Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Highly Selective Hydrogenolysis of Lignin *β*-O-4 Models by Coupled Polyoxometalates/CdS Photocatalytic System

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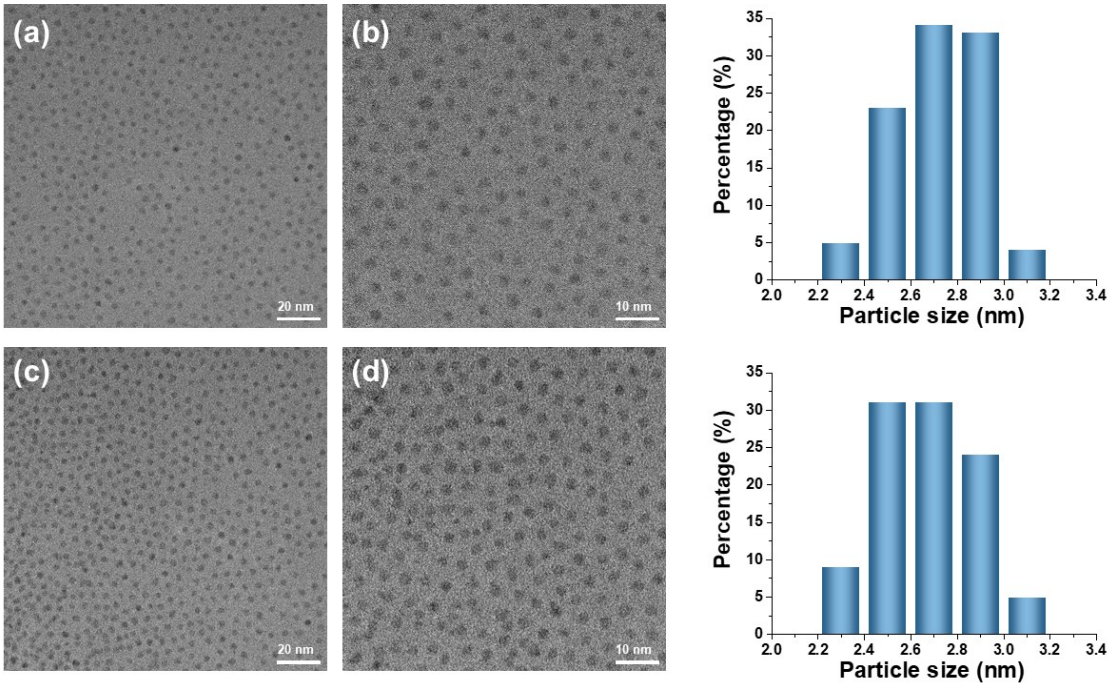


Fig. S1 TEM images (scale bars: (a) 20 nm and (b) 10 nm, respectively) of CdS-OA QDs, the average length was calculated to be 2.73 nm; (scale bars: (c) 20 nm and (d) 10 nm, respectively) of CdS-MPA QDs, the average length was calculated to be 2.66 nm. It was noticed that ligand exchange does almost not affect the size of CdS QDs

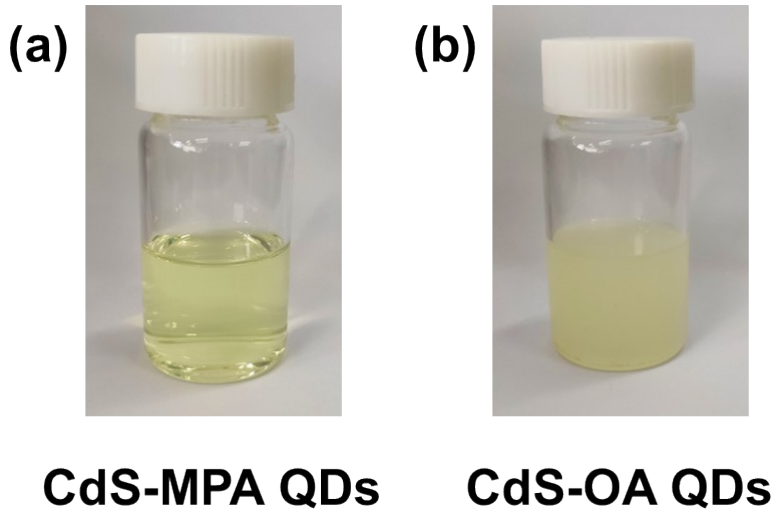


Fig. S2 Digital photos of the reaction solution using different capping agent QDs: (a) CdS-MPA QDs and (b) CdS-OA QDs

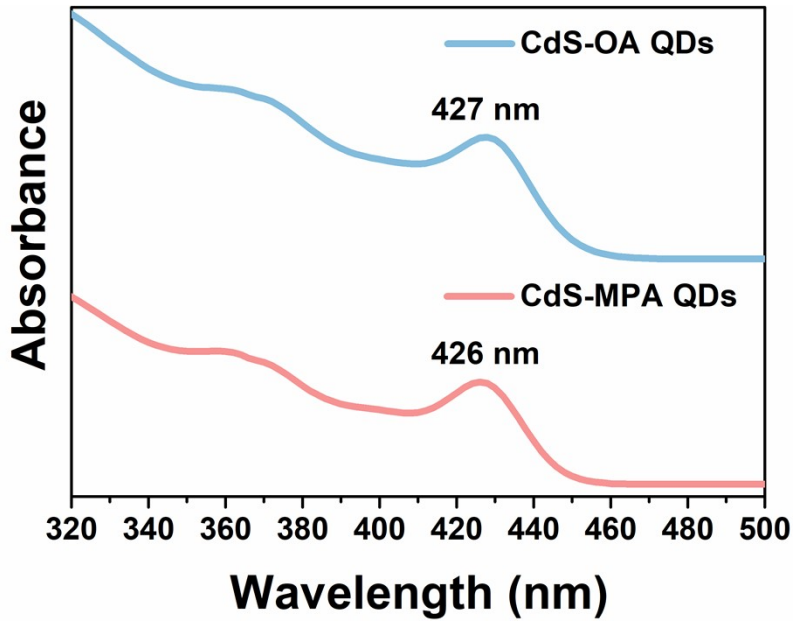


Fig. S3 UV-vis spectra of CdS QDs with different capping agents. Note: the spectrum of OA-CdS was measured in hexane, while the spectra of MPA-CdS samples were measured in water

