Development of a Graphene Oxide-Supported *N*-Heterocyclic Carbene Copper(I) Complex as a Heterogeneous Catalyst for the Selective *N*-Monoalkylation of Amines

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Experimental Section

Graphite mesh, sulfuric acid, sodium nitrate, potassium permanganate, hydrogen peroxide (30%), bromoacetyl bromide, 2-bromopropane and benzimidazole, copper bromide were purchased from Alfa Aesar, TCI, Sigma-Aldrich and Loba. FTIR spectroscopic analysis was recorded on a Perkin Elmer spectrometer between 400 and 4000 cm^{-1} using KBr pellets. FT-Raman spectroscopic analysis was recorded on Bruker RFS 27: stand-alone FT-Raman spectrometer between 50 and 4000 cm^{-1} with 2 cm^{-1} resolutions. The surface morphology was observed by field emission microscope (FESEM) of model FESEM Supra 55 (Carl Zeiss, Germany). The energy-dispersive X-ray spectroscopy (EDX) analysis was carried out on an electron probe microscope (Oxford X-Maxn). Powdered X-ray diffraction (PXRD) of the

catalyst was done by Rigaku Smartlab with CuKα radiation (λ = 0.15418 nm). High-resolution transmission electron microscope (HRTEM) image was observed using thermo scientific Talos F200X G2. X-ray photoelectron (XPS) analysis was performed on a PHI 5000 Versa Probe III,. The thermogravimetric analysis was done using EXSTAR, SI 6300 EXSTAR, Inductively coupled plasma–Optical emission spectroscopy (ICP-OES) was carried out using ICP-OES: Thermo Fisher Scientific USA iCAP 7400 Duo.

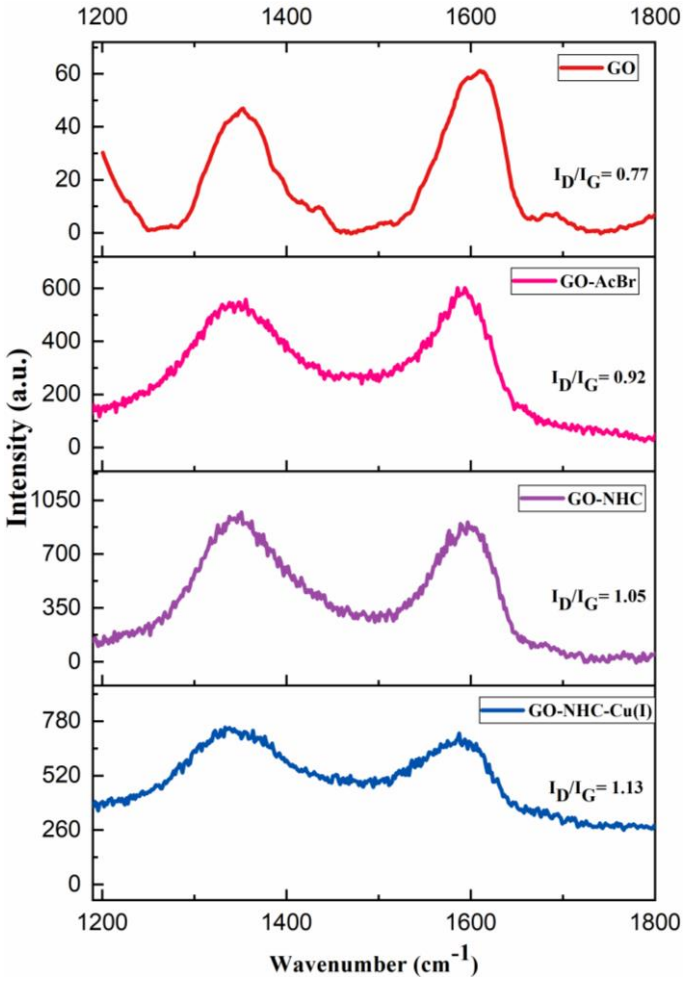
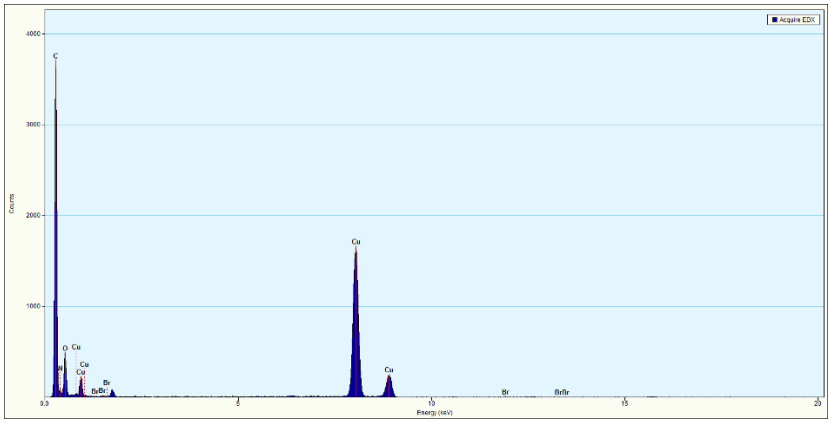


Figure S1. FT-Raman spectra of GO, GO-AcBr, GO-NHC and GO-NHC-Cu



Element	Weight %	Atomic%
C	55.24	82.67
O	4.23	4.76
N	1.10	1.42
Cu	39.23	11.09
Br	0.17	0.03

Figure S2. EDX spectra of GO-NHC-Cu

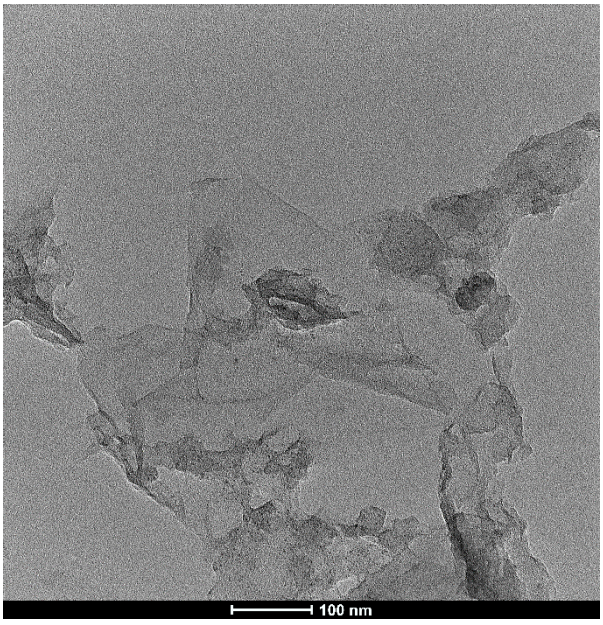


Figure S3. HRTEM micrograph of G-NHC-Cu(I)

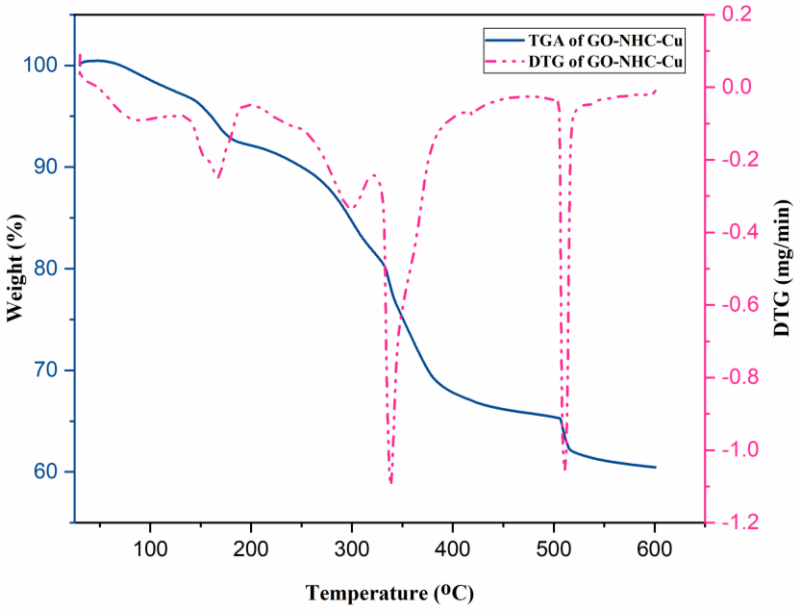


Figure S4. TGA thermogram of GO-NHC-Cu

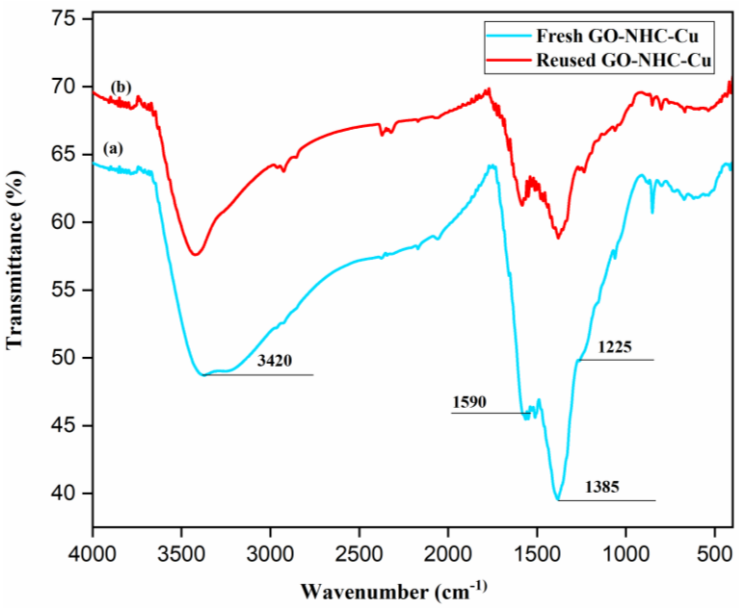


Figure S5. FTIR plot of (a) GO-NHC-Cu (I) fresh and (b) GO-NHC-Cu (I) after the fifth cycle.

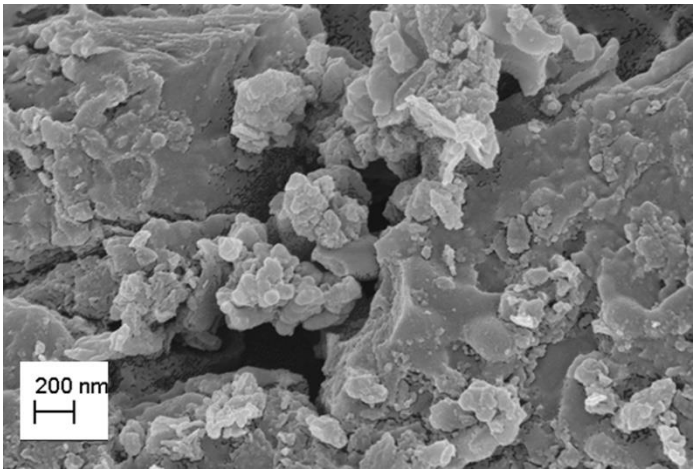
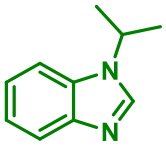


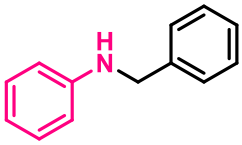
Figure S6. FESEM image of GO-NHC-Cu after the fifth cycle.

Physical and spectral data of N-alkylation



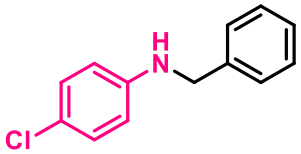
1-isopropyl-1*H*-benzimidazole (L1)

Yellow oil; ^{1}H NMR (DMSO-d_6, 400 MHz):δ 8.32 (s, 1H), 7.69 (d, J = 2.4 Hz, 1H), 7.58 (t, J = 3.6, 1H), 7.20 (d, J = 2.8 Hz, 2H), 7.68 (sept, J = 6.4, 1H), 1.49 (s, 6 H); ^{13}C NMR (DMSO-d_6, 100 MHz) : δ 144.15, 141.92, 133.61, 122.53, 121.85, 119.98, 111.14, 47.49, 22.57.



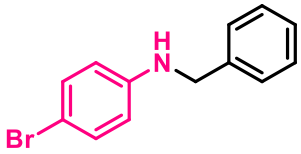
***N*-benzylaniline (Table 2, 3a)**

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.29-7.26 (m, 5H), 7.09 (t, J = 8 Hz, 2H), 6.64 (t, 8Hz, 1H), 6.57 (d, 8 Hz, 2H), 4.25 (s, 2H), 3.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 148.18, 139.46, 129.31, 128.67, 127.55, 127.27, 117.59, 112.87, 48.34.



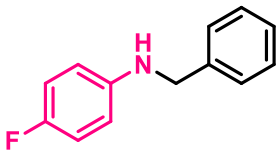
***N*-benzyl-4-chloroaniline (Table 2, 3b)**

Colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.28 (d, J=4.5 Hz, 4H), 7.23-7.21 (m, 1H), 7.04 (d, J=8.9 Hz, 2H), 6.48 (d, J=8.9, 2H), 4.22 (s, 2H), 3.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 146.68, 138.96, 129.10, 128.74, 127.45, 122.11, 113.84, 48.22.



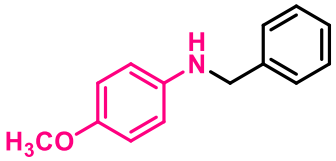
***N*-benzyl-4-bromoaniline (Table 2, 3c)**

Colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.44 (d, J= 4 Hz, 4H), 7.41-7.38 (m, 1H), 7.35-7.33 (m, 2H), 6.57 (d, J= 8.8 Hz, 2H), 4.35 (s, 2H), 4.04 (br, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 147.19, 139.03, 132.09, 128.88, 127.57, 127.55, 114.64, 109.21, 48.30.



