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Supporting Information

The First Report on Chemoselective Biguanide-Catalyzed Henry Reaction under Neat Conditions

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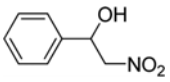
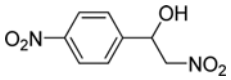
Characterization data for the synthesized β-nitroalcohols:

2-Nitro-1-phenylethanol [Ref. [1a-f]]



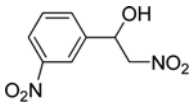
This is a known compound. Llight yellow oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.48 (1H, br s, OH), 4.36-4.7 (2H, m, CH_2), 5.31-5.38 (1H, m, CH), 7.23-7.59 (5H, m). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 70.6, 80.8, 125.7, 128.5, 128.6, 138.1. HRMS (EI): *m/z* Calcd. For $C_8H_9NO_3$: 167.0582, Found: 167.0546.

2-Nitro-1-(4-nitrophenyl)ethanol [Ref. [1a-e, 2]]



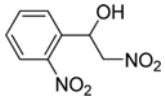
This is a known compound. Light yellow solid; mp 81 °C [lit.[1e] mp 82-83 °C]; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.12 (1H, br s, OH), 4.55-4.59 (2H, m, CH2), 5.50-5.65 (1H, m, CH), 7.61 (2H, d), 8.28 (2H, d). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 69.6, 80.1, 123.8, 126.7, 145.1, 148.0. HRMS (EI): *m/z* Calcd. For $C_8H_8N_2O_5$: 212.0433, Found: 212.0412.

2-Nitro-1-(3-nitrophenyl)ethanol [Ref. [1a, d, e,2]]



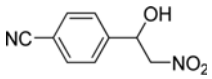
This is a known compound. Light yellow solid; mp 72 °C [lit.[1e] mp 70-71 °C]; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.10 (1H, br s, OH), 4.52-4.62 (2H, m, CH2), 5.51-5.65 (1H, m, CH), 7.58 (1H, t), 7.75 (1H, d), 8.17 (1H, d), 8.28 (1H, s). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 69.9, 80.6, 124.0, 126.9, 145.3, 147.9. HRMS (EI): *m/z* Calcd. For $C_8H_8N_2O_5$: 212.0433, Found: 212.0451.

2-Nitro-1-(2-nitrophenyl)ethanol [Ref. [1c-d, 2]]



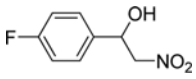
This is a known compound. Dark yellow oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.28 (1H, br s, OH), 4.52-4.87 (2H, m, CH2), 6.02-6.05 (1H, m, CH), 7.52-7.56 (1H, t), 7.72-7.76 (1H, t), 7.93-7.95 (1H, d), 8.05-8.07 (1H, d); ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 70.6, 80.8, 125.7, 128.5, 128.6, 138.1. HRMS (EI): *m/z* Calcd. For $C_8H_8N_2O_5$: 212.0433, Found: 212.0411.

2-Nitro-1-(4-cyanophenyl)ethanol [Ref. [1a]]



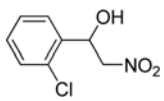
This is a known compound. Colorless oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.20 (1H, br s, OH), 4.51-4.61 (2H, m, CH2), 5.58 (1H, m, CH), 7.50 (2H, d), 7.70 (2H, d). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 70.3, 80.9, 112.2, 118.0, 126.3, 131.8, 144.0. HRMS (EI): *m/z* Calcd. For $C_9H_8N_2O_3$: 192.0535, Found: 192.0511.

1-(4-fluorophenyl)-2-nitroethanol [Ref. [1a-d,f]]



This is a known compound. Colorless oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.57 (1H, br s, OH), 4.41-4.59 (2H, m, CH2), 5.34-5.40 (1H, m, CH), 6.97-7.07 (m, 2H), 7.28-7.35 (m, 2H); ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 70.3, 81.1, 116.1, 127.8, 161.6, 164.1. HRMS (EI): *m/z* Calcd. For $C_8H_8FNO_3$: 185.0488, Found: 185.0412.

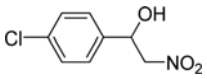
1-(2-Chlorophenyl)-2-nitroethanol [Ref. [1b, d, f, 2]]



This is a known compound. Light yellow oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.55 (1H, br s, OH), 4.42-4.74 (2H, m, CH_2), 5.84-5.90 (1H, m, CH), 7.29- 7.99 (4H, m). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 71.2, 86.3, 127.9, 128.5, 130.7, 131.1, 132.7, 136.5. HRMS (EI): *m/z* Calcd. For

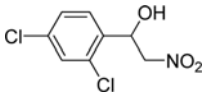
$C_8H_8ClNO_3$: 201.0193, Found: 201.0187.

1-(4-Chlorophenyl)-2-nitroethanol [Ref. [1a-f, 2]]



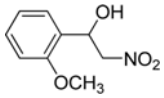
This is a known compound. Light yellow oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.44 (1H, br s, OH), 4.39- 4.59 (2H, m, CH_2), 5.32-5.39 (1H, m, CH), 7.20-766 (4H, m). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 70.1, 80.9, 127.2, 128.983, 134.5, 136.6. HRMS (EI): *m/z* Calcd. For $C_8H_8ClNO_3$: 201.0193, Found: 201.0129.

1-(2,4-Dichlorophenyl)-2-nitroethanol [Ref. [1c]]



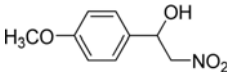
This is a known compound. Colorless oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.55 (1H, br s, OH), 4.42-4.74 (2H, m, CH_2), 5.84-5.90 (1H, m, CH), 7.29- 7.99 (4H, m, Ar). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 67.4, 79.1, 127.9, 128.5, 129.5, 132.0, 134.2, 135.2. HRMS (EI): *m/z* Calcd. For $C_8H_7Cl_2NO_3$: 234.9804, Found: 234.9826.

1-(2-Methoxyphenyl)-2-nitroethanol [Ref. [1c, d, f]]



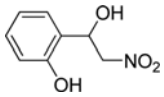
This is a known compound. Light yellow oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.63 (1H, br s, OH), 3.77- 3.88 (3H, m, OCH_3), 4.43- 4.61 (2H, m, CH_2), 5.55-5.61 (1H, m, CH), 6.86-7.40 (4H, m, Ar). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 67.6, 79.8, 110.4, 121.0, 125.9, 127.1, 129.7, 155.9. HRMS (EI): *m/z* Calcd. For $C_9H_{11}NO_4$: 197.0688, Found: 197.0617.

1-(4-Methoxyphenyl)-2-nitroethanol [Ref. [1a-c, f]]



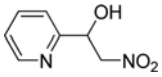
This is a known compound. Light yellow oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 3.10 (1H, br s, OH), 3.80 (3H, m, OCH_3), 4.42-4.62 (2H, m, CH_2), 5.36 (1H, m, CH), 6.92 (4H, d), 7.35 (4H, d). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 55.3, 70.6, 114.3, 127.2, 130.2, 159.9. HRMS (EI): *m/z* Calcd. For $C_9H_{11}NO_4$: 197.0688, Found: 197.0678.

1-(2-Hydroxyphenyl)-2-nitroethanol [Ref. [3]]



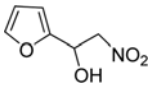
This is a known compound. Yellow oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 4.01 (1H, br s, OH), 4.59-4.91 (2H, m, CH_2), 5.57-5.62 (1H, m, CH), 6.83-7.58 (4H, m, Ar), 11.02 (1H, s, OH). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 70.9, 84.5, 127.4, 128.4, 128.9, 130.6, 131.1, 135.4. HRMS (EI): *m/z* Calcd. For $C_8H_9NO_4$: 183.0531, Found: 183.0522.

1-(2-Pyridyl)-2-nitroethanol [Ref. [4]]



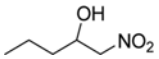
This is a known compound. Light yellow oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 4.40 (1H, br s, OH), 4.64-4.78 (2H, m, CH_2), 5.47 (1H, m, CH), 7.29 (1H, m), 7.44 (1H, m), 7.76 (1H, m), 8.57 (1H, m). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 70.3, 80.7, 120.9, 123.6, 137.4, 148.9, 156.5. HRMS (EI): *m/z* Calcd. For $C_7H_8N_2O_3$: 168.0535, Found: 168.0555.

