Supporting Information

New catalytically active conjugated microporous polymer bearing ordered salen-Cu and porphyrin moieties for Henry reaction in aqueous solution

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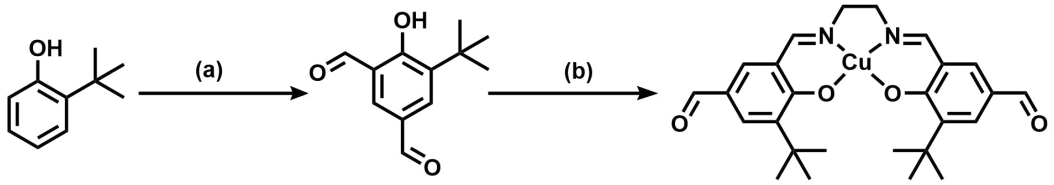
Synthetic procedures

Compound 2 (5-(*tert*-butyl)-4-hydroxyisophthalaldehyde). 2-*tert*-Butylphenol (1.50 g, 0.01 mmol) and hexamethylenetetramine (1.68 g, 0.012 mmol) were placed in a 50 mL of flask, and then trifluoroacetic acid (9 mL) was added. The solution was heated to reflux at 120 °C for 3 hours. After the solution was cooled to room temperature, 10% aq H_2SO_4 (9 mL) was added and the temperature was again raised and kept at 100 °C for 2 hours. After completion of the reaction, the solution was adjusted to pH = 8 with saturated Na_2CO_3 aqueous solution and extracted with 30 mL of $CHCl_3$. The obtained organic phase was dried over anhydrous sodium sulfate, and then concentrated under reduced pressure to obtain a crude product. The crude product was purified on silica gel column using petroleum ether-dichloromethane (2:1, v/v) as eluent to afford compound **2** (1.03 g, 50 % yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 12.40 (s, 1H，O*H*), 9.99 (s, 1H, C*H*O), 9.93 (s, 1H, C*H*O), 8.07 (d, *J* = 2.0 Hz, 1H, Ph-*H*), 7.98 (d, *J* = 2.0 Hz, 1H, Ph-*H*), 1.46 (s, 9H, C(C*H*$_3$)$_3$) ppm.

Salen-Cu. Compound **2** (1.03 g, 5 mmol) and $Cu(OAc)_2$•H_2O (0.50 g, 2.5 mmol) was poured to a round-bottomed flask which contained 25 mL of methanol. Then ethylenediamine (150 mg, 2.5 mmol) was added and the reaction mixture was refluxed for 5 h. After cooling to room temperature, the black precipitate was collected by filtration, washed with cool methanol, and dried under vacuum to give salen-Cu as a black solid in 89 % yield (1.1 g). IR (KBr，cm^{-1}): $\tilde{\nu}$ 2953, 2810, 2712, 1683, 1632, 1596, 1537, 1441, 1392, 1331,1274, 1240, 1201, 1146, 1089, 1034, 995, 932, 890, 798, 733, 679, 639, 587, 490, 420.



1 2 Salen-Cu

(a) i. Hexamethylenetetramine, TFA, 120 °C, reflux, 3h; ii. 10% H_2SO_4, reflux, 2h, (b) Ethylenediamine, $Cu(OAc)_2$•H_2O, CH_3OH, 75 °C, 5h

Scheme S1 Schematic representation for the synthesis of **salen-Cu**.

Characterization of **SP-CMP-Cu**

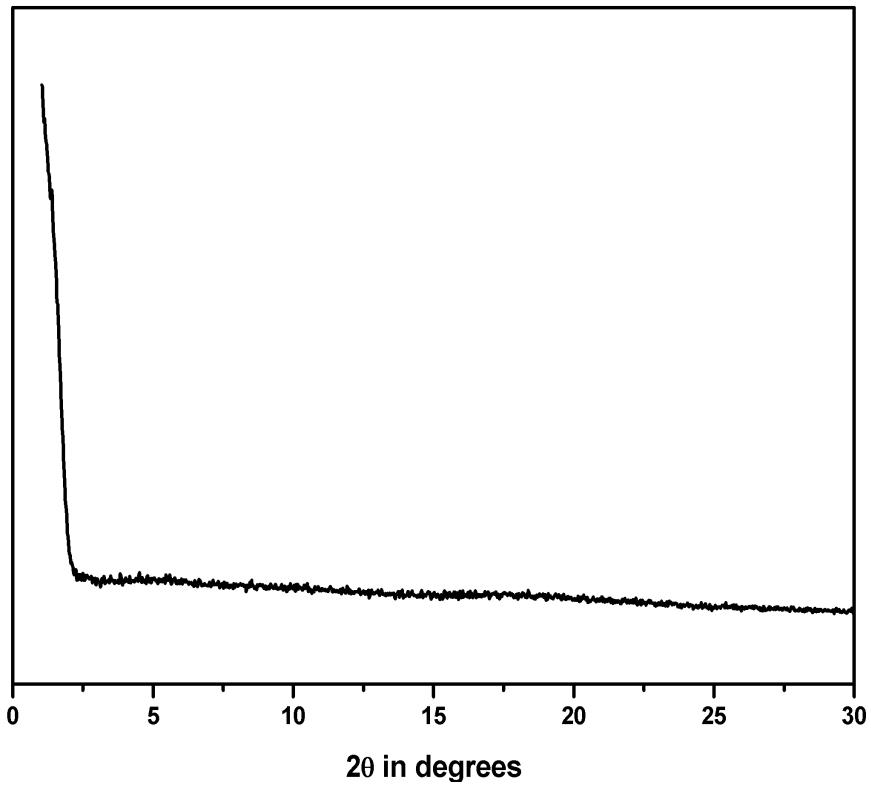


Fig. S1 PXRD of **SP-CMP-Cu.**

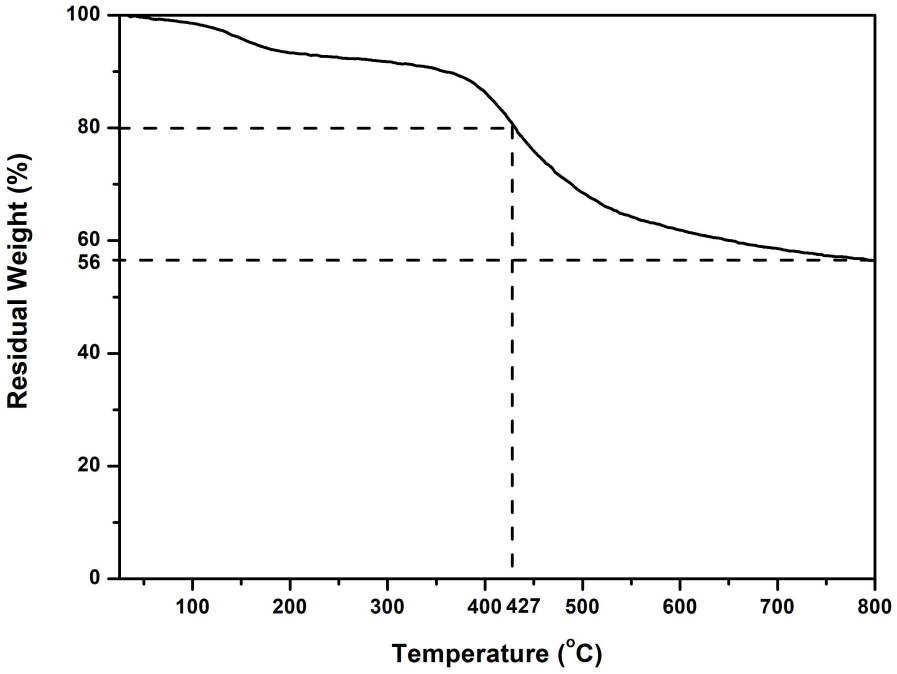


Fig. S2 TGA curve of **SP-CMP-Cu.**

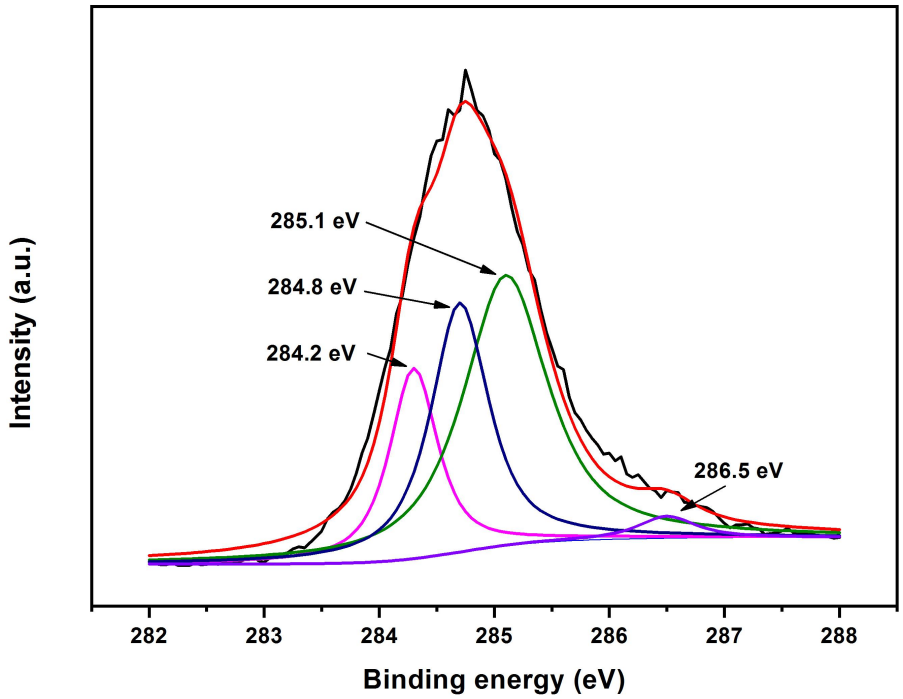


Fig. S3 The XPS spectrum of **SP-CMP-Cu** for C 1s.

