Supporting Information

$Cu(OAc)_2 \cdot H_2O/NH_2NH_2 \cdot H_2O$: An Efficient Catalyst System *in situ* Generating Cu_2O Nanoparticles and HOAc for Huisgen-Click Reaction

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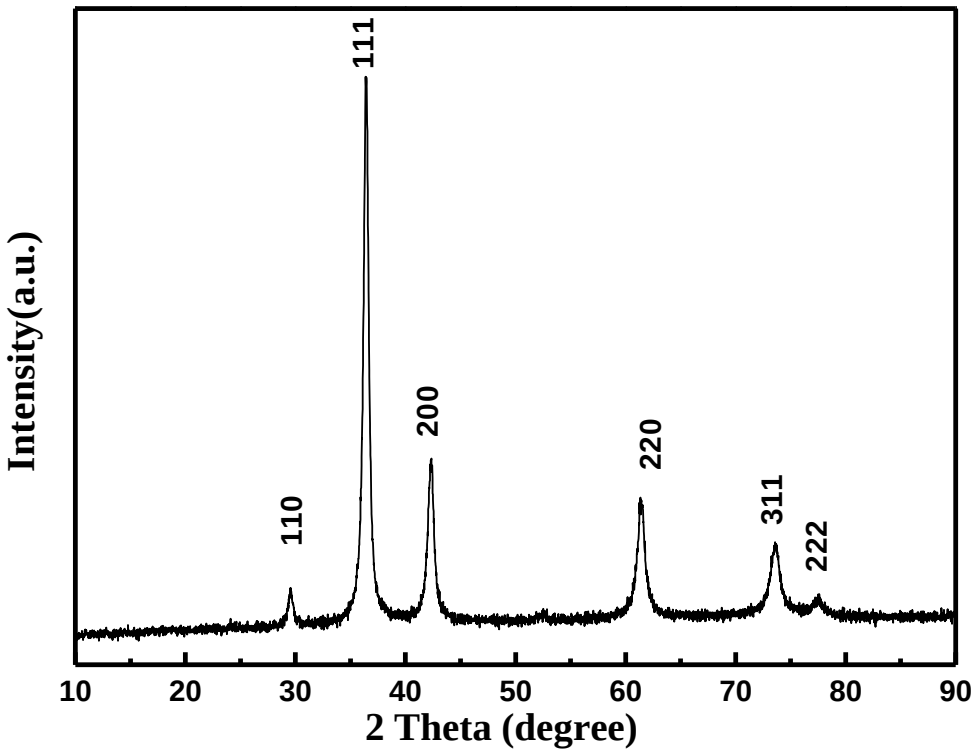
I. General Information:

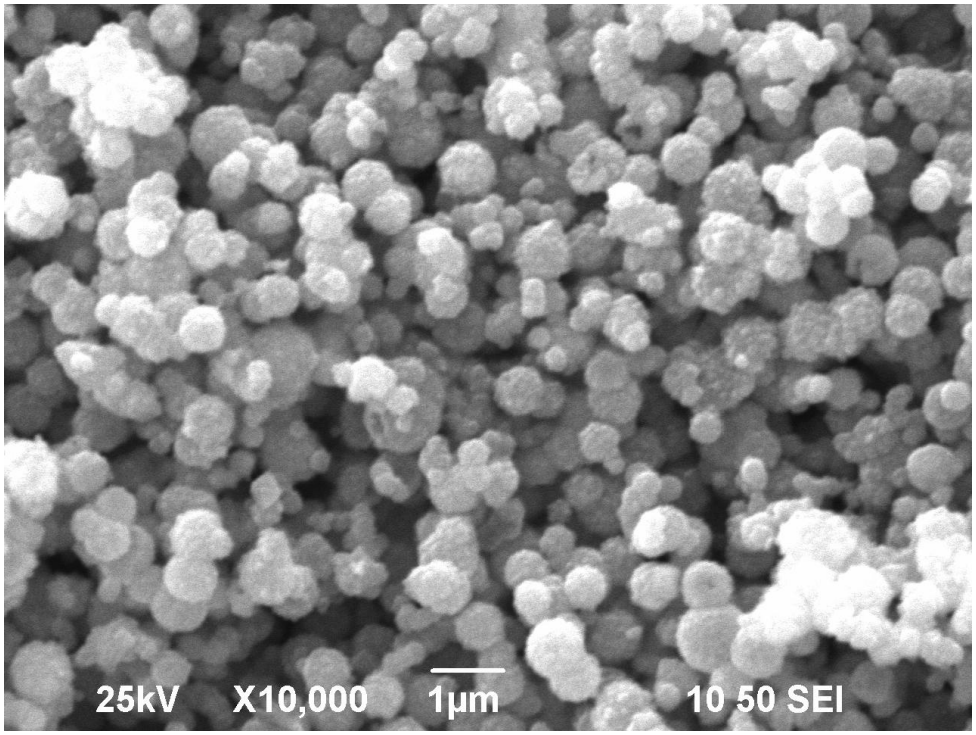
All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. The catalysts were characterized using X-ray powder diffraction (XRD) (Bruker D8 Advance), scanning electron microscope (SEM) (JSM-6390LV) and transmission electron microscope (TEM) (JEM-2100). The products were characterized using ^{1}H NMR and ^{13}C NMR (Bruker Avance/400) which used $CDCl_3$ or DMSO-d6 as the solvent and TMS as internal standard. Data is represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = double of doublets, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constants (J) in Hertz (Hz).

II. Catalyst characterization

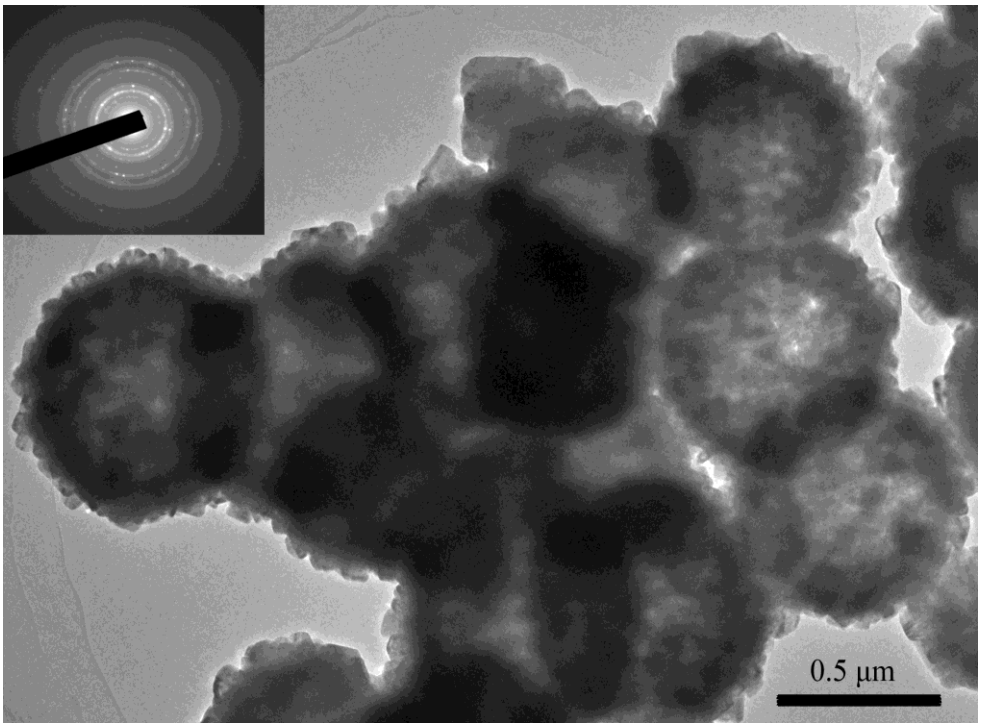
(a) The suspension of catalyst system



(b) XRD pattern of the catalyst



(c) SEM image of the catalyst



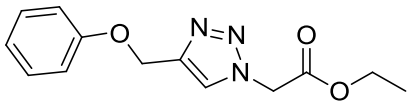
(d) TEM image of the catalyst

XRD peaks at 36.56 °, 42.55 °, 62.77 °and 73.93 °respectively belong to Cu_2O (111), Cu_2O (200), Cu_2O (220) and Cu_2O (311) which clearly demonstrate that the catalysts are Cu_2O. The catalysts are proved to be hollow spherical Cu_2O-NPs of sizes 400-500 nm by SEM and TEM.

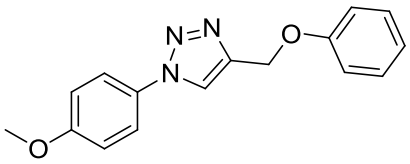
III. General procedure for the synthesis of triazoles

Alkyne (1mmol), azide (1mmol), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol) were dissolved (suspended) in deionized water (1mL) and then $NH_2NH_2 \cdot H_2O$ (0.01 mmol) was added the suspension. The product was precipitated within a short time (**see Table 1** for exact reaction time). After the completion of the reaction, the resulting solution was extracted with EtOAc. The organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed in vacuo to give the corresponding triazoles, which were purified by column chromatography (petroleum ether/EtOAc).

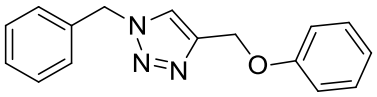
IV. ^{1}H and ^{13}C NMR Data of the Products



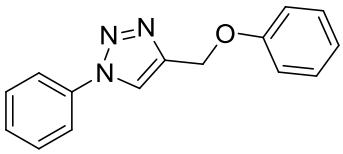
ethyl 2-(4-(phenoxymethyl)-1H-1,2,3-triazol-1-yl)acetate (Table 1, entry 1): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.74 (s, 1H), 7.30-6.94 (m, 5H), 5.21 (s, 2H), 5.13 (s, 2H), 4.23 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.3, 158.2, 144.6, 129.6, 124.3, 121.3, 114.8, 62.4, 61.8, 50.9, 14.0.



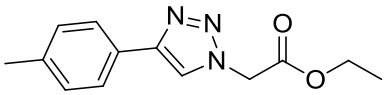
1-(4-methoxyphenyl)-4-(phenoxymethyl)-1H-1,2,3-triazole (Table 1, entry 2): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.97 (s, 1H), 7.64-7.60 (m, 2H), 7.33-7.29 (m, 2H), 7.03-6.99 (m, 5H), 5.28 (s, 2H), 3.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.9, 158.2, 144.8, 130.4, 129.6, 122.3, 121.3, 121.1, 114.8 (2), 62.0, 55.6.



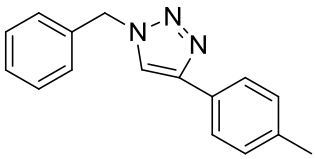
1-benzyl-4-(phenoxymethyl)-1H-1,2,3-triazole (Table 1, entry 3): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.53 (s, 1H), 7.38-7.26 (m, 7H), 6.97 (d, J = 8.0 Hz, 3H), 5.53 (s, 2H), 5.19 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.2, 144.7, 134.5, 129.5, 129.2, 128.8, 128.1, 122.6, 121.3, 114.8, 62.1, 54.3.



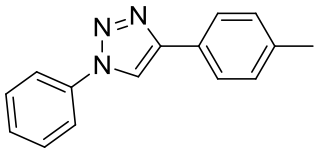
4-(phenoxymethyl)-1-phenyl-1H-1,2,3-triazole (Table 1, entry 4): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.06 (s, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.55-7.43 (m, 3H), 7.32 (t, J = 8.0 Hz, 2H), 7.04-6.98 (m, 3H), 5.31 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.2, 145.1, 137.0, 129.8, 129.6, 128.9, 121.4, 120.9, 120.6, 114.8, 62.0.



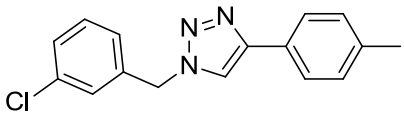
ethyl 2-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)acetate (Table 1, entry 5): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.87 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 8.0 Hz, 2H), 5.19 (s, 2H), 4.28 (q, J = 8.0 Hz, 2H), 2.38 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.4, 148.3, 138.2, 129.5, 127.5, 125.7, 120.7, 62.5, 51.0, 21.3, 14.1.



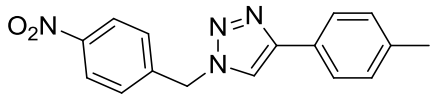
1-benzyl-4-(p-tolyl)-1H-1,2,3-triazole (Table 1, entry 6): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.69 (d, J = 7.6 Hz, 2H), 7.63 (s, 1H), 7.38-7.29 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 5.55 (s, 2H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.3, 138.0, 134.8, 129.5, 129.2, 128.8, 128.1, 127.7, 125.6, 119.2, 54.2, 21.3.



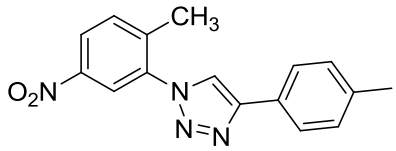
1-phenyl-4-(p-tolyl)-1H-1,2,3-triazole (Table 1, entry 7): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.16 (s, 1H), 7.80 (dd, J = 6.0 Hz, 7.6 Hz, 4H), 7.57-7.26 (m, 5H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.5, 138.3, 137.1, 129.8, 129.6, 128.7, 127.4, 125.8, 120.5, 117.3, 21.3.



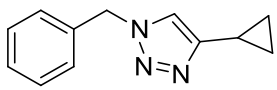
1-(3-chlorobenzyl)-4-(p-tolyl)-1H-1,2,3-triazole (Table 1, entry 8): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.70 (d, J = 8.0 Hz, 2H), 7.66 (s, 1H), 7.35-7.17 (m, 6H), 5.54 (s, 2H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.5, 138.2, 136.7, 135.1, 130.5, 129.5, 129.0, 128.1, 127.5, 126.1, 125.7, 119.2, 53.5, 21.3.



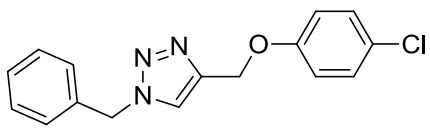
1-(4-nitrobenzyl)-4-(p-tolyl)-1H-1,2,3-triazole (Table 1, entry 9): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.17 (d, J = 8.0 Hz, 2H), 7.75 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 5.65 (s, 2H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.7, 148.0, 141.9, 138.4, 129.6, 128.6, 127.3, 125.6, 124.3, 119.6, 53.1, 21.3.



