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Oxidation Cascade with Oxone: Cleavage of Olefins to Carboxylic Acids

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Abstract

A variety of olefins is shown to be cleaved oxidatively to the corresponding acids with oxone as the reagent. The simple methodology that works well for a range of alkenes, i.e., styrenes, nitrostyrenes, stilbenes, cinnamic acids, chalcones, etc., involves heating of the reactant with oxone in acetonitrile-water mixture (1:1, *v*/*v*) at reflux. The oxidation cascade involves initial dihydroxylation followed by oxidative cleavage and oxidation of the resultant aldehydes to acids.

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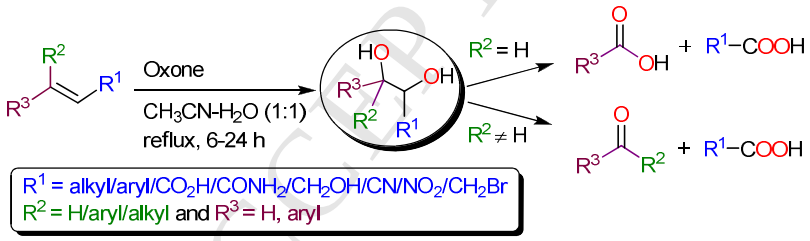
Graphic for TOC



Keywords: Oxidation, Ozonolysis, Oxone, Styrenes, Stilbenes, Cinnamic Acids, Chalcones and Diols.

1. Introduction

Oxidative cleavage of olefins to the corresponding carbonyl compounds, i.e., aldehydes, ketones and acids, is a transformation that is of paramount importance in organic synthesis, and has been investigated immensely in organic synthesis. This reaction may be performed by a variety of reagents based on transition metals such as Mn, Cr, Mo, Ru, Pd, Re, V, Ce, W, Co, In, Os, etc.[1] However, the use of organometallic or metal-based reagents is associated with a serious drawback involving the formation of byproducts that are hazardous and detrimental to the environment. Development of new synthetic methodologies that are green, cost effective and environmentally benign is thus an incessant pursuit. In this regard, although the use of ozone[2] and oxygen[3] is advantageous for oxidative cleavage of olefins, ozone is explosive[2d] and the reactions must be performed in a special apparatus.[2e] Literature reveals a number of metal-free procedures for the cleavage of olefins. For example, Brooks *et al*. showed that styrene can be cleaved with H_2O_2.[4] Incidentally, the strength of H_2O_2 varies with time and its source, which limit its usage. Ochiai and co-workers reported that alkenes can be cleaved oxidatively with ArI in the presence of stoichiometric amounts of iodosobenzene[5a] or *m*-CPBA.[5b] Nicolaou and co-workers introduced a one-pot procedure for the cleavage of olefins by phenyliodonium diacetate (PIDA) reagent, which involves the intermediacy of diol intermediates.[6] Vinod et al. showed that the oxidative cleavage of olefins can be accomplished by *p*-iodobenzoic acid as a catalyst in the presence of oxone in acetonitrile-water at 60 ^{0}C;[7] the active species responsible for the oxidation was shown to be [hydroxy(4-carboxyphenyl)-iodonium]ion.

In continuation of our on-going investigations with IBX[8] and oxone,[9] we recently reported that benzylic alcohols can be oxidized to the corresponding acids in a facile manner using oxone as the terminal oxidant in acetonitrile-water (1:1) at reflux.[9] Given that olefins are reported to undergo dihydroxylation with oxone[7,10] and that the hydroxyl groups are oxidized with oxone in acetonitrile-water (1:1, v/v) at

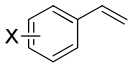
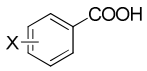
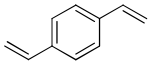
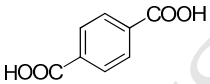
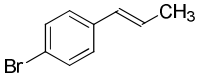
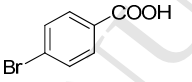
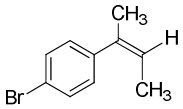
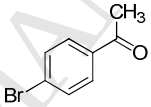
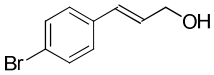
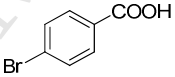
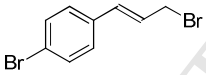
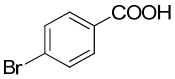
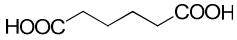
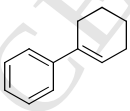
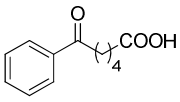
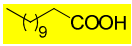
reflux conditions as shown recently by us,[9] we suspected that olefins should be cleaved oxidatively by oxone without any additive. Notwithstanding the finding by Vinod et al. that no oxidative cleavage was observed when styrene was heated in the presence of oxone at 60 °C in acetontrile-water,[7] we investigated the oxidative cleavage of olefins at the reflux conditions. To our delight, oxone was indeed found to be a very good reagent for tandem dihydroxylation followed by oxidative cleavage. In view of its cheap availability and environmentally-benign attributes, oxone is assuming increasing importance in a variety of oxidative transformations as a reagent as well as a co-oxidant.[11] Herein, we report that oxone can be directly employed as a reagent to oxidatively cleave a variety of olefins to the corresponding acids in moderate to excellent isolated yields; ^{1}H NMR monitoring of the reactions as well as the isolation of the diol intermediates in some cases attest to the occurrence of a domino/cascade oxidations[12] with oxone.

2. Results and discussion

At the outset, the reaction of styrene in CH_3CN-H_2O (1:1, *v*/*v*) with oxone was examined at reflux conditions. TLC analyses indicated gradual formation of the diol intermediate and benzoic acid. As oxone is known to decompose in the acidic medium,[13] 3.0 equiv of the reagent was introduced in increments to drive the reaction to completion. At the end of 14 h, the reaction led to benzoic acid in 70% isolated yield. Inspired by this result, a number of olefins were subjected to oxidation likewise. As shown in Table 1, substituents such as bromo, cyano, nitro and carboxy at para position afforded the corresponding acids in 77-93% yields (entries 2-5). The products in similar yields were also isolated for substrates containing substitutents at ortho position as well (entries 7 and 8). However, *p*-methylstyrene was found to yield *p*-methylbenzoic acid in a relatively poor yield (entry 6); we have shown in our previous investigation that alkylaromatics undergo side-chain oxidation with oxone. We attribute the poor isolated yield in this instance to competitive oxidation of the methyl group leading to an intractable mixture of products. Indeed, when the reaction was conducted for 24 h with 5 equiv. of oxone, it gave a mixture of products,

which includes *p*-toluic acid (16%), terephthalic acid (27%) and *p*-formylbenzoic acid (3%); it should be noted that benzaldehyde is an intermediate in the oxidation of toluene, as has been shown by us previously.[9] When the electron rich substrates such as *o*-methylstyrene and *p*-methoxystyrene were reacted with oxone at reflux, formation of messy product mixtures was observed. *o*-Toluic acid and *p*-methoxybenzoic acid were isolated in 8 and 17% yields, respectively (entries 9 and 10). However, when these reactions were conducted only for 12 h by employing 3 equivalents of oxone, 1-*o*-tolylethane-1,2-diol and 1-(*p*-methoxyphenyl)ethane-1,2-diol were obtained in 56 and 30% yields, respectively. Divinylbenzene was found to yield terephthalic acid in an excellent isolated yield, albeit with 8 equivalents of oxone introduced incrementally (entry 11). While the oxidation of *p*-bromo-β-methylstyrene yielded *p*-bromobenzoic acid in 74% yield, that of *p*-bromo-α,β-dimethylstyrene led to *p*-bromoacetophenone in 72% isolated yield (entries 12 and 13). *p*-Bromocinnamyl alcohol and *p*-bromocinnamyl bromide underwent oxidation with 4 equivalents of oxone to provide *p*-bromobenzoic acid in 72 and 81% yields, respectively (entries 14 and 15). The reaction of cyclohexene with oxone yielded adipic acid in 58% yield (entry 16), while its phenyl derivative led to the corresponding keto acid in 63% yield together with benzoic acid in 13% yield (entry 17). The reaction of tridecene with 5 equivalents of oxone over a period of 24 h of reaction duration led to dodecanoic acid in 61% yield (entry 18). Clearly, the results in Table 1 underscore the potential of oxone as a reagent for oxidative cleavage of olefins.

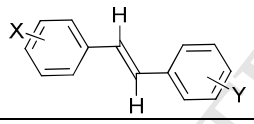
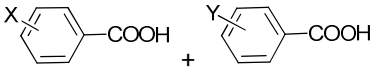
TABLE 1. Results of Oxidative Cleavage of Styrene Using Oxone in CH_3CN-H_2O[a]

Entry	Substrate	Equiv./ Time (h)	Product	Isolated Yield (%)[b]
1	 X = H	3/14		70
2	= *p*-Br	3/12		90
3	= *p*-NO_2	3/14		92
4	= *p*-CN	3/14		93
5	= *p*-CO_2H	3/19		77
6	= *p*-Me	3/24		43
7	= *o*-Br	3/24		77
8	= *o*-NO_2	3/17		82
9	= *o*-Me	5/24		8[c]
10	= *p*-MeO	5/24		17[d]
11		8/21		91
12		4/13		74
13		4/10		72[e]
14		4/14		72
15		4/14		81
16		3/11		58
17		4/20		63[e,f]
18		5/24		61

[a] All reactions were carried out in CH_3CN-H_2O (1:1, v/v) mixture at reflux. [b] Isolated yields unless mentioned otherwise. [c] Isolated from a messy product mixture. [d] 1-(4-Methoxyphenyl)ethane-1,2-diol was isolated in 15% yield. [e] 2 Equiv of H_2SO_4 was added. [f] Benzoic acid was also isolated in 13% yield.

Spurred by the results in Table 1, oxidative cleavage of diarylolefins, i.e., stilbenes, was examined. From TLC monitoring studies of the reaction of parent stilbene with oxone, it was concluded that 5.0 equivalents of oxone is necessary for completion of the reaction. As shown in Table 2, a number of stilbene derivatives containing substituent(s) at para position(s) were found to undergo oxidative cleavage in respectable yields (entries 1-5 and 7). The reaction was found to be highly sluggish for the stilbene substituted at the ortho position, e.g., 2,2'-dibromostilbene (entry 7) suggesting that sterics possibly impede the reaction. In the case of 4-methoxystilbene, the oxidation was found to yield an intractable mixture of products. At least three products, i.e., benzoic acid (35%), *p*-methoxybenzoic acid (8%) and 1-(4-methoxyphenyl)-2-phenylethane-1,2-dione (20%) were isolated (entry 6). We have earlier noted that the oxidation of aromatics containing e-donating groups likewise leads to messy product mixtures due presumably to operation of electron transfer chemistry; this indeed is the limitation with oxone when employed as an oxidant.[9]

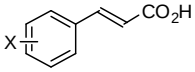
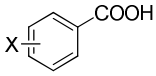
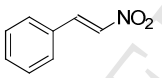
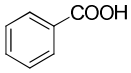
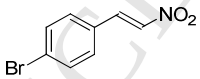
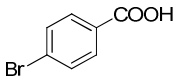
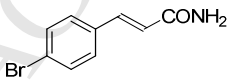
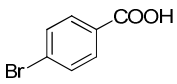
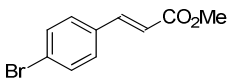
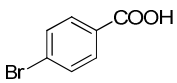
Table 2. Results of Oxidative Cleavage of Stilbenes Using Oxone in CH_3CN-H_2O[a]

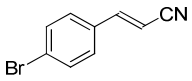
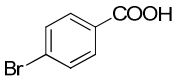
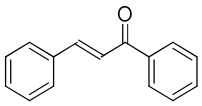
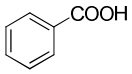
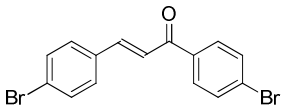
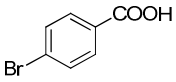
Entry	Substrate		Oxone Equiv/Time (h)	Product(s) Yield (%)[b]	
					
1	X = H	Y = H	5/24	50	
2	X = *p*-Br	Y = *p*-Br	5/22	83	
3	X = H	Y = *p*-Br	5/15	73	78
4	X = H	Y = *p*-NO_2	5/22	80	81
5	X = H	Y = *p*-CN	5/15	79	82
6	X = H	Y = *p*-OMe	4/14	35	8[c]
7	X = *p*-Br	Y = *p*-NO_2	5/18	80	81
8	X = *o*-Br	Y = *o*-Br	6/24	12	12[d]

[a] All reactions were carried out in CH_3CN-H_2O (1:1, v/v) mixture at reflux. [b] Isolated yields unless mentioned otherwise. [c] 1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione was isolated in 20% yield together with other products, see text. [d] The starting material was recovered unreacted in 75% yield.

In logical extension of these studies, the oxone-mediated oxidation of cinnamic acids, cinnamides, cinnamonitriles, nitrostyrene and chalcones was also explored. In Table 3 are consolidated these results; in some instances, more equivalents of oxone was found to be necessary to ensure that the reactions went to completion. As can be seen, all cinnamic acids, with the exception of the parent one and the *p*-methoxy derivative (entries 1 and 7), were found to yield the corresponding benzoic acids in very good yields (entries 2-6). Parent nitrostyrene as well as its *p*-bromo derivative led to the corresponding acids (entries 8 and 9). *p*-Bromocinnamamide, methyl *p*-bromocinnamate and *p*-bromocinnamonitrile yielded *p*-bromobenzoic acid in 76-80% yields (entries 10-12). While the parent chalcone afforded benzoic acid in 49% isolated yield, its bromo-derivative yielded the corresponding *p*-bromobenzoic acid in 80% yield (entries 13 and 14); the reactions were found to be incomplete in both cases even after 24 h.

Table 3. Results of Oxidative Cleavage of Cinnamic Acids, Nitrostyrenes, Cinnamamides and Chalcones Using Oxone in CH_3CN-H_2O[a]

Entry	Substrate	Equiv/ Time (h)	Product	Isolated Yield (%)[b]
1	 X = H	5/20		44
2	= *p*-CN	5/20		90
3	= *o*-CO_2H	5/22		85
4	= *m*-NO_2	5/24		81
5	= *p*-Br	5/30		73
6	= *p*-NO_2	5/20		81
7	= *p*-MeO	5/24		15[c]
8		6/24		76
9		5/24		86
10		5/24		76
11		5/22		80

12		4/18		76
13		6/24		49[d]
14		6/24		80[e]

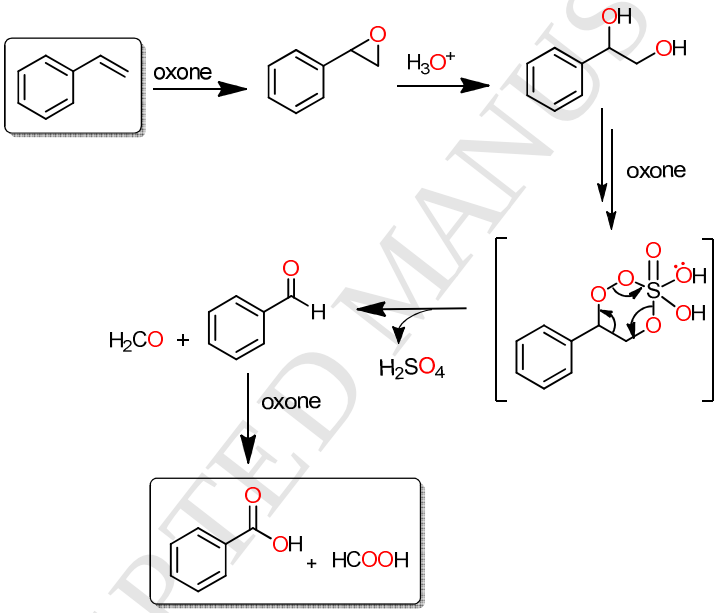
[a] All reactions were carried out in CH_3CN-H_2O (1:1, v/v) mixture at reflux. [b] Isolated yield. [c] Intractable reaction mixture. [d] The starting material was recovered in 26% yield. [e] The starting material was recovered unreacted in 7% .

