Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Transformation of Lignin Model Compounds to N-substituted Aromatics *via* Beckmann Rearrangement

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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 glove box. 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 were reported as parts per million relative to $SiMe_4$.

2-Bromoacetophenone, guaiacol, diisopropylamine, n-BuLi (1.6 M solution in hexane), 3,4-dimethoxybenzaldehyde, 2-bromo-4'-methoxyacetophenone, and the standard substances benzonitrile (**aa1**), 4-methoxybenzonitrile (**aa2**), 3,4-dimethoxybenzonitrile (**aa3**), benzamide (**ab1**), and 4-methoxybenzamide (**ab2**), aniline (**ac1**), 4-methoxyaniline (**ac2**), 3,4-dimethoxyaniline (**ac3**), phenol (**ba1**), 2-methoxyphenol (**ba2**), 2-phenoxyacetic acid, and 2-(2-methoxyphenoxy)acetic acid were purchased from J&K. $NH_2OH{\cdot}HCl$, $NaOAc{\cdot}3H_2O$, 4-acetamido-TEMPO, ethyl (2-methoxyphenoxy)acetate, sodium borohydride, 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 $\mathbf{F^{ox}}$. The oxidized lignin model compounds $\mathbf{A^{ox}}$, [1] $\mathbf{B^{ox}}$, [1] $\mathbf{C^{ox}}$, [1] $\mathbf{D^{ox}}$, [1] $\mathbf{E^{ox}}$, [2] and $\mathbf{F^{ox}}$ [3] were prepared according to a literature procedure.

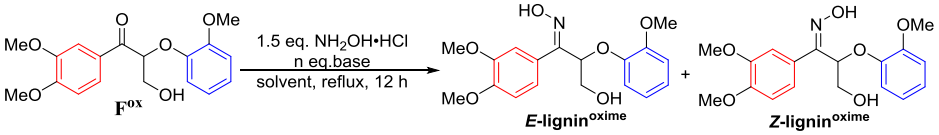
Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV); column chromatography purifications were carried out using silica gel. The reaction mixture was analyzed referred to the standard curves of standards using Waters make High Performance Liquid Chromatograph (HPLC) system equipped with autosampler, C18 column (Length: 150mm, Internal diameter: 4.6mm, 35 ºC) and UV/Vis detector (λ = 220 nm). CH_3OH: H_2O (45:55 or 25:75) was used as a mobile phase with a flow rate of 1.0 mL/min. Mass spectras were recorded on the Bruker MicroTOF Q II.

II. General procedures

1. General procedure for the synthesis of lignin^{oxime}

To a solution of lignin model compounds (10 mmol) in EtOH:H_2O (1:3, 80 mL) was added $NH_2OH{\cdot}HCl$ (15 mmol, 1.5 eq.), $NaOAc{\cdot}3H_2O$ (25 mmol, 2.5 eq.) at room temperature. The mixture was heated to reflux. After the reaction, the mixture was extracted with ethyl acetate for three times and washed with saturated brine. The organic phase was dried by anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The product was purified on silica gel with EtOAc: petroleum ether to provide a mixture of *Z* and *E* isomers.

Table S1. Optimization for the synthesis of lignin^{oxime} [a]

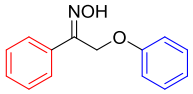


Entry	Base n eq.	Solvent	Conv.[b] (%)	Selctivity[b]	
				Z	E
1	$NaOAc{\cdot}3H_2O$ 1.1	H_2O	7	46	54
2	$NaOAc{\cdot}3H_2O$ 1.1	H_2O:EtOH=3:1	97	42	58

3	NaOAc·3H_2O 1.1	H_2O:EtOH=1:1	90	49	51
4	NaOAc·3H_2O 1.1	EtOH	87	50	50
5	NaOAc·3H_2O 1.5	H_2O:EtOH=3:1	92	55	45
6	NaOAc·3H_2O 3.0	H_2O:EtOH=3:1	>99	51	49
7	NaOAc·3H_2O 5.0	H_2O:EtOH=3:1	62	52	48
8	NaOAc·3H_2O 3.0	EtOH:Tol=1:3	88	62	38
9	NaOAc·3H_2O 3.0	EtOH:1,4-dioxide=1:3	59	56	44
10	NaOAc·3H_2O 3.0	EtOH:$CHCl_3$=1:3	66	61	39
11	Et_3N 3.0	EtOH:H_2O=1:3	75	56	44
12	Et_3N 3.0	Tol	0	-	-

