Electronic Supplementary Material (ESI) for Catalysis Science .

Supporting Information

Efficient Three-Components Coupling Reactions Catalyzed by Cu^{o}-nanoparticles stabilized on Modified Montmorillonite Clay

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1. General information

Bentonite (procured from Gujarat, India) containing quartz, iron oxide etc. as impurities was purified by sedimentation[1] to collect the < 2 μm Montmorillonite rich fraction. The basal spacing (d_{001}) of the air dried samples was about 12.5 Å.[2] The specific surface area determined by N_2 adsorption was 101 m^2/g. The analytical oxide composition of the bentonite determined was SiO_2 : 49.42%; Al_2O_3 : 20.02%; Fe_2O_3 : 7.49%; MgO : 2.82%; CaO : 0.69%; Loss on ignition : 17.51%; others (Na_2O, K_2O and TiO_2): 2.05%.

The Montmorillonite (parent Mont.) was converted to the homoionic Na^+-exchanged form by stirring in 2M NaCl solution for about 78 h, washed and dialysed against distilled water until the conductivity of the water approached that of distilled water. The cation exchange capacity (CEC) was 1.26 meq./g of clay (sample dried at 120 ^oC).[3]

K_2PdCl_4 was purchased from Arora Matthey Ltd., India. Hydrazine hydrate and all the aryl halides, alkenes, alkynes, bases were purchased from M/S Sigma-Aldrich, USA. All the reagents were used as supplied.

IR spectra (4000 - 400 cm^{-1}) were recorded on KBr discs in a Perkin-Elmer system 2000 FT-IR spectrophotometer. Powder XRD spectra were recorded on a Rigaku, Ultima IV X-ray diffractometer from 5 - 80^o 2θ using CuKα source (λ = 1.54 Å). Specific surface area, pore volume, average pore diameter were measured with the Autosorb-1 (Quantachrome, USA). Specific surface area of the samples were measured by adsorption of nitrogen gas at 77 K and applying the Brunauer-Emmett-Teller (BET) calculation. Prior to adsorption, the samples were degassed at 250 ^oC for 3 h. Pore size distributions were derived from desorption isotherms using Barrett-Joyner-Halenda (BJH) method. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) patterns were obtained with Leo 1430 vp operated at 3 and 10 KV. Prior to examination, the samples were coated with gold. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL JEM-2011 electron microscope and the specimens were prepared by dispersing powdered samples in isopropyl alcohol, placing them on a carbon coated copper grid and allowing them to dry. The Pd contents were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using Perkin Elmer, OPTIMA 2000 instrument.

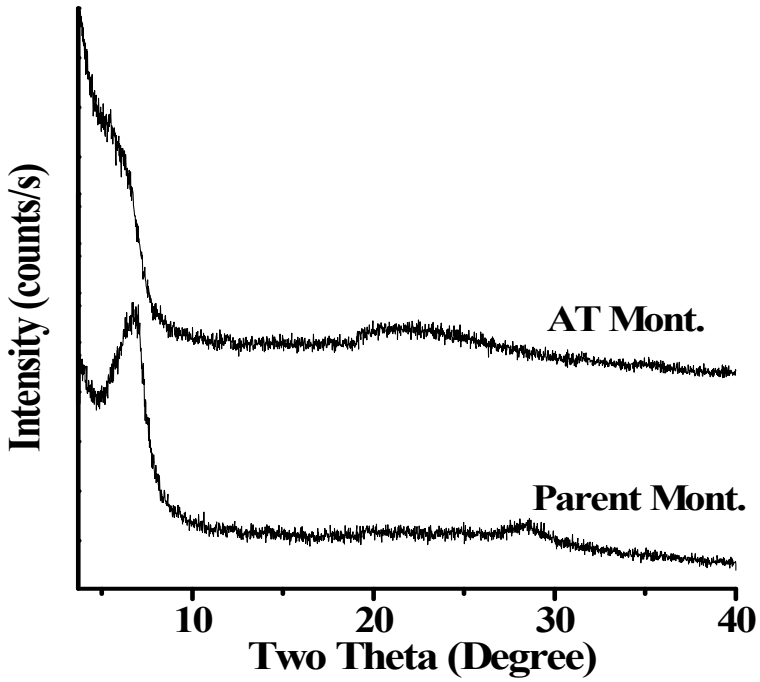


Fig. 1. Powder XRD pattern of different Montmorillonite clay.

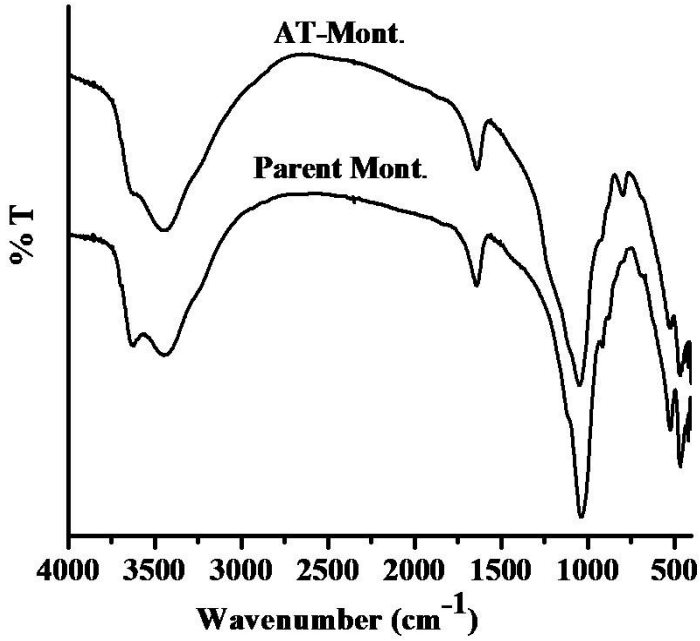


Fig. 2. FTIR spectra of different Montmorillonite clay.

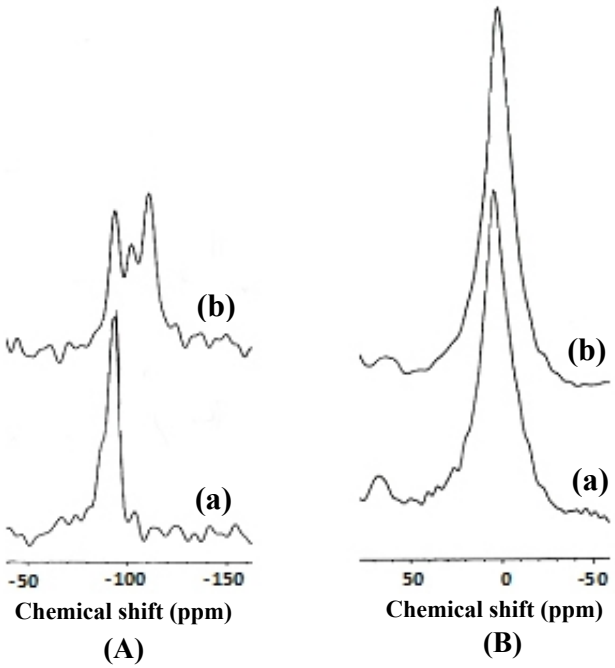
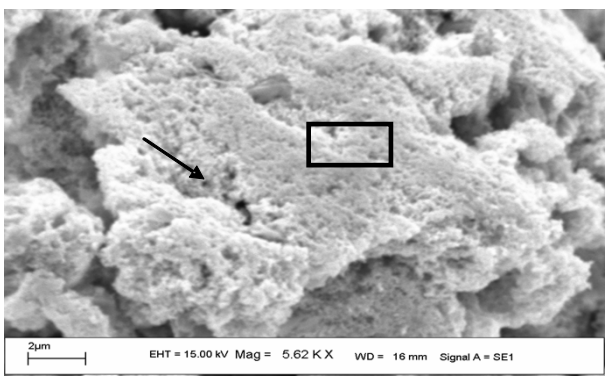
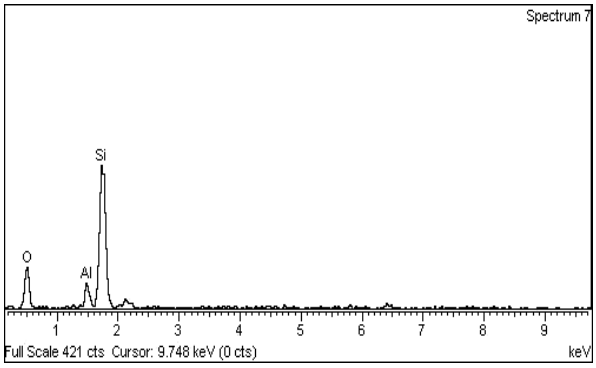


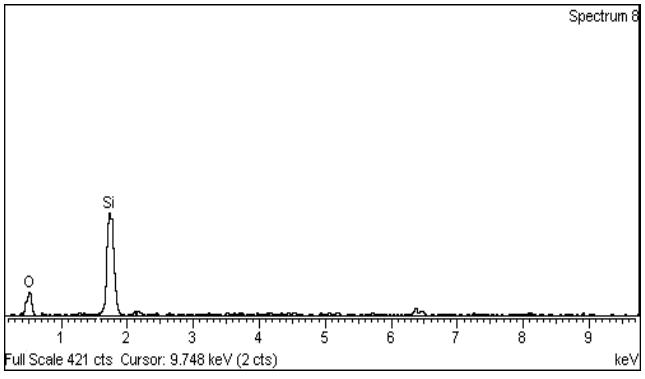
Fig. 3. (A) ^{29}Si and (B) ^{27}Al MAS-NMR spectra of (a) Parent Mont. (b) AT-Mont.



(A)



(B)



(C)

Fig. 4. (A) SEM image of the surface of AT-Mont.; (B) EDX analysis of the surface; (C) EDX spot analysis of pores (indicated by an arrow in (A)).

