**ELECTRONIC SUPPLEMENTARY INFORMATION**

# Efficient synthesis of 4,5-disubstituted-*2H*-1,2,3-triazoles from nitroallylic derivatives *via* cycloaddition-denitration process

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## Table of Contents

## General Experimental

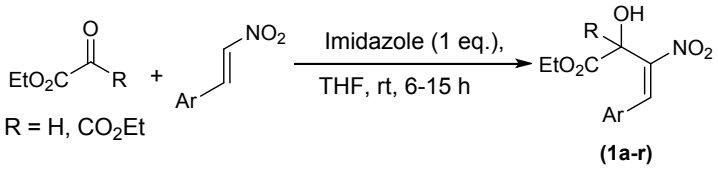
All reagents were purchase from Sigma-Aldrich, TCI, Alfa Aesar, Acros, SDFine, Spectrochem, SRL or AVRA and used without further purification unless otherwise stated. For all reactions carried out under inert atmosphere, solvents were dried over activated 4 Å molecular sieves. The solvents were transfer under nitrogen atmosphere. Silicon oil baths on stirrer hotplates were employed with temperature control *via* thermometer. Reaction progress was monitored by Thin Layer Chromatography (TLC) performed using TLC Silica gel 60 F254. Visualisation was achieved by a combination of ultraviolet light (254 nm) and potassium permanganate solution. Flash column chromatography was performed using silica gel (100-200 mesh) as the stationary phase. All reactions and dried or anhydrous reactions were carried out under nitrogen atmosphere in dried glassware.

Melting points were measured in open capillaries using DBK digital melting point apparatus and are uncorrected. Infra-red spectra were recorded neat on a Perkin-Elmer Spectrum 100 FTIR spectrometer. $^{1}$H NMR and $^{13}$C NMR experiments were recorded using Bruker AVIII400 ($^{1}$H = 400 MHz, $^{13}$C = 101 MHz) with the spectrometers at 300 K. Chemical shifts ($\delta$) are given in ppm relative to TMS and coupling constants ($J$) are quoted in Hz to one decimal place. For spectra recorded in chloroform-*d* ($CDCl_3$) the 7.26 ppm resonance of residual $CHCl_3$ for proton spectra and 77.16 ppm resonance of $CDCl_3$ for carbon spectra were used as internal references. Spectral data for $^{1}$H NMR spectroscopy is reported as follows: Chemical shift (multiplicity, coupling constant, number of protons); and for $^{13}$CNMR spectroscopy: Chemical shift. The following abbreviations were used for multiplicity in $^{1}$H NMR: s (singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublets), td (triplet of doublets), quin (quintuplet), br (broad), m (multiplet), app.(apparent). Mass spectra were recorded using HRMS (ESI-TOF analyzer) equipment. Single crystal X-ray data were collected at 298 K on a Bruker AXS-SMART or OXFORD diffractometer using $\lambda_{Mo-K\alpha}$ = 0.71073 Å radiation. Structures were solved and refined using standard methods, such as SAINTPLUS and ShelXTL.

### Synthesis of Starting Materials

**Synthesis of nitroallylic Alcohols (1a-r)**

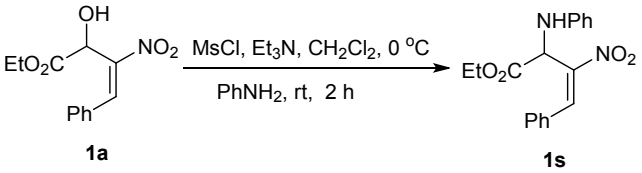
The reaction of various aromatic nitroalkenes with ethyl glyoxylate or diethyl ketomalonate in the presence of imidazole according to Scheme 1. The multifunctional 2-hydroxy-3-nitro-4-arylbut-3-enoates are synthesised as reported in the literature and spectroscopic data matched those reported (**1a-r**).[1]




Scheme 1: Synthesis of multifunctional 2-hydroxy-3-nitro-4-arylbut-3-enoates.

**Synthesis of nitroallylic amine (1s)**

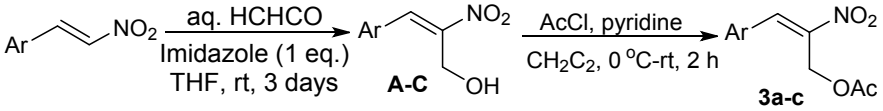
The reaction of nitroallylic alcohol **1a** was treated with methanesulfonyl chloride followed by aniline to form corresponding nitroallylic amine **1s** as reported in the literature and spectroscopic data matched those reported[2] as shown Scheme 2.




Scheme 2: Synthesis of nitroallylic amine.

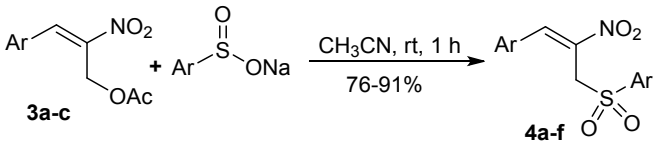
**Synthesis of nitroallylic alcohols and acetates (3a-c)**

The Baylis-Hillman reaction of aromatic nitroalkenes with formalin in the presence of imidazole to form corresponding nitroallylic alcohols (**A-C**) are reported and spectroscopic data matched those reported.[3] These alcohols further converted into corresponding nitroallylic acetates (**3a**-**c**) as reported in the literature[4] (Scheme 3).



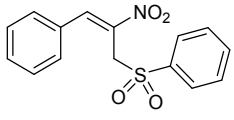

Scheme 3: Synthesis of nitroallylic alcohols and acetates.

## General procedure for synthesis of nitroallylic sulfones (4a-f)

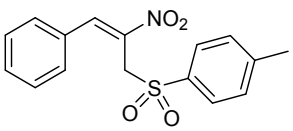



The nitroallylic acetates **3a**-**c** (1 mmol, 1 equiv.) and sodium benzenesulfinate or sodium *p*-toluenesulfinate (2 mmol, 2 equiv.) were mixed in MeCN (3 mL) and stirred at room temperature for 1 h. The solvent was removed under reduced pressure, the reaction mixture was quenched with water and aqueous layer was extracted with ethyl acetate (2x50 mL). The combined organic phase was washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (20% petroleum ether/EtOAc) to afford the pure corresponding sulfones **4a**-**f**.

***(E)-[2-Nitro-3-(phenylsulfonyl)prop-1-en-1-yl]benzene (4a):*** Prepared according to general procedure using **3a** (221 mg, 1 mmol) and sodium benzenesulfinate (328 mg, 2 mmol) to afford the title sulfone **4a** (236 mg, 78%) as a yellow solid. mp: 115-116 °C. IR (neat): *v* = 2924, 1645, 1525, 1446, 1392, 1327, 1182, 1143, 1083, 904, 864, 727 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.91 (d, *J* = 7.2, 2H), 7.71-7.64 (m, 3H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.53-7.44 (m, 3H), 4.81 (s, 2H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 141.3, 140.1, 139.0, 134.6, 131.8, 130.6, 130.1(2C), 129.55(2C), 129.47(2C), 128.4 (2C), 54.9; HRMS (ESI) calculated for $C_{15}H_{13}NO_4SNa$ $[M+Na]^+$: *m/z* 326.0463, found 326.0463.

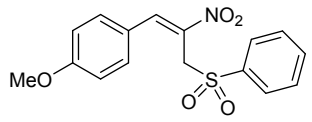



***(E)-1-Methyl-4-[(2-nitro-3-phenylallyl)sulfonyl]benzene (4b):*** Prepared according to general procedure using **3a** (221 mg, 1 mmol) and sodium *p*-toluenesulfinate (356 mg, 2 mmol) to afford the title sulfone **4b** (237 mg, 75%) as a colorless solid. mp: 141-142 °C; IR (neat): *v* = 2933, 1636, 1545, 1457, 1382, 1333, 1180, 1141, 1098, 924, 884, 757 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* =



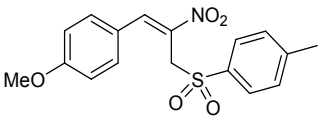
5.8, 1.9 Hz, 2H), 7.52-7.46 (m, 3H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.79 (s, 2H), 2.45 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 145.7, 141.0, 140.3, 136.0, 131.7, 130.6, 130.1(4C), 129.4(2C), 128.4(2C), 54.9, 21.8; HRMS (ESI) calculated for $C_{16}H_{15}NO_4SNa$ [M+Na]$^+$: *m/z* 340.0619, found 340.0621.

***(E)-1-Methoxy-4-[2-nitro-3-(phenylsulfonyl)prop-1-en-1-yl]benzene (4c):*** Prepared



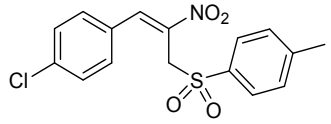

according to general procedure using **3b** (251 mg, 1 mmol) and sodium benzenesulfinate (328 mg, 2 mmol) to afford the title sulfone **4c** (280 mg, 84%) as a yellow solid. mp: 154-156 °C; IR (neat): *v* = 2928, 1649, 1613, 1528, 1448, 1368, 1227, 1187, 1149, 1078, 913, 871, 747 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.94 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 4.84 (s, 2H), 3.89 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 163.0, 141.5, 139.2, 137.5, 134.6, 133.0(2C), 129.5(2C), 128.5(2C), 123.0, 115.1(2C), 55.7, 55.3; HRMS (ESI) calculated for $C_{16}H_{15}NO_5SNa$ [M+Na]$^+$: *m/z* 356.0569, found 356.0569.

***(E)-1-Methoxy-4-(2-nitro-3-tosylprop-1-en-1-yl)benzene (4d):*** Prepared according to



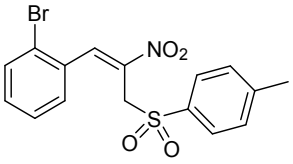

general procedure using **3b** (251 mg, 1 mmol) and sodium *p*-toluenesulfinate (356 mg, 2 mmol) to afford the title sulfone **4d** (308 mg, 89%) as a yellow solid. mp: 143-145 °C; IR (neat): *v* = 2938, 1637, 1616, 1524, 1436, 1364, 1237, 1191, 1135, 1098, 943, 869, 767 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 4.82 (s, 2H), 3.89 (s, 3H), 2.45 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 162.9, 145.7, 141.2, 137.8, 136.3, 133.0(2C), 130.1(2C), 128.5(2C), 123.1, 115.1(2C), 55.7, 55.3, 21.8; HRMS (ESI) calculated for $C_{17}H_{17}NO_5SNa$ [M+Na]$^+$: *m/z* 370.0725, found 370.0725.

***(E)-1-Chloro-4-(2-nitro-3-tosylprop-1-en-1-yl)benzene (4e):*** Prepared according to general




procedure using **3c** (255 mg, 1 mmol) and sodium *p*-toluenesulfinate (356 mg, 2 mmol) to afford the title sulfone **4e** (259 mg, 77%) as a yellow solid. mp: 140-142 °C; IR (neat): *v* = 2924, 1641, 1591, 1527, 1490, 1408, 1327, 1143, 1145, 1087, 1012, 904, 862, 813 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.75 (s, 2H), 2.45 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 145.9, 140.6, 139.7, 138.1, 136.0, 131.5(2C), 130.2(2C), 129.8(2C), 129.1, 128.4(2C), 54.8, 21.9; HRMS (ESI) calculated for $C_{16}H_{14}NO_4SClNa$ [M+Na]$^+$: *m/z* 374.0230, found 374.0230.

***(E)-1-Bromo-2-(2-nitro-3-tosylprop-1-en-1-yl)benzene (4f):*** Prepared according to general



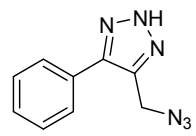

procedure using **3c** (300 mg, 1 mmol) and sodium *p*-toluenesulfinate (356 mg, 2 mmol) to afford the title sulfone **4f** (300 mg, 76%) as a pale-yellow solid. mp: 129-130 °C; IR (neat): *v* = 2922, 1651, 1531, 1463, 1392, 1328, 1247, 1178, 1145, 1085, 1029, 906, 862, 758 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.38-7.28 (m, 3H), 4.66 (s, 2H), 2.45 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 145.8, 141.9, 139.9, 136.0, 133.4, 132.3, 131.4, 130.4, 130.2(2C), 128.4(2C), 128.3, 125.0, 54.5, 21.9;

HRMS (ESI) calculated for $C_{16}H_{14}NO_4SBrNa$ $[M+Na]^+$ and $[M+Na+2]^+$: *m/z* 417.9725 and 419.9704, found 417.9725 and 419.9706.

## General procedure for synthesis of triazoles (5a-c and 6a-f)

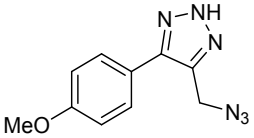
A heat gun-dried Schlenk tube was charged nitroallylic acetate (**3a**-**c**) or nitroallylic sulfone (**4a**-**f**) (0.5 mmol), $NaN_3$ (1.5 mmol for **3a**-**c**) or $NaN_3$ (0.75 mmol for **4a**-**f**) and *p*-TsOH (0.5 mmol) in DMSO (2.5 mL) and stirred at 80 °C under inert atmosphere. The reaction was either complete or appeared to be proceeding no further progress as monitored by TLC. Heating was removed and allowed to room temperature, added water to reaction mixture and extracted with EtOAc (3×40 mL). The combined organic layers was washed with brine (2x40 mL), dried over anhydrous $Na_2SO_4$, and the solvent was removed under reduced pressure. The resulting crude was subjected to flash chromatography on silica gel by eluting with 30-40% petroleum ether/ethyl acetate to afford desired triazoles **5a-c** and **6a-f**.

### *4-(Azidomethyl)-5-phenyl-2H-1,2,3-triazole (5a):*



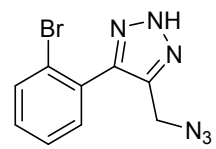
Prepared according to general procedure using **3a** (110.5 mg, 0.5 mmol) to afford the title triazole **5a** (56 mg, 56%) as a black solid. mp: 124-126 °C; IR (neat): *v* = 2924, 2098, 1492, 1448, 1238, 1018, 995, 879, 765 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.71 (dd, *J* = 6.8, 1.5 Hz, 2H), 7.52-7.44 (m, 3H), 4.60 (m, 2H), *one exchangeable proton has not appeared*; $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 144.8, 139.1, 129.2(2C), 129.1, 127.8(2C), 127.5, 45.2; HRMS (ESI) calculated for $C_9H_8N_6Na$ $[M+Na]^+$: *m/z* 223.0708, found 223.0707.

### *4-(Azidomethyl)-5-(4-methoxyphenyl)-2H-1,2,3-triazole (5b):*



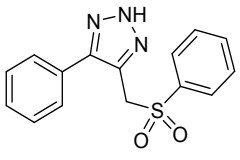
Prepared according to general procedure using **3b** (125.5 mg, 0.5 mmol) to afford the title triazole **5b** (45 mg, 39%) as a pale-yellow solid. mp: 119-120 °C; IR (neat): *v* = 2924, 2098, 1614, 1510, 1463, 1255, 1180, 1024, 883 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 12.15 (bs, 1H), 7.64 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 4.56 (s, 2H), 3.86 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 160.4, 144.3, 138.7, 129.2(2C), 121.4, 114.7(2C), 55.5, 45.3; HRMS (ESI) calculated for $C_{10}H_{10}N_6ONa$ $[M+Na]^+$: *m/z* 253.0814, found 253.0813.

### *4-(Azidomethyl)-5-(2-bromophenyl)-2H-1,2,3-triazole (5c):*



Prepared according to general procedure using **3c** (150 mg, 0.5 mmol) to afford the title triazole **5c** (61 mg, 44%) as a pale-yellow liquid. IR (neat): *v* = 2928, 2099, 1497, 1432, 1245, 1063, 1034, 998, 889, 763 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 7.9, 1H), 7.44-7.37 (m, 2H), 7.35-7.28 (m, 1H), 4.48 (s, 2H), *one exchangeable proton has not appeared*; $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 140.5, 133.34, 133.28, 132.1, 131.1, 130.0, 127.8, 123.6, 45.0; HRMS (ESI) calculated for $C_9H_8BrN_6$ $[M+H]^+$ and $[M+H+2]^+$: *m/z* 278.9994 and 280.9973, found 278.9994 and 280.9974.

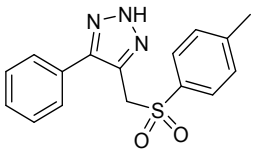
### *5-Phenyl-4-[(phenylsulfonyl)methyl]-1H-1,2,3-triazole* (6a):



Prepared according to general procedure using **4a** (151.5 mg, 0.5 mmol) to afford the title triazole **6a** (111 mg, 74%) as a yellow solid. mp: 124-126 °C; IR (neat): *v* = 2924, 1446, 1319, 1307, 1261, 1151, 1083, 1018, 873, 686 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): *this compound exists in 8.2:1 mixture of isomeric triazoles* δ = 13.09 (bs, 1H), 7.72 (d, *J* = 6.9 Hz, 2H), 7.61-7.38 (m, 8H), 4.68 (s, 2H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 145.5, 138.0,

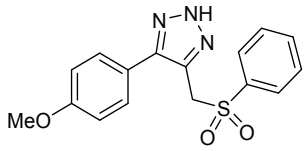
134.3, 134.1, 129.3(2C), 129.2, 129.1(2C), 128.9, 128.6(2C), 128.0(2C), 52.9; HRMS (ESI) calculated for $C_{15}H_{14}N_3O_2S$ $[M+H]^+$: *m/z* 300.0807, found 300.0806.

### *5-Phenyl-4-(tosylmethyl)-1H-1,2,3-triazole (6b):*



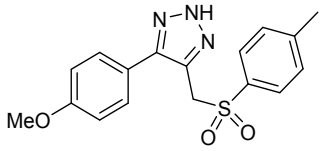
Prepared according to general procedure using **4b** (158.5 mg, 0.5 mmol) to afford the title triazole **6b** (119 mg, 76%) as as a yellow solid. mp: 128-130 °C; IR (neat): *v* = 2924, 1597, 1319, 1301, 1149, 1086, 1018, 813, 698 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): *this compound exists in 13.0:1 mixture of isomeric triazoles*, δ = 12.89 (bs, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.52-7.46 (m, 2H), 7.42-7.36 (m, 3H), 7.19 (d, *J* = 7.9 Hz, 2H), 4.66 (s, 2H), 2.38 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 145.5, 145.4, 134.8, 131.6, 129.9(2C), 129.1, 129.0, 128.9(2C), 128.6(2C), 127.9(2C), 52.9, 21.7; HRMS (ESI) calculated for $C_{16}H_{16}N_3O_2S$ $[M+H]^+$: *m/z* 314.0963, found 314.0963.

### *5-(4-Methoxyphenyl)-4-[(phenylsulfonyl)methyl]-1H-1,2,3-triazole (6c):*



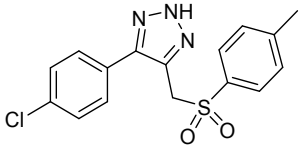
Prepared according to general procedure using **4c** (166.5 mg, 0.5 mmol) to afford the title triazole **6c** (102 mg, 62%) as a yellow solid. mp: 145-146 °C; IR (neat): *v* = 2927, 1614, 1512, 1446, 1305, 1253, 1180, 1151, 1083, 1024, 837, 734 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): *this compound exists in 8.0:1 mixture of isomeric triazoles*, δ = 7.72 (d, *J* = 7.4 Hz, 2H), 7.62-7.52 (m, 2H), 7.48-7.340 (m, 4H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.64 (s, 2H), 3.83 (s, 3H), *one exchangeable proton has not appeared*; $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 160.4, 145.0, 138.1, 134.3, 131.2, 129.4(2C), 129.3, 129.1, 128.6, 120.6, 114.5(2C), 114.3, 55.5, 53.0; HRMS (ESI) calculated for $C_{16}H_{16}N_3O_3S$ $[M+H]^+$: *m/z* 330.0912, found 330.0912.

### *5-(4-Methoxyphenyl)-4-(tosylmethyl)-1H-1,2,3-triazole (6d):*



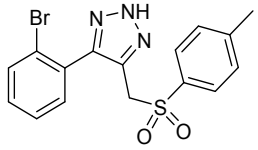
Prepared according to general procedure using **4d** (171.5 mg, 0.5 mmol) to afford the title triazole **6d** (111 mg, 65%) as a yellow solid. mp: 151-153 °C; IR (neat): *v* = 2929, 1612, 1510, 1301, 1253, 1180, 1152, 1085, 1024, 836 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): *this compound exists in 9.9:1 mixture of isomeric triazoles*, δ = 7.56 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.63 (s, 2H), 3.81 (s, 3H), 2.38 (s, 3H), *one exchangeable proton has not appeared*; $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 160.3, 145.3, 144.8, 135.0, 131.3, 129.9(2C), 129.3(2C), 128.6(2C), 114.4(2C), 114.2, 55.4, 53.0, 21.7; HRMS (ESI) calculated for $C_{17}H_{18}N_3O_3S$ $[M+H]^+$: *m/z* 344.1069, found 344.1069.

### *5-(4-Chlorophenyl)-4-(tosylmethyl)-1H-1,2,3-triazole (6e):*



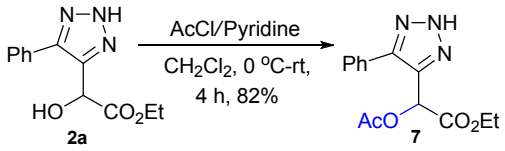
Prepared according to general procedure using **4e** (175.5 mg, 0.5 mmol) to afford the title triazole **6e** (104 mg, 60%) as a pale-yellow solid. mp: 154-156 °C; IR (neat): *v* = 2924, 1597, 1467, 1319, 1301, 1230, 1151, 1089, 1012, 837, 736 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): *this compound exists in 8.5:1 mixture of isomeric triazoles*, δ = 13.21 (bs, 1H), 7.57 (d, *J* = 6.9 Hz, 2H), 7.43 (d, *J* = 7.1 Hz, 2H), 7.34 (d, *J* = 7.0 Hz, 2H), 7.20 (d, *J* = 6.9 Hz, 2H), 4.65 (s, 2H), 2.38 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 145.6, 145.0, 135.2, 134.8, 131.4, 130.0(2C), 129.2(2C), 129.1(2C), 128.5(2C), 127.3, 52.9, 21.7; HRMS (ESI) calculated for $C_{16}H_{14}ClN_3O_2SNa$ $[M+Na]^+$: *m/z* 370.0393, found 370.0394.

### *5-(2-Bromophenyl)-4-(tosylmethyl)-1H-1,2,3-triazole (6f):*



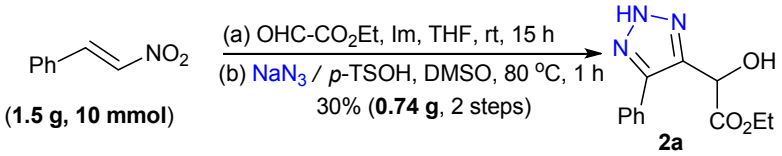
Prepared according to general procedure using **4f** (197 mg, 0.5 mmol) to afford the title triazole **6f** (133 mg, 68%) as a brown-red solid. mp: 151-153 °C; IR (neat): *v* = 2924, 1597, 1454, 1319, 1301, 1149, 1085, 1016, 875, 756 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): *this compound exists in nearly isomeric triazoles* δ = 12.82 (bs, 1H), 7.64-7.58 (m, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.35-7.24 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.16-7.08 (m, 1H), 4.58 (s, 2H), 2.20 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 145.2, 145.0, 134.9, 133.1, 132.3, 130.8, 130.0(2C), 129.8, 128.4(2C), 127.5, 123.0, 53.1, 21.8; HRMS (ESI) calculated for $C_{16}H_{14}N_3O_2SBrNa$ $[M+Na]^+$ and $[M+Na+2]^+$: *m/z* 413.9888 and 415.9867, found 413.9887 and 415.9868.

### *Ethyl 2-acetoxy-2-(5-phenyl-2H-1,2,3-triazol-4-yl)acetate (7):*




To stirred solution of **2a** (123.5 mg, 0.5 mmol), pyridine (120 µL, 1.5 mmol) in dichloromethane (5 mL) at 0 °C was added acetyl chloride (107 µL, 1.5 mmol). After stirring for 4 h at room temperature, the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (2x30 mL). The combined organic layer was washed with brine (30 mL), dried over anhydrous $Na_2SO_4$ and solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel, eluting with 30% petether/ethyl acetate) to afford the pure acetyl triazole **7** (119 mg, 82%) as a pale-yellow liquid. IR (neat): ν = 3302, 1743, 1664, 1529, 1454, 1384, 1236, 1091, 1018, 985 cm-1; 1H NMR (400 MHz, CDCl3): δ = 7.70-7.64 (m, 2H), 7.50-7.43 (m, 3H), 6.41 (s, 1H), 4.21-4.10 (m, 2H), 2.20 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H), *one exchangeable –NH proton has not appeared*; 13C NMR (101 MHz, CDCl3): δ = 170.3, 167.5, 145.1, 137.5, 129.4, 129.1(2C), 128.7, 128.2(2C), 66.4, 62.5, 20.7, 13.9; HRMS (ESI) calculated for $C_{14}H_{15}N_3NaO_4$ $[M+Na]^+$: *m/z* 312.0960, found 312.0961.

### *Representative experimental procedure for one-pot synthesis of triazole (2a):*




The ethyl glyoxylate (4.0 mL, 20 mmol, 50% in toluene) was added to a stirred solution of nitrostyrene (1.5 g, 10 mmol) and imidazole (1.36 g, 20 mmol) in THF (10 mL) at ambient temperature. After 15 h (complete conversion of nitrostyrene as monitored by TLC), the solvent(s) was removed completely under reduced pressure and the residue was dissolved in DMSO (10 mL). Subsequently, $NaN_3$ (0.98 g, 15 mmol) and *p*-TsOH (1.7 g, 10 mmol) were added and stirred at 80 °C under inert atmosphere for 1 h. Heating was removed and allowed to room temperature, added water to reaction mixture and extracted with EtOAc (3×100 mL). The combined organic layers washed with brine (2x100 mL), dried over anhydrous $Na_2SO_4$, and the solvent was removed under reduced pressure. The resulting crude was subjected to flash chromatography (silica gel, eluting with 30-50% petether/ethyl acetate) to afford desired triazole **2a** in 30% (0.74 g for 2 steps) yield.

## Single Crystal X-Ray Data Analysis

***Ethyl 2-[5-(2,4-dichlorophenyl)-2H-1,2,3-triazol-4-yl]-2-hydroxyacetate*** **2n** *(CCDC-1571324):* $C_{12}H_{11}Cl_2N_3O_3$, *Mr* = 316.14, cubic crystal dimensions: 0.24 x 0.24 x 0.24 mm, monoclinic, space group: $P2_1/c$, a = 11.4912(9), b = 7.2015(5), c = 16.5491(13)Å, $\alpha$ = 90°, $\beta$ = 100.277 (2)°, $\gamma$ = 90°, V = 1347.53(18) Å$^3$, Z = 4, $\rho_{calcd}$ = 1.558 g/cm$^3$, $\mu$ = 0.492 mm$^{-1}$, $F_{000}$ = 648.0, $\lambda_{Cu-K\alpha}$ = 1.54184 Å, *T* = 301(2) K, $2\vartheta_{max}$ =148.824°, 22992 reflections measured, 2369 independent reflections ($R_{int}$ = 0.0422), $R_1$ = 0.0465 (observed reflections), *wR* = 0.1179 (all data), largest diff. peak and hole: 0.833 and -0.314 e.Å$^{-3}$.

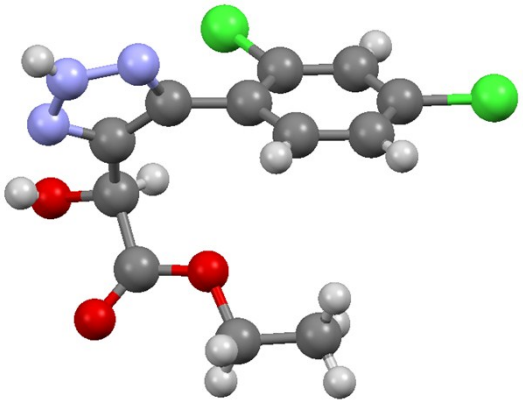


***Figure 1:*** *Crystal structure with ellipsoids drawn at the 50% probability level.*

## References


[1] (a) I. Deb, M. Dadwal, S. M. Mobin and I. N. N. Namboothiri, *Org. Lett*., 2006, *8*, 1201; (b) I. Deb, P. Shanbhag, S. M. Mobin and I. N. N. Namboothiri, *Eur. J. Org. Chem*., 2009, 4091; (c) H.-H. Kuan, R. J. Reddy and K. Chen, *Tetrahedron*, 2010*, 66*, 9875.

[2] R. Gurubrahamam, Y. m. Chen, W.-Y. Huang, Y.-T. Chan, H.-K. Chang, M.-K. Tsai and K. Chen, *Org. Lett.*, 2016, *18*, 3046.

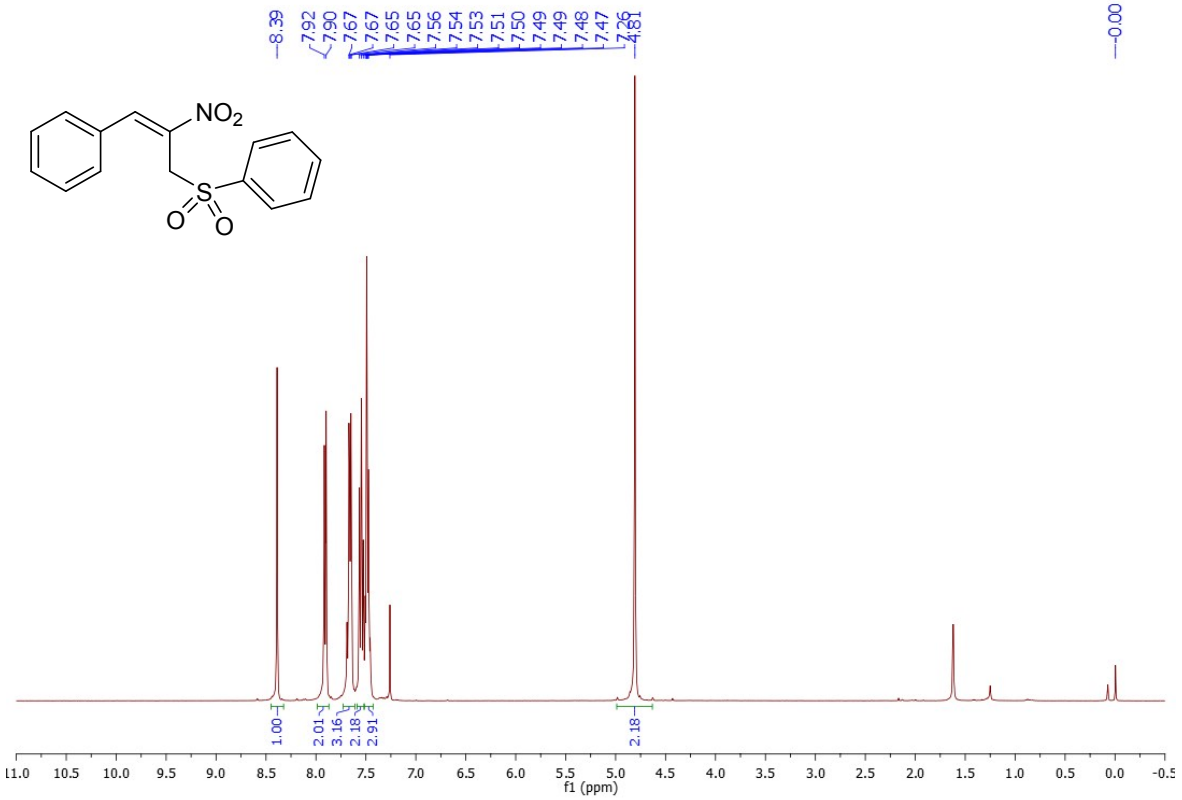
[3] N. Rastogi, I. N. N. Namboothiri and M. Cojocaru, *Tetrahedron Lett*., 2004, *45*, 4745.

