Supplementary Material

S-Scheme Heterojunction $Cs_3Bi_2Br_9/Bi_2WO_6$ for Efficient Photocatalytic Cleavage of C-C Bonds in β-1 Lignin Models

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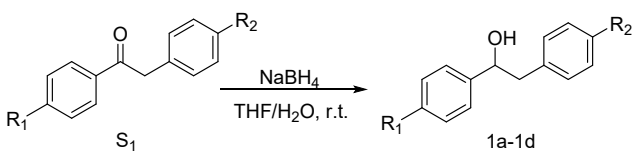
1. Experimental Section

1.1 Synthesis of lignin models. Lignin models were prepared according to a procedure described in the literature.(Wu et al., 2021)



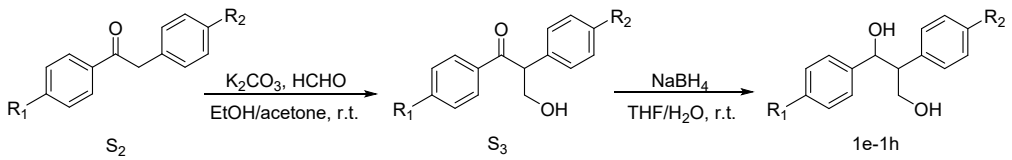
1a: R_1=H, R_2=H

1b: R_1=H, R_2=Me

1c: R_1=OMe, R_2=H

1d: R_1=OMe, R_2=OMe

S_1 (10 mmol, 1 eq.) was added into THF/water solvent (50 mL, v/v = 4/1) in a bottle (100 mL). Afterward, $NaBH_4$ (12 mmol, 1.2 eq.) was added and the mixture was stirred at room temperature (r. t.) for 2 h. Then, an excess of saturated NH_4Cl aqueous solution (30 mL) was added. The crude product was extracted with ethyl acetate (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4. The solvent was then concentrated in vacuo and the resulting white solid was dried at 45 °C for 8 h to obtain the products 1a-1d.



1e: R_1=H, R_2=H

1f: R_1=H, R_2=Me

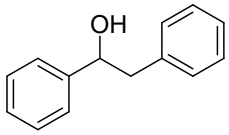
1g: R_1=Me, R_2=H

1h: R_1=OMe, R_2=OMe

To a stirring suspension of K_2CO_3 (4.4 mmol, 1.1 eq.) in ethanol/acetone (v/v = 1/1, 20 mL) and S_2 (4 mmol, 1 eq.) at r. t. under N_2 atmosphere, a water solution of HCHO (36.5-38.0 wt%, 0.6 mL, 7.3 mmol, 1.8 eq.) was added. After 4 h, the reaction mixture was filtered to remove K_2CO_3 and concentrated in vacuo to get a solid product. The crude product was purified on silica gel to obtain S_3.

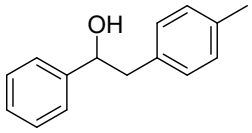
The synthesized S_3 (10 mmol, 1 eq.) was added into THF/water solvent (50 mL, v/v = 4/1) in a bottle (100 mL). Afterward, $NaBH_4$ (12 mmol, 1.2 eq.) was added and the system was stirred at room temperature (r. t.) for 2 h. Then, an excess of saturated NH_4Cl aqueous solution (30 mL) was added. The crude product was extracted with ethyl acetate (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4. The solvent was concentrated in vacuo and the obtained white solid was dried at 45°C for 8 h to obtain the product 1e-1h.

1,2-Diphenylethanol (1a): white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34-7.30 (m, 4H), 7.29-7.22 (m, 3H), 7.17 (d, J = 7.3 Hz, 3H), 5.33 (d, J = 4.7 Hz, 1H), 4.78 (dt, J = 7.7, 5.2 Hz, 1H), 2.91 (t, J = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.7,

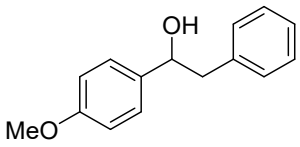


139.1, 129.5, 127.9, 127.8, 126.7, 126.0, 125.8, 73.8, 45.7.

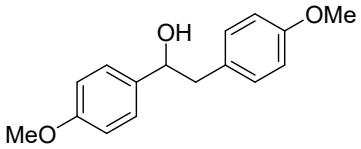
1-Phenyl-2-(p-tolyl)ethan-1-ol (1b): white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.30-7.26 (m, 4H), 7.23-7.18 (m, 1H), 7.02 (s, 4H), 5.25 (d, J = 4.6 Hz, 1H), 4.72 (ddd, J = 7.4, 5.8, 4.6 Hz, 1H), 2.83 (t, J = 7.0 Hz, 2H), 2.254(s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.8, 136.0, 134.6, 129.4, 128.4, 127.8, 126.7, 126.0, 73.9, 45.3, 20.7.



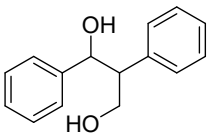
1-(4-Methoxyphenyl)-2-phenylethan-1-ol (1c): white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.23-7.20 (m, 4H), 7.17-7.13 (m, 3H), 6.86-6.83 (m, 2H), 5.20 (d, J = 4.6 Hz, 1H), 4.70 (dt, J = 7.7, 5.3 Hz, 1H), 3.72 (s, 3H), 2.87 (qd, J = 13.4, 6.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.1, 139.2, 137.7, 129.5, 127.8, 127.2, 125.8, 113.2, 73.4, 55.0, 45.7.



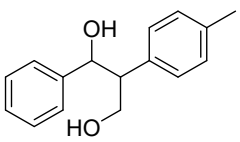
1,2-Bis(4-methoxyphenyl)ethan-1-ol (1d): white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.20-7.12 (m, 2H), 7.09-6.98 (m, 2H), 6.90-6.81 (m, 2H), 6.80-6.73 (m, 2H), 5.14 (d, J = 4.5 Hz, 1H), 4.64 (ddd, J = 7.4, 5.8, 4.4 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 2.80 (dd, J = 16.1, 6.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.1, 157.4, 137.8, 131.1, 130.4, 127.2, 113.2, 113.2, 73.5, 55.0, 54.9, 44.8.



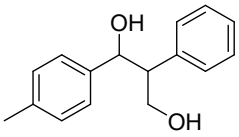
1,2-Diphenylpropane-1,3-diol (1e): white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.24-7.19 (m, 2H), 7.15 (dd, J = 7.6, 5.9 Hz, 5H), 7.10 (dd, J = 7.9, 1.8 Hz, 3H), 5.20 (d, J = 4.5 Hz, 1H), 5.00 (t, J = 5.0 Hz, 1H), 4.54 (t, J = 5.1 Hz, 1H), 3.72 (ddd, J = 10.4, 6.8, 5.2 Hz, 1H), 3.53 (ddd, J = 10.4, 6.9, 5.0 Hz, 1H), 2.90 (td, J = 6.7, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.1, 140.48, 129.5, 127.5, 127.3, 126.4, 126.2, 125.8, 72.2, 62.6, 55.7.



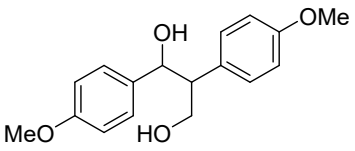
1-Phenyl-2-(p-tolyl)propane-1,3-diol (1f): white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.21-7.19 (m, 2H), 7.18-7.12 (m, 3H), 6.97 (s, 4H), 5.17 (d, J = 4.5 Hz, 1H), 4.99 (t, J = 4.8 Hz, 1H), 4.53 (t, J = 5.1 Hz, 1H), 3.71 (ddd, J = 10.4, 7.1, 5.4 Hz, 1H), 3.49 (ddd, J = 10.4, 6.7, 4.9 Hz, 1H), 2.86 (td, J = 6.9, 5.0 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.1, 137.2, 134.5, 129.4, 127.9, 127.5, 126.3, 126.2, 72.1, 62.7, 55.3, 20.8.



2-Phenyl-1-(p-tolyl)propane-1,3-diol (1g): white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.20-7.15 (m, 2H), 7.15-7.09 (m, 3H), 7.07 (d, J = 8.6 Hz, 2H), 6.81-6.75 (m, 2H), 5.08 (d, J = 4.4 Hz, 1H), 4.92 (t, J = 5.1 Hz, 1H), 4.48 (t, J = 5.1 Hz, 1H), 3.70 (s, 3H), 3.69-3.64 (m, 1H), 3.56-3.43 (m, 1H), 2.86 (m, J = 6.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.8, 140.8, 137.0, 129.5, 127.3, 127.3, 125.8, 112.9, 71.9, 62.7, 55.8, 54.9.



1,2-Bis(4-methoxyphenyl)propane-1,3-diol (1h): white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.10-6.97 (m, 4H), 6.81-6.69 (m, 4H), 5.04 (d, J = 4.4 Hz, 1H), 4.91 (t, J = 4.8 Hz, 1H), 4.47 (t, J = 5.1 Hz, 1H), 3.69 (s, 3H), 3.69 (s, 3H), 3.67-3.61 (m, 1H), 3.47 (dd, J = 5.2, 1.6 Hz, 1H), 2.81 (d, J = 5.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.8, 157.5, 137.1, 132.4, 130.3, 127.3, 112.9, 112.8, 71.8, 62.8, 54.9, 54.9, 54.8.



1.2 Emission decays spectra and kinetic analysis.

The emission decay of photocatalyst was studied and the decay curve for the sample was well fitted with double-exponential function $Y_{(t)}$:(Gan et al., 2023)

$$Y_{(t)} = A_1\exp\left(-\frac{t}{\tau_1}\right) + A_2\exp\left(-\frac{t}{\tau_2}\right) \quad \textbf{(Equation 1)}$$

The average emission time τ_{avg} of photocatalyst was calculated from **Equation (2)**:

$$\tau_{avg} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A\tau_2} \quad \textbf{(Equation 2)}$$

Where A_1, A_2 are functional contributions of time-resolved emission decay lifetime τ_1, τ_2.

1.3 Calculation method for catalytic tests.

The conversion and yield were determined by HPGC analysis with internal standard of acetophenone. The details can be calculated using the following **Equation 3**:

$$Conversion\ (1a) = \left(1 - \frac{R_{(1a)}}{R_{(acetophenone)}} \Big/ \frac{S_{(1a)}}{S_{(acetophenone)}}\right) \times 100\% \quad \textbf{(Equation 3)}$$

$R_{(\mathbf{1a})}$ and $R_{(acetophenone)}$ are the peak areas of the corresponding compounds in the HPGC of the after reaction, $S_{(\mathbf{1a})}$ and $S_{(acetophenone)}$ are the peak areas of the corresponding compounds in the HPGC of the standard samples.

The yield of products (**2a**, **3a**, **4a** and **5a**) were determined by applying the following equations:

$$Yield\ (2a - 4a) = \frac{1}{2} \times \left(\frac{R_{(2a-4a)}}{R_{(acetophenone)}} \Big/ \frac{S_{(2a-4a)}}{S_{(acetophenone)}}\right) \times 100\%\ (Equation\ 4)$$

$$Yield\ (5a) = \left(\frac{R_{(5a)}}{R_{(acetophenone)}} \Big/ \frac{S_{(5a)}}{S_{(acetophenone)}}\right) \times 100\%\ (Equation\ 5)$$

$R_{(\mathbf{2a\text{-}5a})}$ and $R_{(acetophenone)}$ are the peak areas of the corresponding compounds in the HPGC of the after reaction, $S_{(\mathbf{2a\text{-}5a})}$ and $S_{(acetophenone)}$ are the peak areas of the corresponding compounds in the HPGC of the standard samples.

