Supporting Information

Highly Effective C-C Bond Cleavage of Lignin Model Compounds

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I. General information

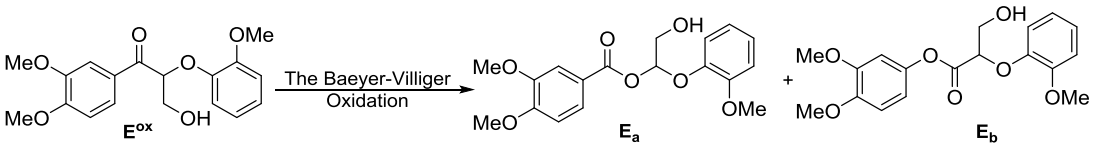
All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, a high-vacuum line, or an argon-filled glovebox. NMR spectra were recorded on a Bruker Avance II 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C) instrument at room temperature. Chemical shifts for ^{1}H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million relative to $SiMe_4$.

2-Bromoacetophenone, guaiacol, diisopropylamine, *n*-BuLi (1.6 M solution in hexanes), 3,4-dimethoxybenzaldehyde, 2-bromo-4'-methoxyacetophenone, and the standard substances methyl benzoate (**1**), phenol (**2**), 2-methoxyphenol (**3**), methyl 4-methoxybenzoate (**4**), methyl 3,4-dimethoxybenzoate (**5**), 4-methoxyphenol (**7**), 3,4-dimethoxyphenol (**9**), benzyl alcohol (**11**), methyl phenylacetate (**12**), diphenylethanone (**F^{ox}**), and benzyl benzoate (**F$_{a'}$**) were purchased from J&K. $(PhCH_2Se)_2$ was purchased from TCI. 4-acetamido-TEMPO, sodium borohydride, ethyl (2-methoxyphenoxy)acetate, m-CPBA, 36 wt% H_2O_2, inorganic salts and solvents were purchased from Titan. All of chemicals were used as received unless otherwise specified as follows. THF were dried over sodium/potassium alloy distilled under nitrogen atmosphere prior to use for the synthesis of lignin model compound **E^{ox}**. The oxidized lignin model compounds **A^{ox}**, [1] **B^{ox}**, [1] **C^{ox}**, [1] **D^{ox}**, [2] and **E^{ox}** [3] were prepared according to a literature procedure.

Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV); column chromatography purifications were carried out using silica gel. The reaction mixture was analyzed using Waters High Performance Liquid Chromatograph (HPLC) system equipped with autosampler, C18 column (Length: 150mm, Internal diameter: 4.6mm, 35 ˚C) and UV/Vis detector (λ = 220 nm). CH_3CN: H_2O (60:40 or 35:65) was used as a mobile phase for Baeyer-Villiger Oxidation products; CH_3OH: H_2O (55:45 or 35:65) was used as a mobile phase for transesterification products with a flow rate of 1.0 mL/min. Mass spectra were recorded on the Bruker MicroTOF Q II.

II. BV oxidation of oxidized lignin model compounds

Table S1. The Baeyer-Villiger Oxidation of **E^{ox}**



Entry	m-CPBA[a] (eq.)	H_2O_2[b] (eq.)	$(PhCH_2Se)_2$ (mol%)	$NaHCO_3$ (eq.)	Solvent	Time (h)	Conv. (%)[c]	Yield (%)[c] E_a	Yield (%)[c] E_b
1	1	-	-	1	CH_2Cl_2	20	88	33	51
2	2	-	-	2	CH_2Cl_2	15	>99	26	66
3	3	-	-	3	CH_2Cl_2	8	>99	35	57
4	-	2	5	-	THF	12	74	31	43
5	-	3	5	-	THF	19	90	37	33
						24	>99	30	38

6	-	4	5	-	THF	12	81	37	37
7	-	4	5	-	THF	24	>99	37	44
8	-	4	10	-	THF	12	88	31	41
9	-	4	20	-	THF	6	82	32	35
10	-	6	5	-	THF	12	97	33	41

[a]Condition: substrate (0.1 mmol, 1.0 eq.), m-CPBA, $NaHCO_3$, 2 mL CH_2Cl_2, at room temperature (~ 25 ˚C). [b]Condition: substrate (0.1 mmol, 1.0 eq.), 36 wt% H_2O_2, $(PhCH_2Se)_2$, 0.5 ml THF, reflux. [c]The yields and conversions were measured by HPLC.

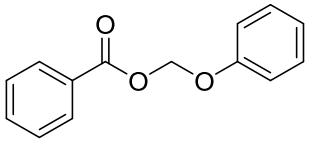
1. General procedure for BV oxidation by m-CPBA

The oxidized model compound (0.1 mmol), m-CPBA (0.2 mmol, 2 eq.) and $NaHCO_3$ (0.2 mmol, 2 eq.) were added to a 5 mL round bottom flask equipped with a stirring bar, subsequently added CH_2Cl_2 (2 mL). The flask was stirred at room temperature for the specified reaction time. Using acetonitrile, the mixture was dissolved to constant volume in a 50 mL volumetric flask and then filtered. The filtrate was measured by HPLC.

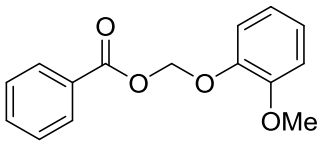
2. General procedure for BV oxidation by H_2O_2

The oxidized model compound (0.1 mmol) and $(PhCH_2Se)_2$ (5 mmol%) were added to a 5 mL round bottom flask equipped with a magnetic stirring bar. THF (0.5 mL) was subsequently added, followed by the addition of H_2O_2 (36 wt% in H_2O) as oxidant. After equipped with a reflux condenser, the mixture was heated to the desired temperature and stirred for the specified reaction time. Using acetonitrile, the mixture was dissolved to constant volume in a 50 mL volumetric flask and then filtered. The filtrate was measured by HPLC.

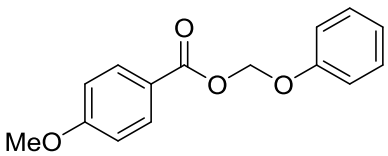
phenoxymethyl benzoate (A_a): Light yellow liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 8.3, 1.3 Hz, 2H, *Ar*), 7.58 (t, *J* = 7.3 Hz, 1H, *Ar*), 7.44 (t, *J* = 8.0 Hz, 2H, *Ar*), 7.35 – 7.31 (m, 2H, *Ar*), 7.12 (d, *J* = 8.5 Hz, 2H, *Ar*), 7.07 (t, *J* = 7.3 Hz, 1H, *Ar*), 6.03 (s, 2H, C*H*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165. 6, 157.1, 133.6, 130.0, 129.8, 129.5, 128.6, 122.9, 116.3, 86.4. HRMS (ESI) calculated for $C_{14}H_{13}O_3$ $[M + H]^+$ 229.0859, found 229.0822.



(2-methoxyphenoxy) methyl benzoate (B_a): Light yellow liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 8.0, 1.5 Hz, 2H, *Ar*), 7.57 (t, *J* = 7.5 Hz, 1H, *Ar*), 7.44 (t, *J* = 7.8 Hz, 2H, *Ar*), 7.15 (dd, *J* = 7.8, 1.3 Hz, 1H, *Ar*), 7.07 (td, *J* = 7.8, 1.5 Hz, 1H, *Ar*), 6.94 – 6.90 (m, 2H, *Ar*), 6.03 (s, 2H, C*H*$_2$), 3.84 (s, 3H, OC*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 150.5, 146.2, 133.5, 130.0, 129.7, 128.5, 124.2, 121.0, 118.0, 112.4, 87.9, 55.9. HRMS (ESI) calculated for $C_{15}H_{15}O_4$ $[M + H]^+$ 259.0965, found 259.1004.

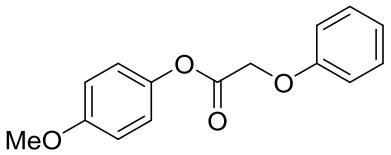


phenoxymethyl 4-methoxybenzoate (C_a): Light yellow liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 9.0 Hz, 2H, *Ar*), 7.33 (t, *J* = 8.0 Hz, 2H, *Ar*), 7.11 (d, *J* = 8.0 Hz, 2H, *Ar*), 7.06 (t, *J* = 7.5 Hz, 1H, *Ar*), 6.92 (d, *J* = 9.0 Hz, 2H, *Ar*), 6.00 (s, 2H, C*H*$_2$), 3.86 (s, 3H, OC*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 163.9, 157.1, 132.1, 129.7, 122.8, 121.8, 116.3, 113.9, 86.2, 55.6. HRMS (ESI)

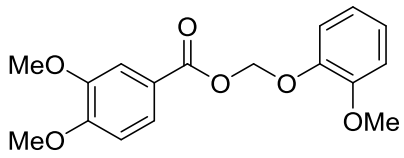


calculated for $C_{15}H_{15}O_4$ [M + H]$^+$ 259.0965, found 259.0945.

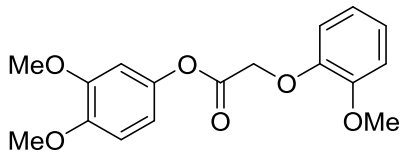
4-methoxyphenyl 2-phenoxyacetate (C_b): White crystal solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 7.8 Hz, 2H, *Ar*), 7.04 – 7.02 (m, 3H, *Ar*), 6.99 (d, *J* = 8.0 Hz, 2H, *Ar*), 6.89 (d, *J* = 9.0 Hz, 2H, *Ar*), 4.85 (s, 2H, C*H*$_2$), 3.79 (s, 3H, OC*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 157.8, 157.6, 143.7, 129.7, 122.1, 122.0, 114.9, 114.6, 65.5, 55.6. HRMS (ESI) calculated for $C_{15}H_{15}O_4$ [M + H]$^+$ 259.0965, found 259.0945.



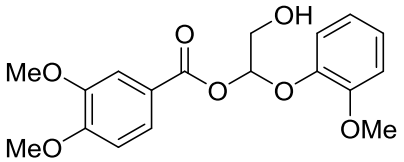
(2-methoxyphenoxy)methyl 3,4-dimethoxybenzoate (D_a): Light yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.5 Hz, 1H, *Ar*), 7.47 (s, 1H, *Ar*), 7.06 (d, *J* = 7.5 Hz, 1H, *Ar*), 6.98 (t, *J* = 7.8 Hz, 1H, *Ar*), 6.84 (t, *J* = 7.8 Hz, 2H, *Ar*), 6.79 (d, *J* = 8.5 Hz, 1H, *Ar*), 5.92 (s, 2H, C*H*$_2$), 3.85 (s, 3H, OC*H*$_3$), 3.82 (s, 3H, OC*H*$_3$), 3.76 (s, 3H, OC*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 153.4, 150.4, 148.6, 146.0, 124.04, 124.00, 121.9, 120.8, 117.9, 112.2, 112.1, 110.3, 87.5, 56.00, 55.97, 55.8. HRMS (ESI) calculated for $C_{17}H_{19}O_6$ [M + H]$^+$ 319.1176, found 319.1164.



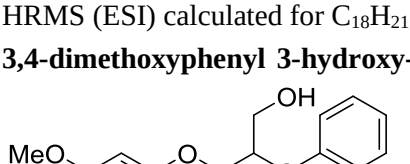
3,4-dimethoxyphenyl 2-(2-methoxyphenoxy)acetate (D_b): White crystal solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.04 – 7.01 (m, 1H, *Ar*), 6.99 – 6.90 (m, 3H, *Ar*), 6.83 (d, *J* = 8.5 Hz, 1H, *Ar*), 6.68 – 6.64 (m, 2H, *Ar*), 4.92 (s, 2H, C*H*$_2$), 3.90 (s, 3H, OC*H*$_3$), 3.86 (s, 3H, OC*H*$_3$), 3.84 (s, 3H, OC*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 150.0, 149.4, 147.2, 147.1, 143.8, 123.0, 120.9, 115.3, 112.7, 112.4, 111.2, 105.5, 66.9, 56.2, 56.1, 56.0. HRMS (ESI) calculated for $C_{17}H_{19}O_6$ [M + H]$^+$ 319.1176, found 319.1139.



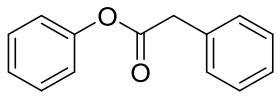
2-hydroxy-1-(2-methoxyphenoxy)ethyl 3,4-dimethoxybenzoate (E_a): red oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 (dd, *J* = 8.5, 2.0 Hz, 1H, *Ar*), 7.51 (d, *J* = 2.0 Hz, 1H, *Ar*), 7.10 (dd, *J* = 8.0, 2.0 Hz, 1H, *Ar*), 7.03 (td, *J* = 7.5, 1.5 Hz, 1H, *Ar*), 6.88 (d, *J* = 8.0 Hz, 1H, *Ar*), 6.85 – 6.81 (m, 2H, *Ar*), 6.59 (dd, *J* = 6.0, 4.0 Hz, 1H, C*H*), 4.06 (dd, *J* = 12.0, 6.0 Hz, 1H, C*H*$_2$), 3.98 (dd, *J* = 11.5, 4.0 Hz, 1H, C*H*$_2$), 3.89 (s, 3H, OC*H*$_3$), 3.87 (s, 3H, OC*H*$_3$), 3.80 (s, 3H, OC*H*$_3$), 3.48 (b s, 1H, O*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9, 153.3, 150.6, 148.5, 145.1, 124.6, 124.0, 121.5, 120.9, 119.9, 112.1, 112.0, 110.1, 97.2, 63.0, 55.82, 55.81, 55.6. HRMS (ESI) calculated for $C_{18}H_{21}O_7$ [M + H]$^+$ 349.1282, found 349.1270.



3,4-dimethoxyphenyl 3-hydroxy-2-(2-methoxyphenoxy)propanoate (E_b): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.10 (dd, *J* = 8.0, 1.5 Hz, 1H, *Ar*), 7.05 (td, *J* = 8.0, 1.5 Hz, 1H, *Ar*), 6.95 – 6.89 (m, 2H, *Ar*), 6.81 (d, *J* = 8.5 Hz, 1H, *Ar*), 6.65 – 6.62 (m, 2H, *Ar*), 4.90 (t, *J* = 4.3 Hz, 1H, C*H*), 4.20 (d, *J* = 4.5 Hz, 2H, C*H*$_2$), 3.87 (s, 3H, OC*H*$_3$), 3.84 (s, 3H, OC*H*$_3$), 3.82 (s, 3H, OC*H*$_3$), 3.61 (b s, 1H, O*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 150.6, 149.4, 147.1, 146.8, 143.9, 124.0, 121.2, 118.8, 112.7, 112.5, 111.2, 105.5, 80.7, 63.3, 56.2, 56.0, 55.9. HRMS (ESI) calculated for $C_{18}H_{21}O_7$ [M + H]$^+$ 349.1282, found 349.1258.



phenyl 2-phenylacetate (F_b): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 6H, *Ar*), 7.30 (t, *J* = 6.8 Hz, 1H, *Ar*), 7.20 (t, *J* = 7.5 Hz, 1H, *Ar*), 7.05 (d, *J* = 7.5 Hz, 2H, *Ar*), 3.85 (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 150.9, 133.6, 129.5, 129.4, 128.9, 127.5, 126.0, 121.6, 41.6.

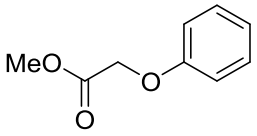


III. Alcoholysis of BV oxidation products

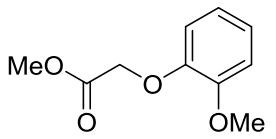
1. General procedure for alcoholysis

BV oxidation product (0.1 mmol, 1.0 eq.) and K_2CO_3 (0.02 mmol, 0.2 eq.) were added to a 5 mL round bottom flask equipped with a magnetic stirring bar, followed by adding CH_3OH (0.5 mL) and stirring at 45 ˚C for 1.5 h. Using methanol, the mixture was dissolved to constant volume in a 50 mL volumetric flask and then filtered. The filtrate was measured by HPLC.

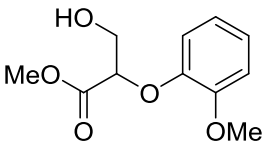
methyl 2-phenoxyacetate (6): Colorless liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.3 Hz, 2H, *Ar*), 7.00 (t, *J* = 7.5 Hz, 1H, *Ar*), 6.91 (d, *J* = 7.5 Hz, 2H, *Ar*), 4.65 (s, 2H, CH_2), 3.81 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 157.9, 129.7, 121.9, 114.7, 65.4, 52.4. HRMS (ESI) calculated for $C_9H_{11}O_3$ $[M + H]^+$ 167.0703, found 167.0676.



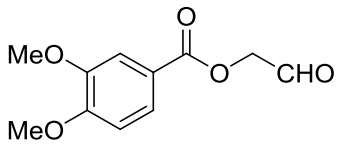
methyl 2-(2-methoxyphenoxy)acetate (8): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.99 (t, *J* = 7.5 Hz, 1H, *Ar*), 6.92 – 6.84 (m, 3H, *Ar*), 4.70 (s, 2H, CH_2), 3.88 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 149.7, 147.2, 122.6, 120.7, 114.5, 112.1, 66.5, 55.9, 52.1. HRMS (ESI) calculated for $C_{10}H_{13}O_4$ $[M + H]^+$ 197.0808, found 197.0804.



methyl 3-hydroxy-2-(2-methoxyphenoxy)propanoate (10): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.07 – 7.01 (m, 2H, *Ar*), 6.93 – 6.88 (m, 2H, *Ar*), 4.67 (dd, *J* = 5.5, 4.0 Hz, 1H, C*H*), 4.03 – 4.00 (m, 2H, CH_2), 3.87 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.11 (t, *J* = 6.8 Hz, 1H, O*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 150.5, 147.0, 123.9, 121.3, 118.4, 112.4, 80.9, 63.2, 56.0, 52.5. HRMS (ESI) calculated for $C_{11}H_{15}O_5$ $[M + H]^+$ 227.0914, found 227.0892.



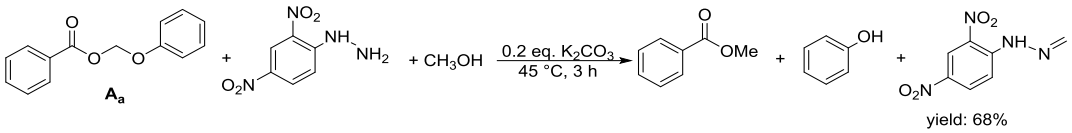
2-oxoethyl 3,4-dimethoxybenzoate (13): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.66 (s, 1H, C*H*O), 7.70 (dd, *J* = 8.5, 1.5 Hz, 1H, *Ar*), 7.52 (d, *J* = 2.0 Hz, 1H, *Ar*), 6.85 (d, *J* = 8.5 Hz, 1H, *Ar*), 4.80 (s, 2H, CH_2), 3.89 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 165.8, 153.6, 148.8, 124.2, 121.3, 112.2, 110.4, 69.0, 56.12, 56.08. HRMS (ESI) calculated for $C_{11}H_{13}O_5$ $[M + H]^+$ 225.0757, found 225.0730.



2. Capture and characterization of formaldehyde by HPLC

To a 5 mL round bottom flask, $\mathbf{A_a}$ (0.1 mmol, 1.0 eq.), K_2CO_3 (0.2 eq.) and 2,4-dinitrophenylhydrazine (1.5 eq.) were added, followed by adding 0.5mL of CH_3OH and

stirring at 45 ºC for 3 h. Using methanol, the mixture was dissolved to constant volume in a 50 mL volumetric flask and then filtered. The filtrate was measured by HPLC. CH_3CN: H_2O (60:40) was used as a mobile phase with a flow rate of 1.0 mL/min and UV/Vis detector (λ = 360 nm).



