Supporting Information

Photocatalytic Pinacol C-C Coupling and Jet Fuel Precursor Production on $ZnIn_2S_4$ nanosheets

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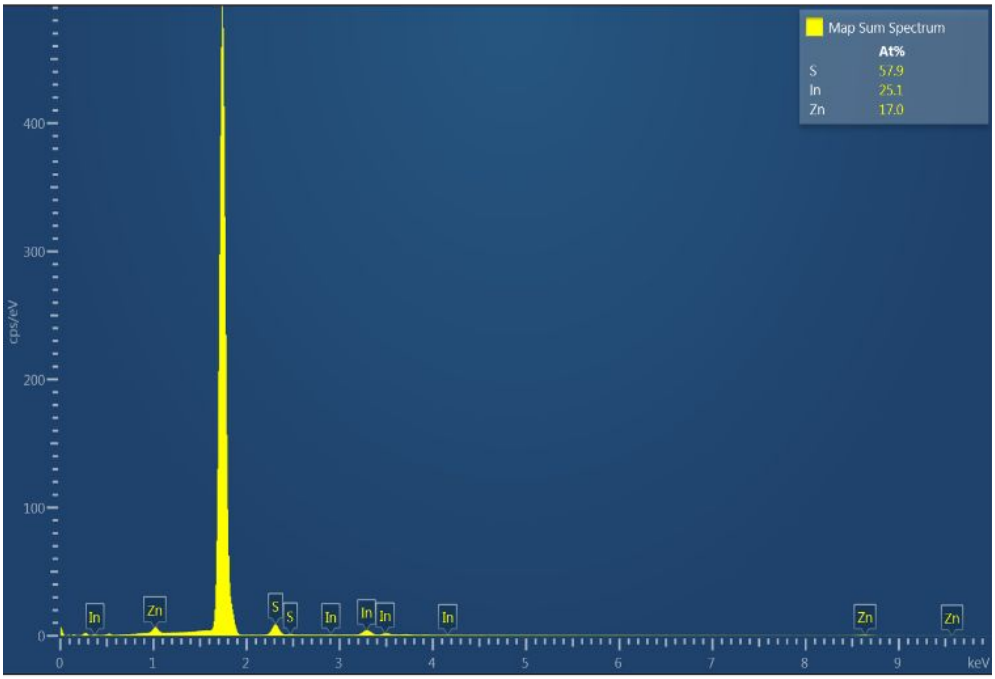


Figure S1. EDX spectrum of $ZnIn_2S_4$, indicating the presence of Zn, In, and S with an atomic ratio ~1:2:4.

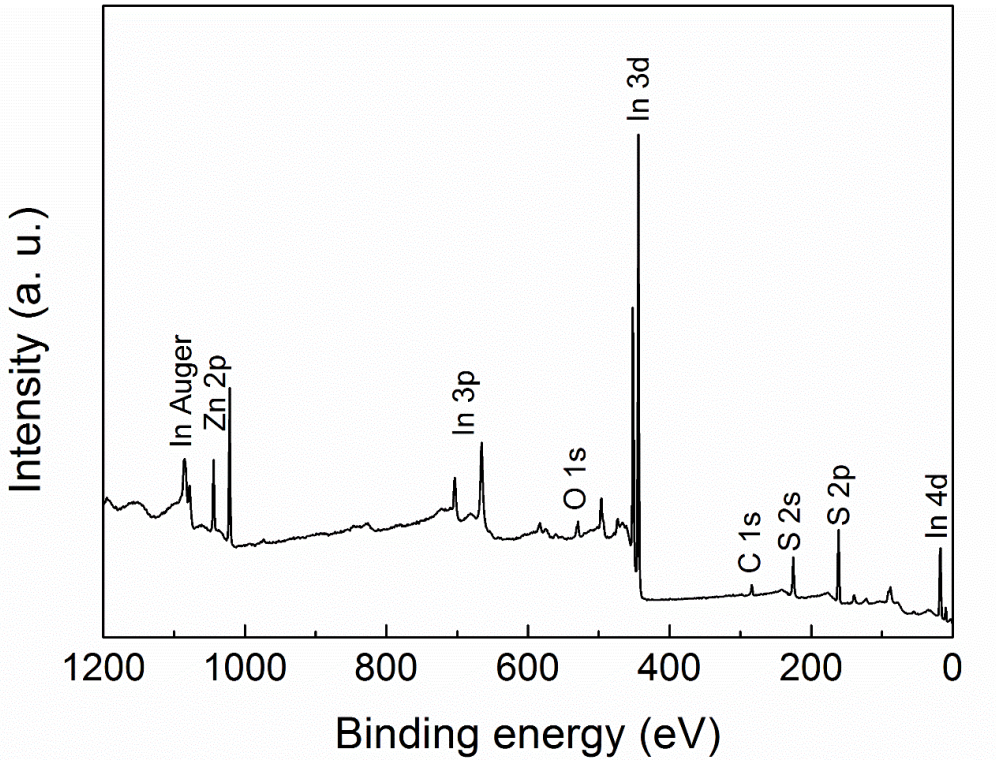
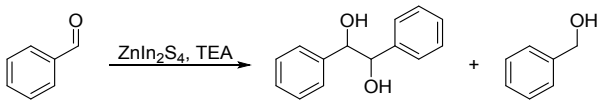


Figure S2. XPS survey spectrum of fresh $ZnIn_2S_4$.

Table S1. Optimization for the photocatalytic C-C coupling of benzaldehyde.[a]



Entry	Photocatalyst	Solvent [b]	Conversion (%)	Hydrobenzoin (%) [c]	Benzyl alcohol (%) [c]
1 [d]	$ZnIn_2S_4$-1	CH_3CN	6.6	6	Trace
2 [d]	$ZnIn_2S_4$-2	CH_3CN	42.5	25.8	16.7
3 [d]	$ZnIn_2S_4$-3	CH_3CN	12.1	5.6	6.5
4 [d]	$ZnIn_2S_4$-4	CH_3CN	20.4	13.3	7.1
5 [d]	$ZnIn_2S_4$-5	CH_3CN	54.9	49.0	5.0
6 [d]	$ZnIn_2S_4$-6	CH3CN	53.2.	29.0	23.2
7 [e]	$ZnIn_2S_4$-5	CH_3CN	-	-	-
8	-	CH_3CN	-	-	-
9 [f]	$ZnIn_2S_4$-5	CH_3CN	-	-	-
10	$ZnIn_2S_4$-5	V/V(CH_3CN:H_2O)=9:1	~100	79.1	21.0
11	$ZnIn_2S_4$-5	V/V(CH_3CN:H_2O)=5:5	~100	90.6	9.4
12	$ZnIn_2S_4$-5	V/V(CH_3CN:H_2O)=3:7	~100	98.1	1.9
13	$ZnIn_2S_4$-5	V/V(CH_3CN:H_2O)=1:9	~100	>99	trace

[a] Reaction condition: benzaldehyde (10 mM), TEA (1 mL), catalyst (10 mg), room temperature, solvent (10 mL), blue LED (450 nm), 2 h. [b] Solvent is degassed by N_2. [c] Yield is determined by HPLC. [d] Catalyst synthesized at different temperatures: 1 is 80 ºC; 2 is 90 ºC; 3 is 100 ºC; 4 is 110 ºC; 5 is 120 ºC; and 6 is 130 ºC. [e] Without light. [f] Without TEA.

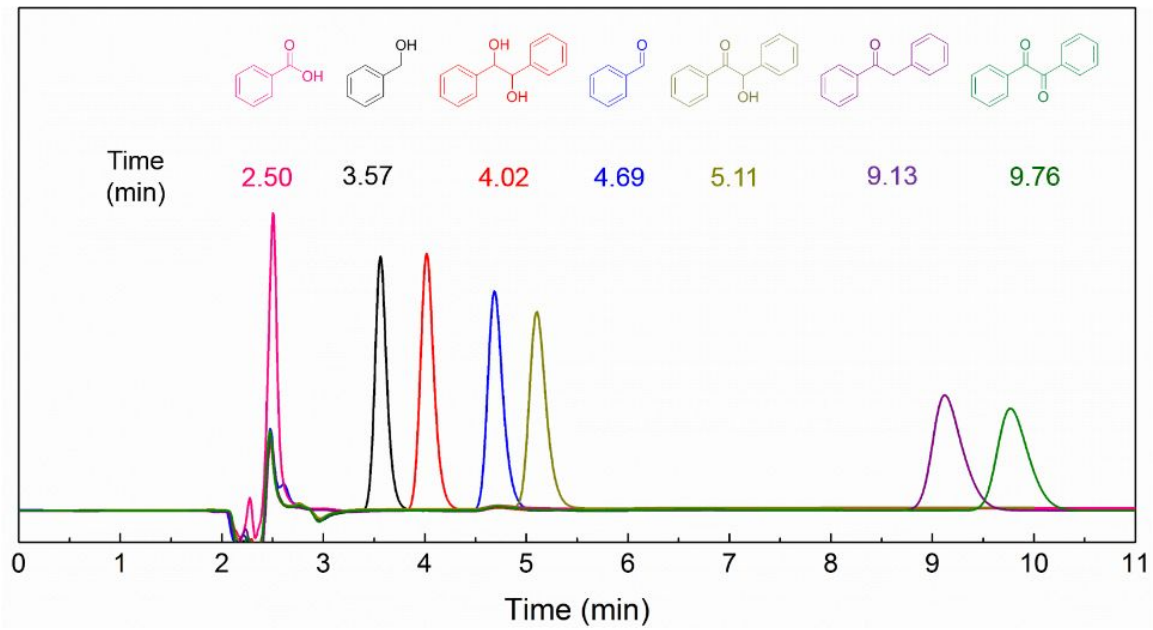
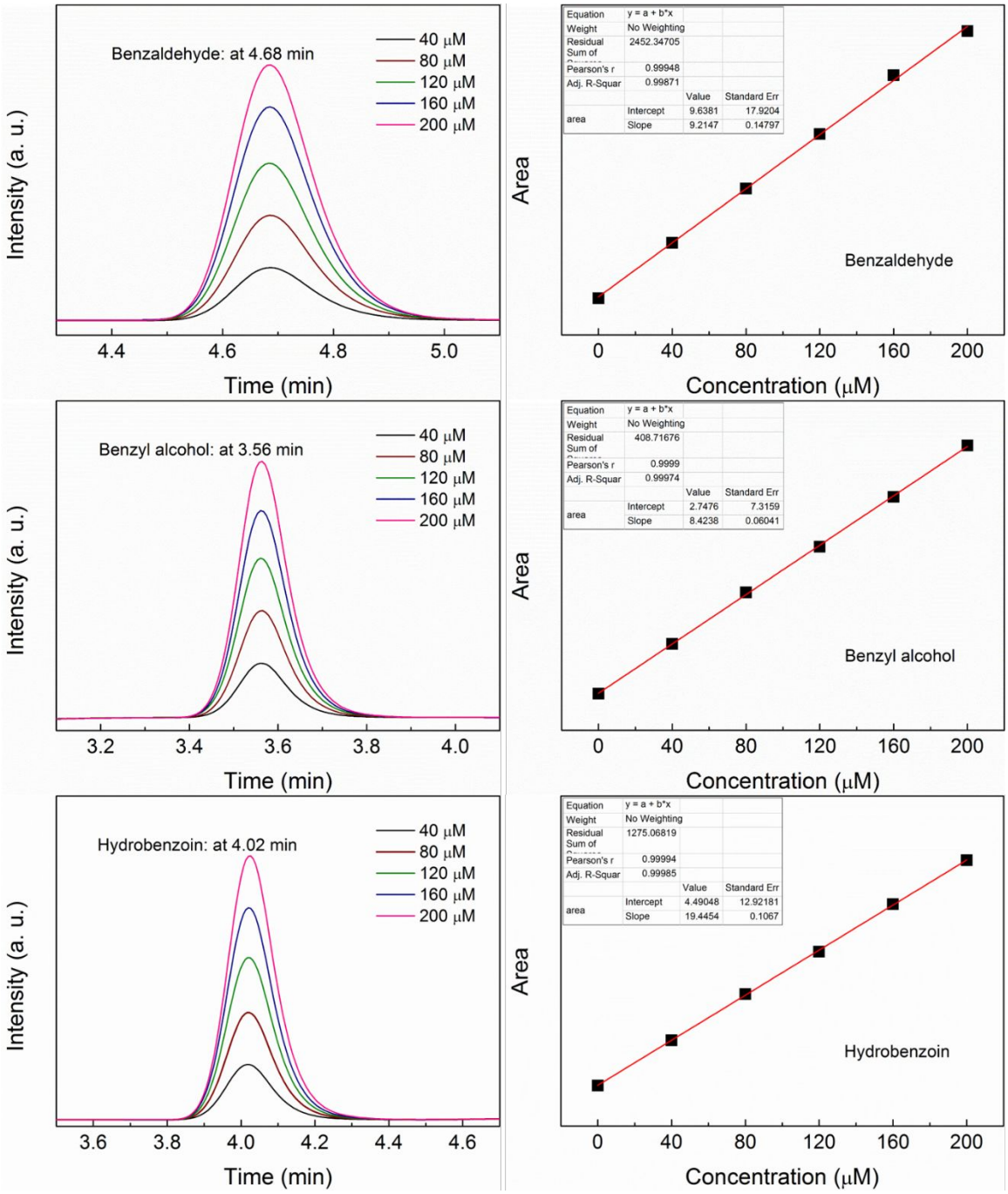


Figure S3. HPLC spectra of benzoic acid, benzyl alcohol, hydrobenzoin, benzaldehyde, benzoin, deoxybenzoin, and benzil. (Conditions: 40% 5 mM ammonium acetate (aq), 60% CH_3CN, 0.5 mL min^{-1}, 11 min).


