Electronic Supplementary Material (ESI) for New Journal of Chemistry.

g-C_3N_4/Uio-66-NH_2 nanocomposites with enhanced visible light photocatalytic activity for hydrogen evolution and oxidation of amines to imines

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Table S1. The content of Zr in Uio-66-NH_2 and CNUIO-x measured by ICP-OES.

Sample	The content of Zr (wt%)
Uio-66-NH_2	27.9
CNUIO-1	13.2
CNUIO-3	6.8
CNUIO-5	5.0
CNUIO-7	3.2
CNUIO-9	2.4

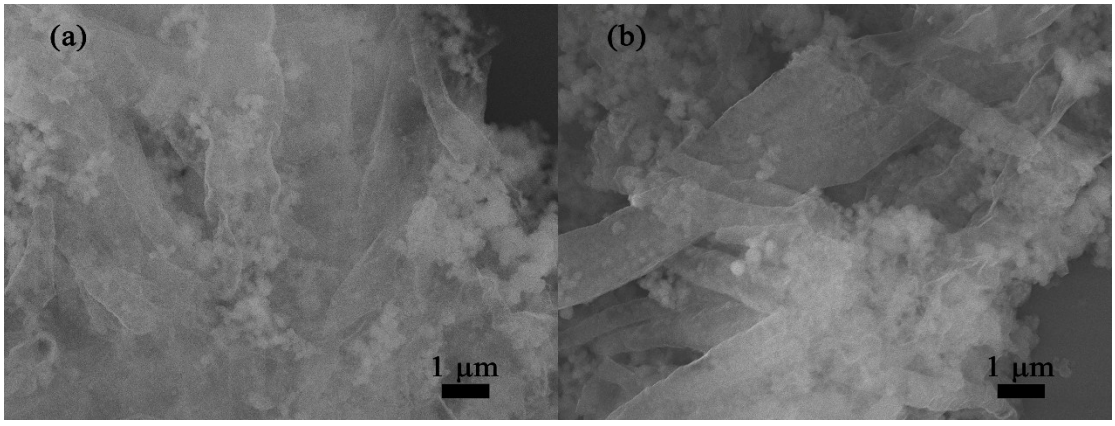

Fig. S1. SEM image of CNUIO-5 before and after five cycles of photocatalytic experiments.

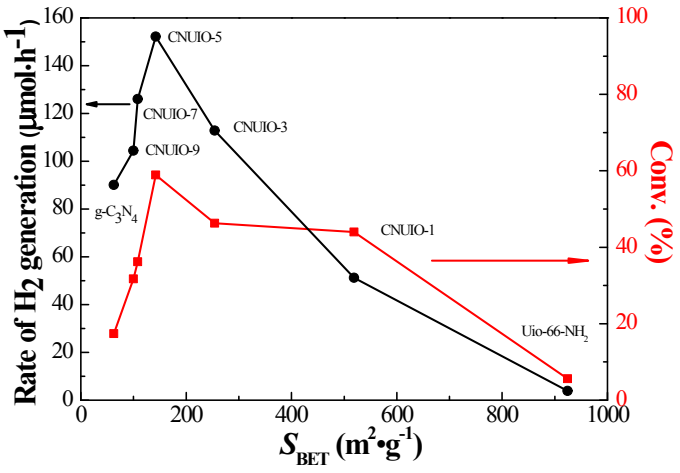

Fig. S2. Plot of the relationship between the photocatalytic activity and S_{BET} using g-C_3N_4, CNUIO-x and Uio-66-NH_2 as photocatalyst, respectively.

The resulted imines were analyzed by NMR and HRMS measurements.

1. *N-benzylidenebenzylamine*

^{1}H NMR (400 MHz, actone-d_6) δ 8.49 (s, 1H), 7.84-7.82 (m, 2H), 7.45-7.43 (m, 3H), 7.38-7.31 (m, 4H), 7.26-7.23 (m, 1H), 4.80 (s, 2H); ^{13}C NMR (100 MHz, actone-d_6) δ 162.32, 140.88, 137.55, 131.44, 129.41, 129.15, 128.95, 128.75, 127.56, 65.44; HRMS (ES$^+$-TOF) calculated for $C_{14}H_{13}N$ ([M+H]$^+$): 196.1121, found 196.1130.

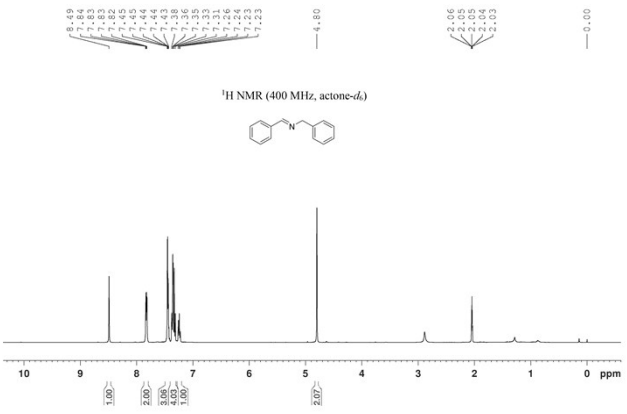

Fig. S3. ^{1}H NMR spectra of *N*-benzylidenebenzylamine.