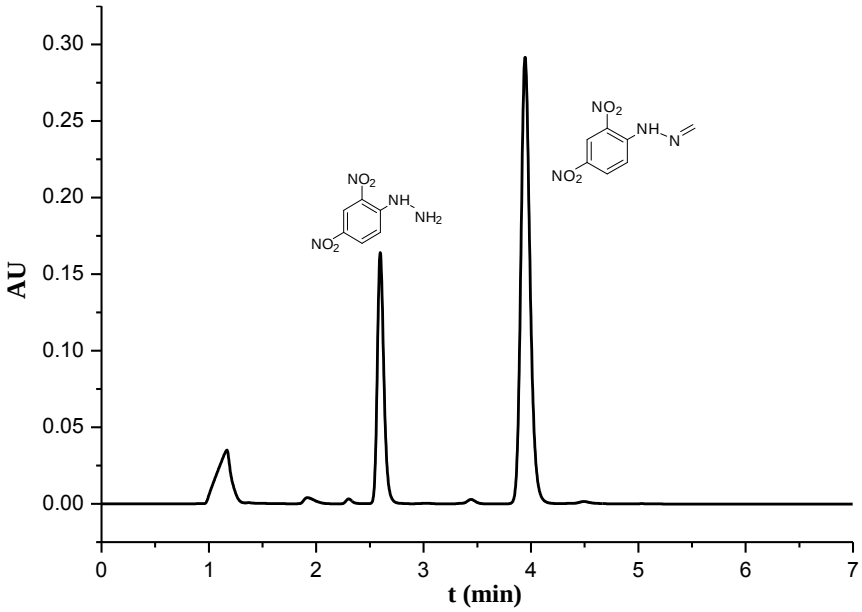
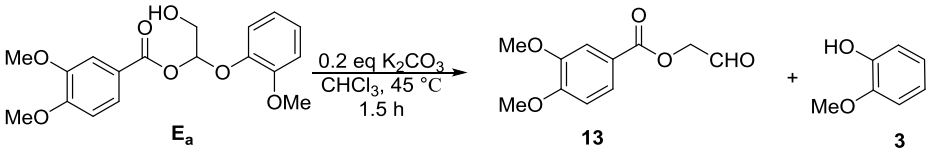


Figure S1. Characterization of captured formaldehyde by HPLC

3. Intramolecular alcoholysis of $\mathbf{E_a}$



BV Oxidation product $\mathbf{E_a}$ (0.1 mmol, 1.0 eq.) and K_2CO_3 (0.2 eq.) were added to a 5 mL round bottom flask, followed by adding $CHCl_3$ and stirring at 45 ºC for specified reaction time. Using methanol, the mixture was dissolved to constant volume in a 50 mL volumetric flask and then filtered. The filtrate was measured by HPLC.

4. In situ NMR reaction of $\mathbf{A_a}$ or $\mathbf{C_b}$

A NMR tube is charged with $\mathbf{A_a}$ or $\mathbf{C_b}$ (0.1 mmol, 1.0 eq.) and K_2CO_3 (0.2 eq.), then 0.6 mL of CD_3OD was subsequently added. The tube was heated at 45 ºC and monitored by ^1H NMR.

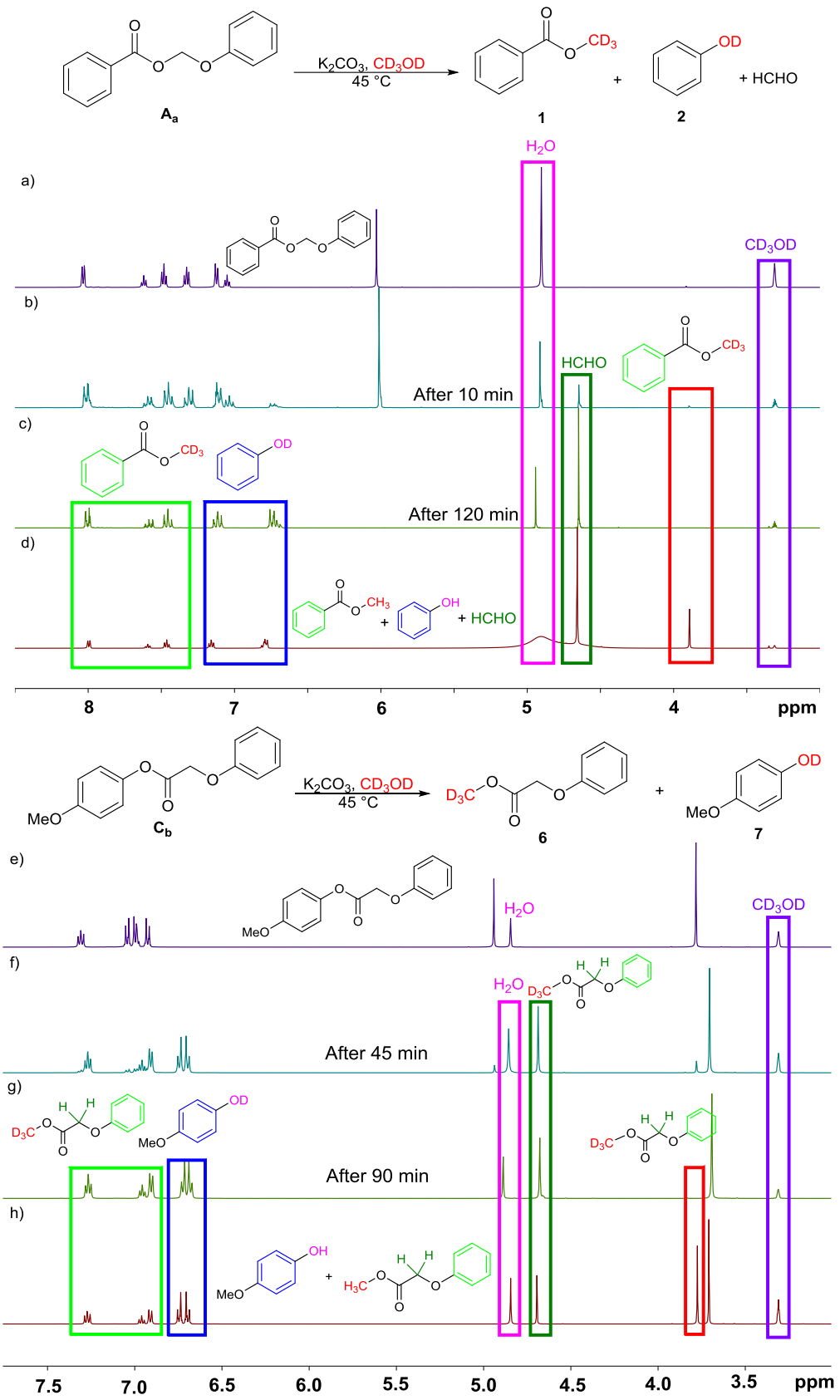
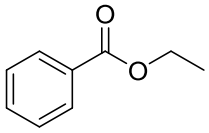


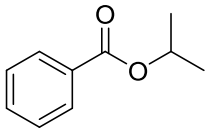
Figure S2. The NMR spectra of a) substrate $\mathbf{A_a}$; b) alcoholysis of $\mathbf{A_a}$ at 10 min; c) alcoholysis of $\mathbf{A_a}$ at 120 min; and d) mixing methyl benzoate (**1**), phenol (**2**) and formaldehyde; e) substrate $\mathbf{C_b}$; f) alcoholysis of $\mathbf{C_b}$ at 45 min; g) alcoholysis of $\mathbf{C_b}$ at 90 min; and h) mixing methyl 2-phenoxyacetate (**6**) and 4-methoxyphenol (**7**).

5. Scope of alcohol source

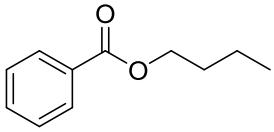
ethyl benzoate: colourless liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 (td, *J* = 8.0, 1.5 Hz, 2H, *Ar*), 7.54 (tt, *J* = 7.5, 1.5 Hz, 1H, *Ar*), 7.42 (t, *J* = 7.8 Hz, 2H, *Ar*), 4.37 (q, *J* = 7.2 Hz, 2H, C*H*$_2$), 1.39 (t, *J* = 7.2 Hz, 3H, C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 132.9, 130.6, 129.6, 128.4, 61.0, 14.4.



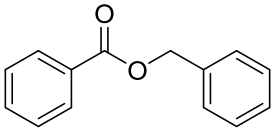
isopropyl benzoate: colorless liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 (td, *J* = 8.0, 1.5 Hz, 2H, *Ar*), 7.56 (tt, *J* = 7.5, 1.5 Hz, 1H, *Ar*), 7.45 (t, *J* = 7.5 Hz, 2H, *Ar*), 5.28 (sept, *J* = 6.5 Hz, 1H, C*H*), 1.40 (d, *J* = 6.5 Hz, 6H, C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 132.8, 131.0, 129.6, 128.4, 68.4, 22.1.



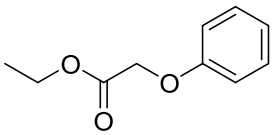
butyl benzoate: colorless liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 (td, *J* = 8.0, 1.5 Hz, 2H, *Ar*), 7.54 (tt, *J* = 7.5, 1.3 Hz, 1H, *Ar*), 7.43 (t, *J* = 7.8 Hz, 2H, *Ar*), 4.33 (t, *J* = 6.8 Hz, 2H, C*H*$_2$), 1.78 – 1.73 (m, 2H, C*H*$_2$), 1.52 – 1.45 (m, 2H, C*H*$_2$), 0.98 (t, *J* = 7.5 Hz, 3H, C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 132.9, 130.7, 129.6, 128.4, 64.9, 30.9, 19.4, 13.9.



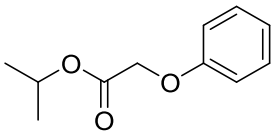
benzyl benzoate: colorless liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.08 (td, *J* = 8.5, 1.5 Hz, 2H, *Ar*), 7.54 (tt, *J* = 7.5, 1.5 Hz, 1H, *Ar*), 7.45 – 7.31 (m, 7H, *Ar*), 5.36 (s, 2H, C*H*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 136.2, 133.1, 130.3, 129.8, 128.7, 128.5, 128.34, 128.26, 66.8.



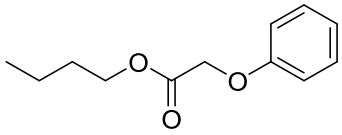
ethyl 2-phenoxyacetate: colorless liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H, *Ar*), 6.99 (tt, *J* = 7.5, 1.0 Hz, 1H, *Ar*), 6.92 – 6.89 (m, 2H, *Ar*), 4.61 (s, 2H, C*H*$_2$), 4.26 (q, *J* = 7.0 Hz, 2H, C*H*$_2$CH$_3$), 1.29 (t, *J* = 7.0 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 157.9, 129.6, 121.8, 114.8, 65.5, 61.4, 14.3.



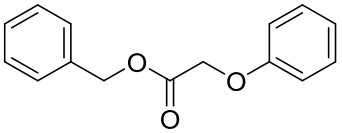
isopropyl 2-phenoxyacetate: colorless liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H, *Ar*), 6.98 (tt, *J* = 7.5, 1.0 Hz, 1H, *Ar*), 6.91 – 6.89 (m, 2H, *Ar*), 5.14 (sept, *J* = 6.0 Hz, 1H, C*H*), 4.58 (s, 2H, C*H*$_2$), 1.26 (d, *J* = 6.0 Hz, 6H, C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 158.0, 129.6, 121.7, 114.8, 69.2, 65.7, 21.8.



butyl 2-phenoxyacetate: colorless liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H, *Ar*), 6.98 (tt, *J* = 7.5, 1.0 Hz, 1H, *Ar*), 6.92 – 6.89 (m, 2H, *Ar*), 4.61 (s, 2H, PhOC*H*$_2$), 4.20 (t, *J* = 6.5 Hz, 2H, COOC*H*$_2$), 1.65 – 1.60 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 1.38 – 1.31 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 0.91 (t, *J* = 7.3 Hz, 3H, C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 157.9, 129.6, 121.8, 114.7, 65.5, 65.2, 30.6, 19.1, 13.7.



benzyl 2-phenoxyacetate: colorless liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 5H, *Ar*), 7.28 – 7.25 (m, 2H, *Ar*), 6.98 (tt, *J* = 7.5, 1.0 Hz, 1H, *Ar*), 6.90 – 6.88 (m, 2H, *Ar*), 5.22 (s, 2H, PhC*H*$_2$O), 4.65 (s, 2H PhOC*H*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 157.9, 135.3, 129.7, 128.7, 128.6, 128.5, 121.9, 114.8, 67.1, 65.5.



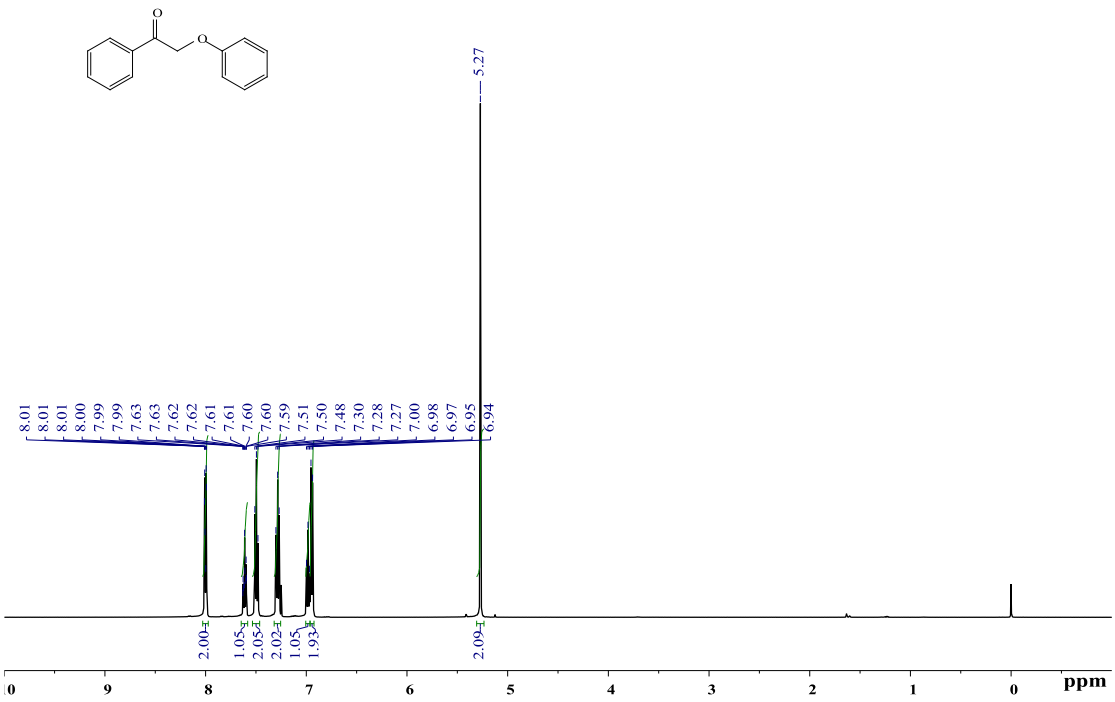
IV. References

(1) J. M. Nichols, L. M. Bishop, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.*, 2010, **132**, 12554–12555.

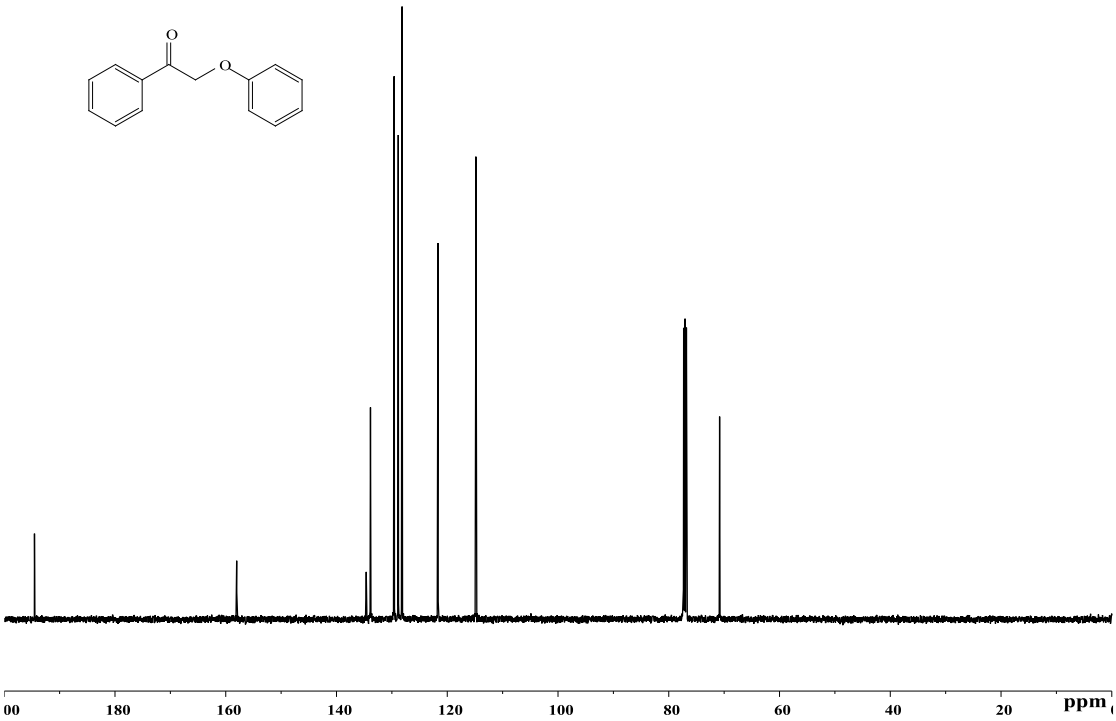
(2) D. W. Cho, R. Parthasarathi, A. S. Pimentel, G. D. Maestas, H. J. Park, U. C. Yoon, D. Dunaway-Mariano, S. Gnanakaran, P. Langan and P. S. Mariano, *J. Org. Chem.*, 2010, **75**, 6549–6562.

(3) A. Rahimi, A. Azarpira, H. Kim, J. Ralph and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 6415–6418.

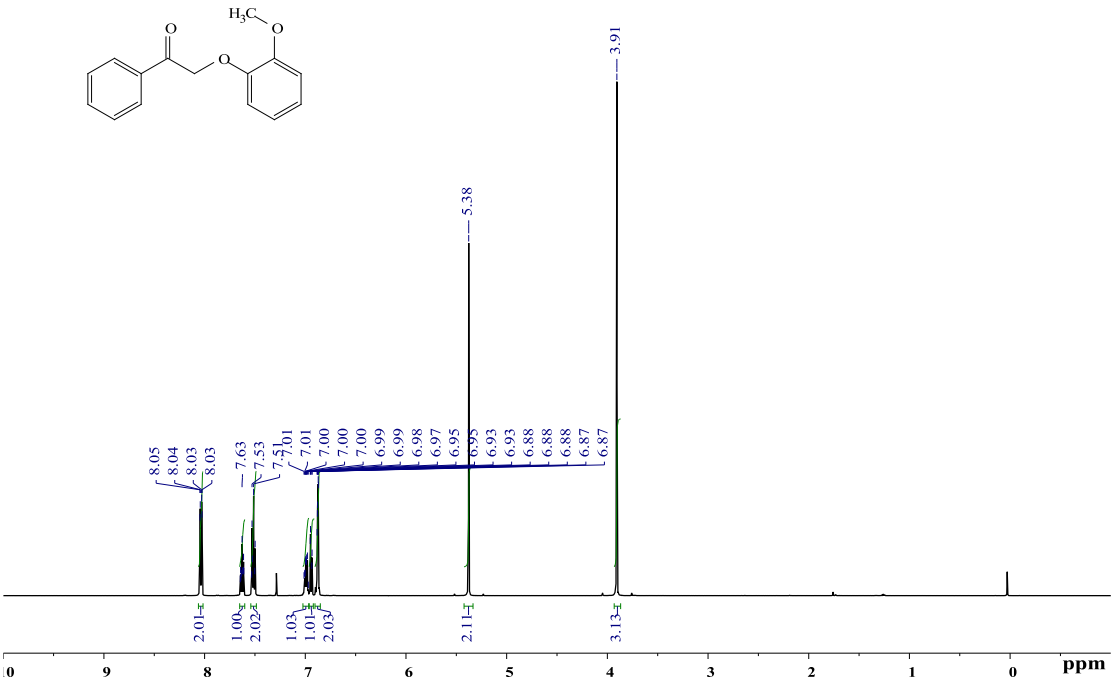
V. NMR spectra



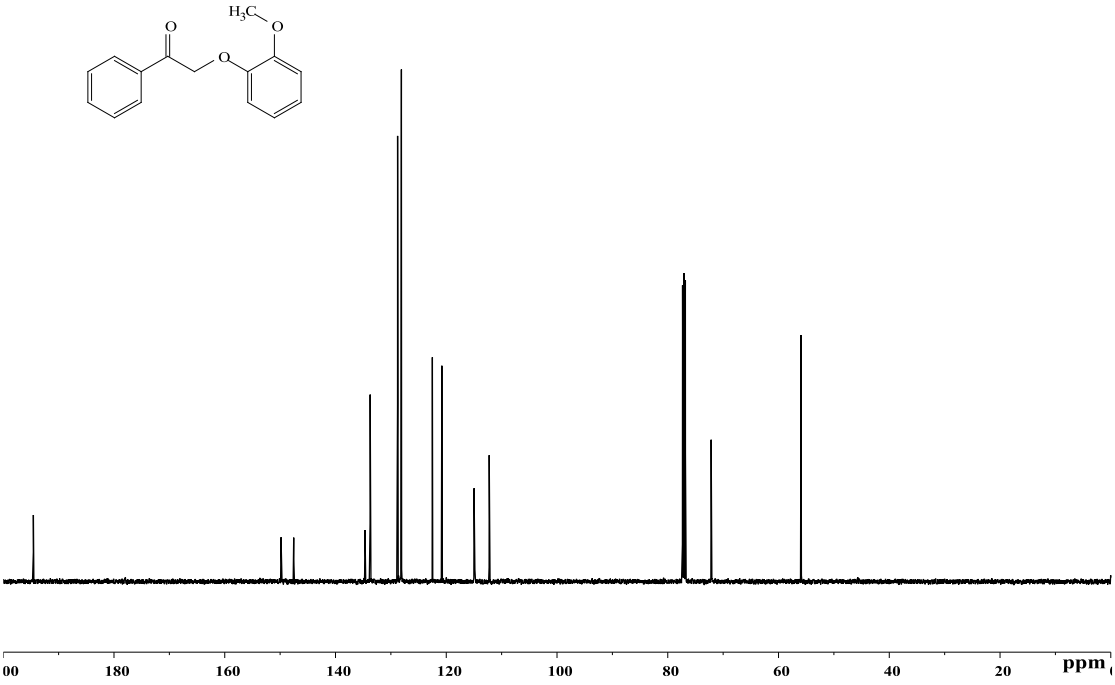
^{1}H NMR spectrum of 2-phenoxy-1-phenylethan-1-one (**A^{ox}**) ($CDCl_3$, 500 MHz)



