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Supporting Information

One-pot Synthesis of Amides via Oxidative Amidation of Aldehydes and Amines Catalyzed by Copper-MOF

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Experimental Section

Materials and methods

All the chemicals were purchased from commercial sources and used without further purification. $Cu_2(BDC)_2(DABCO)$ was synthesized according to the our previously reported procedure [ref]. All reactions were monitored by thin layer chromatography (TLC) using plates coated with Merck 60 HF254 silica under UV light. IR spectra were recorded using Shimadzu 8400s FT-IR spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with BRUKER DRX 500-AVANCE FT-NMR instrument ($CDCl_3$ solution) at 500 MHz and 125 MHz, respectively. Scanning electron microscope (SEM) images were captured with a ZEISS scanning electron microscope at 30 kV with gold coating.

Synthesis of Amides via oxidation amidation of aldehydes catalyzed by $Cu_2(BDC)_2(DABCO)$

To a solution of amine (1 mmol) in CH_3CN (5 mL) was added NCS (1mmol) and the reaction mixture stirred for 1h at room temperature. Then aldehyde (1 mmol), $Cu_2(BDC)_2$DABCO (10% mol) and TBHP 70% (1 mmol) was added and the reaction temperature was increased up to 65 °C and was allowed to stir for 2h. The reaction progress was monitored by TLC. After reaction completion, catalyst filtered and filtrate was evaporated under reduced pressure, and the residue was purified using silicagel column chromatography (hexane/ethyl acetate (4:1)).

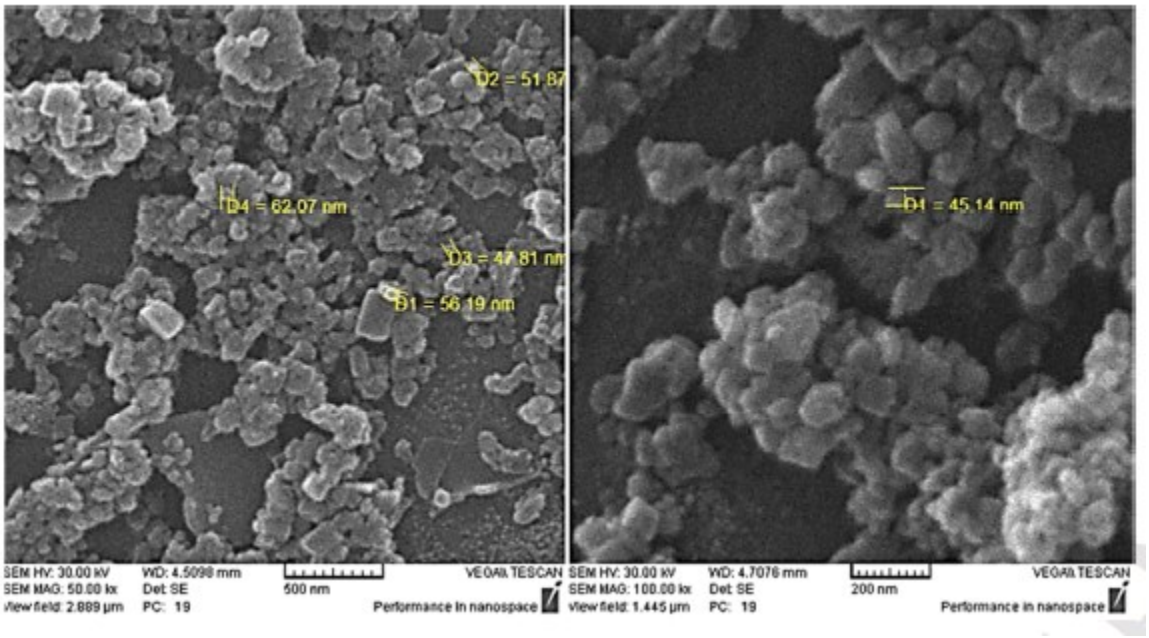

Fig S1. SEM image of $Cu_2(BDC)_2DABCO$ [23a]

***N*-benzylbenzamide**:

White solid; yield:75 %; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 7.1 Hz, 2H), 7.48−7.51(t, J = 7.1 Hz, 1H), 7.41−7.44 (m, 2H), 7.32−7.36 (m, 4H), 7.26−7.31 (m, 1H), 6.44 (brs, 1H), 4.65 (d, J = 5.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 138.2, 134.5, 131.7, 128.9, 128.7, 128.1, 127.7, 127.1, 44.2.

