

SUPPORTING INFORMATION

Green photocatalytic organic transformations by polyoxometalates vs mesoporous TiO₂ nanoparticles: Selective aerobic oxidation of alcohols

Theodoros S. Symeonidis,^a Ioannis Tamiolakis,^b Gerasimos S. Armatas,^b and Ioannis N.
Lykakis,^{a,*}

^aDepartment of Chemistry, Aristotle University of Thessaloniki, University Campus, 54124,
Thessaloniki, Greece; Tel: +30-2310-997871; Fax: +30-2310-997679; E-mail:
lykakis@chem.auth.gr.

^bDepartment of Materials Science and Technology, University of Crete, 71003 Heraklion, Crete,
Greece.

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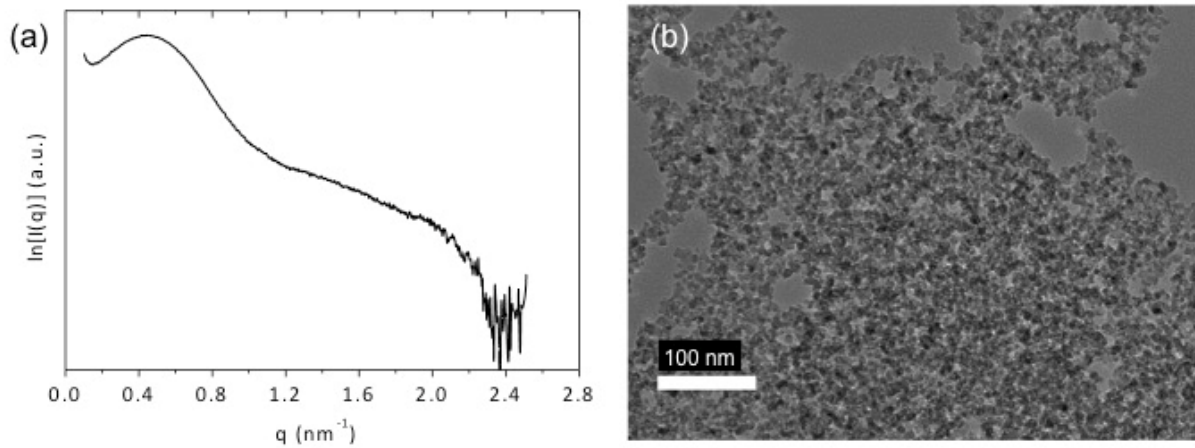


Fig. S1 (a) Small-angle X-ray scattering pattern and (b) typical TEM image of mesoporous DT-MTA catalyst, showing three-dimensional porous ensembles of uniform TiO_2 nanoparticles (*ca.* 7–8 nm in size). The SAXS pattern display a strong scattering peak at $q \sim 0.44 \text{ nm}^{-1}$ which corresponds to an average center-to-center interparticle distance ($d=2\pi/q$) of about 14.3 nm.

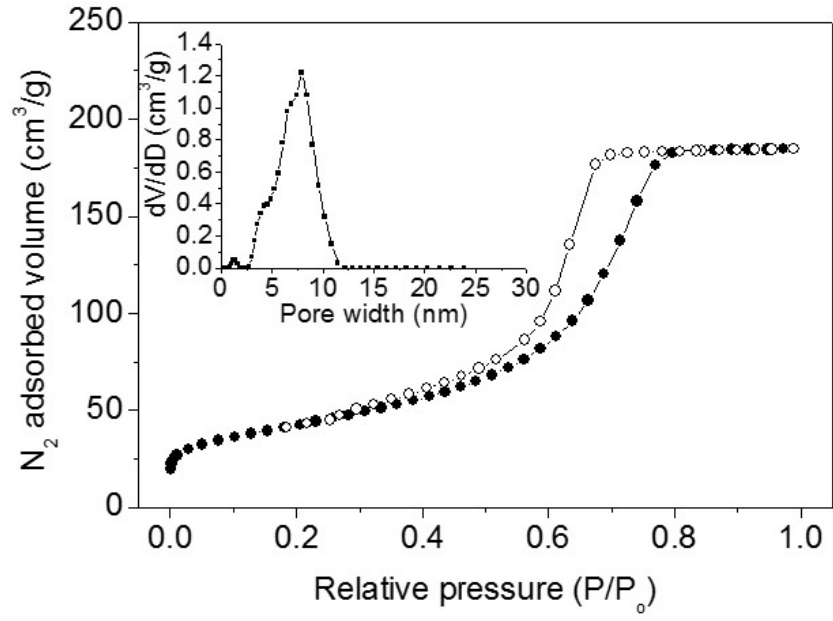


Fig. S2 Nitrogen adsorption-desorption isotherms at -196 °C and NLDFT pore size distribution calculated from the adsorption data (inset) for mesoporous DT-MTA material.

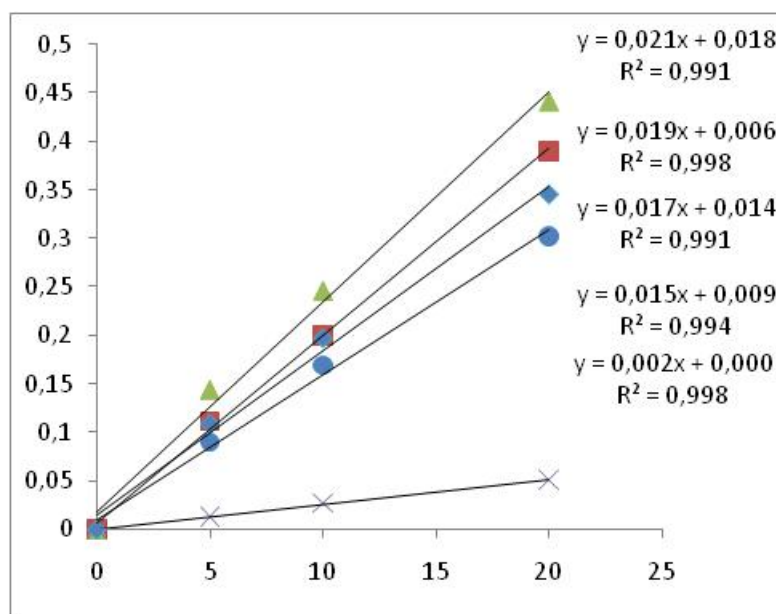


Fig. S3 The pseudo first-order rate plots (x is conversion of substrate at time t) for the photo-oxidation of various *para*-substituted benzyl alcohols catalyzed by mesoporous DT-MTA.

Experimental conditions: 0.1 mmol alcohol, 45 mg catalyst, 20 mL min⁻¹O₂, 3 mL CH₃CN, 5 °C, UV-visible-light irradiation ($\lambda > 320$ nm)

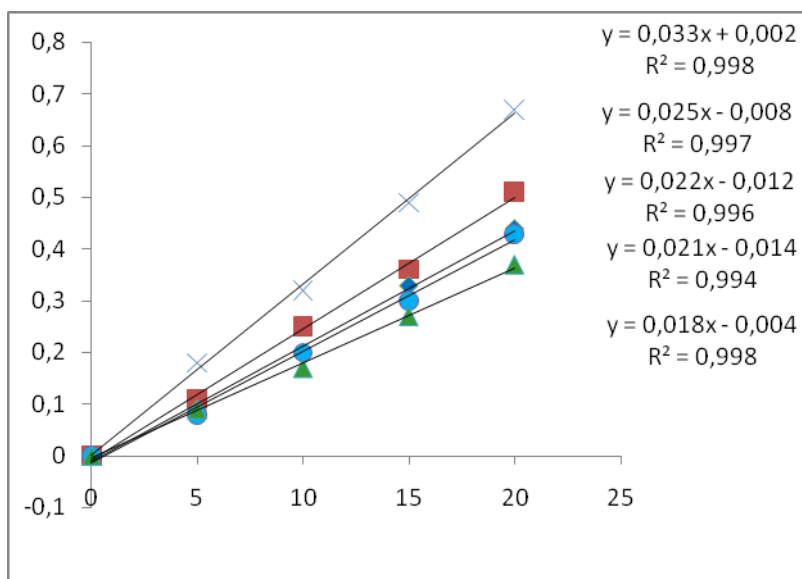


Fig. S4 The pseudo first-order rate plots (x is conversion of substrate at time t) for the photo-oxidation of various *para*-substituted benzyl alcohols catalyzed by decatungstate. *Experimental conditions*: 0.1 mmol alcohol, 3 mg catalyst, 20 mL min⁻¹O₂, 3 mL CH₃CN, 5 °C, UV-visible-light irradiation ($\lambda > 320$ nm).

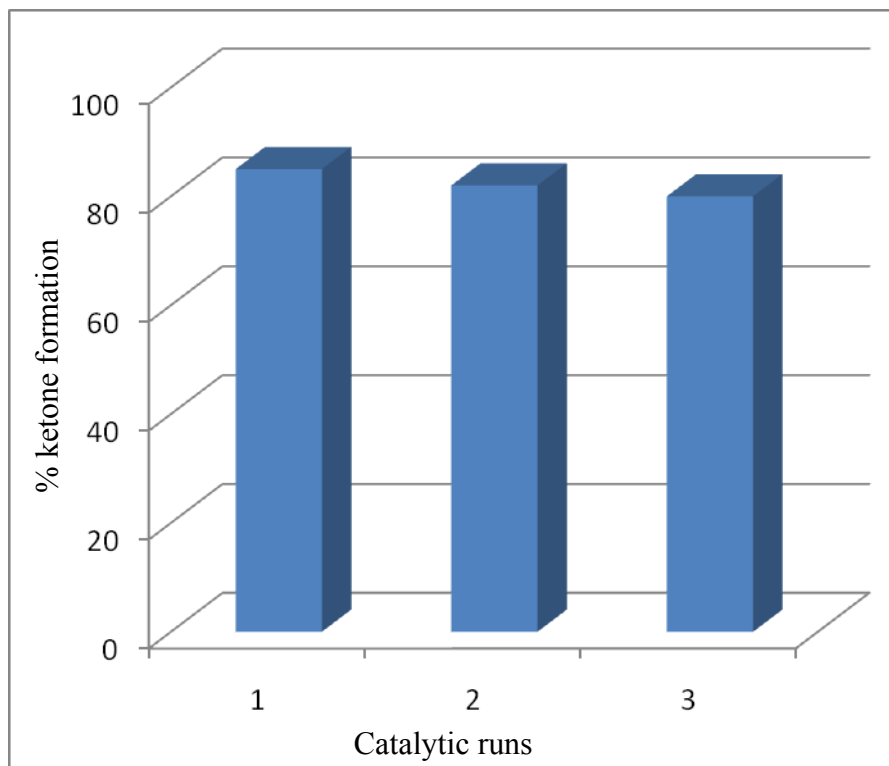
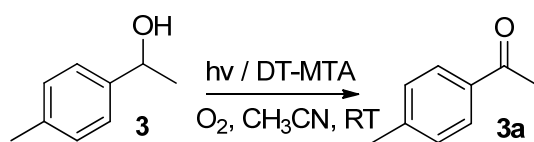


Fig. S5. Recycling study of the mesoporous DT-MTA catalyst (*Experimental conditions: 0.1 mmol of 3, 45 mg of catalyst, 3 mL of CH₃CN, bubbling with O₂, room temperature, t= 2h*).

Table S1. DT-MTA and TBADT catalyzed photooxidation of the *para*-alkyl substitute 1-phenylethanols **3**, **6-8**.

Reaction scheme: $\text{R}^1\text{-C}_6\text{H}_4\text{-CH(OH)CH}_3 \xrightarrow[\text{O}_2/\text{CH}_3\text{CN}]{\text{hv/catalyst}} \text{R}^1\text{-C}_6\text{H}_4\text{-C(=O)CH}_3 + \text{R}^1\text{-C}_6\text{H}_4\text{-CH(OH)CH}_2\text{OOH}$

R ¹	R ²	
H	H	3
CH ₃	H	6
CH ₃	CH ₃	7
Ph	H	8

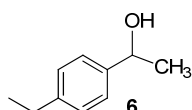
Sub.	Catalyst	Time (min)	Conversion % ^[a]	Relative product yield % ^[b]			
				a	b	c	d
3	TBADT	40	50	>99	-	-	-
3	TBADT	90	82	>99	-	-	-
3	TBADT	120	97	>99	-	-	-
3	DT-MTA	90	35	>99	-	-	-
6	TBADT	10	45	88	4	2	6
6	TBADT	20	78	71	5	10	14
6	TBADT	120	100	25	1	2	72
6	DT-MTA	90	41	90	7	-	3
7	TBADT	10	10	>99	-	-	-
7	TBADT	20	55	85	-	13	2
7	DT-MTA	90	51	91	2	4	3
8	TBADT	20	60	83	7	5	5
8	TBADT	60	80	80	8	6	6
8	DT-MTA	90	35	92	-	-	2 ^[c]

[a] Alcohol (0.1 mmol), decatungstate (5×10^{-4} M), 2 mL CH₃CN, at 5 °C. [b] Determined by ¹H NMR spectroscopy and GC-MS after reduction of hydroperoxides to the corresponding alcohols with PPh₃, error \pm 1%. [c] 6% of the corresponding 4-(1-hydroxyethyl) benzophenone was observed by NMR.

Synthetic procedures and spectroscopic data of alcohols 1-8

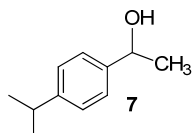
Alcohols **1-5** are commercial available and used without any further purification.

1-(4-ethylphenyl)ethanol (6). This compound was prepared by Grignard reaction using 0.62 g (5.0 mmol) of 4-ethylbenzaldehyde, 0.17 g (7.0 mmol) Mg and 7.0 mmol of MeI in dry ether under Ar atmosphere at 0 °C. 0.71 g of the corresponding aryl alcohol **6** was isolated (94 % yield), after reaction completion monitored by TLC.



^1H NMR (500 MHz, CDCl_3): δ 7.33 (d, 2H, $J = 8.2$ Hz), 7.22 (d, 2H, $J = 8.2$ Hz), 4.89 (q, 1H, $J = 6.5$ Hz), 2.68 (q, 2H, $J = 7.4$ Hz), 1.93 (s, OH), 1.52 (d, 3H, $J = 6.4$ Hz), 1.27 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 143.5, 143.1, 127.9, 125.3, 70.2, 28.5, 25.0, 15.6. MS $m/z =$ 150, 135 (100), 91, 79.

1-(4-isopropylphenyl)ethanol (7). This compound was prepared by Grignard reaction using 0.7 g (5.0 mmol) of 4-isopropylbenzaldehyde, 0.17 g (7.0 mmol) Mg and 7.0 mmol of MeI in dry ether under Argon atmosphere at 0 °C. 0.75 g of the corresponding aryl alcohol **7** was isolated (91 % yield) after reaction completion monitored by TLC.



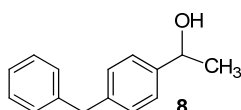
^1H -NMR (500 MHz, CDCl_3): δ 7.35 (d, 2H, $J = 8.1$ Hz), 7.25 (d, 2H, $J = 8.0$ Hz), 4.89 (q, 1H, $J = 6.5$ Hz), 2.95 (m, 1H), 2.05 (s, OH), 1.52 (d, 3H, $J = 6.4$ Hz), 1.29 (t, 3H, $J = 6.9$ Hz). ^{13}C -NMR (125 MHz, CDCl_3): δ 148.1, 143.2, 126.5, 125.4, 70.2, 33.7, 24.9, 23.9. MS $m/z =$ 164, 149 (100), 121, 105, 79.

1-(4-benzylphenyl)ethanol (8). This compound was prepared according to the procedure described below:

1-(4-benzylphenyl)ethanone (8a). To a solution of 5 mmol of diphenyl methane in anhydrous dichloromethane, at 0 °C, were added 6 mmol CH_3COCl and 6 mmol of the AlCl_3 in portions. The reaction mixture was stirred for 6 h and then 30 ml of 10 % HCl at 0 °C was added and the organic layer was extracted with diethylether, washed with 5 % NaHCO_3 and

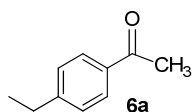
brine, dried and the solvent was removed under evaporation to give the corresponding aryl ketone **8a** in 90 % isolated yield.

To a mixture of LiAlH_4 (2 mmol) in dry ether 20 mL under Argon atmosphere at 0 °C was added dropwise a solution of the aryl ketone **8a** (6 mmol) in dry ether (10 mL). The mixture was heated under reflux for 1 h. The reaction was quenched at 0 °C by addition of 0.1 mL H_2O , 0.1 mL of 15 % NaOH, and 0.3 mL H_2O , followed by filtration. The mixture was washed with 5 % NaHCO_3 and brine, dried and the solvent was removed by evaporation to give the corresponding alcohol **8** in 92 % isolated yield.



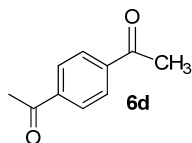
$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.28 (m, 5H), 7.19 (m, 4H), 4.89 (q, 1H, $J = 6.4$ Hz), 3.97 (s, 2H), 1.74 (s, OH), 1.48 (d, 3H, $J = 6.4$ Hz). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 143.5, 141.0, 140.3, 129.0, 128.8, 128.4, 126.1, 125.5, 70.2, 41.6, 25.0. MS $m/z =$ 212, 194, 179, 165, 152, 115, 91 (100), 65.

1-(4-ethylphenyl)ethanone (**6a**)



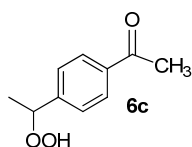
$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.91 (d, 2H, $J = 8.8$ Hz), 7.32 (d, 2H, $J = 8.8$ Hz), 2.74 (q, 2H, $J = 7.6$ Hz), 2.61 (s, 3H), 1.28 (t, 3H, $J = 7.6$ Hz). MS $m/z =$ 148, 133 (100), 105, 77.

1-(4-acetylphenyl)-1-ethanone (**6d**)



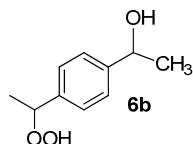
$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.06 (s, 4H), 2.67 (s, 6H). MS $m/z =$ 148, 133 (100), 119, 105, 91.

1-[4-(hydroperoxyethyl) phenyl]-1-ethanone (**6c**)



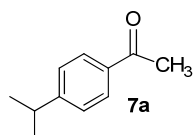
^1H NMR (500 MHz, CDCl_3): δ 8.01 (d, 2H, $J = 8.8$ Hz), 7.88 (s, OOH), 7.32 (d, 2H, $J = 8.8$ Hz), 5.17 (q, 1H, $J = 6.6$ Hz), 2.63 (s, 3H), 1.50 (d, 3H, $J = 6.6$ Hz).

1-[4-(hydroperoxyethyl)phenyl]-1-ethanol (6b)



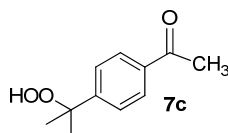
^1H NMR (500 MHz, CDCl_3): δ 7.43 (d, 2H, $J = 8.0$ Hz), 7.39 (d, 2H, $J = 8.0$ Hz), 4.99 (q, 1H, $J = 6.6$ Hz), 4.95 (q, 1H, $J = 6.6$ Hz), 1.53 (d, 3H, $J = 6.6$ Hz), 1.50 (d, 3H, $J = 6.6$ Hz).

1-(4-isopropylphenyl)ethanone (7a)



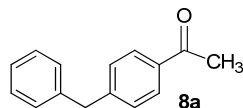
^1H NMR (500 MHz, CDCl_3): δ 7.93 (d, 2H, $J = 8.1$ Hz), 7.34 (d, 2H, $J = 8.1$ Hz), 2.99 (m, 1H), 2.61 (s, 3H), 1.30 (d, 3H, $J = 6.9$ Hz). MS $m/z = 162, 147$ (100), 132, 119, 91, 77.

1-[4-(hydroperoxy-1-methylethyl)phenyl]-1-ethanone (7c)



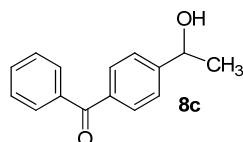
^1H NMR (500 MHz, CDCl_3): δ 8.06 (s, OOH), 7.96 (d, 2H, $J = 8.4$ Hz), 7.60 (d, 2H, $J = 8.4$ Hz), 2.62 (s, 3H), 1.63 (s, 6H).

4-benzyl acetophenone (8a)



^1H NMR (500 MHz, CDCl_3): δ 7.91 (d, 2H, $J = 8.1$ Hz), 7.31 (m, 4H), 7.25 (t, 1H, $J = 7.1$ Hz), 7.20 (d, 2H, $J = 7.4$ Hz), 4.06 (s, 2H), 2.60 (s, 3H). MS $m/z = 210, 195$ (100), 165, 152, 115, 97.

1-(4-benzoylphenyl)-1-ethanol (8c)



^1H NMR (500 MHz, CDCl_3): δ 8.09 (d, 2H, $J = 8.3$ Hz), 7.89 (d, 2H, $J = 8.3$ Hz), 7.83 (d, 2H, $J = 7.8$ Hz), 7.65 (t, 1H, $J = 7.3$ Hz), 7.54 (t, 2H, $J = 7.3$ Hz), 2.70 (s, 3H). MS $m/z = 226, 211, 183, 149, 105$ (100), 77.

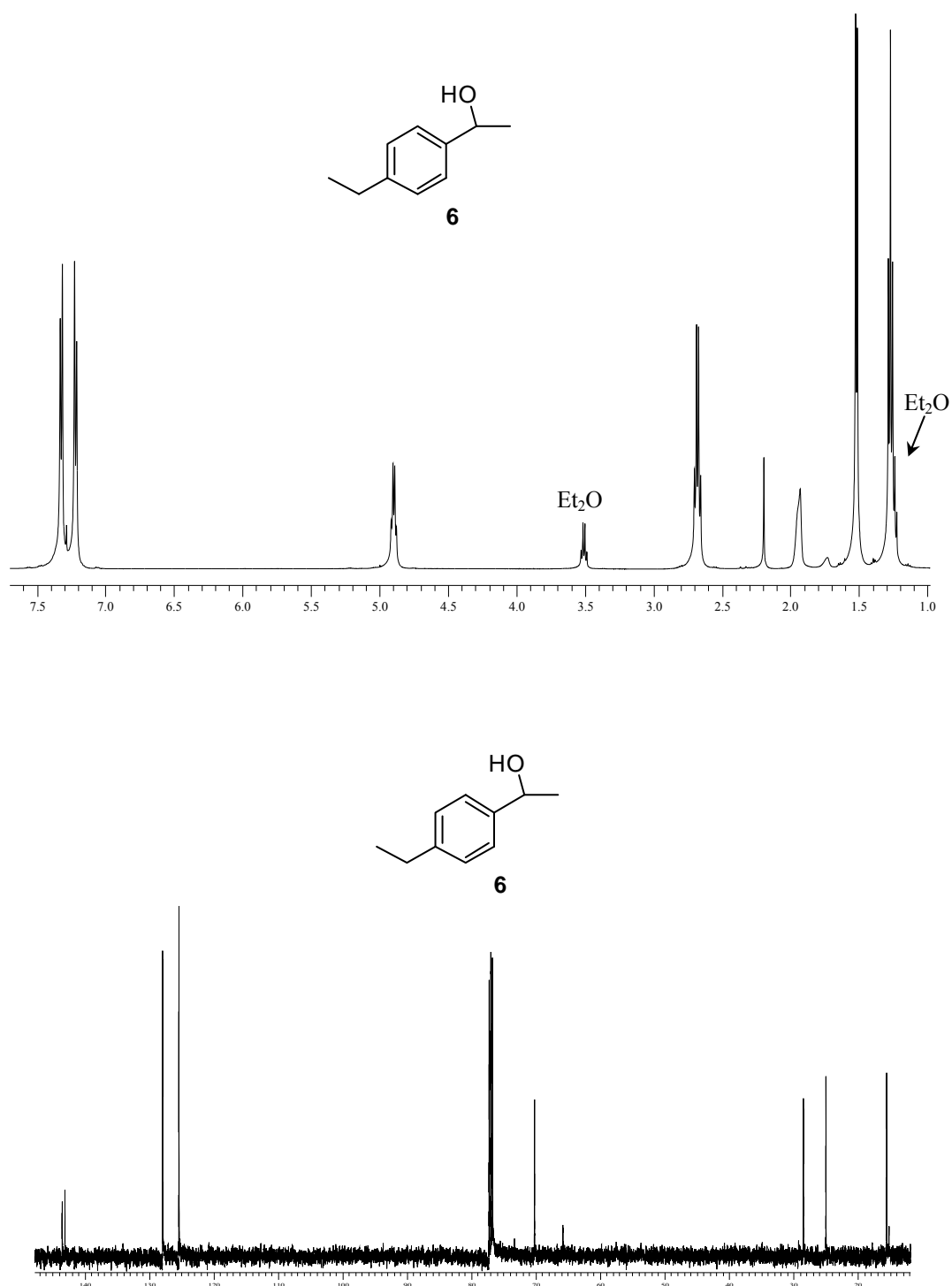
^1H and ^{13}C NMR spectra

Figure S6. ^1H NMR and ^{13}C NMR of the product **6** using CDCl_3 as solvent.

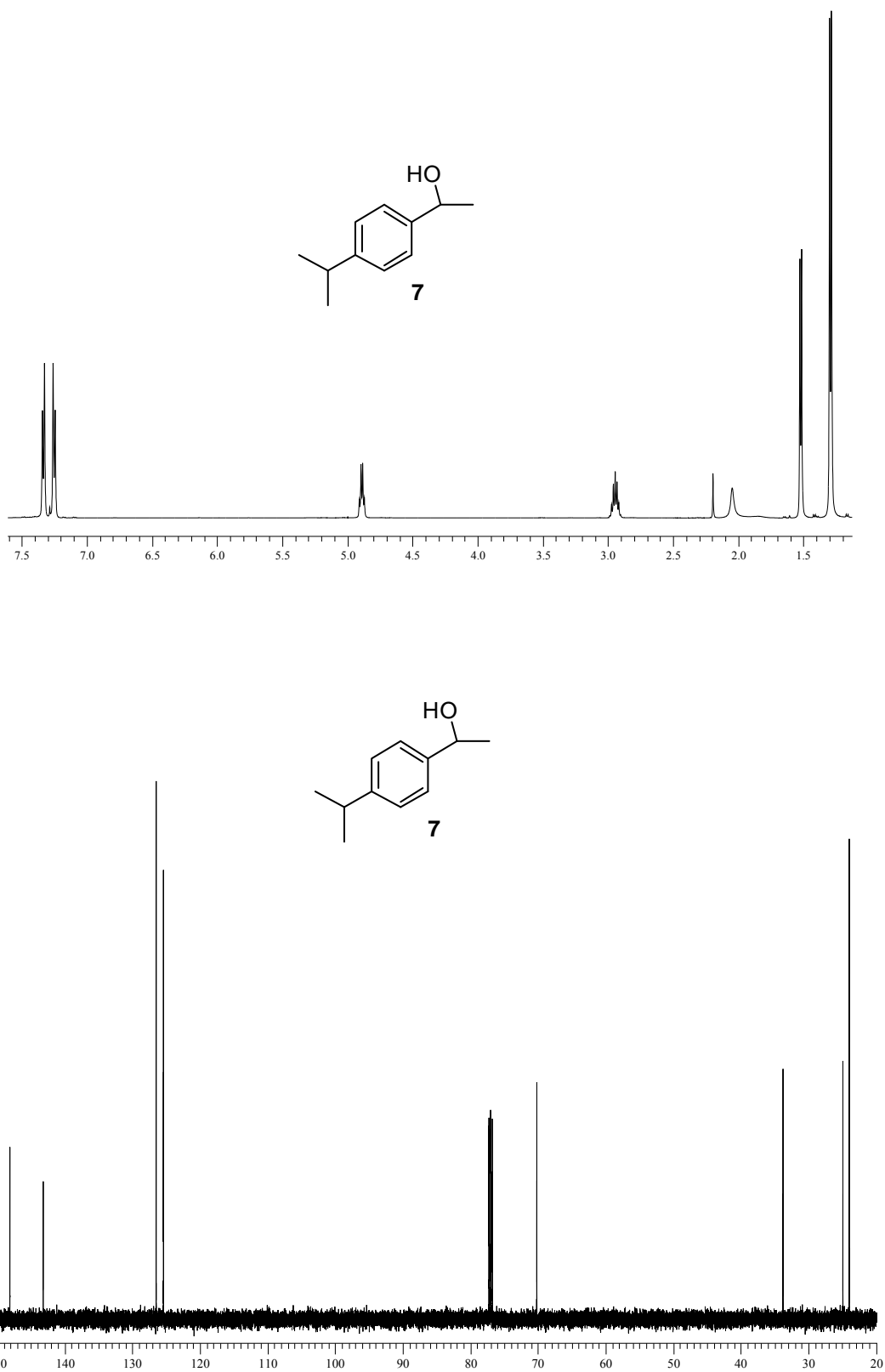


Figure S7. ^1H NMR and ^{13}C NMR of the product **7** using CDCl_3 as solvent.

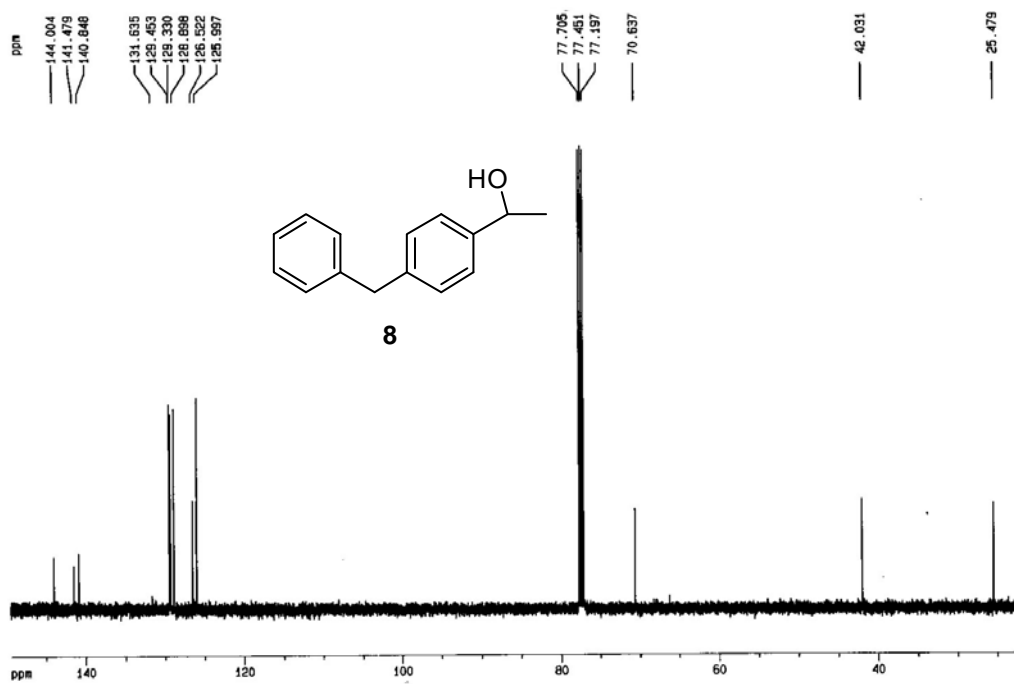
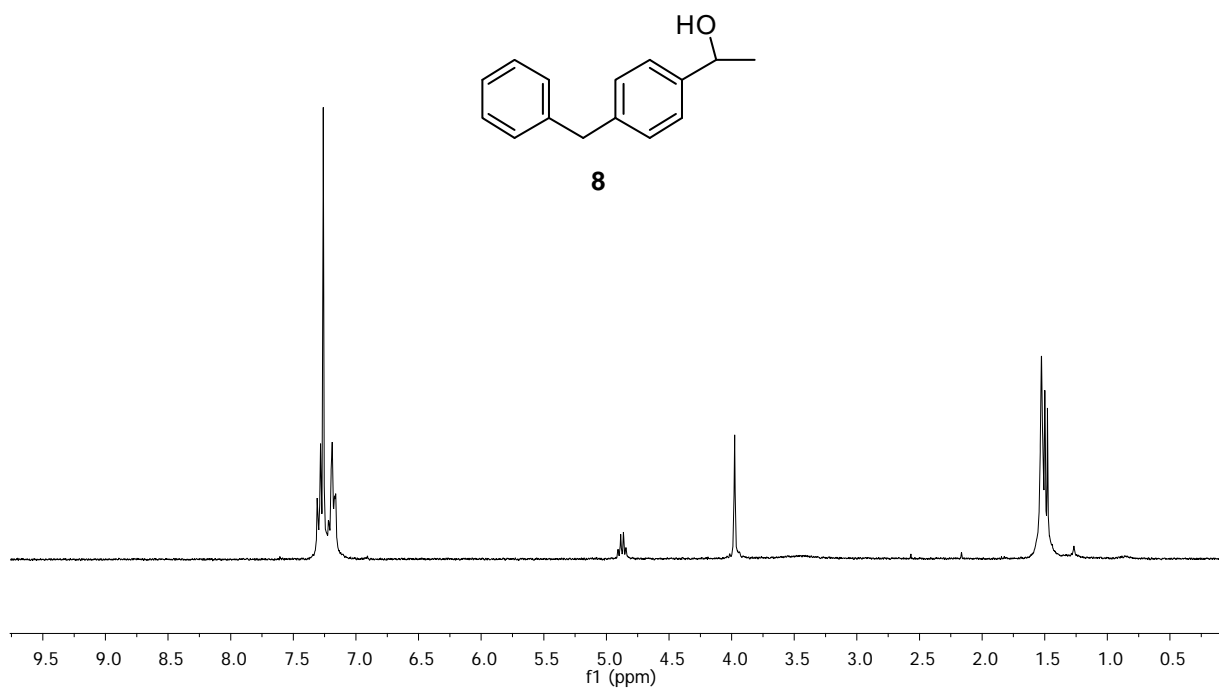


Figure S8. ^1H NMR and ^{13}C NMR of the product **8** using CDCl_3 as solvent.

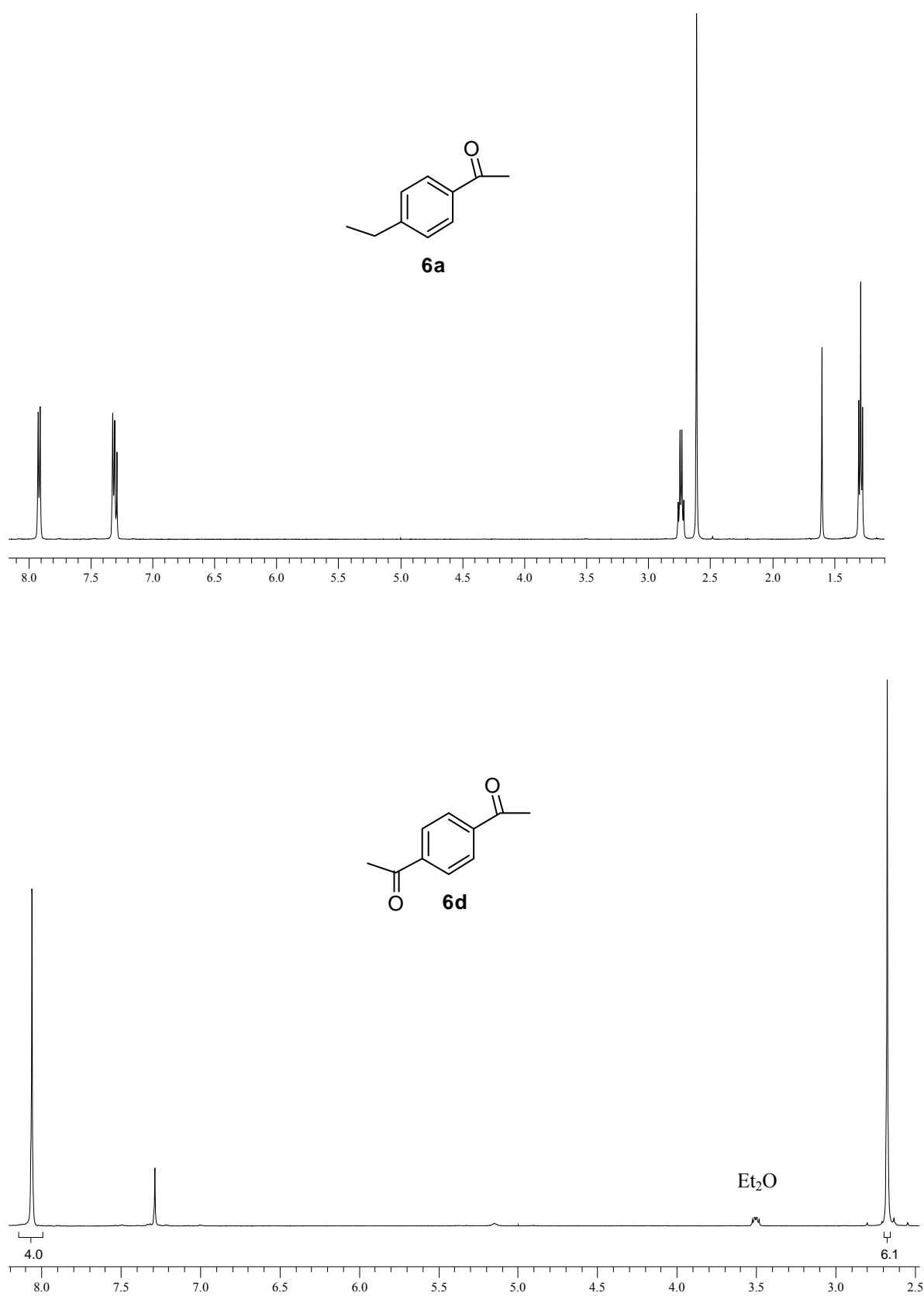


Figure S9. ^1H NMR of the products **6a** and **6d** using CDCl_3 as solvent.

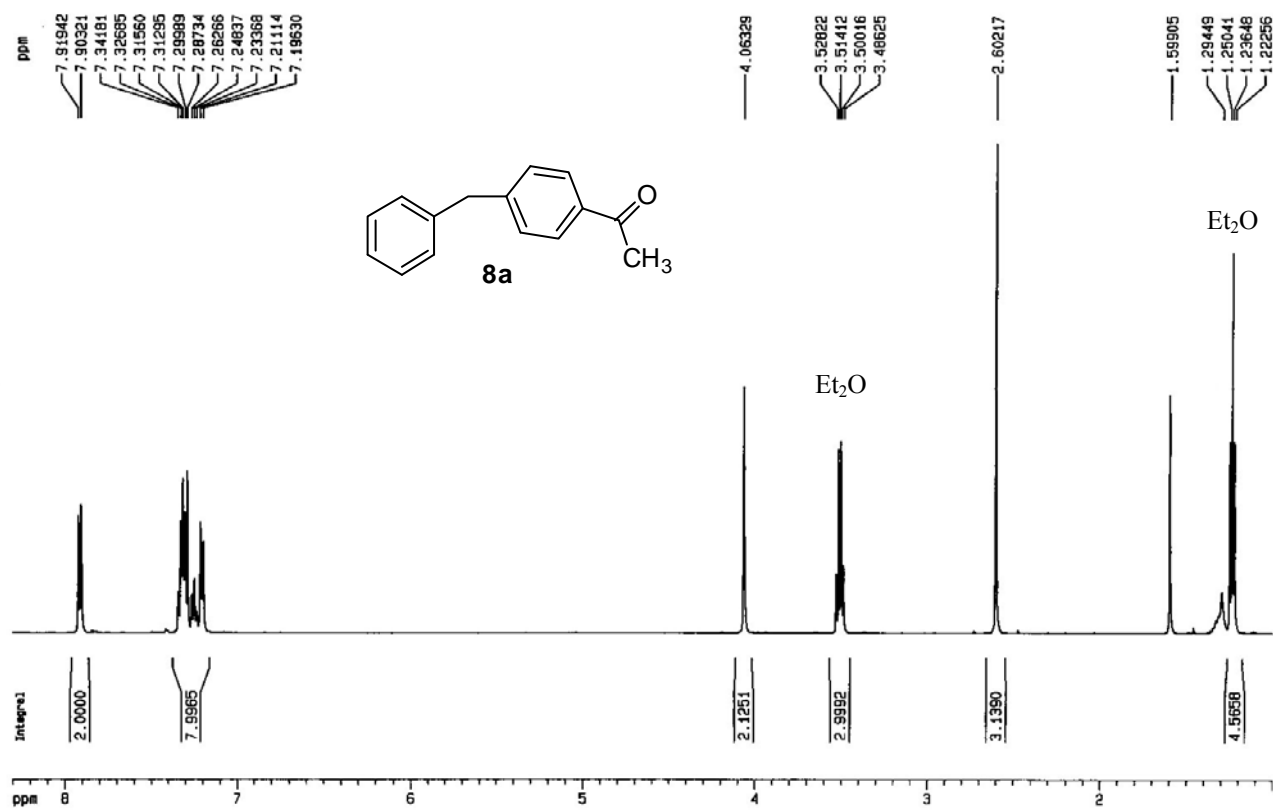


Figure S10. ¹H NMR of the product **8a** using CDCl₃ as solvent.

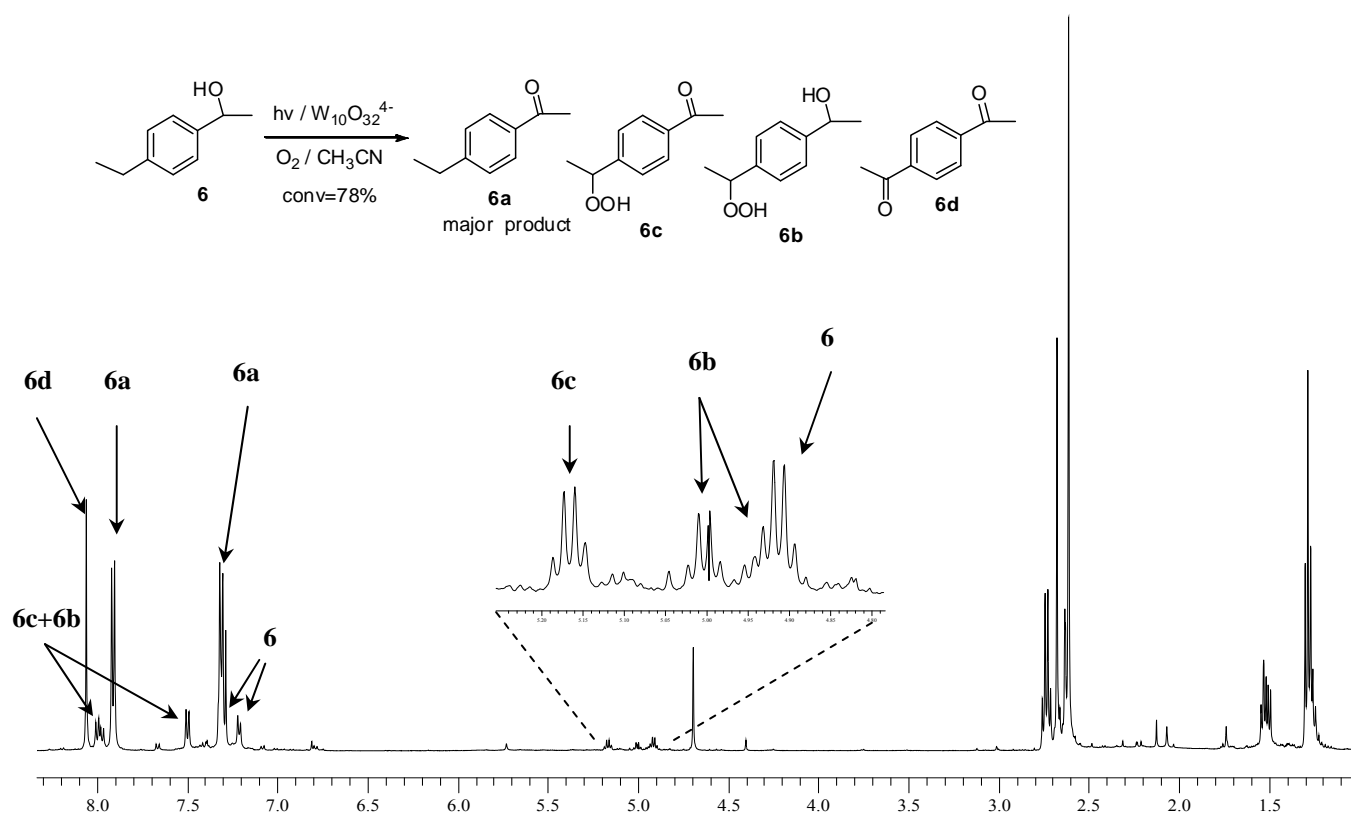


Figure S11. ¹H NMR in CDCl₃ of the crude mixture after photooxidation of **6** catalyzed by W₁₀O₃₂⁴⁻.

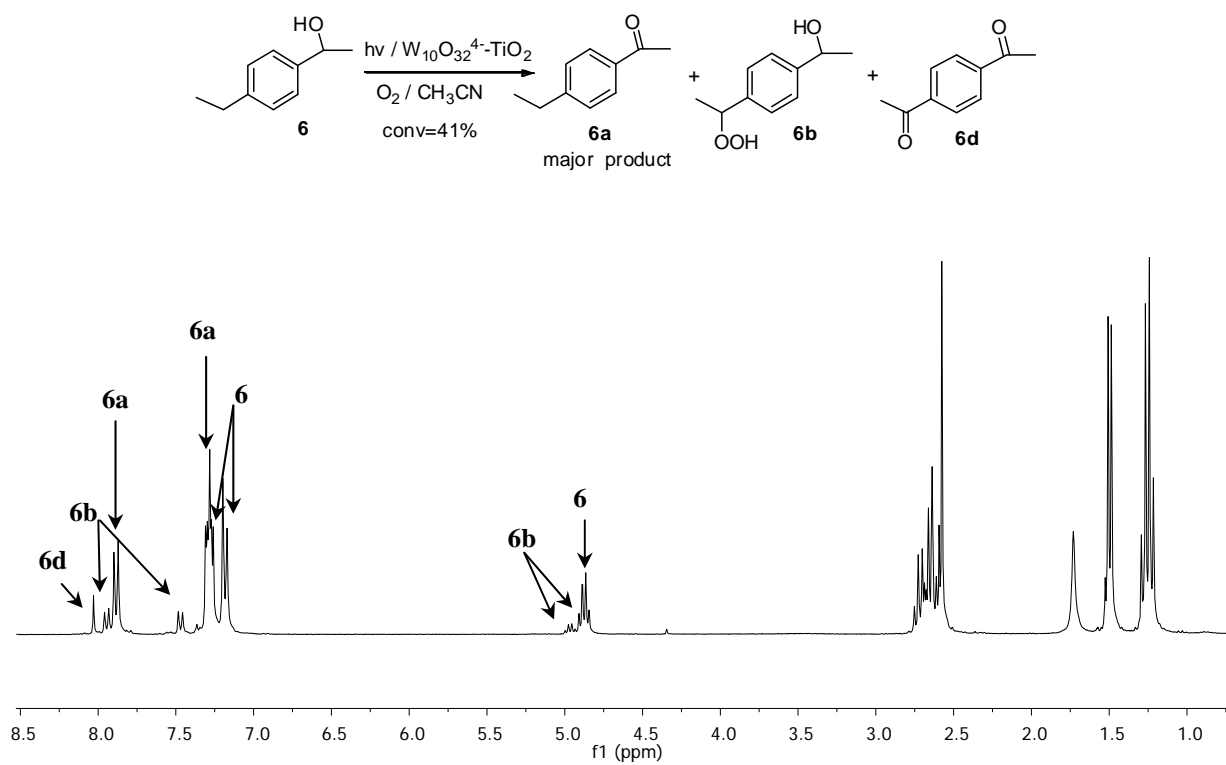


Figure S12. ^1H NMR in CDCl_3 of the crude mixture after photooxidation of **6** catalyzed by DT-MTA.

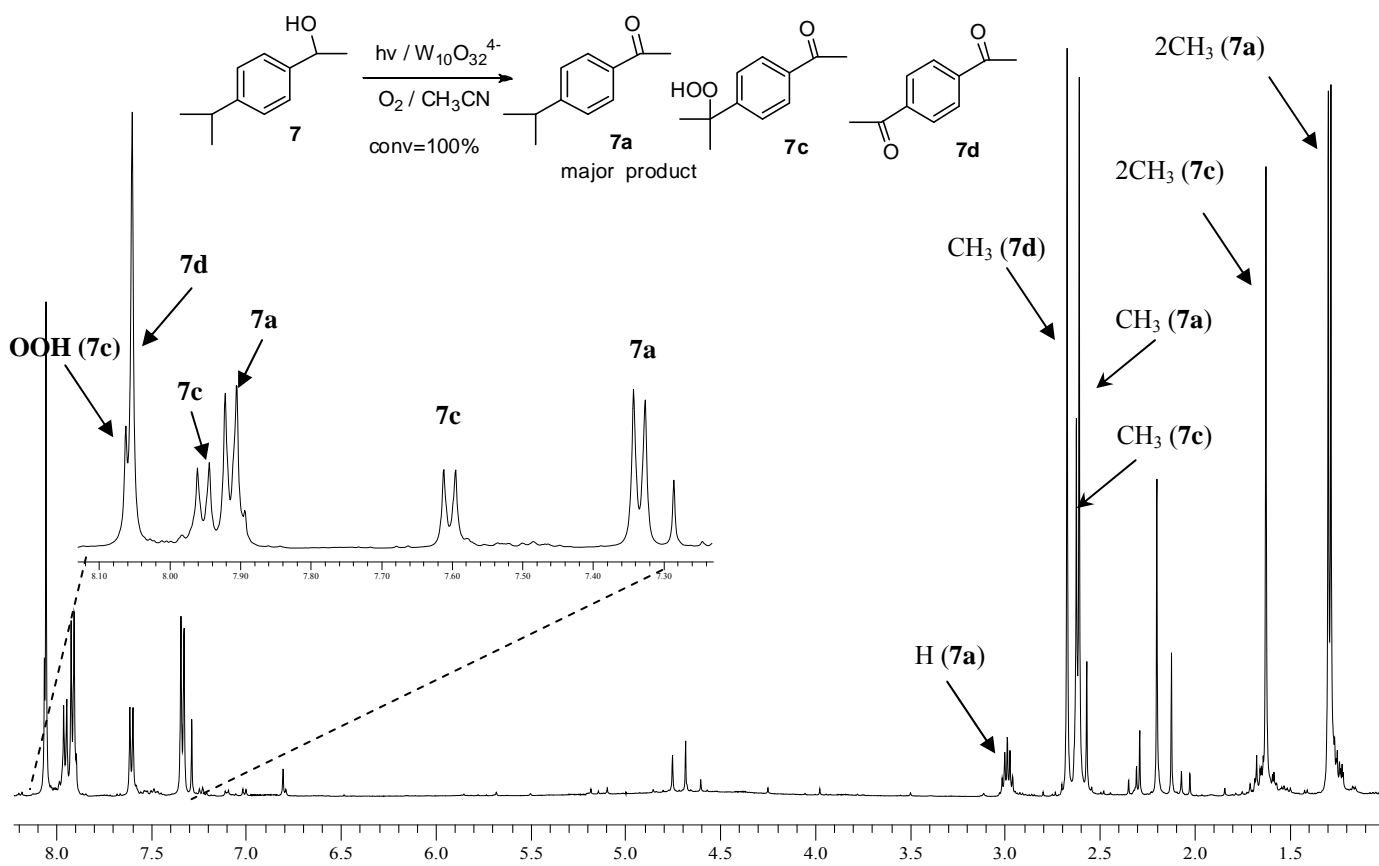


Figure S13. ^1H NMR in CDCl_3 of the crude mixture after photooxidation of **7** catalyzed by $\text{W}_{10}\text{O}_{32}^{4-}$.

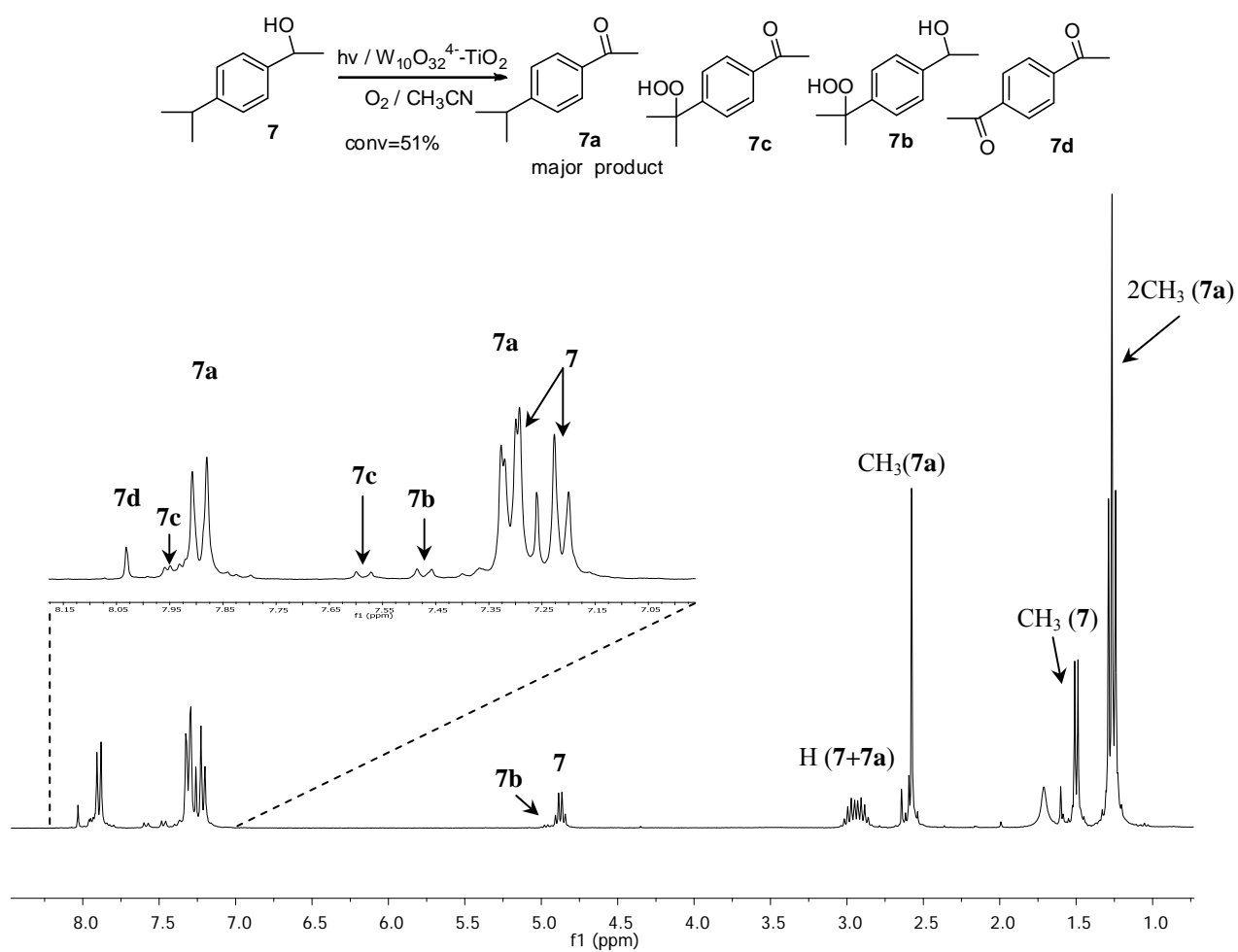


Figure S14. ^1H NMR in CDCl_3 of the crude mixture after photooxidation of **7** catalyzed by DT-MTA.

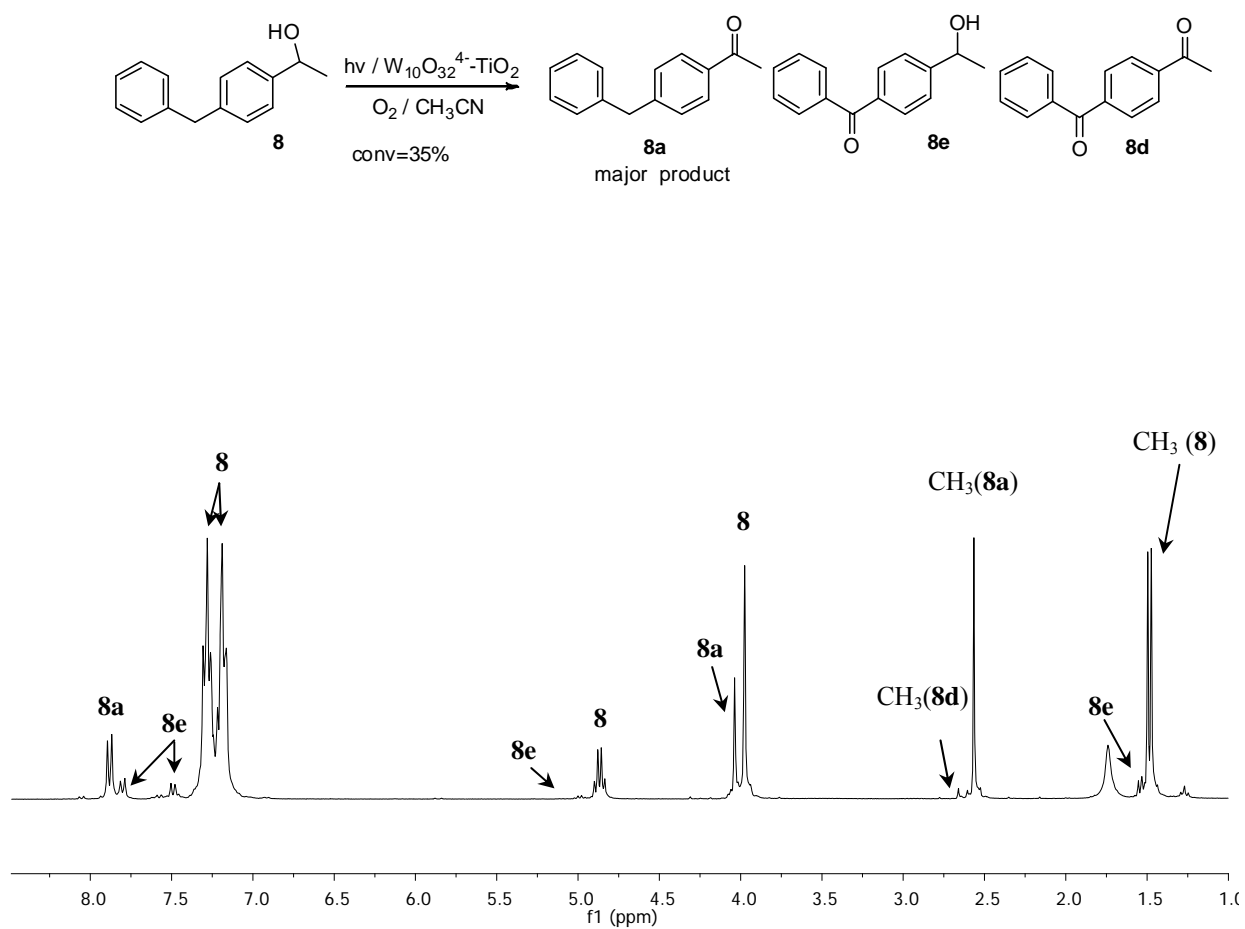


Figure S15. ¹H NMR in CDCl₃ of the crude mixture after photooxidation of **8** catalyzed by DT-MTA.

GC-MS

