Supporting information

Porous Magnesium Carboxylate Framework: Synthesis, X-ray Crystal Structure, Gas Adsorption Property and Heterogeneous Catalytic Aldol Condensation Reaction

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Table S1. Solvent Effect in Aldol Condensation of *p*-nitrobenzaldehyde and Ketons Catalyzed by **1** and calcined catalyst[i]

solvent	ketone	major product	isolated yield (wt %)	selectivity (wt %)
THF	acetone	*β*-aldol product	a) 68 b) 90	a) 100 b) 100
THF	cyclohexanone	*β*-aldol product	a) 58 b) 75	a) 100 b) 100
THF-water (1:1)	acetone	*β*-aldol product	a) 45 b) 50	a) 48 b) 40
THF-water (1:1)	cyclohexanone	*β*-aldol product	a) 40 b) 44	a) 42 b) 36
No solvent	acetone	*β*-aldol product	a) 22 b) 38	a) 100 b) 100
No solvent	cyclohexanone	*β*-aldol product	a) 16 b) 26	a) 100 b) 100

(a), (b), corresponds to the catalytic performance of **1** and calcined catalyst, respectively.

[i]Reaction conditions: Aldehyde (2 mmol), acetone/cyclohexanone (10 mmol), triethylamine (2 mmol), tetrahydrofuran (2 ml) and catalysts (5 mg); temperature = 5-10

°C; for dehydrated compound reaction was performed in nitrogen atmosphere. Yields were isolated after 6 h of reaction.

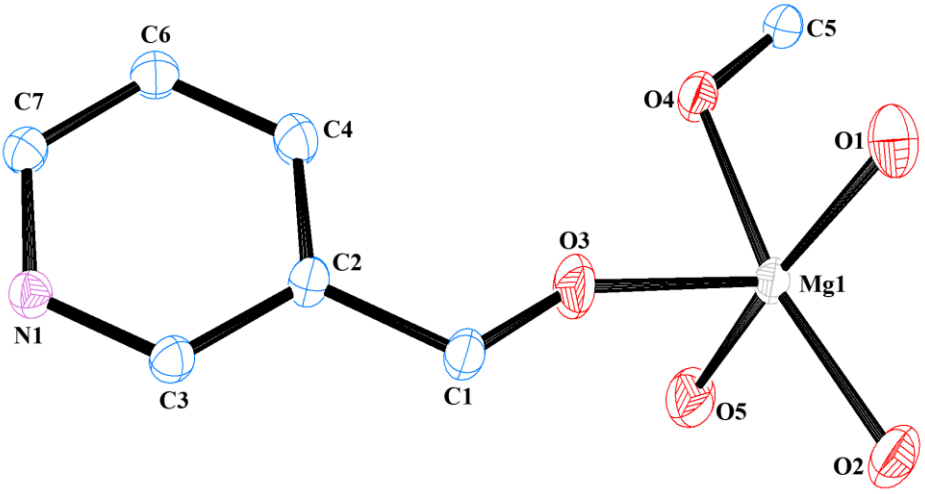


Figure S1. ORTEP diagram of compound **1** with 40% ellipsoid probability.