Benzaldehyde: at 4.68 min
40 μM
80 μM
120 μM
160 μM
200 μM
Intensity (a. u.)
Time (min)
Equation y = a + b*x
Weight No Weighting
Residual Sum of 2452.34705
Pearson's r 0.99948
Adj. R-Squar 0.99871
Value Standard Err
area Intercept 9.6381 17.9204
Slope 9.2147 0.14797
Area
Concentration (μM)
Benzaldehyde
Benzyl alcohol: at 3.56 min
Equation y = a + b*x
Weight No Weighting
Residual Sum of 408.71676
Pearson's r 0.9999
Adj. R-Squar 0.99974
Value Standard Err
area Intercept 2.7476 7.3159
Slope 8.4238 0.06041
Benzyl alcohol
Hydrobenzoin: at 4.02 min
Equation y = a + b*x
Weight No Weighting
Residual Sum of 1275.06819
Pearson's r 0.99994
Adj. R-Squar 0.99985
Value Standard Err
area Intercept 4.49048 12.92181
Slope 19.4454 0.1067
Hydrobenzoin

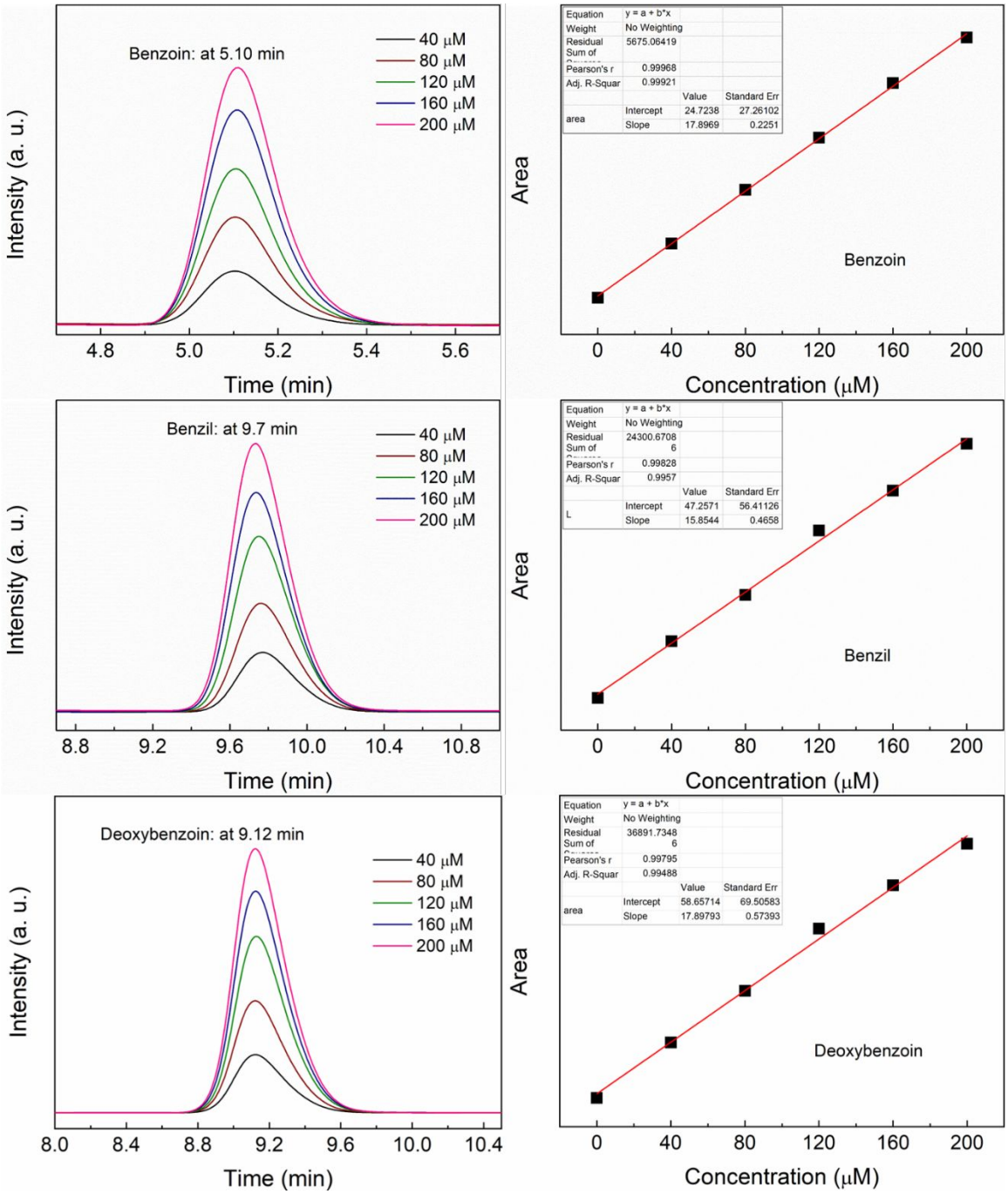


Figure S4. HPLC spectra and calibration curves of benzaldehyde, benzyl alcohol, hydrobenzoin, benzoin, benzil, and deoxybenzoin.

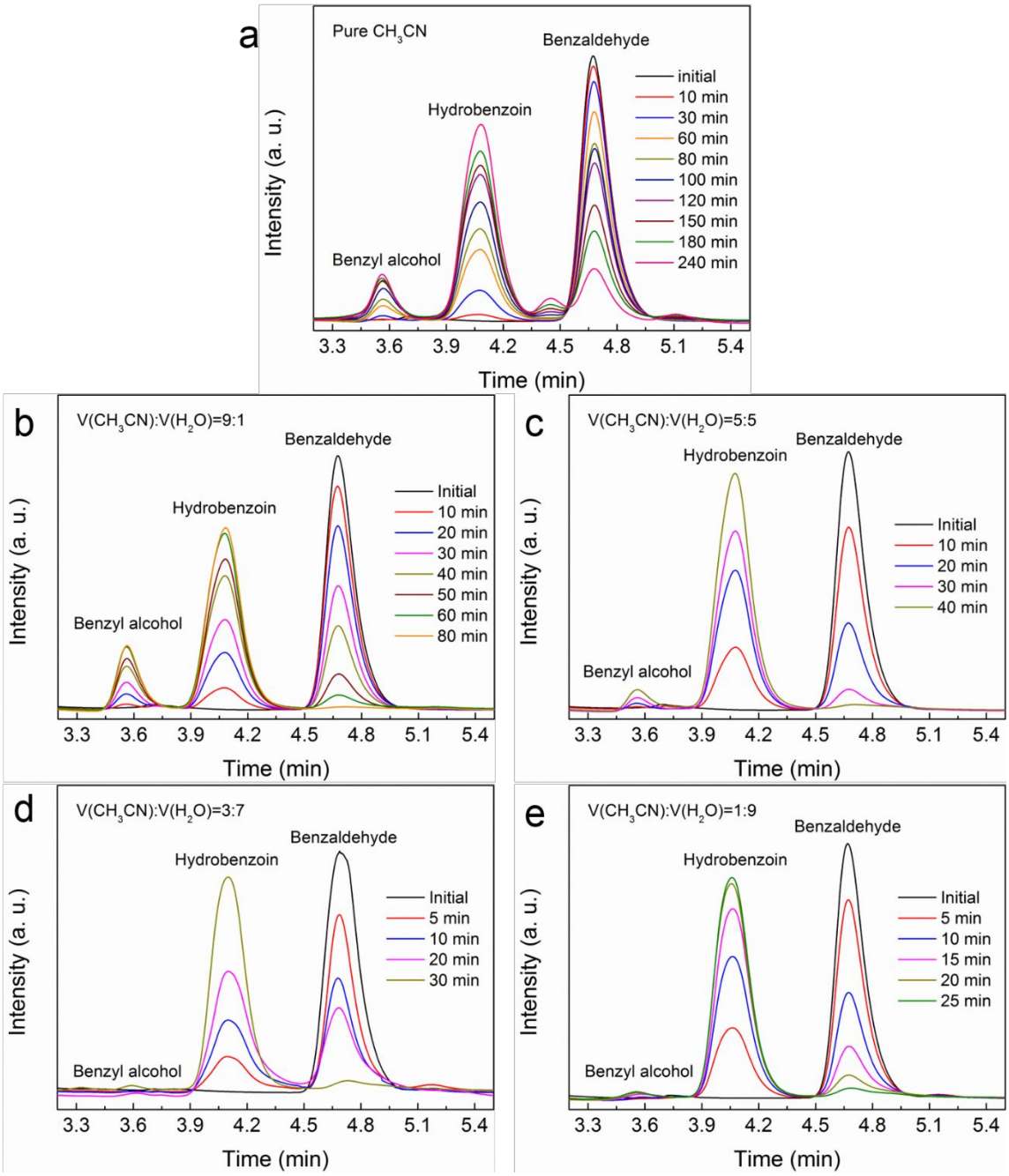


Figure S5. HPLC spectra of photocatalytic upgrading of benzaldehyde over time in pure CH_3CN (a), a mixture with V_{CH3CN}:V_{H2O}=9:1 (b), a mixture with V_{CH3CN}:V_{H2O}=5:5 (c), a mixture with V_{CH3CN}:V_{H2O}=3:7 (d), and a mixture with V_{CH3CN}:V_{H2O}=1:9 (e). (Conditions: 10 mM benzaldehyde, 10 mg $ZnIn_2S_4$, 10 mL solvents, 1 mL TEA, blue LED).

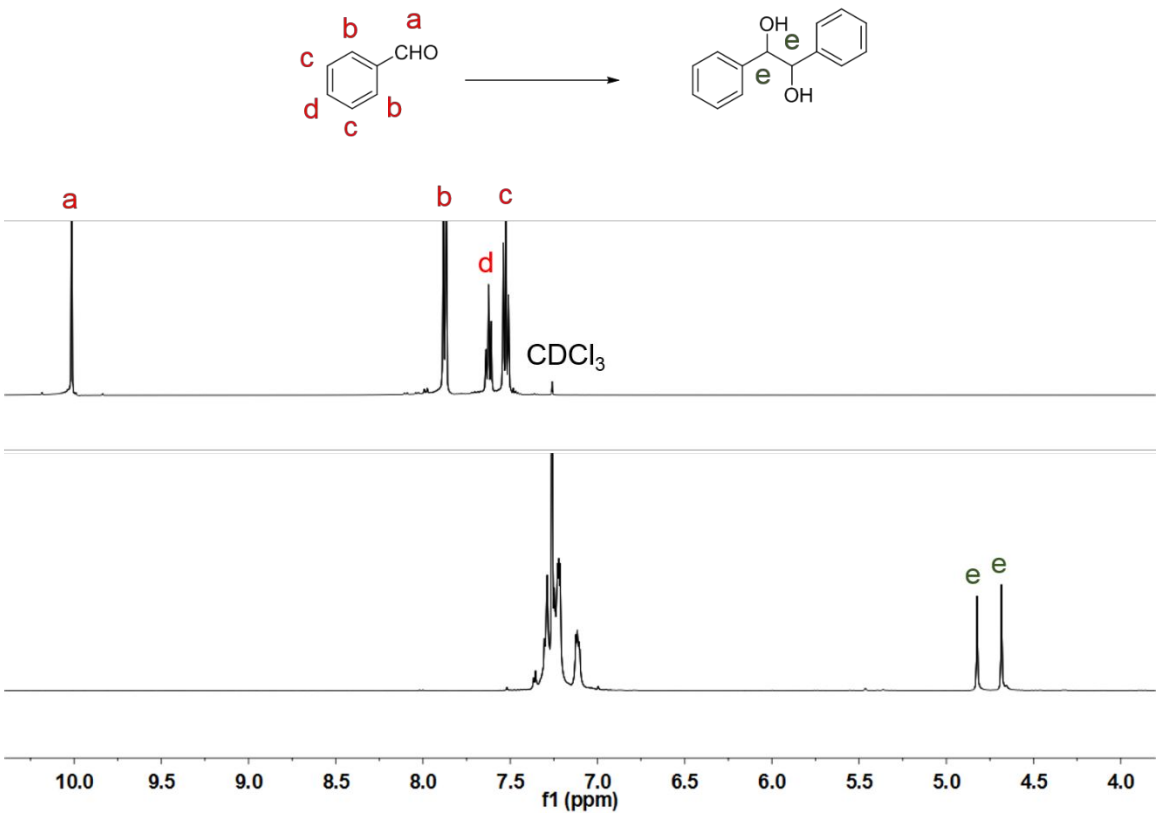


Figure S6. ^{1}H NMR spectra of benzaldehyde (top), and products from benzaldehyde upgrading (bottom). (Condition: 10 mM benzaldehyde, 10 mg $ZnIn_2S_4$, 1 mL CH_3CN, 9 mL H_2O, 1 mL TEA, blue LED, 0.5 h).

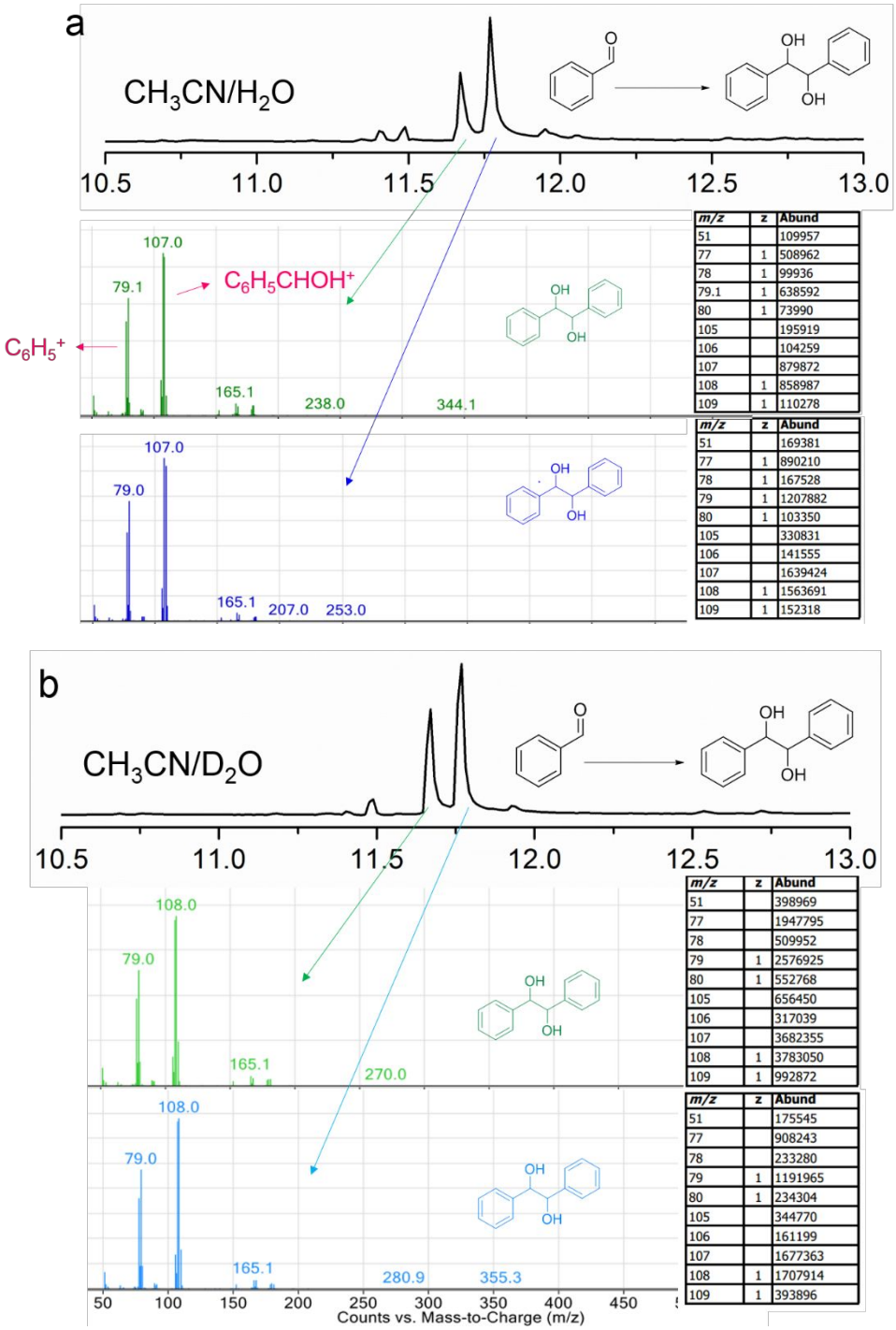


Figure S7. GC-MS spectra after photocatalytic upgrading of benzaldehyde using CH_3CN/H_2O (a) or CH_3CN/D_2O (b) as solvents. (Conditions: 10 mM benzyl alcohol, 10 mg $ZnIn_2S_4$, 1 mL CH_3CN, 9 mL H_2O or D_2O, 1 mL TEA, blue LED, 0.5 h).

