Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Ru(II) and Ru(IV)-dmso complexes catalyzed efficient and selective aqueous phase nitrile hydration reactions under mild conditions

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Table S1. Crystallographic Data for Complex **1**, **2** and **3**.

	1	**2**	**3**
Empirical Formula	$C_6H_{18}Cl_2N_2O_2S_2Ru$	$C_8H_{21}Cl_2NO_3S_3Ru$	$C_6H_{21}Cl_3F_{6.13}NO_3PS_3Ru$
fw	386.31	447.41	606.20
crystal system	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	Pca21	Pbca
a, Å	11.661(2)	13.6347(3)	9.8582(4)
b, Å	8.5427(16)	10.9933(2)	17.8425(7)
c, Å	15.357(3)	11.3070(2)	22.8923(11)
α, deg	90	90	90
β, deg	109.46(2)	90	90
γ, deg	90	90	90
V, $Å^3$	1442.4(5)	1694.81(6)	4026.6(3)
Z	4	4	8
d_{calc}, g cm^{-3}	1.779	1.753	2.000
μ, mm^{-1}	1.732	1.608	1.628
T, K	293(2)	293(2)	293(2)
R_1 all	0.0721	0.0263	0.1058
R_1 [I > 2σ(I)]	0.0656	0.0246	0.0695
wR_2	0.1930	0.0620	0.1529
wR_2 [I > 2σ(I)]	0.1867	0.0609	0.1394
GOF on F^2	1.195	0.966	1.250

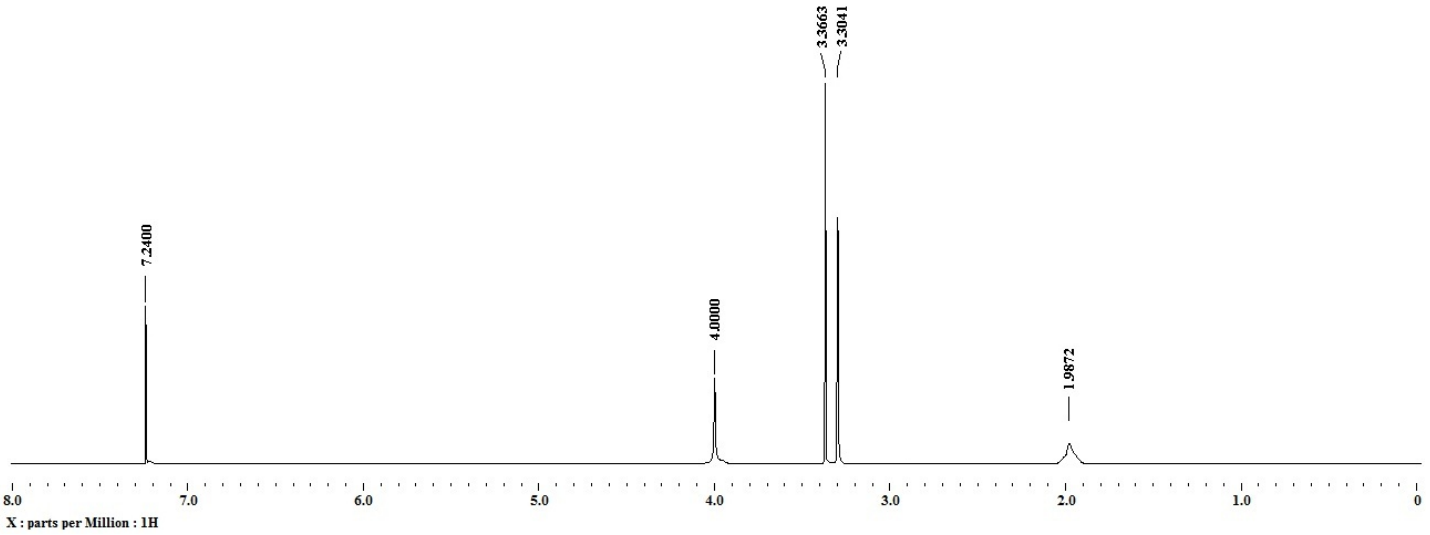


Figure S1. ^{1}H NMR spectrum of complex **1** in $CDCl_3$

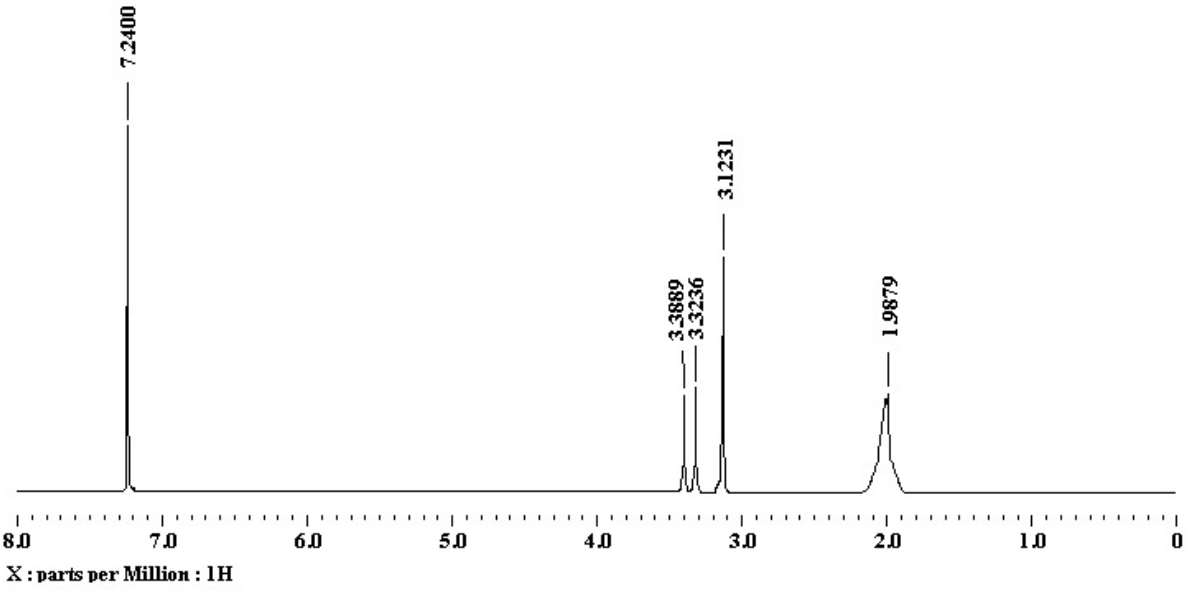


Figure S2. ^{1}H NMR spectrum of complex **2** in $CDCl_3$

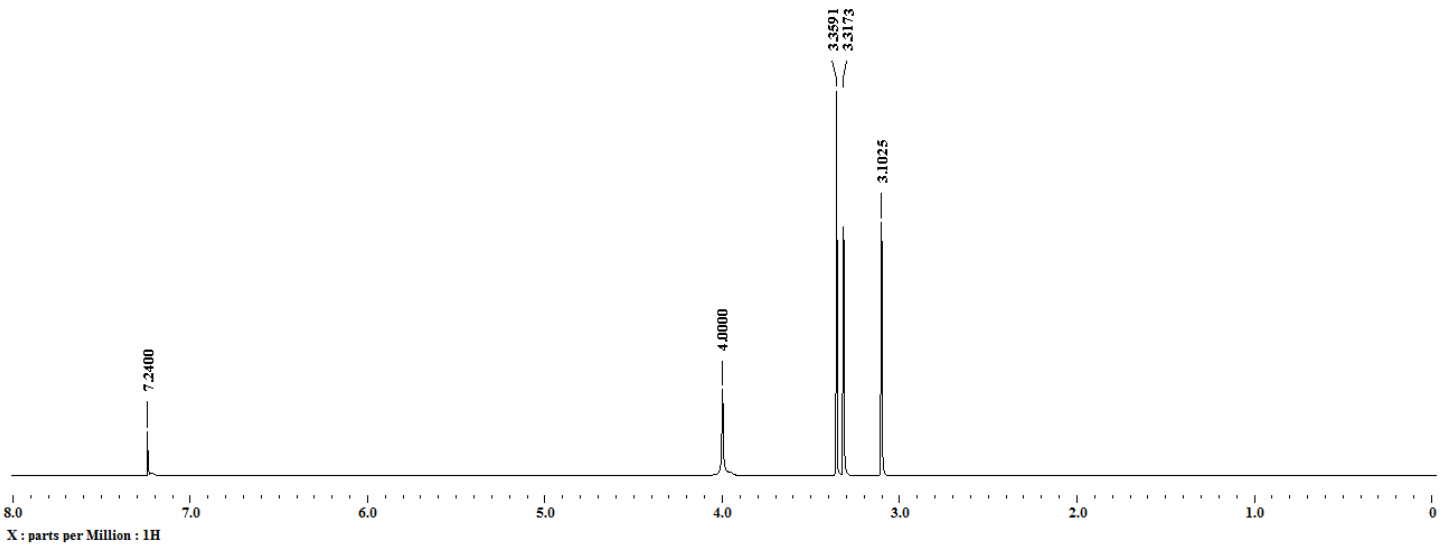


Figure S3. ^{1}H NMR spectrum of complex **3** in $CDCl_3$.

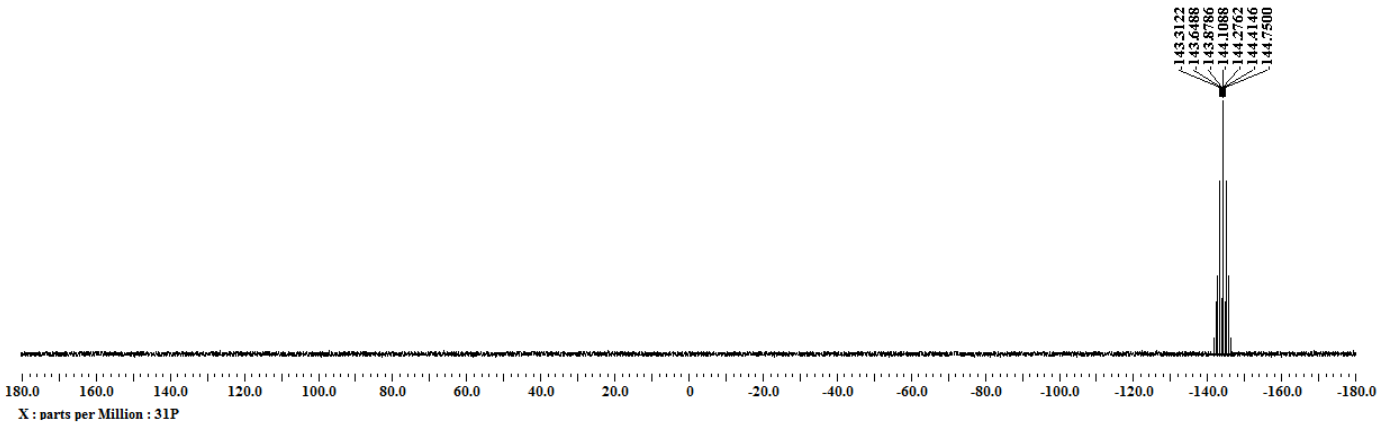


Figure S4. ^{31}P NMR spectrum of complex **3** in $CDCl_3$.

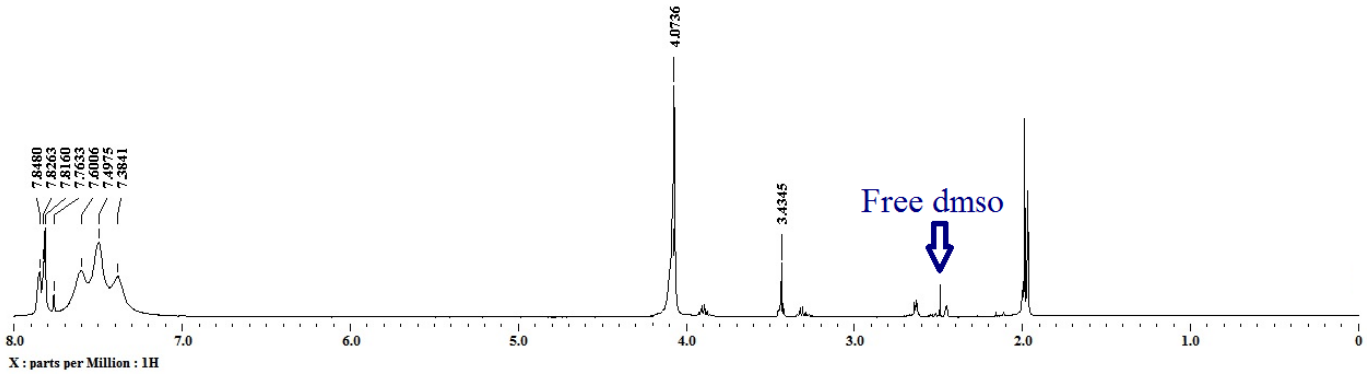


Figure S5. ^{1}H NMR spectrum of the reaction mixture for hydration of benzonitrile after 2 hours catalysed by complex **3** in D_2O.