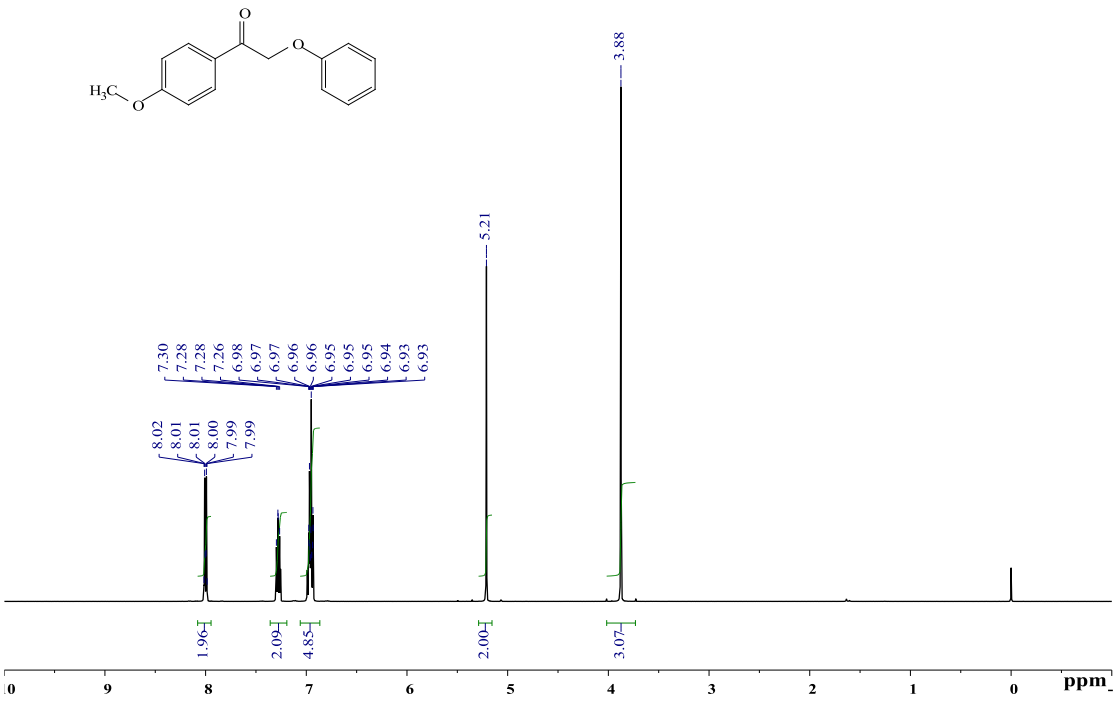
^{13}C NMR spectrum of 2-phenoxy-1-phenylethan-1-one (**A^{ox}**) ($CDCl_3$, 126 MHz)



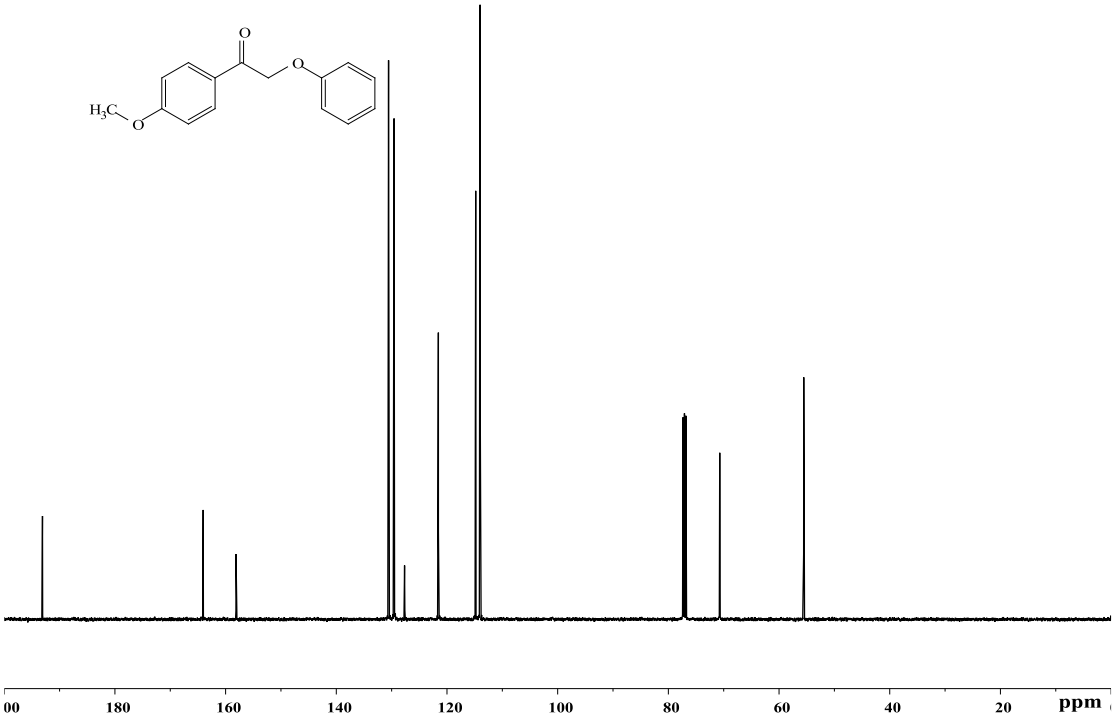
^{1}H NMR spectrum of 2-(2-methoxyphenoxy)-1-phenylethan-1-one (**B^{ox}**) ($CDCl_3$, 500 MHz)



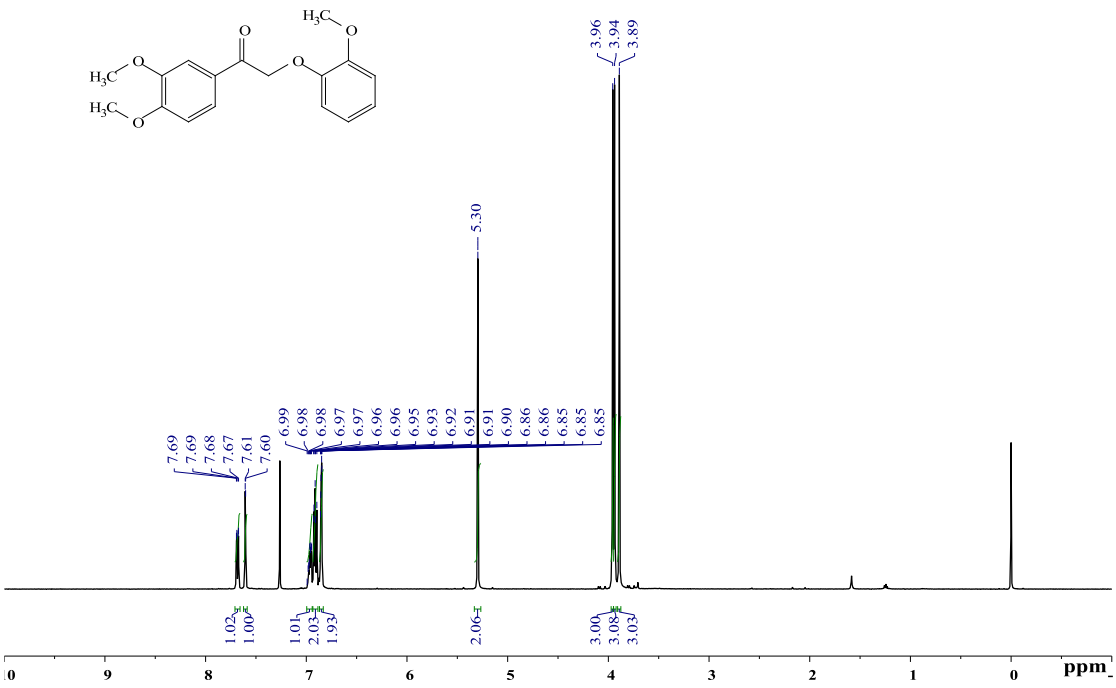
^{13}C NMR spectrum of 2-(2-methoxyphenoxy)-1-phenylethan-1-one (**B^{ox}**) ($CDCl_3$, 126 MHz)



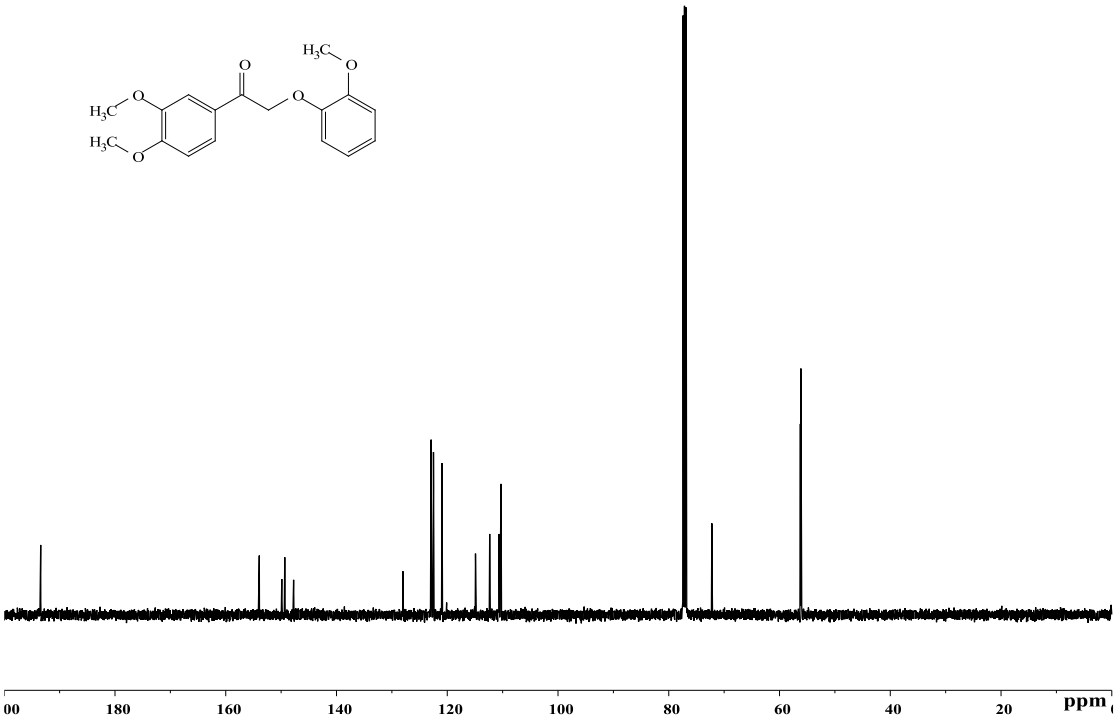
^{1}H NMR spectrum of 1-(4-methoxyphenyl)-2-phenoxyethan-1-one (**C^{ox}**) ($CDCl_3$, 500 MHz)



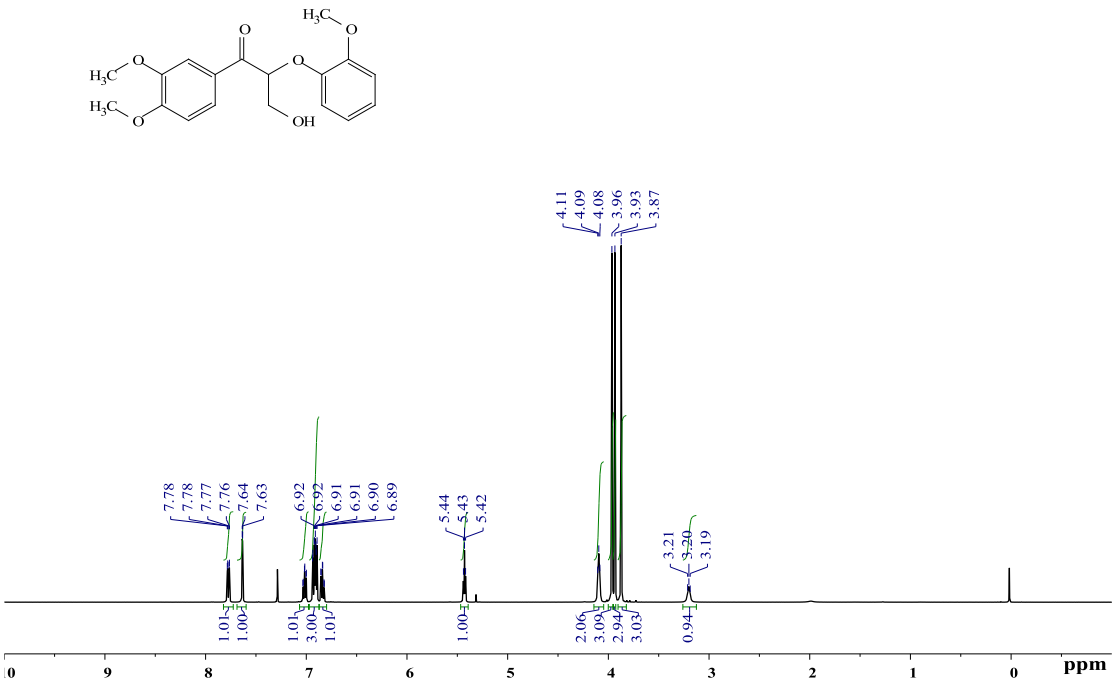
^{13}C NMR spectrum of 1-(4-methoxyphenyl)-2-phenoxyethan-1-one (**C^{ox}**) ($CDCl_3$, 126 MHz)



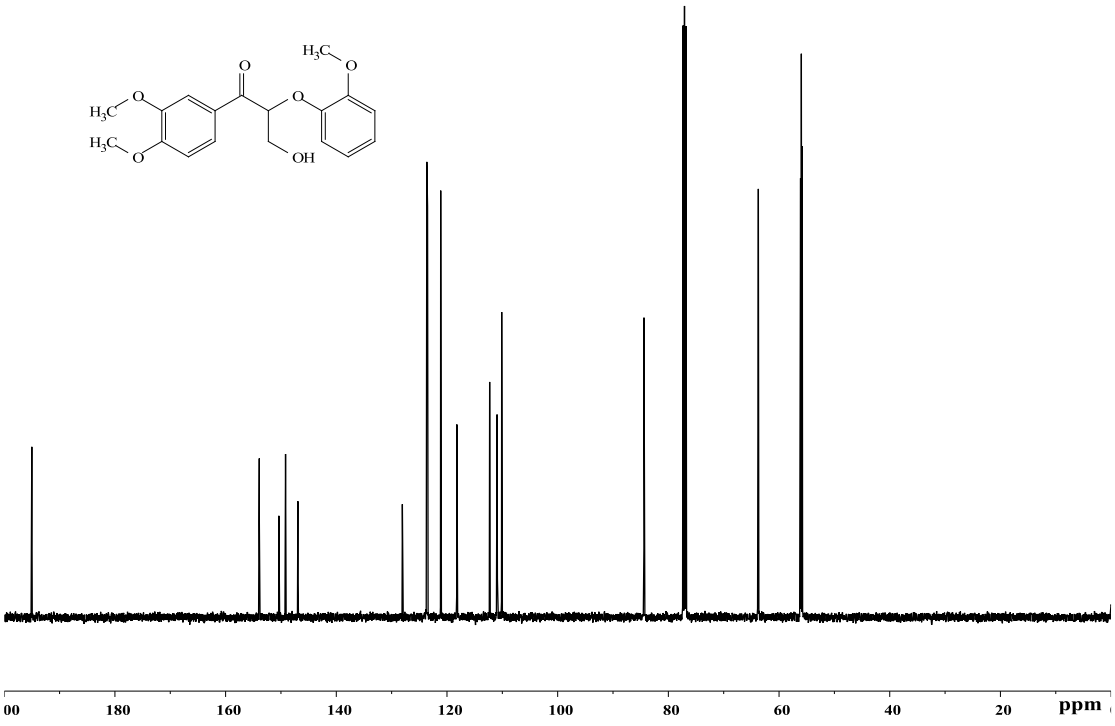
^{1}H NMR spectrum of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one**(D^{ox})** (CD Cl_3, 500 MHz)



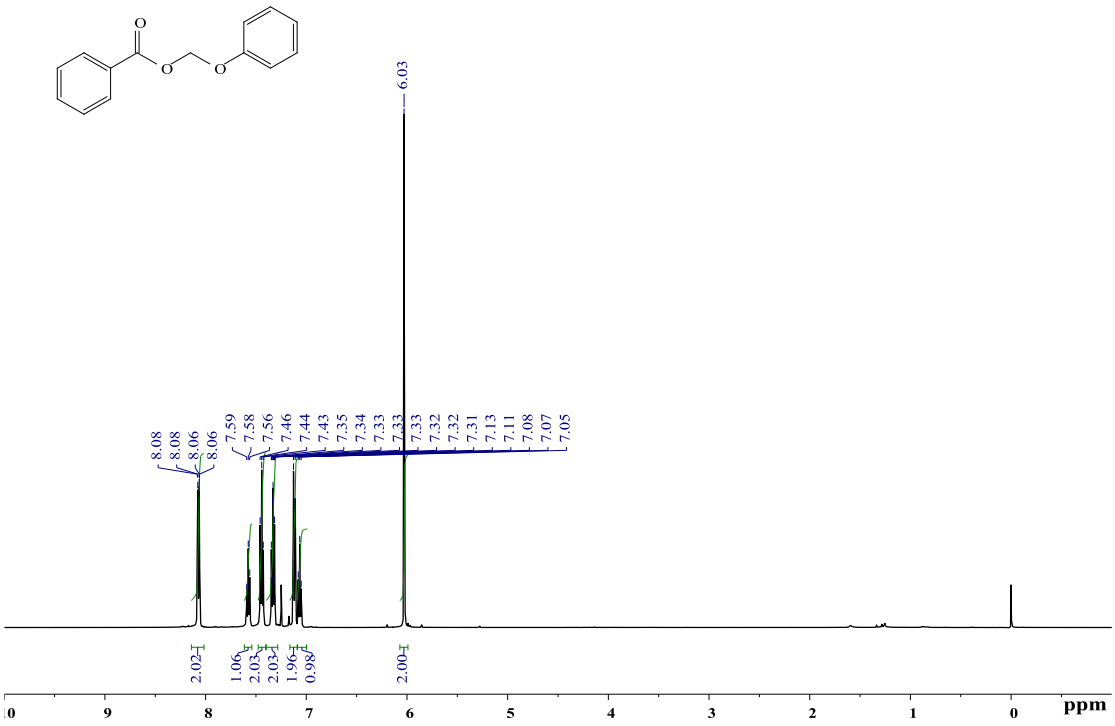
^{13}C NMR spectrum of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one**(D^{ox})** (CD Cl_3, 126 MHz)



