Supporting Information

Copper Immobilized Onto the Triazole Functionalized Magnetic Nanoparticle: A Robust Magnetically Recoverable Catalyst for "Click" Reaction

Firouz Matloubi Moghaddam*, Seyed Ebrahim Ayati

Laboratory of Organic Synthesis and Natural Products, Department of Chemistry,
Sharif University of Technology, Azadi Street, PO Box 111559516
Tehran, Iran

E-mail Address: matloubi@sharif.edu

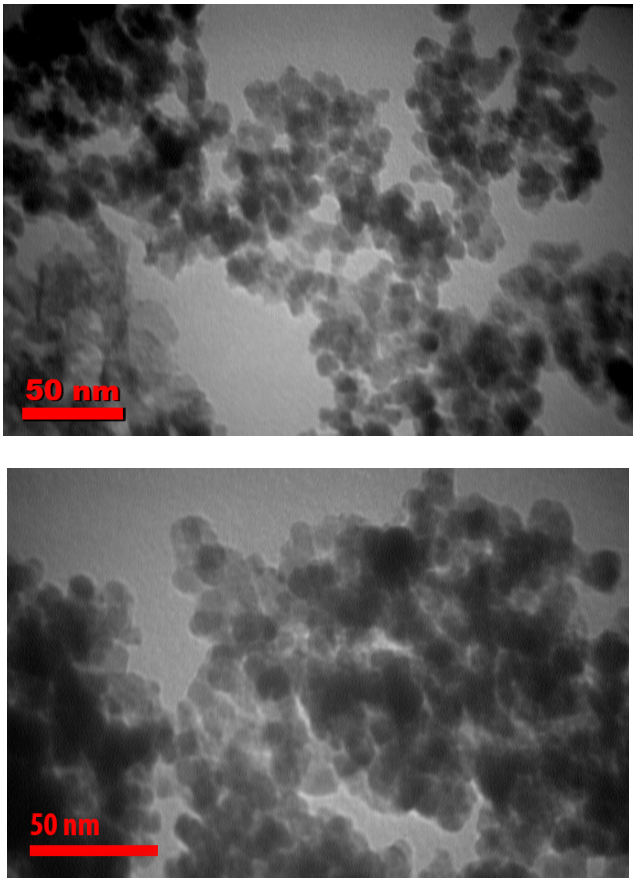
CONTENTS

1. General remarks

All materials used are commercially available and were purchased from Merck and used without any additional purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker (Avance DRX-500) spectrometer using $CDCl_3$ as solvent at room temperature. Chemical shifts δ were reported in ppm relative to tetramethylsilane as an internal standard. FTIR spectra of samples were taken using an ABB Bomem MB-100 FTIR spectrophotometer. The morphology of the catalyst was observed using a Philips XL30 scanning electron microscope (SEM), Thermogravimetric analysis (TGA) was acquired under a nitrogen atmosphere with a TGA Q 50 thermogravimetric analyzer. CHN analysis was done by LECO Truspec.

2. General procedure for the synthesis of triazole

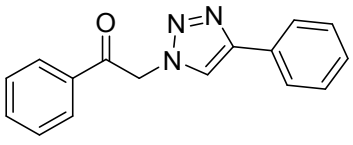
A glass tube was charged with sodium ascorbate (30 mg, 10 mol%), phenyl acetylene (0.5mmol), benzylbromide (0.5 mmol), sodium azide (0.5 mmol), catalyst (5 mg, 0.5mol%) and H_2O/*t*-BuOH with 3/1 ratio (3 mL). The reaction mixture was stirred at 55 ˚C for 4 h and the completion of the reaction was monitored by TLC (EtOAc/ n-hexane, 25:75). In each case, after completion, the product was worked up and purified according to the following procedure: The mixture was diluted with ethyl acetate and water. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure using a rotary evaporator. The residue was purified by recrystallization from ethyl acetate/ n-hexane. In order to reuse the catalyst, the nanomagnetic Cu catalyst was collected using an external magnet, washed with methanol and dried overnight to be ready for the next run.



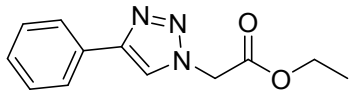
TEM image before and after catalyst recovery

Spectroscopic characterization of the products

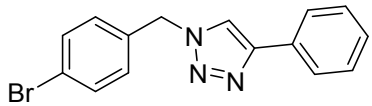
1-Phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethanone[1]:
Colourless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ= 5.93 (s, 2H), 7.36-7.90 (m, 6H), 8.01 (d, *J* = 7.2 Hz, 2H); 8.04 (s, 1H); 8.06 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.4, 121.4, 125.8, 128.2, 128.8, 129.2, 130.5, 133.9, 134.6, 148.2, 190.2



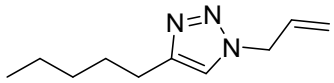
4-Phenyl-(1,2,3-triazole-1-yl)-acetic acid ethyl ester:
^{1}H NMR (400 MHz, $CDCl_3$) δ= 1.33 (3H, t, *J* =7.6 Hz), 4.26 (2H, q, *J* =7.6 Hz), 5.20 (2H, s), 7.34-7.46 (3H, m), 7.85-7.87 (2H, m, ortho to Ar), 7.93 (1H, s); ^{13}C NMR (100MHz, $CDCl_3$) δ = 14.0, 50.9, 62.4, 121.0, 125.8, 128.3, 128.8, 130.3, 148.2, 166.3;



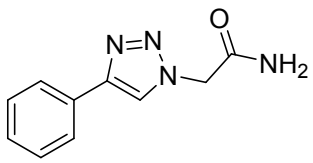
1-(4-bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole[1]:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.69 (2H, s), 7.31-7.36 (1H, m), 7.40-7.44 (4H, m), 7.76 (s, 1 H), 7.81 (2H, d, *J* = 6.8 Hz), 8.22 (2H, d, *J* = 6.8Hz,); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 53.1, 119.7, 124.0, 124.2, 125.7, 128.4, 128.5, 128.8, 130. 0, 141.7, 148.0, 148.6



1-allyl-4-pentyl-1*H*-1,2,3-triazole:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.28 (3H, t), 1.32-1.37 (2H, m), 1.35-1.36 (4H, m), 1.67 (2H, t), 2.27 (2H, t), 4.92 (2H, d), 5.26-5.36 (2H, m), 5.97-6.05 (1H, m), 7.46 (1H, s); ^{13}CNMR (100 MHz, $CDCl_3$) δ = 13.8, 22.4, 25.6, 29.6, 30.9, 31.4, 119.7, 120.4, 130.0, 148.7

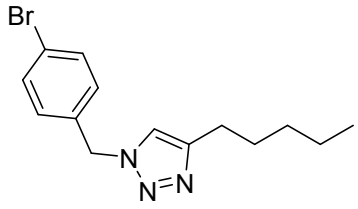


2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)acetamide:
White solid, mp 102-104^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ= 1.62 (2H, broad), 5.93 (2H, s), 7.28 (1H, s), 7.40-7.40 (2H, m), 7.83-7.99 (3H, m, ortho to Ar);^{13}C NMR (100 MHz, $CDCl_3$) δ = 29.70, 109.64, 115.73, 118.78, 126.11, 128.98, 144.50, 185.11

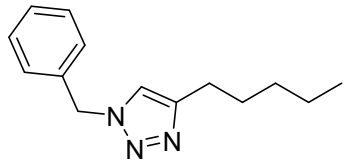


1-(4-bromobenzyl)-4-pentyl-1*H*-1,2,3-triazole:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.85 (3H, t, *J* = 6.9 Hz), 1.27-1.30 (4 H, m), 1.59-1.63 (2H, m), 2.65 (2H, t, *J* = 7.4 Hz), 5.41 (2H, s), 7.09 (2H, d, *J* = 6.3 Hz,), 7.21 (1H, s), 7.46 (2H, d,

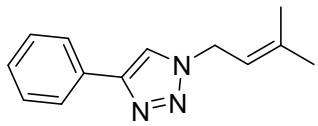
J = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.9, 22.3, 25.6, 29.0, 13.9, 22.3, 25.6, 29.0, 31.4, 53.2, 120.5, 122.6, 129.5, 132.1, 134.0



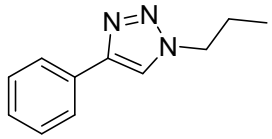
1-Benzyl-4-pentyl-1*H*-1,2,3-triazole[2]:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.87 (3H, t, *J* = 6.9 Hz), 1.29-1.33 (4H, m), 1.61-1.65 (2H, m), 2.67 (2H, t, *J* = 7.4 Hz), 5.49 (2H, s), 7.17 (1H, s), 7.25 (2H, d, *J* = 8.0 Hz), 7.34-7.38 (3H, m,); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.9, 22.3, 25.6, 29.0, 31.4, 53.9, 120.4, 127.9, 128.5, 129.0, 135.0, 148.9



1-(3-methylbut-2-en-1-yl)-4-phenyl-1*H*-1,2,3-triazole:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.81(6H, s), 4.97 (2H, d, *J*= 7.2Hz), 5.46 (1H, t, *J*= 7.2Hz), 7.28-7.36 (3H, m), 7.73 (1H, s), 7.82-7.85 (2H,m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 18.1, 25.7, 48.1, 117.2, 119.2, 126.7, 128.1, 128.8, 139.9, 147.7

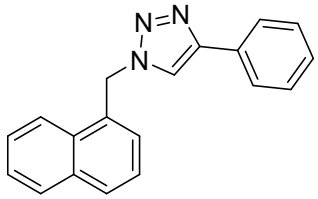


1-propyl-4-phenyl-1*H*-1.2.3-triazole[2]:
White solid, mp 62-64°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.99 (3H, t, *J*= 7.3), 1.97-2.02 (2H, m), 4.37 (2H, t, *J*=7.3), 7.26-7.34 (1H, m, Ar), 7.42 (2H, t, Ar), 7.74 (1H, s), 7.83 (2H, d); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.5, 24.1, 51.9, 119.8 , 126.1, 128.5, 129.2, 130.70, 147.61

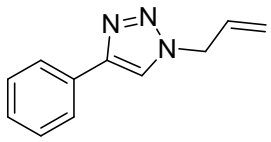


1-(naphthalen-1-ylmethyl)-4-phenyl-1*H*-1,2,3-triazole:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.02 (2H, s), 7.25-7.26 (2H, m), 7.33-7.34 (2H, m), 7.47-7.53 (4H, m), 7.72-7.74(2H, m), 7.90 (2H, d, *J*= 5.2), 8.00 (1H, d, *J*= 5.2); ^{13}C NMR (100

