

Supporting information

Magnetic MIL-101-SO₃H: A highly efficient bifunctional nanocatalyst for the synthesis of 1,3,5-triarylbenzenes and 2,4,6-triaryl pyridines

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spectral data

1,3,5-Triphenylbenzene (2a), C₂₄H₁₈, white solid (0.28 g, 90 %), FT-IR (KBr) cm⁻¹: 1591, 1440, 1410, 871, 751, 695. ¹H NMR (300.13 MHz, CDCl₃), δ 7.82 (s, 3H), 7.75 (d, J=6.9 Hz, 6H), 7.51 (t, J=6.9 Hz, 6H), 7.42 (d, J=7.2 Hz, 3H).

1,3,5-Tri(*p*-tolyl) benzene (2b), C₂₇H₂₄, yellow solid (0.30 g, 85 %), FT-IR (KBr) cm⁻¹: 3020, 2965 1590, 1513, 1450, 1185, 871, 1060, 807, 735, 720. ¹H NMR (300.13 MHz, CDCl₃), δ 7.80 (s, 3H), 7.73 (d, J=8 Hz, 6H), 7.56 (d, J=8 Hz, 6H), 2.32 (s, 9H).

1,3,5-Tris(4-bromophenyl)benzene(2c), C₂₄H₁₅Br₃, yellow solid (0.32, 80%), FT-IR (KBr) cm⁻¹: 3023, 2968 1592, 1515, 1452, 1186, 873, 1064, 810, 738, 723. ¹H NMR (300.13 MHz, CDCl₃), δ 7.68 (s, 3H), 7.60 (d, J=8.5 Hz, 6H), 7.53 (d, J=8.5, 6H).

1,3,5-Tris(4-chlorophenyl)benzene (2d), C₂₄H₁₅Cl₃, yellow solid (0.30, 80%), FT-IR (KBr) cm⁻¹: 3025, 2967, 1591, 1516, 1453, 1184, 875, 1062, 813, 738, 723. ¹H NMR (300.13 MHz, CDCl₃), δ 7.69 (s,3H), 7.60 (d, J=8.5 Hz, 6H), 7.45 (d, J=8.5 Hz, 6H).

1,3,5-Tris(4-fluorophenyl)benzene (2e), $C_{24}H_{15}Cl_3$, yellow solid (0.29, 80%), FT-IR (KBr) cm^{-1} : 3025, 2963, 1593, 1512, 1450, 1183, 871, 1063, 811, 738, 723. 1H NMR (300.13 MHz, $CDCl_3$), δ 7.69 (s, 3H), 7.60 (d, $J=8.5$ Hz, 6H), 7.53 (d, $J=8.5$ Hz, 6H).

1,3,5-Tris(4-methoxyphenyl)benzene (2f), yellow solid (0.27, 75%), FT-IR (KBr) cm^{-1} : 3025, 2985, 1591, 1516, 1453, 1184, 875, 1062, 813, 738, 723. 1H NMR (300.13 MHz, $CDCl_3$), δ 7.65 (s, 3H), 7.61 (d, $J=9$ Hz, 6H), 6.99 (d, $J=8.5$ Hz, 6H).

2,4,6-Triphenylpyridine (4a), $C_{23}H_{17}N$, white solid (0.28 g, 90 %), FT-IR (KBr) cm^{-1} : 1450-1600, 759, 691 1H NMR (300.13 MHz, $CDCl_3$), δ 8.24 (d, $J=7.5$ Hz, 4H), 7.90 (s, 2H), 7.72 (d, $J=6.9$, 2H), 7.21-7.90 (9H, m).

2,6-Diphenyl-4-(*p*-tolyl)pyridine (4b), $C_{24}H_{19}N$, white solid (0.27 g, 85 %), FT-IR (KBr) cm^{-1} : 3020, 2950, 1450-1600, 759, 692. 1H NMR (300.13 MHz, $DMSO-d_6$), δ 8.2 (d, 4H), 7.9 (s, 2H), 7.7 (d, 2H), 7.2-7.9 (9H, m, H-Ar), 2.48 (s, 3H).

4-(4-Chlorophenyl)-2,6-diphenylpyridine (4c), yield: 95, $C_{23}H_{16}ClN$, white solid, FT-IR (KBr) cm^{-1} : 3061, 1599, 1545, 1489, 775, 692, 1H NMR (300.13 MHz, $DMSO-d_6$), δ 8.12 (d, $J=7.2$ Hz, 4H), 8.14 (s, 2H), 7.91 (d, $J=8$ Hz, 2H), 7.41 (d, $J=6.8$ Hz, 2H), 7.28-7.36 (m, 6H).

4-Phenyl-2,6-di-*p*-tolylpyridine (4d), $C_{25}H_{21}N$, white solid (0.29 g, 85 %), FT-IR (KBr) cm^{-1} : 3021, 2952, 1450, 1600, 758, 695. 1H NMR (300.13 MHz, $CDCl_3$), δ 8.13 (d, $J=7.8$ Hz, 4H), 7.87 (s, 2H), 7.76 (d, $J=7.2$ Hz, 2H), 7.47-7.58 (m, 3H), 7.34 (d, $J=7.8$ Hz, 4H), 2.46 (s, 6H).

2,4,6-Tri-*p*-tolylpyridine (4e), $C_{26}H_{23}N$, white solid (0.28, 80 %), FT-IR (KBr) cm^{-1} : 3024, 2952, 1453, 1602, 758, 697. 1H NMR (300.13 MHz, $CDCl_3$), δ 8.13 (d, $J=7.8$ Hz, 4H), 7.87 (s, 2H), 7.79 (d, $J=7.8$ Hz, 2H), 7.34-7.37 (m, 6H), 2.47 (s, 9H).

