Supporting information

Magnetically separable $CuFe_2O_4$/reduced graphene oxide nanocomposites: As a highly active catalyst for solvent free oxidative coupling of amines to imines

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Experimental

1. Catalytic oxidative coupling of benzylamines to imines under N_2 environment: To check the role of oxidant, we performed benzylamine oxidation reaction under N_2 environment. Typically 15 mg of catalyst and 1mmol of benzylamine were taken in a 10 mL round bottom flask. The reaction mixture was then heated at 60 °C for the required time under continuous N_2 flow and the progress of reaction was monitored by thin layer chromatography (TLC). After reaction, the liquid products and the catalyst were separated by centrifugation and the filtrate was passed through the basic alumina-packed column using a mixture of ethyl acetate and hexane (1:9) as eluent. The imine derivatives obtained by this procedure were characterized by ^{1}H NMR.

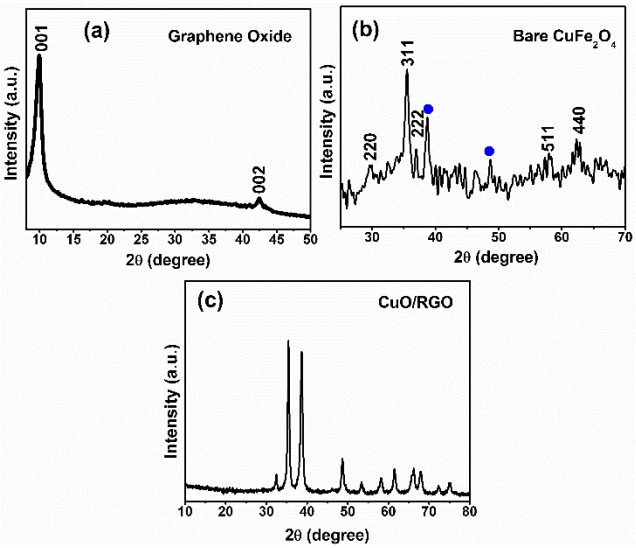
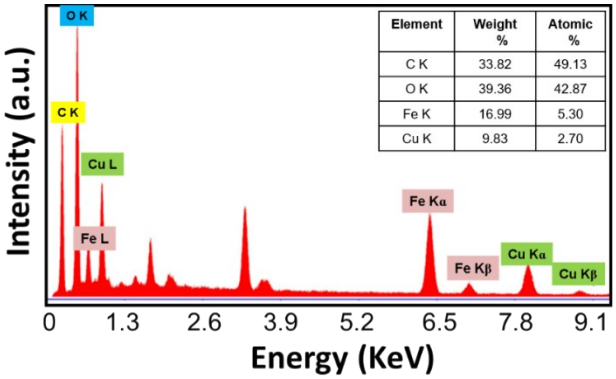


Figure S1. Powder XRD spectrum of (a) graphene oxide, (b) bare $CuFe_2O_4$ NPs (impurity peaks of CuO marked with blue dot) and (c) CuO/RGO nanocomposites.



Element	Weight %	Atomic %
C K	33.82	49.13
O K	39.36	42.87
Fe K	16.99	5.30
Cu K	9.83	2.70

Figure S2. SEM-EDS analysis of CFRNCs.

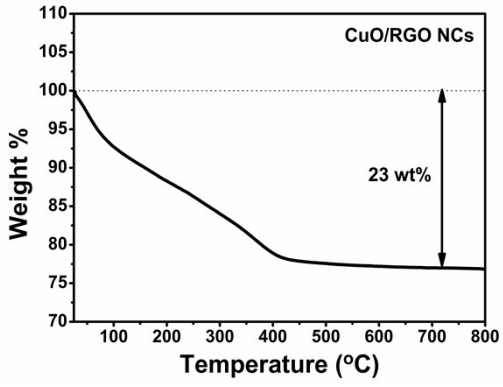


Figure S3. TGA curve of CuO/RGO NCs.

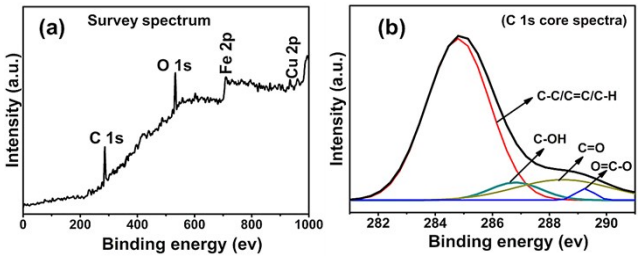


Figure S4. (a) Broad XPS spectrum and (b) C 1s core spectrum of $CuFe_2O_4$/RGO nanocomposites.

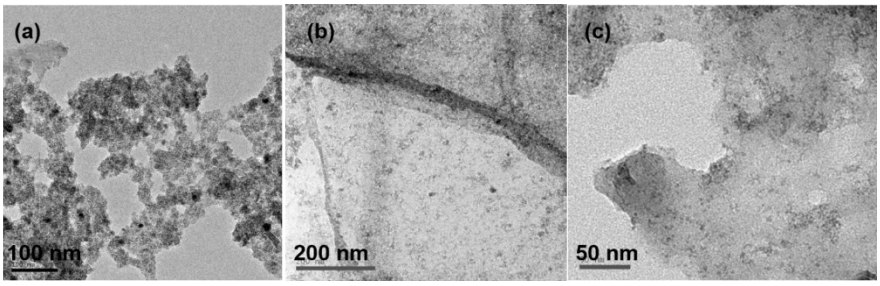


Figure S5. (a-c) Low resolution TEM images of $CuFe_2O_4$/RGO NCs with 15, 45 and 60 wt % graphene content respectively.

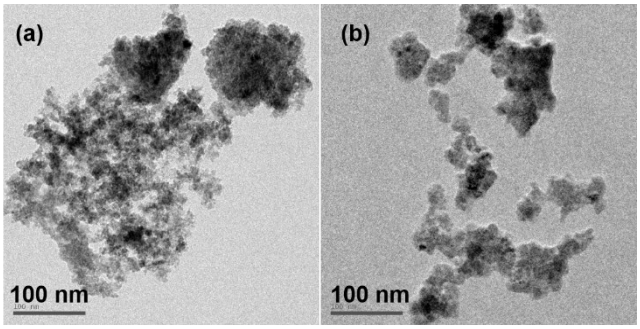


Figure S6. (a-b) Low resolution TEM images of bare $CuFe_2O_4$ NPs.

N-benzylidene-1-phenylmethanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.34 (s, 1H), 7.71-7.70 (m, 2H), 7.4-7.25 (m, 8H), 4.76 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.6, 139.4, 135.6, 130.4, 128.1, 127.9, 127.6, 126.7, 126.4, 64.5.

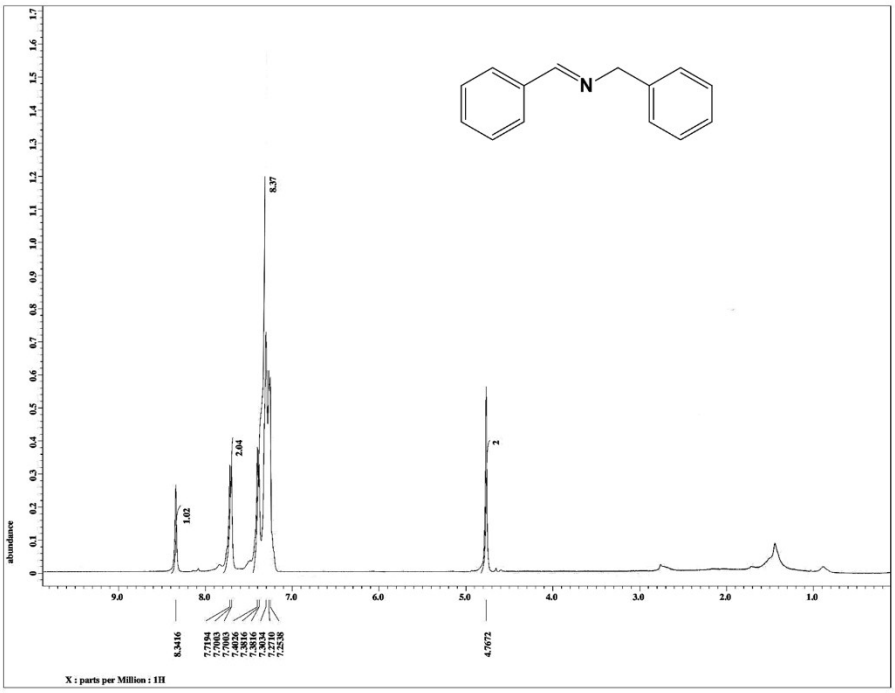


Figure S7. ^{1}H-NMR of N-benzylidene-1-phenylmethanamine.

