Electronic supplementary material (ESI)

Wealth from waste: *M. acuminata* peel waste-derived magnetic nanoparticles as a solid catalyst for Henry reaction

Gunindra Pathak, Kalyani Rajkumari and Samuel Lalthazuala Rokhum*

Department of Chemistry, National Institute of Technology Silchar, Silchar 788010, Assam, India.

†Corresponding author. Tel.: +91 3842 242915; fax: +91 3842-224797;
Email address: rokhum@che.nits.ac.in

Table of content

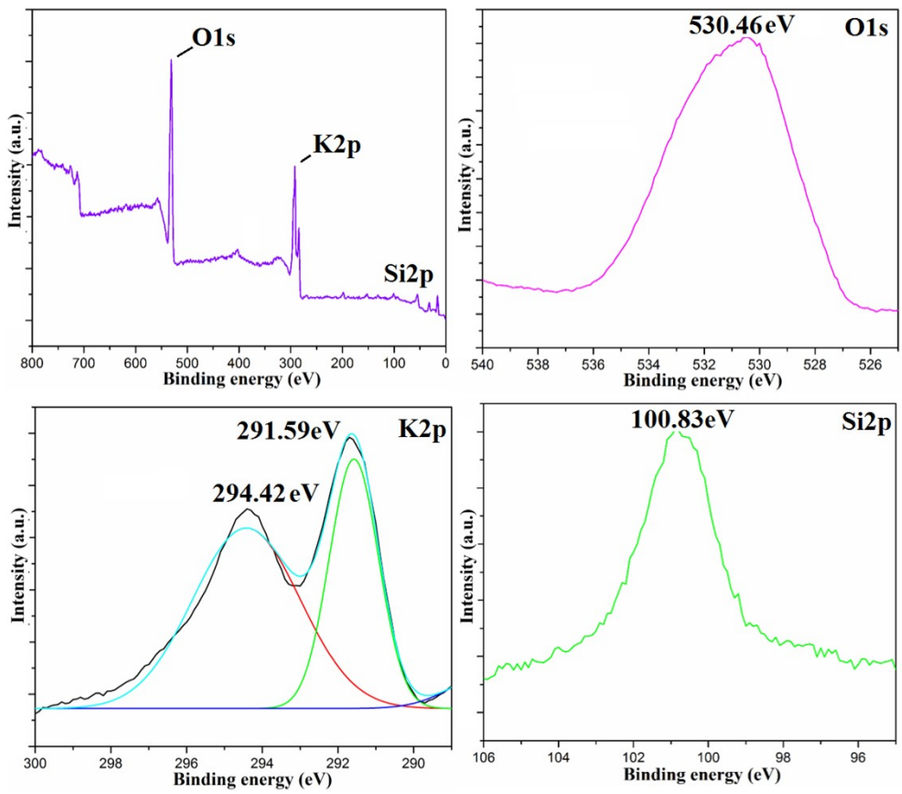


Fig S1: Recovered MABPE@Fe_3O_4 (a) XPS survey spectrum, (b) O1s, (c) K2p and (d) Si2p spectra.

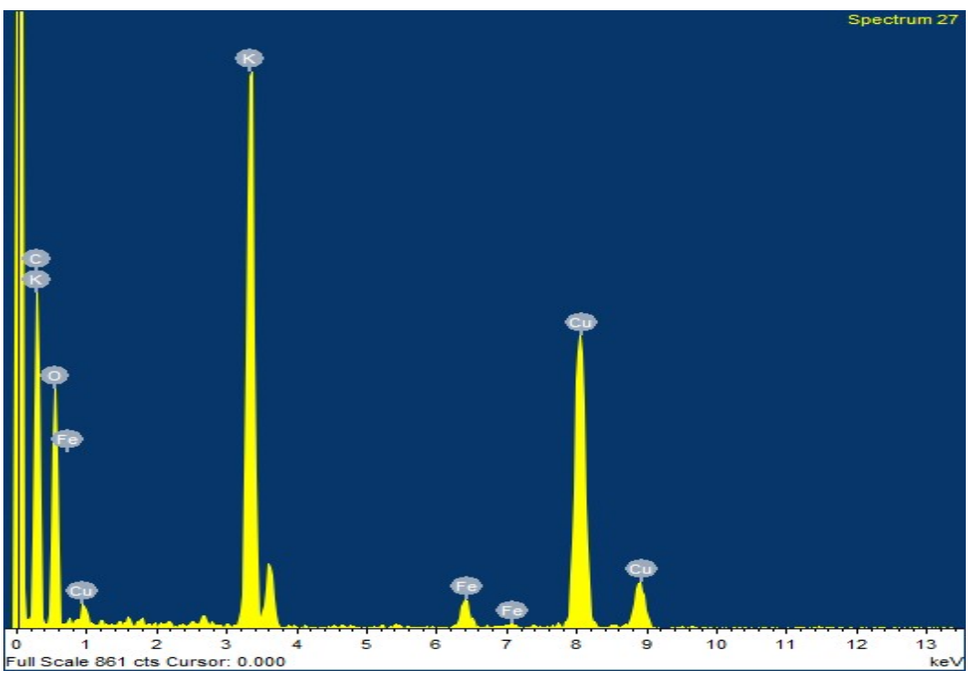


Fig S2: EDX spectrum of the recovered MABPE@Fe_3O_4 nanoparticles

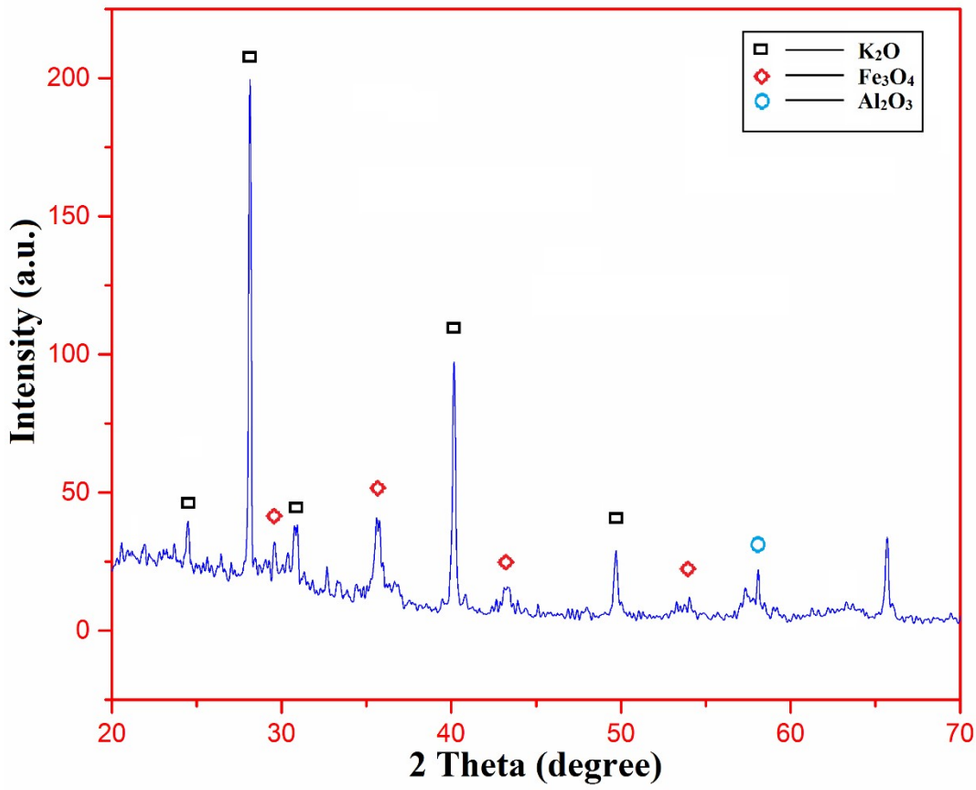


Fig S3: XRD patterns of the recovered MABPE@Fe_3O_4 NPs.

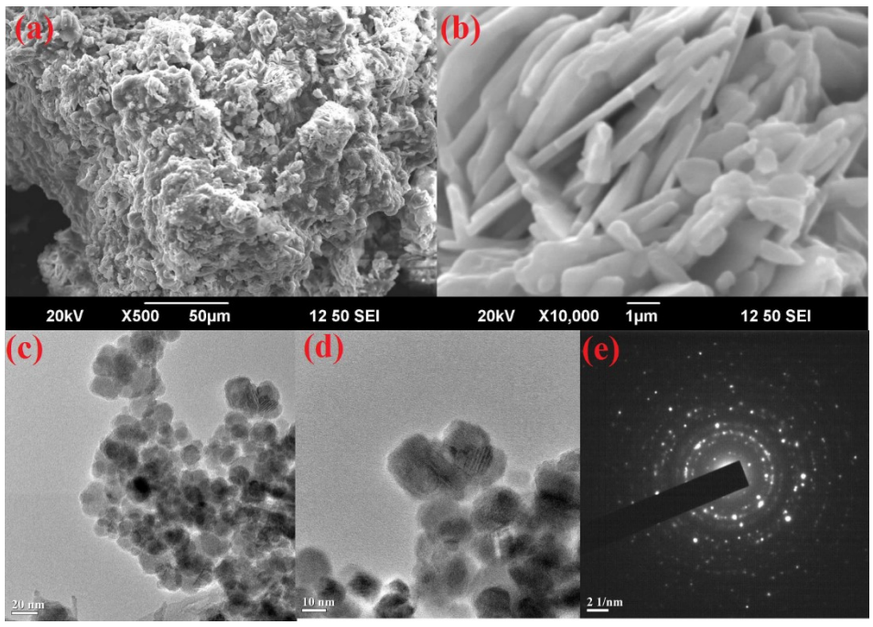


Fig S4: SEM (a-b), TEM (c-d) images of recovered MABPE@Fe_3O_4 nanoparticles at various magnification, SAED pattern (e)

Spectral data:

1-(4-Bromophenyl)-2-nitroethan-1-ol (3b):

Pale yellow oily liquid, 94% yield, IR (KBr, cm^{-1}): ν 3415, 3025, 2939, 2889, 2787, 1550, 1440, 1381, 1331, 1280, 1184, 1120, 840; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.54 (d, *J*= 8.4 Hz, 2H), 7.29 (d, *J*= 8.4 Hz, 2H), 5.44-5.41 (m, 1H), 4.79 (t, *J*= 7.2 Hz, 1H), 4.57-4.50 (m, 1H), 2.03 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 138.05, 132.14, 129.12, 127.68, 122.89, 70.33.

2-Nitro-1-(4-nitrophenyl) ethan-1-ol (3c):

Brownish gummy liquid, 99% yield, IR (KBr, cm^{-1}): ν 3529, 3451, 3019, 1527, 1434, 1222, 1029, 937, 758; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 8.27 (d, *J*= 8.8 Hz, 2H), 7.64 (d, *J*= 8.8 Hz, 2H), 5.63-5.60 (m, 1H), 4.87 (t, *J*= 6.8 Hz, 1H), 4.64-4.58 (m, 1H), 2.01 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 148.09, 145.02, 128.71, 126.96, 124.20, 69.95.

1-(4-Chlorophenyl)-2-nitroethan-1-ol (3d):

Colorless oily liquid, 94% yield, IR (KBr, cm^{-1}): ν 3408, 3035, 2979, 2989, 2756, 1536, 1428, 1389, 1326, 1275, 1185, 1115, 840, 756; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.35 (d, *J*= 8.4 Hz, 2H), 7.18 (d, *J*= 8.4 Hz, 2H), 5.44-5.41 (m, 1H), 4.80 (t, *J*= 7.2 Hz, 1H), 4.56 (d, *J*= 3.6 Hz, 1H), 2.57 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 138.37, 132.67, 129.80, 129.18, 127.37, 70.29.

2-(1-Hydroxy-2-nitroethyl) phenol (3e):

Gummy liquid, 93% yield, IR (KBr, cm^{-1}): ν 3387, 3075, 2914, 1580, 1538, 1362, 1326, 1230, 1105, 1015, 822, 747; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.12 (d, *J*=9.2 Hz, 1H), 7.97 (t, *J*=6.4 Hz, 1H), 7.42 (d, *J*=7.6 Hz, 1H), 7.00 (t, *J*=7.2 Hz, 1H,), 6.81 (s, 1H), 4.31 (t, 1H, *J*=7.2 Hz), 4.23 (t, *J*=6 Hz, 1H), 3.68-3.58 (m, 1H), 1.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 153.94, 131.47, 128.69, 125.87, 121.31, 116.61, 71.22.

2-Nitro-1-(2-nitrophenyl) ethan-1-ol (3f):

Brownish solid, 97% yield, mp: 80-82^{o}C, IR (KBr, cm^{-1}): ν 3305, 3025, 2939, 2889, 2787, 1553, 1432, 1379, 1323, 1281, 1178, 1121, 845; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 8.13 (d, *J*= 7.6 Hz, 1H), 8.07 (d, *J*= 8 Hz, 1H), 7.97 (d, *J*= 7.6 Hz, 1H), 7.56 (t, *J*= 8 Hz, 1H), 6.05 (d, *J*= 9.2 Hz, 1H), 4.87 (d, *J*= 13.6 Hz, 1H), 4.58-4.52 (m, 1H), 2.60 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 134.37, 134.16, 133.81, 131.31, 129.64, 128.77, 124.95, 66.79.

2-Nitro-1-(3-nitrophenyl)ethan-1-ol (g)

Yellowish liquid, 92% yield, IR (KBr, cm^{-1}): ν 3520, 3437, 3028, 1515, 1434, 1218, 1031, 931, 760, ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 8.31 (s, 1H), 8.21 (d, 1H, *J*= 7.2 Hz), 7.78 (d, 1H, *J*= 7.6 Hz), 7.60 (t, 1H, *J*= 8Hz), 5.56 (s, 1H), 5.63-5.60 (m, 1H), 4.67-4.57 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 148.47, 140.38, 132.08, 130.10, 128.21, 123.89, 121.13, 69.80.