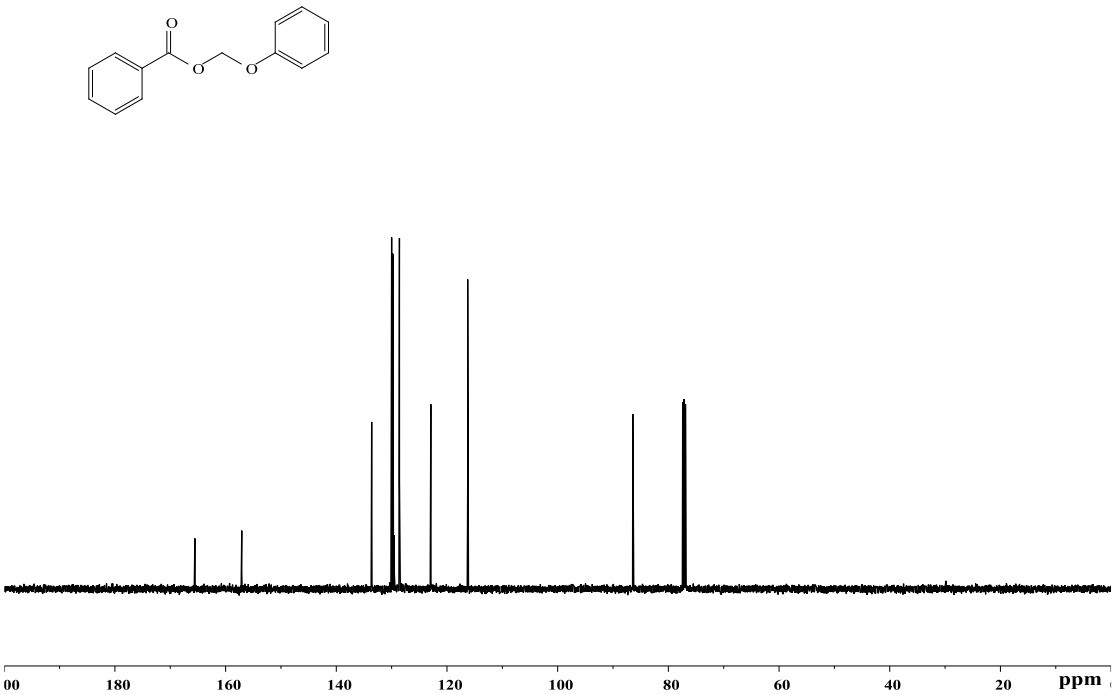
^{1}H NMR spectrum of 1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-1-propanone **(E^{ox})** ($CDCl_3$, 500 MHz)



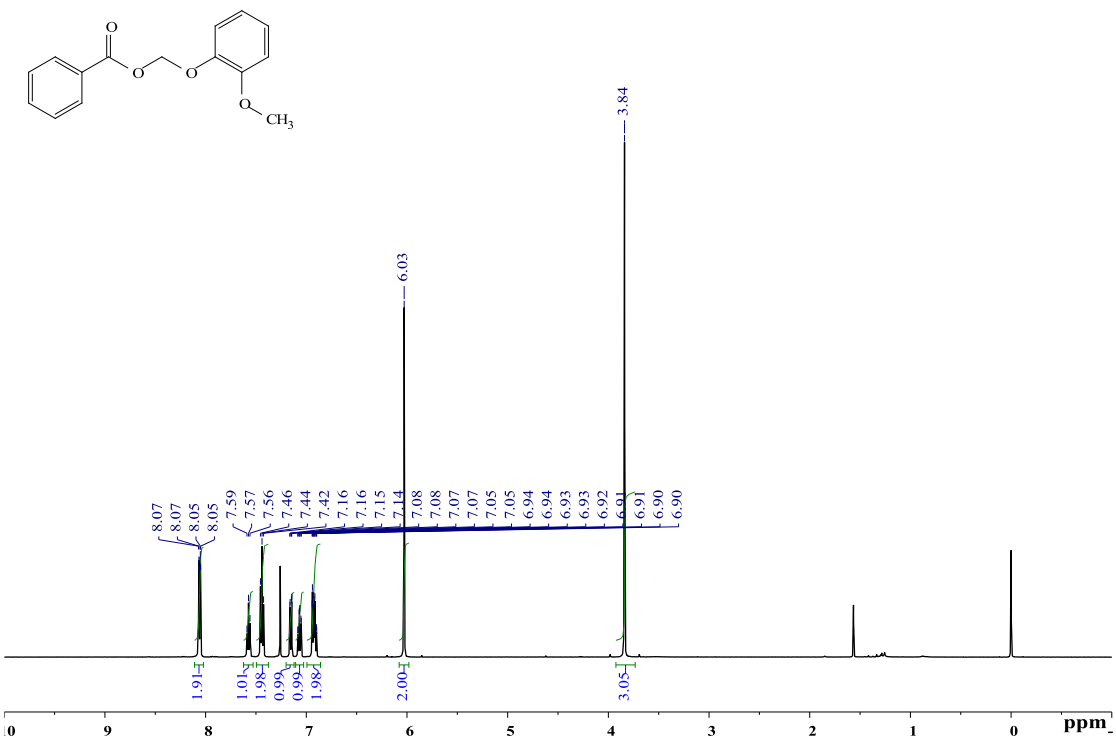
^{13}C NMR spectrum of 1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-1-propanone **(E^{ox})** ($CDCl_3$, 126 MHz)



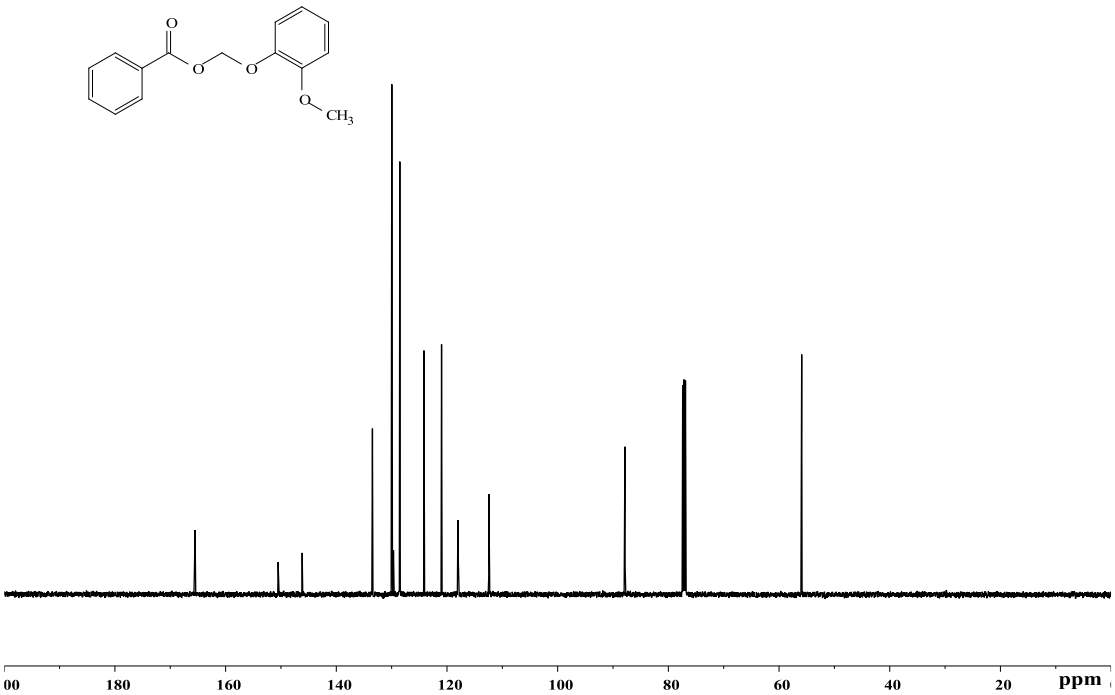
^{1}H NMR spectrum of phenoxymethyl benzoate **(A_a)** ($CDCl_3$, 500 MHz)



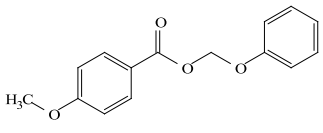
^{13}C NMR spectrum of phenoxymethyl benzoate **(A_a)** ($CDCl_3$, 126 MHz)

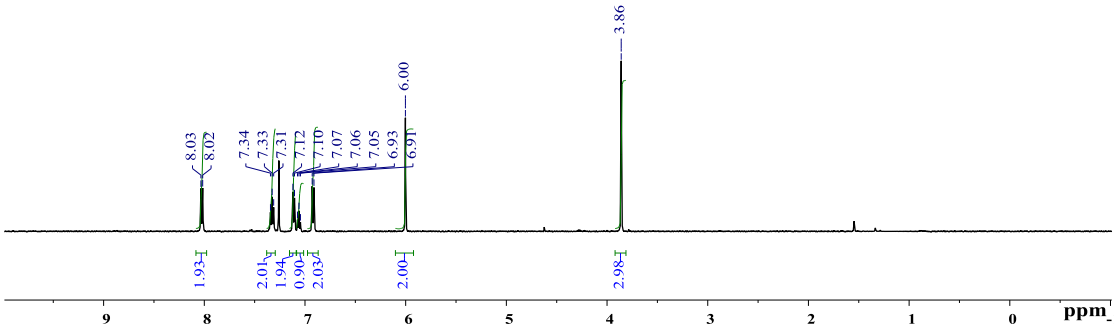


^{1}H NMR spectrum of (2-methoxyphenoxy) methyl benzoate **(B_a)** ($CDCl_3$, 500 MHz)

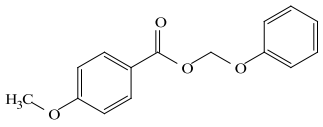


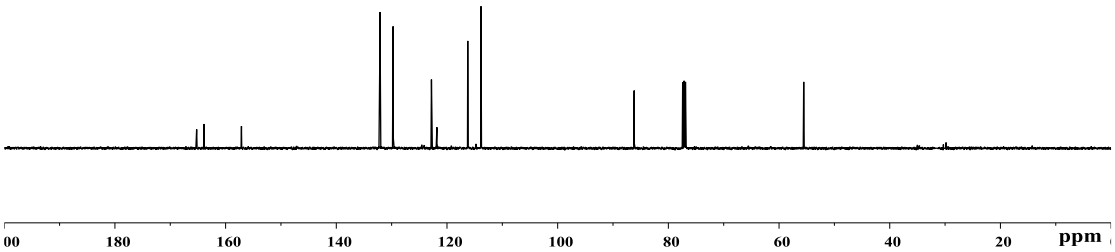
^{13}C NMR spectrum of (2-methoxyphenoxy) methyl benzoate **(B_a)** ($CDCl_3$, 126 MHz)



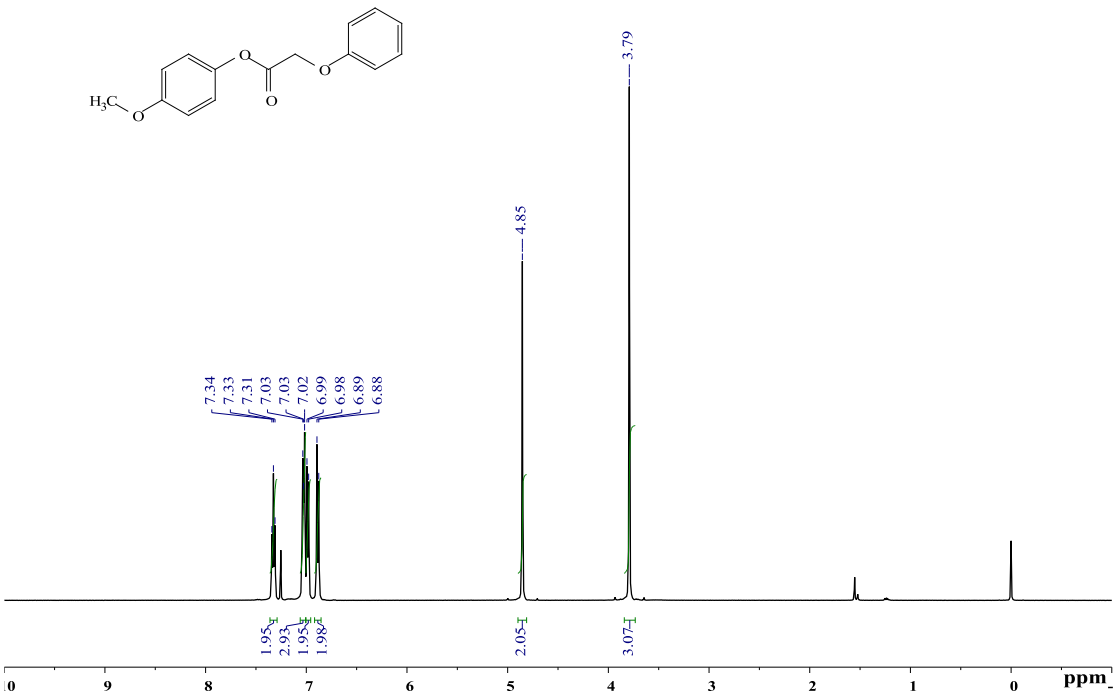


^{1}H NMR spectrum of phenoxymethyl 4-methoxybenzoate **(C_a)** ($CDCl_3$, 500 MHz)

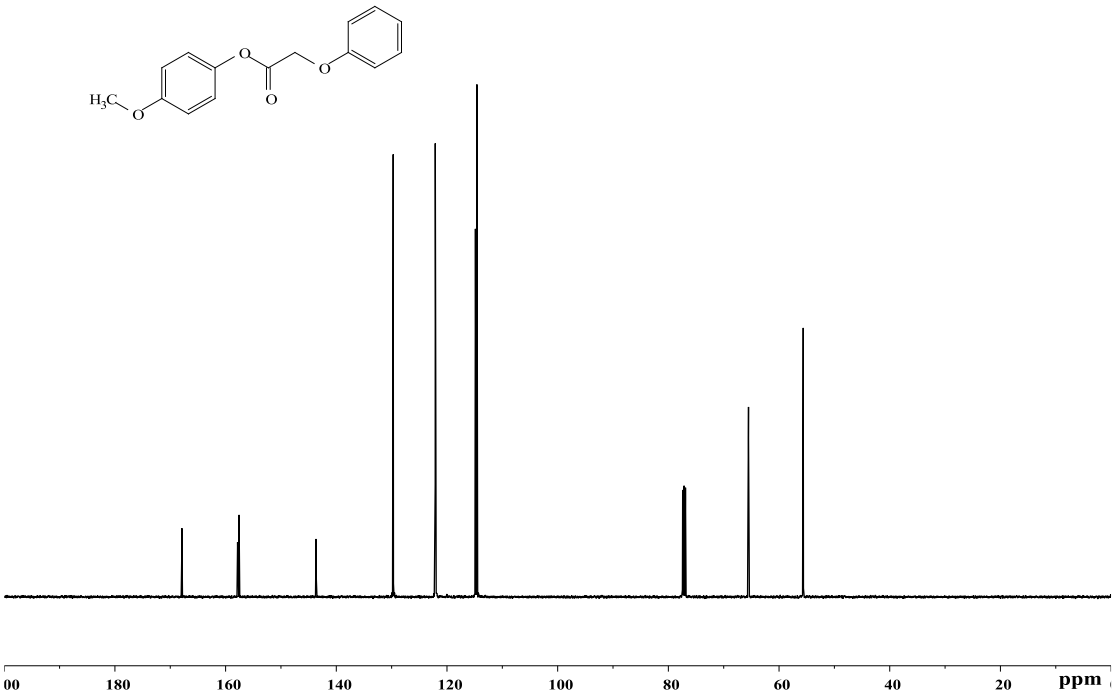




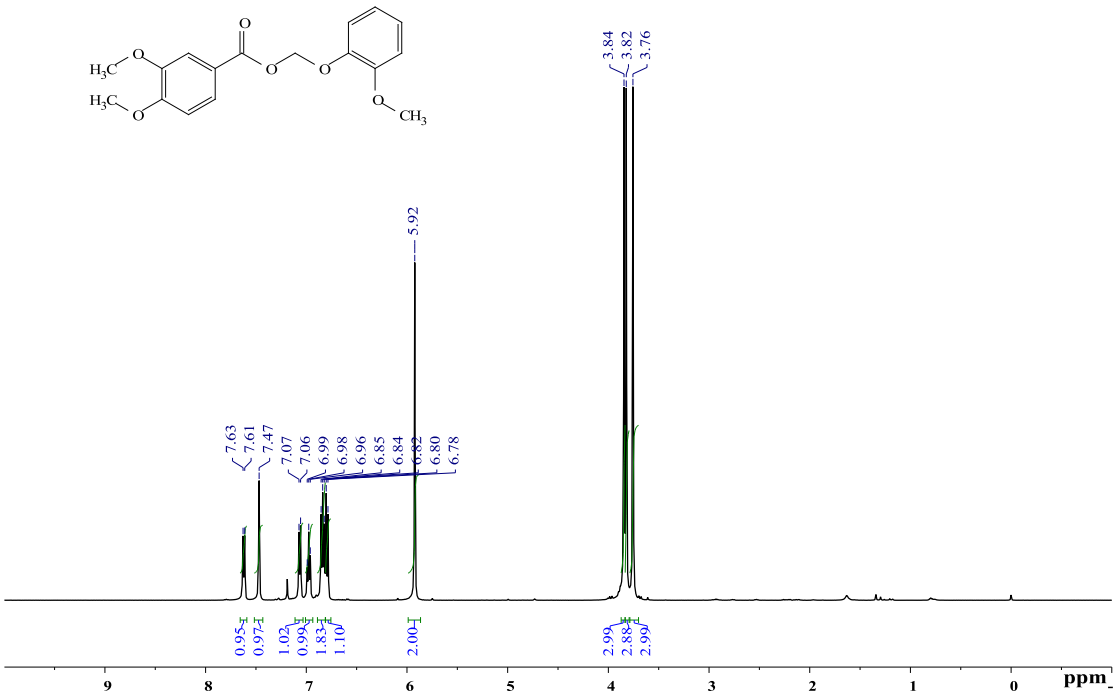
^{13}C NMR spectrum of phenoxymethyl 4-methoxybenzoate **(C_a)** ($CDCl_3$, 126 MHz)



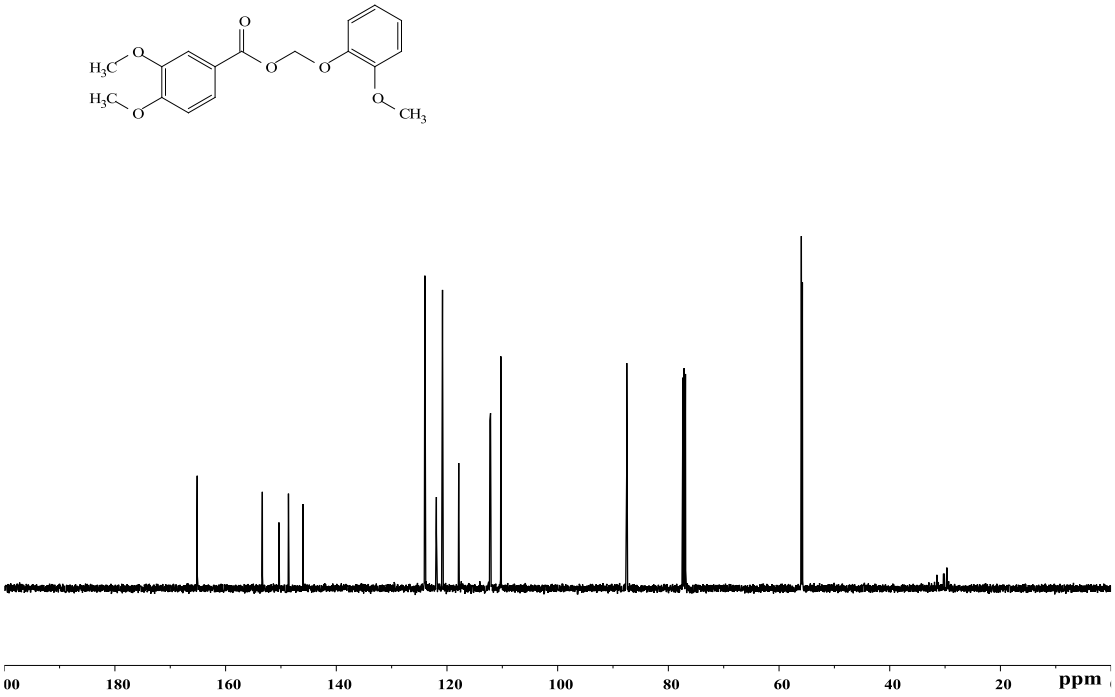
^{1}H NMR spectrum of 4-methoxyphenyl 2-phenoxyacetate **(C_b)** ($CDCl_3$, 500 MHz)