1-(2-methyl-5-nitrophenyl)-4-(p-tolyl)-1H-1,2,3-triazole (Table 1, entry 10): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.29-8.27 (m, 2H), 8.02 (s, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 9.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.2, 146.4, 141.6, 138.6, 136.8, 132.6, 129.6, 126.9, 125.7, 124.2, 121.1, 120.7, 21.3, 18.6.

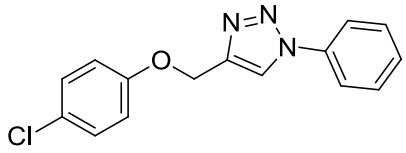


1-benzyl-4-cyclopropyl-1H-1,2,3-triazole (Table 1, entry 11): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.37-7.22 (m, 5H), 7.14 (s, 1H), 5.44 (s, 2H), 1.93-1.86 (m, 1H), 0.92-0.88 (m, 2H), 0.82-0.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 150.7, 134.9, 129.0, 128.6, 128.0, 119.6, 54.0, 7.7, 6.7.

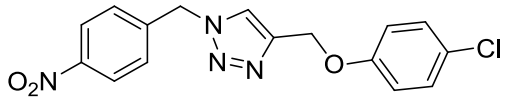


1-benzyl-4-((4-chlorophenoxy)methyl)-1H-1,2,3-triazole (Table 1, entry 12): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.53 (s, 1H), 7.36-7.24 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H),

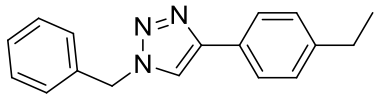
6.88 (d, *J* = 8.0 Hz, 2H), 5.50 (s, 2H), 5.12 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 156.8, 144.1, 134.5, 129.4, 129.2, 128.9, 128.1, 126.1, 122.8, 116.2, 62.3, 54.2.



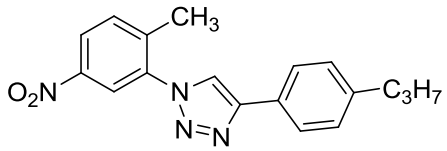
4-((4-chlorophenoxy)methyl)-1-phenyl-1H-1,2,3-triazole (Table 1, entry 13): ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 8.05 (s, 1H), 7.72 (dd, *J* = 8.0 Hz, 2.0 Hz, 2H), 7.54-7.43 (m, 3H), 7.25 (dd, *J* = 6.8 Hz, 2.4 Hz, 2H), 6.95 (dd, *J* = 6.8 Hz, 2.4 Hz, 2H), 5.26 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 156.8, 144.6, 136.9, 129.8, 129.5, 129.0, 126.3, 121.0, 120.6, 116.1, 62.2.



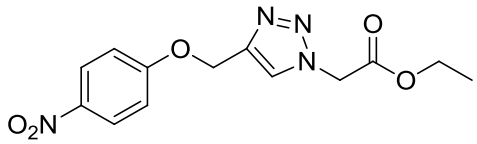
4-((4-chlorophenoxy)methyl)-1-(4-nitrobenzyl)-1H-1,2,3-triazole (Table 1, entry 14): ^{1}H NMR (DMSO-d6, 400 MHz) *δ*: 8.37 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 5.81 (s, 2H), 5.16 (s, 2H). ^{13}C NMR (DMSO-d6, 100 MHz) *δ*: 157.2, 147.6, 143.8, 143.3, 129.7, 129.4, 125.6, 125.1, 124.3, 116.9, 61.8, 52.4.



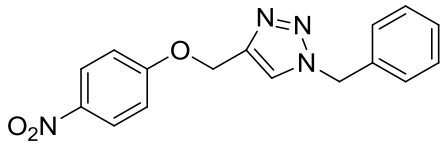
1-benzyl-4-(4-ethylphenyl)-1H-1,2,3-triazole (Table 1, entry 15): ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.71 (d, *J* = 8.0 Hz, 2H), 7.63 (s, 1H), 7.37-7.27 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.53 (s, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 148.3, 144.4, 134.8, 129.1, 128.7, 128.3, 128.0 (2), 125.7, 119.3, 54.2, 28.7, 15.5.



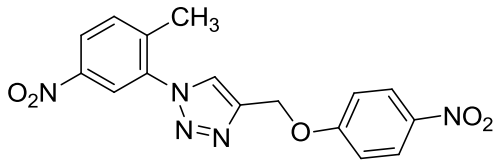
1-(2-methyl-5-nitrophenyl)-4-(4-propylphenyl)-1H-1,2,3-triazole (Table 1, entry 16): ^{1}H NMR (DMSO-d6, 400 MHz) δ: 9.07 (s, 1H), 8.42-8.35 (m, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 2.40 (s, 3H), 1.68-1.58 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H). ^{13}C NMR (DMSO-d6, 100 MHz) δ: 147.3, 146.5, 142.7, 141.6, 136.9, 133.3, 129.3, 128.0, 125.8, 124.5, 123.2, 121.2, 37.4, 24.4, 18.6, 14.0.



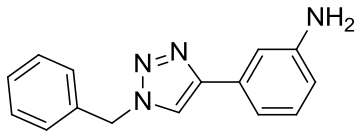
ethyl 2-(4-((4-nitrophenoxy)methyl)-1H-1,2,3-triazol-1-yl)acetate (Table 1, entry 17): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.20 (dd, J = 7.6 Hz, 2.0 Hz, 2H), 7.84 (s, 1H), 7.08 (d, J = 8.0 Hz, 2H), 5.34 (s, 2H), 5.20 (s, 2H), 4.28 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.1, 163.1, 143.2, 141.9, 125.9, 124.5, 114.9, 62.6, 62.4, 51.0, 14.1.



1-benzyl-4-((4-nitrophenoxy)methyl)-1H-1,2,3-triazole (Table 1, entry 18): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.15 (dd, J = 9.2 Hz, 1.2 Hz, 2H), 7.62 (s, 1H), 7.38-7.28 (m, 5H), 7.04 (d, J = 9.2 Hz, 2H), 5.55 (s, 2H), 5.26 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 163.2, 143.1, 141.8, 134.3, 129.2, 128.9, 128.2, 125.9, 123.2, 114.9, 62.4, 54.3.

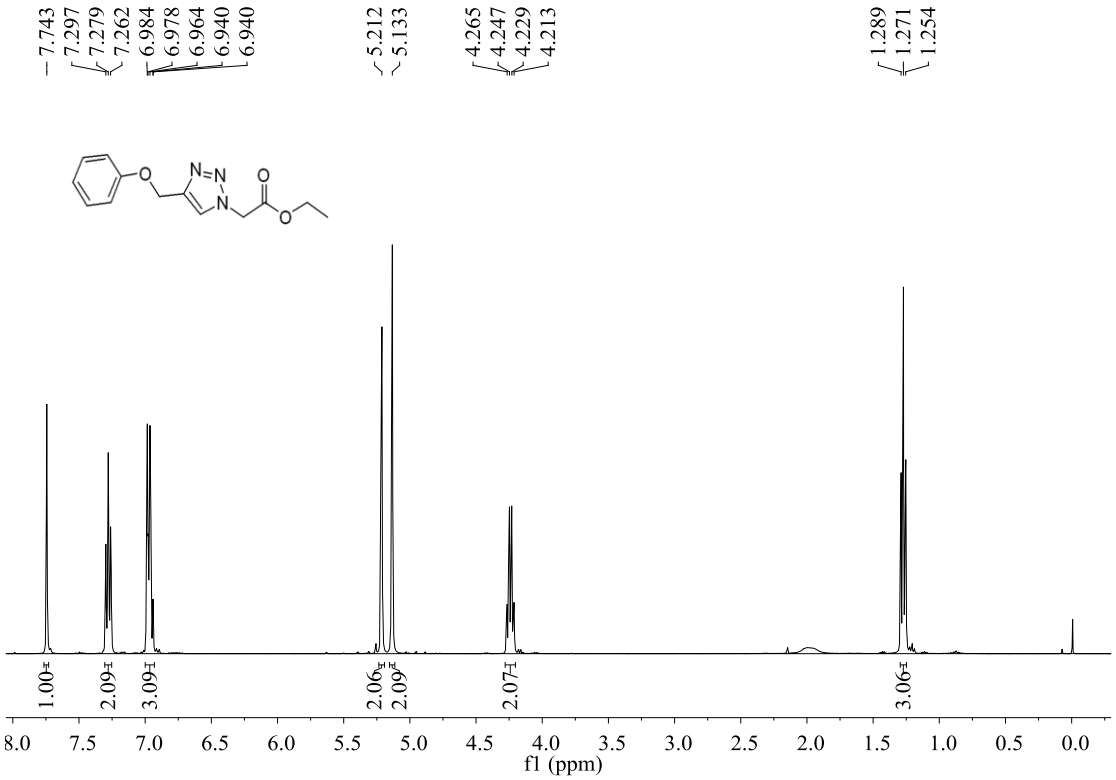


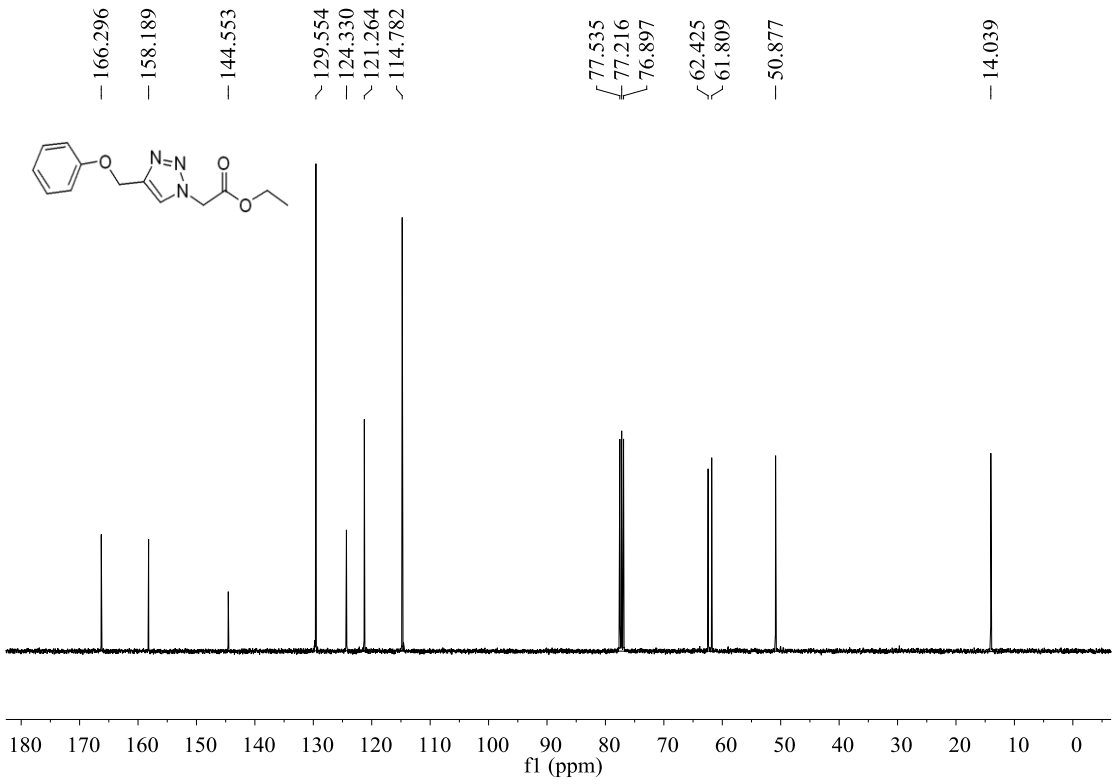
1-(2-methyl-5-nitrophenyl)-4-((4-nitrophenoxy)methyl)-1H-1,2,3-triazole (Table 1, entry 19): ^{1}H NMR (DMSO-d6, 400 MHz) δ: 8.85 (s, 1H), 8.37 (d, J = 6.8 Hz, 2H), 8.26 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 9.2 Hz, 1H), 7.34 (d, J = 9.2 Hz, 2H), 5.46 (s, 2H), 2.32 (s, 3H). 1.68-1.58 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H). ^{13}C NMR (DMSO-d6, 100 MHz) δ: 163.6, 146.5, 142.7, 141.8, 141.5, 136.8, 133.3, 127.3, 126.3, 124.8, 121.5, 115.8, 62.2, 18.4.

