Supporting information

High Efficient and Large-scalable Glucoamylase-catalyzed Henry Reactions

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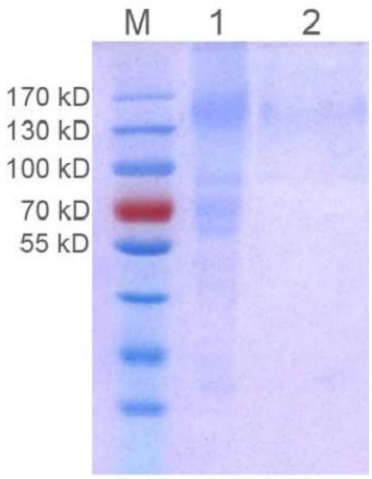
1. Materials and analytical methods

Amyloglucosidase from *Aspergillus niger* [glucoamylase, 1,4-α-D-glucan glucohydrolase, EC 3.2.1.3, ~70 U/mg (One unit corresponds to the amount of enzyme which liberates 1 μmole of glucose per minute at pH 4.8 and 60 °C)] was purchased from Sigma-Aldrich. Glucose (HK) Assay Kit (Product Code GAHK 20) was used as received from Sigma-Aldrich. All reagents, 100-kDa cut off centrifugal ultrafilter (Millipore), and PageRuler Prestained Protein Ladder (Thermo) were obtained from different commercial suppliers and were used without further purification. All reactions were monitored by thin-layer chromatography with Haiyang GF254 silica gel plates. Flash column chromatography was performed using 100–200 mesh silica gel at increased pressure. Enzymatic assay of *An*GA was completed with the method of Spectrophotometric Stop rate Determination.

2. Procedures of *An*GA purification

A centrifugal ultrafiltration strategy was used for the separation and desalting of protein. Briefly, enzyme protein was resolved in ddH_2O and passed through 100-kDa cut off centrifugal ultrafilters. The retentates were washed three times with ddH_2O and then dissolved in 200 μL of ddH_2O. Separated protein was analyzed by SDS-polyacrylamide gel electrophoresis (PAGE) on a 10% gradient gel stained with Coomassie brilliant blue (**Fig. 1s**). When 1mg of purified *An*GA was used to catalyze model Henry reaction, 52% of Henry product was obtained. And its natural activity was 27 U at pH 4.5 and 60 °C.



M - Marker;

1 - commercial enzyme protein (*An*GA);

2 - molecular weight higher than 100 kDa;

Fig. 1s SDS-PAGE analysis of *An*GA

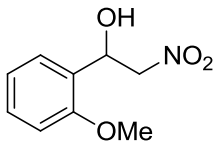
3. Enzymatic assay of *An*GA

Unit definition (U/mg): One unit corresponds to the amount of enzyme which liberates 1 μmole of glucose per minute at pH 4.5 and 60 °C.

The procedures of enzymatic assay were based on literature [1] from Sigma-Aldrich.

4. Characterization of Henry products

1-(2-Methoxyphenyl)-2-nitroethanol (3a) [2, 3]

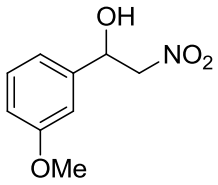


The title compound **3a** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 6/1) to give a light yellow oil (86% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.41 (d, *J* = 8 Hz, 1H), 3.85 (s, 3H), 4.50-4.63 (m, 2H), 5.59 (br s, 1H), 6.89 (d, *J* = 8 Hz, 1H), 6.98 (t, *J* = 8 Hz, 1H), 7.31 (t, *J* = 8 Hz, 1H), 7.40 (d, *J* = 8 Hz, 1H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 55.43, 67.76, 79.91, 110.59, 121.12, 126.12, 127.17, 129.79, 156.04.

1-(3-Methoxyphenyl)-2-nitroethanol (3b) [4, 5]

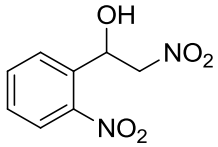


The title compound **3b** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 6/1) to give a yellow oil (77% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.23 (br s, 1H), 3.80 (s, 3H), 4.45-4.59 (m, 2H), 5.39 (d, *J* = 8 Hz, 1H), 6.86-6.94 (m, 3H), 7.29 (t, *J* = 8 Hz, 1H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 55.35, 70.90, 81.25, 111.53, 114.37, 118.12, 130.11, 139.90, 160.02.

2-Nitro-1-(2-nitrophenyl)ethanol (3c) [5-7]

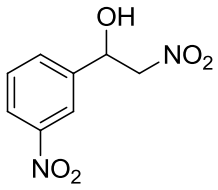


The title compound **3c** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to give a brown oil (95% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.50 (br s, 1H), 4.53-4.59 (m, 1H), 4.84-4.88 (m, 1H), 6.02-6.05 (m, 1H), 7.54-7.57 (m, 1H), 7.75 (t, *J* = 8 Hz, 1H), 7.95 (d, *J* = 8 Hz, 1H), 8.06 (d, *J* = 8 Hz, 1H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 66.81, 80.20, 124.93, 128.71, 129.65, 134.36, 134.49, 147.02.

2-Nitro-1-(3-nitrophenyl)ethanol (3d) [6, 7]



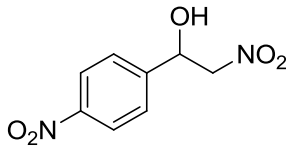
The title compound **3d** was prepared according to the general procedure and purified by column

chromatography (petroleum ether/ethyl acetate = 4/1) to give a white solid (96% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.63 (br s, 1H), 4.62-4.64 (m, 2H), 5.61-5.62 (m, 1H), 7.61 (t, *J* = 8 Hz, 1H), 7.79(d, *J* = 8 Hz, 1H), 8.19 (d, *J* = 8 Hz, 1H), 8.30 (s, 1H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 69.86, 80.72, 121.13, 123.69, 130.12, 132.31, 140.52, 148.34.

2-Nitro-1-(4-nitrophenyl)ethanol (3e) [6, 7]

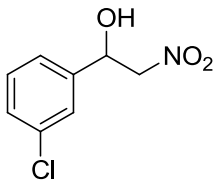


The title compound **3e** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to give a yellow solid (98% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.13 (br s, 1H), 4.58-4.61 (m, 2H), 5.60-5.62 (m, 1H), 7.63 (d, *J* = 8 Hz, 2H), 8.27 (dd, *J* = 8 Hz, 4 Hz, 2H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 69.97, 80.58, 124.21, 126.95, 144.90, 148.19.

1-(3-Chlorophenyl)-2-nitroethanol (3f) [4, 5]

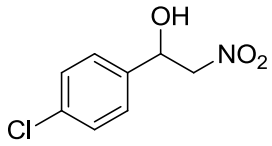


The title compound **3f** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give a yellow oil (52% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.25 (br s, 1H), 4.48-4.52 (m, 1H), 4.54-4.60 (m, 1H), 5.43 (d, *J* = 8 Hz, 1H), 7.26-7.28 (m, 1H), 7.32-7.34 (m, 2H), 7.41 (s, 1 H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 70.29, 80.97, 124.09, 126.22, 129.08, 130.33, 134.97, 140.17.

1-(4-Chlorophenyl)-2-nitroethanol (3g) [4, 8]

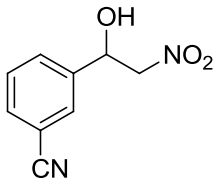


The title compound **3g** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give a yellow oil (82% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.51 (br s, 1H), 4.44-4.48 (m, 1H), 4.51-4.57 (m, 1H), 5.39 (d, *J* = 8 Hz, 1H), 7.29-7.35 (m, 4H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 70.30, 81.04, 127.41, 129.17, 134.71, 136.72.

3-(1-Hydroxy-2-nitroethyl)benzonitrile (3h)[9]

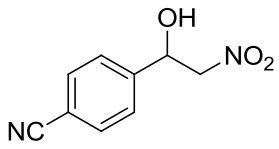


The title compound **3h** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to give a white solid (97% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.39 (br s, 1H), 4.56-4.63 (m, 2H), 5.51-5.55 (m, 1H), 7.52-7.76 (m, 4H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 69.84, 80.80, 113.10, 118.24, 129.71, 129.86, 130.41, 132.47, 139.84.

4-(1-Hydroxy-2-nitroethyl)benzonitrile (3i)[2, 9, 10]



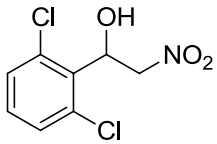
The title compound **3i** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to give a white solid (99% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.31 (d, *J* = 4 Hz, 1H), 4.55-4.60 (m, 2H), 5.53-5.57 (m, 1H), 7.56

(d, *J* = 8 Hz, 2H), 7.70-7.72 (m, 2H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 70.13, 80.74, 118.28, 126.78, 132.79, 143.41.

1-(2,6-Dichlorophenyl)-2-nitroethanol (3j) [9]

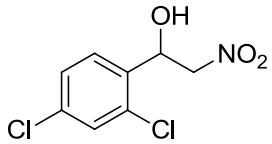


The title compound **3j** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 12/1) to give a light yellow oil (93% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.64 (d, *J* = 8 Hz, 1H), 4.53-4.57 (m, 1H), 5.11-5.17 (m, 1H), 6.20-6.25 (m, 1H), 7.22-7.26 (m, 1H), 7.33-7.35 (m, 2H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 68.51, 77.63, 129.71, 130.64, 132.34, 134.77.

1-(2,4-Dichlorophenyl)-2-nitroethanol (3k) [3, 6, 11]

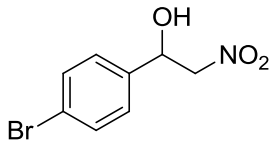


The title compound **3k** was prepared according to the general procedure and purified by column chromatography petroleum ether/ethyl acetate = 12/1) to give a light yellow oil (98% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.38 (d, *J* = 4 Hz, 1H), 4.39-4.45 (m, 1H), 4.62-4.66 (m, 1H), 5.78 (d, *J* = 8 Hz, 1H), 7.33 (d, *J* = 8 Hz, 1H), 7.39 (s, 1H), 7.60 (d, *J* = 8 Hz, 1H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 67.48, 79.20, 127.94, 128.58, 129.41, 132.07, 134.36, 135.08.

1-(4-Bromophenyl)-2-nitroethanol (3l)[2, 5, 11]



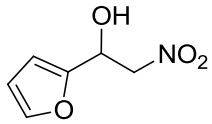
The title compound **3l** was prepared according to the general procedure and purified by column

chromatography (petroleum ether/ethyl acetate = 8/1) to give a yellow oil (89% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.36 (br s, 1H), 4.46 (dd, *J* = 12 Hz, 4 Hz, 1H), 4.52-4.58 (m, 1H), 5.40 (d, *J* = 8 Hz, 1H), 7.26 (d, *J* = 8 Hz, 2H), 7.50-7.53 (m, 2H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 70.35, 80.98, 122.88, 127.70, 132.14, 137.23.

1-(2-Furanyl)-2-nitroethanol (3m) [2, 6]

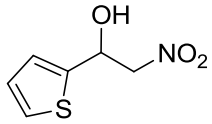


The title compound **3m** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 7/1) to give a yellow oil (6% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 2.89 (br s, 1H), 4.66-4.70 (m, 1H), 4.76-4.82 (m, 1H), 5.48 (dd, *J* = 8 Hz, 4 Hz, 1H), 6.38-6.41 (m, 2H), 7.42-7.43 (m, 1H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 64.88, 78.40, 108.19, 110.67, 143.19, 150.72,

1-(2-thiophenyl)-2-nitroethanol (3n) [6]

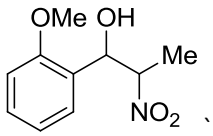


The title compound **3n** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give a yellow oil (8% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.07 (br s, 1H), 4.60-4.64 (m, 1H), 4.70-4.75 (m, 1H), 5.73 (d, *J* = 8 Hz, 1H), 7.01-7.04 (m, 1H), 7.07-7.08 (m, 1H), 7.34-7.35 (m, 1H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 67.12, 80.79, 125.07, 126.19, 127.24, 141.23.

1-(2-Methoxyphenyl)-2-nitroethanol (3o) [12, 13]

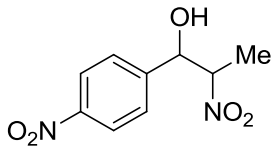


The title compound **3o** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 15/1) to give a colourless oil (*syn* 41% yield) and a white solid (*anti* 31% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ ***syn* isomer:** 1.34 (d, *J* = 8 Hz, 3H), 3.30 (d, *J* = 12 Hz, 1H), 3.90 (s, 3H), 4.97-5.04 (m, 1H), 5.14 (t, *J* = 8 Hz, 1H), 6.92-7.02 (m, 2H), 7.26-7.36 (m, 2H). ***anti* isomer:** 1.49 (d, *J* = 4 Hz, 3H), 3.04 (d, *J* = 4 Hz, 1H), 3.88 (s, 3H), 4.87-4.93 (m, 1H), 5.53-5.55 (m, 1H), 6.90 (d, *J* = 8 Hz, 1 Hz, 1H)； 7.00 (t, *J* = 8 Hz, 1H), 7.29-7.33 (m, 1H), 7.41-7.44 (m, 1H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ ***syn* isomer:** 16.60, 55.45, 74.19, 87.65, 110.99, 121.24, 125.90, 129.02, 130.10, 156.76. ***anti* isomer:** 12.59, 55.40, 70.77, 85.07, 110.39, 120.97, 126.25, 127.66, 129.47, 155.79.

1-(4-nitrophenyl)-2-nitropropan-1-ol (3p) [12, 14]

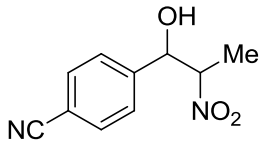


The compound **3p** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give a white solid (87% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 1.38 (d, *J* = 4 Hz, 2H), 1.49 (d, *J* = 8 Hz, 1H), 3.29 (br s, 1H), 4.72-4.80 (m, 1H), 5.18-5.21 (m, 0.58H), 5.57 (s, 0.42H), 7.58-7.60 (m, 2H), 8.23-8.26 (m, 2H).

^{13}CNMR ($CDCl_3$, 400 MHz): δ 11.83, 16.20, 72.93, 75.05, 86.83, 87.83, 123.93, 124.09, 127.05, 127.96, 145.37, 145.67, 147.86, 148.24.

4-(1-hydroxy-2-nitropropyl)benzonitrile (3q) [12, 15]

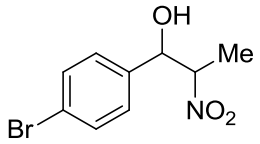


The compound **3q** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 6/1) to give colourless oil (89% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 1.34-1.48 (m, 3H), 3.19 (br s, 1H), 4.68-4.75 (m, 1H), 5.12 (d, *J* = 8 Hz, 0.50H), 5.49 (d, *J* = 4 Hz, 0.50H), 7.52-7.55 (m, 2H), 7.67-7.71 (m, 2H).

^{13}CNMR ($CDCl_3$, 400 MHz): δ 11.86, 16.18, 73.08, 75.24, 86.90, 87.86, 112.05, 112.67, 118.26, 118.42, 126.89, 127.79, 132.54, 132.71, 143.72.

1-(4-bromophenyl)-2-nitropropan-1-ol (3r) [12, 15]

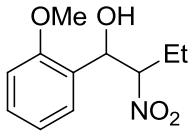


The compound **3r** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 15/1) to give a white solid (65% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 1.32, (d, *J* = 8 Hz, 2H), 1.48 (d, *J* = 8 Hz, 1H), 2.80-2.88 (m, 1H), 4.62-4.75 (m, 1H), 5.00 (d, *J* = 8 Hz, 0.64H), 5.36 (s, 0.36H), 7.24-7.27 (m, 2H), 7.50-7.55 (m, 2H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 11.99, 16.33, 73.32, 75.55, 87.17, 88.17, 122.47, 123.17, 127.74, 128.63, 131.87, 132.14, 137.32, 137.55.

1-(2-Methoxyphenyl)-2-nitrobutan-1-ol (3s) [13, 16]



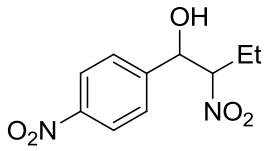
The compound **3s** was prepared according to the general procedure and purified by column

chromatography (petroleum ether/ethyl acetate = 15/1) to give a yellow oil (*anti* 31% yield, *syn* 30% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ ***syn* isomer:** 0.87 (t, *J* = 6 Hz, 3H), 1.37-1.47 (m, 1H), 1.85-1.97 (m, 1H), 3.33 (d, *J* = 8 Hz, 1H), 3.89 (s, 3H), 4.81-4.87 (m, 1H), 5.13 (t, *J* = 10 Hz, 1H), 6.92-7.02 (m, 2H), 7.25-7.36 (m, 2H). ***anti* isomer:** 0.92 (t, *J* = 8 Hz, 3H), 1.86-1.96 (m, 1H), 2.08-2.20 (m, 1H), 3.37 (d, *J* = 8 Hz, 1H), 3.88 (s, 3H), 4.75-4.80 (m, 1H), 5.24 (t, *J* = 6 Hz, 1H), 6.89-7.02 (m, 2H), 7.26-7.34 (m, 2H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ ***syn* isomer:** 10.22, 24.11, 55.47, 73.42, 94.47, 111.00, 121.23, 126.16, 128.93, 130.07, 156.74. ***anti* isomer:** 10.48, 21.70, 55.44, 72.10, 92.58, 110.64, 121.00, 126.02, 128.30, 129.67, 156.18.

1-(4- nitrophenyl)-2-nitrobutan -1-ol (3t) [13, 16]

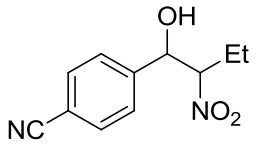


The compound **3t** was prepared according to the general procedure andpurified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give a white solid (87% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 0.89-0.96 (m, 3H), 1.80-2.24 (m, 2H), 3.25-3.29 (m, 1H), 4.57-4.65 (m, 1H), 5.17-5.20 (m, 0.61H), 5.33-5.34 (m, 0.39H), 7.58-7.60 (m, 2H), 8.21-8.26 (m, 2H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 10.05, 10.33, 21.26, 23.82, 73.27, 74.32, 94.16, 94.63, 123.89, 124.11, 127.30, 127.88, 145.73, 147.94, 148.22.

4-(1-Hydroxy-2-nitrobutyl)benzonitrile (3u) [12, 15]

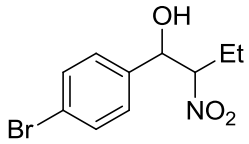


The compound **3u** was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 6/1) to give a white solid (87% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 0.90-0.96 (m, 3H), 1.46-1.50 (m, 1H), 1.81-1.95 (m, 1H), 2.97 (d, *J* = 4 Hz, 1H), 4.53-4.62 (m, 1H), 5.10-5.13 (m, 0.70H), 5.26-5.28 (m, 0.30H), 7.51-7.53 (m, 2H), 7.67-7.72 (m,2H).

^{13}CNMR ($CDCl_3$, 100 MHz): δ 10.07, 10.34, 21.33, 23.79, 73.42, 74.54, 94.23, 94.68, 112.31, 112.76, 118.24, 118.38, 127.12, 127.71, 132.51, 132.73, 144.00.

1-(4-bromophenyl)-2-nitrobutan-1-ol (3v) [12, 15]



The compound **3v** was prepared according to the general procedure andpurified by column chromatography (petroleum ether/ethyl acetate = 15/1) to give a colorless oil (74% yield).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 0.86-0.95 (m, 3H), 1.39-1.46 (m, 1H), 1.79-1.89 (m, 1H), 2.69 (s, 1H), 4.50-4.59 (m, 1H), 5.01 (d, *J* = 8 Hz, 0.77H), 5.14 (d, *J* = 4 Hz, 0.23H), 7.24-7.26 (m, 2H), 7.50-7.55 (m, 2H).