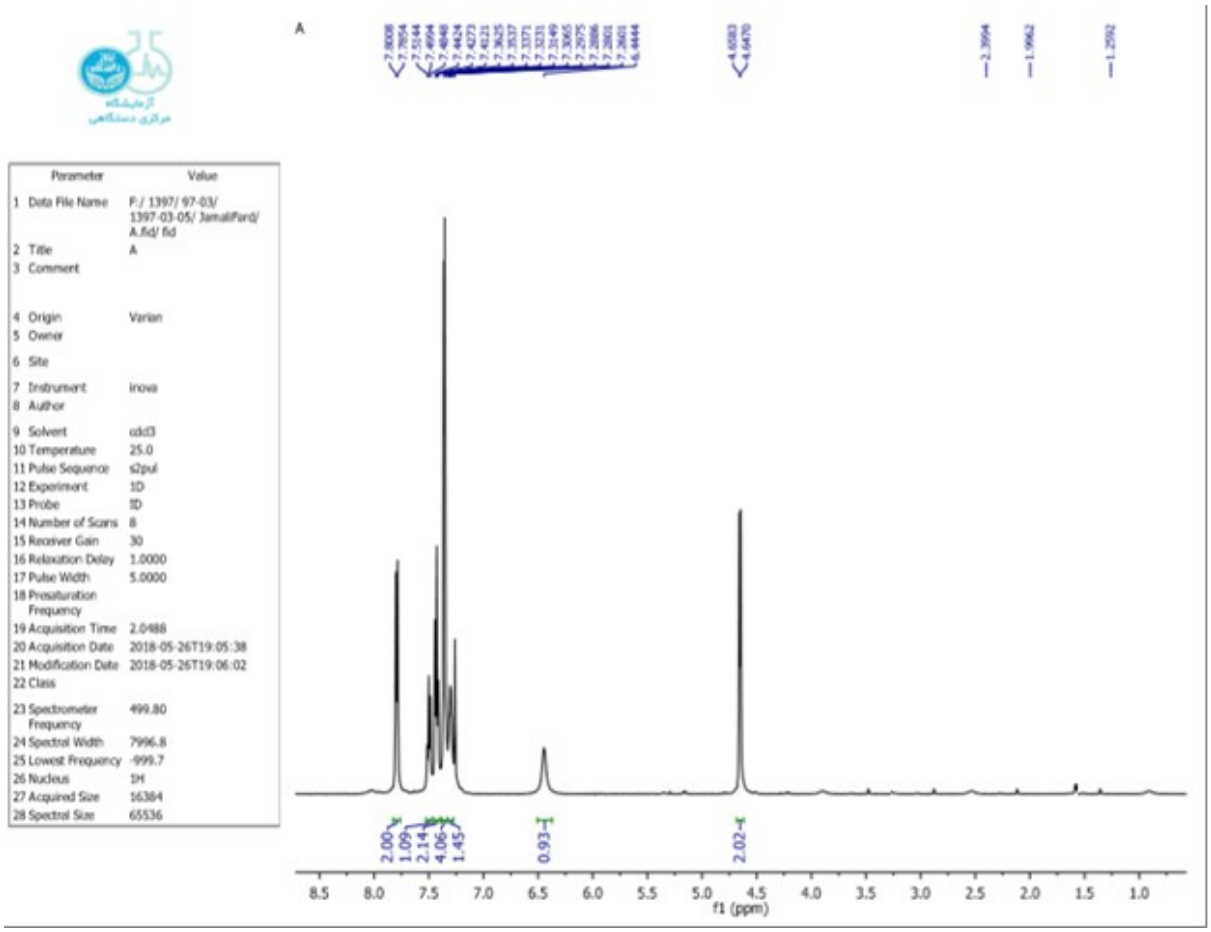

Figure S2. ^{1}H-NMR spectrum of N-benzylbenzamide

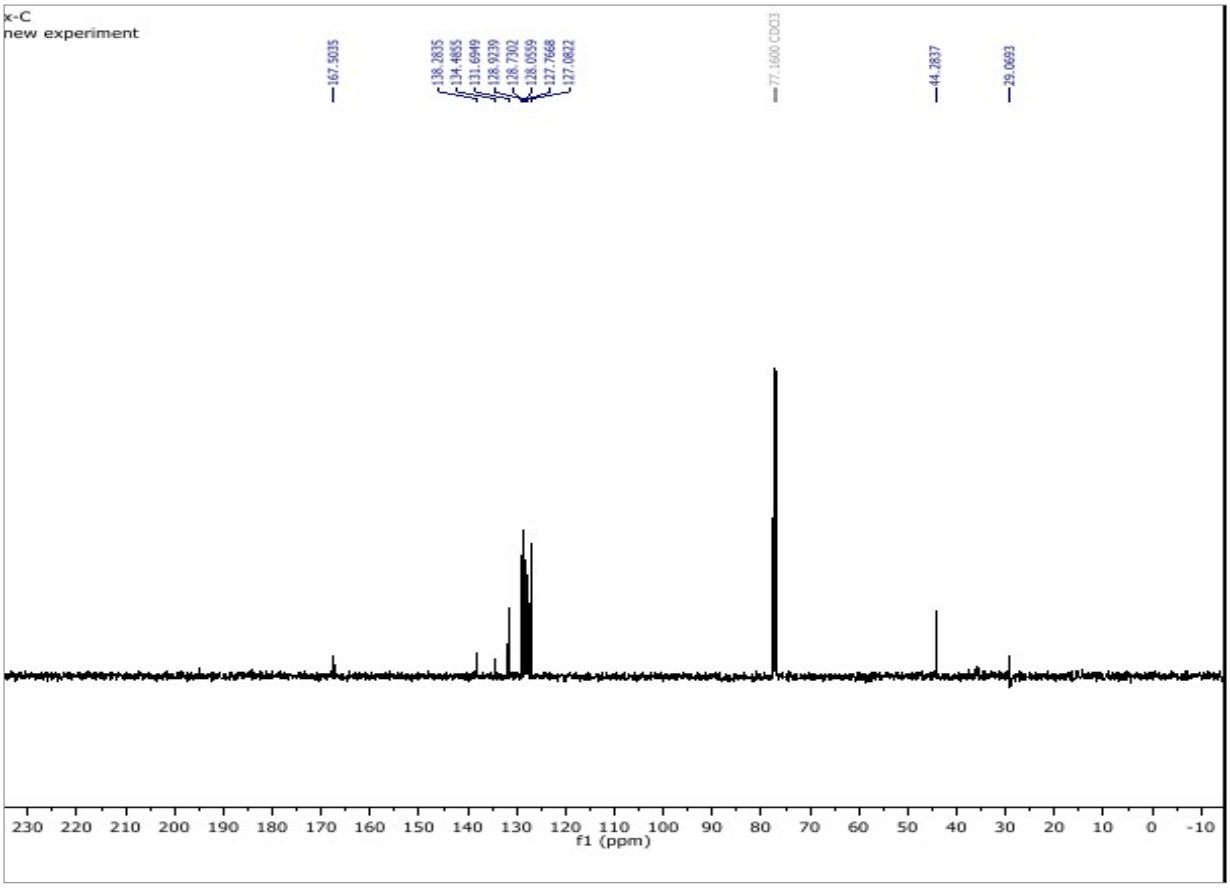

Figure S3. ^{13}C-NMR spectrum of N-benzylbenzamide

N-benzyl-4-nitrobenzamide:

White solid; yield: 74%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.67 (d, 2H, J = 6 Hz), δ 6.47 (bs, 1H), δ 7.36 (m, 5H), δ 7.96 (d, *J* = 9.0 Hz, 2H), δ 8.28 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7, 149.9, 140.3, 137.8, 129.3, 128.5, 128.3, 128.3, 124.2, 44.8.