2,6-Bis(4-chlorophenyl)-4-phenylpyridine (4f), $C_{23}H_{15}Cl_2N$ (0.32, 85 %), FT-IR (KBr) cm^{-1} : 3052, 1489, 1486, 1597, 1524, 760, 694, 1H NMR (300.13 MHz, $DMSO-d_6$), δ 8.36 (d, $J=8.4$ Hz, 4H), 8.23 (s, 2H), 8.04 (d, $J=7.6$ Hz, 2H), 7.50- 7.61 (m, 7H), ^{13}C NMR (75.47 MHz, $DMSO-d_6$).

2,6-Bis(4-chlorophenyl)-4-(4-methoxyphenyl)pyridine (4g), $C_{24}H_{17}Cl_2NO$ (0.32, 80 %), FT-IR (KBr) cm^{-1} : 3052, 1489, 1486, 1597, 1524, 760, 694, 1H NMR (300.13 MHz, $DMSO-d_6$), δ 8.29 (d, $J=8.4$ Hz, 4H), 8.01 (s, 2H), 7.50 (d, $J=7.6$ Hz, 4H), 7.45 (d, $J=6.8$ Hz, 2H), 7.09 (d, $J=8$ Hz, 2H)

Sample: 3Ph-Bn
1H NMR

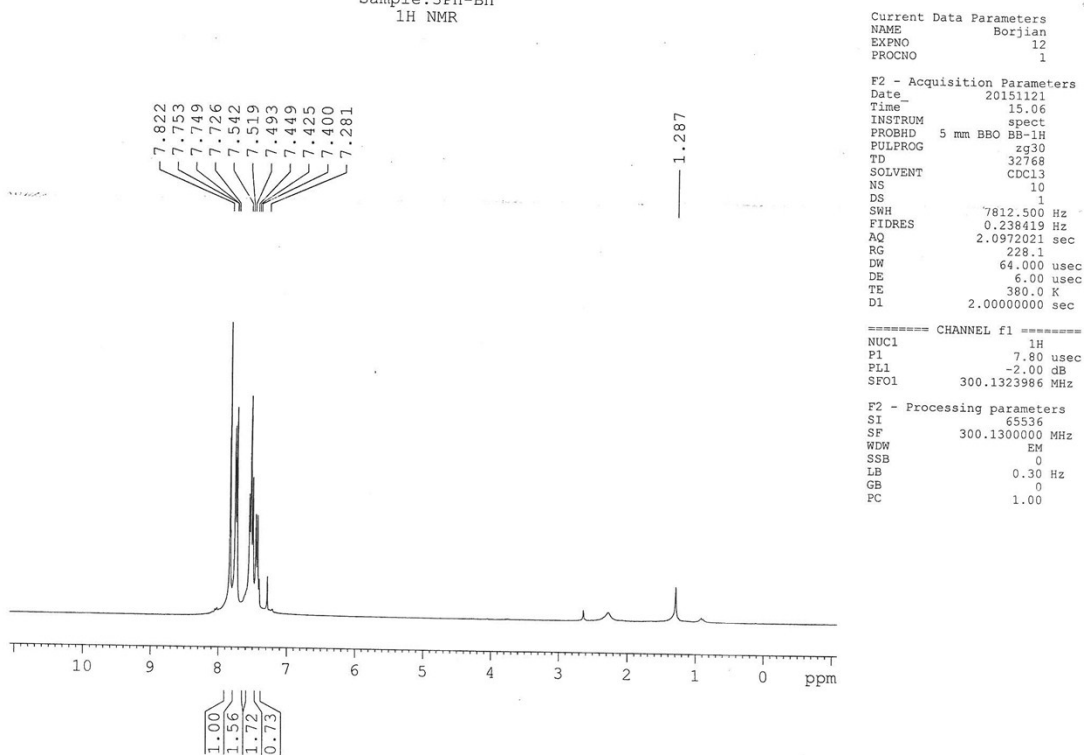


Figure 1. ¹H NMR spectra of 1,3,5-triphenylbenzene (2a)

