Recyclable ruthenium(II) complex supported on magnetic nanoparticles: A regioselective catalyst for alkyne azide cycloaddition

Dong Wang, Lionel Salmon, Jaime Ruiz and Didier Astruc*

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1. General remarks:

All reactions and manipulations were performed in a nitrogen-filled glove-box or under nitrogen using standard Schlenk techniques, unless otherwise noted. Tetrahydrofuran was freshly distilled from sodium/benzophenone. Toluene was distilled from sodium. All commercially available reagents were used as received, unless indicated otherwise.

Flash column chromatography was performed using silica gel (300–400 mesh). ^{1}H NMR spectra were recorded with 300 MHz spectrometer, and ^{13}C NMR spectra were recorded at 75 with 300 MHz spectrometer. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon Villeurbanne, France.

2. Experimental section

Synthesis of compound 5:

The freshly prepared $(Cp^*RuCl_2)_n$ (46 mg, 0.15 mmol) was placed into a 100 mL flask and fitted with a reflux condenser. The flask was purged with nitrogen and 50 mL of absolute ethanol was added. **4** (434 mg, 0.36 mmol) dissolved in 5 mL of THF were added under nitrogen. The mixture was refluxed for 60 h and allowed to cool to room temperature. Then the solvent was removed under vacuum, the obtained solid was washed repeatedly with cold pentane and diethyl ether to afford 326 mg 80 % of **5** as orange microcrystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.41-8.06 (m, 28H), 6.74 (bs, 2H), 3.61 (s, 18H), 2.74-2.92 (m, 4H), 1.58-1.82 (m, 4H), 1.13 (s, 15H), 0.78 (t, *J* = 6.9 Hz, 4H). MS (MALDI-TOF; m/z), calcd. for $C_{60}H_{75}ClN_2O_8P_2RuSi_2$: 1206.3, found: MNa^+ 1228.3. Anal. calcd for $C_{60}H_{75}ClN_2O_8P_2RuSi_2$ C 59.71, H 6.26, N 2.32, found (%) C 59.95, H 6.49, N 2.03.

Synthesis of ruthenium(II) complex supported on magnetic nanoparticles ($Cp^*Ru/SiO_2/\gamma$-Fe_2O_3) 6:

0.16 g of 5 dissolved in 5 mL of dry CH_2Cl_2 were added to a suspension of 0.3 g of magnetic nanoparticles SiO_2/γ-Fe_2O_3 2 in 30 mL of dry toluene. The mixture was then stirred at 90°C under an atmosphere of nitrogen overnight. The dark brown solid material obtained was magnetically separated, washed repeatedly with toluene, CH_2Cl_2, and THF to remove any unanchored species and then dried under vacuum. The obtained catalyst was kept under an atmosphere of nitrogen for further catalytic application.

General procedures for magnetic catalyst 6 - catalyzed cycloaddition of alkynes and organic azides to 1,5-disubstituted 1,2,3-trizoles :

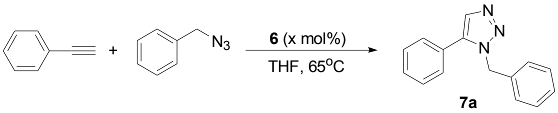
A dried Schlenk tube equipped with a magnetic stirring bar was charged under a nitrogen atmosphere with alkyne (0.5 mmol), organic azide (0.5 mmol), catalyst 6 (2 mol%, 63 mg), and 2 mL of dried THF. The mixture was heated at 65 °C for 3 h. After cooling to room temperature, the mixture was diluted with ethyl acetate. The catalyst was collected by the usage of a lab magnet and then washed with ethyl acetate (3 x 5 mL) and CH_2Cl_2 (3 x 5 mL) and then dried at room temperature under vacuum. During above-mentioned treatment for the reaction, the catalyst was always kept under a nitrogen atmosphere. The combined organic phase was dried over Na_2SO_4

and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum ether /ethyl acetate as eluent) to yield corresponding triazole. And the recovered catalyst was used for the next reaction cycle.

Optimization of catalyst loading

A dried Schlenk tube equipped with a magnetic stirring bar was charged under a nitrogen atmosphere with phenylacetylene (0.5 mmol), benzyl azide (0.5 mmol), catalyst **6** (x mol%), and 2 mL of dried THF. The mixture was heated at 65^{o}C. After cooling to room temperature, the mixture was diluted with ethyl acetate. The catalyst was collected using a lab magnet, washed with ethyl acetate (3 x 5 mL) and CH_2Cl_2 (3 x 5 mL) and dried at room temperature under vacuum. The combined organic phase was dried over Na_2SO_4 and filtered. The filtrate was removed under reduced pressure, which produces the crude product that was further purified by silica gel chromatography (petroleum ether /ethyl acetate as eluent), yielding the corresponding triazole.

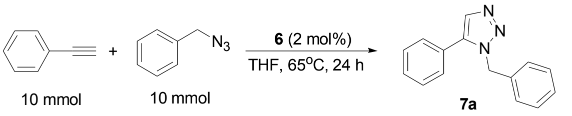
Table S1 Optimization of catalyst loading



Cat. (x mol%)	Time	Yield	Selectivity
2 mol%	3 h	91%	>99.9%
1 mol%	3 h	81%	>99.9%
1 mol%	12 h	87%	99.1%
0.5 mol%	3 h	54%	98.9%
0.5 mol%	12 h	74%	98.3%

Large-scale synthesis of 7a

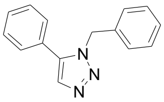
A dried Schlenk tube equipped with a magnetic stir bar was charged under a nitrogen atmosphere with phenylacetylene (10 mmol), benzyl azide (10 mmol), catalyst **6** (2 mol%), and 40 mL of dried THF. The mixture was heated at 65^{o}C in 24 h. After cooling to room temperature, the mixture was diluted with ethyl acetate. The catalyst was collected by the usage of a lab magnet, washed with ethyl acetate (3 x 30 mL) and CH_2Cl_2 (3 x 30 mL) and dried at room temperature under vacuum. The combined organic phase was dried over Na_2SO_4 and filtered. The filtrate was removed under reduced pressure yielding the crude product that was further purified by silica gel chromatography (petroleum ether /ethyl acetate as eluent) to produce the corresponding triazole. Then, the recovered catalyst was used again for the second reaction cycle (Scheme S1).



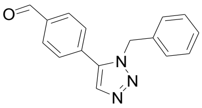
Run 1: 79% yield, 99.3% selectivity
Run 2: 73% yield, 98.4% selectivity

Scheme S1 Cycloaddition reaction between phenylacetylene and benzyl azide in 10-mmol scale.

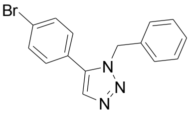
3. Spectral data of the compounds:



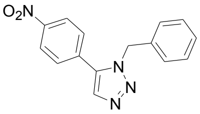
1-Benzyl-5-phenyl-1H-[1,2,3]triazole[1] **: 7a** was isolated as a white solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.77 (s, 1H), 7.41-7.48 (m, 3H), 7.27-7.34 (m, 5H), 7.09-7.13 (m, 2H), 5.58 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 138.17, 135.59, 133.22, 129.89, 129.55, 128.99, 128.84, 128.13, 127.14, 126.87, 51.77.



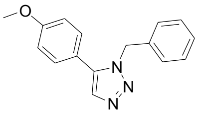
4-(3-Benzyl-3H-[1,2,3]triazol-4-yl)-benzaldehyd[1] **: 7b** was isolated as a white solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 10.08 (s, 1H), 7.93-7.97 (m, 2H), 7.84 (s, 1H), 7.45-7.48 (m, 2H), 7.29-7.33 (m, 3H), 7.07-7.12 (m, 2H), 5.62 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 191.30, 136.99, 136.70, 135.11, 133.87, 132.76, 130.12, 129.45, 129.01, 128.44, 127.06, 52.27.



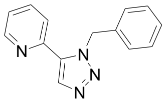
1-Benzyl-5-(4-bromo-phenyl)-1H-[1,2,3]triazole: 7c was isolated as a pale yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.76 (s, 1H), 7.57 (d, J = 8.7 Hz, 2H), 7.30-7.34 (m, 3H), 7.08-7.15 (m, 4H), 5.56 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 137.14, 135.32, 133.51, 132.24, 130.45, 128.97, 128.34, 127.08, 125.86, 124.04, 51.97. IR (cm^{-1}): 3439, 3064, 1603, 1550, 1481, 1242, 1210, 1113, 1074, 1008, 974, 824, 728, 584. TOF HRMS: calcd. for $C_{15}H_{12}N_3NaBr$ $[M+Na]^+$: 336.0106, found: 336.0109.



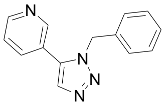
1-Benzyl-5-(4-nitro-phenyl)-1H-[1,2,3]triazole: 7d was isolated as a yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 8.26-8.30 (m, 2H), 7.86 (s, 1H), 7.45-7.50 (m, 2H), 7.31-7.34 (m, 3H), 7.06-7.10 (m, 2H), 5.63 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 148.28, 136.09, 134.90, 134.14, 133.37, 129.76, 129.11, 128.57, 126.99, 124.16, 52.39. IR (cm^{-1}): 3439, 3103, 1957, 1603, 1518, 1454, 1353, 1108, 974, 854, 729, 584. TOF HRMS: calcd. for $C_{15}H_{13}N_4O_2$ $[M]^+$: 281.1033, found: 281.1043.



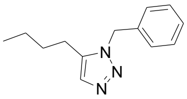
1-Benzyl-5-(4-methoxy-phenyl)-1H-[1,2,3]triazole [2] **: 7e** was isolated as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.58 (s, 1H), 7.15-7.20 (m, 3H), 7.05-7.09 (m, 2H), 6.97-7.00 (m, 2H), 6.81-6.84 (m, 2H), 5.42 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 160.52, 138.02, 135.72, 133.05, 130.24, 128.84, 128.11, 127.12, 118.96, 114.44, 55.41, 51.68.



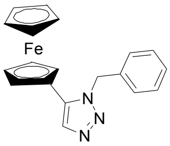
2-(3-Benzyl-3H-[1,2,3]triazol-4-yl)-pyridine [3] **: 7f** was isolated as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.72 (d, J = 4.8 Hz, 1H), 8.04 (s, 1H), 7.73-7.79 (m, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.26-7.32 (m, 6H), 6.20 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 149.55, 147.02, 137.08, 136.16, 135.65, 133.68, 128.52, 127.89, 123.37, 123.30, 122.82, 53.13.



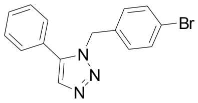
3-(3-Benzyl-3H-[1,2,3]triazol-4-yl)-pyridine [3] **: 7g** was isolated as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.66 (s, 1H), 8.52 (s, 1H), 7.79 (d, J = 2.1 Hz, 1H), 7.51-7.55 (m, 1H), 7.24-7.36 (m, 4H), 7.03-7.06 (m, 2H), 5.57 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 150.60, 149.28, 136.18, 135.02, 134.88, 133.96, 129.01, 128.44, 127.04, 123.60, 123.35, 52.18.



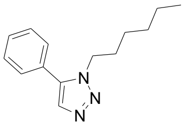
1-Benzyl-5-butyl-1H-[1,2,3]triazole [1] **: 7h** was isolated as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.46 (s, 1H), 7.27-7.34 (m, 3H), 7.12-7.15 (m, 2H), 5.48 (s, 2H), 2.48 (t, J = 7.8 Hz, 2H), 1.43-1.53 (m, 2H), 1.17-1.35 (m, 2H), 0.84 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 137.48, 135.11, 132.51, 128.92, 128.23, 127.08, 51.58, 29.88, 22.81, 22.14, 13.61.