3. Mechanism of Oxidation

We believe that the initial double bond oxidation is a common step in the oxidation of all substrates for which the results are collected in Tables 1-3. Oxone has been reported to convert olefins to epoxides,[14] which under the employed conditions of the reaction open up to give diols; it should be noted that the solution of oxone in acetonitrile-water (1:1, v/v) is strongly acidic, and we have found that the pH of the solutions of oxone in acetonitrile-water (1:1, v/v) mixture employed for oxidations described herein is typically ~3-4. Thus, the initially formed epoxides should be expected to open up in acetontrile-water to give the corresponding diols. We have indeed isolated the diol intermediates in some cases, e.g., styrene (entry 1, Table 1), *p*-methylstyrene (entry 6, Table 1) and 1-phenylcyclohexene (entry 15, Table 1), when the reactions were run for a short period. Indeed, the fact that the reaction of styrene with oxone in CH_3CN-H_2O (1:1, v/v) leads to dihydroxy products has previously been shown by Vinod and co-workers.[7] Further, the formation of diol intermediates is clearly revealed in the ^{1}H NMR monitoring of the reactions for some cases, e.g., *p*-nitrocinnamic acid, stilbene and *4,4'*-dibromostilbene, cf. Supplementary Information. The oxidative cleavage of diols presumably occurs via formation of the cyclic hypervalent sulfur intermediate with oxone and subsequent decomposition to the latter to aldehyde/s (Scheme 1). The fact that only dihydroxylated products are observed at 60 ^{0}C and that the reflux condition leads to cleavage products suggests that the initial epoxidation followed by opening is much faster than

equilibrium formation of the 6-membered cyclic hypervalent sulfur intermediate that collapses to the carbonyl compounds, cf. Scheme 1. When the product is aldehyde, it subsequently undergoes rapid oxidation with oxone; the latter, i.e., oxidation of the aldehyde to the corresponding acid, is a well-known reaction.[15] Clearly, a cascade of oxidations that include dihydroxylation, cleavage to the aldehydes followed by further oxidation the latter to the corresponding acids occur in tandem.

Scheme 1. Mechanism of Oxidative Cleavage of Styrene.



4. Conclusions

We have found that the cheap and environmentally-benign oxone can be employed directly for oxidative cleavage of a number of olefins that include dialkyl, diaryl and alkyl aryl olefins, cinnamic acids, cinnamyl alcohols, cinnamamides and chalcones to the corresponding acids. The oxidations proceed via initial dihydroxylation of olefins to the diols. Of course, the aldehydes that are produced undergo further

oxidation with oxone to the corresponding carboxylic acids under the employed conditions of reaction. The procedure that involves heating of the substrate in CH_3CN-H_2O (1:1, v/v) mixture with incremental addition of oxone is simple, convenient and cost-effective for a cascade oxidation of olefins, i.e., dihydroxylation, oxidative cleavage and oxidation of aldehydes, and thus should constitute an invaluable addition to the repertoire of transformations accomplished by oxone as a reagent.

5. Experimental Section

5.1. General

Solvents were distilled prior to use and double distilled water was used for all the reactions. All reactions were carried out in an open atmosphere without any precaution. The products were isolated by column chromatography with a silica gel of 100−200 μm particle size. NMR spectra were recorded with 400 and 500 MHz spectrometers.

5.2. General Procedure for the Oxidative Cleavage of Olefins. To a solution of the olefin (0.5-1.2 mmol) in 16 mL of acetonitrile-water (1:1) mixture at reflux was introduced oxone incrementally over the entire duration of the reaction. Progress of the reaction in each case was monitored by TLC analysis. After completion of the reaction as judged by TLC analysis, the reaction mixture was cooled to rt, and the organic matter was extracted with ethyl acetate. The combined organic extract was dried over anhyd Na_2SO_4 and concentrated in vacuo. The residue was subjected to a short-pad silica gel column chromatography to isolate pure product/s. All the products were characterized by their ^{1}H NMR spectral data.

5.2.1. Benzoic Acid.[9] Colorless solid; R_f (25% EtOAc/pet. ether) 0.37; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (t, J = 7.3, 2H), 7.62 (t, J = 7.8 Hz, 1H), 8.12 (d, J = 7.3 Hz, 2H).

5.2.2. *p*-Bromobenzoic Acid.[9] Colorless solid; R_f (50% EtOAc/pet. ether) 0.48; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.62 (d, J = 8.55 Hz, 2H), 7.96 (d, J = 8.55 Hz, 2H).

5.2.3. ***p*-Nitrobenzoic Acid.**[9] Colorless solid; R_f (10% CH_3OH/EtOAc) 0.32; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, J = 8.8 Hz, 2H), 8.33 (d, J = 8.8 Hz, 2H).

5.2.4. ***o*-Bromobenzoic Acid.**[9] Colorless solid; R_f (50% EtOAc/pet. ether) 0.49; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.43 (m, 2H), 7.72 (d, J = 8.2 Hz, 1H), 8.02 (dd, J_1 = 7.3 Hz, J_2 = 2.1 Hz, 1H).

5.1.5. **Adipic Acid.**[9] Colorless solid; R_f (10% MeOH/EtOAc) 0.24; mp 146-148 °C (lit. mp 147.5-149 °C). ^1H NMR (acetone-d_6, 500 MHz) δ 1.63-1.67 (m, 4H), 2.30-2.35 (m, 4H).

5.2.6. ***o*-Nitrobenzoic Acid.**[9] Colorless solid; R_f (10% CH_3OH/EtOAc) 0.31; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.73 (m, 2H), 7.86–7.92 (m, 2H).

5.2.7. ***p*-Cyanobenzoic Acid.**[9] Colorless solid; R_f (50% EtOAc/pet. ether) 0.19; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.98 (d, J = 8.6 Hz, 2H), 8.07 (d, J = 8.6 Hz, 2H).

5.2.8. ***p*-Bromoacetophenone.**[9] Colorless solid; R_f (10% EtOAc/pet. ether) 0.43; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.58 (s, 3H), 7.60 (d, J = 8. 5 Hz, 2H), 7.82 (d, J = 8.5 Hz, 2H).

5.2.9. **Terephthalic Acid.**[9] Colorless solid; R_f (10% CH_3OH/EtOAc) 0.2; ^1H NMR (DMSO-d_6, 500 MHz) δ 8.03 (s, 4H), 12.7 (bs, 2H).

5.2.10. **1-Phenylcyclohexane-1,2-diol.**[9] Colorless solid; R_f (50% EtOAc/pet. ether) 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 1.37-1.45 (m, 1H), 1.51-1.55 (m, 1H), 1.64-1.73 (m, 3H), 1.82-1.88 (m, 3H), 3.96-3.99 (m, 1H), 7.26 (t, J = 7.7 Hz, 1H), 7.37 (t, J = 7.4 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H).

5.2.11. **6-Phenyl-6-oxo-hexanoic Acid.**[7] Colorless solid; R_f (75% EtOAc/pet. ether) 0.4; ^1H NMR (400 MHz, $CDCl_3$) δ 1.74-1.81 (m, 4H), 2.42 (t, J = 6.9 Hz, 2H), 3.01 (t, J = 6.9 Hz, 2H), 7.45 (t, J = 7.7 Hz, 1H), 7.54 (t, J = 7.4 Hz, 2H), 7.95 (d, J = 8.7 Hz, 2H).

5.2.12. **1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione.**[16] Yellow solid; R_f (25% EtOAc/pet. ether) 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 3.99 (s, 3H), 6.98 (d, J = 8.8 Hz, 2H), 7.5 (t, J = 7.5 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.94-7.98 (m, 4H).

5.2.13. ***p*-Toluic Acid.**[17] Colorless solid; R_f (25% EtOAc/pet. ether) 0.37; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 7.4 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 8.1 Hz, 2H).

5.2.14. **4-Methoxybenzoic Acid.**[17] Colorless solid; R_f (50% EtOAc/pet. ether) 0.4; ^1H NMR (500 MHz, CDCl3) δ 3.88 (s, 2H), 6.95 (d, J = 9.0 Hz, 2H), 8.07 (d, J = 9.0 Hz, 2H).

5.1.15. *m*-Nitrobenzoic Acid.[17] Colorless solid; R_f (10% MeOH/EtOAc) 0.31; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.7 (m, 1H), 8.5 (m, 2H), 8.96 (m, 1H).

5.2.16. 1-Phenylethane-1,2-diol.[18] Colorless solid; R_f (50% EtOAc/pet. ether) 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66-3.74 (m, 2H), 4.82-4.84 (dd, 1H), 7.31-7.37 (m, 5H).

5.2.17. 1-(4-Tolyl)ethane-1,2-diol.[18] Colorless solid; R_f (50% EtOAc/pet. ether) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62-3.72 (m, 2H), 4.78 (m, 1H), 7.17-7.25 (m, 5H).

5.2.18. Phthalic Acid.[19] Colorless solid; R_f (25% MeOH/EtOAc) 0.2; ^{1}H NMR (500 MHz, $CDCl_3$+DMSO-d_6) δ 8.34 (b, 2H), 7.55-7.56 (m, 2H), 7.32-7.33 (m, 2H).

5.2.19. Isophthalic Acid.[19] Colorless solid; R_f (10% CH_3OH/EtOAc) 0.23; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.63 (t, J = 7.7 Hz, 1H), 8.16 (dd, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 2H), 8.48 (s, 1H).

5.2.20. Dodecanoic acid.[20] Colorless solid; R_f (50% EtOAc/pet. ether) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 6.6 Hz, 3H), 1.2-1.31(m, 1H), 1.61(m, 2H), 2.33 (t, J = 7.5 Hz, 2H).

5.2.21. *o*-Toluic acid.[19] Colorless solid; R_f (25% EtOAc/pet. ether) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (s, 3H), 7.26 (m, 2H), 7.45 (m, 1H), 8.06 (dd, J = 7.5 Hz, J_1 = 1.8 Hz, 1H).

5.2.22. 1-(*p*-Methoxyphenyl)ethane-1,2-diol.[18] Colorless solid; R_f (50% EtOAc/pet. ether) 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59-3.68 (m, 2H), 3.78 (s, 3H), 4.74 (q, J = 3.6 Hz, 1H), 6.87 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H).

5.2.23. 1-*o*-Tolylethane-1,2-diol.[18] Colorless solid; R_f (50% EtOAc/pet. ether) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.61-3.7 (m, 2H), 5.05 (m, 1H), 7.12 – 7.22 (m, 2H), 7.47 (2H, J = 7.32 Hz, 2H). .

5.2.24. *p*-Formylbenzoic acid.[21] Colorless solid; R_f (EtOAc) 0.25; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.02 (d, J = 8.6 Hz, 2H), 8.13 (d, J = 8.6 Hz, 2H), 10.1 (s, 1H).

Acknowledgments. JNM is thankful to the Department of Science and Technology, India for generous financial support. KNP gratefully acknowledges the senior research fellowship from CSIR, New Delhi.

Supplementary Data Available. ^{1}H and ^{13}C NMR spectral reproductions for the products of oxidations and ^{1}NMR spectral reproductions for monitoring of the oxidations of cinnamic acid, *p*-nitrocinnamic acid, stilbene, *4,4'*-dibromostilbene and chalcone.

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SUPPORTING INFORMATION

Oxidation Cascade with Oxone: Cleavage of Olefins to Carboxylic Acids

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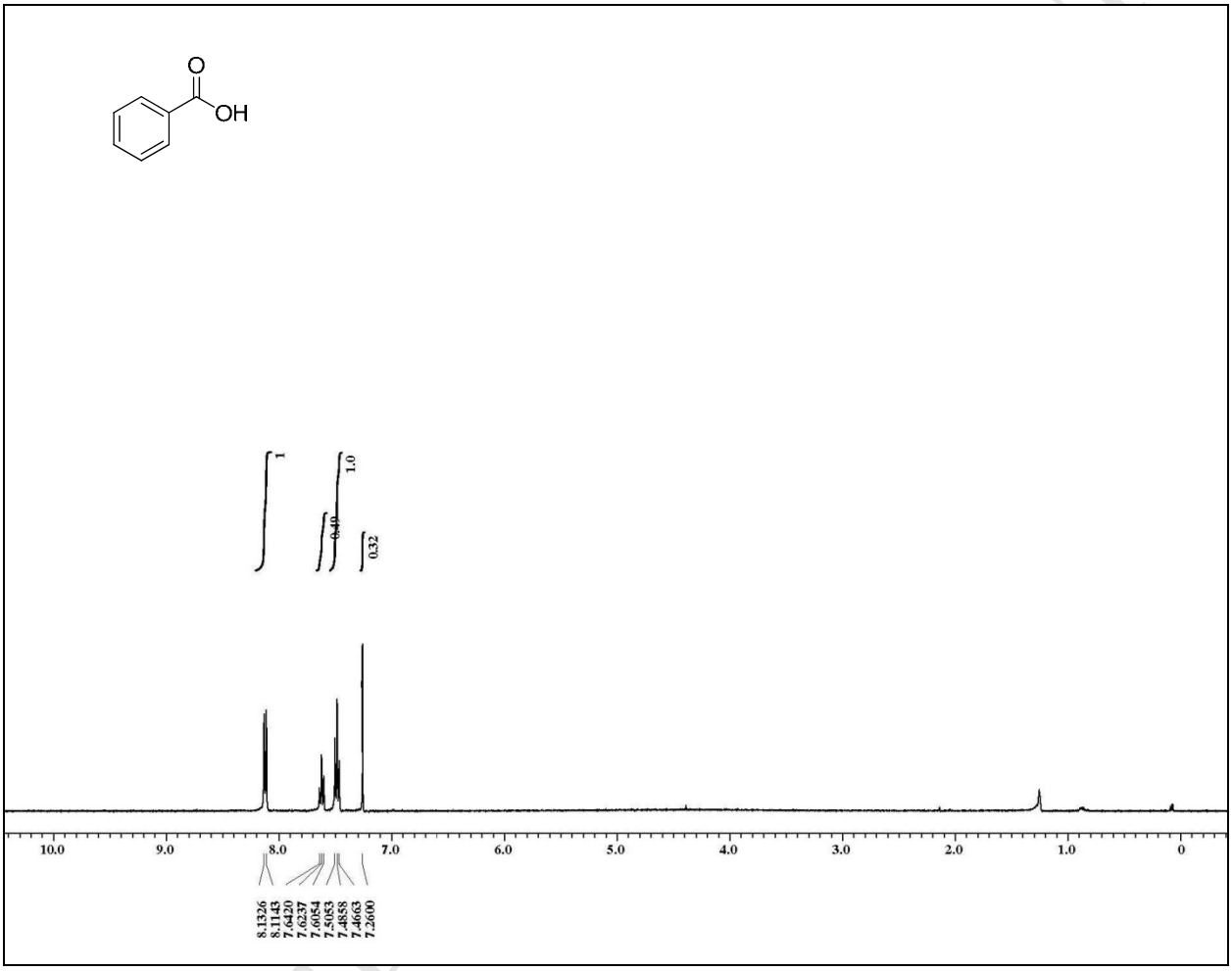


FIGURE S1. ^{1}H NMR spectrum of benzoic acid in $CDCl_3$.

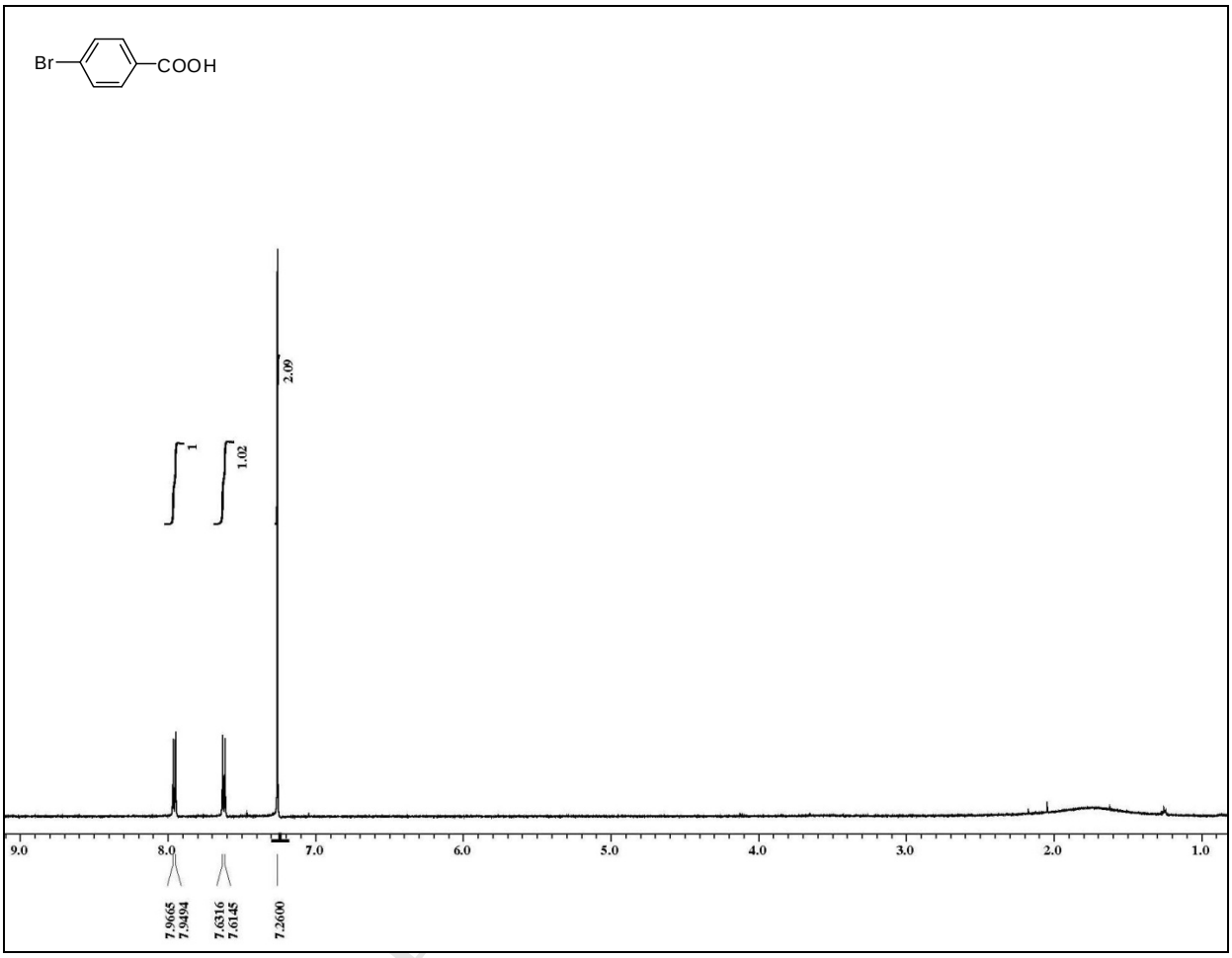


FIGURE S2. ^{1}H NMR spectrum of *p*-bromobenzoic acid in $CDCl_3$.