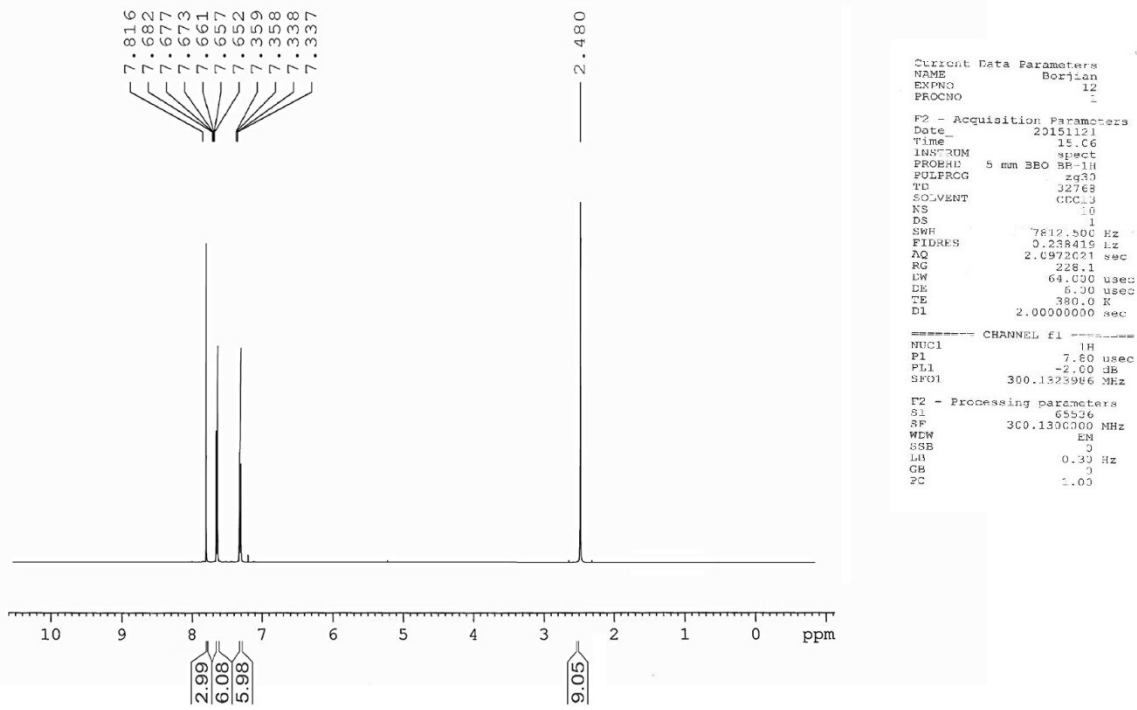


Figure 2. ^1H NMR spectra of 1,3,5-tri(p-tolyl)benzene (2b)

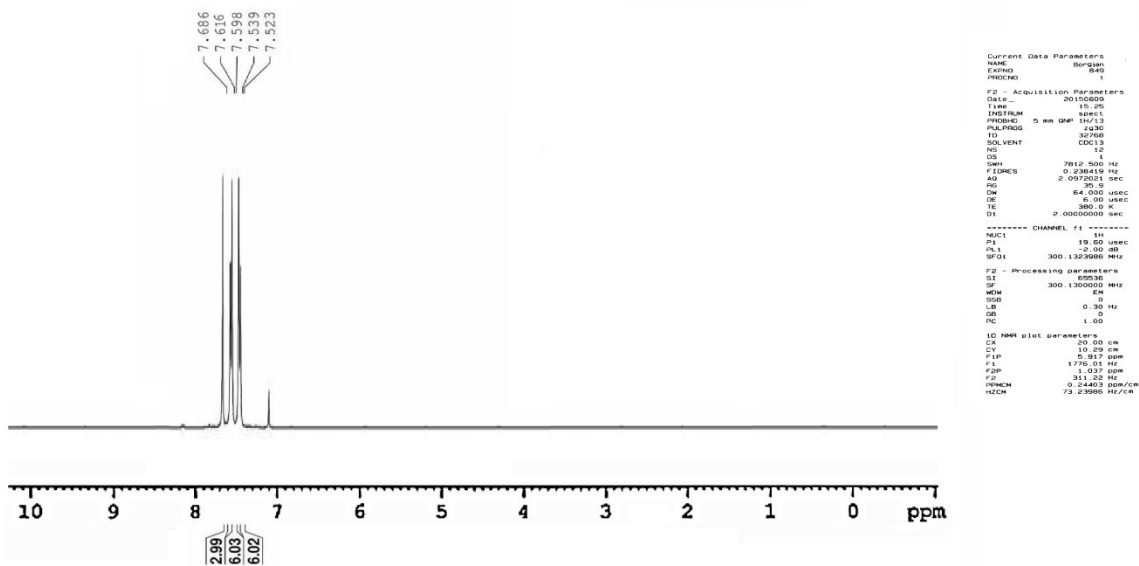


Figure 3. ^1H NMR spectra of 1,3,5-tris(4-bromophenyl)benzene (2c)

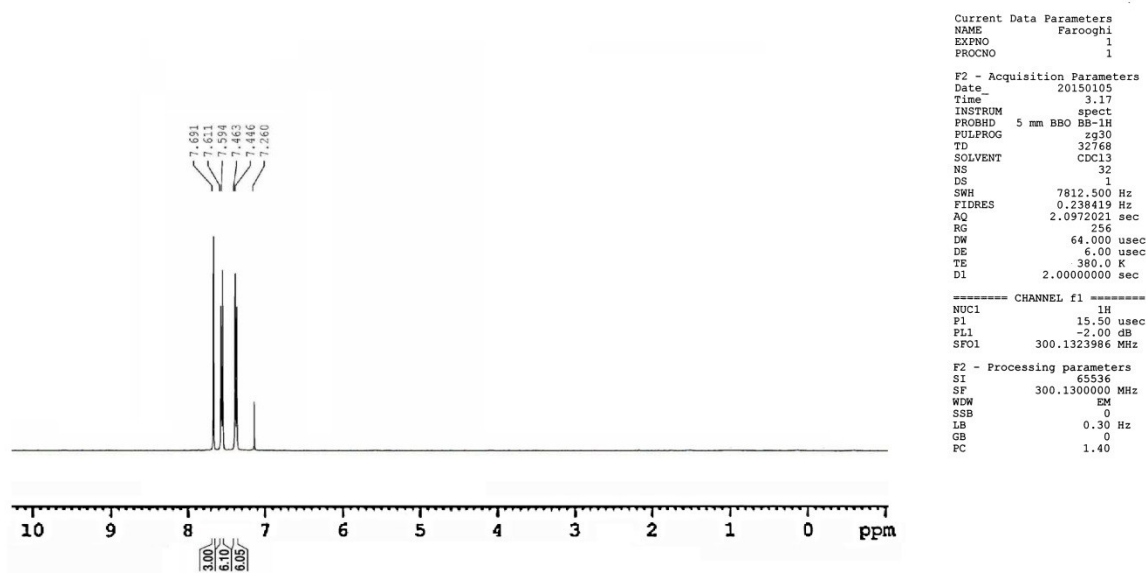


Figure 4. ¹H NMR spectra of 1,3,5-tris(4-chlorophenyl)benzene (2d)

