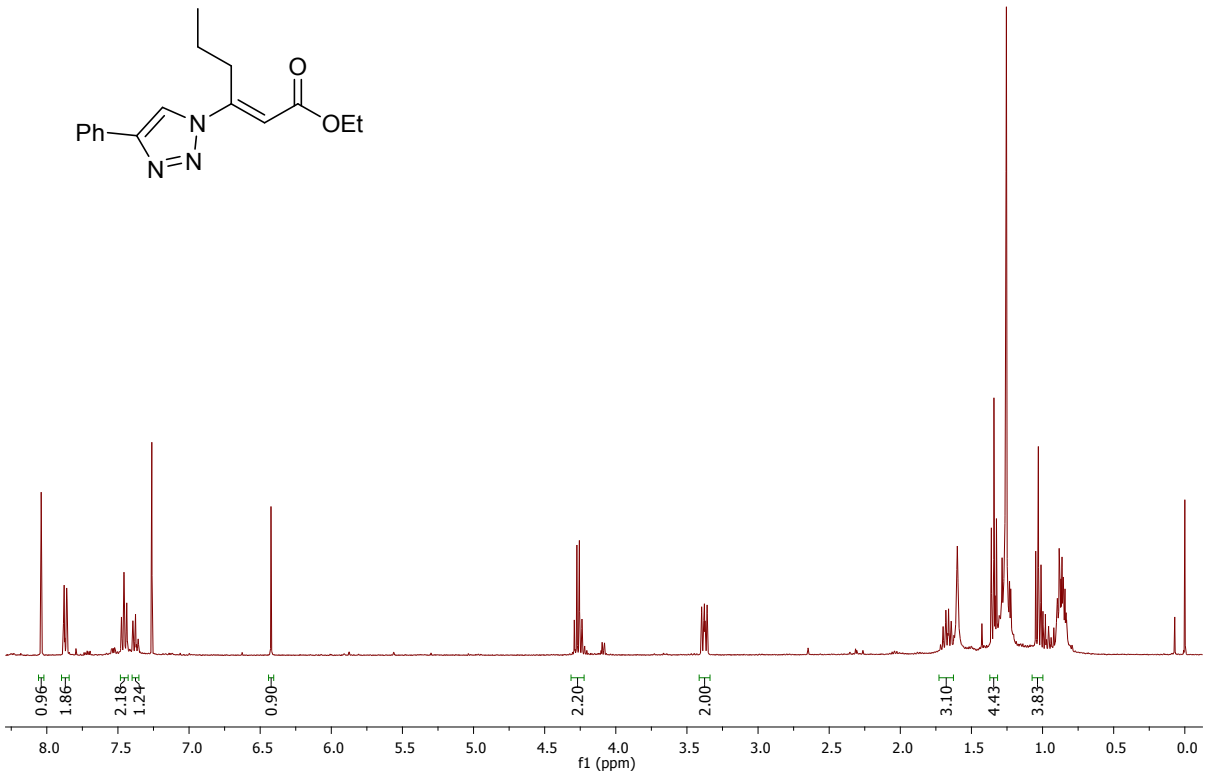
^{13}C NMR spectrum for compound **4r** in $CDCl_3$, 100 MHz



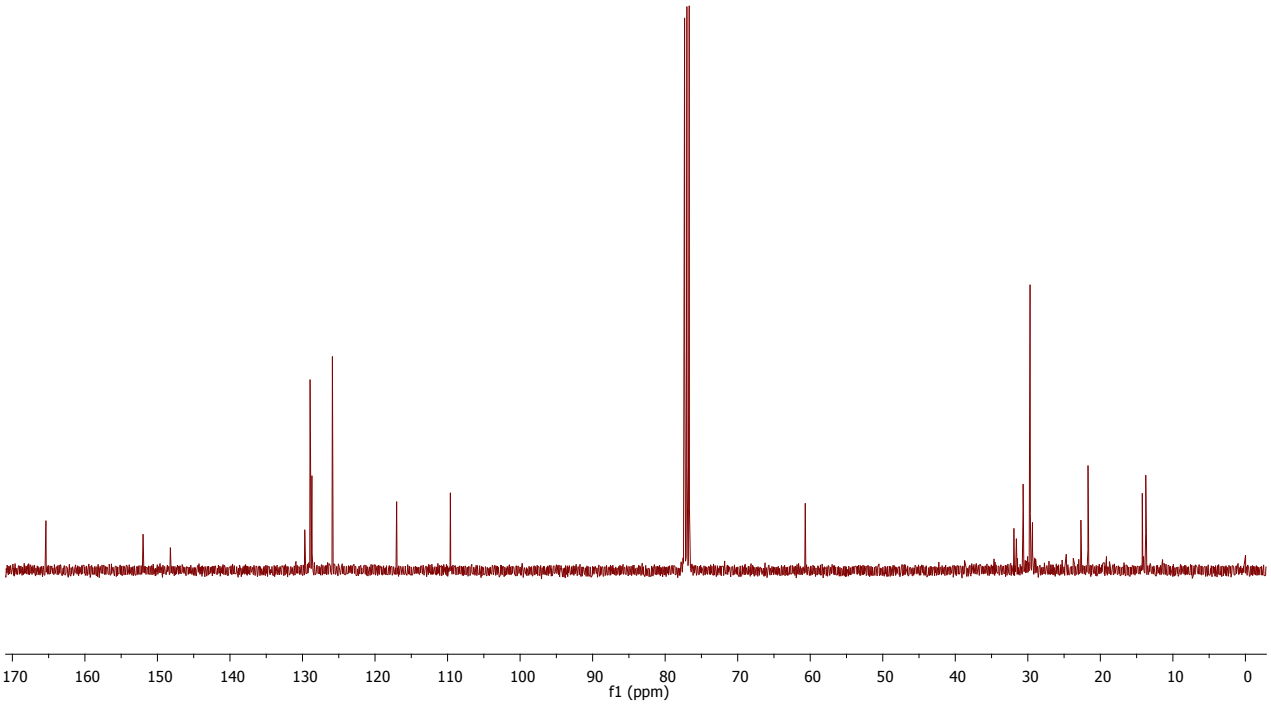
^{1}H NMR spectrum for compound **4s** in $CDCl_3$, 400 MHz



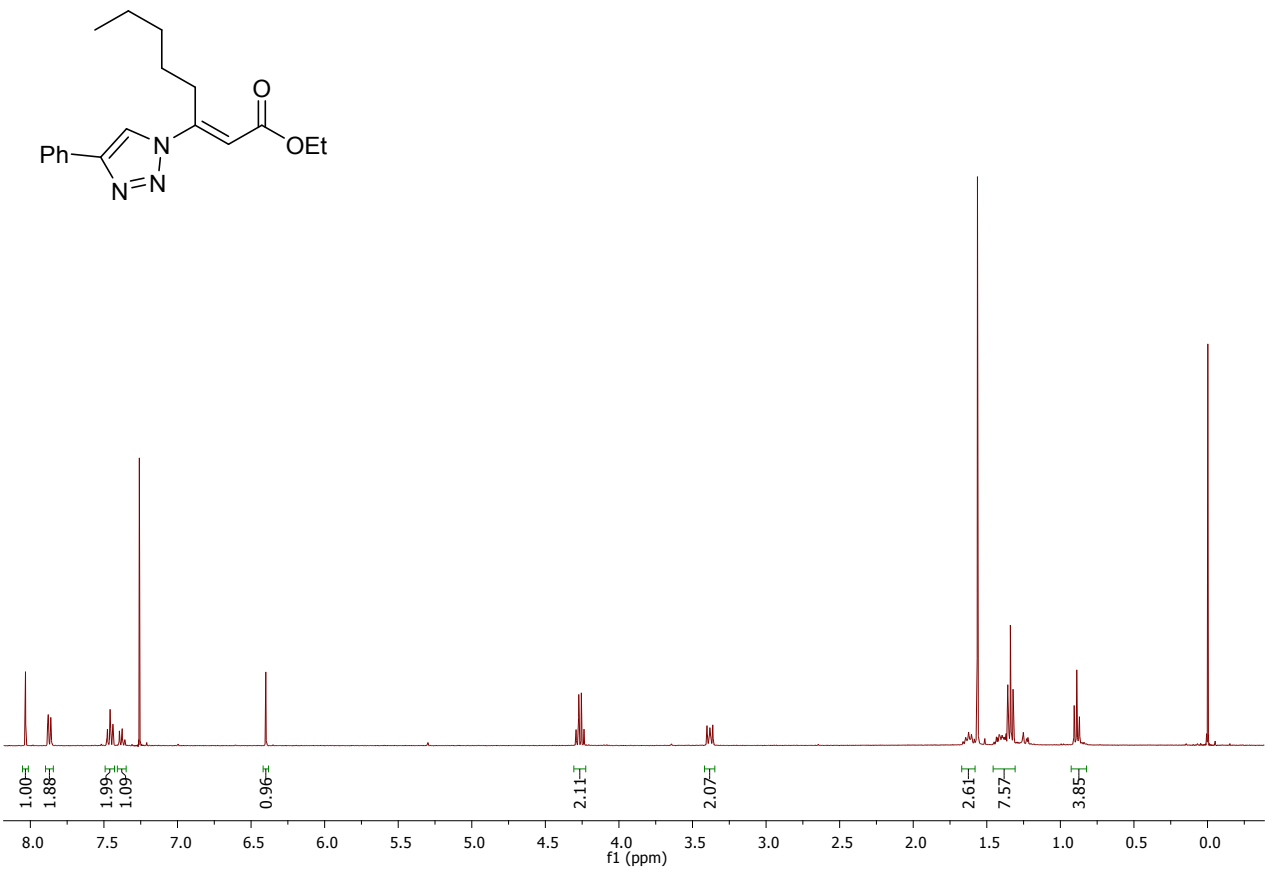
^{13}C NMR spectrum for compound **4s** in $CDCl_3$, 100 MHz



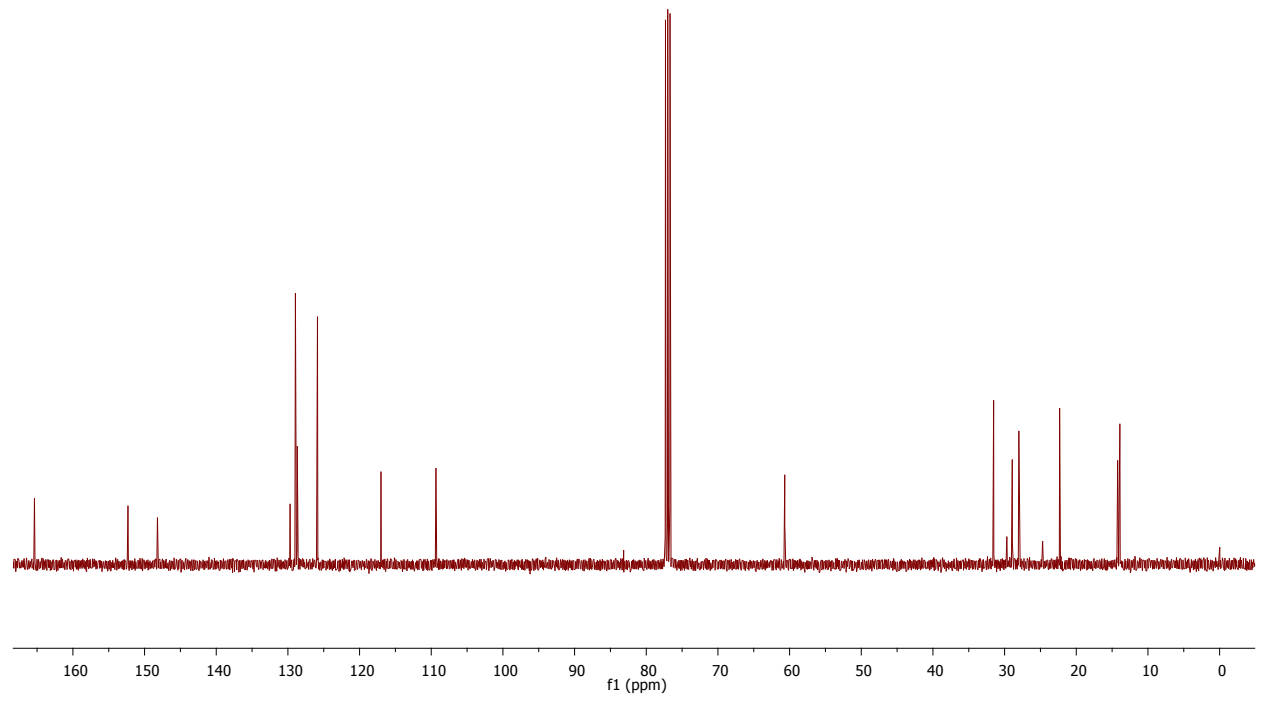
