# Electronic Supplementary Information

# Solvent Assisted Photochemical Formation of New Keto[3,3]paracyclophane

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## Experimental Section

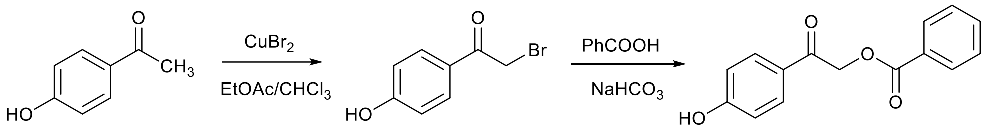
## General Information

All reagents and solvents were purchased from commercial suppliers and were used without further purification. The reaction was monitored through thin layer chromatography on silica gel 60 $F_{254}$ plate (Merck, Darmstadt, Germany). Column chromatography was done on silica gel (BioSphere silica gel 60um 60A; BioMec, Seoul, South Korea). $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker Auto-Sampler-HR-MAS 500 MHz-NMR Spectrometry. IR spectra were recorded on Functional Anal-ATR-FTIR Spectrometer (IdentifyIR® Portable FT-IR Spectrometer; Smiths Detection, London, United Kingdom). High-resolution mass spectra (HR-MS) were acquired under ESI condition on a High resolution LC/MSMS spectrometer Triple TOF 5600+(AB Sciex, USA).

## Synthesis

### 2-(4-(4-hydroxyphenethoxy)phenyl)-2-oxoethyl benzoate (3)

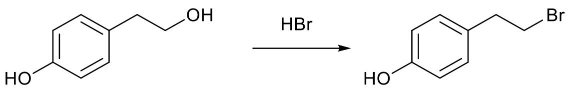
A. Synthesis of 4-hydroxyphenethoxy benzoate



Copper (II) bromide (3.6 g, 16 mmol) was added into an oven-dried 100 mL two-neck round bottom flask with chloroform (12 mL) and ethyl acetate (13 mL). The flask was then refluxed with stirring at 80°C. Then 4-hydroxyacetophenone (1.0 g, 7.3 mmol) was dissolved in ethyl acetate (15 mL) and poured in the reaction mixture. After 2~3 h, the reaction was monitored by thin layer chromatography (TLC). The reaction was continued until the complete consumption of 4-hydroxyacetophenone. When the reaction was over, the mixture was cooled and precipitates were filtered. The filtrate then went through evaporation by a rotary evaporator to get rid of the solvents. The product was dissolved in ethyl acetate (30 mL), washed twice with water (30 mL each) and once with brine (30 mL). The organic layer was then dried over $MgSO_4$. After filtration, the solvent was evaporated under vacuum. The crude product of 2-bromo-1-(4-hydroxyphenyl)ethan-1-one was obtained (1.6 g), which was used for the next step without further purification.

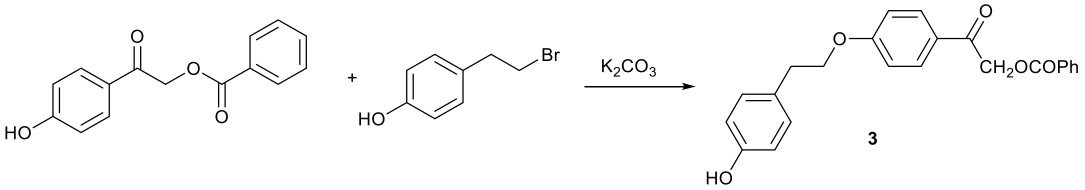
To a 100 mL, two-neck, round bottom flask charged with benzoic acid (1.12 g, 9.17 mmol), sodium bicarbonate (0.77 g, 9.2 mmol), acetone (30 mL) were added and refluxed at 60°C for 30 min with stirring. 2-bromo-1-(4-hydroxyphenyl)ethan-1-one (1.6 g) dissolved in acetone (10 mL) was added to the reaction mixture in droplets, and the resulting mixture was additionally refluxed for 72 hr. The reaction was monitored through thin layer chromatography (TLC). After completion of the reaction, the mixture was filtered to remove precipitates, and the filtrate was evaporated under vacuum at room temperature to remove acetone. 5% hydrochloric acid was added to the residue and was stirred for 10 min. Ethyl acetate was added to the mixture and the organic layer was extracted. The organic layer was washed twice with water and once with brine, and it was dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator. The solid material was recrystallized with ethyl acetate/n-hexane solution to give 0.71g of the colorless solid (36 % yield).

B. Synthesis of 4-(2-bromoethyl)phenol

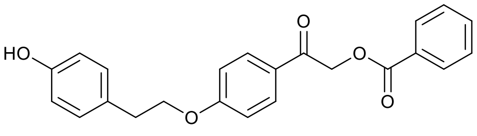


4-(2-hydroxyethyl)phenol (0.40 g, 2.9 mmol) and hydrobromic acid(HBr, 48%) (0.4 mL, 3.5 mmol) were added to a 25 mL round bottom flask and refluxed at 80°C for 2 hr with stirring. Then, after cooling the reaction mixture, diethyl ether and water were added for work-up. The organic layer was washed twice with water and once with brine, and dried with anhydrous $MgSO_4$. After removing the solvent on a rotary evaporator, the resulting liquid product (0.57g) was obtained, which was used for the next step without purification.

C. Synthesis of 2-(4-(4-hydroxyphenethoxy)phenyl)-2-oxoethyl benzoate (**3**)



To a 100 mL, two-neck, round bottom flask, 2-(4-hydroxyphenyl)-2-oxoethyl benzoate (0.71 g, 2.8 mmol) and $K_2CO_3$ (0.46 g, 3.3 mmol) were dissolved in acetone (40 mL) and refluxed at 60°C for 30 min with stirring. 4-(2-bromoethyl)phenol (0.56 g, 2.8 mmol) was added in the reaction mixture and reaction proceeded for 60 hr. The reaction was monitored by thin layer chromatography (TLC). When the substrates were consumed, the precipitates were filtered, and the filtrate was evaporated under vacuum. The product was dissolved in ethyl acetate and washed twice with water, once with brine. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was evaporated. The crude product was then purified over silica gel column chromatography (ethyl acetate/n-hexane=1/1.5, v/v), to give 2-(4-(4-hydroxyphenethoxy)phenyl)-2-oxoethyl benzoate (0.45 g, 44%)



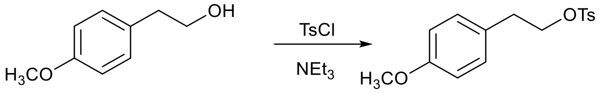
**3**

$R_f$ = 0.24 (ethyl acetate/n-hexane = 1/1.5, v/v); $^1$H NMR (500 MHz, $CDCl_3$) δ(ppm) 8.14 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.93 (d, *J* = 8.9 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.53 (s, 2H), 4.70 (s, OH), 4.20 (t, *J* = 7.0 Hz, 2H), 3.06 (t, *J* = 7.0 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ(ppm) 190.7, 166.2, 163.4, 154.4, 133.3, 130.2, 130.1, 130.0, 129.7, 129.4, 128.4, 127.2, 115.4, 114.6, 69.2, 66.2, 34.7.; IR(ATR) 3354 cm$^{-1}$ (-OH), 1671cm$^{-1}$ (C=O); HRMS (ESI): calculated for $C_{23}H_{20}O_5$ $(M+H)^+$

377.1384, Found 377.1386.

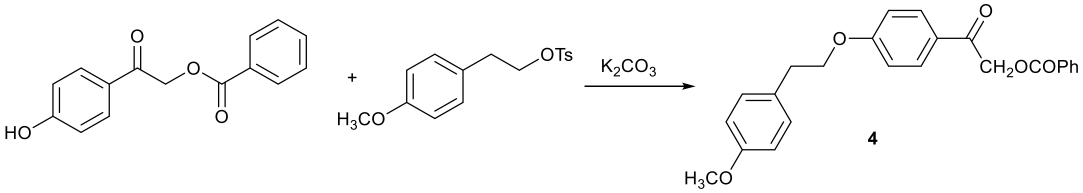
**2-(4-(4-methoxyphenethoxy)phenyl)-2-oxoethyl benzoate (4)**

A. Synthesis of 2-(4-methoxyphenyl)ethyl-4-methylbenzenesulfonate

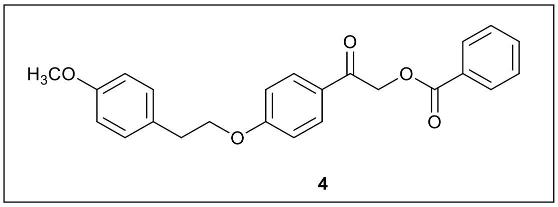


To a 100 mL Erlenmeyer flask, 4-methoxyphenethyl alcohol (0.91 g, 6.0 mmol) and p-toluenesulfonyl chloride (1.3 g, 6.6 mmol) were dissolved in methylene chloride (20 mL). Triethylamine (0.67 g, 6.6 mmol) dissolved in methylene chloride (4 mL) were added to the mixture and stirred at room temperature. The reaction was monitored by thin layer chromatography (TLC) (ethyl acetate/n-hexane = 1/1.5, v/v). After completion of the reaction, 38% HCl was added to the reaction mixture and stirred for 5 min. The organic layer was washed with $NaHCO_3$ aqueous solution and once with brine, and dried with anhydrous $MgSO_4$. The solvent was evaporated by a rotary evaporator. The solid material was recrystallized with ethyl acetate/n-hexane solution. The resulting light yellow solid product (1.4g, 75%) was obtained.

B. Synthesis of 2-(4-(4-methoxyphenethoxy)phenyl)-2-oxoethyl benzoate (**4**)



To a 100 mL, two-neck, round bottom flask, 2-(4-hydroxyphenyl)-2-oxoethyl benzoate (0.2 g, 0.78 mmol) and $K_2CO_3$ (0.23 g, 1.7 mmol) were dissolved in acetone (40 mL) and refluxed at 60°C for 1 hr with stirring. 2-(4-methoxyphenyl)ethyl-4-methylbenzenesulfonate (0.24 g, 0.78 mmol) was added in the reaction mixture and reaction proceeded for 72 hr. The reaction was monitored by thin layer chromatography (TLC). When the substrates were consumed, the precipitates were filtered, and the filtrate was evaporated under vacuum. The product was dissolved in ethyl acetate and washed twice with water, once with brine. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was evaporated. The crude product was then purified over silica gel column chromatography (ethyl acetate/n-hexane=1/1.5, v/v) and recrystallization (ethyl acetate/n-hexane and acetone), to give 2-(4-(4-methoxyphenethoxy)phenyl)-2-oxoethyl benzoate (0.13 g, 42%).



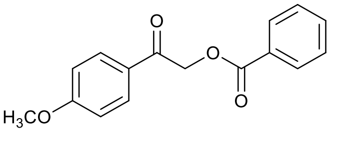
**4**

$R_f$ = 0.81 (ethyl acetate/n-hexane = 1/1.5, v/v); $^1$H NMR (500 MHz, $CDCl_3$) δ(ppm) 8.14 (dd, *J* =

8.2, 1.1 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.53 (s, 2H), 4.21 (t, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.07 (t, *J* = 7.0 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ(ppm) 190.6, 166.1, 163.4, 158.4, 133.3, 130.1, 130.0 (d, *J* = 2.1 Hz), 129.7, 129.5, 128.4, 127.3, 114.6, 114.0, 69.2, 66.2, 55.3, 34.7.; IR(ATR) 1697cm$^{-1}$ (C=O); HRMS (ESI): calculated for $C_{24}H_{22}O_5$ $(M+H)^+$ 391.1540, Found 391.1537.

**2-(Benzoyloxy)-1-(4-methoxyphenyl)ethanone (*p*MP)[1]**

This compound was prepared by the same method as that of 4-hydroxyphenethoxy benzoate shown above.



***p*MP**

$R_f$ = 0.35 (ethyl acetate/n-hexane = 1/3, v/v); $^{1}$H NMR (500 MHz, $CDCl_3$) δ(ppm) 8.14 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 5.54 (s, 2H), 3.88 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ(ppm) 190.6, 166.1, 164.1, 133.3, 130.2, 130.0, 129.5, 128.4, 127.4, 114.1, 66.2, 55.5.

## Photochemical Experiments

### General procedure

Irradiation in NMR tubes

A reactant solution in a deuterated solvent (typically 0.01-0.02 M) was irradiated with 313 nm light (solution filter) of 450 W Hanovia medium pressure mercury arc lamp after degassed by bubbling with Ar gas. The course of the reaction was monitored by $^{1}$H NMR spectra taken at regular intervals. Identification of the photoproducts was based on comparison of their $^{1}$H NMR spectra with those of authentic samples. For quantitative analysis, methyl benzoate was used as an internal standard.

Preparative scale irradiation

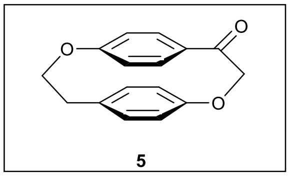
A large test tube containing the sample solution (typically 0.01-0.02 M) was fitted with a rubber septum and the sample was degassed by bubbling with argon for 10 min. The test tube was then irradiated by attaching them close to an immersion well with a Pyrex filtered light of 450 W Hanovia medium pressure mercury arc lamp. After irradiation to >90 % conversion, the resulting photoproducts were isolated by routine purification methods using silica gel column chromatography. Each of the isolated products was identified by analyzing its spectroscopic data and by X-ray crystallography if necessary.

Quantum yield measurements

The same method that was described above in the NMR scale photolysis was used except that another sample solution containing valerophenone (actinometer)[2] was irradiated in parallel. The reaction conversions were always kept below 20 % to avoid the interference of photoproducts.