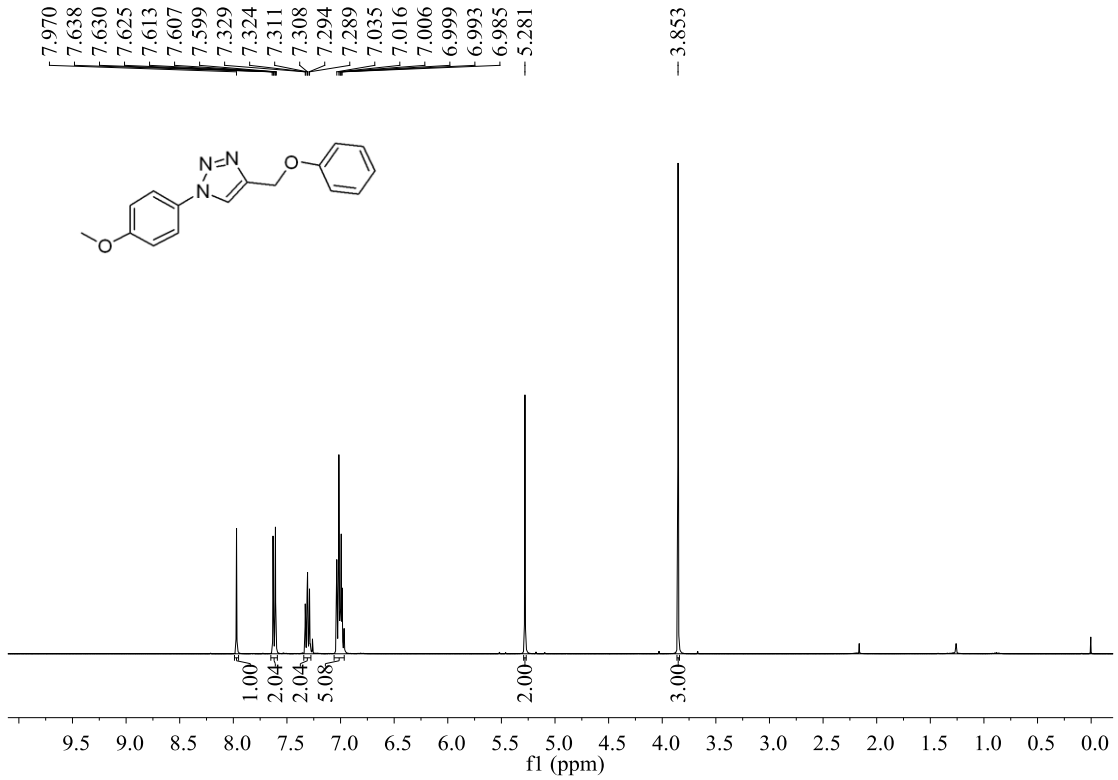


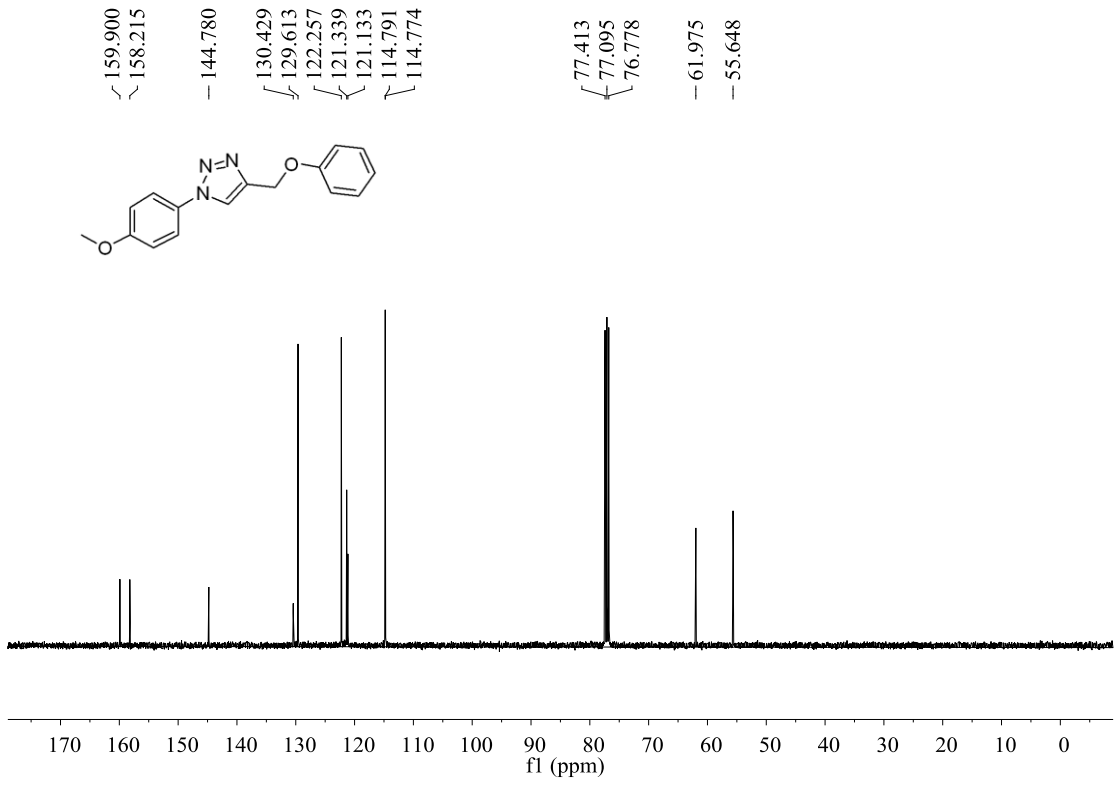
3-(1-benzyl-1H-1,2,3-triazol-4-yl)aniline (Table 1, entry 20): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.61 (s, 1H), 7.38-7.28 (m, 5H), 7.23 (s, 1H), 7.16 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 5.55 (s, 2H), 3.35 (br s, 2H, NH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.3, 146.8, 134.7, 131.4, 129.7, 129.1, 128.8, 128.1, 119.6, 116.1, 115.0, 112.3, 54.2.

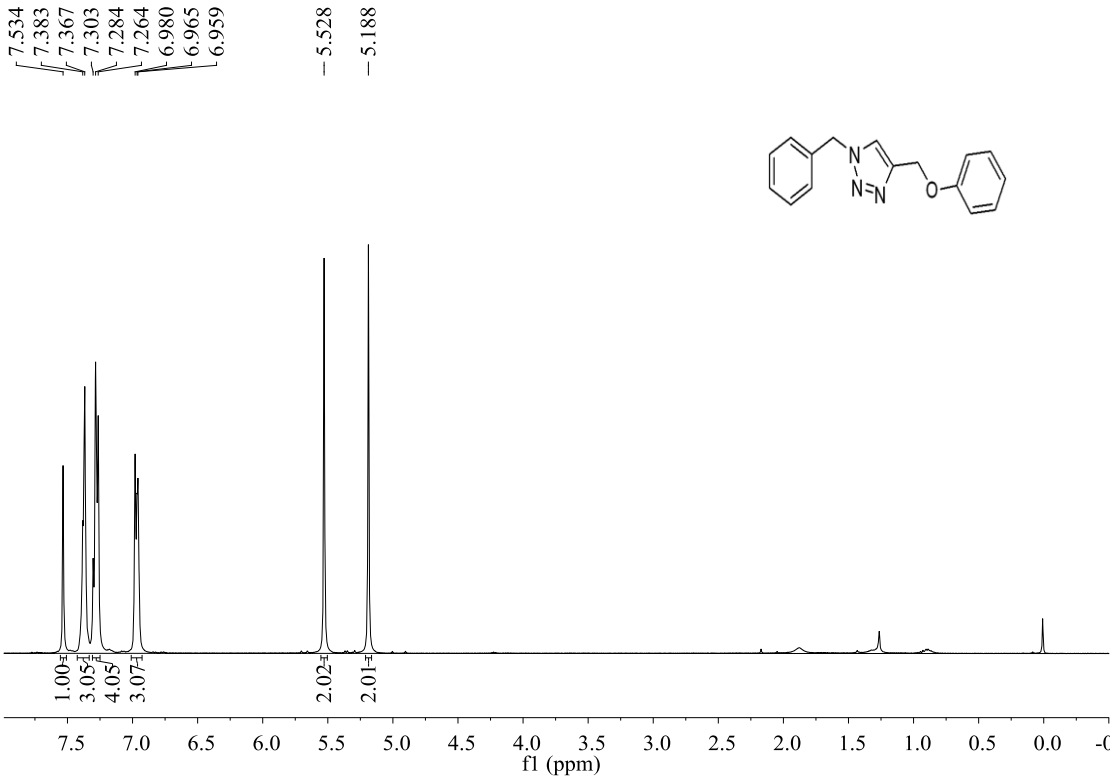
V. ^{1}H and ^{13}C NMR Spectra of the Products

