Supplementary Information

Biorenewable carbon-supported Ru catalyst for *N*-Alkylation of Amines with Alcohols and Selective Hydrogenation of Nitroarenes

Vishakha Goyal,[a, b] Naina Sarki,[a, b] Mukesh Kumar Poddar,[a] Deependra Tripathi,[a] Anjan Ray,[a, b] and Kishore Natte*[a, b]

[a]Chemical and Material Sciences Division, Light Stock Processing Division, Analytical Sciences Division, CSIR-Indian Institute of Petroleum (CSIR-IIP), Haridwar Road, Mohkampur, Dehradun 248005, India

[b]Academy of Scientific and Innovative Research (AcSIR), CSIR-HRDC Campus, Joggers Road, Kamla Nehru Nagar, Ghaziabad, Uttar Pradesh 201 002, India

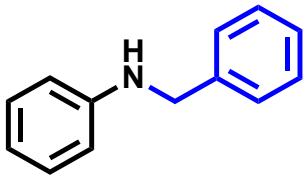
*Corresponding author: kishore.natte@iip.res.in or kishorenatte@gmail.com

Section S1: General Considerations.

NMR spectra obtained at 25 °C on a Bruker AVANCE III 500 MHz spectrometer using $CDCl_3$ or DMSO-d^6 as solvent. Gas chromatography mass spectrometry (GC-MS) analysis was performed using 5977A MSD attached to a 7890B, an Agilent GC system equipped with a 30 m × 0.32 mm id and 0.25 μm mid-polarity capillary column (DB35MS, 35% phenyl/ 65% dimethylpolysiloxane). Transmission electron microscopy (TEM) analysis performed on a JEM 2100 (JEOL, Japan) microscope and samples were deposited on a Lacey carbon formvar Cu grid upon dispersing in ethanol. X-Ray Diffraction (XRD) patterns of powdered samples were recorded on *PROTO AXRD benchtop X-Ray Diffractometer* at 40 kV and 30 mA using Ni *β*-filtered Cu K*α* radiation (l=1.5406 Å) over a 2 theta range of 10-80 degree. X-ray photoelectron spectroscopy analysis of catalyst was carried out using ESCA+, omicron nanotechnology, Oxford Instrument Germany equipped with monochromator Aluminum Source (Al ka radiation *hv*=1486.7ev). The binding energy measurements corrected with reference to the C1s core carbon (284.6ev). Raman Spectra of catalysts obtained on HorbiaJobinYvon Lab Ram HR Evolution Spectrometer equipped with CCD (charged coupled device) detector using an excitation laser wavelength of 633 nm.

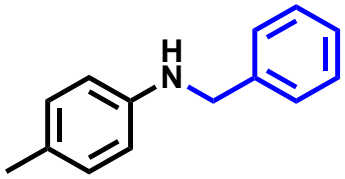
Section S2. ^{1}H and ^{13}C spectral data of *N*-alkylamines and anilines

N-benzylaniline



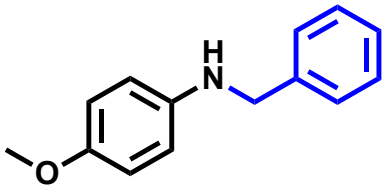
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 5H), 7.17 (m, 2H), 6.70 (t, *J* = 7.3 Hz, 2H), 6.62 (d, *J* = 8.1 Hz, 1H), 4.30 (s, 2H), 3.99 (s, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.21, 139.50, 129.34, 128.71, 127.58, 127.30, 117.62, 112.90, 48.36.

N-benzyl-4-methylaniline



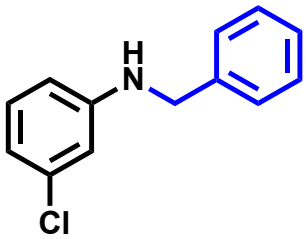
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.15 (m, 5H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.47 (d, *J* = 8.2 Hz, 2H), 4.21 (s, 2H), 2.15 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.84, 138.58, 128.69, 127.54, 126.44, 112.28, 47.57, 19.16.

N-benzyl-4-methoxyaniline



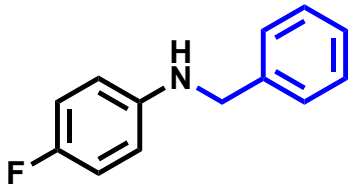
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4H), 7.26 (m, 1H), 6.81 – 6.70 (m, 2H), 6.64 – 6.54 (m, 2H), 4.28 (s, 2H), 3.73 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.21, 142.47, 139.70, 128.62, 127.58, 114.93, 114.14, 55.83, 49.27, 29.74.

N-benzyl-3-chloroaniline



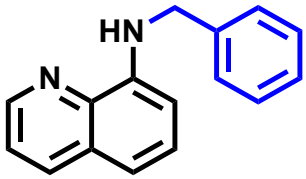
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 5H), 7.24 – 7.19 (m, 1H), 7.13 – 7.06 (t, 1H), 6.99 (t, 1H), 6.65 – 6.54 (m, 2H), 6.41 (d, 2H), 4.25 (s, 1H), 4.23 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.15, 137.68, 133.96, 129.16, 127.69, 126.40, 116.35, 111.78, 111.41, 47.03.

N-benzyl-4-fluoroaniline



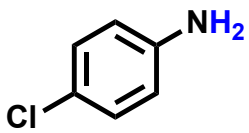
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.18 (m, 5H), 6.92 – 6.82 (m, 2H), 6.67 – 6.50 (m, 2H), 4.30 (s, 2H), 3.92 (s, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.83, 154.96, 144.50, 139.25, 128.70, 127.52, 127.34, 115.79, 115.61, 113.68, 48.94.

N-benzylquinolin-8-amine



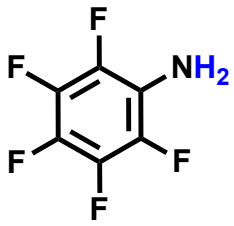
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 – 8.68 (m, 1H), 8.05 (m, 1H), 7.44 (m, 2H), 7.37 – 7.24 (m, 5H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.62 (m, 2H), 4.55 (s, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.96, 144.59, 139.25, 138.24, 136.07, 128.65, 127.79, 127.45, 127.16, 121.45, 114.18, 105.17, 47.72, 29.75.

4-chloroaniline



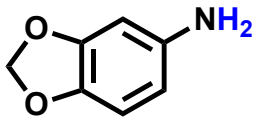
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 2), 6.60 (d, *J* = 5.8 Hz, 2H), 3.65 (s, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.96, 129.13, 123.16, 116.25.

Pentafluoroaniline



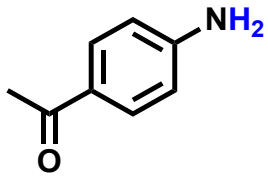
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.04 – 3.54 (s, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 139.09 (s), 137.59 (s), 137.05 (s), 135.82 (s), 134.30 (s), 132.40 (s), 121.88 (s).

Benzo[d][1,3]dioxol-5-amine



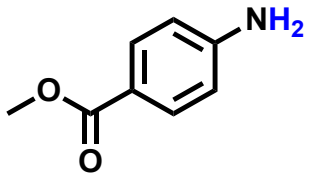
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (d, *J* = 8.2 Hz, 1H), 6.29 (d, *J* = 4.7 Hz, 1H), 6.13 (m, 1H), 5.86 (s, *J* = 5.6 Hz, 2H), 3.39 (s, *J* = 130.6 Hz, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.21, 141.40, 140.37, 108.59, 106.89, 100.68, 98.09.

1-(4-Aminophenyl)ethanone



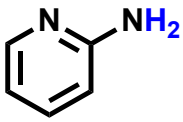
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 4.20 (s, 2H), 2.50 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 196.62, 151.26, 130.84, 127.76, 113.72, 83.56, 26.13.

Methyl 4-aminobenzoate



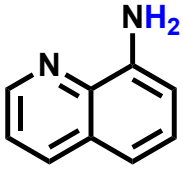
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 4.10 (s, 2H), 3.85 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.24, 150.92, 131.62, 119.62, 113.80, 51.65.

2-Aminopyridine



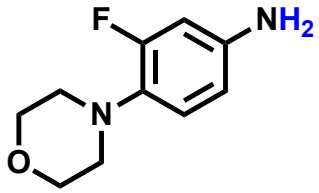
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 4.4 Hz, 1H), 7.45 – 7.37 (m, 1H), 6.68 – 6.59 (m, 1H), 6.48 (d, *J* = 8.3 Hz, 1H), 4.83 – 4.48 (s, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.57, 151.33, 148.07, 137.73, 113.89, 108.63, 22.28.

Quinolin-8-amine



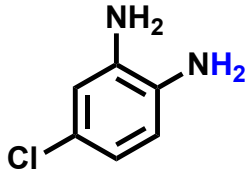
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (m, 1H), 8.07 (m, 1H), 7.44 – 6.89 (m, 4H), 4.99 (s, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.47, 143.95, 136.02, 128.86, 127.39, 121.37, 116.08, 110.07.

3-Fluoro-4-morpholinoaniline



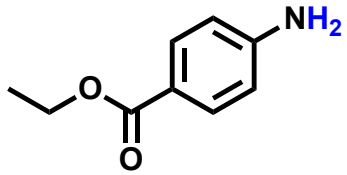
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.79 (t, *J* = 8.9 Hz, 1H), 6.42 (ddd, *J* = 8.6, 8.1, 1.6 Hz, 2H), 3.93 – 3.79 (m, 4H), 3.06 – 2.90 (m, 4H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.73, 155.77, 142.79, 131.78, 120.21, 110.66, 103.84, 67.18, 51.76.

4-Chlorobenzene-1,2-diamine



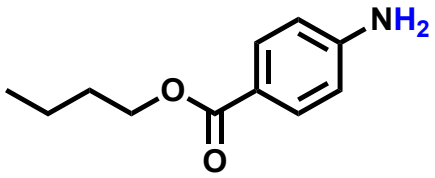
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (s, *J* = 1.7 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 3.39 (m, 4H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.13, 133.08, 124.82, 119.65, 117.55, 116.25.

Ethyl 4-aminobenzoate



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.17 – 3.96 (s, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.21, 141.40, 140.37, 108.59, 106.89, 100.68, 98.09.

Butyl 4-aminobenzoate



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 4.26 (t, *J*= 6.6 Hz, 2H), 4.18 – 4.02 (m, 2H), 1.83 – 1.68 (m, 2H), 1.54 – 1.42 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.82, 150.76, 131.57, 113.79, 64.25, 30.90, 19.33, 13.83.