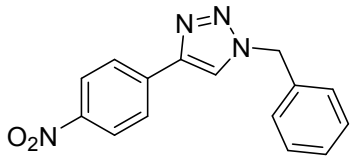
MHz, $CDCl_3$) δ = 52.8, 119.8, 123.3, 125.7, 126.0, 126.8, 127.8, 128.3, 128.5, 129.1, 129.3, 130.2, 130.5, 130.9, 131.6, 134.3



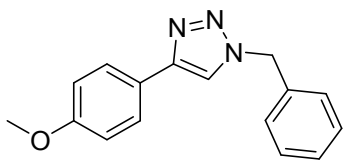
1-allyl-4-phenyl-1*H*-1.2.3-triazole[2]:
White solid, mp 58-60°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ= 5.01-5.04 (2H, d, *J* =6.2 Hz), 5.33-5.40 (2H, dd, *J* =8 Hz & 16.86 Hz), 6.03-6.12 (1H, m), 7.28-7.44 (3H, m), 7.78 (1H, s), 7.82-7.85 (2H, d, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ= 51.1, 119.9, 120.5, 126.1, 128.5, 129.2, 131.0, 131.7, 147.3



1-benzyl-4-(4-nitrophenyl)-1*H*-1,2,3-triazole
Yellow solid, mp: 166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.61(2H, s), 7.33-7.43(5H, m), 7.81(1H, s), 7.96(2H, d, *J*=8.8 Hz), 8.23(2H, d, *J*=8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 54.4, 120.9, 124.2, 126.1, 128.2, 129.0, 129.3, 134.2, 136.8, 145.9, 147.3.

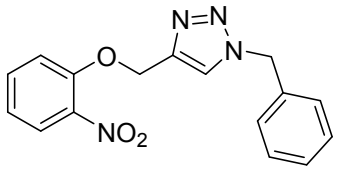


1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole
White solid; ^{1}H NMR (400 MHz, DMSO-d6) δ= 3.75 (3H, s), 5.59 (2H, s), 6.95 (2H, d, *J* = 10 Hz), 7.29-7.35 (4H, m), 7.27 (1H, d, *J* = 8.5), 8.24 (1H, s), 8.45 (1H, s); ^{13}C NMR (100 MHz, DMSO-d6) δ= 53.6, 55.6, 114.7, 121.1, 123.8, 127.1, 128.4, 128.7, 129.3, 136.5, 147.2, 159.6.

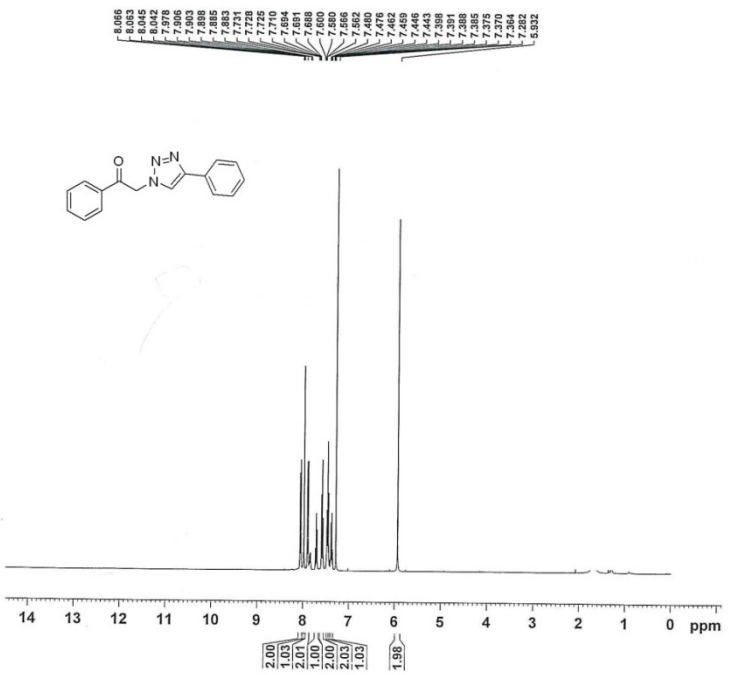


1-benzyl-4-((2-nitrophenoxy)methyl)-1*H*-1,2,3-triazole

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ= 5.35 (2H, s), 5.53 (2H, s), 7.05-7.06 (1H, d, *J* =7.4 Hz), 7.26-7.37 (6H, m), 7.53 (1H, d), 7.64 (1H, s), 7.82- 7.84 (1H, t); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 54.7, 64.3, 115.9, 121.5, 123.5, 126.1, 128.5, 129.3, 129.6, 134.7, 140.6, 151.9



