Electronic Supplementary Information

A cobalt-based metal-organic framework as a sustainable catalyst for base-free transfer hydrogenation of biomass-derived carbonyl compounds

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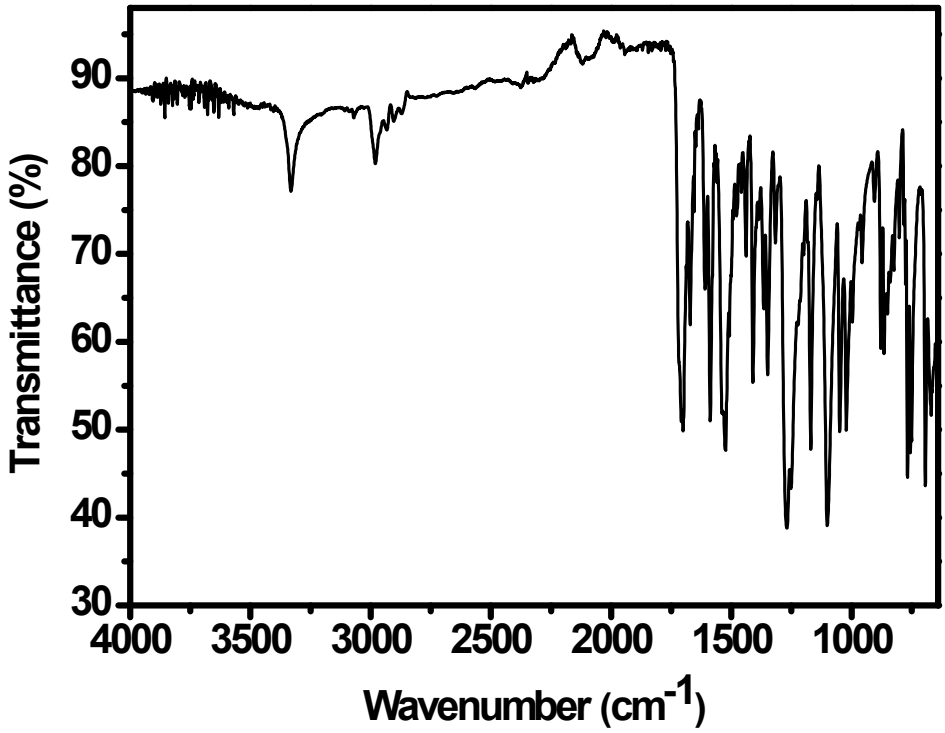

Figure S1. FTIR spectrum of **L2**.

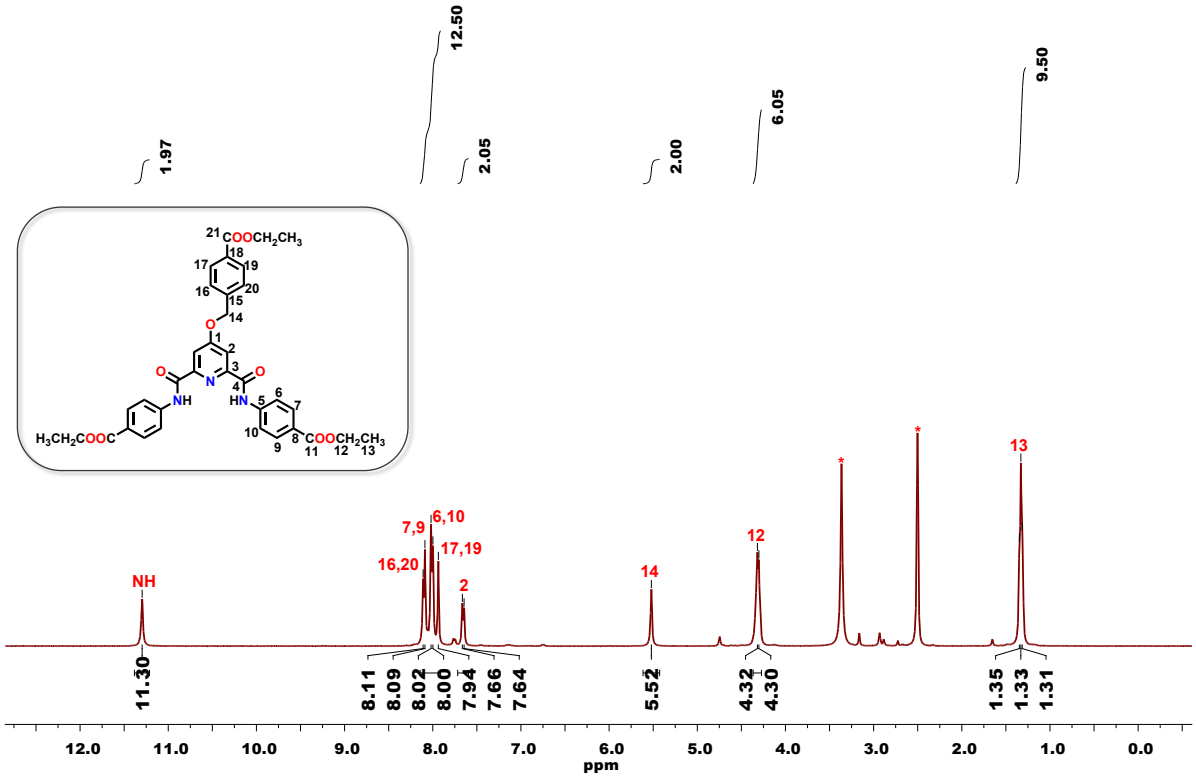

Figure S2. ^{1}H NMR spectrum of **L2** in DMSO-d_6 solvent where * represents the residual solvent and/or adventitious water peak.

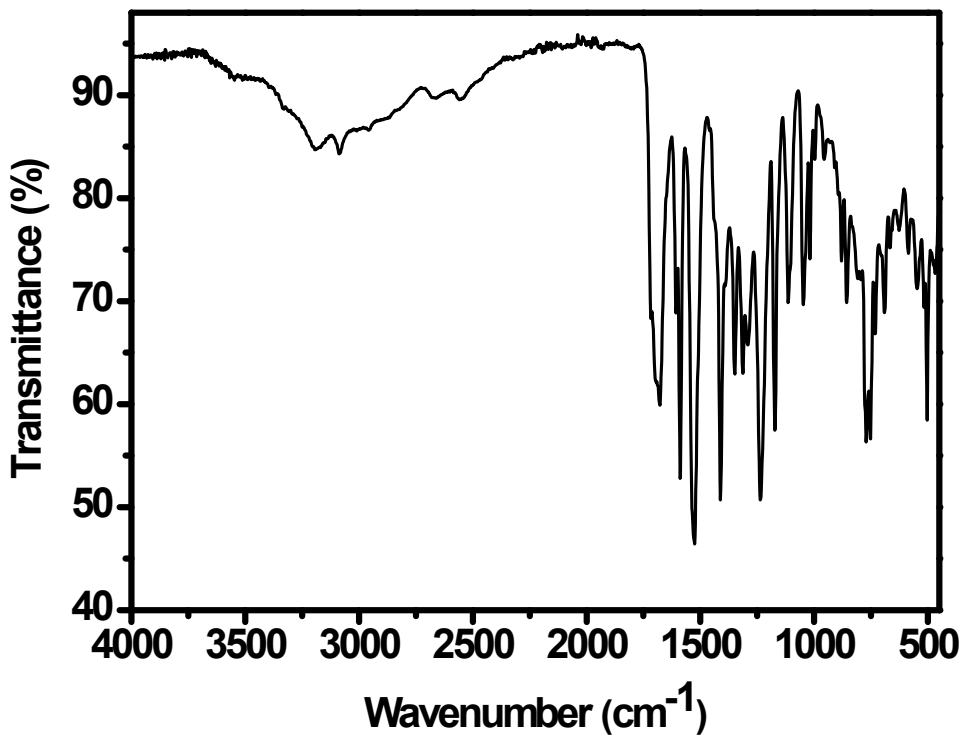

Figure S3. FTIR spectrum of ligand **L3**.

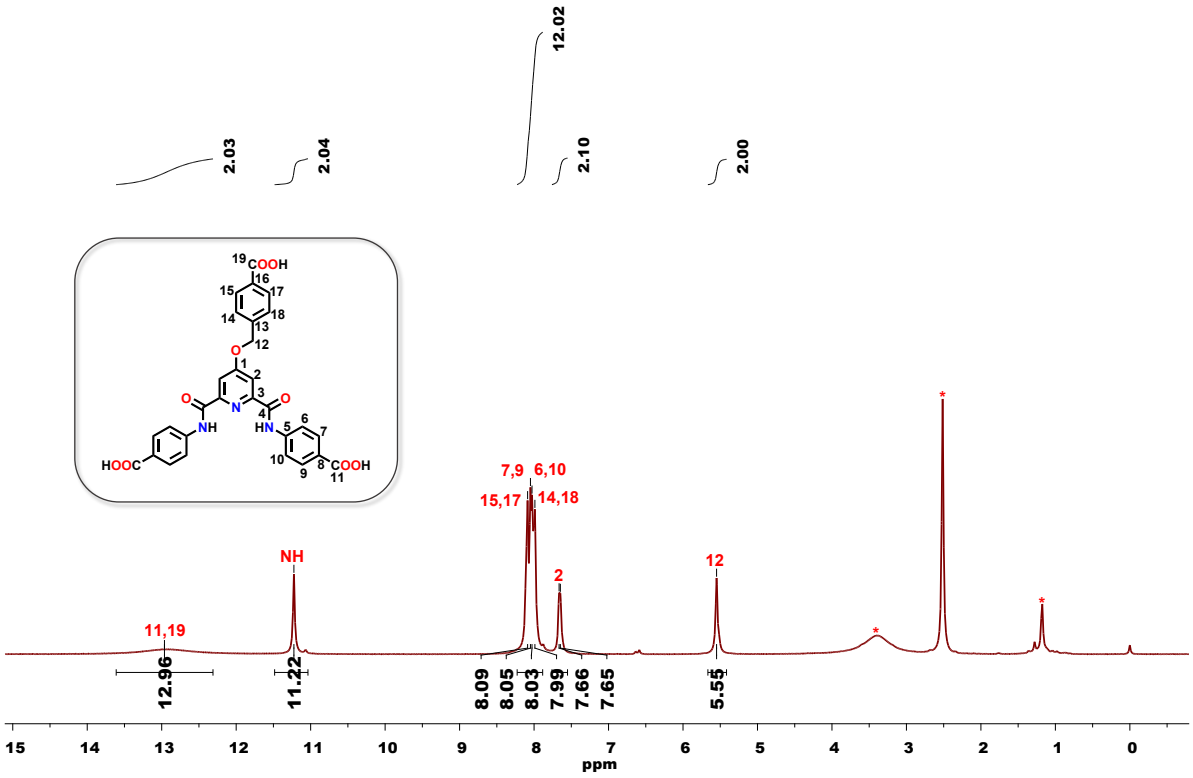

Figure S4. ^{1}H NMR spectrum of ligand **L3** in DMSO-d_6 solvent where * represents the residual solvent and/or adventitious water peak.

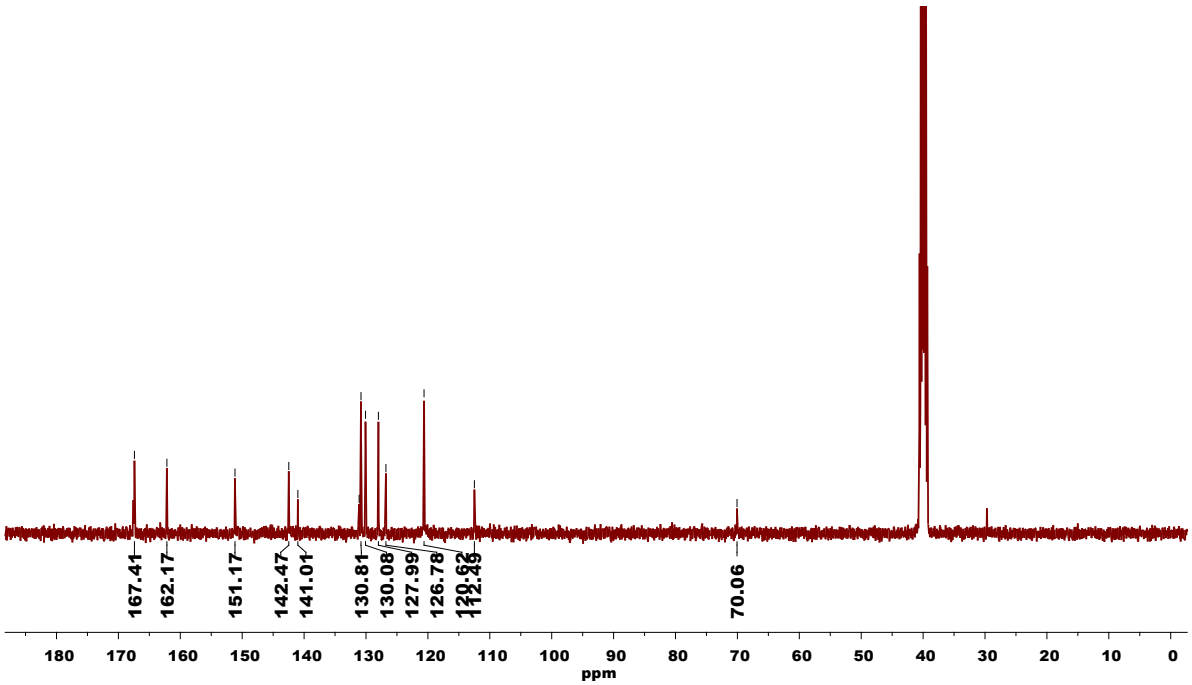

Figure S5. ^{13}C NMR spectrum of ligand **L3** in DMSO-d_6 solvent where * represents the residual solvent peak.

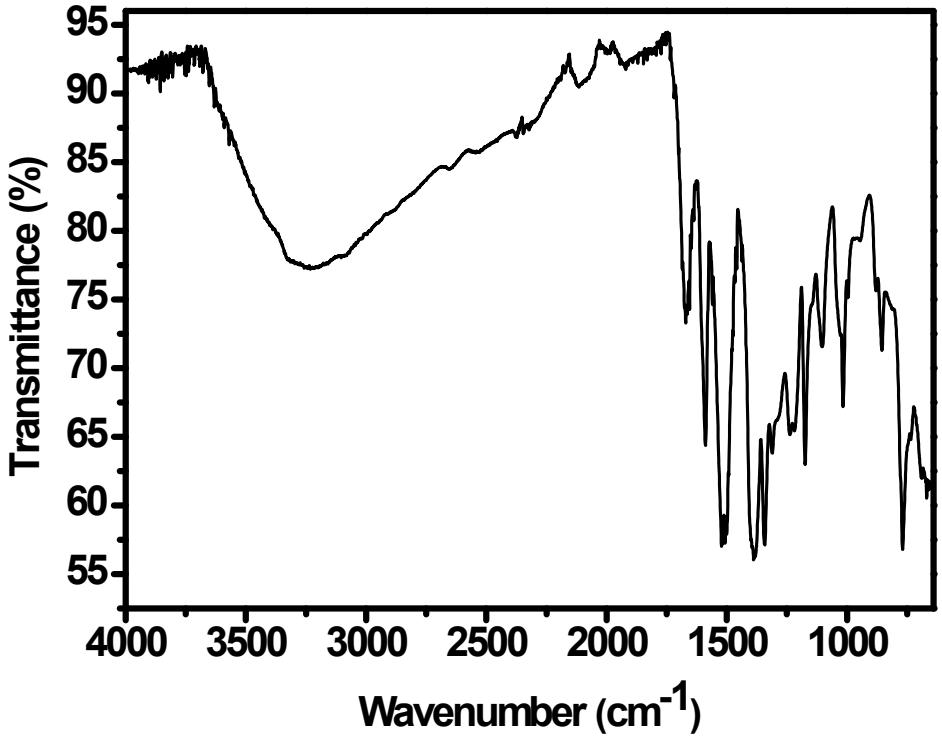

Figure S6. FTIR spectrum of MOF **1**.

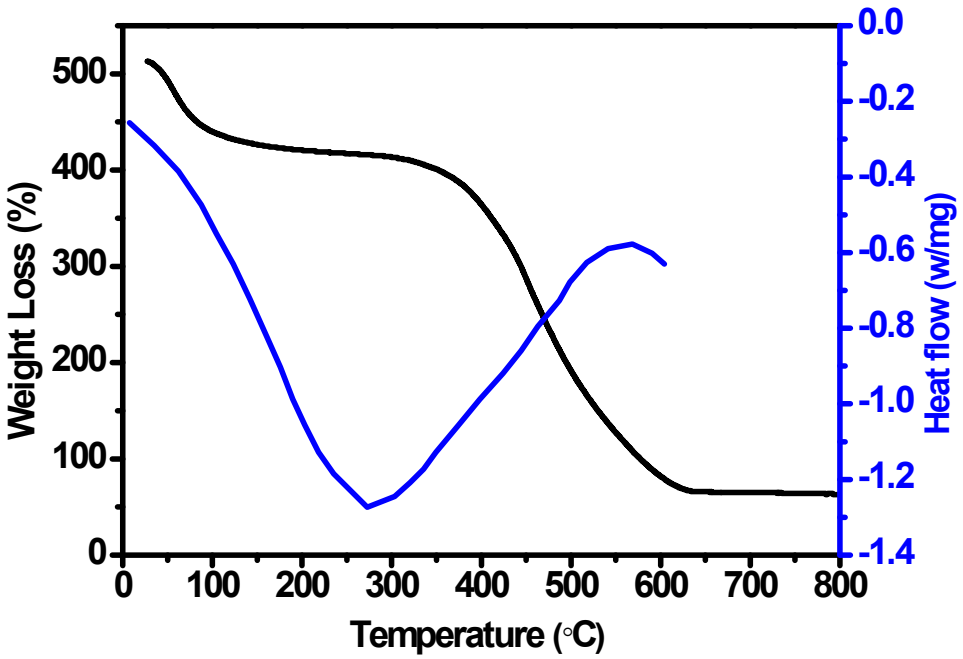

Figure S7. Thermal Gravimetric Analysis (TGA, black trace) and Differential Scanning Calorimetric (DSC, blue trace) plots for MOF **1**.

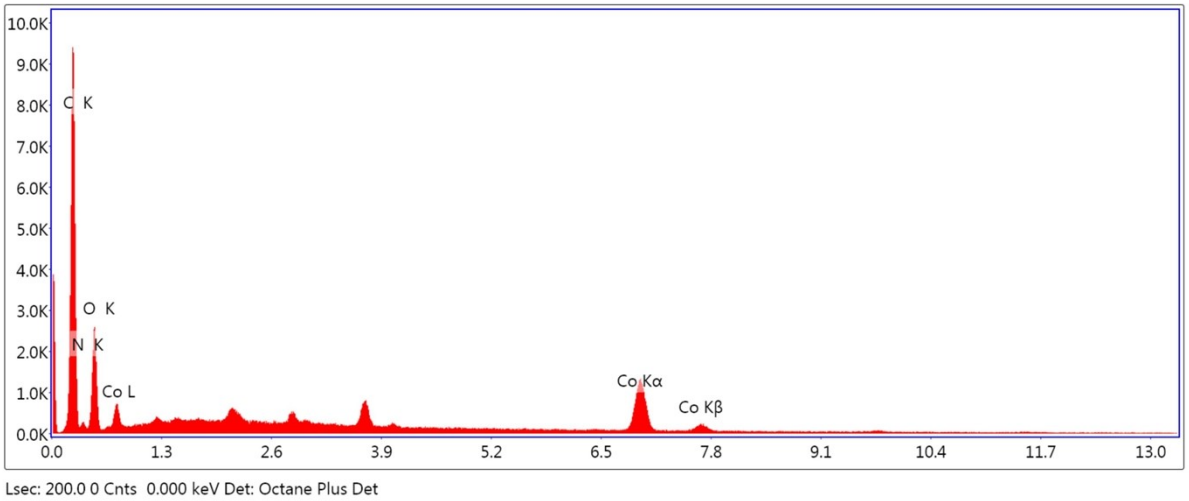

Figure S8. EDX spectrum of MOF **1**.

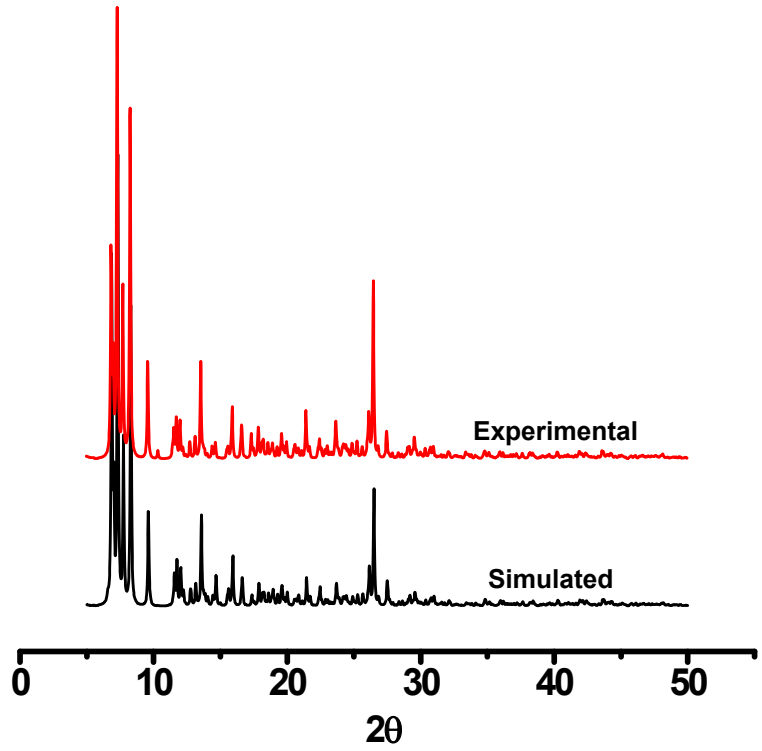

Figure S9. X-ray powder diffraction patterns for as-synthesized MOF **1** (red trace) and the one simulated from Mercury 3.0 using the single crystal diffraction data (black trace).

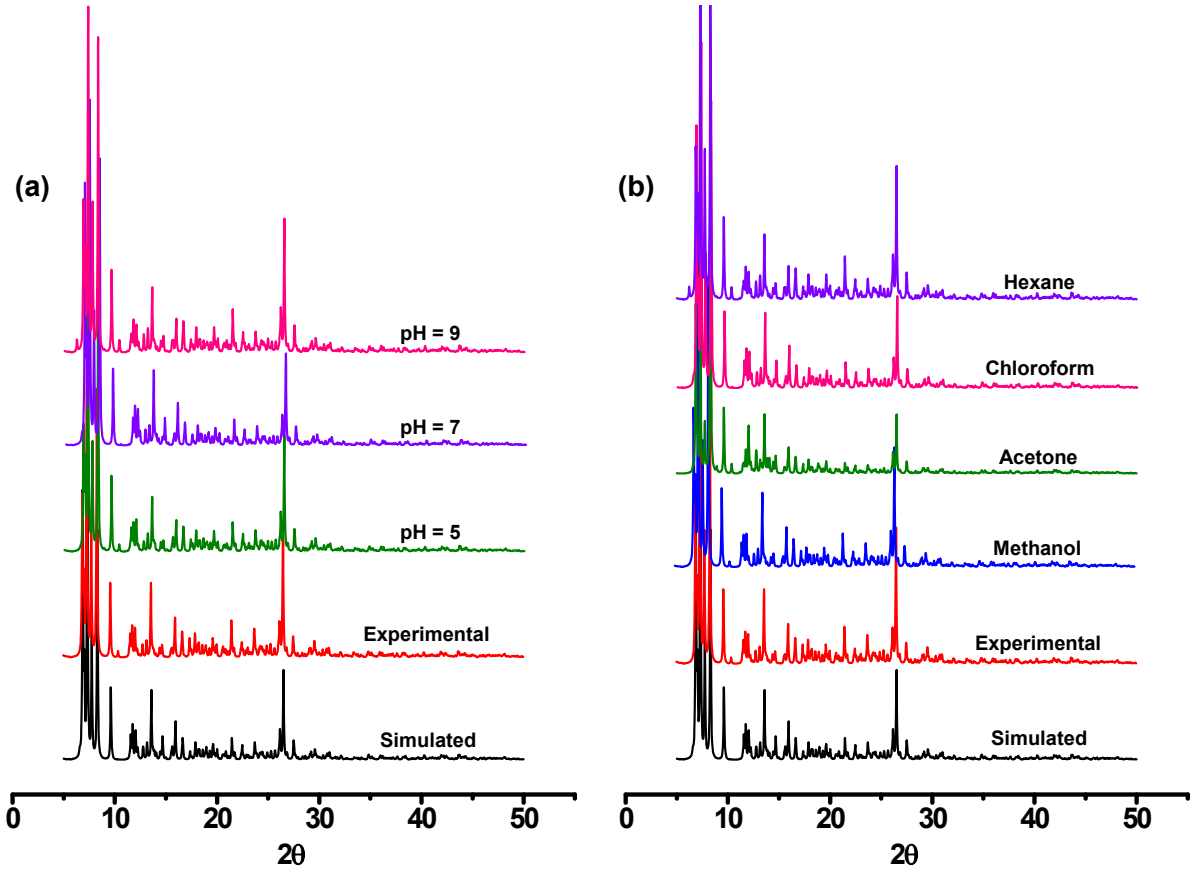

Figure S10. (a) X-ray powder diffraction patterns of as-synthesized MOF **1**, its simulated patterns, and after treatment with different (a) pHs and (b) organic solvents.

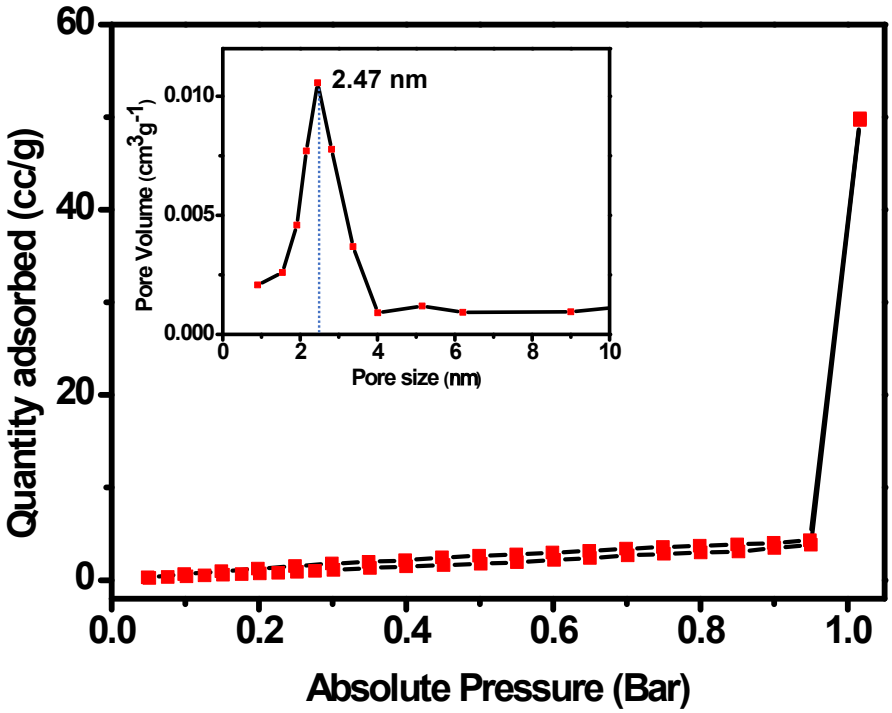

Figure S11. N_2 sorption isotherm measured for MOF **1** at 77 K. Black and red traces respectively denote sorption and desorption plots. Inset shows the pore size distribution plot.

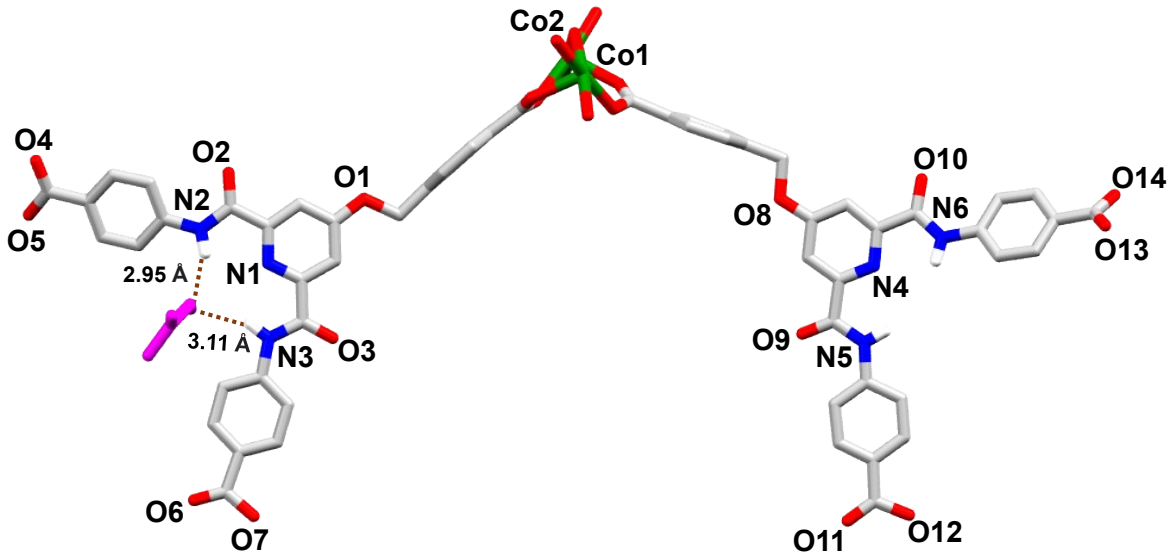

Figure S12. Asymmetric unit of MOF **1**. Colour codes; green, Co; blue, N; red, O; grey, C; pink, DMF. The hydrogen atoms, except for amidic protons, have been omitted for clarity.

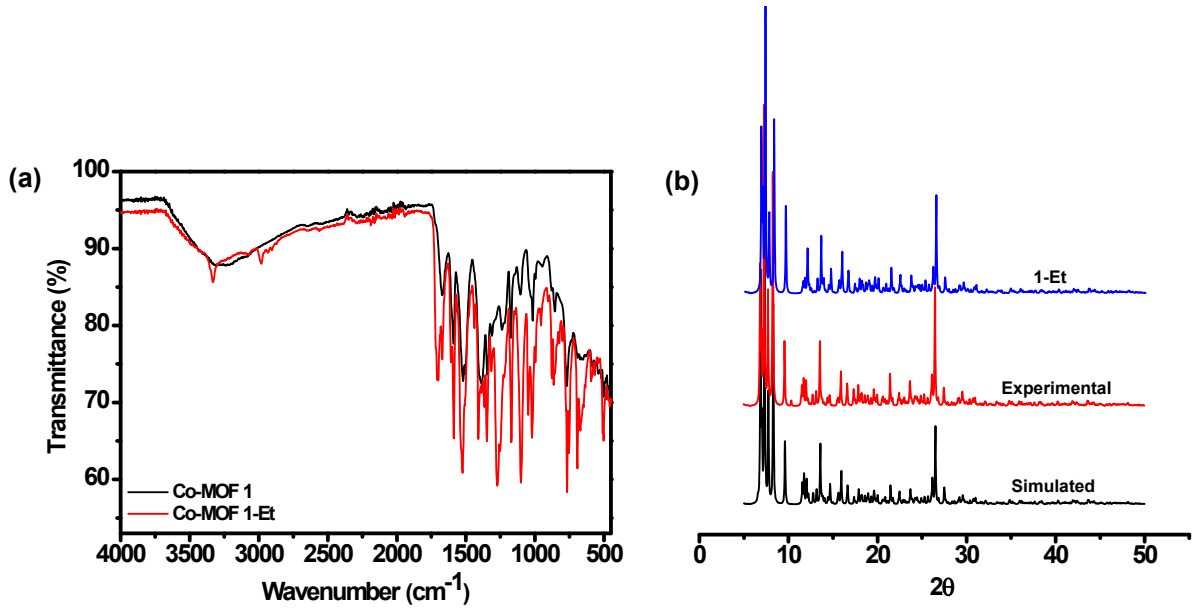

Figure S13. (a) FTIR spectra of MOF **1** (black trace) and **1-Et** (red trace); (b) X-ray powder diffraction patterns for as-synthesized **1** (red trace); its simulated one (black trace); and for **1-Et** (blue trace).

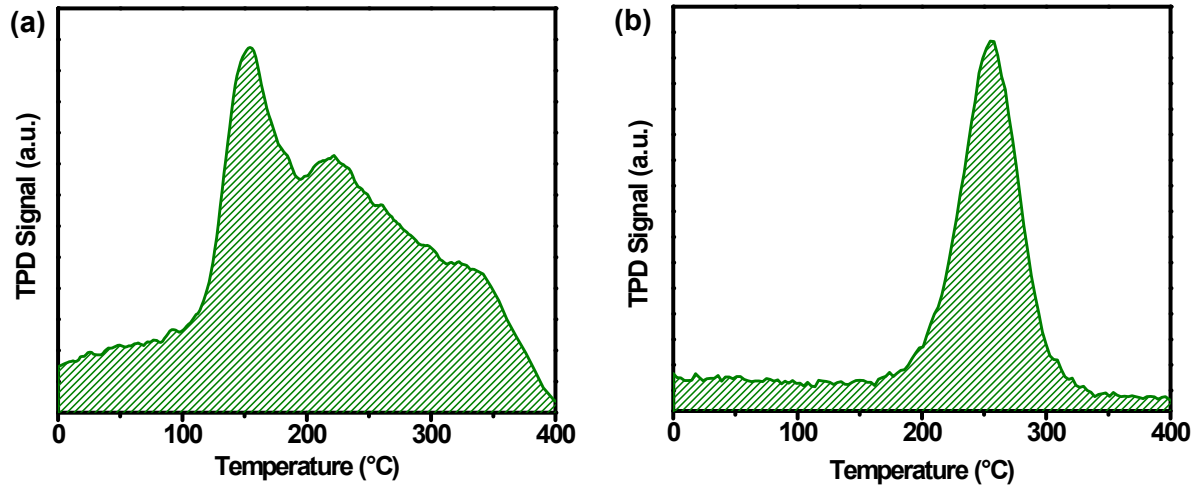

Figure S14. (a) NH_3-TPD profile; and (b) CO_2-TPD profile for MOF **1**. TDP: temperature-programmed desorption.

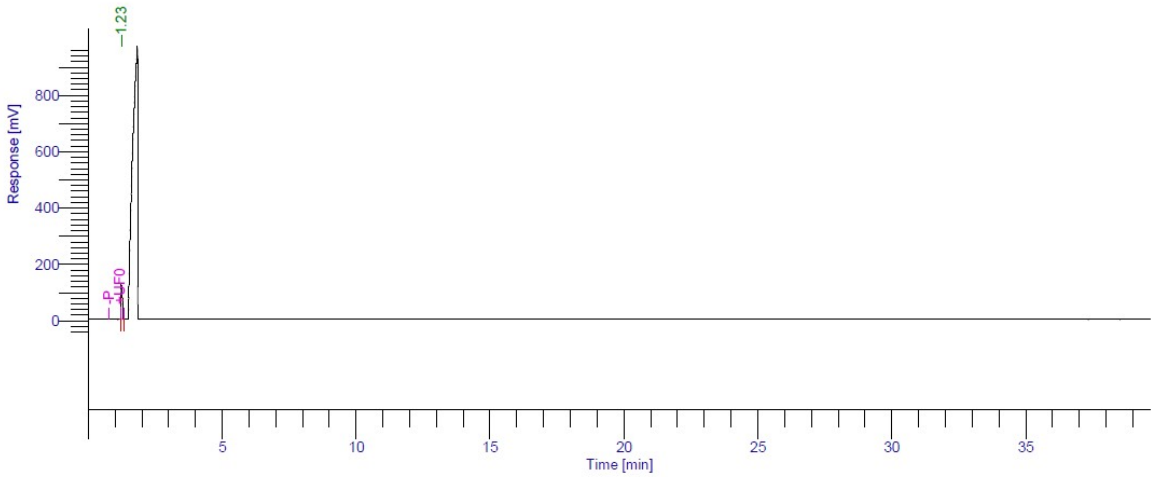

Figure S15(a). Gas chromatogram (in ethyl acetate) for the detection of in-situ generated acetone (at ca. 1.21 min.) in a catalytic reaction mixture.

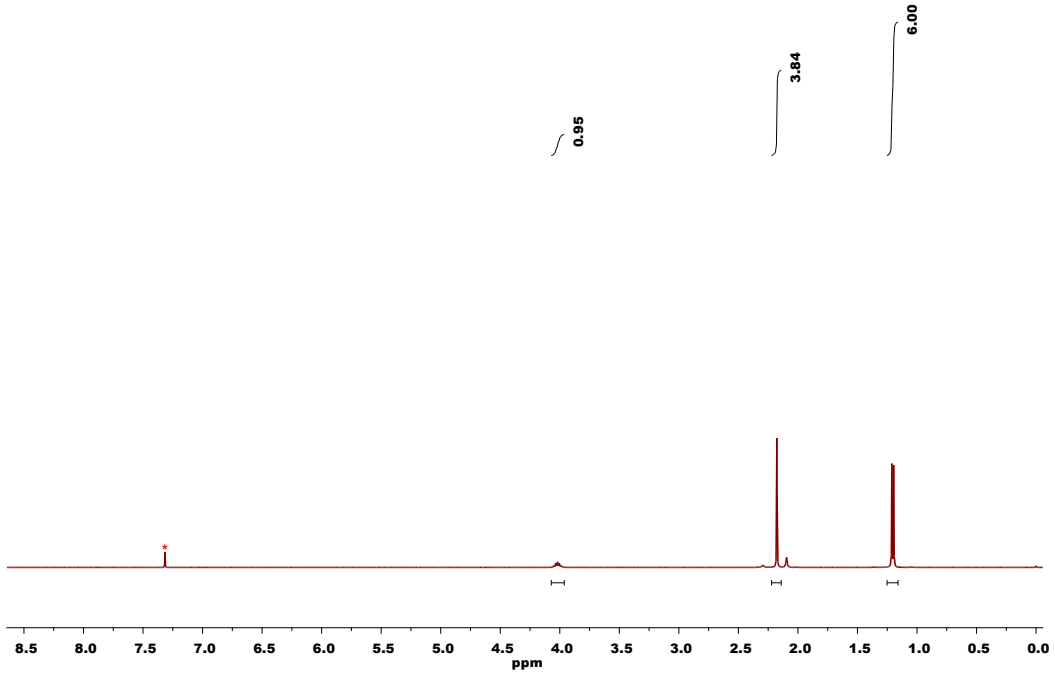

Figure S15(b). ^{1}H NMR spectrum of in-situ formed acetone (at ca. 2.2 ppm) in $CDCl_3$ solvent where * represents the residual solvent peak. The spectrum also exhibits the presence of isopropyl alcohol used as a solvent.