^{1}H and ^{13}C NMR copies of *N*-alkylamines and anilines

Figure S1: ^{1}HNMR spectra of *N*-benzylaniline

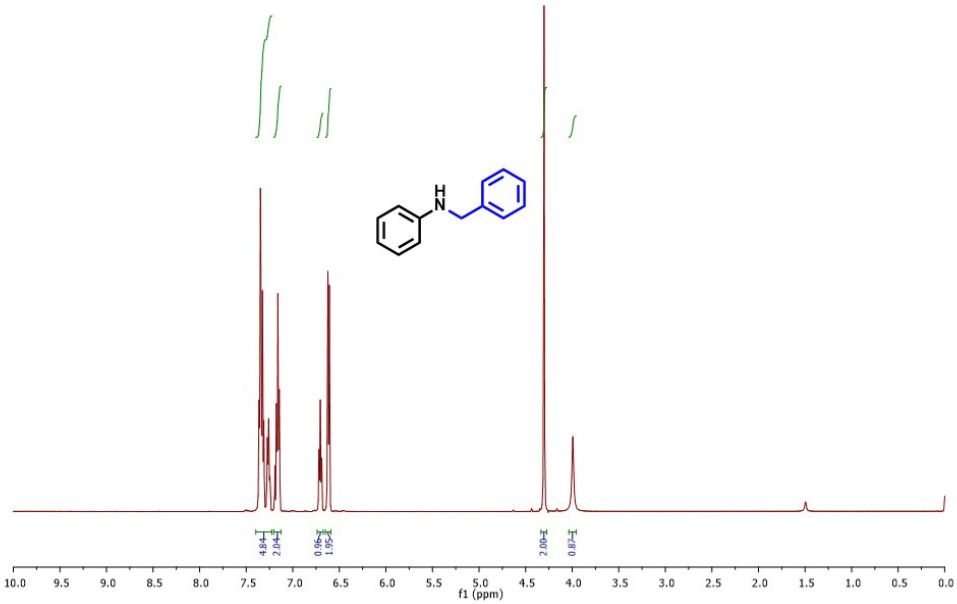


Figure S2: ^{13}CNMR spectra of *N*-benzylaniline

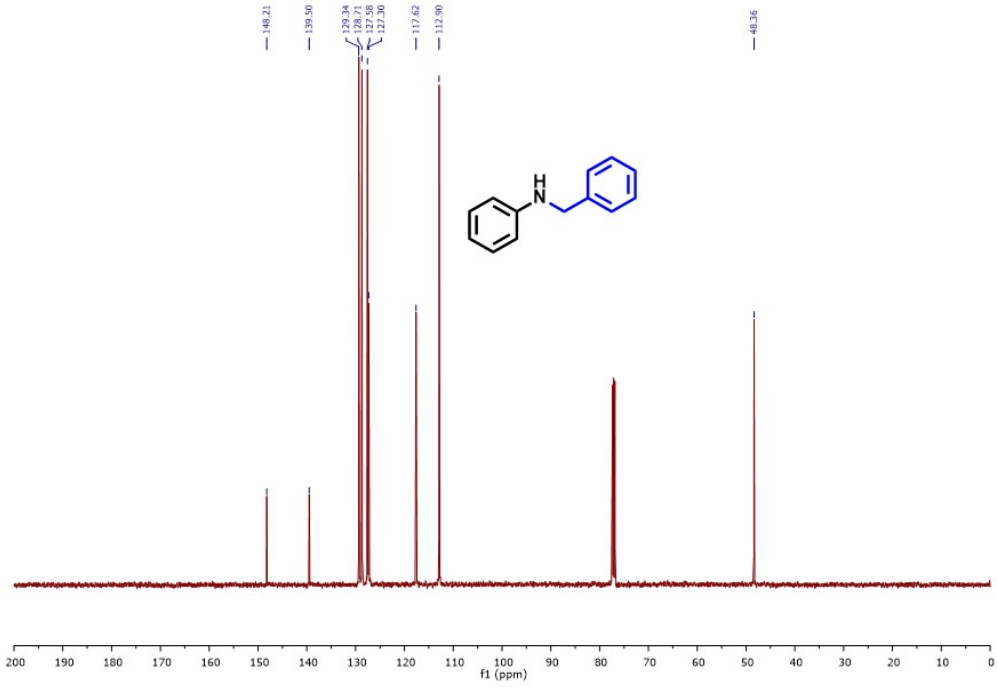


Figure S3: ^{1}HNMR spectra of *N*-benzyl-4-methylaniline

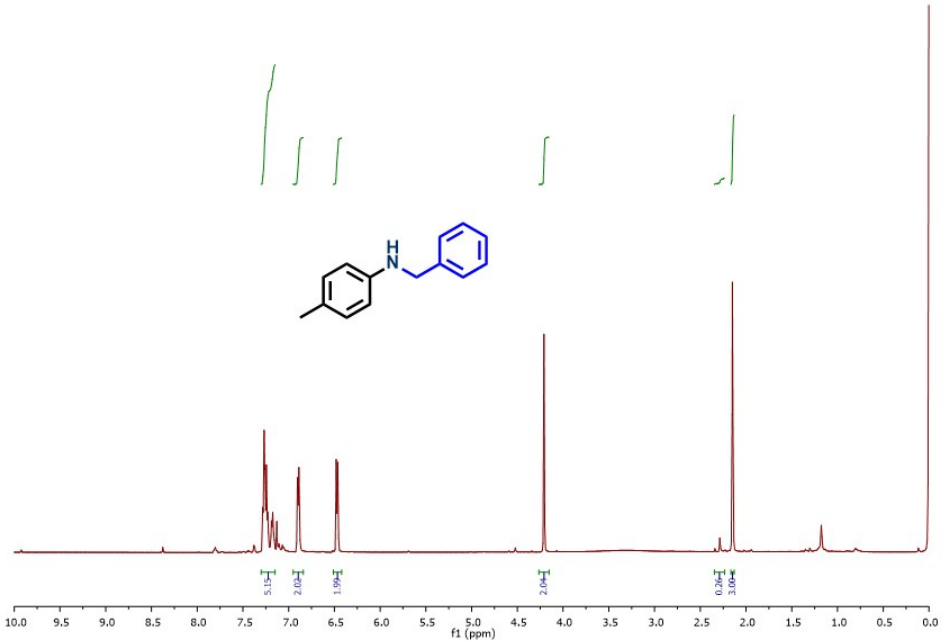


Figure S4: ^{13}CNMR spectra of *N*-benzyl-4-methylaniline

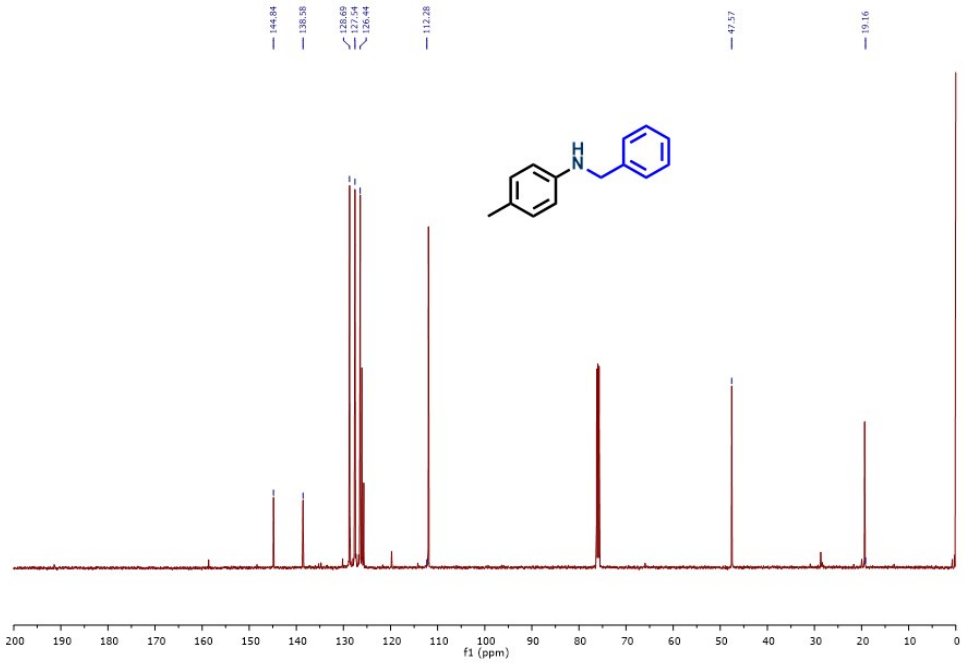


Figure S5: ^{1}HNMR spectra of *N*-benzyl-4-methoxyaniline