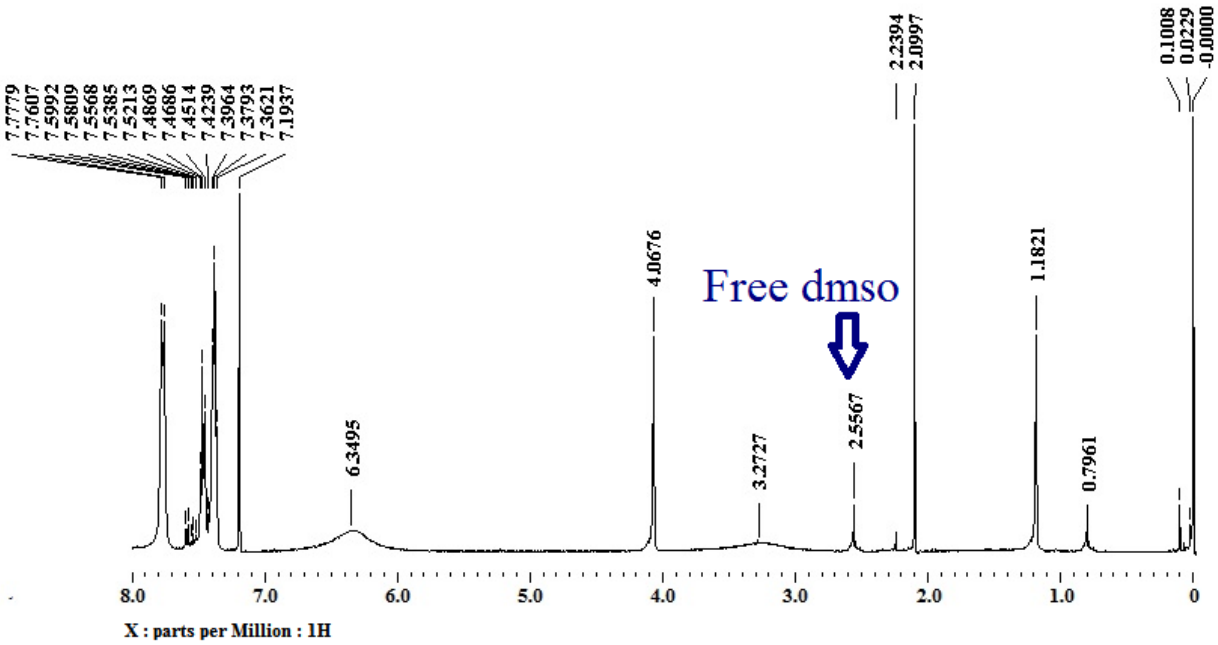


Figure S6. ^{1}H NMR spectrum of the reaction mixture for hydration of benzonitrile after 12 hours catalysed by complex **3** in D_2O.

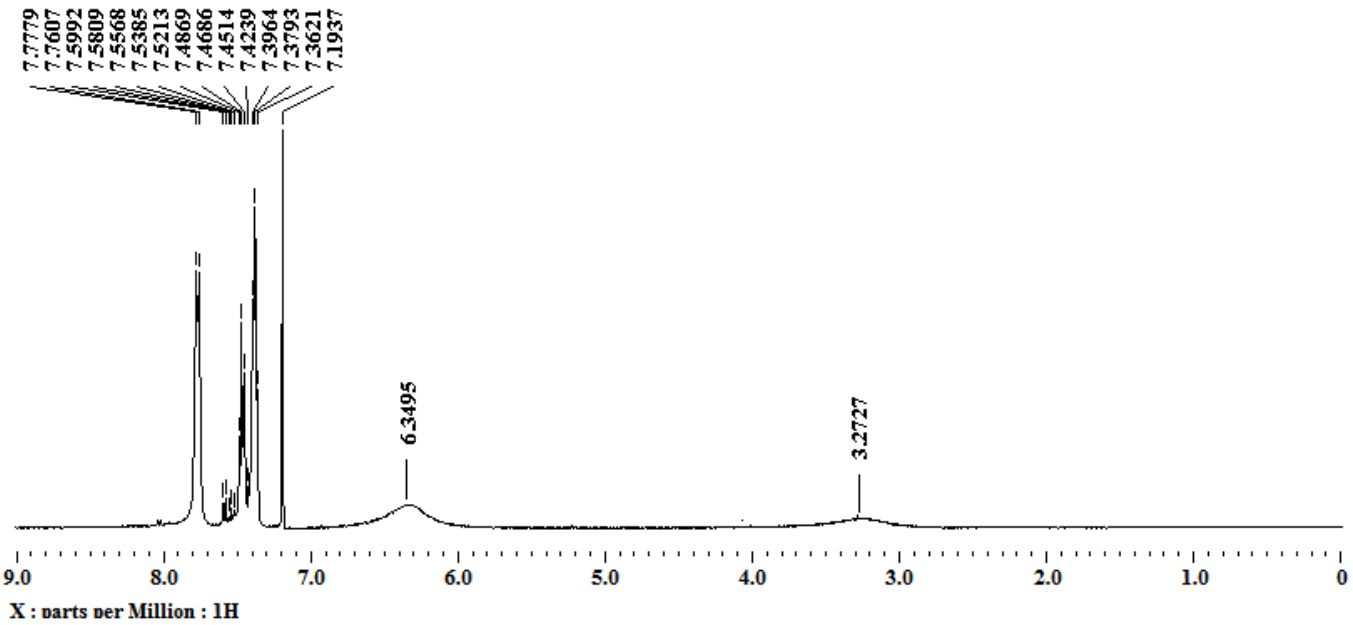


Figure S7. ^{1}H NMR spectrum of the reaction mixture for hydration of benzonitrile after 24 hours catalysed by complex **3** in D_2O.

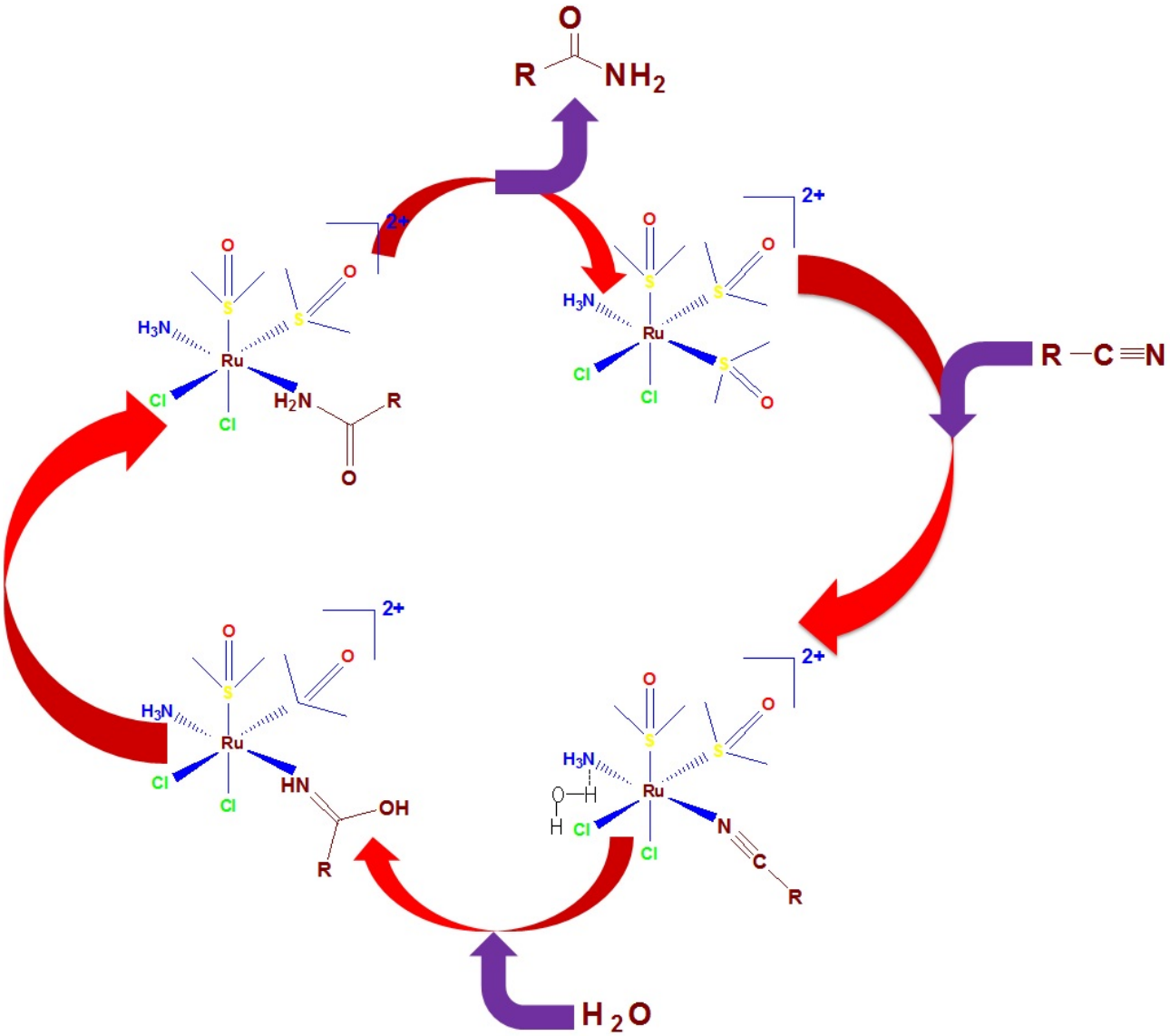


Figure S8. The proposed reaction mechanism for Ru(IV)/Ru(II) complex catalyzed hydration of nitrile with H_2O in air.