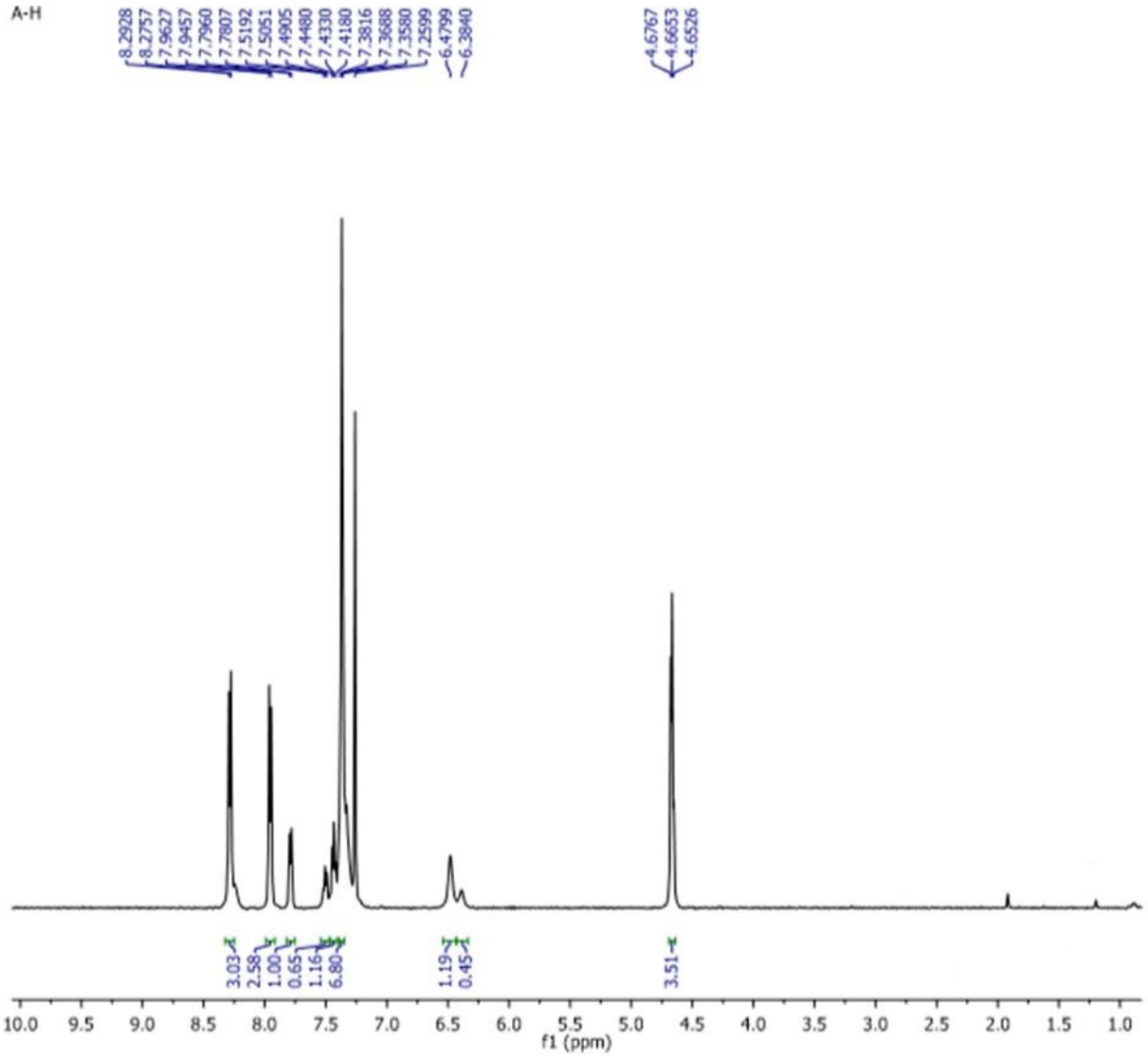

Figure S4. ^{1}H-NMR spectrum of N-benzyl-4-nitrobenzamide

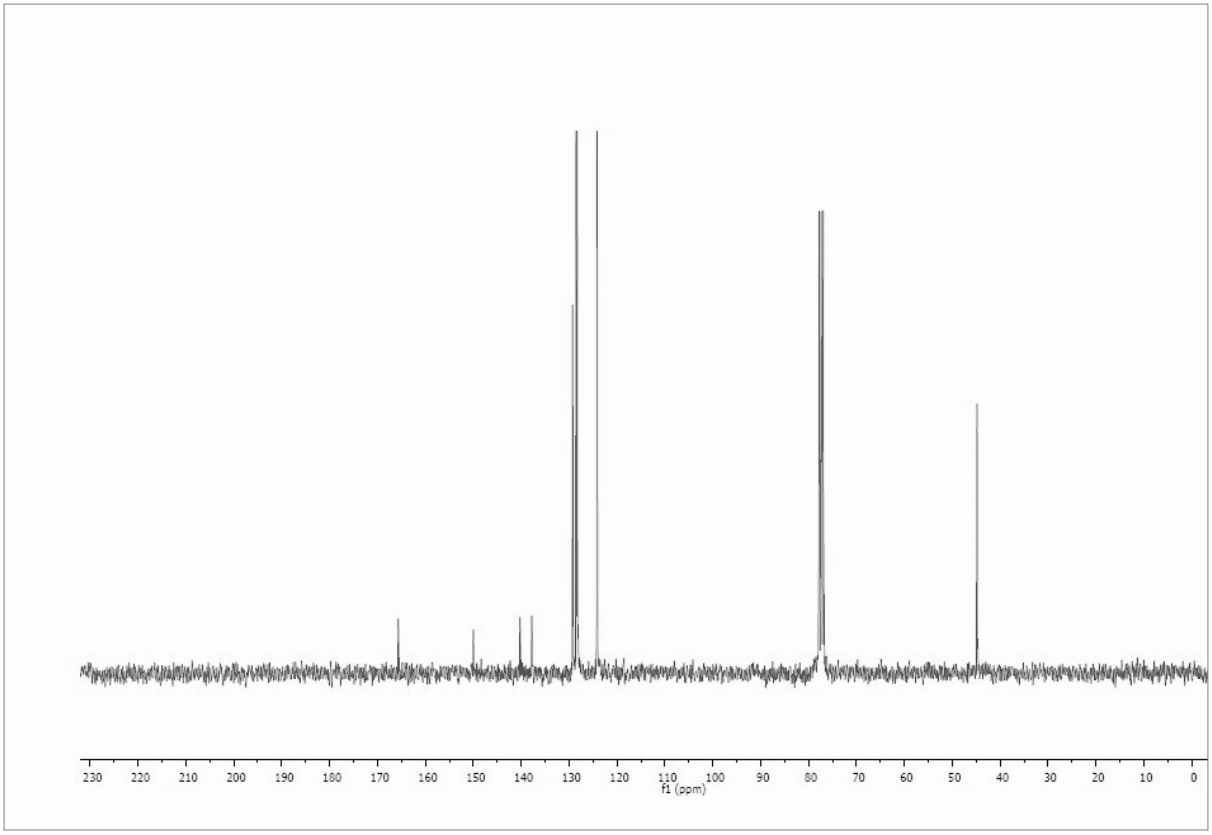

Figure S5. ^{13}C-NMR spectrum of N-benzyl-4-nitrobenzamide

***N*-benzyl-4-cyanobenzamide:**

White solid; yield: 72%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.65 (d, 2H, J = 5.6 Hz), δ 6.68 (bs, 1H), δ 7.34-7.36 (m, 2H, CH of Ar), δ 7.49-7.66 (m, 2H, CH of Ar), δ 7.71-7.87 (m, 2H, CH of Ar), δ 7.87-7.92 (m, 3H, CH of Ar).