^{1}H NMR spectrum for compound **4t** in $CDCl_3$, 400 MHz



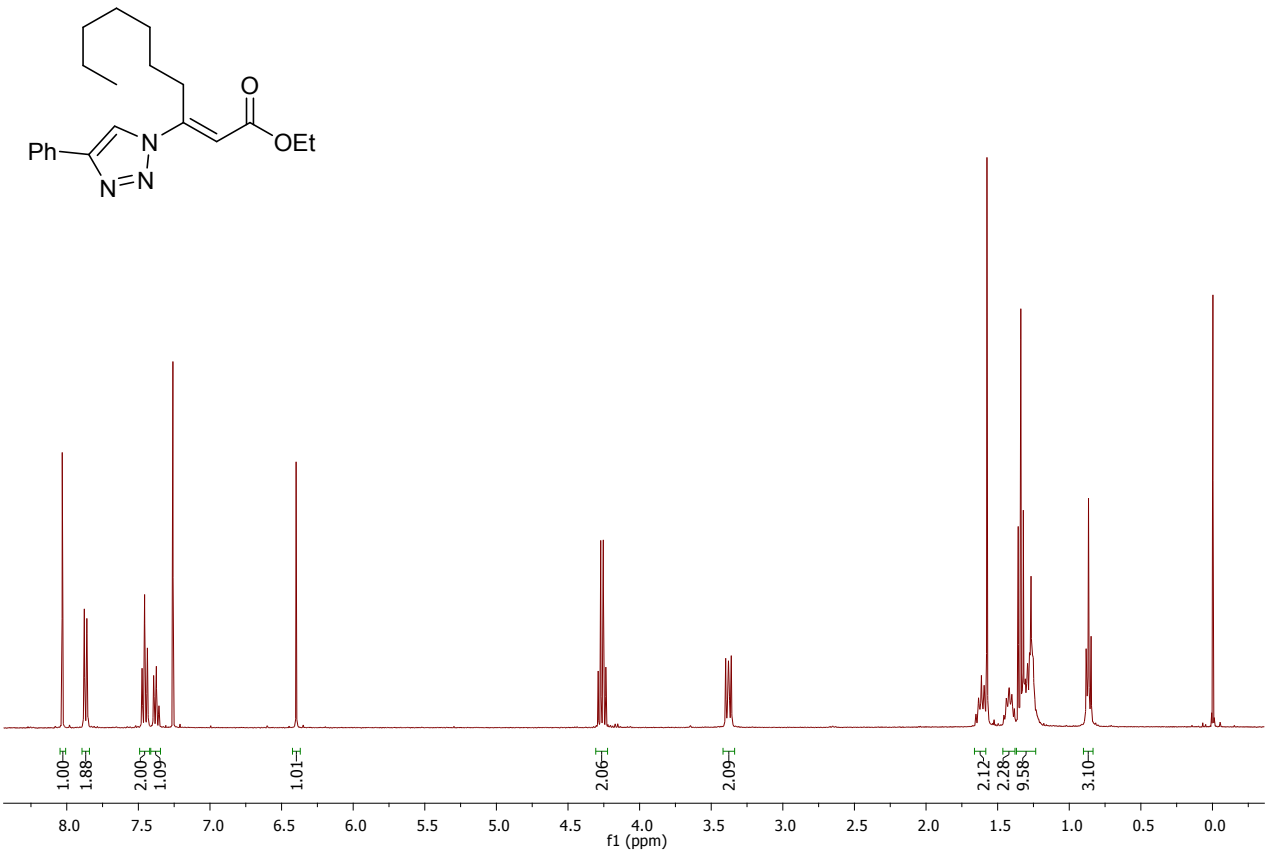
^{13}C NMR spectrum for compound **4t** in $CDCl_3$, 100 MHz