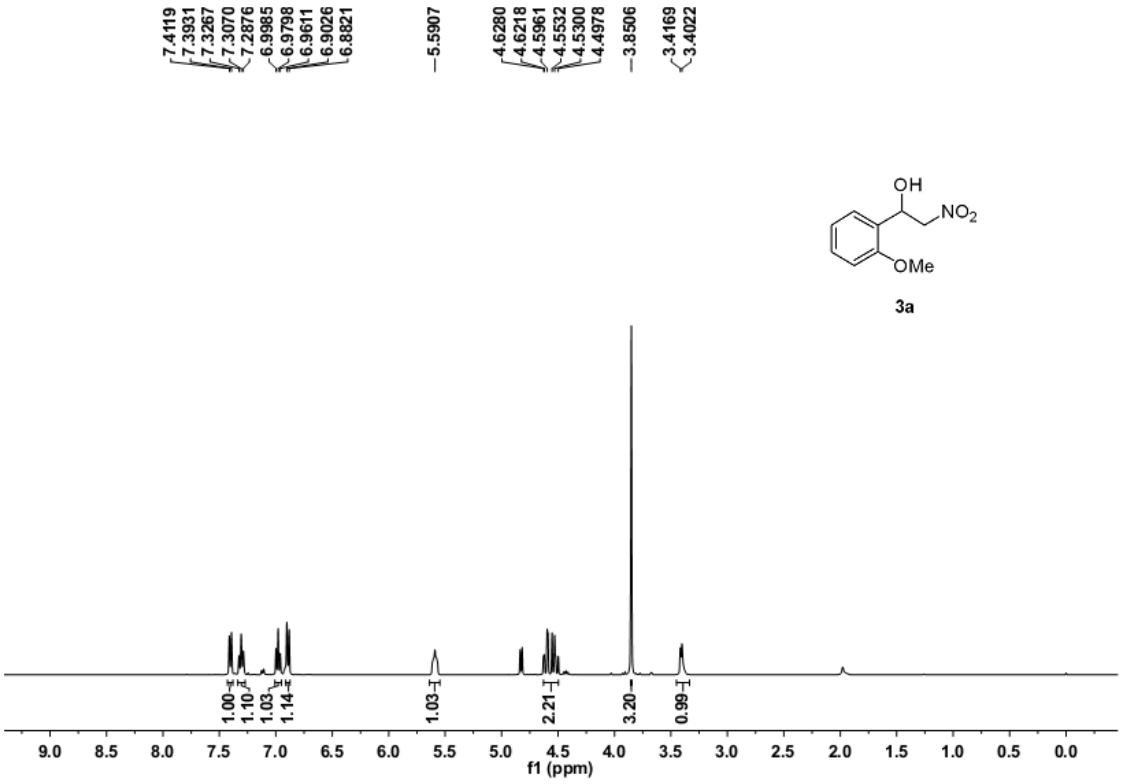
^{13}CNMR ($CDCl_3$, 100 MHz): δ 10.06, 10.36, 21.33, 23.88, 73.62, 74.82, 94.44, 94.96, 122.71, 123.18, 127.95, 128.55, 131.90, 132.18, 137.57, 137.66.

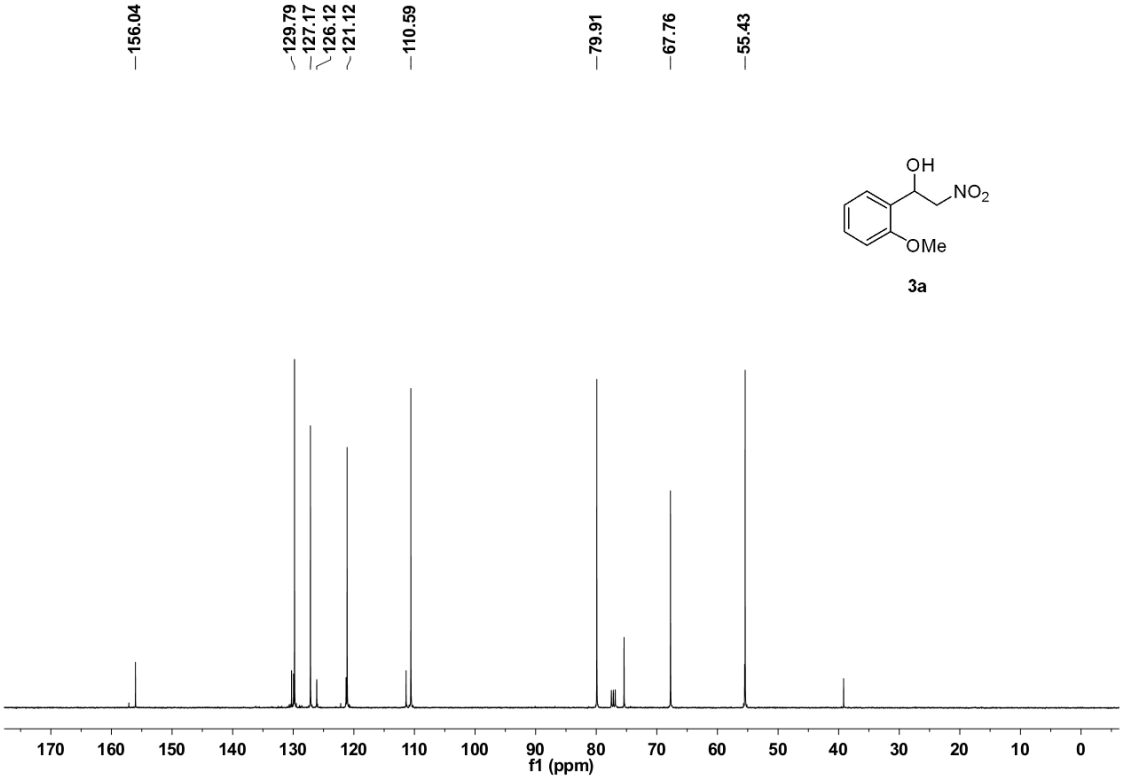
5. List of the obvious difference between *syn*- and *anti*- isomers on ^{1}HNMR

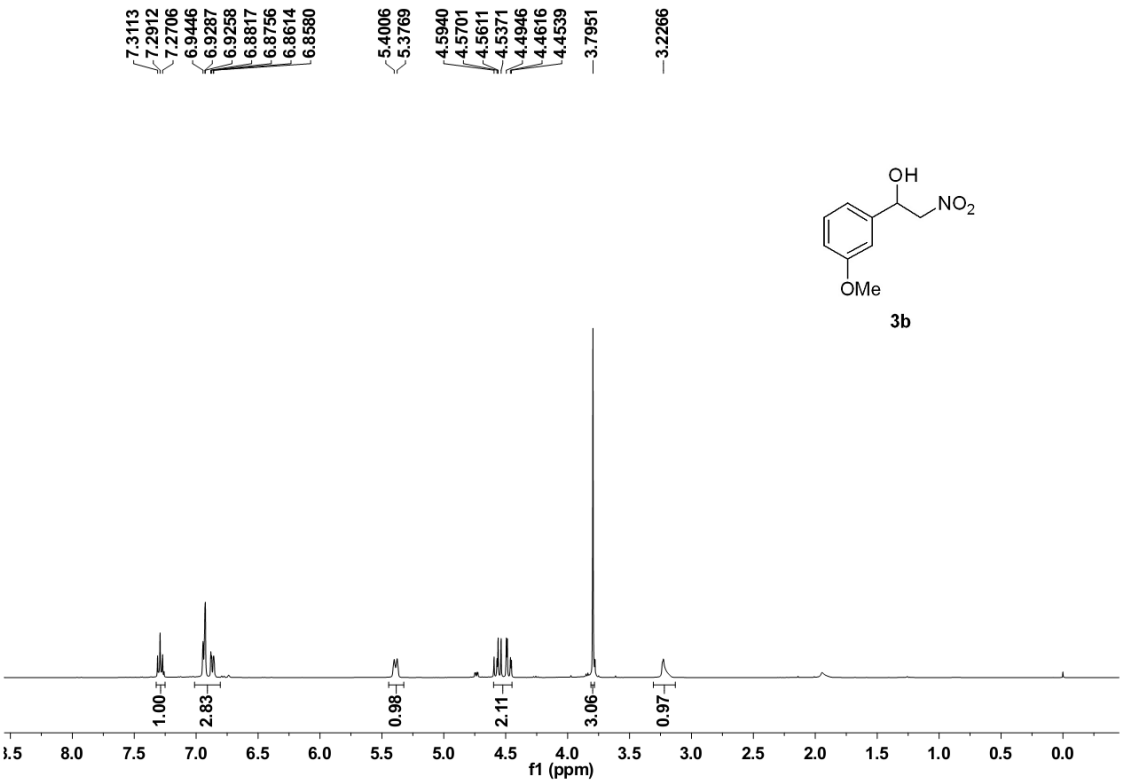
Entry	Product	^{1}HNMR (-CHOH) [ppm]

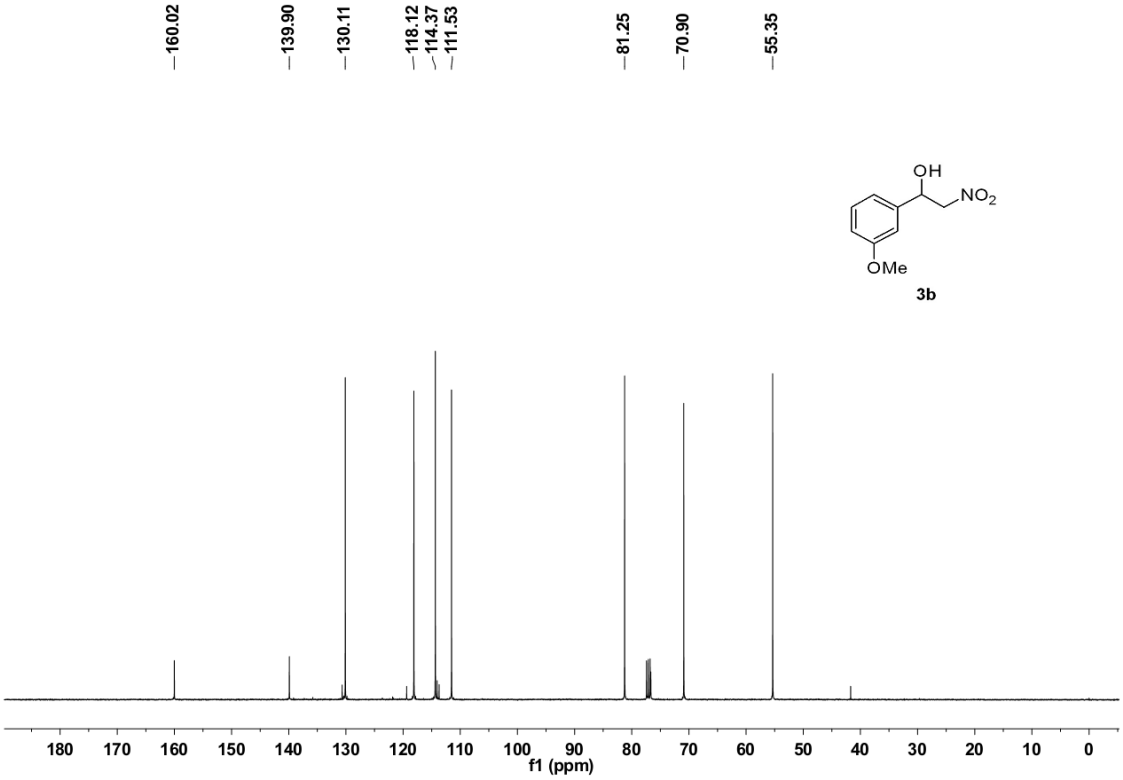
		syn	*anti*
1	**3o**	5.14 (t, *J* = 8 Hz)	5.53-5.55 (m)
2	**3p**	5.18-5.21 (m)	5.57 (s)
3	**3q**	5.12 (d, *J* = 8 Hz)	5.49 (d, *J* = 4 Hz)
4	**3r**	5.00 (d, *J* = 4 Hz)	5.36 (s)
5	**3s**	5.13 (t, *J* = 10 Hz)	5.24 (t, *J* = 6 Hz)
6	**3t**	5.17-5.20 (m)	5.33-5.34 (m)
7	**3u**	5.10-5.13 (m)	5.26-5.28 (m)
8	**3v**	5.01 (d, *J* = 8 Hz)	5.14 (d, *J* = 4 Hz)

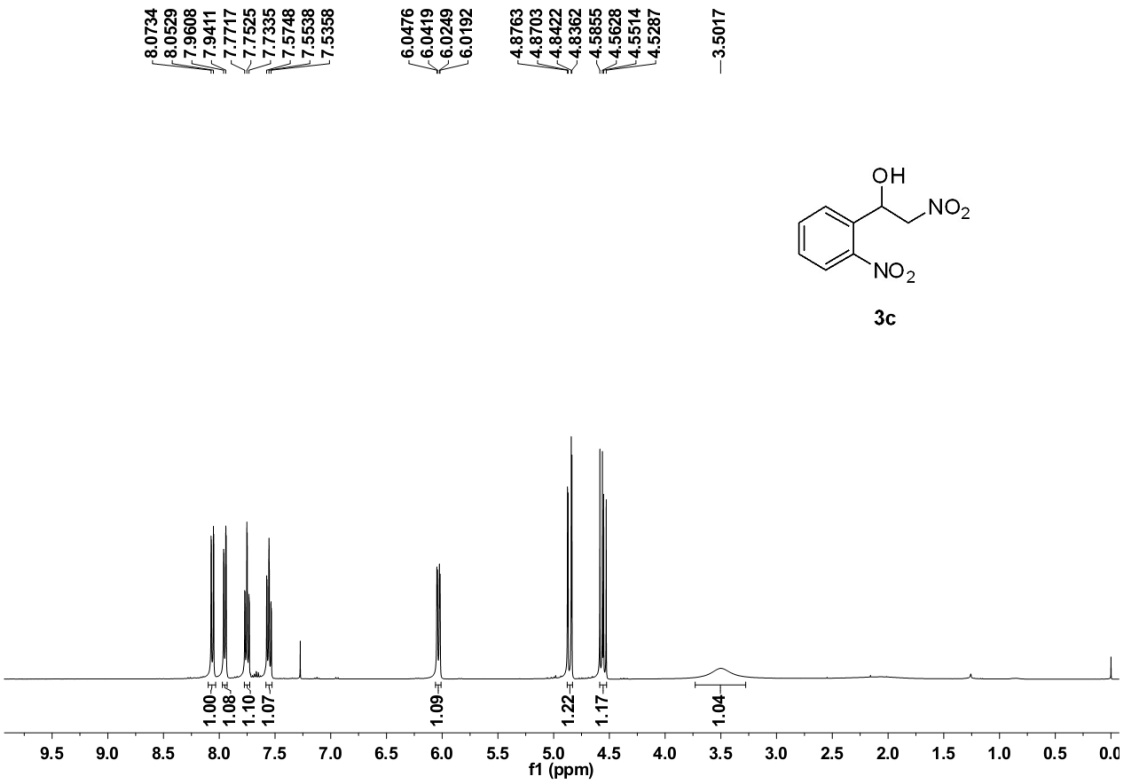
6. ^{1}HNMR and ^{13}CNMR spectra for Henry products

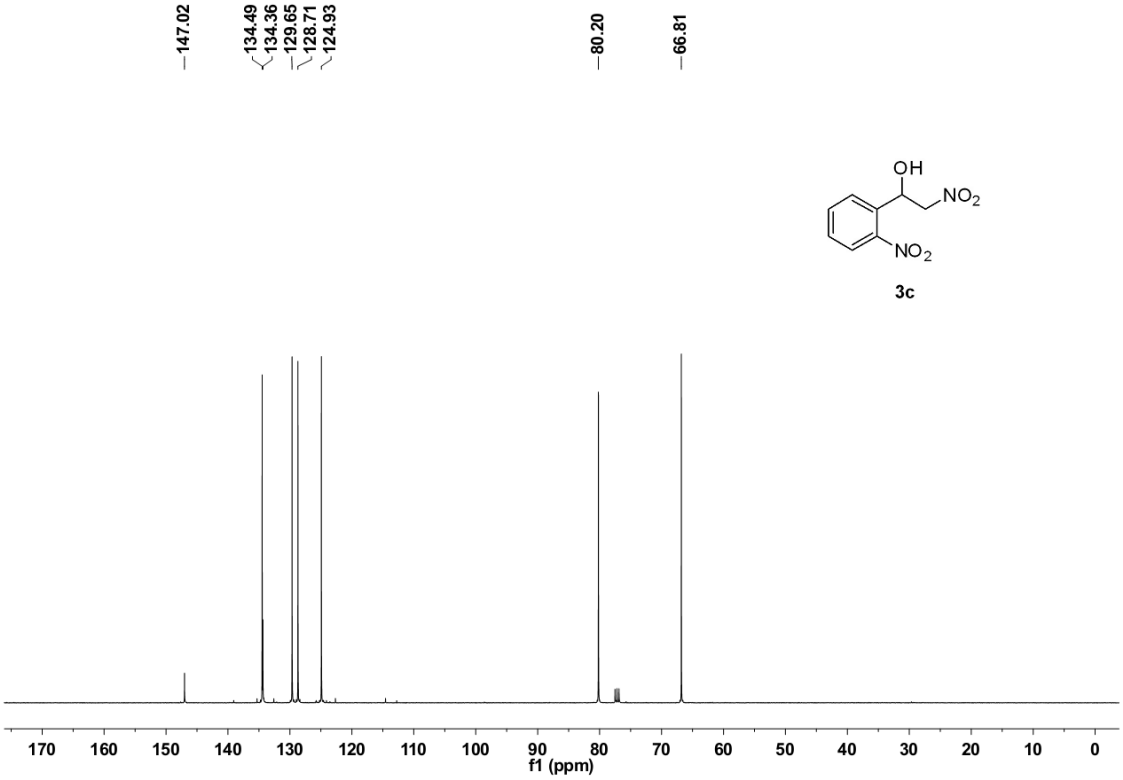


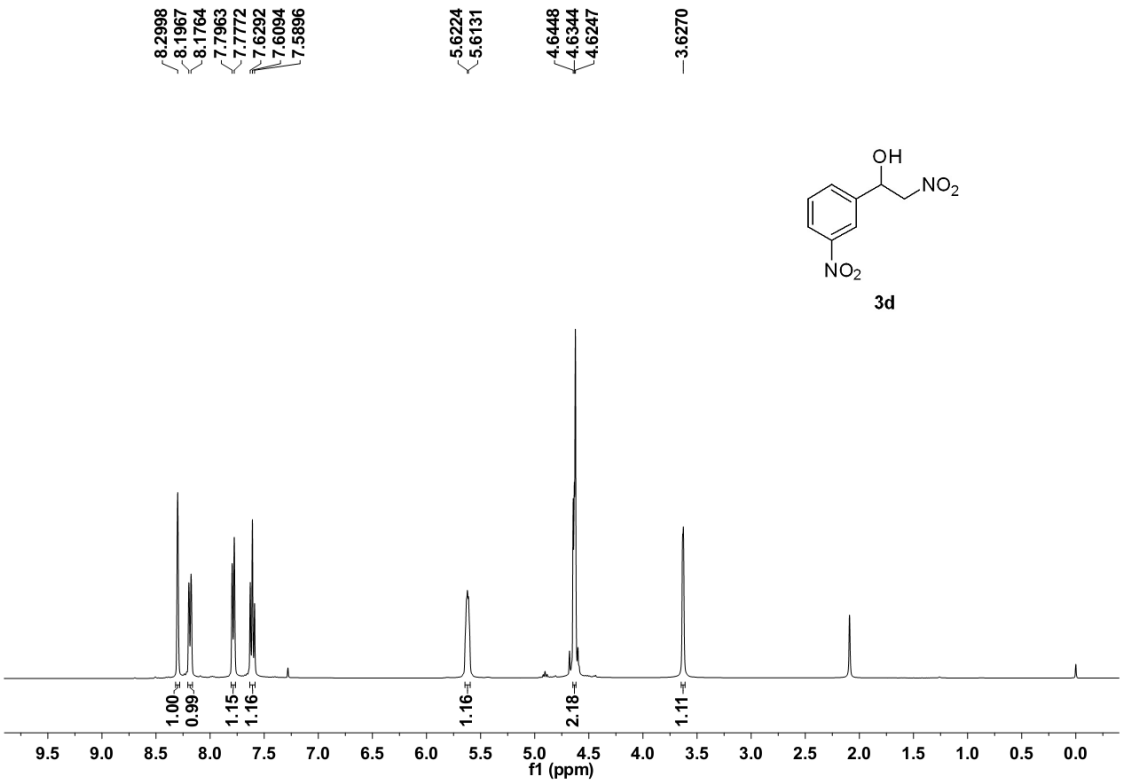


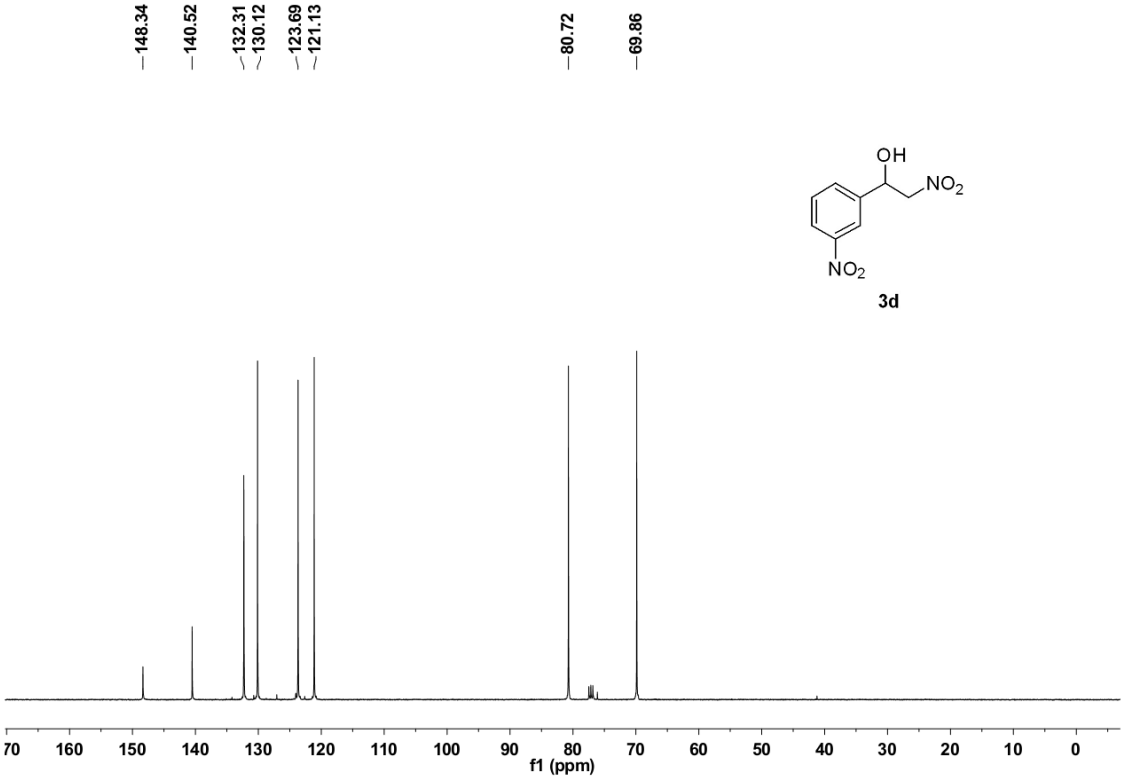



160.02
139.90
130.11
118.12
114.37
111.53
81.25
70.90
55.35
OH
NO2
OMe
3b
f1 (ppm)