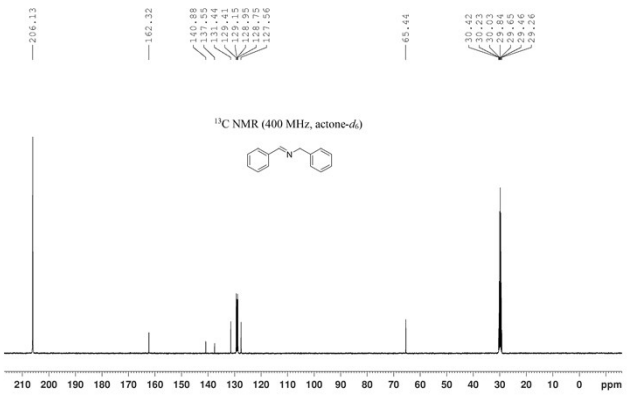

Fig. S4. ^{13}C NMR spectra of *N*-benzylidenebenzylamine.

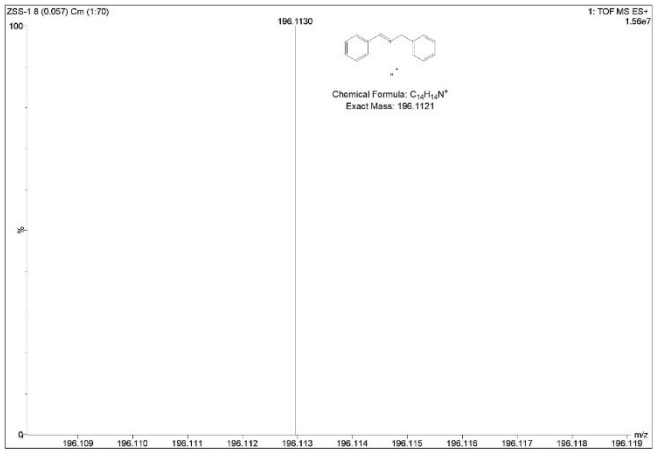

Fig. S5. HRMS spectra of *N*-benzylidenebenzylamine.

2. *(E)-N-(4-fluorobenzylidene)(4-fluorophenyl)methanamine*

^{1}H NMR (400 MHz, actone-d_6) δ 8.48 (s, 1H), 7.90-7.86 (m, 2H), 7.42-7.38 (m, 2H), 7.24-7.20 (m, 2H), 7.12-7.08 (m, 2H), 4.78 (s, 2H); ^{13}C NMR (100 MHz, actone-d_6) δ 165.24 (d, *J* = 244.9 Hz), 162.80 (d, *J* = 239.1 Hz), 161.27, 137.06 (d, *J* = 2.8 Hz), 134.15 (d, *J* = 2.8 Hz), 131.23 (d, *J* = 8.7 Hz), 130.65 (d, *J* = 7.9 Hz), 116.48 (d, *J* = 21.9 Hz), 115.90 (d, *J* = 21.2 Hz), 64.53; HRMS (ES^{+}-TOF) calculated for $C_{14}H_{11}F_2N$ ([M+H]$^{+}$): 232.0932, found 232.0942.

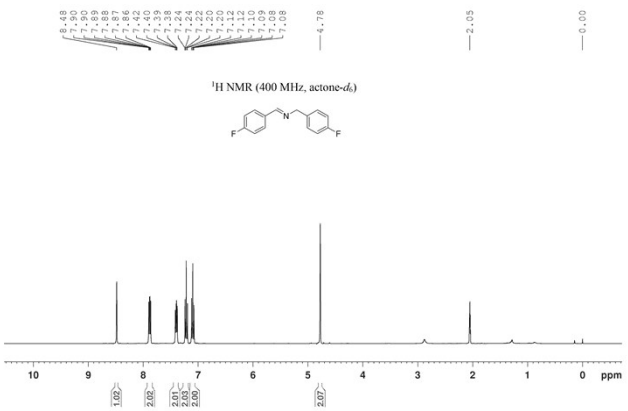

Fig. S6. ^{1}H NMR spectra of (*E*)-*N*-(4-fluorobenzylidene)(4-fluorophenyl)methanamine.

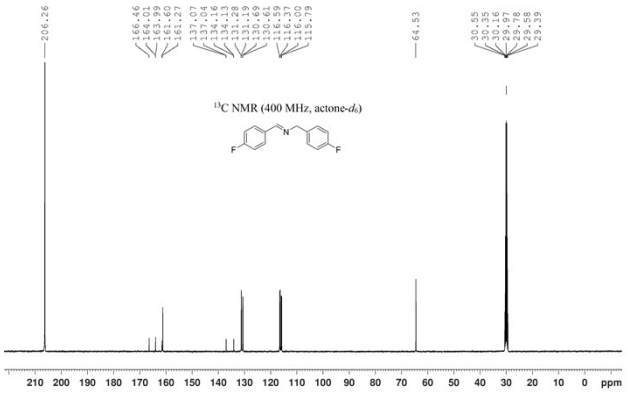

Fig. S7. ^{13}C NMR spectra of (*E*)-*N*-(4-fluorobenzylidene)(4-fluorophenyl)methanamine.

