

Supporting Information

Selectivity in the photo-Fries rearrangement of some aryl benzoates in green and sustainable media. Preparative and mechanistic studies.

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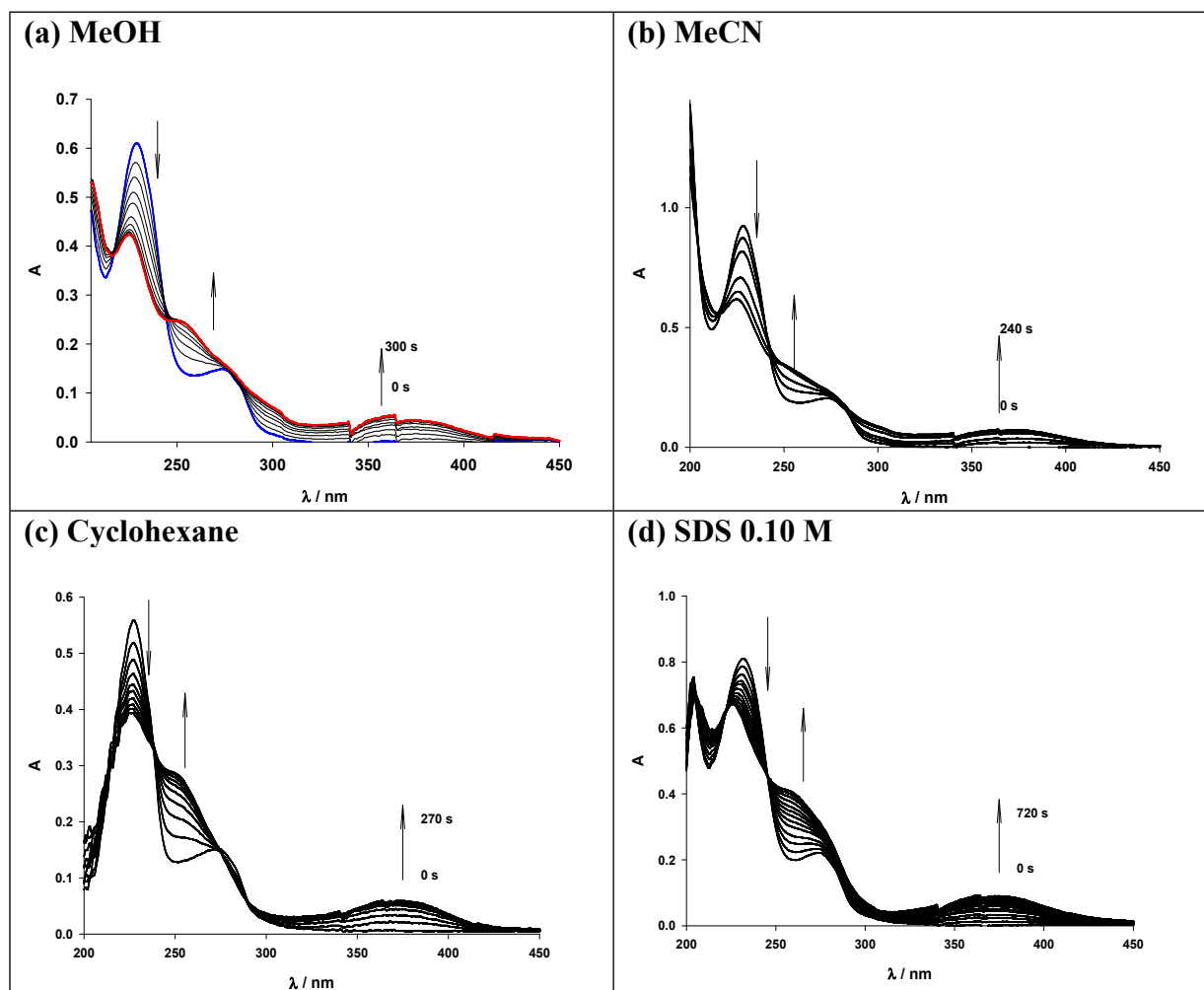
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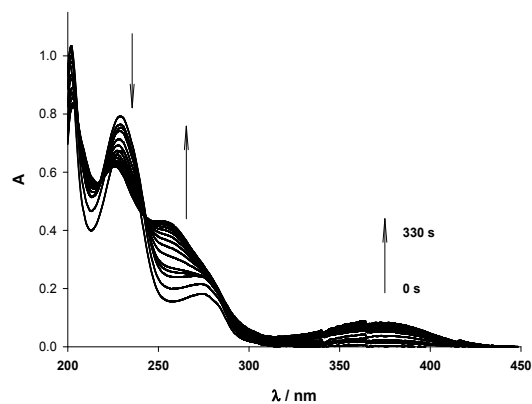
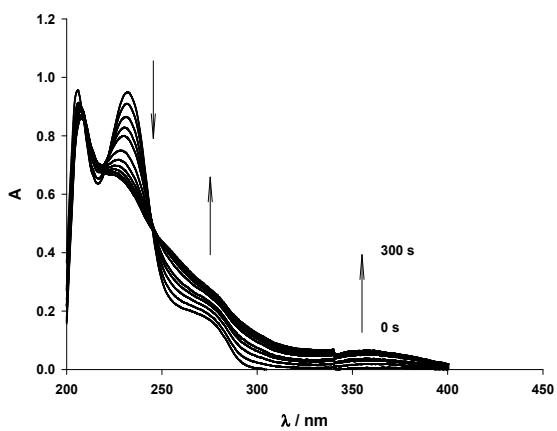
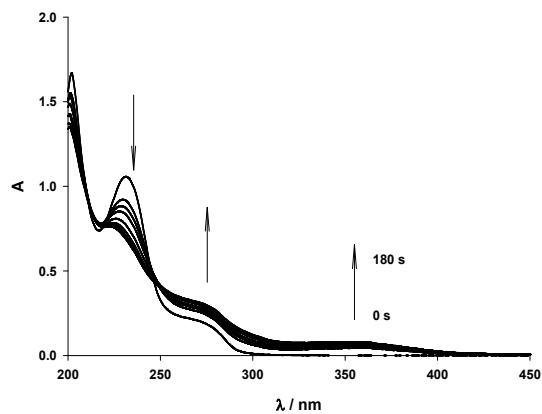
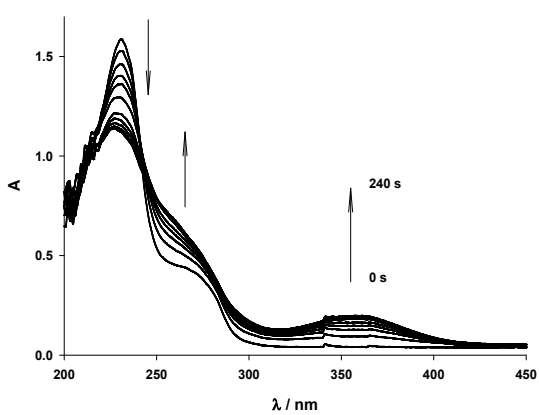
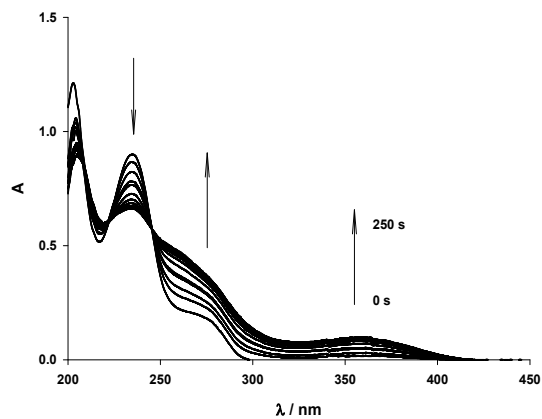
1. Time-resolved UV-visible absorption spectroscopy under steady-state.

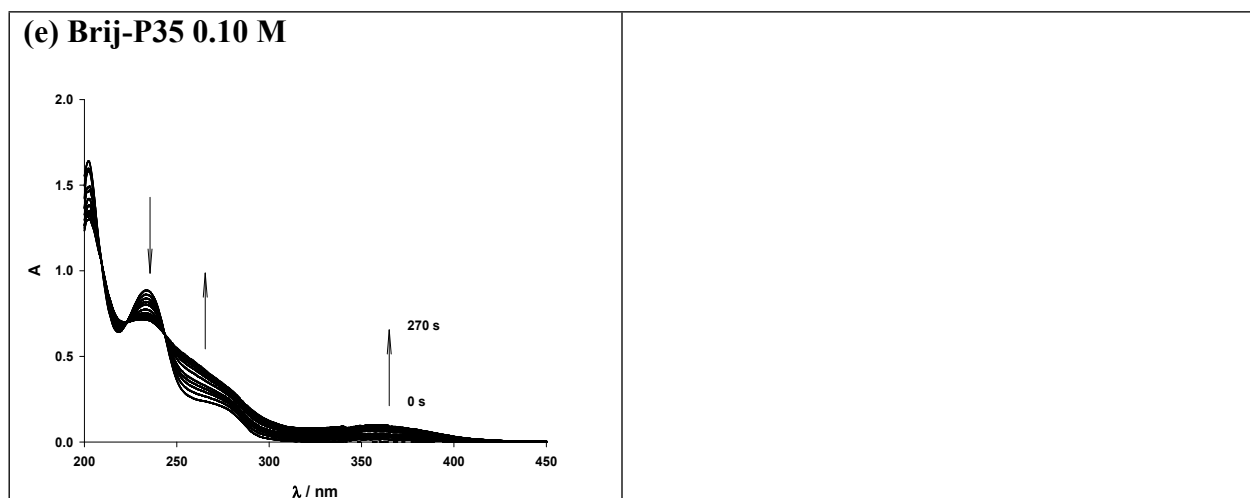
UV-visible spectroscopy was used to follow the photochemical reaction of the aryl benzoates (**1** – **8**) in homogeneous (MeOH, MeCN and cyclohexane) and heterogeneous media (SDS 0.10 mol.dm⁻³ and Brij-P35 0.10 mol.dm⁻³ solutions). The concentration of the aryl benzoates was 5.0x10⁻⁵ mol.dm⁻³ in all the solvents studied and the solutions, placed in UV-visible absorption stoppered quartz cuvettes, were irradiated with 8 germicide lamps (18 W) at 254 nm under inert atmosphere.

Figure S1. UV-visible spectral change vs time of aryl benzoates **1** - **8** in all the solvents studied.

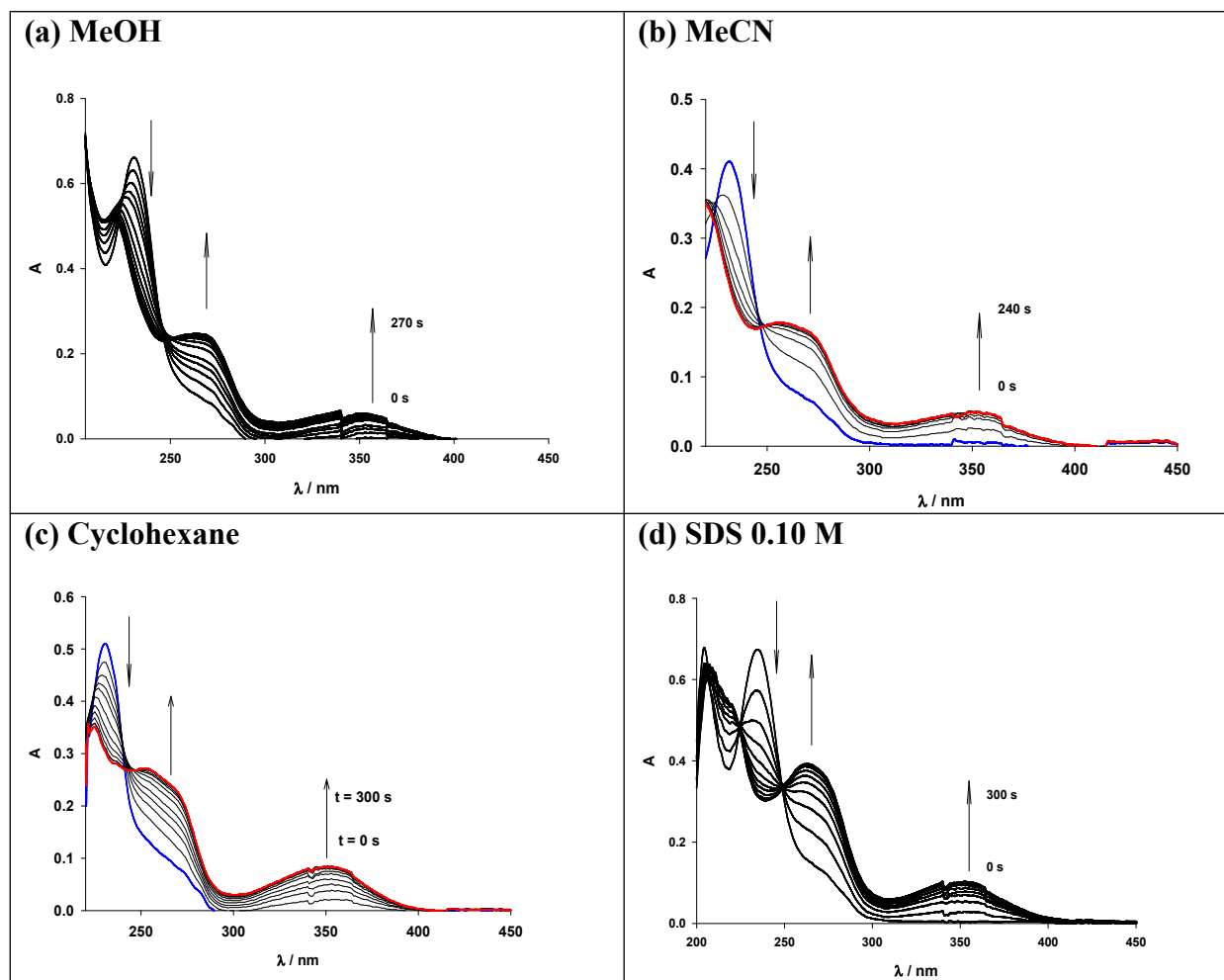
1.1. *p*-Methoxyphenyl benzoate (**1**).

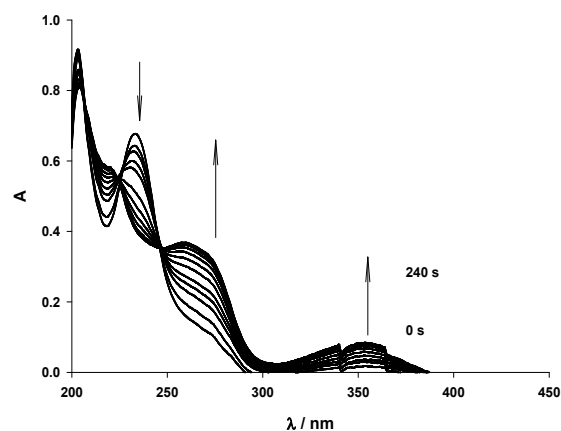
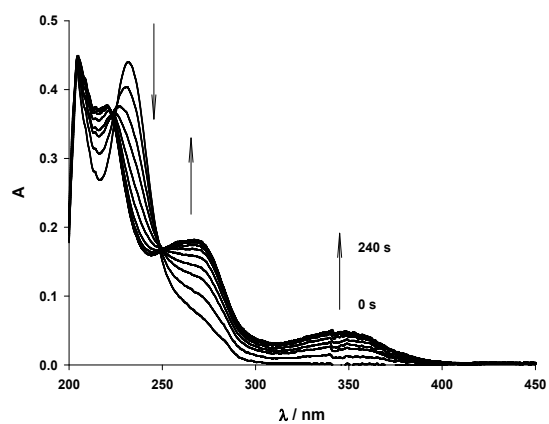
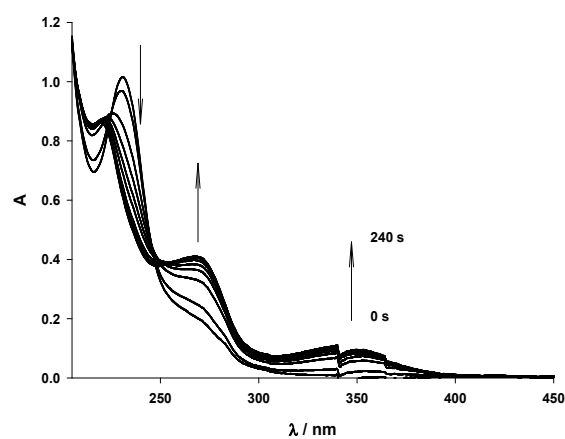
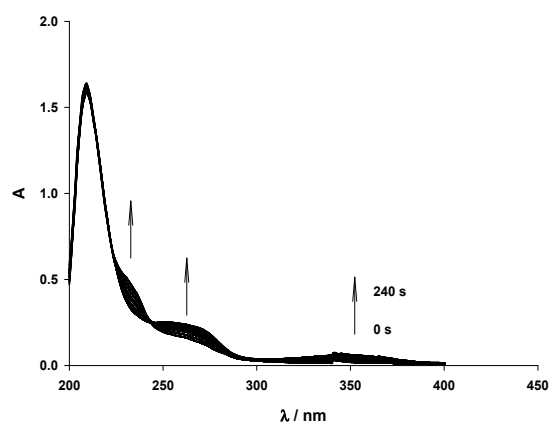
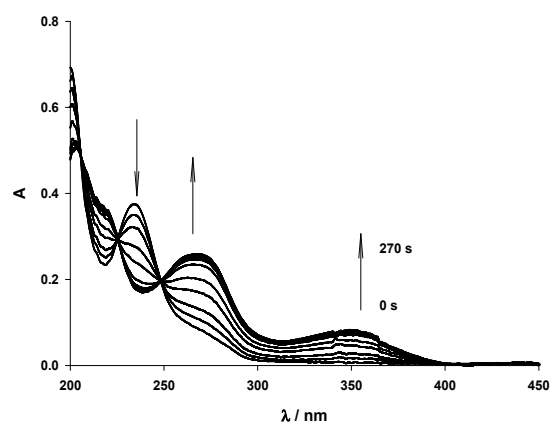


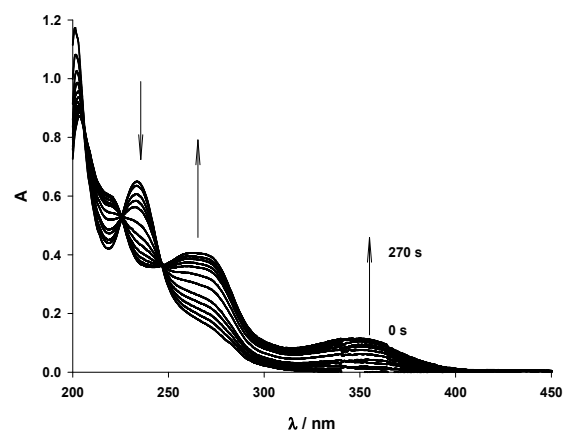
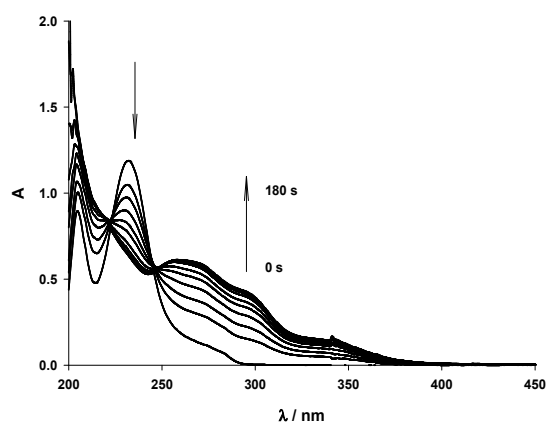
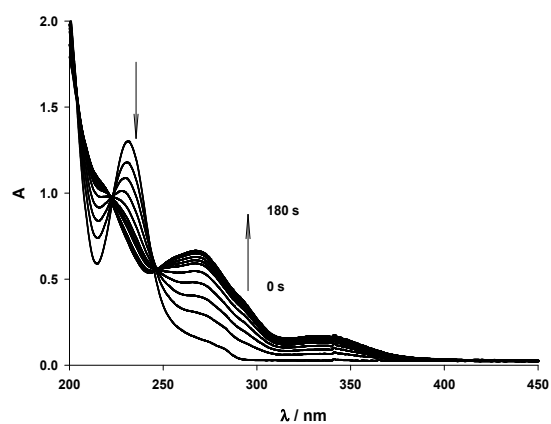
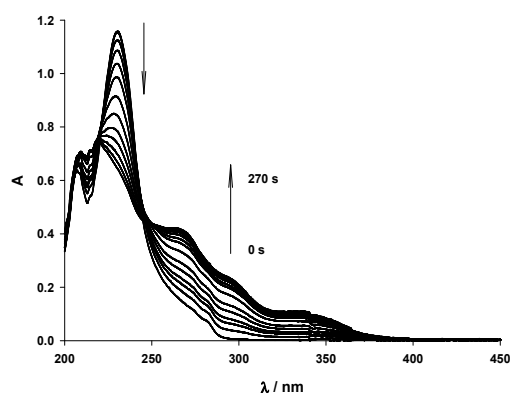
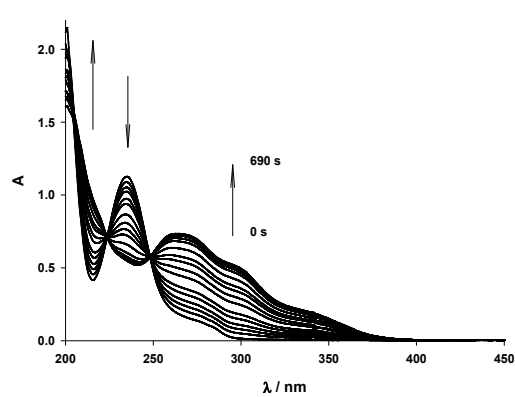
(e) Brij-P35 0.10 M**1.2. *p*-Phenoxyphenyl benzoate (2).****(a) MeOH****(b) MeCN****(c) Cyclohexane****(d) SDS 0.10 M**

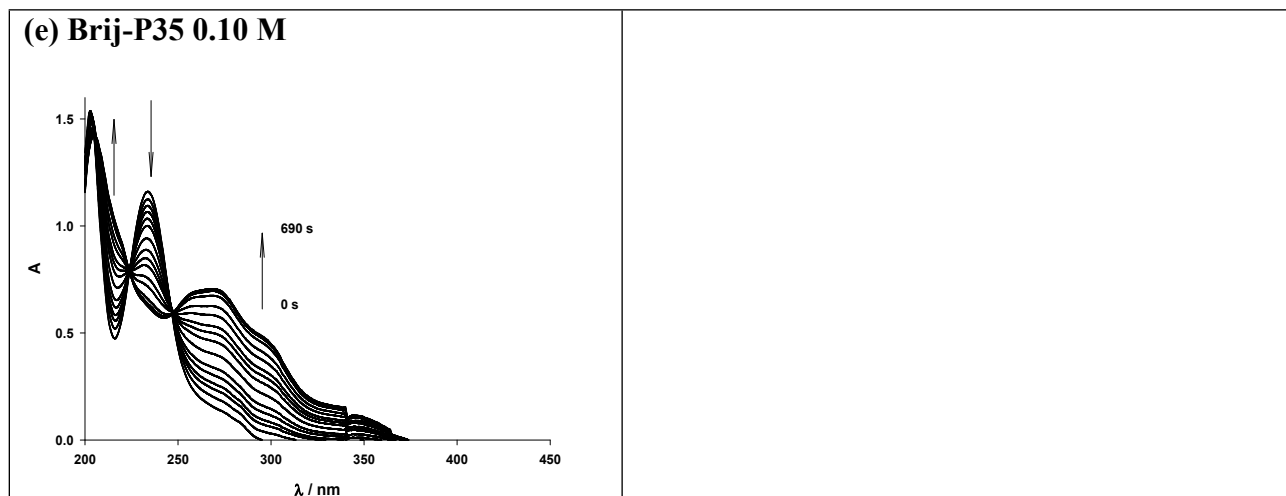


1.3. *p*-Methylphenyl benzoate (3).

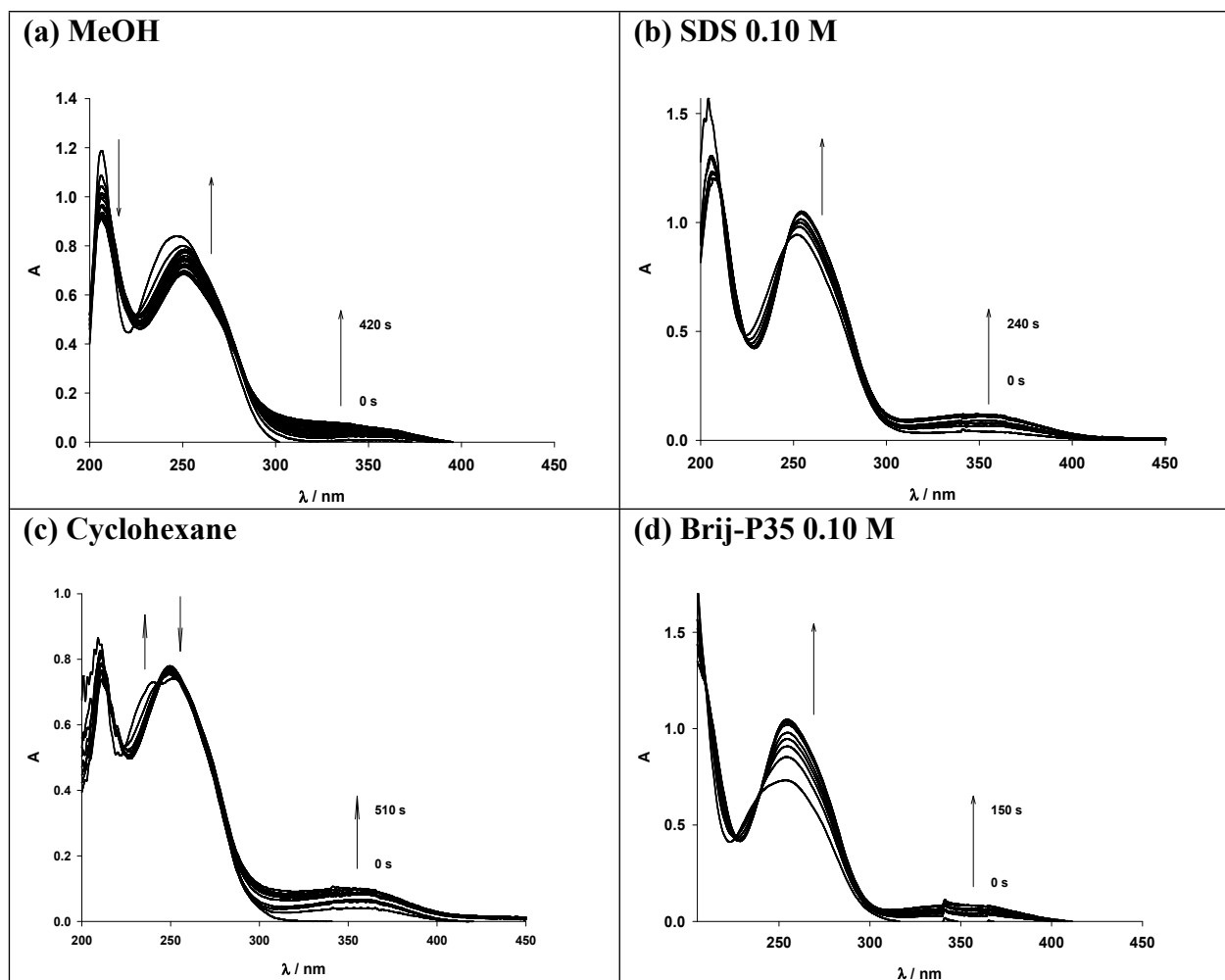


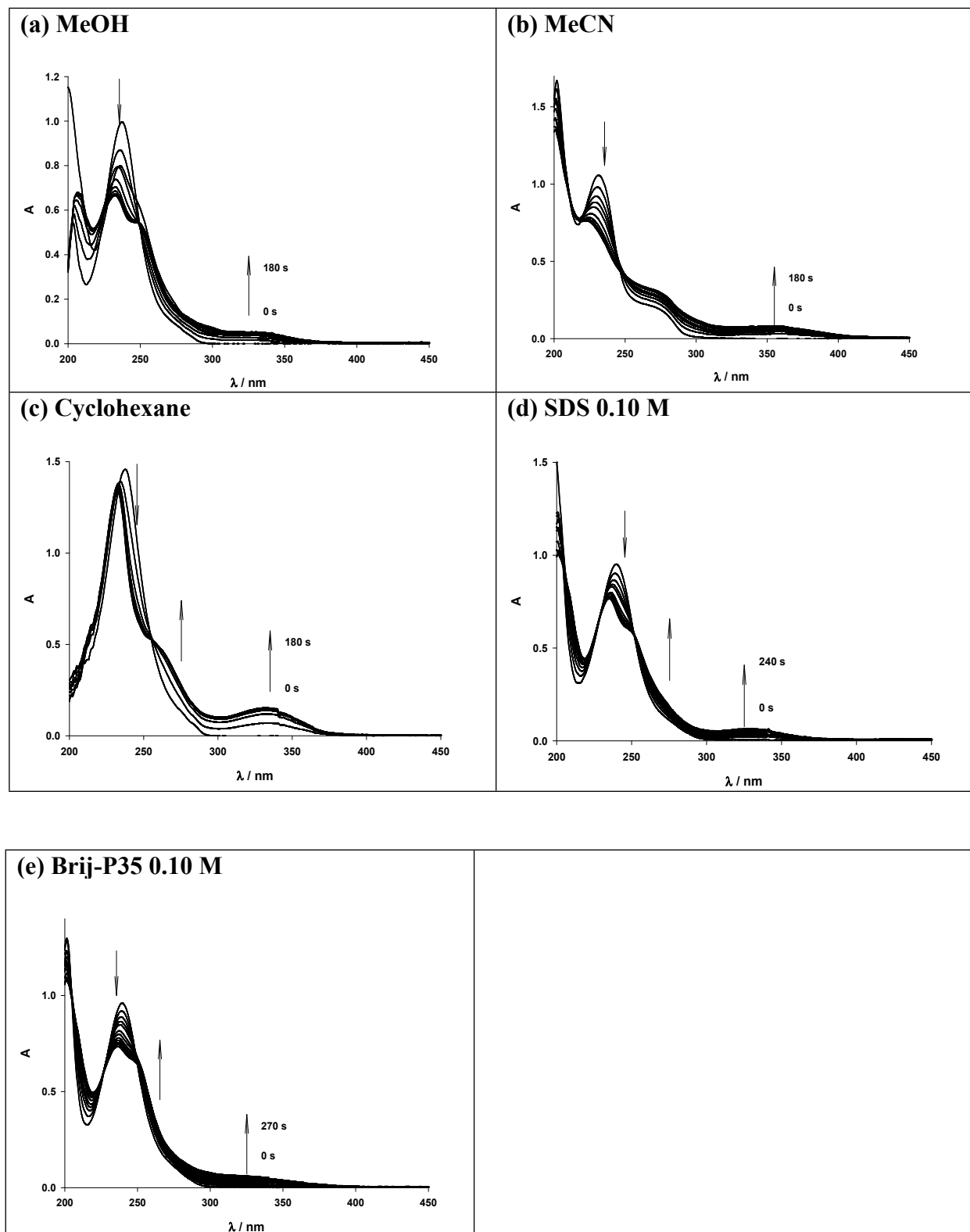
(e) Brij-P35 0.10 M**1.4. *p*-t-Butylphenyl benzoate (4).****(a) MeOH****(b) MeCN****(c) Cyclohexane****(d) SDS 0.10 M**

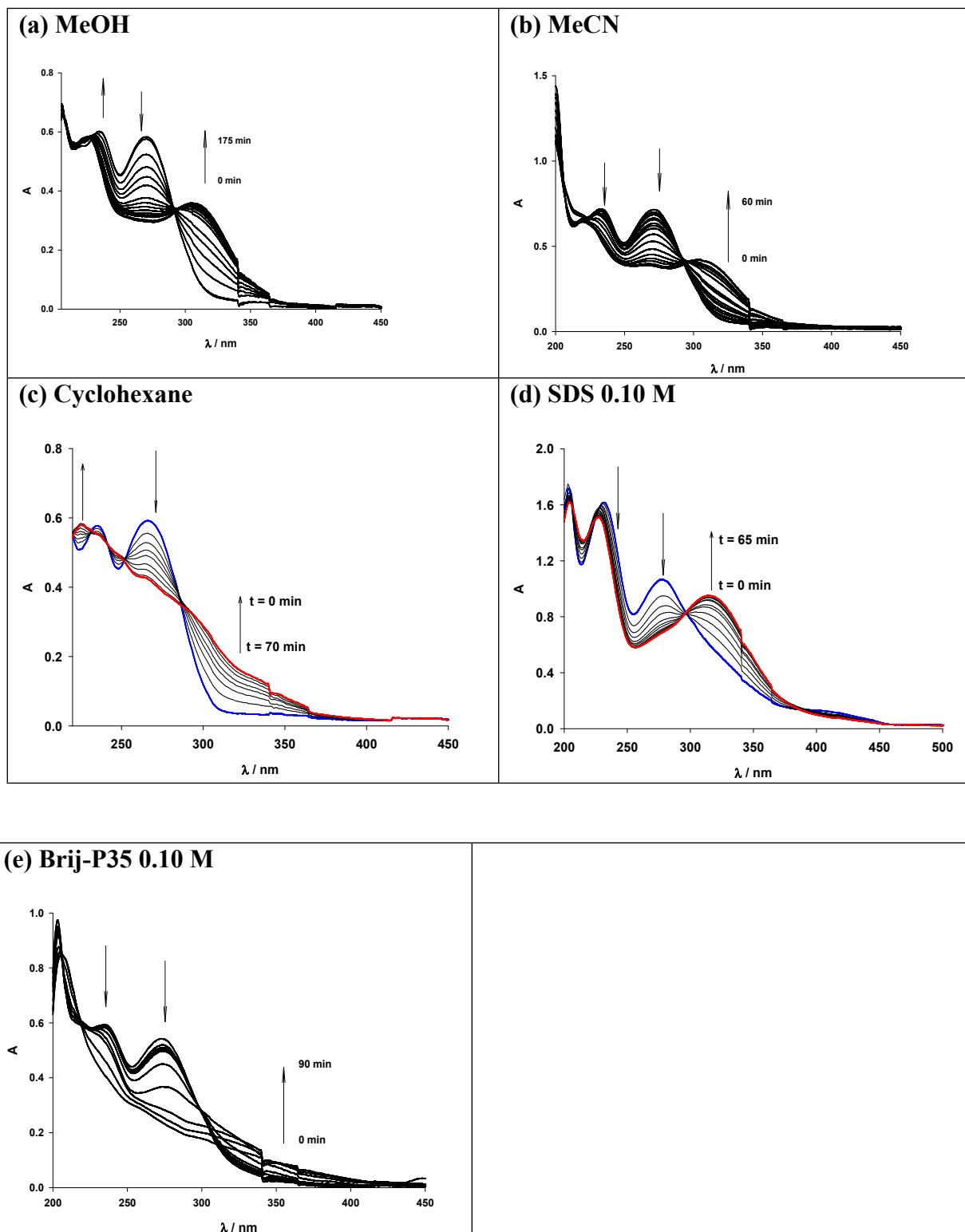
(e) Brij-P35 0.10 M**1.5. Phenyl benzoate (5).****(a) MeOH****(b) MeCN****(c) Cyclohexane****(d) SDS 0.10 M**



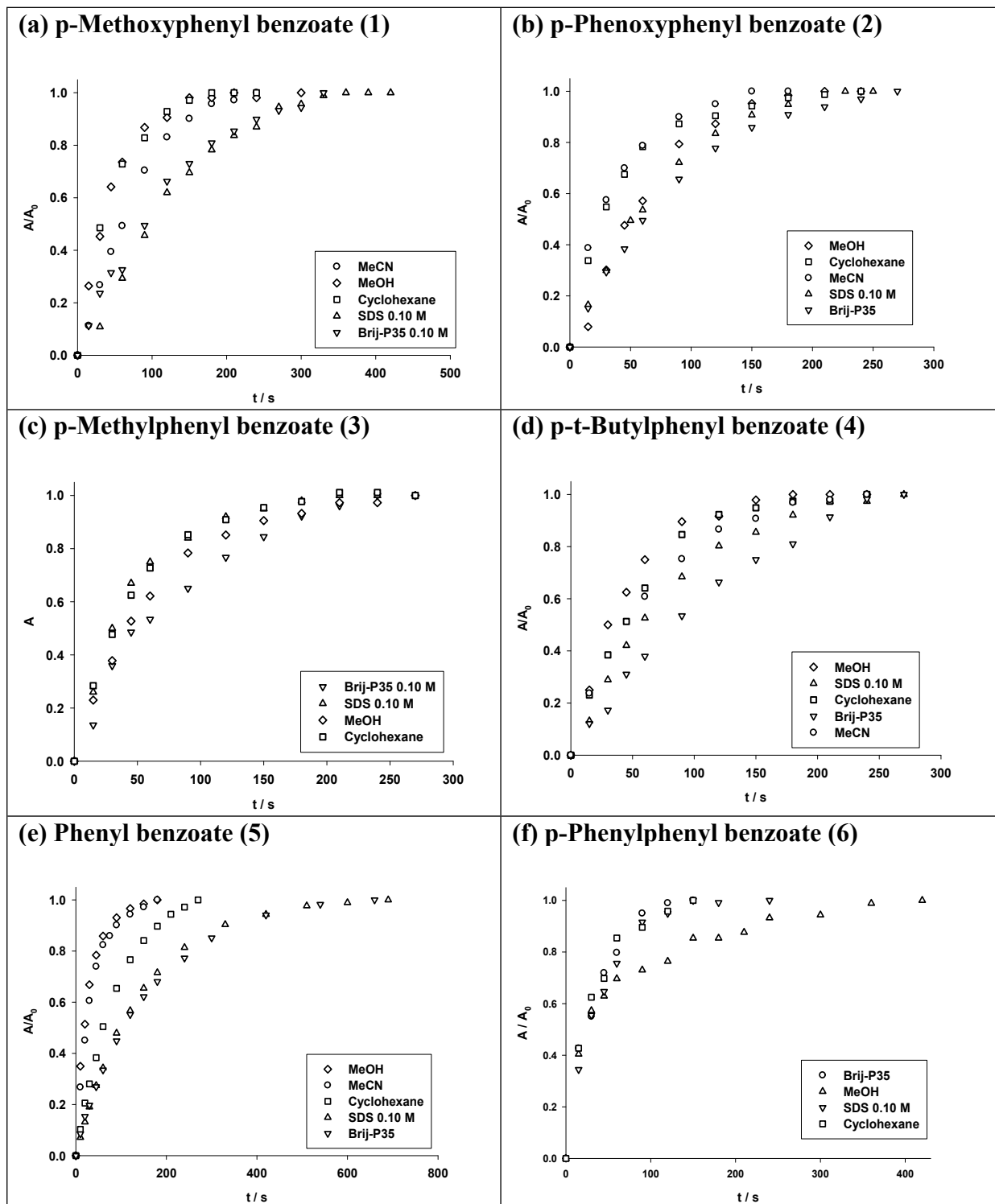
1.6. p-Phenylphenyl benzoate (6).