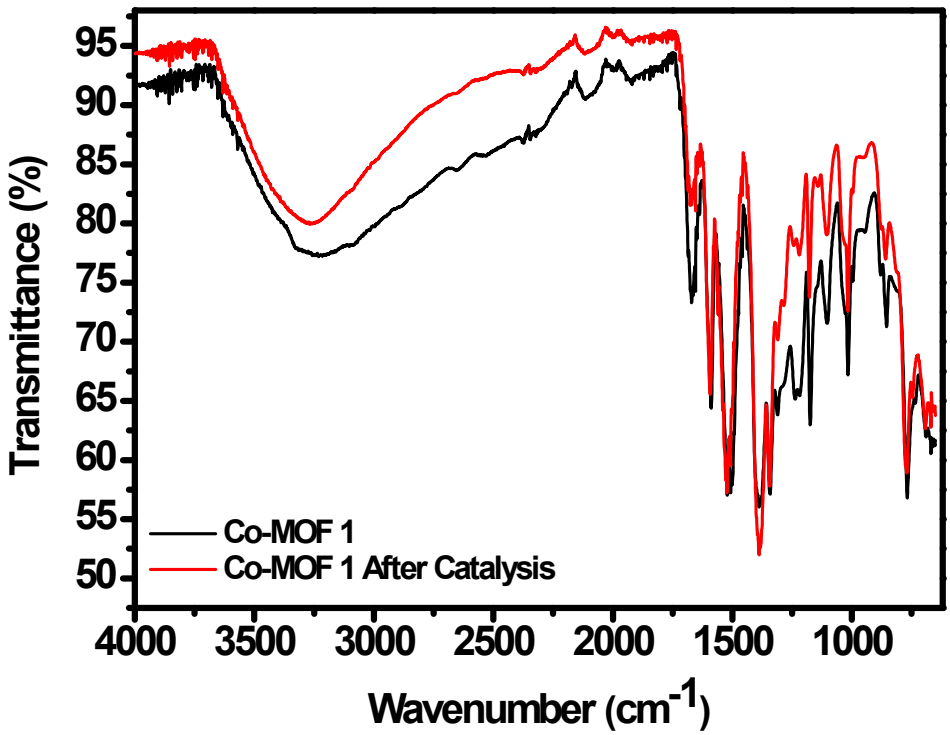

Figure S16. FTIR spectra of MOF **1** before (black trace) and after the TH reaction (red trace).

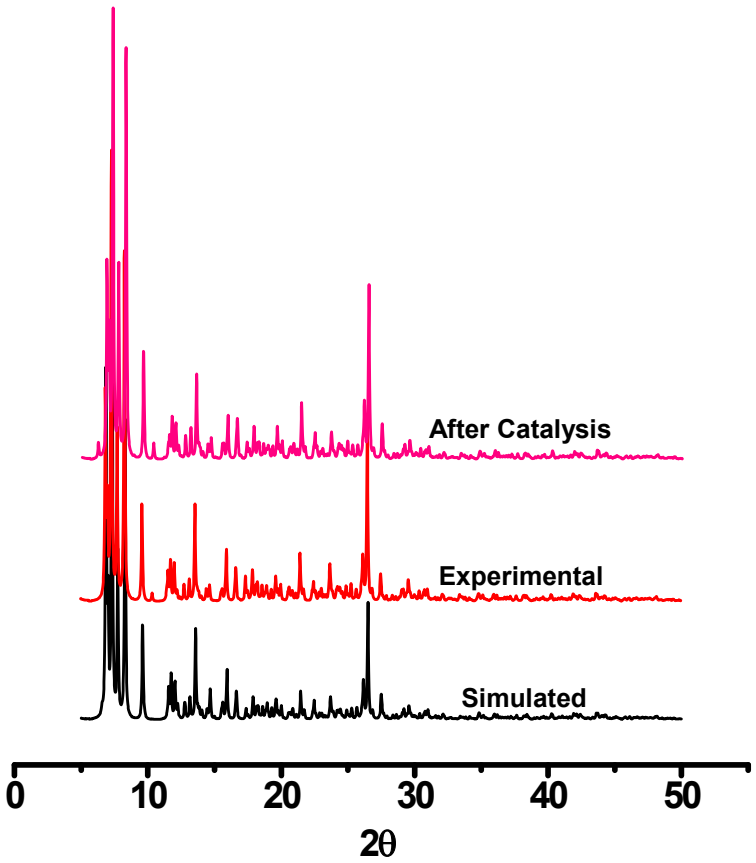

Figure S17. X-ray powder diffraction patterns for as-synthesized **1** (red trace); its simulated one (black trace); and after the TH reaction (pink trace).

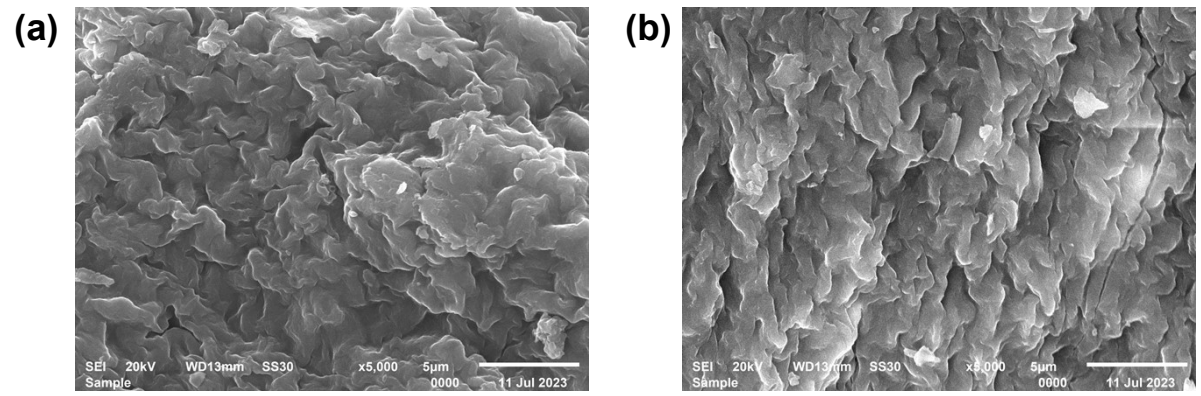

Figure S18. SEM images of (a) as-synthesized MOF **1** and (b) after the TH reaction.

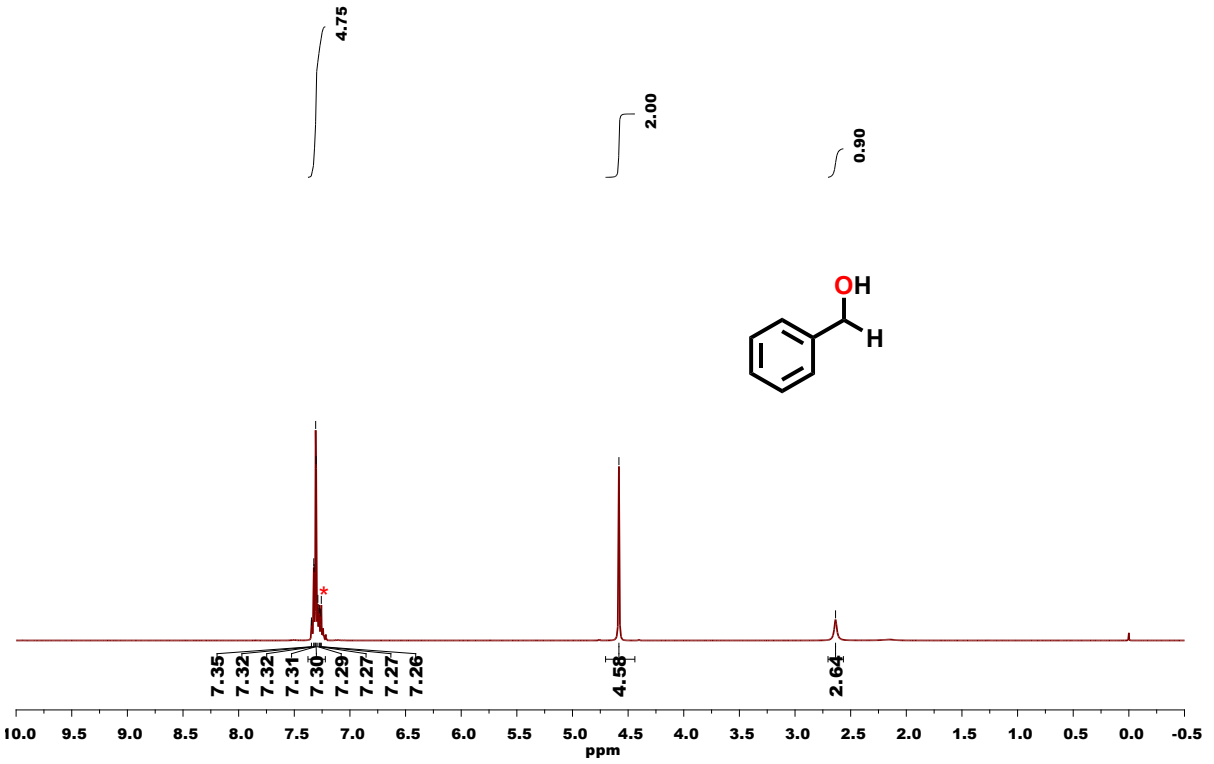

Figure S19. ^{1}H NMR spectrum of product **1** (benzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

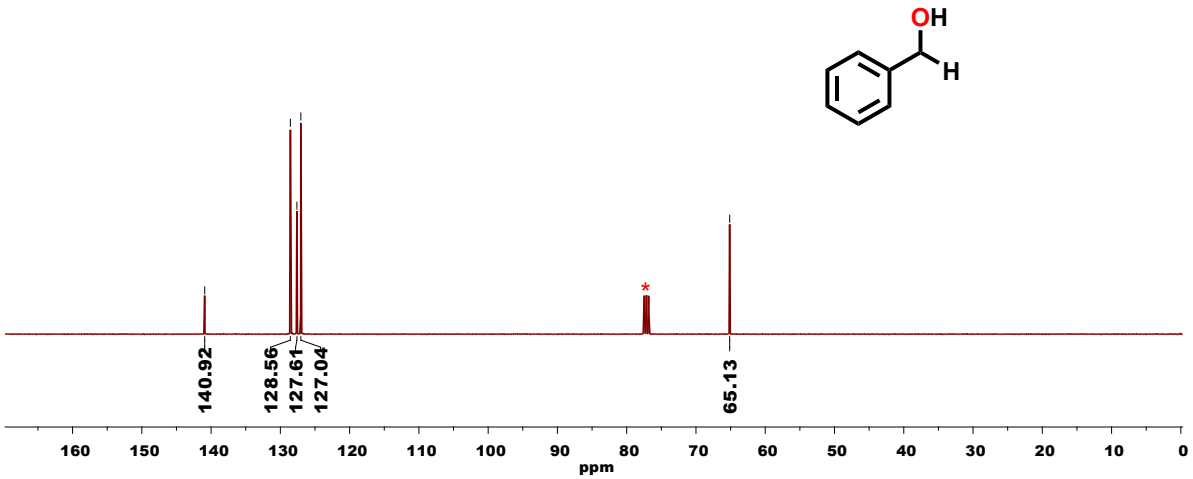

Figure S20. ^{13}C NMR spectrum of product **1** (benzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

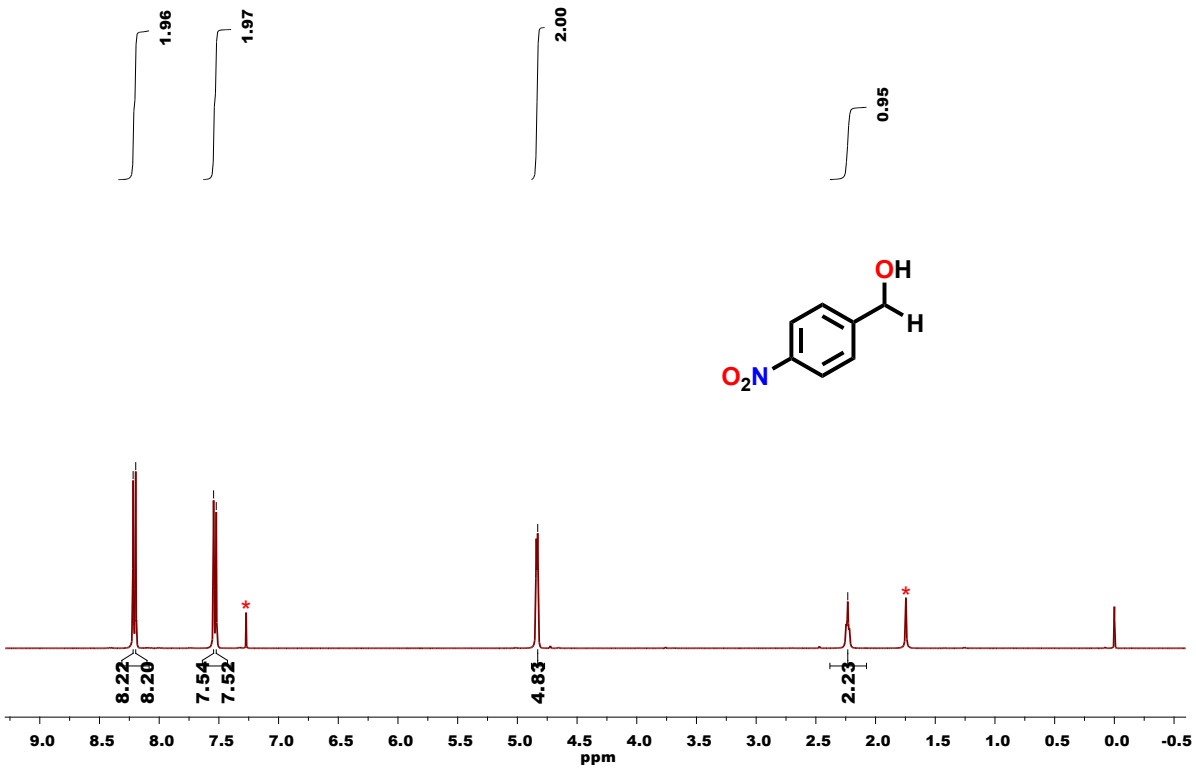

Figure S21. ^{1}H NMR spectrum of product **2** (4-nitrobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

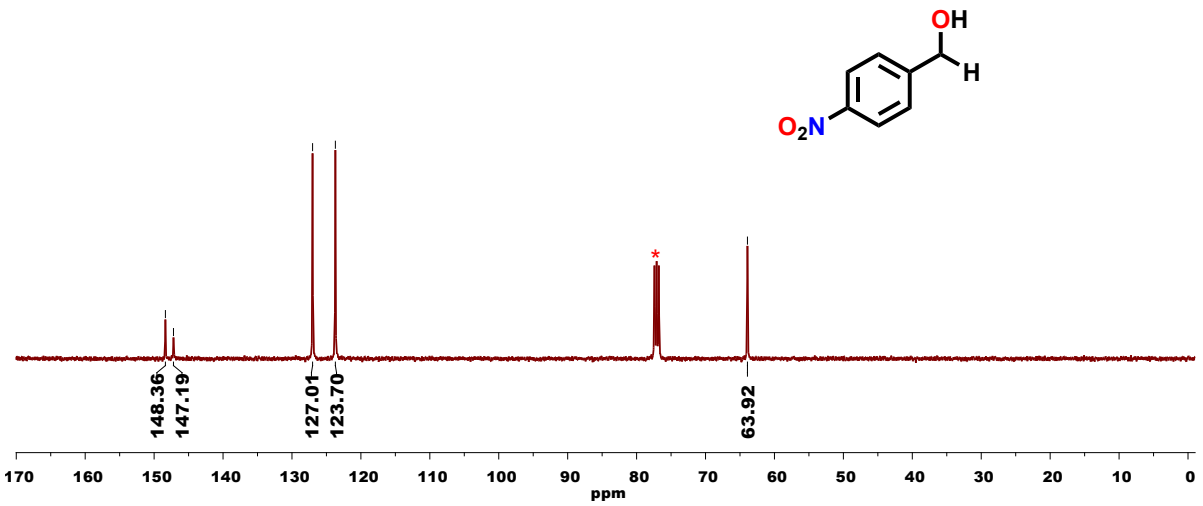

Figure S22. ^{13}C NMR spectrum of product **2** (4-nitrobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

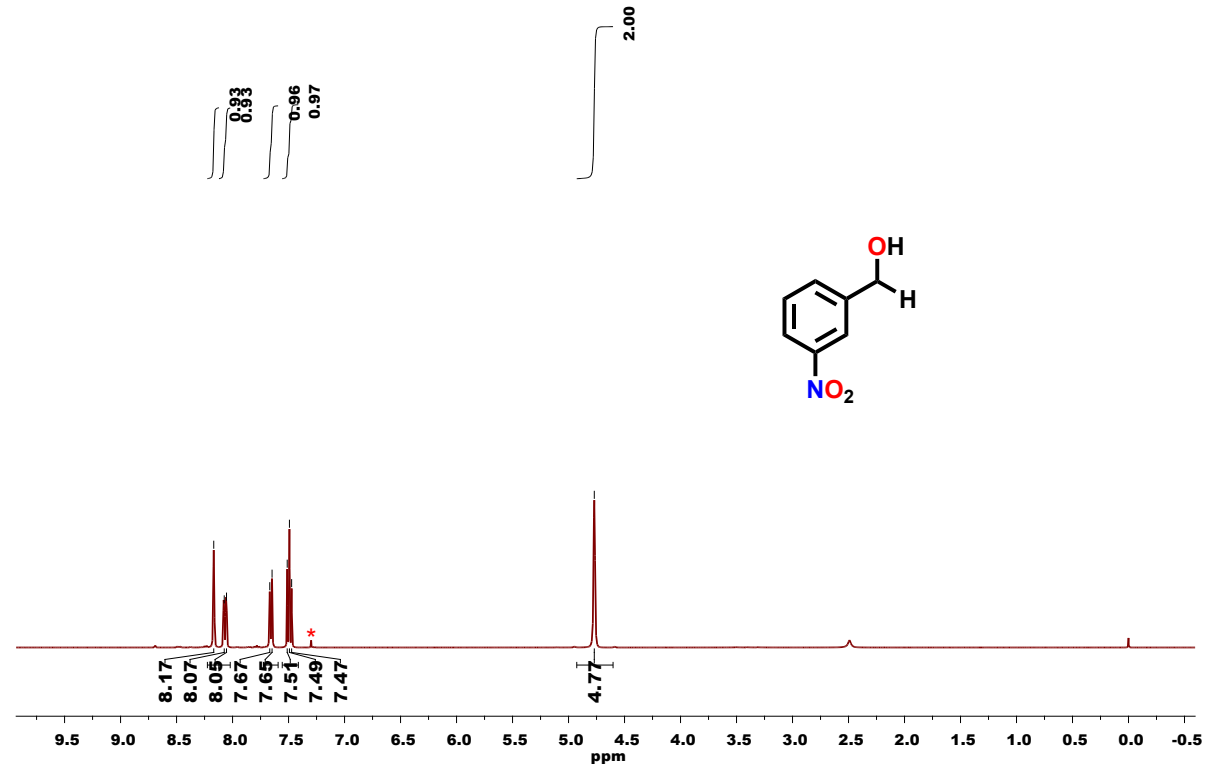

Figure S23. ^{1}H NMR spectrum of product **3** (3-nitrobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

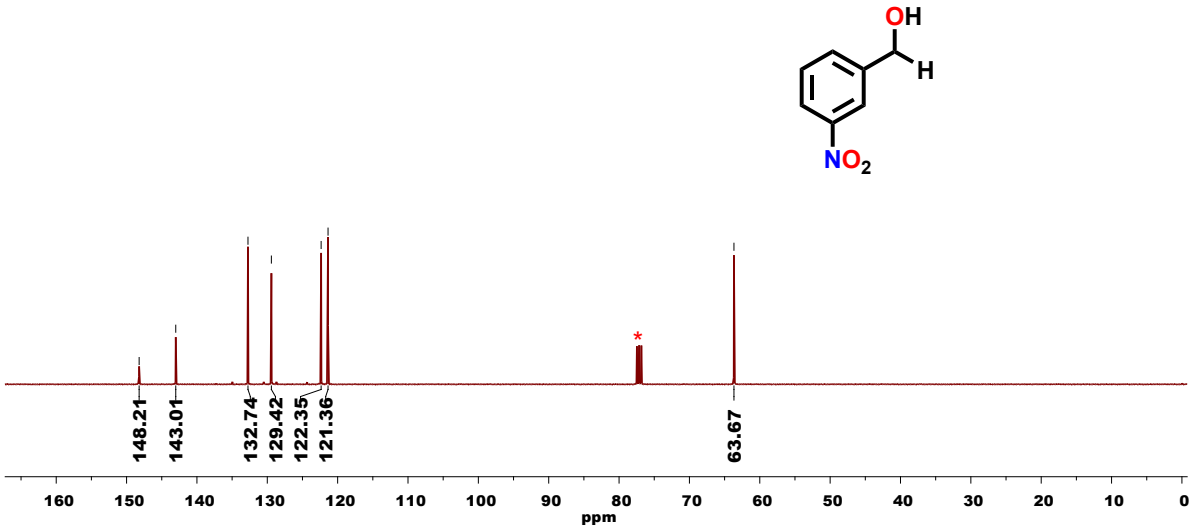

Figure S24. ^{13}C NMR spectrum of product **3** (3-nitrobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

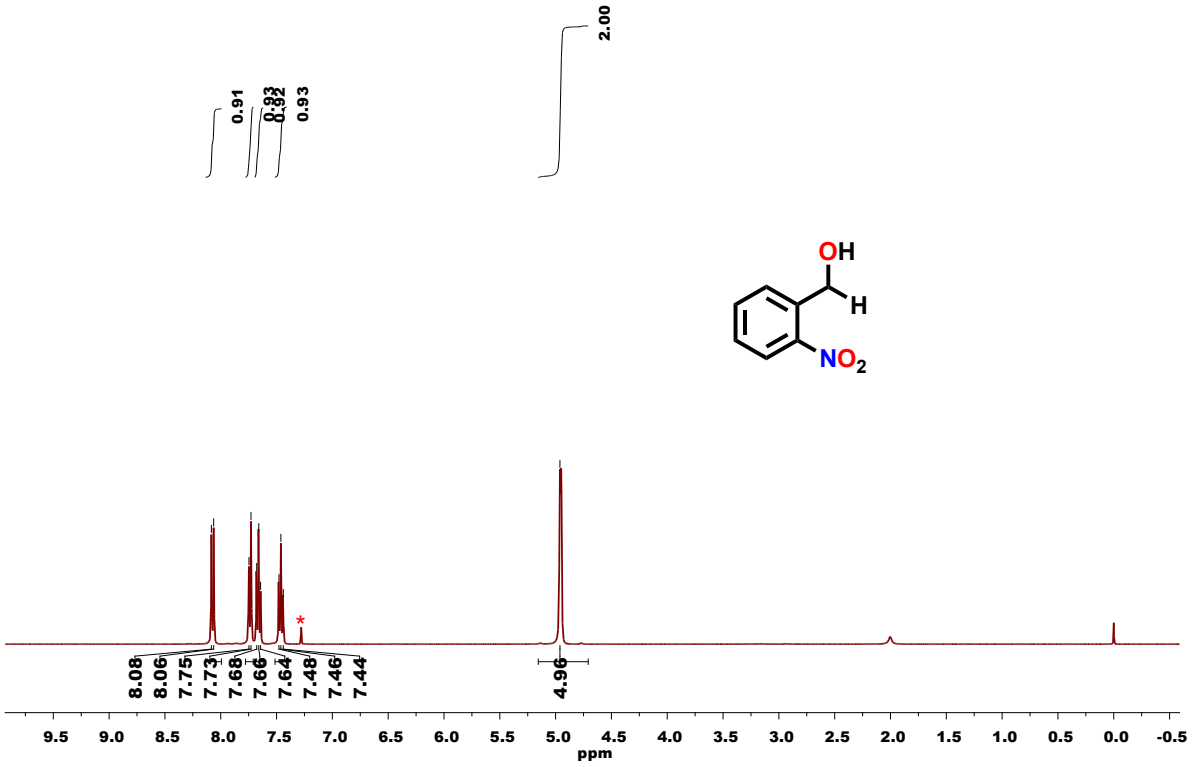

Figure S25. ^{1}H NMR spectrum of product **4** (2-nitrobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

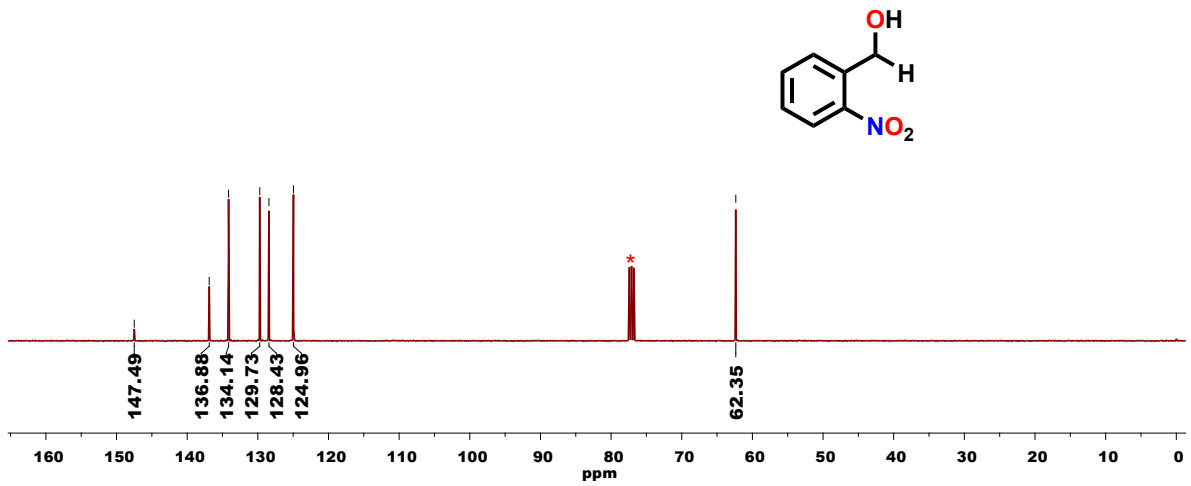

Figure S26. ^{13}C NMR spectrum of product **4** (2-nitrobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

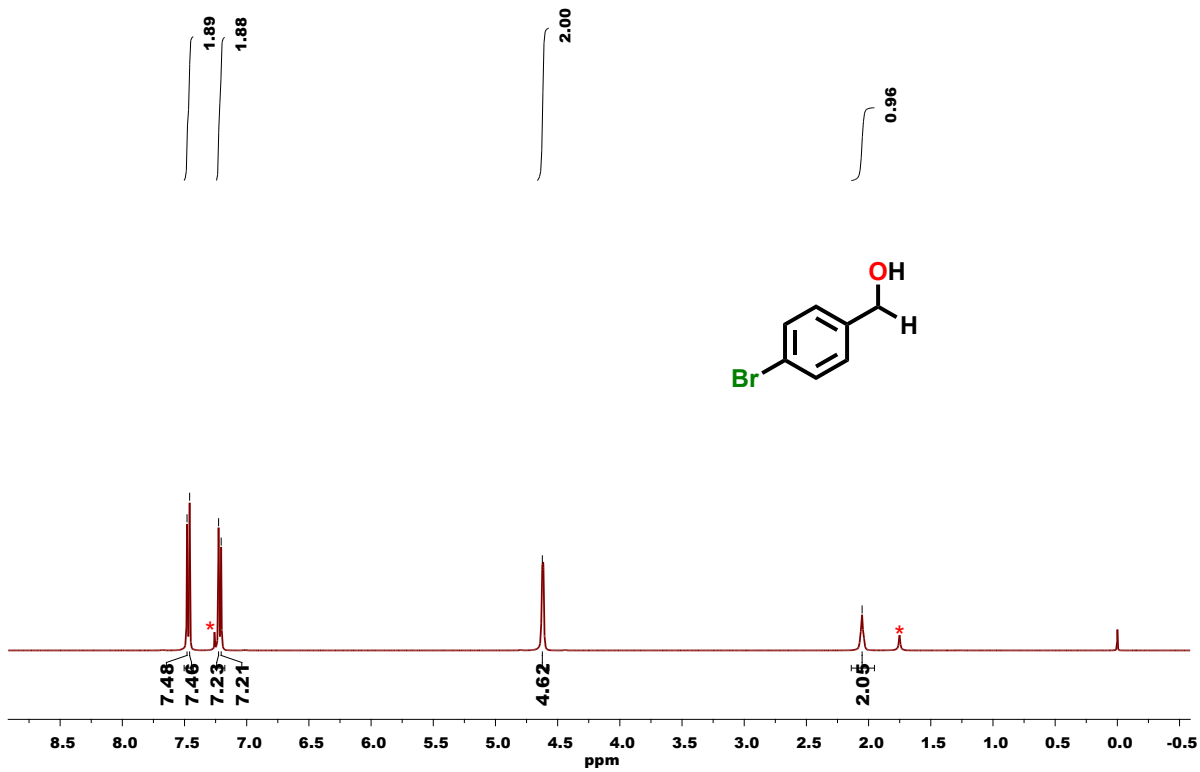

Figure S27. ^{1}H NMR spectrum of product **5** (4-bromobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

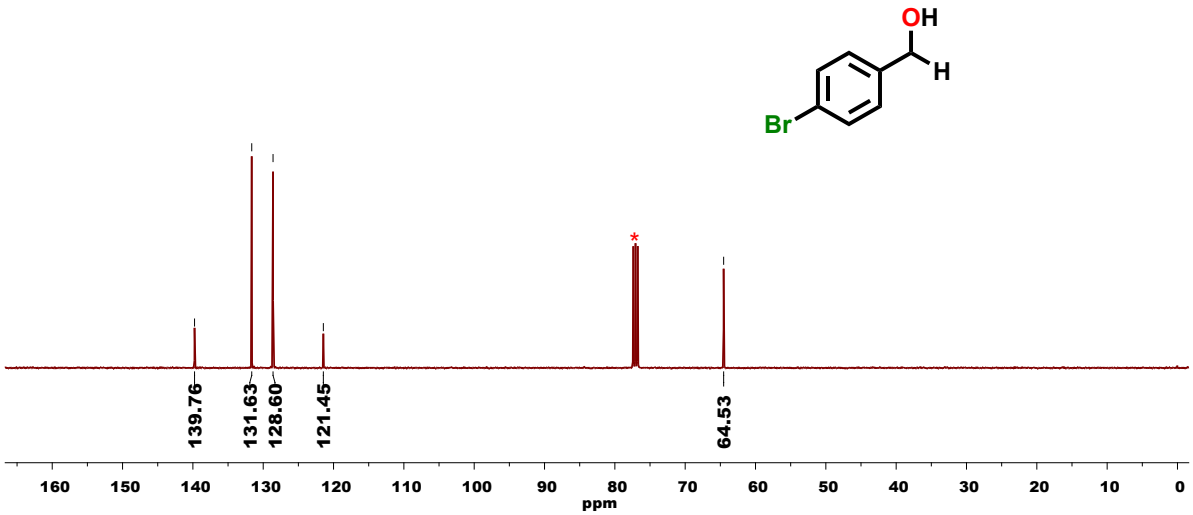

Figure S28. ^{13}C NMR spectrum of product **5** (4-bromobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

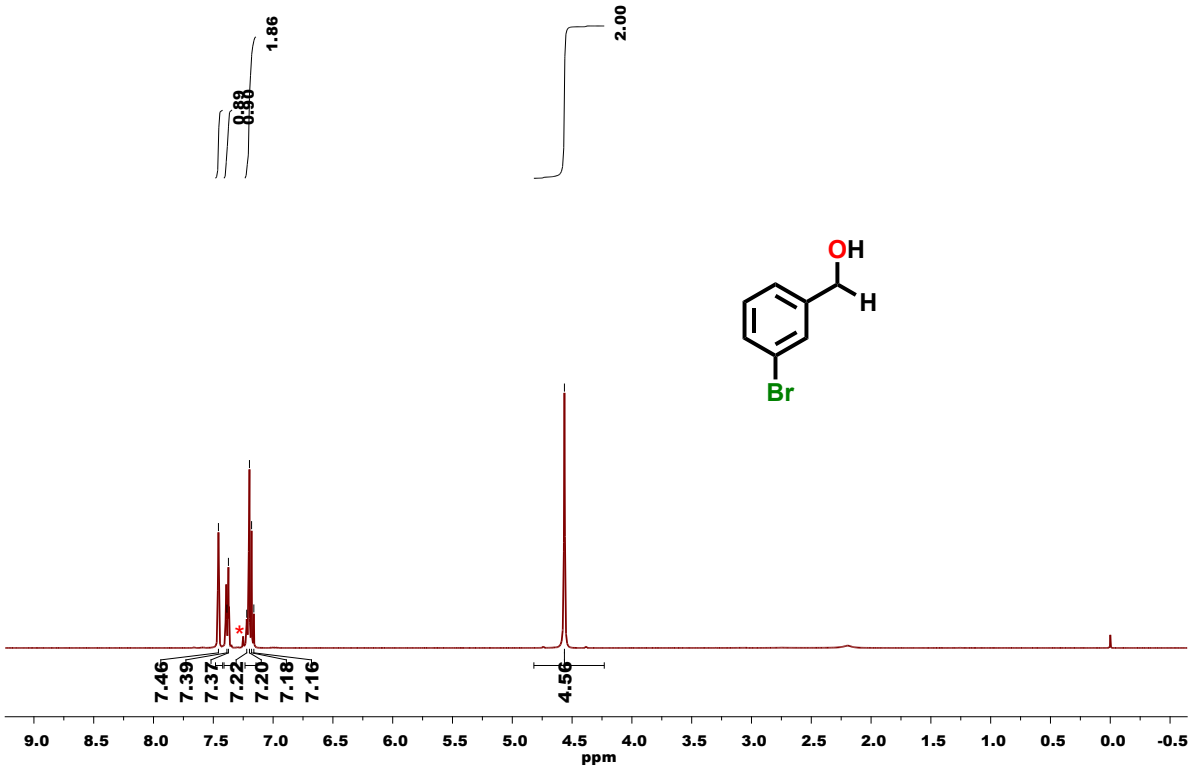

Figure S29. ^{1}H NMR spectrum of product **6** (3-bromobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

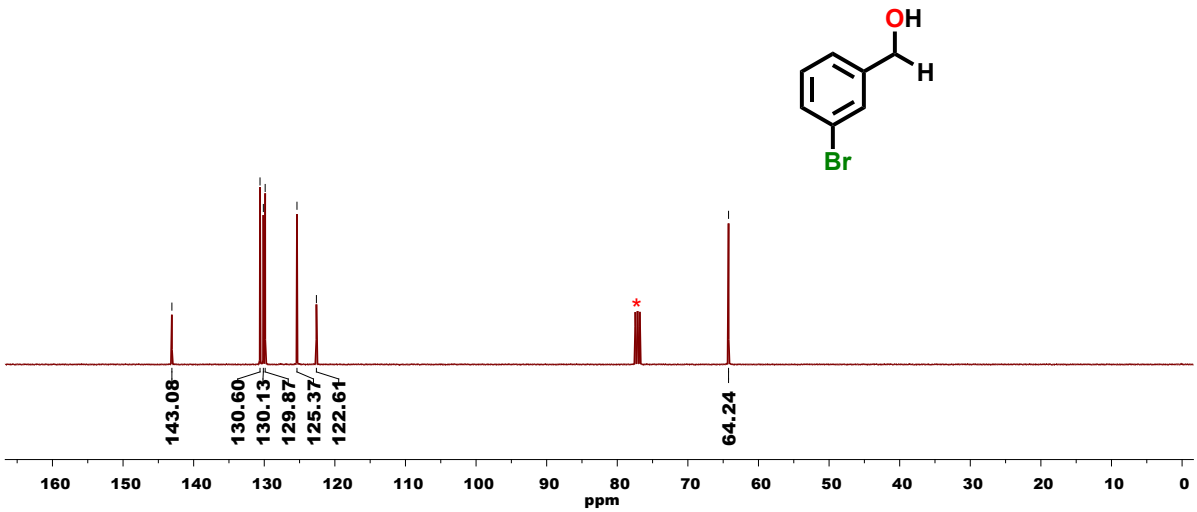

Figure S30. ^{13}C NMR spectrum of product **6** (3-bromobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