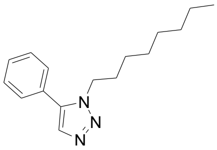
1-Benzyl-5- ferrocenyl-1H-[1,2,3]triazole [4] **: 7i was** isolated as a golden yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.78 (s, 1H), 7.30-7.38 (m, 3H), 7.11 (d, J = 7.2 Hz, 2H), 5.67 (s, 2H), 4.37 (s, 2H), 4.32 (s, 2H), 4.06 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 136.55, 135.86, 132.93, 128.97, 128.08, 126.57, 70.59, 69.75, 69.61, 68.37, 51.72.



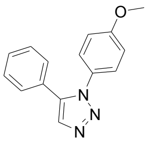
1-(4-Bromo-benzyl)-5-phenyl-1H-[1,2,3]triazole[5]**: 7j** was isolated as a pale yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.76 (s, 1H), 7.41-7.50 (m, 5H), 7.25-7.30 (m, 2H), 6.96-7.00 (m, 2H), 5.52 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 138.12, 134.47, 133.29, 131.91, 129.65, 129.06, 128.93, 128.79, 126.65, 122.22, 51.13.



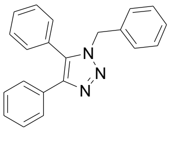
1-Hexyl-5-phenyl-1H-[1,2,3]triazole[6]**: 7k** was isolated as a pale yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.65 (s, 1H), 7.46-7.51 (m, 3H), 7.35-7.38 (m, 2H), 4.32 (t, J = 7.4 Hz, 2H), 1.75-1.82 (m, 2H), 1.19-1.26 (m, 6H), 0.80 (t, J = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 137.67, 132.95, 129.40, 129.07, 128.71, 127.31, 48.28, 31.01, 30.02, 26.06, 22.33, 13.88.



1-Octyl-5-phenyl-1H-[1,2,3]triazole[7]**: 7l** was isolated as a pale yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.65 (s, 1H), 7.46-7.48 (m, 3H), 7.35-7.38 (m, 2H), 4.32 (t, J = 7.2 Hz, 2H), 1.75-1.85 (m, 2H), 1.17-1.24 (m, 10H), 0.83 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 137.86, 133.15, 129.58, 129.26, 128.91, 127.52, 48.48, 31.85, 30.25, 29.15, 29.02, 26.58, 22.76, 14.24.



1-(4-Methoxy-phenyl)-5-phenyl-1H-[1,2,3]triazole[8]**: 7m** was isolated as a pale yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.89 (s, 1H), 7.25-7.40 (m, 7H), 6.95-6.98 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 160.10, 137.73, 133.22, 129.64, 128.86, 128.57, 126.91, 126.64, 114.52, 55.60.



1-Benzyl-4,5-diphenyl-1H-[1,2,3]triazole[1]**: 8** was isolated as a white solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.46-7.50 (m, 2H), 7.32-7.40 (m, 3H), 7.14-7.21 (m, 7H), 7.05-7.08 (m, 2H), 6.93-6.96 (m, 2H), 5.33 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 144.59, 135.47, 134.00, 131.04, 130.18, 129.79, 129.27, 128.78, 128.54, 128.23, 127.94, 127.79, 127.59, 126.81, 52.11.

4. References

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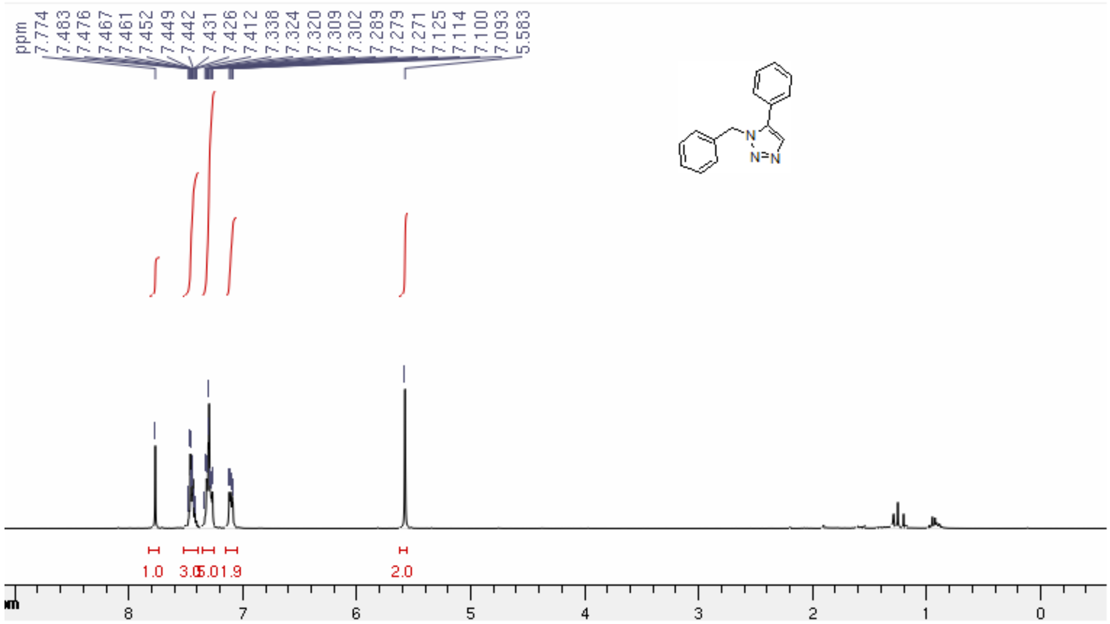
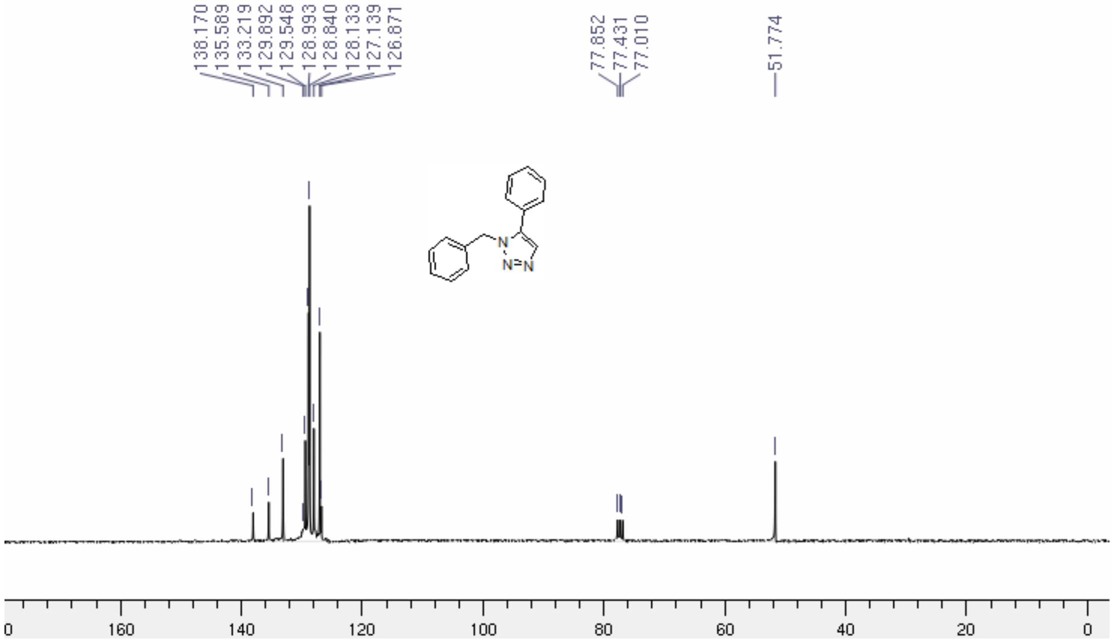
8. L. Wu, Y. Chen, M. Tang, X. Song, G. Chen, X. Song and Q. Lin, *Synlett* 2012, **23**, 1529.

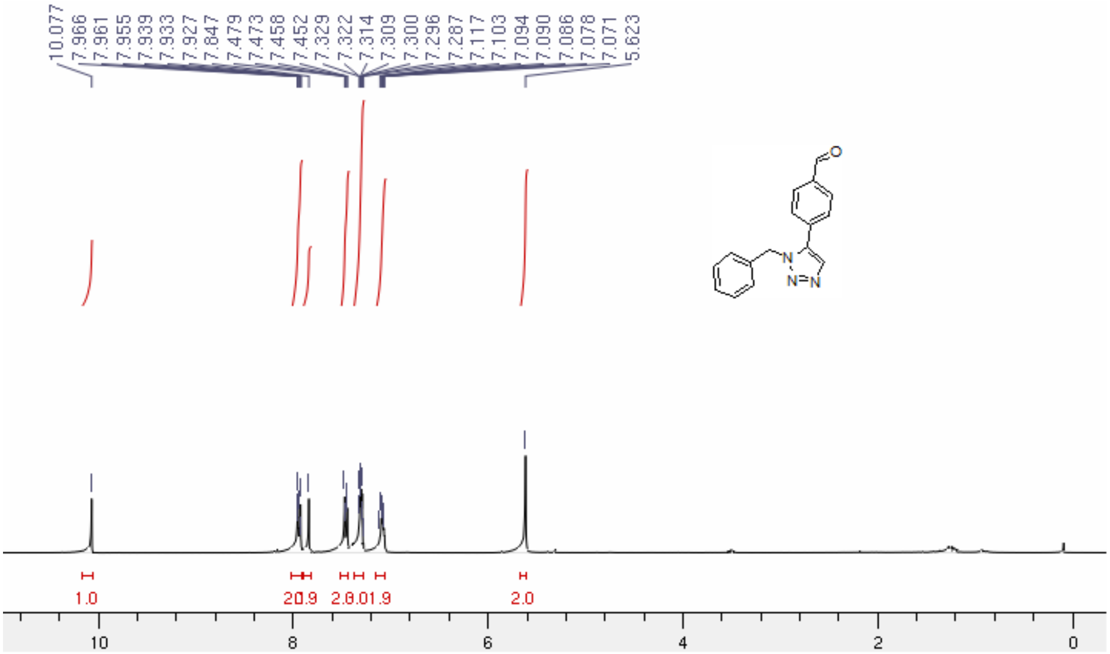
5. NMR spectra of the products

7a:





7b: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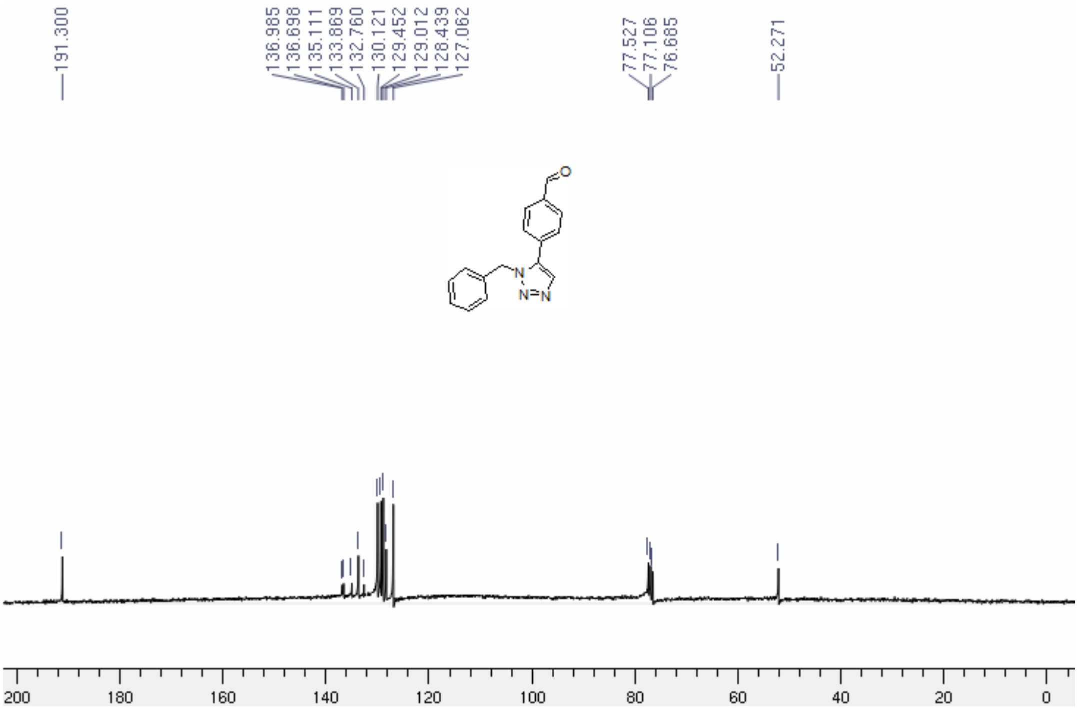
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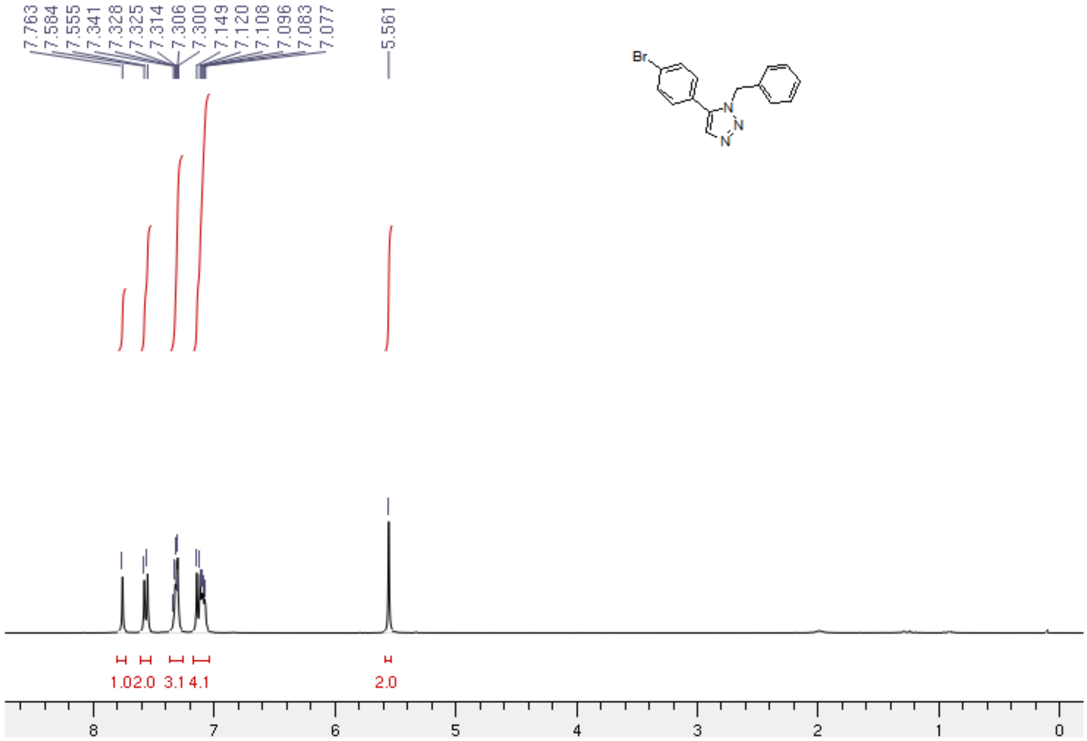
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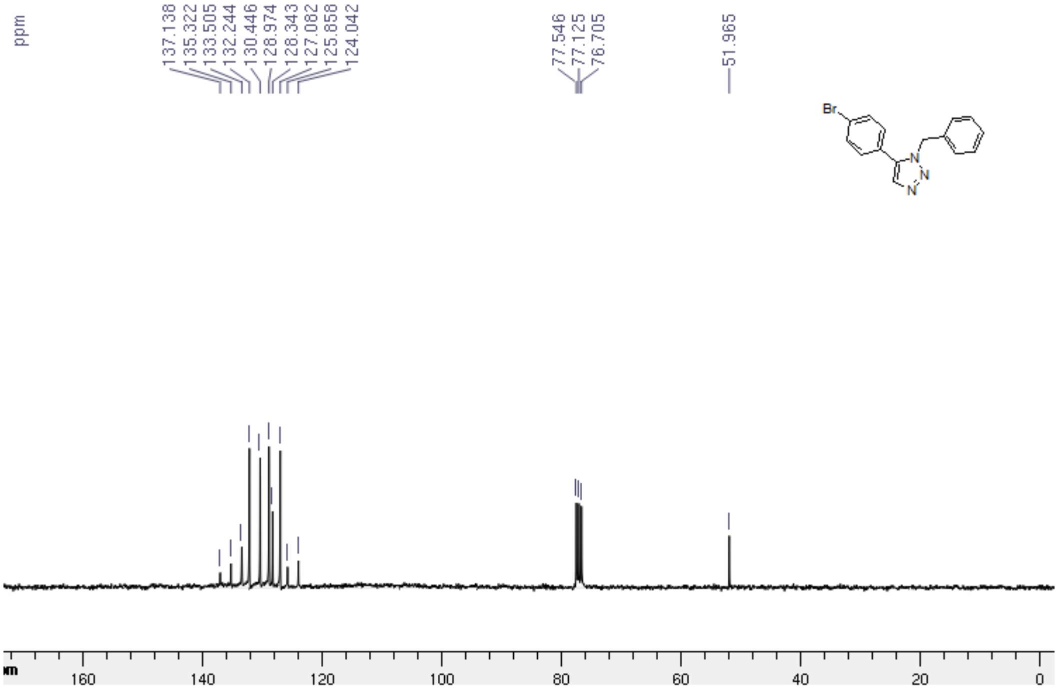
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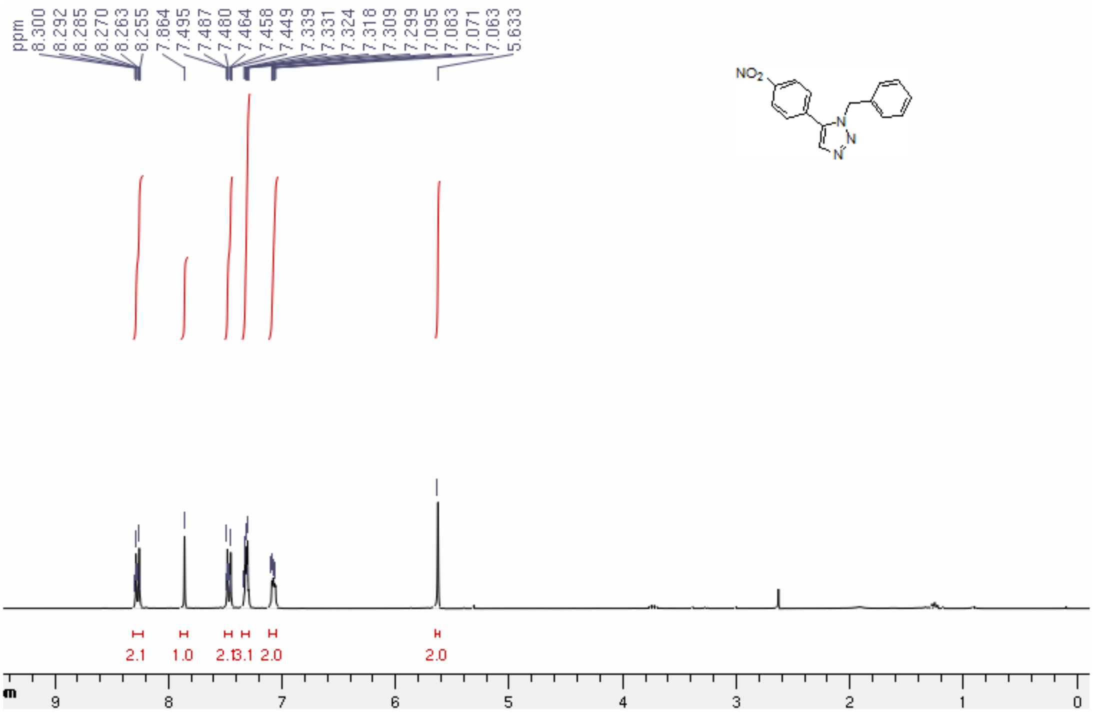
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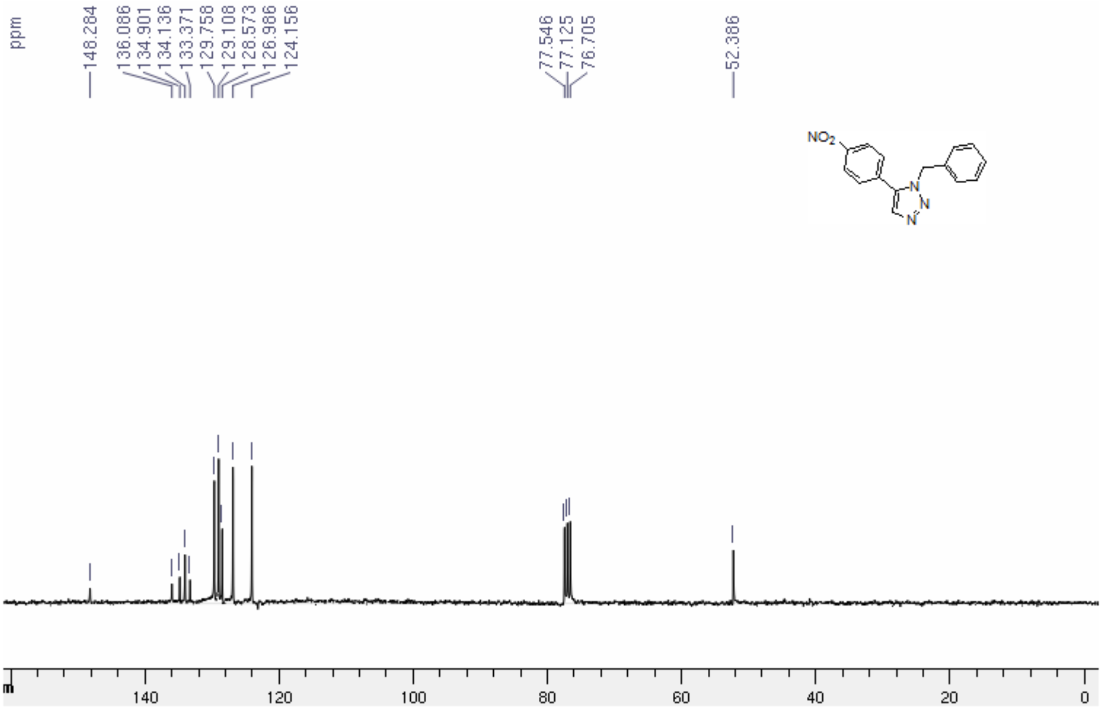
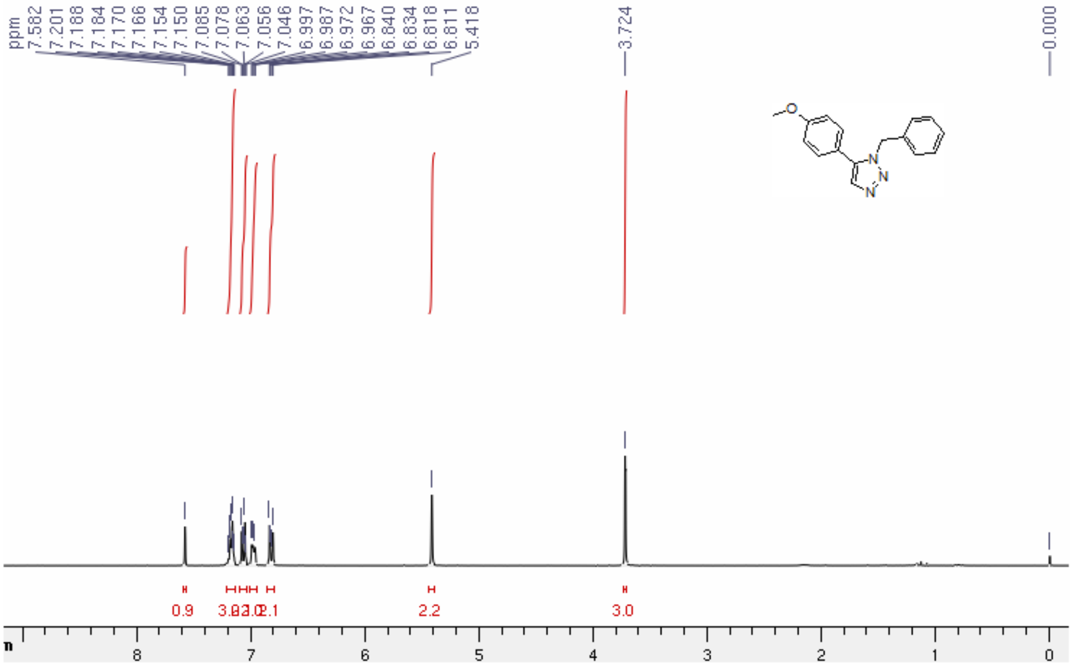
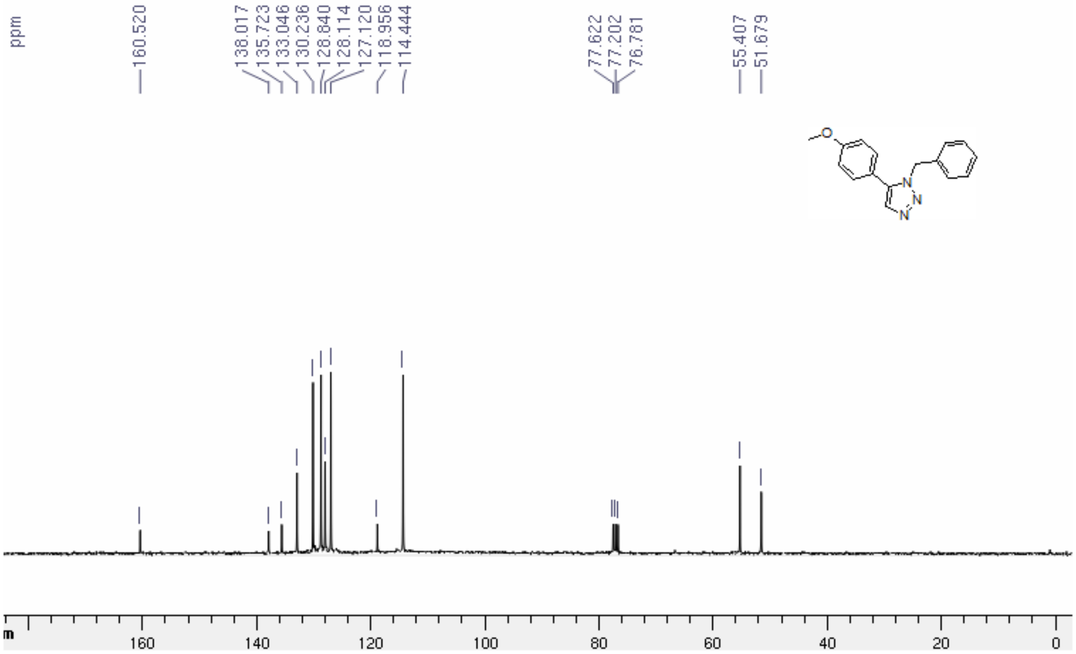
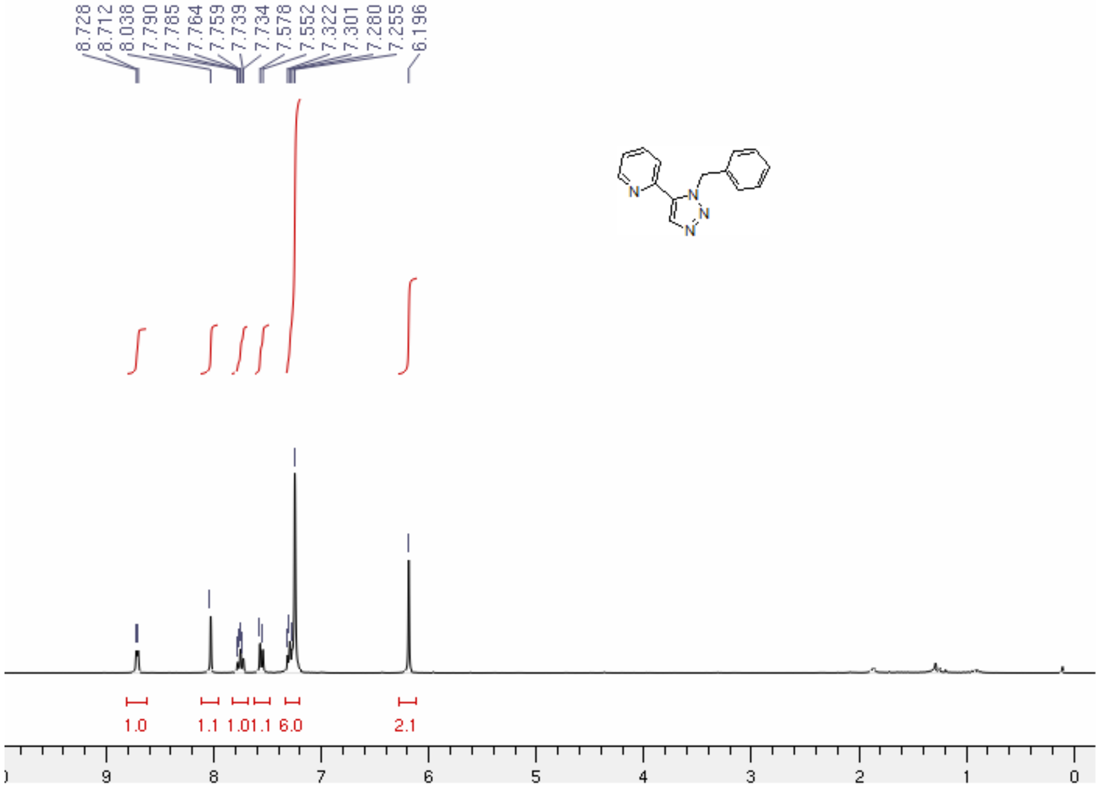