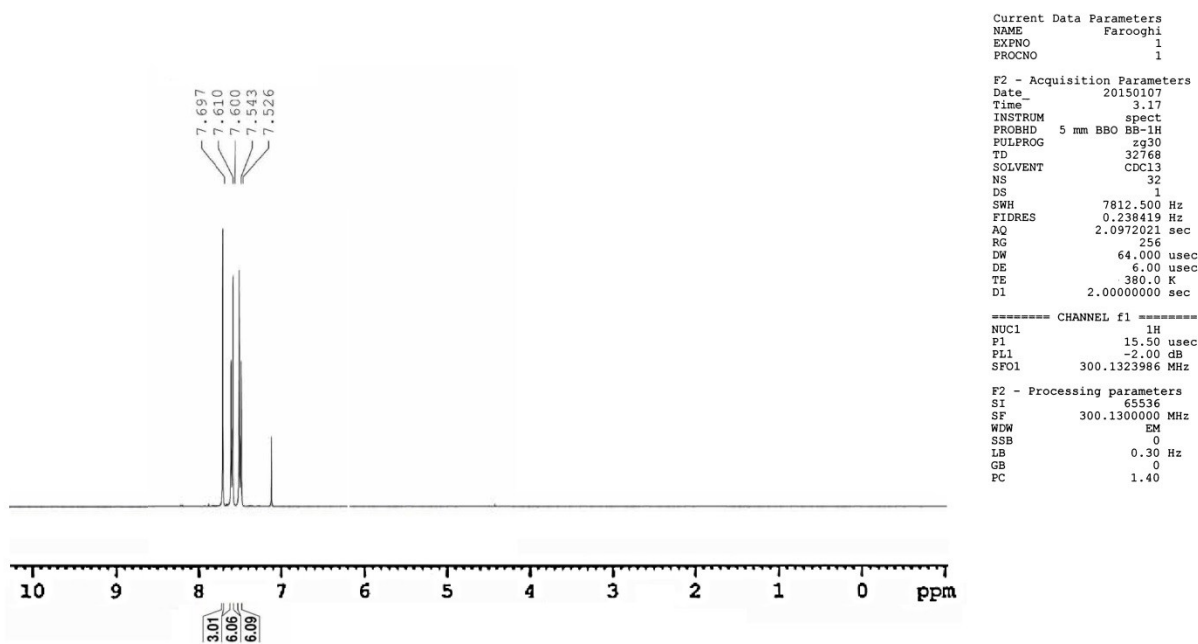


Figure 5. ¹H NMR spectra of 1,3,5-tris(4-fluorophenyl)benzene (2e)

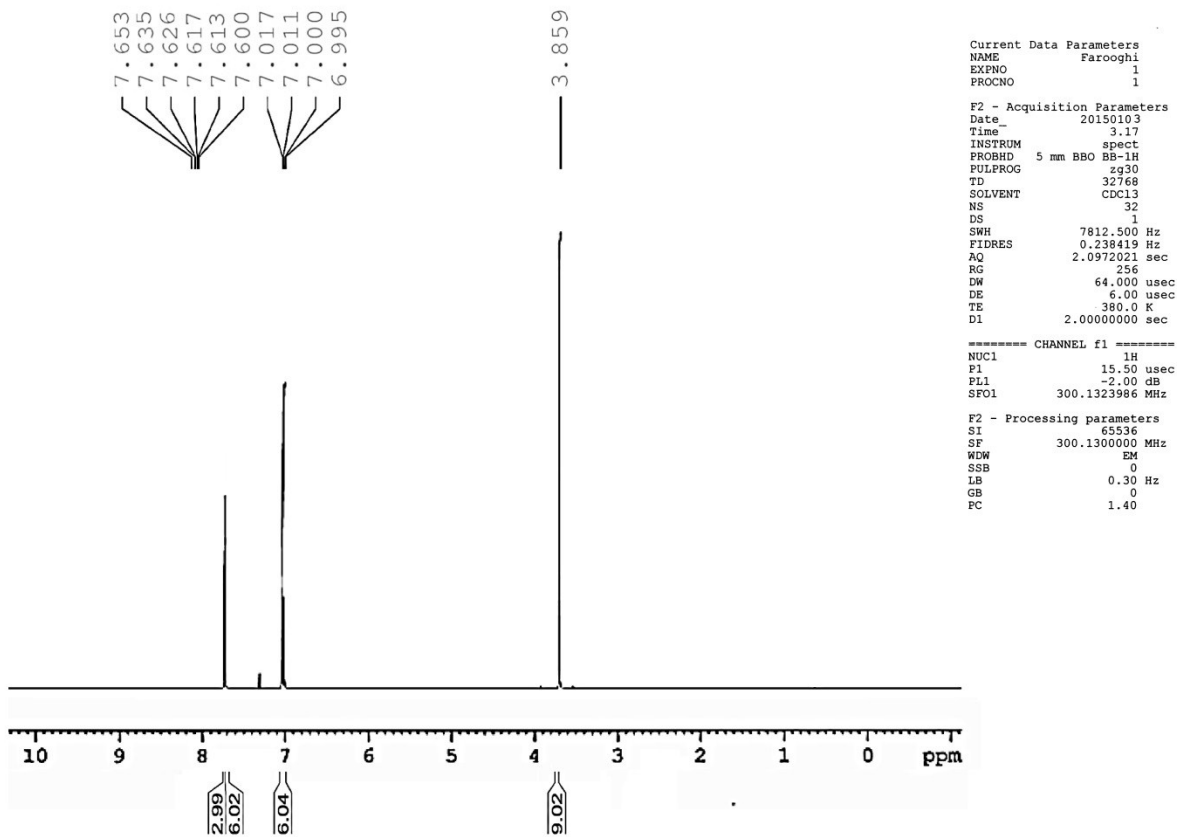


Figure 6. ¹H NMR spectra of 1,3,5-tris(4-methoxyphenyl)benzene (2f)