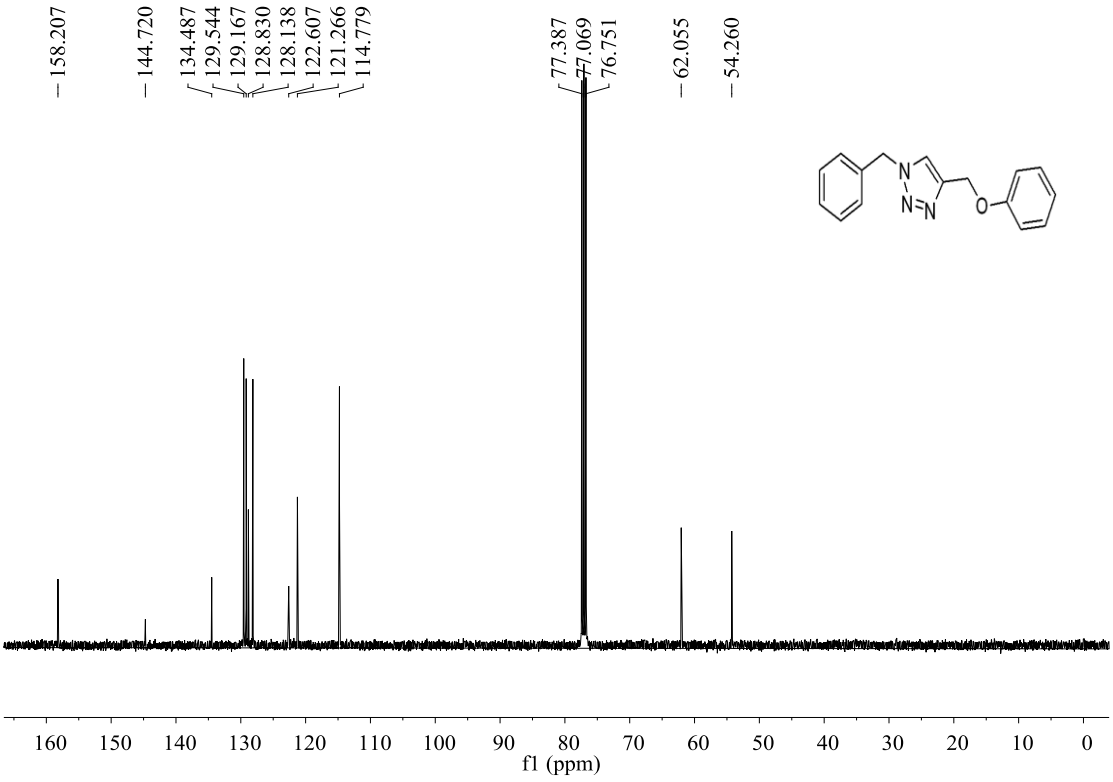


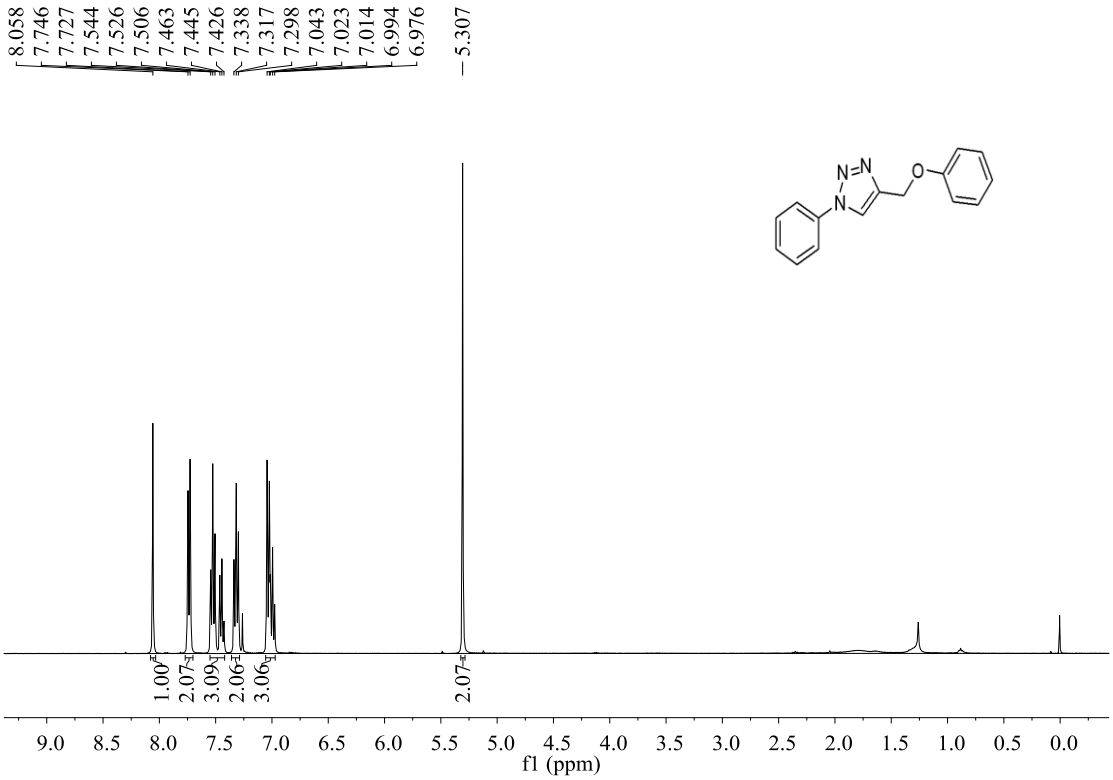


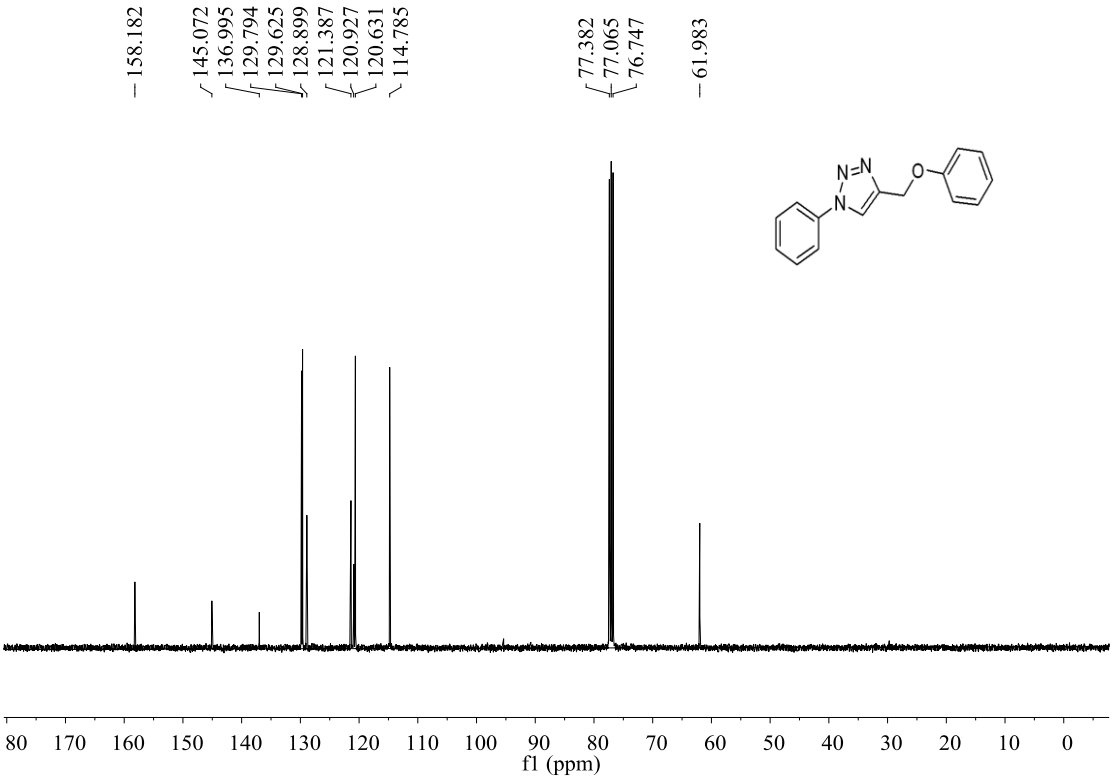


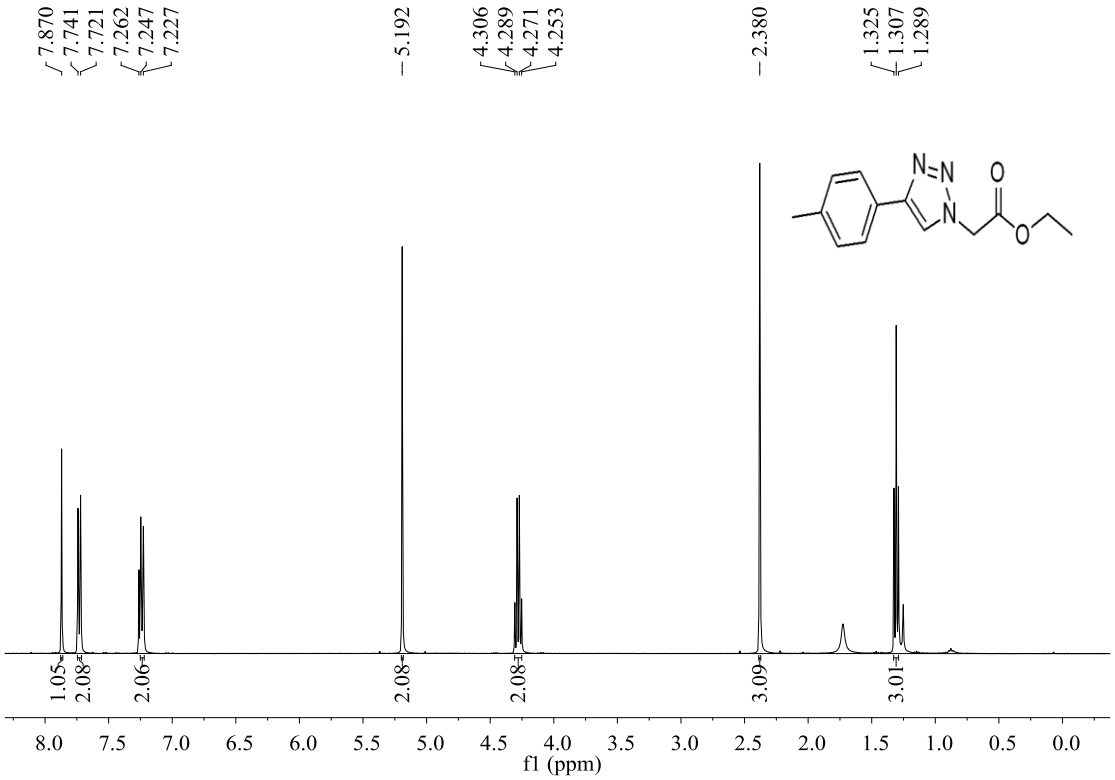


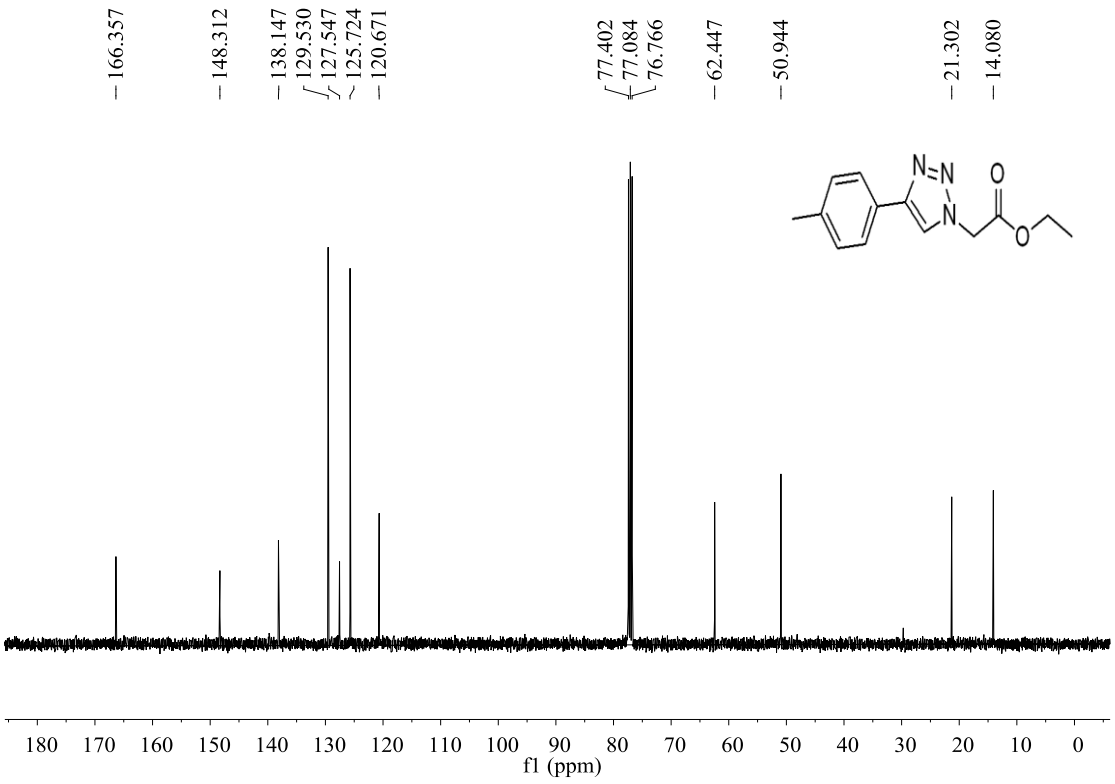


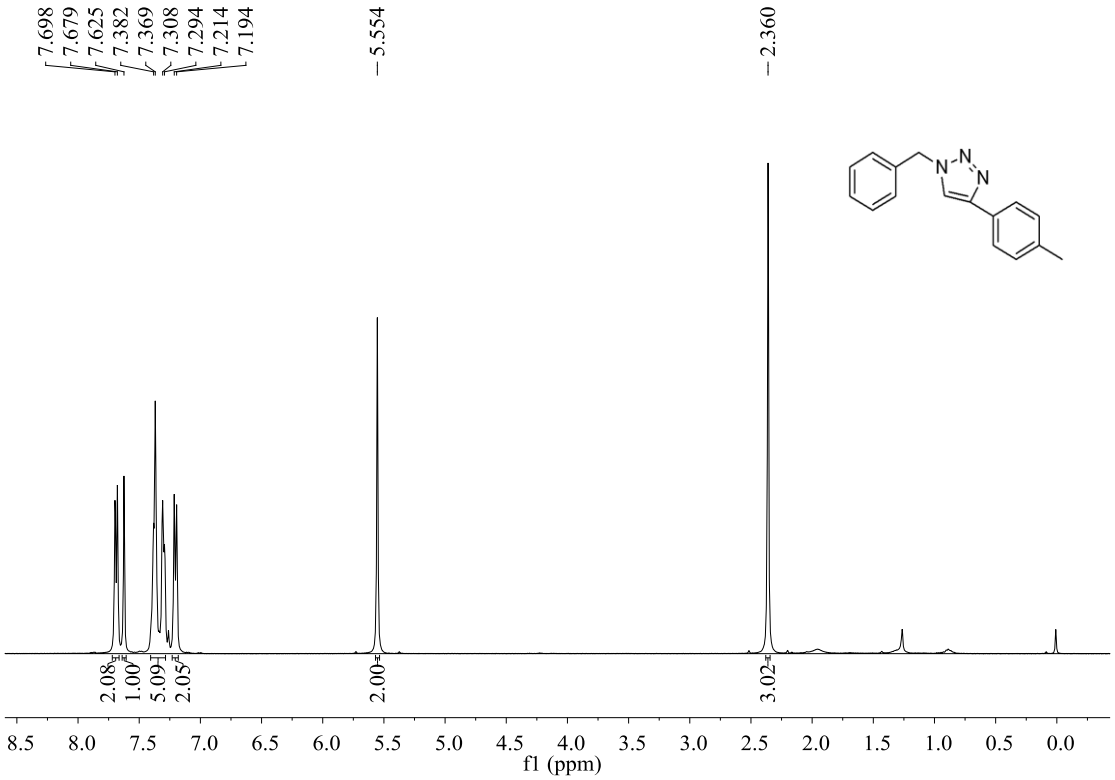


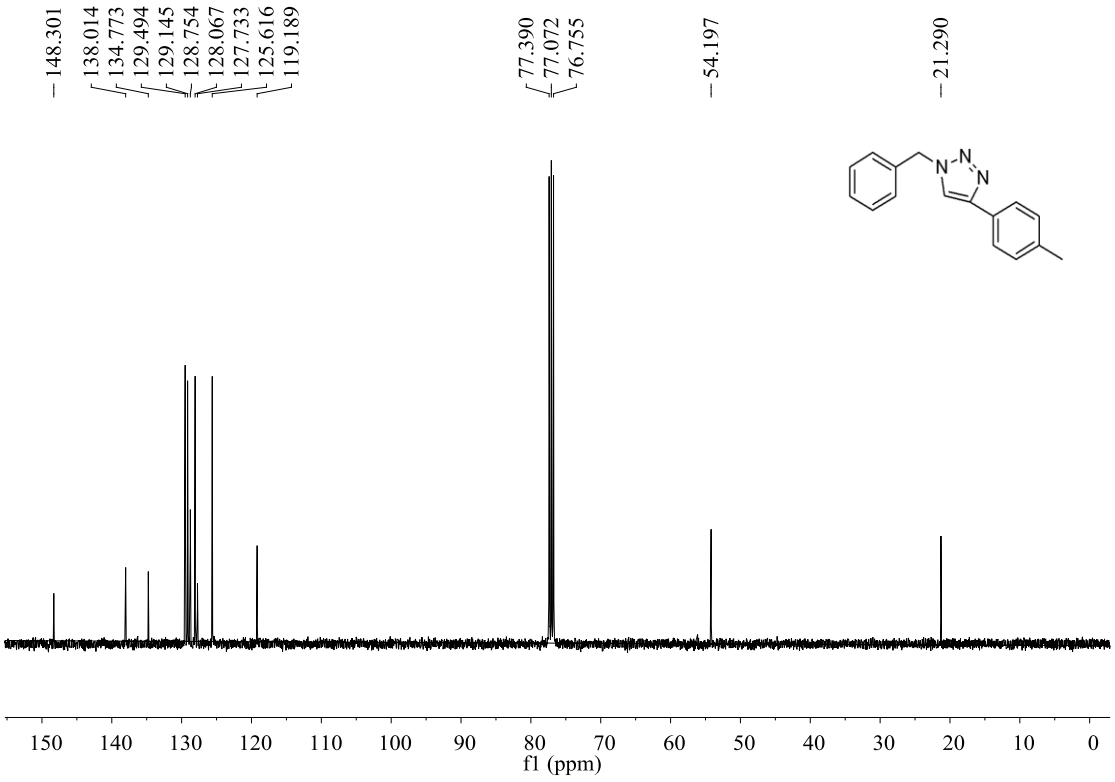


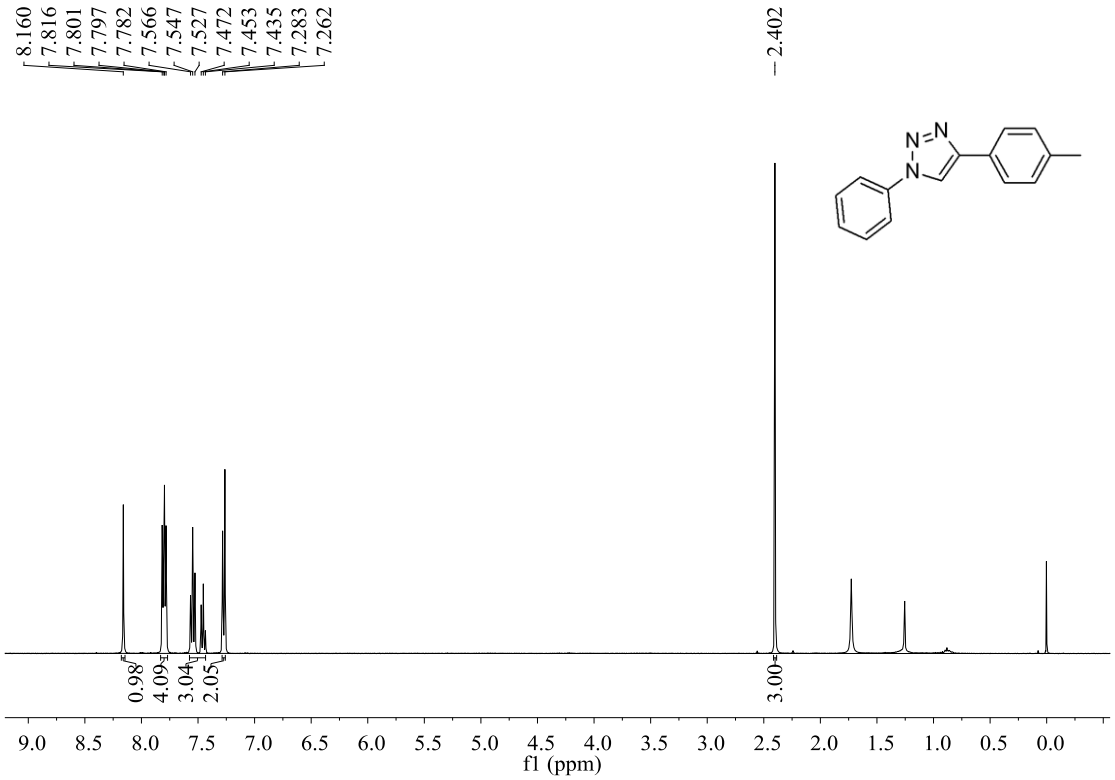


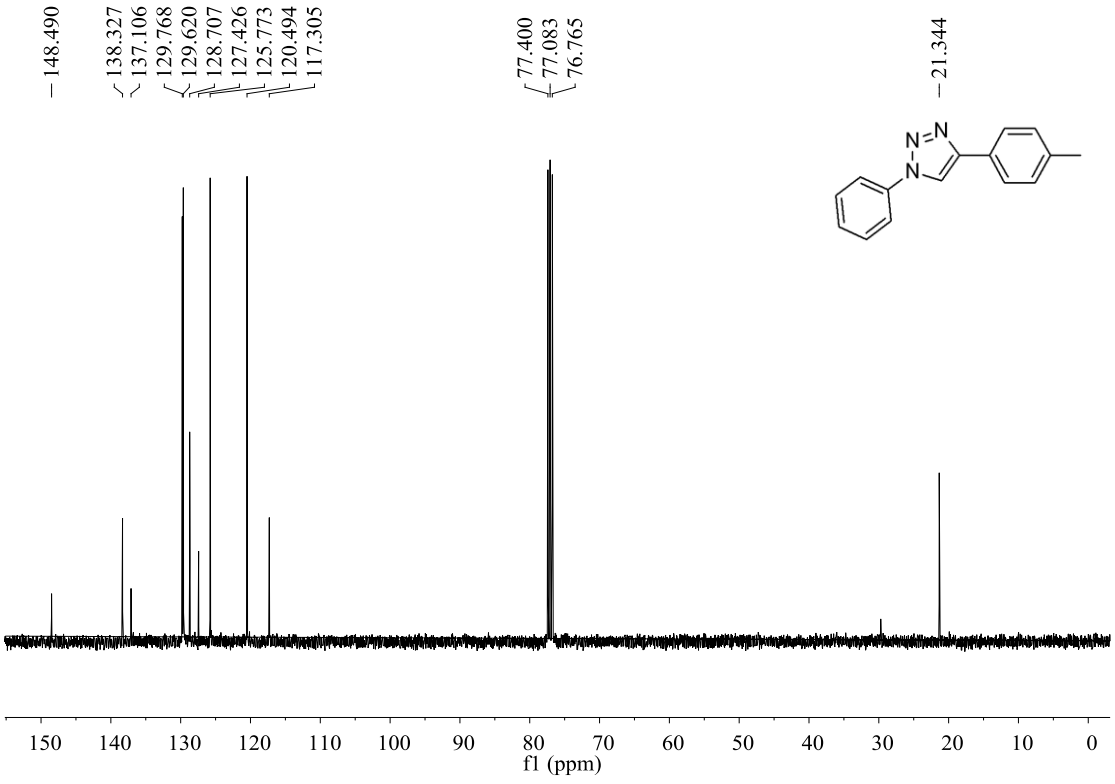


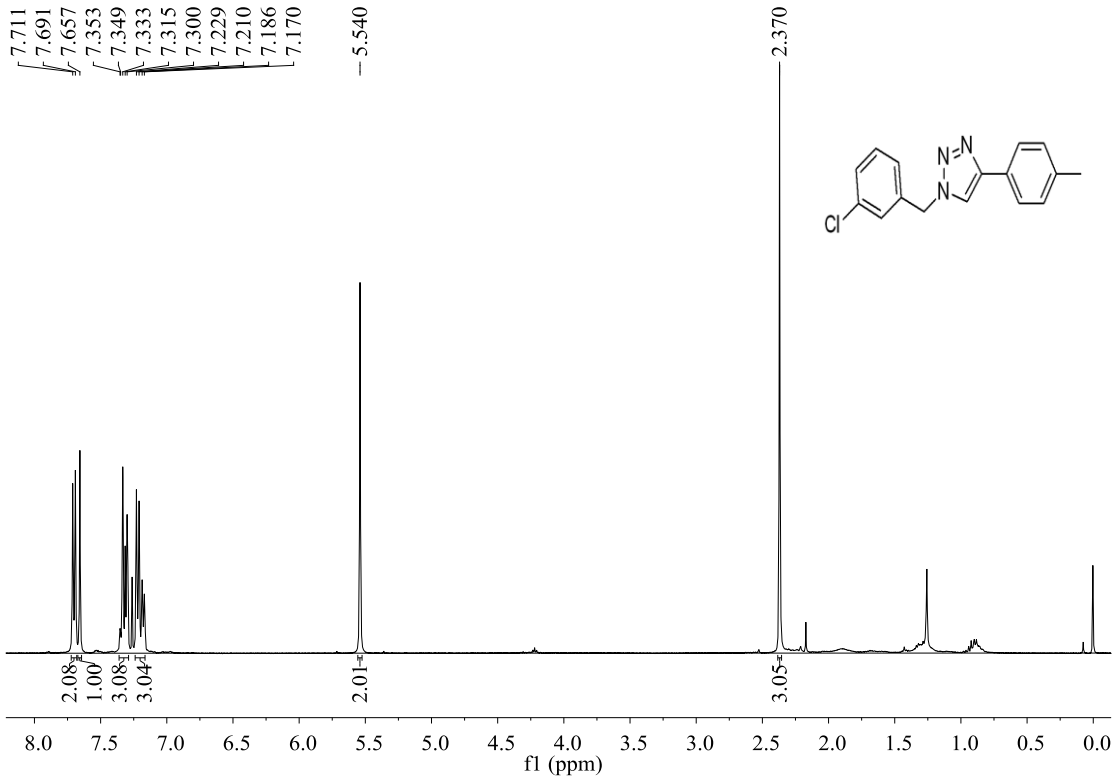


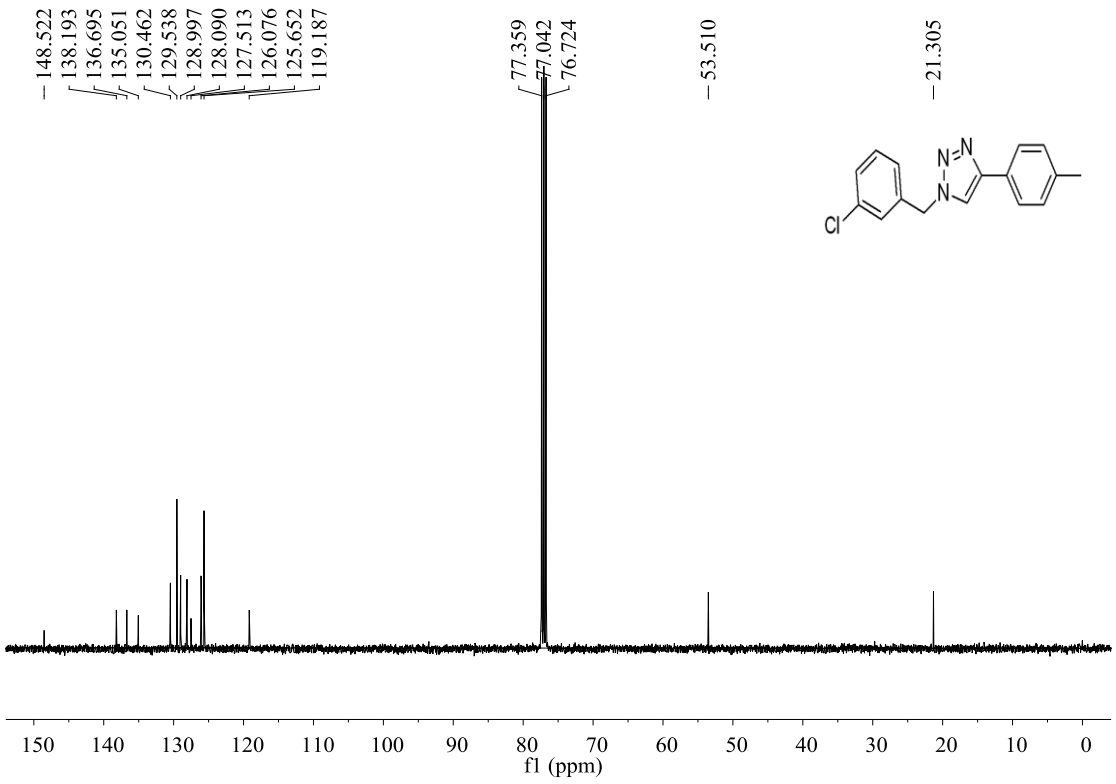