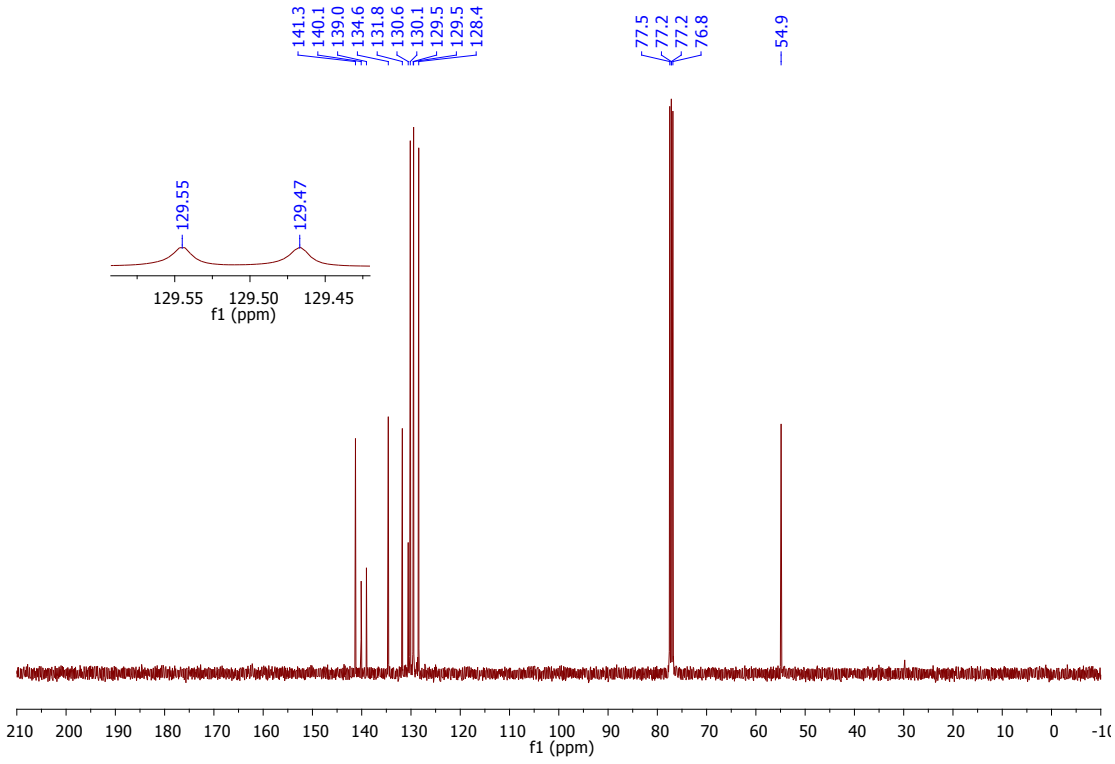
[4] C.-L. Cao, Y.-Y. Zhou, J. Zhou, X.-L. Sun, Y. Tang, Y.-X. Li, G.-Y. Li and J. Sun, *Chem.-Eur. J*., 2009, *15*, 11384.

# $^{1}$H NMR and $^{13}$C NMR Spectra of New Compounds

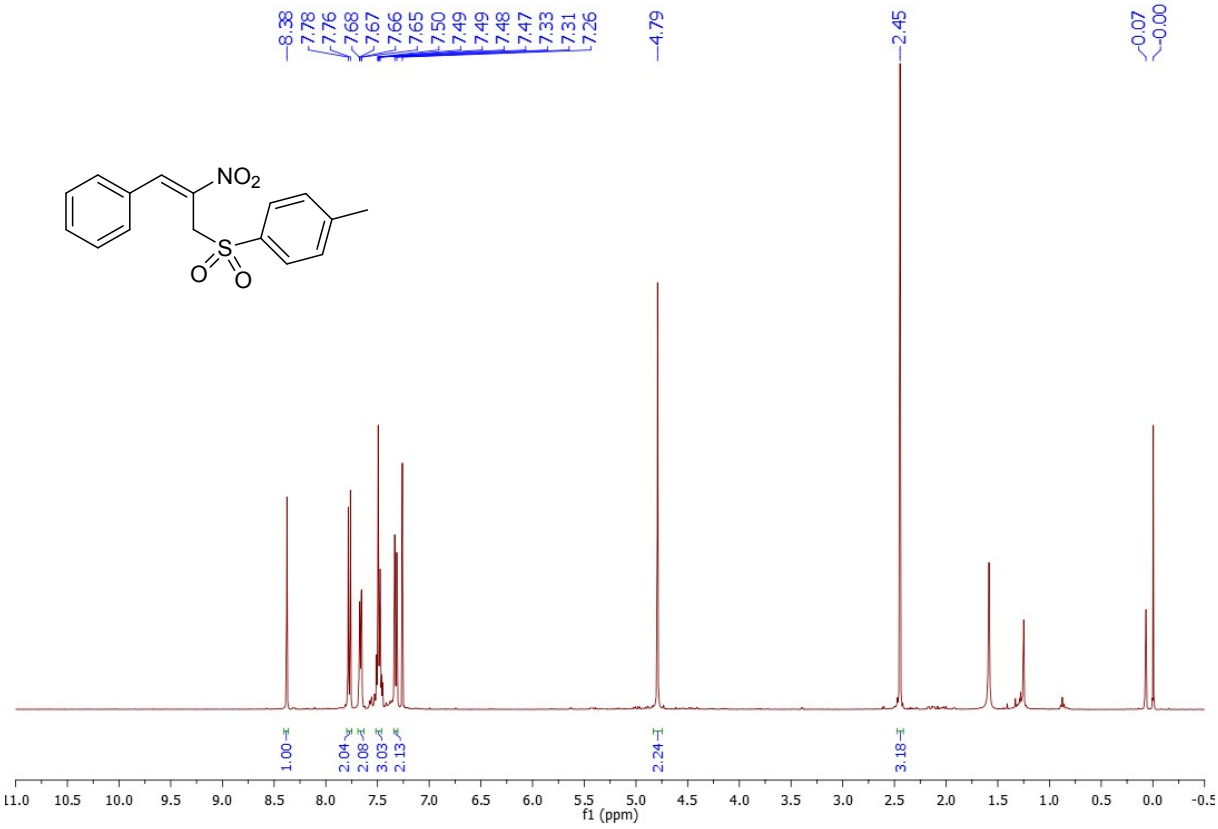
**(Note**: *Common laboratory solvents as trace impurities, peaks at δ 1.25 and δ 1.58 refers to grease and moisture respectively in a $^{1}$H NMR recorded in $CDCl_3$. In a $^{13}$C NMR recorded in $CDCl_3$, a peak at δ 29.7 represents to grease*; *Ref*. H. E. Gottlie, V. Kotlyar and A. Nudelman, *J. Org. Chem*., 1997, **62**, 7512).

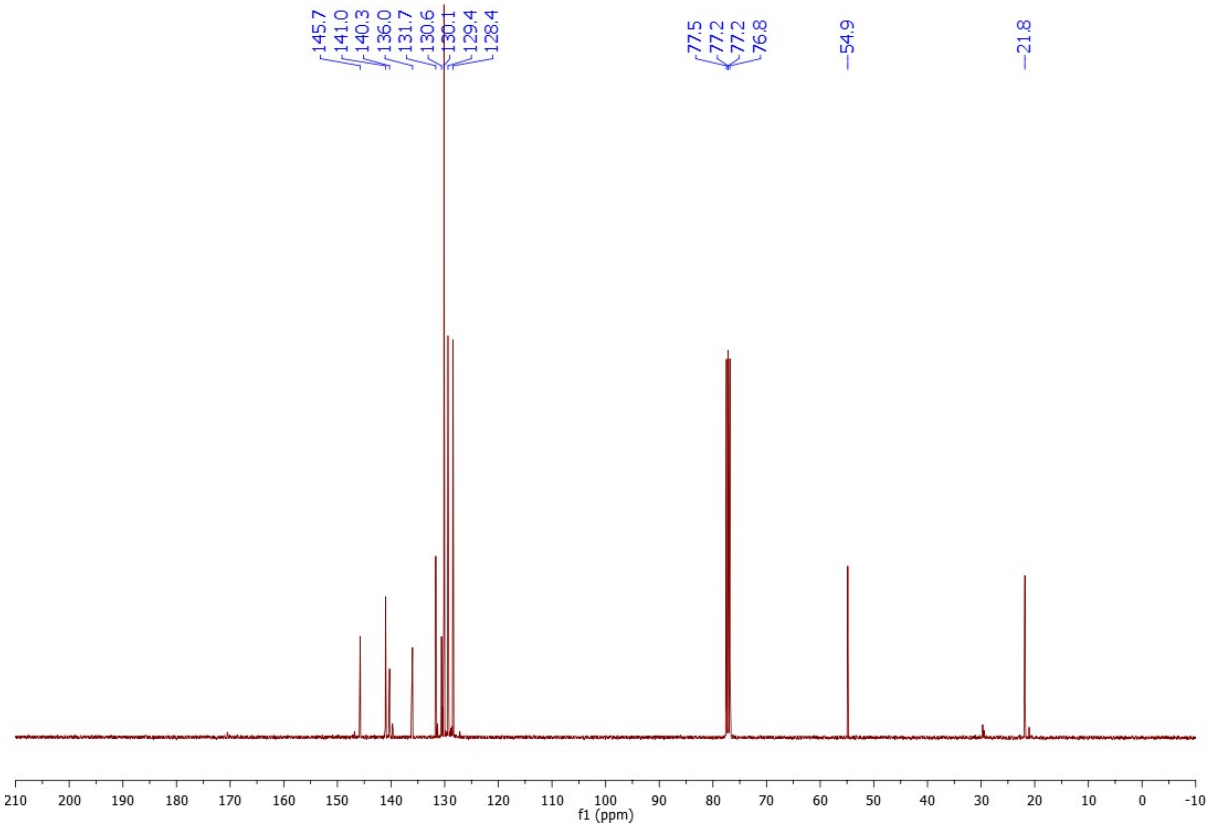
***(E)-[2-Nitro-3-(phenylsulfonyl)prop-1-en-1-yl]benzene (4a): $^{1}$H and $^{13}$C in $CDCl_3$***



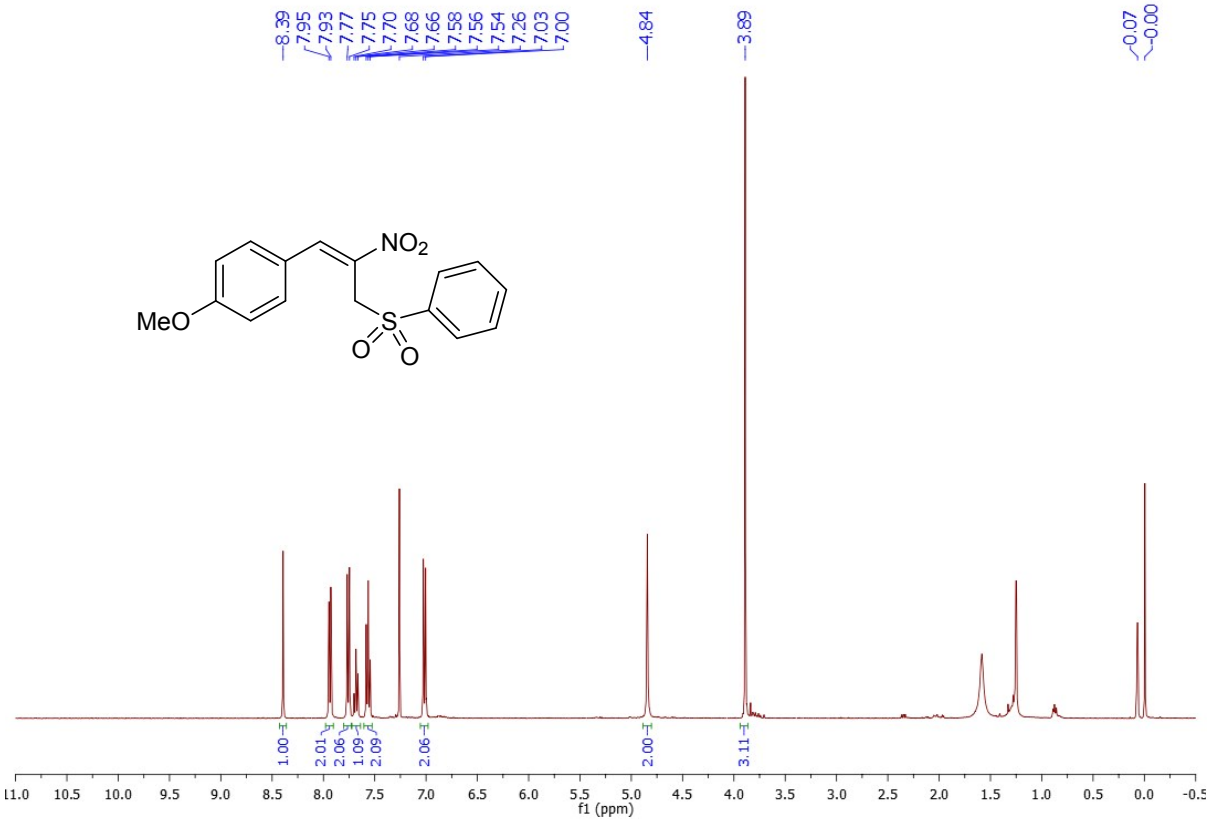



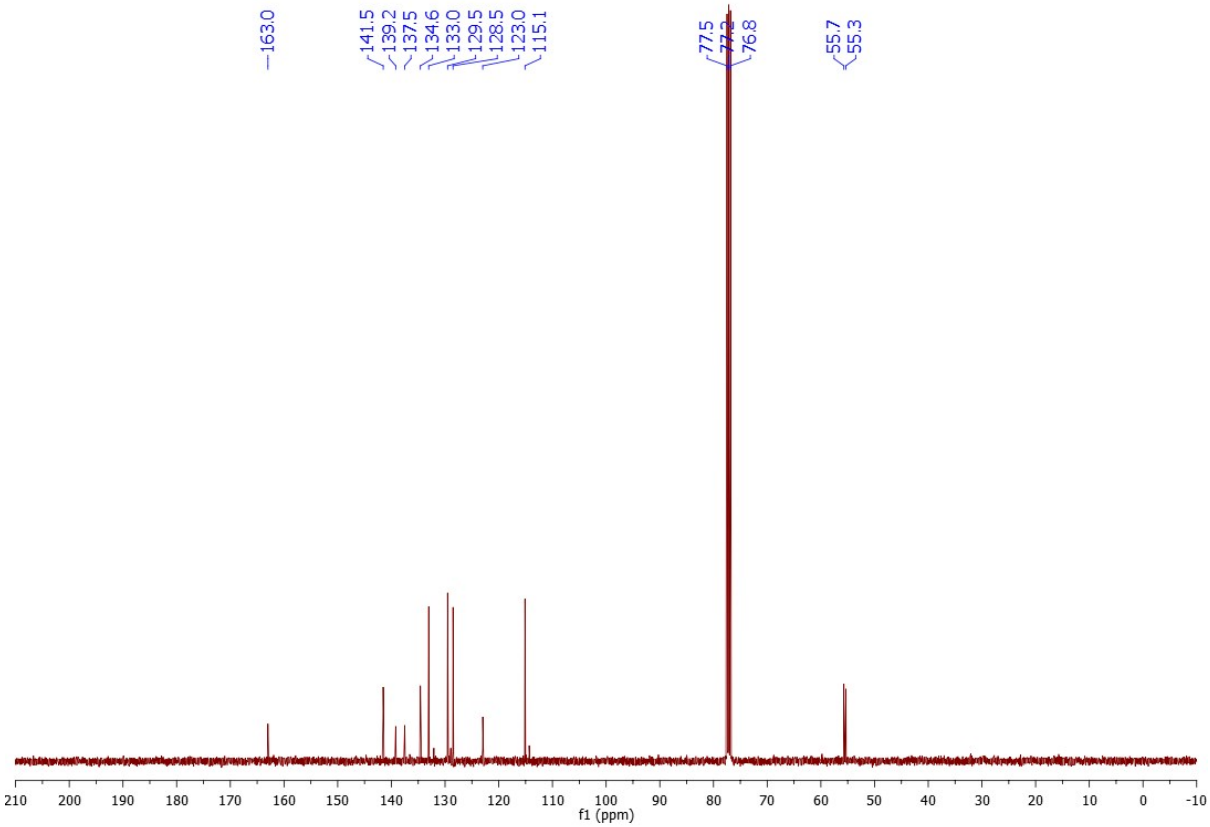
***(E)-1-Methyl-4-[(2-nitro-3-phenylallyl)sulfonyl]benzene (4b): $^{1}H$ and $^{13}C$ in $CDCl_3$***



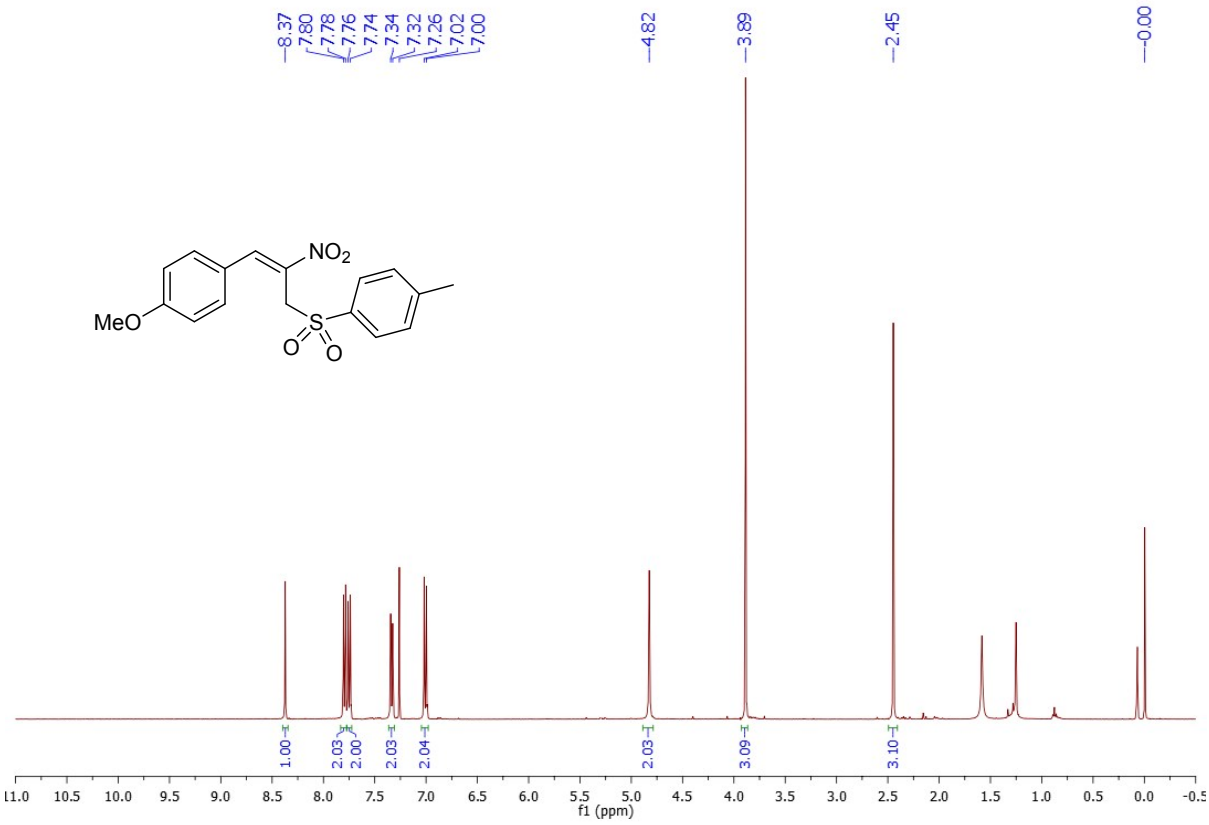



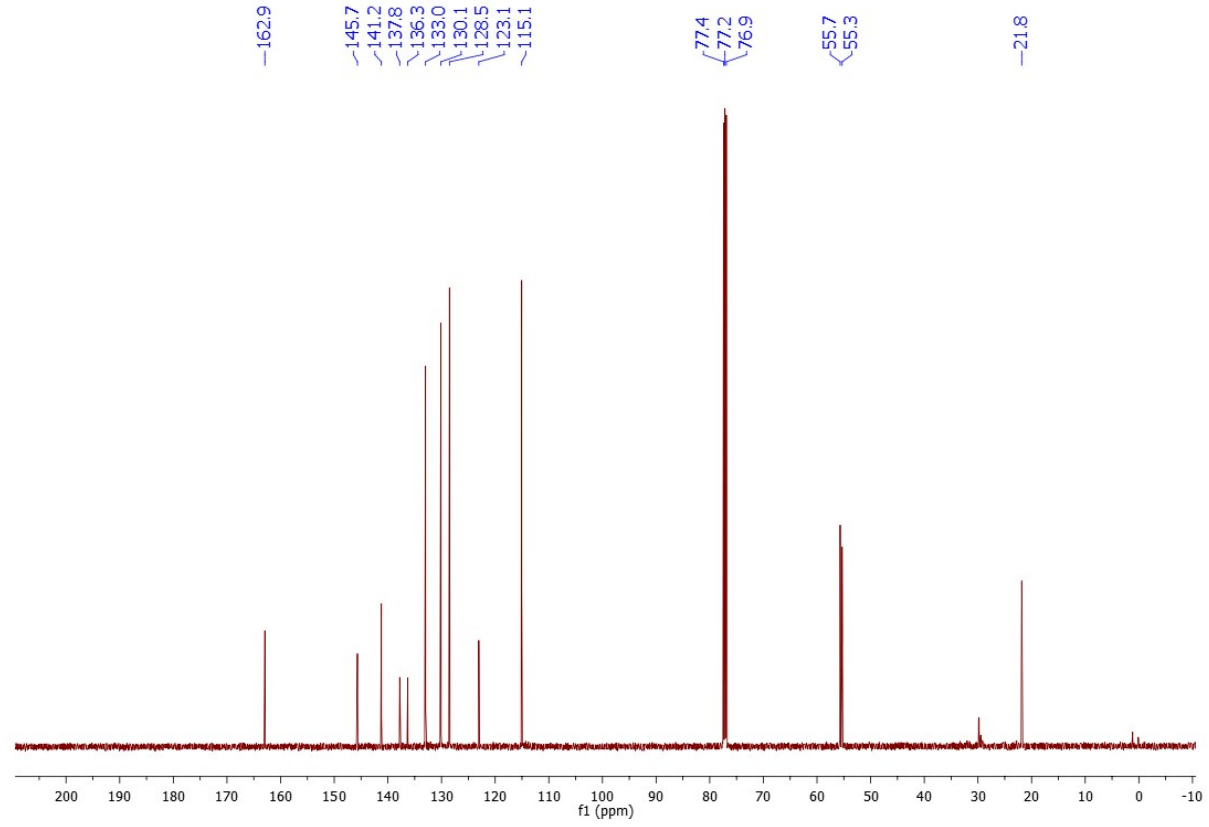
***(E)-1-Methoxy-4-[2-nitro-3-(phenylsulfonyl)prop-1-en-1-yl]benzene (4c): $^{1}H$ and $^{13}C$ in $CDCl_3$***



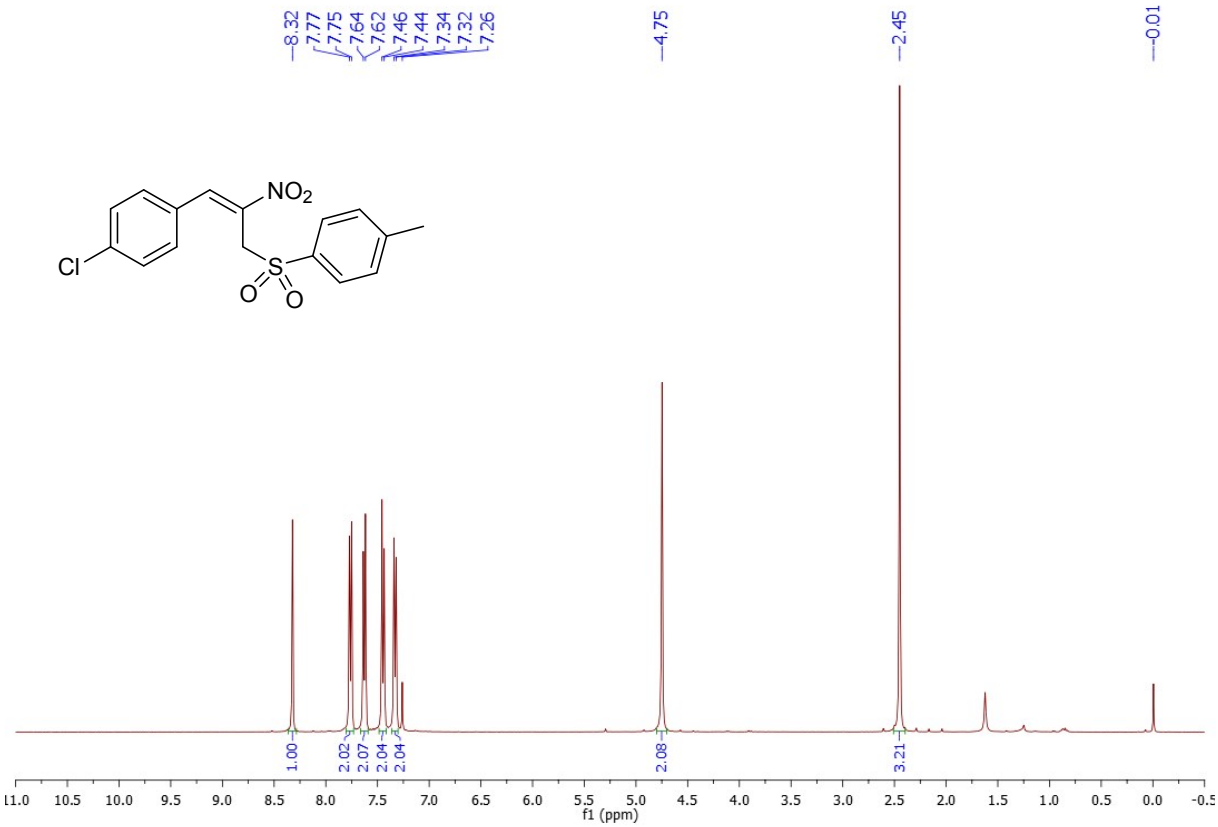



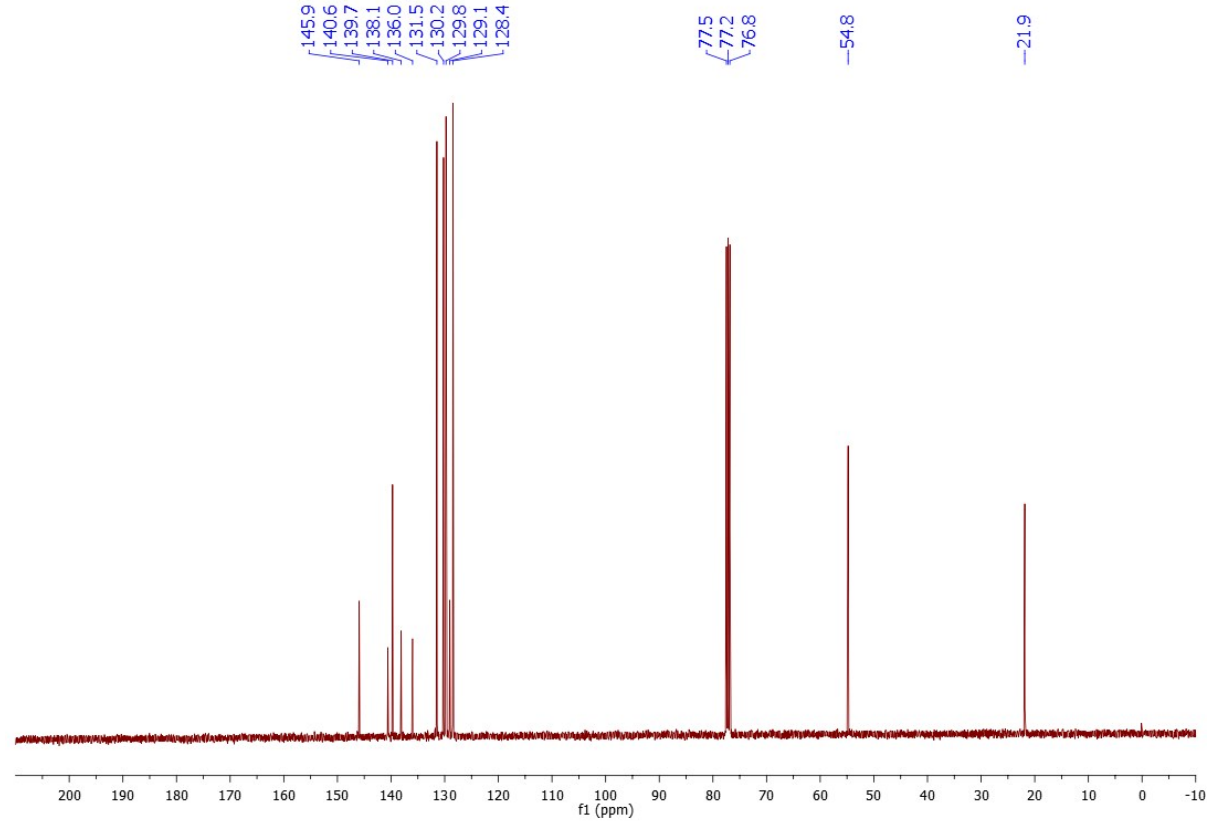
***(E)-1-Methoxy-4-(2-nitro-3-tosylprop-1-en-1-yl)benzene (4d): $^{1}H$ and $^{13}C$ in $CDCl_3$***