1-(Furan-2-yl)-2-nitroethanol [Ref. [1a, c-f]]



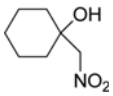
This is a known compound. Dark yellow oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 2.99 (1H, br s, OH), 4.61-4.81 (2H, m, CH_2), 5.47 (1H, m, CH), 6.86-7.40 (4H, m).^{13}C NMR (50.03 MHz; $CDCl_3$) δ 64.7, 78.3, 108.1, 110.6, 143.1, 150.7. HRMS (EI): *m/z* Calcd. For $C_6H_7NO_4$: 157.0375, Found: 157.0311.

1-Nitropentan-2-ol [Ref. [5, 6]]



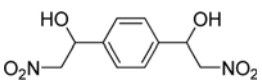
This is a known compound. Colorless oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 0.93-0.97 (m, 3H), 1.41-1.59 (m, 4H), 2.52 (brs, 1H), 4.00-4.47 (m, 3H). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 13.7, 18.4, 35.7, 68.4, 80.6. HRMS (EI): *m/z* Calcd. For $C_5H_{11}NO_3$: 133.0739, Found: 133.0777.

1-(Nitromethyl)cyclohexanol [Ref. [7]]



This is a known compound. Colorless oil; ^{1}H NMR (200 MHz; $CDCl_3$) δH 1.38-1.64 (10H, m, CH_2, 2.78 (1H, br s, OH), 4.37 (2H, s, CH_2). ^{13}C NMR (50.03 MHz; $CDCl_3$) δ 21.5, 27.1, 40.1, 64.3, 80.2. HRMS (EI): *m/z* Calcd. For $C_7H_{13}NO_3$: 159.0895, Found: 159.0874.

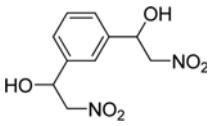
1,1'-(1,4-Phenylene)bis(2-nitroethanol)



This is an unknown compound. White-off solid; mp 165 C; ^{1}H NMR (200 MHz; DMSO) δH 4.38-4.57 (2H, m, CH_2), 4.77-4.84 (2H, m, CH_2), 5.20-5.25 (2H, m, CH), 6.04-6.07 (2H, OH), 7.39 (4H); ^{13}C NMR (50.03 MHz; DMSO) δ 69.7, 81.6, 126.3, 140.2; MS *m/z* (relative intensity %): 256 (M^+), 148 (100), 133 (40), 103 (30), 91 (25), 77 (35), 51 (10).

HRMS (EI): *m/z* Calcd. For $C_{10}H_{12}N_2O_6$: 256.0695, Found: 256.0672.

1,1'-(1,3-Phenylene)bis(2-nitroethanol)



This is an unknown compound. Yellow oil; ^{1}H NMR (200 MHz; DMSO) δH 4.53-4.66 (2H, m, CH_2), 4.81-4.91 (2H, m, CH_2), 5.29-5.36 (2H, m, CH), 6.21-6.23 (2H, OH), 7.32-7.67 (3H, m), 7.79 (1H, s); ^{13}C NMR (50.03 MHz; DMSO) δ 69.6, 81.4, 121.0,127.0, 129.6, 140.2; MS *m/z* (relative intensity %): 256 (M^+), 252 (75), 209 (45), 191 (30), 161 (45), 148 (60), 133 (98), 117 (100), 103 (55), 91(75), 77 (50), 51 (15). HRMS (EI): *m/z* Calcd. For $C_{10}H_{12}N_2O_6$: 256.0695, Found: 256.0618.

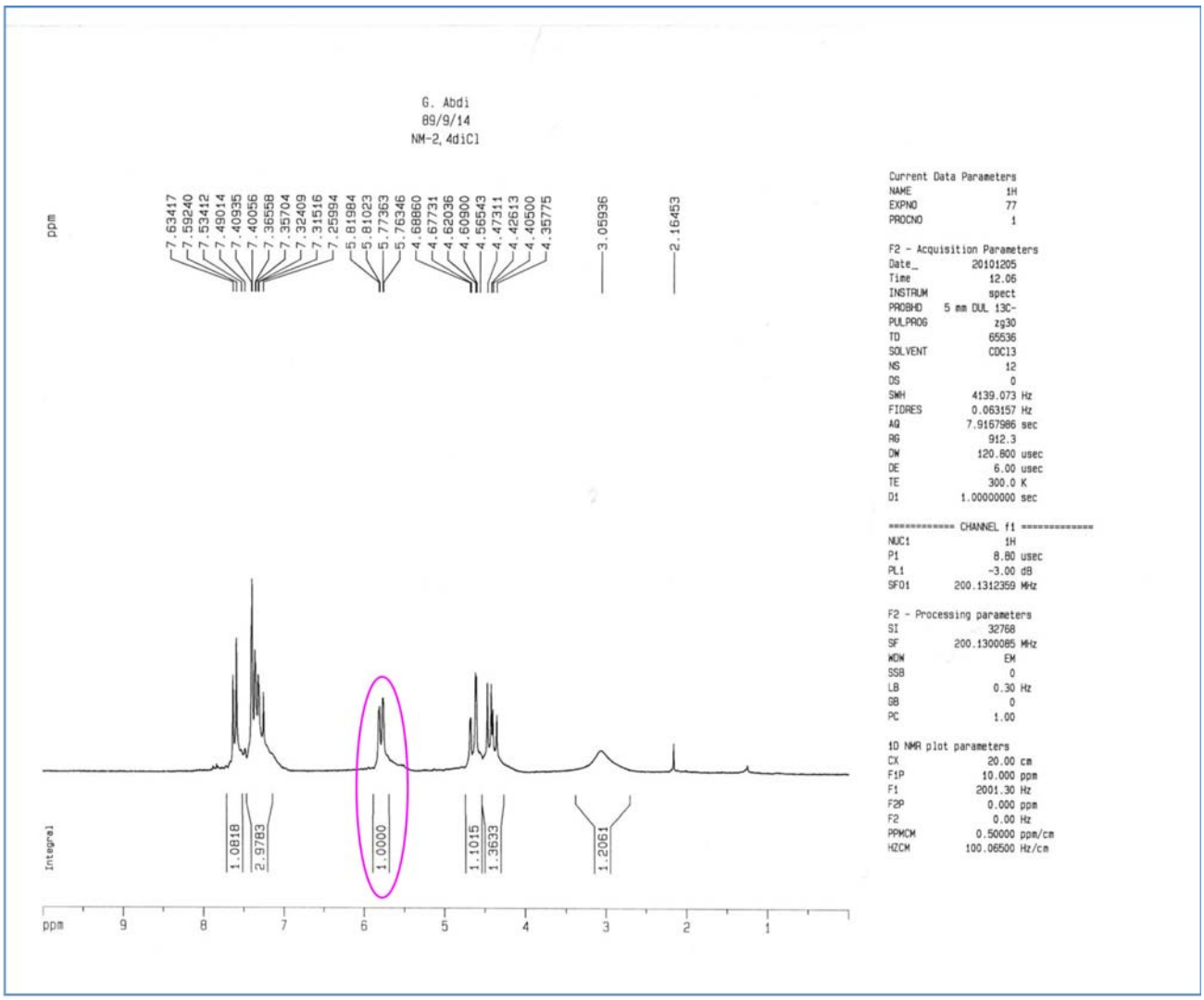


Figure S-1 ^{1}H NMR spectrum for compound 1-(2,4-Dichlorophenyl)-2-nitroethanol (Table 1 Entry 3 and Table 2 Entry 11)