ppm
148.284
136.086
134.901
134.136
133.371
129.758
129.108
128.573
126.986
124.156
77.546
77.125
76.705
52.386
NO2
N
N
N
140
120
100
80
60
40
20
0

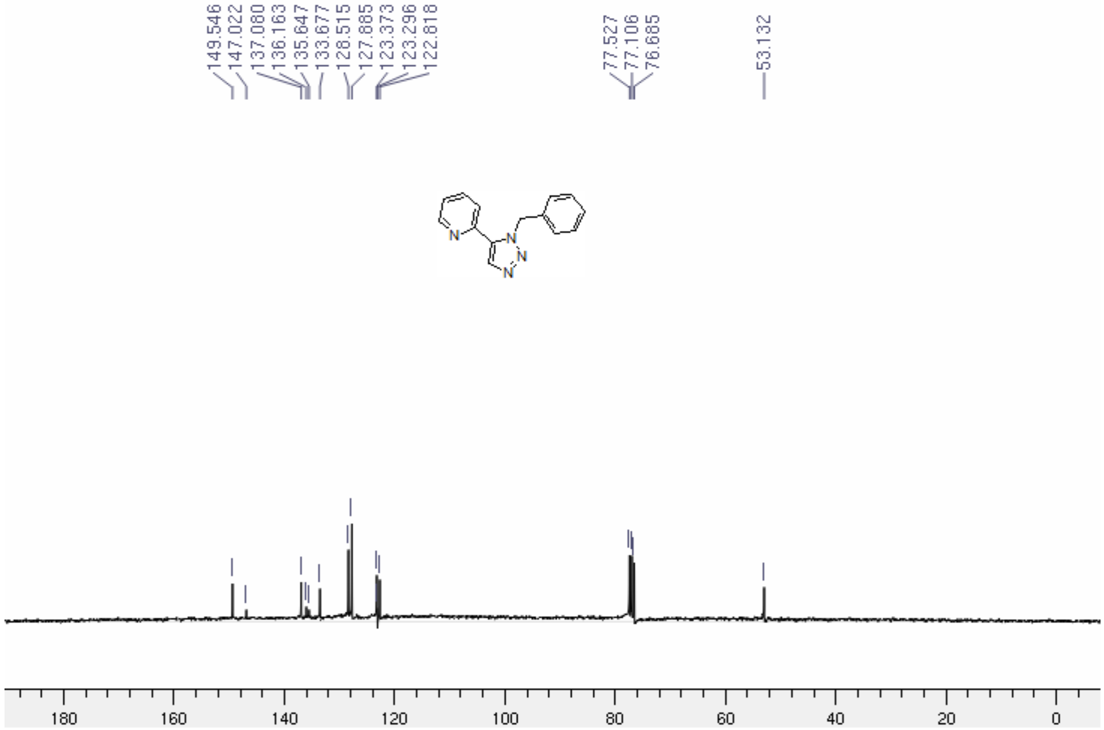
7e:


ppm
7.582
7.201
7.188
7.184
7.170
7.166
7.154
7.150
7.085
7.078
7.063
7.056
7.046
6.997
6.987
6.972
6.967
6.840
6.834
6.818
6.811
5.418
3.724
0.000
O
N
N
N
0.9
3.923.02.1
2.2
3.0
8
7
6
5
4
3
2
1
0