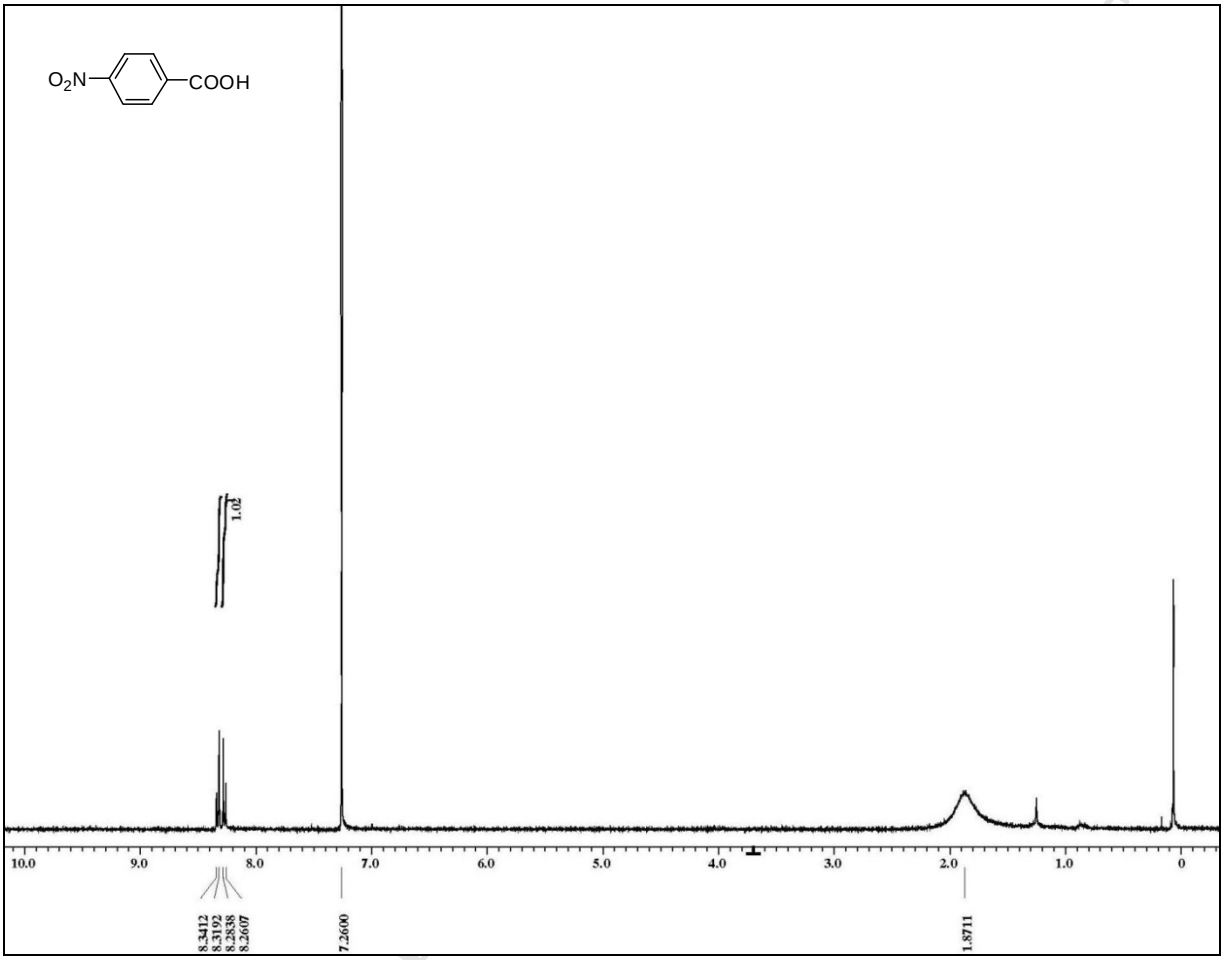
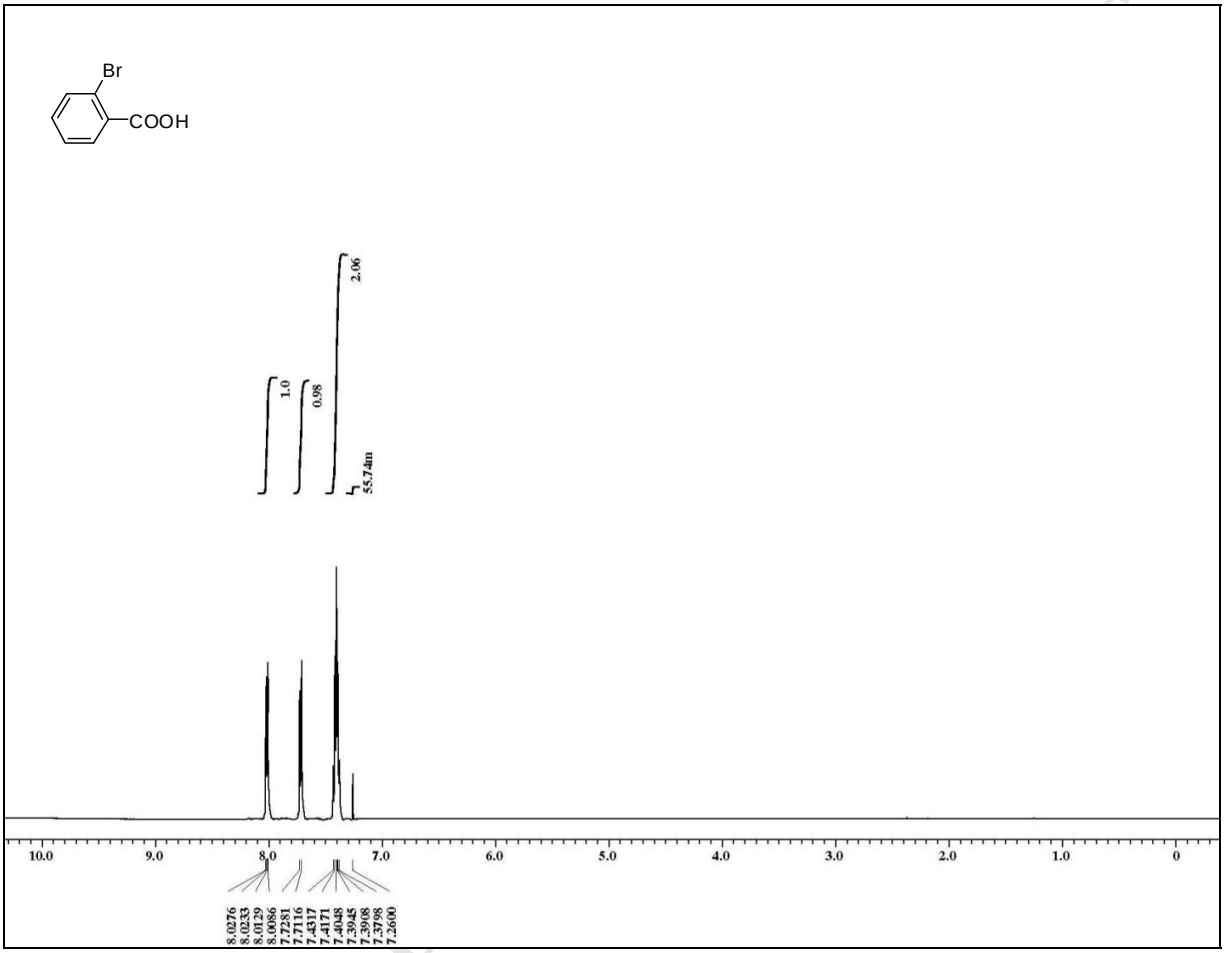


FIGURE S3. ^{1}H NMR spectrum of *p*-nitrobenzoic acid in $CDCl_3$.



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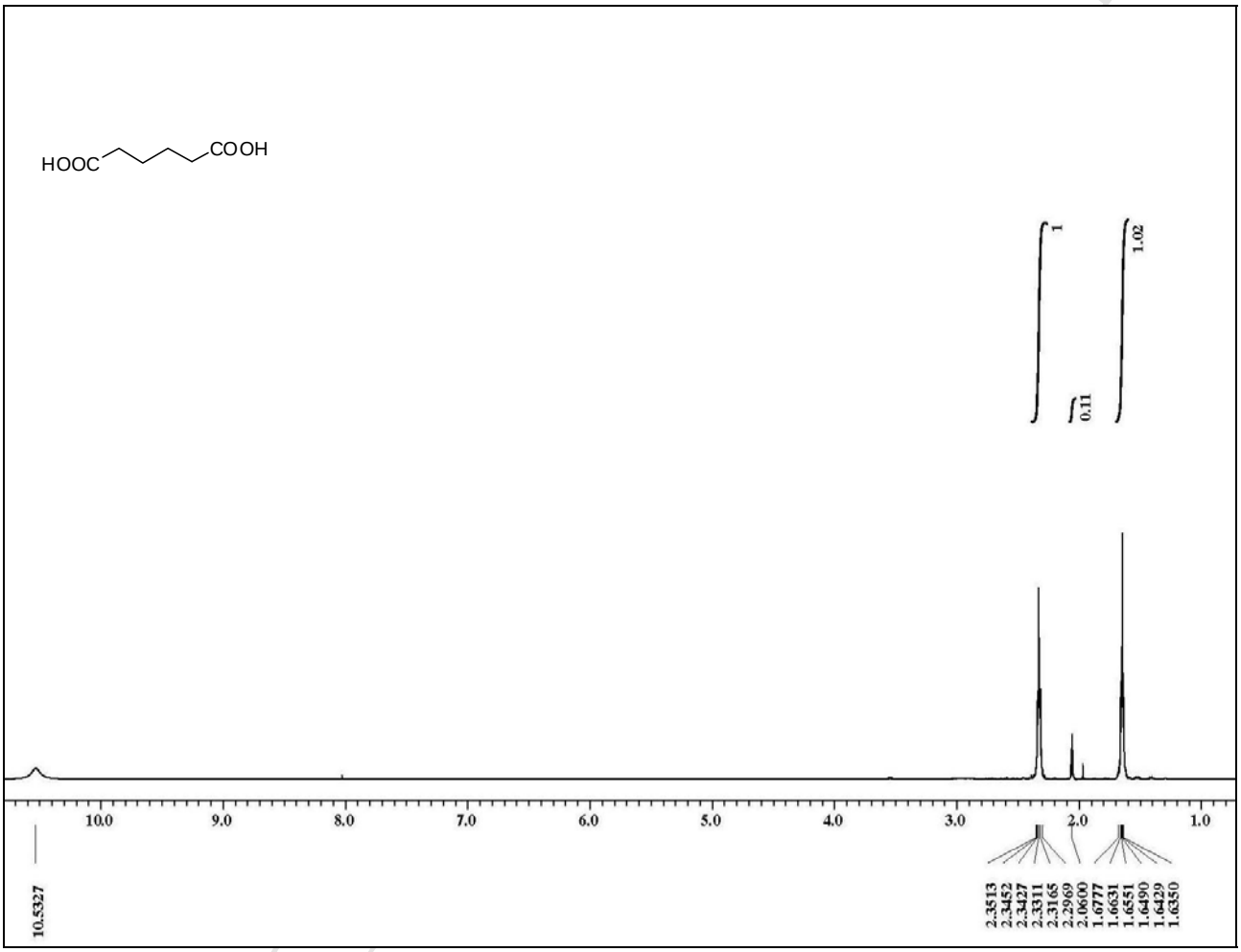

FIGURE S5. ^{1}H NMR spectrum of hexane-1,6-dicarboxylic acid in acetone-d_6.

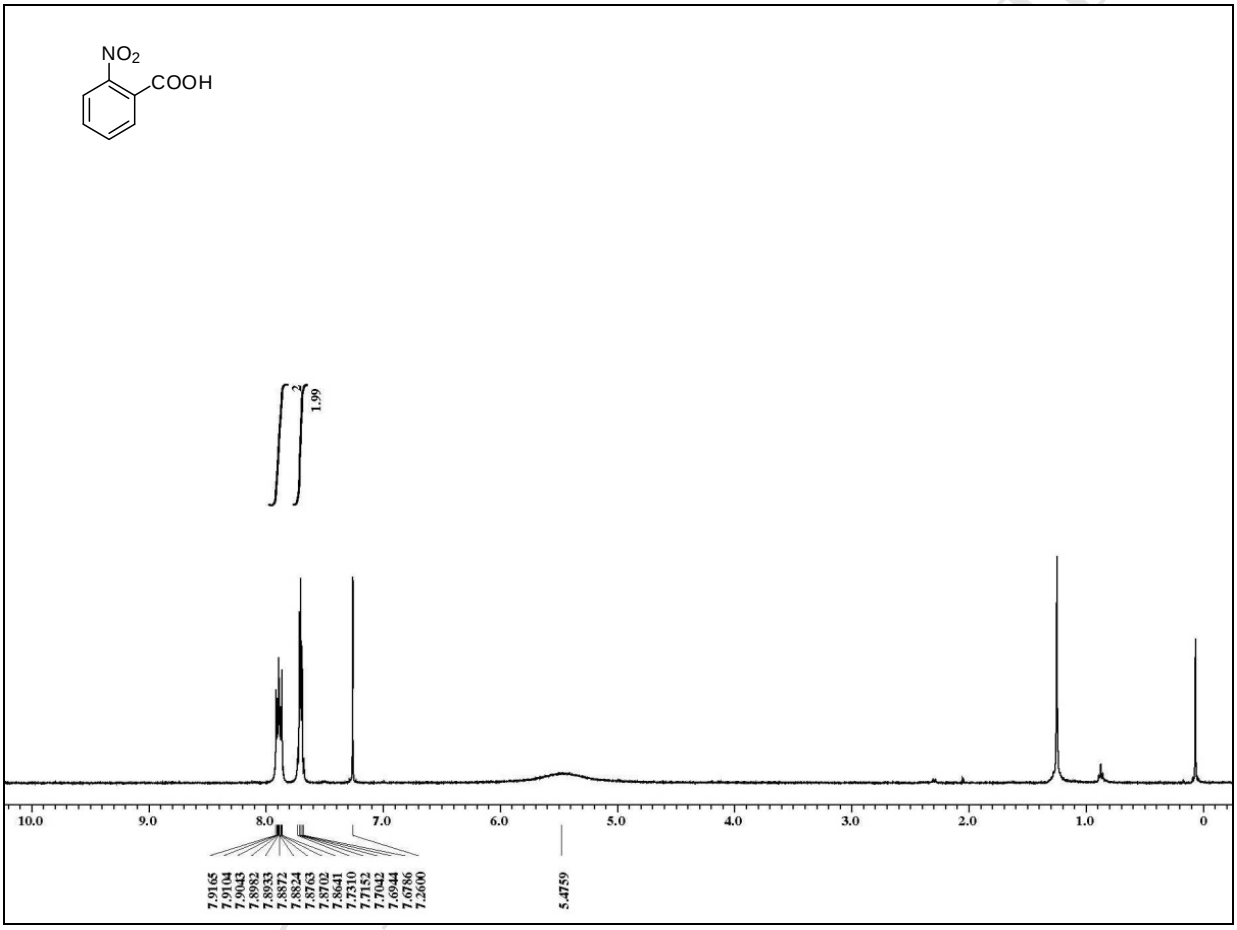

FIGURE S6. ^{1}H NMR spectrum of *o*-nitrobenzoic acid in $CDCl_3$.

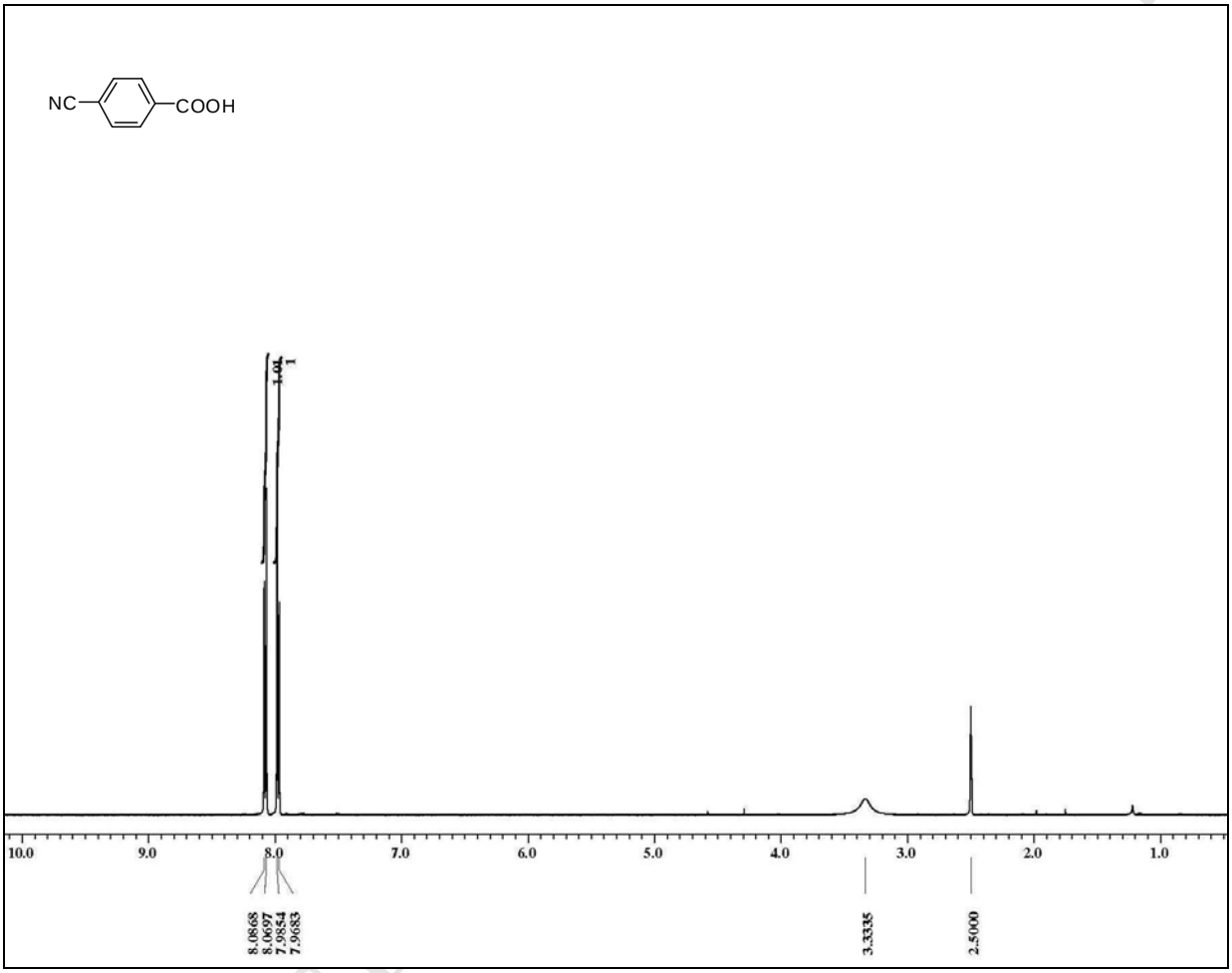

FIGURE S7. ^{1}H NMR spectrum of *p*-cyanobenzoic acid in DMSO-d_6.

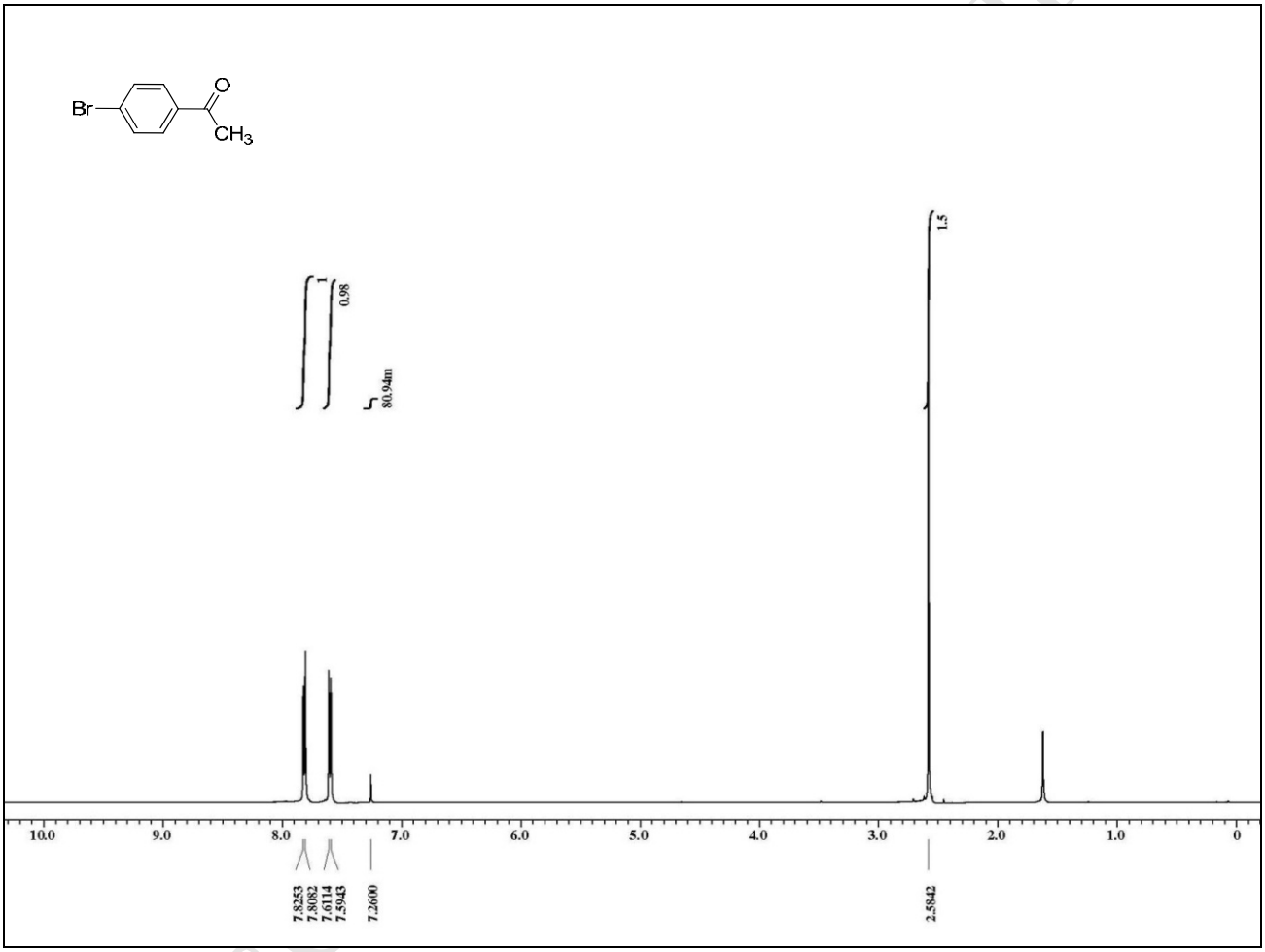

FIGURE S8. ^{1}H NMR spectrum of *p*-bromoacetophenone in $CDCl_3$.

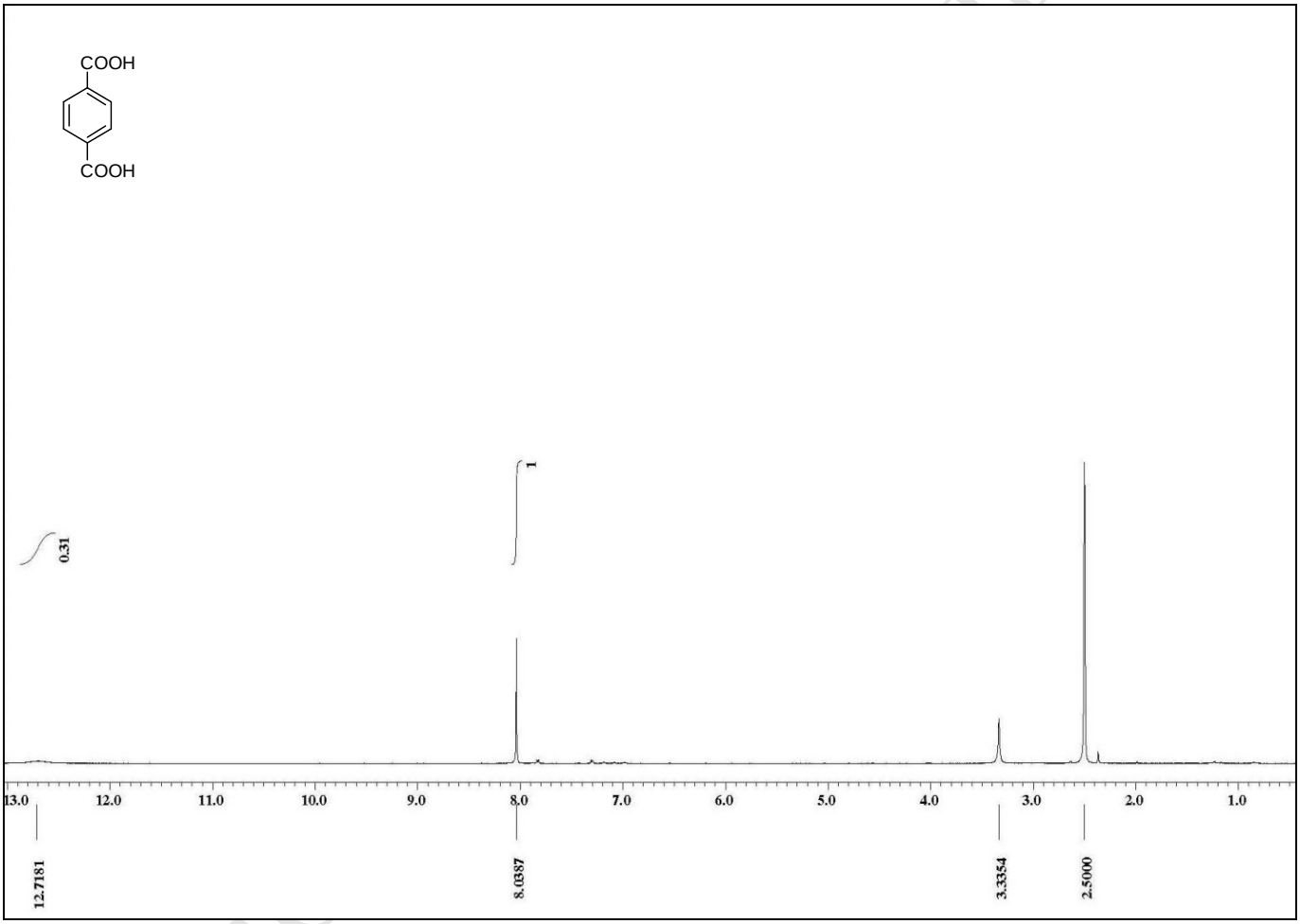

FIGURE S9. ^{1}H NMR spectrum of benzene-1,4-dicarboxylic acid in DMSO-d_6.

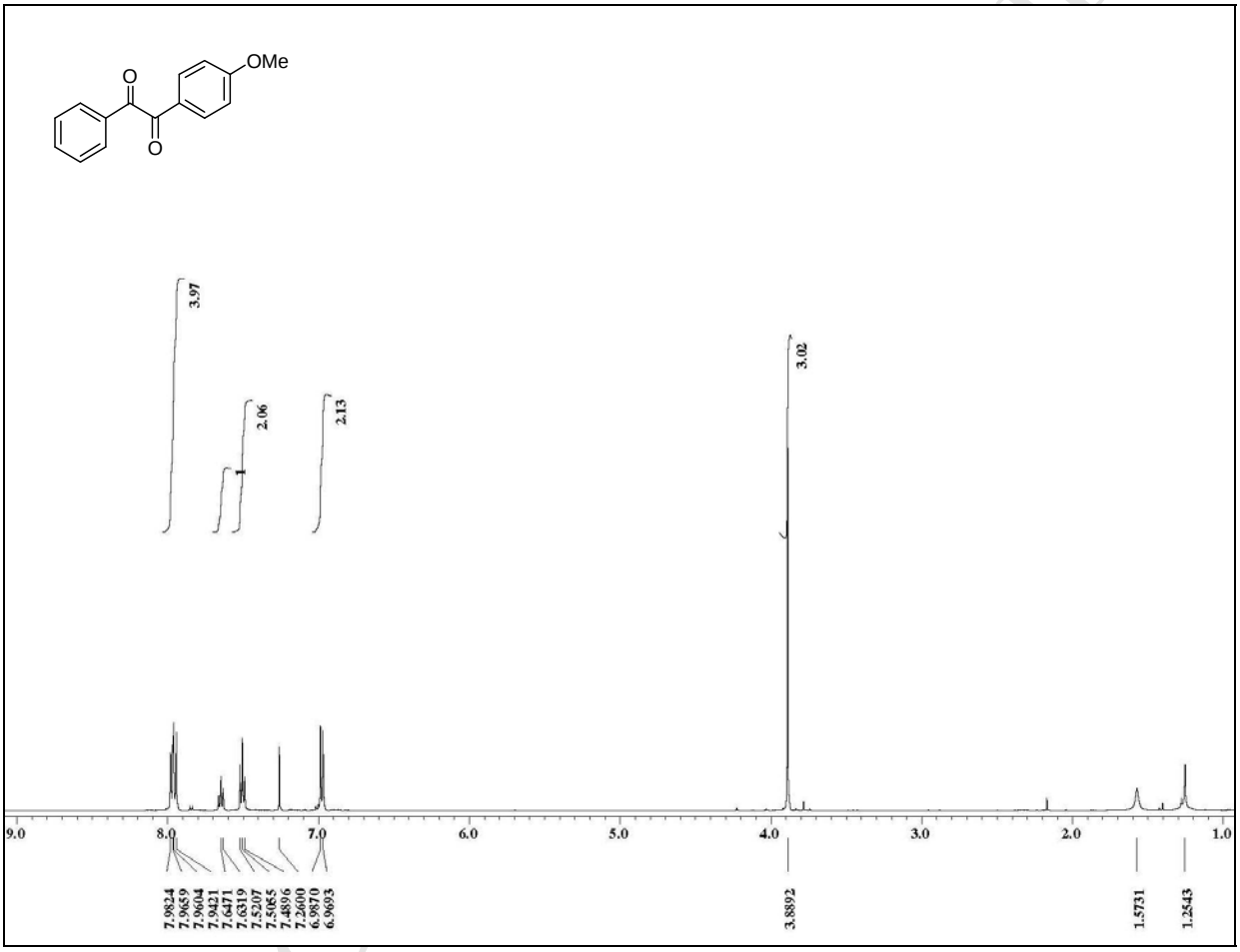

FIGURE S10. ^{1}H NMR spectrum of 1-(4-methoxyphenyl)-2-phenylethane-1,2-dione in $CDCl_3$.

