Supplementary Information (SI) for Materials Advances.

Efficient and selective *N*-benzylation of amines using Pd doped La-BDC MOF catalyst

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Experimental Details

1. General

All the amines used were of analytical grade Pd(NO_3)$_2$, *p*-phenylenediamine, aniline, *o*-toludine, *p*-toludine, *p*-anisidine, cyclohexylamine, *p*-chloro aniline, *p*-bromo aniline, benzylamine, *p*-hydroxy aniline, *p*-aminobenzoic acid, *p*-nitro aniline were used as received from Sigma Aldrich. Lanthanum nitrate, Benzenedicarboxylate, *N*,*N*-Dimethylformamide (DMF) and sodium borohydride (analytical grade) were purchased from Loba Chemicals. Ethanol was purchased from SD Fine Chemicals Limited, India. All the chemicals were >99% pure. Reaction analysis was performed on TLC grade-silica gel G254, and the spots were visualized under iodine chamber. Column chromatography technique was used to isolate pure methylated product over silica gel (60-120 mesh size) with hexane-ethyl acetate mixture as eluent. All glassware was washed with dilute HNO_3 acid and rinsed thoroughly with distilled water prior to use and dried.

2. Characterization Methods

FTIR spectra of Pd@La-BDC MOF, was determined by a Fourier Transform Infrared Spectroscope (FTIR Nicolet 5700, Thermo Corp.,). The powder X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (D5000, Siemens) using Cu Kα radiation ($\lambda = 0.15418$ nm). HR-TEM images of Pd@La-BDC was conducted using a JEOL JSM7500F HR-TEM at 5 kV accelerating voltage and at 30,000 times magnification. Samples prepared for FE-SEM were analysed by an EDS detector (Oxford Instruments software Aztec.) attachment for the JEOL JSM-7500F at 20 kV accelerating voltage. Reaction analysis was performed on TLC grade- silica gel G254, and the spots were visualized under iodine chamber. Column chromatography technique was utilized to isolate pure alkylated amines over silica gel (60-120 mesh size) with hexane-ethyl acetate mixture as eluent. Al-MOF was kept under vacuum at 150 ºC for 1h, prior to use. NMR spectra were recorded on Bruker Avance-II FTNMR spectrometer (500 MHz) using $CDCl_3$ and d6-DMSO, and chemical shifts were recorded relative to tetramethyl silane (TMS) as internal standard.

3. Representative procedure for La-BDC MOF synthesis

The solvothermal method has been employed to synthesize La-BDC MOF, similar to the one reported in literature [21]. In a 30 mL 1:1 water-DMF mixture, 10 mmol of each of the salt lanthanum nitrate and BDC were dissolved and the whole mixture was moved to a 150 mL teflon-lined autoclave and kept at 120 °C in a pre-heated oven for 24h. Upon allowing the contents were then allowed to cool to room temperature, the MOF precipitated out. The solid thus obtained was filtered and washed with distilled water. Before being used, the filtered solid was activated for 4 hours by placing it in a vacuum oven maintained at 100 °C.

4. Representative procedure for Pd supported La-BDC MOF synthesis

To prepare Pd loaded MOF, 5 mg of palladium nitrate was loaded into a pre-formed solution containing 100 mg of La-BDC MOF in 40 mL ethanol. The in-situ reduction of palladium ions was done by addition of 10% solution of sodium borohydride in water. The mixture was stirred continuously over magnetic stirrer for 1h for reduction to complete. The Pd loaded MOF thus obtained was filtered off from the solution and washed with 20 mL ethanol and 20 mL water. The isolated solid Pd@La-BDC MOF was dried in a vacuum oven at 100°C for 24 hours.

5. Representative procedure for catalytic *N*-benzylation reaction

The *N*-Benzylation reactions were carried out under autoclave conditions. The Teflon tube was charged with 10 mmol of amine, 50 mmol benzyl alcohol, 2-3 mL toluene, 2 mg KOH and 10 mol% of MOF catalyst. The Teflon tube was sealed with Teflon tape before being immersed into a preheated furnace. After commencement of time, the reaction mixture was cooled and the heterogenous catalyst was filtered off. The percentage yields of all the products were ascertained using GC analysis and adding n-hexadecane as the standard. After completion of the reaction, 20 mL of n-hexadecane was added to the reaction mixture, which was diluted with ethyl acetate and subjected to filtration over a plug of silica and then analysed with GC. All the products were obtained over silica gel column eluted with hexane-ethyl acetate mixture.

6. Kinetic Study for the *N*-benzylation of Aniline

The kinetic studies were carried out in a glass reactor equipped with magnetic stirrer. To establish the reaction kinetics, varying amounts of benzyl alcohol (0.1 mol-0.4 mol) and aniline (0.1 mol-0.4 mol) in toluene were made to react at 150 °C (while varying only one reactant at a time), with 10 mol% of MOF catalyst. Dodecane (0.2 mmol) was added as an external standard. At different intervals, about 50 µL aliquots were withdrawn. Each aliquot was diluted with ethyl acetate before being centrifuged, and the supernatant thus isolated was examined on a gas chromatogram.

Characterization Data:

(Compound 5a): *N*-Benzylaniline **(Figure S1, S2):** Yellow liquid; ^{1}H-NMR (500 MHz, $CDCl_3$): 3.99 (br s, 1H), 4.27 (s, 2H), 6.58-6.70 (m, 3H), 7.12-7.25 (m, 3H), 7.28-7.49 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 48.3, 117.6, 127.3, 127.6, 128.7, 129.0, 129.3, 129.8, 139.5.

(Compound 5b): *N*-Benzyl-*p*-toluidine **(Figure S3, S4):** Yellow liquid; ^{1}H-NMR (500 MHz, $CDCl_3$): 2.24 (s, 3H), 4.31 (s, 2H), 6.57-6.59 (m, 2H), 6.98-7.00 (m, 2H), 7.26-7.38 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): 20.4, 48.7, 113.1, 126.9, 127.1, 127.5, 128.6, 129.7, 139.5, 145.7.

(Compound 5d): *N*-Benzyl-*p*-anisidine **(Figure S5, S6):** Yellow liquid; ^{1}H-NMR (500 MHz, $CDCl_3$): 3.72 (s, 3H), 4.27 (s, 2H), 6.58-6.60 (m, 2H), 6.75-6.77 (m, 2H), 7.23-7.27 (m, 1H), 7.31-7.37 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 49.2, 55.8, 114.1, 114.9, 127.1, 127.5, 128.6, 139.7, 142.4, 152.2.

(Compound 5e): *N*-Benzyl-*p*-chloroaniline **(Figure S7, S8):** Yellow liquid; ^{1}H-NMR (500 MHz, $CDCl_3$): 4.09 (br s, 1H), 4.32 (s, 2H), 6.52-6.54 (m, 2H), 6.62-6.72 (m, 1H), 7.08-7.37 (m, 6H), 4.34 (t, 2H), 7.75-7.80 (m, 2H), 9.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 48.3, 117.6, 127.4, 127.5, 128.6, 128.7, 139.4, 148.1.