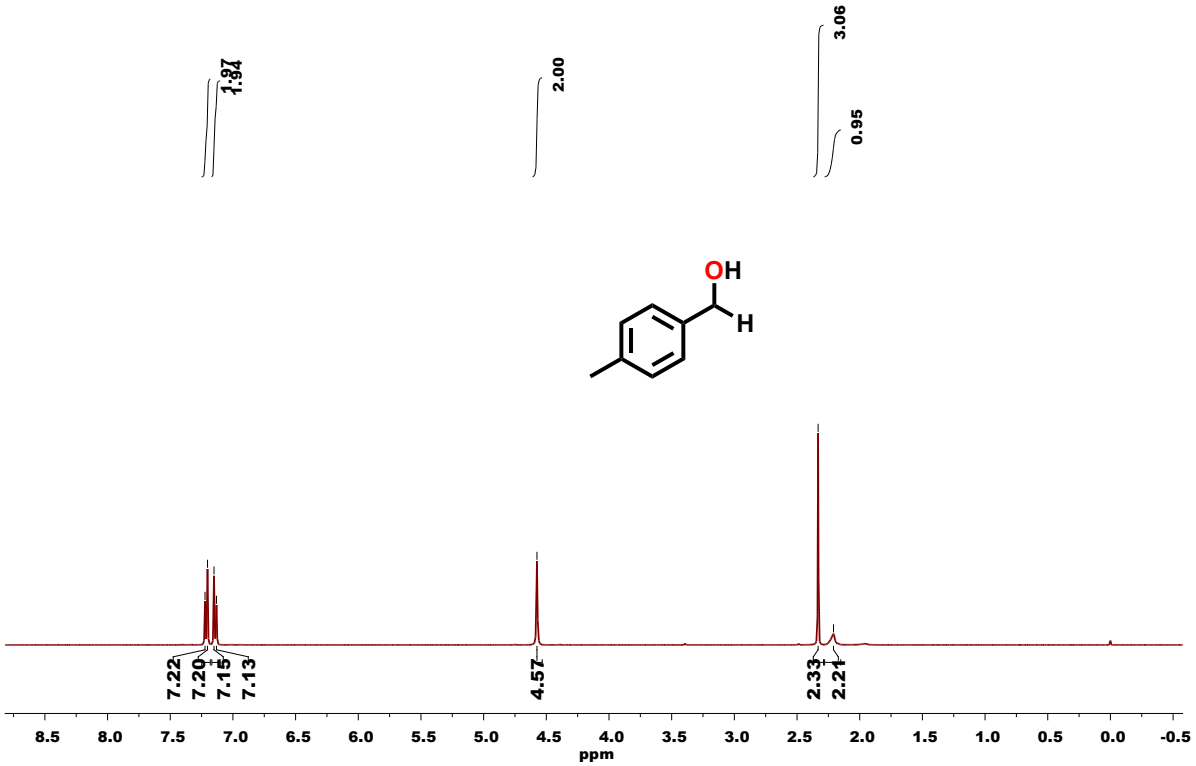

Figure S31. ^{1}H NMR spectrum of product **7** (4-methylbenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

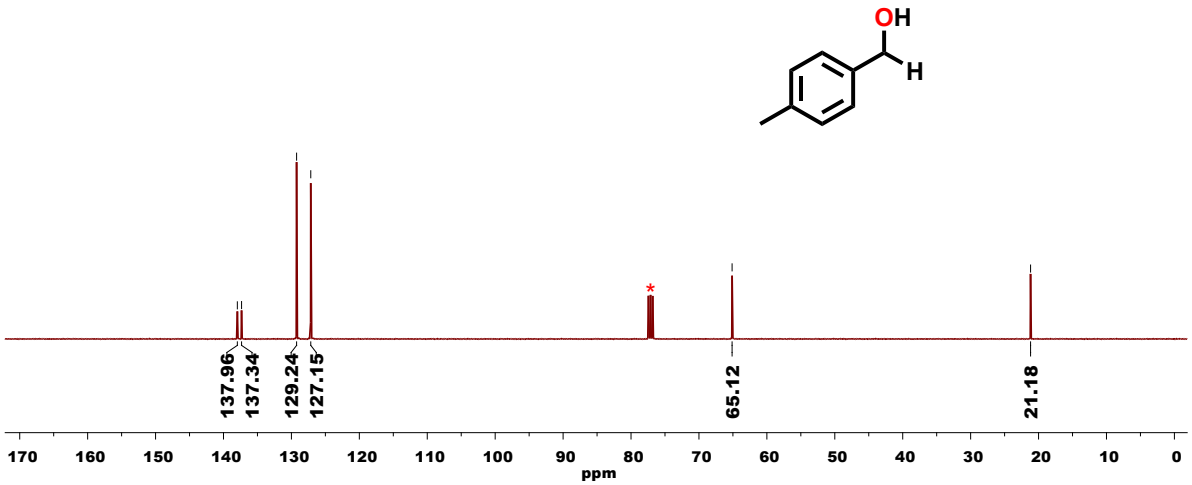

Figure S32. ^{13}C NMR spectrum of product **7** (4-methylbenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

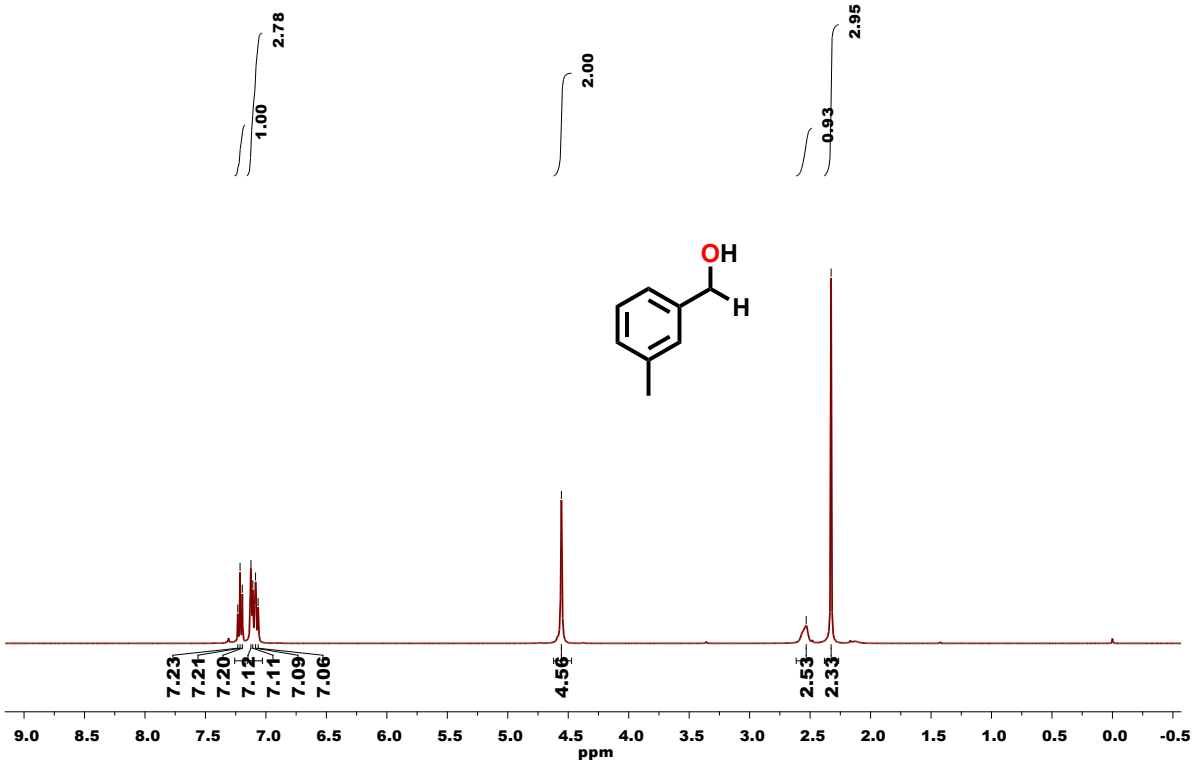

Figure S33. ^{1}H NMR spectrum of product **8** (3-methylbenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

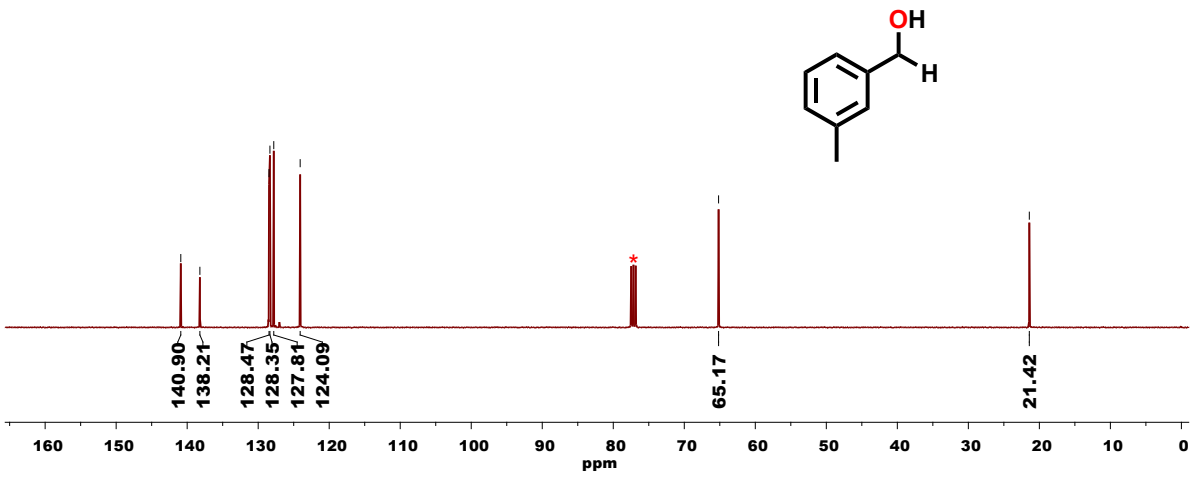

Figure S34. ^{13}C NMR spectrum of product **8** (3-methylbenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

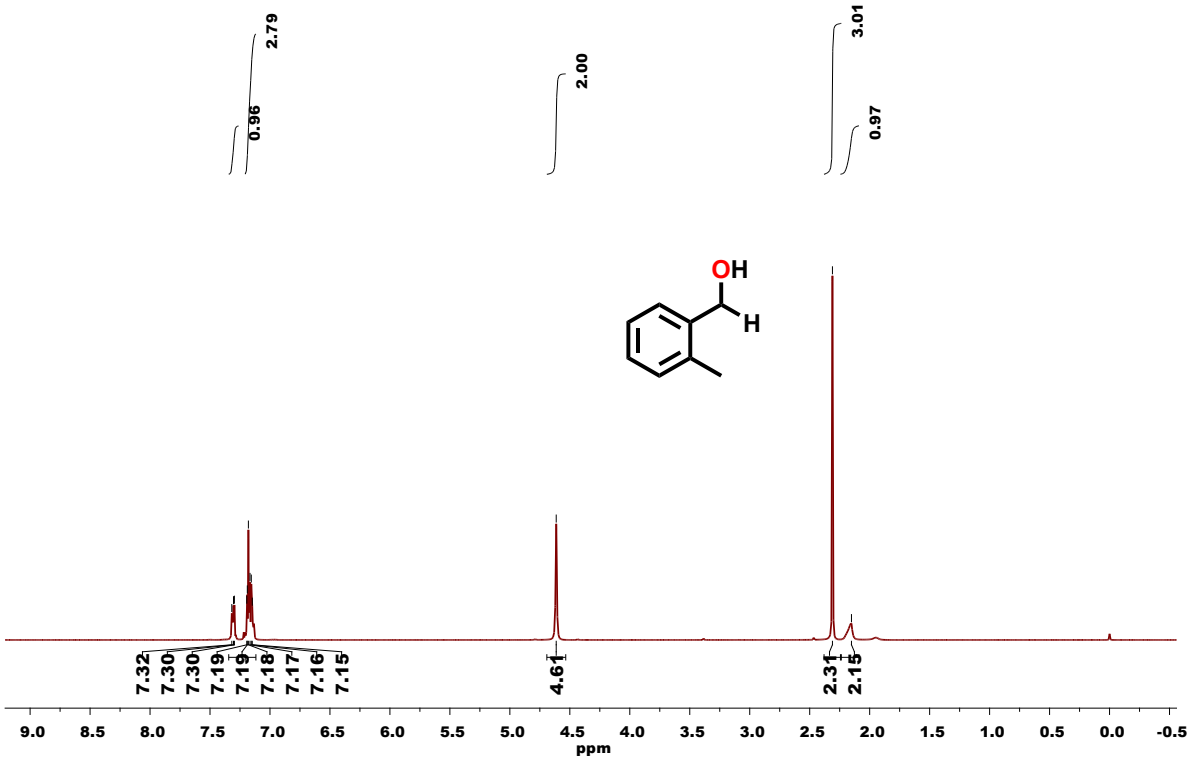

Figure S35. ^{1}H NMR spectrum of product **9** (2-methylbenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

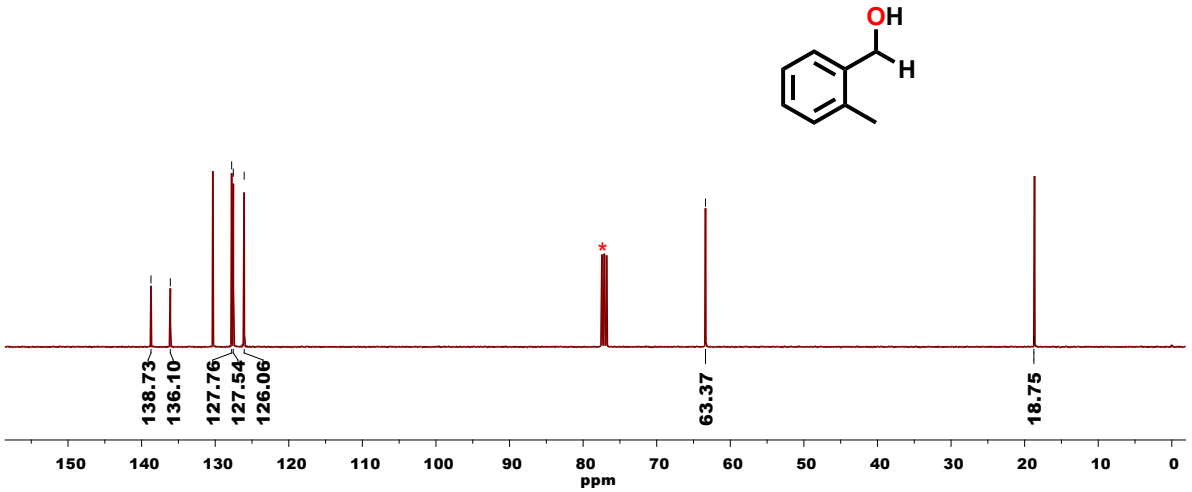

Figure S36. ^{13}C NMR spectrum of product **9** (2-methylbenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

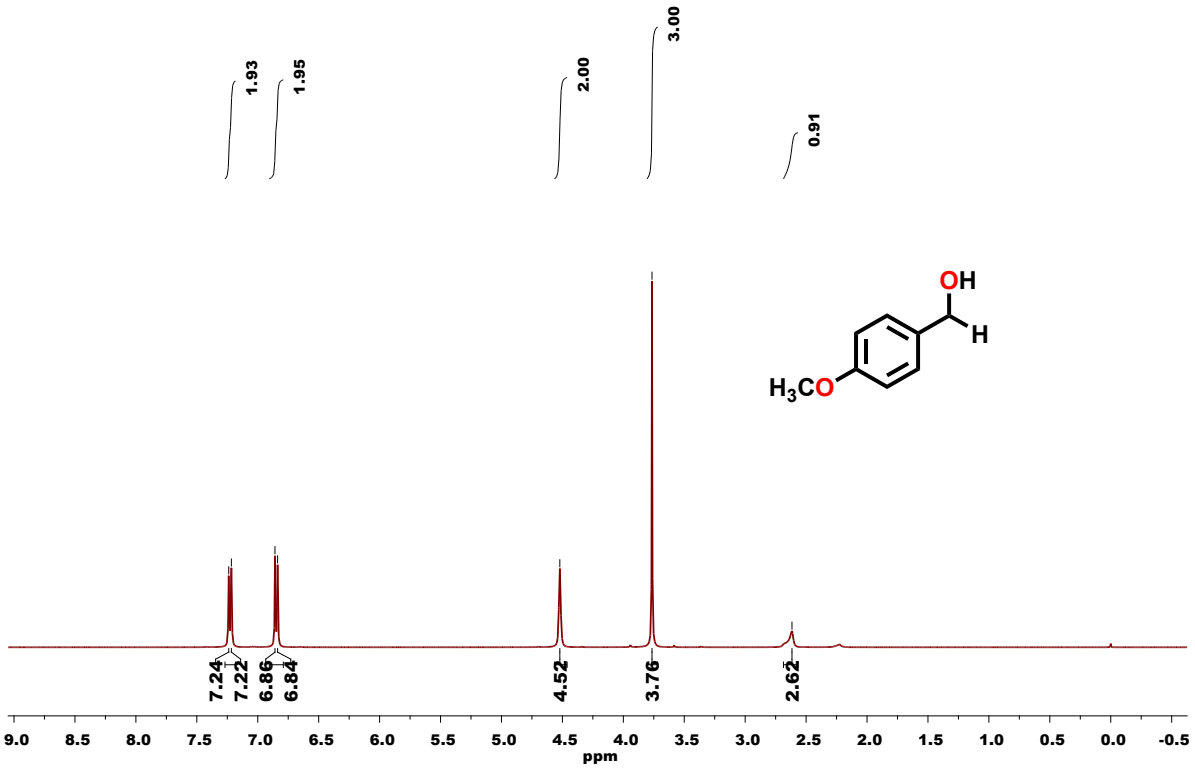

Figure S37. ^{1}H NMR spectrum of product **10** (4-methoxybenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

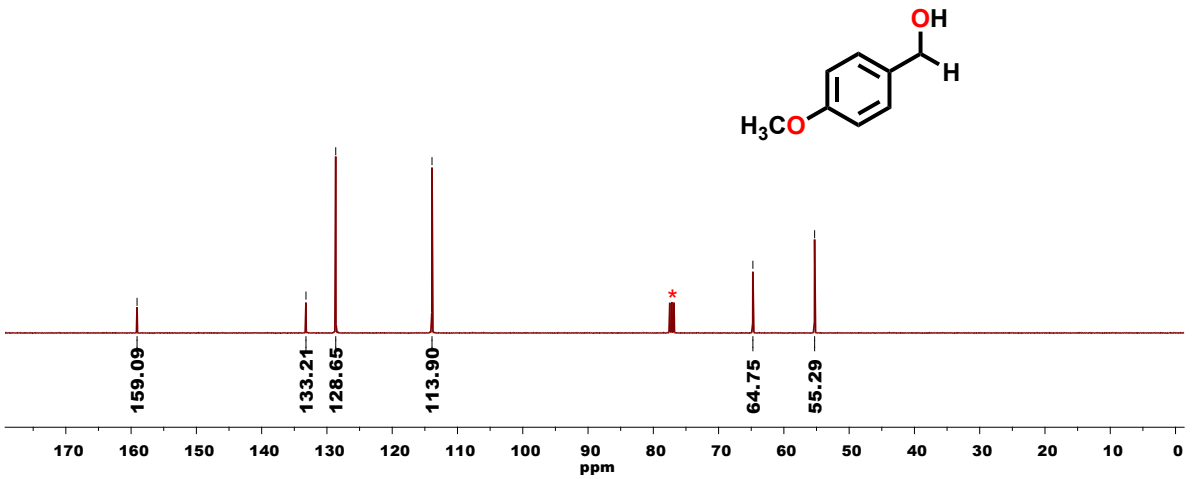

Figure S38. ^{13}C NMR spectrum of product **10** (4-methoxybenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

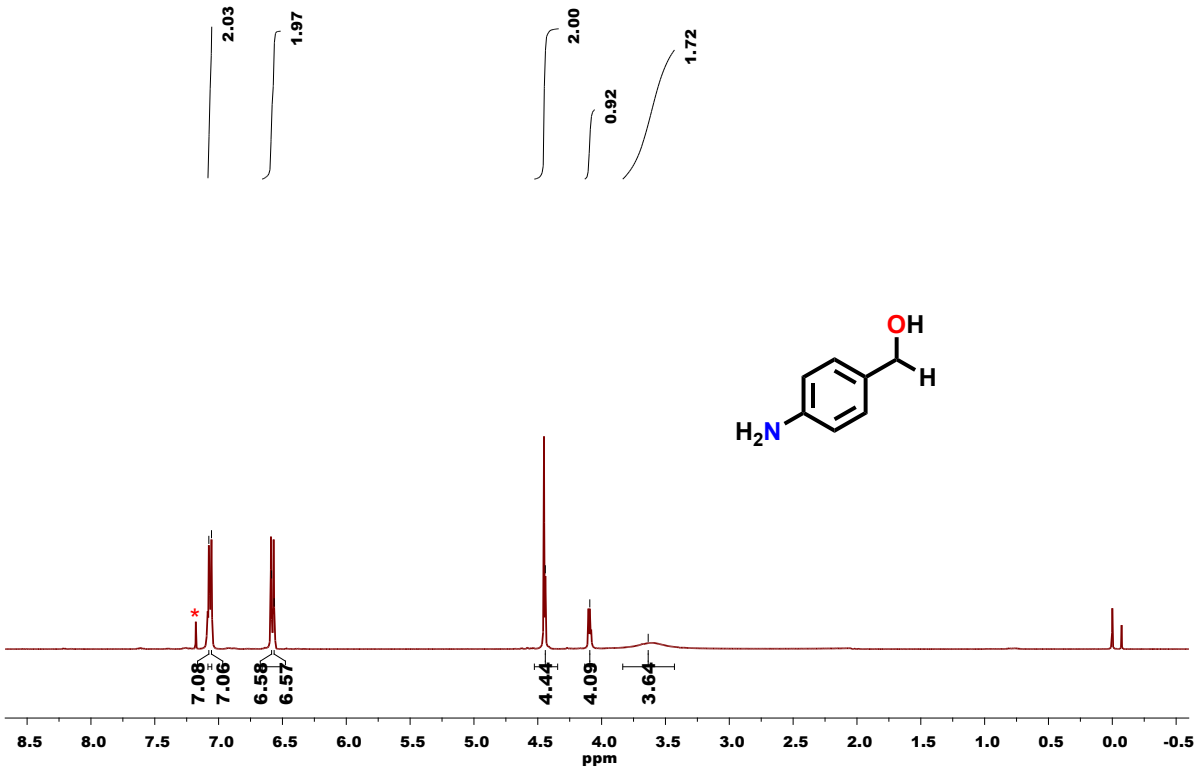

Figure S39. ^{1}H NMR spectrum of product **11** (4-aminobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

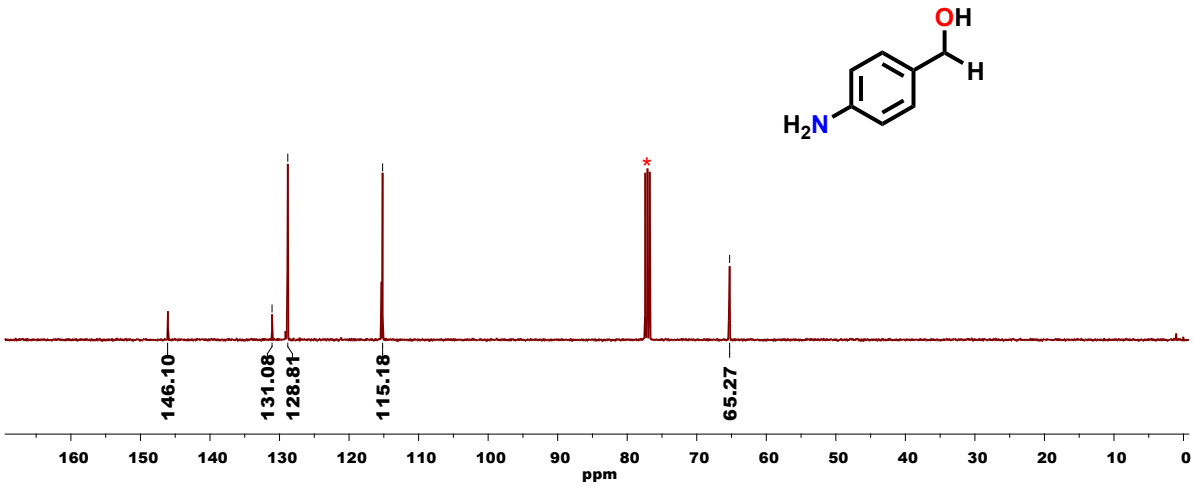

Figure S40. ^{13}C NMR spectrum of product **11** (4-aminobenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

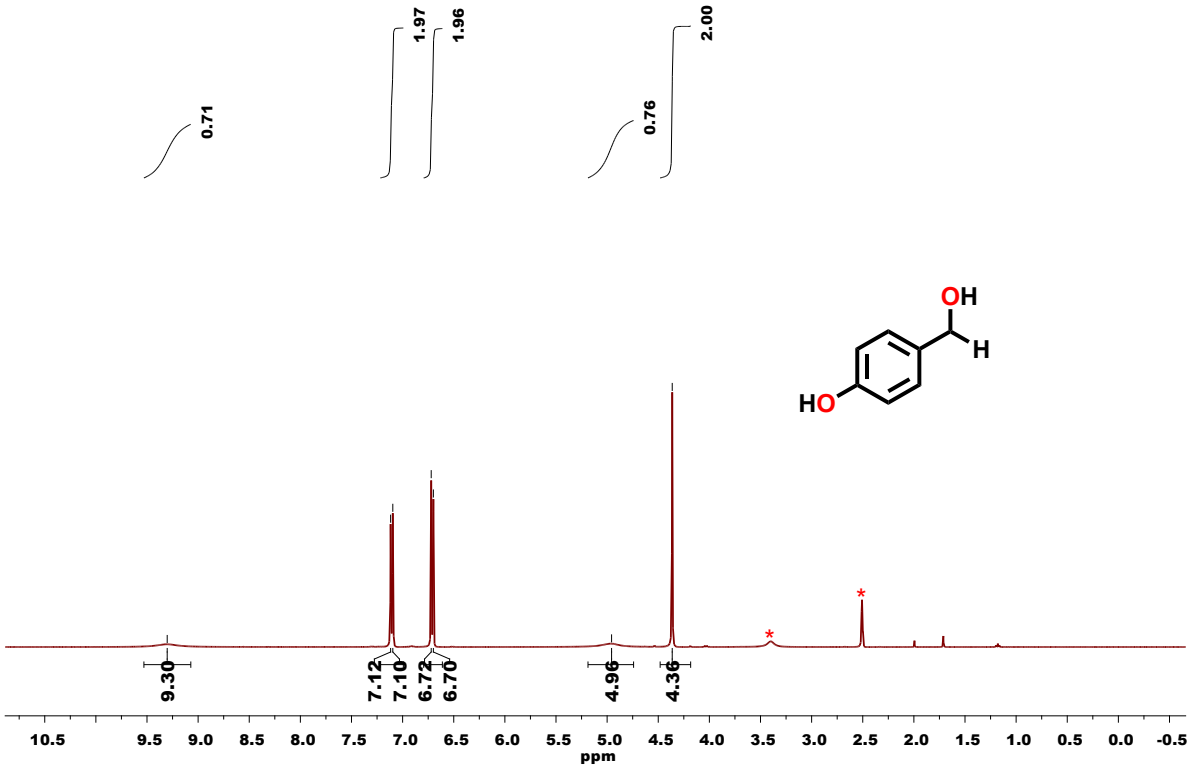

Figure S41. ^{1}H NMR spectrum of product **12** (4-hydroxybenzyl alcohol) in (DMSO-*d6*) solvent where * represents the residual solvent and/or adventitious water peaks.

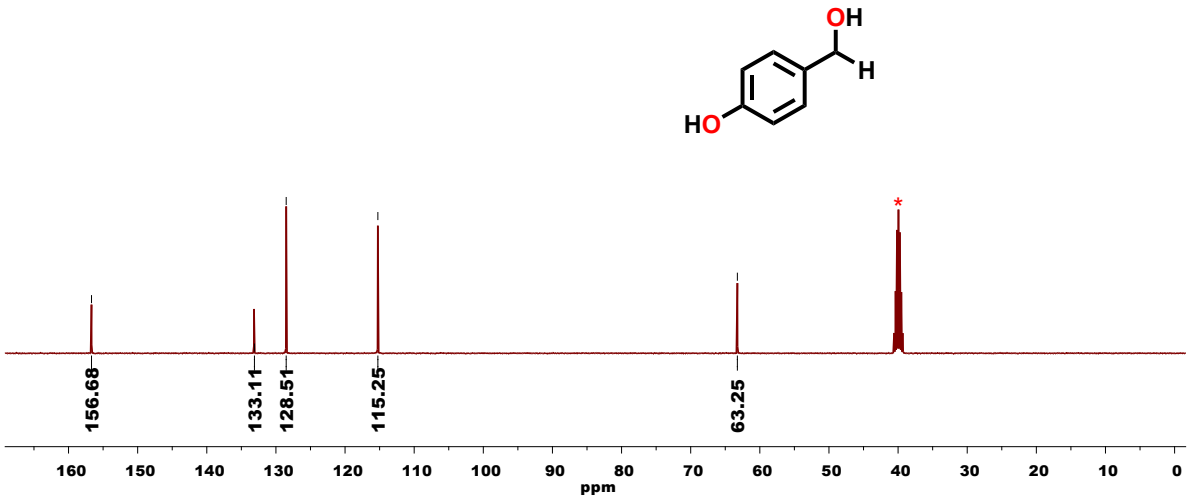

Figure S42. ^{13}C NMR spectrum of product **12** (4-hydroxybenzyl alcohol) in (DMSO-*d6*) solvent where * represents the residual solvent peak.

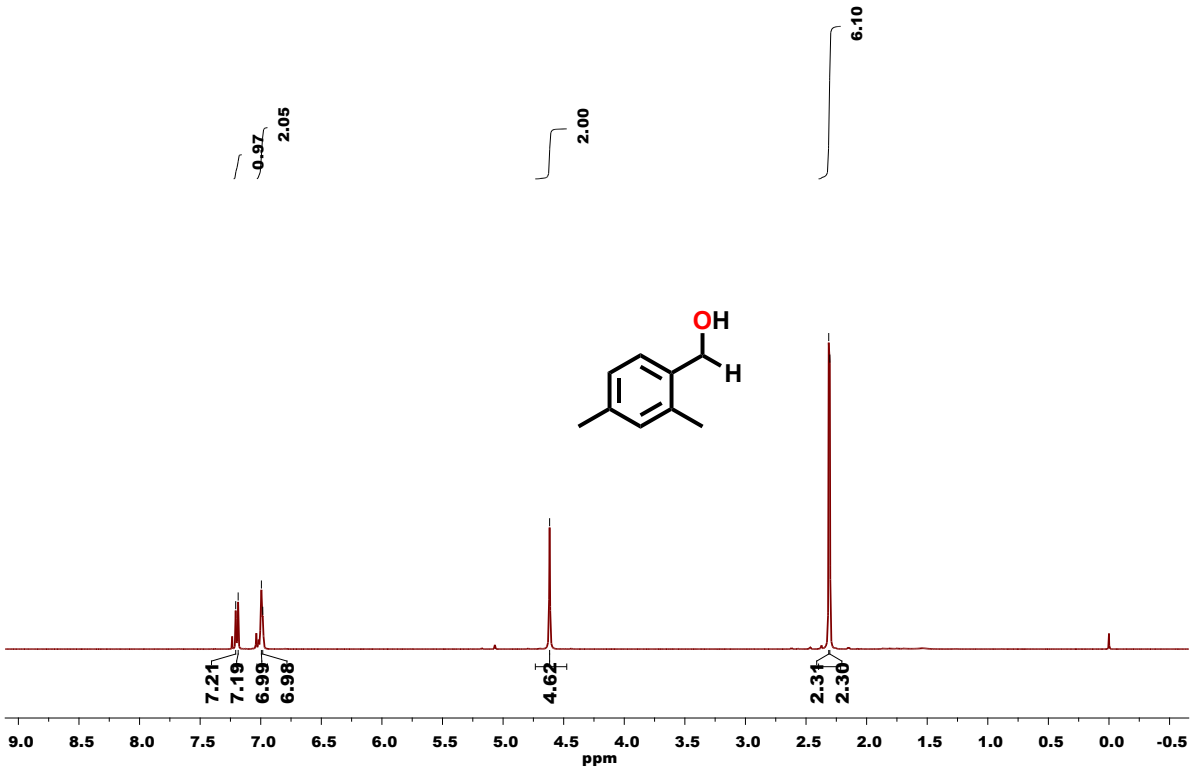

Figure S43. ^{1}H NMR spectrum of product **13** (2,5-dimethylbenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

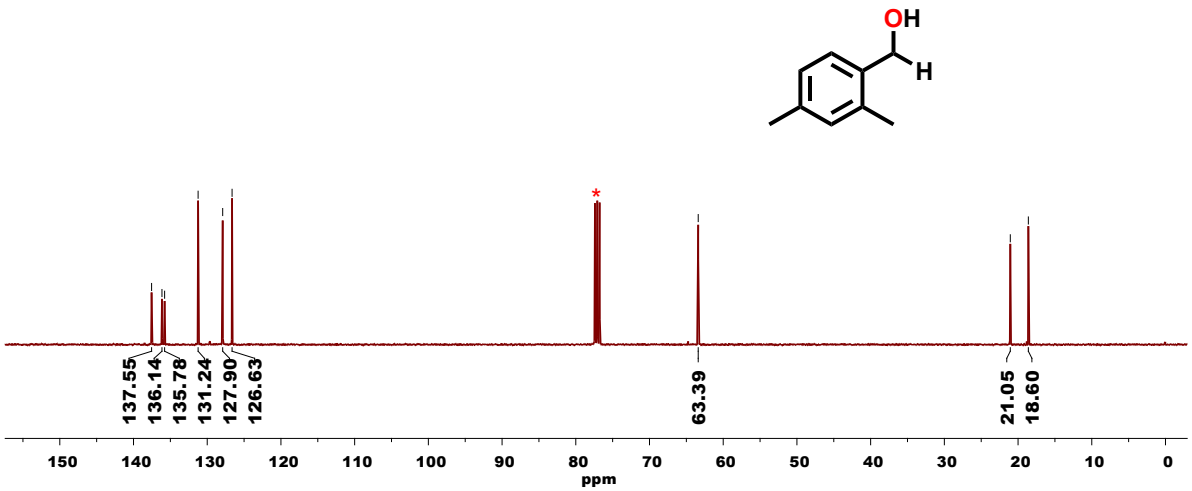

Figure S44. ^{13}C NMR spectrum of product **13** (2,5-dimethylbenzyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

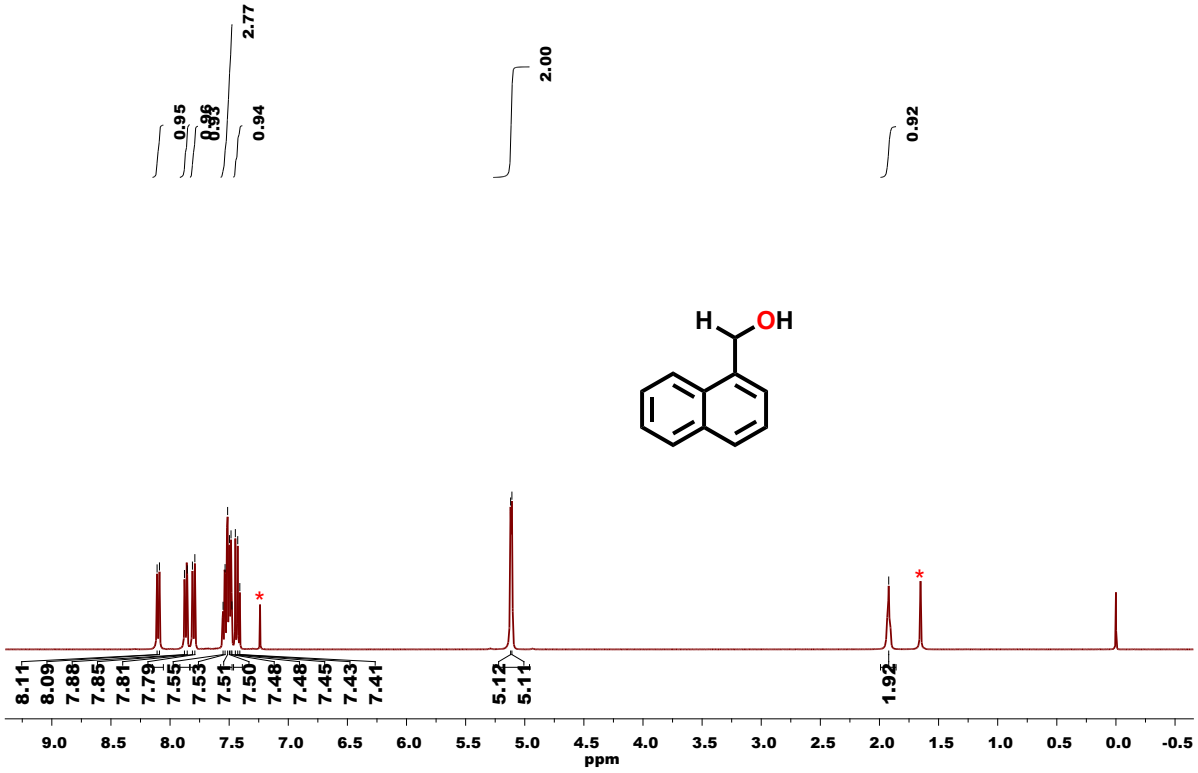

Figure S45. ^{1}H NMR spectrum of product **14** (1-napthalenemethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

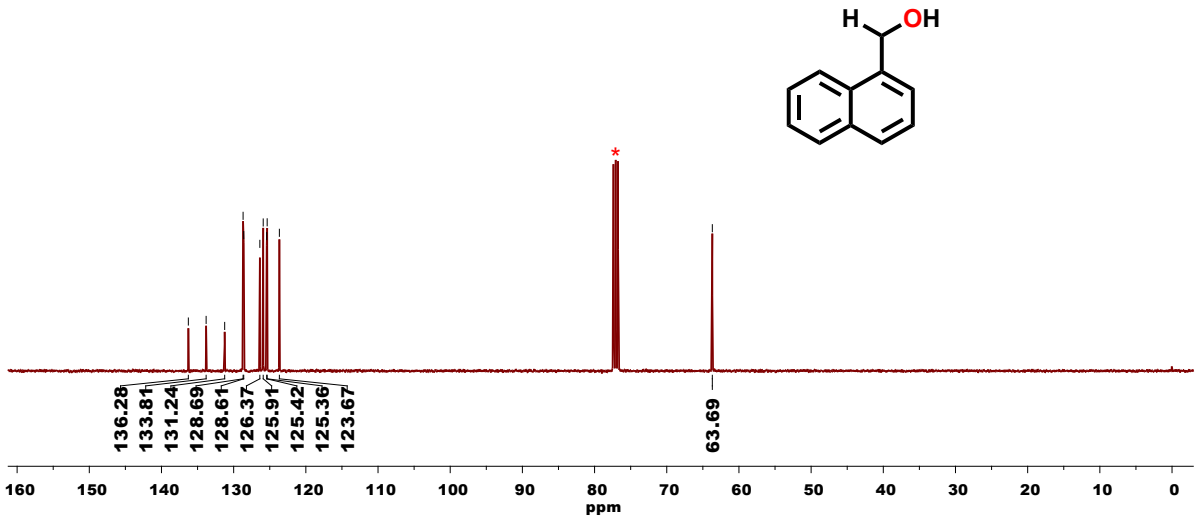

Figure S46. ^{13}C NMR spectrum of product **14** (1-napthalenemethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

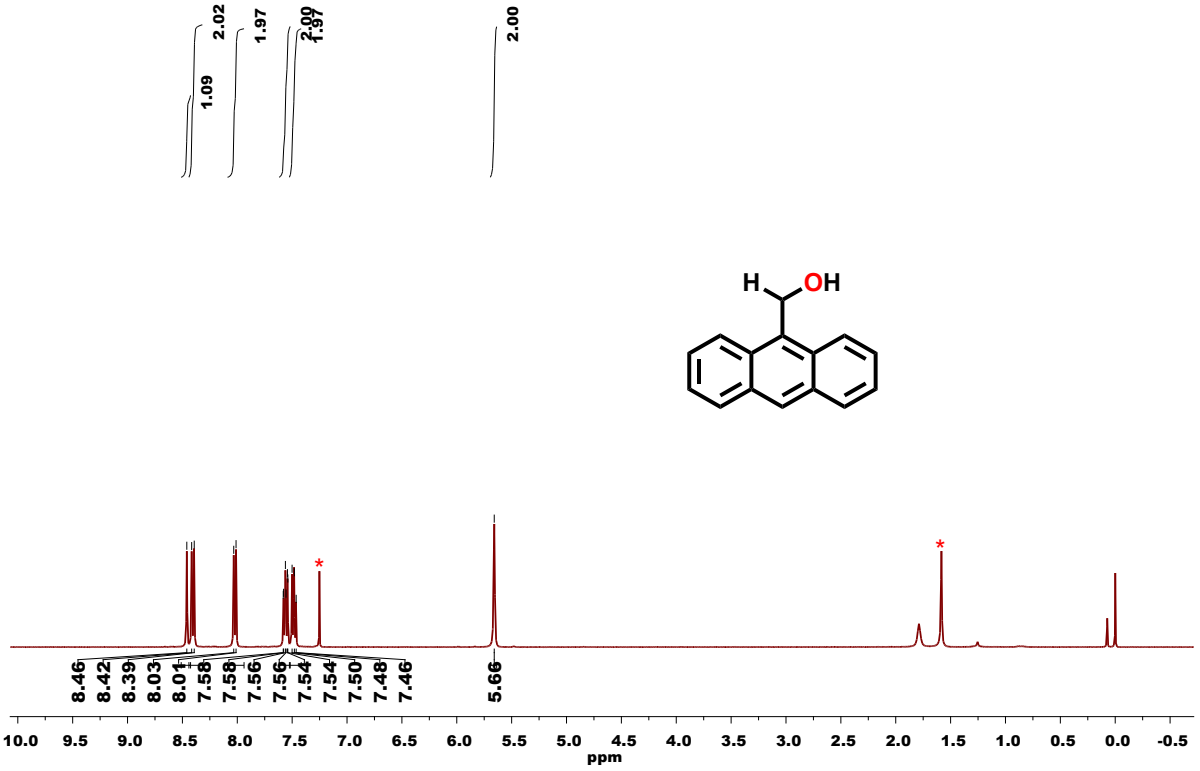

Figure S47. ^{1}H NMR spectrum of product **15** (9-anthracenemethanol) in $CDCl_3$ solvent where * represents the residual solvent peak and/or adventitious water peaks.