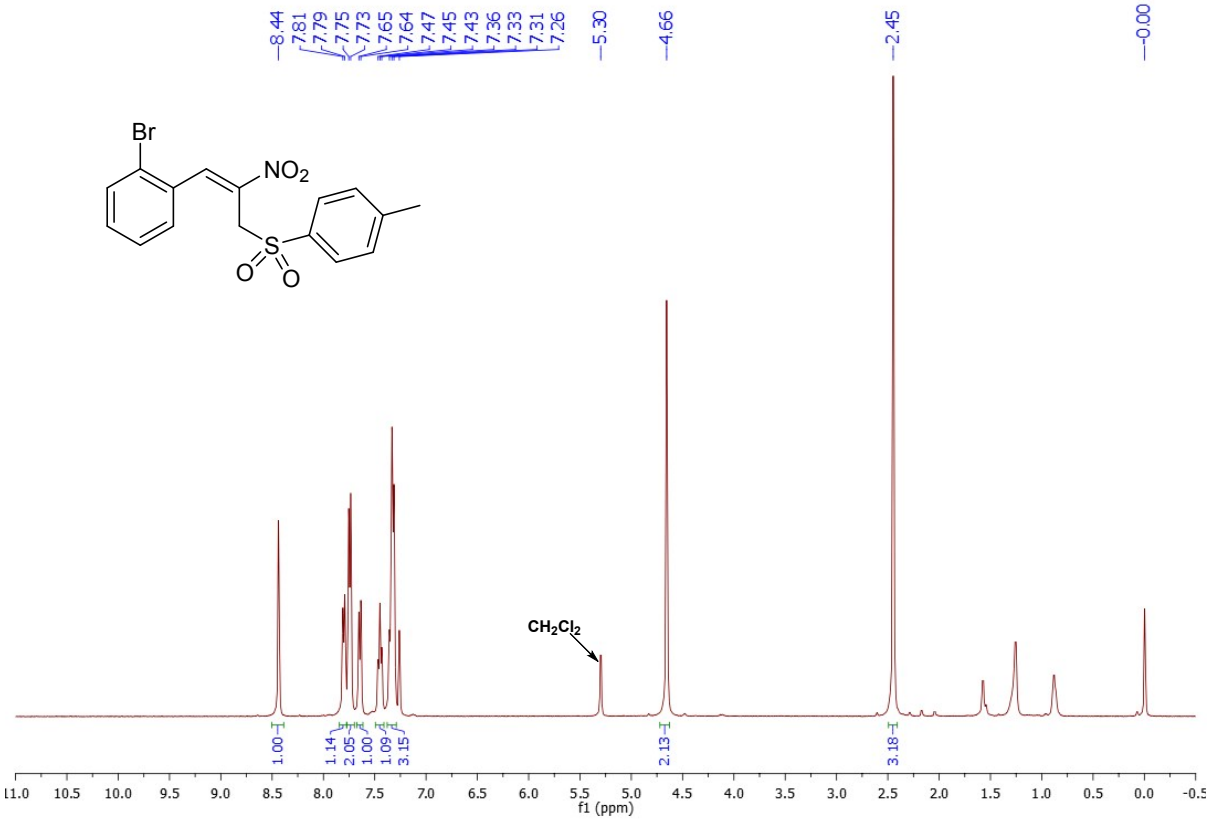



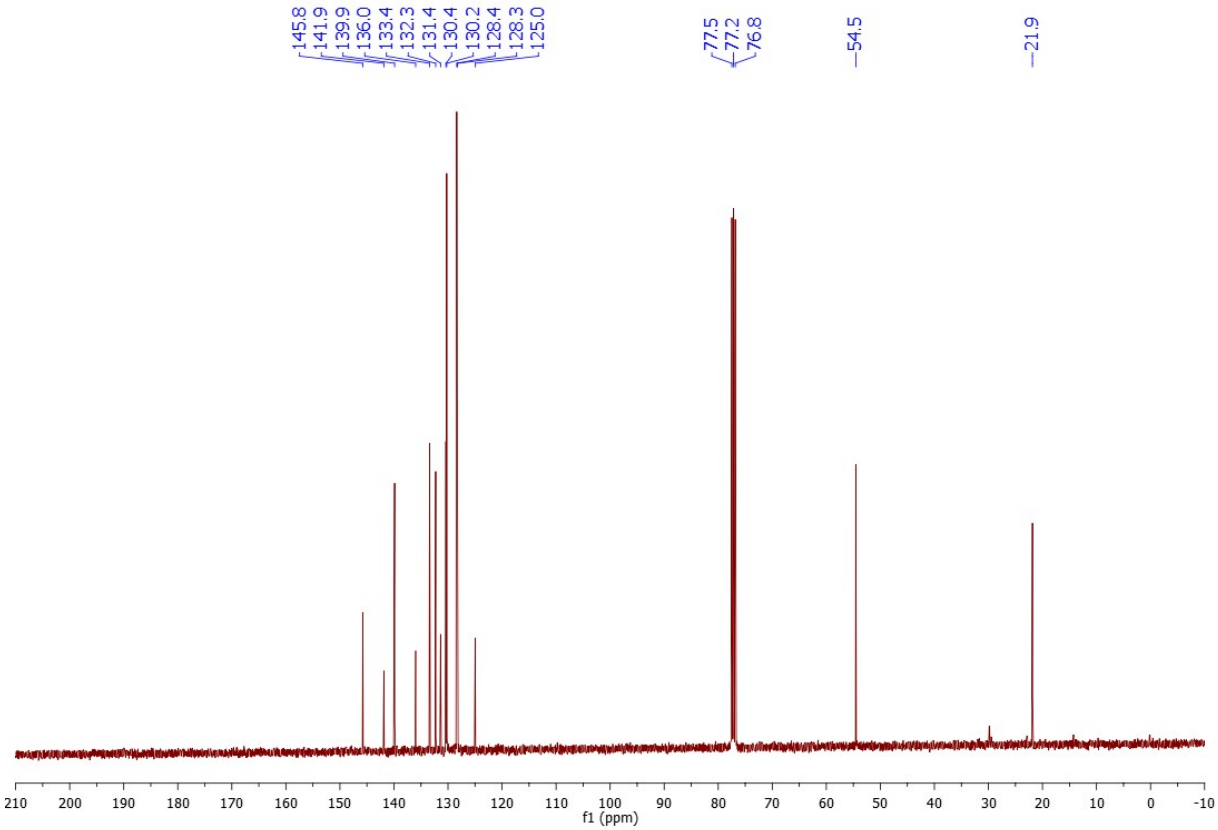
***(E)-1-Chloro-4-(2-nitro-3-tosylprop-1-en-1-yl)benzene (4e): $^{1}H$ and $^{13}C$ in $CDCl_3$***



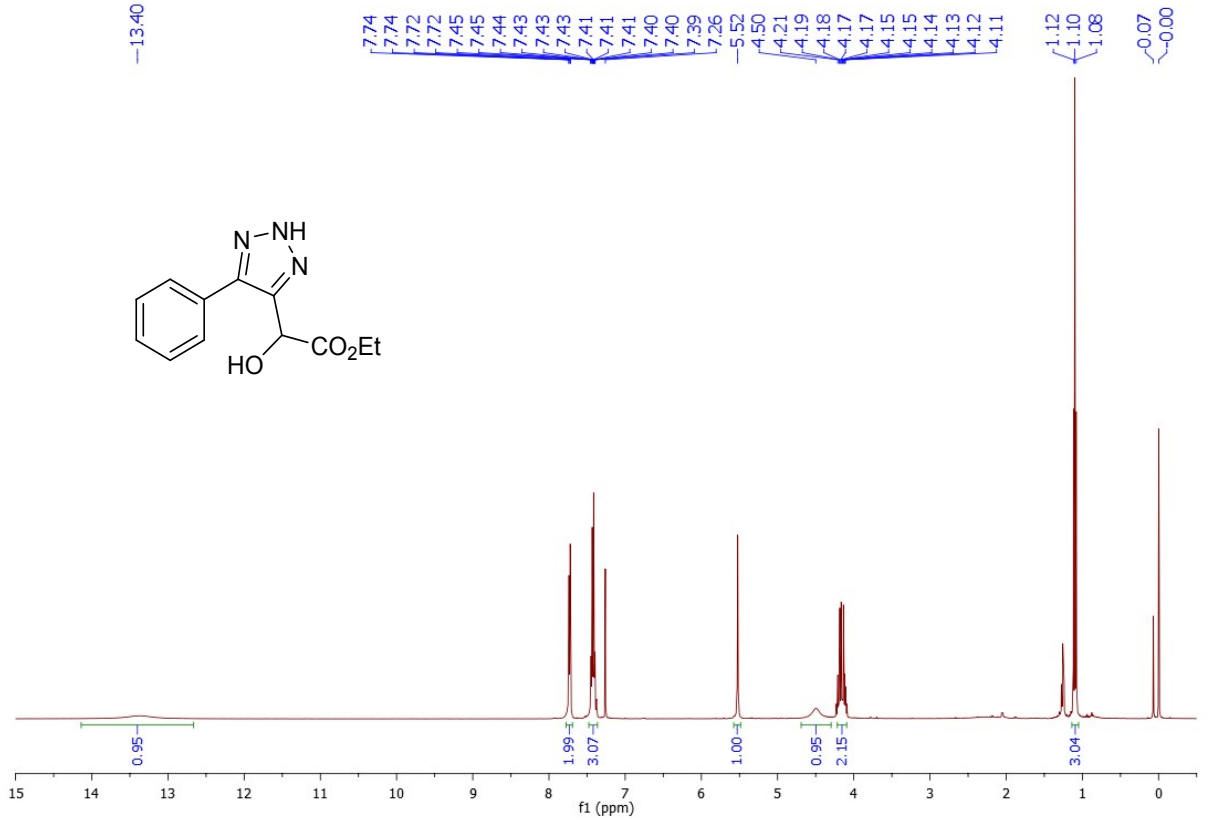



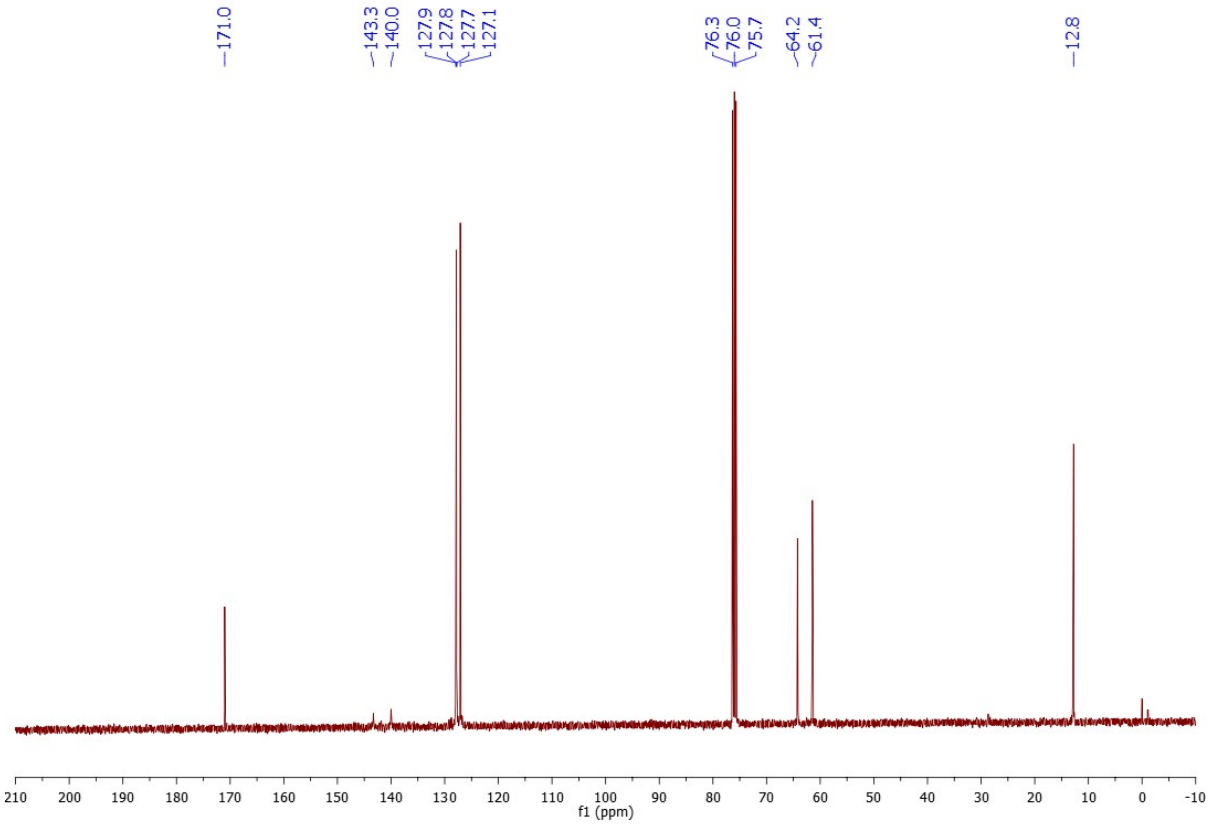
***(E)-1-Bromo-2-(2-nitro-3-tosylprop-1-en-1-yl)benzene (4f): $^{1}H$ and $^{13}C$ in $CDCl_3$***



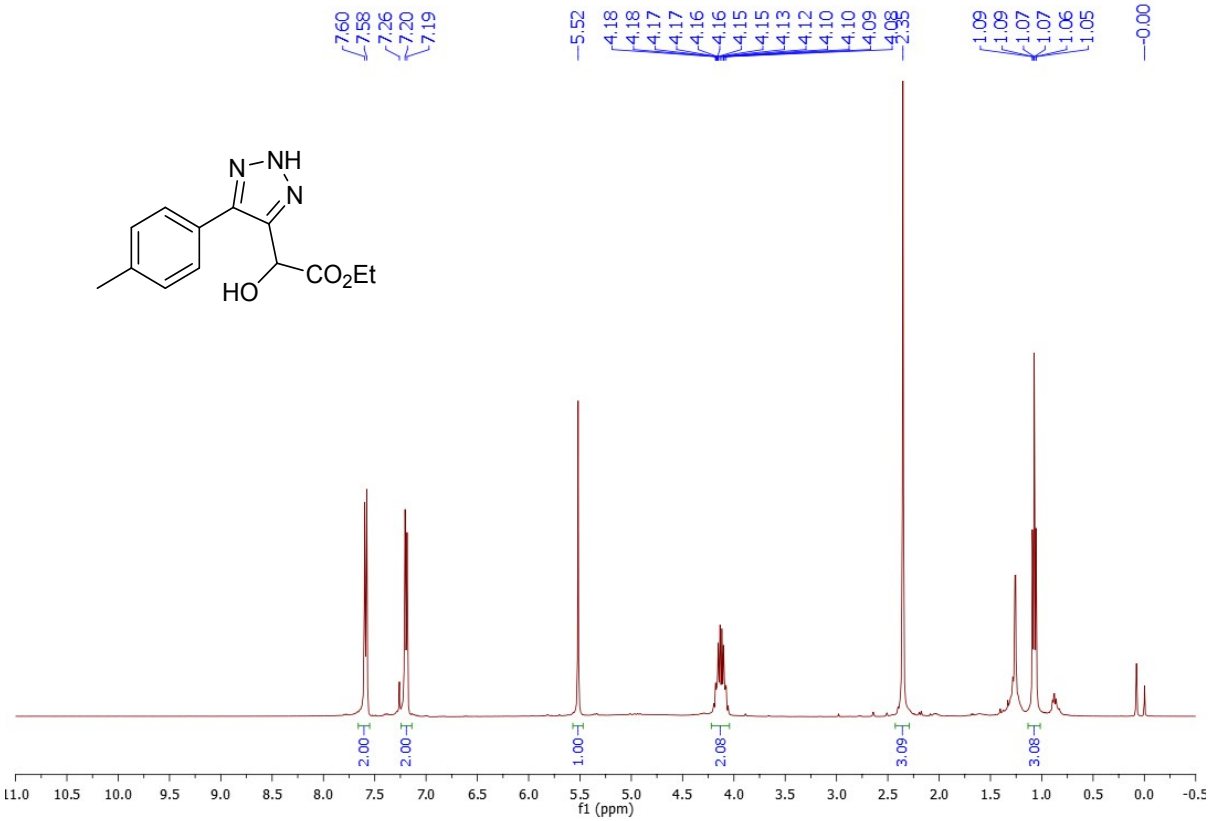



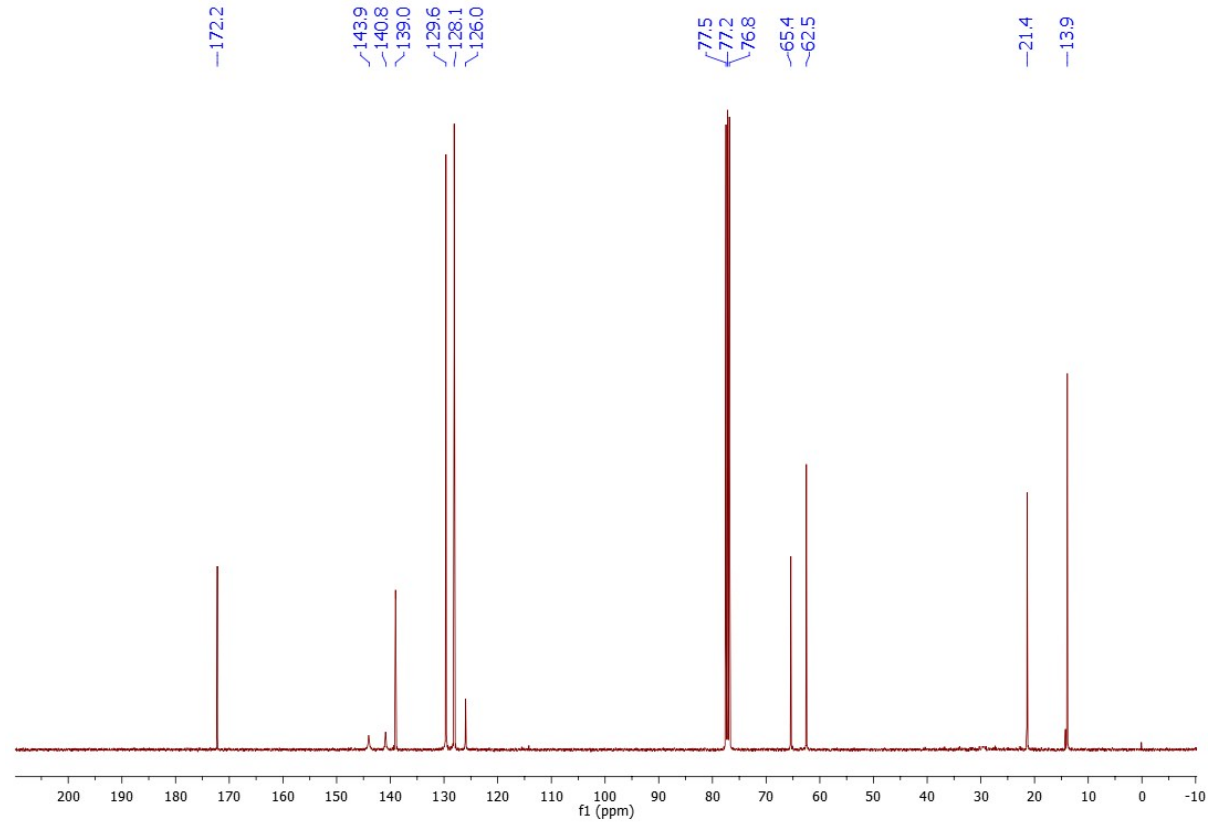
***Ethyl 2-hydroxy-2-(5-phenyl-1H-1,2,3-triazol-4-yl)acetate (2a): $^{1}H$ and $^{13}C$ in $CDCl_3$***



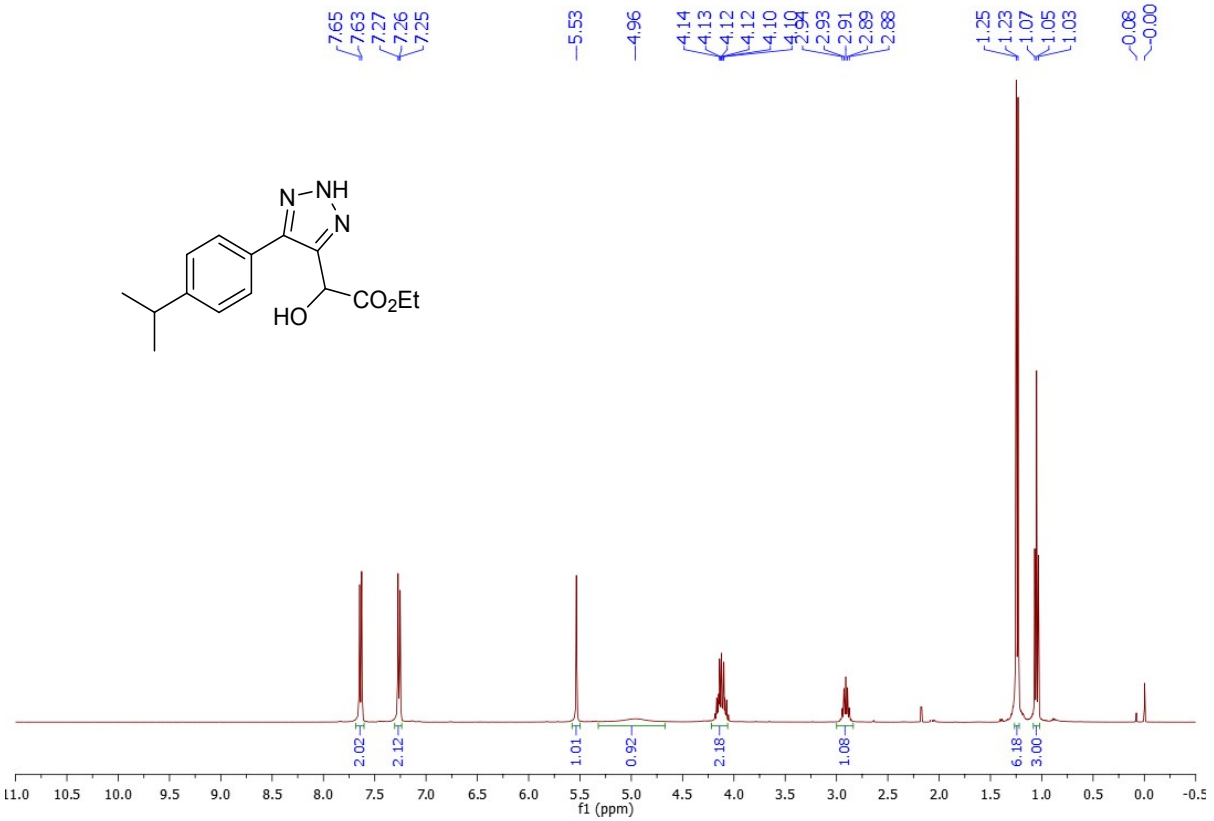



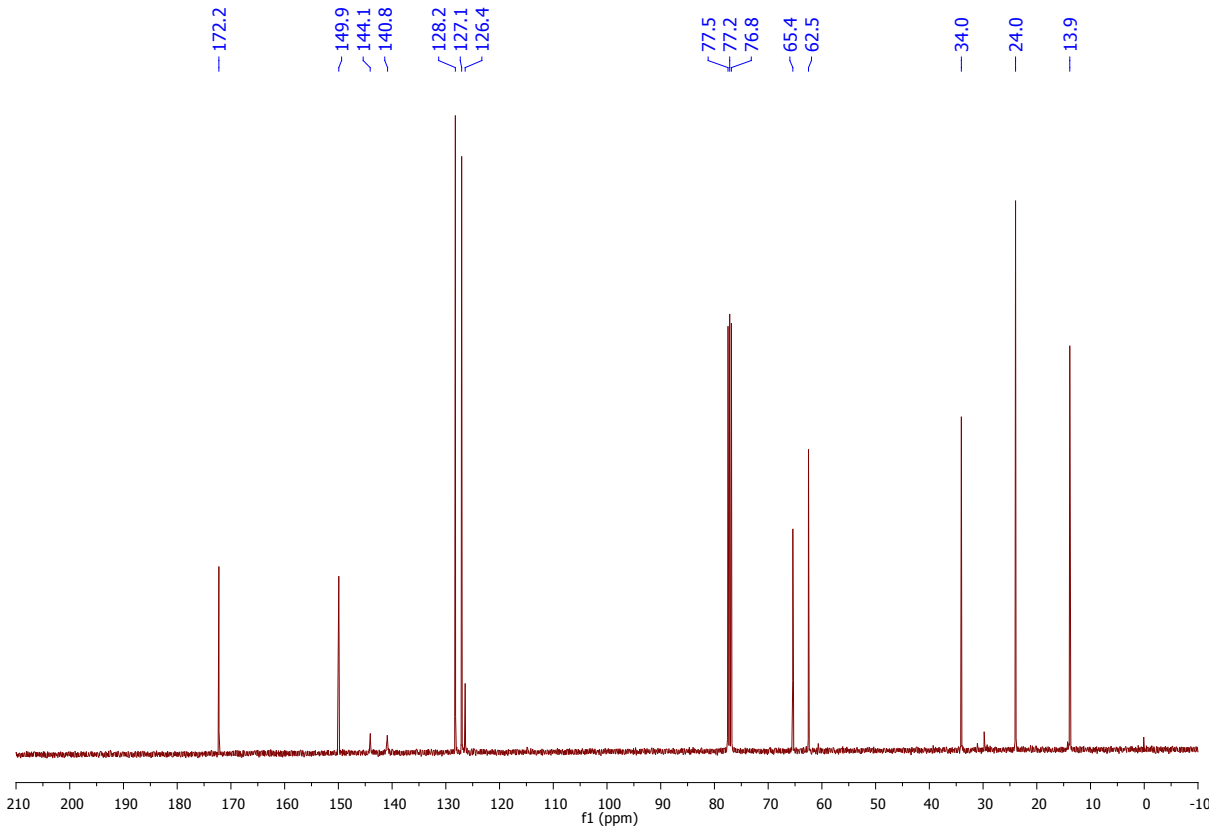
***Ethyl 2-hydroxy-2-[5-(4-methylphenyl)-1H-1,2,3-triazol-4-yl]acetate (2b): $^{1}H$ and $^{13}C$ in $CDCl_3$***



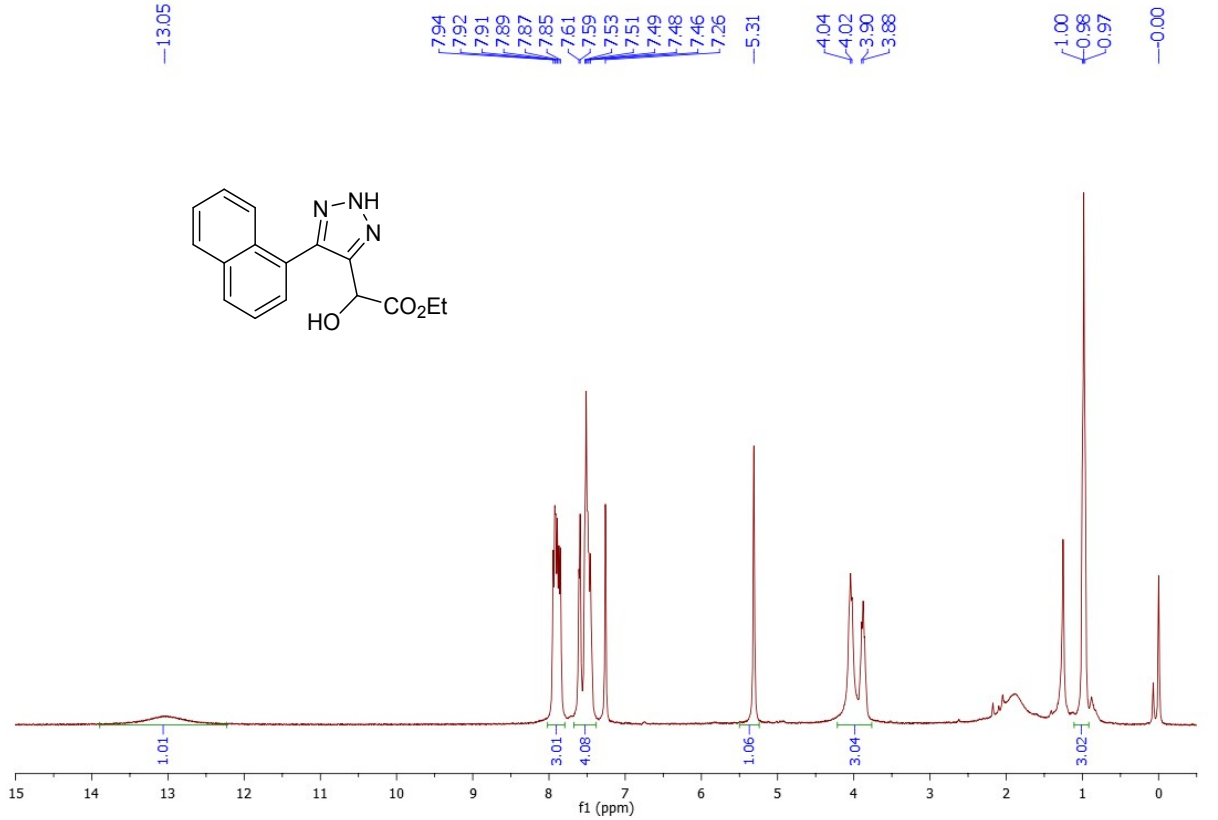



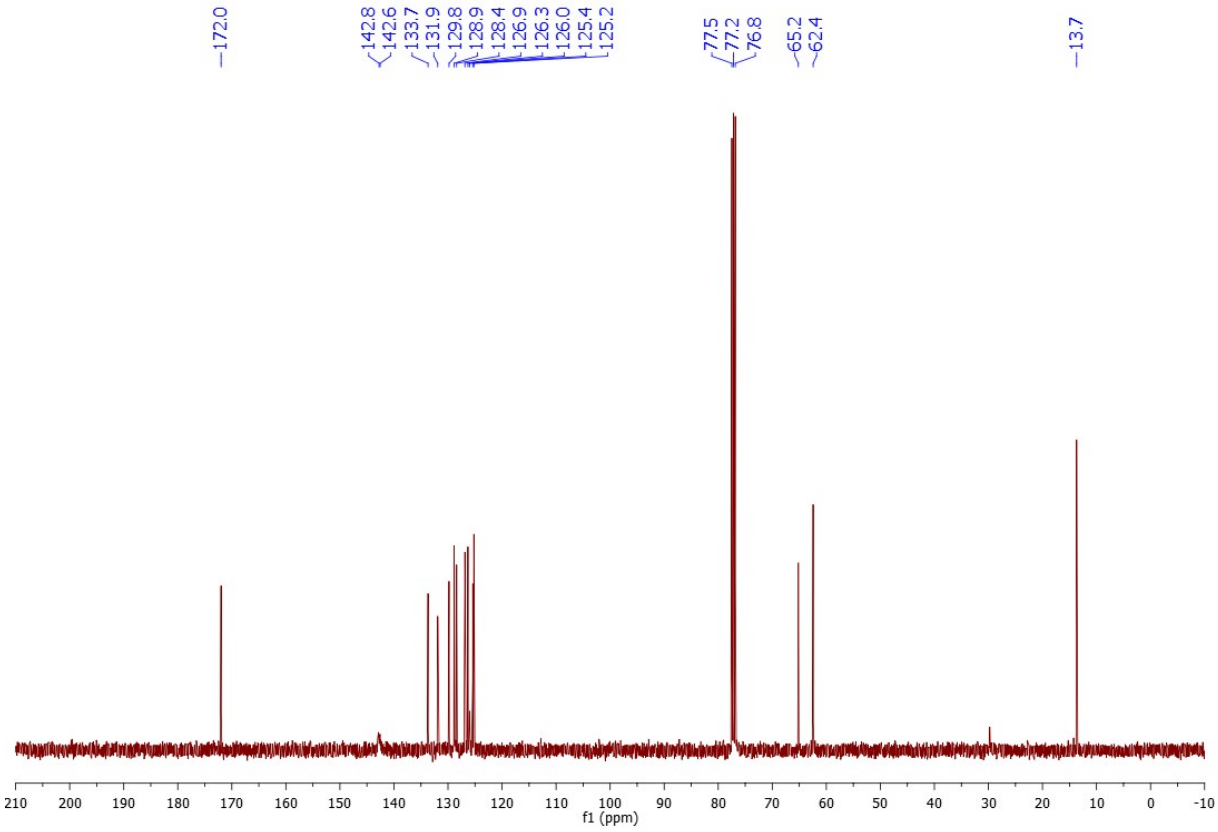
***Ethyl 2-hydroxy-2-[5-(4-isopropylphenyl)-1H-1,2,3-triazol-4-yl]acetate (2c): $^{1}H$ and $^{13}C$ in $CDCl_3$***