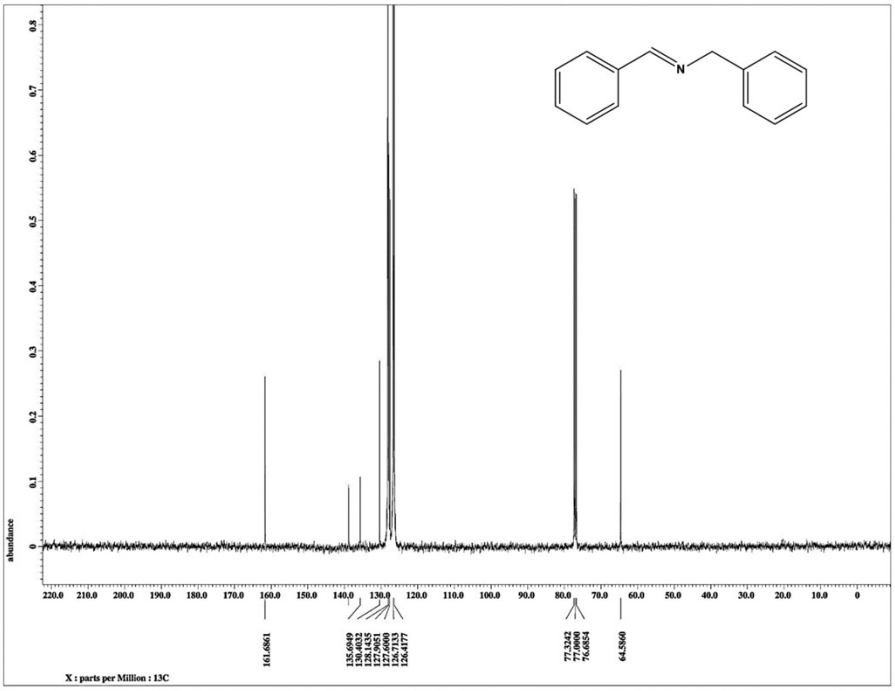


Figure S8. ^{13}C NMR of N-benzylidene-1-phenylmethanamine.

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C14 H13 N	196.1117	10	Find by Molecular Feature	195.1045

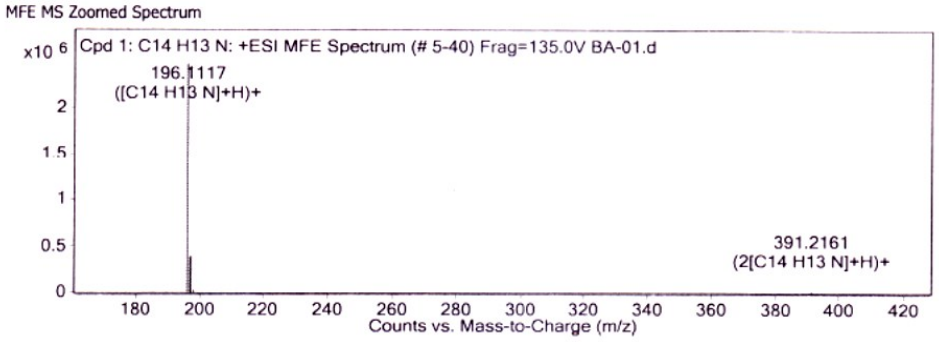


Figure S9. Mass spectra of N-benzylidene-1-phenylmethanamine.

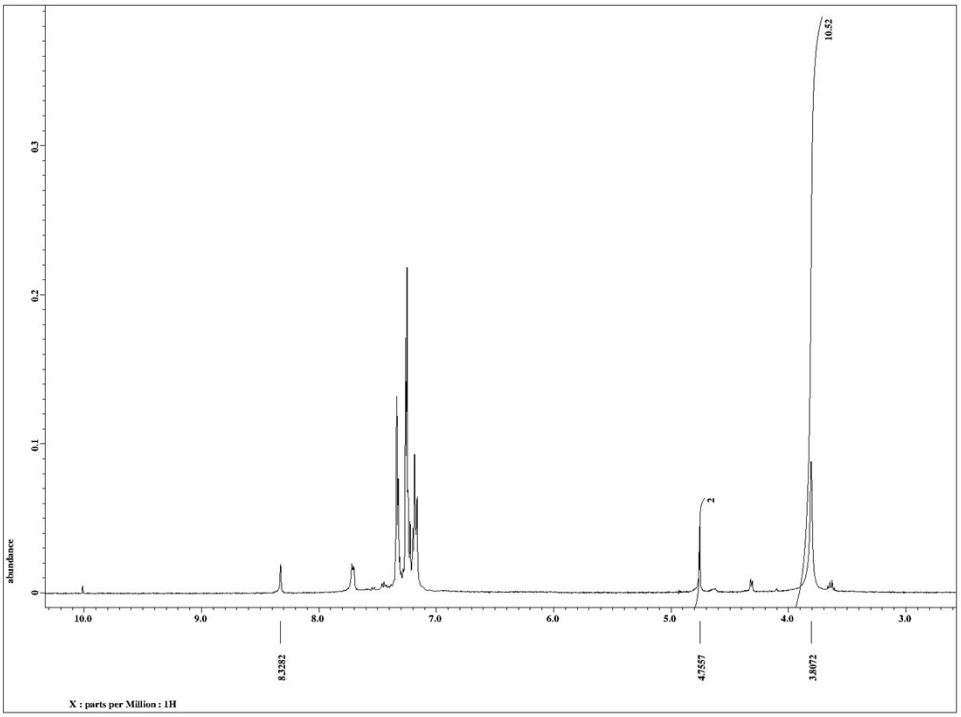


Figure S10. ^{1}H-NMR of benzylamine oxidation reaction under N_2 environment.

N-(4-chlorobenzylidene)-1-(4-chloro phenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.33 (s, 1H), 7.68 (d, 2H, J = 8.4 Hz), 7.37 (d, 2H, J = 8.3 Hz), 7.31-7.26 (m, 4H), 4.75 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ_C 160.8, 137.5, 136.8, 134.3, 132.7, 129.4, 129.2, 128.9, 128.6, 64.1

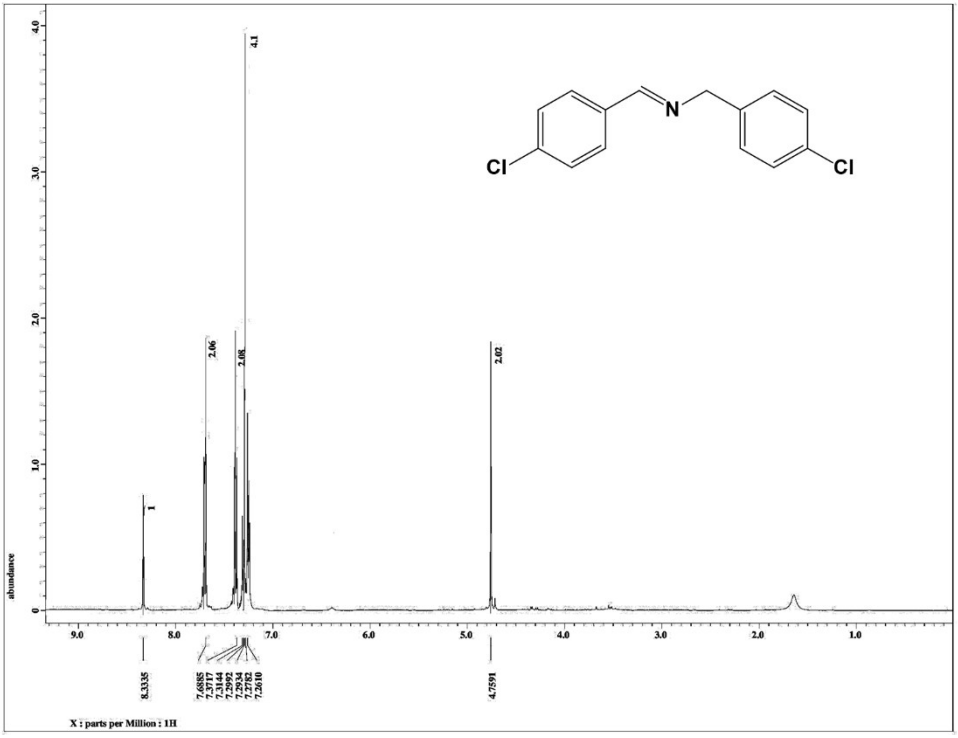


Figure S11. ^{1}H-NMR of N-(4-chlorobenzylidene)-1-(4-chloro phenyl)methanamine.

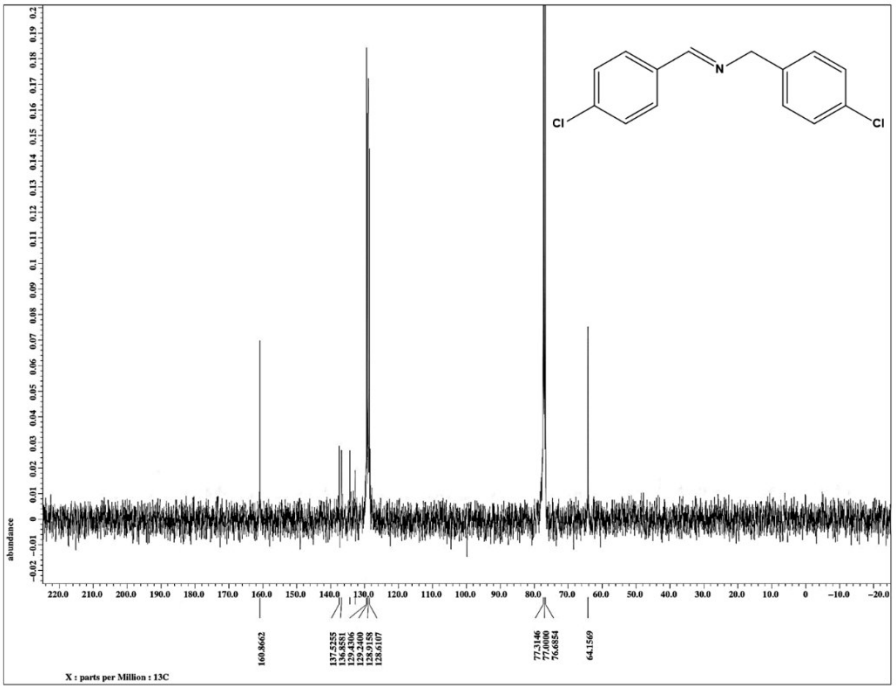


Figure S12. ^{13}C NMR of N-(4-chlorobenzylidene)-1-(4-chloro phenyl)methanamine.