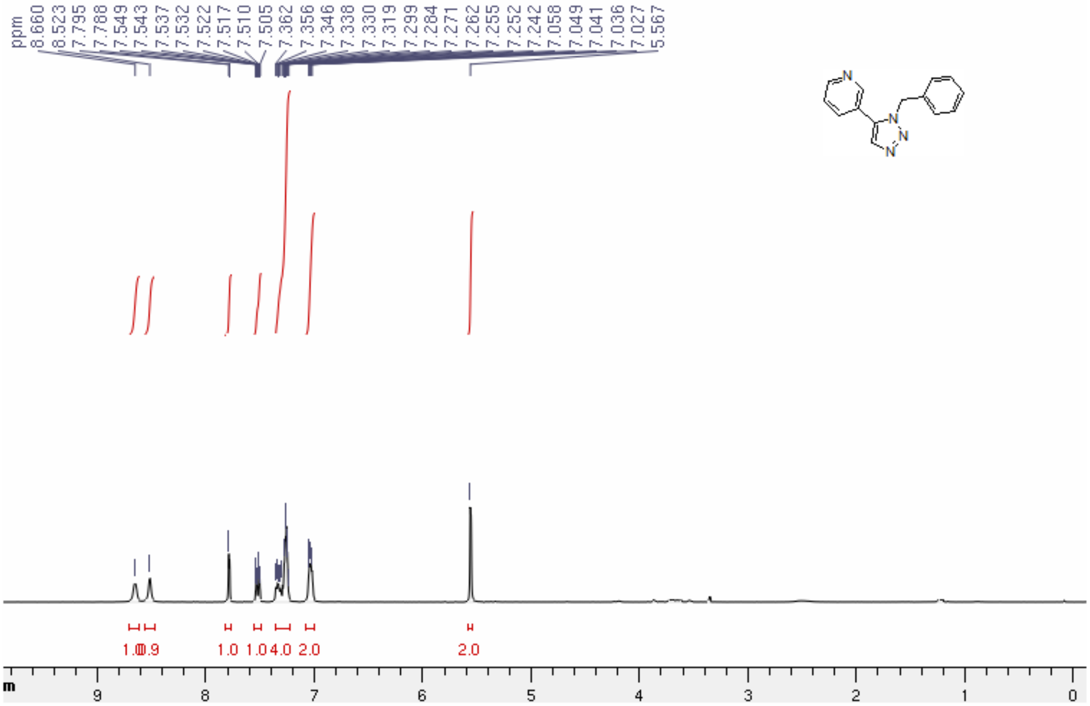

ppm
160.520
138.017
135.723
133.046
130.236
128.840
128.114
127.120
118.956
114.444
77.622
77.202
76.781
55.407
51.679
O
N
N
N
160
140
120
100
80
60
40
20
0

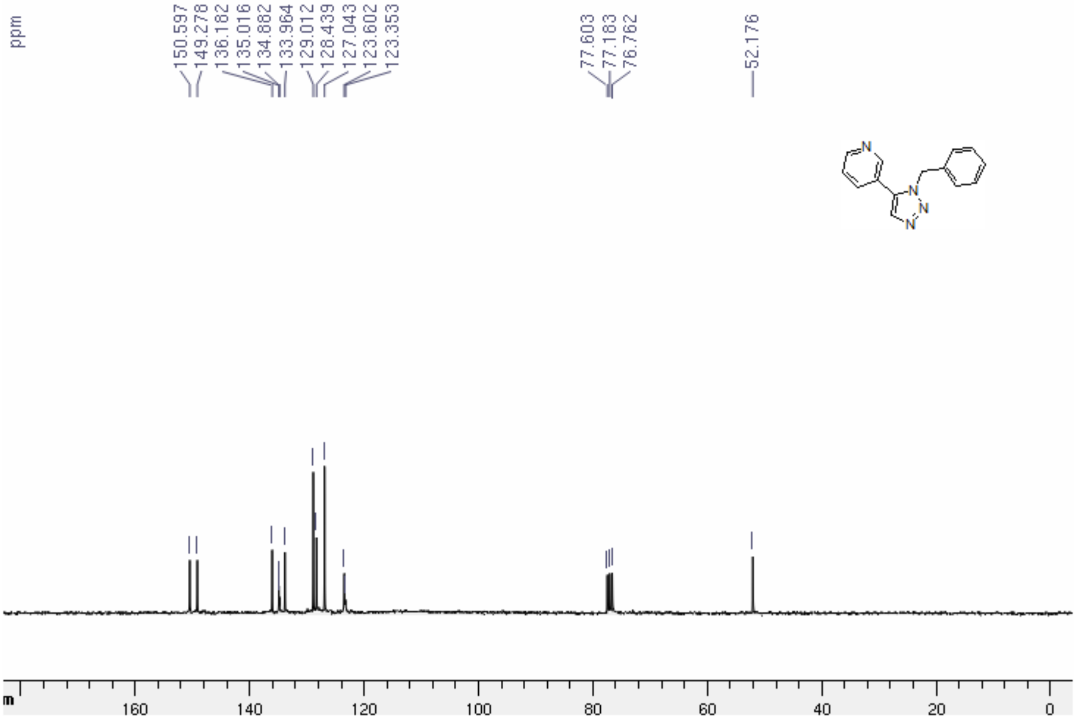
7f:


8.728
8.712
8.038
7.790
7.785
7.764
7.759
7.739
7.734
7.578
7.552
7.322
7.301
7.280
7.255
6.196
N
N
N
N
1.0
1.1
1.0
1.1
6.0
2.1
9
8
7
6
5
4
3
2
1
0

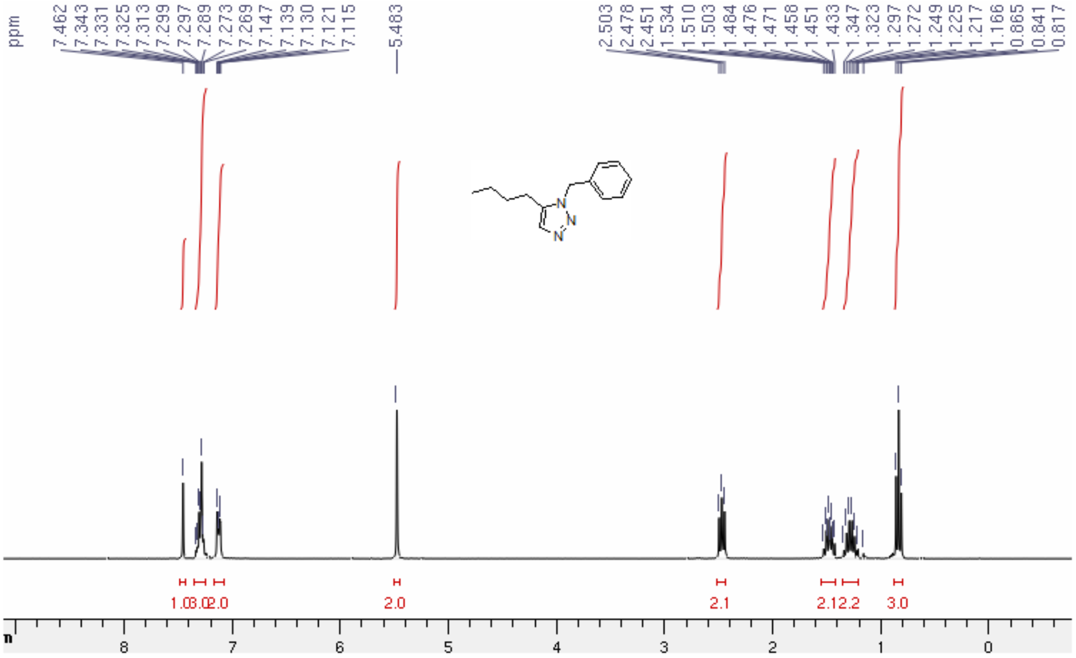

149.546
147.022
137.080
136.163
135.647
133.677
128.515
127.885
123.373
123.296
122.818
77.527
77.106
76.685
53.132
N
N
N
N
180
160
140
120
100
80
60
40
20
0

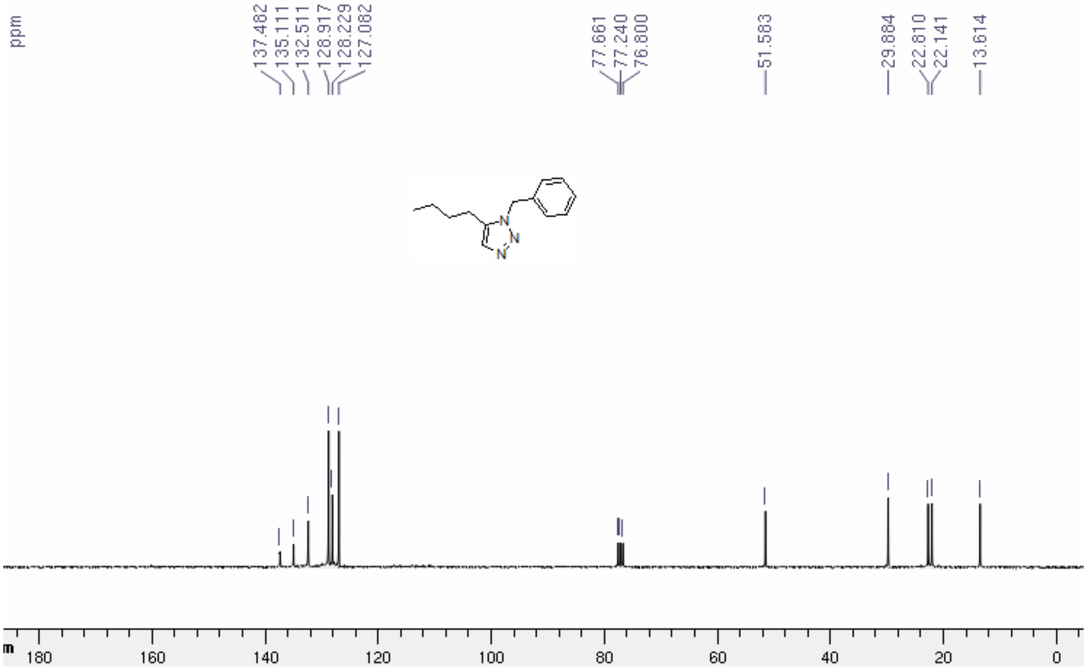
7g:


ppm
8.660
8.523
7.795
7.788
7.549
7.543
7.537
7.532
7.522
7.517
7.510
7.505
7.362
7.356
7.346
7.338
7.330
7.319
7.299
7.284
7.271
7.262
7.255
7.252
7.242
7.058
7.049
7.041
7.036
7.027
5.567
1.0
0.9
1.0
1.0
4.0
2.0
2.0
9
8
7
6
5
4
3
2
1
0
N
N
N
N

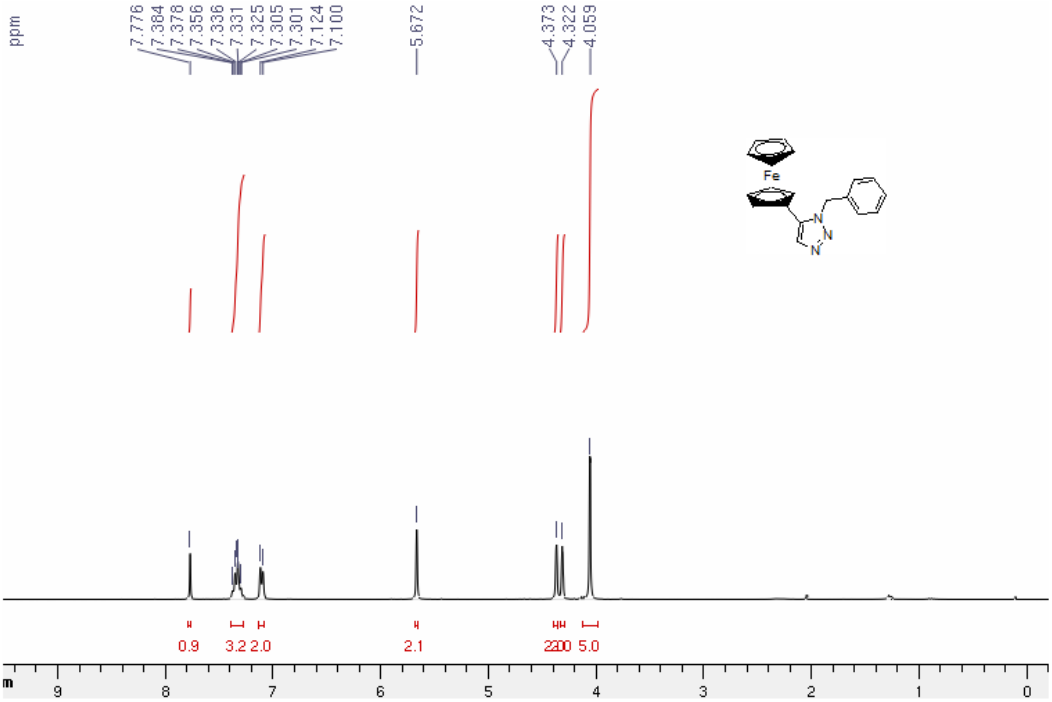

ppm
150.597
149.278
136.182
135.016
134.882
133.964
129.012
128.439
127.043
123.602
123.353
77.603
77.183
76.762
52.176
160
140
120
100
80
60
40
20
0
N
N
N
N