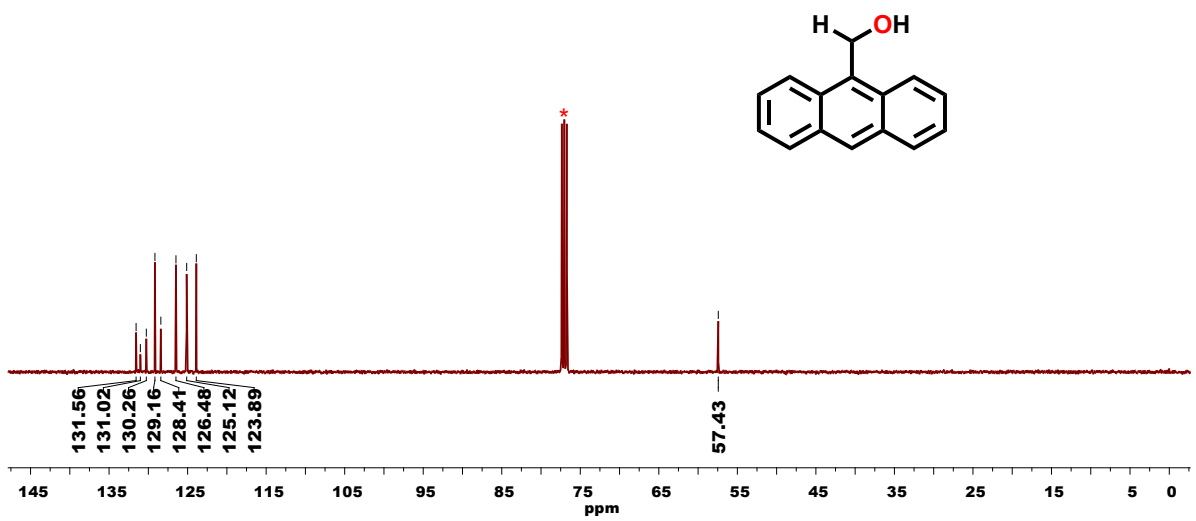

Figure S48. ^{13}C NMR spectrum of product **15** (9-anthracenemethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

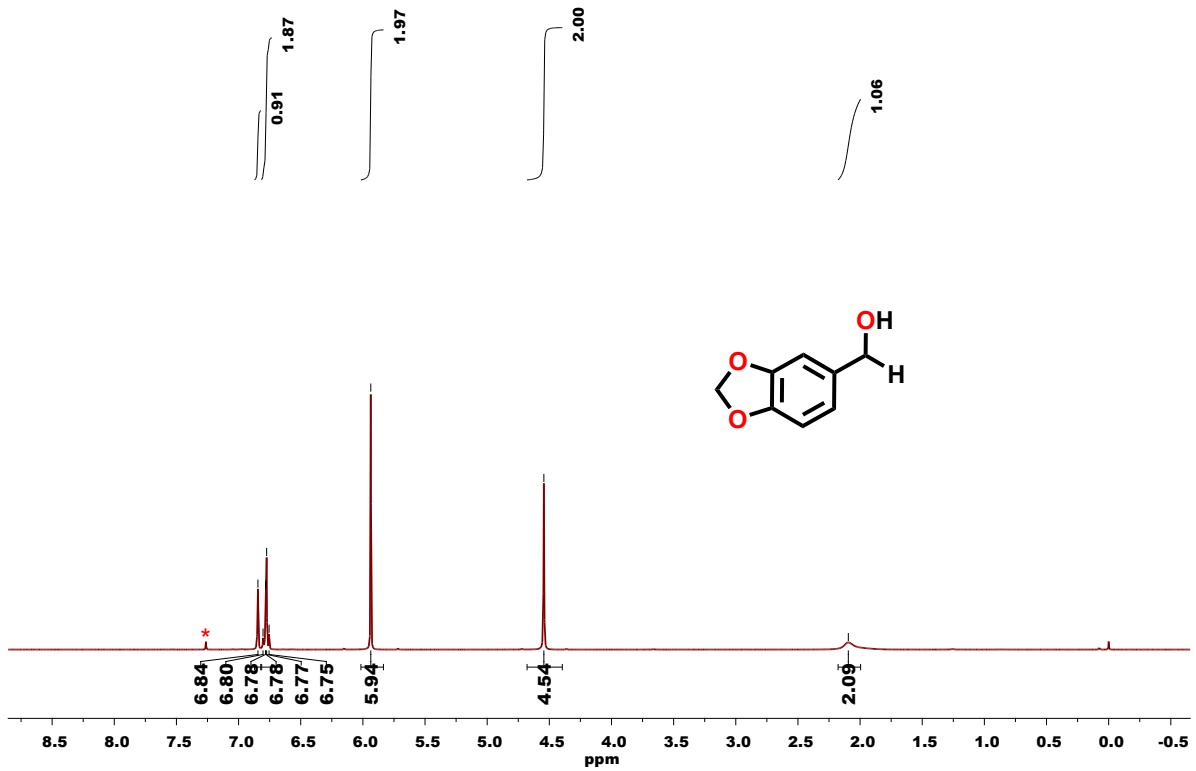

Figure S49. ^{1}H NMR spectrum of product **16** (1,3-benzenedioxol-5-ylmethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

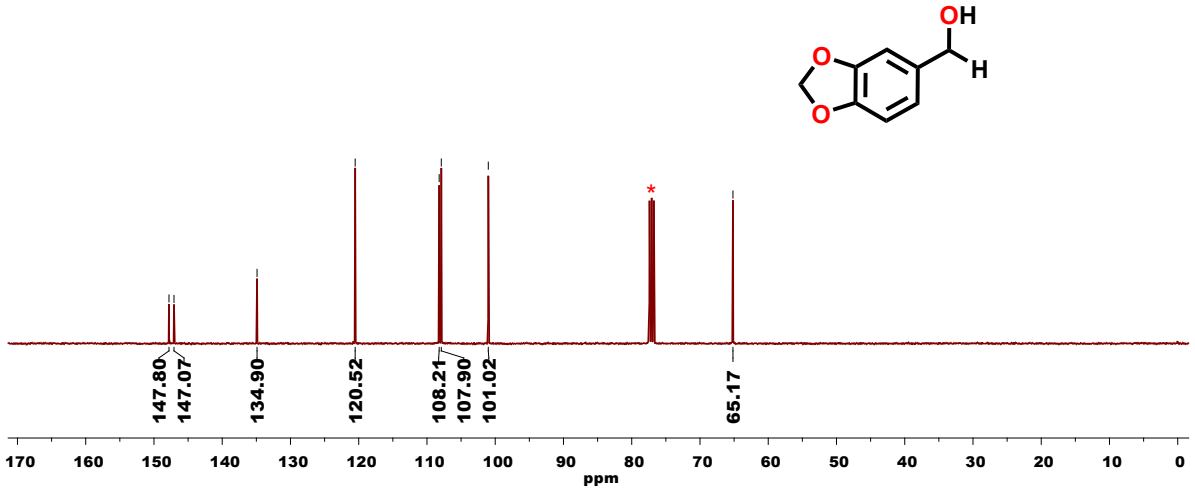

Figure S50. ^{13}C NMR spectrum of product **16** (1,3-benzenedioxol-5-ylmethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

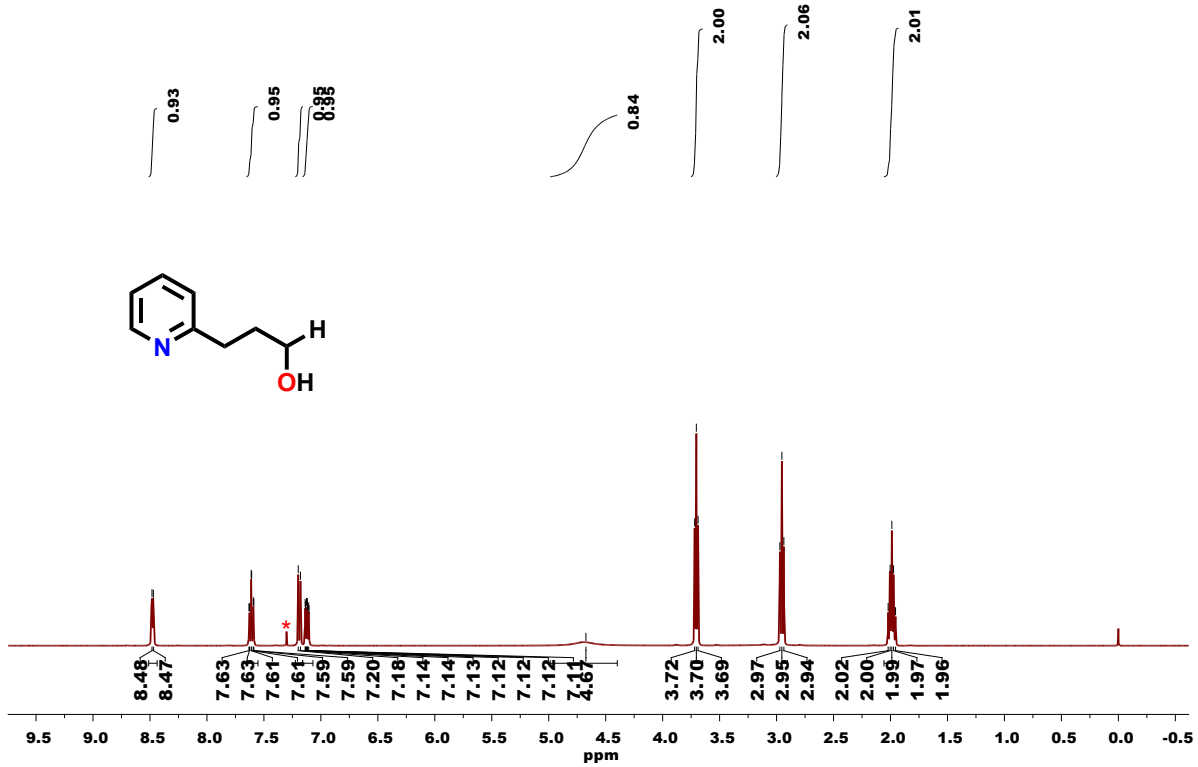

Figure S51. ^{1}H NMR spectrum of product **17** (2-pyridinepropanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

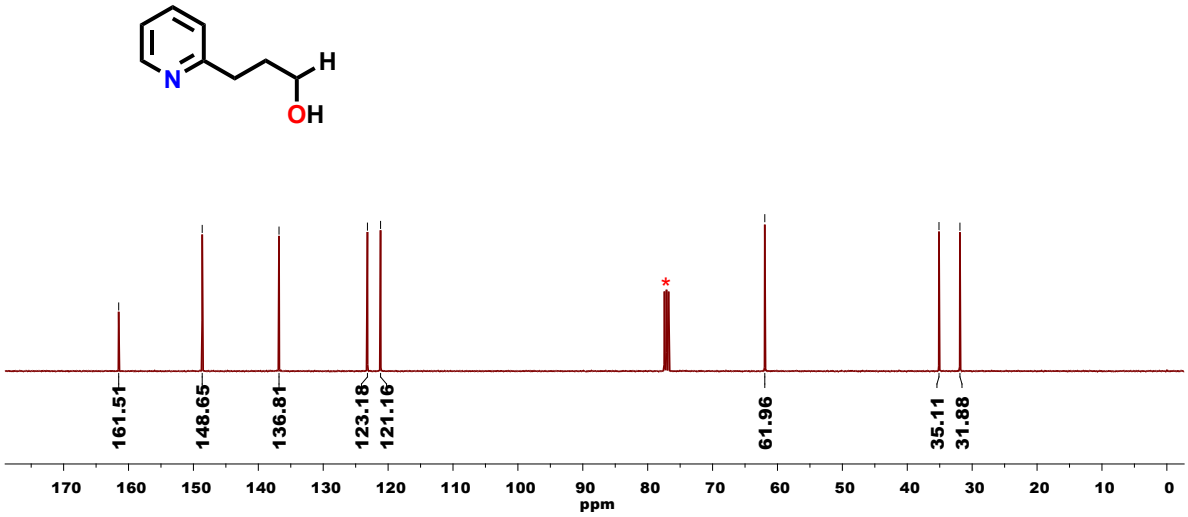

Figure S52. ^{13}C NMR spectrum of product **17** (2-pyridinepropanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

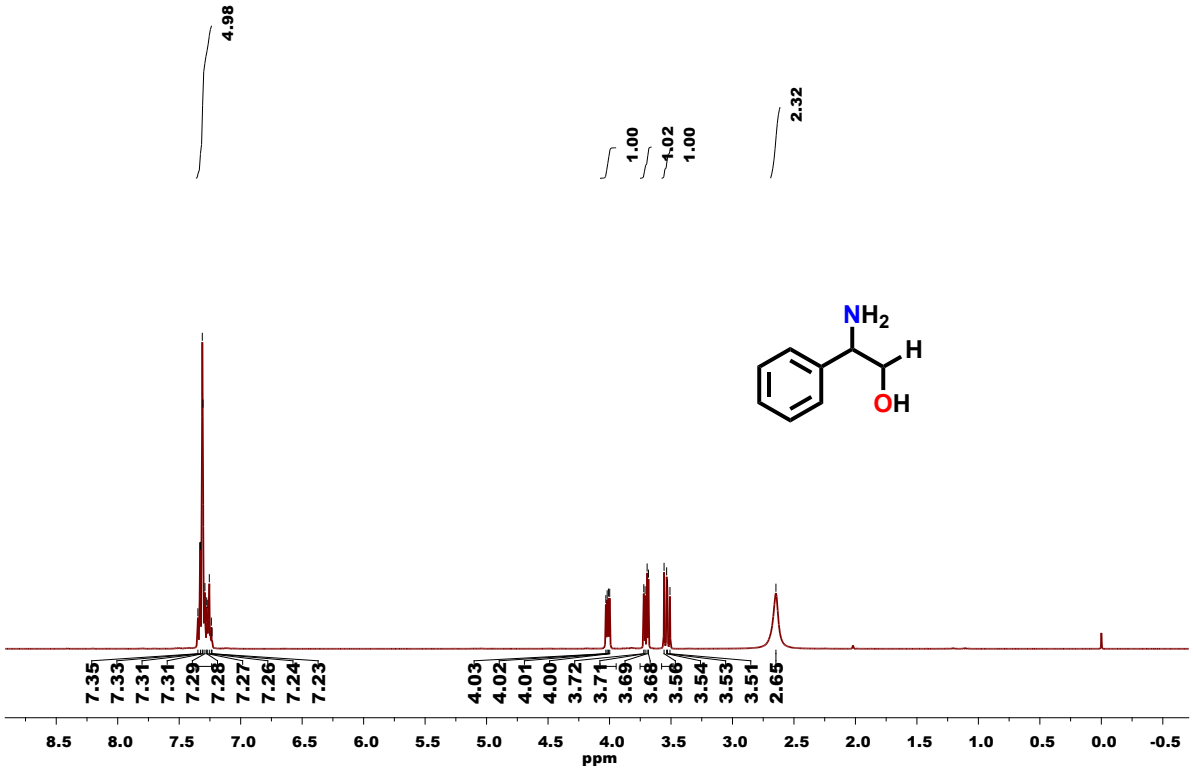

Figure S53. ^{1}H NMR spectrum of product **18** (2-amino-2-phenylethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

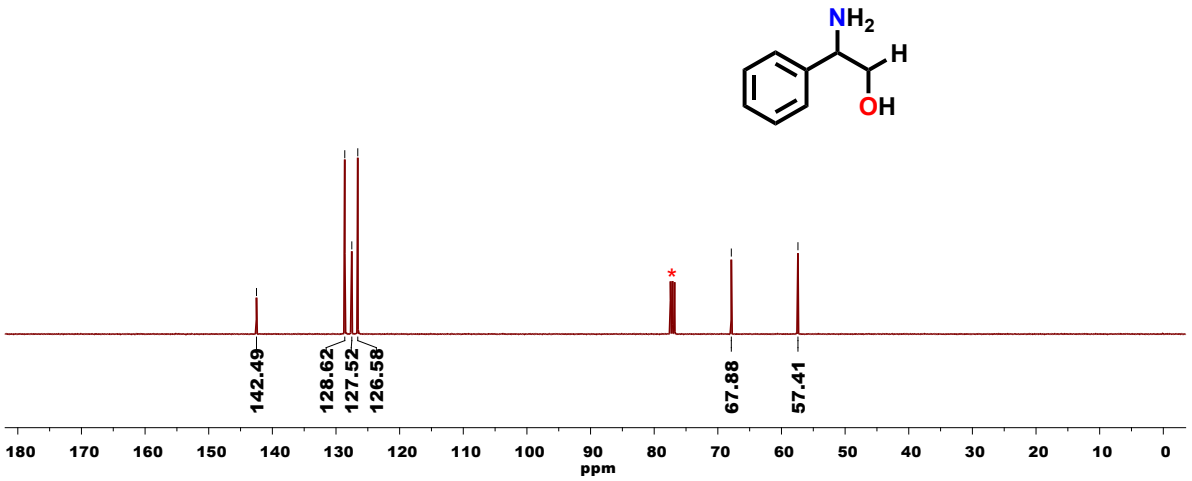

Figure S54. ^{13}C NMR spectrum of product **18** (2-amino-2-phenylethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

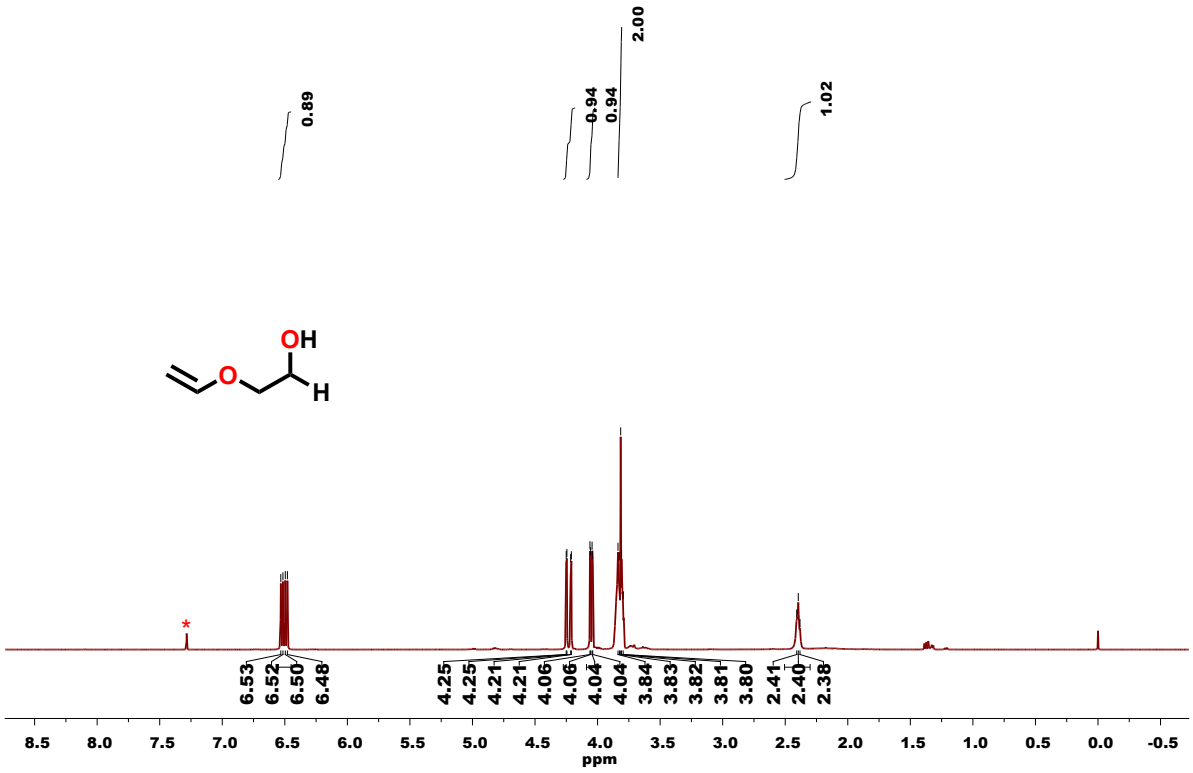

Figure S55. ^{1}H NMR spectrum of product **19** (2-(vinyloxy)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

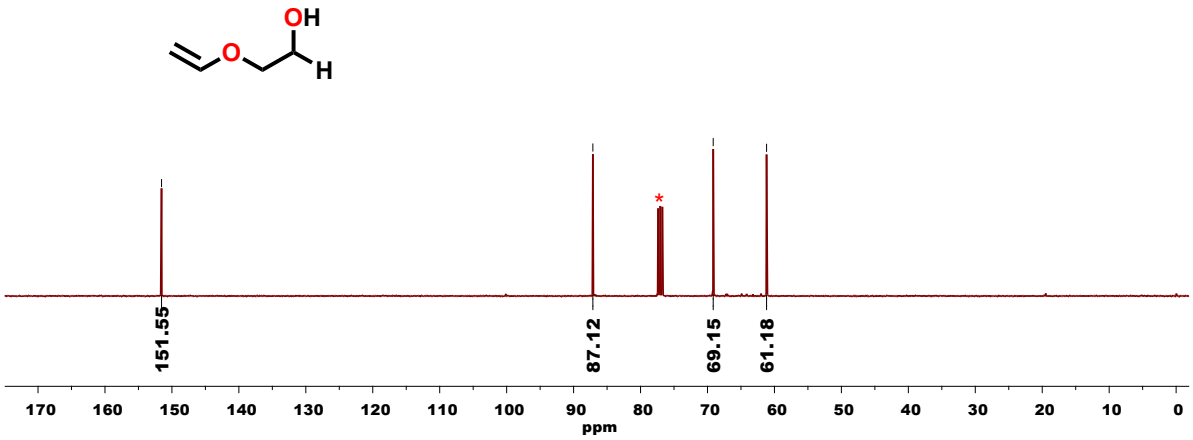

Figure S56. ^{13}C NMR spectrum of product **19** (2-(vinyloxy)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

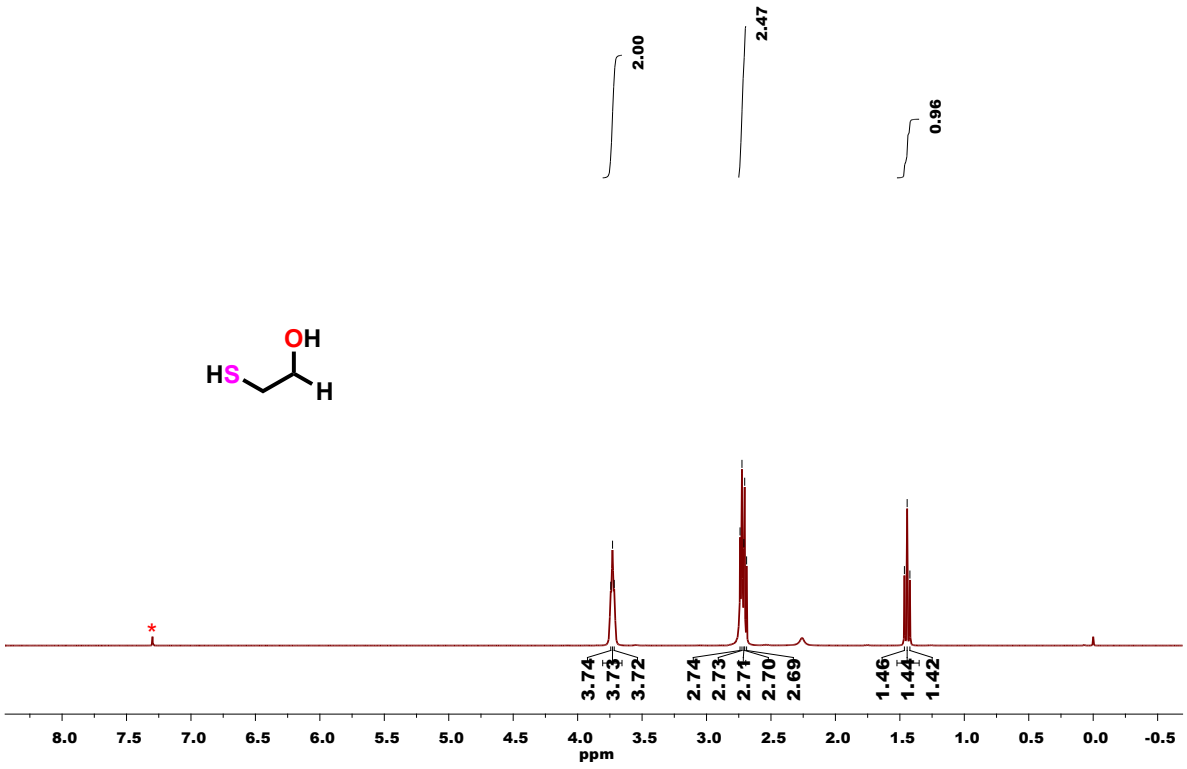

Figure S57. ^{1}H NMR spectrum of product **20** (2-mercaptoethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

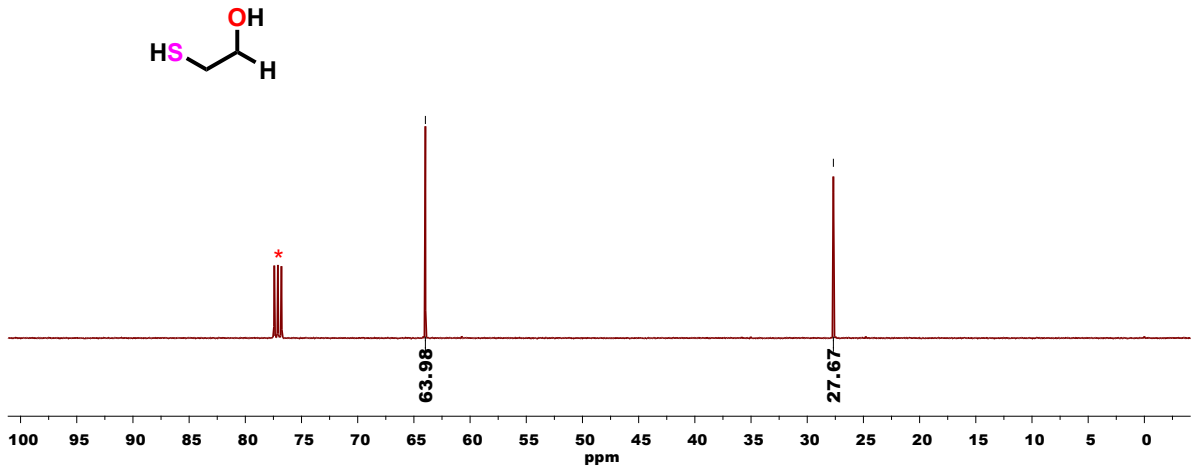

Figure S58. ^{13}C NMR spectrum of product **20** (2-mercaptoethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

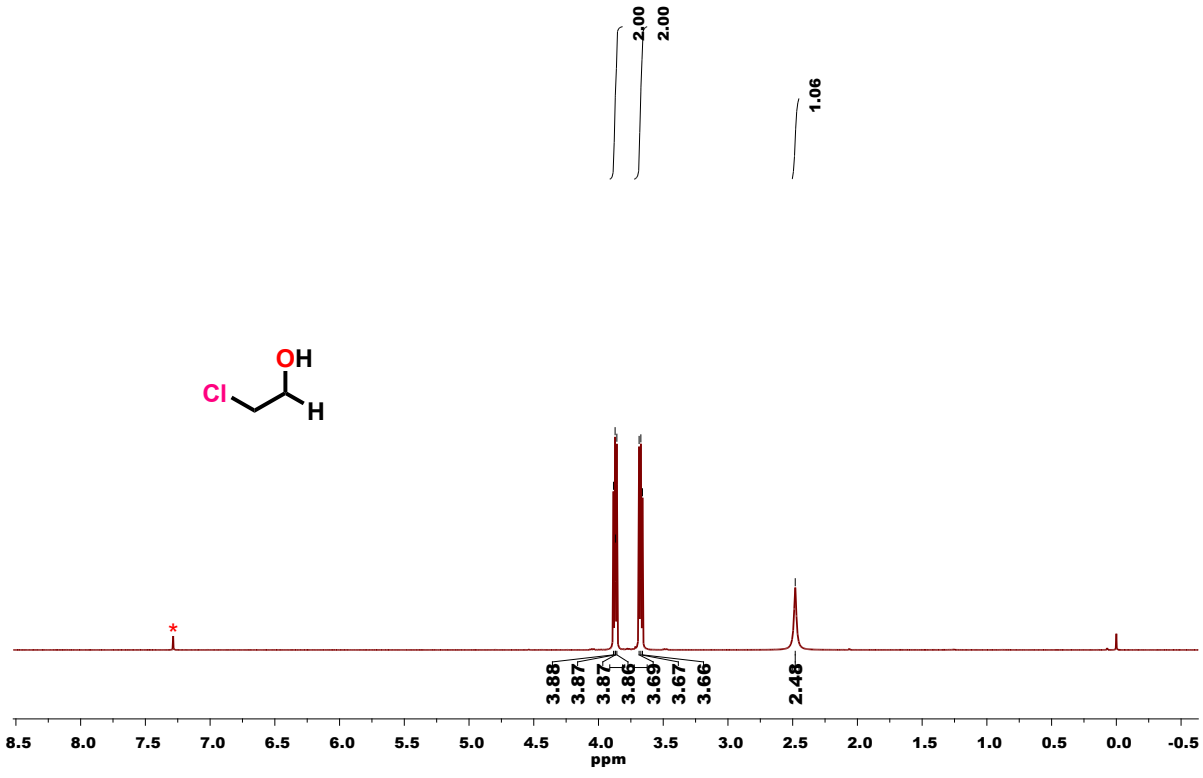

Figure S59. ^{1}H NMR spectrum of product **21** (2-chloroethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

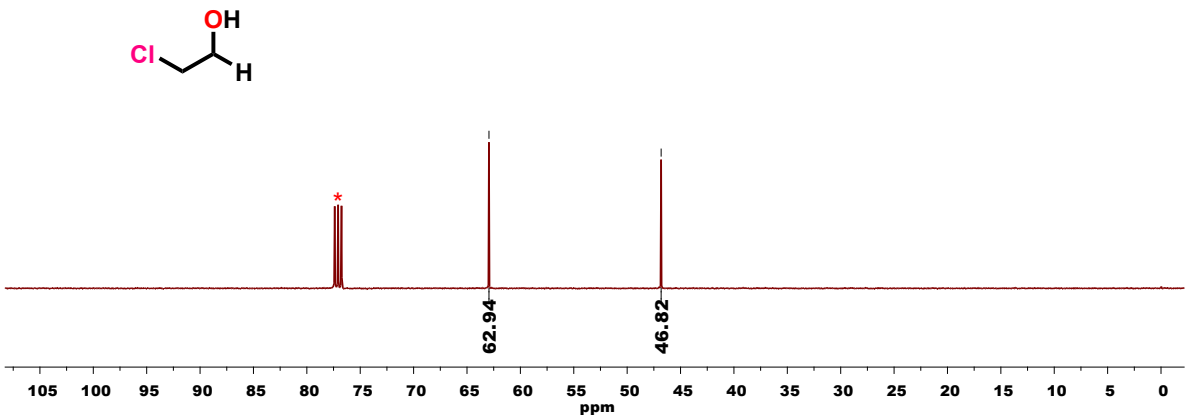

Figure S60. ^{13}C NMR spectrum of product **21** (2-chloroethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

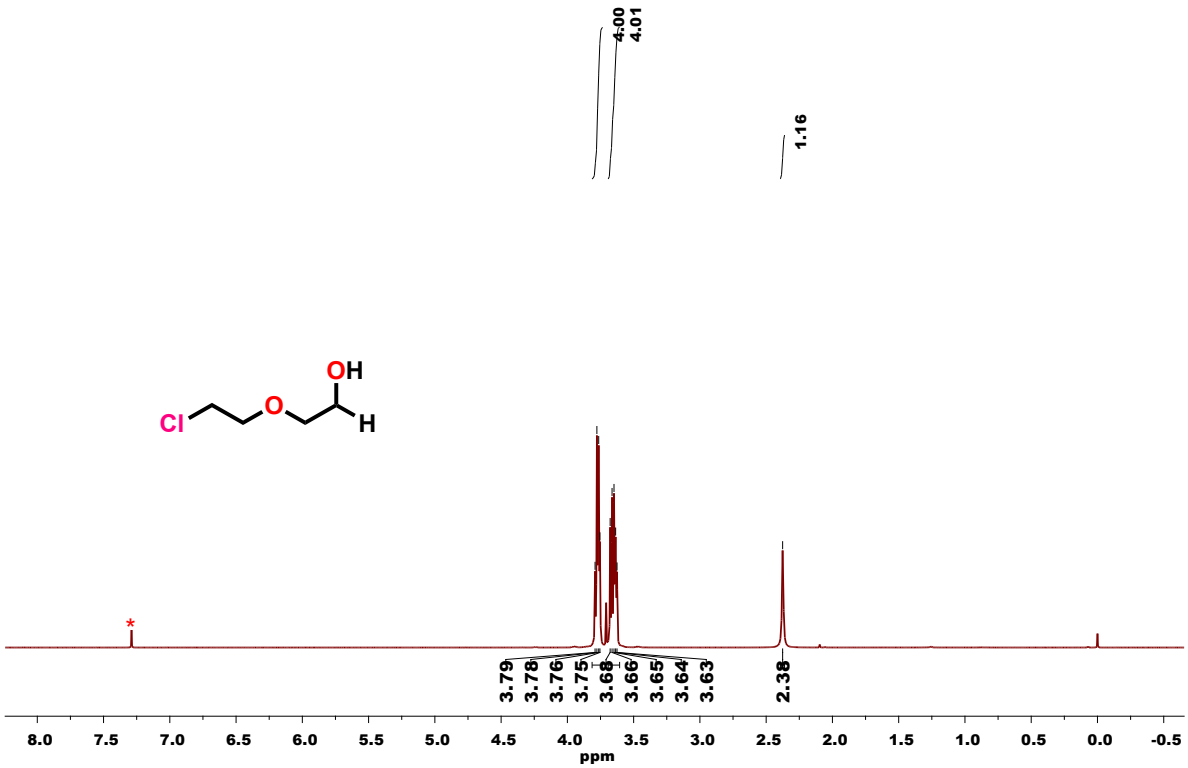

Figure S61. ^{1}H NMR spectrum of product **22** (2-(2-chloroethoxy)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

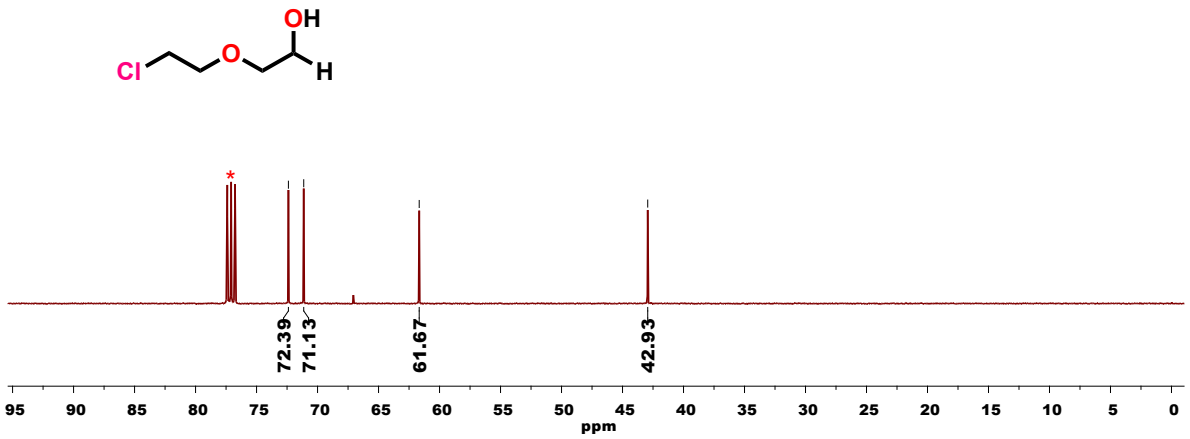

Figure S62. ^{13}C NMR spectrum of product **22** (2-(2-chloroethoxy)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

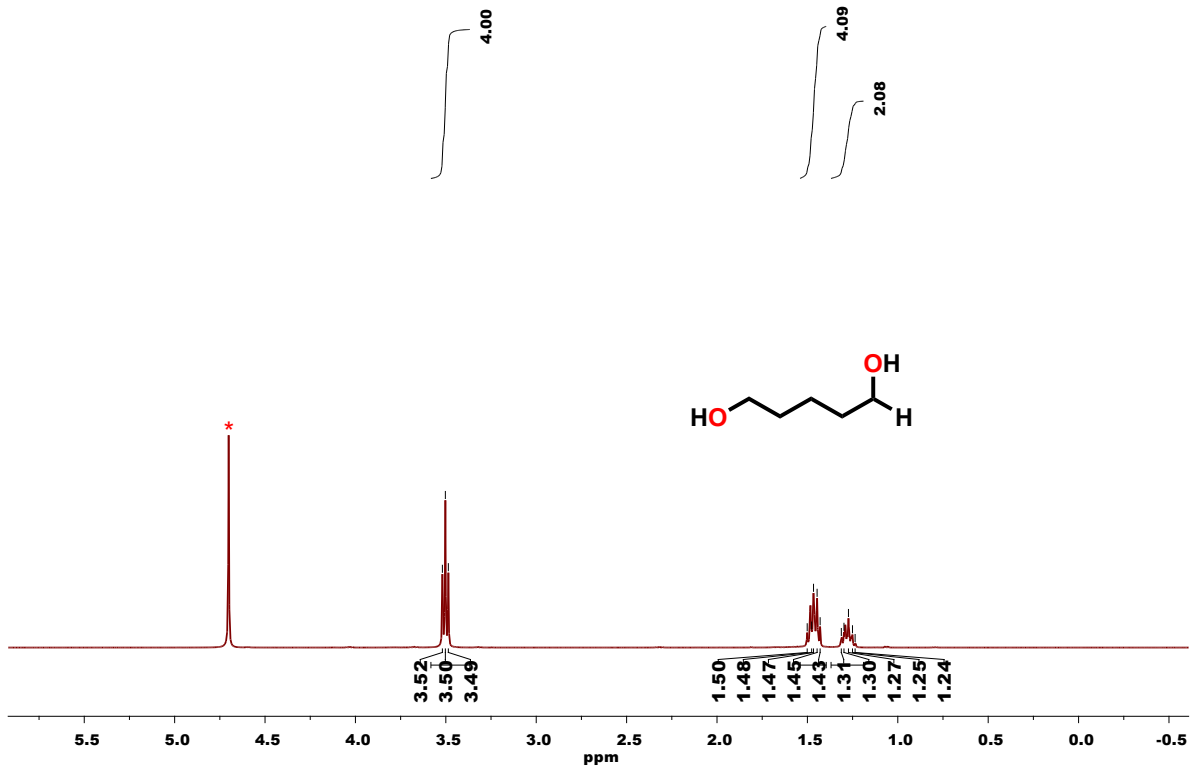

Figure S63. ^{1}H NMR spectrum of product **23** (1,5-pentanediol) in D_2O solvent where * represents the residual solvent peak.