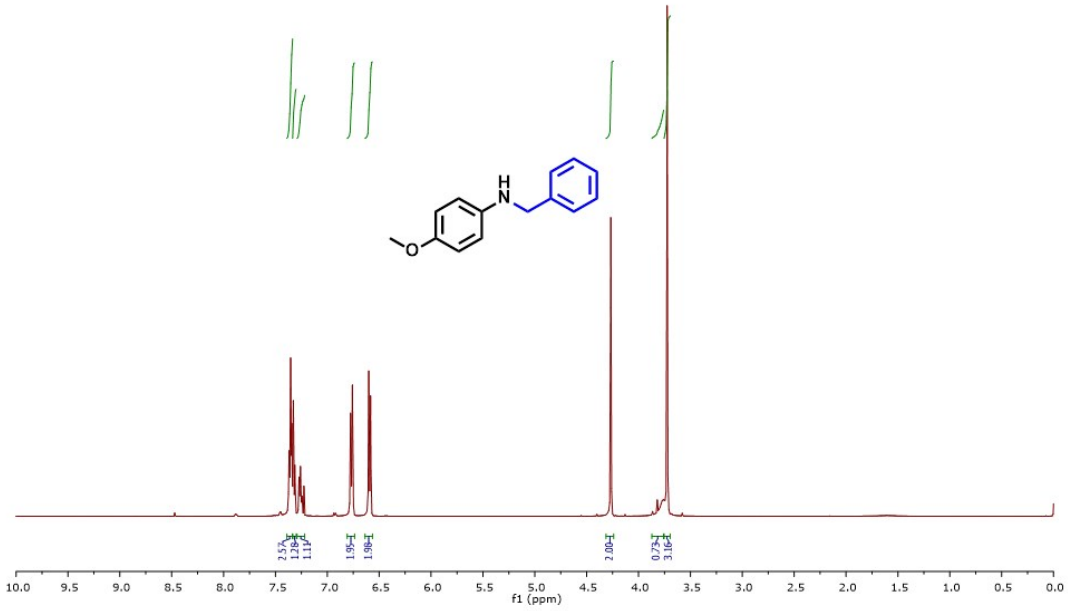


Figure S6: ^{13}CNMR spectra of *N*-benzyl-4-methoxyaniline

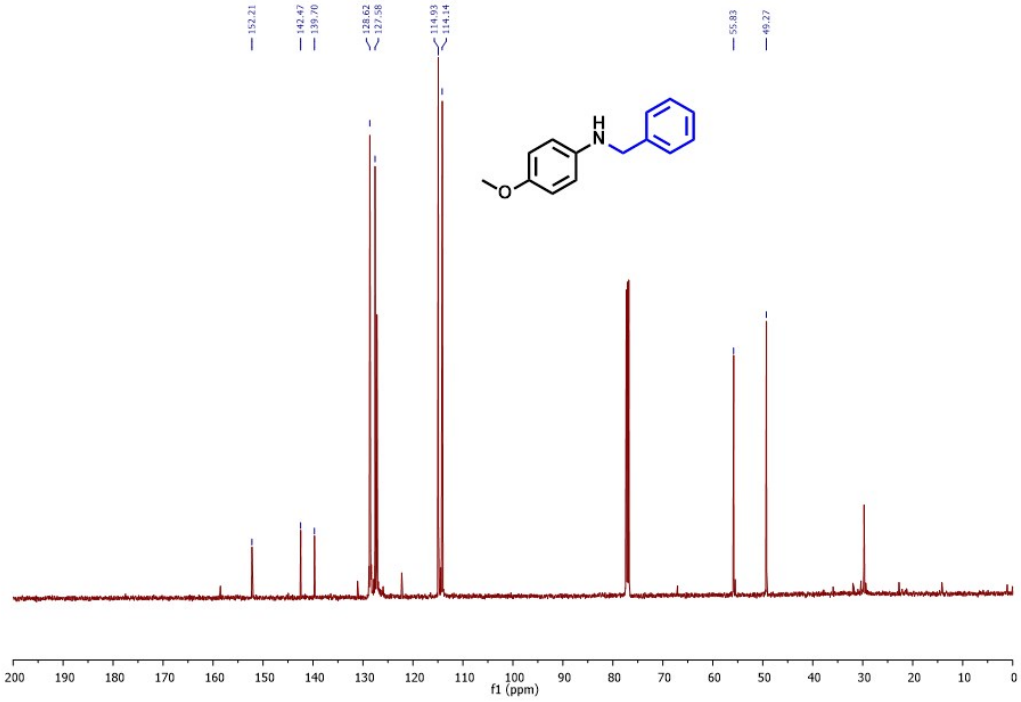


Figure S7: ^{1}HNMR spectra of *N*-benzyl-3-chloroaniline

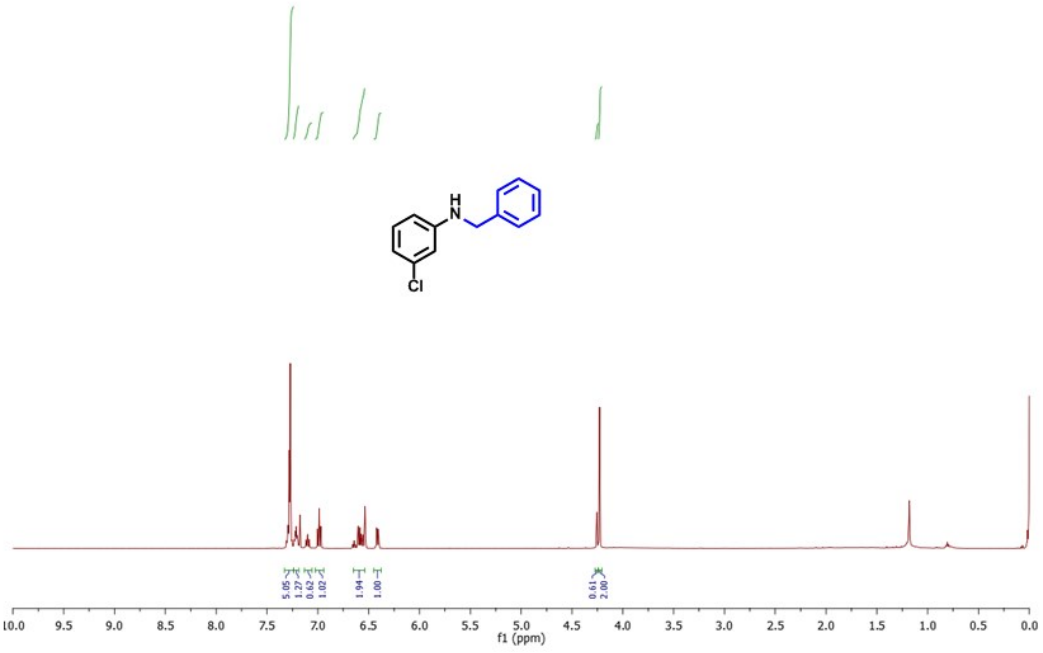


Figure S8: ^{13}CNMR spectra of *N*-benzyl-3-chloroaniline

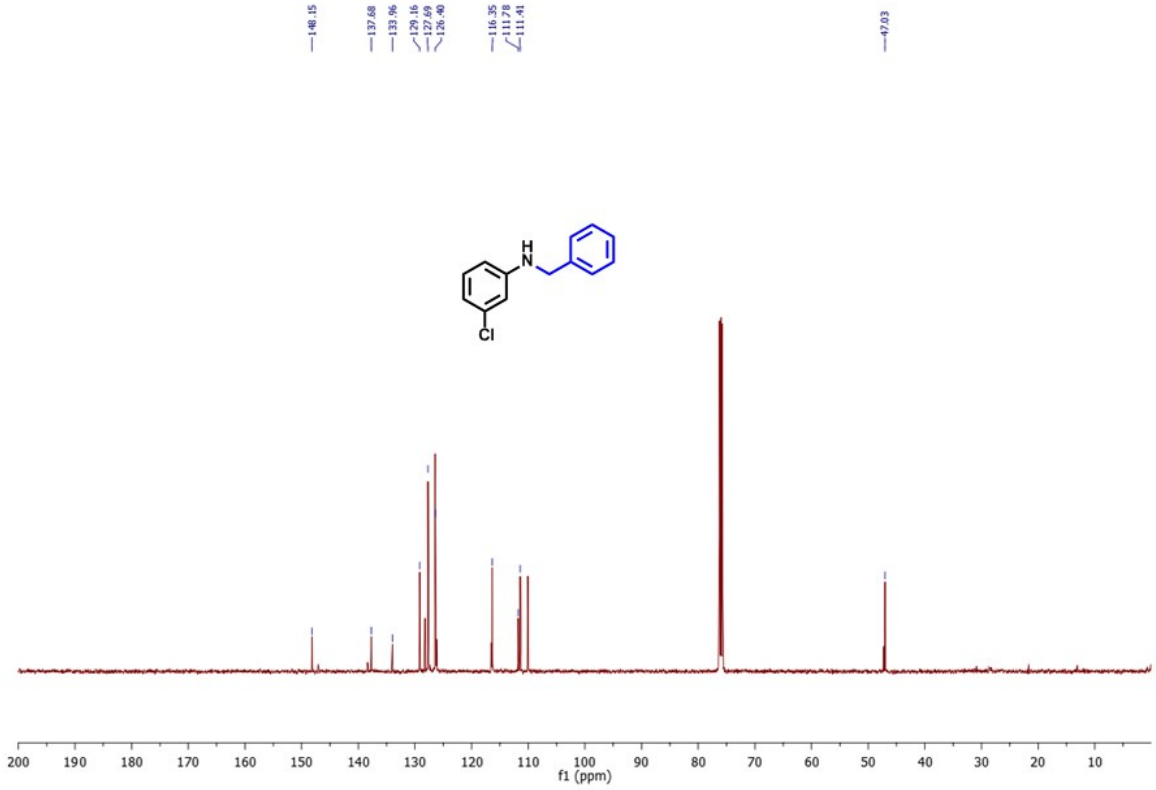


Figure S9: [1]HNMR spectra of *N*-benzyl-4-fluoroaniline

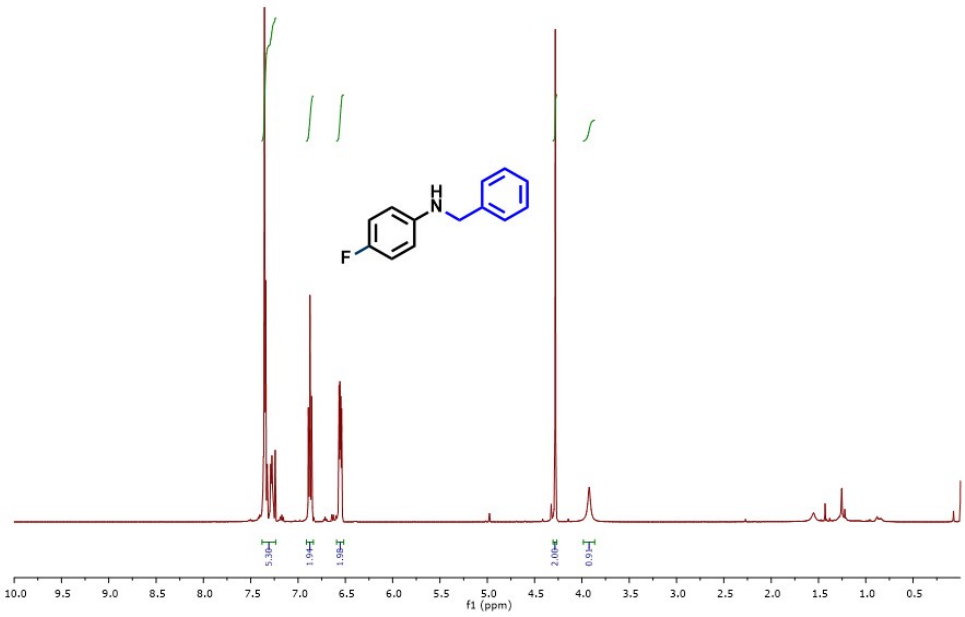


Figure S10: [13]CNMR spectra of *N*-benzyl-4-fluoroaniline

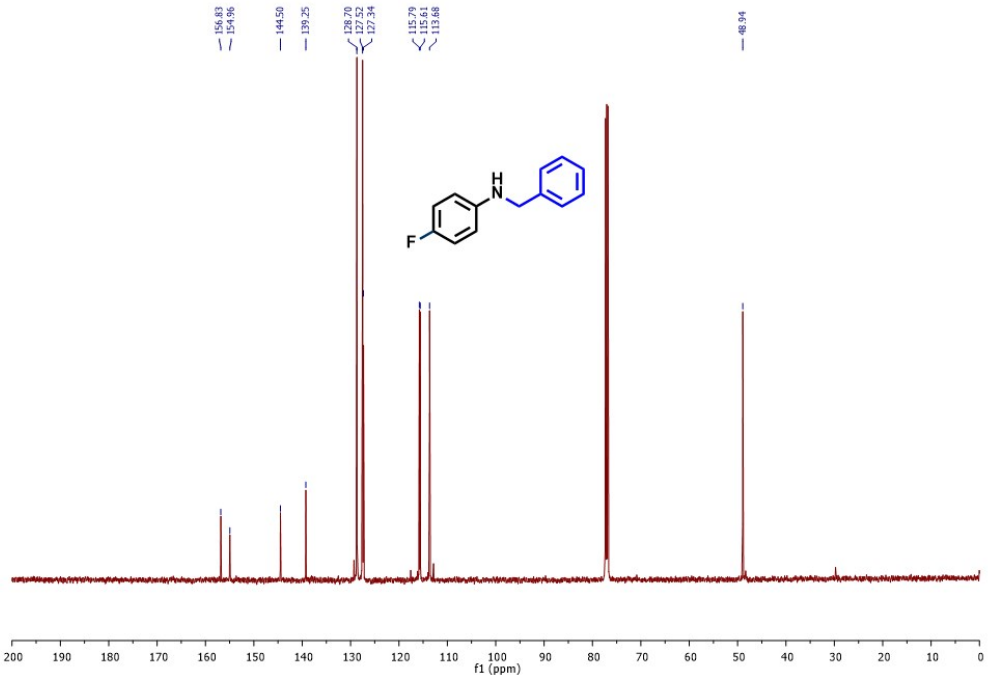