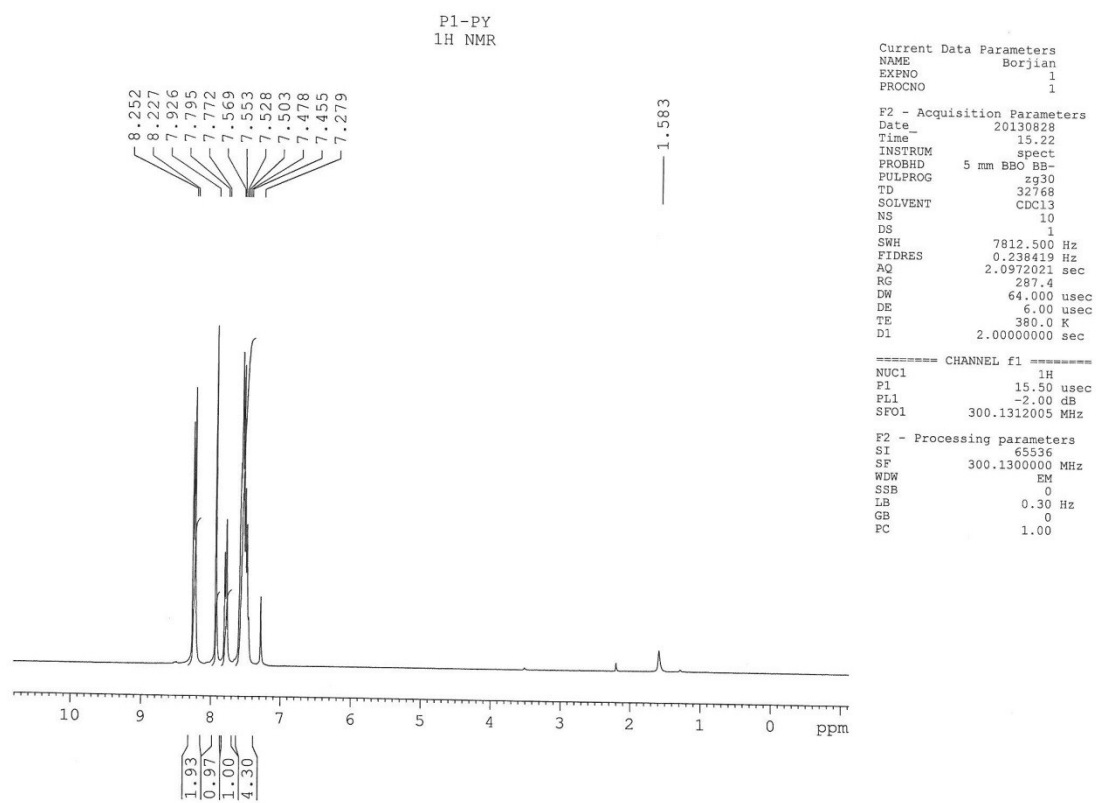


Figure 7. ^1H NMR spectra of 2,4,6-triphenyl pyridine (4a)

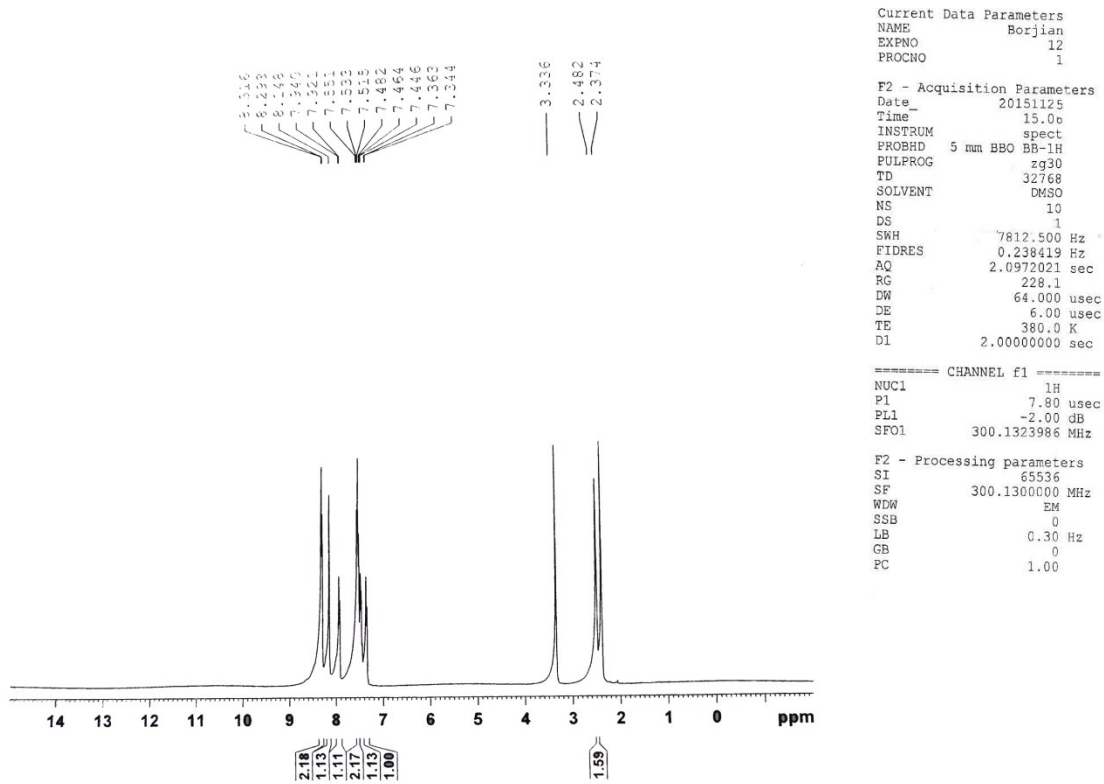


Figure 8. ¹H NMR spectra of 2,6-diphenyl-4-(p-tolyl)pyridine (4b)