(Compound 5g): *N*-Benzyl-benzylamine **(Figure S9, S10):** Yellow liquid; ^{1}H-NMR (500 MHz, $CDCl_3$): 4.66 (s, 4H), 5.01 (br s, 1H), 7.39-7.49 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): 64.5, 127.2, 127.5, 128.5, 141.2.

(Compound 5h): *N*-benzyl indole **(Figure S11, S12):** Viscous yellow liquid; ^{1}H-NMR (500 MHz, $CDCl_3$): 4.28 (s, 2H), 6.89-7.79 (m, 11H); ^{13}C NMR (125 MHz, $CDCl_3$): 51.6, 126.2, 127.5, 128.0, 128.4, 128.8, 129.0, 129.3, 129.4, 131.4, 131.8, 133.1, 135.1.

(Compound 5i): *N*-benzyl methyl glycinate **(Figure S13, S14):** Viscous yellow liquid; ^{1}H-NMR (500 MHz, $CDCl_3$): 3.26 (s, 2H), 3.50 (s, 3H), 4.00 (br s, 1H) 4.27 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 41.2, 49.1, 54.7, 122.5, 123.1, 125.1, 128.7, 169.9.

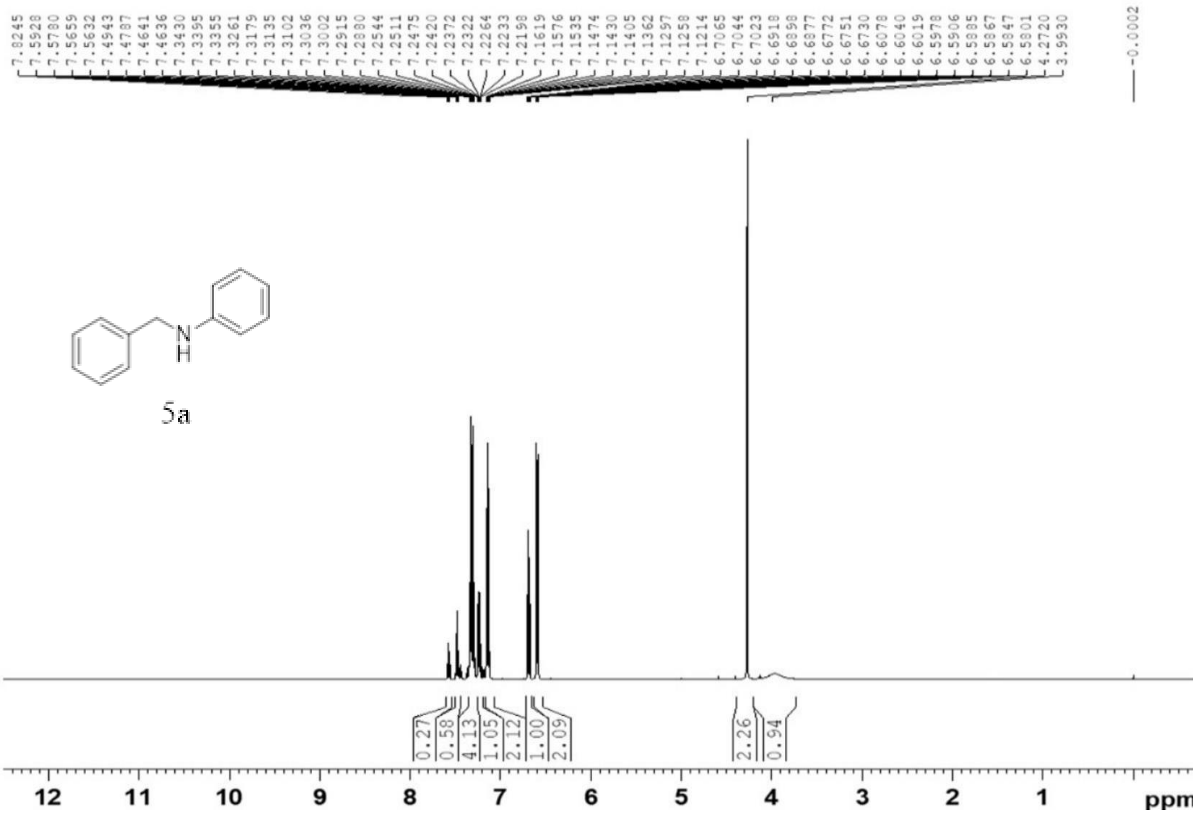

Figure S1. ^{1}H-NMR Spectra of *N*-Benzylaniline

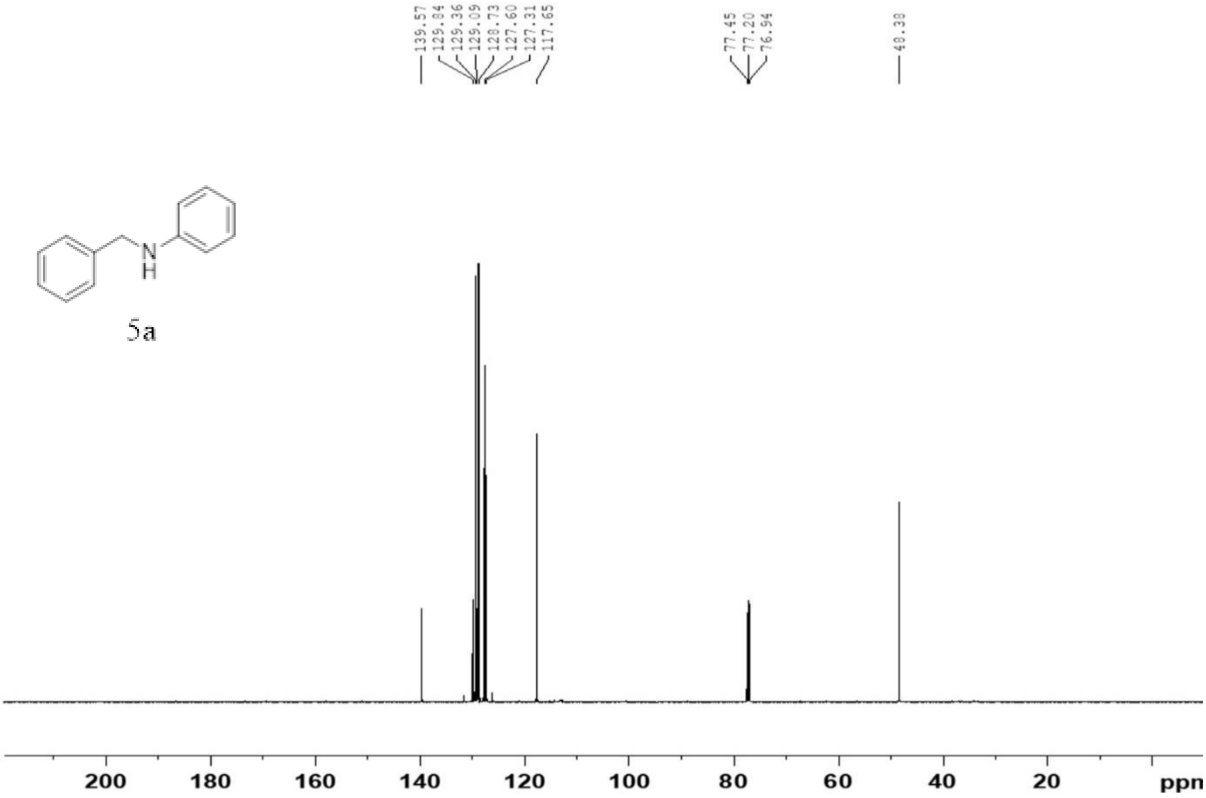