1.7. p-Cyanophenyl benzoate (7).

1.8. p-Nitrophenyl benzoate (8).

2. Relative absorption profiles (A/A_0) versus time in homogeneous and heterogeneous media



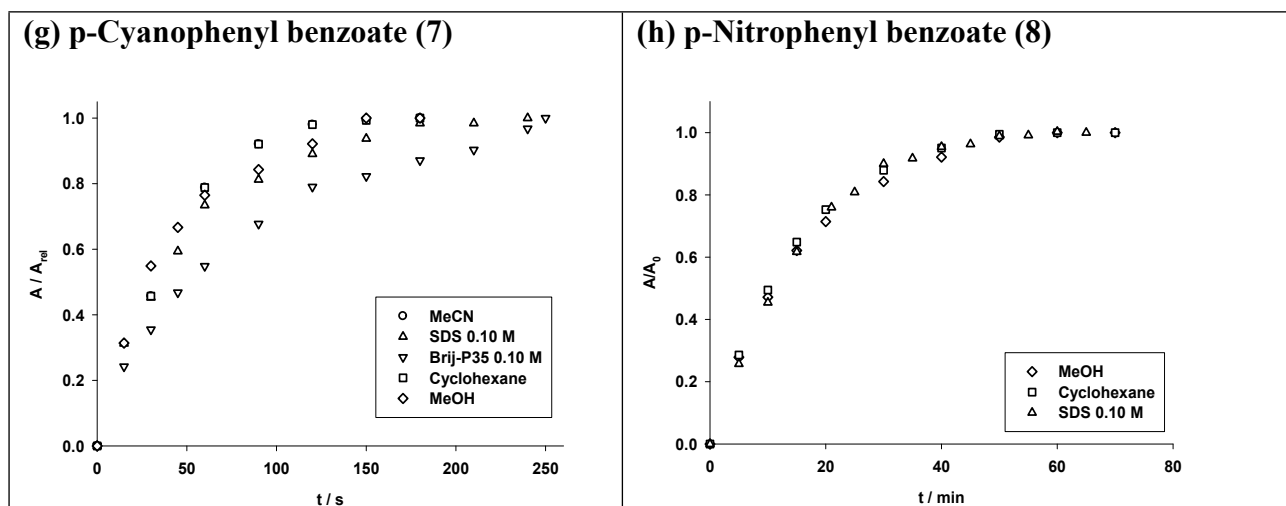


Figure S2. Relative absorption profiles versus time of aryl benzoates **1 – 8** in all the solvents studied.

3. (a) NMR spectroscopy of the photoreaction mixture (6 h irradiation) of 4-cyanophenyl benzoate (**7**) in cyclohexane under N₂ atmosphere.

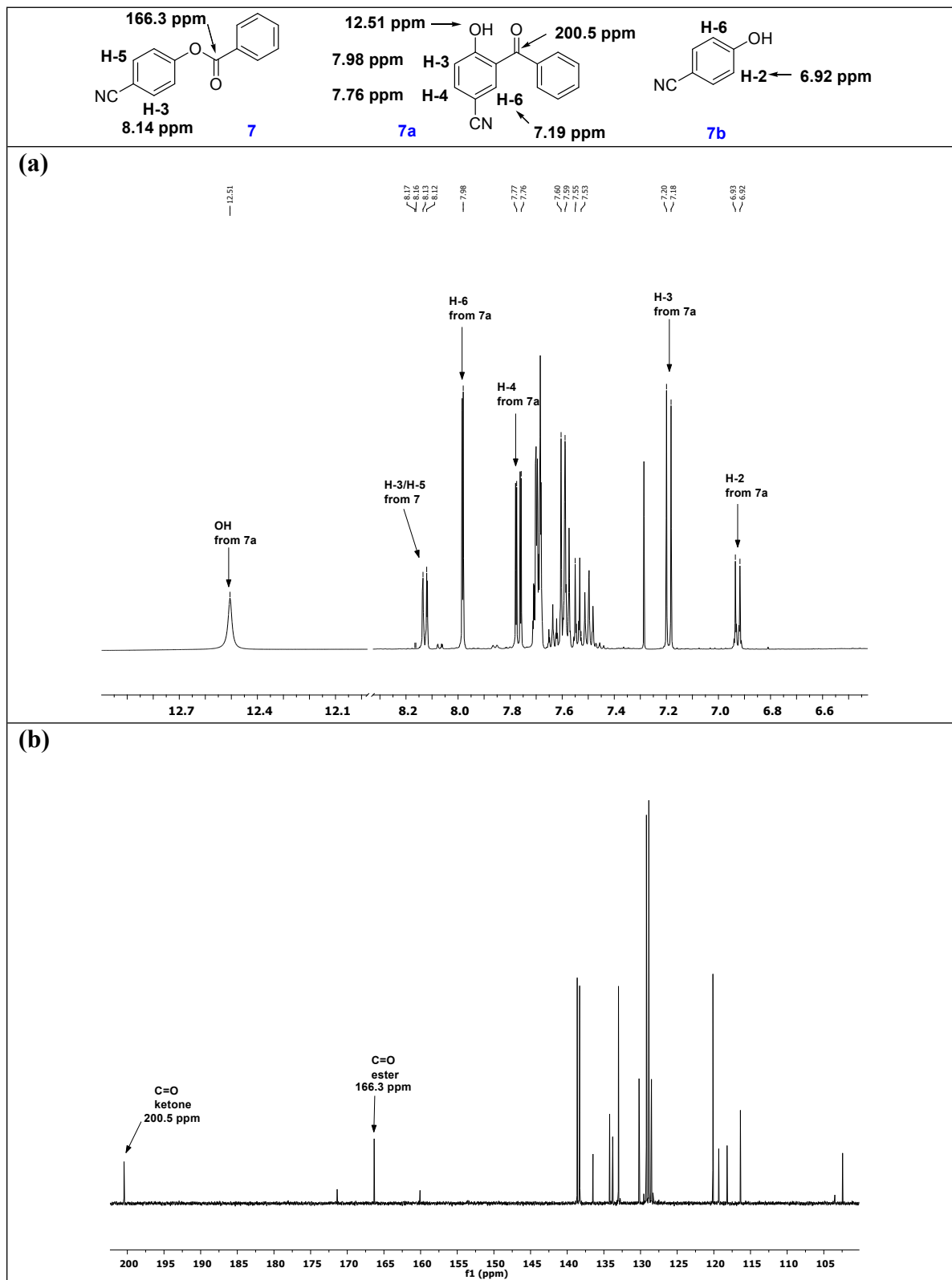


Figure S3. (a) ¹H-NMR and (b) ¹³C-NMR spectra of the photoreaction mixture of compound **7** in cyclohexane after 6 h of irradiation with $\lambda_{\text{exc}} = 254$ nm.

(b) NMR spectroscopy of the photoreaction mixture (6 h irradiation) of 4-methoxyphenyl benzoate (**1**) in SDS (0.10 M) solution under nitrogen atmosphere.

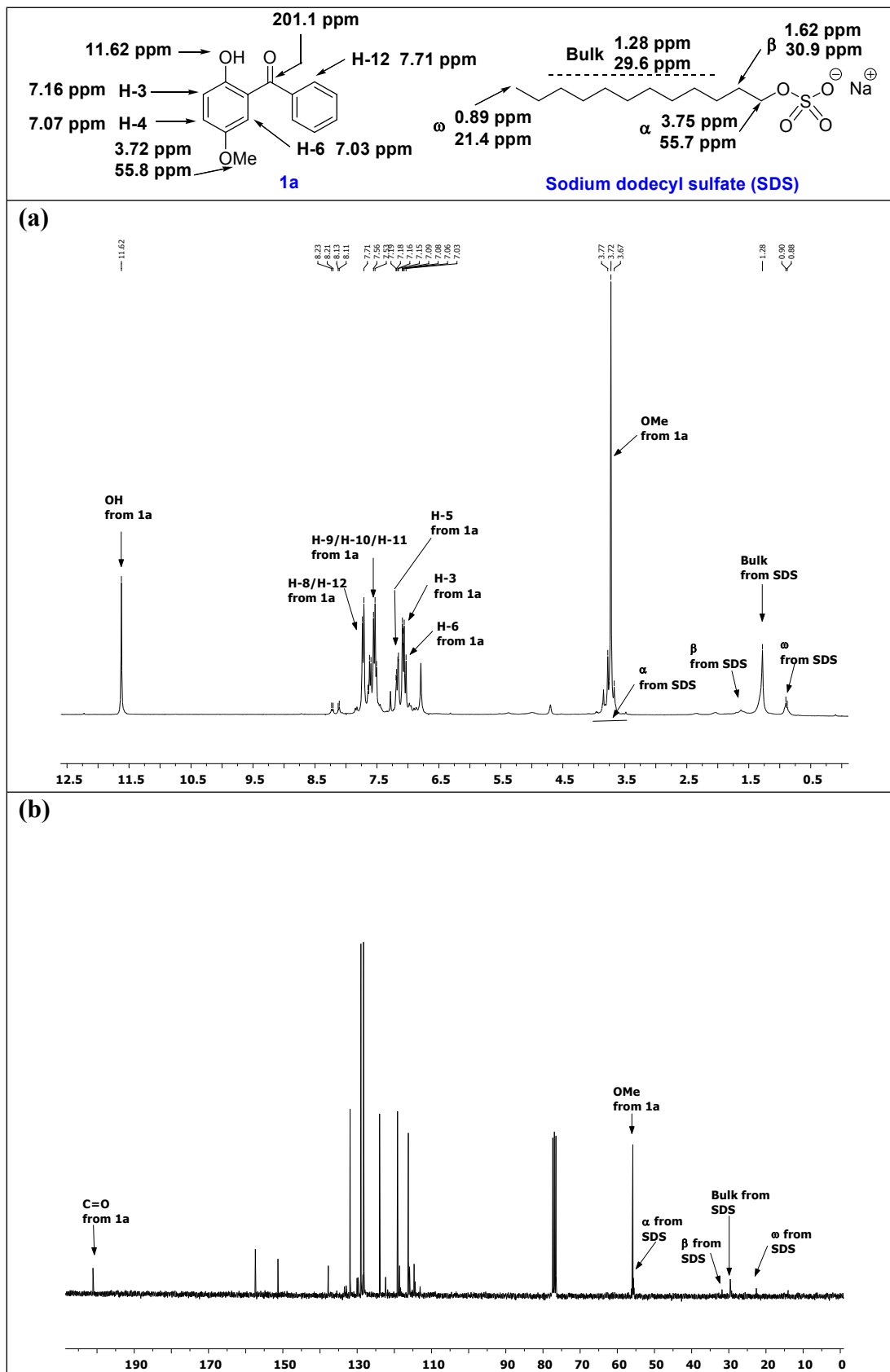


Figure S4. (a) ^1H -NMR and **(b)** ^{13}C -NMR spectra of the photoreaction mixture of compound **1** in SDS (0.10 M) after 6 h of irradiation with $\lambda_{\text{exc}} = 254$ nm.

3. Determination of the constants of binding K_b showed in Table 3.

The constants of binding (K_b) between aryl benzoates and micelles of SDS and Brij-P35 were carried out using UV-visible spectroscopy and applying a methodology that have been early reported for aryl acetamide.^{S1} Linear relationships were observed when plotting $(A - A_0)^{-1}$ and the reciprocal of the concentration of the surfactant (see **Figure S5**) according to equation 1 whose mathematical deduction was described in the main text of the manuscript. A and A_0 are the absorbance at the maxima wavelength of the benzoates in the presence and absence of surfactant (Surf), respectively, and ε_S and ε_C are the molar absorptivity of the benzoates and the complex. Also, in **Figure S5** were included the linear regression fittings for benzoates **1** (p -MeO), **3** (p -Me), **5** (p -H), **6** (p -Ph), **7** (p -CN) and **8** (p -NO₂).

$$\frac{A_0}{(A - A_0)} = \frac{\varepsilon_S}{\varepsilon_C} + \frac{\varepsilon_S}{\varepsilon_C \cdot K_b} \frac{1}{[\text{Surf}]} = A_0 \frac{1}{\Delta A} \quad (1)$$

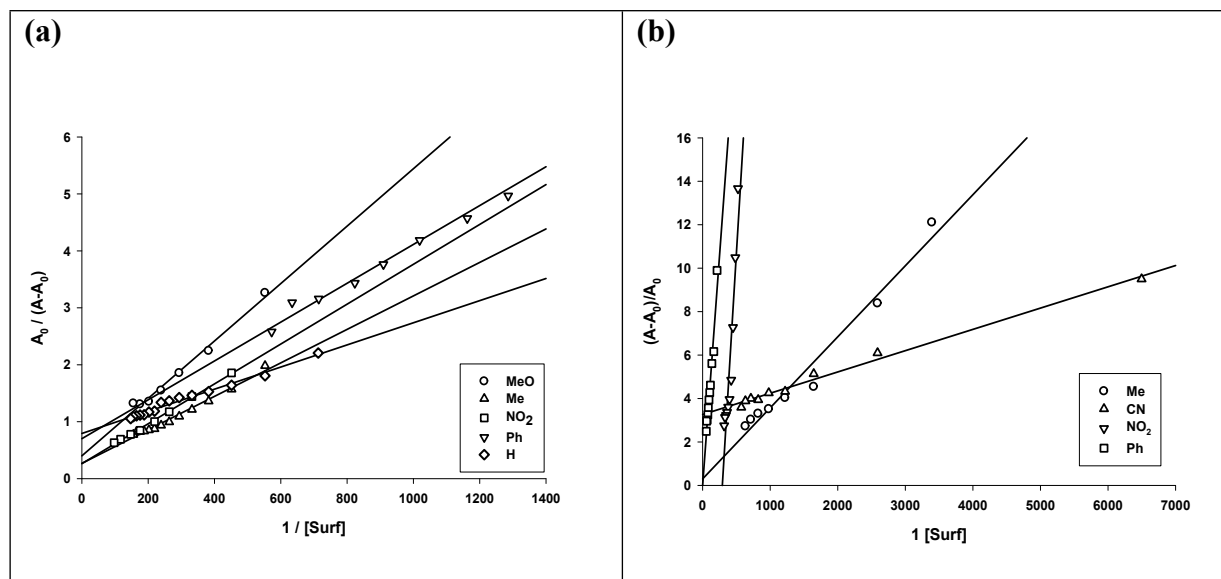


Figure S5. Plots of reciprocal of $(A_0/(A - A_0))$ vs reciprocal of concentration of surfactants in water at room temperature: **(a)** SDS and **(b)** Brij-P35.

Finally, from the ratio between the slope and the intercept obtained after fitting the experimental data with a linear regression it was easily to calculate the K_b values which were already collected in Table 3 for aryl benzoates (**1** – **8**) with different surfactants in the main text.

4. 2D NOESY NMR spectra in micellar media.

In the following figures (**Figure S6, S7 and S8**) are shown the contour plots of 2D NOESY experiments performed in D₂O mixing a surfactant with an aryl benzoate in *ca.* 1:1 molar ratio. Positive cross-peaks between diagnostic signals of the substrate and the surfactants, respectively, were highlighted with gray frame insets in the corresponding contour plots.

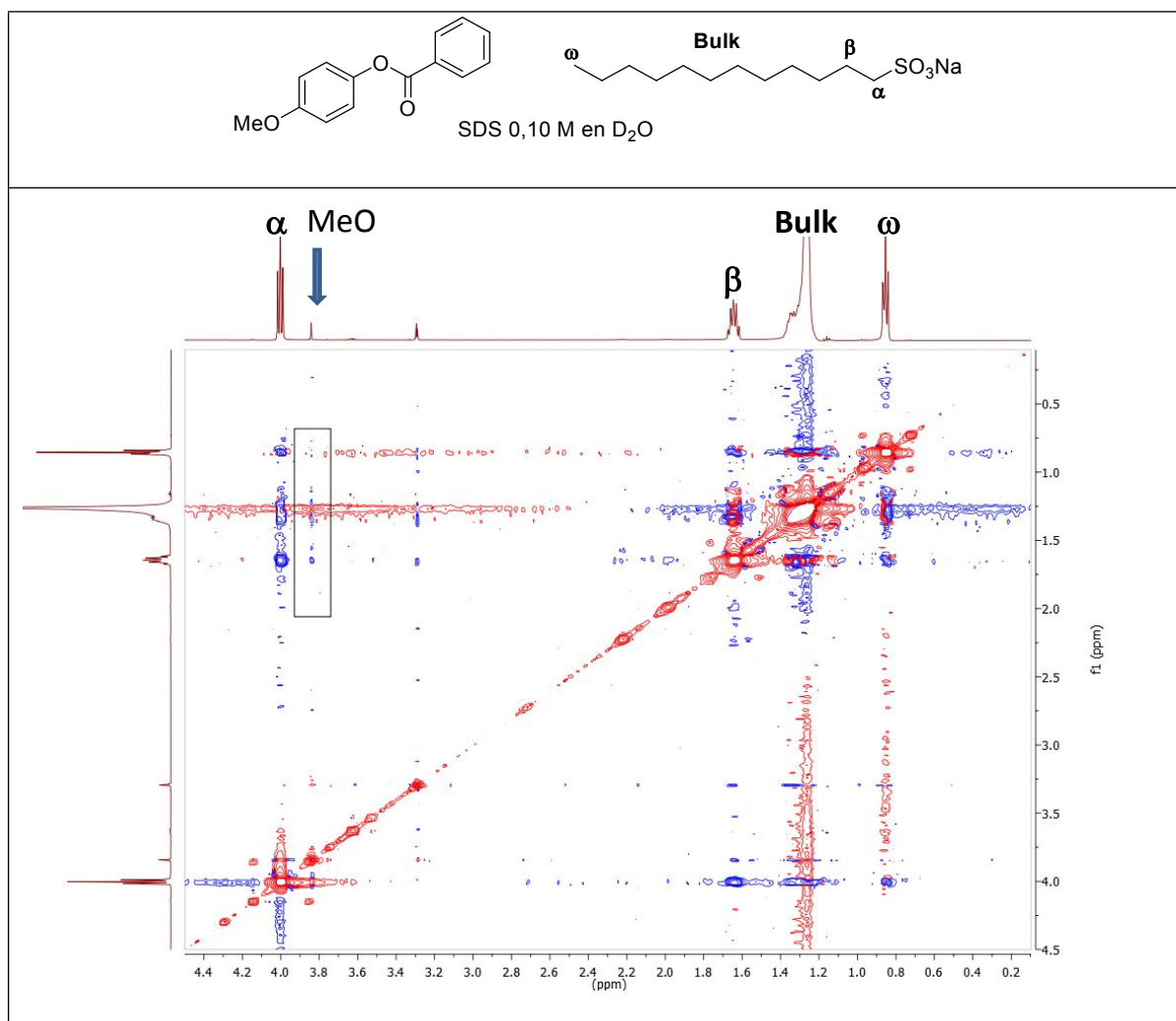


Figure S6. 2D NOESY counter plot of a solution of SDS (7 mM) and **1** (10 mM) in D₂O at room temperature.

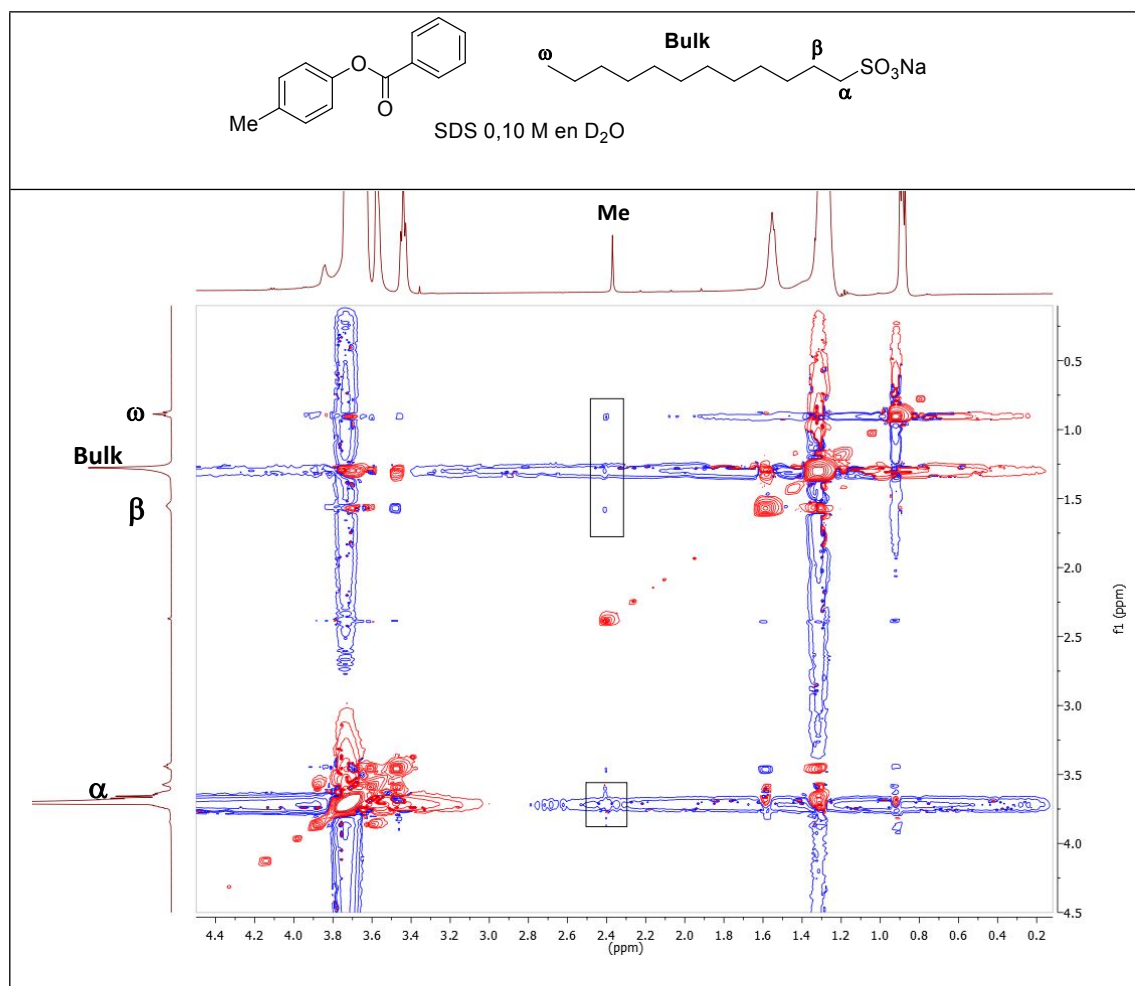


Figure S7. 2D NOESY counter plot of a solution of SDS (7 mM) and **3** (10 mM) in D₂O at room temperature.

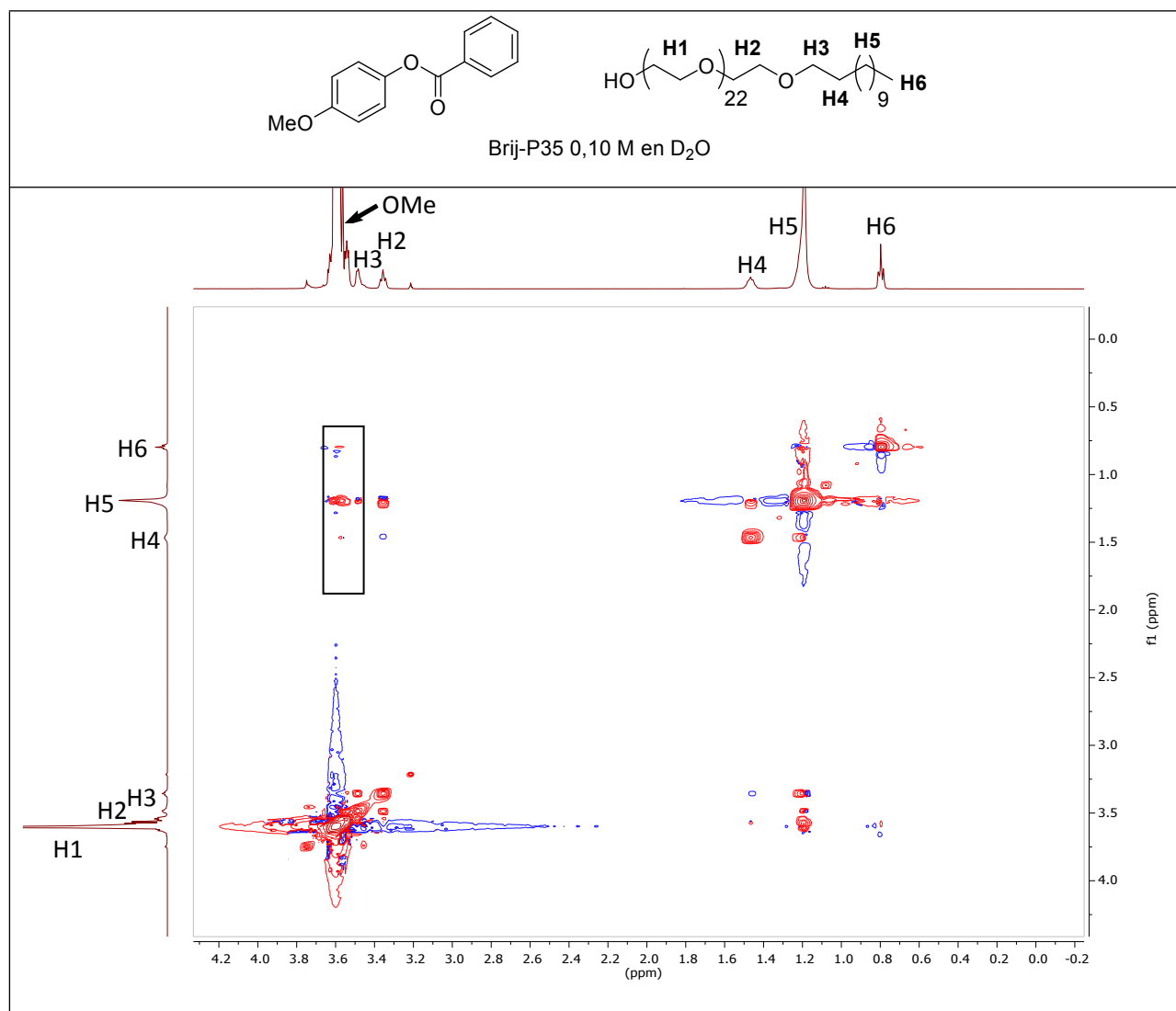
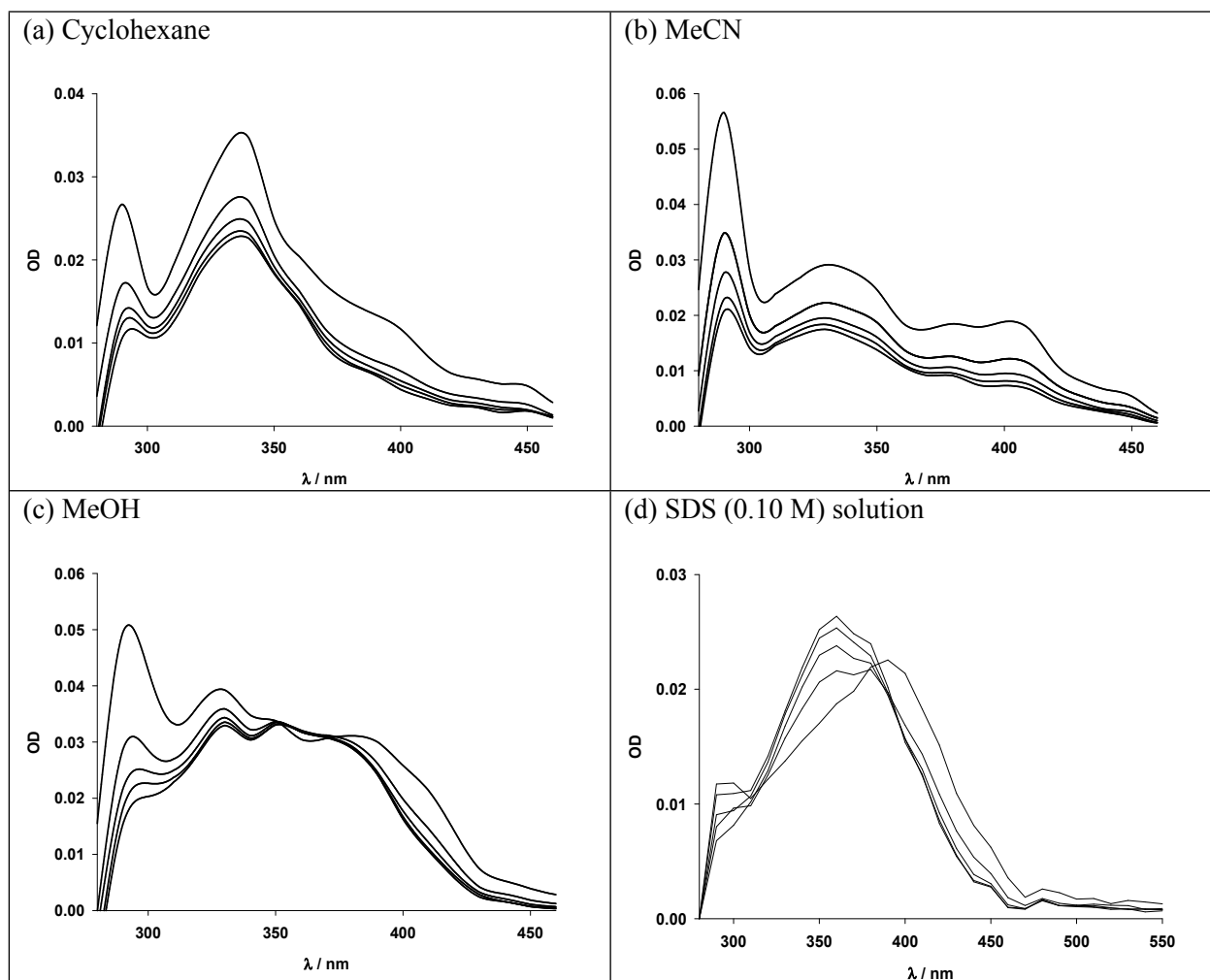


Figure S8. 2D NOESY counter plot of a solution of Brij-P35 (7 mM) and **1** (10 mM) in D₂O at room temperature.

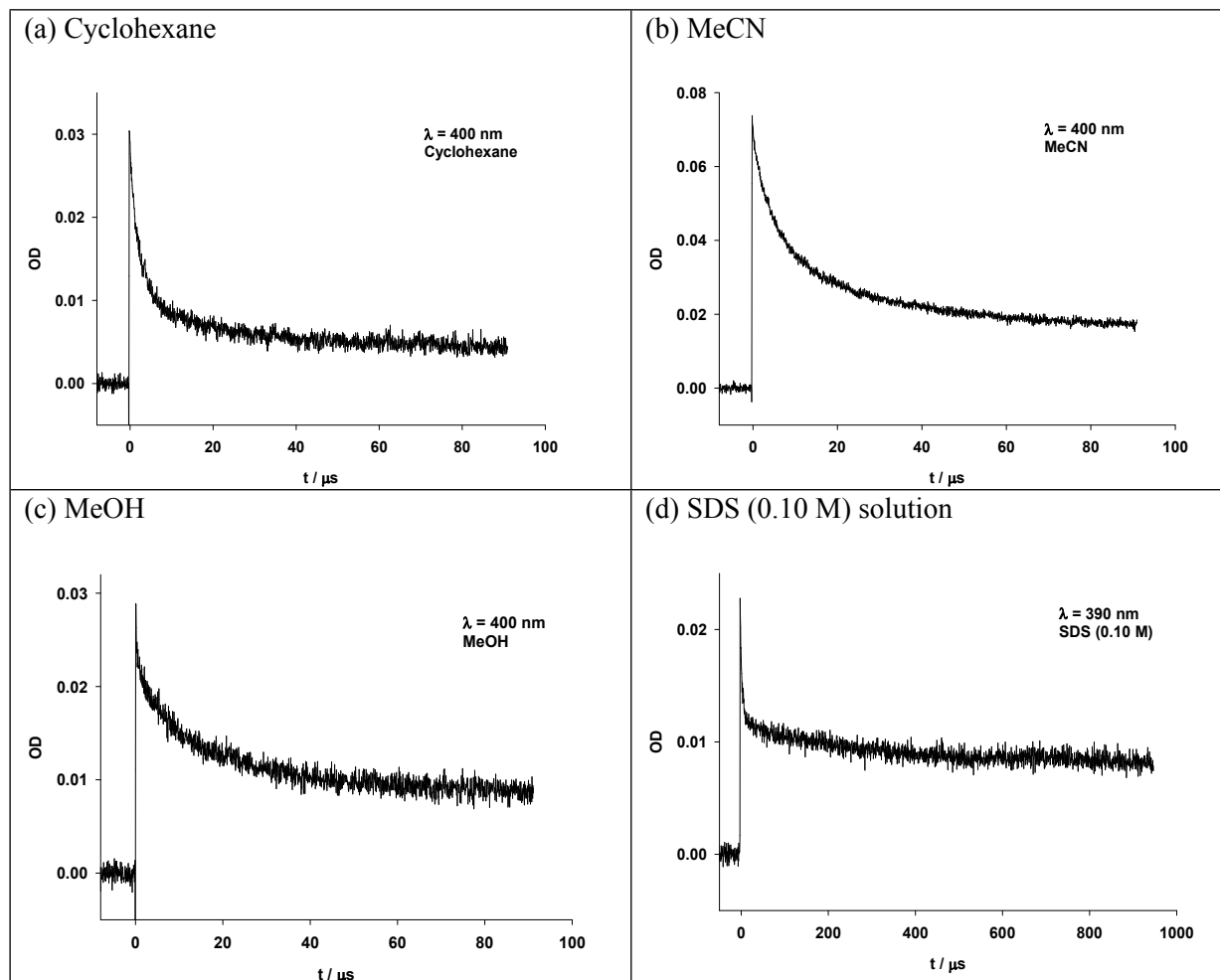
5. Time-resolved absorption spectroscopy.