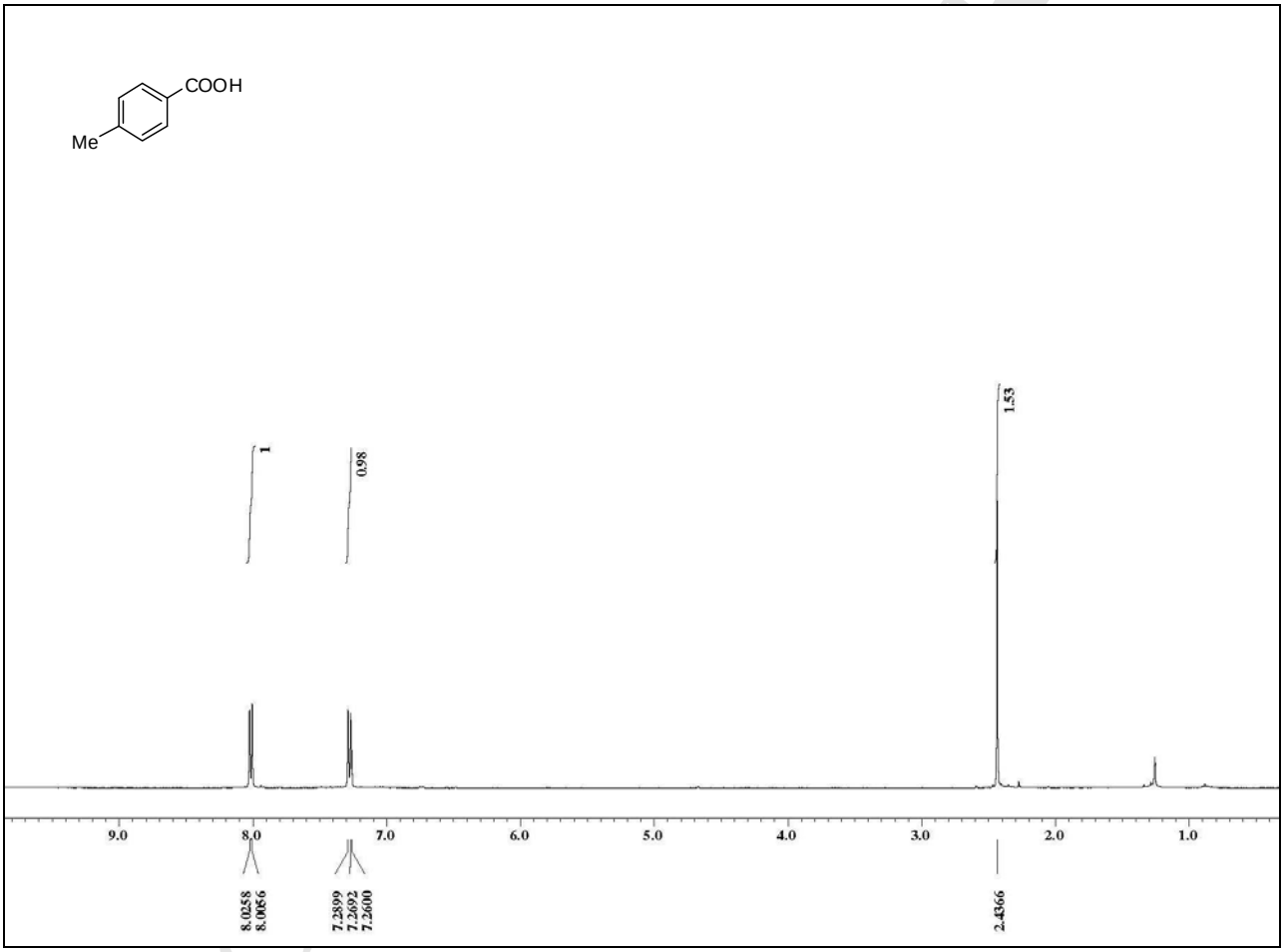

FIGURE S11. ^{1}H NMR spectrum of 4-toluic acid in $CDCl_3$.

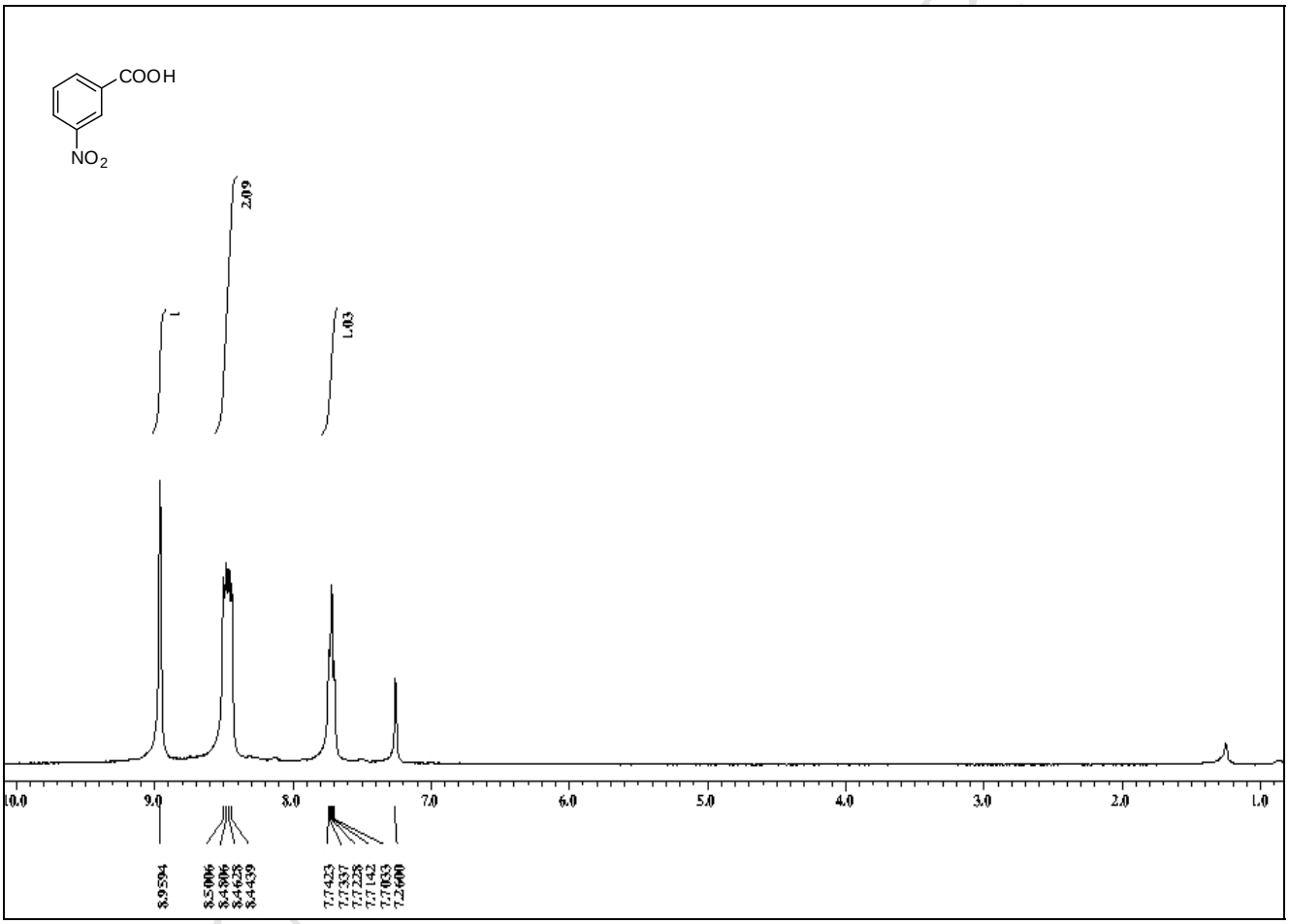

FIGURE S12. ^{1}H NMR spectrum of 4-nitrobenzoic acid in $CDCl_3$.

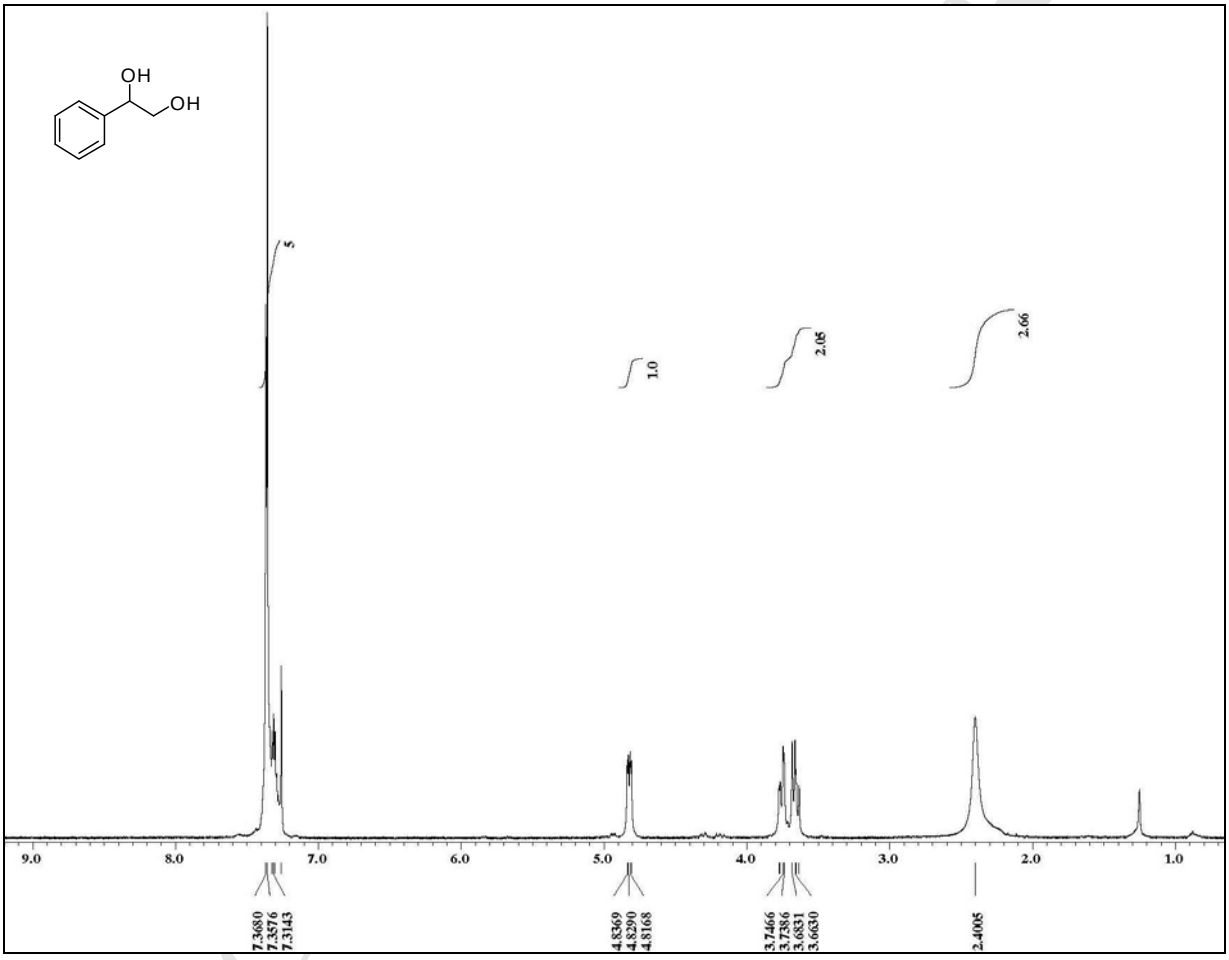

FIGURE S13. ^{1}H NMR spectrum of 1-phenylethane-1,2-diol in $CDCl_3$.

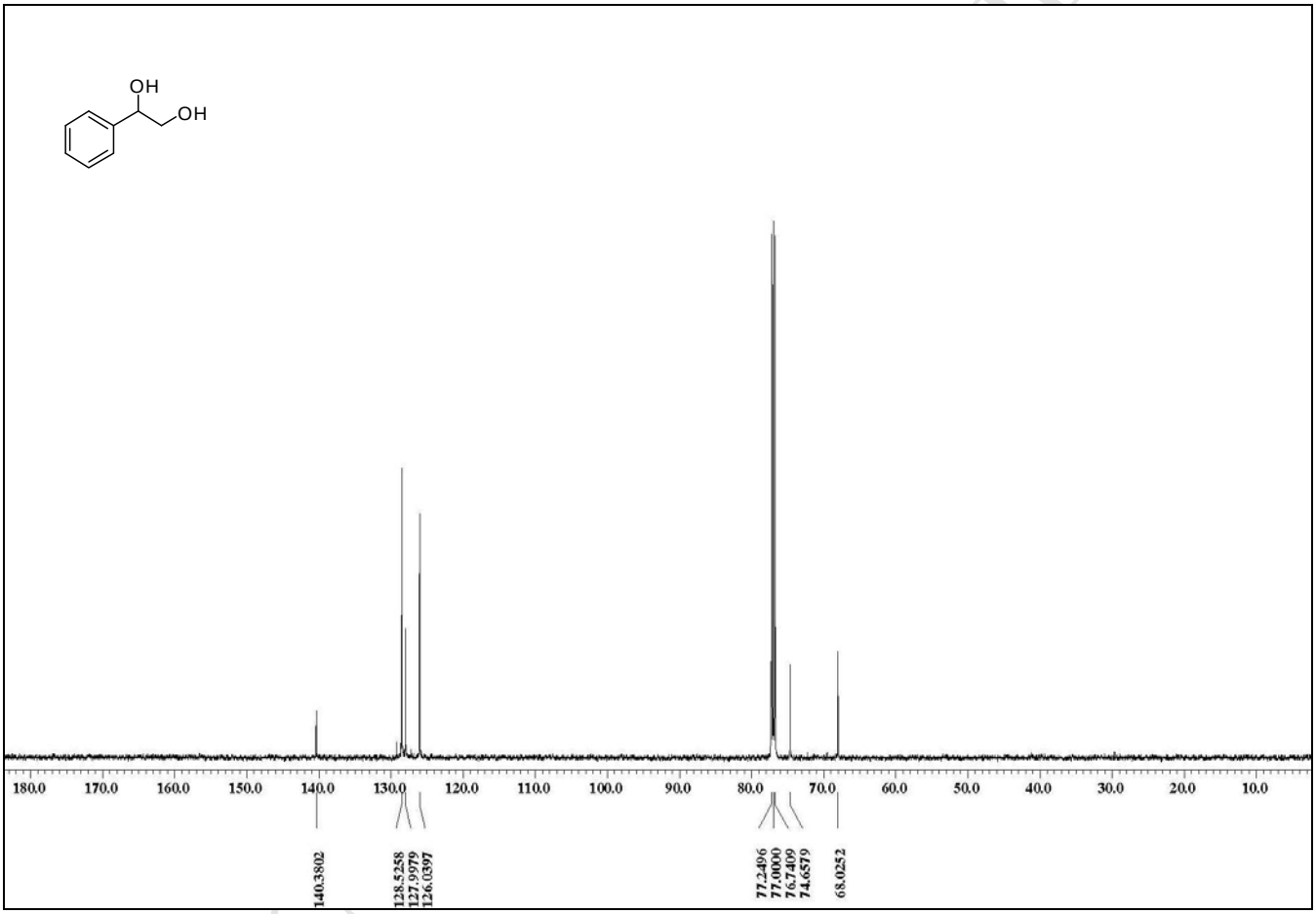

FIGURE S14. ^{13}C NMR spectrum of 1-phenylethane-1,2-diol in $CDCl_3$.

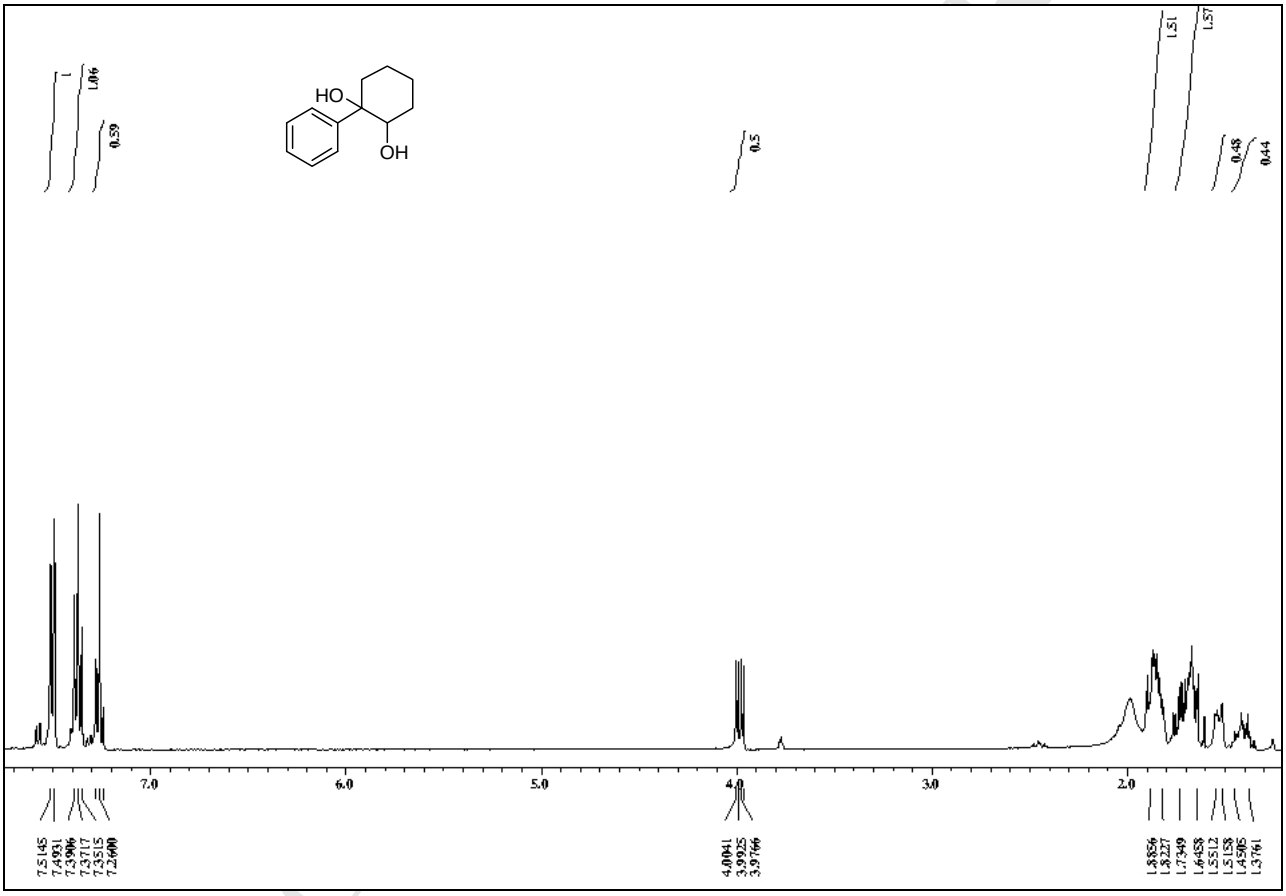

FIGURE S15. ^{1}H NMR spectrum of 1-phenylcyclohexane-1,2-diol in $CDCl_3$.