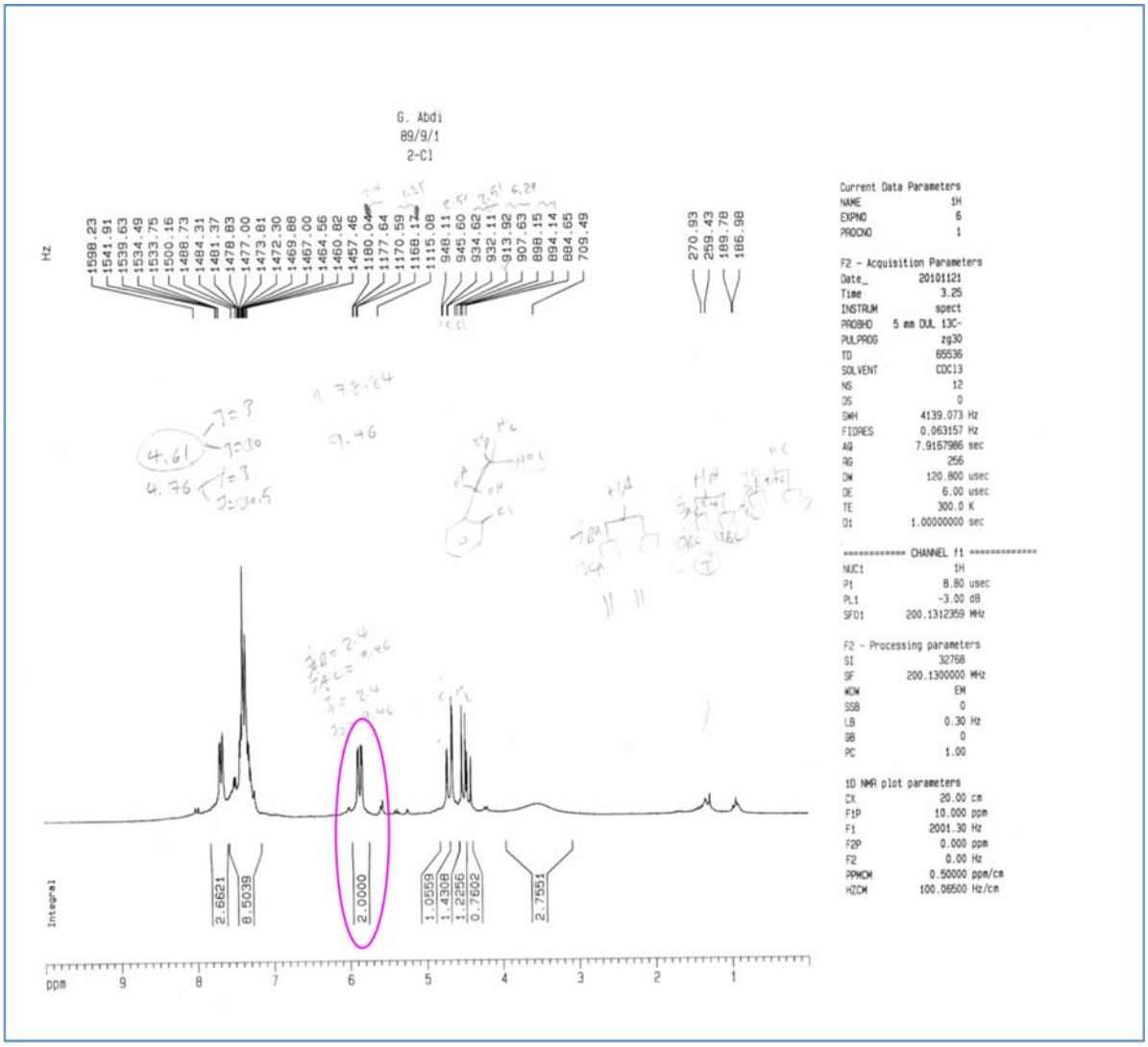


Figure S-2 ^{1}H NMR spectrum for compound 1-(2-Chlorophenyl)-2-nitroethanol (Table 2 Entry 7)

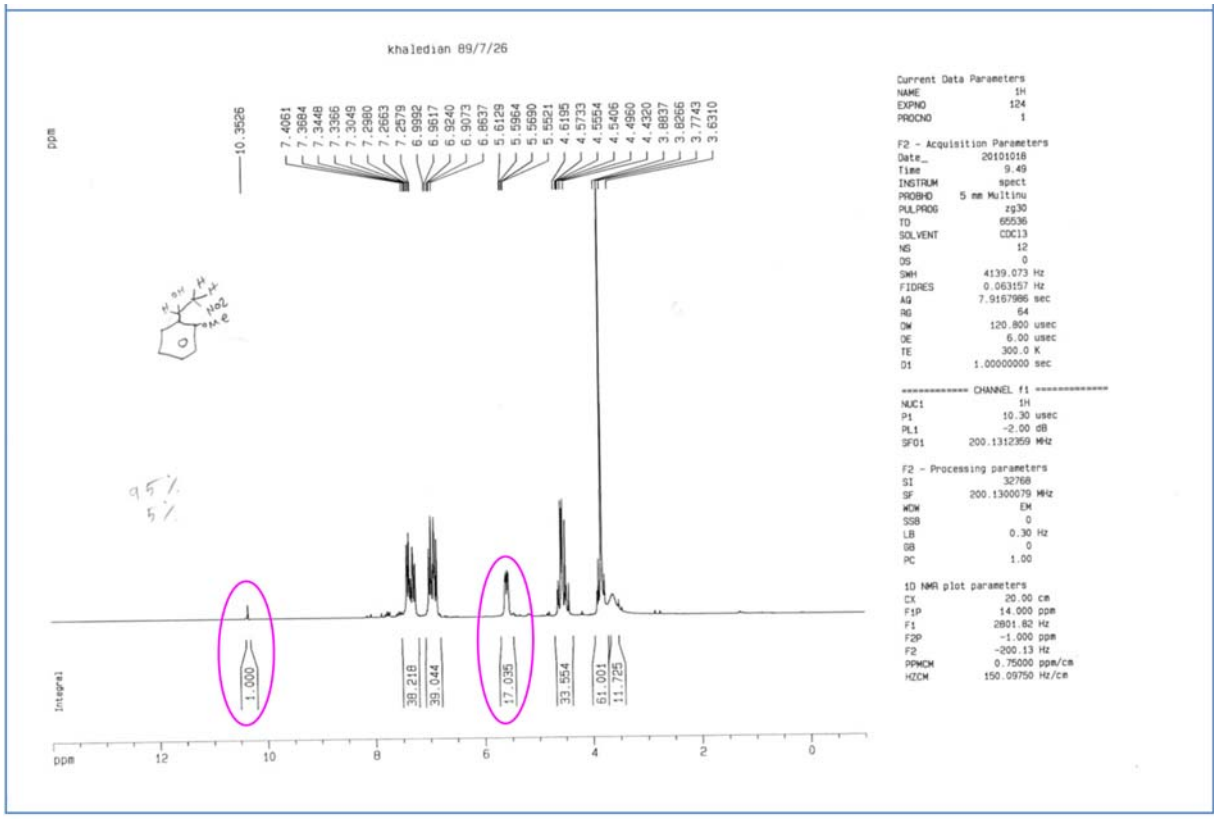


Figure S-3 ^{1}H NMR spectrum for compound 1-(2-Methoxyphenyl)-2-nitroethanol (Table 2 Entry 11)