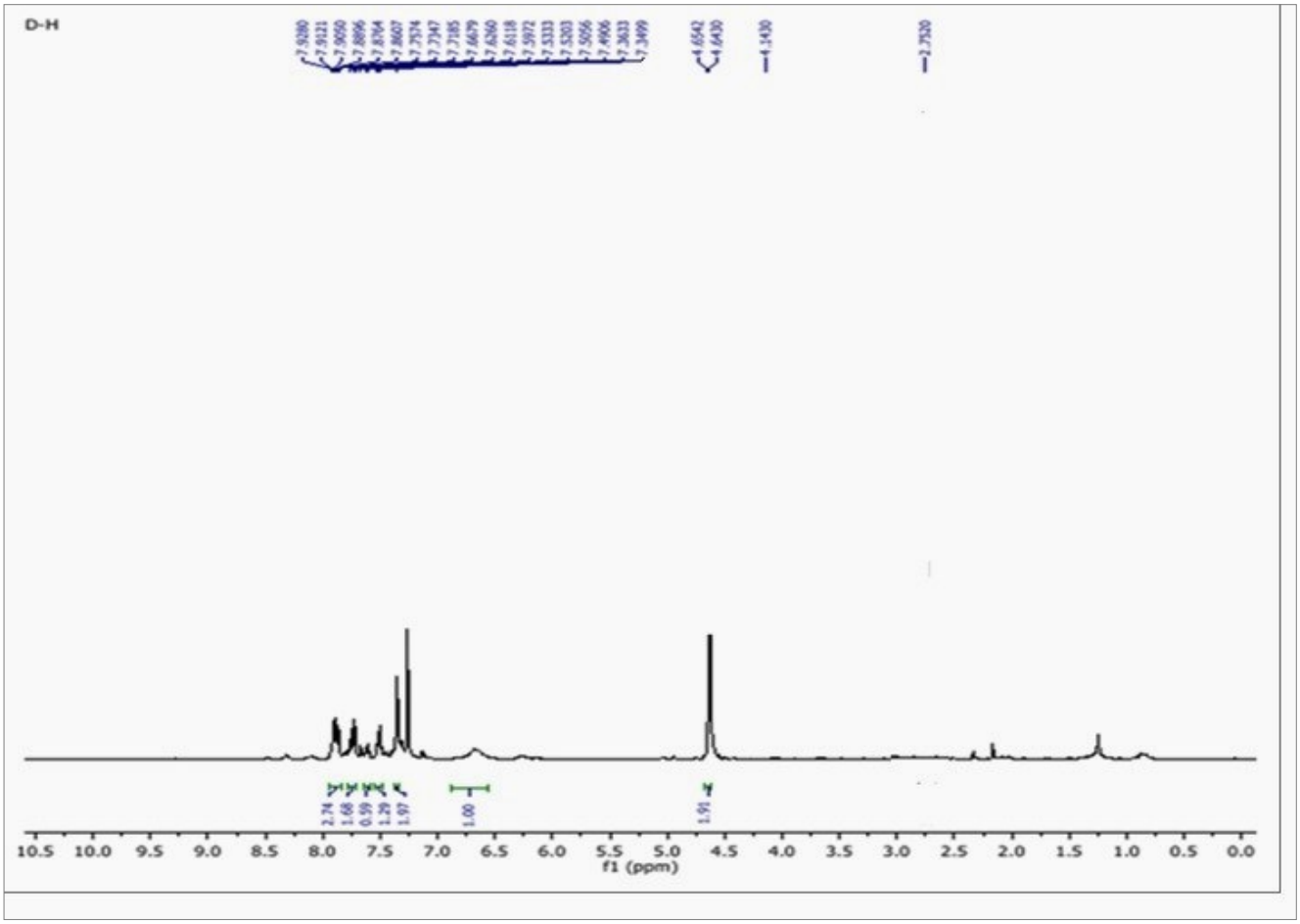

Figure S6. ^{1}H-NMR spectrum of N-benzyl-4-cyanobenzamide

N-benzyl-4-bromobenzamide:

Pale yellow solid; yield: 76%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.65 (d, 2H, J = 5.5 Hz), δ 6.42 (bs, 1H), δ 7.31-7.39 (m, 5H, CH of Ar), δ 7.57-7.59 (m, 2H, CH of Ar), δ 7.66-7.68 (m, 2H, CH of Ar).

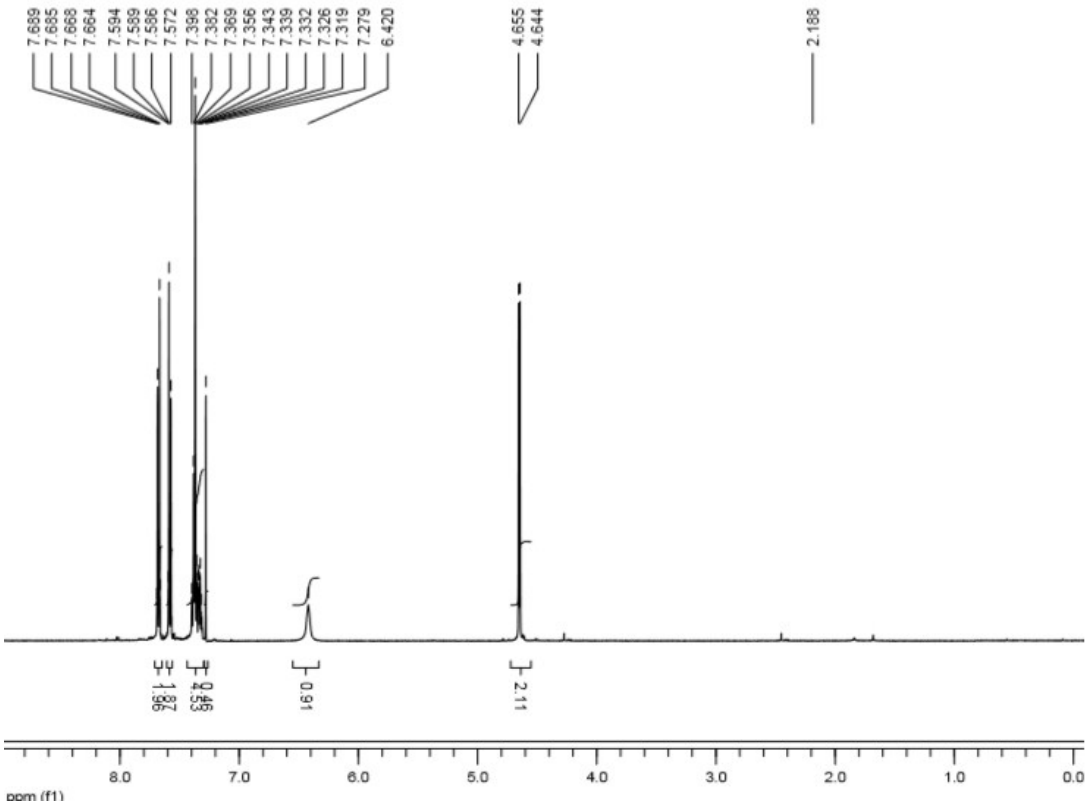

Figure S7. ^{1}H-NMR spectrum of N-benzyl-4-bromobenzamide

N-(2-chlorobenzyl)benzamide:

white solid; yield: 72%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.72 (d, 2H, J = 5.6 Hz), δ 6.66 (bs, 1H), δ 7.23-7.25 (m, 2H, CH of Ar), δ 7.37-7.50 (m, 5H, CH of Ar), δ 7.77-7.79 (m, 2H, CH of Ar).

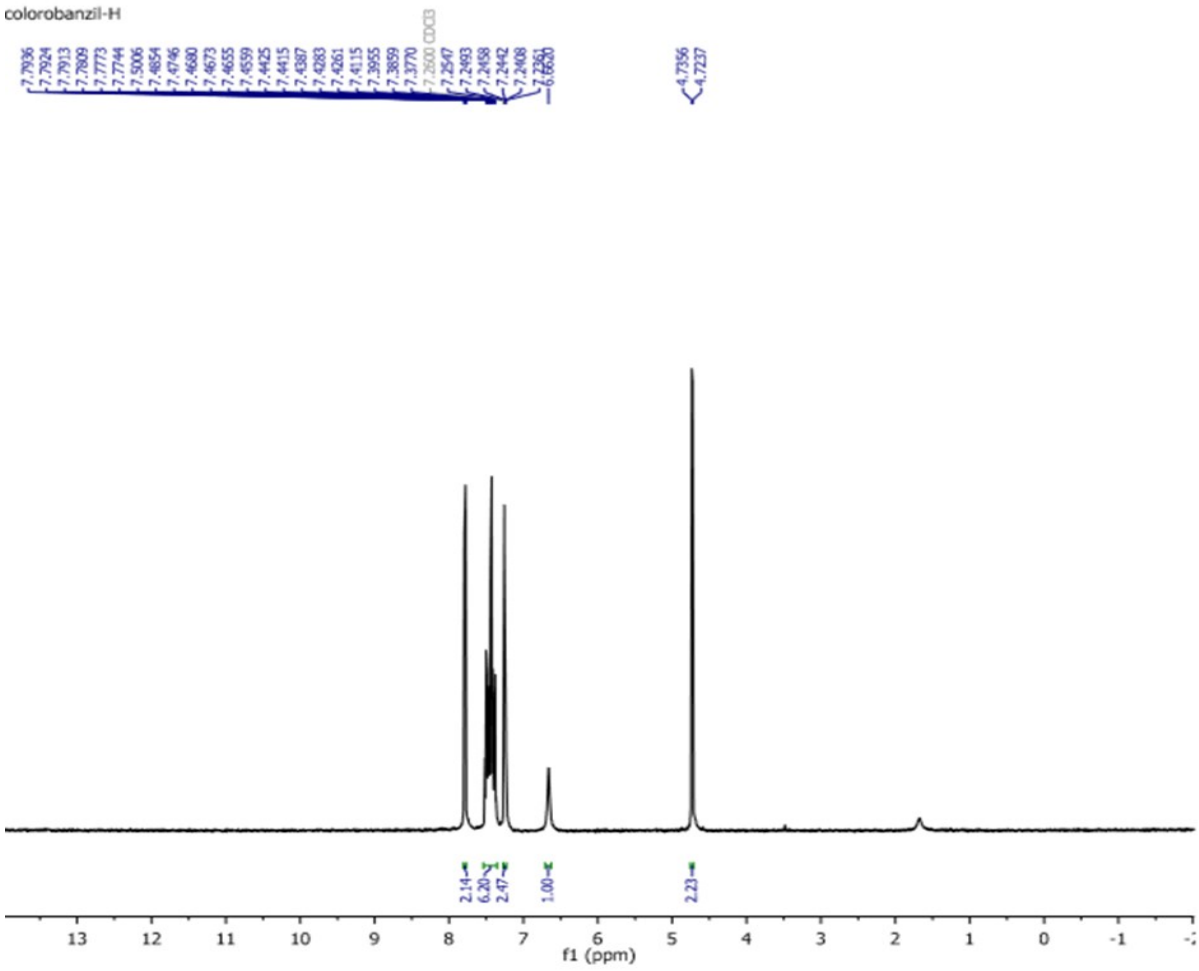

Figure S8. ^{1}H-NMR spectrum of N-(2-chlorobenzyl)benzamide

N-benzyl-4-methylbenzamide:

White solid; yield: 74%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3H, Me), 4.63 (d, 2H, J = 5.0 Hz), δ 6.49 (bs, 1H), δ 7.22 (d, ^{3}j= 8.0 Hz, 2H, CH of Ar), δ 7.27-7.36 (m, 5H, CH of Ar), δ 7.69 (d, ^{3}j= 8.0 Hz, 2H, CH of Ar).

