Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Carboxymethylpullulans Promoted Cu_2O-Catalyzed Huisgen-Click Reaction

Weiwei Zhang, Baoqi Ren, Yuqin Jiang*, Zhiguo Hu*

Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, P. R. China.

E-mail: jiangyuqin@htu.cn; zghu@htu.cn.

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I. General Information

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. 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). The pH values of different amount of CMP in water were measured by a model PHS-3C pH meter (Shanghai Precision & Scientific Instrument Co., Ltd).

II. Procedure for the synthesis of CMP

Pullulan (5 g, 30.86 mmol) in 20 mL water was dispersed in 6 mL isopropyl alcohol. NaOH (1.82 g, 45.75 mmol) in 5 mL water was added to the mixture above at 70 °C and stirred for 15 mins. $ClCH_2COONa$ (3.6 g 30 mmol) was added together with 5 mL of water and 3 mL of isopropyl. The reaction mixture was vigorously stirred at 70 °C for 4 h. Then, the same amount of the addition of NaOH and $ClCH_2COONa$ was repeated. The reaction was continued stirring and heating at 70 °C for another 3 h. The reaction mixture was precipitated with methanol and dialyzed against deionized water. The H^+ form of CMP was obtained by dialysis against 0.1 M HCl for 2-3 h. Then, the excess of HCl was removed by dialysis against water for 3 day. The purified polymer was obtained by lyophilization.

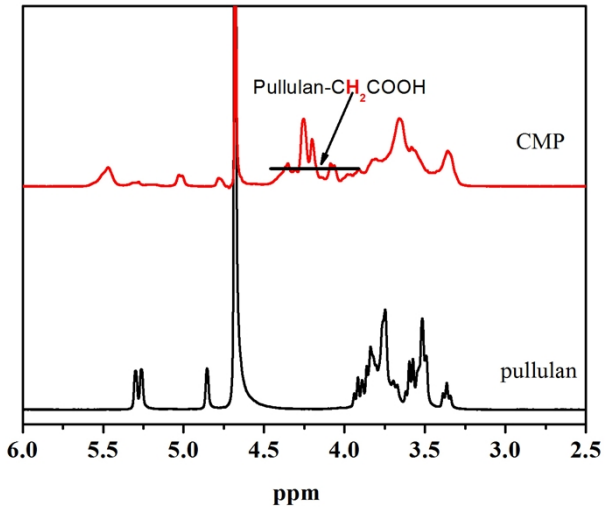


Figure 1. ^{1}H NMR of pullulan and CMP

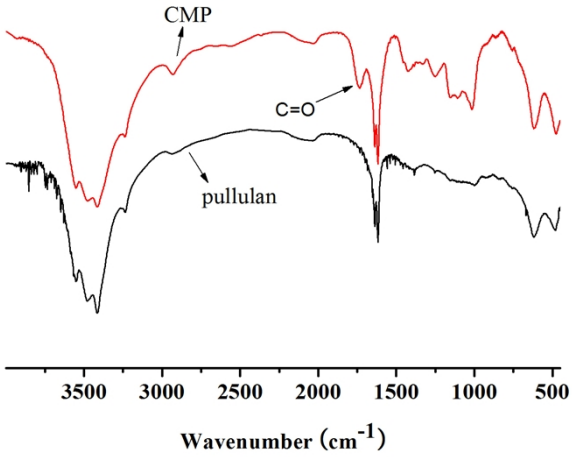


Figure 2. IR of pullulan and CMP

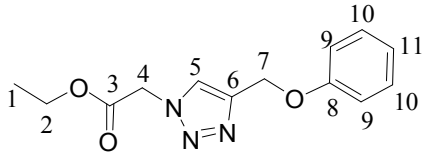
III. General procedure for the synthesis of triazoles and the recyclability of CMP

Alkyne (1mmol), azide (1mmol), CMP (5 mol%) and Cu_2O (0.5 mol%) were dissolved (suspended) in deionized water (2 mL) and the reaction temperature was elevated to 60 °C. After the completion of the reaction, the resulting solution was extracted by 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).

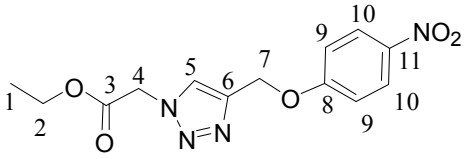
Recyclability of the CMP for the model reaction

Propargyl phenyl ether (10.0 mmol), azide benzyl (10.0 mmol), CMP (5 mol%) and Cu_2O (0.5 mol%) were dissolved (suspended) in deionized water (20 mL) and the reaction temperature was elevated to 60 °C. After the completion of the reaction, the resulting solution was extracted by 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). The water phase was added propargyl phenyl ether (10.0 mmol), azide benzyl (10.0 mmol) and Cu_2O (0.5 mol%) again and the reaction repeated the above procedure for another 5 cycles.

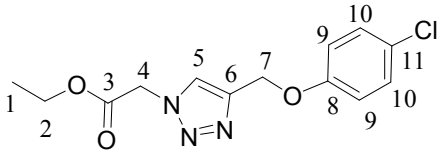
IV. ^{1}H and ^{13}C NMR Data of the Products

3a: 

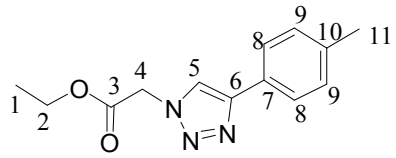
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.75 (s, 1H), 7.30-6.94 (m, 5H), 5.22 (s, 2H), 5.14(s, 2H), 4.23 (q, J = 6.8 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.3 (C-3), 158.2 (C-8), 144.6 (C-6), 129.6 (C-10), 124.3 (C-5), 121.3 (C-11), 114.8 (C-9), 62.4 (C-2), 61.8 (C-7), 50.9 (C-4), 14.0 (C-1).

3b: 

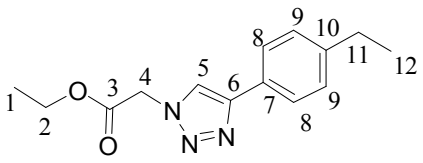
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.18 (d, J = 8.8 Hz, 2H), 7.82 (s, 1H), 7.07 (d, J = 9.2 Hz, 2H), 5.32 (s, 2H), 5.18 (s, 2H), 4.27 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 3.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.1 (C-3), 163.1 (C-8), 143.2 (C-6), 141.9 (C-11), 125.9 (C-10), 124.5 (C-5), 114.9 (C-9), 62.6 (C-2), 62.4 (C-7), 51.0 (C-4), 14.1 (C-1).

3c: 

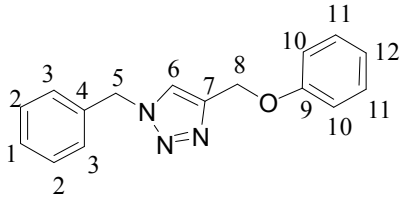
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.74 (s, 1H), 7.20 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 5.17 (s, 2H), 5.14 (s, 2H), 4.24 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.2 (C-3), 156.8 (C-8), 144.2 (C-6), 129.4 (C-10), 126.2 (C-11), 124.2 (C-5), 116.2 (C-9), 62.5 (C-2), 62.2 (C-7), 50.9 (C-)4, 14.0 (C-1).

3d: 

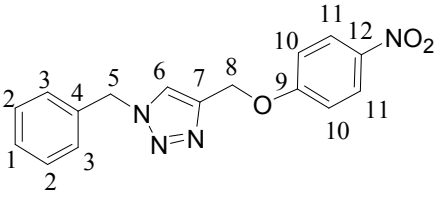
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.87 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 5.19 (s, 2H), 4.28 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.3 (C-3), 148.3 (C-6), 138.2 (C-10), 129.5 (C-9), 127.5 (C-7), 125.7 (C-8), 120.6 (C-5), 62.5 (C-2), 51.0 (C-4), 21.3 (C-11), 14.1 (C-1).

3e: 

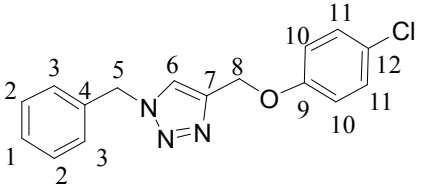
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.88 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 5.18 (s, 2H), 4.26 (q, J = 7.2 Hz, 2H), 2.67 (q, J = 7.2 Hz, 2H), 1.31-1.23 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.4 (C-3), 148.3 (C-6), 144.5 (C-10), 128.3 (C-9), 127.8 (C-7), 125.8 (C-8), 120.7 (C-5), 62.4 (C-2), 50.9 (C-4), 28.7 (C-11), 15.5 (C-1), 14.1 (C-12).

3f : 

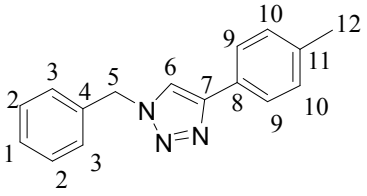
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.53 (s, 1H), 7.38-7.26 (m, 7H), 6.97 (d, J = 8.4 Hz, 3H), 5.53 (s, 2H), 5.19 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.2 (C-9), 144.7 (C-7), 134.5 (C-4), 129.5 (C-11), 129.2 (C-3), 128.8 (C-1), 128.1 (C-2), 122.6 (C-6), 121.3 (C-12), 114.8 (C-10), 62.1 (C-8), 54.3 (C-5).

3g: 

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.13 (d, J = 9.2 Hz, 2H), 7.60 (s, 1H), 7.36-7.26 (m, 5H), 7.02 (d, J = 9.2 Hz, 2H), 5.53 (s, 2H), 5.24 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 163.2 (C-9), 143.1 (C-7), 141.8 (C-12), 134.3 (C-4), 129.2 (C-3), 128.9 (C-1), 128.2 (C-2), 125.9 (C-11), 123.2 (C-6), 114.9 (C-10), 62.4 (C-8), 54.3 (C-5).

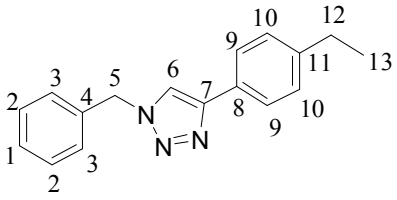
3h: 

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.53 (s, 1H), 7.39-7.24 (m, 5H), 7.20 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 9.2 Hz, 2H), 5.50 (s, 2H), 5.12 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 156.8 (C-9), 144.1 (C-7), 134.5 (C-4), 129.4 (C-11), 129.2 (C-3), 128.9 (C-1), 128.1 (C-2), 126.1 (C-12), 122.8 (C-6), 116.2 (C-10), 62.3 (C-8), 54.2 (C-5).



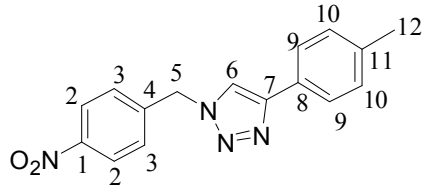
3i:

^{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 (C-8), 138.0 (C-4), 134.8 (C-11), 129.5 (C-3), 129.2 (C-1), 128.8 (C-10), 128.1 (C-2), 127.7 (C-8), 125.6 (C-9), 119.2 (C-6), 54.2 (C-5), 21.3 (C-12).



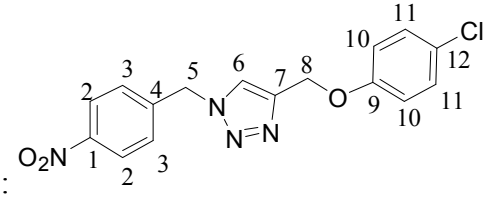
3j:

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.72 (d, J = 8.0 Hz, 2H), 7.64 (s, 1H), 7.38-7.29 (m, 5H), 7.23 (d, J = 8.0 Hz, 2H), 5.55 (s, 2H), 2.66 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.3 (C-7), 144.4 (C-11), 134.8 (C-4), 129.1 (C-3), 128.7 (C-1), 128.3 (C-10), 128.0 (C-2, 8), 125.7 (C-9), 119.3 (C-6), 54.2 (C-5), 28.7 (C-12), 15.5 (C-13).



3k:

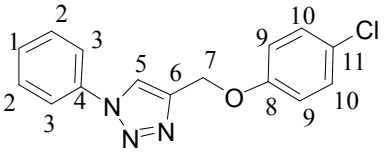
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.17 (d, J = 8.4 Hz, 2H), 7.75 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 5.65 (s, 2H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.7 (C-1), 148.0 (C-7), 141.9 (C-4), 138.4 (C-11), 129.6 (C-3), 128.6 (C-10), 127.3 (C-8), 125.6 (C-9), 124.3 (C-2), 119.6 (C-6), 53.1 (C-5), 21.3 (C-12).



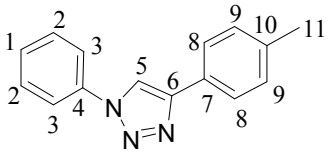
3l :

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.20 (d, J = 8.4 Hz, 2H), 7.62 (s, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 5.65 (s, 2H), 5.17 (s, 2H).

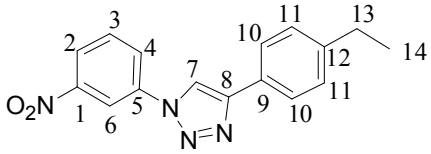
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 156.7 (C-9), 148.1 (C-1), 144.8 (C-7), 141.5 (C-4), 129.5 (C-11), 128.6 (C-3), 126.3 (C-12), 124.3 (C-2), 123.0 (C-6), 116.1 (C-10), 62.2 (C-8), 53.2 (C-5).

