

Supplementary Materials

Facile Synthesis of COF-Supported Reduced Pd-based Catalyst for One-Pot Reductive Amination of Aldehydes

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General methods

All reactions were conducted under dry nitrogen atmosphere using magnetic stirring. The solvent EtOH (AR, water $\leq 0.3\%$), DMF (Biotechnology grade, $\geq 99.9\%$), CH_2Cl_2 (Standard for GC, $\geq 99.7\%$, 50–150 ppm Isoamylene stabilizer), MeOH ($\geq 99.9\%$ (GC)) using in this research were bought from Shanghai Aladdin Bio-Chem Technology Co., LTD and used directly without any further purification.

GC of products was recorded by GC-2014C (Shimadzu, Japan) with HP5 column (30 m $\times$ 250 μm $\times$ 0.25 μm) and FID detector. GC-MS of products was determined by TRACE 1300ISQ GC-MS (Thermo Fisher Scientific, America) with TG-5MS column (30 m $\times$ 250 μm $\times$ 0.25 μm). ^1H NMR spectra were recorded on a Bruker 400 at 400 MHz in CDCl_3 and referenced internally to the residual CHCl_3 peak (7.26 ppm). ^{13}C NMR spectra were recorded at 75 MHz in CDCl_3 and referenced to the central peak of CDCl_3 (77.0 ppm). Chemical shifts are reported in ppm (δ scale). Powder X-ray diffraction (XRD) patterns were recorded by an X'Pert Pro system, using $\text{Cu-K}\alpha$ radiation with a $\Delta 2\theta = 0.02^\circ$ in the 2.5° to 50° 2θ range (X'Pert PRO MPD, PANalytical, Netherlands). X-ray photoelectron spectroscopy (XPS) was recorded with an AXIS Ultra DLD (Kratos, Britain) and the standard C 1s peak was used as a reference for correcting the shifts. Field-emission scanning electron microscope (FESEM) images were acquired on a JEOL JSM-6700 electron microscope (JEOL, Japan). Fourier Transform infrared spectroscopy (FTIR) was mainly used for group structure analysis of materials, qualitative and quantitative analysis of materials, especially qualitative analysis of the functional group characteristic absorption frequency. IR spectra were recorded on a Bruker Tensor 27 spectrometer with dried KBr (Berlin, Germany). The N_2 adsorption-desorption isotherms were measured with a Tristar 3010 isothermal nitrogen sorption analyzer (Micromeritics, Florida, USA) at 77 K after the samples were degassed in a vacuum at 120 $^\circ\text{C}$ for 10 h.

General procedure for SJ02, Pd-SJ04 and Reduced COF-supported Pd-SJ04 catalysts synthesis

1.1. Synthesis of SJ02.

The SJ02 was synthesized by reacting 2,4,6-Trihydroxy-benzene-1,3,5-tricarbaldehyde (200 mg, 0.92 mmol) with 6-(5-aminopyridin-2-yl)pyridin-3-amine (215.2 mg, 1.11 mmol) for 1 h in presence of anhydrous ethanol (60 mL) at room temperature. The reaction products were gathered and dispersed into DMF at 153 $^\circ\text{C}$ –160 $^\circ\text{C}$ for 4 h. After isolated by filtration, the resulting powder was then immersed in anhydrous ethanol at 80 $^\circ\text{C}$ for 2 h. Finally, the powder material was dried under vacuum condition and heated at 80 $^\circ\text{C}$ for 24 h.

1.2. Synthesis of Pd-SJ04.

Pre-synthesized SJ02 (165 mg) was dispersed in 10–20 mL of CH_2Cl_2 , and $\text{Pd}(\text{OAc})_2$ (20 mg, 0.089 mmol) was added. The reaction mixture was stirred at temperature for 24 h. Then the residue was recovered by filtration and washed with CH_2Cl_2 in Soxhlet extractor for 24 h. Finally, the so prepared sample of Pd-SJ04 was further dried at 80 $^\circ\text{C}$ in vacuum drying oven.

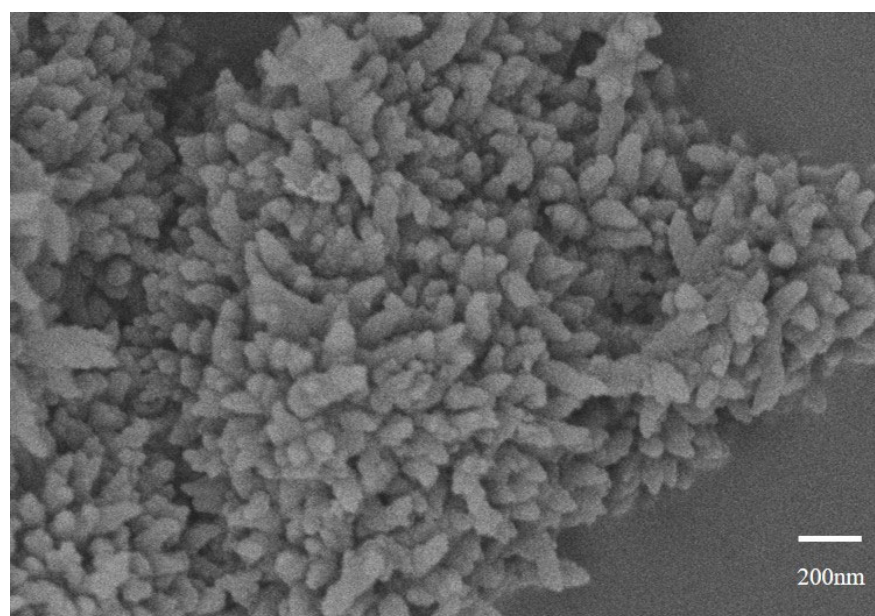
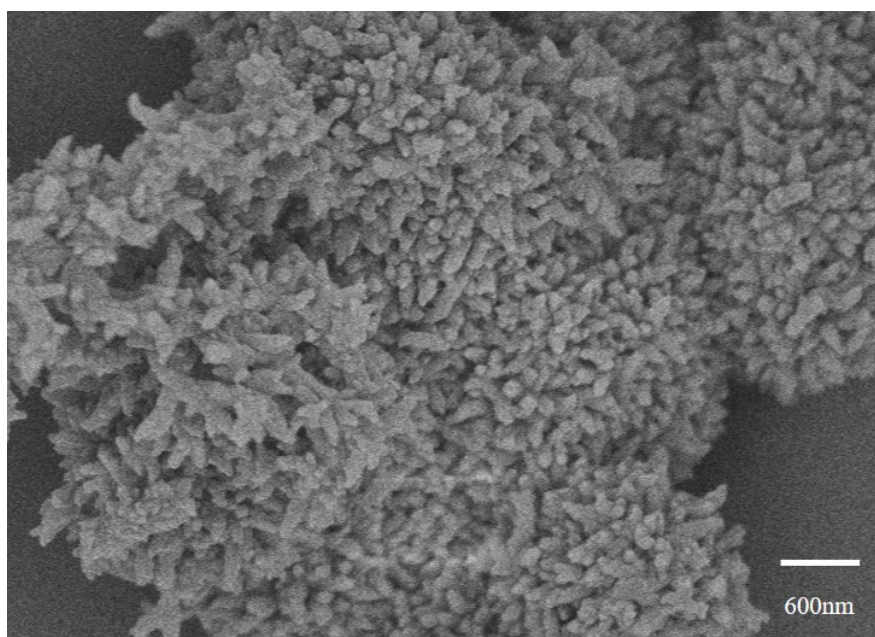
1.3. Synthesis of Reduced COF-supported Pd-SJ04

The Pd-SJ04 (148 mg) and sodium borohydride (3.97 mg, 1.5 times the molar amount of Pd) are stirred in methanol solution for 24 h. Finally, Reduced COF-supported Pd-SJ04 was further dried at 90 $^\circ\text{C}$ for 12 h under vacuum.

1.4. General procedure for catalytic reductive amination reaction

In a typical run for catalytic activity test of Reduced COF-supported Pd-SJ04, to a high-pressure reaction kettle with Teflon coated stir bar, purged with hydrogen, was transferred aldehyde substance (0.5 mmol), Reduced COF-supported Pd-SJ04 catalyst (5 mg) and 2M methanol ammonia

solution (5 mL). The reaction mixture was filled with hydrogen to 1–3 MPa, and then the reactor was allowed to vigorously stir at 50–110 °C for a reasonable time (2–12 h). The whole reaction is carried out in the reactor produced by KEMI. After the reaction was carried out at the setting time, the product was obtained and was analysis directly. Conversions and selectivity were determined by ¹H NMR spectroscopy or GC chromatography.



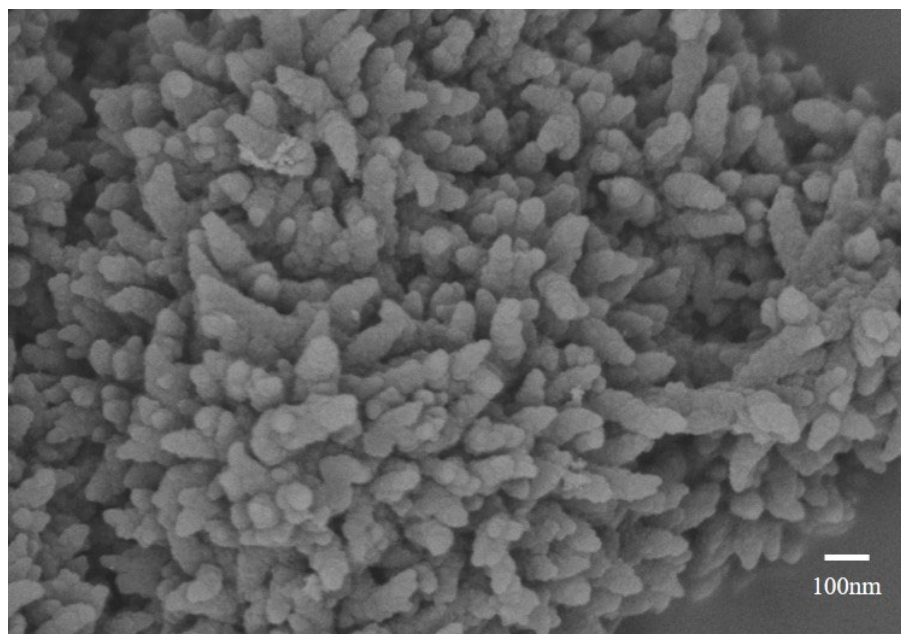


Figure S1. SEM images of Reduced COF-supported Pd-SJ04.

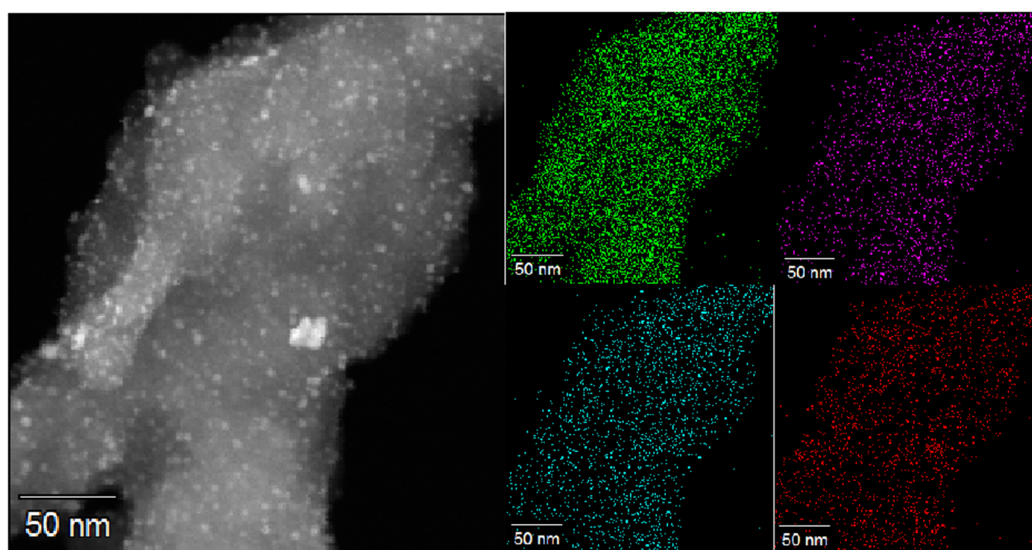


Figure S2. TEM mapping of Reduced COF-supported Pd-SJ04.

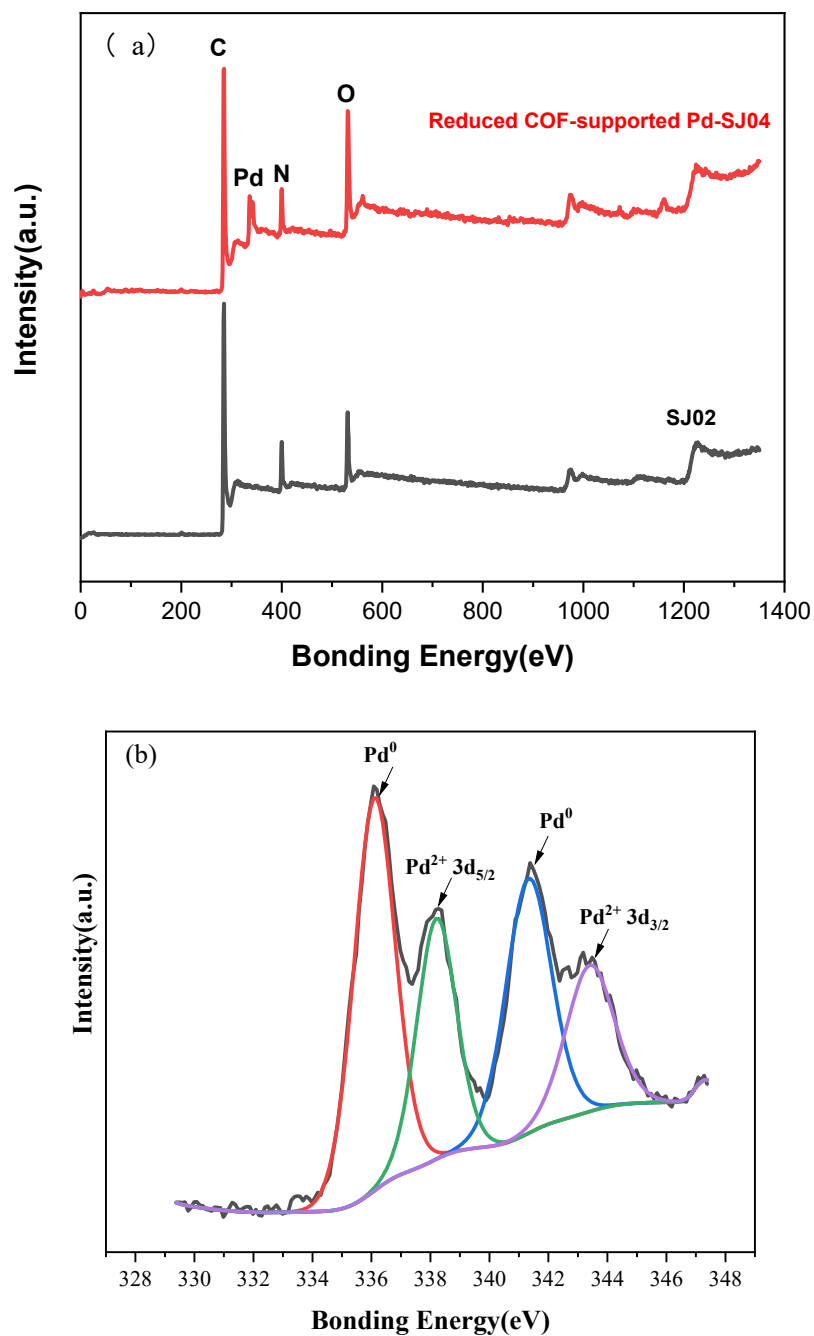


Figure S3. (a) The survey spectra and (b) high-resolution XPS spectra of Pd3d for Reduced COF-supported Pd-SJ04.

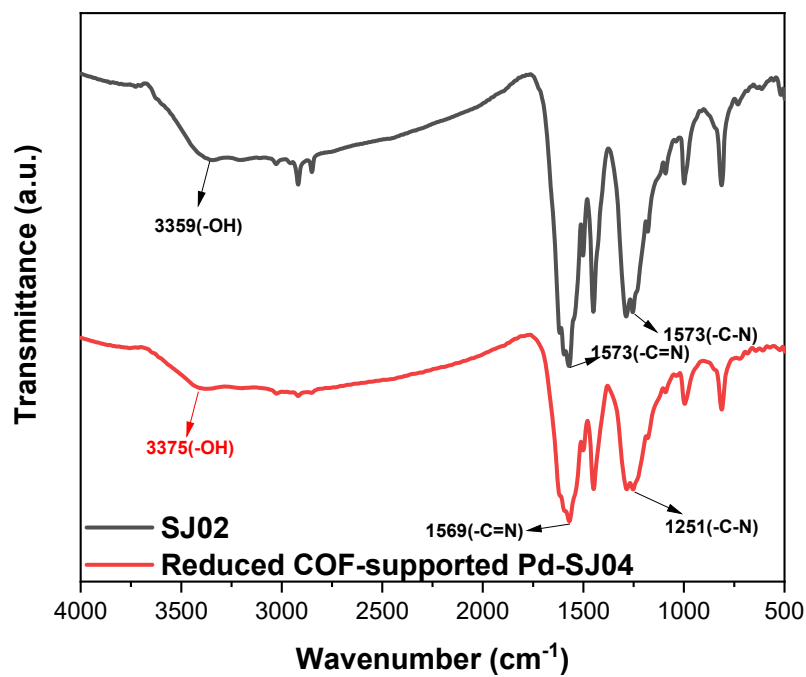


Figure S4. The FTIR spectra of SJ-02 and Reduced COF-supported Pd-SJ04.

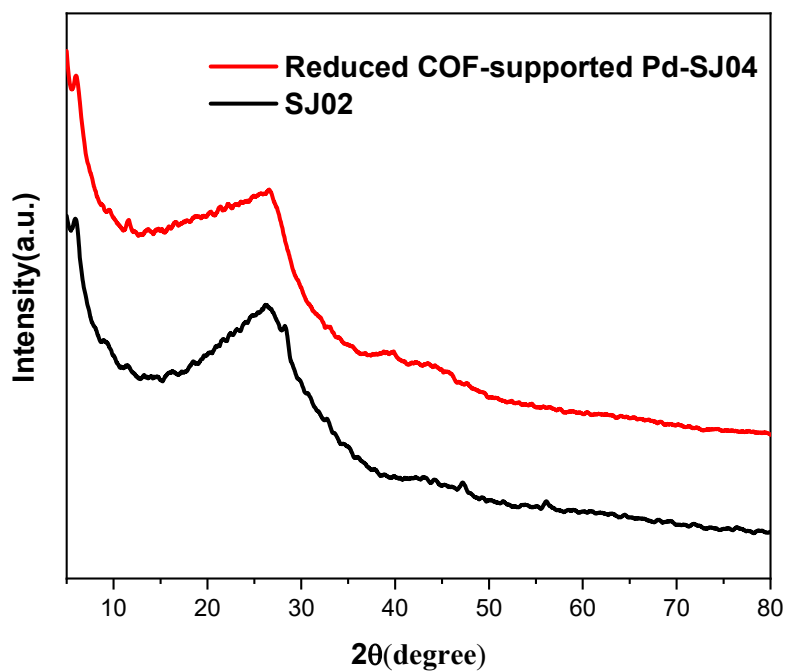


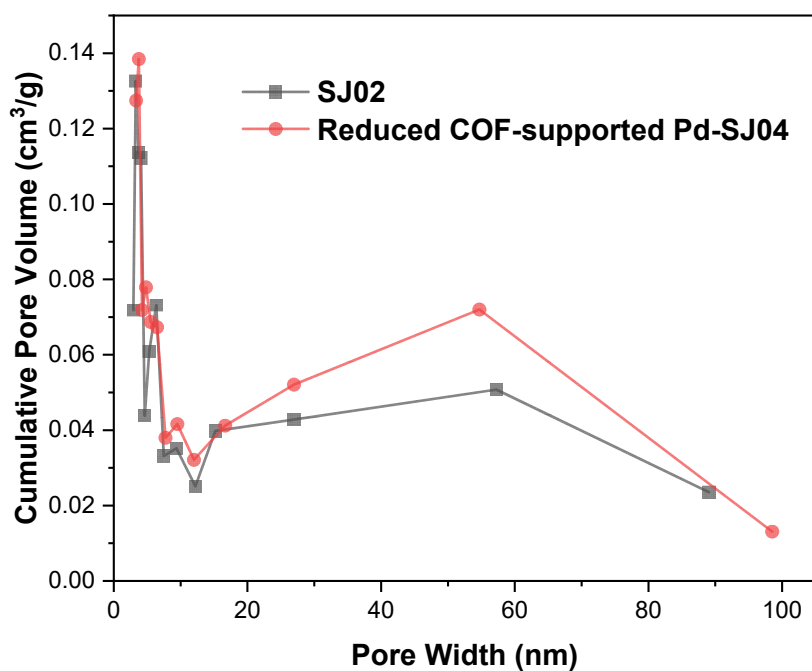
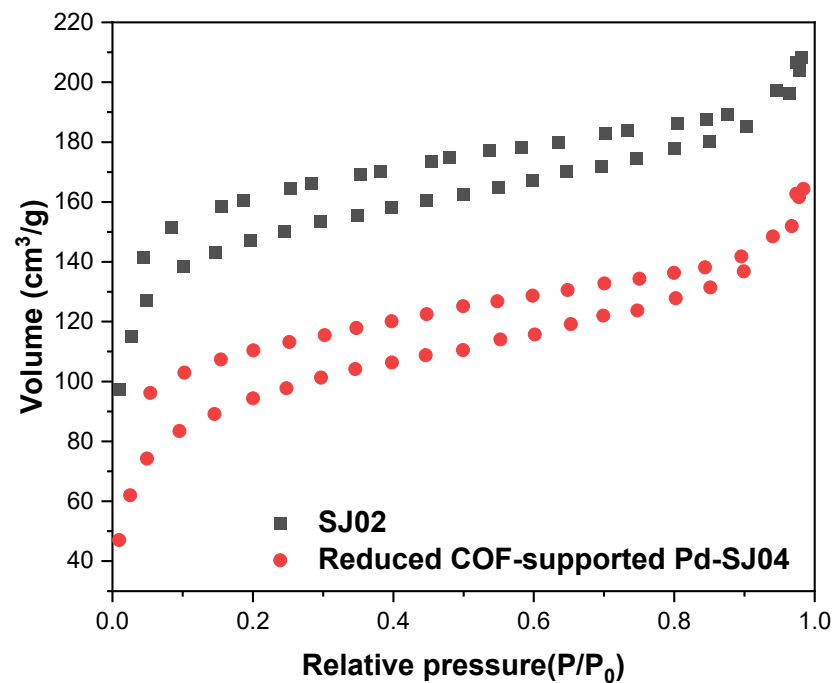
Figure S5. XRD patterns of SJ-02 and Reduced COF-supported Pd-SJ04.

Figure S6. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of SJ-02 and Reduced COF-supported Pd-SJ04.

Table S1. Comparison with Other Reported Catalysts for the Hydrogenation of Alkynes.

catalyst	Conversion (%)	Selectivity (%)	ref
Reduced COF-supported Pd-SJ04	100	87.57	This work
Pd NW	97	93	[1]
Pt-MnOx/TiO ₂	92	70	[2]
Co-nanoparticles	100	92	[3]

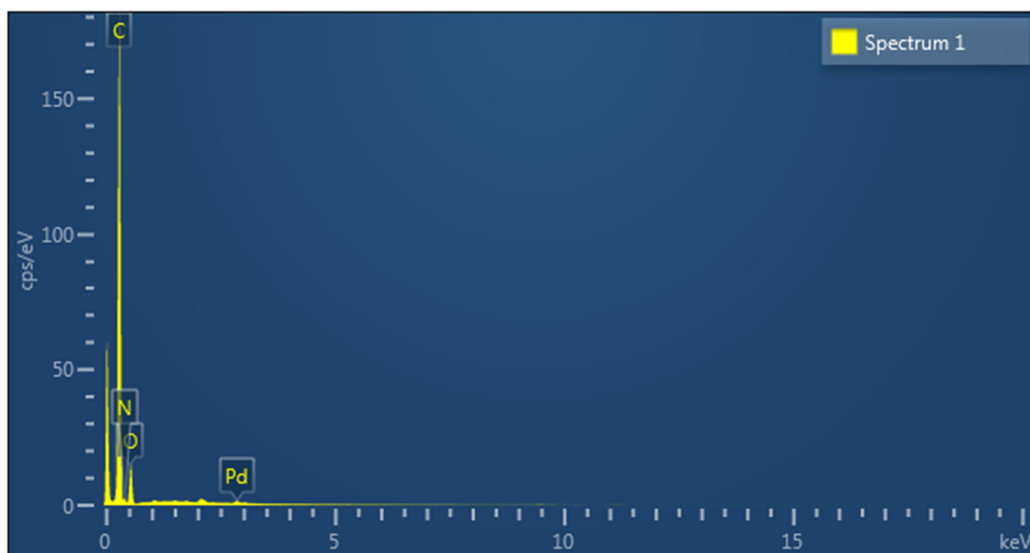


Figure S7. Elemental analysis of Reduced COF-supported Pd-SJ04.

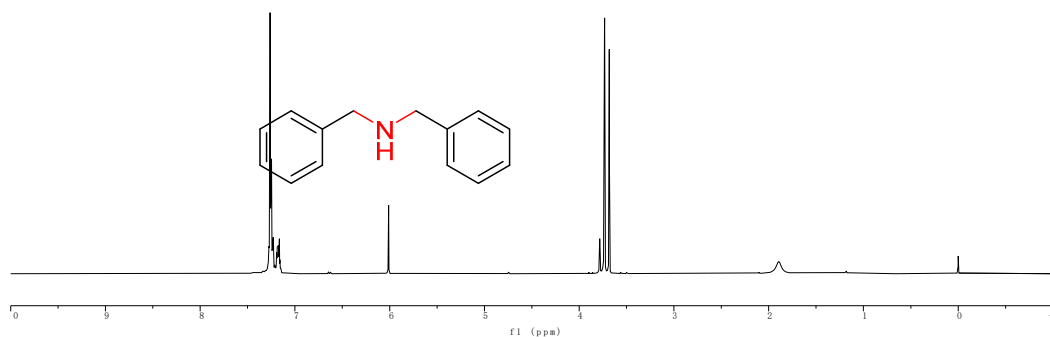
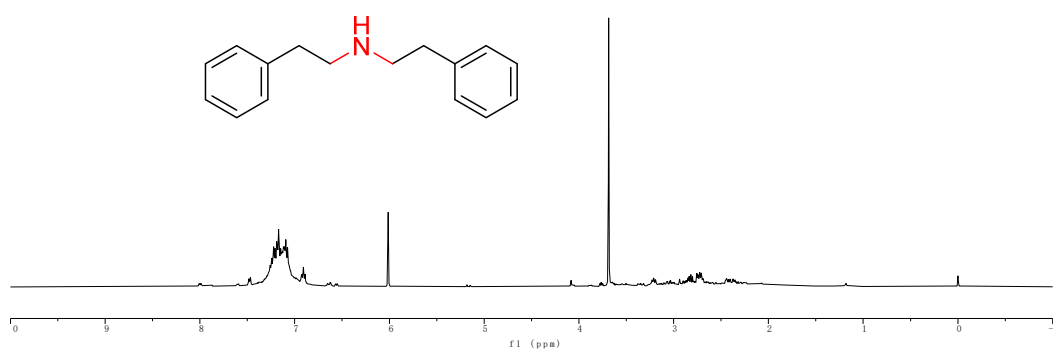
Table S2. Specific surface area, pore volume, pore diameter of SJ-02 and Reduced COF-supported Pd-SJ04.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{cm}^3 \text{g}^{-1}$)	d_{pore} (nm)	constant C
SJ02	559.531	0.322	1.152	280.799
Reduced COF-supported Pd-SJ04	347.076	0.254	2.929	140.019

Table S3. The element contents of the as-prepared catalysts determined by TEM spectrum.

Sample	C (wt. %)	N (wt. %)	O (wt. %)	Pd (wt. %)
Reducibility Pd-SJ02	75.80	5.85	7.48	10.87

NMR and GC-MS spectra

Figure S8. ^1H NMR spectra of phenylacetylene.Figure S9. ^1H NMR spectra of diphenethylamine.

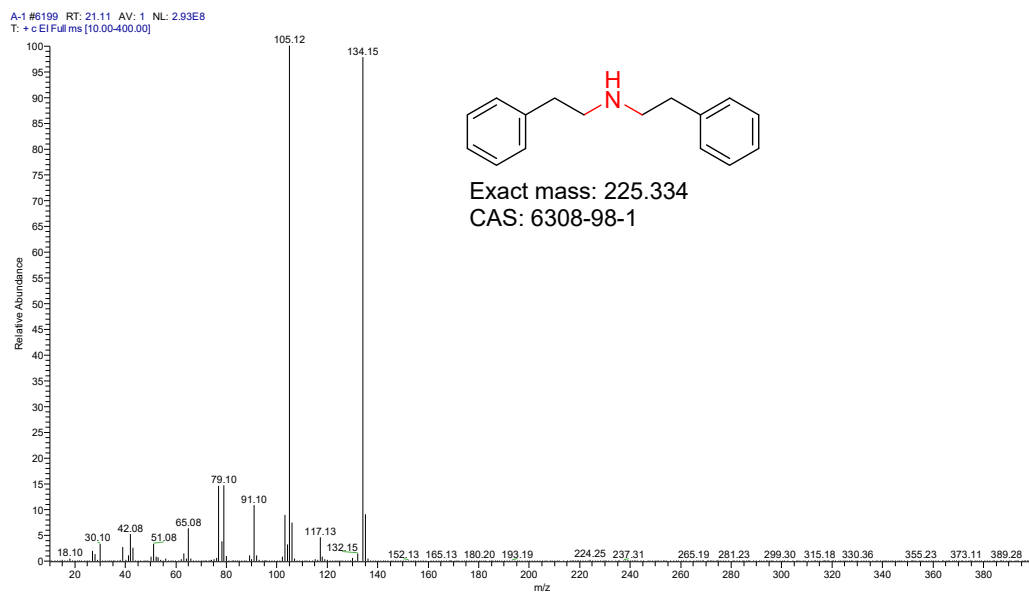
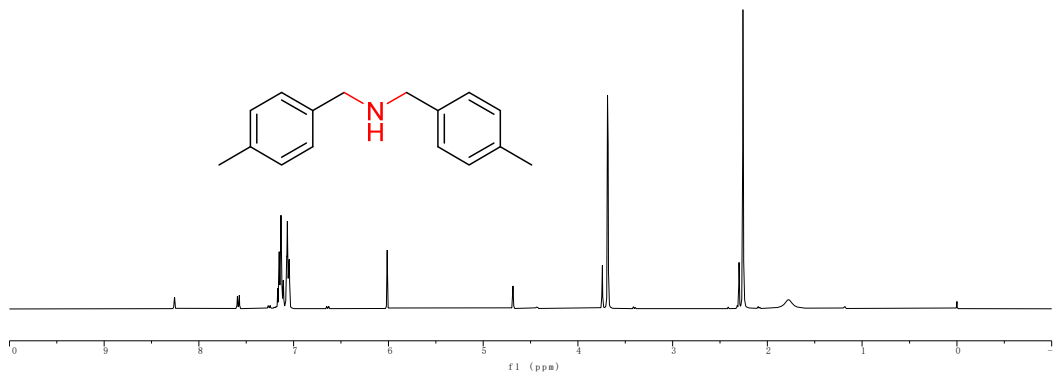
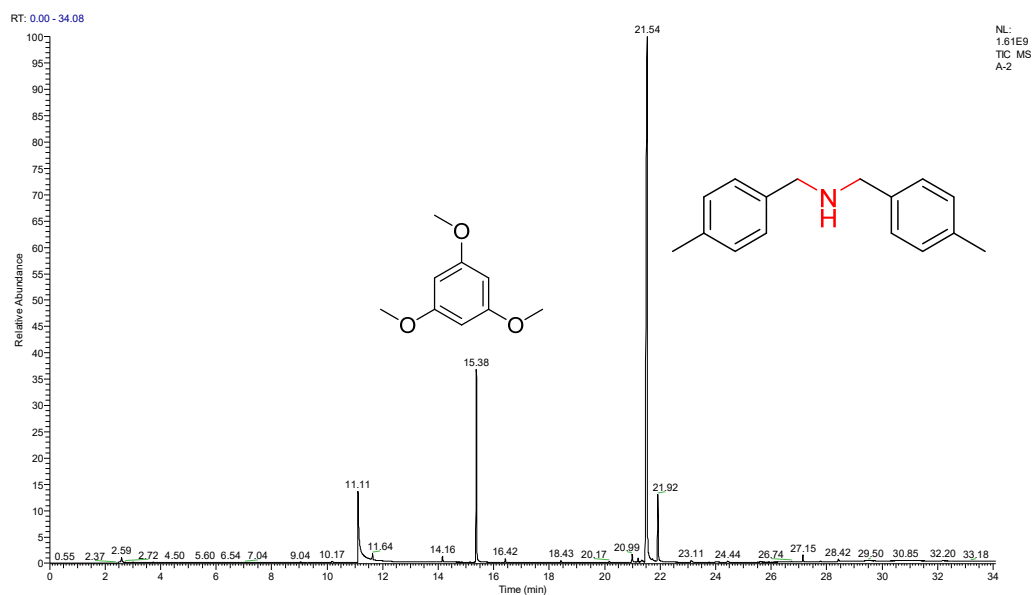


Figure S10. GC-MS spectra of diphenethylamine.

Figure S11. ¹H NMR spectra of bis(4-methylbenzyl)amine.

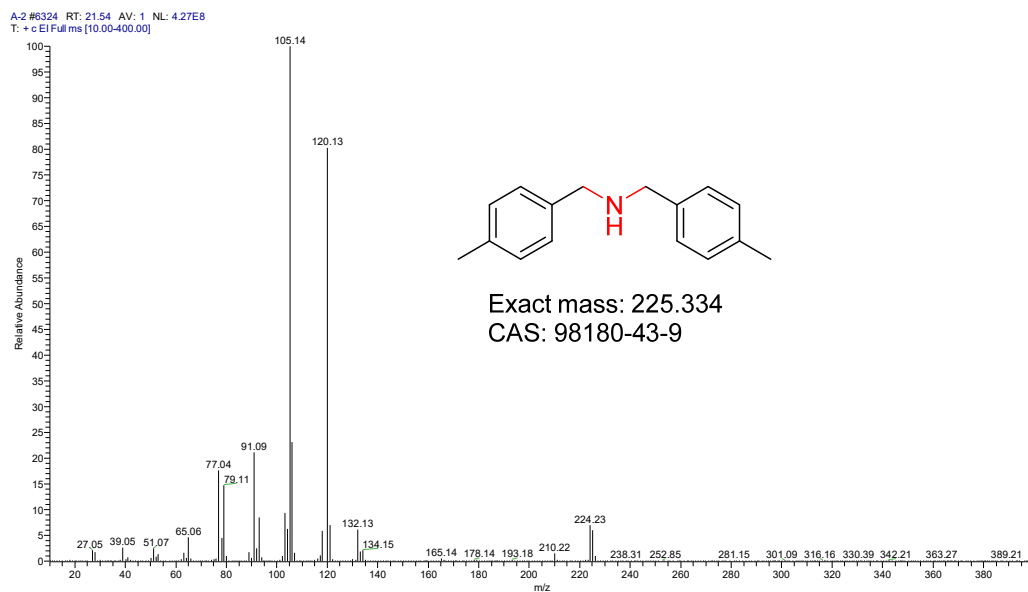


Figure S12. GC-MS spectra of bis(4-methylbenzyl)amine.

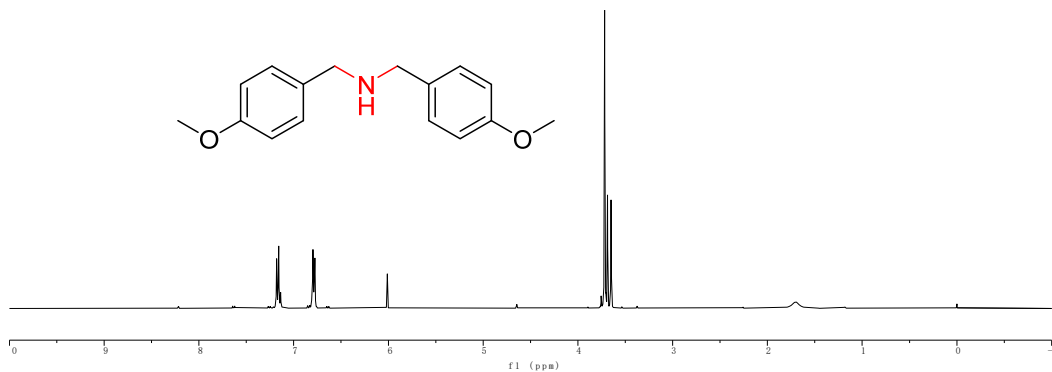
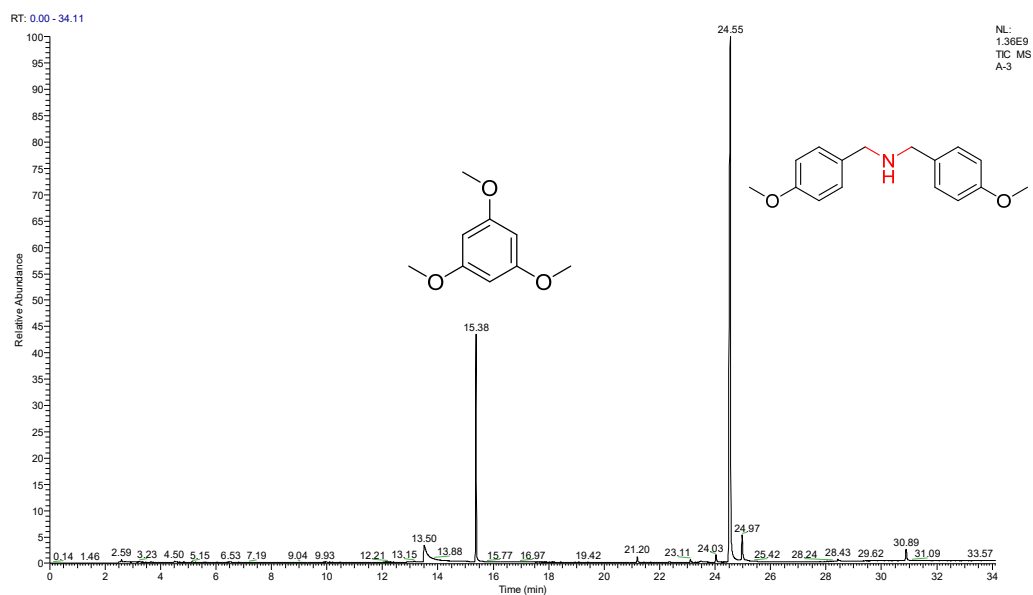


Figure S13. ¹H NMR spectra of N,N-bis(p-methoxybenzyl)amine.



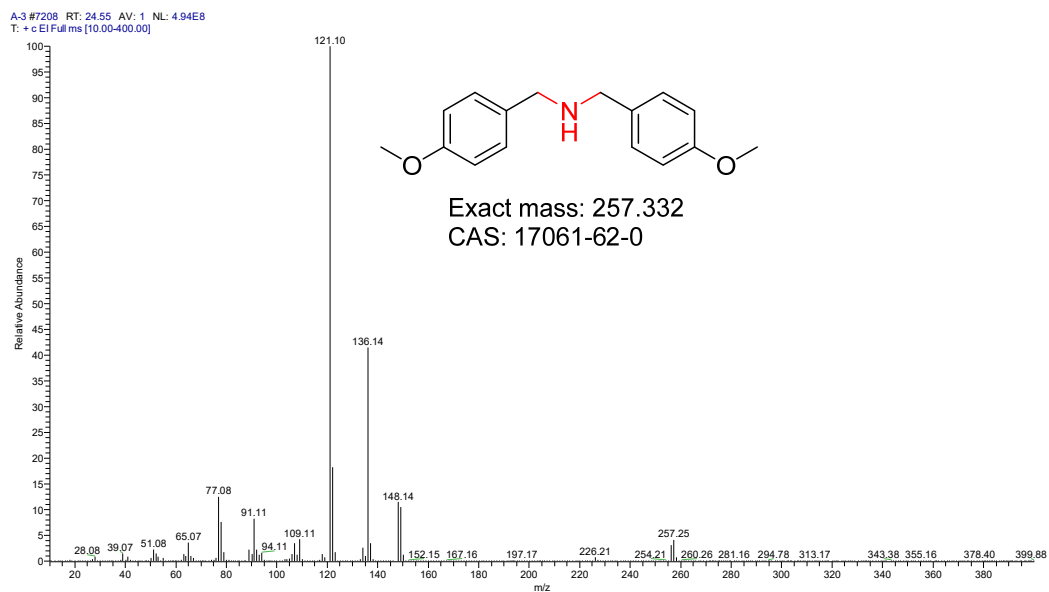


Figure S14. GC-MS spectras of N,N-bis(p-methoxybenzyl)amine.

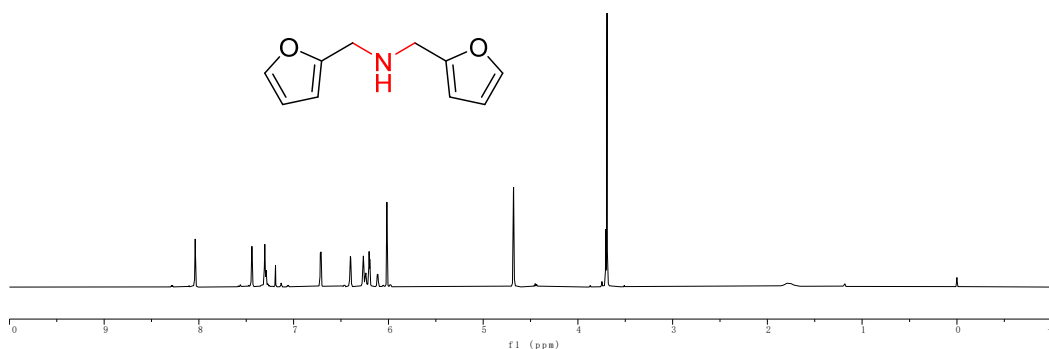
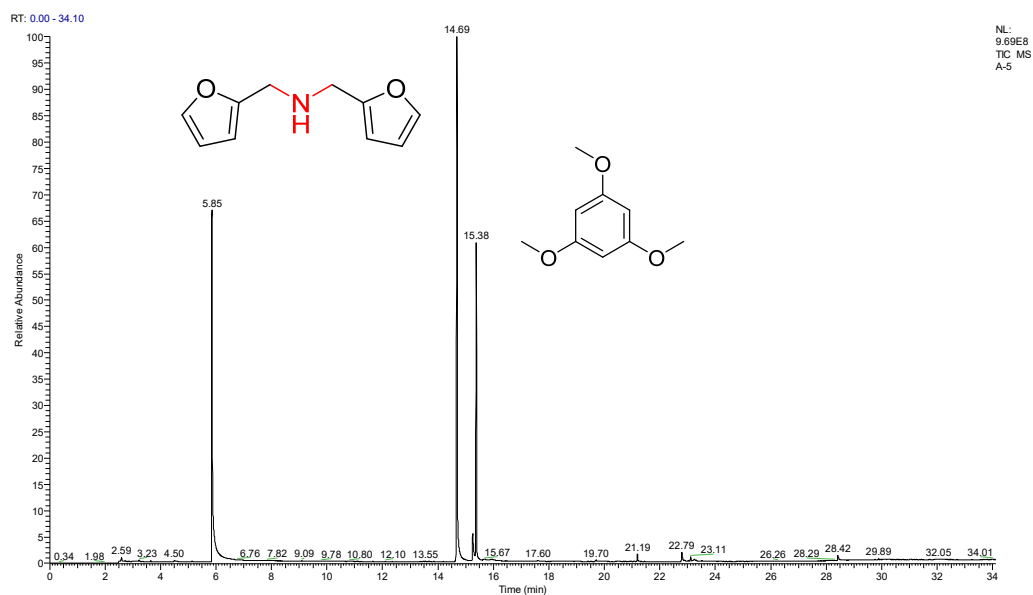


Figure S15. ¹H NMR spectras of bis((furan-2-yl)methyl)amine.



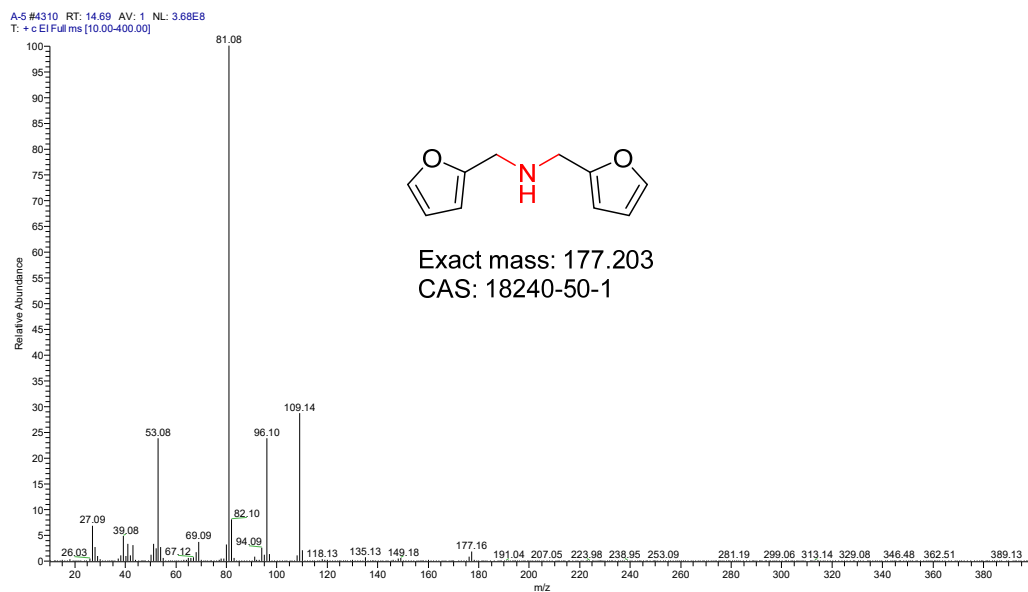


Figure S16. GC-MS spectras of bis((furan-2-yl)methyl)amine.

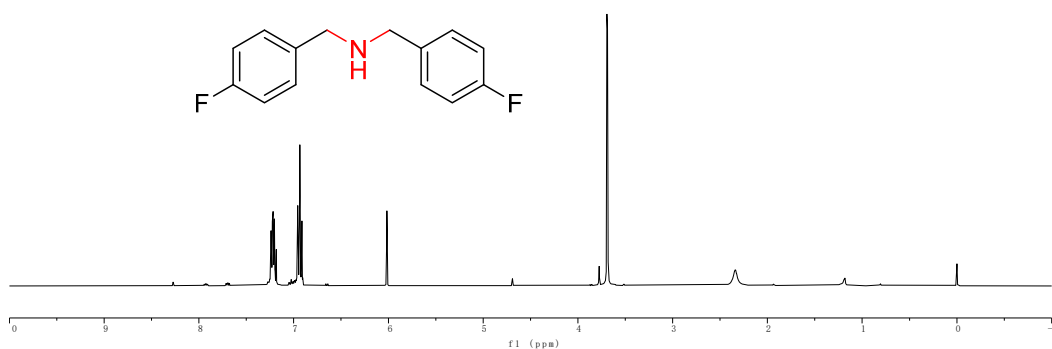
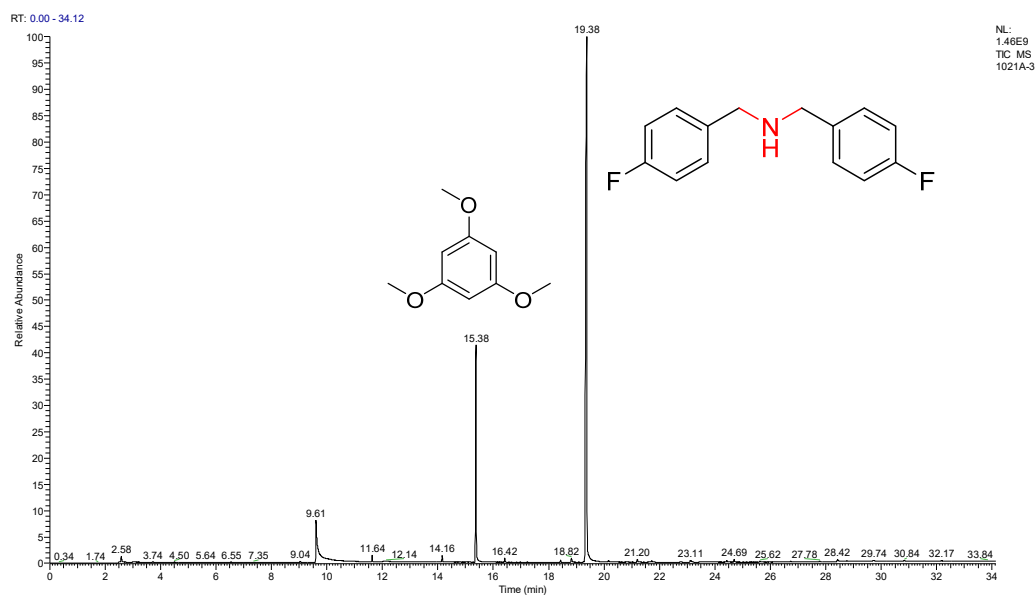


Figure S17. ¹H NMR spectras of 1-(4-fluorophenyl)-N-[(4-fluorophenyl)methyl]methanamine.



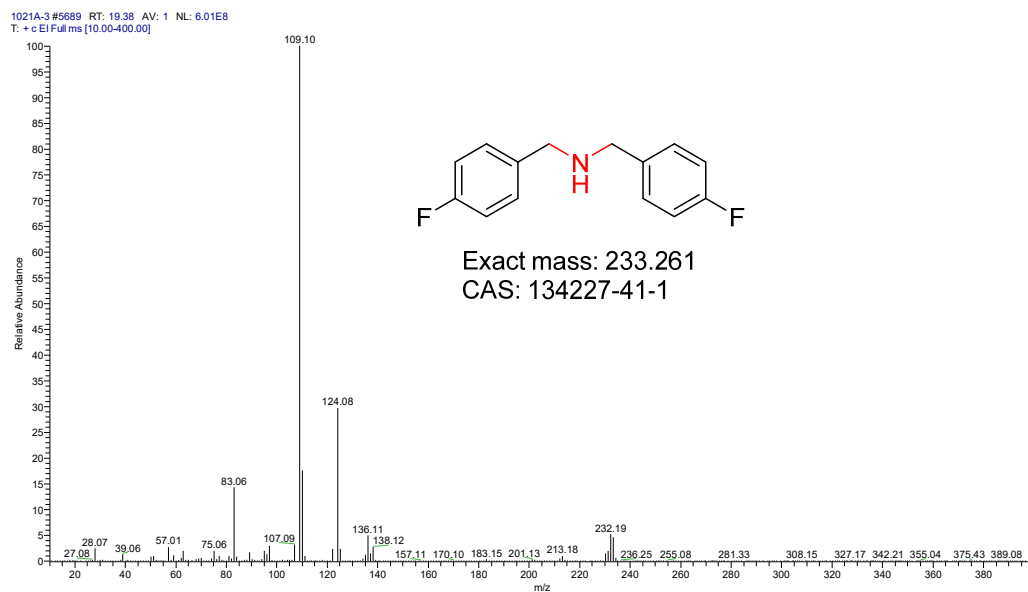


Figure S18. GC-MS spectra of 1-(4-fluorophenyl)-N-[(4-fluorophenyl)methyl]methanamine.

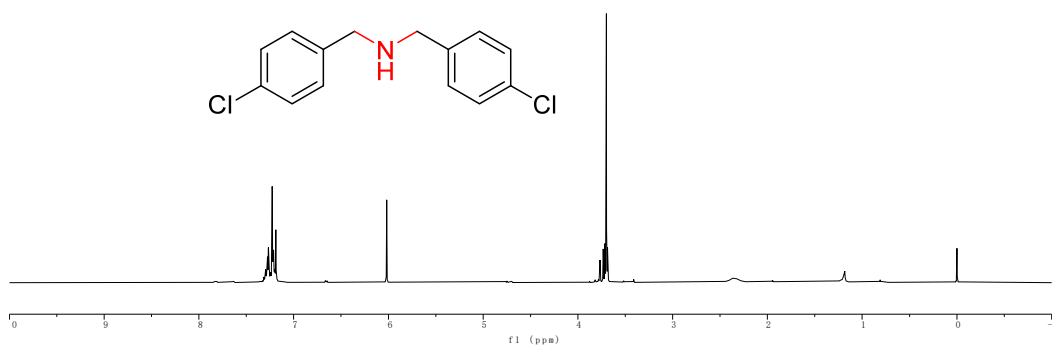
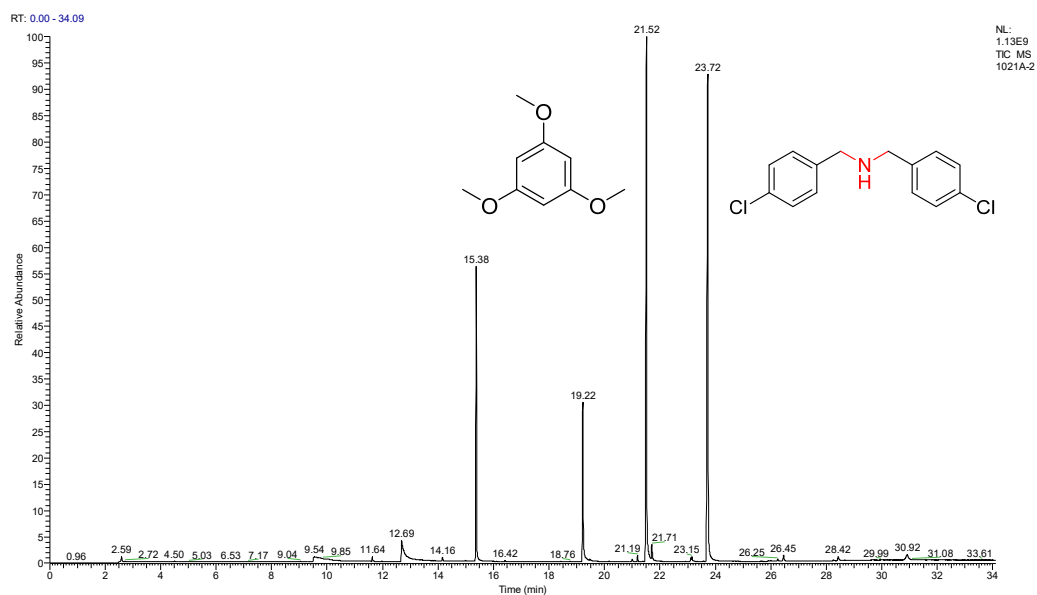


Figure S19. ¹H NMR spectra of N,N-bis(4-chlorobenzyl)amine.



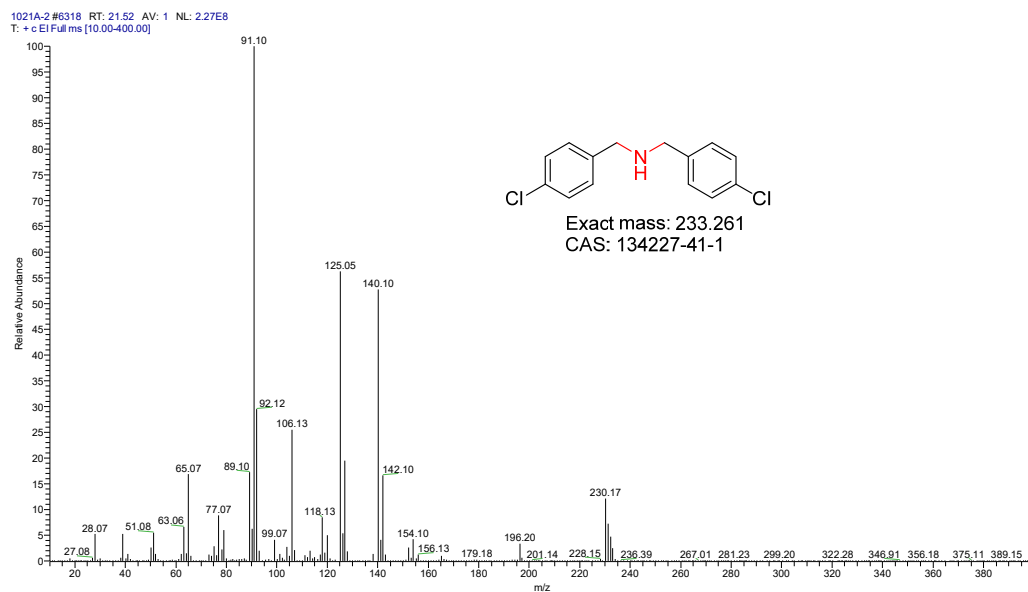


Figure S20. GC-MS spectras of N,N-bis(4-chlorobenzyl)amine.

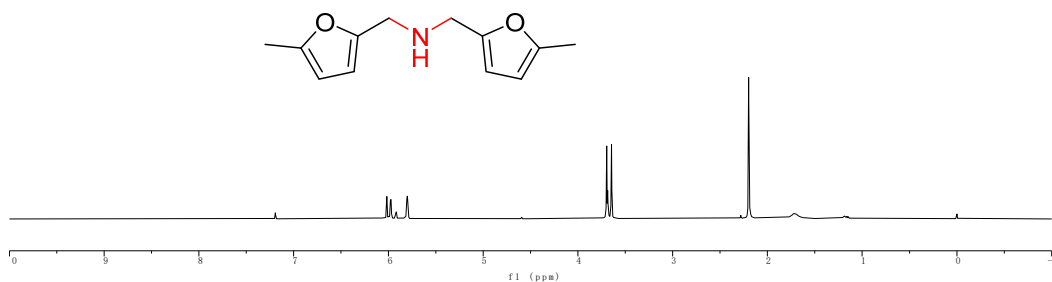
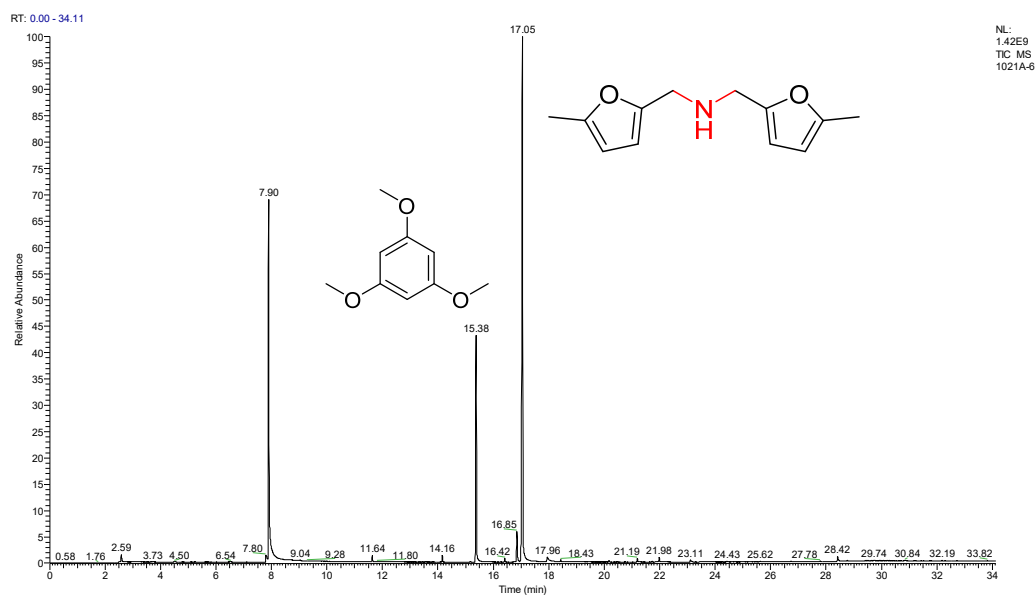


Figure S21. ¹H NMR spectras of bis-(5-methyl-furan-2-ylmethyl)-amine.



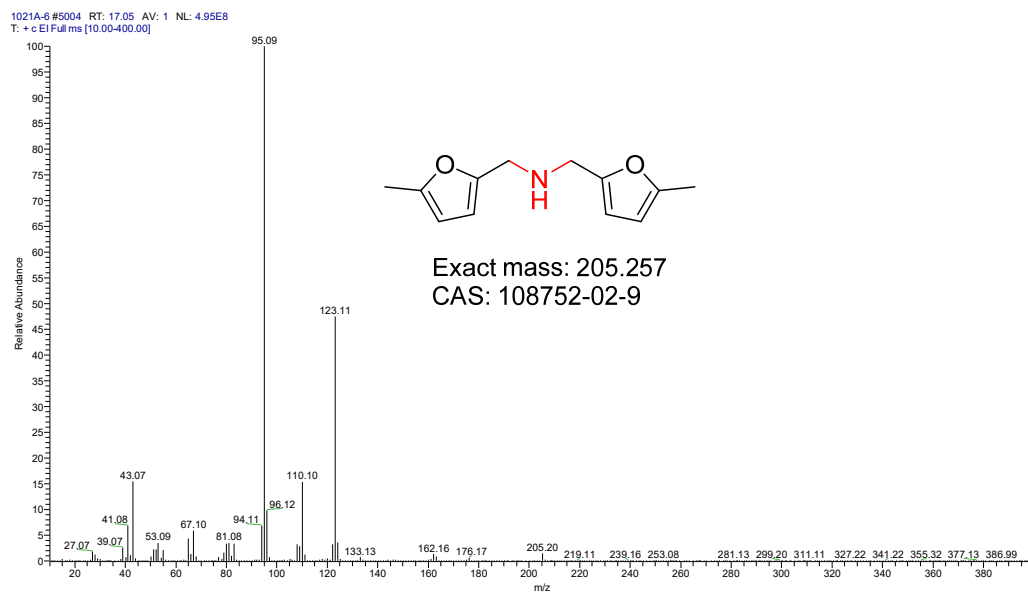


Figure S22. GC-MS spectras of bis-(5-methyl-furan-2-ylmethyl)-amine.

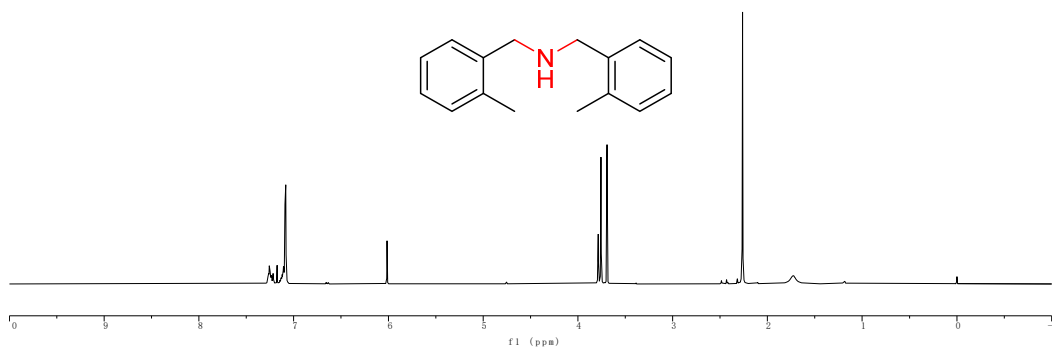
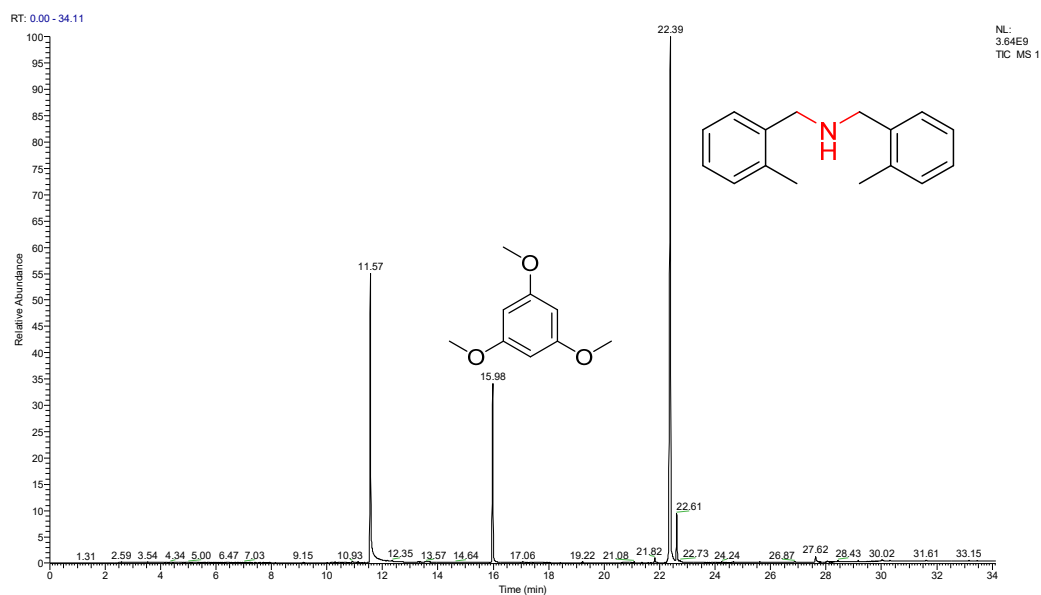


Figure S23. ¹H NMR spectras of bis(2-methylbenzyl)amine.



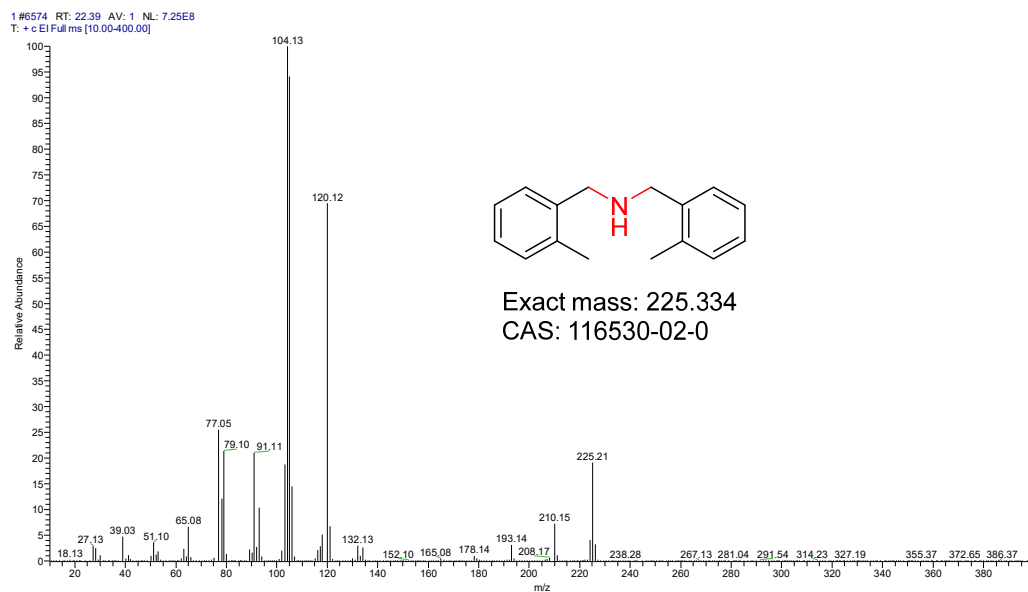


Figure S24. GC-MS spectras of bis(2-methylbenzyl)amine.

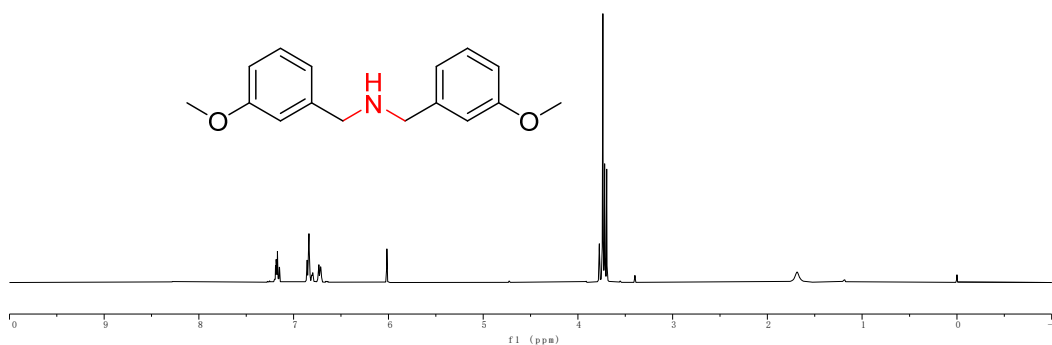
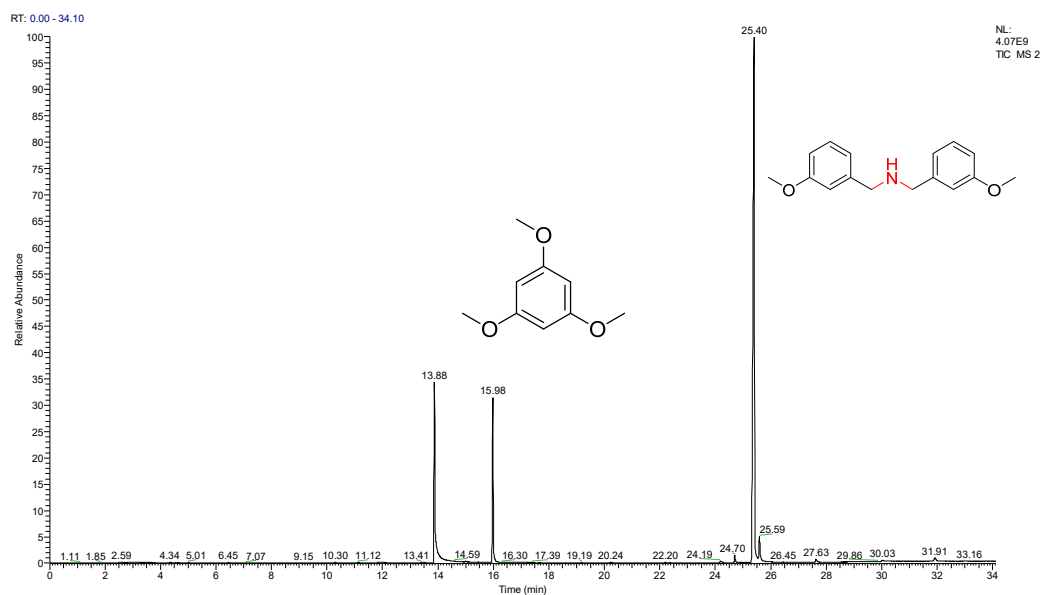


Figure S25. ¹H NMR spectras of N,N-bis(m-methoxybenzyl)amine.



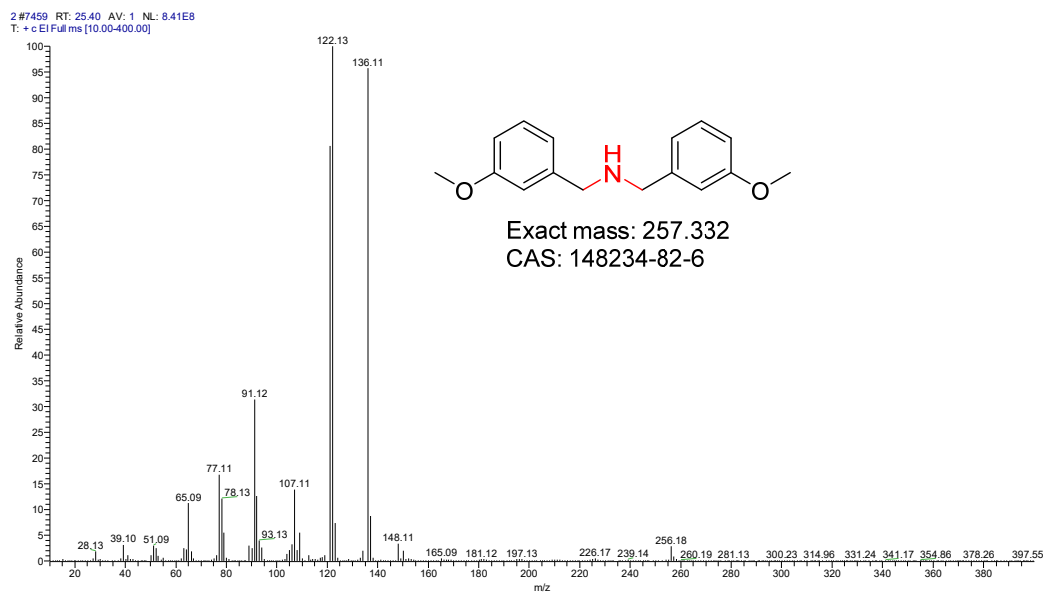


Figure S26. GC-MS spectras of N,N-bis(m-methoxybenzyl)amine.

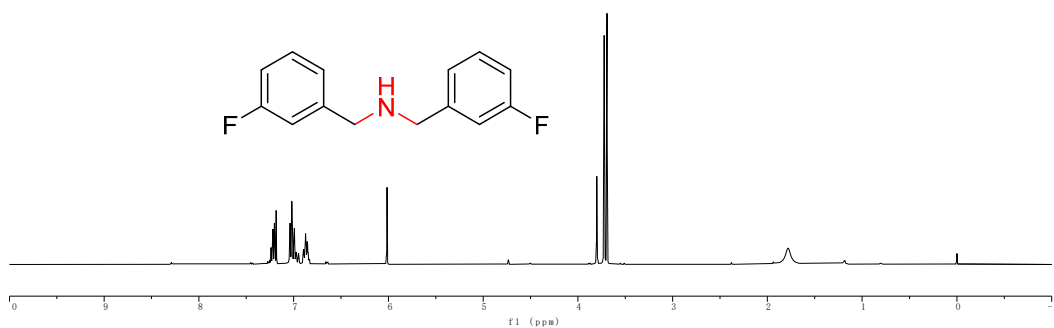
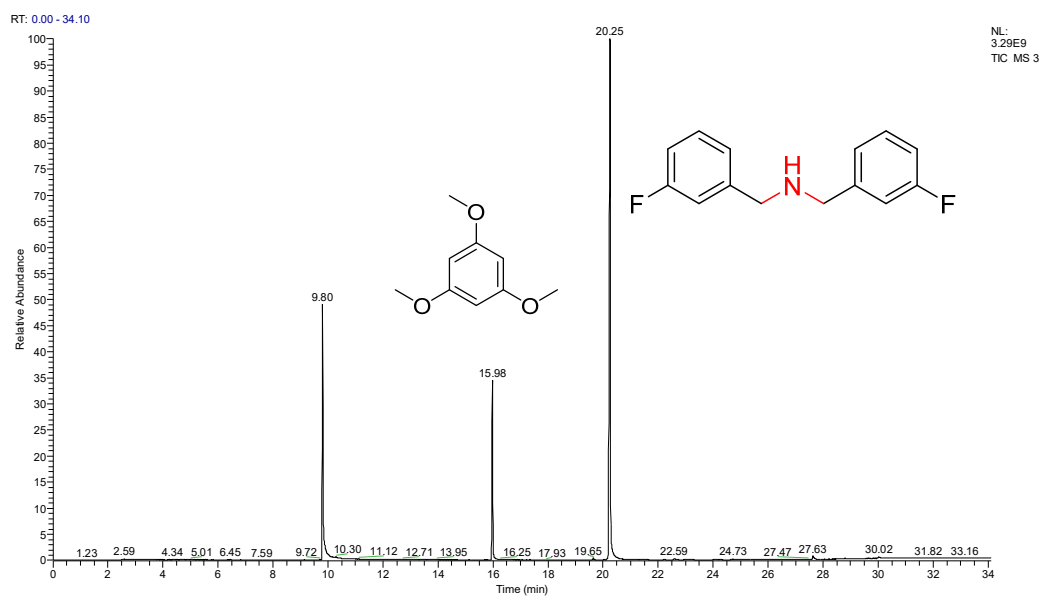


Figure S27. ¹H NMR spectras of bis(3-fluorobenzyl)amine.



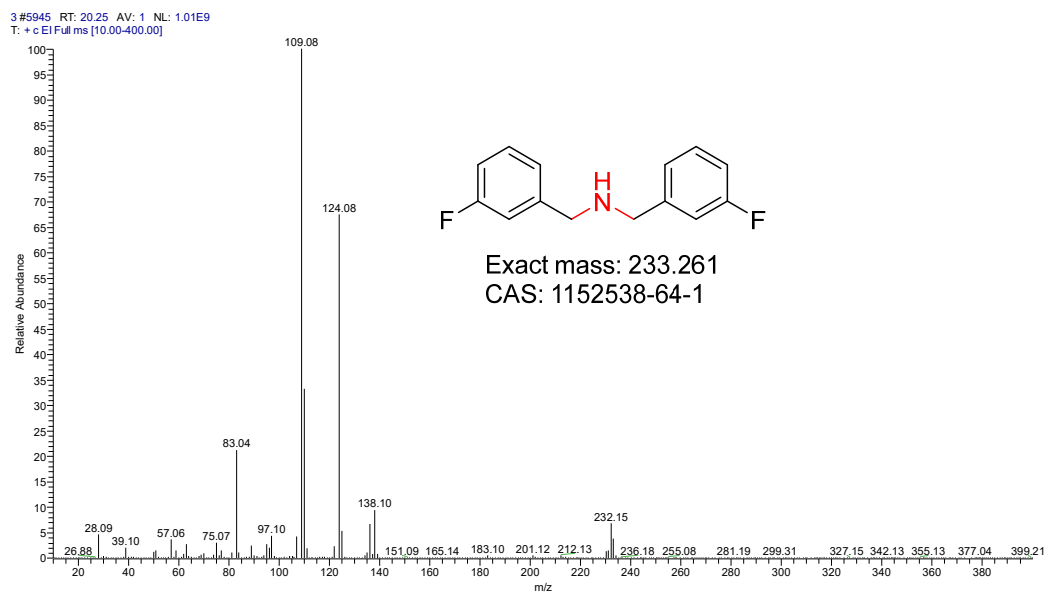
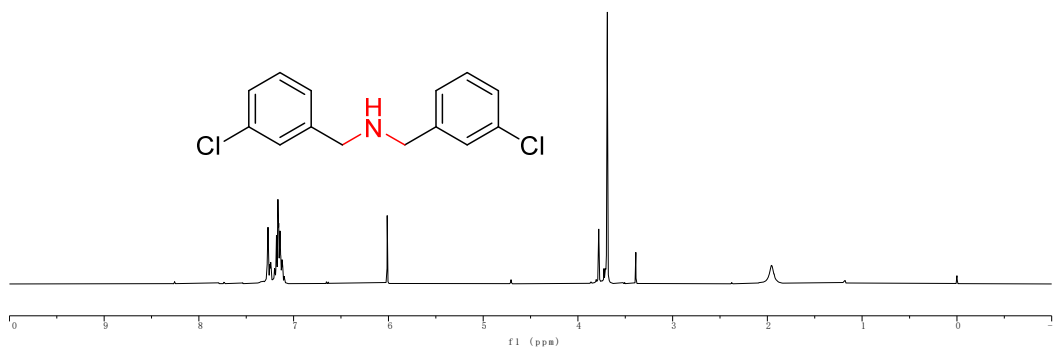
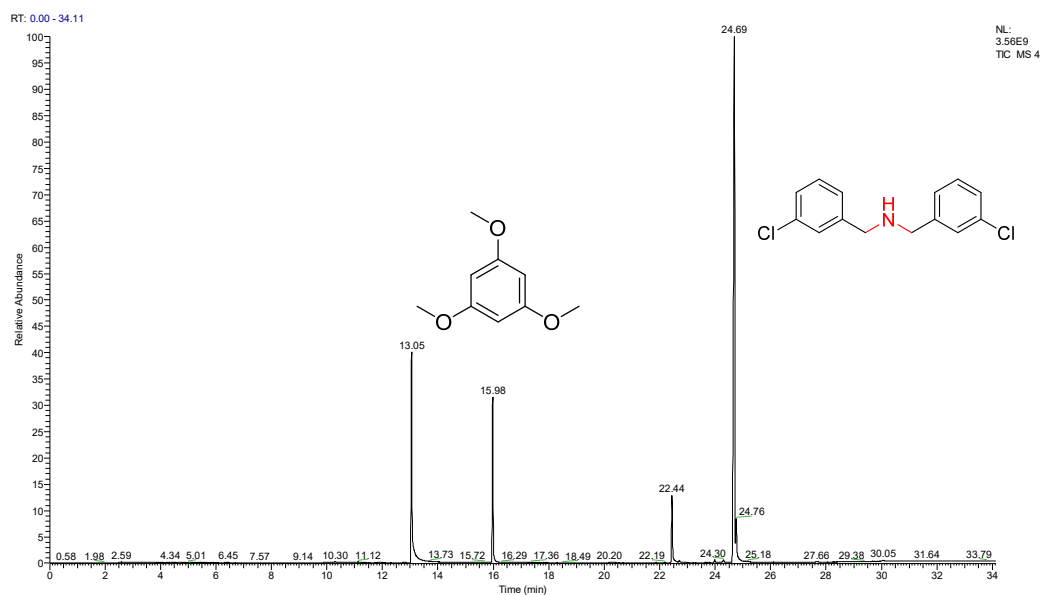


Figure S28. GC-MS spectras of bis(3-fluorobenzyl)amine.

Figure S29. ¹H NMR spectra of N,N-bis(3-chlorobenzyl)amine.

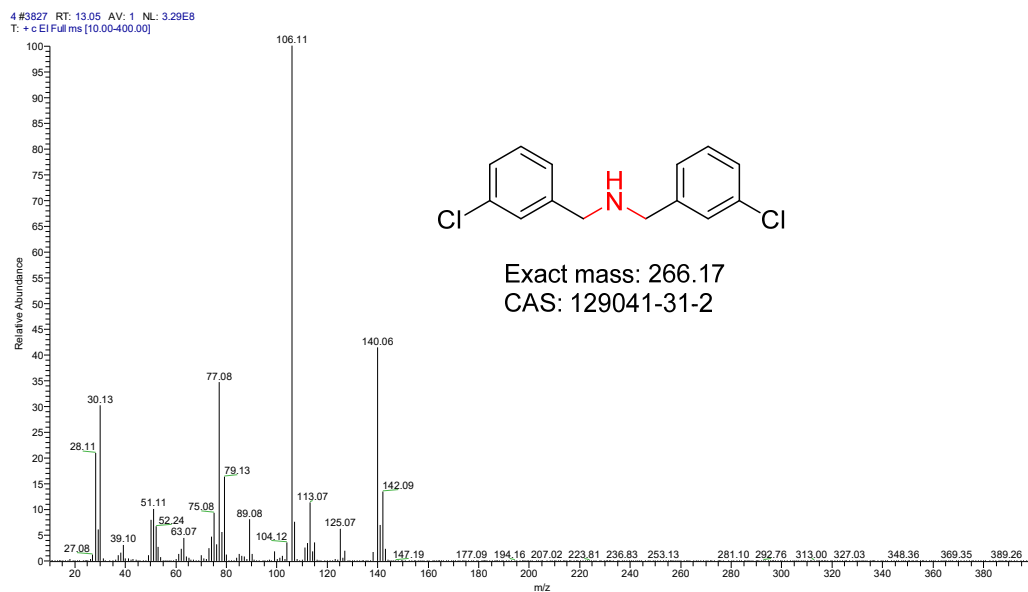


Figure S30. GC-MS spectras of N,N-bis(3-chlorobenzyl)amine.

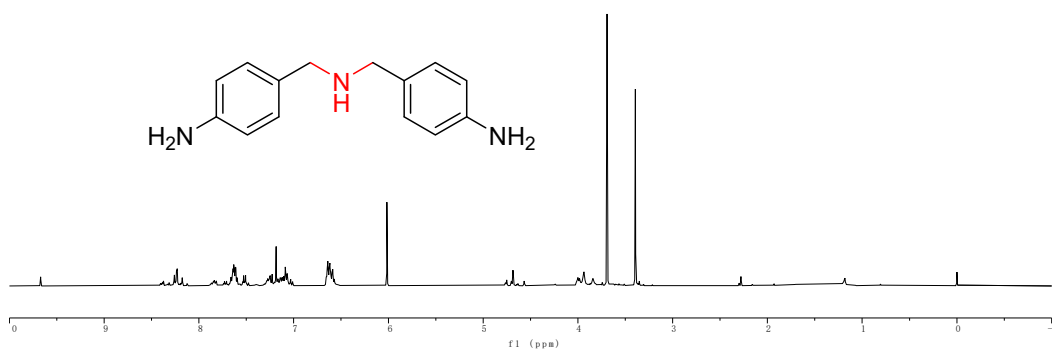


Figure S31. ^1H NMR spectra of bis(4-aminobenzyl)amine.

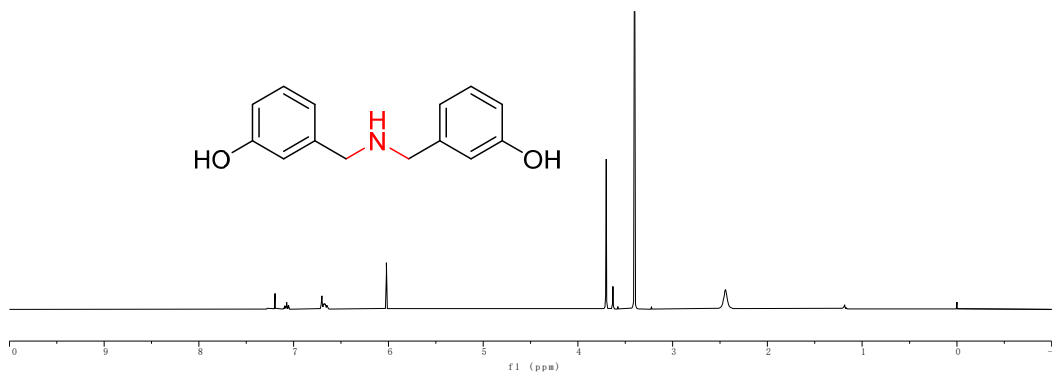


Figure S32. ^1H NMR spectra of N,N-bis(3-hydroxybenzyl)amine.

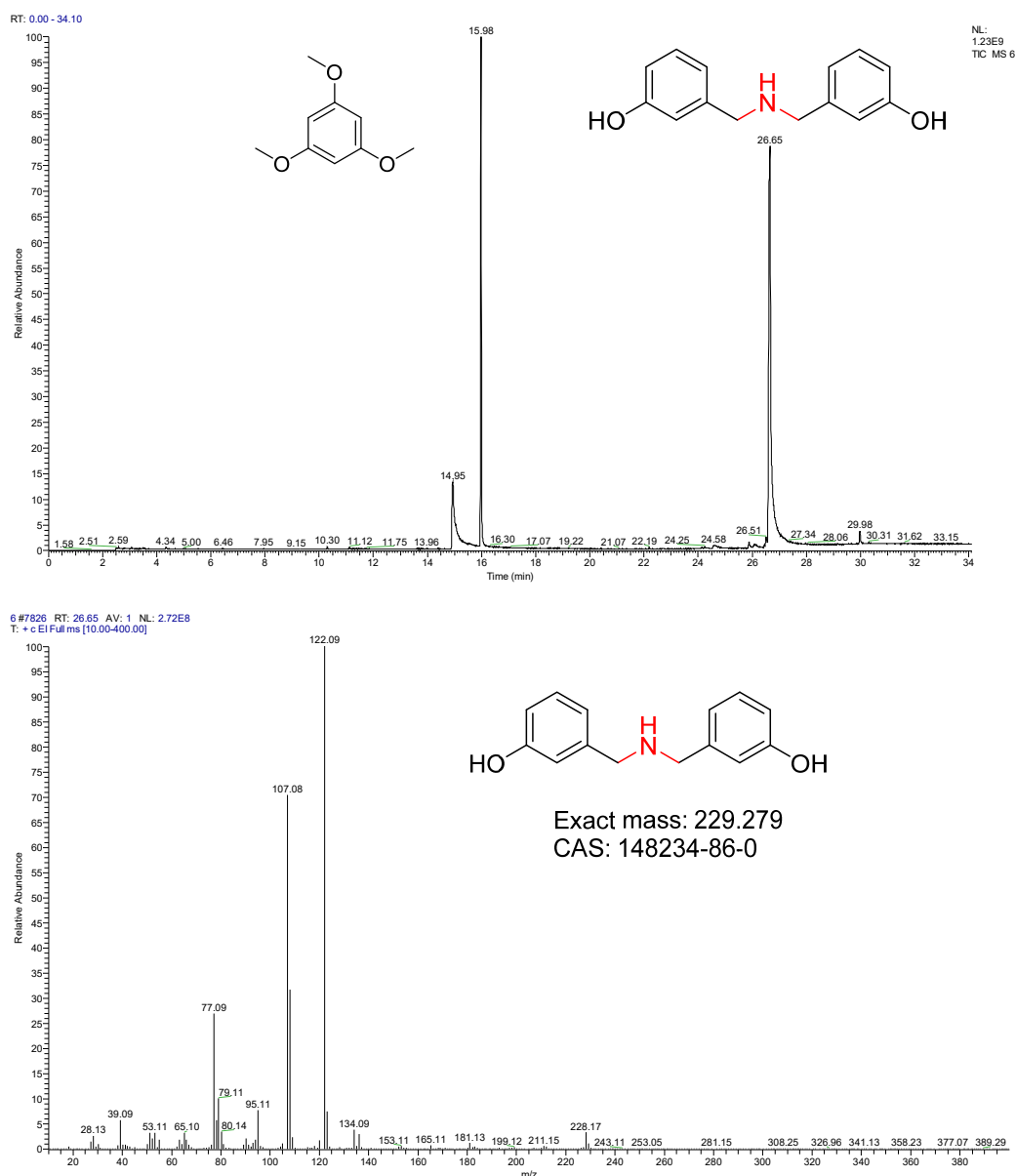


Figure S33. GC-MS spectra of N,N-bis(3-hydroxybenzyl)amine.

Reference

1. Qi, F.; Hu, L.; Lu, S.; Cao, X.; Gu, H., Selective synthesis of secondary amines by Pt nanowire catalyzed reductive amination of aldehydes and ketones with ammonia. *Chem Commun (Camb)* **2012**, 48 (77), 9631–9633.
2. Nakamura, Y.; Kon, K.; Touchy, A. S.; Shimizu, K.-i.; Ueda, W., Selective Synthesis of Primary Amines by Reductive Amination of Ketones with Ammonia over Supported Pt catalysts. *ChemCatChem* **2015**, 7 (6), 921–924.
3. Senthamarai, T.; Chandrashekar, V. G.; Gawande, M. B.; Kalevaru, N. V.; Zbořil, R.; Kamer, P. C. J.; Jagadeesh, R. V.; Beller, M., Ultra-small cobalt nanoparticles from molecularly-defined Co–salen complexes for catalytic synthesis of amines. *Chemical Science* **2020**, 11 (11), 2973–2981.