2-Nitro-1-(p-tolyl) ethan-1-ol (3h):

Colorless oil, 75% yield, IR (KBr, cm^{-1}): ν 3429, 3018, 2408, 1553, 1433, 1221, 1035, 963, 777, 677; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.27-7.26 (dd, *J*= 7.6 Hz, 1H), 7.20-7.18 (dd, *J*= 8 Hz, 1H), 7.10 (d, *J*= 8 Hz, 2H), 5.41-5.38 (m, 1H), 4.74-4.71 (m, 1H), 4.61-4.55 (m, 1H), 2.34 (s, 3H), 1.52 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 139.04, 138.89, 129.93, 129.67, 125.89, 70.90, 21.16.

2-Nitro-1-(3,4,5-trimethoxyphenyl)ethan-1-ol (3i)

Gummy liquid, 70% yield, IR (KBr, cm^{-1}): ν 3422, 3026, 1547, 1420, 1215, 1040, 967, 781, 670; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.61 (s, 2H), 5.42-5.39 (m, 1H), 4.63-4.57 (m, 1H), 4.53-4.48 (m, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 1.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 153.66, 133.83, 107.28, 102.71, 81.31, 71.16, 60.85, 56.23.

1-Nitropentan-2-ol (3j):

Colorless oil, 90% yield, IR (KBr, cm^{-1}): ν 3352, 2860, 1605, 1515, 1196, 1162, 833; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 4.45 (d, *J*=2 Hz, 1H), 4.42 (d, *J*=2 Hz, 1H), 4.35-4.30 (m, 1H), 2.27 (s, 1H), 1.49-1.38 (m, 2H), 1.35-1.25 (m, 2H), 1-0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 68.39, 35.71, 18.43, 13.76.

1-(4-Chlorophenyl)-2-nitropropan-1-ol (3l):

Colorless oily liquid, 97% yield, IR (KBr, cm^{-1}): ν 3401, 3025, 2949, 2889, 2786, 1546, 1438, 1381, 1323, 1281, 1179, 1121, 845, 786; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.81 (d, *J*= 7.6 Hz, 2H), 7.52 (d, *J*= 7.6 Hz, 2H), 5.01 (d, *J*= 8.8 Hz, 1H), 4.75-4.69 (m, 1H), 2.64 (s, 1H), 1.47 (d, J= 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 136.87, 131.47, 128.32, 127.40, 88.25, 31.77, 16.33.

2-Nitro-1-(4-nitrophenyl) propan-1-ol (3m):

Pale yellow solid, 99% yield, mp: 90-91^{o}C, IR (KBr, cm^{-1}): ν 3434, 3332, 3021, 2884, 2790, 1540, 1439, 1313, 1231, 1222, 1180, 780; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 8.25 (dd, 2H, *J*= 8.4 Hz), 7.60 (d, 2H, *J*= 8 Hz), 5.21 (d, 1H, *J*= 8 Hz), 4.82-4.70 (m, 1H), 1.39 (d, 3H, *J*=6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 148.16, 145.73, 127.97, 127.05, 124.07, 123.75, 87.83, 75.04, 16.18.

2-nitro-1-(3-nitrophenyl)propan-1-ol (3n)

Pale yellow solid, 95% yield, mp: 74-75^{o}C , IR (KBr, cm^{-1}): ν 3429, 3329, 3021, 2887, 2785, 1542, 1432, 1321, 1235, 1217, 1177, 762; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.27 (t, 1H, *J*=

7.6 Hz), 8.25-8.21 (m, 1H), 7.75 (d, 1H, *J*= 8 Hz), 7.62 (t, 1H, *J*= 8 Hz), 5.19 (d, 1H, *J*= 8.8 Hz), 4.83-4.73 (m, 1H), 1.40 (d, 3H, *J*= 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 148.42, 140.71, 133.01, 130.09, 124.01, 121.96, 87.84, 74.99, 16.25

2-Nitro-1-(p-tolyl)propan-1-ol (3o):

Colorless oily liquid, 87% yield, IR (KBr, cm^{-1}): ν 3354, 3015, 2929, 2898, 2780, 1550, 1441, 1377, 1345, 1284, 1179, 1110; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.24 (d, *J*= 8 Hz, 2H), 7.20 (d, *J*= 7.2 Hz, 2H), 5.30 (s, 1H), 4.96 (d, *J*= 8.8 Hz, 1H), 4.77-4.70 (m, 1H), 2.35 (s, 1H), 1.48-1.47 (dd, *J*= 6.8 Hz, 1H), 1.29-1.27 (dd, *J*= 6.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 129.16, 128.89, 126.35, 125.40, 87.98, 75.62, 20.69, 15.95;

2-Nitrohexan-3-ol (3p):

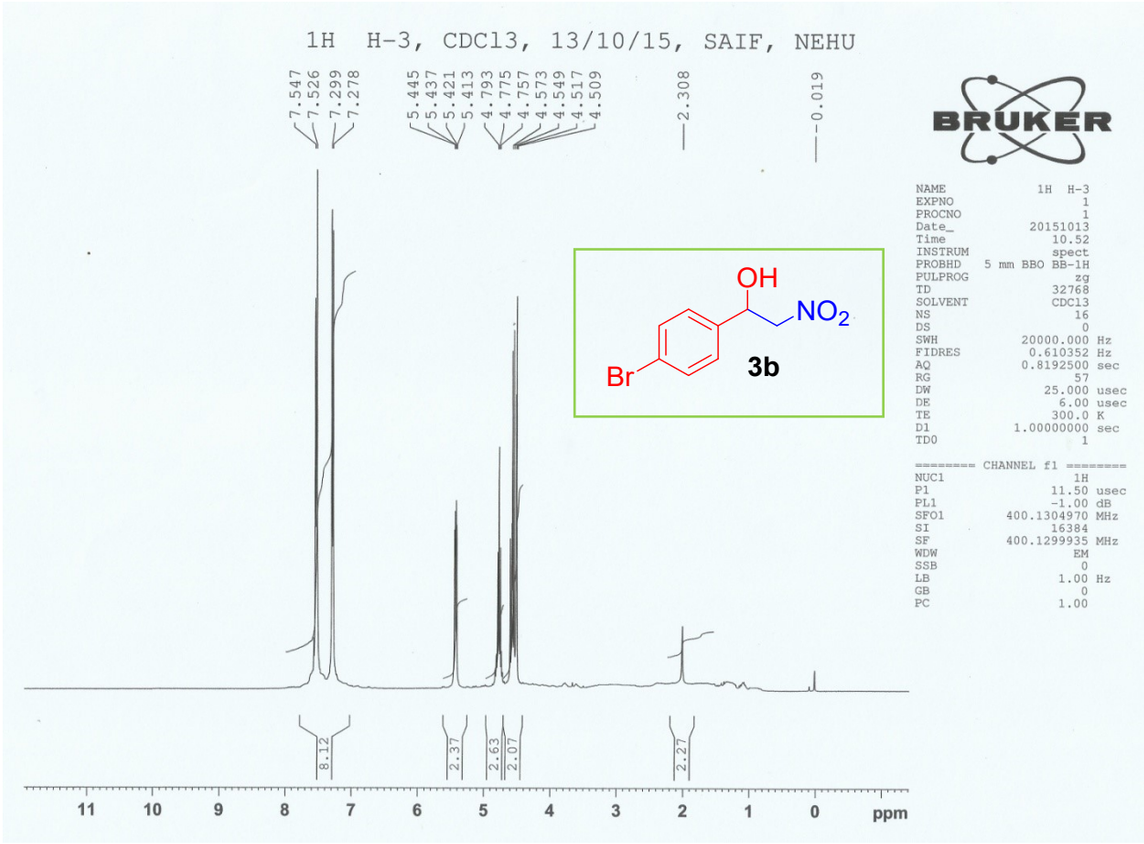
Colorless liquid, 90% yield, IR (KBr, cm^{-1}): ν 1840, 1632, 1531, 1439, 1371, 1221, 1016, 839; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 4.57-4.48 (m, 1H), 4.22-4.18 (m, 1H), 3.94-3.89 (m, 1H), 1.56-1.35 (m, 7H), 0.95 (t, 3H, J= 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 87.83, 72.65, 35.06, 18.95, 14.02, 13.76.

2-Nitrotetradecan-3-ol (3q):

Colorless liquid, 90% yield, IR (KBr, cm^{-1}): ν 1850, 1622, 1547, 1450, 1386, 1225, 1024, 848; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 4.18-4.15 (m, 1H), 3.91-3.88 (m, 1H), 2.44 (s, 1H), 1.54-1.37 (m, 20H), 0.89 (t, *J*= 6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 86.17, 72.90, 33.05, 33.92, 31.71, 29.52, 29.32, 24.92, 22.65, 16.13, 14.09;

2-methyl-2-nitro-1-(4-nitrophenyl)propan-1-ol (3r)

Whitish solid, 97% yield, IR (KBr, cm^{-1}): ν 3527, 3445, 3023, 1519, 1428, 1217, 1036, 942, 764; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 8.23 (d, 2H, *J*= 8.8 Hz), 7.59 (d, 2H, *J*=8.4 Hz), 5.44 (s, 1H), 1.57 (s, 3H), 1.47 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 147.96, 145.43, 130.54, 128.55, 127.86, 123.40, 91.77, 74.30, 23.93, 19.29.



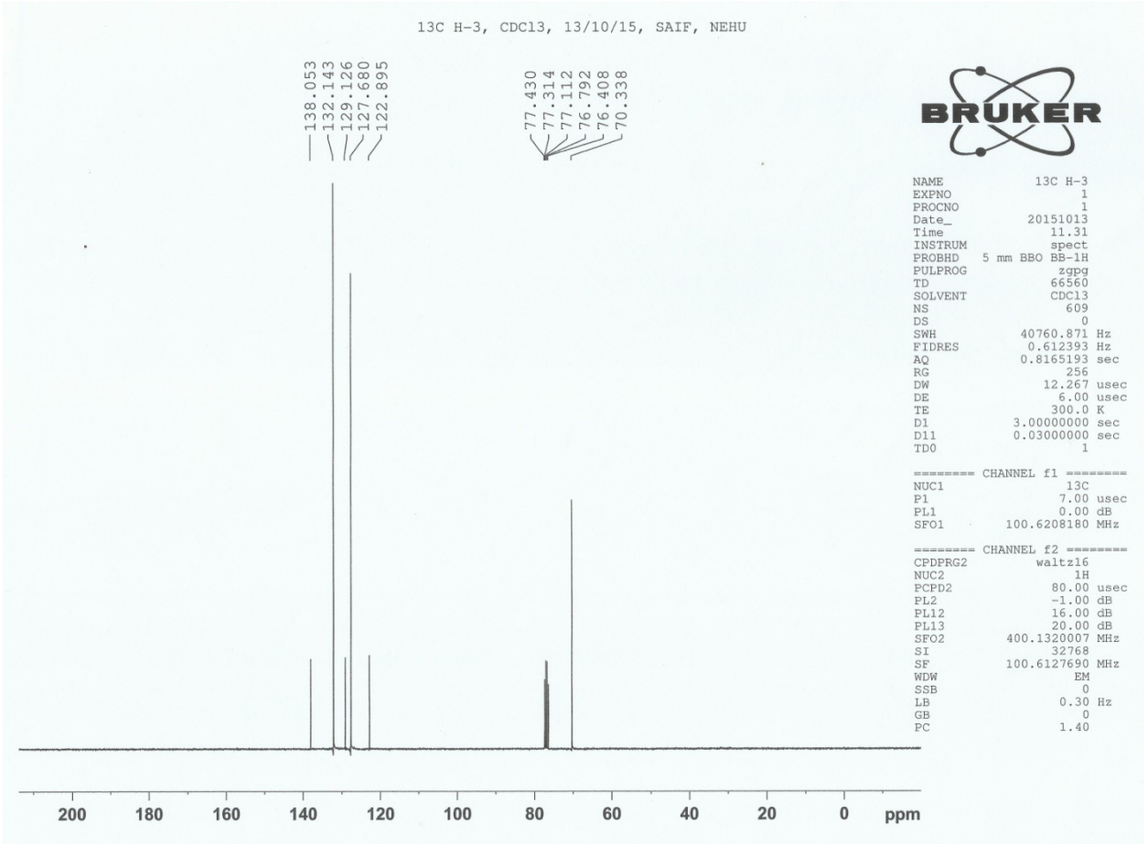
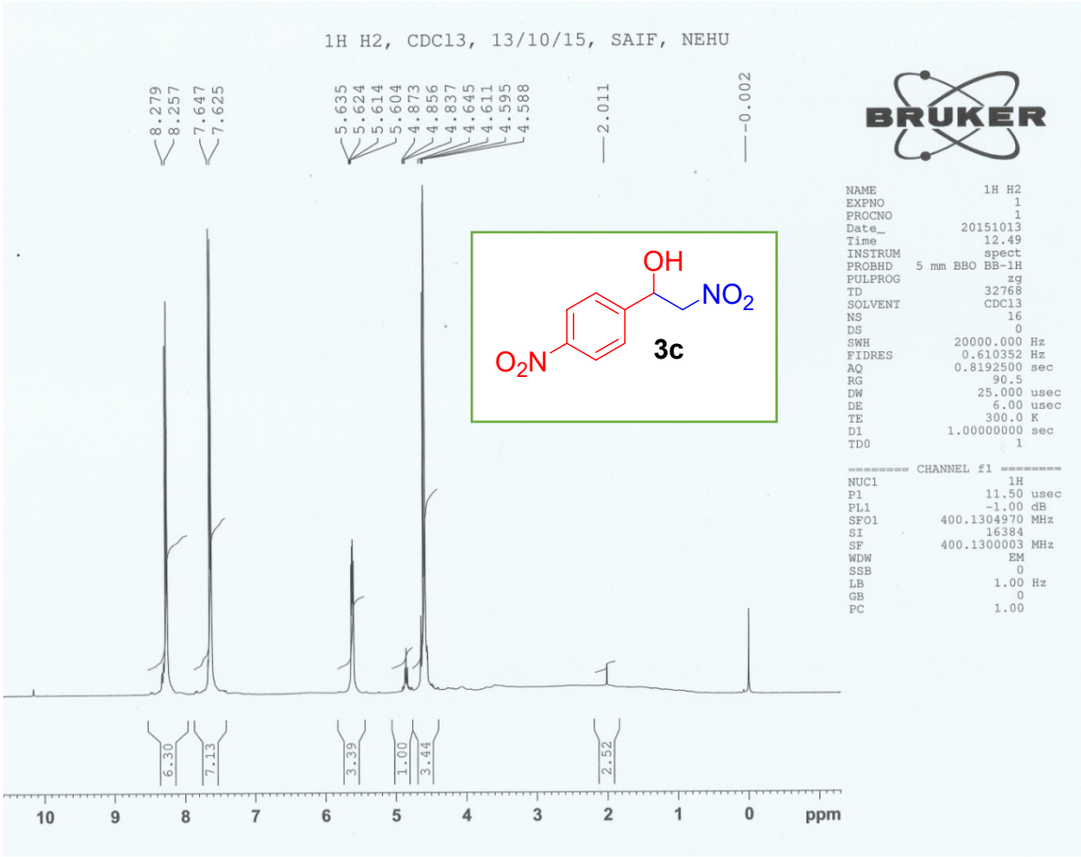