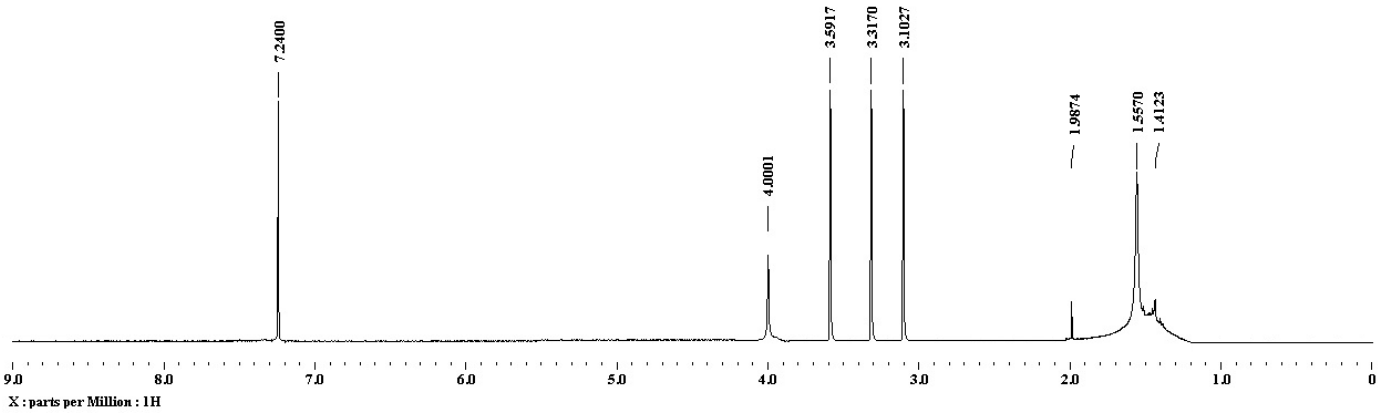
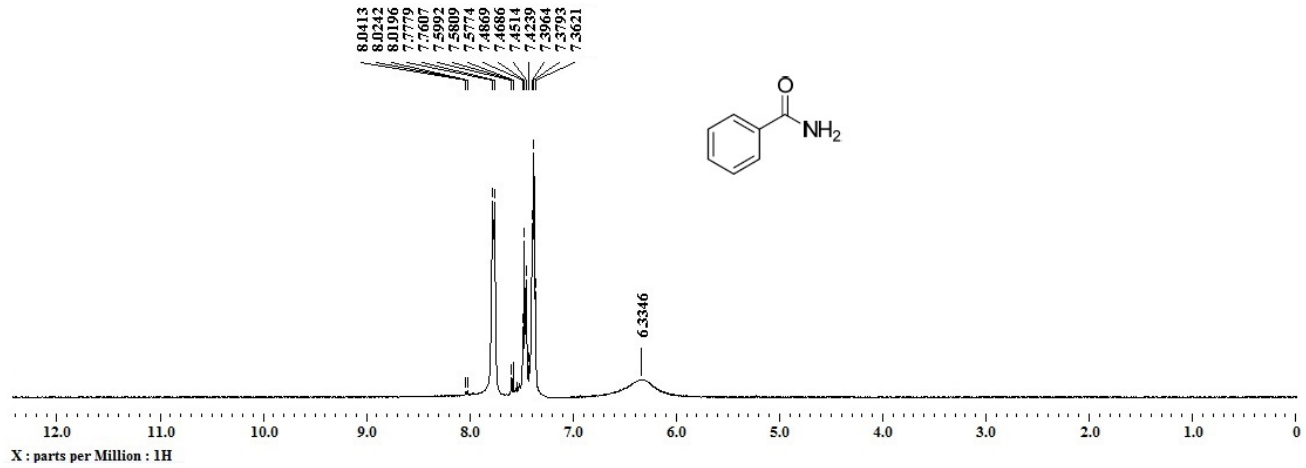
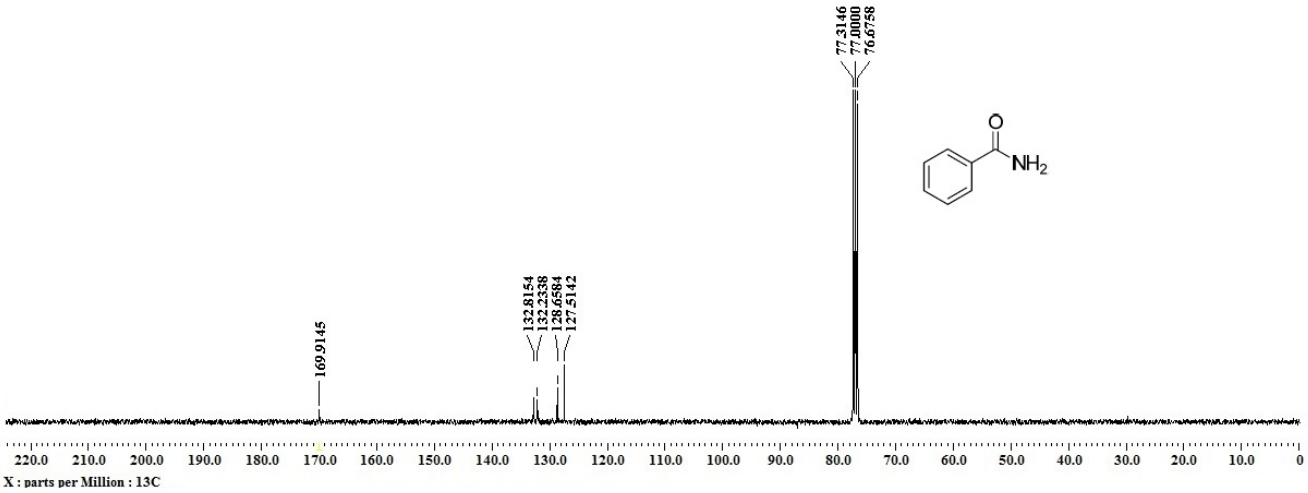


Figure S9. ^{1}H NMR spectrum of complex **3** in aqueous solution after 4 weeks in $CDCl_3$ solution.

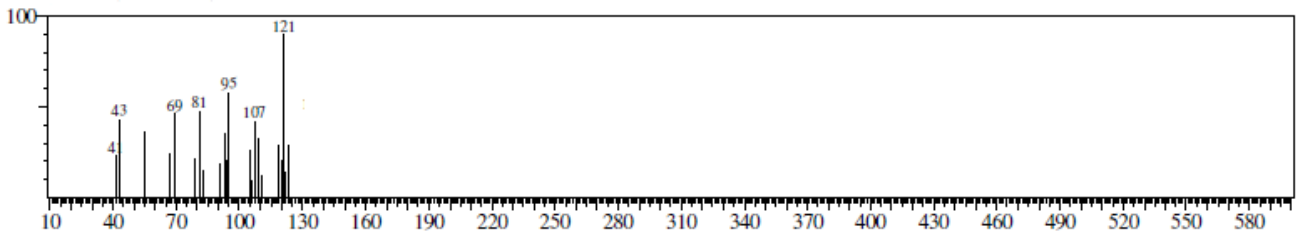
Characterization of the Products and References

Benzamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, 1H, J = 6.8 Hz), 7.77-7.57 (m, 2H, J = 7.0 Hz), 7.48-7.36 (m, 2H, J = 7.3 Hz), 6.33 (b, 2H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 169.91, 132.81, 132.23, 128.65, 127.51 ppm; MS (EI): m/z (%): 121(M^+).[1]

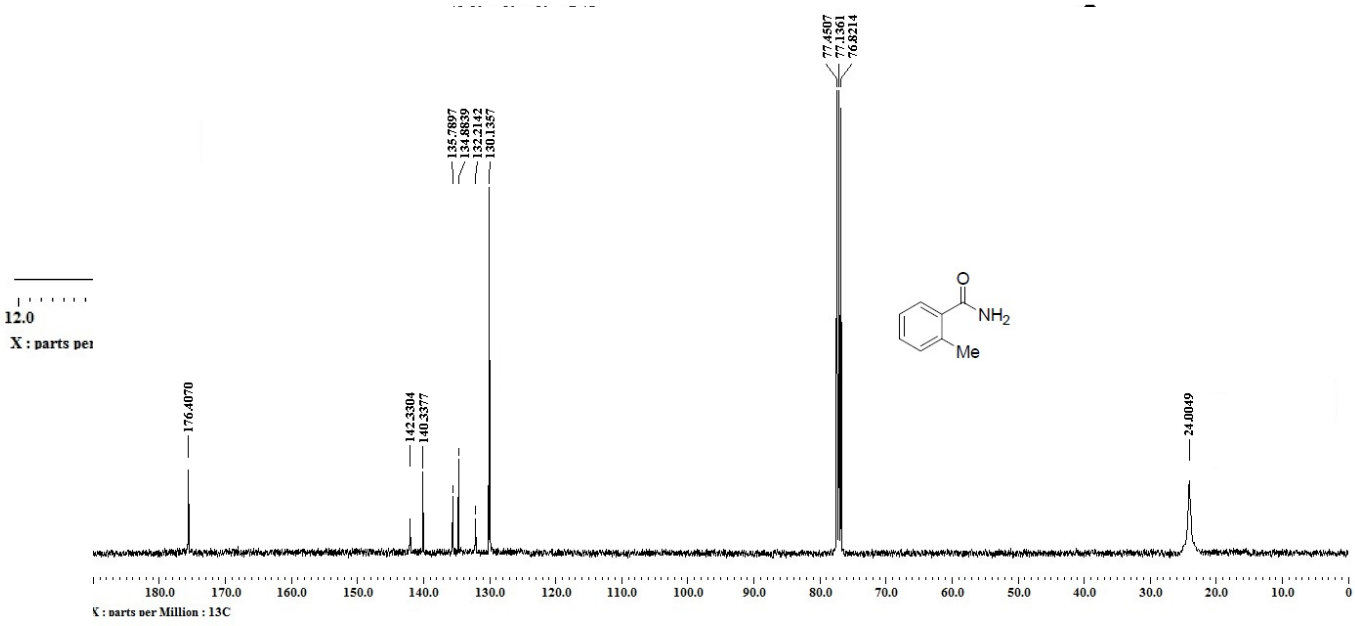




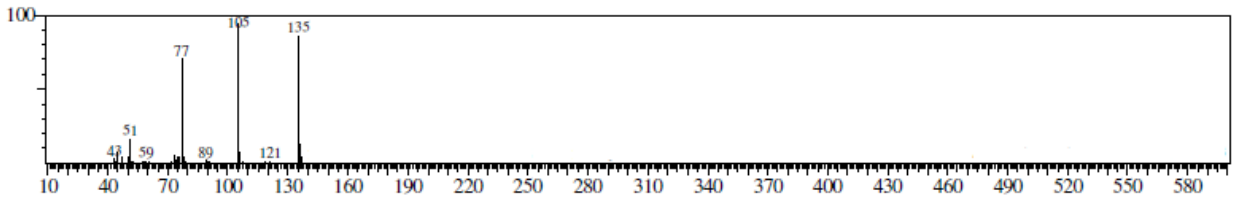
GC chromatogram for hydration of benzonitrile after 24 hours (Benzamide 8.23 min)



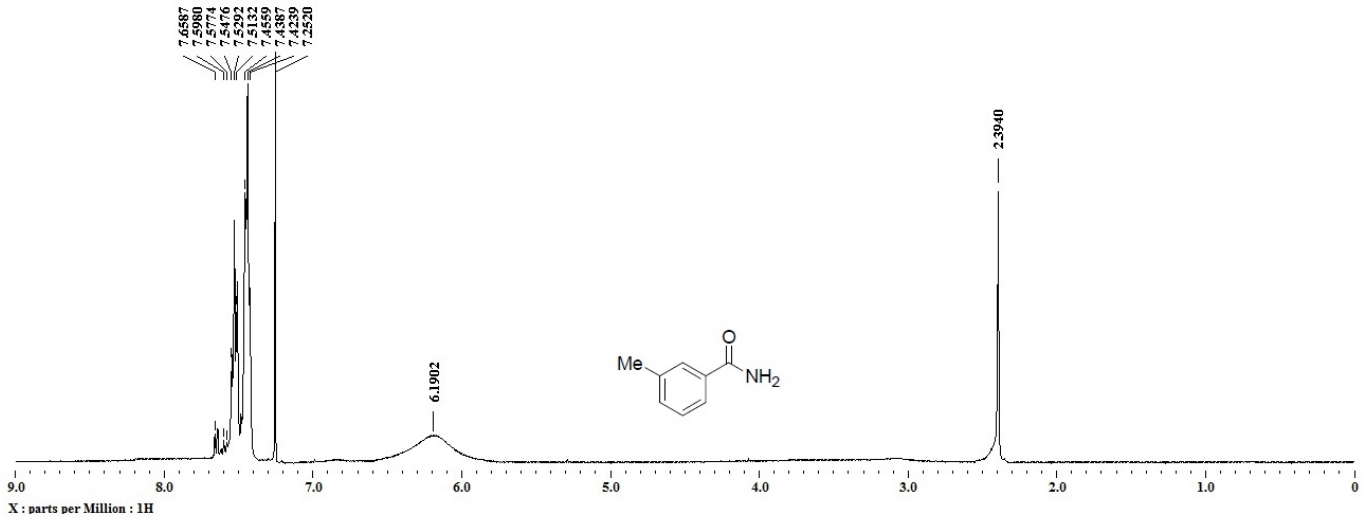
2-Methylbenzamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (s, 1H), 7.36-7.30 (m, 3H, J = 5.9 Hz), 7.24-7.21 (m, 2H, J = 6.8 Hz), 6.34 (b, 2H), 2.37(s, 3H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 176.40, 142.33, 140.33, 135.78, 134.88, 132.21, 130.13, 24.00 ppm; MS (EI): m/z (%): 135(M^+).[2]