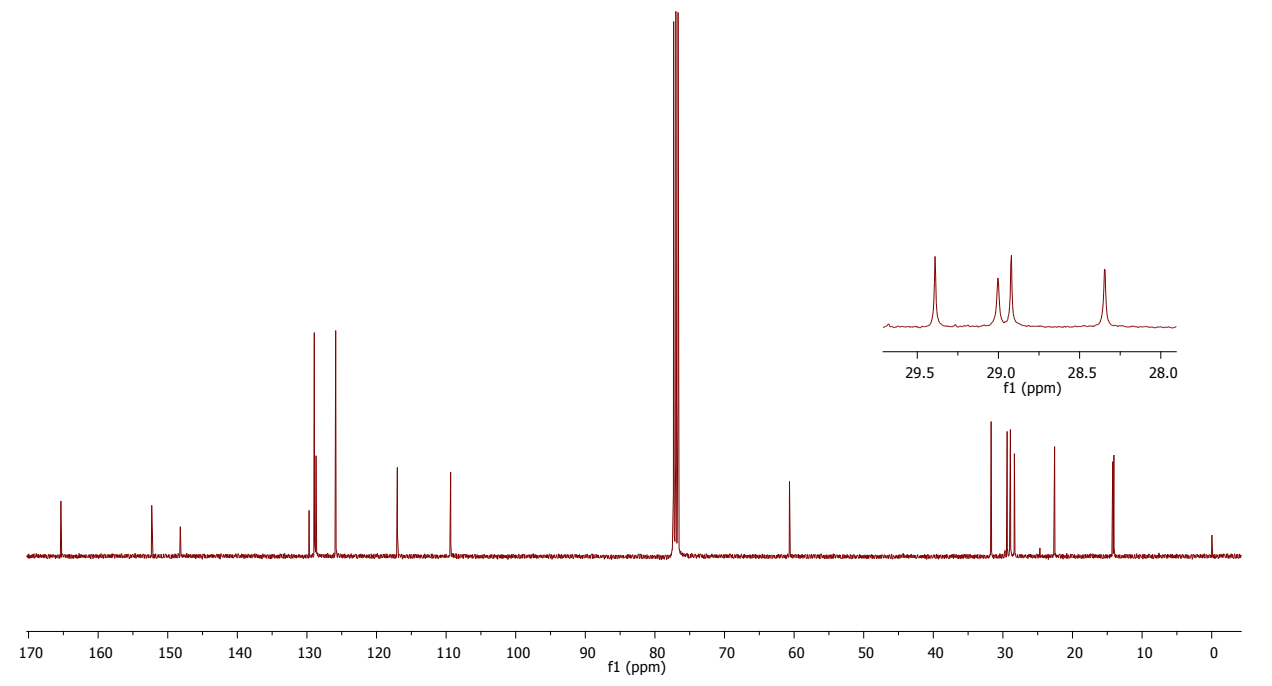
^{1}H NMR spectrum for compound **4u** in $CDCl_3$, 400 MHz



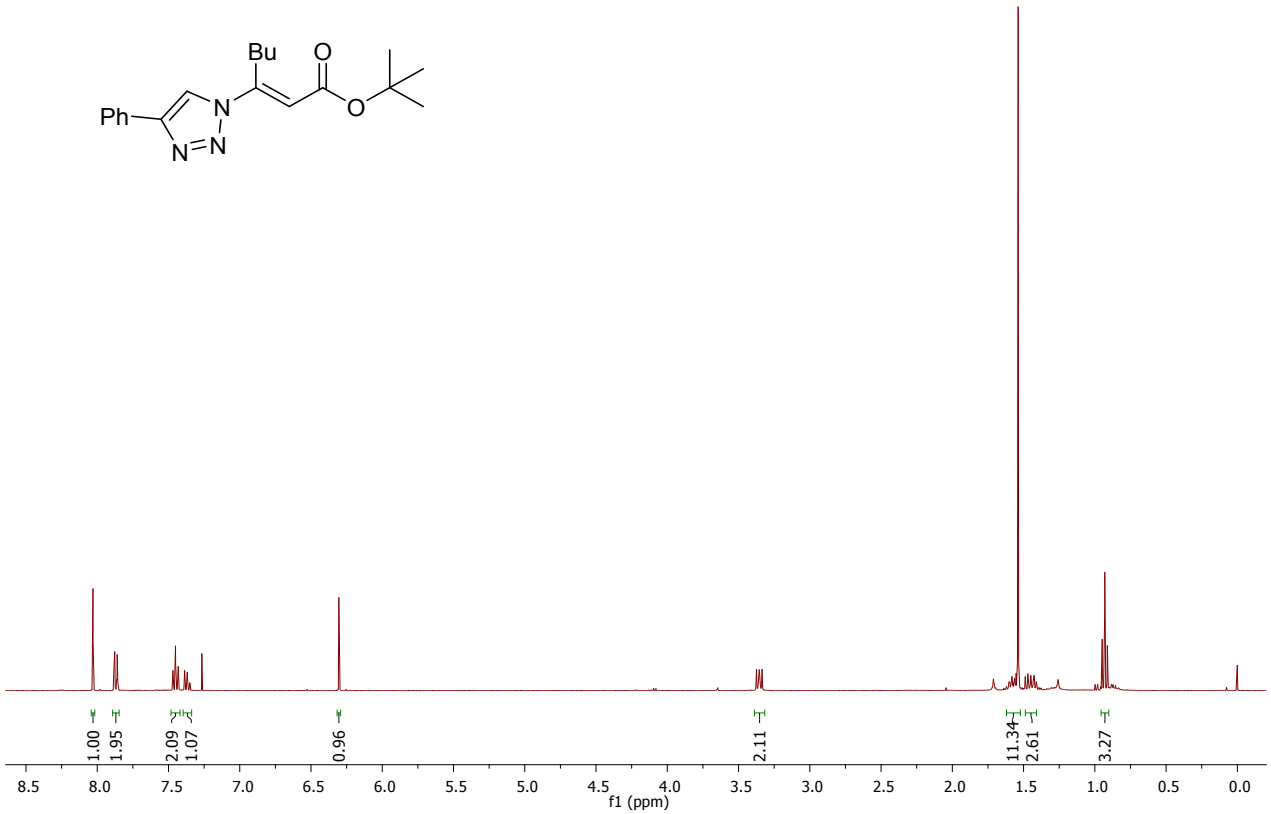
^{13}C NMR spectrum for compound **4u** in $CDCl_3$, 100 MHz