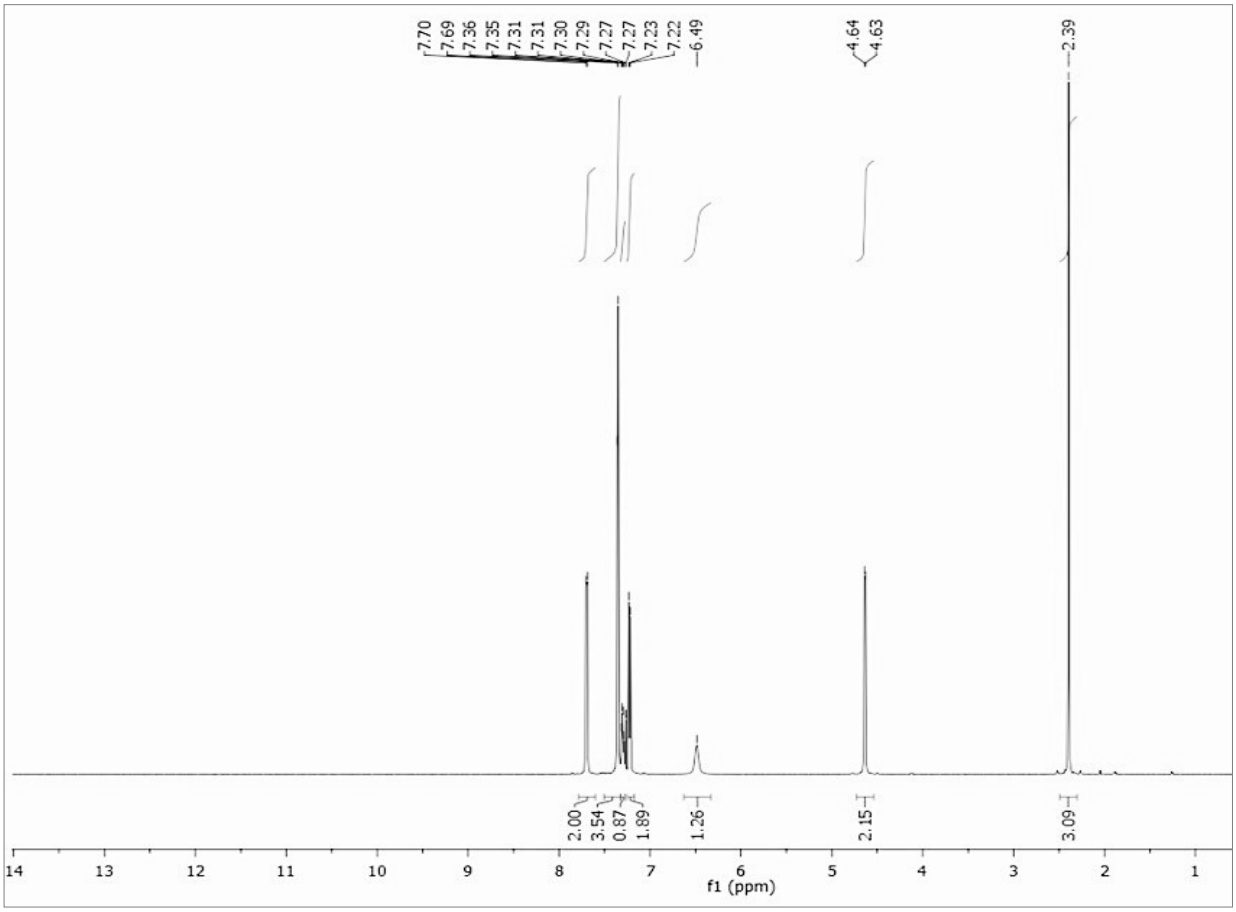

Figure S9. ^{1}H-NMR spectrum of N-benzyl-4-methylbenzamide

N-(2-chlorobenzyl)-4-methylbenzamide:

Pale yellow solid; yield: 69%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.42 (s, 3H, Me), 4.73 (d, 2H, ^{3}J = 5.9 Hz), δ 6.69 (t, 1H, ^{3}J = 5.9 Hz), δ 7.22-7.35 (m, 5H, CH of Ar), δ 7.27-7.40 (m, 2H, CH of Ar), δ 7.41-7.71 (m, 2H, CH of Ar).

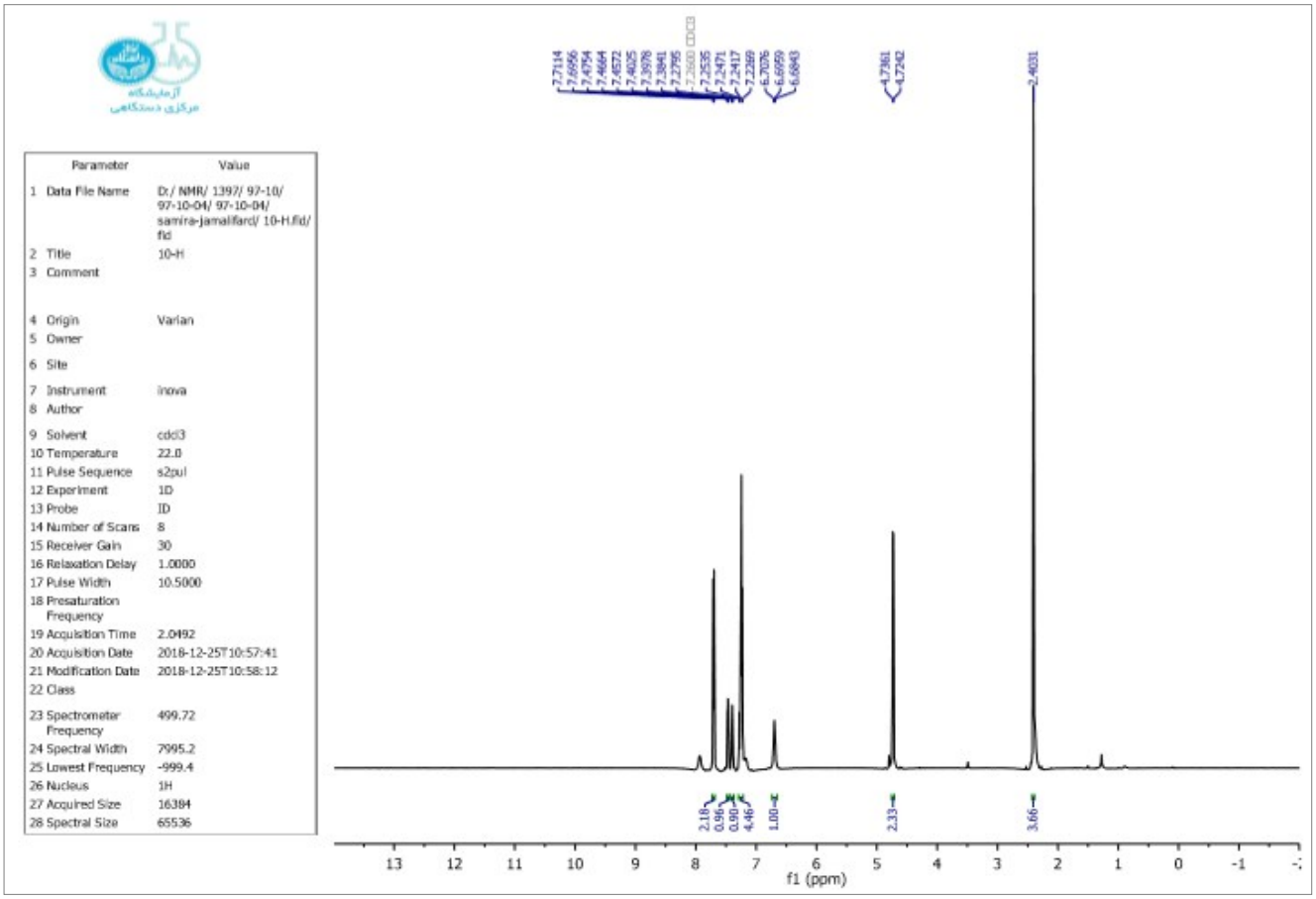

Figure S10. ^{1}H-NMR spectrum of N-(2-chlorobenzyl)-4-methylbenzamide

N-propylbenzamide:

White solid; yield: 70%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96 (t, 3H, ^{3}J = 7.4 Hz, Me), 1.60-1.65 (m, 2H, CH_2), 3.39-3.34 (m, 2H, CH_2), δ 6.20 (brs, 1H, NH), δ 7.42-7.47 (m, 3H, CH of Ar), δ 7.71-7.76 (m, 2H, CH of Ar).