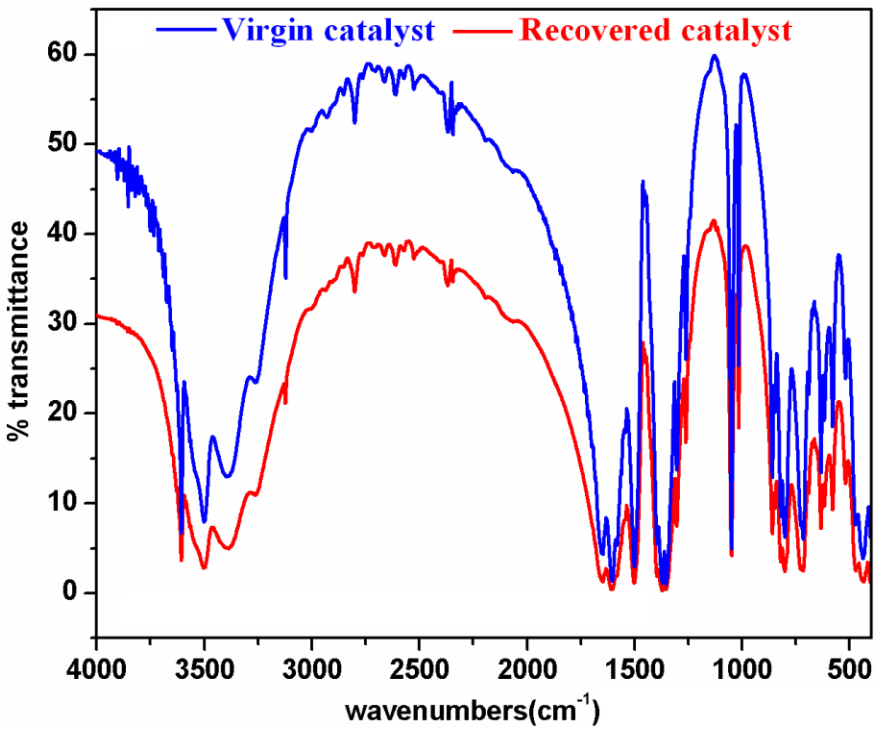


Figure S2. Comparison of IR spectra of pure and recovered catalyst for **1**

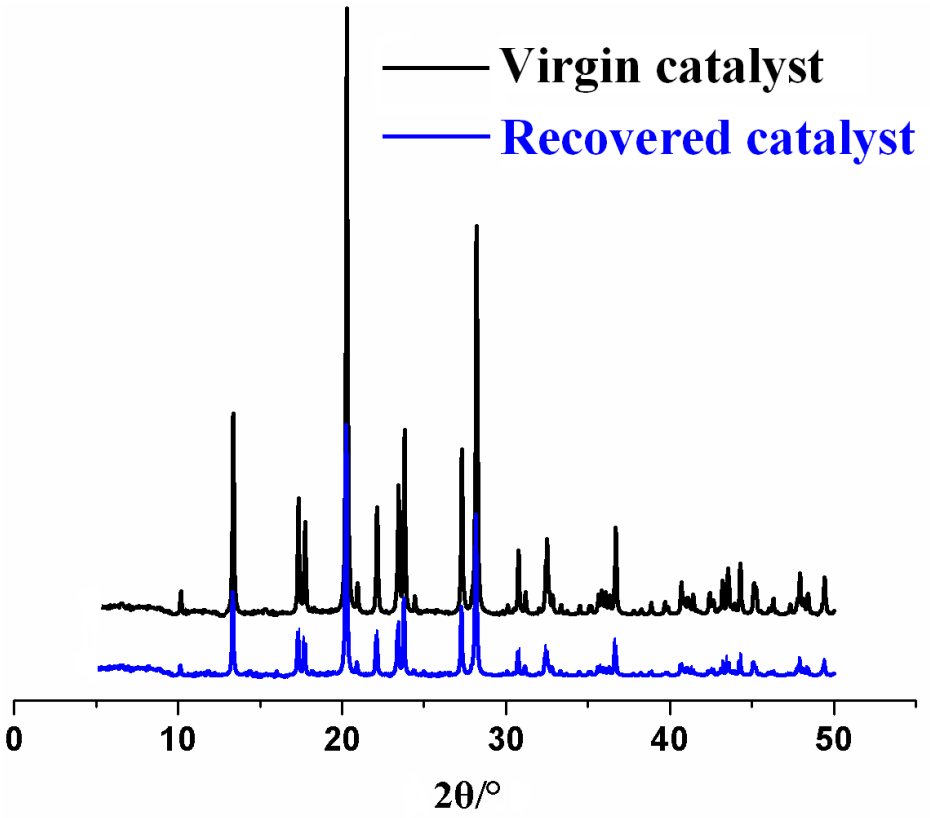


Figure S3. X-ray powder pattern of virgin catalyst and recovered catalyst for **1**