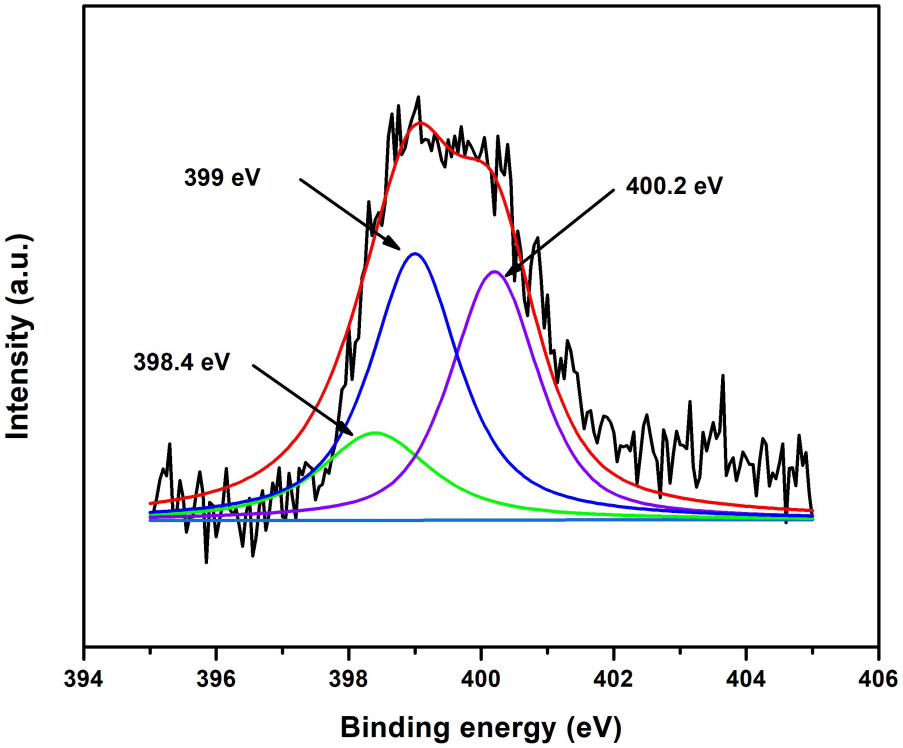


Fig. S4 The XPS spectrum of **SP-CMP-Cu** for N 1s.

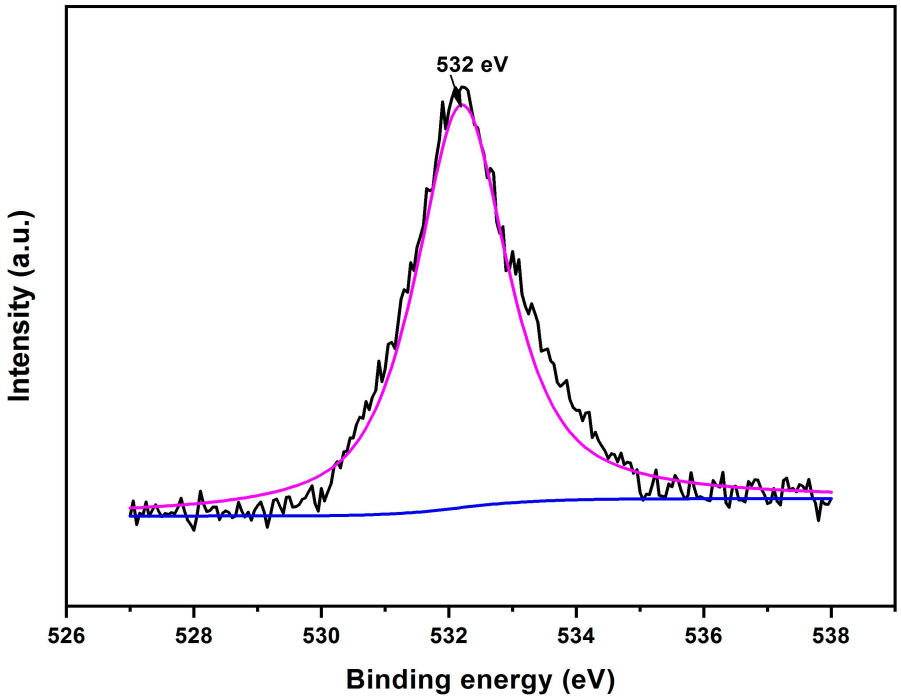


Fig. S5 The XPS spectrum of **SP-CMP-Cu** for O 1s.

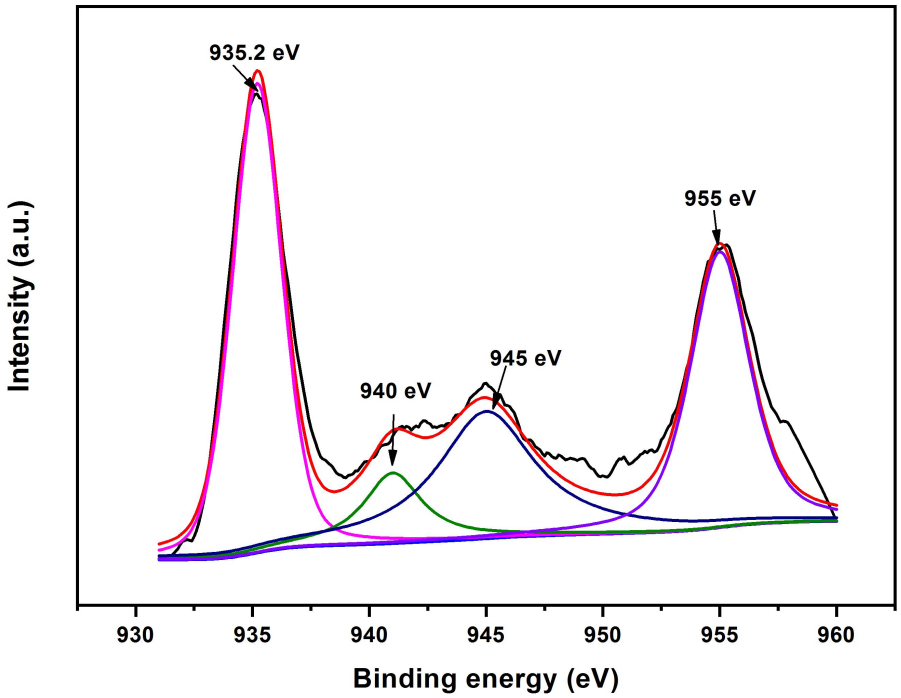


Fig. S6 The XPS spectrum of **SP-CMP-Cu** for Cu 2p.

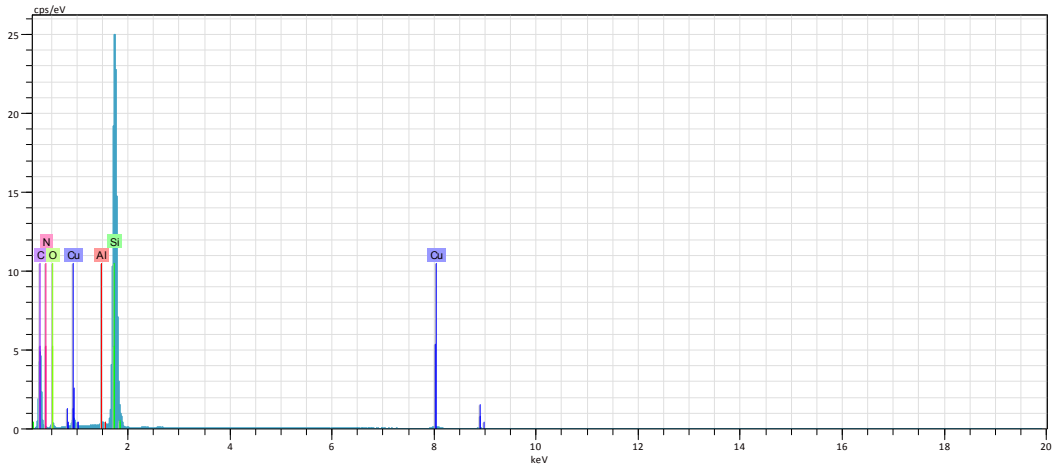


Fig. S7 Energy-dispersive X-ray elemental mapping image of **SP-CMP-Cu.**

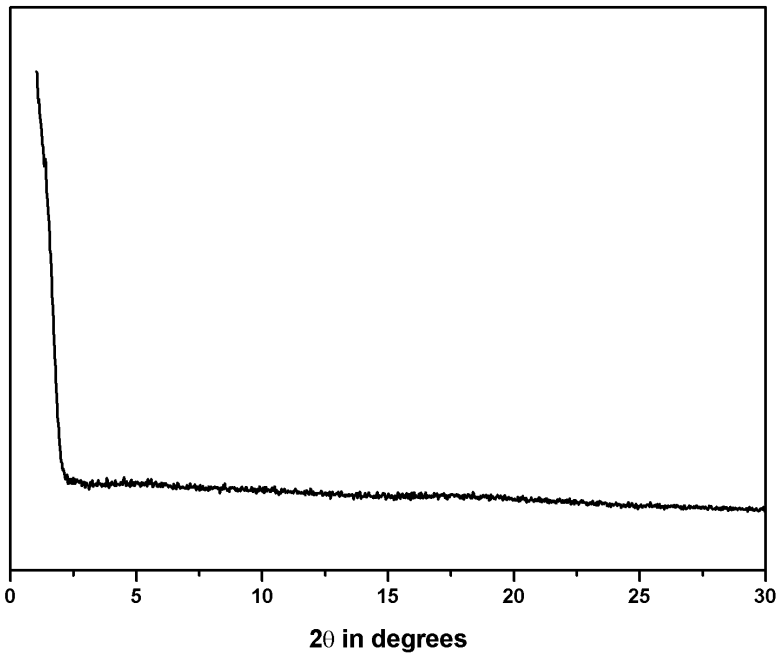


Fig. S8 PXRD of the recovered **SP-CMP-Cu** after five successive reactions.