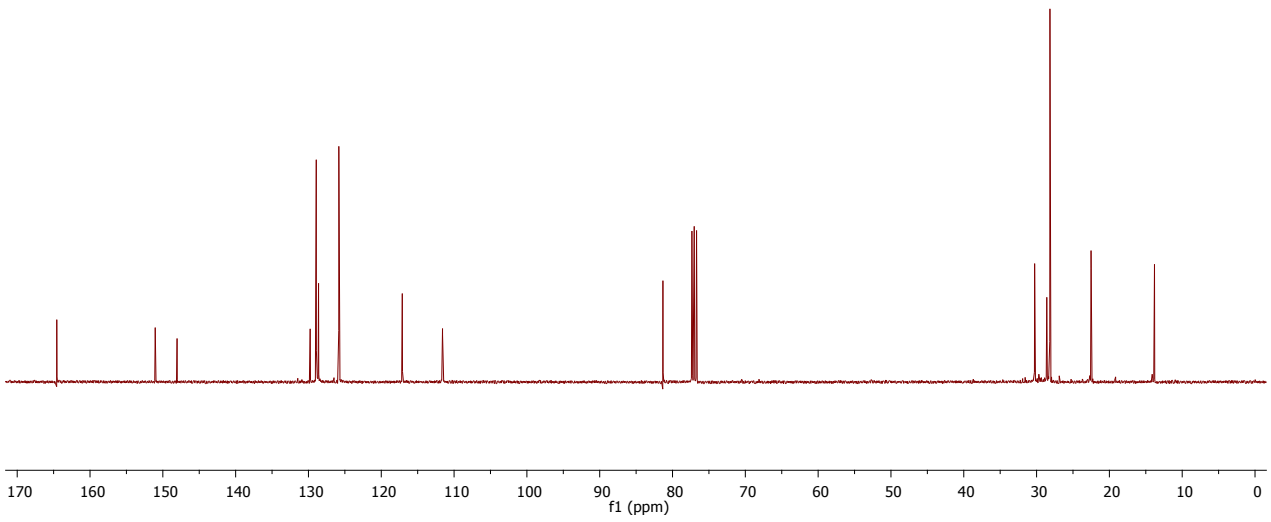
^{1}H NMR spectrum for compound **4v** in $CDCl_3$, 400 MHz



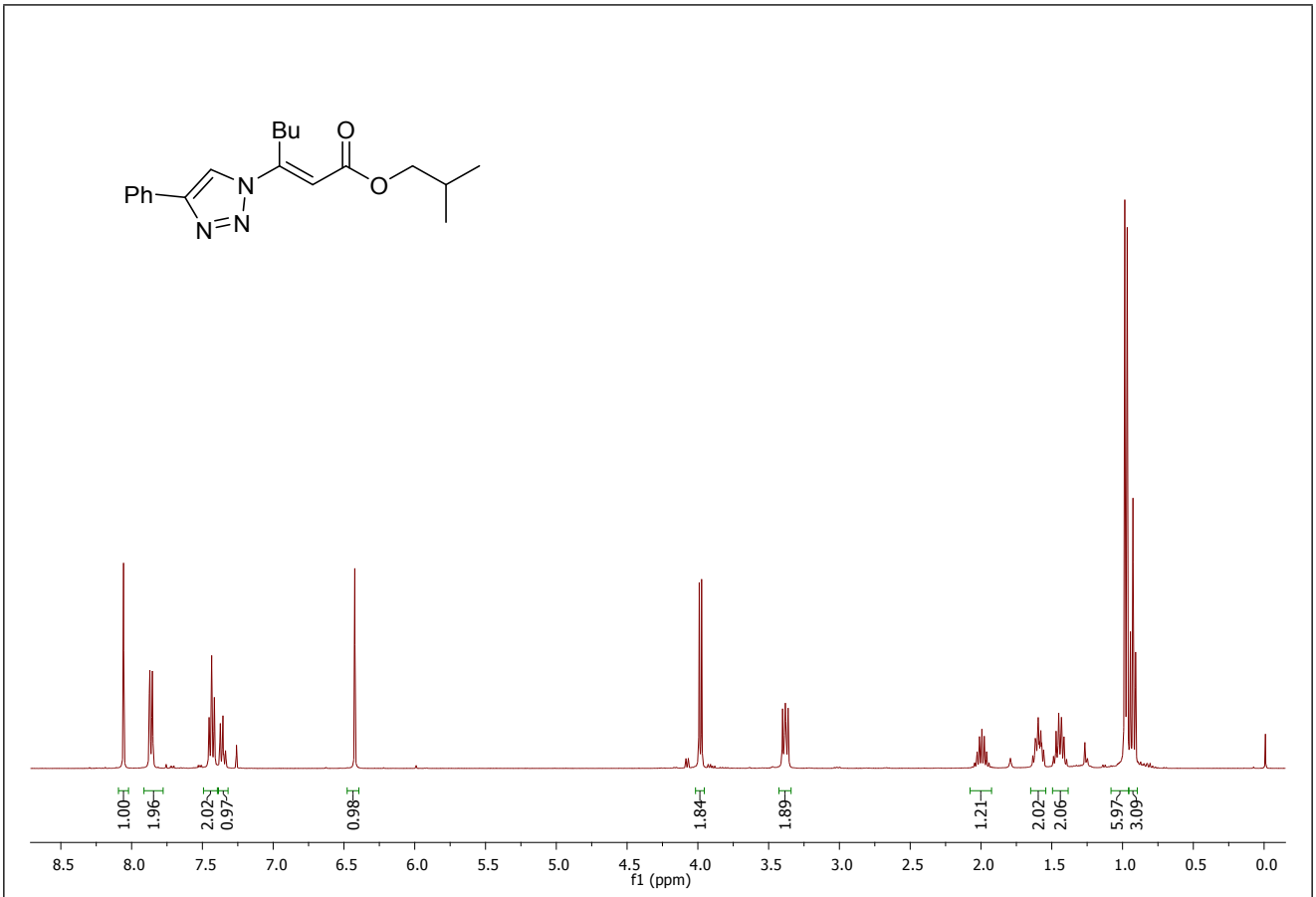