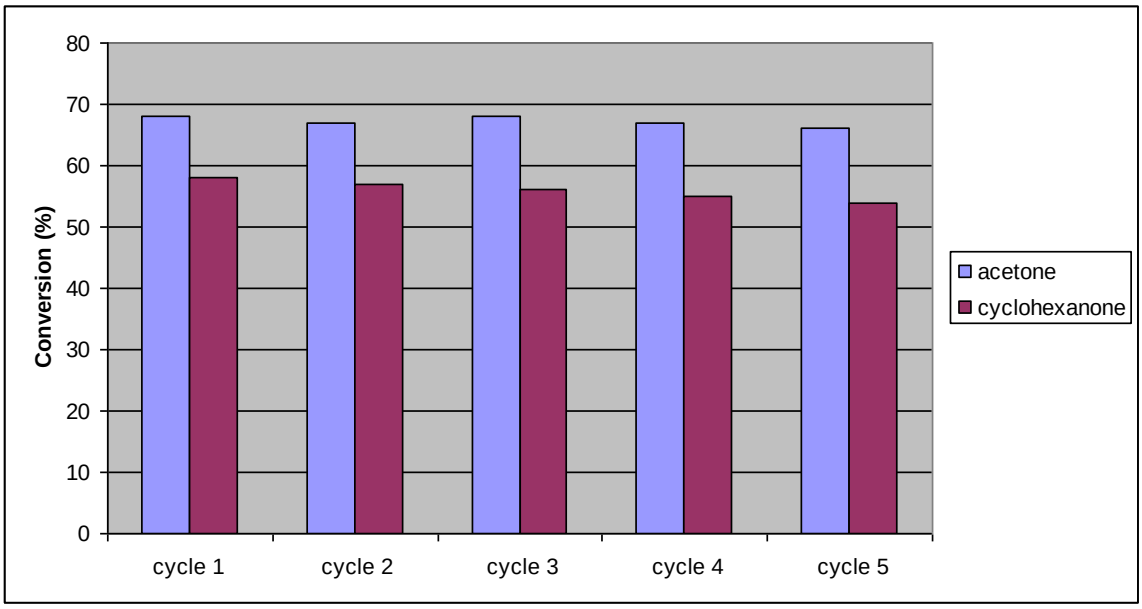


Figure S4. Aldol condensation of *p*-nitrobenzaldehyde and ketons catalyzed by **1** in five successive runs

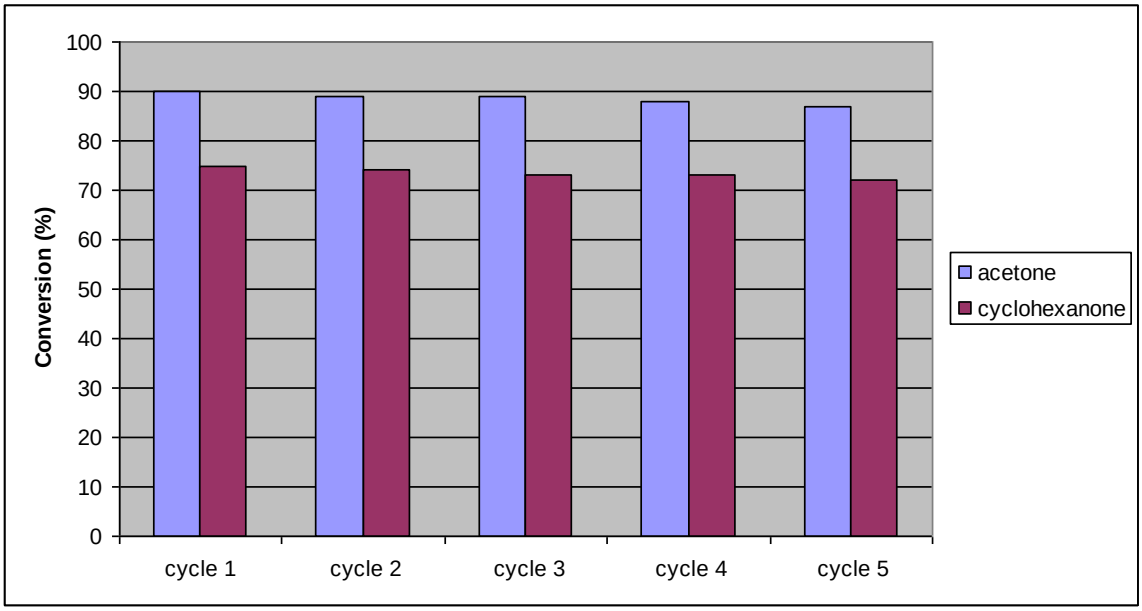


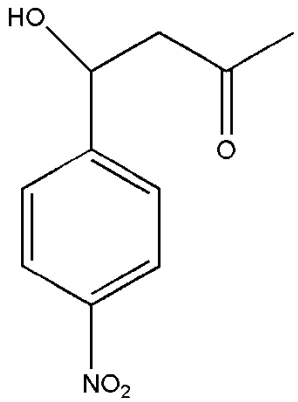
Figure S5. Aldol condensation of *p*-nitrobenzaldehyde and ketons catalyzed by calcined complex in five successive runs