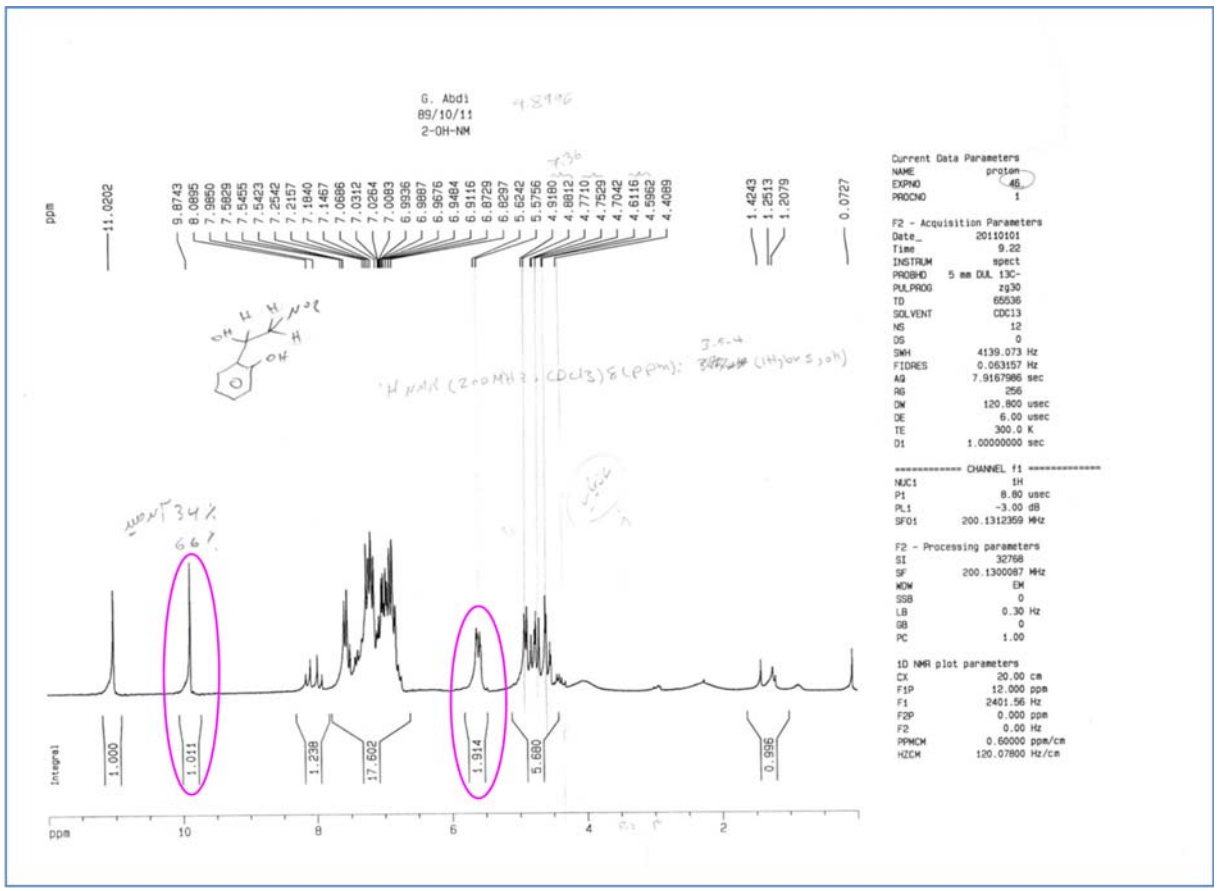


Figure S-4 ^{1}H NMR spectrum for compound 1-(2-Hydroxyphenyl)-2-nitroethanol (Table 2 Entry 13)

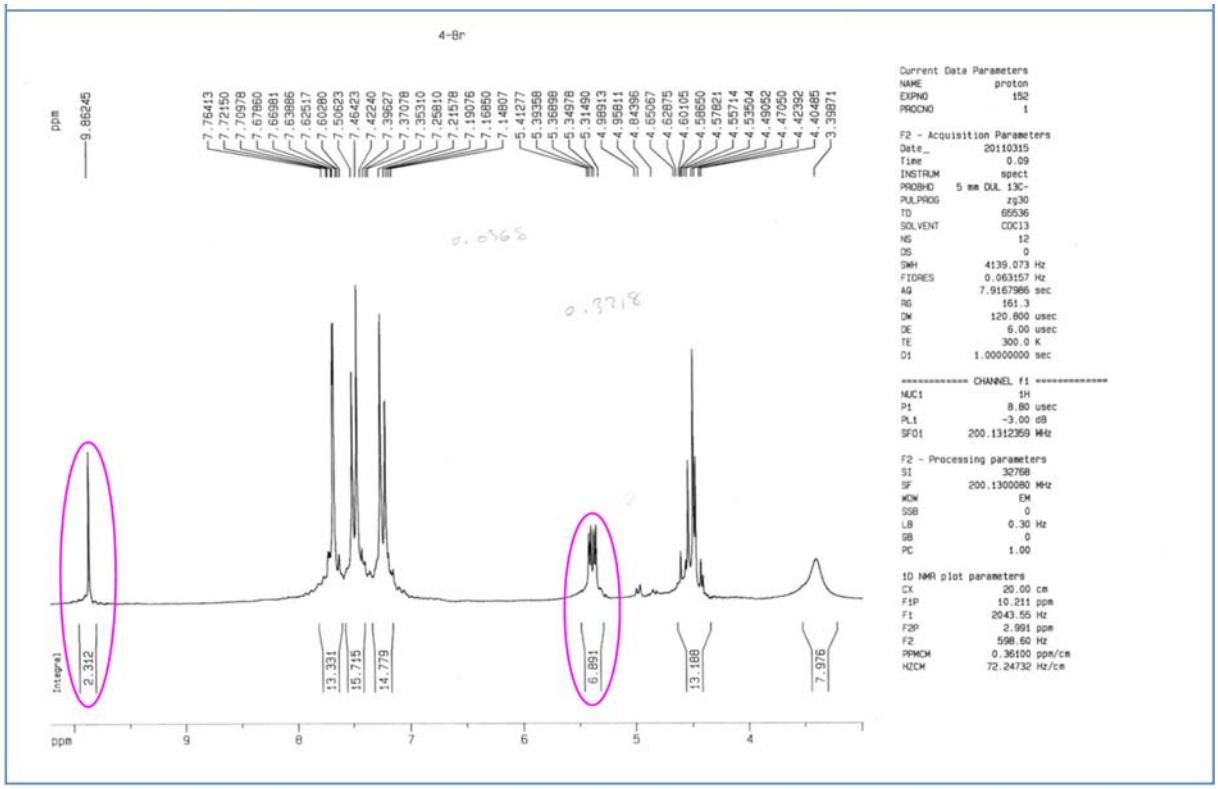


Figure S-5 ^{1}H NMR spectrum for compound 1-(4-Chlorophenyl)-2-nitroethanol (Table 2 Entry 9)

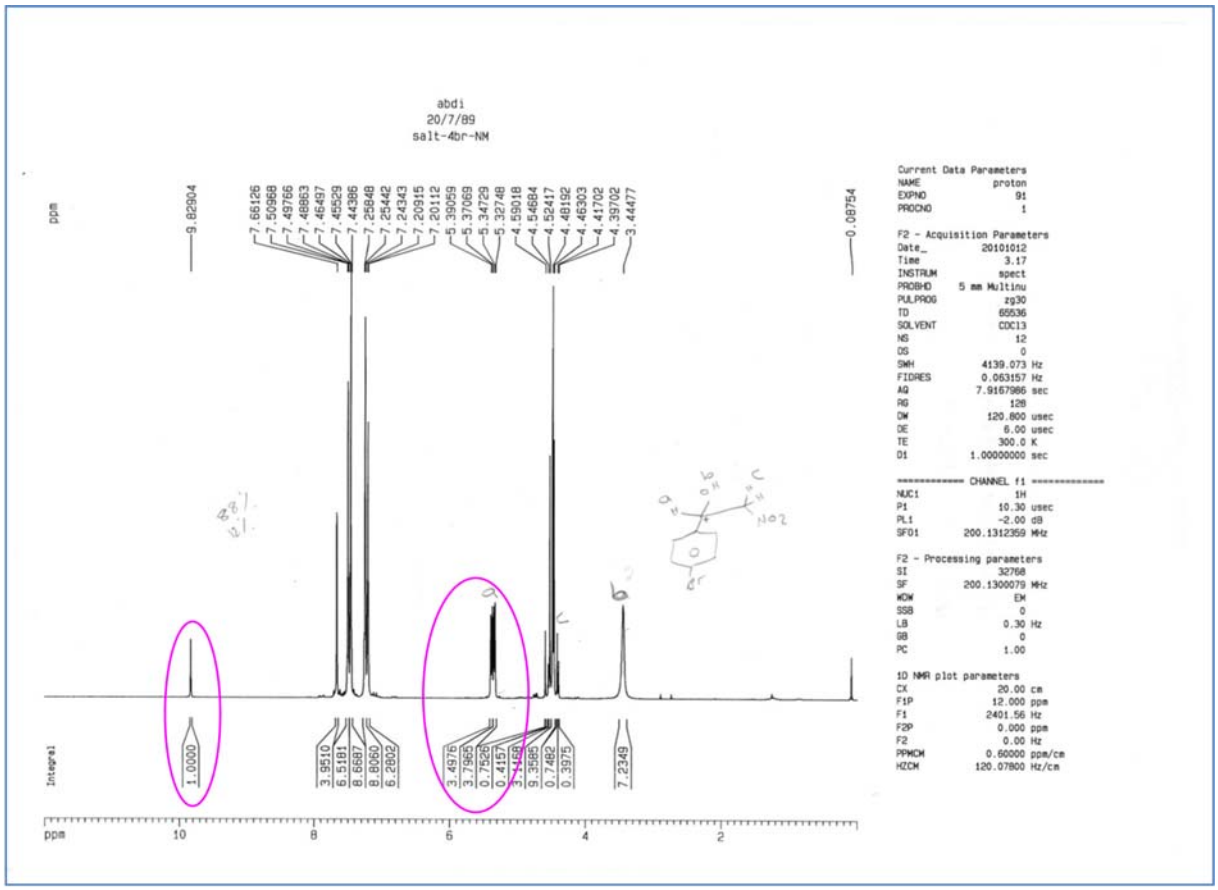


Figure S-6 ^{1}H NMR spectrum for compound 1-(4-Bromophenyl)-2-nitroethanol (Table 2 Entry 8)

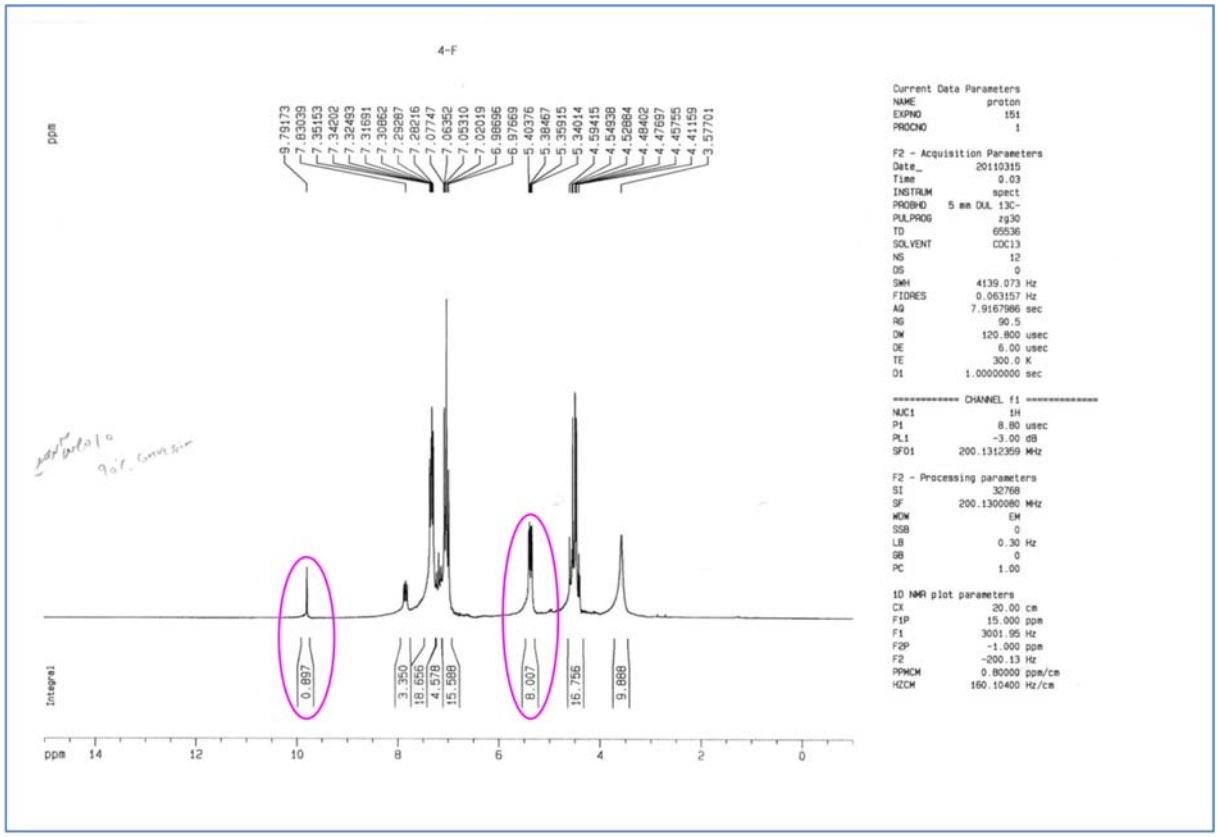


Figure S-7 ^{1}H NMR spectrum for compound 1-(4-Flourophenyl)-2-nitroethanol (Table 2 Entry 6)

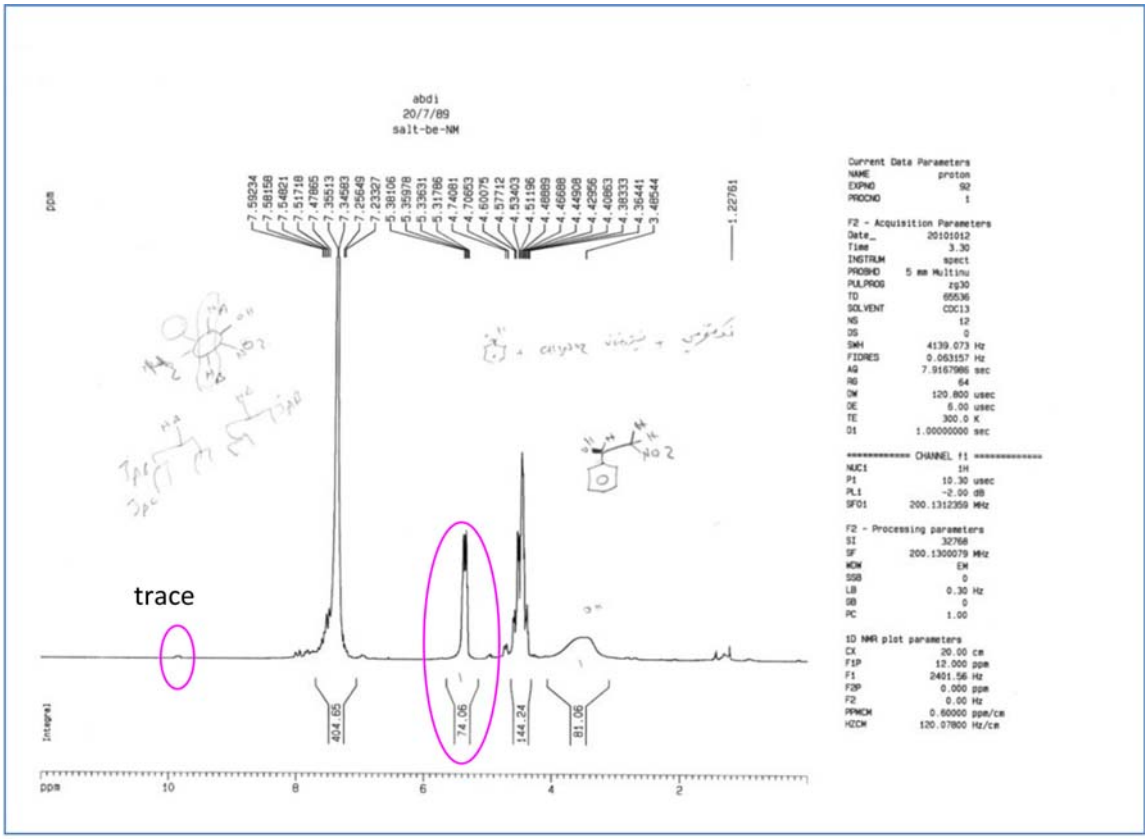


Figure S-8 ^{1}H NMR spectrum for compound 1-phenyl-2-nitroethanol (Table 2 Entry 1)