3m: 

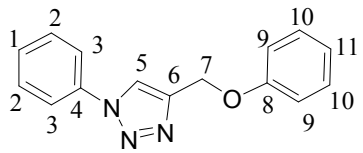
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05 (s, 1H), 7.72 (dd, J = 8.0 Hz, 2.0 Hz, 2H), 7.54-7.44 (m, 3H), 7.25 (dd, J = 6.8 Hz, 2.4 Hz, 2H), 6.95 (dd, J = 6.8 Hz, 2.4 Hz, 2H), 5.26 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ:156.8 (C-8), 144.6 (C-6), 136.9 (C-4), 129.8 (C-10), 129.5 (C-1), 129.0 (C-2), 126.3 (C-11), 121.0 (C-5), 120.6 (C-3), 116.1 (C-9), 62.2 (C-7).

3n: 

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.16 (s, 1H), 7.80 (dd, J = 7.6 Hz, 6.0 Hz, 4H), 7.57-7.26 (m, 5H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.5 (C-6), 138.3 (C-4), 137.1 (C-10), 129.8 (C-1), 129.6 (C-2), 128.7 (C-9), 127.4 (C-7), 125.8 (C-8), 120.5 (C-5), 117.3 (C-3), 21.3 (C-11).

3o: 

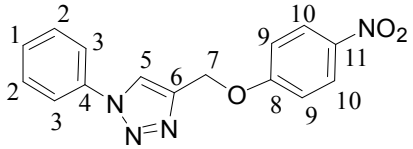
^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.44 (s, 1H), 8.73 (s, 1H), 8.40 (d, J = 7.6 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.88 (t, J = 8.0 Hz, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 2.63 (q, J = 7.2 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 149.0 (C-8), 148.2 (C-1), 144.6 (C-12), 137.7 (C-5), 132.0 (C-3), 128.8 (C-11), 127.8 (C-9), 126.2 (C-4), 125.8 (C-7), 123.4 (C-10), 119.9 (C-2), 114.8 (C-6), 28.4 (C-13), 15.9 (C-14).

3p: 

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.06 (s, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.54-7.45 (m,

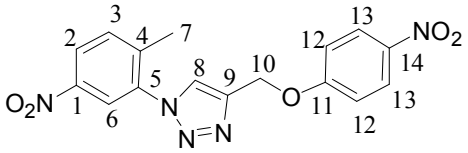
3H), 7.32 (t, J = 8.0 Hz, 2H), 7.04-6.98 (m, 3H), 5.31 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.2 (C-8), 145.1 (C-6), 137.0 (C-4), 129.8 (C-10), 129.6 (C-1), 128.9 (C-2), 121.4 (C-5), 120.9 (C-11), 120.6 (C-3), 114.8 (C-9), 62.0 (C-7).

3q:



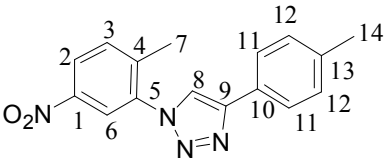
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.21 (tt, J = 9.2 Hz, 2.0 Hz, 2H), 8.13 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.54 (t, J = 8.0 Hz, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.12 (dd, J = 7.2 Hz, 2.0 Hz, 2H), 5.39 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 163.1 (C-8), 143.5 (C-6), 141.9 (C-11), 136.8 (C-4), 129.9 (C-1), 129.1 (C-2), 126.0 (C-10), 121.4 (C-5), 120.6 (C-3), 114.9 (C-9), 62.4 (C-7).

3r:



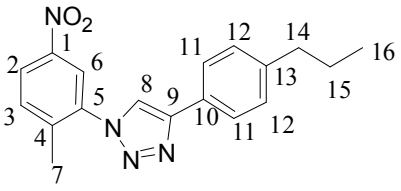
^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.85 (s, 1H), 8.37 (d, J = 6.8 Hz, 2H), 8.26 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 9.2 Hz, 1H), 7.33 (d, J = 9.2 Hz, 2H), 5.46 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 163.6 (C-11), 146.5 (C-1), 142.7 (C-4), 141.8 (C-9), 141.5 (C-14), 136.8 (C-5), 133.3 (C-3), 127.3 (C-8), 126.3 (C-2), 124.8 (C-13), 121.5 (C-6), 115.8 (C-12), 62.2 (C-10), 18.4 (C-7).

3s:



^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.30-8.27 (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 (C-9), 146.4 (C-1), 141.6 (C-4), 138.6 (C-5), 136.8 (C-13), 132.6 (C-3), 129.6 (C-12), 126.9 (C-10), 125.7 (C-8), 124.2 (C-11), 121.1 (C-2), 120.7 (C-6), 21.3 (C-14), 18.6 (C-7).

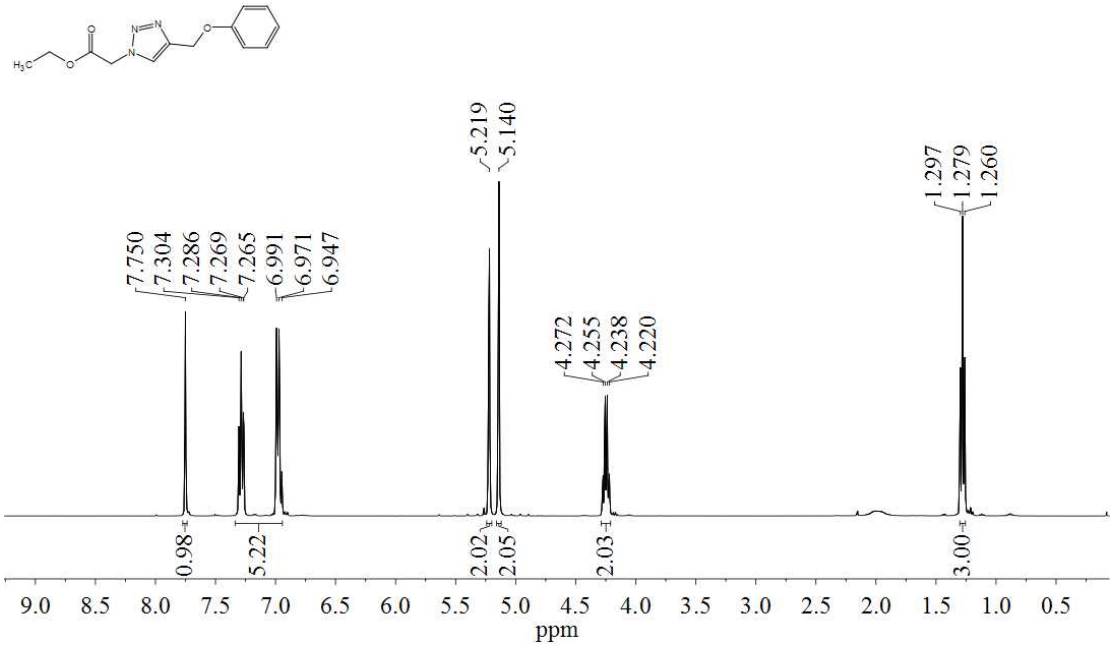
3t:

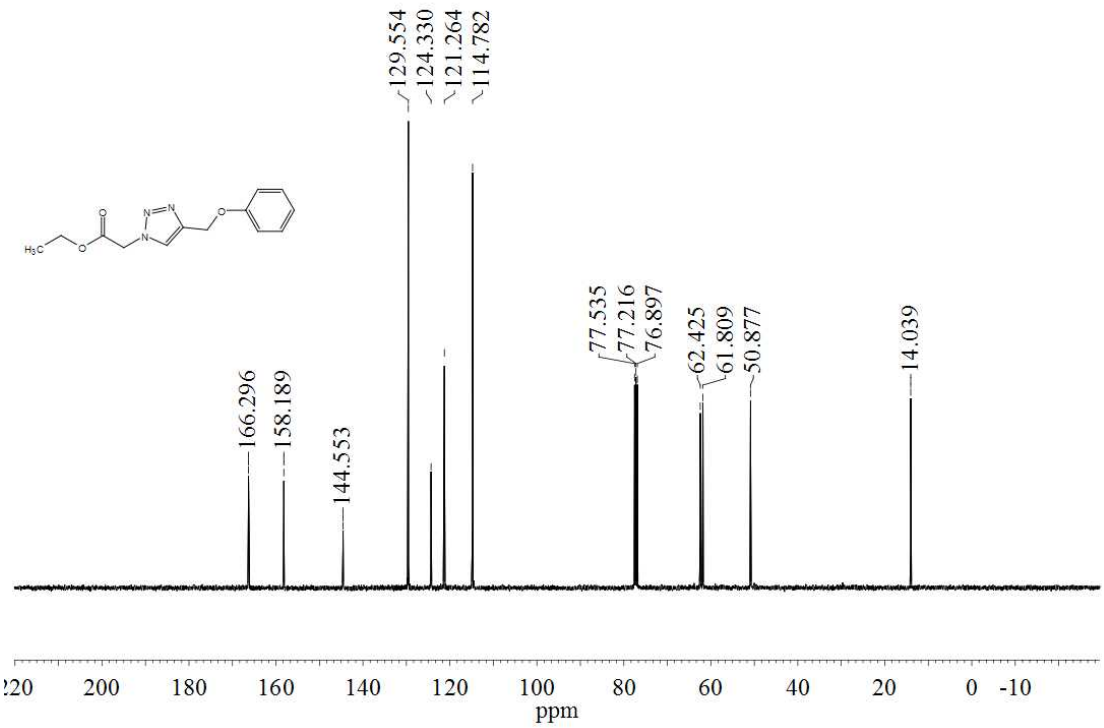


^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.07 (s, 1H), 8.42-8.35 (m, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 2.40 (s, 3H), 1.68-1.58 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 147.3 (C-9), 146.5 (C-1), 142.7 (C-4), 141.6 (C-13), 136.9 (C-5), 133.3 (C-3), 129.3 (C-10), 128.0 (C-12), 125.8 (C-8), 124.5 (C-2), 123.2 (C-6), 121.2 (C-11), 37.4 (C-14), 24.4 (C-15), 18.6 (C-7), 14.0 (C-16).

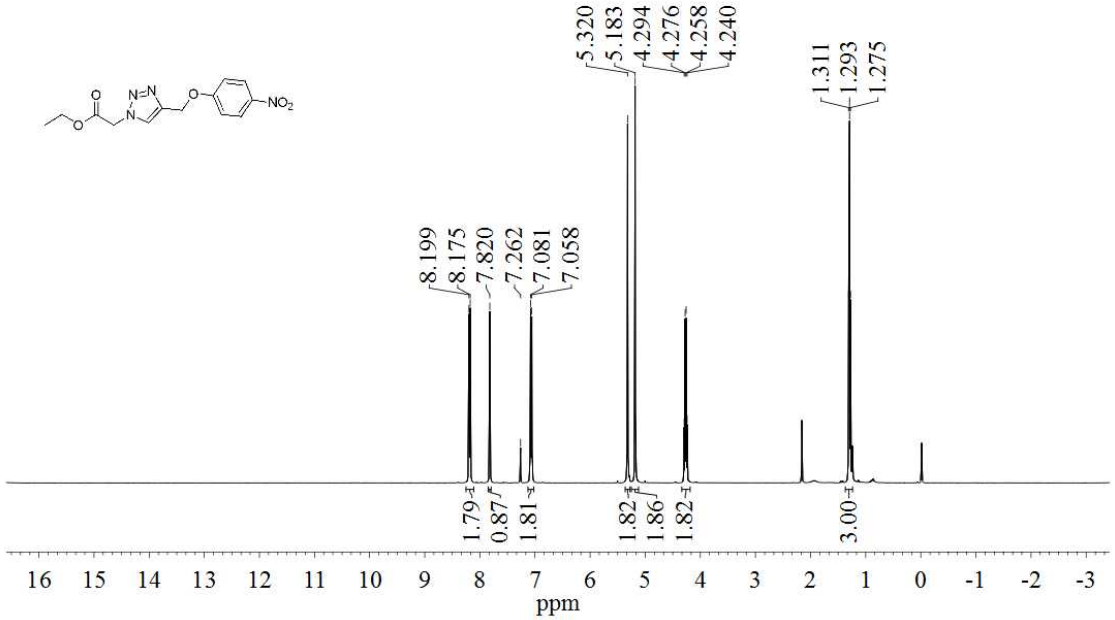
V. ^{1}H and ^{13}C NMR Spectra of the Products

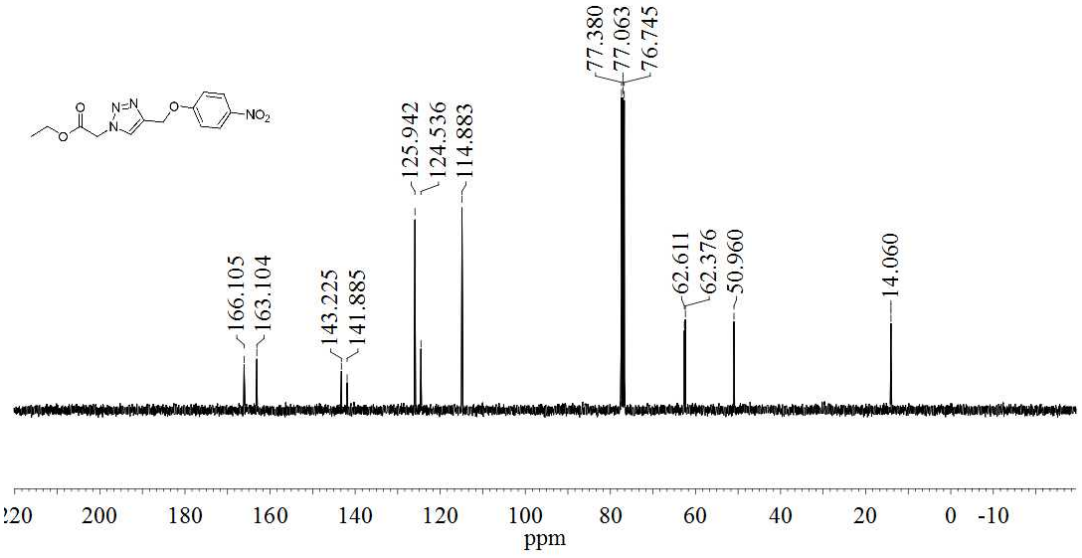
3a:



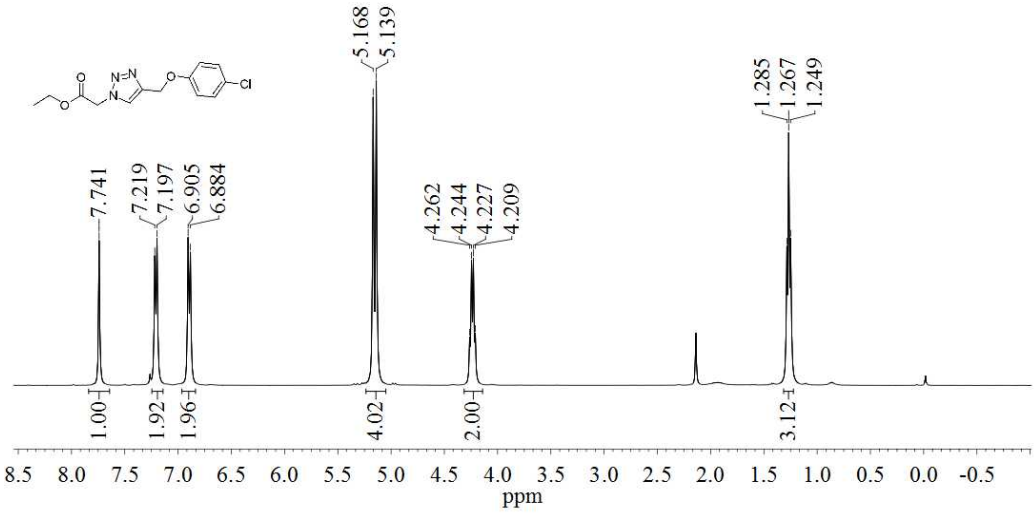


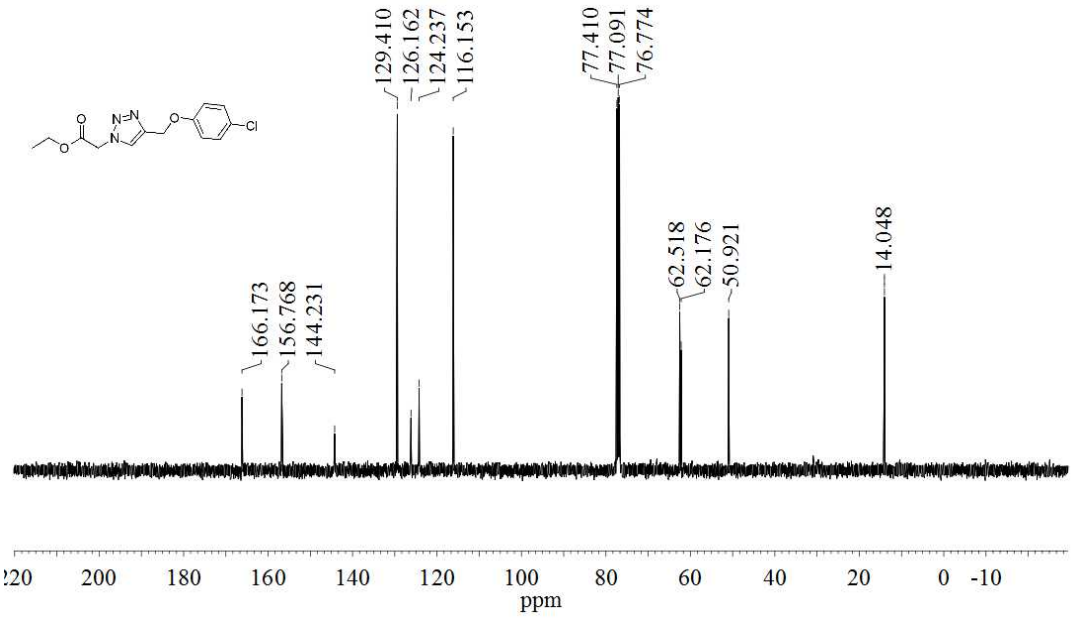
3b:


5.320
5.183
4.294
4.276
4.258
4.240
1.311
1.293
1.275
8.199
8.175
7.820
7.262
7.081
7.058
1.79
0.87
1.81
1.82
1.86
1.82
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

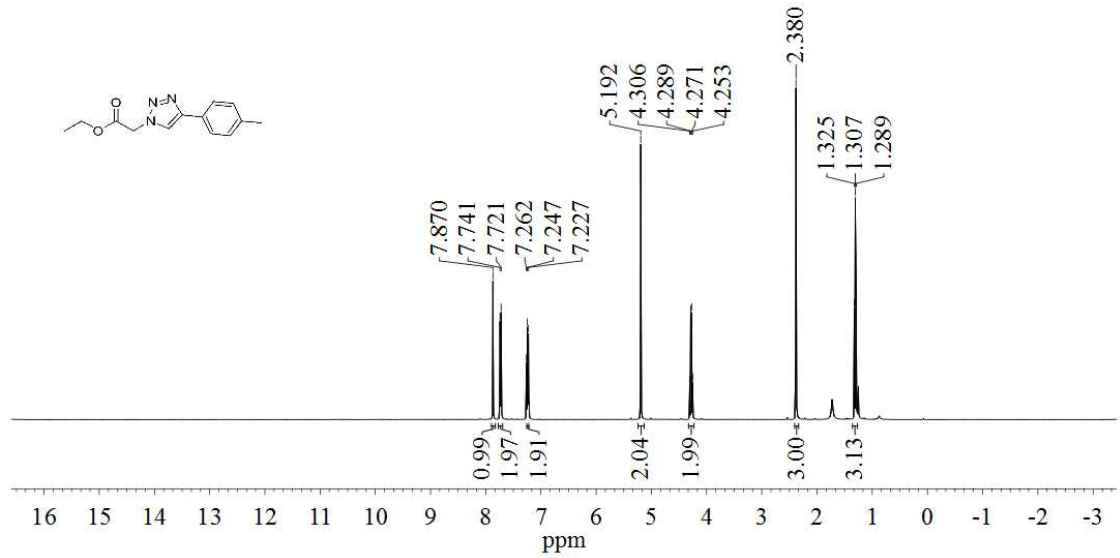

77.380
77.063
76.745
125.942
124.536
114.883
166.105
163.104
143.225
141.885
62.611
62.376
50.960
14.060
220 200 180 160 140 120 100 80 60 40 20 0 -10
ppm

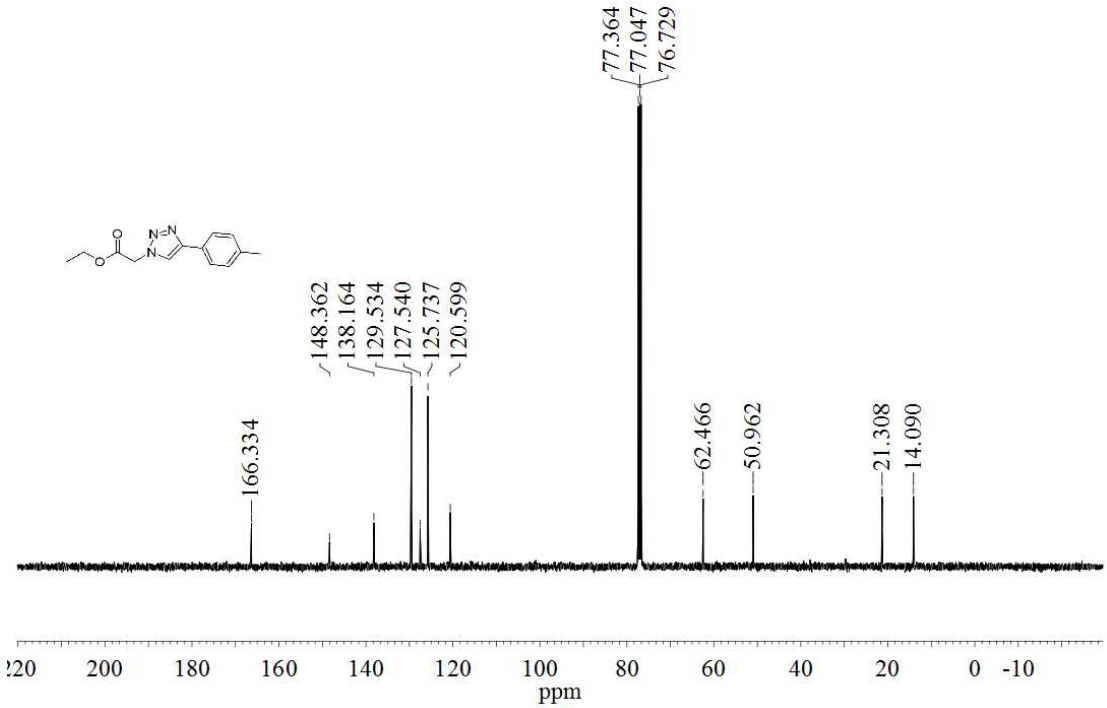
3c:


5.168
5.139
1.285
1.267
1.249
7.741
7.219
7.197
6.905
6.884
4.262
4.244
4.227
4.209
1.00
1.92
1.96
4.02
2.00
3.12
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 -0.5
ppm

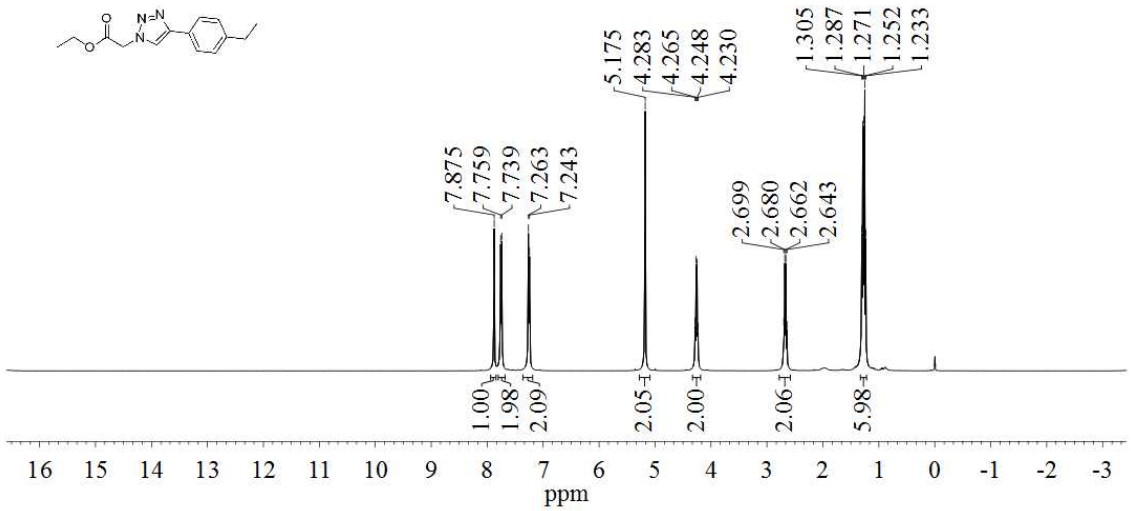

129.410
126.162
124.237
116.153
77.410
77.091
76.774
166.173
156.768
144.231
62.518
62.176
50.921
14.048
220 200 180 160 140 120 100 80 60 40 20 0 -10
ppm

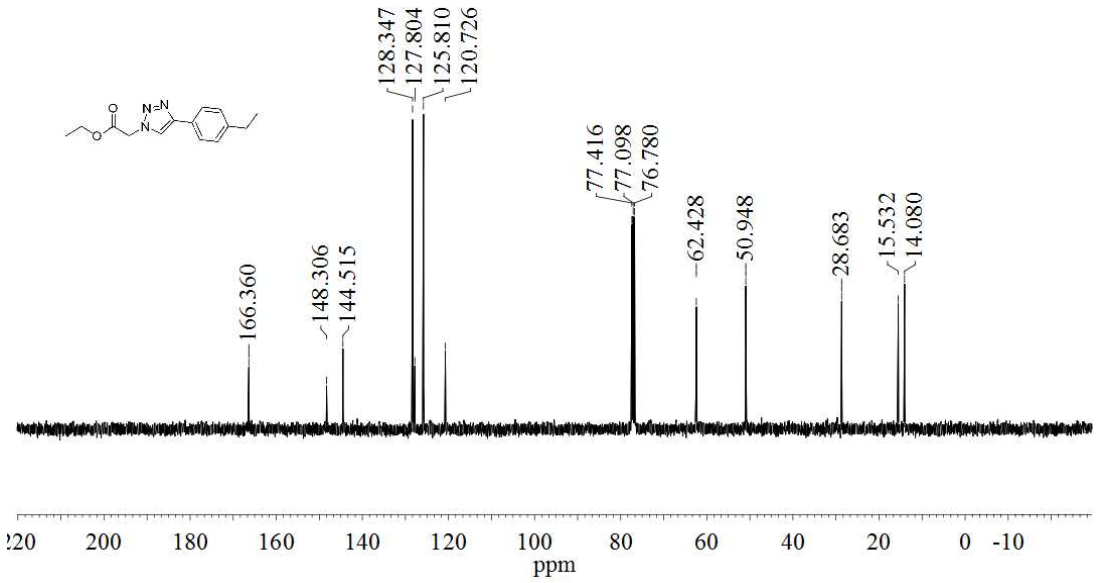
3d:


7.870
7.741
7.721
7.262
7.247
7.227
5.192
4.306
4.289
4.271
4.253
2.380
1.325
1.307
1.289
0.99
1.97
1.91
2.04
1.99
3.00
3.13
ppm

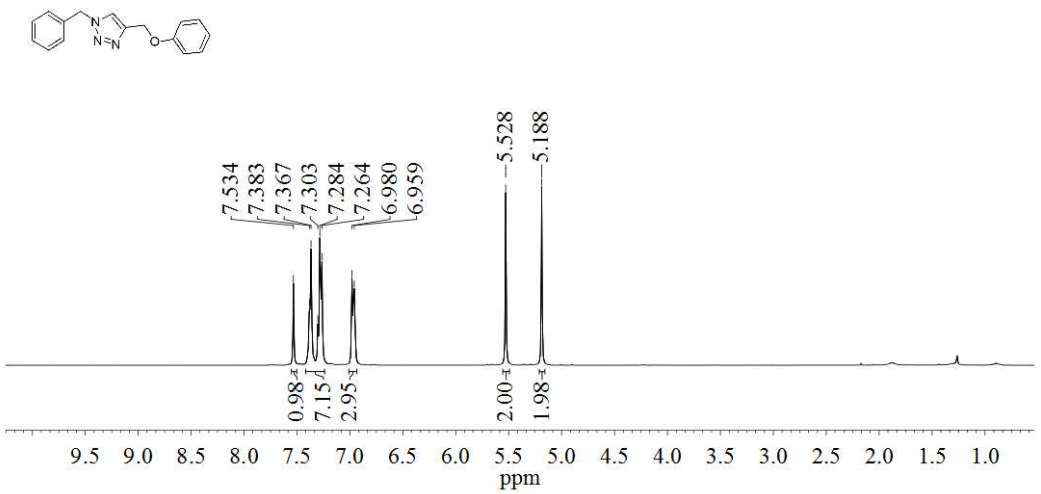

77.364
77.047
76.729
148.362
138.164
129.534
127.540
125.737
120.599
166.334
62.466
50.962
21.308
14.090
ppm

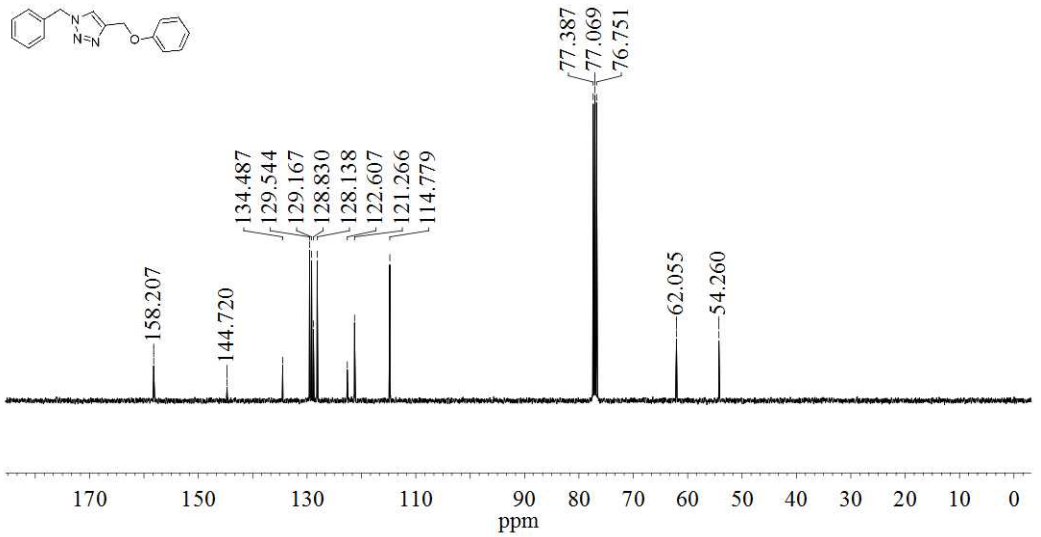
3e:


7.875
7.759
7.739
7.263
7.243
5.175
4.283
4.265
4.248
4.230
2.699
2.680
2.662
2.643
1.305
1.287
1.271
1.252
1.233
1.00
1.98
2.09
2.05
2.00
2.06
5.98
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

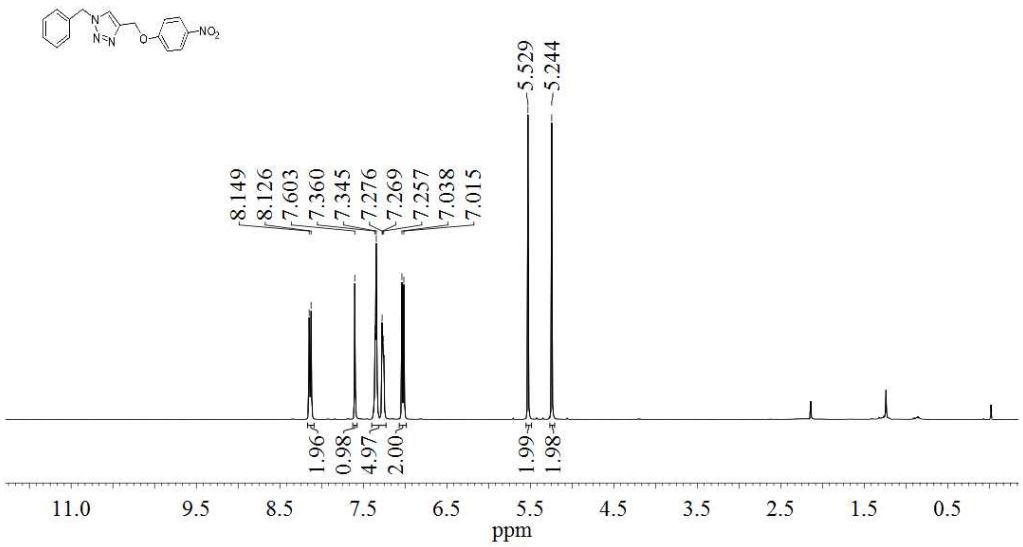

128.347
127.804
125.810
120.726
77.416
77.098
76.780
166.360
148.306
144.515
62.428
50.948
28.683
15.532
14.080
220 200 180 160 140 120 100 80 60 40 20 0 -10
ppm

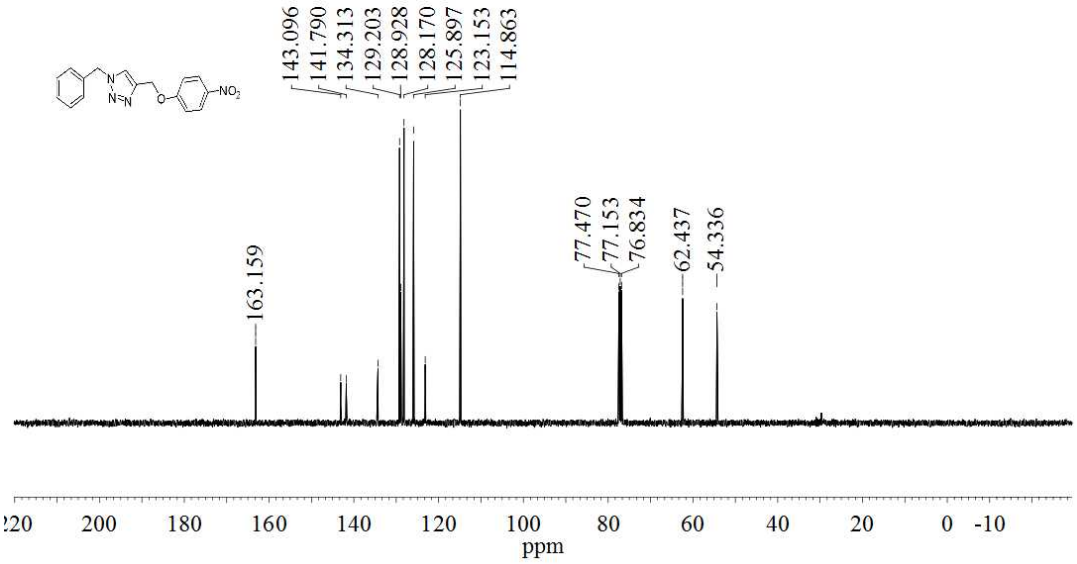
3f:


7.534
7.383
7.367
7.303
7.284
7.264
6.980
6.959
5.528
5.188
0.98
7.15
2.95
2.00
1.98
9.5 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
ppm

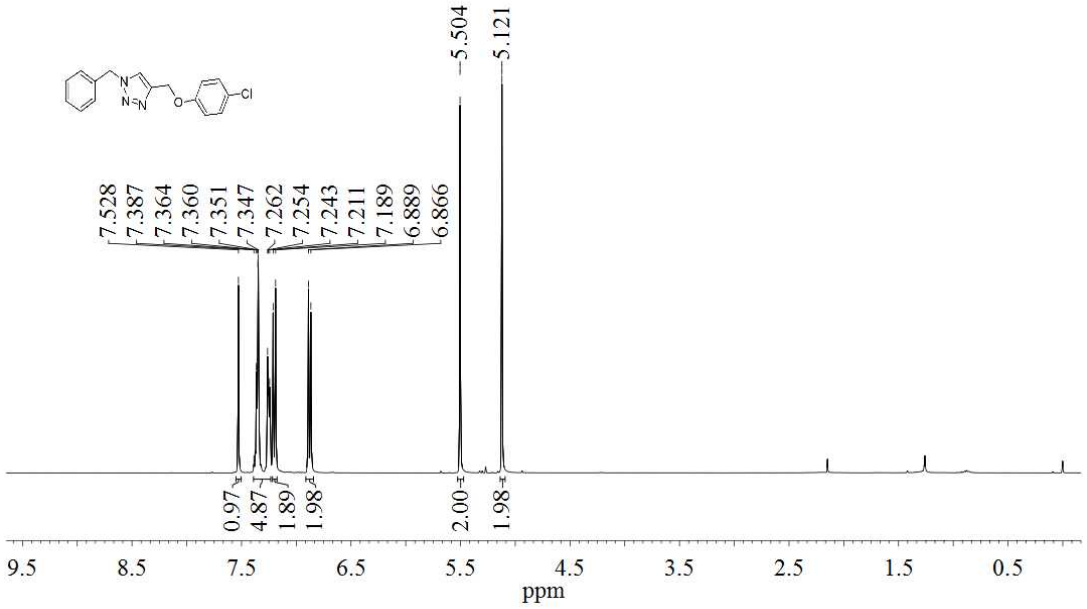

158.207
144.720
134.487
129.544
129.167
128.830
128.138
122.607
121.266
114.779
77.387
77.069
76.751
62.055
54.260
170 150 130 110 90 80 70 60 50 40 30 20 10 0
ppm

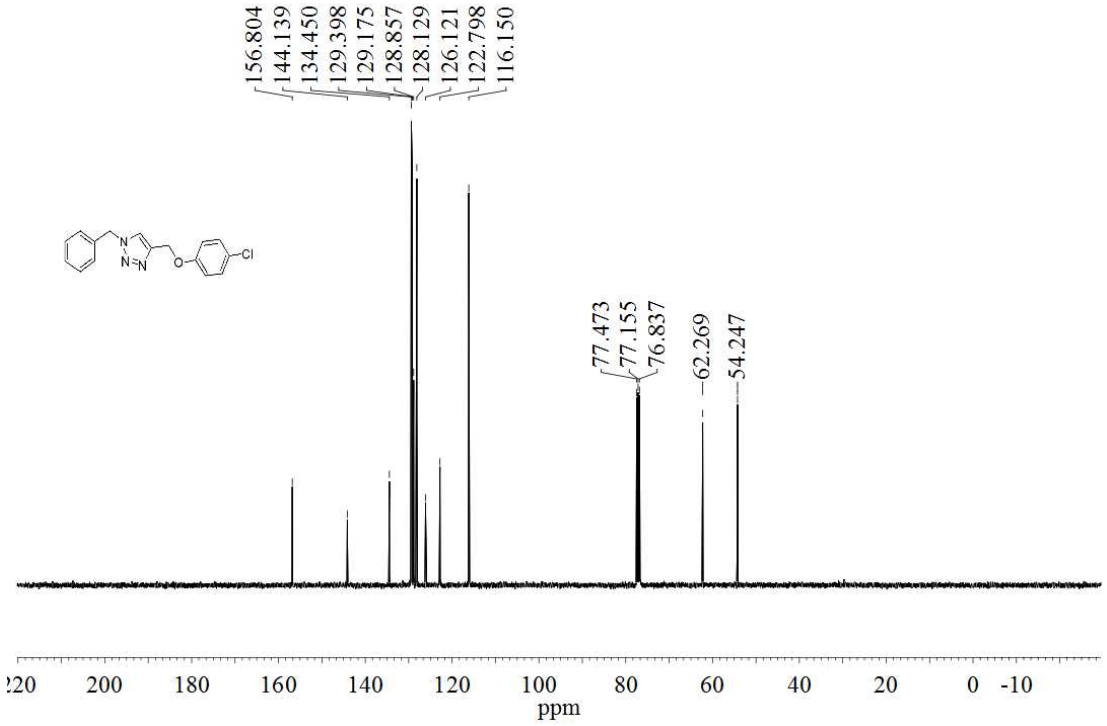
3g:


8.149
8.126
7.603
7.360
7.345
7.276
7.269
7.257
7.038
7.015
5.529
5.244
1.96
0.98
4.97
2.00
1.99
1.98
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm

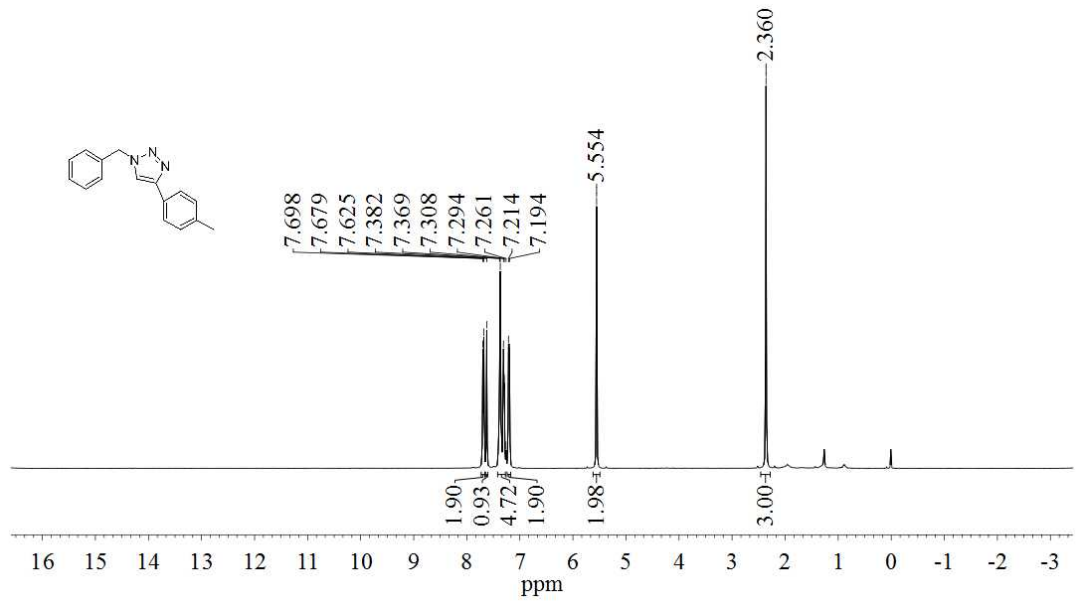

143.096
141.790
134.313
129.203
128.928
128.170
125.897
123.153
114.863
77.470
77.153
76.834
62.437
54.336
163.159
220
200
180
160
140
120
100
80
60
40
20
0
-10
ppm

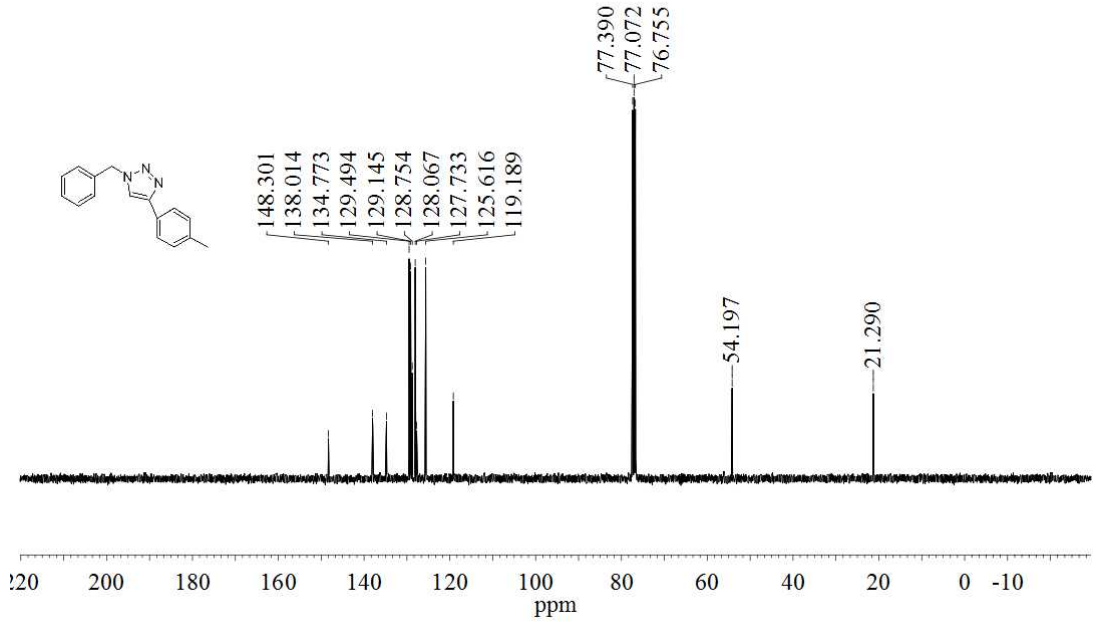
3h:


5.504
5.121
7.528
7.387
7.364
7.360
7.351
7.347
7.262
7.254
7.243
7.211
7.189
6.889
6.866
0.97
4.87
1.89
1.98
2.00
1.98
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm

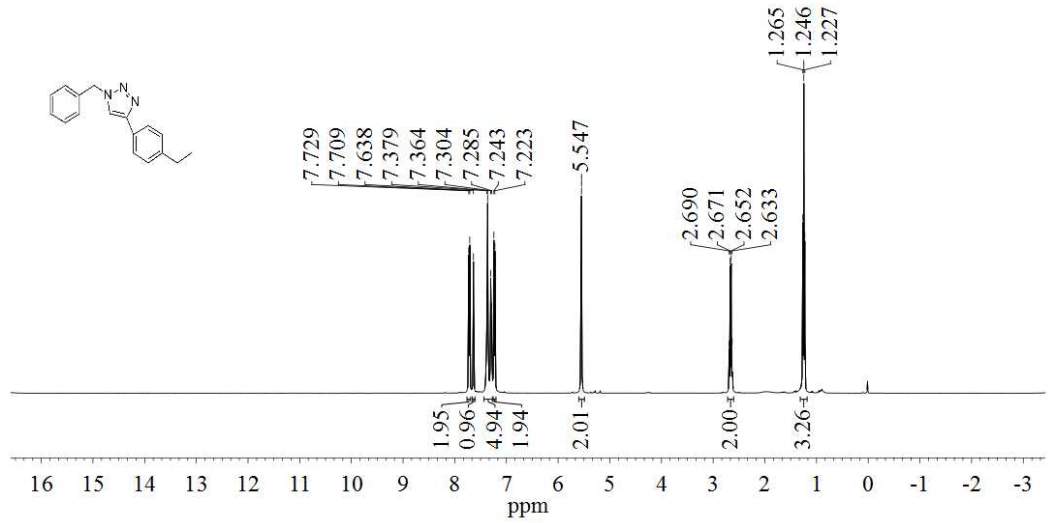

156.804
144.139
134.450
129.398
129.175
128.857
128.129
126.121
122.798
116.150
77.473
77.155
76.837
62.269
54.247
220
200
180
160
140
120
100
80
60
40
20
0
-10
ppm

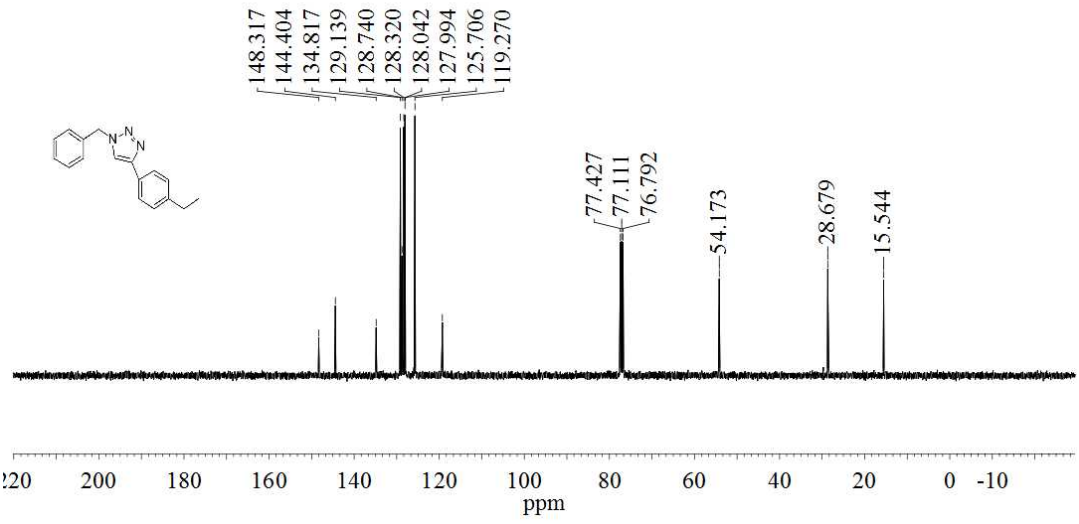
3i:


7.698
7.679
7.625
7.382
7.369
7.308
7.294
7.261
7.214
7.194
5.554
2.360
1.90
0.93
4.72
1.90
1.98
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

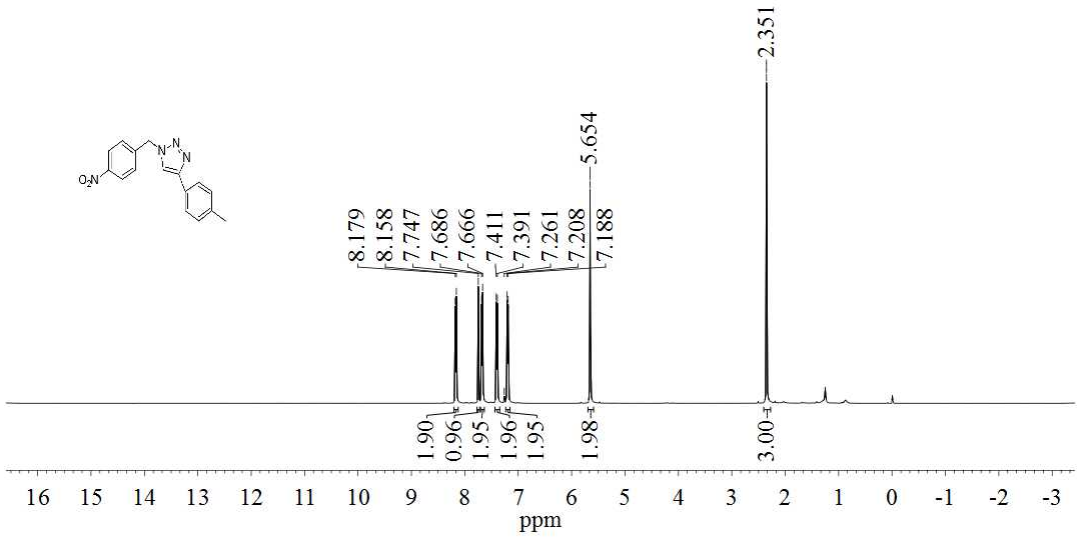

77.390
77.072
76.755
148.301
138.014
134.773
129.494
129.145
128.754
128.067
127.733
125.616
119.189
54.197
21.290
220 200 180 160 140 120 100 80 60 40 20 0 -10
ppm

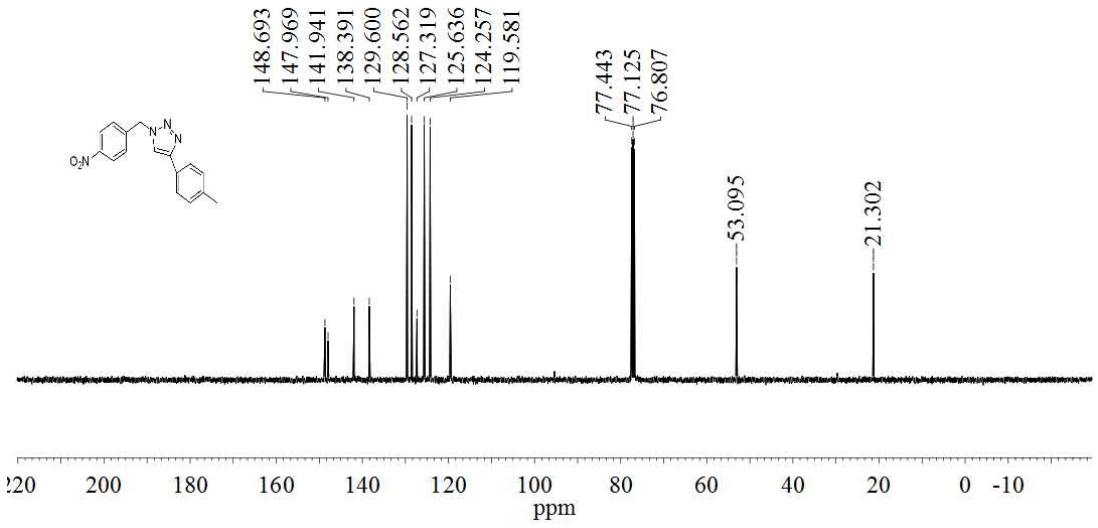
3j:


7.729
7.709
7.638
7.379
7.364
7.304
7.285
7.243
7.223
5.547
2.690
2.671
2.652
2.633
1.265
1.246
1.227
1.95
0.96
4.94
1.94
2.01
2.00
3.26
ppm