## Characterization of the Photoproducts

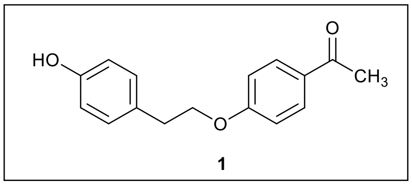
### 2,6-dioxa-1,5(1,4)-dibenzenacyclooctaphan-4-one (5)



**5**

$R_f$ = 0.58 (ethyl acetate/chloroform = 1/7, v/v); $^1$H NMR (500 MHz, $CDCl_3$) δ(ppm) 7.16 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 8.2 Hz, 2H), 4.80 (s, 2H), 4.58 (t, *J* = 5.4 Hz, 2H), 2.95 (t, *J* = 5.4 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ(ppm) 195.8, 163.0, 156.2, 133.4, 133.2, 132.4, 131.4, 121.8, 118.1, 76.2, 70.4, 37.6.; IR ($CHCl_3$) 1674cm$^{-1}$ (C=O); HRMS (ESI): calculated for $C_{16}H_{14}O_3$ $(M+H)^+$ 255.1016, Found 255.1011.

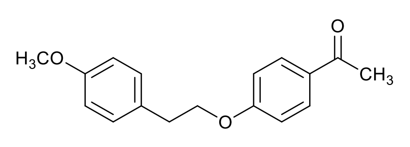
### 1-(4-(4-hydroxyphenethoxy)phenyl)ethanone (1)[3]



**1**

$^1$H NMR (500 MHz, $CDCl_3$) δ(ppm) 7.92 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.14 (s, OH), 4.19 (t, *J* = 7.0 Hz, 2H), 3.05 (t, *J* = 7.0 Hz, 2H), 2.56 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ(ppm) 197.1, 162.8, 154.4, 130.6, 130.2 (d, *J* = 8.5 Hz), 129.8, 115.4, 114.2, 69.1, 34.7, 26.3.

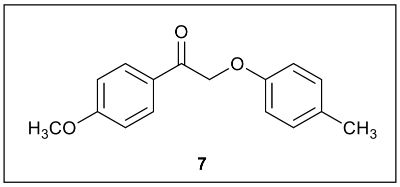
### 1-(4-(4-methoxyphenethoxy)phenyl)ethanone (2)[3]



**2**

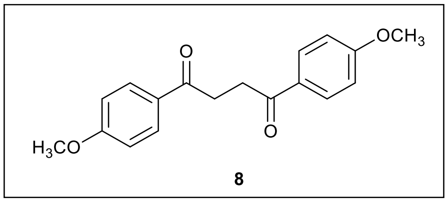
$^1$H NMR (500 MHz, $CDCl_3$) δ(ppm) 7.92 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.19 (t, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.06 (t, *J* = 7.1 Hz, 2H), 2.55 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ(ppm) 196.8, 162.8, 158.4, 130.6, 130.3, 129.8 (d, *J* = 18.8 Hz), 114.2, 114.0, 69.1, 55.2, 34.7, 26.3.; IR(ATR) 1671cm$^{-1}$ (C=O)

### 1-(4-methoxyphenyl)-2-(p-tolyloxy)ethanone (7)[4]



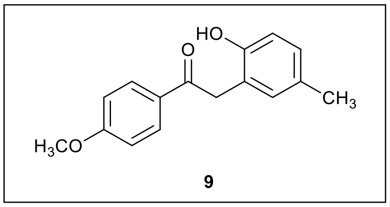
$^1$H NMR (500 MHz, CDCl$_3$) δ(ppm) 8.00 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.18 (s, 2H), 3.88 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ(ppm) 193.4, 164.0, 156.0, 130.8, 130.6, 130.0, 127.7, 114.6, 114.0, 71.0, 55.5, 20.5.

### 1,4-bis(4-methoxyphenyl)butane-1,4-dione (8)[5]



$^1$H NMR (500 MHz, CDCl$_3$) δ(ppm) 8.02 (d, *J* = 8.9 Hz, 4H), 6.95 (d, *J* = 8.9 Hz, 4H), 3.88 (s, 6H), 3.40 (s, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ(ppm) 197.4, 163.5, 130.4, 129.9, 113.7, 55.5, 32.3.

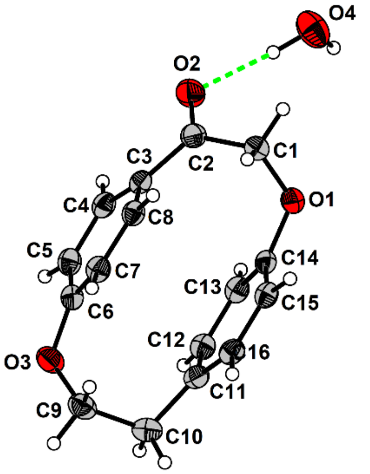
### 2-(2-hydroxy-5-methylphenyl)-1-(4-methoxyphenyl)ethanone (9)



$^1$H NMR (500 MHz, CDCl$_3$) δ(ppm) 8.09 (d, *J* = 8.9 Hz, 2H), 8.00 (s, OH), 7.03 – 6.93 (m, 4H), 6.87 (d, *J* = 8.8 Hz, 1H), 4.18 (s, 2H), 3.89 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ(ppm) 199.9, 164.4, 153.7, 131.6, 131.3, 129.9, 129.4, 128.7, 121.0, 117.7, 114.1, 55.6, 40.8, 20.4.; IR(ATR) 3419cm$^{-1}$ (-OH), 1666cm$^{-1}$ (C=O); HRMS (ESI): calculated for $C_{16}H_{16}O_3$ $(M+H)^+$ 257.1172, Found 257.1165.

## Crystallography analysis of **2,6-dioxa-1,5(1,4)-dibenzenacyclooctaphan-4-one** (5)

White crystals of purified 2,5-dioxa-1,4(1,4)-dibenzenacycloheptaphan-7-one for X-ray crystallography analysis were obtained from a dichloromethane/hexane solution under slow evaporation. A colorless plate-like specimen of $C_{16}H_{16}O_4$, approximate dimensions 0.020 mm x 0.100 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda$ = 0.71073 Å).



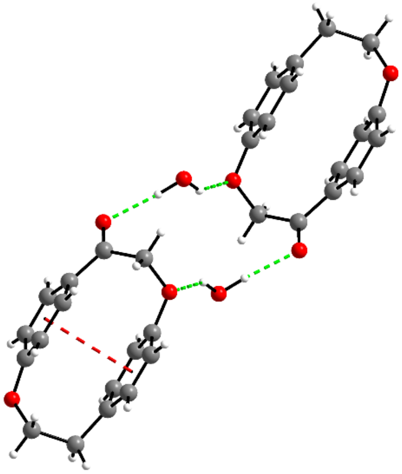


**Table S1: Data collection details**

| Axis | dx/ mm | 2θ/ ° | ω/° | φ/° | χ/° | Width/° | Frames | Time/ s | Wavelength/Å | Voltage/ kV | Current/ mA | Temperature/K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Phi | 60.561 | 0.00 | 0.00 | 0.00 | 54.74 | 1.00 | 180 | 1.20 | 0.71073 | 50 | 30.0 | n/a |
| Phi | 60.561 | 0.00 | 0.00 | 180.00 | 54.74 | 1.00 | 180 | 1.20 | 0.71073 | 50 | 30.0 | n/a |
| Omega | 60.561 | 18.54 | -174.46 | -105.00 | 54.74 | 1.00 | 206 | 10.00 | 0.71073 | 50 | 30.0 | n/a |
| Omega | 60.561 | 18.54 | -174.46 | 102.00 | 54.74 | 1.00 | 206 | 10.00 | 0.71073 | 50 | 30.0 | n/a |
| Omega | 60.561 | 18.54 | -174.46 | 0.00 | 54.74 | 1.00 | 206 | 10.00 | 0.71073 | 50 | 30.0 | n/a |
| Omega | 60.561 | 18.54 | -174.46 | -156.00 | 54.74 | 1.00 | 206 | 10.00 | 0.71073 | 50 | 30.0 | n/a |

| Axis | dx/mm | 2θ/° | ω/° | φ/° | χ/° | Width/° | Frames | Time/s | Wavelength/Å | Voltage/kV | Current/mA | Temperature/K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Omega | 60.561 | 18.54 | -174.46 | 153.00 | 54.74 | 1.00 | 206 | 10.00 | 0.71073 | 50 | 30.0 | n/a |
| Omega | 60.561 | 27.81 | -165.19 | 0.00 | 54.74 | 1.00 | 206 | 10.00 | 0.71073 | 50 | 30.0 | n/a |
| Phi | 60.561 | 18.54 | 31.54 | 0.00 | 54.74 | 1.00 | 360 | 10.00 | 0.71073 | 50 | 30.0 | n/a |
| Phi | 60.561 | 0.00 | 0.00 | 0.00 | 54.74 | 360.00 | 1 | 108.00 | 0.71073 | 50 | 30.0 | n/a |

A total of 1957 frames were collected. The total exposure time was 4.58 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 52457 reflections to a maximum θ angle of 28.28° (0.75 Å resolution), of which 3236 were independent (average redundancy 16.210, completeness = 99.8%, $R_{int}$ = 6.23%, $R_{sig}$ = 2.59%) and 1977 (61.09%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.1109(2) Å, b = 10.9261(4) Å, c = 16.7893(5) Å, β = 93.4920(10)°, volume = 1302.01(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 9455 reflections above 20 σ(I) with $4.45° < 2\theta < 52.65°$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.907. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9880 and 0.9980.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{16}H_{16}O_4$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 190 variables converged at R1 = 5.01%, for the observed data and wR2 = 20.41% for all data. The goodness-of-fit was 1.001. The largest peak in the final difference electron density synthesis was 0.205 $e^-/Å^3$ and the largest hole was -0.225 $e^-/Å^3$ with an RMS deviation of 0.048 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.389 $g/cm^3$ and F(000), 576 $e^-$.

**Table S2. Sample and crystal data.**

| | |
|---|---|
| **Chemical formula** | $C_{16}H_{16}O_4$ |
| **Formula weight** | 272.29 g/mol |
| **Temperature** | 296(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal size** | 0.020 x 0.100 x 0.120 mm |
| **Crystal habit** | colorless plate |

| | | |
|---|---|---|
| **Crystal system** | monoclinic | |
| **Space group** | P $2_1$/c | |
| **Unit cell dimensions** | a = 7.1109(2) Å | α = 90° |
| | b = 10.9261(4) Å | β = 93.4920(10)° |
| | c = 16.7893(5) Å | γ = 90° |
| **Volume** | 1302.01(7) Å$^3$ | |
| **Z** | 4 | |
| **Density (calculated)** | 1.389 g/cm$^3$ | |
| **Absorption coefficient** | 0.100 mm$^{-1}$ | |
| **F(000)** | 576 | |

**Table S3. Data collection and structure refinement.**

| | | |
|---|---|---|
| **Theta range for data collection** | 2.23 to 28.28° | |
| **Index ranges** | -9<=h<=9, -14<=k<=14, -22<=l<=22 | |
| **Reflections collected** | 52457 | |
| **Independent reflections** | 3236 [R(int) = 0.0623] | |
| **Coverage of independent reflections** | 99.8% | |
| **Absorption correction** | Multi-Scan | |
| **Max. and min. transmission** | 0.9980 and 0.9880 | |
| **Structure solution technique** | direct methods | |
| **Structure solution program** | SHELXT 2018/2 (Sheldrick, 2018) | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Refinement program** | SHELXL-2018/3 (Sheldrick, 2018) | |
| **Function minimized** | $\Sigma w(F_o^2 - F_c^2)^2$ | |
| **Data / restraints / parameters** | 3236 / 0 / 190 | |
| **Goodness-of-fit on $F^2$** | 1.001 | |
| **Final R indices** | 1977 data; I>2σ(I) | $R_1$ = 0.0501, $wR_2$ = 0.1357 |
| | all data | $R_1$ = 0.1011, $wR_2$ = 0.2041 |

| | |
|---|---|
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.1000P)^2+0.7958P]$<br>where $P=(F_o^2+2F_c^2)/3$ |
| **Extinction coefficient** | 0.0200(50) |
| **Largest diff. peak and hole** | 0.205 and -0.225 eÅ$^{-3}$ |
| **R.M.S. deviation from mean** | 0.048 eÅ$^{-3}$ |

**Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$).**

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.8467(3) | 0.5961(2) | 0.40122(14) | 0.0479(6) |
| C2 | 0.8741(3) | 0.4668(2) | 0.36968(14) | 0.0474(6) |
| C3 | 0.9055(3) | 0.45549(19) | 0.28404(13) | 0.0398(5) |
| C4 | 0.8120(3) | 0.36444(19) | 0.23837(14) | 0.0436(5) |
| C5 | 0.7893(3) | 0.3749(2) | 0.15680(14) | 0.0464(6) |
| C6 | 0.8584(3) | 0.4783(2) | 0.11930(14) | 0.0440(5) |
| C7 | 0.9803(3) | 0.5564(2) | 0.16213(14) | 0.0448(5) |
| C8 | 0.9990(3) | 0.5466(2) | 0.24374(14) | 0.0412(5) |
| C9 | 0.7742(4) | 0.6245(2) | 0.01650(15) | 0.0562(6) |
| C10 | 0.5944(4) | 0.6843(3) | 0.04313(15) | 0.0563(7) |
| C11 | 0.5825(3) | 0.6898(2) | 0.13240(14) | 0.0442(5) |
| C12 | 0.4887(3) | 0.5983(2) | 0.17131(14) | 0.0445(5) |
| C13 | 0.5081(3) | 0.5854(2) | 0.25326(14) | 0.0436(5) |
| C14 | 0.6225(3) | 0.6652(2) | 0.29737(13) | 0.0395(5) |
| C15 | 0.6998(3) | 0.7655(2) | 0.26124(14) | 0.0433(5) |
| C16 | 0.6796(3) | 0.7770(2) | 0.17922(14) | 0.0448(5) |
| O1 | 0.6585(2) | 0.64039(16) | 0.37841(9) | 0.0495(4) |
| O2 | 0.8505(3) | 0.37842(17) | 0.41238(11) | 0.0646(6) |
| O3 | 0.7956(3) | 0.49847(16) | 0.04196(10) | 0.0569(5) |
| O4 | 0.7147(4) | 0.4378(3) | 0.56735(15) | 0.0841(7) |