Fig S5: ^{1}H and ^{13}C-NMR spectra of 1-(4-Bromophenyl)-2-nitroethan-1-ol (**3b**)



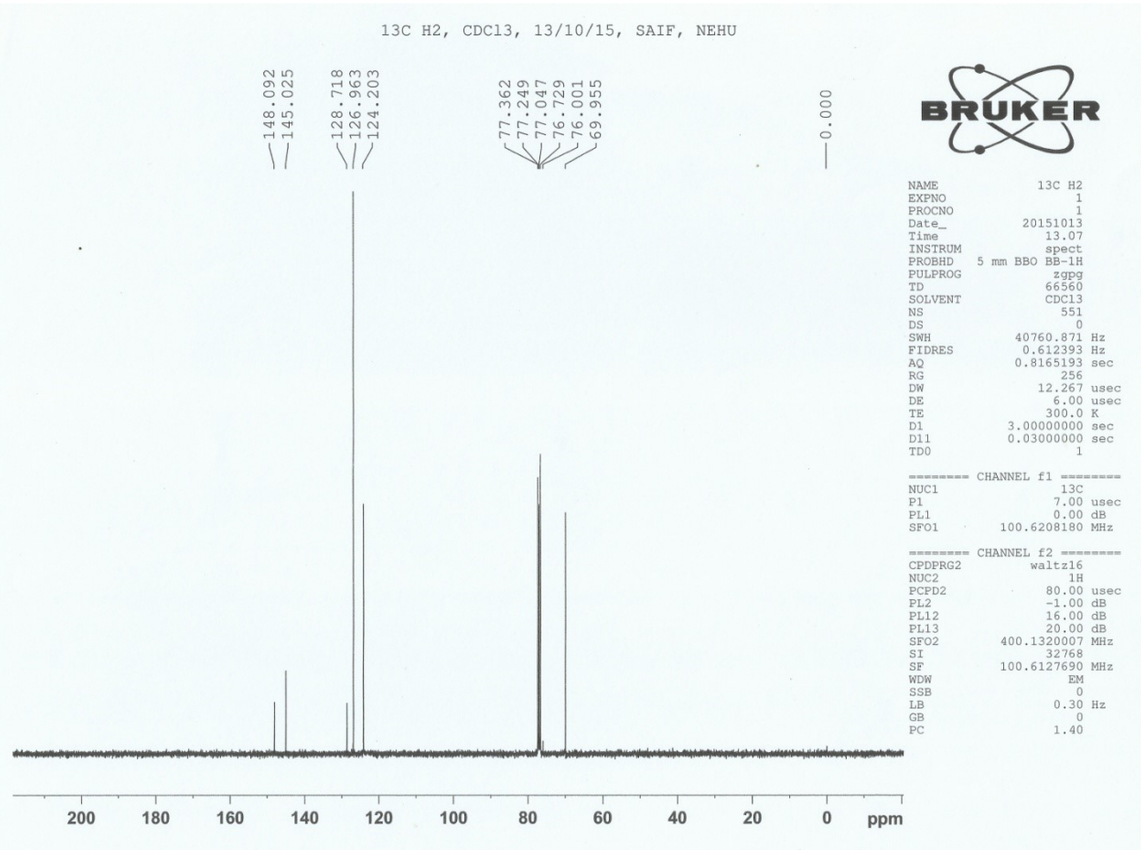
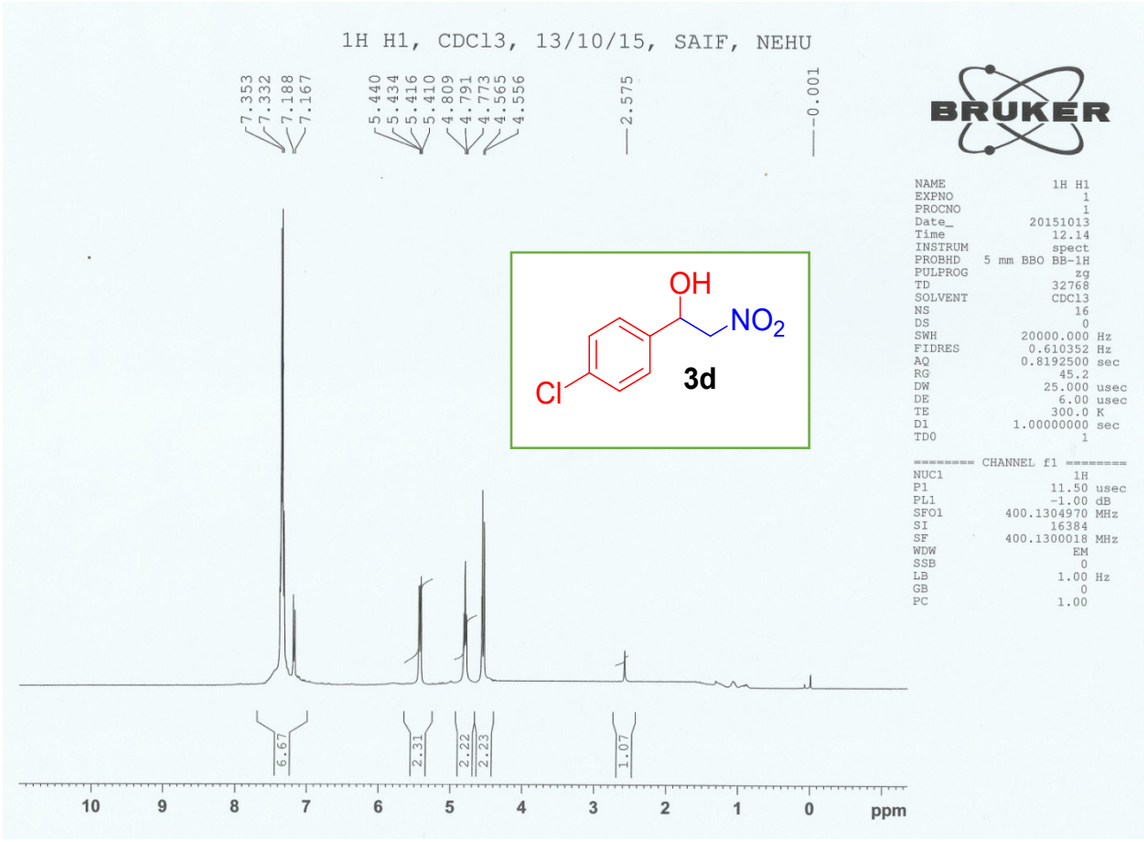


Fig S6: ^{1}H and ^{13}C-NMR spectra of 2-Nitro-1-(4-nitrophenyl) ethan-1-ol (**3c**)



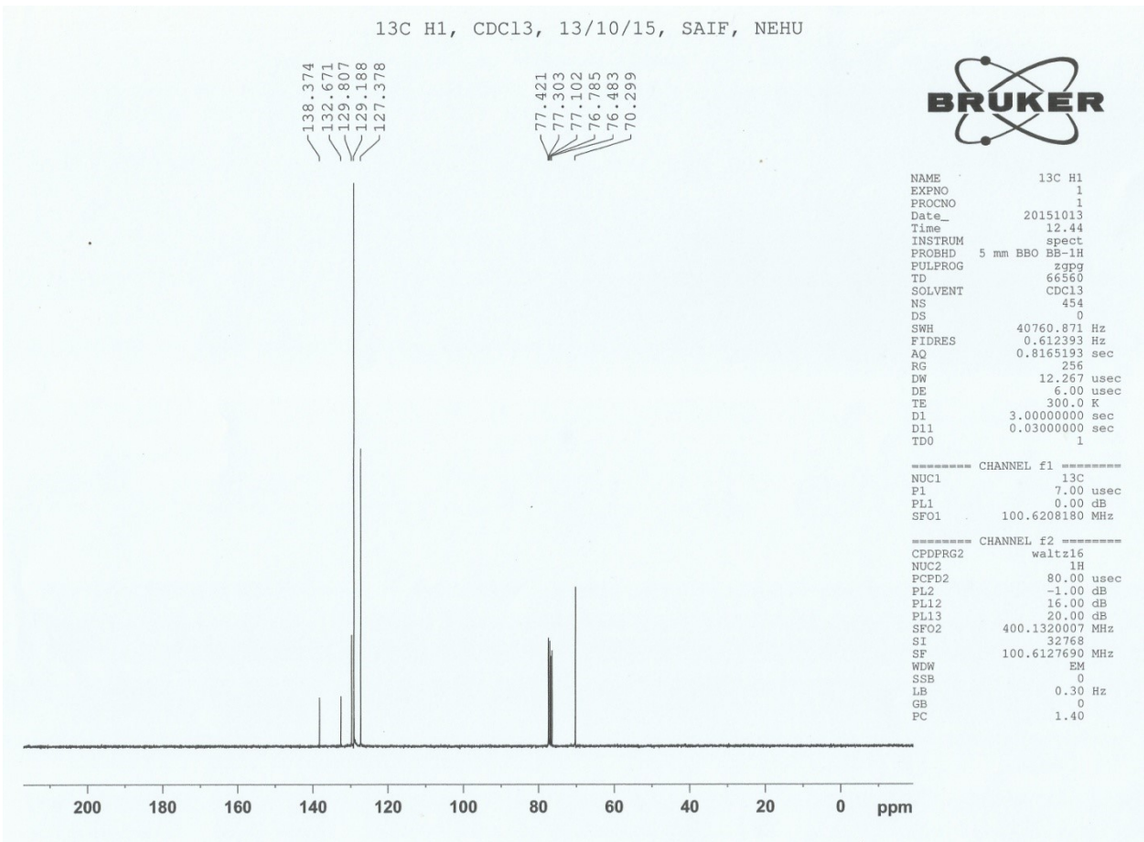
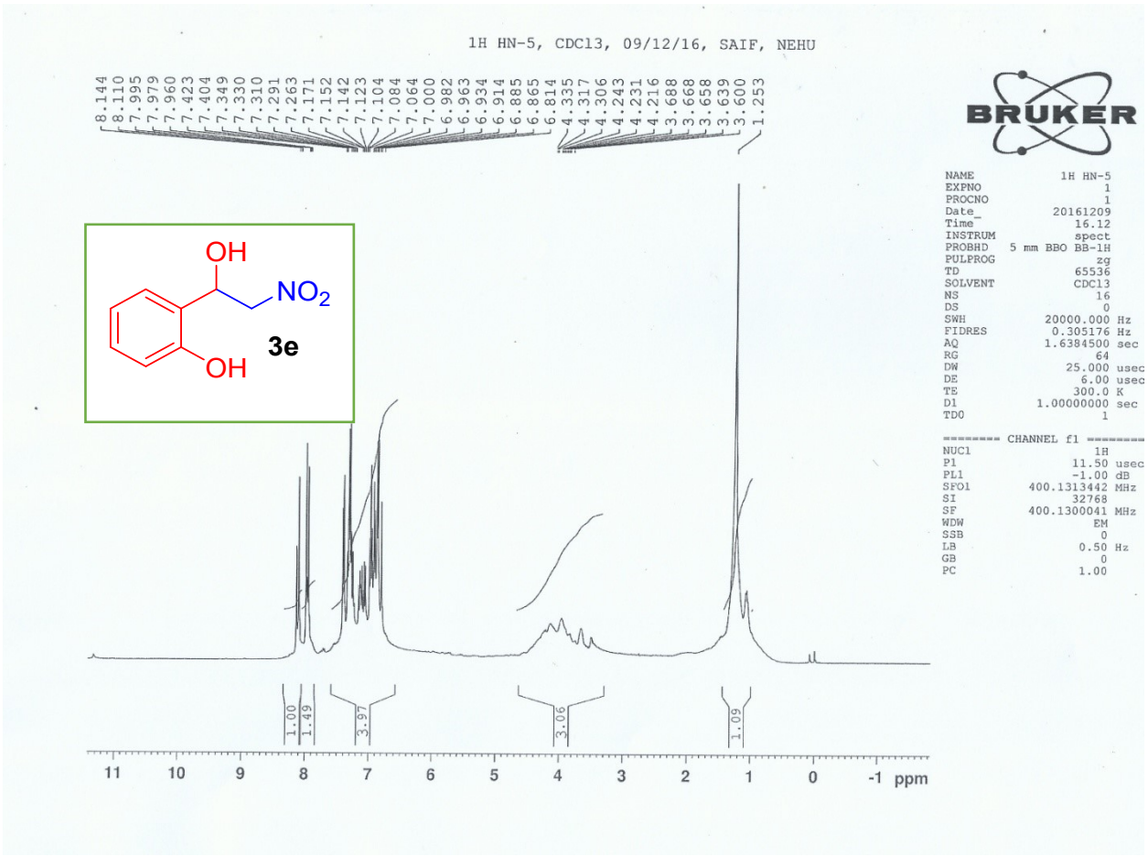


Fig S7: ^{1}H and ^{13}C-NMR spectra of 1-(4-Chlorophenyl)-2-nitroethan-1-ol (**3d**)