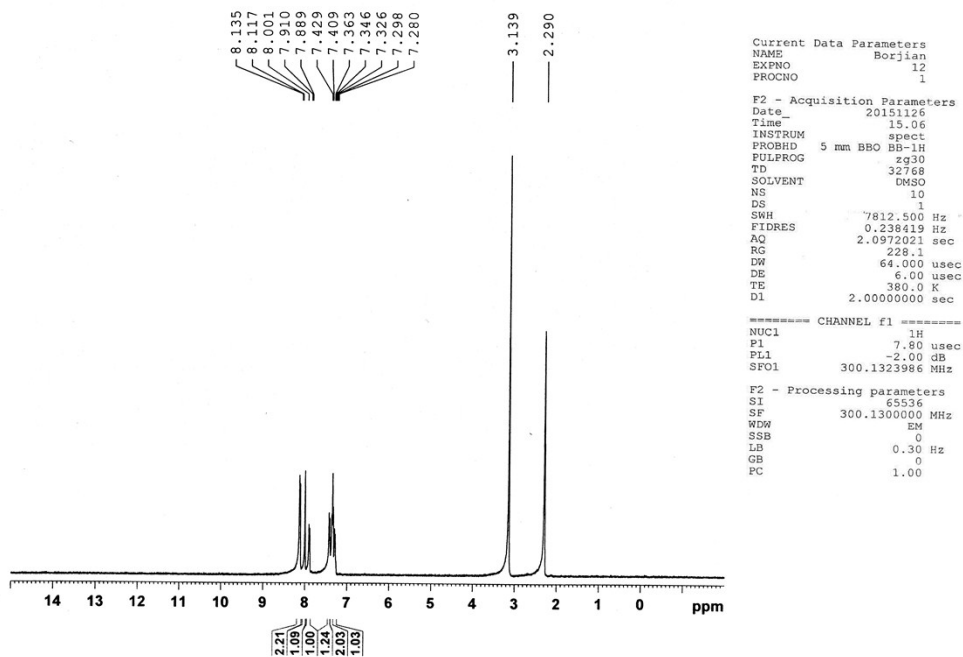


Figure 9. 4-(4-chlorophenyl)-2,6-diphenylpyridine (4c)

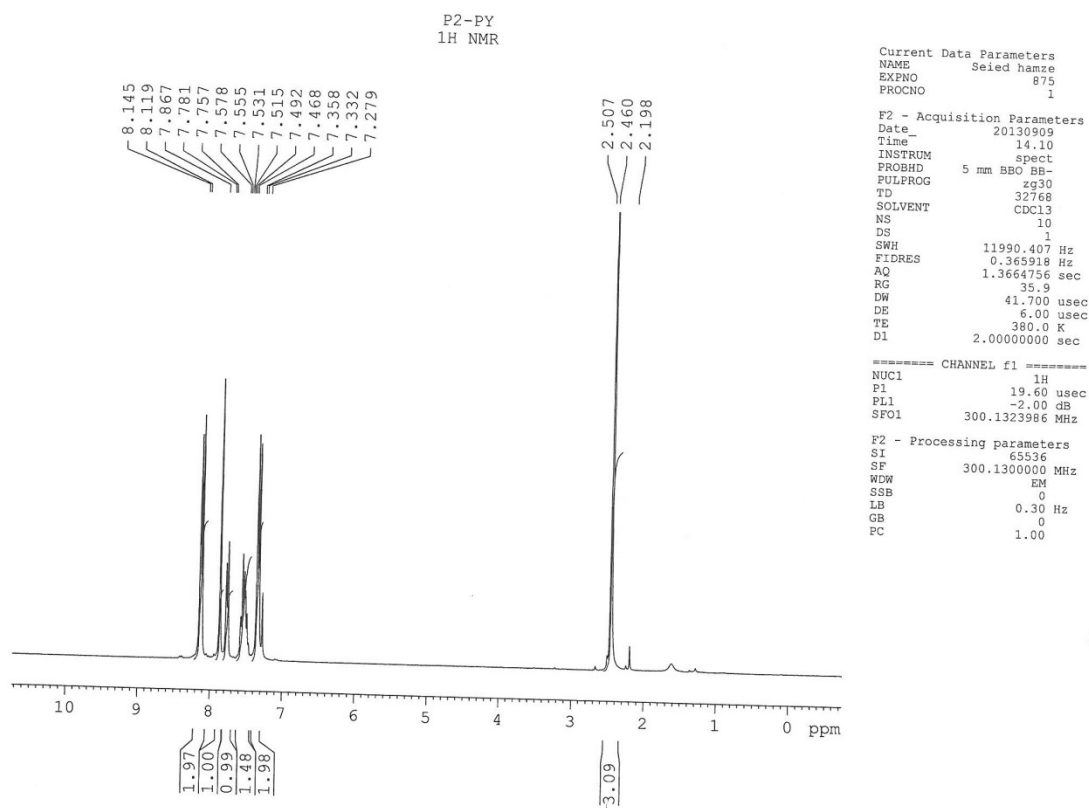


Figure 10. ^1H NMR spectra of 4-phenyl-2,6-di-p-tolylpyridine (4d)