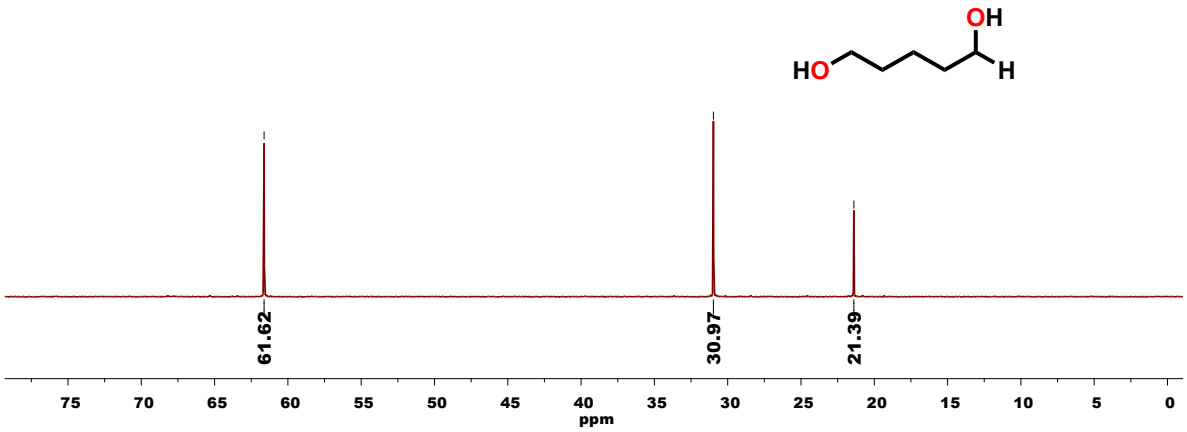

Figure S64. ^{13}C NMR spectrum of product **23** (1,5-pentanediol) in D_2O solvent.

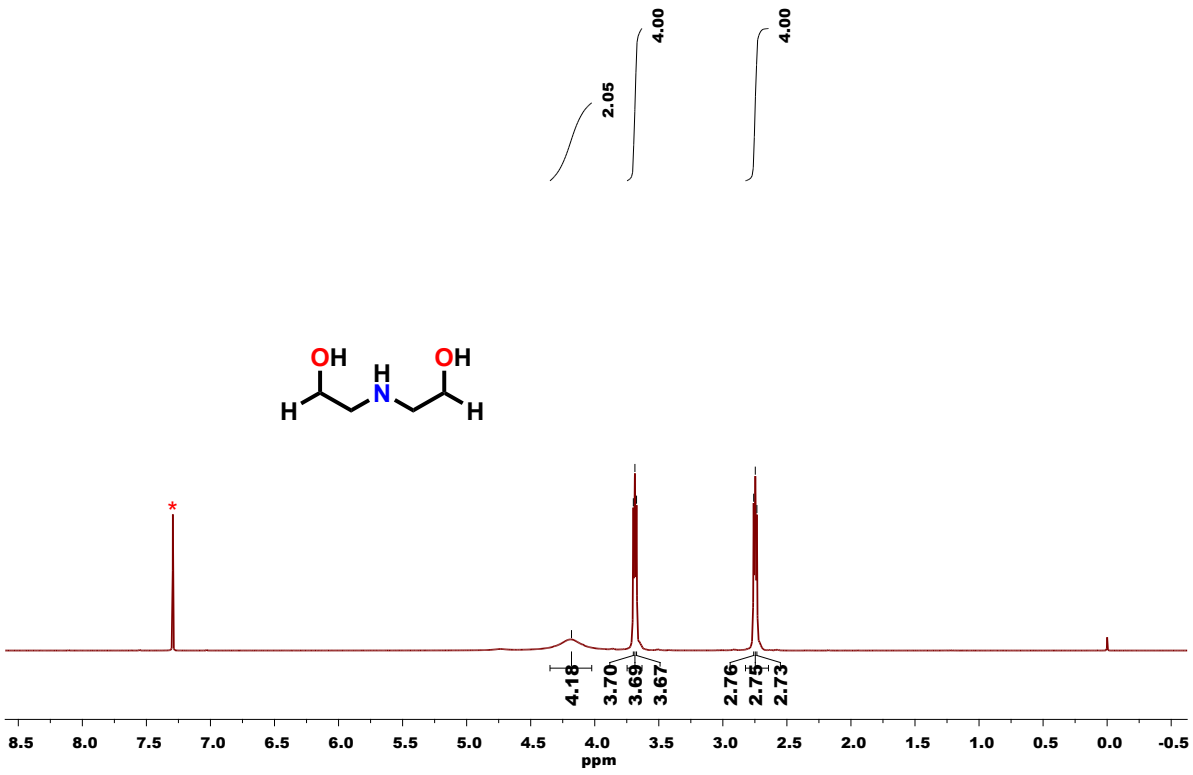

Figure S65. ^{1}H NMR spectrum of product **24** (2,2'-azanediylbis(ethan-1-ol)) in $CDCl_3$ solvent where * represents the residual solvent peak.

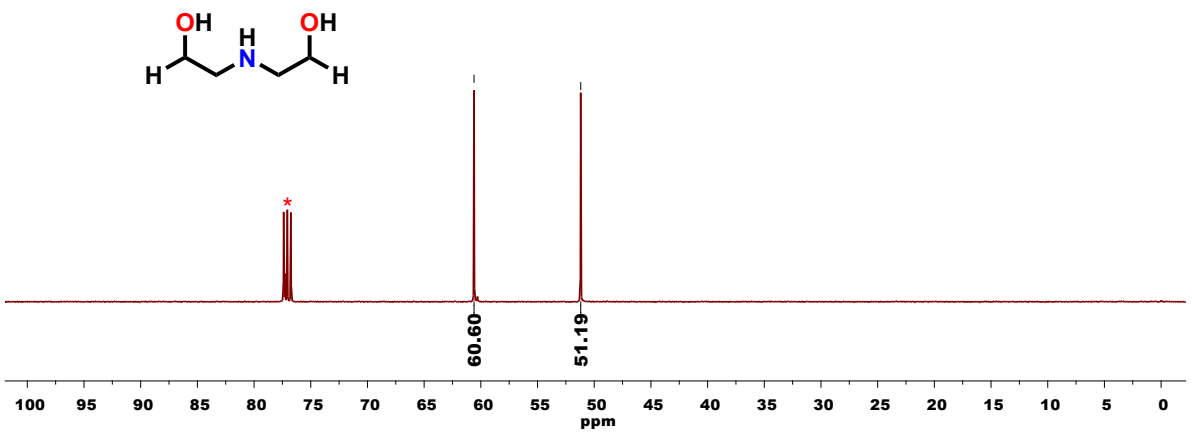

Figure S66. ^{13}C NMR spectrum of product **24** (2,2'-azanediylbis(ethan-1-ol)) in $CDCl_3$ solvent where * represents the residual solvent peak.

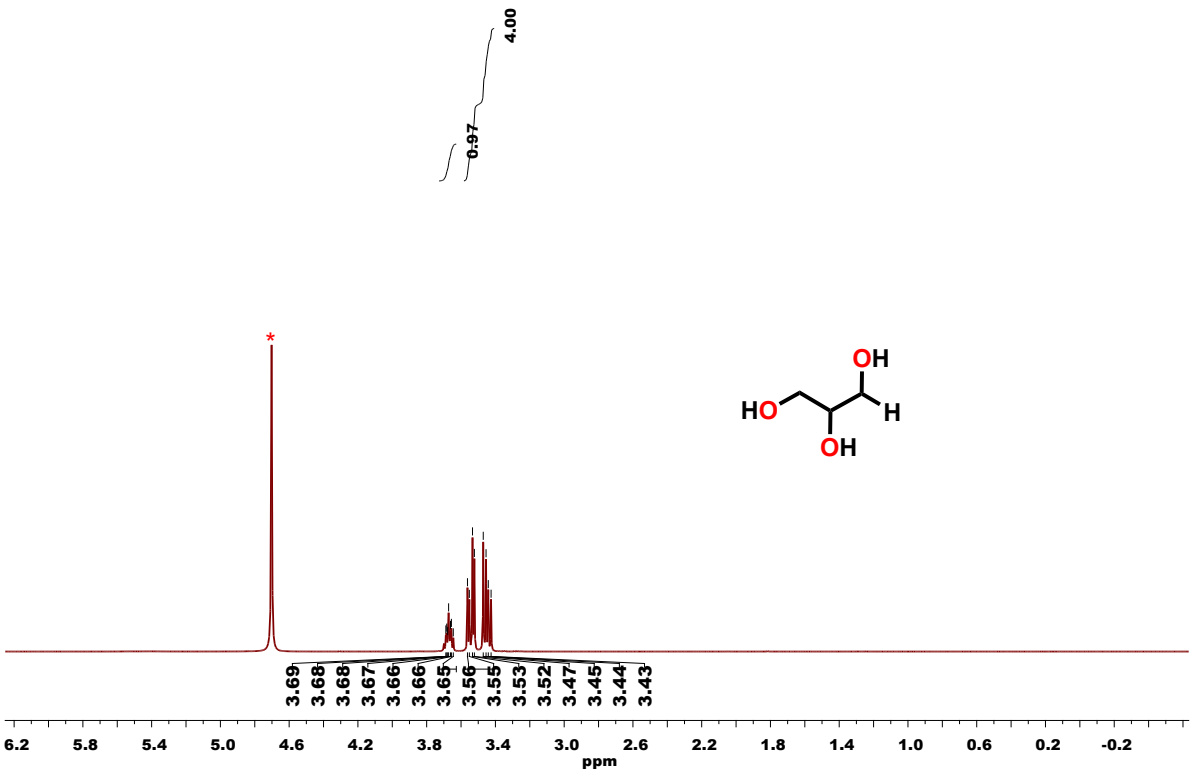

Figure S67. ^{1}H NMR spectrum of product **25** (1,2,3-propanetriol) in D_2O solvent where * represents the residual solvent peak.

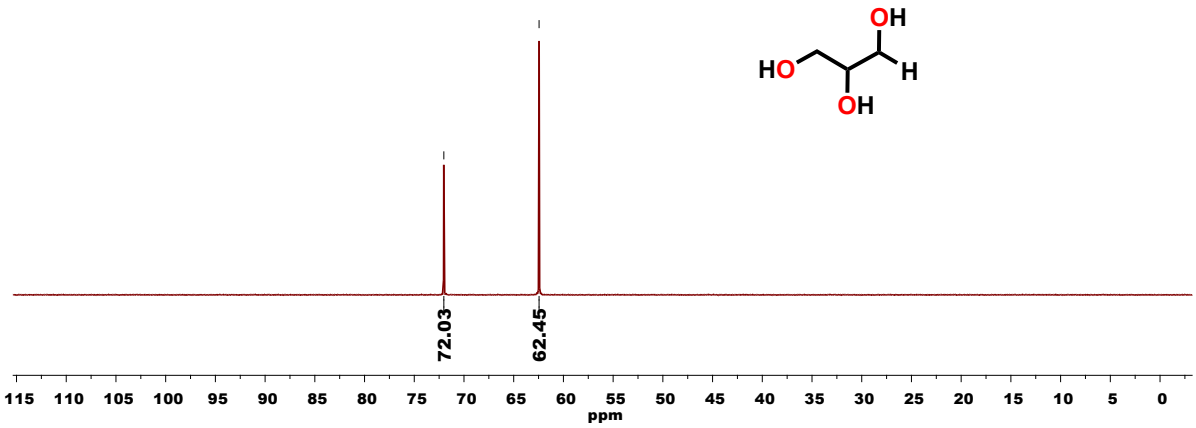

Figure S68. ^{13}C NMR spectrum of product **25** (1,2,3-propanetriol) in D_2O solvent.

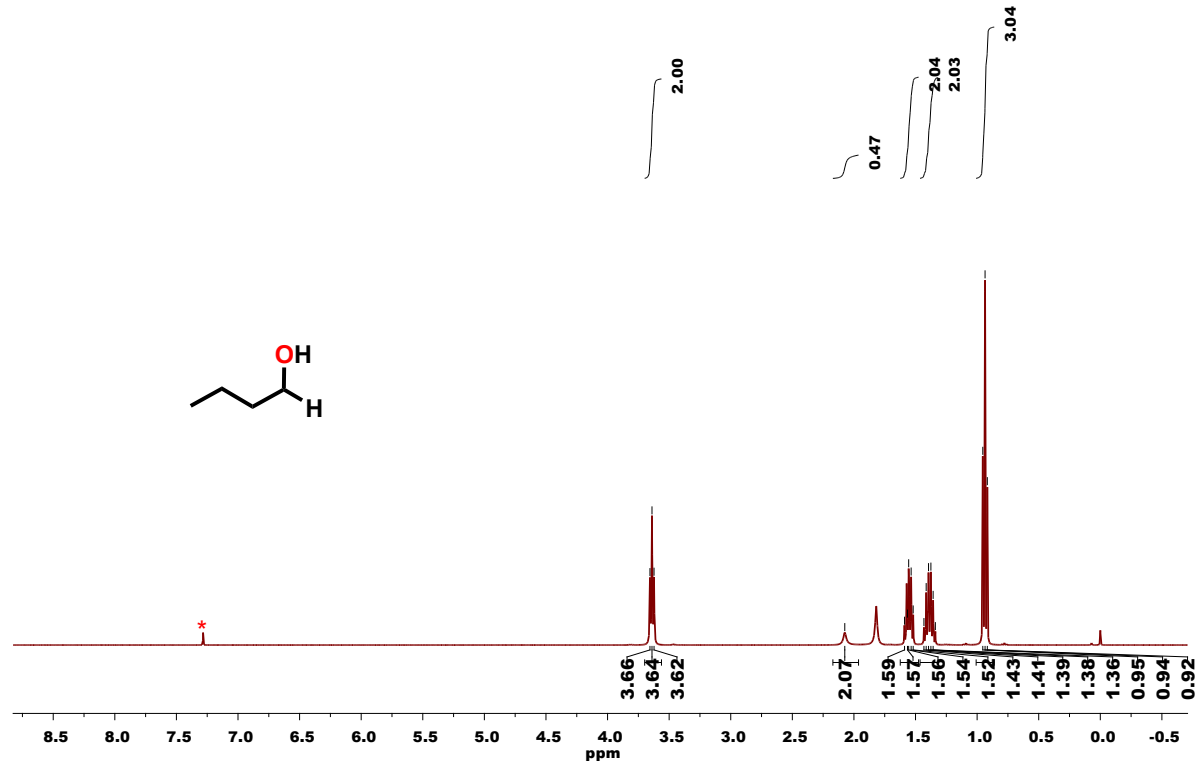

Figure S69. ^{1}H NMR spectrum of product **26** (1-butanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

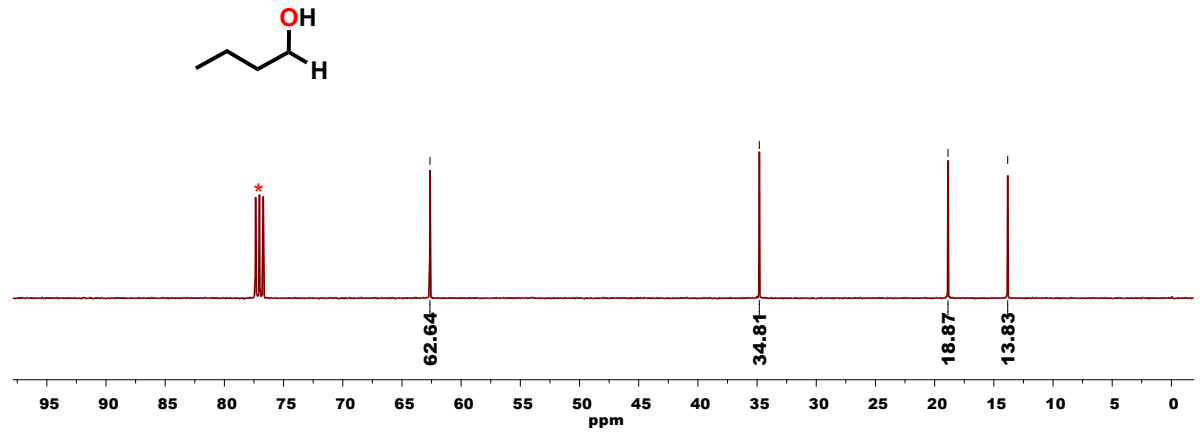

Figure S70. ^{13}C NMR spectrum of product **26** (1-butanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

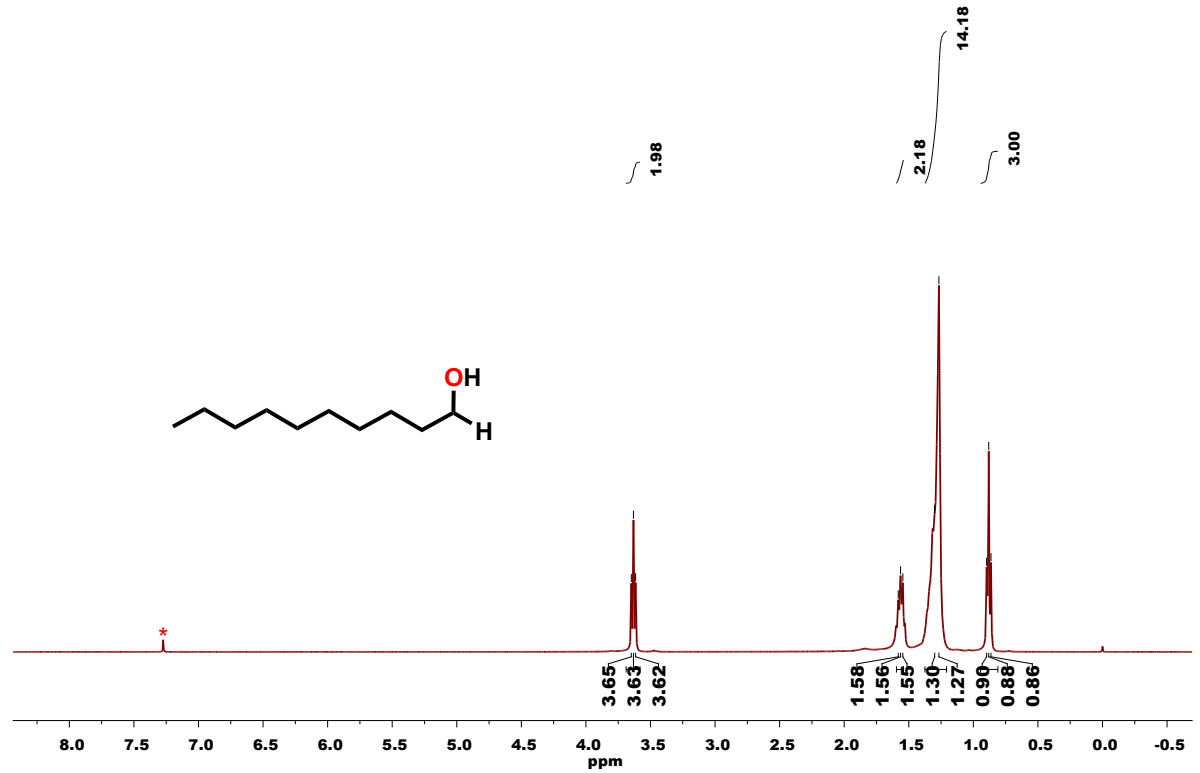

Figure S71. ^{1}H NMR spectrum of product **27** (1-decanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

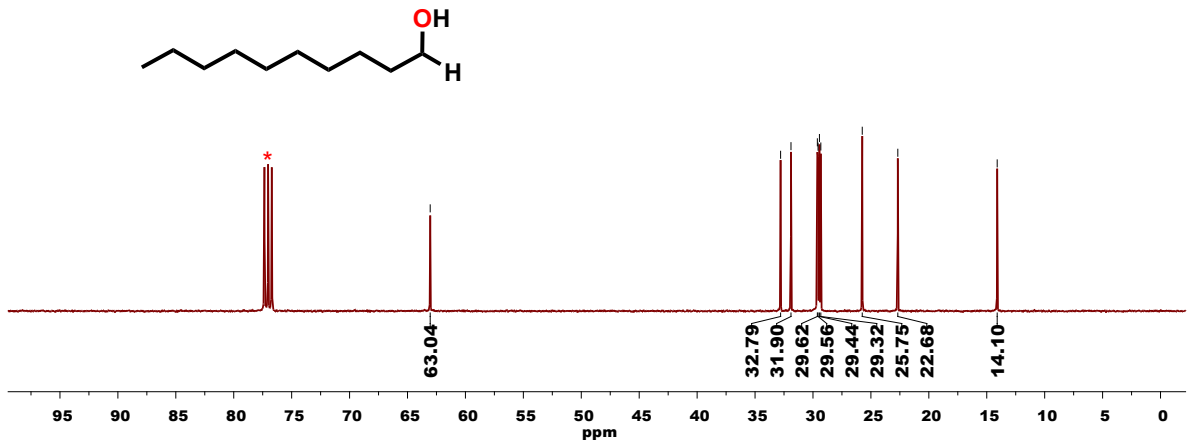

Figure S72. ^{13}C NMR spectrum of product **27** (1-decanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

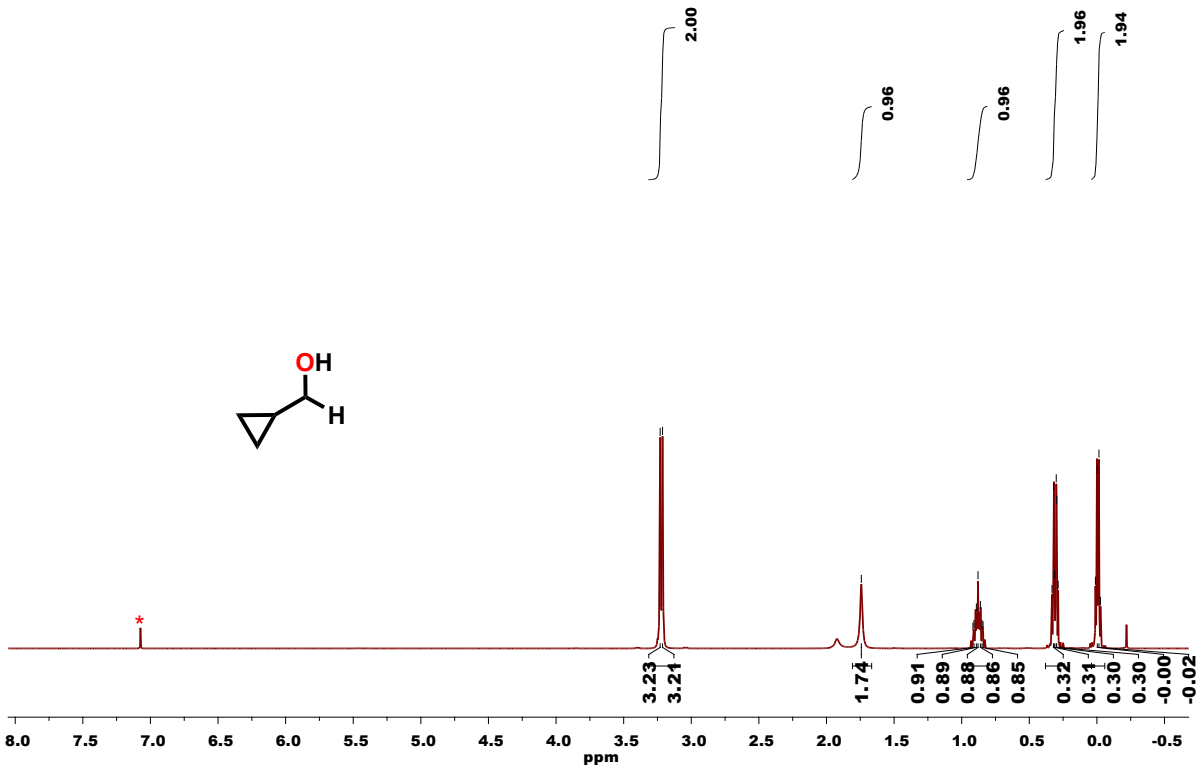

Figure S73. ^{1}H NMR spectrum of product **28** (cyclopropylmethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

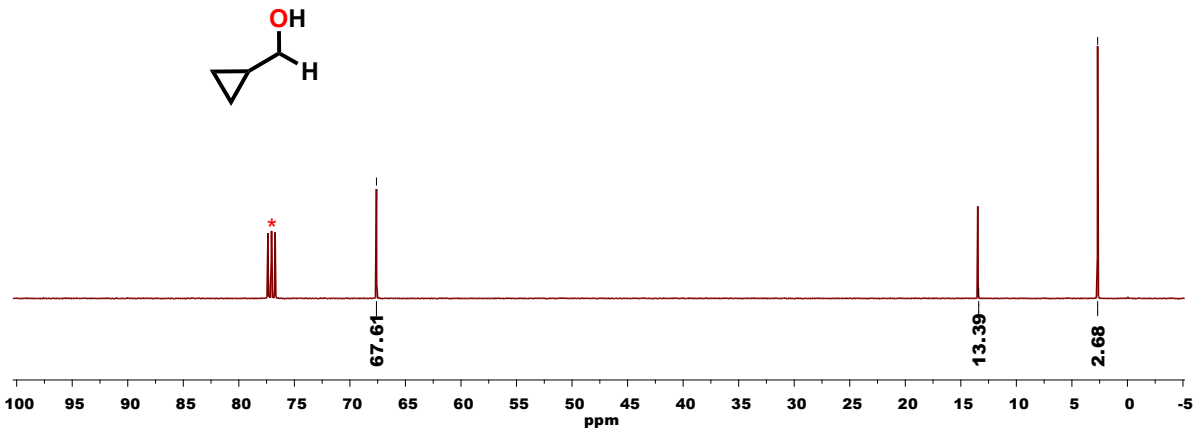

Figure S74. ^{13}C NMR spectrum of product **28** (cyclopropylmethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

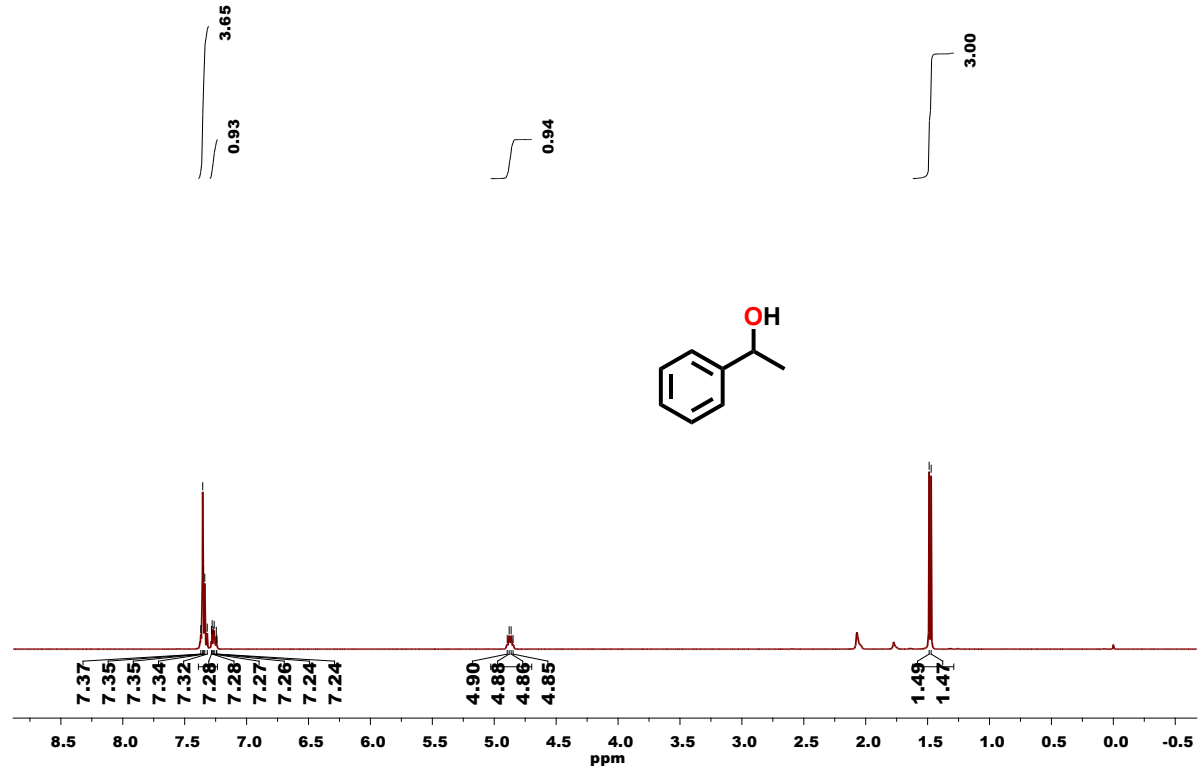

Figure S75. ^{1}H NMR spectrum of product **29** (1-phenylethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

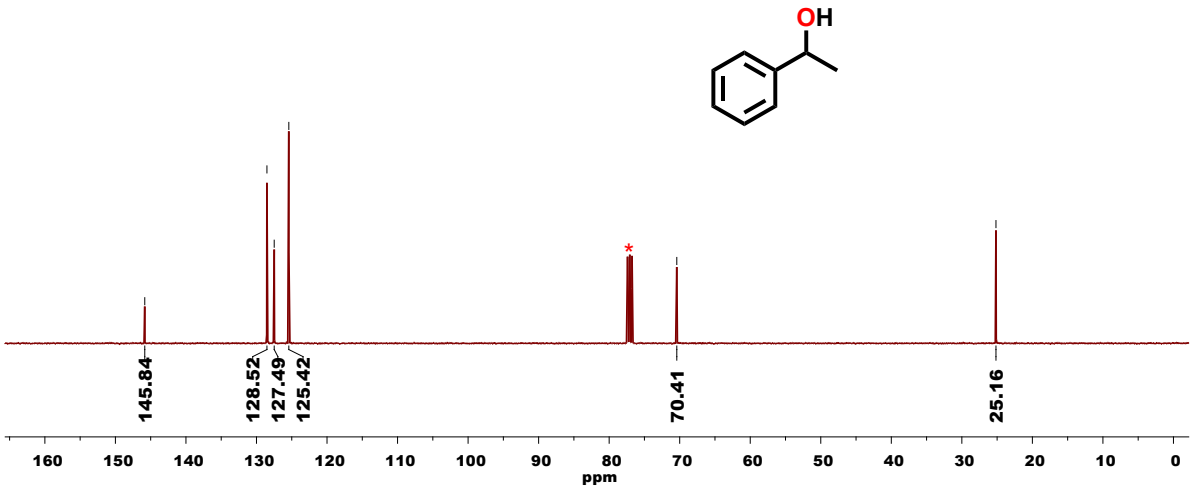

Figure S76. ^{13}C NMR spectrum of product **29** (1-phenylethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

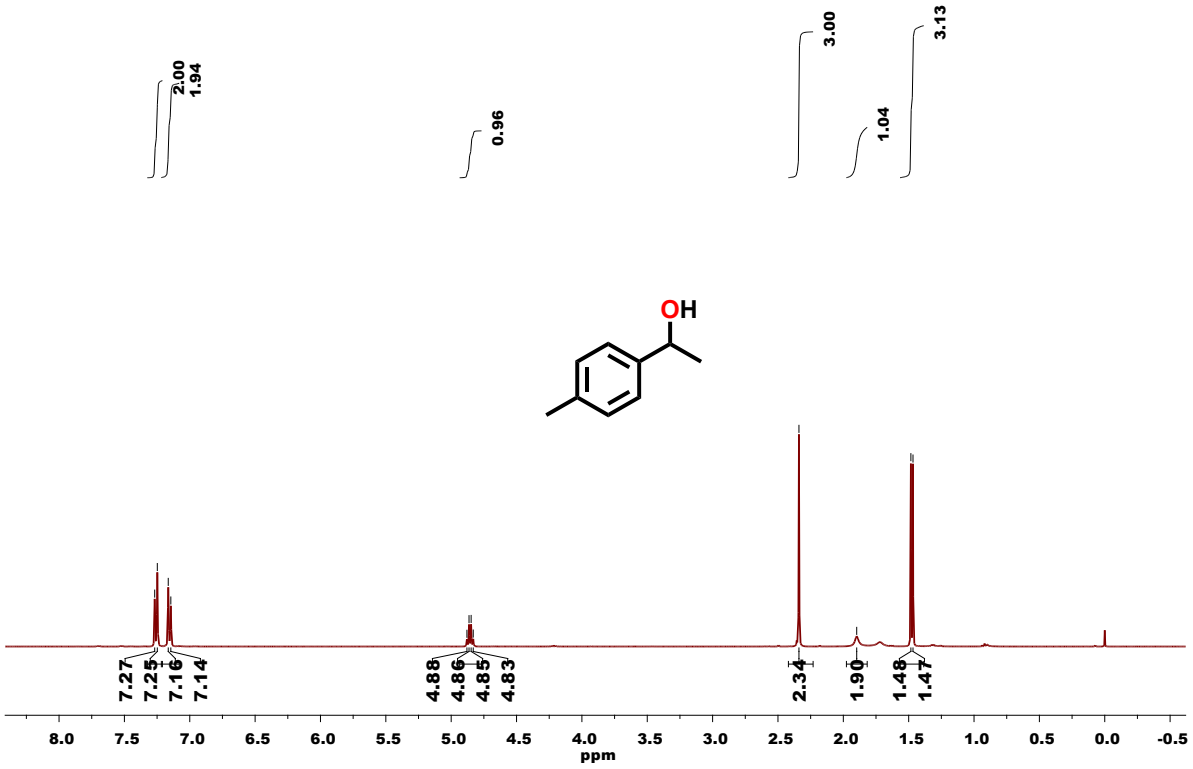

Figure S77. ^{1}H NMR spectrum of product **30** (1-(4-methylphenyl)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