General Information

All chemicals were purchased from Aldrich and were used as received except benzaldehyde. All solvents used were analytical grade and were used as received from Merck India Pvt. Ltd. Benzaldehyde, acetone and tetrahydrofuran was distilled before use. Benzaldehyde was kept over NaA molecular sieves to trap possible traces of benzoic acid. All reactions were carried out in air, without any special precautions. Column chromatography was performed over silica gel (mesh 60-120) and hexane/ethyl acetate combination was used as the eluent. ^{1}H NMR spectra were recorded at ambient temperature in $CDCl_3$ with tetramethylsilane as internal standard. The chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz, respectively on Bruker Avance 300 instrument. Elemental analysis of the products was performed by using Perkin-Elmer 240C elemental analyzer.

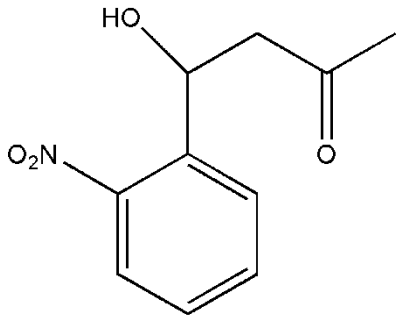
Characterization of Products

4-hydroxy-4-(4-nitrophenyl)-butan-2-one (Table 3, entry 1):



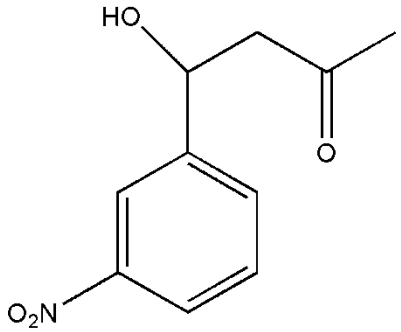
Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.07 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 5.20 (m, 1H), 3.57 (br s, 1H), 2.81 (m, 2H), 2.15 (s, 3H); Anal. Calcd. for $C_{10}H_{11}NO_4$: C, 57.41%; H, 5.30%; N, 6.69%. Found: C, 57.6%; H, 5.4%; N, 6.6%.

4-hydroxy-4-(2-nitrophenyl)-butan-2-one (Table 3, entry 2):



Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.75 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 10.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 5.52 (m, 1H), 3.93 (br s, 1H), 2.86 (d, *J* = 17.2 Hz, 1H), 2.63 (dd, *J* = 17.2, 9.3 Hz, 1H), 2.06 (s, 3H); Anal. Calcd. for $C_{10}H_{11}NO_4$: C, 57.41%; H, 5.30%; N, 6.69%. Found: C, 57.6%; H, 5.4%; N, 6.5%.

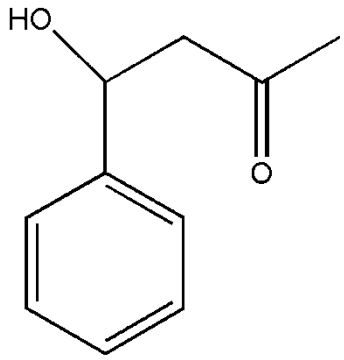
4-hydroxy-4-(3-nitrophenyl)-butan-2-one (Table 3, entry 3):



Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.12 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.0Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 5.17 (m, 1H), 3.69 (br s, 1H), 2.81 (m,

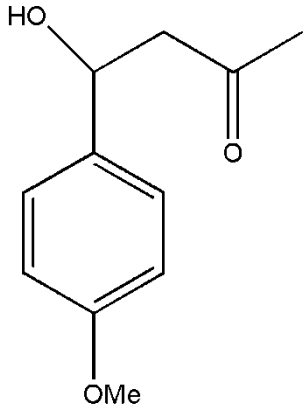
2H), 2.13 (s, 3H); Anal. Calcd. for $C_{10}H_{11}NO_4$: C, 57.41%; H, 5.30%; N, 6.69%. Found: C, 57.7%; H, 5.4%; N, 6.5%.