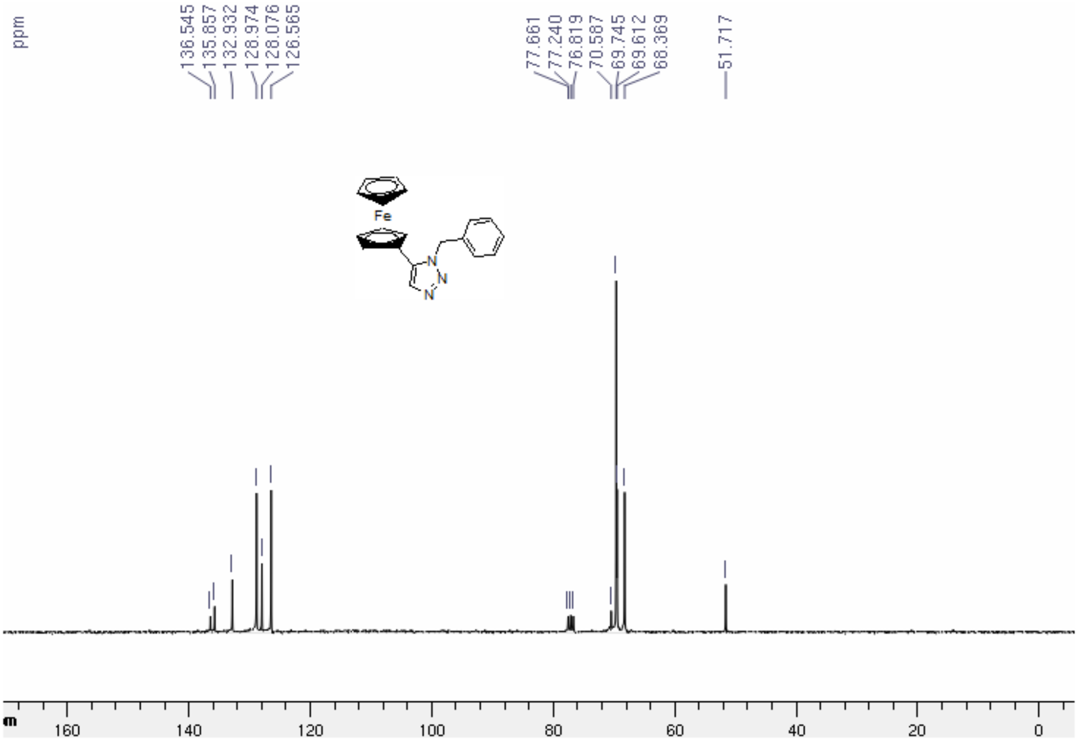
7h:


ppm
7.462
7.343
7.331
7.325
7.313
7.299
7.297
7.289
7.273
7.269
7.147
7.139
7.130
7.121
7.115
5.483
2.503
2.478
2.451
1.534
1.510
1.503
1.484
1.476
1.471
1.458
1.451
1.433
1.347
1.323
1.297
1.272
1.249
1.225
1.217
1.166
0.865
0.841
0.817
N
N
N
1.0
3.0
2.0
2.0
2.1
2.1
2.2
3.0
8
7
6
5
4
3
2
1
0

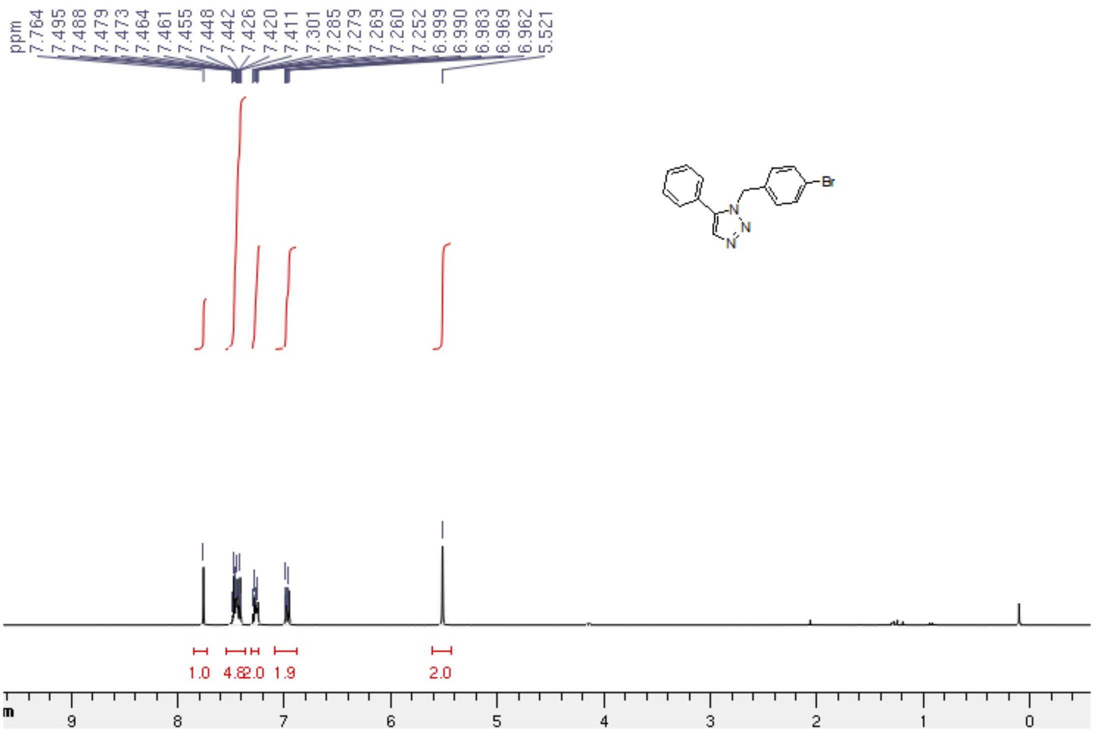

ppm
137.482
135.111
132.511
128.917
128.229
127.082
77.661
77.240
76.800
51.583
29.884
22.810
22.141
13.614
N
N
N
180
160
140
120
100
80
60
40
20
0

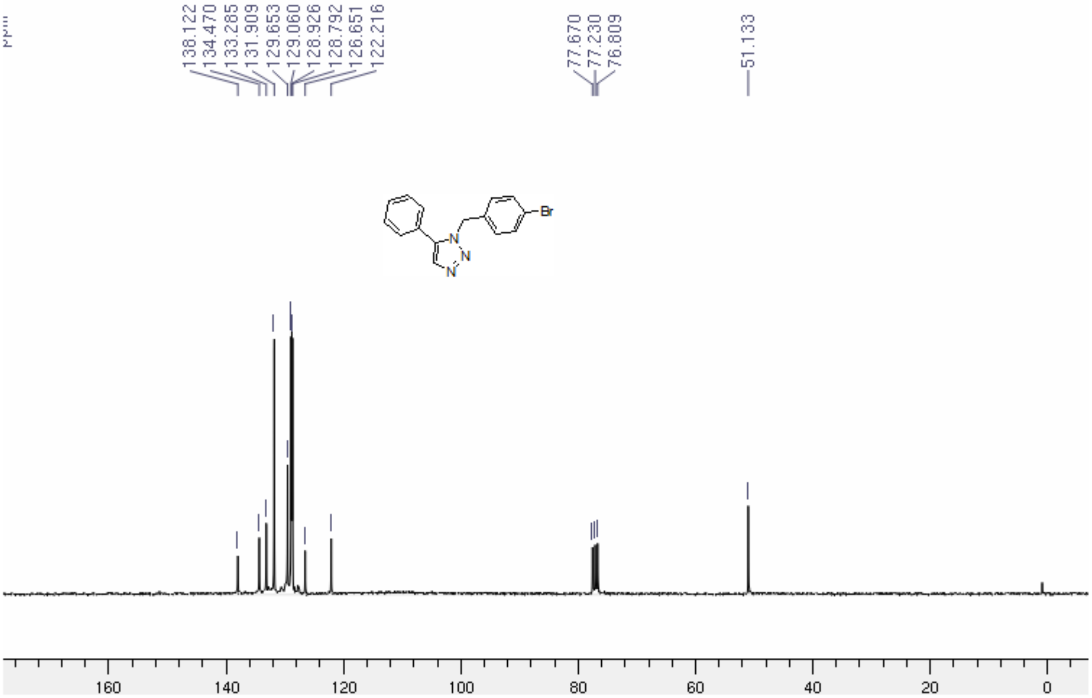
7i:


ppm
7.776
7.384
7.378
7.356
7.336
7.331
7.325
7.305
7.301
7.124
7.100
5.672
4.373
4.322
4.059
Fe
N
N
N
0.9
3.2
2.0
2.1
2.0
2.0
5.0
m
9
8
7
6
5
4
3
2
1
0

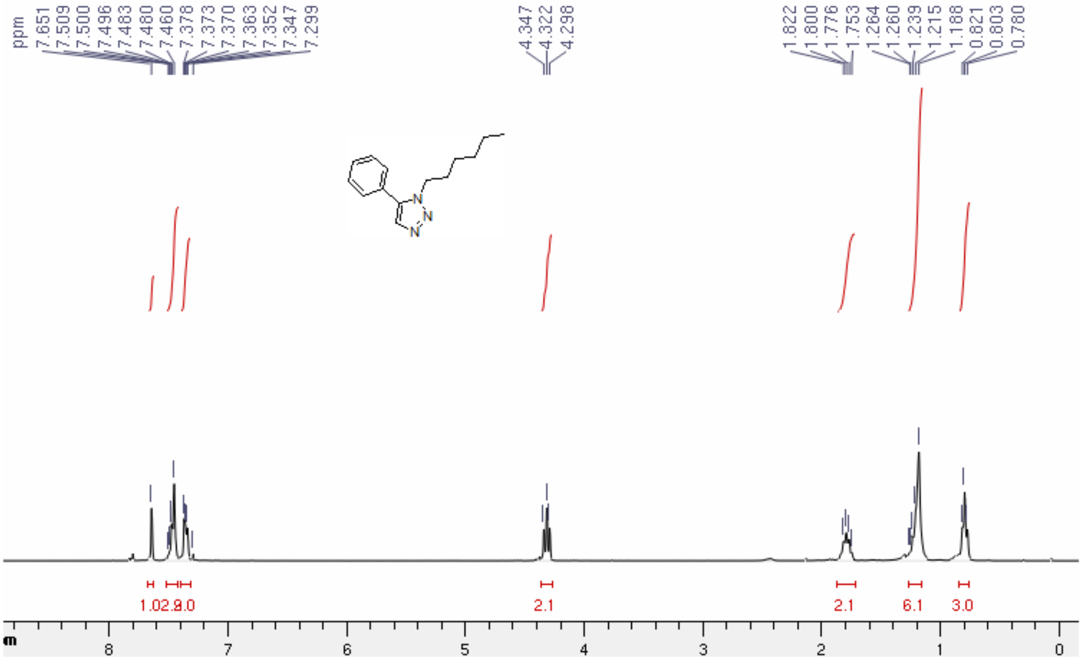

ppm
136.545
135.857
132.932
128.974
128.076
126.565
77.661
77.240
76.819
70.587
69.745
69.612
68.369
51.717
Fe
N
N
N
m
160
140
120
100
80
60
40
20
0

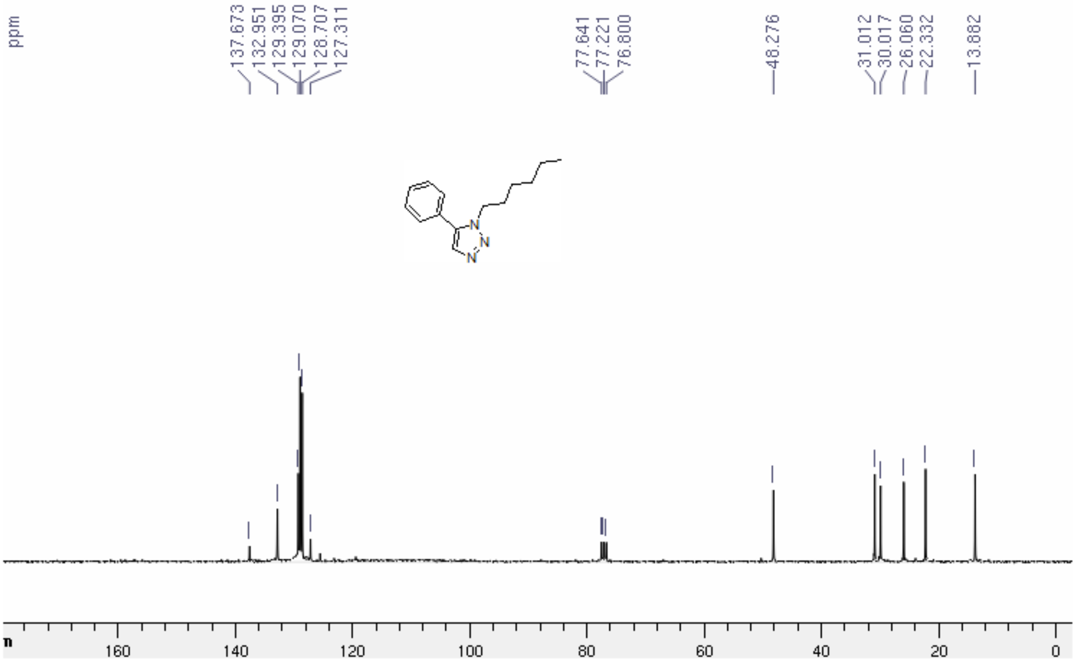
7j:


ppm
7.764
7.495
7.488
7.479
7.473
7.464
7.461
7.455
7.448
7.442
7.426
7.420
7.411
7.301
7.285
7.279
7.269
7.260
7.252
6.999
6.990
6.983
6.969
6.962
5.521
N
N
N
Br
1.0
4.8
2.0
1.9
2.0
9
8
7
6
5
4
3
2
1
0

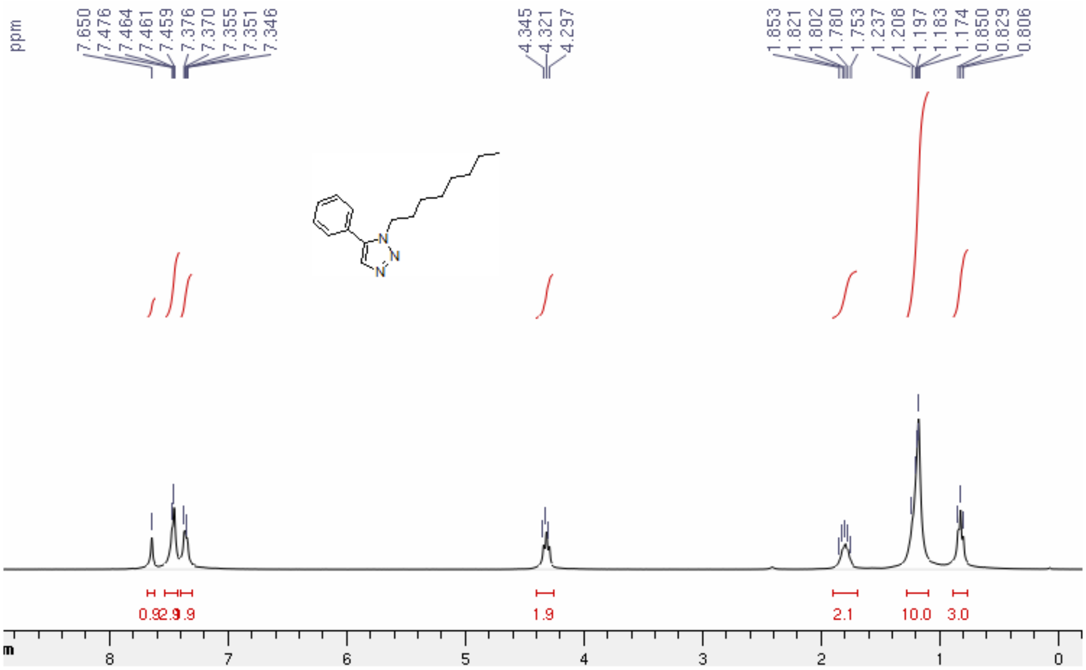

138.122
134.470
133.285
131.909
129.653
129.060
128.926
128.792
126.651
122.216
77.670
77.230
76.809
51.133
N
N
N
Br
160
140
120
100
80
60
40
20
0

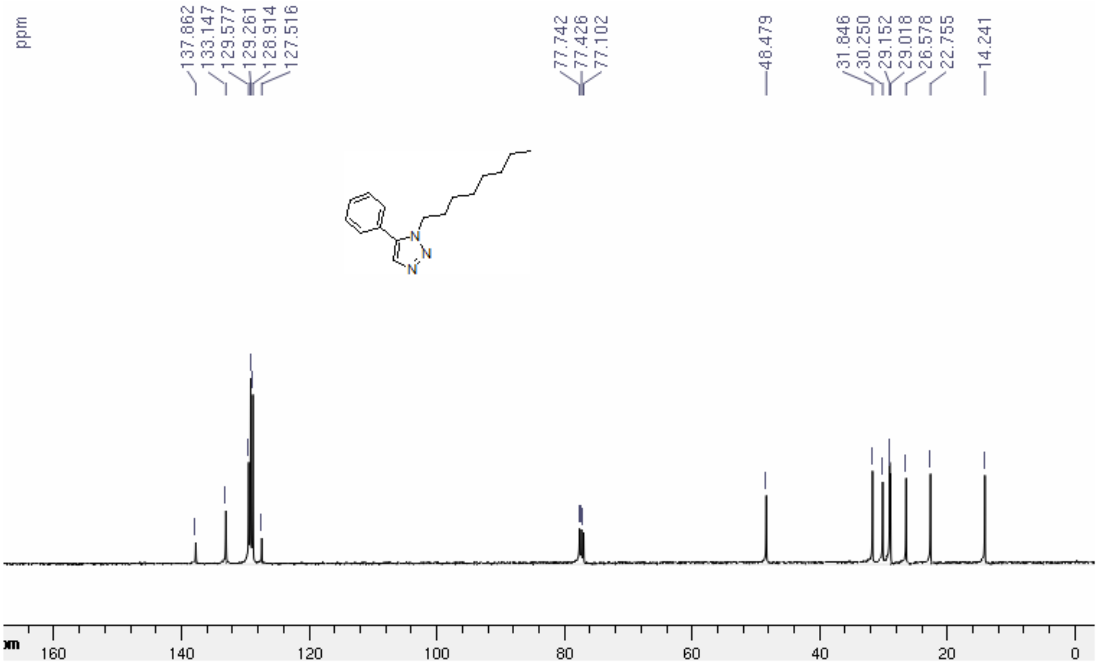
7k:


ppm
7.651
7.509
7.500
7.496
7.483
7.480
7.460
7.378
7.373
7.370
7.363
7.352
7.347
7.299
4.347
4.322
4.298
1.822
1.800
1.776
1.753
1.264
1.260
1.239
1.215
1.188
0.821
0.803
0.780
N
N
N
1.0
2.9
3.0
2.1
2.1
6.1
3.0
m
8
7
6
5
4
3
2
1
0

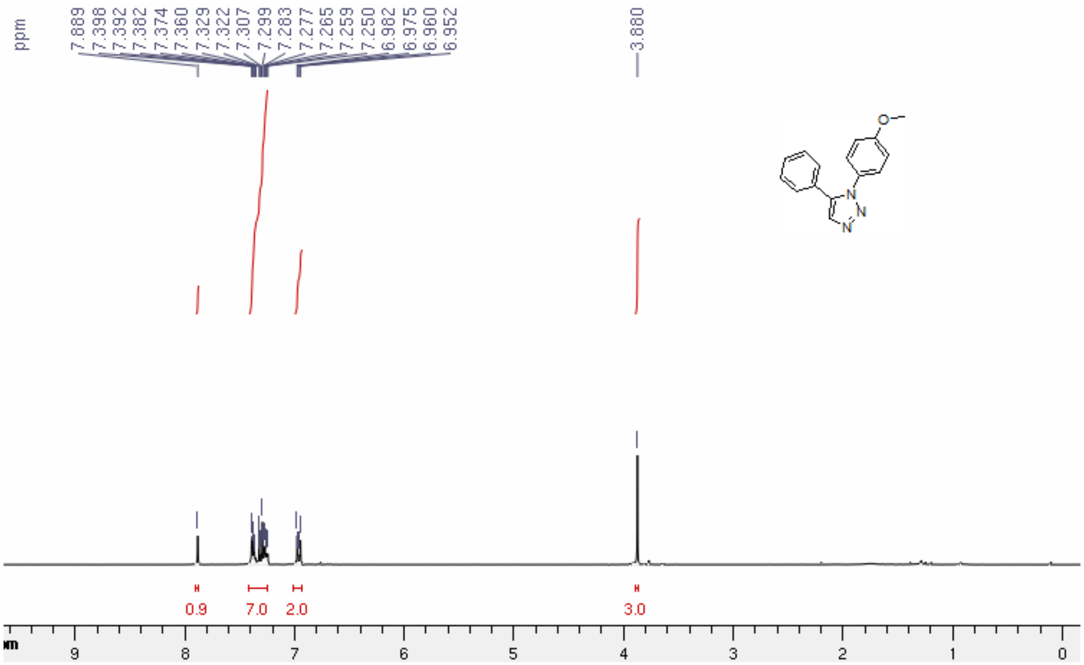

ppm
137.673
132.951
129.395
129.070
128.707
127.311
77.641
77.221
76.800
48.276
31.012
30.017
26.060
22.332
13.882
N
N
N
n
160
140
120
100
80
60
40
20
0

7l:


ppm
7.650
7.476
7.464
7.461
7.459
7.376
7.370
7.355
7.351
7.346
4.345
4.321
4.297
1.853
1.821
1.802
1.780
1.753
1.237
1.208
1.197
1.183
1.174
0.850
0.829
0.806
N
N
N
0.9
2.9
1.9
1.9
2.1
10.0
3.0
8
7
6
5
4
3
2
1
0


ppm
137.862
133.147
129.577
129.261
128.914
127.516
77.742
77.426
77.102
48.479
31.846
30.250
29.152
29.018
26.578
22.755
14.241
N
N
N
160
140
120
100
80
60
40
20
0