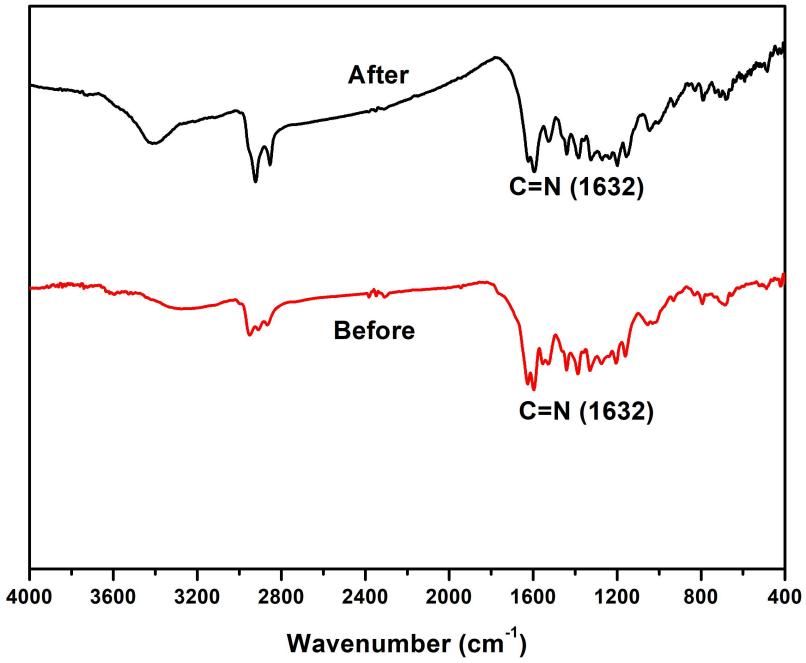


Fig. S9 FT-IR spectra of the original **SP-CMP-Cu** (red) and the recovered **SP-CMP-Cu** after five successive reactions (black).

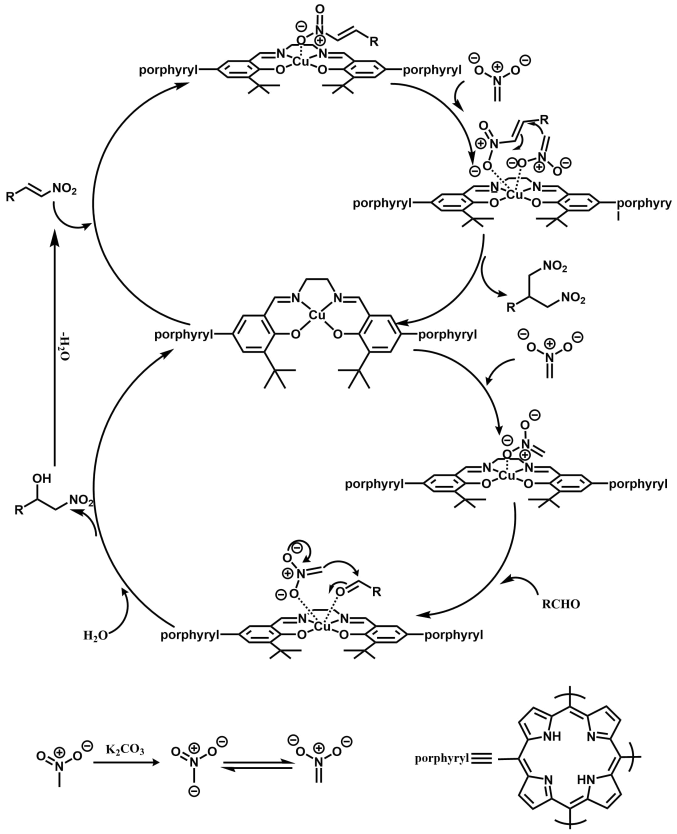
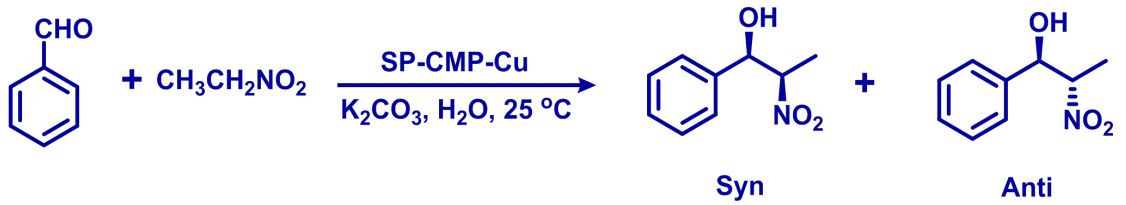


Fig. S10 Proposed mechanism of the Henry reaction with **SP-CMP-Cu.**

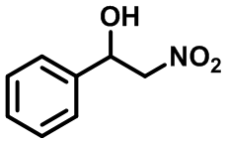


Reaction conditions: benzaldehyde (2 mmol), K_2CO_3 (1 mmol), **SP-CMP-Cu** (5 mg), and nitroethane (20 mmol) in 2 mL of H_2O at 25 °C for 12 h. The conversion of benzaldehyde was determined by ^1H NMR.

Scheme S2 The Henry reaction of benzaldehyde with nitroethane catalyzed by **SP-CMP-Cu**

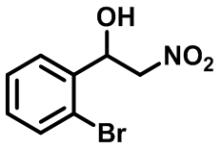
^{1}H NMR Spectral Data

2-nitro-1-phenylethan-1-ol



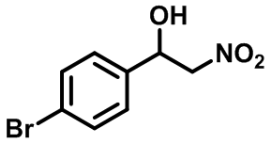
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 3.8 Hz, 5H), 5.45 (dt, J = 9.5, 3.3 Hz, 1H), 4.60 (ddd, J = 13.3, 9.5, 1.0 Hz, 1H), 4.53–4.47 (m, 1H), 2.91 (dd, J = 11.5, 3.8 Hz, 1H) ppm.

1-(2-bromophenyl)-2-nitroethan-1-ol



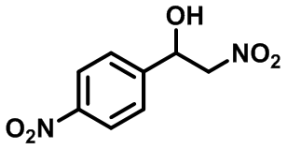
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.62 (m, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.23 (td, J = 7.7, 1.7 Hz, 1H), 5.80 (dt, J = 9.8, 3.1 Hz, 1H), 4.68 (dd, J = 13.7, 2.3 Hz, 1H), 4.43 (dd, J = 13.6, 9.6 Hz, 1H), 3.10 (dt, J = 9.6, 4.2 Hz, 1H) ppm.

1-(4-bromophenyl)-2-nitroethan-1-ol



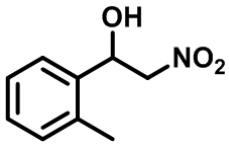
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.51 (m, 2H), 7.30 (d, J = 8.2 Hz, 2H), 5.45 (dt, J = 9.3, 3.5 Hz, 1H), 4.58 (dd, J = 13.5, 9.3 Hz, 1H), 4.50 (dd, J = 13.5, 3.2 Hz, 1H), 2.86 (d, J = 3.8 Hz, 1H) ppm.

2-nitro-1-(4-nitrophenyl)ethan-1-ol



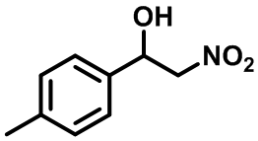
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 5.73–5.54 (m, 1H), 4.60 (d, J = 7.9 Hz, 2H), 3.29–3.12 (m, 1H) ppm.

2-nitro-1-(*o*-tolyl)ethan-1-ol



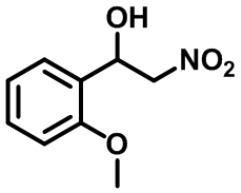
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.50 (m, 1H), 7.29–7.25 (m, 2H), 7.21–7.17 (m, 1H), 5.69 (dt, J = 9.7, 3.1 Hz, 1H), 4.55 (dd, J = 13.4, 9.7 Hz, 1H), 4.44 (dd, J = 13.4, 2.6 Hz, 1H), 2.69 (dq, J = 7.9, 2.6 Hz, 1H), 2.39 (s, 3H) ppm.