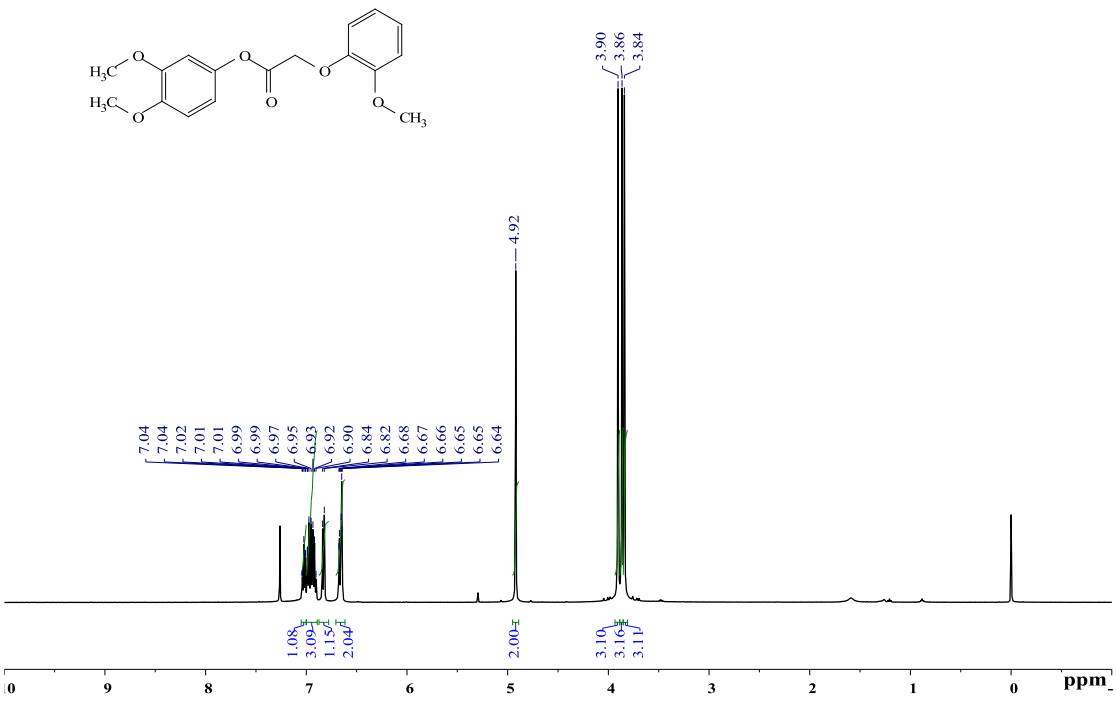
^{13}C NMR spectrum of 4-methoxyphenyl 2-phenoxyacetate **(C_b)** ($CDCl_3$, 126 MHz)



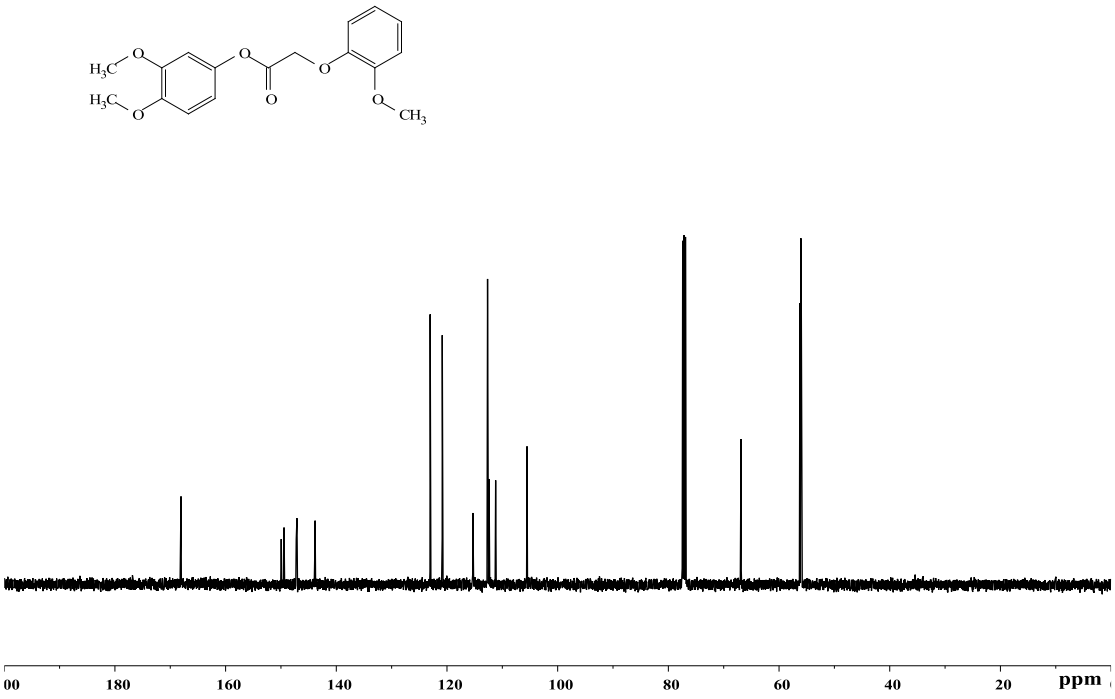
^{1}H NMR spectrum of (2-methoxyphenoxy)methyl 3,4-dimethoxybenzoate **(D_a)** ($CDCl_3$, 500 MHz)



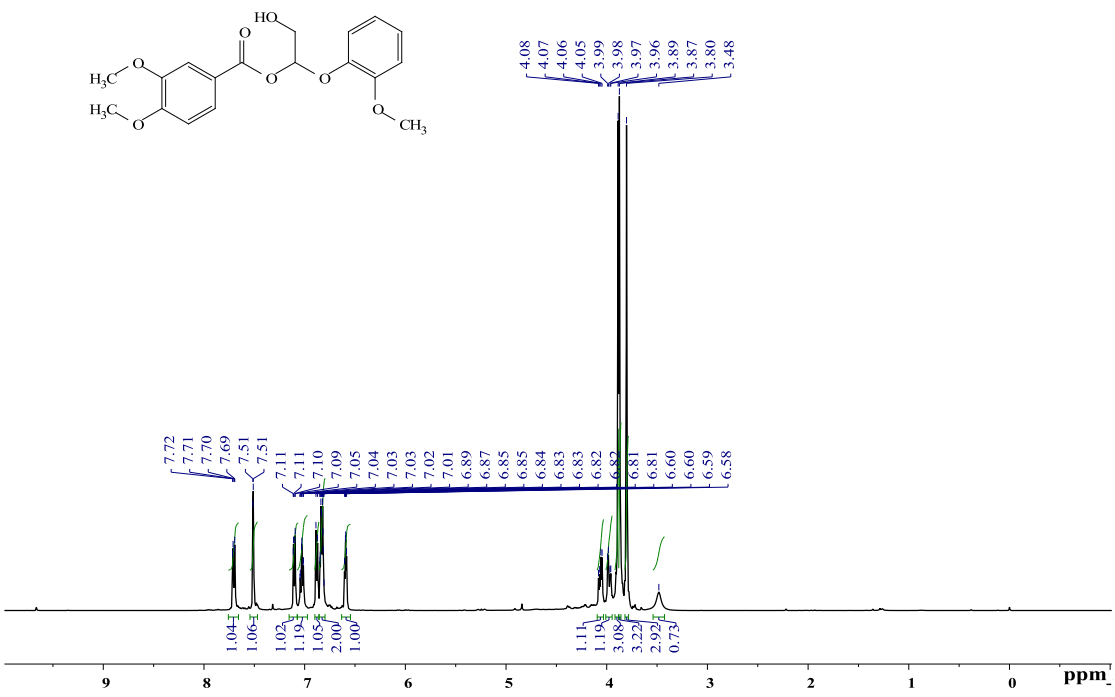
^{13}C NMR spectrum of (2-methoxyphenoxy)methyl 3,4-dimethoxybenzoate **(D_a)** ($CDCl_3$, 126 MHz)



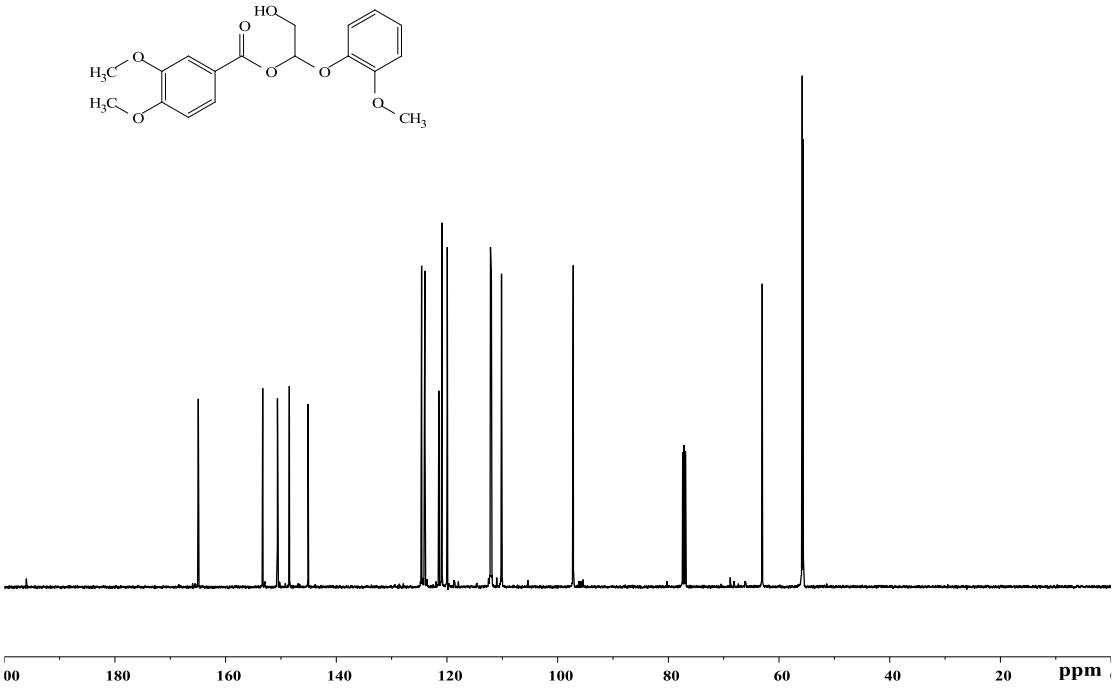
^{1}H NMR spectrum of 3,4-dimethoxyphenyl 2-(2-methoxyphenoxy)acetate **(D_b)** ($CDCl_3$, 500 MHz)



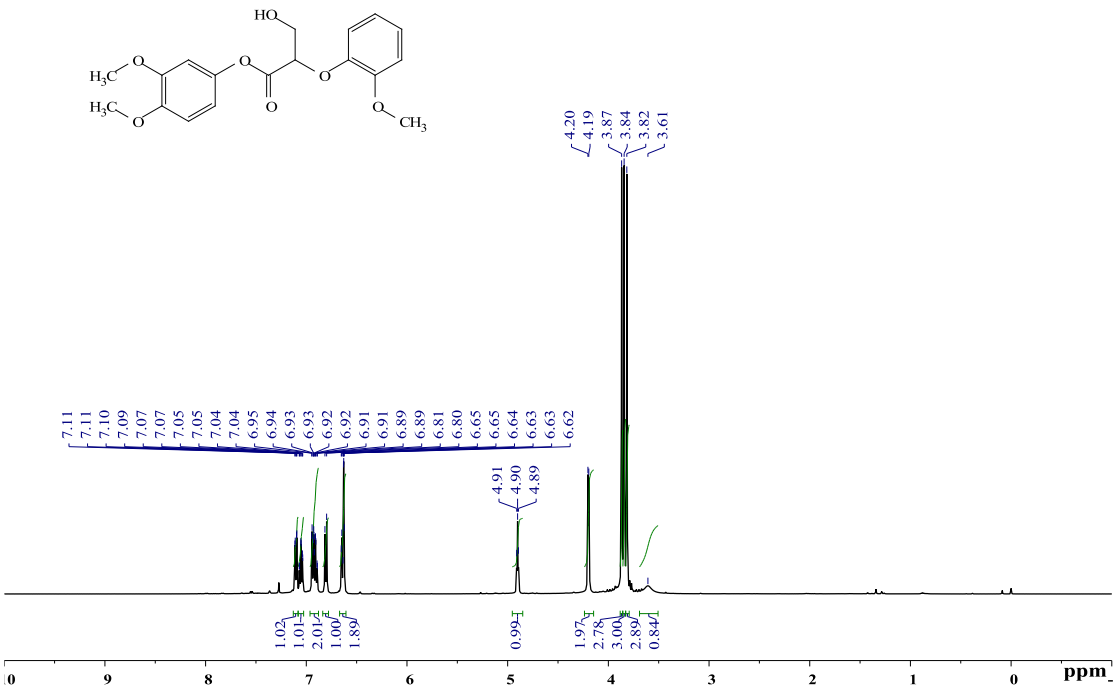
^{13}C NMR spectrum of 3,4-dimethoxyphenyl 2-(2-methoxyphenoxy)acetate **(D_b)** ($CDCl_3$, 126 MHz)



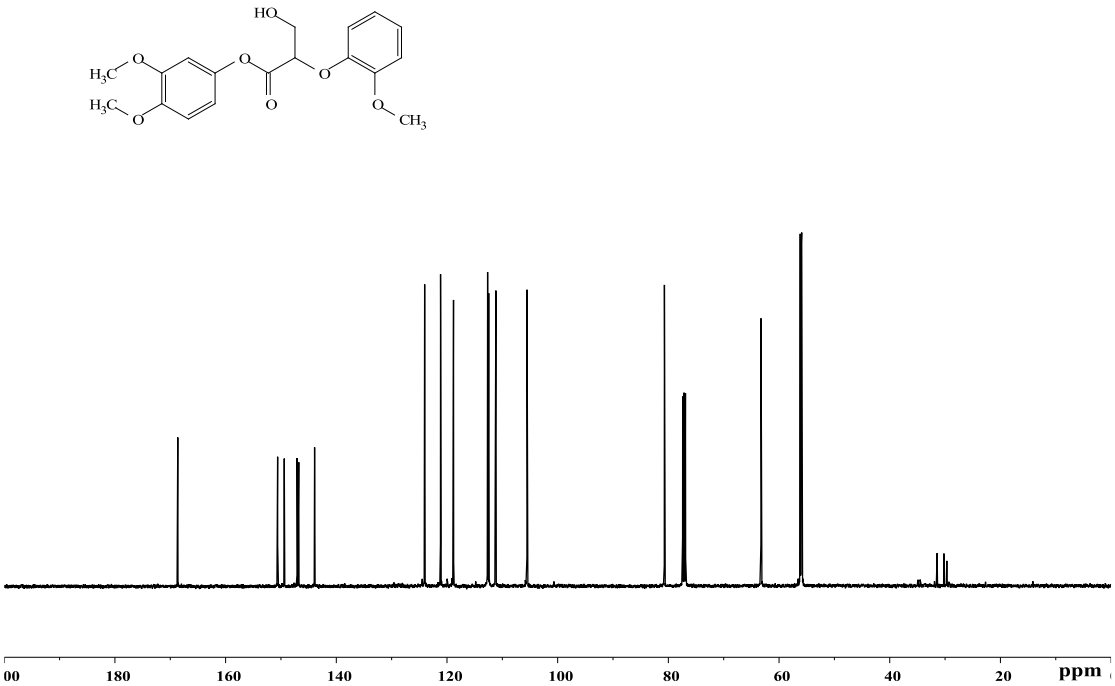
^{1}H NMR spectrum of 2-hydroxy-1-(2-methoxyphenoxy)ethyl 3,4-dimethoxybenzoate **(E_a)** ($CDCl_3$, 500 MHz)



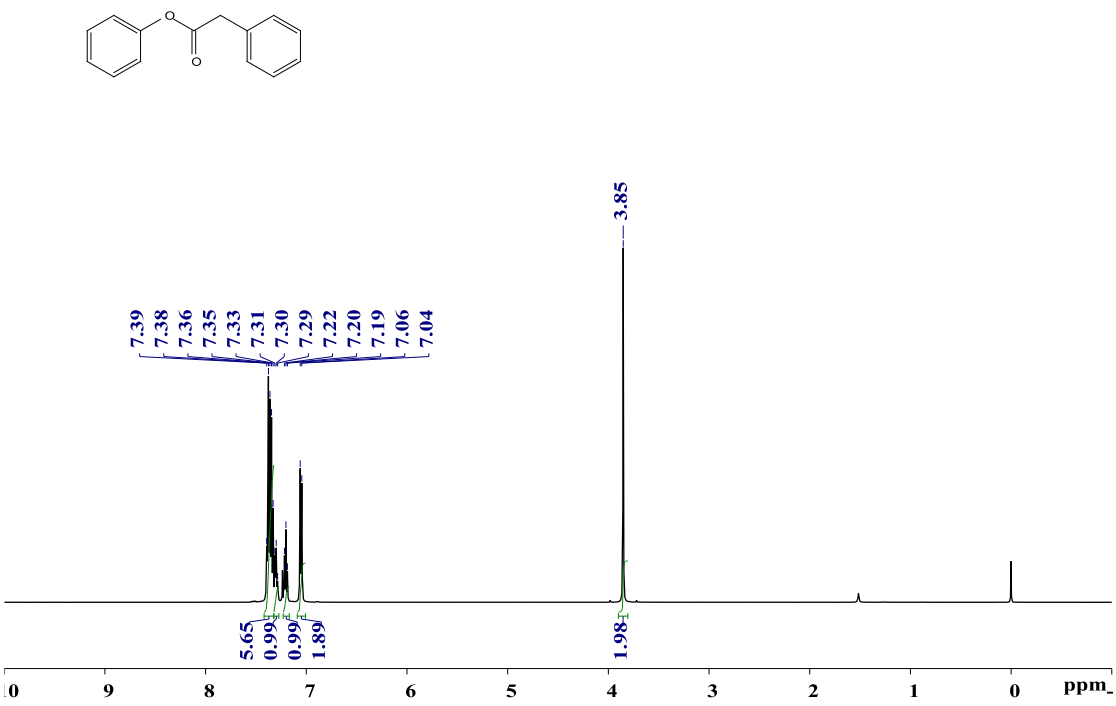
^{13}C NMR spectrum of 2-hydroxy-1-(2-methoxyphenoxy)ethyl 3,4-dimethoxybenzoate **(E_a)** ($CDCl_3$, 126 MHz)



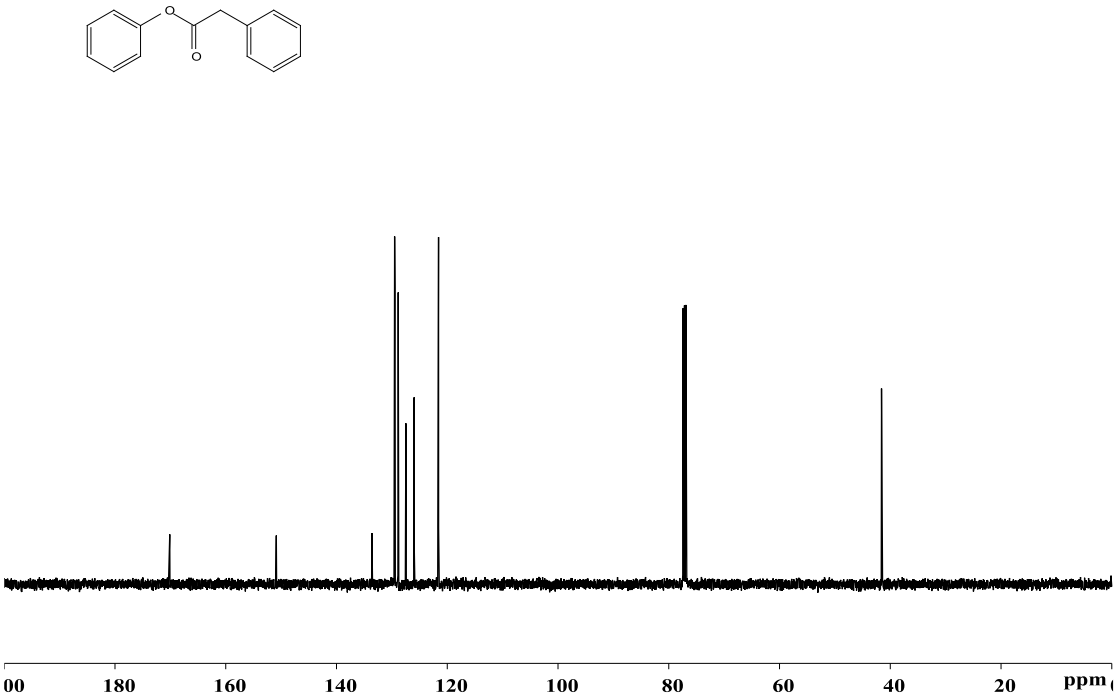
^{1}H NMR spectrum of 3,4-dimethoxyphenyl 3-hydroxy-2-(2-methoxyphenoxy)propanoate **(E_b)** ($CDCl_3$, 500 MHz)