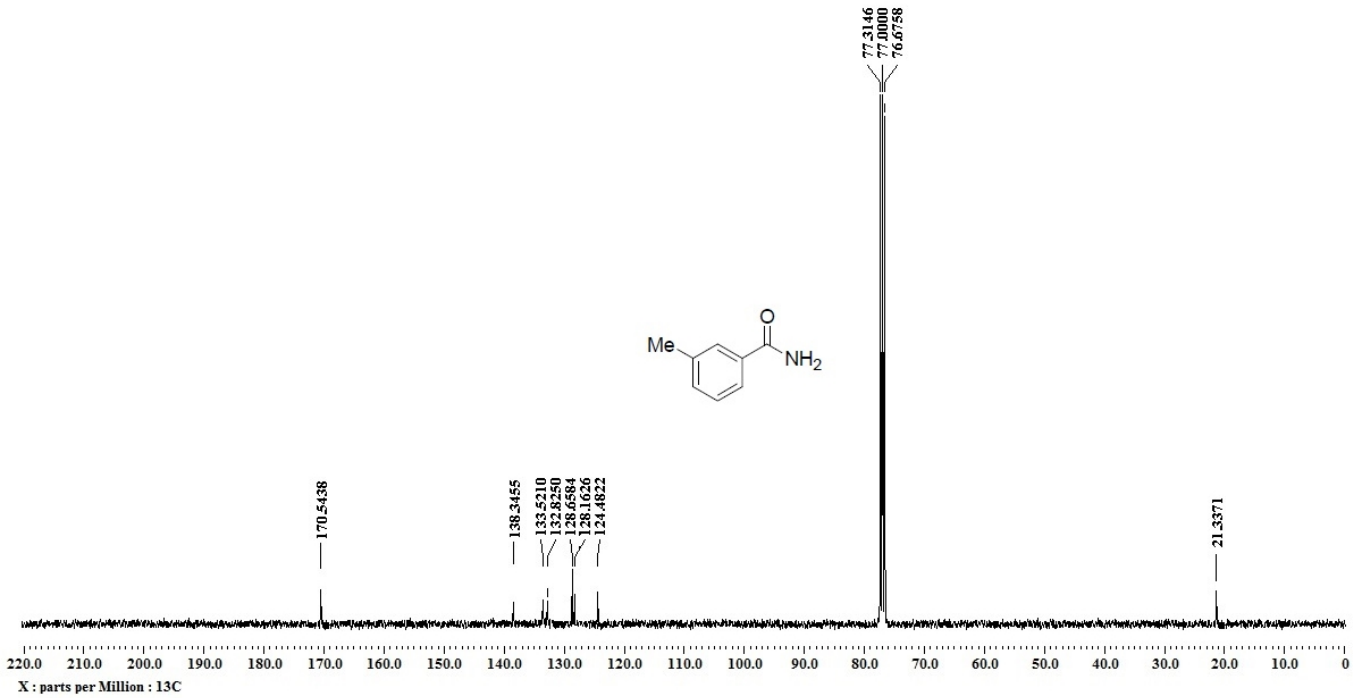


GC chromatogram for hydration of 2-methylbenzonitrile after 24 hours (2-methylbenzamide 8.83 min)

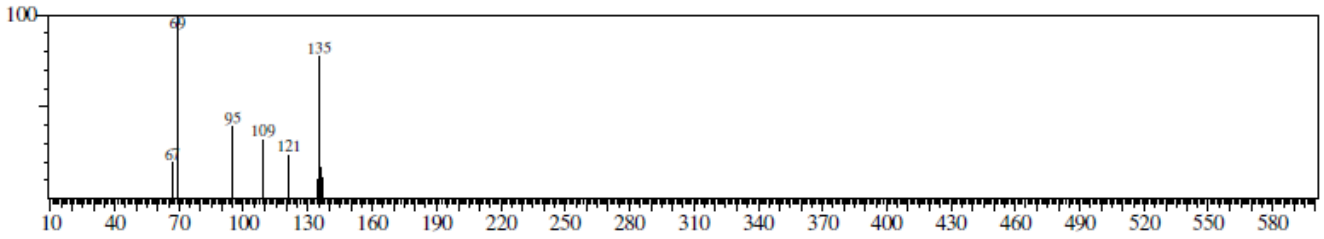


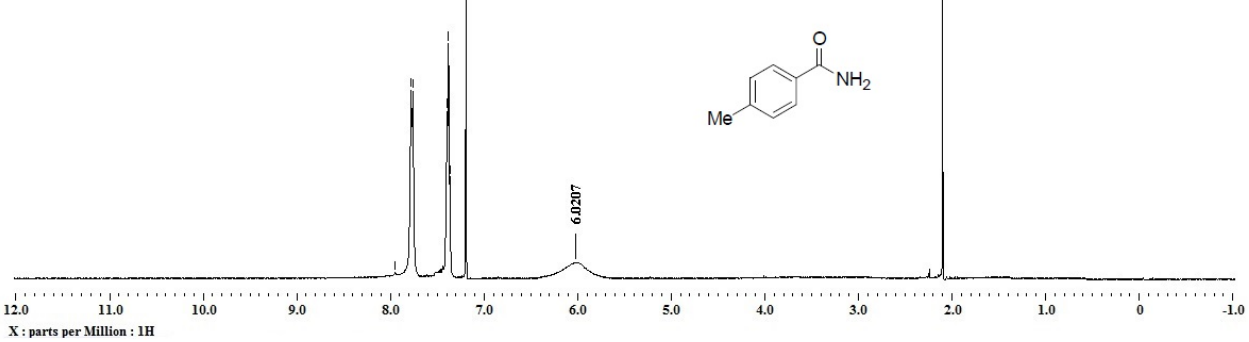
3-Methylbenzamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (s, 1H), 7.59-7.51 (m, 1H, J = 6.4 Hz), 7.45-7.42 (m, 2H, J = 5.9 Hz), 6.19 (b, 2H), 2.39 (s, 3H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 170.54, 138.34, 133.52, 132.82, 128.65, 128.16, 124.48, 21.33 ppm; MS (EI): m/z (%): 135(M^+).[1]



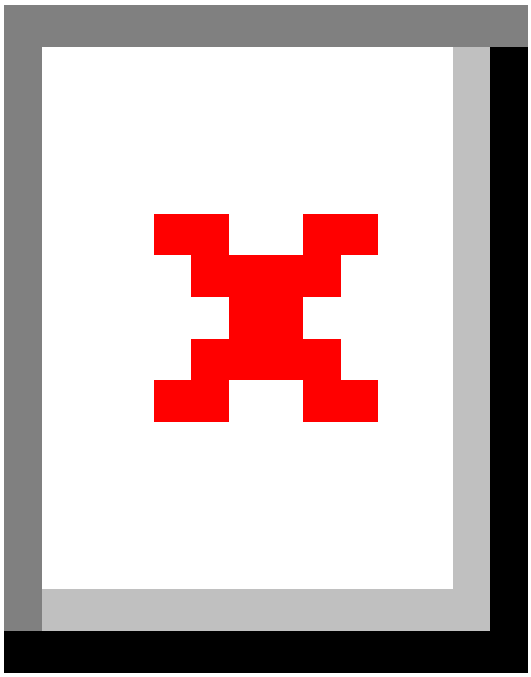


GC chromatogram for hydration of 3-methylbenzonitrile after 24 hours (3-methylbenzamide 9.28 min)



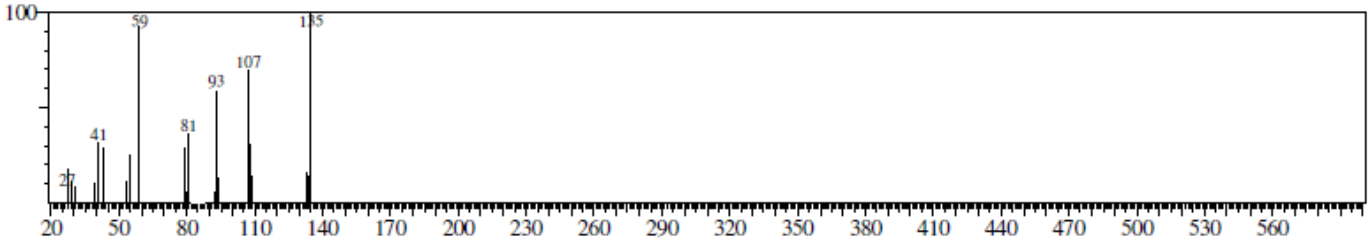


4-Methylbenzamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (b, 1H), 7.76 (d, 2H, J = 6.8 Hz), 7.39-7.36 (m, 2H, J = 6.8 Hz), 6.02 (b, 2H), 2.09 (s, 3H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ =

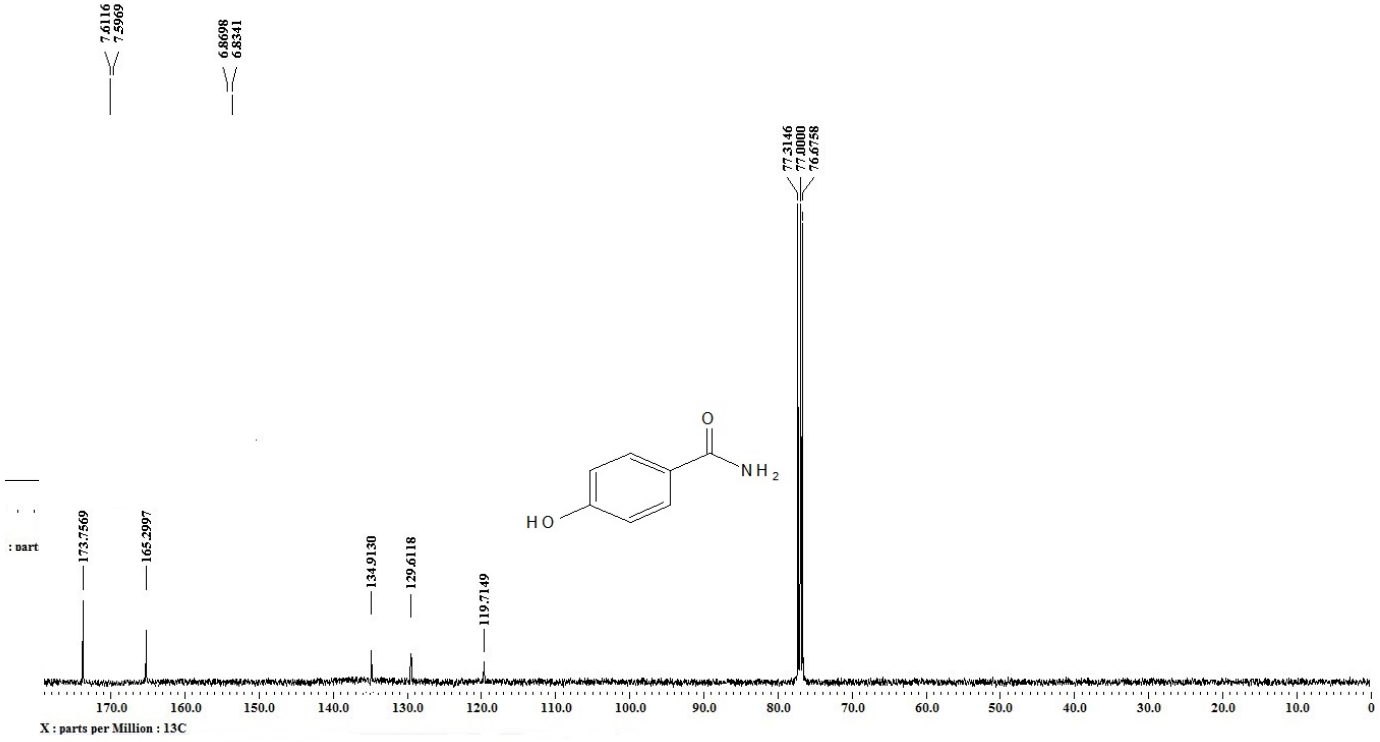


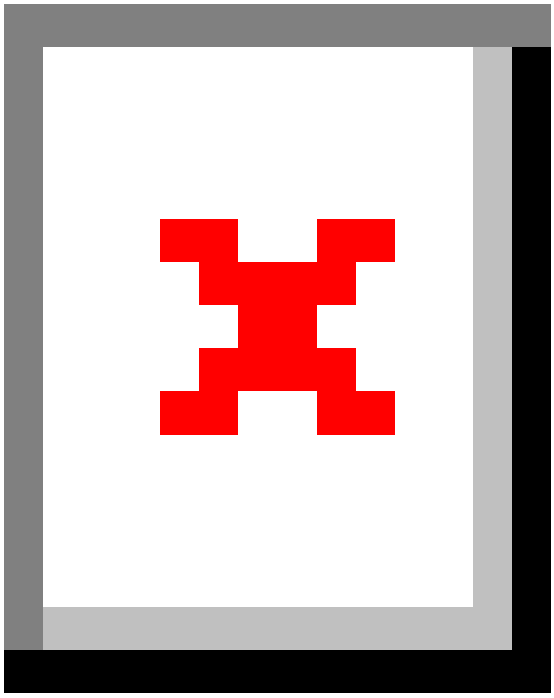
169.35, 142.54, 130.53, 129.25, 127.51, 21.48 ppm; MS (EI): m/z (%): 135(M^+).[1]