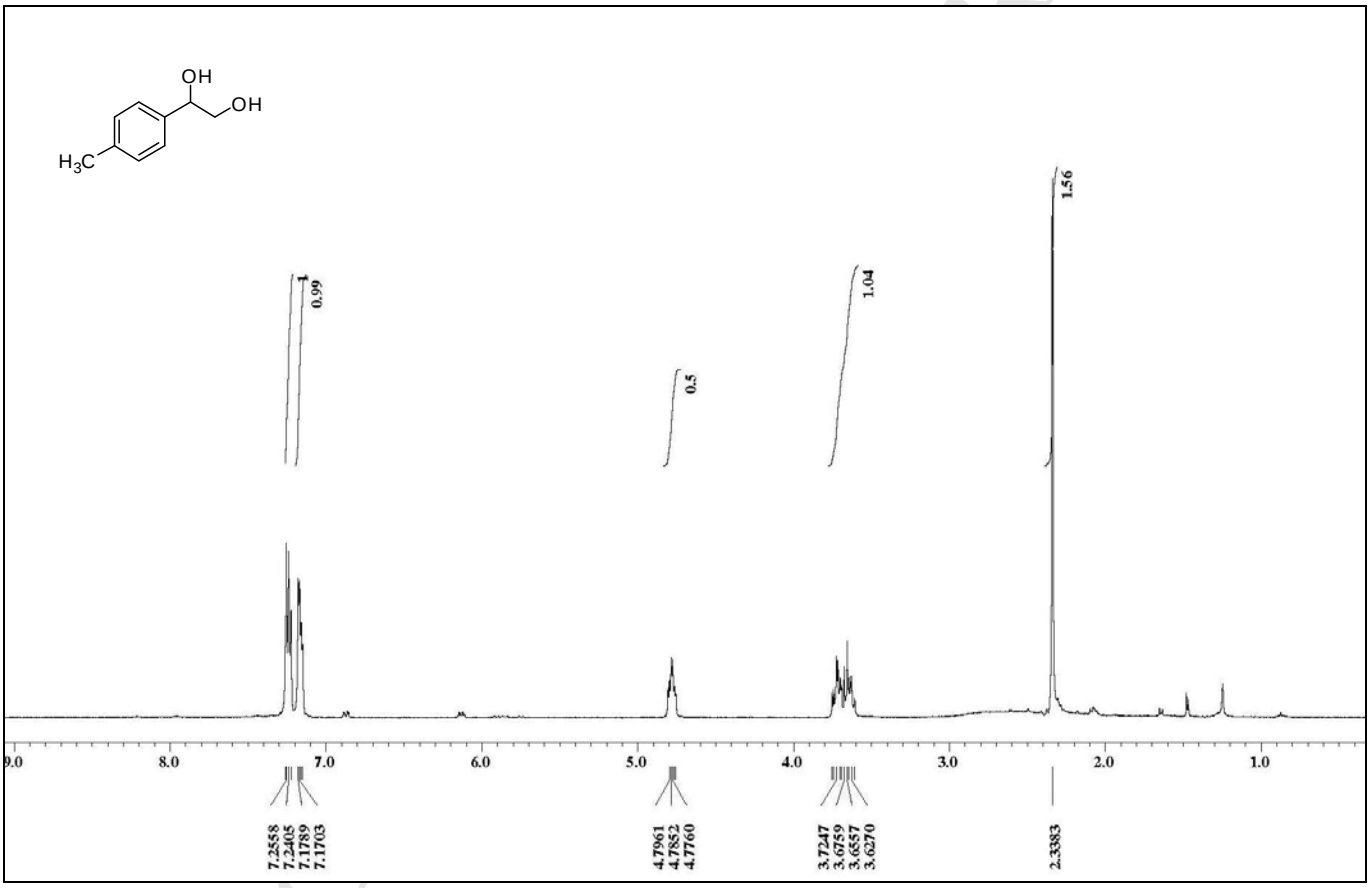

FIGURE S16. ^{1}H NMR spectrum of 1-(4-tolyl)ethane-1,2-diol in $CDCl_3$.

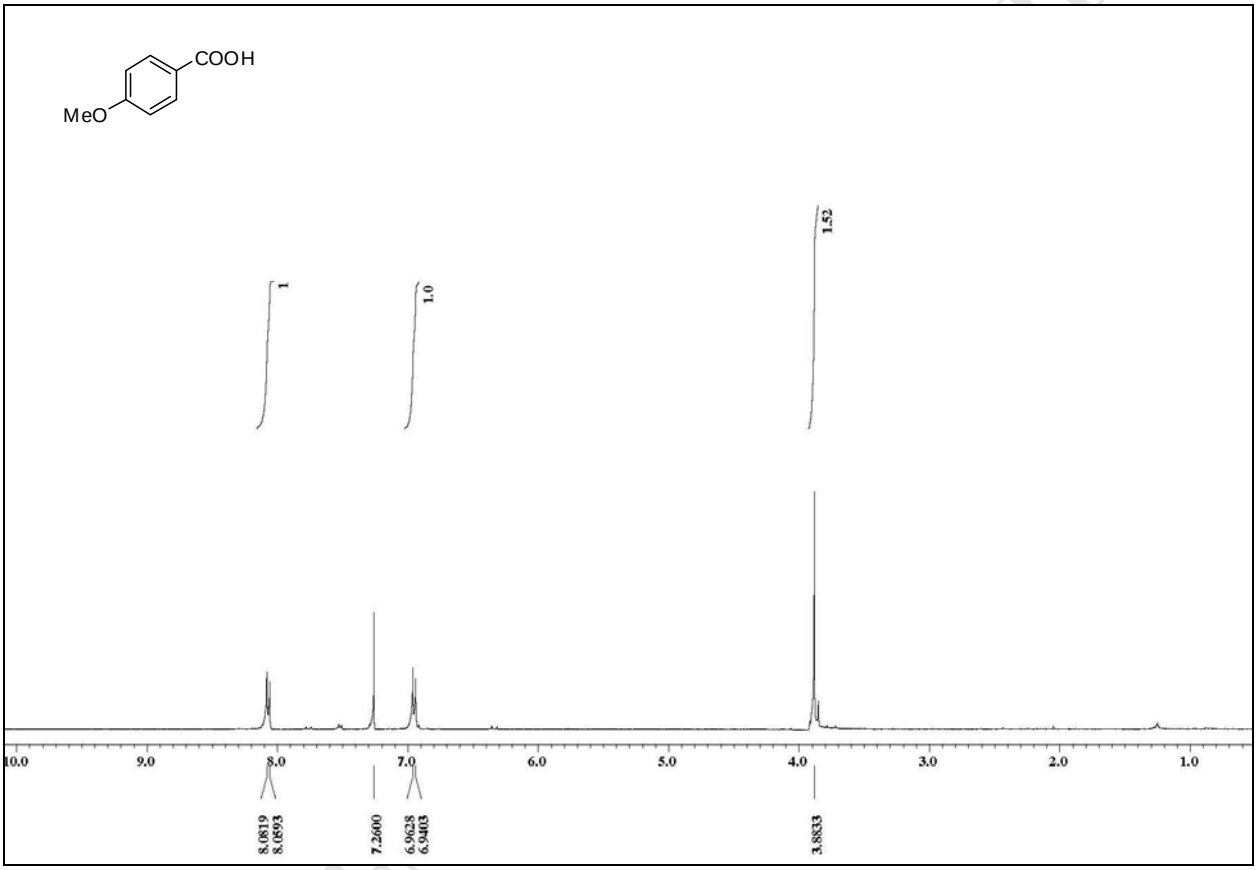

FIGURE S17. ^{1}H NMR spectrum of 4-methoxy benzoic acid in $CDCl_3$.

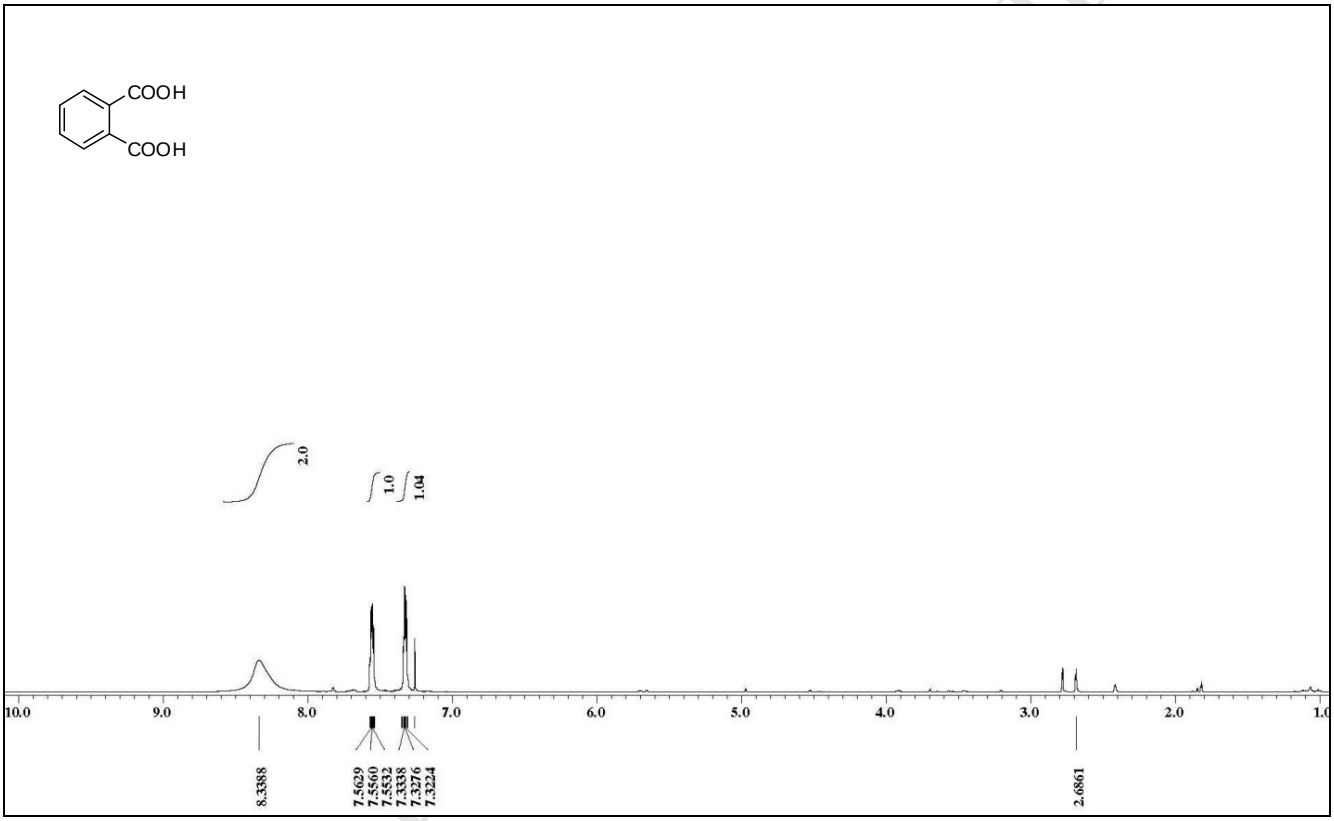

FIGURE S18. ^{1}H NMR spectrum of *o*-phthalic acid acid in $CDCl_3$+DMSO-d_6.

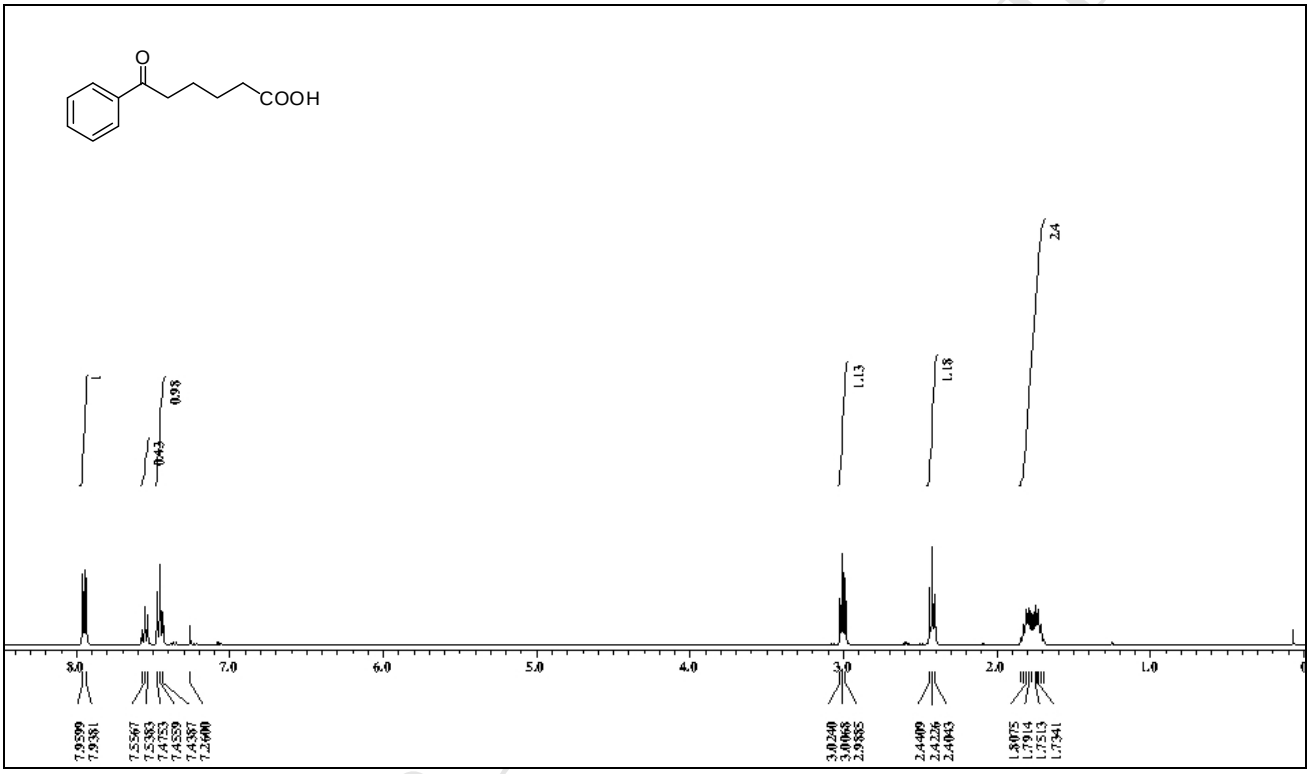

FIGURE S19. ^{1}H NMR spectrum of 6-phenyl-6-oxo-hexanoic acid in $CDCl_3$.

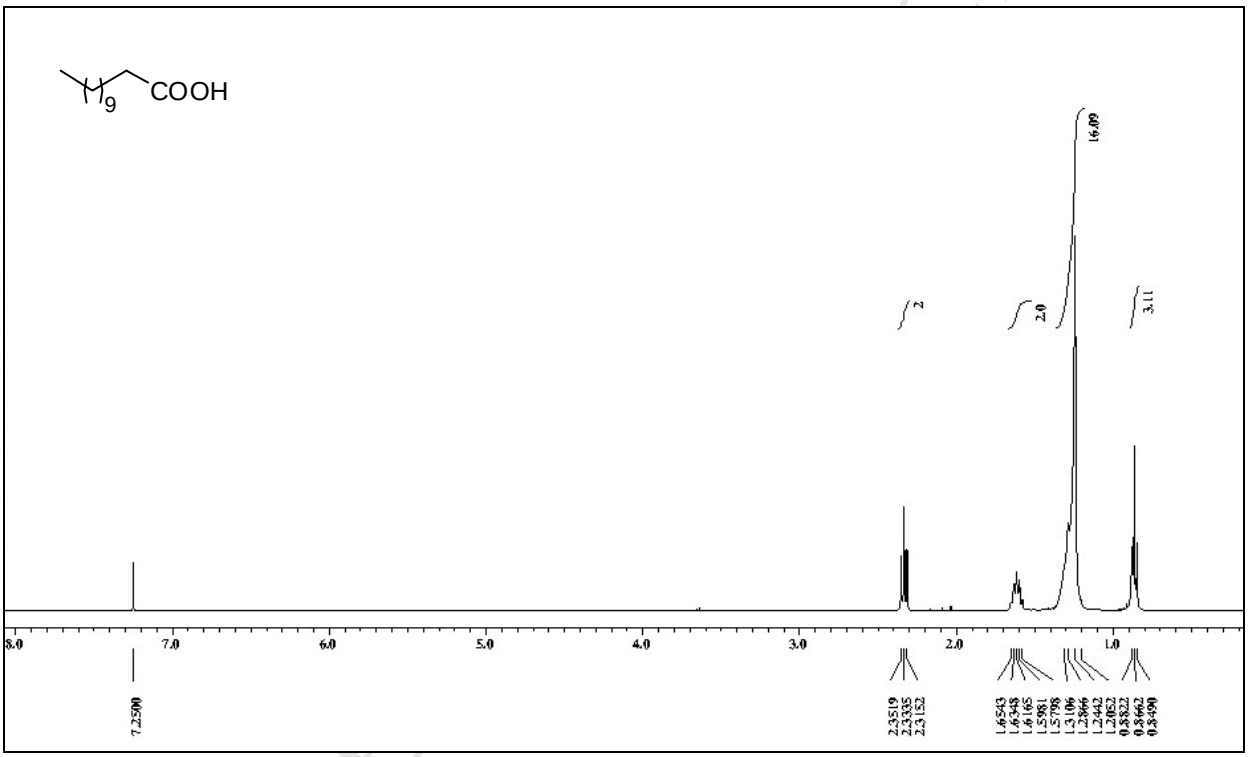

FIGURE S20. ^{1}H NMR spectrum of dodecanoic acid in $CDCl_3$.