Figure S9 shows some representative time-resolved transient absorption spectra of aryl benzoates and the decay traces of the corresponding substituted fenoxyl radical transients located at *ca* 400 nm after excitation with a laser pulse (266 nm) of a solution of the aryl benzoates ($3.0 \times 10^{-3} \text{ mol dm}^{-3}$) in homogeneous (MeOH, MeCN and cyclohexane) and in heterogeneous (SDS 0.10 mol dm^{-3} solution) under nitrogen atmosphere at room temperature.

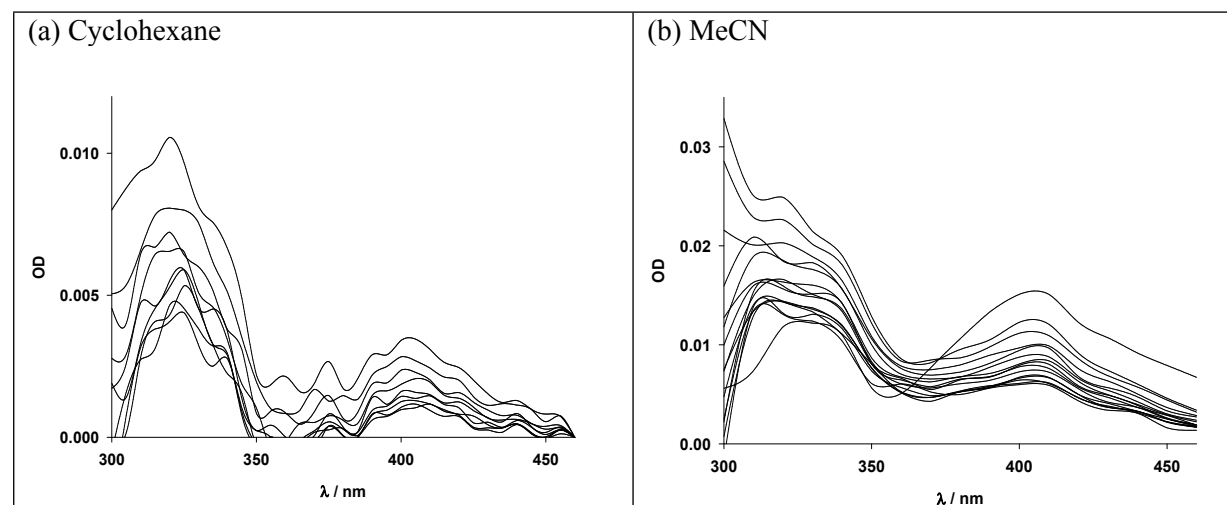
(i) Time-resolved transient absorption spectra of *p*-methoxyphenyl benzoate (**1**).

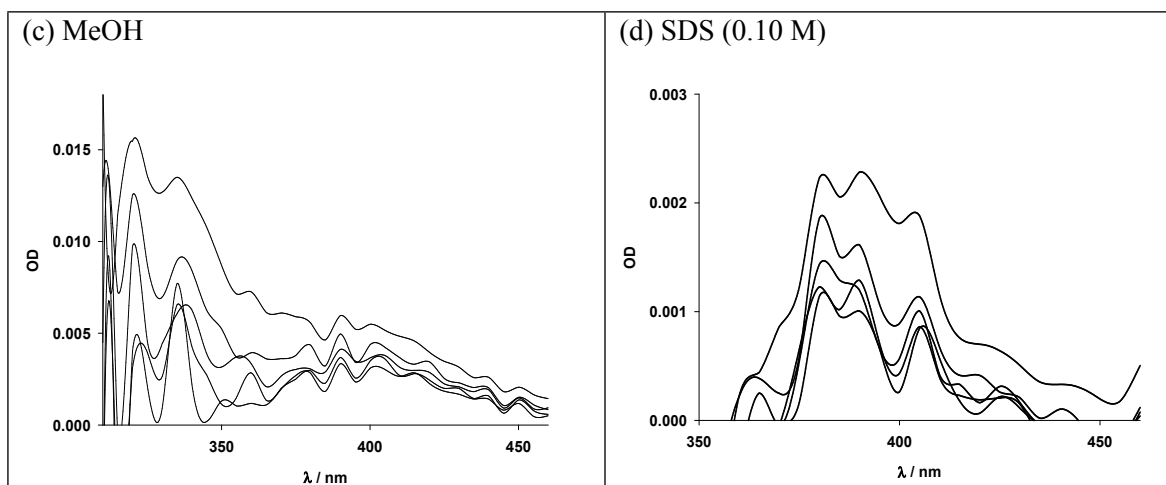


(ii) Transient decay traces of *p*-methoxyphenyl benzoate (**1**).

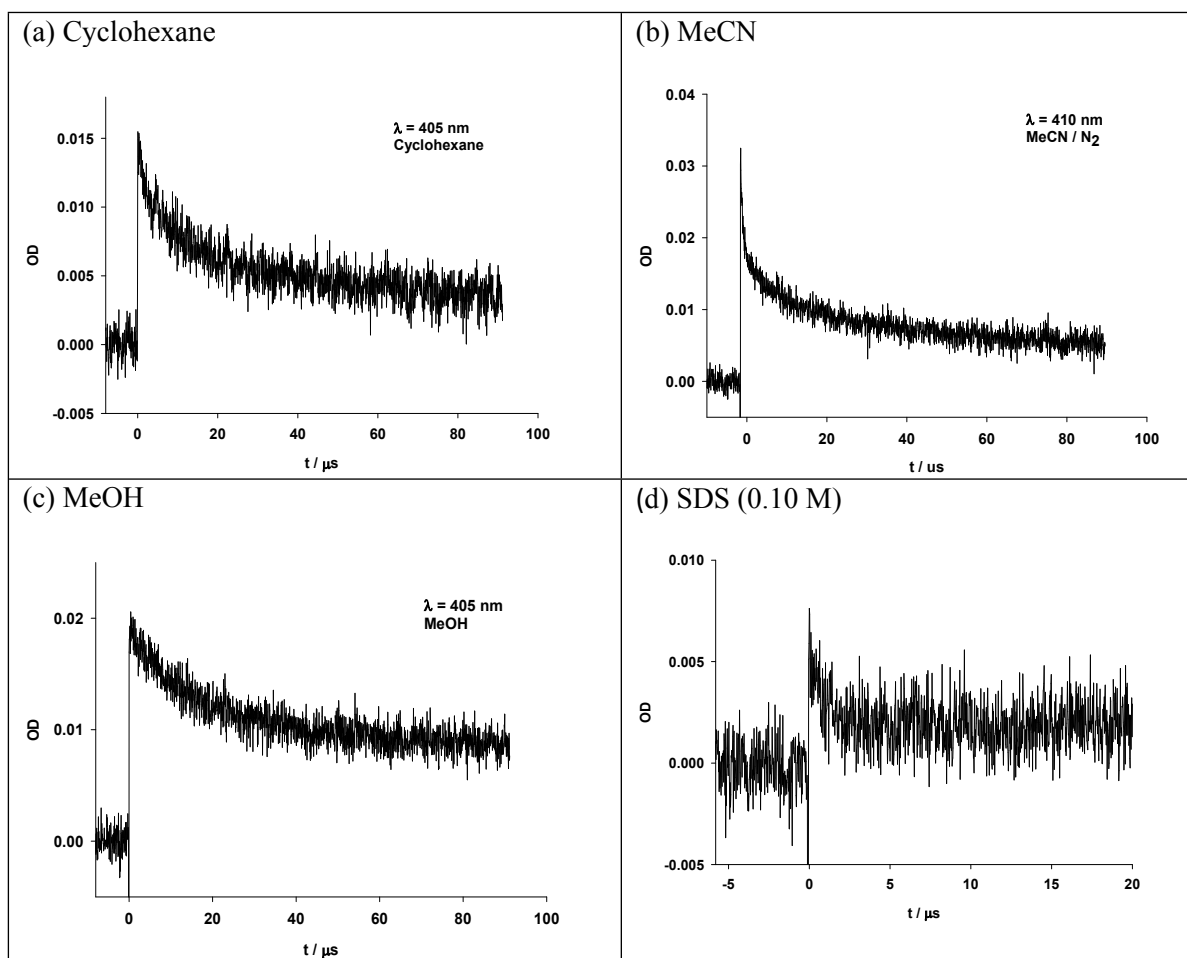


(iii) Time-resolved transient absorption spectra of *p*-phenoxyphenyl benzoate (**2**).

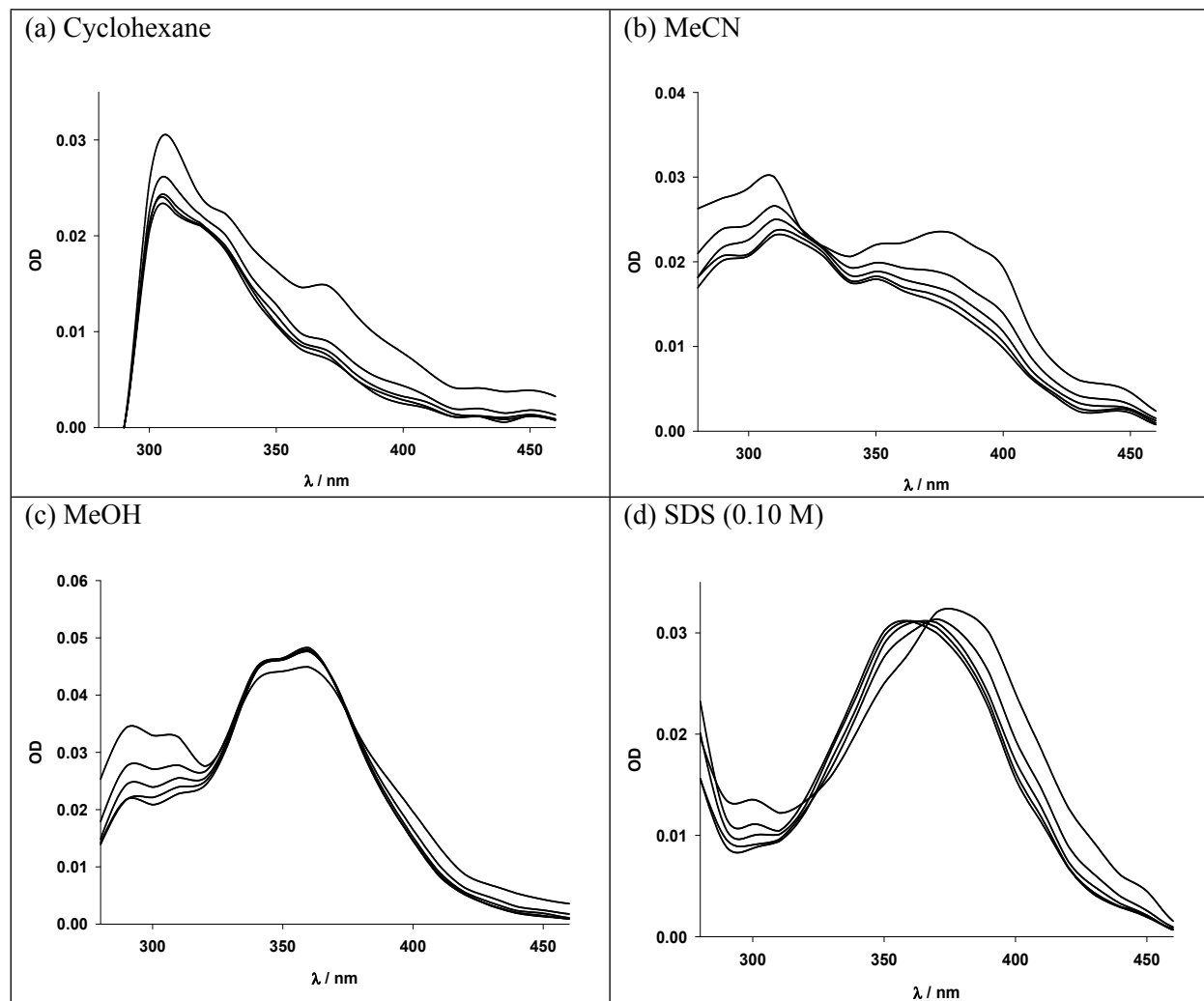




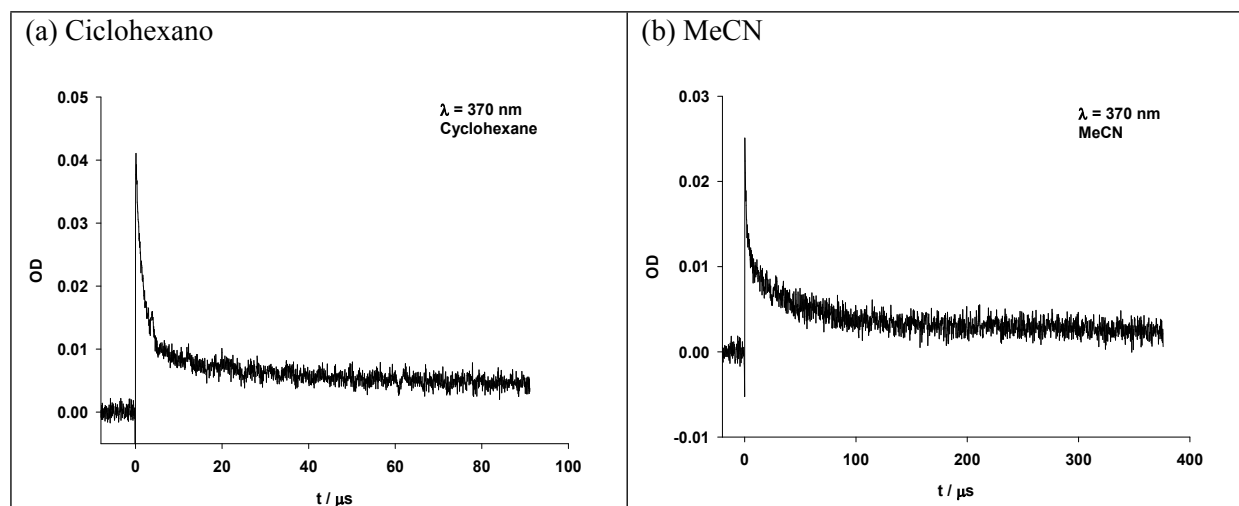
(iv) Transient decay traces of *p*-phenoxyphenyl benzoate (**2**).

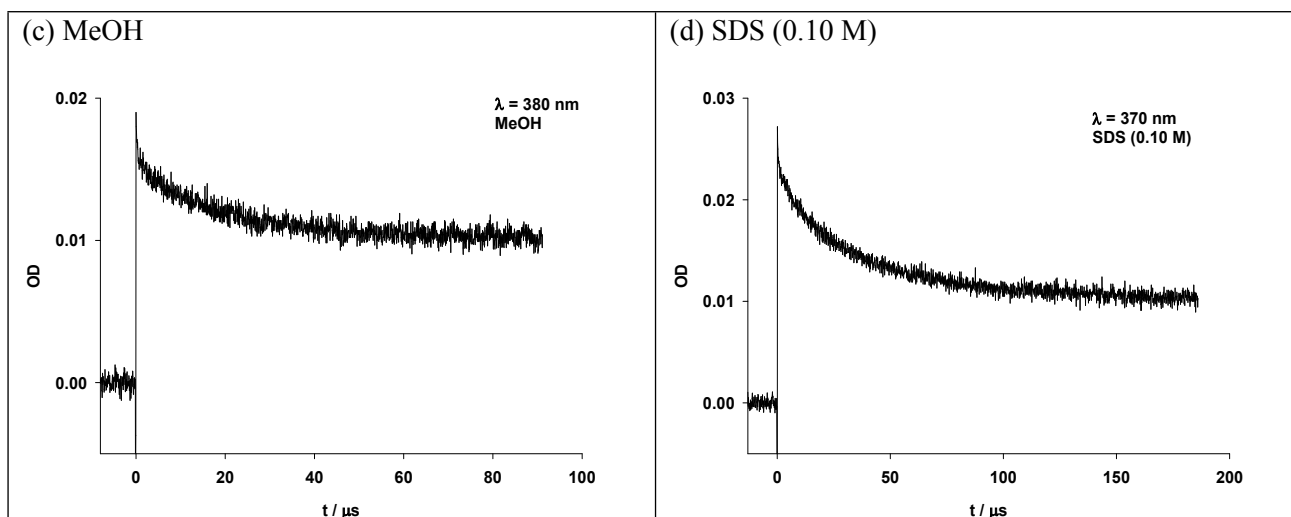


(v) Time-resolved transient absorption spectra of *p*-methylphenyl benzoate (**3**).

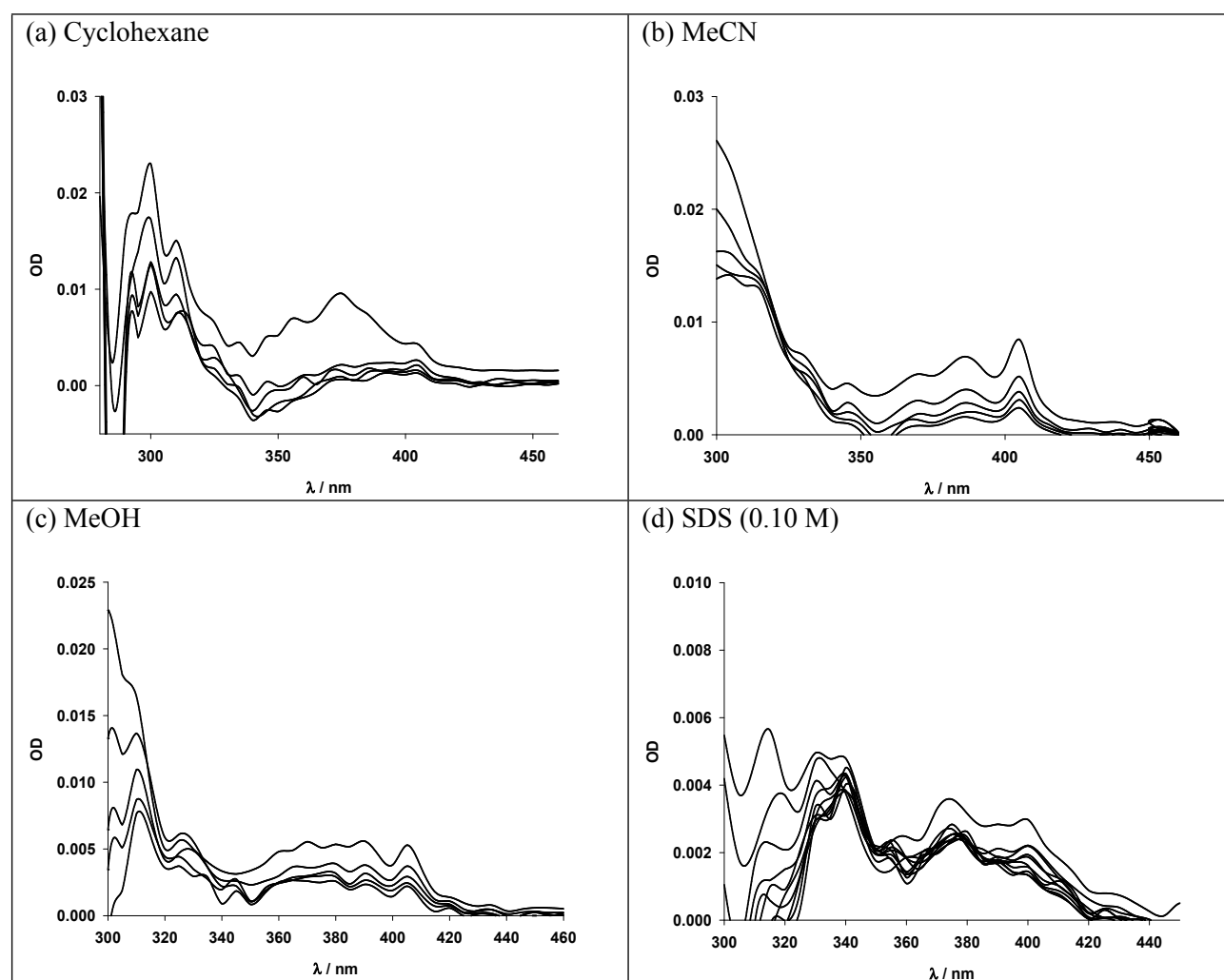


(vi) Transient decay traces of *p*-methylphenyl benzoate (**3**).

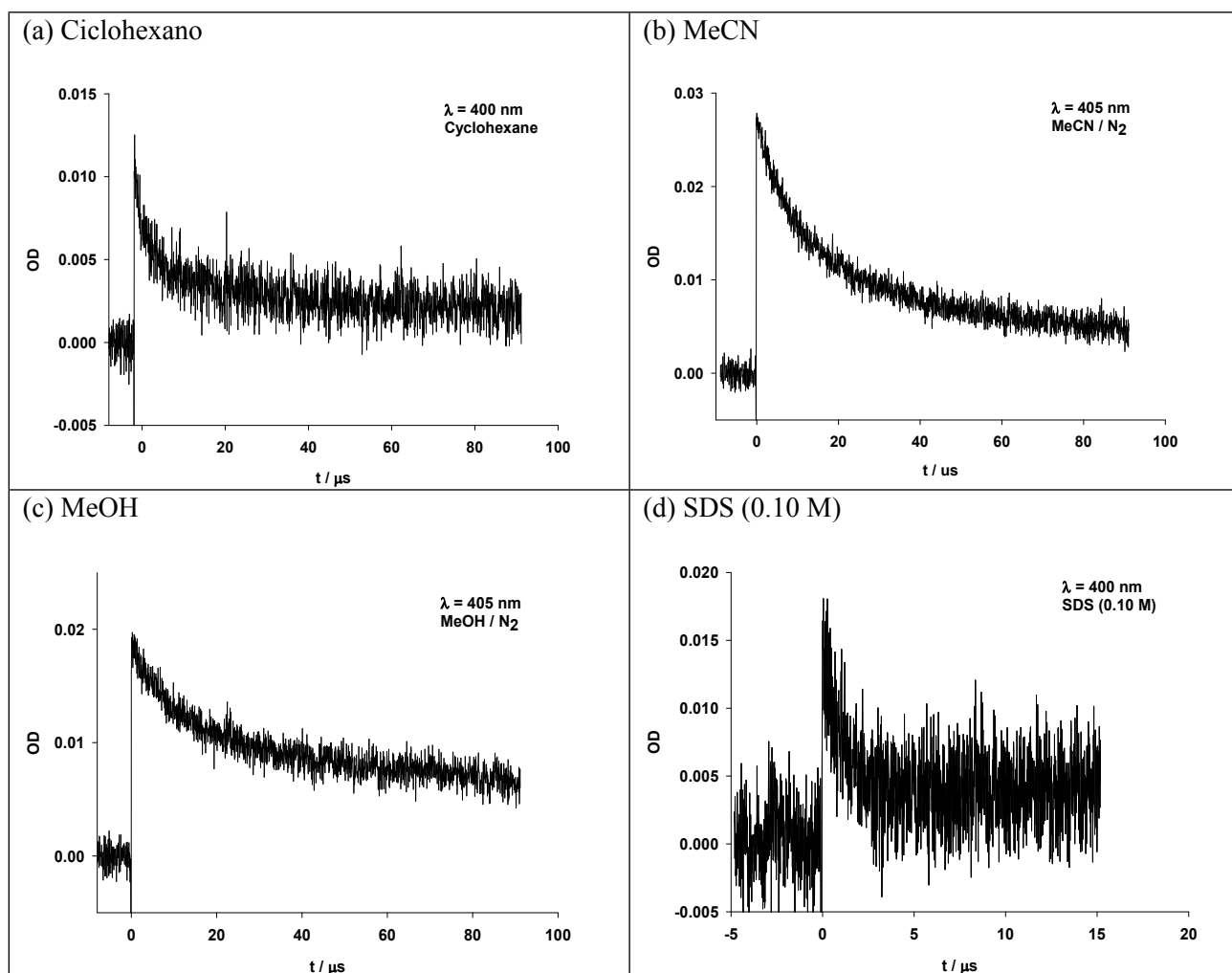




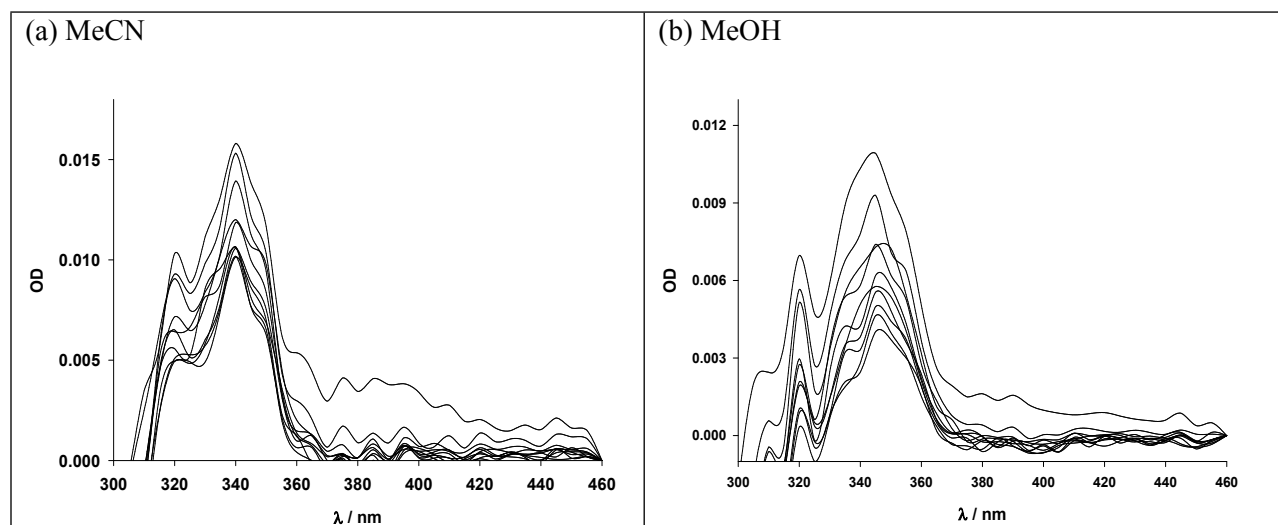
(vii) Time-resolved transient absorption spectra of *p*-*t*-butylphenyl benzoate (**4**).



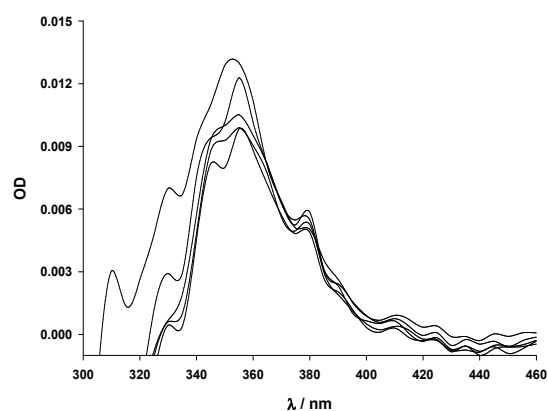
(viii) Transient decay traces of *p*-*t*-butylphenyl benzoate (**4**).



(ix) Time-resolved transient absorption spectra of *p*-phenylphenyl benzoate (**6**).



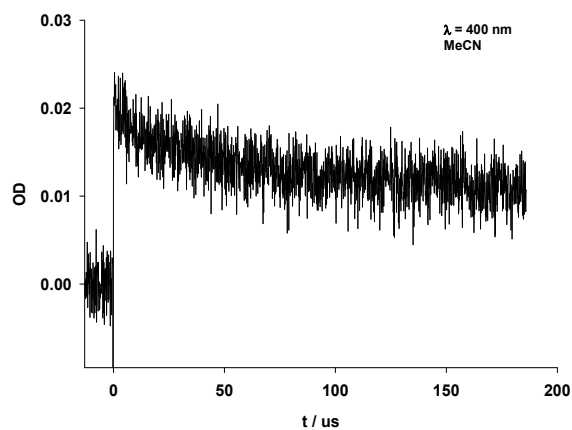
(c) SDS (0.10 M)



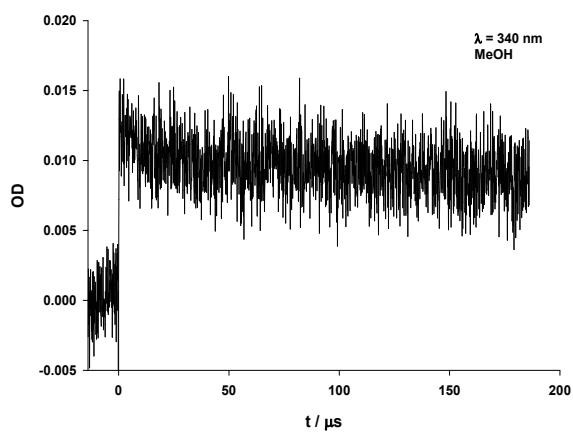
(d) The substrate is insoluble cyclohexane.

(x) Transient decay traces of *p*-phenylphenyl benzoate (6).

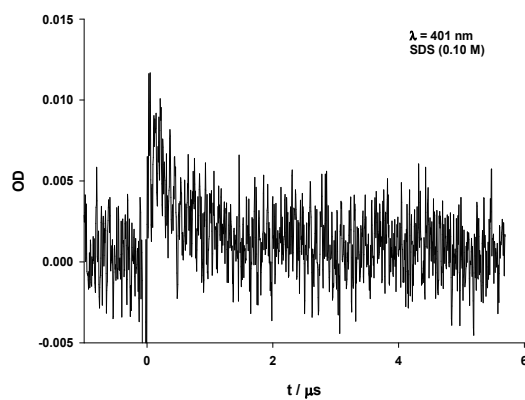
(a) MeCN



(b) MeOH

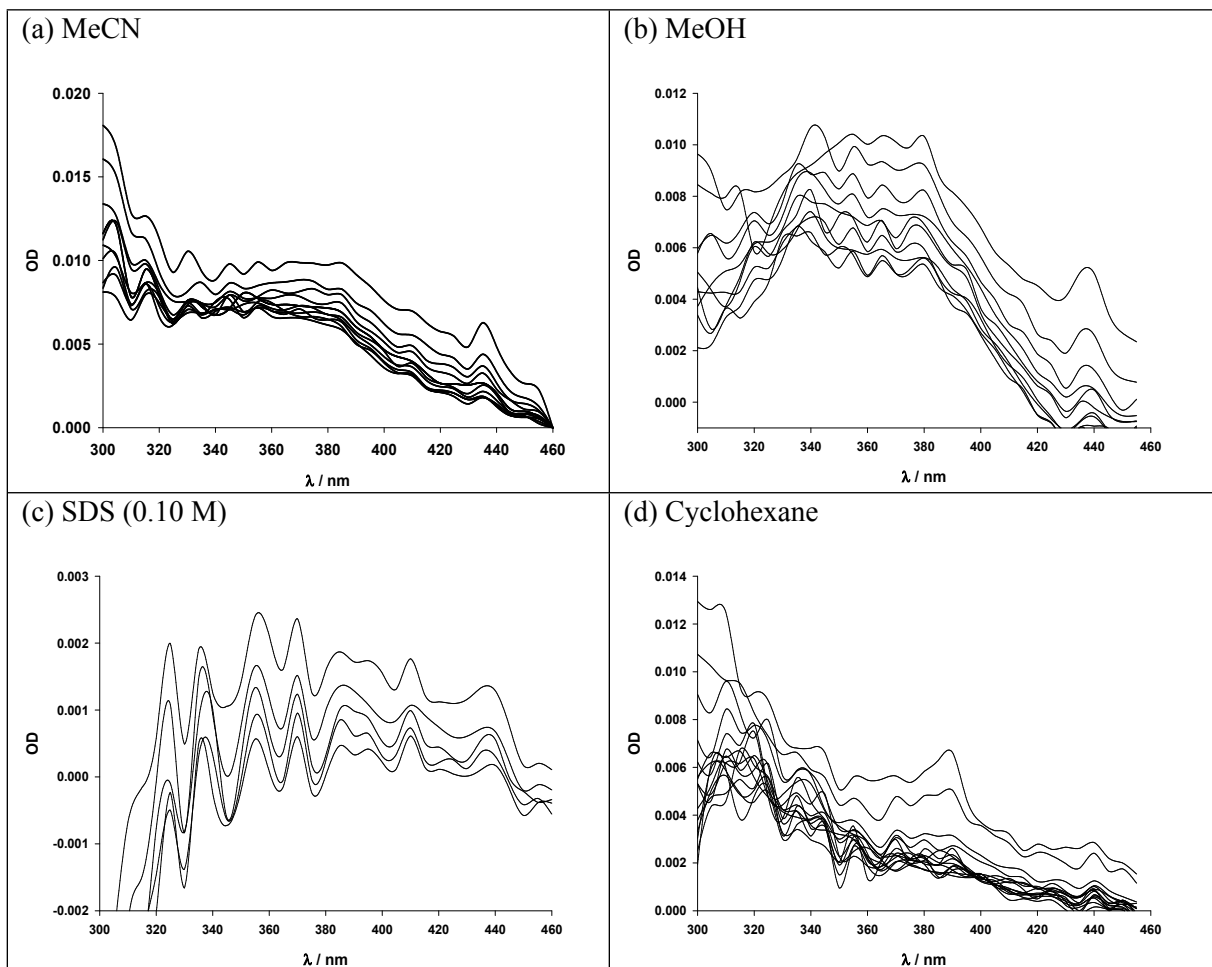


(c) SDS (0.10 M)

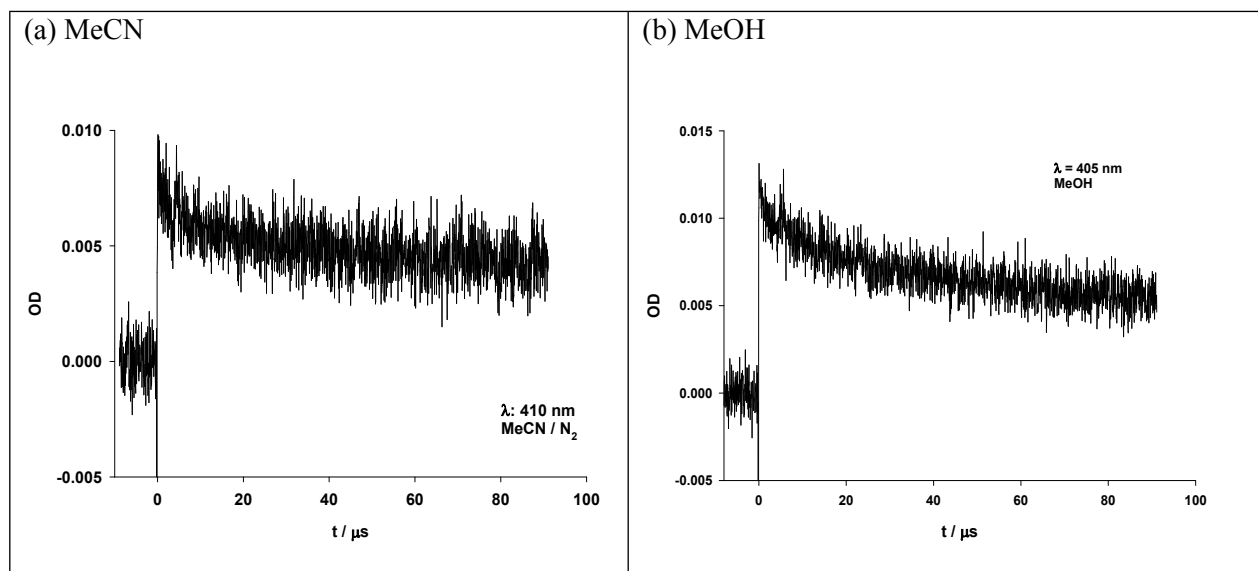


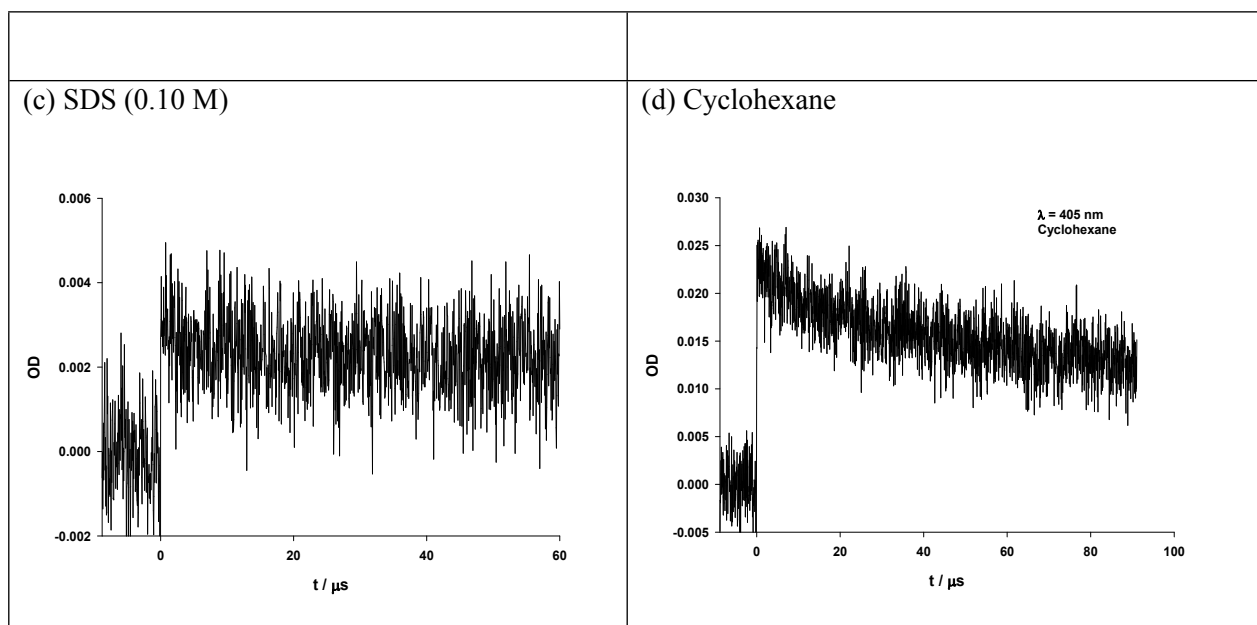
(d) The substrate is insoluble cyclohexane.