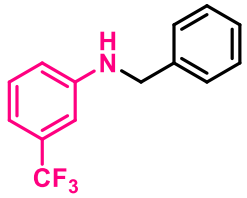
***N*-benzyl-4-fluoroaniline (Table 2, 3d)**

Colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.39-7.36 (m, 5H), 6.91 (t, J=8.4 Hz, 2H), 6.59 (dd, J=7.5, 4.6 Hz, 2H), 4.31 (s, 2H), 3.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 154.75 (d, J=234.9 Hz), 144.52, 139.28, 128.72, 127.54, 115.60 (d, J=22.3 Hz), 113.71 (d, 7.4 Hz), 48.94 Hz.



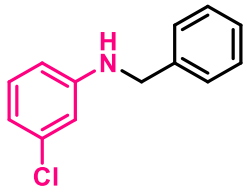
***N*-benzyl-4-methoxyaniline (Table 2, 3e)**

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.44-7.35 (m, 5H), 6.87-6.84 (m, 2H), 6.68-6.66 (m, 2H), 4.33 (s, 2H), 3.80 (s, 3H), 3.71(s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 152.30, 142.46, 139.77, 128.70, 127.67, 127.27, 114.99, 114.28, 55.85, 49.32.



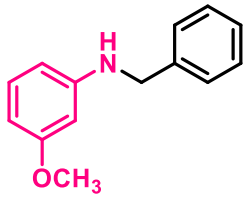
***N*-benzyl-3-(trifluroylmethyl)aniline (Table 2, 3f)**

Colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.38-7.30 (m, 6H), 6.97-6.95 (m, 1H), 6.86 (s, 1H), 6.77-6.75 (m, 1H), 4.36 (s, 2H), 4.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 148.22, 138.57, 131.41 (q, J_{C-F}=31.5 Hz), 129.68, 128.80, 127.54, 122.98, 115.72, 113.93 (q, J_{C-F}=3.8 Hz), 109.06(q, J_{C-F}=3.8 Hz), 48.13.



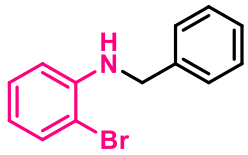
***N*-benzyl-3-chloroaniline(Table 2, 3g)**

Colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42-7.37 (m, 5H), 7.12 (t, J= 8 Hz, 1H), 6.74 (dd, J=8 , J=1.2 Hz, 1H), 6.67 (t, J= 2 Hz, 1H), 6.53 (dd, J=8.4, J=1.6 Hz, 1H), 4.33 (s, 2H), 4.07 (br, s). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 149.26, 138.81, 135.09, 130.34, 128.84, 127.58, 127.54, 117.52, 112.64, 111.27, 48.16.



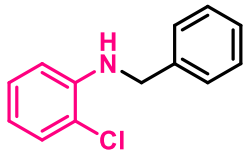
***N*-benzyl-3-methoxyaniline (Table 2, 3h)**

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.39-7.26 (m, 5H), 7.08 (t, J=8 Hz, 1H), 6.30-6.26 (m, 2H), 6.20 (s, 1H), 4.32 (s, 2H), 4.06 (br, 1H), 3.75 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 160.83, 149.57, 139.33, 130.02, 128.66, 127.54, 127.27, 106, 102.68, 98.87, 55.09, 48.34.



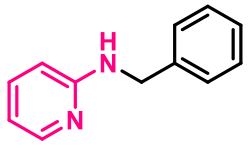
***N*-benzyl-2-bromoaniline (Table 2, 3i)**

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.49-7.47 (m, 1H), 7.40-7.37(m, 4H), 7.31-7.33 (m, 1H), 7.18-7.14 (m, 1H), 6.65-6.59 (m, 2H), 4.80 (s, 1H), 4.44(d, J=4.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 144.83, 138.73, 132.44, 128.79, 128.55, 127.40, 127.28, 118.02, 111.67, 48.03, 21.19.



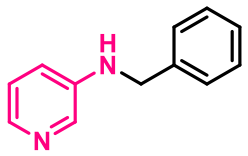
***N*-benzyl-2-chloroaniline (Table 2, 3j)**

Colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.33 (m, 5H), 7.32-7.29 (m, 2H), 7.11 (t, J=7.6 Hz, 1H), 6.66 (t, J= 8 Hz, 1H), 4.81 (br, s), 4.42 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 143.85, 138.75, 129.15, 128.77, 127.40, 127.32, 119. 15, 117.48, 111.57, 47.88



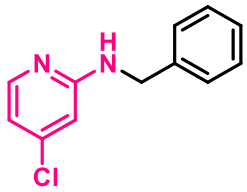
***N*-benzyl-(2-pyridyl)amine (Table 2, 3k)**

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 8.08 (d, J=4.8 Hz, 1H), 7.42-7.34 (m, 5H), 7.29-7.26(m, 1H), 6.60-6.57 (m, 1H), 6.38 (d, J=8.4, 1H), 5.05(b, 1H), 4.50 (d, J=5.6, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ158.66, 148.13, 139.15, 137.60, 128.67, 127.40, 127.27, 113.15, 106.78, 46.34.



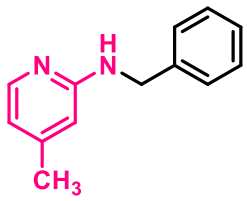
***N*-benzyl-(3-pyridyl)amine ((Table 2, 3l)**

Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 8.02 (d, J= 2 Hz, 1H), 7.90 (d, 4.4 Hz, 1H), 7.32-7.31 (m, 4H), 7.26-7.25 (m, 1H), 7.03-6.99 (m, 1H), 6.84-6.81 (m, 1H), 4.80 (s, 1H), 4.27 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 144.40, 138.67, 138.16, 135.75, 128.85, 127.43, 127.38, 123.90, 118.72, 47.63.



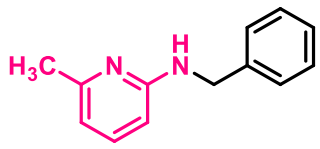
N-benzyl-4-chloropyridin-2-amine (Table 2, 3m)

Colourless solid, ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.96 (d, J=5.6 Hz, 1 H), 7.35-7.30 (m, 5H), 6.60 (d, J=4H Hz, 1H), 6.38 (s, 1H), 5.17 (br, 1H), 4.47 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 159.50, 149.13, 144.90, 138.50, 128.76, 127.48, 127.40, 113.67, 106.28, 46.28.



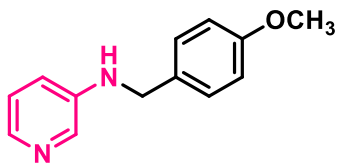
N-benzyl-4-methylpyridin-2-amine(Table 2, 3n)

Colourless solid, ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.94(d, J= 5.2 Hz, 1H), 7.35- 7.27 (m, 5H), 6.44 (d, J=5.2 Hz, 1H), 6.21 (s, 1H), 5.17 (s, 1H), 4.48 (d, J= 4.8 Hz 2H), 2.21 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 158.56, 149.18, 146.89, 139.07, 128.67, 127.35, 127.26, 114.73, 107.16, 46.33, 21.33.



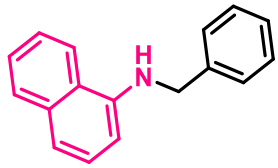
N-benzyl-6-methylpyridin-2-amine (Table 2, 3o)

Colourless solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.29 (m, 6H), 6.48 (d, J= 7.6 Hz, 1H), 6.18 (d, J= 8.4 Hz, 1H), 5.32 (br, 1H), 4.48 (d, J= 6 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 158.49, 156.93, 139.33, 138.07, 128.64, 127.33, 127.19, 112.51, 102.98, 46.51, 24.35.



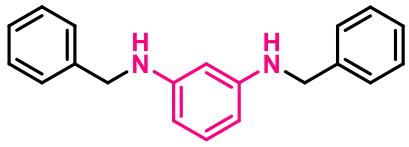
***N*-(4-methoxybenzyl)pyridine-3-amine (Table 2, 3p)**

Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 8.03 (d, J= 2.8 Hz, 1H), 7.93 (d, J=4, 1H), 7.27-7.25 (m, 2H), 7.07-7.03 (m,1H) 6.89-6.84 (m, 3H), 4.24 (s, 3H), 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 159.01, 144.15, 138.67, 136.04, 130.50, 128.76, 123.78, 118.63, 114.15, 55.32, 47.3.



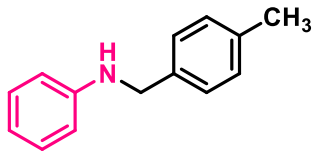
N-Benzylnaphthalen-1-amine (Table 2, 3q)

Colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.99-7.89 (m, 2H), 7.65-7.46 (m, 9H), 6.78 (d, J= 7.2, 1H), 4.81 (br, s), 4.58 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 143.45, 139.35, 134.54, 129.25, 128.94, 127.93, 127.60, 126.91, 126.00, 124.97, 120.21, 117.84, 104.99, 48.70.



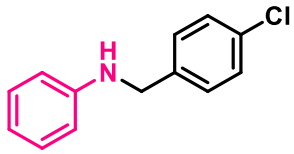
***N,N'*-Dibenzylpyridine-2,6-diamine(Table 2, 3r)**

Colourless solid, ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.35-7.29 (m, 11H), 5.75 (d, J=8 Hz, 2H), 4.95 (s, 2H), 4.44 (d, J=5.6 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 157.53, 139.67, 139.47, 128.59, 127.42, 127.15, 95.07, 46.37, 29.75.



***N*-(4-methyl)benzylaniline (Table 2, 3s)**

Colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.42-7.30 (m, 6H), 6.88 (dd, J=18, 11.9 Hz, 1H), 6.78 (d, J=7.6 Hz, 2H), 4.40 (s, 2H), 4.08 (s, 1H), 2.51 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 148.42, 136.99, 136.59, 129.50, 129.44, 127.70, 127.64, 117.64, 113.02, 48.20, 21.31.



***N*-(4-chloro)benzylaniline (Table 2, 3t)**

Colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.37-7.31 (m, 4 H), 7.17 (t, J=7.6 Hz, 2 H), 6.73 (t, J= 7.2 Hz, 1 H), 6.62 (d, J= 8 Hz, 2 H), 4.32 (s, 2H), 4.07 (br, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 147.83, 138.00, 132.88, 129.32, 128.77, 117.82, 112.90, 47.62.

^{1}H and ^{13}C NMR spectra of organic products

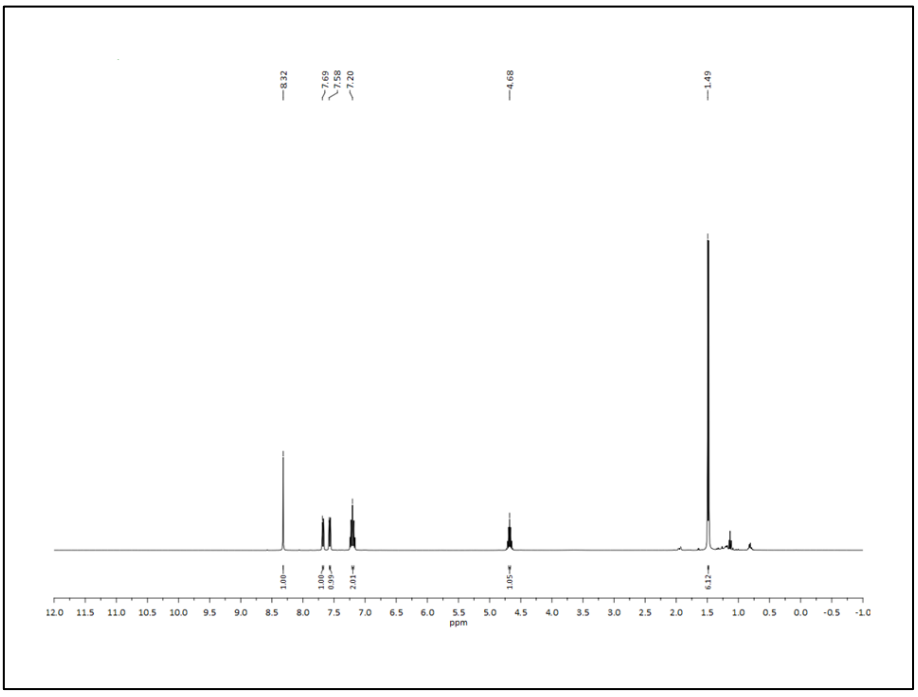


Figure S7. ^{1}H NMR of 1-isopropyl-1*H*-benzimidazole (L1)

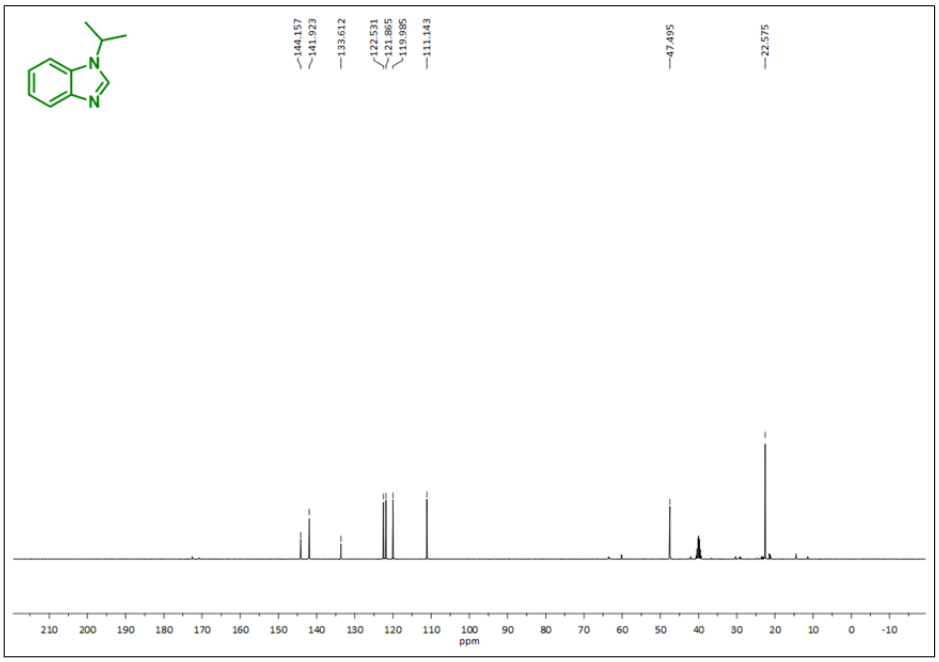


Figure S8. ^{13}C NMR of 1-isopropyl-1*H*-benzimidazole (L1)

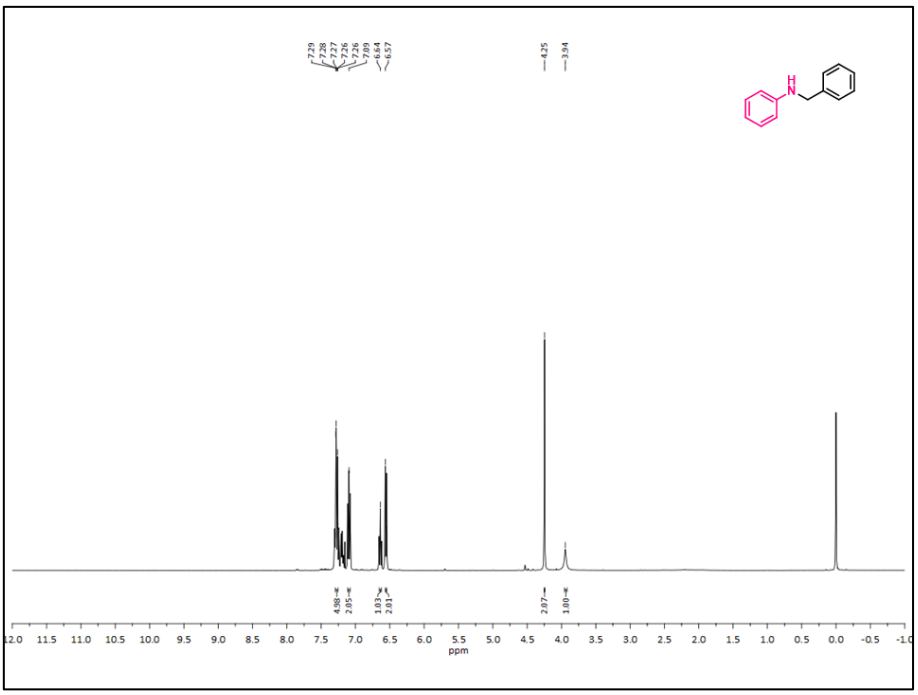


Figure S9. ^{1}H NMR of *N*-benzylaniline

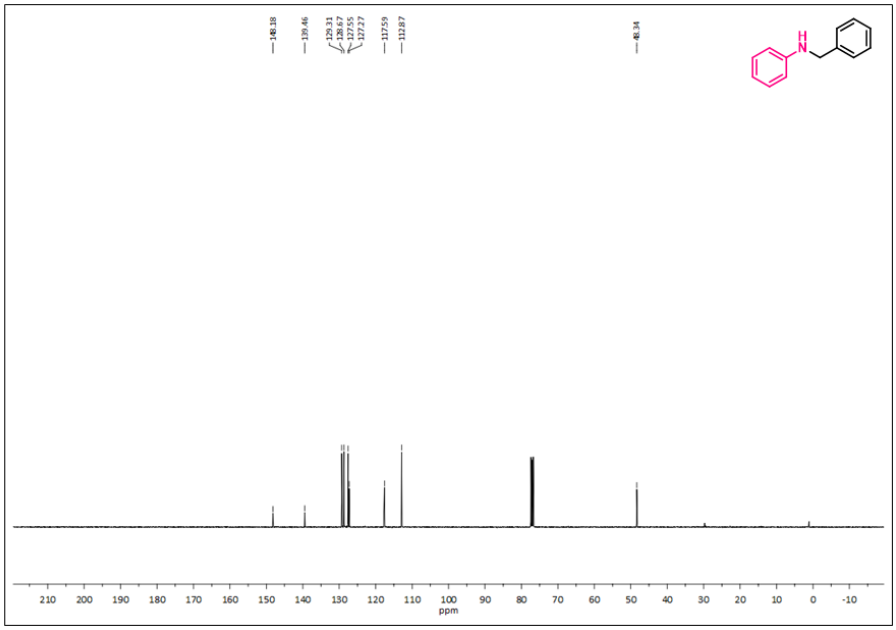


Figure S10. ^{13}C NMR of *N*-benzylaniline

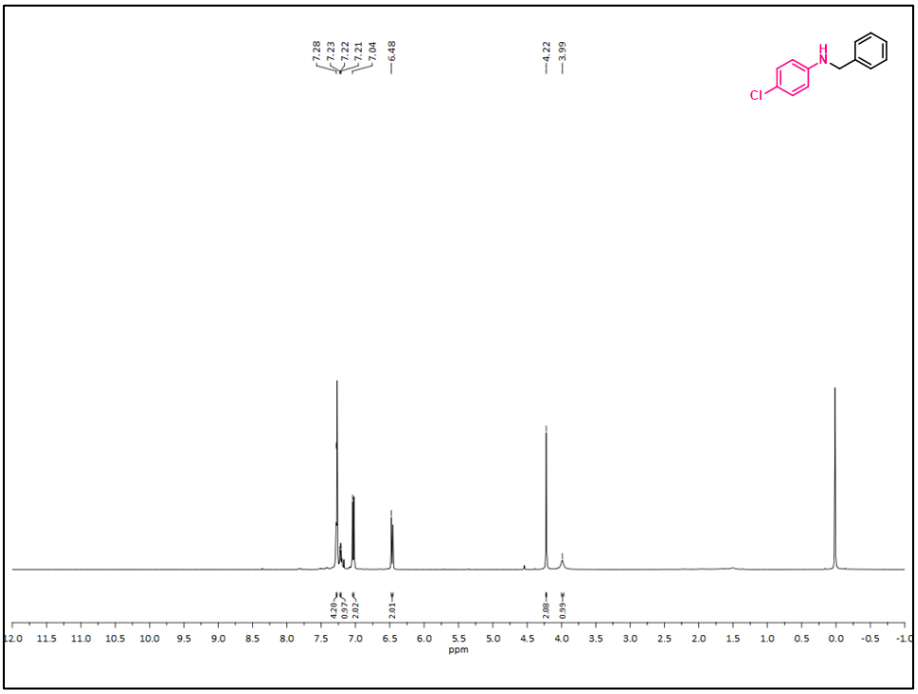


Figure S11. ^{1}H NMR of *N*-benzyl-4-chloroaniline

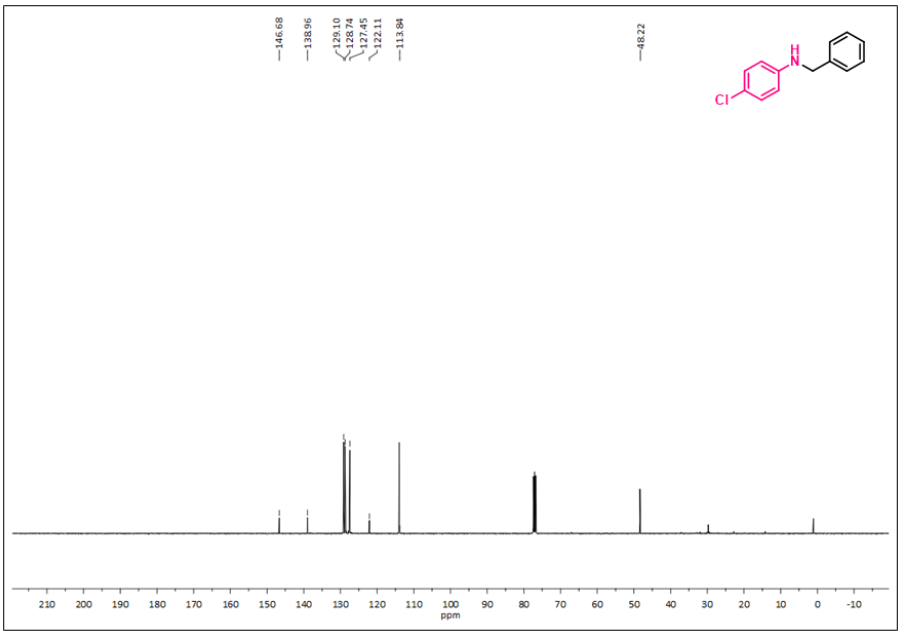


Figure S12. ^{13}C NMR of *N*-benzyl-4-chloroaniline

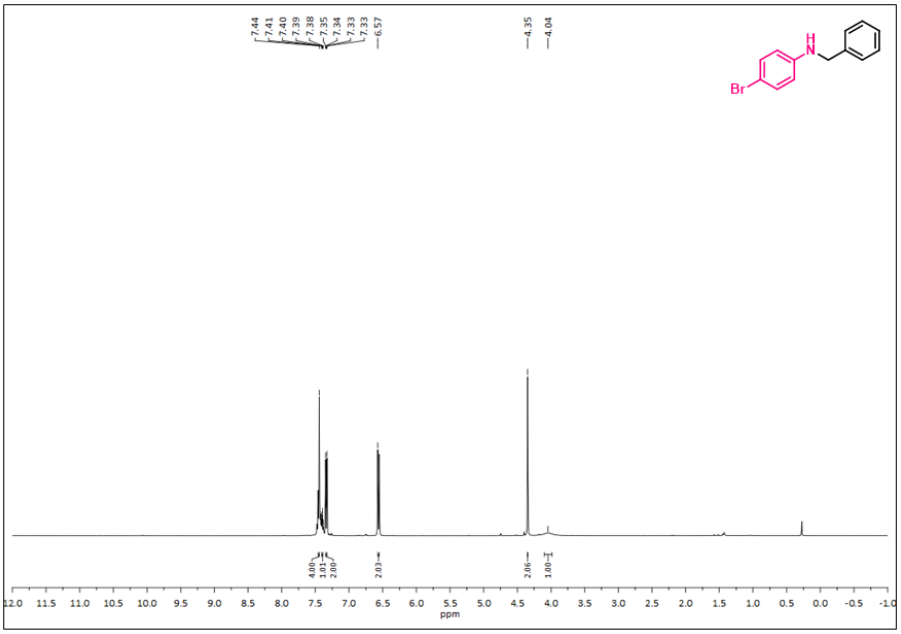


Figure S13. ^{1}H NMR of *N*-benzyl-4-bromoaniline

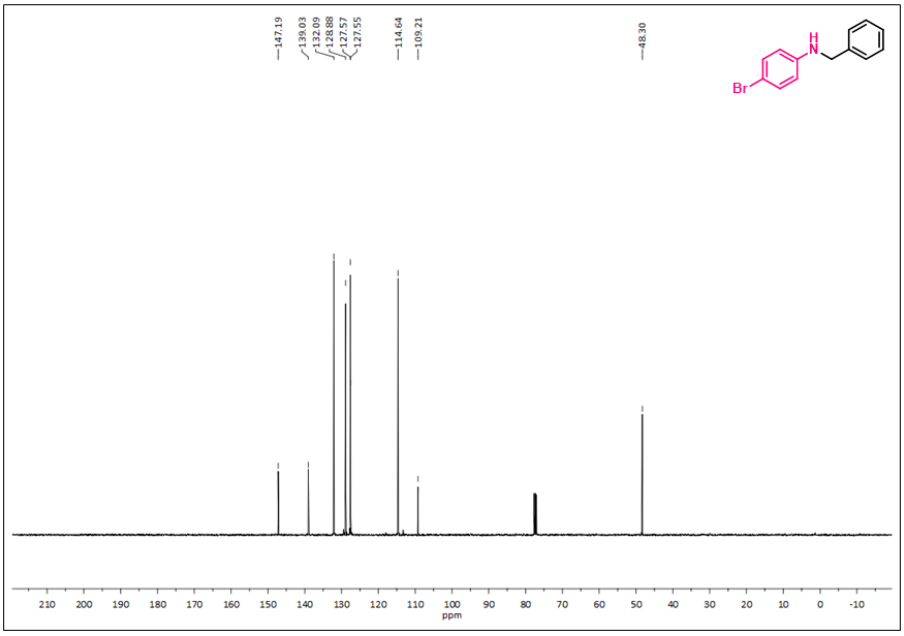


Figure S14. ^{13}C NMR of *N*-benzyl-4-bromoaniline

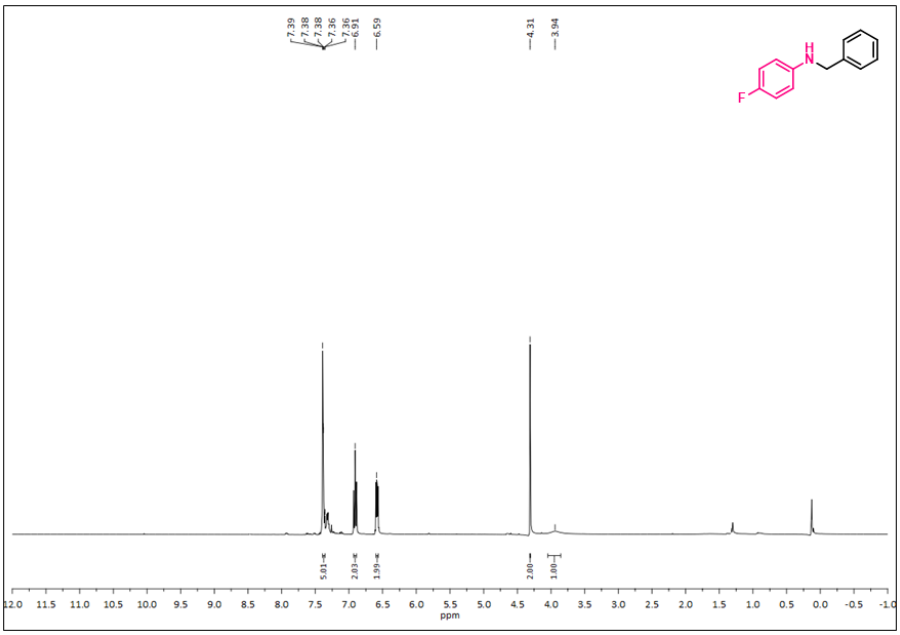


Figure S15. ^{1}H NMR of *N*-benzyl-4-fluoroaniline

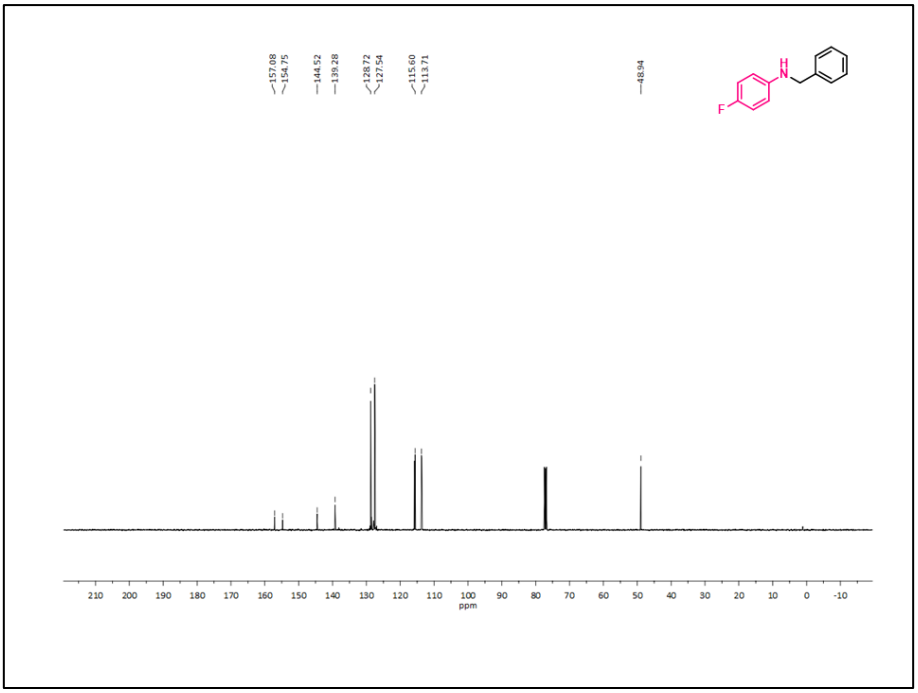


Figure S16. ^{13}C NMR of *N*-benzyl-4-fluoroaniline

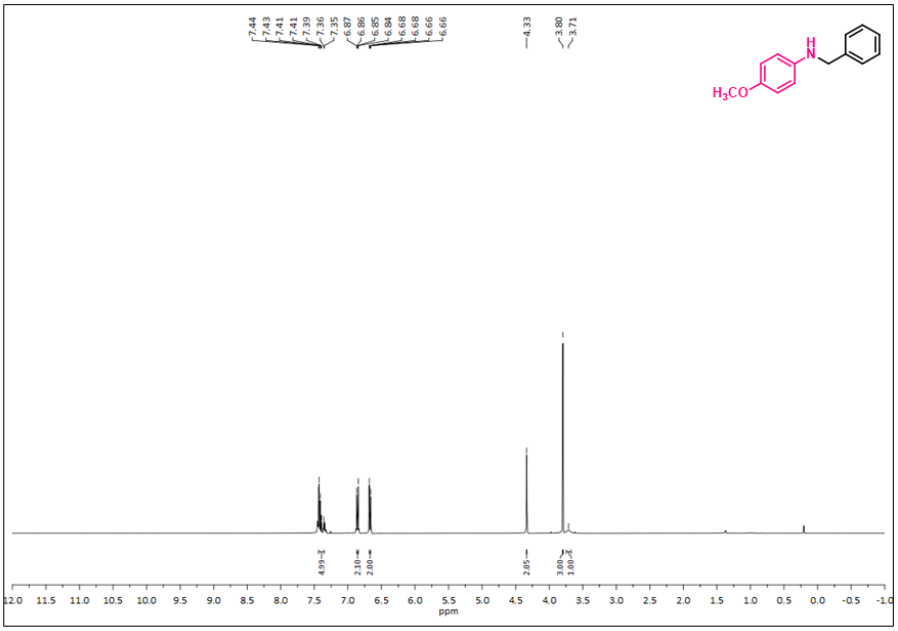


Figure S17. ^{1}H NMR of *N*-benzyl-4-methoxyaniline

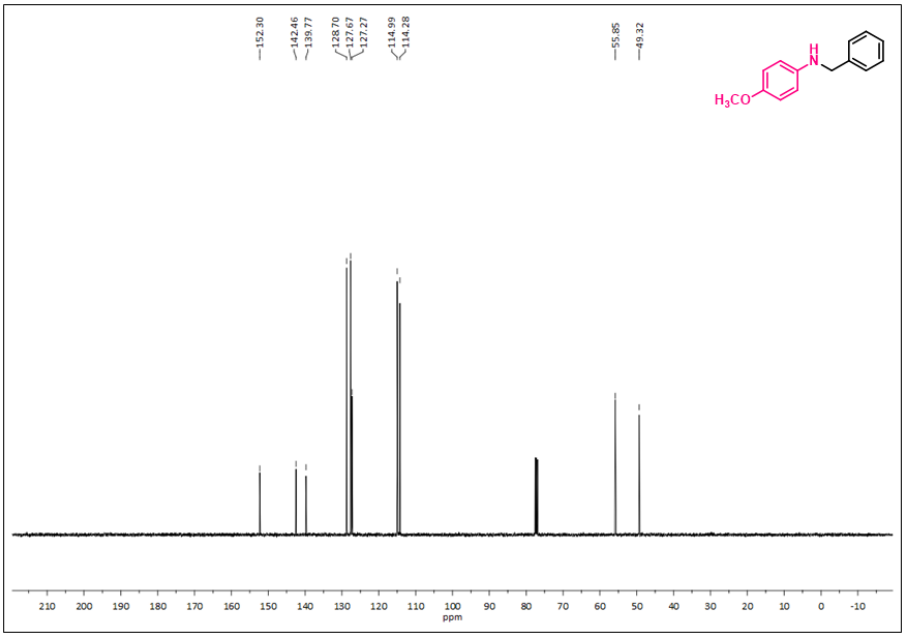


Figure S18. ^{13}C NMR of *N*-benzyl-4-methoxyaniline

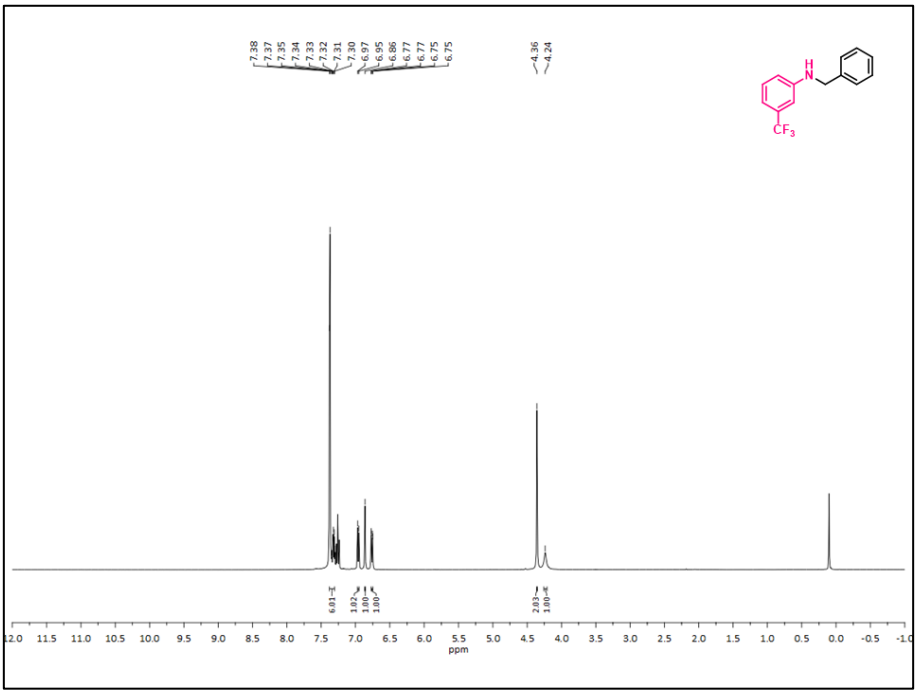


Figure S19. ^{1}H NMR of *N*-benzyl-3-(trifluroylmethyl)aniline

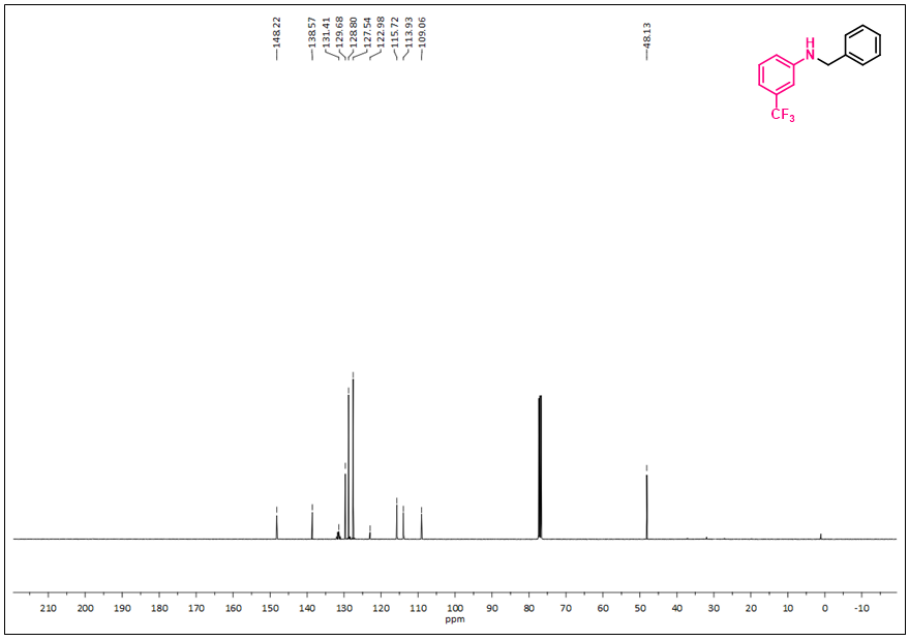


Figure S20. ^{13}C NMR of *N*-benzyl-3-(trifluroylmethyl)aniline

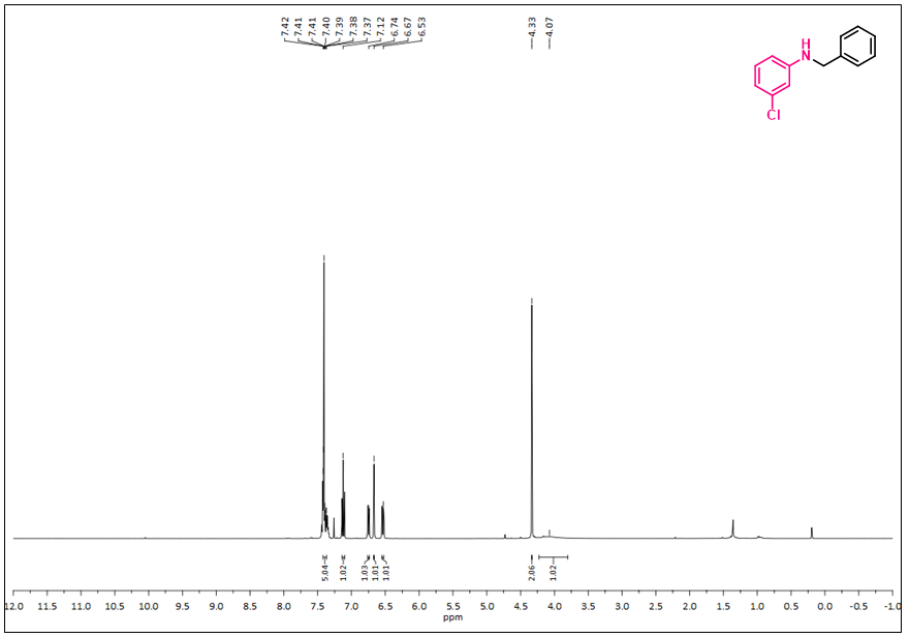


Figure S21. ^{1}H NMR of *N*-benzyl-3-chloroaniline

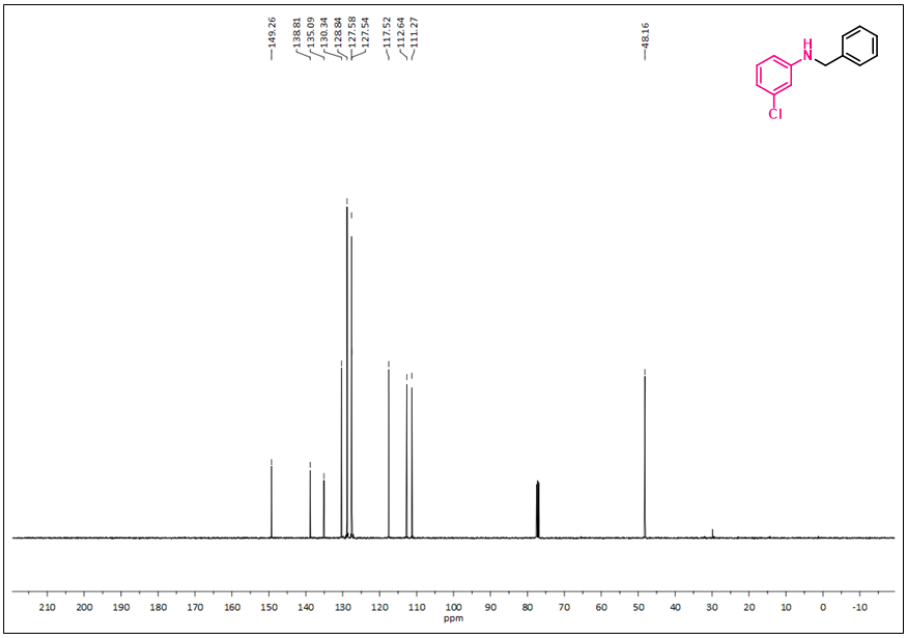


Figure S22. ^{13}C NMR of *N*-benzyl-3-chloroaniline

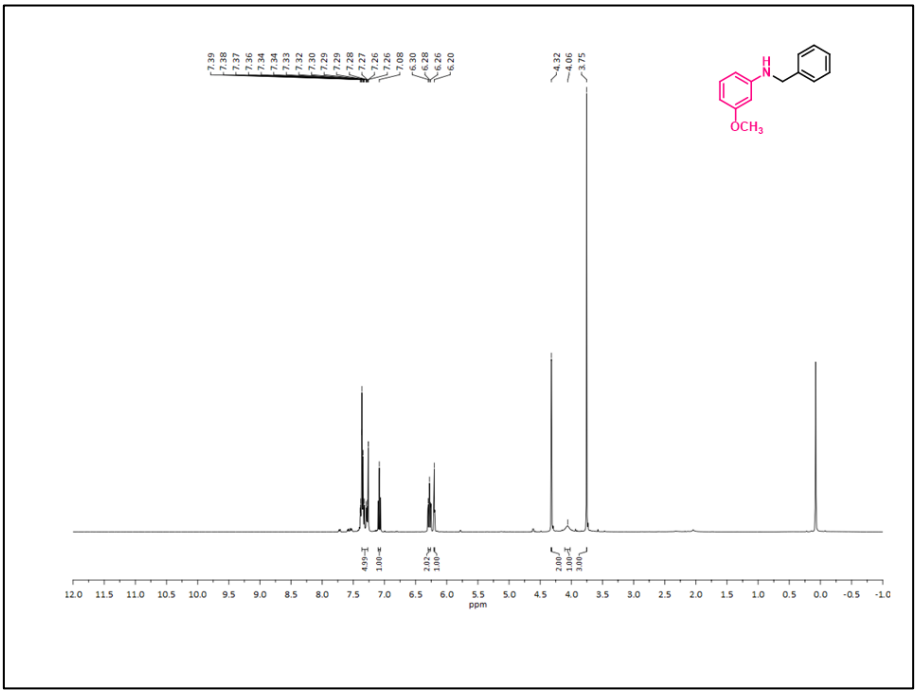


Figure S23. ^{1}H NMR of *N*-benzyl-3-methoxyaniline

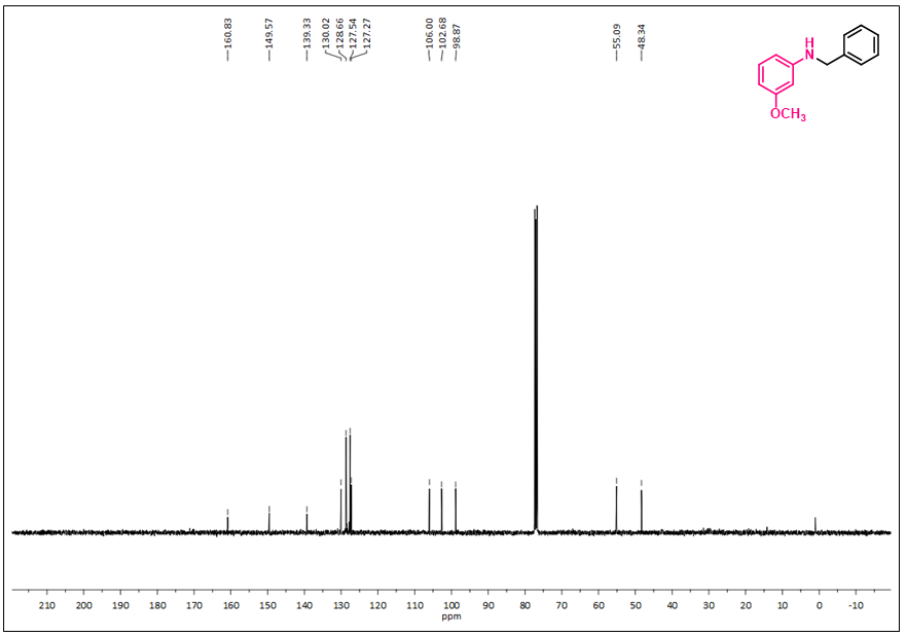


Figure S24. ^{13}C NMR of *N*-benzyl-3-methoxyaniline

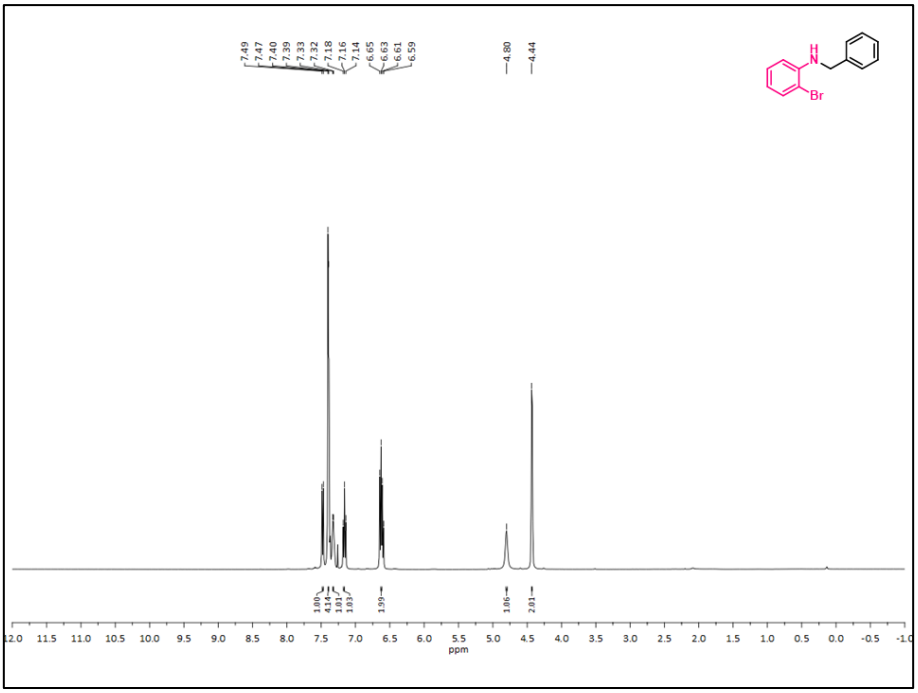


Figure S25. ^{1}H NMR of *N*-benzyl-2-bromoaniline

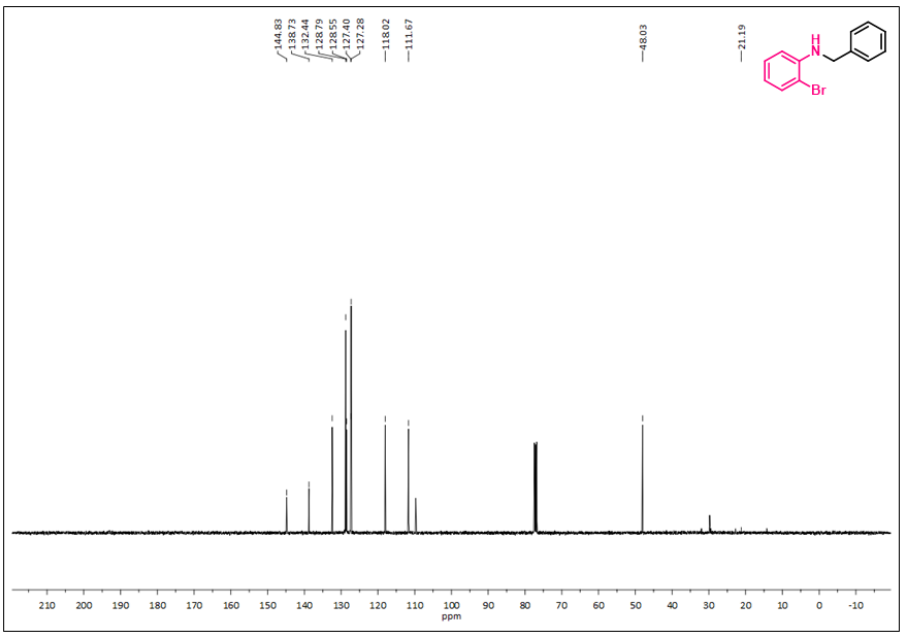


Figure S26. ^{13}C NMR of *N*-benzyl-2-bromoaniline

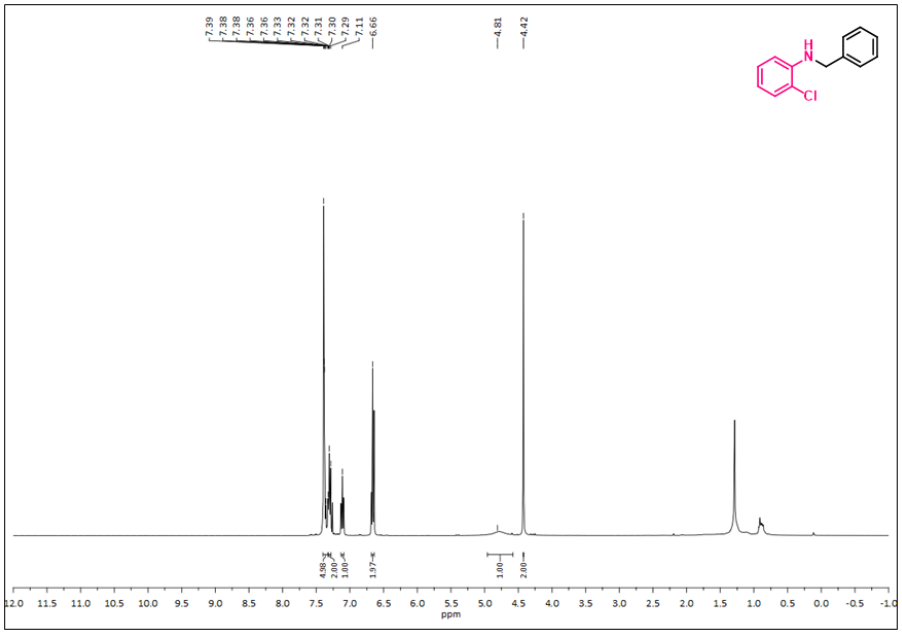


Figure S27. ^{1}H NMR of *N*-benzyl-2-chloroaniline

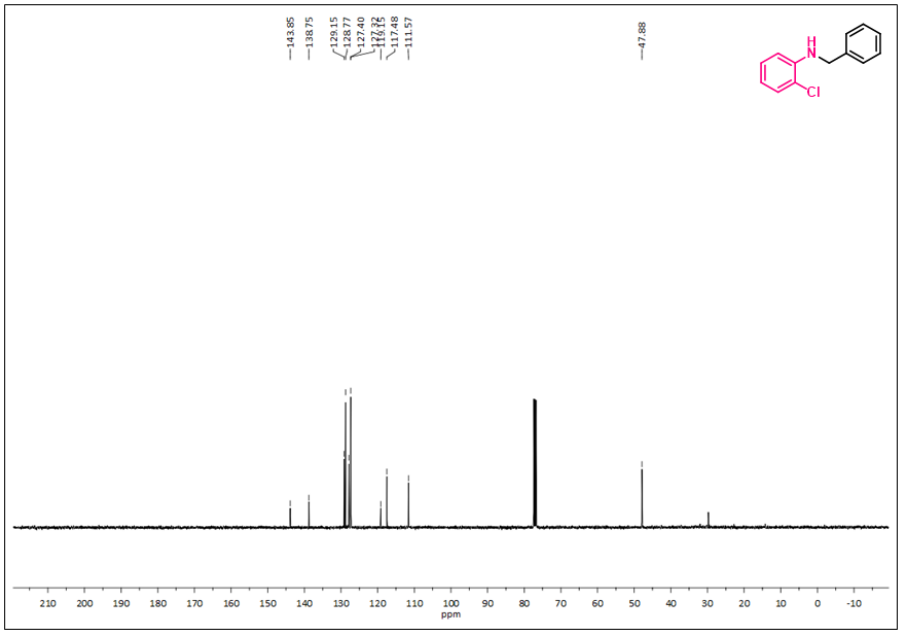


Figure S28. ^{13}C NMR of *N*-benzyl-2-chloroaniline

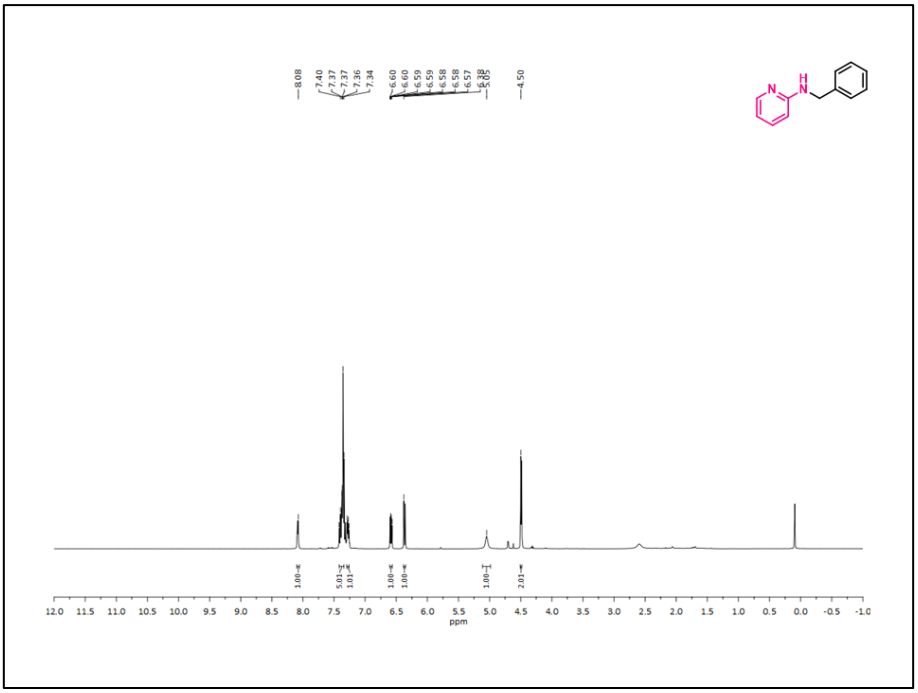


Figure S29. ^{1}H NMR of *N*-benzyl-(2-pyridyl)amine

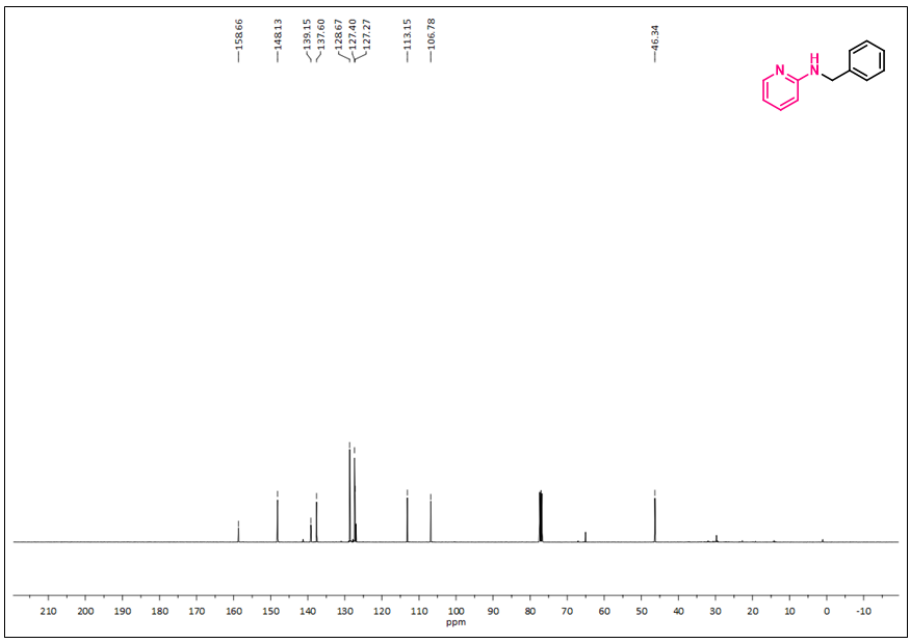


Figure S30. ^{13}C NMR of *N*-benzyl-(2-pyridyl)amine

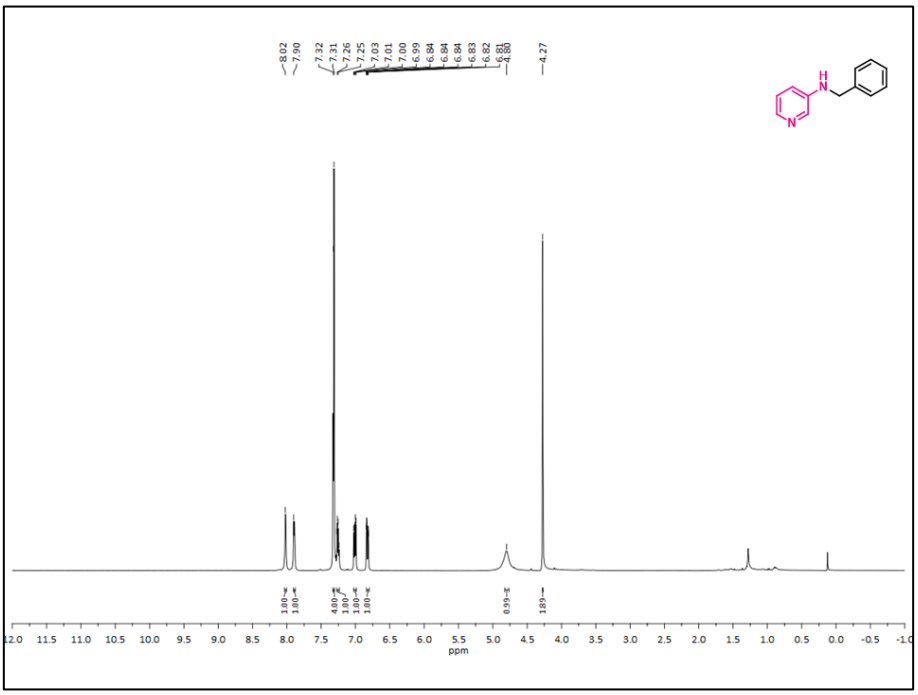


Figure S31. ^{1}H NMR of *N*-benzyl-(3-pyridyl)amine

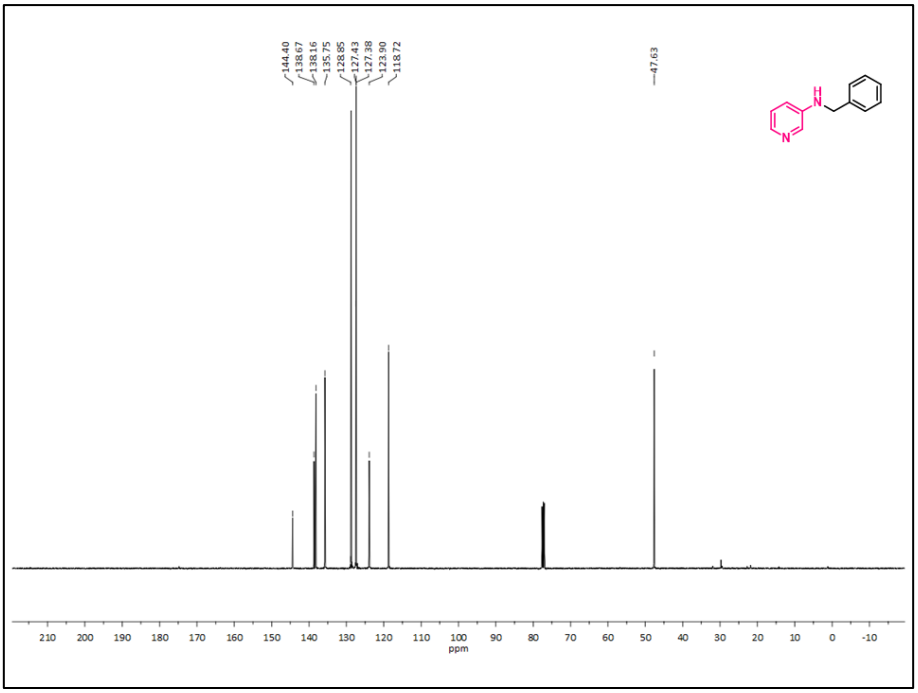


Figure S32. ^{13}C NMR of *N*-benzyl-(3-pyridyl)amine

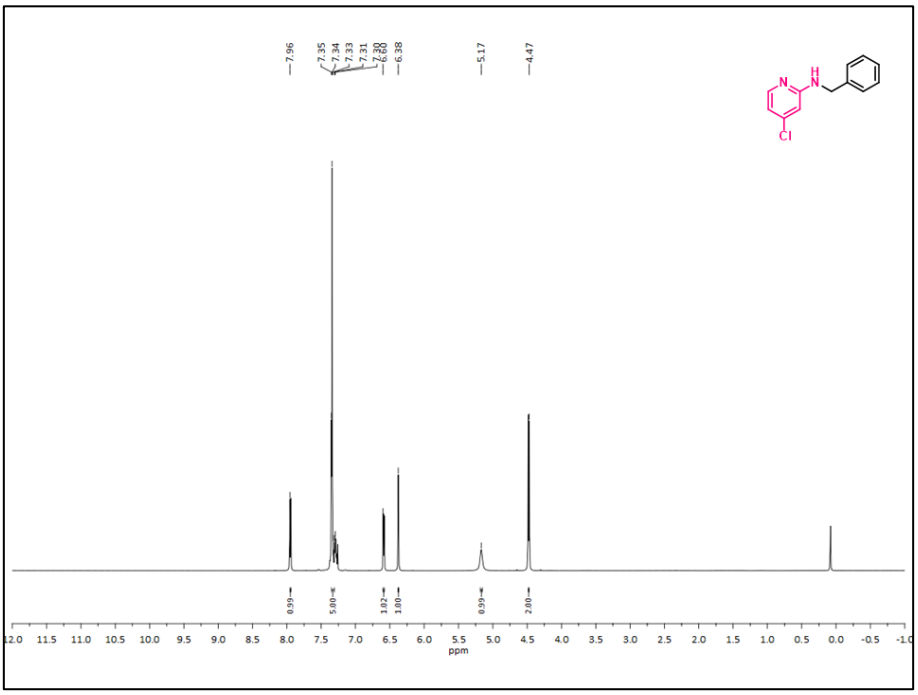


Figure S33. ^{1}H NMR of N-benzyl-4-chloropyridin-2-amine

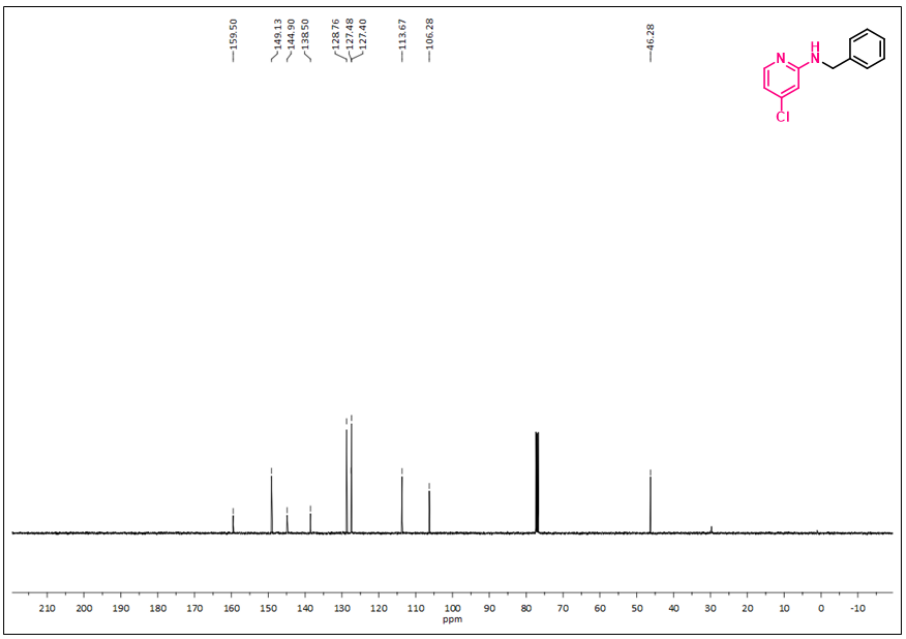


Figure S34. ^{13}C NMR of N-benzyl-4-chloropyridin-2-amine

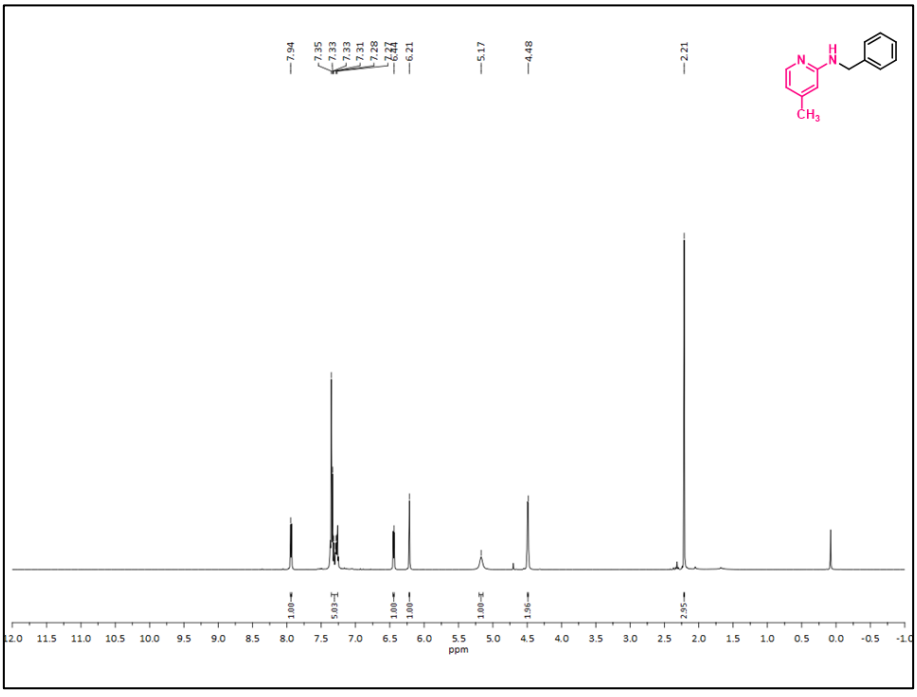


Figure S35. ^{1}H NMR of N-benzyl-4-methylpyridin-2-amine

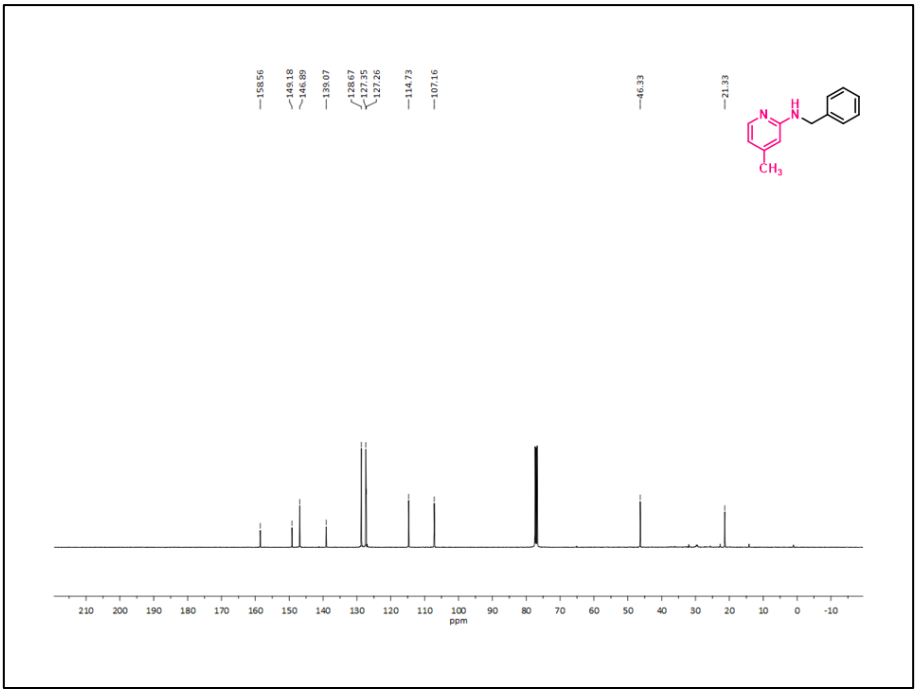


Figure S36. ^{13}C NMR of N-benzyl-4-methylpyridin-2-amine

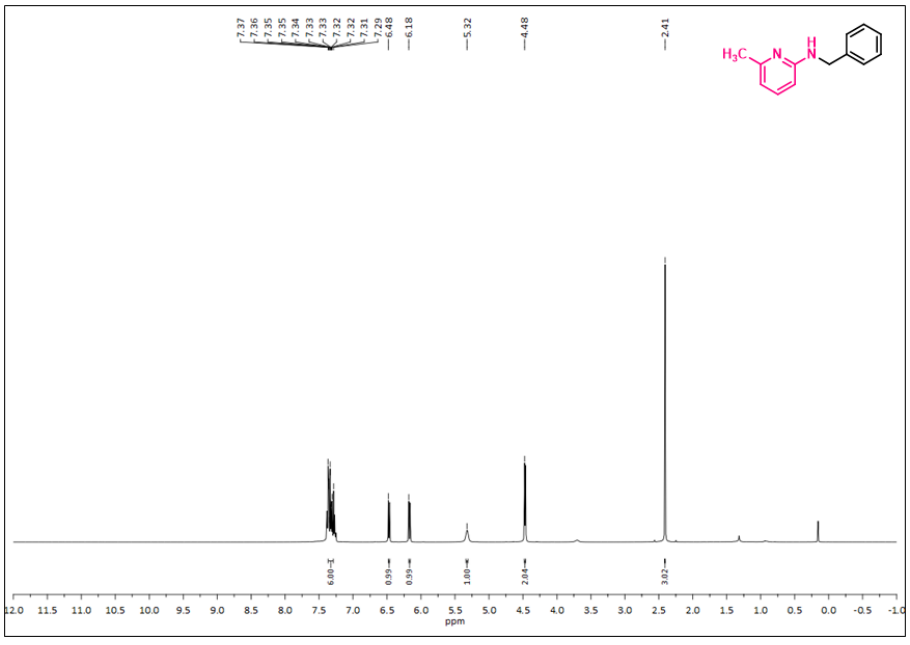


Figure S37. ^{1}H NMR of N-benzyl-6-methylpyridin-2-amine

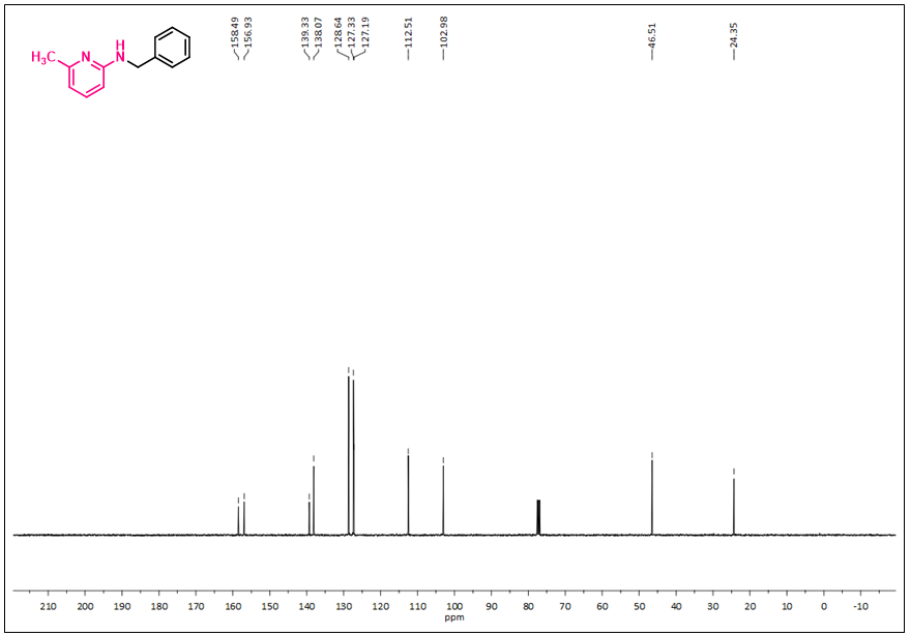


Figure S38. ^{13}C NMR of N-benzyl-6-methylpyridin-2-amine

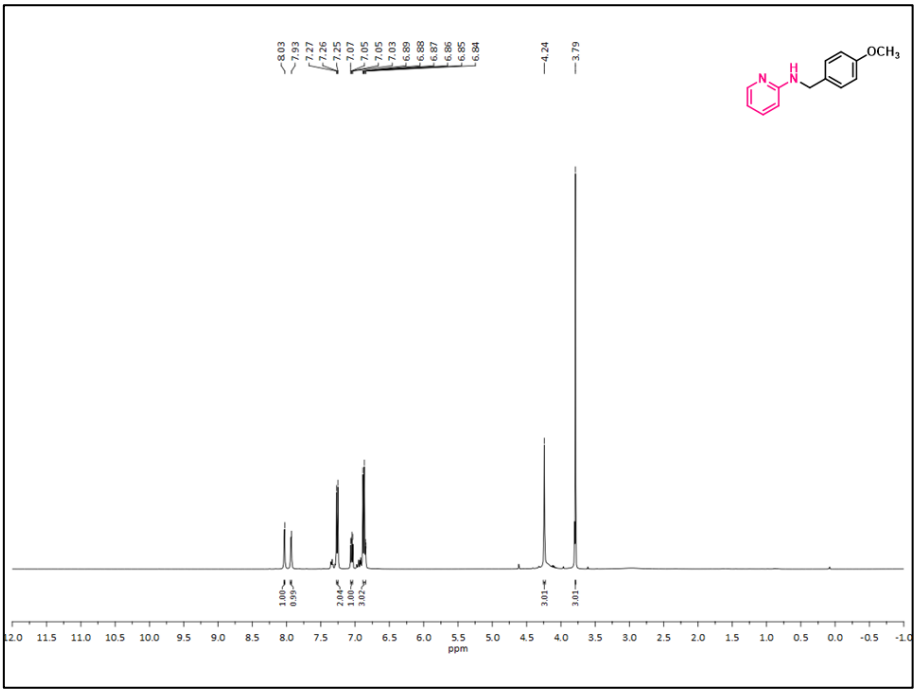


Figure S39. ^{1}H NMR of *N*-(4-methoxybenzyl)pyridine-3-amine

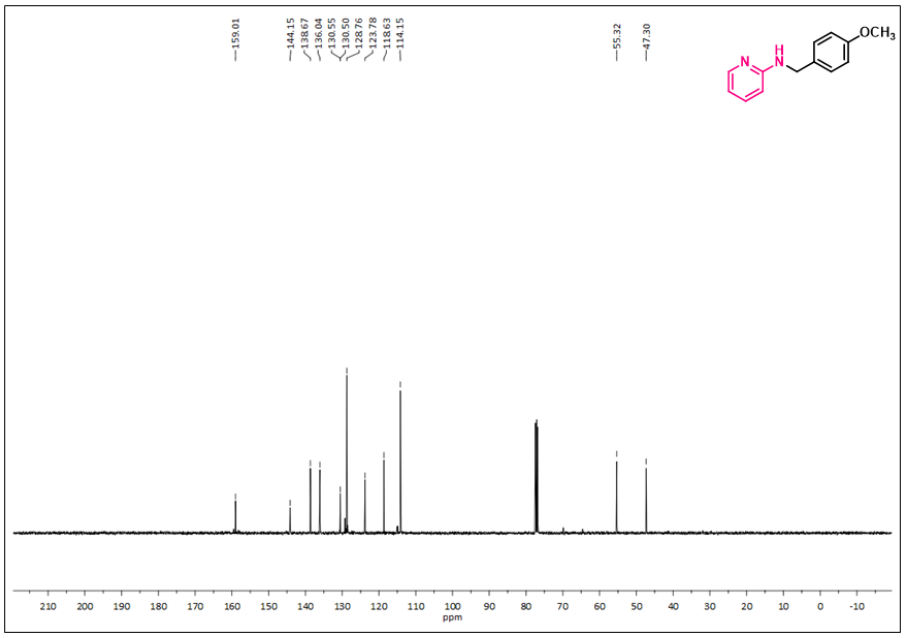


Figure S40. ^{13}C NMR of *N*-(4-methoxybenzyl)pyridine-3-amine

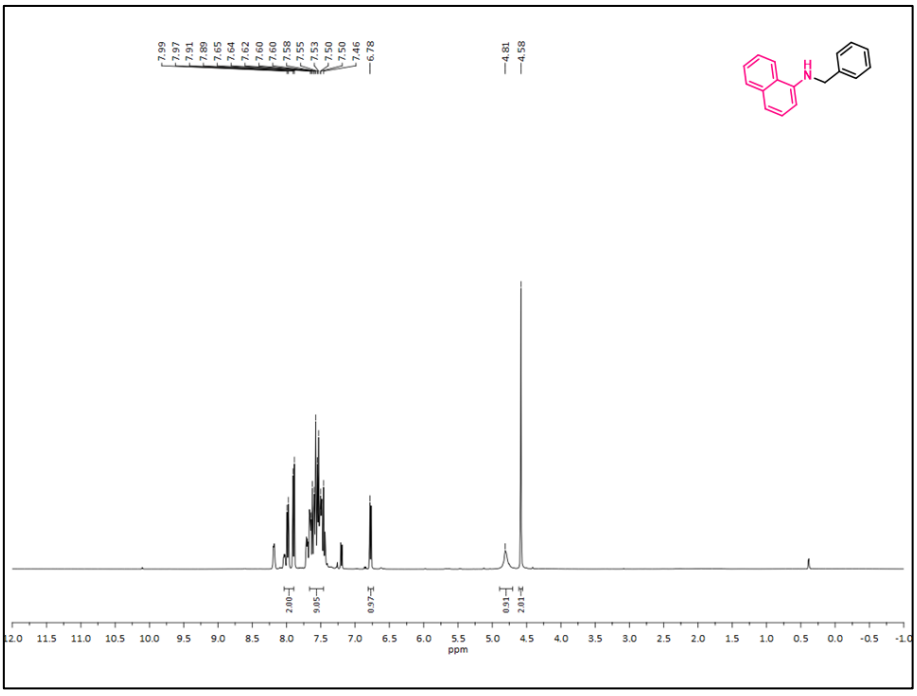


Figure S41. ^{1}H NMR of N-Benzylnaphthalen-1-amine

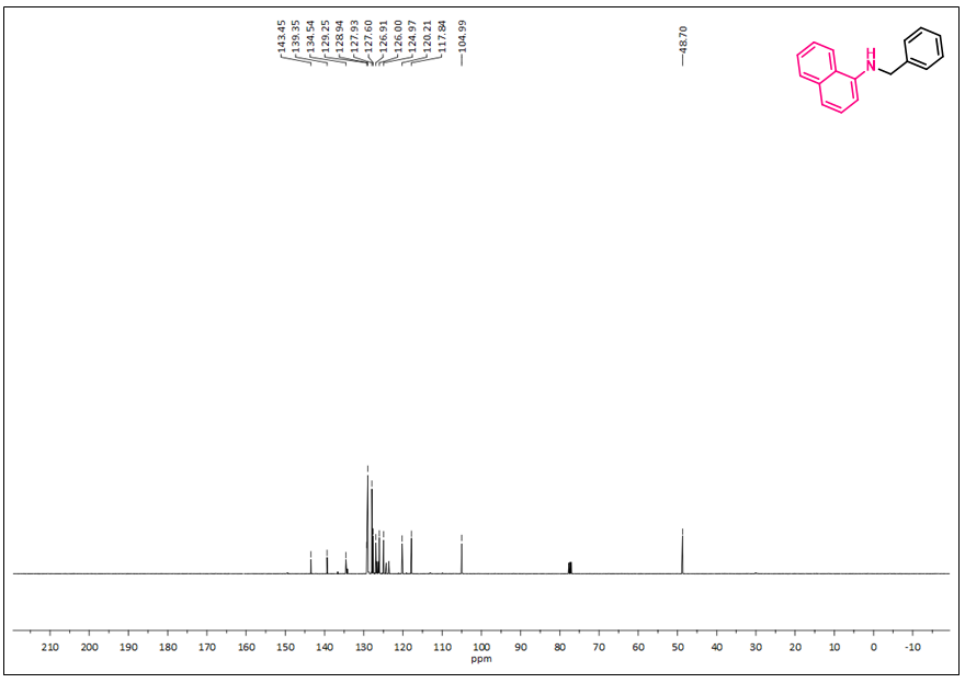


Figure S42. ^{13}C NMR of N-Benzylnaphthalen-1-amine

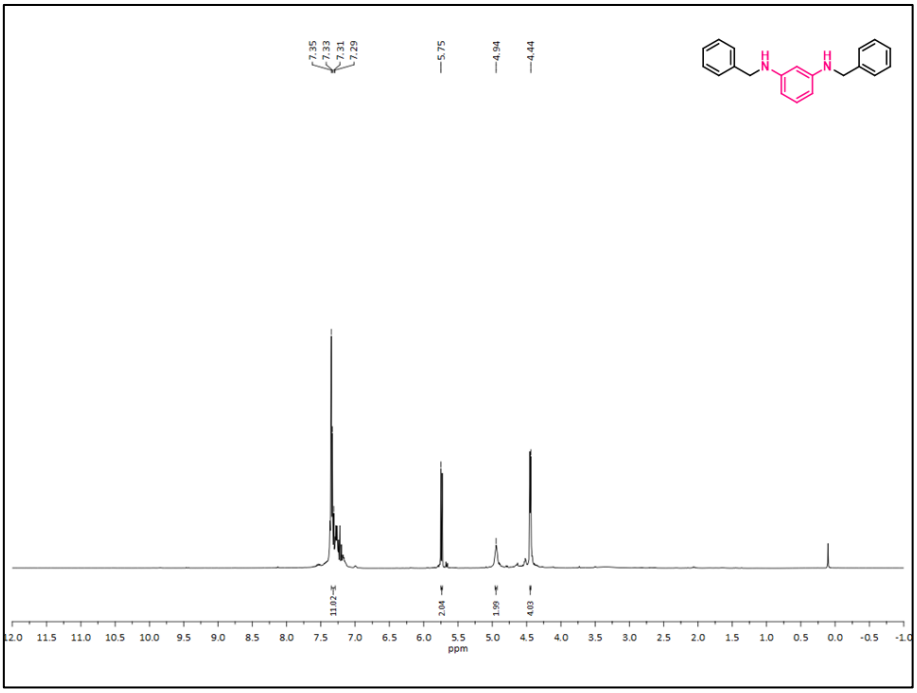


Figure S43. ^{1}H NMR of *N,N'*-Dibenzylpyridine-2,6-diamine

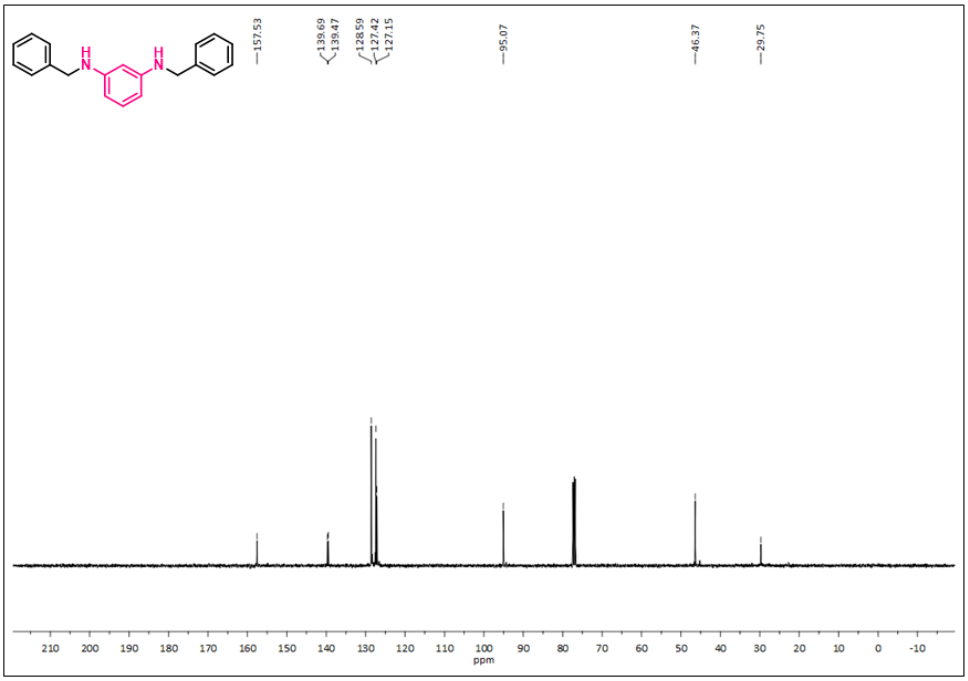


Figure S44. ^{13}C NMR of *N,N'*-Dibenzylpyridine-2,6-diamine

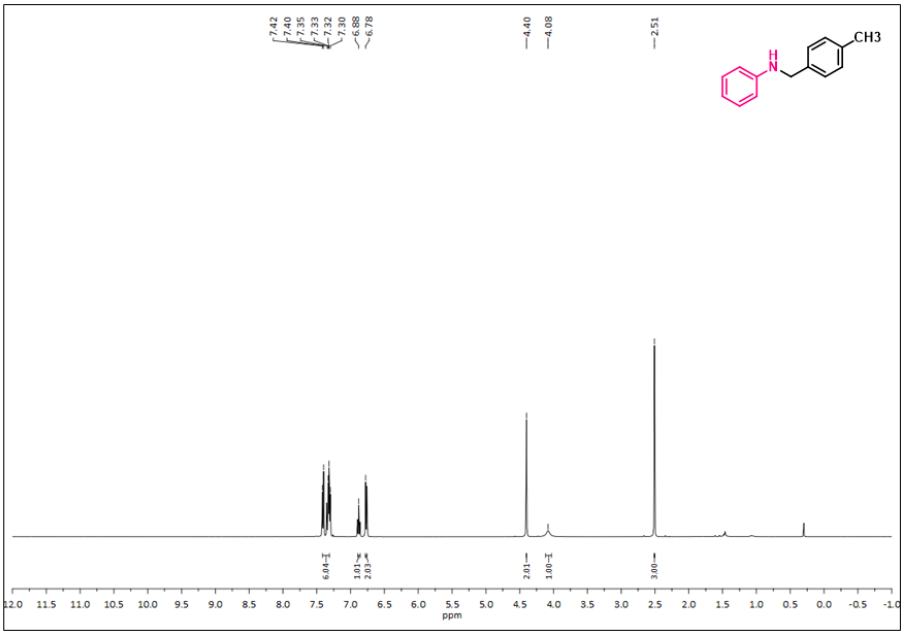


Figure S45. ^{1}H NMR of *N*-(4-methyl)benzylaniline

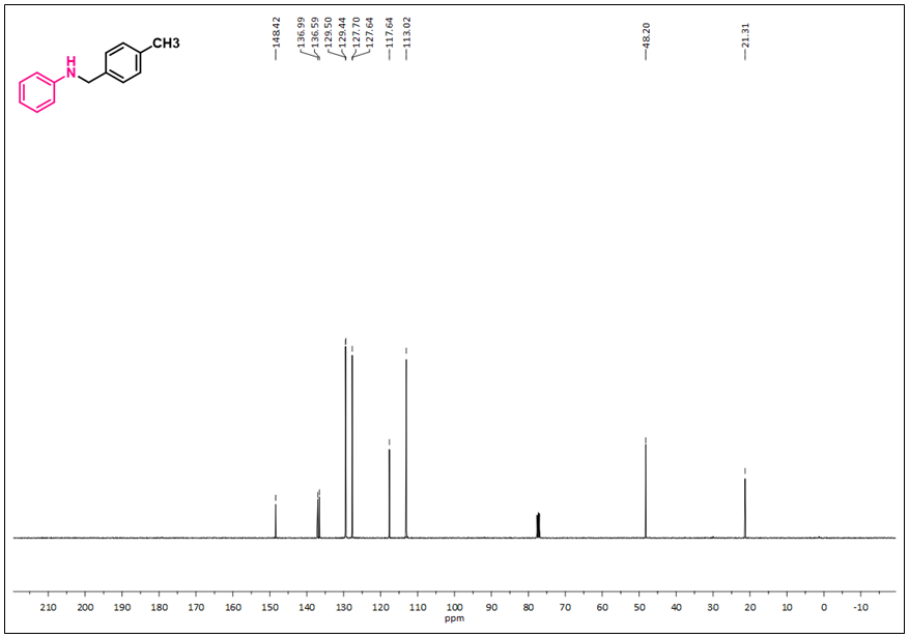


Figure S46. ^{13}C NMR of *N*-(4-methyl)benzylaniline

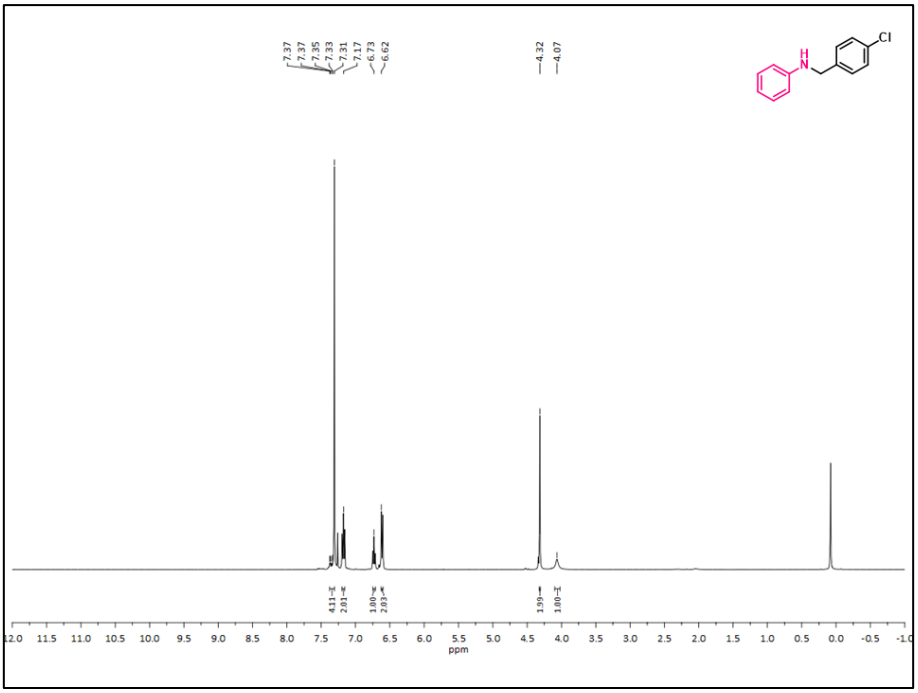


Figure S47. ^{1}H NMR of *N*-(4-chloro)benzylaniline

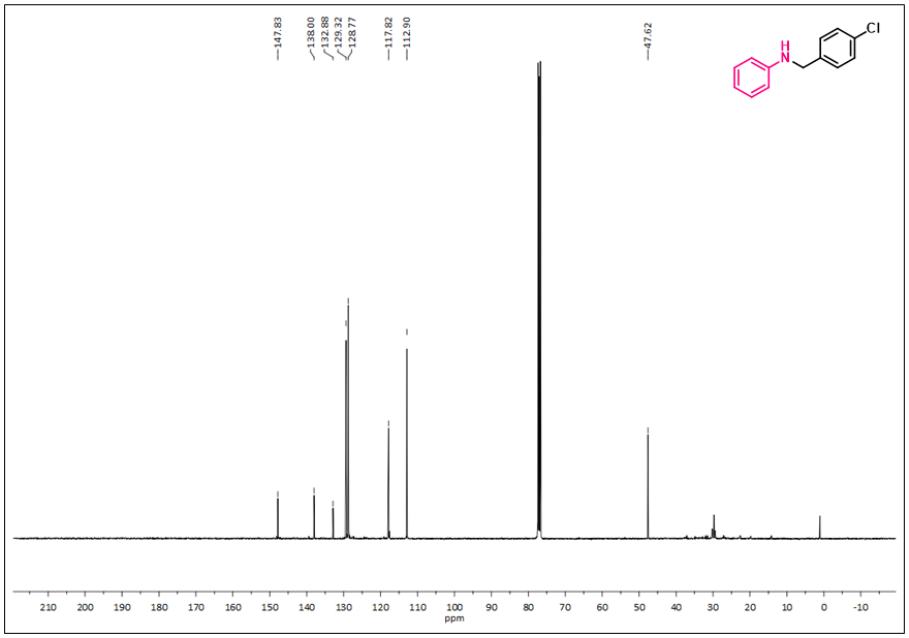
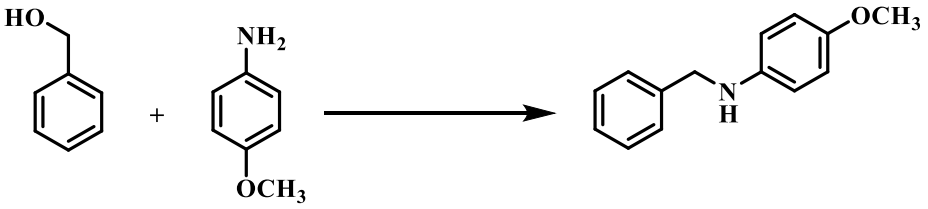


Figure S48. ^{13}C NMR of *N*-(4-chloro)benzylaniline



M.Wt (g/mol)	**108.14**	**123.15**	**213.12**
mmol	**1**	**1**	**0.959**
Amount (g)	**0.112**	**0.123**	**0.204**

Figure S49. Green Chemistry Metric calculation

a) E-factor: $$\frac{(\text{total mass of stiochiomtric reactant}) - (\text{total mass of product formed})}{\text{Mass of product}}$$

$$= \frac{(0.112+0.123)-0.204}{0.204}$$

$$= 0.15$$

b) Atom economy: $$\frac{(\text{M.Wt of product})}{\sum(\text{M.Wt of stiochiometric reactants})} \times 100$$

$$= \frac{213.12}{108.14+123.15} \times 100$$

$$= 92.14\%$$

c) Carbon efficiency: $\frac{[(\text{No.of moles of product})(\text{No.of carbons in product})}{\sum[(\text{No.of moles of reactant})(\text{No.of carbon in reactant})]} \times 100$

$$= \frac{0.959 \times 14}{(1 \times 7)+(1 \times 7)} \times 100$$

$$=95.9\%$$

d) Process mass intensity: $\frac{\sum(\text{mass of stiochiometric reactants})}{\text{mass of products}}$

$$= \frac{0.112+0.123}{0.204}$$

$$=1.15$$

Alternatively Process mass intensity = E-factor+1

$$= 0.15+1$$

$$=1.15$$

e) Reaction mass efficiency: $\frac{\text{mass of product}}{\sum(\text{mass of stiochiometric reactants})} \times 100$

$$= \frac{0.204}{0.112+0.123} \times 100$$

$$= 86.80\%$$

References

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65. Yu, X.; Jiang, L.; Li, Q.; Xie, Y.; Xu, Q. Palladium-Catalyzed *N*-Alkylation of Amides and Amines with Alcohols Employing the Aerobic Relay Race Methodology. *Chin. J. Chem.* **2012**, *30*, 2322–2332. https://doi.org/10.1002/cjoc.201200462.
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