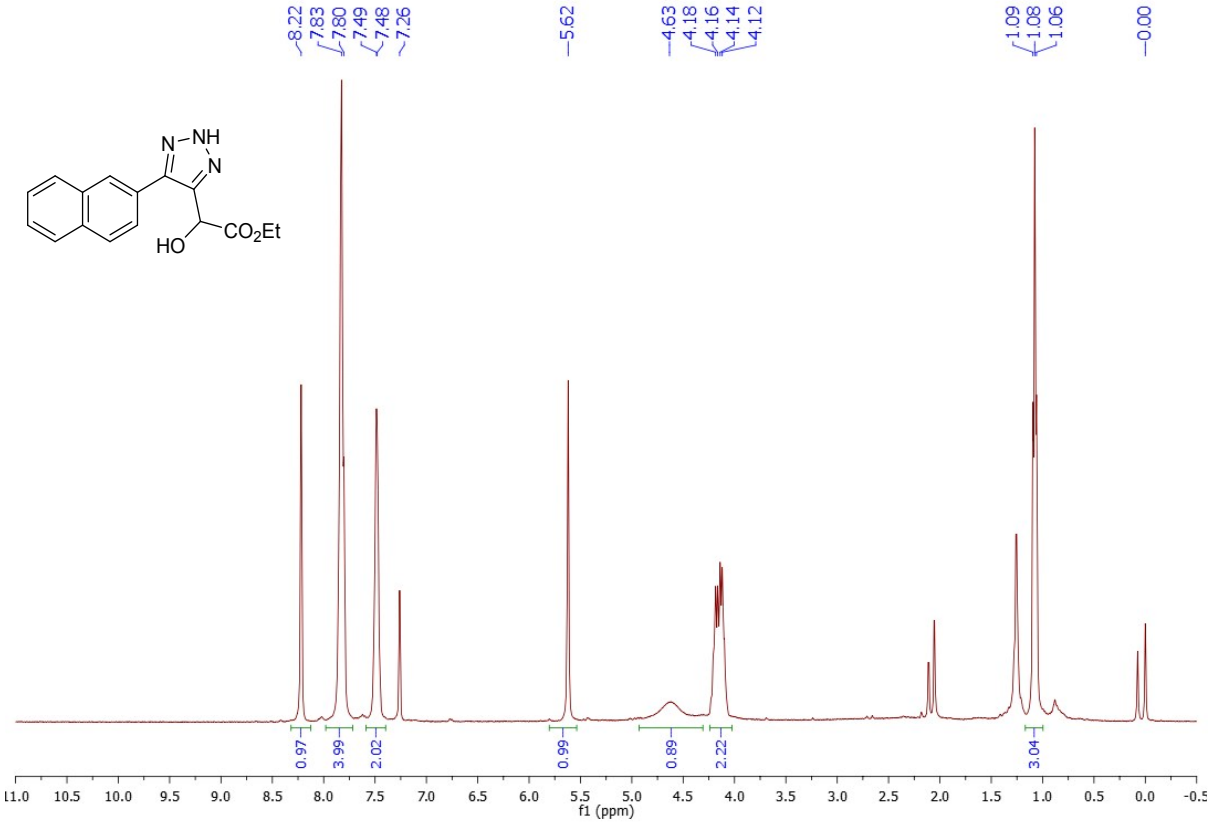



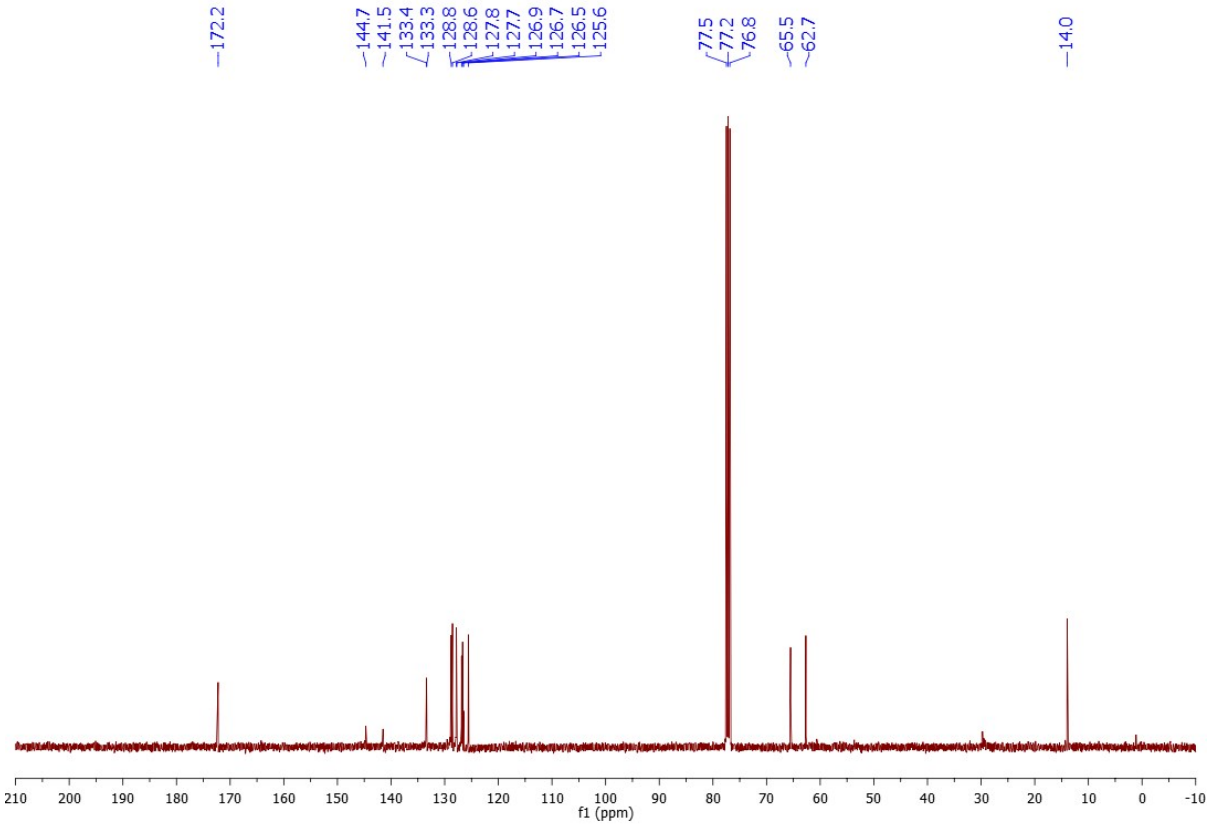
***Ethyl 2-hydroxy-2-[5-(naphthalen-1-yl)-1H-1,2,3-triazol-4-yl]acetate (2d): $^{1}H$ and $^{13}C$ in $CDCl_3$***



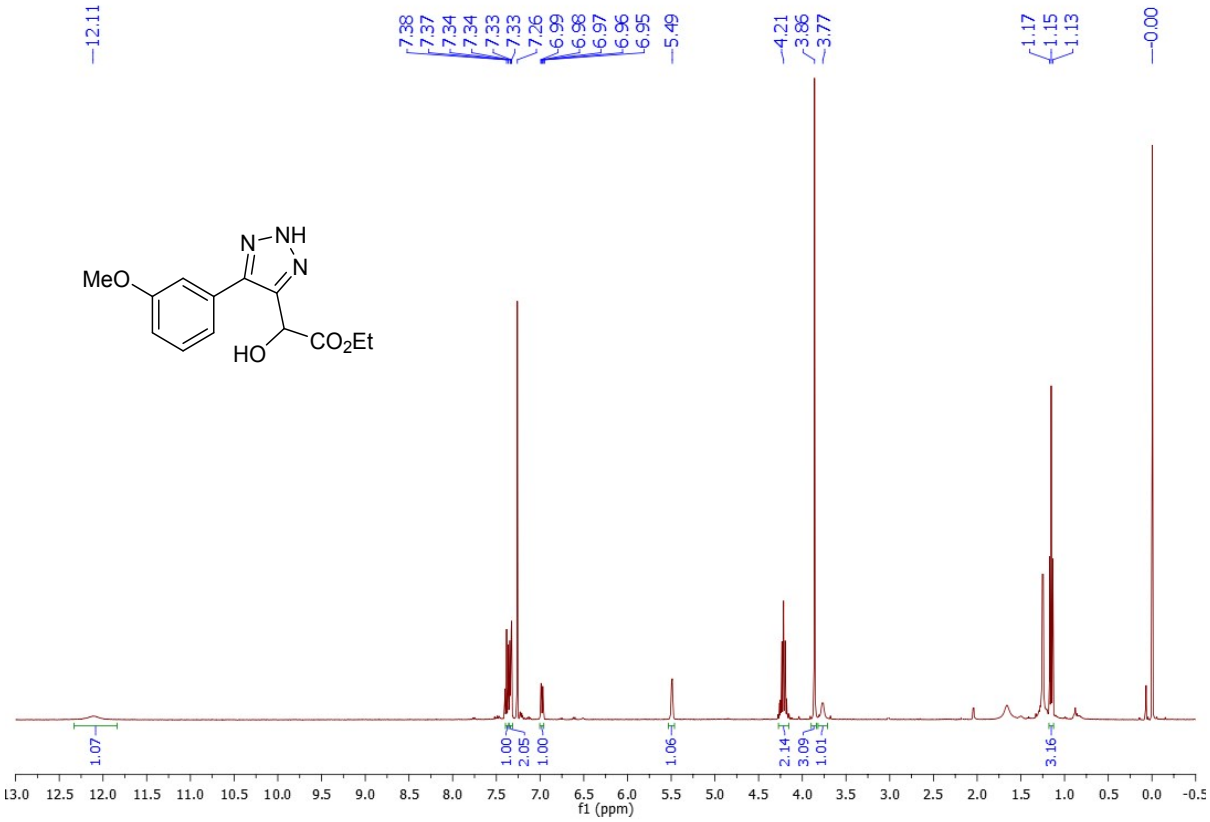



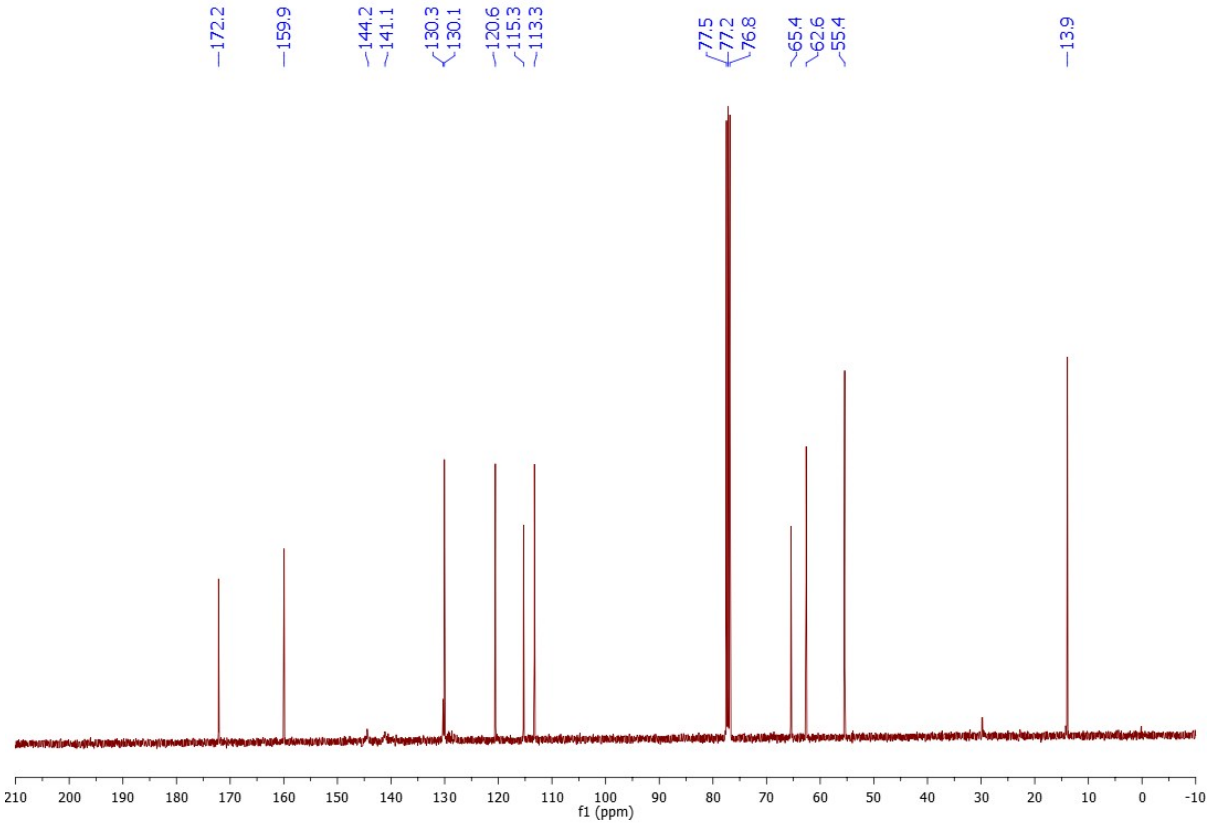
***Ethyl 2-hydroxy-2-[5-(naphthalen-2-yl)-2H-1,2,3-triazol-4-yl]acetate (2e): $^{1}H$ and $^{13}C$ in $CDCl_3$***



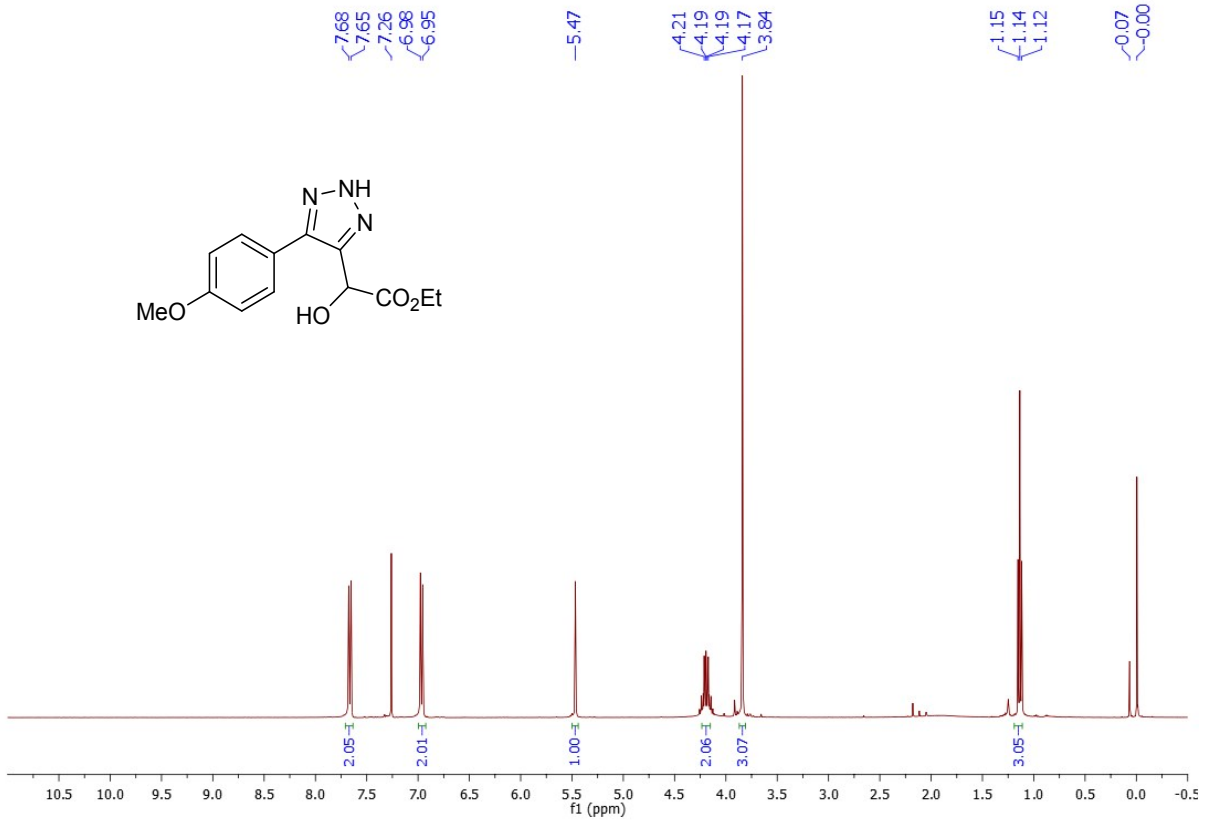



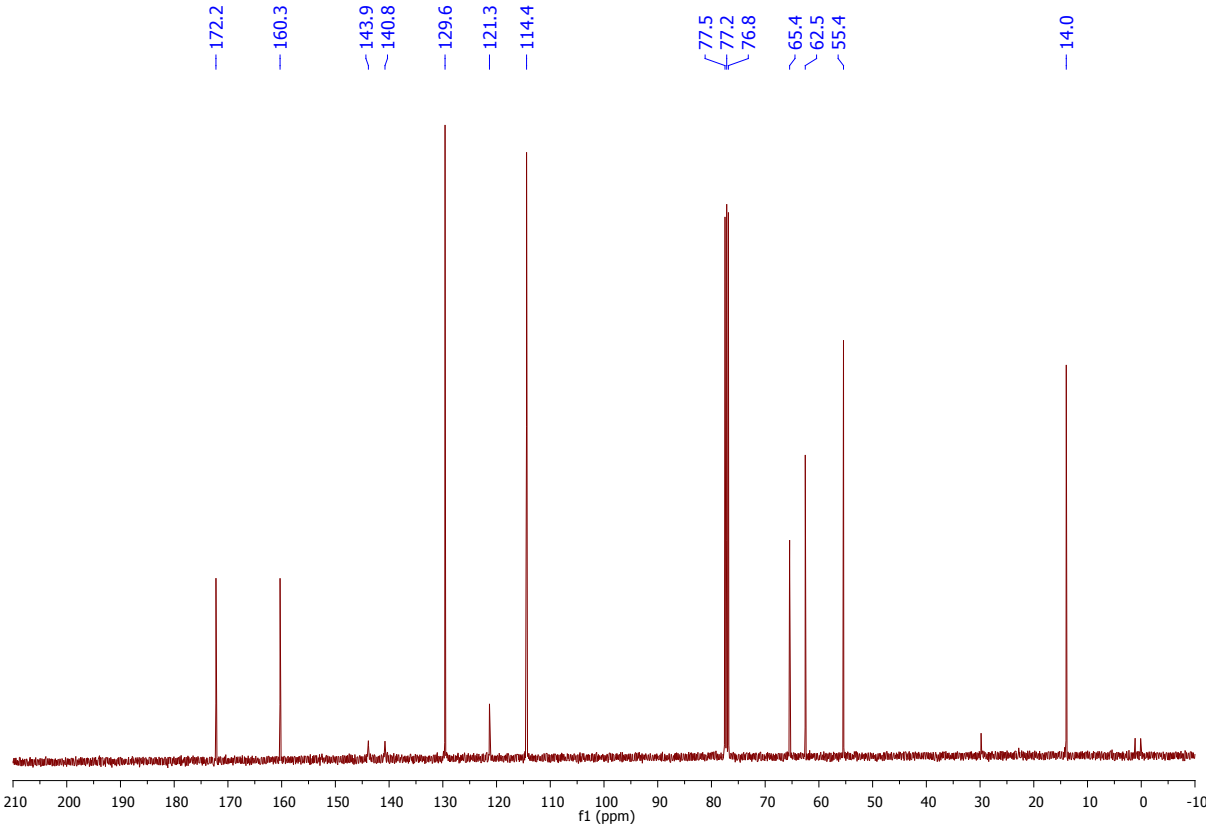
***Ethyl 2-hydroxy-2-[5-(3-methoxyphenyl)-1H-1,2,3-triazol-4-yl]acetate (2f): $^{1}H$ and $^{13}C$ in $CDCl_3$***



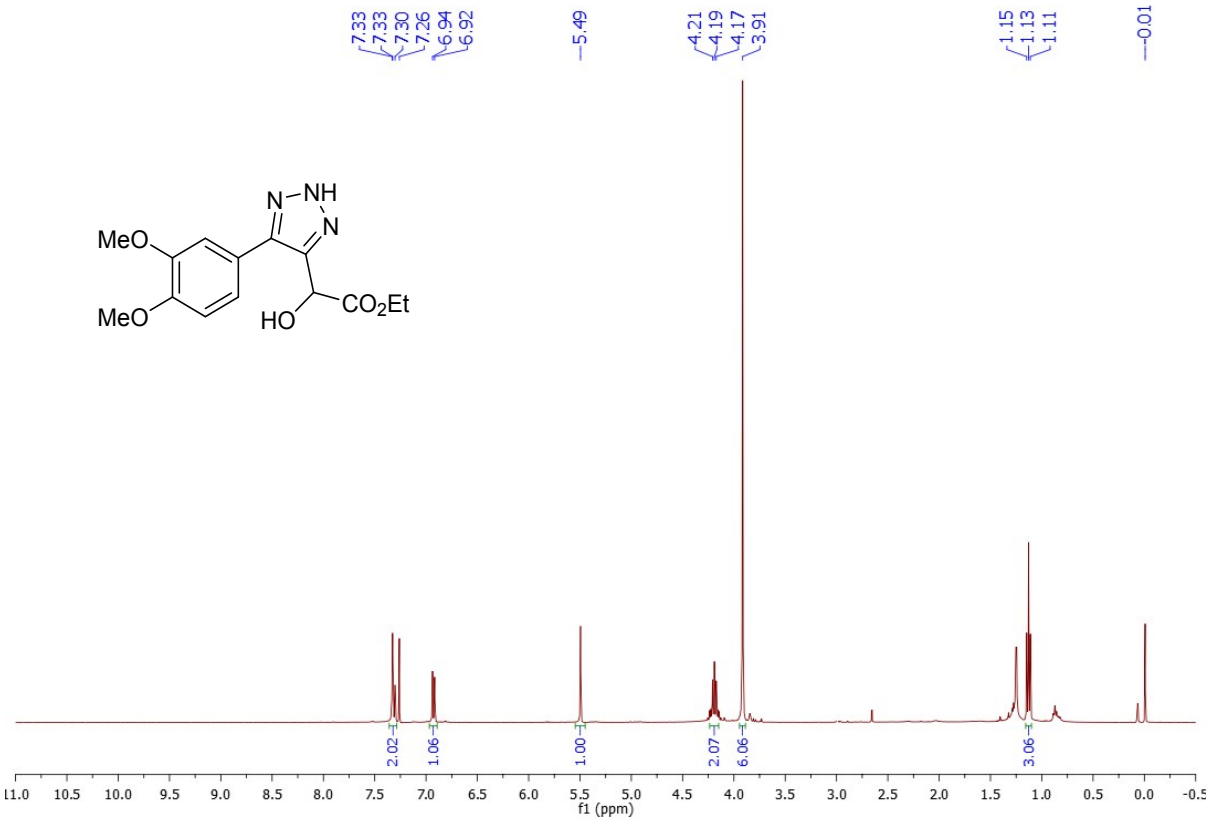



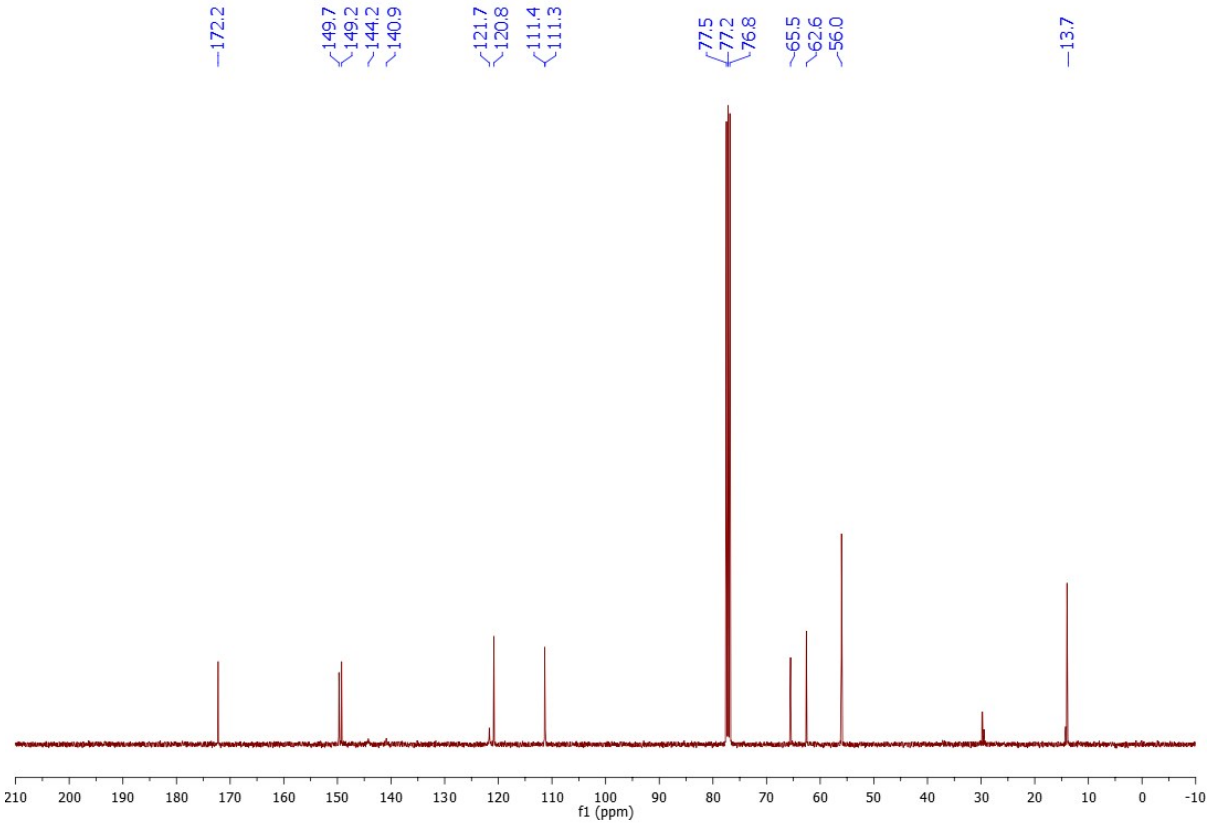
***Ethyl 2-hydroxy-2-[5-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl]acetate (2g): $^{1}H$ and $^{13}C$ in $CDCl_3$***



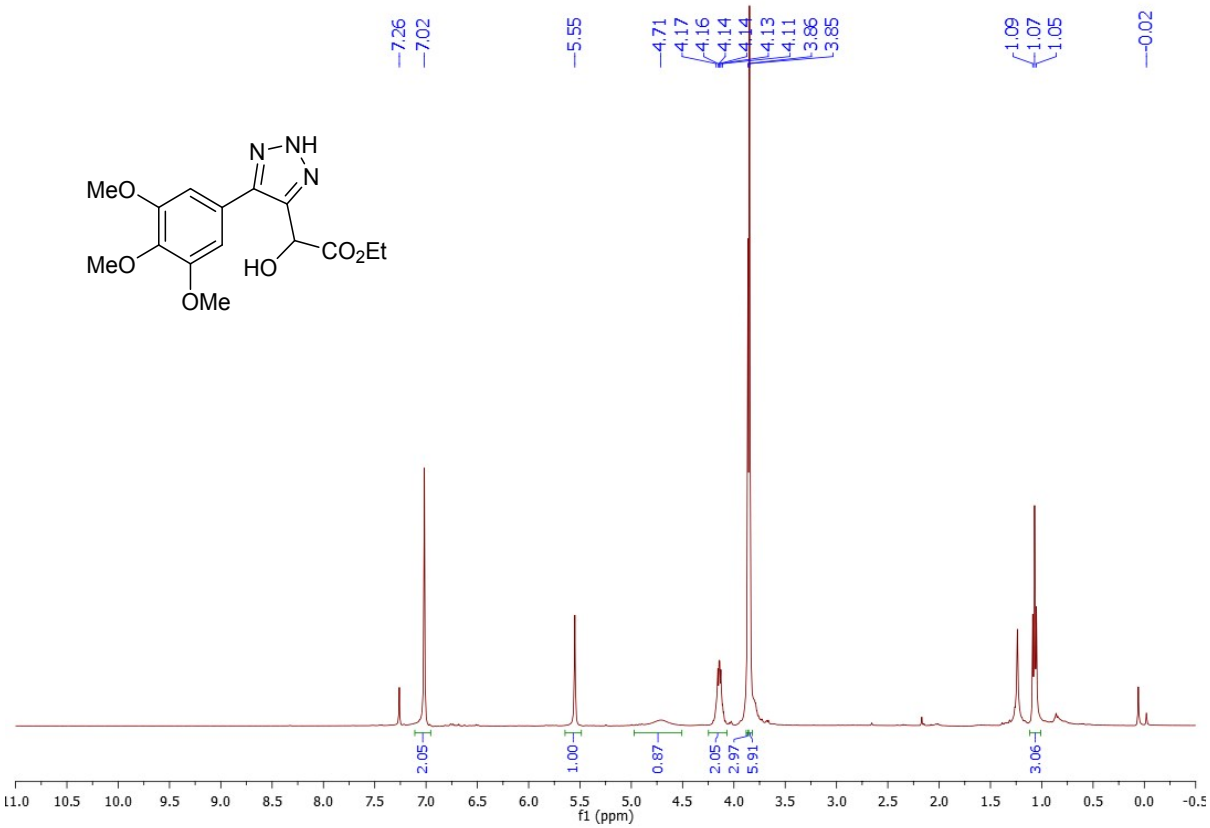



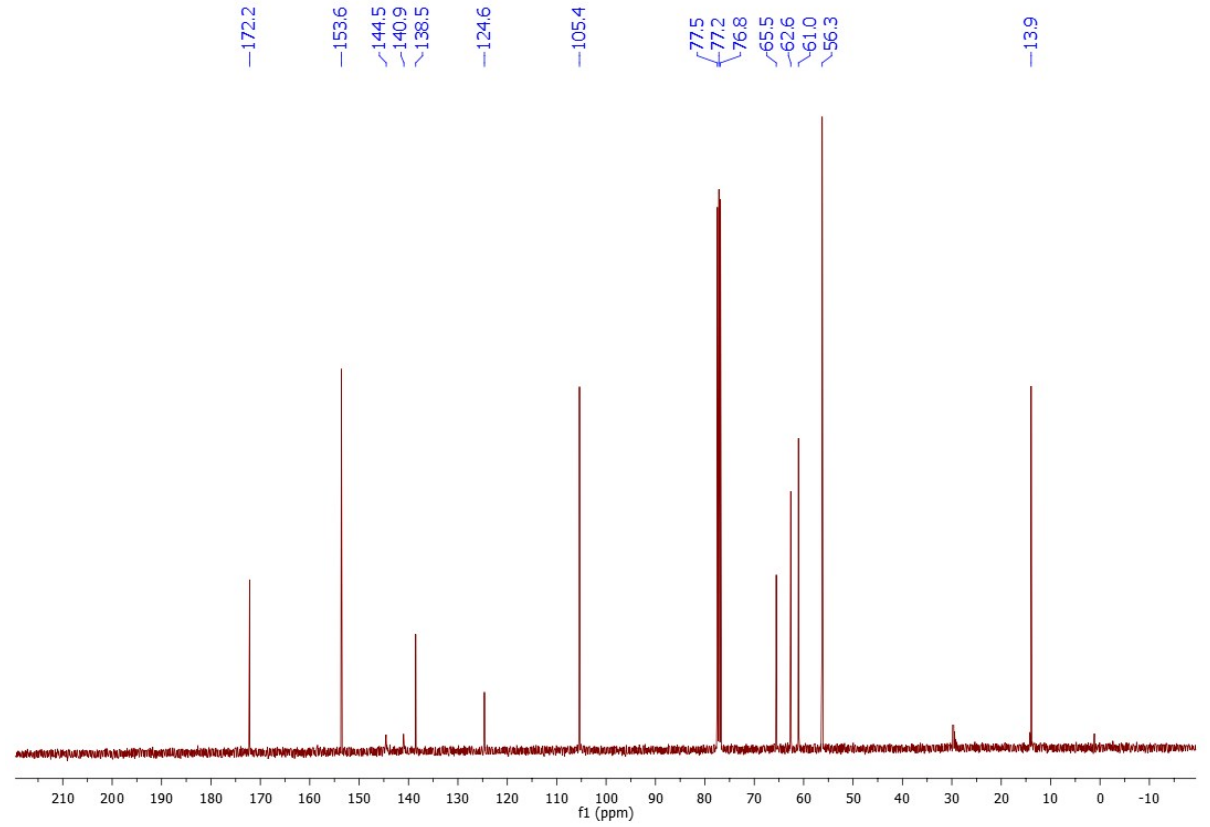
***Ethyl 2-[5-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-4-yl]-2-hydroxyacetate (2h): $^{1}H$ and $^{13}C$ in $CDCl_3$***