N-(4-fluorobenzylidene)-1-(4-fluorophenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.32 (s, 1H), 7.82-7.70 (m, 2H), 7.45-7.36 (m, 2H), 7.25-7.15 (m, 4H), 4.74 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 165.52, 163.0, 162.8, 160.6, 160.5, 134.7 (d, $J_{C,F}$ = 2.9 Hz), 132.1 (d, $J_{C,F}$ = 2.9 Hz), 130.1 (d, $J_{C,F}$ = 8.6 Hz), 129.4 (d, $J_{C,F}$ = 8.6 Hz), 115.2 (d, $J_{C,F}$ = 21.1 Hz),115.0 (d, $J_{C,F}$ = 21.1 Hz), 64.0

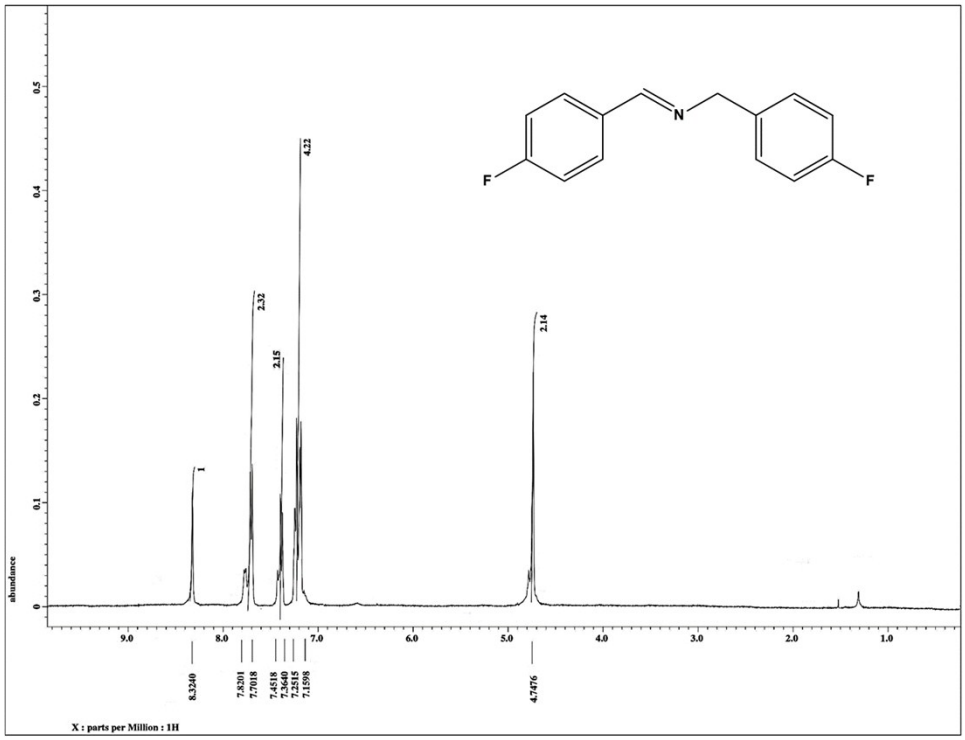


Figure S13. ^{1}H-NMR of N-(4-fluorobenzylidene)-1-(4-fluorophenyl)methanamine.

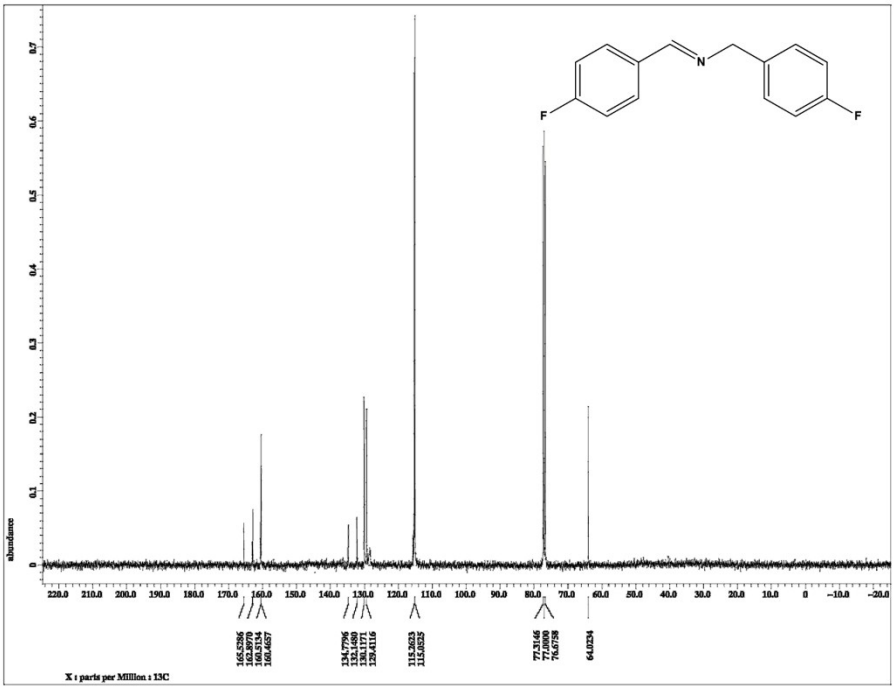


Figure S14. ^{13}C NMR of N-(4-fluorobenzylidene)-1-(4-fluorophenyl)methanamine.

N-(2-methylbenzylidene)-1-(o-tolyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.67 (s, 1H), 7.93-7.91 (m, 1H), 7.30-7.17 (m, 7H), 4.83 (s, 2H), 2.50 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 160.4, 137.5, 137.4, 135.9, 134.0, 130.6, 130.1, 129.9, 128.1, 127.5, 126.8, 126.0, 125.9, 63.1, 19.2, 19.1.

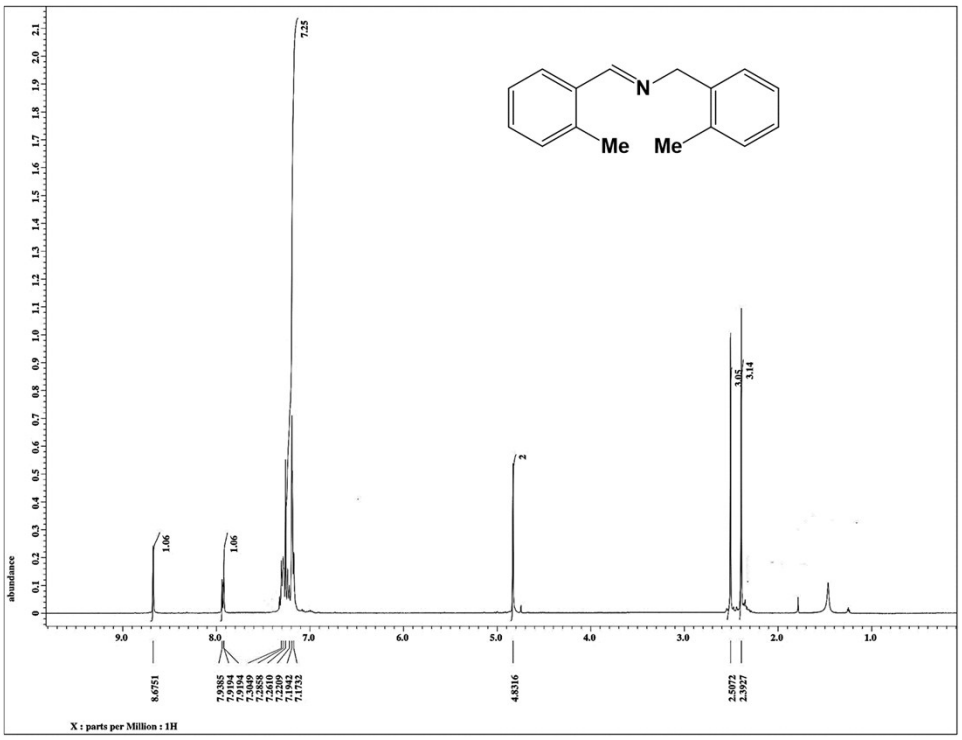


Figure S15. ^{1}H-NMR of N-(2-methylbenzylidene)-1-(o-tolyl)methanamine.