(xi) Time-resolved transient absorption spectra of *p*-cyanophenyl benzoate (7).

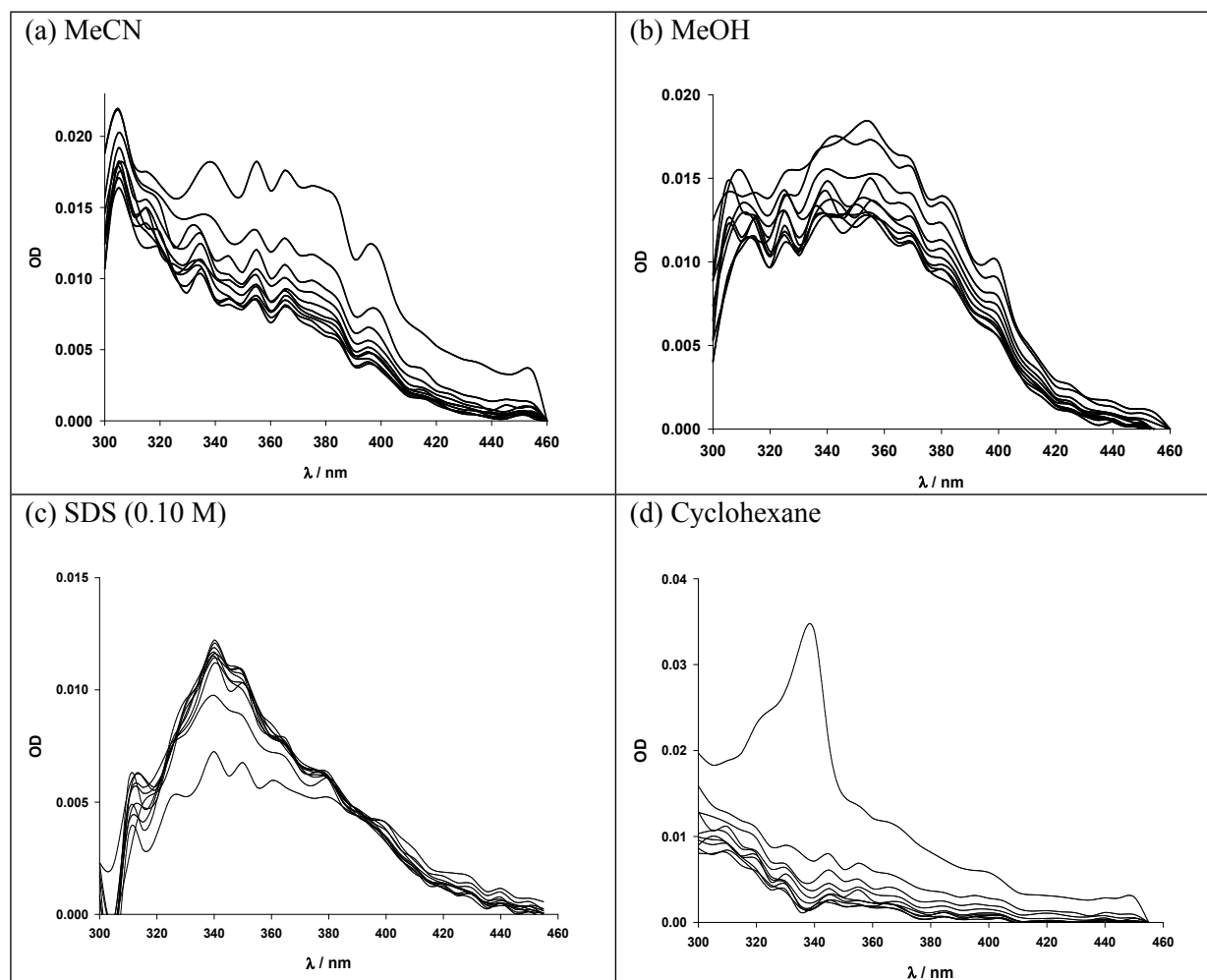


(xii) Transient decay traces of *p*-cyanophenyl benzoate (7).





(xiii) Time-resolved transient absorption spectra of phenyl benzoate (**5**).



(xiv) Transient decay traces of phenyl benzoate (5).

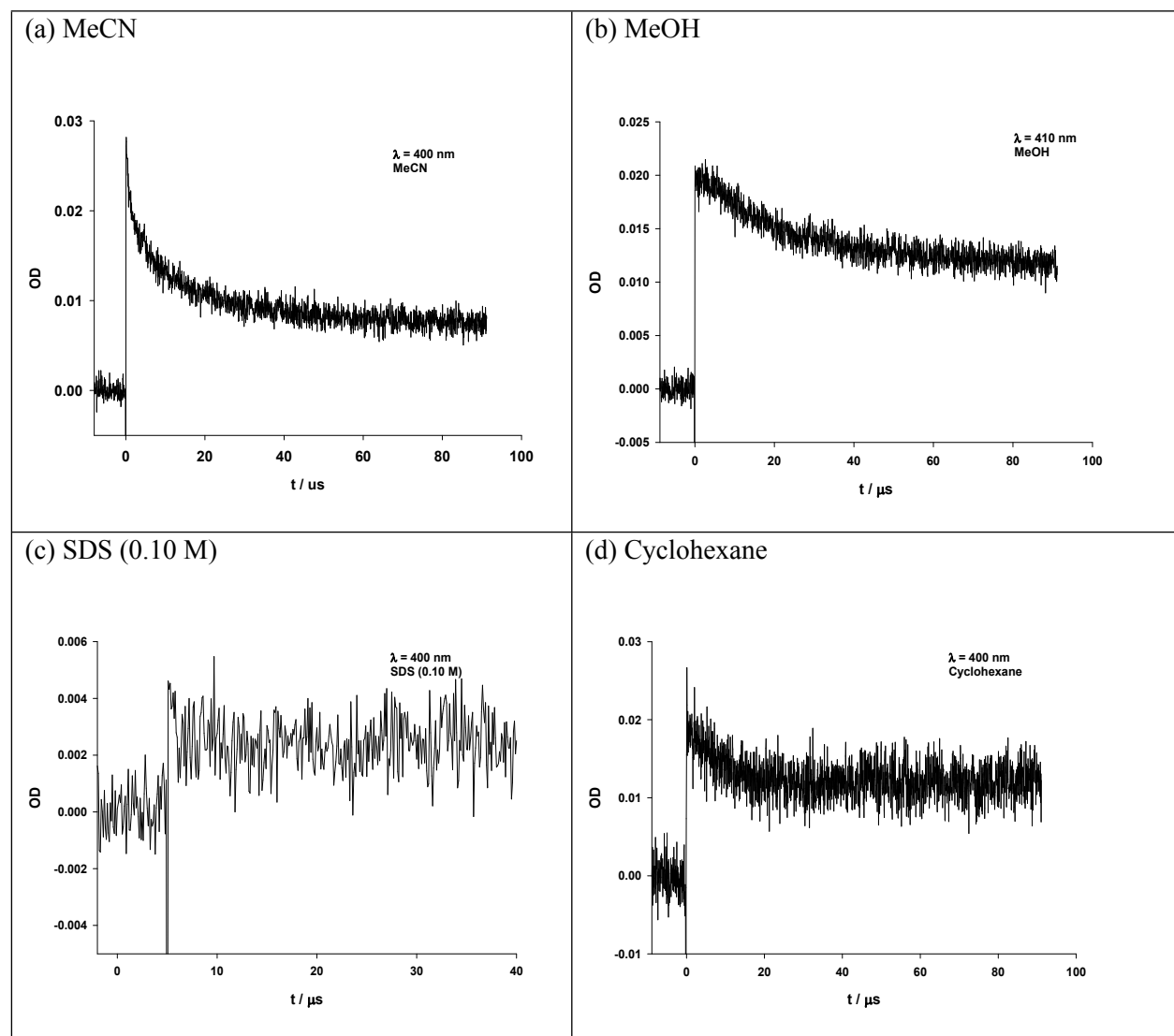
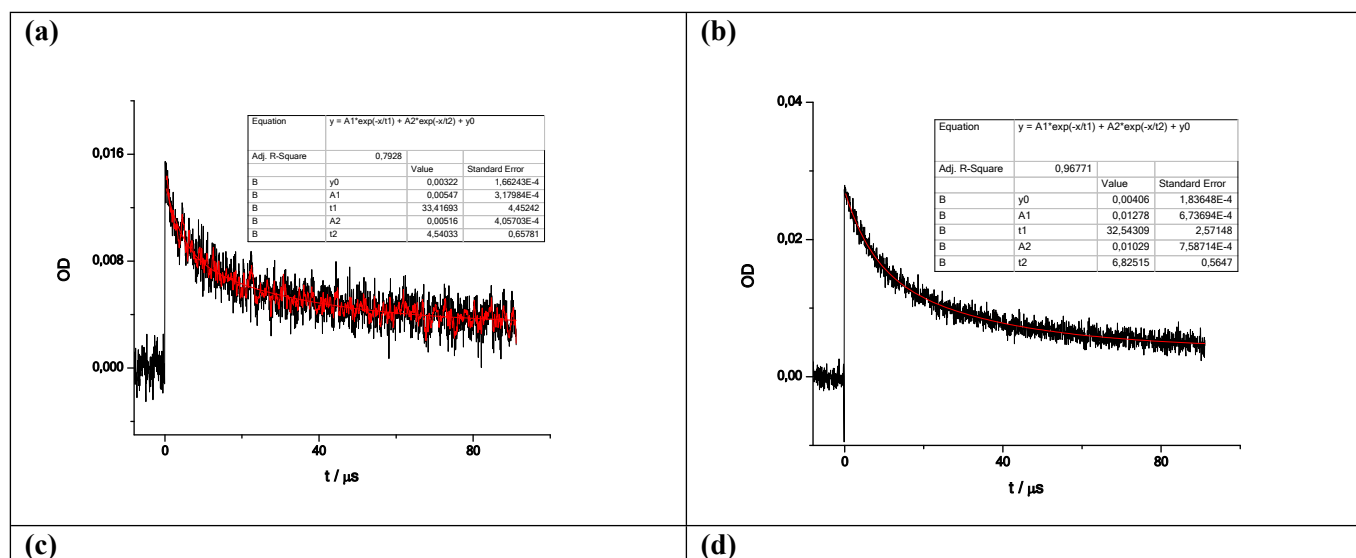


Figure S9. Transient absorption spectra and decay traces of 4-substituted phenoxy radicals recorded after a laser pulse (100 μs ; λ_{exc} : 266 nm) of N_2 -saturated solutions (5.1×10^{-4} M) in homogeneous and heterogeneous media.

6. Determination of the rate constants k_E and k_R in homogeneous and heterogeneous media.

Non-linear regression fitting has been applied to the transient decay traces of 4-substituted phenoxy radicals showing a bi-exponential decay behavior of the experimental values obtained for all the substrates studied. Some examples are already shown in Figure 8 in the main text. Therefore, two half lifetime values were obtained; viz. τ_E and τ_R . The short lifetime (τ_R) was assigned to the *ortho*-acyl migration process while the large lifetime (τ_E) was assigned to the 4-substituted phenoxy radical out-of-cage escape process by comparison with earlier published data regarding thiyl radicals.^{S2} Some representative examples of the primary experimental data are shown in the following plots together with the bi-exponential decay fitting and the statistics data (see **Figure S10**).



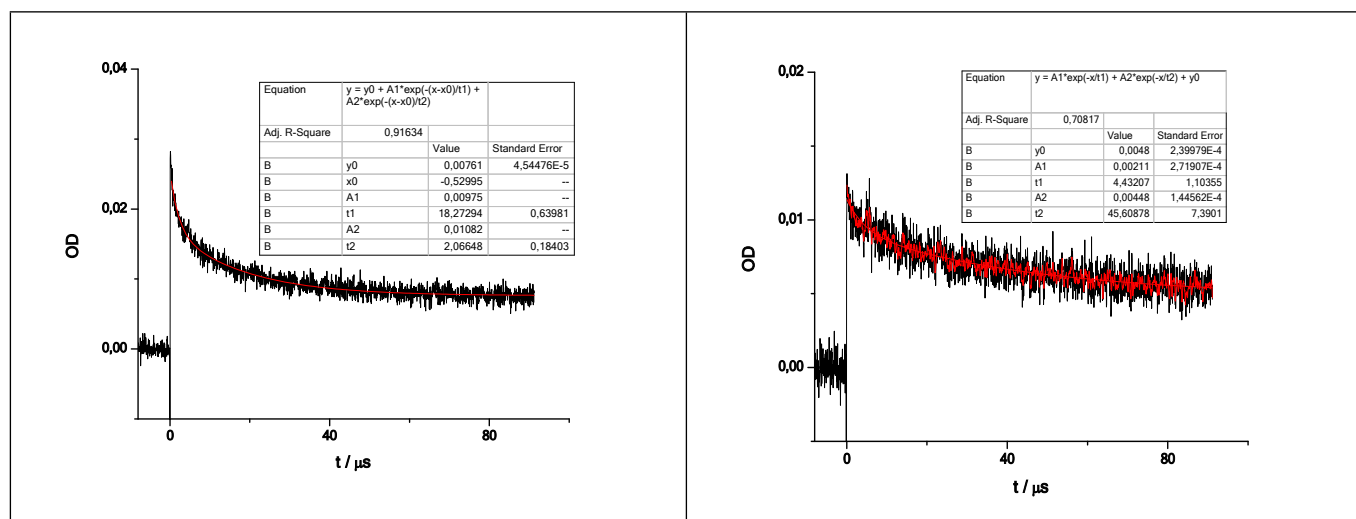


Figure S10. Decay traces from 4-substituted phenoxyl radical transients (1×10^{-4} mol dm $^{-3}$) recorded after laser pulse (266 nm) under N $_2$ atmosphere: (a) *p*-phenoxyphenyl benzoate (**2**) in MeCN; (b) *p*-*t*-butylphenyl benzoate (**4**) in cyclohexane; (c) phenyl benzoate (**5**) in MeCN and (d) *p*-cyanophenyl benzoate (**7**) in MeOH.

The out-of-cage process of 4-substituted phenoxy radicals is a unimolecular pathway, therefore, the following equation (2) holds.

$$\tau_E = \frac{1}{k_E} \quad (2)$$

Then, the rate constants (k_E) can be easily obtained from the experimental half lifetime values and these values are already shown in Table 4 and Table 5 (see manuscript).

On the other hand, the rate constants of the *ortho* coupling reaction (k_R) were determined from the experimental optical density (OD) shown in **Figure S9** which were converted to molar concentration applying Lambert-Beer law. The absorption coefficients of the 4-substituted phenoxy radicals are known.^{S3} Then, plotting the reciprocal of the radical concentration against time, nice linear plots were obtained. **Figure S11** shows the linear plots and also the best linear regression fitting for the experiments done in different homogeneous and heterogeneous media.

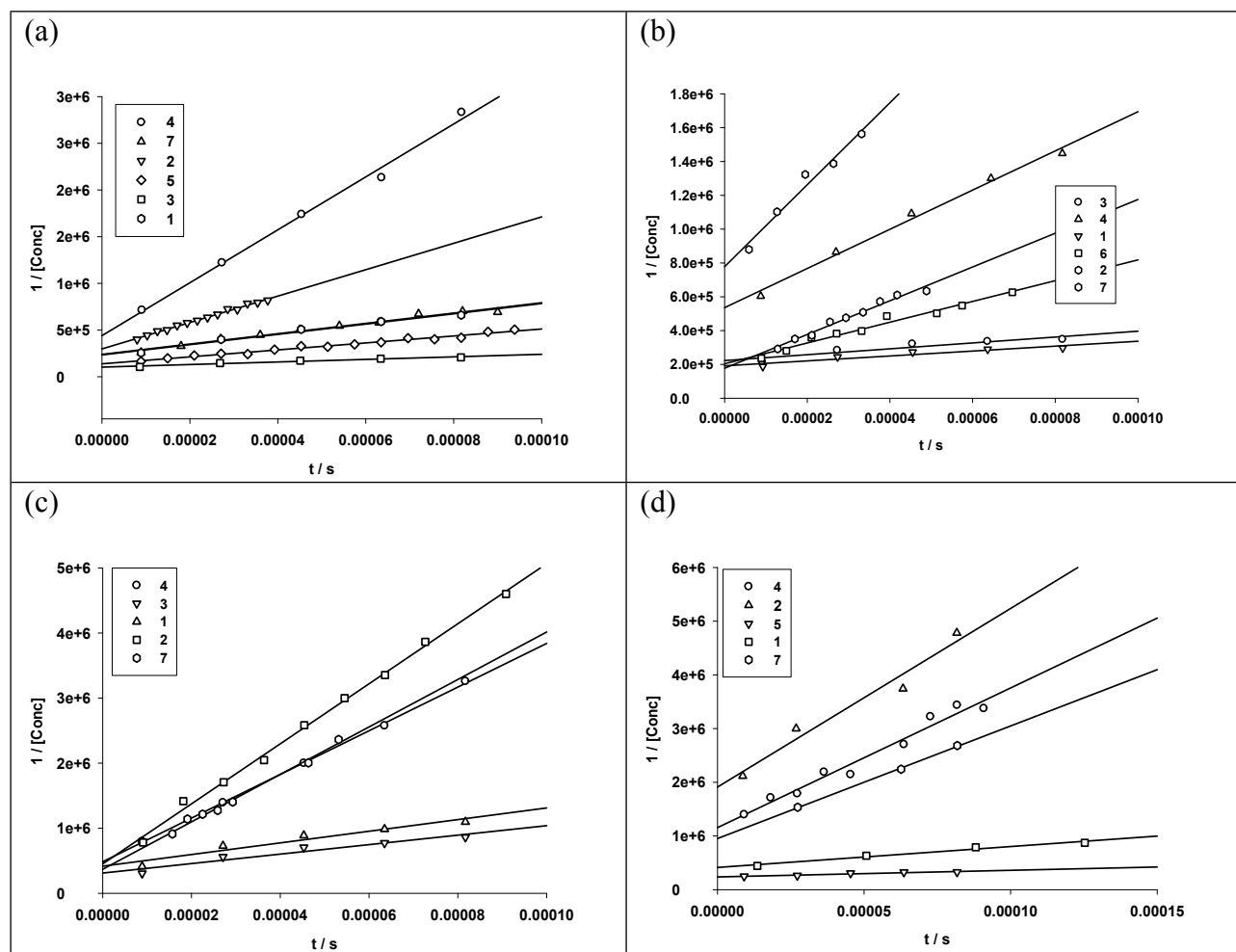


Figure S11. Reciprocal of the concentration of transient 4-substituted phenoxy radical vs. time plots recorded under N_2 in: (a) MeCN; (b) MeOH; (c) Cyclohexane and (d) SDS 0.10 M solution. The numbers shown in the insets are those of the aryl benzoates already shown in Table 2 (see main text).

From the slopes of the best linear regression shown in **Figure S11** the bimolecular rate constants, k_R , were easily obtained under all the conditions examined which are already collected in Tables 4 (see manuscript).

For the case of phenyl benzoate (**5**) the bimolecular rate constants of formation of the *ortho*-benzoylcyclohexadienones (k_{ortho}) and *para*-cyclohexadienone (k_{para}) in homogeneous media were obtained from the slopes of the best linear regression shown in **Figure S12**.

The assignment of the rate constants k_{ortho} and k_{para} was done taking into account that the migration of the benzoyl group to the *ortho* position is more rapid than the migration of the same group to the *para* position because the last pathway requires rotation of the phenoxyl radical to approach the benzoyl group. This assignment is in agreement with the chemical yield obtained in micellar solution where the rotation is confined within the micellar core. Compare the yield of the 2-hydroxybenzophenone (**5a**): 90% in SDS and 92% in Brij-P35, with the yield of 4-hydroxybenzophenone which is *ca* 8 – 10 % in both micellar media. Additionally, in homogeneous media a similar trend was observed that is in agreement with this assignment.

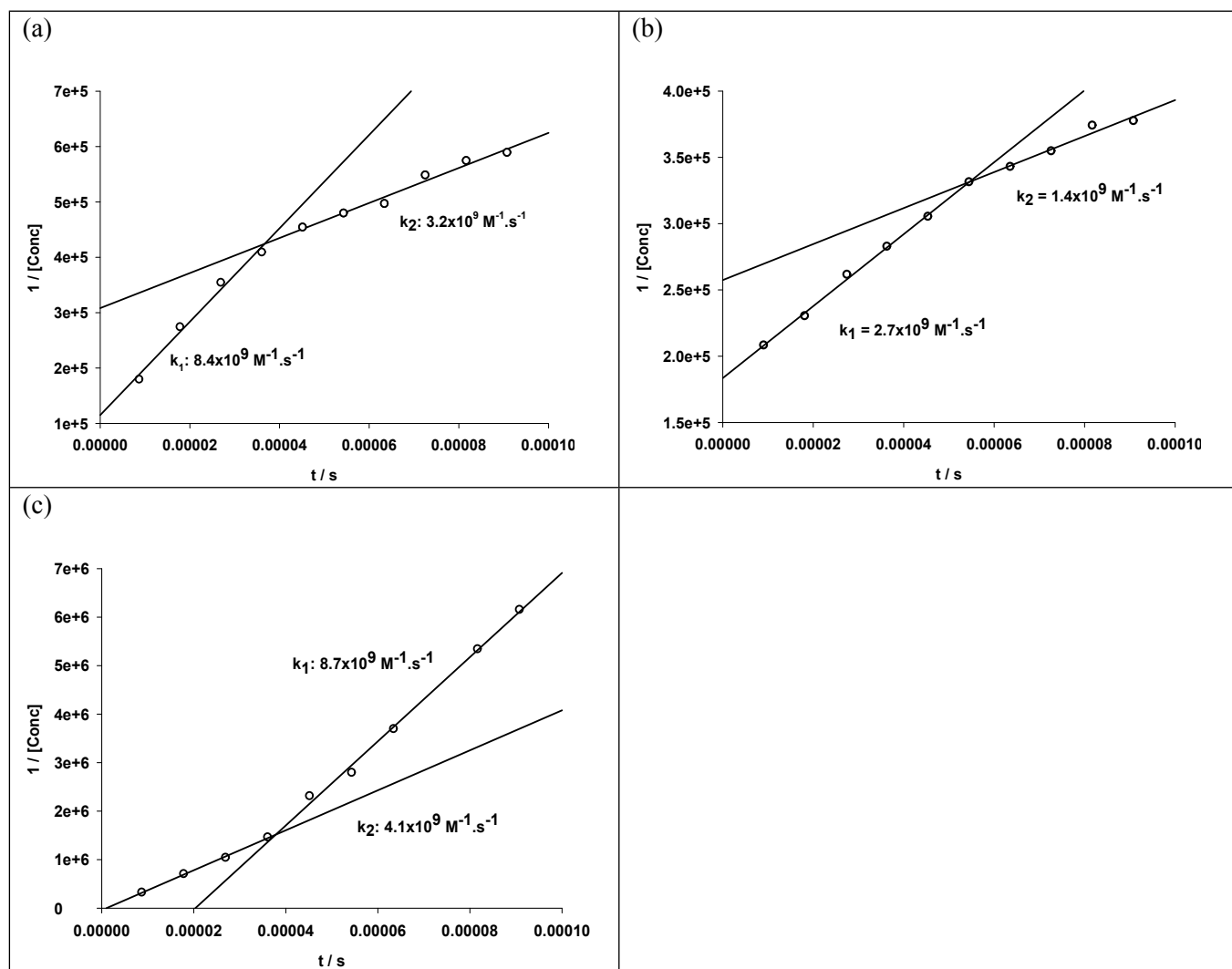
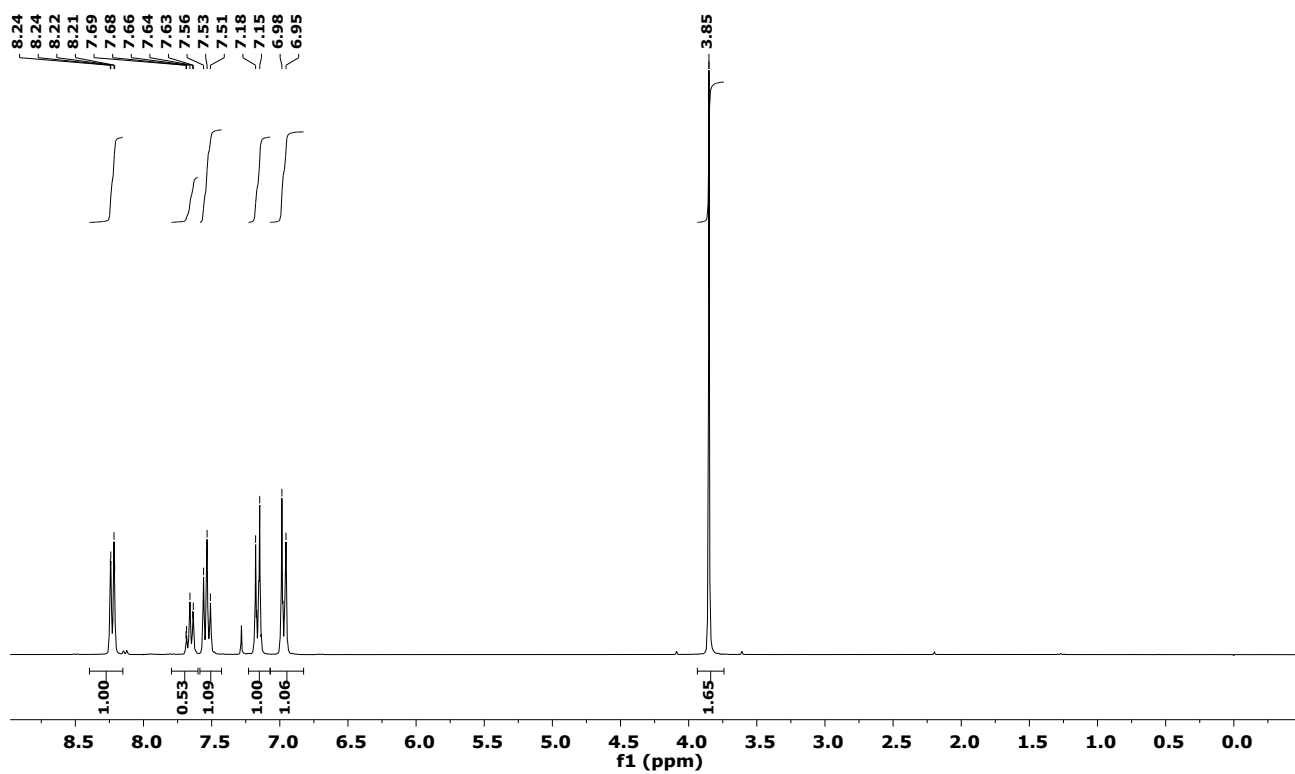
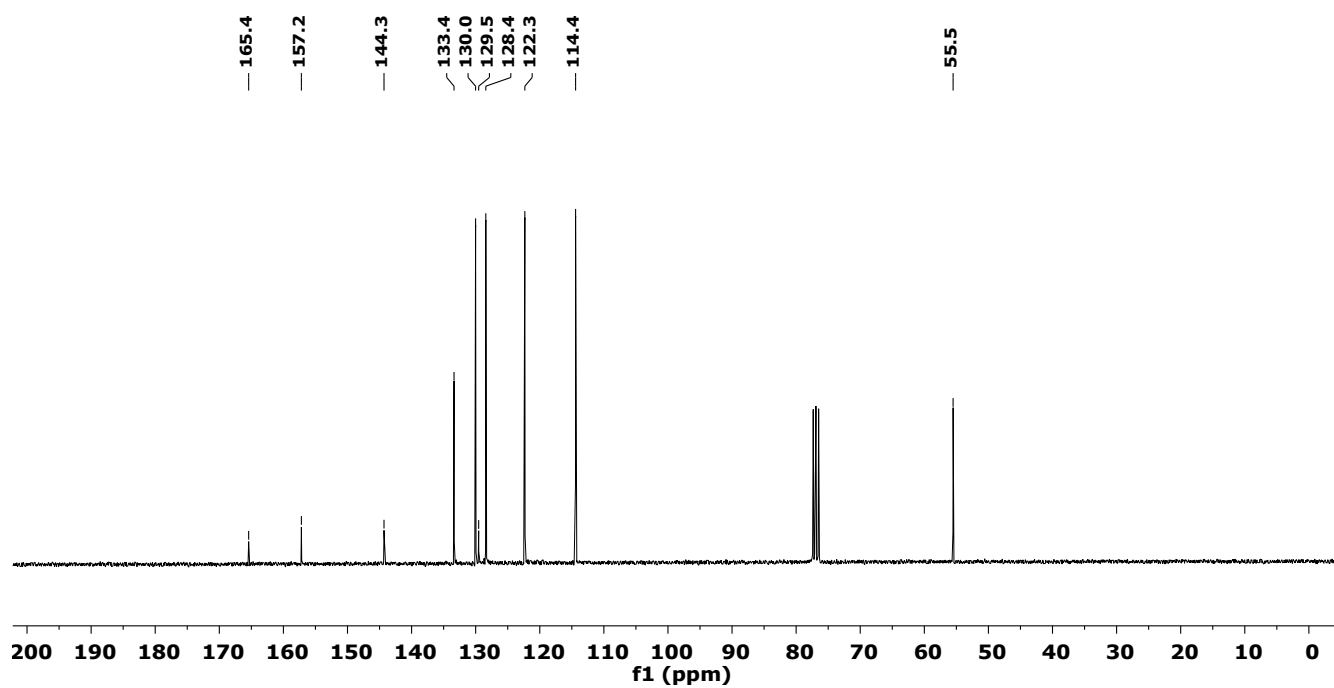


Figure S12. Reciprocal of the concentration of transient phenoxyl radical vs. time plots recorded under N₂ in: (a) MeCN; (b) MeOH and (c) Cyclohexane. Absorption wavelength: 400 nm.

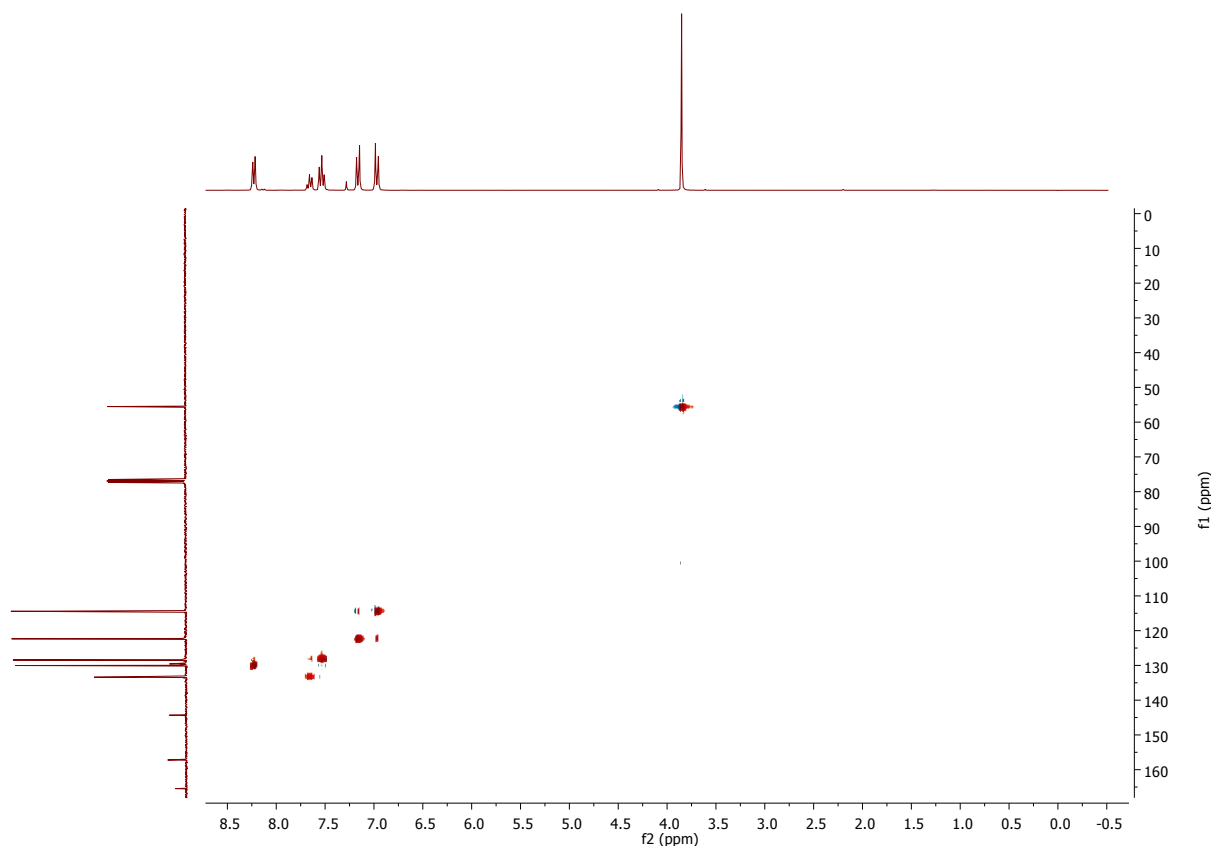
7. References

- [S1] Iguchi, D.; Erra-Balsells, R.; Bonesi, S. M., Photo-Fries rearrangement of aryl acetamides: regioselectivity induced by the aqueous micellar green environment, *Photochem. Photobiol. Sci.* **2016**, *15*, 106 – 116, 2016.
- [S2] (a) Gadosy, T. A.; Shukla, D.; Johnston, L. J., Generation, characterization, and deprotonation of phenol radical cations, *J. Phys. Chem. A* **1999**, *103*, 8834-8839. (b) Bonesi, S. M.; Crespi, S.; Merli, D.; Manet, I.; Albini, A., Direct irradiation of aryl sulfides: hemolytic fragmentation and sensitized S-oxidation, *J. Org. Chem.* **2017**, *82*, 9054–9065.
- [S3] Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C., Reaction of t-butoxy radicals with phenols. Comparison with the reactions of carbonyl triplets, *J. Am. Chem. Soc.* **1981**, *103*, 4162 - 4166.