^{1}H-NMR and ^{13}C-NMR spectra of the products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8.042
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7.710
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7.688
7.680
7.580
7.566
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7.480
7.476
7.462
7.459
7.446
7.443
7.398
7.391
7.388
7.385
7.375
7.370
7.364
7.282
5.932
O
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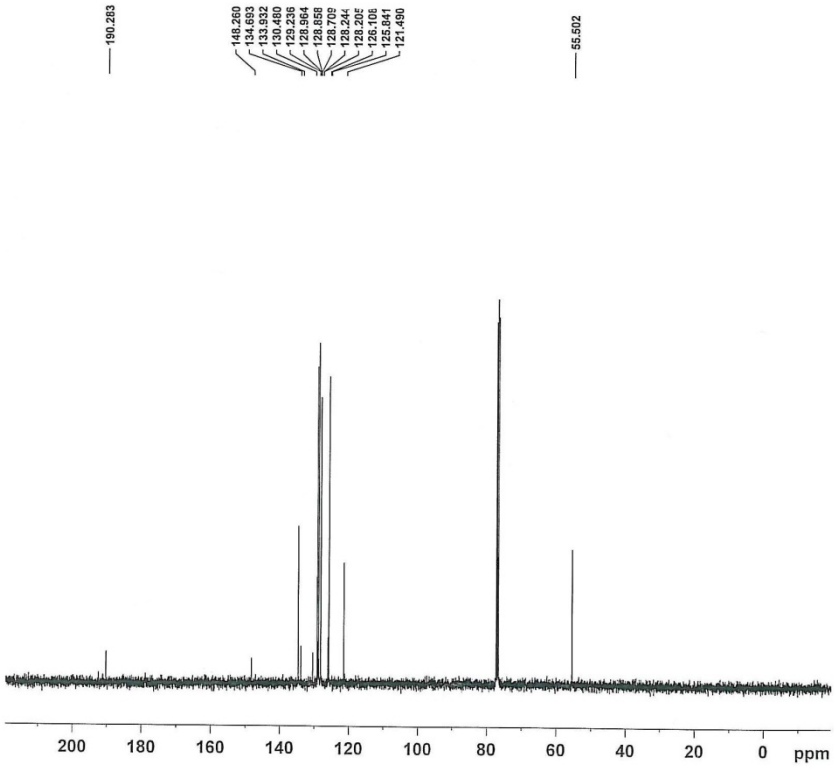
1.00
2.00
2.03
1.03
1.98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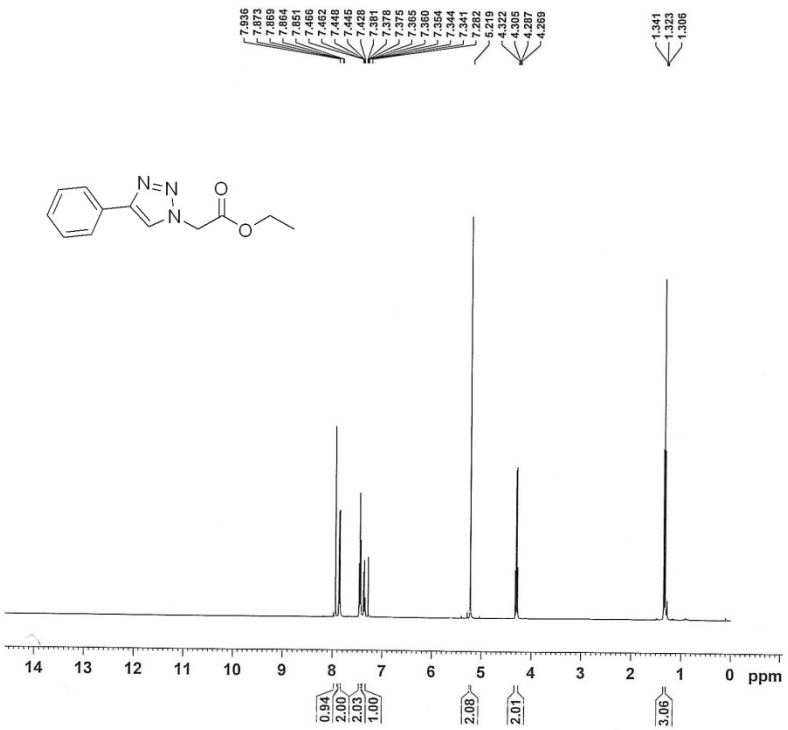
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4.322
4.305
4.287
4.269
1.341
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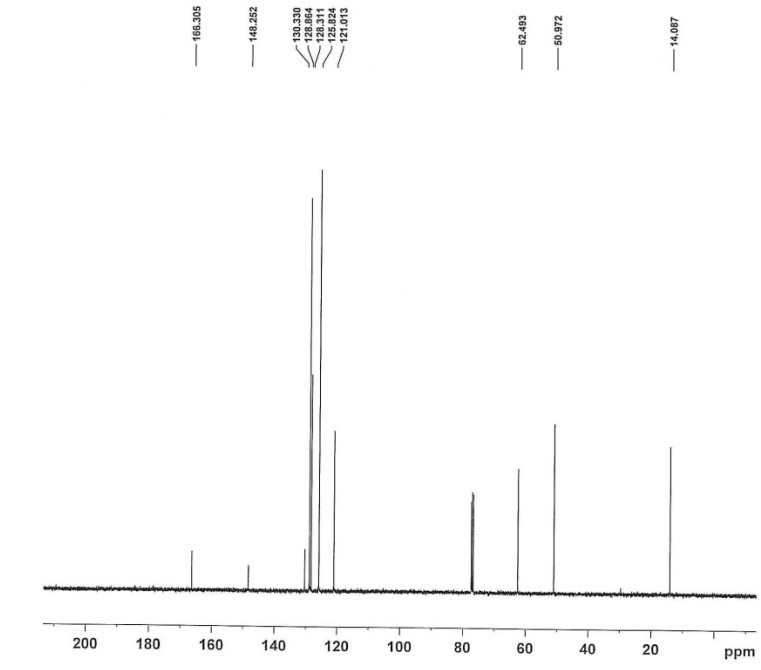
3.06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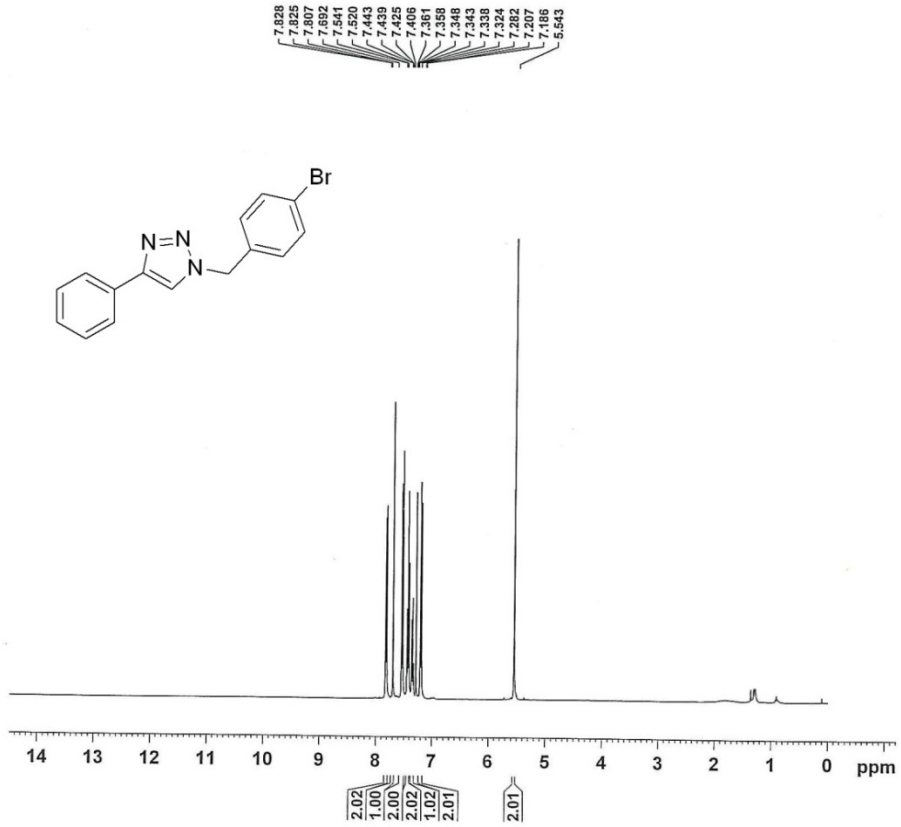
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7.343
7.338
7.324
7.282
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7.186
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Br
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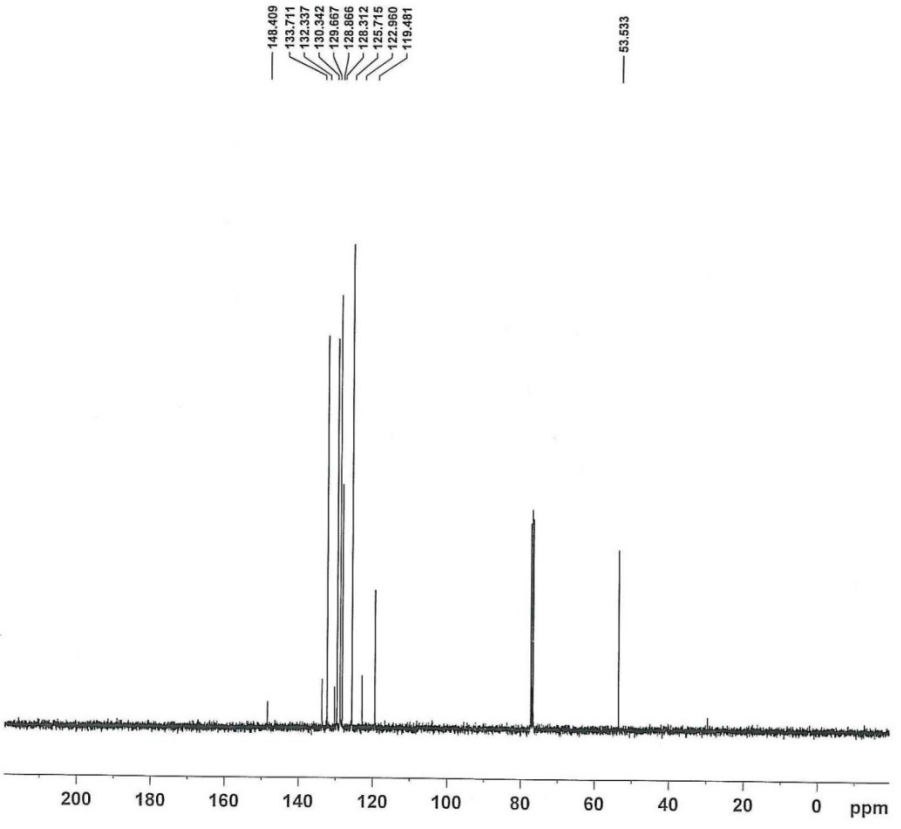
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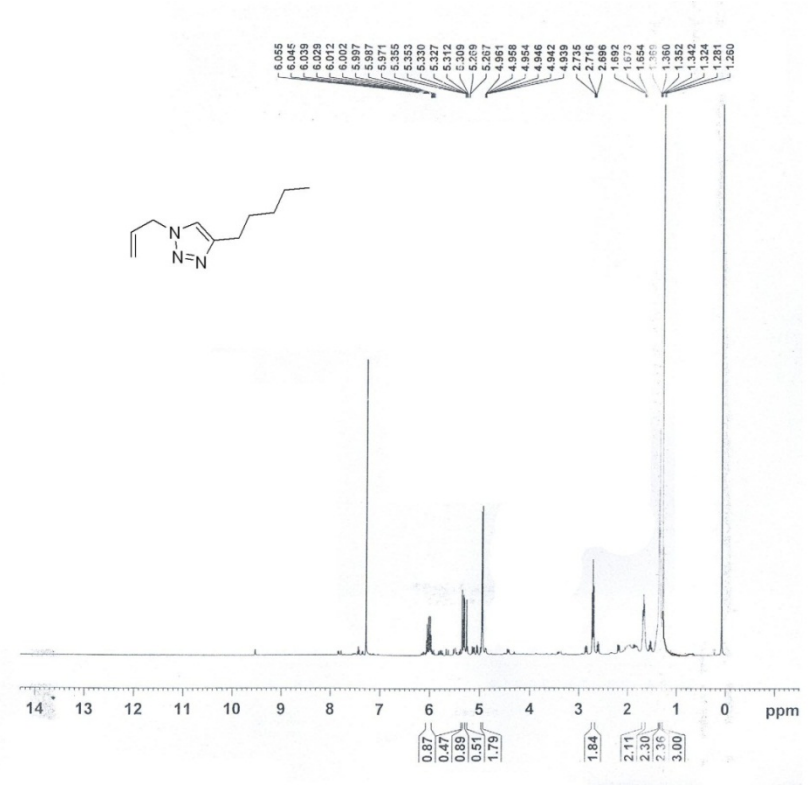
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5.309
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5.267
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4.958
4.954
4.946
4.942
4.939
2.715
2.696
1.692
1.673
1.654
1.360
1.352
1.342
1.324
1.281
1.260
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
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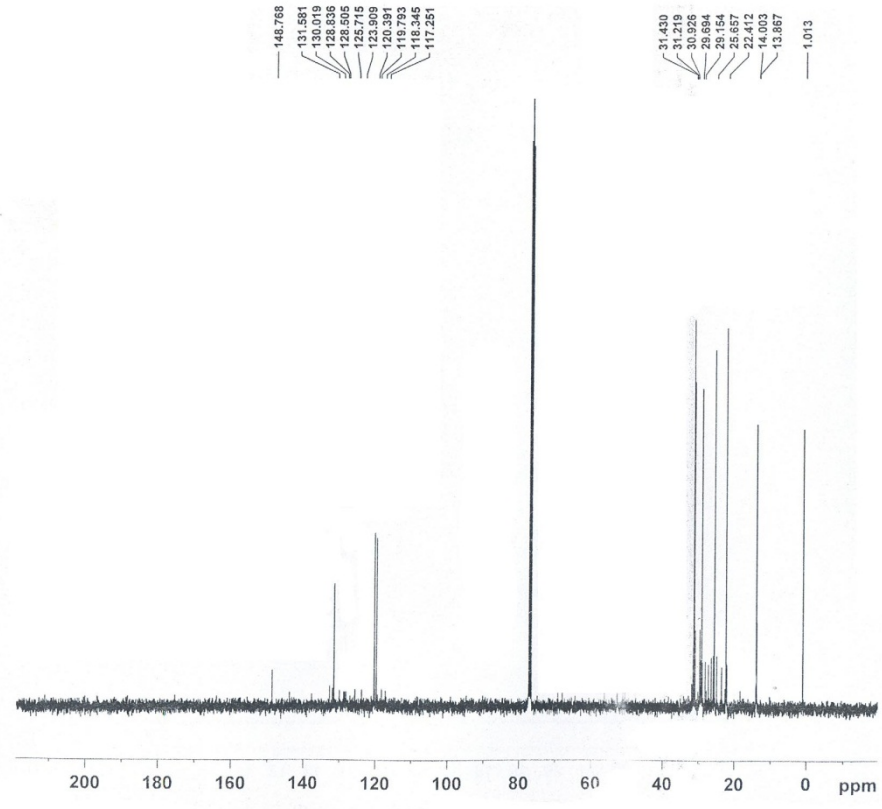
2.36
3.00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125.715
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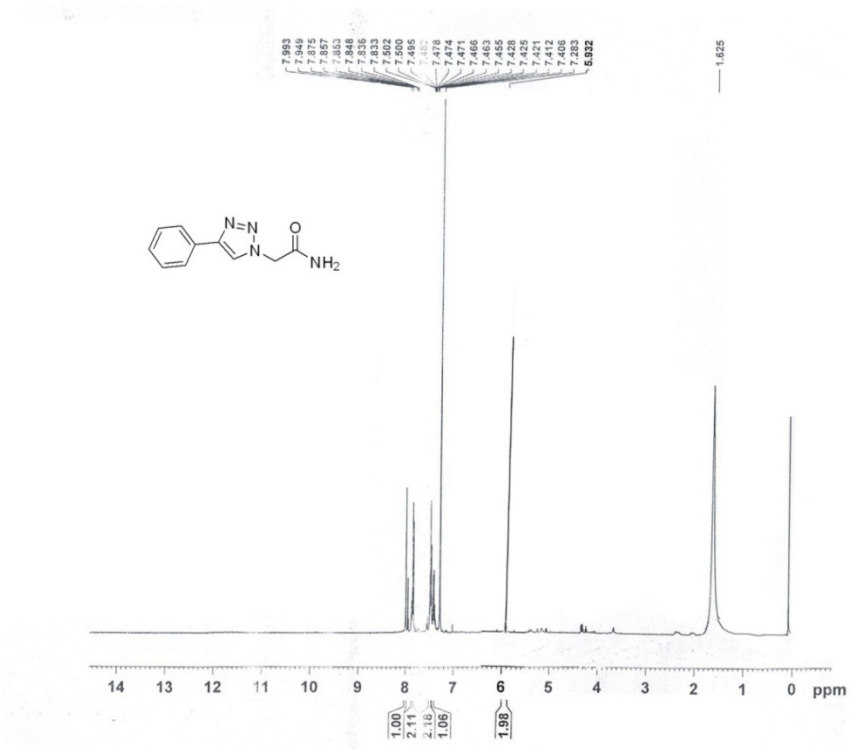
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7.848