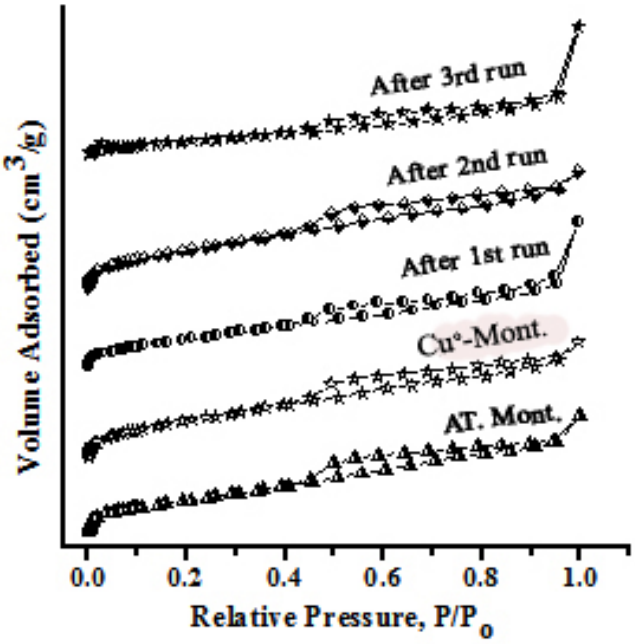
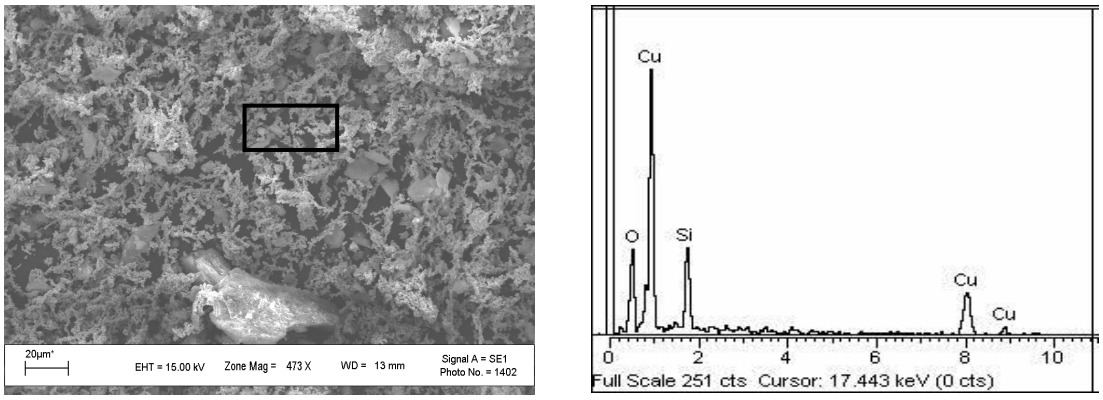


Fig. 5. N_2 adsorption / desorption isotherms of AT-Mont., Cu^o-Mont. and recovered catalysts.



(A) (B)

Fig. 6: (A) SEM image of the surface of AT-Mont. after supporting the Cu^{o}-nanoparticles (B) EDX spot analysis of the pores.

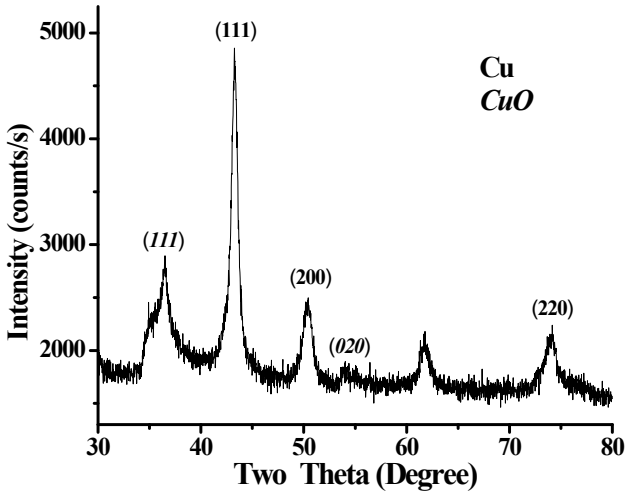
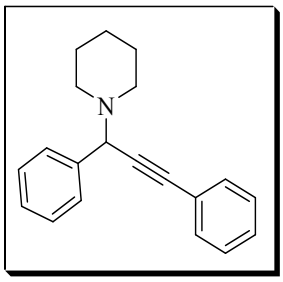


Fig. 7. Powder XRD pattern of recovered catalyst.

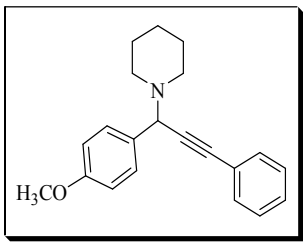
2. ^{1}H and ^{13}C NMR data of the synthesized Propargylamines:

(i) 1-(1,3-diphenylprop-2-ynyl)piperidine (**Entry 1**):



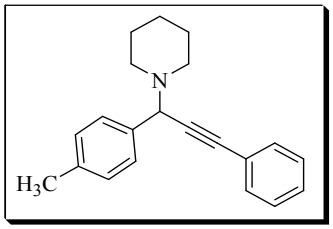
Pale yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.38-1.65 (m, 6H), δ 2.54-2.57 (t, 4H), δ 4.79 (s, 1H), δ 7.24-7.35 (m, 6H), δ 7.50-7.53 (m, 2H), δ 7.61-7.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 24.66, 26.22, 50.74, 62.43, 86.10, 87.94, 123.38, 127.23, 128.13-128.34, 128.51-128.75, 131.87, 138.59; MS m/z 275 (M^+).

(ii) 1-(1-(4-Methoxyphenyl)-3-phenylprop-2-ynyl)-piperidine (**Entry 2**):



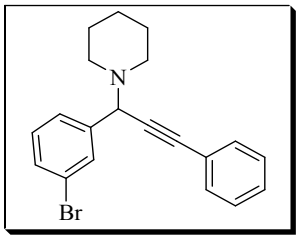
Dark yellowish oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.41-1.67 (m, 6H), δ 2.52-2.55 (t, 4H), δ 3.81 (s, 3H), δ 4.73 (s, 1H), δ 6.87-6.90 (m, 2H), δ 7.30-7.38 (m, 3H), δ 7.48-7.54 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 24.55, 26.21, 50.64, 55.27, 61.83, 86.44, 87.75, 113.46-113.68, 123.43, 128.10, 128.34, 129.75,130.64,131.85, 159.07; MS m/z 304 (M^+).

(iii) 1-(3-phenyl-1-p-tolylprop-2-ynyl)piperidine (**Entry 3**):



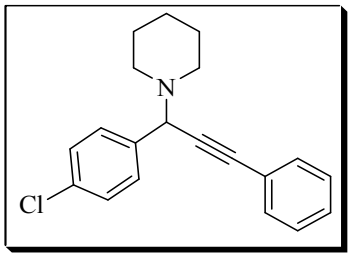
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.34-1.60 (m, 6H), δ 2.34 (s, 3H), δ 2.41-2.62 (m, 4H), δ 4.75 (s, 1H), δ7.05-7.14 (1H, m), δ 7.30-7.49 (m, 4H), δ7.49-7.53 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 21.25, 24.61, 26.30, 50.78, 62.24, 81.75, 86.48, 121.89, 123.51, 128.14-129.93, 131.92, 132.60, 135.62, 137.19; MS m/z 289 (M^+).

(iv) 1-(1-(3-Bromophenyl)-3-phenylprop-2-ynyl)piperidine (**Entry 4**):



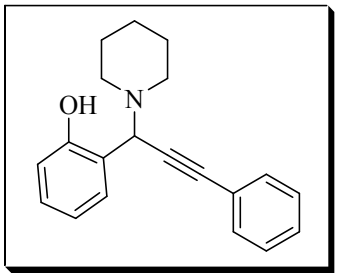
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.33-1.66 (m, 6H), δ 2.51-2.52 (d, 4H), δ 2.41-2.62 (m, 4H), δ 4.74 (s, 1H), δ7.16-7.40 (5H, m), δ 7.49-7.58 (m, 3H), δ7.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 24.55, 26.31, 50.81, 61.94, 81.80, 85.18, 88.67, 121.91- 123.17, 137.22-, 132.62, 141.37; MS m/z 355 (M^+).

(v) 1-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl)piperidine (**Entry 5**):



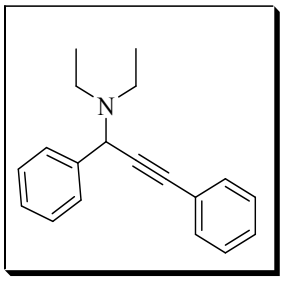
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.31-1.51 (m, 6H), δ 2.51-2.54 (t, 4H), δ 4.76 (s, 1H), δ 7.30-7.34 (m, 6H), δ 7.49-7.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 24.53, 26.27, 50.74, 61.79, 74.29, 81.79, 85.45, 123.20, 128.33-128.56, 129.47, 129.97, 131.94, 132.60, 134.81; MS m/z 309 (M^+).

(vi) 2-(3-(4-phenyl-1(piperidin-1-yl)prop-2-ynyl)phenol (**Entry 6**):



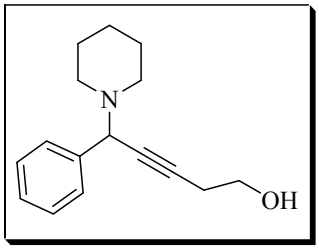
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.21-1.67 (m, 6H), δ 2.68-2.75 (m, 4H), δ 5.09 (s, 1H), δ 6.83-6.85 (2H, m), δ 7.19-7.25 (m, 1H), δ 7.33-7.37 (m, 3H), δ 7.51-7.56 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 23.07, 24.06, 38.40, 61.13, 82.42, 89.90, 116.42, 117.64, 121.35, 122.66, 128.48-128.64, 129.27-129.43, 131.94, 132.54, 151.72; MS m/z 391 (M^+).

(vii) (1,3-Diphenyl-prop-2-ynyl)diethylamine (**Entry 7**):



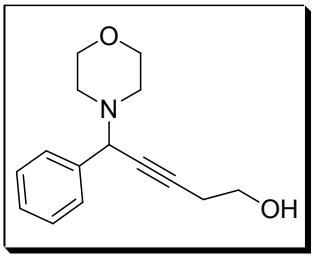
Pale yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.97-1.04 (m, 6H), δ 2.40-2.62 (m, 4H), δ 4.97 (s, 1H), δ 7.24-7.27 (m, 5H), δ 7.41-7.44 (m, 3H), δ 7.59-7.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 13.64, 44.65, 57.09, 74.03, 81.63, 86.17, 121.86, 123.46, 127.33-129.26, 131.85, 132.56, 139.89; MS m/z 263 (M^+).