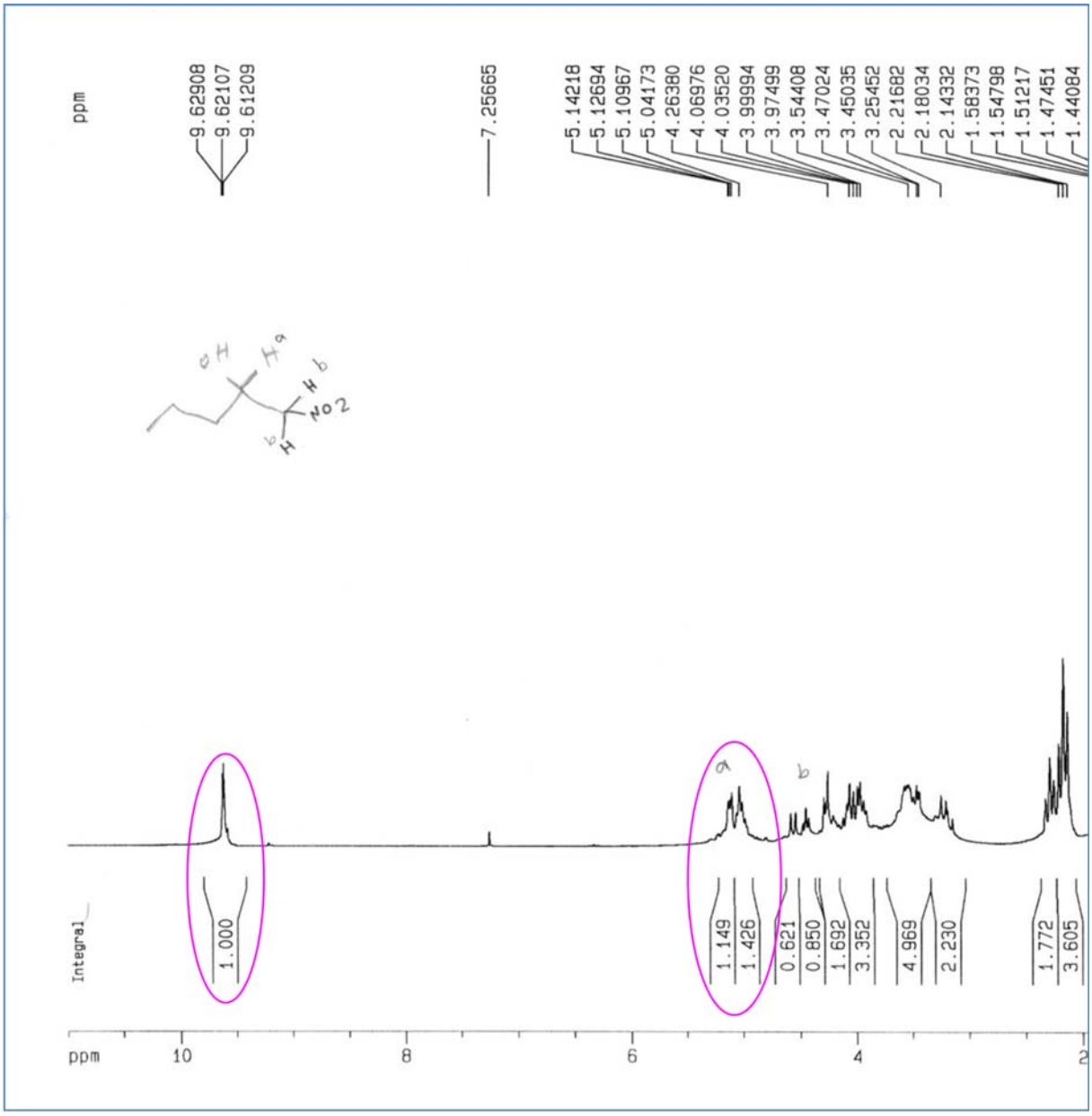


Figure S-9 ^{1}H NMR spectrum for compound 1-Nitropentan-2-ol (Table 2 Entry 18)

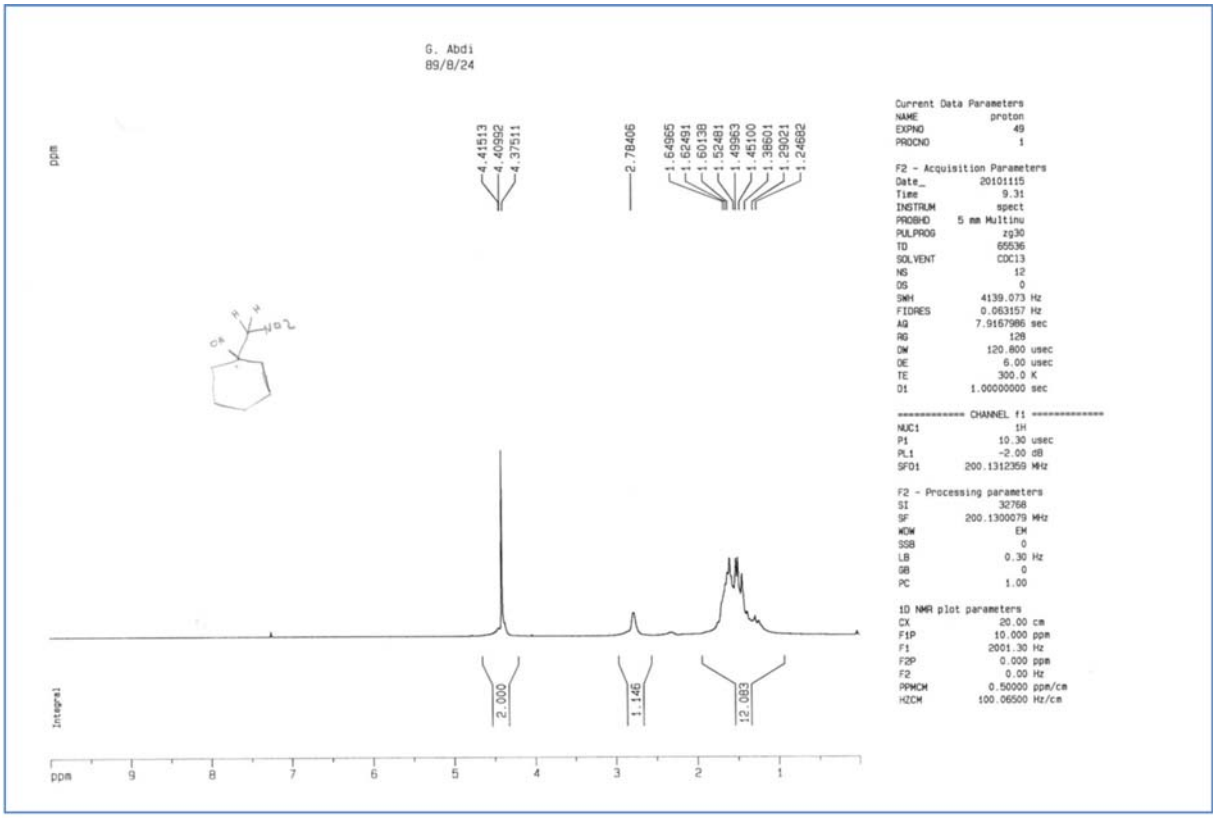


Figure S-10 ^{1}H NMR spectrum for compound 1-(Nitromethyl)cyclohexanol (Table 2 Entry 19)