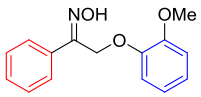
[a]Condition: substrate (0.1 mmol, 1 eq.), NH_2OH·HCl (n eq.), base (n eq.), and 0.8 ml solvent, reflux, 12 h. [b]The conversion and seletivity were measured by ^{1}H NMR.

2-phenoxy-1-phenylethan-1-one oxime (A^{oxime}): white solid. ^{1}H NMR (500 MHz, DMSO-d_6)



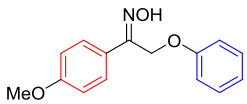
δ 11.92 (s, 3H, -O*H*), 11.42 (s, 1H, -O*H*), 7.68 – 7.65 (m, 9H, -*Ar*), 7.43 – 7.34 (m, 13H, -*Ar*), 7.28 – 7.25 (m, 9H, -*Ar*), 6.98 – 6.92 (m, 13H, -*Ar*), 5.26 (s, 7H, -CH_2), 4.96 (s, 2H -CH_2). ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.1, 157.9, 152.9, 151.0, 134.3, 131.8, 129.5, 129.5, 128.8, 128.6, 128.3, 128.0, 126.4, 120.9, 114.9, 114.3, 69.2, 58.6. HRMS (ESI) calculated for $C_{14}H_{14}NO_2$ $[M + H]^+$ 228.1019, found 228.0993.

2-(2-methoxyphenoxy)-1-phenylethan-1-one oxime (B^{oxime}): white solid. ^{1}H NMR (500 MHz,



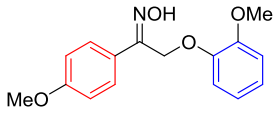
DMSO-d_6) δ 11.86 (s, 3H, -O*H*), 11.39 (s, 1H, -O*H*), 7.71 – 7.68 (m, 8H, -*Ar*), 7.43 – 7.34 (m, 12H, -*Ar*), 7.05 – 7.03 (m, 4H, -*Ar*), 6.95 – 6.85 (m, 12H, -*Ar*), 5.22 (s, 6H, -CH_2), 4.92 (s, 2H, -CH_2), 3.66 (s, 12H, -OCH_3). ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.9, 151.1, 149.4, 149.2, 147.6, 147.6, 134.4, 131.9, 128.8, 128.7, 128.2, 127.9, 126.4, 121.7, 121.5, 120.7, 120.7, 114.8, 113.5, 112.6, 112.5, 70.3, 59.4, 55.5. HRMS (ESI) calculated for $C_{15}H_{16}NO_3$ $[M + H]^+$ 258.1125, found 258.1090.

1-(4-methoxyphenyl)-2-phenoxyethan-1-one oxime (C^{oxime}): white solid. ^{1}H NMR (500 MHz,



DMSO-d_6) δ 11.70 (s, 5H, -O*H*), 11.36 (s, 1H, -O*H*), 7.75 – 7.72 (m, 2H, -*Ar*), 7.63 – 7.60 (m, 10H, -*Ar*), 7.29 – 7.24 (m, 13H, -*Ar*), 6.98 – 6.91 (m, 32H, -*Ar*), 5.23 (s, 10H, -CH_2), 4.94 (s, 2H, -CH_2), 3.77 (s, 3H, -OCH_3), 3.75 (s, 14H, -OCH_3). ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.8, 159.5, 158.1, 157.9, 152.4, 150.1, 130.5, 129.5, 129.4, 127.7, 126.7, 123.8, 120.9, 114.9, 114.3, 113.7, 113.3, 69.2, 58.5, 55.1. HRMS (ESI) calculated for $C_{15}H_{16}NO_3$ $[M + H]^+$ 258.1125, found 258.1090.