2-nitro-1-(*p*-tolyl)ethan-1-ol



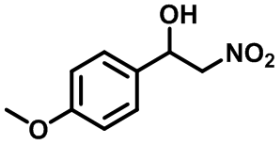
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 5.43 (dq, J = 9.4, 3.0 Hz, 1H), 4.61 (ddd, J = 13.3, 9.6, 1.2 Hz, 1H), 4.49 (ddd, J = 13.3, 3.1, 1.3 Hz, 1H), 2.71 (dd, J = 10.8, 3.7 Hz, 1H), 2.36 (s, 3H) ppm.

1-(2-methoxyphenyl)-2-nitroethan-1-ol

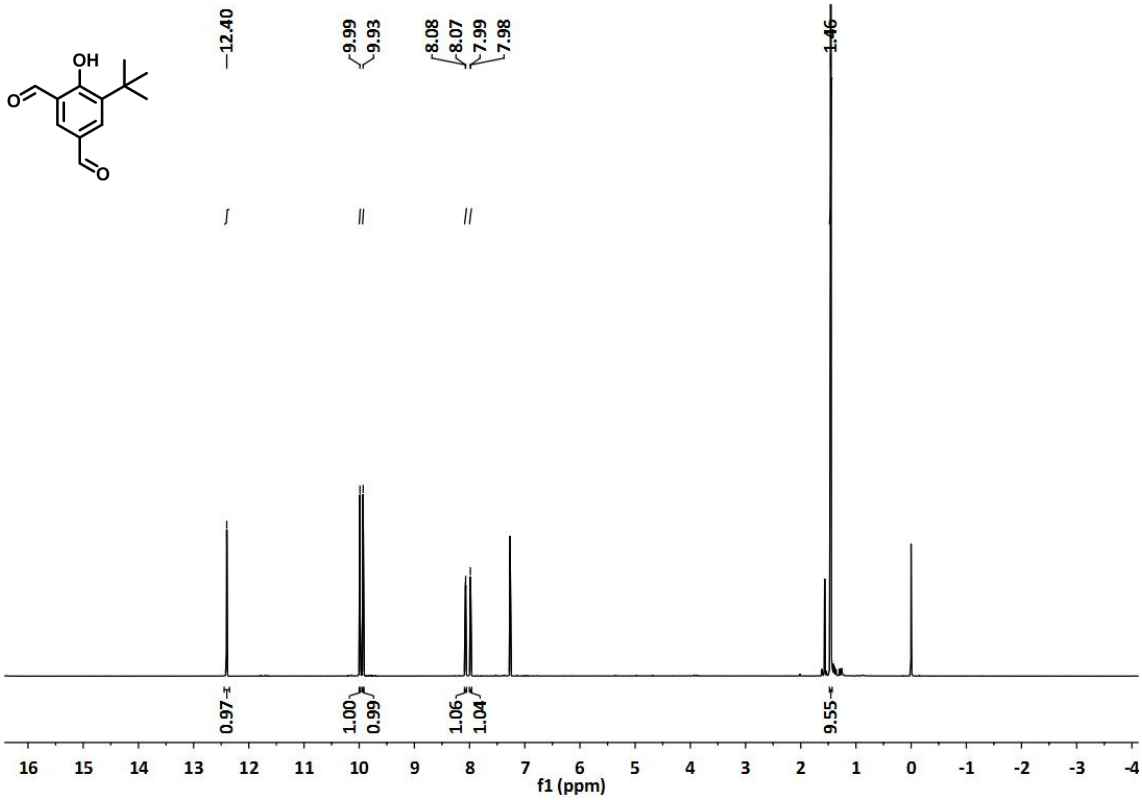


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, J = 7.6, 1.7 Hz, 1H), 7.33 (td, J = 7.8, 1.7 Hz, 1H), 7.01 (td, J = 7.5, 1.0 Hz, 1H), 6.91 (dd, J = 8.3, 1.0 Hz, 1H), 5.63 (ddd, J = 9.2, 6.0, 3.2 Hz, 1H), 4.68–4.54 (m, 2H), 3.89 (s, 3H), 3.16–3.11 (m, 1H) ppm.