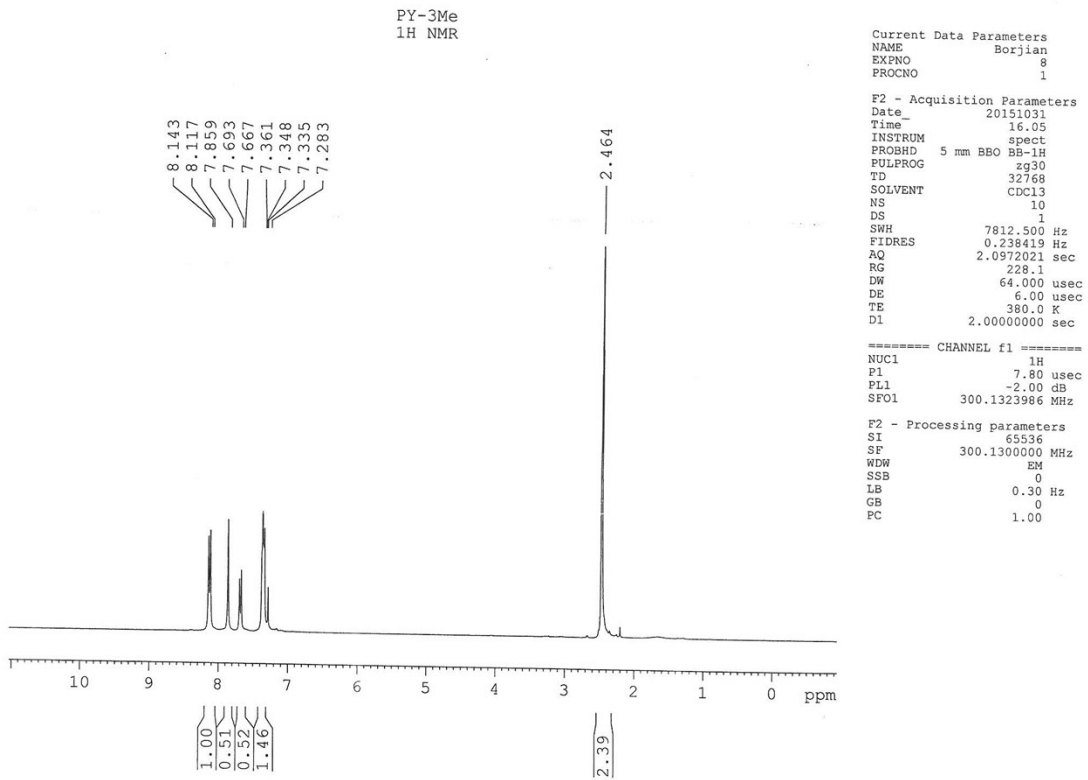


Figure 11. ¹H NMR spectra of 2,4,6-tri-p-tolylpyridine (4e)

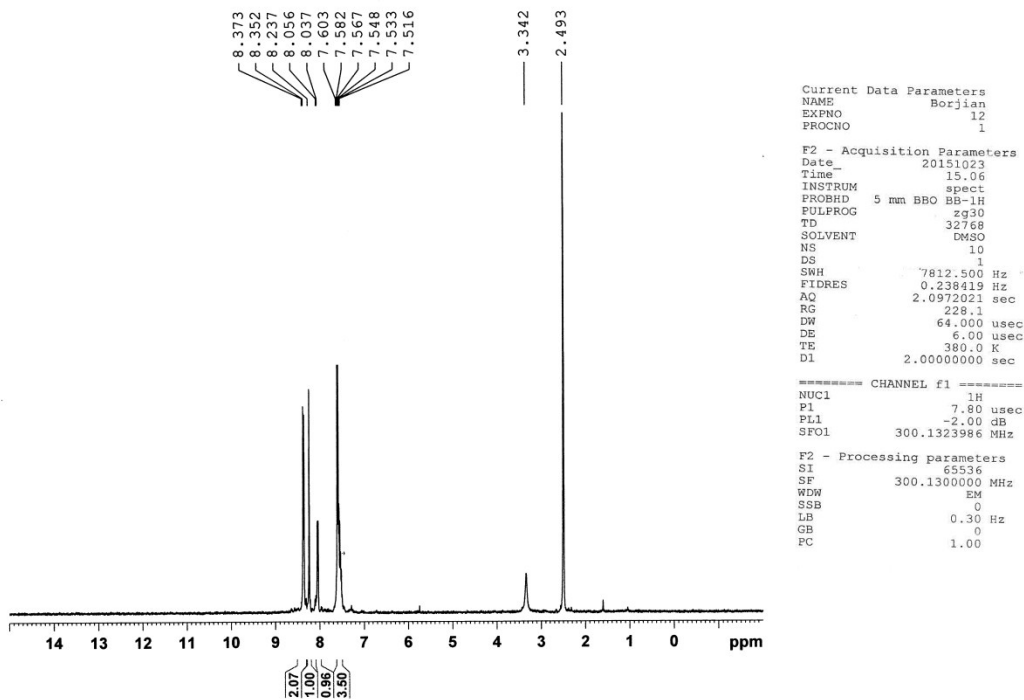


Figure 12. ¹H NMR spectra of 2,6-bis(4-chlorophenyl)-4-phenylpyridine (4f)