**Table S5. Bond lengths (Å).**

| | | | |
|---|---|---|---|
| C1-O1 | 1.452(3) | C1-C2 | 1.526(3) |

| | | | |
|---|---|---|---|
| C1-H1A | 0.97 | C1-H1B | 0.97 |
| C2-O2 | 1.220(3) | C2-C3 | 1.474(3) |
| C3-C8 | 1.394(3) | C3-C4 | 1.399(3) |
| C4-C5 | 1.374(3) | C4-H4 | 0.93 |
| C5-C6 | 1.397(3) | C5-H5 | 0.93 |
| C6-O3 | 1.365(3) | C6-C7 | 1.385(3) |
| C7-C8 | 1.373(3) | C7-H7 | 0.93 |
| C8-H8 | 0.93 | C9-O3 | 1.447(3) |
| C9-C10 | 1.527(4) | C9-H9A | 0.97 |
| C9-H9B | 0.97 | C10-C11 | 1.507(3) |
| C10-H10A | 0.97 | C10-H10B | 0.97 |
| C11-C12 | 1.387(3) | C11-C16 | 1.392(3) |
| C12-C13 | 1.382(3) | C12-H12 | 0.93 |
| C13-C14 | 1.377(3) | C13-H13 | 0.93 |
| C14-C15 | 1.382(3) | C14-O1 | 1.396(3) |
| C15-C16 | 1.382(3) | C15-H15 | 0.93 |
| C16-H16 | 0.93 | O4-H41 | 0.95(5) |
| O4-H42 | 1.04(7) | | |

**Table S6. Bond angles (°).**

| | | | |
|---|---|---|---|
| O1-C1-C2 | 110.60(19) | O1-C1-H1A | 109.5 |
| C2-C1-H1A | 109.5 | O1-C1-H1B | 109.5 |
| C2-C1-H1B | 109.5 | H1A-C1-H1B | 108.1 |
| O2-C2-C3 | 122.8(2) | O2-C2-C1 | 120.3(2) |
| C3-C2-C1 | 116.5(2) | C8-C3-C4 | 117.8(2) |
| C8-C3-C2 | 121.3(2) | C4-C3-C2 | 119.9(2) |
| C5-C4-C3 | 120.7(2) | C5-C4-H4 | 119.7 |
| C3-C4-H4 | 119.7 | C4-C5-C6 | 119.5(2) |
| C4-C5-H5 | 120.2 | C6-C5-H5 | 120.2 |
| O3-C6-C7 | 123.5(2) | O3-C6-C5 | 117.1(2) |
| C7-C6-C5 | 119.3(2) | C8-C7-C6 | 119.3(2) |
| C8-C7-H7 | 120.3 | C6-C7-H7 | 120.3 |
| C7-C8-C3 | 121.3(2) | C7-C8-H8 | 119.3 |
| C3-C8-H8 | 119.3 | O3-C9-C10 | 113.3(2) |

| | | | |
|---|---|---|---|
| O3-C9-H9A | 108.9 | C10-C9-H9A | 108.9 |
| O3-C9-H9B | 108.9 | C10-C9-H9B | 108.9 |
| H9A-C9-H9B | 107.7 | C11-C10-C9 | 114.0(2) |
| C11-C10-H10A | 108.7 | C9-C10-H10A | 108.7 |
| C11-C10-H10B | 108.7 | C9-C10-H10B | 108.7 |
| H10A-C10-H10B | 107.6 | C12-C11-C16 | 117.6(2) |
| C12-C11-C10 | 119.8(2) | C16-C11-C10 | 122.2(2) |
| C13-C12-C11 | 121.4(2) | C13-C12-H12 | 119.3 |
| C11-C12-H12 | 119.3 | C14-C13-C12 | 119.4(2) |
| C14-C13-H13 | 120.3 | C12-C13-H13 | 120.3 |
| C13-C14-C15 | 120.2(2) | C13-C14-O1 | 118.0(2) |
| C15-C14-O1 | 121.8(2) | C16-C15-C14 | 119.3(2) |
| C16-C15-H15 | 120.3 | C14-C15-H15 | 120.3 |
| C15-C16-C11 | 121.2(2) | C15-C16-H16 | 119.4 |
| C11-C16-H16 | 119.4 | C14-O1-C1 | 115.68(16) |
| C6-O3-C9 | 117.20(18) | H41-O4-H42 | 100.(4) |

**Table S7. Torsion angles (°).**

| | | | |
|---|---|---|---|
| O1-C1-C2-O2 | -95.9(3) | O1-C1-C2-C3 | 76.6(3) |
| O2-C2-C3-C8 | -155.8(2) | C1-C2-C3-C8 | 31.9(3) |
| O2-C2-C3-C4 | 36.1(3) | C1-C2-C3-C4 | -136.2(2) |
| C8-C3-C4-C5 | -9.6(3) | C2-C3-C4-C5 | 158.9(2) |
| C3-C4-C5-C6 | -0.7(3) | C4-C5-C6-O3 | -165.2(2) |
| C4-C5-C6-C7 | 12.7(3) | O3-C6-C7-C8 | 163.8(2) |
| C5-C6-C7-C8 | -14.0(3) | C6-C7-C8-C3 | 3.5(3) |
| C4-C3-C8-C7 | 8.3(3) | C2-C3-C8-C7 | -160.1(2) |
| O3-C9-C10-C11 | 61.1(3) | C9-C10-C11-C12 | -94.5(3) |
| C9-C10-C11-C16 | 78.5(3) | C16-C11-C12-C13 | -7.3(3) |
| C10-C11-C12-C13 | 166.0(2) | C11-C12-C13-C14 | 0.2(3) |

|  |  |  |  |
|---|---|---|---|
| C12-C13-C14-C15 | 7.4(3) | C12-C13-C14-O1 | -171.85(19) |
| C13-C14-C15-C16 | -7.6(3) | O1-C14-C15-C16 | 171.64(19) |
| C14-C15-C16-C11 | 0.2(3) | C12-C11-C16-C15 | 7.1(3) |
| C10-C11-C16-C15 | -166.1(2) | C13-C14-O1-C1 | 107.0(2) |
| C15-C14-O1-C1 | -72.2(3) | C2-C1-O1-C14 | -69.8(2) |
| C7-C6-O3-C9 | -31.3(3) | C5-C6-O3-C9 | 146.5(2) |
| C10-C9-O3-C6 | -78.8(3) |  |  |

**Table S8. Anisotropic atomic displacement parameters (Å$^2$).**

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

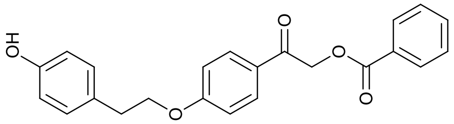
|  | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0501(13) | 0.0530(13) | 0.0403(12) | -0.0025(10) | -0.0001(10) | 0.0048(10) |
| C2 | 0.0452(12) | 0.0516(13) | 0.0455(13) | 0.0048(10) | 0.0038(10) | 0.0044(10) |
| C3 | 0.0369(10) | 0.0377(10) | 0.0447(12) | 0.0009(9) | 0.0032(9) | 0.0061(8) |
| C4 | 0.0453(12) | 0.0333(10) | 0.0526(13) | 0.0025(9) | 0.0074(10) | 0.0032(9) |
| C5 | 0.0494(13) | 0.0372(11) | 0.0526(14) | -0.0076(10) | 0.0039(10) | -0.0012(9) |
| C6 | 0.0461(12) | 0.0443(12) | 0.0420(12) | -0.0031(9) | 0.0065(9) | 0.0042(9) |
| C7 | 0.0407(11) | 0.0444(12) | 0.0501(13) | 0.0020(10) | 0.0096(9) | -0.0018(9) |
| C8 | 0.0354(10) | 0.0406(11) | 0.0477(12) | -0.0037(9) | 0.0031(9) | 0.0006(8) |
| C9 | 0.0686(16) | 0.0599(15) | 0.0404(13) | 0.0059(11) | 0.0053(11) | -0.0017(12) |
| C10 | 0.0581(15) | 0.0619(16) | 0.0481(14) | 0.0103(12) | -0.0043(11) | -0.0005(12) |
| C11 | 0.0410(11) | 0.0451(12) | 0.0464(12) | 0.0051(10) | 0.0009(9) | 0.0042(9) |
| C12 | 0.0364(11) | 0.0453(12) | 0.0515(13) | -0.0028(10) | 0.0007(9) | -0.0026(9) |
| C13 | 0.0386(11) | 0.0406(11) | 0.0526(13) | 0.0034(10) | 0.0112(9) | -0.0016(9) |
| C14 | 0.0374(10) | 0.0416(11) | 0.0401(11) | -0.0004(9) | 0.0078(8) | 0.0057(8) |
| C15 | 0.0414(11) | 0.0361(11) | 0.0524(13) | -0.0029(9) | 0.0039(9) | 0.0012(9) |
| C16 | 0.0435(12) | 0.0370(11) | 0.0542(14) | 0.0068(10) | 0.0070(10) | -0.0004(9) |

|  | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0486(9) | 0.0591(10) | 0.0415(9) | -0.0008(7) | 0.0092(7) | 0.0071(7) |
| O2 | 0.0862(14) | 0.0548(11) | 0.0540(11) | 0.0115(9) | 0.0139(9) | 0.0032(10) |
| O3 | 0.0733(12) | 0.0558(11) | 0.0412(9) | -0.0036(7) | 0.0000(8) | -0.0027(8) |
| O4 | 0.0773(16) | 0.110(2) | 0.0662(15) | -0.0124(13) | 0.0182(12) | -0.0200(13) |

**Table S9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$).**

|  | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1A | 0.8659 | 0.5962 | 0.4589 | 0.057 |
| H1B | 0.9393 | 0.6504 | 0.3799 | 0.057 |
| H4 | 0.7648 | 0.2961 | 0.2635 | 0.052 |
| H5 | 0.7282 | 0.3136 | 0.1268 | 0.056 |
| H7 | 1.0487 | 0.6148 | 0.1359 | 0.054 |
| H8 | 1.0755 | 0.6018 | 0.2727 | 0.049 |
| H9A | 0.7735 | 0.6277 | -0.0413 | 0.067 |
| H9B | 0.8819 | 0.6711 | 0.0378 | 0.067 |
| H10A | 0.5865 | 0.7669 | 0.0220 | 0.068 |
| H10B | 0.4867 | 0.6390 | 0.0204 | 0.068 |
| H12 | 0.4111 | 0.5445 | 0.1416 | 0.053 |
| H13 | 0.4445 | 0.5234 | 0.2784 | 0.052 |
| H15 | 0.7647 | 0.8246 | 0.2918 | 0.052 |
| H16 | 0.7319 | 0.8443 | 0.1548 | 0.054 |
| H41 | 0.737(7) | 0.410(4) | 0.515(3) | 0.133(17) |
| H42 | 0.570(10) | 0.423(6) | 0.568(3) | 0.18(2) |

## Spectroscopic Data



**3**

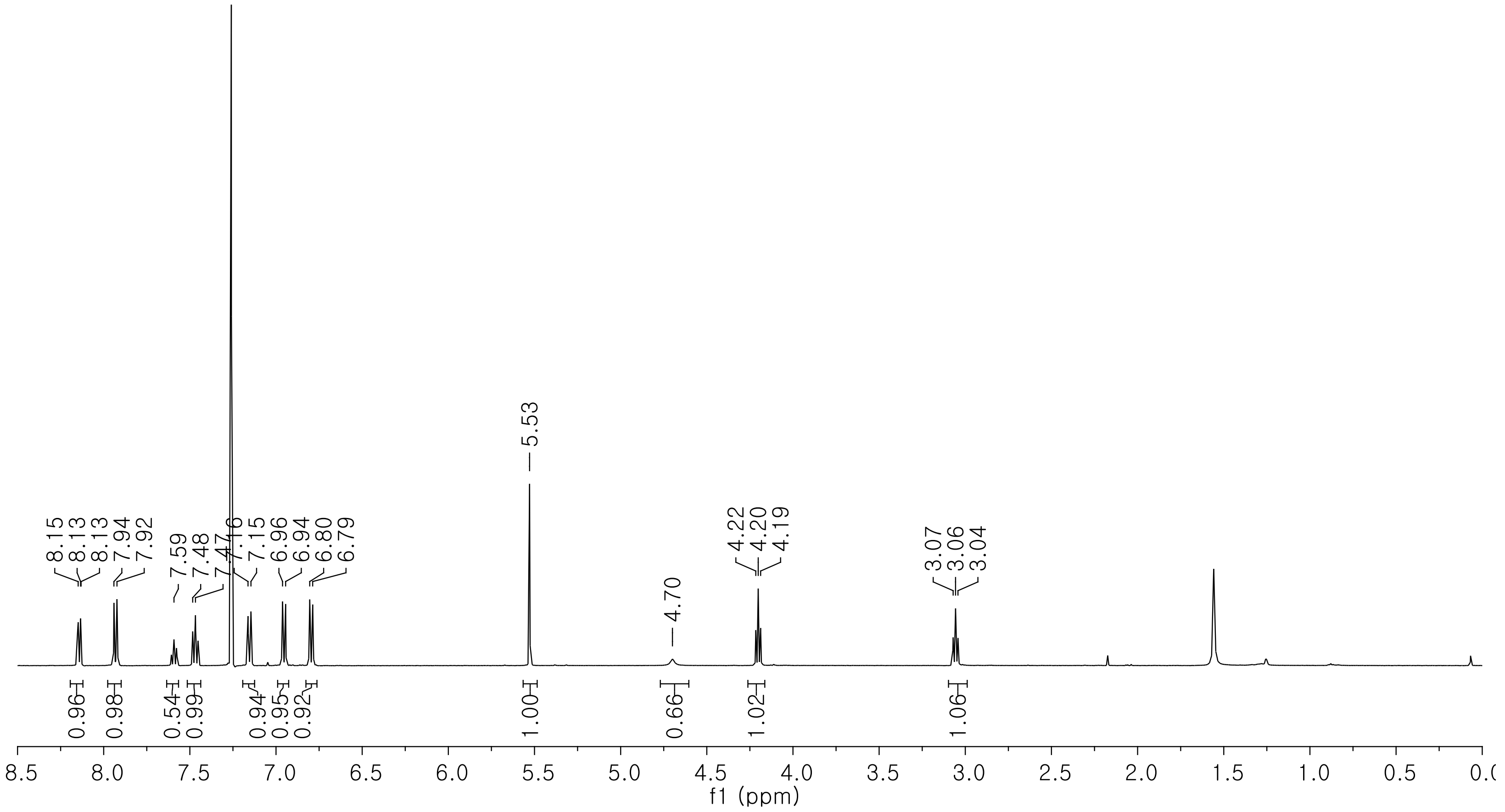


Figure S1. $^1$H NMR Spectrum (500 MHz, $CDCl_3$) of 2-(4-(4-hydroxyphenethoxy)phenyl)-2-oxoethyl benzoate (**3**)