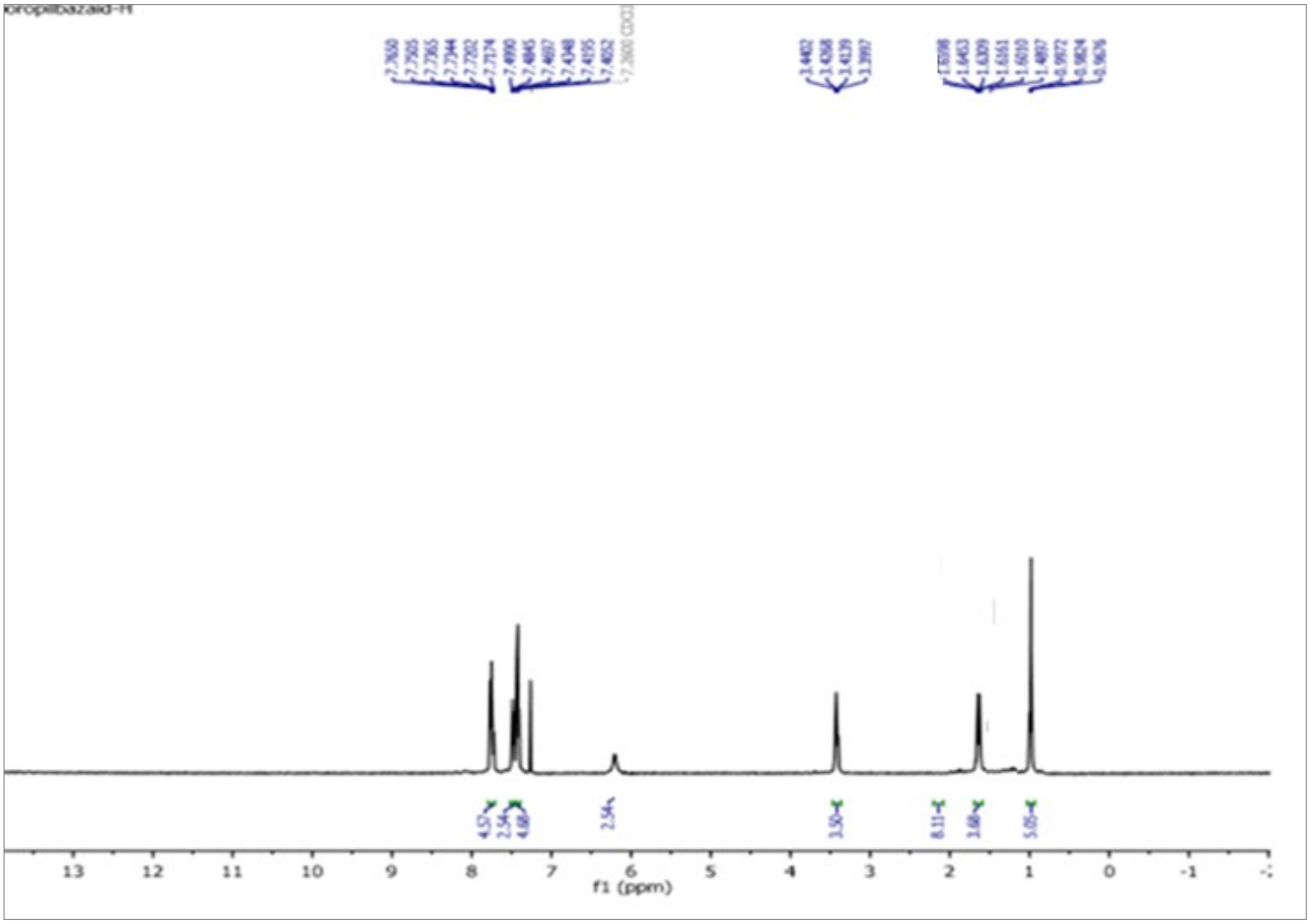

Figure S11. ^{1}H-NMR spectrum of N-propylbenzamide

4-bromo-N-propylbenzamide:

White solid; yield: 72%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.95-0.99 (m, 3H, Me), 1.61-1.66 (m, 2H, CH_2), 3.38-3.42 (m, 2H, CH_2), δ 6.10 (brs, 1H, NH), δ 7.53-7.63 (m, 4H, CH of Ar).