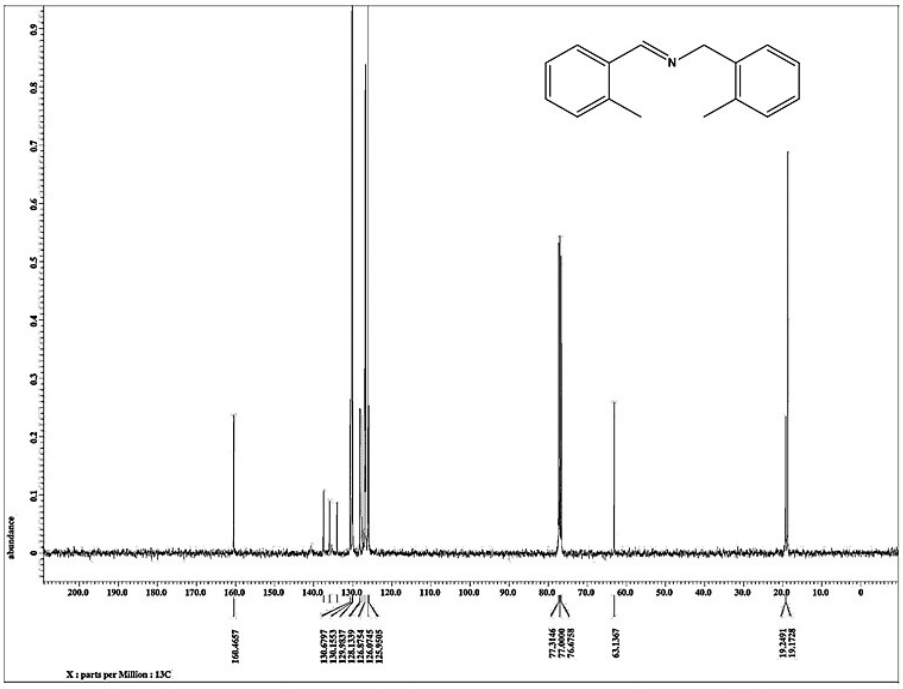


Figure S16. ^{13}C NMR of N-(2-methylbenzylidene)-1-(o-tolyl)methanamine.

N-(4-(trifluoromethyl)benzylidene)-1-(4(trifluoromethyl)phenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.67 (s, 1H), 7.91 (d, 2H, J = 7.83 Hz), 7.38-7.26 (m, 4H), 7.18 (d, 2H, J = 7.83 Hz), 4.83 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.13, 142.9, 138.9, 132.7, 132.3, 128.4, 128.0, 125.6 (q, $J_{C,F}$ = 3.8 Hz), 125.4(q, $J_{C,F}$ = 3.8 Hz), 122.4, 64.3.

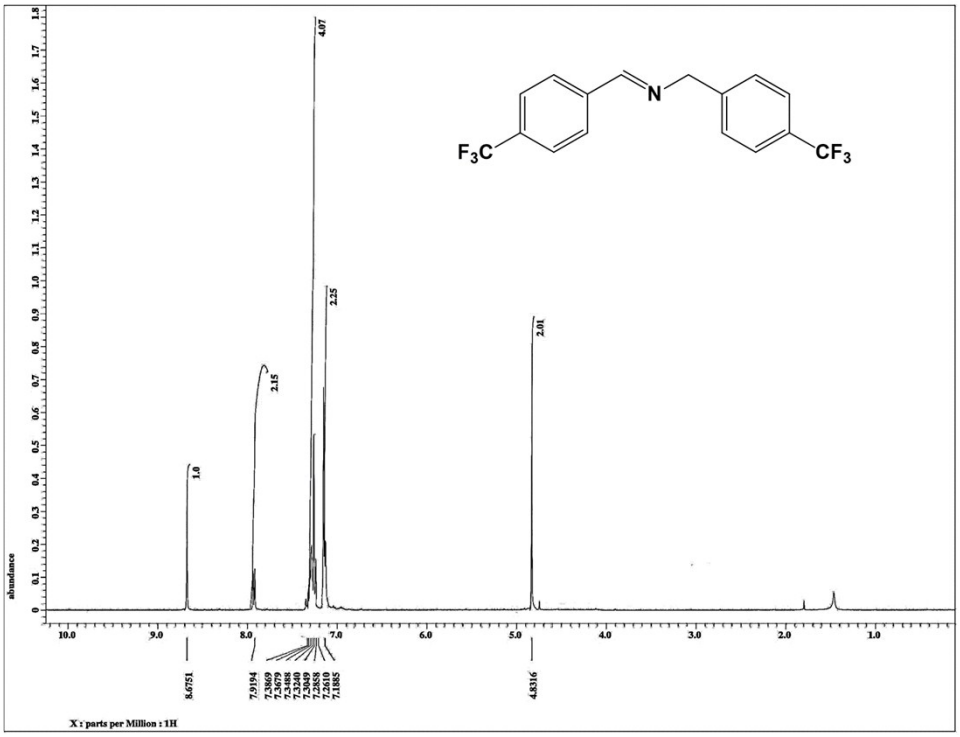


Figure S17. ^{1}H-NMR of N-(4-(trifluoromethyl)benzylidene)-1-(4(trifluoromethyl)phenyl)methanamine.

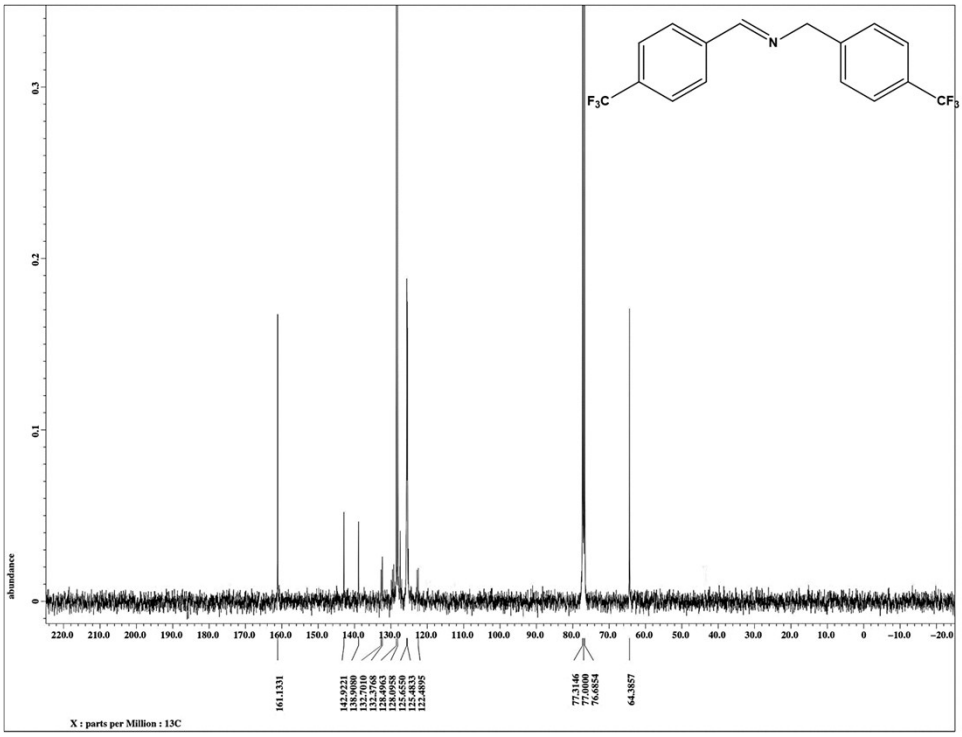


Figure S18. ^{13}C NMR of N-(4-(trifluoromethyl)benzylidene)-1-(4(trifluoromethyl)phenyl)methanamine.

N-(4-methoxybenzylidene)-1-(4-methoxyphenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.29 (s, 1H), 7.71 (d, 2H, J = 8.6), 7.22 (d, 2H, J = 8.7), 6.88-6.86 (m, 4H), 4.72 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.4, 160.7, 158.3, 131.4, 129.6, 129.0, 128.1, 113.78, 113.72, 64.2, 55.16, 55.10.

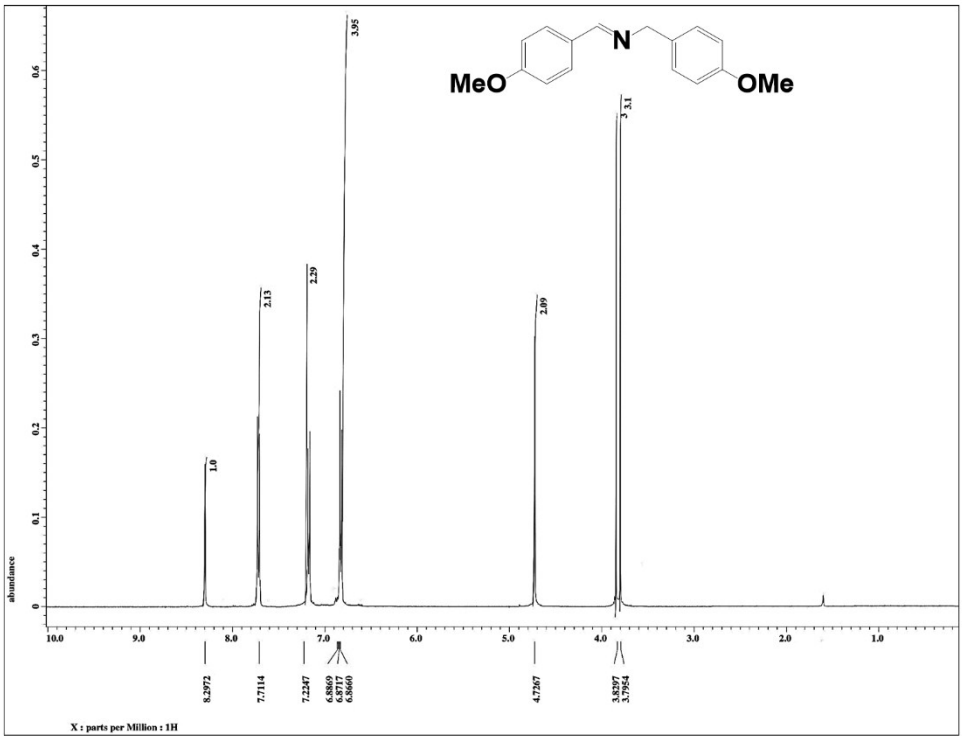


Figure S19. ^{1}H-NMR of N-(4-methoxybenzylidene)-1-(4-methoxyphenyl)methanamine.