Figure S2. ^{13}C-NMR Spectra of *N*-Benzylaniline

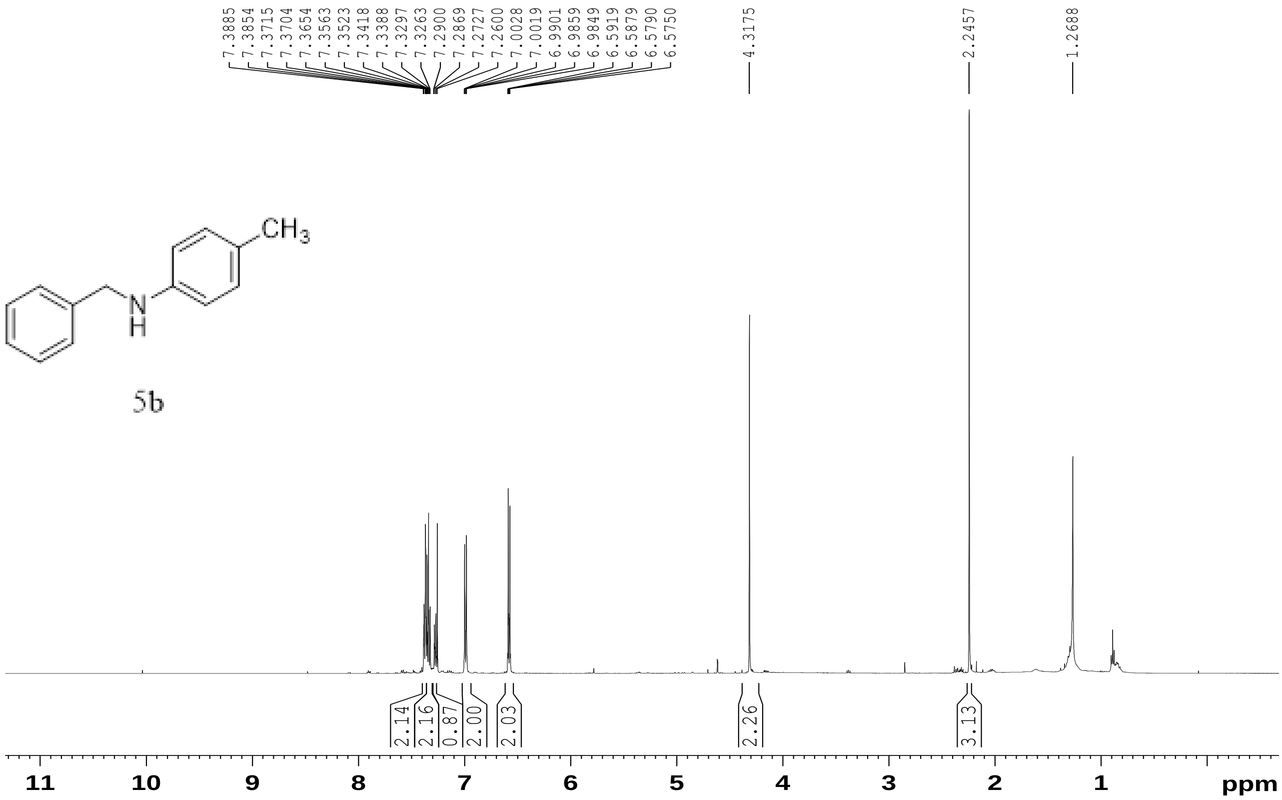

Figure S3. ^{1}H-NMR Spectra of *N*-Benzyl-*p*-toluidine

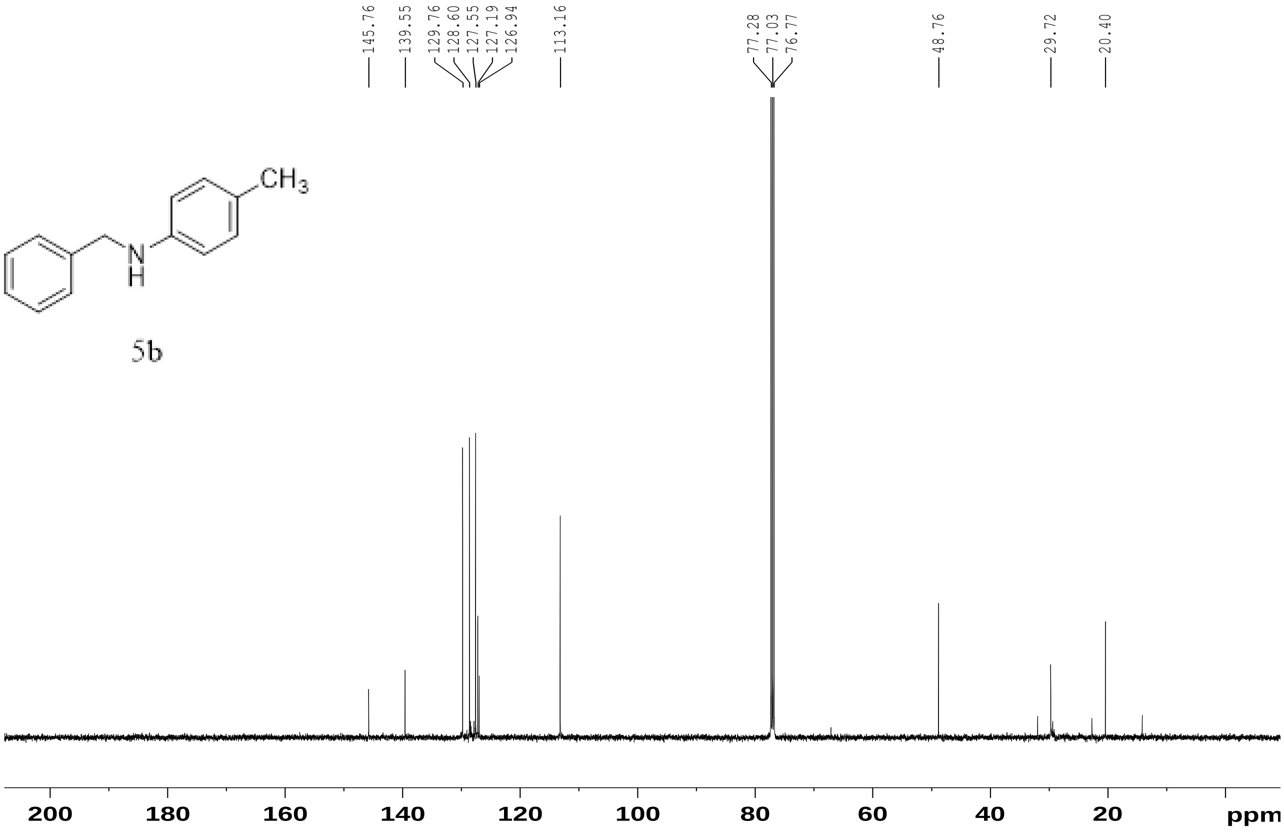

Figure S4. ^{13}C-NMR Spectra of *N*-Benzyl-*p*-toluidine

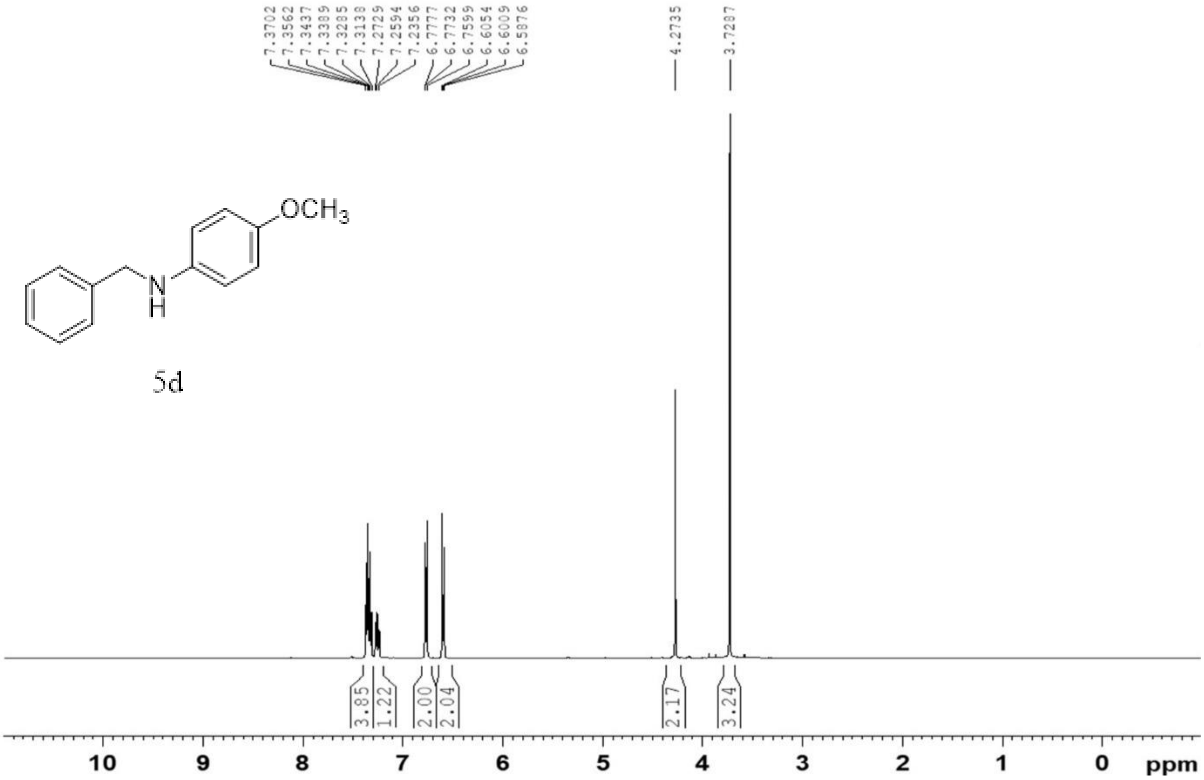

Figure S5. ^{1}H-NMR Spectra of *N*-Benzyl-*p*-Anisidine