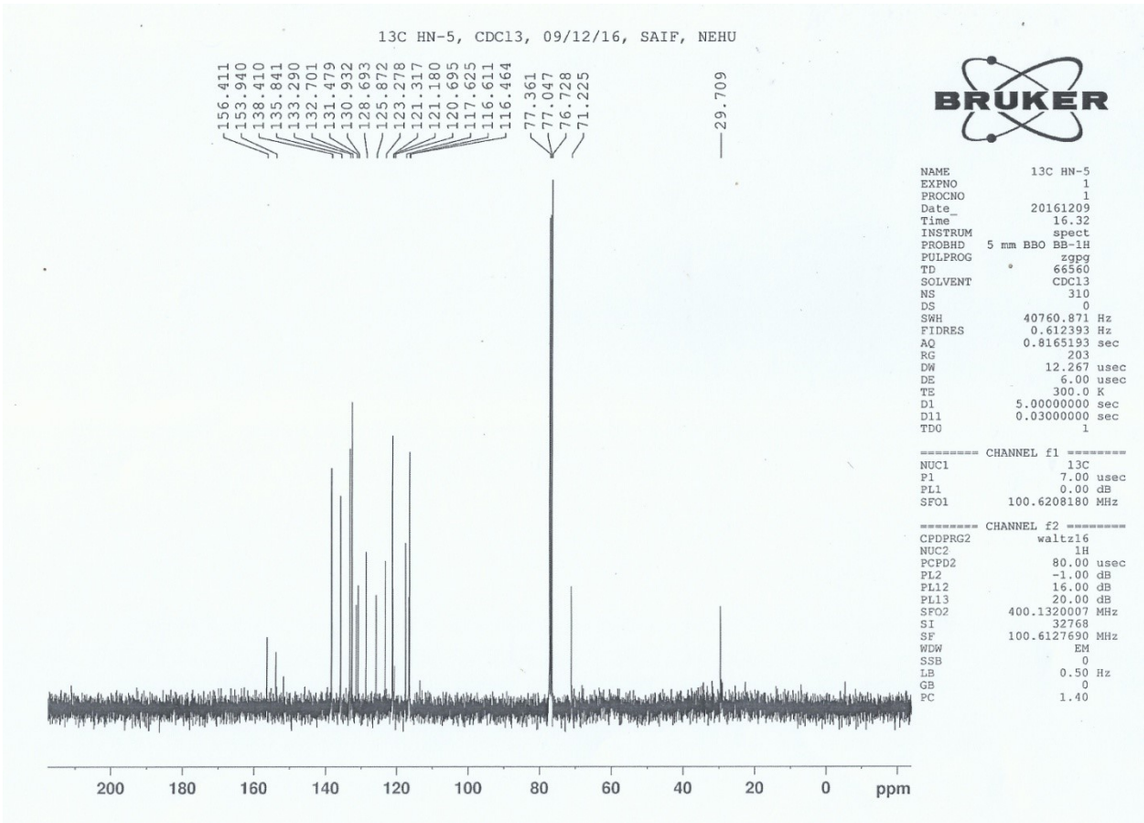
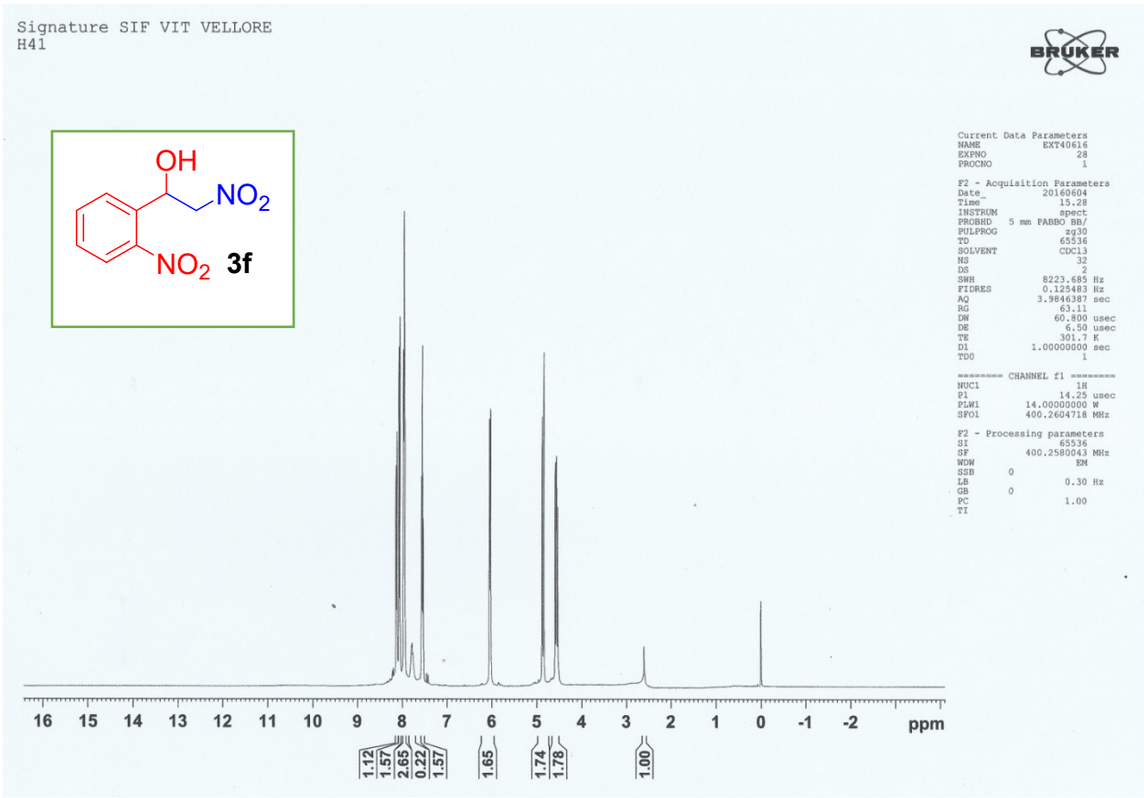


Fig S8: ^{1}H and ^{13}C-NMR spectra of 2-(1-Hydroxy-2-nitroethyl) phenol (**3e**)



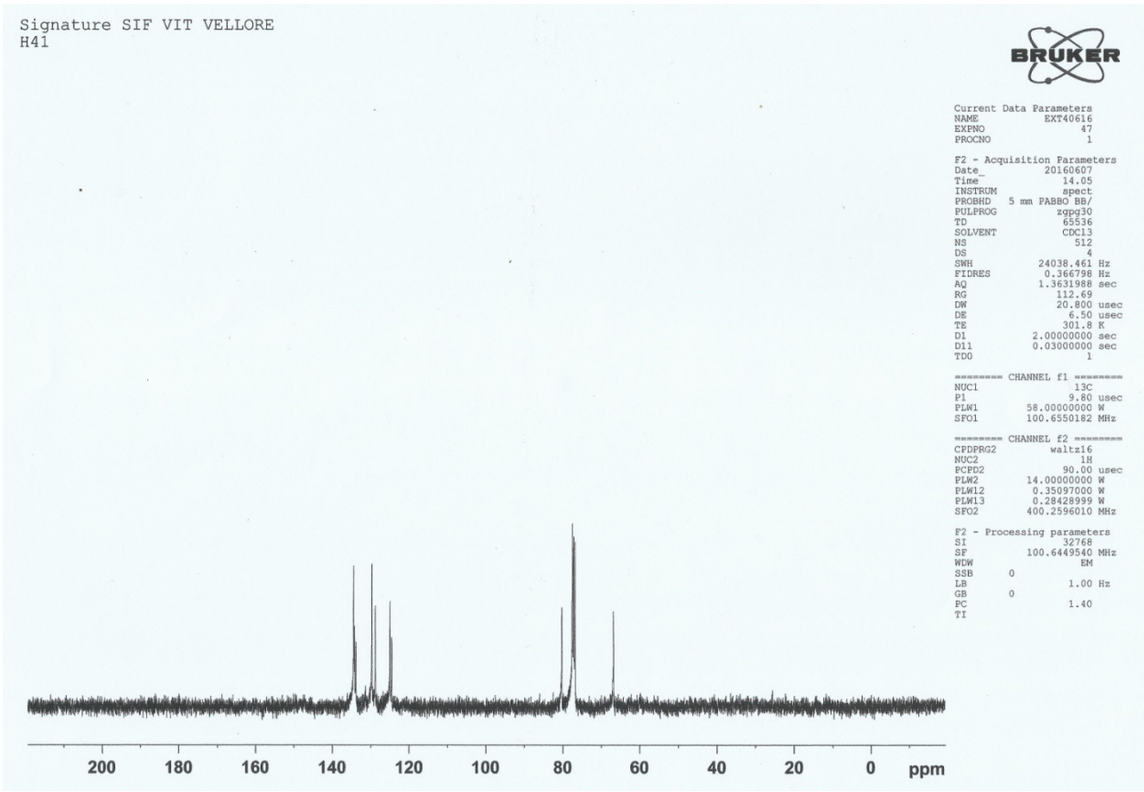
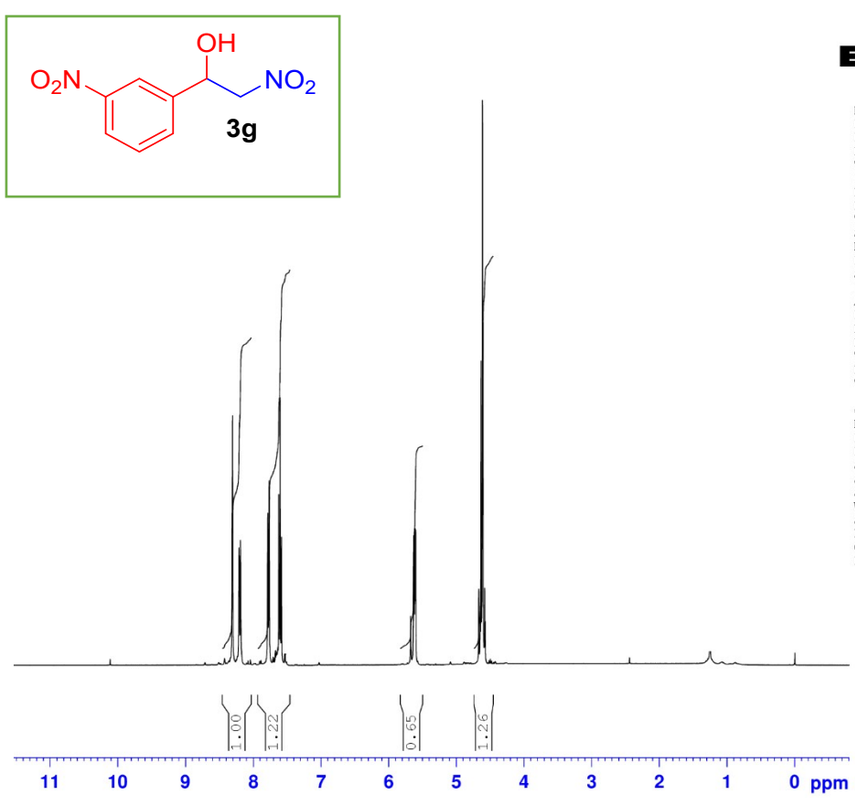
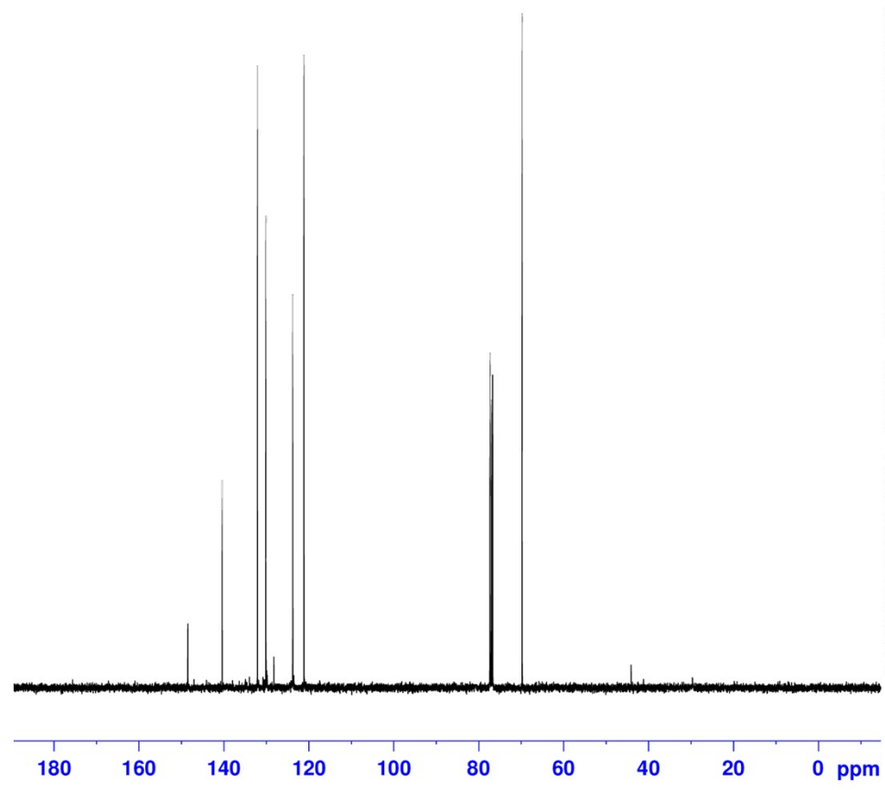


Fig S9: ^{1}H and ^{13}C-NMR spectra of 2-Nitro-1-(2-nitrophenyl)ethan-1-ol (**3f**)




```
NAME                  1H K13
EXPNO                    1
PROCNO                   1
Date_             20180614
Time                 14.29
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG                 zg
TD                  131072
SOLVENT              CDCl3
NS                       8
DS                       0
SWH           20000.000 Hz
FIDRES            0.152588 Hz
AQ                3.2768500 sec
RG                    80.6
DW                  25.000 usec
DE                   6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.50 usec
PL1                  -1.00 dB
SFO1          400.1312578 MHz
SI                    65536
SF            400.1299979 MHz
WDW                     EM
SSB                      0
LB                    0.50 Hz
GB                       0
PC                    1.00
```