Figure S11: ^{1}HNMR spectra ofN-benzylquinolin-8-amine

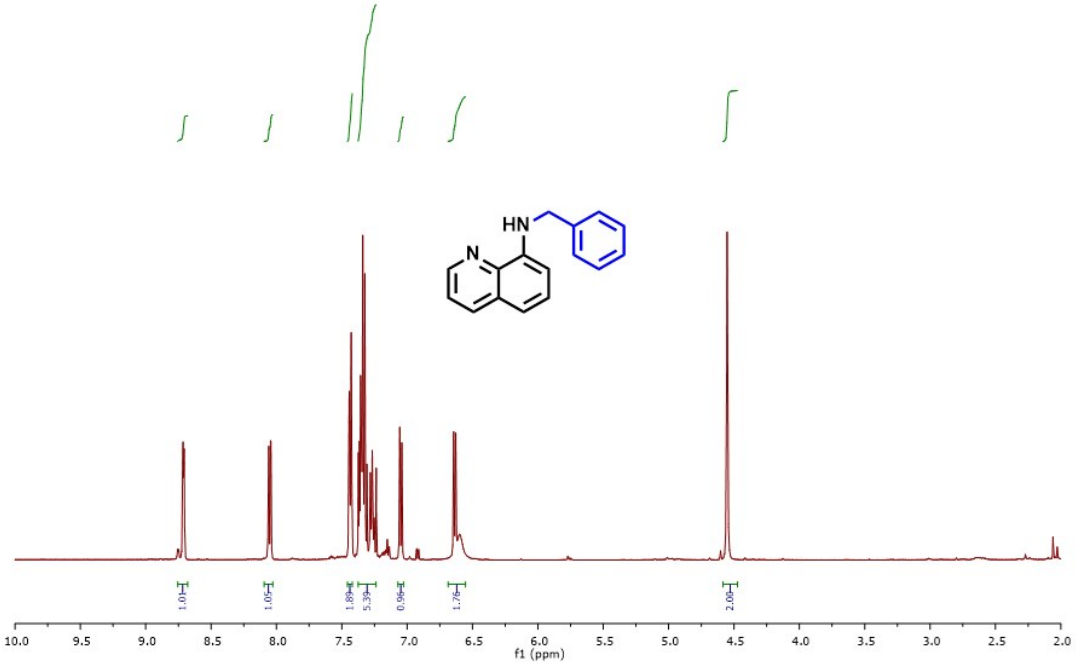


Figure S12: ^{13}CNMR spectra of N-benzylquinolin-8-amine

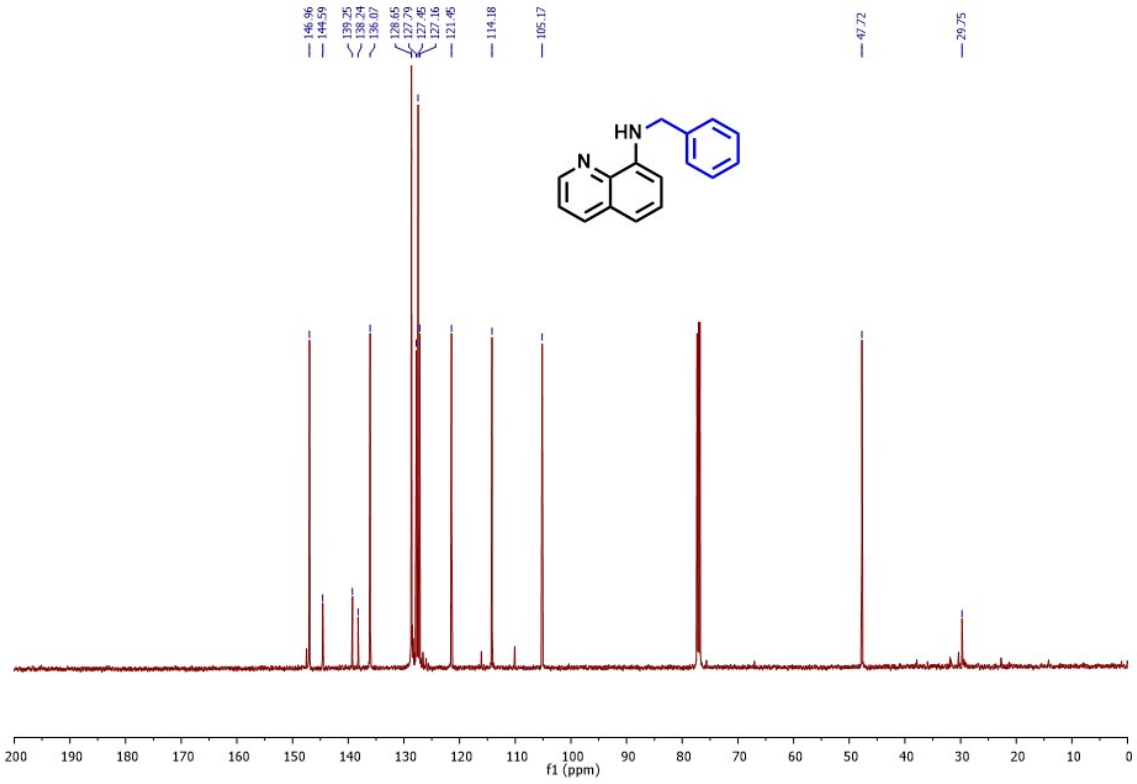
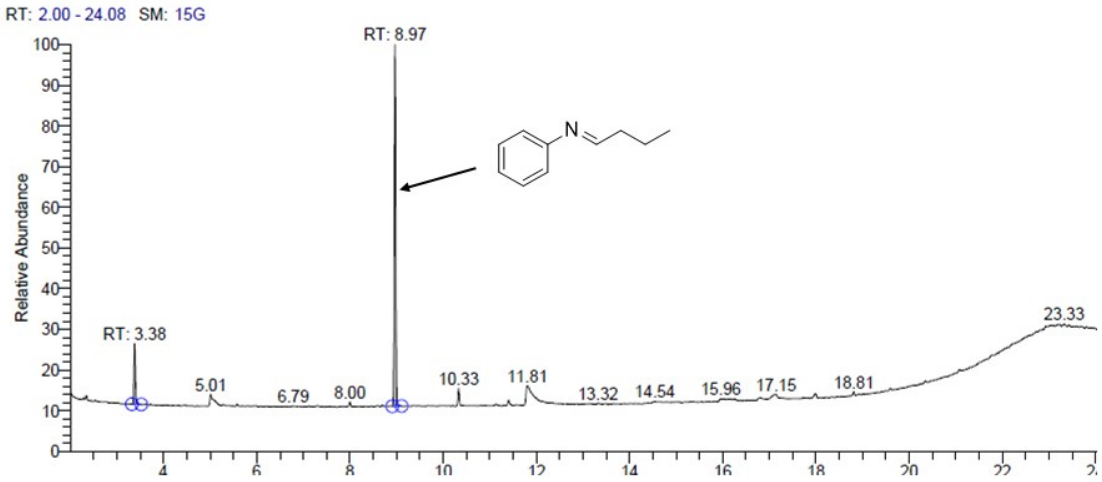


Figure S13:GCMS spectra of N-butylideneaniline



Library Search Results Table

RT	Compound Name	Probability	Molecular Weight	Library
8.97	N-Phenylpyrrolidine	49.65	147	mainlib
8.97	Benzenamine, N-3-butenyl-	41.94	147	mainlib
8.97	1-Benzylazetidine	2.01	147	mainlib