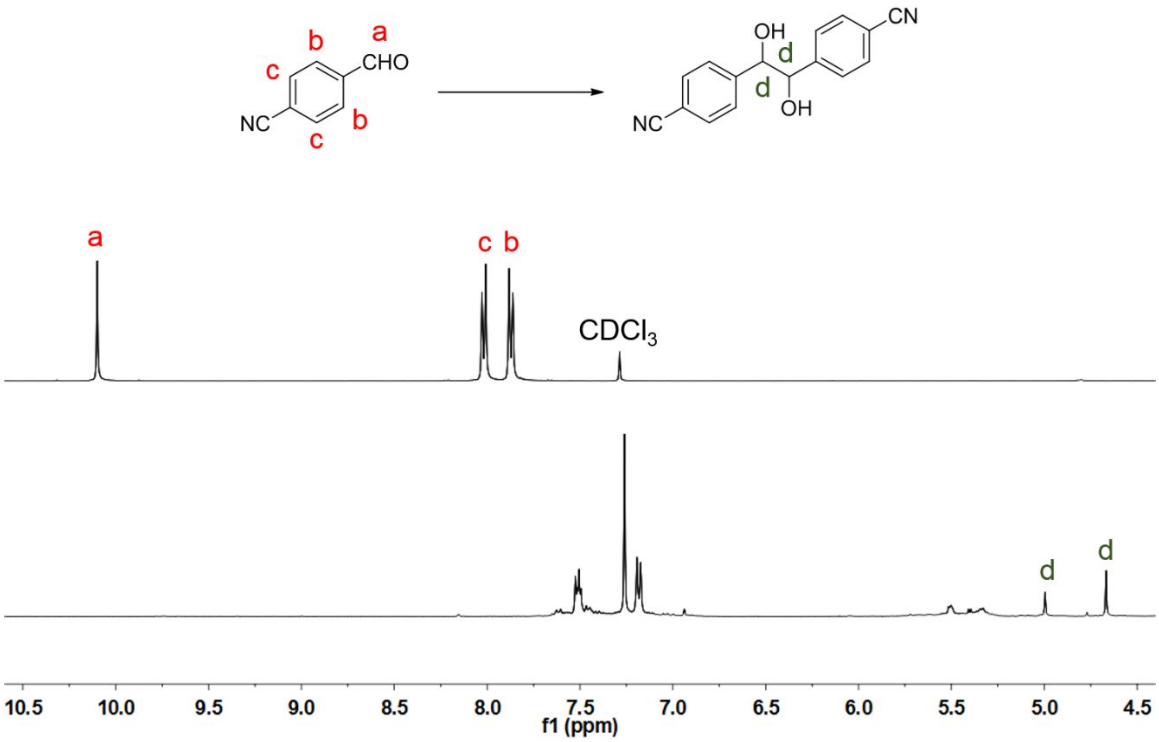


Figure S8. ^{1}H NMR spectra of 4-cyanobenzaldehyde (top), and products from 4-cyanobenzaldehyde upgrading (bottom). (Condition: 10 mM 4-cyanobenzaldehyde, 10 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, 1 mL TEA, blue LED, 0.5 h).

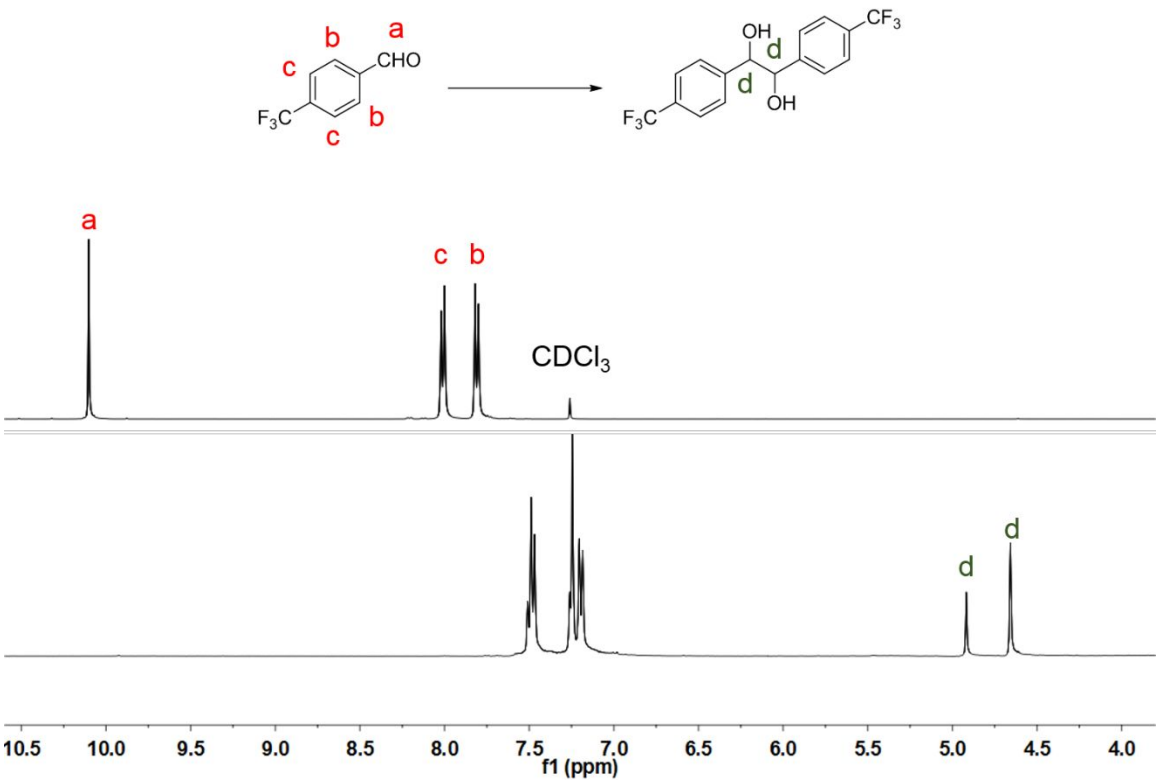


Figure S9. ^{1}H NMR spectra of 4-(trifluoromethyl)benzaldehyde (top), and products from 4-(trifluoromethyl)benzaldehyde upgrading (bottom). (Condition: 10 mM 4-(trifluoromethyl)benzaldehyde, 10 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, 1 mL TEA, blue LED, 0.5 h).

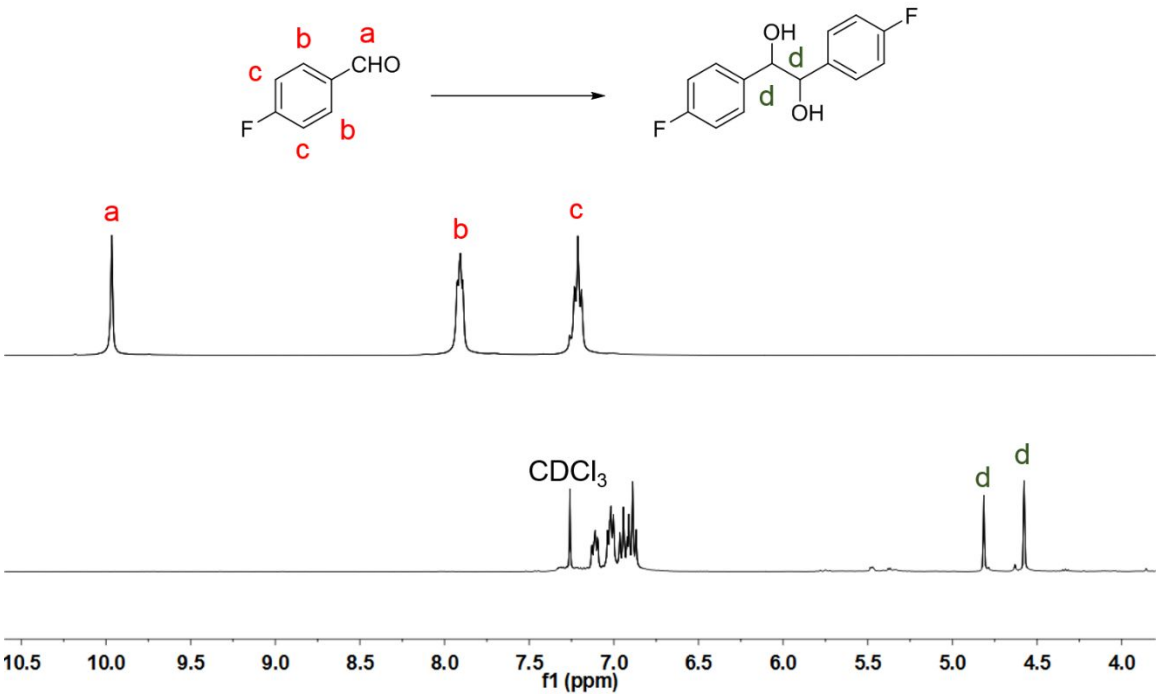


Figure S10. ^{1}H NMR spectra of 4-fluorobenzaldehyde (top), and products from 4-fluorobenzaldehyde upgrading (bottom). (Condition: 10 mM 4-fluorobenzaldehyde, 10 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, 1 mL TEA, blue LED, 0.5 h).

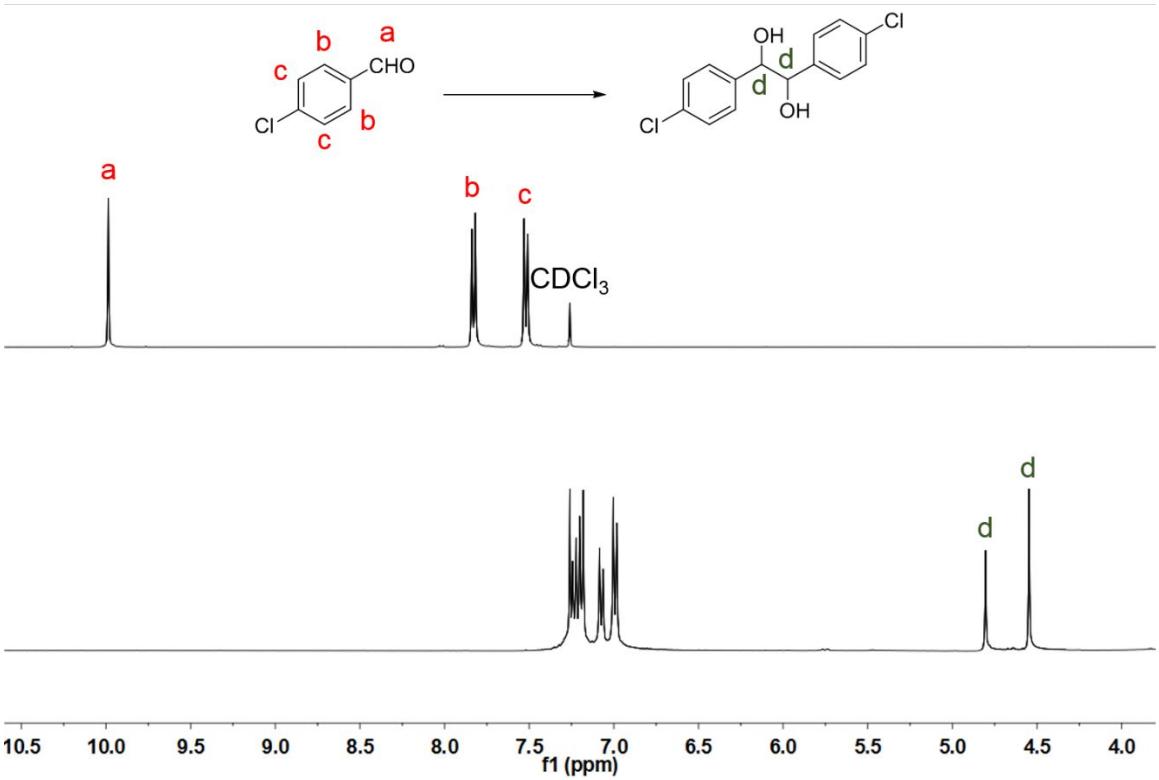


Figure S11. ^{1}H NMR spectra of 4-chlorobenzaldehyde (top), and products from 4-chlorobenzaldehyde upgrading (bottom). (Condition: 10 mM 4-chlorobenzaldehyde, 10 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, 1 mL TEA, blue LED, 0.5 h).

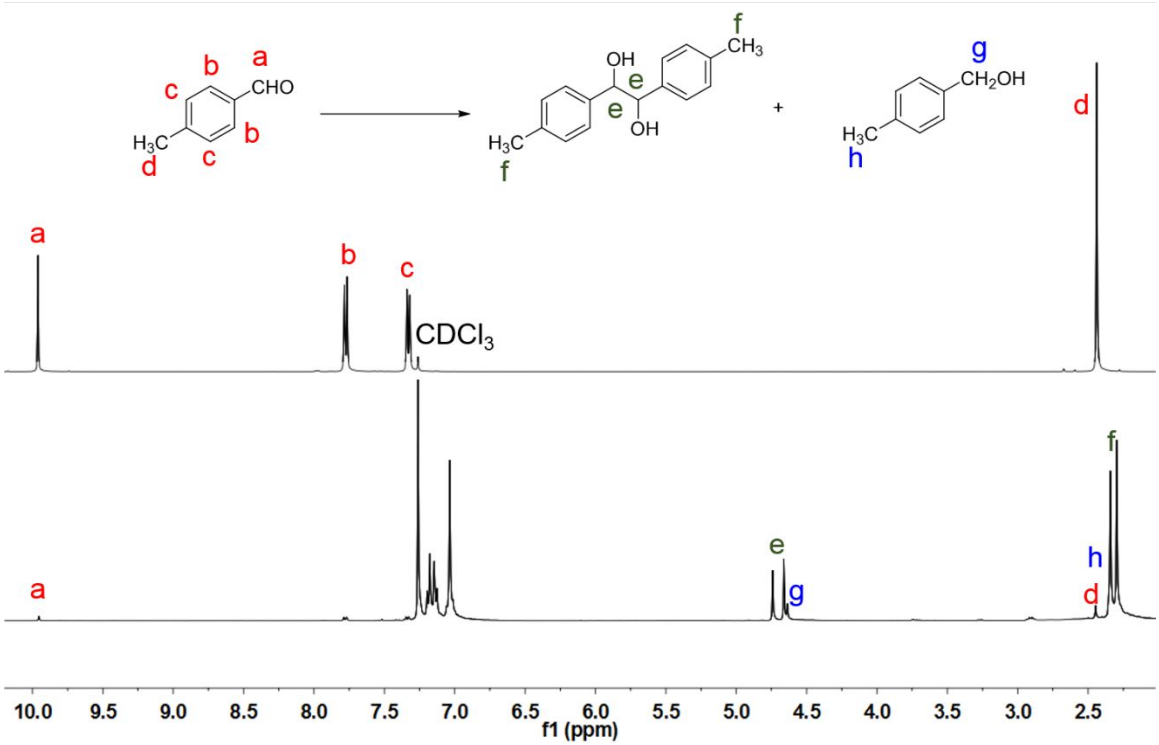


Figure S12. ^1H NMR spectra of 4-methylbenzaldehyde (top), and products from 4-methylbenzaldehyde upgrading (bottom). (Condition: 10 mM 4-methylbenzaldehyde, 10 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, 1 mL TEA, blue LED, 0.5 h).