^{13}C NMR spectrum for compound **4v** in $CDCl_3$, 100 MHz



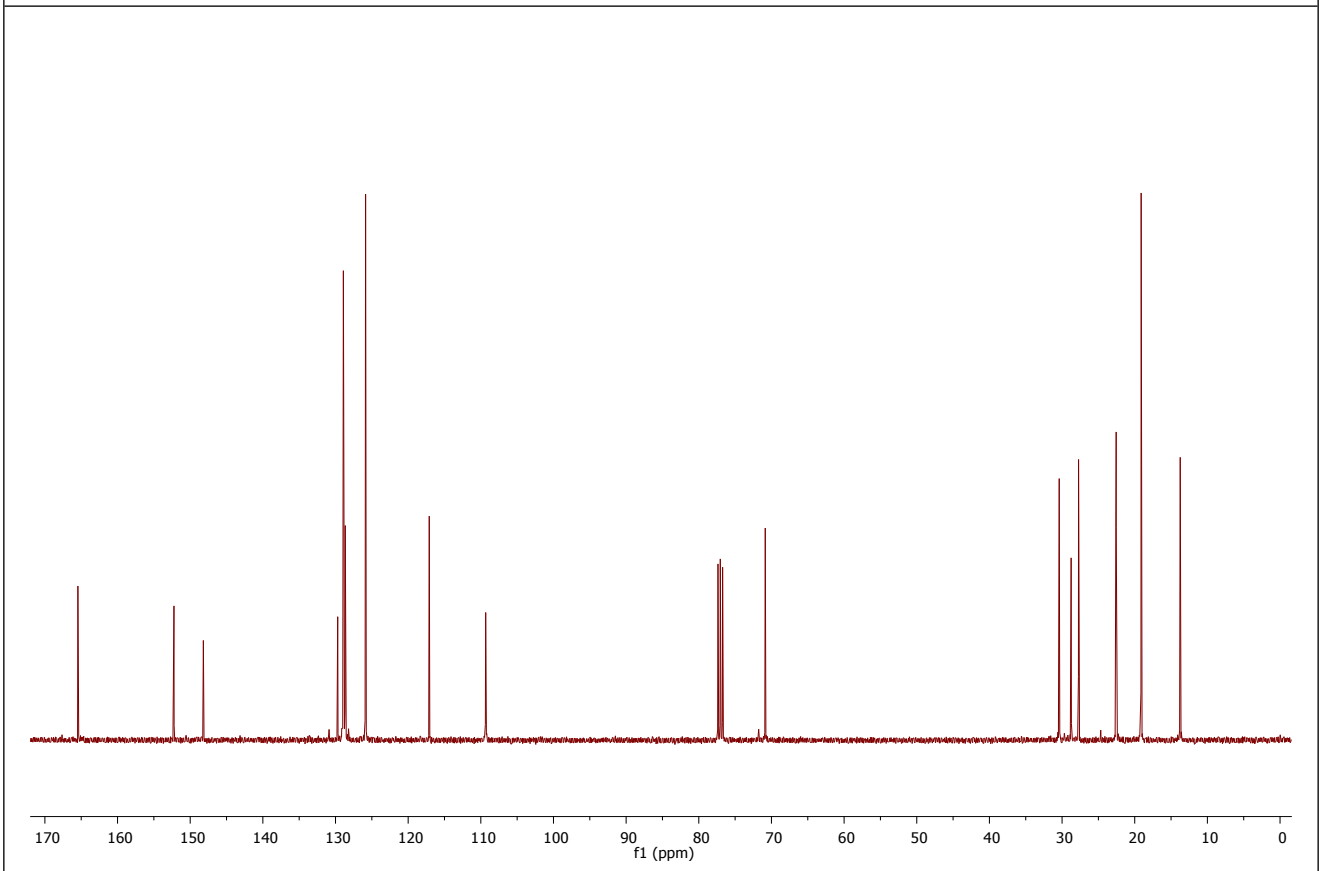
^{1}H NMR spectrum for compound **4w** in $CDCl_3$, 400 MHz



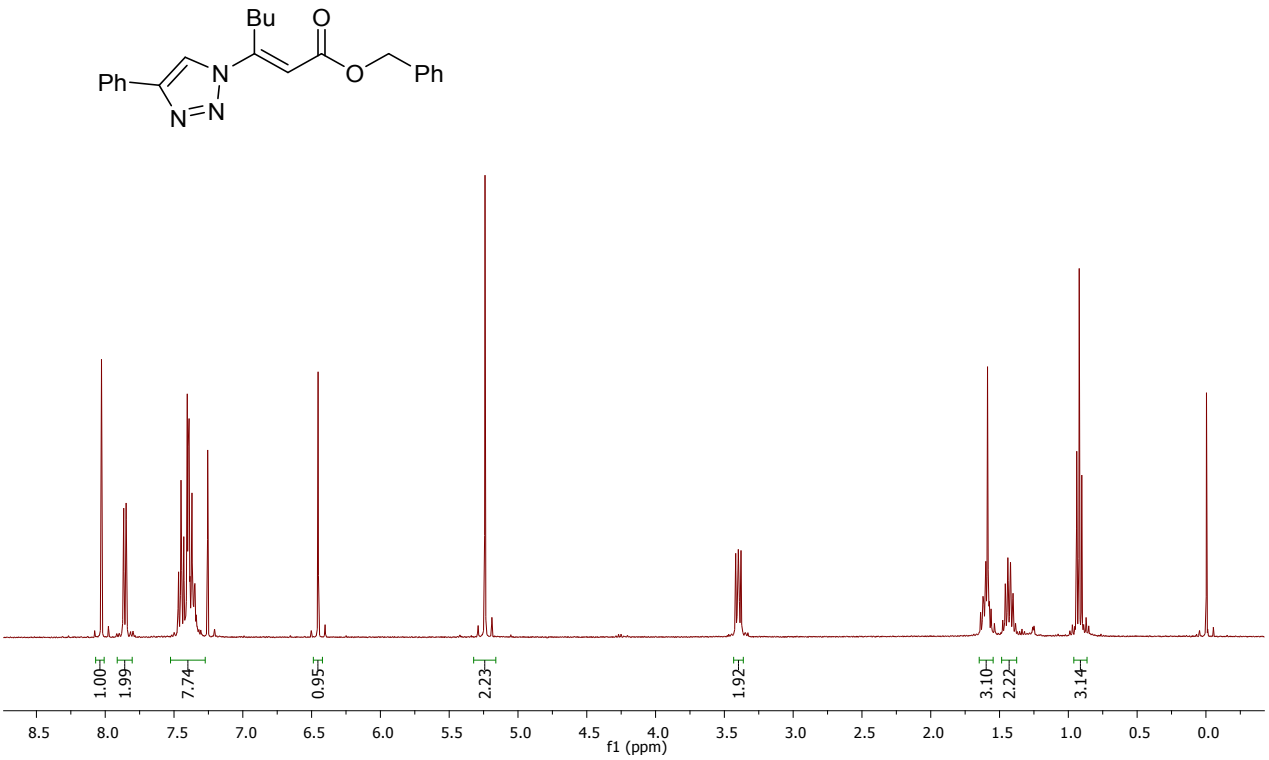