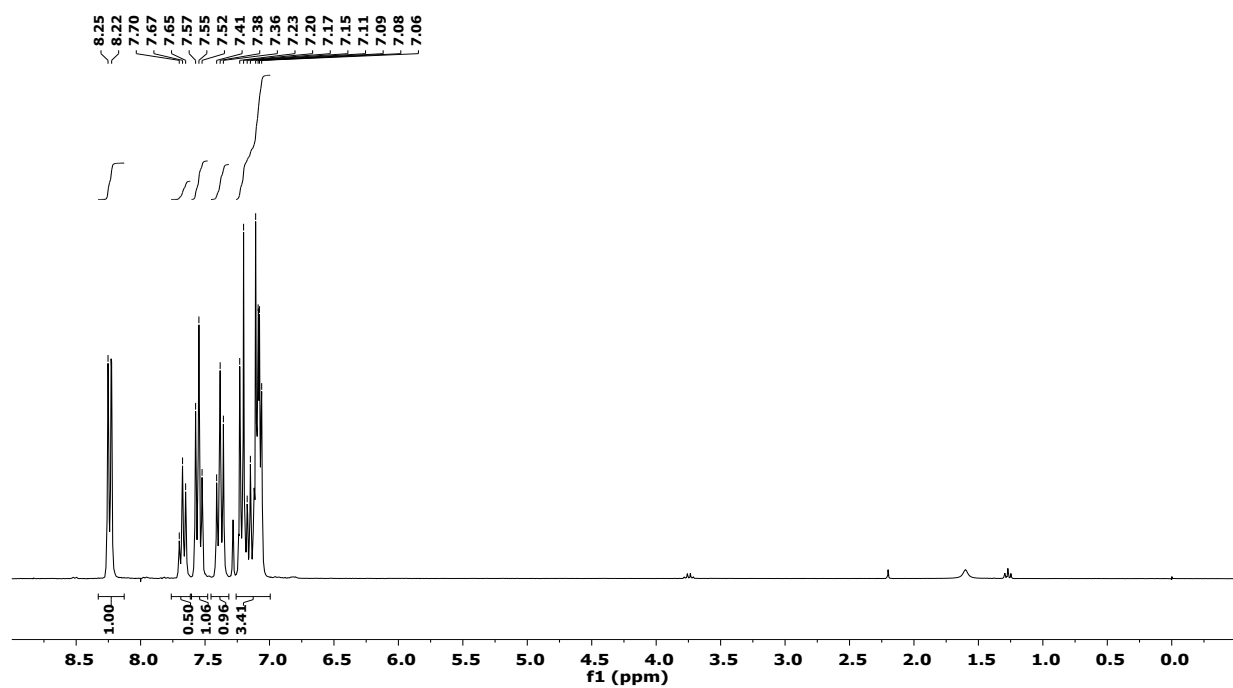
8. Copy of the ^1H and ^{13}C spectra of aryl benzoates (1-8).**(a) *p*-Methoxyphenyl benzoate (1).** Copy of the ^1H -NMR (300 MHz), CDCl_3 .Copy of the ^{13}C -NMR (300 MHz), CDCl_3 .



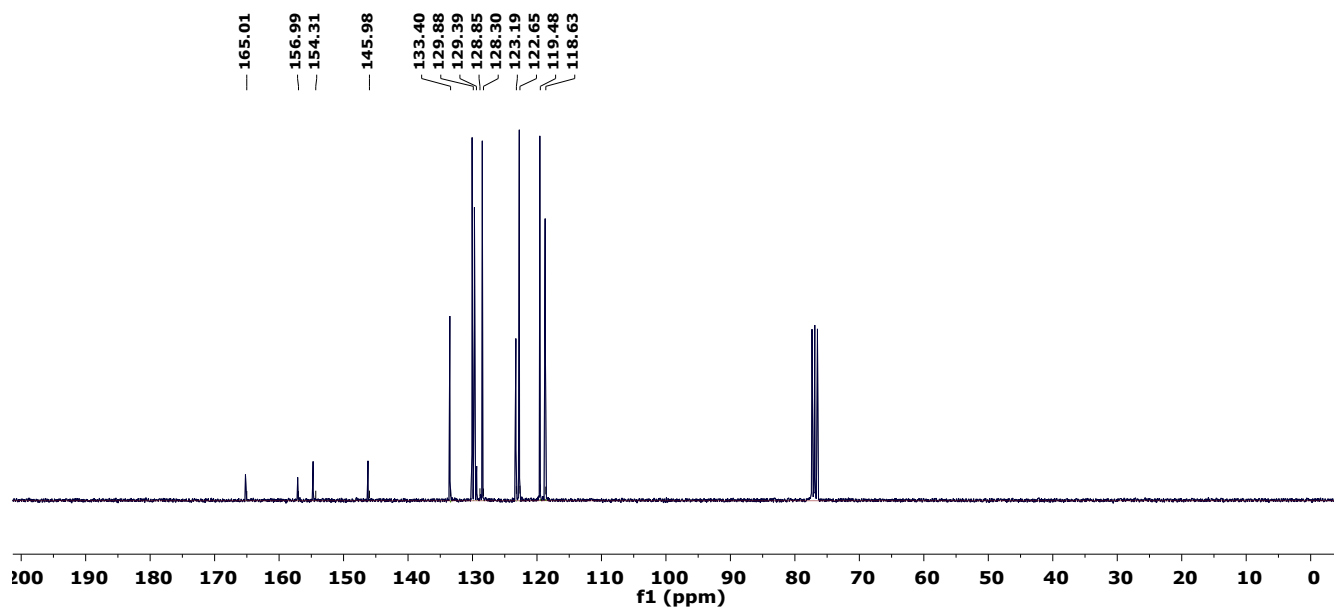
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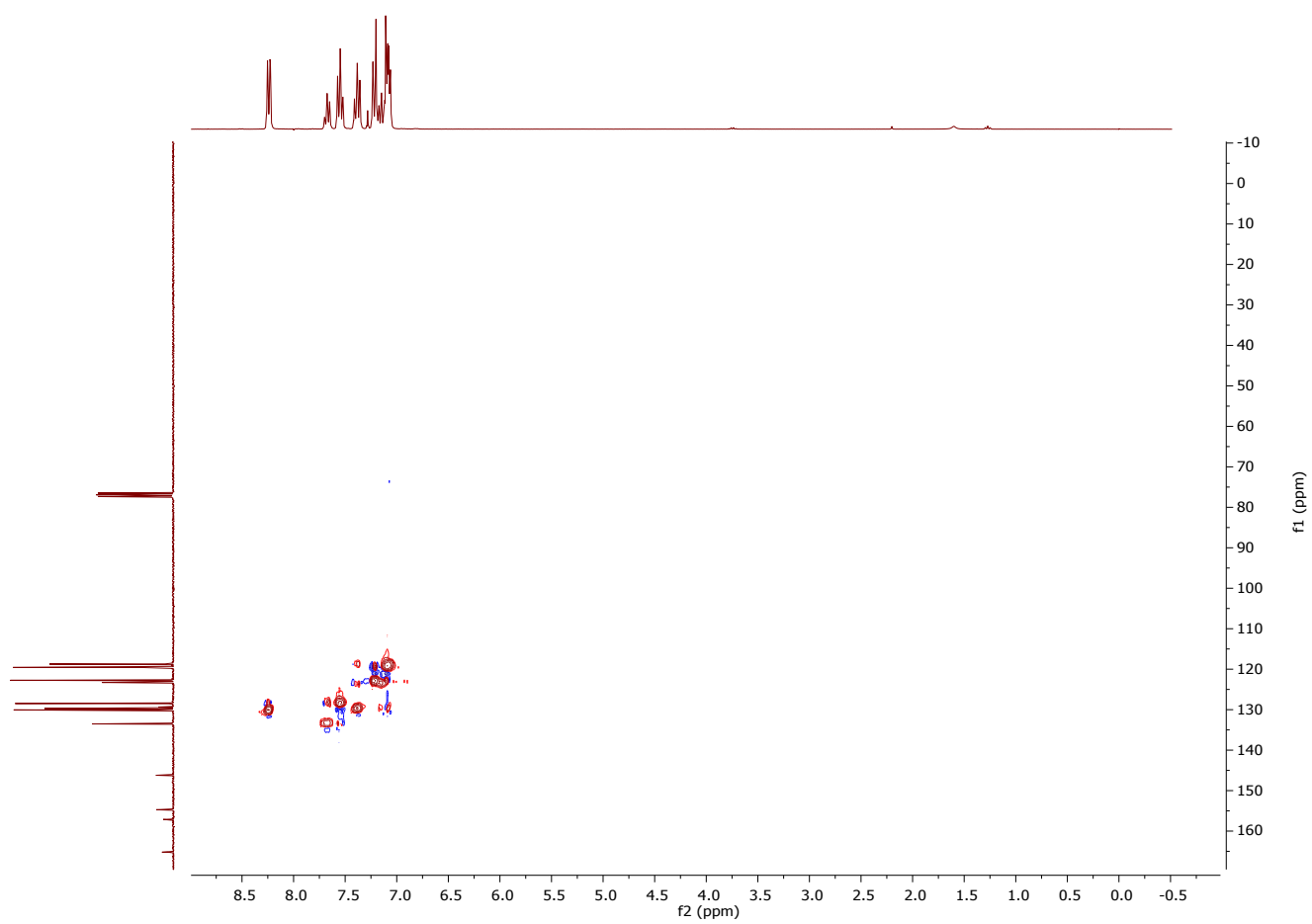
(b) *p*-Phenoxyphenyl benzoate (2). Copy of the ¹H-NMR (300 MHz), CDCl₃.



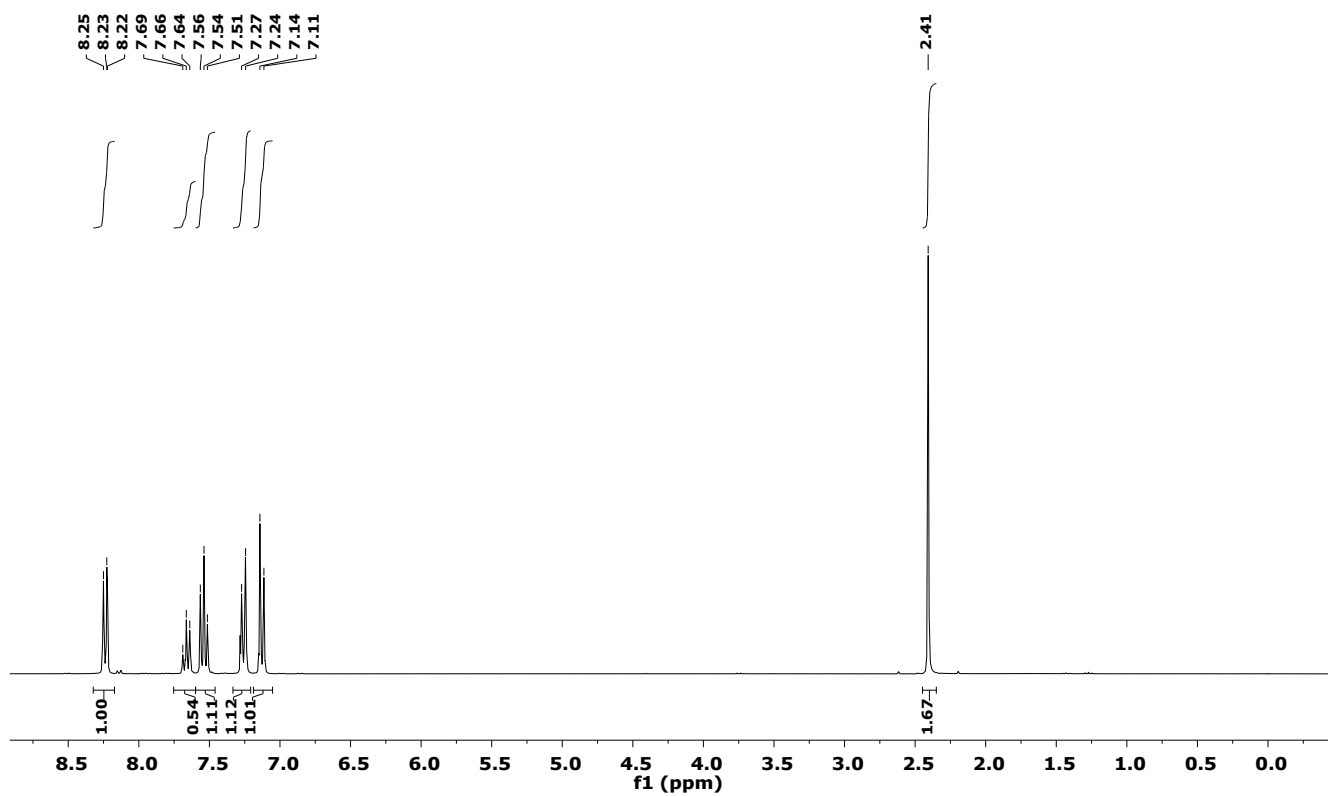
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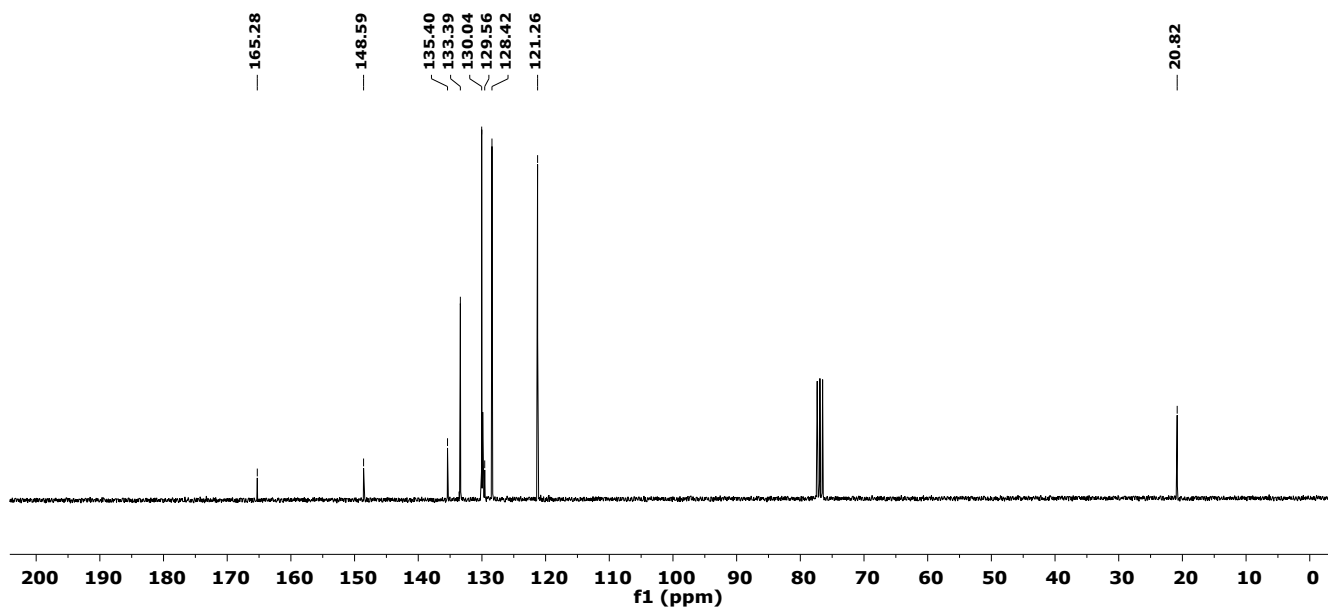
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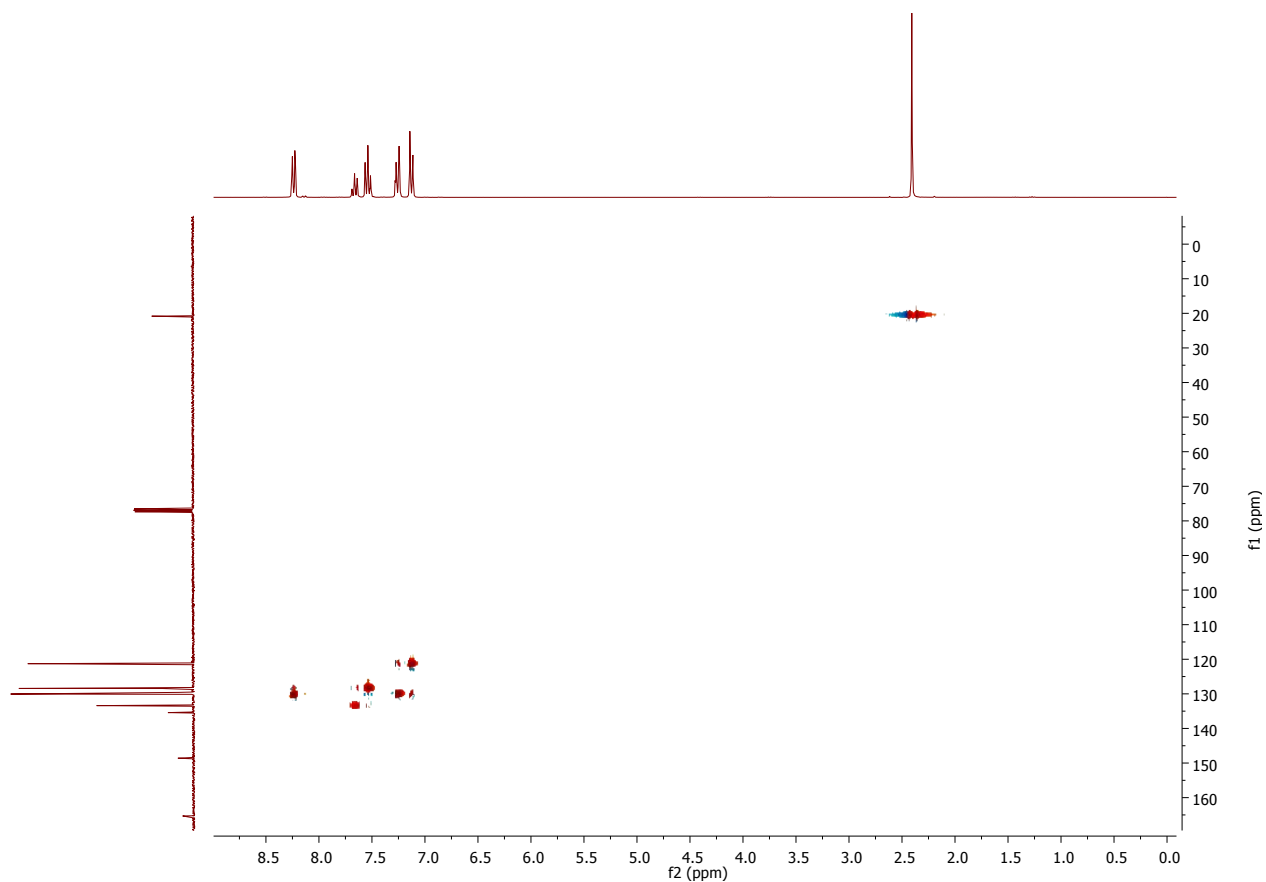
(c) *p*-Methylphenyl benzoate (3). Copy of the ^1H -NMR (300 MHz), CDCl_3 .



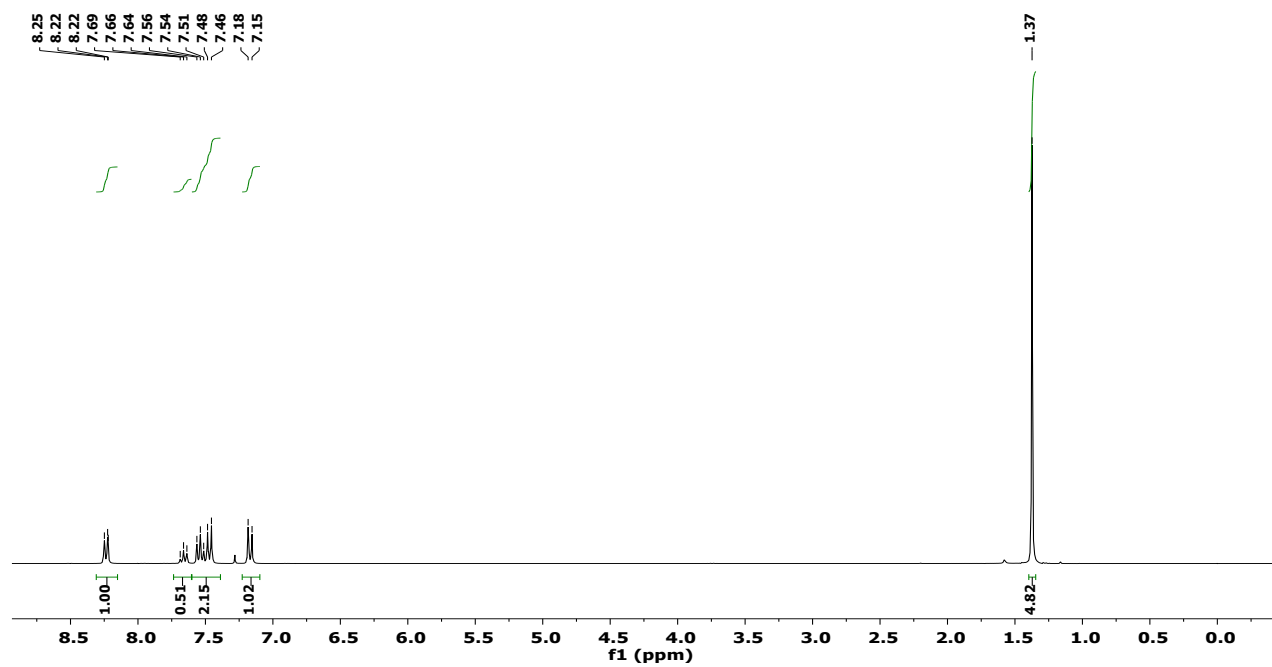
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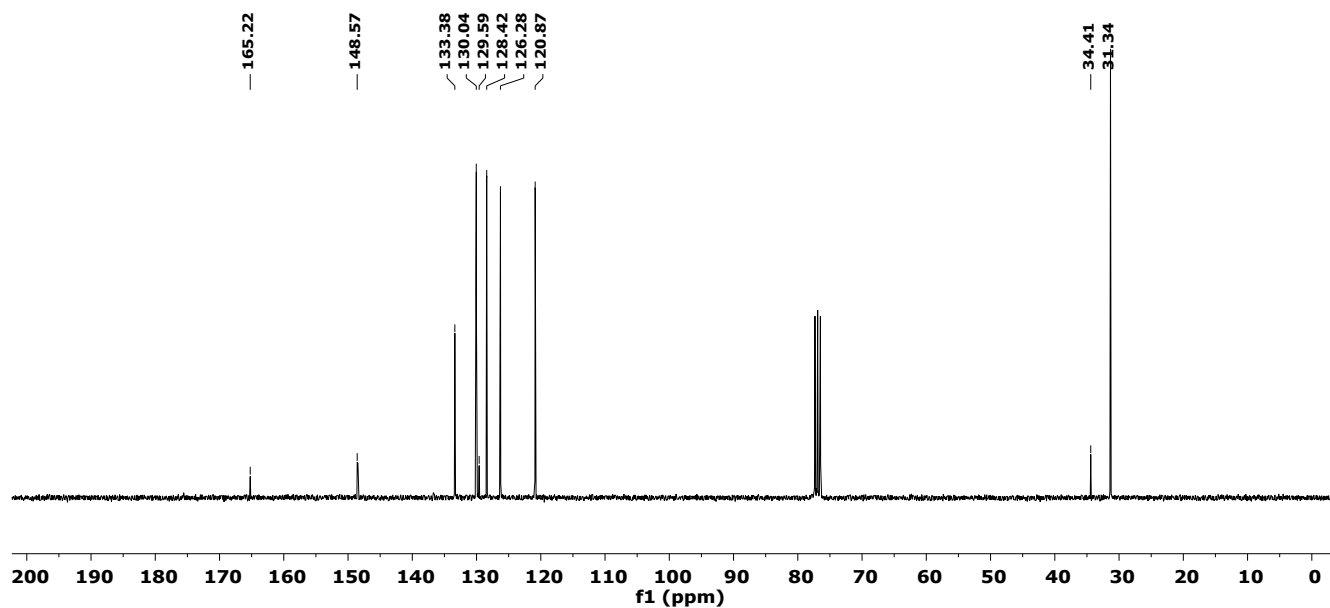
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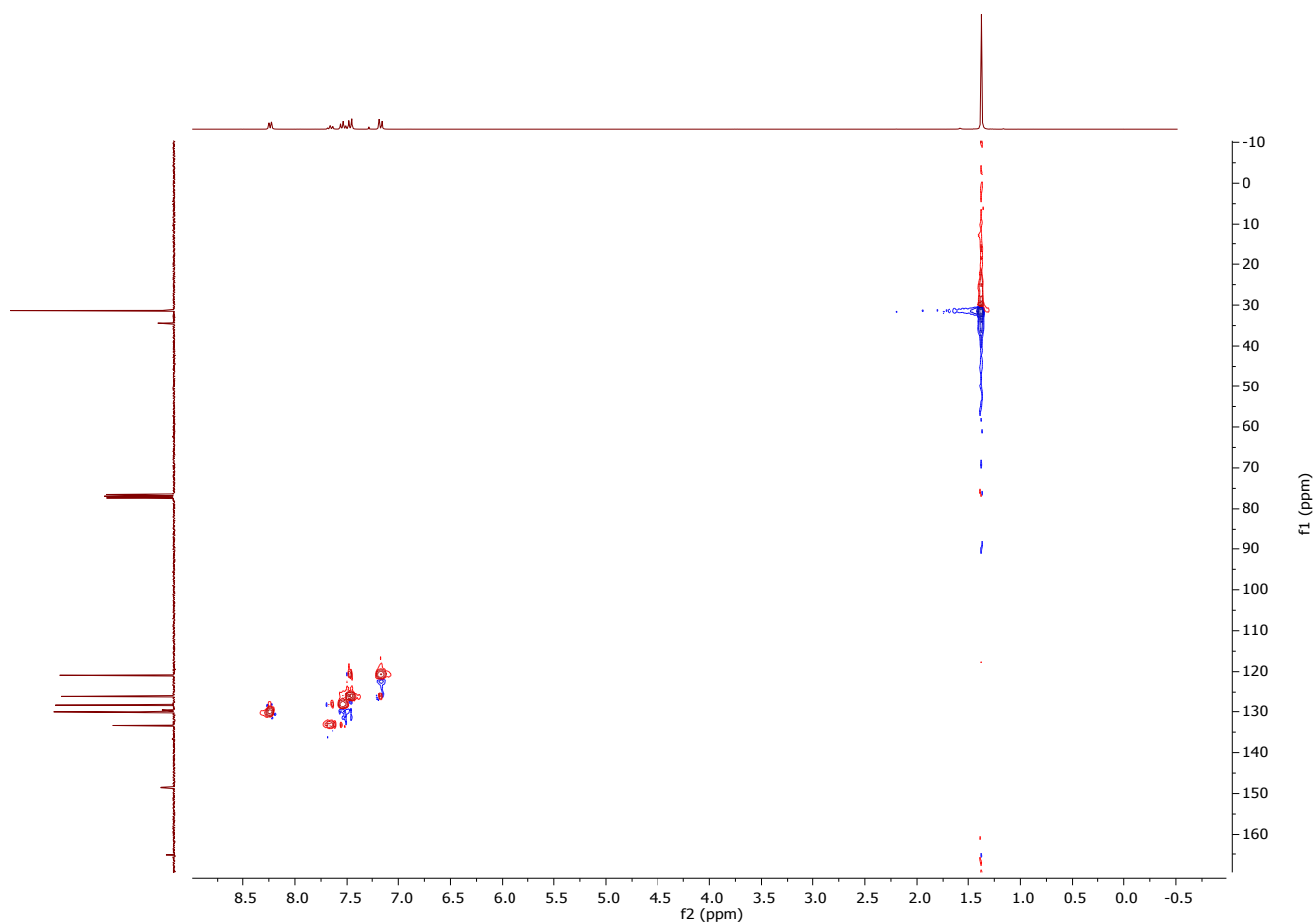
(d) *p*-t-Butylphenyl benzoate (4). Copy of the ^1H -NMR (300 MHz), CDCl_3 .



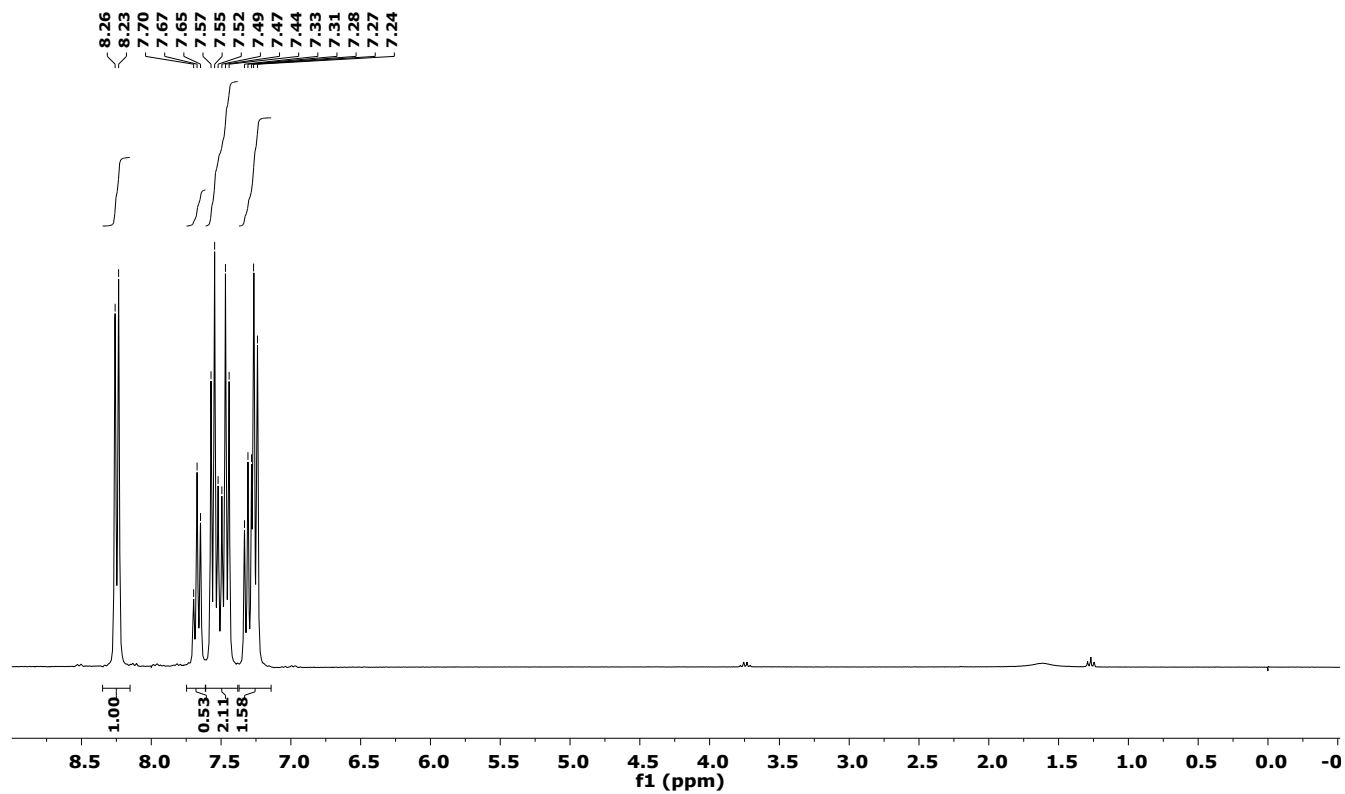
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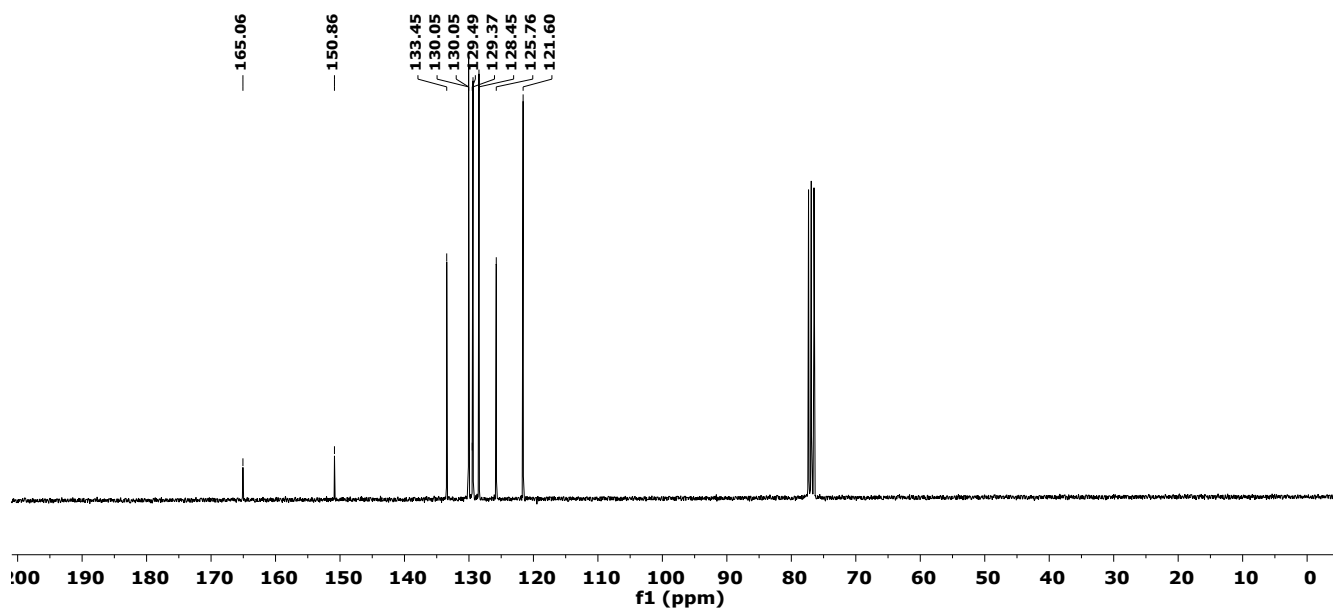
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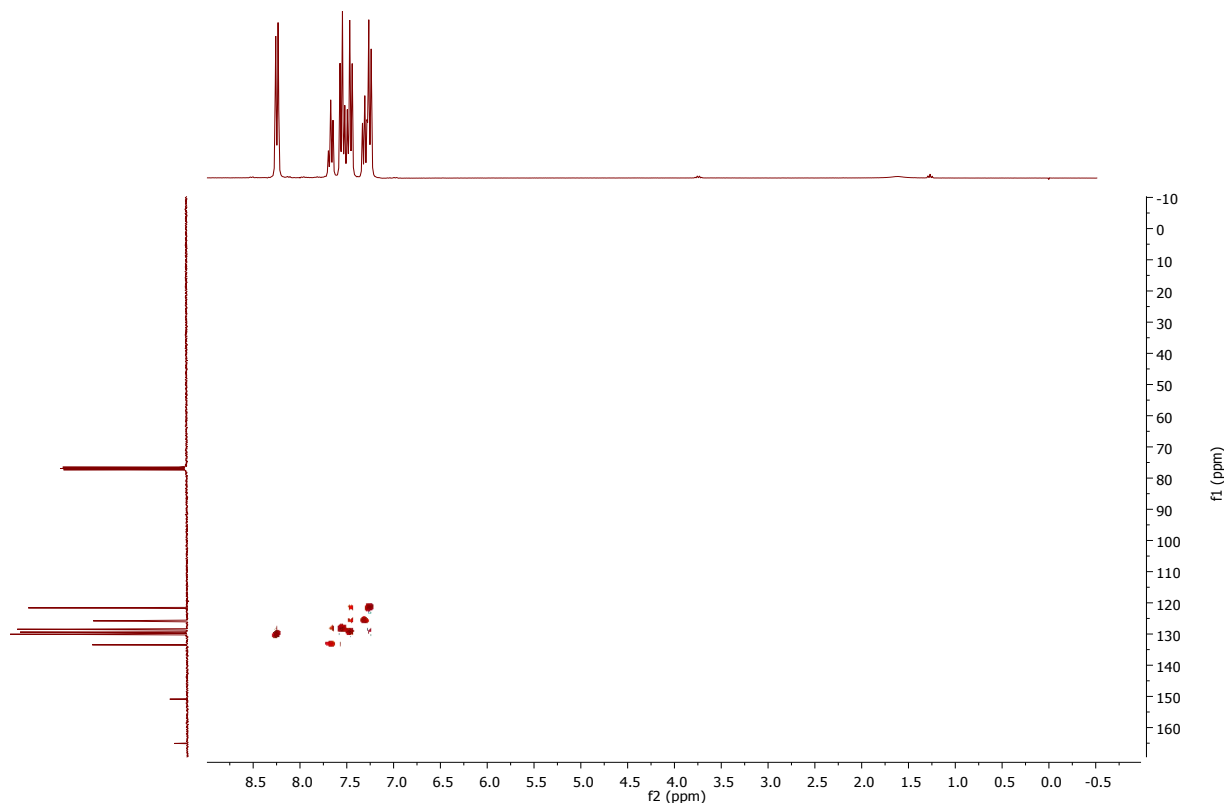
(e) Phenyl benzoate (5). Copy of the ¹H-NMR (300 MHz), CDCl₃.