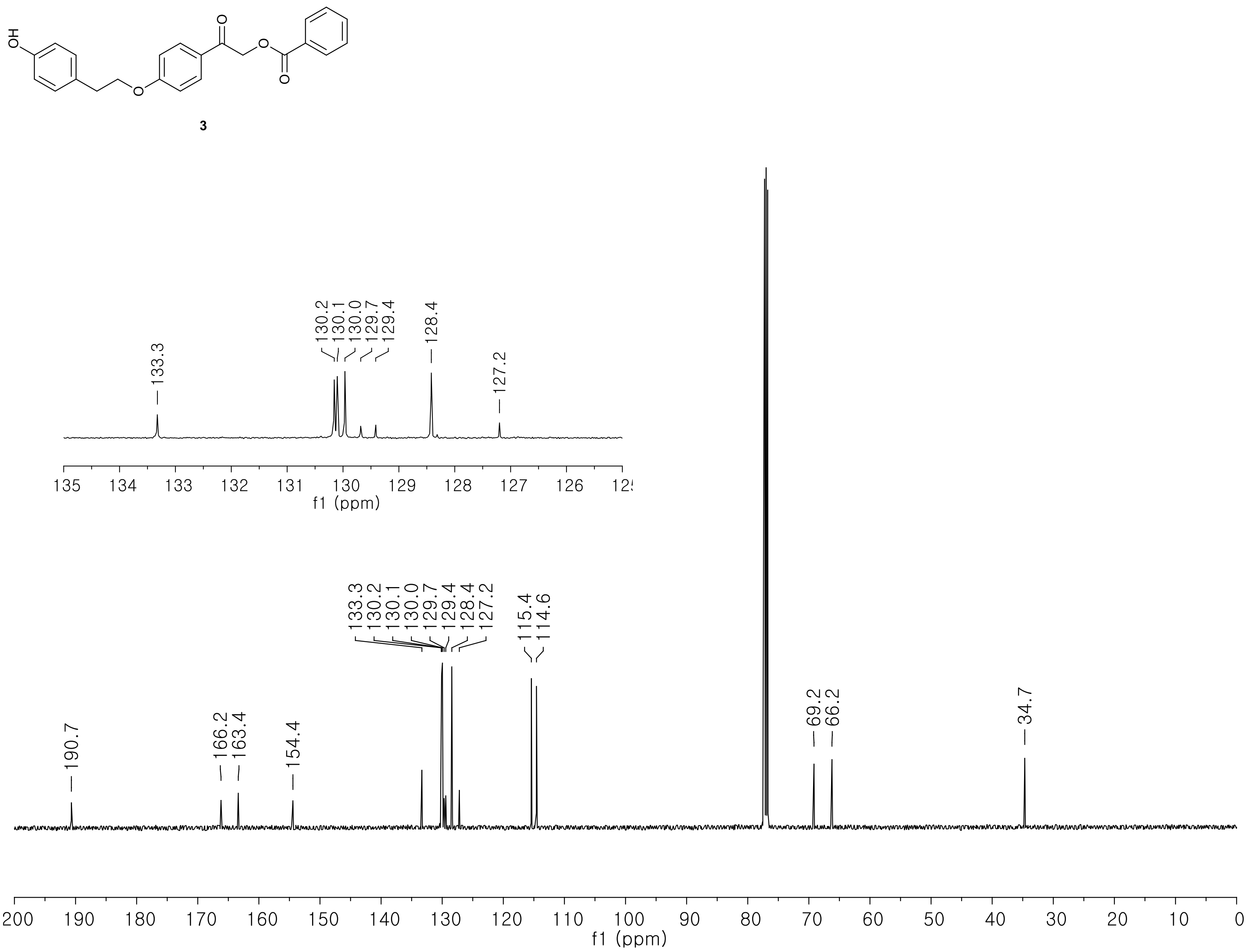


Figure S2. $^{13}$C NMR Spectrum (125 MHz, $CDCl_3$) of 2-(4-(4-hydroxyphenethoxy)phenyl)-2-oxoethyl benzoate (**3**)

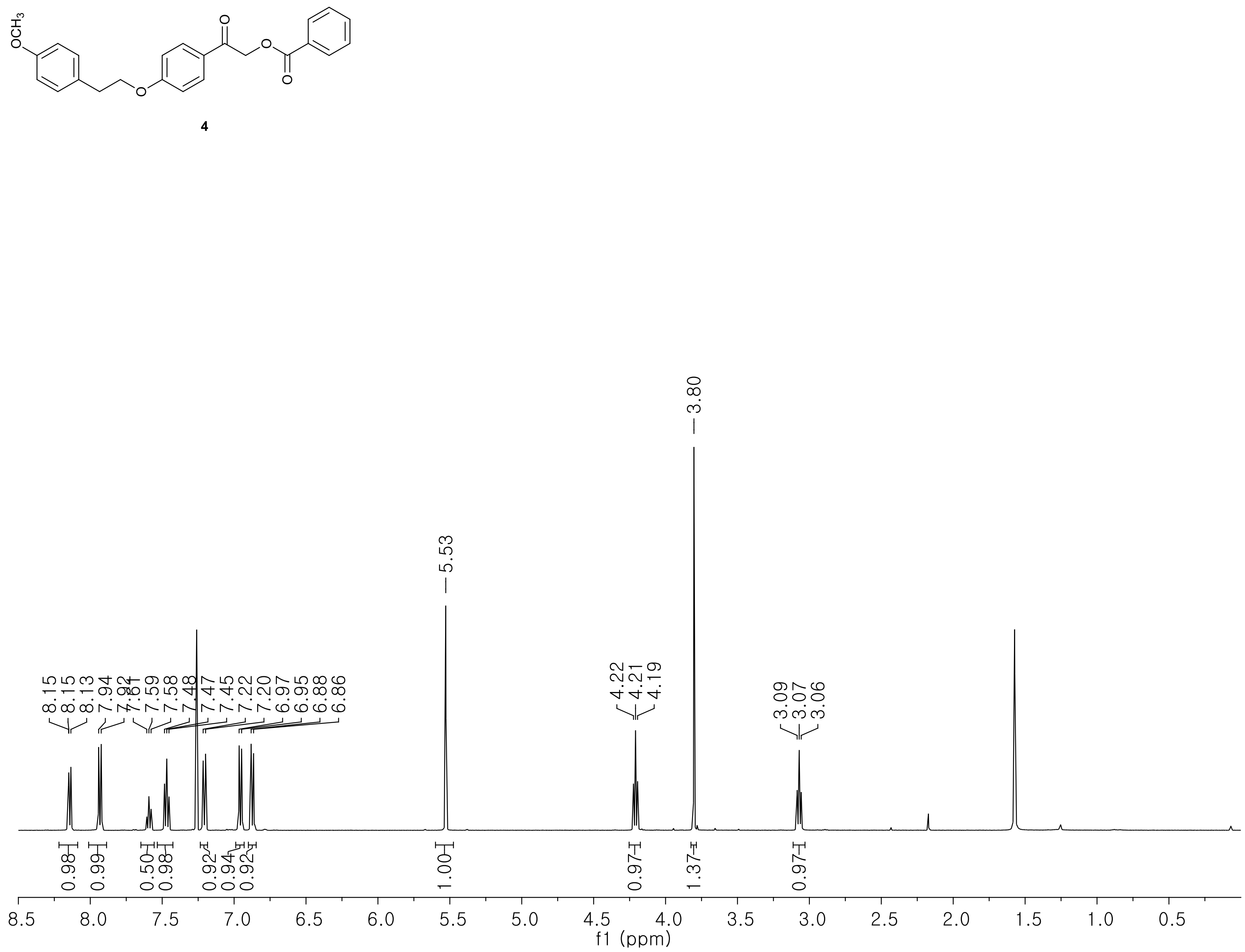
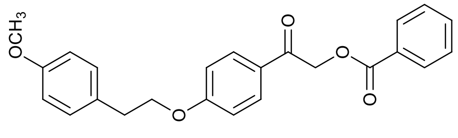


Figure S3. $^{1}$H NMR Spectrum (500 MHz, $CDCl_3$) of 2-(4-(4-methoxyphenethoxy)phenyl)-2-oxoethyl benzoate (**4**)



**4**

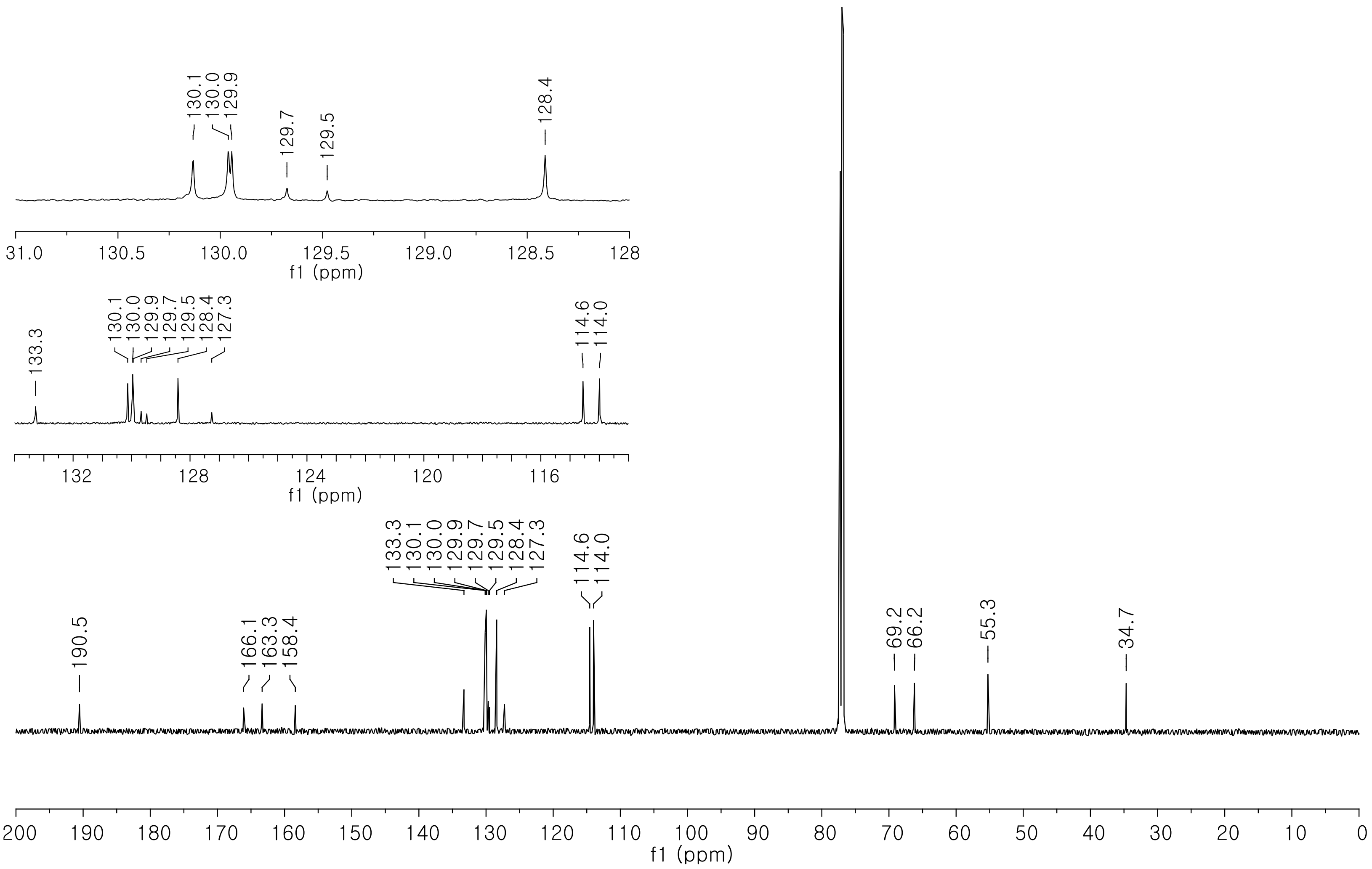


Figure S4. $^{13}$C NMR Spectrum (125 MHz, $CDCl_3$) of 2-(4-(4-methoxyphenethoxy)phenyl)-2-oxoethyl benzoate (**4**)