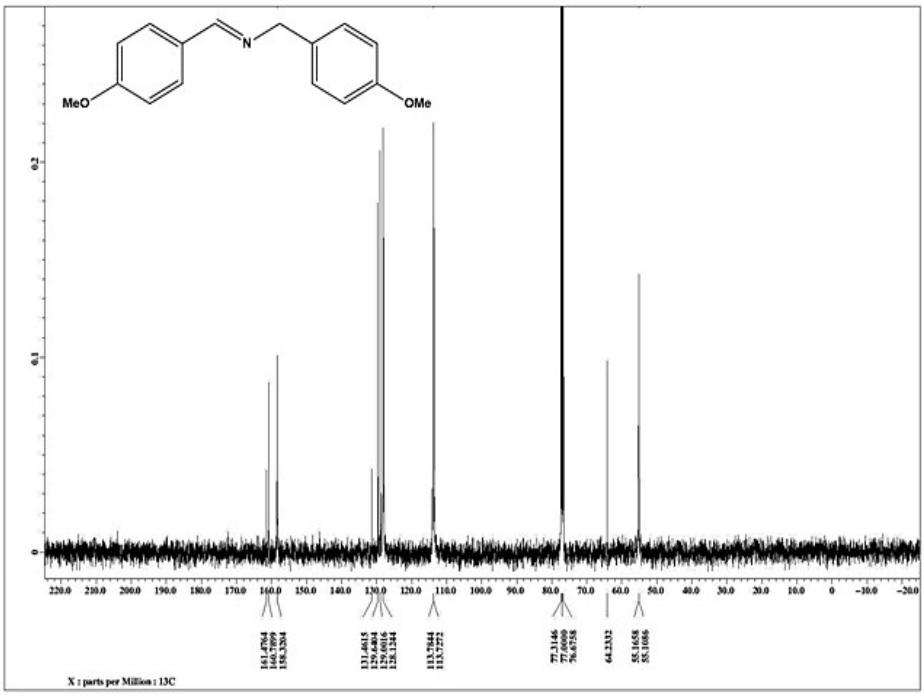


Figure S20. ^{13}C NMR of N-(4-methoxybenzylidene)-1-(4-methoxyphenyl)methanamine.

N-(4-methylbenzylidene)-1-(p-tolyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.36 (s, 1H), 7.70 (d, 2H, J = 8.2 Hz), 7.28-7.16 (m, 6H), 4.79 (s, 2H), 2.41 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.9, 140.3, 136.6, 136.3, 133.5, 129.5, 129.1, 128.3, 128.1, 64.6, 21.4, 21.1.

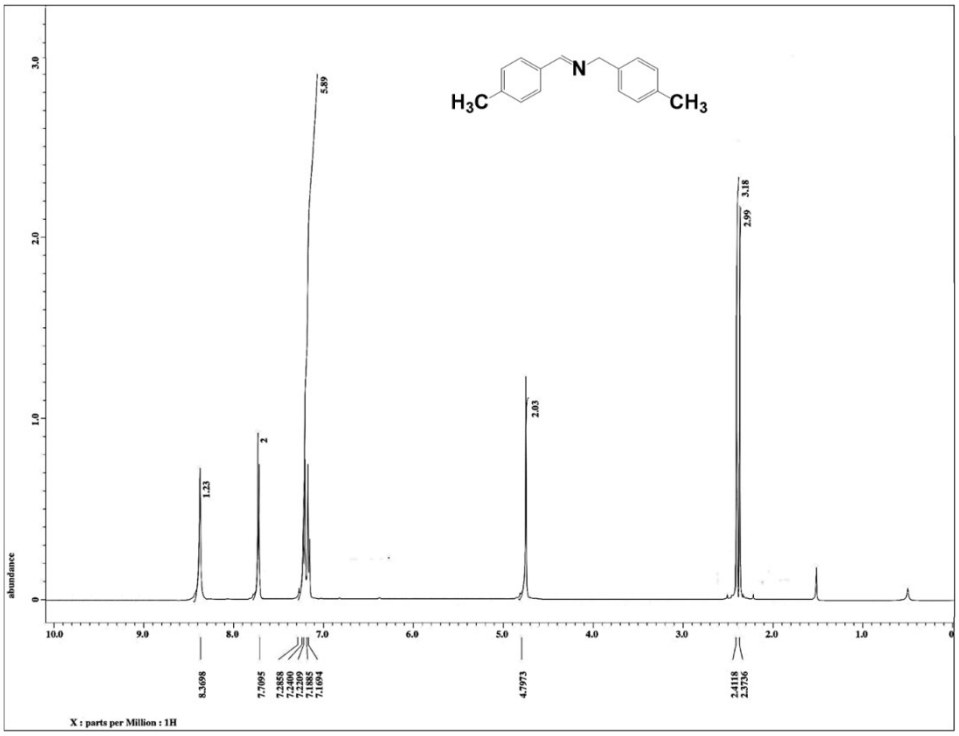


Figure S21. ^{1}H NMR of N-(4-methylbenzylidene)-1-(p-tolyl)methanamine.

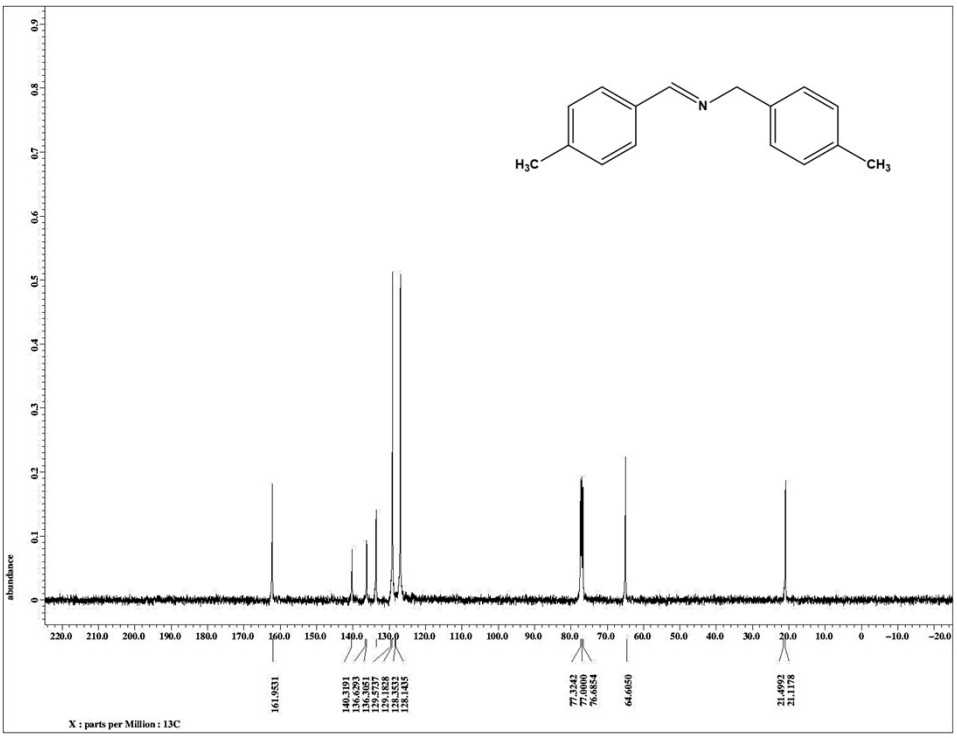


Figure S22. ^{13}C NMR of N-(4-methylbenzylidene)-1-(p-tolyl)methanamine.

N-(3-methoxybenzylidene)-1-(3-methoxyphenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.3 (s, 1H), 7.31 – 7.22 (m, 1H), 6.94 – 6.89 (m, 3H), 6.86-6.76 (m, 4H), 4.78(s, 2H), 3.82 (s, 3H), 3.79(s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.1, 159.9, 159.8, 140.8, 137.6, 129.6, 129.5, 121.7, 120.3, 117.6, 113.7, 112.5, 111.6, 64.7, 55.4, 55.2.