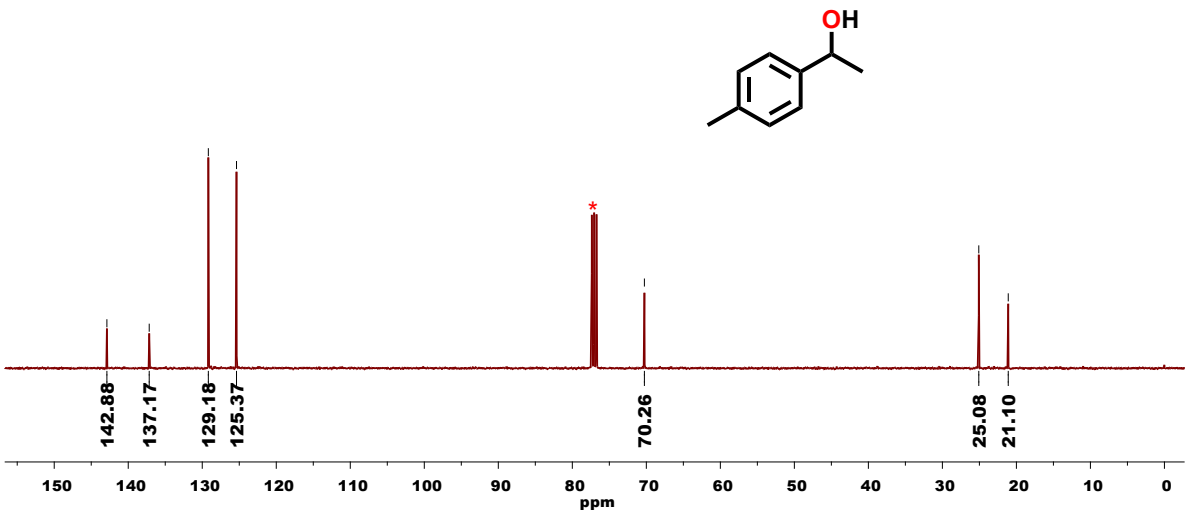

Figure S78. ^{13}C NMR spectrum of product **30** (1-(4-methylphenyl)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

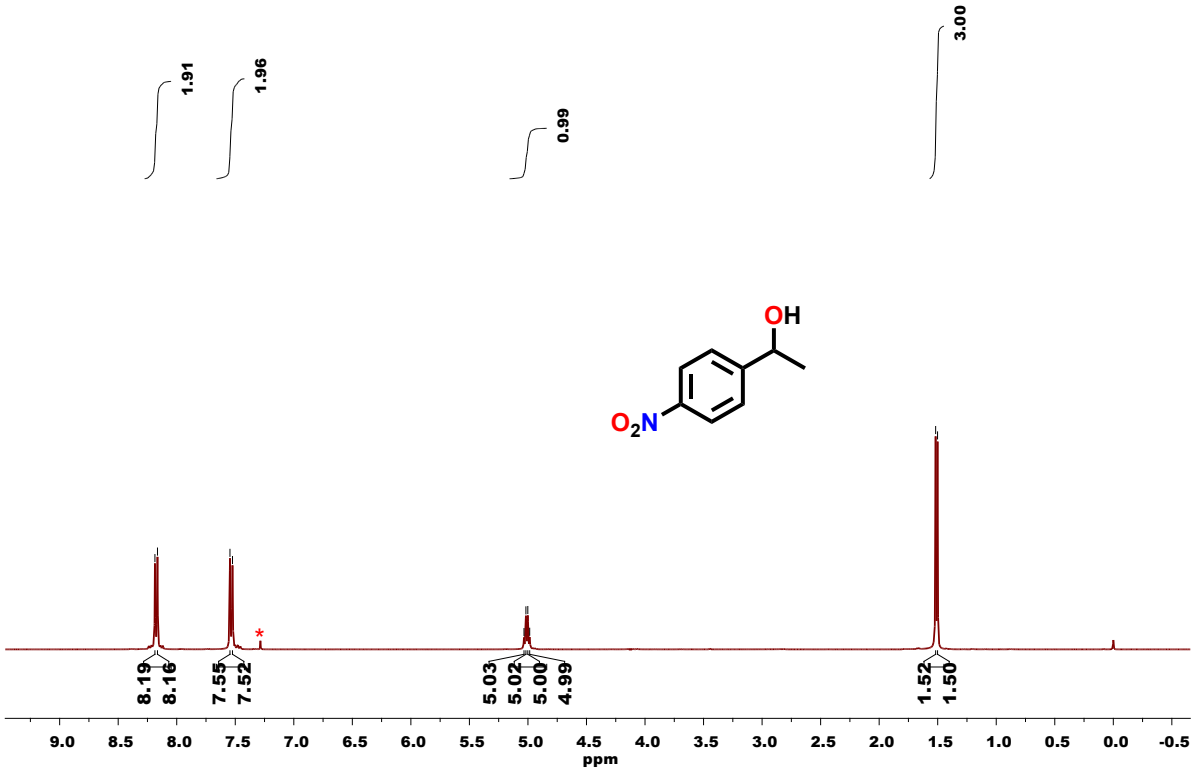

Figure S79. ^{1}H NMR spectrum of product **31** (1-(4-nitrophenyl)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

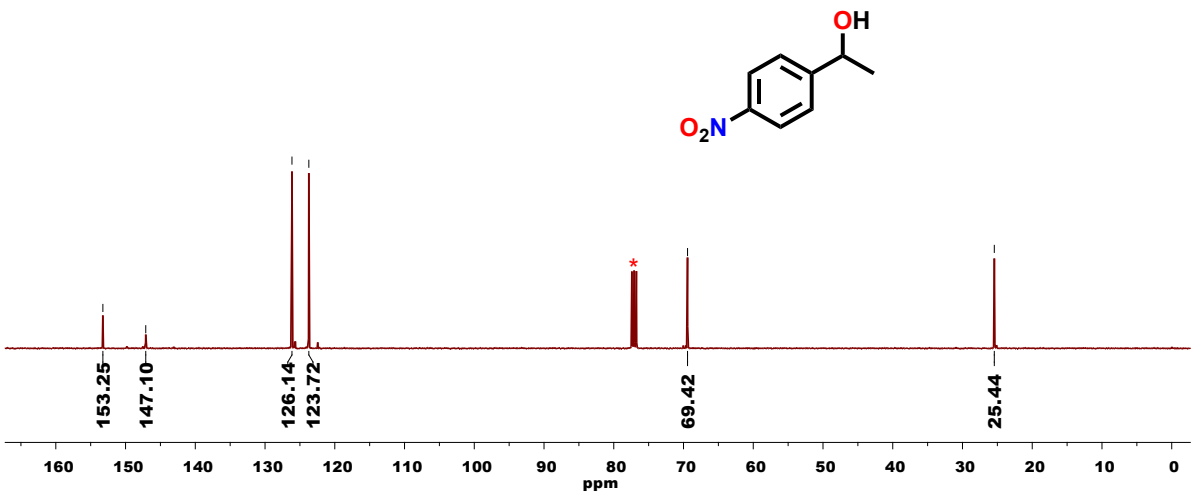

Figure S80. ^{13}C NMR spectrum of product **31** (1-(4-nitrophenyl)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

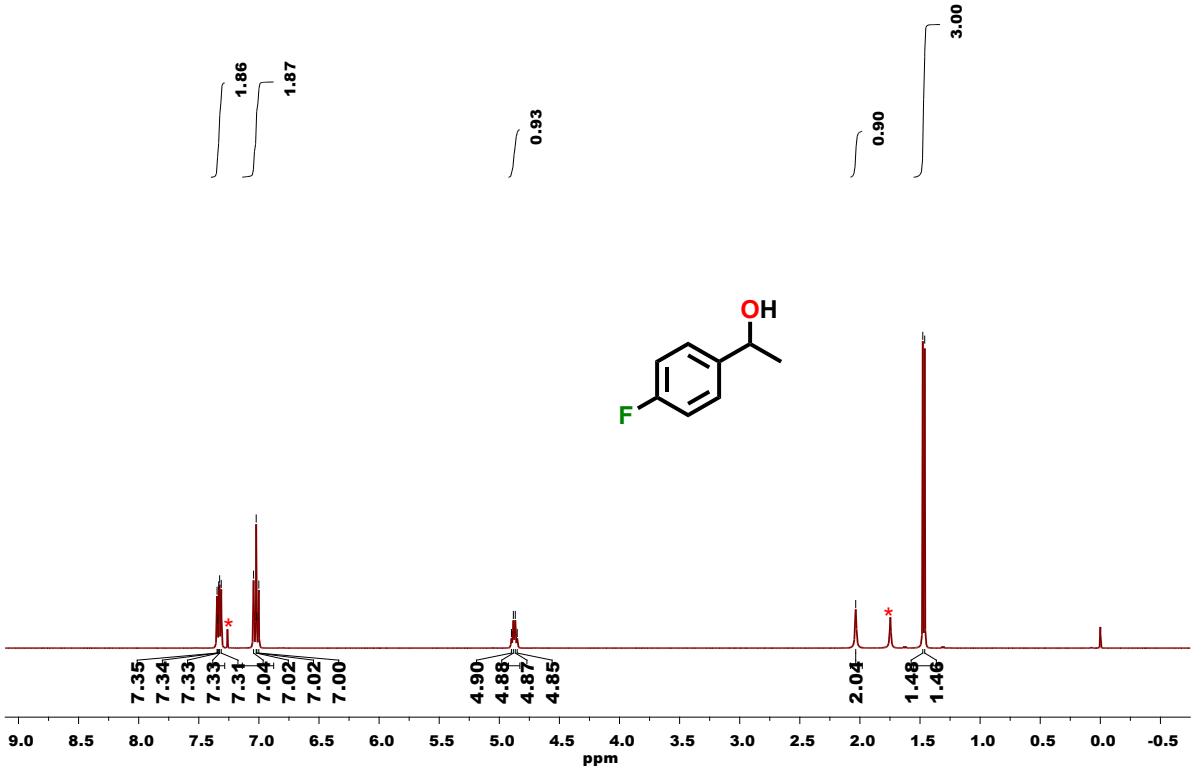

Figure S81. ^{1}H NMR spectrum of product **32** (1-(4-fluorophenyl)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

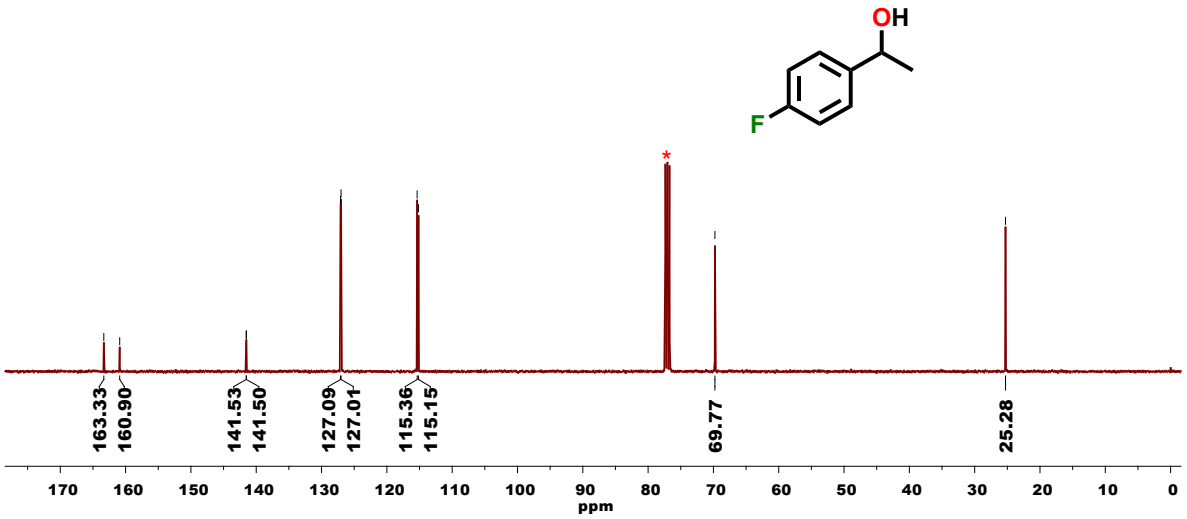

Figure S82. ^{13}C NMR spectrum of product **32** (1-(4-fluorophenyl)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

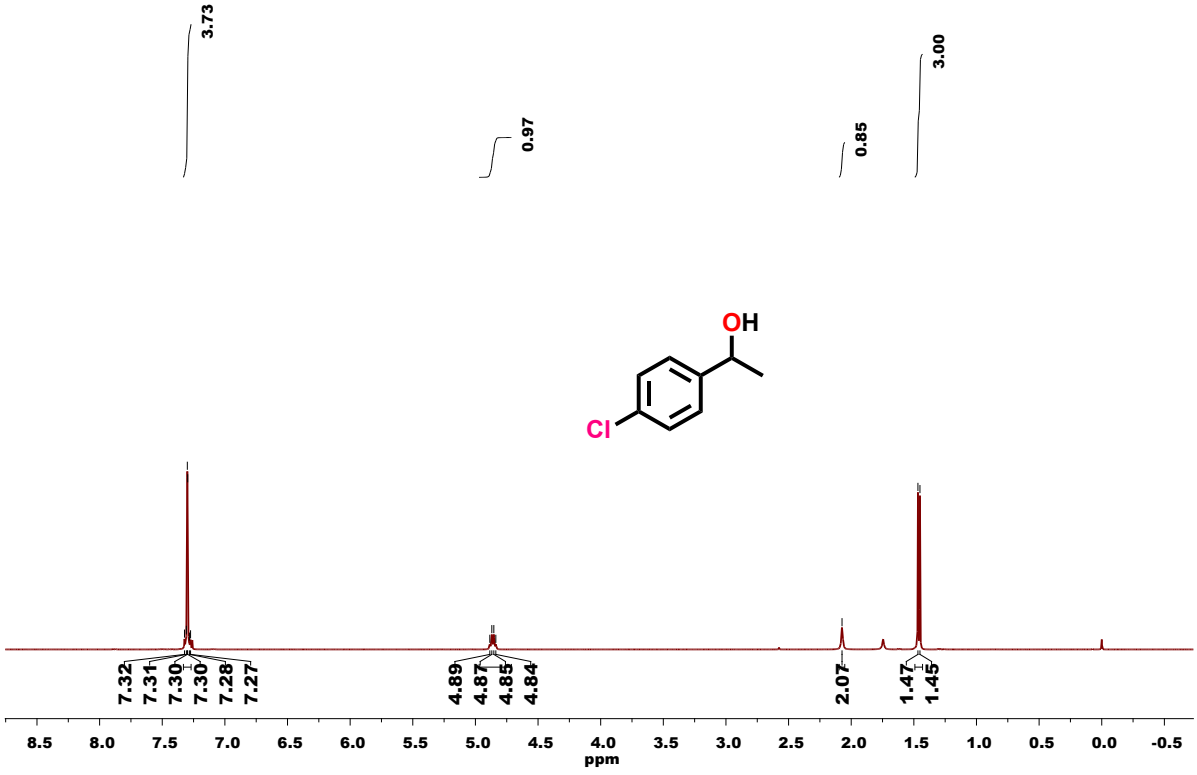

Figure S83. ^{1}H NMR spectrum of product **33** (1-(4-chlorophenyl)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

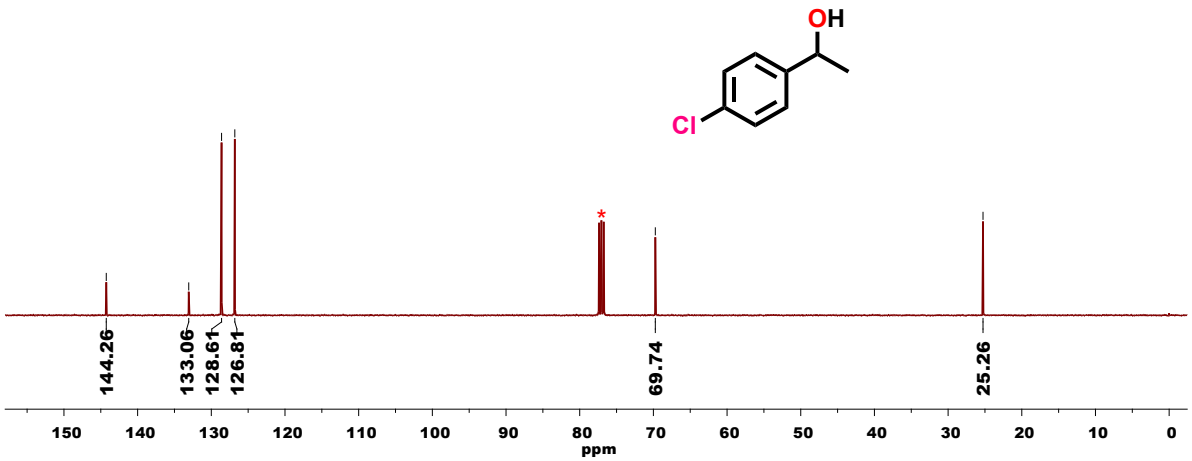

Figure S84. ^{13}C NMR spectrum of product **33** (1-(4-chlorophenyl)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

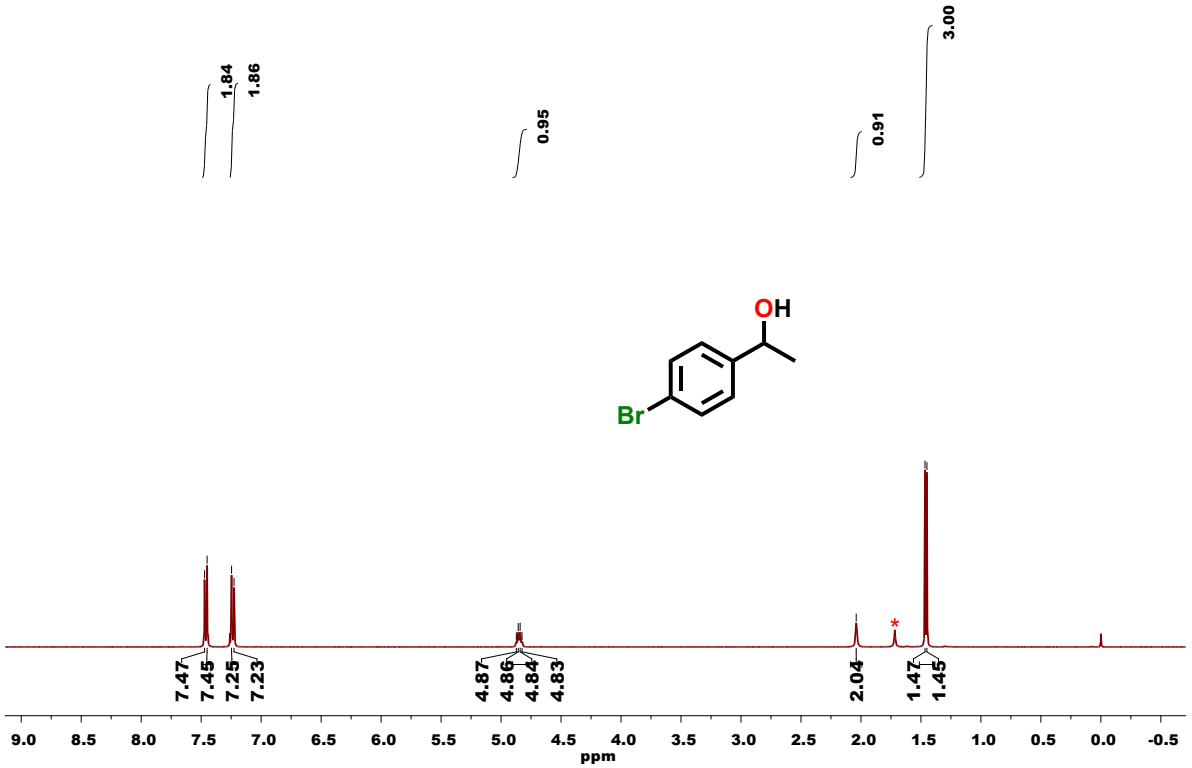

Figure S85. ^{1}H NMR spectrum of product **34** (1-(4-bromophenyl)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

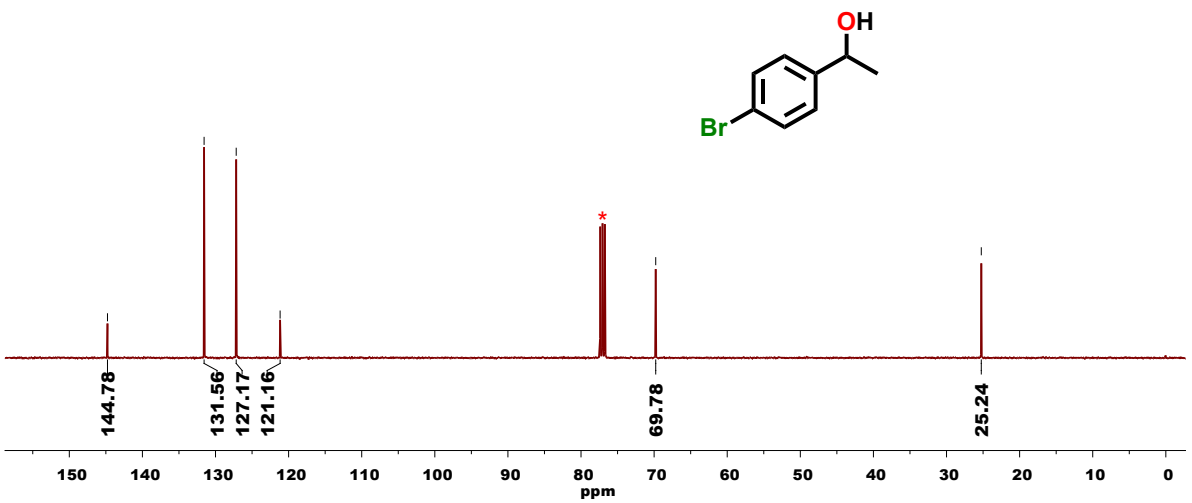

Figure S86. ^{13}C NMR spectrum of product **34** (1-(4-bromophenyl)ethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

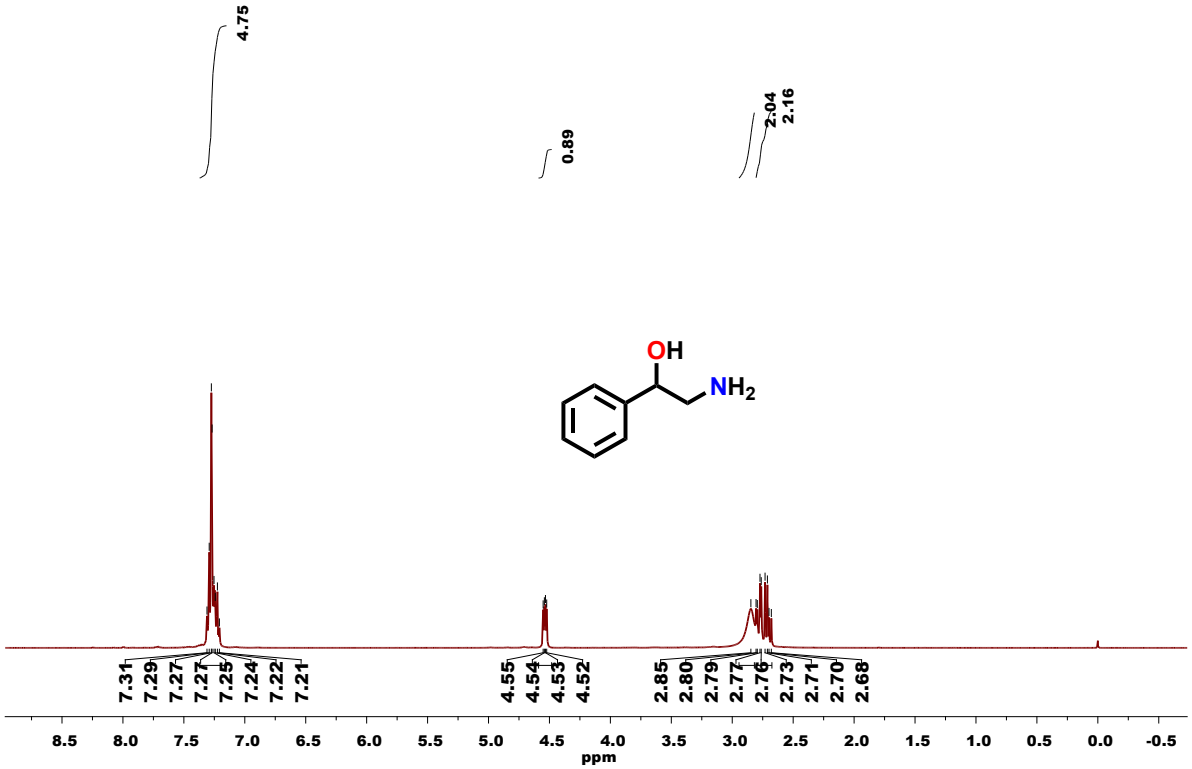

Figure S87. ^{1}H NMR spectrum of product **35** (2-amino-1-phenylethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

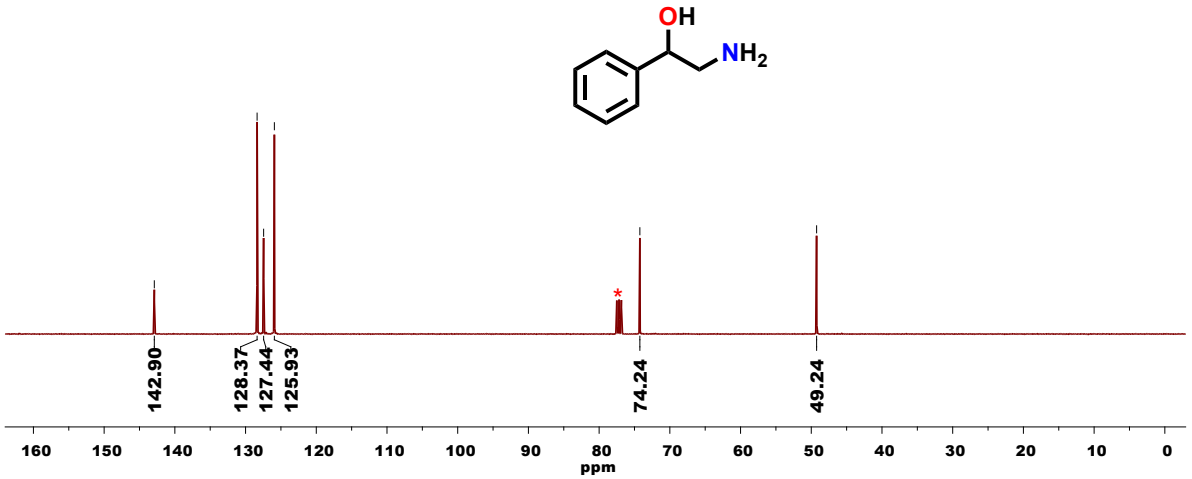

Figure S88. ^{13}C NMR spectrum of product **35** (2-amino-1-phenylethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

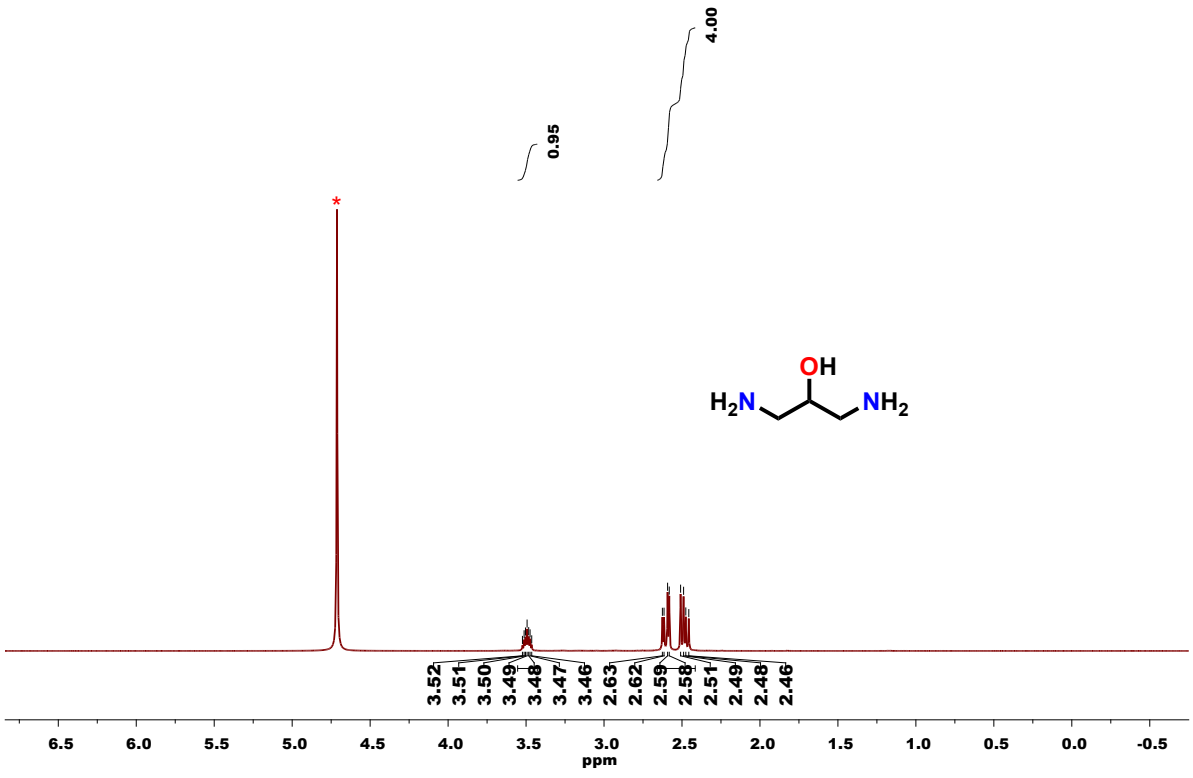

Figure S89. ^{1}H NMR spectrum of product **36** (1,3-diaminopropanol) in D_2O solvent where * represents the residual solvent peak.

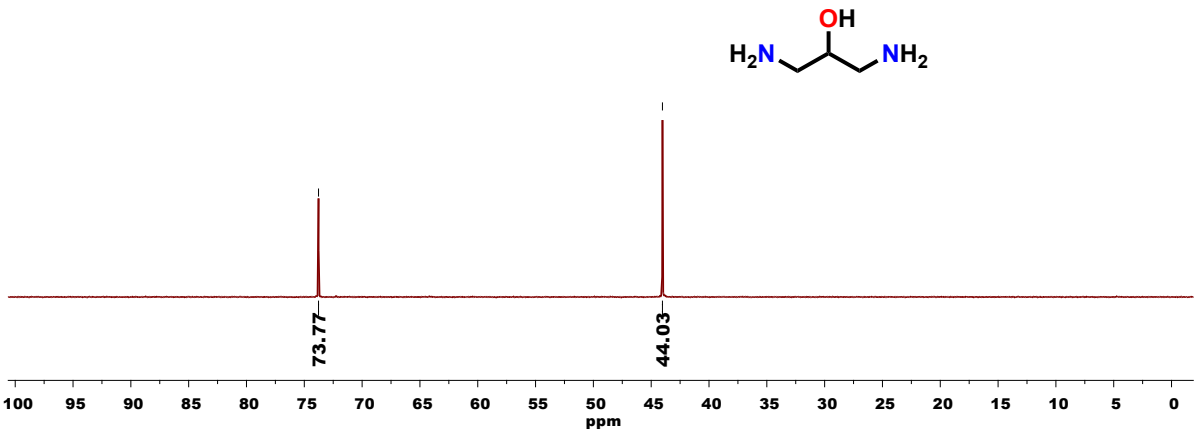

Figure S90. ^{13}C NMR spectrum of product **36** (1,3-diaminopropanol) in D_2O solvent.