1-(4-methoxyphenyl)-2-nitroethan-1-ol



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 5.41 (dt, J = 9.6, 3.3 Hz, 1H), 4.61 (dd, J = 13.2, 9.6 Hz, 1H), 4.48 (dd, J = 13.3, 3.1 Hz, 1H), 3.82 (s, 3H), 2.72 (d, J = 3.4 Hz, 1H) ppm.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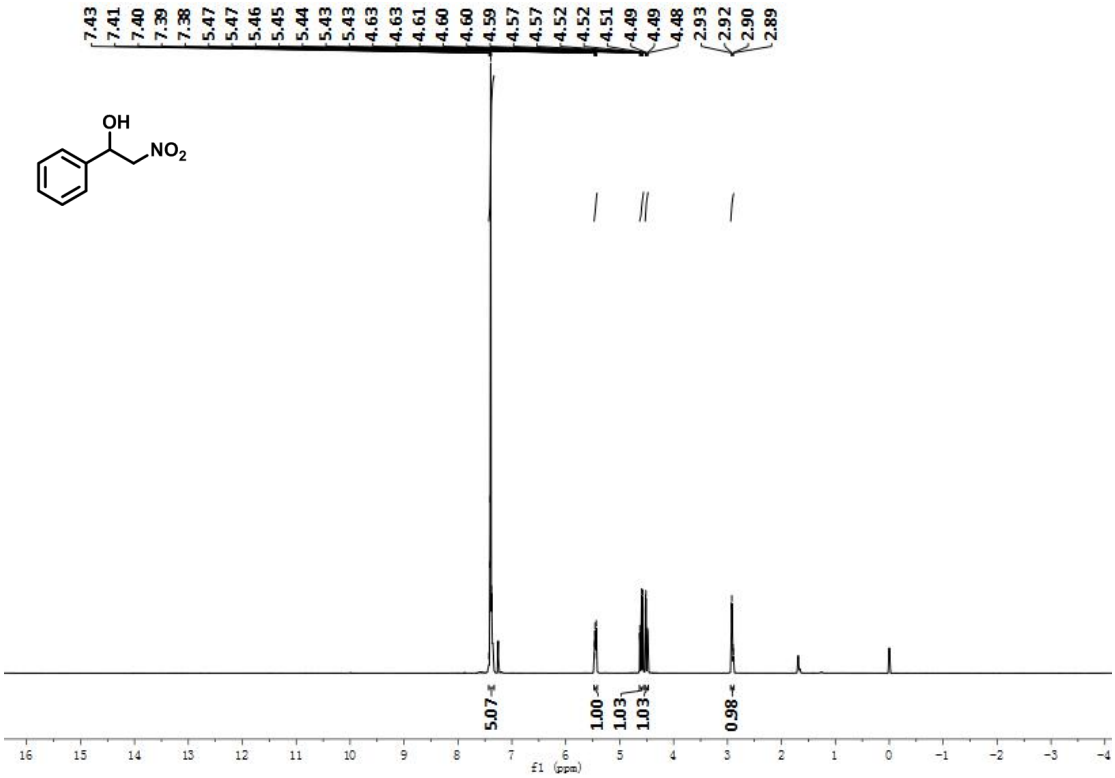
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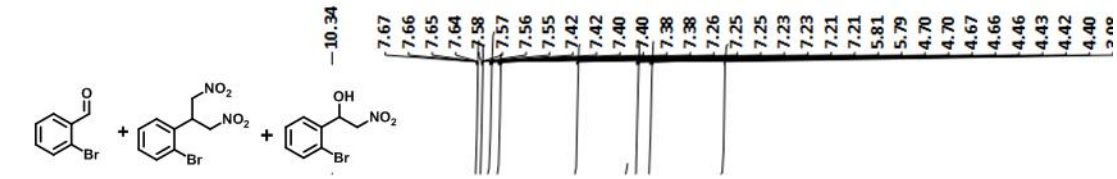
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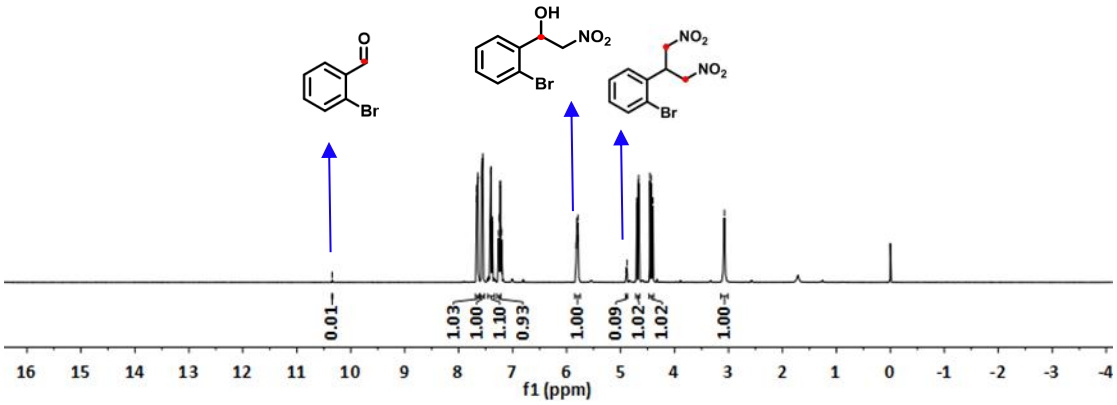
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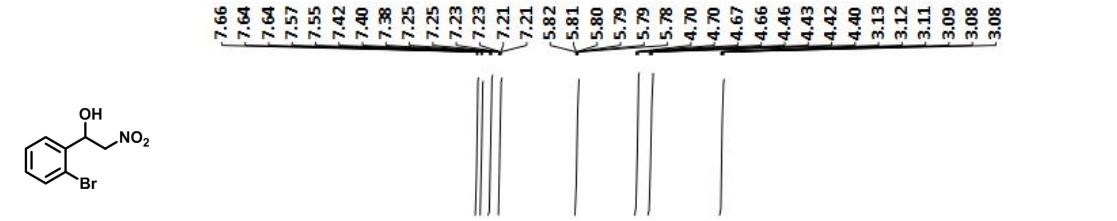
f1 (ppm)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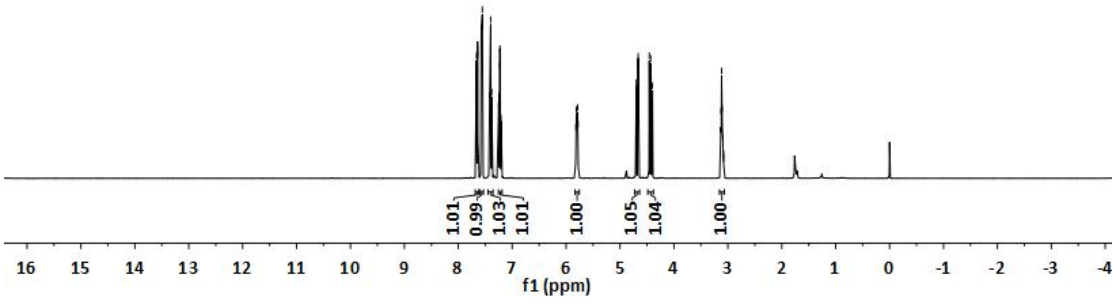
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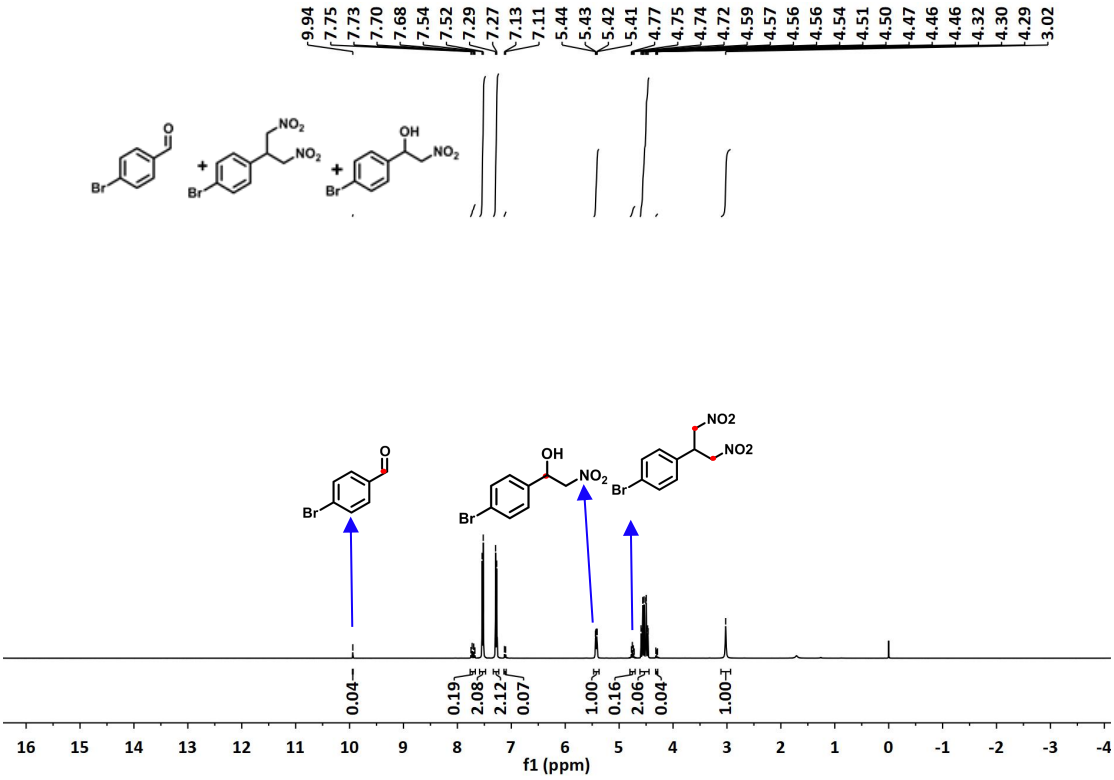
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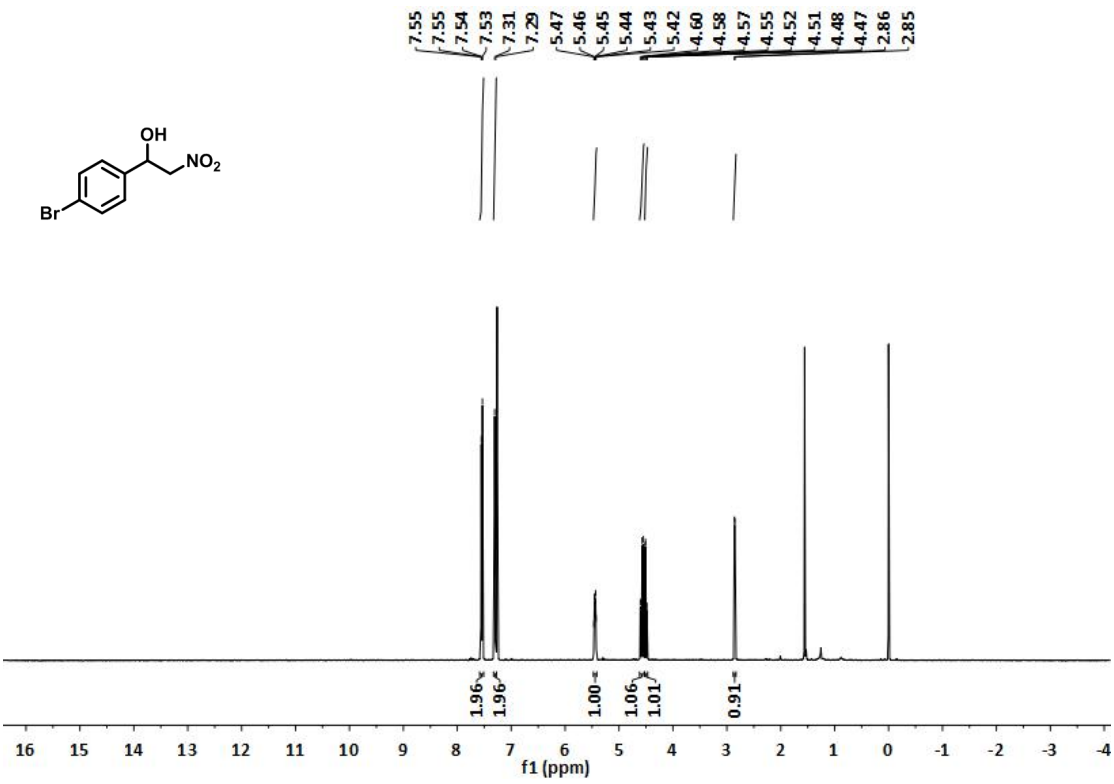
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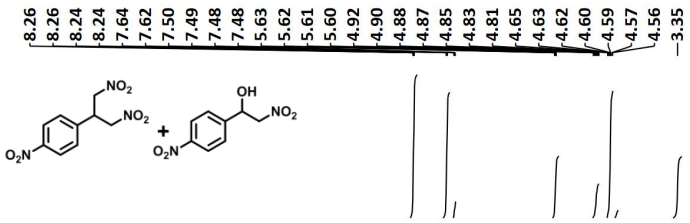
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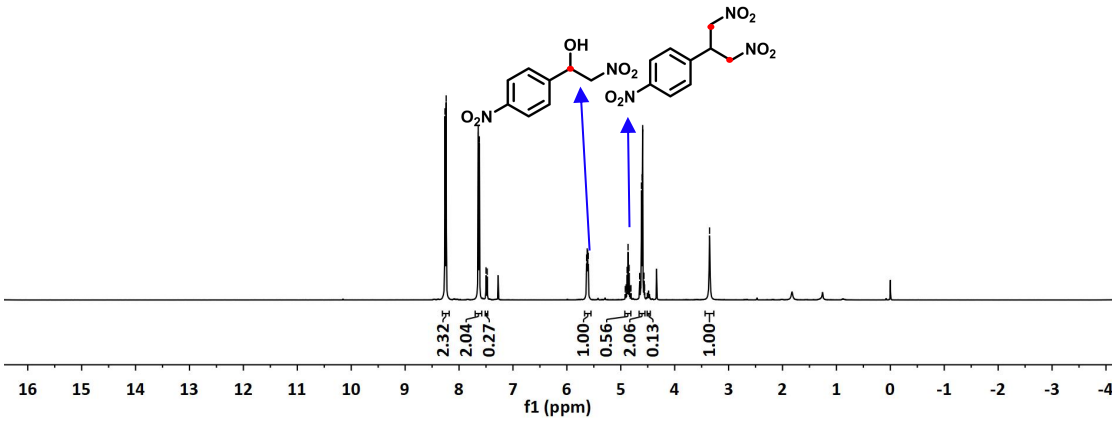