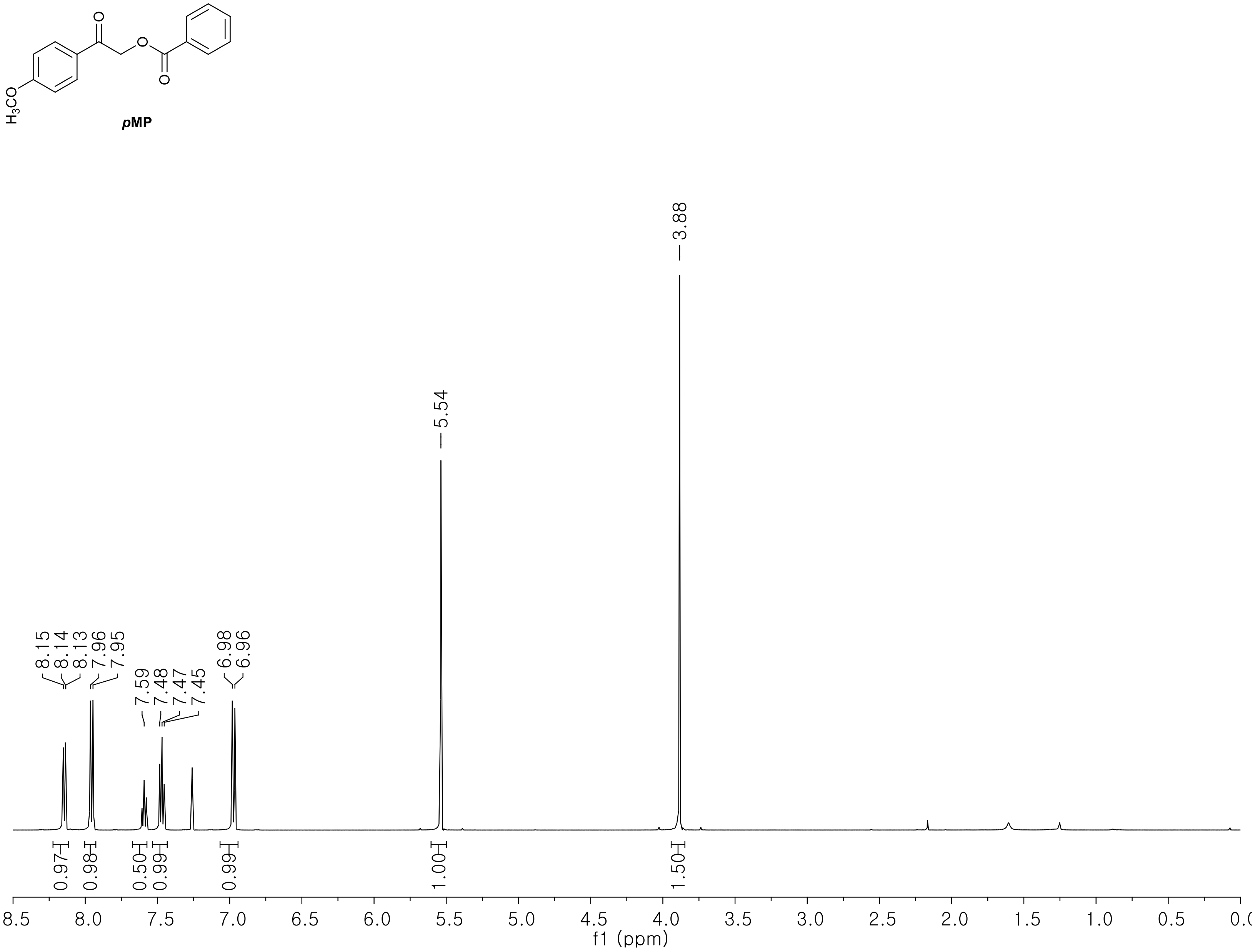


Figure S5. $^1$H NMR Spectrum (500 MHz, $CDCl_3$) of 2-(benzoyloxy)-1-(4-methoxyphenyl)-ethanone (***p*MP**)

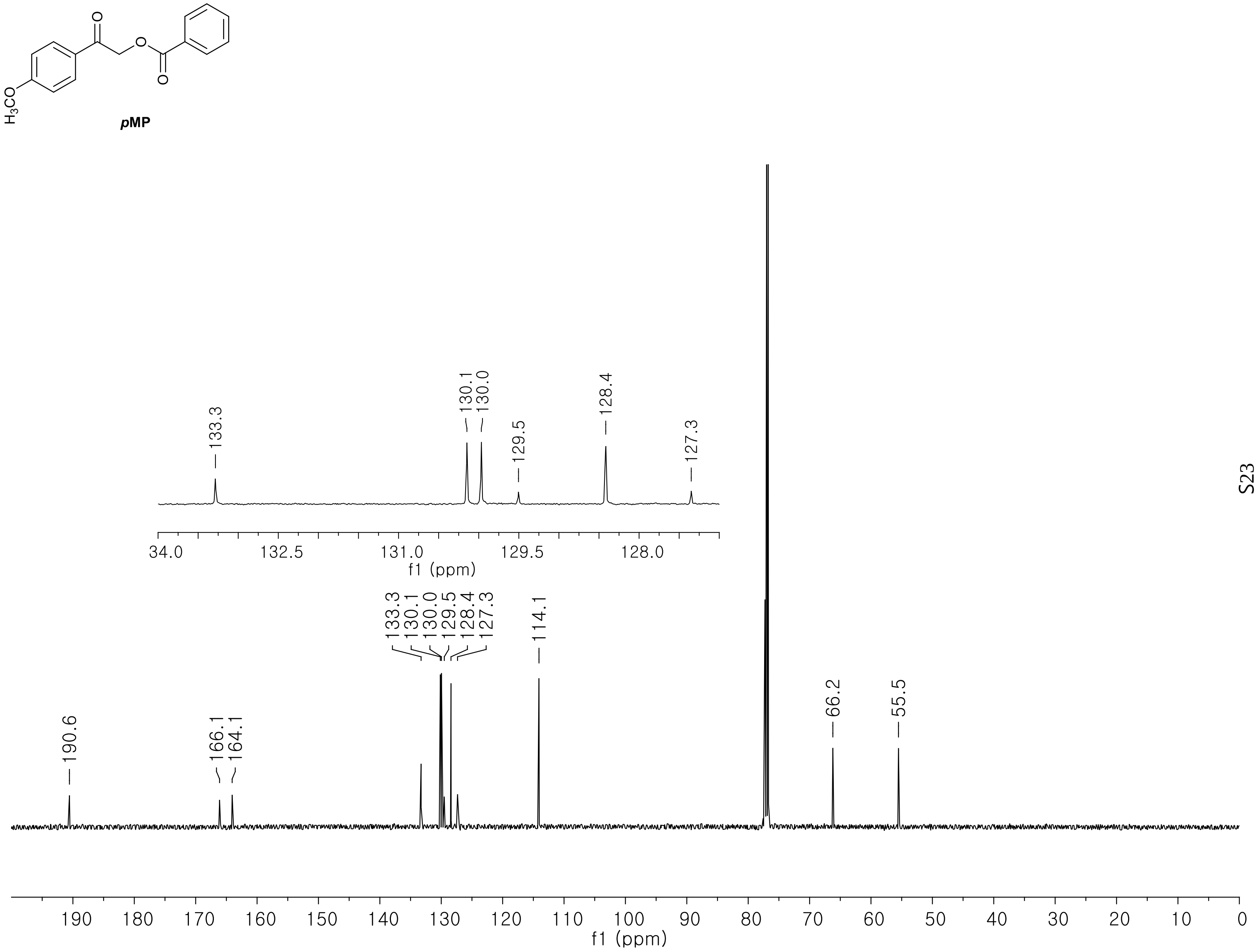


Figure S6. $^{13}$C NMR Spectrum (125 MHz, $CDCl_3$) of 2-(benzoyloxy)-1-(4-methoxyphenyl)-ethanone (***p*MP**)

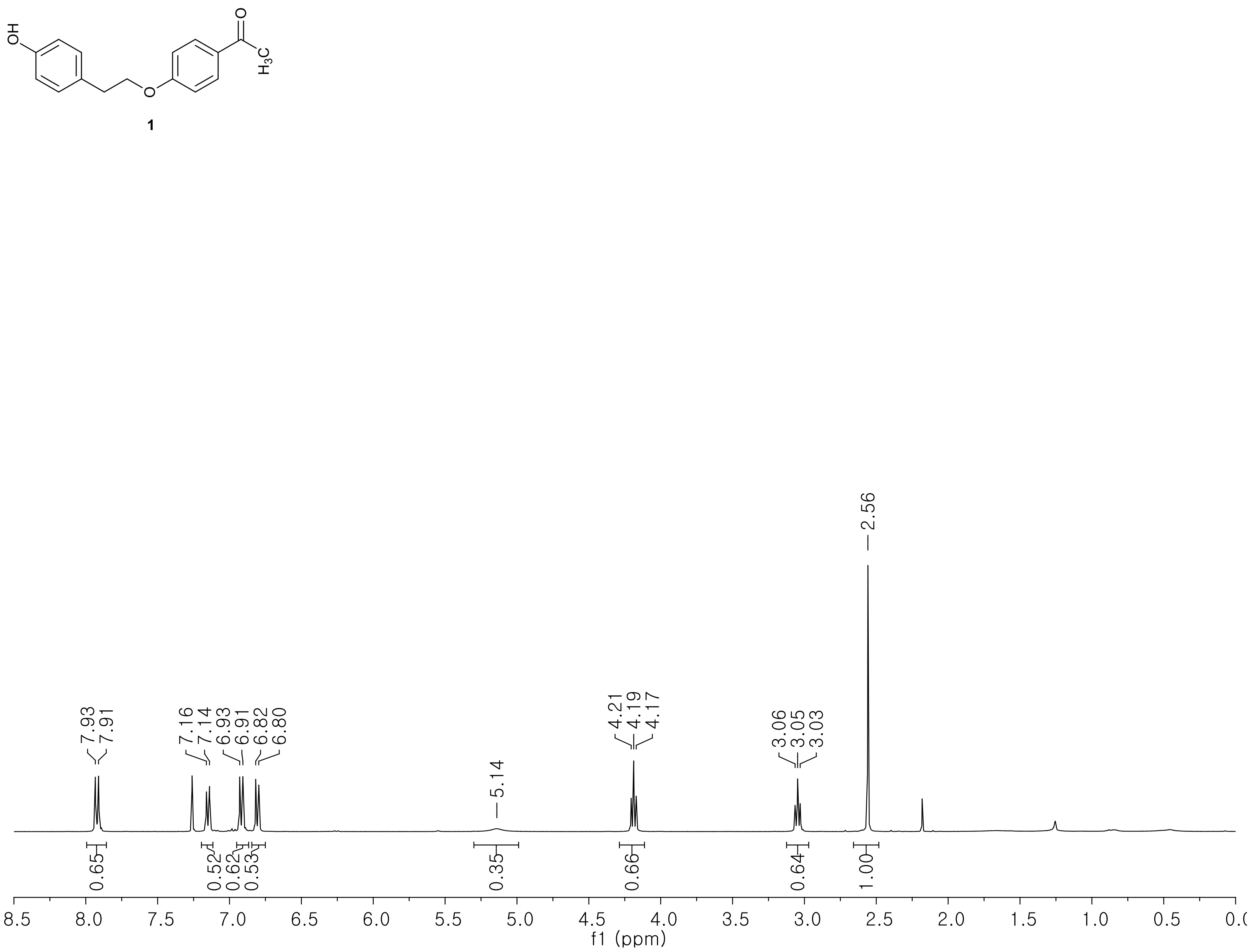


Figure S7. $^{1}$H NMR Spectrum (500 MHz, $CDCl_3$) of 1-(4-(4-hydroxyphenethoxy)phenyl)-ethanone (**1**)

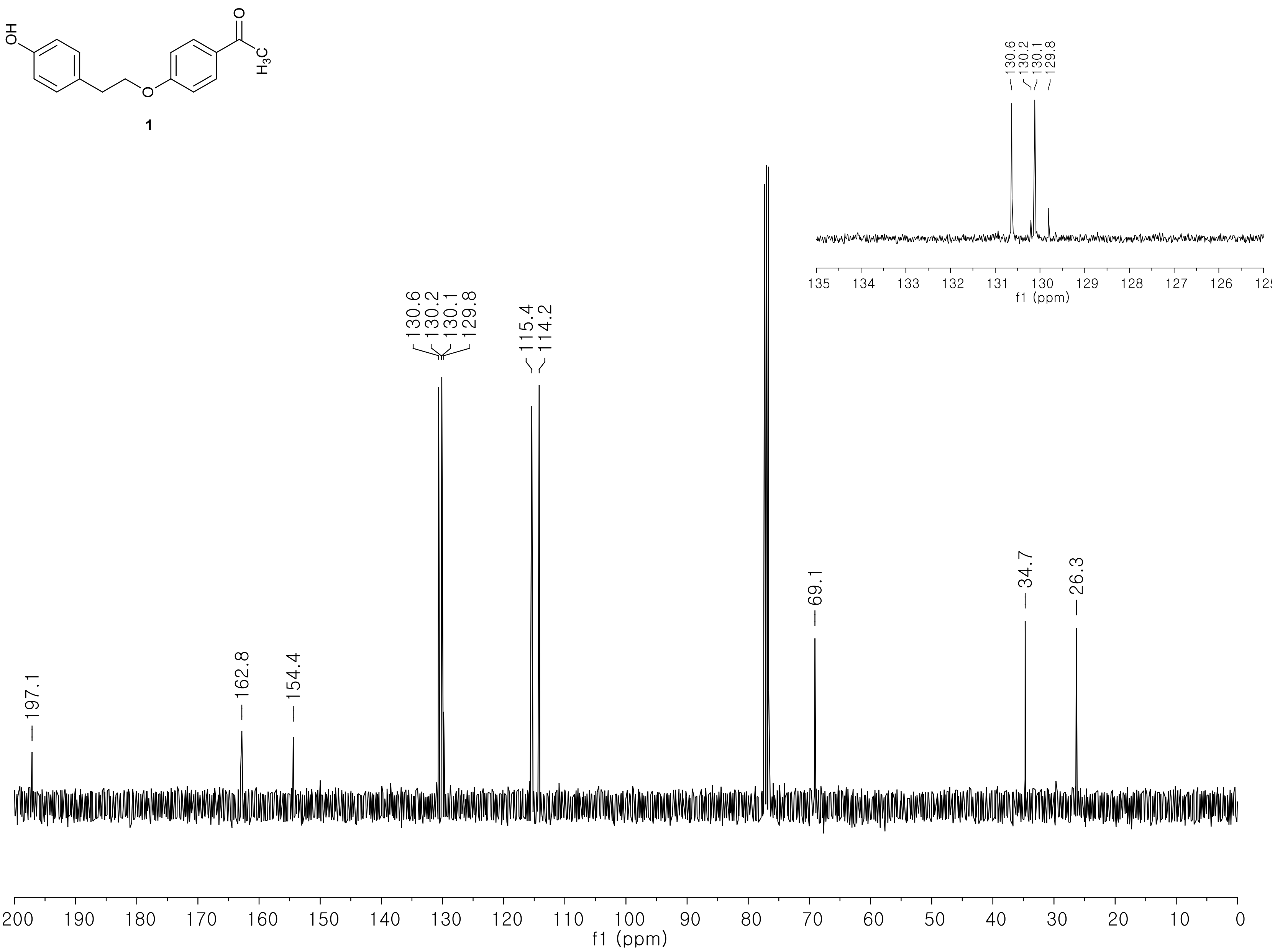
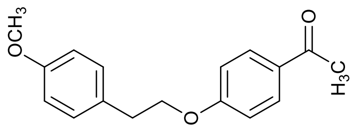