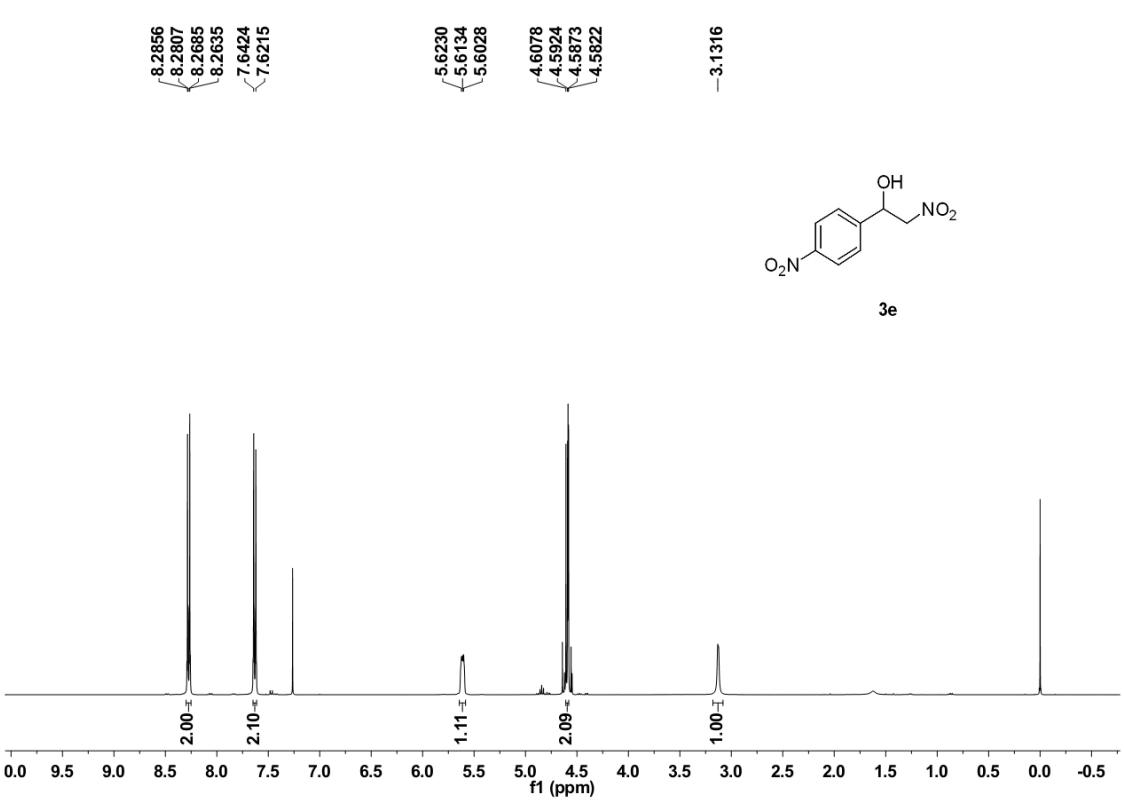

8.0734
8.0529
7.9608
7.9411
7.7717
7.7525
7.7335
7.5748
7.5538
7.5358
6.0476
6.0419
6.0249
6.0192
4.8763
4.8703
4.8422
4.8362
4.5855
4.5628
4.5514
4.5287
3.5017
OH
NO2
NO2
3c
1.00
1.08
1.10
1.07
1.09
1.22
1.17
1.04
f1 (ppm)