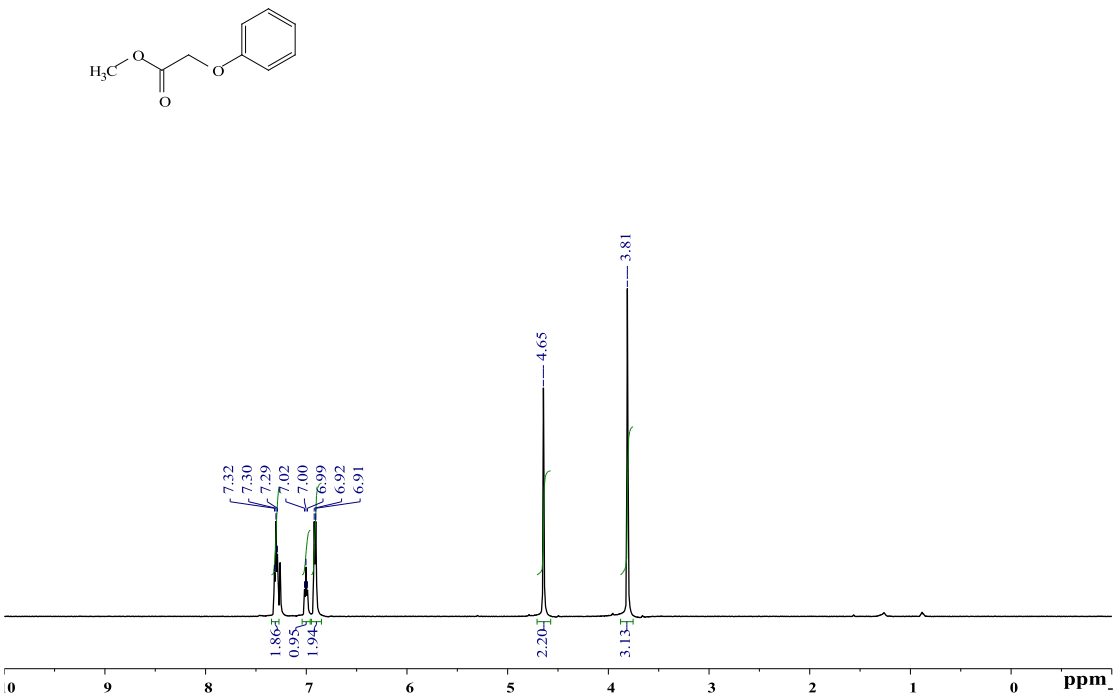
^{13}C NMR spectrum of 3,4-dimethoxyphenyl 3-hydroxy-2-(2-methoxyphenoxy)propanoate **(E_b)** ($CDCl_3$, 126 MHz)



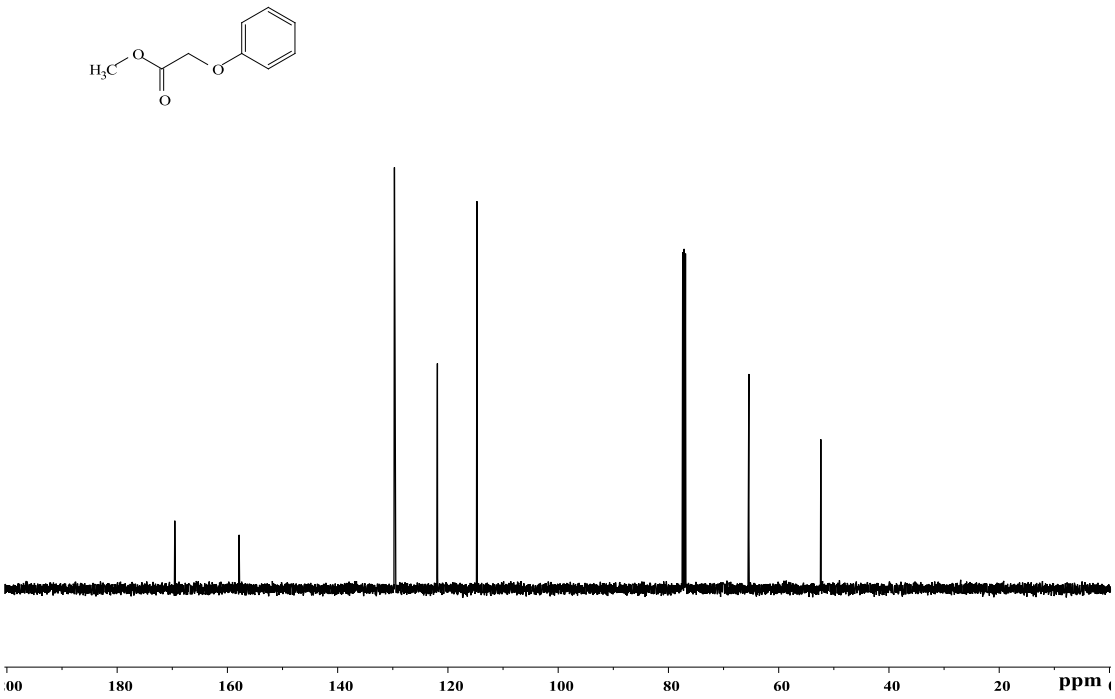
^{1}H NMR spectrum of phenyl 2-phenylacetate **(F_b)** ($CDCl_3$, 500 MHz)



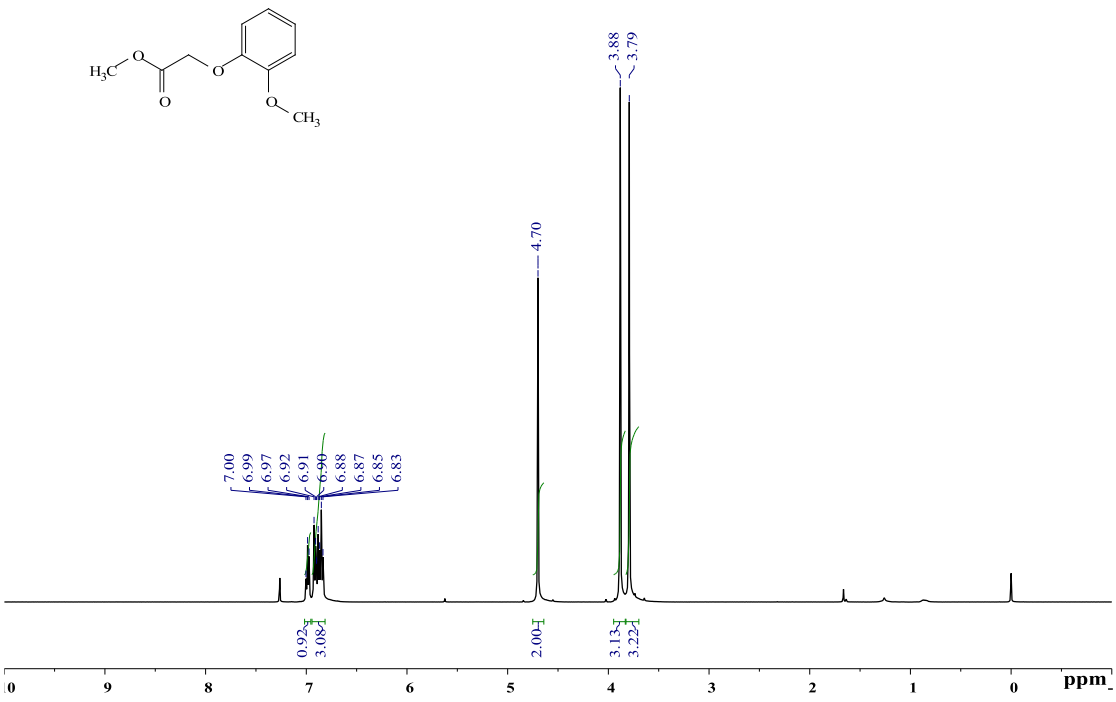
^{13}C NMR spectrum of phenyl 2-phenylacetate **(F_b)** ($CDCl_3$, 126 MHz)



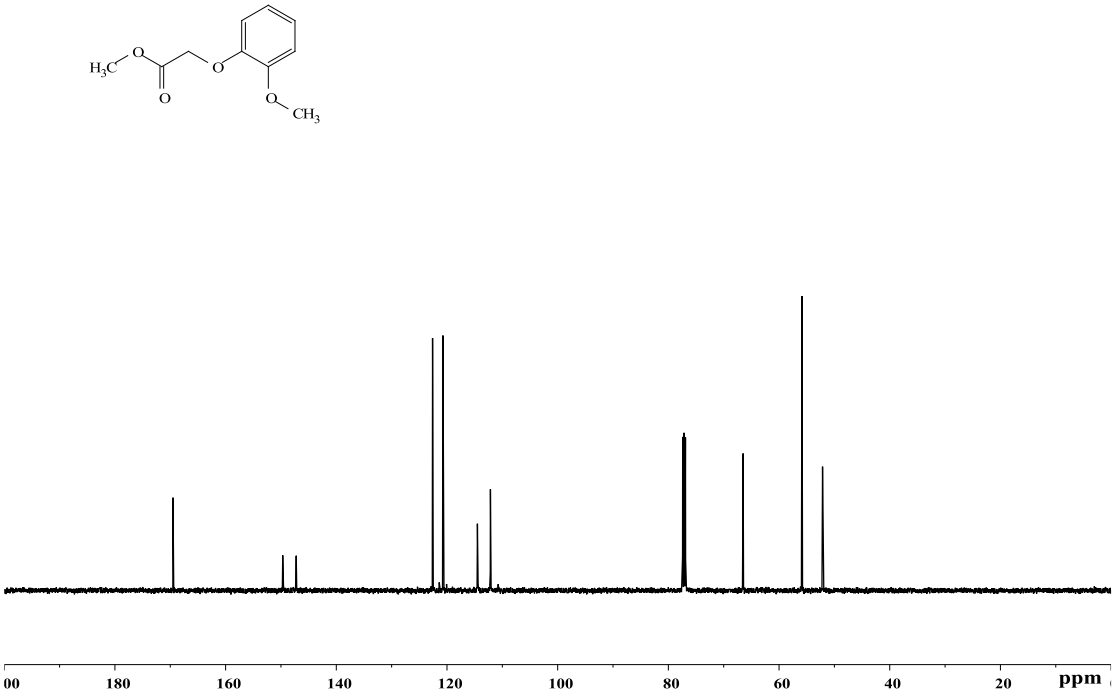
^{1}H NMR spectrum of methyl 2-phenoxyacetate **(6)** ($CDCl_3$, 500 MHz)



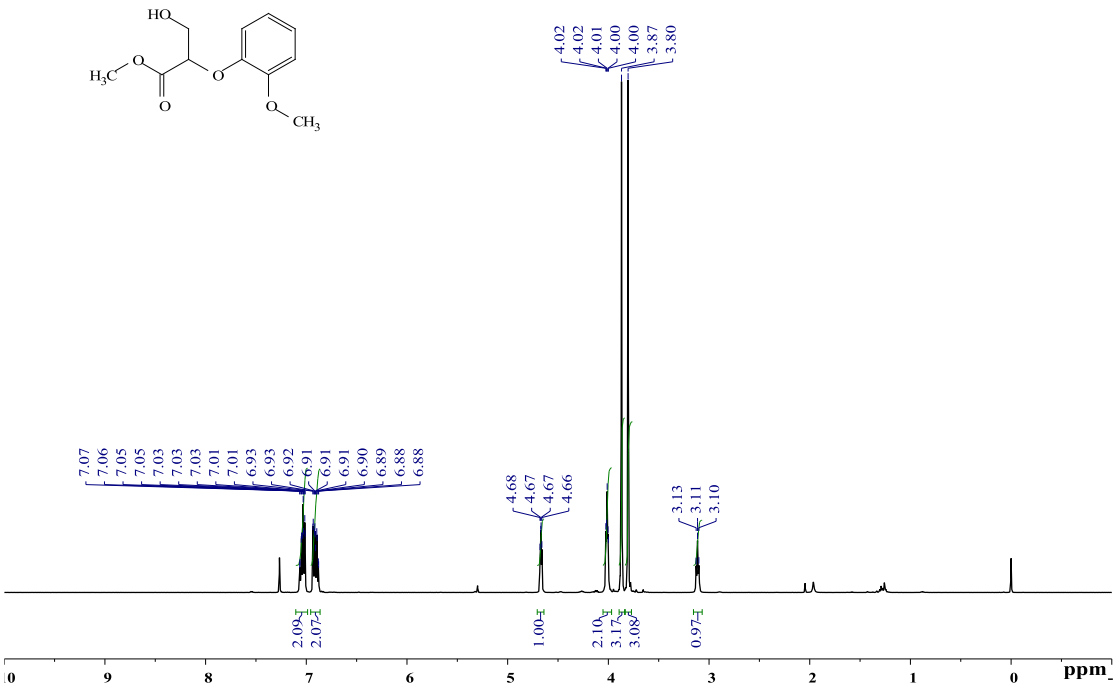
^{13}C NMR spectrum of methyl 2-phenoxyacetate **(6)** ($CDCl_3$, 126 MHz)



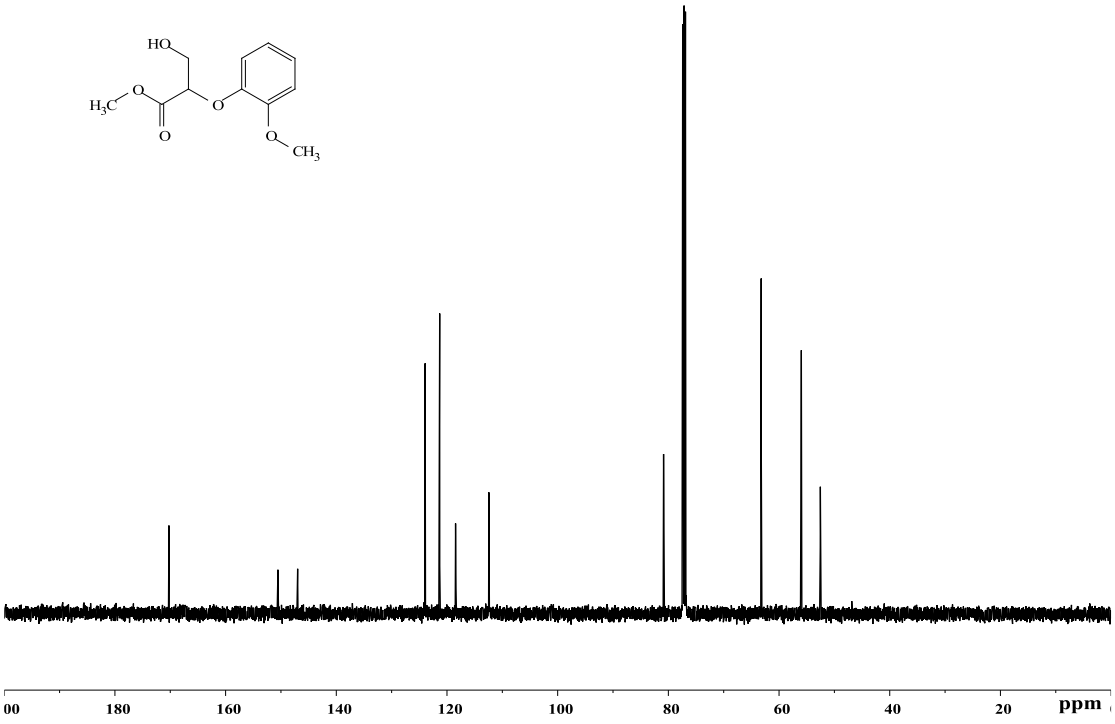
^{1}H NMR spectrum of methyl 2-(2-methoxyphenoxy)acetate **(8)** ($CDCl_3$, 500 MHz)



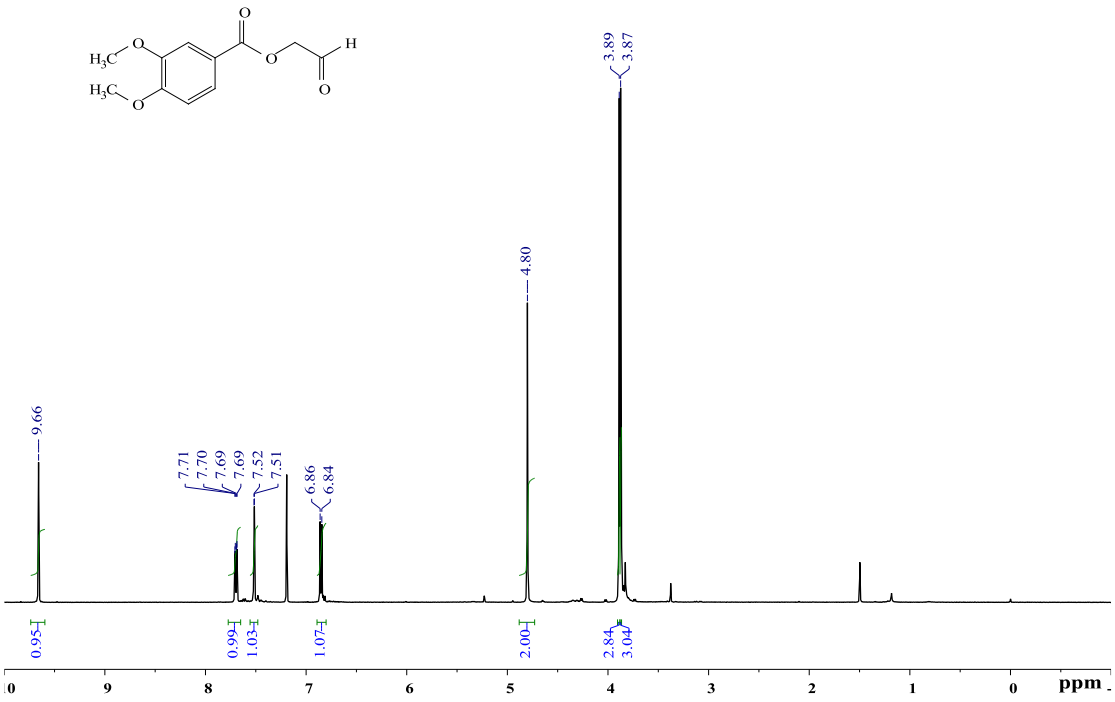
^{13}C NMR spectrum of methyl 2-(2-methoxyphenoxy)acetate **(8)** ($CDCl_3$, 126 MHz)



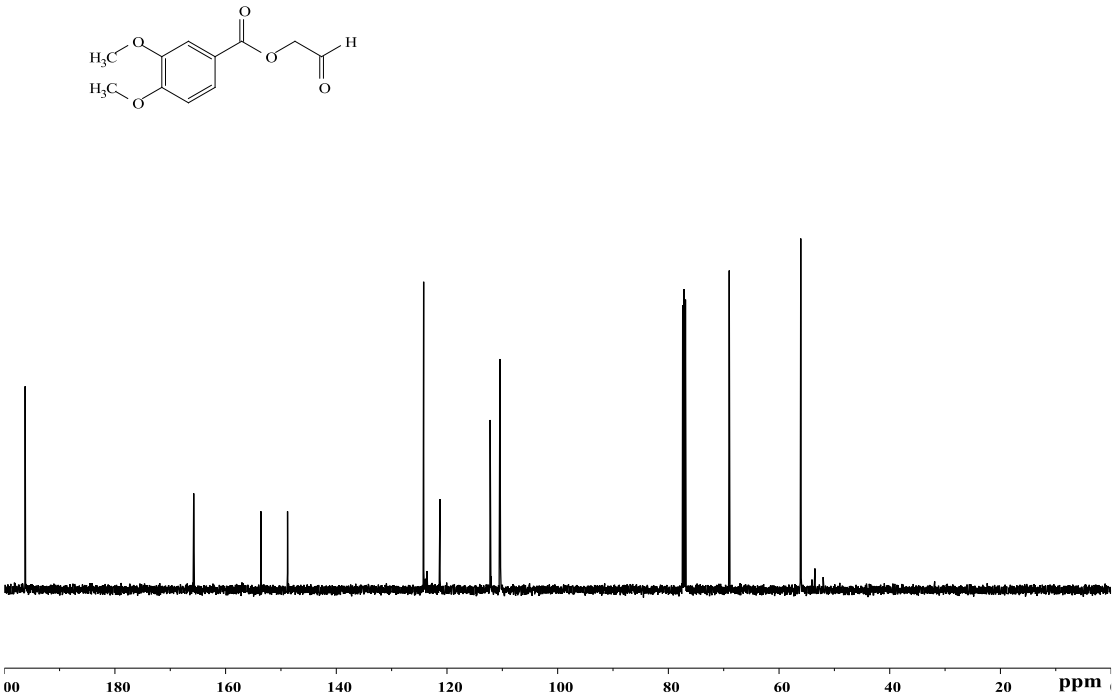
^{1}H NMR spectrum of methyl 3-hydroxy-2-(2-methoxyphenoxy)propanoate **(10)** ($CDCl_3$, 500 MHz)