GC chromatogram for hydration of 4-methylbenzonitrile after 24 hours (4-methylbenzamide 9.88 min)

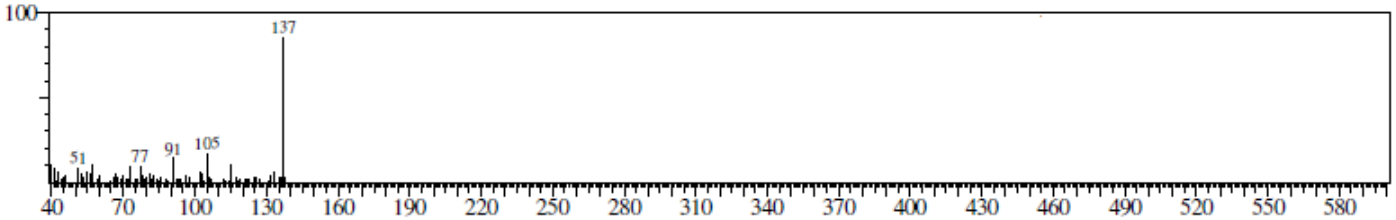


4-Hydroxybenzamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (d, 2H, J = 5.8 Hz), 6.85 (d, 2H, J = 14.2 Hz), 3.63 (s, 1H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 173.75, 165.29, 134.91, 129.61, 119.71 ppm; MS (EI): m/z (%): 137(M^+).[3]

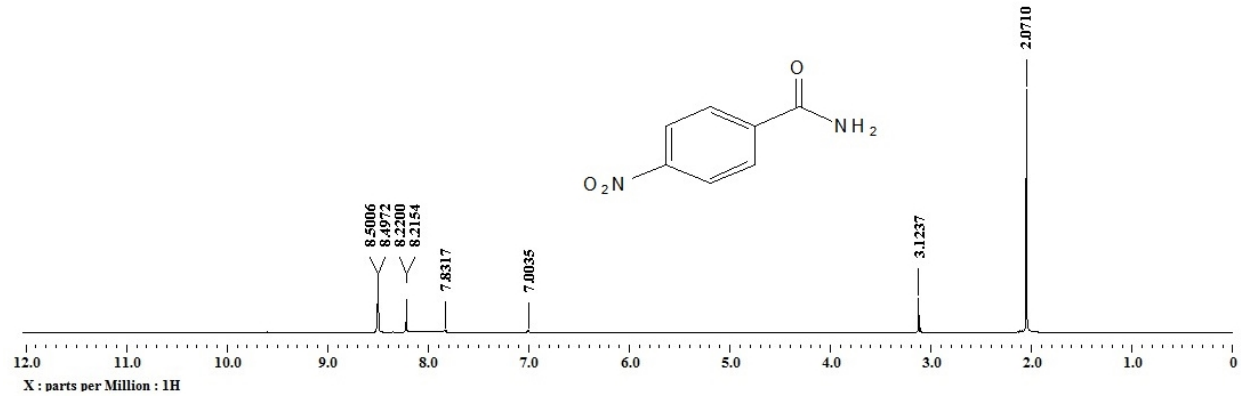


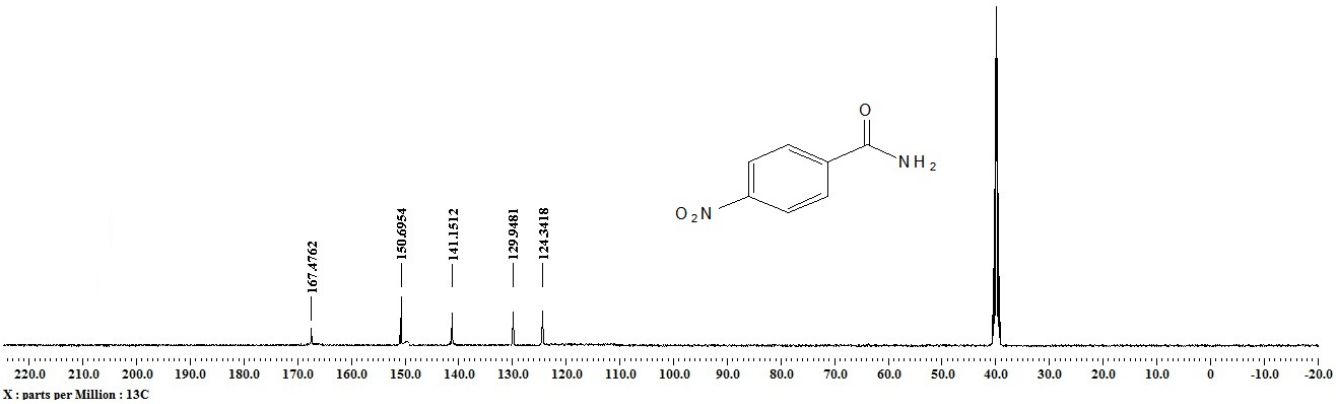


GC chromatogram for hydration of 4-hydroxybenzonitrile after 24 hours (4-hydroxybenzamide 9.99 min)

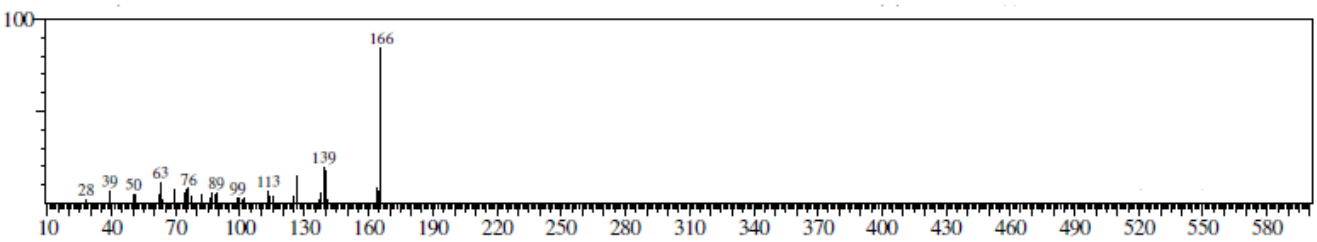


4-Nitrobenzamide: ^{1}H NMR (400 MHz, Acetone-d_6) δ = 8.49 (d, 2H, J = 1.3 Hz), 8.21 (d, 2H, J = 1.28 Hz), 7.83(s, 1H), 7.00 (s, 1H) ppm; ^{13}C (400 MHz, Acetone-d_6): δ = 167.47, 150.69, 141.15, 129.94, 124.34 ppm; MS (EI): m/z (%): 166(M^+).[4]

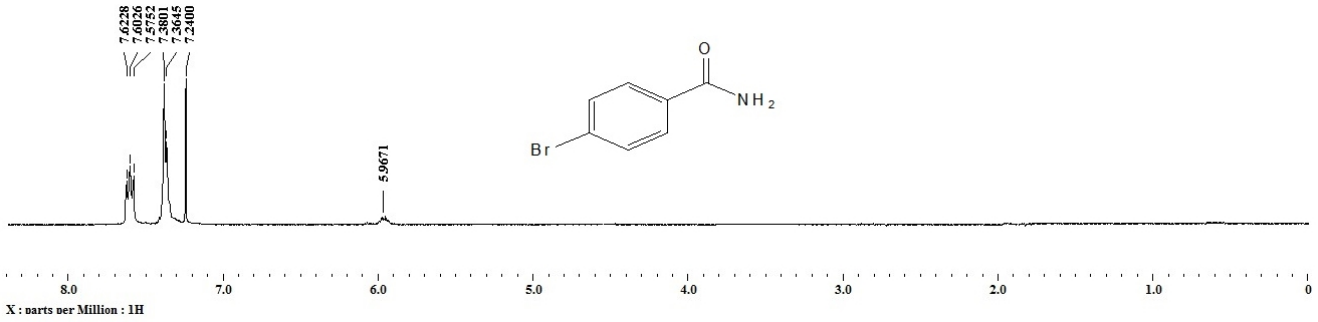


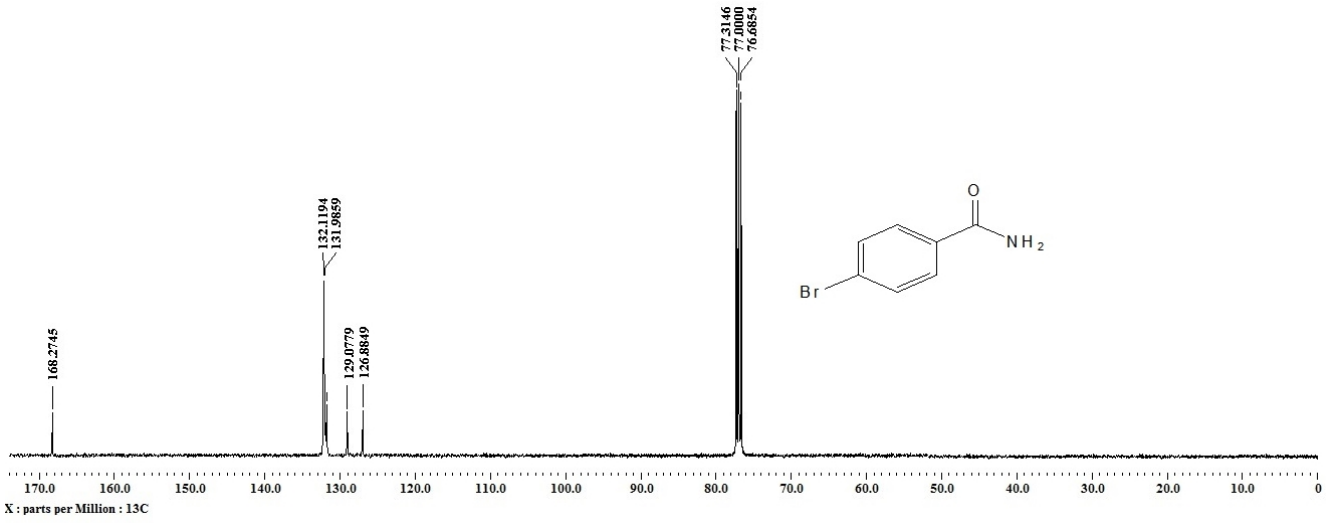


GC chromatogram for hydration of 4-nitrobenzonitrile after 24 hours (4-nitrobenzamide 11.88 min)

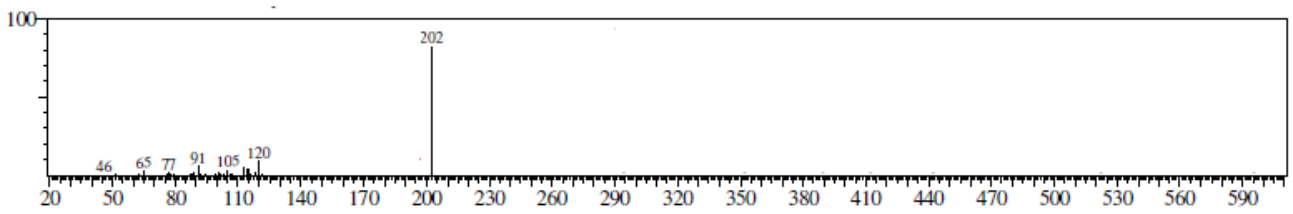


4-Bromobenzamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (t, 2H, J = 8.0 Hz), 7.37 (d, 2H, J = 6.2 Hz), 5.96 (b, 2H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 168.27, 132.11, 131.98, 129.07, 126.88, ppm; MS (EI): m/z (%): 202(M^+).[5]

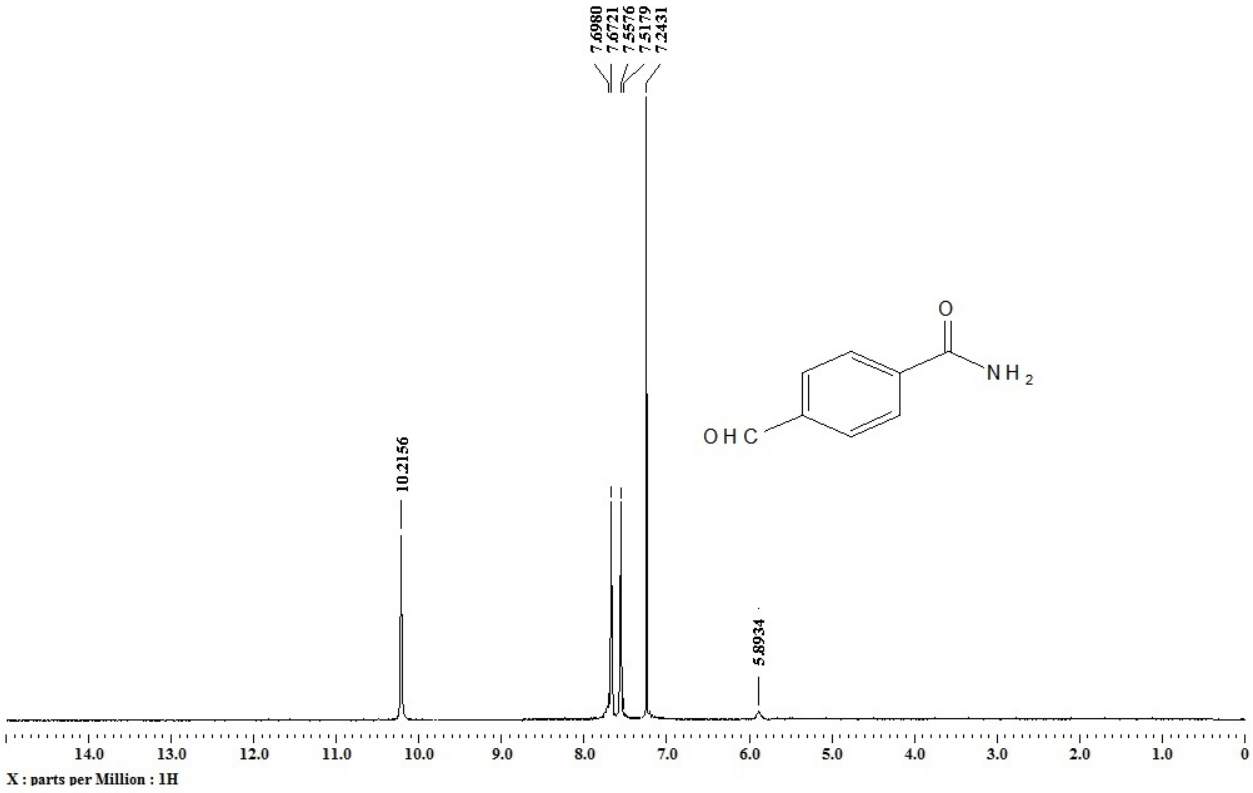


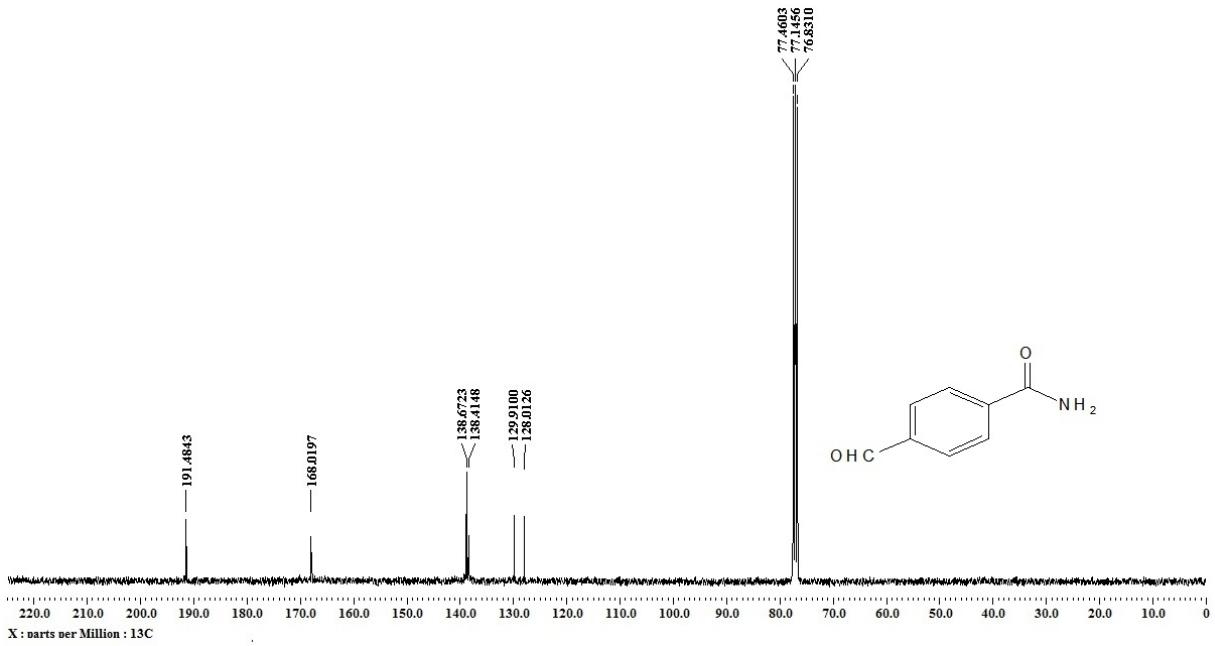


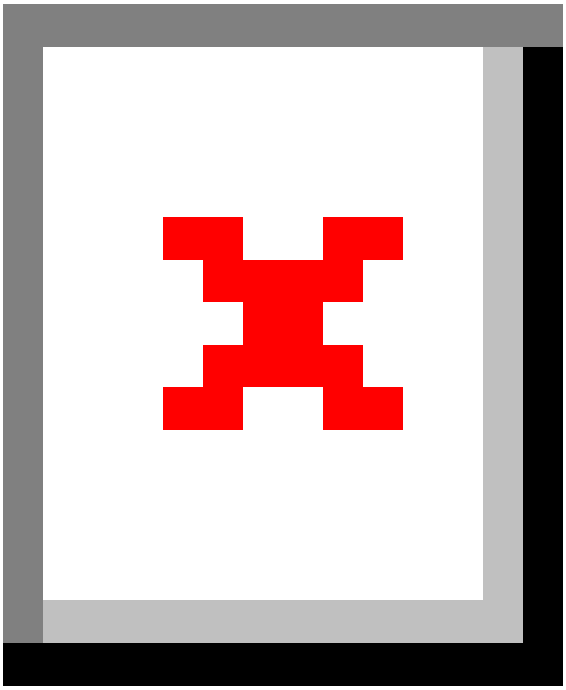
GC chromatogram for hydration of 4-bromobenzonitrile after 24 hours (4-bromobenzamide 11.28 min)



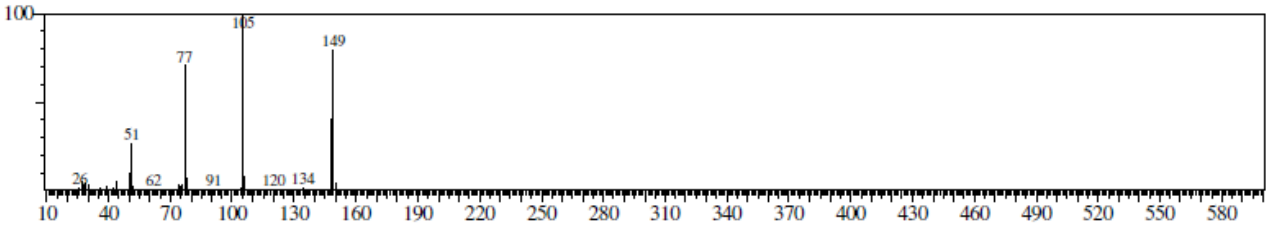
4-formylbenzamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.21(s, 1H), 7.68 (d, 2H, J = 10.3 Hz), 7.53 (d, 2H, J = 15.8 Hz), 5.89 (b, 2H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 191.48, 168.01, 138.67, 138.41, 129.91, 128.01 ppm; MS (EI): m/z (%): 149(M^+).[6]



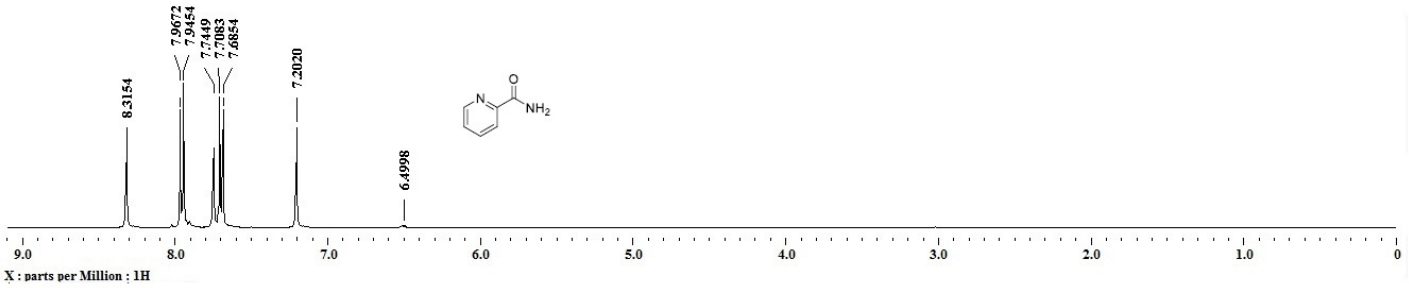


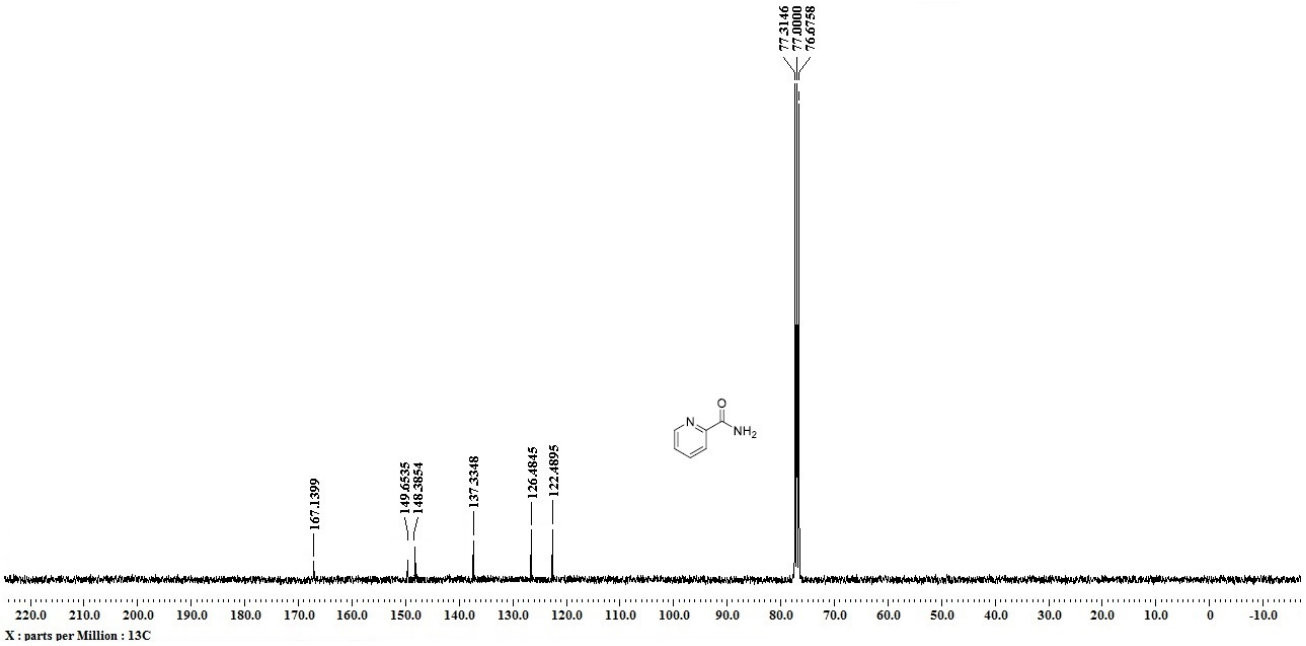


GC chromatogram for hydration of 4-formylbenzonitrile after 24 hours (4-formylbenzamide 11.98 min)