Figure S14: ^{1}HNMR spectra of 4-chloroaniline

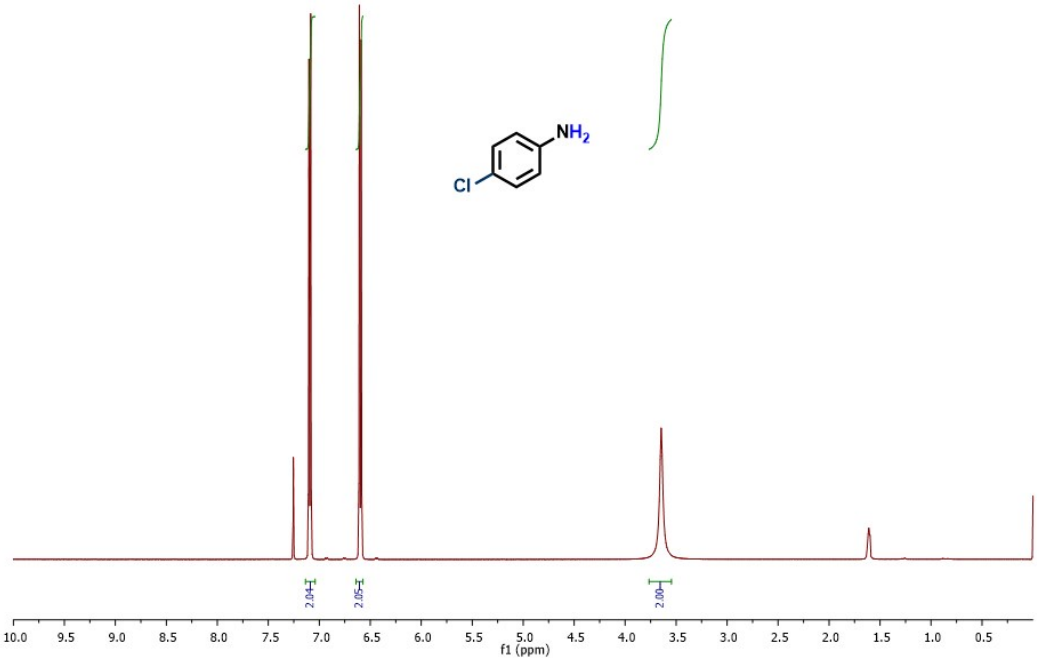


Figure S15: ^{13}CNMR spectra of4-chloroaniline

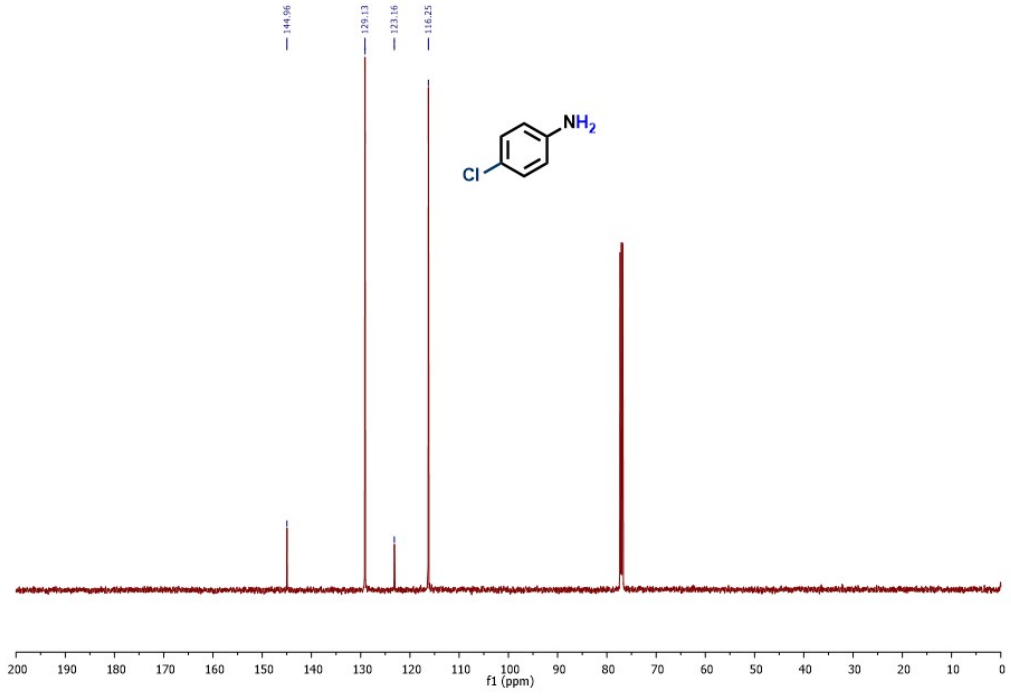


Figure S16: ^{1}HNMR spectra of pentafluoroaniline

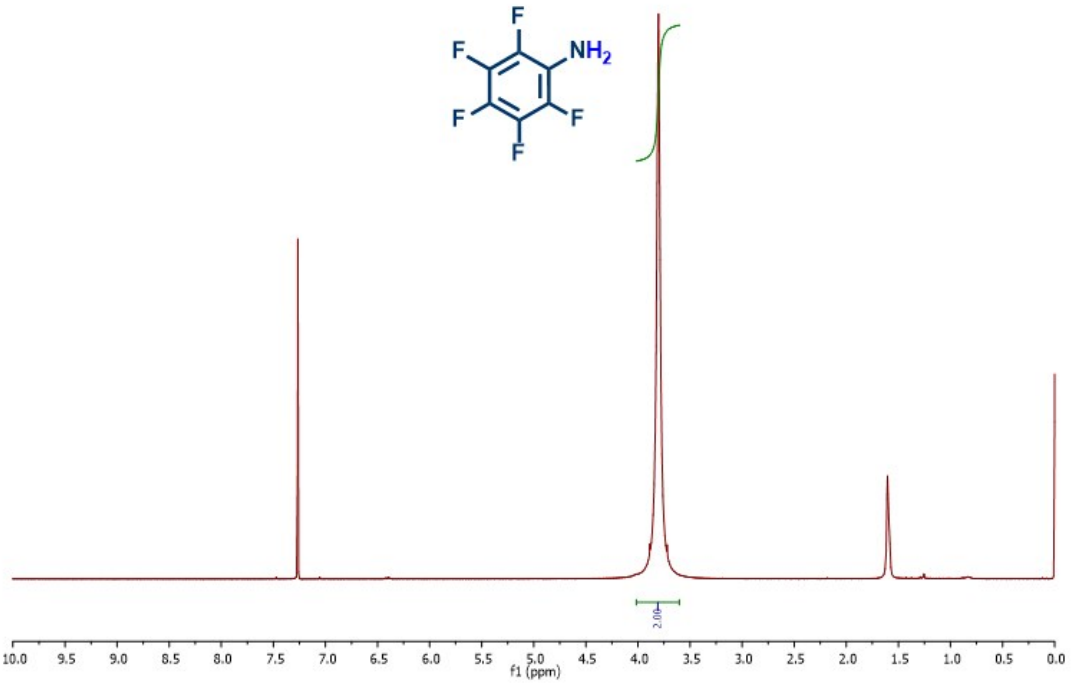


Figure S17: ^{13}CNMR spectra of pentafluoroaniline

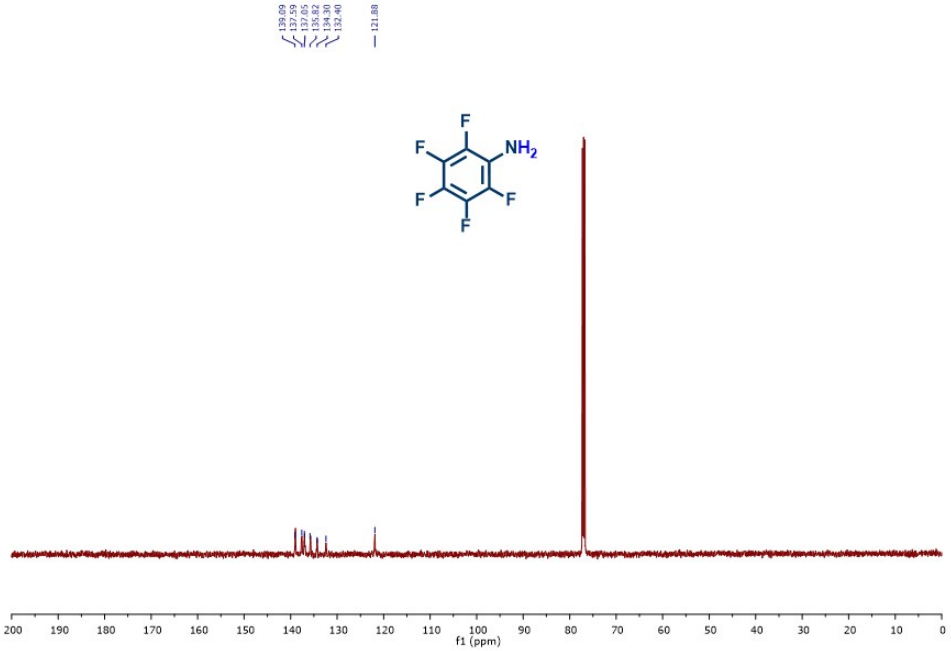


Figure S18: ^{1}HNMR spectra of Benzo[d][1,3]dioxol-5-amine

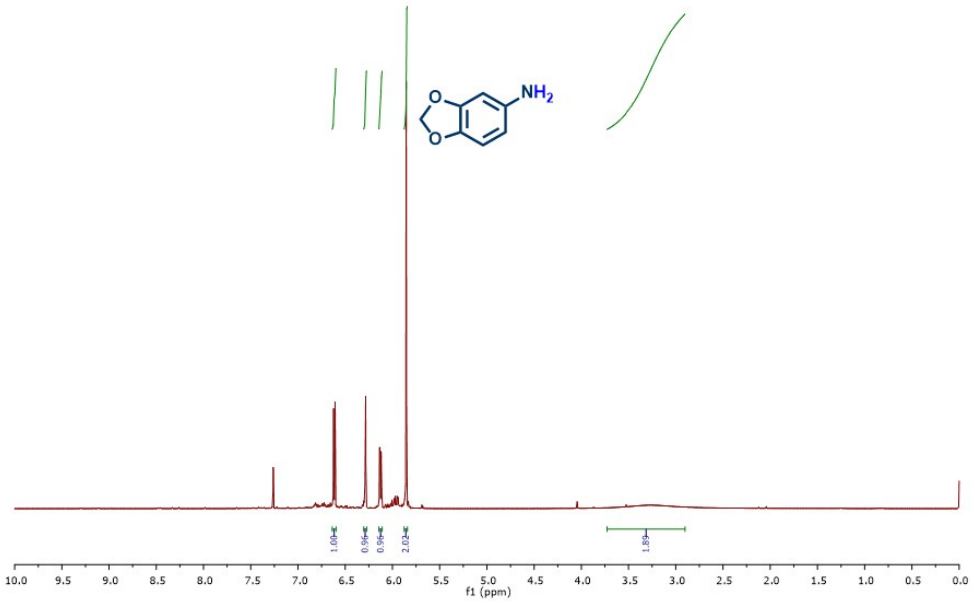


Figure S19: ^{13}CNMR spectra of Benzo[d][1,3]dioxol-5-amine