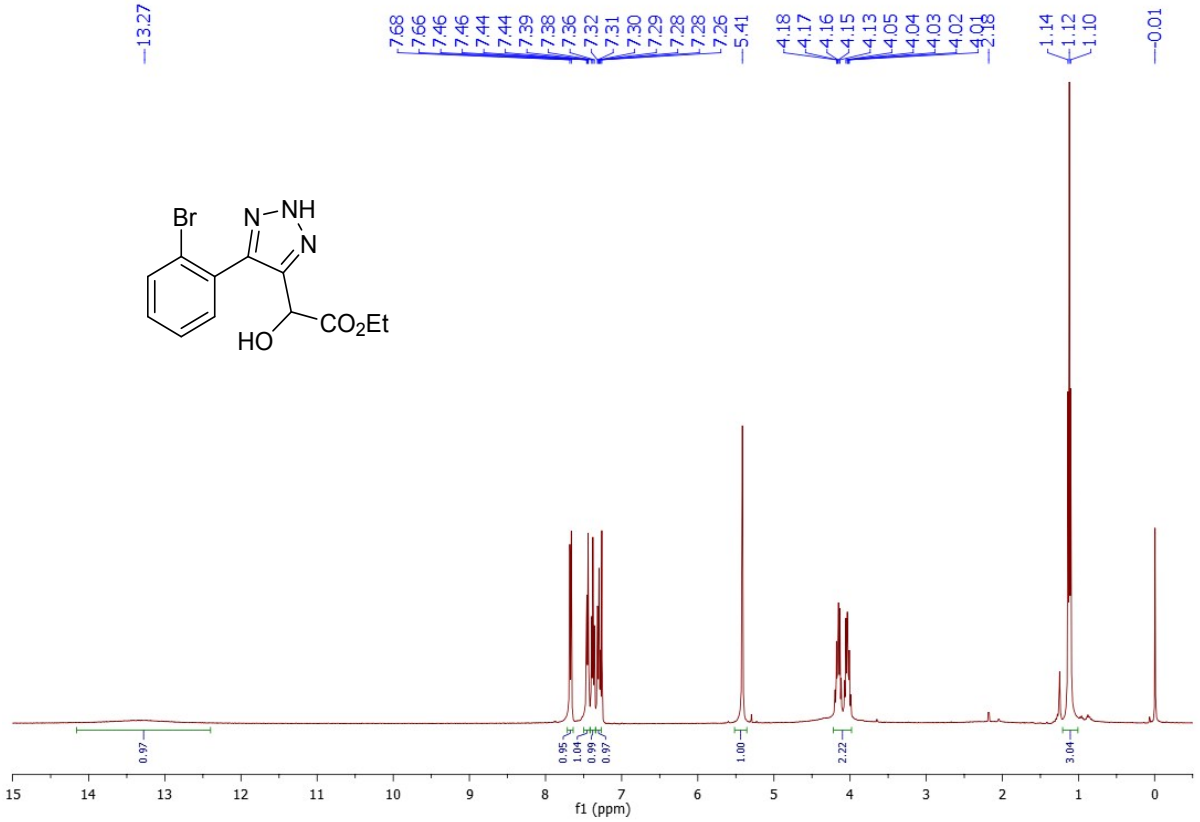



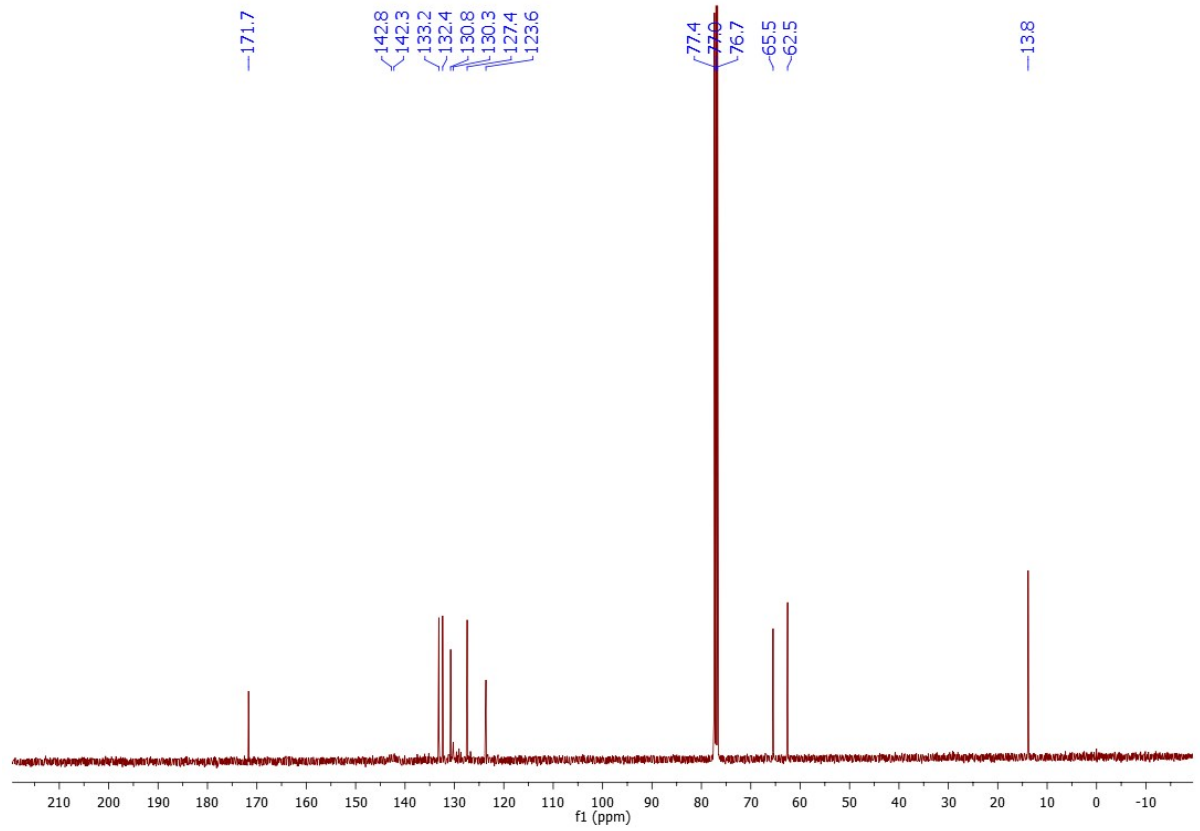
***Ethyl 2-hydroxy-2-[5-(3,4,5-trimethoxyphenyl)-1H-1,2,3-triazol-4-yl]acetate (2i): $^{1}H$ and $^{13}C$ in $CDCl_3$***



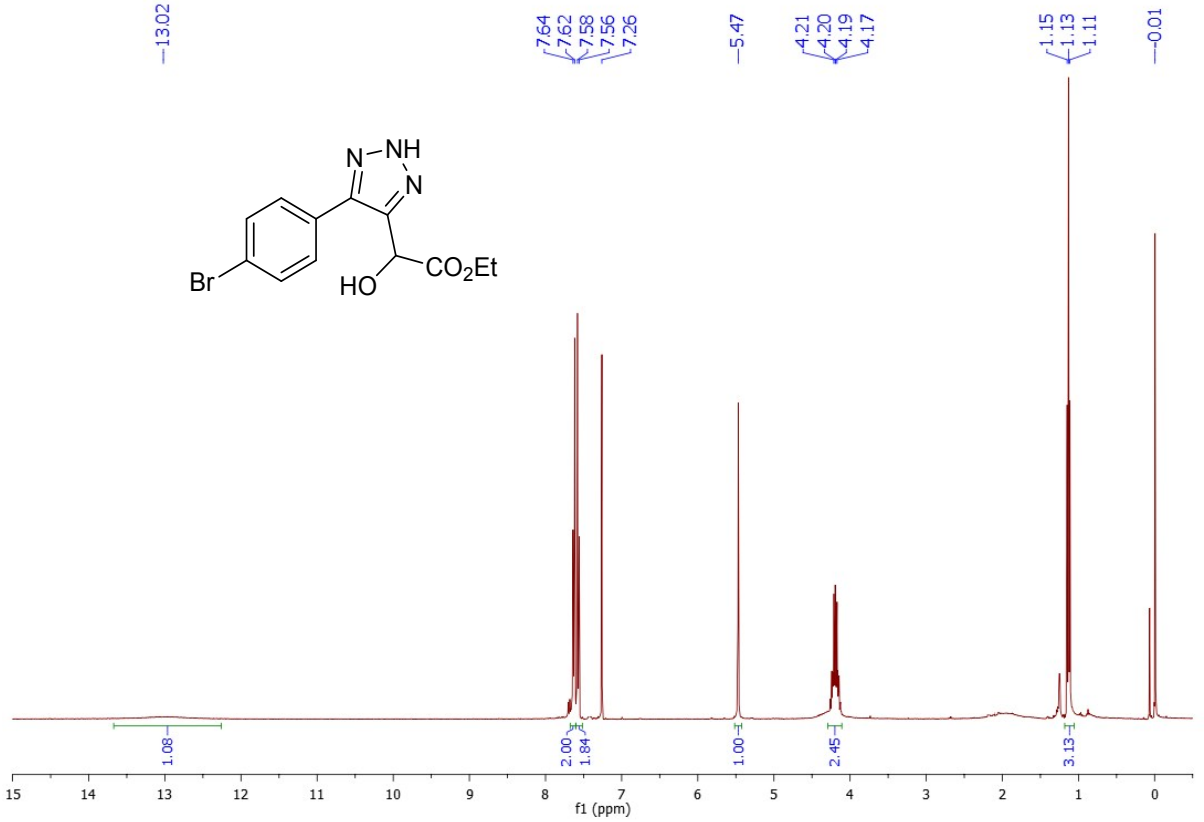



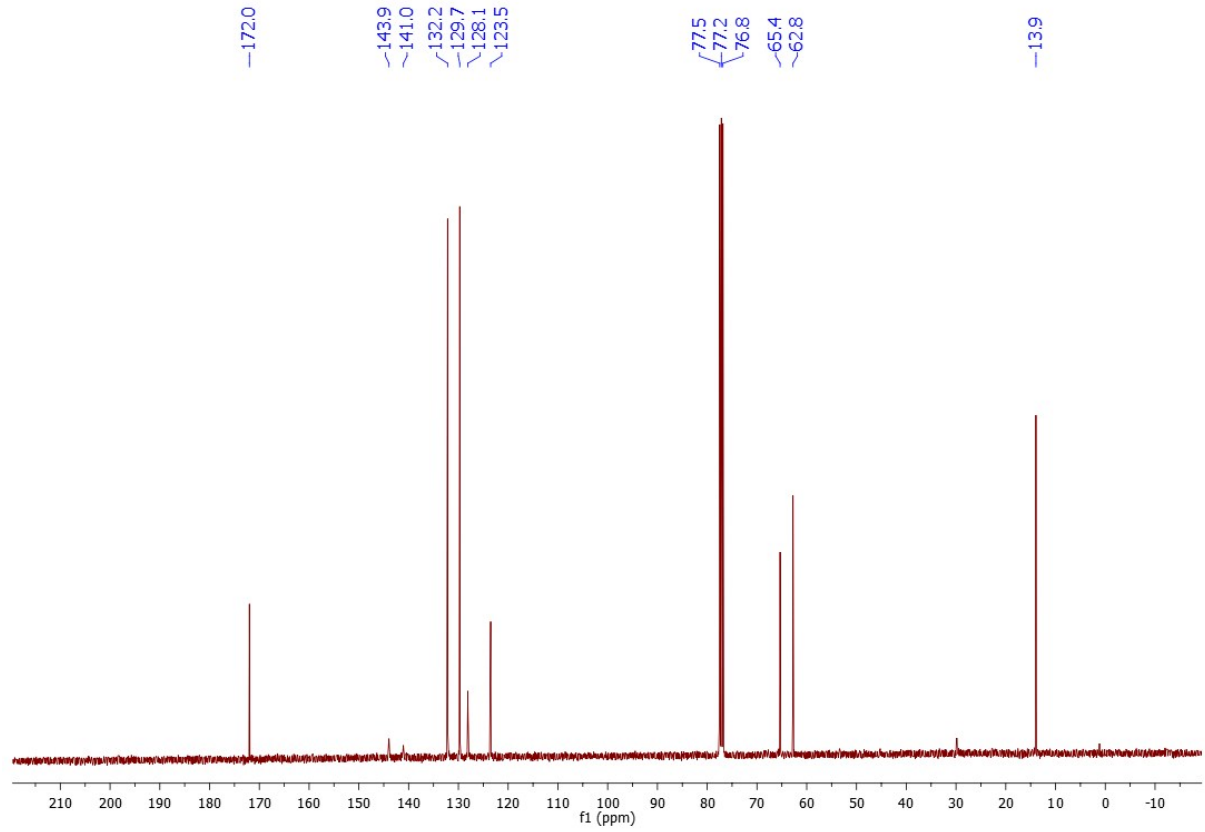
***Ethyl 2-[5-(2-bromophenyl)-1H-1,2,3-triazol-4-yl]-2-hydroxyacetate (2j): $^{1}H$ and $^{13}C$ in $CDCl_3$***



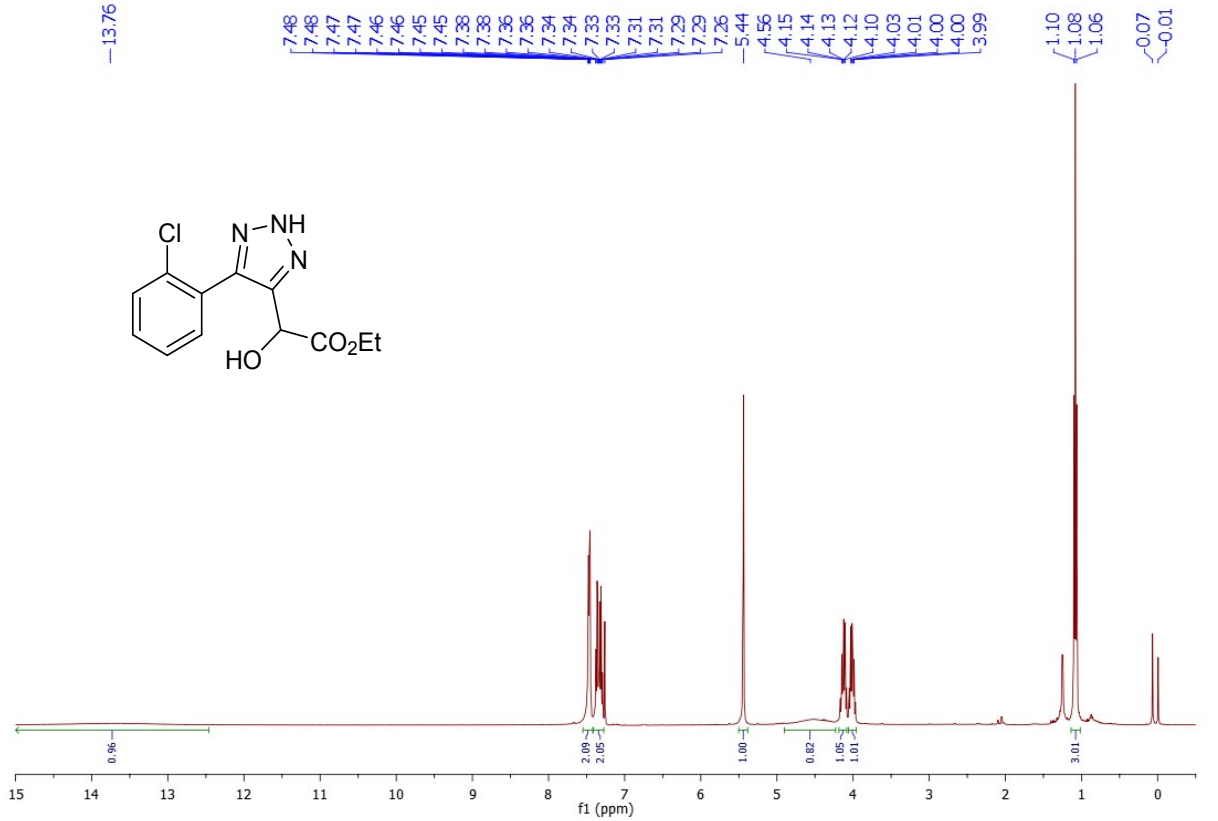



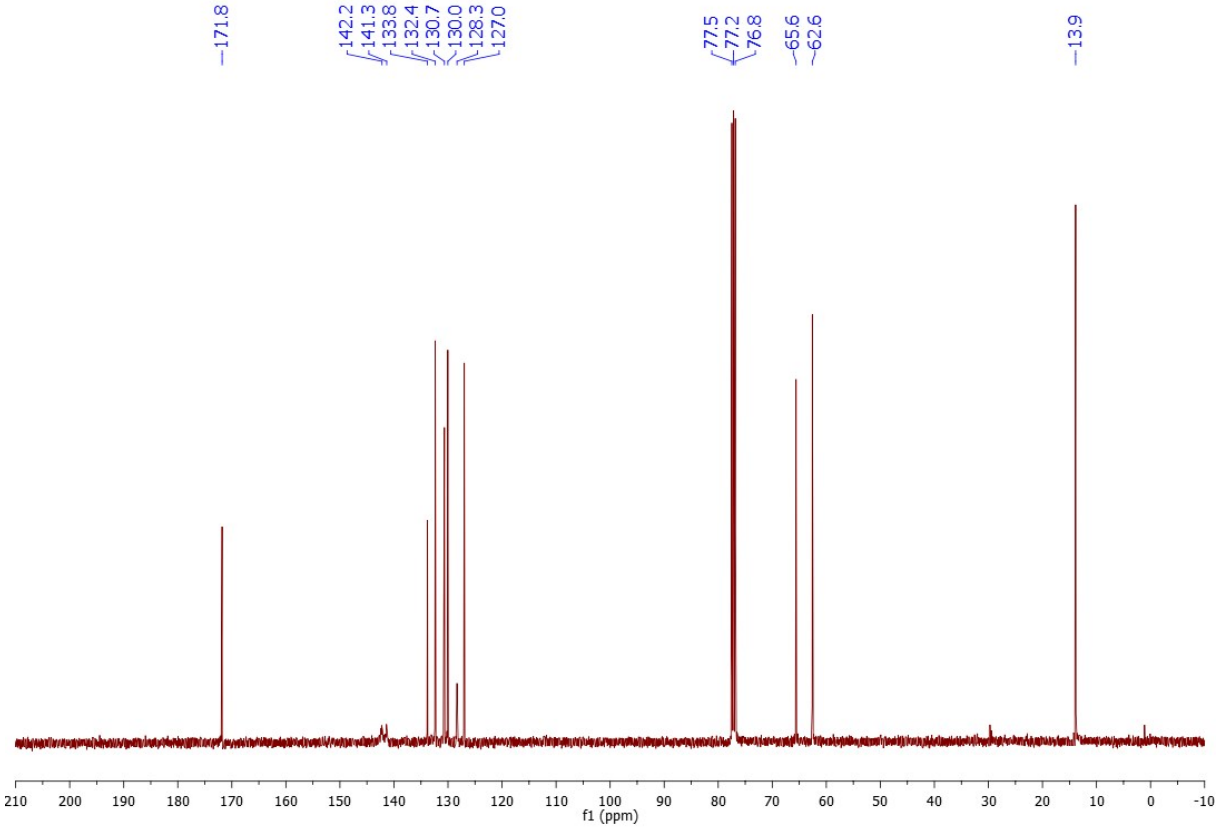
***Ethyl 2-[5-(4-bromophenyl)-1H-1,2,3-triazol-4-yl]-2-hydroxyacetate (2k): $^{1}H$ and $^{13}C$ in $CDCl_3$***



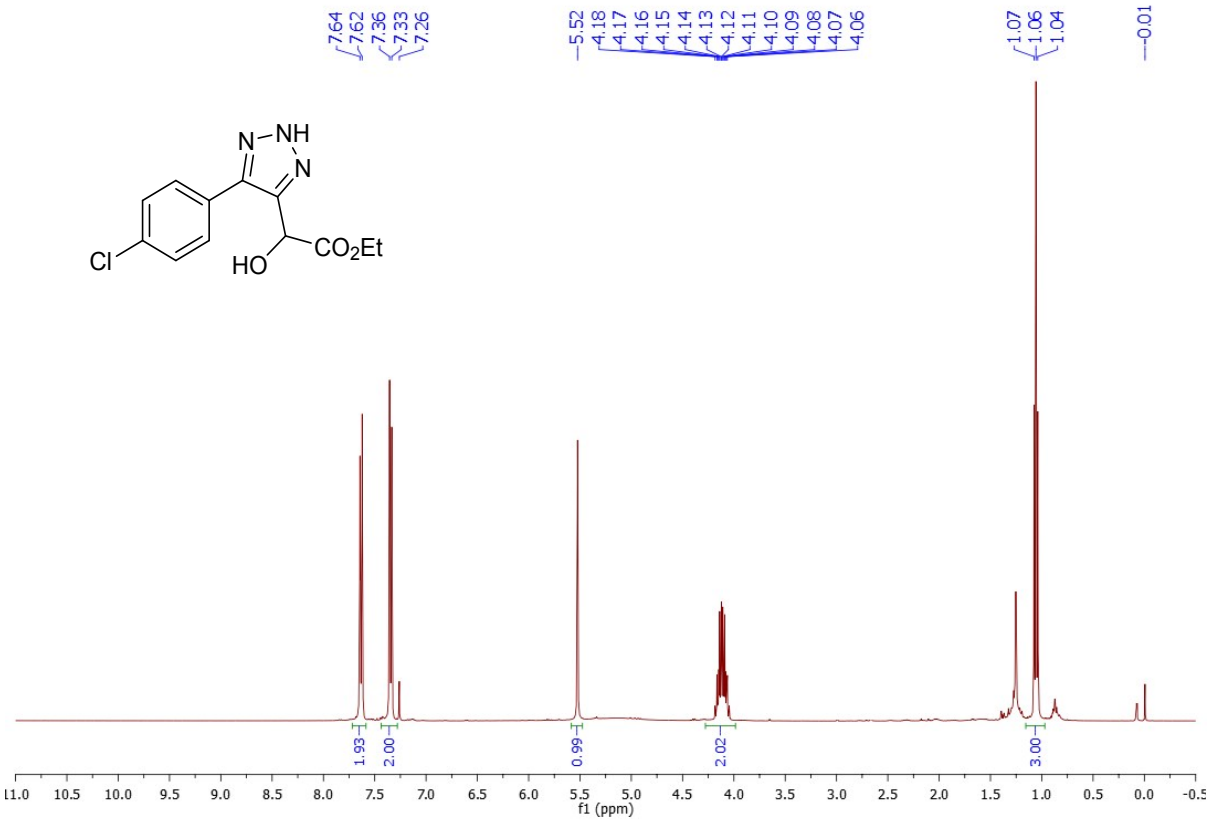



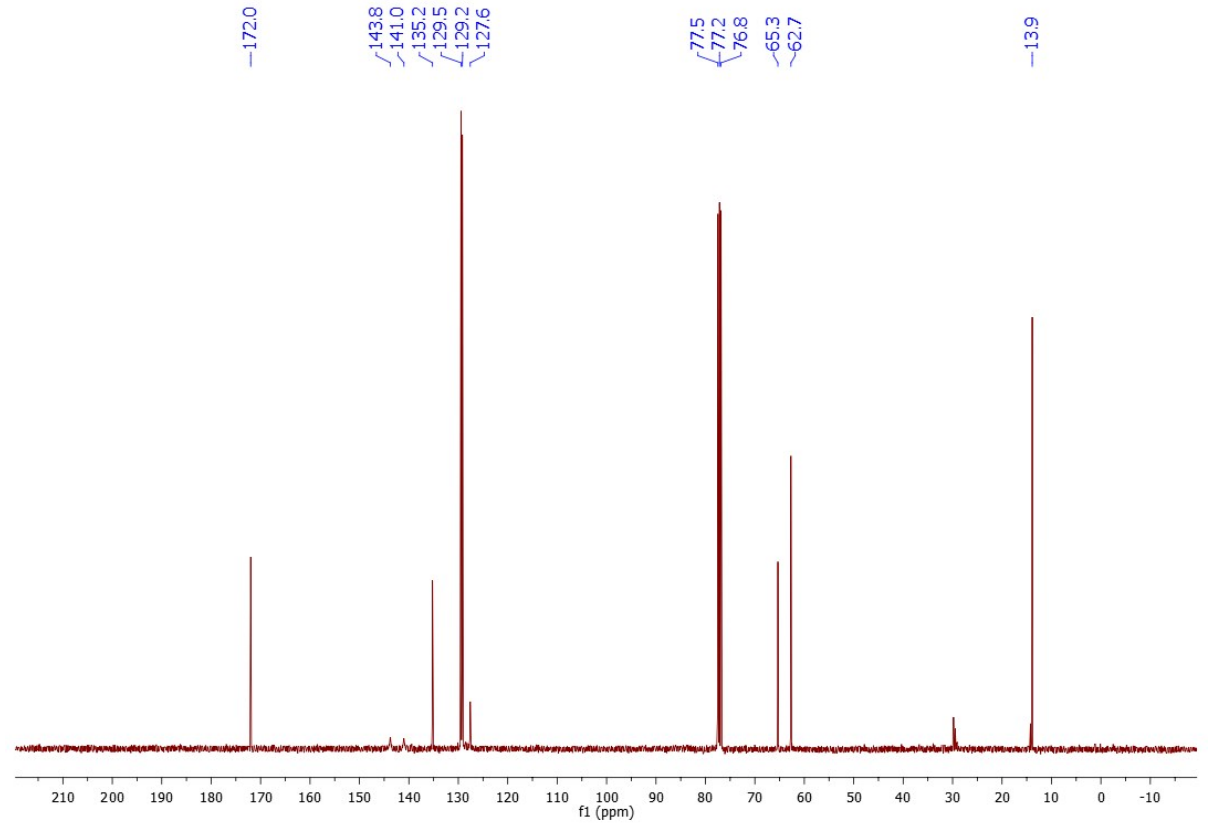
***Ethyl 2-[5-(2-chlorophenyl)-1H-1,2,3-triazol-4-yl]-2-hydroxyacetate (2l): $^{1}H$ and $^{13}C$ in $CDCl_3$***



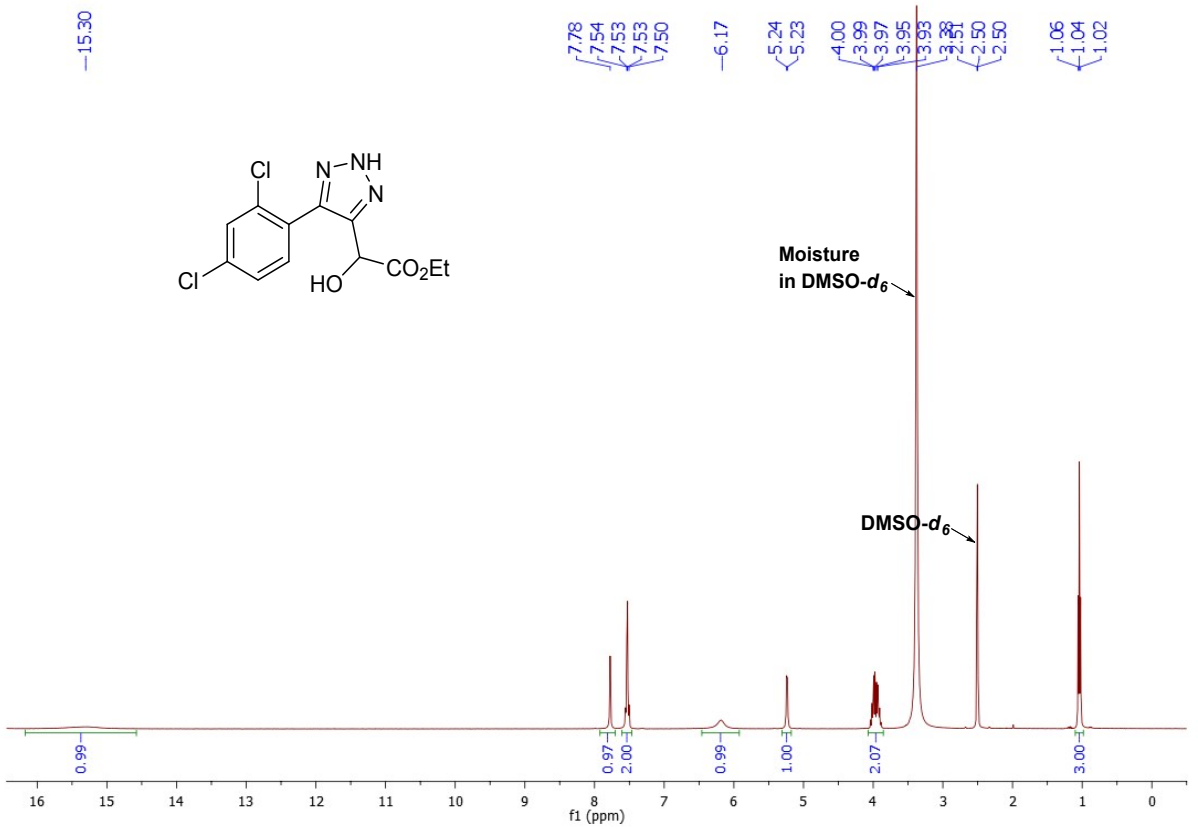



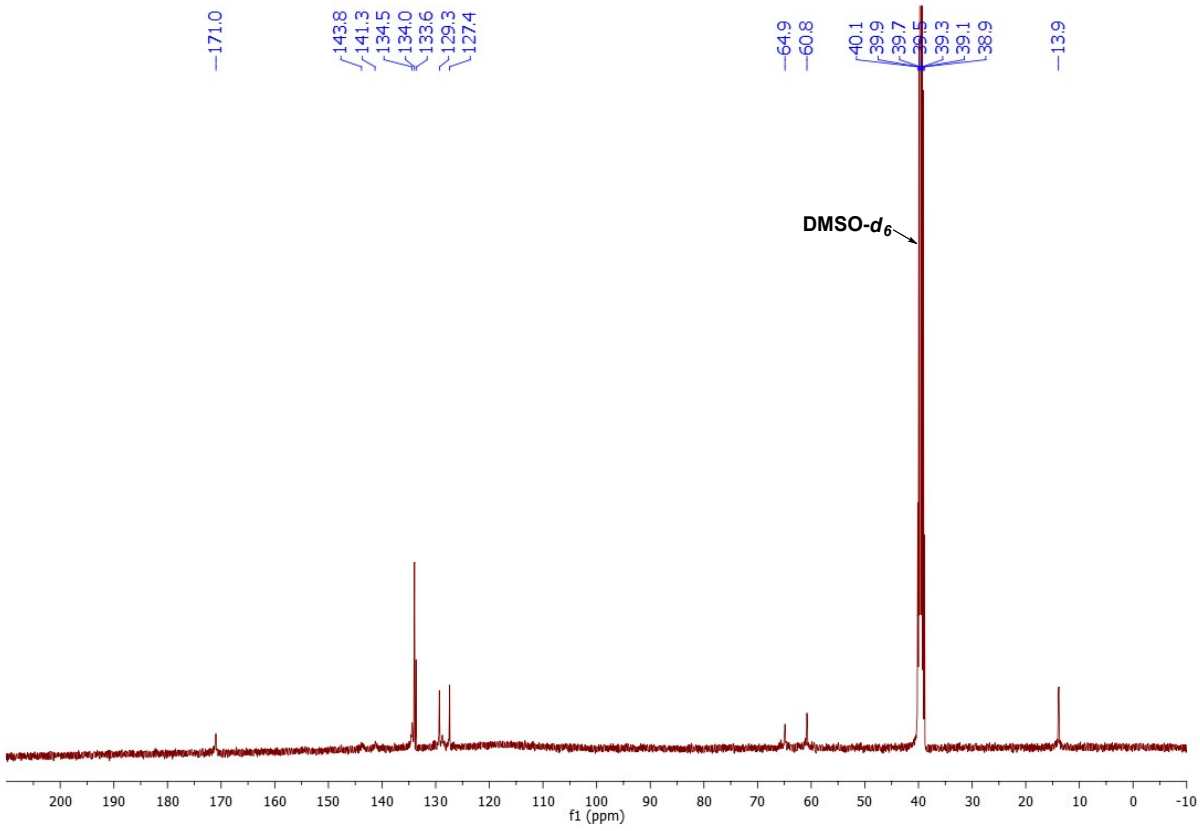
***Ethyl 2-[5-(4-chlorophenyl)-1H-1,2,3-triazol-4-yl]-2-hydroxyacetate (2m): $^{1}H$ and $^{13}C$ in $CDCl_3$***