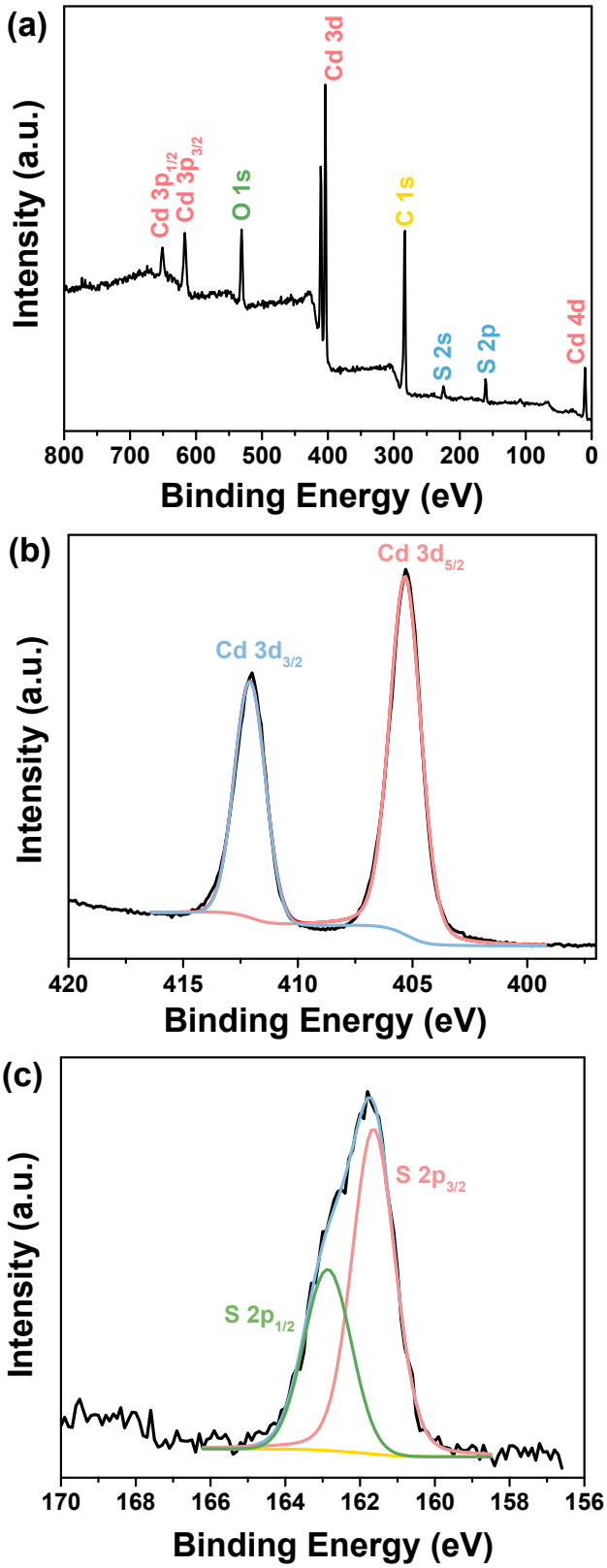


Fig. S4 (a) The survey XPS spectra of CdS-MPA QDs, and corresponding high resolution XPS signals of (b) Cd 3d, (c) S 2p

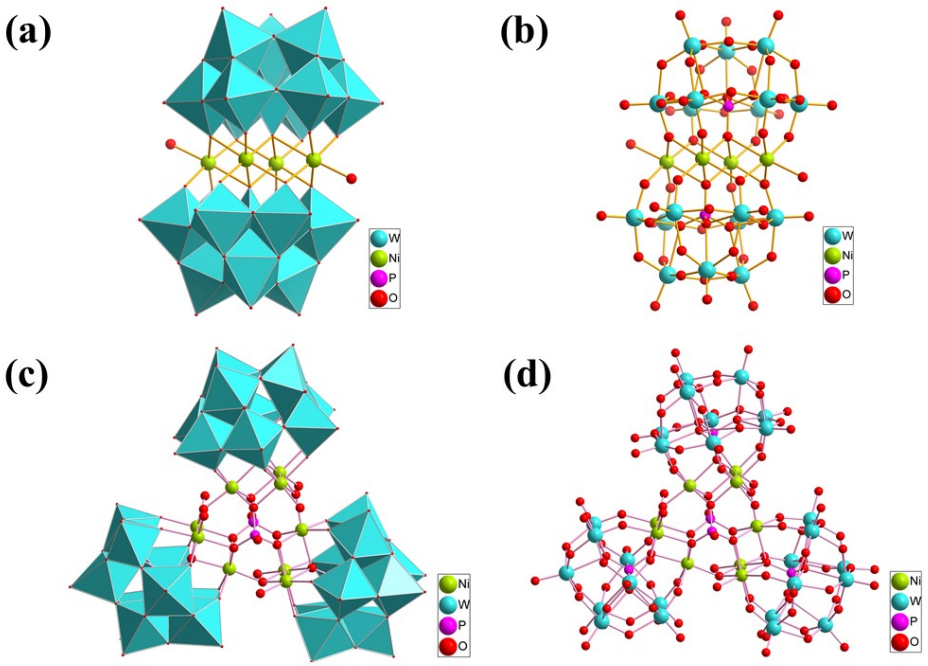


Fig. S5 Polyhedral and ball-and-stick representations of two polyoxometalates: (a-b) $\mathbf{Ni_4P_2}$ and (c-d) $\mathbf{Ni_9P_3}$

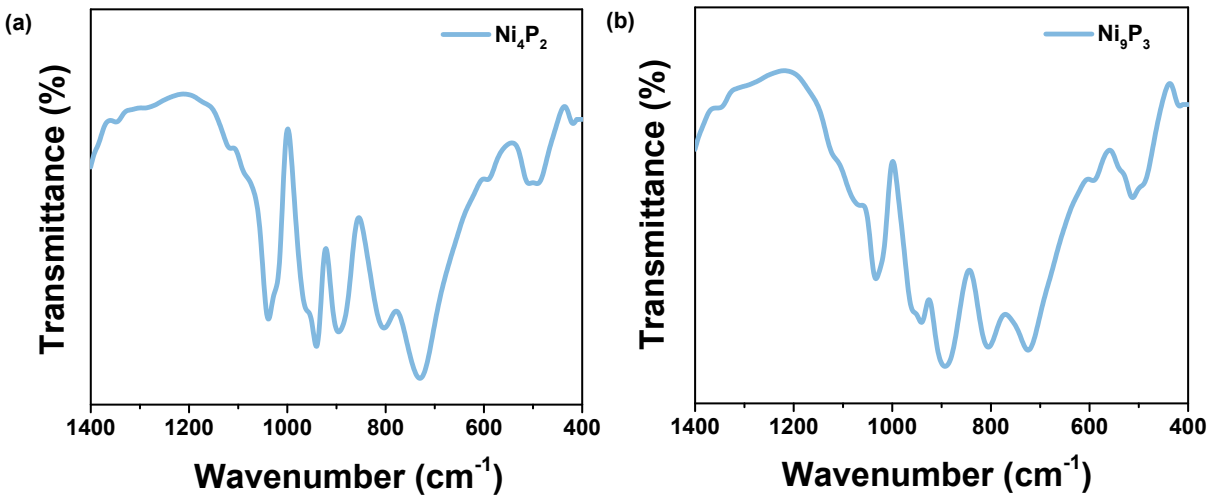


Fig. S6 FT-IR spectra of (a) $\mathbf{Ni_4P_2}$, (b) $\mathbf{Ni_9P_3}$, ~ 2 wt % in KBr