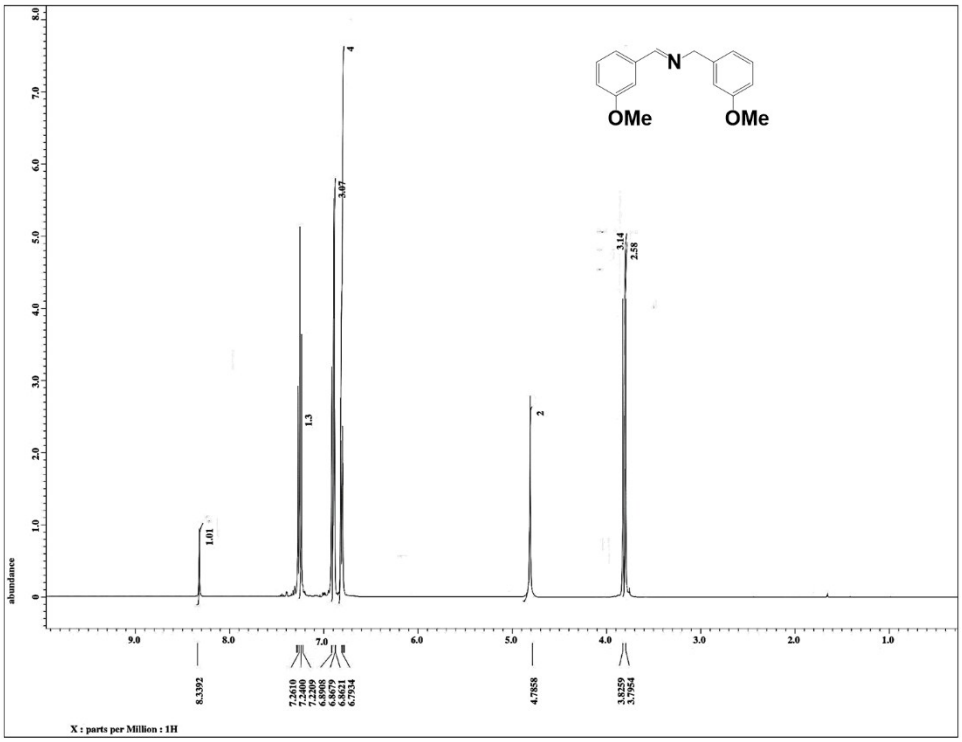


Figure S23. ^{1}H-NMR of N-(3-methoxybenzylidene)-1-(3-methoxyphenyl)methanamine.

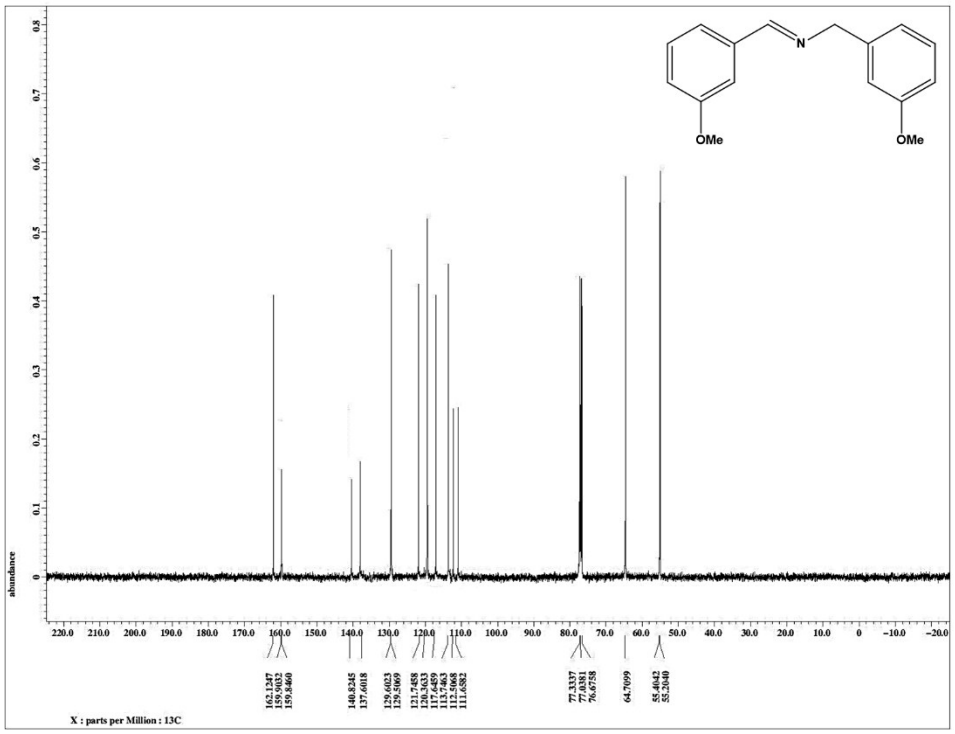


Figure S24. ^{13}C NMR of N-(3-methoxybenzylidene)-1-(3-methoxyphenyl)methanamine.

N-(2-chlorobenzylidene)-1-(2-chlorophenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.86 (s, 1H), 8.12-8.10 (m, 2H), 7.42-7.17 (m, 6H), 4.94 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 159.7, 136.7, 135.2, 133.3, 133.0, 131.6, 129.7, 129.6, 129.2, 128.3, 128.2, 127.0, 126.8, 62.1.

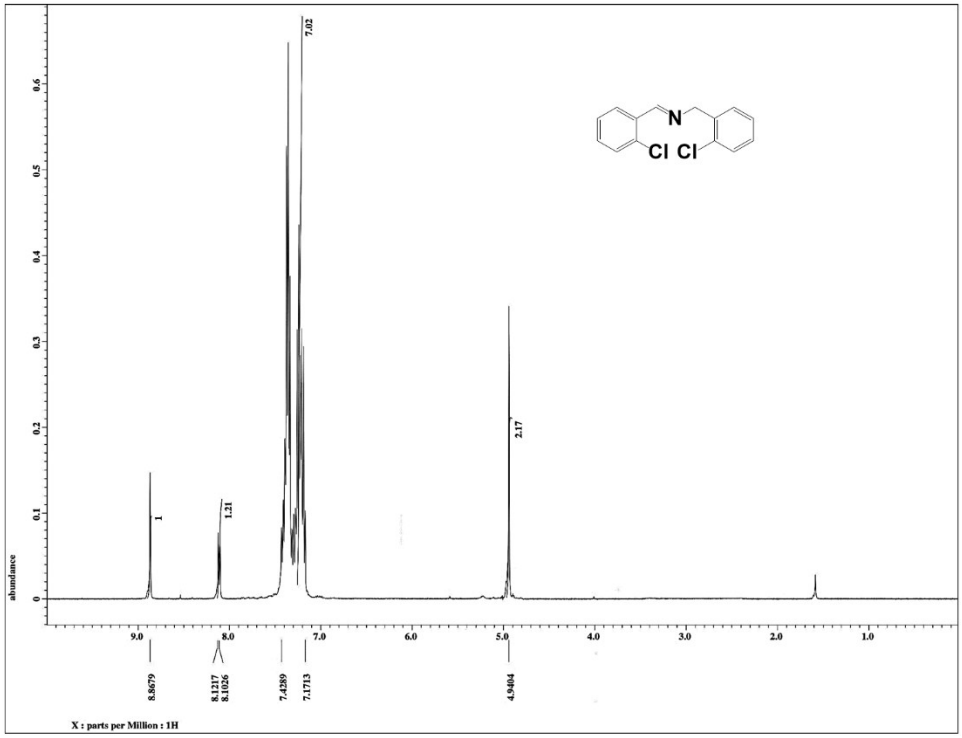


Figure S25. ^{1}H-NMR of N-(2-chlorobenzylidene)-1-(2-chlorophenyl)methanamine.

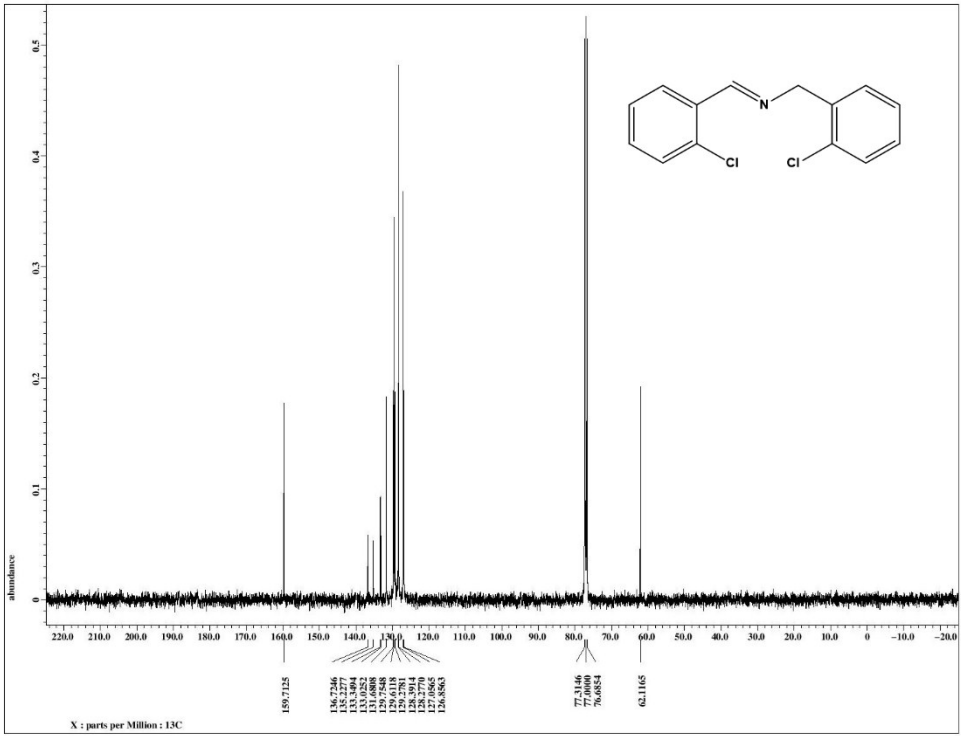


Figure S26. ^{13}C NMR of N-(2-chlorobenzylidene)-1-(2-chlorophenyl)methanamine.