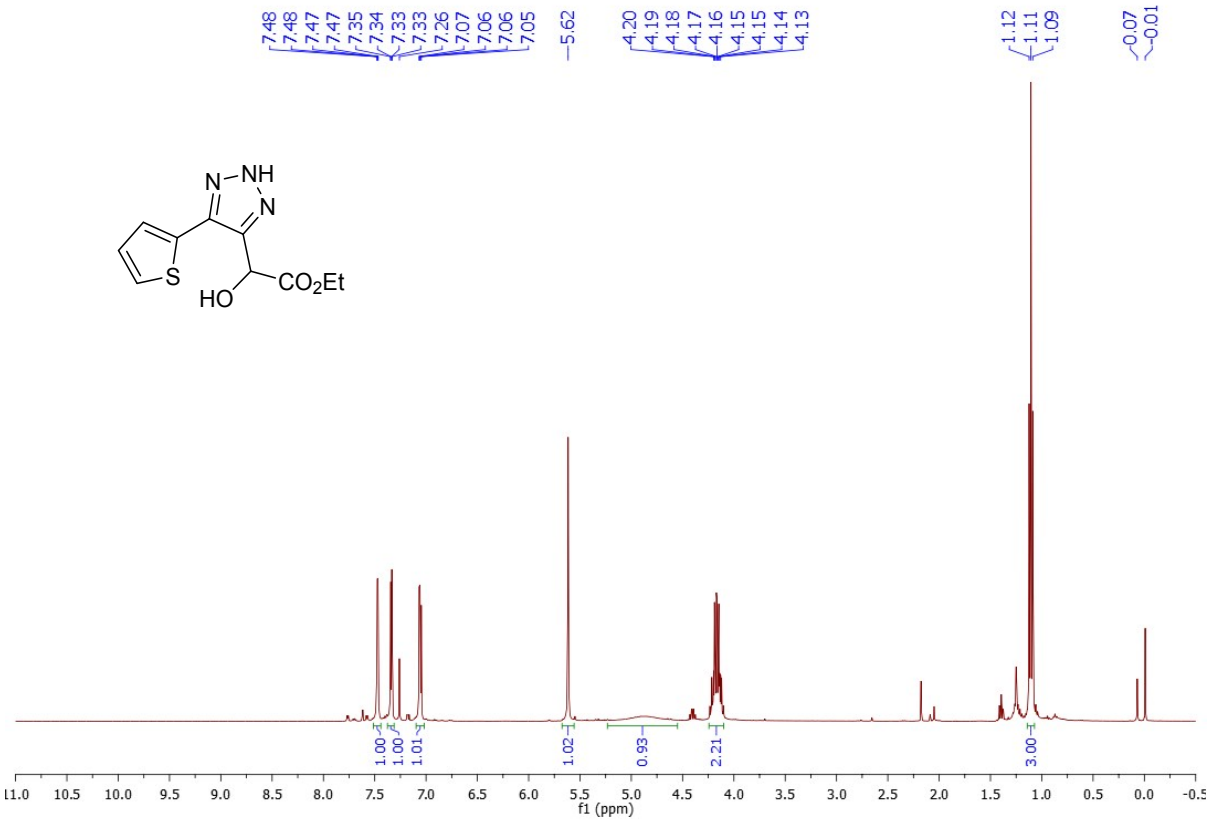



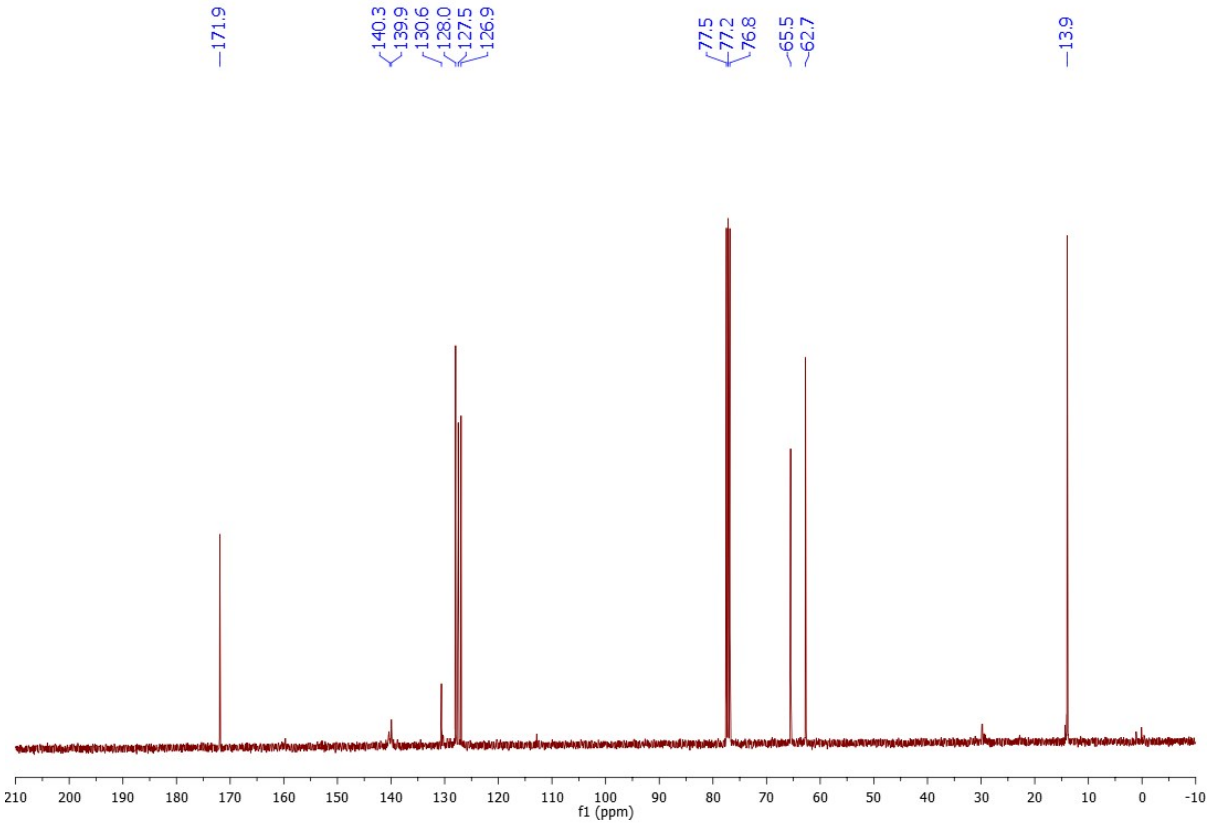
***Ethyl 2-[5-(2,4-dichlorophenyl)-1H-1,2,3-triazol-4-yl]-2-hydroxyacetate (2n): $^{1}H$ and $^{13}C$ in DMSO-$d_6$***



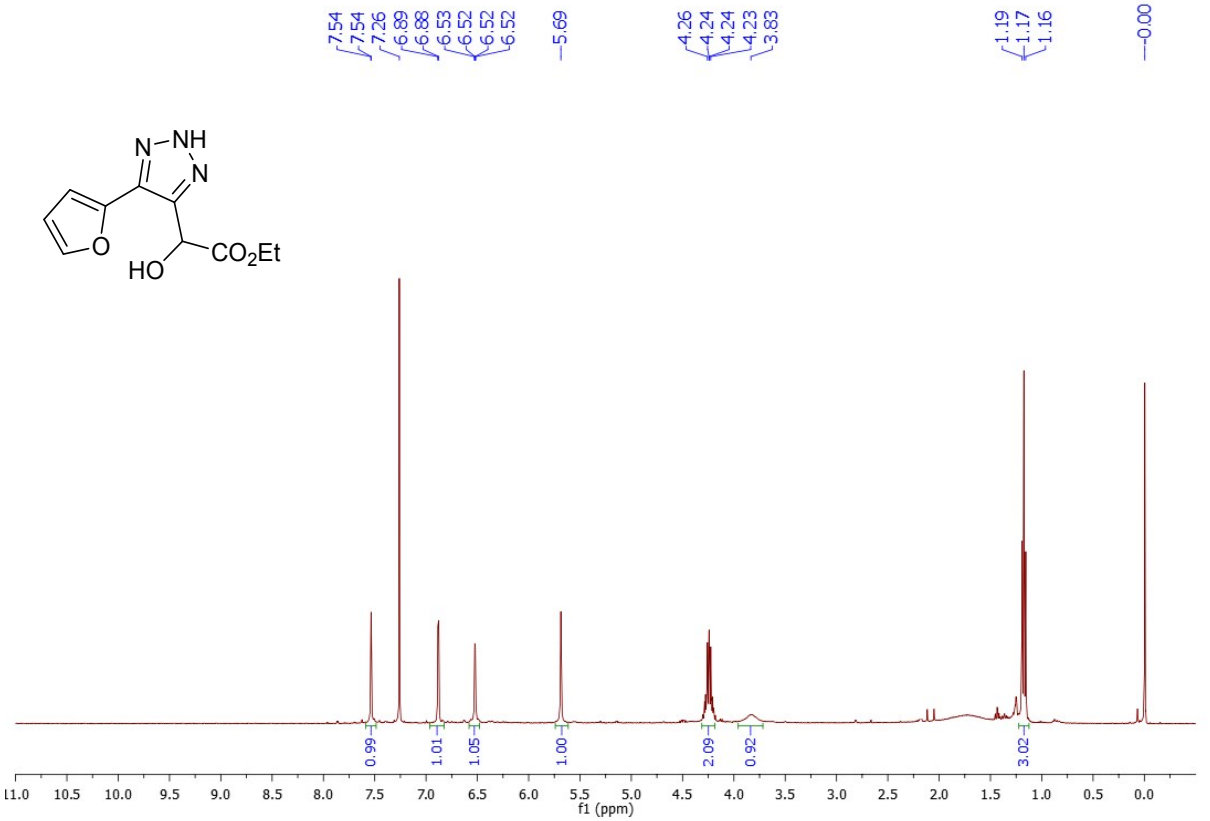



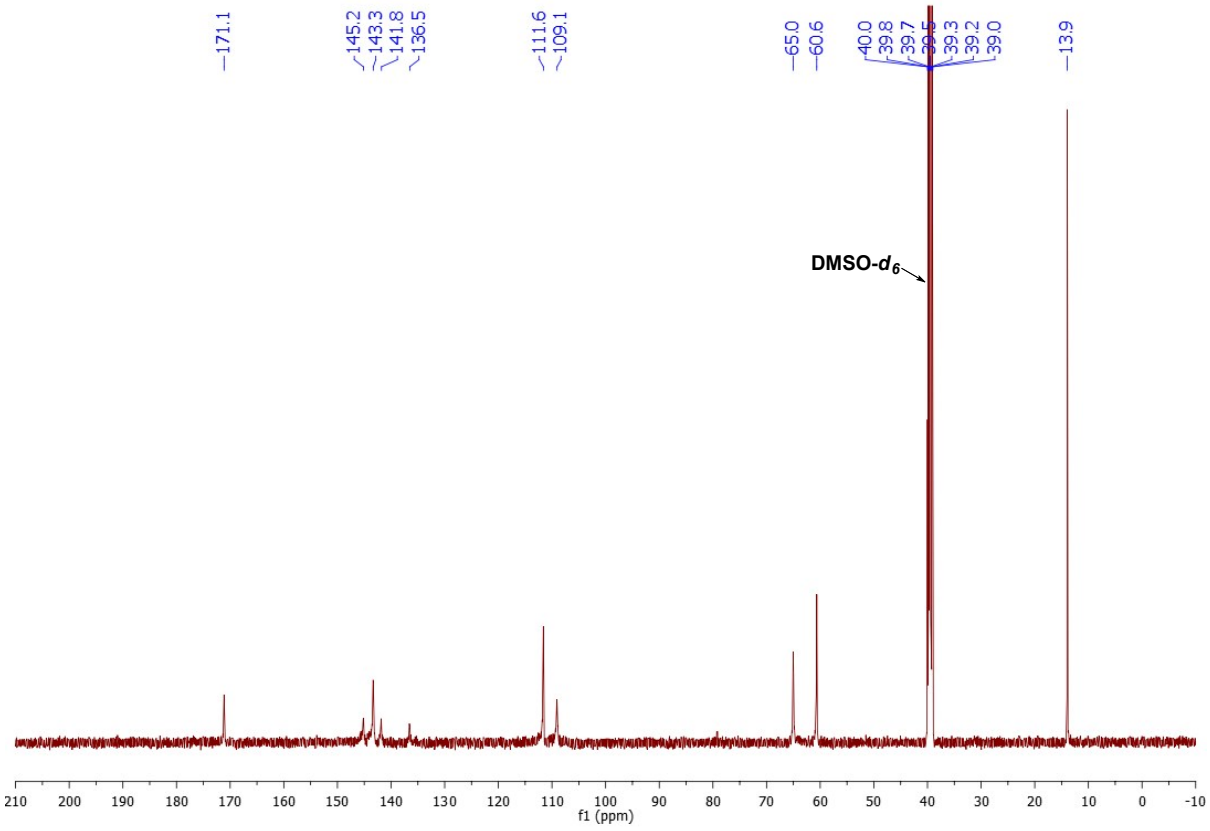
***Ethyl 2-hydroxy-2-[5-(thiophen-2-yl)-1H-1,2,3-triazol-4-yl]acetate (2o): $^{1}H$ and $^{13}C$ in $CDCl_3$***



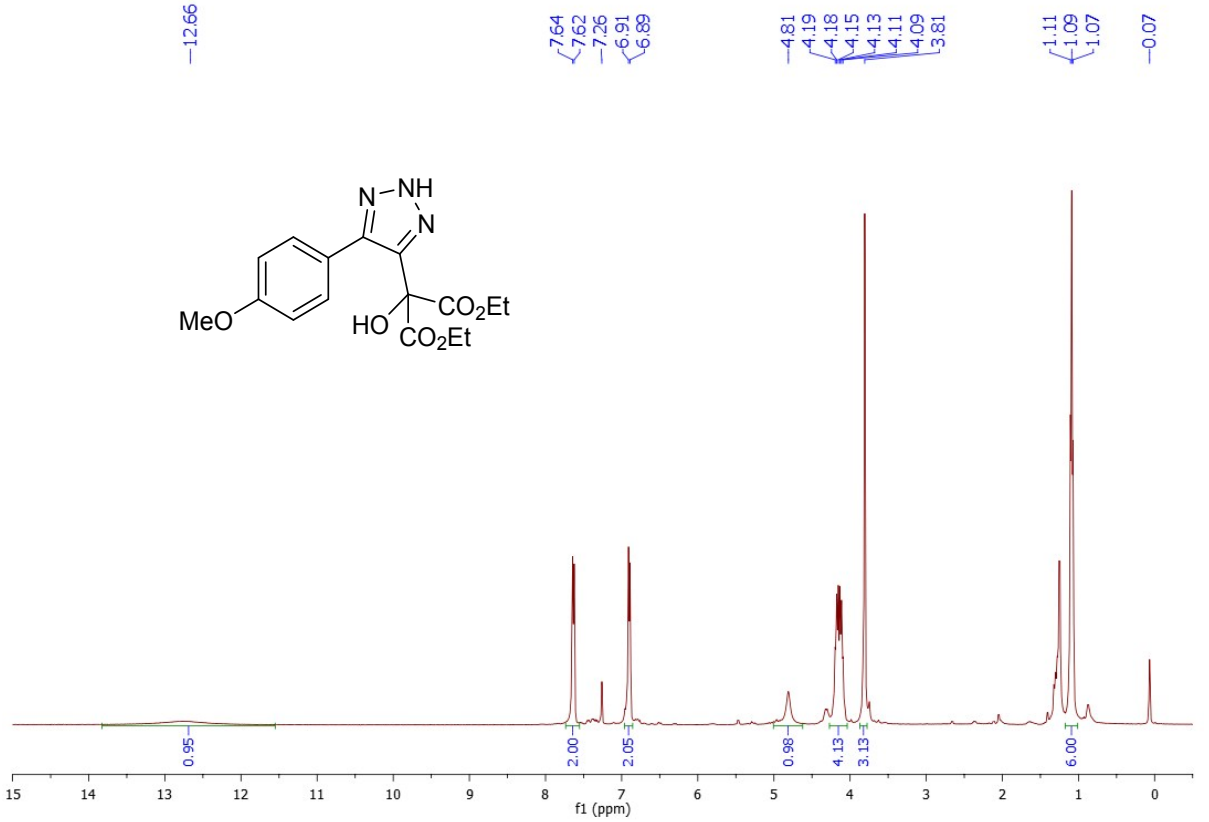



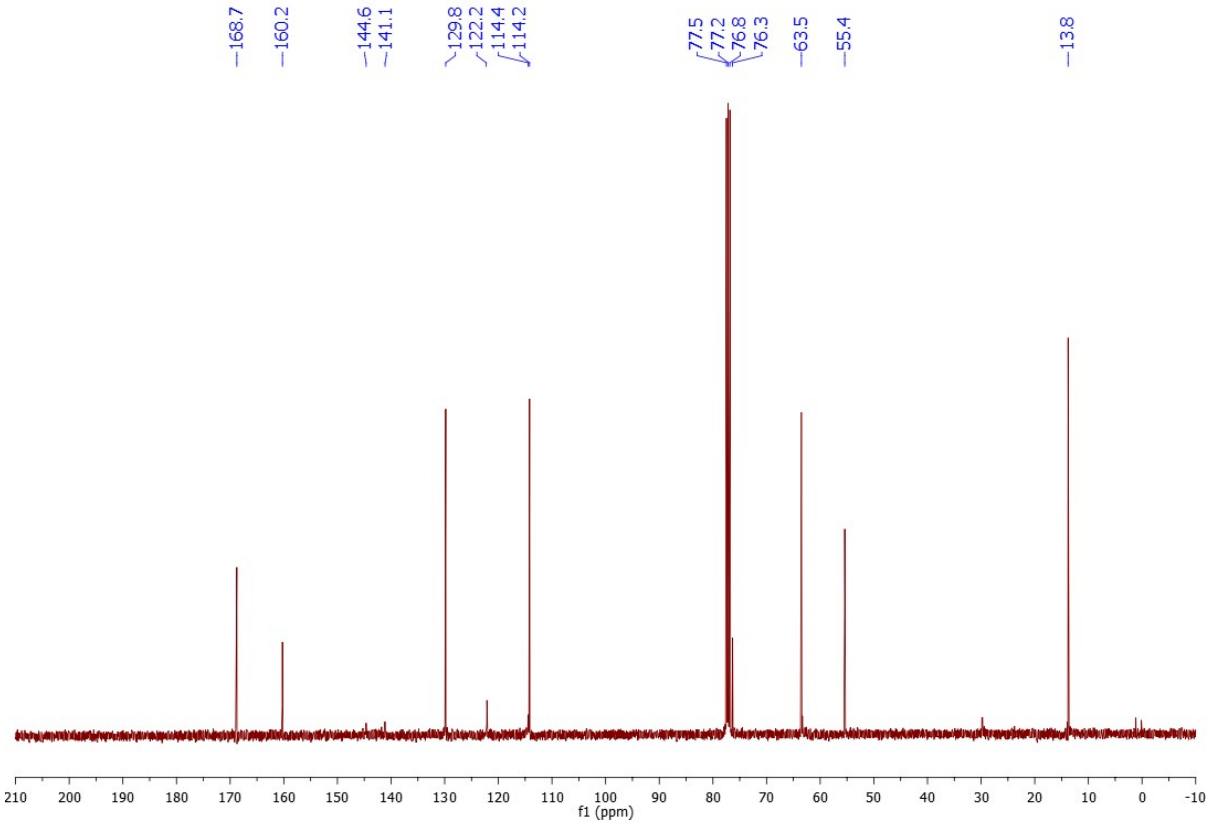
***Ethyl 2-[5-(furan-2-yl)-1H-1,2,3-triazol-4-yl]-2-hydroxyacetate (2p): $^{1}H$ ($CDCl_3$)and $^{13}C$ (DMSO-$d_6$)***



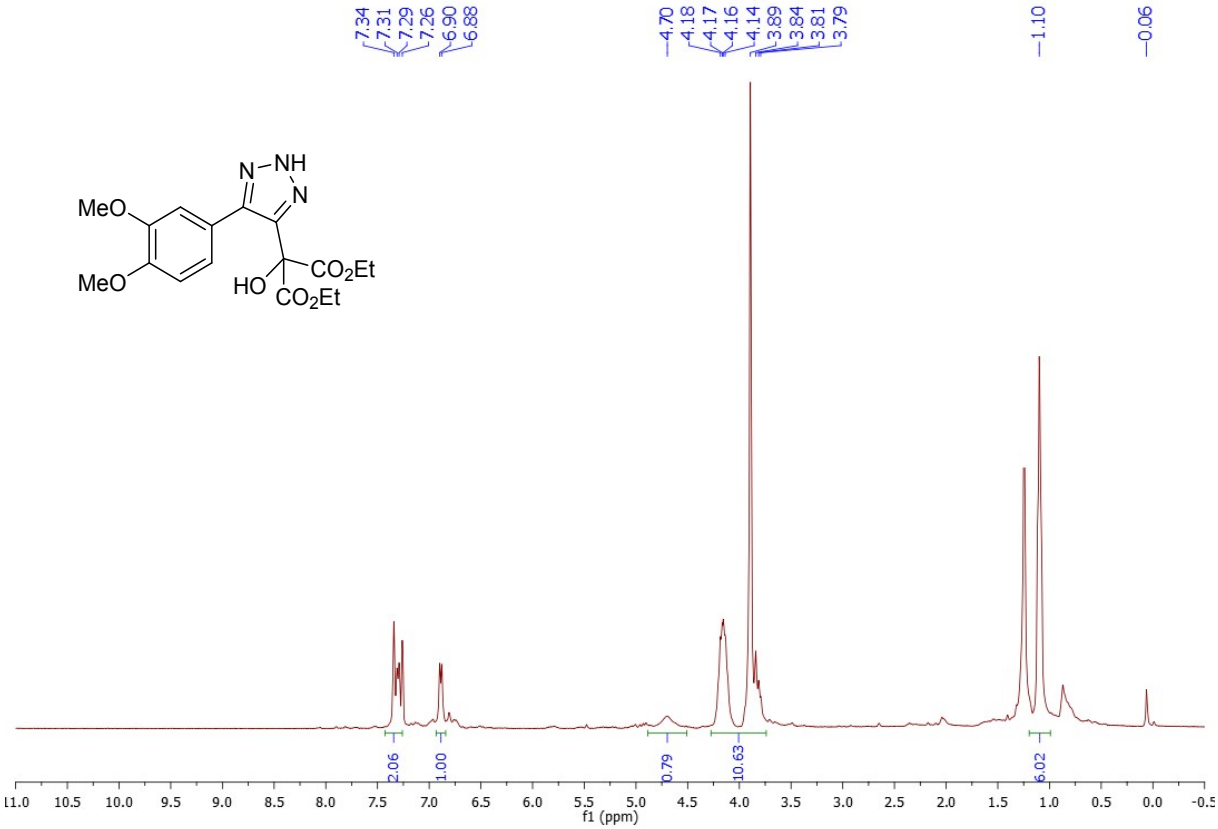



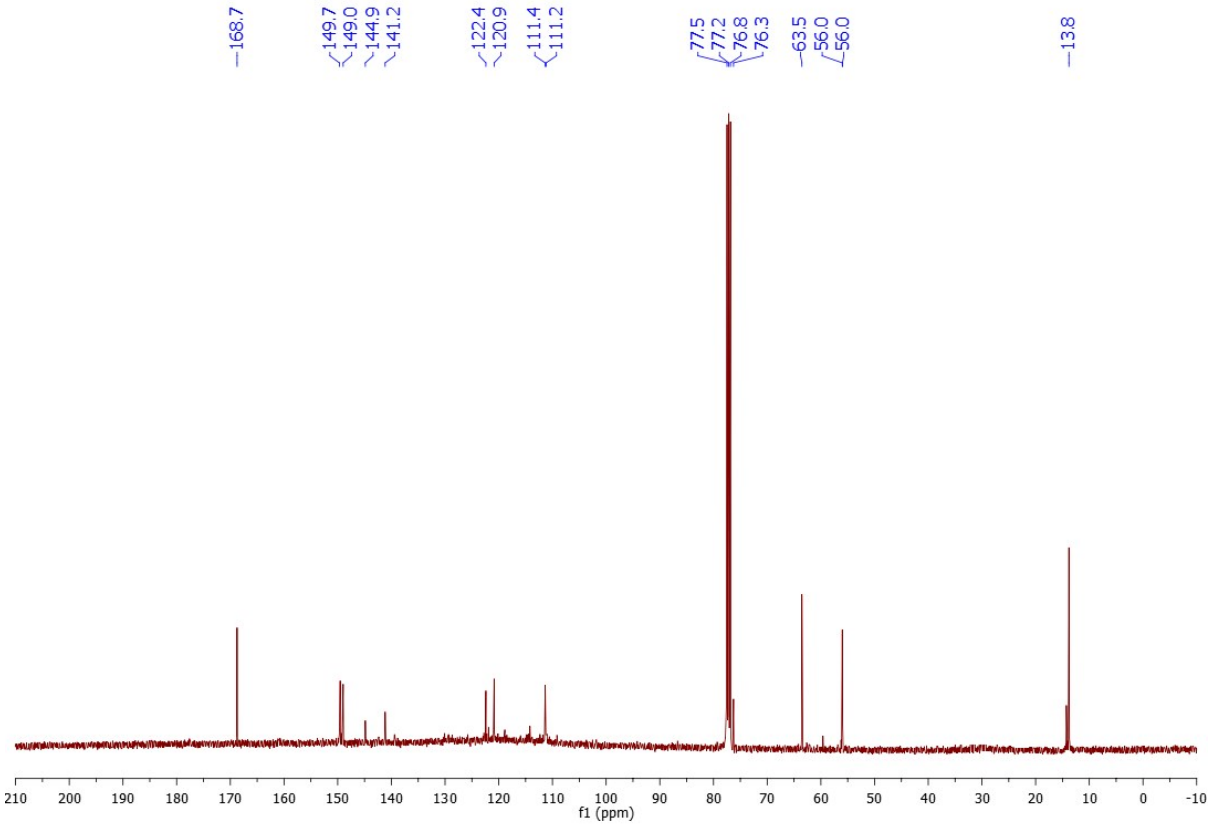
***Diethyl 2-hydroxy-2-[5-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl]malonate (2q): $^{1}H$ and $^{13}C$ in $CDCl_3$***