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7.466
7.463
7.455
7.428
7.425
7.421
7.412
7.406
7.283
5.932
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N
NH2
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2.18
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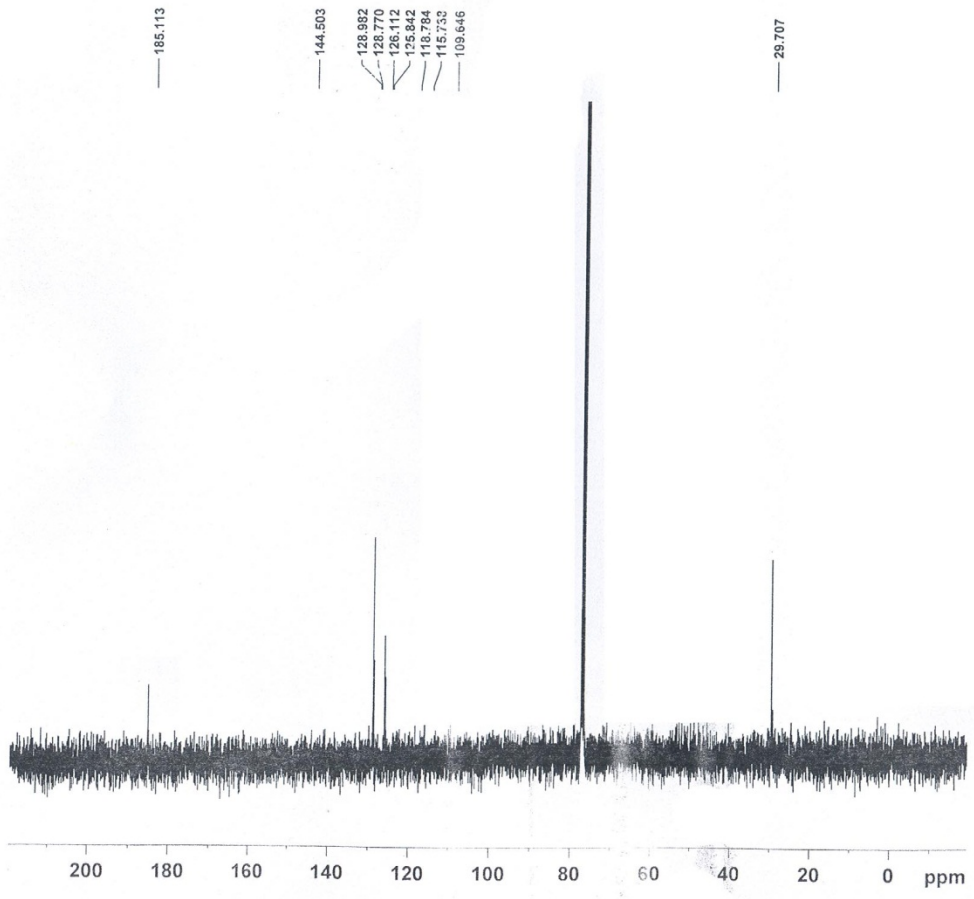
1.98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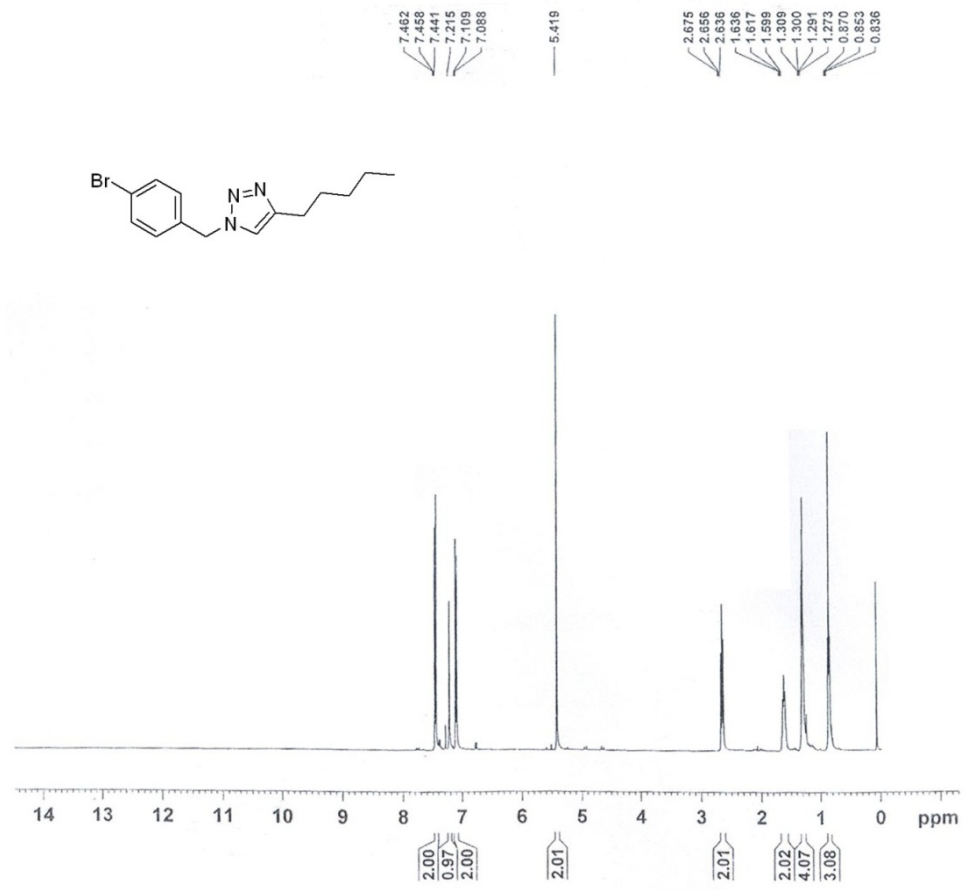
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7.088
5.419
2.675
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2.636
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1.599
1.309
1.300
1.291
1.273
0.870
0.853
0.836
Br
N=N
N
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
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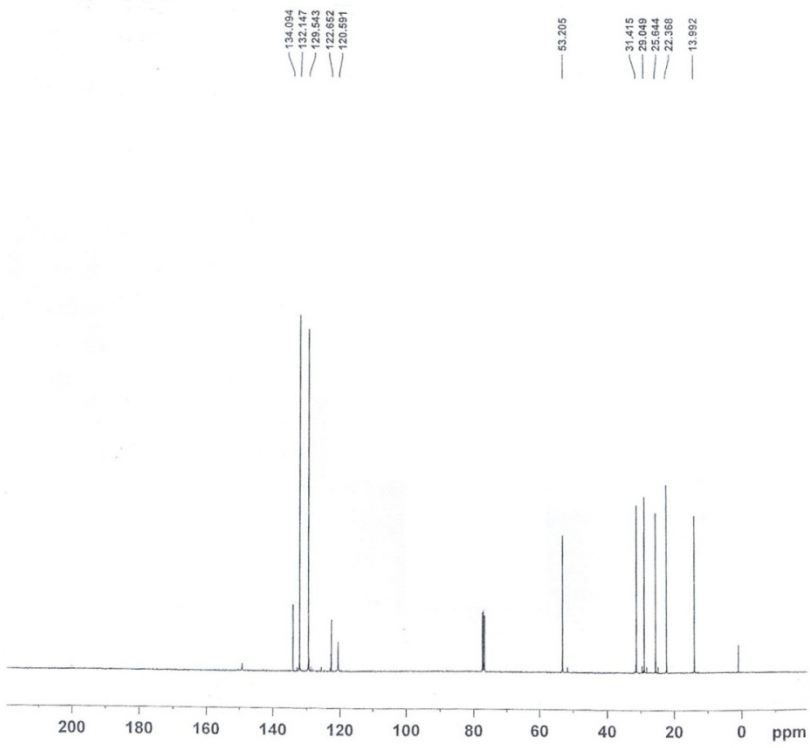
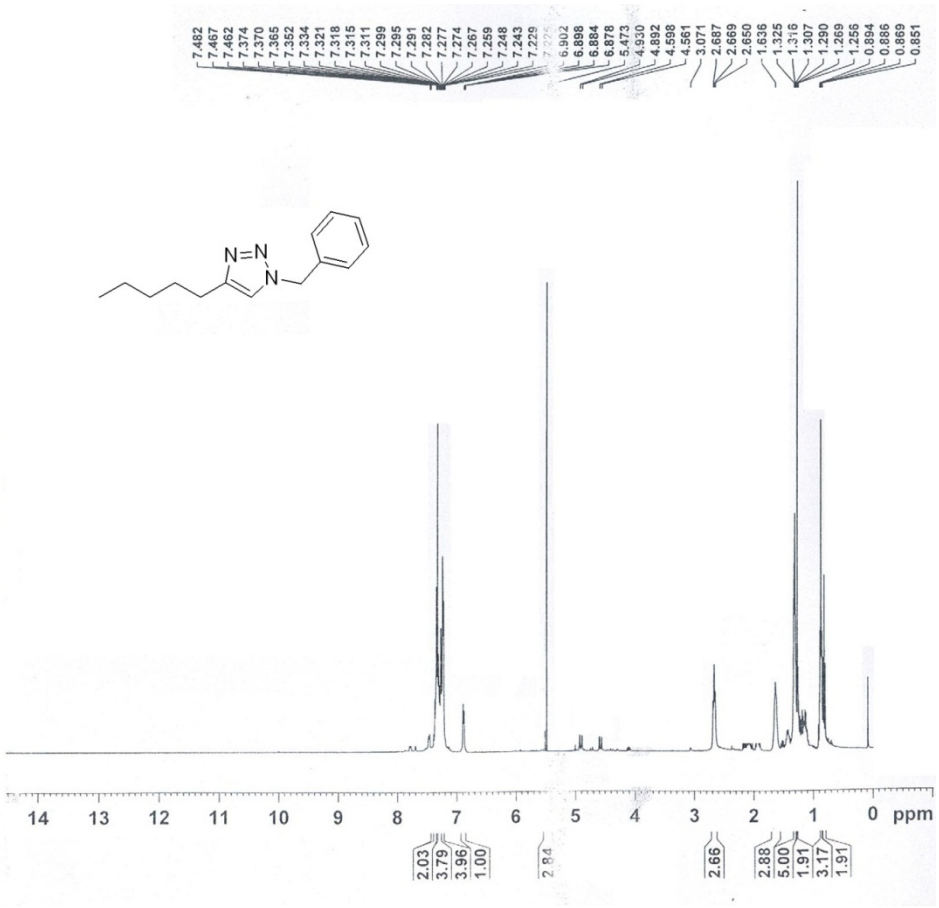
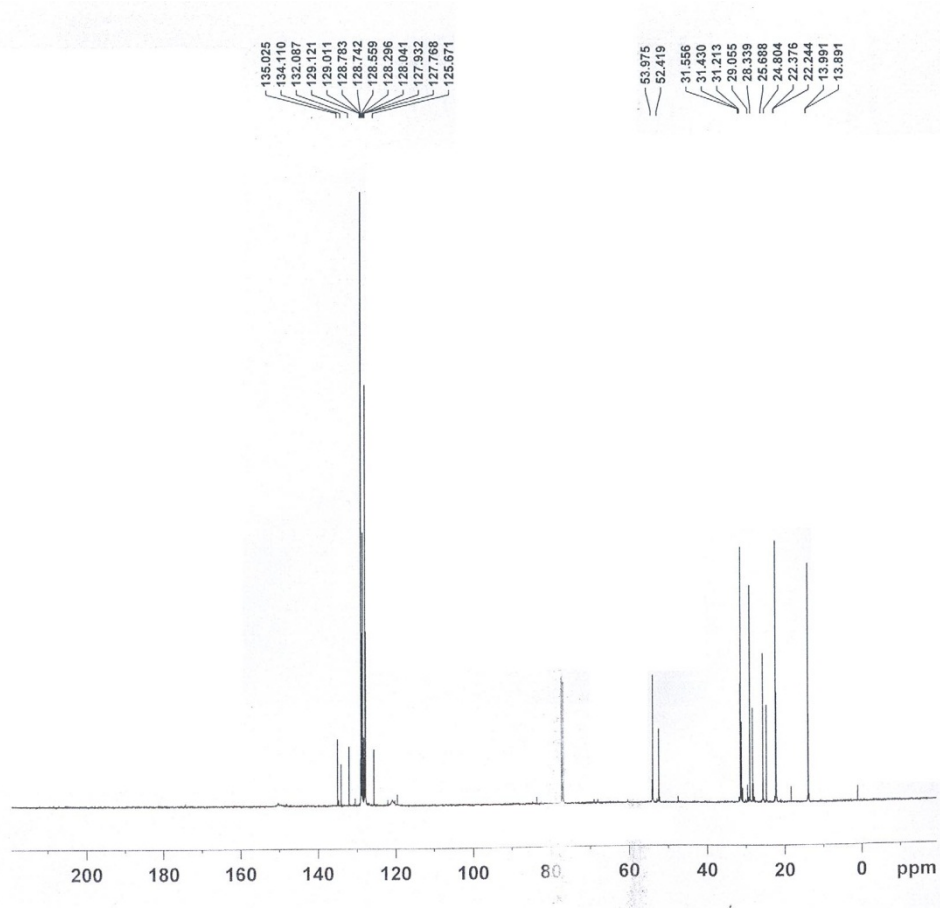
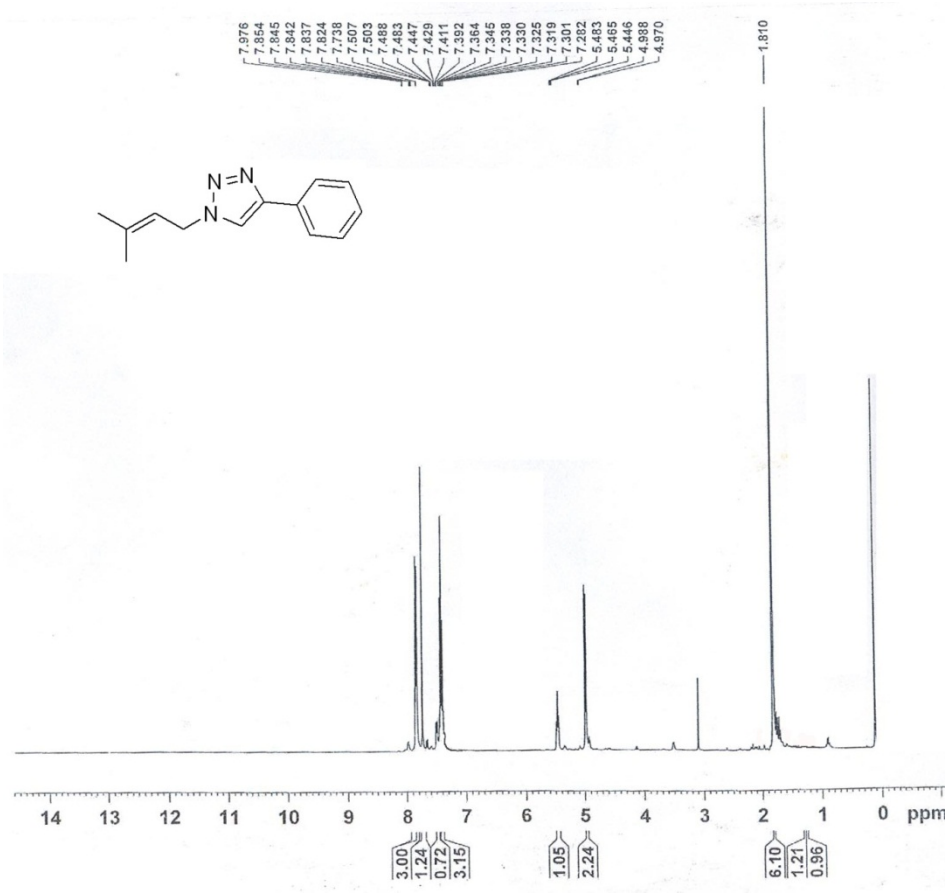
0.97
2.00
2.01
2.01
2.02
4.07
3.08