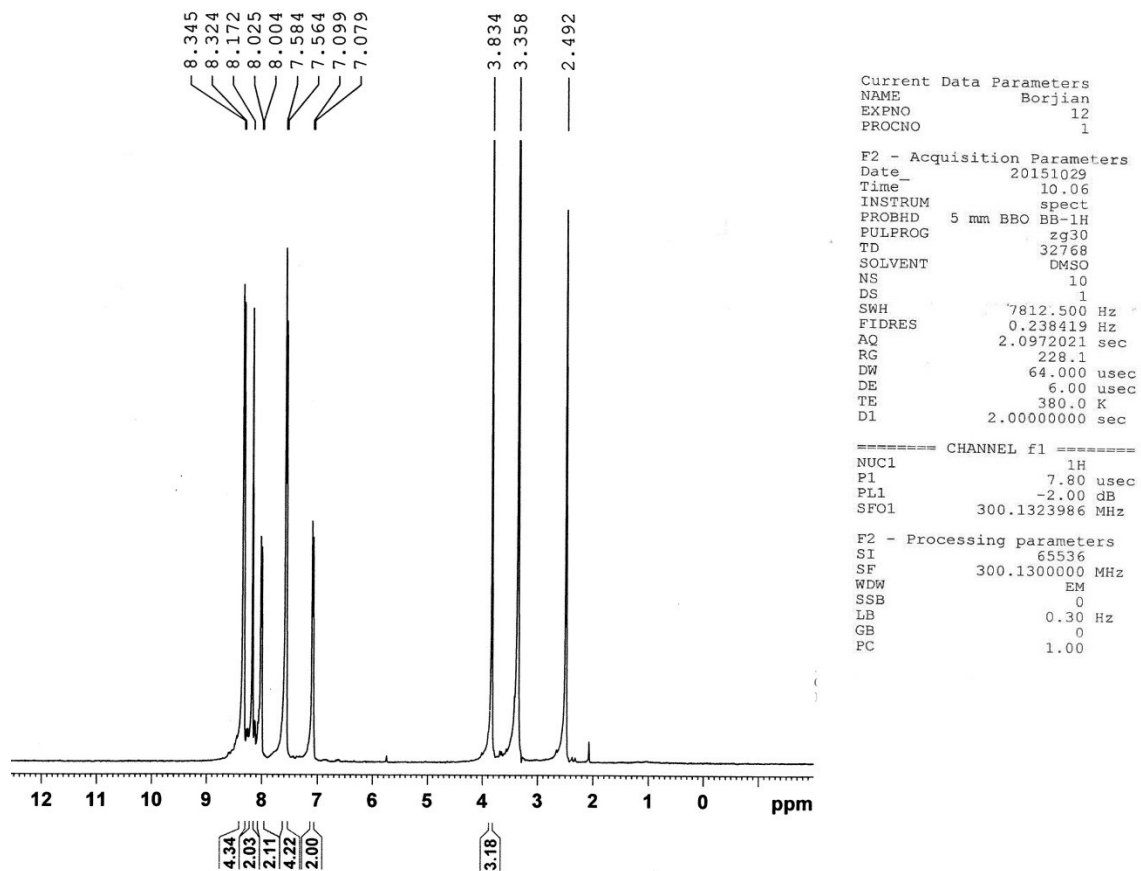


Figure 13. ¹H NMR spectra of 2,6-bis(4-chlorophenyl)-4-(4-methoxyphenyl)pyridine (4g)

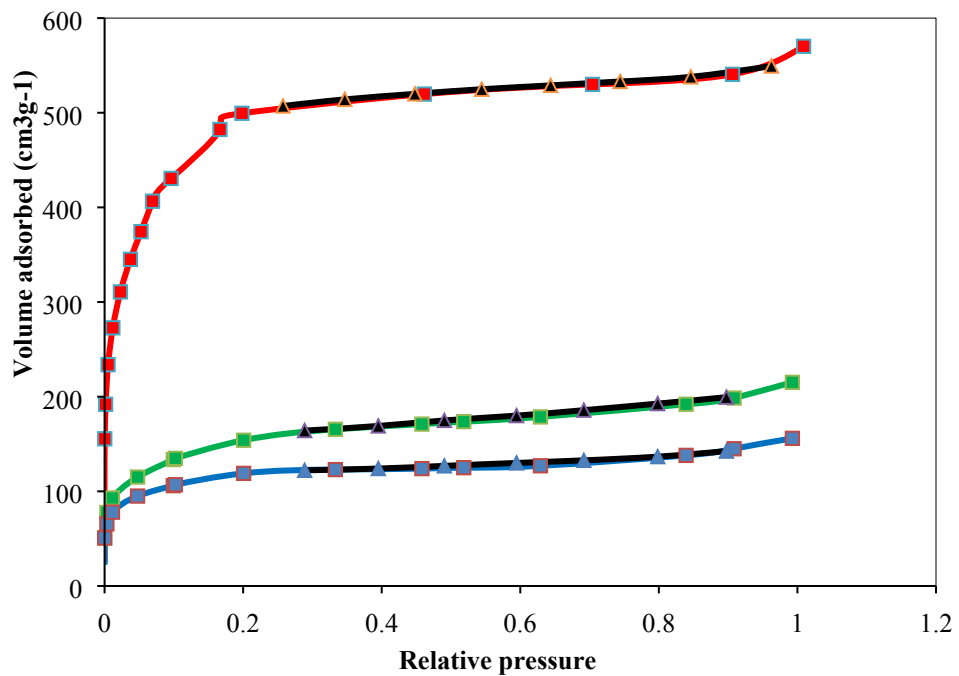


Figure 14. N₂ adsorption-desorption isotherms at 77 K for MIL-101(red),magnetic MIL-101 (green) and magnetic MIL-101-SO₃H nanocatalyst(blue)