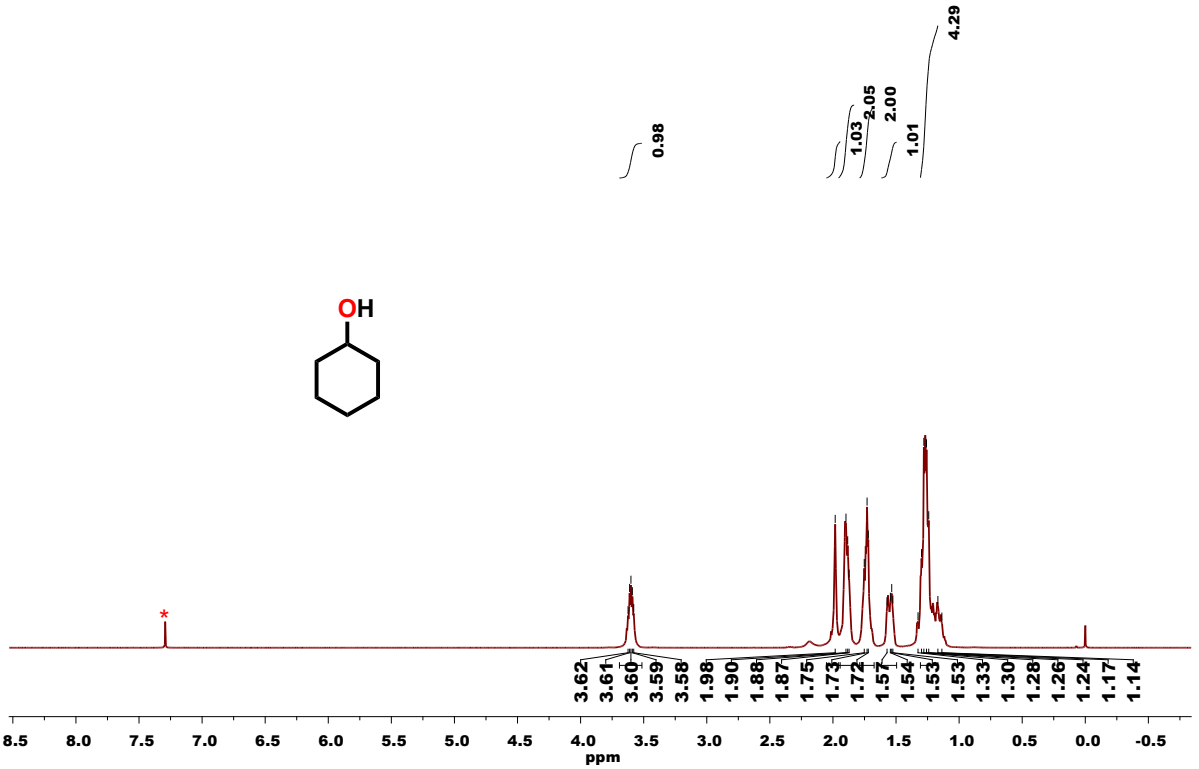

Figure S91. ^{1}H NMR spectrum of product **37** (cyclohexanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

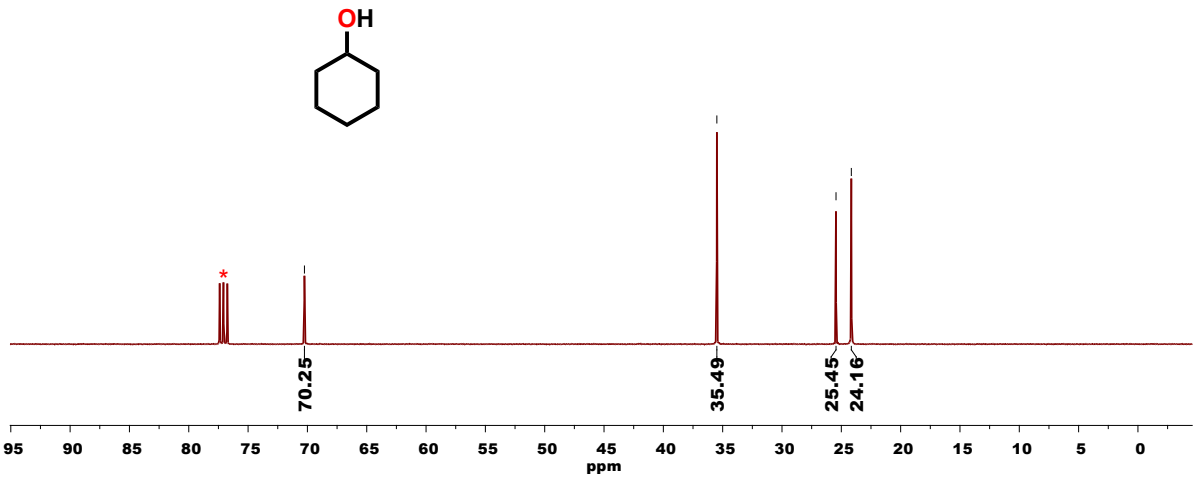

Figure S92. ^{13}C NMR spectrum of product **37** (cyclohexanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

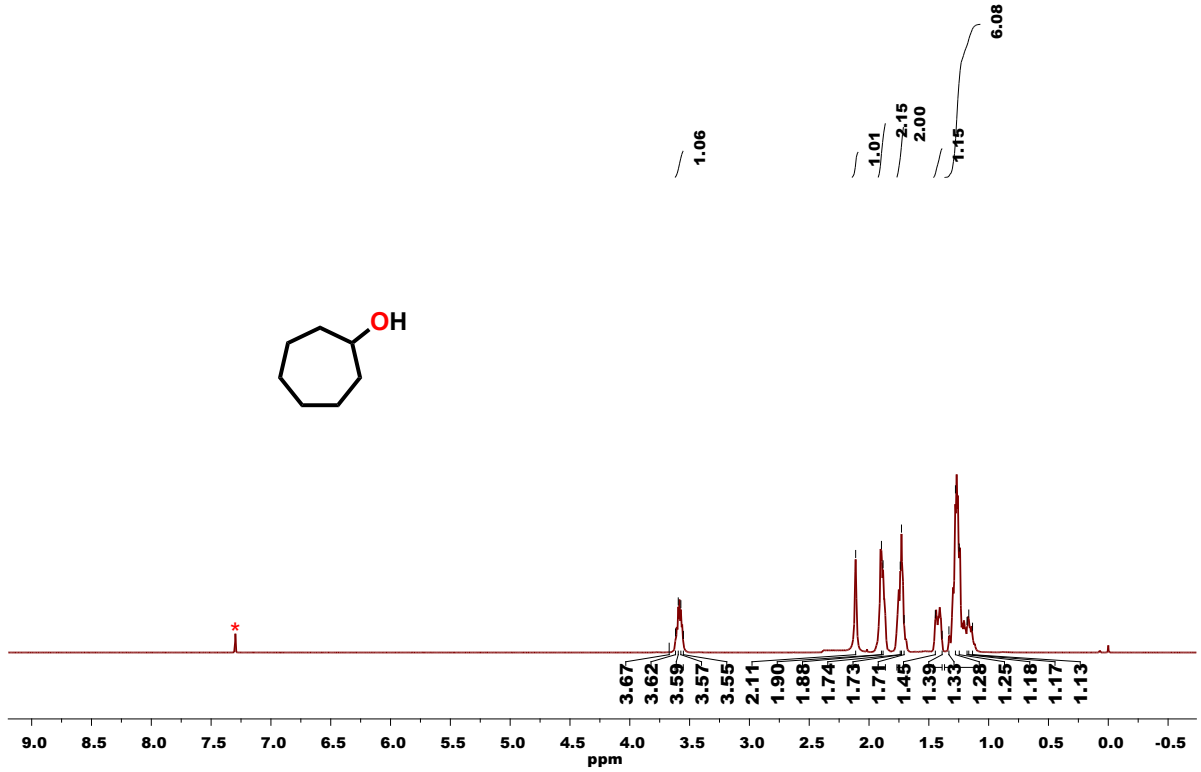

Figure S93. ^{1}H NMR spectrum of product **38** (cycloheptanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

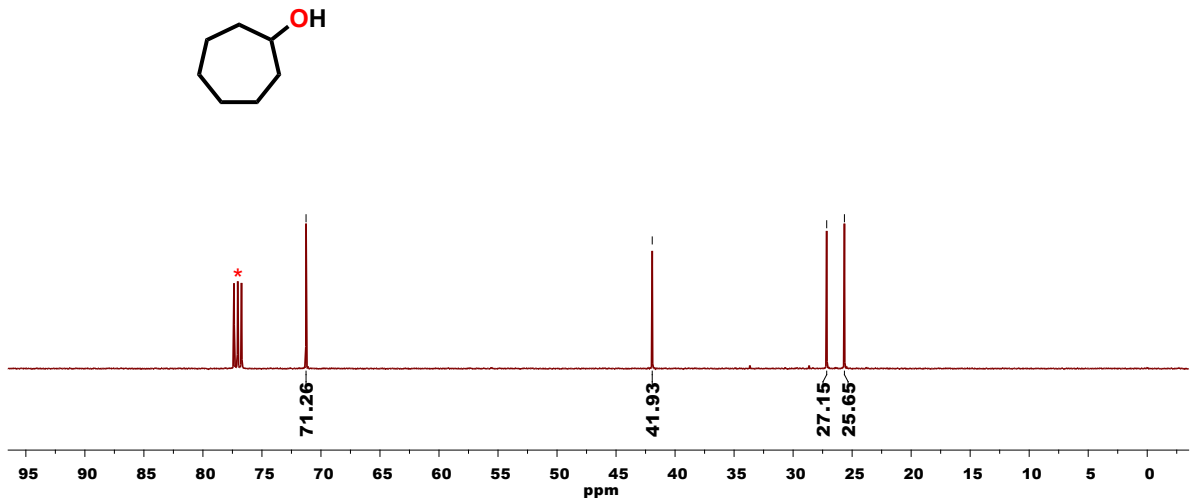

Figure S94. ^{13}C NMR spectrum of product **38** (cycloheptanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

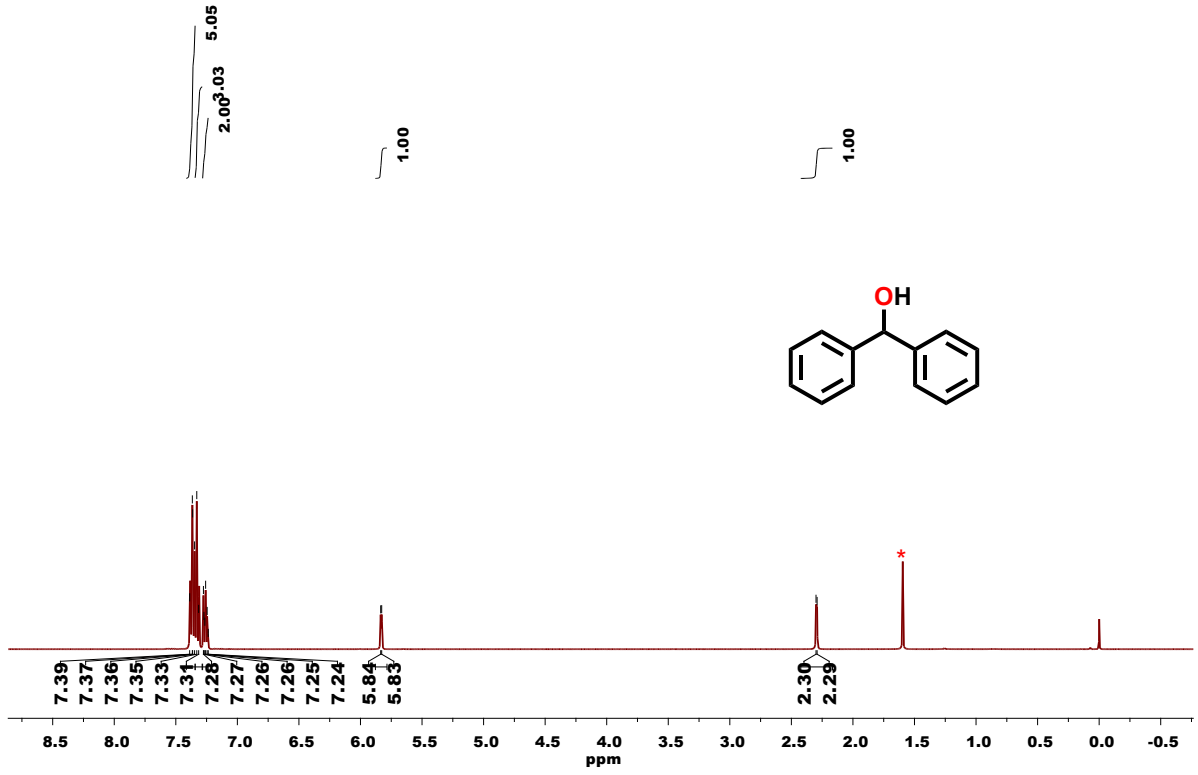

Figure S95. ^{1}H NMR spectrum of product **39** (diphenylmethanol) in $CDCl_3$ solvent where * represents the residual solvent and/or adventitious water peaks.

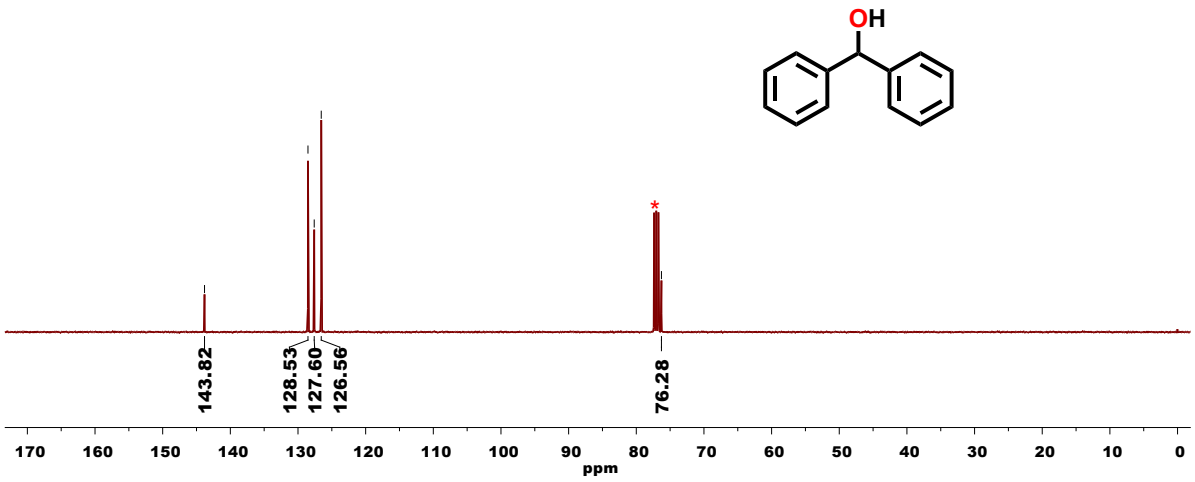

Figure S96. ^{13}C NMR spectrum of product **39** (diphenylmethanol) in $CDCl_3$ solvent where * represents the residual solvent peak.

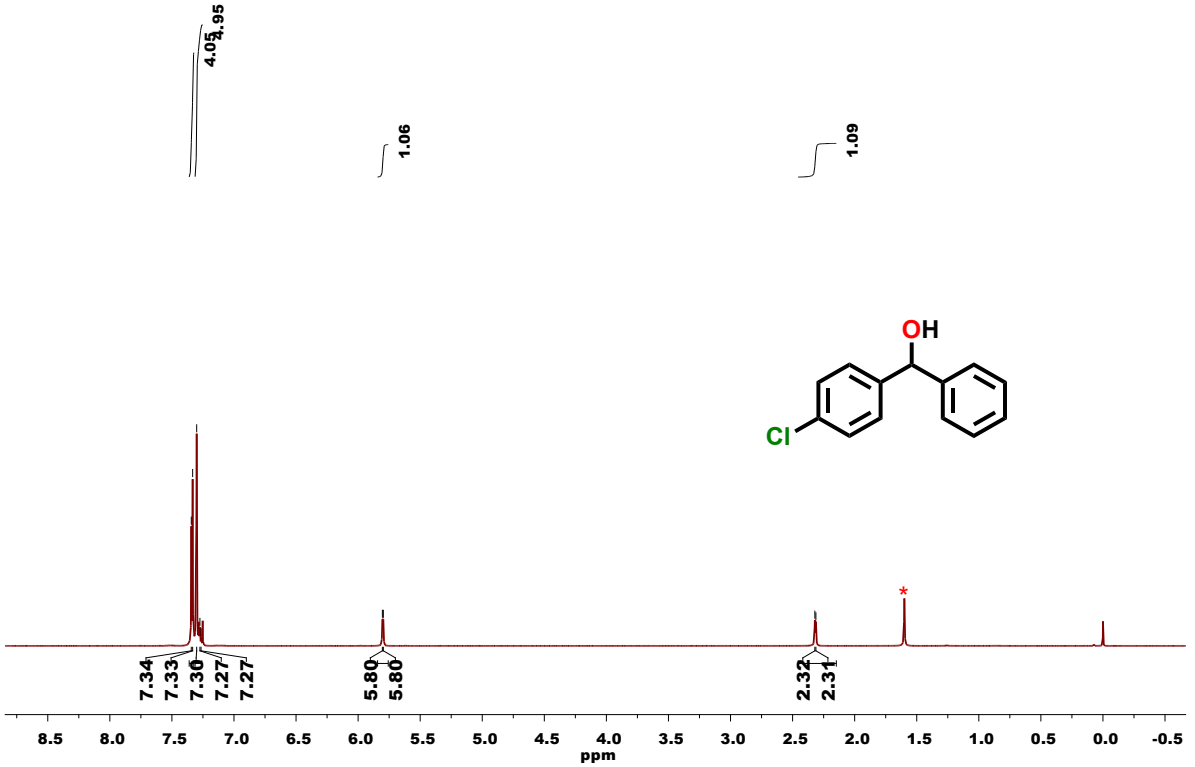

Figure S97. ^{1}H NMR spectrum of product **40** (4-chlorobenzhydrol) in $CDCl_3$ solvent where * represents the residual solvent and/or adventitious water peaks.

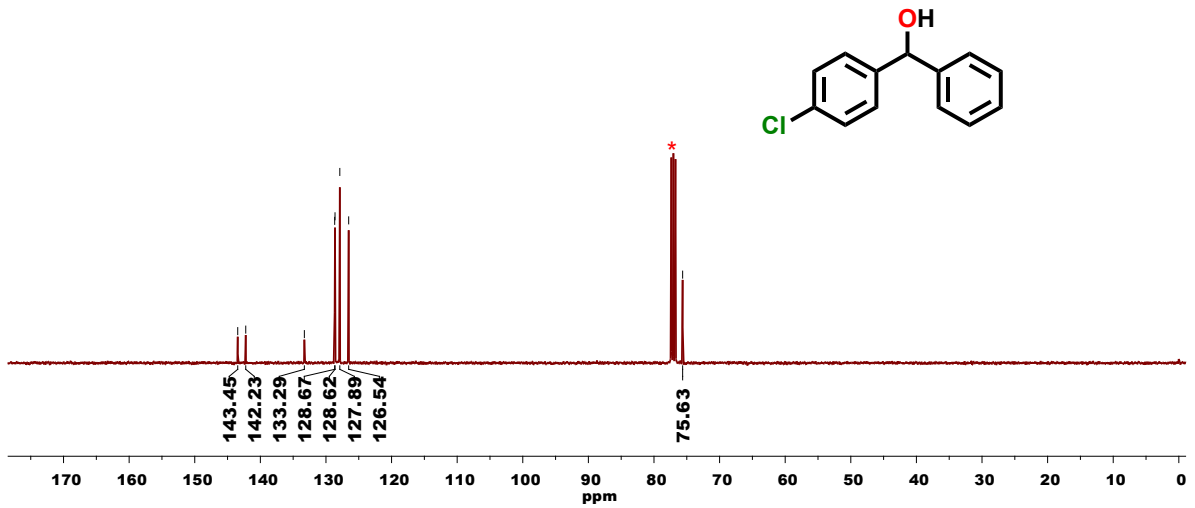

Figure S98. ^{13}C NMR spectrum of product **40** (4-chlorobenzhydrol) in $CDCl_3$ solvent where * represents the residual solvent peak.

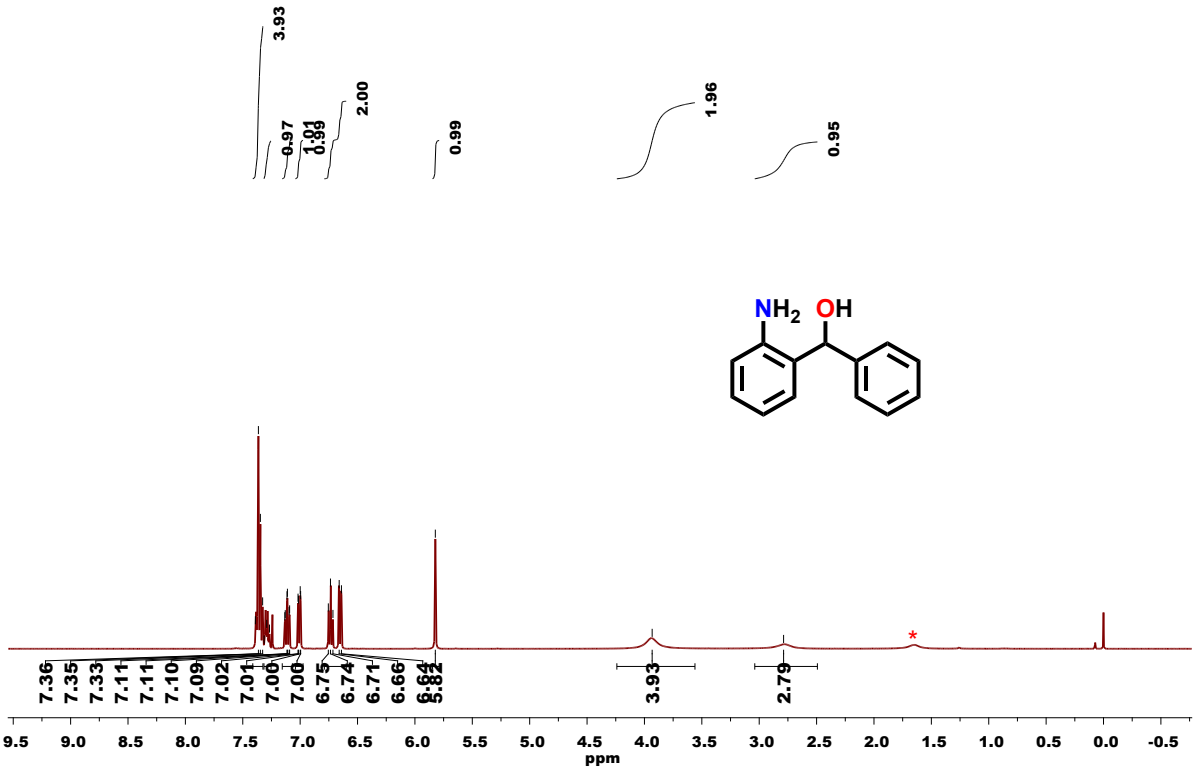

Figure S99. ^{1}H NMR spectrum of product **41** (2-aminobenzhydrol) in $CDCl_3$ solvent where * represents the residual solvent and/or adventitious water peaks.

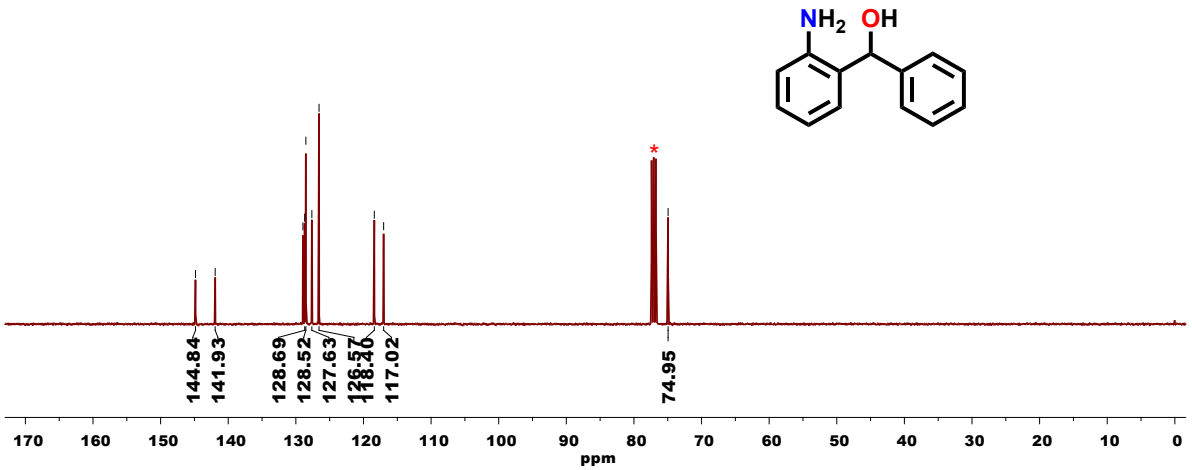

Figure S100. ^{13}C NMR spectrum of product **41** (2-aminobenzhydrol) in $CDCl_3$ solvent where * represents the residual solvent peak.

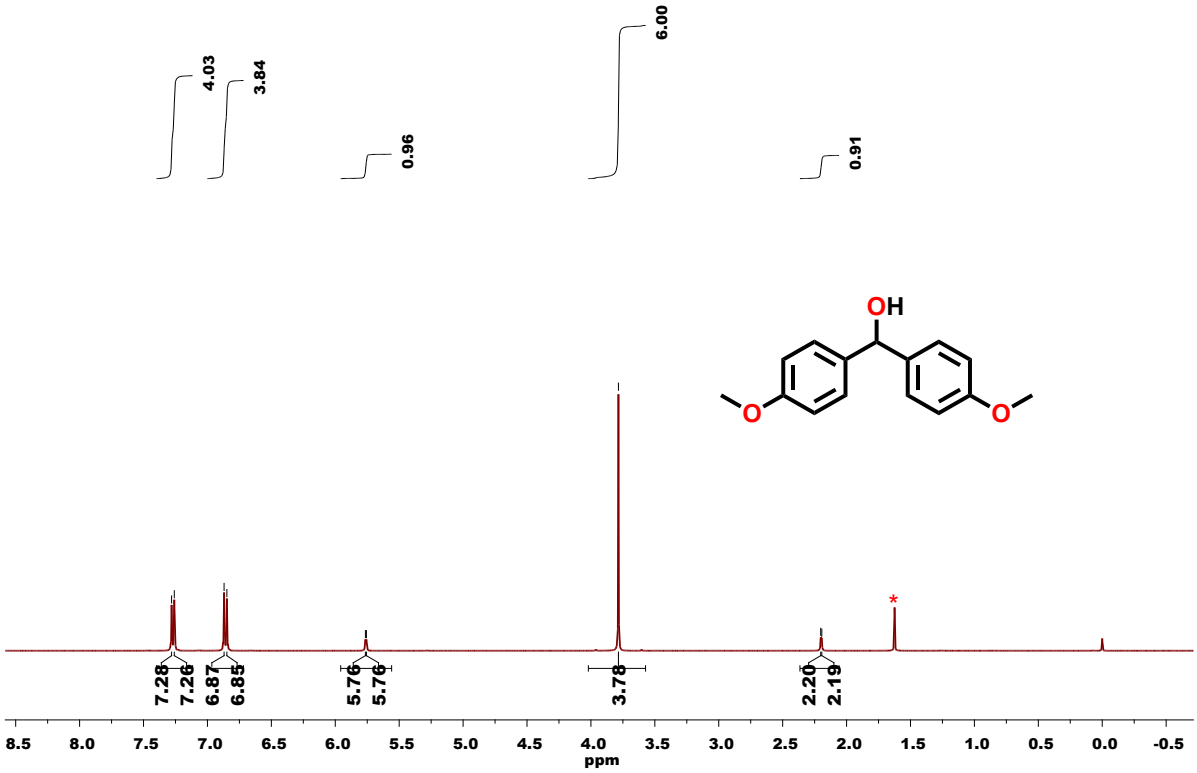

Figure S101. ^{1}H NMR spectrum of product **42** (4,4'-dimethoxybenzhydrol) in $CDCl_3$ solvent where * represents the residual solvent and/or adventitious water peaks.

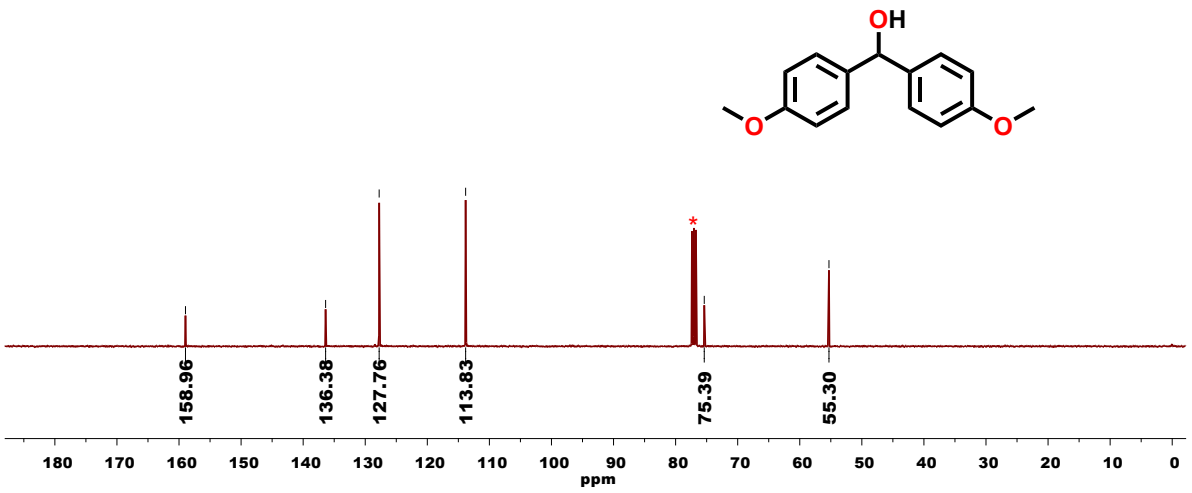

Figure S102. ^{13}C NMR spectrum of product **42** (4,4'-dimethoxybenzhydrol) in $CDCl_3$ solvent where * represents the residual solvent peak.

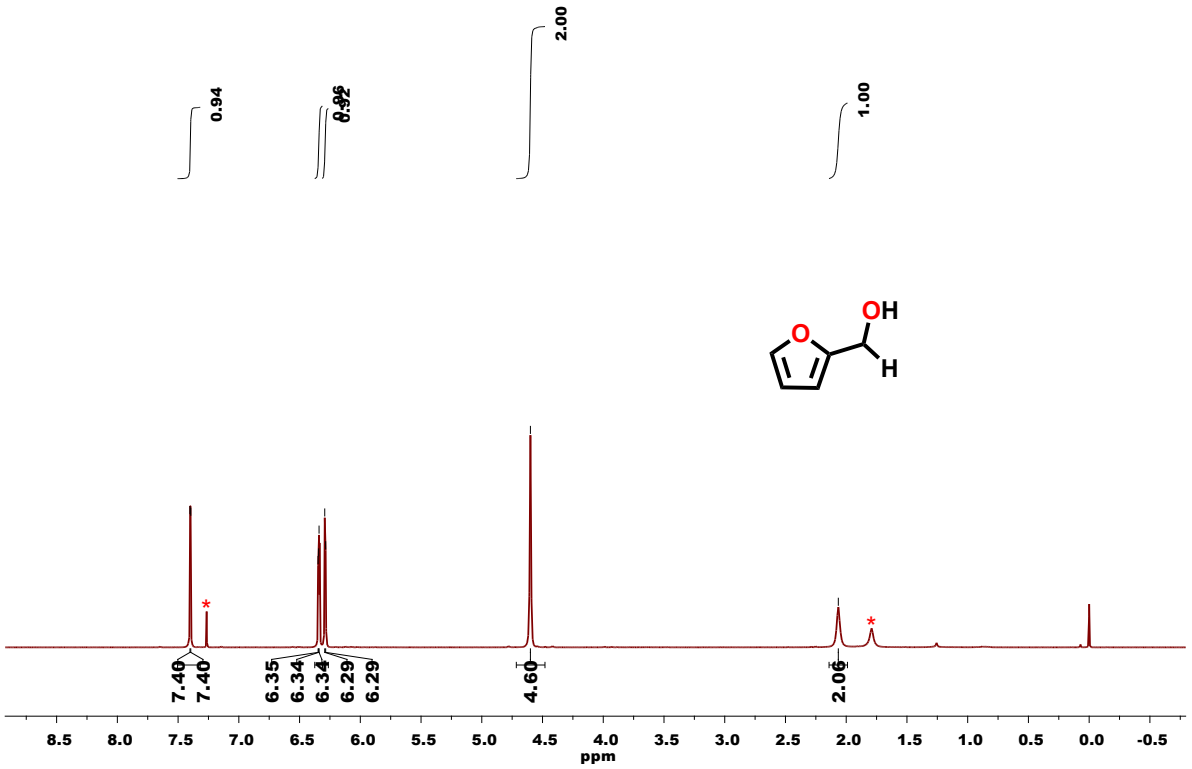

Figure S103. ^{13}C NMR spectrum of product **43** (furfuryl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

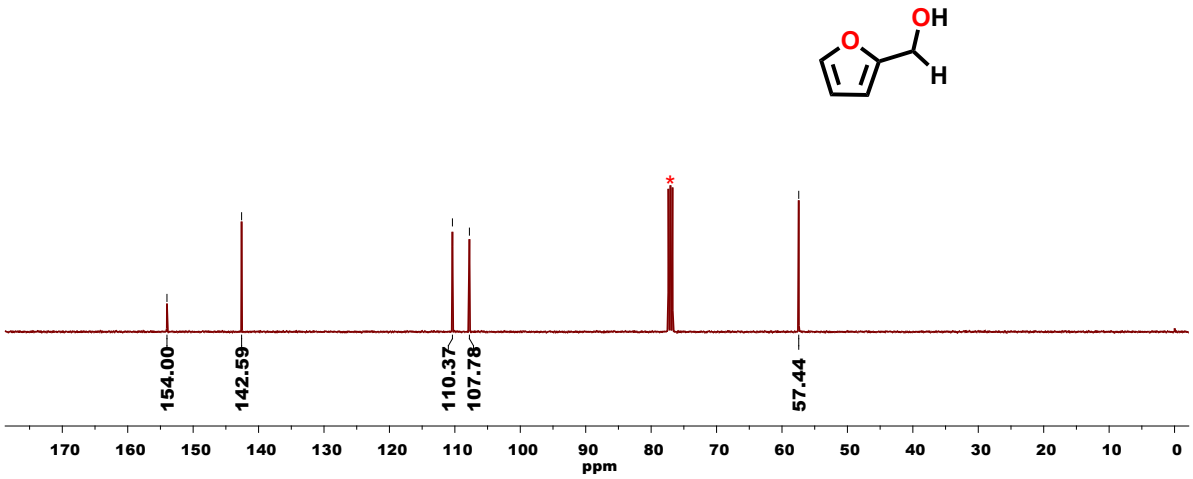

Figure S104. ^{13}C NMR spectrum of product **43** (furfuryl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

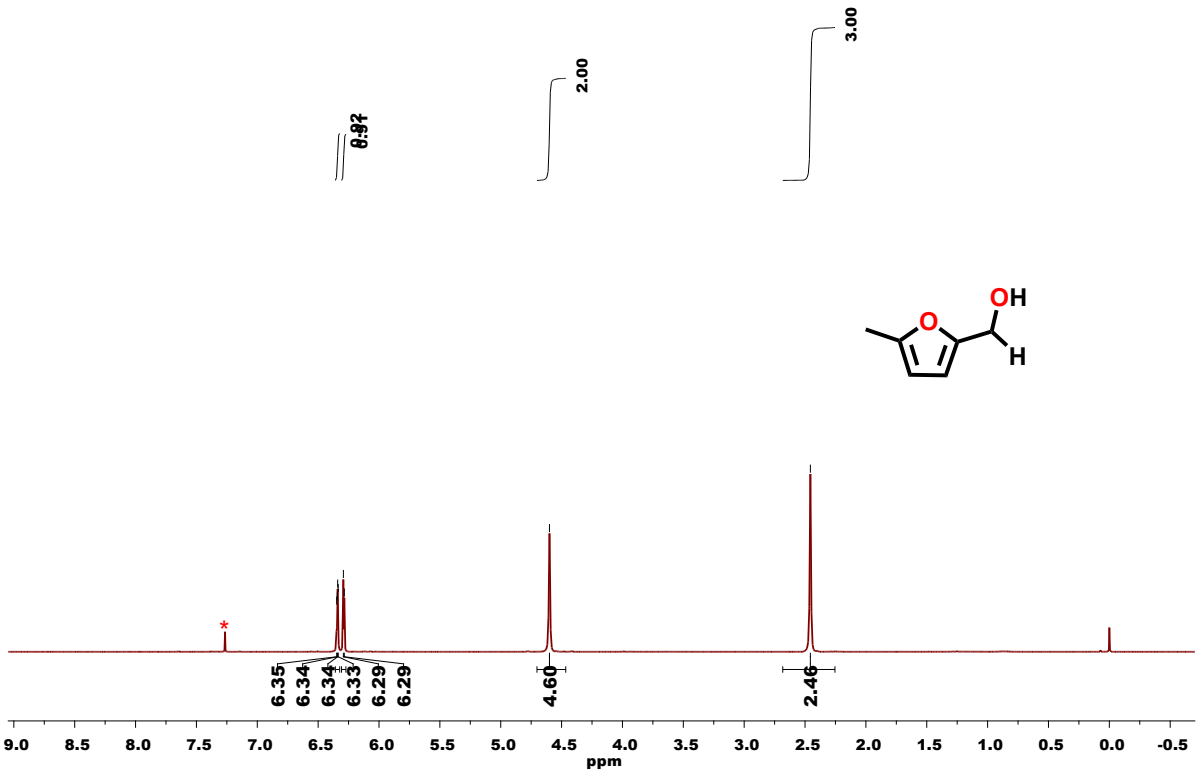

Figure S105. ^{1}H NMR spectrum of product **44** (5-methylfurfuryl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

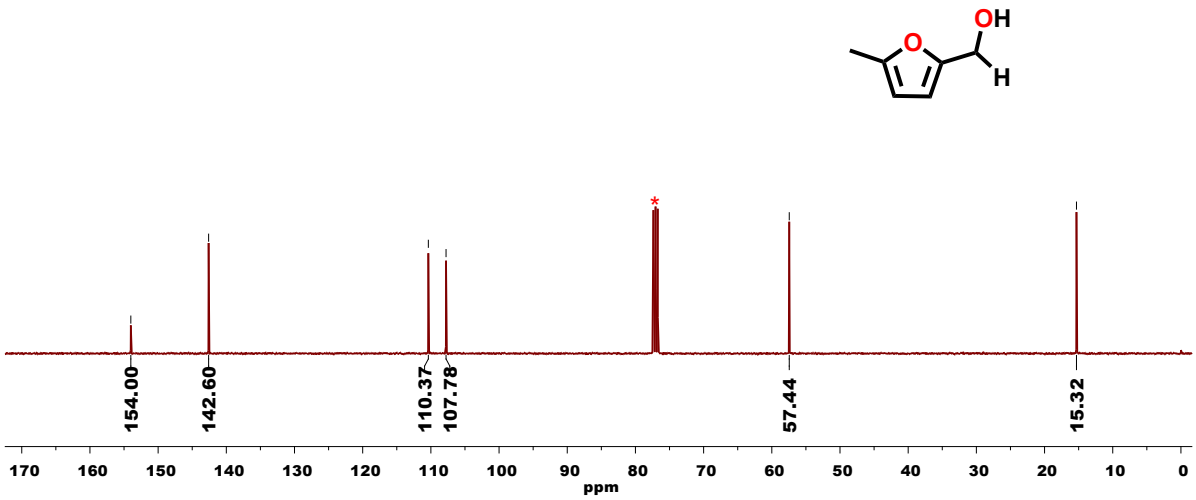

Figure S106. ^{13}C NMR spectrum of product **44** (5-methylfurfuryl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

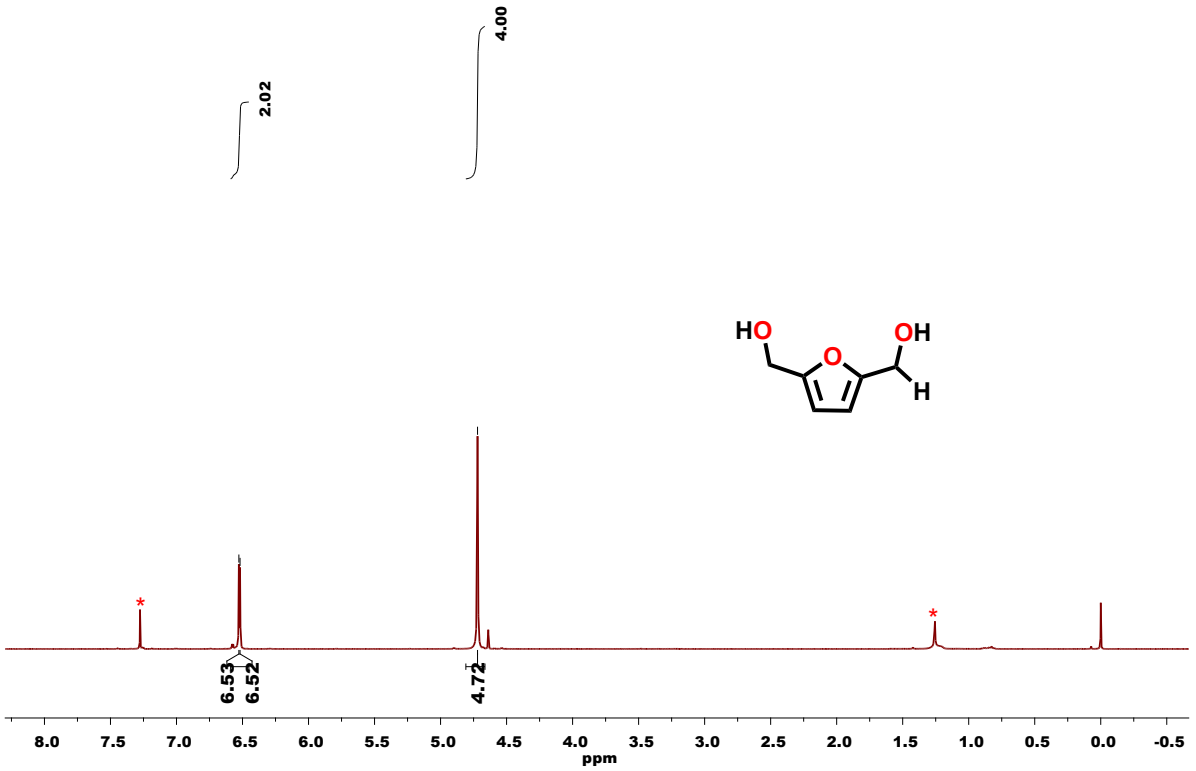

Figure S107. ^{1}H NMR spectrum of product **45** (5-(hydroxymethyl)furfuryl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

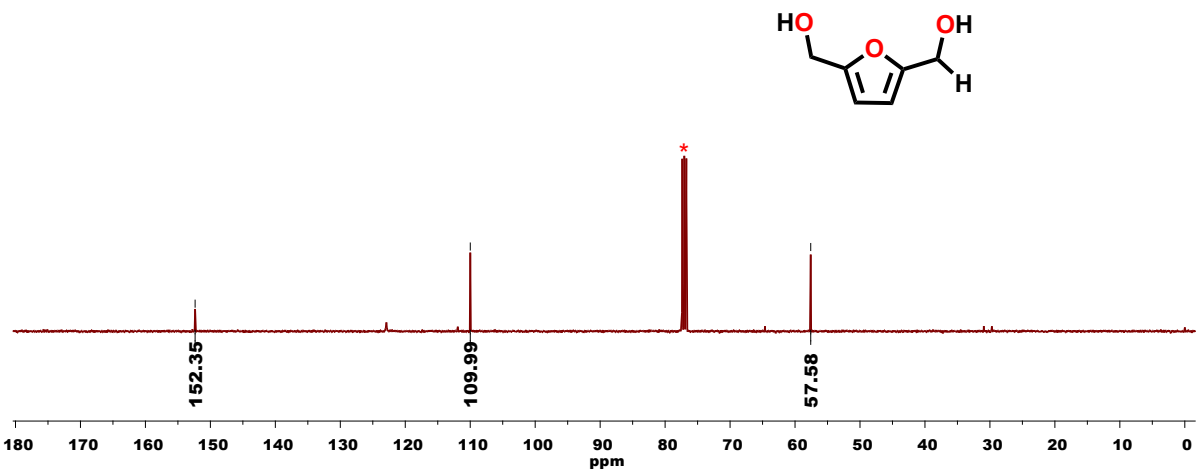

Figure S108. ^{13}C NMR spectrum of product **45** (5-(hydroxymethyl)furfuryl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

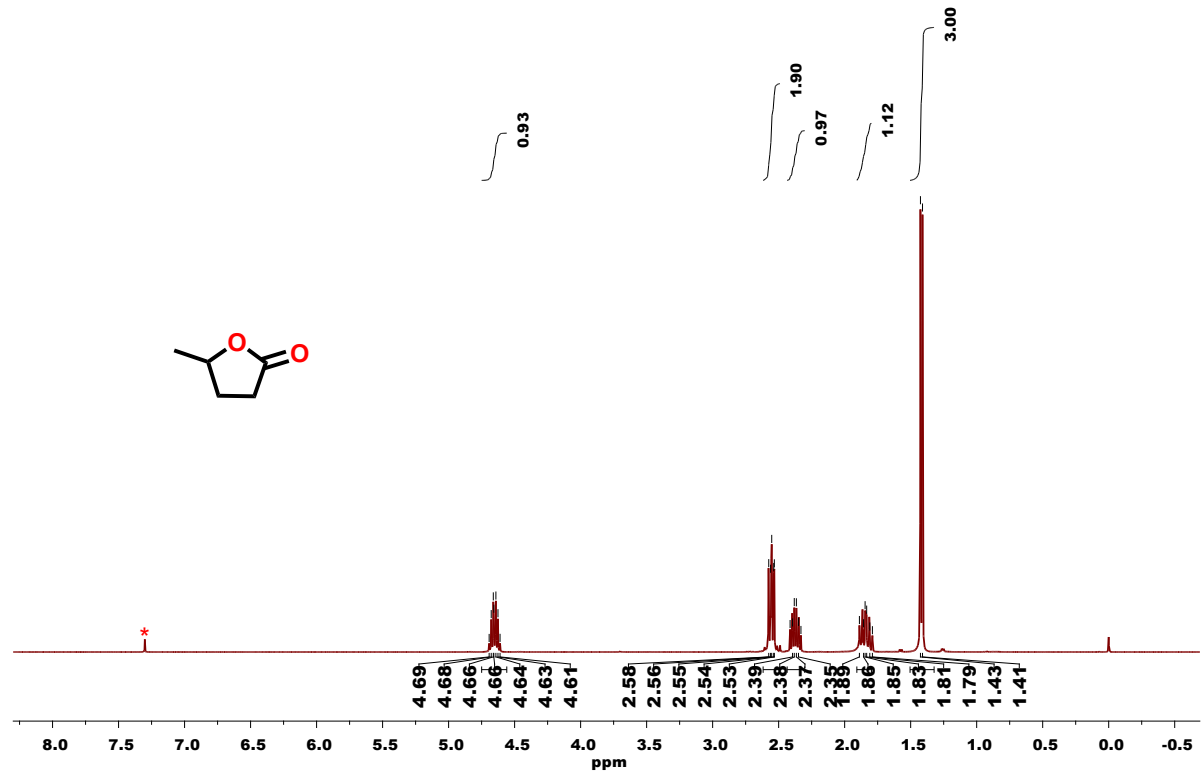

Figure S109. ^{1}H NMR spectrum of product **46** (gamma-valerolactone) in $CDCl_3$ solvent where * represents the residual solvent peak.