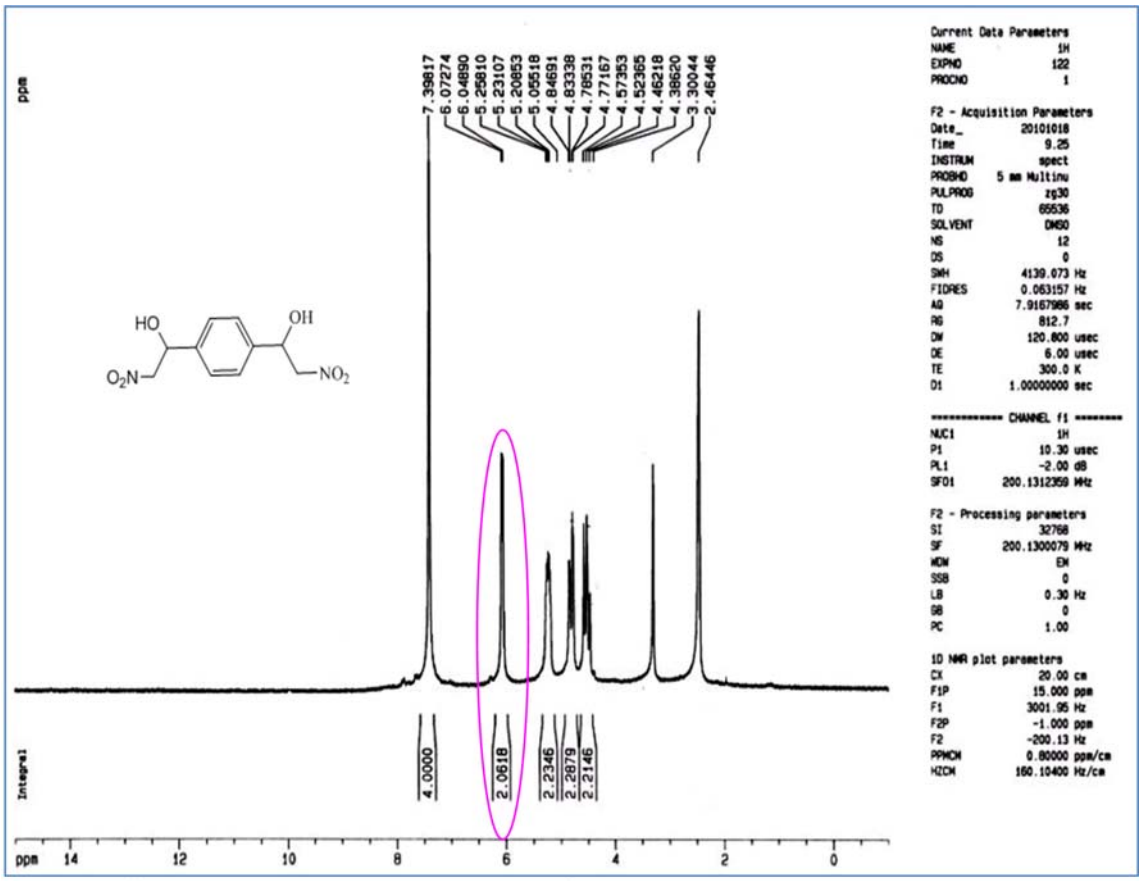


Figure S-11 ^{1}H NMR spectrum of newly synthesized 1,1'-(1,4-Phenylene)bis(2-nitroethanol) (Table 2 Entry 14)

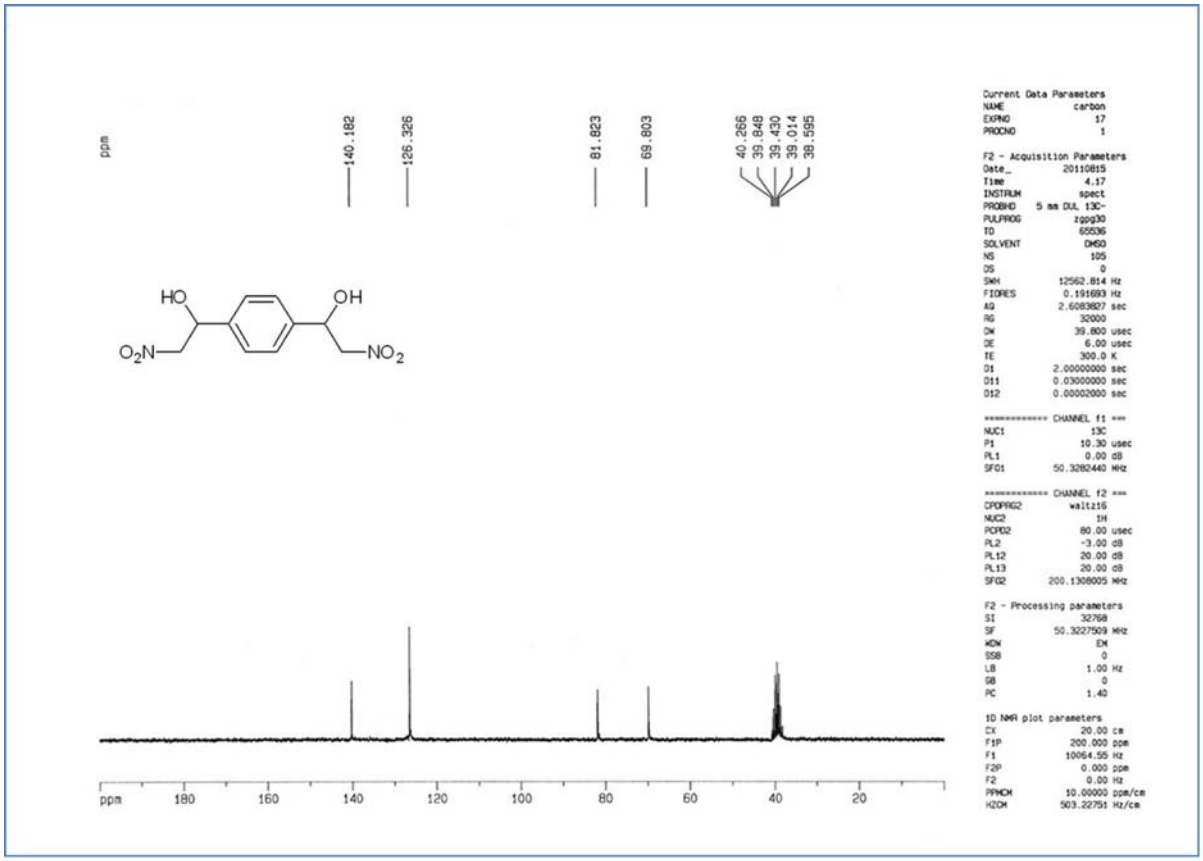


Figure S-12 ^{13}C NMR spectrum of newly synthesized 1,1'-(1,4-Phenylene)bis(2-nitroethanol) (Table 2 Entry 14)