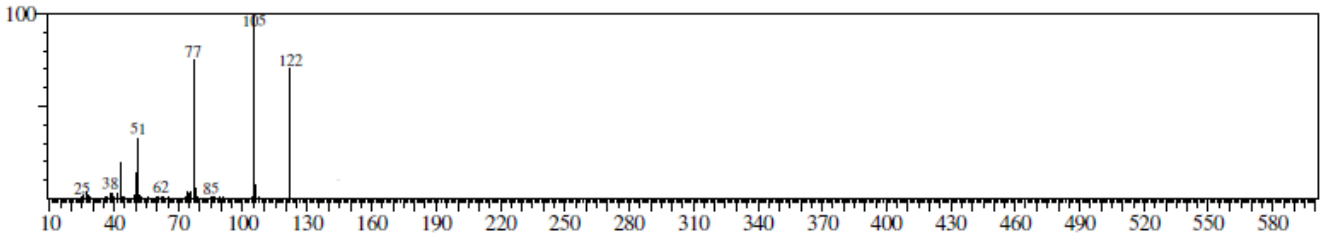


Picolinamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31(s, 1H), 7.95 (d, 1H, J = 8.7 Hz), 7.71 (t, 2H, J = 14.6 Hz), 6.49 (b, 2H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 167.13, 149.65, 148.38, 137.33, 126.48, 122.48 ppm; MS (EI): m/z (%): 122(M^+).[7]

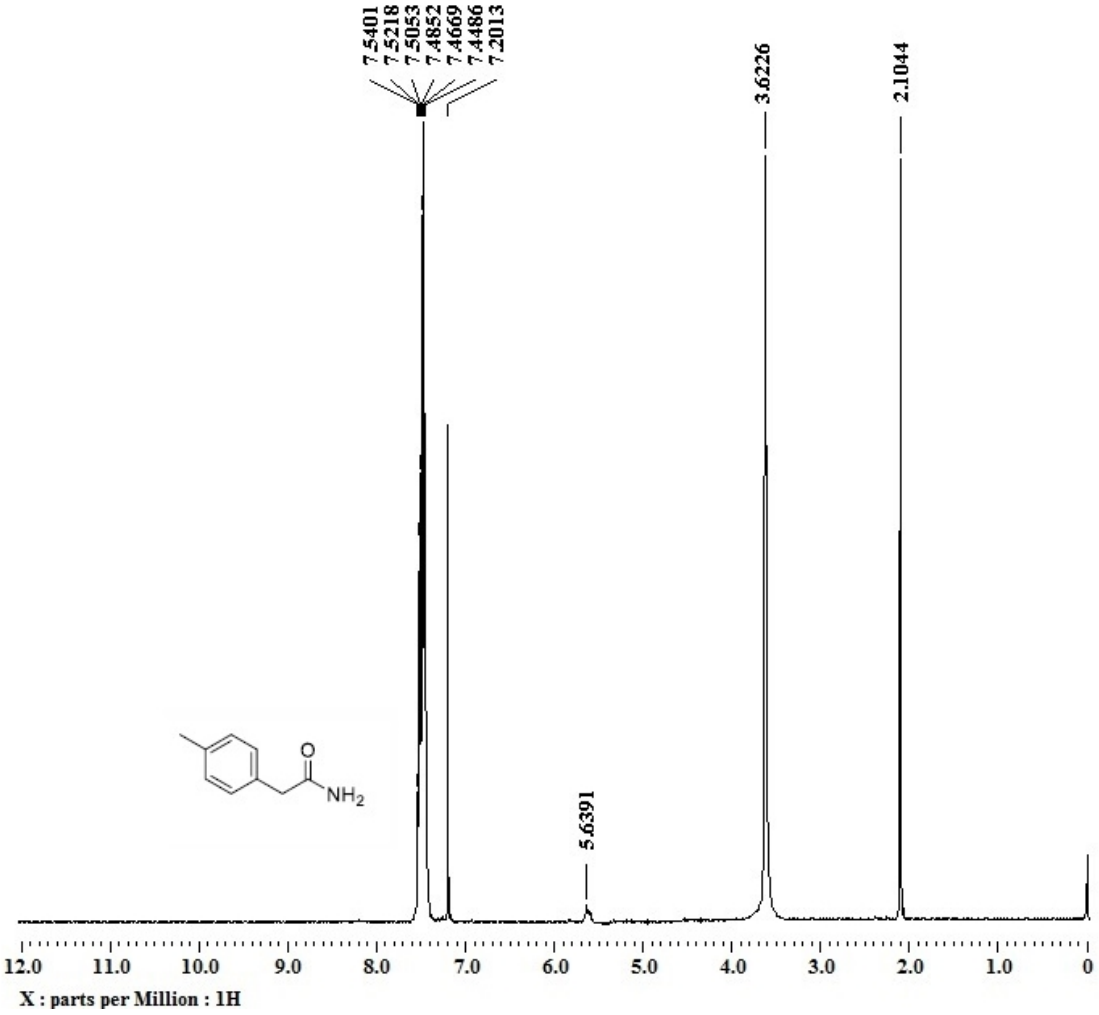


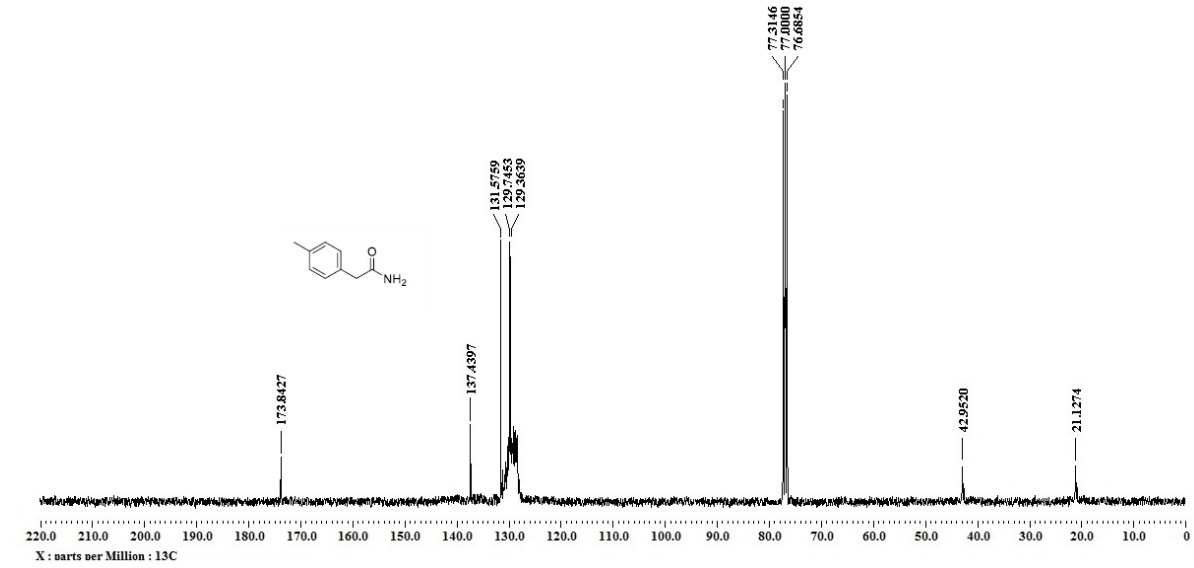


GC chromatogram for hydration of 2-cyanopyridine after 24 hours (Picolinamide 4.24 min)

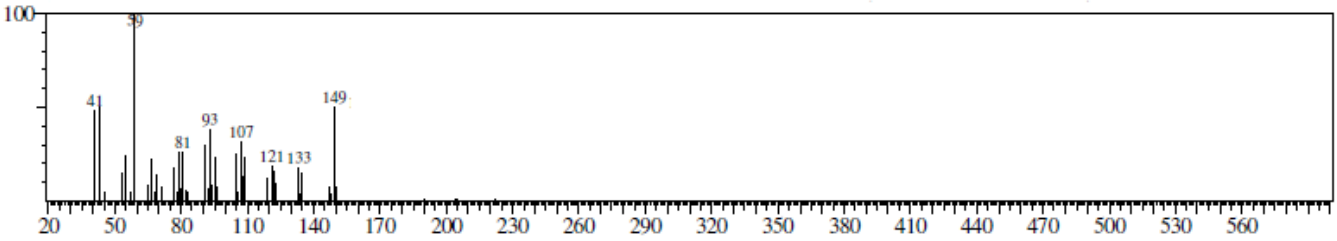


4-(*p*-tolyl)-acetamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54(m, 4H, J = 7.3 Hz), 5.63 (b, 2H), 3.62(s, 2H), 2.10(s, 3H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 173.84, 137.43, 131.57, 129.74, 129.36, 42.95, 21.12 ppm; MS (EI): m/z (%): 149(M^+).[8]

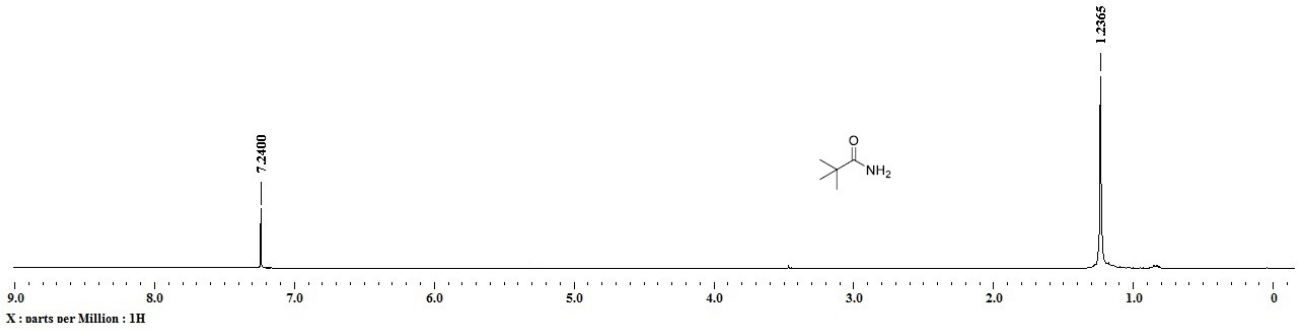


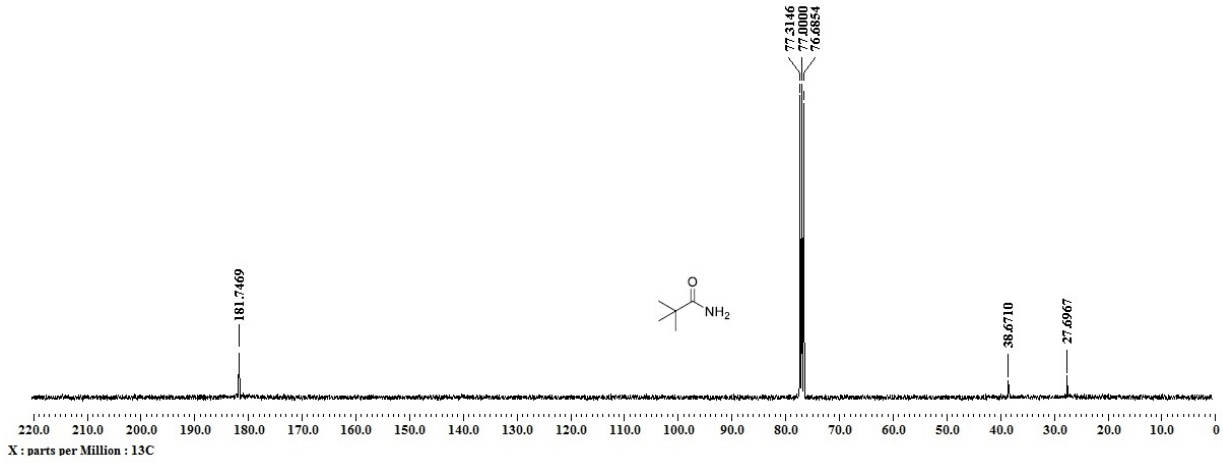


GC chromatogram for hydration of 4-methylbenzyl cyanide after 24 hours (4-(*p*-tolyl)-acetamide 6.54 min)

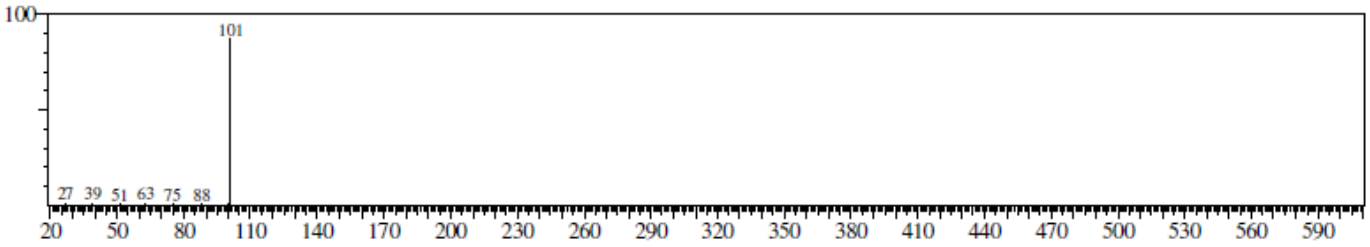


Pivalamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.23(s, 9H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 181.74, 38.67, 27.69 ppm; MS (EI): m/z (%): 101(M^+).[9]