(viii) 5-phenyl-5-(piperidin-1-yl)pent-3-yn-1-ol (**Entry 8**):



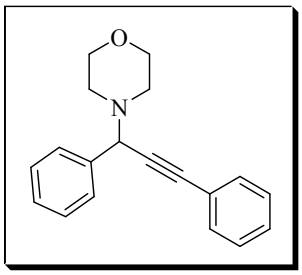
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.38-1.42 (m, 4H), δ 2.08-2.17 (m, 4H), δ 2.44-2.61 (m, 5H), δ 3.72-3.79 (m, 2H), δ 4.53 (s, 1H), δ 7.26-7.61 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 23.30, 24.57, 25.85, 50.68, 60.63, 61.22, 62.08, 66.70, 74.72, 78.57, 84.36, 126.76, 127.62, 128.08-128.67, 137.91; MS m/z 243 (M^+).

(ix) 5-Morpholino-5-phenylpent-3-yn-1-ol (**Entry 9**):



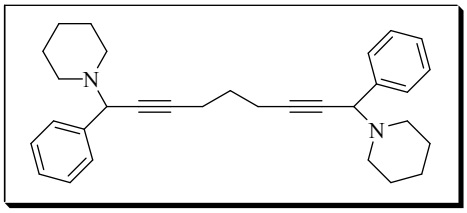
Pale yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.53-2.62 (m, 4H), δ 3.40-3.80 (m, 8H), δ 4.53 (s, 1H), δ 5.30 (s, 1H), δ 7.26-7.61 (m, 4H), δ 8.06 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 23.22, 40.62, 45.81, 49.53, 67.08-67.20, 89.09, 127.07, 128.81,129.74, 134.45, 136.40; MS m/z 245 (M^+).

(x) 4-(1,3-diphenylprop-2-ynyl)morpholine (**Entry 10**):



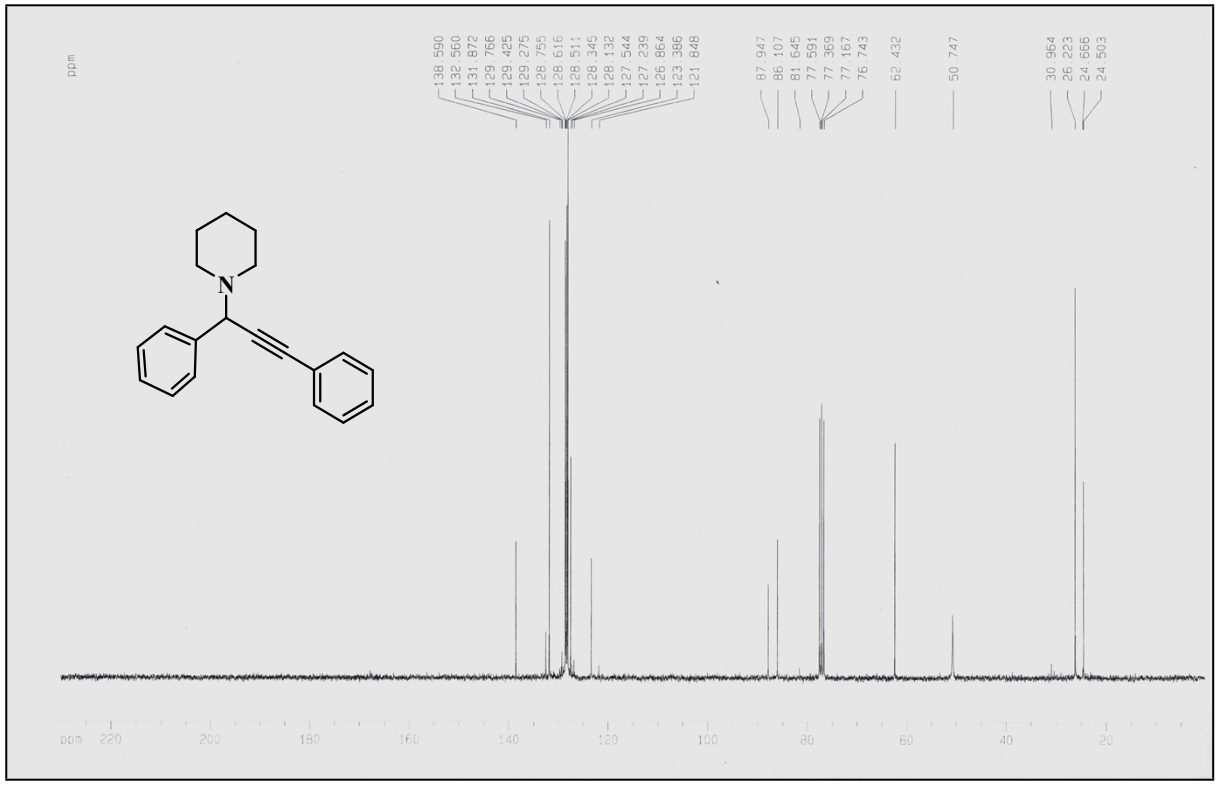
Pale yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.62-2.65 (t, 4H), δ 3.72-3.75 (t, 4H), δ 4.79 (s, 1H), δ 7.24-7.39 (m, 6H), δ 7.49-7.53 (m, 2H), δ 7.62-7.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 49.89, 62.06, 67.16, 85.02, 88.54, 122.97, 127.82, 128.34, 128.62, 131.83, 137.77; MS m/z 277 (M^+).

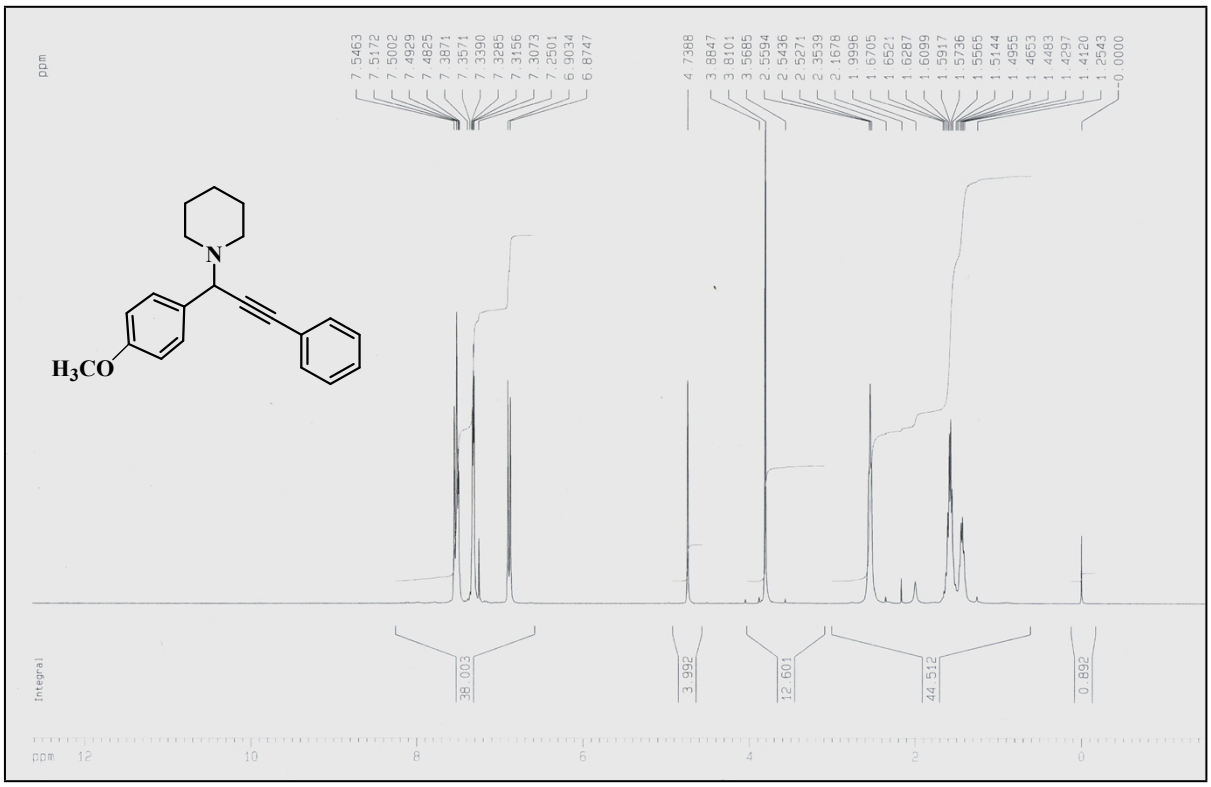
(xi) 1-(1,9-diphenyl-9-(piperidin-1-yl)nona-2,7-diynyl)piperidine (**Entry 11**):



Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.25-1.59 (m, 10H), δ 1.77-1.82 (m, 4H), δ 2.36-2.47 (m, 12H), δ 4.54 (s, 2H), δ 7.23-7.42 (6H, m), δ 7.53-7.55 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 17.56, 17.68, 24.42, 26.06, 27.92, 50.54, 61.95, 68.84, 83.62, 86.60, 127.34, 127.96, 128.54, 138.78; MS m/z 438 (M^+).