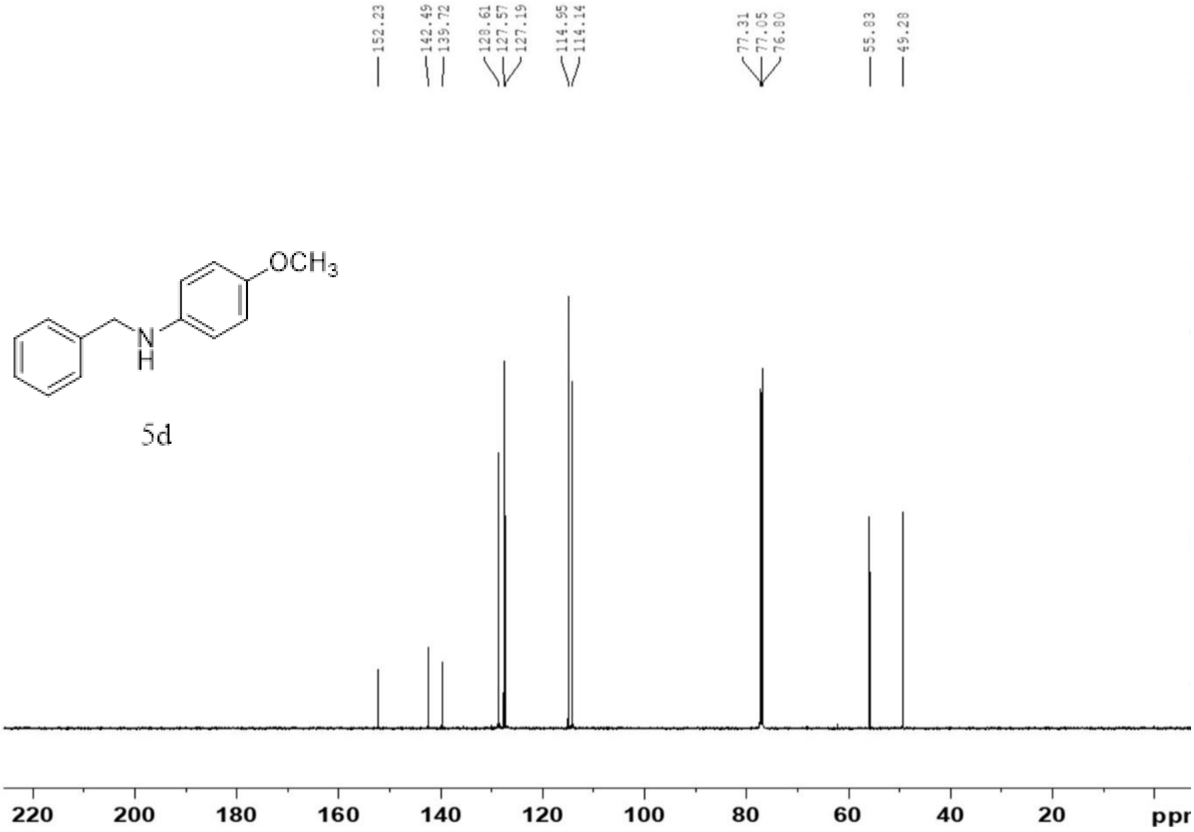

Figure S6. ^{13}C-NMR Spectra of *N*-Benzyl-*p*-Anisidine

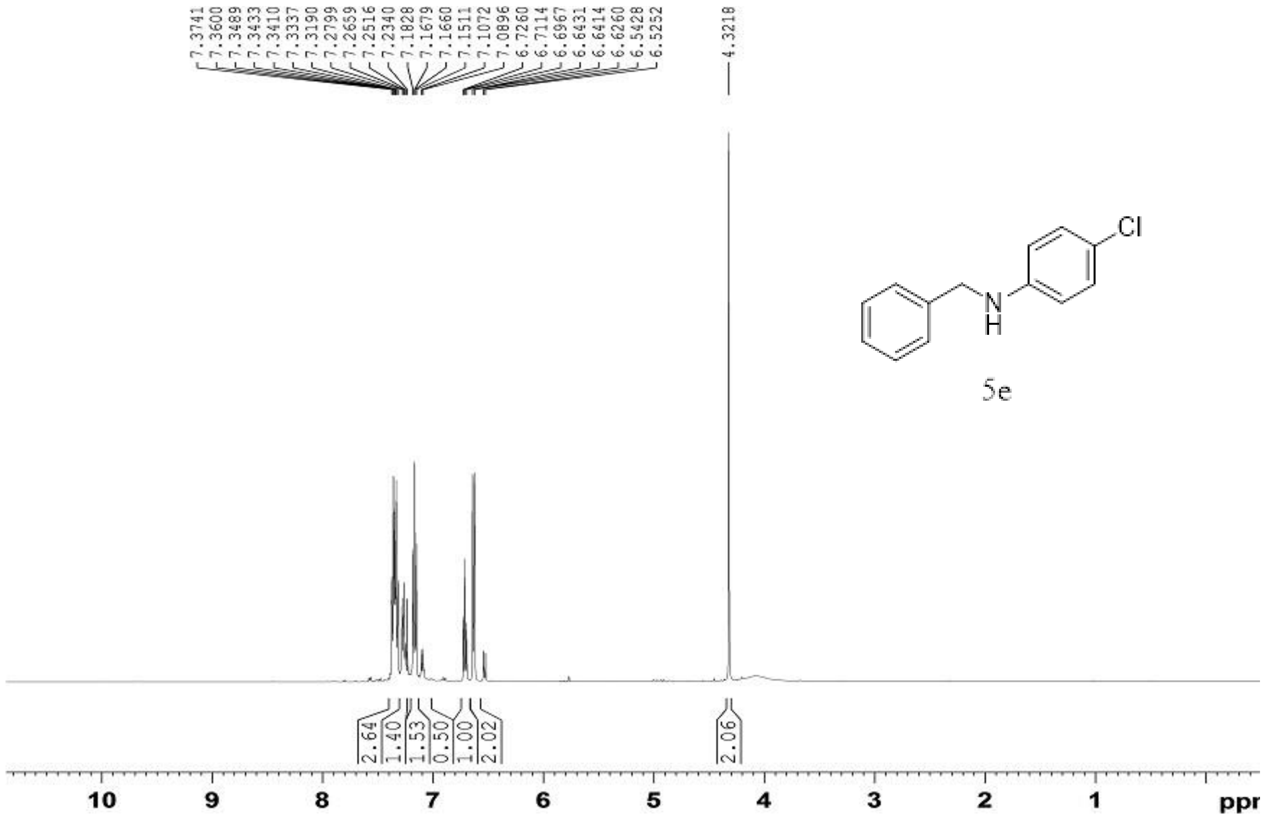

Figure S7. ^{1}H-NMR Spectra of *N*-Benzyl-*p*-chloroaniline

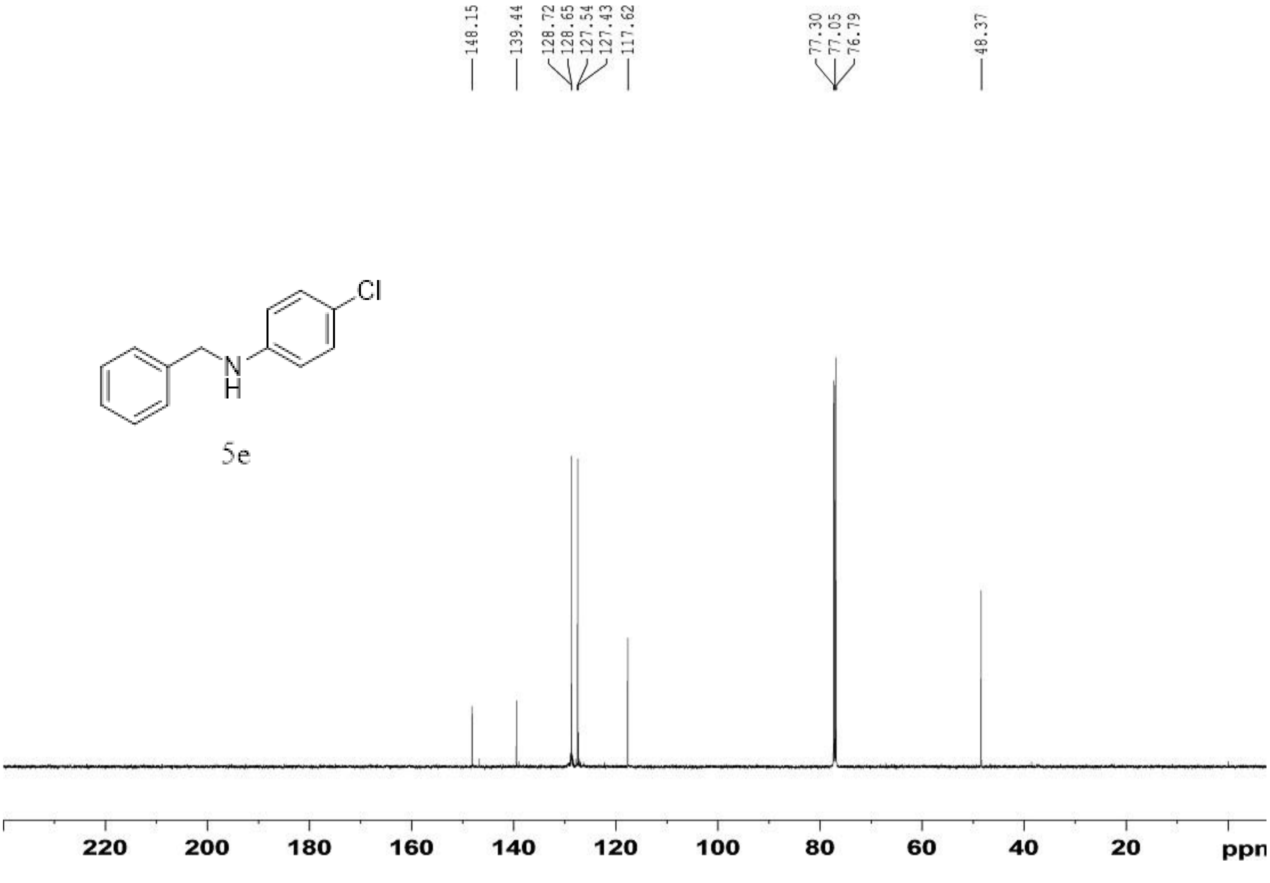

Figure S8. ^{13}C-NMR Spectra of *N*-Benzyl-*p*-chloroaniline