Figure S8. $^{13}$C NMR Spectrum (125 MHz, $CDCl_3$) of 1-(4-(4-hydroxyphenethoxy)phenyl)-ethanone (**1**)



**2**

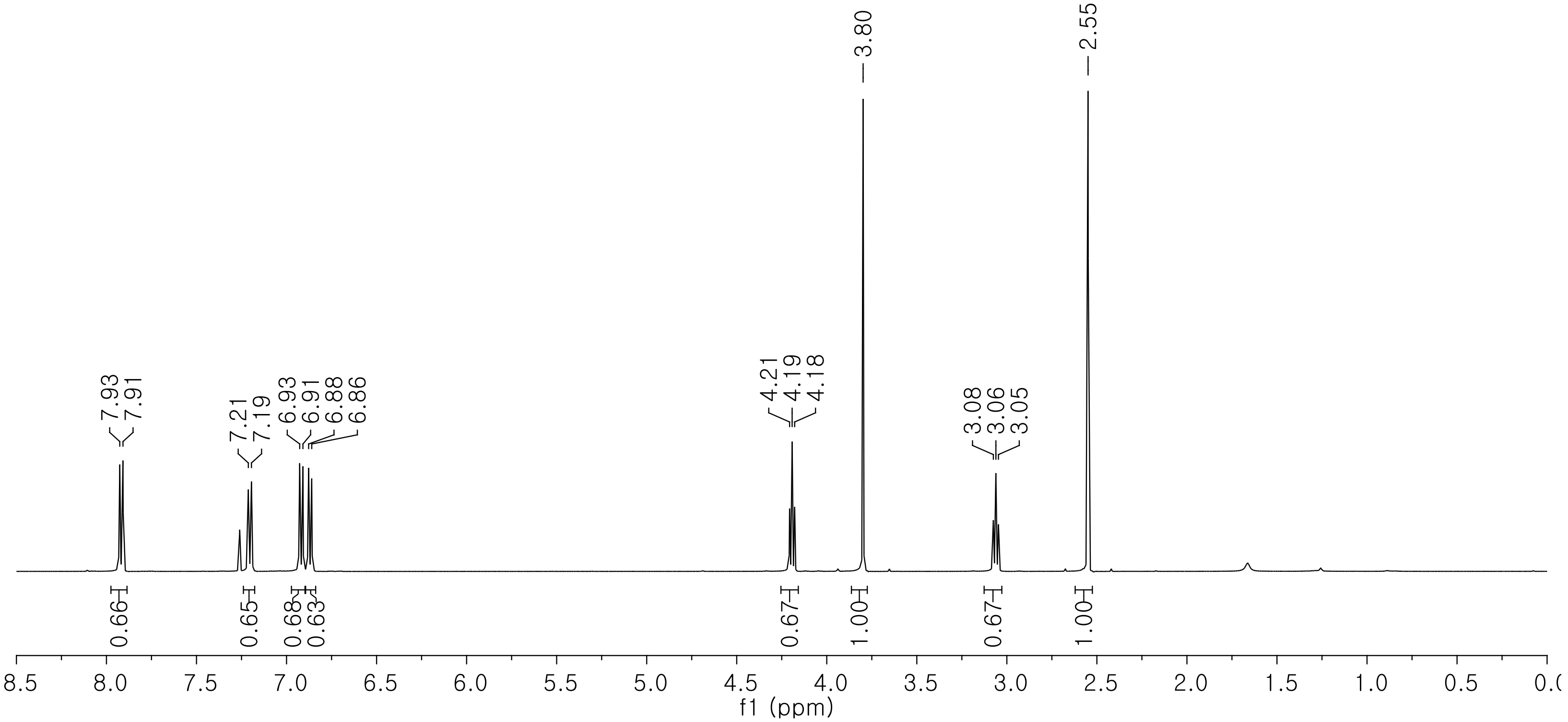


Figure S9. $^1$H NMR Spectrum (500 MHz, $CDCl_3$) of 1-(4-(4-methoxyphenethoxy)phenyl)-ethanone (**2**)

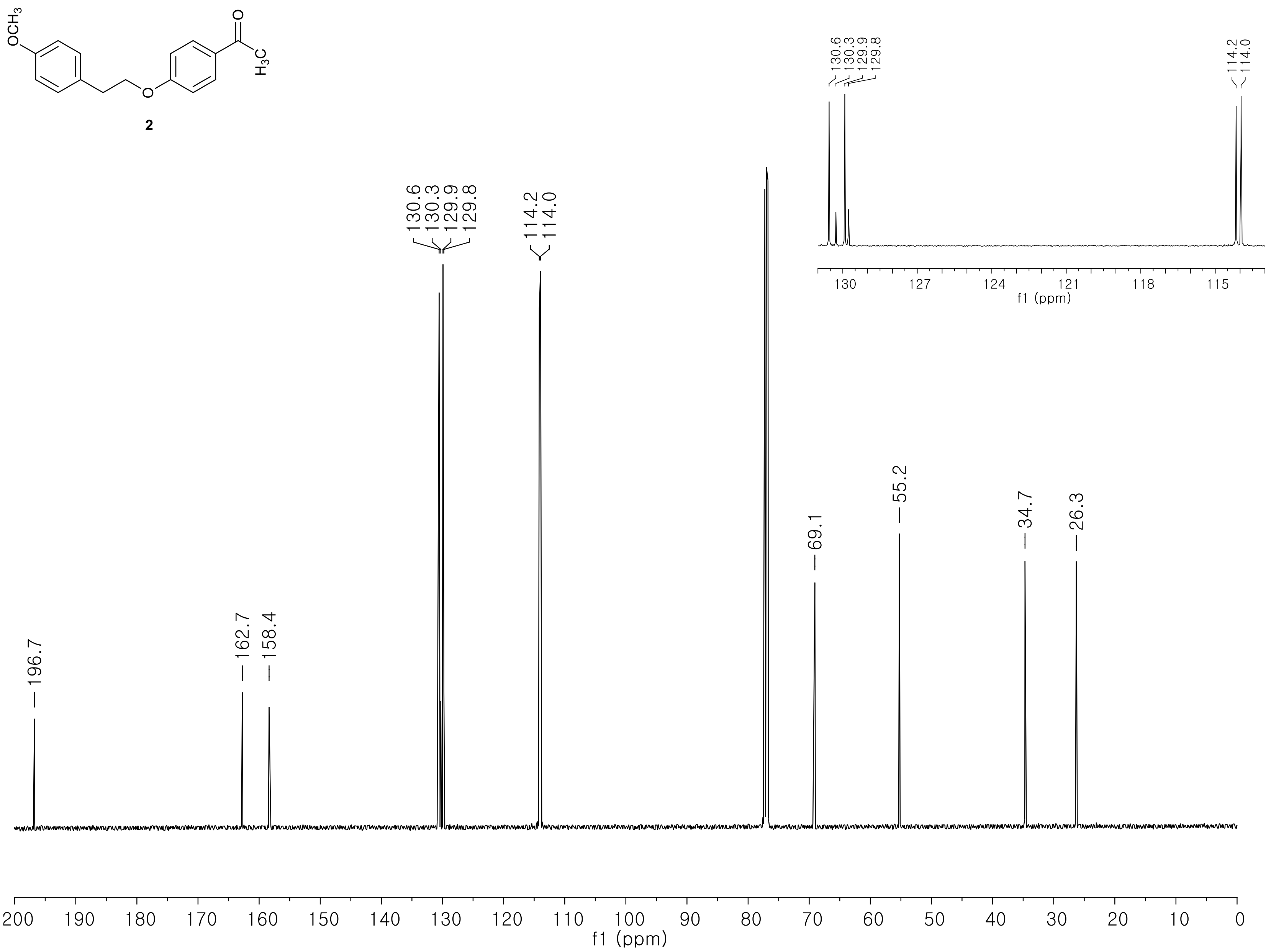
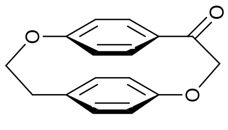


Figure S10. $^{13}$C NMR Spectrum (125 MHz, CDCl$_3$) of 1-(4-(4-methoxyphenethoxy)phenyl)-ethanone (**2**)



**5**

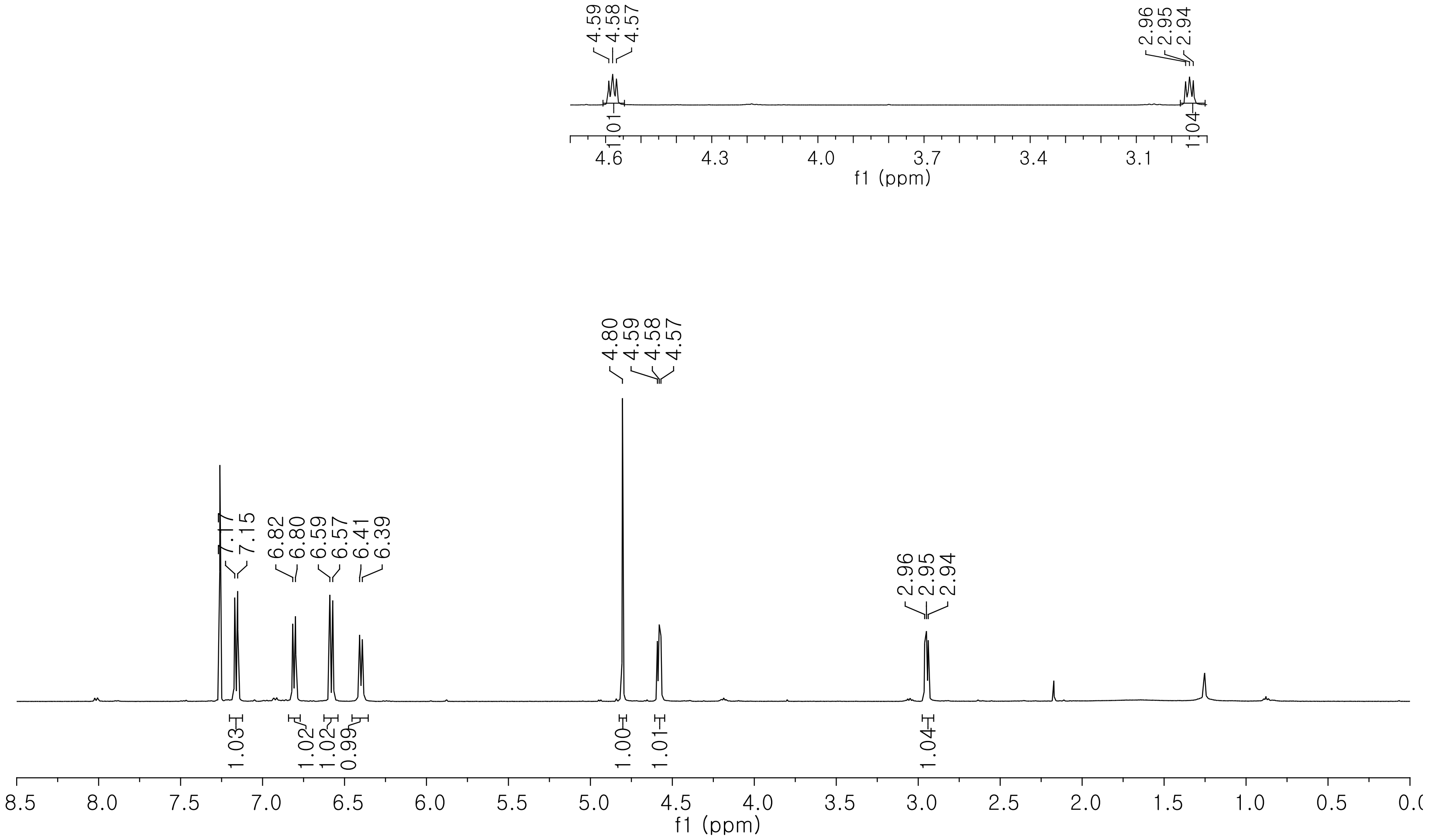


Figure S11. $^1$H NMR Spectrum (500 MHz, $CDCl_3$) of 2,6-dioxa-1,5(1,4)-dibenzena-cyclooctaphan-4-one (5)