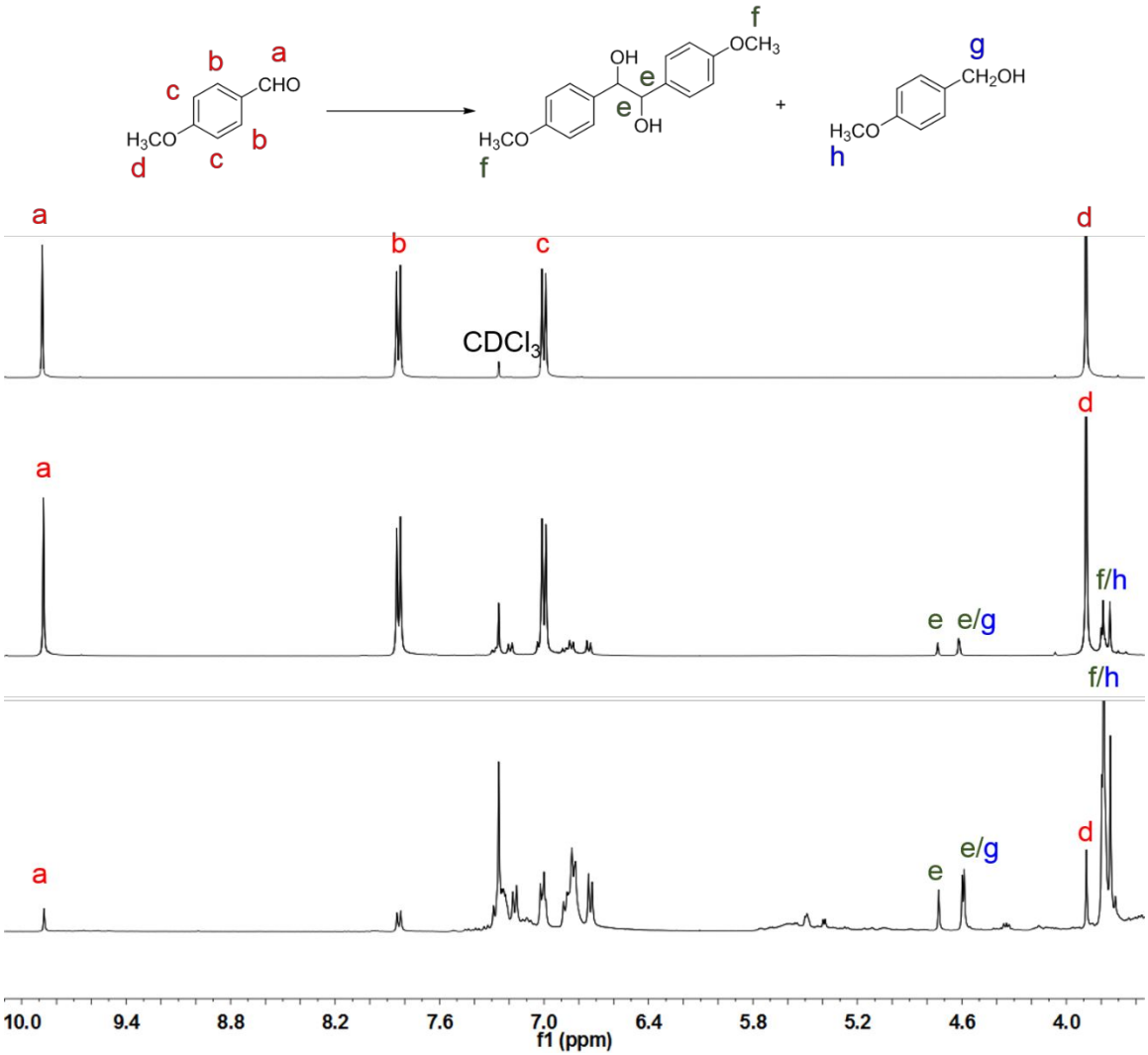


Figure S13. ^{1}H NMR spectra of 4-methoxybenzaldehyde (top), products from 4-methoxybenzaldehyde upgrading after 0.5 h (middle), and products from 4-methoxybenzaldehyde upgrading after 6 h (bottom). (Condition: 10 mM 4-methoxybenzaldehyde, 10 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, 1 mL TEA, blue LED, 0.5 h or 6 h).

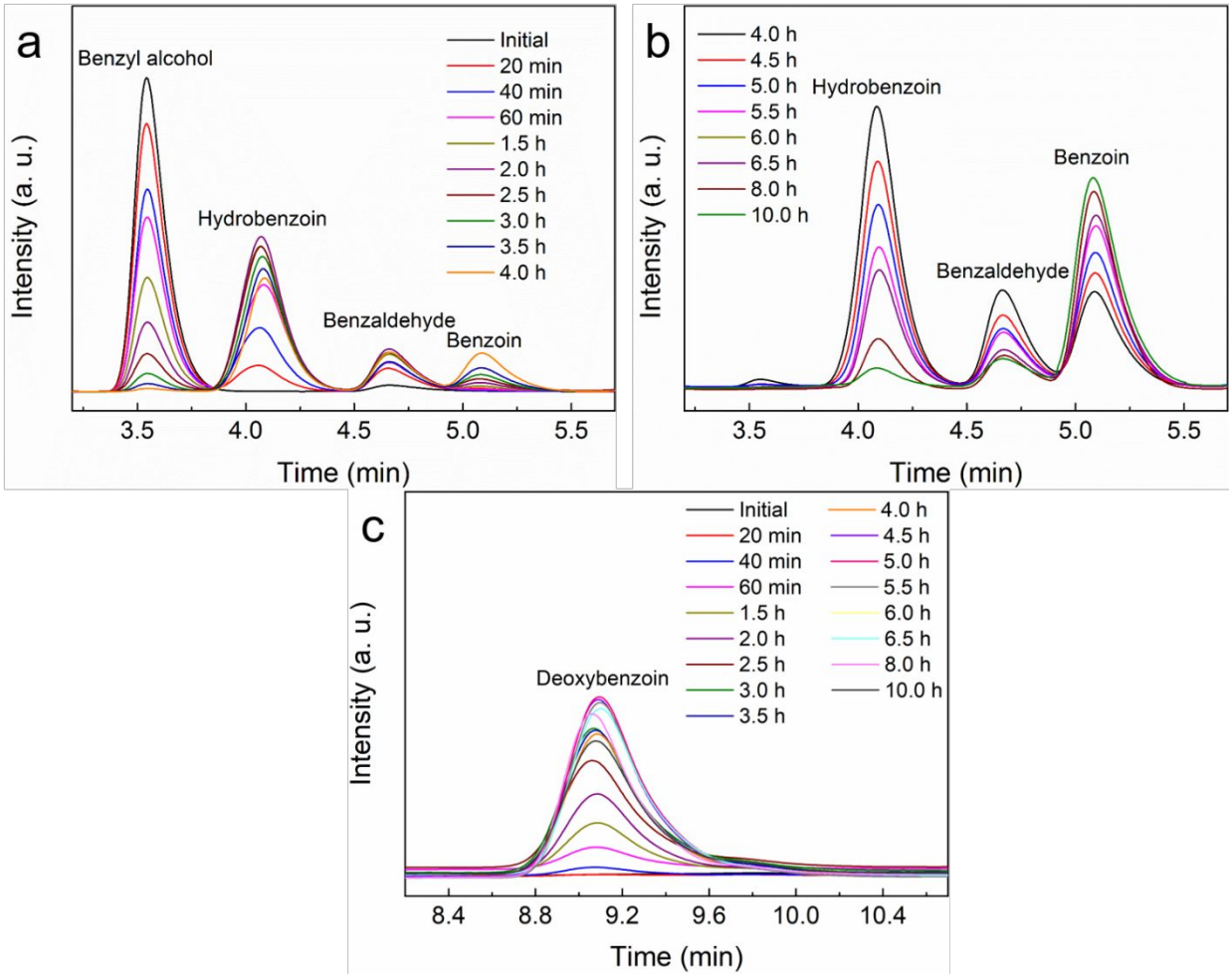


Figure S14. HPLC spectra of photocatalytic upgrading of benzyl alcohol over time. (Conditions: 10 mM benzyl alcohol, 10 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, blue LED, 10 h).

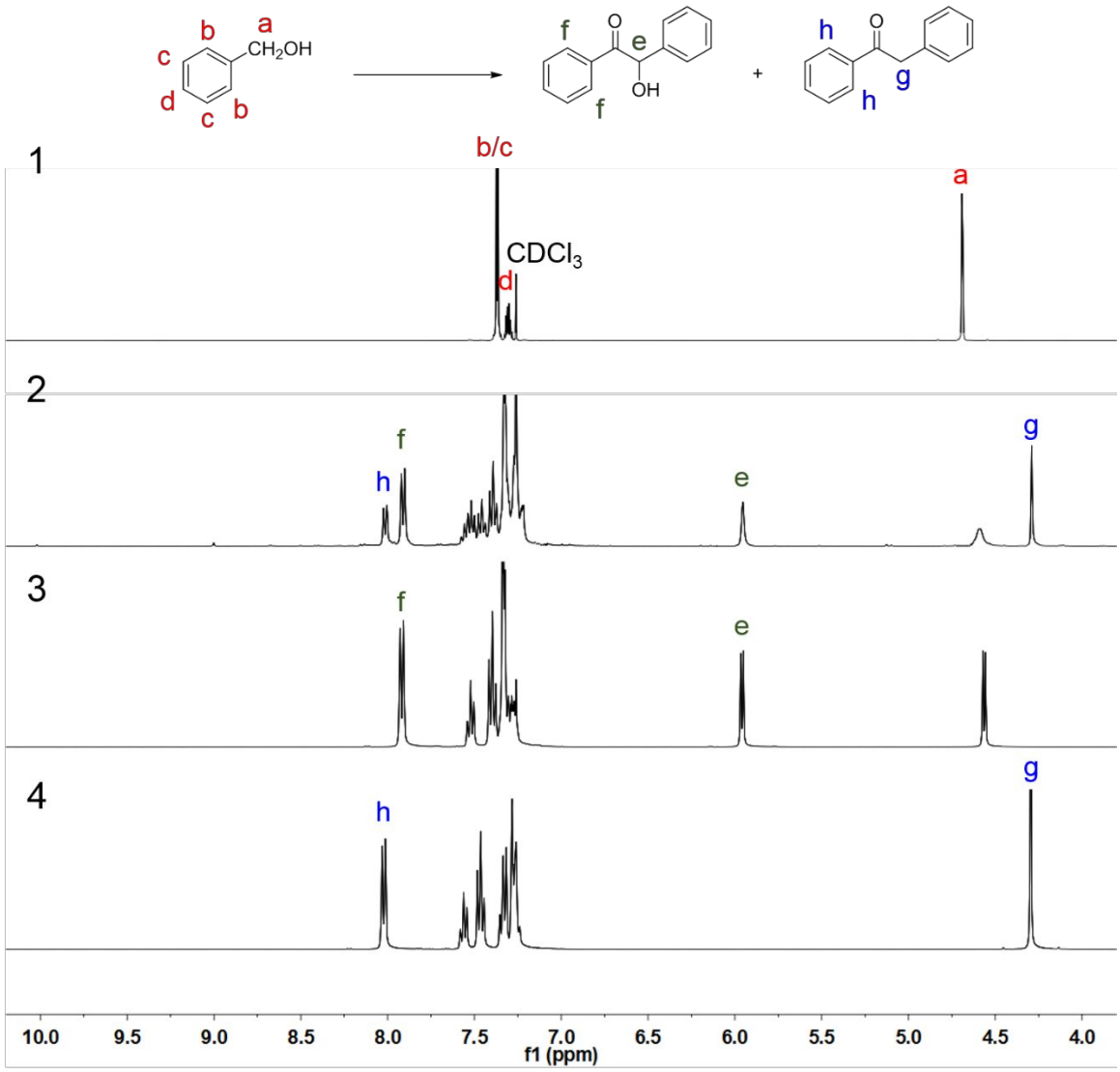


Figure S15. ^{1}H NMR spectra of benzyl alcohol (1), products from benzyl alcohol upgrading (2), standard benzoin (3) and standard deoxybenzoin (4). (Condition: 10 mM benzyl alcohol, 10 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, blue LED, 10 h).

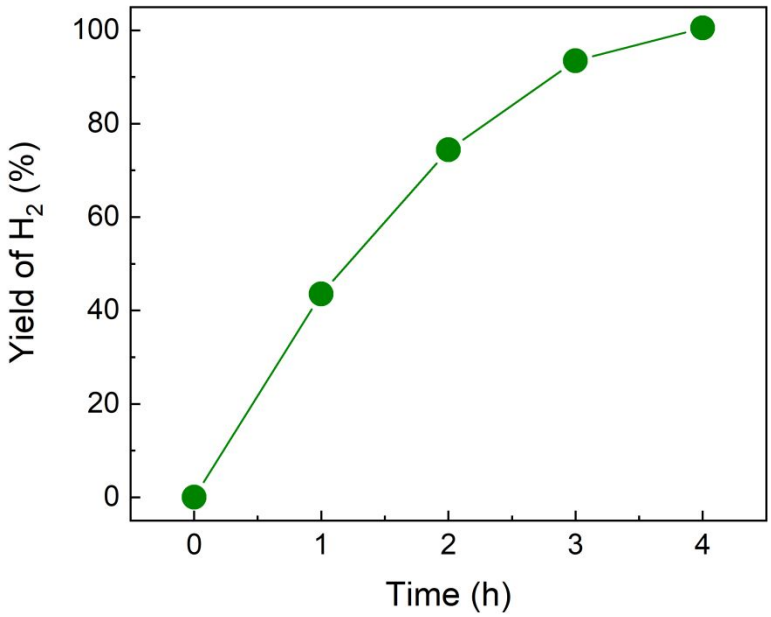


Figure S16. Yield of H_2 change over time. Conditions: 10 mM benzyl alcohol, 10 mg $ZnIn_2S_4$, room temperature, 3 mL CH_3CN, 7 mL H_2O, blue LED, 4 h.

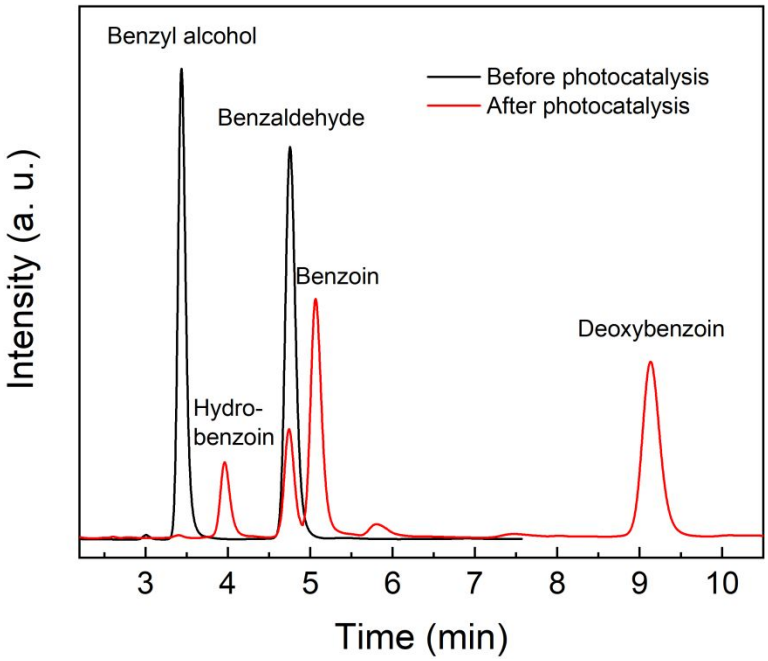


Figure S17. HPLC spectra of heterocoupling between benzyl alcohol and benzaldehyde before and after photocatalysis. Conditions: 10 mM benzaldehyde, 10 mM benzyl alcohol, 10 mg $ZnIn_2S_4$, room temperature, 7 mL H_2O, 3 mL CH_3CN, blue LED, 14 h.

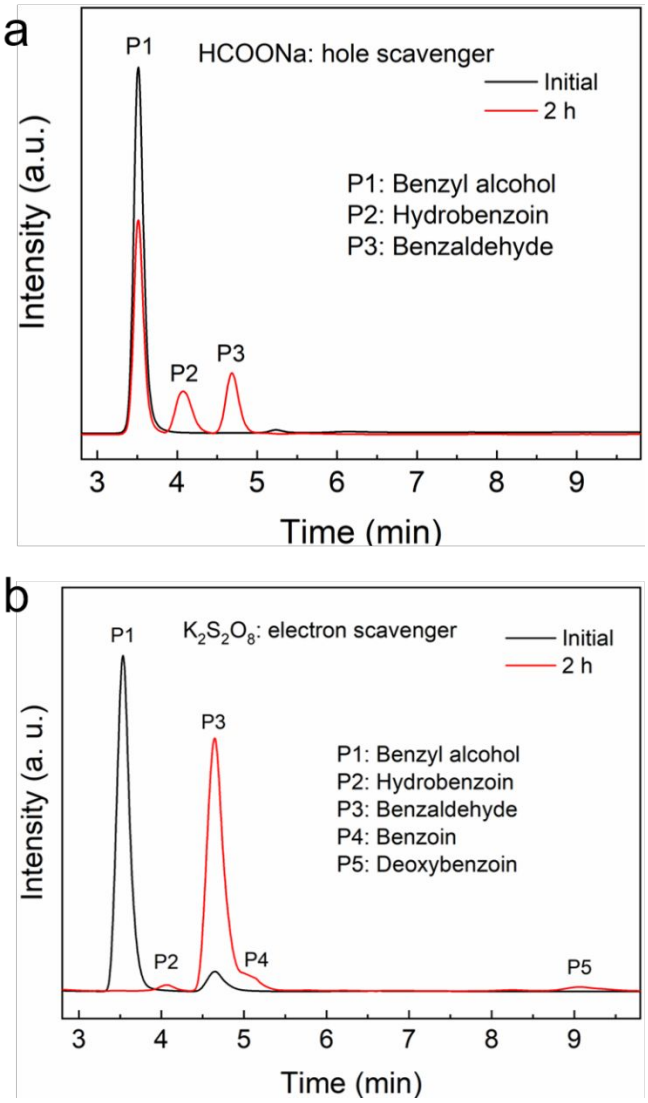


Figure S18. HPLC spectra of photocatalytic upgrading of benzyl alcohol over time using HCOONa as hole scavenger (a) and $K_2S_2O_8$ as electron scavenger (b). (Conditions: 10 mM benzyl alcohol, 10 mM scavenger, 10 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, blue LED, 2 h).

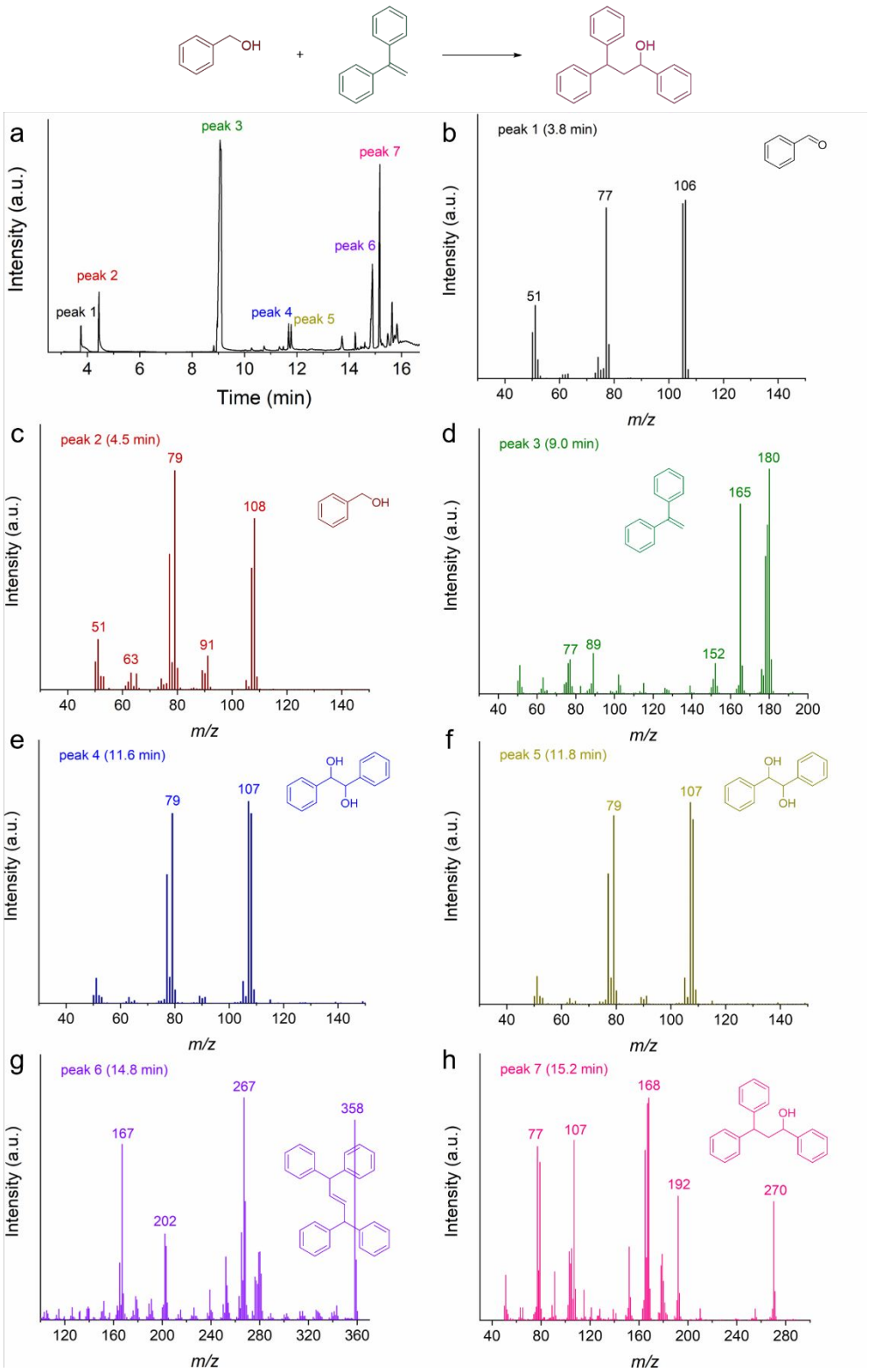


Figure S19. GC-MS spectra of the mixture after radical trapping experiment. Conditions: 2.5 mmol benzyl alcohol, 5 mmol 1,1-diphenylethylene, 50 mg $ZnIn_2S_4$, 25 mL CH_3CN, blue LED, 60 h.

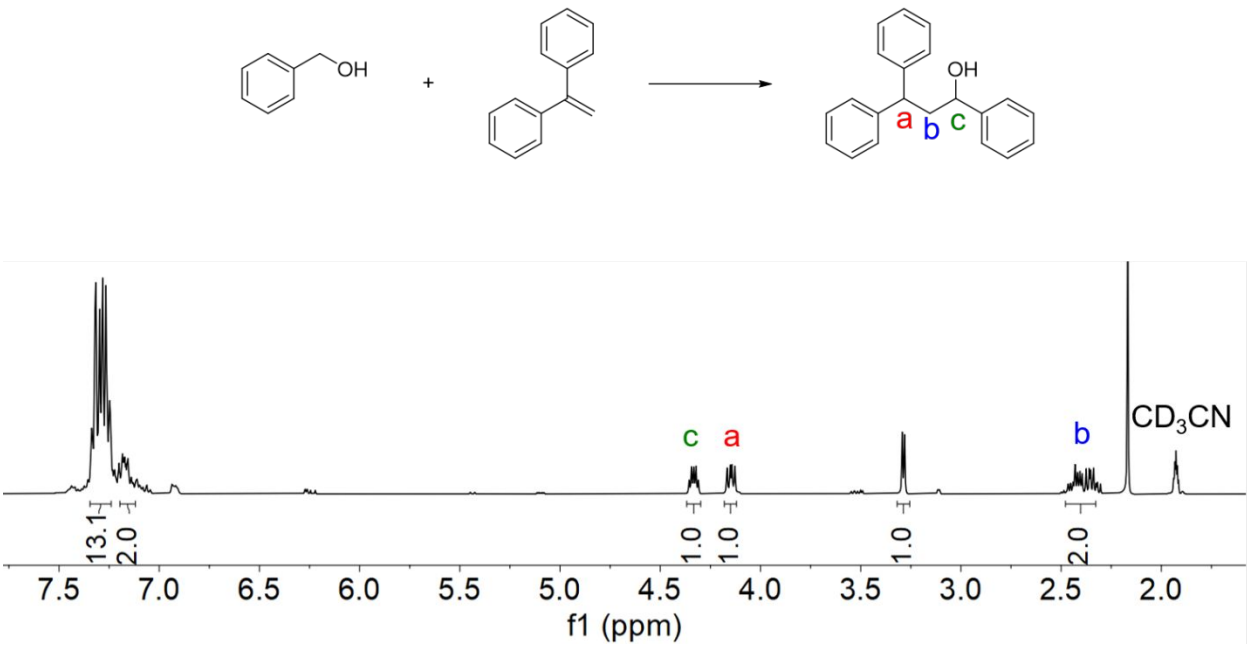


Figure S20. ^{1}H NMR spectrum of the purified 1,3,3-triphenyl-1-propanol after radical trapping experiment. Conditions: 2.5 mmol benzyl alcohol, 5 mmol 1,1-diphenylethylene, 50 mg $ZnIn_2S_4$, 25 mL CH_3CN, blue LED, 60 h.

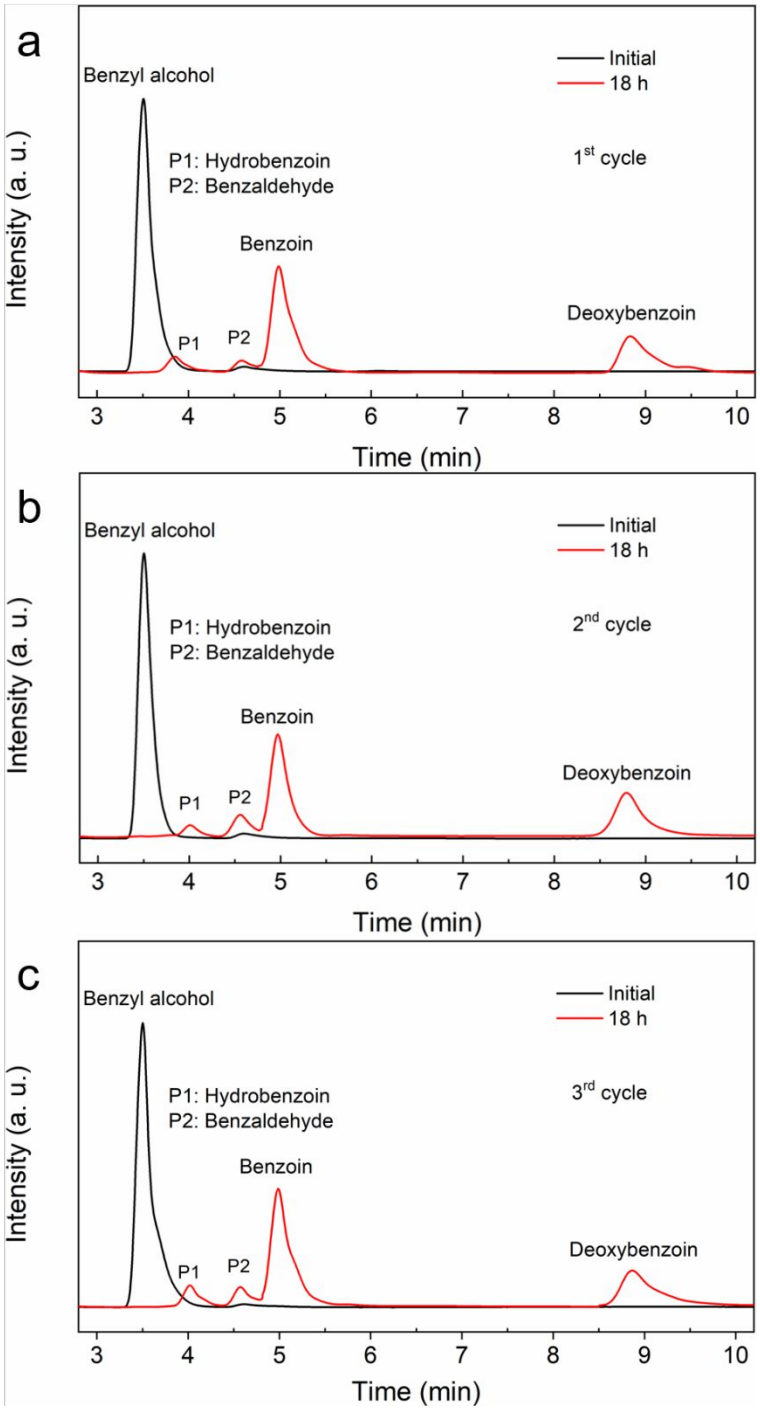


Figure S21. HPLC spectra of benzyl alcohol upgrading before and after photocatalysis by three consecutive cycles. (a) 1st cycle, (b) 2nd cycle, and (c) 3rd cycle. (Conditions: 10 mM benzyl alcohol, 20 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, blue LED, 18 h).

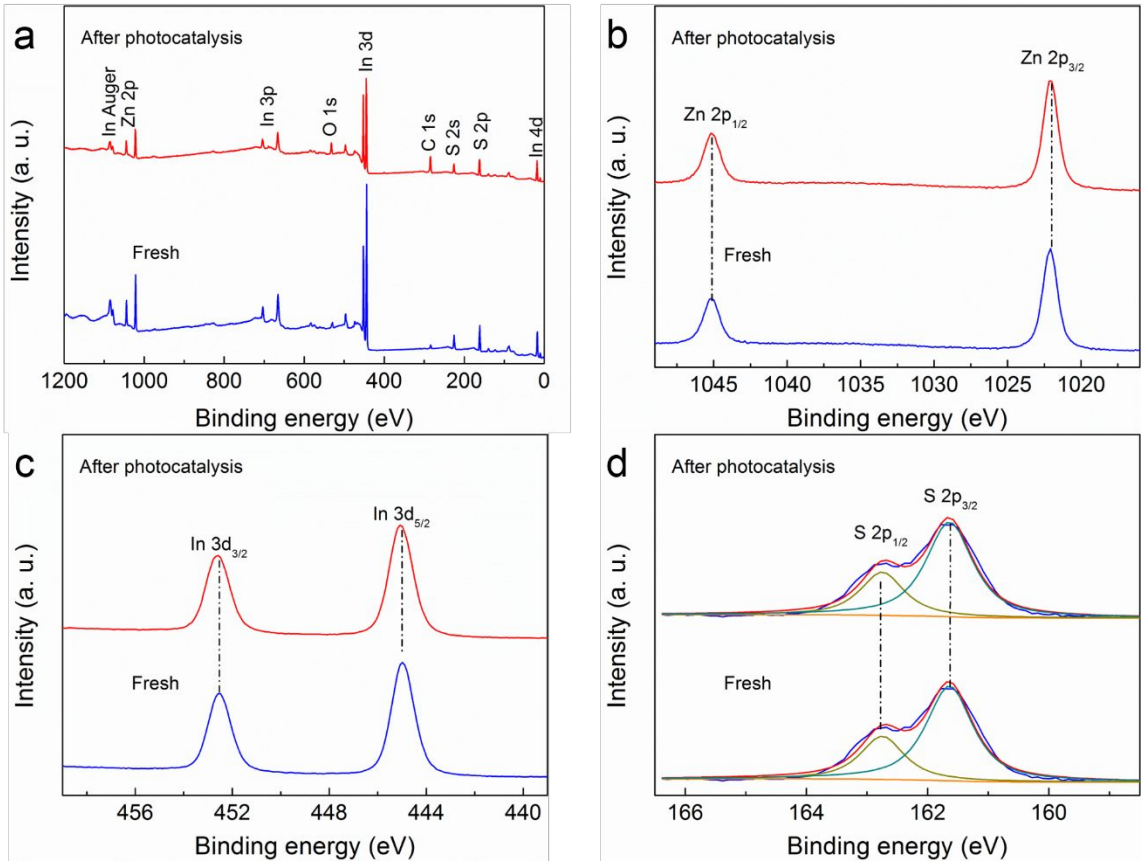


Figure S22. XPS spectra of $ZnIn_2S_4$ before and after photocatalysis including survey (a), high-resolution Zn 2p (b), In 3d (c), and S 2p (d).

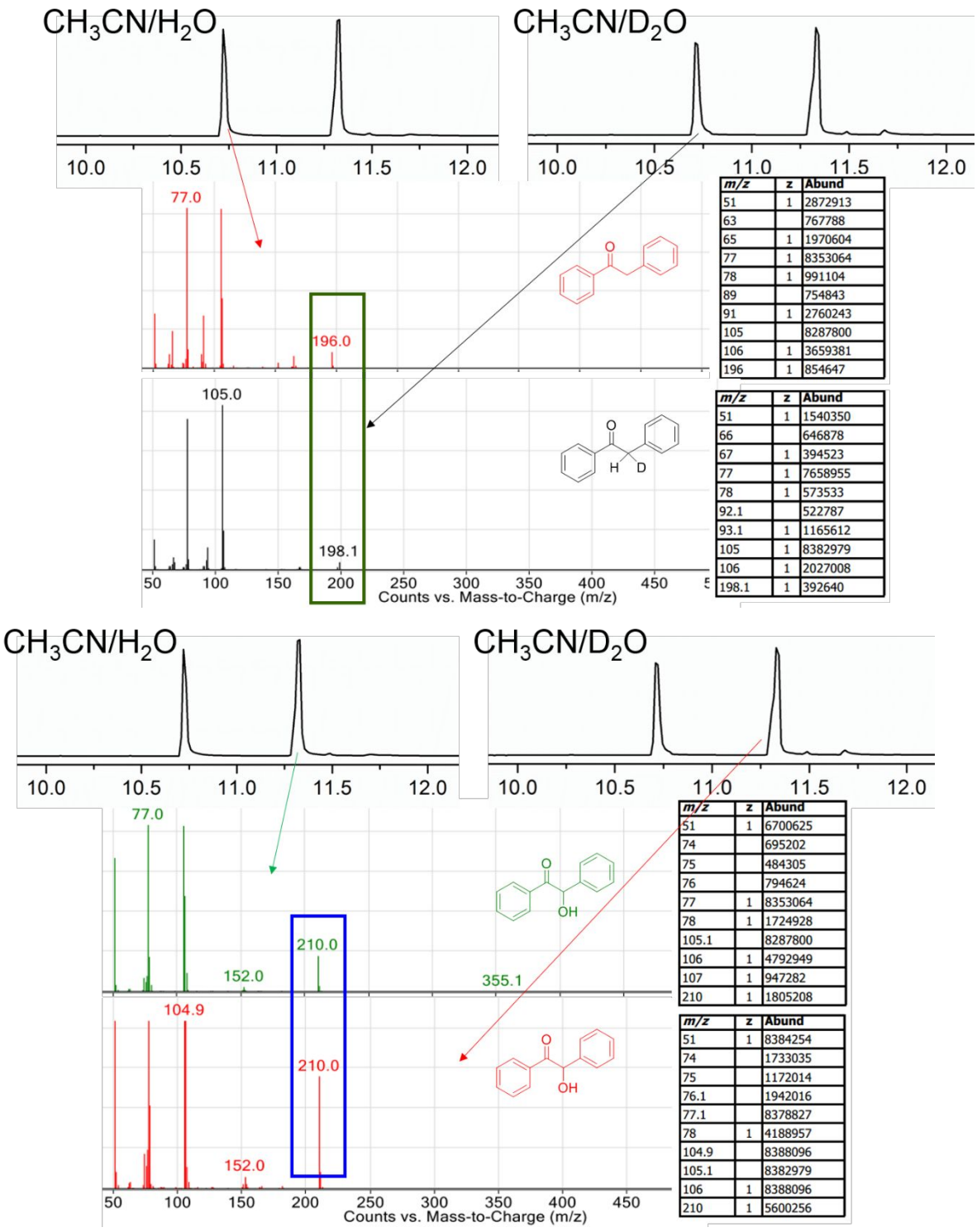


Figure S23. GC-MS spectra from photocatalytic upgrading of benzyl alcohol using CH_3CN/H_2O or CH_3CN/D_2O as solvents. (Conditions: 10 mM benzyl alcohol, 10 mg $ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O or D_2O, blue LED, 18 h).

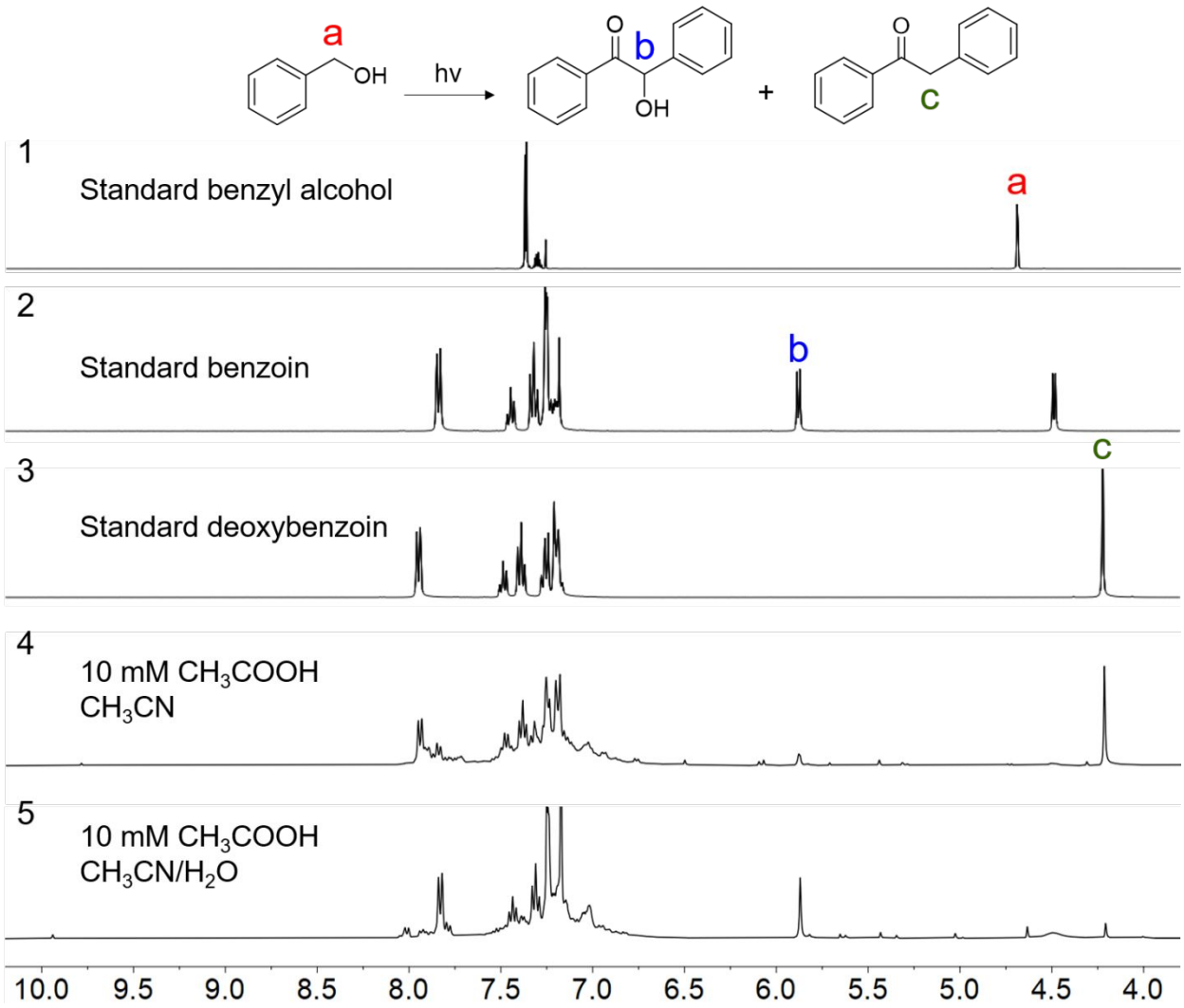


Figure S24. ^{1}H NMR spectra of photocatalytic coupling of benzyl alcohol. ^{1}H NMR spectra of (1) benzyl alcohol, (2) benzoin, (3) deoxybenzoin, (4) products from benzyl alcohol coupling (condition: 10 mM benzyl alcohol, 10 mM acetic acid, 10 mg $ZnIn_2S_4$, 10 mL CH_3CN, blue LED, 6 h), and (4) products from benzyl alcohol coupling (condition: 10 mM benzyl alcohol, 10 mM acetic acid, 10 mg $ZnIn_2S_4$, 7 mL CH_3CN, 3 mL H_2O, blue LED, 18 h).

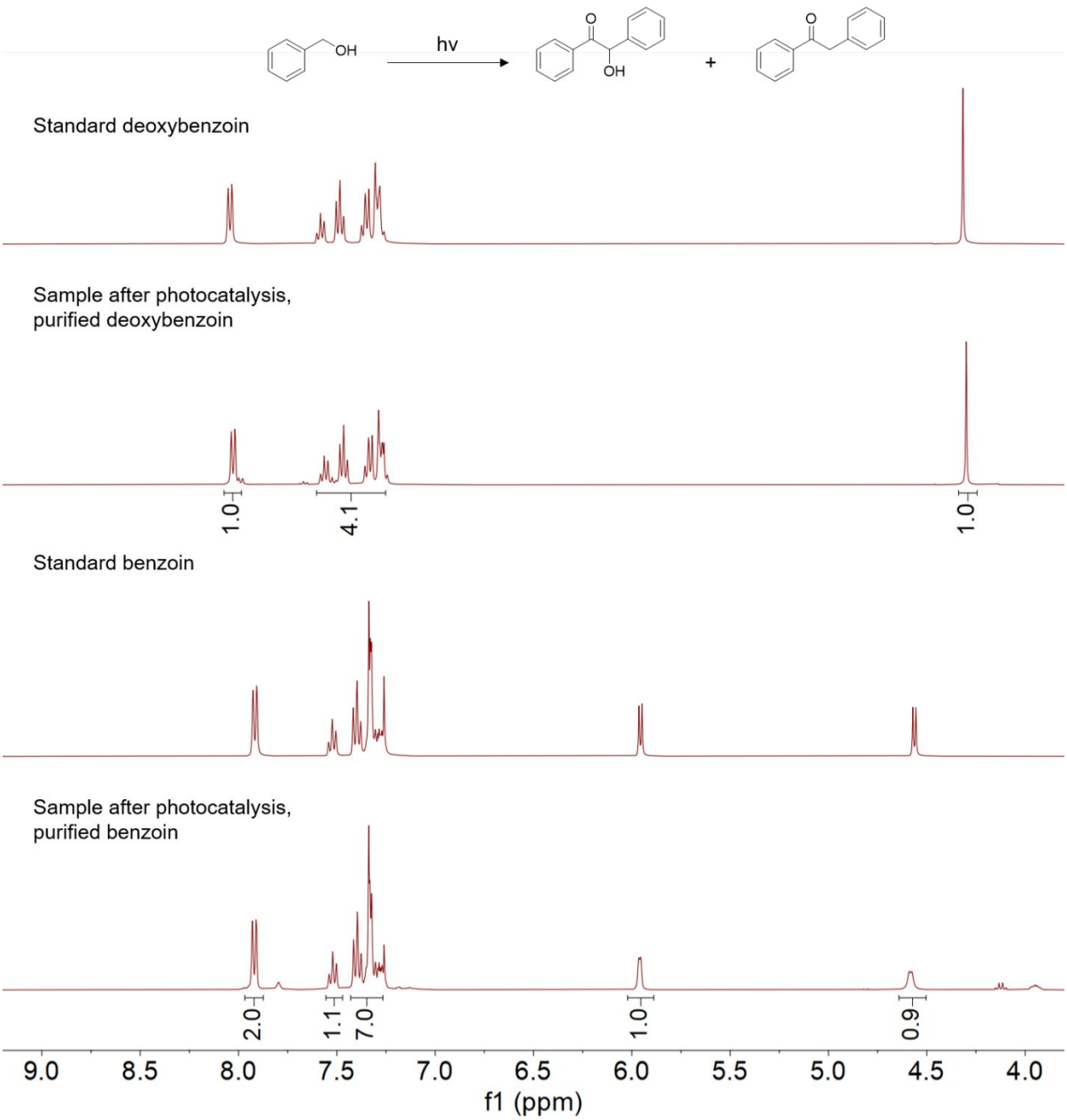


Figure S25. ^{1}H NMR spectra of standard deoxybenzoin, chromatography purified deoxybenzoin after photocatalysis, standard benzoin, and chromatography purified benzoin after photocatalysis. Conditions: (1) 10 mM benzyl alcohol, 10 mM acetic acid, 10 mg $ZnIn_2S_4$, 10 mL CH_3CN, blue LED, 6 h; (2) 10 mM benzyl alcohol, 10 mM acetic acid, 10 mg $ZnIn_2S_4$, 7 mL CH_3CN, 3 mL H_2O, blue LED, 18 h.

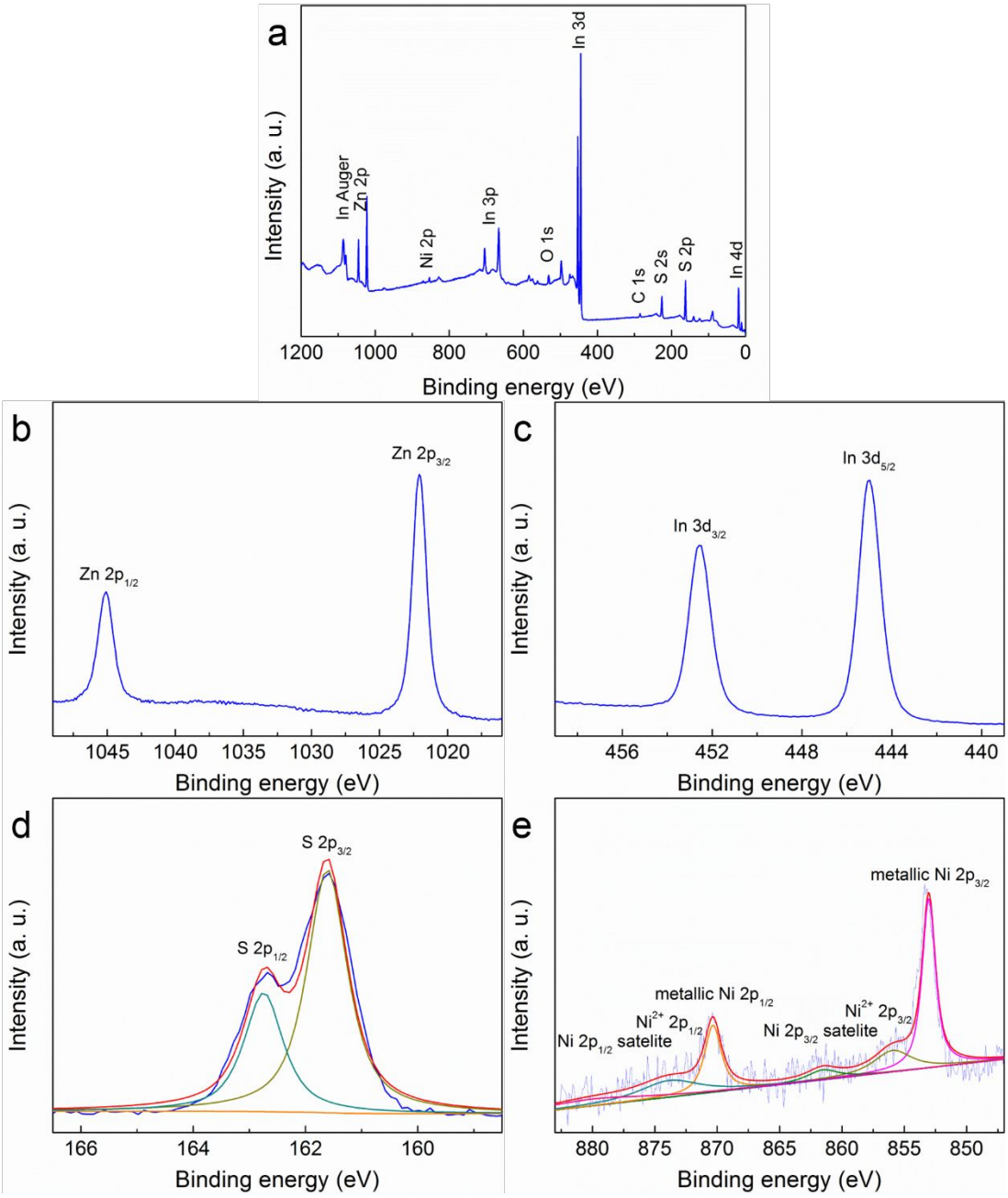


Figure S26. XPS spectra of fresh Ni/$ZnIn_2S_4$ including survey (a), high-resolution Zn 2p (b), In 3d (c), S 2p (d) and Ni 2p (e).

Table S2. ICP-AES of Ni/$ZnIn_2S_4$.

Element	Wt%
Ni	2.0
Zn	12.7
In	45.0
S	40.3

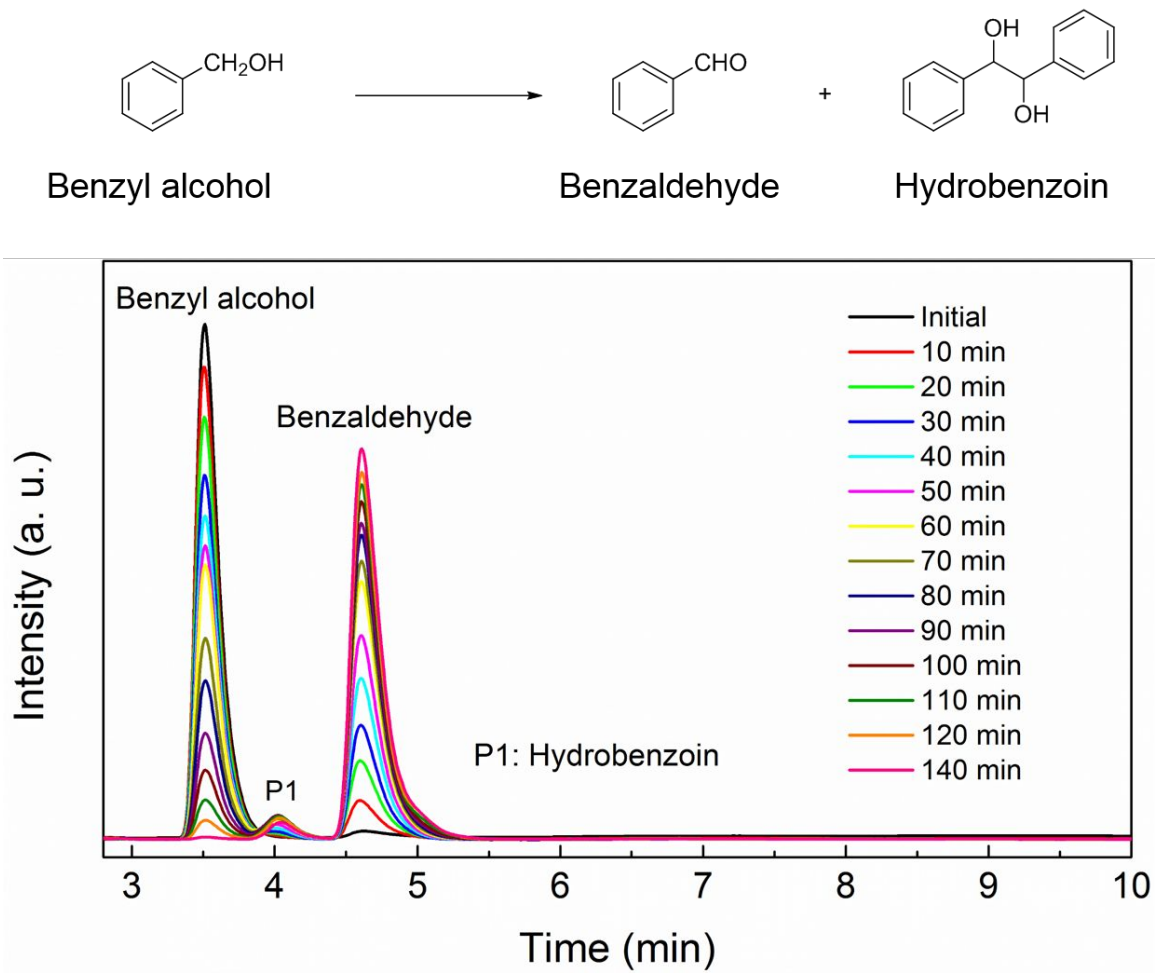


Figure S27. HPLC spectra of photocatalytic upgrading of benzyl alcohol over time. (Conditions: 10 mM benzyl alcohol, 10 mg Ni/$ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, blue LED, 2.4 h).

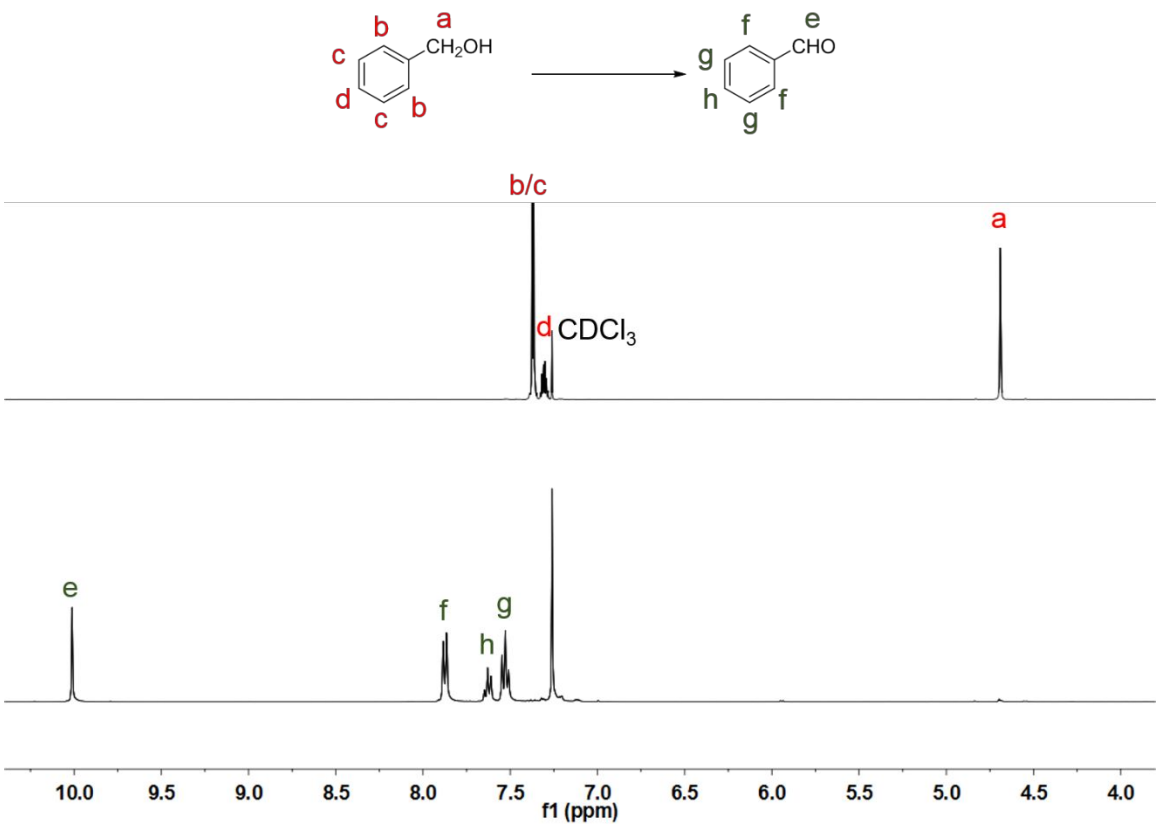


Figure S28. ^{1}H NMR spectra of benzyl alcohol (top), and products from benzyl alcohol upgrading (bottom). (Condition: 10 mM benzyl alcohol, 10 mg Ni/$ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, blue LED, 2.4 h).

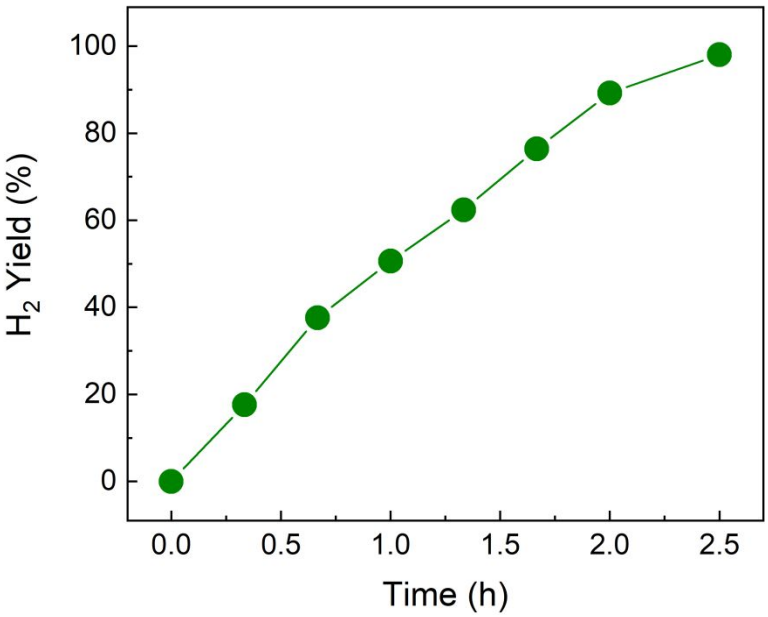


Figure S29. Yield of H_2 change over time. Conditions: 10 mM benzyl alcohol, 10 mg Ni/$ZnIn_2S_4$, room temperature, 3 mL CH_3CN, 7 mL H_2O, 2.5 h.

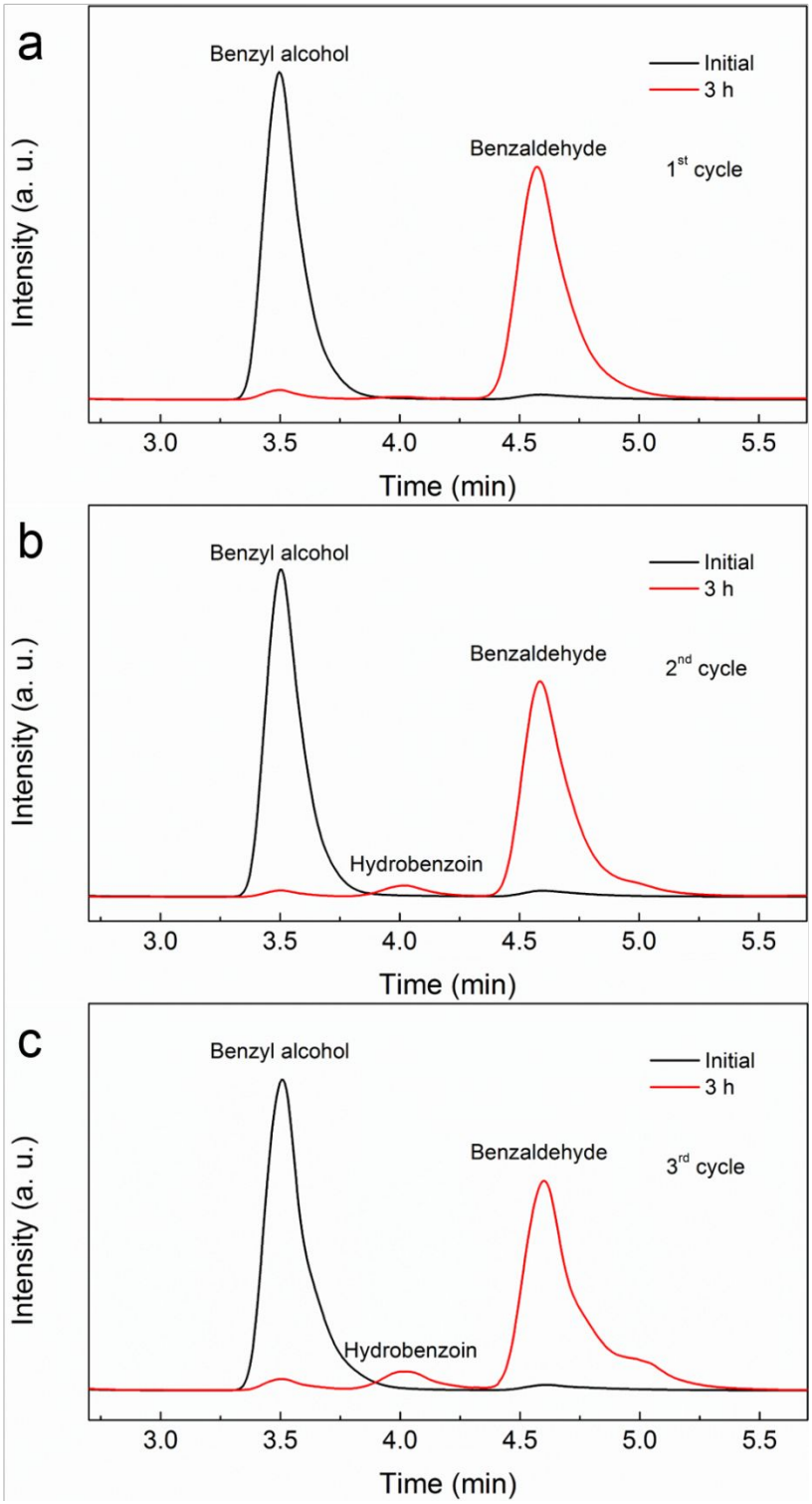


Figure S30. HPLC spectra of benzyl alcohol upgrading before and after photocatalysis by three consecutive cycles. (a) 1st cycle, (b) 2nd cycle, and (c) 3rd cycle. (Conditions: 10 mM benzyl alcohol, 20 mg Ni/$ZnIn_2S_4$, 3 mL CH_3CN, 7 mL H_2O, blue LED, 2.4 h).

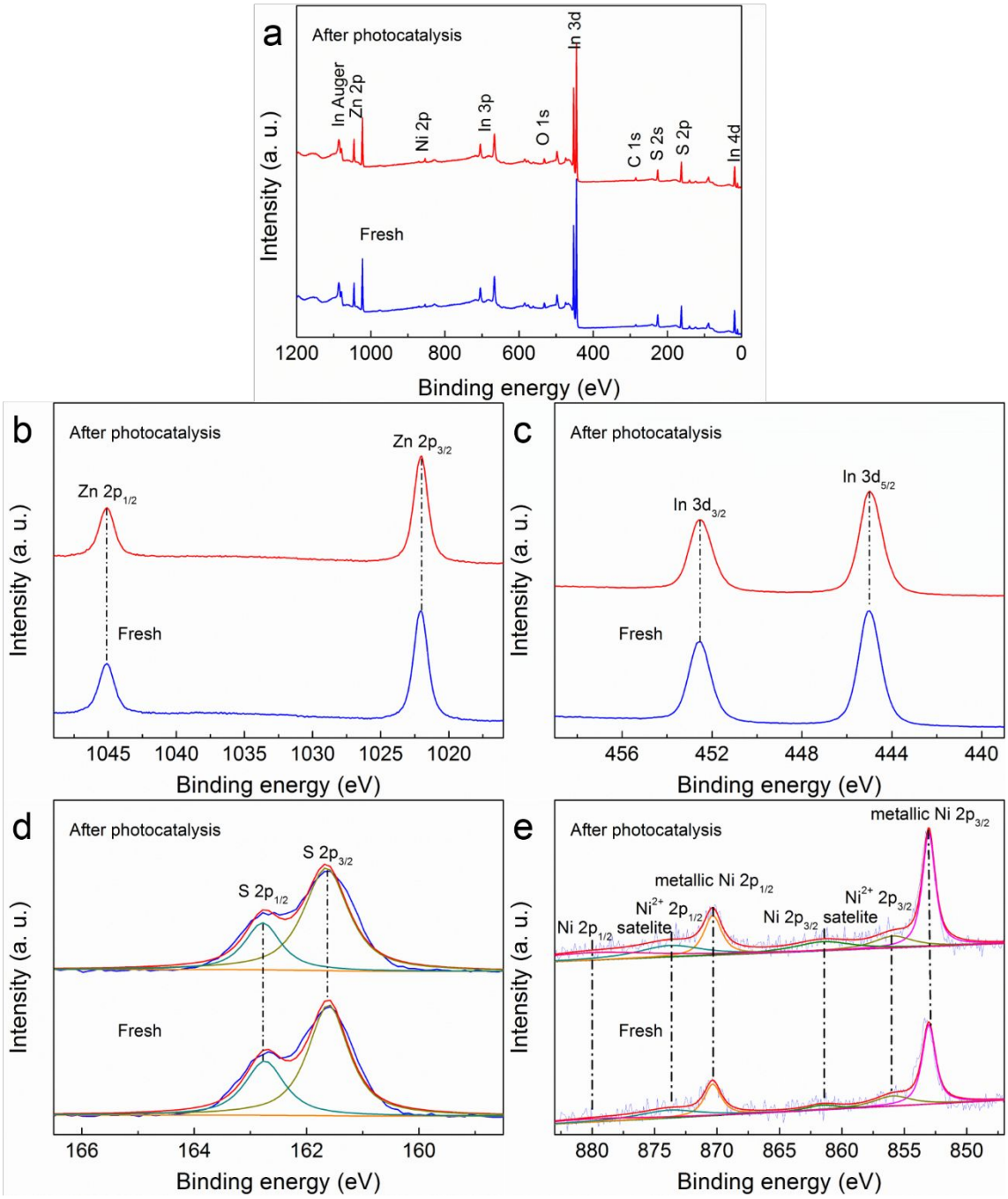


Figure S31. XPS spectra of $Ni/ZnIn_2S_4$ before and after photocatalysis including survey (a), high-resolution Zn 2p (b), In 3d (c), S 2p (d) and Ni 2p (e).

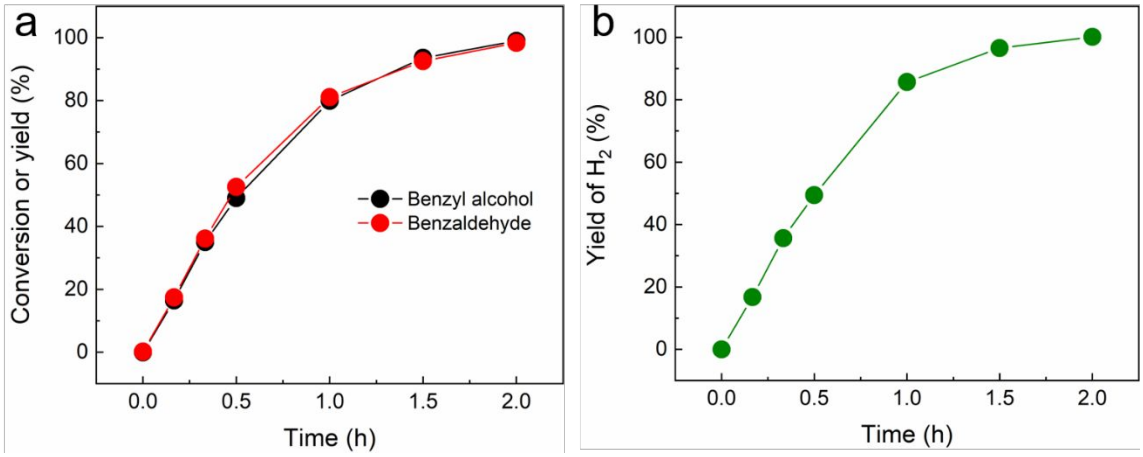
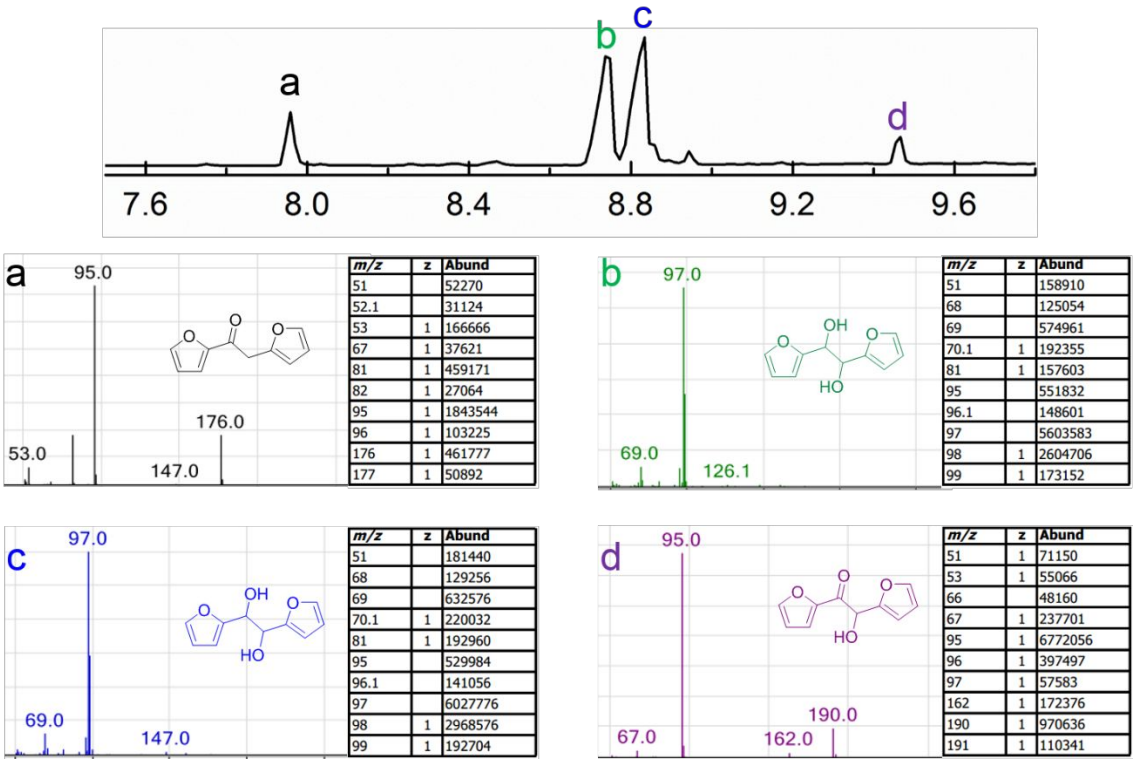


Figure S32. (a) Conversion of benzyl alcohol and yield of benzaldehyde change over time. (b) Yield of H_2 change over time. Conditions: 10 mM benzyl alcohol, 10 mg $NiS/ZnIn_2S_4$, room temperature, 3 mL CH_3CN, 7 mL H_2O, blue LED, 2 h.



m/z	z	Abund
51		52270
52.1		31124
53	1	166666
67	1	37621
81	1	459171
82	1	27064
95	1	1843544
96	1	103225
176	1	461777
177	1	50892

m/z	z	Abund
51		158910
68		125054
69		574961
70.1	1	192355
81	1	157603
95		551832
96.1		148601
97		5603583
98	1	2604706
99	1	173152

m/z	z	Abund
51		181440
68		129256
69		632576
70.1	1	220032
81	1	192960
95		529984
96.1		141056
97		6027776
98	1	2968576
99	1	192704

m/z	z	Abund
51	1	71150
53	1	55066
66		48160
67	1	237701
95	1	6772056
96	1	397497
97	1	57583
162	1	172376
190	1	970636
191	1	110341

Figure S33. GC-MS spectra after photocatalytic coupling of furfural and furfural alcohol. (Conditions: 10 mM furfural, 10 mM furfural alcohol, 10 mg $ZnIn_2S_4$, 9 mL CH_3CN, 1 mL H_2O, blue LED, 16 h).

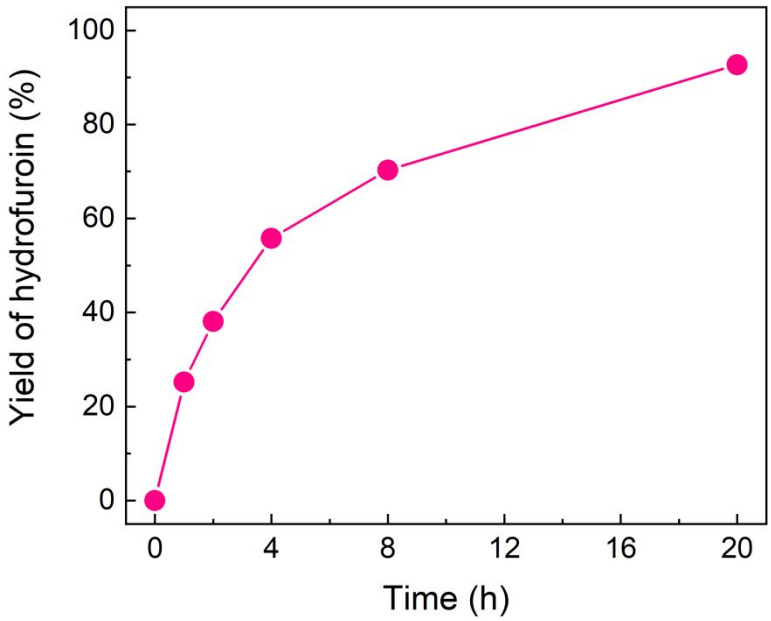


Figure S34. Yield of hydrofuroin over time. Conditions: 10 mM furfural, 10 mM furfural alcohol, 10 mg $ZnIn_2S_4$, 9 mL CH_3CN, 1 mL H_2O, Blue LED.

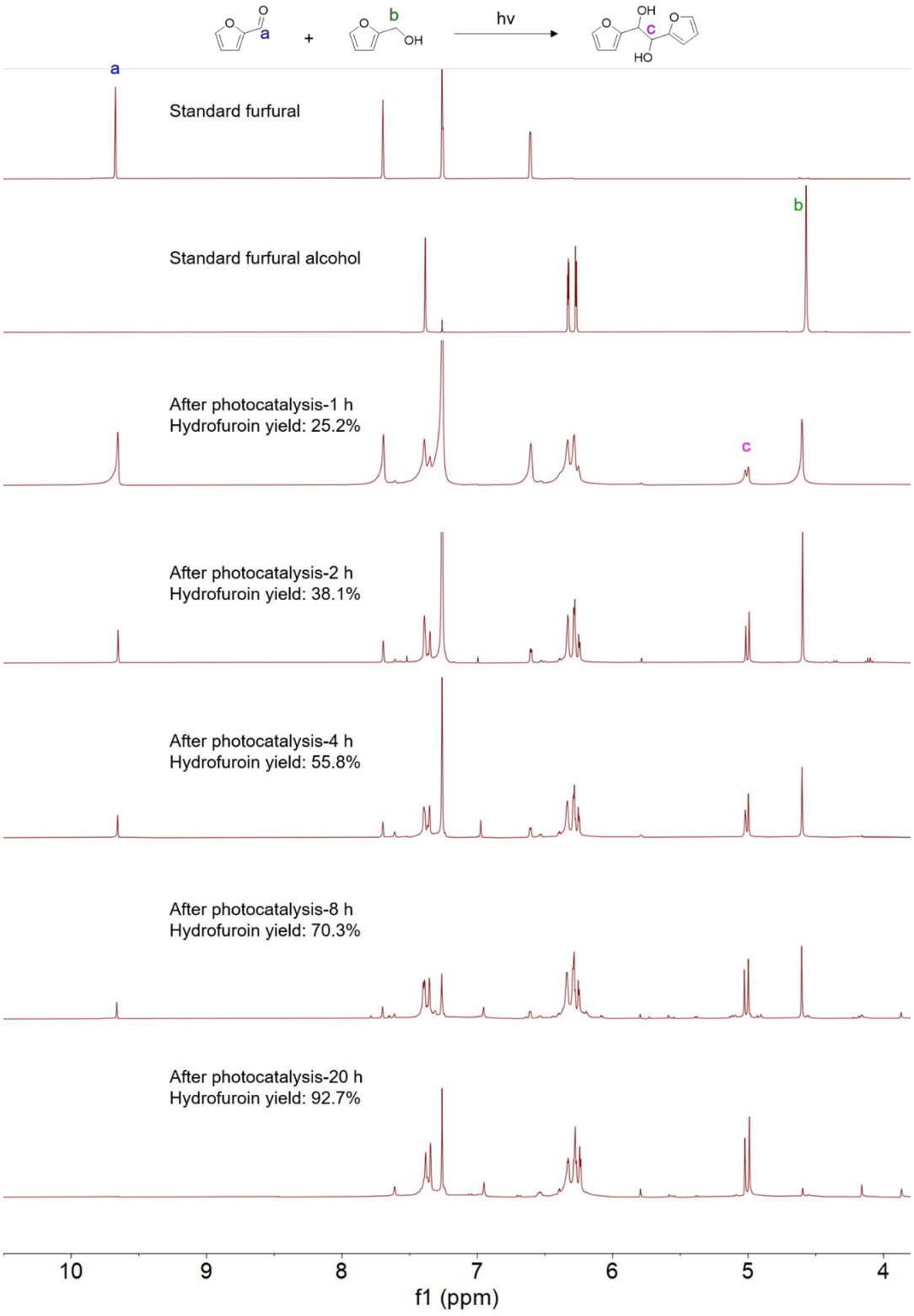


Figure S35. ^{1}H NMR spectra of heterocoupling between furfural and furfural alcohol after different photocatalysis time. Conditions: 10 mM furfural, 10 mM furfural alcohol, 10 mg $ZnIn_2S_4$, 9 mL CH_3CN, 1 mL H_2O, Blue LED.

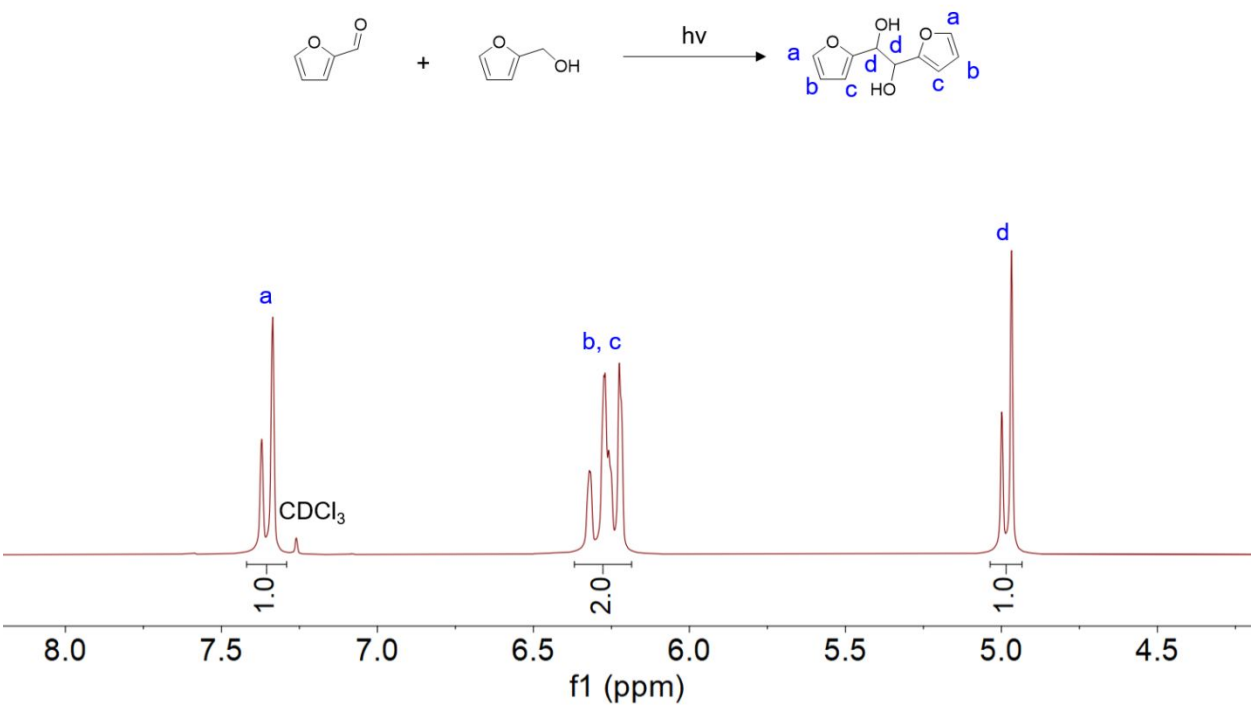


Figure S36. ^{1}H NMR spectrum of the purified hydrofuroin obtained from photocatalysis. Conditions: 20 mM furfural, 20 mM furfural alcohol, 500 mg $ZnIn_2S_4$, 450 mL CH_3CN, 50 mL H_2O, 4 Blue LEDs, 60 h.