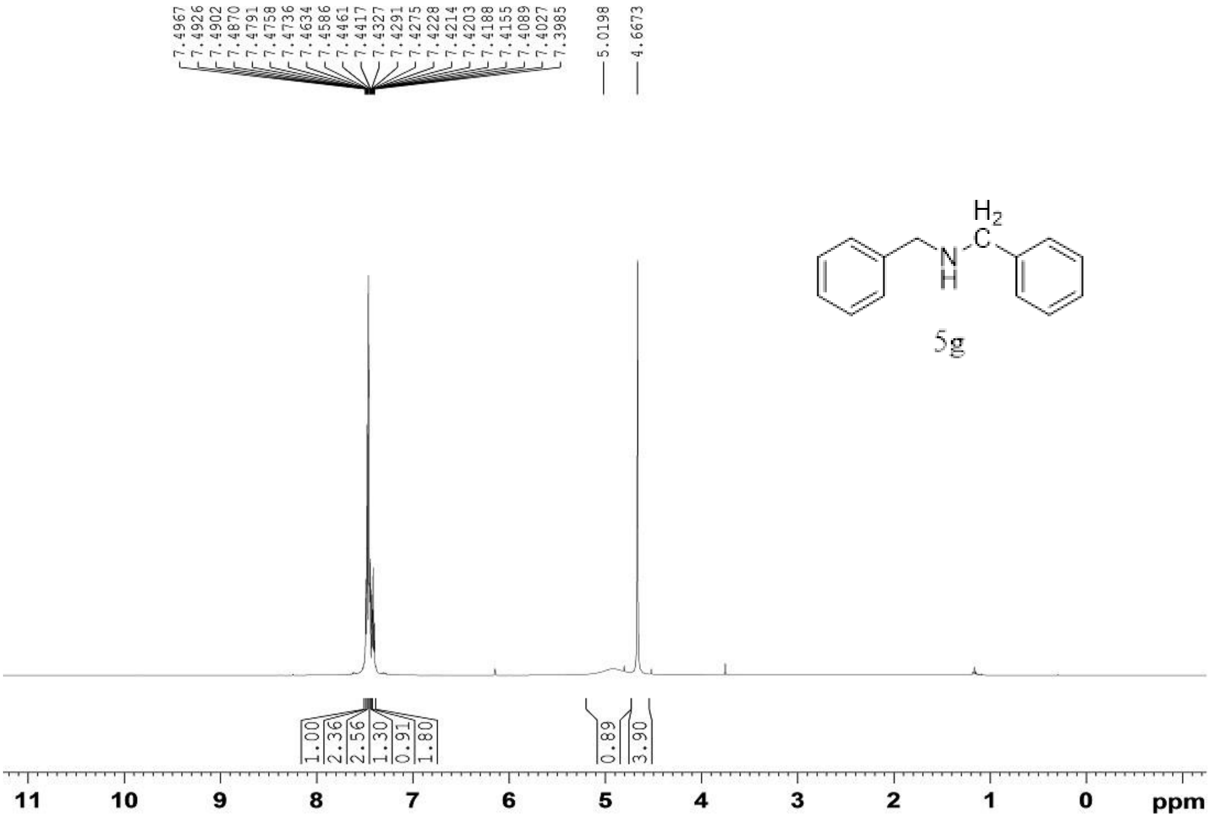

Figure S9. ^{1}H-NMR Spectra of *N*-Benzyl-benzylamine

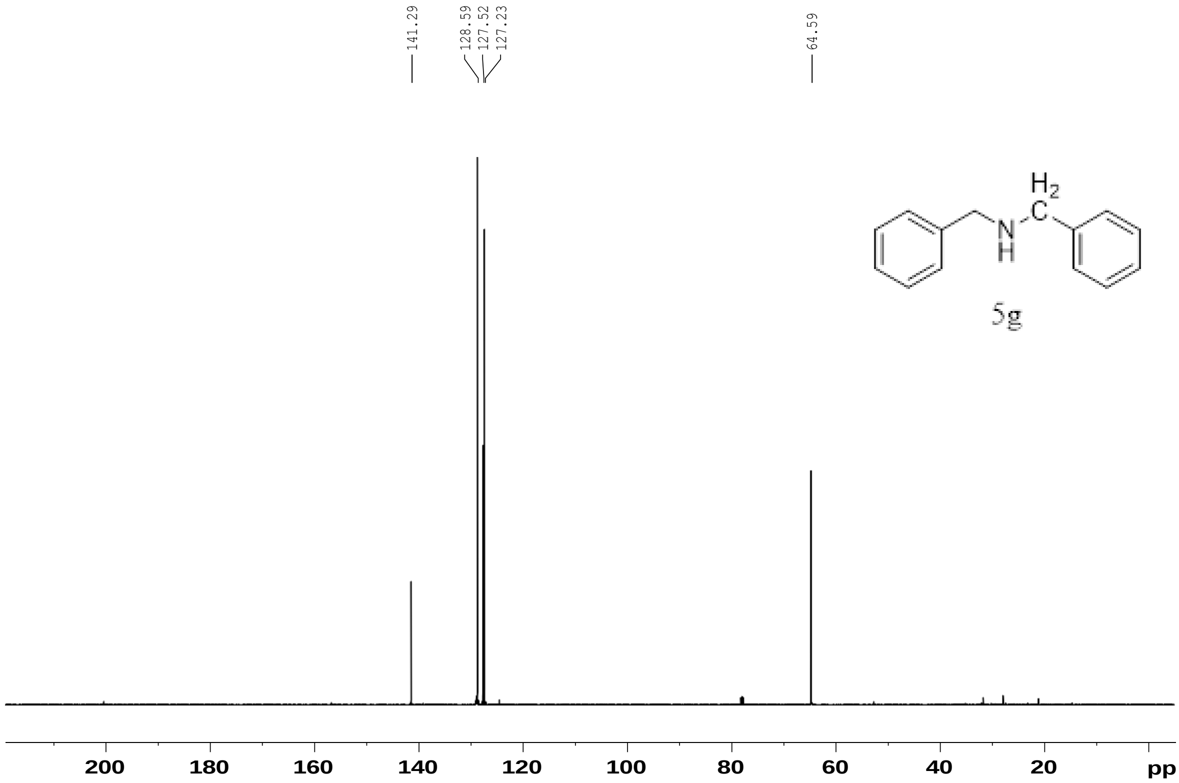

Figure S10. ^{13}C-NMR Spectra of *N*-Benzyl-benzylamine

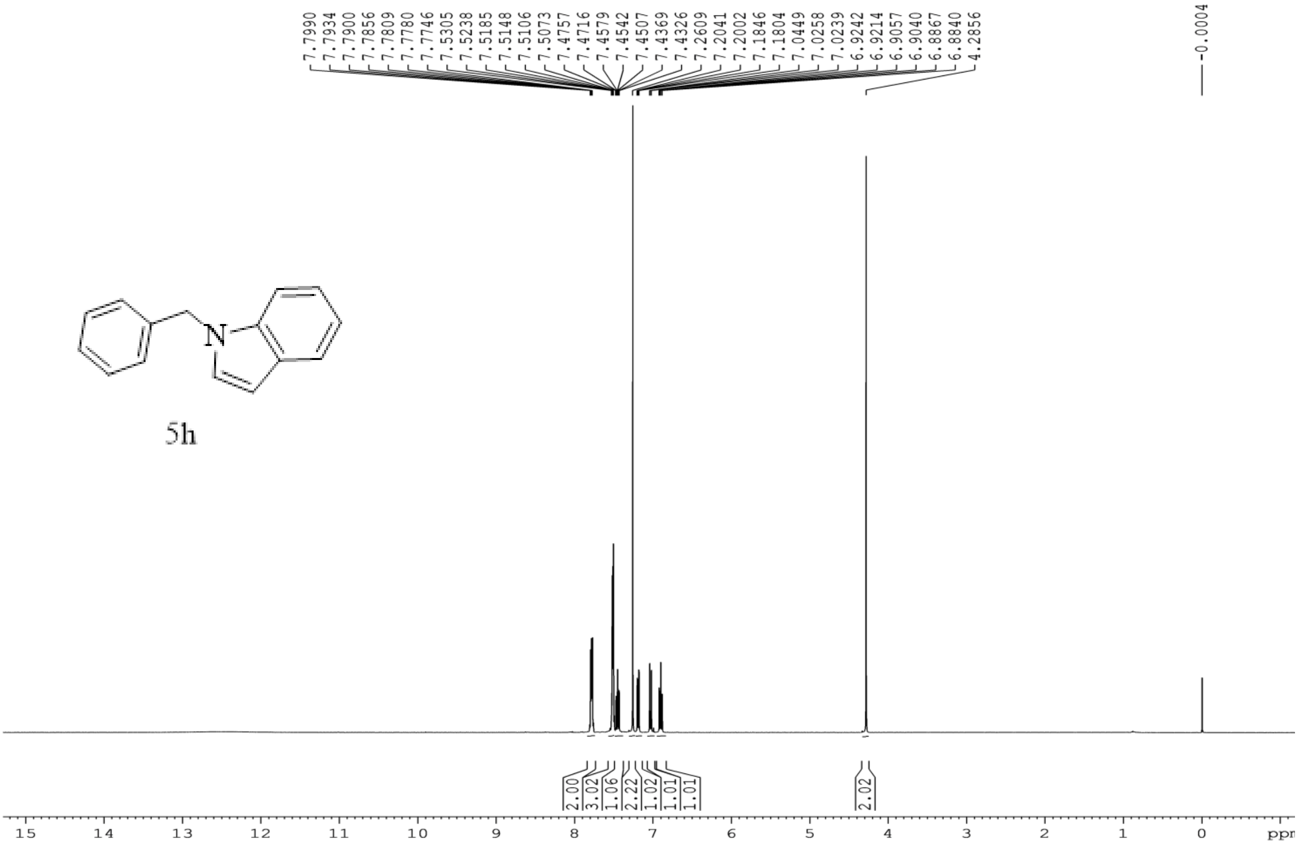

Figure S11. ^{1}H-NMR spectra of *N*-Benzyl indole