134.094
132.147
129.643
122.652
120.691
53.205
31.415
29.049
25.644
22.368
13.992
200 180 160 140 120 100 80 60 40 20 0 ppm


7.482
7.467
7.462
7.374
7.370
7.365
7.352
7.334
7.321
7.318
7.315
7.311
7.299
7.295
7.291
7.282
7.277
7.274
7.267
7.259
7.248
7.243
7.229
6.902
6.898
6.884
6.878
5.473
4.930
4.892
4.598
4.561
3.071
2.687
2.669
2.650
1.636
1.325
1.316
1.307
1.290
1.269
1.256
0.894
0.886
0.869
0.851
N=N
N
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.03
3.79
3.96
1.00
2.84
2.66
2.88
5.00
1.91
3.17
1.91


135.025
134.110
132.087
129.121
129.011
128.783
128.742
128.559
128.296
128.041
127.932
127.768
125.671
53.975
52.419
31.556
31.430
31.213
29.055
28.339
25.688
24.804
22.376
22.244
13.991
13.891
200 180 160 140 120 100 80 60 40 20 0 ppm


7.976
7.854
7.845
7.842
7.837
7.824
7.738
7.507
7.503
7.488
7.483
7.447
7.429
7.411
7.392
7.364
7.345
7.338
7.330
7.325
7.319
7.301
7.282
5.483
5.465
5.446
4.988
4.970
1.810
N=N
N
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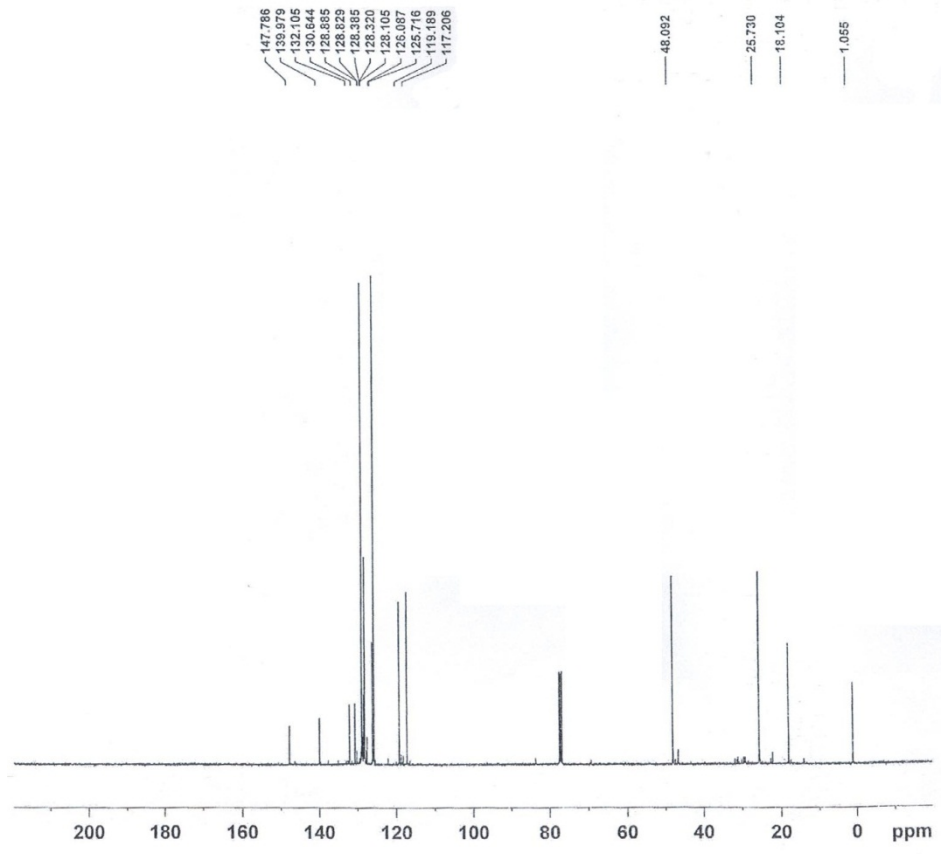
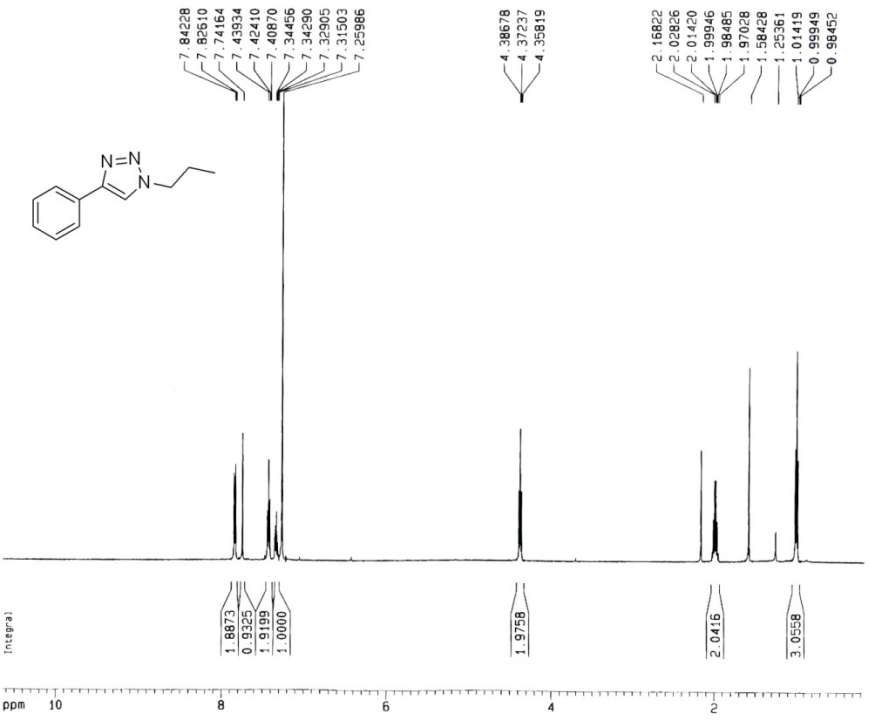
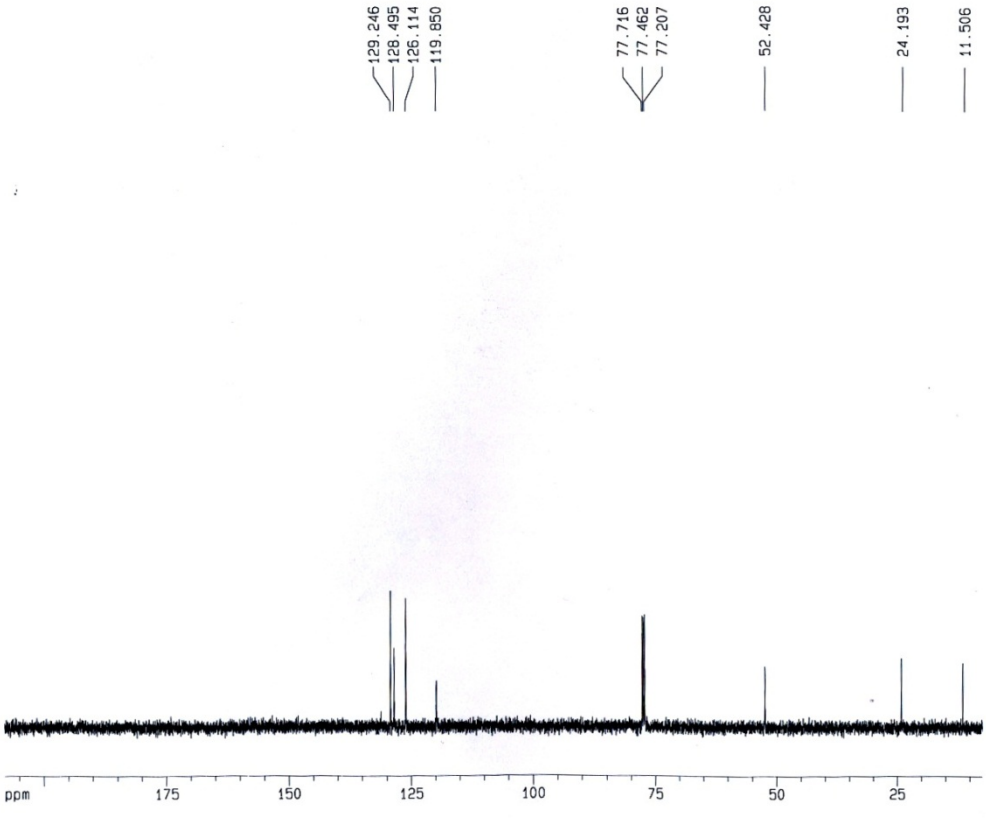
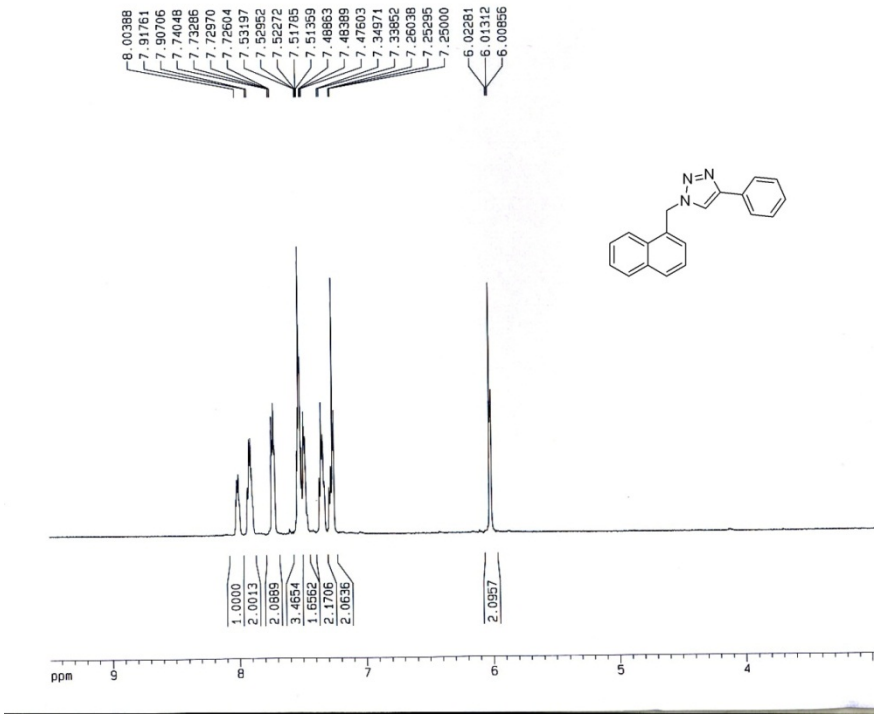
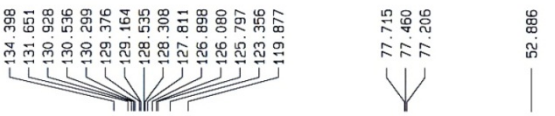
3.00
1.24
0.72
3.15
1.05
2.24
6.10
1.21
0.96


147.786
139.979
132.105
130.644
128.885
128.829
128.385
128.320
128.105
126.087
125.716
119.189
117.206
48.092
25.730
18.104
1.055
200 180 160 140 120 100 80 60 40 20 0 ppm


7.84228
7.82610
7.74164
7.43934
7.42410
7.40870
7.34456
7.34290
7.32905
7.31503
7.25986
4.38678
4.37237
4.35819
2.16822
2.02826
2.01420
1.99946
1.98485
1.97028
1.58428
1.25361
1.01419
0.99949
0.98452
N=N
N
Integral
1.8873
0.9325
1.9199
1.0000
1.9758
2.0416
3.0558
ppm
10
8
6
4
2


129.246
128.495
126.114
119.850
77.716
77.462
77.207
52.428
24.193
11.506
ppm
175
150
125
100
75
50
25


8.00388
7.91761
7.90706
7.74048
7.73286
7.72970
7.72604
7.53197
7.52952
7.52272
7.51785
7.51359
7.48863
7.48389
7.47603
7.34971
7.33852
7.26038
7.25295
7.25000
6.02281
6.01312
6.00856
1.0000
2.0013
2.0889
3.4654
1.6562
2.1706
2.0636
2.0957
ppm
9
8
7
6
5
4


134.398
131.651
130.928
130.536
130.299
129.376
129.164
128.535
128.308
127.811
126.898
126.080
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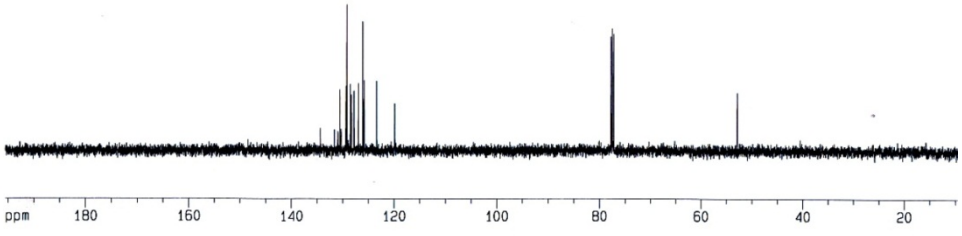
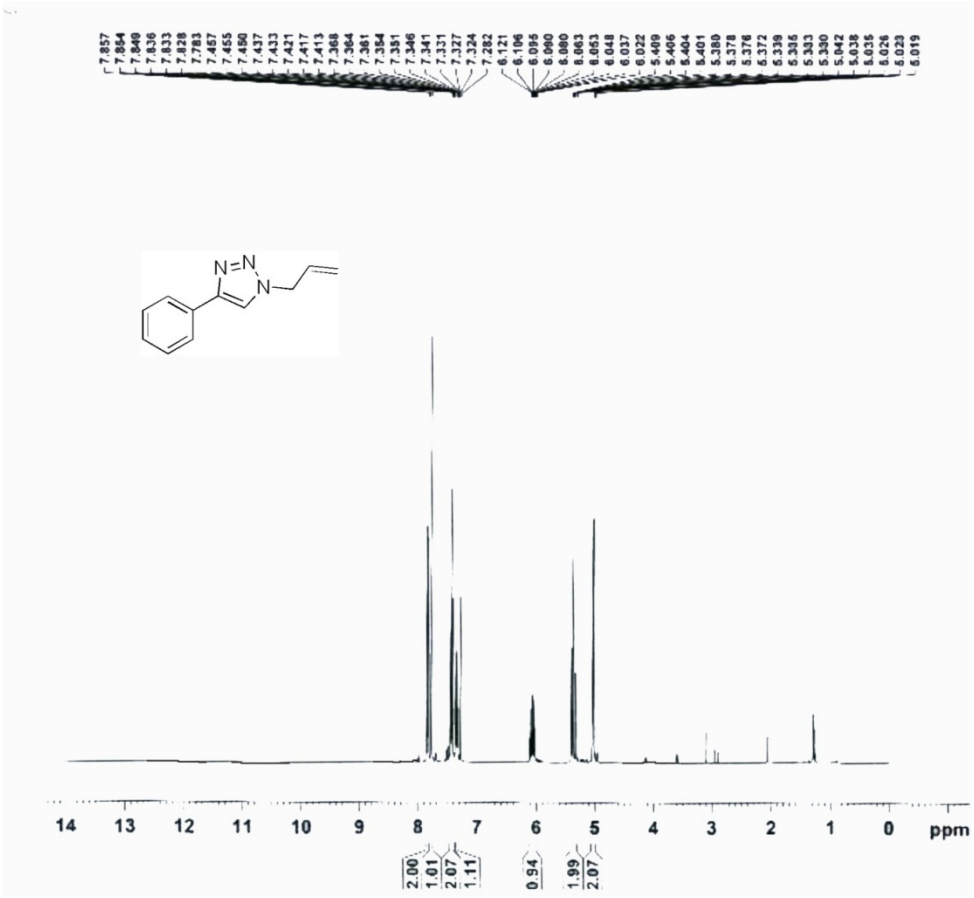
123.356
119.877
77.715
77.460
77.206
52.886