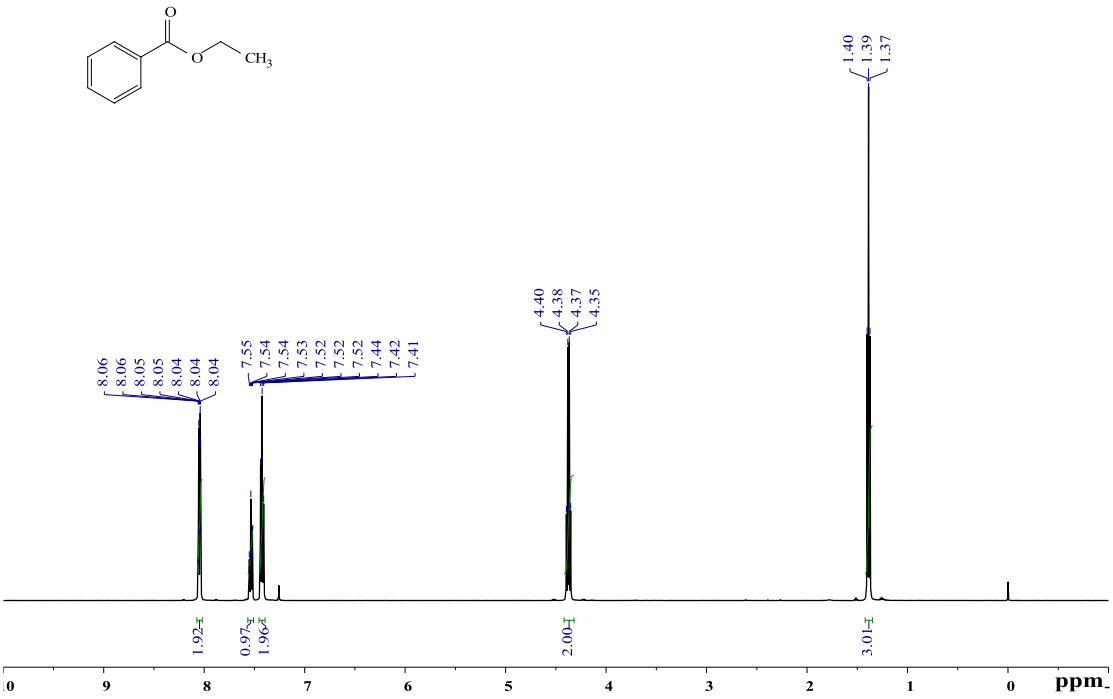
^{13}C NMR spectrum of methyl 3-hydroxy-2-(2-methoxyphenoxy)propanoate **(10)** ($CDCl_3$, 126 MHz)



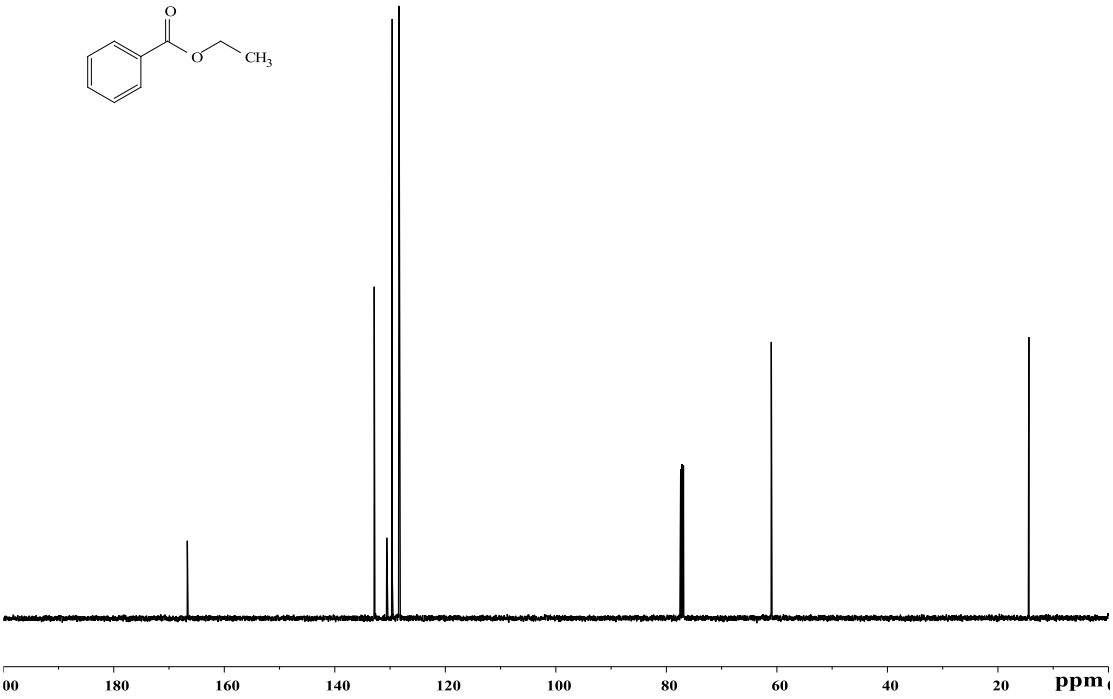
^{1}H NMR spectrum of 2-oxoethyl 3,4-dimethoxybenzoate **(13)** ($CDCl_3$, 500 MHz)



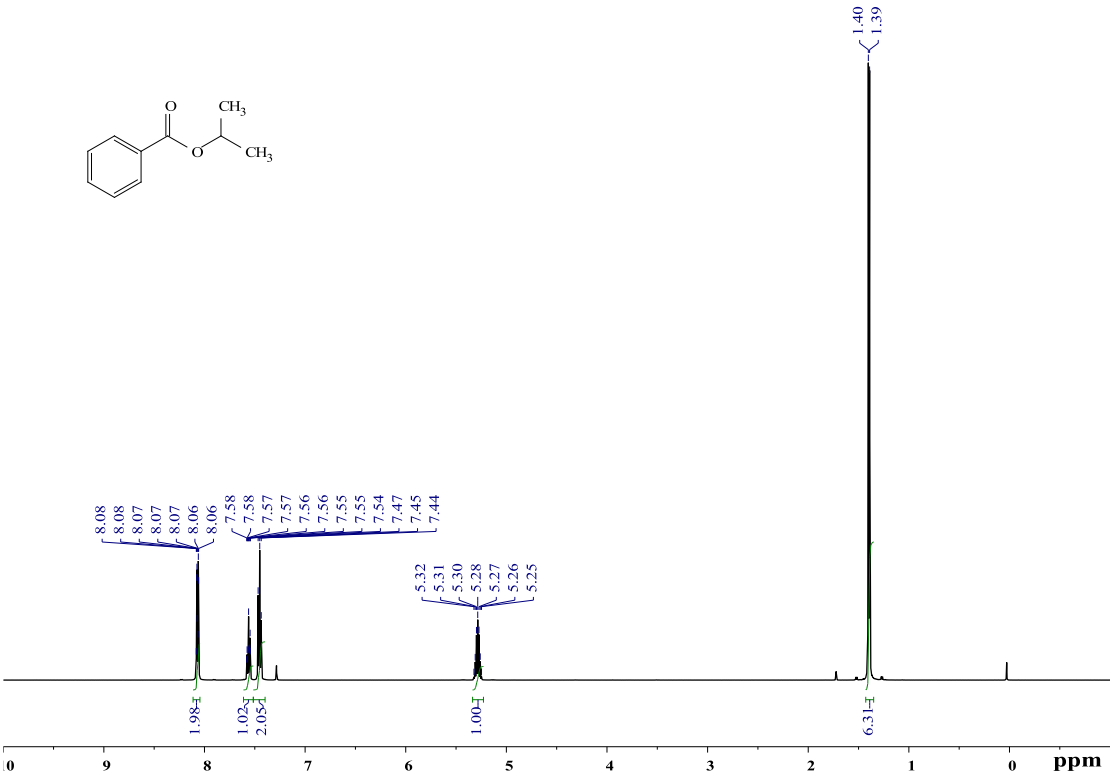
^{13}C NMR spectrum of 2-oxoethyl 3,4-dimethoxybenzoate **(13)** ($CDCl_3$, 126 MHz)



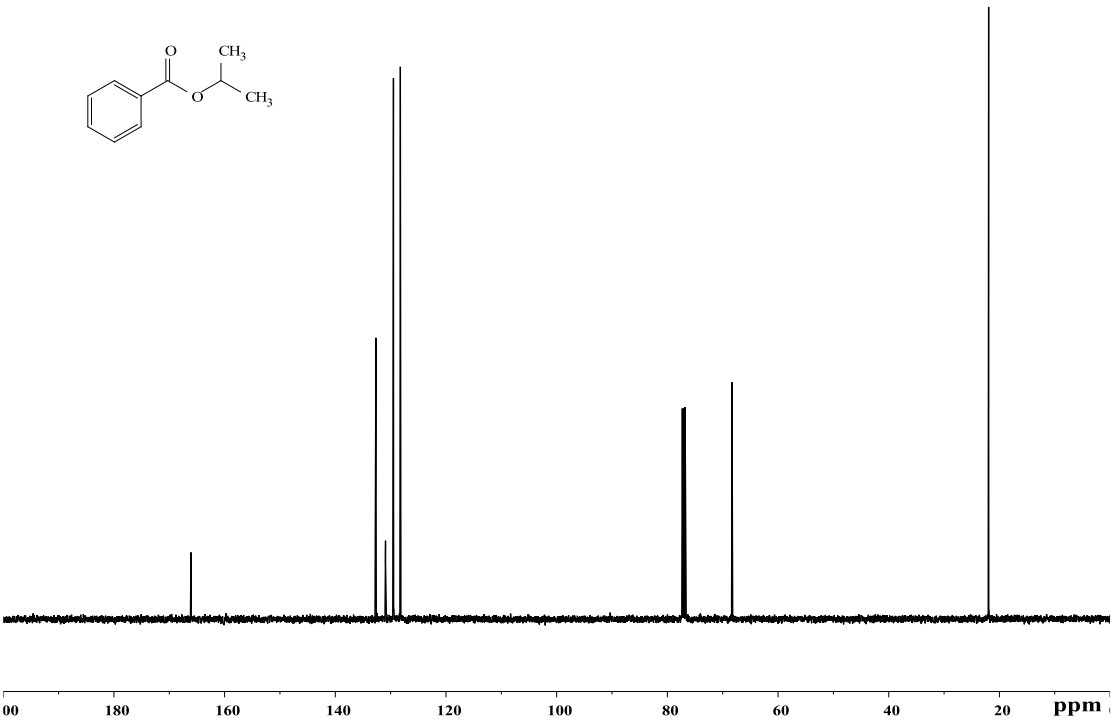
^{1}H NMR spectrum of ethyl benzoate ($CDCl_3$, 500 MHz)



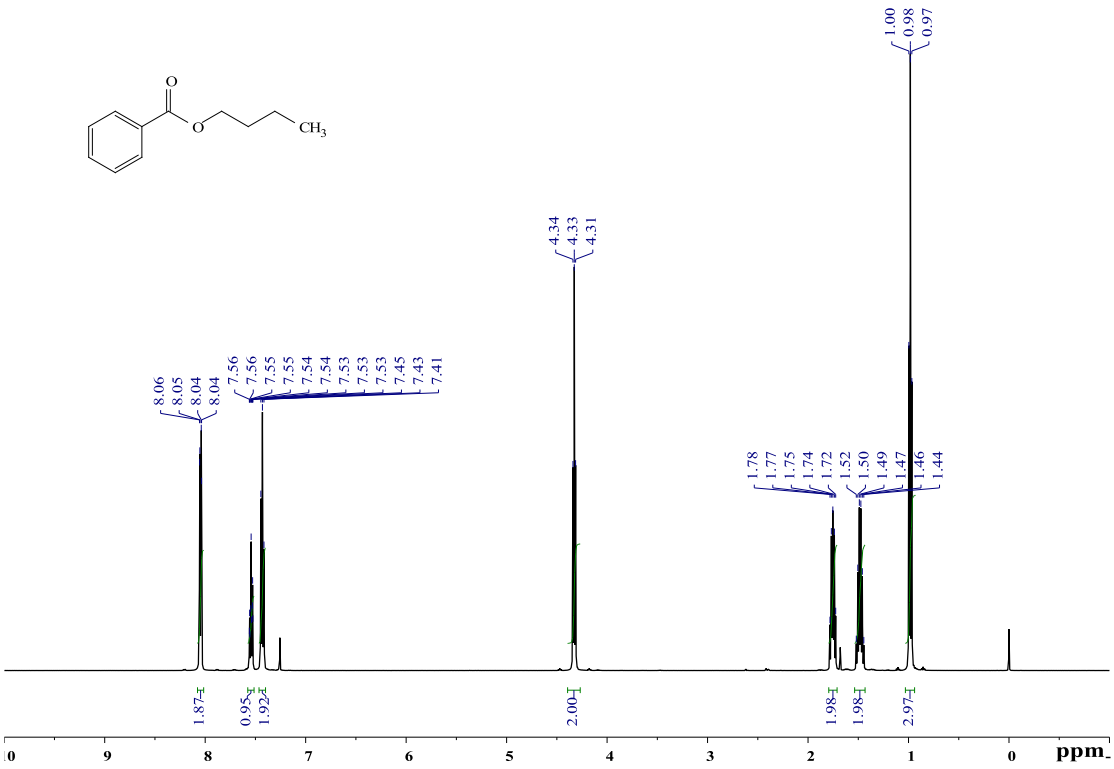
^{13}C NMR spectrum of ethyl benzoate ($CDCl_3$, 126 MHz)



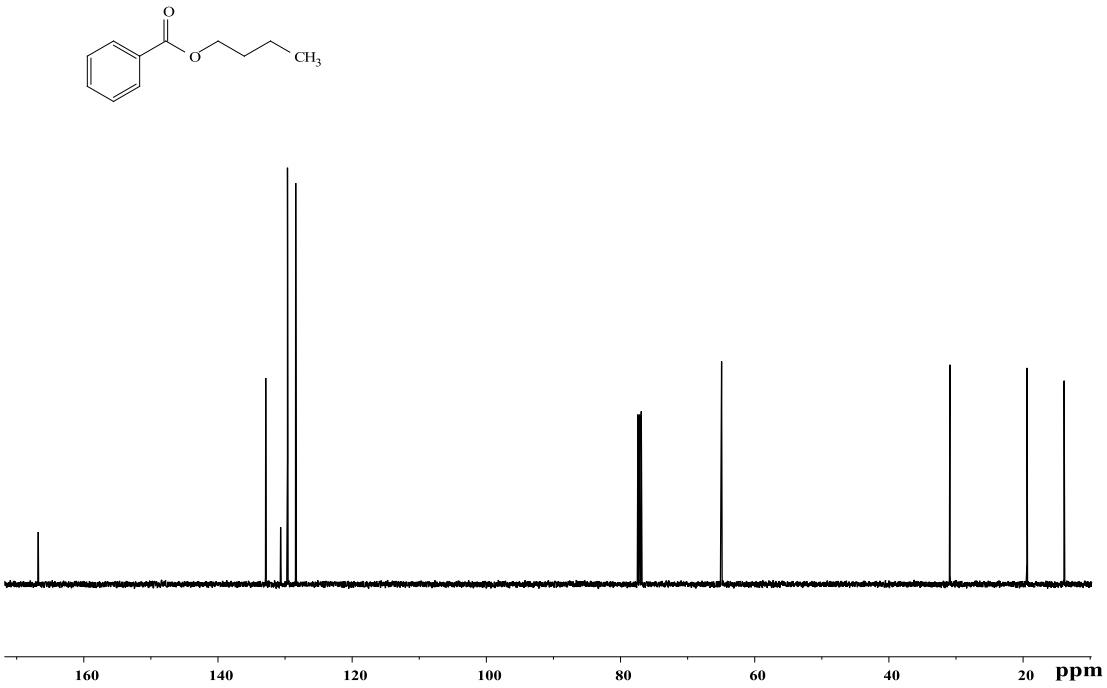
^{1}H NMR spectrum of isopropyl benzoate ($CDCl_3$, 500 MHz)



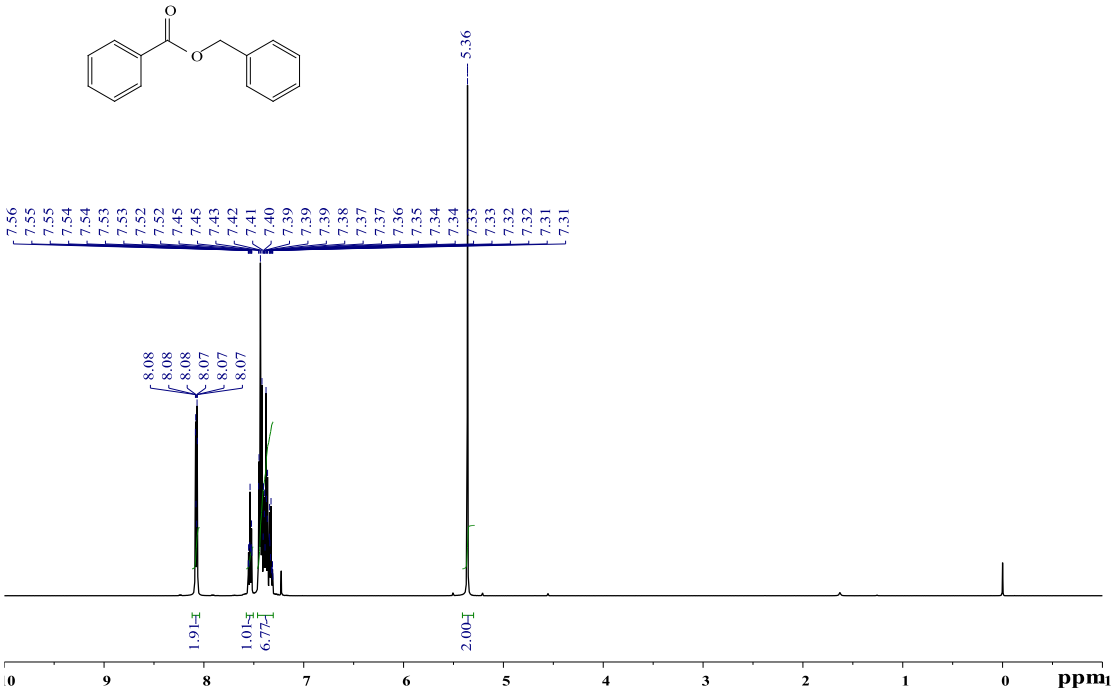
^{13}C NMR spectrum of isopropyl benzoate ($CDCl_3$, 126 MHz)



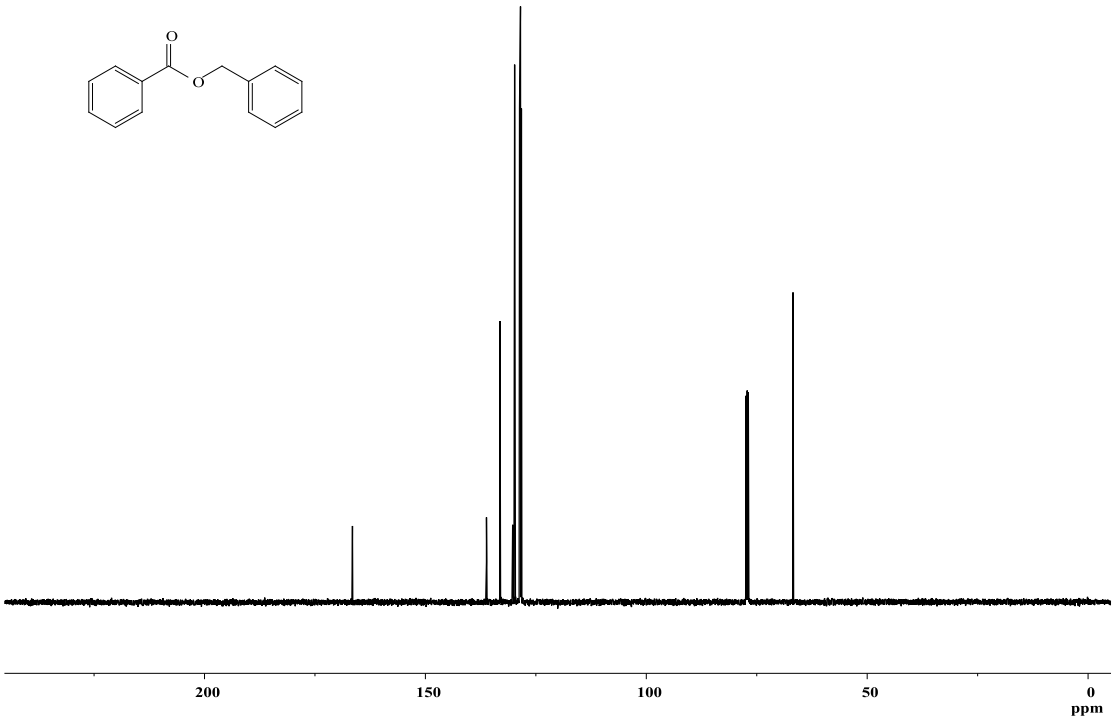
^{1}H NMR spectrum of butyl benzoate ($CDCl_3$, 500 MHz)



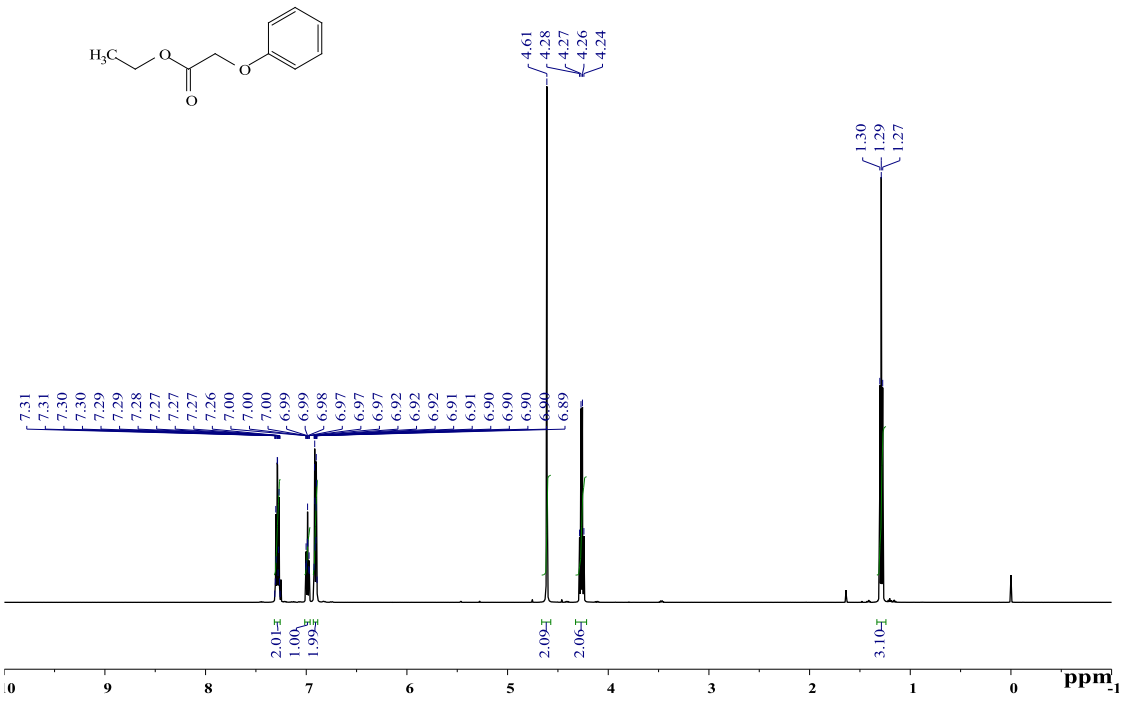
^{13}C NMR spectrum of butyl benzoate ($CDCl_3$, 126 MHz)



^{1}H NMR spectrum of benzyl benzoate ($CDCl_3$, 500 MHz)

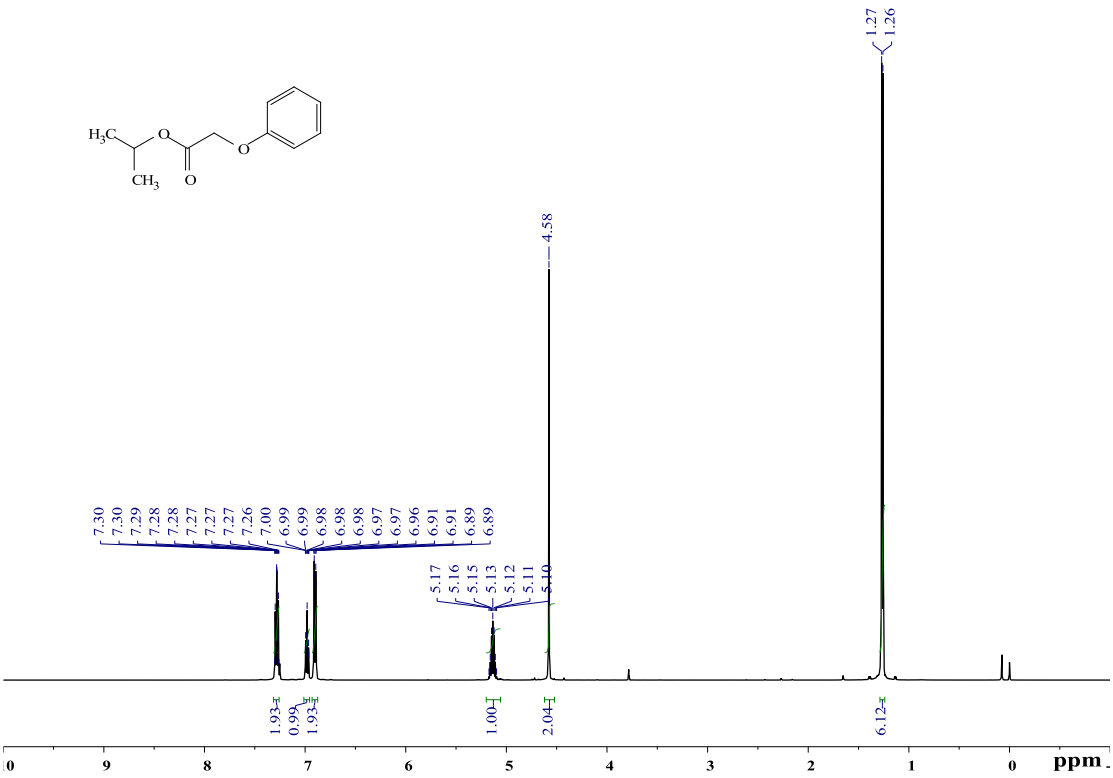


^{13}C NMR spectrum of benzyl benzoate ($CDCl_3$, 126 MHz)

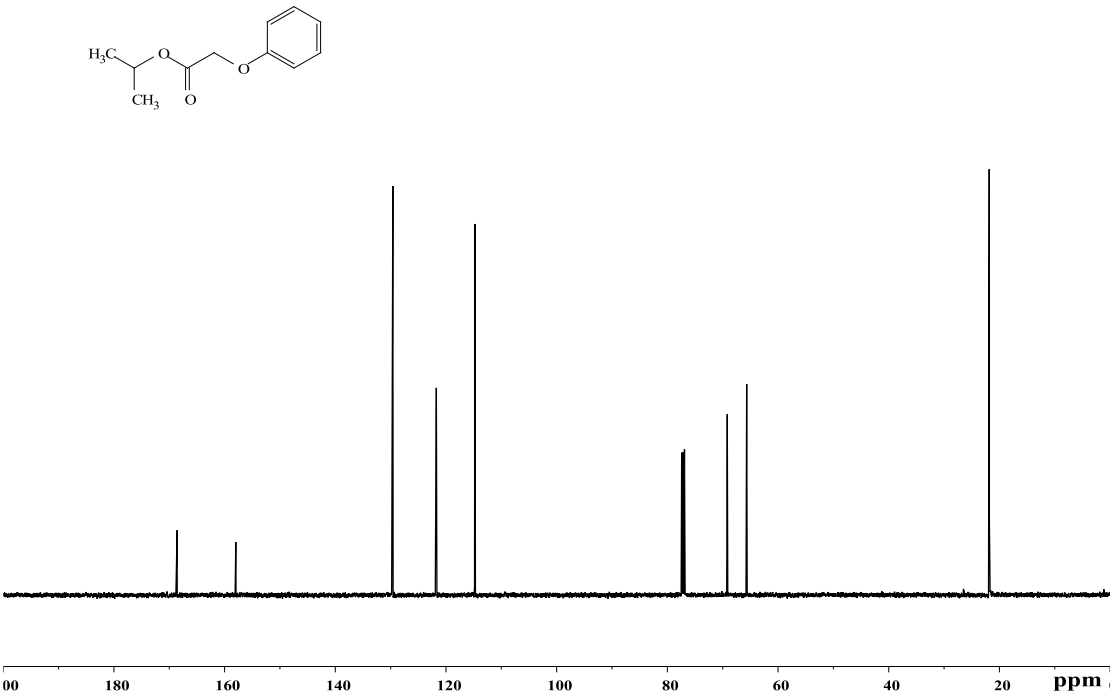


^{1}H NMR spectrum of ethyl 2-phenoxyacetate ($CDCl_3$, 500 MHz)

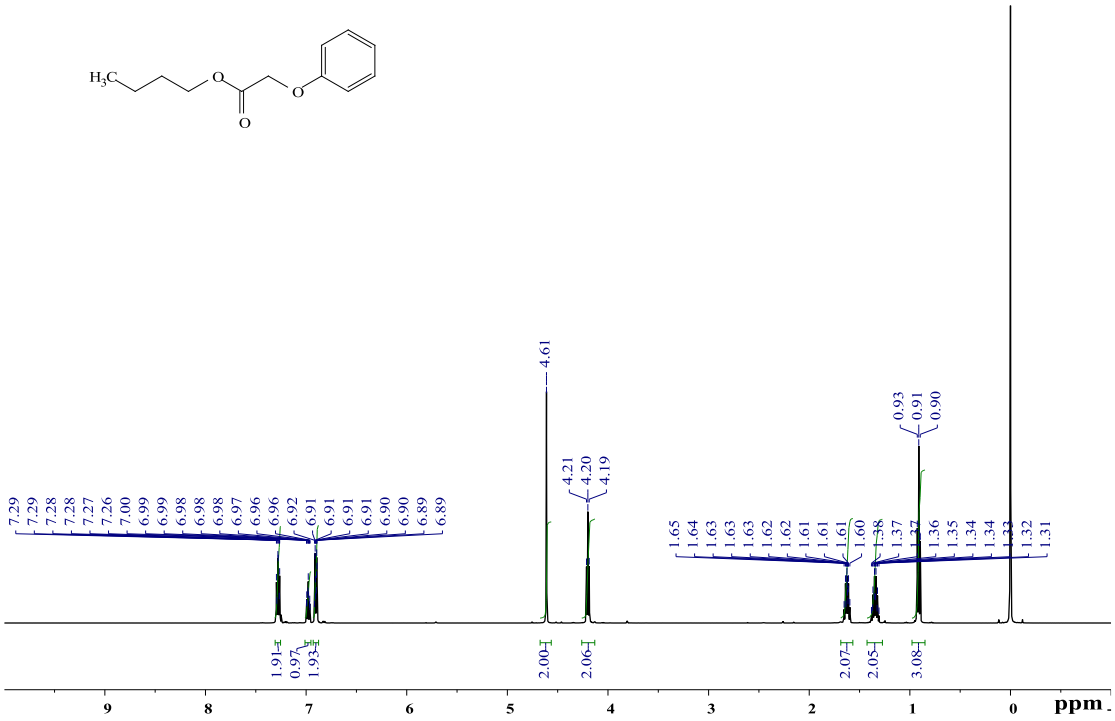
^{13}C NMR spectrum of ethyl 2-phenoxyacetate ($CDCl_3$, 126 MHz)



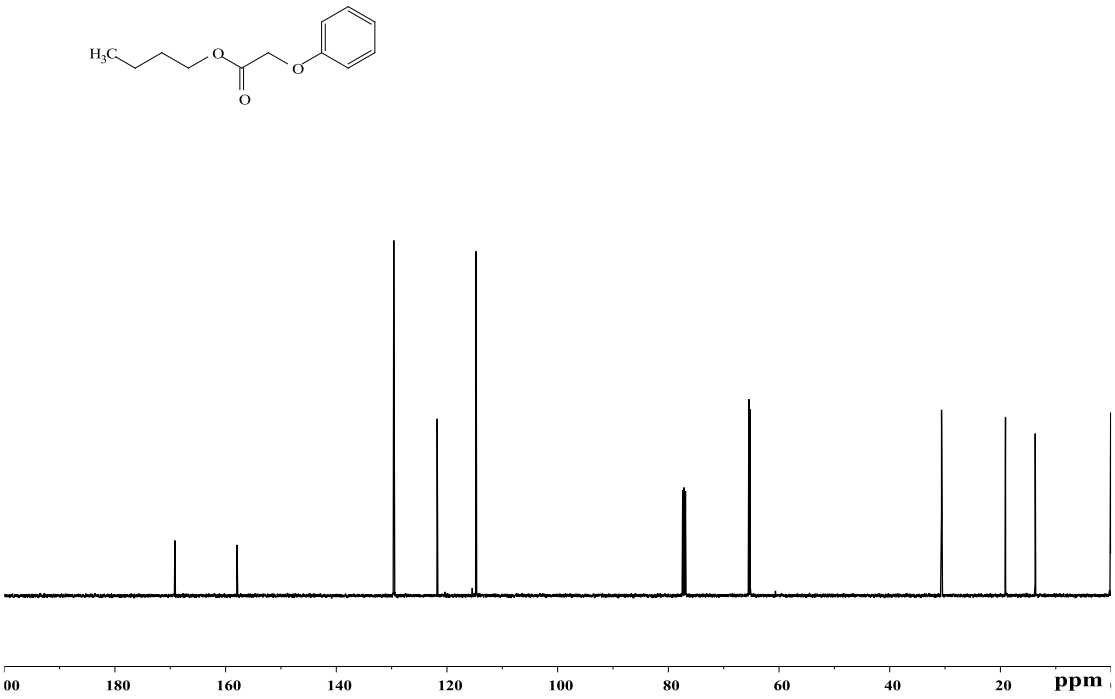
^{1}H NMR spectrum of isopropyl 2-phenoxyacetate ($CDCl_3$, 500 MHz)



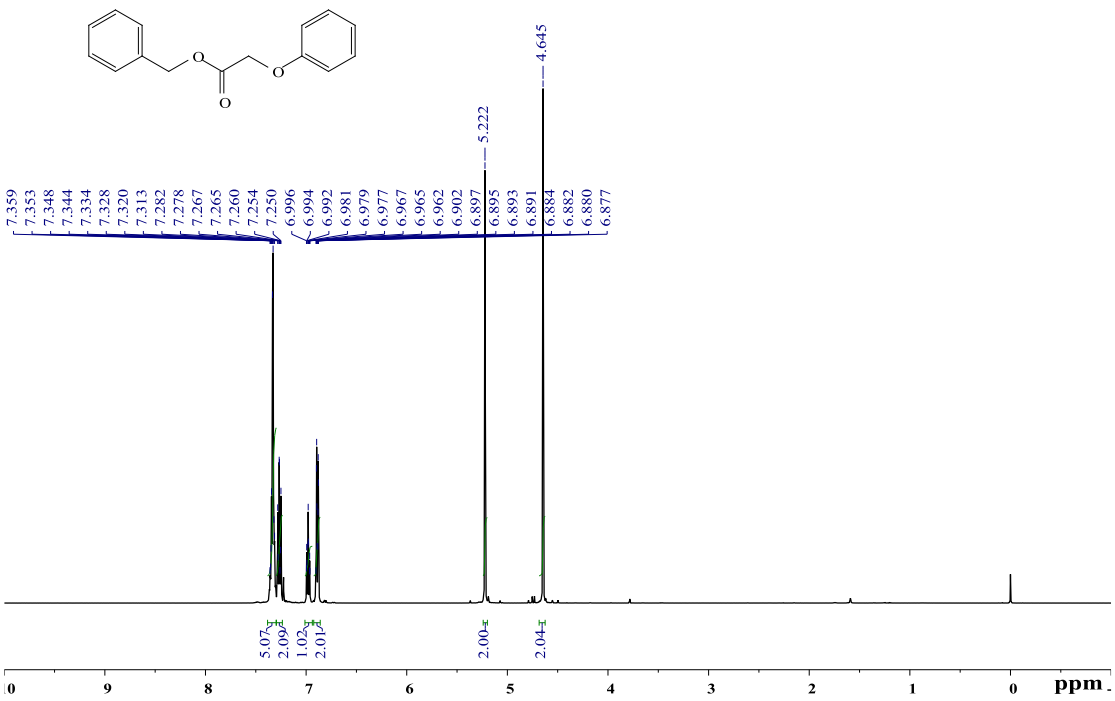
^{13}C NMR spectrum of isopropyl 2-phenoxyacetate ($CDCl_3$, 126 MHz)



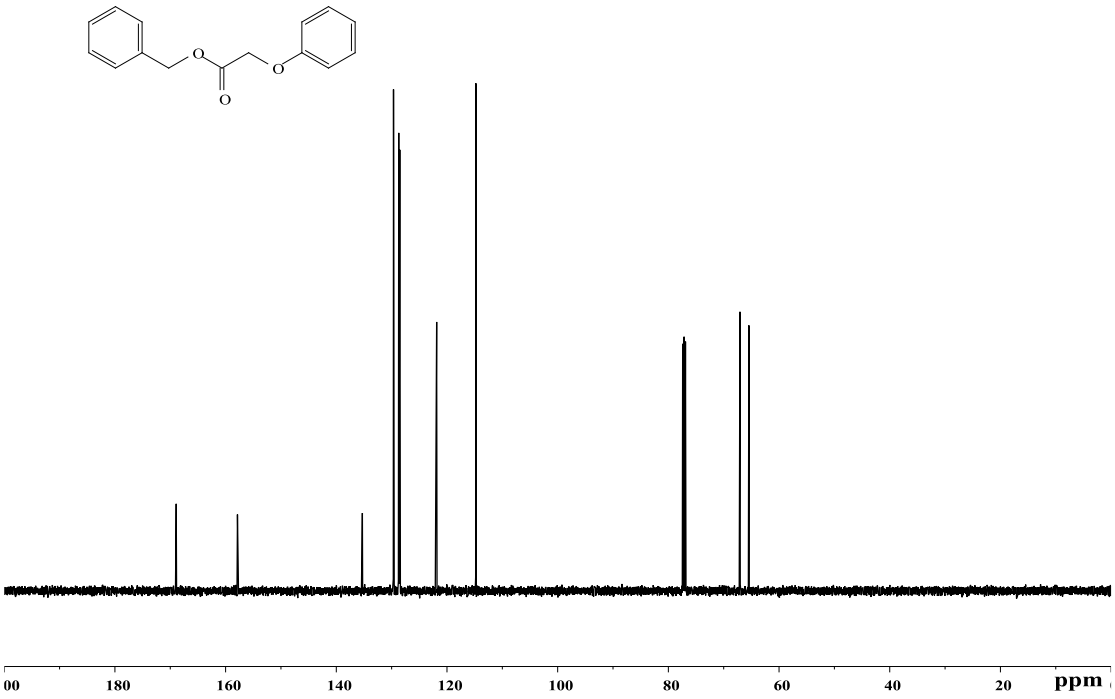
^{1}H NMR spectrum of butyl 2-phenoxyacetate ($CDCl_3$, 500 MHz)



^{13}C NMR spectrum of butyl 2-phenoxyacetate ($CDCl_3$, 126 MHz)



^{1}H NMR spectrum of benzyl 2-phenoxyacetate ($CDCl_3$, 500 MHz)



^{13}C NMR spectrum of benzyl 2-phenoxyacetate ($CDCl_3$, 126 MHz)