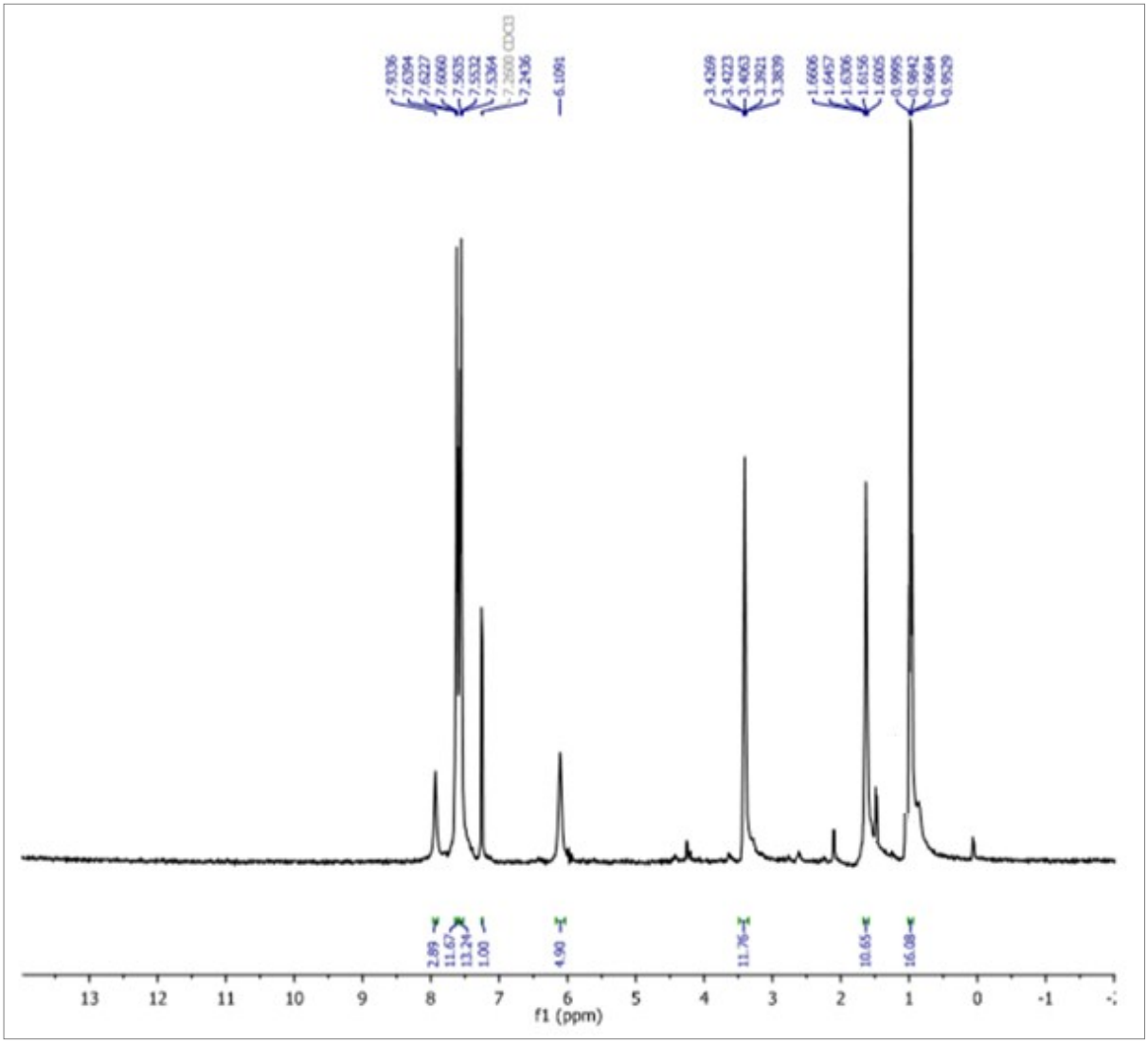

Figure S12. ^{1}H-NMR spectrum of 4-bromo-N-propylbenzamide

4-methyl-N-propylbenzamide:

White solid; yield: 68%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94-0.98 (m, 3H, Me), 1.61-1.66 (m, 2H, CH_2), 3.38-3.42 (m, 2H, CH_2), 6.20 (brs, 1H, NH), 7.16-7.22 (m, 2H, CH of Ar), 7.95-7.97 (m, 2H, CH of Ar).

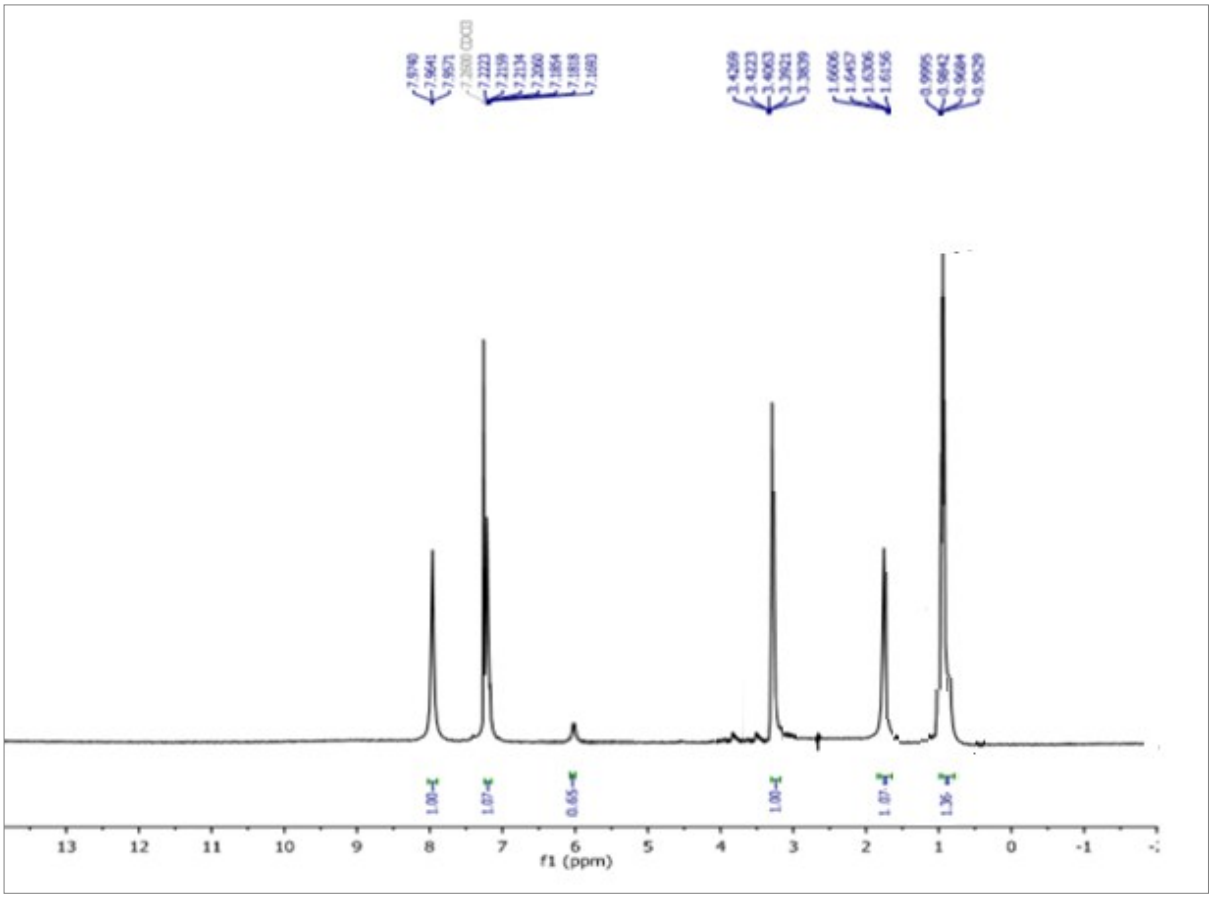

Figure S13. ^{1}H-NMR spectrum of 4-methyl-N-propylbenzamide