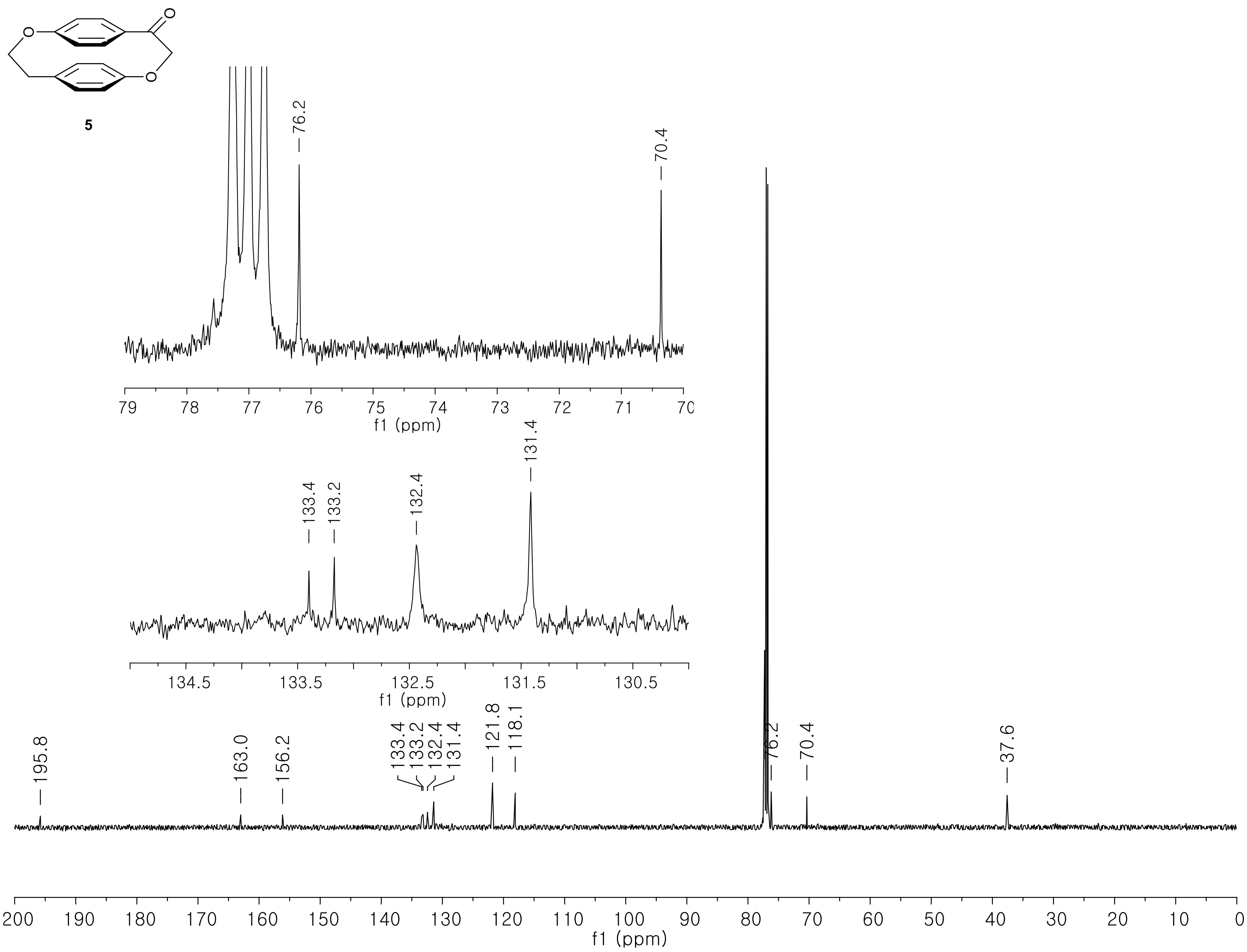
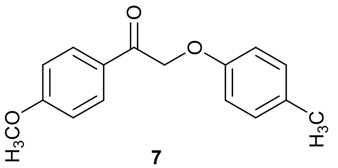


Figure S12. $^{13}$C NMR Spectrum (125 MHz, $CDCl_3$) of 2,6-dioxa-1,5(1,4)-dibenzenacy-clooctaphan-4-one (5)



**7**

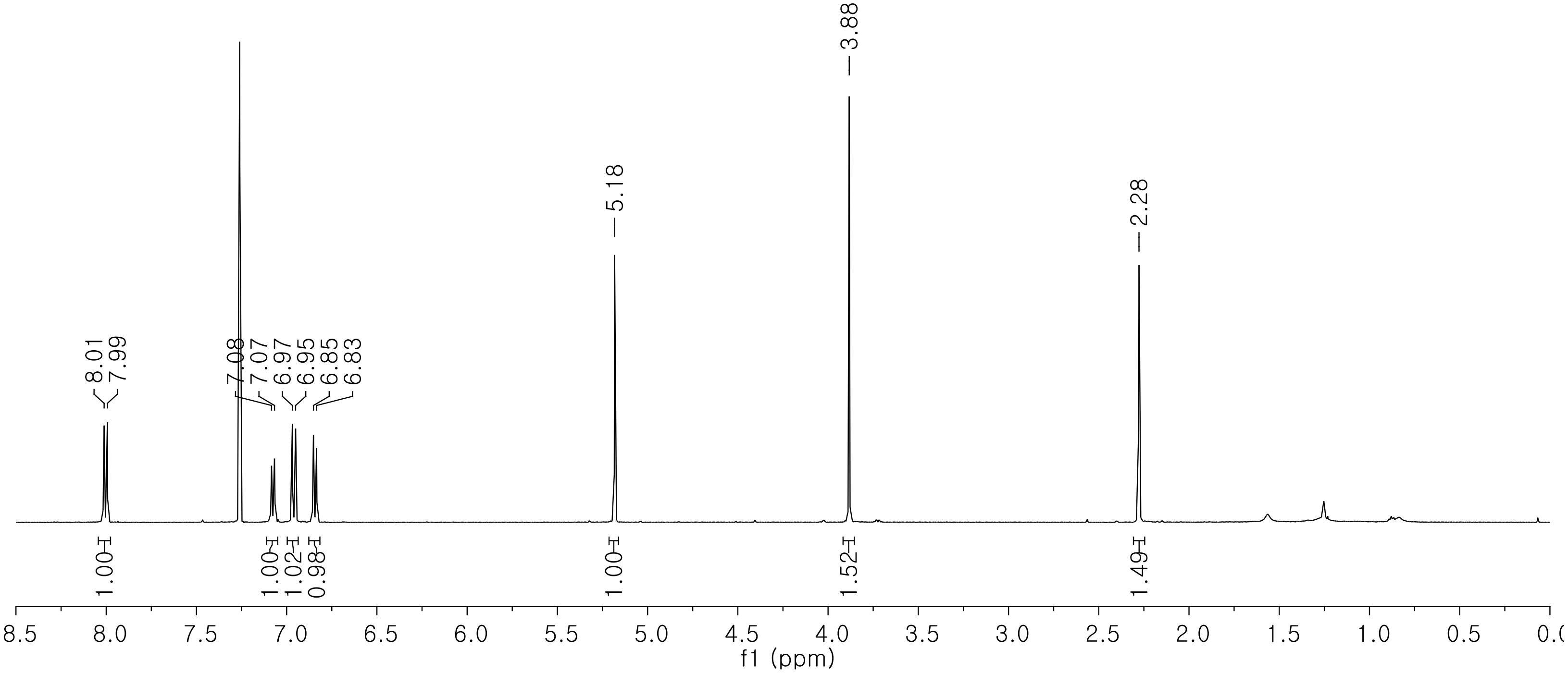


Figure S13. $^1$H NMR Spectrum (500 MHz, $CDCl_3$) of 1-(4-methoxyphenyl)-2-(p-tolyloxy)-ethanone (**7**)

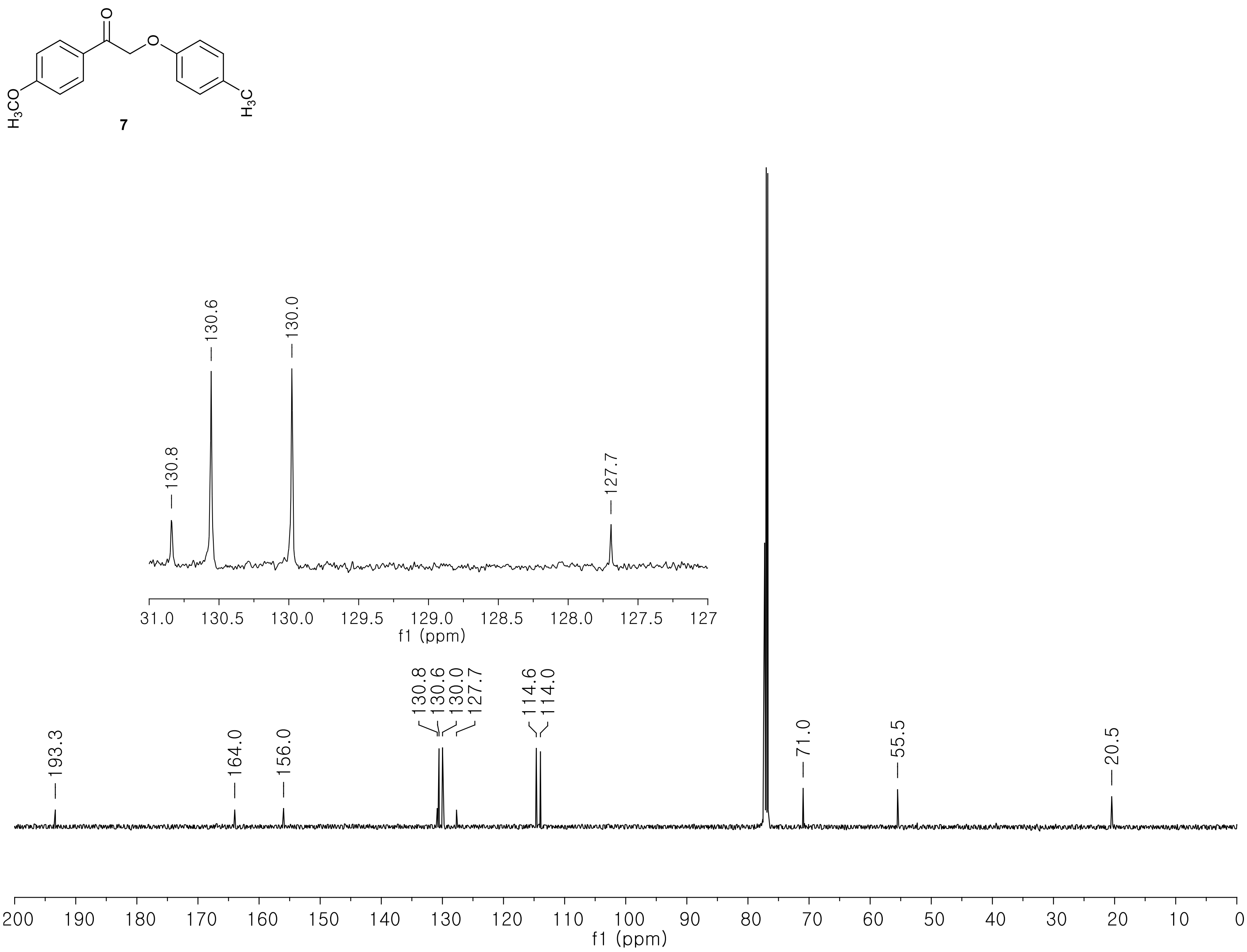


Figure S14. $^{13}$C NMR Spectrum (125 MHz, CDCl$_3$) of 1-(4-methoxyphenyl)-2-(p-tolyloxy)-ethanone (**7**)