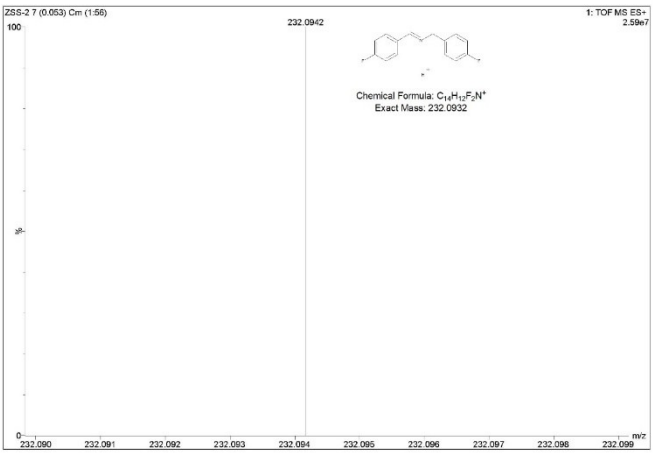

Fig. S8. HRMS spectra of (*E*)-*N*-(4-fluorobenzylidene)(4-fluorophenyl)methanamine.

3. ***(E)-N-(4-chlorobenzylidene)(4-chlorophenyl)methanamine***

^{1}H NMR (400 MHz, actone-d_6) δ 8.51 (s, 1H), 7.86-7.84 (m, 2H), 7.51-7.48 (m, 2H), 7.41-7.36 (m, 4H), 4.80 (s, 2H); ^{13}C NMR (100 MHz, actone-d_6) δ 161.75, 139.88, 137.09, 136.38, 133.08, 130.67, 130.59, 129.81, 129.37, 64.54; HRMS (ES$^+$-TOF) calculated for $C_{14}H_{11}Cl_2N$ ([M+H]$^+$): 264.0341, found 264.0352.

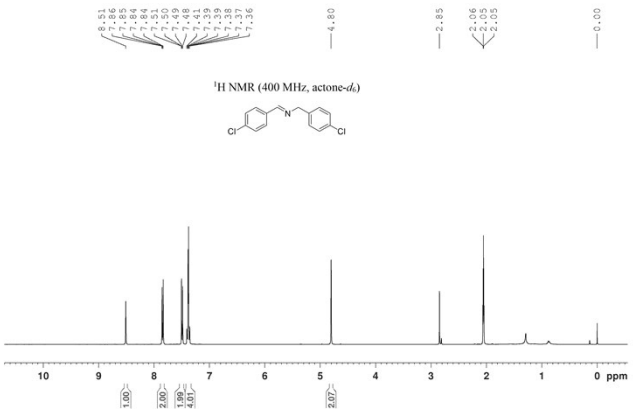

Fig. S9. ^{1}H NMR spectra of (*E*)-*N*-(4-chlorobenzylidene)(4-chlorophenyl)methanamine.

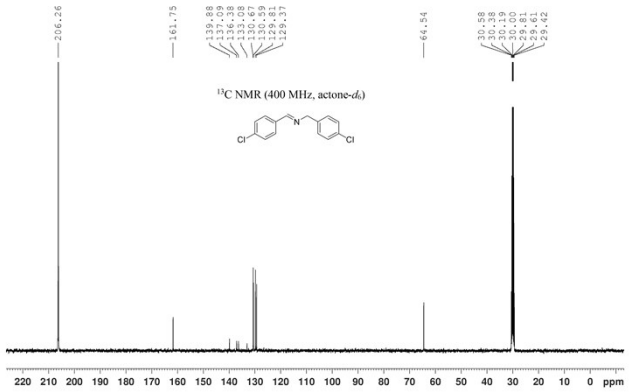

Fig. S10. ^{13}C NMR spectra of (*E*)-*N*-(4-chlorobenzylidene)(4-chlorophenyl)methanamine.

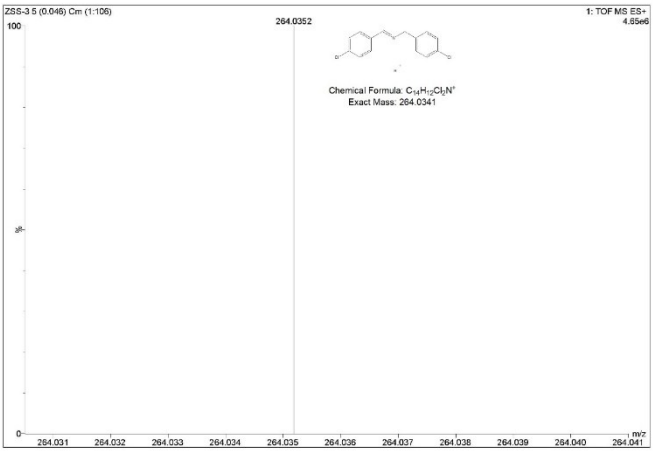

Fig. S11. HRMS spectra of (*E*)-*N*-(4-chlorobenzylidene)(4-chlorophenyl)methanamine.