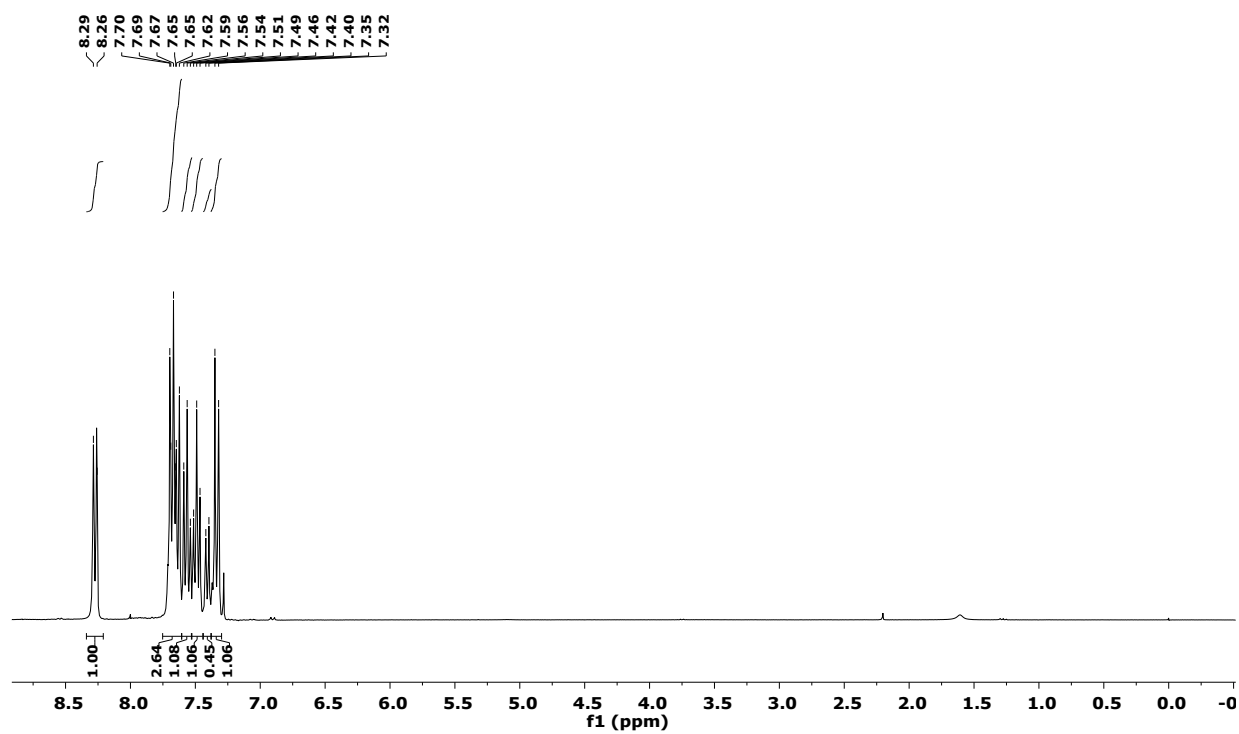
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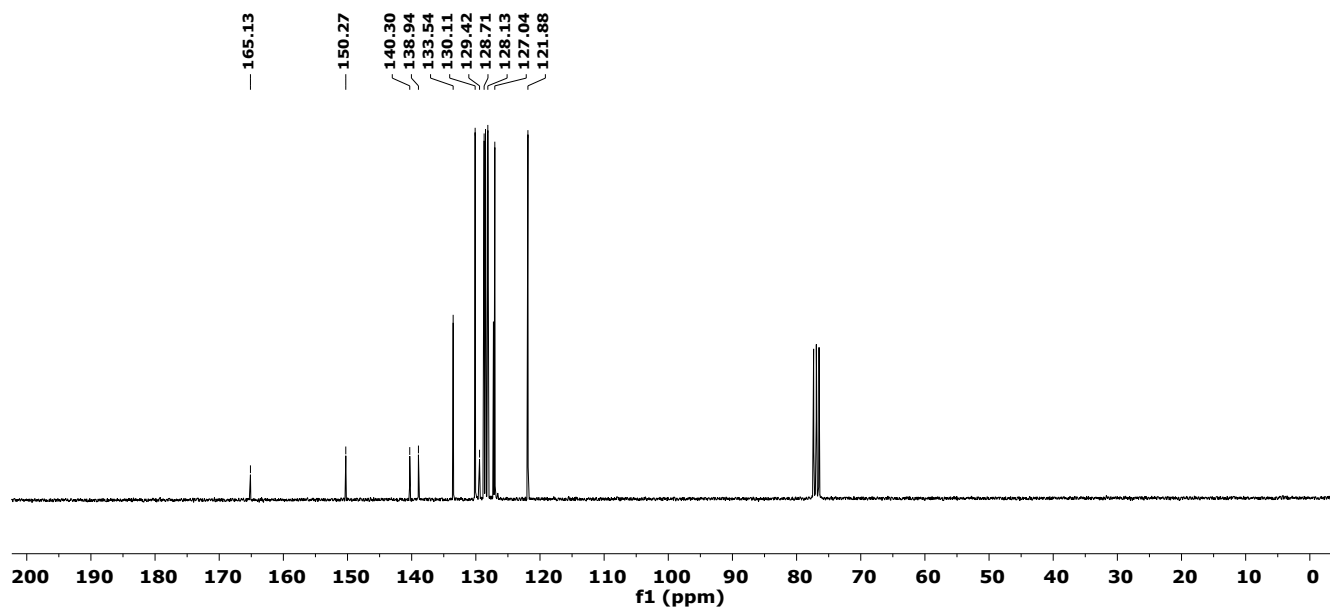
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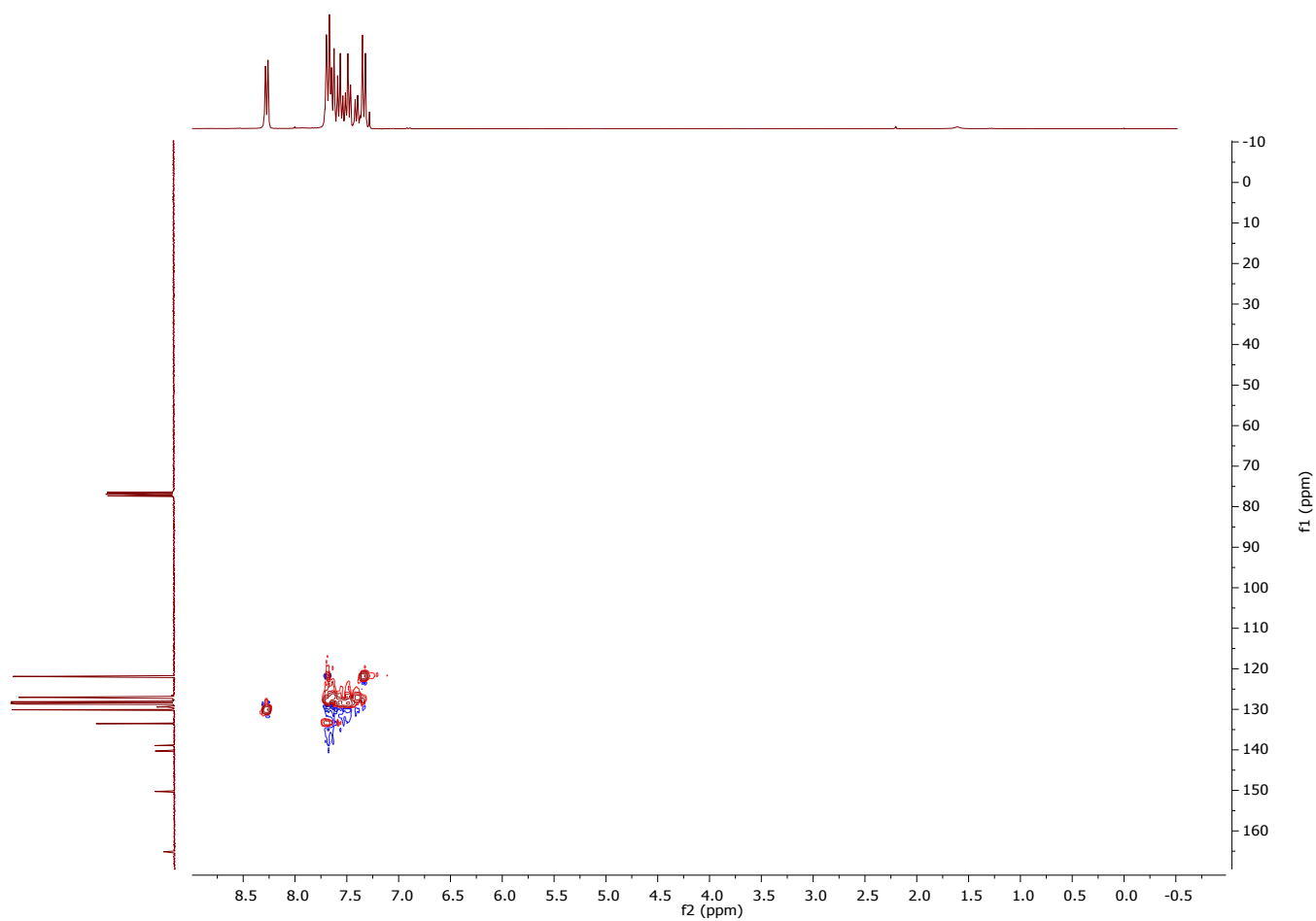
(f) *p*-Phenylphenyl benzoate (6). Copy of the ^1H -NMR (300 MHz), CDCl_3 .



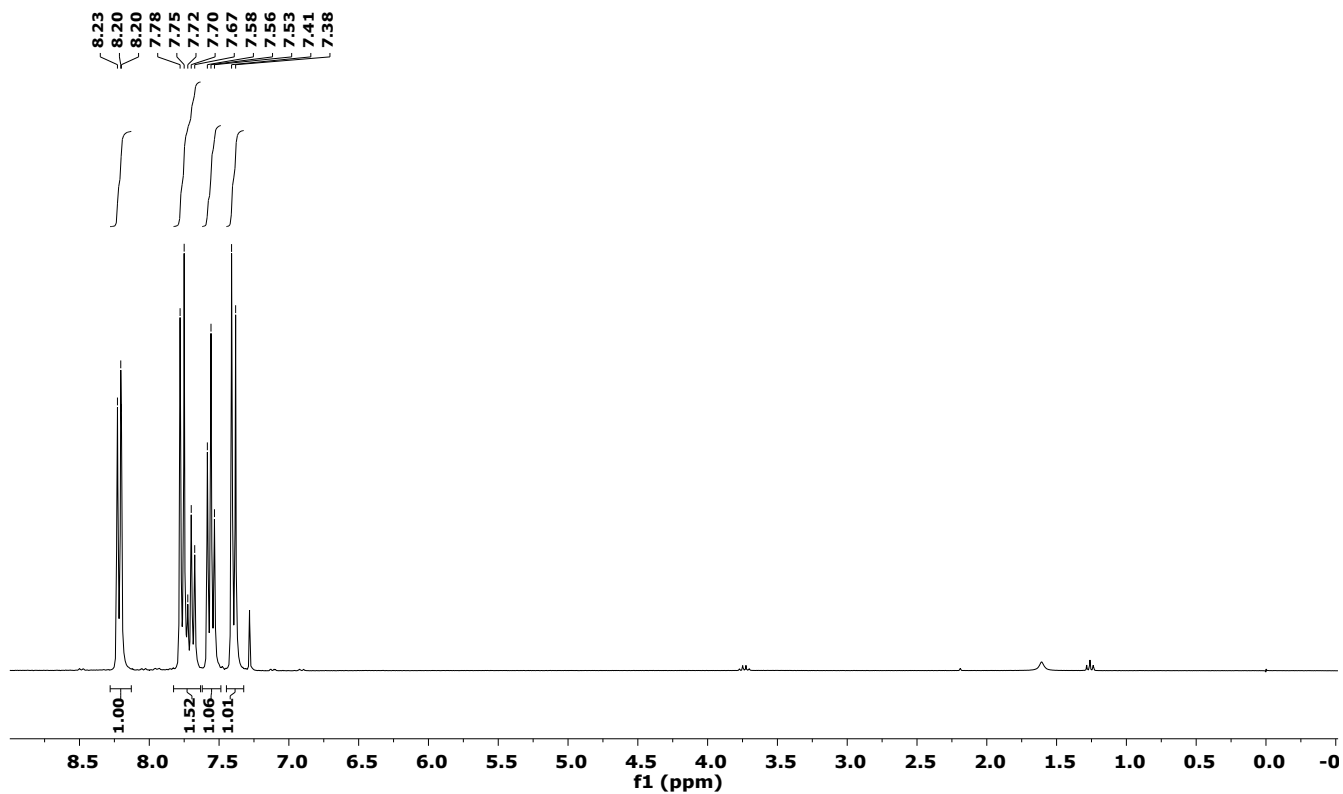
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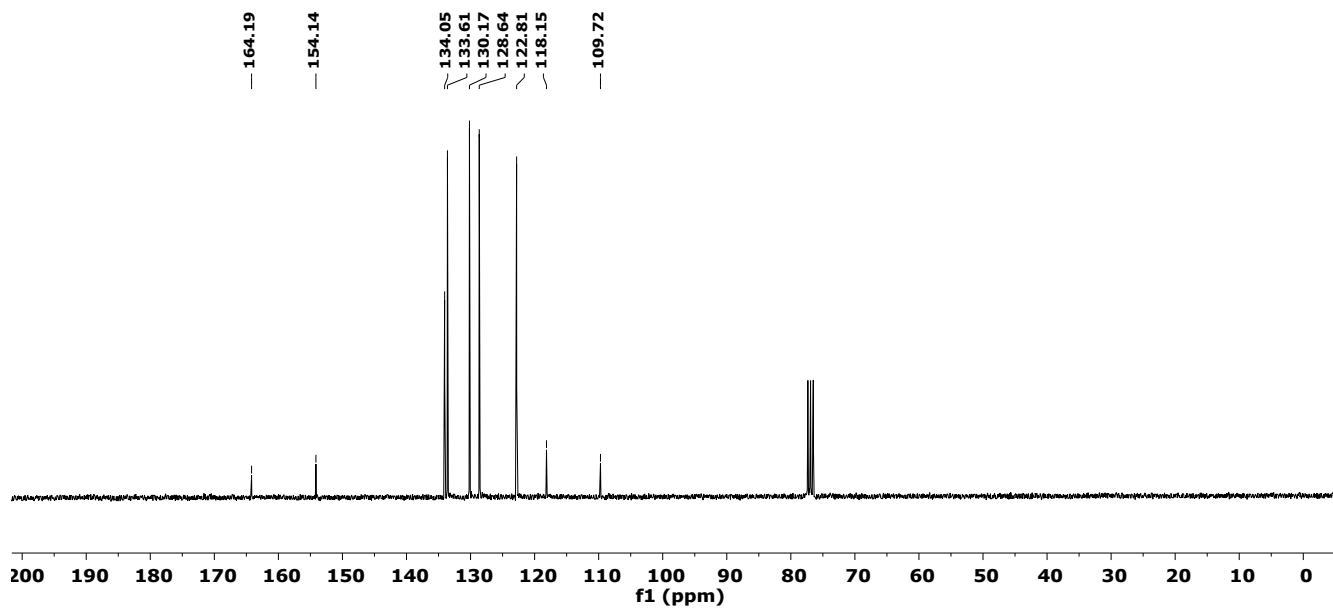
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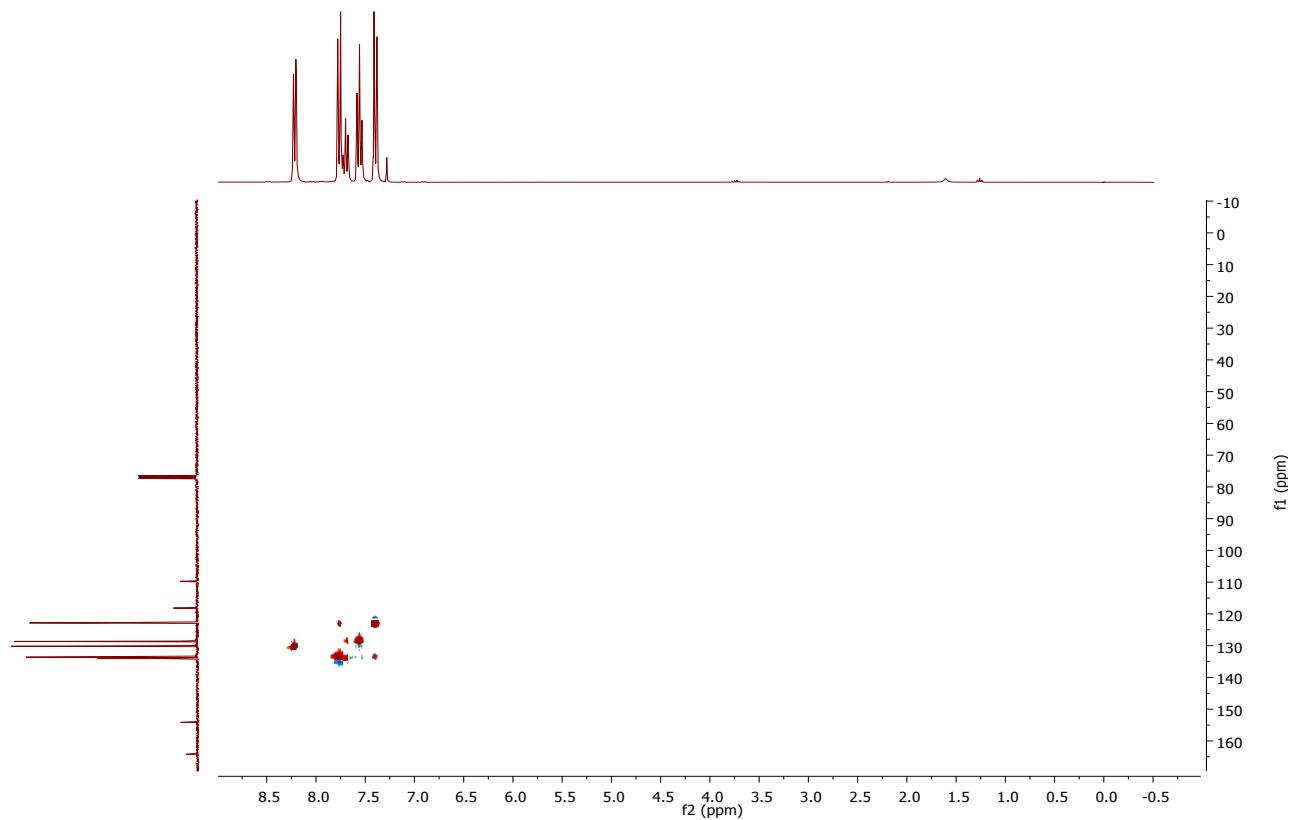
(f) *p*-Cyanophenyl benzoate (7). Copy of the ¹H-NMR (300 MHz), CDCl₃.



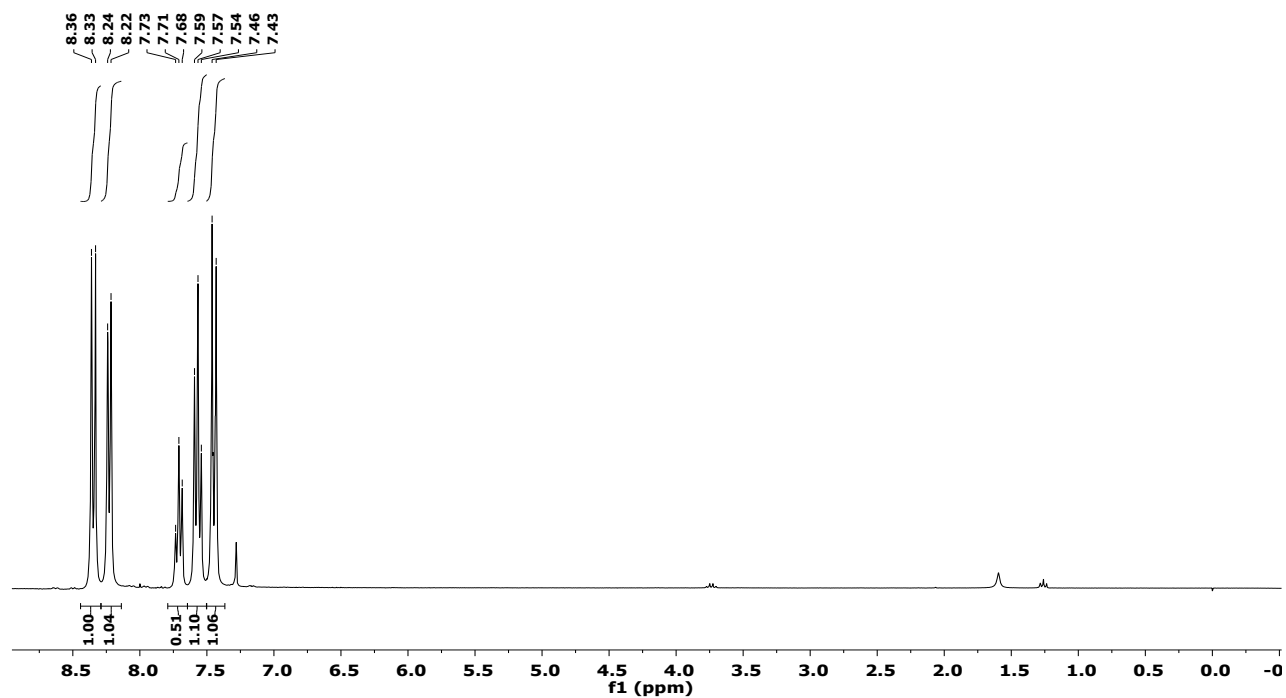
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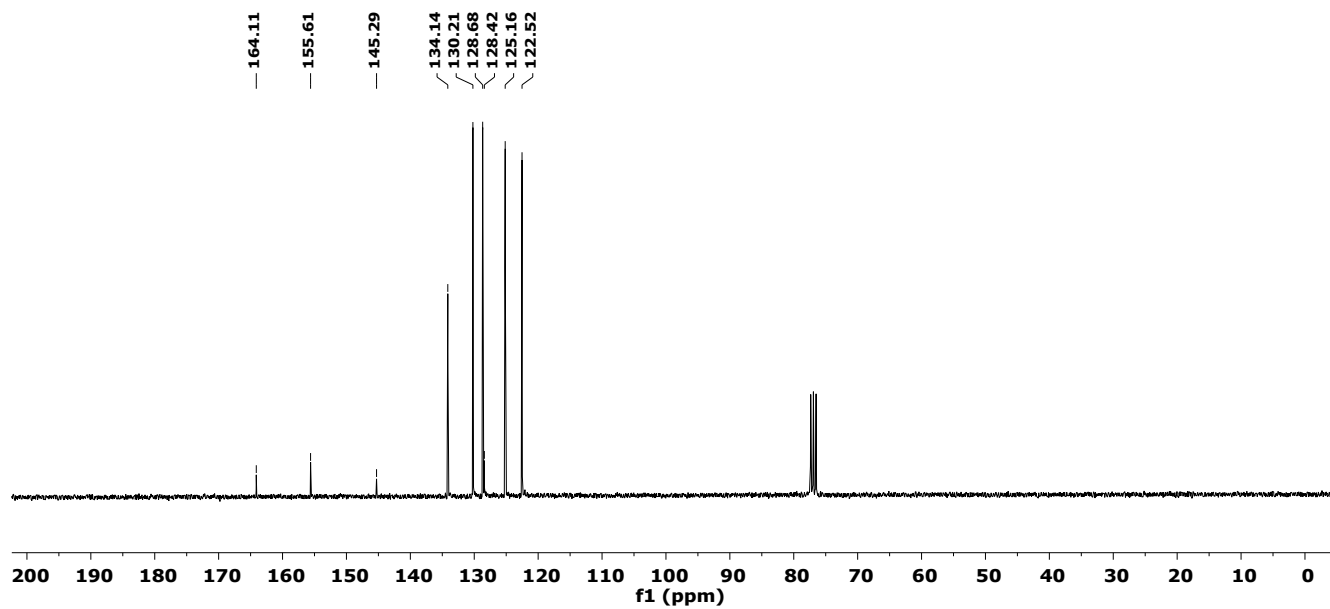
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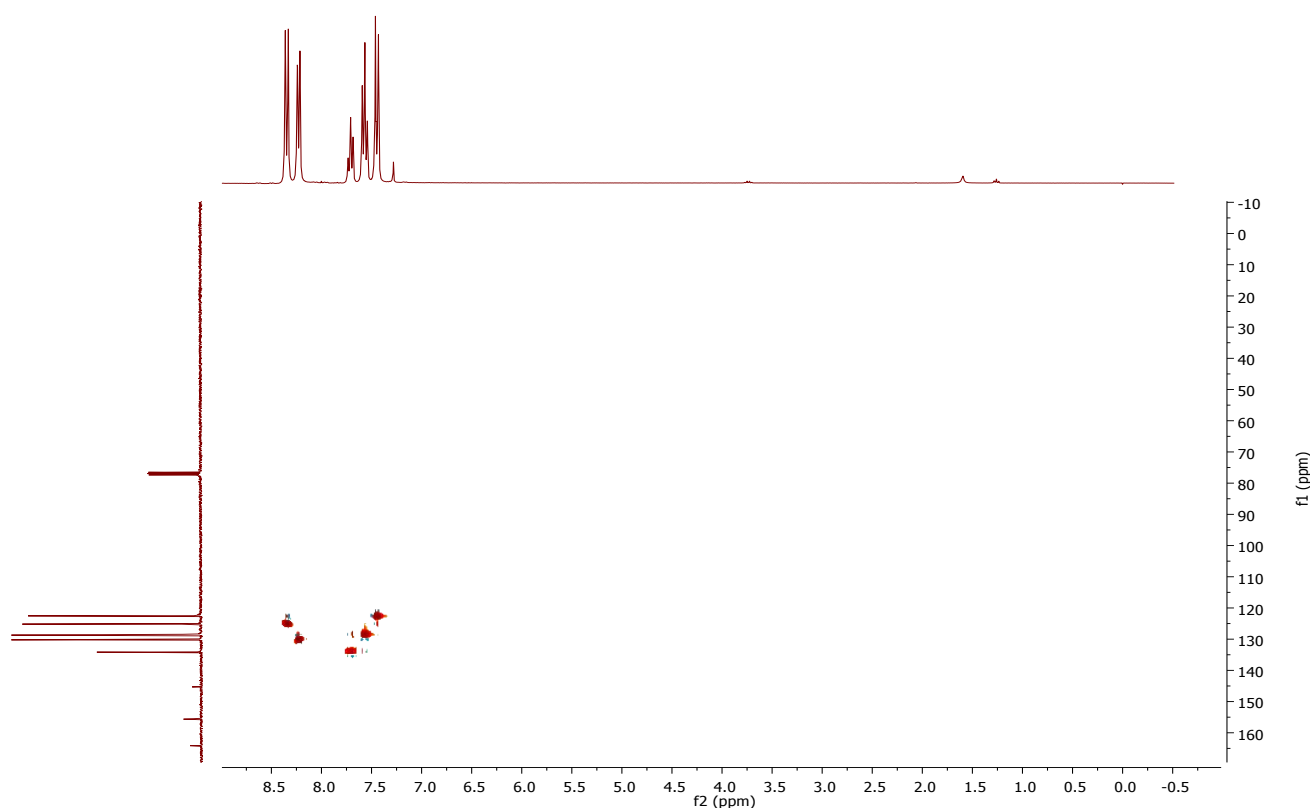
(g) *p*-Nitrophenyl benzoate (**8**). Copy of the ^1H -NMR (300 MHz), CDCl_3 .



Copy of the ^{13}C -NMR (300 MHz), CDCl_3 .

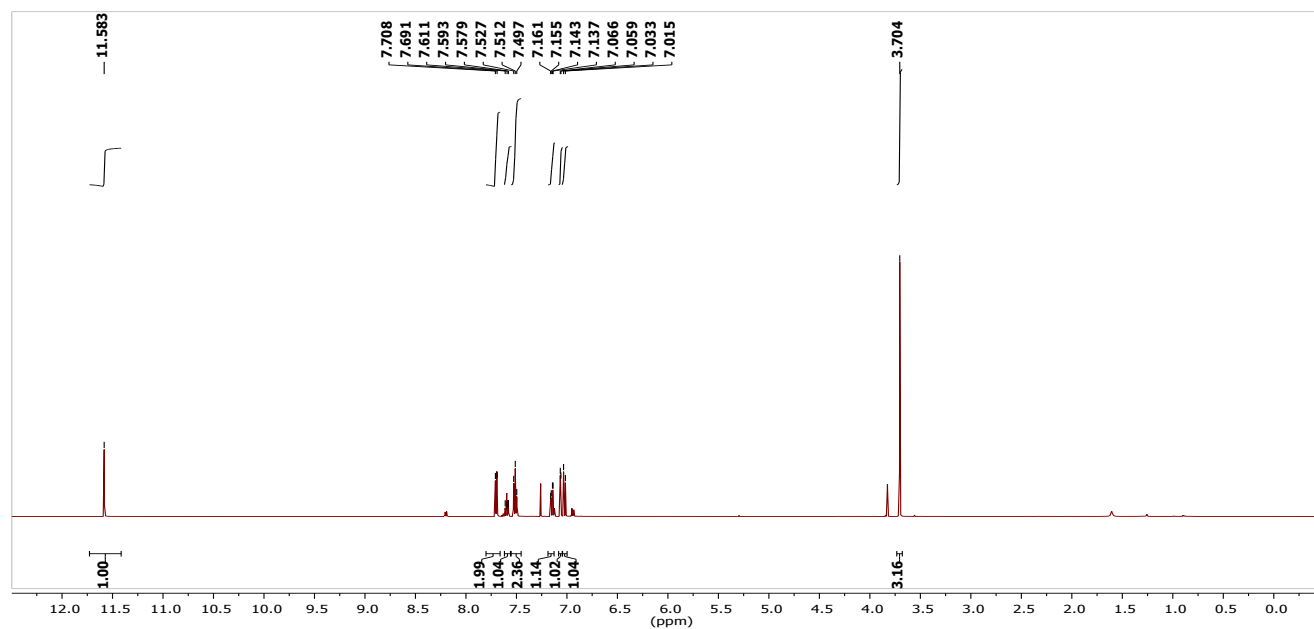


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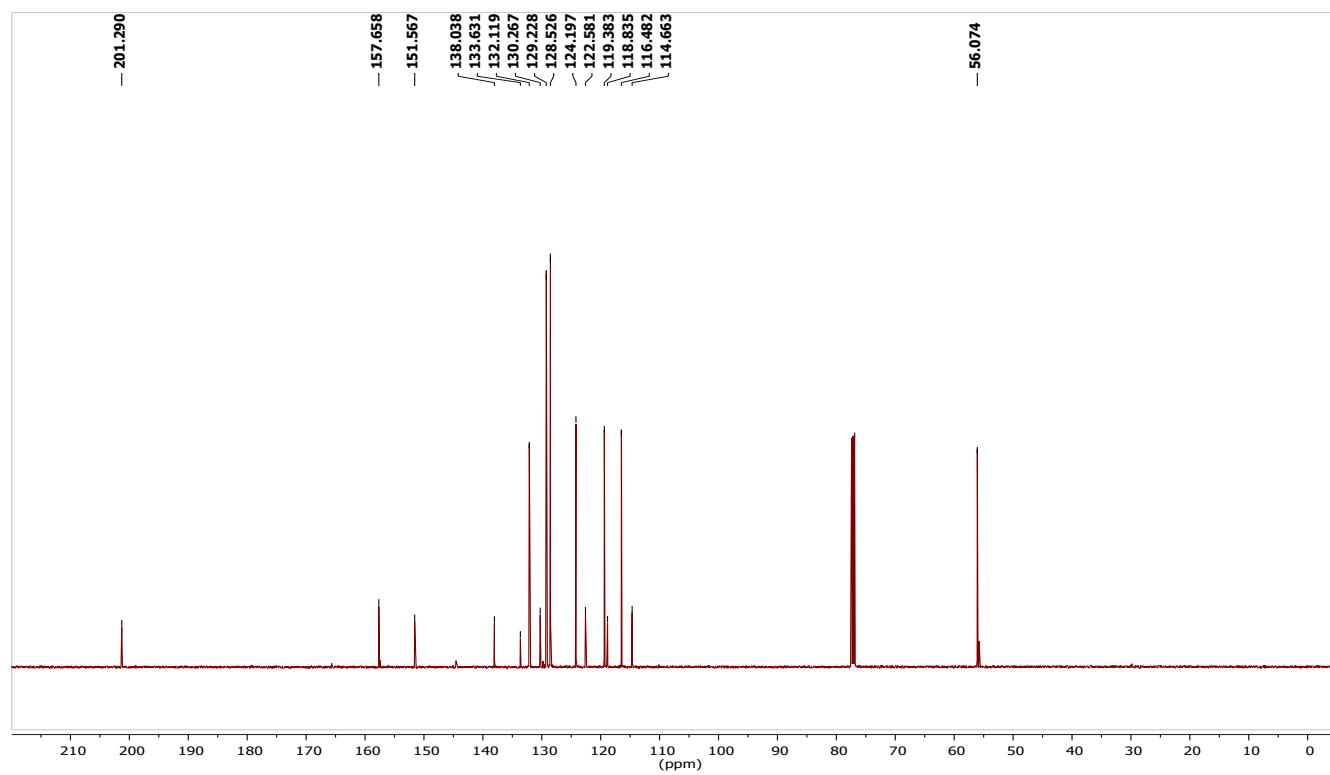


9. Copy of the ¹H and ¹³C spectra of 2-hydroxy-5-substituted benzophenones (1a-8a).

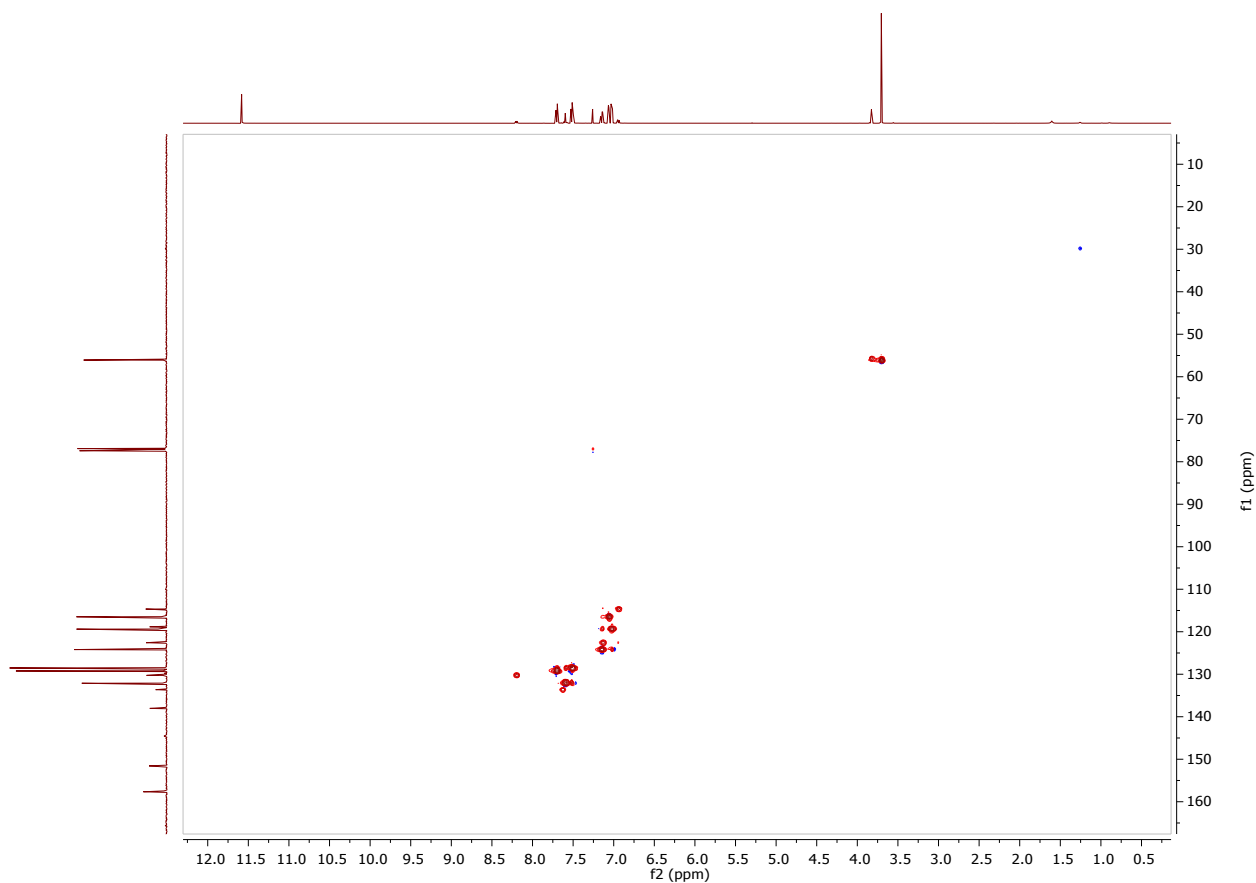
(a) 2-Hydroxy-5-methoxy benzophenone (1a). Copy of the ^1H -NMR (500 MHz), CDCl_3 .