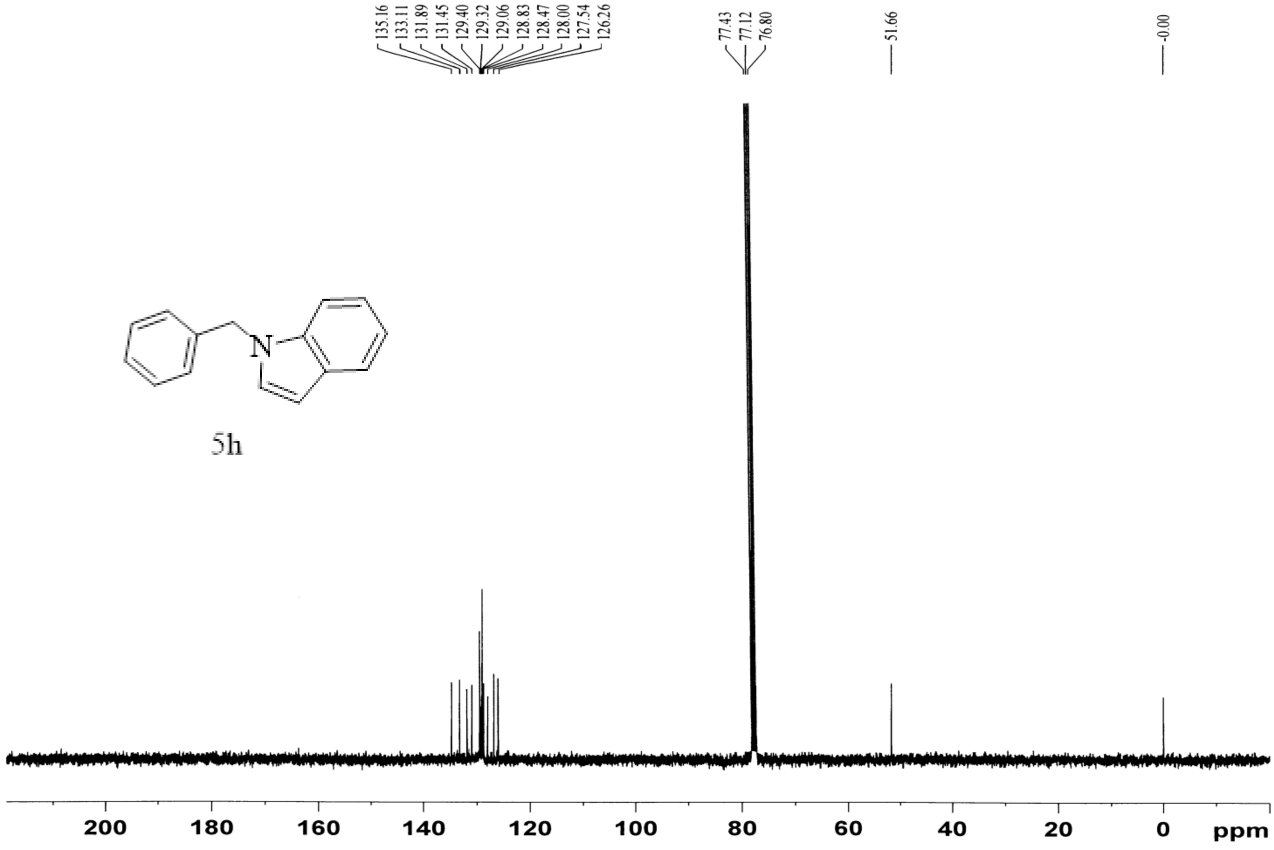

Figure S12. ^{13}C-NMR spectra of *N*-Benzyl indole

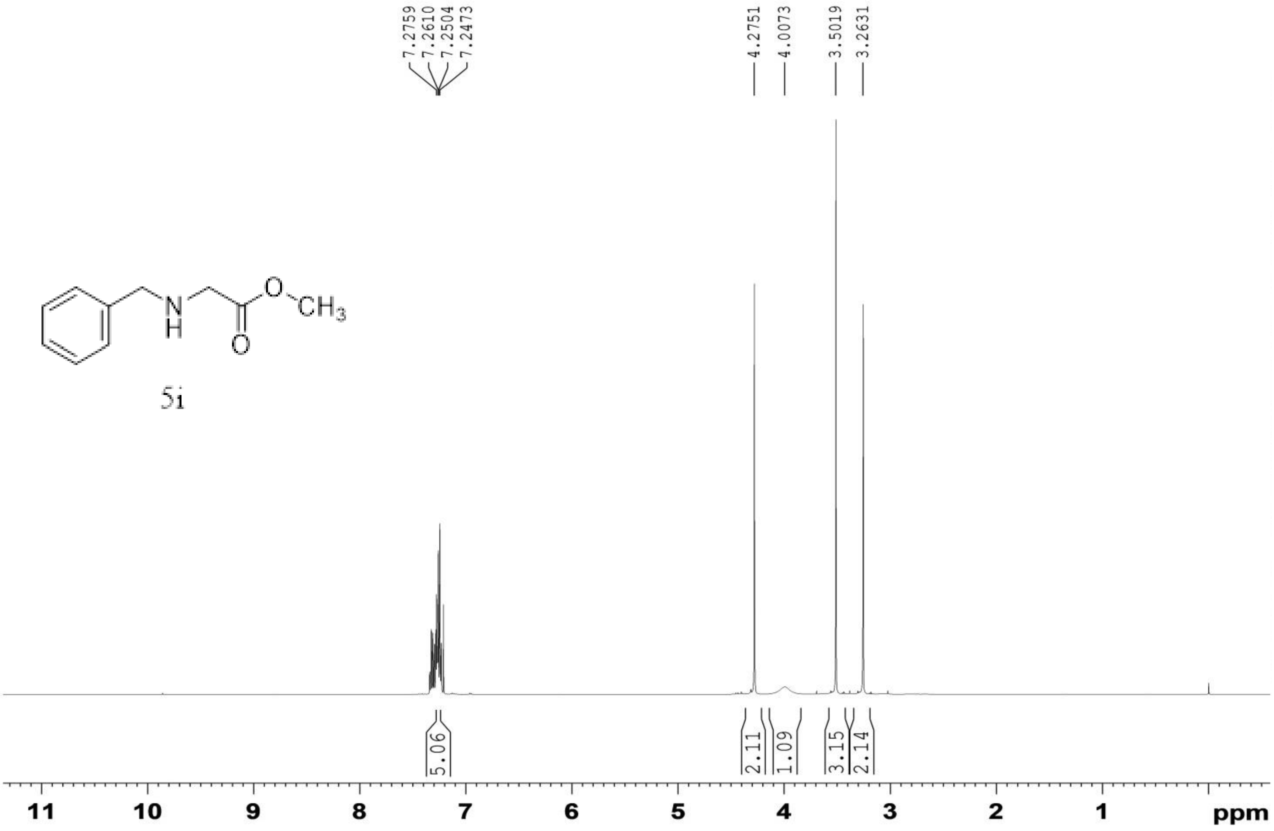

Figure S13. ^{1}H-NMR spectra of *N*-Benzyl methyl glycinate

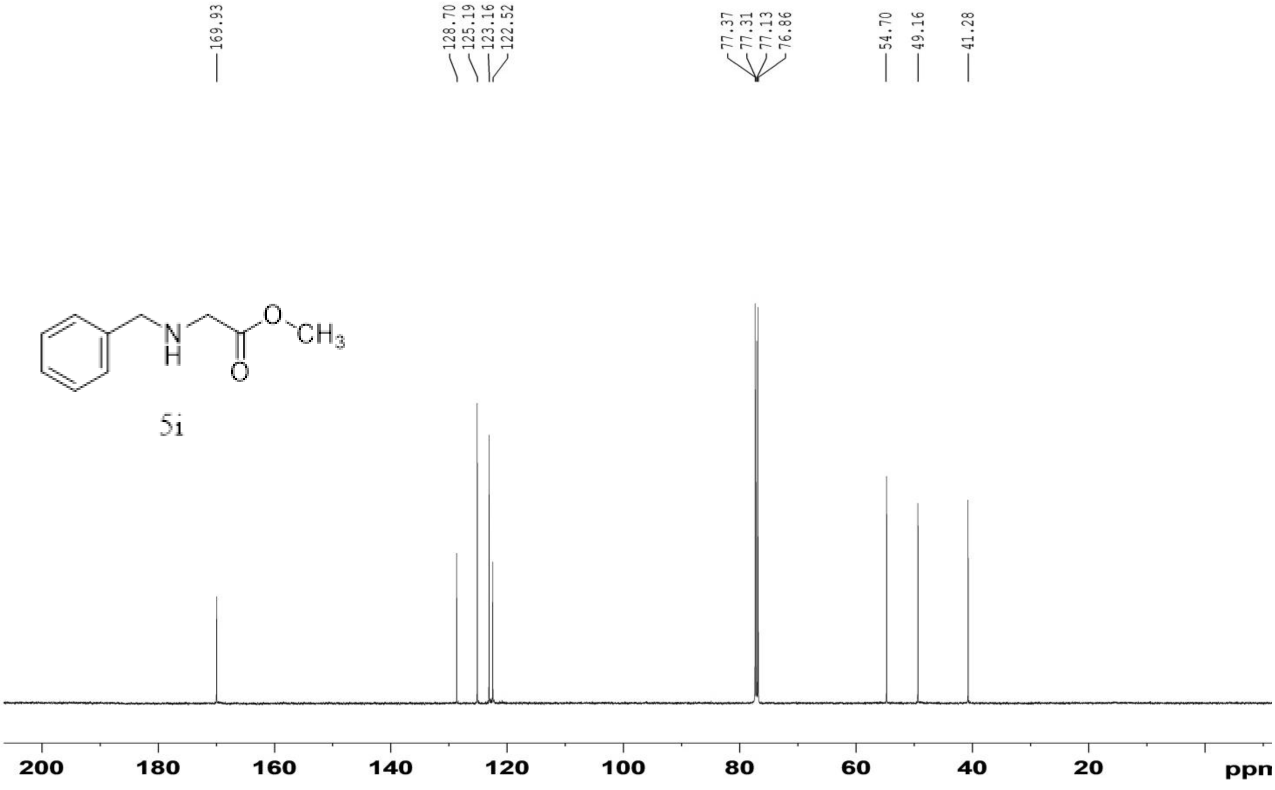

Figure S14. ^{13}C-NMR spectra of *N*-Benzyl methyl glycinate