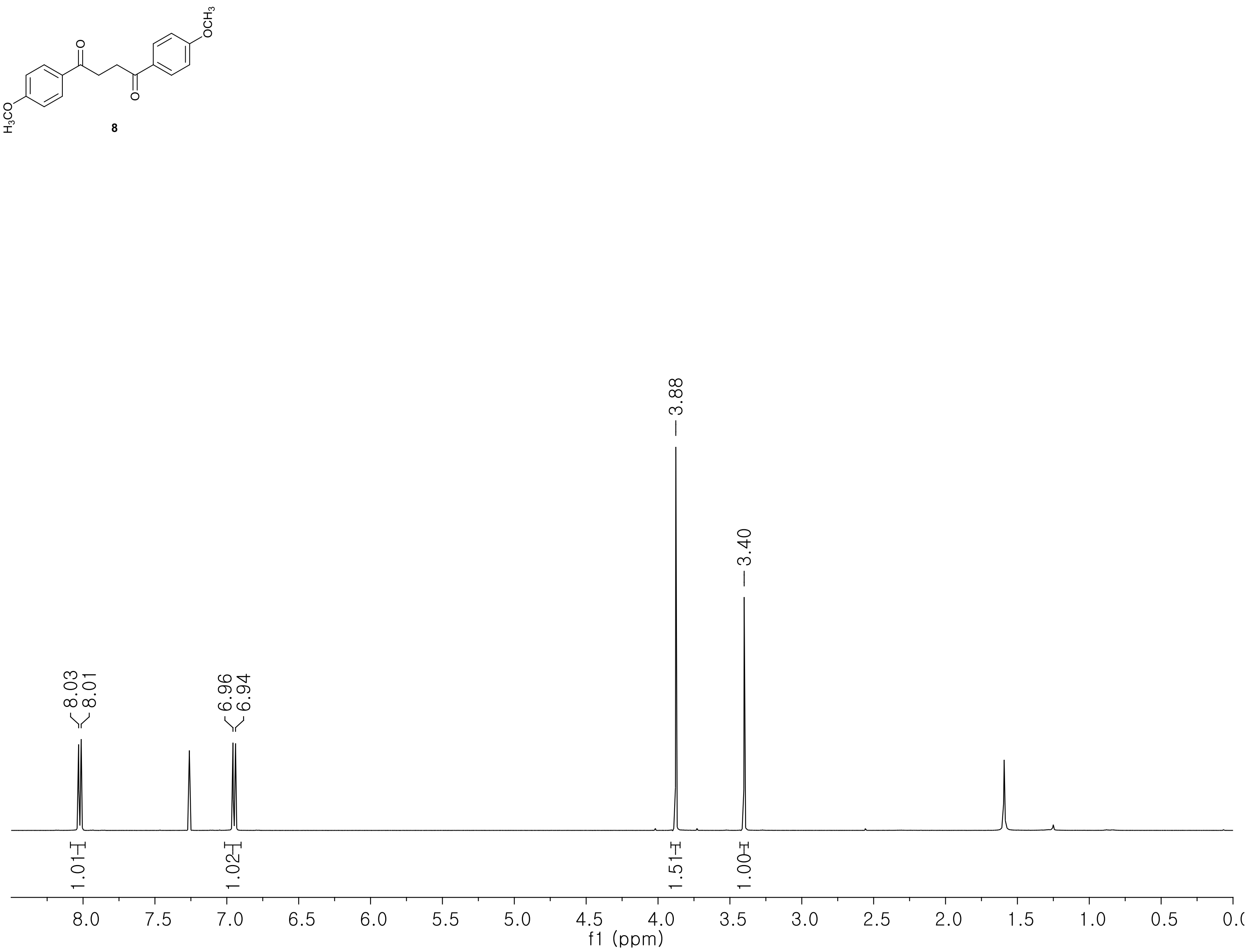


Figure S15. $^1$H NMR Spectrum (500 MHz, $CDCl_3$) of 1,4-bis(4-methoxyphenyl)butane-1,4-dione (**8**)

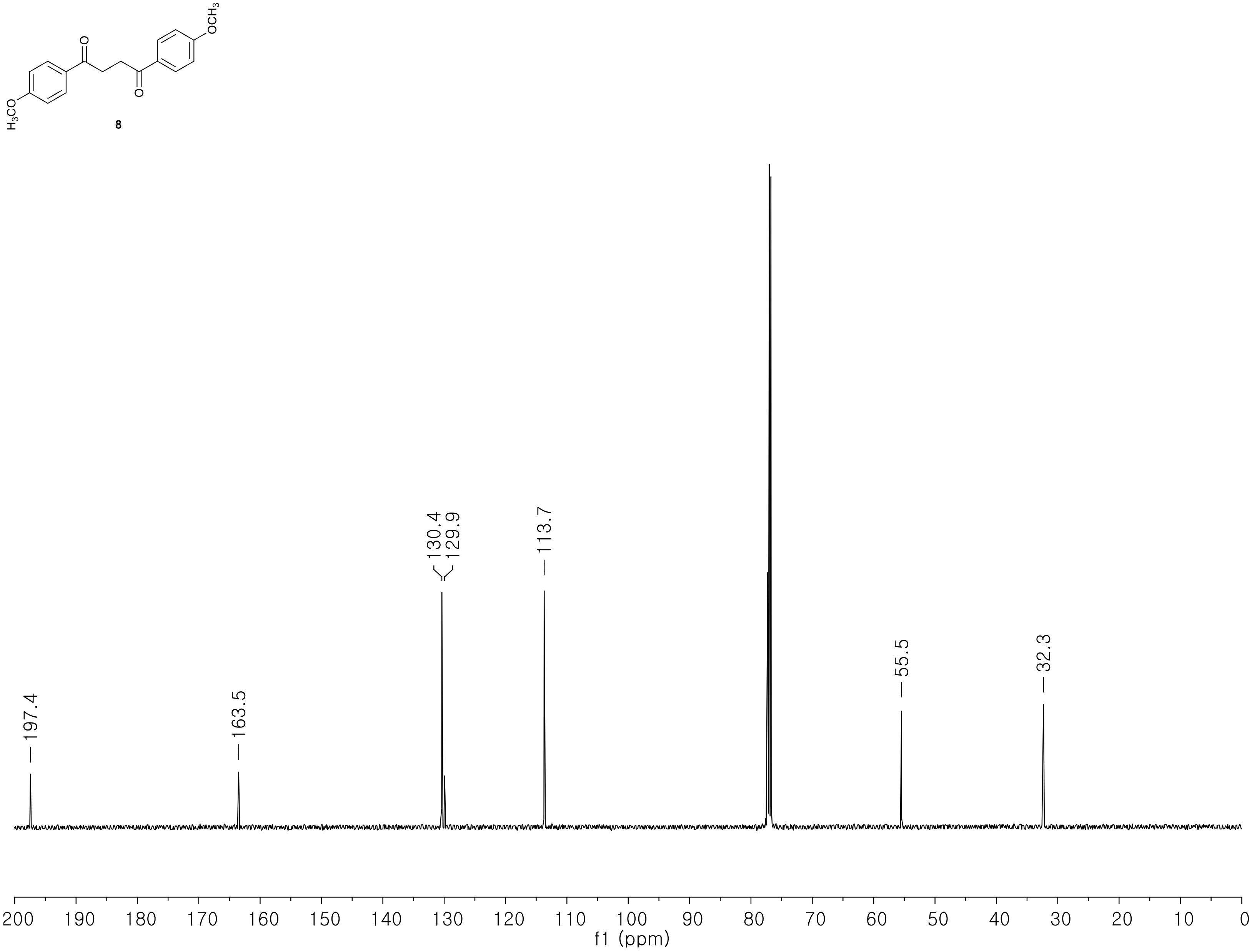


Figure S16. $^{13}$C NMR Spectrum (125 MHz, CDCl$_3$) of 1,4-bis(4-methoxyphenyl)butane-1,4-dione (**8**)

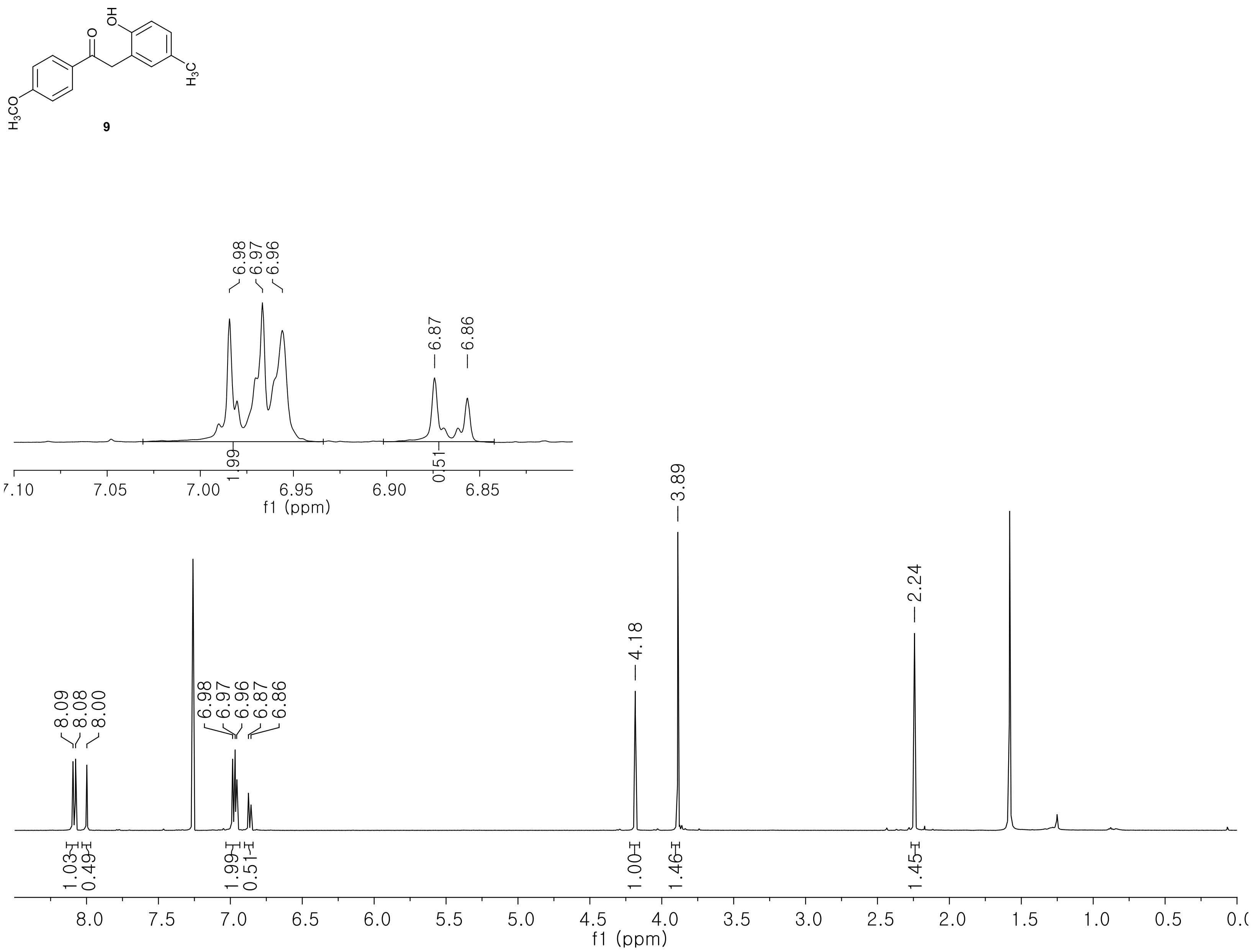


Figure S17. $^{1}$H NMR Spectrum (500 MHz, $CDCl_3$) of 2-(2-hydroxy-5-methylphenyl)-1-(4-methoxyphenyl)ethanone (**9**)

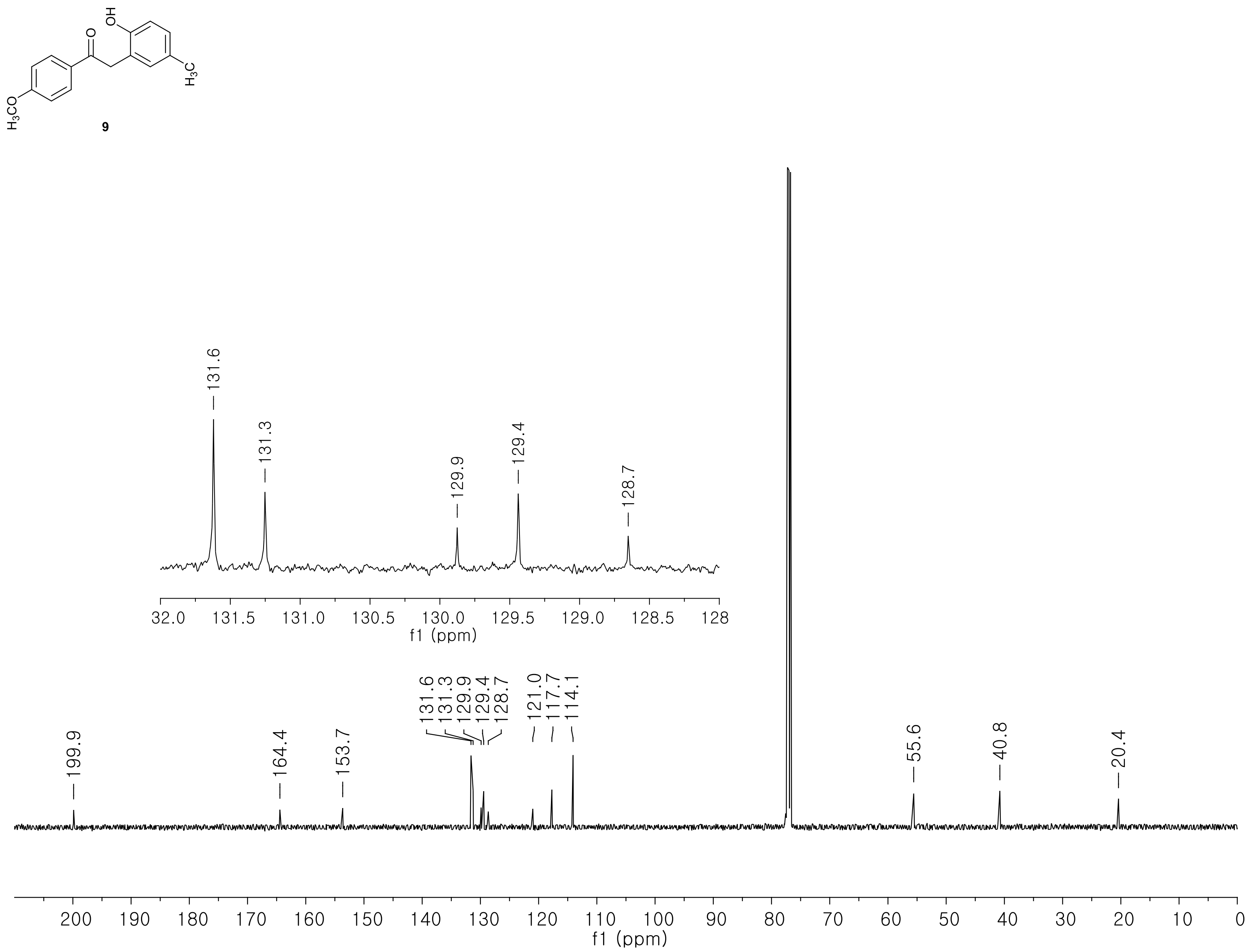


Figure S18. $^{13}$C NMR Spectrum (125 MHz, CDCl$_3$) of 2-(2-hydroxy-5-methylphenyl)-1-(4-methoxyphenyl)ethanone (**9**)

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