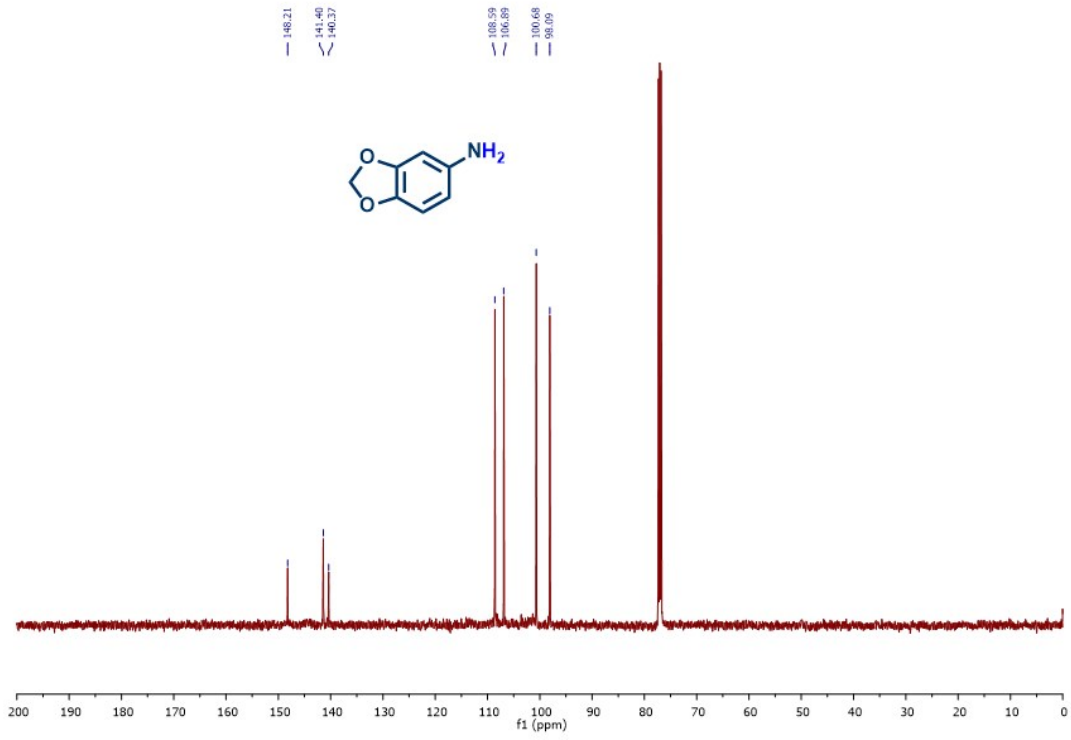


Figure S20: ^{1}HNMR spectra of 1-(4-Aminophenyl)ethanone

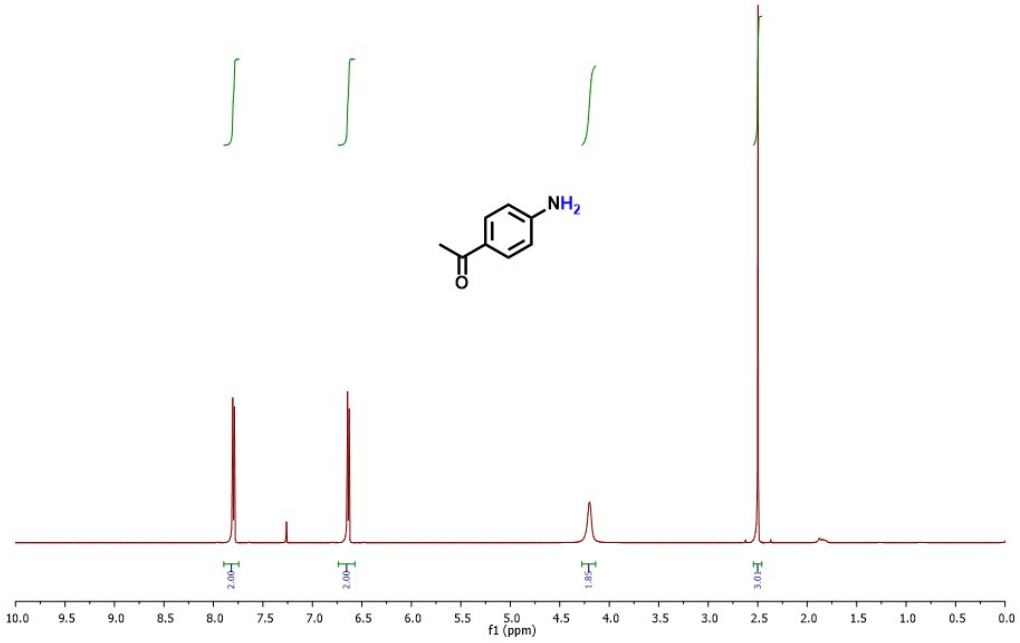


Figure S21: ^{13}CNMR spectra of1-(4-Aminophenyl)ethanone

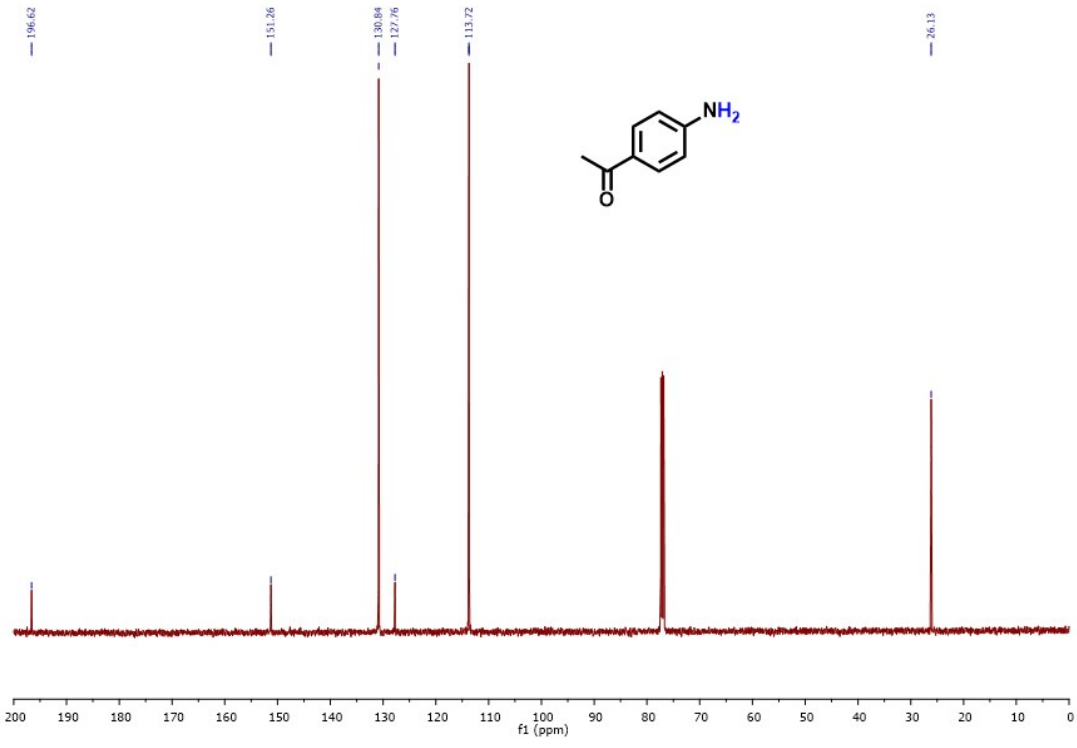


Figure S22: ^{1}HNMR spectra of Methyl 4-aminobenzoate

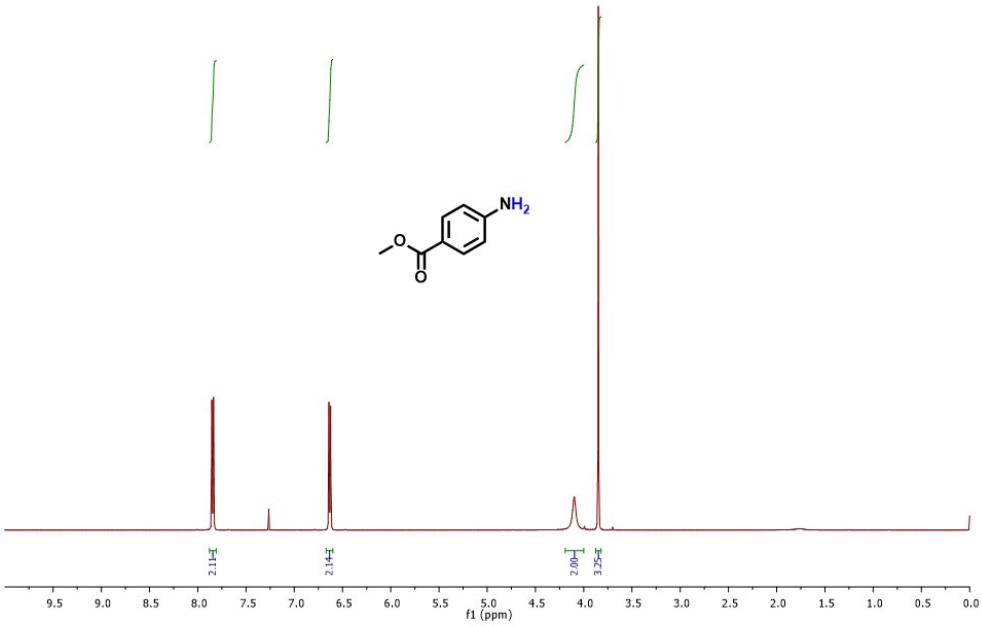


Figure S23: ^{13}CNMR spectra of Methyl 4-aminobenzoate

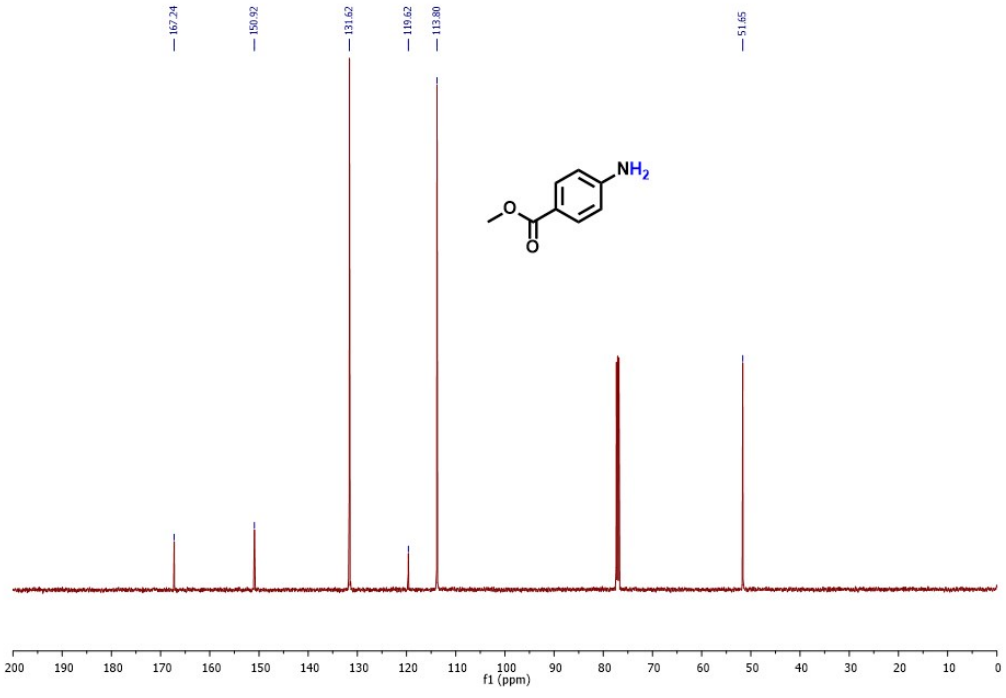


Figure S24: ^{1}HNMR spectra of 2-Aminopyridine

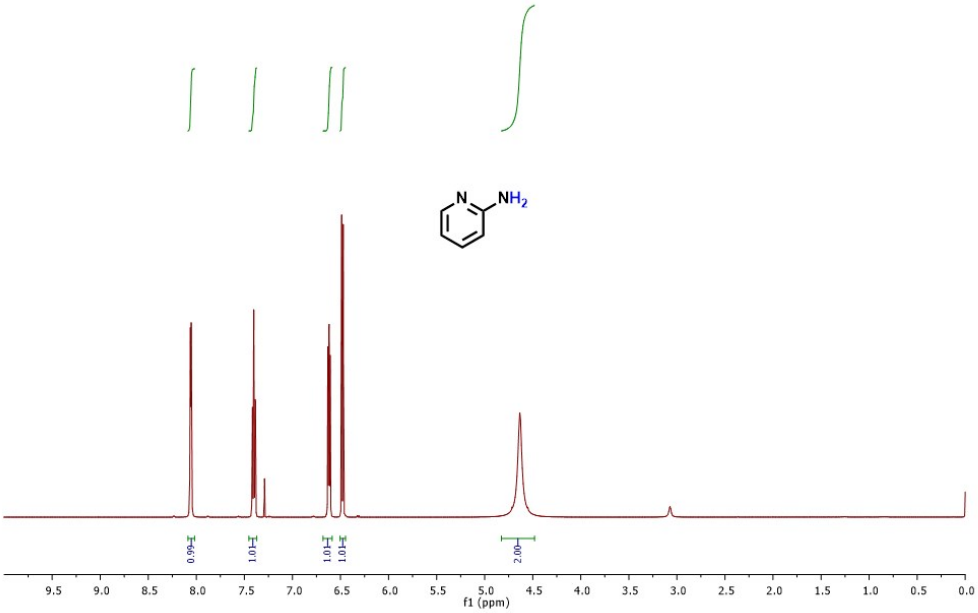


Figure S25: ^{13}CNMR spectra of 2-Aminopyridine

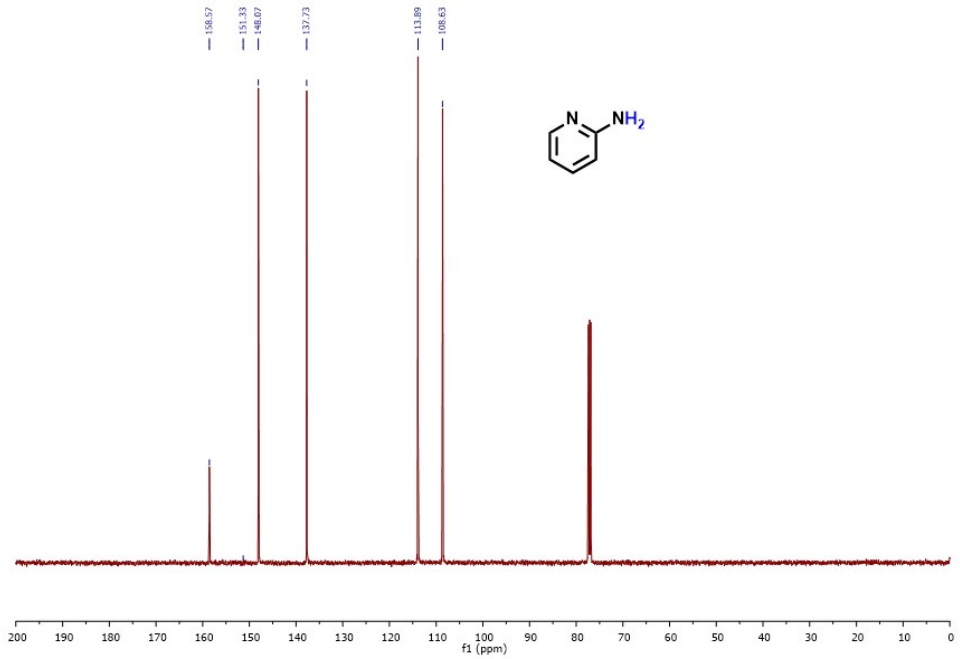


Figure S26: ^{1}HNMR spectra of 8-Aminoquinoline

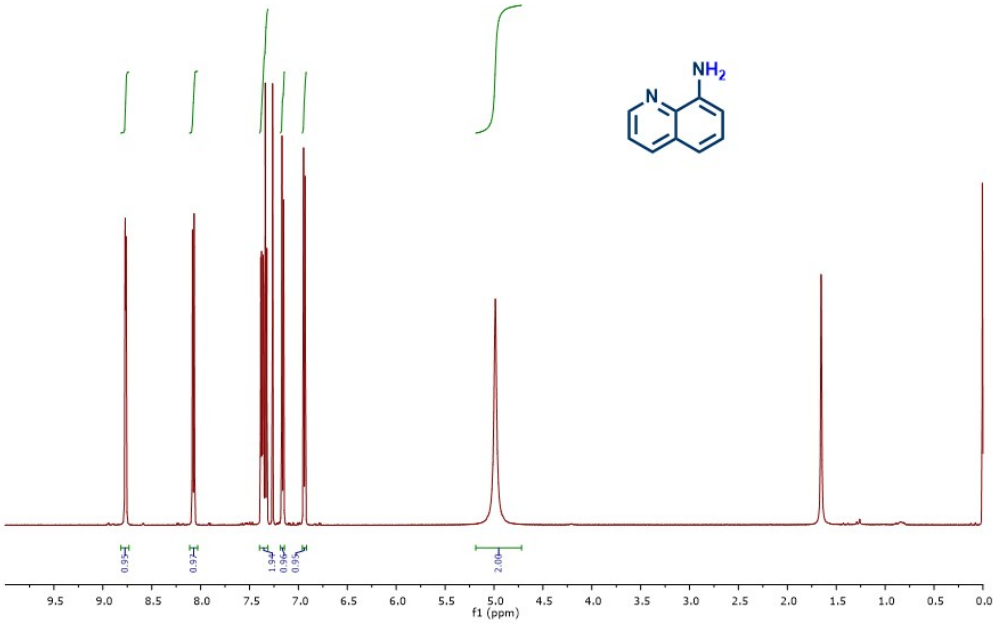


Figure S27: ^{13}CNMR spectra of 8-Aminoquinoline

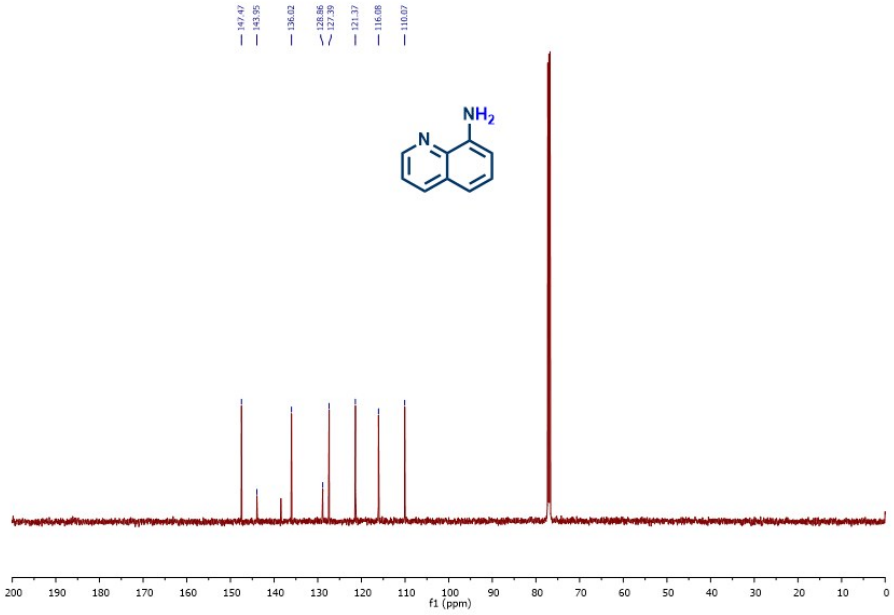


Figure S28: ^{1}HNMR spectra of 3-Fluoro-4-morpholinoaniline

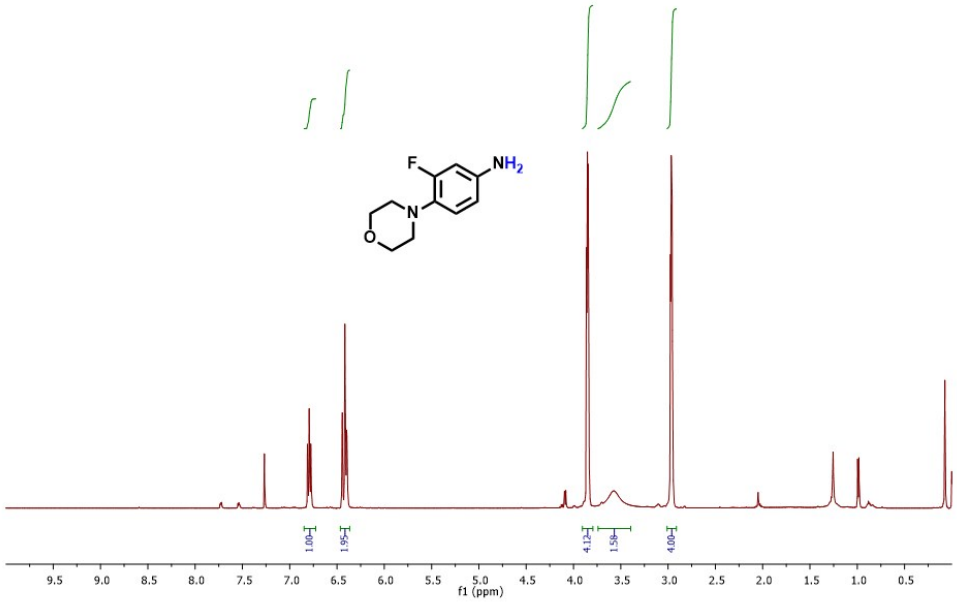


Figure S29: ^{13}CNMR spectra of 3-Fluoro-4-morpholinoaniline

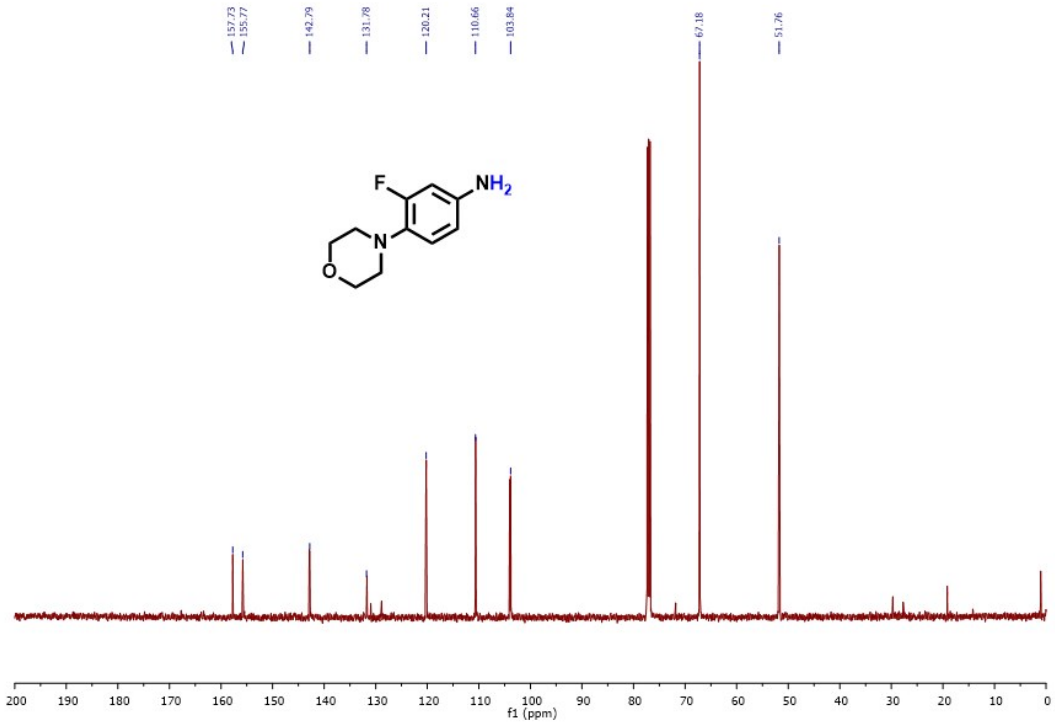


Figure S30:[1]HNMR spectra of 4-Chlorobenzene-1,2-diamine

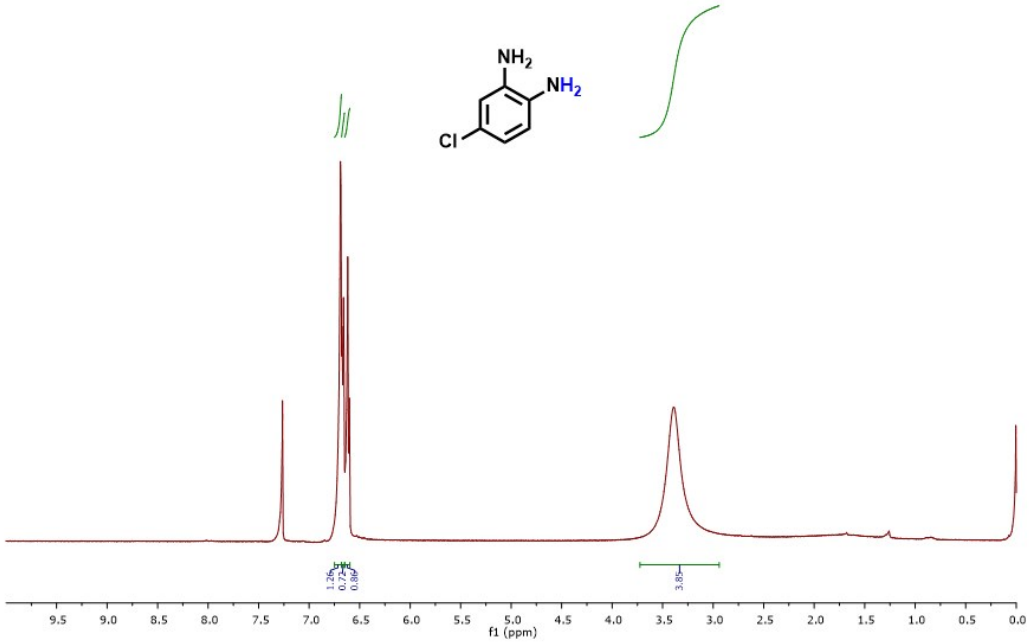


Figure S31:[13]CNMR spectra of 4-Chlorobenzene-1,2-diamine

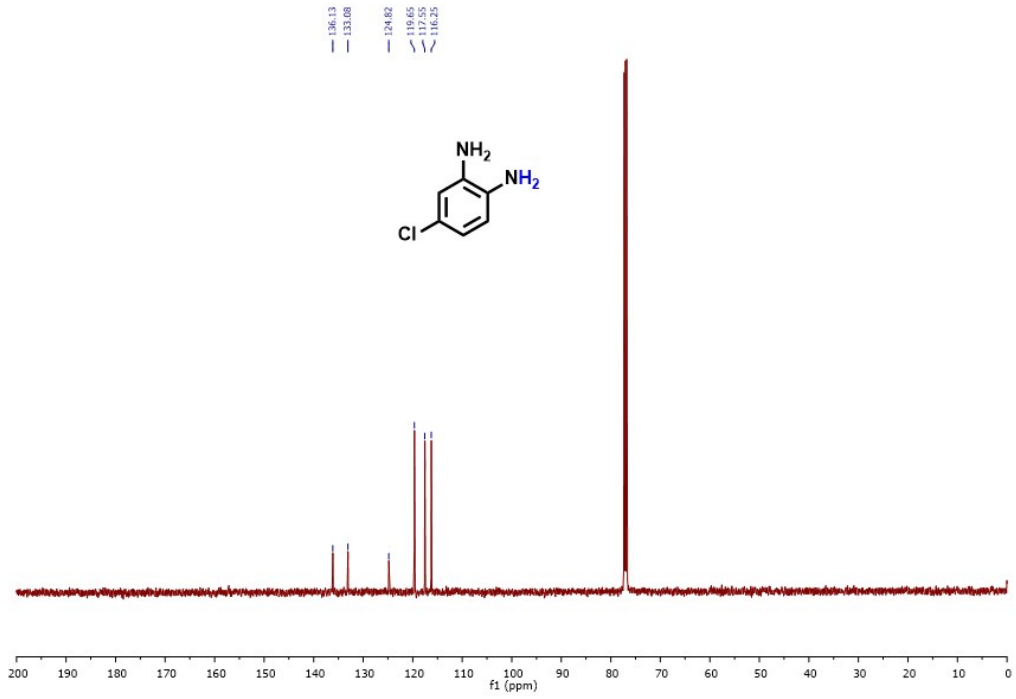


Figure S32: ^{1}HNMR spectra of Ethyl 4-aminobenzoate

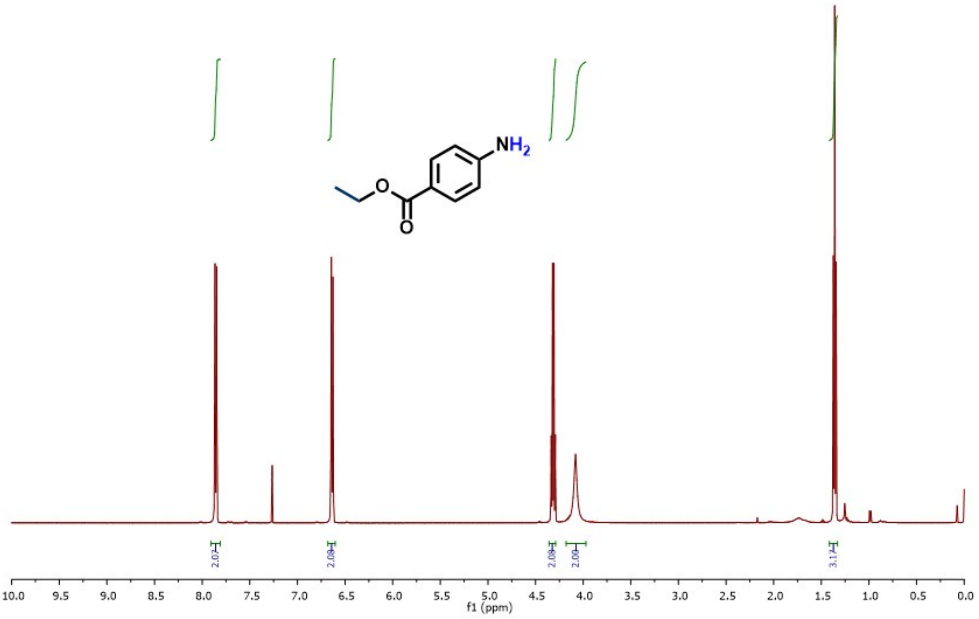


Figure S33: ^{13}CNMR spectra of Ethyl 4-aminobenzoate

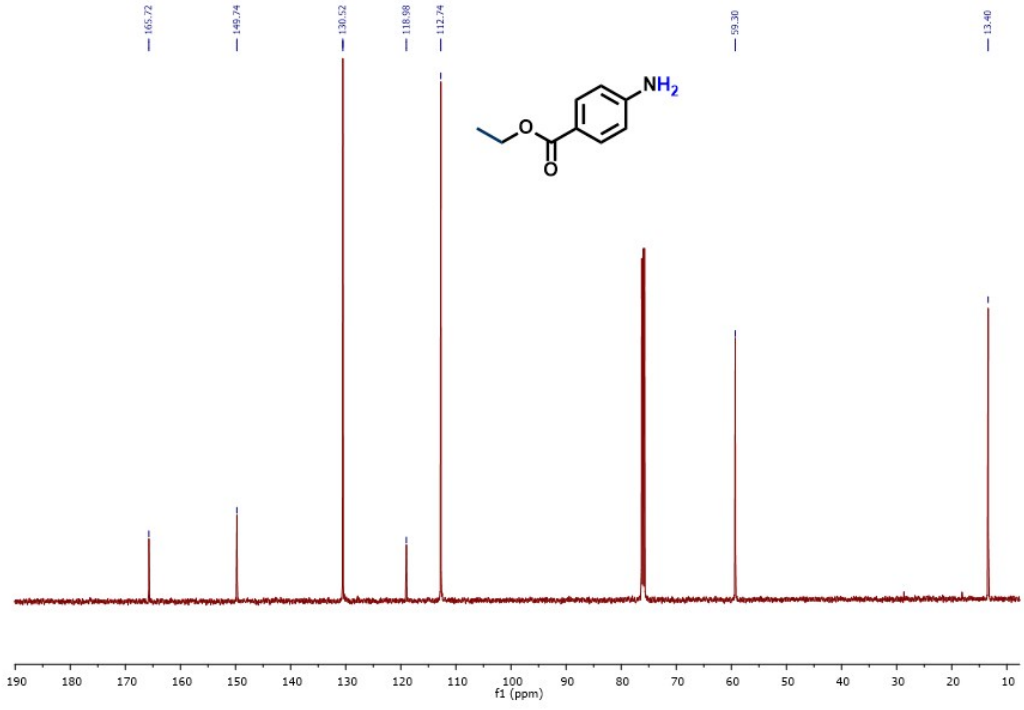


Figure S34: ^{1}HNMR spectra of Butyl 4-aminobenzoate

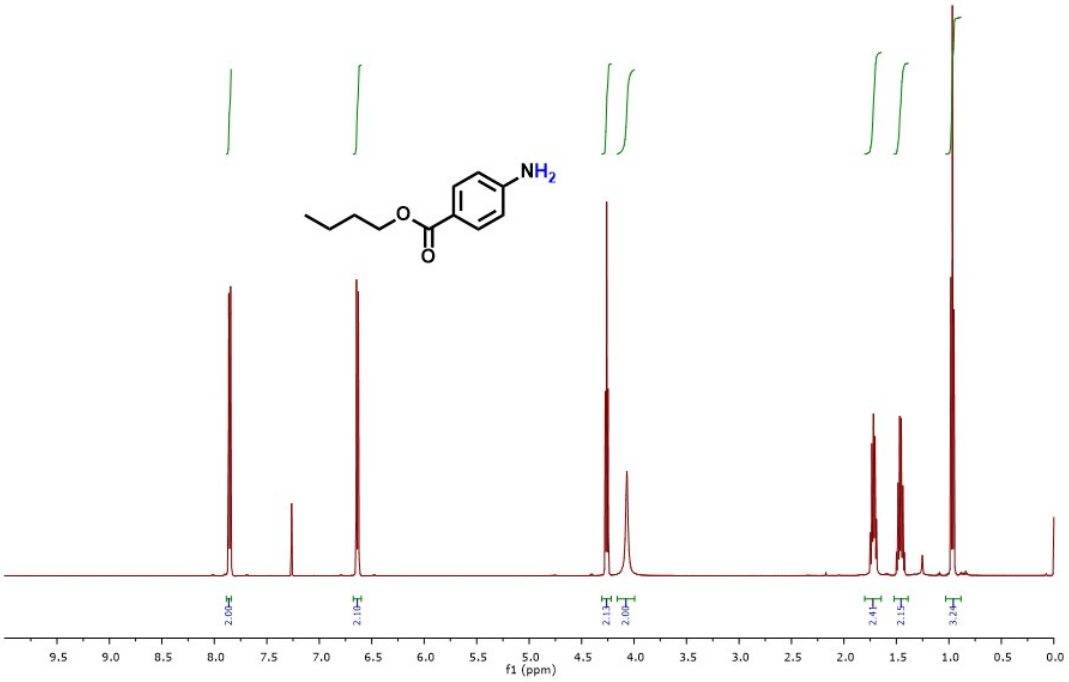


Figure S35: ^{13}CNMR spectra of Butyl 4-aminobenzoate