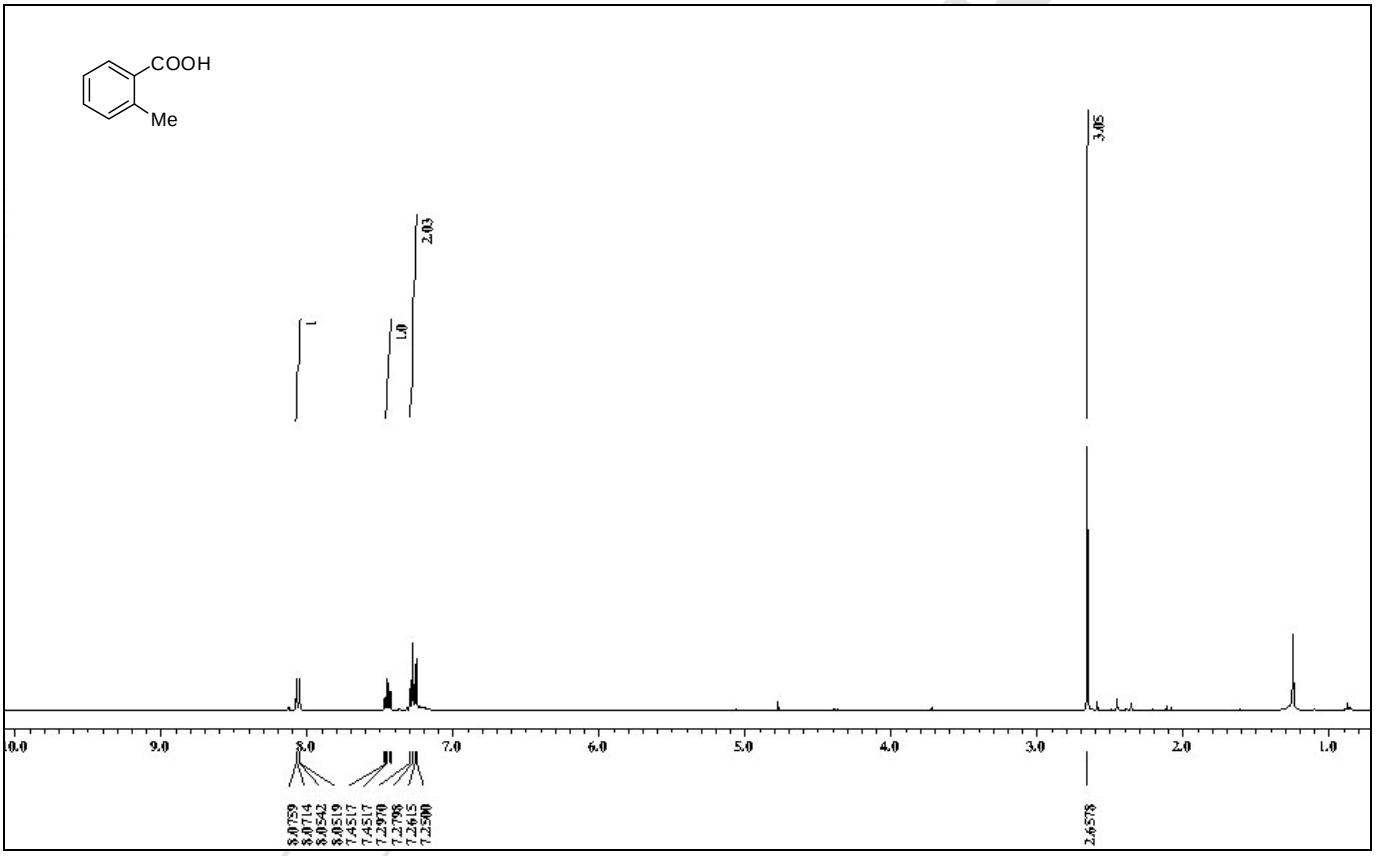

FIGURE S21. ^{1}H NMR spectrum of *o*-toluic acid in $CDCl_3$.

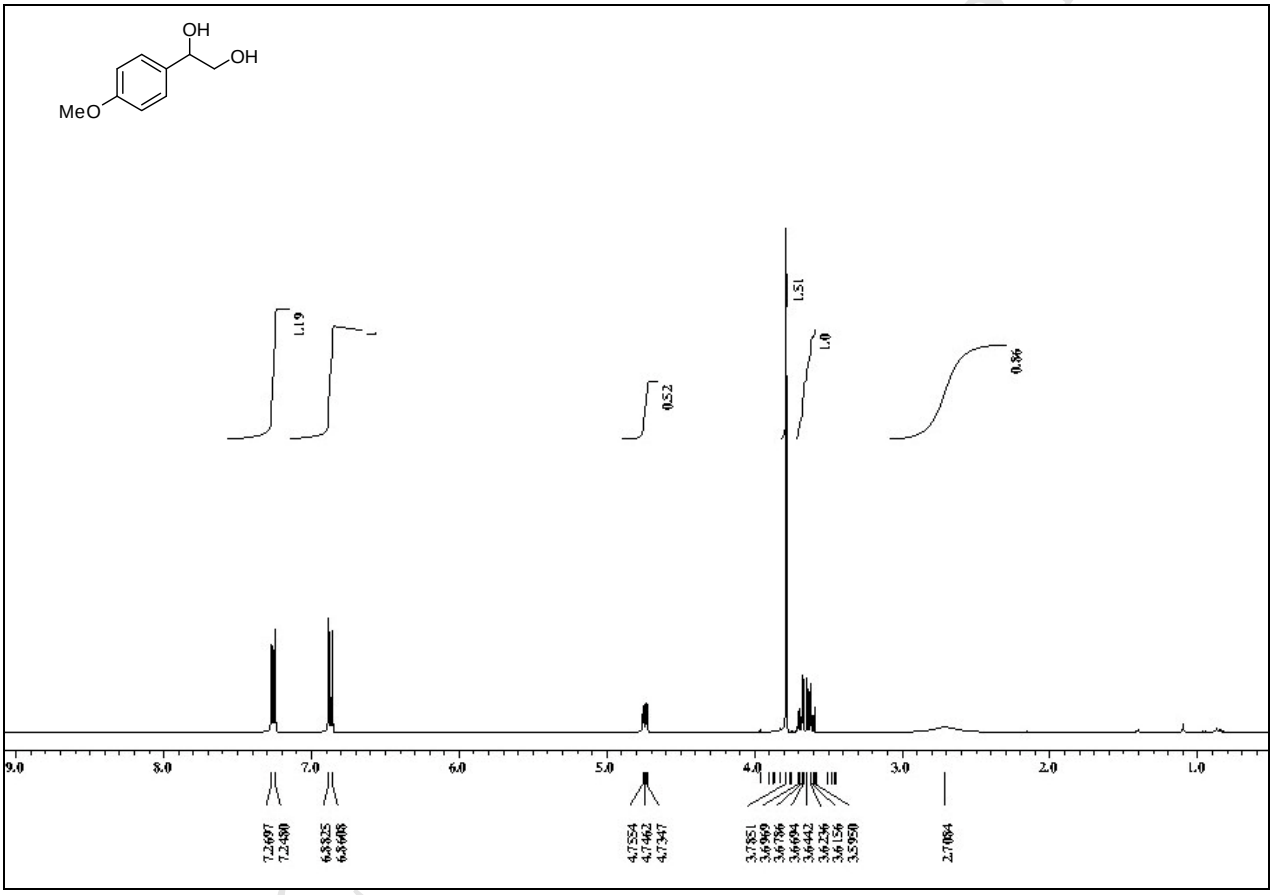

FIGURE S22. ^{1}H NMR spectrum of 1-(*p*-methoxyphenyl)ethane-1,2-diol in $CDCl_3$.

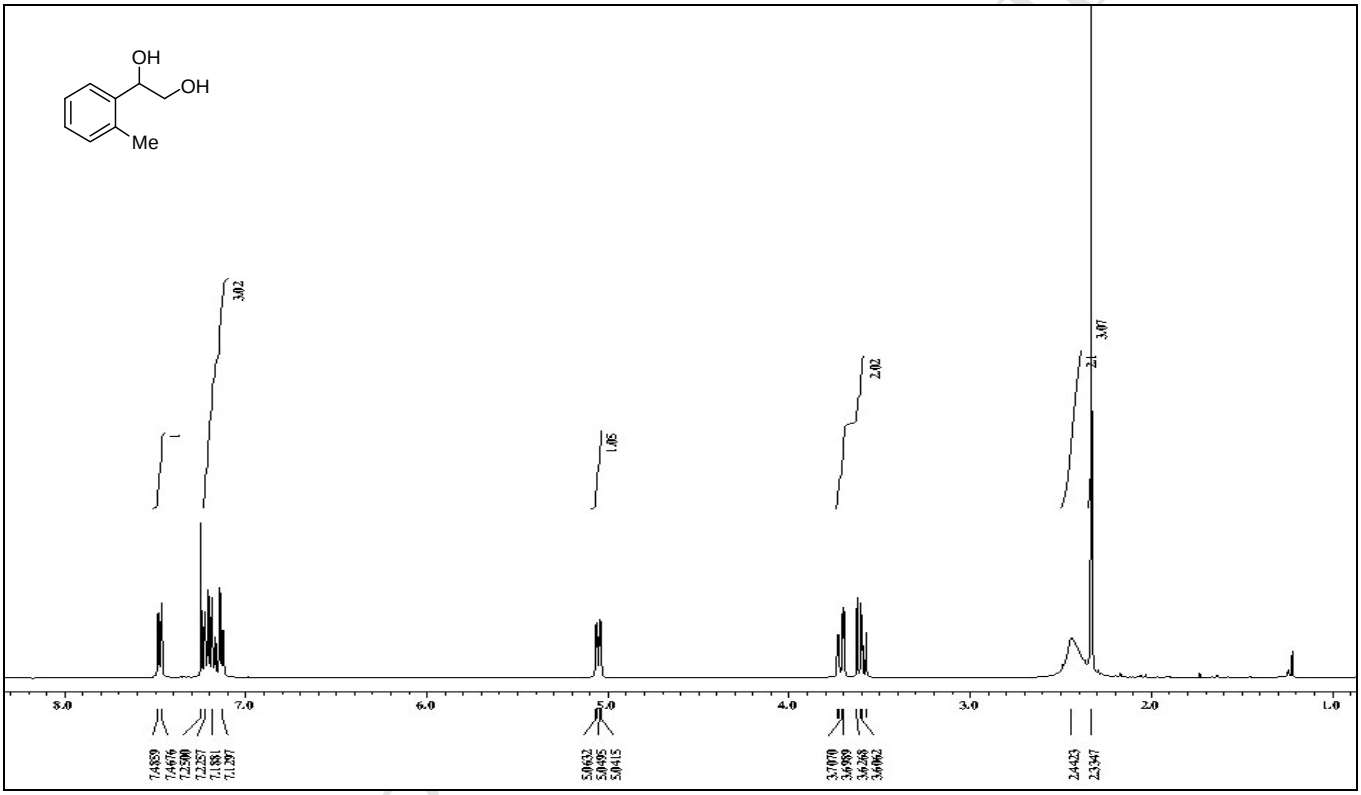

FIGURE S23. ^{1}H NMR spectrum of 1-*o*-tolylethane-1,2-diol in $CDCl_3$.

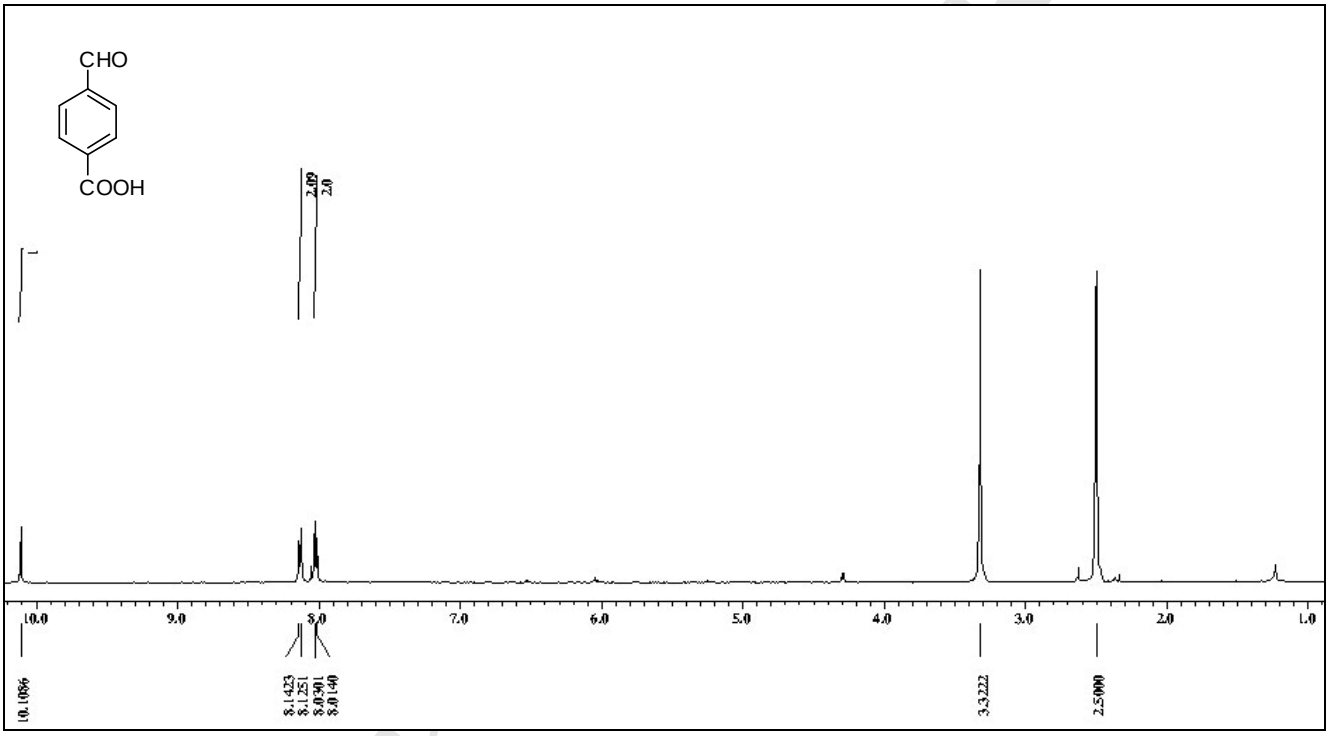

FIGURE S24. ^{1}H NMR spectrum of *p*-formylbenzoic acid in DMSO-d_6.