NO2
O2N
+
OH
NO2
O2N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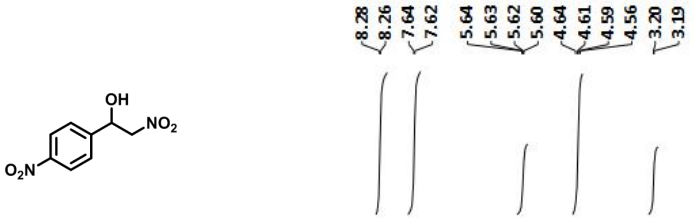
f1 (ppm)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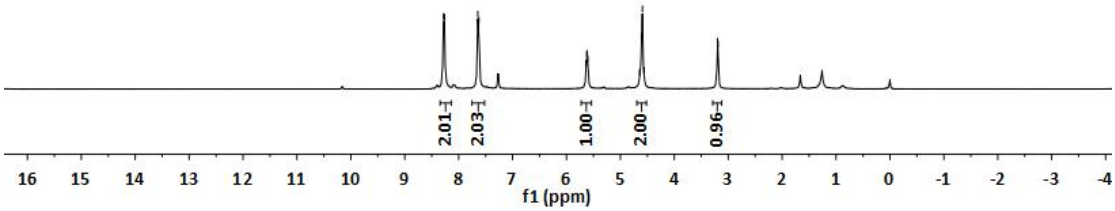
4.61
4.59
4.56
3.20
3.19
OH
NO2
O2N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2.03
1.00
2.00
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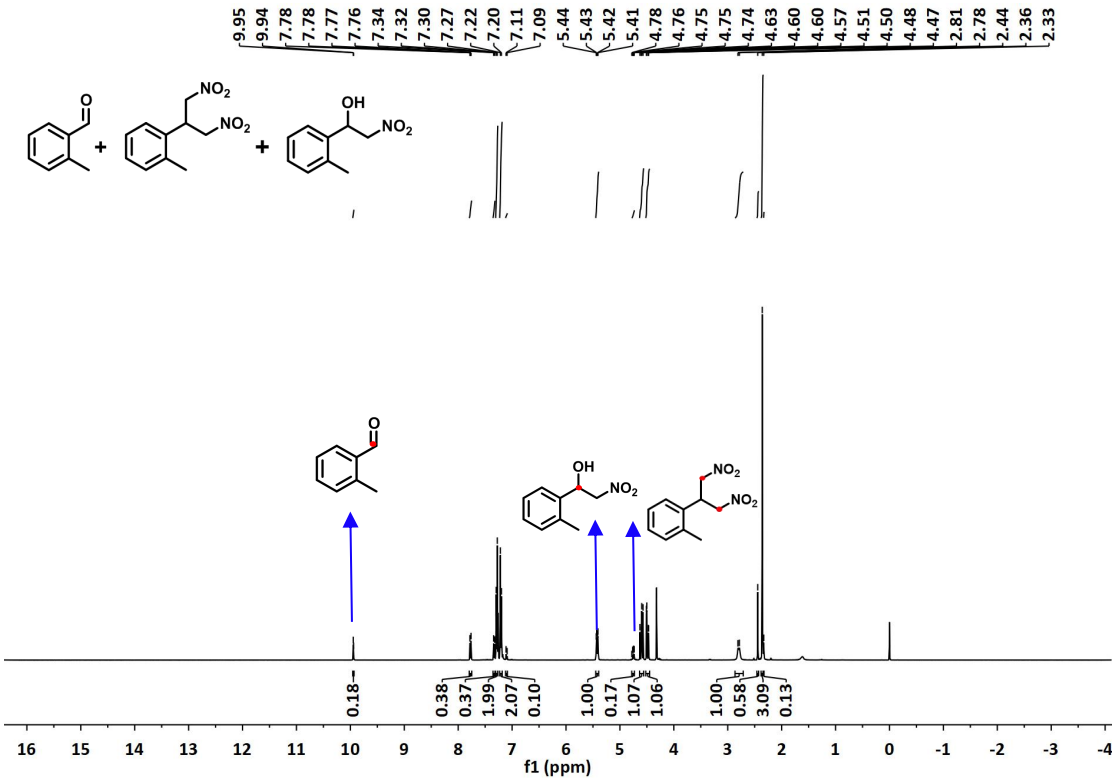
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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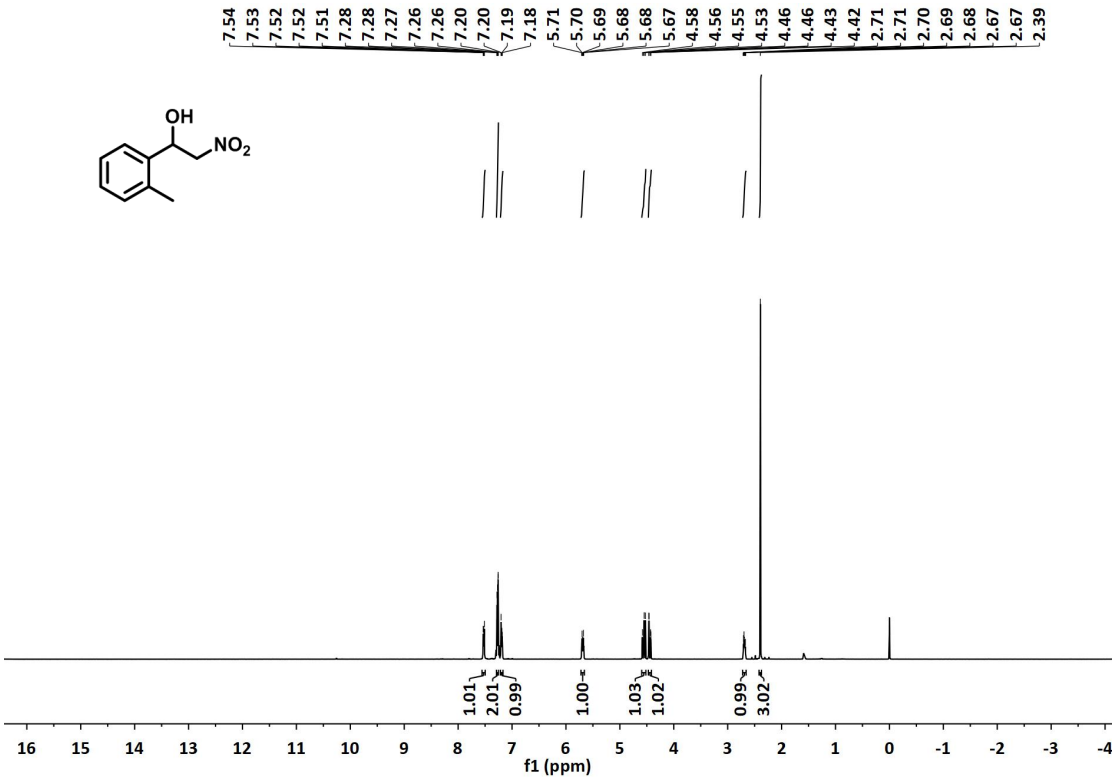
NO2
NO2
OH
NO2
0.18 0.38 0.37 1.99 2.07 0.10 1.00 0.17 1.07 1.06 1.00 0.58 3.09 0.13
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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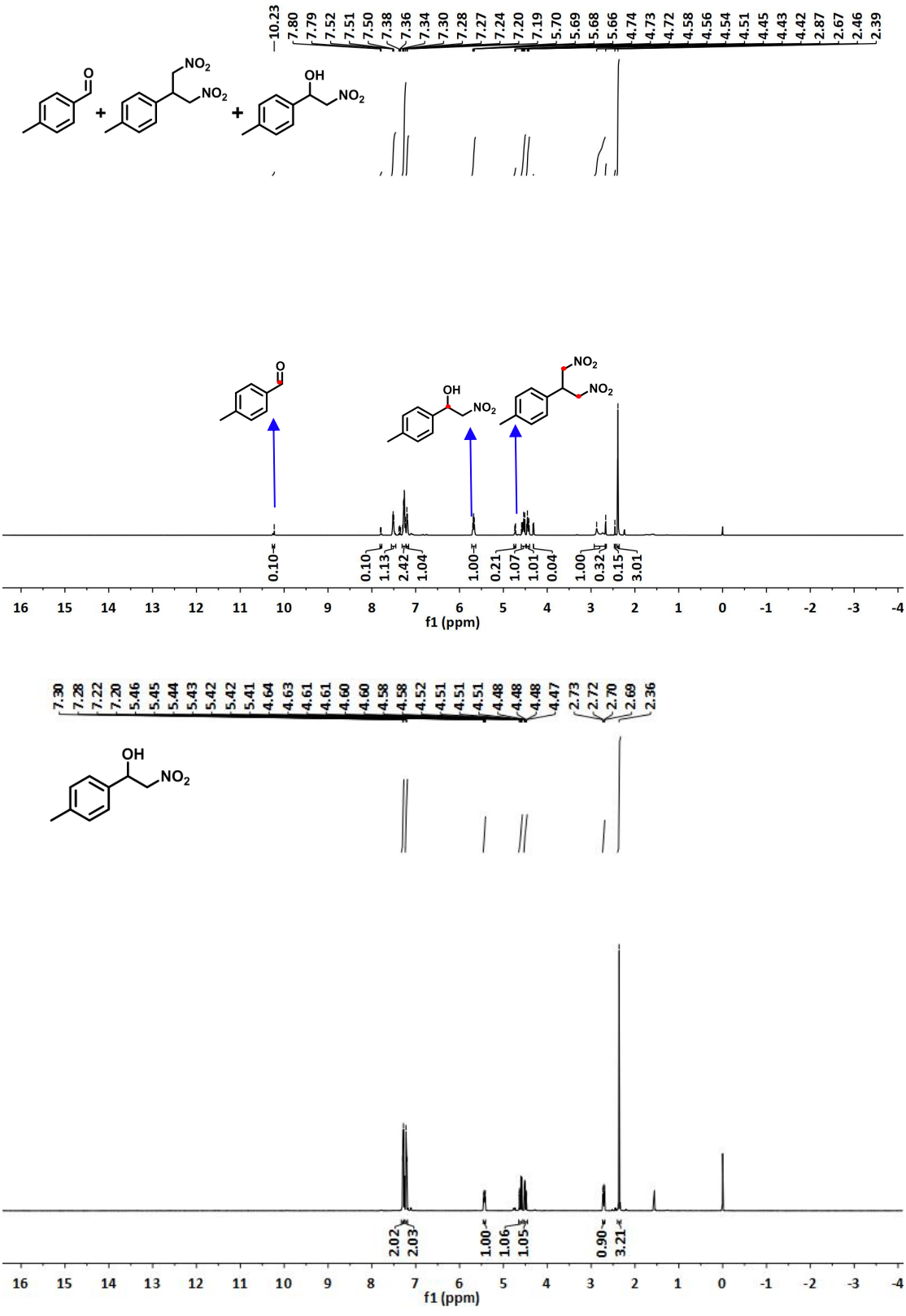
OH
NO2
1.01 2.01 0.99 1.00 1.03 1.02 0.99 3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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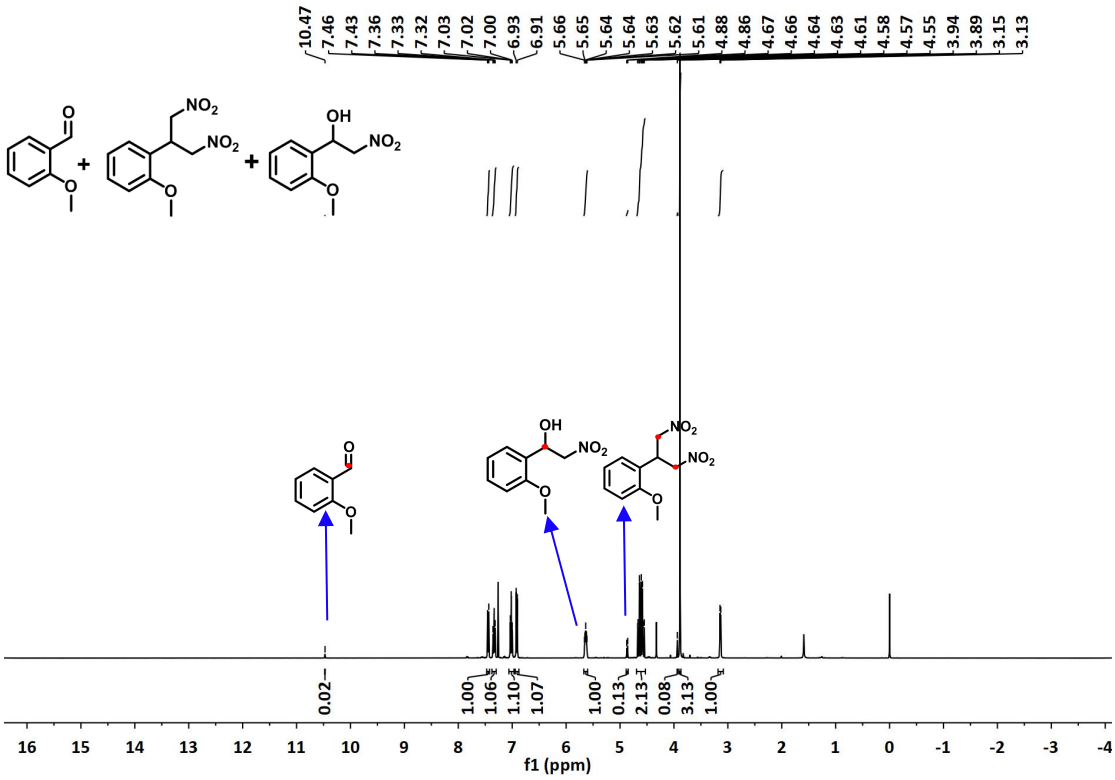
7.79
7.52
7.51
7.50
7.38
7.36
7.34
7.30
7.28
7.27
7.24
7.20
7.19
5.70
5.69
5.68
5.66
4.74
4.73
4.72
4.58
4.56
4.54
4.51
4.45
4.43
4.42
2.87
2.67
2.46
2.39
O
NO2
NO2
OH
NO2
0.10
0.10
1.13
2.42
1.04
1.00
0.21
1.07
1.01
0.04
1.00
0.32
0.15
3.01
f1 (ppm)
7.30
7.28
7.22
7.20
5.46
5.45
5.44
5.43
5.42
5.42
5.41
4.64
4.63
4.61
4.61
4.60
4.60
4.58
4.58
4.52
4.51
4.51
4.51
4.48
4.48
4.48
4.47
2.73
2.72
2.70
2.69
2.36
OH
NO2
2.02
2.03
1.00
1.06
1.05
0.90
3.21
f1 (ppm)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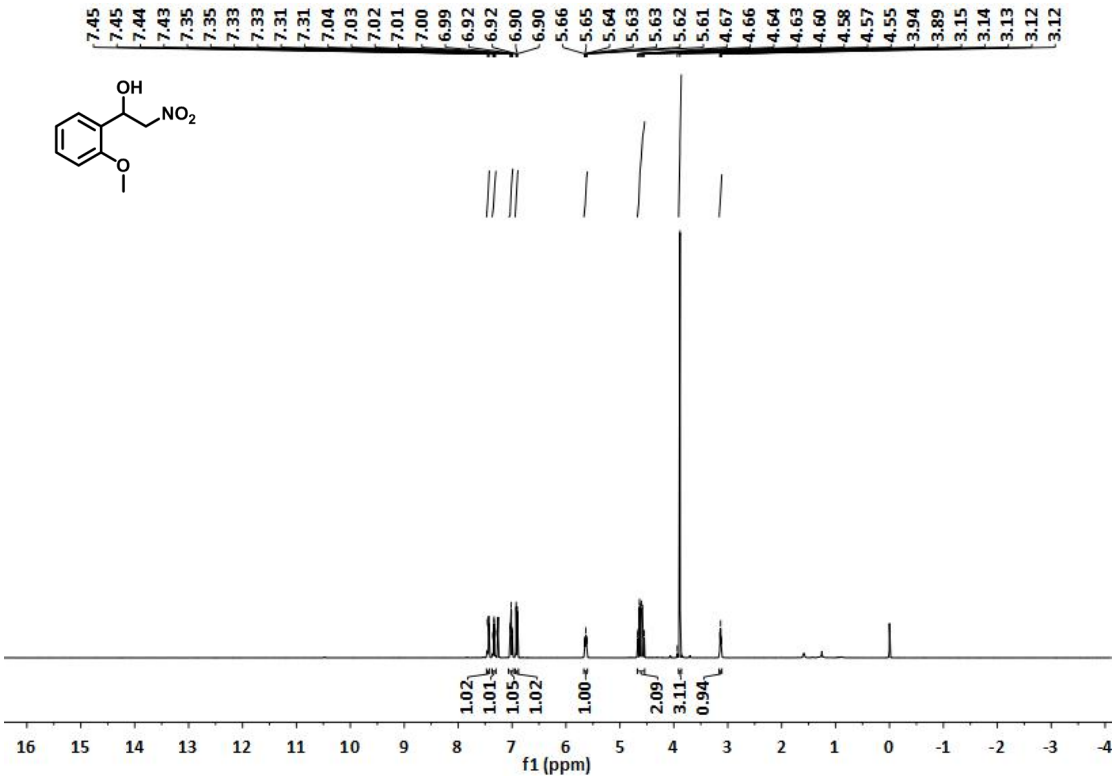
7.46
7.43
7.36
7.33
7.32
7.03
7.02
7.00
6.93
6.91
5.66
5.65
5.64
5.64
5.63
5.62
5.61
4.88
4.86
4.67
4.66
4.64
4.63
4.61
4.58
4.57
4.55
3.94
3.89
3.15
3.13
NO2
NO2
OH
NO2
O
O
O
O
0.02
1.00
1.06
1.10
1.07
1.00
0.13
2.13
0.08
3.13
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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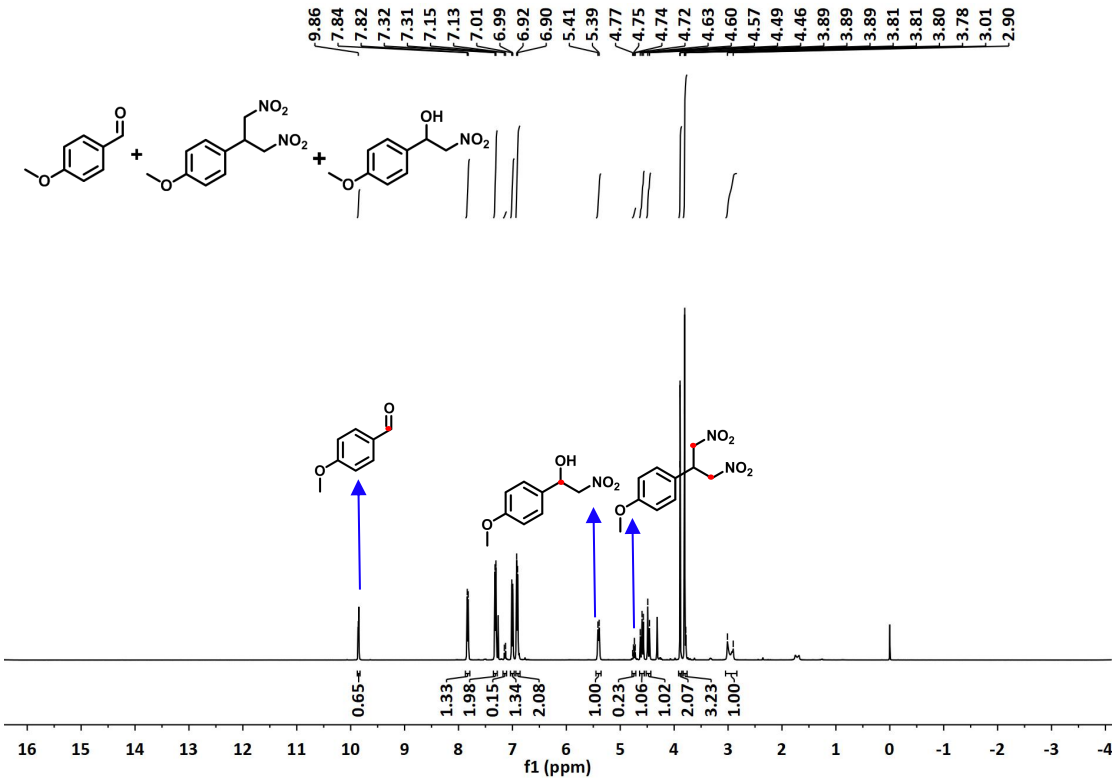
7.44
7.43
7.35
7.35
7.33
7.33
7.31
7.31
7.04
7.03
7.02
7.01
7.00
6.99
6.92
6.92
6.90
6.90
5.66
5.65
5.64
5.63
5.63
5.62
5.61
4.67
4.66
4.64
4.63
4.60
4.58
4.57
4.55
3.94
3.89
3.15
3.14
3.13
3.12
3.12
OH
NO2
O
1.02
1.01
1.05
1.02
1.00
2.09
3.11
0.94
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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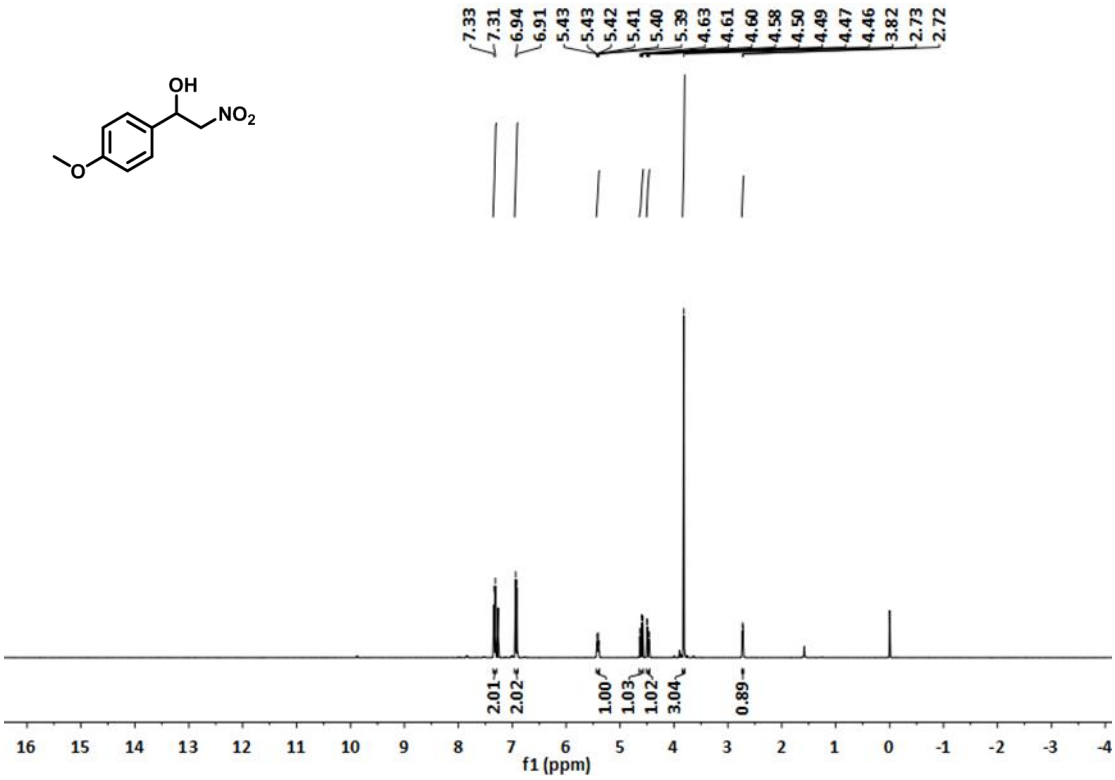
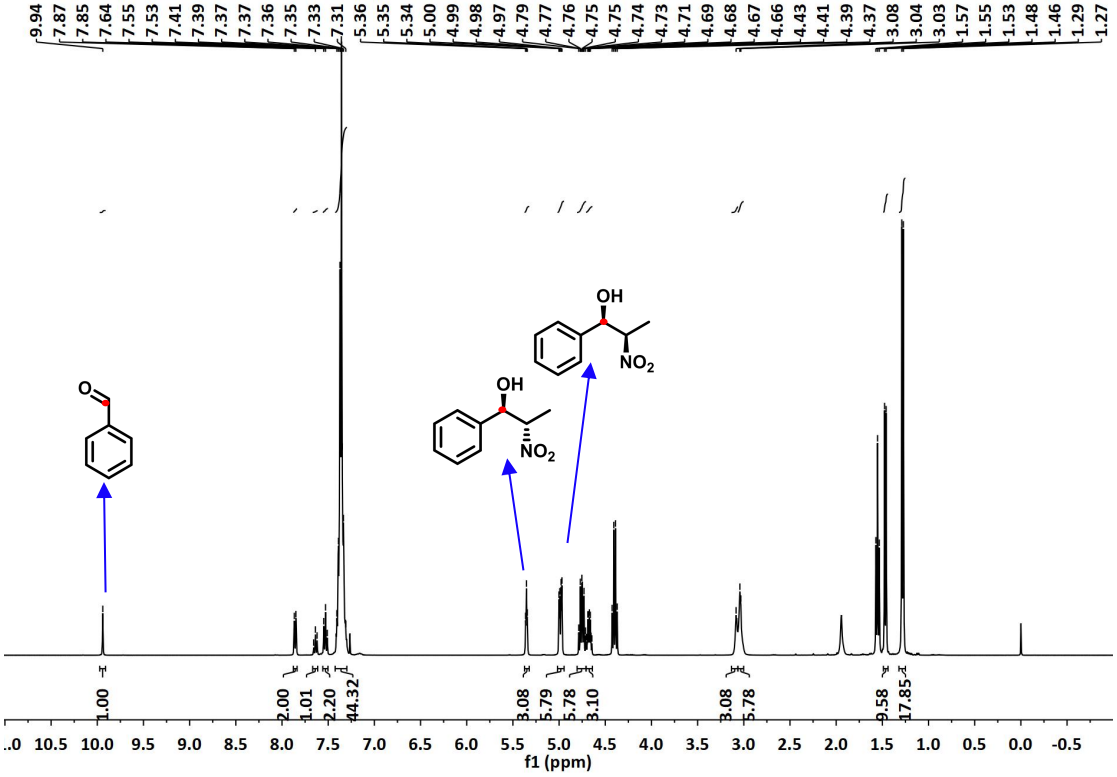
7.84
7.82
7.32
7.31
7.15
7.13
7.01
6.99
6.92
6.90
5.41
5.39
4.77
4.75
4.74
4.72
4.63
4.60
4.57
4.49
4.46
3.89
3.89
3.89
3.81
3.81
3.80
3.78
3.01
2.90
0.65
1.33
1.98
0.15
1.34
2.08
1.00
0.23
1.06
1.02
2.07
3.23
1.00
f1 (ppm)


7.33
7.31
6.94
6.91
5.43
5.43
5.42
5.41
5.40
5.39
4.63
4.61
4.60
4.58
4.50
4.49
4.47
4.46
3.82
2.73
2.72
2.01
2.02
1.00
1.03
1.02
3.04
0.89
f1 (ppm)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7.85
7.64
7.55
7.53
7.41
7.39
7.37
7.37
7.36
7.35
7.33
7.31
5.36
5.35
5.34
5.00
4.99
4.98
4.97
4.79
4.77
4.76
4.75
4.75
4.74
4.73
4.71
4.69
4.68
4.67
4.66
4.43
4.41
4.39
4.37
3.08
3.04
3.03
1.57
1.55
1.53
1.48
1.46
1.29
1.27
O
OH
NO2
OH
NO2
1.00
2.00
1.01
2.20
44.32
3.08
5.79
5.78
3.10
3.08
5.78
9.58
17.85
..0 10.5 10.0 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)