2. Results and Discussion

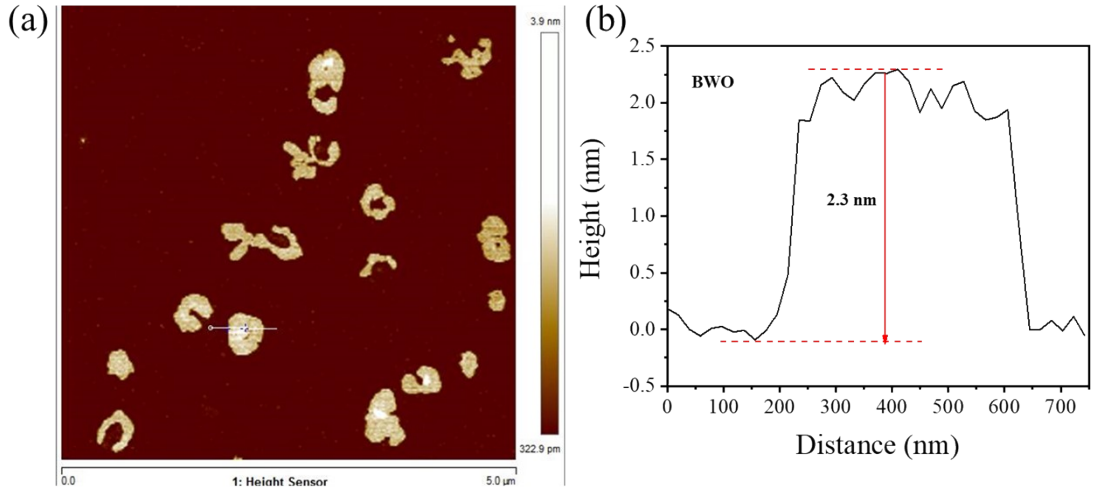


Fig. S1. (a) AFM image of BWO. (b)The AFM height cutaway view of BWO.

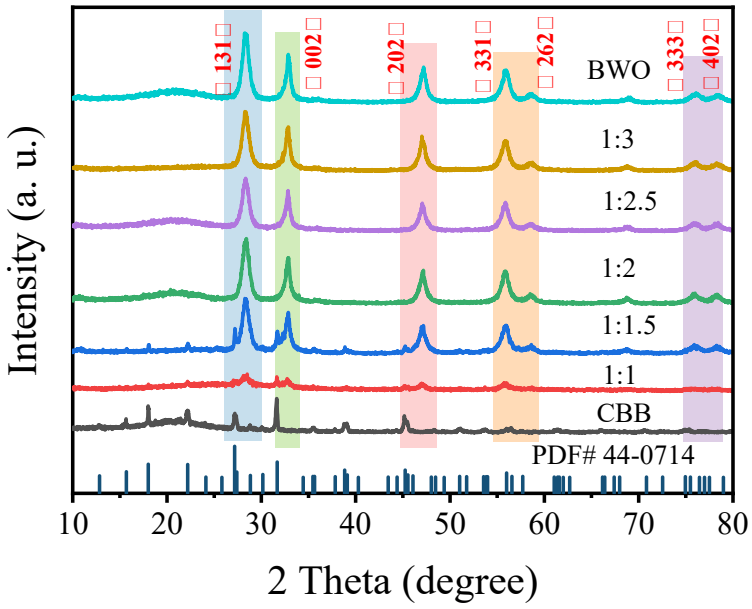


Fig. S2. XRD patterns of the as-prepared samples.

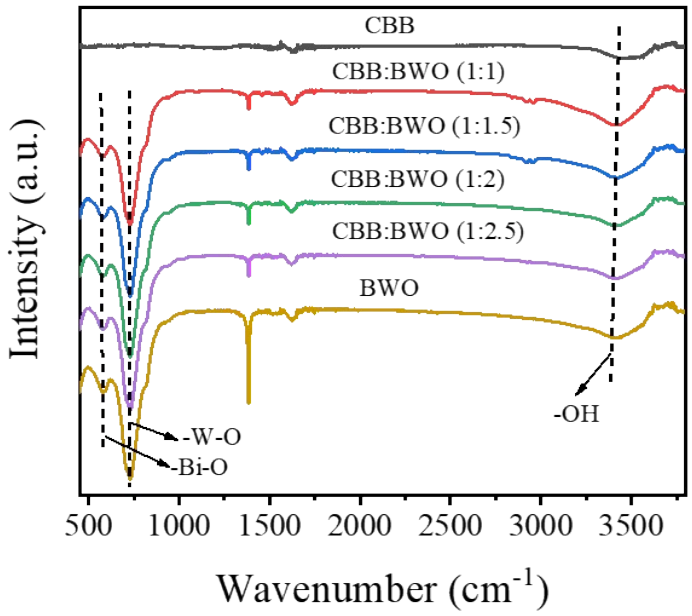


Fig. S3. FTIR spectra of the as-prepared samples.

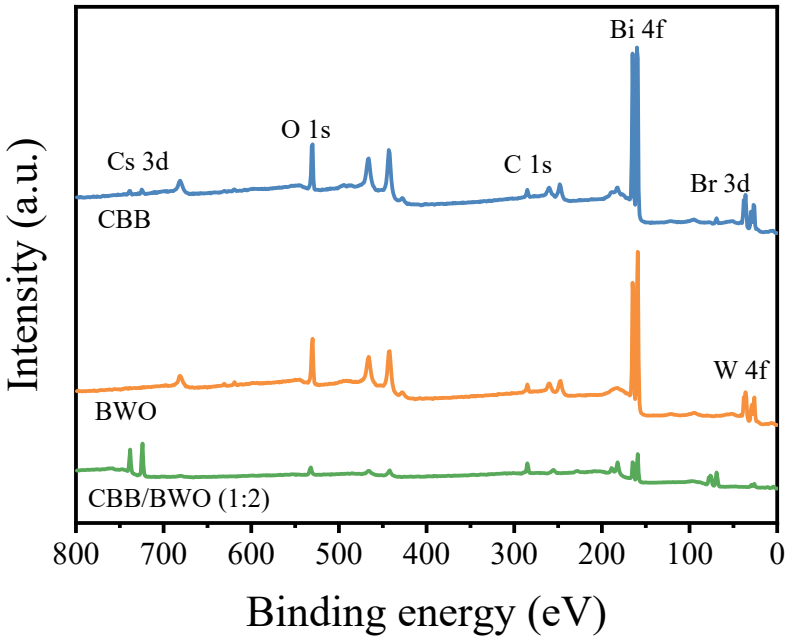


Fig. S4. Full XPS spectra of pristine CBB, BWO and CBB/BWO (1:2).

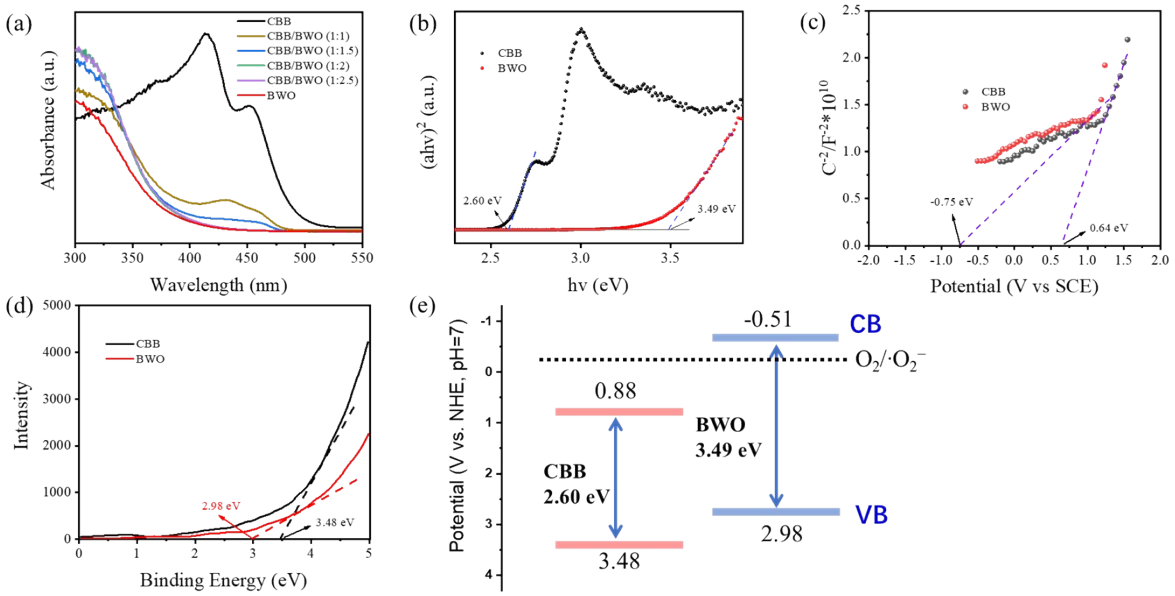


Fig. S5. (a) UV-vis DRS of CBB, BWO, and different ratios of composites. (b) Kubelka-Munk plots. (c) Mott-Schottky plots. (d) XPS valence band spectroscopy of CBB and BWO. (e) Band structures of CBB and BWO.

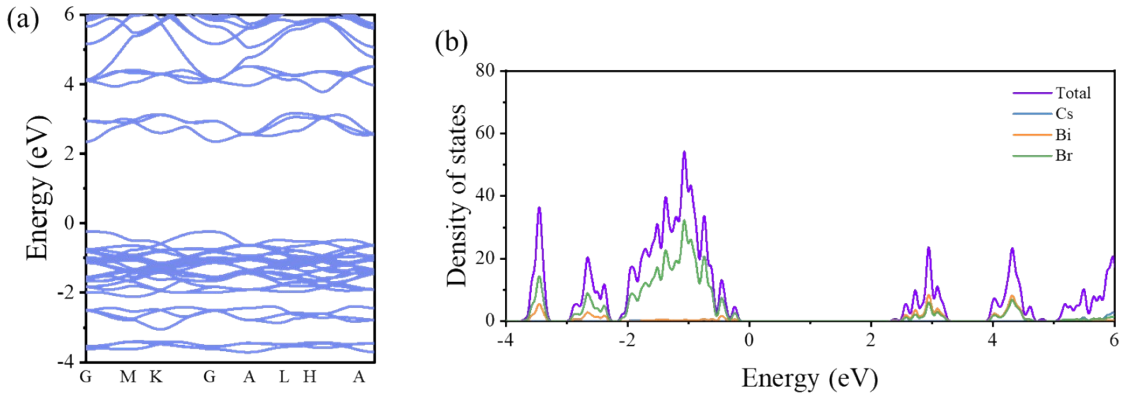


Fig. S6. (a) Electronic band structures of CBB (001) facet. (b) The density of states (DOS) of CBB (001) facet.

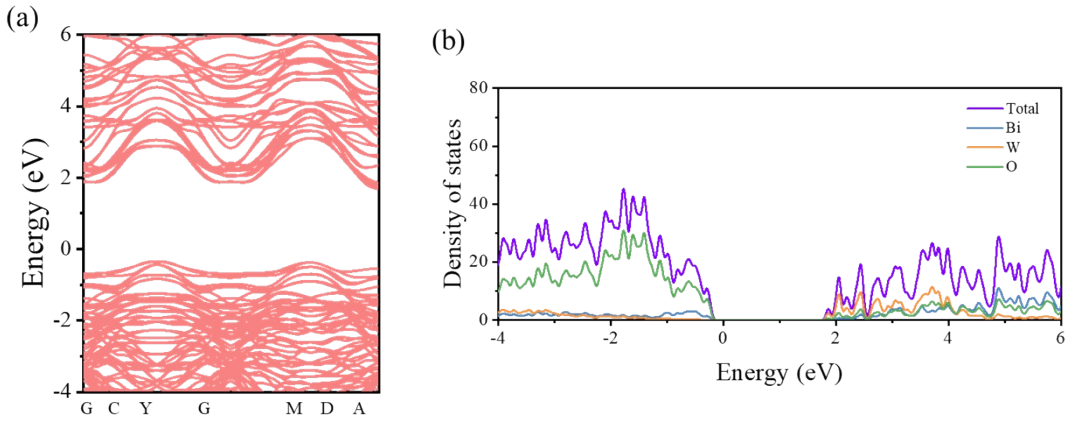


Fig. S7. (a) Electronic band structures of BWO (100) facet. (b) The density of states (DOS) of BWO (100) facet.