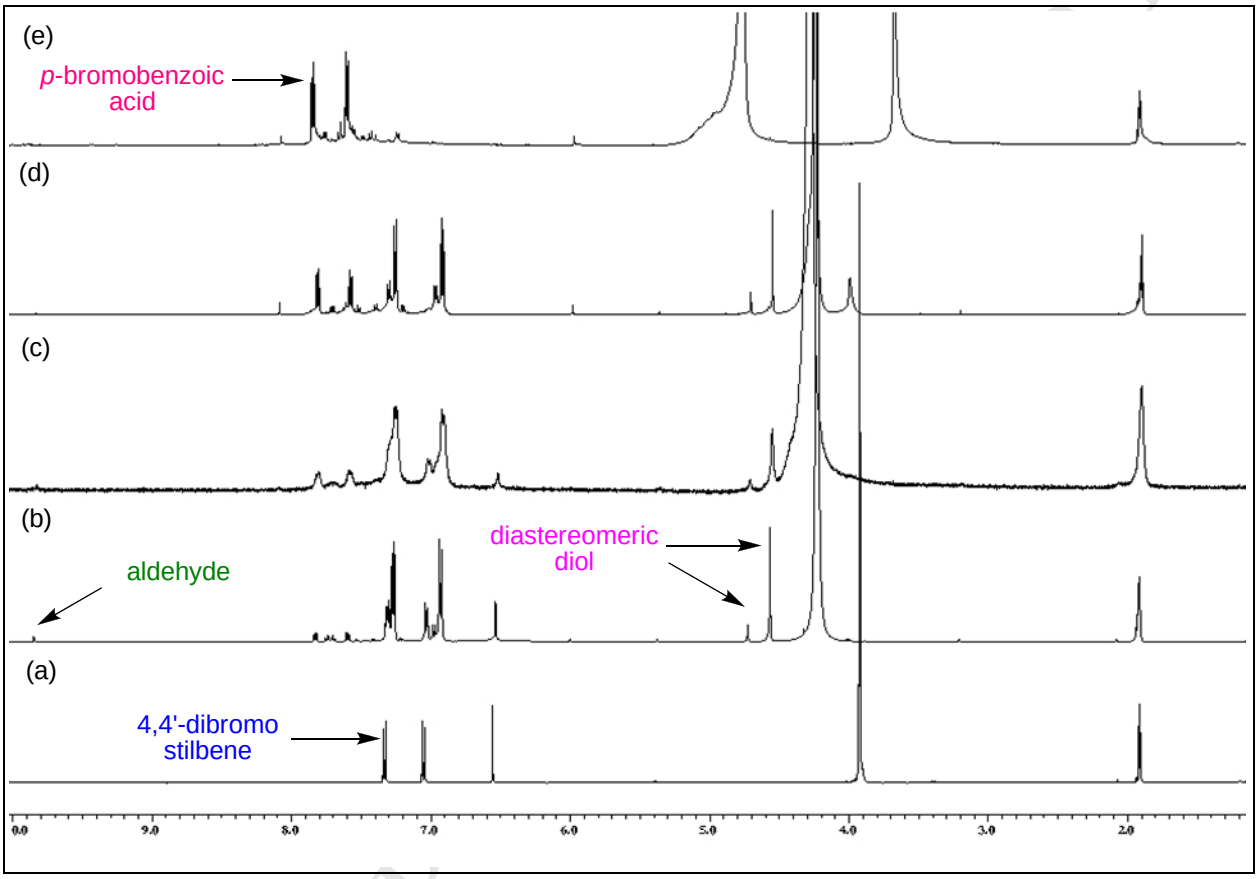

FIGURE S25. ^{1}H Monitoring of oxidation of *4,4'*-dibromostilbene in CD_3CN-D_2O (1:1) with oxone (5 equiv) at reflux. [a] 0 h, before addition of oxone, [b] after 2 h, [c] after 4 h, [d] after 10 h and [e] after 24 h.

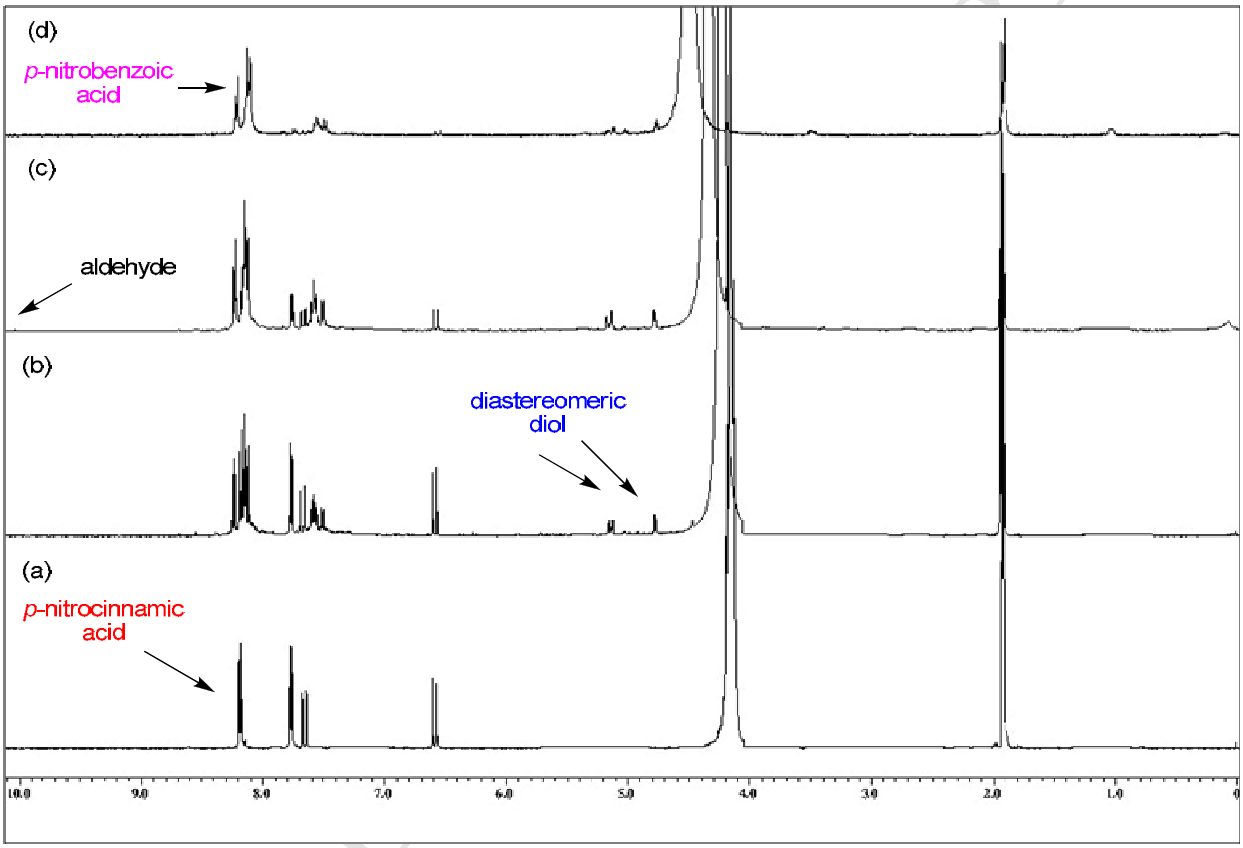

FIGURE S26. ^{1}H Monitoring of the oxidation of *p*-nitrocinnamic acid in CD_3CN-D_2O (1:1) with oxone (5 equiv) at reflux. [a] Before addition of oxone, 0 h [b] after 2h, [c] after 4 h and [d] after 10 h.

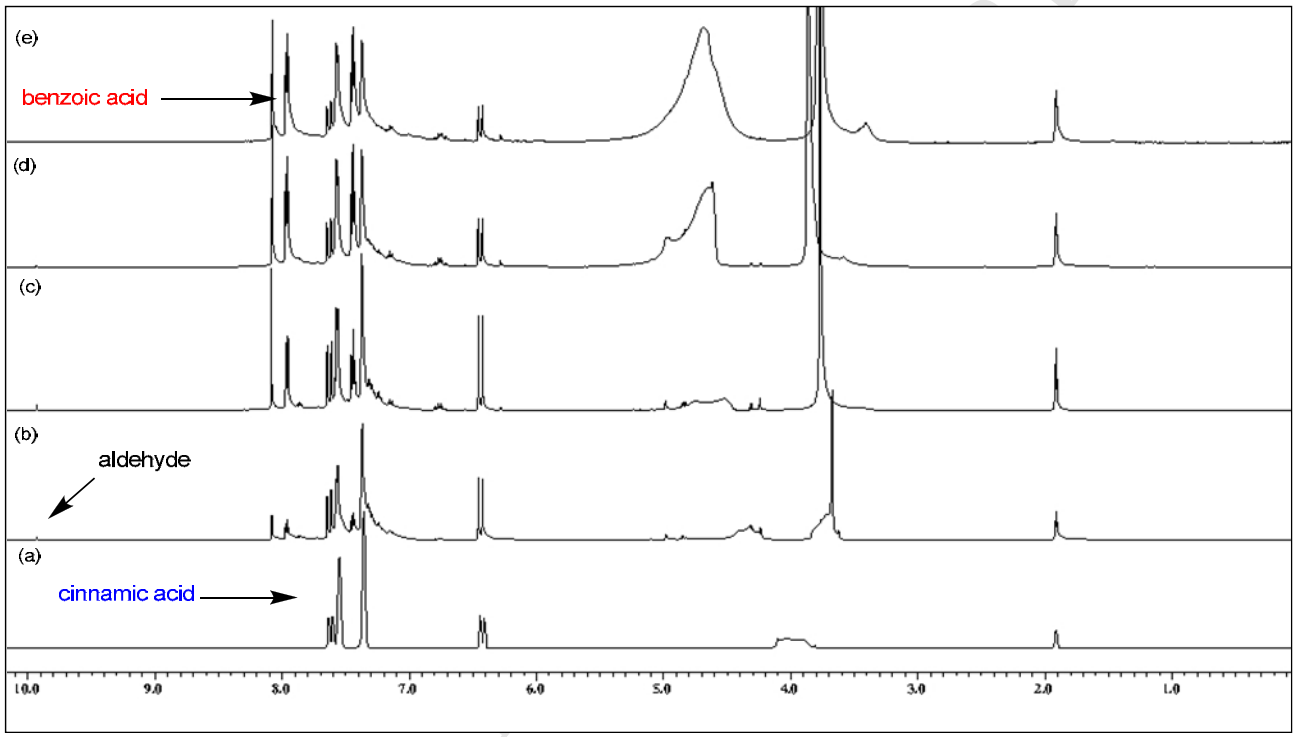

FIGURE S27. ^{1}H NMR Monitoring of the oxidation of cinnamic acid in CD_3CN-D_2O (1:1) with oxone (5 equiv) at reflux. [a] Before addition of oxone, 0 h, [b] after 2h, [c] after 4 h, [d] after 10 h and [e] after 20 h.

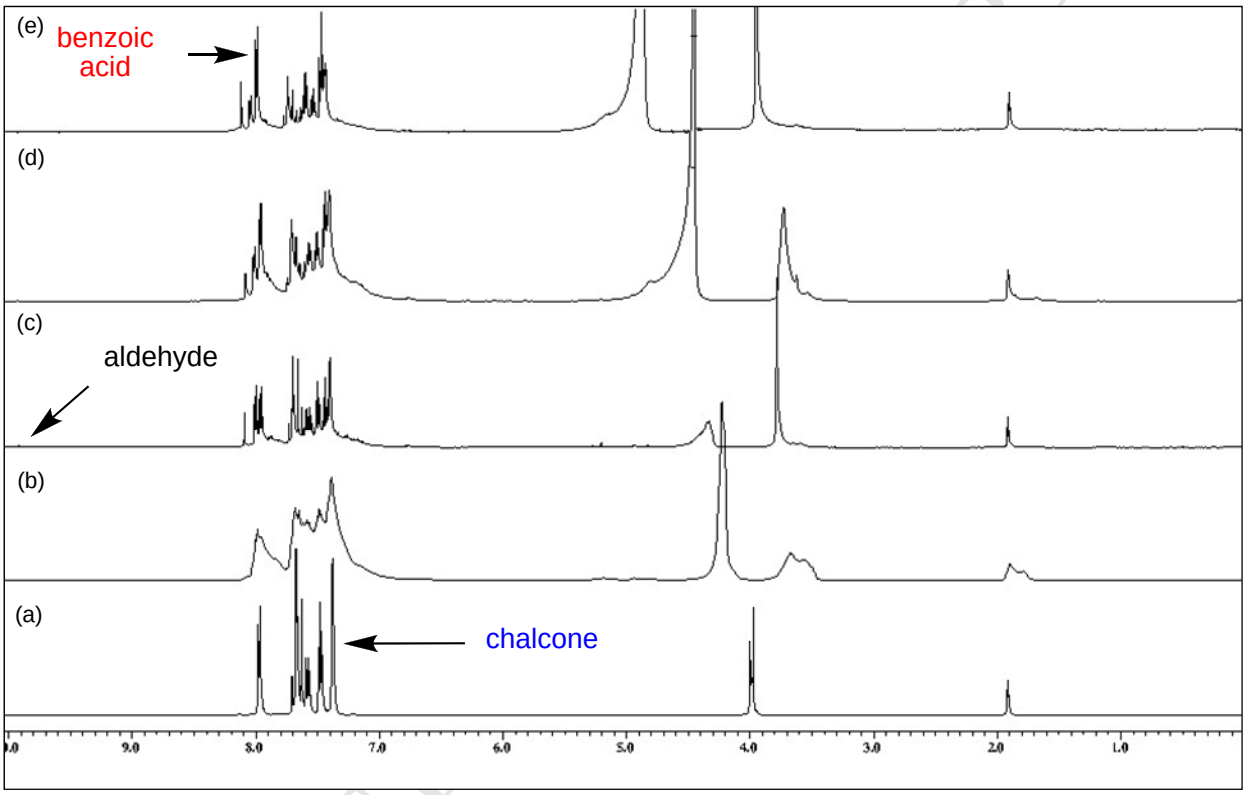

FIGURE S28. ^{1}H NMR monitoring of the oxidation of chalcone in CD_3CN-D_2O (1:1) with oxone (5 equiv) at reflux. [a] Before addition of oxone, 0 h, [b] after 2 h, [c] after 4 h, [d] after 10 h, and [e] after 24 h.

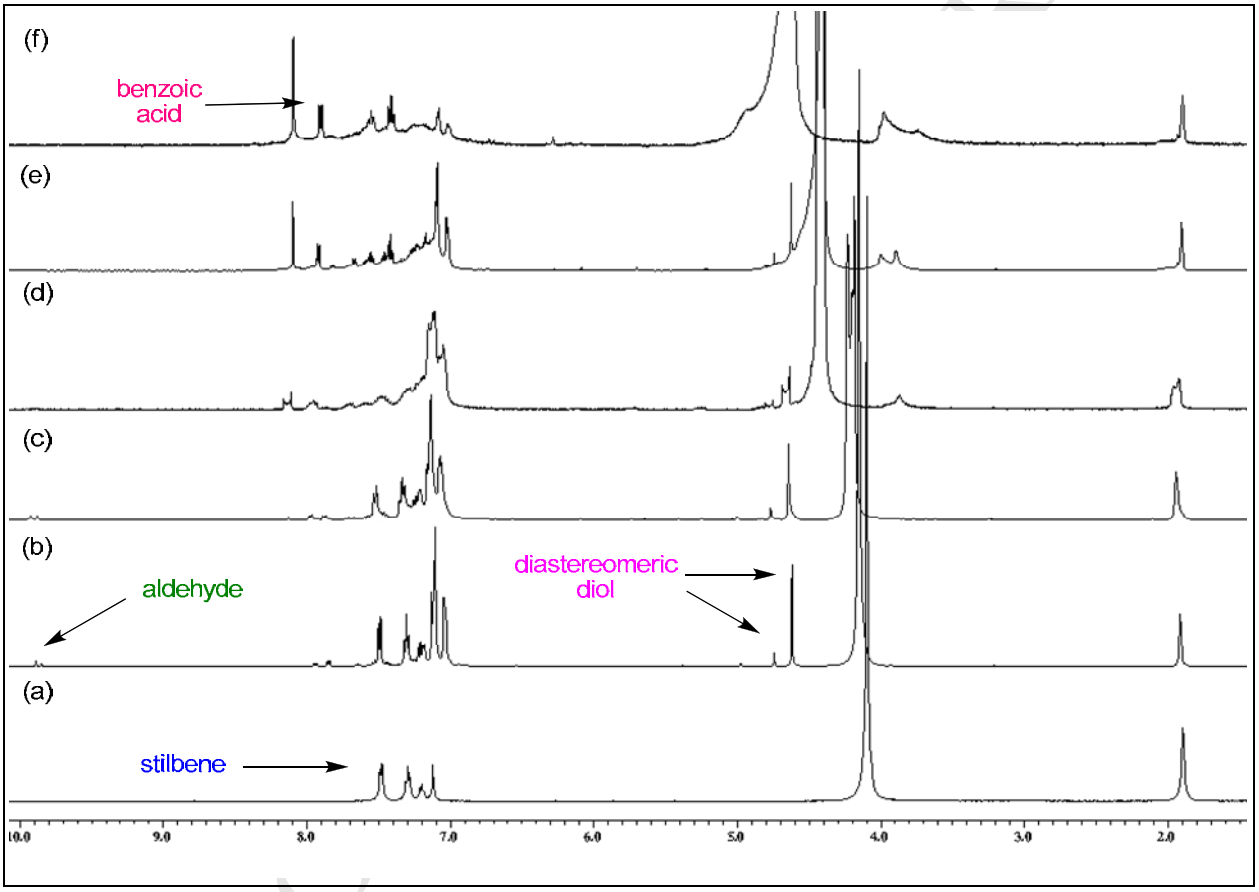

FIGURE S29. ^{1}H NMR monitoring of the oxidation of stilbene in CD_3CN-D_2O (1:1) with oxone (5 equiv) at reflux. [a] Before addition of oxone, 0 h, [b] after 2 h, [c] after 4 h, [d] after 10 h, [e] after 20 h, and [f] after 24 h.