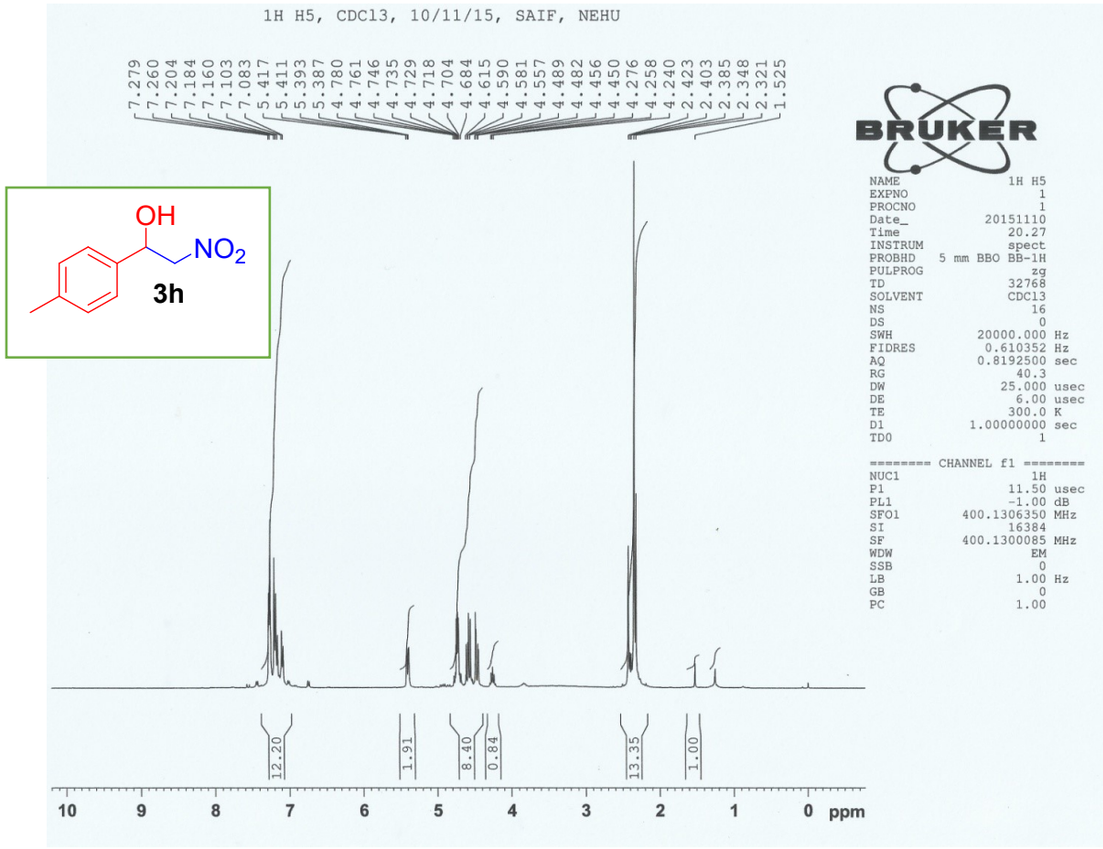



```
NAME                 13C K13
EXPNO                    1
PROCNO                   1
Date_             20180614
Time                 15.01
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg
TD                   66560
SOLVENT              CDCl3
NS                     312
DS                       0
SWH           40760.871 Hz
FIDRES            0.612393 Hz
AQ                0.8165193 sec
RG                     362
DW                  12.267 usec
DE                   6.00 usec
TE                  300.0 K
D1              5.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.00 usec
PL1                   0.00 dB
SFO1          100.6208180 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 16.00 dB
PL13                 20.00 dB
SFO2          400.1320007 MHz
SI                    32768
SF            100.6127690 MHz
WDW                     EM
SSB                      0
LB                    0.50 Hz
GB                       0
PC                    1.40
```

Fig S10: ^{1}H and ^{13}C-NMR spectra of 2-nitro-1-(3-nitrophenyl)ethan-1-ol (**3g**)



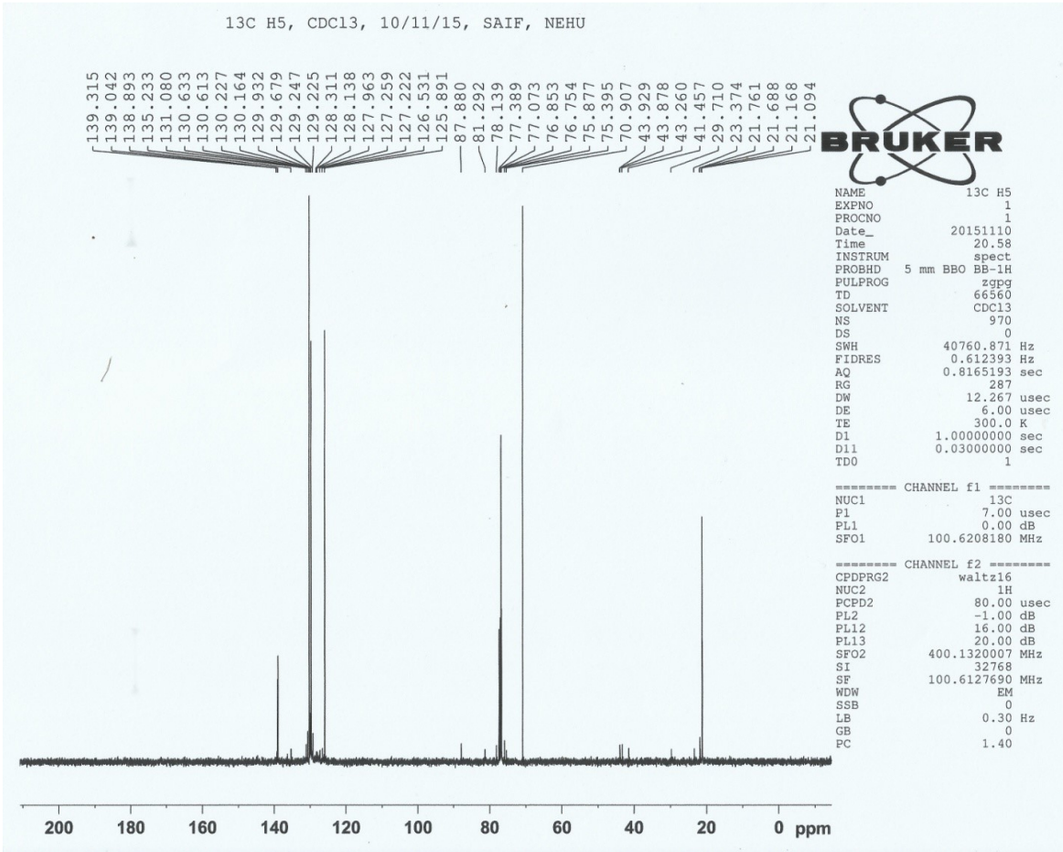


Fig S11: ^{1}H and ^{13}C-NMR spectra of 2-Nitro-1-(p-tolyl) ethan-1-ol (**3h**)

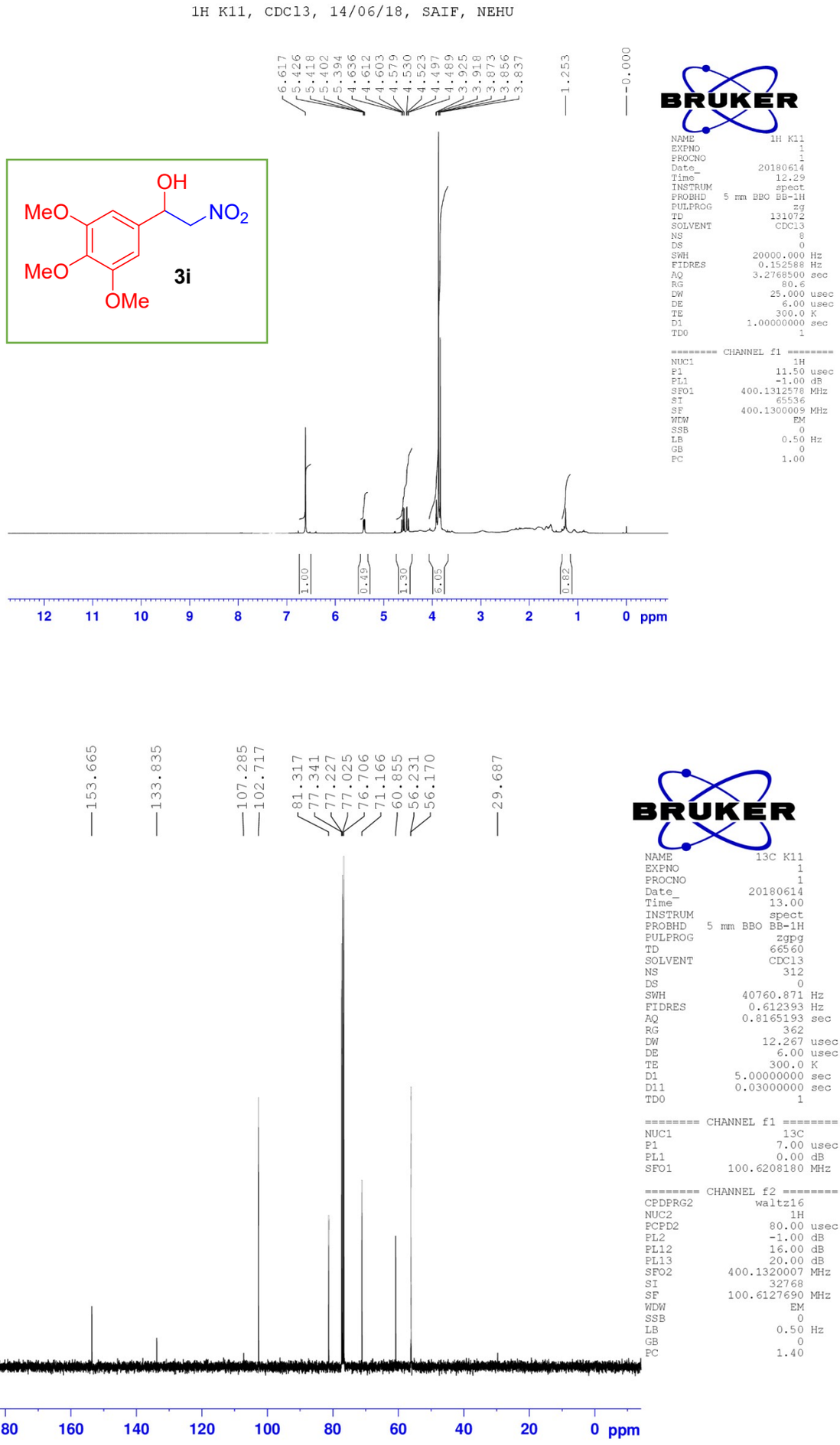
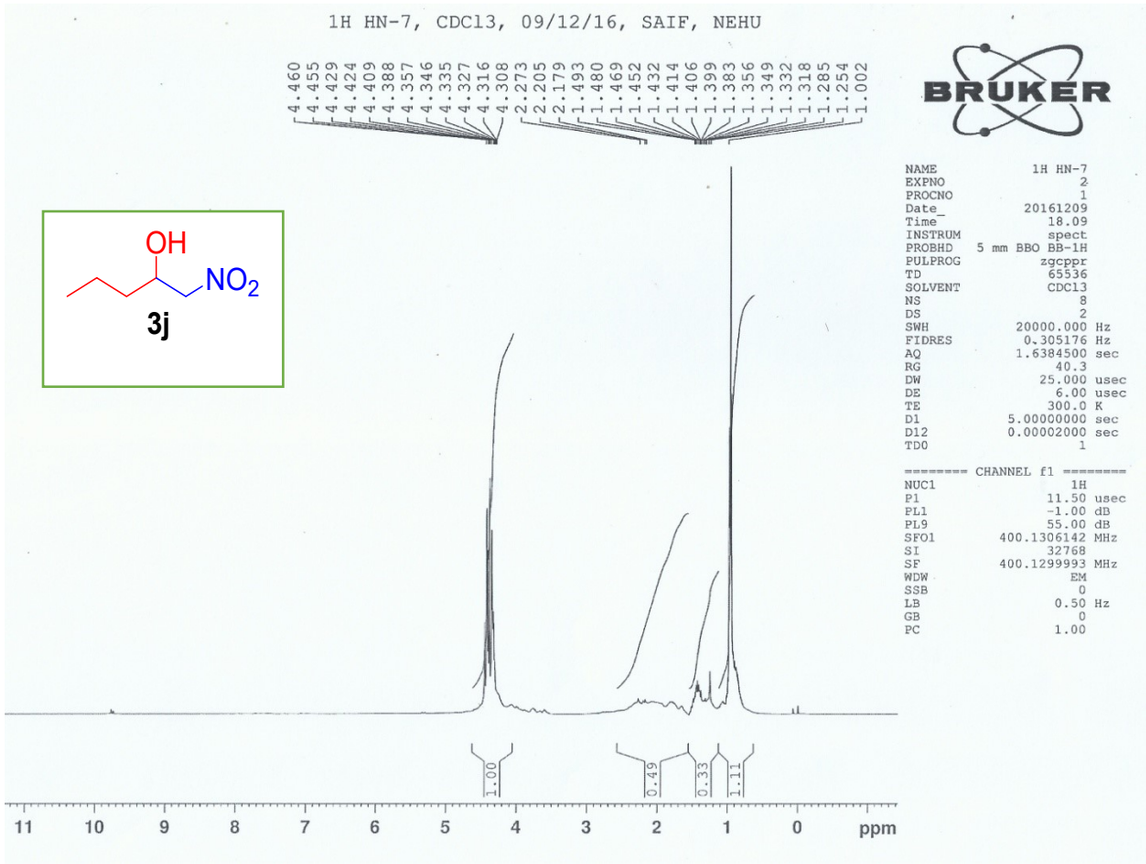


Fig S12: ^{1}H and ^{13}C-NMR spectra of 2-nitro-1-(3,4,5-trimethoxyphenyl)ethan-1-ol (**3i**)