N-(3,4-dichlorobenzylidene)-1-(3,4-dichlorophenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.29 (s, 1 H), 7.88 (d, J = 1.9 Hz, 1 H), 7.59-7.57 (dd, J = 8.3, 2 Hz), 7.50 (d ,J = 8.4 Hz, 1 H), 7.39 (d, J = 8.2 Hz, 2H), 7.16-7.13 (dd, J = 8.2, 2 Hz, 1 H), 4.74 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 160.02, 139.03, 135.61, 135.09, 133.16, 132.99, 130.69, 130.43, 129.75, 127.34, 127.18, 63.51

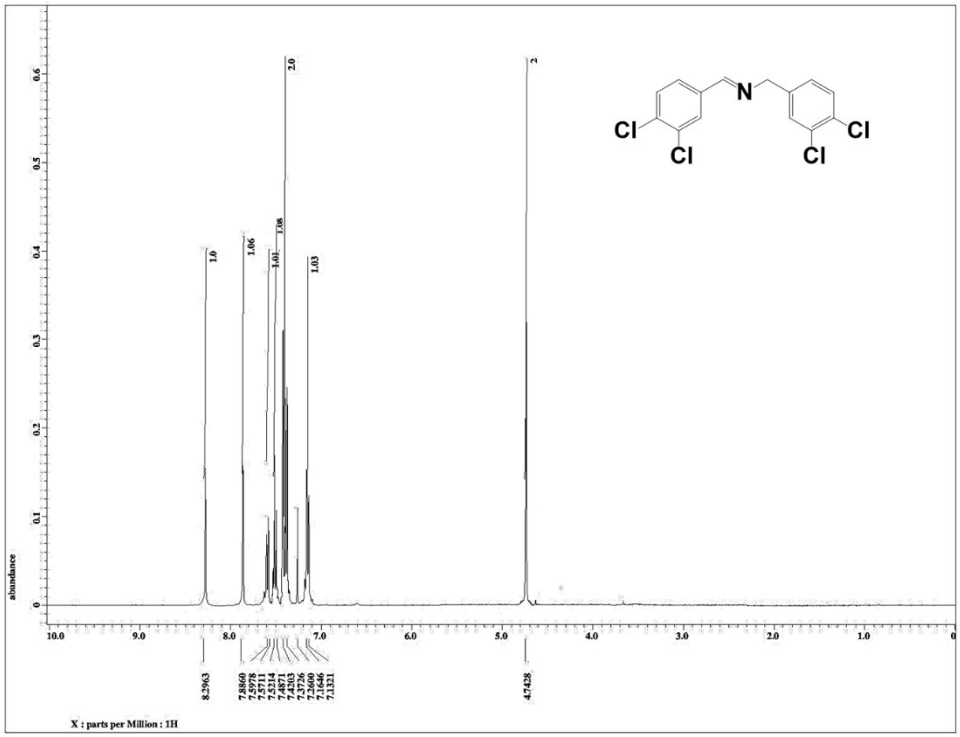


Figure S27. ^{1}H-NMR of N-(3,4-dichlorobenzylidene)-1-(3,4-dichlorophenyl)methanamine.

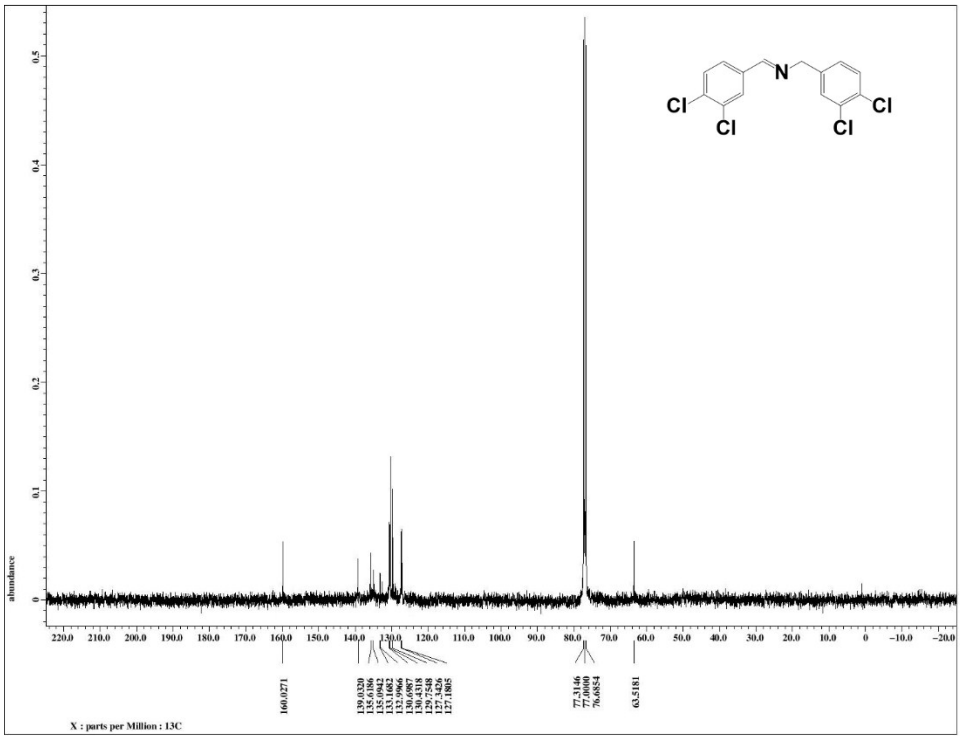


Figure S28. ^{13}C NMR of N-(3,4-dichlorobenzylidene)-1-(3,4-dichlorophenyl)methanamine.

N-(3-(trifluoromethyl)benzylidene)-1-(3-trifluoromethyl)phenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.46 (s, 1 H), 8.06 (s, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.71-7.67 (m, 1H), 7.59-7.42 (m, 5H), 4.88 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 160.9, 139.9, 136.5, 131.4 (q, J = 0.9 Hz), 131.2 (q, J = 1 Hz), 131.0 (q, J = 30.6 Hz), 130.9 (q, J = 30.4 Hz), 129.2, 129.1, 127.4 (q, J = 3.6 Hz), 125(q, J = 3.6 Hz), 124.6 (q, J = 3.6 Hz), 124.0 (q, J = 270 Hz), 123.7 (q, J = 3.6 Hz),123.6 (q, J = 270 Hz), 64.4

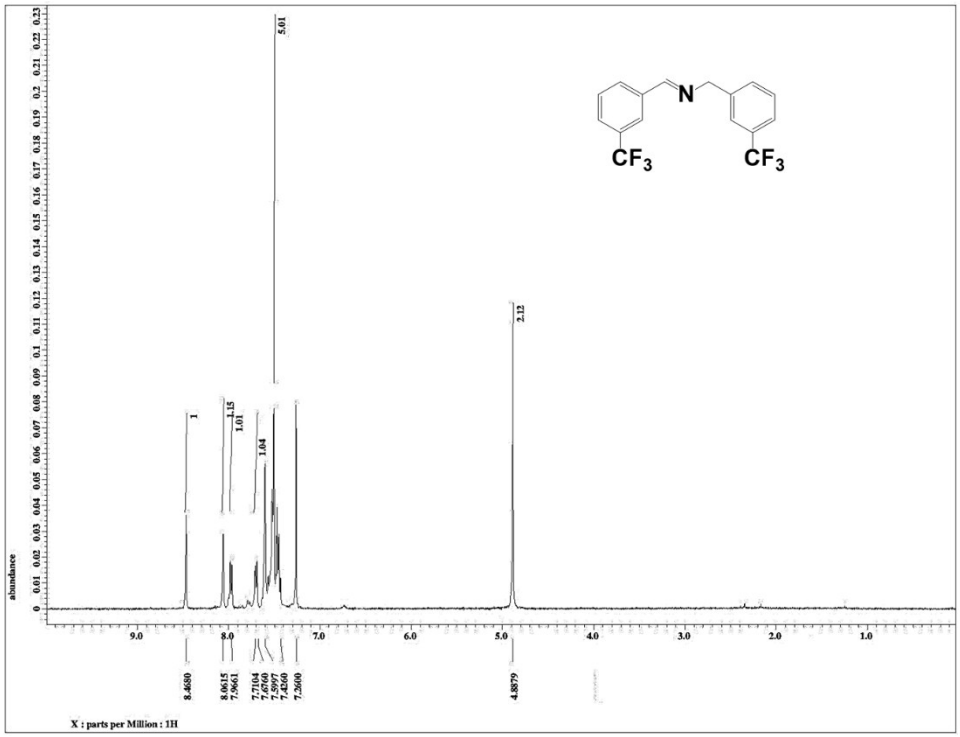


Figure S29. ^{1}H-NMR of N-(3-(trifluoromethyl)benzylidene)-1-(3-trifluoromethyl)phenyl)methanamine.

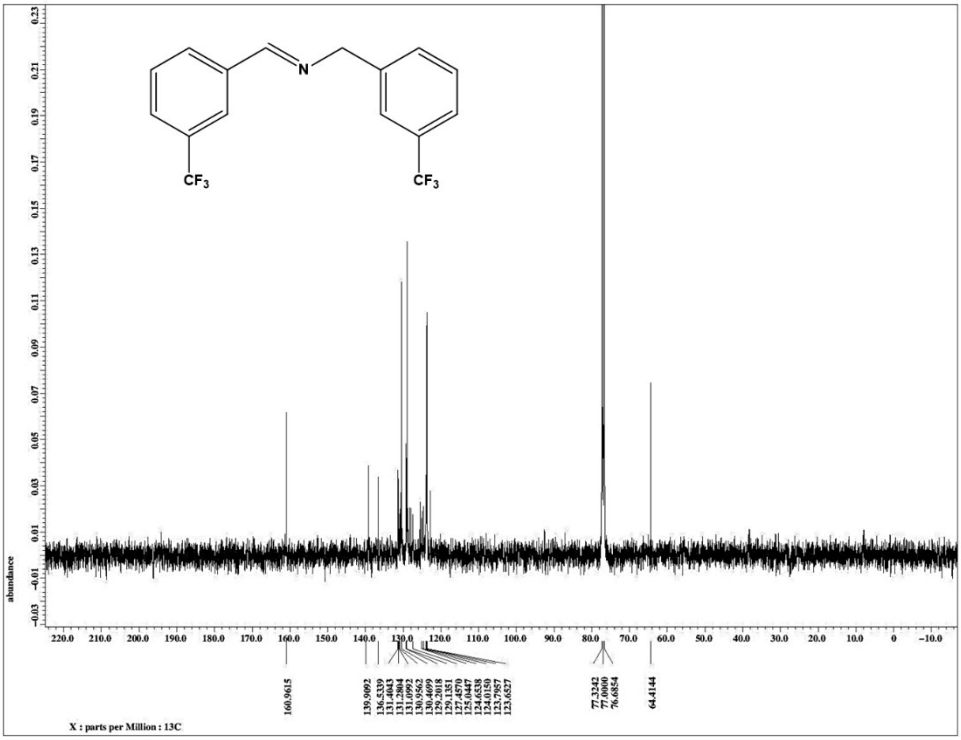


Figure S30. ^{13}C NMR of N-(3-(trifluoromethyl)benzylidene)-1-(3-trifluoromethyl)phenyl)methanamine.

N-(2-methoxybenzylidene)-1-(2-methoxyphenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.82 (s, 1H), 8.01 (dd, J = 7.6, 1.5 Hz, 1 H), 7.29-7.19 (m, 3 H), 6.98-6.85 (m, 4 H), 4.81 (s, 2H), 3.85(s, 3H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 158.7, 158.3, 156.9, 131.7, 129.0, 128.0, 127.8, 127.4, 124.7, 120.6, 120.4, 110.9, 110.2, 59.5, 55.4, 55.2.

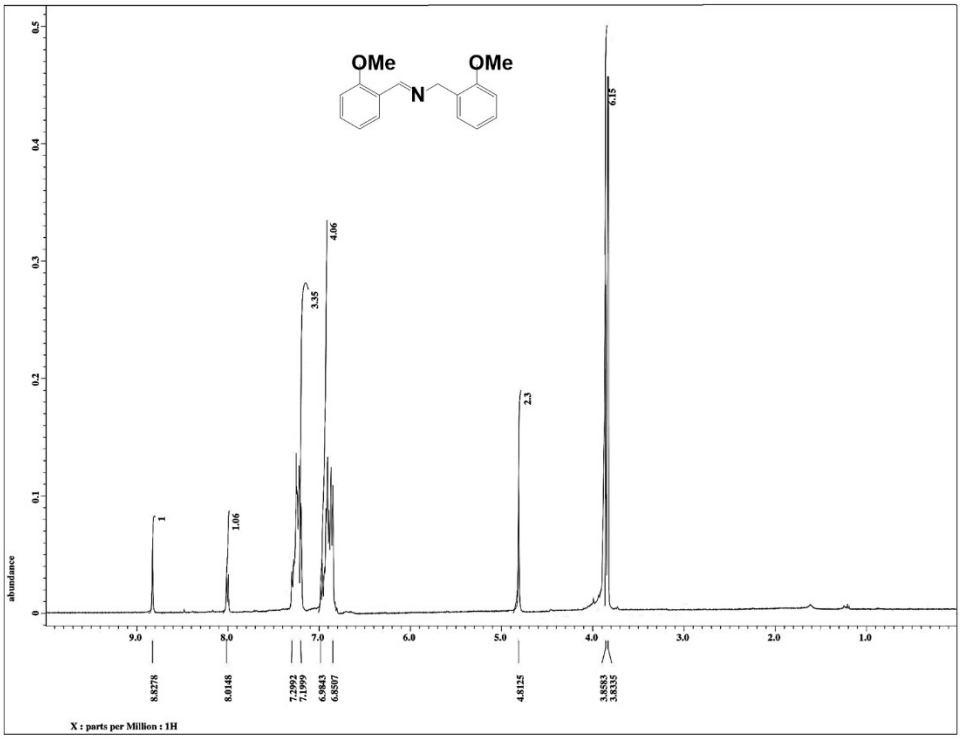


Figure S31. ^{1}H-NMR of N-(2-methoxybenzylidene)-1-(2-methoxyphenyl)methanamine.

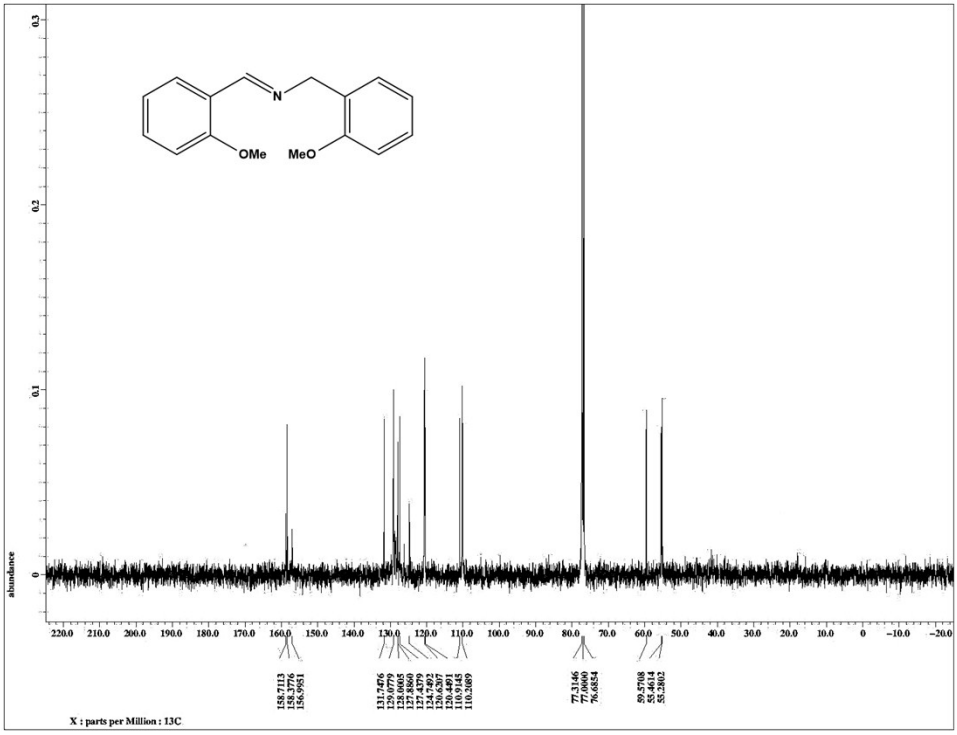


Figure 32. ^{13}C NMR of N-(2-methoxybenzylidene)-1-(2-ethoxyphenyl)methanamine.

Table S1. Comparison of catalytic activity of $CuFe_2O_4$/RGO NCs with some recent nanocatalysts.

Sr. No.	Catalyst	Time (h)	Oxidant	Temp. (°C)	TOF (h^{-1})	Ref.
1	Au/CeO2	4	O_2 (3 atm.)	130	2.4	S1
2	$Au/Ce_{0.9}Fe_{0.1}O_{2-\delta}$	4	Bubbling	130	3.2	S1
3	Au/SBA-NH2	24	O_2 (1 atm.)	100	4.9	S2
4	Au–Pd/Fiber	24	O_2 (5 atm.)	100	3.7	S3
5	Meso Cs/MnO_x	3	Balloon	110	1.1	S4
7	**$CuFe_2O_4$/RGO**	**8**	**Air**	**60**	**2.72**	**This work**

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