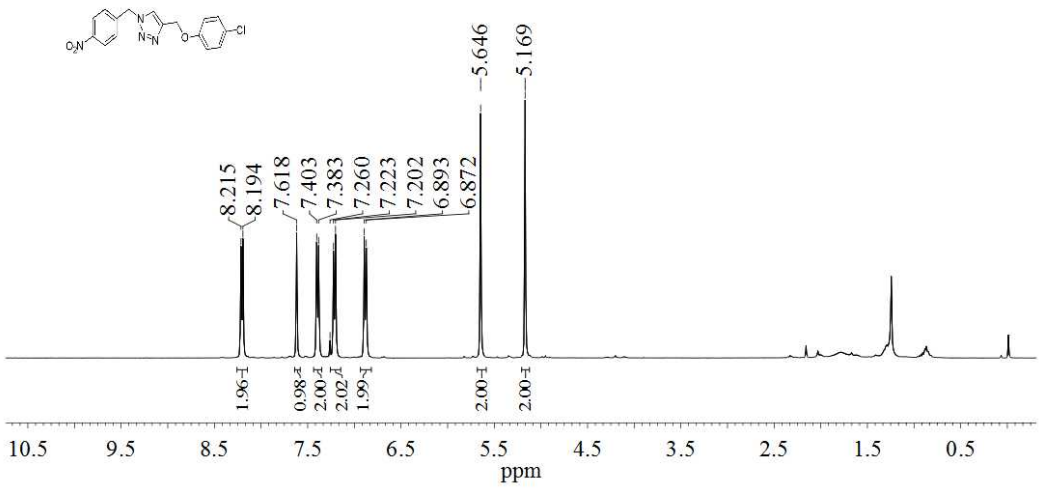

148.317
144.404
134.817
129.139
128.740
128.320
128.042
127.994
125.706
119.270
77.427
77.111
76.792
54.173
28.679
15.544
ppm

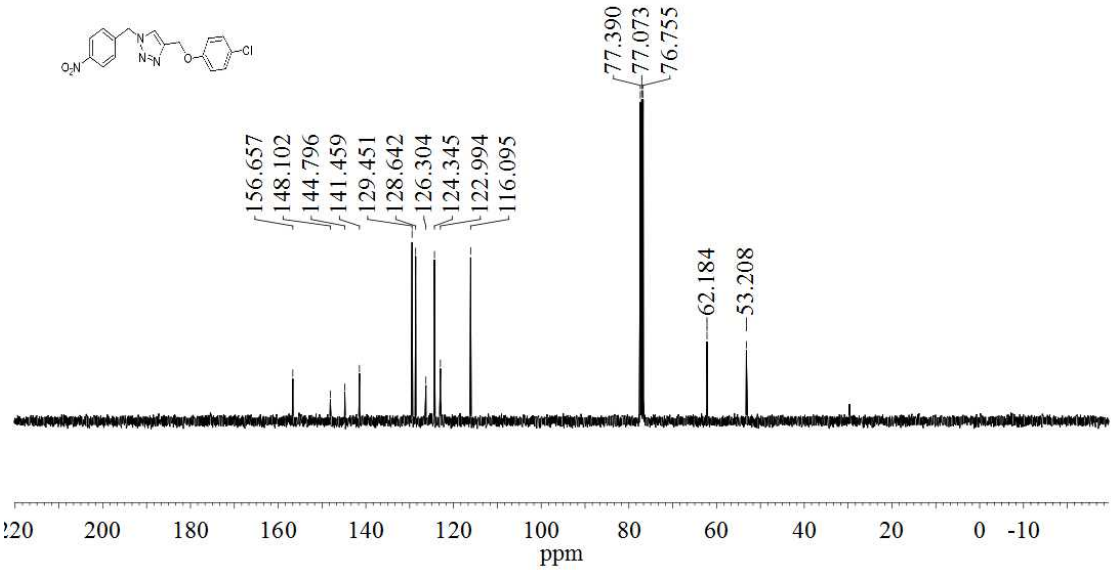
3k:


8.179
8.158
7.747
7.686
7.666
7.411
7.391
7.261
7.208
7.188
5.654
2.351
1.90
0.96
1.95
1.96
1.95
1.98
3.00
ppm

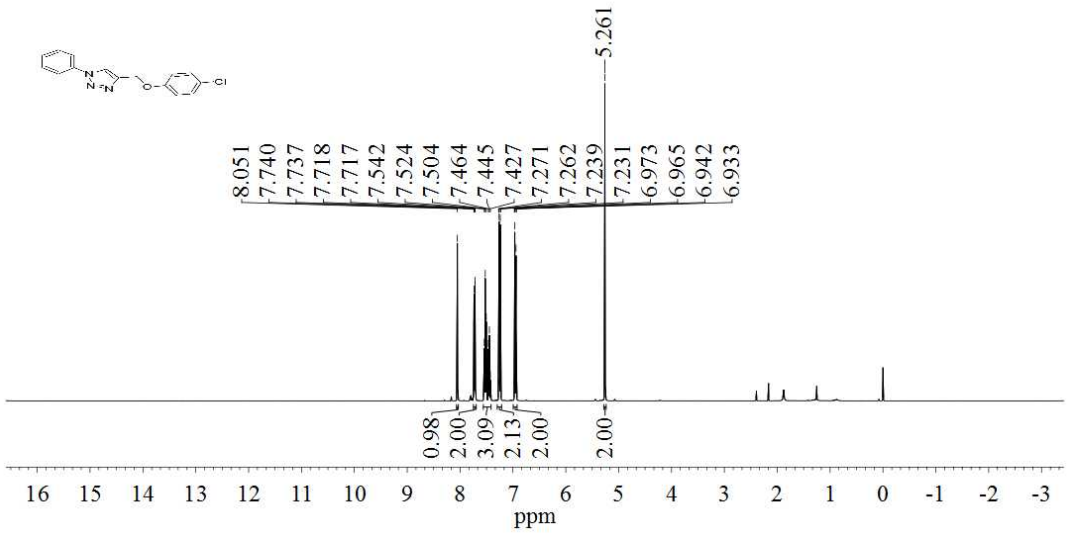

148.693
147.969
141.941
138.391
129.600
128.562
127.319
125.636
124.257
119.581
77.443
77.125
76.807
53.095
21.302
ppm

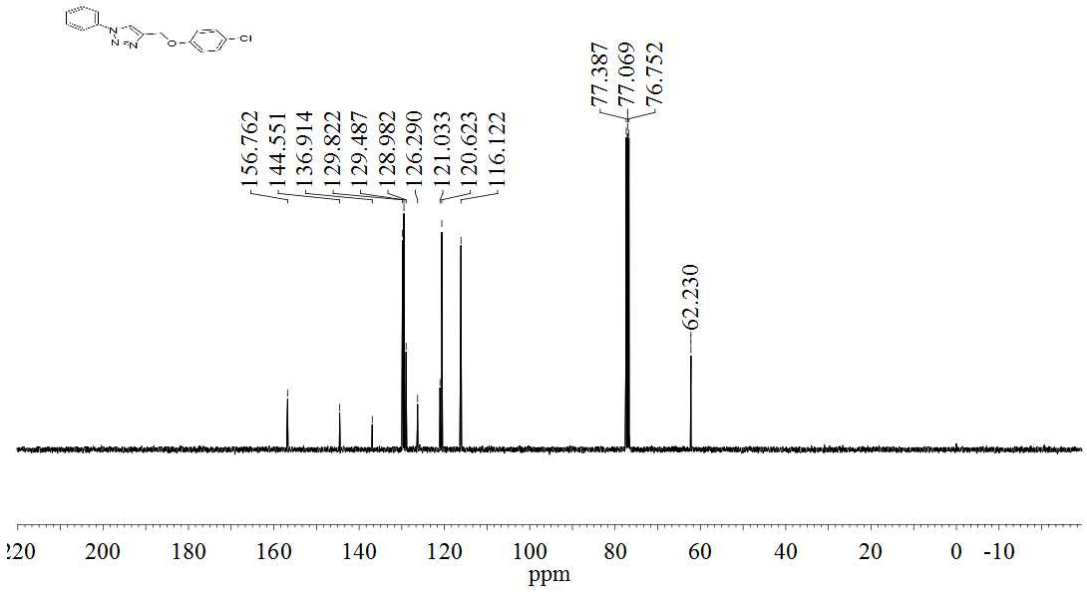
3l:


8.215
8.194
7.618
7.403
7.383
7.260
7.223
7.202
6.893
6.872
5.646
5.169
1.96
0.98
2.00
2.02
1.99
2.00
2.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm

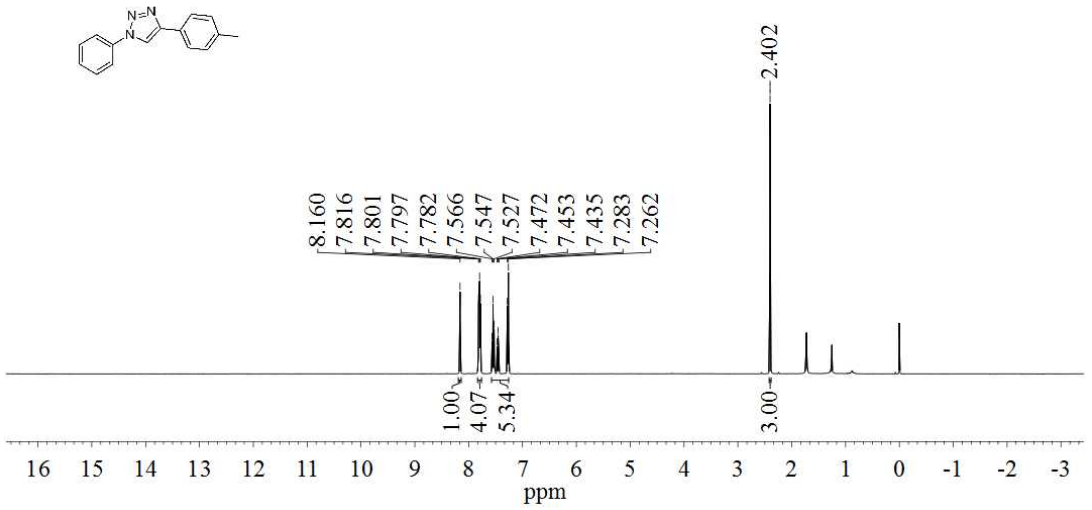

156.657
148.102
144.796
141.459
129.451
128.642
126.304
124.345
122.994
116.095
77.390
77.073
76.755
62.184
53.208
220
200
180
160
140
120
100
80
60
40
20
0
-10
ppm

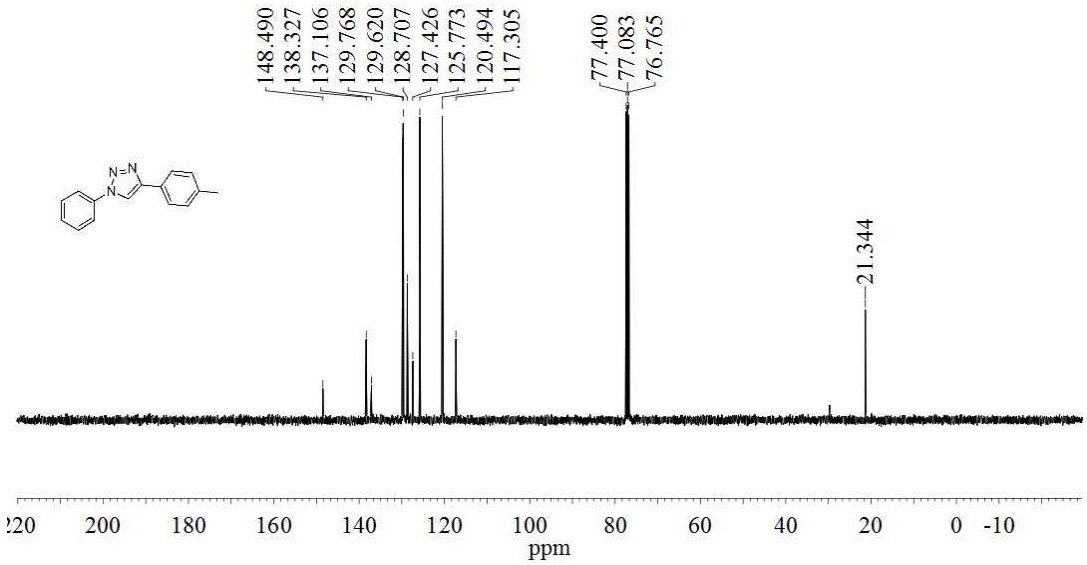
3m:


8.051
7.740
7.737
7.718
7.717
7.542
7.524
7.504
7.464
7.445
7.427
7.271
7.262
7.239
7.231
6.973
6.965
6.942
6.933
5.261
0.98
2.00
3.09
2.13
2.00
2.00
ppm

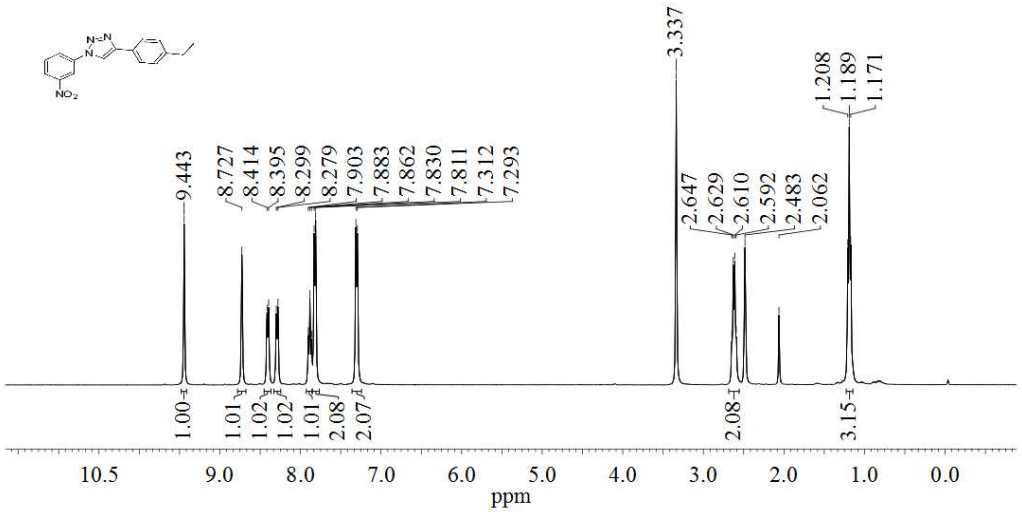

156.762
144.551
136.914
129.822
129.487
128.982
126.290
121.033
120.623
116.122
77.387
77.069
76.752
62.230
ppm