4-hydroxy-4-phenylbutan-2-one (Table 3, entry 4):



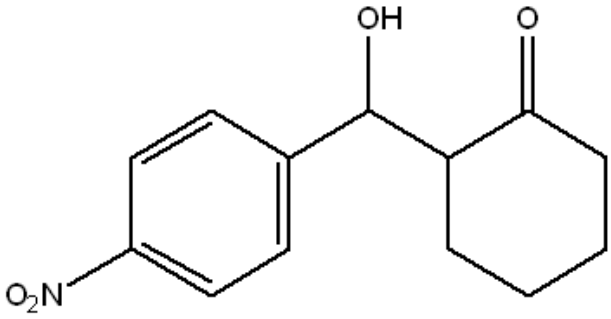
Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.3 (m, 5H), 5.16 (m, 1H), 3.25 (br s, 1H), 2.88 (m, 2H), 2.15 (s, 3H); Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15%; H, 7.27%. Found: C, 73.3%; H, 7.1%.

4-hydroxy-4-(4-methoxyphenyl)-butan-2-one (Table 3, entry 5):



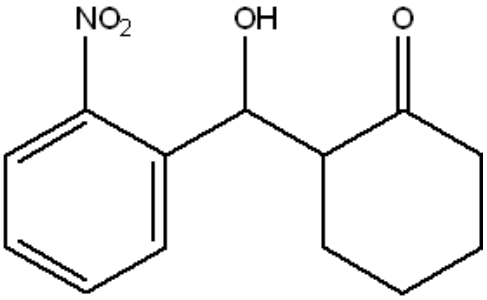
Pale yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.2 (d, *J* = 8.8 Hz, 2H), 6.9 (d, *J* = 8.8 Hz, 2H), 4.9 (d, *J* = 8.2 Hz, 1H), 4.05 (br s, 1H), 3.8 (s, 3H), 2.75 (m, 2H), 2.15 (s, 3H); Anal. Calcd. for $C_{13}H_{14}O_3$: C, 68.02%; H, 7.27%. Found: C, 67.8%; H, 7.2%.

2-(Hydroxy-(4-nitrophenyl)-methyl)-cyclohexan-1-one (Table 3, entry 6):



Pale yellow densed oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.21 (d, *J* = 9 Hz, 2H), 7.5 (d, *J* = 8.7 Hz, 2H), 4.94 (d, *J* = 8.2 Hz, 1H), 3.96 (br s, 1H), 2.75-2.8 (m, 1H), 2.36-2.49 (m, 2H), 2.07-2.14 (m,1H), 1.59-1.88 (m, 5H); Anal. Calcd. for $C_{13}H_{15}NO_4$: C, 62.64%; H, 6.07%; N, 5.62%. Found: C, 62.8%; H, 6.2%; N, 5.7%.

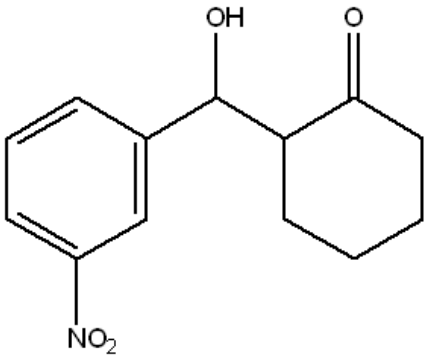
2-(Hydroxy-(2-nitrophenyl)-methyl)-cyclohexan-1-one (Table 3, entry 7):



Pale yellow densed oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.86 (dd, *J* = 8.2 Hz, 1 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1 Hz, 1H), 7.65 (td, *J* = 7.9 Hz, 1.3 Hz, 1H), 7.44 (td, *J* = 7.9 Hz, 1 Hz, 1H), 5.48 (d, *J* = 8.2 Hz, 1H), 3.88 (br s, 1H), 2.74-2.8 (m, 1H), 2.36-2.48 (m,

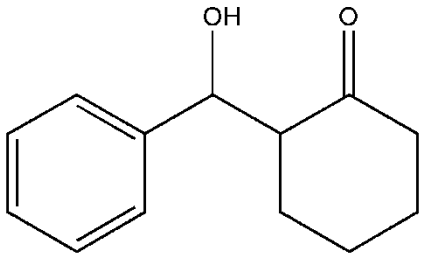
2H), 2.07-2.15 (m,1H), 1.56-1.9 (m, 5H); Anal. Calcd. for $C_{13}H_{15}NO_4$: C, 62.64%; H, 6.07%; N, 5.62%. Found: C, 62.6%; H, 6%; N, 5.6%.