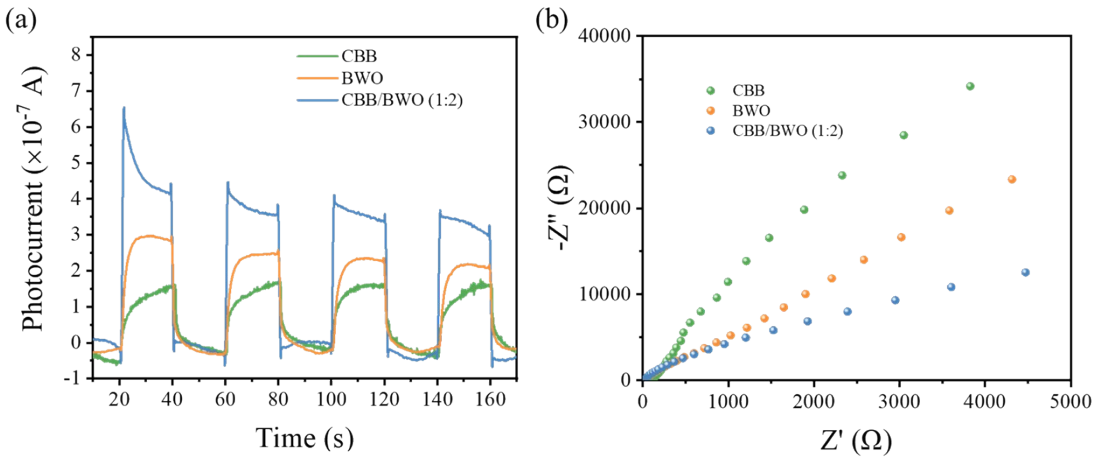


Fig. S8. (a) Transient photocurrent response and (b) Nyquist plots of CBB, BWO and CBB/BWO (1:2).

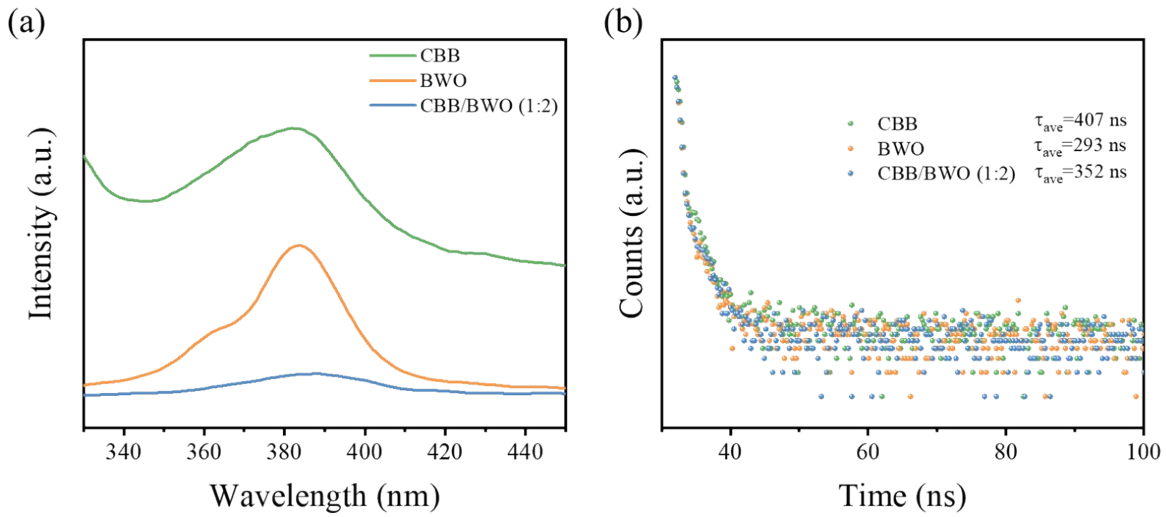
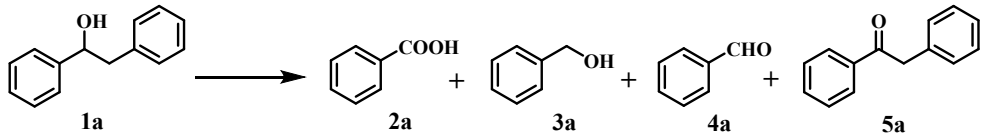


Fig. S9. (a) Photoluminescence (PL) spectra and (b) TRPL spectra of CBB, BWO and CBB/BWO (1:2) at emission wavelengths of 385 nm.

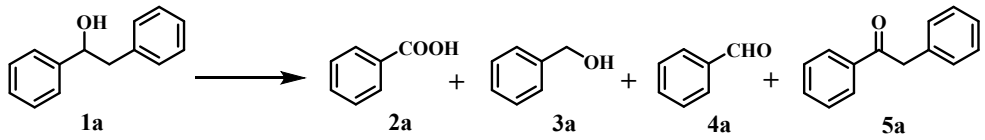
Table S1. Photocatalytic activity of different photocatalysts for cleavage of substrate **1a**.[a]



Entry	P. C.	Conversion (%)	Yield (%)[b]				$S_{Cα-Cβ}$ (%)
			2a	3a	4a	5a	
1	CBB	12	0	0	1	8	8
2	CBB/BWO (1:1)	54	1	1	34	16	67
3	CBB/BWO (1:1.5)	62	1	1	42	13	71
4	CBB/BWO (1:2)	99	21	1	62	12	85
5	CBB/BWO (1:2.5)	99	8	1	74	13	84
6	CBB/BWO (1:3)	99	25	0	58	11	84
7	BWO	50	3	2	38	5	86

[a]Reaction conditions: 0.10 mmol **1a**, 3.0 mL CH_2Cl_2, 20 mg catalys, 30 W blue LEDs, O_2, 12 h. [b]The quantification was performed by means of HPGC analysis using acetophenone as an internal standard.

Table S2. Control Experiment.[a]

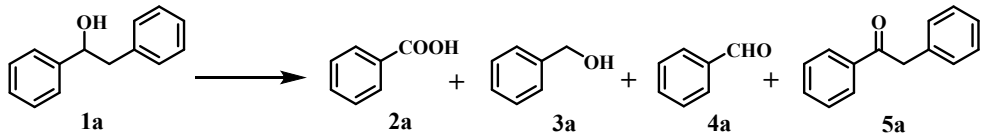


1a 2a 3a 4a 5a

Entry	Conditions	Conversion (%)	Yield (%)[b]				$S_{Cα-Cβ}$ (%)
			2a	3a	4a	5a	
1	CBB/BWO (1:2)	99	21	1	62	12	85
2	No P.C.	0	0	0	0	0	0
3	No light	0	0	0	0	0	0
4	MPA	0	0	0	0	0	0
5	CsBr	0	0	0	0	0	0
6	$BiBr_3$	60	0	0	0	55	0
7	$Bi(NO_3)_3·5H_2O$	0	0	0	0	0	0
8	$Na_2WO_4·2H_2O$	0	0	0	0	0	0

[a]Reaction conditions: 0.10 mmol **1a**, 3.0 mL CH_2Cl_2, 20 mg CBB/BWO (1:2), 30 W blue LEDs, O_2, 12 h. [b]The quantification was performed by means of HPGC analysis using acetophenone as an internal standard.

Table S3. Catalytic performances of varying amounts of CBB/BWO (1:2).[a]

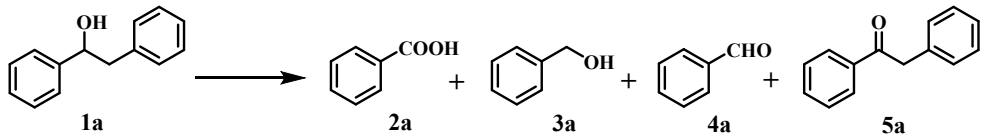


1a 2a 3a 4a 5a

Entry	CBB/BWO (mg)	Conversion (%)	Yield (%)[b]				$S_{Cα-Cβ}$ (%)
			2a	3a	4a	5a	
1	5	48	3	2	35	7	83
2	10	81	9	3	58	11	86
3	15	94	6	2	71	14	84
4	20	99	21	1	62	12	85
5	25	93	12	2	59	18	79

[a]Reaction conditions: 0.10 mmol **1a**, 3.0 mL CH_2Cl_2, CBB/BWO (1:2), 30 W blue LEDs, O_2, 12 h. [b]The quantification was performed by means of HPGC analysis using acetophenone as an internal standard.

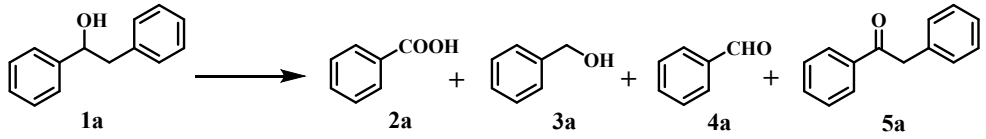
Table S4. Catalytic performances of CBB/BWO (1:2) with different solvents.[a]



Entry	Solvent	Conversion (%)	Yield (%)[b]				$S_{Cα-Cβ}$ (%)
			2a	3a	4a	5a	
1	CH_3CN	36	2	0	8	25	26
2	1,2-Dichloroethane	95	8	1	36	23	48
3	Acetone	18	0	0	0	17	0
4	CH_2Cl_2	99	21	1	62	12	85
5	CH_3CH_2OH	15	0	0	0	14	0
6	1,4-Dioxane	17	0	0	0	16	0
7	N,N-Dimethylformamide	4	0	0	0	3	0

[a]Reaction conditions: 0.10 mmol **1a**, 3.0 mL solvent, 20 mg CBB/BWO (1:2), 30 W blue LEDs, O_2, 12 h. [b]The quantification was performed by means of HPGC analysis using acetophenone as an internal standard.

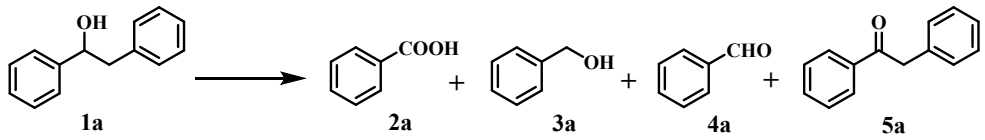
Table S5. Catalytic performances of CBB/BWO (1:2) with different reaction time.[a]



Entry	Time	Conversion (%)	Yield (%)[b]				$S_{Cα-Cβ}$ (%)
			2a	3a	4a	5a	
1	1 h	8	0	0	4	3	50
2	2 h	25	0	1	15	7	64
3	3 h	40	0	1	27	7	70
4	4 h	55	1	2	38	12	74
5	5 h	68	2	2	46	11	74
6	6 h	80	3	2	56	15	76
7	8 h	89	4	2	63	14	77
8	10 h	95	9	2	67	15	82
9	12 h	99	7	1	75	15	84

[a]Reaction conditions: 0.10 mmol **1a**, 3.0 mL CH_2Cl_2, 20 mg CBB/BWO (1:2), 30 W blue LEDs, O_2. [b]The quantification was performed by means of HPGC analysis using acetophenone as an internal standard.

Table S6. Catalytic performances of CBB/BWO (1:2) with different reaction atmosphere.[a]



Entry	Atmosphere	Conversion (%)	Yield (%)[b]				$S_{Cα-Cβ}$ (%)
			2a	3a	4a	5a	
1	O_2	99	21	1	62	12	85
2	Ar	6	0	0	2	2	31
3	air	55	0	2	41	4	78

[a]Reaction conditions: 0.10 mmol **1a**, 3.0 mL CH_2Cl_2, 20 mg CBB/BWO (1:2), 30 W blue LEDs, 12 h. [b]The quantification was performed by means of HPGC analysis using acetophenone as an internal standard.