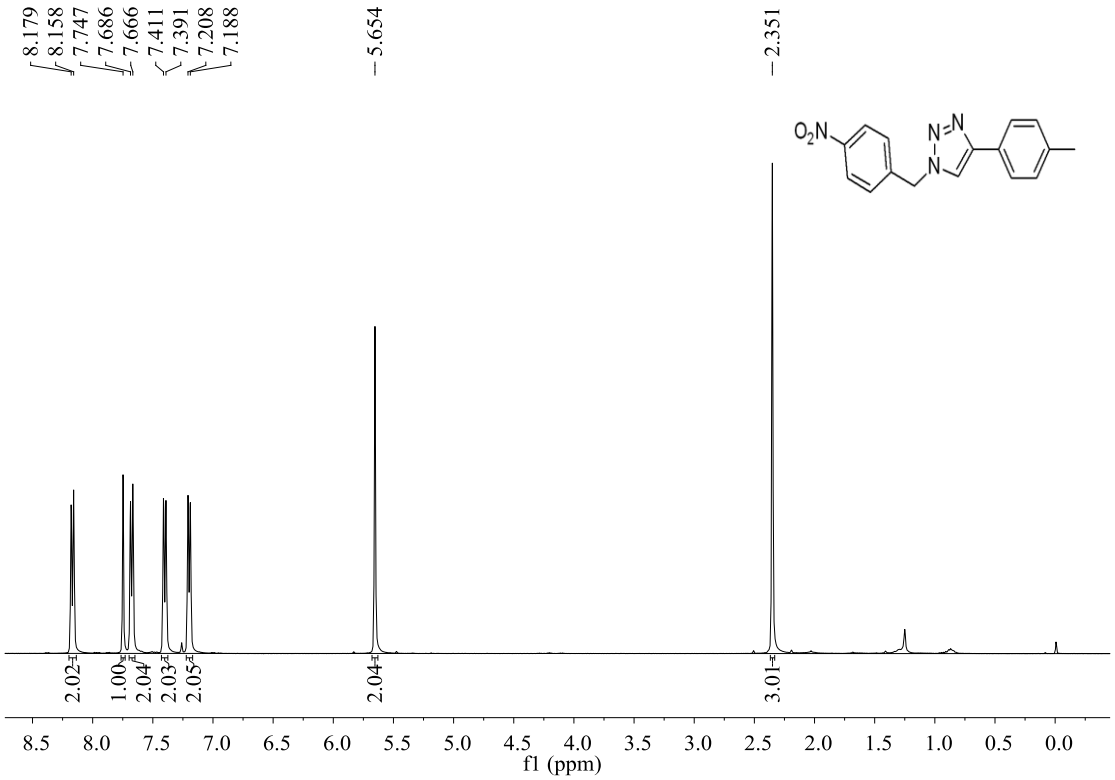








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8.158
7.747
7.686
7.666
7.411
7.391
7.208
7.188
5.654
2.351
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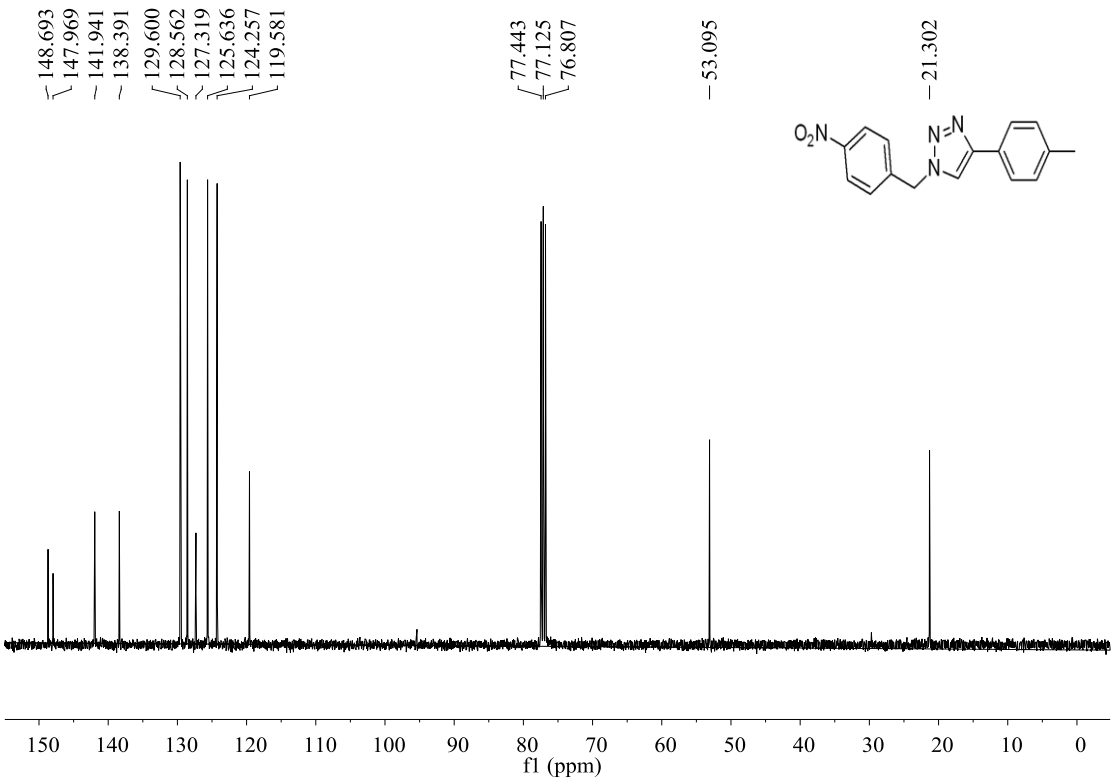
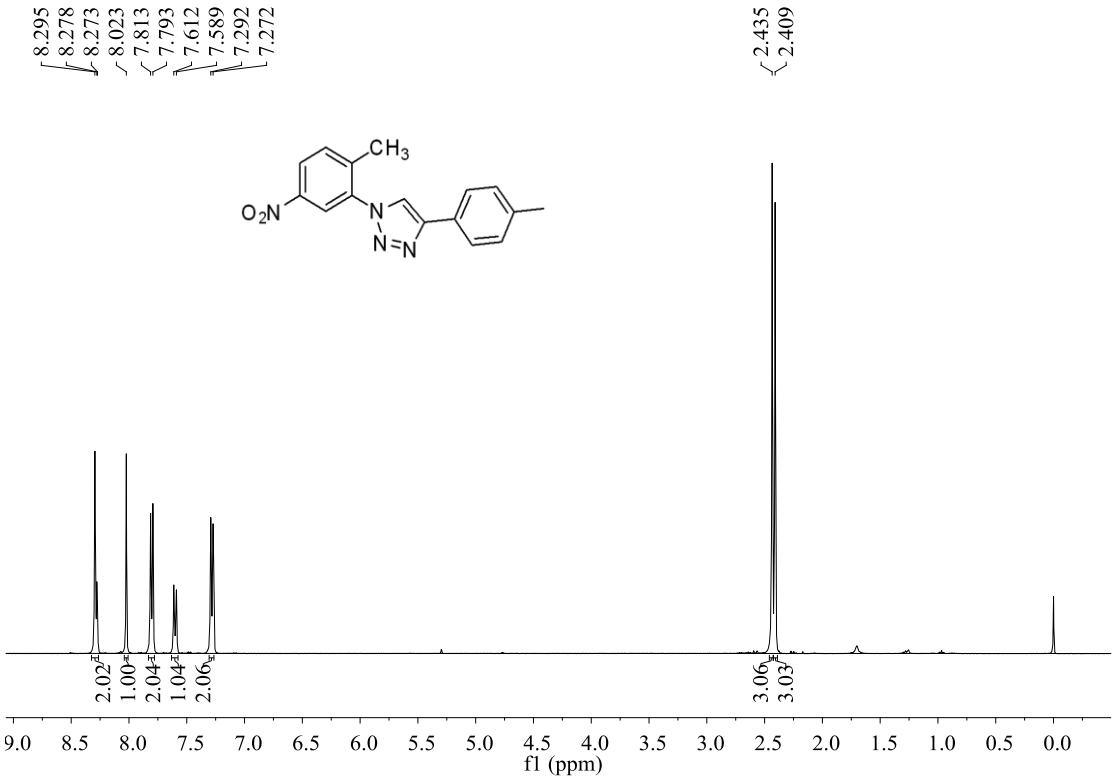
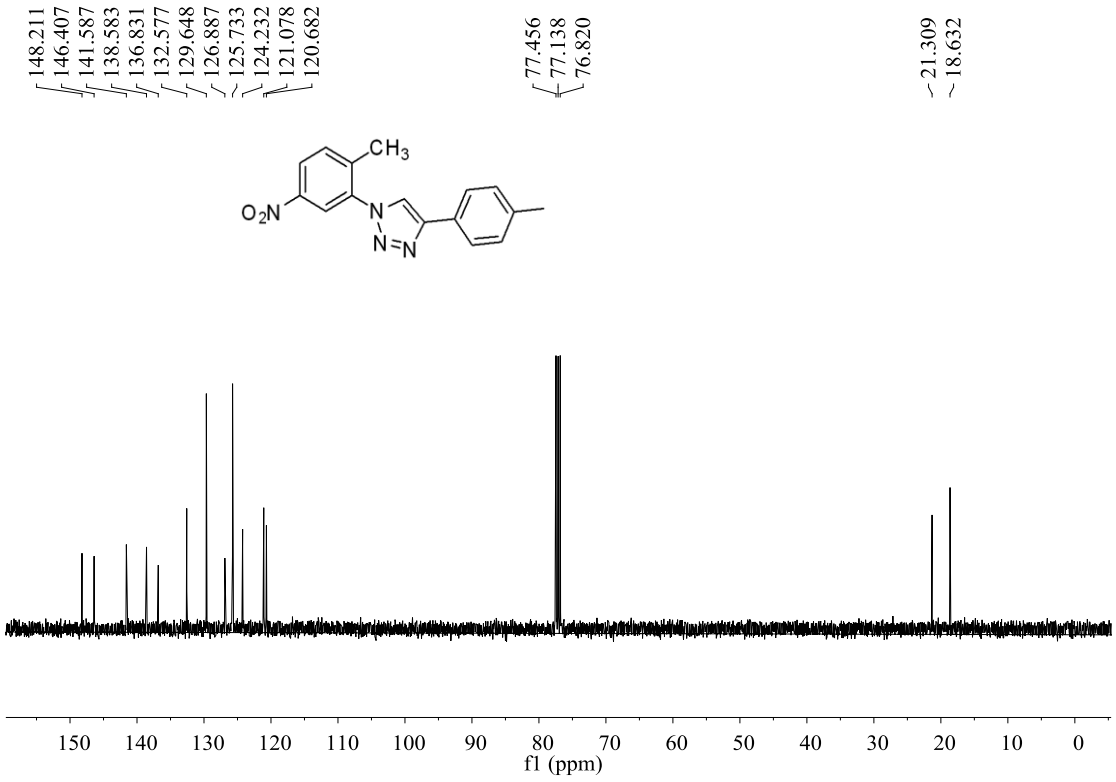
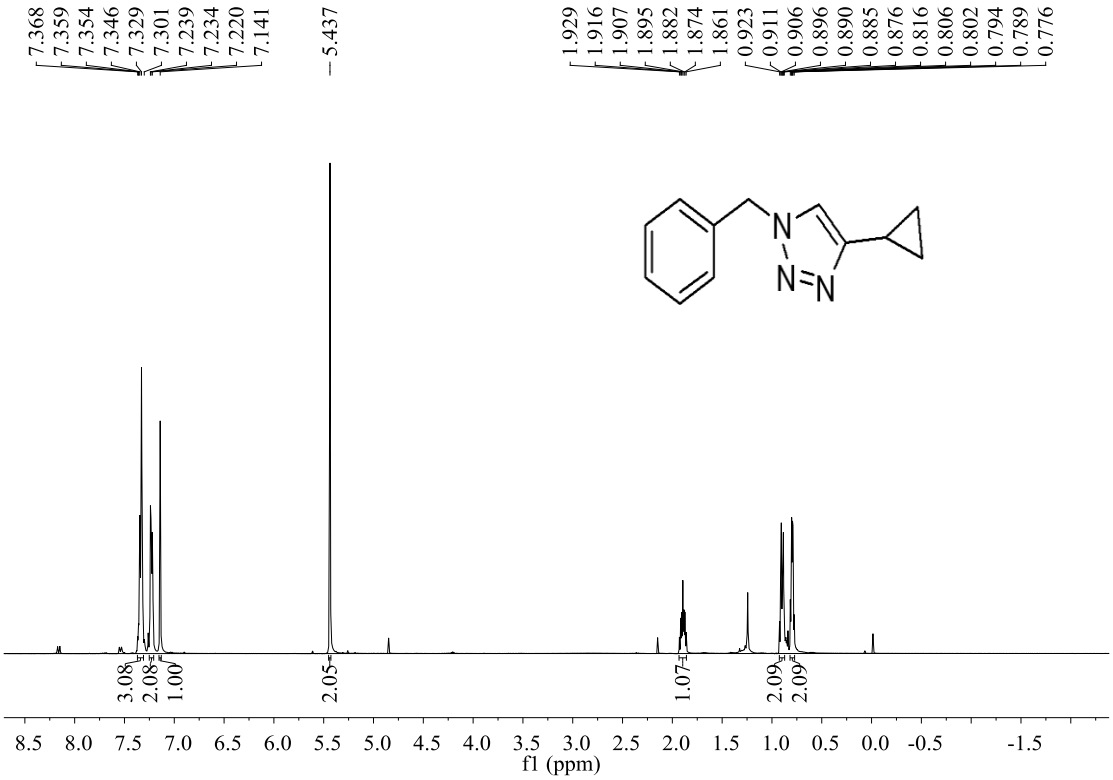
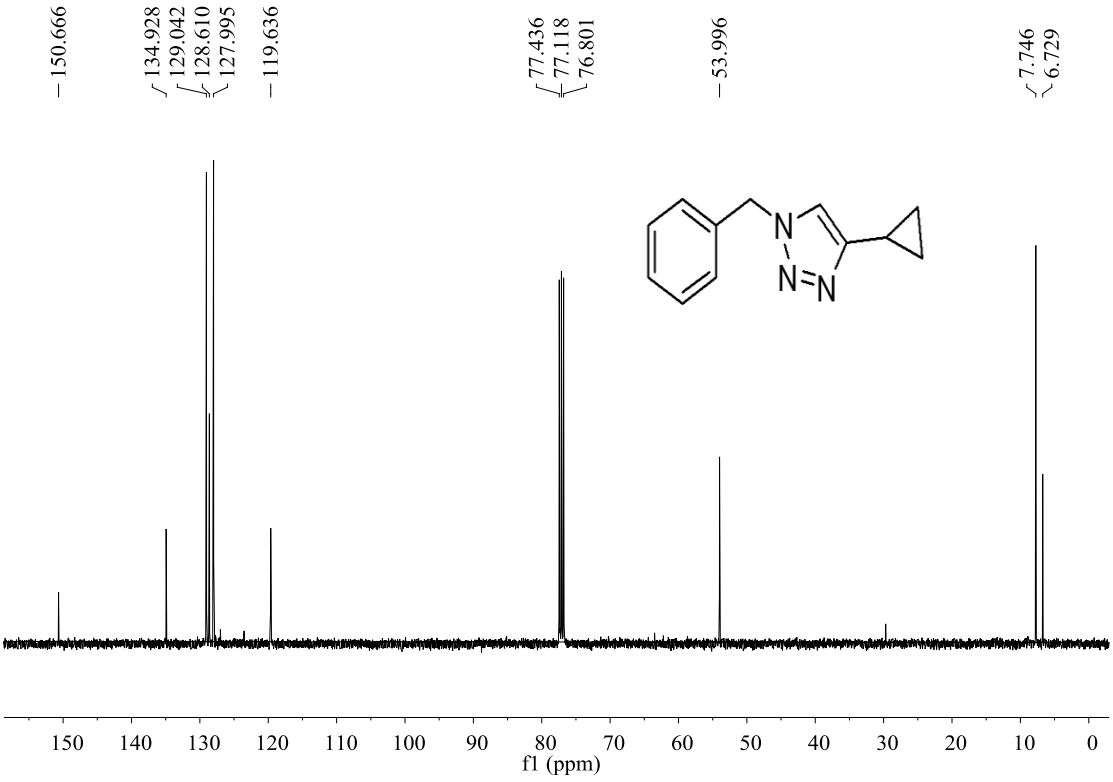
1.00
2.04
2.03
2.05
2.04
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

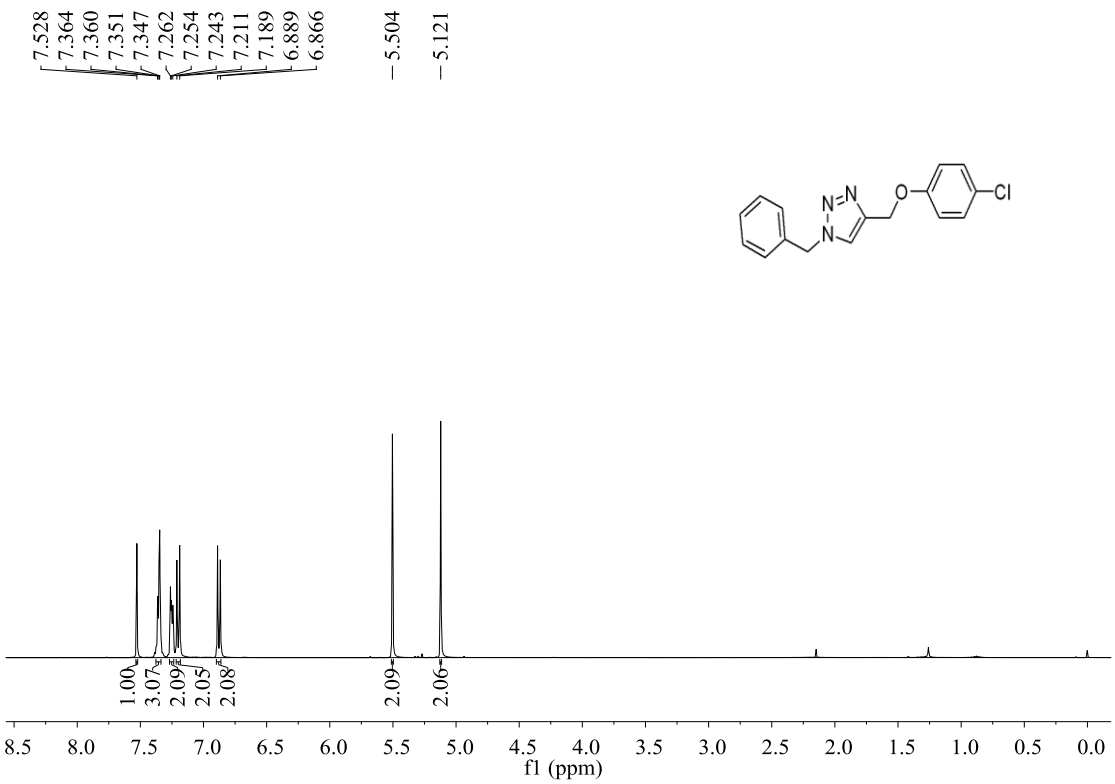

148.693
147.969
141.941
138.391
129.600
128.562
127.319
125.636
124.257
119.581
77.443
77.125
76.807
53.095
21.302
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

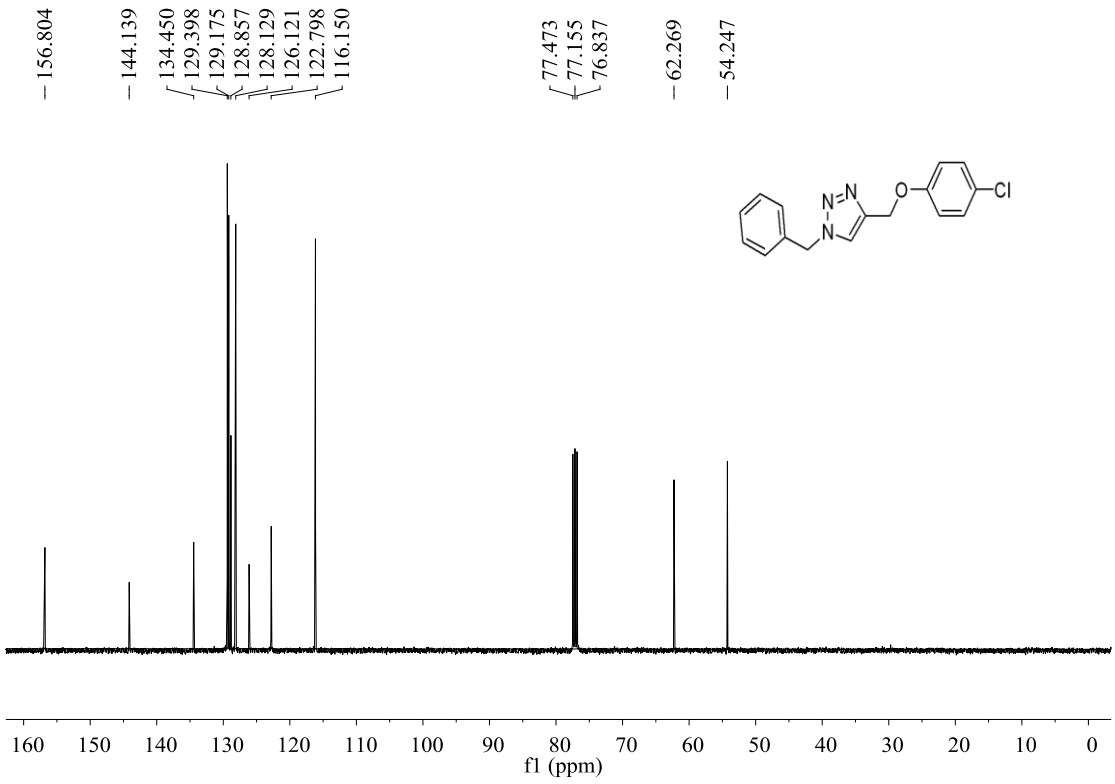

8.295
8.278
8.273
8.023
7.813
7.793
7.612
7.589
7.292
7.272
2.435
2.409
CH3
O2N
N
N=N
2.02
1.00
2.04
1.04
2.06
3.06
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

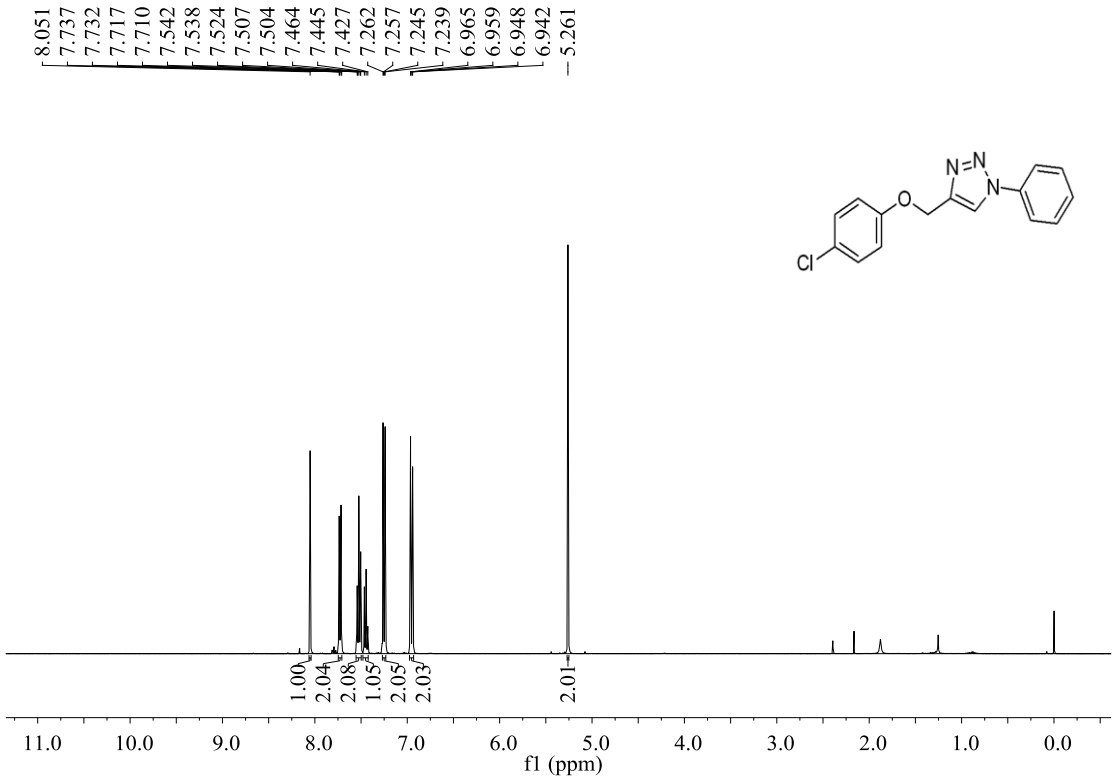

148.211
146.407
141.587
138.583
136.831
132.577
129.648
126.887
125.733
124.232
121.078
120.682
77.456
77.138
76.820
21.309
18.632
CH3
O2N
N
N=N
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