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

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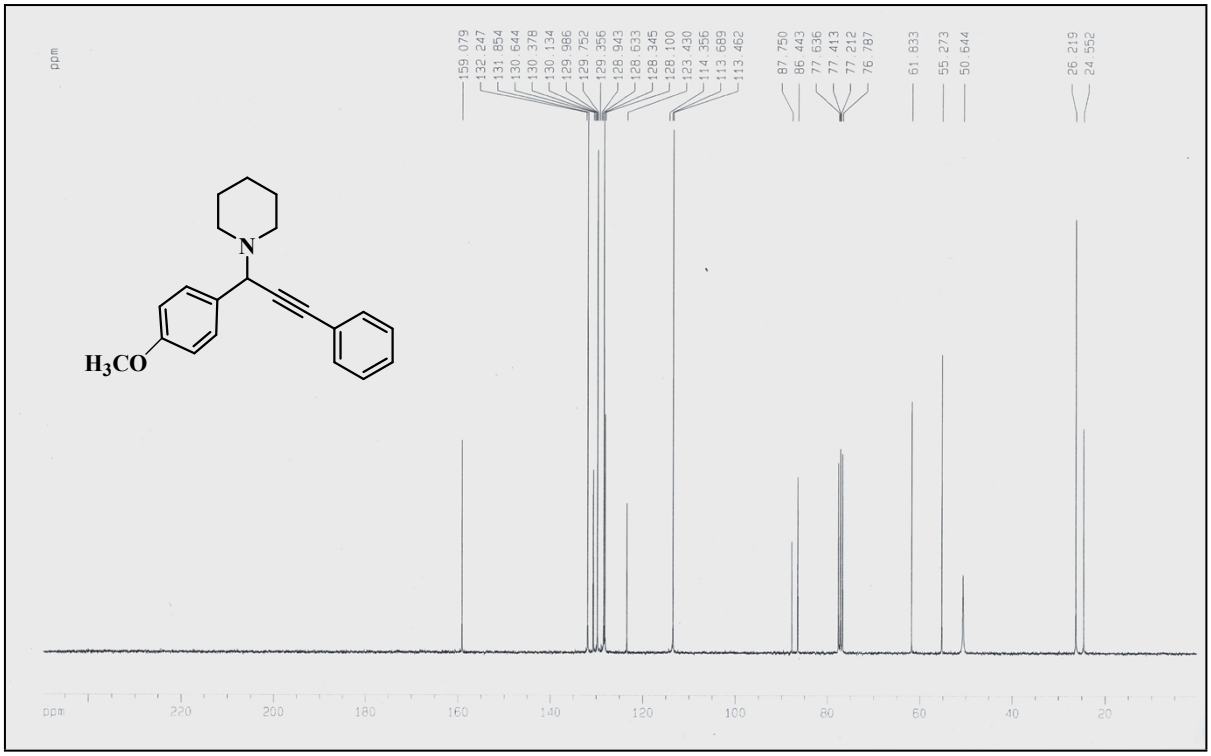
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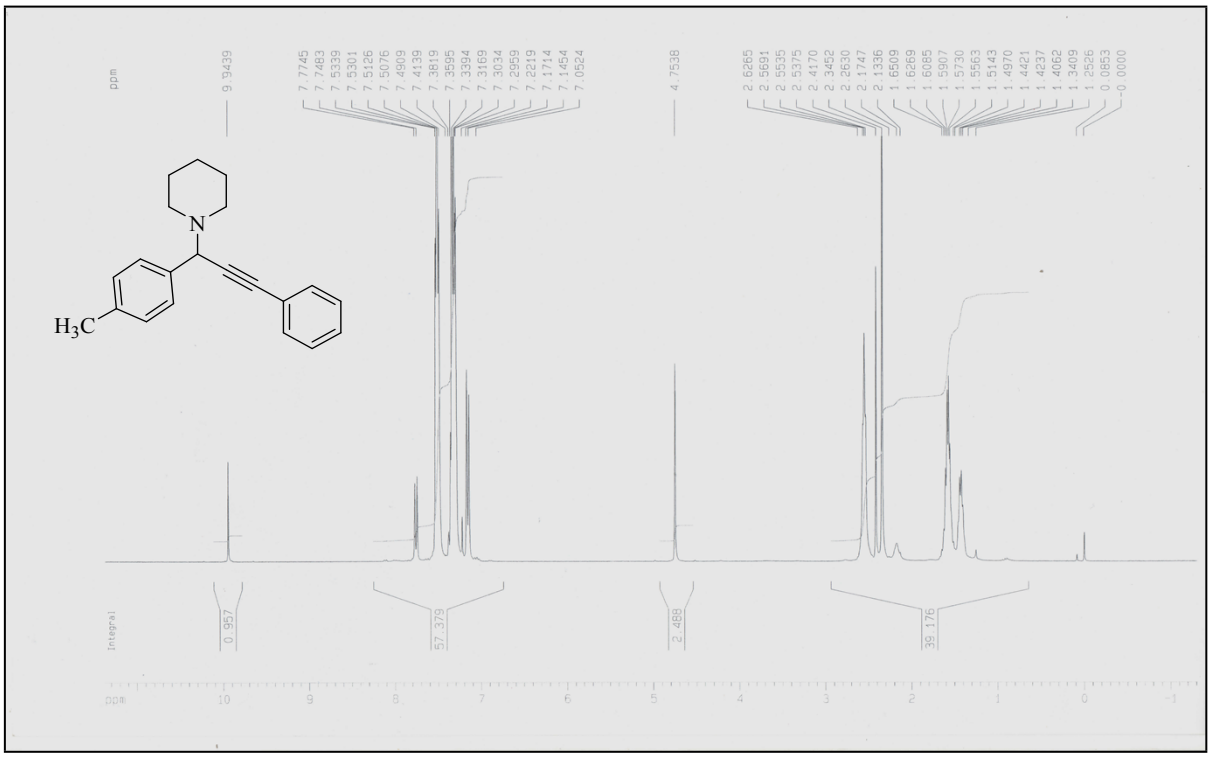
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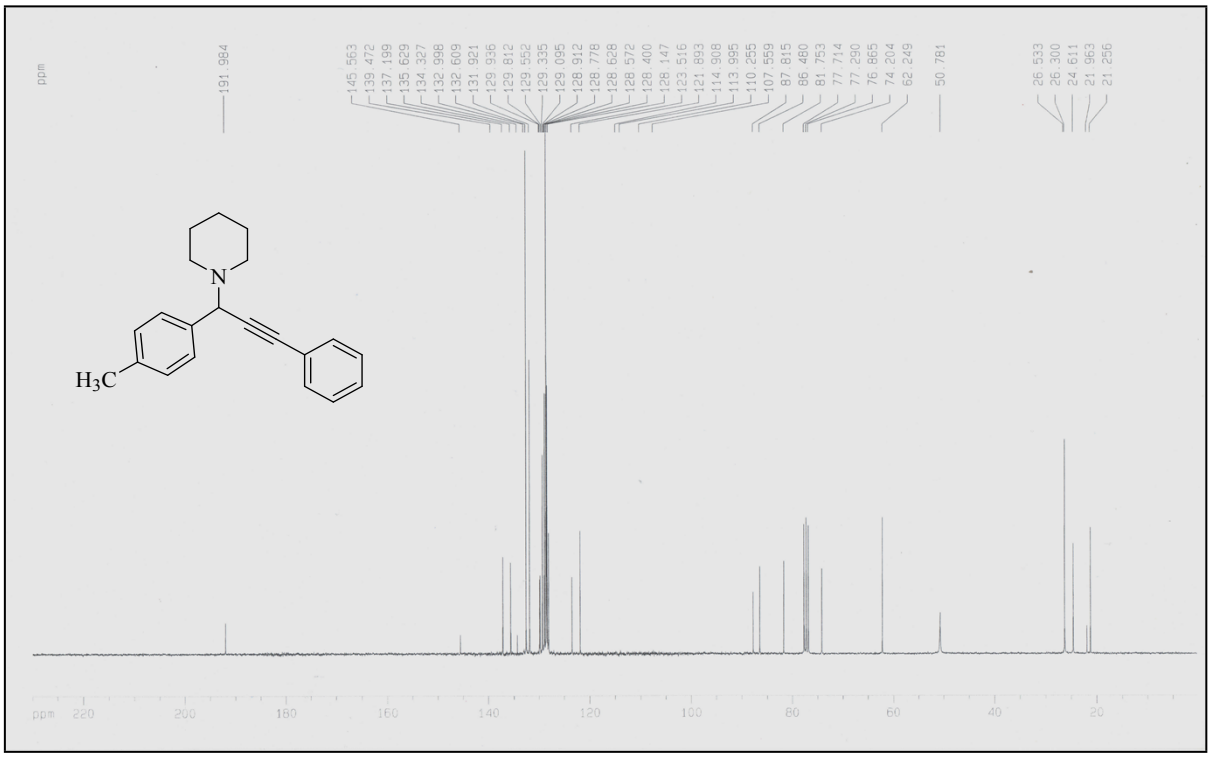
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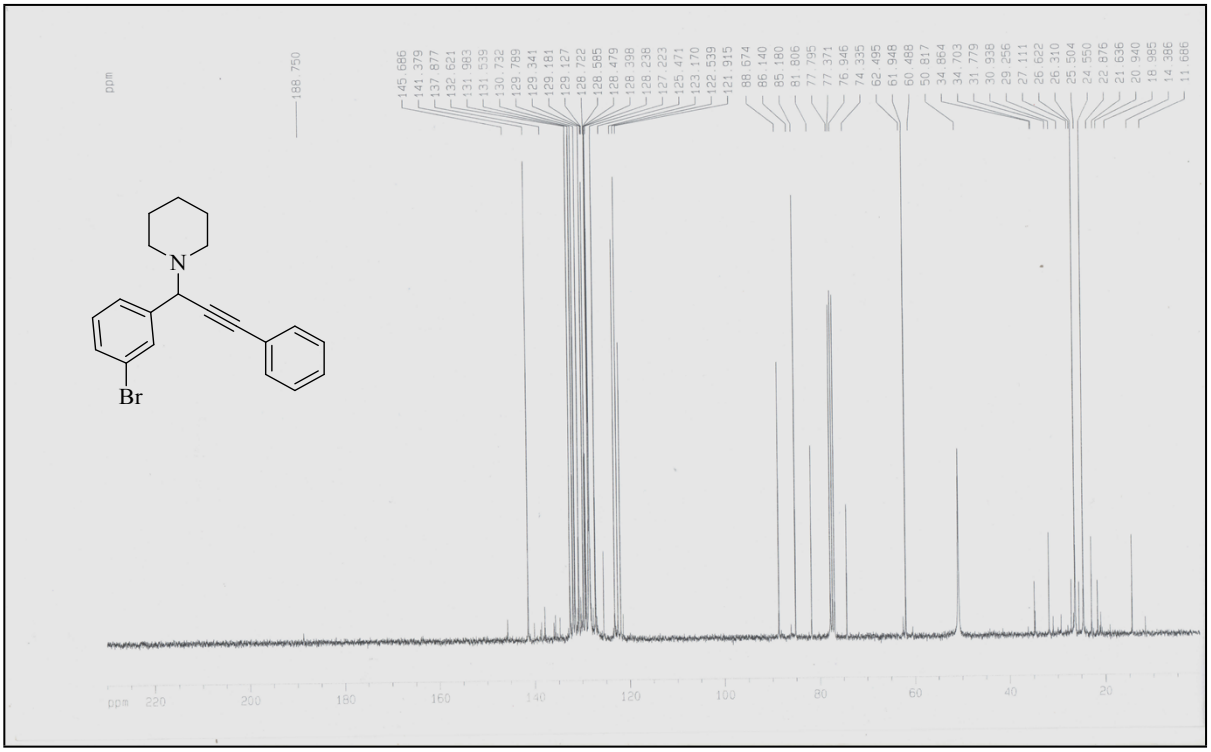
Br
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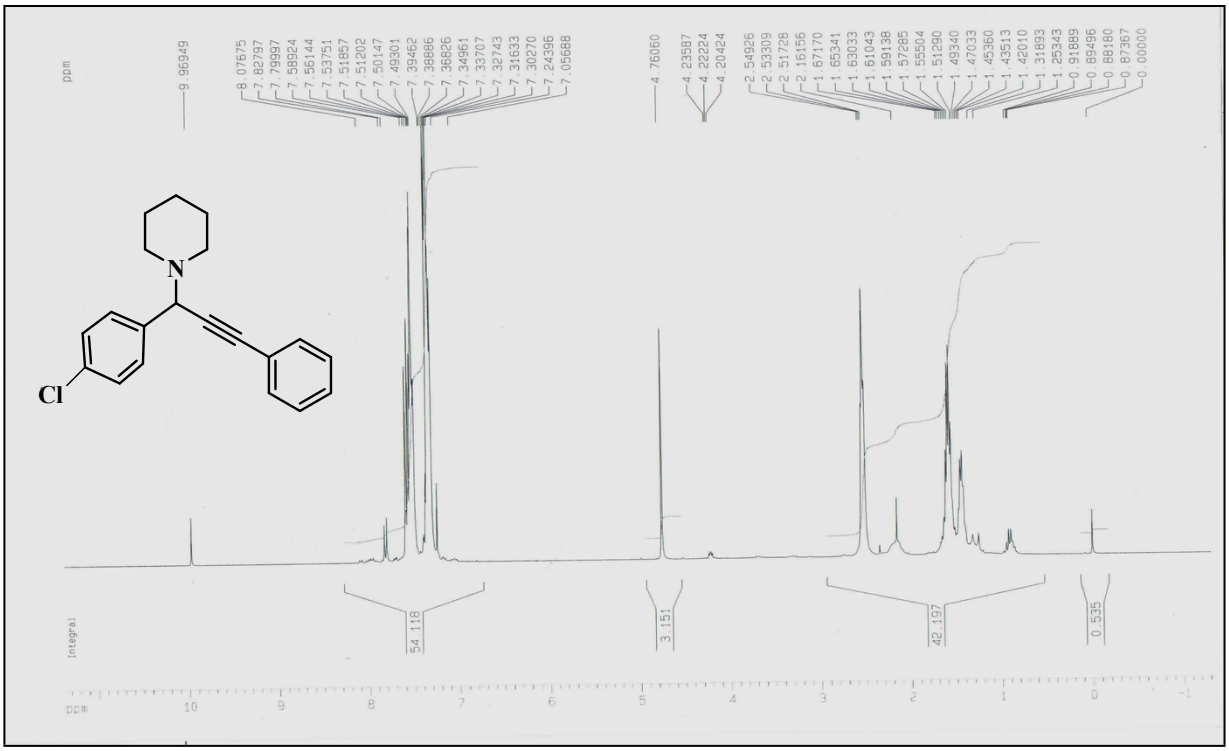
130.732
129.789
129.341
129.181
129.127
128.722
128.585
128.479
128.398
128.238
127.223
125.471
123.170
122.539
121.915
88.674
86.140
85.180
81.806
77.795
77.371
76.946
74.335
62.495
61.948
60.488
50.817
34.864
34.703
31.779
30.938
29.256
27.111
26.622
26.310
25.504
24.550
22.876
21.636
20.940
18.985
14.386
11.686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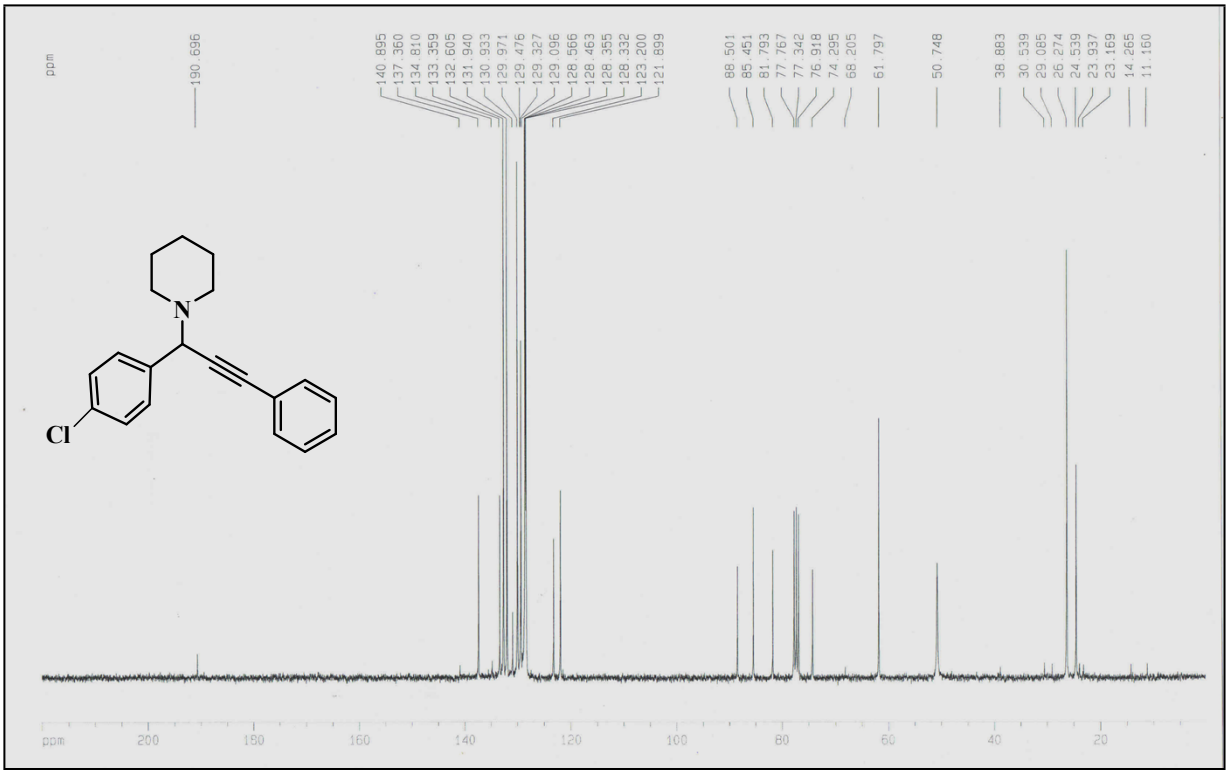
7.50147
7.49301
7.39462
7.38886
7.36826
7.34961
7.33707
7.32743
7.31633
7.30270
7.24396
7.05688
4.76060
4.23587
4.22224
4.20424
2.54926
2.53309
2.51728
2.16156
1.67170
1.65341
1.63033
1.61043
1.59138
1.57285
1.55504
1.51290
1.49340
1.47033
1.45360
1.43513
1.42010
1.31893
1.25343
0.91889
0.89496
0.88180
0.87367
0.00000
N
Cl
Integral
54.118
3.151
42.197
0.535
ppm