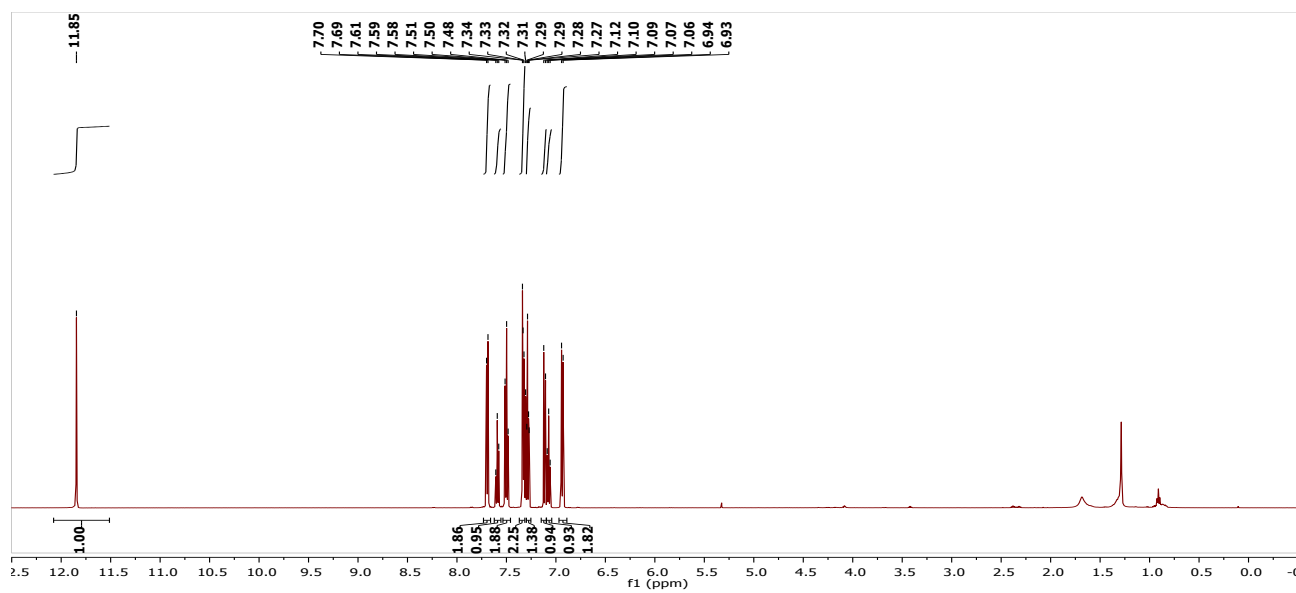
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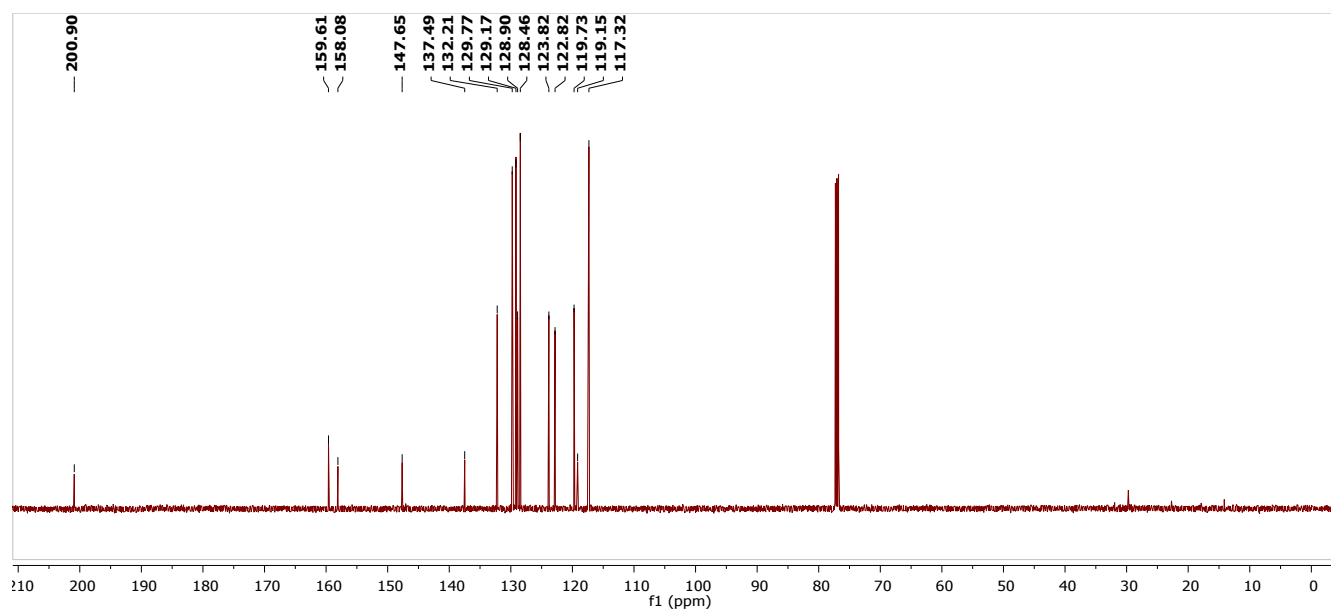
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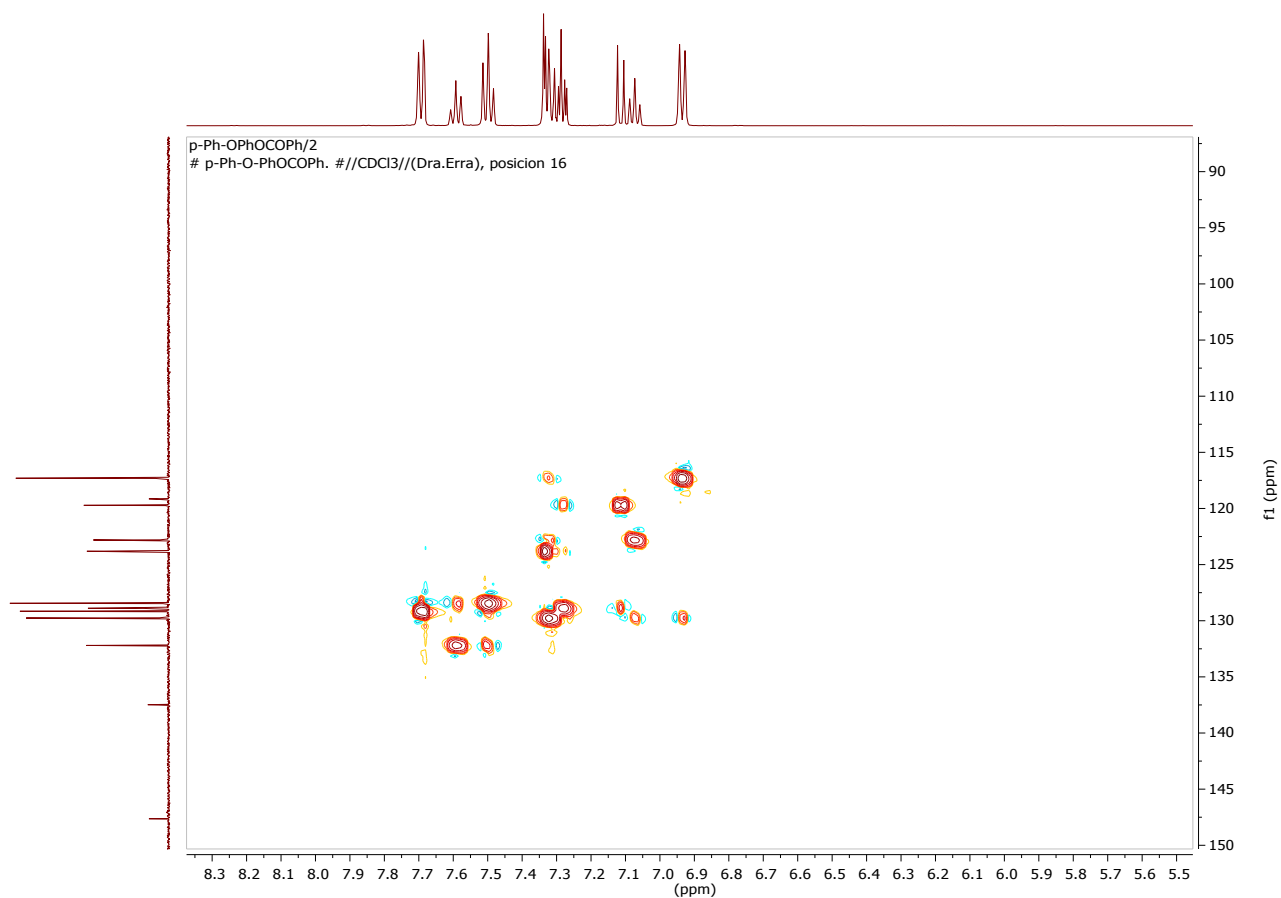
(b) 2-Hydroxy-5-phenoxy benzophenone (2a). Copy of the ^1H -NMR (500 MHz), CDCl_3 .



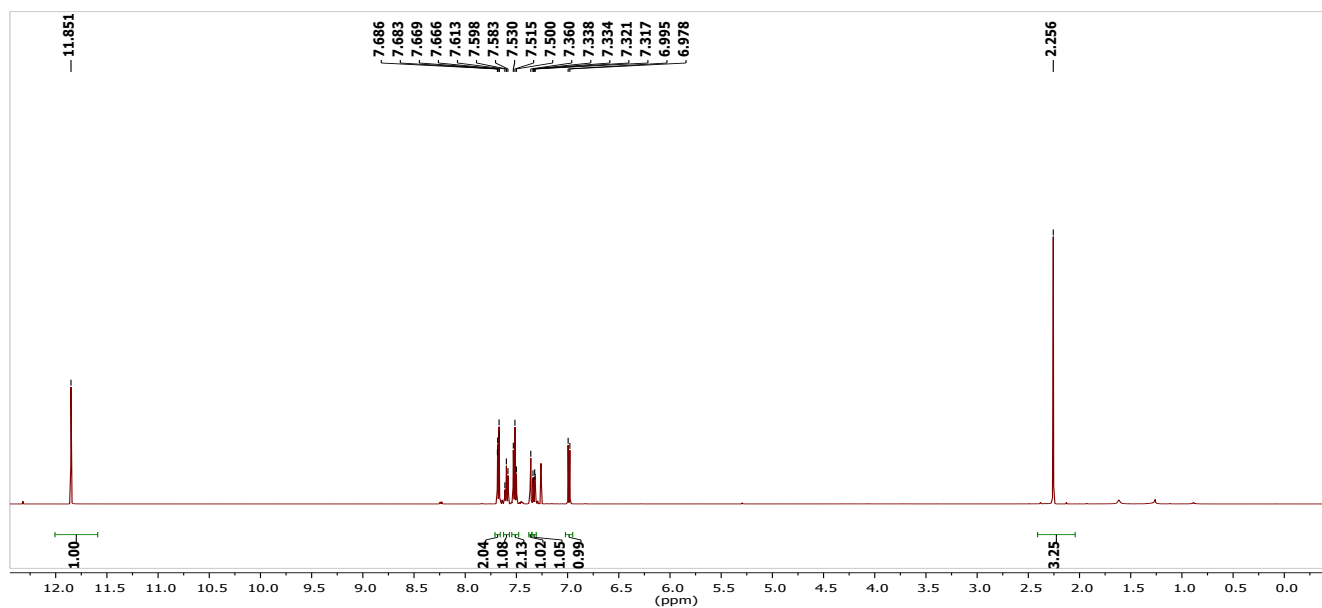
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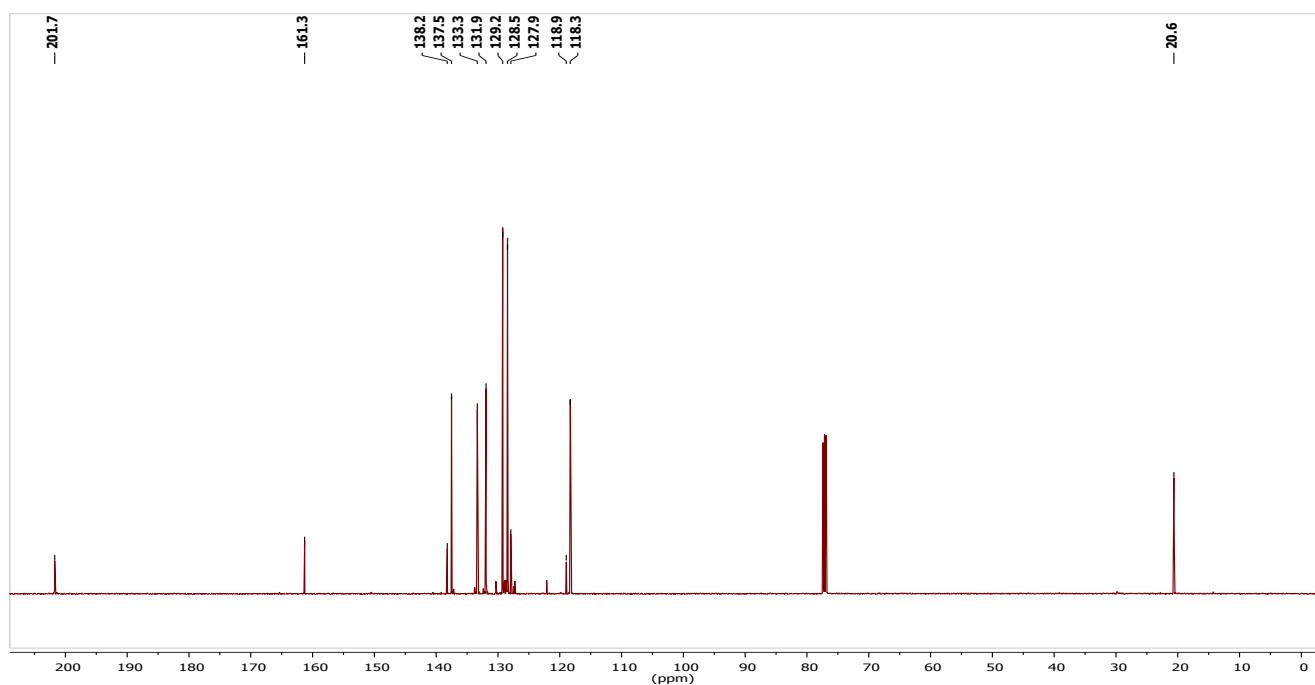
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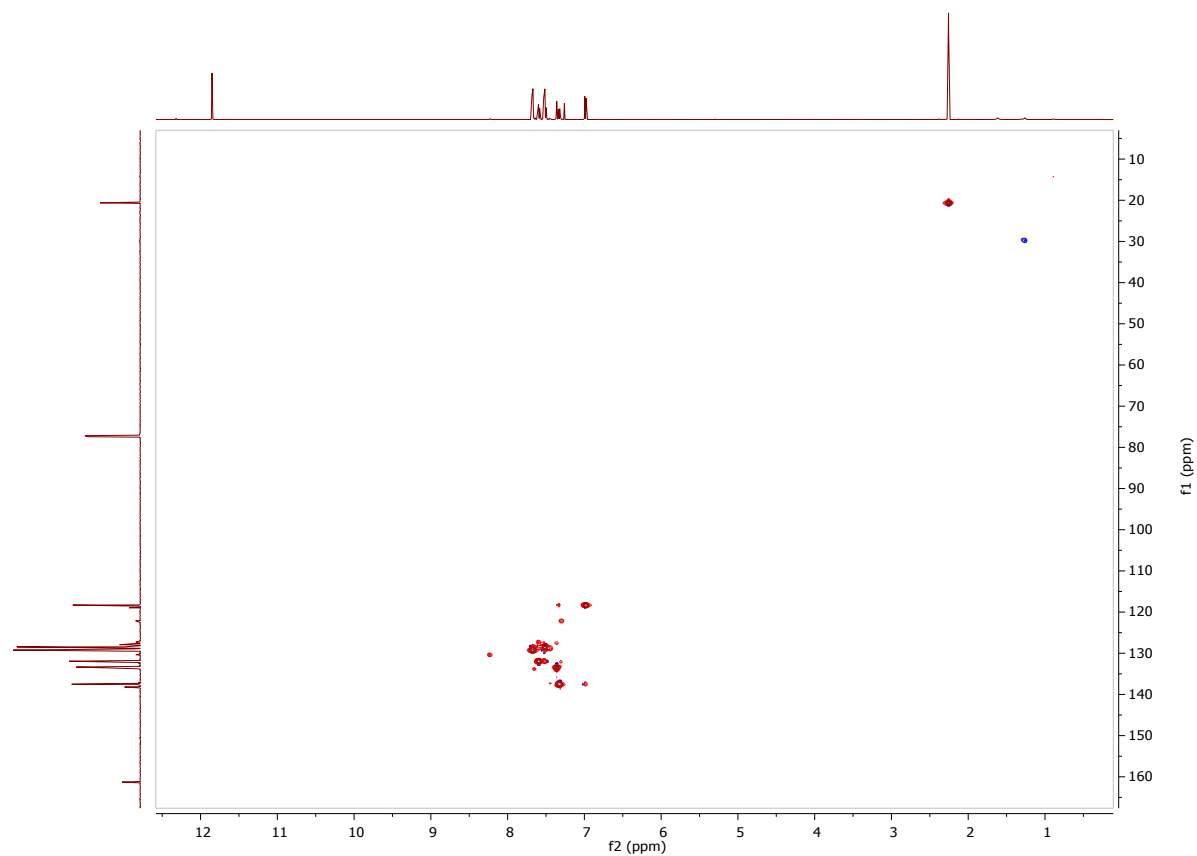
(c) 2-Hydroxy-5-methyl benzophenone (3a). Copy of the ^1H -NMR (300 MHz), CDCl_3 .



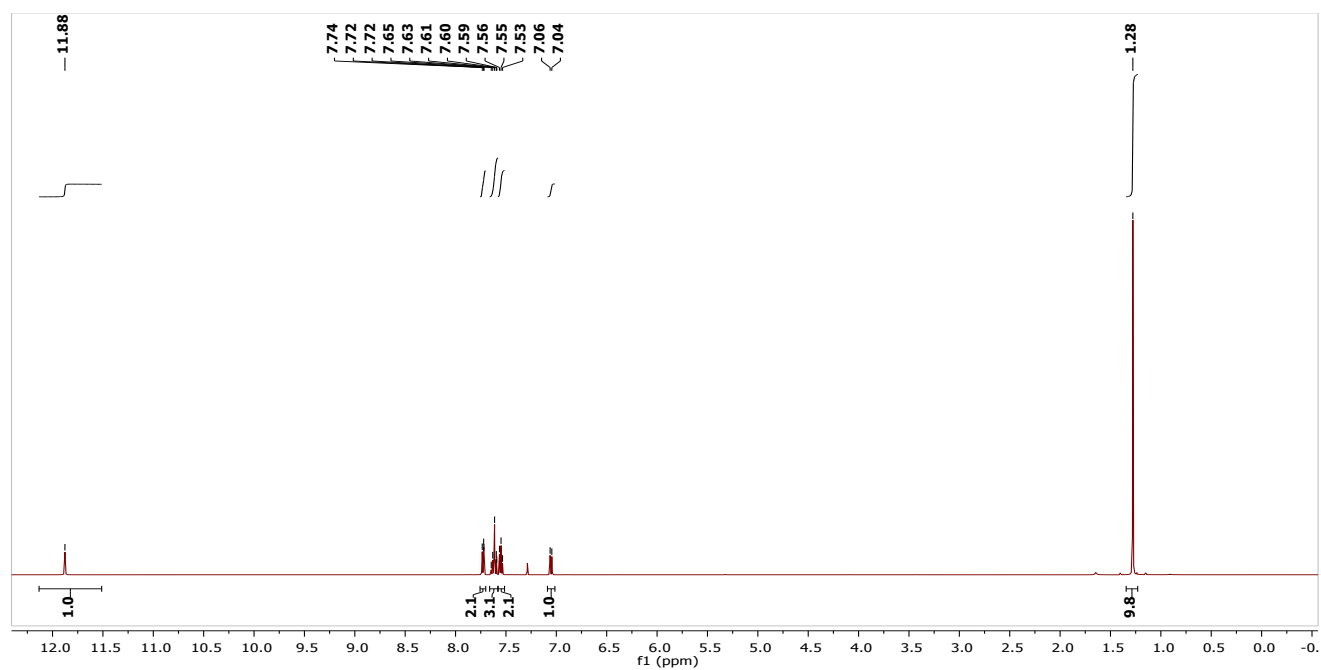
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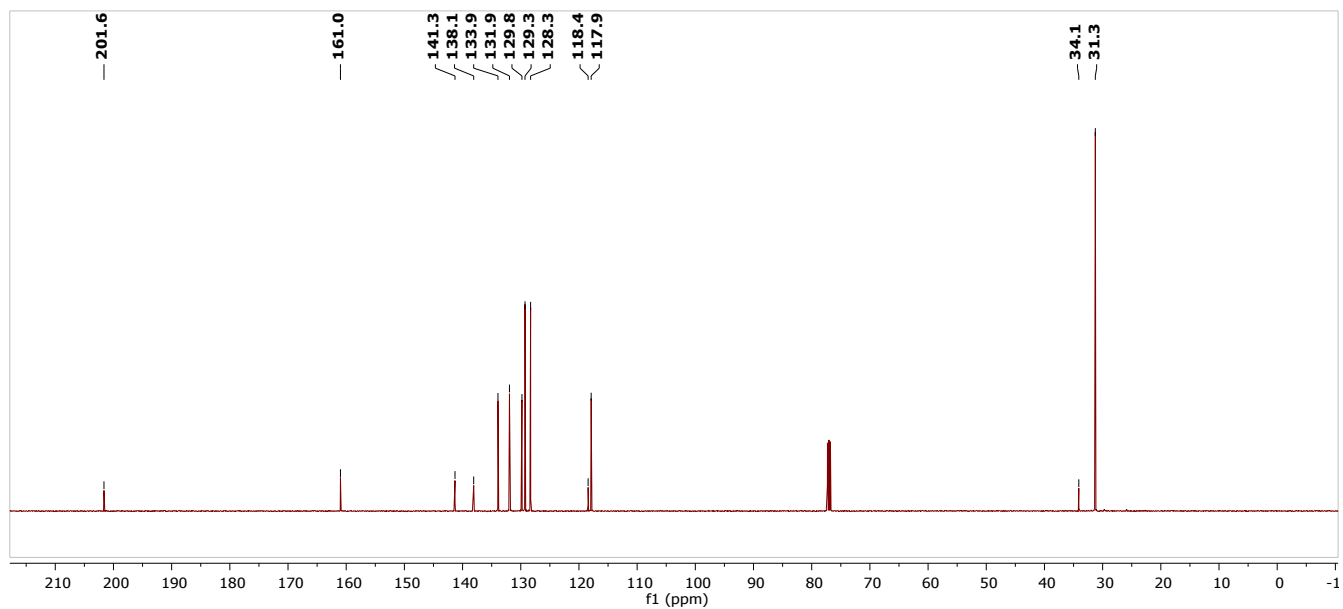
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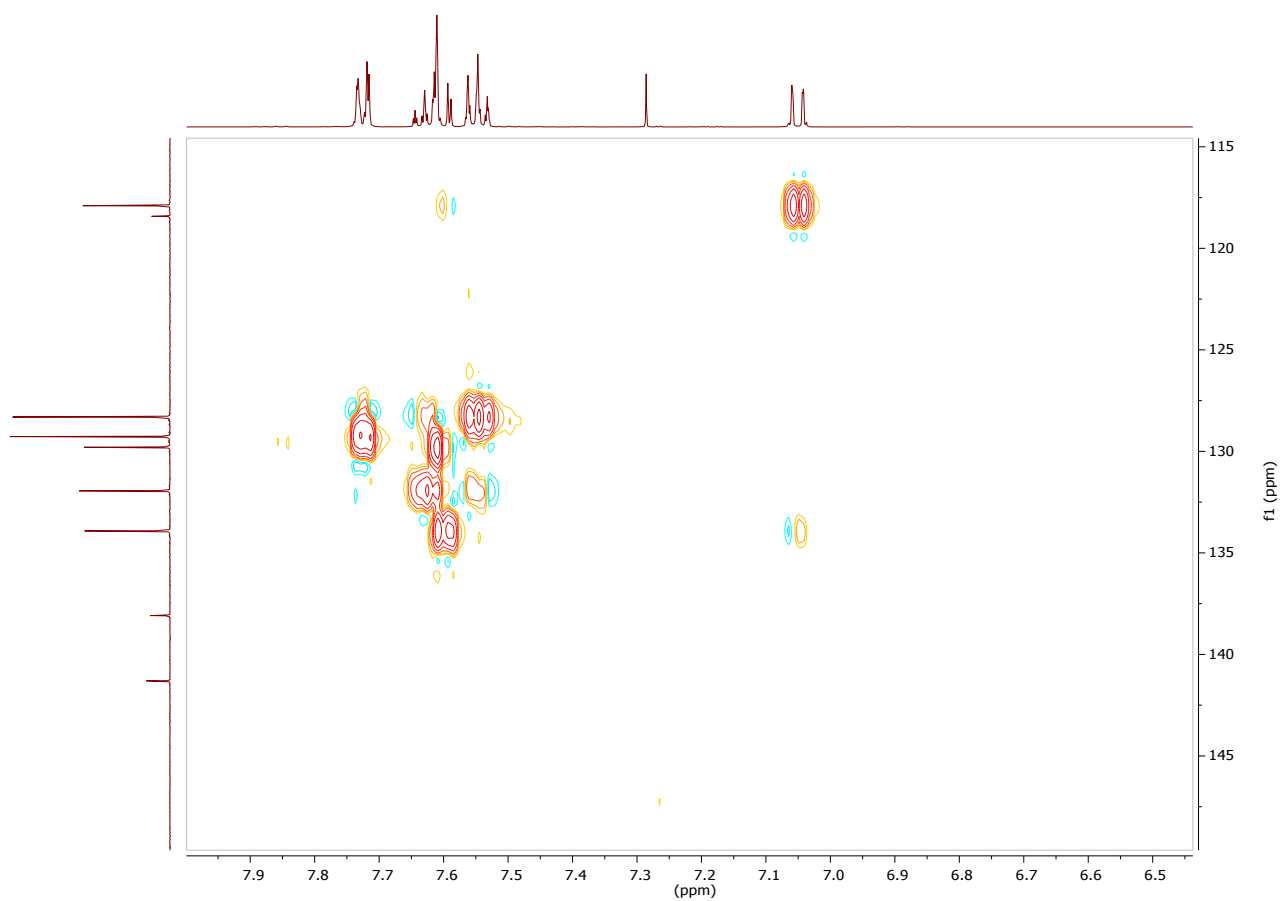
(d) 2-Hydroxy-5-*t*-butyl benzophenone (4a). Copy of the ^1H -NMR (500 MHz), CDCl_3 .



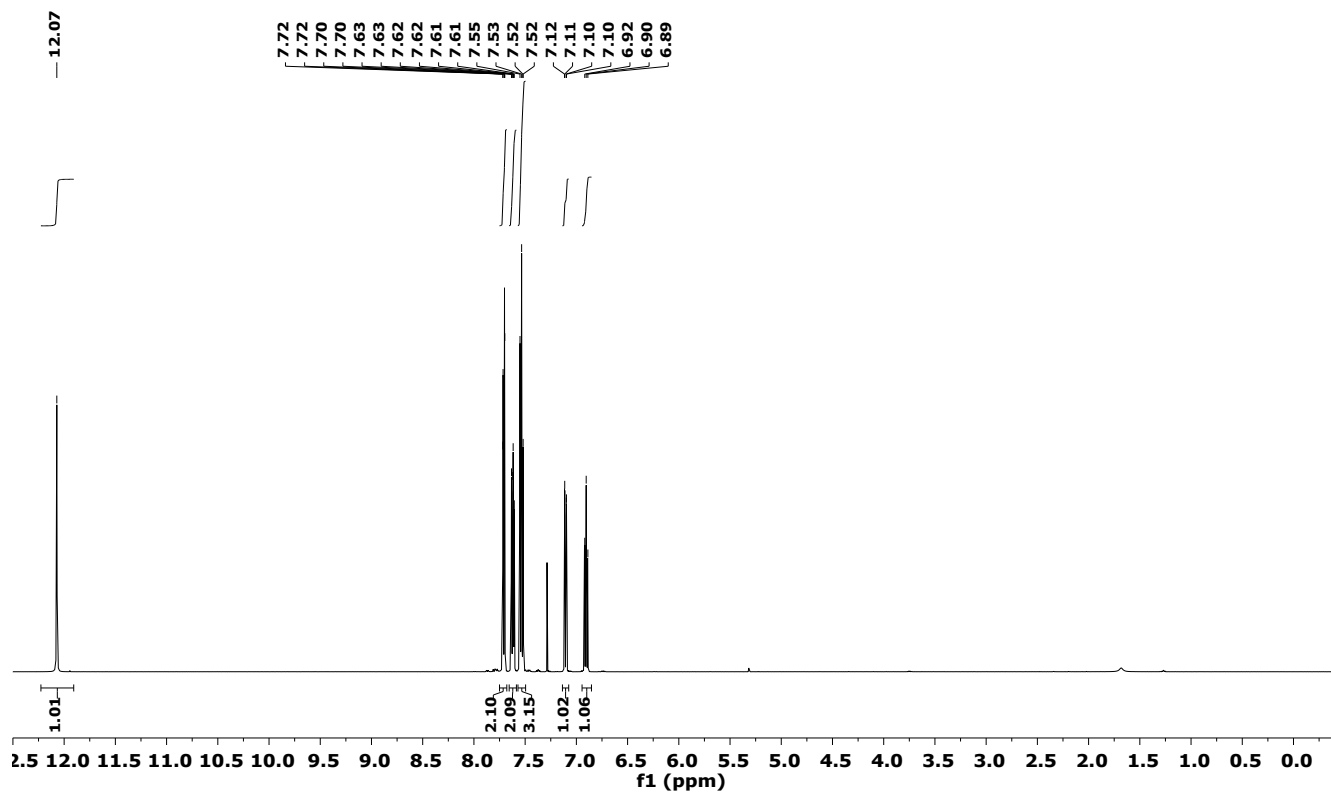
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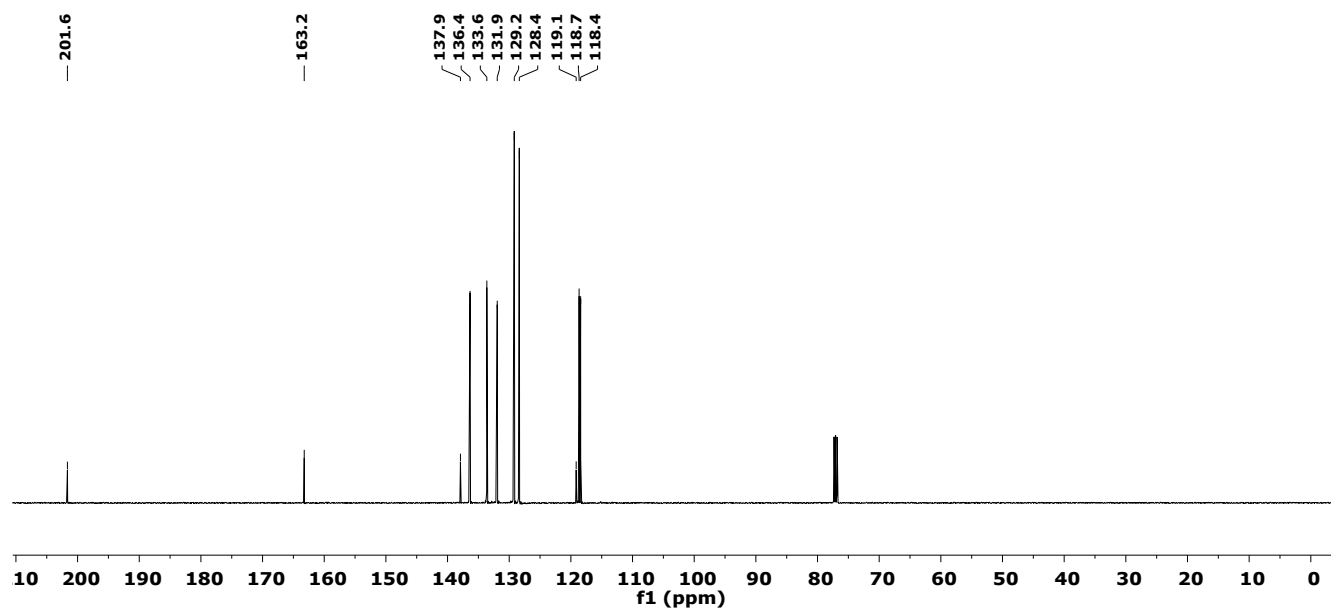
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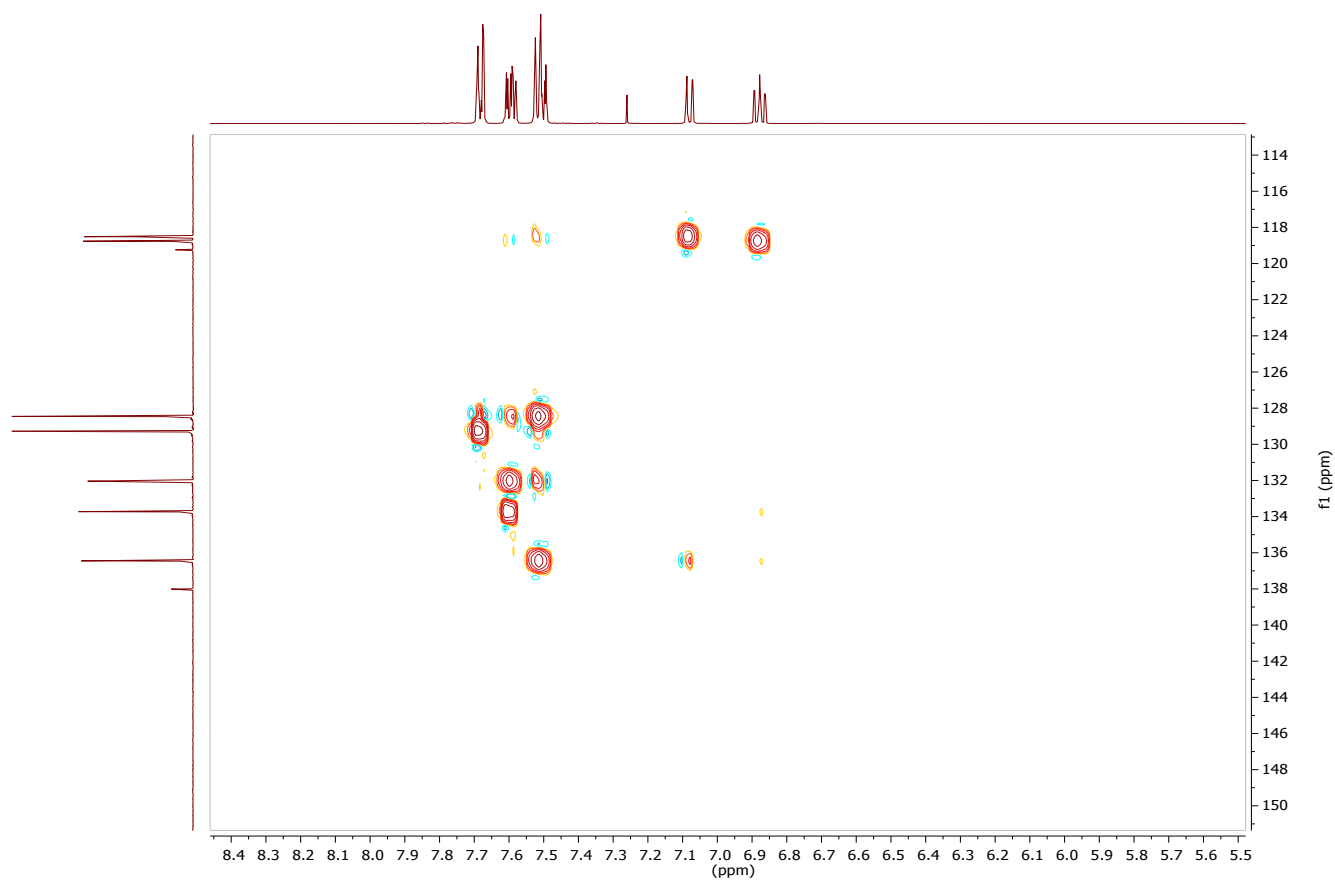
(e) 2-Hydroxybenzophenone (5a). Copy of the ¹H-NMR (500 MHz), CDCl₃.