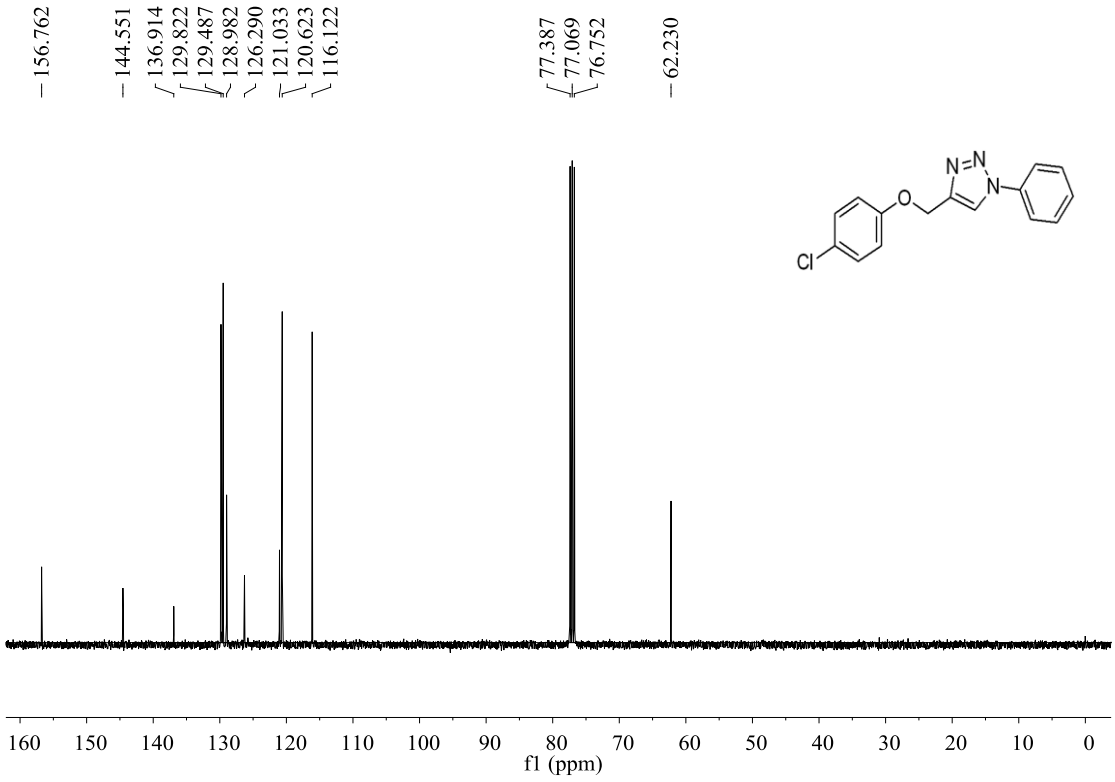


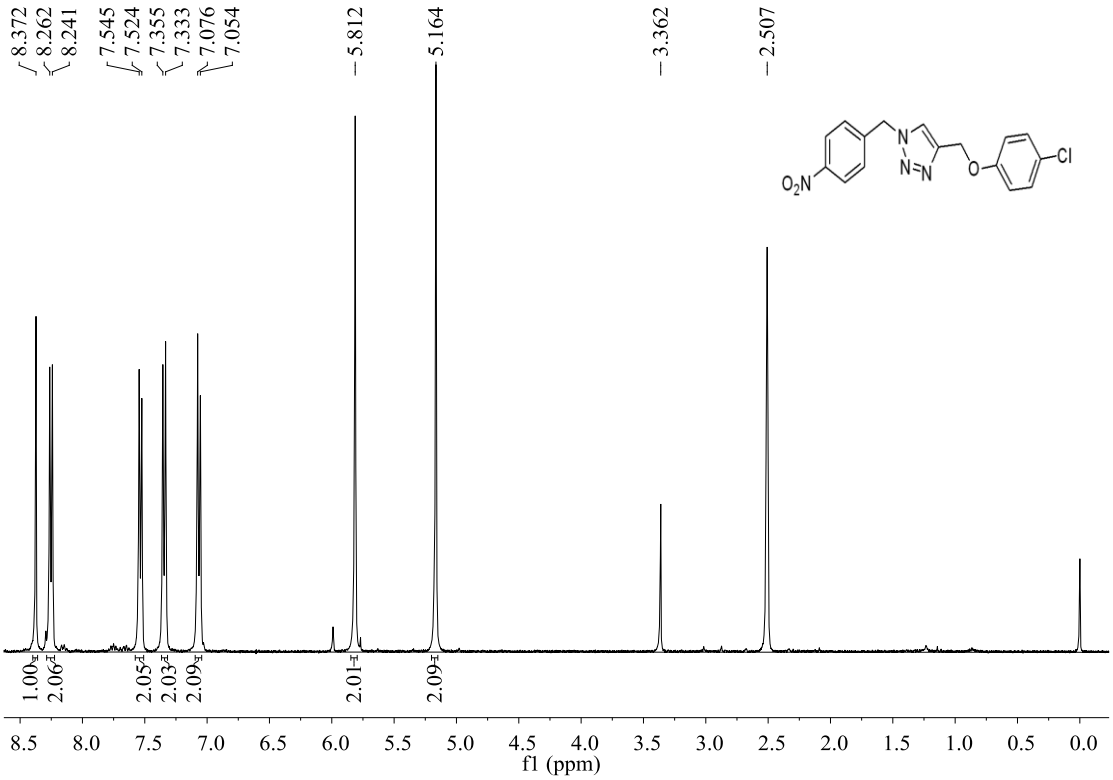








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8.262
8.241
7.545
7.524
7.355
7.333
7.076
7.054
5.812
5.164
3.362
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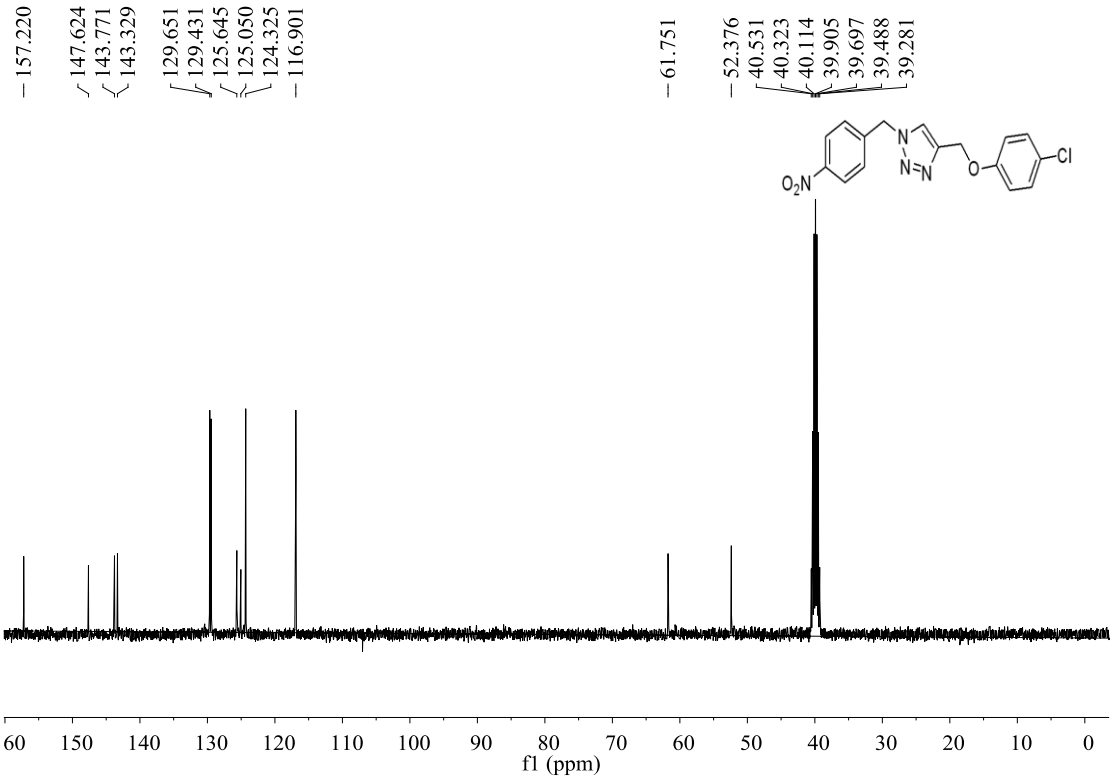
1.00
2.06
2.05
2.03
2.09
2.01
2.09
f1 (ppm)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143.771
143.329
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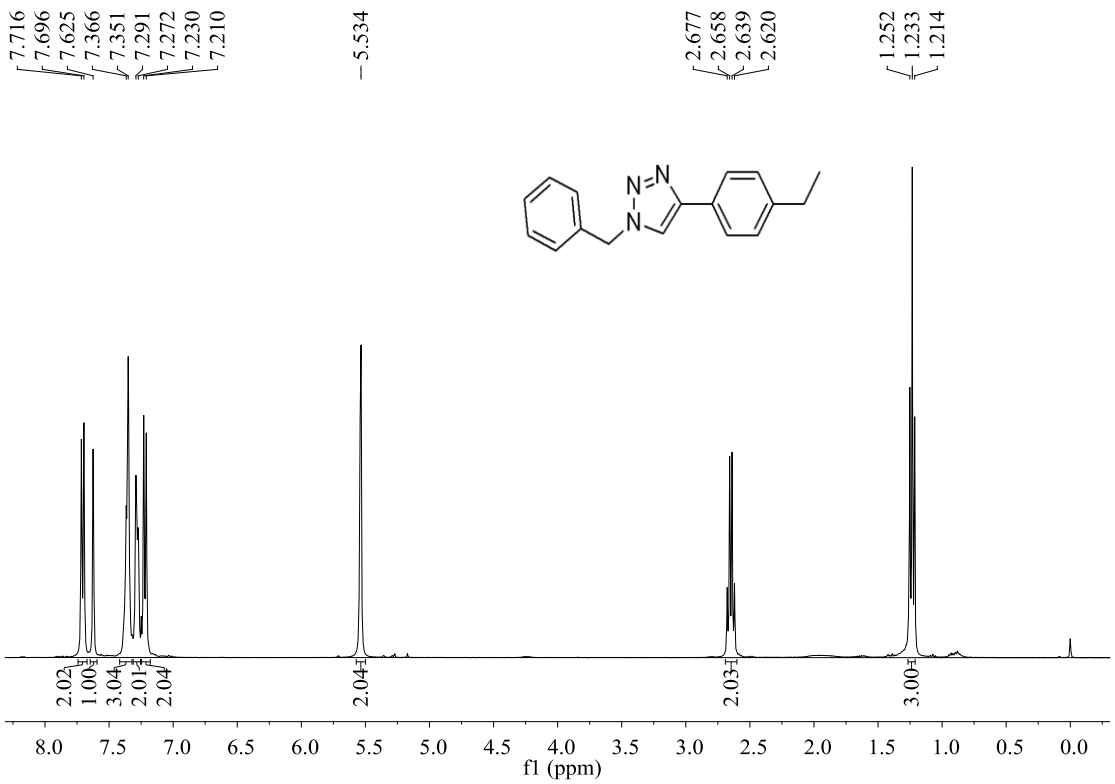
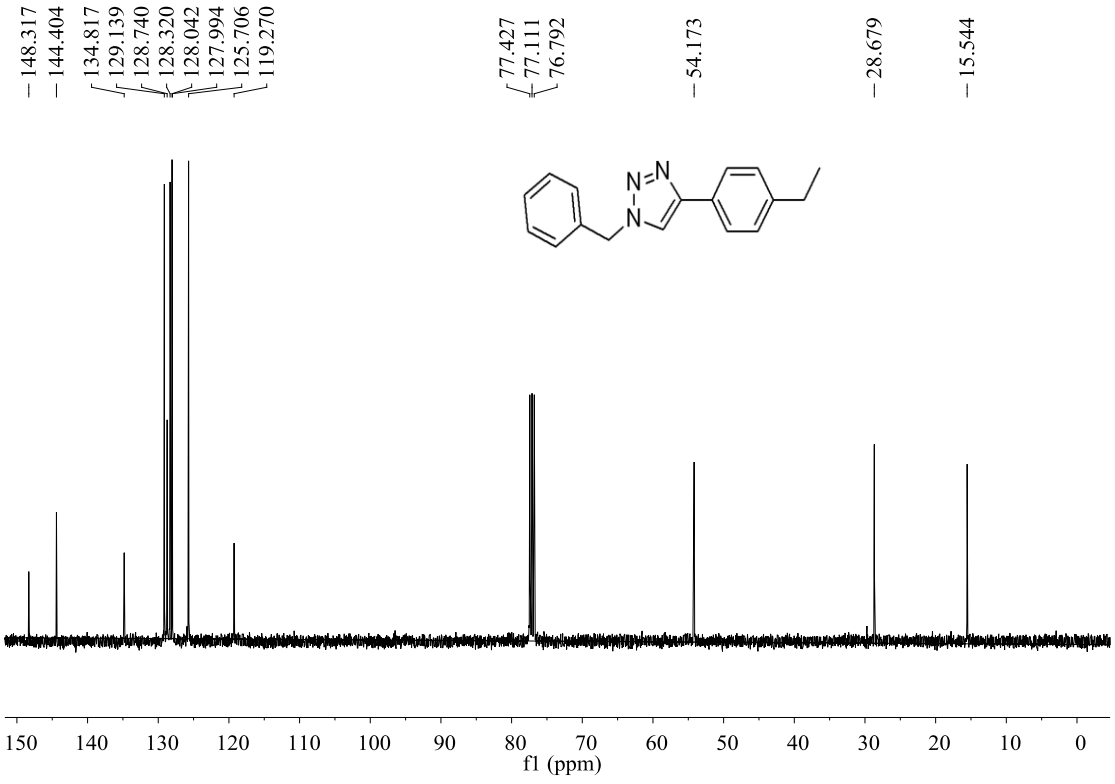
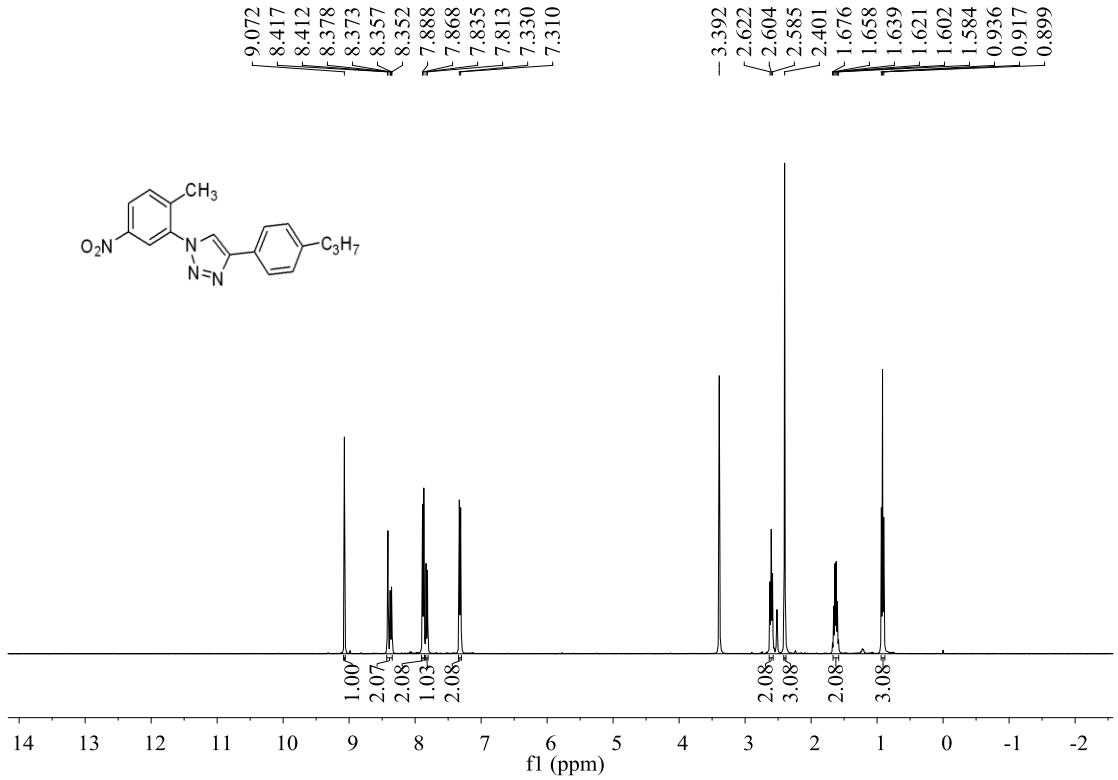
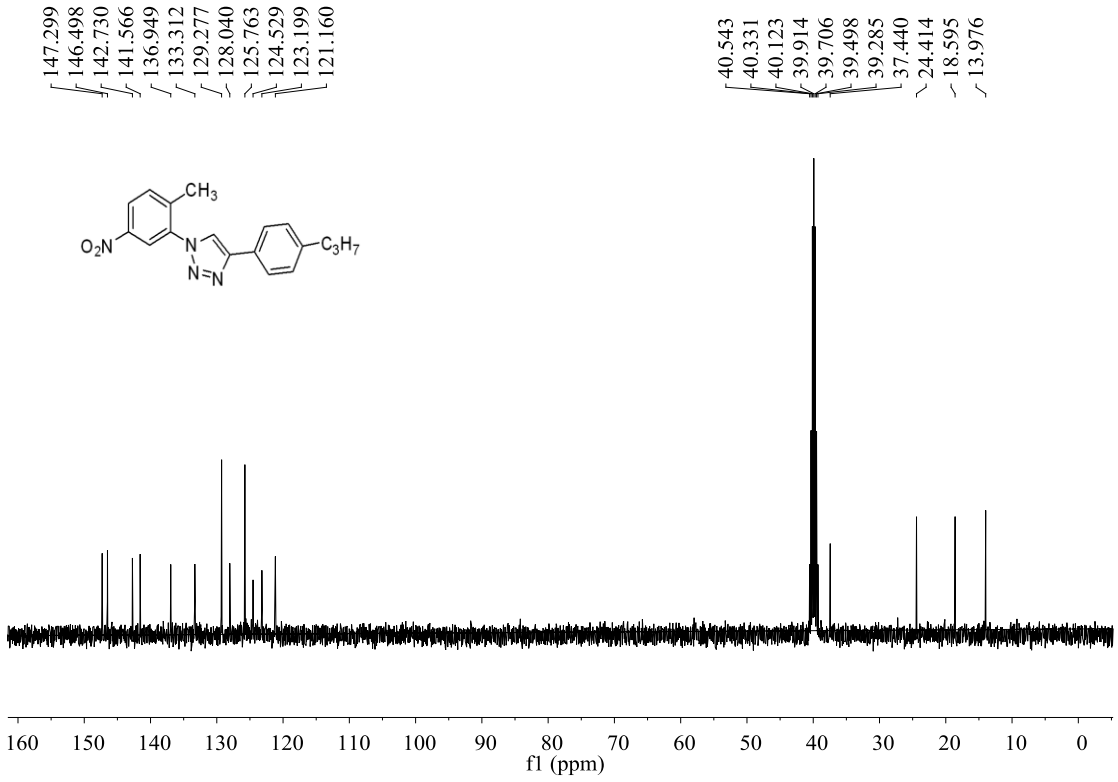
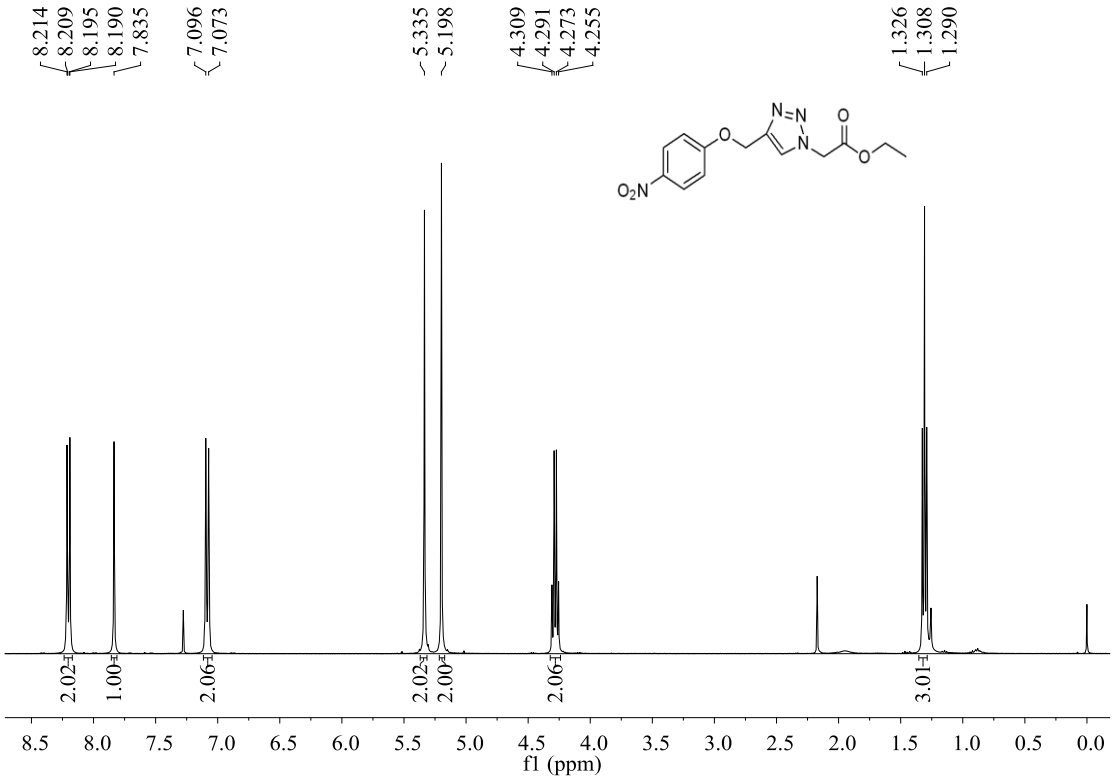
129.431
125.645
125.050
124.325
116.901
61.751
52.376
40.531
40.323
40.114
39.905
39.697
39.488
39.281
f1 (ppm)

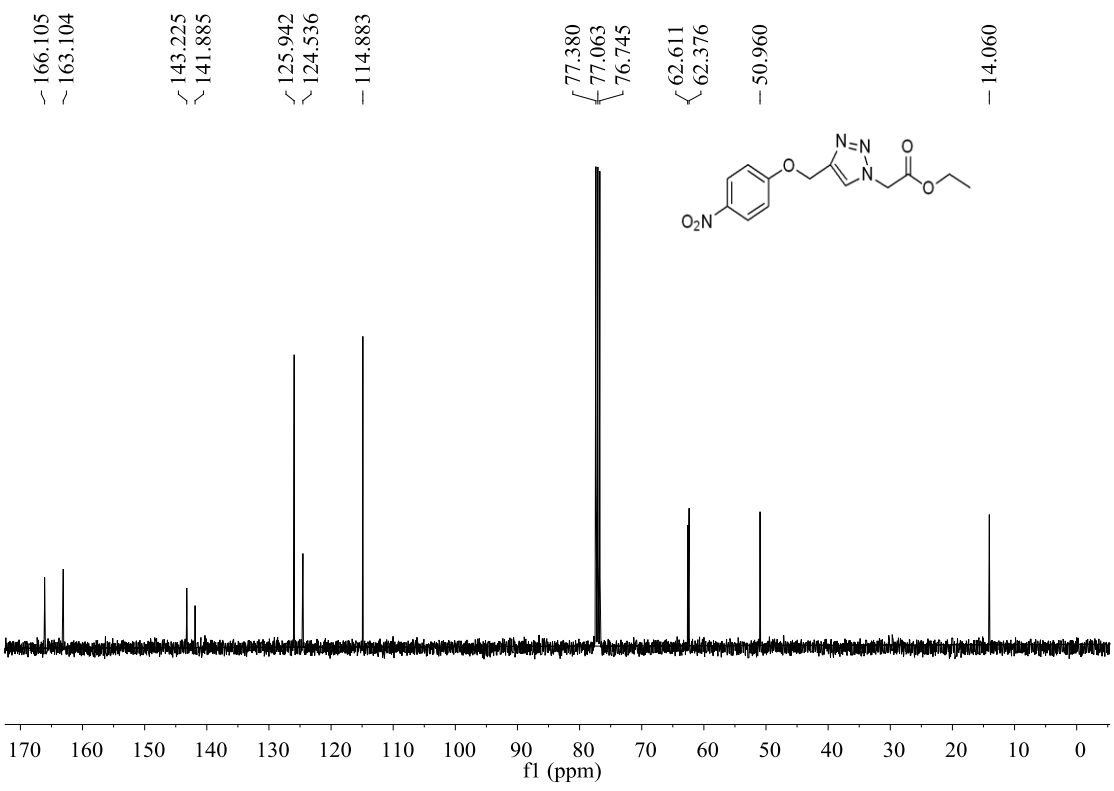









8.214
8.209
8.195
8.190
7.835
7.096
7.073
5.335
5.198
4.309
4.291
4.273
4.255
1.326
1.308
1.290
2.02
1.00
2.06
2.02
2.00
2.06
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.105
163.104
143.225
141.885
125.942
124.536
114.883
77.380
77.063
76.745
62.611
62.376
50.960
14.060
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)