7m:


ppm
7.889
7.398
7.392
7.382
7.374
7.360
7.329
7.322
7.307
7.299
7.283
7.277
7.265
7.259
7.250
6.982
6.975
6.960
6.952
3.880
O
N
N
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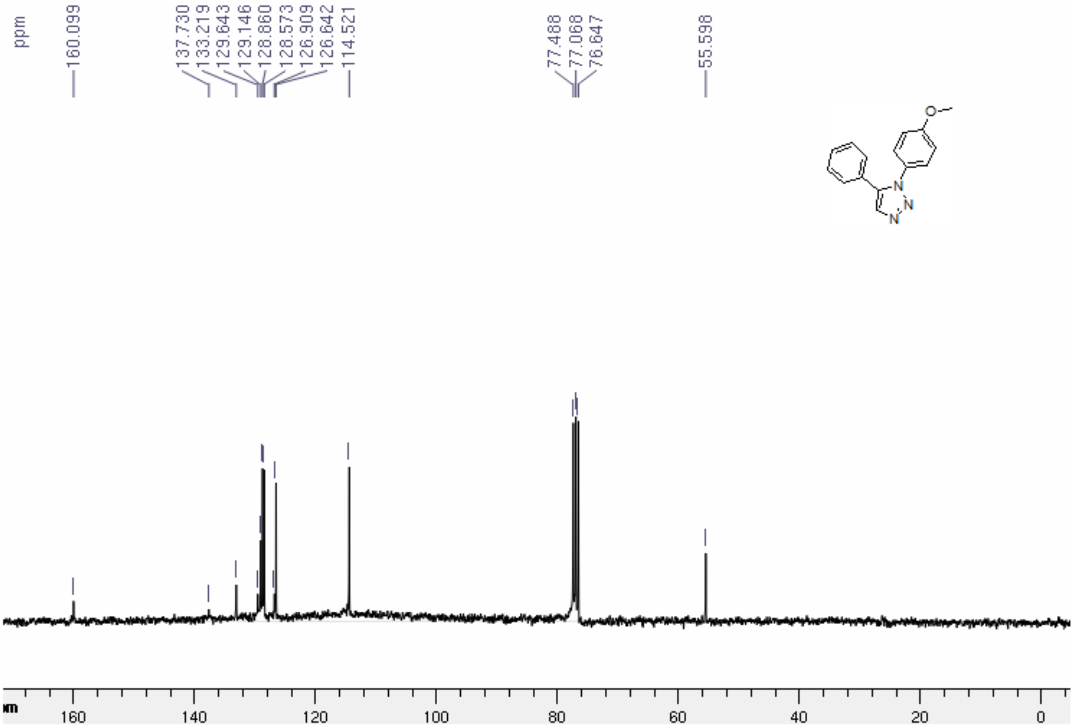
0.9
7.0
2.0
3.0
9
8
7
6
5
4
3
2
1
0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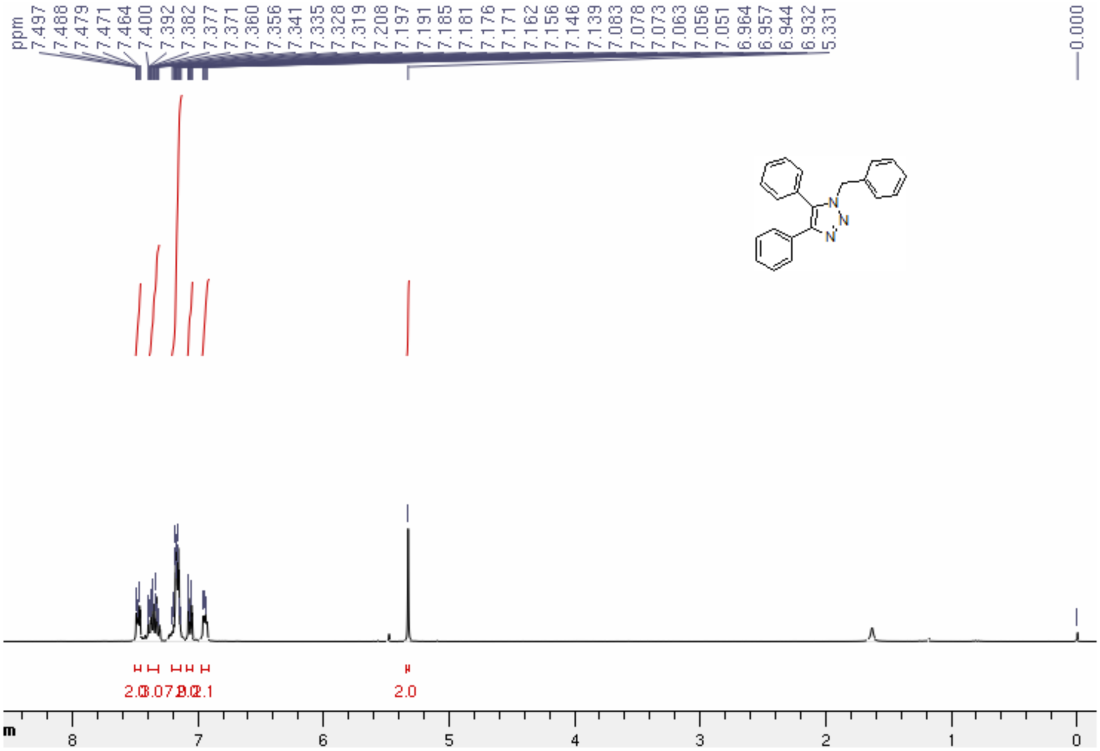
129.643
129.146
128.860
128.573
126.909
126.642
114.521
77.488
77.068
76.647
55.598
O
N
N
N
160
140
120
100
80
60
40
20
0

8:


ppm
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7.479
7.471
7.464
7.400
7.392
7.382
7.377
7.371
7.360
7.356
7.341
7.335
7.328
7.319
7.208
7.197
7.191
7.185
7.181
7.176
7.171
7.162
7.156
7.146
7.139
7.083
7.078
7.073
7.063
7.056
7.051
6.964
6.957
6.944
6.932
5.331
0.000
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N
N
2.03.072.02.02.1
2.0
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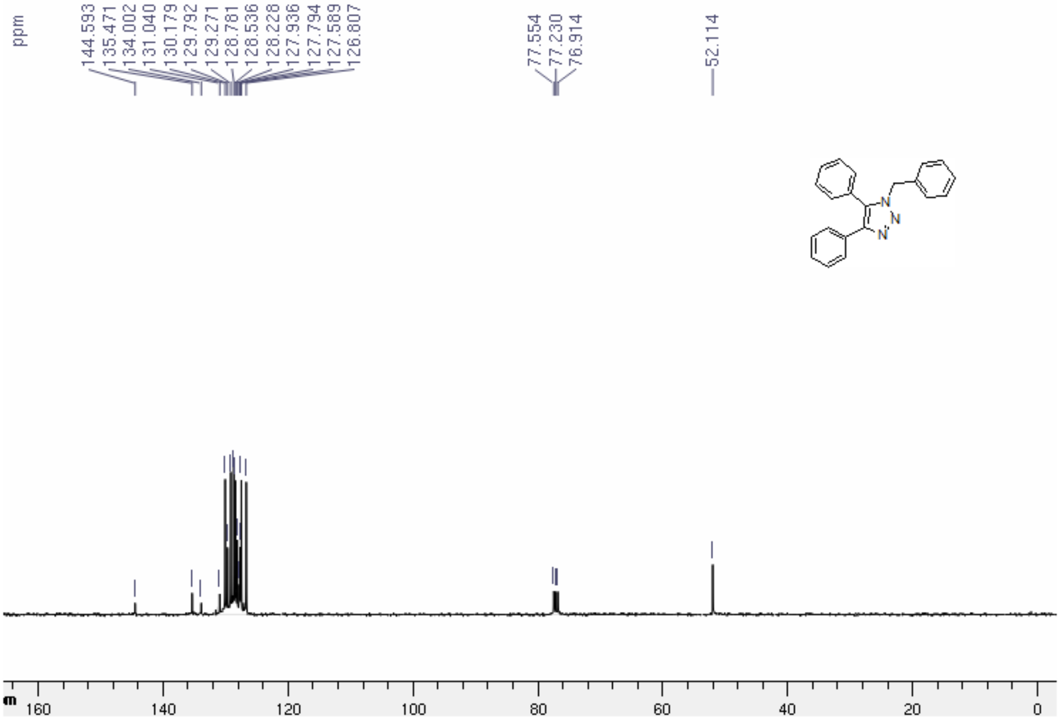
7
6
5
4
3
2
1
0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144.593
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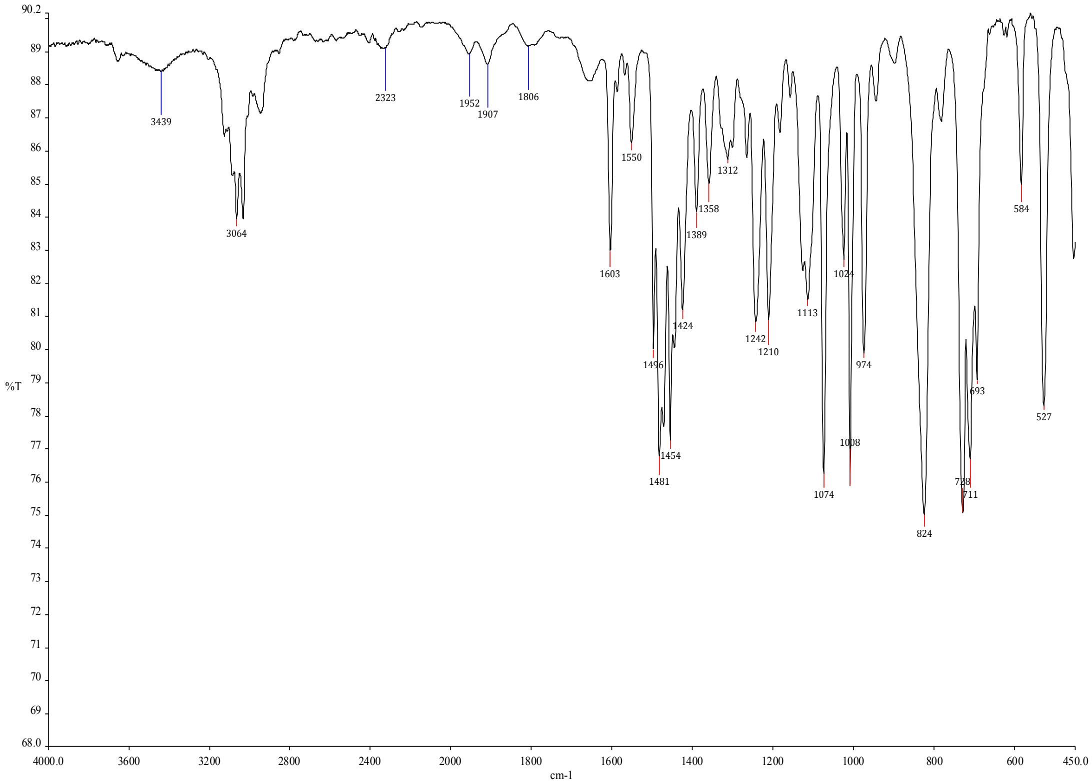
134.002
131.040
130.179
129.792
129.271
128.781
128.536
128.228
127.936
127.794
127.589
126.807
77.554
77.230
76.914
52.114
N
N
N
160
140
120
100
80
60
40
20
0

6. IR spectrums of 7c and 7d

7c:



7d: