Photochemical upcycling of polystyrene waste by $BiCl_3$

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Supporting information

Contents

I. General information

All the chemicals were purchased either from Sigma Aldrich, TCI chemicals, BLD Pharma, Avra chemicals, Alfa Aesar, ChemScene and used without further purification unless mentioned. Reagent-grade solvents were purchased from SD Fine Chemicals (India) and used as received. $CDCl_3$ and DMSO-d_6 were purchased from either Cambridge Isotope Laboratories or Sigma Aldrich and used as received. Styrene was filtered through a plug of alumina to remove any stabilizers prior to use. All NMR spectra ^1H (400 MHz / 500 MHz), $^{13}C\{^1H\}$ (100 MHz / 125MHz) were recorded by a Bruker Avance 400 MHz NMR/ 500 MHz spectrometer at an ambient temperature. ^1H NMR chemical shifts are reported relative to TMS and are referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm, DMSO- d^6: 2.5 ppm), whereas ^{13}C NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm, DMSO-d^6: 39.5 ppm). ^1H NMR yield was calculated using mesitylene as an internal standard. Abbreviations used for signal multiplicity: ^1H-NMR: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, and m = multiplet.

GC-MS data was acquired using the GCMS-QP2010 SE SHIMADZU system.

FTIR and UV data were acquired using PerkinElmer Spectrum One instrument and Shimadzu UV-3600 spectrometer respectively.

EPR data was acquired using JES-X320 EPR Spectrometer with X band and Q band.

GPC data was acquired using Malvern instrument calibrated with narrow-distribution polystyrene standards and THF as the mobile phase at 30 °C.

TEM measurements were performed on a JEOL JEM-2100F field emission transmission electron microscope operating at 200 kV. The TEM samples were prepared on carbon-coated copper grids by drop-casting 1– 2 µL of the diluted sample.

XPS data were obtained using a Thermo Fischer Scientific K-alpha instrument with Al Kα as X-ray source.

Dynamic light Scattering (DLS) analysis was performed using the HORIBA scientific SZ-100 instrument.

CHNS(O) analysis was done using Elementar Unicube analyser.

Commercially available, pre-coated TLC-sheets ALUGRAM® Xtra Sil G/UV254 were purchased from MACHEREY-NAGEL GmbH & Co. KG. Column chromatography was performed using silica gel (100-200 mesh).

II. Safety Precaution

The user must wear personal protective equipment (lab coat, safety glasses, and gloves) while dealing with O_2 gas. Benzene is a highly volatile and flammable solvent, and inhalation must be prevented. Exposure to benzene without adequate safety measures can lead to various health effects and diseases, including cancer.[1]

III. Photochemical reaction setup

Figure S1: Kessil lamp used for the reaction

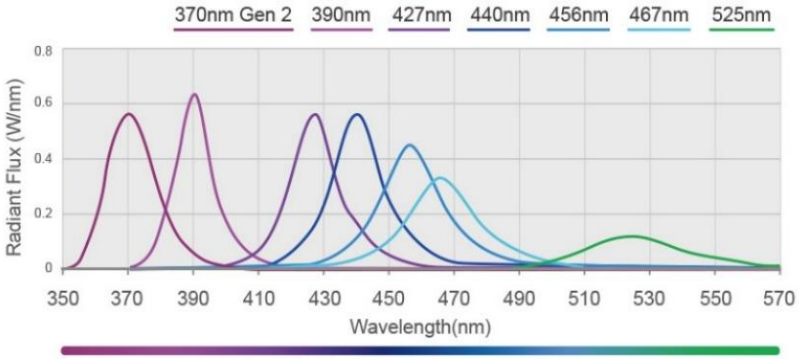


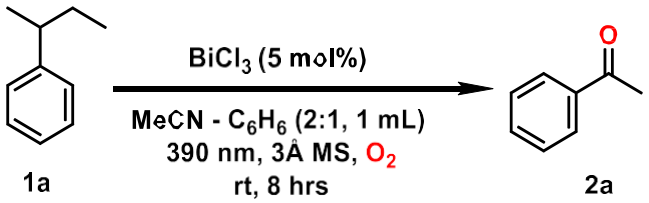
Figure S2: Emission spectrum of the Kessil® PR160L-390 nm lamp (Source: Kessil)

Figure S3 : Photo of the reaction setup employed

Kessil lamps PR160L were used as the irradiation source. For all experiments, the intensity of the Kessil lamps was controlled at the maximum level, with a power consumption of 390 nm (max 52W). The average intensity is 399 mW/cm². The photon flux for the lamp was calculated using actinometry measurements with potassium ferrioxalate.

IV. General procedure for alkylarene oxidation

Scheme S1. Experimental procedure for alkylarene oxygenation



NMR Scale reactions

In a Teflon tube equipped with a magnetic stir bar, $BiCl_3$ (3.2 mg, 0.01 mmol, 5 mol%) and the alkylarene (0.2 mmol) were added along with the solvent MeCN/C_6H_6 (2:1, 1 mL). The reaction mixture was purged with O_2 for 1 minute and the tube equipped with the oxygen balloon was placed in the reactor and irradiated with blue LED (390 nm, 40 W) for 8 hours. The solvent was evaporated under reduced pressure and ^1H NMR checked using mesitylene as the internal standard.

For product isolation

In a Teflon tube equipped with a magnetic stir bar, $BiCl_3$ (7.9 mg, 0.025 mmol, 5 mol%) and the alkylarene (0.5 mmol) were added along with the solvent MeCN/C_6H_6 (2:1, 2.5 mL). The reaction mixture was purged with O_2 for 1 minute and the tube equipped with the oxygen balloon was placed in the reactor and irradiated with blue LED (390 nm, 40 W) for 8 hours. The solvent was evaporated under reduced pressure, and the residue was either purified by column chromatography (ethyl acetate/hexane mixture) or isolated by acid-base extraction to give the pure product.

V. Optimization of reaction conditions for small molecules

Table S1. Solvent screening

S. No	Solvent	Yield[a]
1	MeCN	40%
2	Acetone	50%
3	THF	0
4	MeOH	0
5	DCM	32%
7	HFIP	0
8	EtOAc	32%
8	Benzene	0
9	MeCN-C_6H_6 (1:1)	62%
10	MeCN-C_6H_6 (2:1)	63%
11	Acetone-C_6H_6 (1:1)	54%

Table S2. Catalyst mol% screening

S. No	Catalyst mol%	Yield[a]
1	5	63%
2	10	63%

Table S3. Light source screening

S. No	Light source (nm)	Yield[a]
1	365	60%
2	370	65%
3	390	63%
4	427	36%

Table S4. Solvent volume screening

S. No	Solvent volume (mL)	Yield[a]
1	1	63%
2	2	62%

Table S5. Effect of chloride additives

S. No	Equiv of TBACl added	Yield[a]
1	1	65%
2	2	63%
3	3	66%

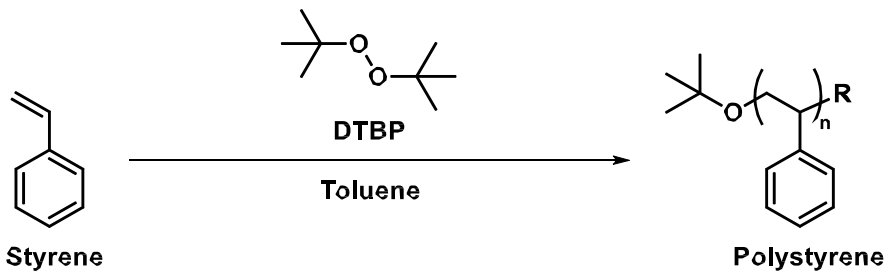
Table S6. Control experiments

S. No	Conditions	Yield[a]
1	Without light	0
2	Without oxygen	0
3	Without $BiCl_3$	0
4	Without chloride additive	63%
5	Without 3Å MS	43%

(a - These values are the average of two trials with an error bar of 5%)

VI. General procedure for polystyrene synthesis

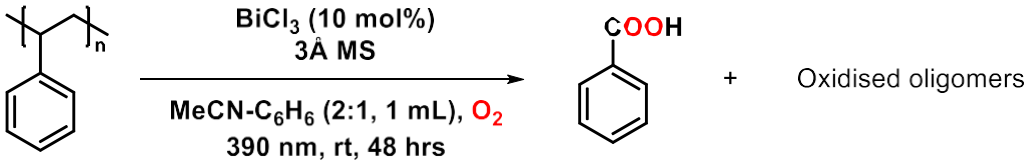
Scheme S2. Experimental procedure for polystyrene preparation



The polystyrene was prepared following a previous literature report.[2] The styrene was first purified by passing through an alumina column. 10 mL toluene and 0.1 equiv Di-tert-butyl peroxide (DTBP) were then added to the round-bottom flask and fitted with a reflux condenser. It was then refluxed for about 4 hours and then allowed to cool to room temperature. The solution was slowly dripped into methanol (15 times more than the amount of toluene taken for the reaction) with vigorous stirring. Precipitated polystyrene was collected and dried under vacuum.

VII. General procedure for polystyrene degradation

Scheme S3. Experimental procedure for polystyrene degradation



NMR Scale reactions

In a Teflon tube equipped with a magnetic stir bar, $BiCl_3$ (6.3 mg, 0.02 mmol, 10 mol%) and the PS (0.2 mmol, based on the repeat unit) were added along with the solvent MeCN/C_6H_6 (2:1, 1 mL). The reaction mixture was purged with O_2 for 1 minute and the tube equipped with the oxygen balloon was placed in the reactor and irradiated with blue LED (390 nm, 40 W) for 48 hours. The solvent was evaporated under reduced pressure and ^1H NMR checked using mesitylene as the internal standard.

For product isolation

In a Teflon tube equipped with a magnetic stir bar, $BiCl_3$ (15.8 mg, 0.05 mmol, 10 mol%) and the PS (0.5 mmol) were added along with the solvent MeCN/C_6H_6 (2:1, 2.5 mL). The reaction mixture was purged with O_2 for 1 minute and the tube equipped with the oxygen balloon was placed in the reactor and irradiated with blue LED (390 nm, 40 W) for 48 hours. The solvent was evaporated under reduced pressure, and the residue was isolated by acid-base extraction to give the pure product.

Table S7. Optimization table for polystyrene degradation

S. No	Condition	Yield[a]
1	5 mol% catalyst and 24 hours	27%
2	5 mol% catalyst and 48 hours	33%
3	5 mol% catalyst and 72 hours	34%
4	10 mol% catalyst and 24 hours	30%
5	10 mol% catalyst and 48 hours	50%

6	10 mol% catalyst and 72 hours	48%
7	50 mol% catalyst and 48 hours	50%

(a - These values are the average of two trials with an error bar of 5%)

VIII. General procedure for polystyrene degradation from a mixture of plastic waste

In a Teflon tube equipped with a magnetic stir bar, $BiCl_3$ (6.3 mg, 0.02 mmol, 10 mol%) and the following plastic waste were added along with the solvent MeCN/C_6H_6 (2:1, 1 mL) – Polypropylene (PP - 20 mg), Polyethylene terephthalate (PET - 20 mg), Low density polyethylene (LDPE - 20 mg) and polystyrene (PS - 20.8 mg). The reaction mixture was purged with O_2 for 1 minute, and the tube equipped with the oxygen balloon was placed in the reactor and irradiated with blue LED (390 nm, 40 W) for 48 hours. The solvent was evaporated under reduced pressure and ^{1}H NMR checked using mesitylene as the internal standard.

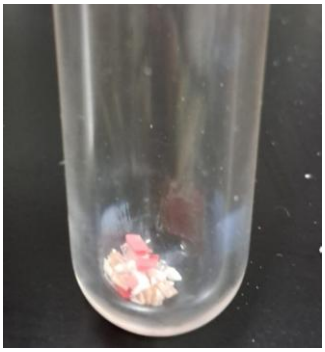
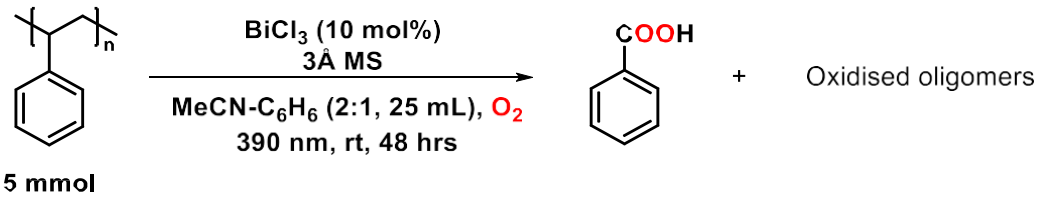


Figure S4: Degradation of PS from a mixture of plastic waste

IX. General procedure for Large-scale polystyrene degradation using PS

Scheme S4. Experimental procedure for large-scale polystyrene degradation

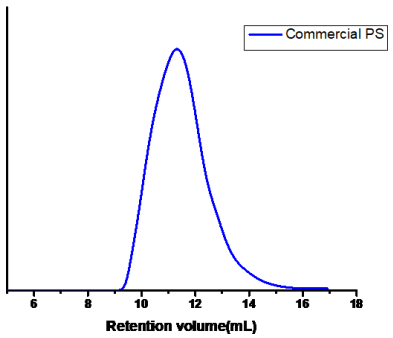


In a Schlenk tube equipped with a magnetic stir bar, $BiCl_3$ (157.7 mg, 0.5 mmol, 10 mol%) and the PS pellet (5 mmol) were added along with the solvent MeCN/C_6H_6 (2:1, 25 mL). The reaction mixture was purged with O_2 for 1 minute and the tube equipped with the oxygen balloon was placed in the reactor and irradiated with blue LED (390 nm, 40 W) for 48 hours. The solvent was evaporated under reduced pressure, and the residue was isolated by acid-base extraction to give the pure product.

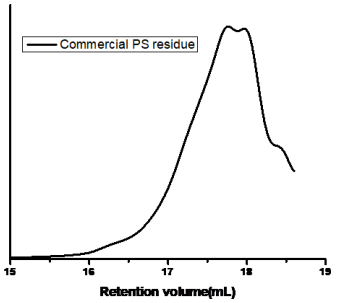
X. GPC analysis of synthesized PS and commercial pellets

The molecular weight characteristics of the polystyrene (PS) samples were analyzed using Gel Permeation Chromatography (GPC) calibrated with narrow-distribution polystyrene standards and THF as the mobile phase at 30 °C.

1) Commercial pellet

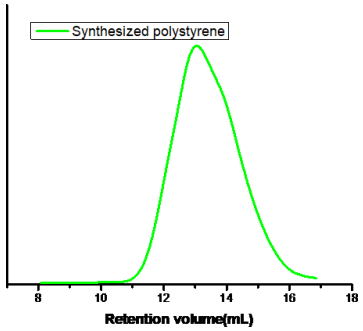


A1-Commercial Polystyrene(PS)	
Mn(g/mol)	1,00,723
Mw(g/mol)	2,14,707
Mw/Mn(g/mol)	2.132
M-H a	0.696

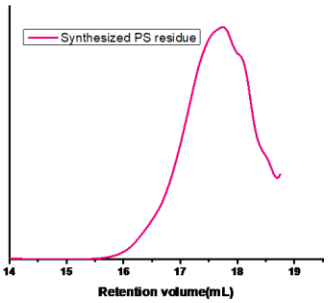


A2-Commercial PS residue	
Mn(g/mol)	10,384
Mw(g/mol)	15,209
Mw/Mn(g/mol)	1.465
M-H a	0.094

2) Synthesised PS



B1-Synthesized Polystyrene	
Mn(g/mol)	18,532
Mw(g/mol)	32,628
Mw/Mn(g/mol)	1.761
M-H a	0.642



B2- Synthesized PS residue	
Mn(g/mol)	14,477
Mw(g/mol)	19,632
Mw/Mn(g/mol)	1.356
M-H a	0.173

XI. CHNS(O) analysis of the post-reaction mixture after PS degradation

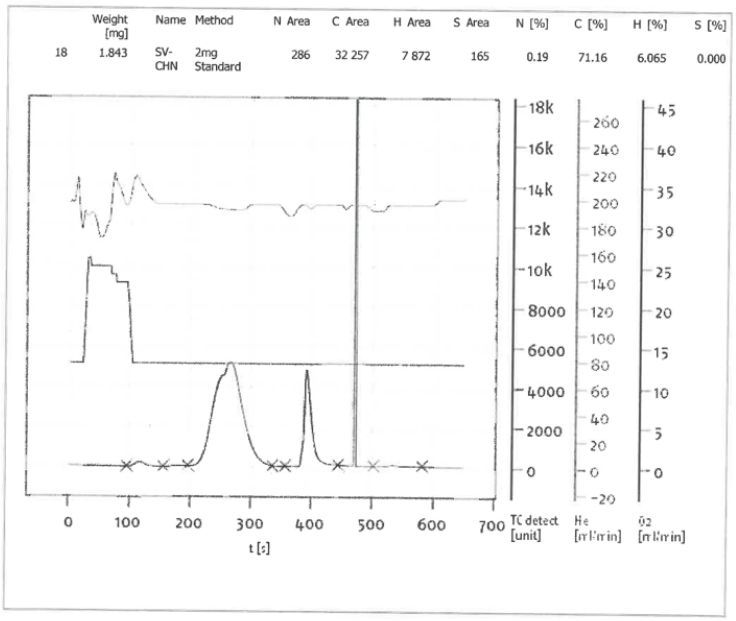
CHNS/OXYGEN REPORT

Samples

	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]
18	1.843	SV-CHN	2mg Standard	286	32 257	7 872	165	0.19	71.16	6.065	0.000

CHNS/OXYGEN REPORT

	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]
18	1.843	SV-CHN	2mg Standard	286	32 257	7 872	165	0.19	71.16	6.065	0.000



Parameters

Temperatures

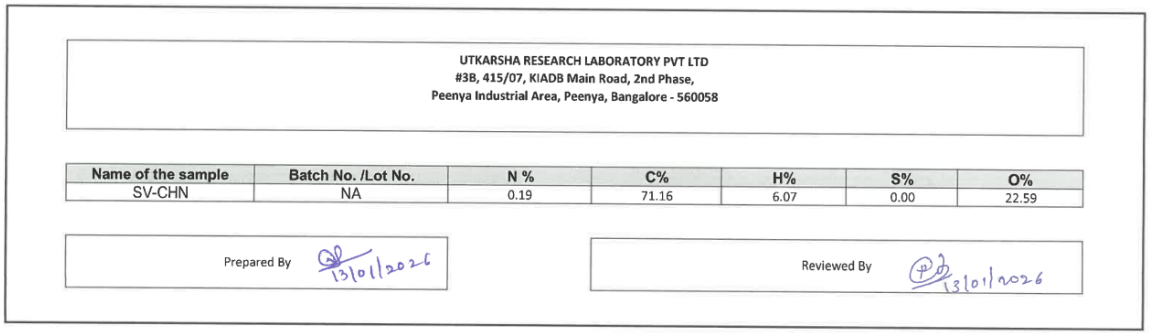
Comb. tube	0
Reduct. tube	0
Ads.col.standby	60
Ads.col.cooltemp.	90

Time values

Flush time	45
O2 delay	20
Integrator reset delay peak N	10
Integrator reset delay peak C	1
Integrator reset delay peak H	1
Integrator reset delay peak S	2

Methods

Name	O2 dosing time	Autozero delay N	Autozero delay C	Autozero delay S	Peak anticipation N	Peak anticipation C	Peak anticipation H	Peak anticipation S	Desorpt.CO2	Desorpt.H2O	Desorpt.SO2
2mg Standard	70	10	2	10	50	120	100	100	60	140	210



UTKARSHA RESEARCH LABORATORY PVT LTD
#3B, 415/07, KIADB Main Road, 2nd Phase,
Peenya Industrial Area, Peenya, Bangalore - 560058

Name of the sample	Batch No. /Lot No.	N %	C%	H%	S%	O%
SV-CHN	NA	0.19	71.16	6.07	0.00	22.59

Prepared By 13/01/2026

Reviewed By 13/01/2026

We performed CHNS(O) analysis on the solid residue to determine the carbon balance of the solid phase. The analysis yielded the following values: %C – 71.16, %H – 6.07 and %O – 22.59.

Theoretically, if only benzoic acid were formed, then the expected carbon percentage would be 68.8%. From the analysis of the post-reaction mixture, we obtained 71.16% carbon content, which is higher than pure benzoic acid but lower than the expected carbon content of the starting polystyrene (92%). This slightly higher value than pure benzoic acid suggests that the oxidation is not complete, and it is a mixture of benzoic acid and partially oxidised oligomers. Since the presence of inorganic carbon is unlikely in our system, CHNS(O) analysis, which provides an estimate of total carbon content, can be considered equivalent to the total organic carbon content.

Theoretically, the carbon balance for complete oxidation of PS to benzoic acid cannot be 100%, as the conversion of PS (C_8) to benzoic acid (C_7) requires a loss of one carbon per monomer unit.

Therefore, maximum carbon recovery possible =Carbon in product/Carbon in reactant
= 7/8 = 87.5%

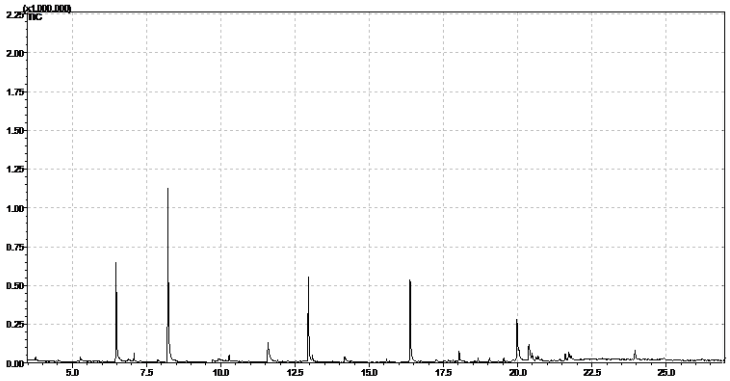
Calculation of the carbon balance for our reaction

The reaction was performed on a 0.2 mmol scale with 20.83 mg of PS. After the reaction, 17.4 mg of residue was obtained, from which a CHNS(O) analysis was performed.

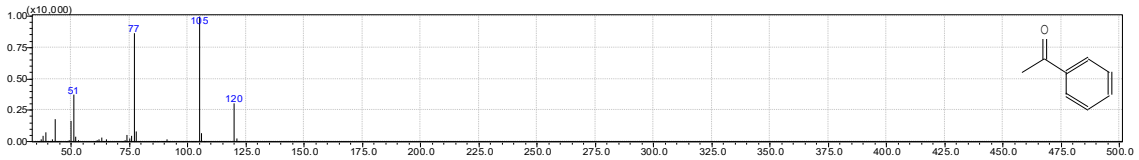
Amount of PS taken = 20.83 mg
%C in PS = 92.25%
Amount of C in 20.83 mg PS = 20.83 x (0.9225)
= 19.22 mg
Amount of residue obtained after the reaction = 17.4 mg
%C in residue as detected by CHNS(O) analysis = 71.16%
Amount of C in residue = 17.4 x (0.7116)
= 12.38 mg
Carbon recovery = C in residue/C in PS
Carbon recovery = 64.4%

The 23% difference between the theoretical maximum (87.5%) and our value (64.4%) is attributed to the loss of volatile organic compounds, such as acetophenone (detected in crude GC), during the drying process.

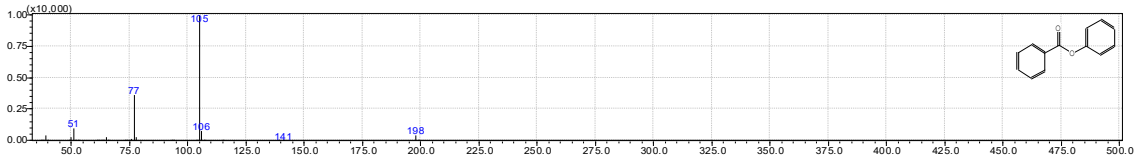
Analysis of the crude organic layer before solvent evaporation



Retention time – 8.283 min

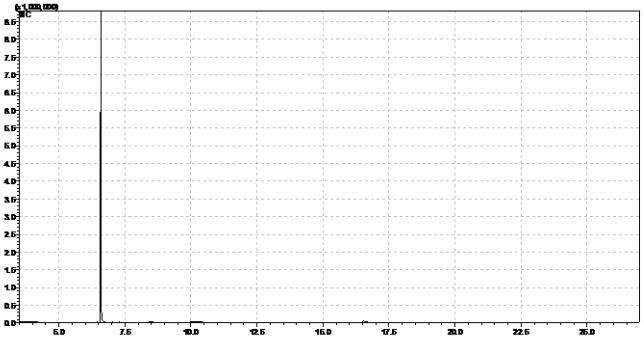


Retention time – 16.456 min



GC-MS of the crude organic layer

After evaporating the solvent and adding mesitylene as the internal standard, the GC-MS analysis revealed no small molecules and only a peak corresponding to mesitylene was seen.



GC-MS of the mixture after solvent evaporation

Therefore, the unaccounted carbon is attributed to the loss of volatile organic compounds and the expected C_1 loss during the degradation of PS to benzoic acid.

XII. Evaluation of catalyst stability

1) Transmission electron microscopy (TEM) analysis

The reaction was carried out under standard reaction conditions, using 0.2 mmol of

alkylarene and 5 mol% of catalyst in a 2:1 mixture of MeCN and C_6H_6. After the completion of the reaction, the solvent was evaporated under reduced pressure and the mixture was completely dried. The solution was then diluted with acetonitrile, and the resulting mixture was drop-cast onto a carbon-coated copper grid (200 nm mesh size). After completely drying the sample (at least 24 h at rt), it was analyzed by JEOL JEM-2100F field emission transmission electron microscope operating at 200 kV.

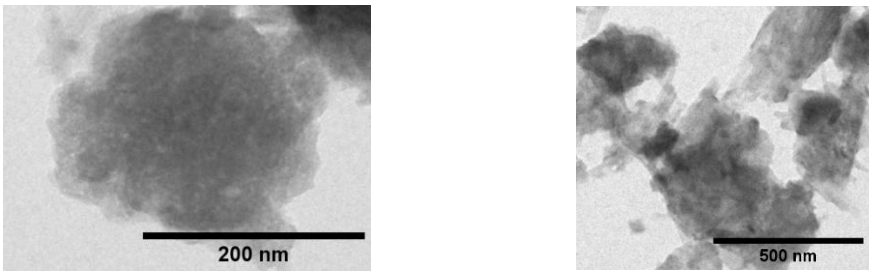


Figure S5: TEM images of the post-reaction mixture

2) X-ray photoelectron spectroscopy (XPS) analysis

The reaction was carried out under standard reaction conditions, using 0.2 mmol of alkylarene and 5 mol% of catalyst in a 2:1 mixture of MeCN and C_6H_6. After the completion of the reaction, the solvent was evaporated under reduced pressure and the mixture was dried. It was then diluted with acetonitrile and made into a solution. A 5 × 5 mm glass slide was cut and ultrasonicated in IPA solvent. After the glass slide was completely dried, the post-reaction mixture was drop-cast (2-3 drops) onto the glass slide and left to dry in the desiccator. It was then analysed using a Thermo Fisher Scientific K-alpha instrument with an Al Kα X-ray source.

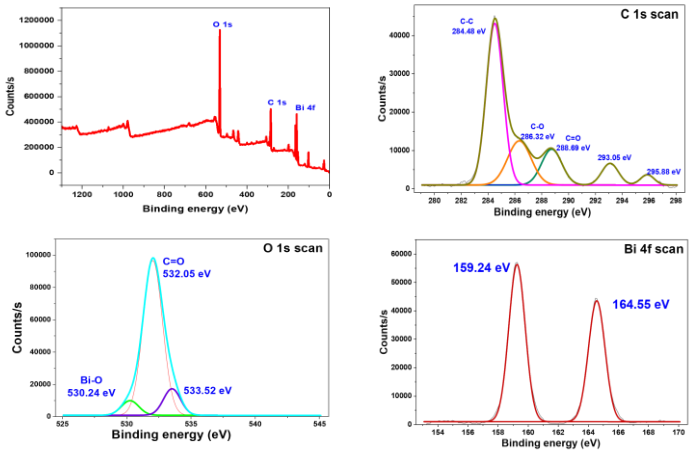


Figure S6: XPS spectra of the post-reaction mixture – Overall spectra, C 1s scan, O 1s scan and Bi 4f scan

3) Dynamic light scattering (DLS) analysis

The reaction was carried out under standard reaction conditions, using 0.2 mmol of alkylarene and 5 mol% of catalyst in a 2:1 mixture of MeCN and C_6H_6. After the

completion of the reaction, the solvent was evaporated under reduced pressure and the mixture was dried. Then it was diluted to 0.2 wt% in MeCN, and 1 mL of this solution was analysed.

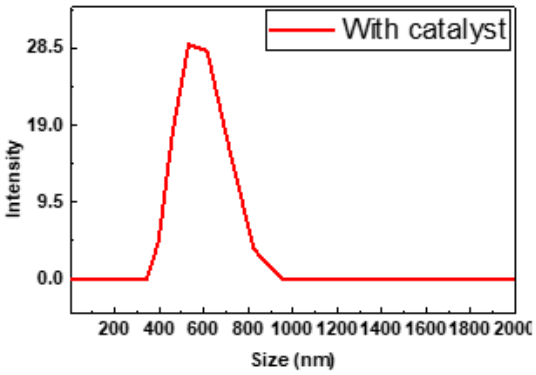


Figure S7: DLS analysis of the post-reaction mixture

4) Filtration test

In a Teflon tube, 0.4 mmol of alkylarene and 10 mol% catalyst were taken along with 2 mL of MeCN-C_6H_6 (2:1). The mixture was irradiated for 90 minutes, and a small aliquot was taken for GC-MS analysis. Then, 1 mL of the reaction mixture was passed through a 0.1 µm syringe filter and transferred to another Teflon tube (both tubes now have approximately a reaction scale of 0.2 mmol). Both the Teflon tubes were then irradiated and analysed every 30 minutes by GC-MS to check for conversion.

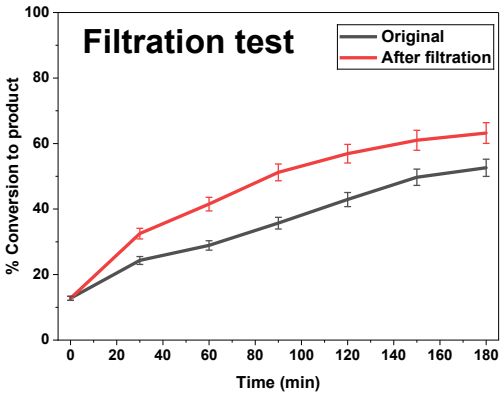


Figure S8: Filtration test for assessing the homogeneity of the catalyst

5) Recyclability test

In a Teflon tube, 0.2 mmol of alkylarene and 5 mol% catalyst were taken along with 1 mL of MeCN-C_6H_6 (2:1). The mixture was irradiated for 8 hours, and a small aliquot was taken for GC-MS analysis. Then, a fresh batch of reactant was added to the same reaction vessel without recovering the catalyst, and the reaction was carried out for an additional 8 hours. After this, a small aliquot was analysed by GC-MS.

Four cycles of this type of in-situ recyclability were done.

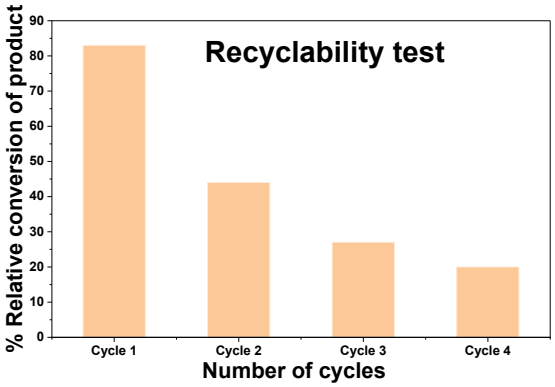


Figure S9: Recyclability test for checking the stability of the catalyst

6) ICP-OES analysis

In a Teflon tube, 0.2 mmol of alkylarene, along with 5 mol% catalyst, was taken along with 1 mL of MeCN-C_6H_6 (2:1) and irradiated for 8 hours. After the reaction completion, the solvent was evaporated, and the mixture was completely dried. The weight of the crude mixture was recorded. Then the mixture was digested using 1:1 mixture of concentrated HCl and HNO_3 (total 10 mL) and heated at 60 °C for 24 hours. Then 550 µL of this stock was taken and diluted to 4 mL by using 2 wt% HNO_3 and analysed.

```
==========================================================================================
Batch ID: 27122025
Sequence No.: 5                                  Autosampler Location:
Sample ID: SV-IPC-3                              Date Collected: 27-12-2025 10:42:41
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time (before sample):

------------------------------------------------------------------------------------------
Replicate Data: SV-IPC-3
                          Net       Corrected            Calib.              Sample  Analysis
Repl# Analyte          Intensity   Intensity       Conc. Units          Conc. Units     Time
  1   Bi 223.061        327723.9    329823.1       26.80 mg/L           26.80 mg/L    10:43:27

------------------------------------------------------------------------------------------
Mean Data: SV-IPC-3
                 Mean Corrected          Calib.                      Sample
Analyte             Intensity      Conc. Units      Std.Dev.      Conc. Units      Std.Dev.   RSD
Bi 223.061          329823.1       26.80 mg/L                     26.80 mg/L
```

Calculation of Bi content in the reaction mixture

Amount of crude product = 10.9 mg
Volume to which dilution was done for digestion = 10 mL = 0.010 L
For ICP-OES analysis, 550 µL of the stock solution was taken and diluted with 2 wt% HNO_3 to give a final volume of 4 mL.
$V_{(aliquot)}$ = 0.55 mL
$V_{(final)}$ = 4 mL
Dilution factor = 4/(0.55) = 7.27

From ICP-OES Data

$C_{(measured)}$ = 26.80 mg/L

Accounting for the correction due to dilution

$C_{(stock)}$ = 26.80 x 7.27 = 194.84 mg/L

So, the mass of Bi in the stock digest

$m(Bi) = C_{(stock)} \times V_{(stock)}$ = 194.84 mg/L x 0.010 L = 1.95 mg

weight percent of Bi = 1.95/10.9 = 17.88%

Amount of Bi recovered along with product = 194.8 ppm

Amount of Bi in initially added catalyst = (208.98/315.34) x (3.2)
= 2.12 mg

Recovery = 1.95/2.12 = 91.9%

XIII. Calculation of E-metrics

$$\text{E factor} = \frac{\text{Mass of waste (kg)}}{\text{Mass of product (kg)}}$$

Mass of waste = Mass of total input materials – Mass of product

Mass of input materials

1) 0.2 mmol PS = 20.83 mg
2) $BiCl_3$ (5 mol%) = 3.2 mg
3) 3 A Molecular sieves = 75 mg
4) MeCN (0.67 mL) = 0.67 mL x 0.786 g/mL = 526.62 mg
5) C_6H_6 (0.33 mL) = 0.33 mL x 0.874 g/mL = 288.42 mg

Total mass of input = 914.07 mg

Mass of benzoic acid (product) = 0.5 x 0.2 mmol
= 0.01 mmol
= 12.21 mg

Mass of waste = 914.07 – 12.21 = 901.86

E factor = 73.86

Comparison of E-metrics with previous literature reports based on Fe and Cu

SNo	Work	Total mass of input (without purification) (mg)	Yield of product (%)	Mass of product (mg)	E-factor
1	Our work (0.2 mmol scale)	20.83 (PS) + 3.2 ($BiCl_3$) + 75 (MS) + 815.04 (total solvent)	50	12.21	73.86
2	Chem. Sci., 2025, 16, 2004 (0.1 mmol scale reaction)	10.415 (PS) + 0.672 ($CuCl_2$) + 2.22 ($CaCl_2$) + 262.2 (C_6H_6) + 1021.8 (Total MeCN) + 4.83 ($Cu(NO_3)_2.3H_2O$)	65	7.94	163.04
3	Chin. J. Chem. 2021, 39, 3225—3230 (0.4 mmol scale reaction)	41.66 (PS) + 6.49 ($FeCl_3$) + 11.12 (TBACl) + 11.95 (Cl_3CCH_2OH) + 3160 (acetone)	67	32.73	97.73

4	ChemSusChem 2021, 14, 5049 – 5056 (0.5 mmol scale reaction)	52.075(PS) + 1.2675($FeCl_2$) + 1590(DCM) + 628.8 (MeCN)	65	39.689	56.248
5	J. Am. Chem. Soc. 2022, 144, 5745−5749 (0.19 mmol scale reaction)	20 (PS) + 2 ($FeCl_3$) + 197.5 (acetone)	14 mol% (23 mol% total products)	3.28	65.92

XIV. Calculation of apparent quantum yield and energetics

Chemical actinometry [3,4]

a) Measurement of photon flux

Solution A – Potassium ferrioxalate hydrate (737 mg, 1.50 mmol) was dissolved in aq. H_2SO_4 (0.05 M, 10 mL) to afford a 0.15 M ferrioxalate solution.

Solution B - 1,10-Phenanthroline monohydrate (25 mg, 0.13 mmol), NaOAc (5.63 g, 68.63 mmol) were dissolved in aq. H_2SO_4 (0.5 M, 25 mL).

Both solutions were stored in the dark. The photon flux of the 390 nm LED was determined first. For this, 1 mL of solution A was added to 4 glass vials. Two of the vials were stored in dark conditions, and two were irradiated using a 390 nm LED for 60 seconds. Then 315 µL of solution B was added to all four vials, and they were left to stir in the dark for 60 minutes to facilitate the coordination of Fe(II) by phenanthroline. The absorbance at 510 nm was then measured for all four solutions. The difference in absorbance ($\Delta A_{510\ nm}$) between the average absorbance of the irradiated and non-irradiated samples at 510 nm was then determined.

The amount of Fe(II) was calculated according to Beer-Lambert's law

$$n(Fe^{II}) = \frac{V \times \Delta A_{510\ nm}}{l \times \varepsilon}$$

V (total volume of solution) = 1.315 mL (0.001315 L), l (path length of the cuvette) = 1.0 cm, and ε (molar extinction coefficient of the ferrioxalate actinometer at λ = 510 nm) = 11100 $L \cdot mol^{-1} \cdot cm^{-1}$.

$$n(Fe^{II}) = \frac{0.001315\ L \times 2.806}{1\ cm \times 11100\ L \cdot mol^{-1} \cdot cm^{-1}}$$

$$= 3 \times 10^{-7}\ mol$$

Photon flux was determined by the following equation

$$Photon\ Flux(\phi_q) = \frac{nFe(II)}{\Phi_F \times t \times f}$$

Where Φ_F corresponds to the quantum yield of the ferrioxalate actinometer (1.13 at 390 nm) [5,6], t is the irradiation time for solution A (60 s), and f is the fraction of light absorbed by the actinometer at λ = 390 nm. The value of f is calculated using the following equation,

$$f = 1 - 10^{-A}$$

where A is the absorption of the ferrioxalate solution at 390 nm. When absorbance is greater than 2, f ≈1.

By employing the formula, the photon flux was determined to be 0.0442 x 10^{-7} mol s^{-1}

Determining the quantum yield for the reaction in the case of the model substrate

In a Teflon tube equipped with a magnetic stir bar, $BiCl_3$ (3.2 mg, 0.01 mmol, 5 mol%) and the alkylarene (0.2 mmol) were added along with the solvent MeCN/C_6H_6 (2:1, 1 mL). The reaction mixture was purged with O_2 for 1 minute, and the tube equipped with the oxygen balloon was placed in the reactor and irradiated with blue LED (390 nm, 40 W) for 2 hours. The solvent was evaporated under reduced pressure, and ^1H NMR was checked using mesitylene as the internal standard. The yield of acetophenone was 24.7% (0.0494 mmol).

The quantum yield (Φ) was calculated as follows:

$$\text{Quantum yield}(\Phi) = \frac{n(\text{product})}{\Phi_q \times t \times f_r}$$

where the photon flux (Φ_q) is 0.0442 x 10^{-7} mol s^{-1}, t is the reaction time (2 hours = 7200 s), and f_r is the fraction of light absorbed by the reaction mixture ($f_r = 1 - 10^{-A} = 1 - 10^{-0.253} = 0.4415$).

The quantum yield has been calculated to be 3.51, indicating a radical chain propagation mechanism.

Energy usage in the case of polystyrene degradation

E_{input} = Power x Irradiation time = 40 W x 48 h = 1920 Wh = 1.92 kWh

Energy consumed per gram of BA formed = $E_{(input)}$ / Mass of BA (in g)

We obtained 50% benzoic acid = 0.5 x 24.424 = 12.212 mg

Energy consumed per gram of benzoic acid formed = 1.92 kWh / 0.0122212 g

= 157.22 kWh g^{-1}

While this energy is high compared to industrial standards, a direct comparison with previous reports based on the energy consumed per gram of product formed may not be accurate, as the literature reports differ in the scale of the reaction. For example, a 0.2 mmol scale and a 1 mmol scale may both utilise the same 40 W, but the values will be highly inflated for the 0.2 mmol scale due to the lower value of the denominator (mass of product) while calculating energy consumed per gram of product formed.

Therefore, this cannot be a limitation of the chemical efficiency, but rather a geometrical constraint, where a broad beam of light irradiating a smaller vessel results in a loss of energy to the surroundings. When the same process is performed on an industrial scale or in a flow reactor, the value is expected to decrease.
However, compared to thermal methods, our reaction operates under ambient conditions, as pyrolysis requires a high temperature of around 300–450 °C, which typically consumes more than 1000 W, resulting in a very high energy cost. Furthermore, the calculated AQY of 3.51 indicates an effective radical chain mechanism, highlighting that the inflation is not due to chemical inefficiency.

XV. Mechanistic investigation

(a) Radical trapping experiments

In a Teflon tube equipped with a magnetic stir bar, $BiCl_3$ (3.2 mg, 0.01 mmol, 5 mol%), trapping agent (2 equiv) and the alkylarene (0.2 mmol) were added along with the solvent $MeCN/C_6H_6$ (2:1, 1 mL). The reaction mixture was purged with O_2 for 1 minute, and the tube equipped with the oxygen balloon was placed in the reactor and irradiated with blue LED (390 nm, 40W) for 8 hours. The solvent was evaporated under reduced pressure, and GC-MS and ^1H NMR were obtained using mesitylene as the internal standard wherever applicable.

Scheme S5. Radical trapping experiments

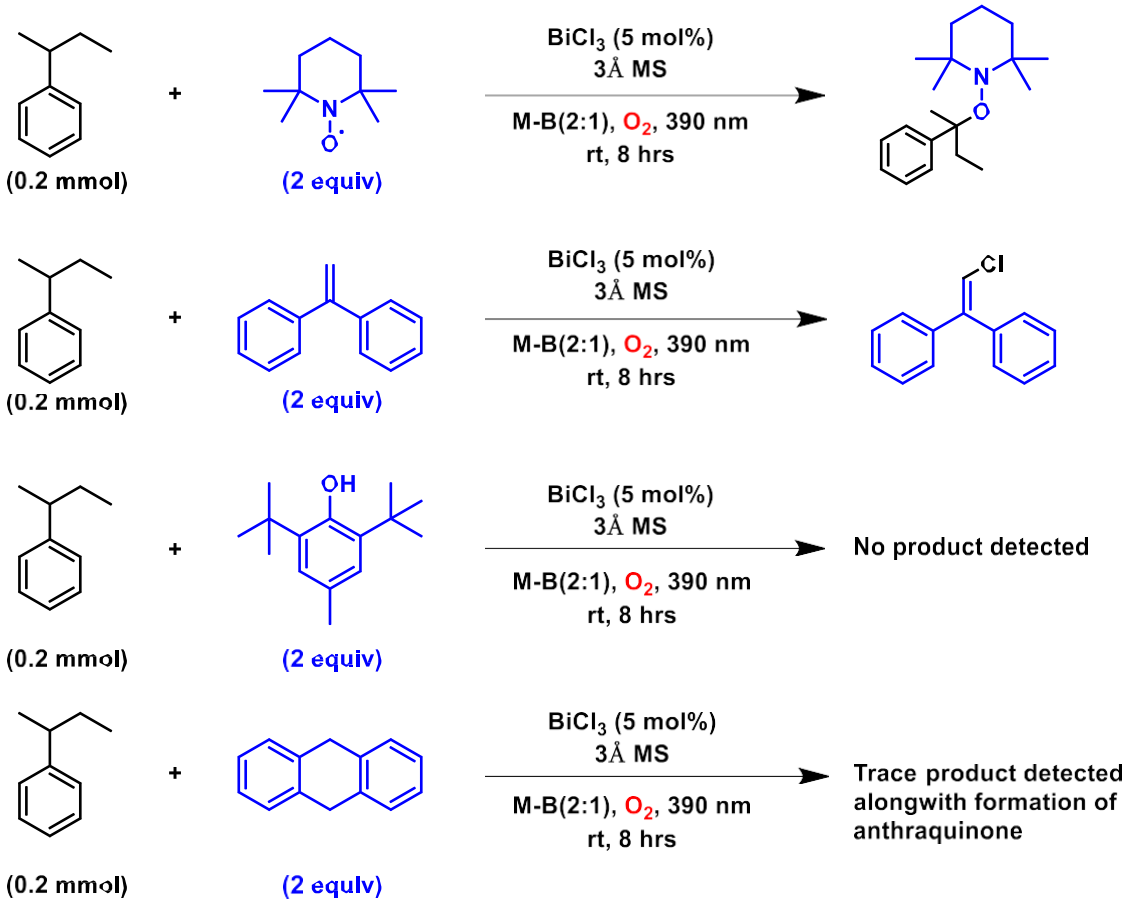


Table S8. Radical scavenging test

S. No	Radical trap	Yield
1	TEMPO	n.d
2	1,1-Diphenylethylene	Trace product
3	BHT	n.d
4	9,10-Dihydroanthracene	Trace product

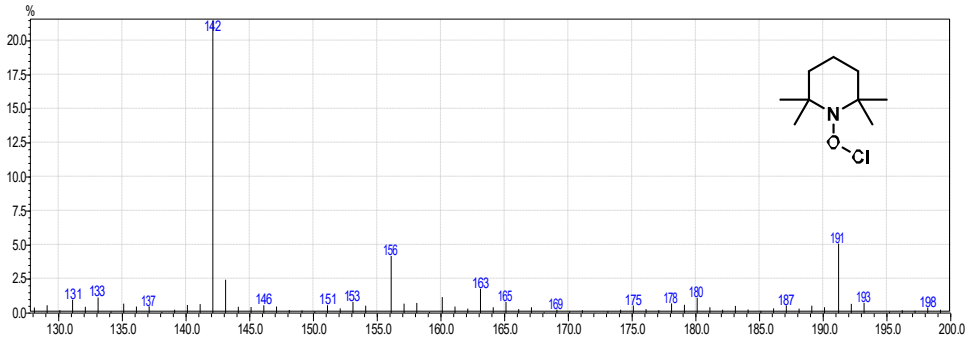


Figure S10. Mass spectra of TEMPO trapped chlorine radical

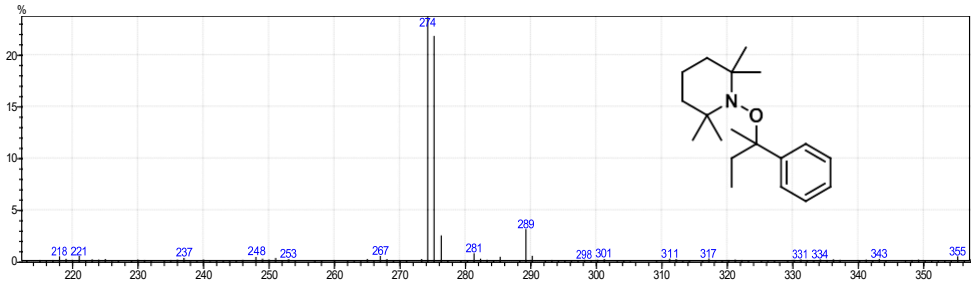


Figure S11. Mass spectra of TEMPO trapped benzylic radical

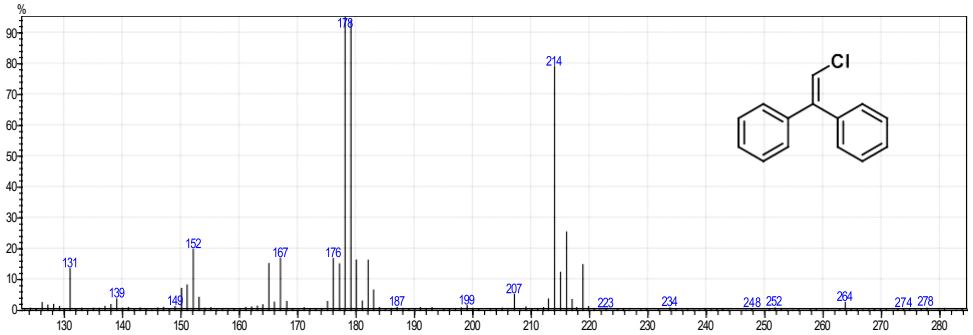
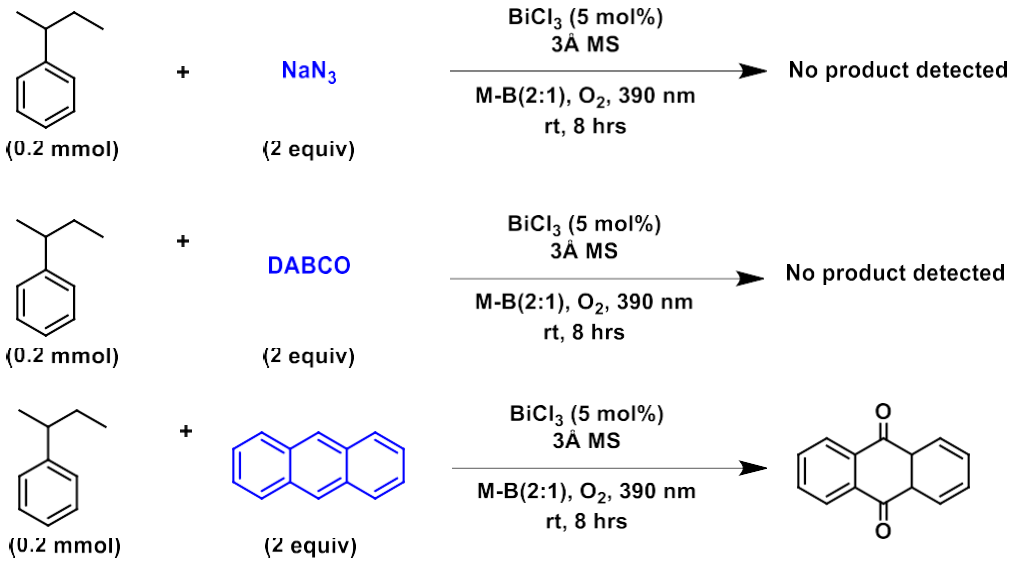


Figure S12. Mass spectra of DPE trapped chlorine radical

Test for singlet oxygen

In a teflon tube equipped with a magnetic stir bar, $BiCl_3$ (3.2 mg, 0.01 mmol, 5 mol%), quencher (NaN_3, DABCO and Anthracene, 2 equiv) and the alkylarene (0.2 mmol) were added along with the solvent MeCN/C_6H_6 (2:1, 1 mL). The reaction mixture was purged with O_2 for 1 minute, and the tube equipped with the oxygen balloon was placed in the reactor and irradiated with blue LED (390 nm, 40 W) for 8 hours. The solvent was evaporated under reduced pressure, and GC-MS and ^1H NMR were obtained using mesitylene as the internal standard.

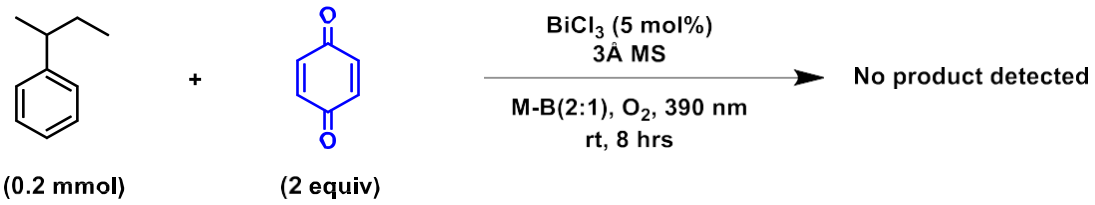
Scheme S6. Scavenging experiments for singlet oxygen detection



Test for superoxide ion

In a Teflon tube equipped with a magnetic stir bar, $BiCl_3$ (3.2 mg, 0.01 mmol, 5 mol%), p-benzoquinone (2 equiv) and the alkylarene (0.2 mmol) were added along with the solvent $MeCN/C_6H_6$ (2:1, 1 mL). The reaction mixture was purged with O_2 for 1 minute, and the tube equipped with the oxygen balloon was placed in the reactor and irradiated with blue LED (390 nm, 40 W) for 8 hours. The solvent was evaporated under reduced pressure, and GC-MS and ^1H NMR were obtained using mesitylene as the internal standard.

Scheme S7. Scavenging experiment for superoxide detection



EPR study for detecting the presence of singlet oxygen

To investigate the formation of singlet oxygen through energy transfer during the reaction, an EPR study was conducted to corroborate the results obtained from scavenger experiments. The reaction was conducted under standard conditions along with 2 equiv of TEMP (2,2,6,6-tetramethylpiperidine), which is EPR silent. TEMP reacts with singlet oxygen to produce TEMPO, which is an EPR-active compound.

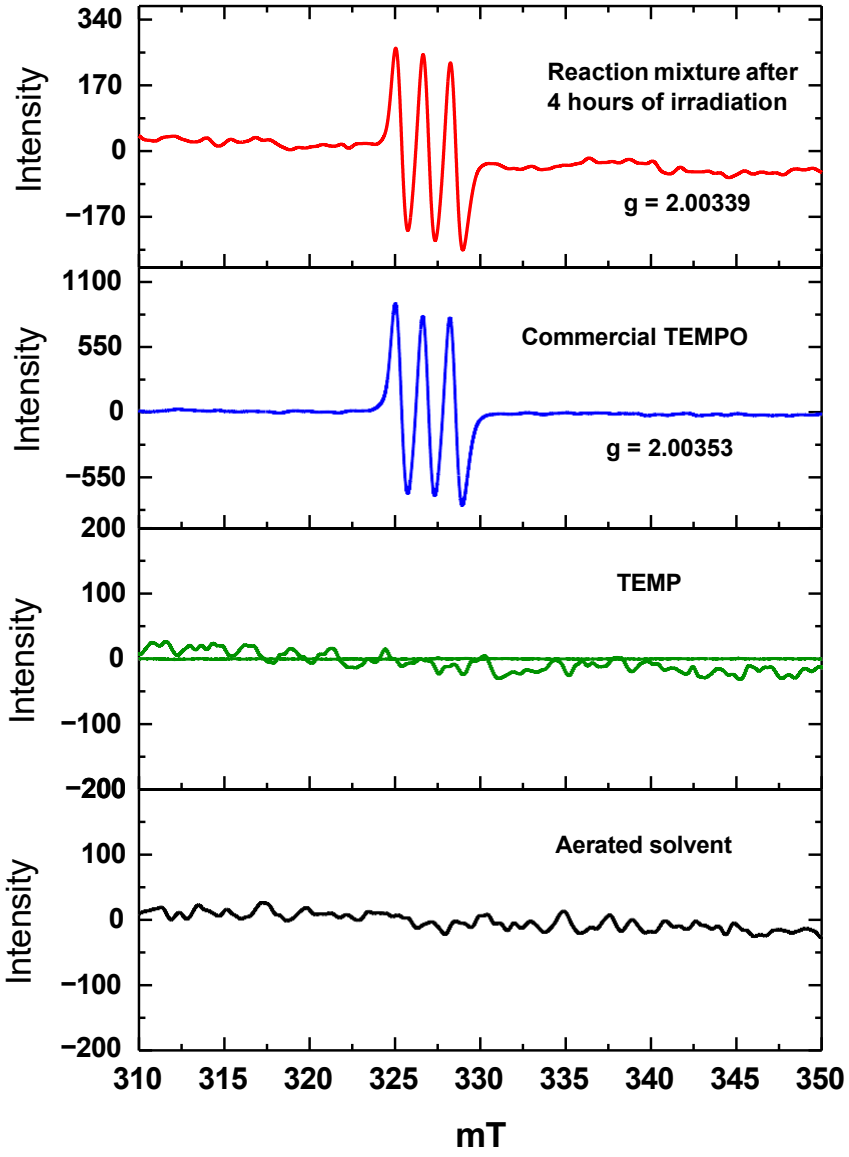


Figure S13. EPR spectra depicting the formation of TEMPO from the reaction mixture containing TEMP

The signal characteristic of TEMPO was obtained from the reaction mixture and was also verified by recording an EPR of pure TEMPO. There was no signal from the aerated solvent kept in the dark and the pure TEMP reagent. This proves the generation of singlet oxygen in the reaction system.

(b) UV Vis spectra

The absorption spectra was measured using Shimadzu spectrometer. Solutions of $BiCl_3$ and TBACl were made in MeCN at a concentration of 0.1mM

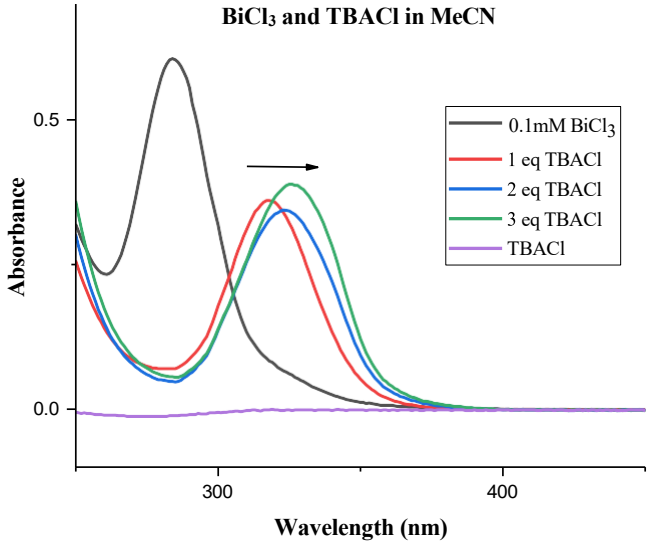


Figure S14. UV Vis spectra of $BiCl_3$ with additional chloride additive

Shift in the absorption maxima was seen on sequential addition of 1 and 2 equiv of TBACl, corresponding to the formation of $(BiCl_4)^-$ and $(BiCl_5)^{2-}$. On adding the third equiv, no further shift was seen.

XVI. DFT study

All the DFT calculations were performed using the Gaussian 16 program.[7] During the first trial, the ground state structures, and transition states were optimised using PBE functional and Def2-TZVPP basis set.[8,9] With this functional and basis set, we obtained a negative activation energy for the hydrogen abstraction by the chlorine radical (Refer Fig S15). So we performed the calculations using the functional BHandHLYP and aug-cc-pVDZ basis set, which is known to give a positive barrier height for the same.[10,11] So we revisited all our calculations using the above-mentioned functional and basis set.

The ground states were optimized with solvent effects of acetonitrile using the SMD model[12] with the BHandHLYP functional and the aug-cc-pVDZ basis set.[13,14] For the reactant, intermediates, and products, the ground state energy was obtained with zero imaginary frequency, and the TS geometry was optimized with 1 imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed to confirm if the reaction path connects the reactant and products.

To get mechanistic insight for the formation of singlet oxygen during the reaction, the ground state structure of $BiCl_3$ was optimized with solvent effects of acetonitrile by using the SMD model with the PBE functional. Def2-TZVPP basis set was

used. The excited state was modelled using the optimised ground state geometry of $BiCl_3$ with solvent effects of acetonitrile by using SMD model with PBE method. TDA was used for singlet and triplet energy state calculation.[15]

All the 3D structures were generated using CYLview20 software.

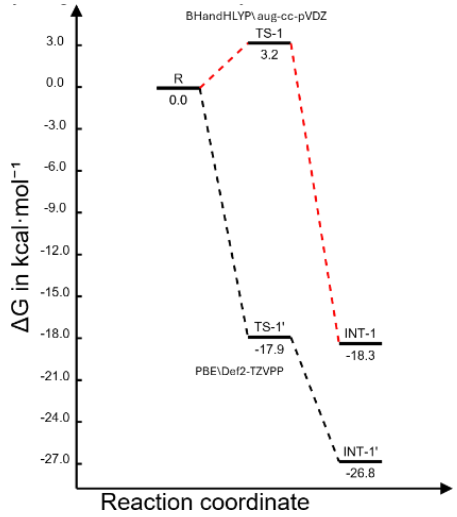
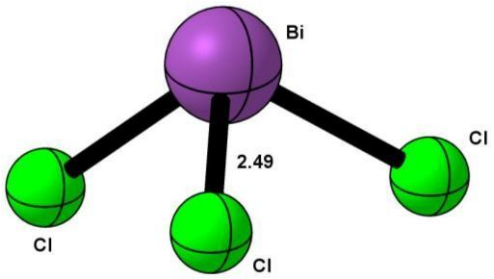


Figure S15. Comparison of the activation barriers using 2 different functionals and basis sets.

Probing the feasibility of energy transfer from $BiCl_3$ to triplet oxygen

Coordinates of optimized ground state $BiCl_3$



Imaginary Frequency	= 0
Electronic Energy	= -1594.909768 H
EE + Thermal Free Energy Correction	= -1594.941250 H

Symbol	X	Y	Z
Bi	0.00005000	0.87281600	0.01336300
Cl	-0.00220100	-0.43879000	2.12654300
Cl	1.85171500	-0.38974200	-1.06788300
Cl	-1.84956500	-0.38928300	-1.07202400

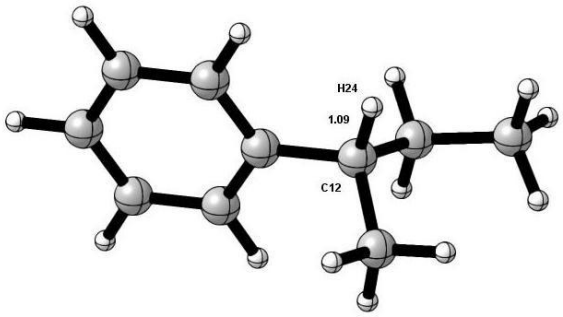
Energy of first excited singlet state = 4.9163 eV

Energy of first excited triplet state = 4.6262 eV

The generation of singlet oxygen by energy transfer from the first triplet excited state of $BiCl_3$ to ground state triplet oxygen is feasible by comparison of the energy values. Singlet oxygen has two possible states, and its lower energy state $^1\Delta_g$ is long-lived and has an energy of 0.98 eV.[16] Since the energy of the triplet state of $BiCl_3$ is higher, energy transfer is thermodynamically feasible.

Coordinates of optimized structures of intermediates and transition states involved in the mechanism

1) Substrate R



Imaginary Frequency = 0

Electronic Energy = -389.300685 H

EE + Thermal Free Energy Correction = -389.117475 H

	X	Y	Z
C	-2.04907100	-0.16848300	-0.39740100
C	-0.65885400	-0.20687000	-0.35806100
C	0.05847500	0.54670300	0.56937100
C	-0.65958300	1.34482300	1.46294400
C	-2.04735900	1.38711300	1.42876000
C	-2.74987900	0.62974700	0.49699900
H	-2.58317700	-0.76274000	-1.12881700
H	-0.12273100	-0.83272300	-1.06178100
H	-0.13144000	1.94202300	2.19545000

H	-2.58332600	2.01361600	2.13144100
H	-3.83186700	0.66336400	0.46954200
C	1.57063400	0.48992600	0.60565800
C	2.06174000	-0.17201800	1.90046500
H	1.53850000	-1.12414200	2.01825500
H	1.77146100	0.44996700	2.75161200
C	3.56180900	-0.42516700	1.94173000
H	3.83080400	-0.98275700	2.84130100
H	3.88446500	-1.01249100	1.07802200
H	4.13439900	0.50349100	1.94932000
C	2.18928500	1.87086900	0.38803500
H	1.79648900	2.33237000	-0.51960800
H	1.97431200	2.53700500	1.22637100
H	3.27226400	1.80298900	0.28241500
H	1.88313700	-0.14874000	-0.22456100

2) Chlorine radical

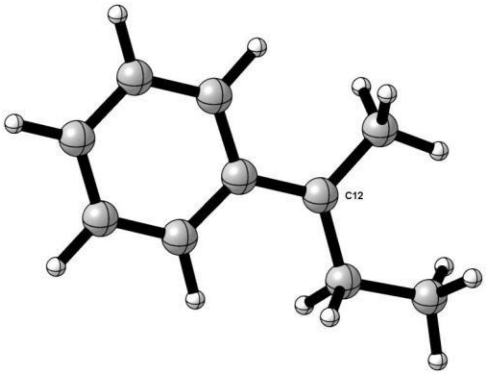
Imaginary Frequency = 0

Electronic Energy = -460.154580 H

EE + Thermal Free Energy Correction = -460.170257 H

	X	Y	Z
Cl	-0.06456200	1.44189400	0.00000000

3) Substrate radical (Int-1)



Imaginary Frequency = 0

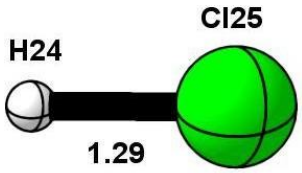
Electronic Energy = -388.659374 H

EE + Thermal Free Energy Correction = -388.490351 H

	X	Y	Z
C	-2.08357700	-0.54208400	0.53968900
C	-0.71948600	-0.53625600	0.77038700
C	0.00947700	0.67695000	0.87535600
C	-0.73373300	1.87719200	0.73079100
C	-2.09763400	1.86062000	0.50000500
C	-2.78885000	0.65322800	0.40191500
H	-2.60659300	-1.48782800	0.46570800
H	-0.20813300	-1.48238800	0.87167700
H	-0.23151500	2.83125000	0.80100800
H	-2.63126000	2.79748300	0.39482200
H	-3.85613100	0.64398800	0.22129200
C	1.41734800	0.69499300	1.11395800
C	2.15734400	-0.60975600	1.25476300
H	1.98817400	-1.20965200	0.35360300
H	1.70210600	-1.18768900	2.06679400
C	3.65568900	-0.52947900	1.50373100

H	4.06549900	-1.53781600	1.58437600
H	4.17784200	-0.02473500	0.68891200
H	3.88720400	-0.00361600	2.43172400
C	2.12782700	2.00854800	1.21642900
H	2.02686700	2.59281400	0.29571100
H	1.71620500	2.62635000	2.02116800
H	3.18923100	1.88748900	1.40960000

4) HCl (Int-1)



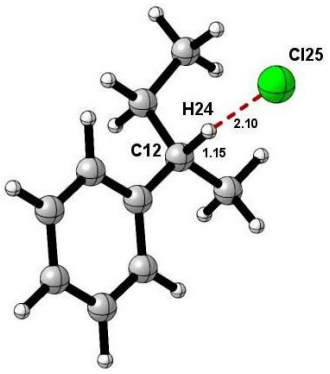
Imaginary Frequency = 0

Electronic Energy = -460.815407 H

EE + Thermal Free Energy Correction = -460.826548 H

	X	Y	Z
Cl	-1.09932300	0.69583900	0.00000000
H	-2.39096300	0.69583900	0.00000000

5) TS-1



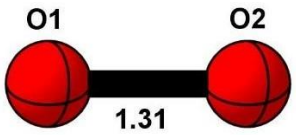
Imaginary Frequency = 1

Electronic Energy = -849.457575 H

EE + Thermal Free Energy Correction = -849.282575 H

	X	Y	Z
C	-2.00334500	-0.60004900	0.28384000
C	-0.63939800	-0.57389800	0.39150400
C	0.05726400	0.64611300	0.66730700
C	-0.70873100	1.84230100	0.77014600
C	-2.07302500	1.80733400	0.67504200
C	-2.73476400	0.58799600	0.43028200
H	-2.51880900	-1.52677600	0.07264900
H	-0.07214500	-1.48073800	0.24421000
H	-0.21112500	2.77995700	0.96199800
H	-2.65174100	2.71368700	0.78943200
H	-3.81320500	0.57220400	0.34218100
C	1.51622800	0.63500800	0.78125400
C	2.06769600	-0.48382200	1.69178400
H	1.55857100	-1.42123800	1.47767800
H	1.80859000	-0.21501200	2.71976300
C	3.56718700	-0.70727300	1.58040300
H	3.85344100	-1.56330200	2.19429900
H	3.85860600	-0.91884800	0.55055500
H	4.14141700	0.15090900	1.92933600
C	2.17712600	1.98027900	1.02464500
H	1.84161800	2.73037600	0.31018900
H	1.97163700	2.34356600	2.03418500
H	3.25520900	1.88959800	0.91413800
H	1.81018800	0.31415300	-0.28603900
Cl	2.59757900	-0.04518700	-2.20183600

6) Superoxide



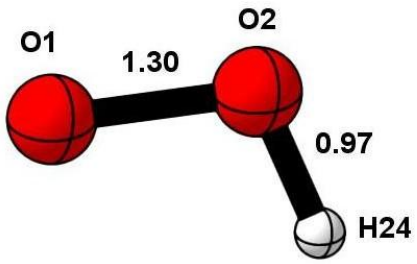
Imaginary Frequency = 0

Electronic Energy = -150.389729 H

EE + Thermal Free Energy Correction = -150.406493 H

	X	Y	Z
O	-1.82601400	0.22238200	0.00000000
O	-3.13759500	0.22238200	0.00000000

7) OOH radical



Imaginary Frequency = 0

Electronic Energy = -150.867224 H

EE + Thermal Free Energy Correction = -150.874498 H

	X	Y	Z
O	-0.51113900	-1.51649500	0.00000000
H	-0.80751700	-0.59266400	0.00000000
O	0.79022500	-1.48375200	0.00000000

8) Chloride ion

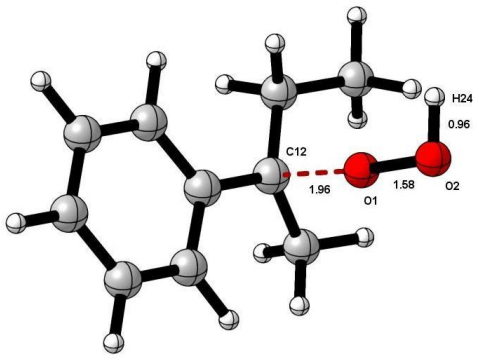
Imaginary Frequency = 0

Electronic Energy = -460.384670 H

EE + Thermal Free Energy Correction = -460.399693 H

	X	Y	Z
Cl	1.26307900	0.94917800	0.00000000

9) TS-2



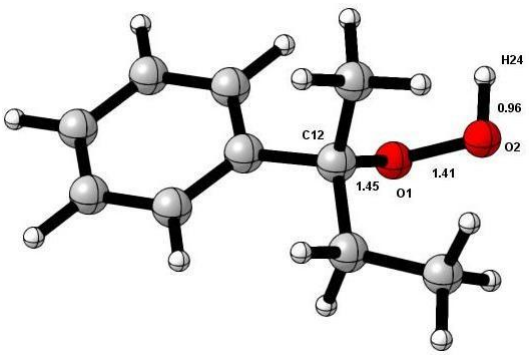
Imaginary Frequency = 1

Electronic Energy = -539.478281 H

EE + Thermal Free Energy Correction = -539.298539 H

	X	Y	Z
C	-0.55447500	-0.61606800	-0.13389400
C	0.80350200	-0.60773400	0.14728300
C	1.51398300	0.59808400	0.28240900
C	0.79245900	1.79350100	0.11171800
C	-0.56258000	1.78242900	-0.17609700
C	-1.24772300	0.57758400	-0.29868700
H	-1.07449300	-1.56167000	-0.22209300
H	1.30641200	-1.55410900	0.27521400
H	1.29293100	2.74668700	0.19019700
H	-1.08787400	2.72025900	-0.30617200
H	-2.30745300	0.56994900	-0.51989500
C	2.95542900	0.61041400	0.56086600
C	3.64035400	-0.71064200	0.79343700
H	3.35287900	-1.40553400	0.00637600
H	3.24614500	-1.12661900	1.72882400
C	5.15916800	-0.66451400	0.87544500
H	5.54924000	-1.68000600	0.95981200
H	5.59362900	-0.21408600	-0.01880000
H	5.50937200	-0.10586400	1.74359200
C	3.55042400	1.79311000	1.25910200
H	3.07184800	2.73015900	0.99306600
H	3.44780400	1.65774800	2.34230700
H	4.61306600	1.88394900	1.04330300
O	3.52045600	1.01408900	-1.27611900
O	3.93997800	1.22350000	-2.78354900
H	4.12277200	0.30969200	-3.01855700

10) Int-2



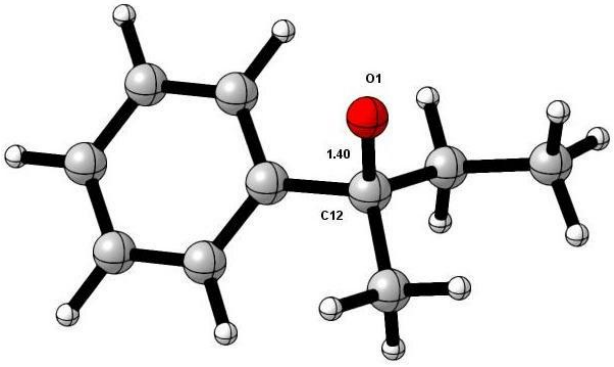
Imaginary Frequency = 0

Electronic Energy = -539.600090 H

EE + Thermal Free Energy Correction = -539.410138 H

	X	Y	Z
C	-0.63070700	-0.52403000	0.50922800
C	0.75872800	-0.52449100	0.58932600
C	1.50714700	0.51239300	0.03676000
C	0.82362600	1.55097900	-0.60052800
C	-0.56091500	1.55092100	-0.68746000
C	-1.29700600	0.51071300	-0.13067700
H	-1.18962200	-1.34072900	0.94860200
H	1.24372200	-1.34661300	1.09339800
H	1.37951600	2.36737700	-1.03962400
H	-1.06655100	2.36562300	-1.19083200
H	-2.37781000	0.50873500	-0.19615600
C	3.03089200	0.57897600	0.14477100
C	3.64334700	-0.76217300	0.55548700
H	3.22824000	-1.53592700	-0.09245600
H	3.30346400	-0.98234600	1.56875200
C	5.16210200	-0.85925900	0.52140400
H	5.46297300	-1.84619000	0.87837000
H	5.55228800	-0.73553500	-0.48728400
H	5.64025900	-0.11896900	1.16355500
C	3.41400600	1.70072900	1.10352200
H	3.02174800	2.65724800	0.75863500
H	2.98025000	1.48938100	2.08053400
H	4.49152900	1.78485500	1.21780700
O	3.41243700	0.90382000	-1.21563800
O	4.71527200	1.44441200	-1.27665900
H	4.54245300	2.38604200	-1.34532300

11) Alkoxy radical (Int-3)



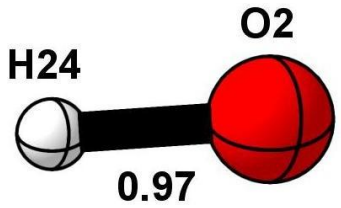
Imaginary Frequency = 0

Electronic Energy = -463.834307 H

EE + Thermal Free Energy Correction = -463.661084 H

	X	Y	Z
C	0.52892300	-1.22034500	-0.45904600
C	1.91526600	-1.18342400	-0.40698700
C	2.58346100	-0.03836700	0.03391000
C	1.83029600	1.07089100	0.41202900
C	0.44115300	1.02846100	0.37295100
C	-0.21467700	-0.11414600	-0.06540200
H	0.02924300	-2.11584200	-0.80662400
H	2.47817200	-2.05432700	-0.71178000
H	2.31341200	1.97509200	0.75095100
H	-0.12776800	1.89559800	0.68386200
H	-1.29645000	-0.14281100	-0.10079500
C	4.11912800	-0.03848500	0.08764000
C	4.61508400	-1.11548500	1.06660100
H	4.14624500	-2.06068000	0.79379800
H	4.25484400	-0.85420000	2.06386000
C	6.12640100	-1.29599600	1.08823900
H	6.38951800	-2.14768100	1.71792500
H	6.51591800	-1.49275400	0.08689000
H	6.64066300	-0.42136400	1.48756300
C	4.70993500	1.33124900	0.39975600
H	4.31190800	2.08827500	-0.27418600
H	4.50200800	1.62360200	1.42945300
H	5.79014700	1.29895500	0.26840000
O	4.44425600	-0.38537300	-1.22635700

12) Hydroxyl radical (Int-3)



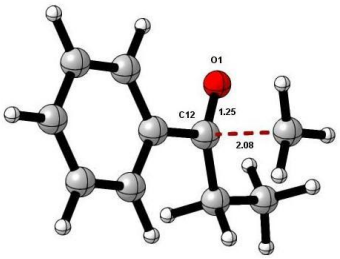
Imaginary Frequency = 0

Electronic Energy = -75.723005 H

EE + Thermal Free Energy Correction = -75.731278 H

	X	Y	Z
O	-1.88907700	0.55544300	0.00000000
H	-2.21314100	1.47056900	0.00000000

13) TS-4a



Imaginary Frequency = 1

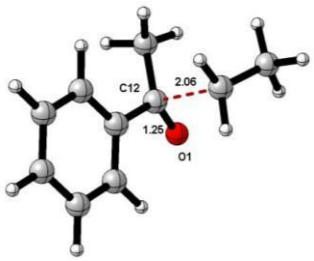
Electronic Energy = -463.808366 H

EE + Thermal Free Energy Correction = -463.639734 H

	X	Y	Z
C	2.66972500	-0.97206600	-0.30833000
C	1.29366000	-1.14933000	-0.32490700
C	0.43373300	-0.07148700	-0.11649100
C	0.98195300	1.19063500	0.11003500
C	2.35970700	1.36966900	0.12735900
C	3.20848400	0.28977700	-0.08153600
H	3.32370700	-1.81886600	-0.47524200
H	0.87291900	-2.12854200	-0.50522400
H	0.34215600	2.04467800	0.28030900
H	2.76987800	2.35596800	0.30383000
H	4.28202100	0.43044200	-0.06920100

C	-1.05955000	-0.30798000	-0.16835400
C	-1.94488900	0.90428600	-0.44186300
H	-1.58502100	1.31878100	-1.38907300
H	-1.78241400	1.67639900	0.30735500
C	-3.42205800	0.58094500	-0.56042400
H	-3.97825100	1.48759300	-0.80461000
H	-3.60441100	-0.15168100	-1.34596100
H	-3.82679900	0.18299100	0.37108100
C	-1.34996500	-0.50758800	1.88142800
H	-0.73209100	-1.36560300	2.11090500
H	-0.98385900	0.45240900	2.22229500
H	-2.41874800	-0.66539200	1.93727000
O	-1.46498200	-1.44131300	-0.50197100

14) TS-4b



Imaginary Frequency = 1

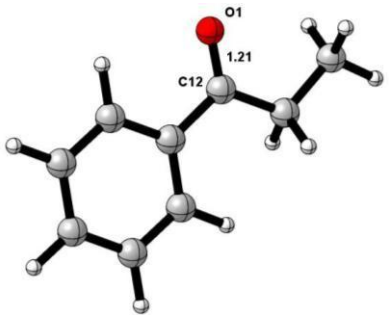
Electronic Energy = -463.815583 H

EE + Thermal Free Energy Correction = -463.646629 H

	X	Y	Z
C	2.51274200	-1.20454400	-0.01291900
C	1.16891300	-1.16657500	0.32863200
C	0.45615400	0.03199500	0.28812500
C	1.12092500	1.19421700	-0.10096000
C	2.46831000	1.15830500	-0.44156400
C	3.16867100	-0.04028800	-0.39992800
H	3.05181000	-2.14298200	0.02515700
H	0.65927500	-2.06941600	0.63473700
H	0.59675200	2.13839200	-0.14265300
H	2.97074200	2.07031900	-0.73846400
H	4.21814900	-0.06802700	-0.66502800
C	-1.00087500	0.03372600	0.68674600

C	-1.78031000	-0.27720200	-1.19920000
H	-1.27679800	-1.21048100	-1.41939800
H	-1.33462700	0.58977200	-1.67314000
C	-3.26625500	-0.32629200	-1.13924000
H	-3.64718800	-0.54686000	-2.14385800
H	-3.61644900	-1.11589800	-0.47499000
H	-3.69923800	0.62465900	-0.83038300
C	-1.63674200	1.37226500	1.01181400
H	-1.14352800	1.77394000	1.90077600
H	-1.54413000	2.10598200	0.21435700
H	-2.68797400	1.22026800	1.24332000
O	-1.45666200	-0.98580000	1.25698000

15) Propiophenone (Int-4a)



Imaginary Frequency = 0

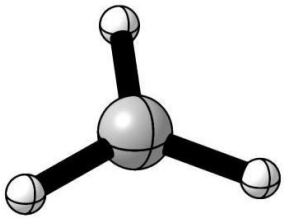
Electronic Energy = -424.014326 H

EE + Thermal Free Energy Correction = -423.877927 H

	X	Y	Z
C	2.73216500	0.00688300	-1.01755100
C	1.41078000	0.41674500	-1.09202500
C	0.55594300	0.25959200	0.00102300
C	1.05035300	-0.31647500	1.17188600
C	2.37492000	-0.72736000	1.24721300
C	3.21692200	-0.56661200	0.15418400
H	3.38651400	0.13290600	-1.87068400
H	1.02674300	0.86323700	-1.99849900
H	0.41015800	-0.44927100	2.03207000
H	2.74888000	-1.17297000	2.15988700
H	4.24943100	-0.88740700	0.21373300

C	-0.86256400	0.71587600	-0.12242500
C	-1.78652200	0.54168400	1.05471900
H	-1.33695400	1.05333200	1.90934400
H	-1.79421300	-0.51954000	1.31604300
C	-3.19520400	1.04400700	0.80976100
H	-3.80452400	0.88378600	1.70034000
H	-3.20200300	2.11025200	0.58113700
H	-3.66500800	0.51862900	-0.02234800
O	-1.25116900	1.21523600	-1.15730400

16) Methyl radical (Int-4a)



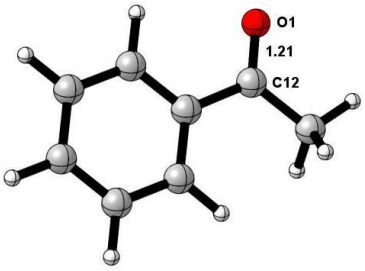
Imaginary Frequency = 0

Electronic Energy = -39.813626 H

EE + Thermal Free Energy Correction = -39.803145 H

	X	Y	Z
C	-2.57676300	-2.46079100	-1.06156600
H	-2.82719400	-1.84765100	-1.91727600
H	-1.55270800	-2.77030900	-0.89902600
H	-3.35061000	-2.76581400	-0.36947100

17) Acetophenone (Int-4b)



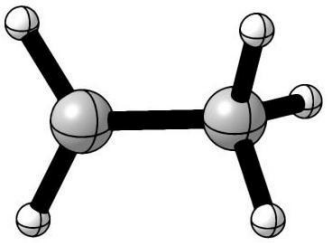
Imaginary Frequency = 0

Electronic Energy = -384.723034 H

EE + Thermal Free Energy Correction = -384.613595 H

	X	Y	Z
C	-0.00804700	-2.27948000	-0.47947100
C	1.34990800	-2.48027900	-0.29434500
C	2.15011900	-1.46617800	0.23661700
C	1.56565100	-0.24627400	0.57837300
C	0.20396100	-0.04465700	0.39284300
C	-0.58354900	-1.05955100	-0.13543900
H	-0.62082700	-3.07100200	-0.89162000
H	1.80523600	-3.42434900	-0.55901200
H	2.16498000	0.55362600	0.98957200
H	-0.24136000	0.90477900	0.66069900
H	-1.64506300	-0.90171200	-0.27994100
C	3.60942800	-1.71782100	0.42259000
O	4.08971400	-2.78815500	0.11128500
C	4.46818200	-0.63053600	0.99781900
H	5.49349200	-0.98452900	1.06993200
H	4.43025800	0.25780100	0.36440100
H	4.10757800	-0.34349400	1.98734000

18) Ethyl radical (Int-4b)



Imaginary Frequency = 0

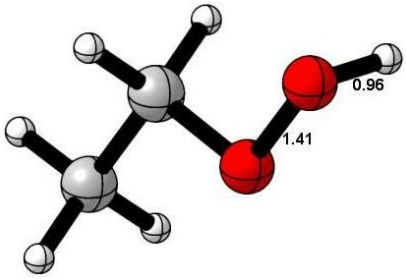
Electronic Energy = -79.111410 H

EE + Thermal Free Energy Correction = -79.075073 H

	X	Y	Z
C	-2.81647900	-1.66807300	0.57216000
H	-2.24532100	-1.54828400	1.48445200
H	-2.54818200	-2.48430400	-0.08704700
C	-4.04268800	-0.86911900	0.33348900
H	-4.92563100	-1.33408500	0.79659800

H	-3.96045900	0.13386000	0.75921100
H	-4.26274000	-0.77536200	-0.73251100

19) EtOOH



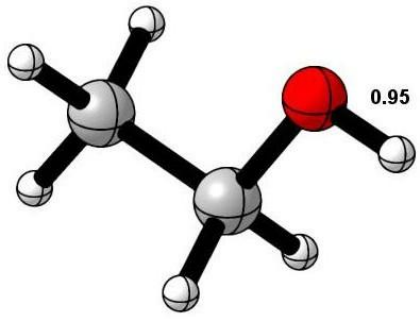
Imaginary Frequency = 0

Electronic Energy = -230.081541 H

EE + Thermal Free Energy Correction = -230.023281 H

	X	Y	Z
C	-0.55199900	0.19394500	-0.00144200
C	0.95410100	0.14466500	-0.05481300
H	-0.87509400	1.23388400	-0.06958200
H	-0.99378300	-0.35774500	-0.83281300
H	-0.92472100	-0.22063800	0.93659600
H	1.33129900	0.55568800	-0.99505800
H	1.40048100	0.69333100	0.77710100
O	1.33084100	-1.22232400	0.03966800
O	2.74005600	-1.28796200	0.04500100
H	2.94861600	-1.45167700	-0.87869600

20) EtOH



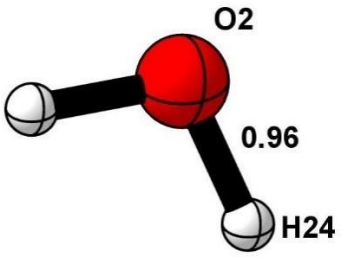
Imaginary Frequency = 0

Electronic Energy = -154.975486 H

EE + Thermal Free Energy Correction = -154.918798 H

	X	Y	Z
C	-0.56794100	0.20072400	-0.00001400
C	0.93876400	0.22012200	-0.00017800
H	-0.95392700	1.22206500	0.00020400
H	-0.94876500	-0.31063100	-0.88664200
H	-0.94855300	-0.31091300	0.88654500
H	1.31100100	0.74555000	-0.88519200
H	1.31117600	0.74544500	0.88483100
O	1.40588800	-1.12303500	-0.00029600
H	2.36050300	-1.11809400	-0.00102800

21) H_2O



Imaginary Frequency = 0

Electronic Energy = -76.409268 H

EE + Thermal Free Energy Correction = -76.405608 H

	X	Y	Z
O	-1.90836200	0.55232700	0.00000000
H	-1.70159400	1.48603900	0.00000000
H	-1.05879800	0.11335900	0.00000000

22) Hydrogen atom

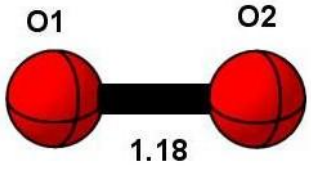
Imaginary Frequency = 0

Electronic Energy = -0.497663 H

EE + Thermal Free Energy Correction = -0.508317 H

	X	Y	Z
H	0.77023500	2.21932100	0.00000000

23) Singlet oxygen



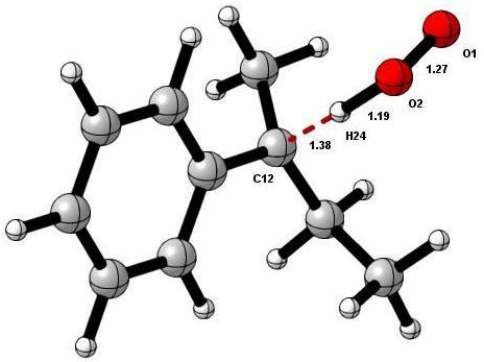
Imaginary Frequency = 0

Electronic Energy = -150.211017 H

EE + Thermal Free Energy Correction = -150.225788 H

	X	Y	Z
O	-1.89108000	0.22238200	0.00000000
O	-3.07252900	0.22238200	0.00000000

24) TS-1'



Imaginary Frequency = 1

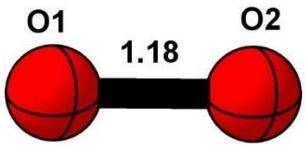
Electronic Energy = -539.511568 H

EE + Thermal Free Energy Correction = -539.335923 H

	X	**Y**	**Z**
C	0.15339200	-2.12794700	-0.71673200
H	0.60201000	-2.60107200	0.15795000
H	-0.22158100	-2.92170700	-1.36488600
C	1.17850400	-1.28551400	-1.46921800
H	2.02271900	-1.92233200	-1.73580600
H	0.75081900	-0.94326900	-2.41801100
C	1.72546300	-0.07435400	-0.73767300
C	3.13376900	0.29194500	-1.14448500

H	3.12944700	0.59543600	-2.19769900
H	3.54212900	1.11697200	-0.56453900
H	3.80154200	-0.56461200	-1.05312200
C	0.81068300	1.05739300	-0.44983100
C	1.23111000	2.10954000	0.37928400
C	-0.48367900	1.12603900	-0.98216000
C	0.39717300	3.17931000	0.66210600
H	2.21930600	2.08763700	0.81825400
C	-1.31458300	2.20401700	-0.70856800
H	-0.84600900	0.34606900	-1.63495900
C	-0.88177300	3.23428800	0.11706100
H	0.74590100	3.97380400	1.30984200
H	-2.30503200	2.23850600	-1.14462000
H	-1.53281000	4.07162700	0.33396600
H	-0.70119400	-1.54317300	-0.37782000
H	1.97210000	-0.55314000	0.53800600
O	2.24404700	-0.94111200	1.62422600
O	3.33004600	-1.58805000	1.57253300

25) Triplet oxygen



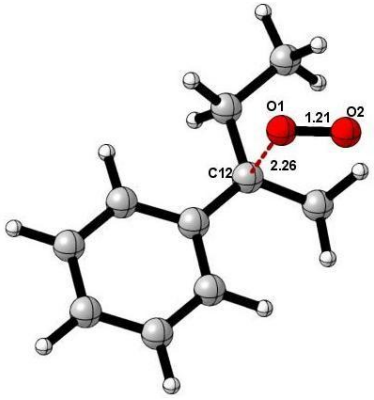
Imaginary Frequency = 0

Electronic Energy = -150.278421 H

EE + Thermal Free Energy Correction = -150.294225 H

	X	Y	Z
O	-1.89017900	0.22238200	0.00000000
O	-3.07343000	0.22238200	0.00000000

26) TS-2'b



Imaginary Frequency = 1

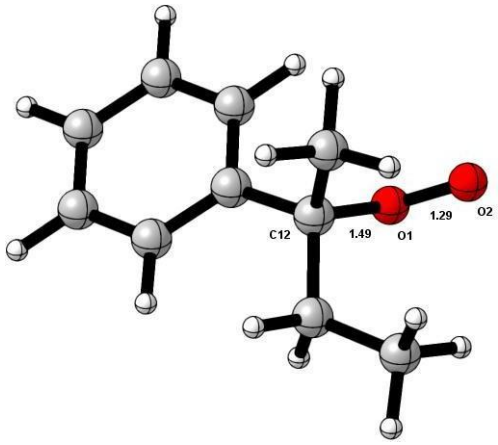
Electronic Energy = -538.933016 H

EE + Thermal Free Energy Correction = -538.761997 H

	X	Y	Z
C	-1.41392000	-1.63807600	0.00187500
C	-0.05267700	-1.61992800	0.26248900
C	0.67598800	-0.41342600	0.27955500
C	-0.04048100	0.77095100	0.01034600
C	-1.39852400	0.74746400	-0.25681000
C	-2.09838200	-0.45637200	-0.26101100
H	-1.94455200	-2.58194400	0.00575900
H	0.44295800	-2.55659700	0.46823300
H	0.46749500	1.72352500	-0.00486400
H	-1.91671600	1.67519900	-0.46507200
H	-3.16114600	-0.47188900	-0.46641200
C	2.10512500	-0.40329400	0.53490600
C	2.79890600	-1.70772200	0.81428000
H	2.50648600	-2.43940700	0.06037300
H	2.41232400	-2.09322400	1.76601200
C	4.31820400	-1.65721900	0.88691000
H	4.70481700	-2.66083000	1.06994000
H	4.75525200	-1.29971900	-0.04624500
H	4.67124400	-1.01678100	1.69531500
C	2.80861700	0.84003800	0.94264900
H	2.20818900	1.73690200	0.83329600
H	3.11184000	0.76293700	1.99118300
H	3.72601400	0.97505400	0.36260300

O	2.69411100	-0.32941800	-1.64922000
O	3.48445800	0.54310100	-1.93658800

27) INT-2'b



Imaginary Frequency = 0

Electronic Energy = -538.968564 H

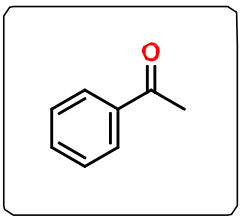
EE + Thermal Free Energy Correction = -538.791741 H

	X	Y	Z
C	-1.42009700	-1.51199900	0.43025300
C	-0.03386900	-1.50076000	0.55008700
C	0.71039400	-0.41677500	0.09238100
C	0.03266100	0.65551800	-0.49125300
C	-1.34829000	0.64293100	-0.61905000
C	-2.08251400	-0.44344600	-0.15602600
H	-1.97954300	-2.36413900	0.79488900
H	0.45160200	-2.34898800	1.00877500
H	0.58726100	1.50999500	-0.85500500
H	-1.85201300	1.48320200	-1.08006700
H	-3.16080900	-0.45498700	-0.25278900
C	2.22292800	-0.34120900	0.24443400
C	2.87063300	-1.69281300	0.54429200
H	2.50168100	-2.41767600	-0.18246700
H	2.50948700	-2.01202600	1.52236900
C	4.39147800	-1.71550800	0.54729600
H	4.73063400	-2.72971800	0.76393700
H	4.80621400	-1.43039400	-0.41962200
H	4.81424400	-1.05928200	1.30806700
C	2.60154700	0.73208800	1.24838800

H	2.18460600	1.69652900	0.96322500
H	2.18093000	0.44836600	2.21274100
H	3.67720500	0.83287100	1.35351300
O	2.66979600	0.04730400	-1.11880500
O	3.73353600	0.77326000	-1.15811300

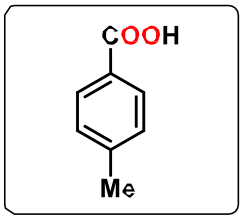
XVII. Characterisation of products

Acetophenone



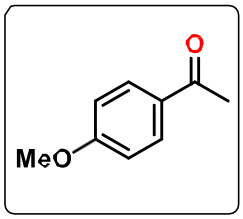
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 2.59 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 198.3, 137.2, 133.2, 128.6, 128.4, 26.7.

p-Toluic acid



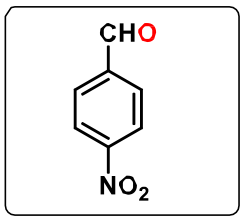
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.13 (brs, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 172.6, 144.8, 130.4, 129.4, 126.7, 21.9.

4-methoxyacetophenone



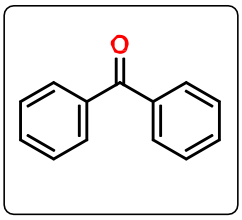
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 2.48 (s, 3H) $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 196.7, 163.4, 130.5, 130.2, 113.6, 55.4, 26.2

4-nitrobenzaldehyde



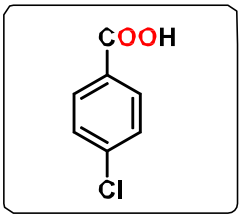
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.16 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 190.5, 151.2, 140.2, 130.6, 124.5

Benzophenone



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.0 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 4H) $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 196.9, 137.7, 132.5, 130.2, 128.4

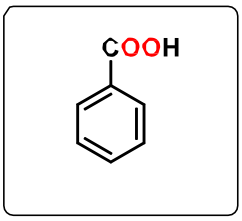
4-Chlorobenzoic acid



^{1}H NMR (400 MHz, DMSO d^{6}): δ 13.16 (brs, 1H), 7.92 (d, *J* = 6.3 Hz, 2H), 7.54 (d, *J* = 6.4 Hz, 2H) ^{13}C{^{1}H} NMR (100 MHz, DMSO d^{6}): δ 166.5, 137.8, 131.2, 129.6, 128.7

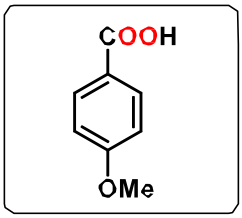
(3.4 ppm in ^{1}H NMR - Water from DMSO d^{6})

Benzoic acid



^{1}H NMR (400 MHz, $CDCl_3$): δ 11.08 (brs, 1H), 8.14 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H) ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 172.5, 134.0, 130.4, 129.4, 128.6

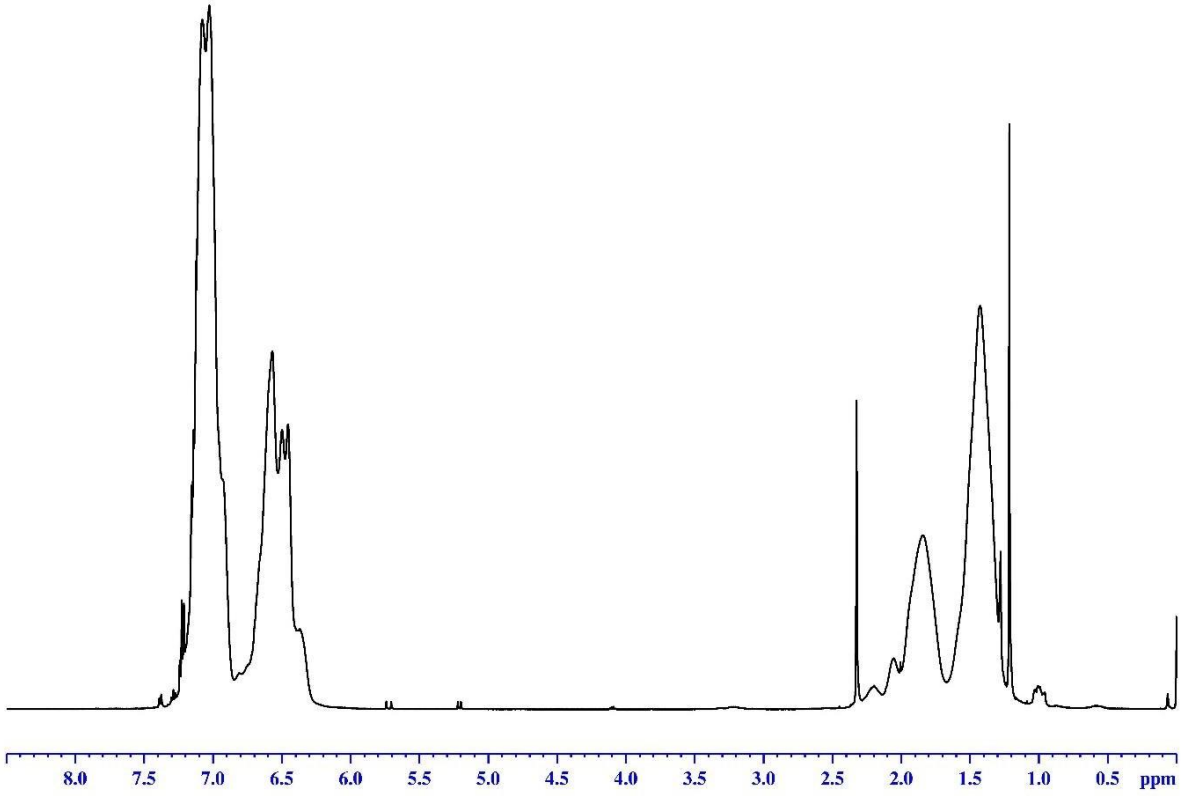
4-methoxybenzoic acid



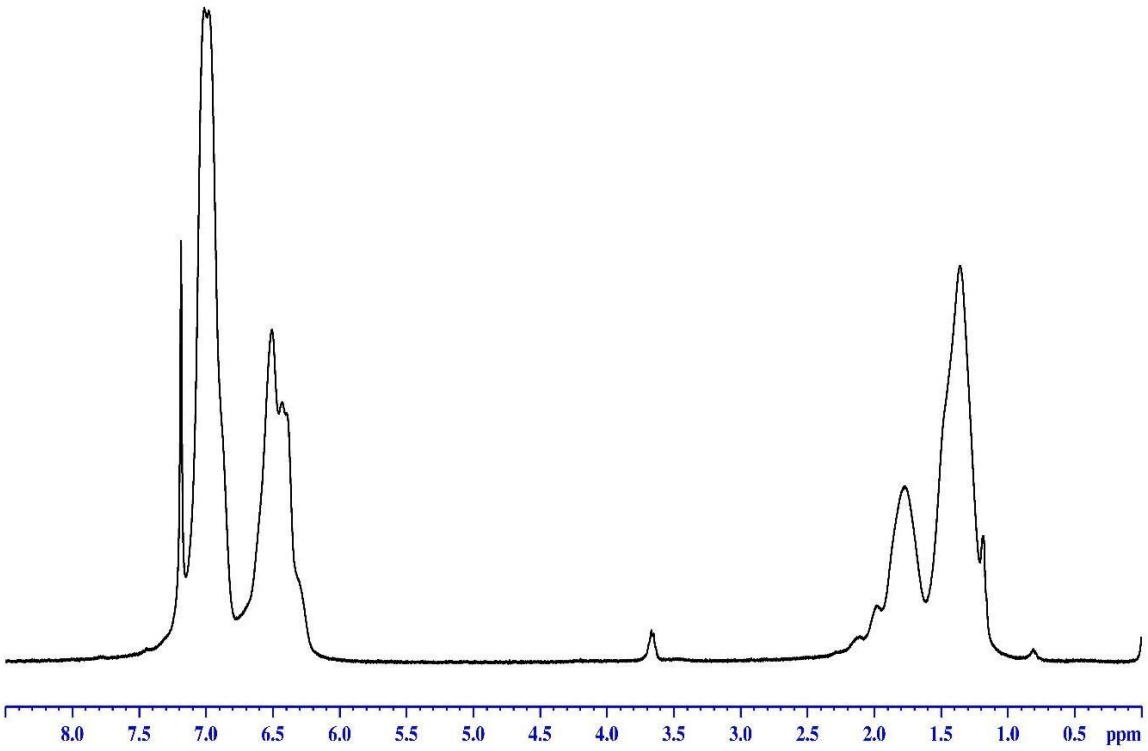
^{1}H NMR (400 MHz, DMSO-d^{6}): δ 12.61 (brs, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 3H) ^{13}C{^{1}H} NMR (100 MHz, DMSO-d^{6}): δ 167.1, 162.9, 131.4, 123.1, 113.9, 55.5

NMR Spectra

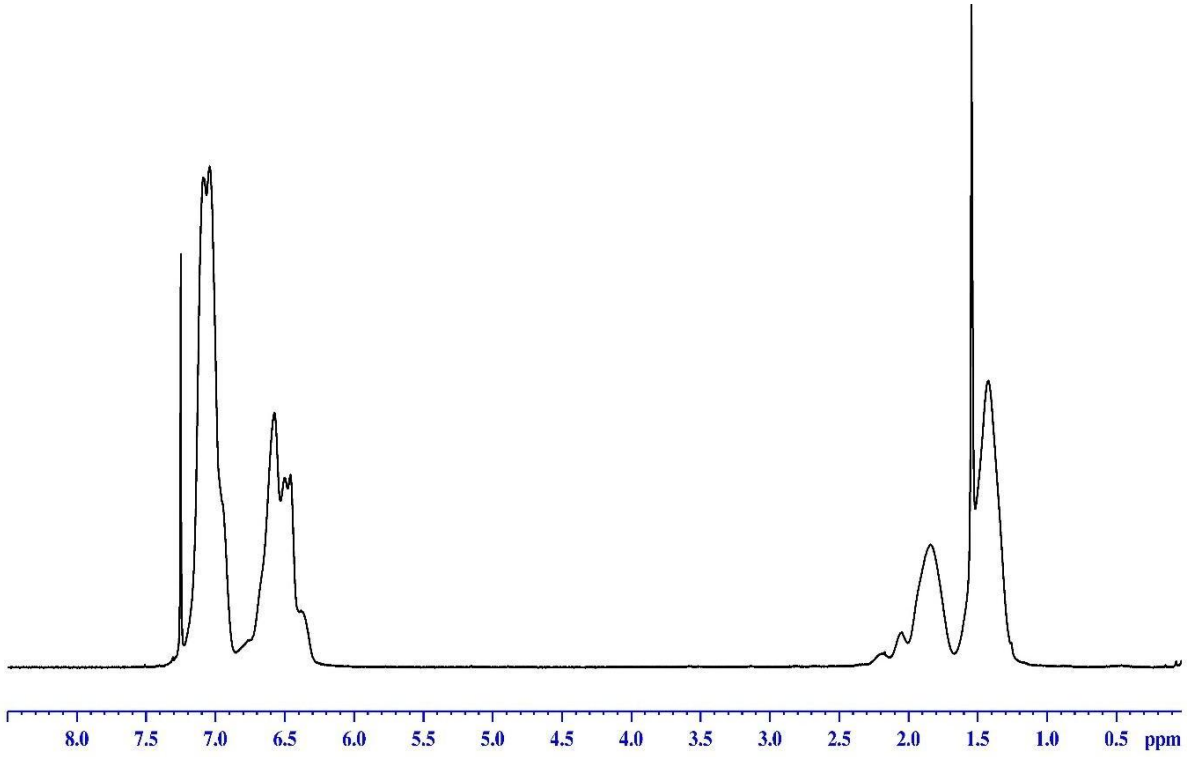
^1H NMR of synthesised polystyrene in $CDCl_3$



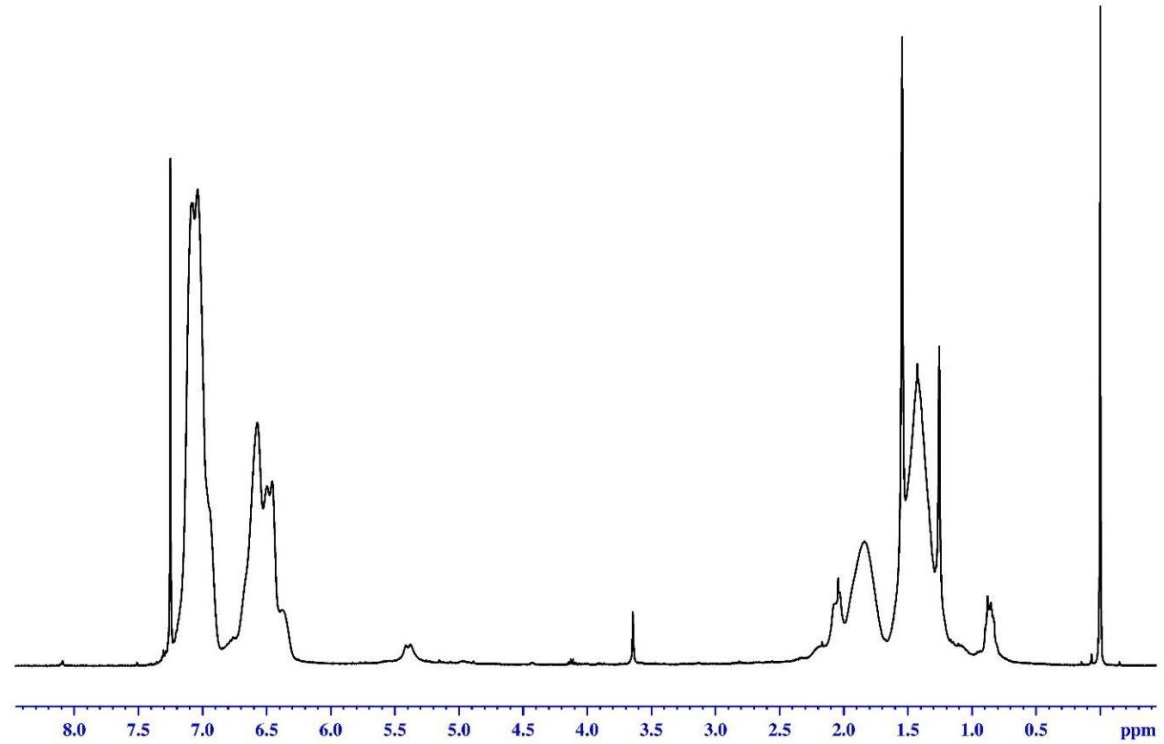
^1H NMR of expanded polystyrene foam in $CDCl_3$



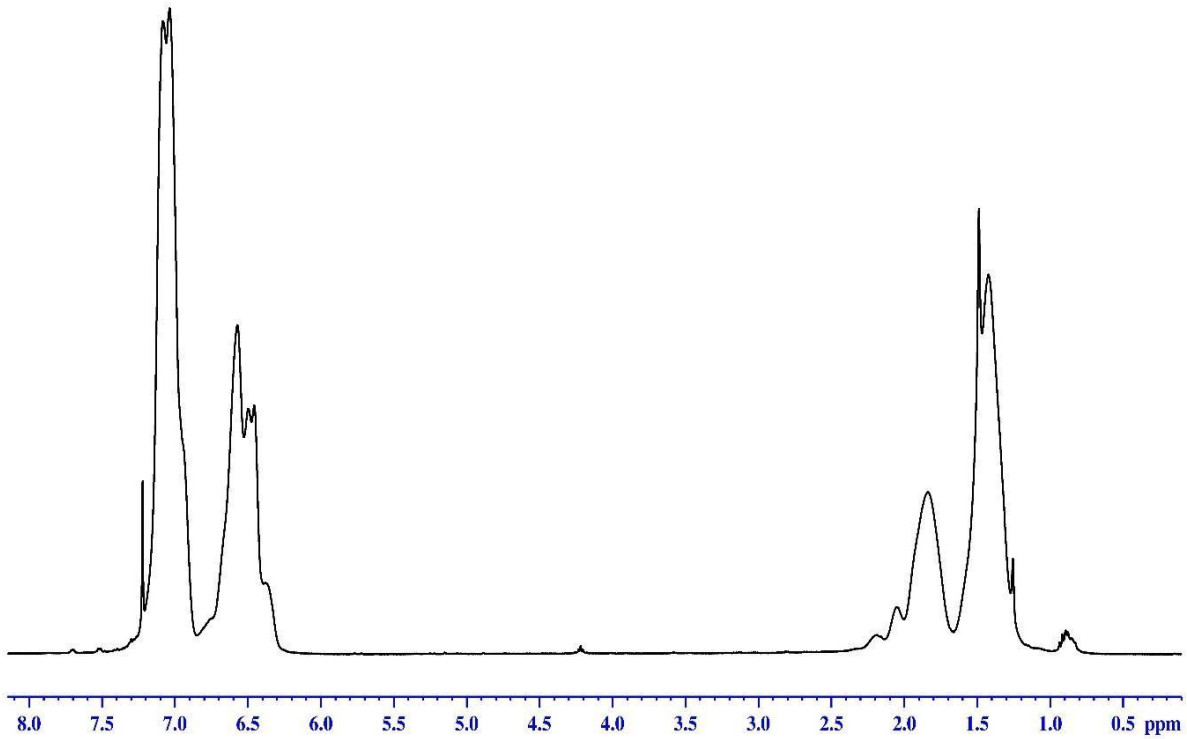
^{1}H NMR of Commercial PS pellet in $CDCl_3$



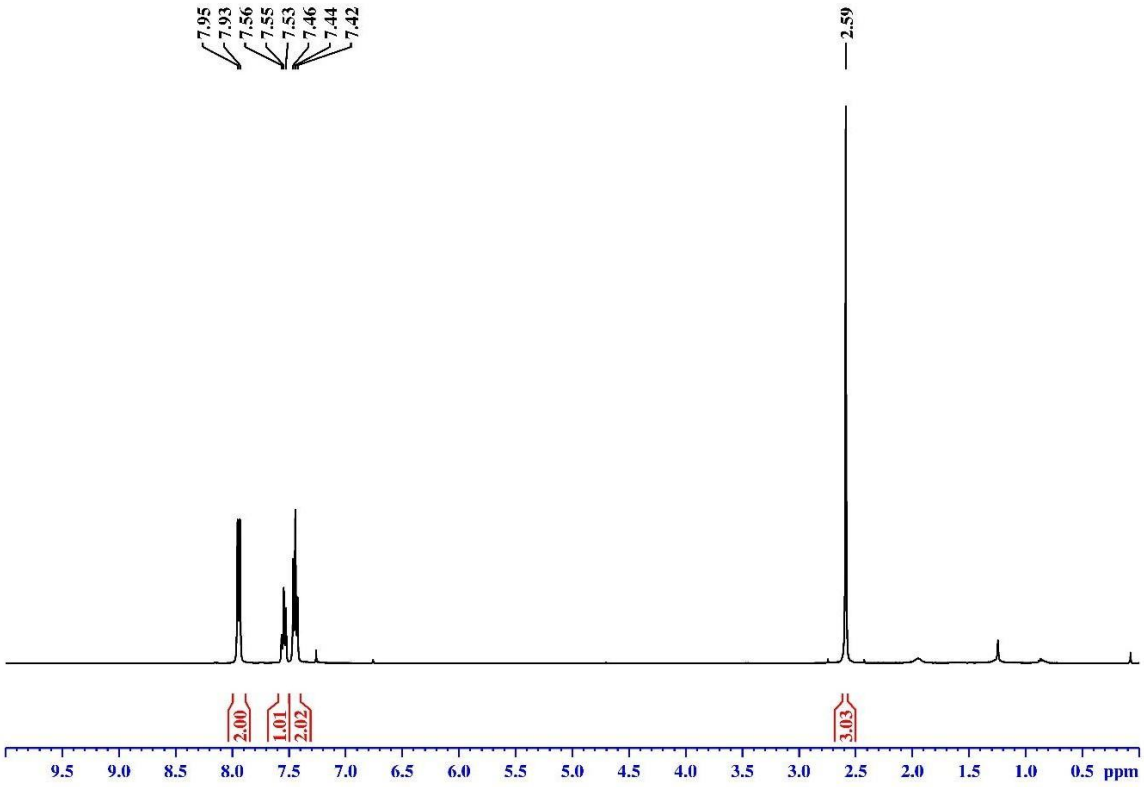
^{1}H NMR of yoghurt cup in $CDCl_3$



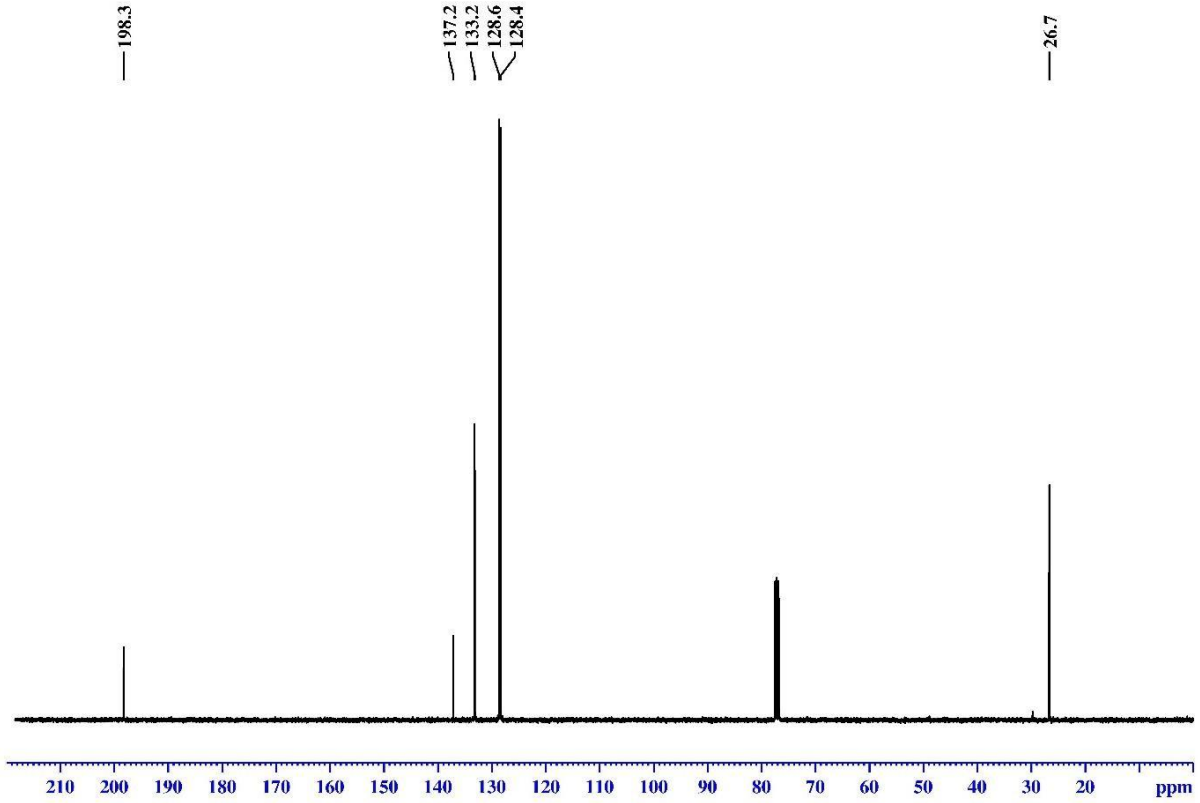
^{1}H NMR of plastic ruler in $CDCl_3$



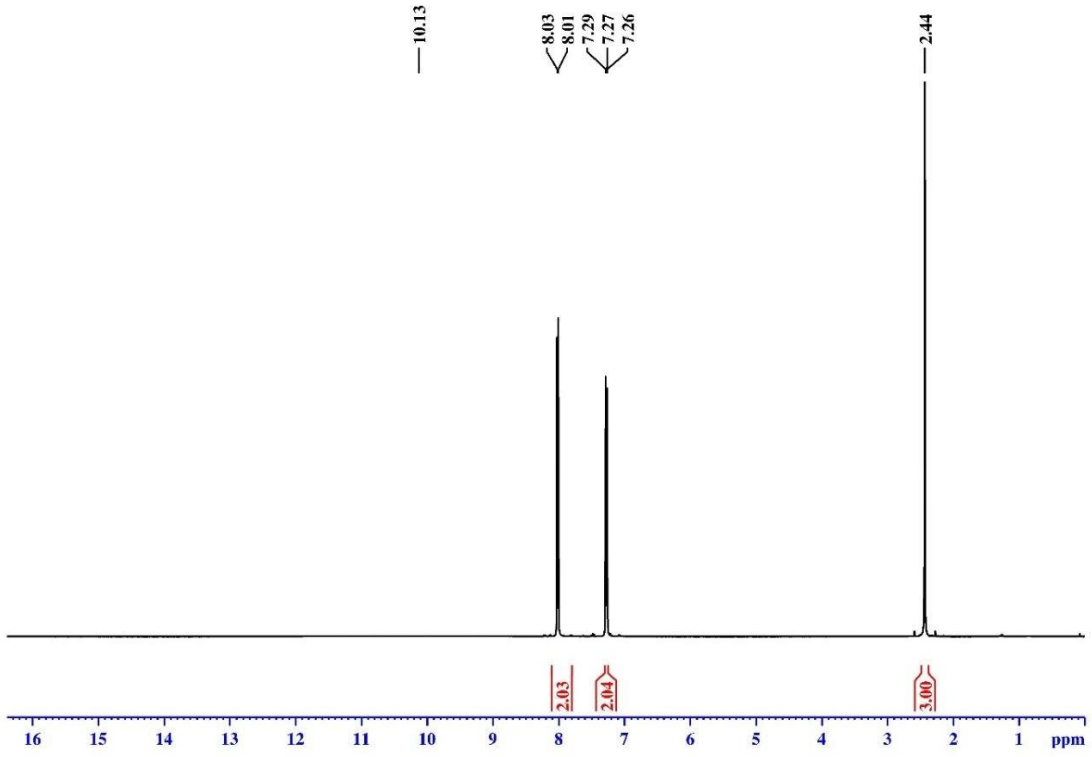
^{1}H NMR of acetophenone



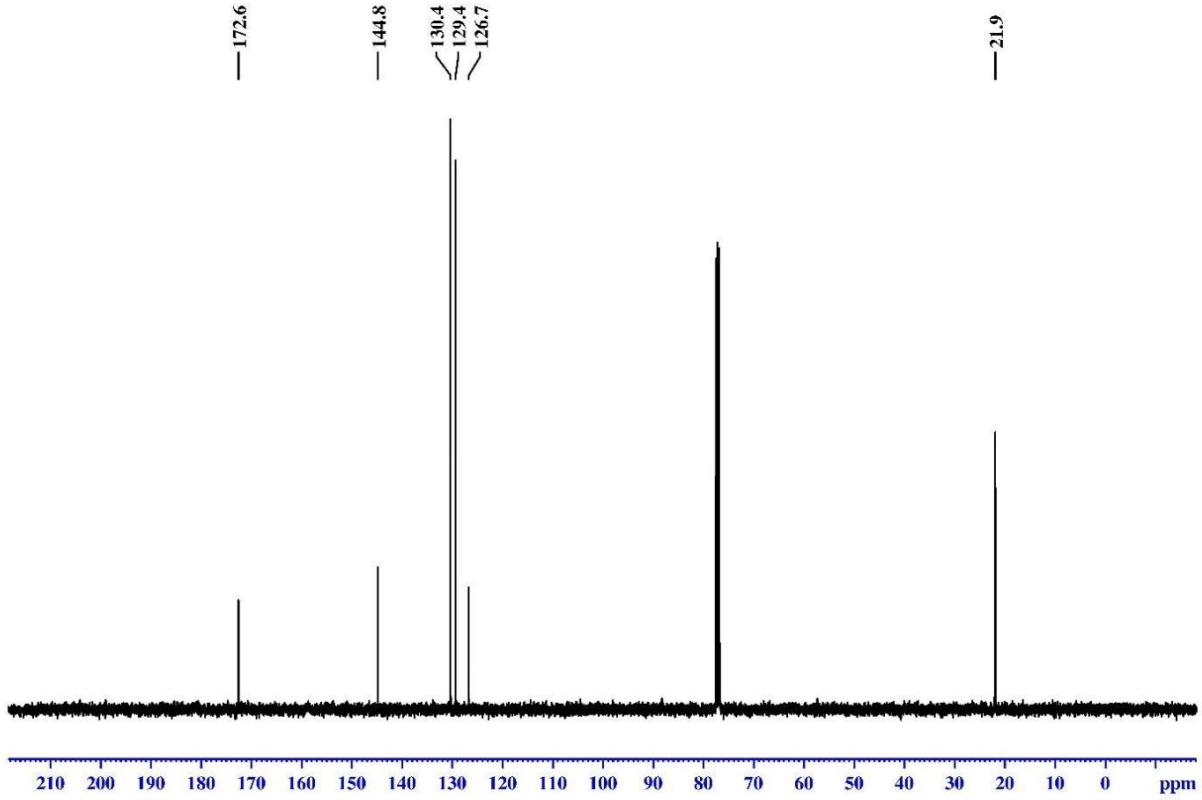
^{13}C NMR of acetophenone



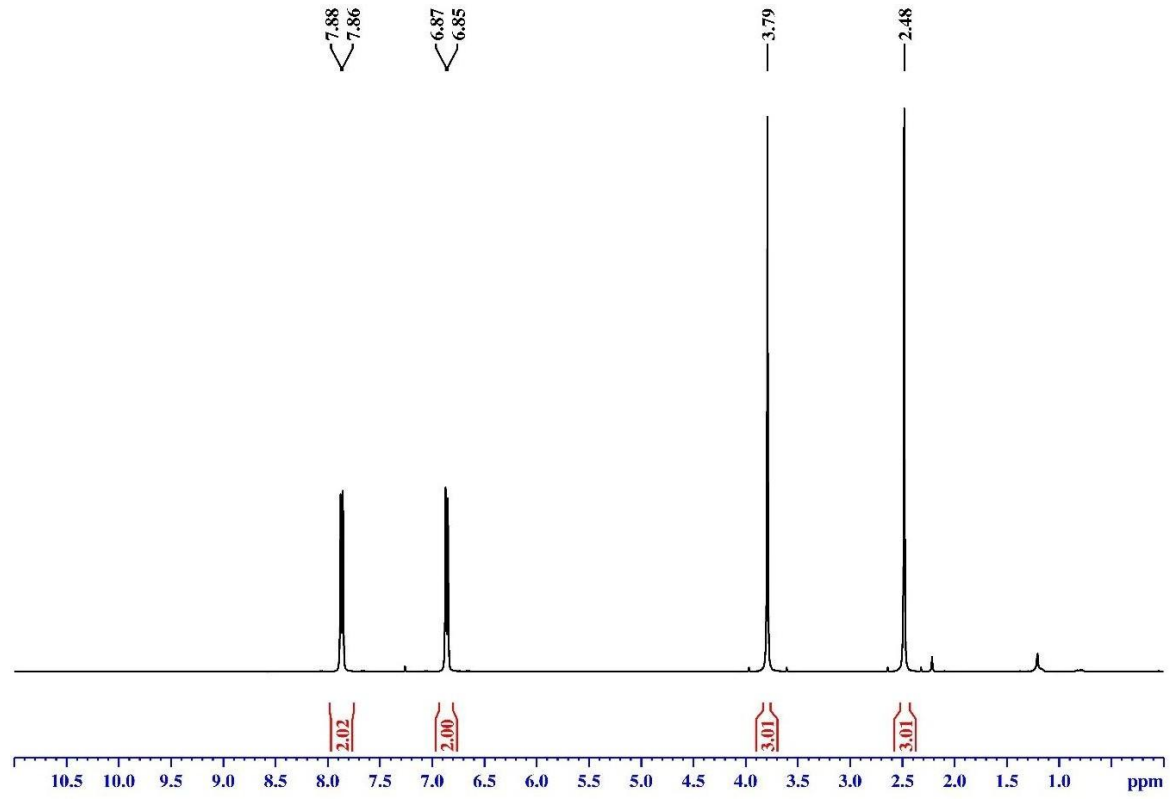
^{1}H NMR of p-Toluic acid



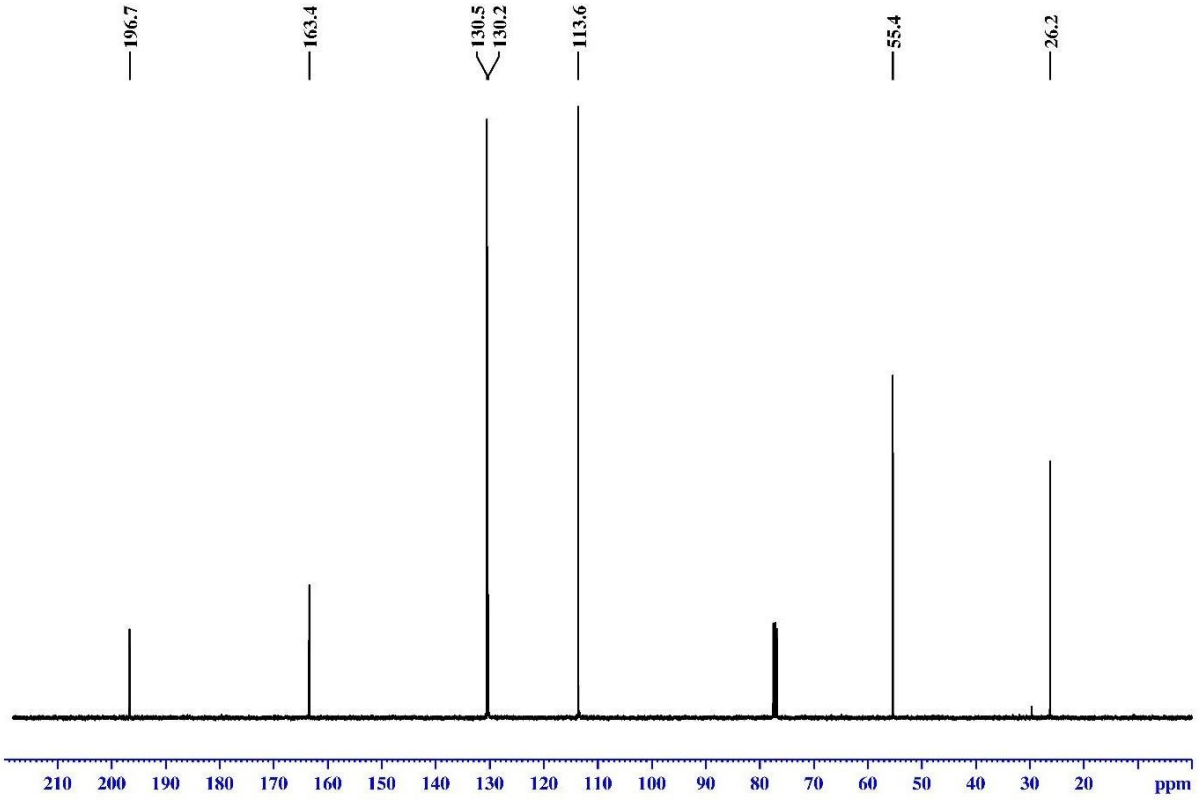
^{13}C NMR of p-Toluic acid



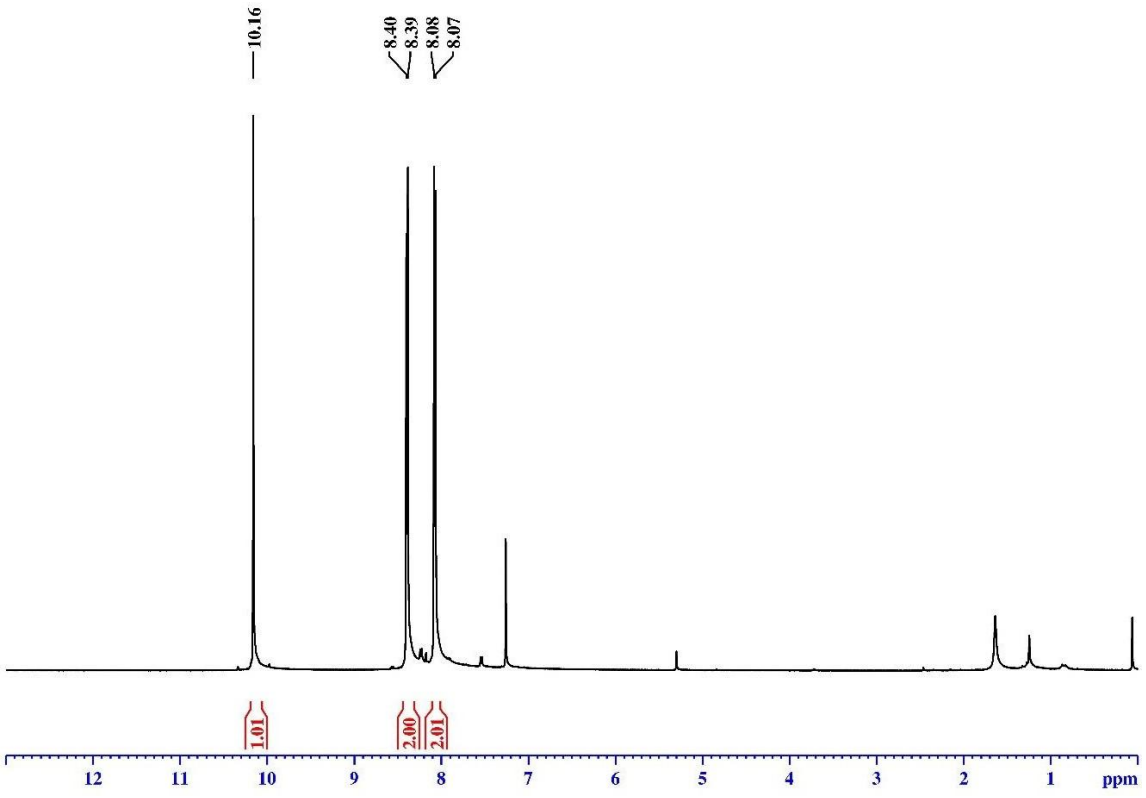
^{1}H NMR of 4-methoxyacetophenone



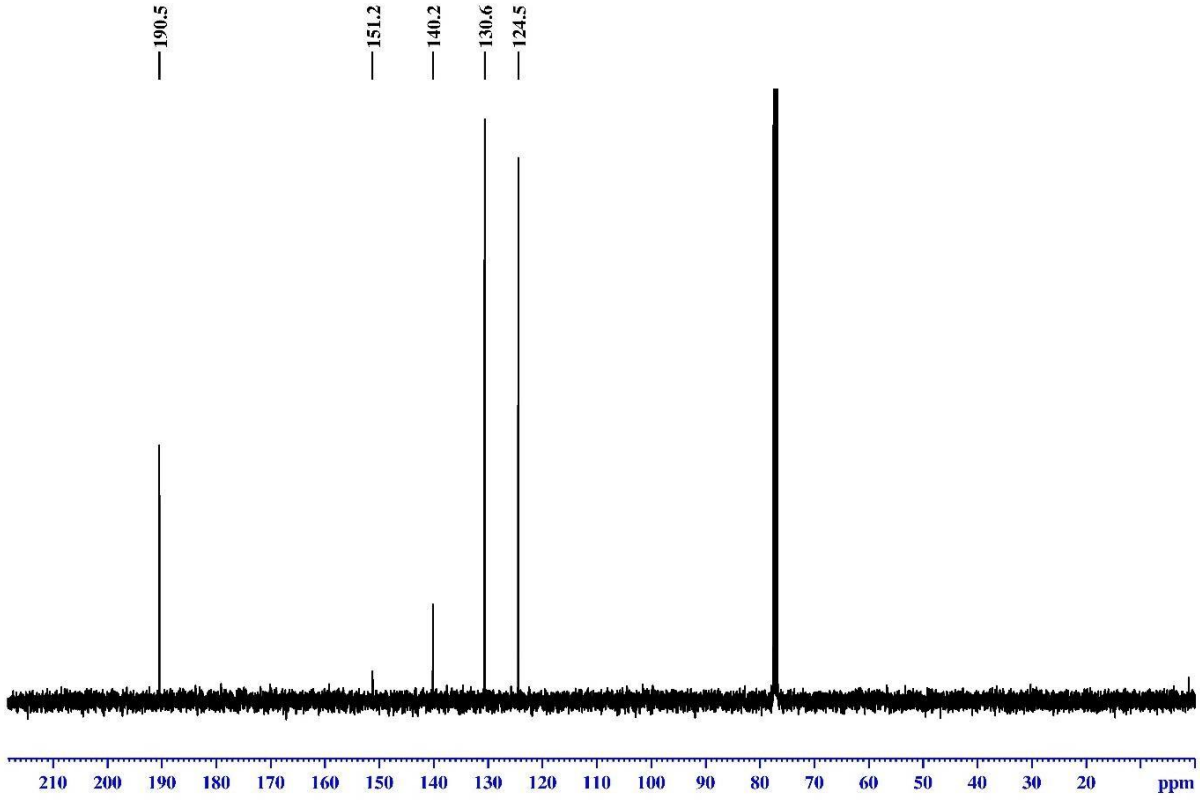
^{13}C NMR of 4-methoxyacetophenone



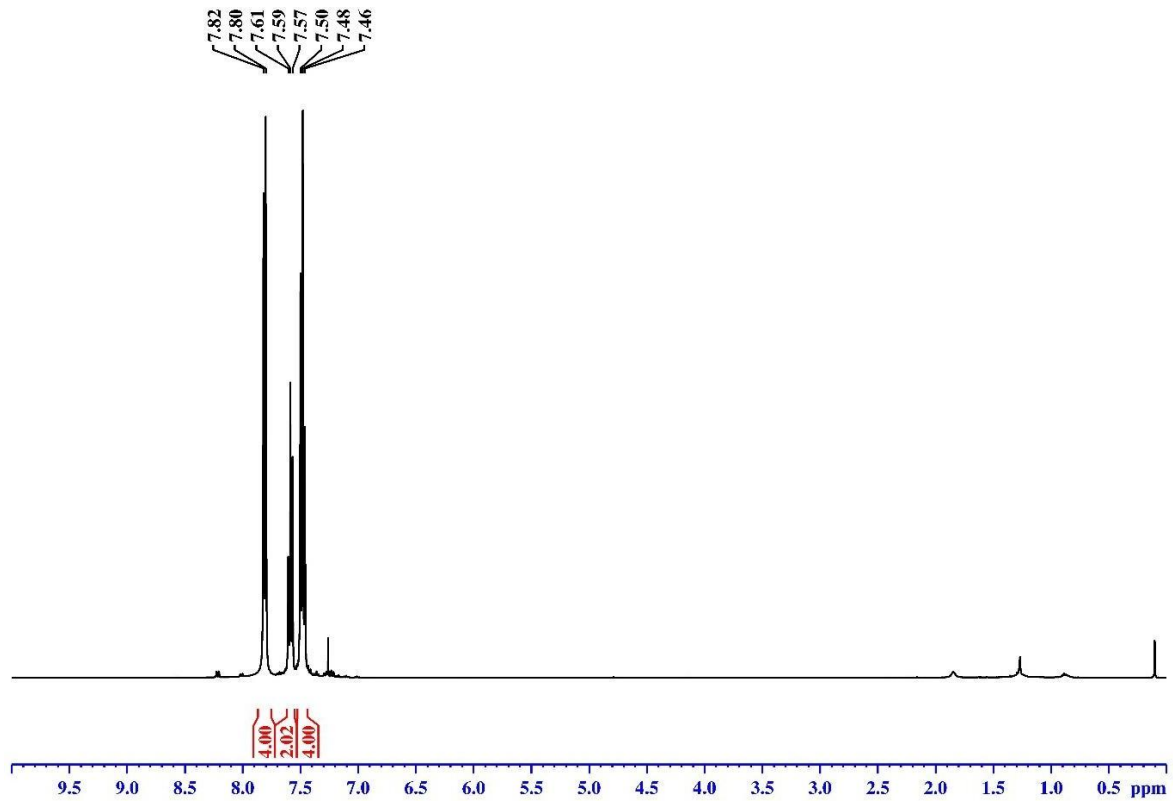
^{1}H NMR of 4-nitrobenzaldehyde



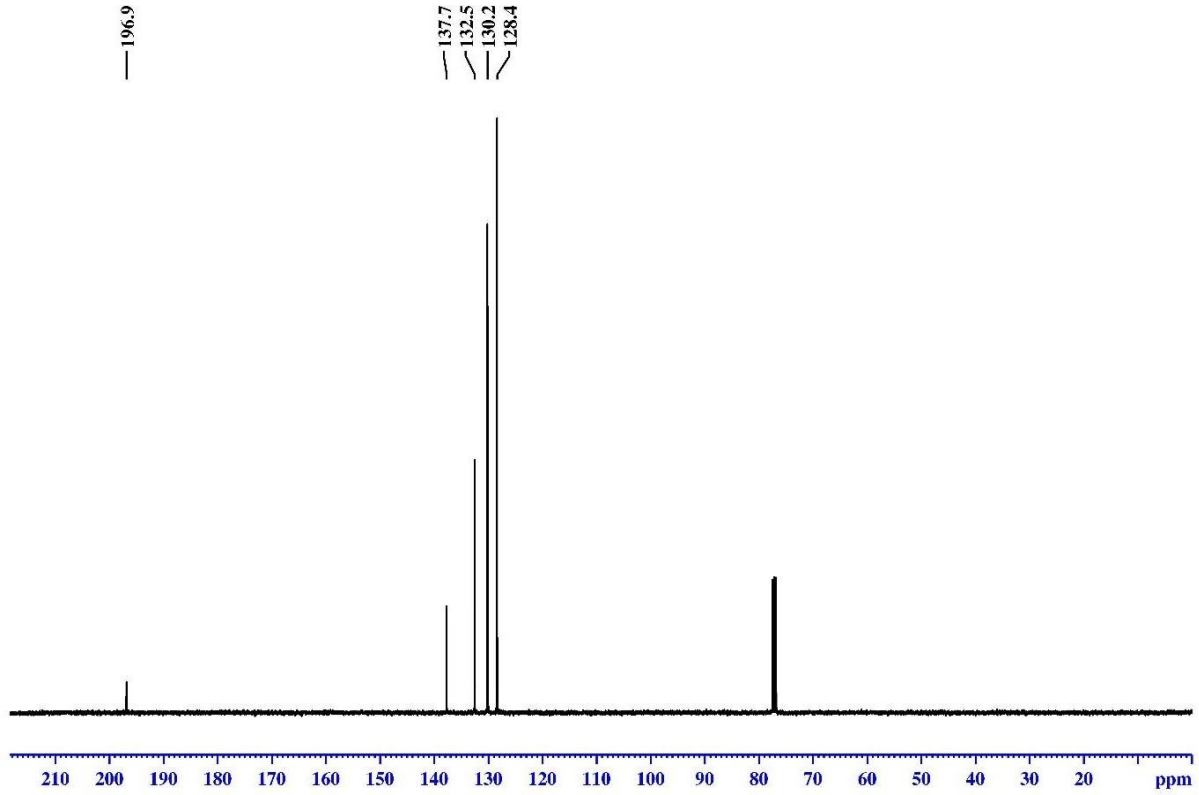
^{13}C NMR of 4-nitrobenzaldehyde



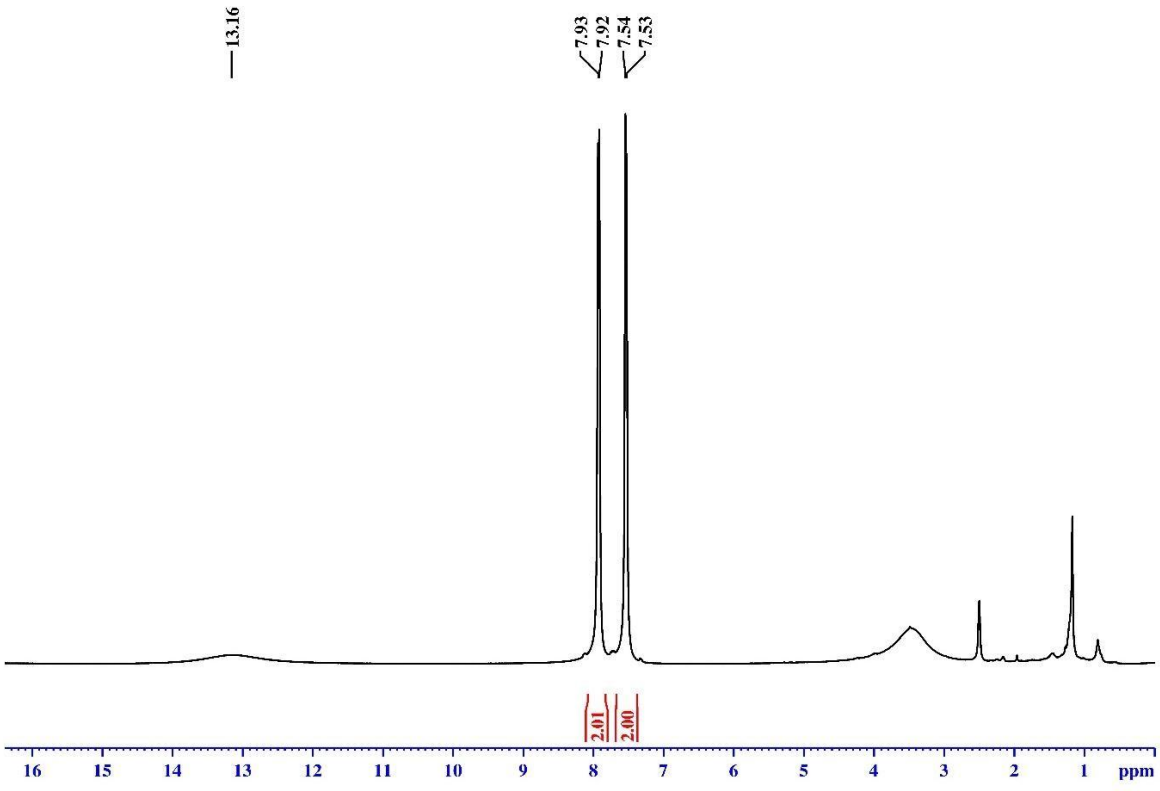
^{1}H NMR of benzophenone



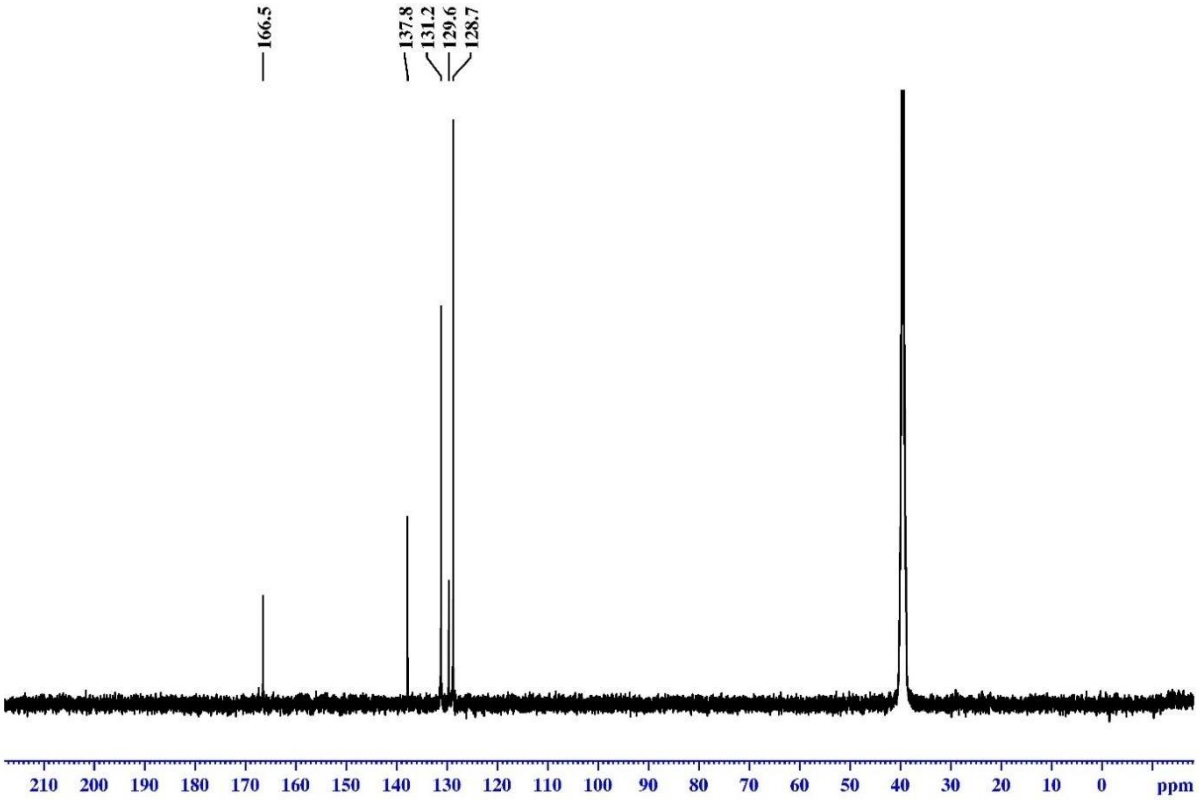
^{13}C NMR of benzophenone



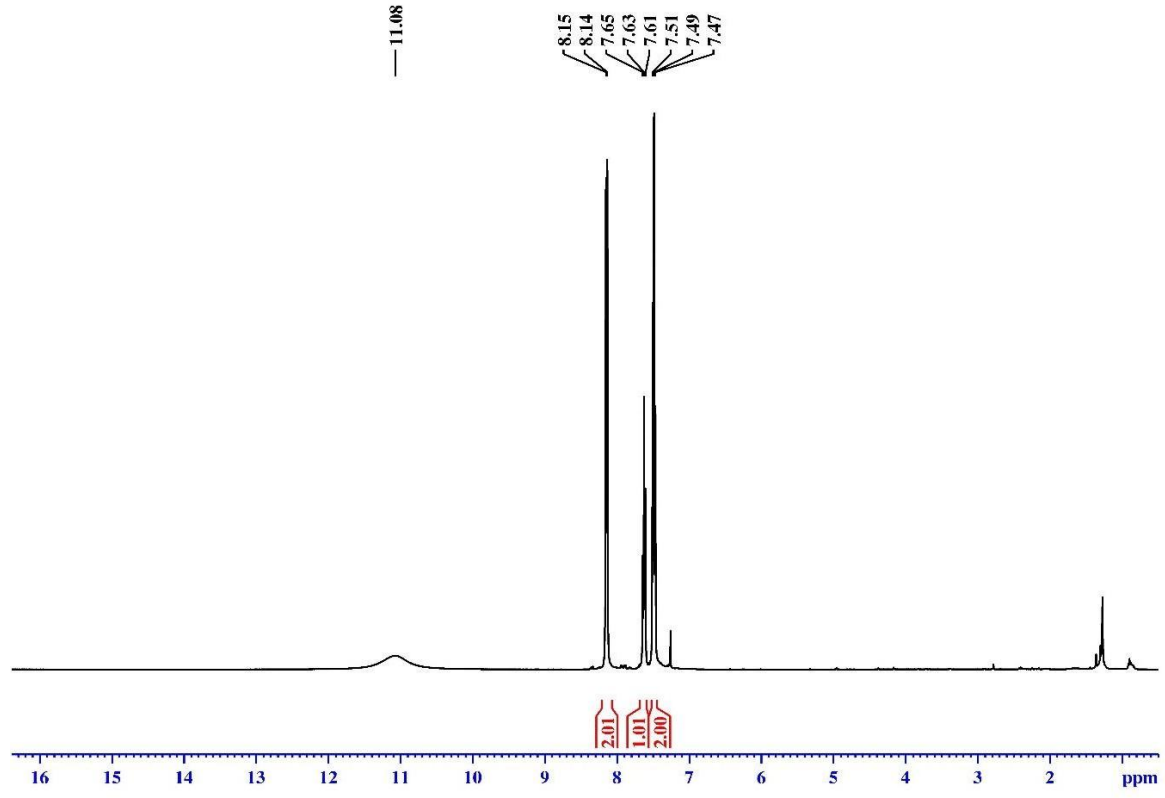
^{1}H NMR of 4-chlorobenzoic acid



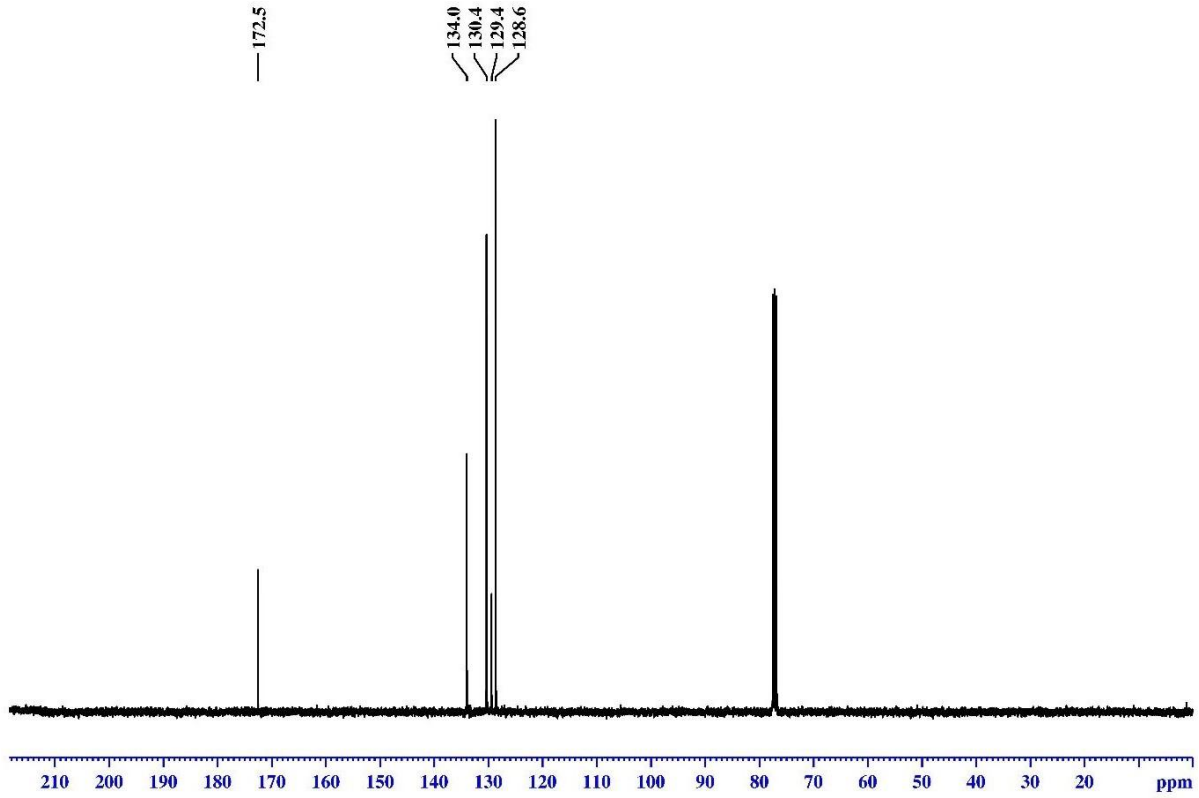
^{13}C NMR of 4-chlorobenzoic acid



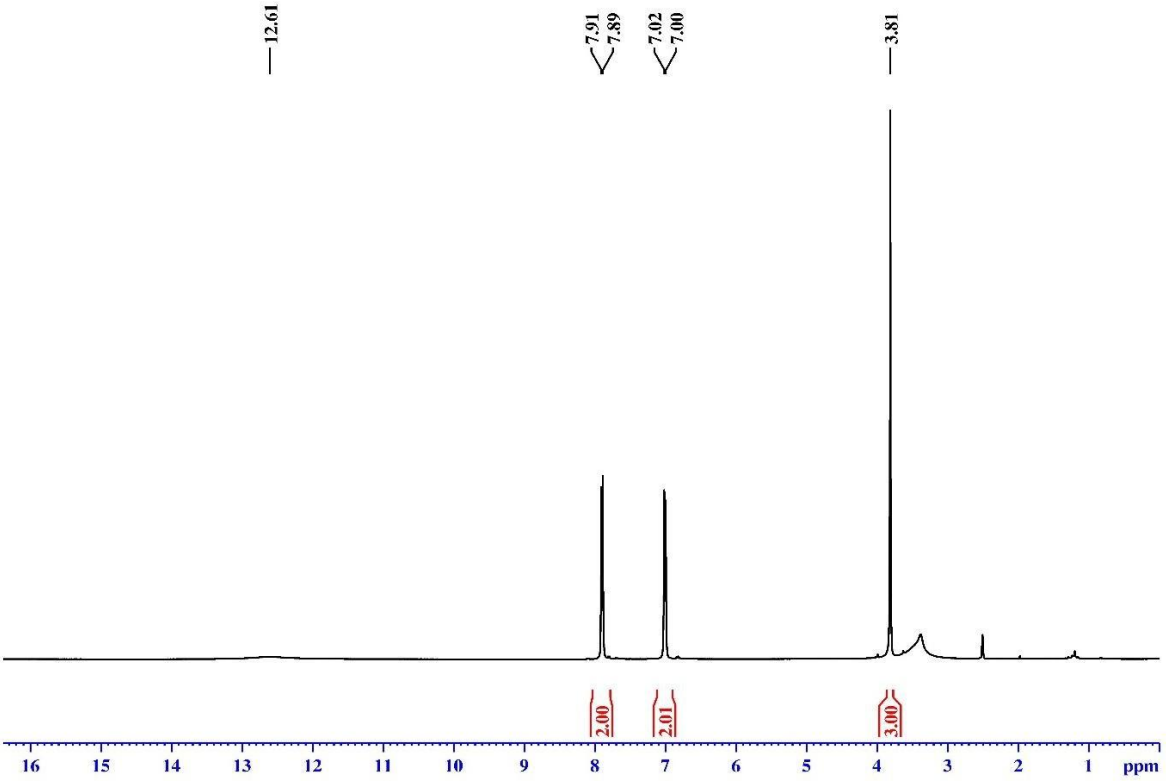
^{1}H NMR of benzoic acid



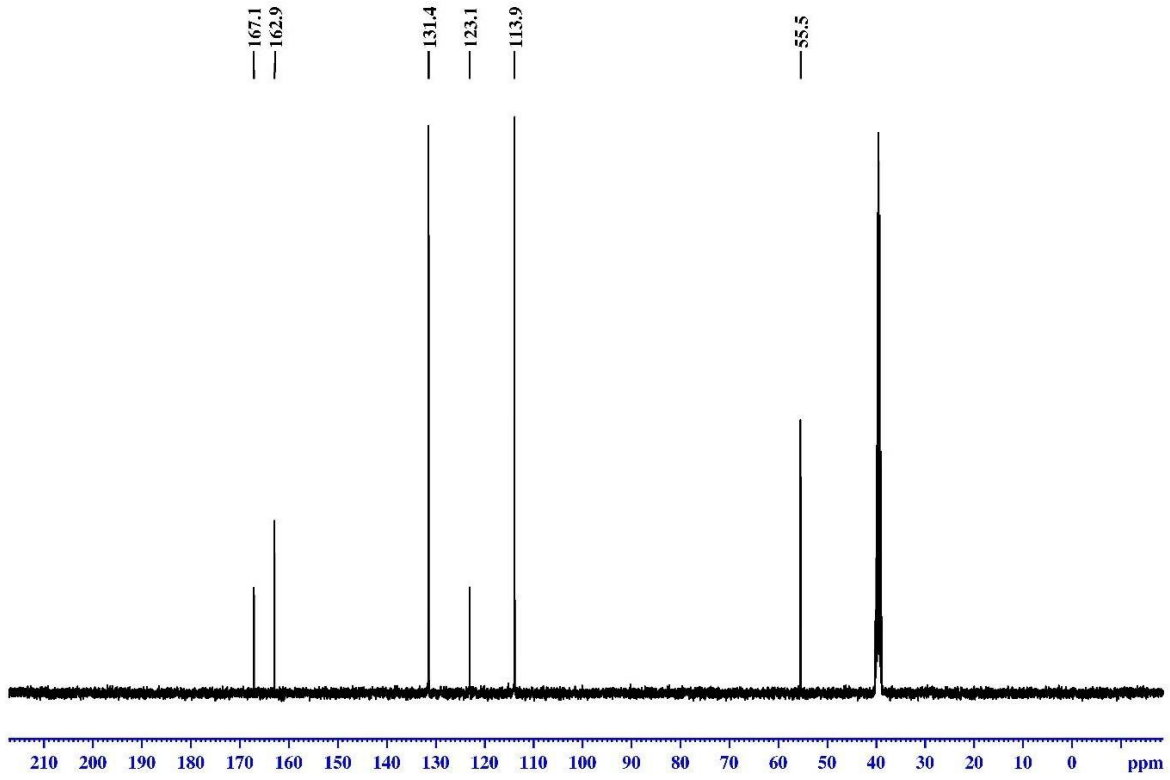
^{13}C NMR of benzoic acid



^{1}H NMR of 4-Methoxybenzoic acid



^{13}C NMR of 4-Methoxybenzoic acid



XVIII. References

1) https://www.ncbi.nlm.nih.gov/books/NBK591300/
2) J. Wm. Wackerly, J. F. Dunne, *J. Chem. Educ*. 2017, **94**, 1790-1793.
3) B. Ghorai, B. Sahana, D. P. Hari, *Angew. Chem. Int. Ed*. 2025, e202506747
4) J. Patra, A. M. Nair, C.M.R. Volla, *Chem. Sci*., 2024, **15**, 7136
5) C.G. Hatchard and C.A. Parker, *Proc. R. Soc. Lond*., 1956, **235**, 518–536
6) H.J. Kuhn, S.E. Braslavsky and R. Schmidt, Pure Appl. Chem., 2004, 76, 2105–2146.
7) *Gaussian 16 Rev*. *C.01*; Wallingford, CT, 2016.
8) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*. 2005, **7**, 3297-3305.
9) A. Schafer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* 1994, **100**, 5829-5835.
10) G. C. Tiu, F. M. Tao, *Chem. Phys. Lett*. 2006, **428**, 42-48.
11) R. J. O'Reilly, B. Chan, M. S. Taylor, S. Ivanic, G. B. Bacskay, C. J. Easton, L. Radom, *J. Am. Chem. Soc*. 2011, **133**, 16553-16559.
12) A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*. 2009, **113**, 6378-6396.
13) T. H. Dunning, *J. Chem. Phys.* 1989, **90**, 1007– 1023.
14) J. G. Hill, *Int. J. Quantum Chem*. 2013, **113**, 21-34.
15) S. Hirata, M. H. Gordon, *Chem. Phys. Lett*. 1999, **314**, 291-299.
16) M. C. DeRosa, R. J. Crutchley, *Coord. Chem. Rev*. 2002, **233-234**, 351-371.