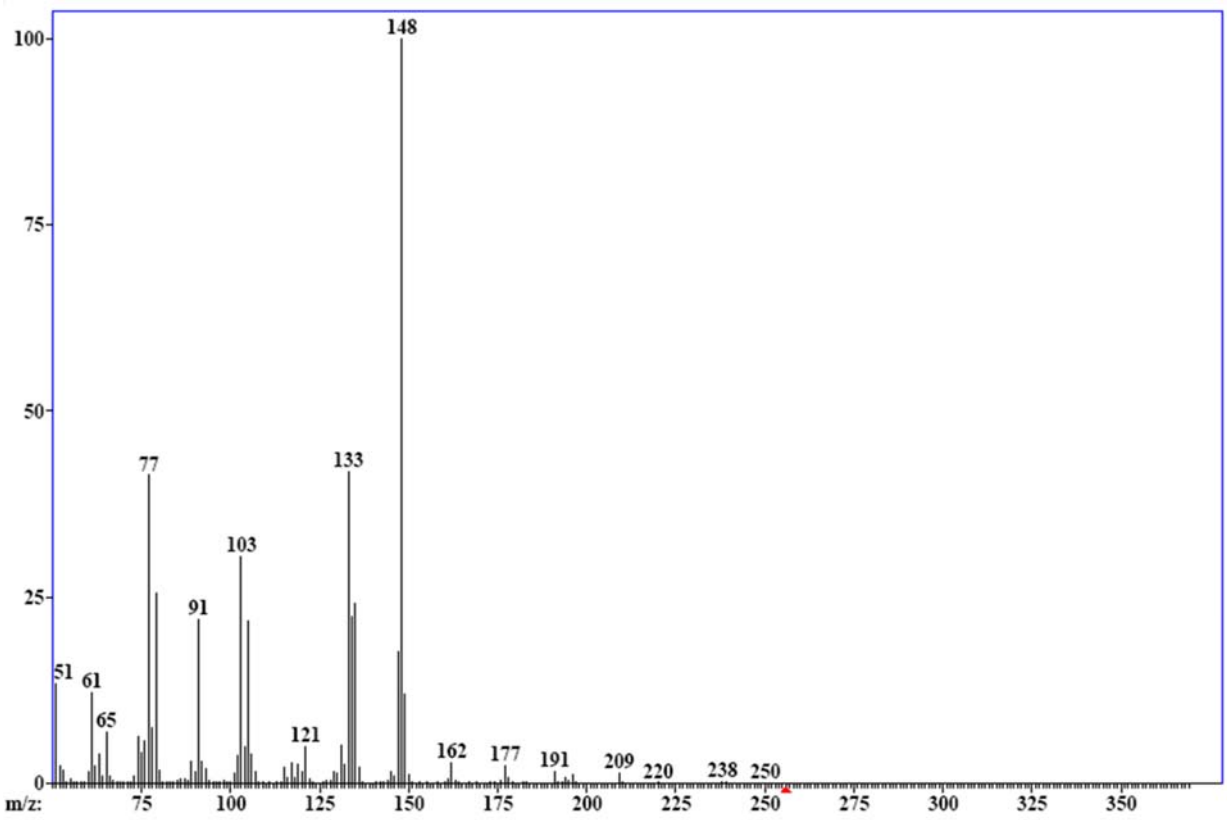


Figure S-13 MS spectrum of newly synthesized 1,1'-(1,4-Phenylene)bis(2-nitroethanol) (Table 2 Entry 14)

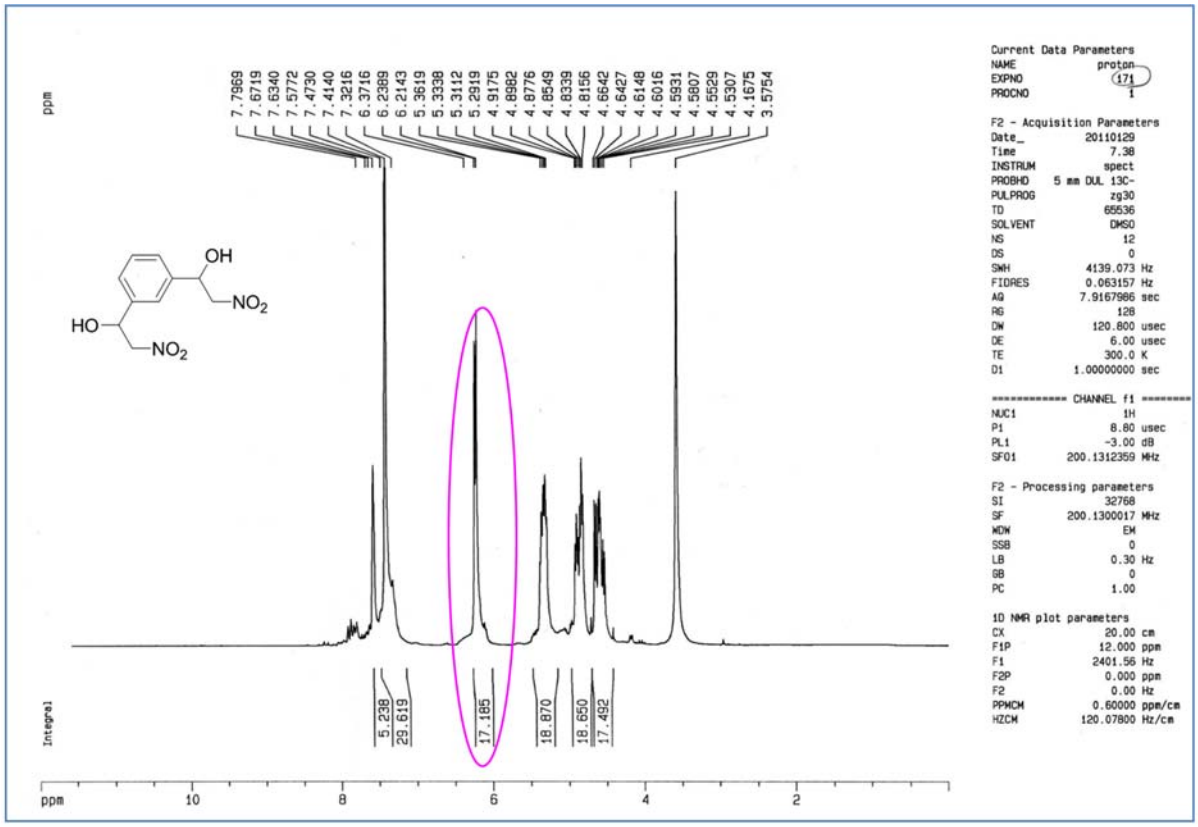


Figure S-14 ^{1}H NMR spectrum of newly synthesized 1,1'-(1,3-Phenylene)bis(2-nitroethanol) (Table 2 Entry 15)

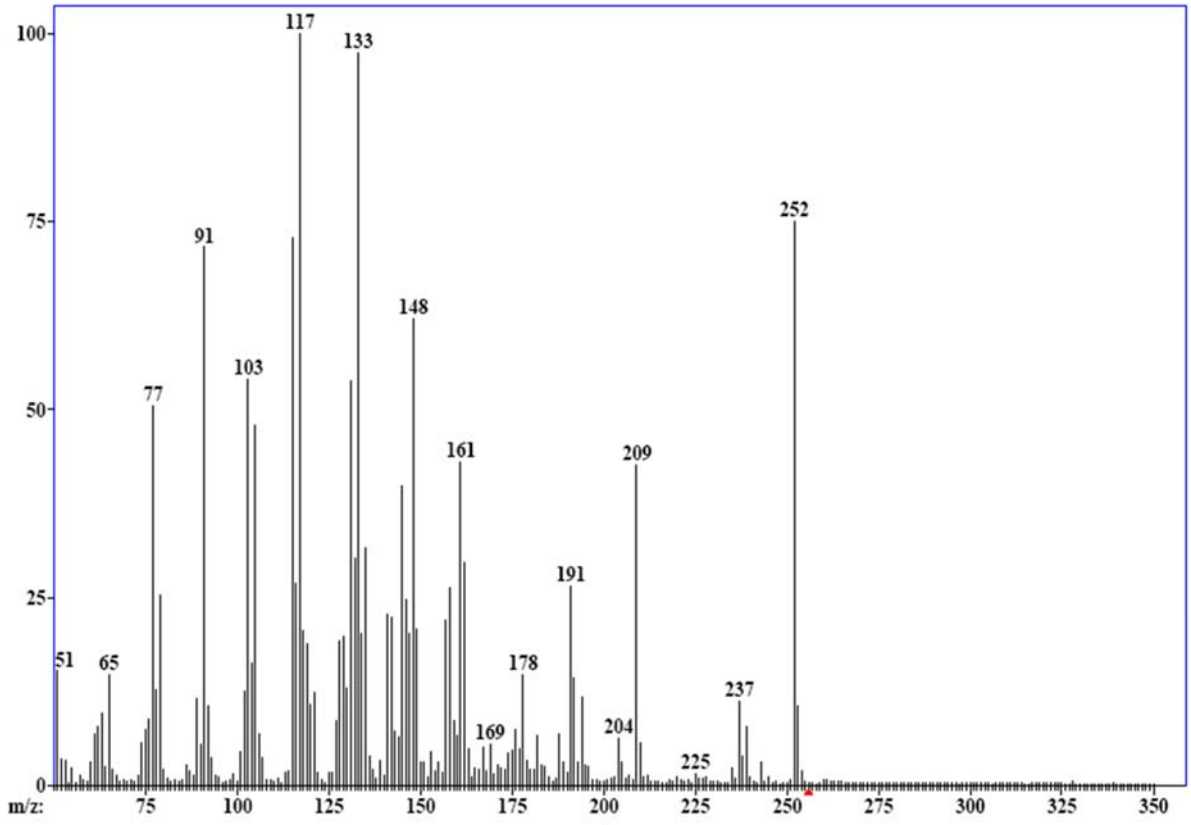


Figure S-15 MS spectrum of newly synthesized 1,1'-(1,3-Phenylene)bis(2-nitroethanol) (Table 2 Entry 15)

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