^{13}C NMR spectrum for compound **4w** in $CDCl_3$, 100 MHz



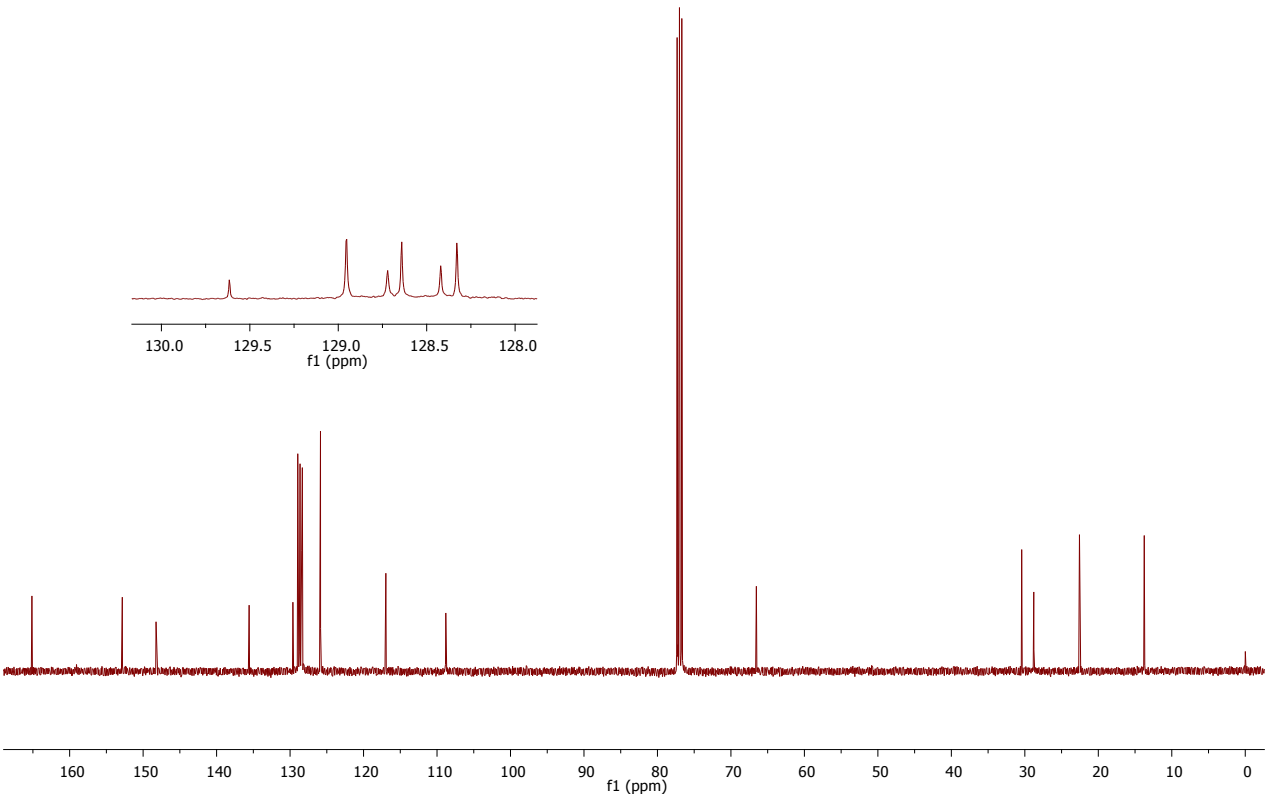
^{1}H NMR spectrum for compound **4x** in $CDCl_3$, 400 MHz



^{13}C NMR spectrum for compound **4x** in $CDCl_3$, 100 MHz



^{1}H NMR spectrum for compound **4y** in $CDCl_3$, 400 MHz



^{13}C NMR spectrum for compound **4y** in $CDCl_3$, 100 MHz