Cu(II) PBS-bridged PMOs catalyzed one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles in water through click chemistry

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Supporting Information

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3. ^{1}H NMR and ^{13}C NMR spectra of isolated compounds

1. General information: ^{1}H and ^{13}C NMR spectra were recorded on Agilent Innova 400 MHz spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS), which is used as an internal standard, and coupling constants (J) are reported in hertz (Hz). Splitting patterns of proton are described as s, d, dd, t, q, br s and m stand for the resonance multiplicities singlet, doublet, doublet of doublet, triplet, quartet, broad singlet and multiplet, respectively.

2. Recyclability of the Cu(II) PBS-bridged PMO catalyst: We carried out catalyst-recycling experiments by using benzyl bromide, sodium azide and phenylacetylene as the model reaction. Remarkably, the used Cu(II)–PBS-HPMO catalyst exhibited without any significant loss of activity and selectivity in terms of desired product up to five cycles.

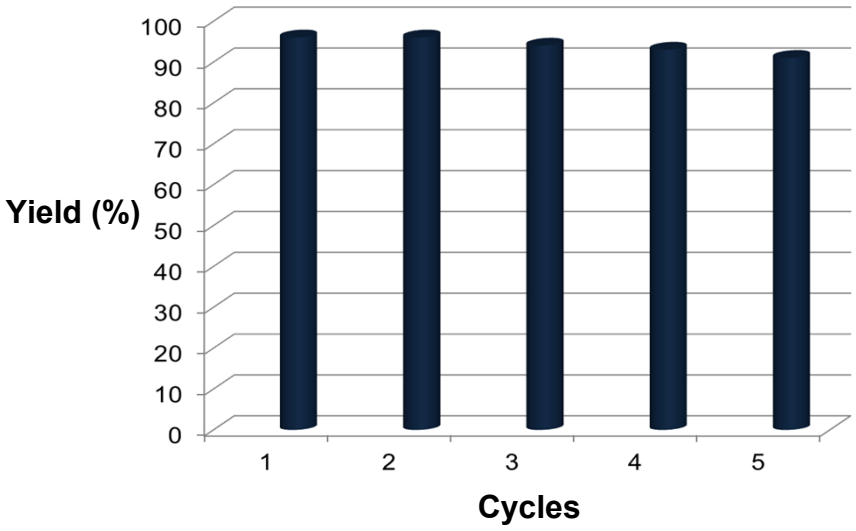
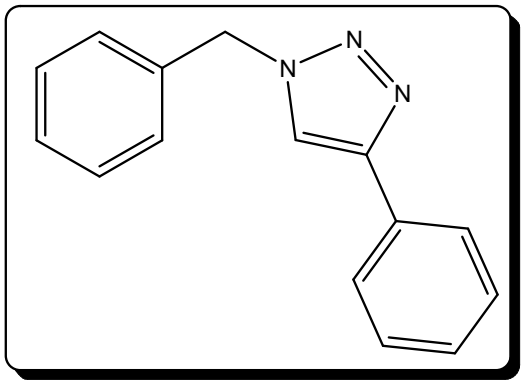


Figure 1. Recycling of Cu(II)-PBS-HPMO catalyst for the reaction between benzyl bromide, sodium azide and phenylacetylene.

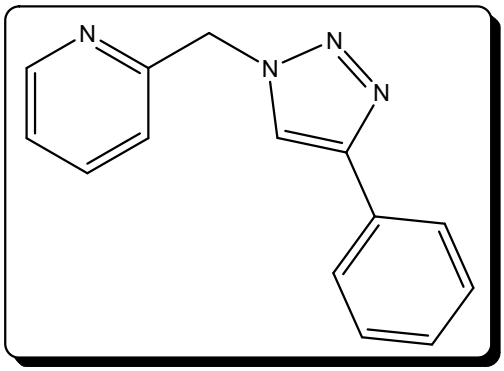
2. ^{1}H NMR and ^{13}C NMR of isolated compounds:

Table 5, Entry 2: 1-Benzyl-4-phenyl-1*H*-1,2,3,-triazole:



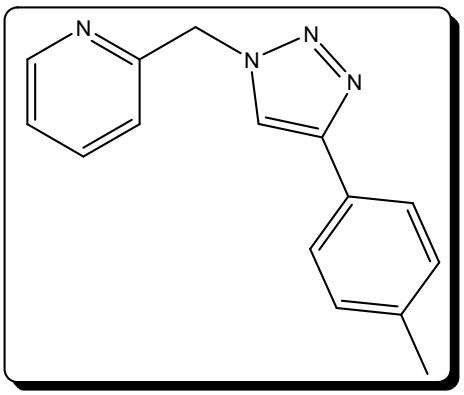
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.80-7.78 (m, 2H), 7.65 (s, 1H), 7.41-7.36 (m, 5H), 7.33-7.29 (m, 3H), 7.27-7.24 (m, 1H), 5.57 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 148.2, 134.6, 130.4, 129.1, 128.7, 128.1, 128.0, 127.1, 125.6, 119.4, 54.2 ppm.

Table 5, Entry 3: 2-((4-Phenyl-1*H*-1,2,3-triazol-1-yl)methyl)pyridine:



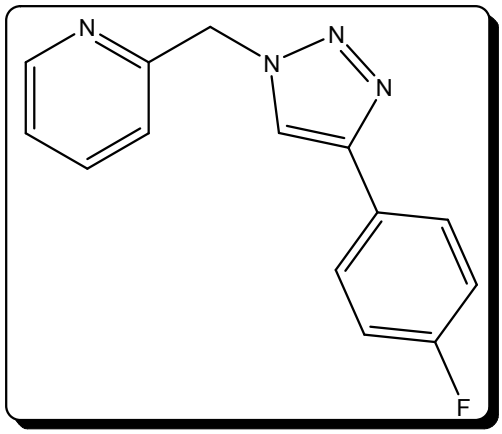
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 8.62-8.59 (m, 1H), 7.97-7.93 (m, 1H), 7.84-7.82 (m, 2H), 7.72-7.67 (m, 1H), 7.43-7.39 (m, 2H), 7.34-7.26 (m, 3H), 5.70 (s, 2H) ppm; ^{13}C NMR($CDCl_3$, 25 ^{0}C) δ 154.4, 149.7, 148.2, 137.3, 130.4, 128.7, 128.1, 125.7, 123.4, 122.4, 120.1, 55.7 ppm.

Table 5, Entry 4: 2-((4-*p*-Tolyl-1*H*-1,2,3-triazol-1-yl)methyl)pyridine:



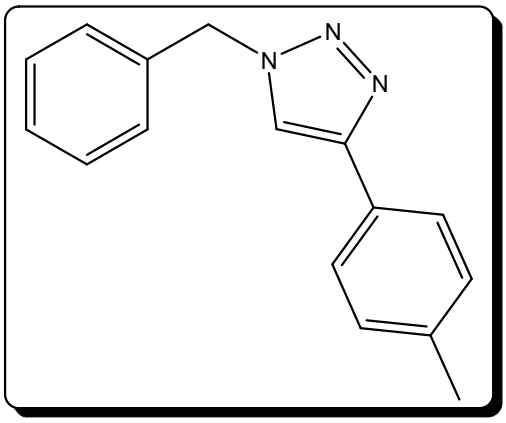
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 8.60 (s, 1H), 7.88 (s, 1H), 7.71-7.66 (m, 3H), 7.28-7.26 (m, 1H), 7.23-7.20 (m, 3H), 5.68 (s, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 154.5, 149.6, 148.2, 137.9, 137.3, 129.4, 127.6, 125.5, 123.4, 122.4, 119.8, 55.6, 21.2 ppm.

Table 5, Entry 5: 2-((4-(4-Fluorophenyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine:



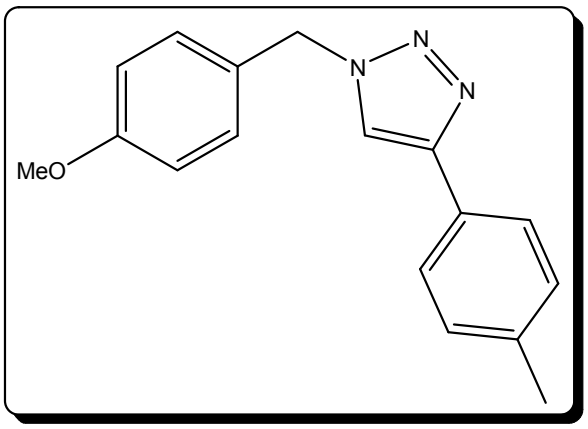
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 8.61-8.60 (d, *J* = 4.39 Hz, 1H), 7.89 (s, 1H), 7.81-7.76 (m, 2H), 7.72-7.67 (m, 1H), 7.29-7.24 (m, 2H), 7.11-7.07 (m, 2H), 5.69 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 163.8, 154.3, 149.7, 147.3, 137.4, 127.4, 127.3, 126.7, 126.6, 123.5, 122.5, 119.9, 115.8, 115.6, 55.6 ppm.

Table 5, Entry 6: 1-Benzyl-4-*p*-tolyl-1*H*-1,2,3-triazole:



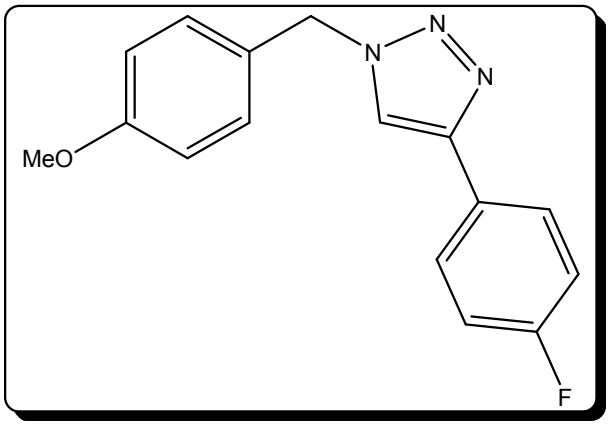
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.71-7.67 (m, 2H), 7.61 (s, 1H), 7.39-7.35 (m, 5H), 7.21-7.17 (m, 2H), 5.56 (s, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 148.2, 137.9, 134.6, 129.4, 129.0, 128.6, 127.9, 127.6, 125.5, 119.1, 54.1, 21.2 ppm.

Table 5, Entry 7: 1-(4-Methoxybenzyl)-4-*p*-tolyl-1*H*-1,2,3-triazole:



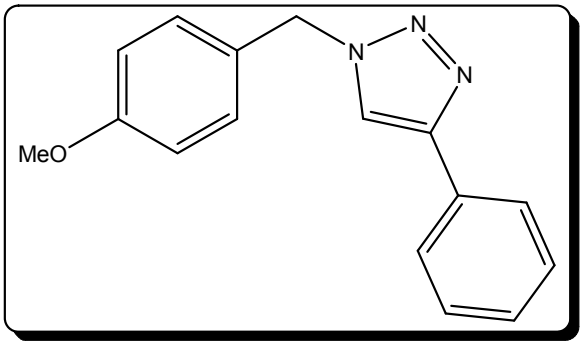
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.68-7.66 (d, *J* = 8.05 Hz, 1H), 7.57 (s, 1H), 7.27-7.18 (m, 4H), 6.92-6.88 (m, 2H), 5.48 (s, 3H), 3.80 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 159.9, 148.1, 137.9, 129.6, 129.4, 127.7, 126.6, 125.5, 118.8, 114.4, 55.3, 53.7, 21.2 ppm.

Table 5, Entry 8: 1-(4-Methoxybenzyl)-4-(4-fluorophenyl)-1*H*-1,2,3-triazole:



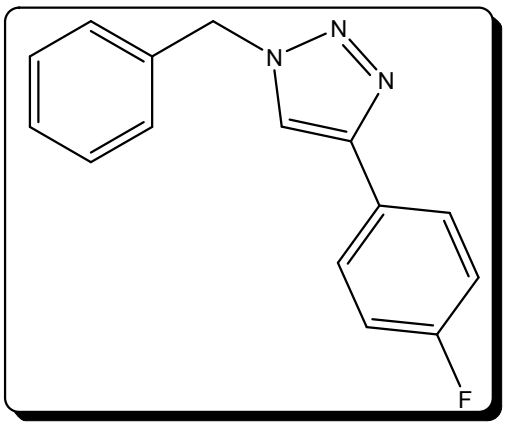
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.76–7.71 (m, 2H), 7.56 (s, 1H), 7.27-7.24 (m, 2H), 7.09-7.04 (m, 2H), 6.92-6.88 (m, 2H), 5.48 (s, 2H), 3.80 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 163.7, 159.8, 147.1, 129.6, 127.3, 127.2, 126.7, 126.4, 118.9, 115.7, 115.5, 114.4, 55.2, 53.7 ppm.