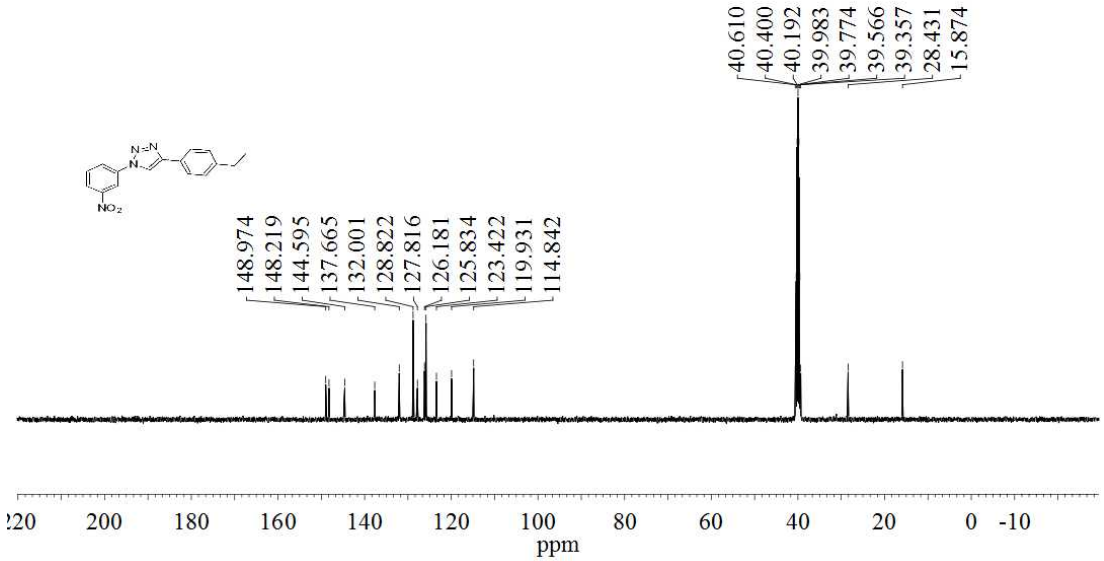
3n:


8.160
7.816
7.801
7.797
7.782
7.566
7.547
7.527
7.472
7.453
7.435
7.283
7.262
2.402
1.00
4.07
5.34
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

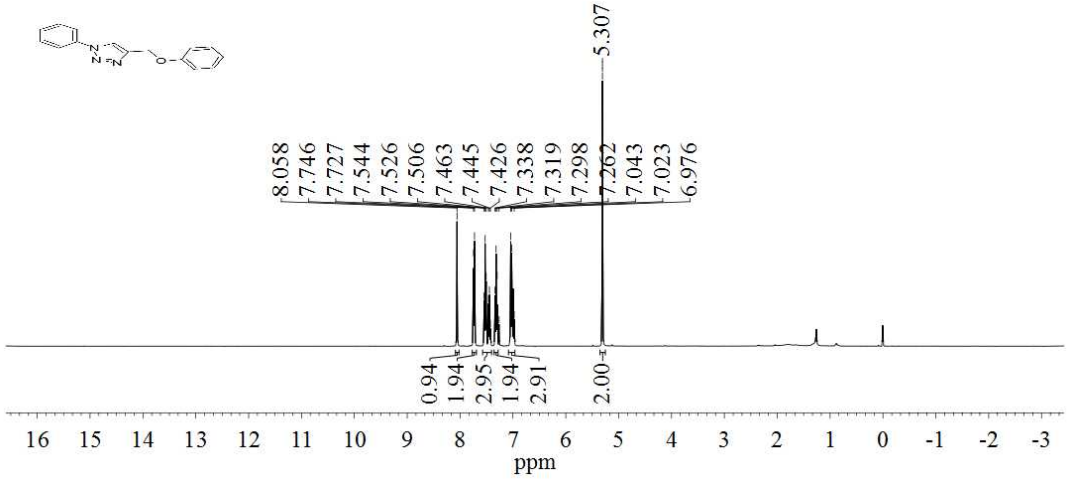

148.490
138.327
137.106
129.768
129.620
128.707
127.426
125.773
120.494
117.305
77.400
77.083
76.765
21.344
220 200 180 160 140 120 100 80 60 40 20 0 -10
ppm

3o:


9.443
8.727
8.414
8.395
8.299
8.279
7.903
7.883
7.862
7.830
7.811
7.312
7.293
3.337
2.647
2.629
2.610
2.592
2.483
2.062
1.208
1.189
1.171
1.00
1.01
1.02
1.02
1.01
2.08
2.07
2.08
3.15
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


40.610
40.400
40.192
39.983
39.774
39.566
39.357
28.431
15.874
148.974
148.219
144.595
137.665
132.001
128.822
127.816
126.181
125.834
123.422
119.931
114.842
220
200
180
160
140
120
100
80
60
40
20
0
-10
ppm

3p:


5.307
8.058
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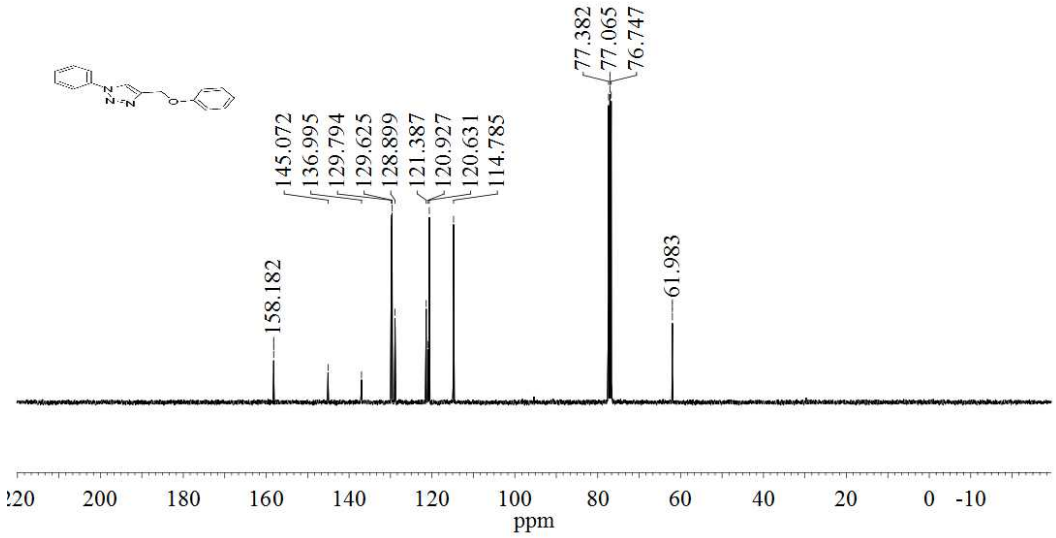
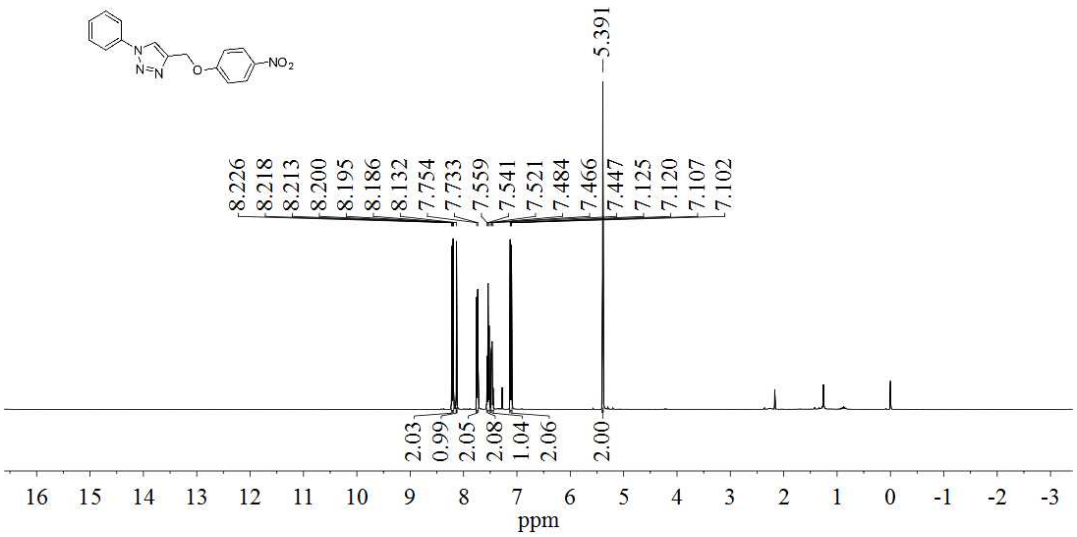
7.727
7.544
7.526
7.506
7.463
7.445
7.426
7.338
7.319
7.298
7.262
7.043
7.023
6.976
0.94
1.94
2.95
1.94
2.91
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm


77.382
77.065
76.747
145.072
136.995
129.794
129.625
128.899
121.387
120.927
120.631
114.785
158.182
61.983
220 200 180 160 140 120 100 80 60 40 20 0 -10
ppm

3q: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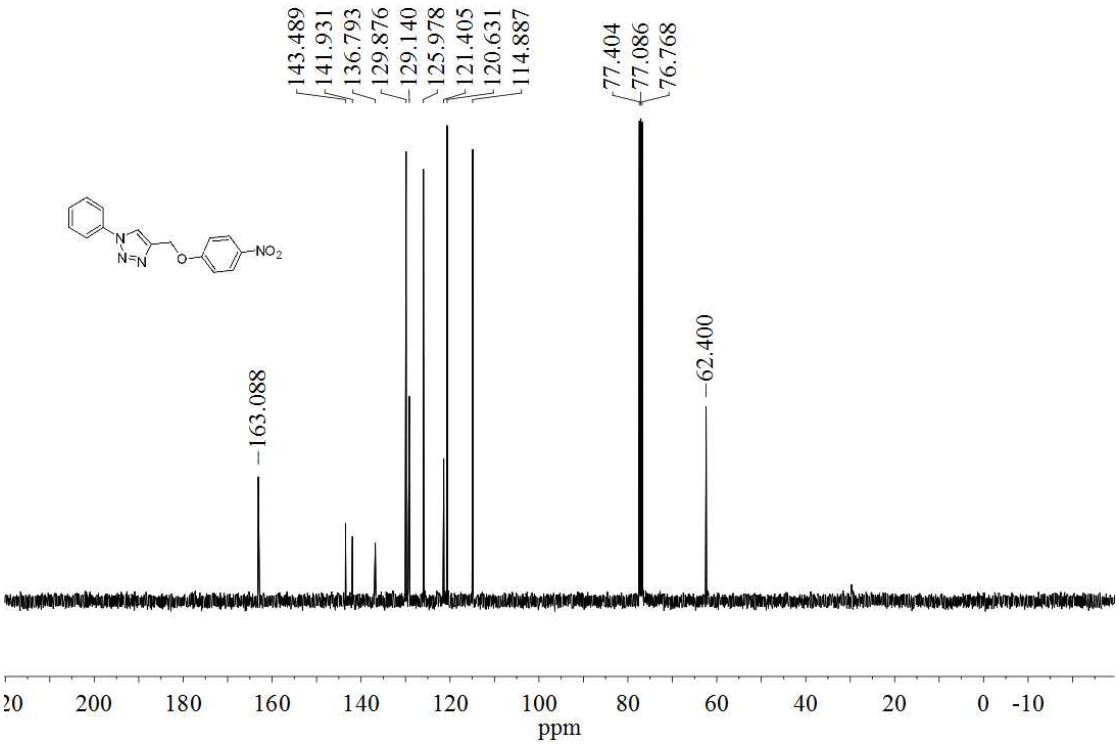
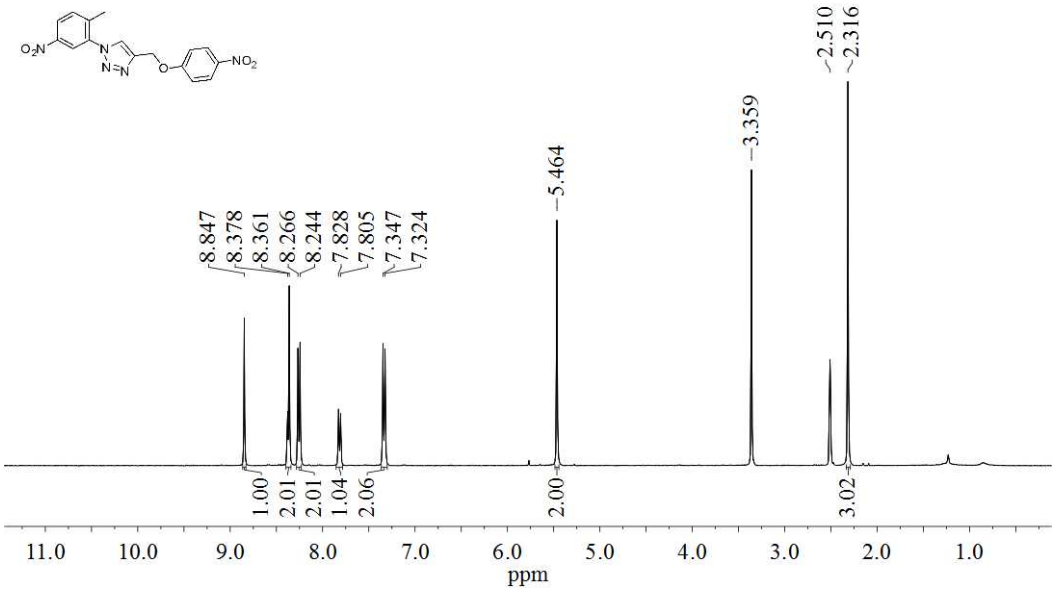
8.226
8.218
8.213
8.200
8.195
8.186
8.132
7.754
7.733
7.559
7.541
7.521
7.484
7.466
7.447
7.125
7.120
7.107
7.102
2.03
0.99
2.05
2.08
1.04
2.06
2.00
ppm