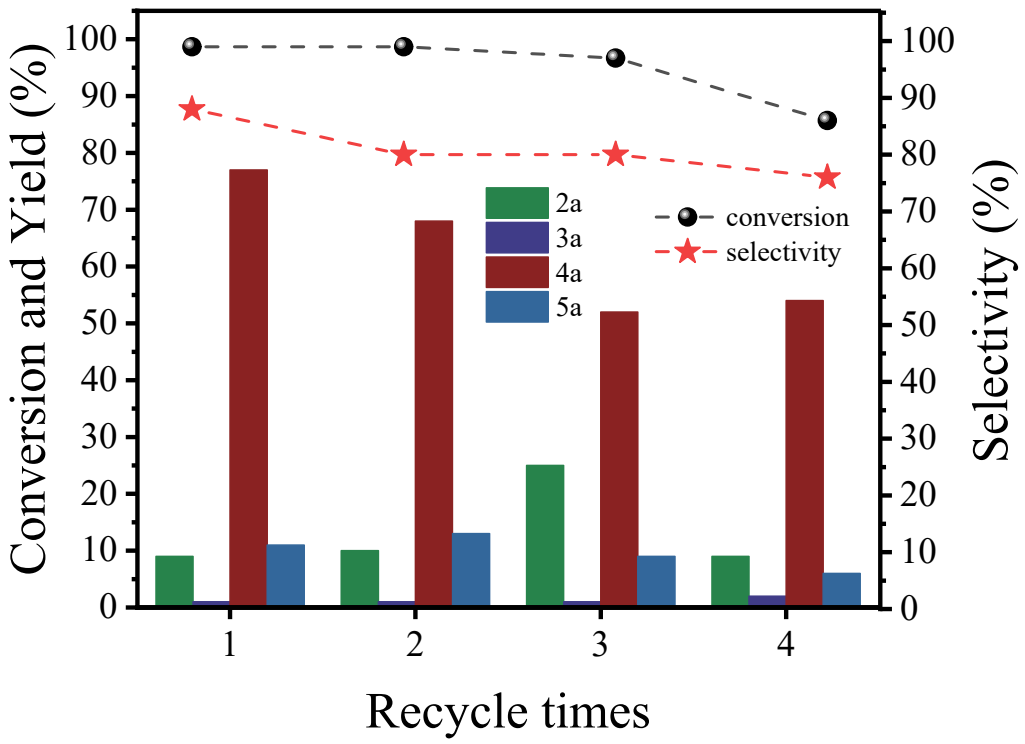


Fig. S10. Recycling experiment.

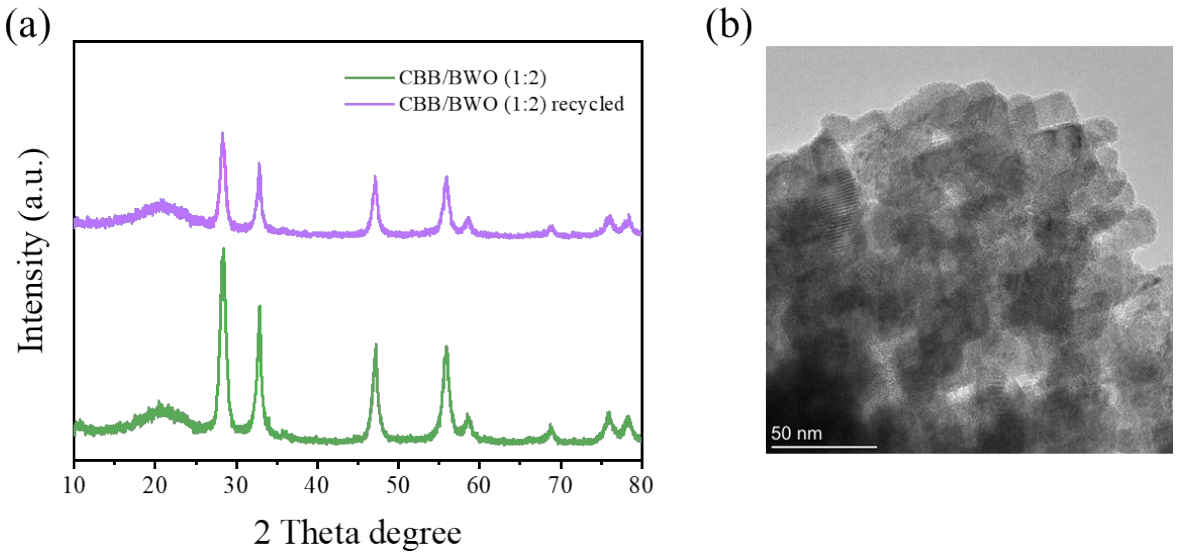


Fig. S11. (a) The XRD pattern and (b) TEM of the recycled CBB/BWO (1:2) after 4th catalytic cycle obtained via centrifugation.

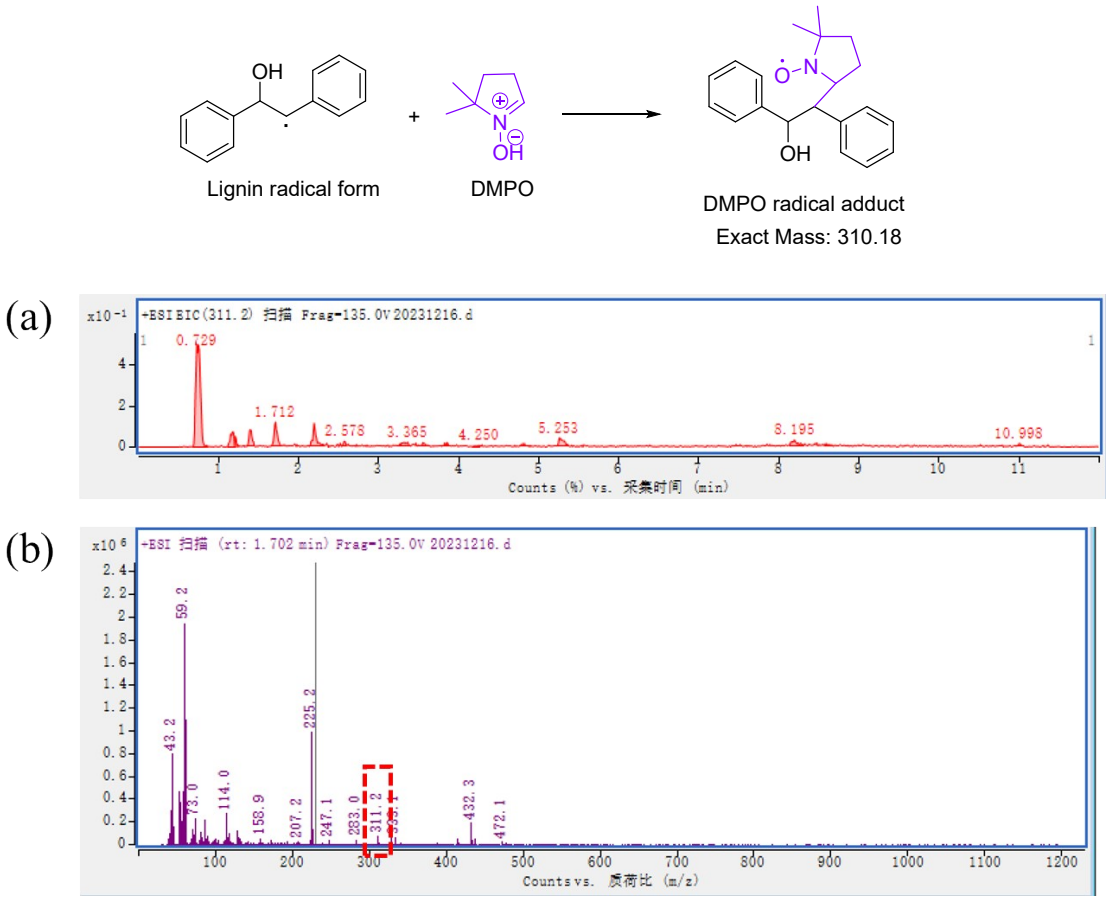


Fig. S12. HPLC-MS analysis of DMPO-captured experiments. (a) HPLC spectra of ion (Mw = 311). (b) Fragment information of ion (Mw = 311) at retention time of 1.702 min.

3. NMR Spectra

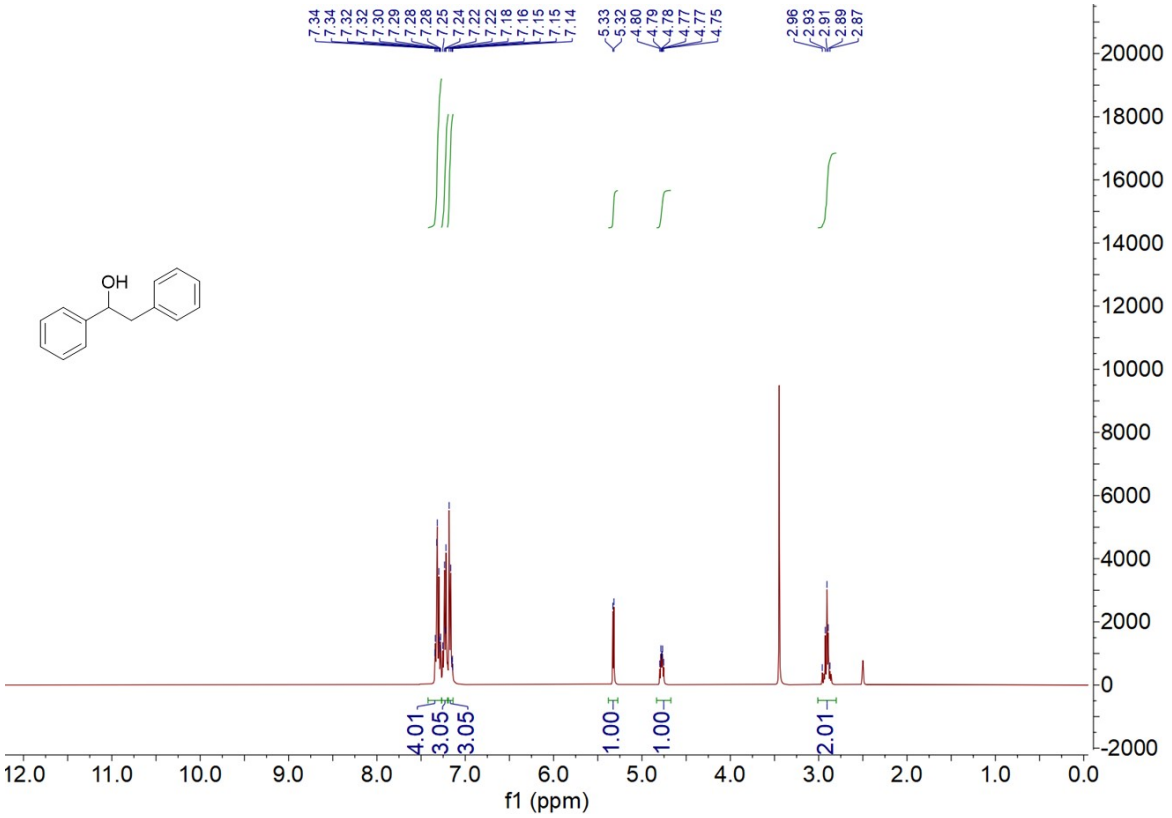


Fig. S13. [1]H NMR spectrum of 1,2-diphenylethan-1-ol (1a) (DMSO-d_6, 400 MHz).

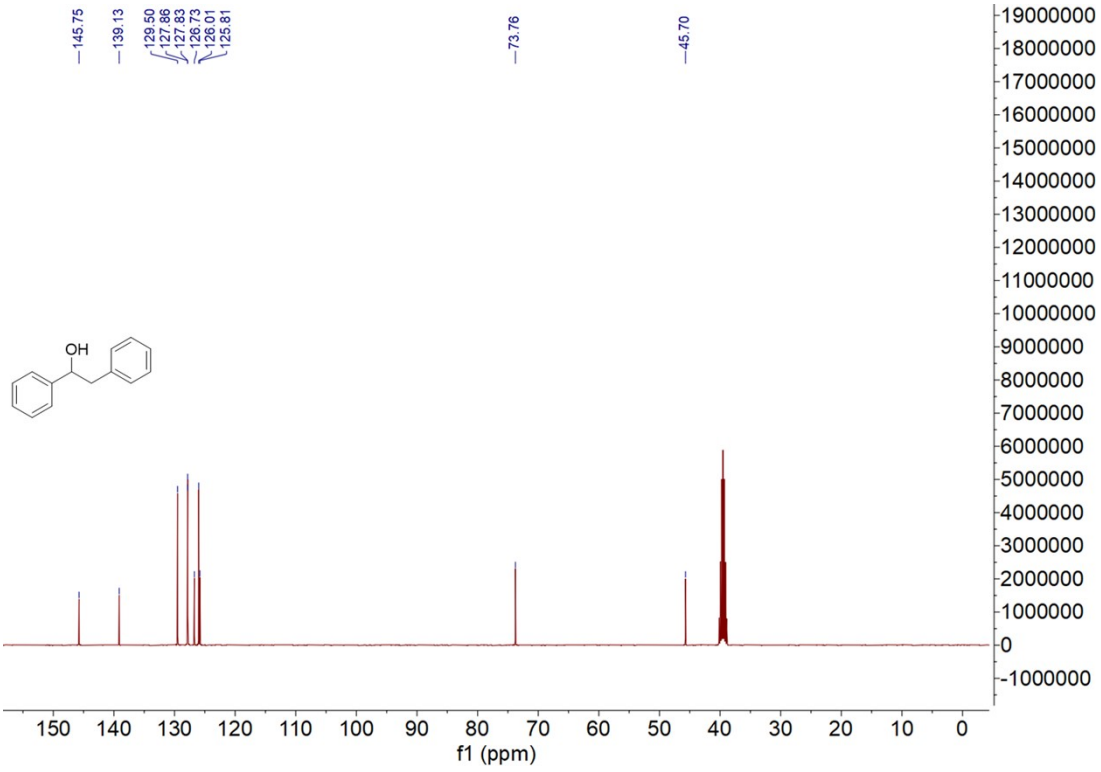


Fig. S14. [13]C NMR spectrum of 1,2-diphenylethan-1-ol (1a) (DMSO-d_6, 101 MHz).

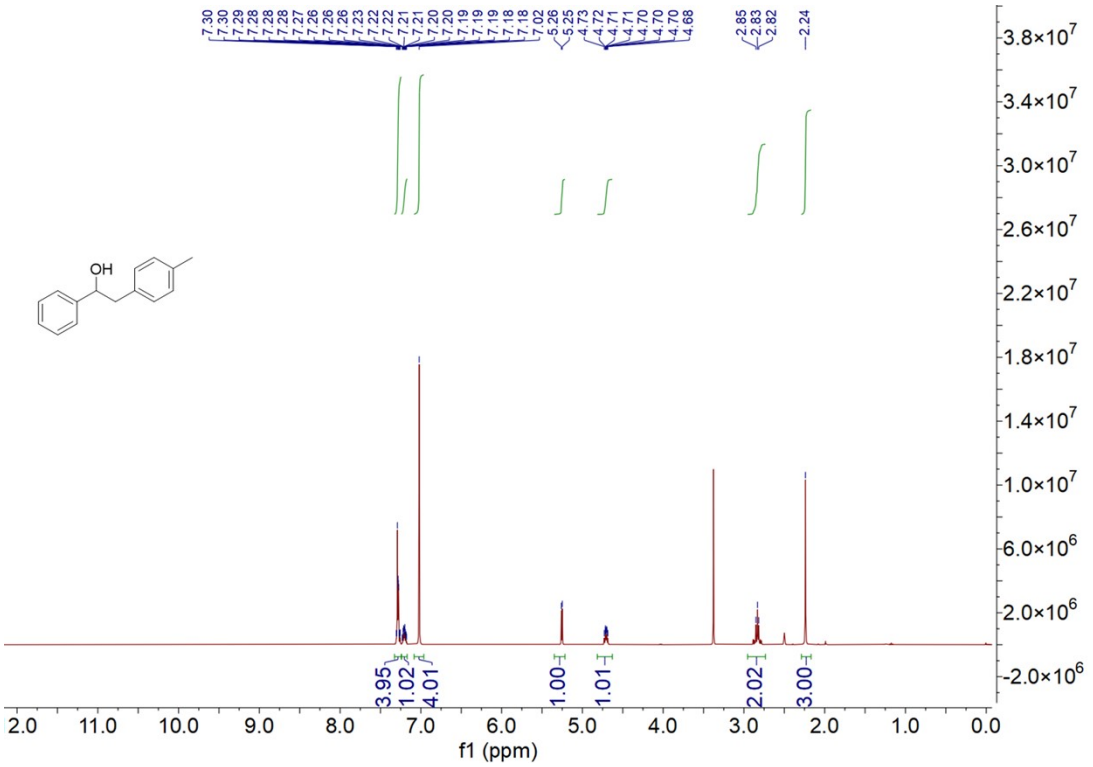


Fig. S15. ^{1}H NMR spectrum of 1-phenyl-2-(p-tolyl)ethan-1-ol (1b) (DMSO-d_6, 400 MHz).

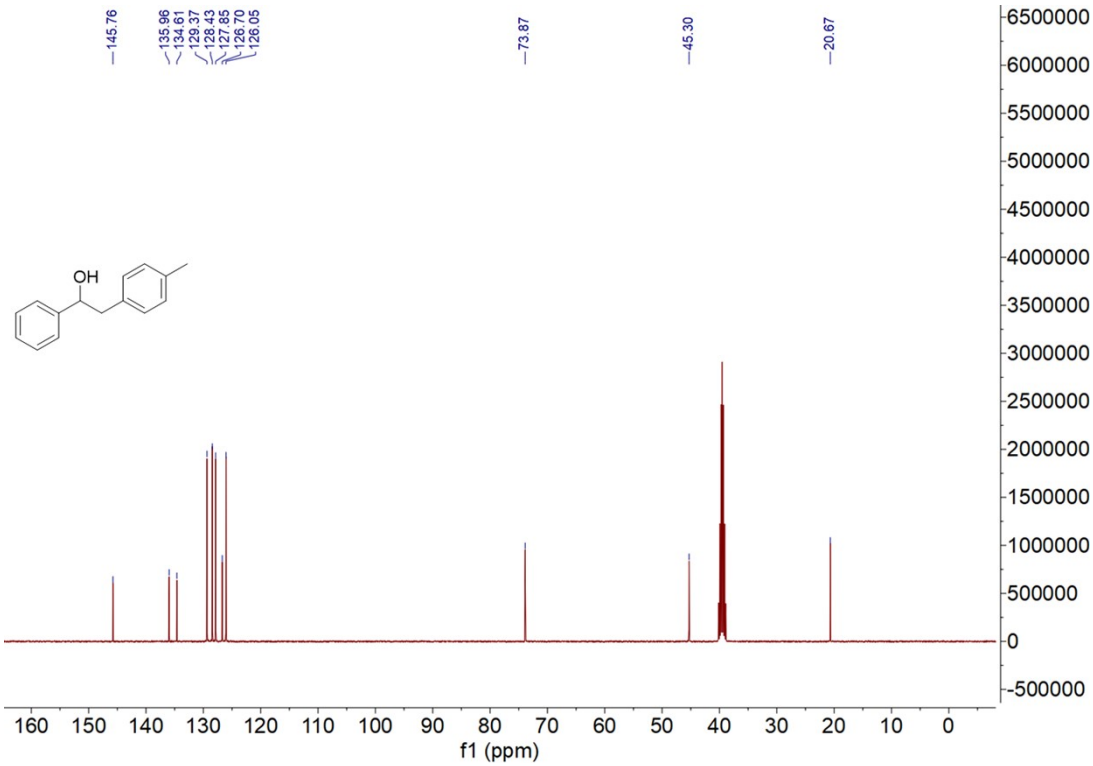


Fig. S16. ^{13}C NMR spectrum of 1-phenyl-2-(p-tolyl)ethan-1-ol (1b) (DMSO-d_6, 101 MHz).

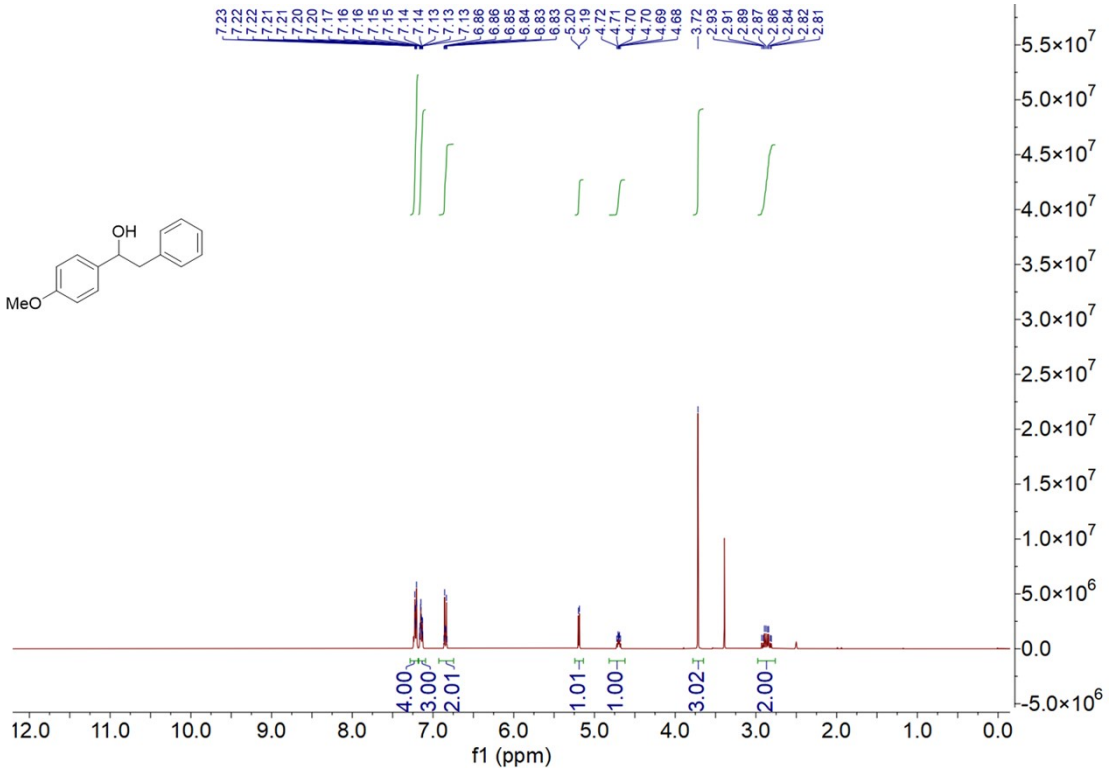


Fig. S17. ^{1}H NMR spectrum of 1-(4-methoxyphenyl)-2-phenylethan-1-ol (1c) (DMSO-d_6, 400 MHz).

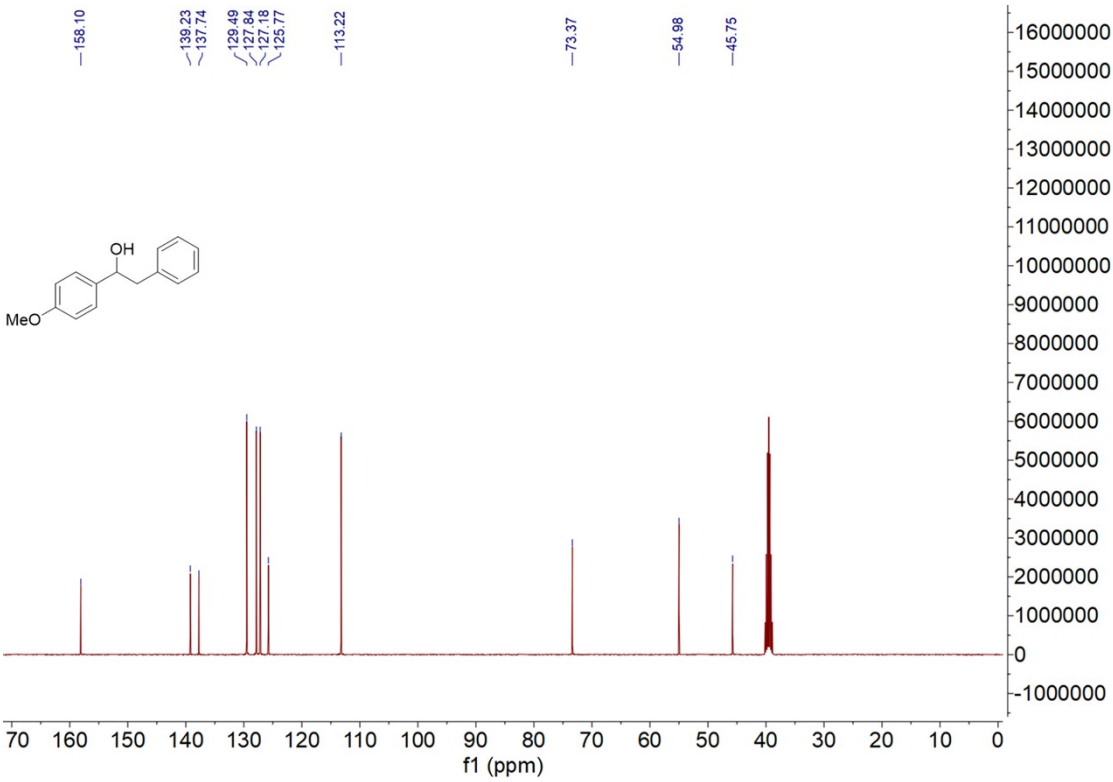


Fig. S18. ^{13}C NMR spectrum of 1-(4-methoxyphenyl)-2-phenylethan-1-ol (1c) (DMSO-d_6, 101 MHz).

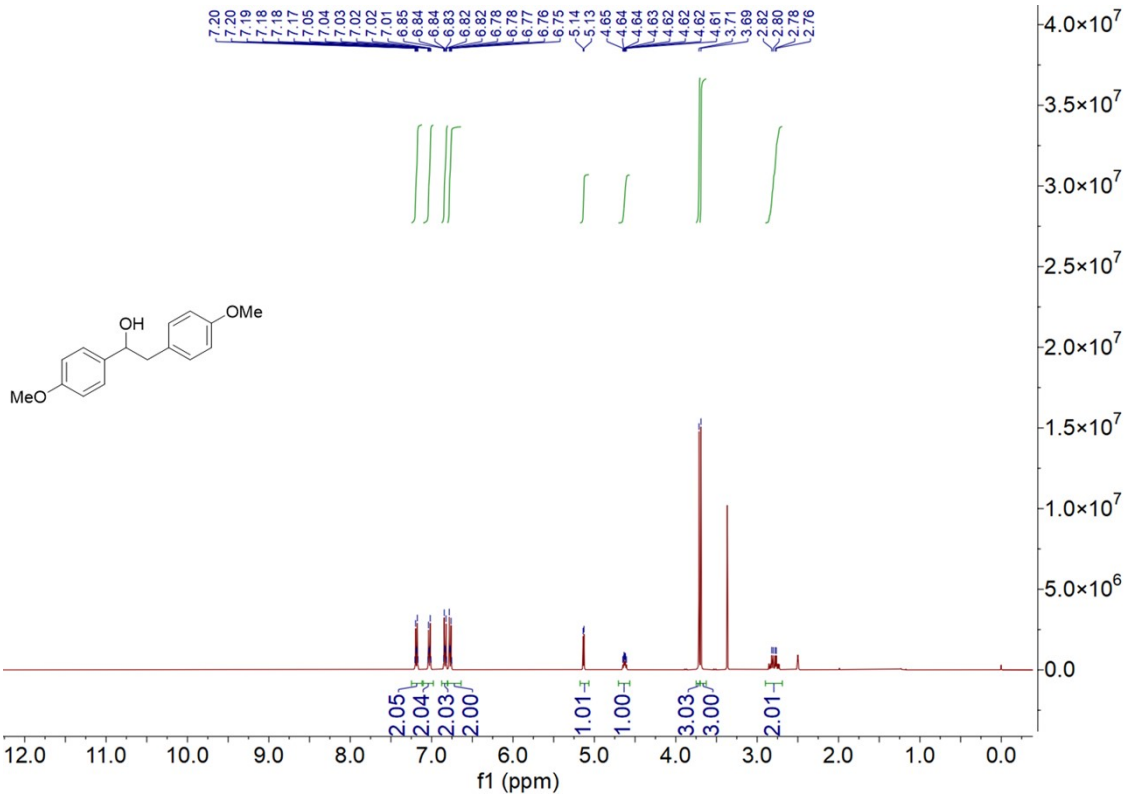


Fig. S19. ^{1}H NMR spectrum of 1,2-bis(4-methoxyphenyl)ethan-1-ol (1d) (DMSO-d_6, 400 MHz).

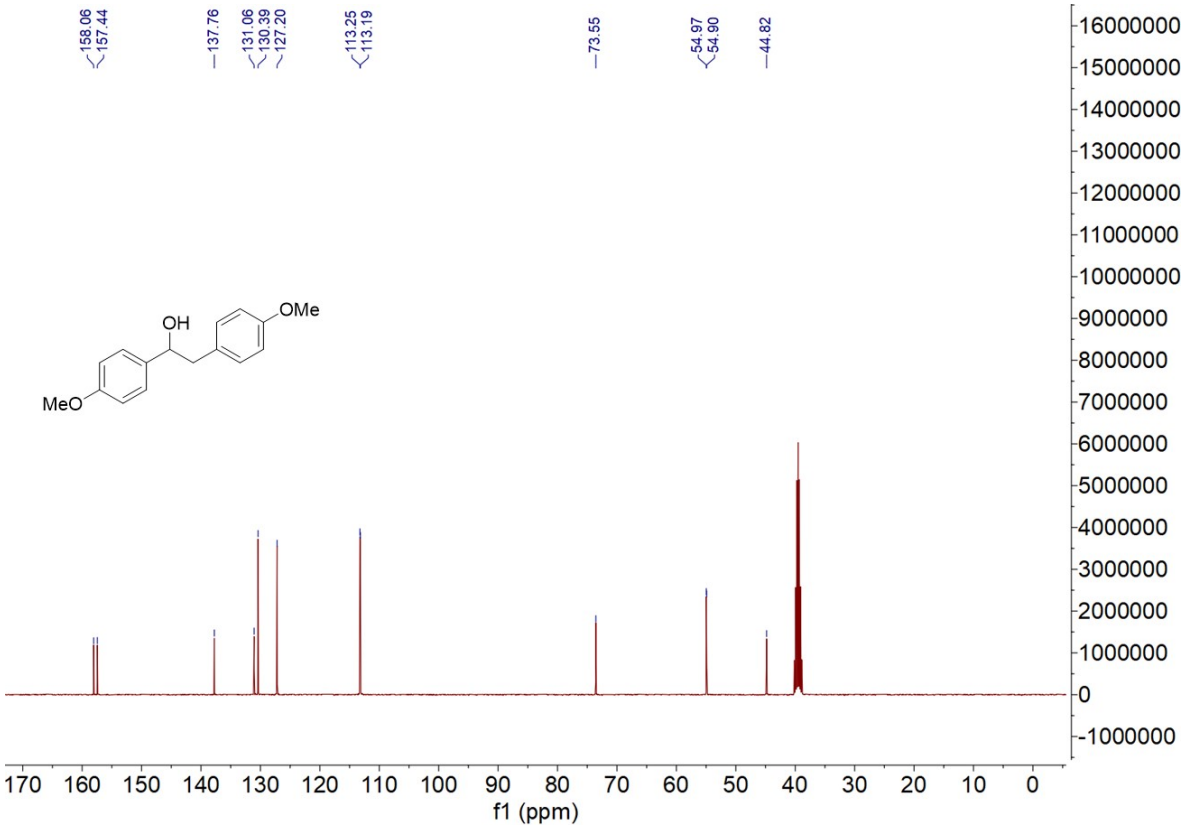


Fig. S20. ^{13}C NMR spectrum of 1,2-bis(4-methoxyphenyl)ethan-1-ol (1d) (DMSO-d_6, 101 MHz).

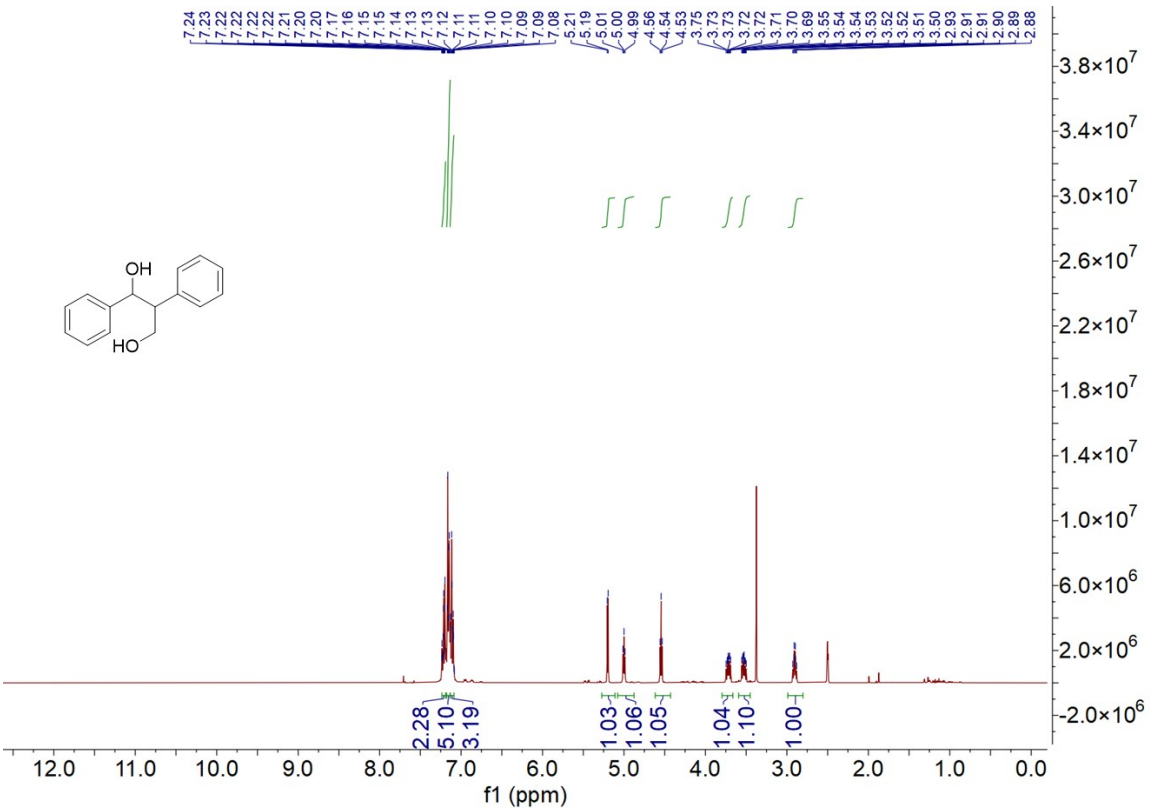


Fig. S21. ^{1}H NMR spectrum of 1,2-diphenylpropane-1,3-diol (1e) (DMSO-d_6, 400 MHz).

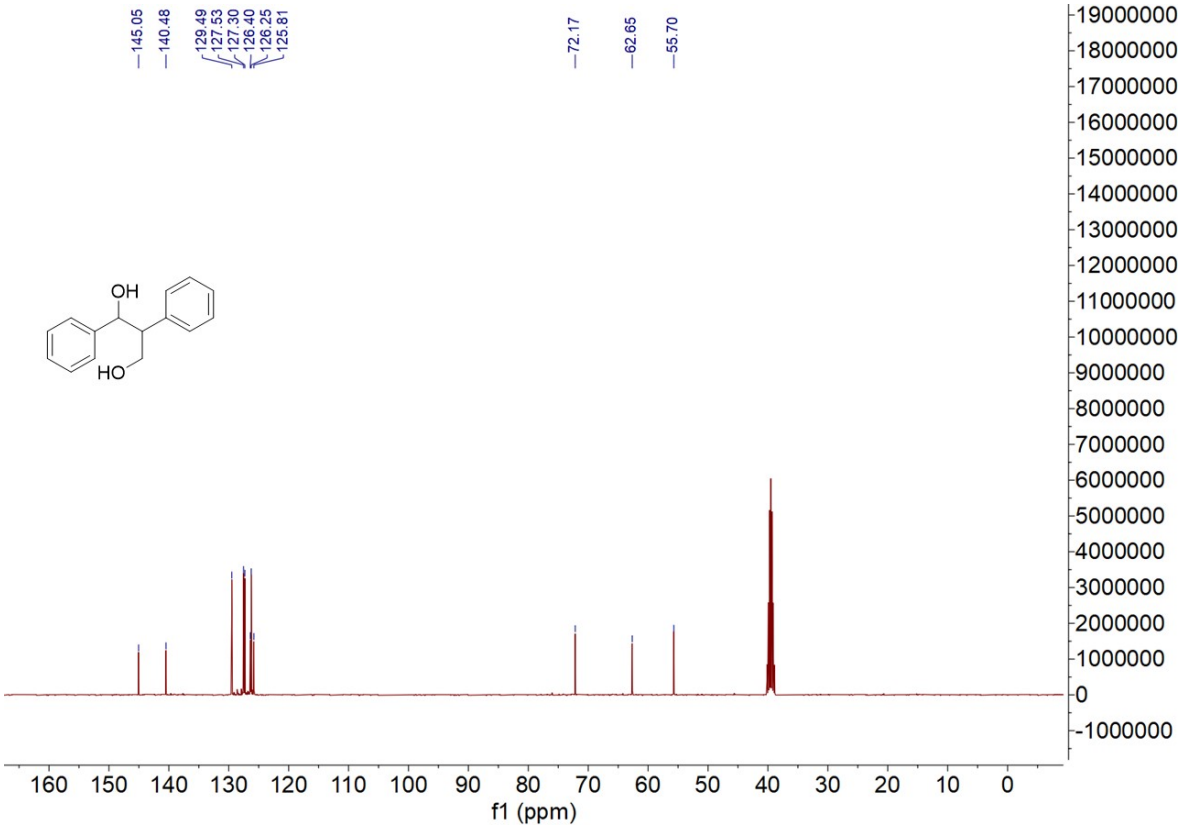


Fig. S22. ^{13}C NMR spectrum of 1,2-diphenylpropane-1,3-diol (1e) (DMSO-d_6, 101 MHz).

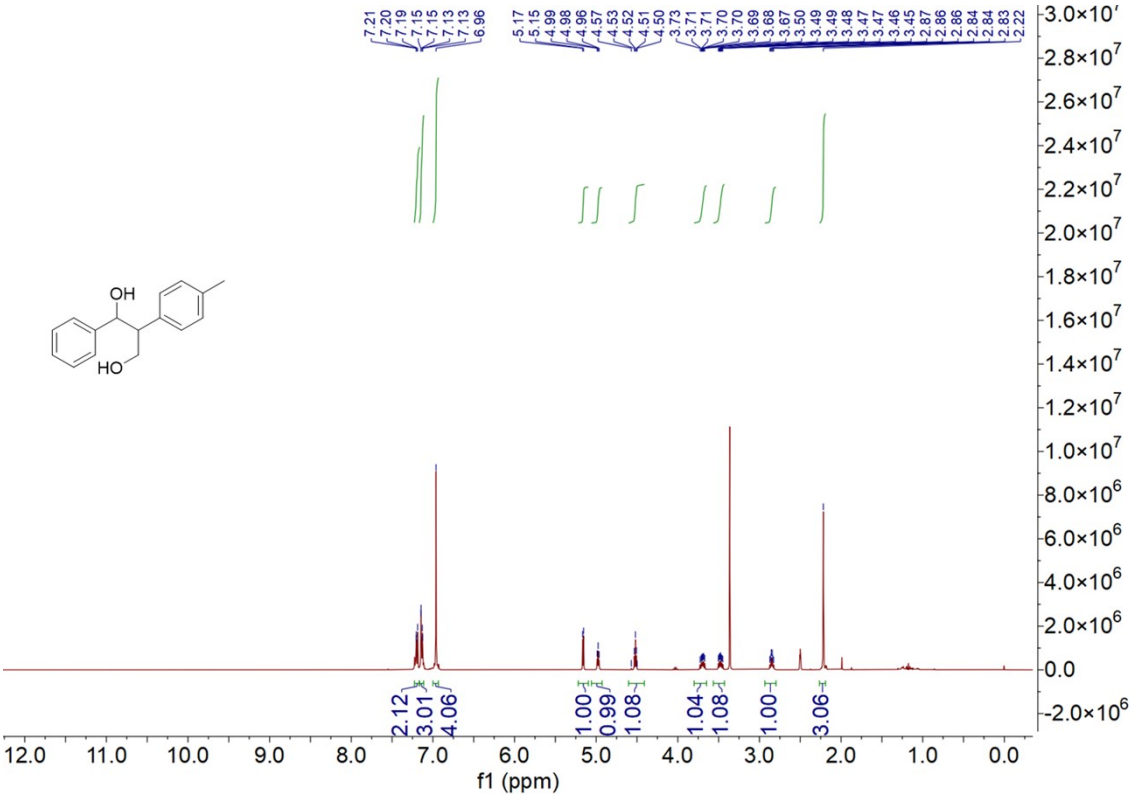


Fig. S23. [1]H NMR spectrum of 1-phenyl-2-(p-tolyl)propane-1,3-diol (1f) (DMSO-d_6, 400 MHz).

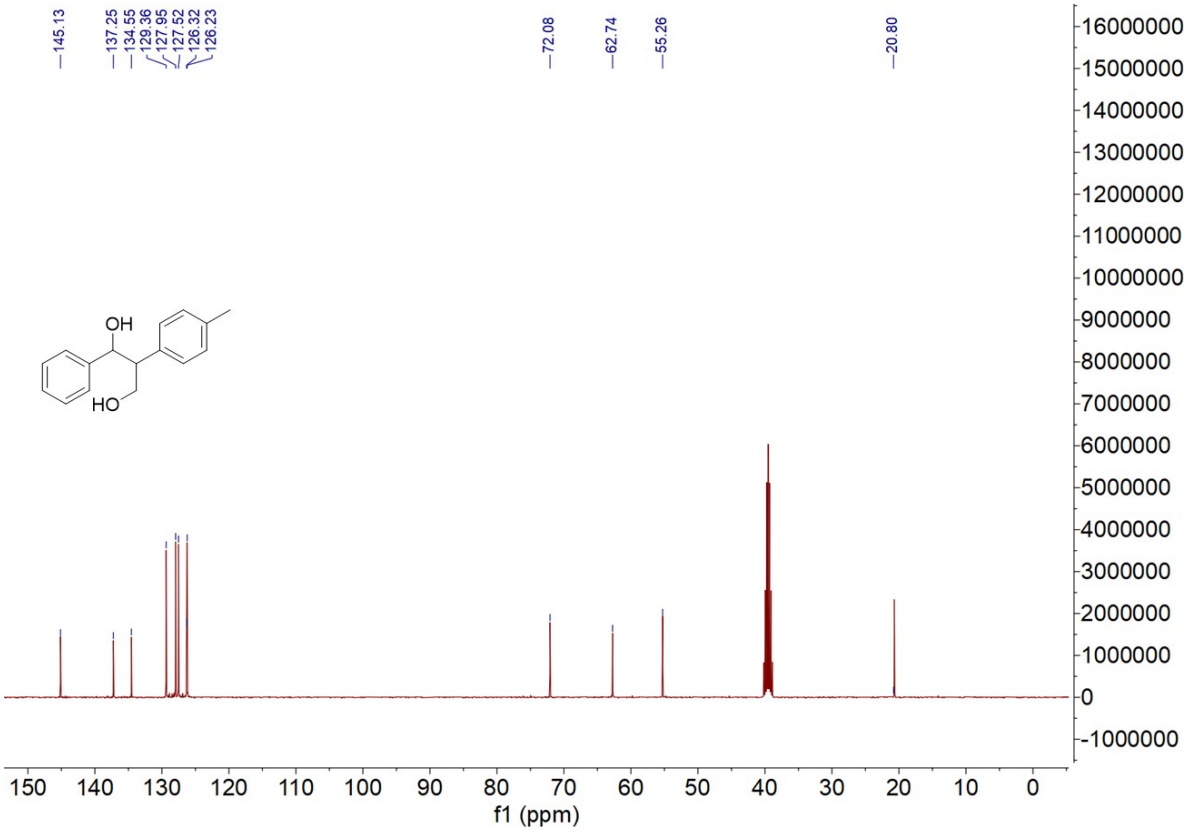


Fig. S24. [13]C NMR spectrum of 1-phenyl-2-(p-tolyl)propane-1,3-diol (1f) (DMSO-d_6, 101 MHz).

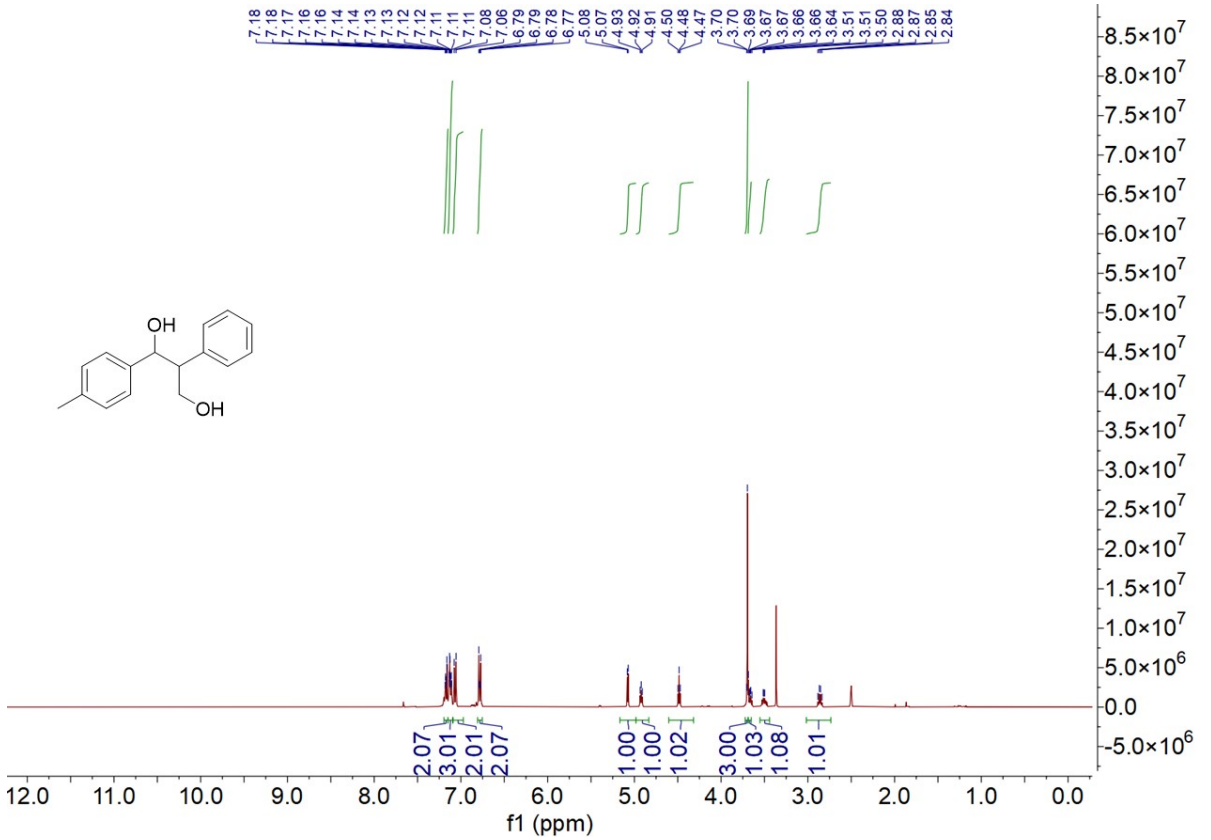


Fig. S25. ^{1}H NMR spectrum of 2-phenyl-1-(p-tolyl)propane-1,3-diol (1g) (DMSO-d_6, 400 MHz).

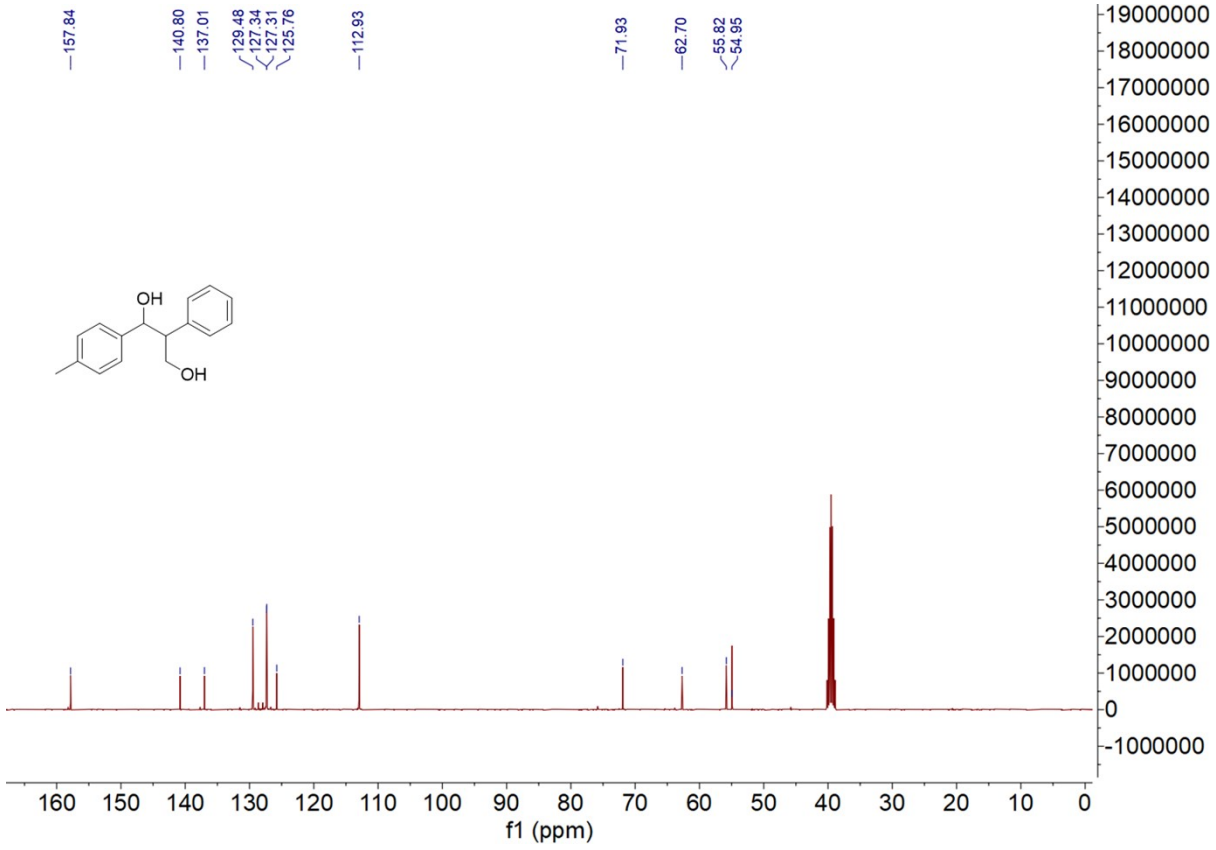


Fig. S26. ^{13}C NMR spectrum of 2-phenyl-1-(p-tolyl)propane-1,3-diol (1g) (DMSO-d_6, 101 MHz).

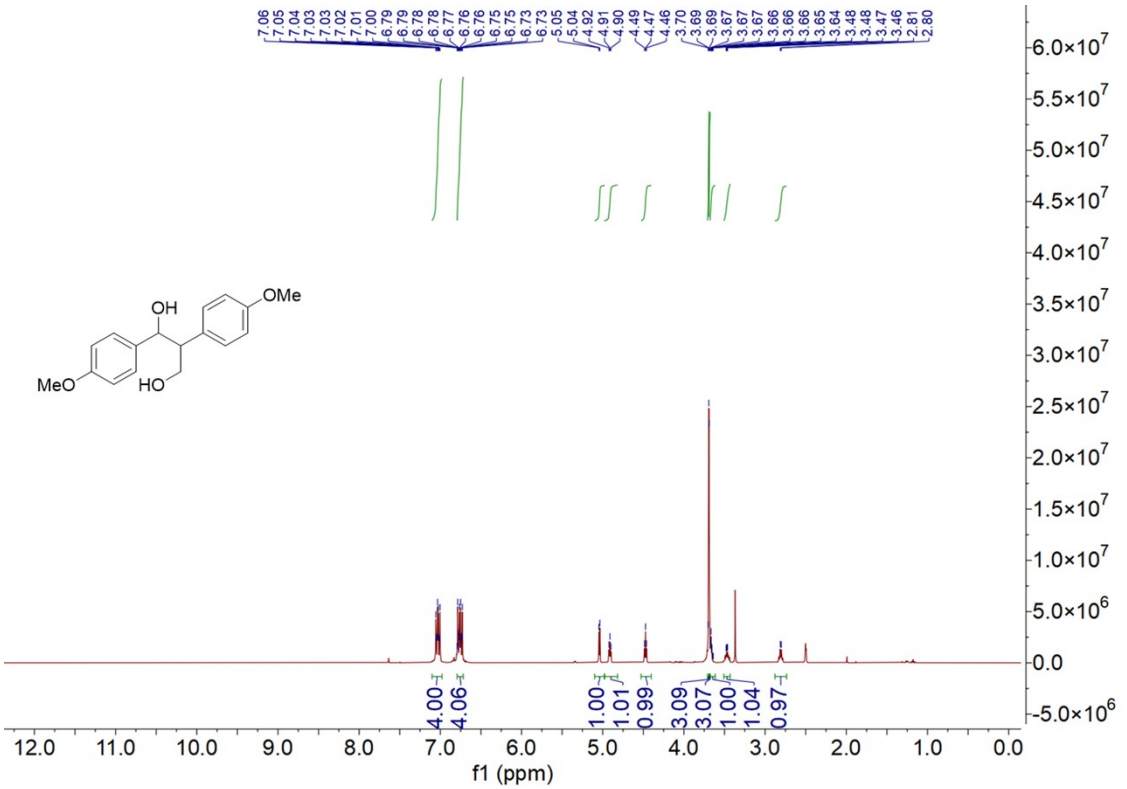


Fig. S27. ^{1}H NMR spectrum of 1,2-bis(4-methoxyphenyl)propane-1,3-diol (1h) (DMSO-d_6, 400 MHz).

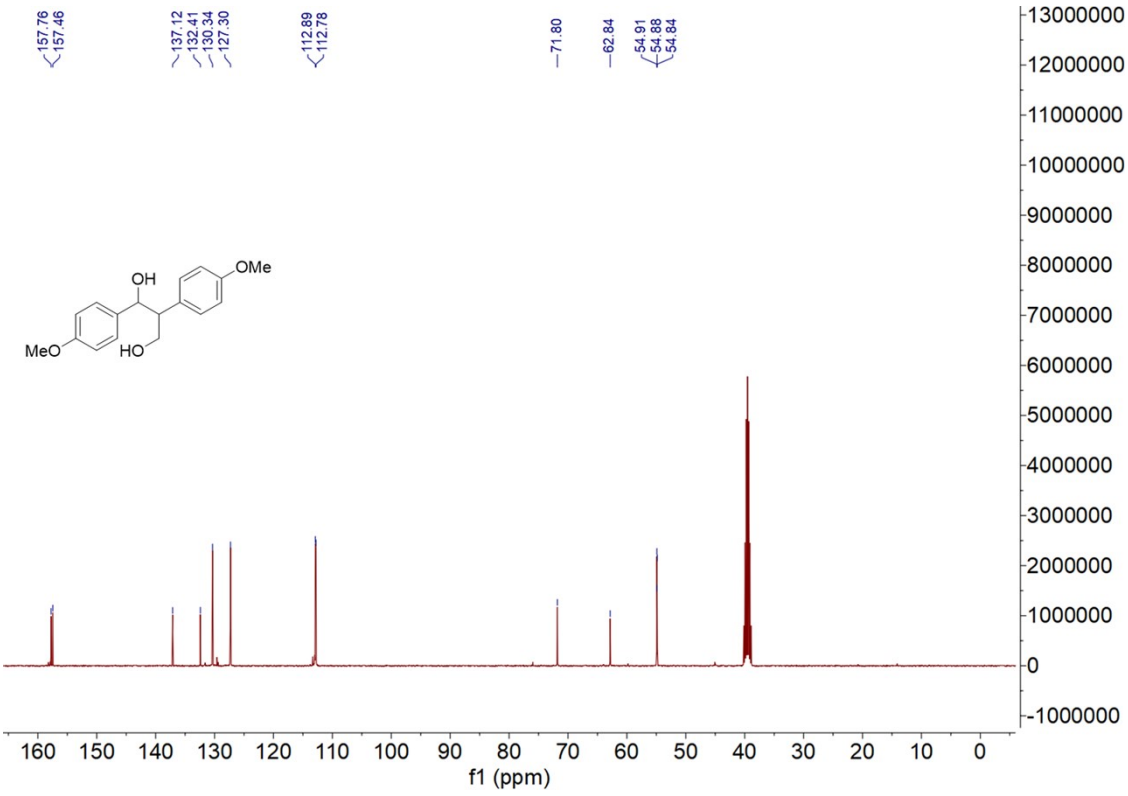


Fig. S28. ^{13}C NMR spectrum of 1,2-bis(4-methoxyphenyl)propane-1,3-diol (1h) (DMSO-d_6, 101 MHz).

4. References

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Wu, X., Lin, J., Zhang, H., Xie, S., Zhang, Q., Sels, B.F., Wang, Y., 2021. Z-scheme nanocomposite with high redox ability for efficient cleavage of lignin C-C bonds under simulated solar light. Green Chem. 23(24), 10071-10078. https://doi.org/10.1039/d1gc03455c.