2-(Hydroxy-(3-nitrophenyl)-methyl)-cyclohexan-1-one (Table 3, entry 8):



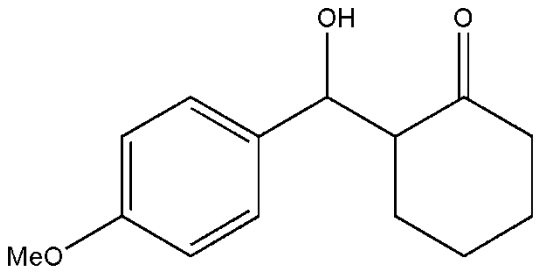
Pale yellow densed oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.21 (dd, *J* = 8.2 Hz, 1 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1 Hz, 1H), 7.65 (td, *J* = 7.9 Hz, 1.3 Hz, 1H), 7.43 (td, *J* = 7.9 Hz, 1 Hz, 1H), 4.9 (d, *J* = 8.2 Hz, 1H), 4.08 (br s, 1H), 2.75-2.81 (m, 1H), 2.35-2.49 (m, 2H), 2.07-2.15 (m,1H), 1.56-1.88 (m, 5H); Anal. Calcd. for $C_{13}H_{15}NO_4$: C, 62.64%; H, 6.07%; N, 5.62%. Found: C, 62.7%; H, 6.2%; N, 5.6%.

2-(Hydroxy (phenyl)-methyl)-cyclohexan-1-one (Table 3, entry 9):



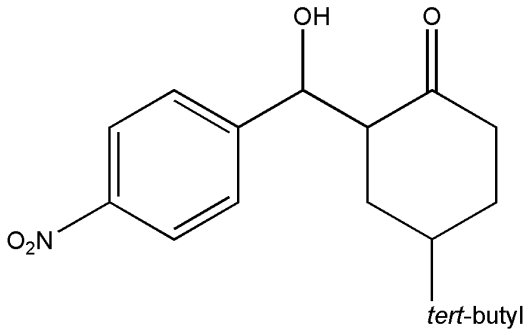
Pale yellow densed oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.20-7.37 (m, 5H), 5.05 (m, 1H), 3.96 (br s, 1H), 2.73-2.8 (m, 1H), 2.33-2.47 (m, 2H), 2.05-2.13 (m,1H), 1.53-1.9 (m, 5H); Anal. Calcd. for $C_{13}H_{16}O_2$: C, 74.44%; H, 7.90%. Found: C, 74.6%; H, 7.9%.

2-(Hydroxy-(4-methoxy-phenyl)-methyl)-cyclohexan-1-one (Table 3, entry 10):



Pale yellow densed oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.28 (d, *J* = 8.8 Hz, 2H), 6.9 (d, *J* = 8.8 Hz, 2H) 4.90 (d, *J* = 8.2 Hz, 1H), 4.05 (br s, 1H), 3.85 (s, 3H), 2.75-2.81 (m, 1H), 2.33-2.49 (m, 2H), 2.05-2.15 (m,1H), 1.55-1.9 (m, 5H); Anal. Calcd. for $C_{16}H_{18}O_3$: C, 71.77%; H, 7.74%. Found: C, 71.6%; H, 7.6%.

2-(Hydroxy-(4-nitrophenyl)-methyl)-4-(*tert*-butyl)-cyclohexan-1-one (Table 3, entry 11):



Pale yellow solid, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.20 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 2H), 5.48 (s, 1H), 3.96 (d, *J* = 3.4 Hz,1H), 2.11-2.67 (m, 4H), 1.43-1.62 (m, 4H), 0.81 (s, 9H); Anal. Calcd. for $C_{17}H_{23}NO_4$: C, 66.86%; H, 7.59%; N, 4.59%. Found: C, 66.8%; H, 7.6%; N, 4.6%.

References

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[3] Lopez, R. F.; Kofoed, J.; Machuqueiro, M.; Darbre, T. *Eur. J. Org. Chem*. **2005**, 5268-5276.

[4] Wu, C.; Fu, X.; Li, S. *Tetrahedron* **2011**, 67, 4283-4290.