4. *(E)-N-(4-bromobenzylidene)(4-bromophenyl)methanamine*

^{1}H NMR (400 MHz, actone-d_6) δ 8.47 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.77 (s, 2H); ^{13}C NMR (100 MHz, actone-d_6) δ 161.86, 140.23, 136.64, 132.75, 132.31, 130.90, 130.84, 125.52, 121.12, 64.54; HRMS (ES$^+$-TOF) calculated for $C_{14}H_{11}Br_2N$ ([M+H]$^+$): 351.9331, found 351.9339.

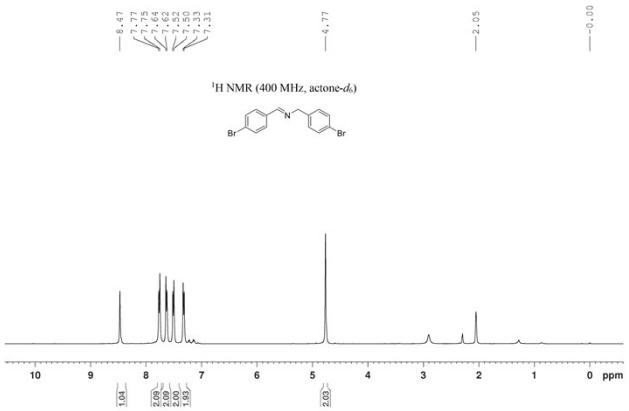

Fig. S12. ^{1}H NMR spectra of (*E*)-*N*-(4-bromobenzylidene)(4-bromophenyl)methanamine.

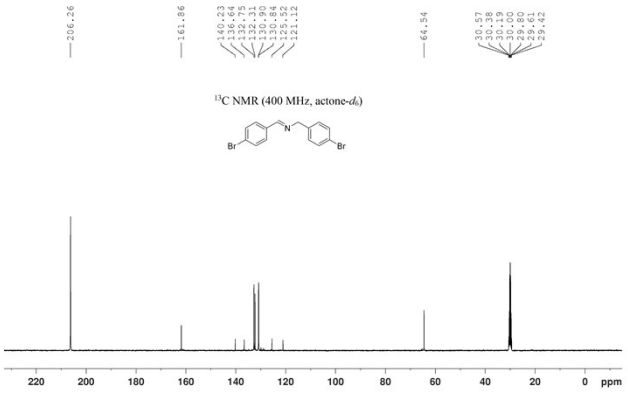

Fig. S13. ^{13}C NMR spectra of (*E*)-*N*-(4-bromobenzylidene)(4-bromophenyl)methanamine.

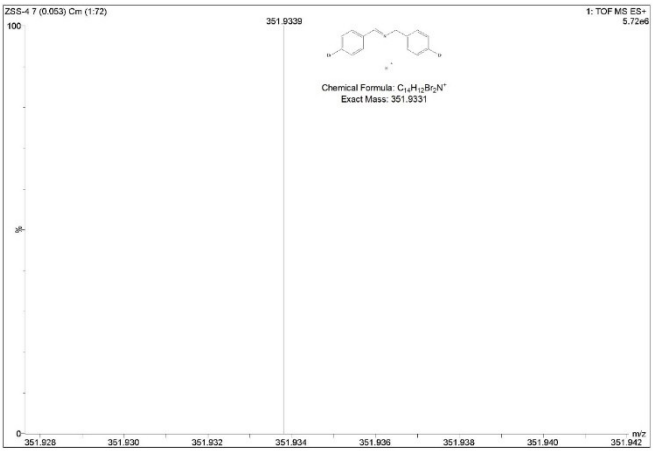

Fig. S14. HRMS spectra of (*E*)-*N*-(4-bromobenzylidene)(4-bromophenyl)methanamine.

5. *(E)-N-(4-methoxybenzylidene)(4-methoxyphenyl)methanamine*

^{1}H NMR (400 MHz, actone-d_6) δ 8.37 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 7.5 Hz, 2H), 4.68 (s, 2H), 3.83 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, actone-d_6) δ 162.72, 161.18, 159.67, 133.17, 130.57, 129.98, 114.85, 114.60, 64.98, 55.79, 55.55; HRMS (ES^{+}-TOF) calculated for $C_{16}H_{17}NO_2$ ([M+H]$^{+}$): 256.1332, found 256.1337.

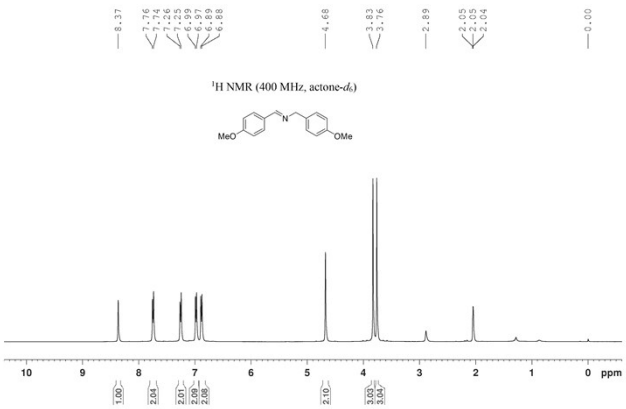

Fig. S15. ^{1}H NMR spectra of (*E*)-*N*-(4-methoxybenzylidene)(4-methoxyphenyl)methanamine.

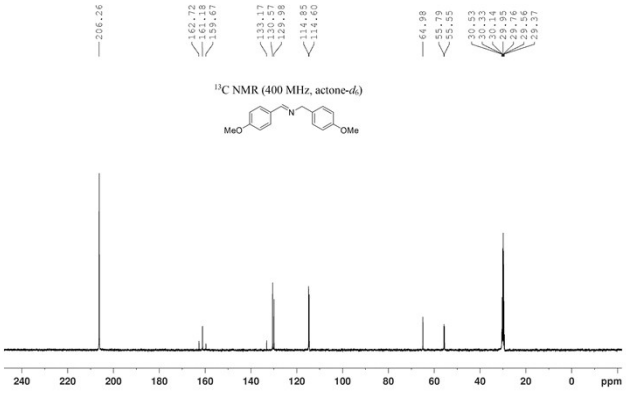

Fig. S16. ^{13}C NMR spectra of (*E*)-*N*-(4-methoxybenzylidene)(4-methoxyphenyl)methanamine.

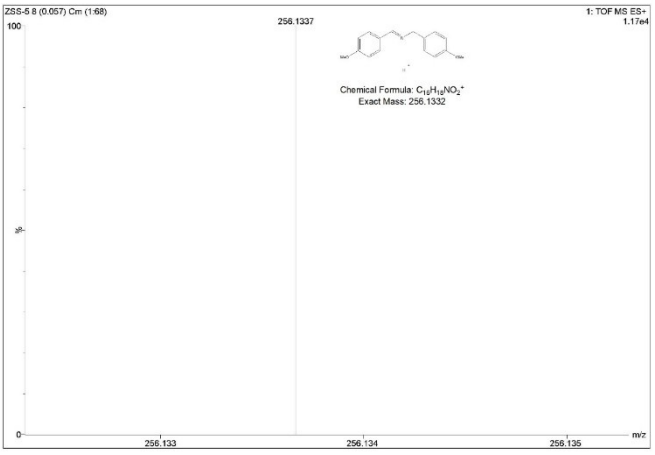

Fig. S17. HRMS spectra of (*E*)-*N*-(4-methoxybenzylidene)(4-methoxyphenyl)methanamine.

6. ***(E)-N-(4-methylbenzylidene)(4-methylphenyl)methanamine***

^{1}H NMR (400 MHz, actone-d_6) δ 8.42 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.24 (t, *J* = 8.2 Hz, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.72 (s, 2H), 2.36 (s,3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, actone-d_6) δ 162.03, 141.71, 138.14, 137.04, 135.26, 130.22, 129.92, 129.11, 128.90, 65.42, 21.59, 21.25; HRMS (ES$^+$-TOF) calculated for $C_{16}H_{17}N$ ([M+H]$^+$): 224.1434, found 224.1453.

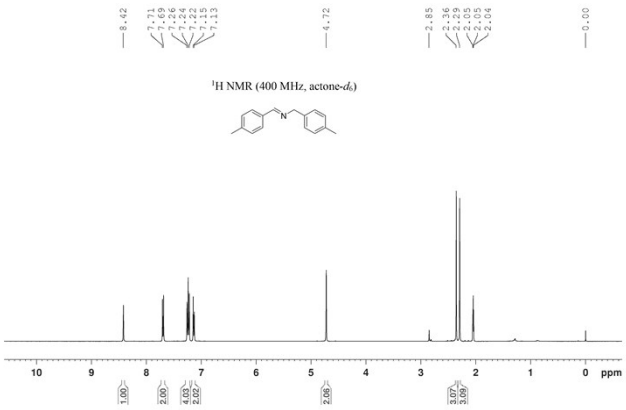

Fig. S18. ^{1}H NMR spectra of (*E*)-*N*-(4-methylbenzylidene)(4-methylphenyl)methanamine.

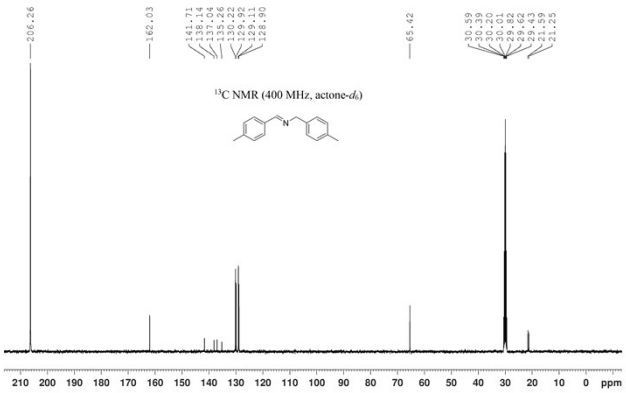

Fig. S19. ^{13}C NMR spectra of (*E*)-*N*-(4-methylbenzylidene)(4-methylphenyl)methanamine.

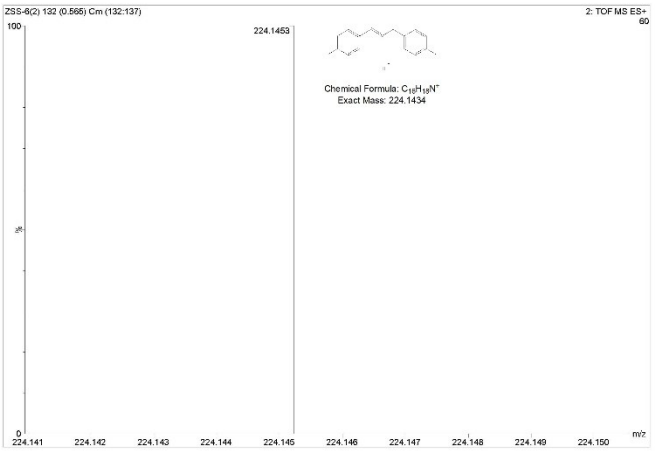

Fig. S20. HRMS spectra of (*E*)-*N*-(4-methylbenzylidene)(4-methylphenyl)methanamine.

7. *(E)-N-(3-methylbenzylidene)(3-methylphenyl)methanamine*

^{1}H NMR (400 MHz, actone-d_6) δ 8.44 (s, 1H), 7.64 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.35-7.26 (m, 2H), 7.21-7.13 (m, 3H), 7.06 (d, *J* = 7.4 Hz, 1H), 4.75 (s, 2H), 2.36 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, actone-d_6) δ 162.45, 140.96, 139.15, 138.70, 137.76, 132.29, 129.64, 129.48, 129.22, 128.39, 126.50, 126.05, 65.73, 21.57, 21.41; HRMS (ES$^+$-TOF) calculated for $C_{16}H_{17}N$ ([M+H]$^+$): 224.1434, found 224.1443.

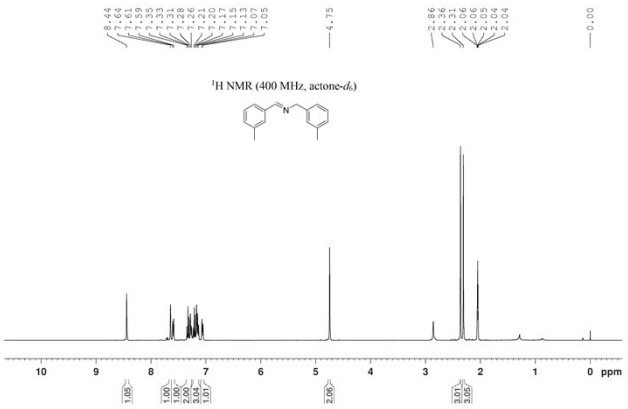

Fig. S21. ^{1}H NMR spectra of (*E*)-*N*-(3-methylbenzylidene)(3-methylphenyl)methanamine.

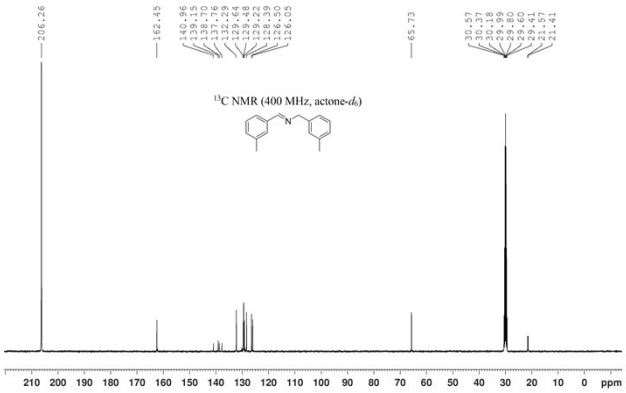

Fig. S22. ^{13}C NMR spectra of (*E*)-*N*-(3-methylbenzylidene)(3-methylphenyl)methanamine.

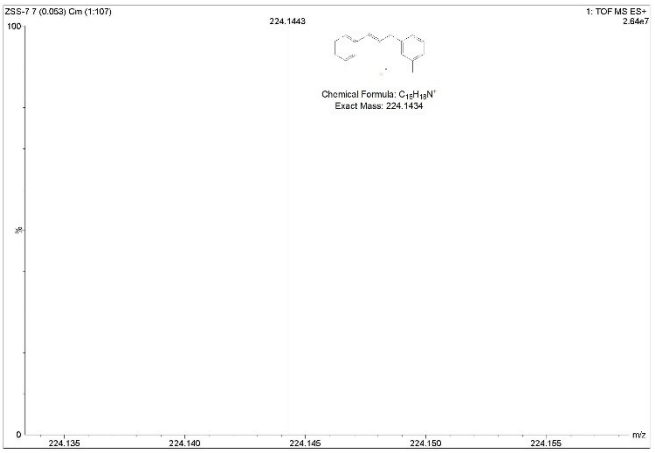

Fig. S23. HRMS spectra of (*E*)-*N*-(3-methylbenzylidene)(3-methylphenyl)methanamine.

8. *(E)-N-(2-methylbenzylidene)(2-methylphenyl)methanamine*

^{1}H NMR (400 MHz, actone-d_6) δ 8.79 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.33-7.30 (m, 2H), 7.26-7.21 (m, 2H), 7.18-7.14 (m, 3H), 4.81 (s, 2H), 2.53 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, actone-d_6) δ 161.29, 139.35, 138.74, 137.06, 135.49, 131.89, 131.08, 130.92, 129.23, 128.78, 127.83, 126.96, 126.88, 64.14, 19.75, 19.47; HRMS (ES^{+}-TOF) calculated for $C_{16}H_{17}N$ ([M+H]$^{+}$): 224.1434, found 224.1441.

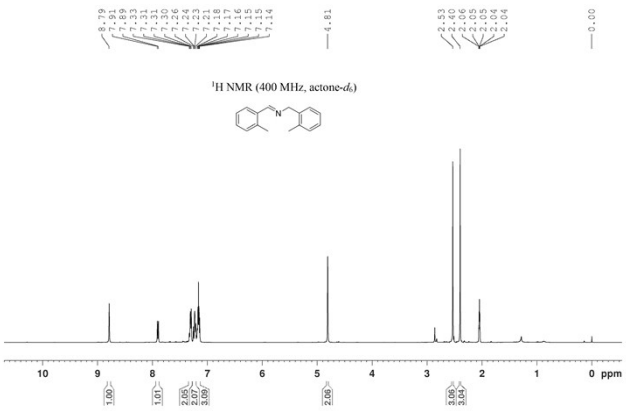

Fig. S24. ^{1}H NMR spectra of (*E*)-*N*-(2-methylbenzylidene)(2-methylphenyl)methanamine.

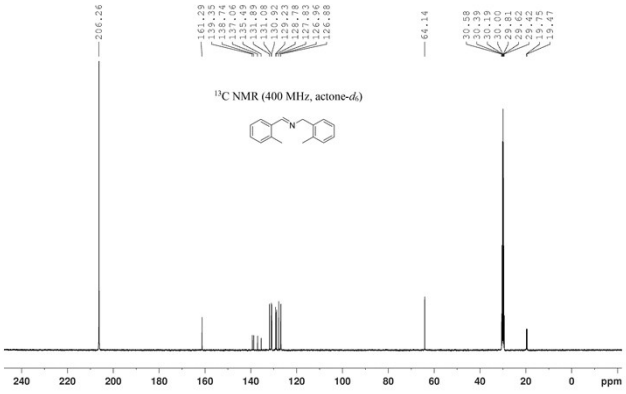

Fig. S25. ^{13}C NMR spectra of (*E*)-*N*-(2-methylbenzylidene)(2-methylphenyl)methanamine.

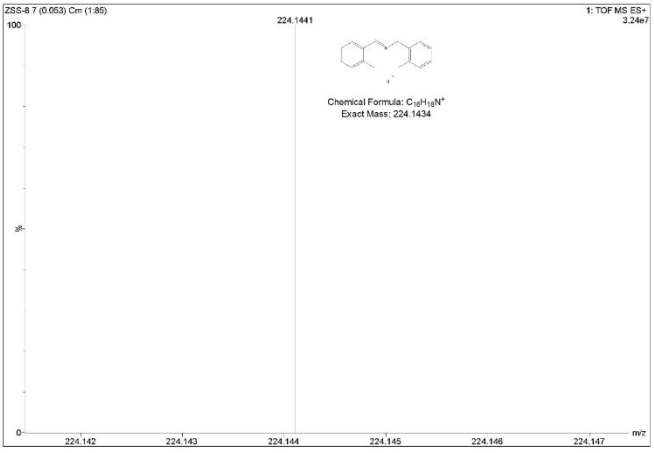

Fig. S26. HRMS spectra of (*E*)-*N*-(2-methylbenzylidene)(2-methylphenyl)methanamine.

Table S2. Comparison of the H_2 production rates over CNUIO-5 and some reported g-C_3N_4 compounds.

	Catalyst	H_2 evolution rate (μmol·h^{-1})	Reference
1	Uio-66/g-C_3N_4	10.0	[1]
2	Na_x-C_3N_4/Pt@Uio-66	1.4	[2]
3	g-C_3N_4-Co_2P-0.1 mM K_2HPO_4	27.8	[3]
4[a]	CN-AB-CuS	17.4	[4]
5	g-C_3N_4–Cu_3P	8.0	[5]
6	H-g-C_3N_4	15.2	[6]
7	HM-CN	25.1	[7]
8	g-C_3N_4-0.5%Ni-1.0%NiS	25.8	[8]
9[b]	g-C_3N_4-0.5%CB-1.0%	18.3	[9]
10	M-CN	15.6	[10]
11	CNUIO-5	152.2	Our work

[a] Acetylene black (AB); [b] Carbon black (CB).

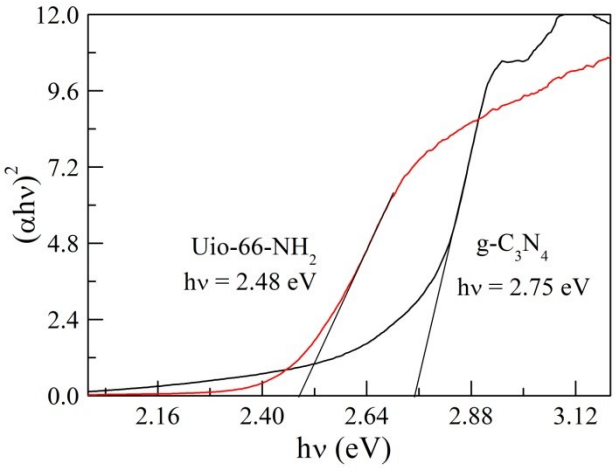

Fig. S27. The band gaps of g-C_3N_4 and Uio-66-NH_2.

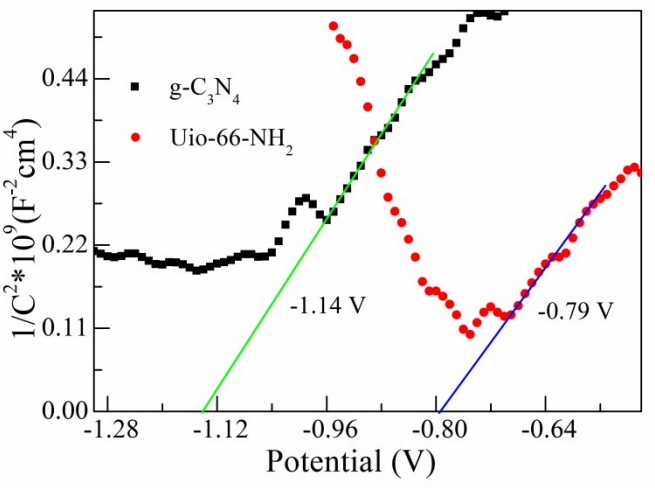

Fig. S28. Mott-Schottky plots of g-C_3N_4 and Uio-66-NH_2.

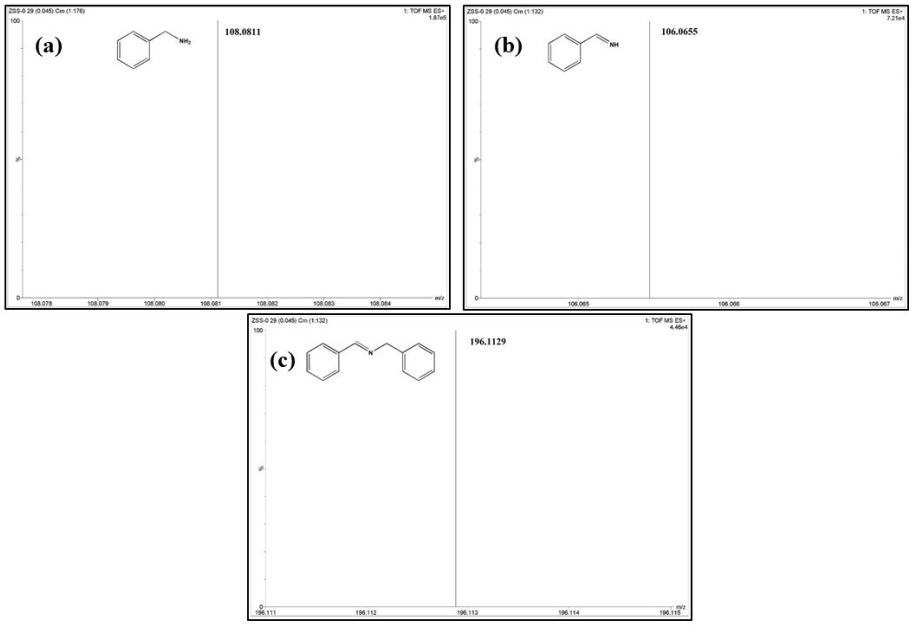

Fig. S29. HRMS spectra of benzylamine (a), phenylmethanimine (b) and *N*-benzylidenebenzylamine (c).

References

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[10] M. J. Zhou, Z. H. Hou, L. Zhang, Y. Liu, Q. Z. Gao and X. B. Chen, *Sustainable Energy Fuels.*, 2017, 1, 317-323.