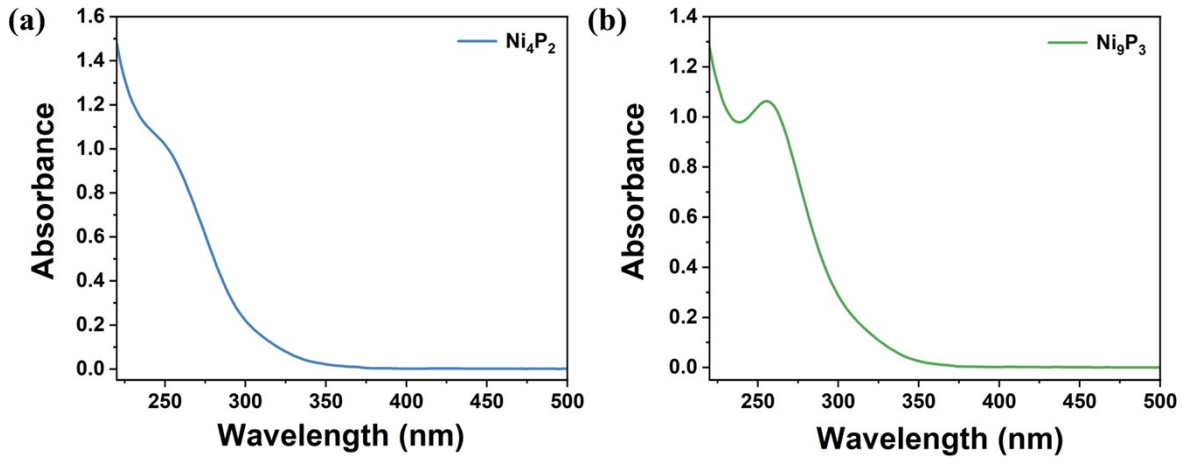


Fig. S7 UV-vis spectra of $\mathbf{Ni_9P_3}$ and $\mathbf{Ni_4P_2}$ catalyst at the same concentration (0.0016 mM)

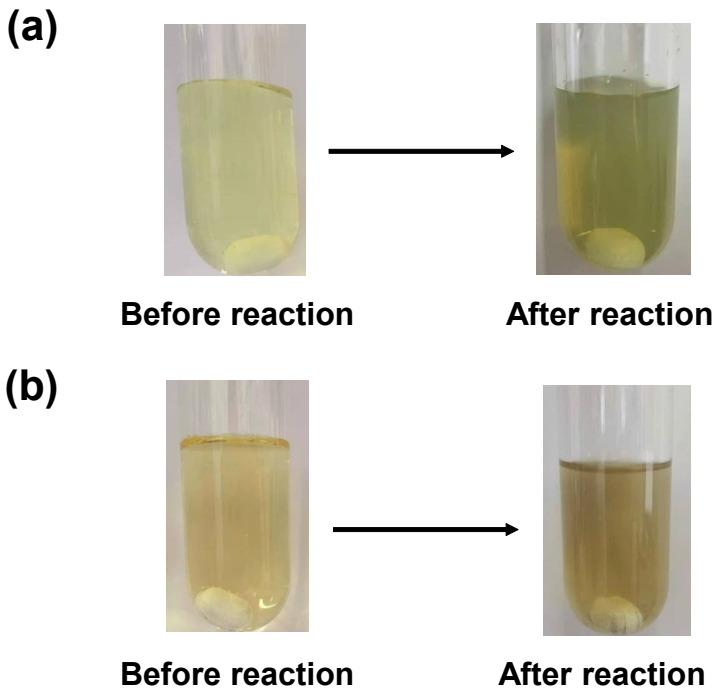


Fig. S8 Digital photos of the reaction solution before and after photocatalysis using (a) 0.1 mM of $\mathbf{Ni_9P_3}$ catalyst and (b) 0.9 mM of $NiCl_2$. Reaction conditions: 10 mM of PP-one (**1a**), 1 μM of CdS-MPA QDs, 10 mL of iso-propanol/H_2O (3/2), blue LED (450 nm), 8h, Ar/CH_4 (4/1) atmosphere

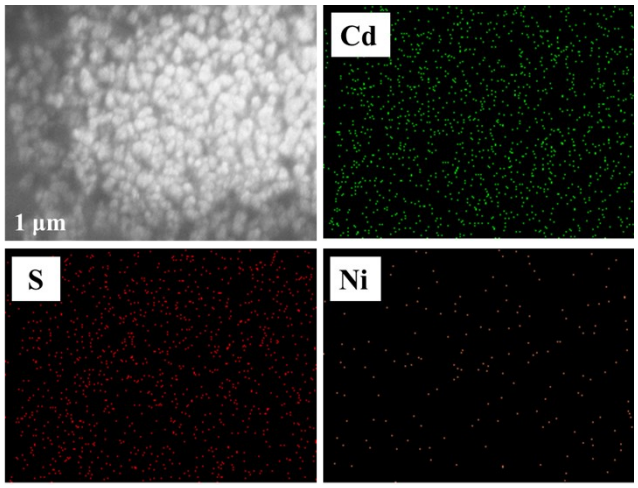


Fig. S9 SEM and corresponding elemental mapping images of isolated CdS-MPA QDs from $NiCl_2$-catalyzed post-reaction solution. Reaction conditions: 10 mM of PP-one (**1a**), 1 µM of CdS-MPA QDs, 10 mL of iso-propanol/H_2O (3/2), blue LED (450 nm), 8h, Ar/CH_4 (4/1) atmosphere

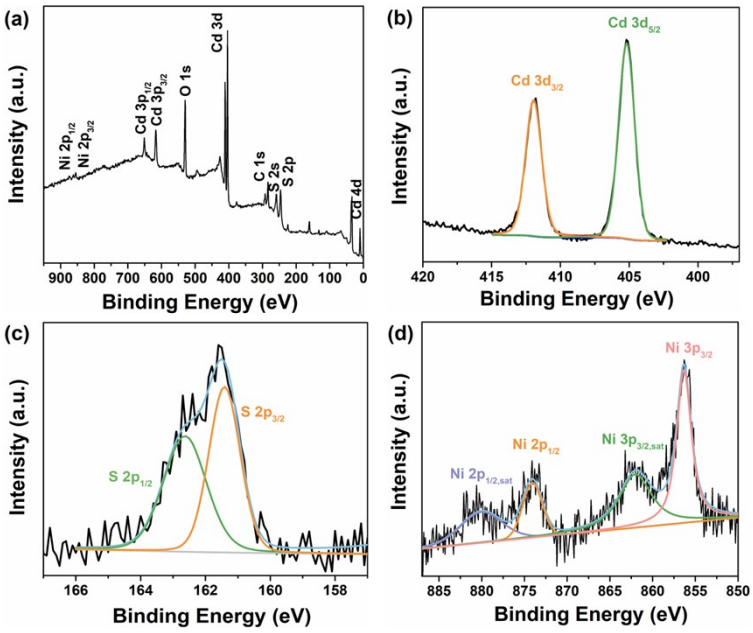


Fig. S10 High resolution XPS spectra of (a) Full XPS spectrum, (b) Cd 3d, (c) S 2p, and (d) Ni 2p signals of isolated CdS-MPA QDs from $NiCl_2$-catalyzed post-reaction solution after photocatalysis for 8 h

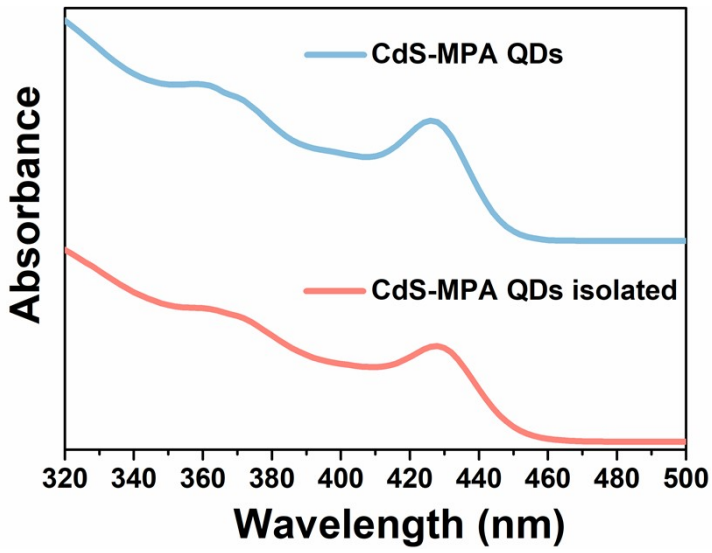


Fig. S11 UV-vis spectra of CdS-MPA QDs before and after photocatalysis

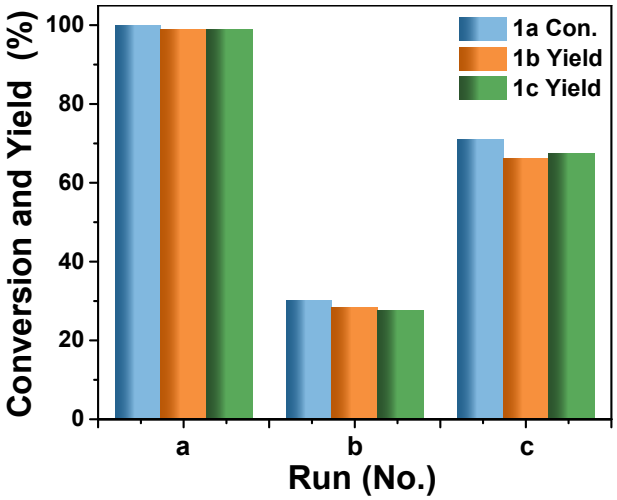


Fig. S12 Photocatalytic hydrogenolysis of PP-one. (a) the first run using fresh CdS-MPA QDs and **Ni_9P_3** catalyst, (b) the second run using isolated CdS-MPA QDs and no fresh **Ni_9P_3** catalyst was added in this cycle, (c) the third run using isolated CdS-MPA QDs and fresh **Ni_9P_3** catalyst. Standard reaction conditions: 10 mM of PP-one (**1a**), 1 μM of CdS-MPA QDs, 0.1 mM of **Ni_9P_3** catalyst, 10mL of iso-propanol/H_2O (3/2), blue LED (450 nm), 8h, Ar/CH_4 (4/1) atmosphere

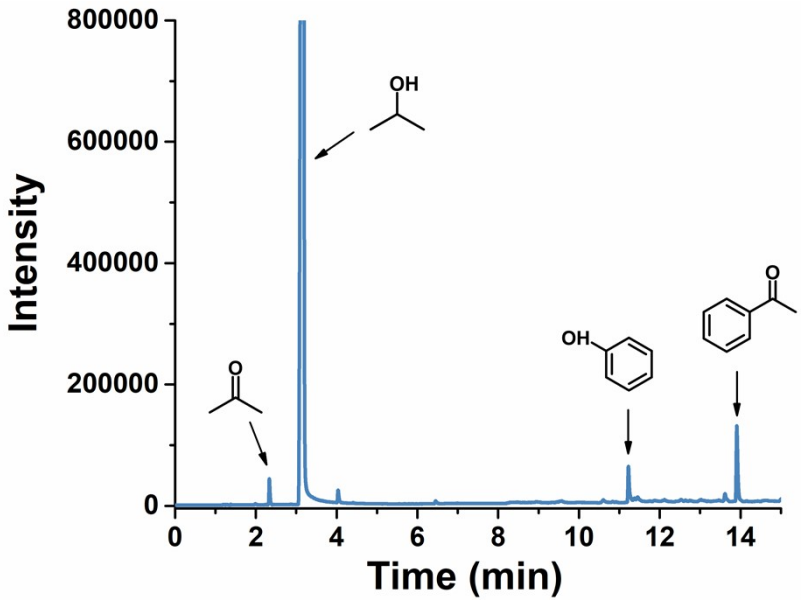


Fig. S13 Gas chromatography (GC) from the photocatalytic hydrogenolysis of PP-one. Reaction conditions: 10 mM of PP-one (1a), 1 μM of CdS-MPA QDs, 0.1 mM of **Ni_9P_3**, 10mL of iso-propanol/H_2O (3/2), blue LED (450 nm), 8h, Ar/CH_4 (4/1) atmosphere

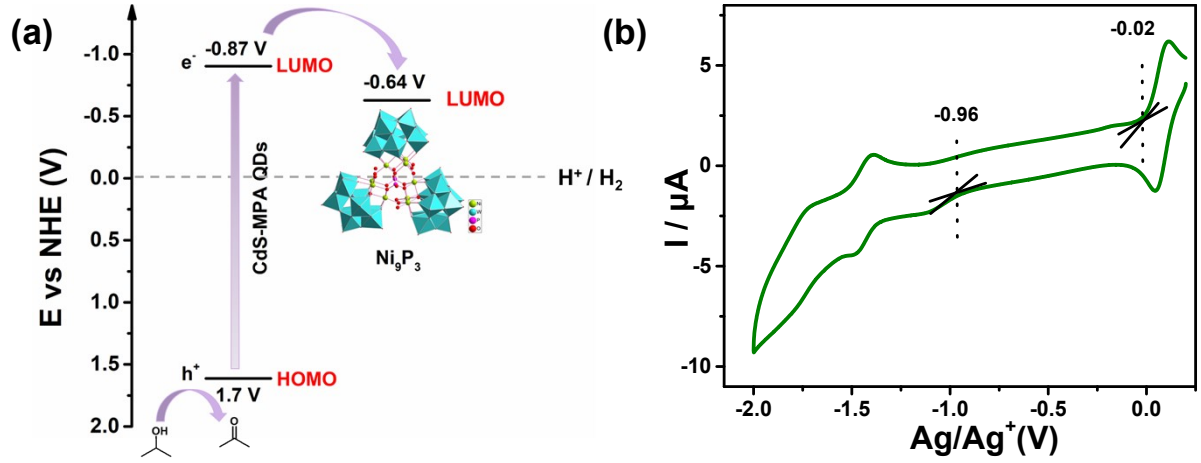
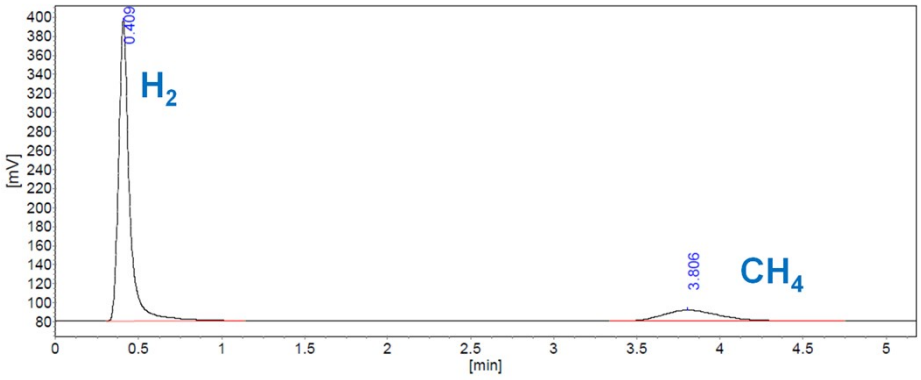


Fig. S14 (a) Schematic energy level diagram for photocatalytic hydrogenolysis of PP-one; (b) Cyclic voltammogram of **Ni_9P_3** (0.1 mM) in 0.1 M $TBAPF_6$ and 0.01M $AgNO_3$ acetonitrile solution using glassy carbon working electrode, Ag/Ag^+ reference electrode, and Pt silk counter electrode; Scan rate: 100 mV/s. The measured potential was expressed by converting to normal hydrogen electrode (NHE)



Analysis result table

Entry	Retention time (min)	Peak height (uV)	Peak area (uV*s)	Area percentage %
1	0.409	315679	1438574	83.0850
2	3.806	11702	292874	16.9150

Fig. S15 Gas chromatography (GC) trace of hydrogen gas produced from the photocatalytic hydrogenolysis of PP-one. Reaction conditions: 10 mM of PP-one (**1a**), 1 μM of CdS-MPA QDs, 0.1 mM of $\mathbf{Ni_9P_3}$, 10mL of iso-propanol/H_2O (3/2), blue LED (450 nm), 8h, Ar/CH_4 (4/1) atmosphere

Table S1 Semiconductor Photocatalysts for Lignin Conversion

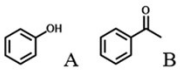
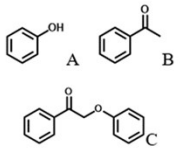
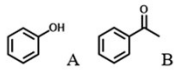
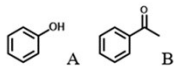
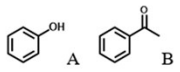
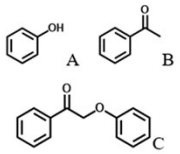
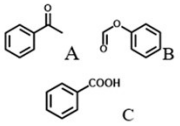
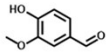
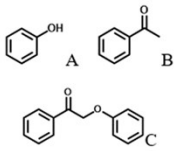
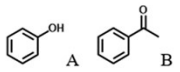
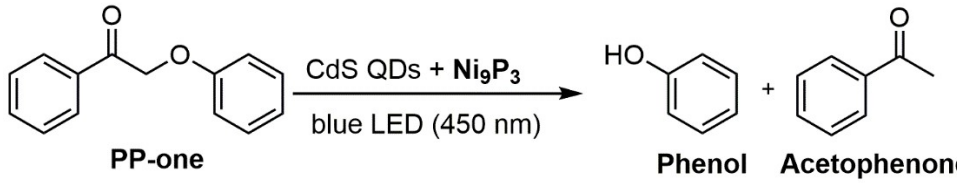
Entry	Catalyst	Heterogeneous/Homogeneous	Substrate concentration	Reaction time	Product	Conv. [%]	Yield [%]	Ref.
1	CdS-MPA QDs (1 μM) + **Ni_9P_3** (0.1 mM)	Homogeneous	10 mM	8 h		99	A: 99 B: 99	This work
2	$ZnIn_2S_4$ (5 mg)	Heterogeneous	100 mM	4 h		99	A: 83 B: 90 C: 6	4
3	Ni/CdS (20 mg)	Heterogeneous	5 mM	8 h		100	A: 99 B: 99	9
4	CdS (10mg)	Heterogeneous	20 mM	3 h		99	A: 93 B: 91	37
5	Pb/$ZnIn_2S_4$ (10 mg), TiO_2 (5 mg)	Heterogeneous	133 mM	33 h		94	A: 94 B: 76	50
6	$Zn_4In_2S_7$ (10 mg)	Heterogeneous	20 mM	4 h		99	A: 82 B: 86 C: 10	51
7	Mesoporous g-C_3N_4 (10 mg)	Heterogeneous	50 mM	10 h		96	A: 51 B: 30 C: 21	54
8	In_2S_3 (20 mg)	Heterogeneous	0.16 mM	8.384 min		N.A.	N.A.	55
9	$Zn_4In_2S_7$ (10mg)	Heterogeneous	20 mM	2 h		93	A: 70 B: 51 C: 17	56
10	$Cd_xZn_{1-x}S$ (10 mg)	Heterogeneous	20 mM	2 h		93	A: 85 B: 36	57
11	Ligand-controlled CdS QDs (15 mg)	Heterogeneous	Native lignin	8 h	Aromatic monomers	27	N.A.	58

Table S2 Screening of Reaction Conditions for Photocatalytic Hydrogenolysis of PP-one[a]



Entry	Conv. (%)	Product Yield (%)		H_2 (μmol)	Acetone (μmol)
		Phenol	Acetophenone		
1	99.3	99.3	98.8	142.3	205.3
2[b]	0	0	0	0	78.4
3[c]	48.5	48.4	43.1	17.9	76.7
4[d]	43.5	42.8	21.8	405.2	276.3

[a] Reaction conditions: 10mM of 2-phenoxy-1-phenylethan-1-one, 1 μM of CdS-MPA QDs, 0.1 mM of $\mathbf{Ni_9P_3}$, 10 mL of isopropanol/H_2O (3/2), blue LED (450 nm), Ar/CH_4 (4/1) atmosphere, 8 h. [b] with 10mM $K_2S_2O_8$. [c] with 10mM $Na_2C_2O_4$. [d] with 2 wt % Pt

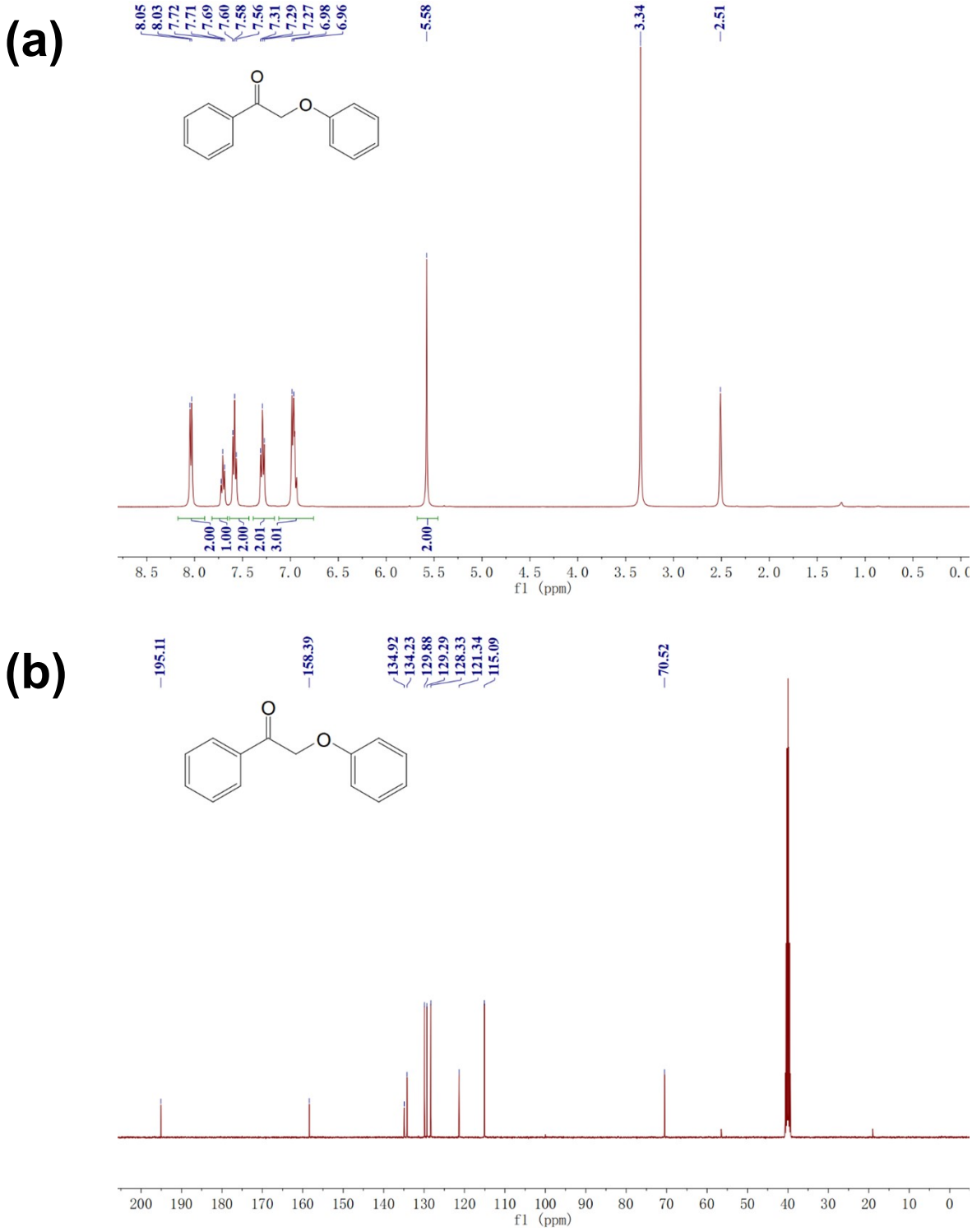


Fig. S16 (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra of compound 2-phenoxy-1-phenylethan-1-one (**1a**)

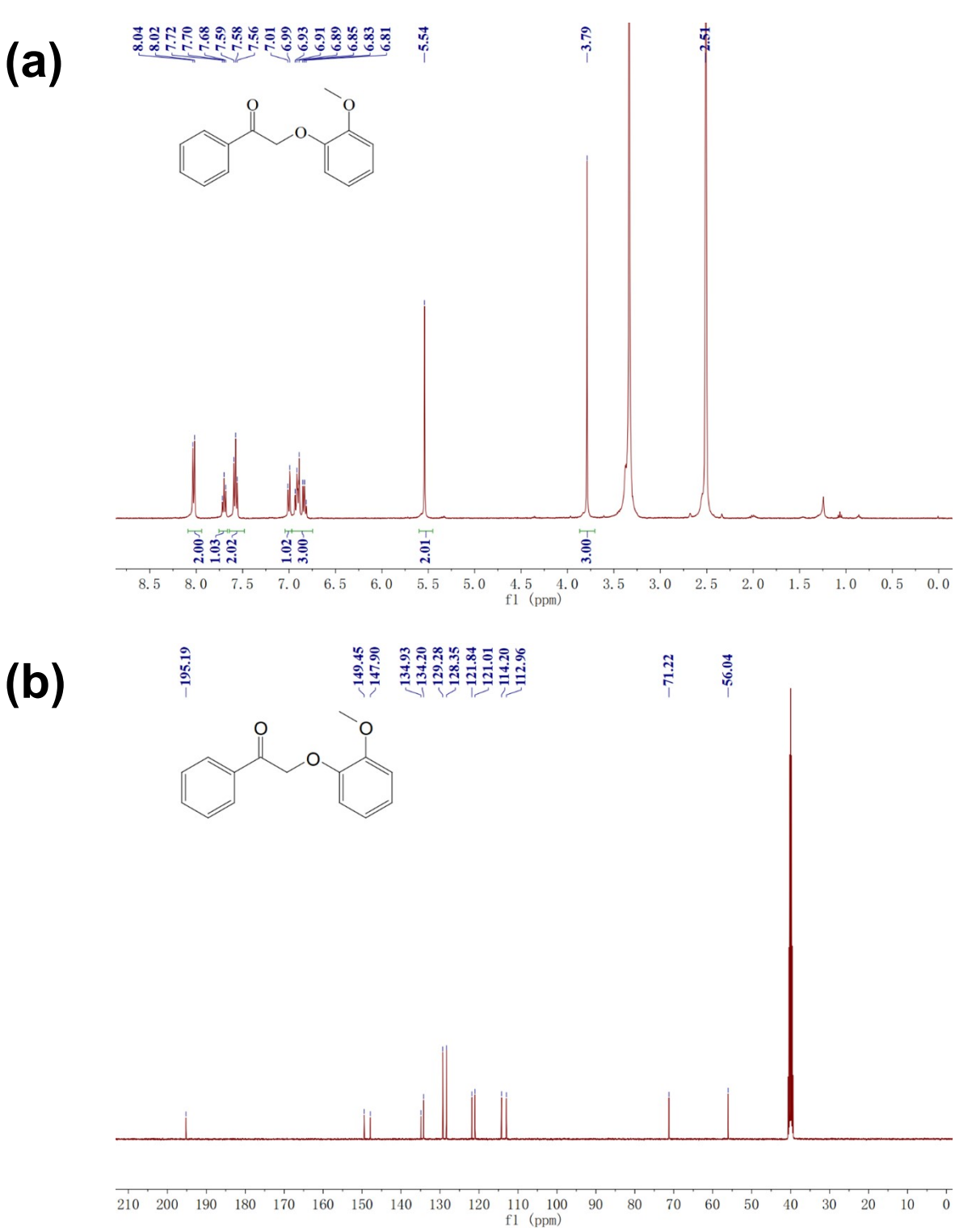


Fig. S17 (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra of compound 2-(2-methoxyphenoxy)-1-phenylethan-1-on (**2a**)

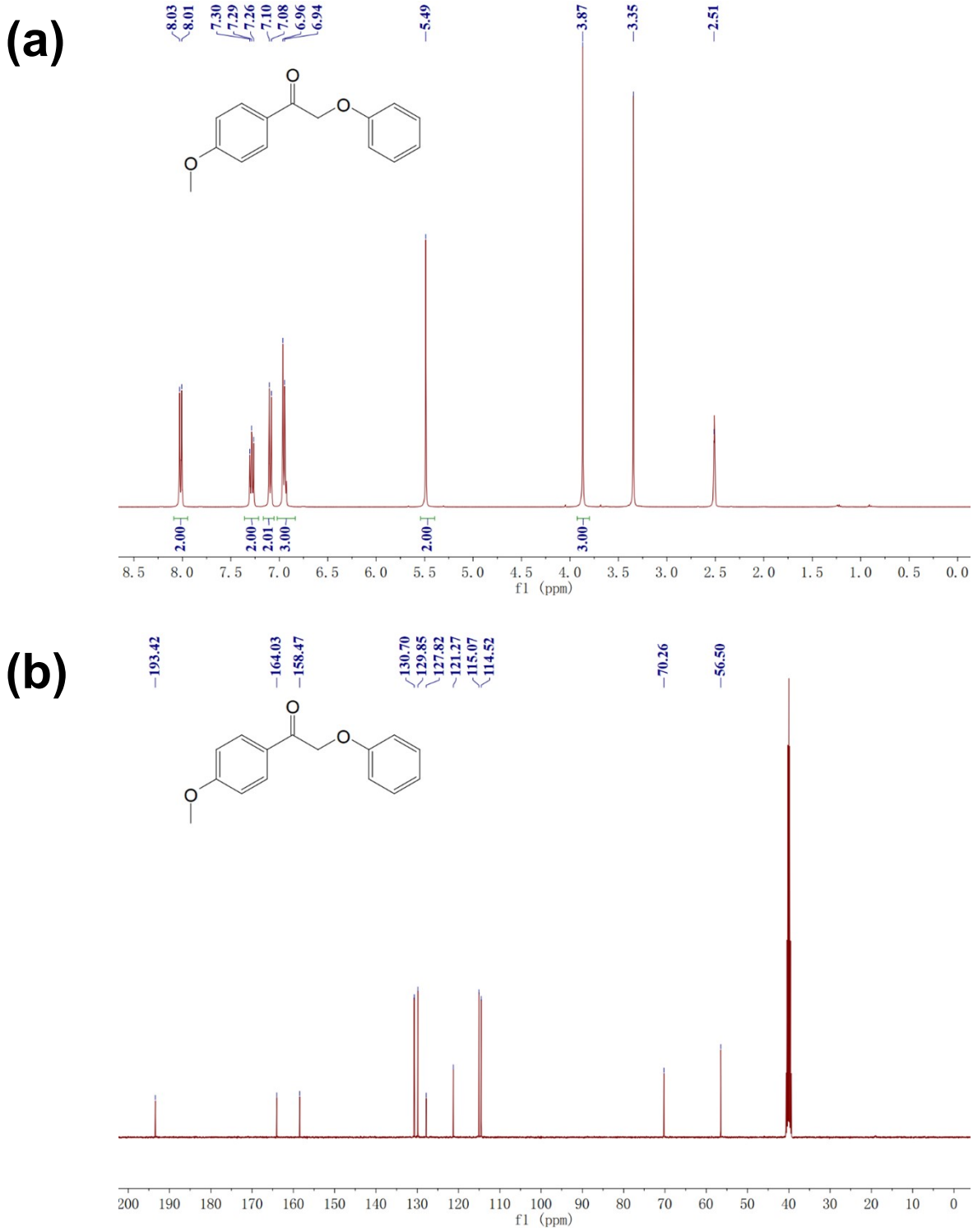


Fig. S18 (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra of compound 1-(4-methoxyphenyl)-2-phenoxyethan-1-one (**3a**)

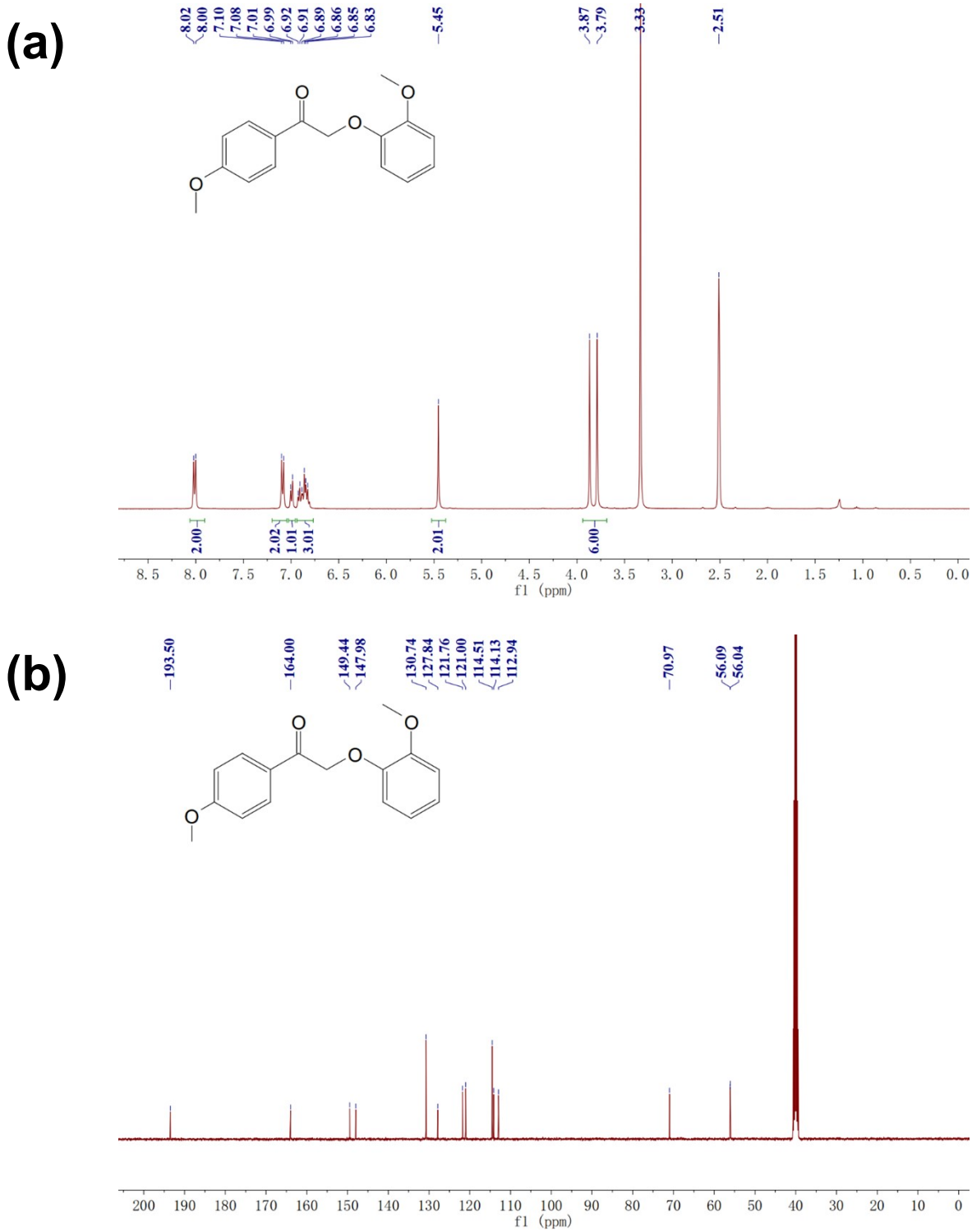


Fig. S19 (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra of compound 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**4a**)

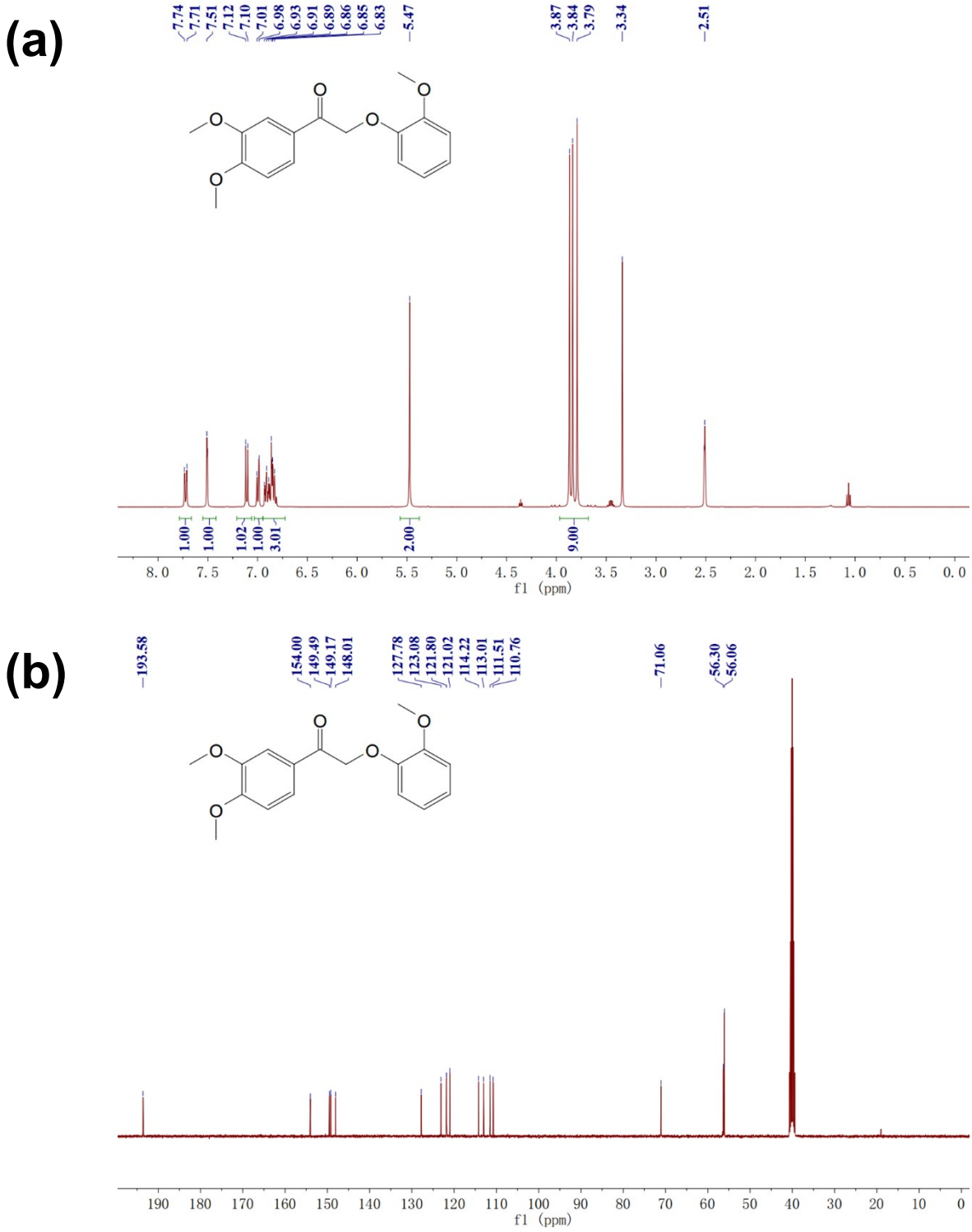


Fig. S20 (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra of compound 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (**5a**)

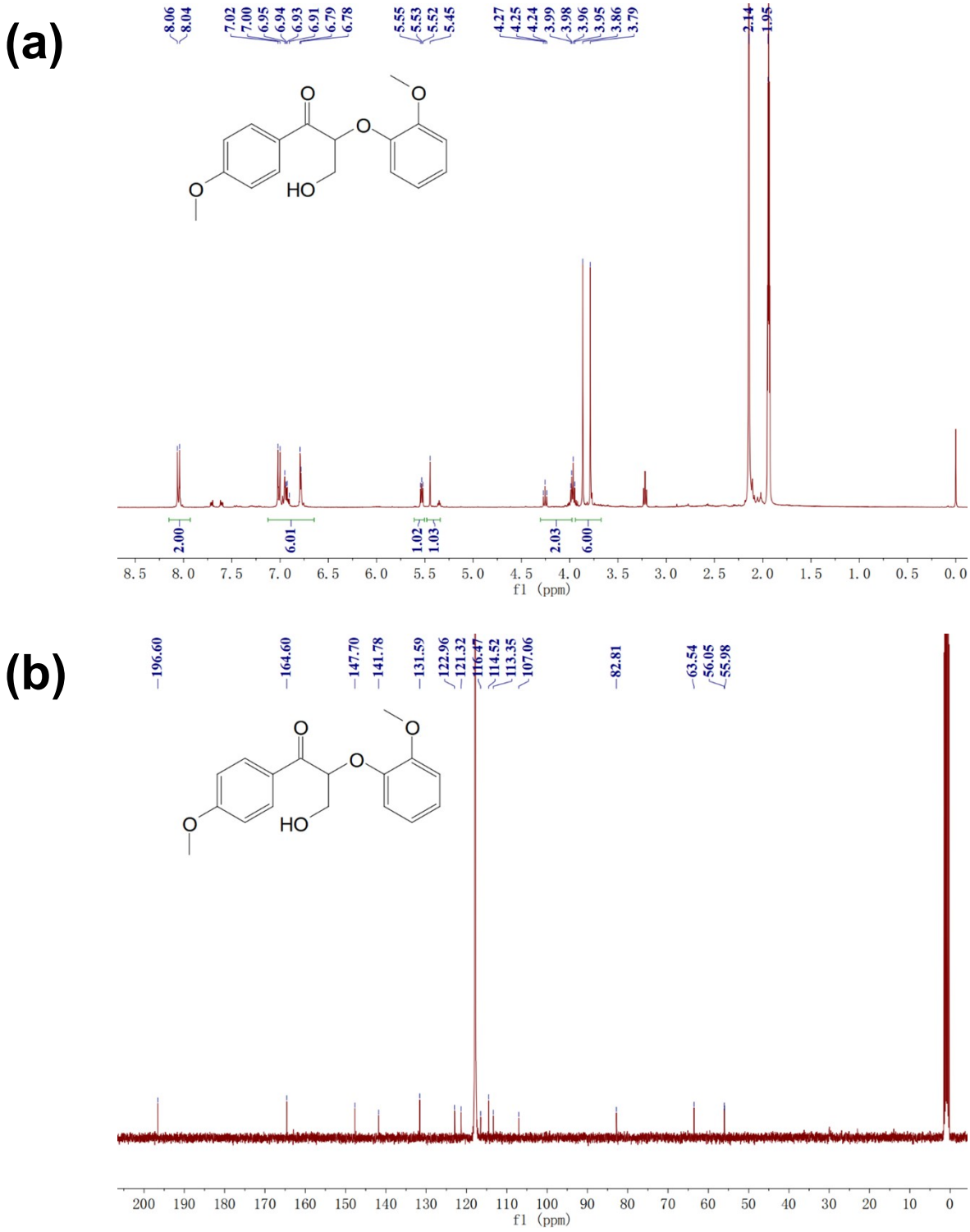


Fig. S21 (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra of compound 3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (**6a**)

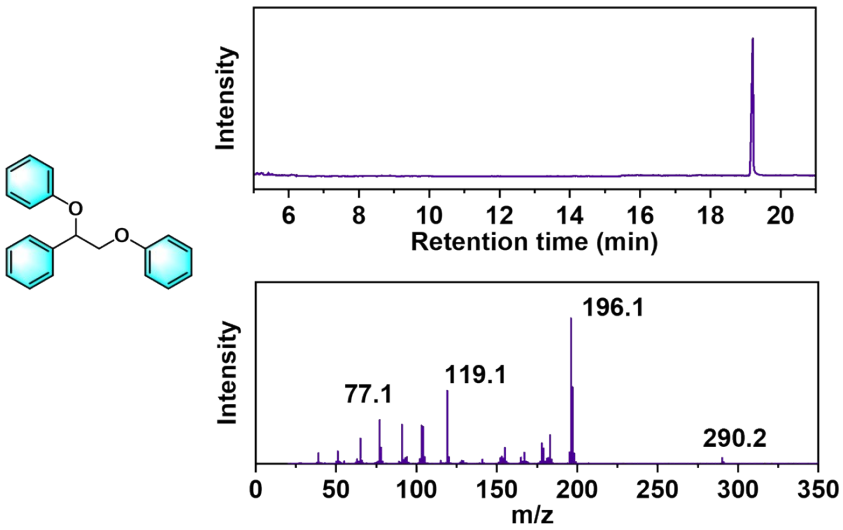


Fig. S22 The structure and GC-MS spectra of compound ((1-phenylethane-1,2-diyl)bis(oxy))dibenzene (**7a**)