ppm
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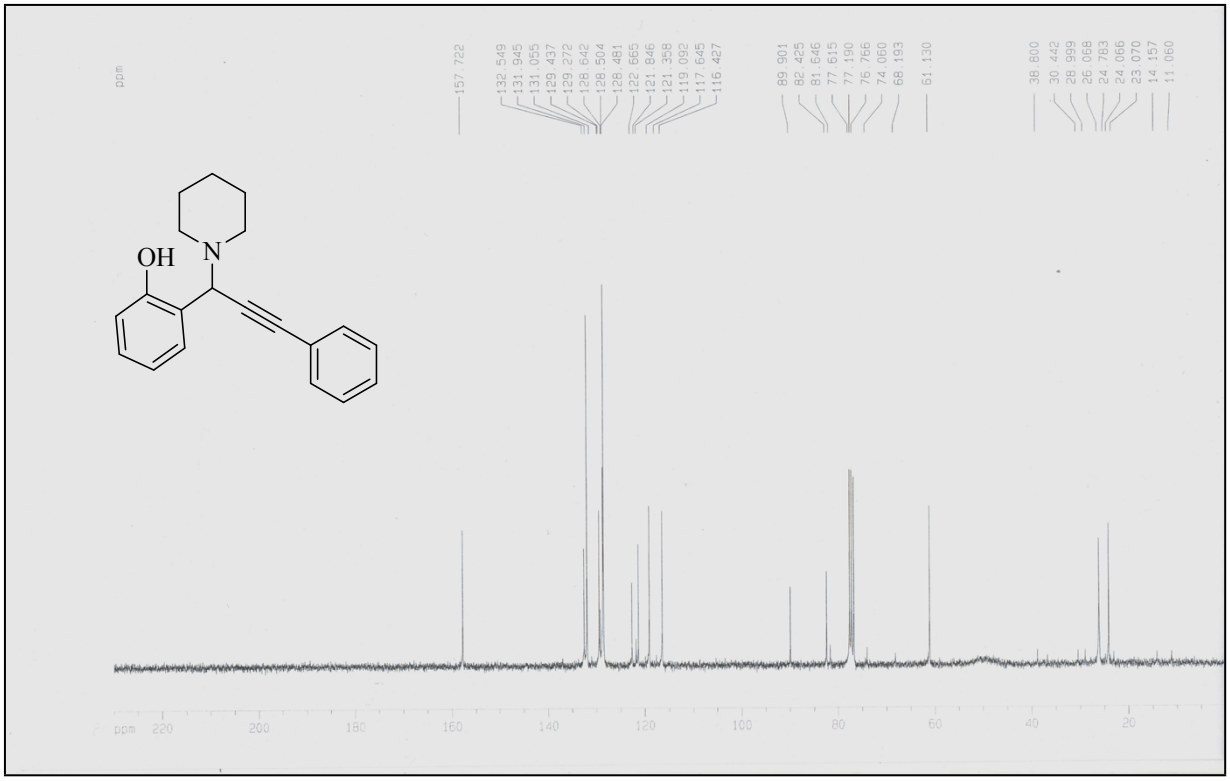
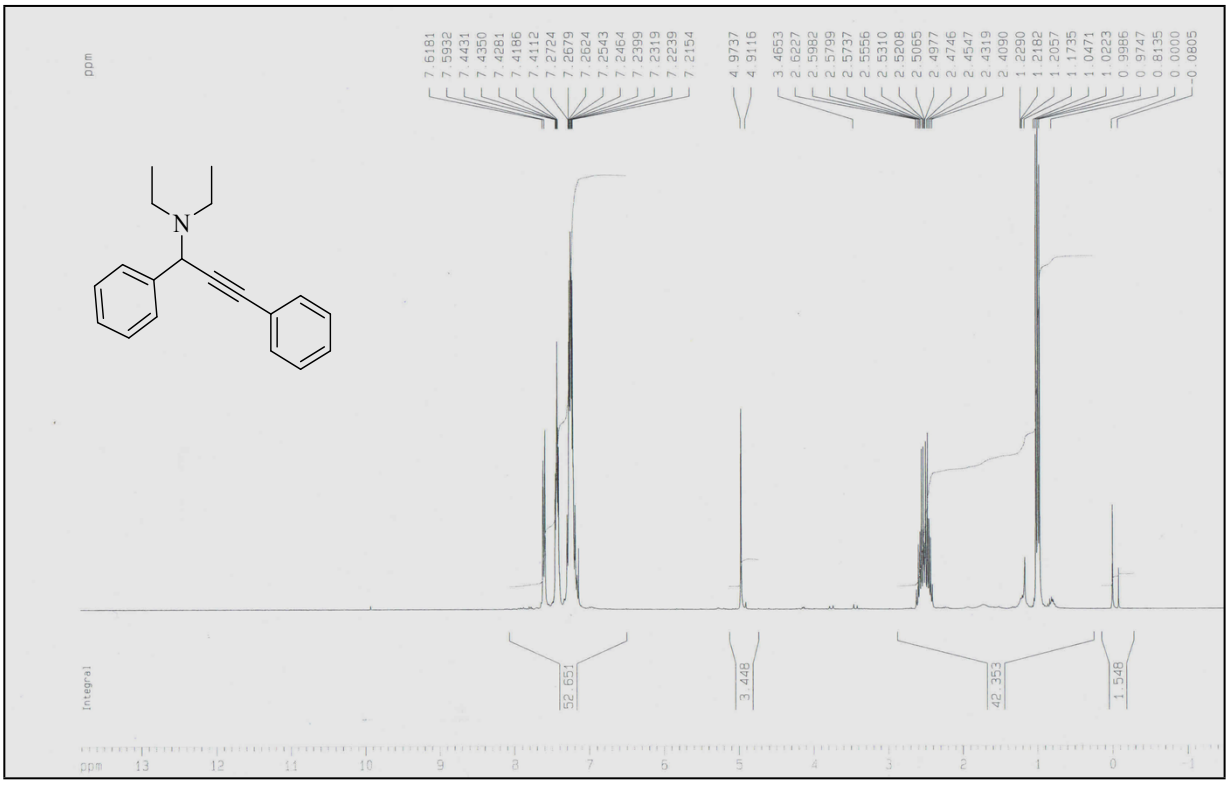
134.810
133.359
132.605
131.940
130.933
129.971
129.476
129.327
129.096
128.566
128.463
128.355
128.332
123.200
121.899
88.501
85.451
81.793
77.767
77.342
76.918
74.295
68.205
61.797
50.748
38.883
30.539
29.085
26.274
24.539
23.937
23.169
14.265
11.160
N
Cl
ppm


OH
N


OH
N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7.4350
7.4281
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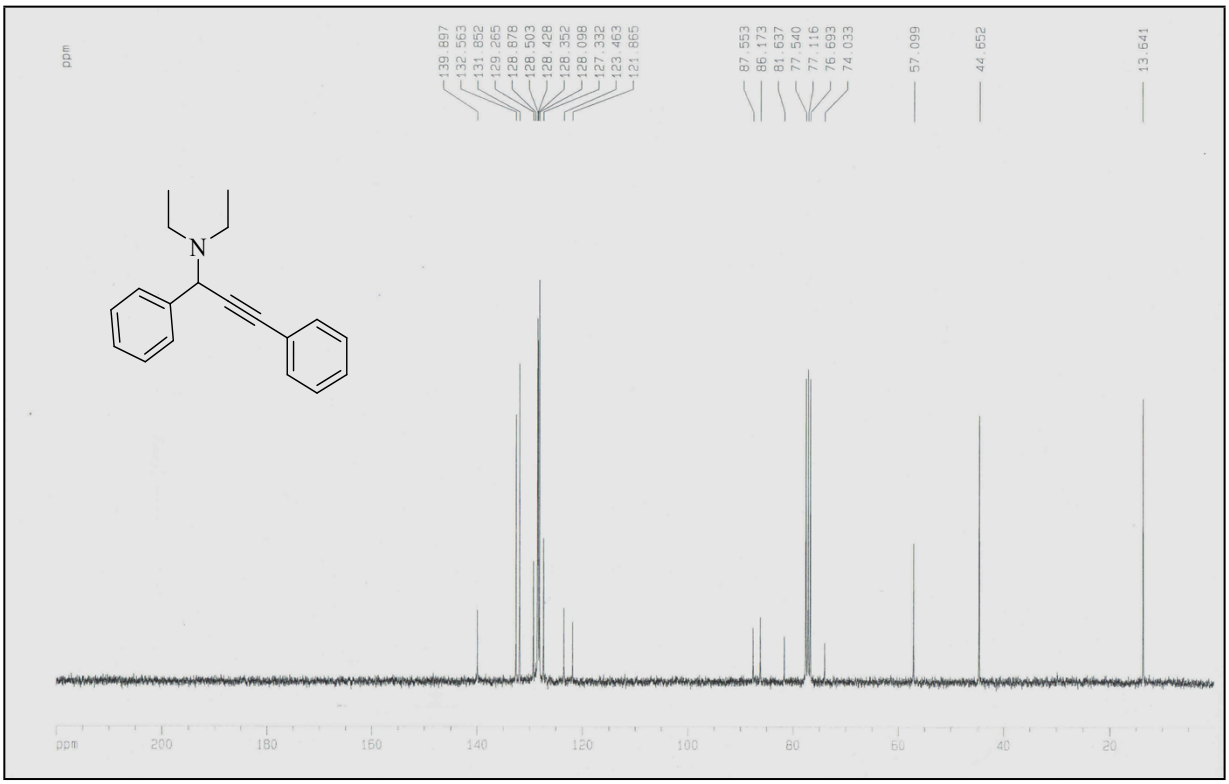
7.4112
7.2724
7.2679
7.2624
7.2543
7.2464
7.2399
7.2319
7.2239
7.2154
4.9737
4.9116
3.4653
2.6227
2.5982
2.5799
2.5737
2.5556
2.5310
2.5208
2.5065
2.4977
2.4746
2.4547
2.4319
2.4090
1.2290
1.2182
1.2057
1.1735
1.0471
1.0223
0.9986
0.9747
0.8135
0.0000
-0.0805
Integral
52.651
3.448
42.353
1.548
ppm 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1


ppm
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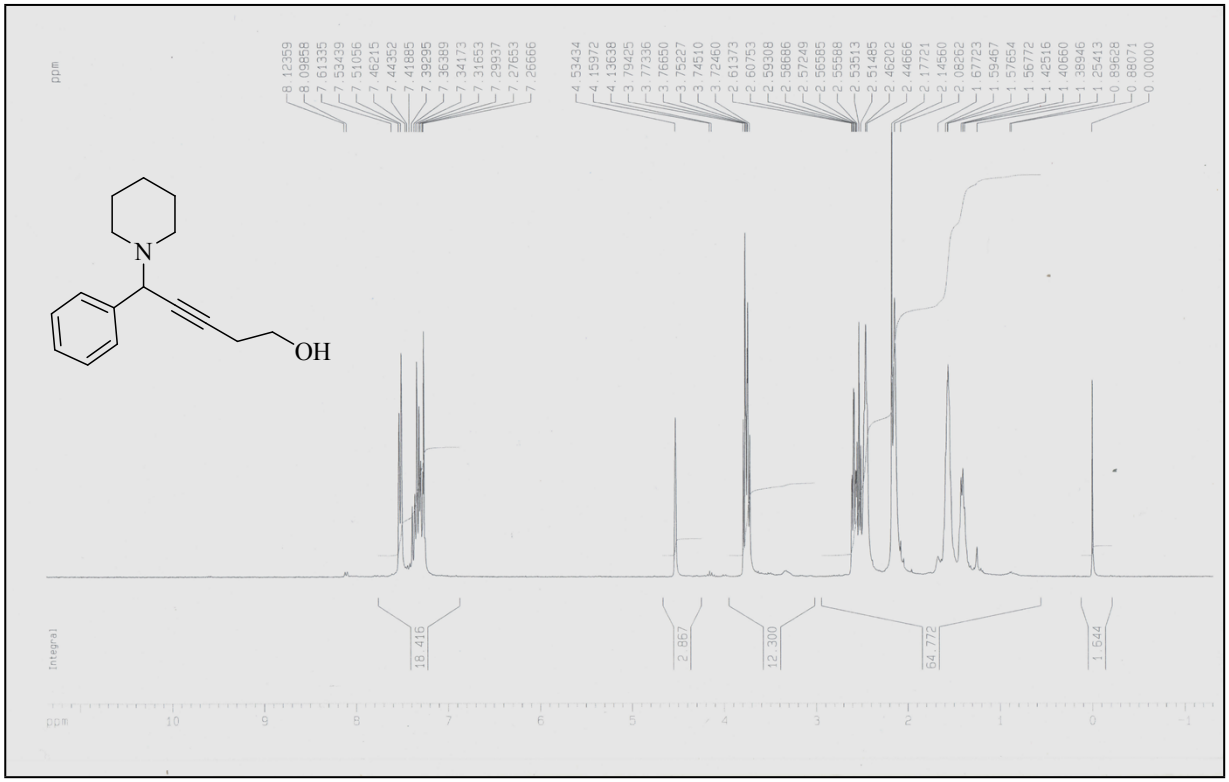
129.265
128.878
128.503
128.428
128.352
128.098
127.332
123.463
121.865
87.553
86.173
81.637
77.540
77.116
76.693
74.033
57.099
44.652
13.641
ppm 200 180 160 140 120 100 80 60 40 20


ppm
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7.61335
7.53439
7.51056
7.46215
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7.41885
7.39295
7.36389
7.34173
7.31653
7.29937
7.27653
7.26666
4.53434
4.15972
4.13638
3.79425
3.77336
3.76650
3.75227
3.74510
3.72460
2.61373
2.60753
2.59308
2.58686
2.57249
2.56585
2.55588
2.53513
2.51485
2.46202
2.44666
2.17721
2.14560
2.08262
1.67723
1.59467
1.57654
1.56772
1.42516
1.40660
1.38946
1.25413
0.89628
0.88071
0.00000
N
OH
Integral
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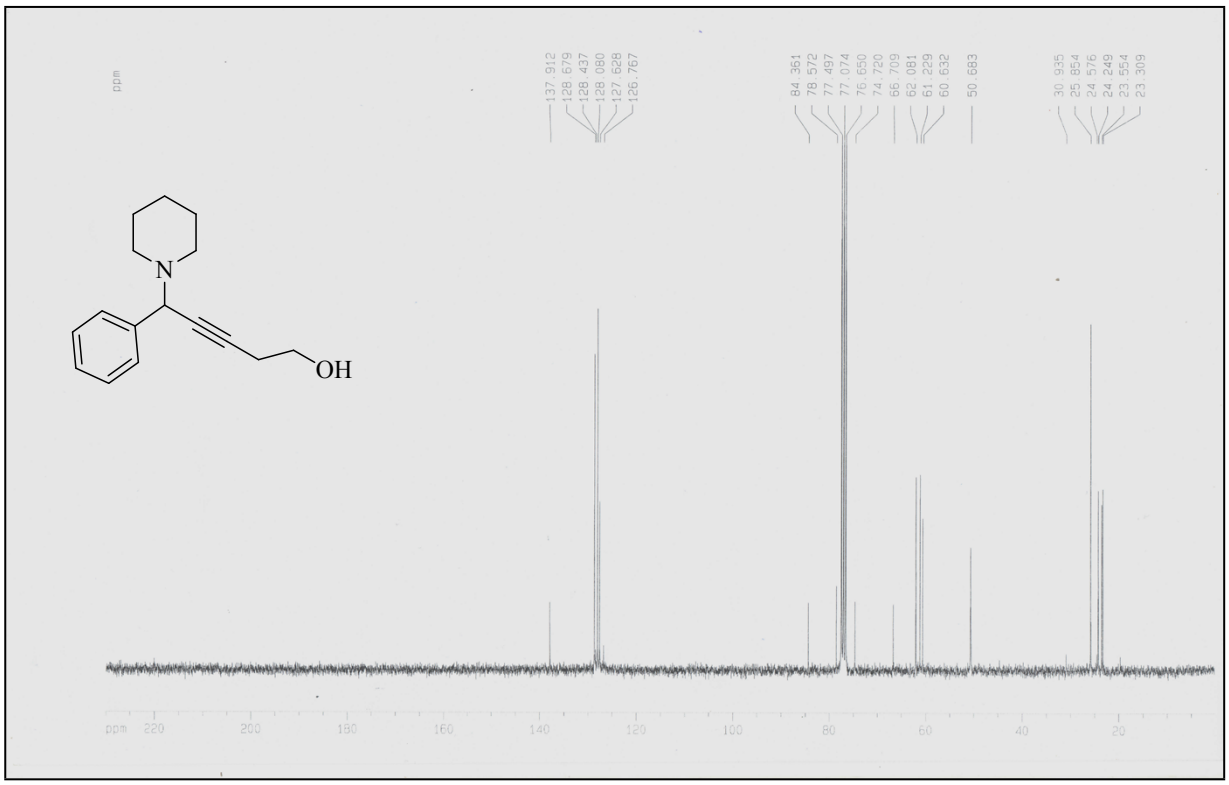
2.857
12.300
64.772
1.644
ppm


ppm
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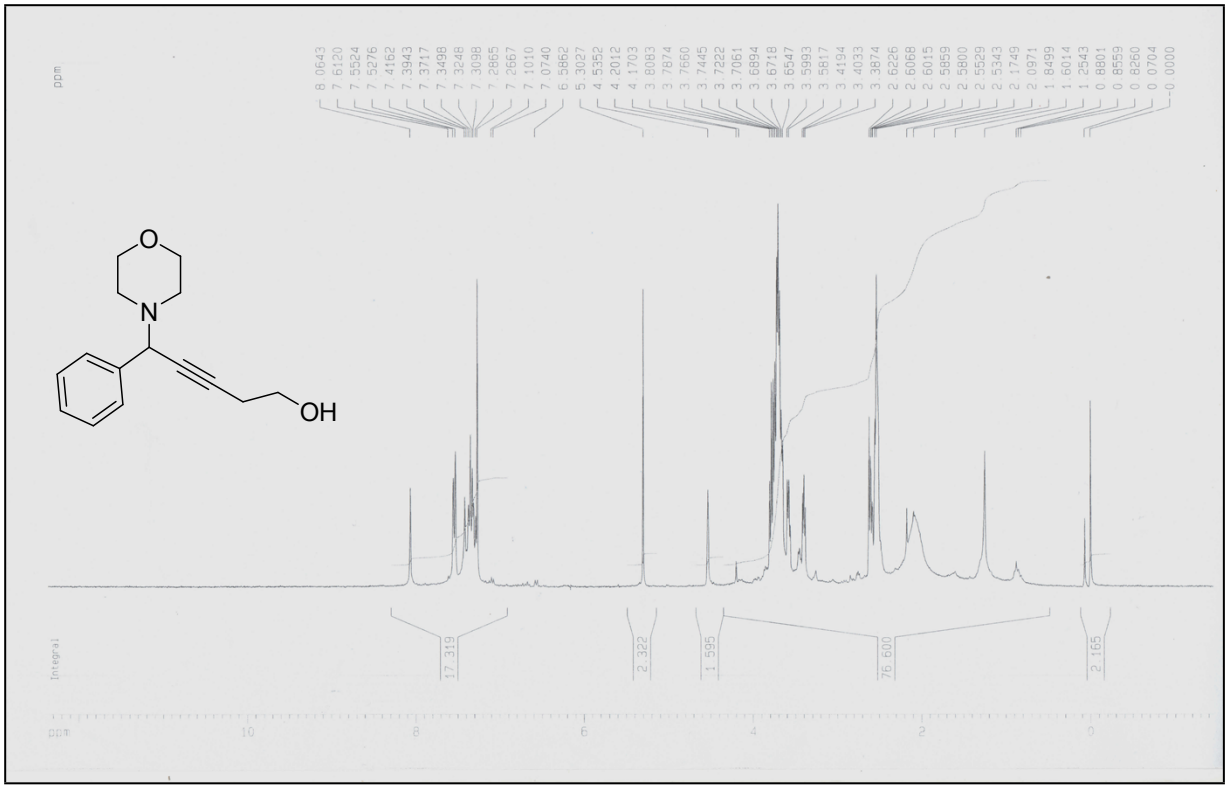
128.437
128.080
127.628
126.767
84.361
78.572
77.497
77.074
76.650
74.720
66.709
62.081
61.229
60.632
50.683
30.935
25.854
24.576
24.249
23.554
23.309
N
OH
ppm


O
N
OH
ppm
Integral
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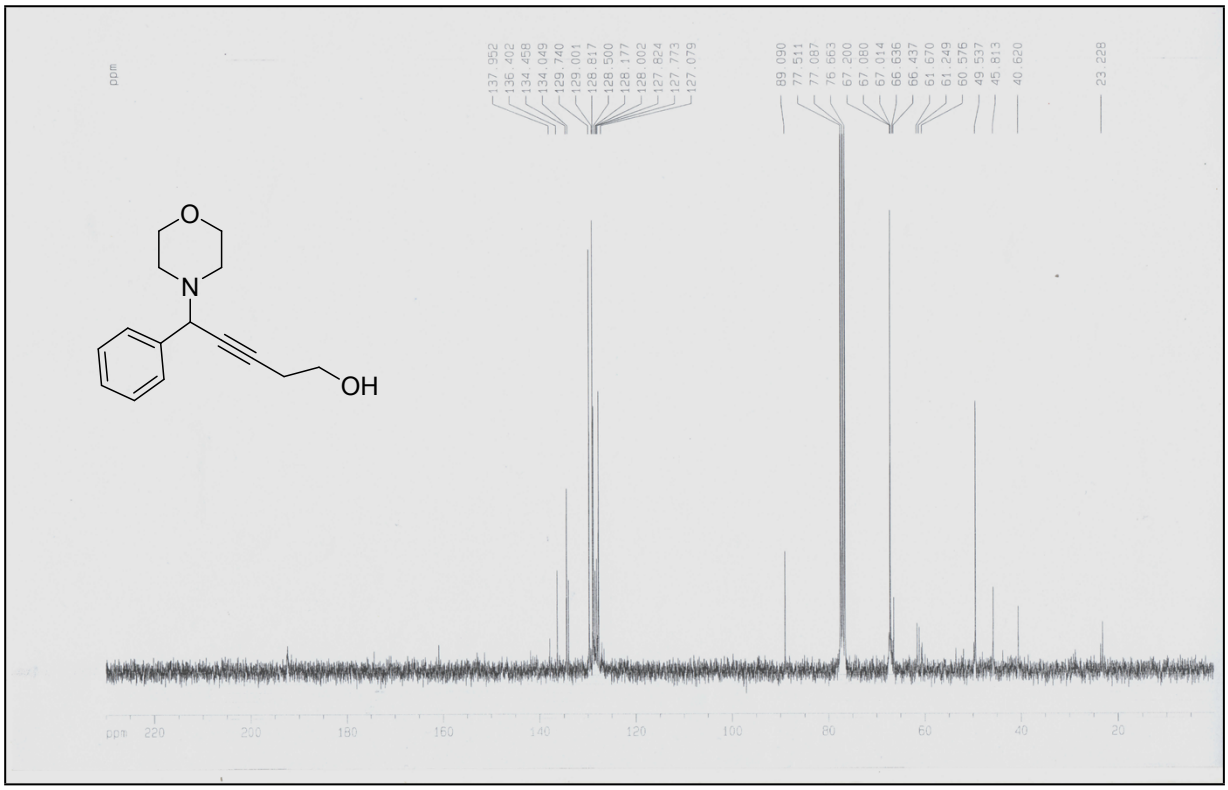
2.322
1.595
76.600
2.165


O
N
OH
ppm
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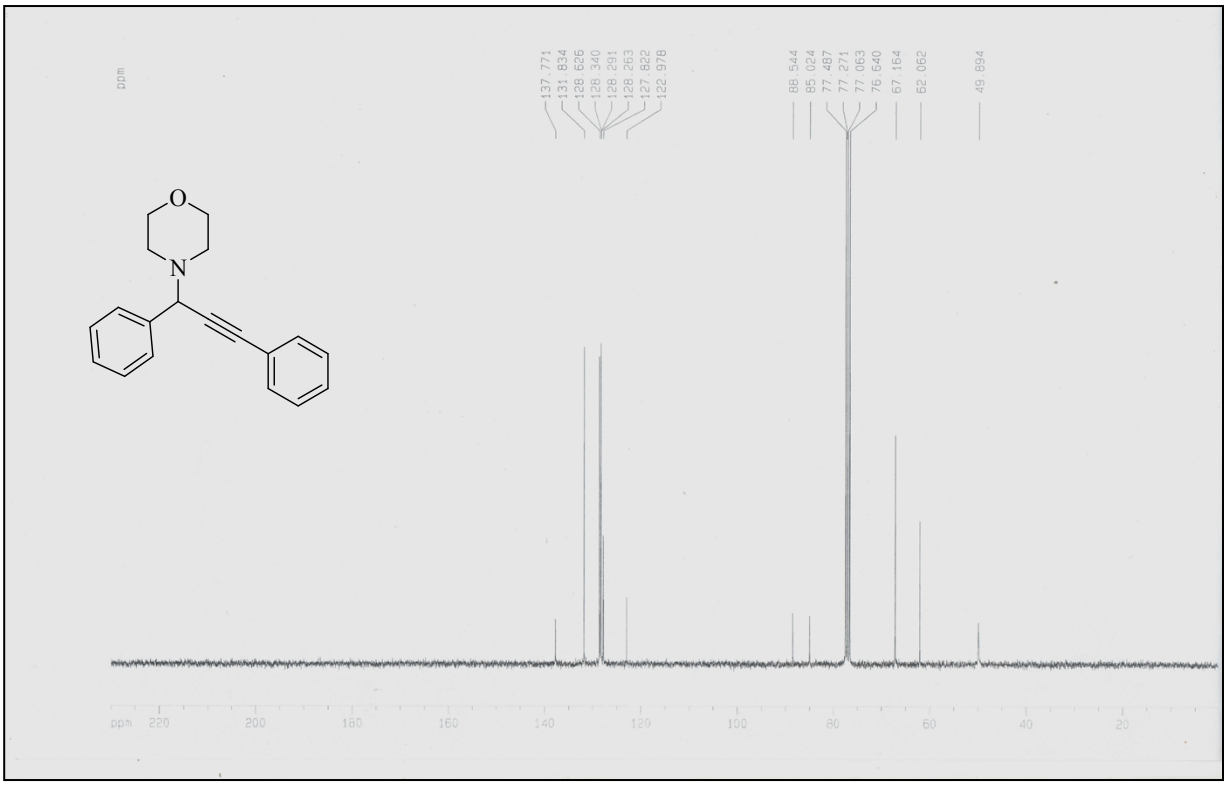
134.049
129.740
129.001
128.817
128.500
128.177
128.002
127.824
127.773
127.079
89.090
77.511
77.087
76.663
67.200
67.080
67.014
66.636
66.437
61.670
61.249
60.576
49.537
45.813
40.620
23.228


ppm
7.6474
7.6237
7.5311
7.5198
7.5137
7.5080
7.4997
7.4428
7.3937
7.3712
7.3448
7.3374
7.3262
7.3167
7.3021
7.2778
7.2425
4.7952
3.7915
3.7776
3.7538
3.7400
3.7260
3.6910
3.6776
2.6525
2.6379
2.6238
2.4131
2.3493
2.1601
2.1410
2.0395
1.3009
1.2553
0.8962
0.8808
-0.0000
Integral
50.492
4.732
20.234
23.954
0.588
ppm
10
9
8
7
6
5
4
3
2
1
0
-1


ppm
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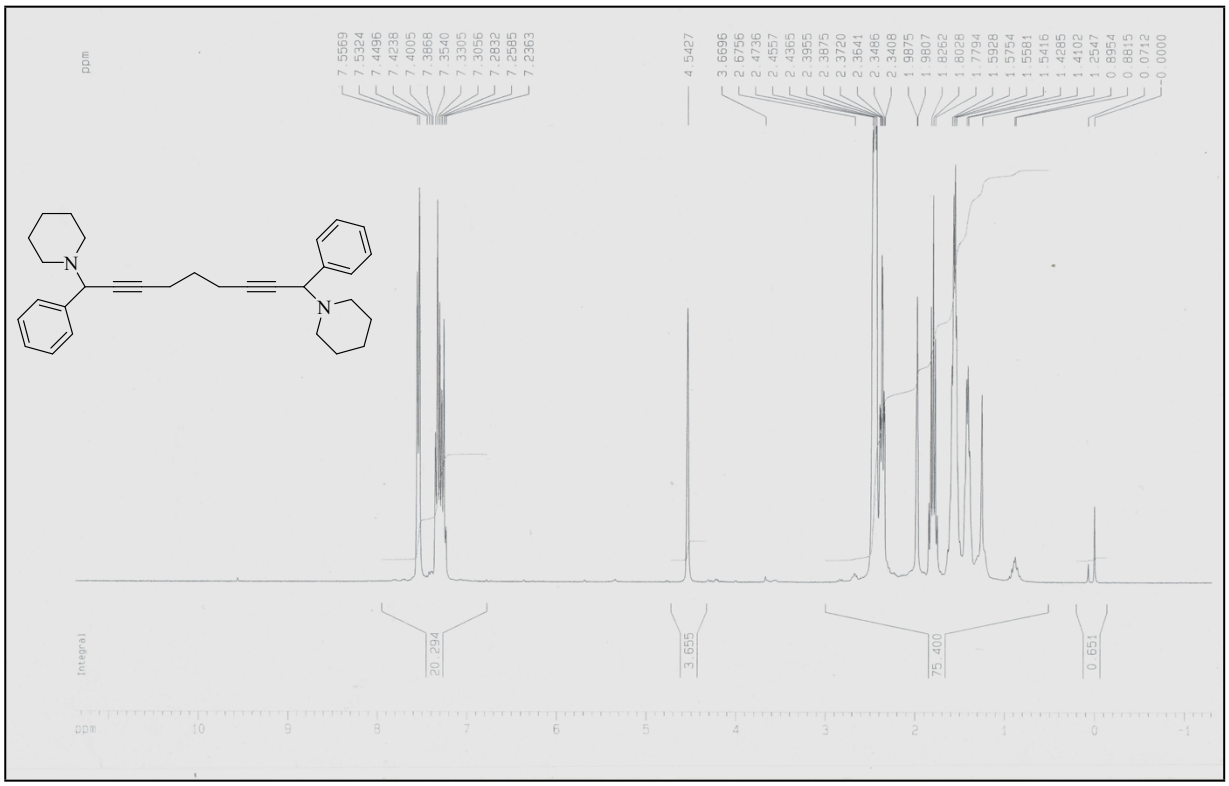
128.291
128.263
127.822
122.978
88.544
85.024
77.487
77.271
77.063
76.640
67.164
62.062
49.894
ppm
220
200
180
160
140
120
100
80
60
40
20


ppm
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7.4238
7.4005
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7.3540
7.3305
7.3056
7.2832
7.2585
7.2363
4.5427
3.6696
2.6756
2.4736
2.4557
2.4365
2.3955
2.3875
2.3720
2.3641
2.3486
2.3408
1.9875
1.9807
1.8262
1.8028
1.7794
1.5928
1.5754
1.5581
1.5416
1.4285
1.4102
1.2547
0.8954
0.8815
0.0712
-0.0000
Integral
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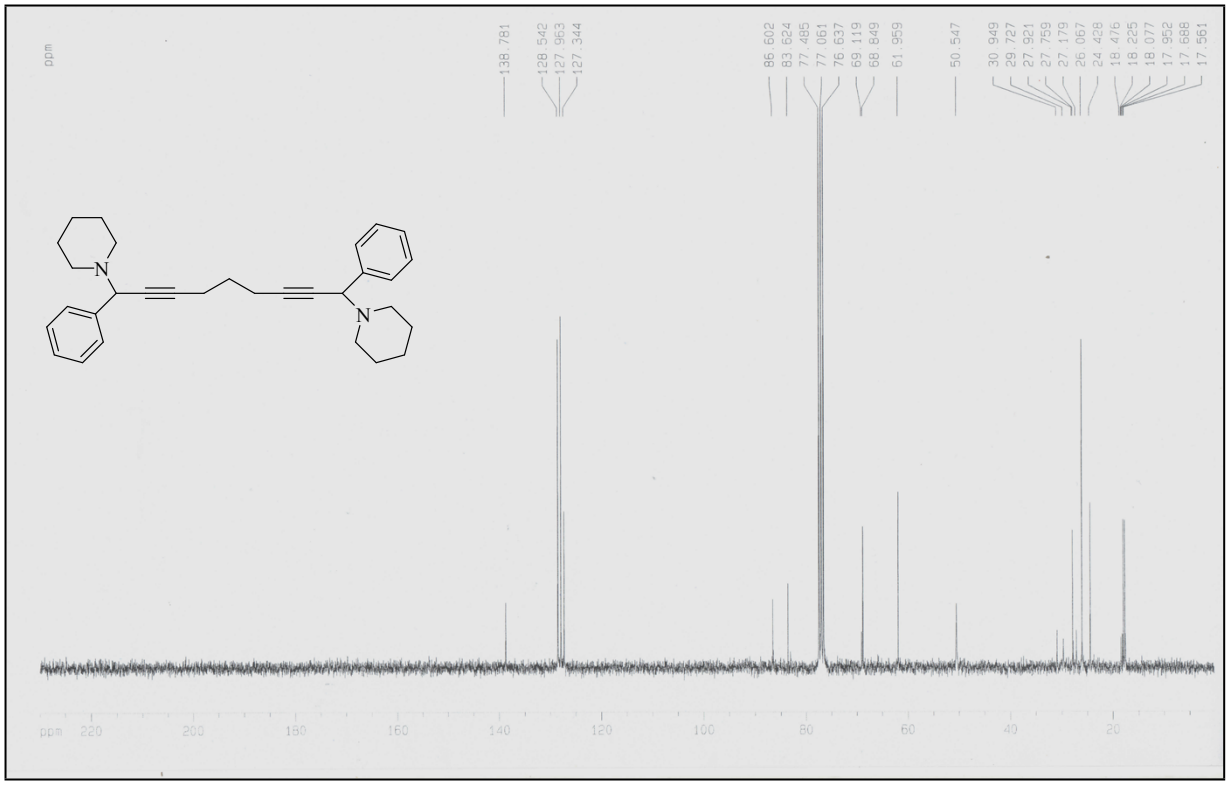
3.655
75.400
0.651
ppm
10
9
8
7
6
5
4
3
2
1
0
-1


ppm
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128.542
127.963
127.344
86.602
83.624
77.485
77.061
76.637
69.119
68.849
61.959
50.547
30.949
29.727
27.921
27.759
27.179
26.067
24.428
18.476
18.225
18.077
17.952
17.688
17.561
ppm
220
200
180
160
140
120
100
80
60
40
20

References

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[2] M. Borah, J. N. Ganguli, D. K. Dutta, *J. Colloid. Interface Sci.* **2001**, 233,171.

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