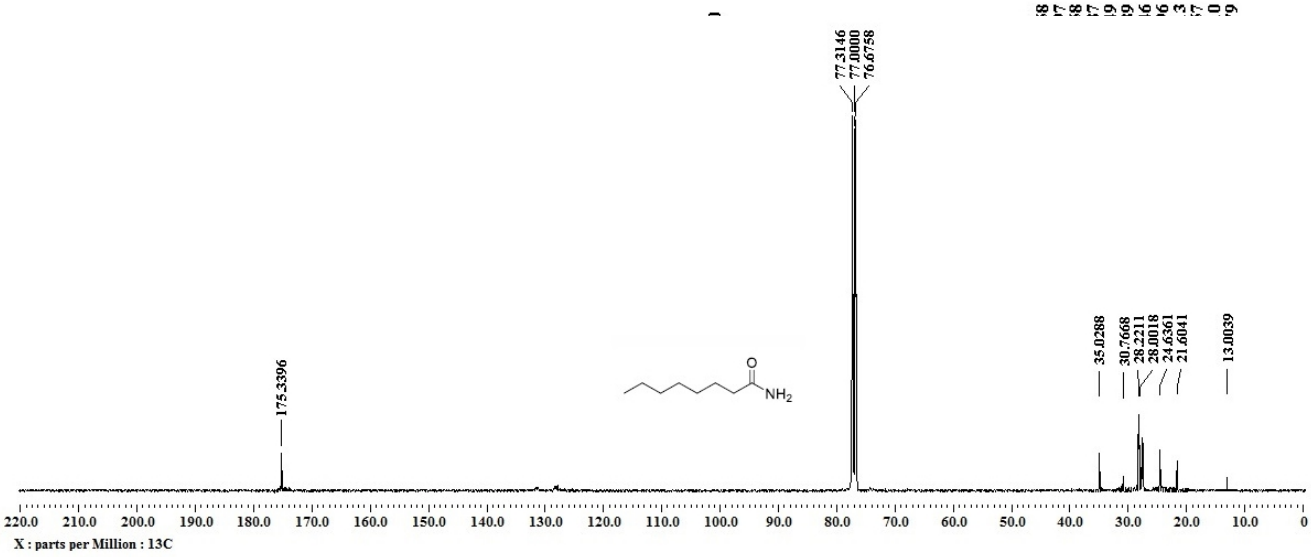


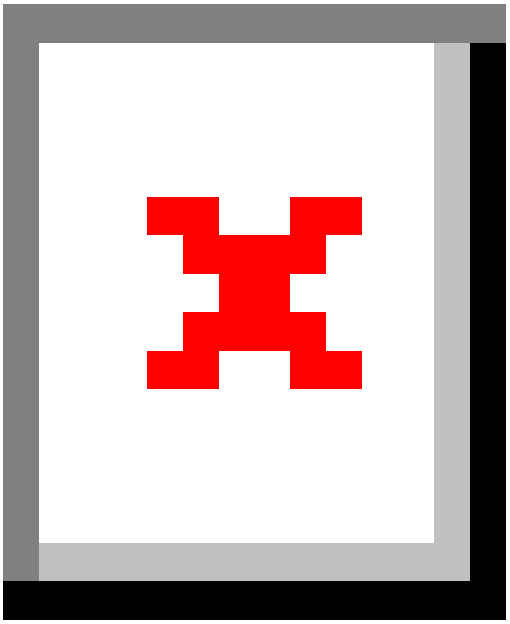


GC chromatogram for hydration of pivalonitrile after 24 hours (pivalamide 3.44 min)

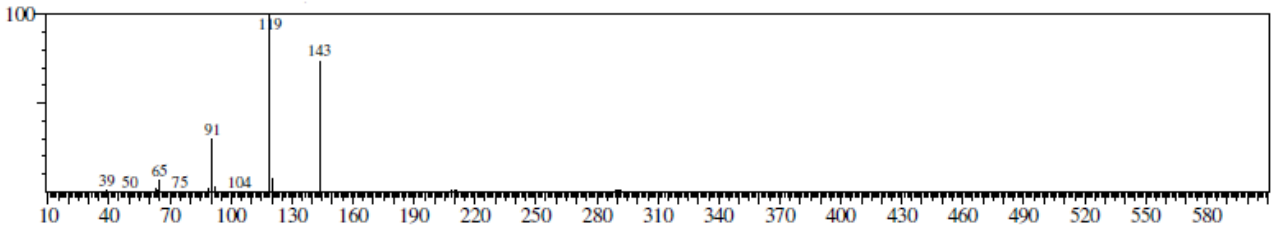


Octamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.24(b, 1H), 5.59(b, 1H), 2.15 (s, 2H), 1.67(s, 2H), 1.23-139(m, 8H, J=9.5 Hz), 0.81-0.91(m, 2H, J= 7.3 Hz) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 175.33, 35.02, 30.76, 28.22, 28.00, 24.63, 21.60, 13.00 ppm; MS (EI): m/z (%): 143(M^+).[8]

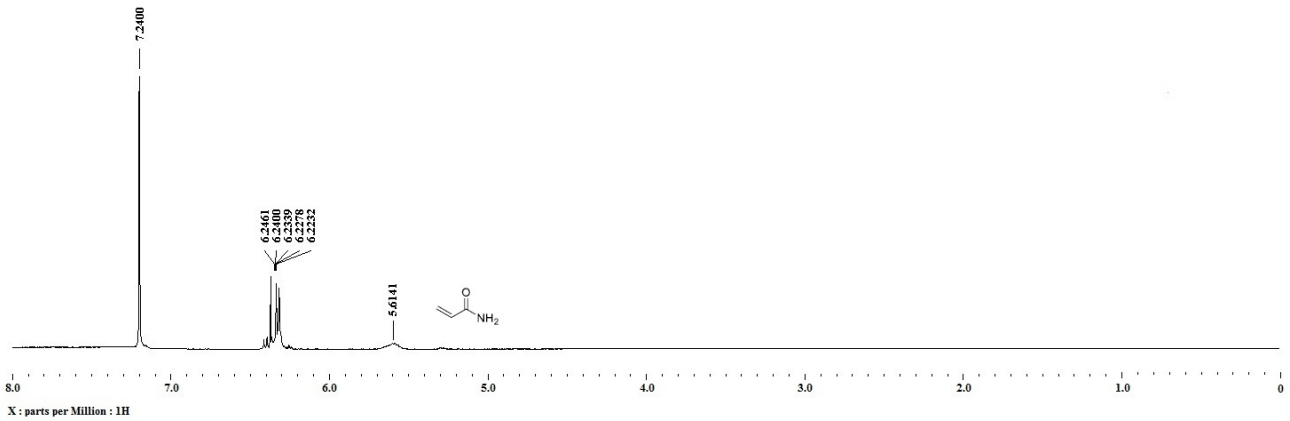


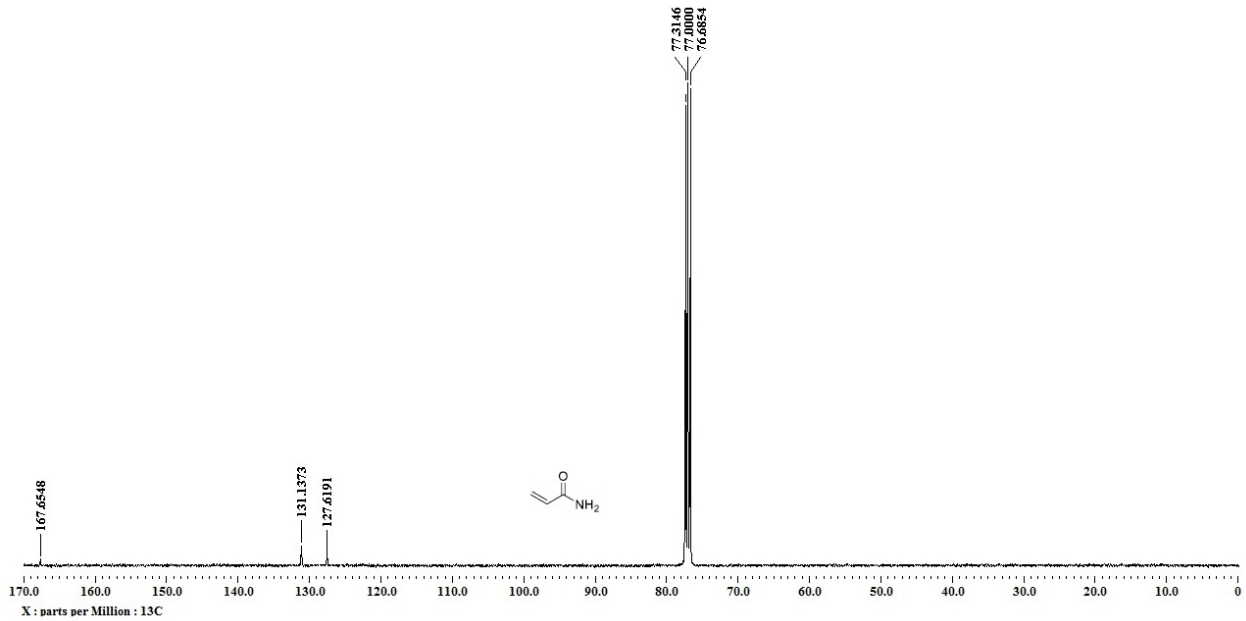


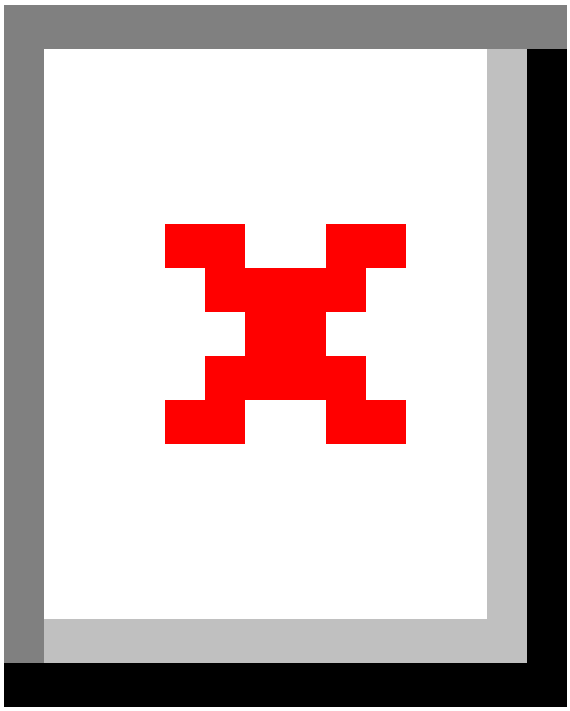
GC chromatogram for hydration of heptyl cyanide after 24 hours (octamide 5.54 min)



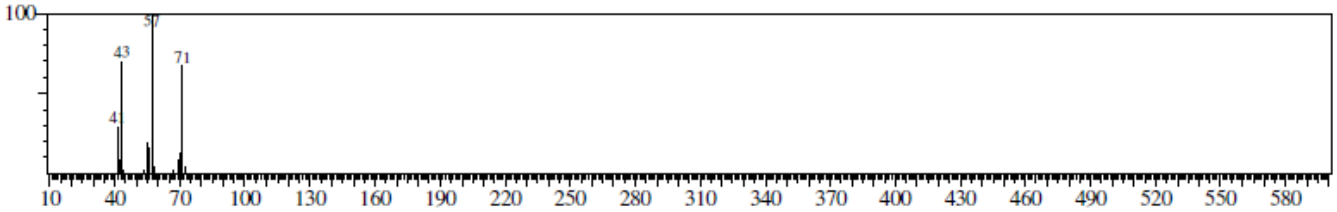
Acrylamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.22-6.24(m, 3H), 5.61(b, 2H) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 167.65, 131.13, 127.61 ppm; MS (EI): m/z (%): 71(M^+).[9]







GC chromatogram for hydration of acrylonitrile after 24 hours (acrylamide 5.04 min)



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