ppm
180
160
140
120
100
80
60
40
20


7.857
7.854
7.840
7.836
7.833
7.828
7.783
7.457
7.455
7.450
7.437
7.433
7.421
7.417
7.413
7.368
7.364
7.361
7.354
7.351
7.346
7.341
7.331
7.327
7.324
7.282
6.121
6.106
6.095
6.090
6.080
6.063
6.048
6.037
6.022
5.409
5.406
5.404
5.401
5.380
5.378
5.378
5.372
5.339
5.336
5.333
5.330
5.042
5.038
5.035
5.026
5.023
5.019
N=N
N
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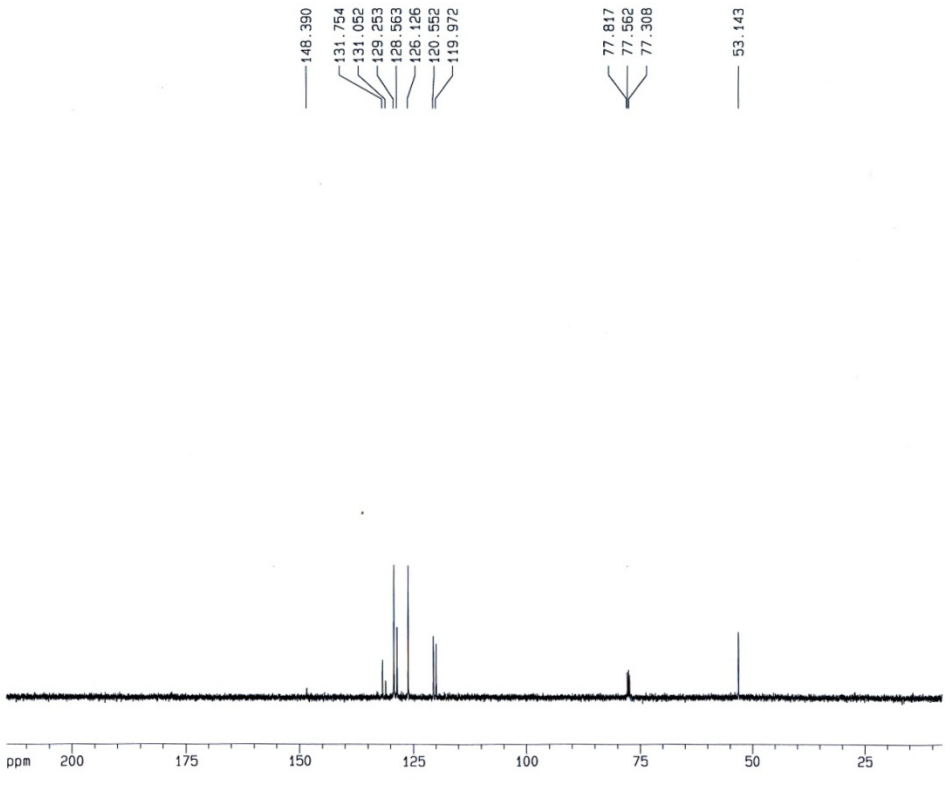
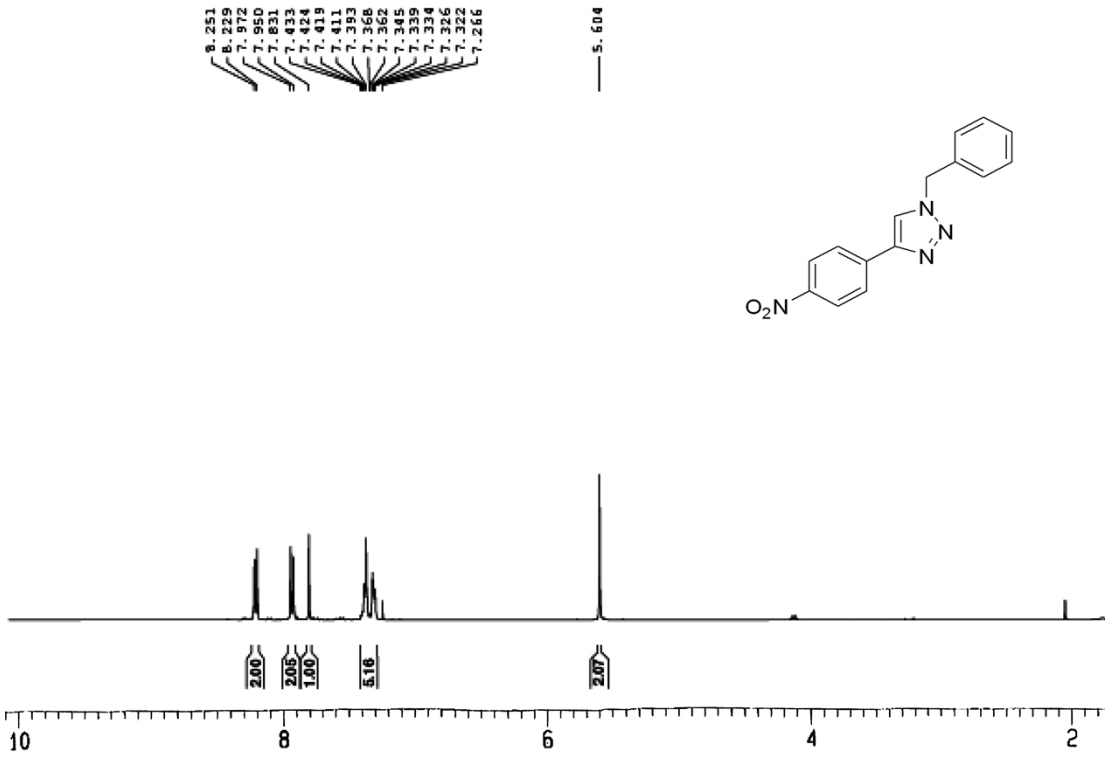
2.00
1.01
2.07
1.11
0.94
1.99
2.07


148.390
131.754
131.052
129.253
128.563
126.126
120.552
119.972
77.817
77.562
77.308
53.143
ppm 200 175 150 125 100 75 50 25