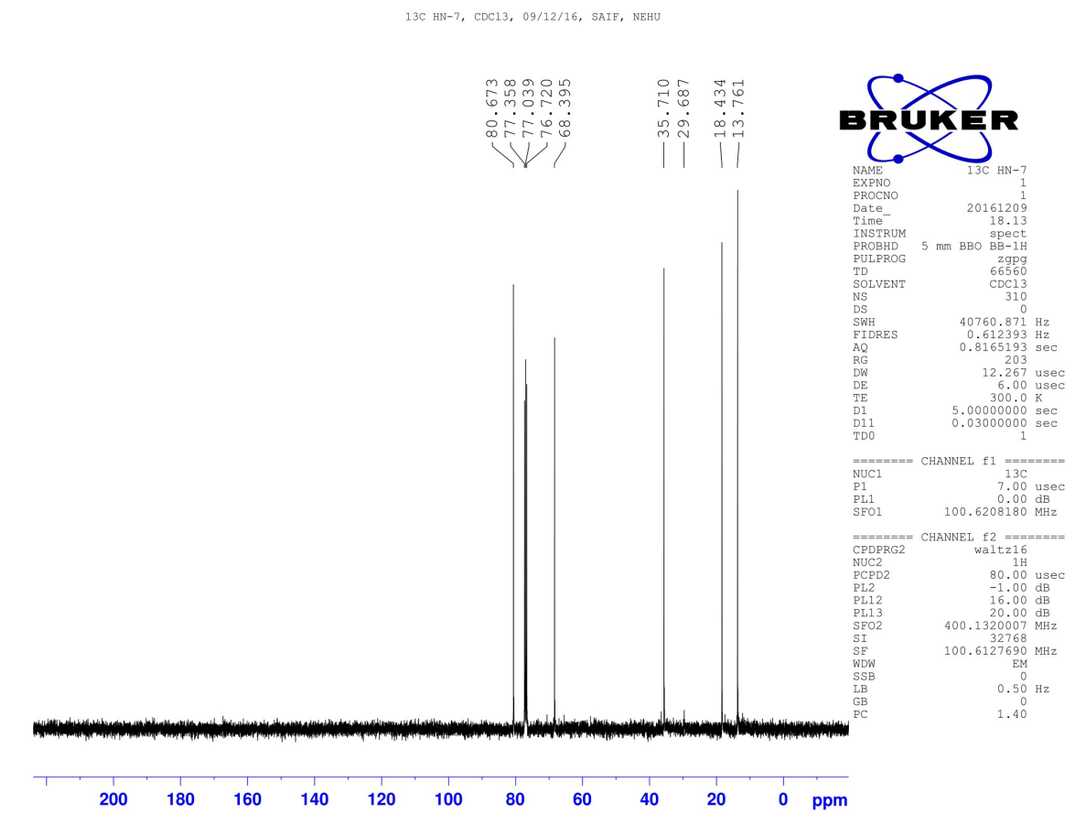
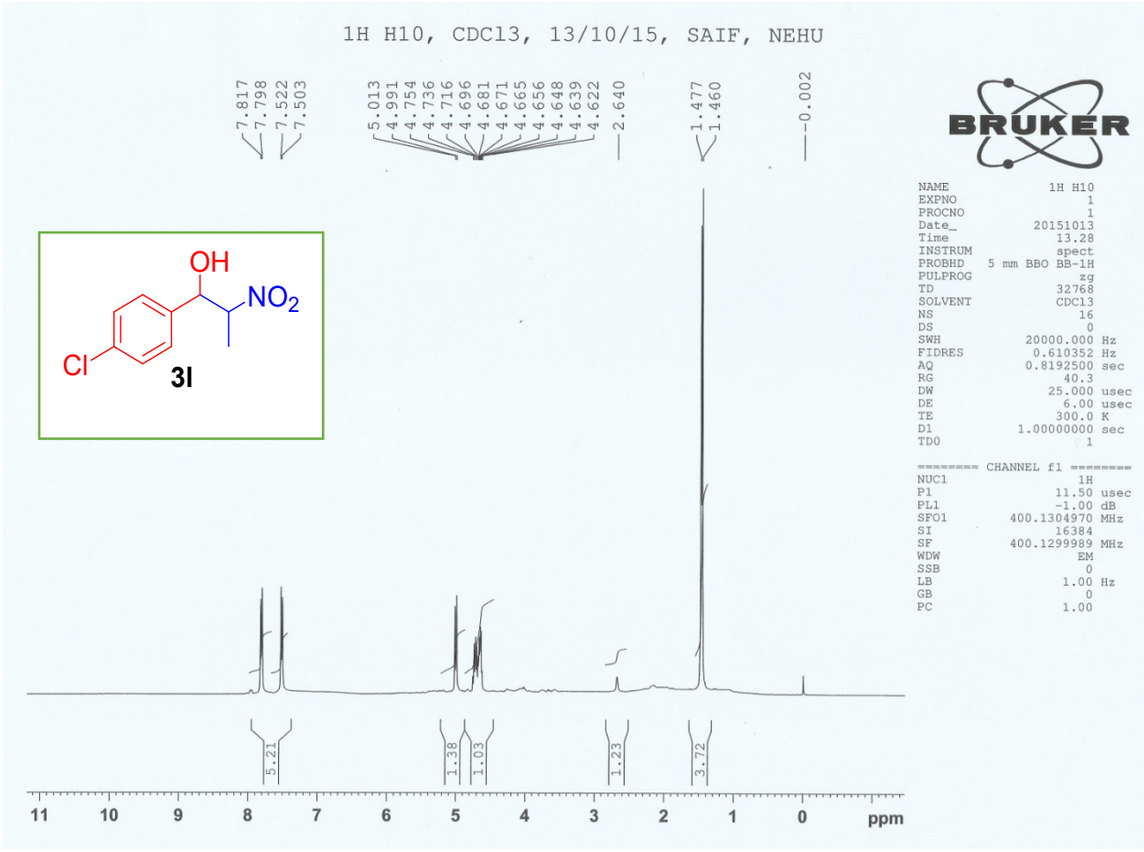


Fig S13: ^{1}H and ^{13}C-NMR spectra of 1-Nitropentan-2-ol (**3j**)



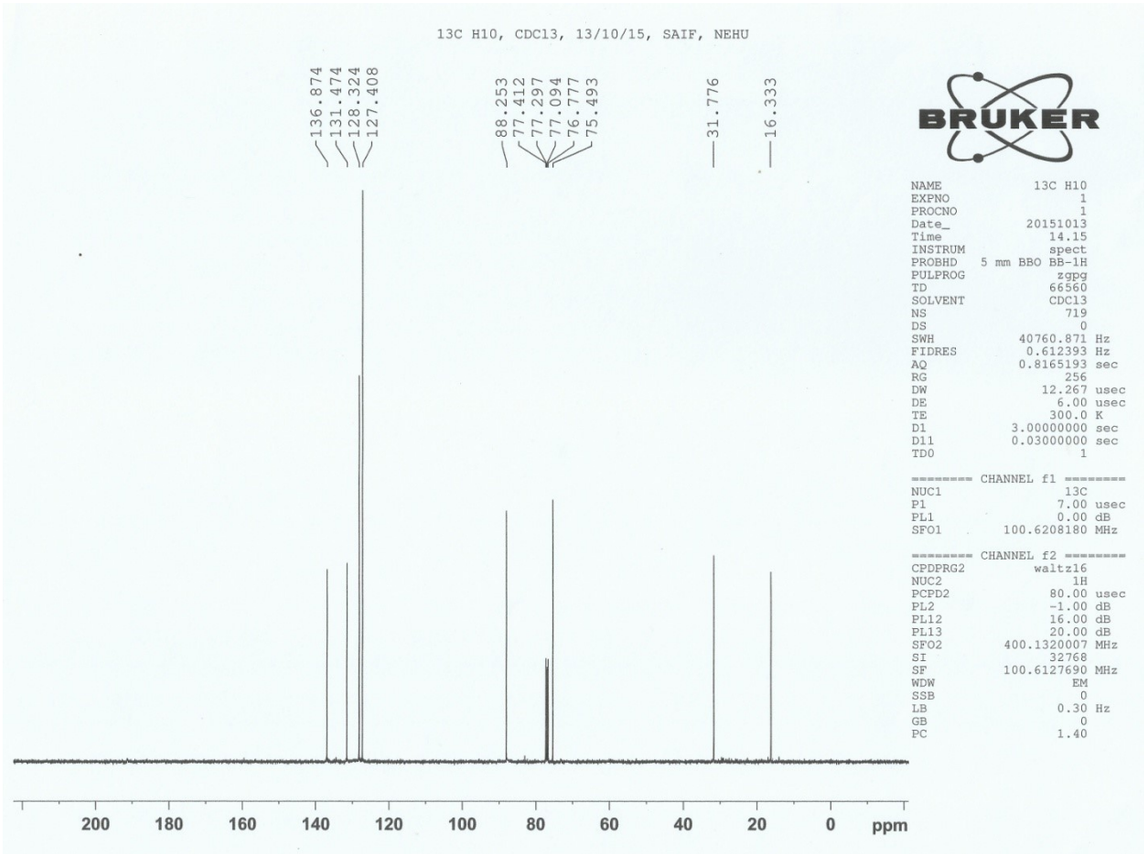
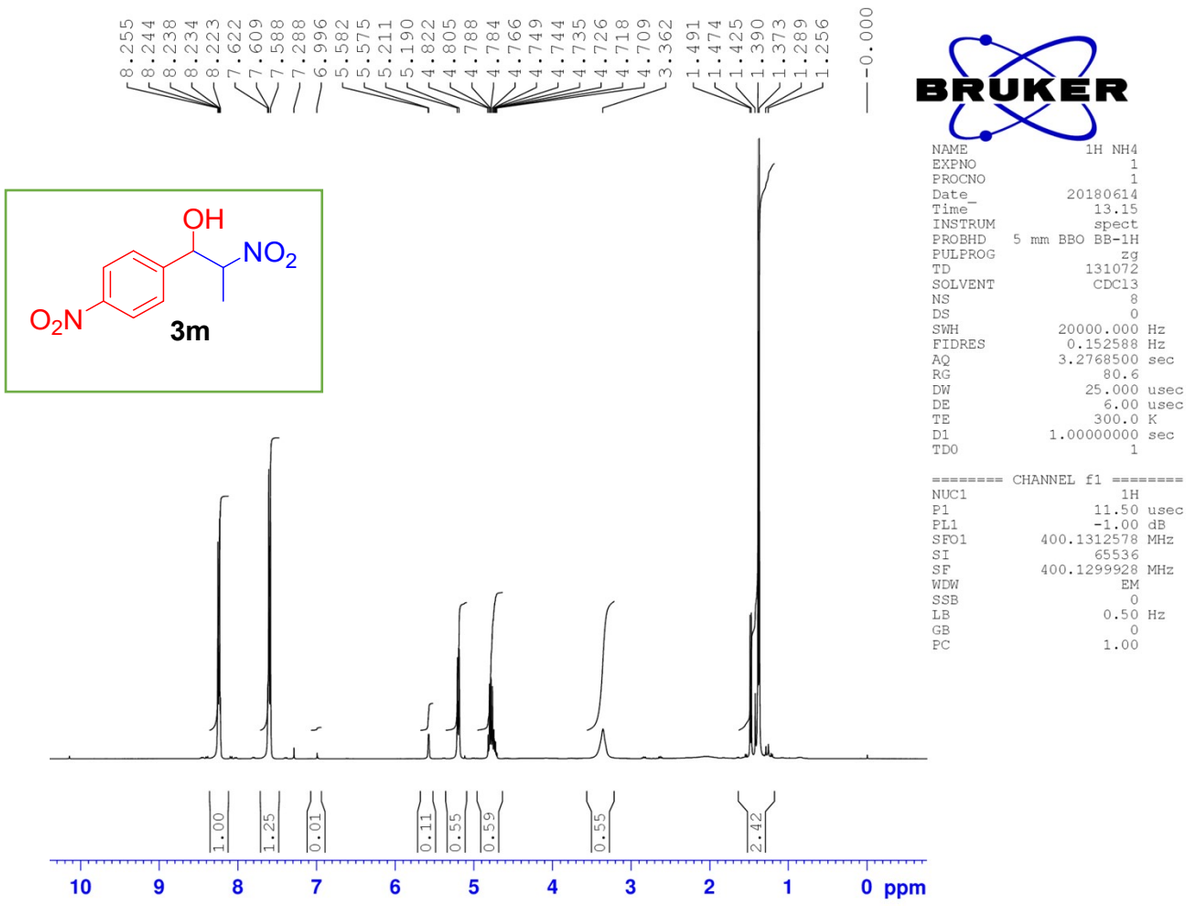


Fig S14: ^{1}H and ^{13}C-NMR spectra of 1-(4-Chlorophenyl)-2-nitropropan-1-ol (**3l**)



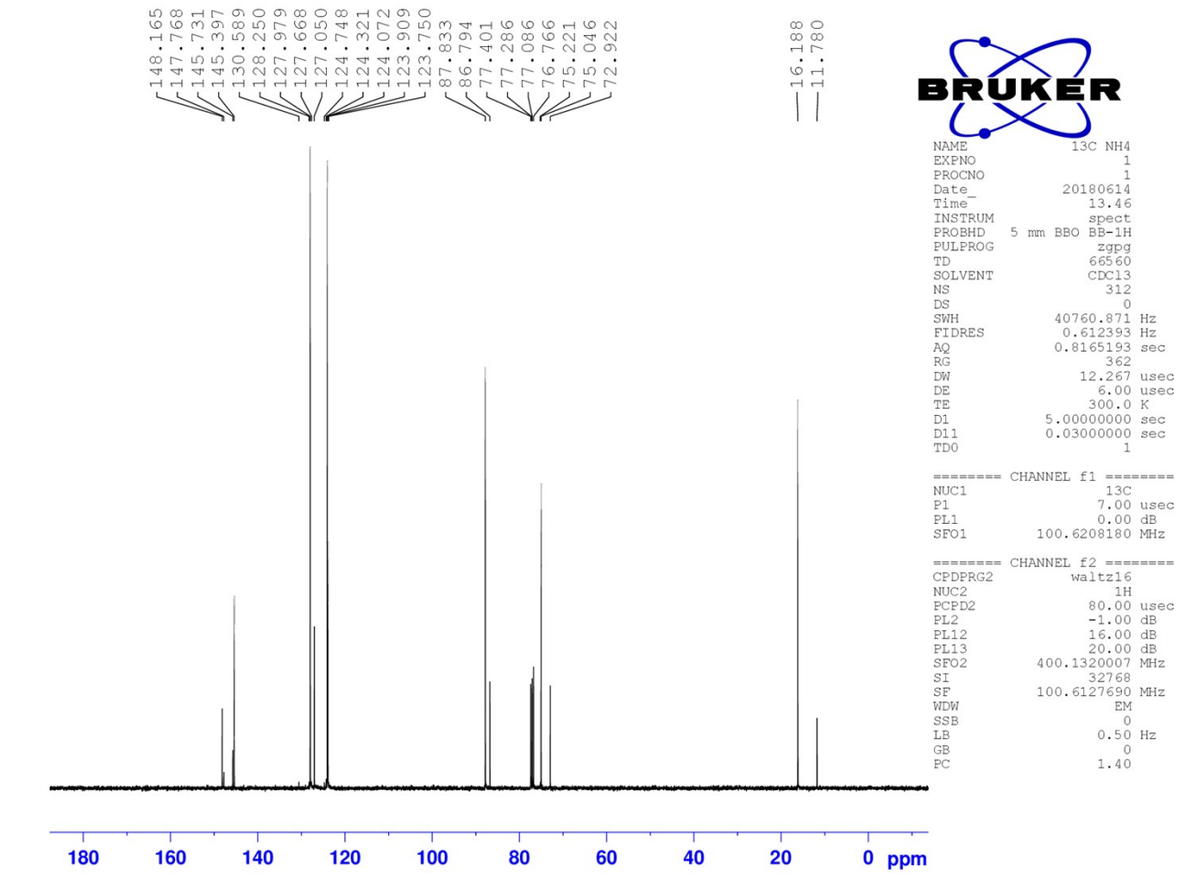


Fig S15: ^{1}H and ^{13}C-NMR spectra of 2-Nitro-1-(4-nitrophenyl) propan-1-ol (**3m**)