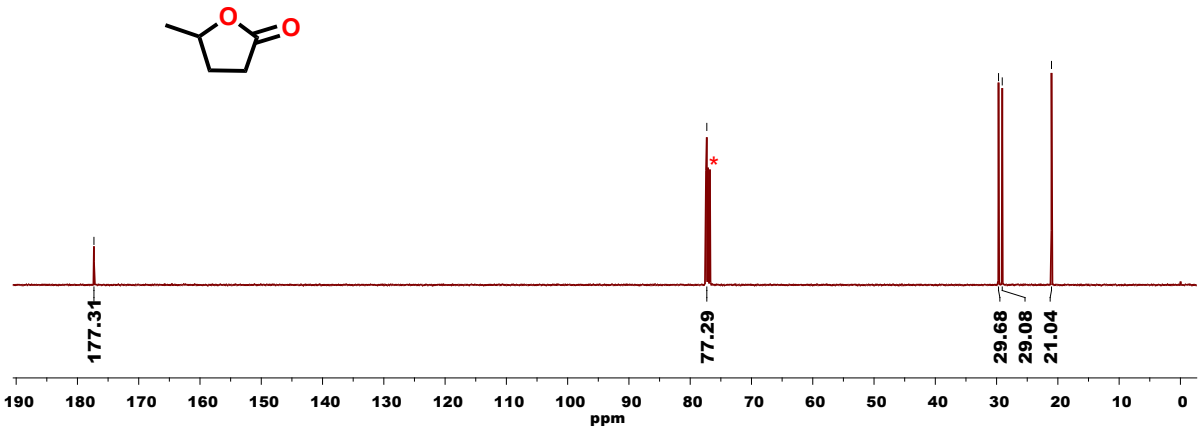

Figure S110. ^{13}C NMR spectrum of product **46** (gamma-valerolactone) in $CDCl_3$ solvent where * represents the residual solvent peak.

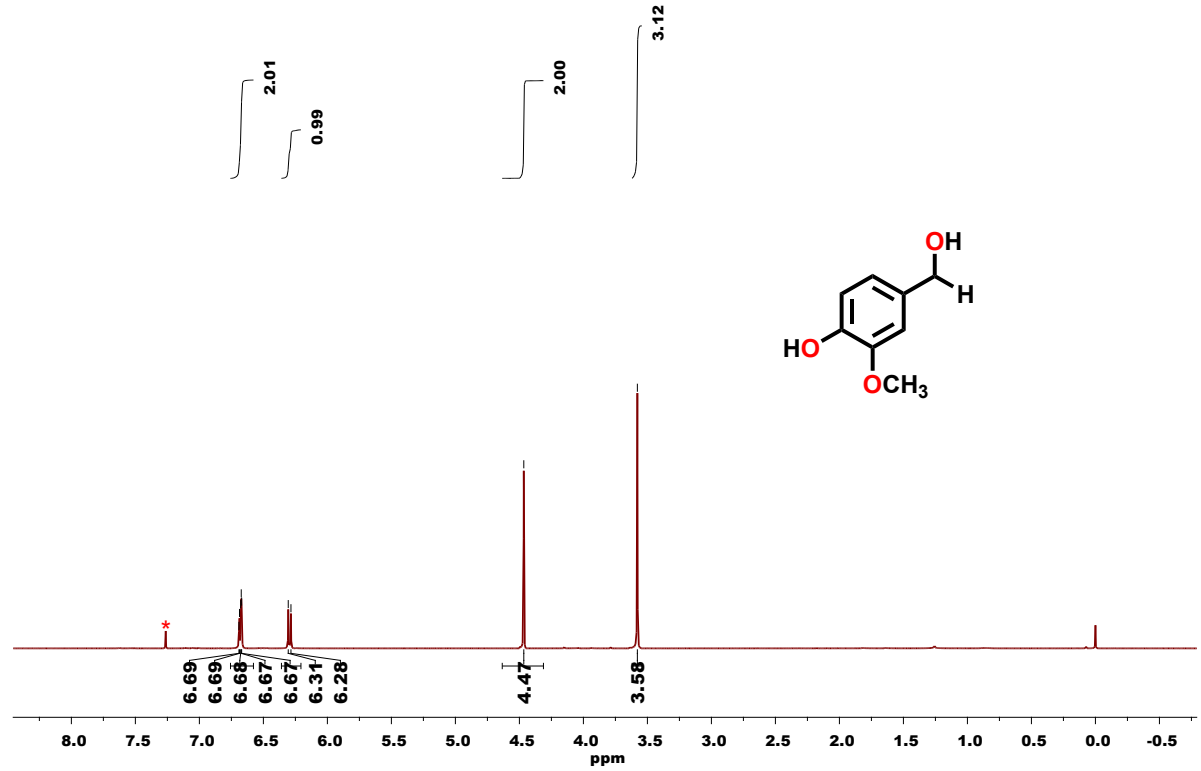

Figure S111. ^{1}H NMR spectrum of product **47** (vanillyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

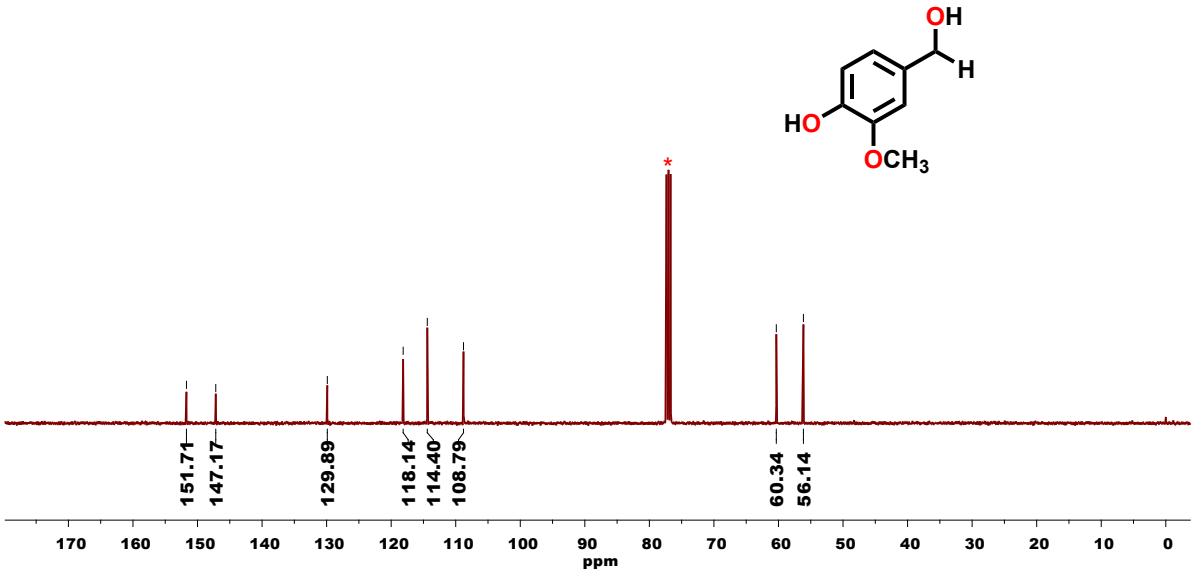

Figure S112. ^{13}C NMR spectrum of product **47** (vanillyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

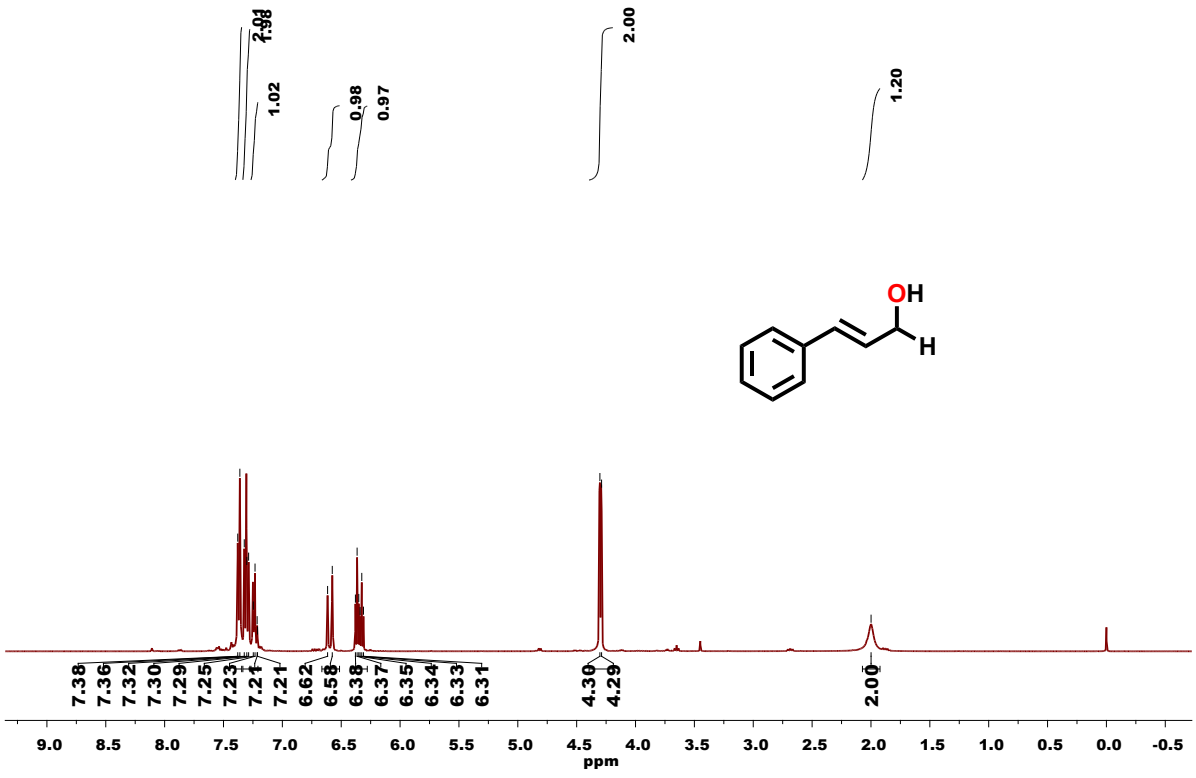

Figure S113. ^{1}H NMR spectrum of product **48** (cinnamyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

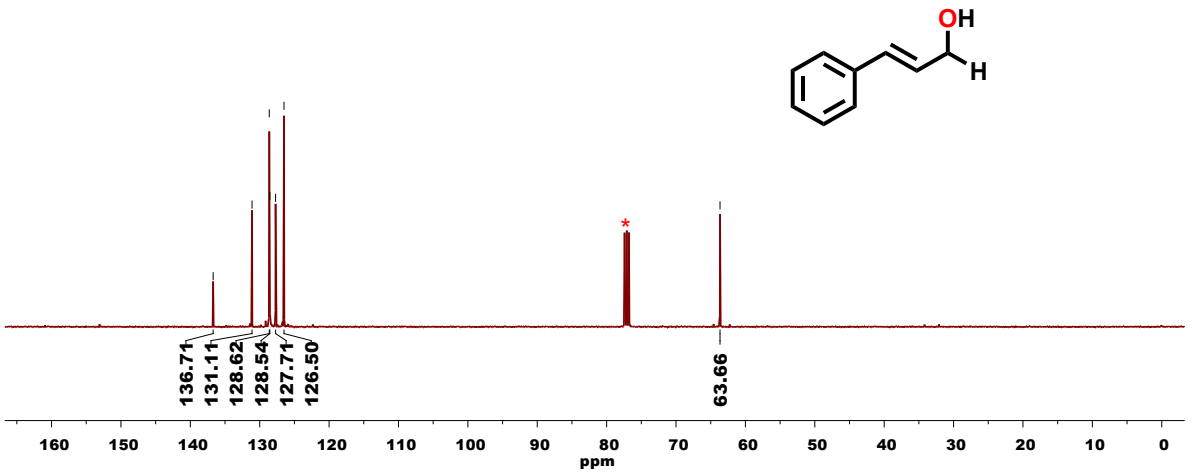

Figure S114. ^{13}C NMR spectrum of product **48** (cinnamyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

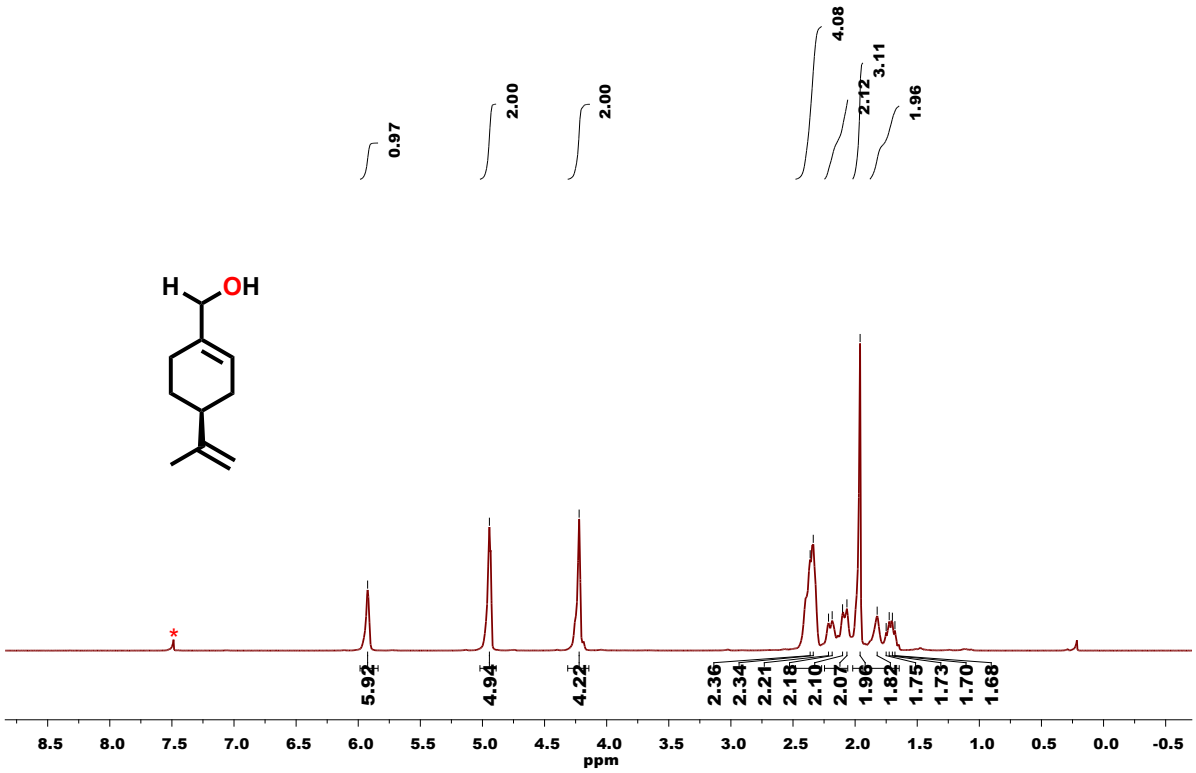

Figure S115. ^{1}H NMR spectrum of product **49** (perillyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

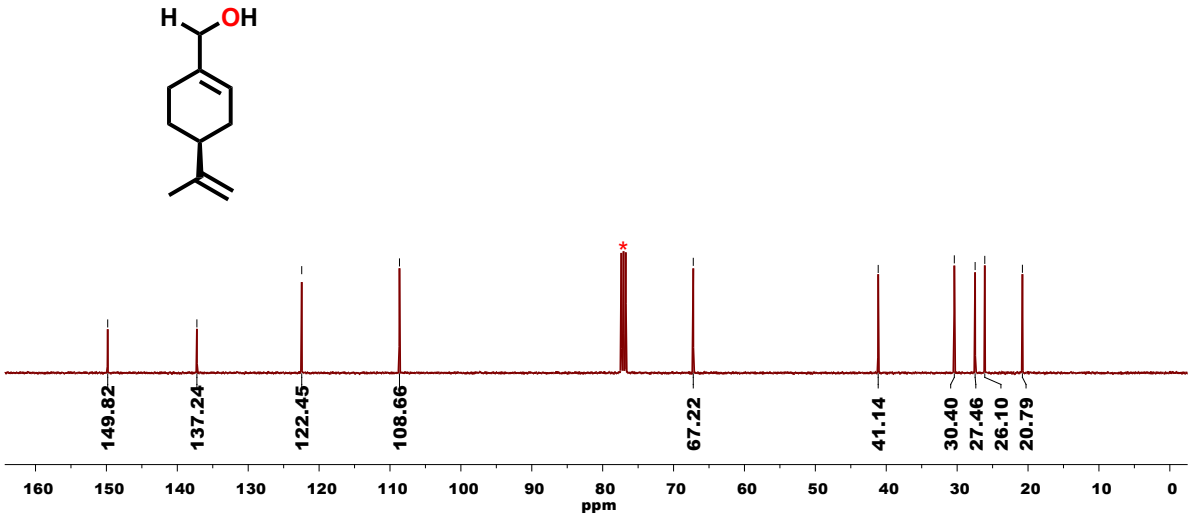

Figure S116. ^{13}C NMR spectrum of product **49** (perillyl alcohol) in $CDCl_3$ solvent where * represents the residual solvent peak.

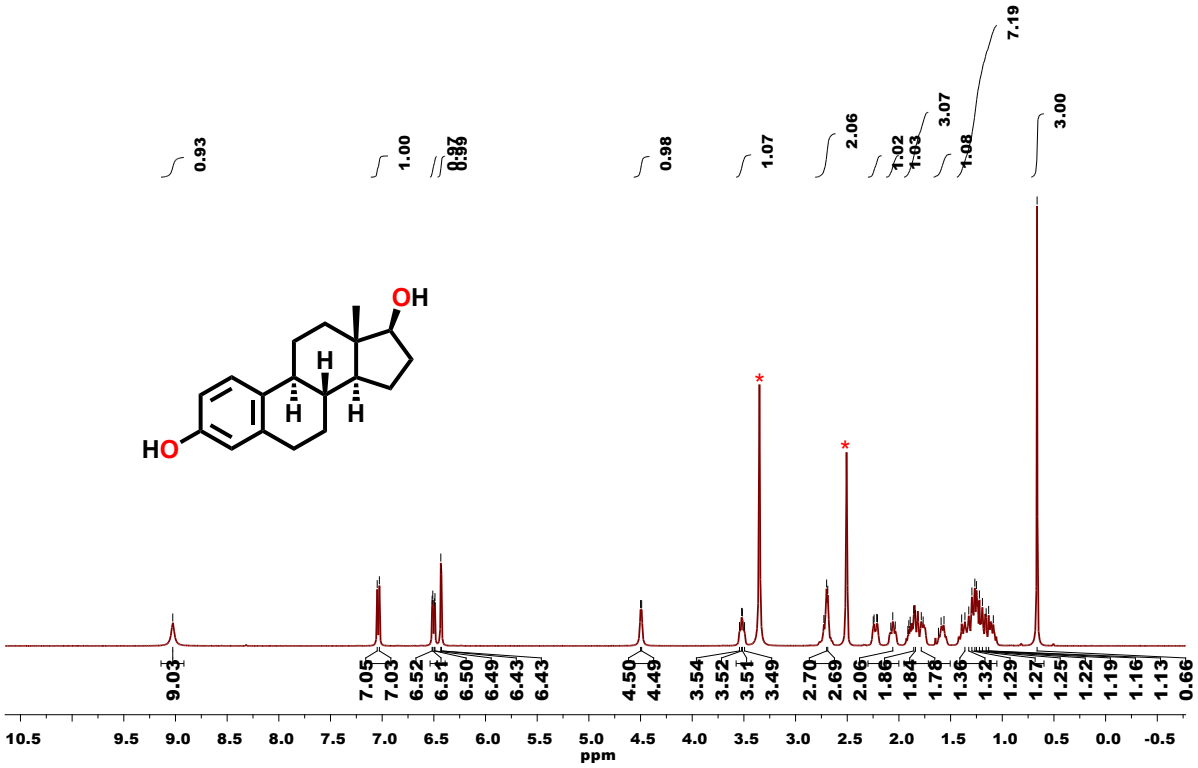

Figure S117. ^{1}H NMR spectrum of product **50** (estradiol) in (DMSO-*d6*) solvent where * represents the residual solvent and/or adventitious water peaks.

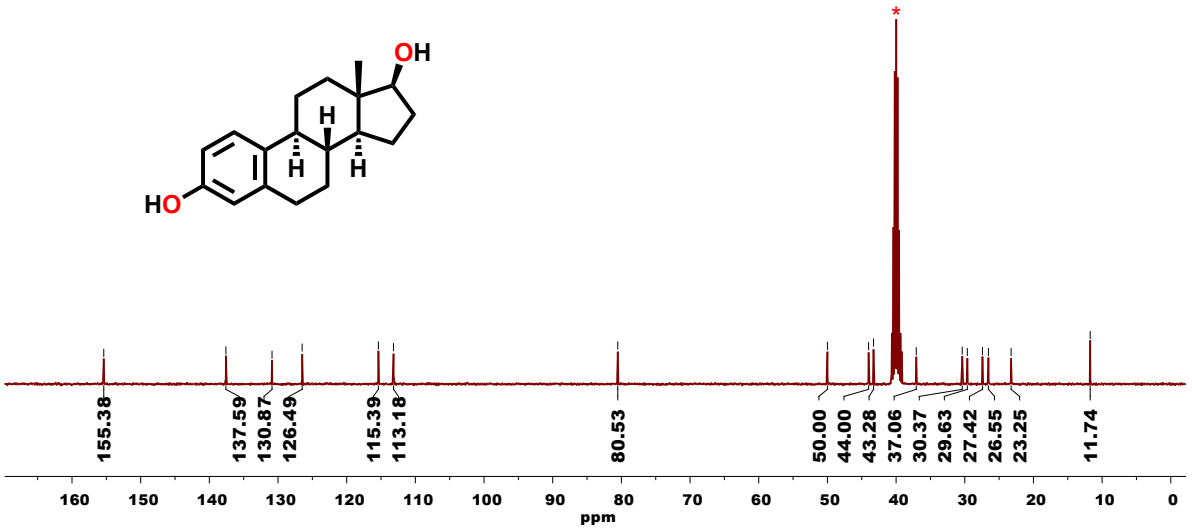

Figure S118. ^{13}C NMR spectrum of product **50** (estradiol) in (DMSO-*d6*) solvent where * represents the residual solvent peak.

Table S1. Crystallographic data collection and structure refinement parameters for MOF **1**.

	1
Empirical formula	$C_{128}H_{110}N_{14}O_{51}Co_4$
Formula weight	2896.01
Temperature/K	296.15
Crystal system	monoclinic
Space group	*C*2/*c*
a/Å	27.2275(13)
b/Å	14.6648(5)
c/Å	43.1167(16)
α/°	90
β/°	99.068(2)
γ/°	90
Volume/Å^3	17000.7(12)
Z	4
ρ_{calc}g/cm^3	1.131
μ/mm^{-1}	0.459
F(000)	5968.0
Crystal size/mm^3	0.23 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.818 to 56.71
Index ranges	-36 ≤ h ≤ 36, -19 ≤ k ≤ 18, -57 ≤ l ≤ 57
Reflections collected	135294
Independent reflections	21223 [R_{int} = 0.1064, R_{sigma} = 0.0731]
Data/restraints/parameters	21223/0/896
Goodness-of-fit on F^2	1.031
Final *R* indexes [I>=2σ (I)]	R_1 = 0.1026, wR_2 = 0.2824
Final *R* indexes [all data]	R_1 = 0.1481, wR_2 = 0.3159
Largest diff. peak/hole / e Å^{-3}	1.72/-1.55
CCDC No.	2334280

Table S2. Selected bond distances (Å) for MOF **1**.

Bond	**1**
Co(2)-O(19)	2.173(2)
Co(2)-O(14)$^{\#1}$	2.073(3)
Co(2)-O(16)	2.057(4)
Co(2)-O(18)	2.038(4)
Co(2)-O(23)	2.085(4)
Co(2)-O(20)	2.133(4)
Co(1)-O(4)$^{\#2}$	2.110(4)
Co(1)-O(17)	2.051(6)
Co(1)-O(15)	2.102(5)
Co(1)-O(22)	2.061(8)
Co(1)-O(21)	2.102(7)
Co(1)-O(20)	2.091(5)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$+X,2-Y,-1/2+Z; $^{\#2}$+X,2-Y,1/2+Z

Table S3. Selected bond angles (°) for MOF **1**.

Bond	1
O(14) $^{\#1}$-Co(2)-O(19)	87.22(12)
O(14) $^{\#1}$-Co(2)-O(23)	88.24(16)
O(14) $^{\#1}$-Co(2)-O(20)	91.75(15)
O(16)-Co(2)-O(19)	85.76(15)
O(16)-Co(2)-O(14) $^{\#1}$	85.31(15)
O(16)-Co(2)-O(23)	170.34(18)
O(16)-Co(2)-O(20)	94.82(17)
O(18)-Co(2)-O(19)	89.01(15)
O(18)-Co(2)-O(14) $^{\#1}$	175.2(2)
O(18)-Co(2)-O(16)	97.36(18)
O(18)-Co(2)-O(23)	88.60(19)
O(18)-Co(2)-O(20)	91.98(17)
O(23)-Co(2)-O(19)	86.74(17)
O(23)-Co(2)-O(20)	92.56(19)
O(20)-Co(2)-O(19)	178.78(16)
O(17)-Co(1)-O(4) $^{\#2}$	84.2(2)
O(17)-Co(1)-O(15)	94.7(2)
O(17)-Co(1)-O(22)	87.4(3)
O(17)-Co(1)-O(21)	174.0(3)
O(17)-Co(1)-O(20)	95.2(2)
O(15)-Co(1)-O(4) $^{\#2}$	178.2(2)
O(15)-Co(1)-O(21)	89.3(2)
O(22)-Co(1)-O(4) $^{\#2}$	93.3(3)
O(22)-Co(1)-O(15)	88.1(3)
O(22)-Co(1)-O(21)	88.3(4)
O(22)-Co(1)-O(20)	176.0(2)
O(21)-Co(1)-O(4) $^{\#2}$	91.8(2)
O(20)-Co(1)-O(4) $^{\#2}$	89.92(17)
O(20)-Co(1)-O(15)	88.7(2)
O(20)-Co(1)-O(21)	89.3(3)
Co(2)-O(19)-Co(2) $^{\#3}$	132.3(2)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$+X,2-Y,-1/2+Z; $^{\#2}$+X,2-Y,1/2+Z; $^{\#3}$1-X,+Y,3/2-Z

Table S4. Zero pass CHEM 21 green metrics toolkit parameters.

Yield, conversion, selectivity, AE, RME

Reactant (Limiting Reactant First)	Mass (g)	MW	Mol	Catalyst	Mass (g)	Reagent	Mass (g)	Reaction solvent	Volume (cm^3)	Density ($g\ ml^{-1}$)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density ($g\ ml^{-1}$)	Mass (g)
Furfural	1.00	96.08	0.01	[Co]	0.03			Isopropanol	2.00	0.79	1.58			ethyl acetate	15.00	0.90	13.50
Isopropanol	0.62	60.10	0.01								0.00						0.00
Total	1.62	156.18			0.03		0.00				1.58		0.00				13.50

$$AE = \frac{molecular\ weight\ of\ product}{total\ molecualr\ weight\ of\ reactants} \times 100$$

$$RME = \frac{mass\ of\ isolated\ product}{total\ mass\ of\ reactants} \times 100$$

		Flag
Yield	99.9	99.9
Conversion	100.0	100.0
Selectivity	99.9	99.9
AE	62.8	
RME	63.0	

	mass	mw	mol
Product	1.020	98.100	0.0103976
	mass		
Unreacted limiting reactant	0.000		

Solvents (Zero Pass)

Highly hazardous solvents (Red flag for any of the following)	List Highly Hazardous Solvents Below
Et_2O, Benzene, CCl_4, chloroform, DCE, nitromethane, CS_2, HMPA	None

Health and Safety (Zero Pass)

Health & safety (Red flag for any of the following)		List substances plus the red flagged H-codes below
Highly explosive	H200, H201, H202, H203	None
Explosive thermal runaway	H240	None
Fatally toxic	H300, H310, H330	None
Mutagenic	H350	None
Repro-toxic	H360	None
Serious environmental implications	H420	None

Table S5. First pass CHEM 21 green metrics toolkit parameters.

Yield, AE, RME, MI/PMI and OE

Reactant (Limiting Reactant First)	Mass (g)	MW	Mol	Catalyst	Mass (g)	Reagent	Mass (g)	Reaction solvent	Volume (cm^3)	Density ($g\ ml^{-1}$)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density ($g\ ml^{-1}$)	Mass (g)
Furfural	1.00	96.08	0.01	[Co]	0.03			Isopropanol	2.00	0.79	1.58			ethyl acetate	15.00	0.90	13.50
Isopropanol	0.62	60.10	0.01								0.00						0.00
Total	1.62	156.18			0.03		0.00				1.58		0.00				13.50

$$RME = \frac{mass\ of\ isolated\ product}{total\ mass\ of\ reactants} \times 100$$

$$AE = \frac{molecular\ weight\ of\ product}{total\ molecular\ weight\ of\ reactants} \times 100$$

$$mass\ intensity = \frac{total\ mass\ in\ a\ process\ or\ process\ step}{mass\ of\ product}$$

$$OE = \frac{RME}{AE} \times 100$$

		Flag
Yield	99.9	99.9
Conversion	100.0	100.0
Selectivity	99.9	99.9
AE	62.8	
RME	63.0	OE 100.2
PMI total	16.4	
PMI Reaction	3.2	
PMI reactants, reagents, catalyst	1.6	
PMI reaction solvents	1.5	
PMI Workup	13.2	
PMI Workup chemical	0.0	
PMI workup solvents	13.2	

	Mass	MW	Mol
Product	1.020	98.100	0.010397554
	mass		
Unreacted limiting	0.00		

Solvents (First Pass)

		List solvents below
Preferred solvents	**water,** EtOH, nBuOH, AcOipr, AcOnBu, PhOMe, MeOH, tBuOH, BnOH, ethylene glycol, acetone, MEK, MIBK, **AcOEt,** sulfolane	2-propanol
Problematic solvents: (acceptable only if substitution does not offer	DMSO, cyclohexanone, DMPU, AcOH, Ac2O, Acetonitrile, AcOMe, THF, heptane, Me-cyclohexane, toluene, xylene,	
Hazardous solvents: These solvents have significant health and/or safety	dioxane, pentane, TEA, diisopropyl ether, DME, DCM, DMF, DMA, NMP, methoxyethanol, hexane	
Highly hazardous solvents: The	Et.O. Benzene. CCl.. chloroform. DCE. nitromethane. CS..	

Catalyst/enzyme (First Pass)		**Tick**			**Tick**
Catalyst or enzyme used, **or** reaction takes place without **any** catalyst/reagents.	Green Flag	√	Facile recovery of catalyst/enzyme	Green Flag	√
Use of stoichiometric quantities of reagents	Amber Flag		catalyst/enzyme not recovered	Amber Flag	
Use of reagents in excess	Red Flag				

Critical elements

Supply remaining	Flag colour	Note element
5-50 years	Red Flag	
50-500 years	Amber Flag	
+500 years	Green Flag	Co

Energy (First Pass)		**Tick**			**Tick**
Reaction run between 0 to 70°C	Green Flag	√	Reaction run at reflux	Red Flag	
Reaction run between -20 to 0 or 70 to 140°C	Amber Flag		Reaction run 5°C or more below the solvent boiling point	Green Flag	√
Reaction run below -20 or above 140°C	Red Flag				

Batch/flow		**Tick**	**Work Up**		**List**
Flow	Green Flag		quenching	Green Flag	Filtration & Evaporation
Batch	Amber Flag		filtration		
			centrifugation		
			crystallisation		
			Low temperature distillation/evaporation/		
			solvent exchange, quenching into aqueous	Amber Flag	
			chromatography/ion exchange		
			high temperature	Red Flag	
			multiple recrystallisation		

Health & safety				**List substances and H-codes**	**List substances and H-codes**	**List substances and H-codes**
	Red Flag	**Amber Flag**	**Green Flag**			
Highly explosive	H200, H201, H202, H203	H205, H220, H224	If no red or amber flagged H codes present then green flag			Acetophenone: H227, H302, H318;
Explosive thermal runaway	H230, H240, H250	H241		None	None	Isopropanol: H225, H319, H336;
Toxic	H300, H310, H330	H301, H311, H331,				1-Phenylethan-1-ol: H227, H302;
Long Term toxicity	H340, H350, H360, H370,	H341, H351, H361,				Acetone: H225, H319, H336.
Environmental implications	H400, H410, H411, H420	H401, H412				

Use of chemicals of environmental concern		**List substances of very high concern**
Chemical identified as Substances of Very High Concern by	Red Flag	None