8.251
8.229
7.972
7.950
7.831
7.433
7.424
7.419
7.411
7.393
7.368
7.362
7.345
7.339
7.334
7.326
7.322
7.266
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O2N
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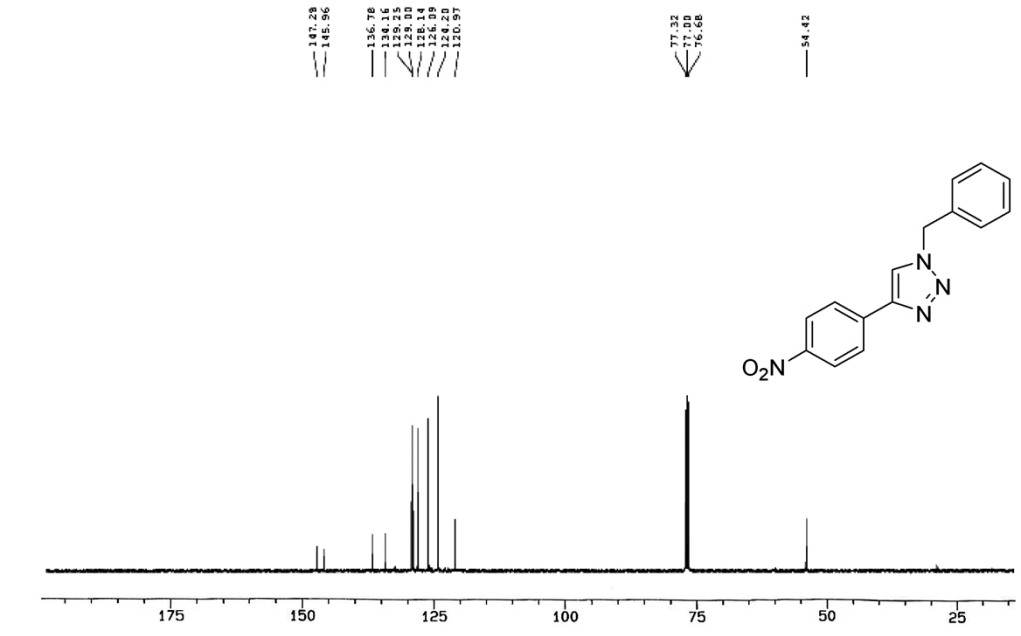
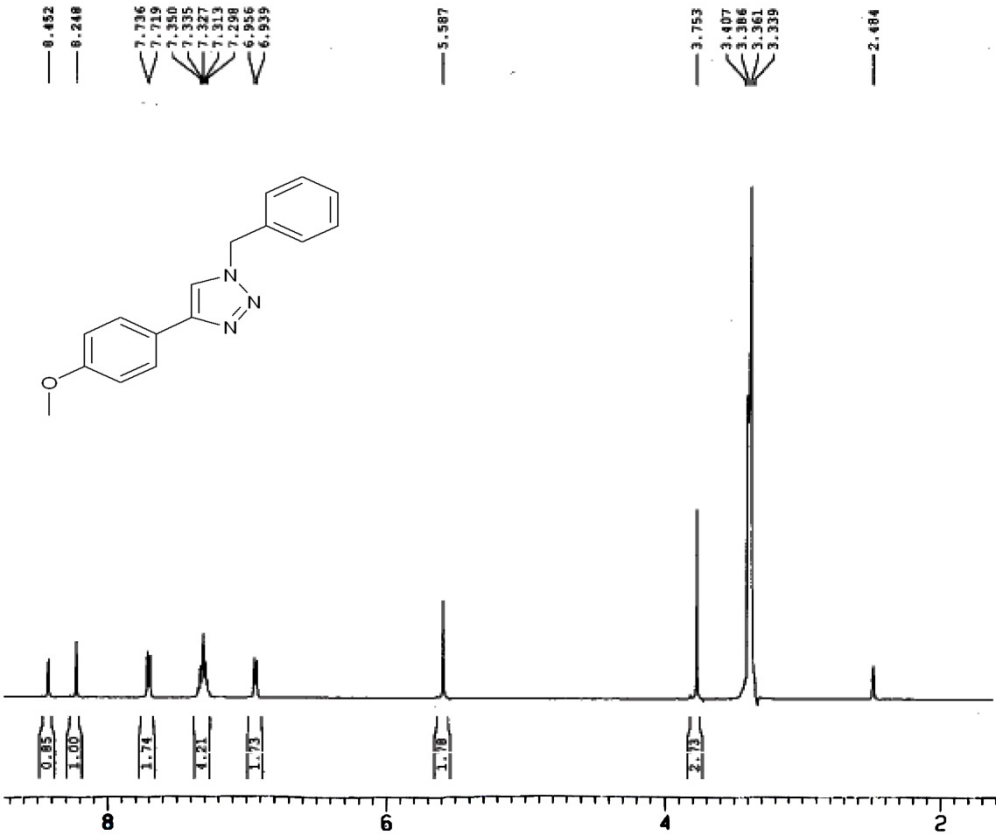
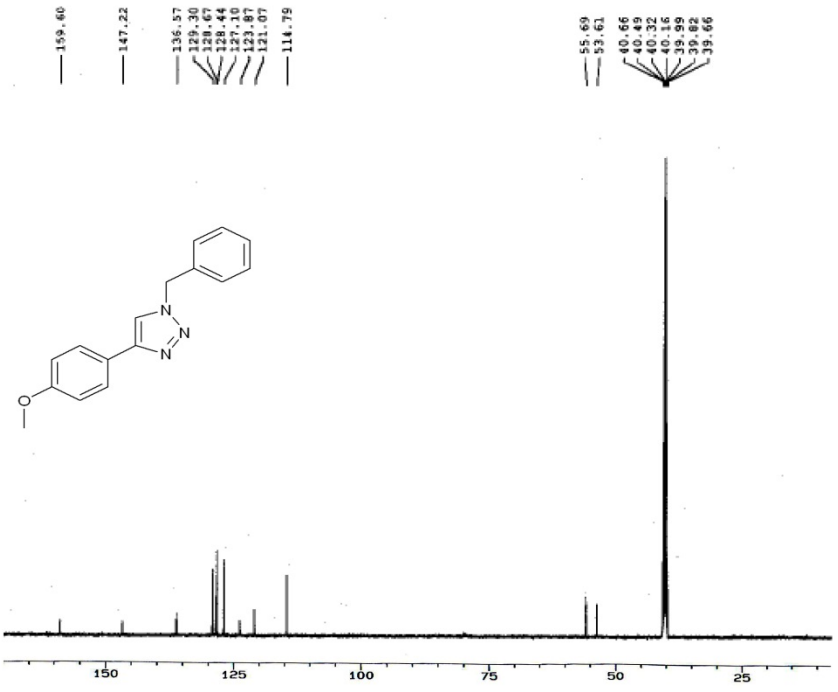
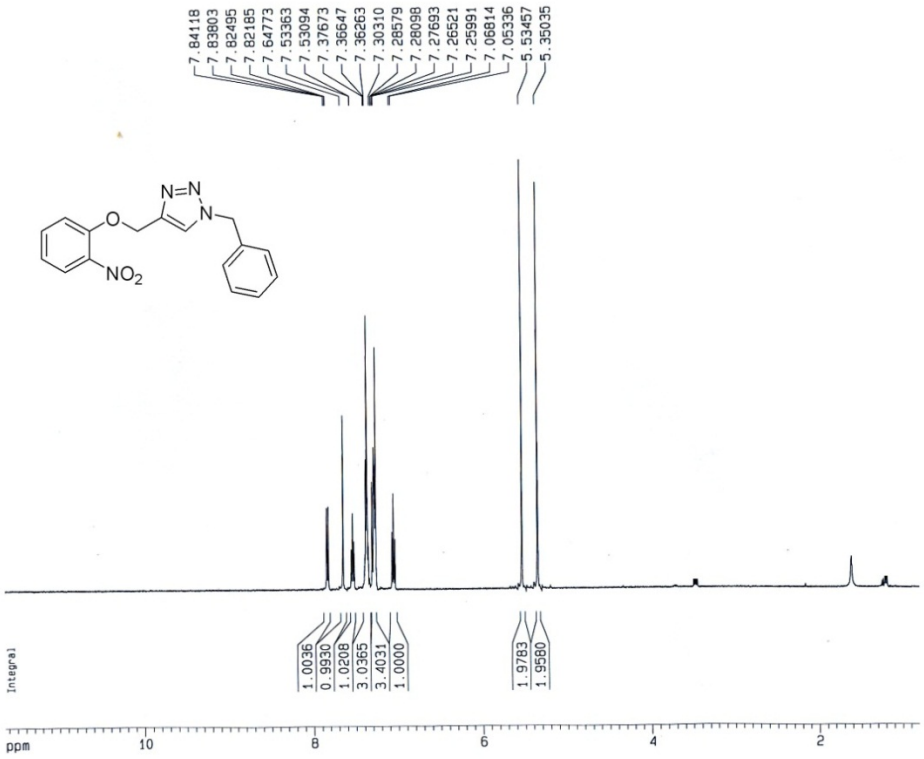
1.00
5.16
2.07
10
8
6
4
2


147.28
145.96
136.78
134.16
129.25
129.00
128.14
126.38
124.28
120.97
77.32
77.00
76.68
54.42
O2N
175
150
125
100
75
50
25


8.452
8.248
7.736
7.719
7.350
7.335
7.327
7.313
7.298
6.956
6.939
5.587
3.753
3.407
3.386
3.361
3.339
2.484
0.85
1.00
1.74
4.21
1.73
1.78
2.13
8
6
4
2


159.60
147.22
136.57
129.30
128.67
128.44
127.10
123.87
121.07
114.79
55.69
53.61
40.66
40.49
40.32
40.16
39.99
39.82
39.66
150
125
100
75
50
25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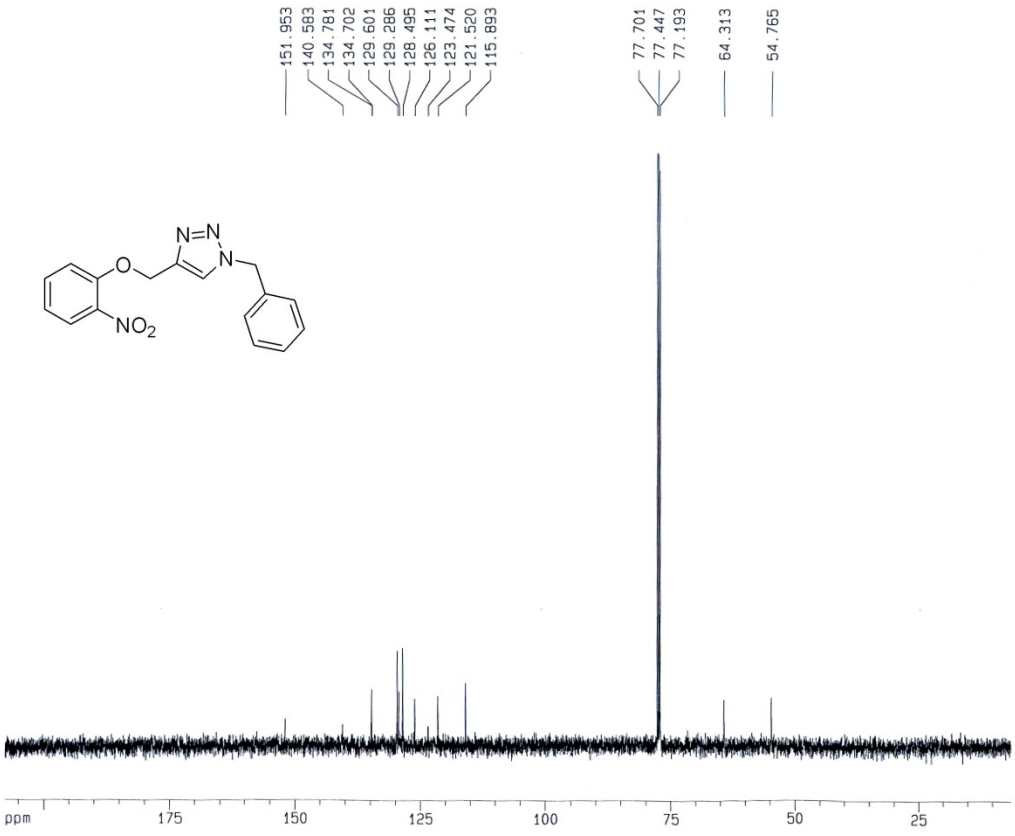
7.82495
7.82185
7.64773
7.53363
7.53094
7.37673
7.36647
7.36263
7.30310
7.28579
7.28098
7.27693
7.26521
7.25991
7.06814
7.05336
5.53457
5.35035
N=N
N
O
NO2
Integral
1.0036
0.9930
1.0208
3.0365
3.4031
1.0000
1.9783
1.9580
ppm
10
8
6
4
2


151.953
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134.781
134.702
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129.286
128.495
126.111
123.474
121.520
115.893
77.701
77.447
77.193
64.313
54.765
N=N
N
O
NO2
ppm
175
150
125
100
75
50
25

References:

[1] M. Boominathan, N. Pugazhenthiran, M. Nagaraj, S. Muthusubramanian, S. Murugesan, N. Bhuvanesh, *ACS Sus. Chem. Eng*., 2013, **1**, 1415.
[2] S. R. Kale, S. S. Kahandal, B. G. Manoj, R. V. Jayaram, *RSC Adv.*, 2013,**3**, 8184.