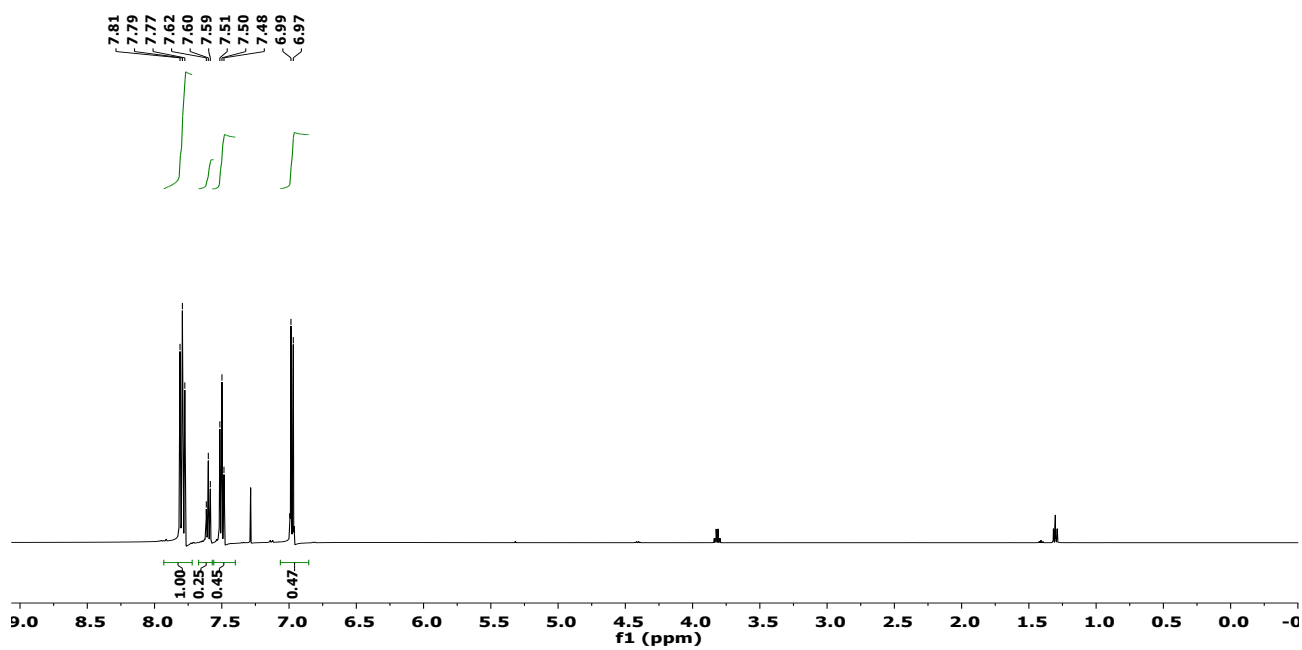
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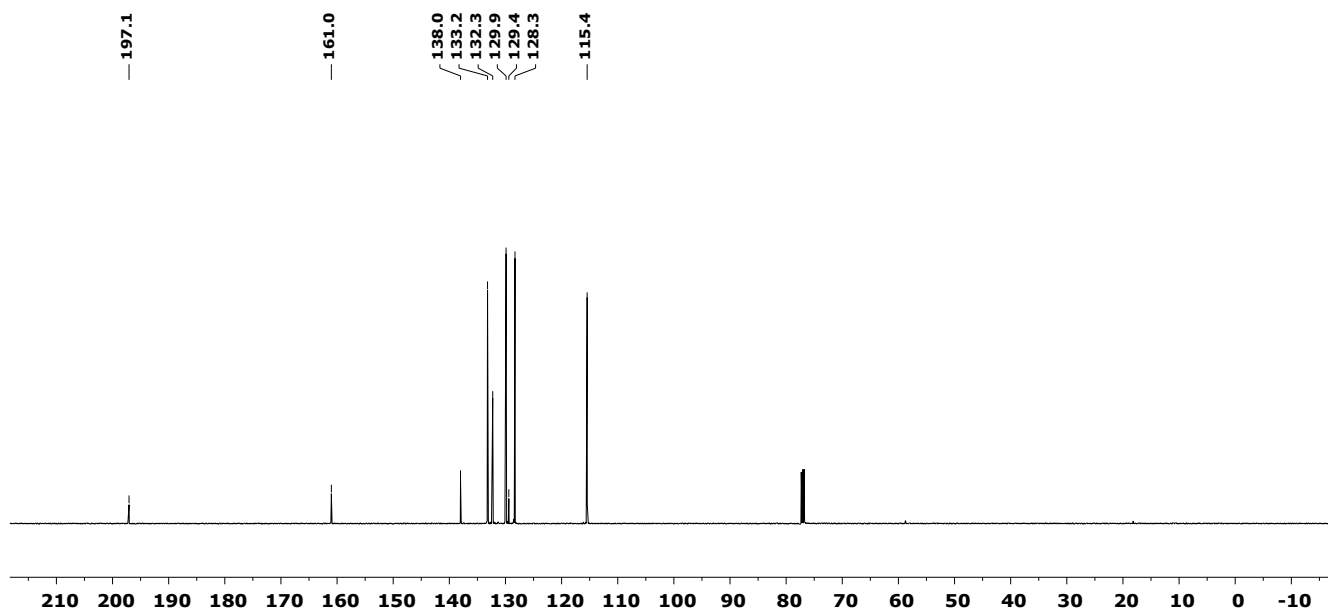
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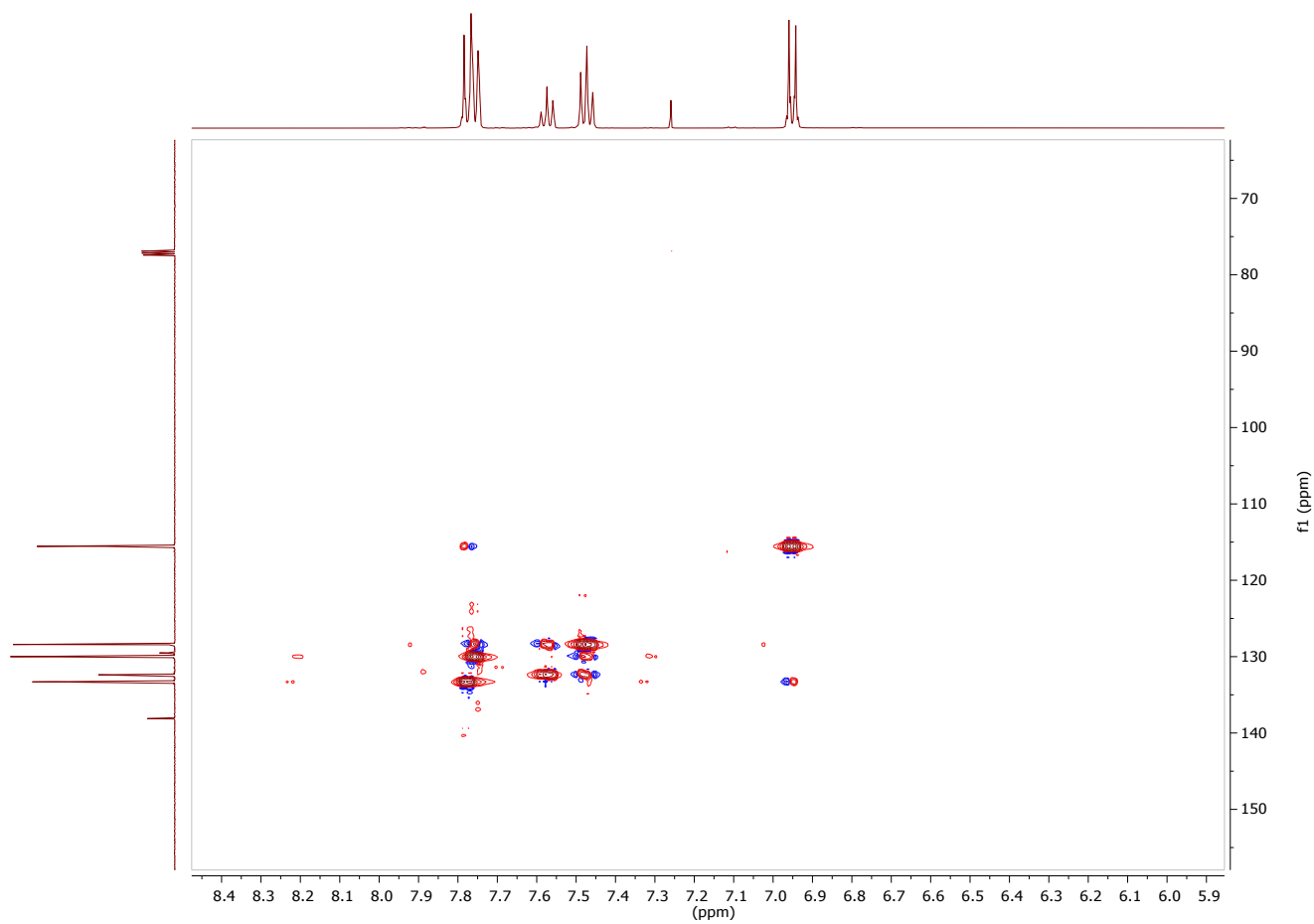
(f) 4-Hydroxybenzophenone (5b). Copy of the ^1H -NMR (500 MHz), CDCl_3 .



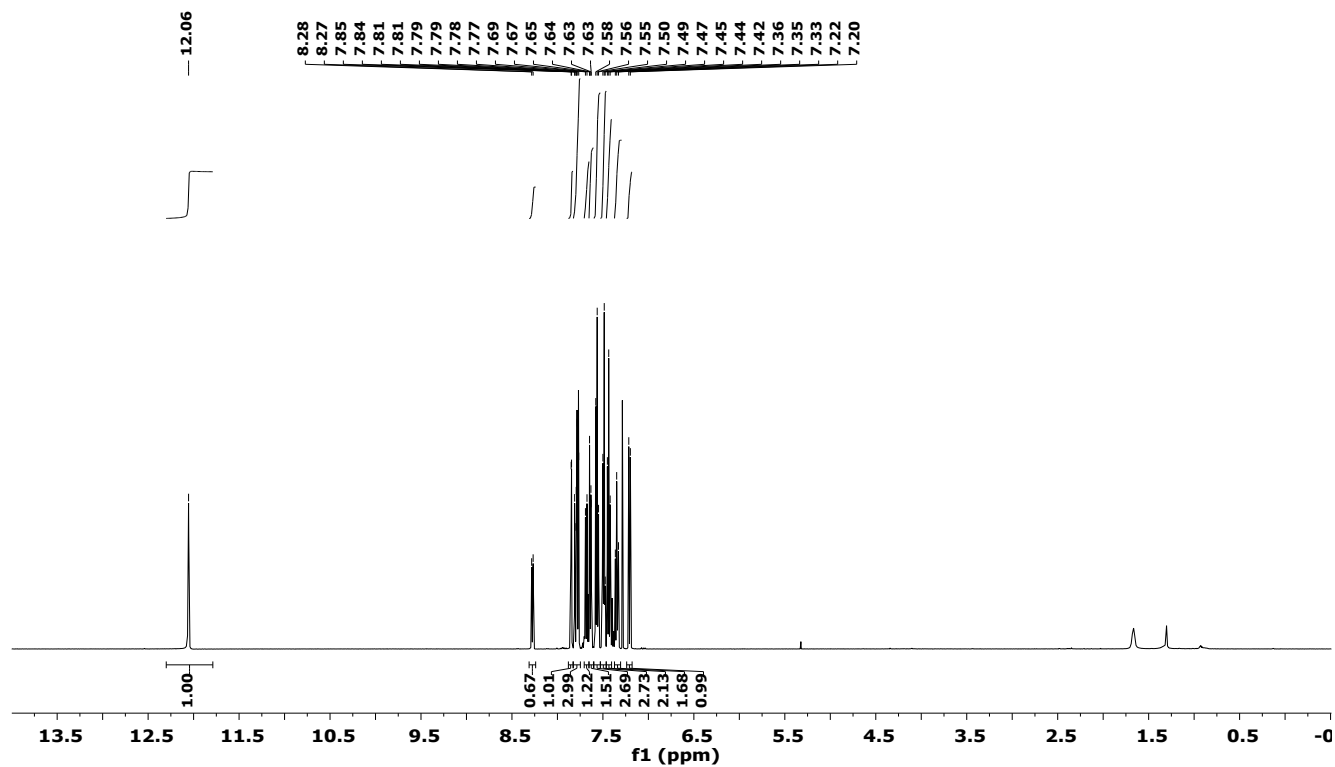
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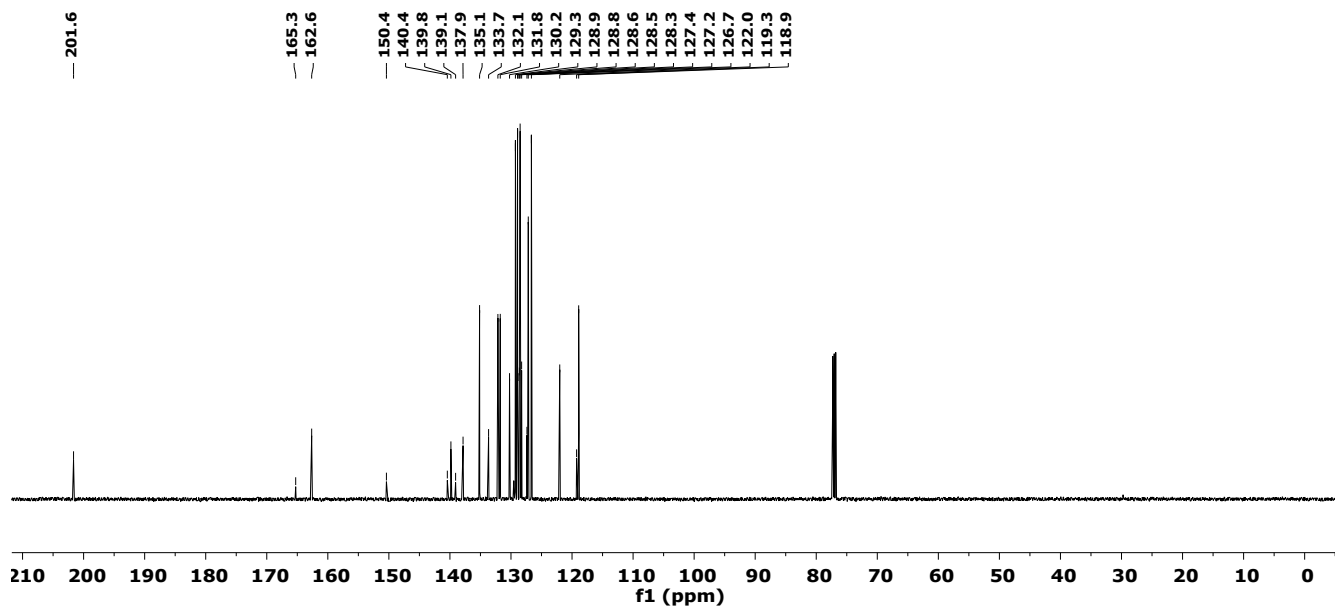
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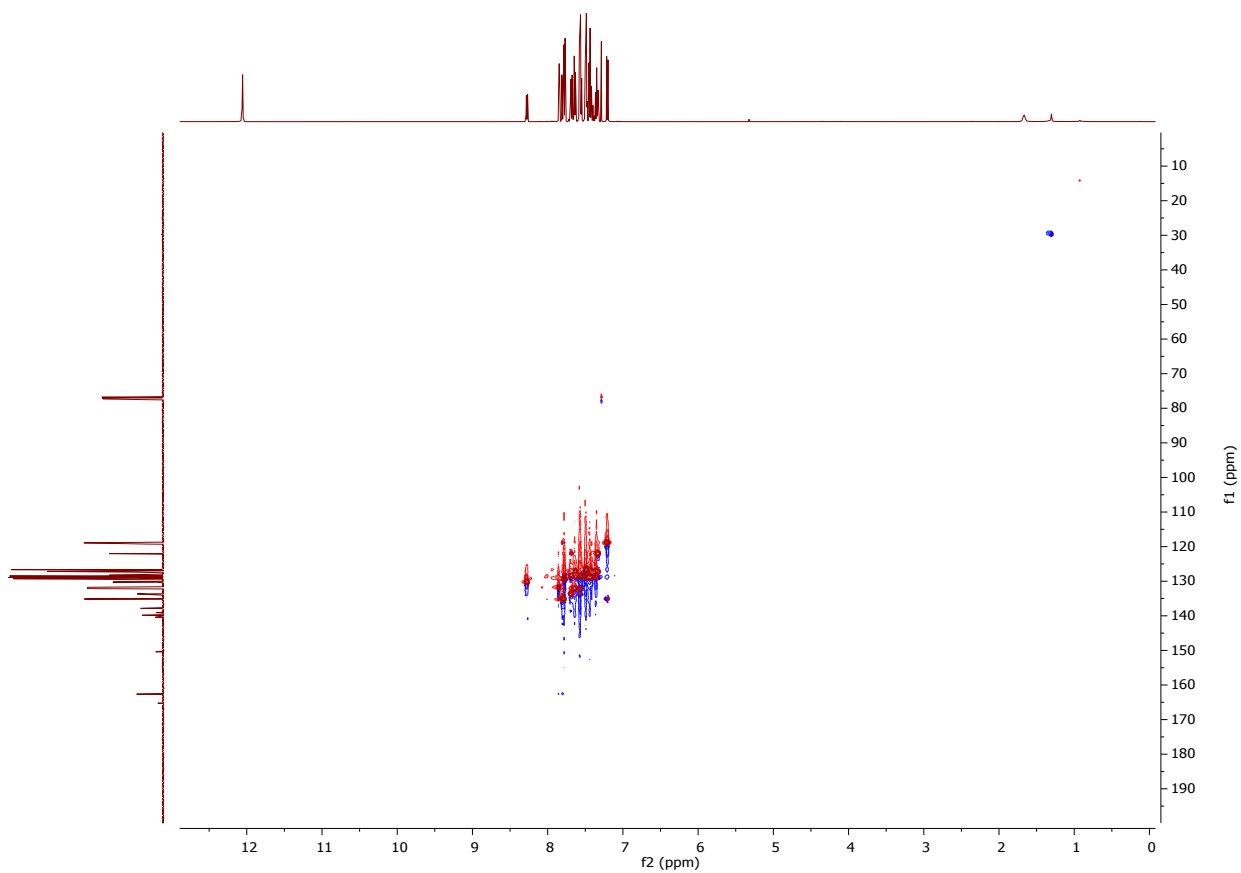
(g) 2-Hydroxy-5-phenyl benzophenone (6a). Copy of the ¹H-NMR (500 MHz), CDCl₃.



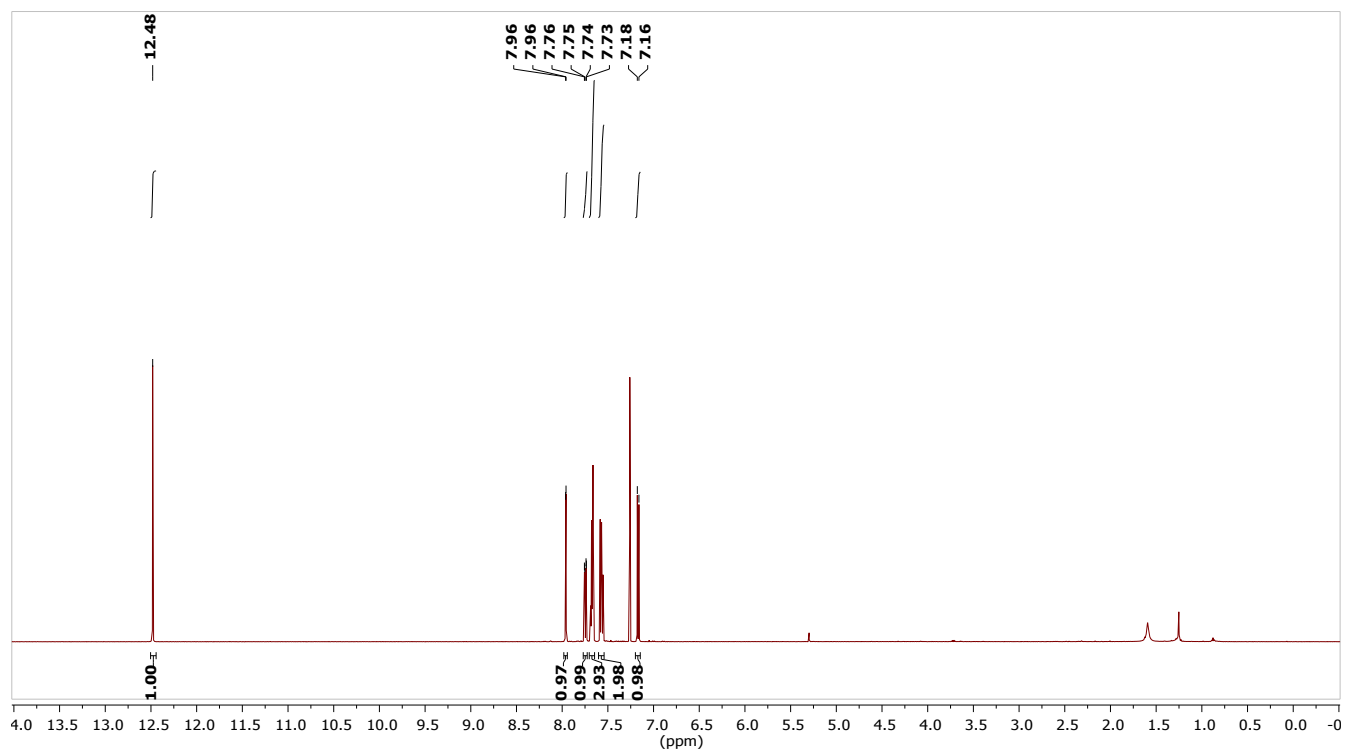
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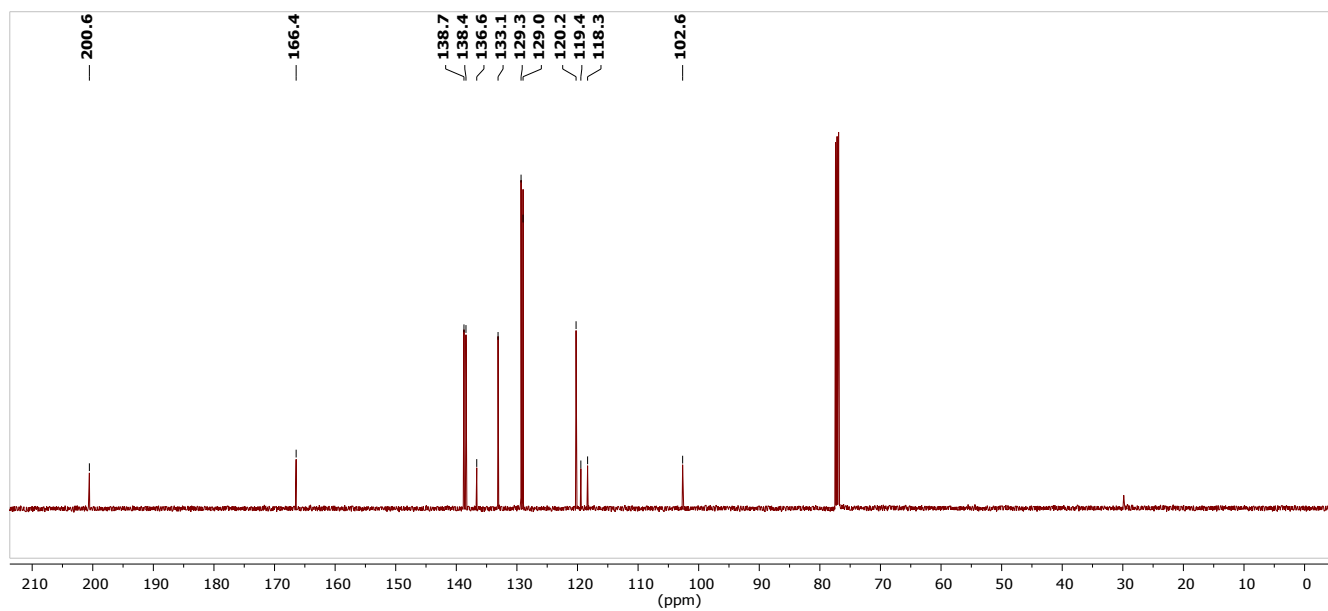
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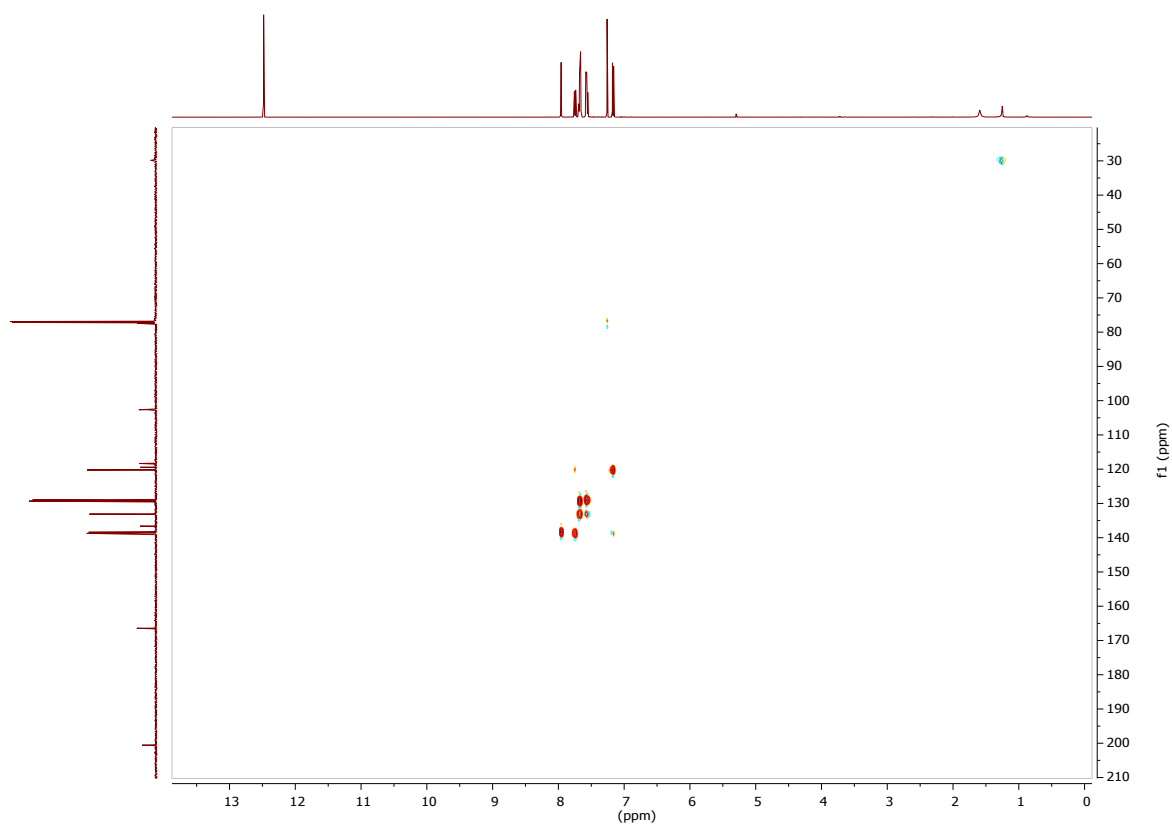
(h) 2-hydroxy-5-cyano benzophenone (7a). Copy of the ^1H -NMR (500 MHz), CDCl_3 .



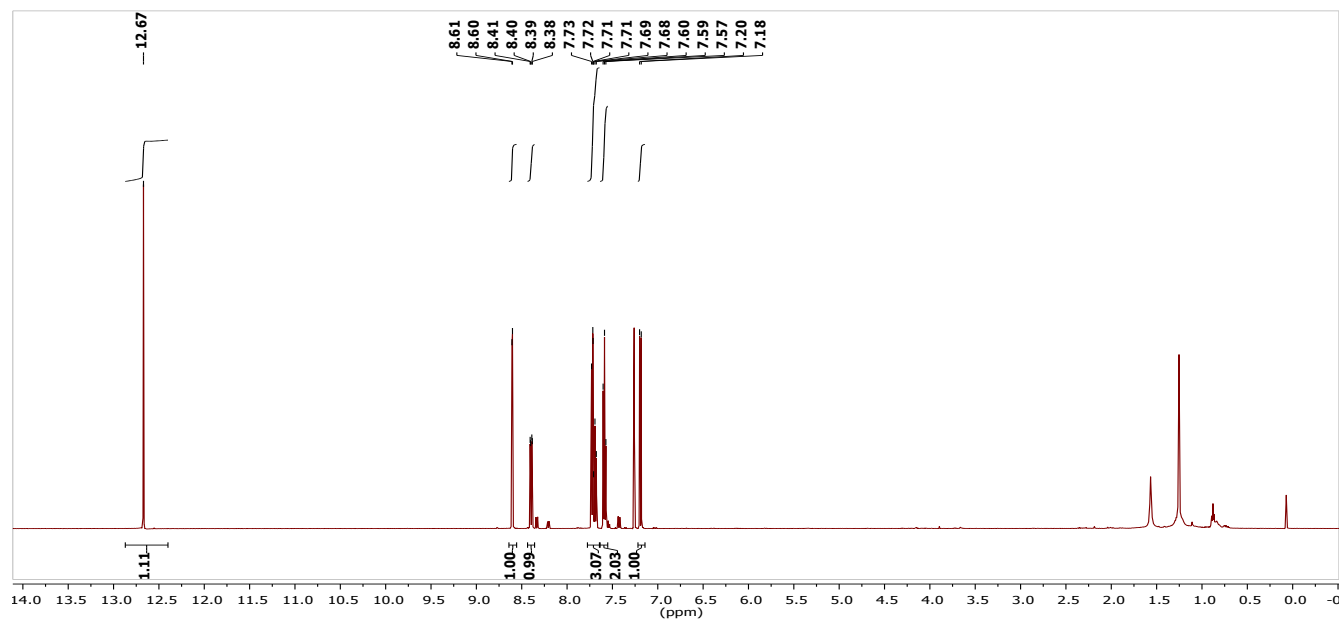
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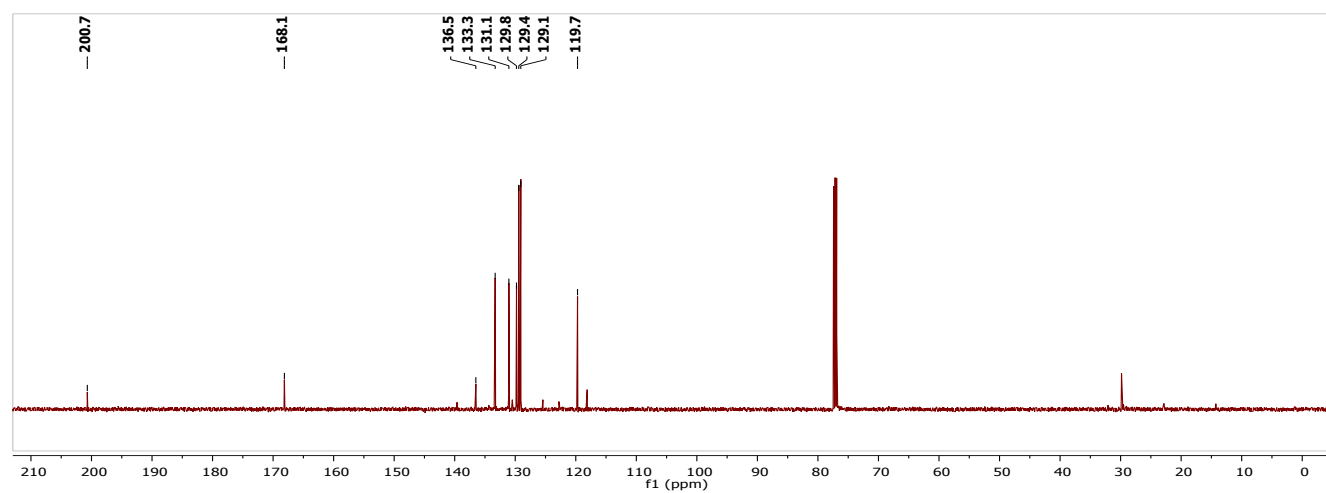
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(j) 2-Hydroxy-5-nitro benzophenone (8a). Copy of the ¹H-NMR (500 MHz), CDCl₃.



Copy of the ^{13}C -NMR (500 MHz), CDCl_3 .



Copy of the HSQC (500 MHz), CDCl_3 .