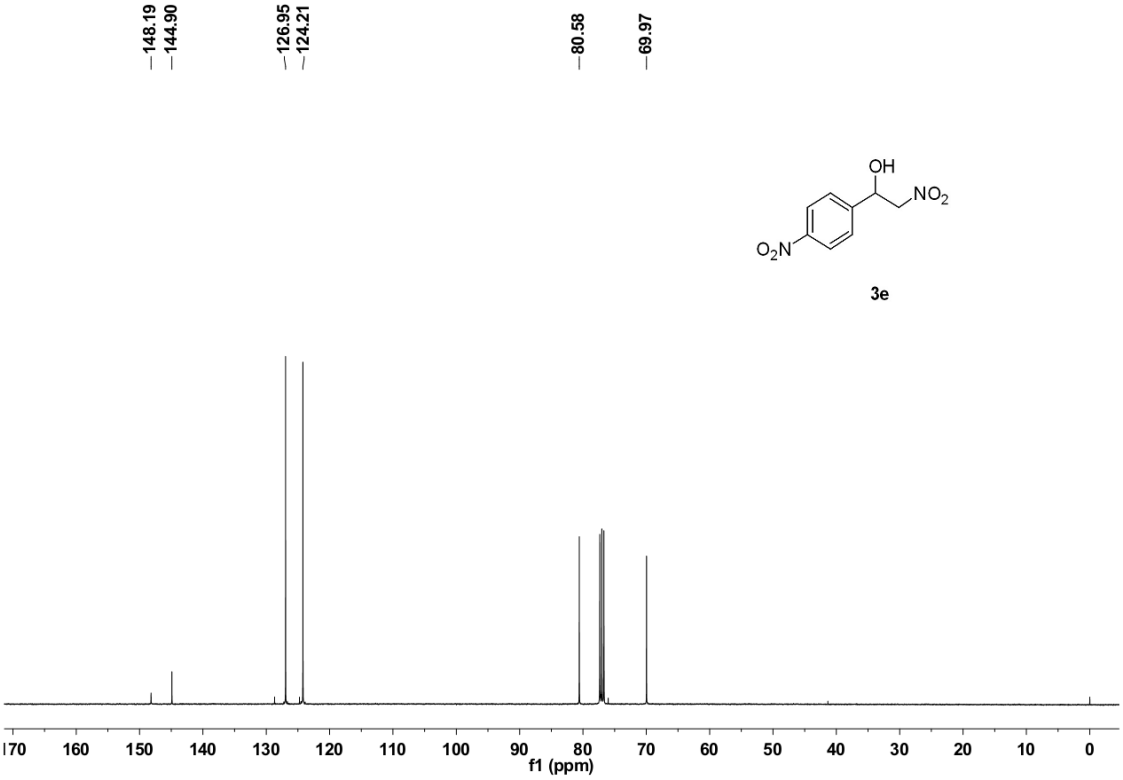


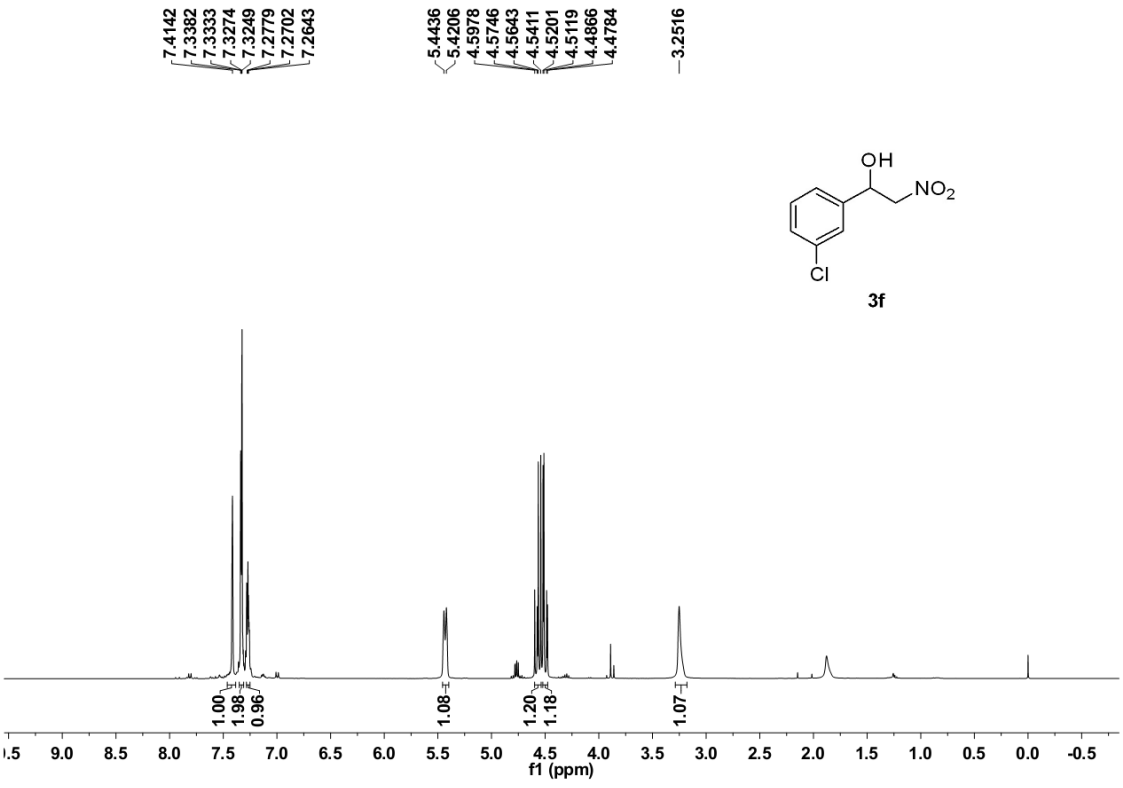


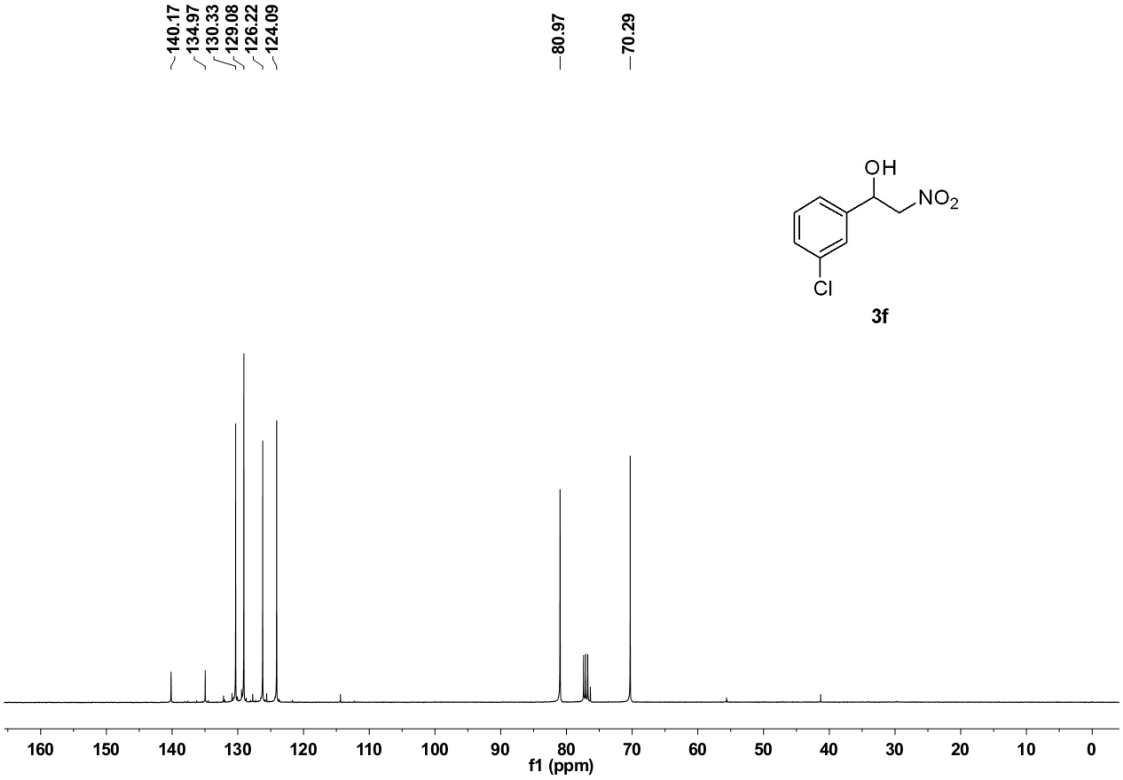
3d

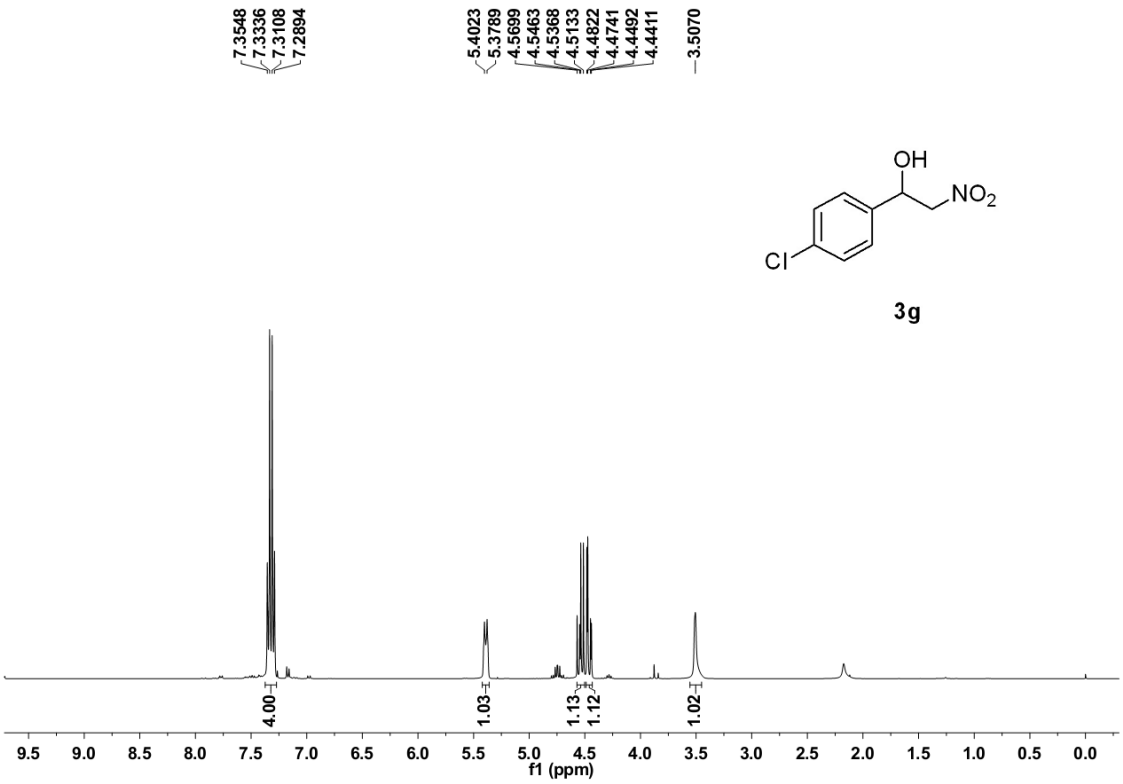


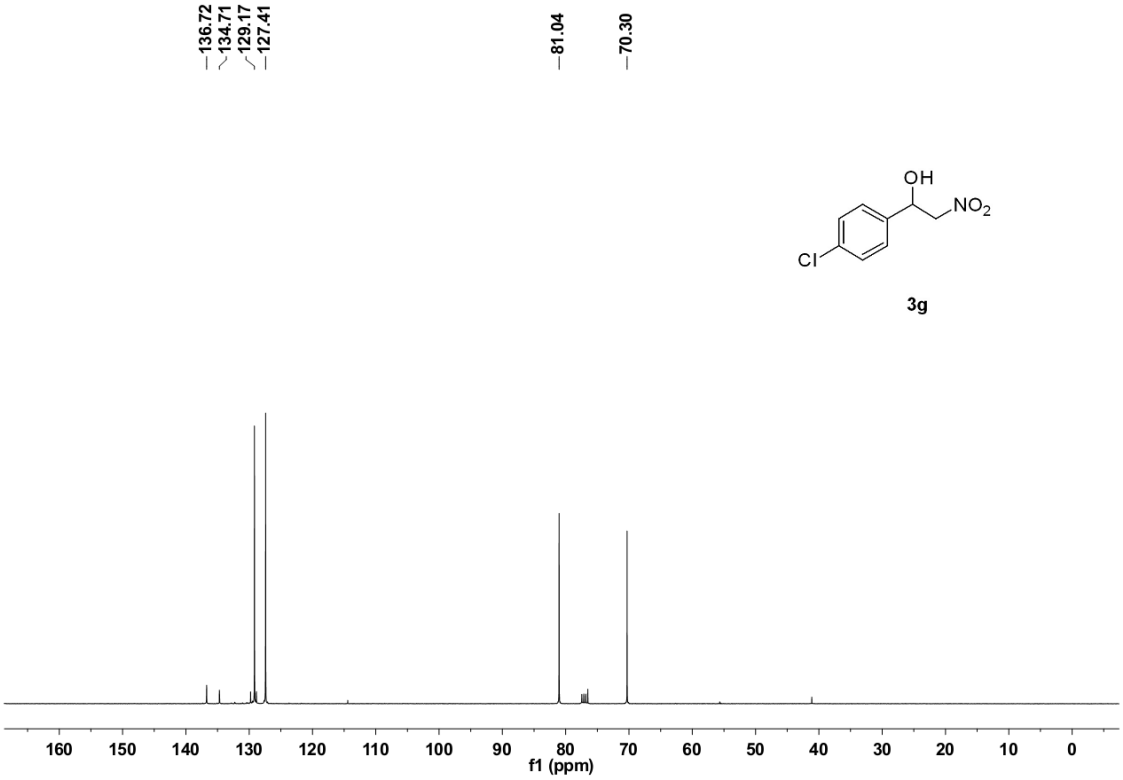
3e

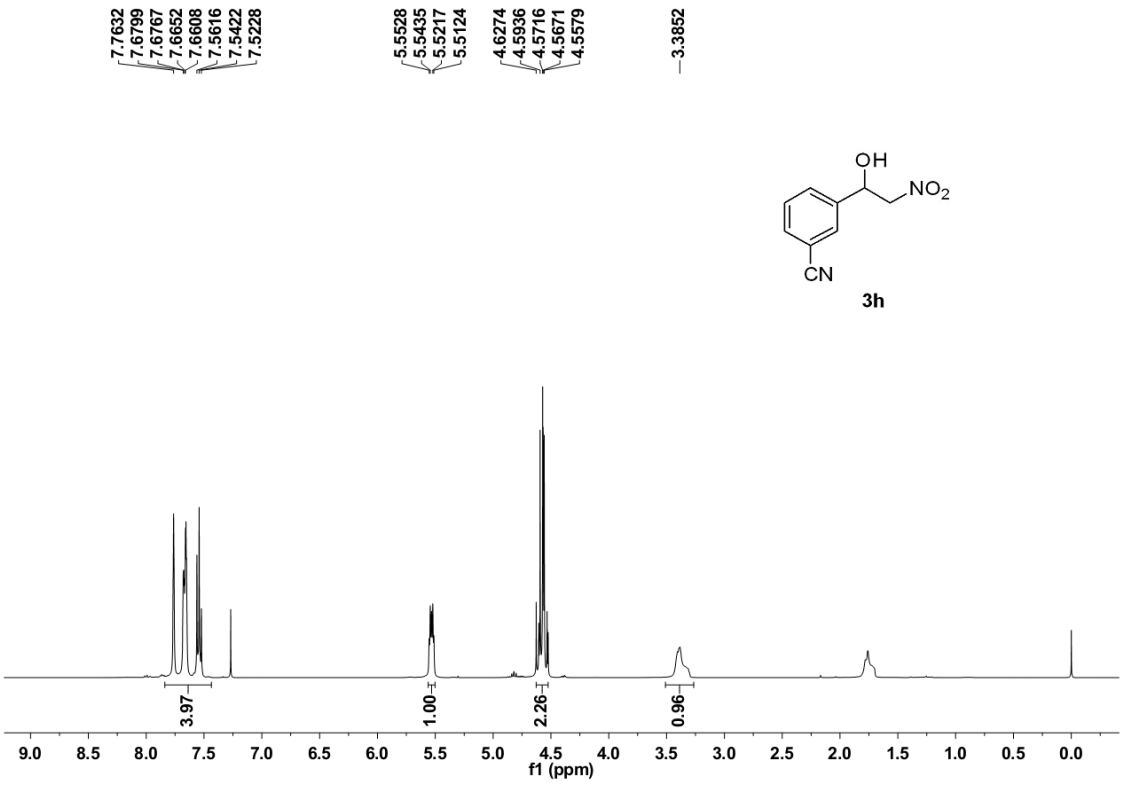


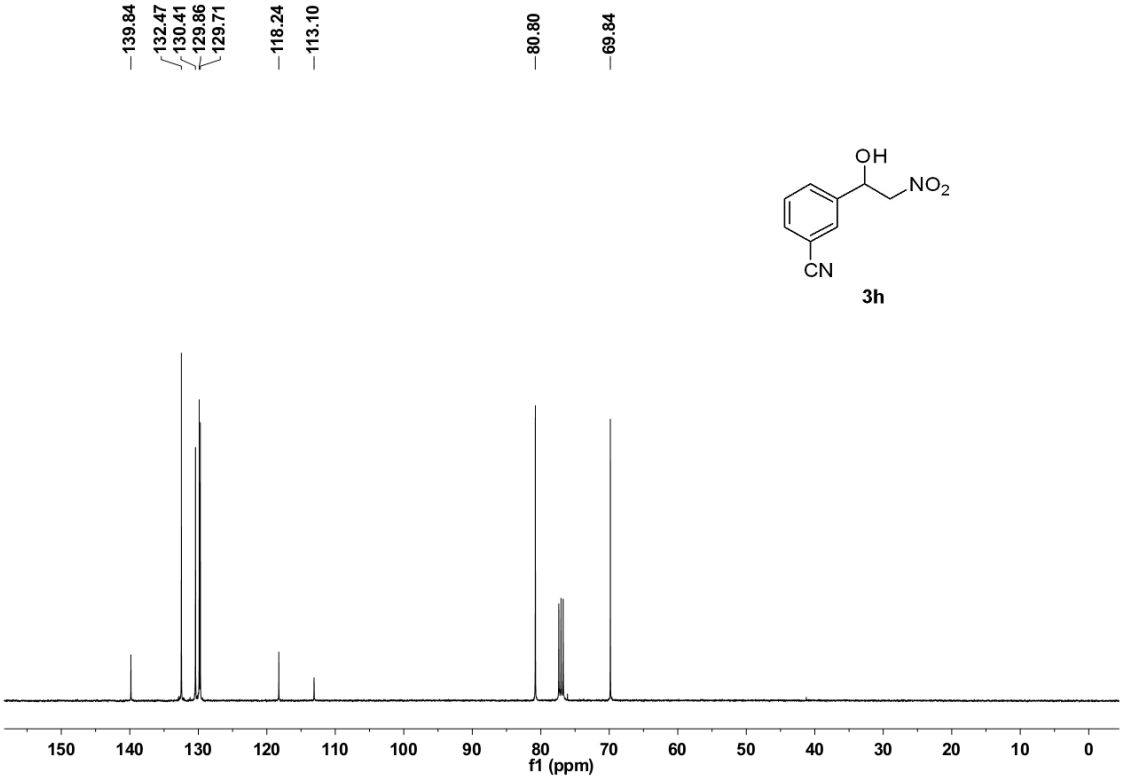


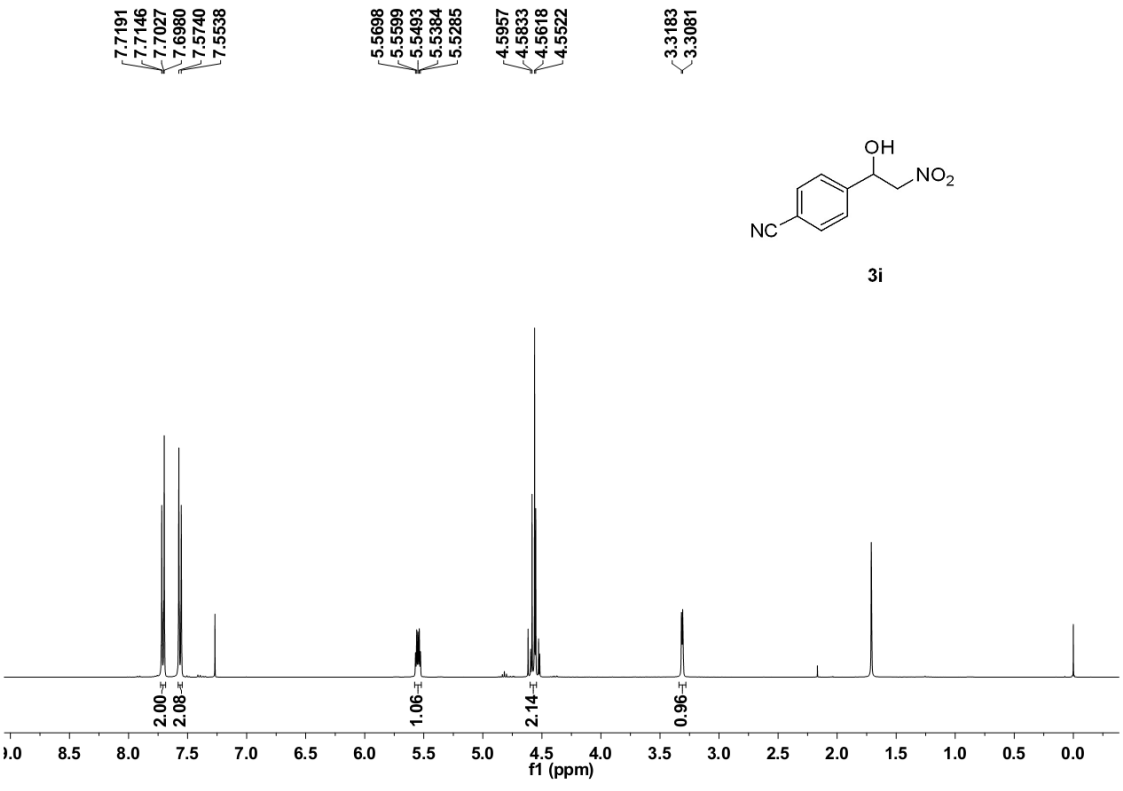


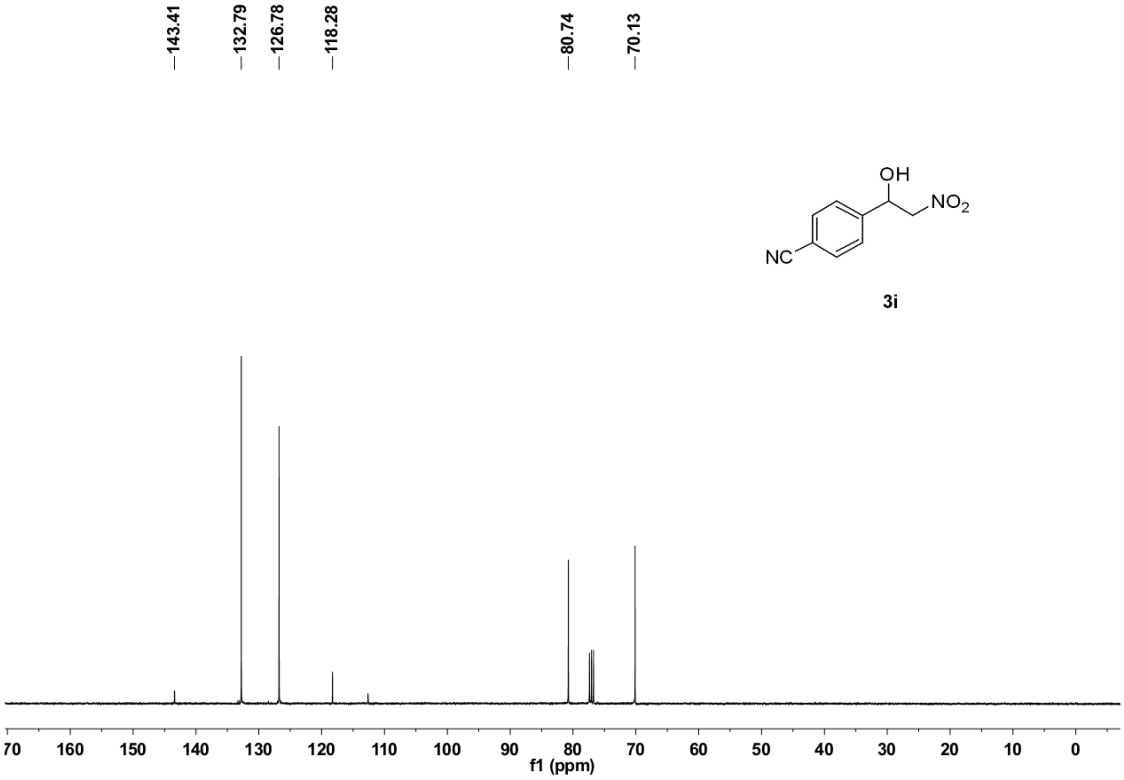


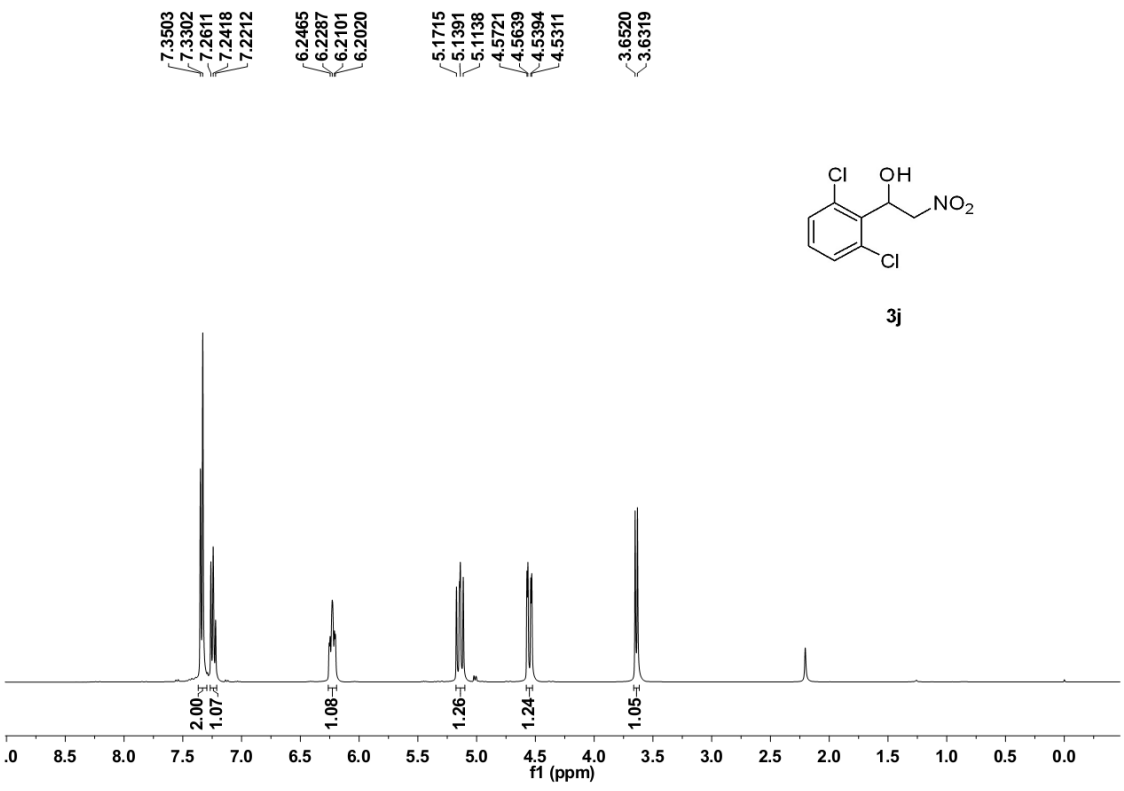


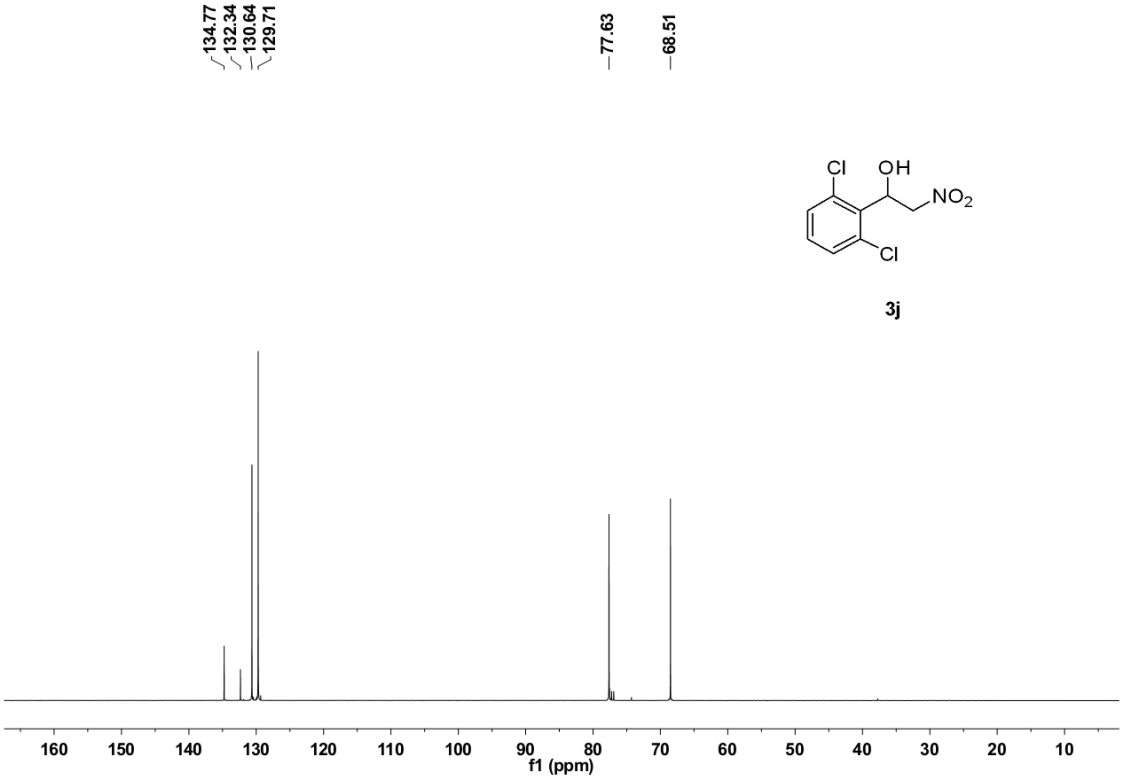