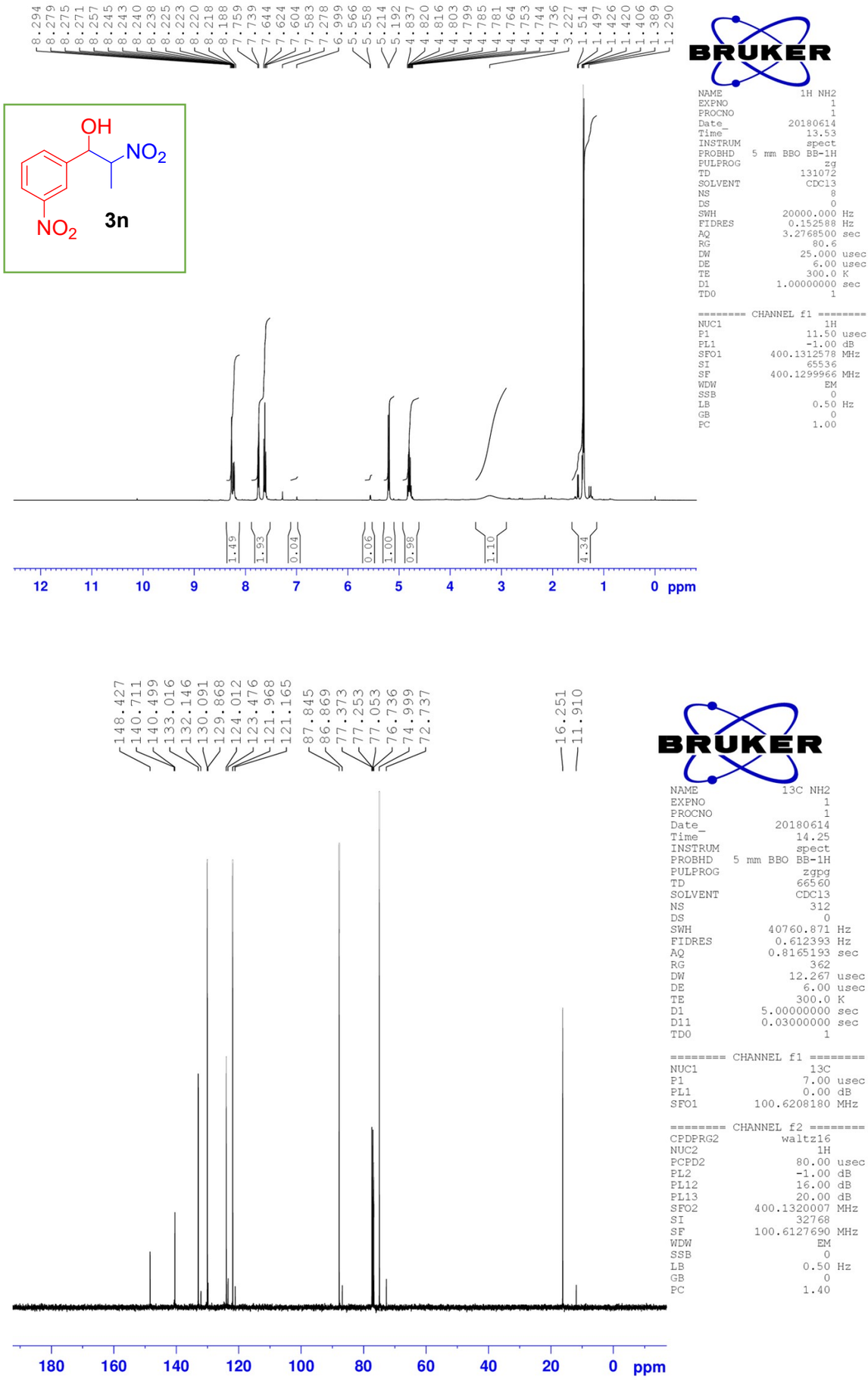
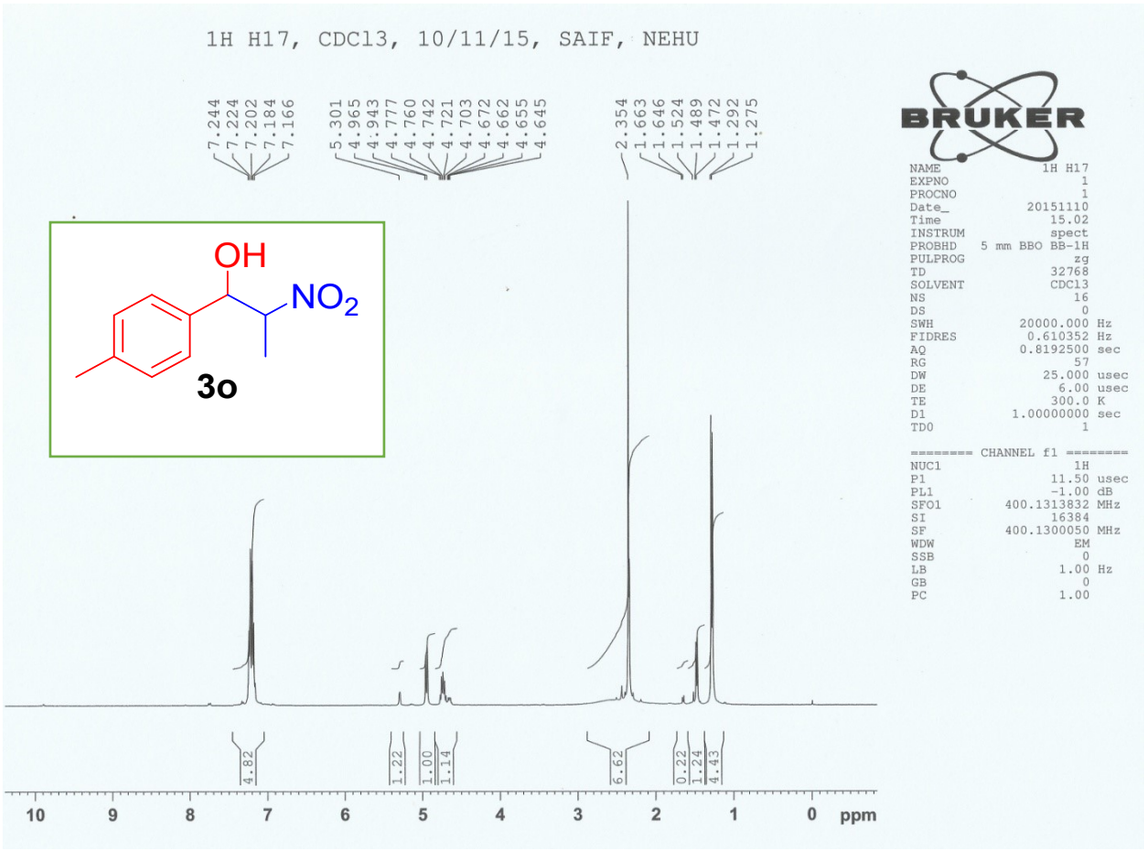


Fig S16: ^{1}H and ^{13}C-NMR spectra of 2-nitro-1-(3-nitrophenyl)propan-1-ol (**3n**)



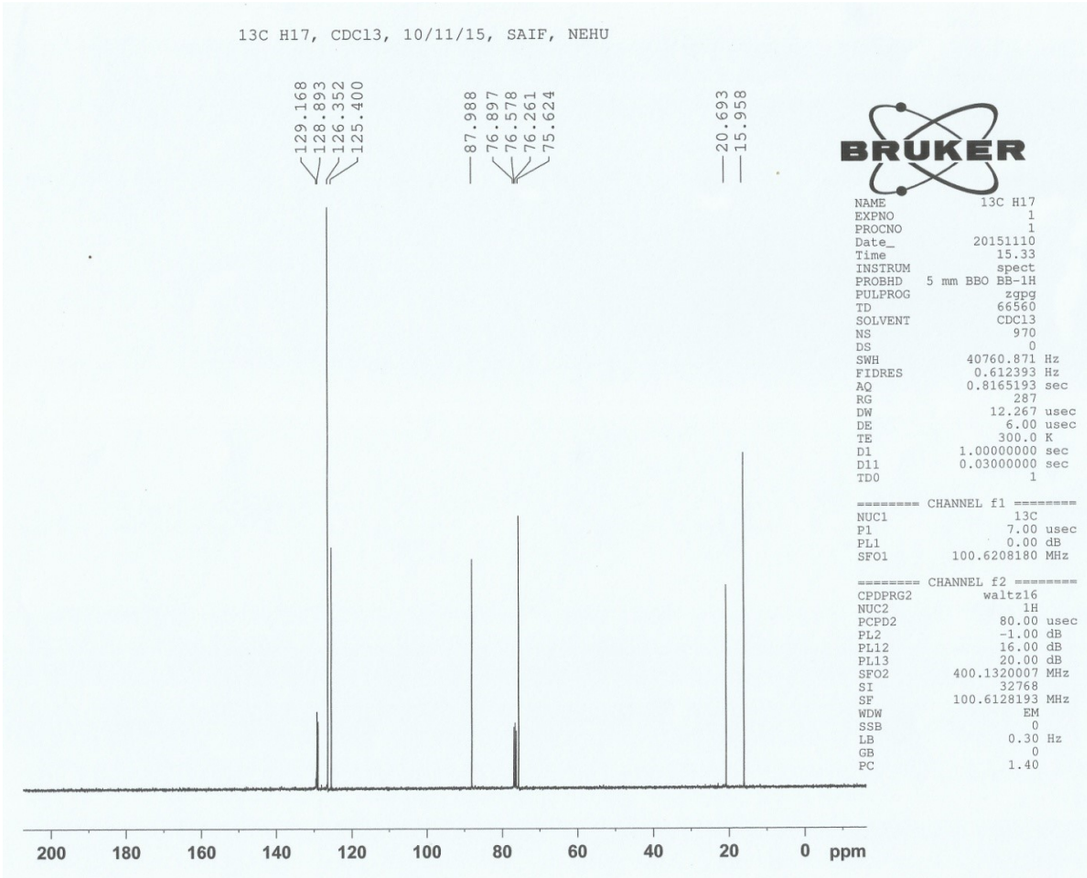
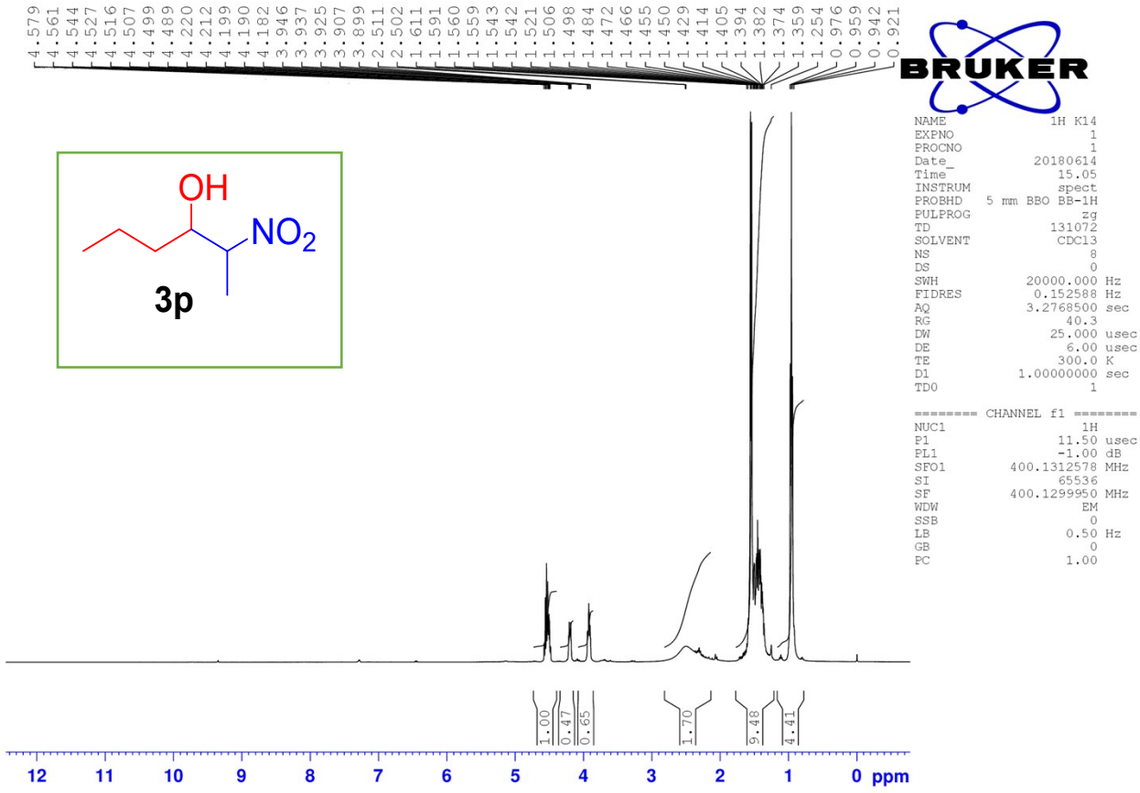