143.489
141.931
136.793
129.876
129.140
125.978
121.405
120.631
114.887
77.404
77.086
76.768
163.088
62.400
ppm

3r: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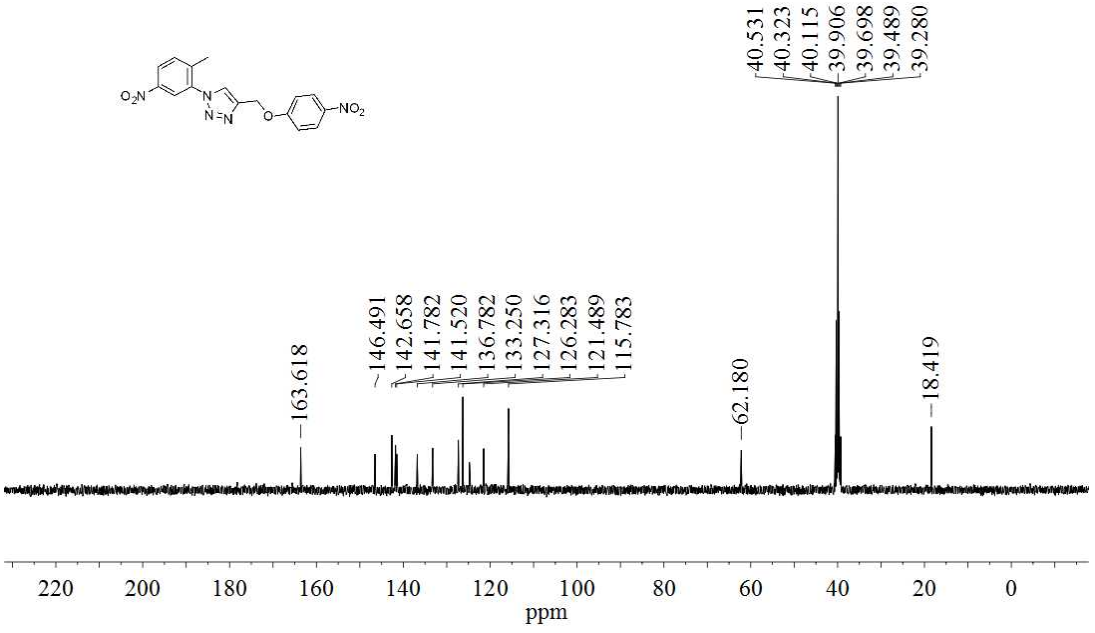
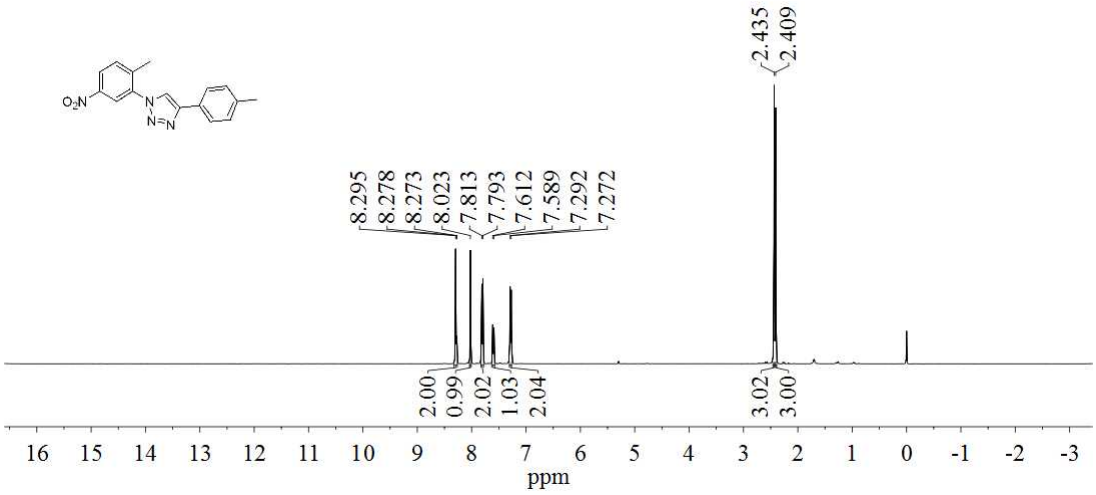
8.378
8.361
8.266
8.244
7.828
7.805
7.347
7.324
5.464
3.359
2.510
2.316
1.00
2.01
2.01
1.04
2.06
2.00
3.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm


40.531
40.323
40.115
39.906
39.698
39.489
39.280
163.618
146.491
142.658
141.782
141.520
136.782
133.250
127.316
126.283
121.489
115.783
62.180
18.419
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3s: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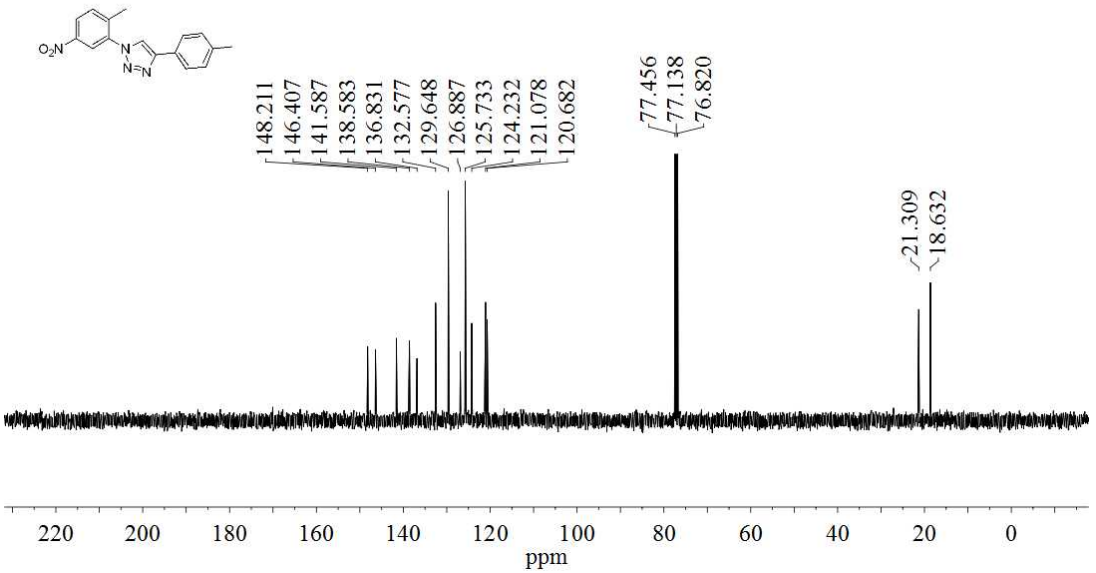
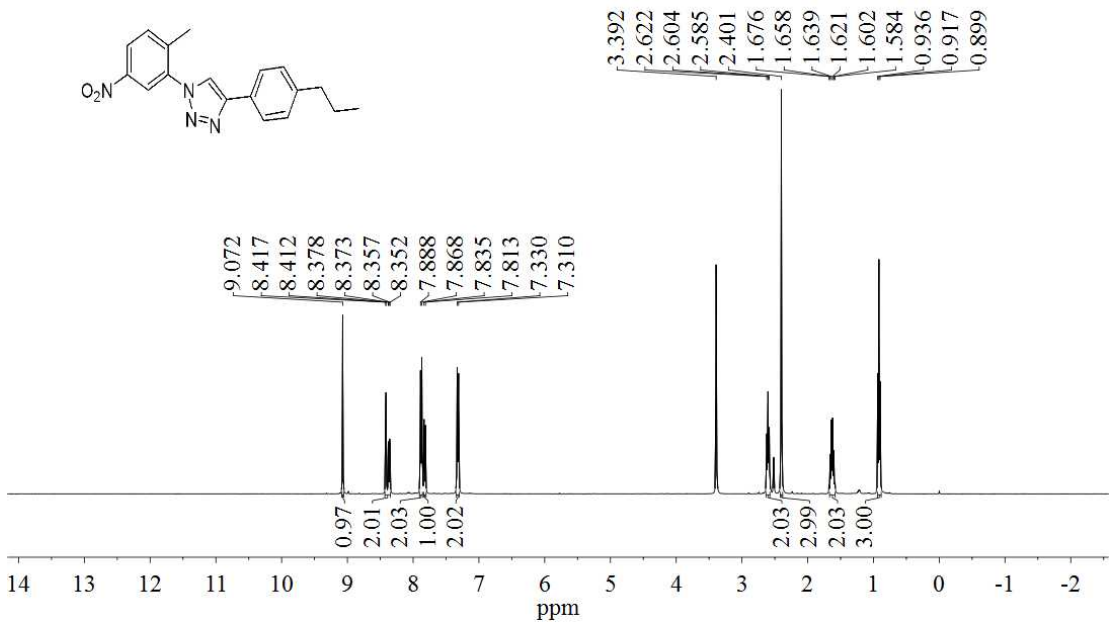
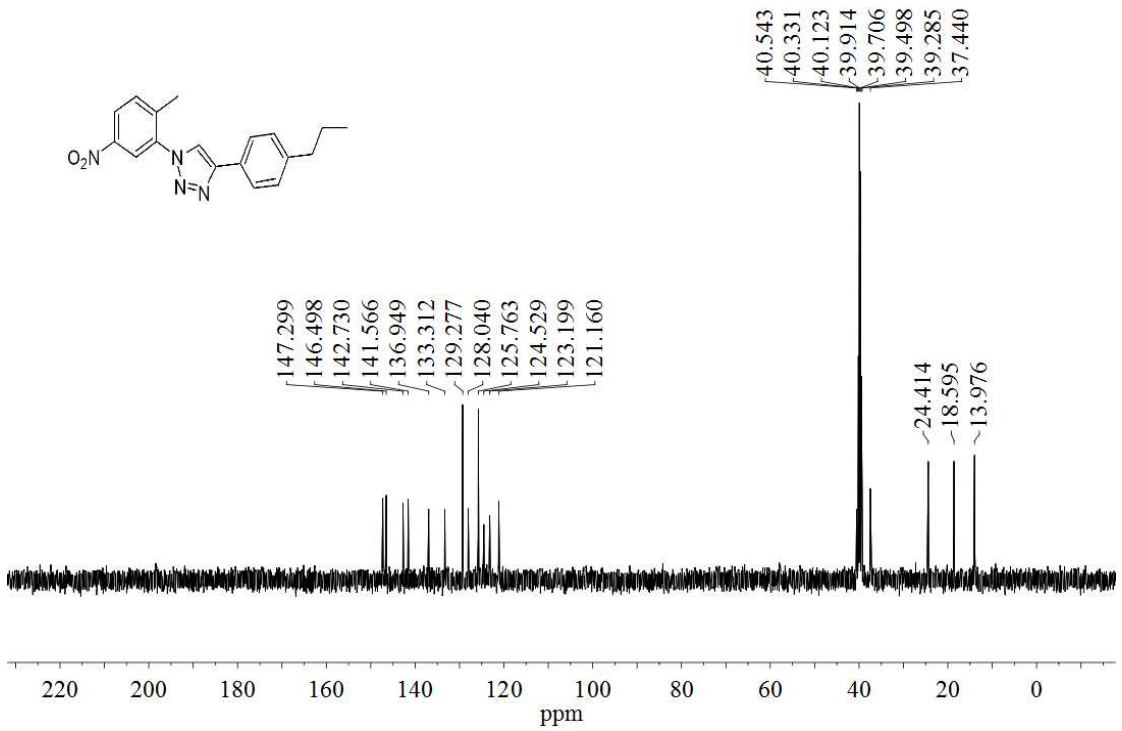
8.278
8.273
8.023
7.813
7.793
7.612
7.589
7.292
7.272
2.435
2.409
2.00
0.99
2.02
1.03
2.04
3.02
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm


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
220 200 180 160 140 120 100 80 60 40 20 0
ppm

3t:


3.392
2.622
2.604
2.585
2.401
1.676
1.658
1.639
1.621
1.602
1.584
0.936
0.917
0.899
9.072
8.417
8.412
8.378
8.373
8.357
8.352
7.888
7.868
7.835
7.813
7.330
7.310
0.97
2.01
2.03
1.00
2.02
2.03
2.99
2.03
3.00
ppm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40.331
40.123
39.914
39.706
39.498
39.285
37.440
147.299
146.498
142.730
141.566
136.949
133.312
129.277
128.040
125.763
124.529
123.199
121.160
24.414
18.595
13.976
ppm