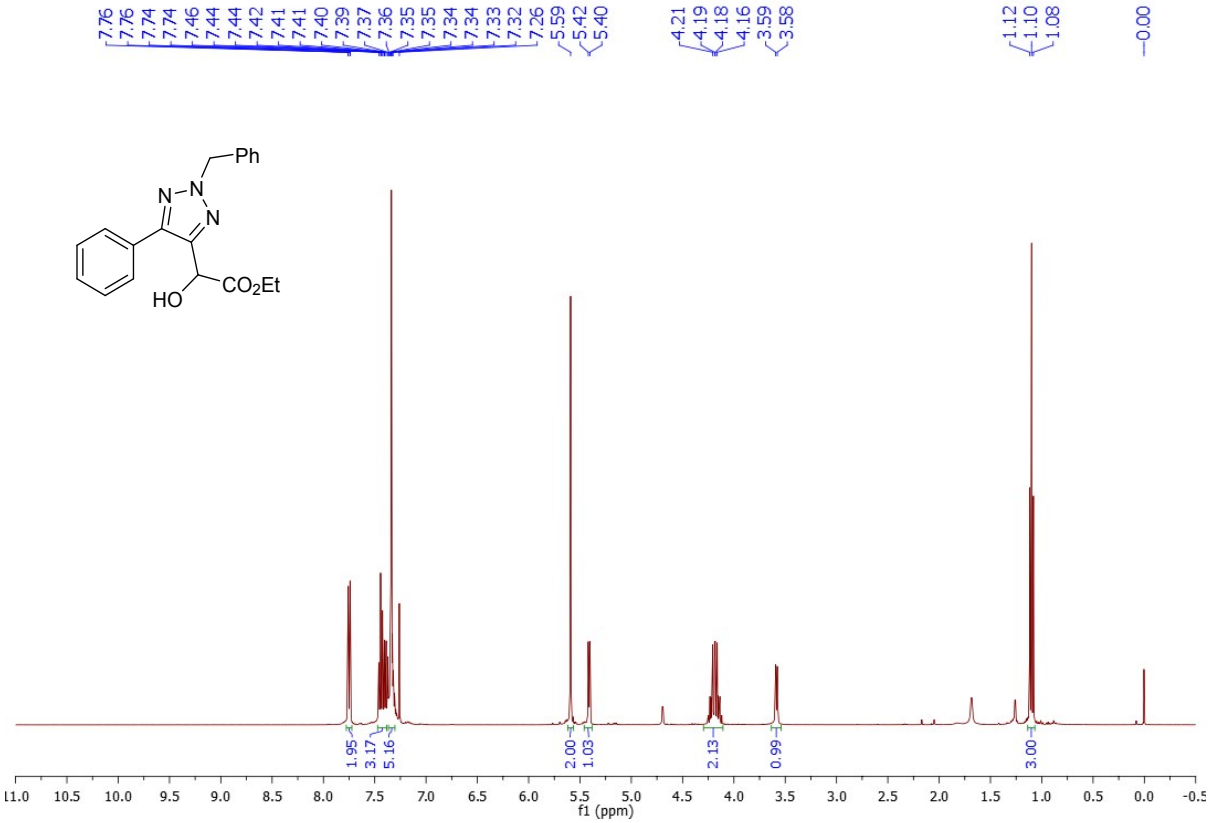



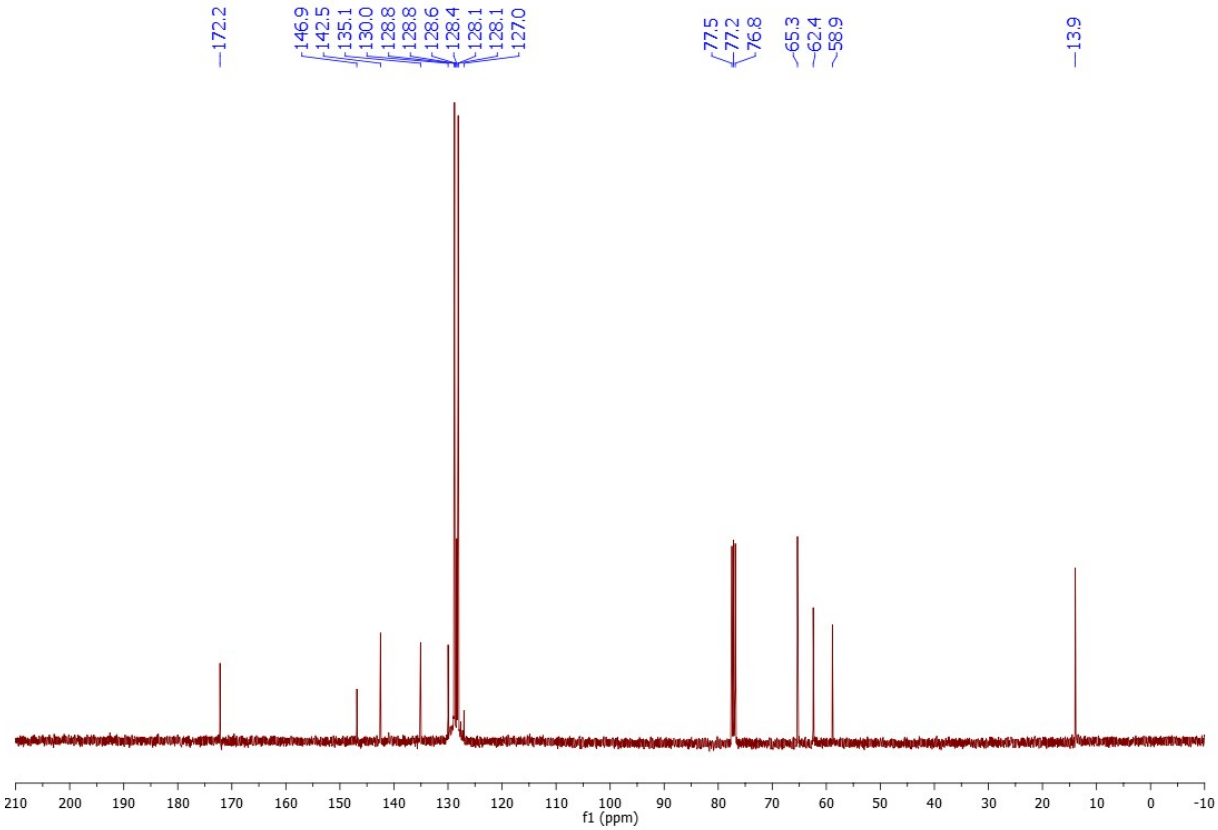
***Diethyl 2-[5-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-4-yl]-2-hydroxymalonate (2r): $^{1}H$ and $^{13}C$ in $CDCl_3$***



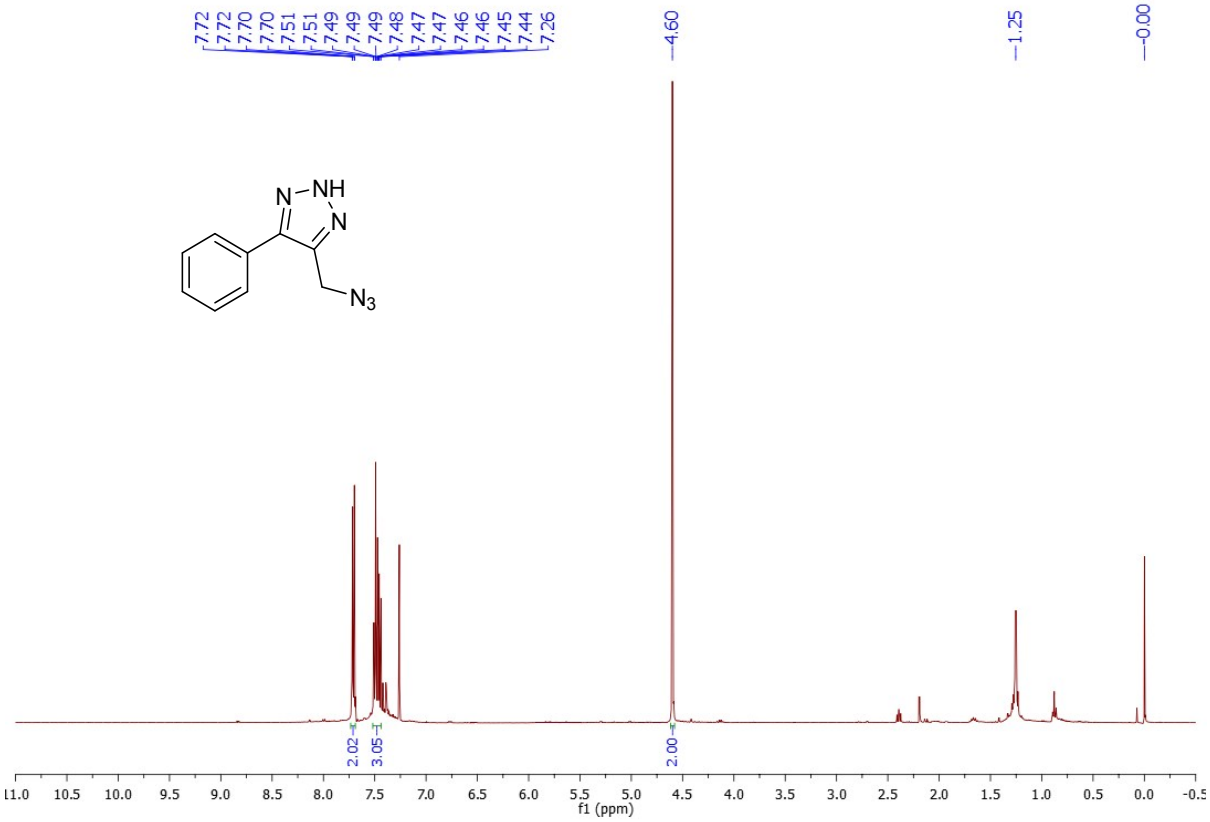



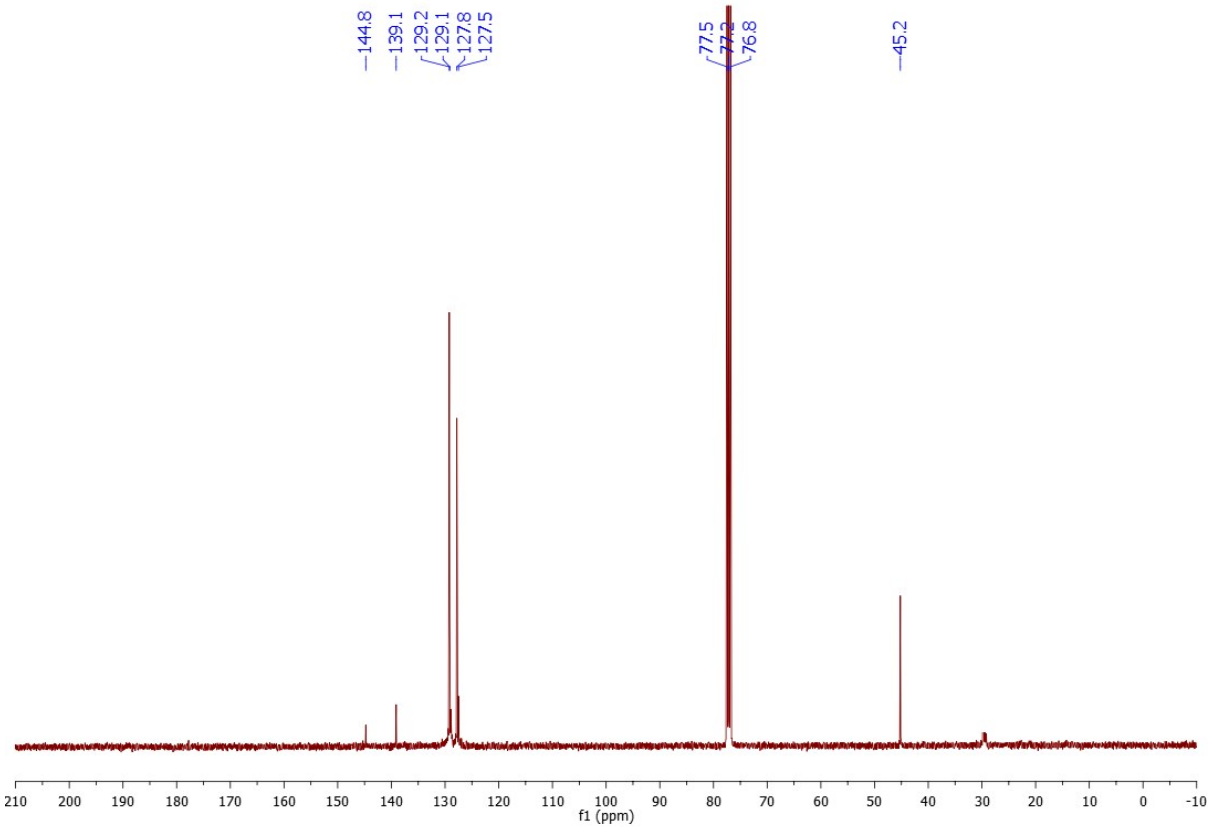
***Ethyl 2-(2-benzyl-5-phenyl-2H-1,2,3-triazol-4-yl)-2-hydroxyacetate (2t): $^{1}H$ and $^{13}C$ in $CDCl_3$***



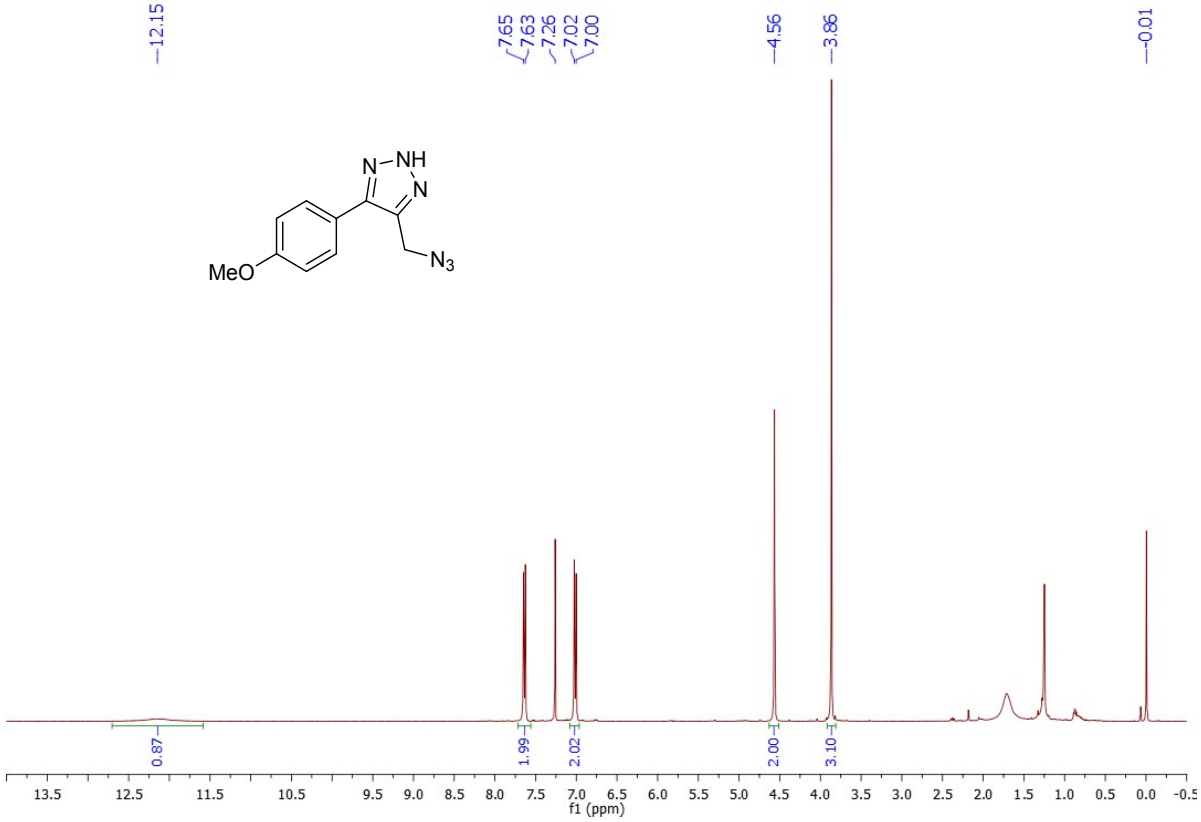



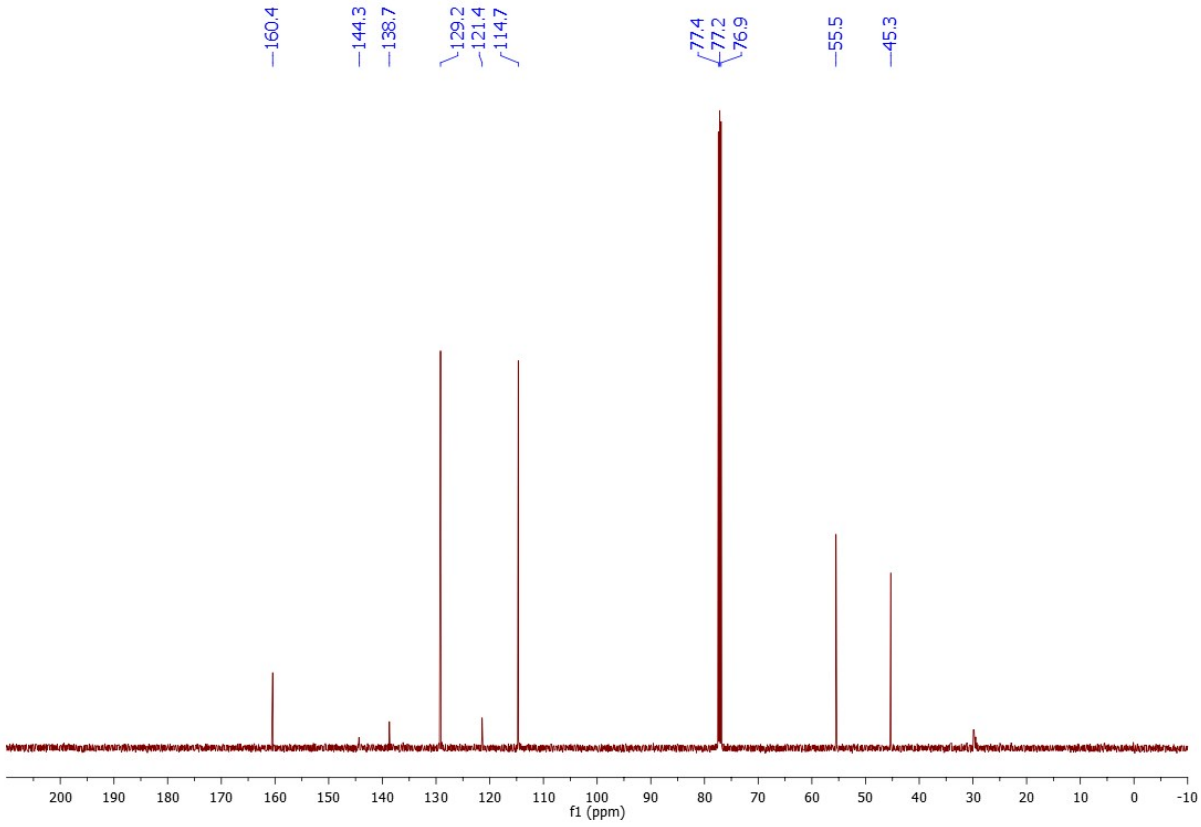
***4-(Azidomethyl)-5-phenyl-2H-1,2,3-triazole (5a): $^{1}H$ and $^{13}C$ in $CDCl_3$***



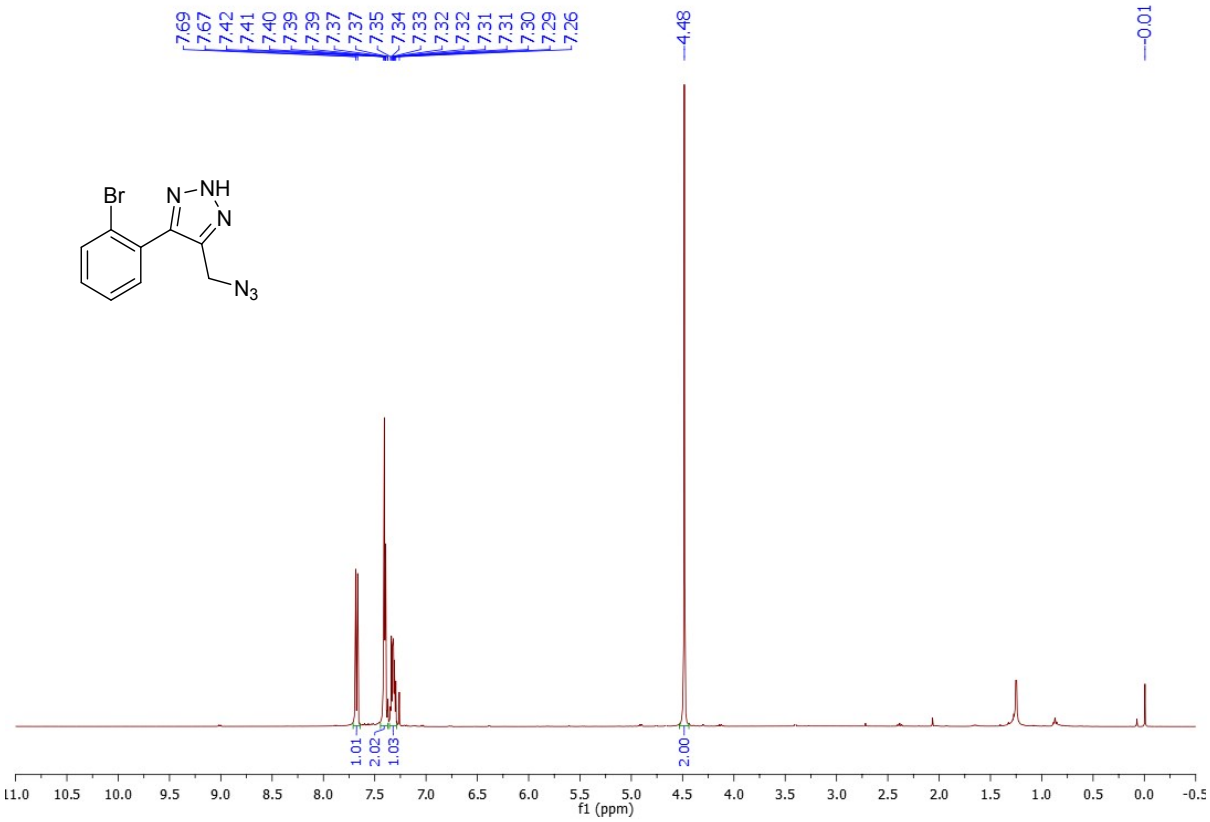



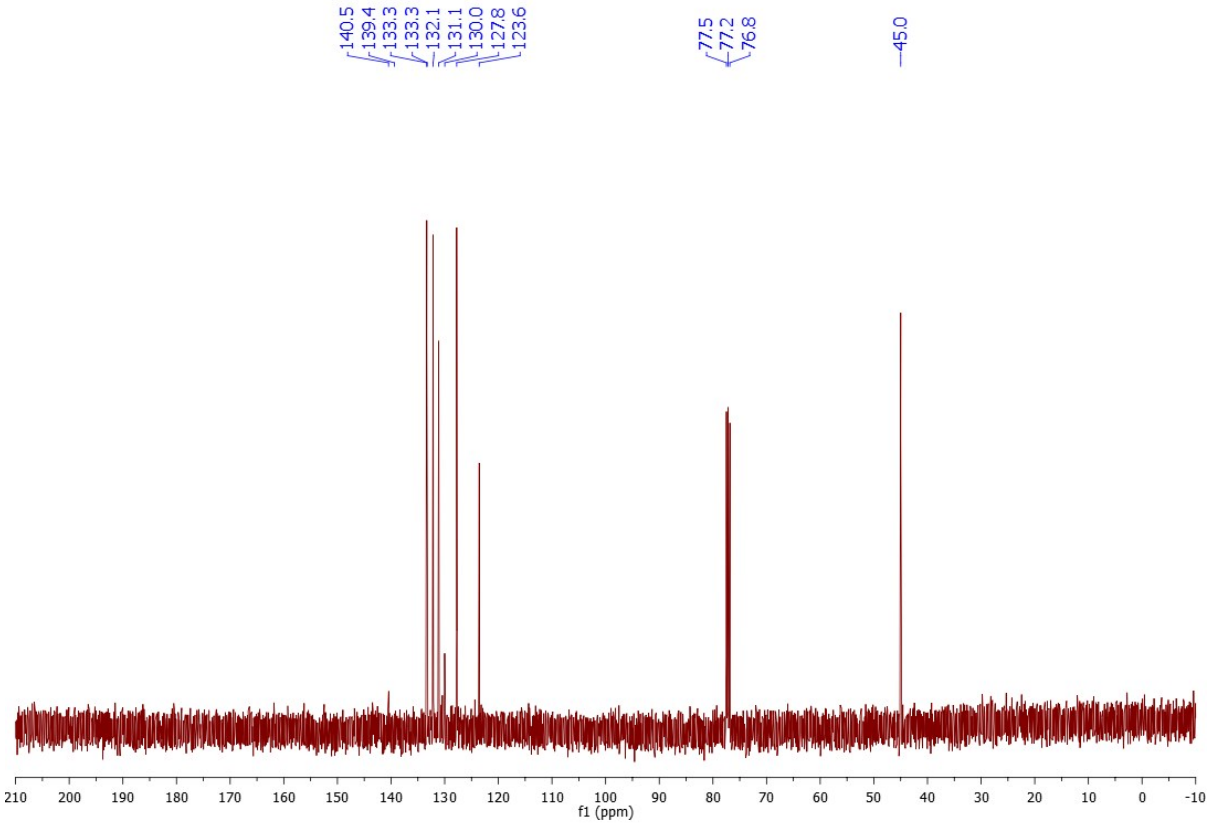
***4-(Aidomethyl)-5-(4-methoxyphenyl)-2H-1,2,3-triazole (5b): $^{1}H$ and $^{13}C$ in $CDCl_3$***



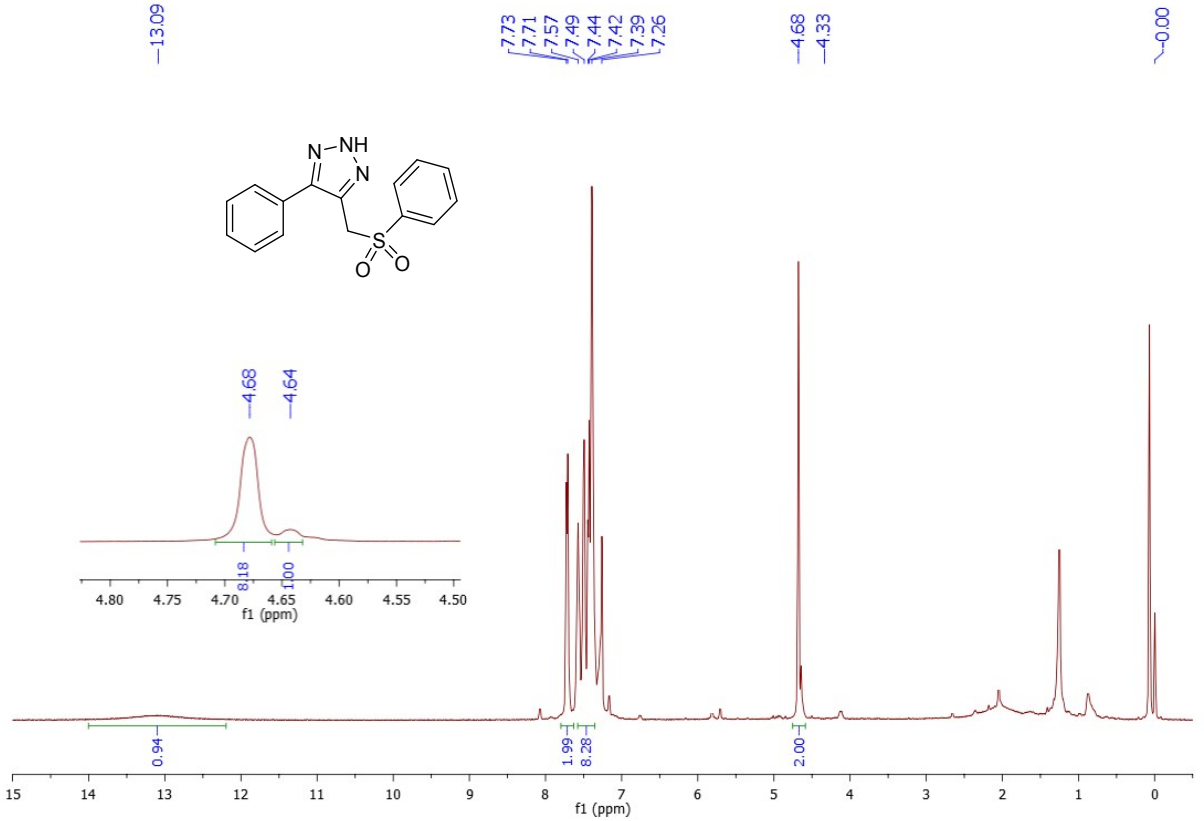



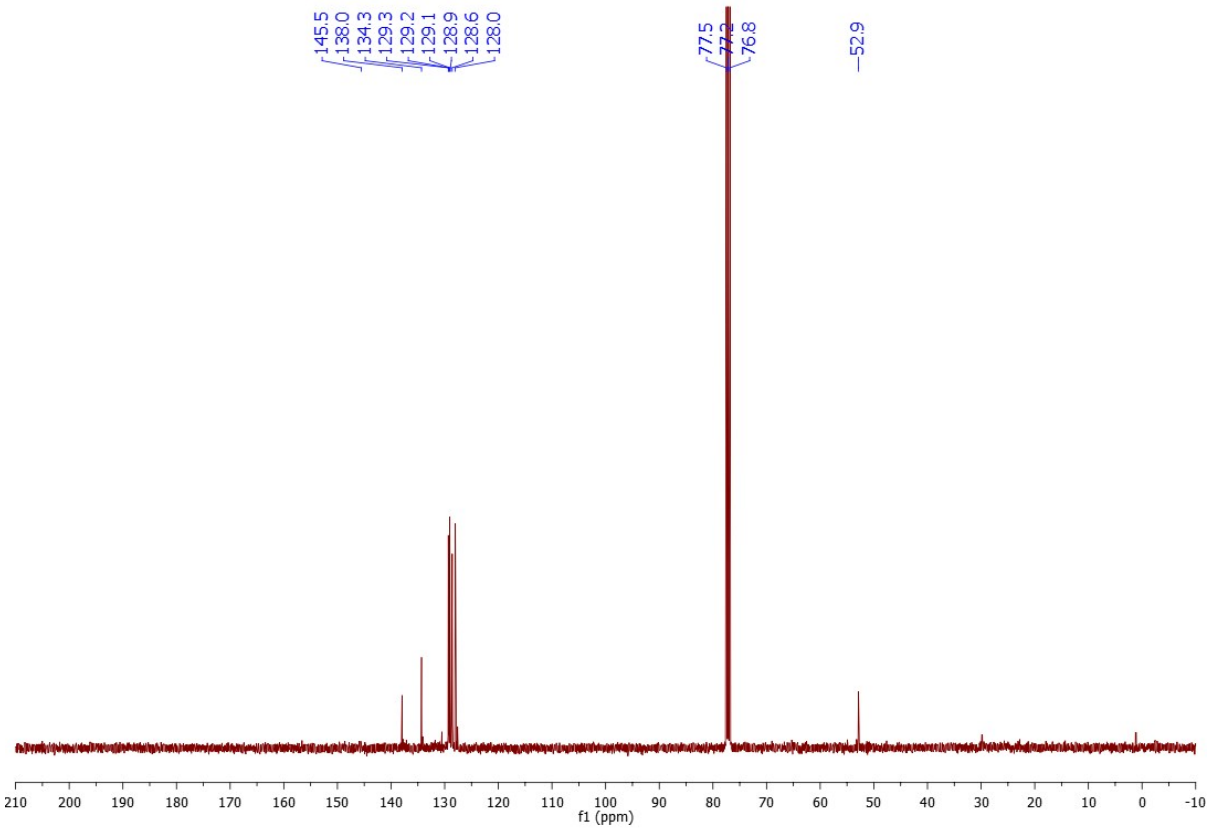
***4-(Azidomethyl)-5-(2-bromophenyl)-2H-1,2,3-triazole (5c): $^{1}H$ and $^{13}C$ in $CDCl_3$***



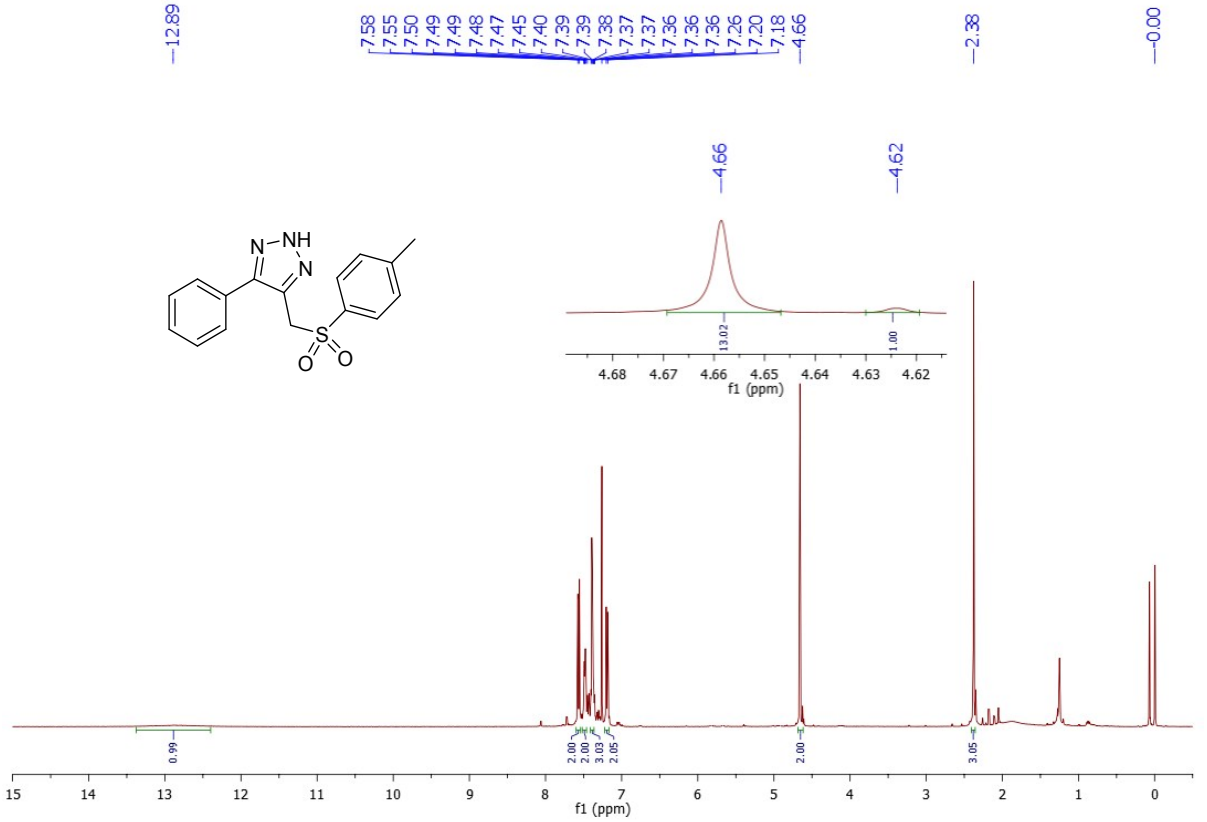



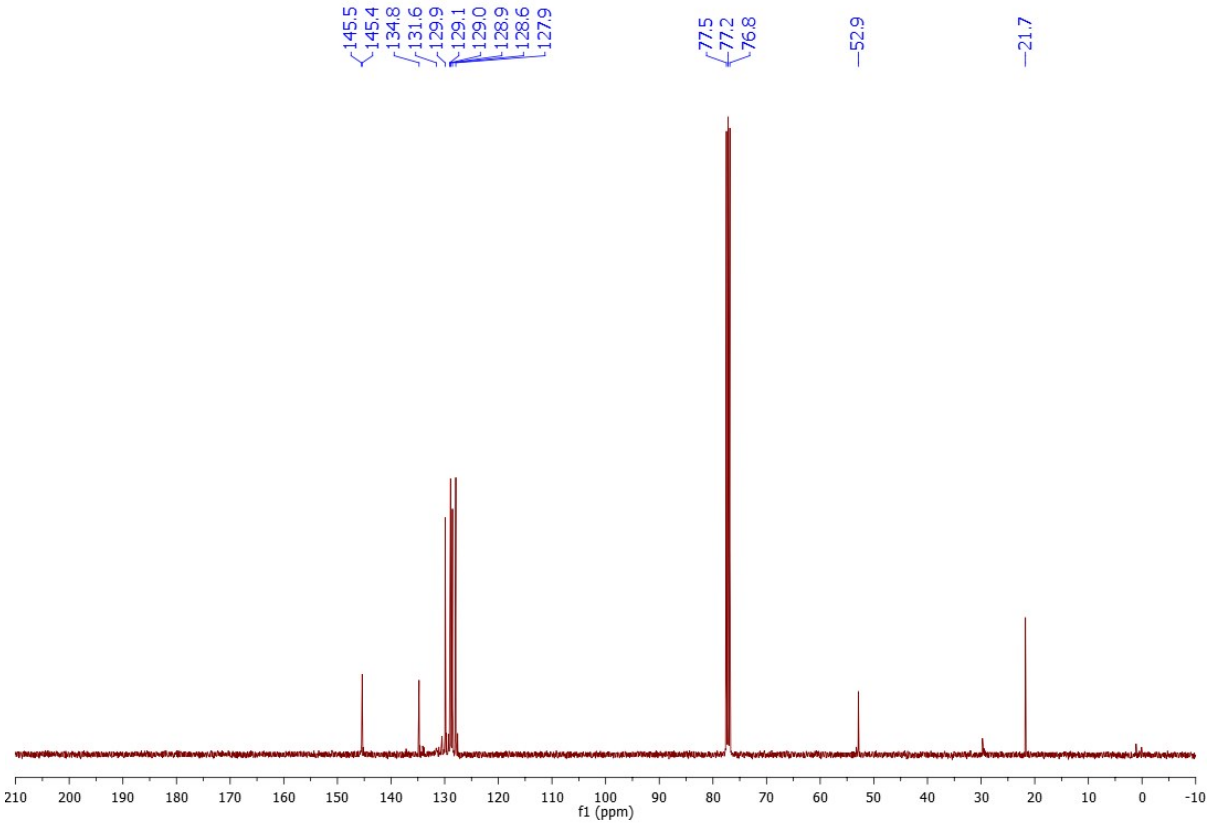
***5-Phenyl-4-[(phenylsulfonyl)methyl]-1H-1,2,3-triazole (6a): $^{1}H$ and $^{13}C$ in $CDCl_3$***



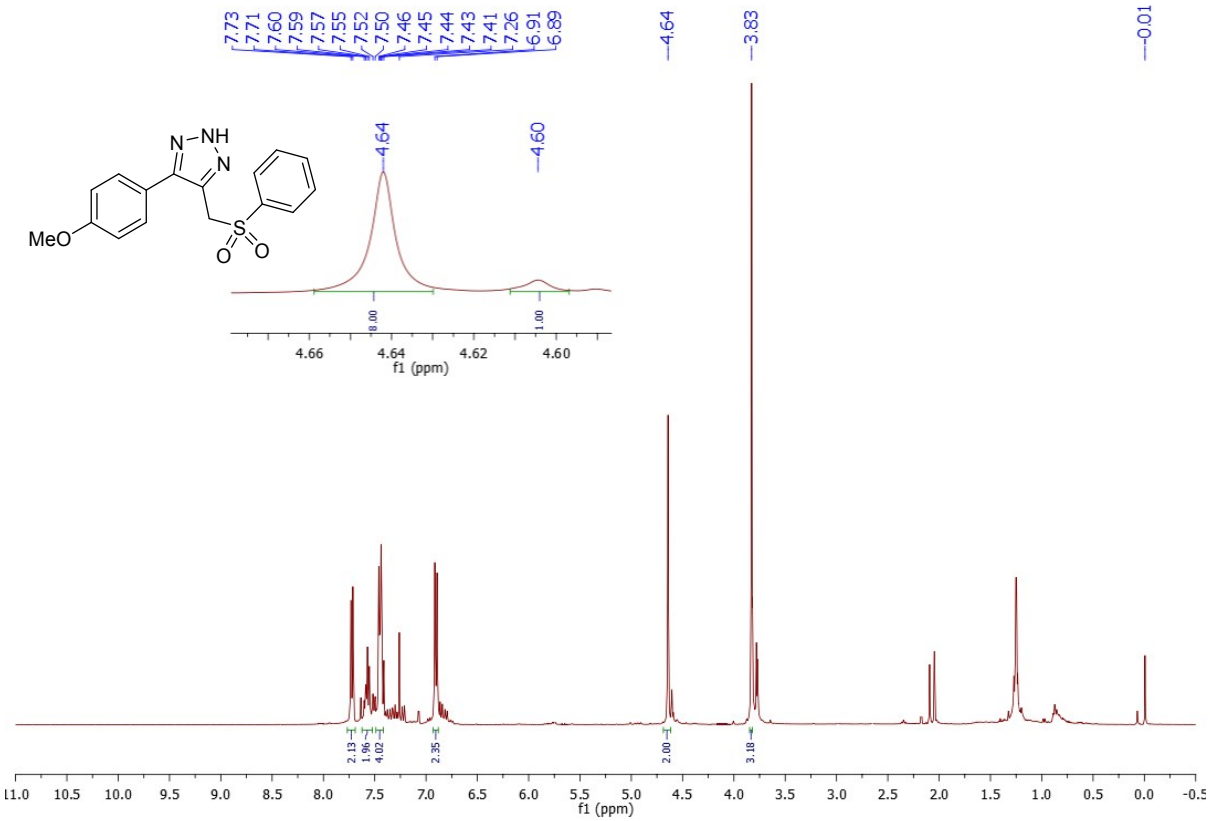



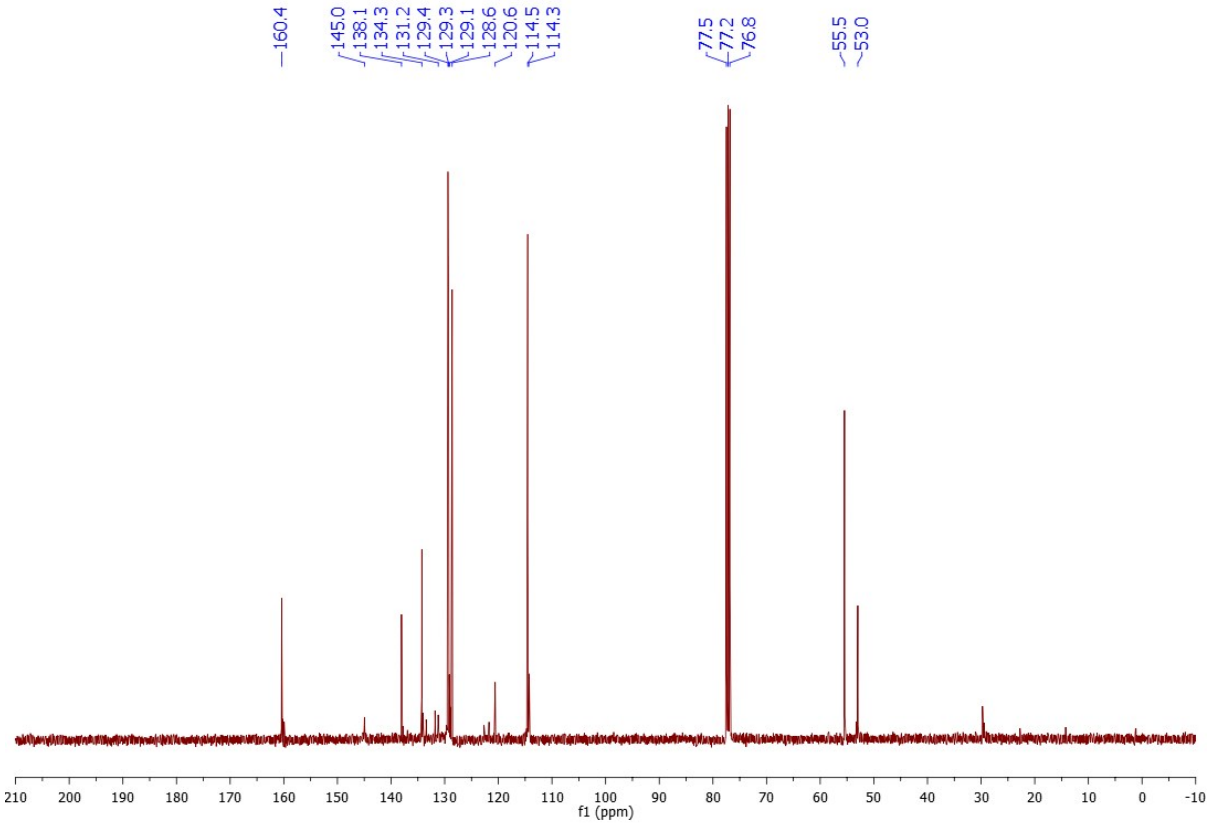
***5-Phenyl-4-(tosylmethyl)-1H-1,2,3-triazole (6b): $^{1}H$ and $^{13}C$ in $CDCl_3$***



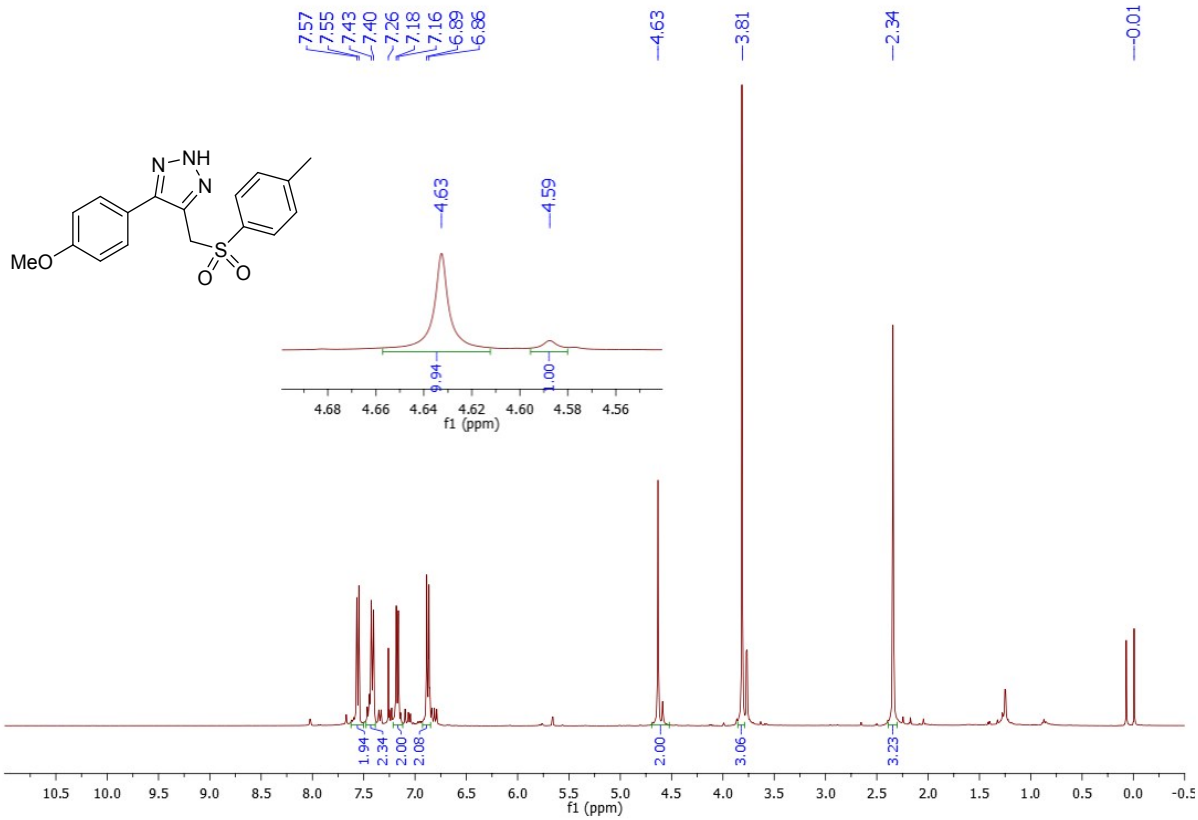



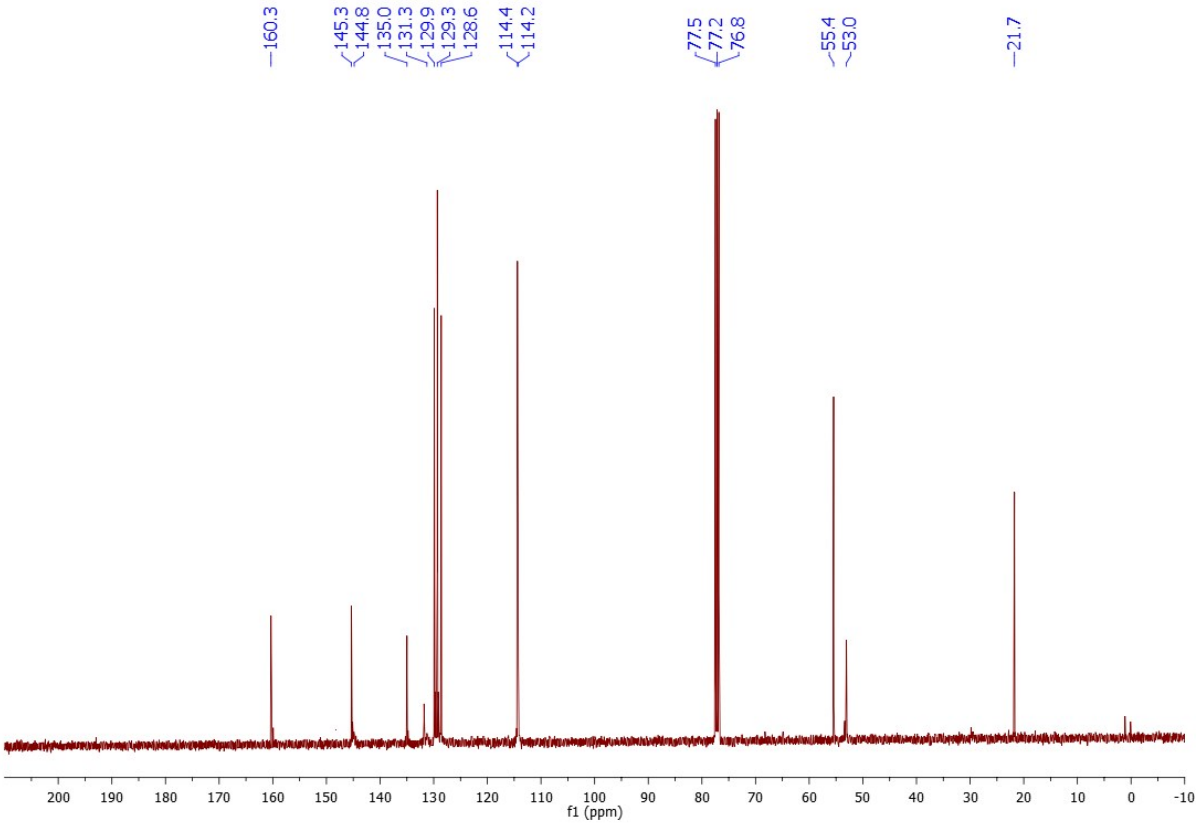
***5-(4-Methoxyphenyl)-4-[(phenylsulfonyl)methyl]-1H-1,2,3-triazole (6c): $^{1}H$ and $^{13}C$ in $CDCl_3$***



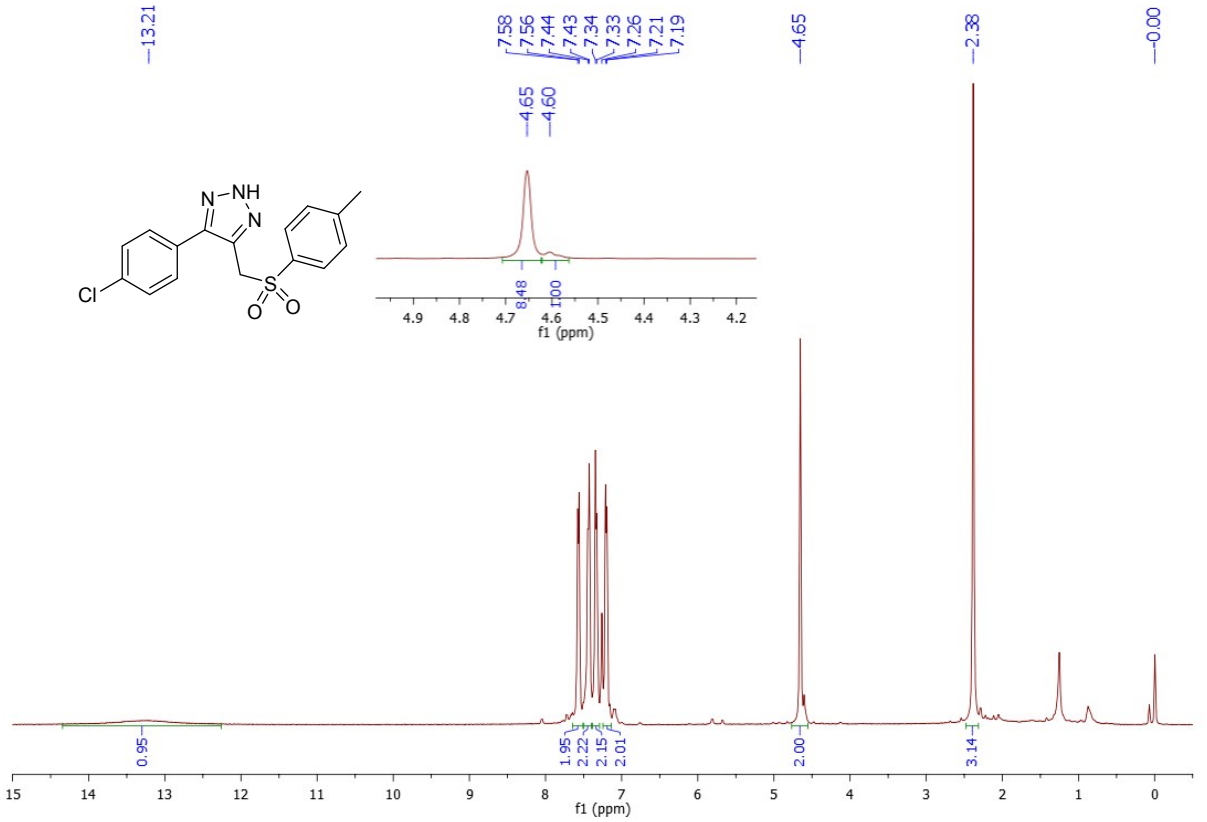



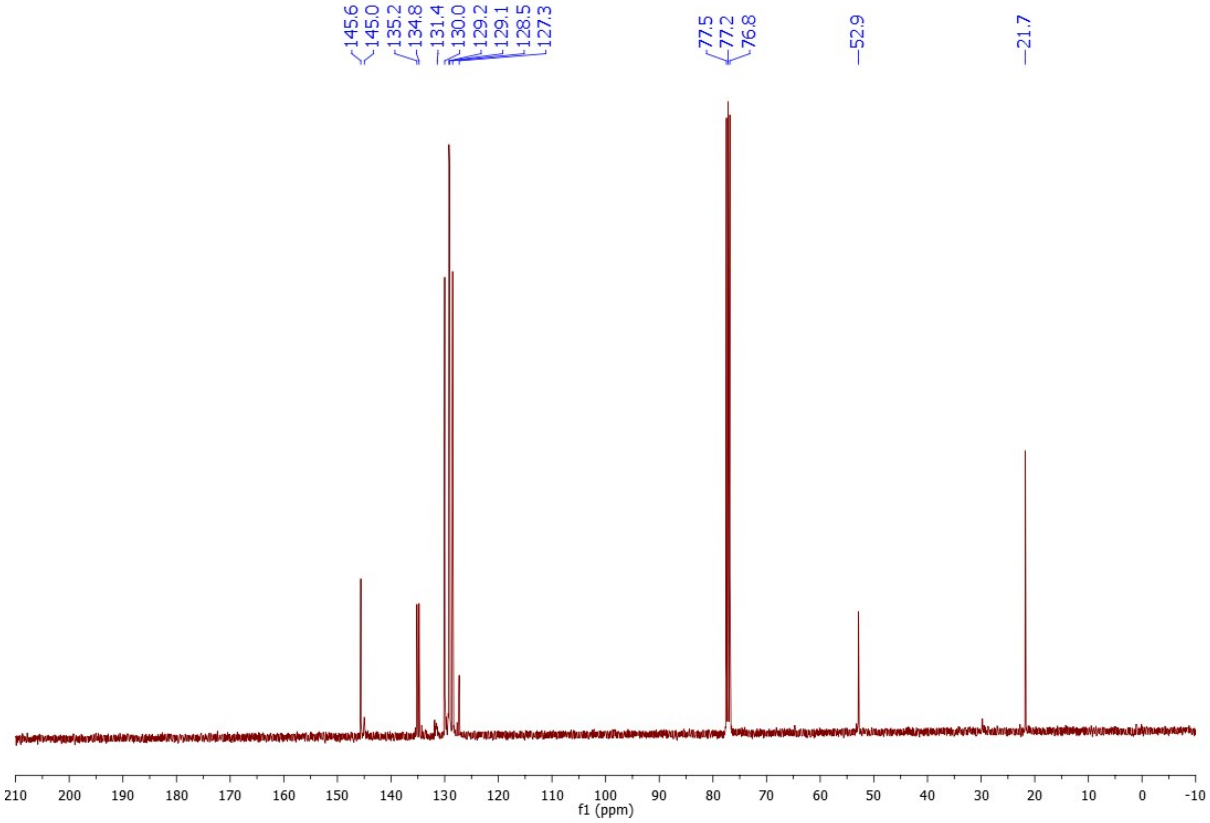
***5-(4-Methoxyphenyl)-4-(tosylmethyl)-1H-1,2,3-triazole (6d): $^{1}H$ and $^{13}C$ in $CDCl_3$***



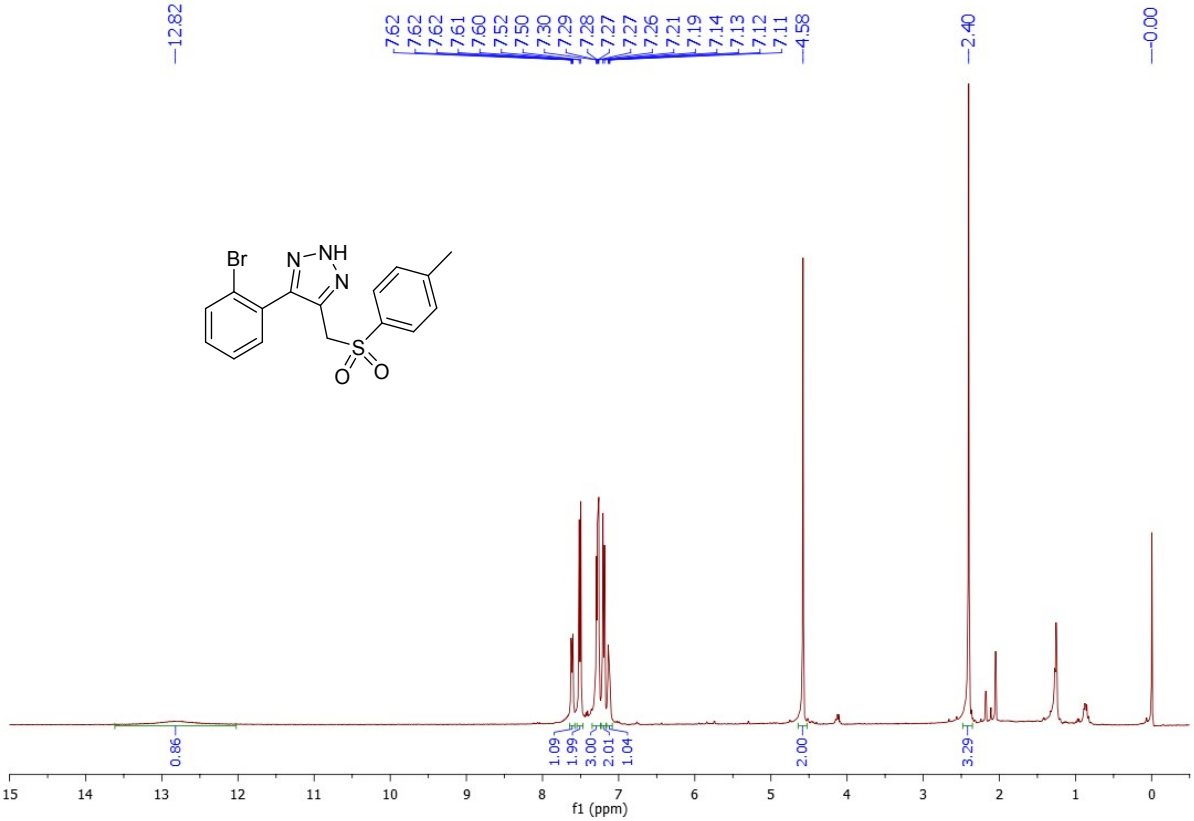



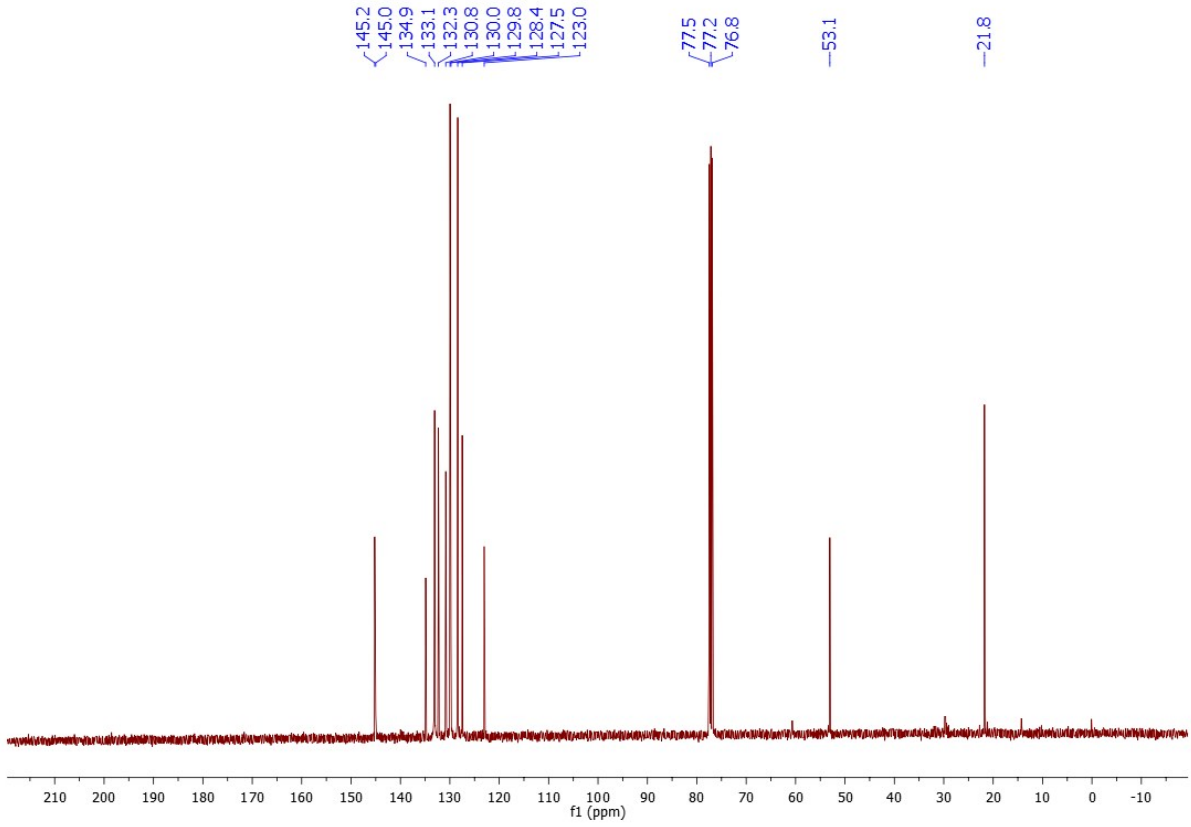
***5-(4-Chlorophenyl)-4-(tosylmethyl)-1H-1,2,3-triazole (6e): $^{1}H$ and $^{13}C$ in $CDCl_3$***



***5-(2-Bromophenyl)-4-(tosylmethyl)-1H-1,2,3-triazole (6f): $^{1}H$ and $^{13}C$ in $CDCl_3$***



***Ethyl 2-acetoxy-2-(5-phenyl-2H-1,2,3-triazol-4-yl)acetate (7): $^{1}H$ and $^{13}C$ in $CDCl_3$***