Fig S17: ^{1}H and ^{13}C-NMR spectra of 2-Nitro-1-(p-tolyl) propan-1-ol (**3o**)



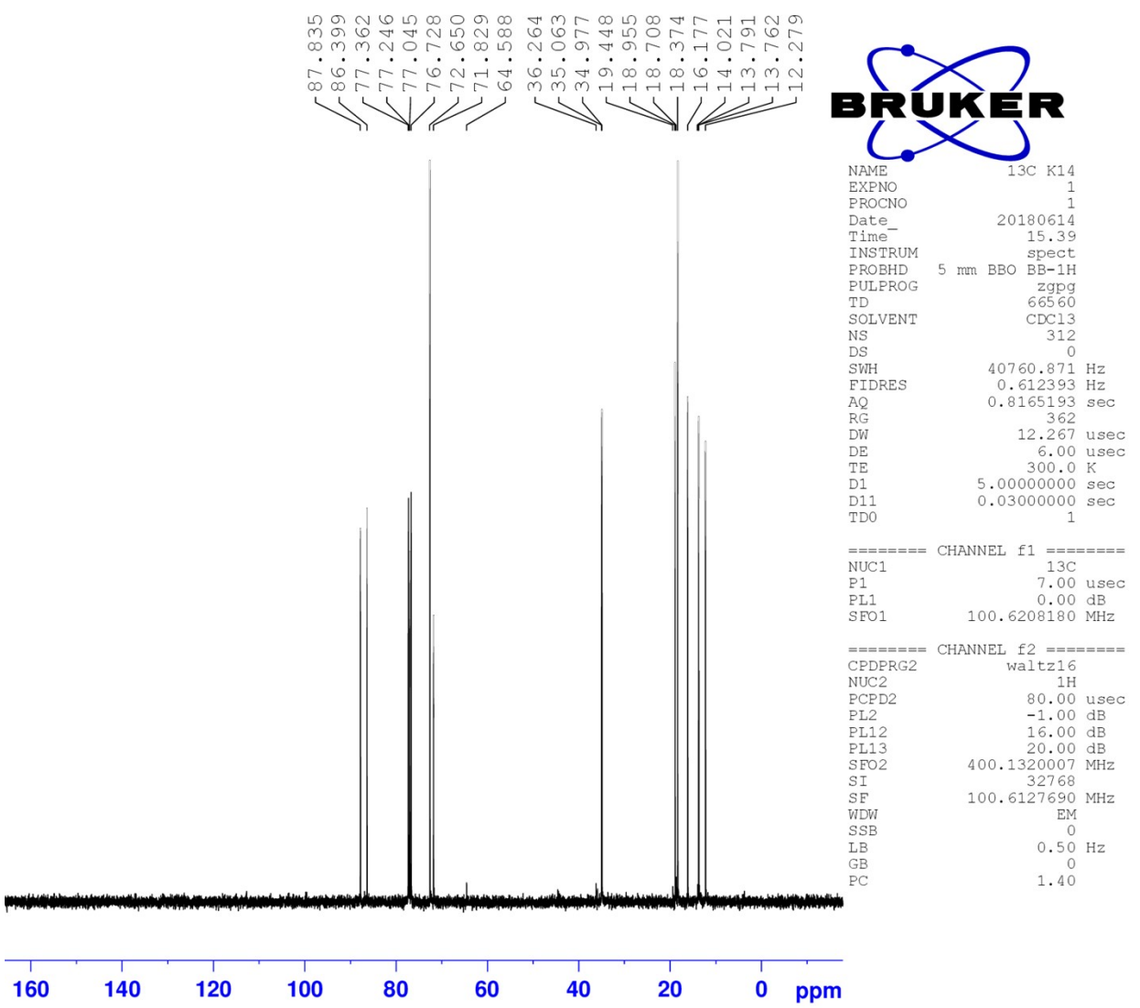
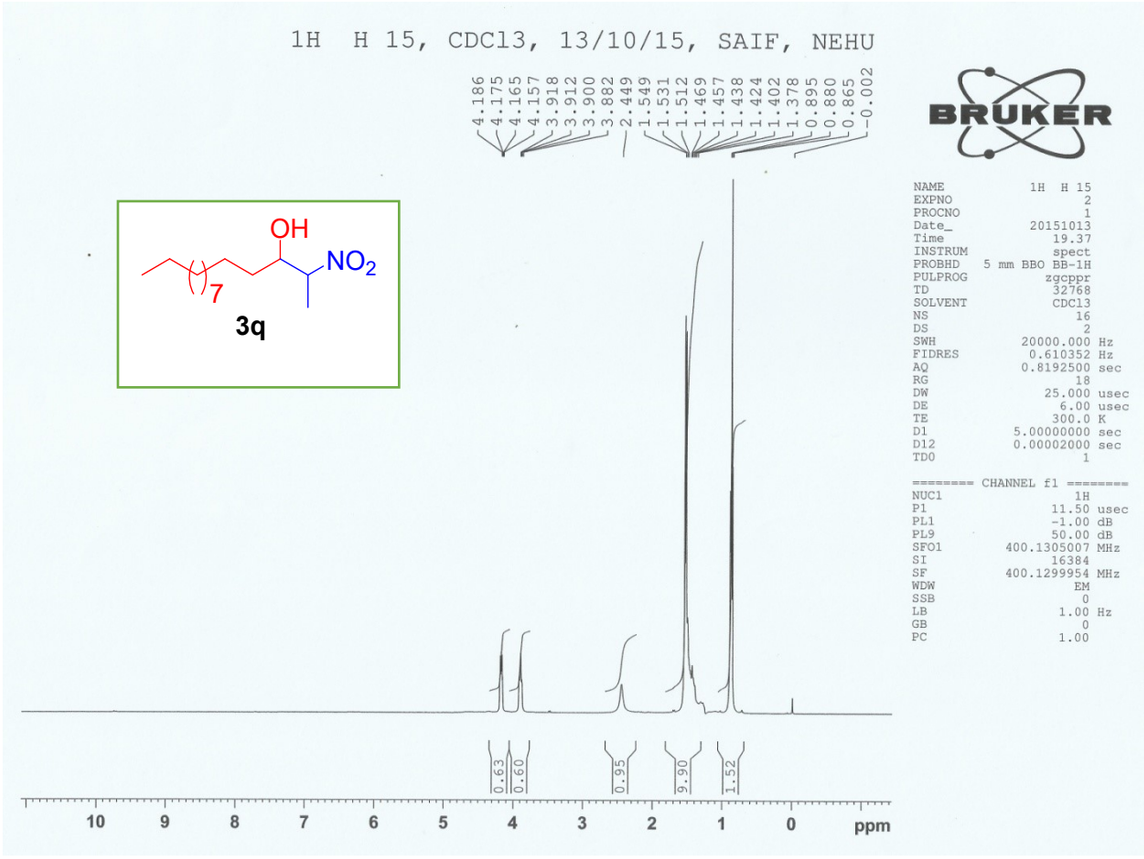


Fig S18: ^{1}H and ^{13}C-NMR spectra of 2-Nitrohexan-3-ol (**3p**)



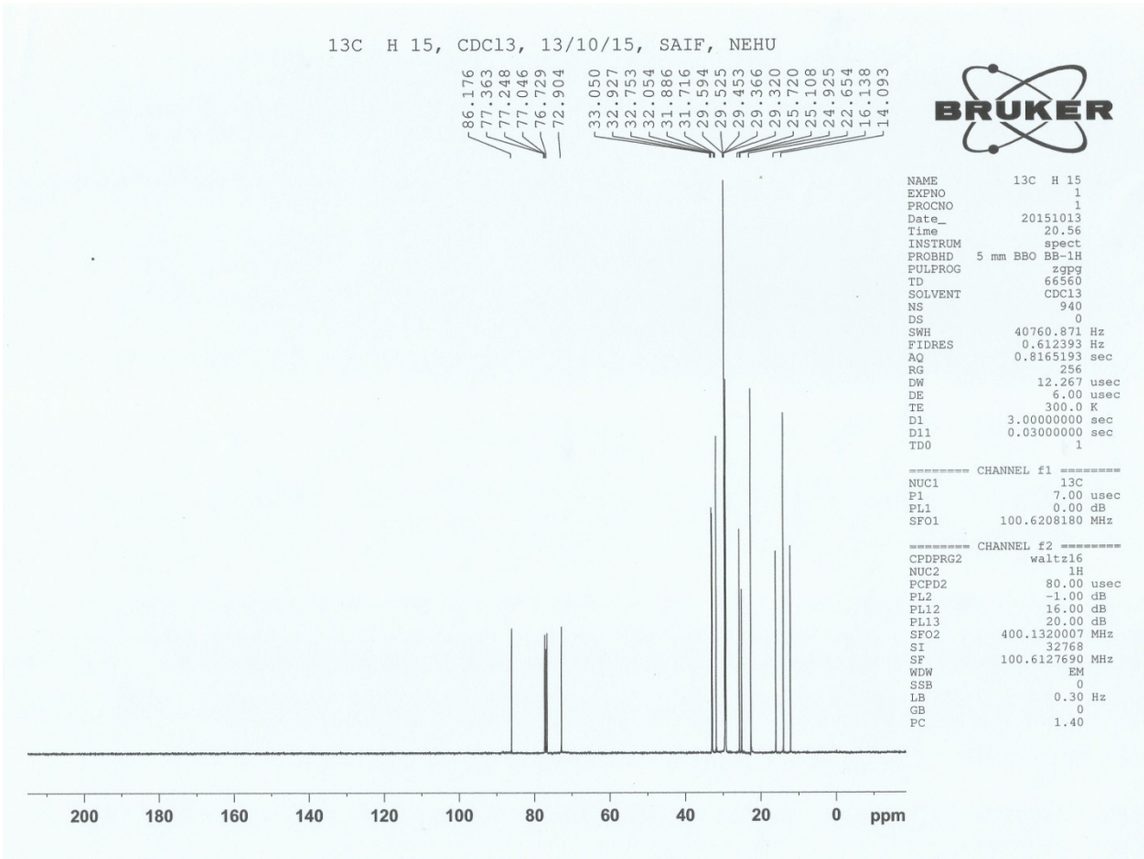


Fig S19: ^{1}H and ^{13}C-NMR spectra of 2-Nitrotetradecan-3-ol (**3q**)

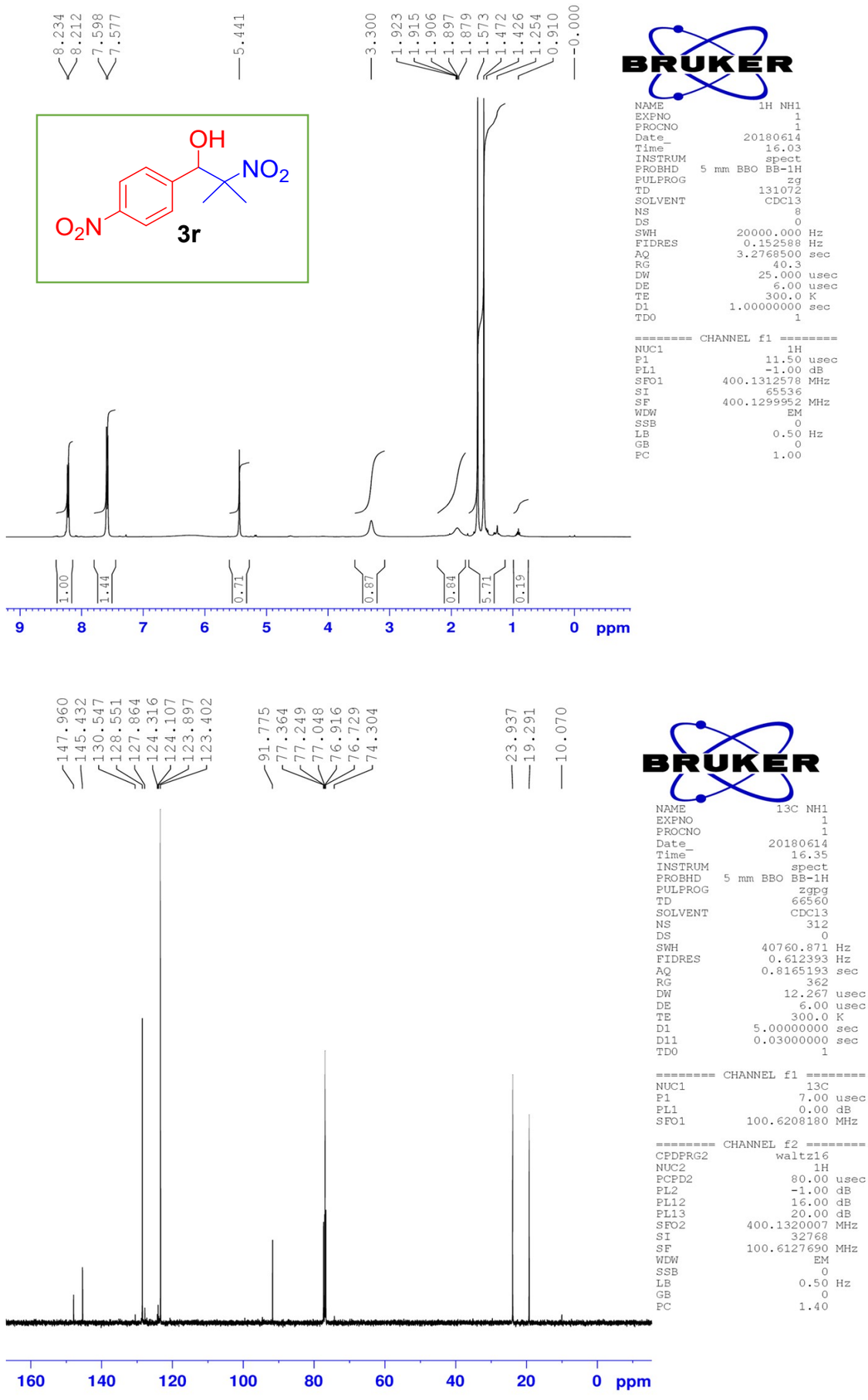


Fig S20: ^{1}H and ^{13}C-NMR spectra of 2-methyl-2-nitro-1-(4-nitrophenyl)propan-1-ol (**3r**)