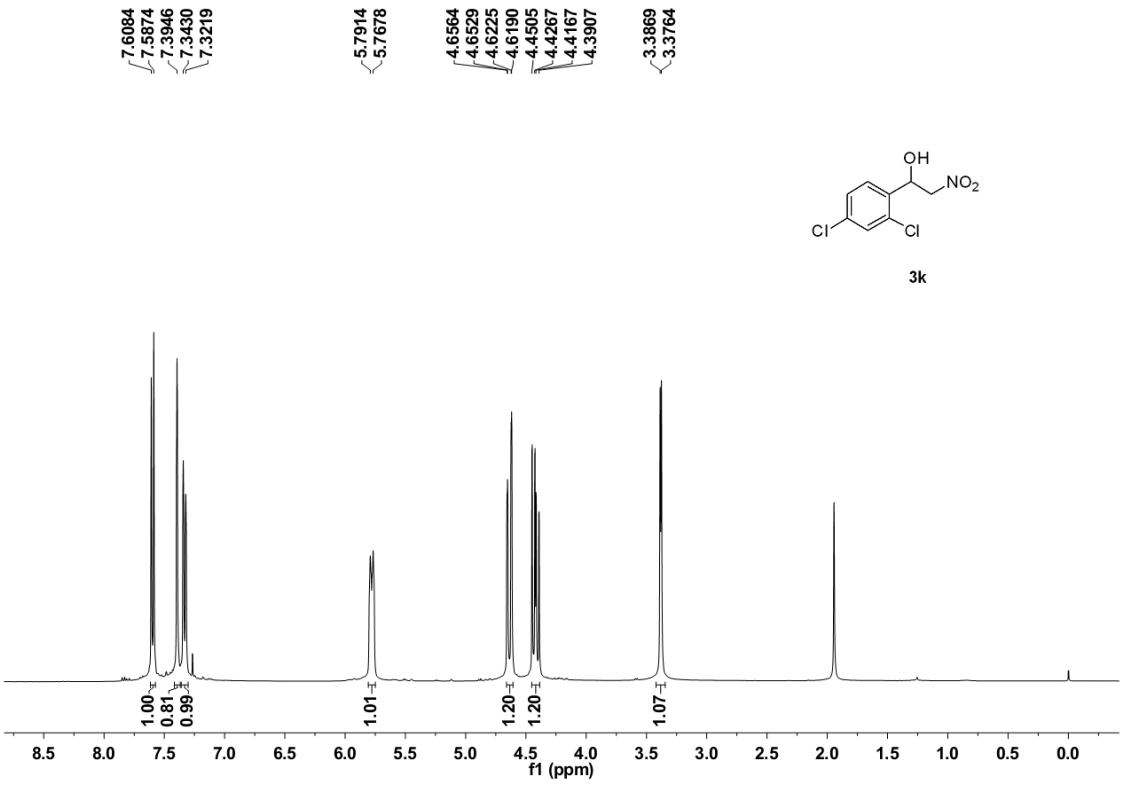




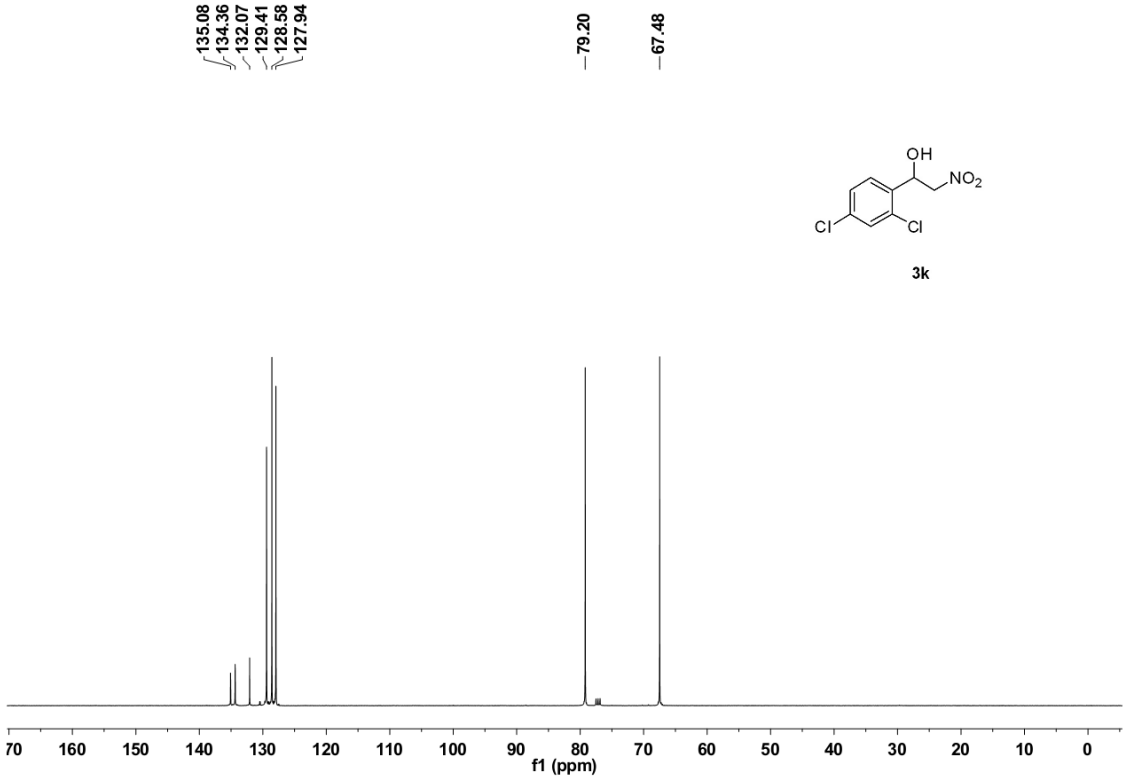




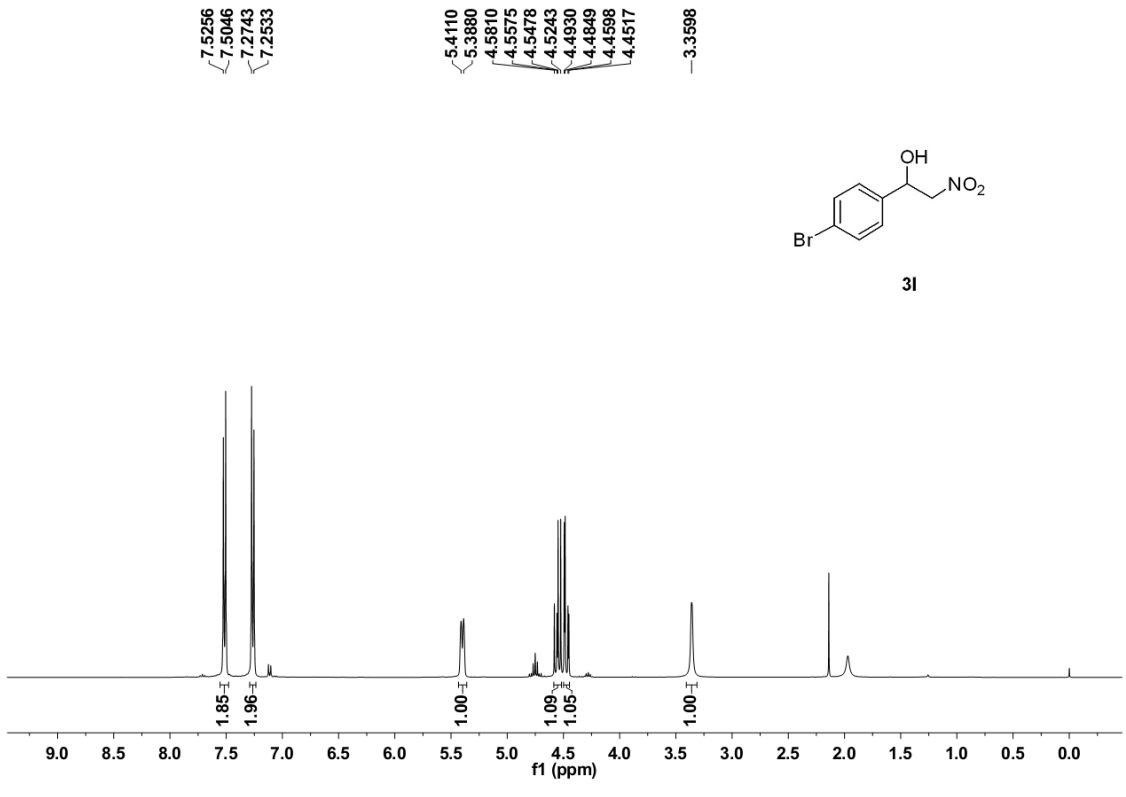
3j



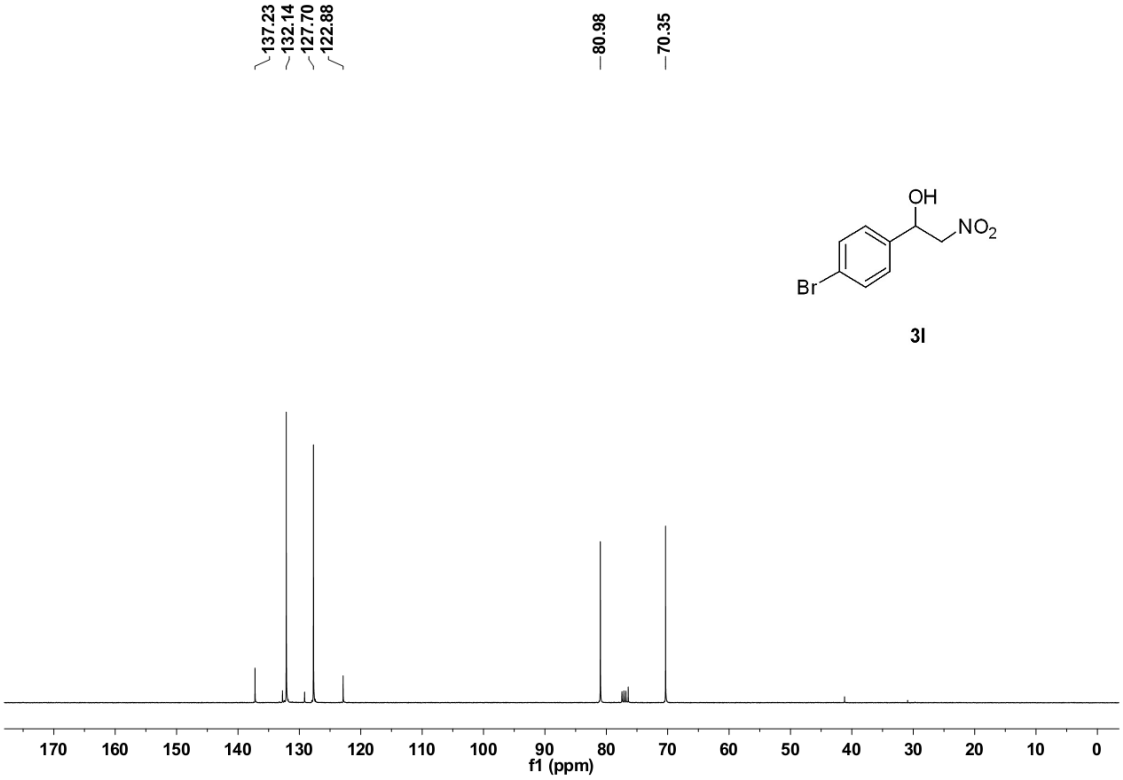
3k

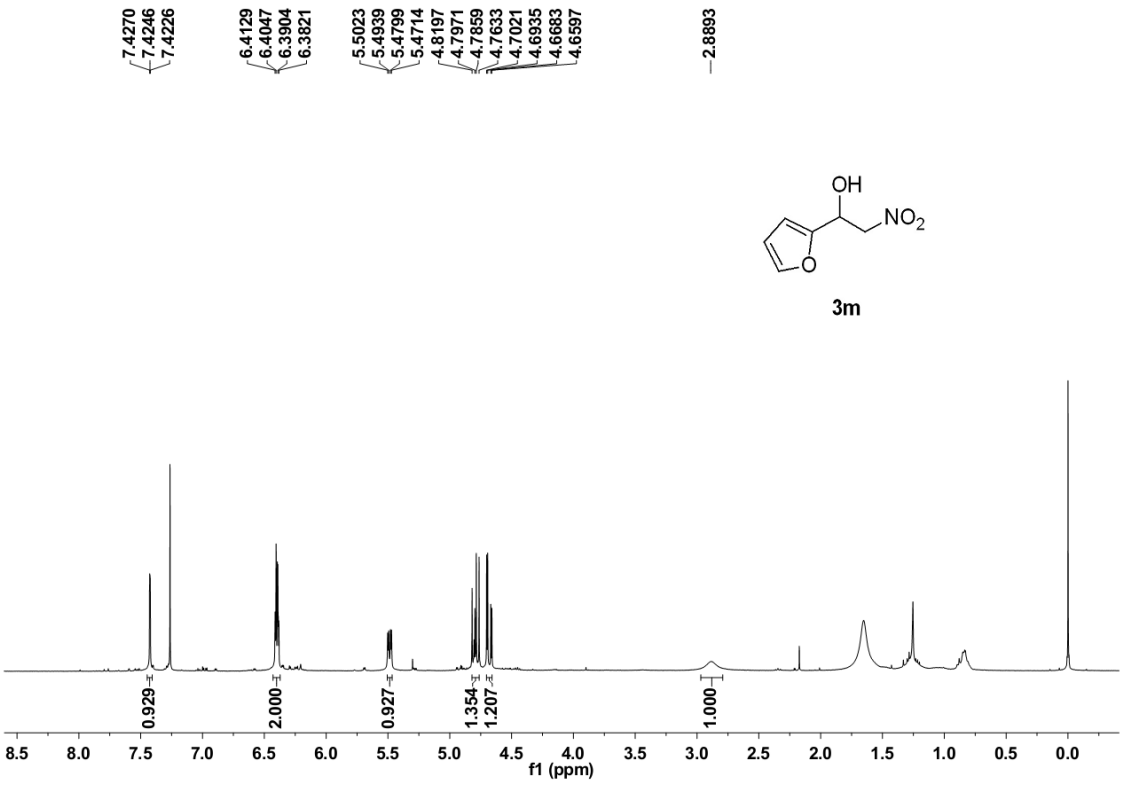


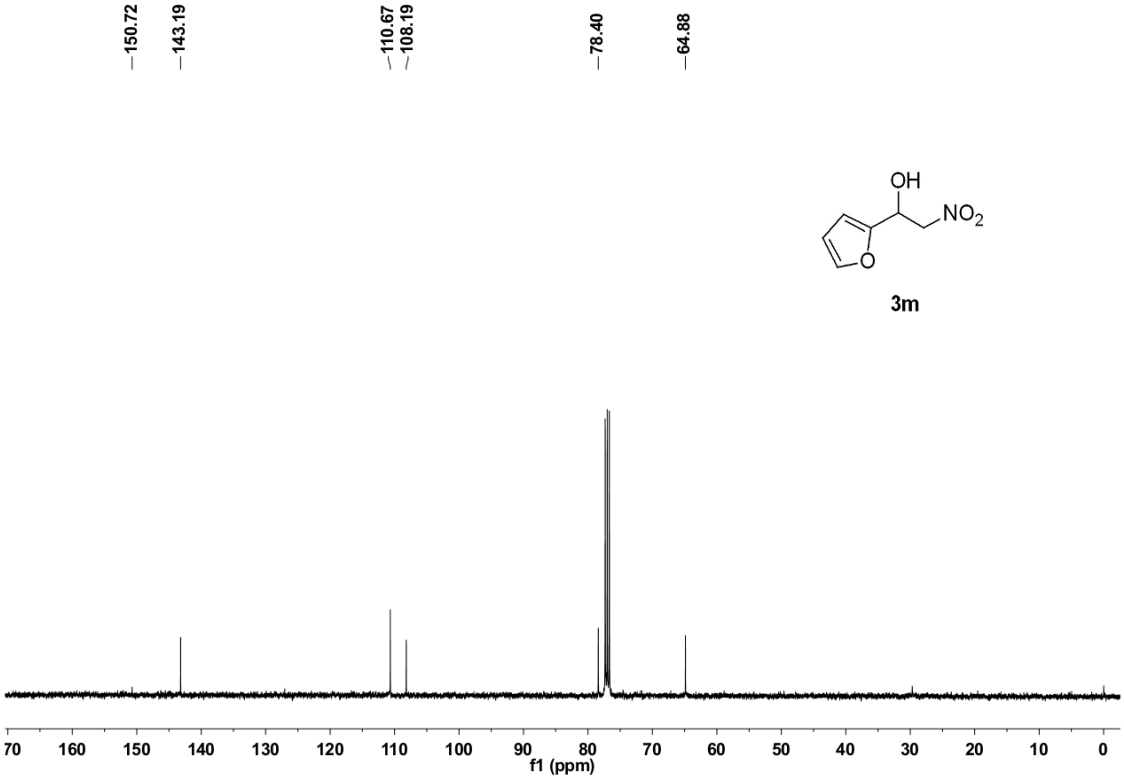
3k

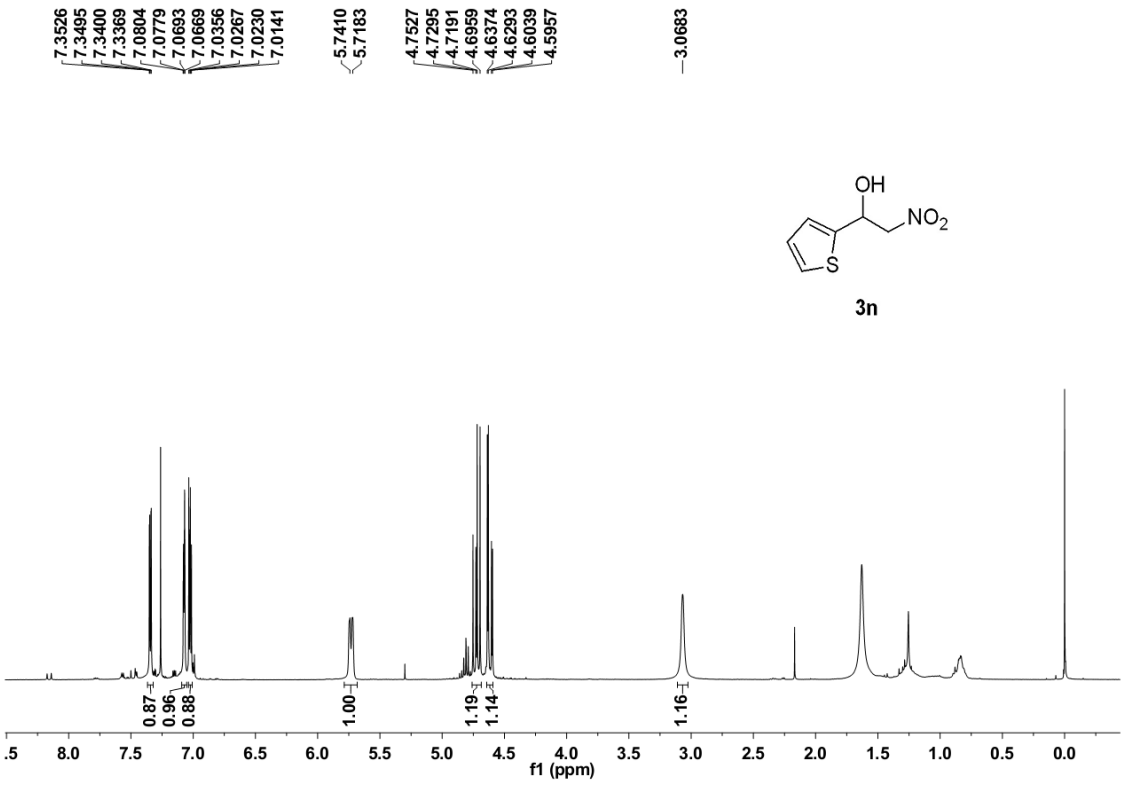


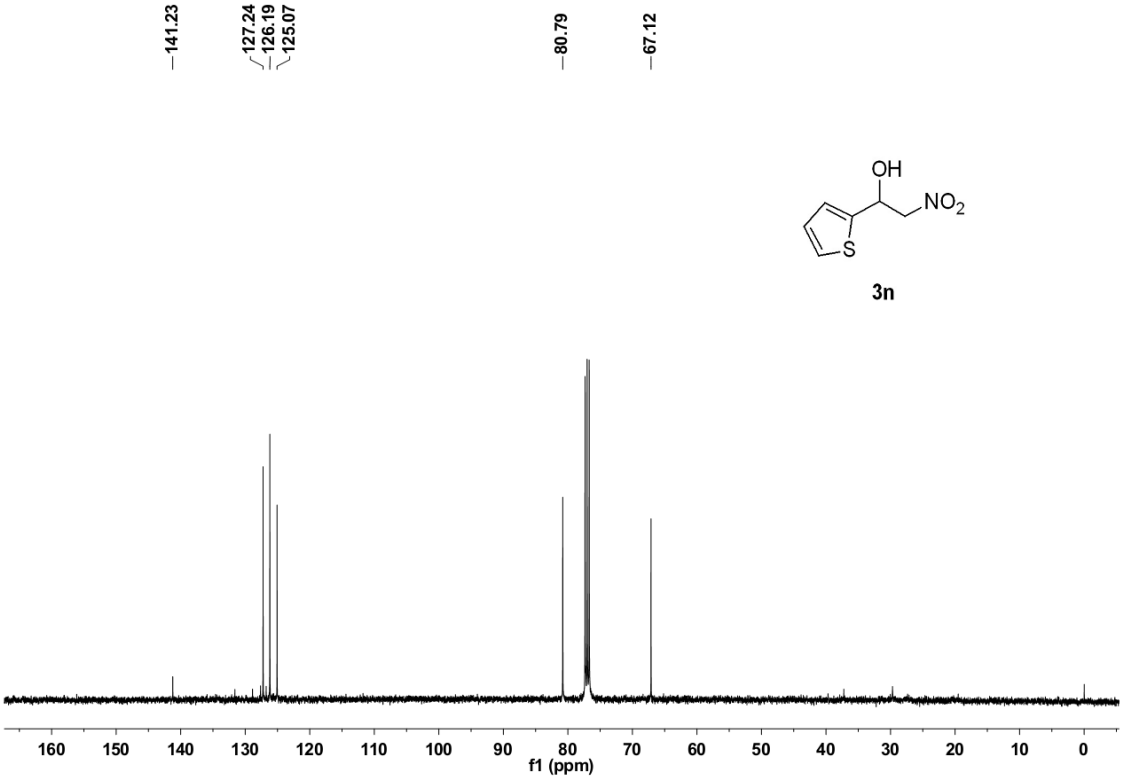
3l

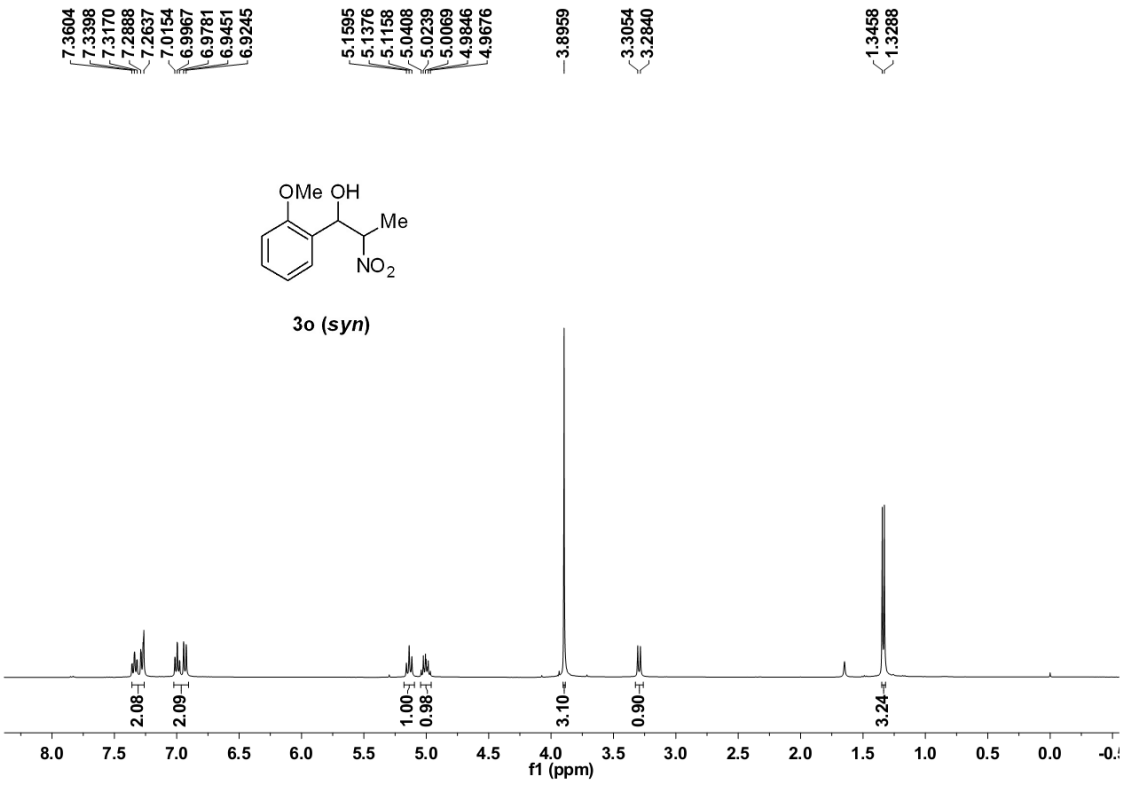

137.23
132.14
127.70
122.88
80.98
70.35
OH
NO2
Br
3l
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

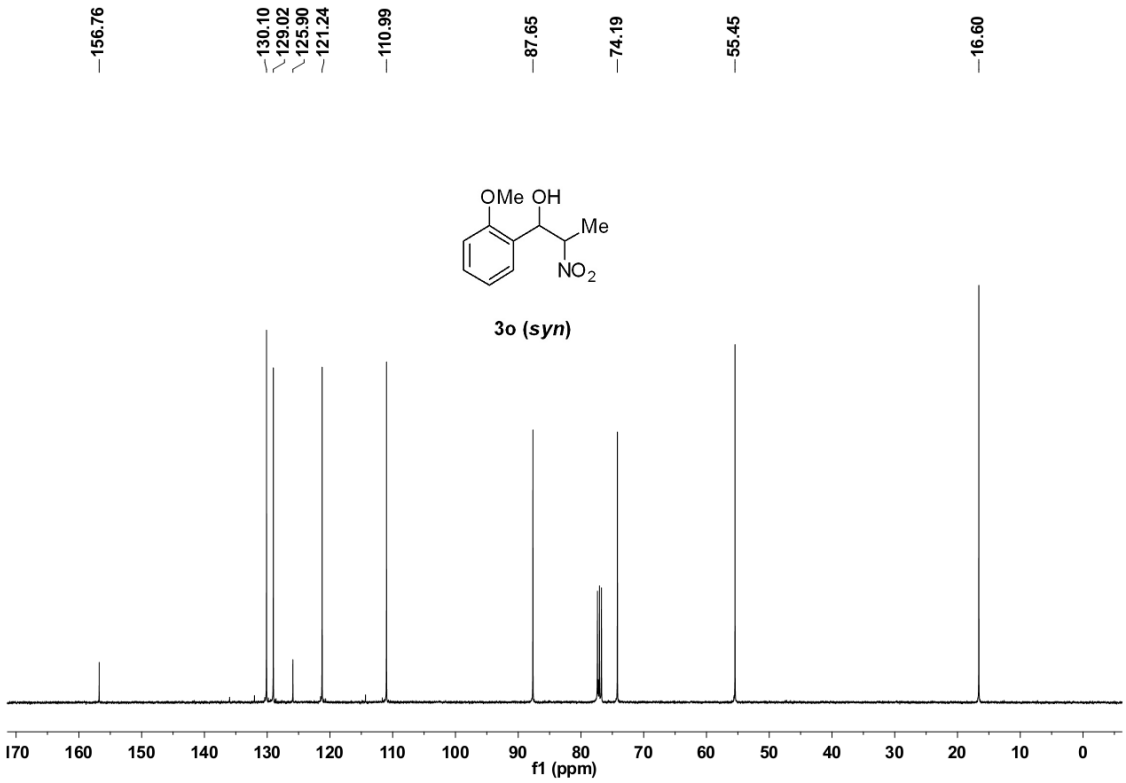

7.4270
7.4246
7.4226
6.4129
6.4047
6.3904
6.3821
5.5023
5.4939
5.4799
5.4714
4.8197
4.7971
4.7859
4.7633
4.7021
4.6935
4.6683
4.6597
2.8893
OH
NO2
O
3m
0.929
2.000
0.927
1.354
1.207
1.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

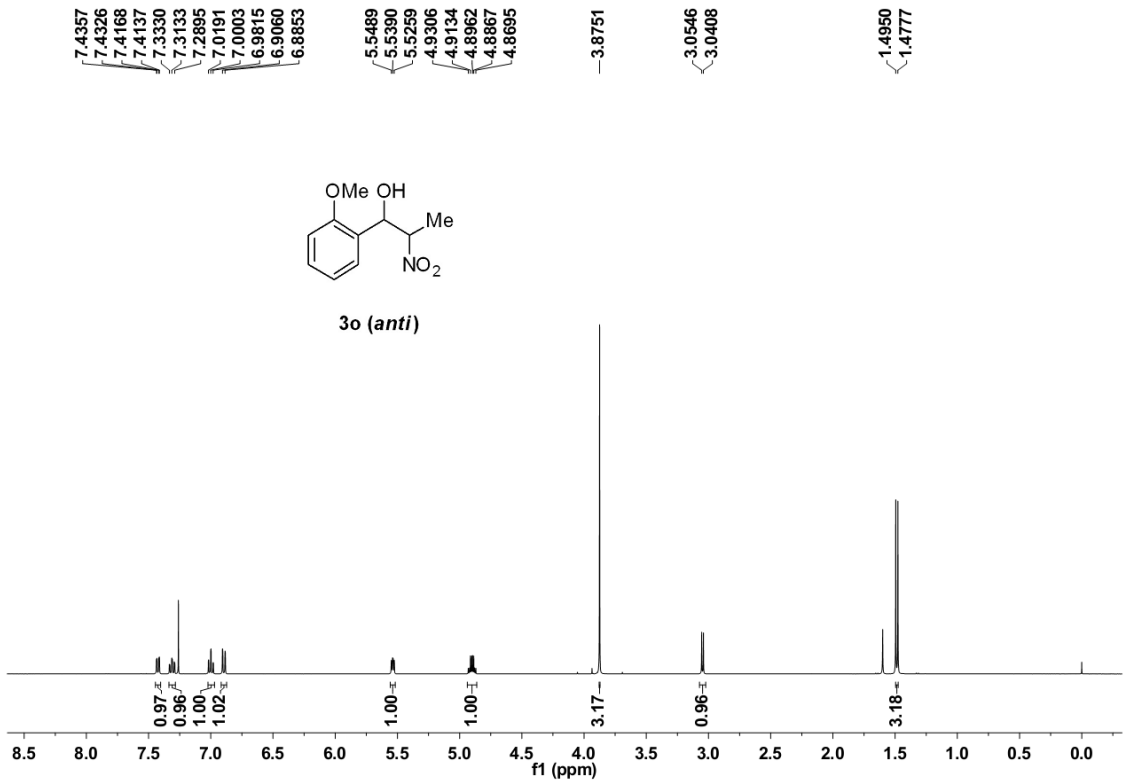

150.72
143.19
110.67
108.19
78.40
64.88
OH
NO2
O
3m
f1 (ppm)

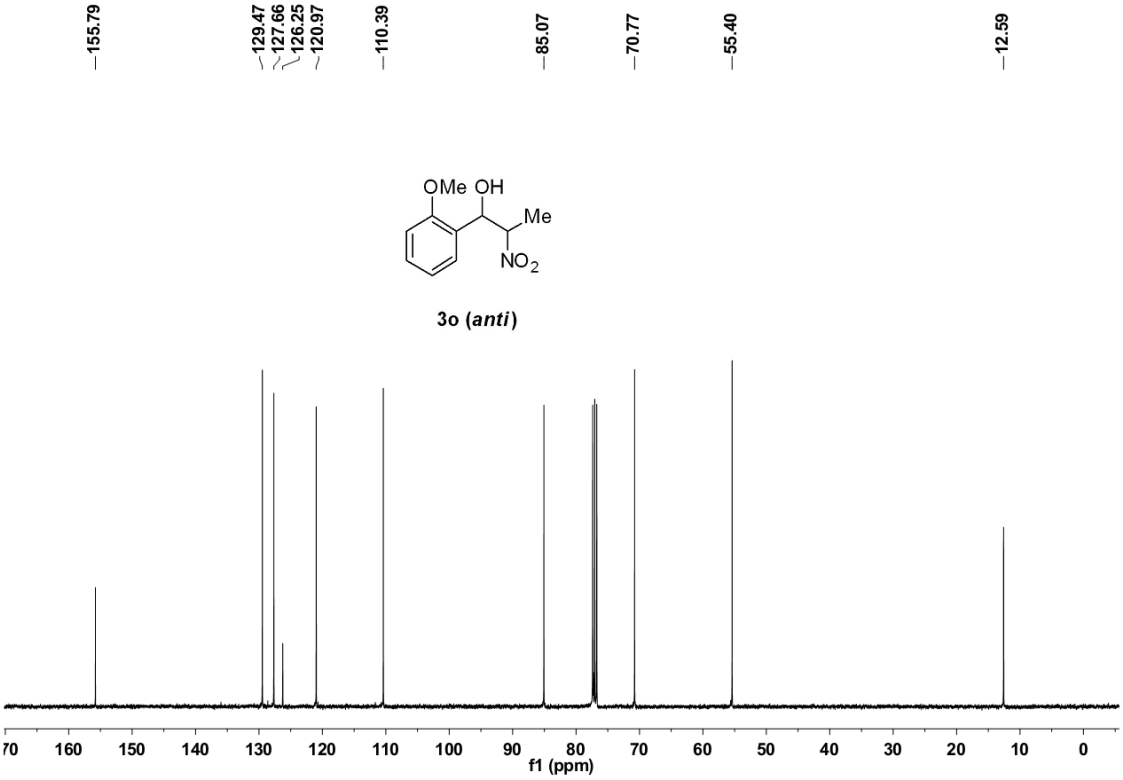

7.3526
7.3495
7.3400
7.3369
7.0804
7.0779
7.0693
7.0669
7.0356
7.0267
7.0230
7.0141
5.7410
5.7183
4.7527
4.7295
4.7191
4.6959
4.6374
4.6293
4.6039
4.5957
3.0683
OH
NO2
S
3n
0.87
0.96
0.88
1.00
1.19
1.14
1.16
f1 (ppm)



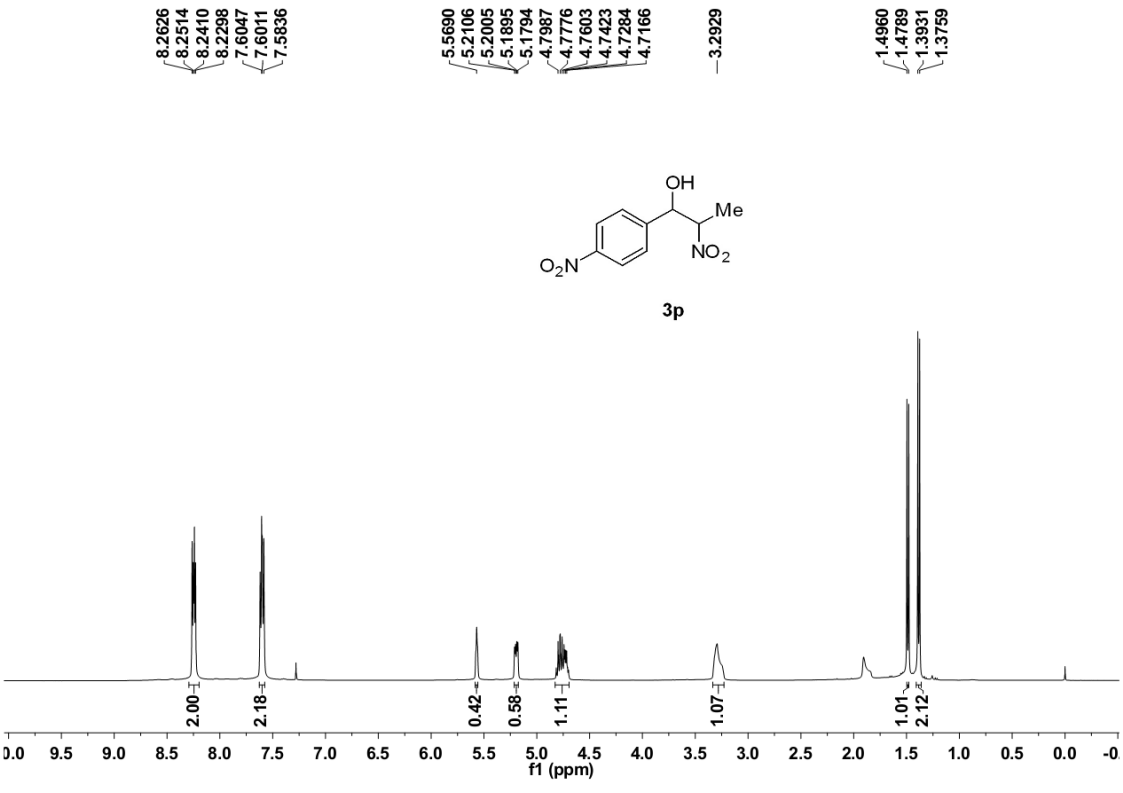



156.76
130.10
129.02
125.90
121.24
110.99
87.65
74.19
55.45
16.60
OMe OH
Me
NO2
3o (syn)
f1 (ppm)

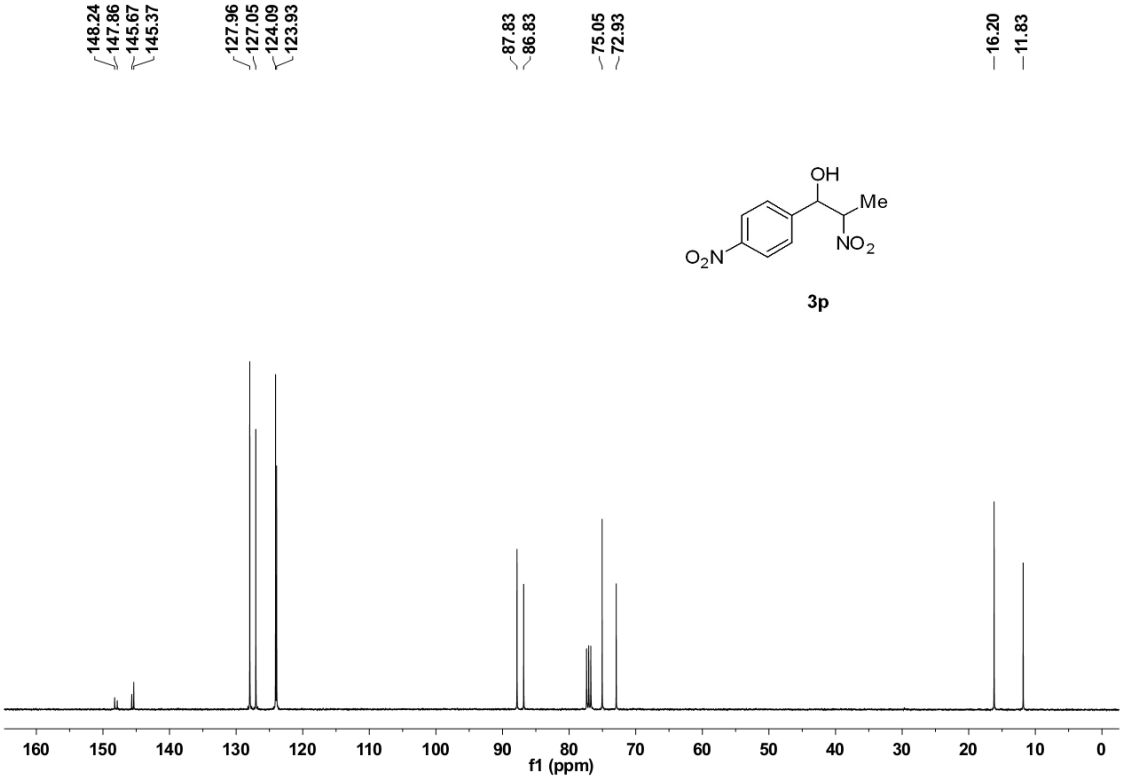

7.4357
7.4326
7.4168
7.4137
7.3330
7.3133
7.2895
7.0191
7.0003
6.9815
6.9060
6.8853
5.5489
5.5390
5.5259
4.9306
4.9134
4.8962
4.8867
4.8695
3.8751
3.0546
3.0408
1.4950
1.4777
OMe OH
Me
NO2
3o (anti)
0.97
0.96
1.00
1.02
1.00
1.00
3.17
0.96
3.18
f1 (ppm)



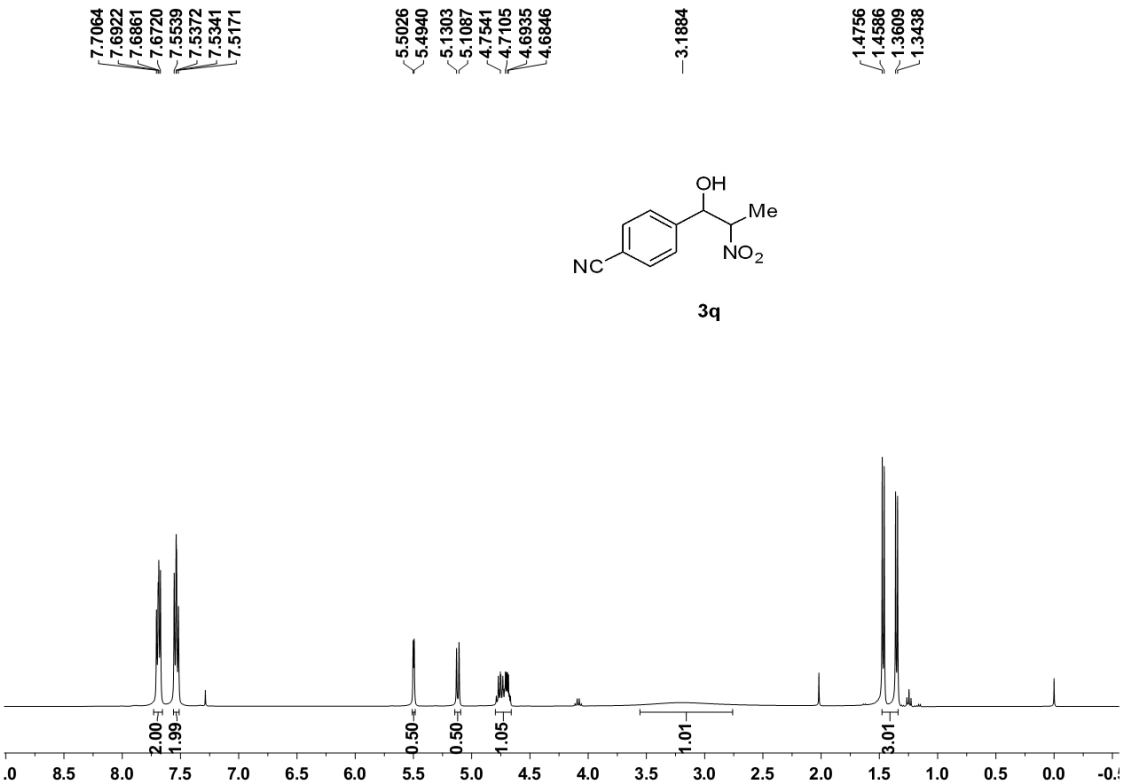
3o (*anti*)



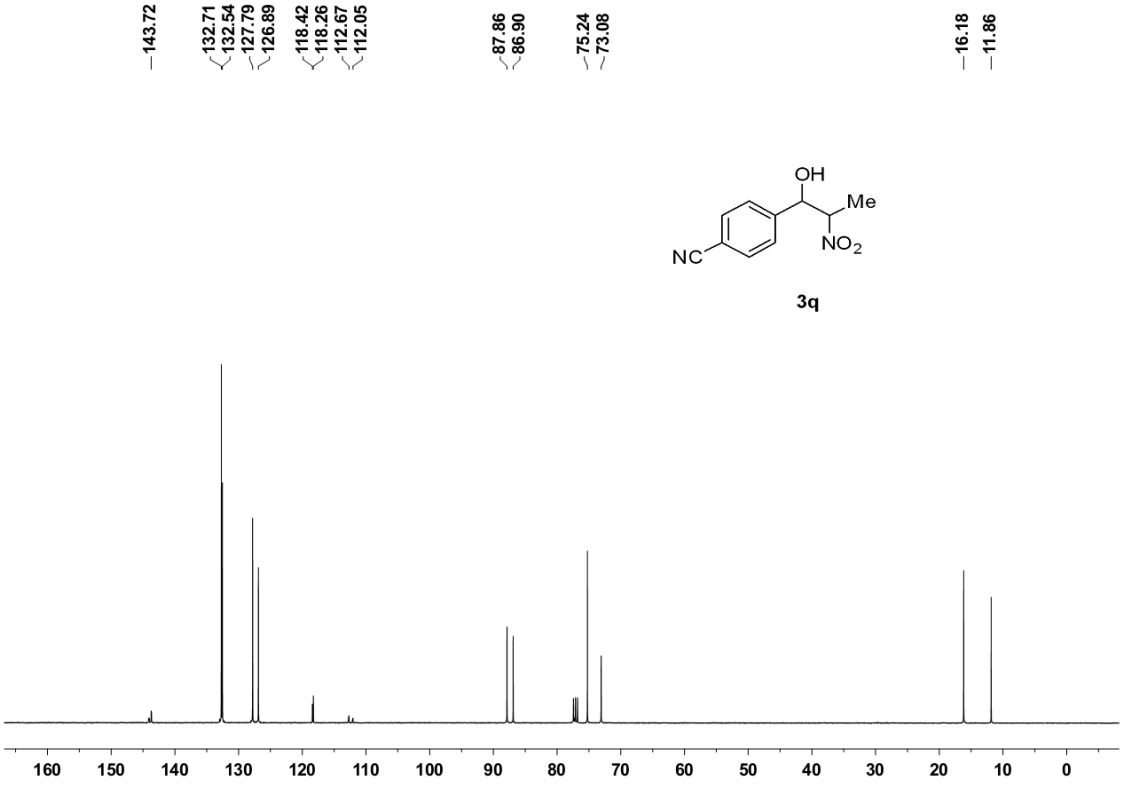
3p


148.24
147.86
145.67
145.37
127.96
127.05
124.09
123.93
87.83
86.83
75.05
72.93
16.20
11.83
OH
Me
NO2
O2N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

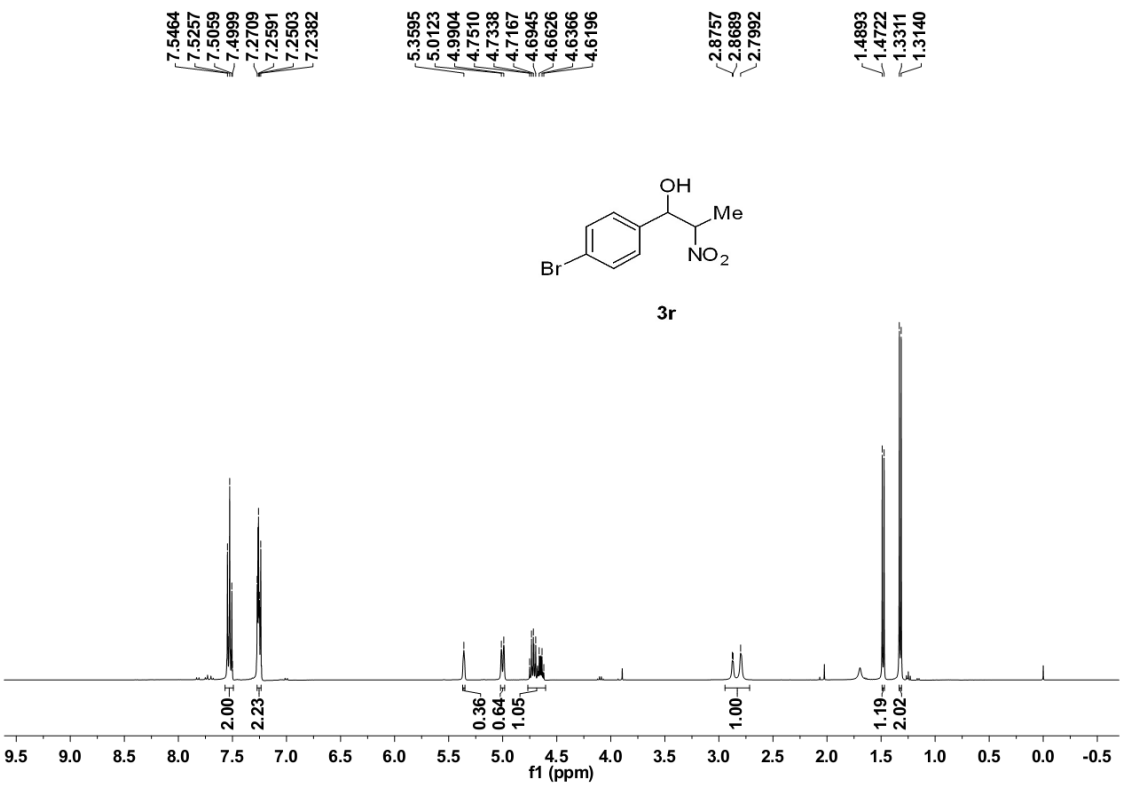
3p


7.7064
7.6922
7.6861
7.6720
7.5539
7.5372
7.5341
7.5171
5.5026
5.4940
5.1303
5.1087
4.7541
4.7105
4.6935
4.6846
3.1884
1.4756
1.4586
1.3609
1.3438
OH
Me
NO2
NC
2.00
1.99
0.50
0.50
1.05
1.01
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

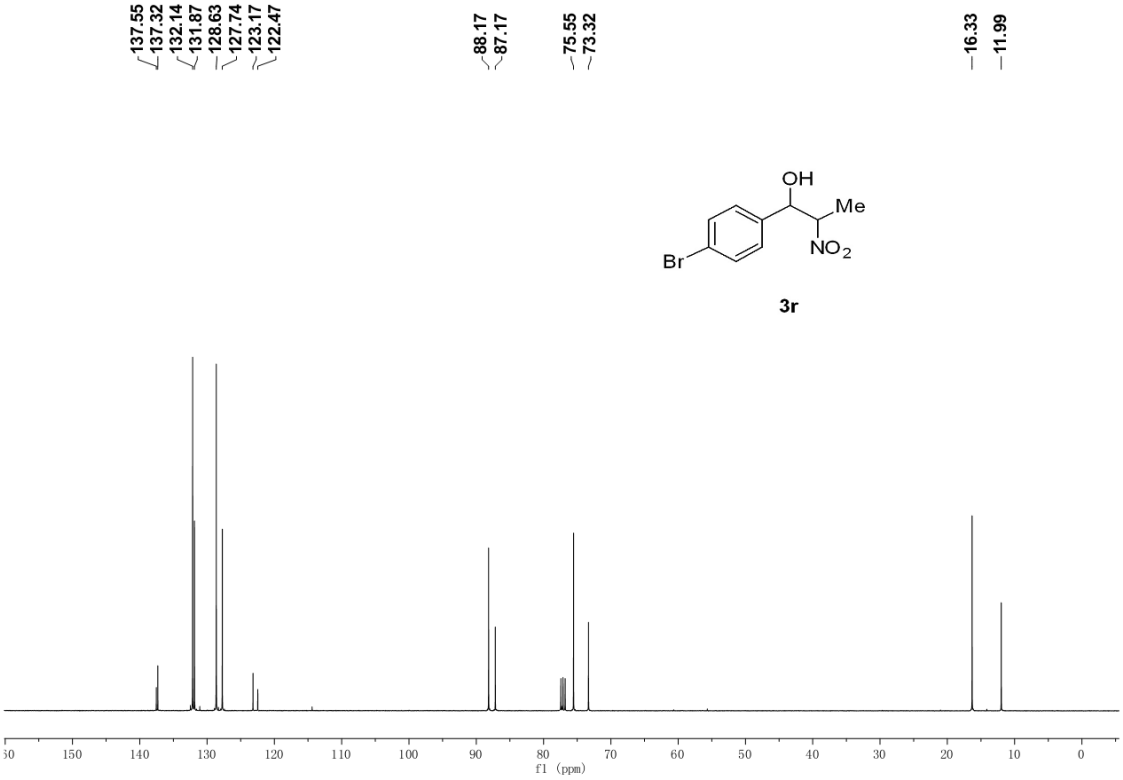
3q


143.72
132.71
132.54
127.79
126.89
118.42
118.26
112.67
112.05
87.86
86.90
75.24
73.08
16.18
11.86
OH
Me
NO2
NC
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

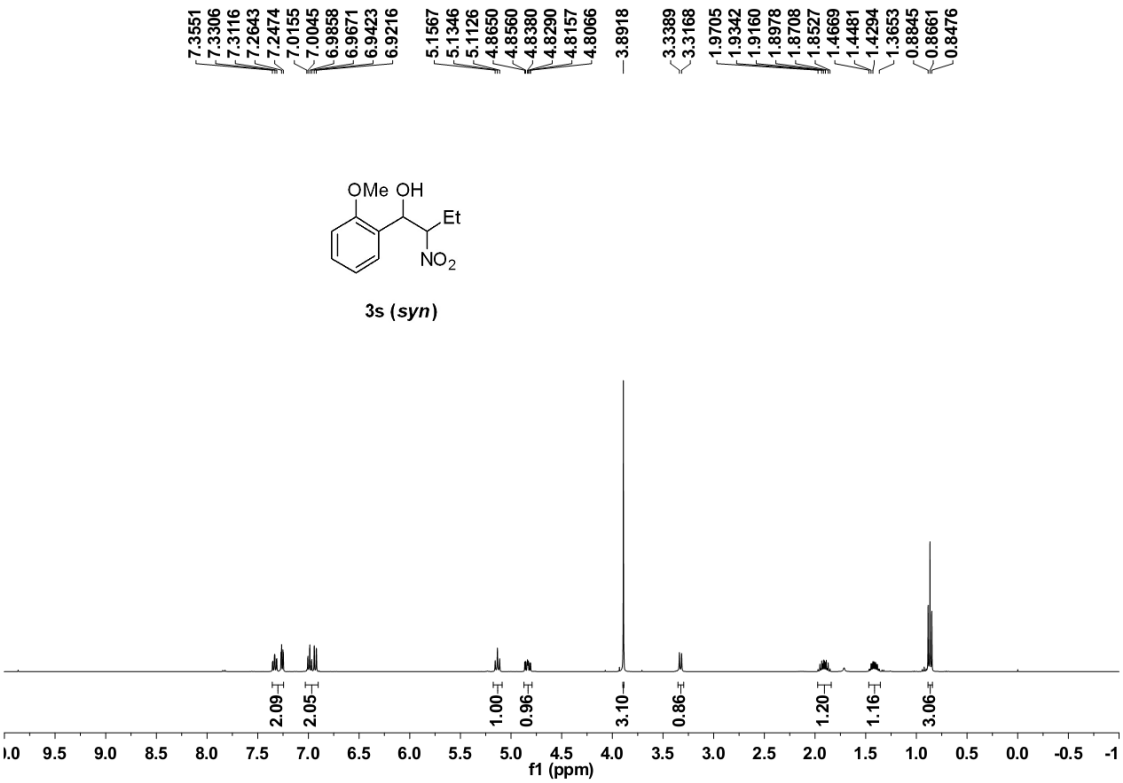
3q


7.5464
7.5257
7.5059
7.4999
7.2709
7.2591
7.2503
7.2382
5.3595
5.0123
4.9904
4.7510
4.7338
4.7167
4.6945
4.6626
4.6366
4.6196
2.8757
2.8689
2.7992
1.4893
1.4722
1.3311
1.3140
OH
Me
NO2
Br
2.00
2.23
0.36
0.64
1.05
1.00
1.19
2.02
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
0.5
0.0
-0.5
f1 (ppm)

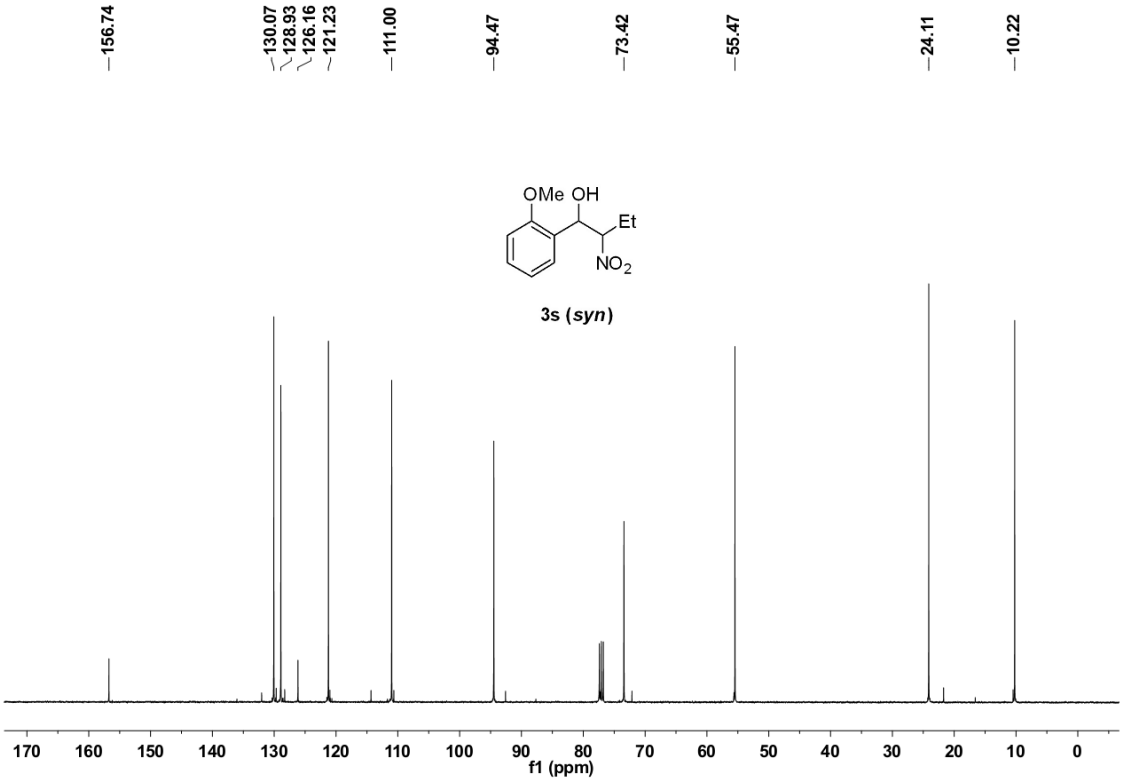
3r

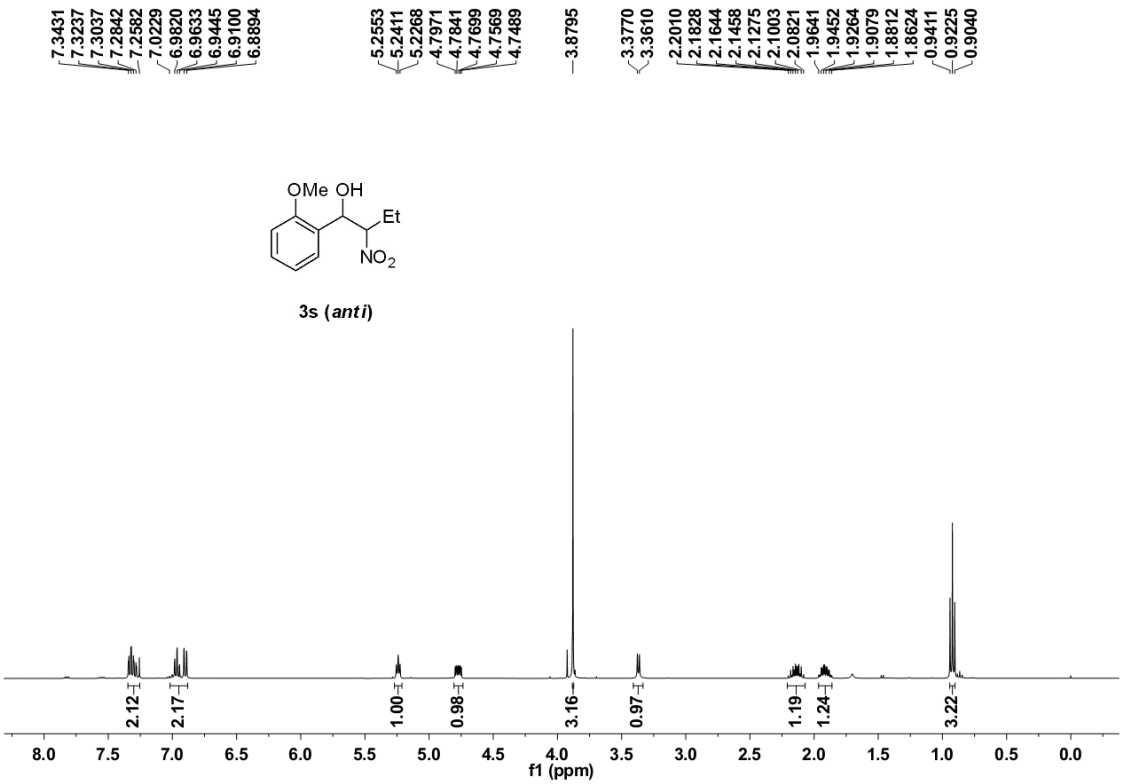

137.55
137.32
132.14
131.87
128.63
127.74
123.17
122.47
88.17
87.17
75.55
73.32
16.33
11.99
OH
Me
NO2
Br
f1 (ppm)

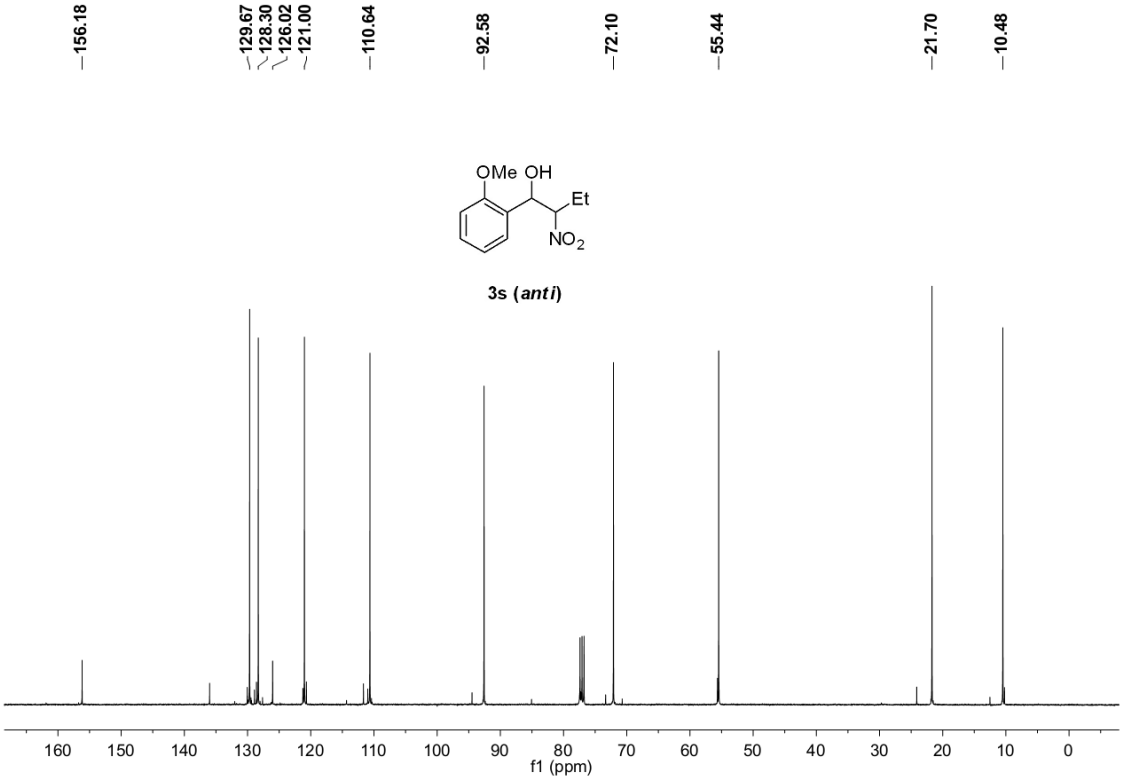
3r


7.3551
7.3306
7.3116
7.2643
7.2474
7.0155
7.0045
6.9858
6.9671
6.9423
6.9216
5.1567
5.1346
5.1126
4.8650
4.8560
4.8380
4.8290
4.8157
4.8066
3.8918
3.3389
3.3168
1.9705
1.9342
1.9160
1.8978
1.8708
1.8527
1.4669
1.4481
1.4294
1.3653
0.8845
0.8661
0.8476
OMe OH
Et
NO2
2.09
2.05
1.00
0.96
3.10
0.86
1.20
1.16
3.06
f1 (ppm)

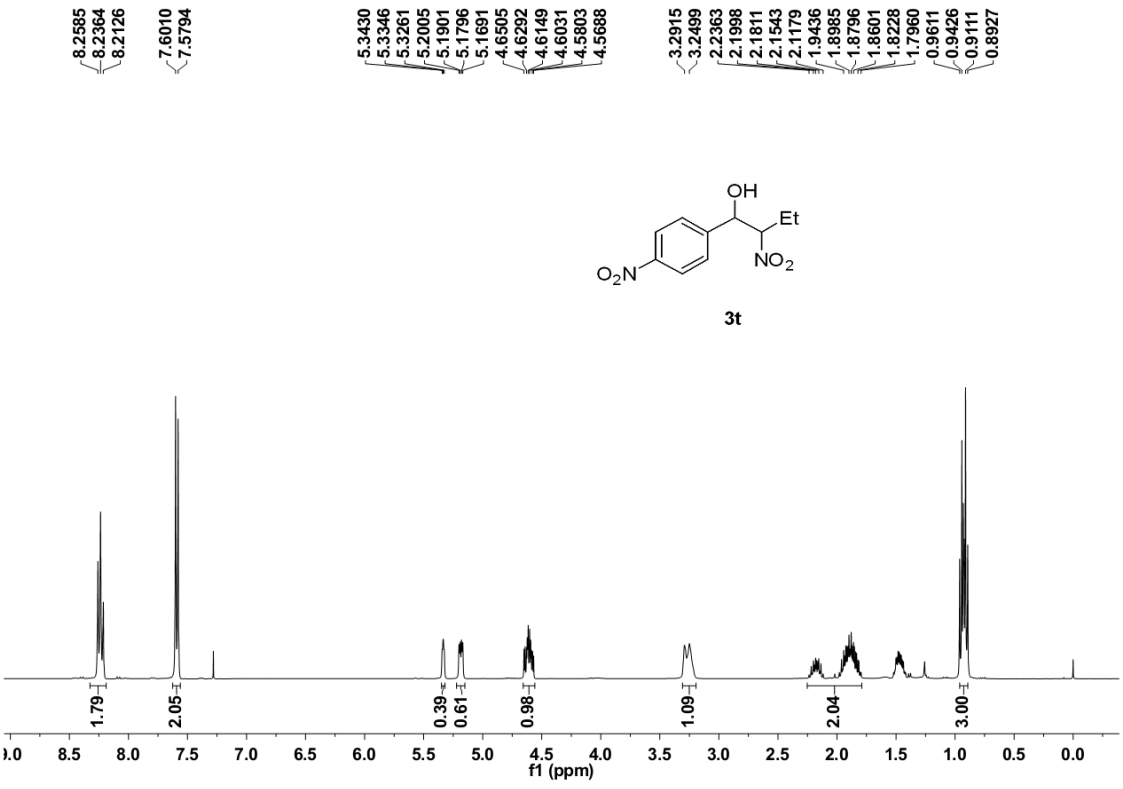
3s (*syn*)



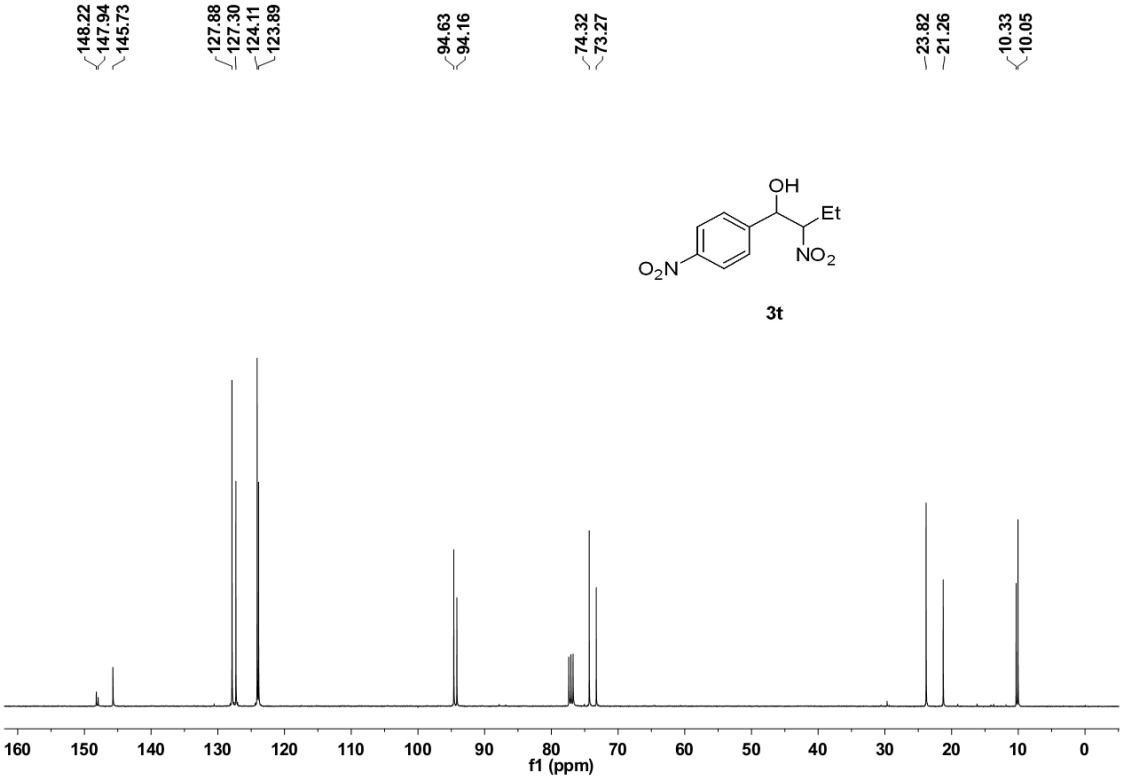



156.18
129.67
128.30
126.02
121.00
110.64
92.58
72.10
55.44
21.70
10.48
OMe OH
Et
NO2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

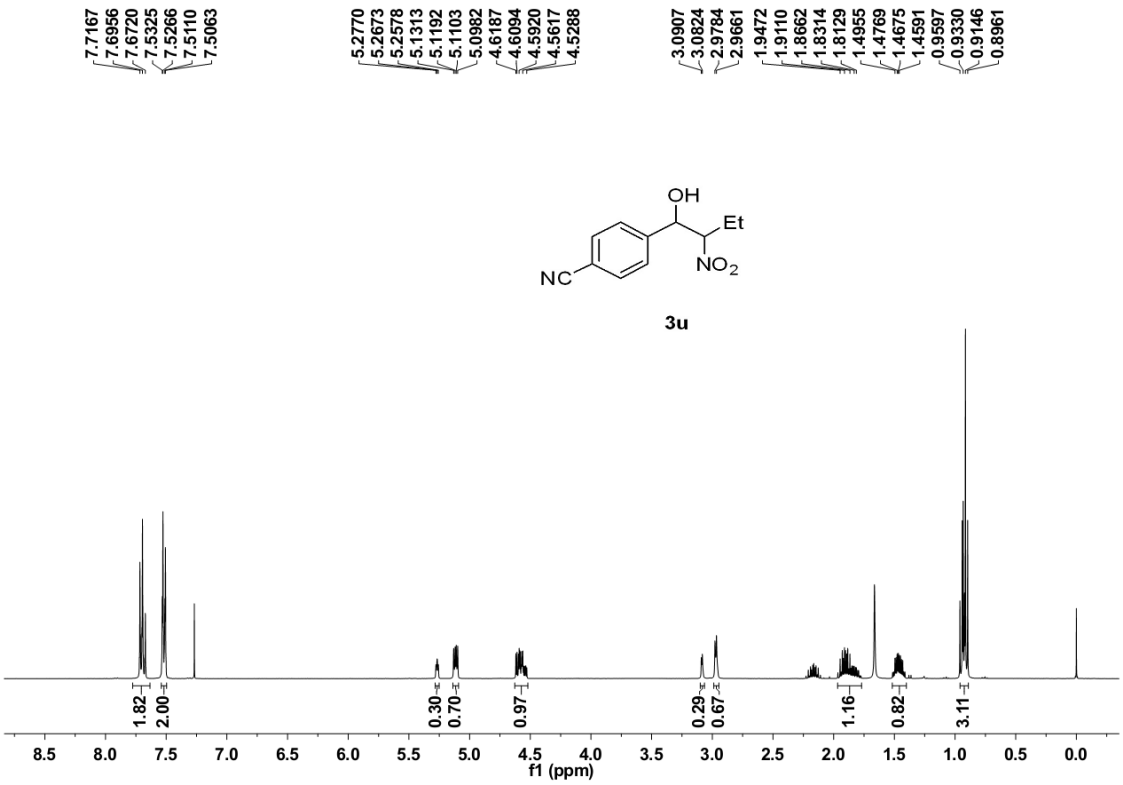
3s (*anti*)


8.2585
8.2364
8.2126
7.6010
7.5794
5.3430
5.3346
5.3261
5.2005
5.1901
5.1796
5.1691
4.6505
4.6292
4.6149
4.6031
4.5803
4.5688
3.2915
3.2499
2.2363
2.1998
2.1811
2.1543
2.1179
1.9436
1.8985
1.8796
1.8601
1.8228
1.7960
0.9611
0.9426
0.9111
0.8927
OH
Et
NO2
O2N
1.79
2.05
0.39
0.61
0.98
1.09
2.04
3.00
f1 (ppm)

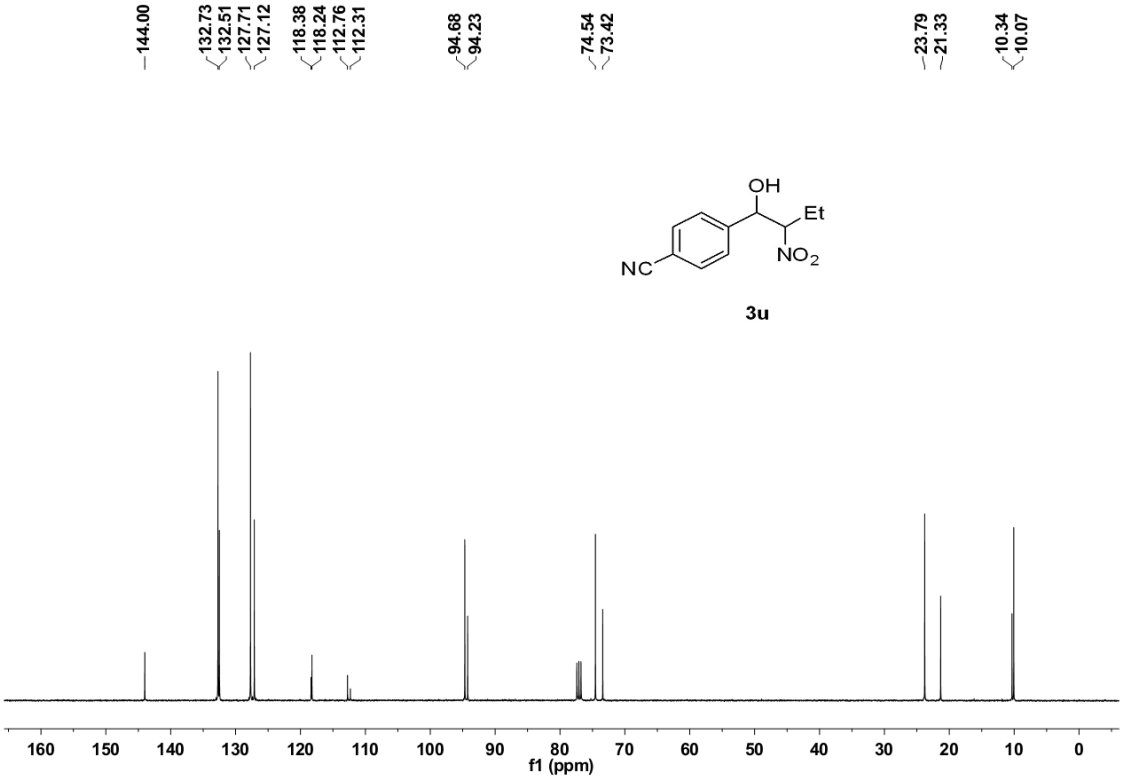
3t

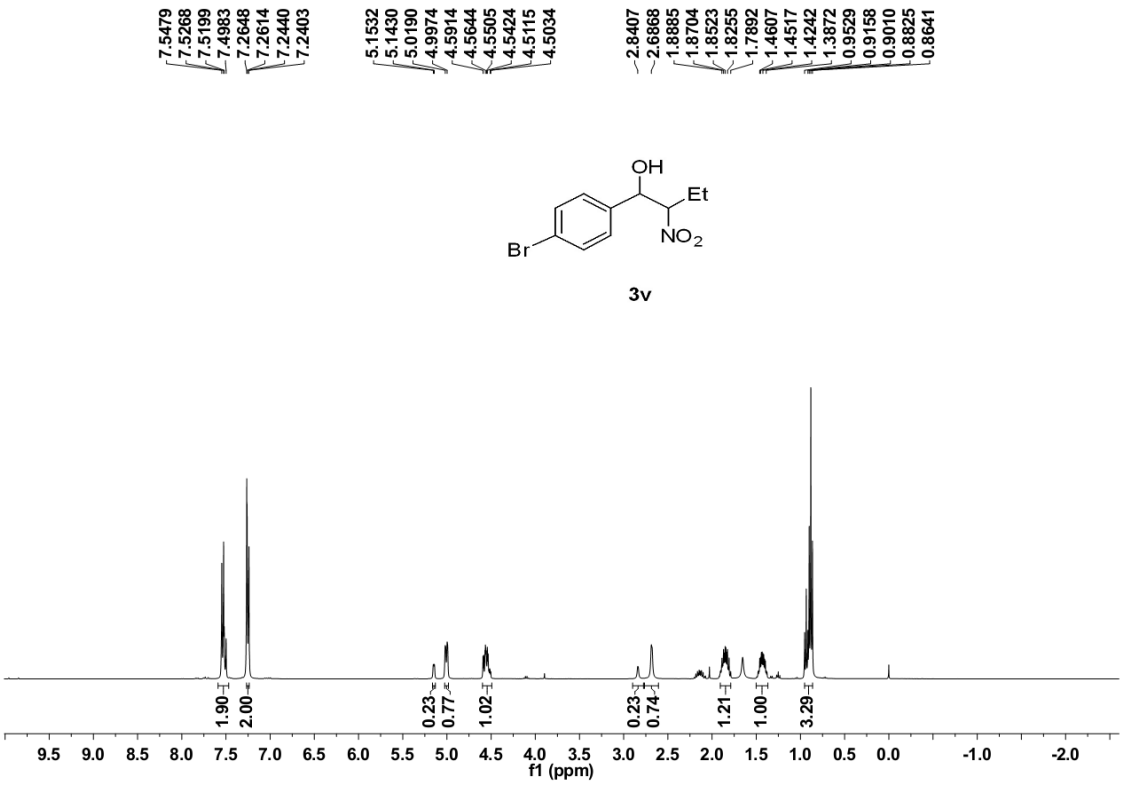

148.22
147.94
145.73
127.88
127.30
124.11
123.89
94.63
94.16
74.32
73.27
23.82
21.26
10.33
10.05
OH
Et
NO2
O2N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

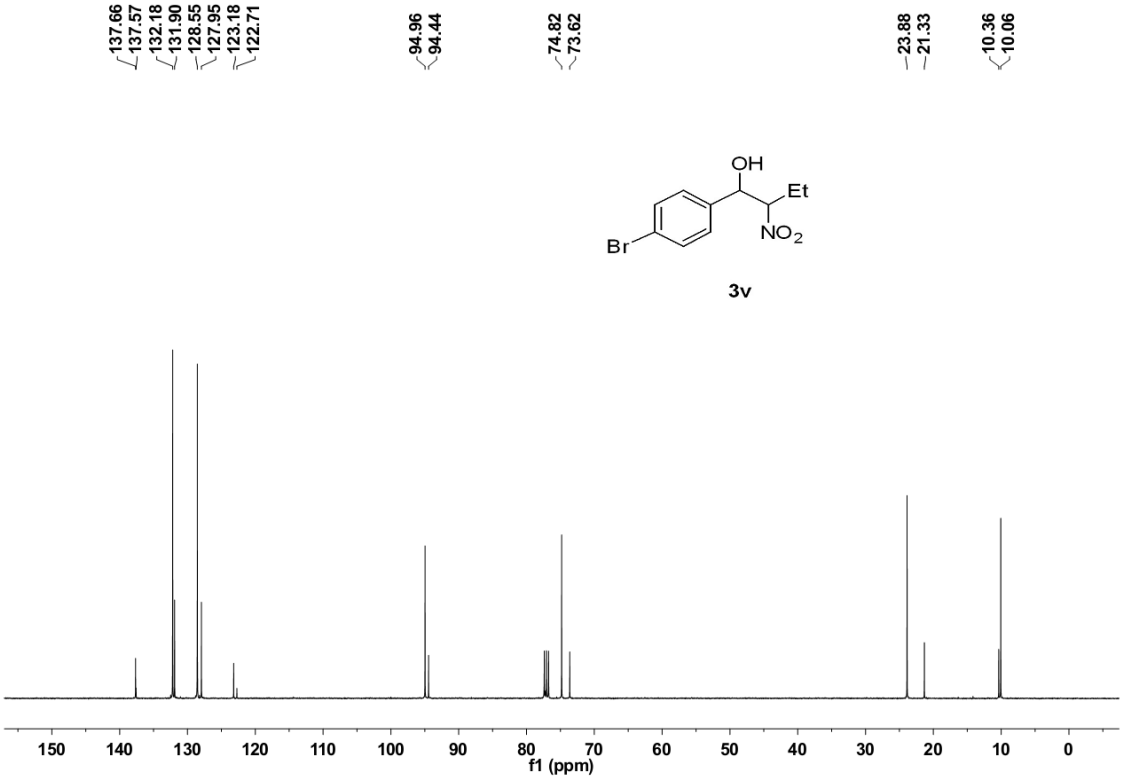
3t


7.7167
7.6956
7.6720
7.5325
7.5266
7.5110
7.5063
5.2770
5.2673
5.2578
5.1313
5.1192
5.1103
5.0982
4.6187
4.6094
4.5920
4.5617
4.5288
3.0907
3.0824
2.9784
2.9661
1.9472
1.9110
1.8662
1.8314
1.8129
1.4955
1.4769
1.4675
1.4591
0.9597
0.9330
0.9146
0.8961
OH
Et
NO2
NC
1.82
2.00
0.30
0.70
0.97
0.29
0.67
1.16
0.82
3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3u


144.00
132.73
132.51
127.71
127.12
118.38
118.24
112.76
112.31
94.68
94.23
74.54
73.42
23.79
21.33
10.34
10.07
OH
Et
NO2
NC
3u
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.5479
7.5268
7.5199
7.4983
7.2648
7.2614
7.2440
7.2403
5.1532
5.1430
5.0190
4.9974
4.5914
4.5644
4.5505
4.5424
4.5115
4.5034
2.8407
2.6868
1.8885
1.8704
1.8523
1.8255
1.7892
1.4607
1.4517
1.4242
1.3872
0.9529
0.9158
0.9010
0.8825
0.8641
OH
Et
NO2
Br
3v
1.90
2.00
0.23
0.77
1.02
0.23
0.74
1.21
1.00
3.29
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 0.5 0.0 -1.0 -2.0
f1 (ppm)



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