Table 5, Entry 9: 1-(4-Methoxybenzyl)-4-phenyl-1*H*-1,2,3-triazole:



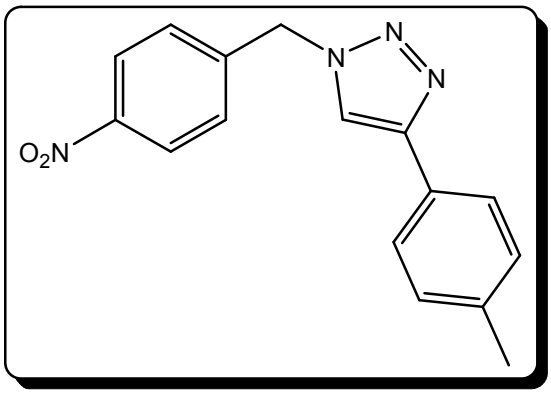
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.79-7.77 (m, 2H), 7.61 (s, 1H), 7.40-7.36 (m, 2H), 7.32-7.25 (m, 3H), 6.91-6.89 (m, 2H), 5.49 (s, 2H), 3.80 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 159.8, 148.0, 130.5, 129.5, 128.7, 128.0, 126.5, 125.5, 119,2, 114.4, 55.2, 53.6 ppm.

Table 5, Entry 10: 1-Benzyl-4-(4-fluorophenyl)-1*H*-1,2,3-triazole:



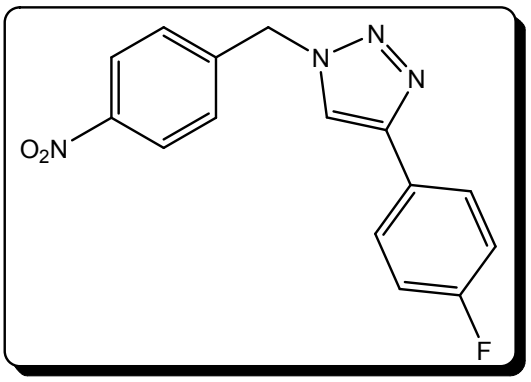
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.78-7.74 (m, 2H), 7.61 (s,1H), 7.41-7.36 (m, 3H), 7.32-7.29 (m, 2H), 7.11-7.05 (m, 2H), 5.56 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 163.8, 147.3, 134.5, 129.1, 128.8, 128.0, 127.4, 127.3, 126.7, 119.1, 115.8, 115.6, 54.2 ppm.

Table 5, Entry 12: 1-(4-Nitrobenzyl)-4-*p*-tolyl-1*H*-1,2,3-triazole:



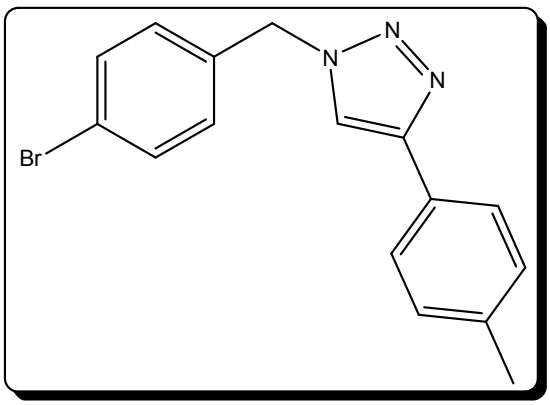
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 8.24-8.22 (d, *J* = 8.42 Hz, 2H), 7.70-7.68 (t, *J* = 4.7 Hz, 3H), 7.44-7.42 (d, *J* = 8.05 Hz, 2 H), 7.23-7.21 (d, 8.42 Hz, 2H), 5.68 (s, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 147.9, 141.7, 138.3, 129.5, 128.4, 127.2, 125.5, 124.2, 53.07, 21.22 ppm.

Table 5, Entry 13: 1-(4-Nitrobenzyl)-4-(4-fluorophenyl)-1*H*-1,2,3-triazole:



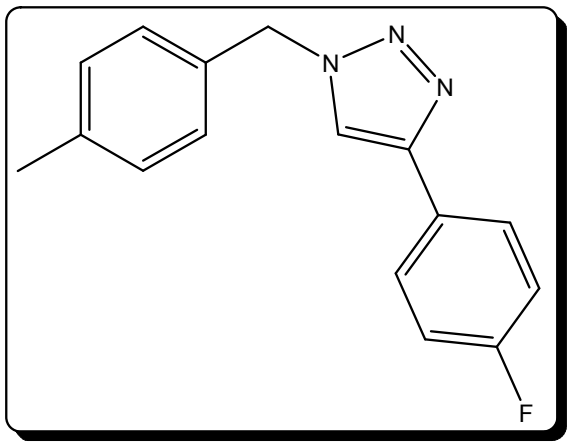
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 8.25–8.23 (d, *J* = 8.42 Hz, 2H), 7.79-7.76 (dd, *J* = 3.66, 8.42 Hz, 2H), 7.69 (s, 1H), 7.45-7.43 (d, *J* = 8.05 Hz, 2H), 7.13-7.08 (t, *J* = 8.42 Hz, 2H), 5.69 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 164.0, 148.1, 141.5, 128.5, 127.5, 127.4, 127.3, 126.3, 124.3, 116.0, 115.8, 53.2 ppm.

Table 5, Entry 14: 1-(4-Bromobenzyl)-4-*p*-tolyl-1*H*-1,2,3-triazole:



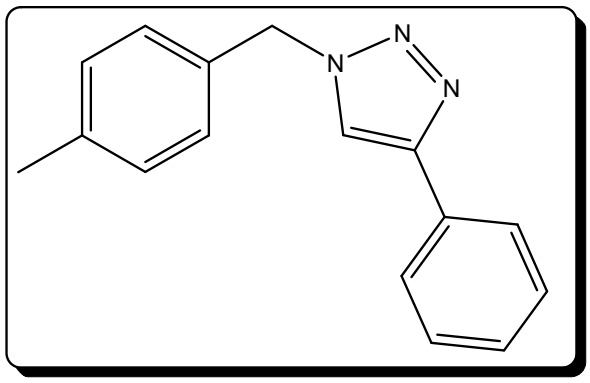
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.70-7.68 (d, *J* = 7.69 Hz, 2H), 7.51-7.49 (d, *J* = 8.42 Hz, 2H), 7.22-7.16 (m, 4H), 5.51 (s, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 138.0, 133.7, 132.7, 129.5, 129.4, 127.4, 125.5, 122.8, 119.0, 53.4, 21.2 ppm.

Table 5, Entry 19: 4-(4-Fluorophenyl)-1-(4-methylbenzyl)-1*H*-1,2,3-triazole:



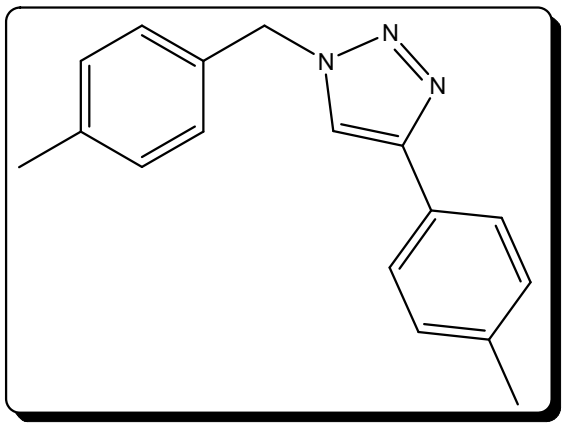
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.76-7.72 (m, 2H), 7.58 (s, 1H), 7.21-7.17 (m, 4H), 7.08-7.04 (m, 2H), 5.50 (s, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 163.7, 147.2, 138.7, 131.4, 129.7, 128.0, 127.3, 127.2, 126.7, 119.1, 115.7, 115.5, 54.0, 21.1 ppm.

Table 5, Entry 20: 1-(4-Methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole:



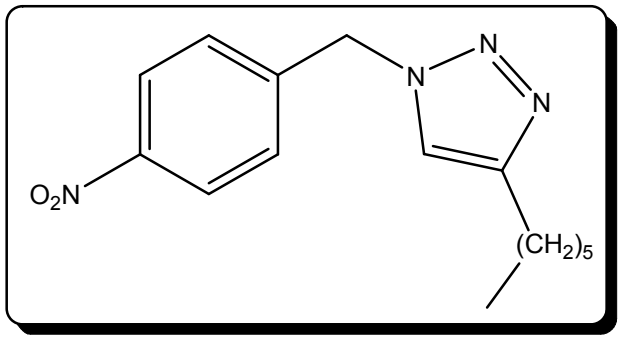
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.79-7.76 (m, 2H), 7.62 (s, 1H), 7.40-7.36 (m, 2H), 7.31-7.28 (m, 1H), 7.22-7.17 (m, 4H), 5.52 (s, 1H), 2.35 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 148.0, 138.6, 131.5, 130.5, 129.7, 128.7, 128.0, 125.6, 119.3, 53.9, 21.1 ppm.

Table 5, Entry 21: 1-(4-Methylbenzyl)-4-*p*-tolyl-1*H*-1,2,3-triazole:



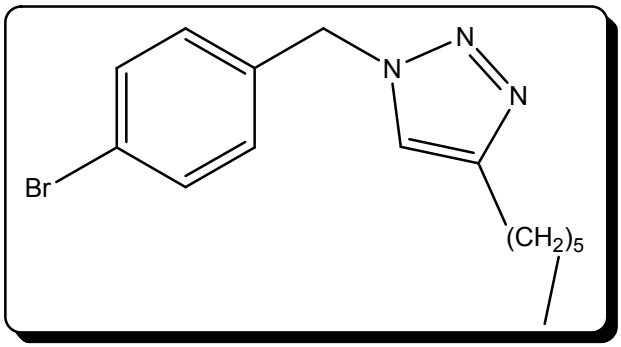
^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.68-7.65 (m, 2H), 7.58 (s, 1H), 7.22-7.17 (m, 6H), 5.51 (s, 2H), 2.35 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 138.6, 137.9, 131.6, 129.7, 129.4, 128.1, 127.7, 125.5, 54.0, 21.2, 21.1 ppm.

Table 5, Entry 22: 1-(4-Nitrobenzyl)-4-hexyl-1*H*-1,2,3-triazole:



^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 8.14-8.11 (m, 2H), 7.32-7.21 (m, 3H), 5.54 (s, 2H), 2.65-2.40 (m, 2H), 1.61-1.44 (m, 2H), 1.25-1.15 (m, 6H), 0.80-0.77 (t, *J* = 6.59 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 149.4, 147.8, 142.0, 128.3, 127.7, 124.1, 124.0, 120.7, 52.8, 31.4, 29.2, 28.8, 25.5, 22.4, 13.9 ppm.

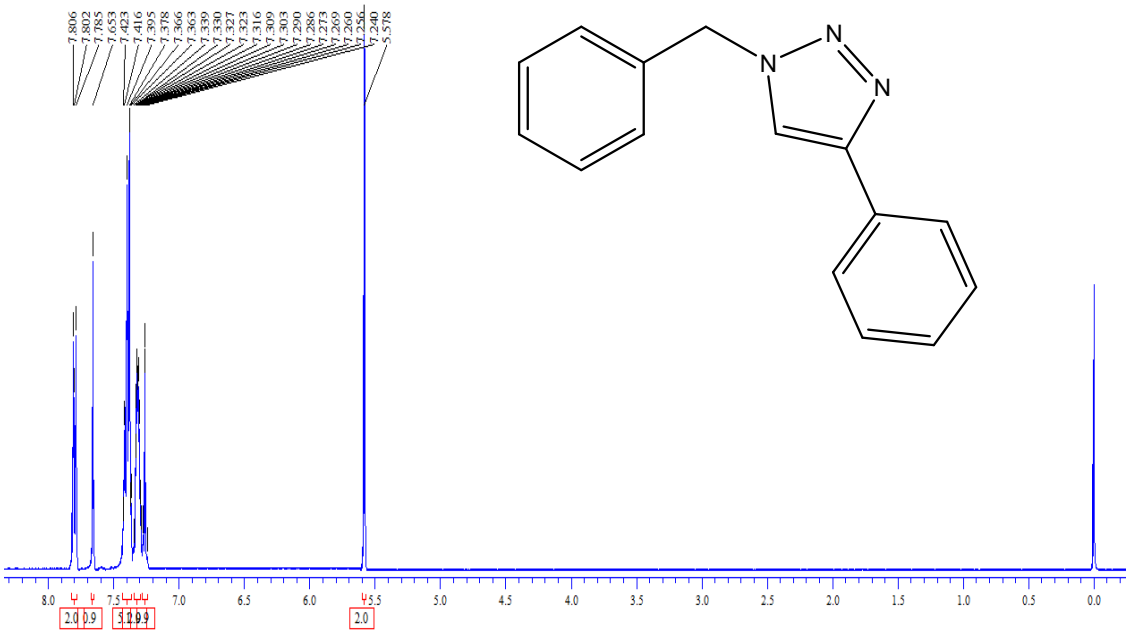
Table 5, Entry 23: 1-(4-Bromobenzyl)-4-hexyl-1*H*-1,2,3-triazole:



^{1}H NMR ($CDCl_3$, 25 ^{0}C) δ 7.42-7.40 (d, *J* = 8.42 Hz 2H), 7.12 (s, 1H), 7.005-6.93 (m, 2H), 5.36 (s, 2H), 2.62-2.38 (t, *J* = 7.69 Hz, 2H), 1.59-1.40 (m, 2H), 1.25-1.15 (m, 6H), 0.80-0.77 (t, *J* = 6.95 Hz, 3H) ppm, ^{13}C NMR ($CDCl_3$, 25 ^{0}C) δ 149.1, 133.9, 132.1, 129.4, 128.7, 122.6, 120.4, 53.1, 31.4, 29.2, 28.8, 25.6, 22.4, 13.9 ppm.

3. ^{1}H NMR and ^{13}C NMR spectra of isolated compounds

Table 5, Entry 2: 1-Benzyl-4-phenyl-1*H*-1,2,3,-triazole:



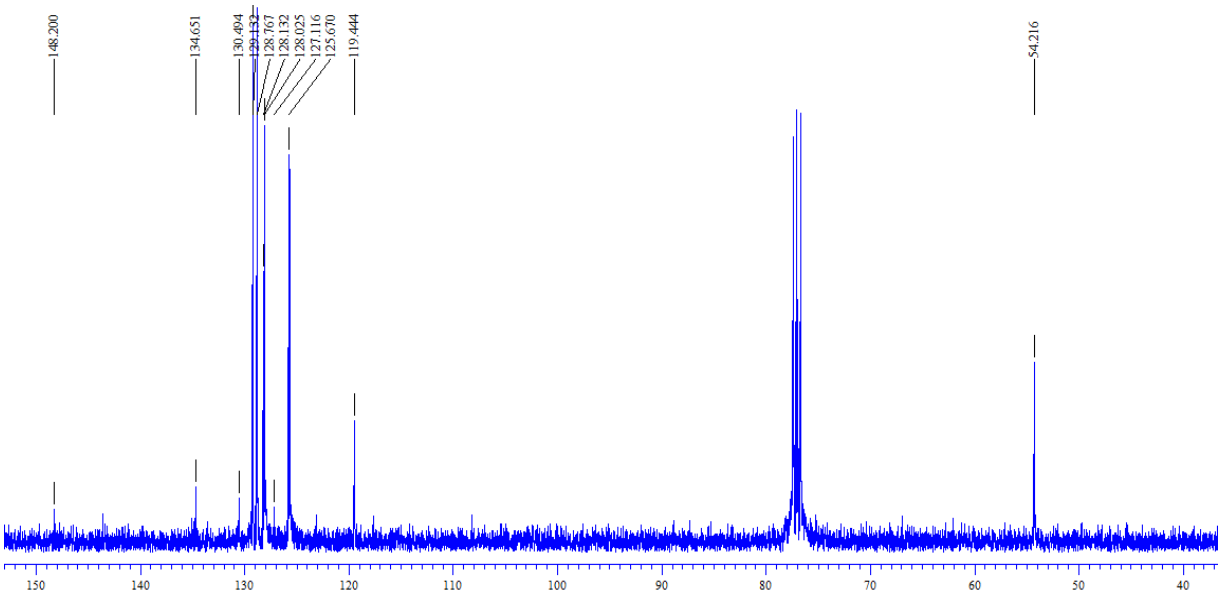
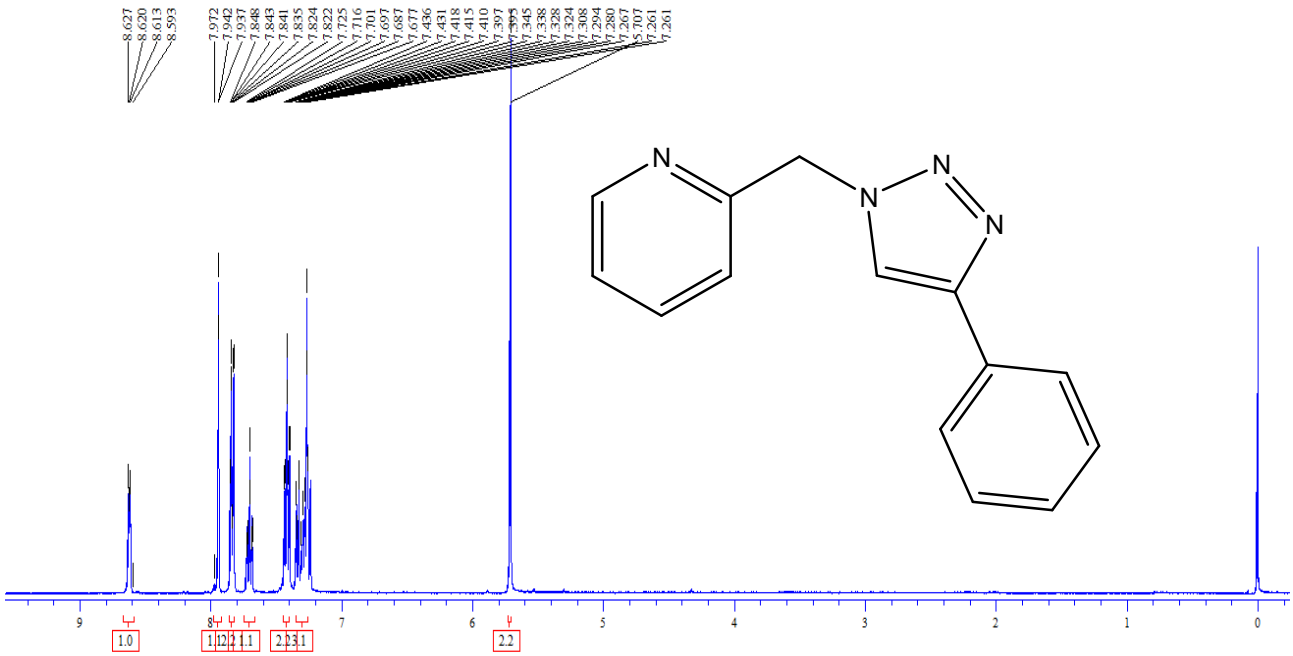


Table 5, Entry 3: 2-((4-Phenyl-1*H*-1,2,3-triazol-1-yl)methyl)pyridine:



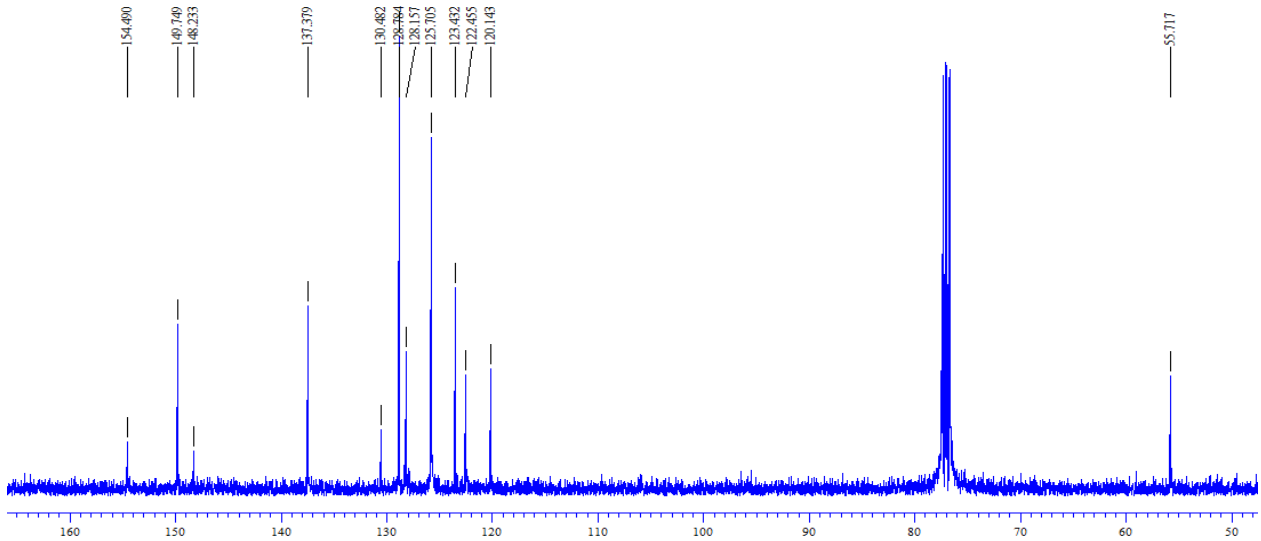
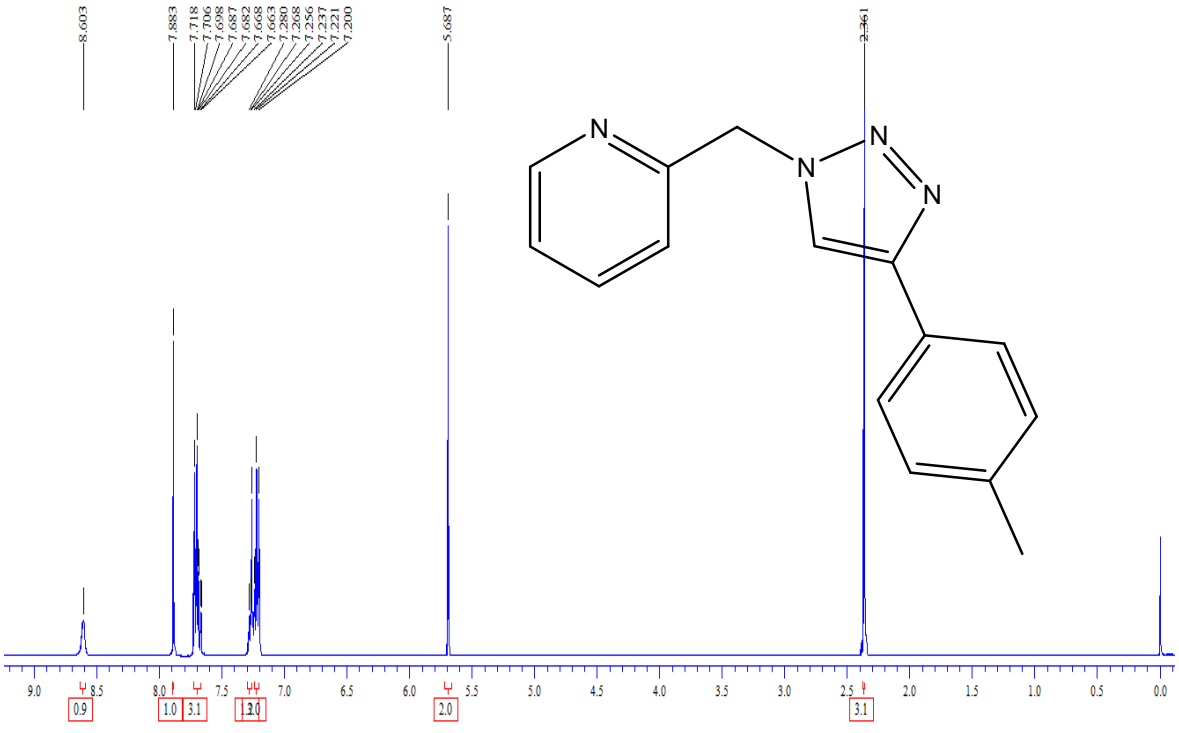


Table 5, Entry 4: 2-((4-*p*-Tolyl-1*H*-1,2,3-triazol-1-yl)methyl)pyridine:



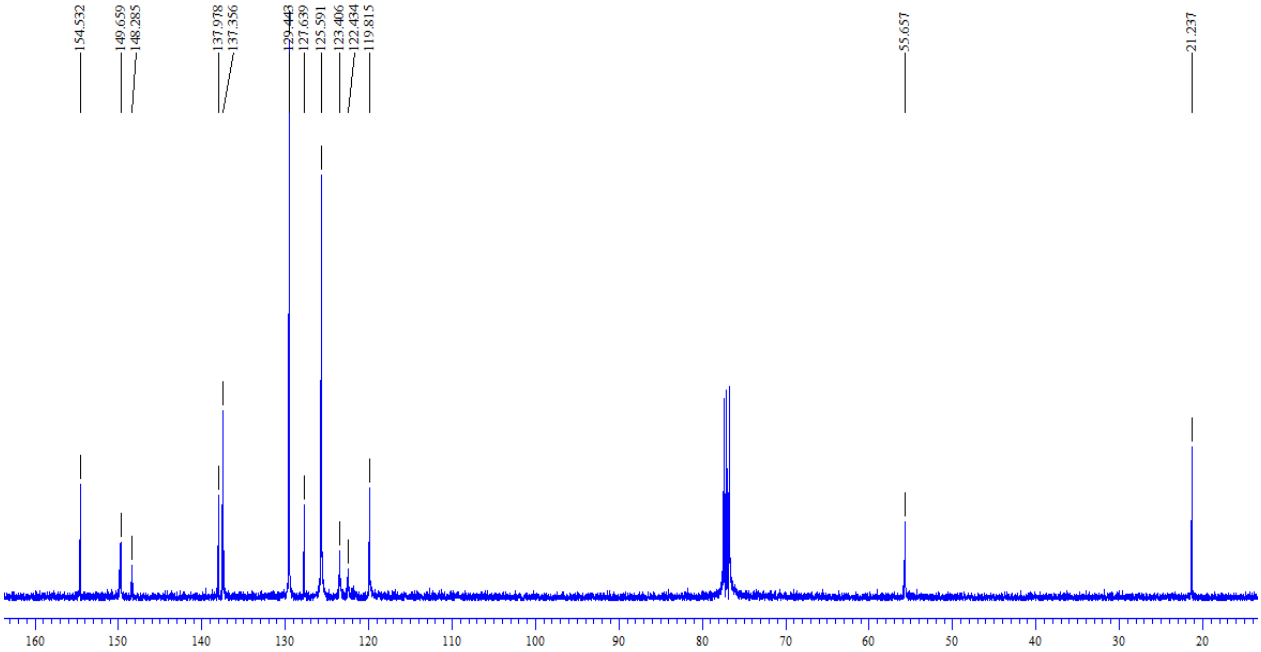
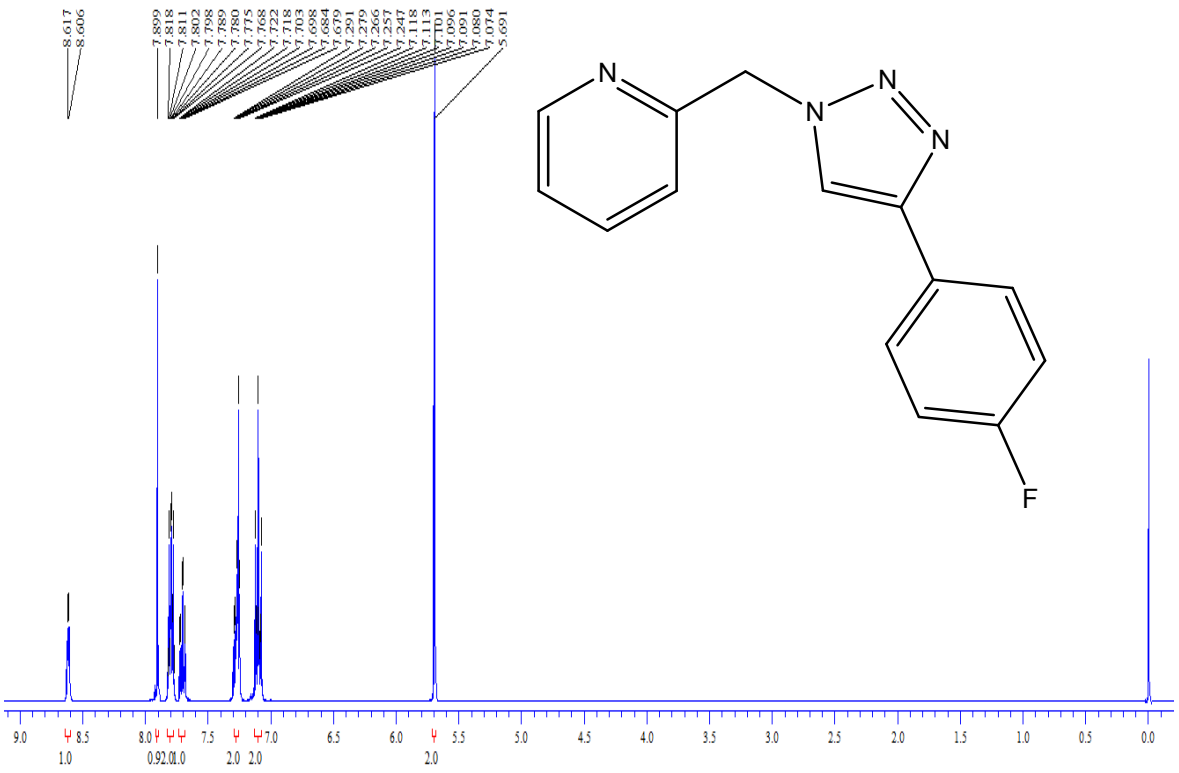


Table 5, Entry 5: 2-((4-(4-Fluorophenyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine:



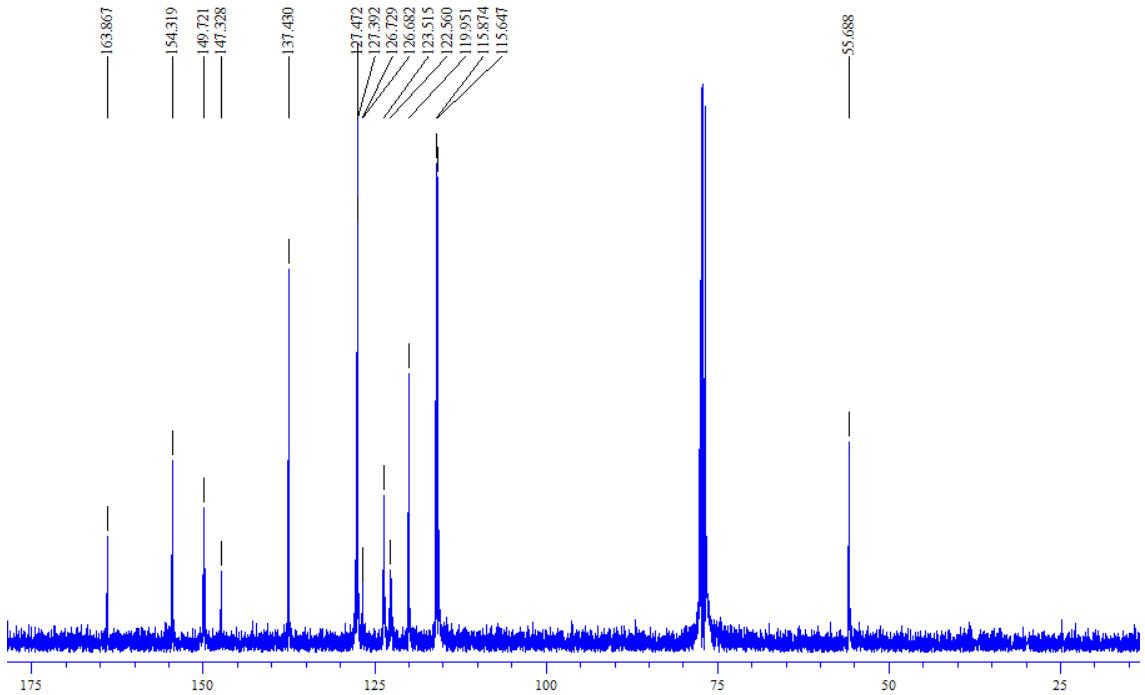
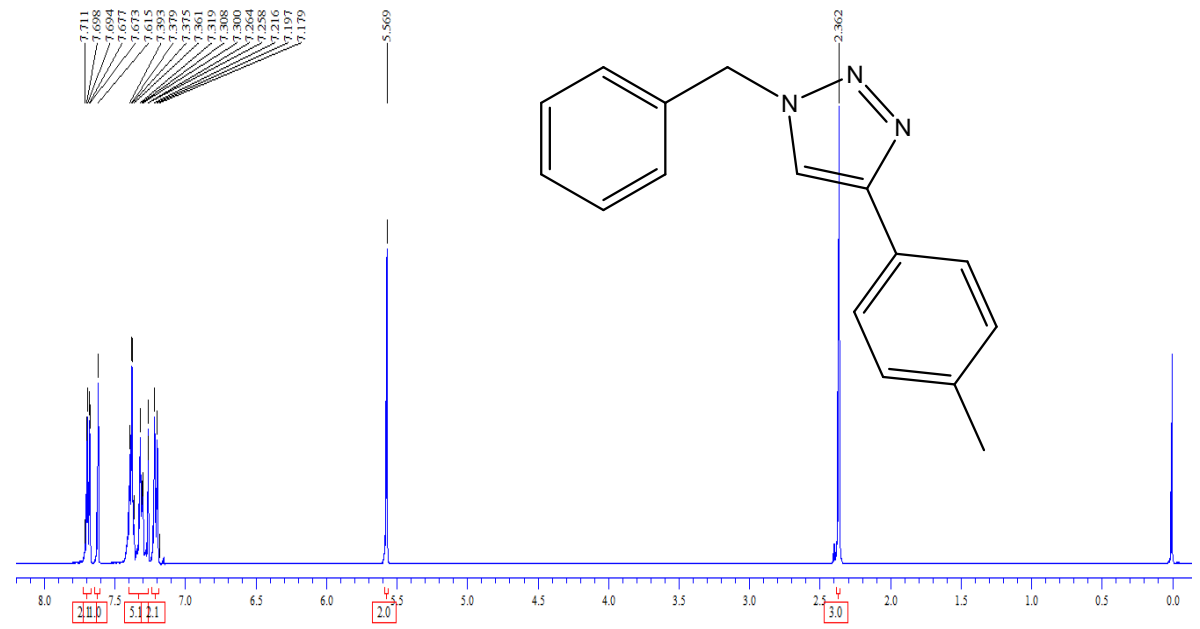


Table 5, Entry 6: 1-Benzyl-4-*p*-tolyl-1*H*-1,2,3-triazole:



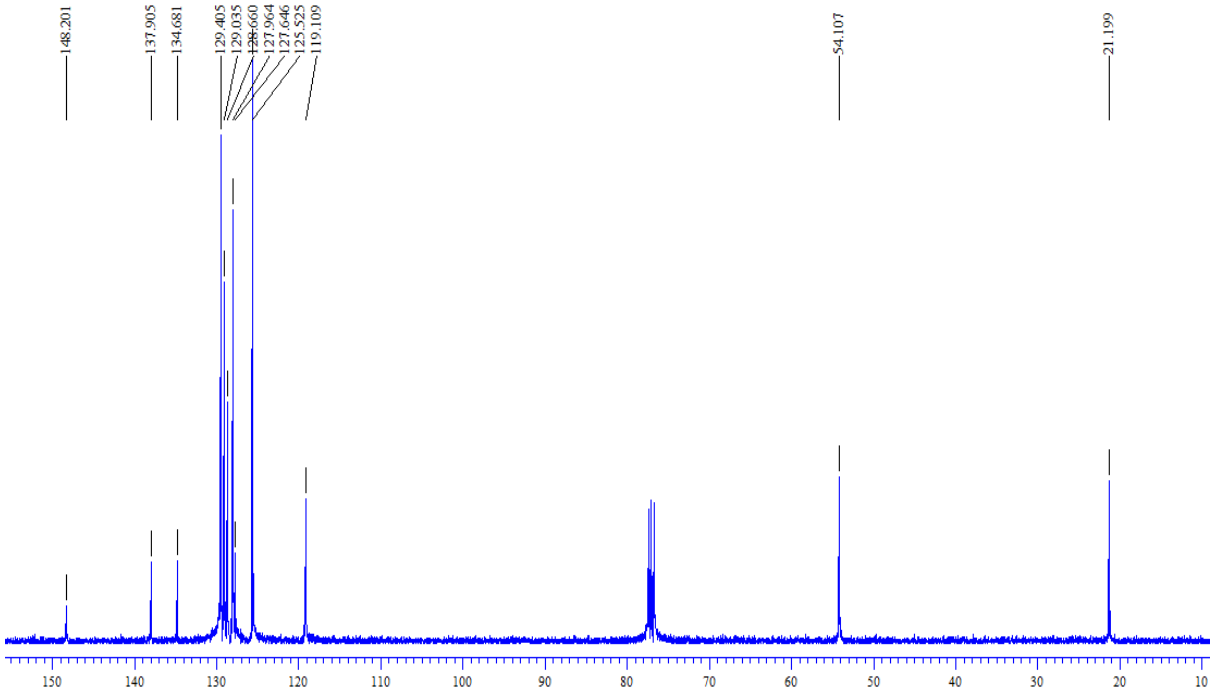
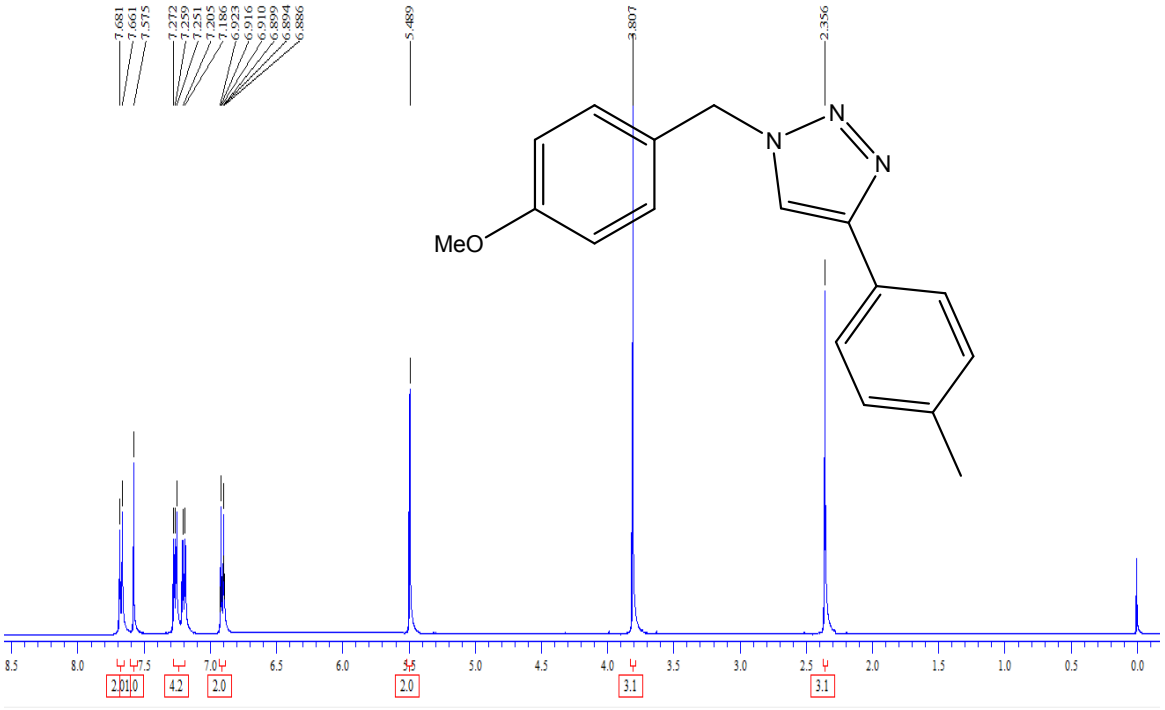


Table 5, Entry 7: 1-(4-Methoxybenzyl)-4-*p*-tolyl-1*H*-1,2,3-triazole:



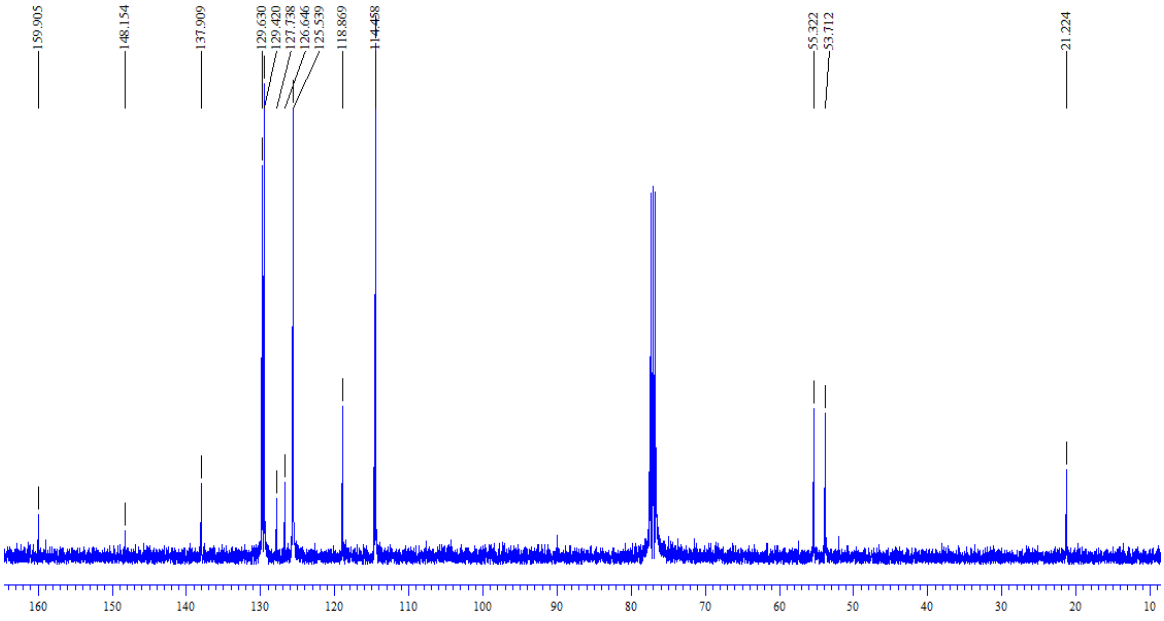
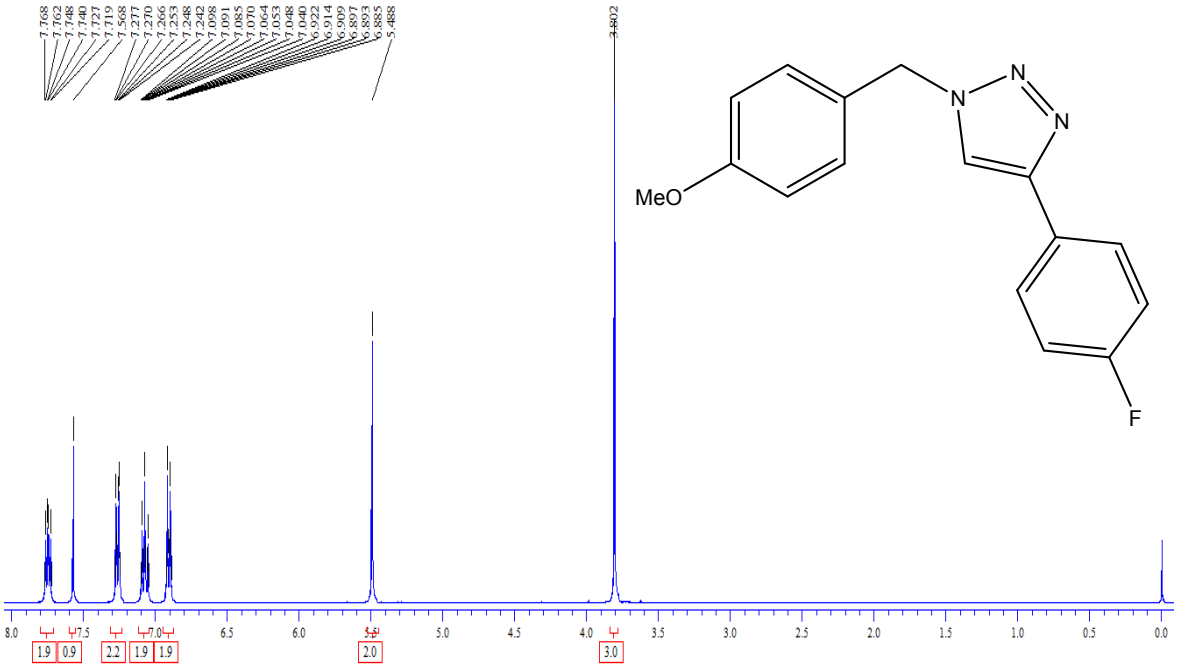


Table 5, Entry 8: 1-(4-Methoxybenzyl)-4-(4-fluorophenyl)-1*H*-1,2,3-triazole:



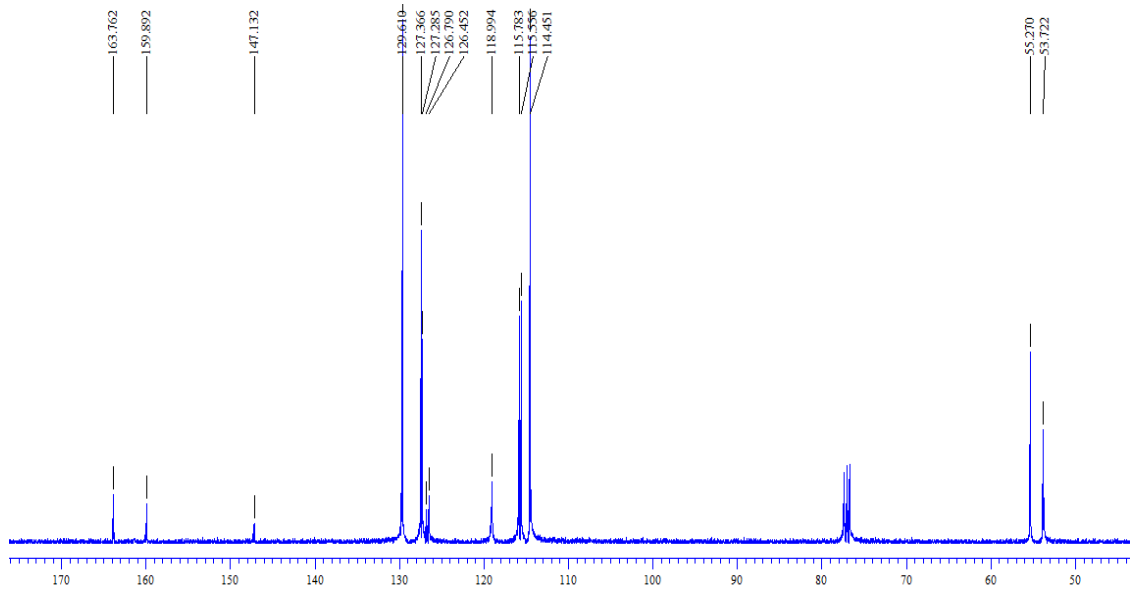
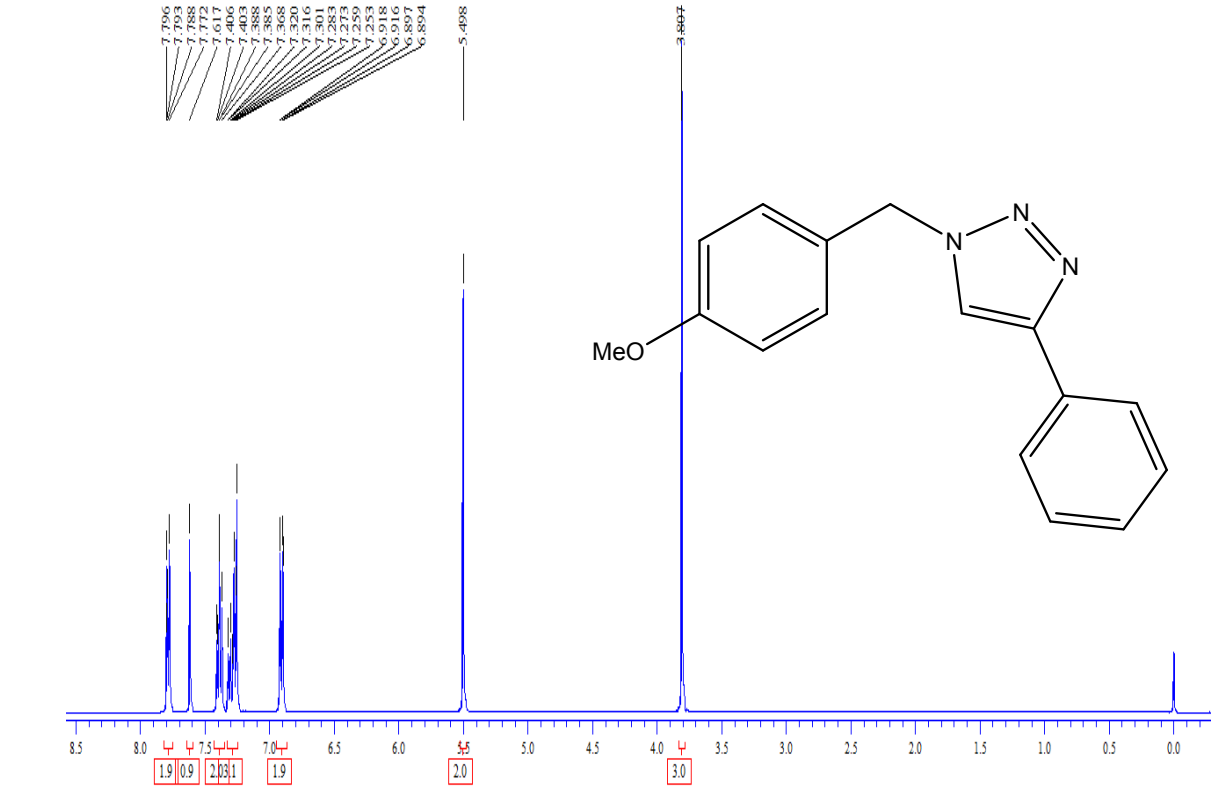


Table 5, Entry 9: 1-(4-Methoxybenzyl)-4-phenyl-1*H*-1,2,3-triazole:



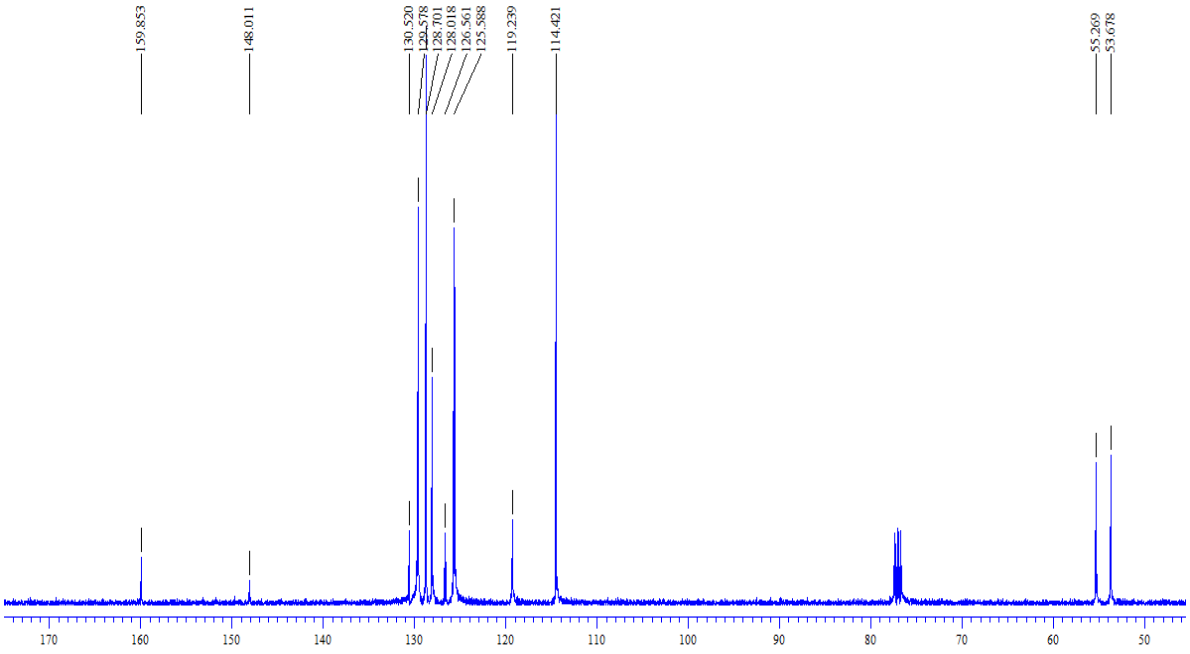
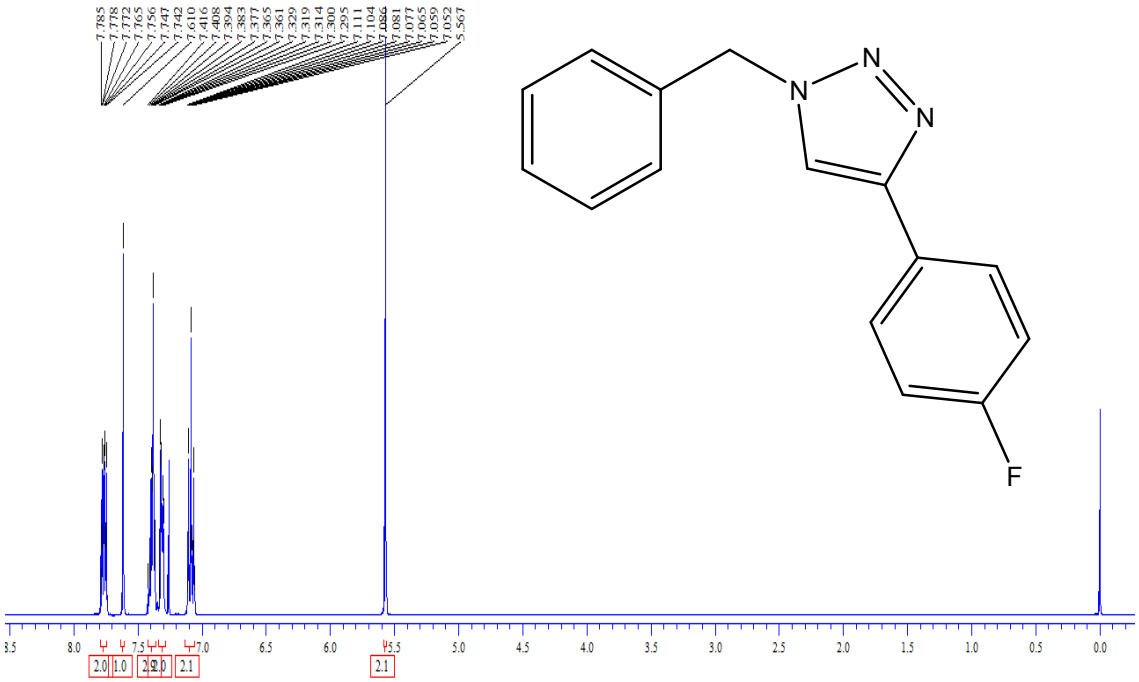


Table 5, Entry 10: 1-Benzyl-4-(4-fluorophenyl)-1*H*-1,2,3-triazole:



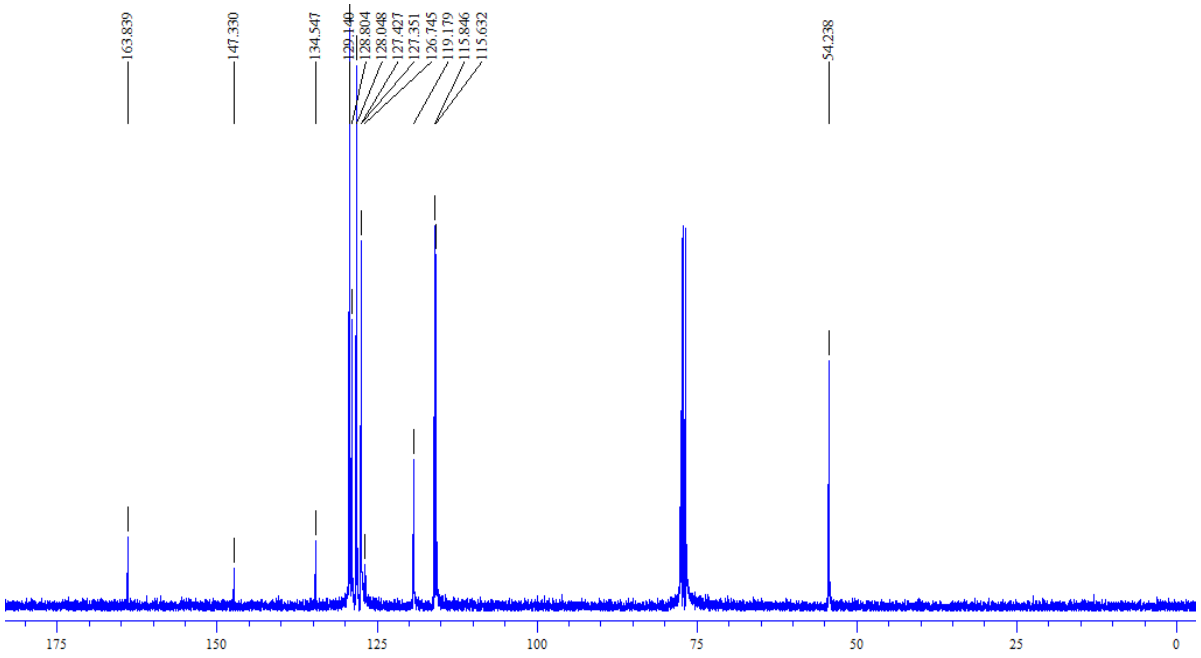
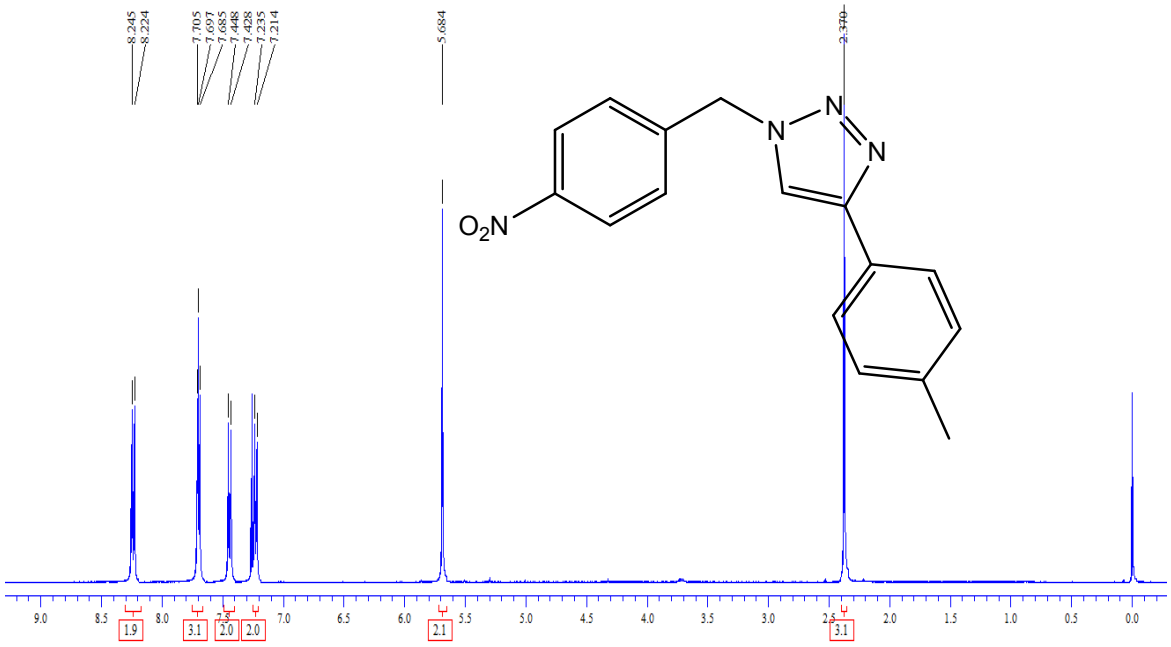


Table 5, Entry 12: 1-(4-Nitrobenzyl)-4-*p*-tolyl-1*H*-1,2,3-triazole:



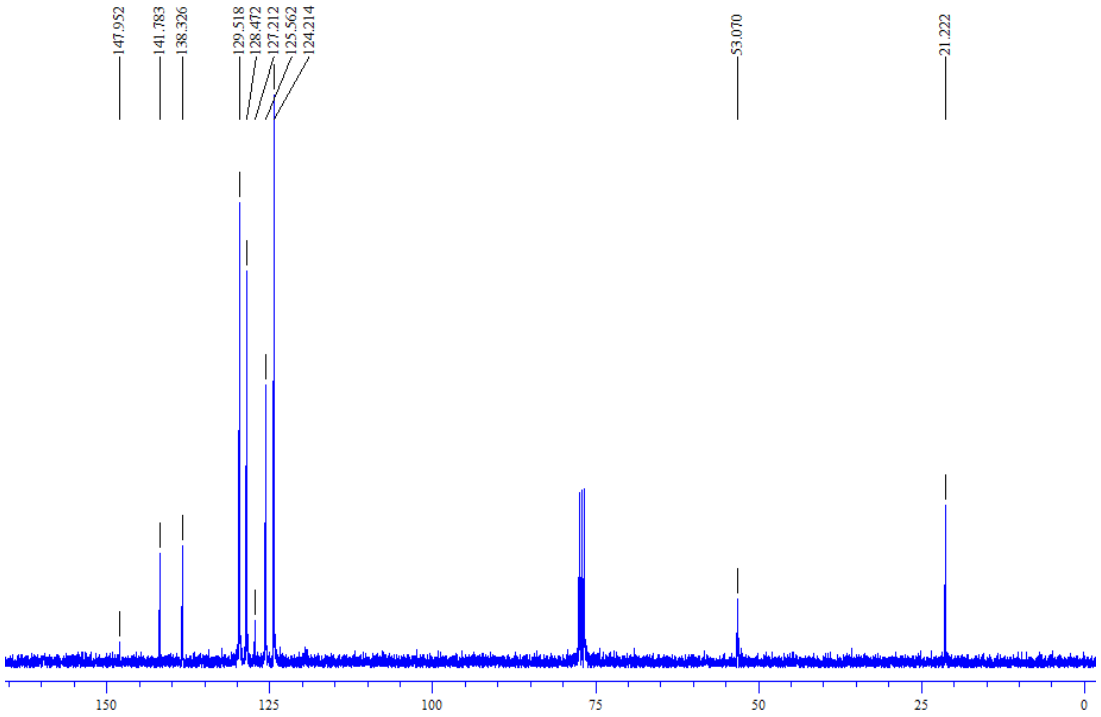
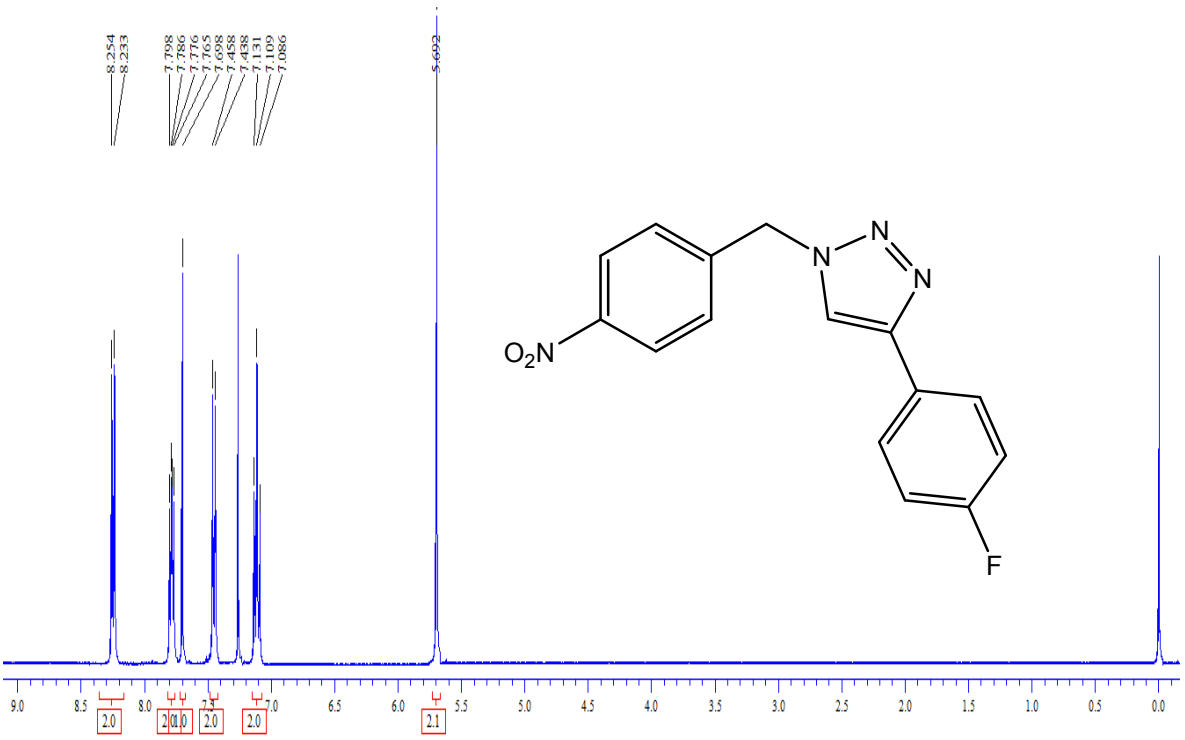


Table 5, Entry 13: 1-(4-Nitrobenzyl)-4-(4-fluorophenyl)-1*H*-1,2,3-triazole:



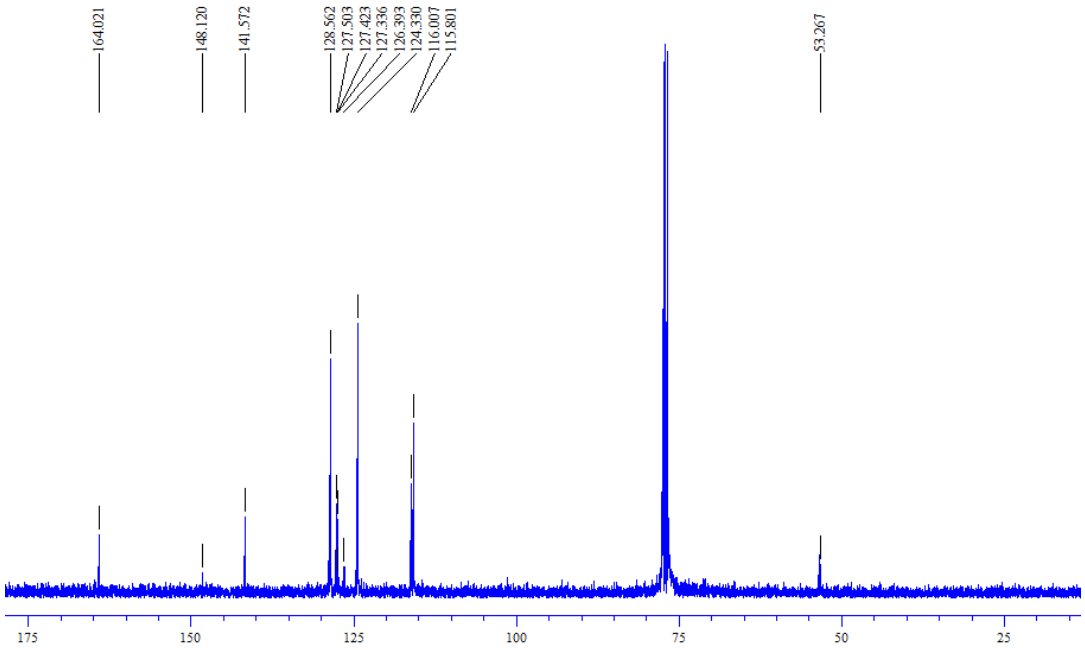
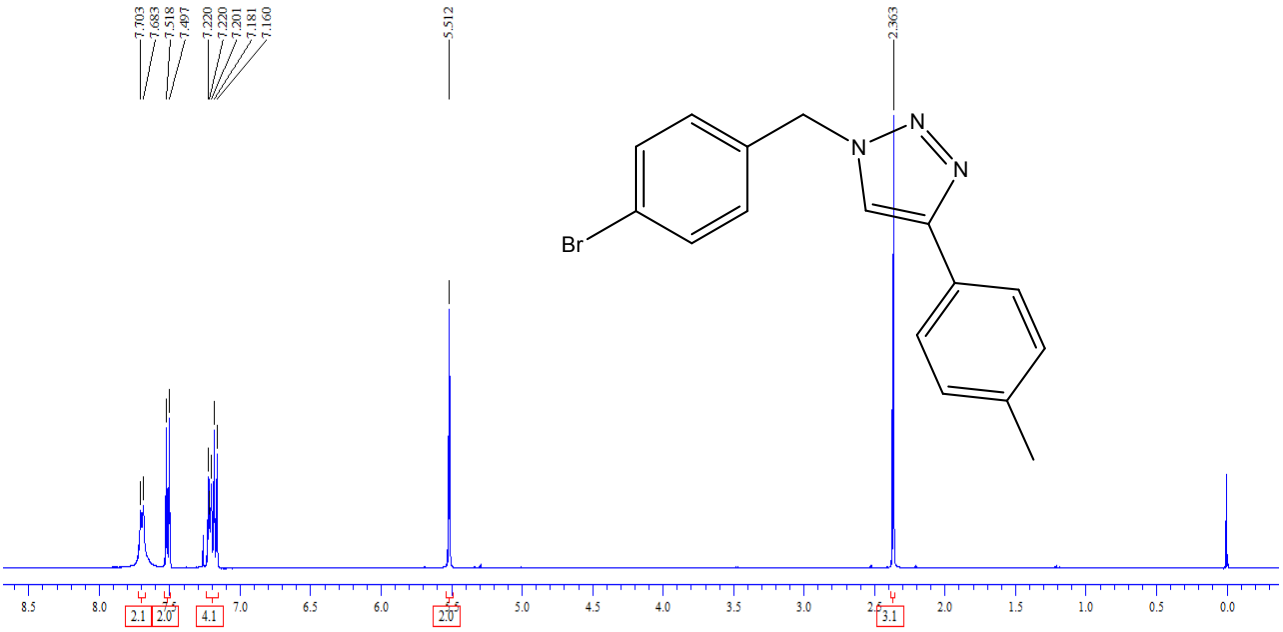


Table 5, Entry 14: 1-(4-Bromobenzyl)-4-*p*-tolyl-1*H*-1,2,3-triazole:



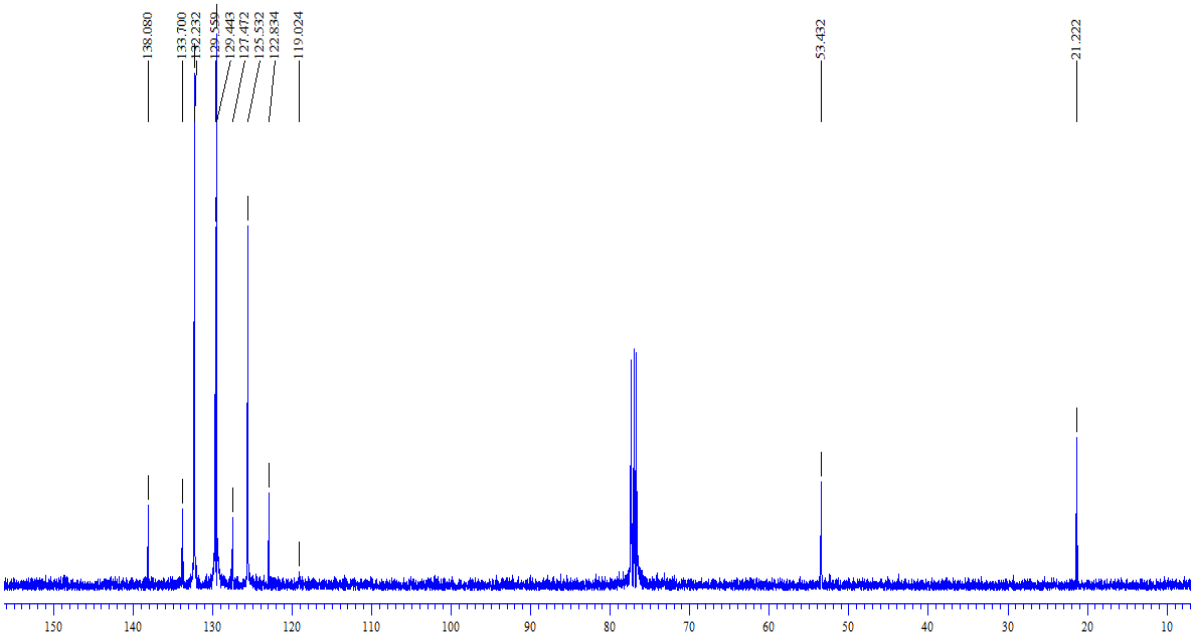
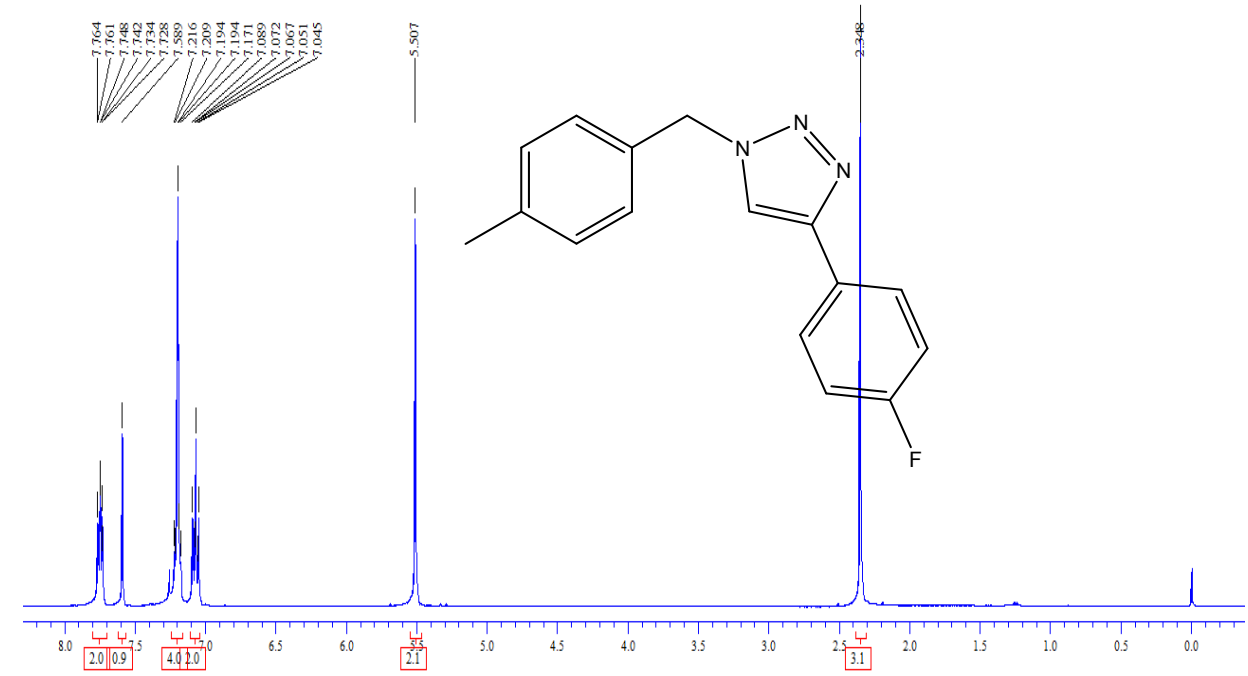


Table 5, Entry 19: 4-(4-Fluorophenyl)-1-(4-methylbenzyl)-1*H*-1,2,3-triazole:



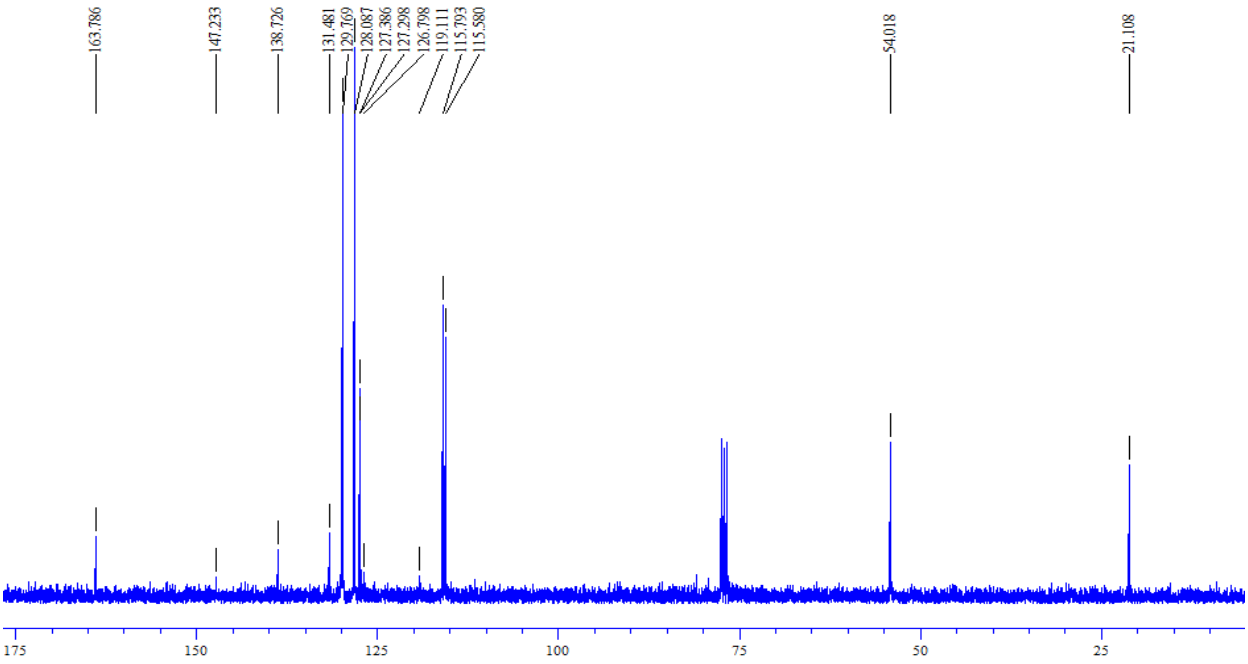
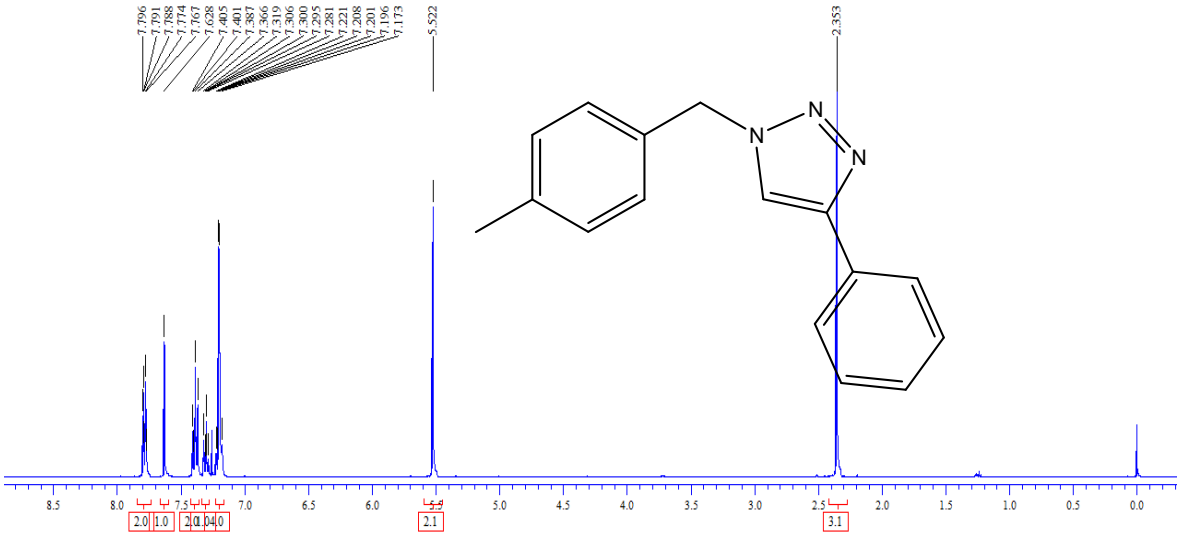


Table 5, Entry 20: 1-(4-Methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole:



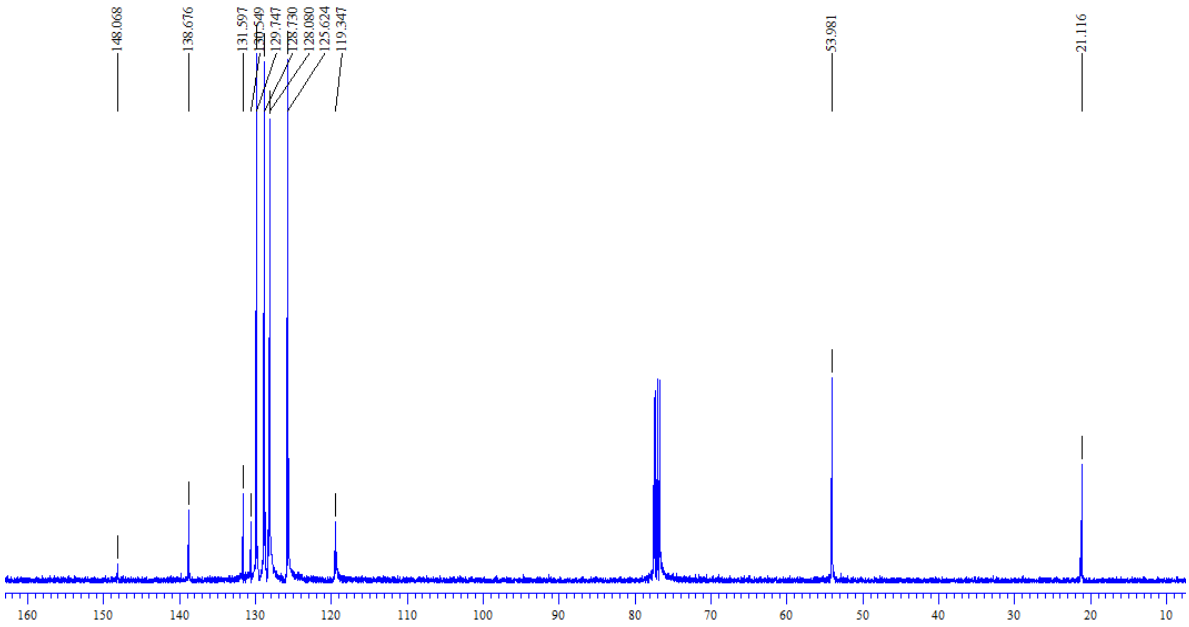


Table 5, Entry 21: 1-(4-Methylbenzyl)-4-*p*-tolyl-1*H*-1,2,3-triazole:

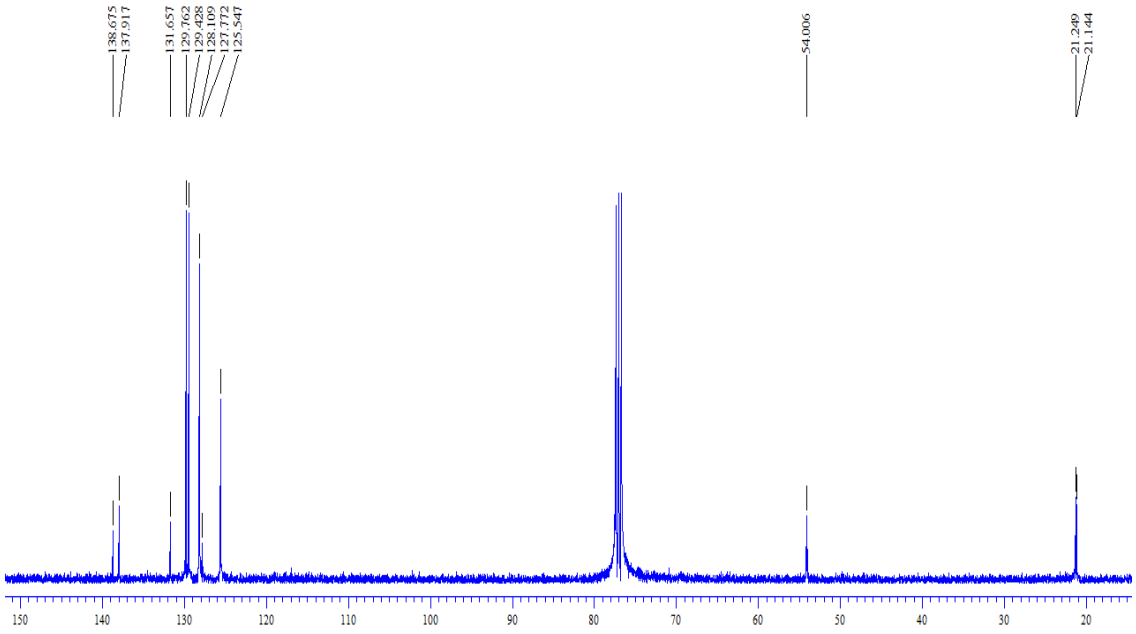
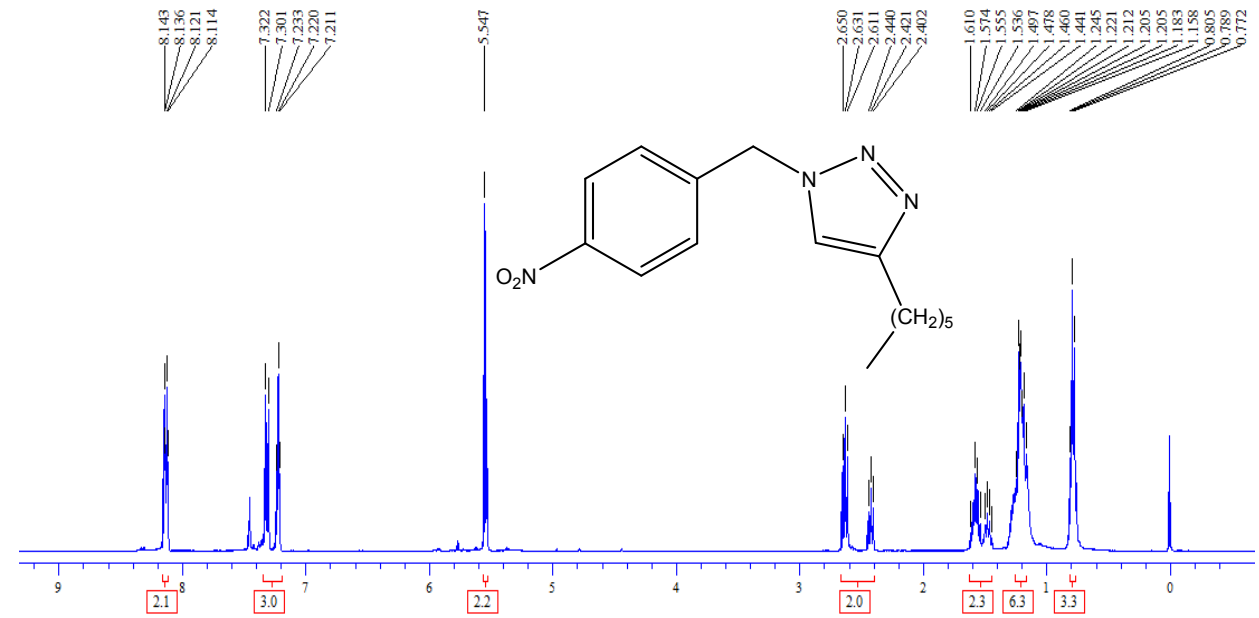


Table 5, Entry 22: 1-(4-Nitrobenzyl)-4-hexyl-1*H*-1,2,3-triazole:



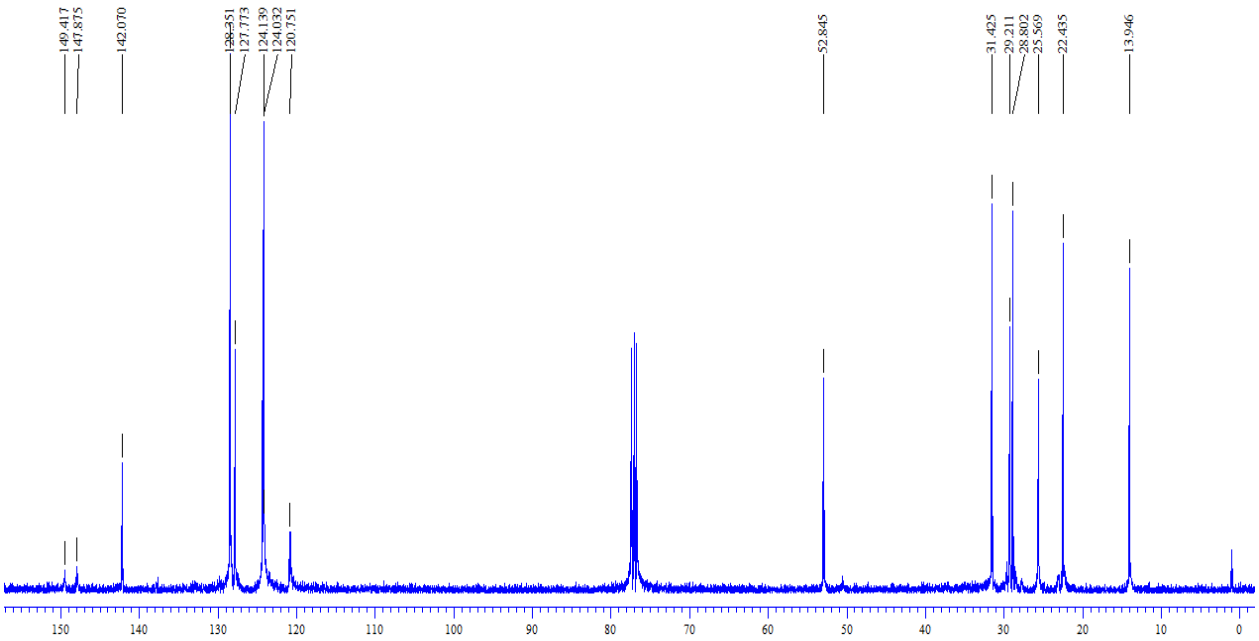


Table 5, Entry 23: 1-(4-Bromobenzyl)-4-hexyl-1*H*-1,2,3-triazole: