Nickel-decorated g-C_3N_4 hollow sphere as an efficient photocatalyst for hydrogen evolution and oxidation of amines to imines

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The resulted imines were analyzed by NMR and HRMS.

1. ***N-benzylidenebenzylamine***

^{1}H NMR (400 MHz, actone-d_6) δ 8.49 (s, 1H), 7.84-7.82 (m, 2H), 7.46-7.43 (m, 3H), 7.38-7.32 (m, 4H), 7.26-7.23 (m, 1H), 4.80 (s, 2H); ^{13}C NMR (100 MHz, actone-d_6) δ 162.34, 140.90, 137.58, 131.47, 129.44, 129.17, 128.98, 128.77, 127.58, 65.47; HRMS (ES^+-TOF) calculated for $C_{14}H_{13}N$ ($[M+H]^+$): 196.1121, found 196.1130.

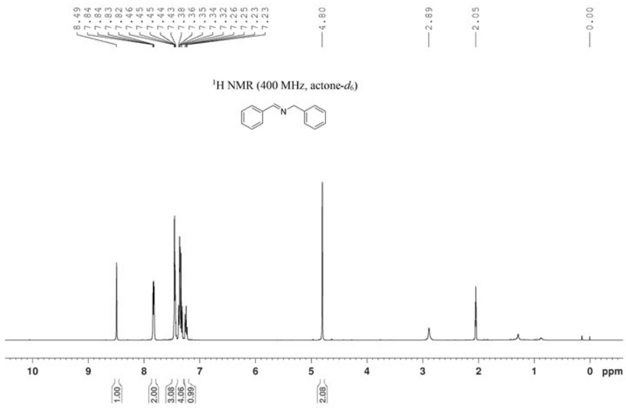

Fig. S1. ^{1}H NMR spectra of *N*-benzylidenebenzylamine.

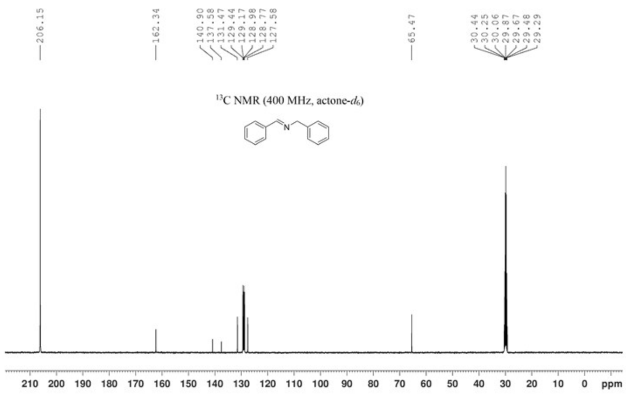

Fig. S2. ^{13}C NMR spectra of *N*-benzylidenebenzylamine.

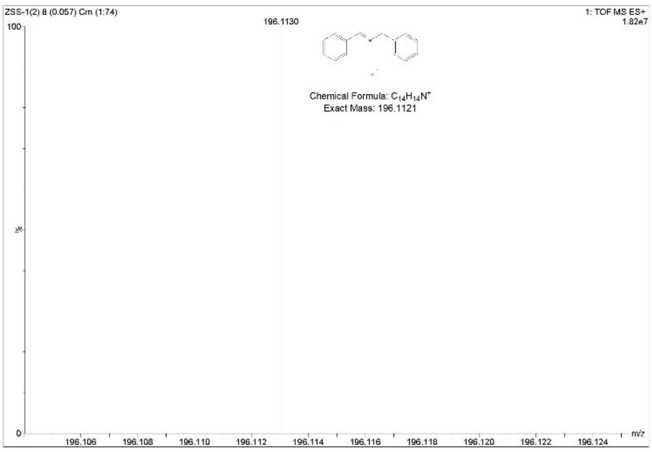

Fig. S3. HRMS spectra of *N*-benzylidenebenzylamine.

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

^{1}H NMR (400 MHz, actone-d_6) δ 8.48 (s, 1H), 7.90-7.87 (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 165.17 (d, J = 245.0 Hz), 162.74 (d, J = 241.0 Hz), 161.20, 136.99 (d, J = 3.0 Hz), 134.08 (d, J = 2.8 Hz), 131.17 (d, J = 8.6 Hz), 130.58 (d, J = 8.0 Hz), 116.41 (d, J = 21.9 Hz), 115.83 (d, J = 21.2 Hz), 64.47; HRMS (ES$^+$-TOF) calculated for $C_{14}H_{11}F_2N$ ([M+H]$^+$): 232.0932, found 232.0940.

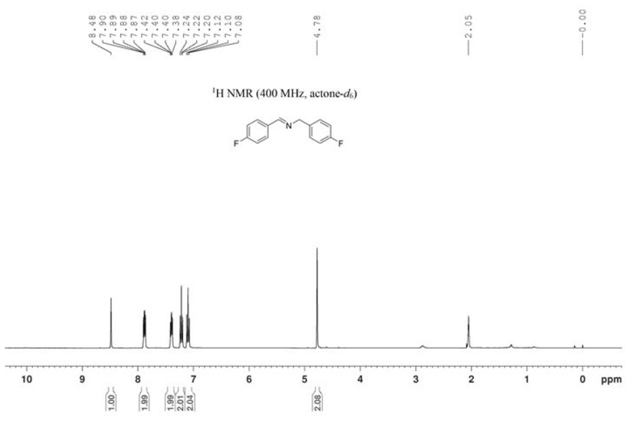

Fig. S4. ^{1}H NMR spectra of (*E*)-*N*-(4-fluorobenzylidene)(4-fluorophenyl)methanamine.

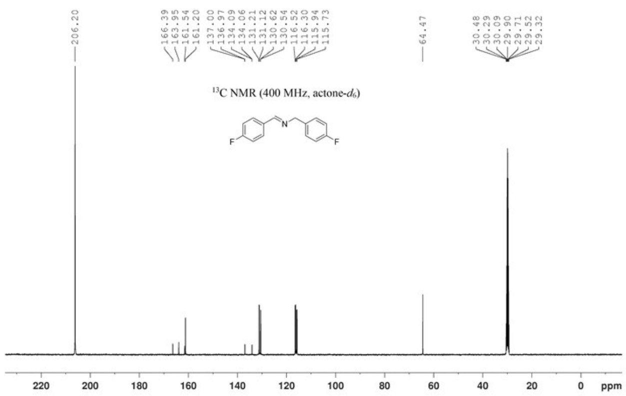

Fig. S5. ^{13}C NMR spectra of (*E*)-*N*-(4-fluorobenzylidene)(4-fluorophenyl)methanamine.

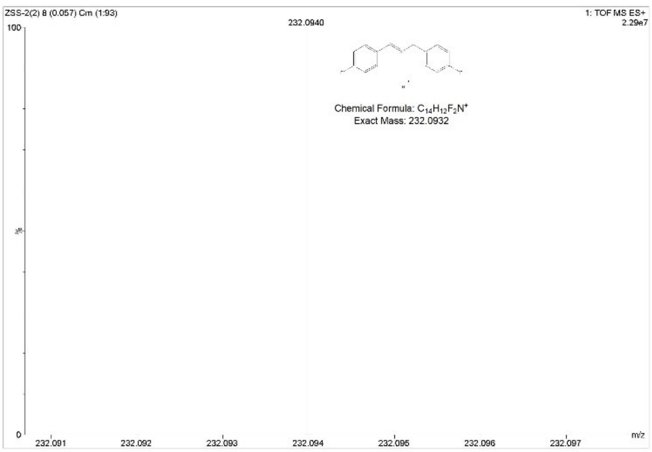

Fig. S6. HRMS spectra of (*E*)-*N*-(4-fluorobenzylidene)(4-fluorophenyl)methanamine.

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

^{1}H NMR (400 MHz, actone-d_6) δ 8.51 (s, 1H), 7.85-7.83 (m, 2H), 7.50-7.48 (m, 2H), 7.41-7.35 (m, 4H), 4.80 (s, 2H); ^{13}C NMR (100 MHz, actone-d_6) δ161.70, 139.83, 137.04, 136.33, 133.03, 130.62, 130.54, 129.76, 129.31, 64.49; HRMS (ES$^+$-TOF) calculated for $C_{14}H_{11}Cl_2N$ ($[M+H]^+$): 264.0341, found 264.0346.

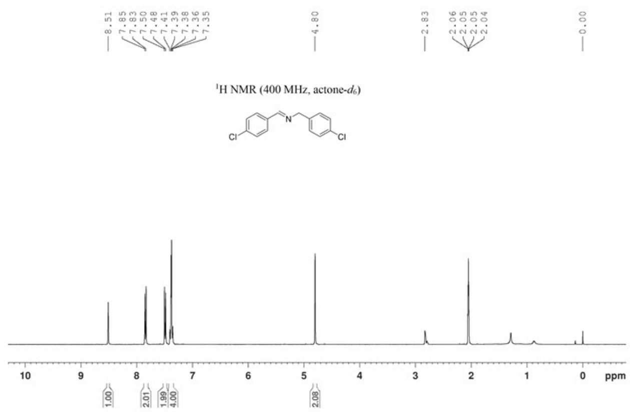

Fig. S7. ^{1}H NMR spectra of (*E*)-*N*-(4-chlorobenzylidene)(4-chlorophenyl)methanamine.

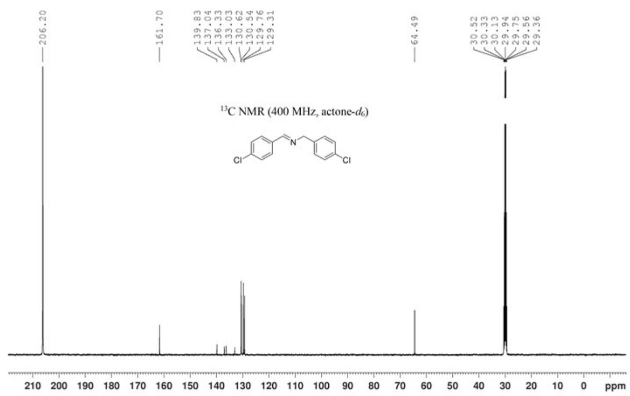

Fig. S8. ^{13}C NMR spectra of (*E*)-*N*-(4-chlorobenzylidene)(4-chlorophenyl)methanamine.

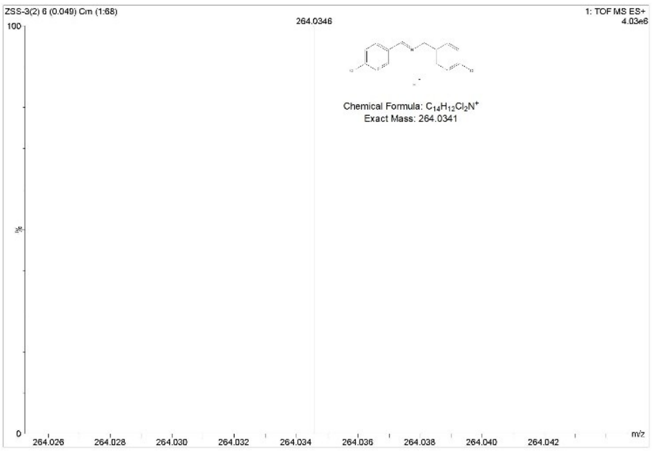

Fig. S9. HRMS spectra of (*E*)-*N*-(4-chlorobenzylidene)(4-chlorophenyl)methanamine.

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 = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 4.77 (s, 2H); ^{13}C NMR (100 MHz, actone-d_6) δ 161.80, 140.16, 136.57, 132.69, 132.24, 130.84, 130.78, 125.45, 121.06, 64.48; HRMS (ES$^+$-TOF) calculated for $C_{14}H_{11}Br_2N$ ([M+H]$^+$): 351.9331, found 351.9338.

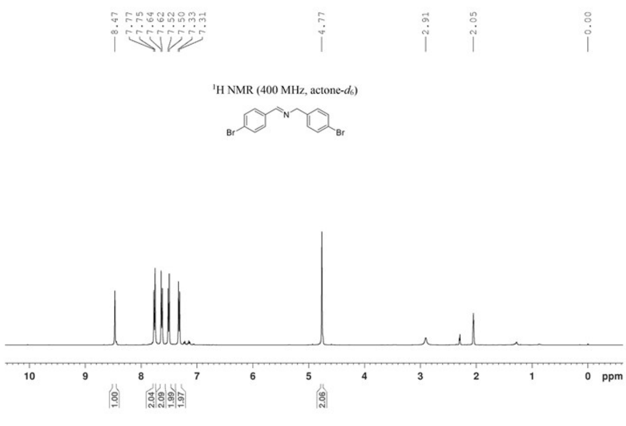

Fig. S10. ^{1}H NMR spectra of (*E*)-*N*-(4-bromobenzylidene)(4-bromophenyl)methanamine.

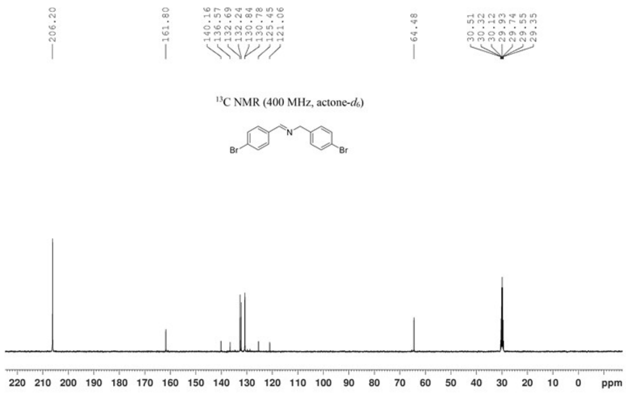

Fig. S11. ^{13}C NMR spectra of (*E*)-*N*-(4-bromobenzylidene)(4-bromophenyl)methanamine.

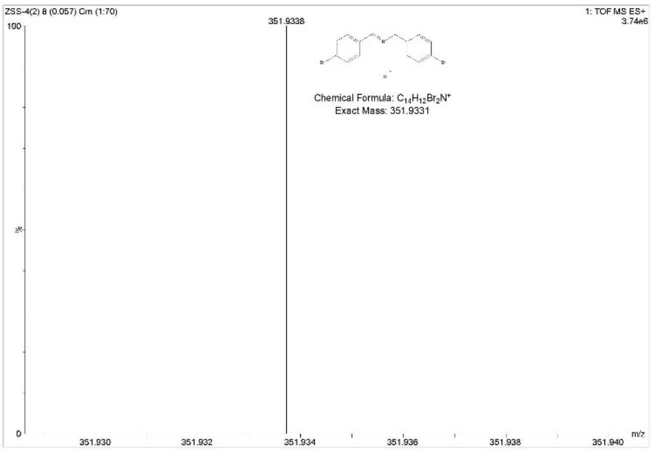

Fig. S12. HRMS spectra of (*E*)-*N*-(4-bromobenzylidene)(4-bromophenyl)methanamine.

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

^{1}H NMR (400 MHz, actone-d_6) δ 8.37 (s, 1H), 7.76-7.74 (m, 2H), 7.27-7.25 (m, 2H), 6.99-6.97 (m, 2H), 6.90-6.87 (m, 2H), 4.68 (s, 2H), 3.83 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, actone-d_6) δ 162.68, 161.13, 159.63, 133.20, 130.52, 129.93, 114.80, 114.55, 64.93, 55.74, 55.50; HRMS (ES^{+}-TOF) calculated for $C_{16}H_{17}NO_2$ ([M+H]$^{+}$): 256.1332, found 256.1337.

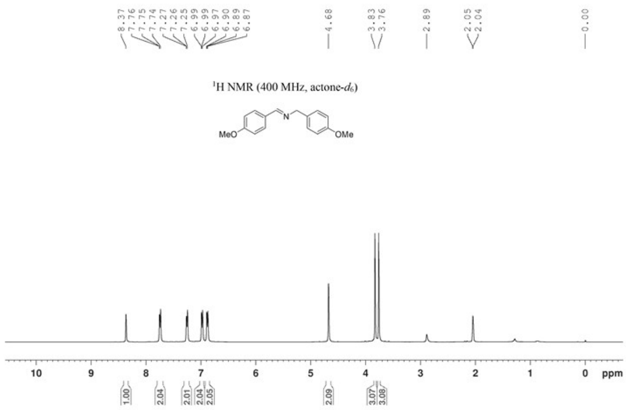

Fig. S13. ^{1}H NMR spectra of (*E*)-*N*-(4-methoxybenzylidene)(4-methoxyphenyl)methanamine.

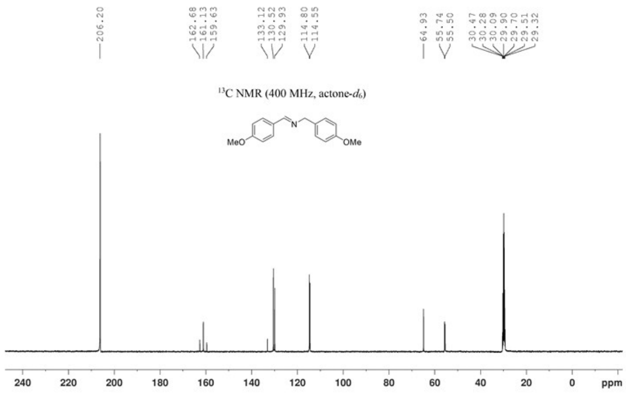

Fig. S14. ^{13}C NMR spectra of (*E*)-*N*-(4-methoxybenzylidene)(4-methoxyphenyl)methanamine.

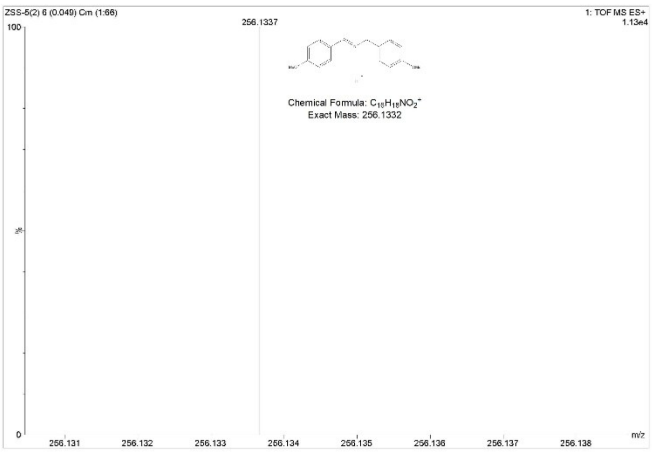

Fig. S15. HRMS spectra of (*E*)-*N*-(4-methoxybenzylidene)(4-methoxyphenyl)methanamine.

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 161.98, 141.65, 138.09, 136.99, 135.21, 130.16, 129.87, 129.06, 128.85, 65.37, 21.54, 21.19; HRMS (ES^{+}-TOF) calculated for $C_{16}H_{17}N$ ([M+H]$^{+}$): 224.1434, found 224.1450.

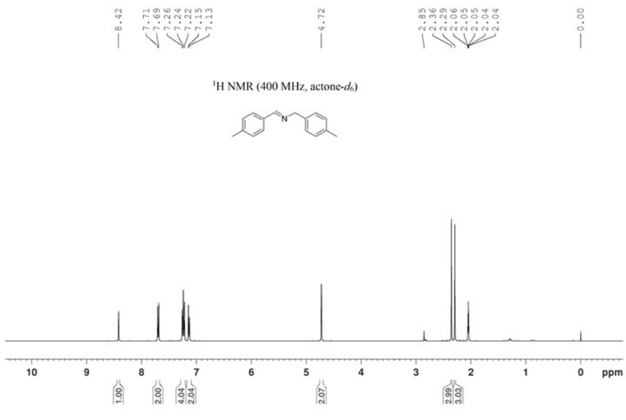

Fig. S16. ^{1}H NMR spectra of (*E*)-*N*-(4-methylbenzylidene)(4-methylphenyl)methanamine.

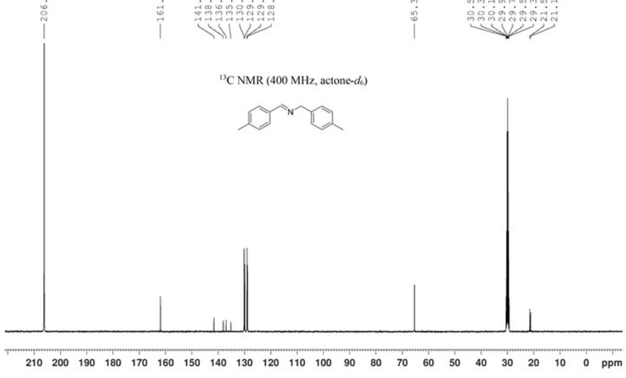

Fig. S17. ^{13}C NMR spectra of (*E*)-*N*-(4-methylbenzylidene)(4-methylphenyl)methanamine.

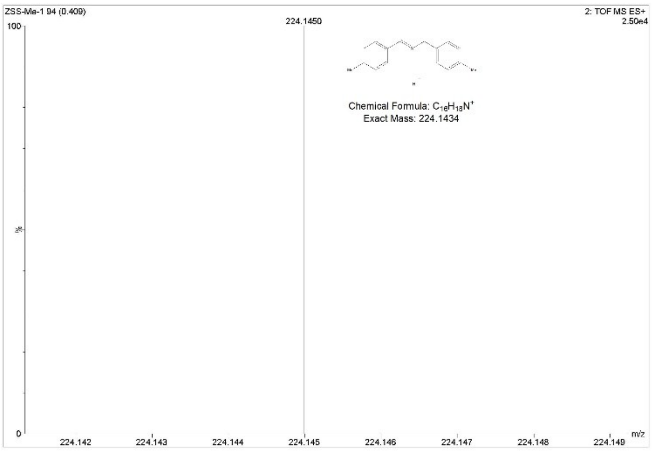

Fig. S18. HRMS spectra of (*E*)-*N*-(4-methylbenzylidene)(4-methylphenyl)methanamine.

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), 7.35-7.13 (m, 5H), 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 162.38, 140.88, 139.07, 138.62, 137.67, 132.21, 129.56, 129.41, 129.15, 128.32, 126.43, 125.97, 65.65, 21.49, 21.33; HRMS (ES$^+$-TOF) calculated for $C_{16}H_{17}N$ ($[M+H]^+$): 224.1434, found 224.1442.

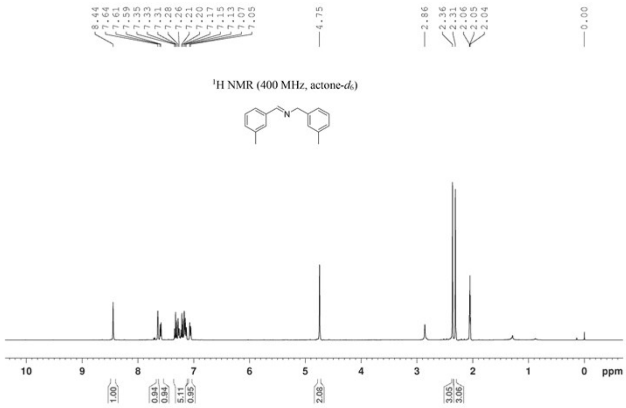

Fig. S19. ^{1}H NMR spectra of (*E*)-*N*-(3-methylbenzylidene)(3-methylphenyl)methanamine.

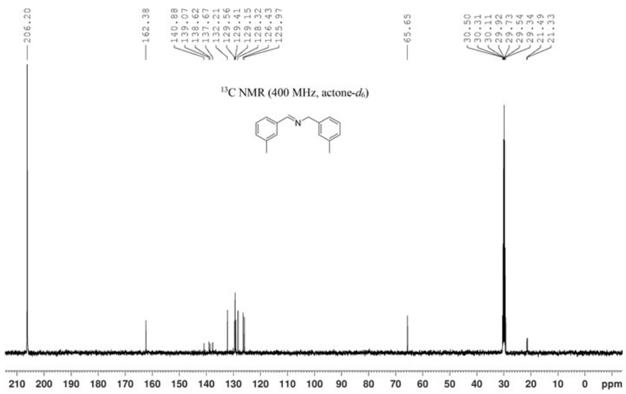

Fig. S20. ^{13}C NMR spectra of (*E*)-*N*-(3-methylbenzylidene)(3-methylphenyl)methanamine.

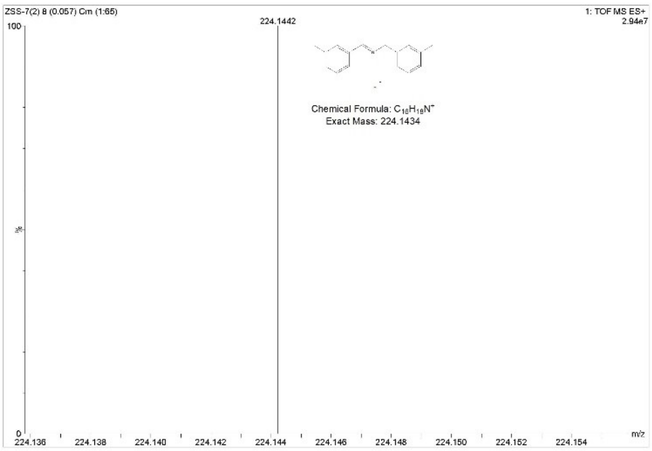

Fig. S21. HRMS spectra of (*E*)-*N*-(3-methylbenzylidene)(3-methylphenyl)methanamine.

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

^{1}H NMR (400 MHz, actone-d_6) δ 8.79 (s, 1H), 7.64 (s, 1H), 7.91-7.89 (m, 1H), 7.33-7.30 (m, 2H), 7.26-7.21 (m, 2H), 7.19-7.14 (m, 3H), 4.81 (s, 2H), 2.53 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, actone-d_6) δ 161.22, 139.28, 138.67, 137.00, 135.42, 131.82, 131.01, 130.85, 129.16, 128.71, 127.76, 126.90, 126.81, 64.07, 19.68, 19.40; HRMS (ES$^+$-TOF) calculated for $C_{16}H_{17}N$ ([M+H]$^+$): 224.1434, found 224.1444.

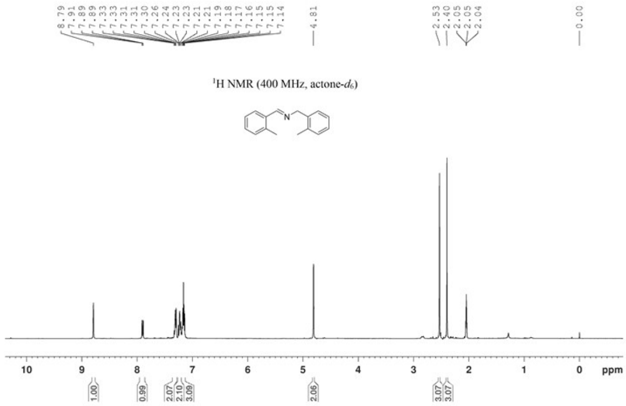

Fig. S22. ^{1}H NMR spectra of (*E*)-*N*-(2-methylbenzylidene)(2-methylphenyl)methanamine.

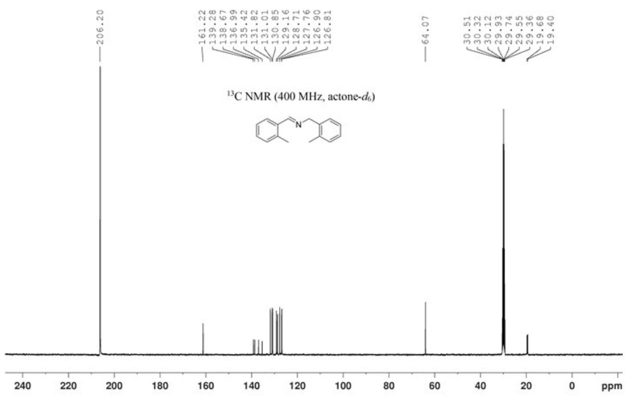

Fig. S23. ^{13}C NMR spectra of (*E*)-*N*-(2-methylbenzylidene)(2-methylphenyl)methanamine.

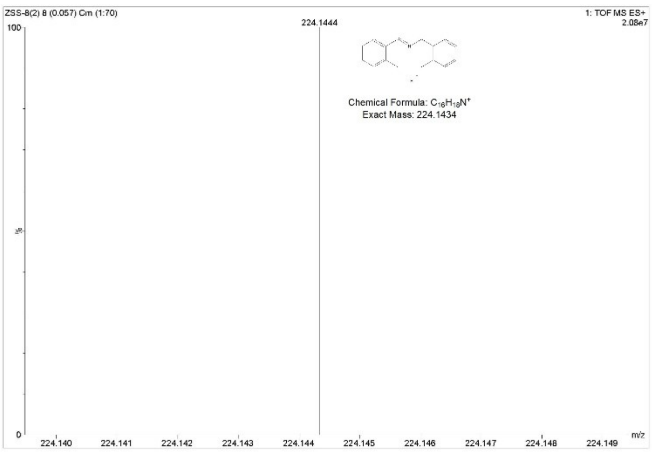

Fig. S24. HRMS spectra of (*E*)-*N*-(2-methylbenzylidene)(2-methylphenyl)methanamine.

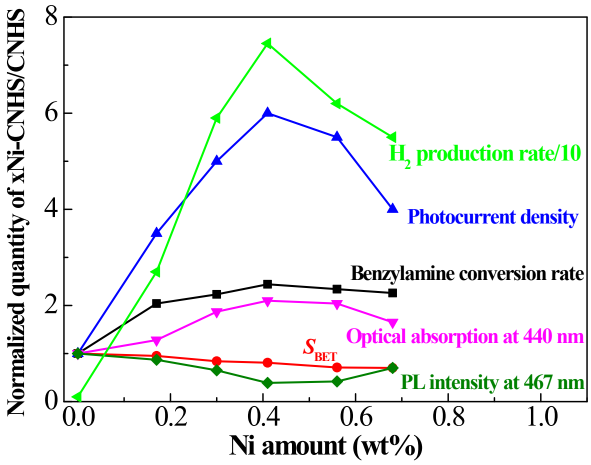

Fig. S25. Plots of the normalized photocatalytic activity, S_{BET}, optical absorption at 440 nm, photocurrent density, and PL intensity at 467 nm of xNi-CNHS/CNHS versus Ni amount. (The H_2 production rate is divided by 10 for comparison)

Table S1. The H_2 production rates of 0.41Ni-CNHS and some reported Ni compounds/g-C_3N_4 photocatalysts

Catalyst	Morphology	S_{BET} ($m^2.g^{-1}$)	H_2 evolution rate ($\mu mol \cdot g^{-1} \cdot h^{-1}$)	Ref.
0.41 Ni-CNHS	Hollow sphere	86.8	596	This work
2 wt % Ni_2P/g-C_3N_4	Bulk	-	85	[1]
2 wt % Ni_2P-sg-CN	Bulk	130.0	330	[2]
1% Ni_2P/g-C_3N_4	Bulk	-	362	[3]
0.5 mol% $Ni(OH)_2$-g-C_3N_4	Nanosheet	56.7	152	[4]
Ni_3N-g-C_3N_4	Nanosheet	-	300	[5]
3 wt% Ni_3N/g-C_3N_4	Nanosheet	-	170	[6]
g-C_3N_4/NiB7.5 wt%	Nanosheet	56.4	464	[7]
NiO/g-C_3N_4	Nanosheet	26.2	68	[8]
2 wt% NiS_2-g-C_3N_4	Nanosheet	-	410	[9]
7 wt% NiS_2-g-C_3N_4	Bulk	-	716	[10]
1.25 wt% NiS/C_3N_4	Mesoporous	76.8	482	[11]
2 wt % Ni-SCN	Nanosheet	85.0	3628	[12]
10% Ni/CM-C_3N_4	Loose tremella-like structure	35.3	314	[13]
Ni-SCN5	Nanosheet	60.4	2021	[14]
7.4 wt % Ni/g-C_3N_4	Nanosheet	-	4318	[15]
10Ni@g-C_3N_4	Nanosheet	-	168	[16]
0.73 wt% Ni-g-C_3N_4	Bulk	142.0	260	[17]
15 wt% Ni_3C/g-C_3N_4	Nanosheet	53.8	304	[18]
0.5%Ni-1.0%NiS/g-C_3N_4	**Nanosheet**	**60.9**	**515**	**[19]**

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