2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one oxime (D^{oxime}): white solid. ^{1}H



NMR (500 MHz, DMSO-d_6) δ 11.64 (s, 3H, -O*H*), 11.34 (s, 1H, -O*H*), 7.77 (d, J = 8.5 Hz, 2H, -*Ar*), 7.64 (d, J = 8.5 Hz, 7H, -*Ar*), 7.05 – 7.03 (m, 5H, -*Ar*), 6.98 – 6.85 (m, 22H, -*Ar*), 5.18 (s, 7H, -CH_2), 4.90 (s, 2H, -CH_2), 3.78 (s, 4H, -OCH_3), 3.76 (s, 9H, -OCH_3), 3.68 (s, 12H, -OCH_3). ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.8, 159.5, 152.4, 150.1, 149.4, 149.1, 147.6, 130.6, 127.7, 126.9, 123.9, 121.6, 121.5, 120.7, 120.7, 114.7, 113.7, 113.4, 113.3, 112.5, 112.4, 70.4, 59.3, 55.5, 55.1. HRMS (ESI) calculated for $C_{16}H_{18}NO_4$ $[M + H]^+$ 288.1231, found 288.1195.

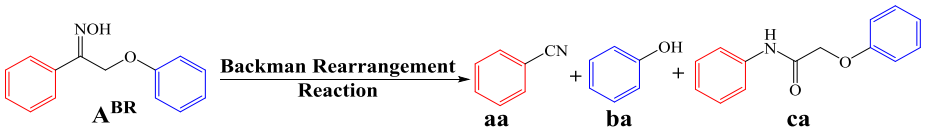
1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one oxime (E^{oxime}): white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.68 (s, 7H, -O*H*), 11.36 (s, 1H, -O*H*), 7.46 – 7.24 (m, 17H, -*Ar*), 7.07 – 6.87 (m, 42H, -*Ar*), 5.19 (s, 14H, -CH_2), 4.91 (s, 2H, -CH_2), 3.72 (d, J = 32.0 Hz, 76H, -OCH_3). ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.3, 150.1, 149.6, 149.5, 149.3, 149.2, 148.4, 147.9, 147.6, 127.0, 124.2, 122.2, 121.6, 121.5, 120.7, 120.7, 119.5, 114.7, 113.4, 112.8, 112.4, 111.3, 111.0, 109.4, 70.5, 59.3, 55.5, 55.5, 55.3. HRMS (ESI) calculated for $C_{17}H_{20}NO_5$ $[M + H]^+$ 318.1336, found 318.1329.

1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one oxime (F^{oxime}): white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.70 (s, 1H, -NO*H*), 11.07 (s, 1H, -NO*H*), 7.34 (d, *J* = 2.0 Hz, 1H, -*Ar*), 7.30 (dd, *J* = 8.5, 2.0 Hz, 1H, -*Ar*), 7.12 (dd, *J* = 8.0, 2.0 Hz, 1H, -*Ar*), 7.03 – 6.76 (m, 11H, -*Ar*), 5.88 (dd, *J* = 7.5, 3.5 Hz, 1H, -C*H*), 5.19 (t, *J* = 5.8 Hz, 1H, -CH_2OH), 5.02 (t, *J* = 6.5 Hz, 1H, -C*H*), 4.97 (t, *J* = 5.8 Hz, 1H, -CH_2OH), 3.97 (dt, *J* = 12.5, 6.5 Hz, 1H, -CH_2OH), 3.76 (s, 3H, -OCH_3), 3.75 – 3.71 (m, 9H, -OCH_3), 3.70 (s, 3H, -OCH_3), 3.67 (s, 3H, -OCH_3), 3.57 (dt, *J* = 11.5, 6.0 Hz, 1H, -CH_2OH). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.2, 152.2, 149.6, 149.3, 148.9, 148.8, 147.8, 147.8, 146.9, 126.1, 123.7, 121.6, 121.5, 121.1, 120.6, 120.5, 120.1, 115.4, 112.7, 112.5, 112.4, 112.1, 111.0, 111.0, 110.8, 81.1, 73.6, 61.8, 61.7, 55.5, 55.5, 55.4, 55.4, 55.3, 55.2. HRMS (ESI) calculated for $C_{18}H_{22}NO_6$ $[M + H]^+$ 348.1442, found 348.1436.

2. General procedure for the BR reaction of lignin^{oximes}

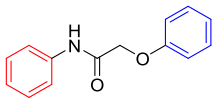
A mixture of *Z* and *E* lignin^{oxime} (0.1 mmol) was added to a 5 mL round bottom flask equipped with a magnetic stirring bar. A solution of $SOCl_2$ (0.5 eq.) in dry CH_3CN 0.5ml was subsequently added dropwise at 80°C with a syringe. The mixture was stirred for 2 min at 80°C. After the reaction, it was quenched by saturated sodium bicarbonate solution. Using acetonitrile, the mixture was dissolved to constant volume in a 25 mL volumetric flask and then filtered. The filtrate was measured by HPLC.

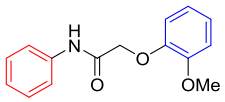
Table S2. Optimization for BR reaction of lignin$^{oximes\ a}$

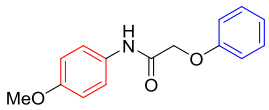


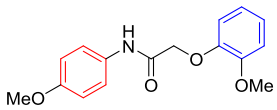
Entry	Conditions			Products and yields [b] (%)		
	$SOCl_2$ (eq.)	T (°C)	t (min)	**aa**	**ba**	**ca**
1	$SOCl_2$ 0.5	25	2	15	15	47
2	$SOCl_2$ 0.5	40	2	21	17	53
3	$SOCl_2$ 0.5	60	2	30	28	53
4	**$SOCl_2$ 0.5**	**80**	**2**	**33**	**27**	**63**
5	$SOCl_2$ 0.3	80	10	36	47	31
6	$SOCl_2$ 0.1	80	10	17	22	12
7	PCl_5 0.5	80	2	31	27	44

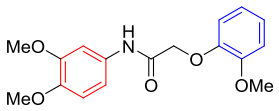
[a] Optimization reactions were performed on a 0.1 mmol scale. [b]The yields measured by HPLC.

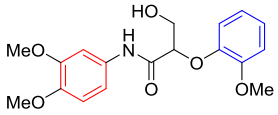
2-phenoxy-N-phenylacetamide (A^{BR}): white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.29 (s, 
1H, -N*H*CO), 7.60 (d, *J* = 8.0 Hz, 2H, -*Ar*), 7.36 (t, *J* = 7.5 Hz, 4H, -*Ar*), 7.16 (t, *J* = 7.5 Hz, 1H, -*Ar*), 7.07 (t, *J* = 7.5 Hz, 1H, -*Ar*), 7.00 (d, *J* = 8.0 Hz, 2H, -*Ar*), 4.62 (s, 2H, -CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 157.1, 137.0, 130.0, 129.2, 125.0, 122.6, 120.2, 115.0, 67.8. HRMS (ESI) calculated for $C_{14}H_{14}NO_2$ $[M + H]^+$ 228.1019, found 228.0993.

2-(2-methoxyphenoxy)-N-phenylacetamide (B^{BR}): white solid. ^{1}H NMR (500 MHz, Chloroform- 
d) δ 8.96 (s, 1H, -N*H*CO), 7.61 (d, *J* = 8.5 Hz, 2H, -*Ar*), 7.36 (t, *J* = 8.0 Hz, 2H, -*Ar*), 7.14 (t, *J* = 7.3 Hz, 1H, -*Ar*), 7.10 – 7.07 (m, 1H, -*Ar*), 7.00 (dd, *J* = 8.0, 1.5 Hz, 1H, -*Ar*), 7.00 – 6.96 (m, 2H, -*Ar*), 4.66 (s, 2H, -CH_2), 3.94 (s, 3H, -OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 150.0, 147.4, 137.4, 129.2, 124.7, 123.8, 121.5, 119.9, 116.8, 112.3, 70.7, 56.0. HRMS (ESI) calculated for $C_{15}H_{16}NO_3$ $[M + H]^+$ 258.1125, found 258.1090.

N-(4-methoxyphenyl)-2-phenoxyacetamide (C^{BR}): white solid. ^{1}H NMR (500 MHz, Chloroform- 
d) δ 8.21 (s, 1H, -N*H*CO), 7.49 (d, *J* = 8.0 Hz, 2H, -*Ar*), 7.35 (t, *J* = 7.5 Hz, 2H, -*Ar*), 7.06 (t, *J* = 7.0 Hz, 1H, -*Ar*), 6.99 (d, *J* = 7.5 Hz, 2H, -*Ar*), 6.89 (d, *J* = 7.5 Hz, 2H, -*Ar*), 4.60 (s, 2H, -CH_2), 3.80 (s, 3H, -OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 157.1, 156. 9, 130.0, 122.5, 122.1, 114.9, 114.3, 67.8, 55.6. HRMS (ESI) calculated for $C_{15}H_{16}NO_3$ $[M + H]^+$ 258.1125, found 258.1090.

2-(2-methoxyphenoxy)-N-(4-methoxyphenyl) acetamide (D^{BR}): white solid. ^{1}H NMR (500 MHz, 
Chloroform-*d*) δ 8.82 (s, 1H, -N*H*CO), 7.52 – 7.48 (m, 2H, -*Ar*), 7.07 – 7.04 (m, 1H, -*Ar*), 7.01 – 6.98 (m, 1H, -*Ar*), 6.97 – 6.93 (m, 2H, -*Ar*), 6.90 – 6.87 (m, 2H, -*Ar*), 4.65 (s, 2H, -CH_2), 3.94 (s, 3H, -OCH_3), 3.80 (s, 3H, -OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 156.7, 150.0, 147.5, 130.5, 123.7, 121.7, 121.5, 116.7, 114.3, 112.3, 70.6, 56.1, 55.6. HRMS (ESI) calculated for $C_{16}H_{18}NO_4$ $[M + H]^+$ 288.1231, found 288.1195.

N-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) acetamide (E^{BR}): white solid. ^{1}H NMR (500 
MHz, Chloroform-*d*) δ 8.86 (s, 1H, -N*H*CO), 7.43 (d, *J* = 2.0 Hz, 1H, -*Ar*), 7.09 (t, *J* = 7.5 Hz, 1H, -*Ar*), 7.03 (d, *J* = 7.5 Hz, 1H, -*Ar*), 7.00 – 6.96 (m, 2.0H, -*Ar*), 6.86 (d, *J* = 8.5 Hz, 1H, -*Ar*), 4.67 (s, 2H, -CH_2), 3.97 (s, 3H, -OCH_3), 3.92 (s, 3H, -OCH_3), 3.89 (s, 3H, -OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 150.0, 149.3, 147.50, 146.2, 131.0, 123.8, 121.6, 116.9, 112.3, 112.0, 111.5, 105.0, 70.8, 56.3, 56.1, 56.1. HRMS (ESI) calculated for $C_{17}H_{20}NO_5$ $[M + H]^+$ 318.1336, found 318.1329.

N-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy) propanamide (F^{BR}): white solid. 
^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.15 (s, 1H, N*H*CO), 7.45 (d, *J* = 3.5 Hz, 1H, *Ar*), 7.16 – 7.11 (m, 2H, *Ar*), 7.01 – 6.97 (m, 3H, *Ar*), 6.85 (d, *J* = 9.0 Hz, 1H, *Ar*), 4.66 (t, *J* = 5.0 Hz, 1H, C*H*), 4.14 – 4.13 (m, 2H, CH_2OH), 3.97 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 2.76 (brs, 1H, O*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 150.7, 149.2, 147.1, 146.2, 131.1, 124.8, 121.9, 119.7, 112.5,

111.8, 111.5, 104.7, 83.8, 63.3, 56.3, 56.1, 56.1. HRMS (ESI) calculated for $C_{18}H_{22}NO_6$ $[M + H]^+$ 348.1442, found 348.1436.

2-(3,4-dimethoxyphenyl) oxazole (aa3'): slight yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.67 (s, 1H, -OC*H*CHN), 7.63 (dd, *J*=8.5, 2.0, 1H, -*Ar*), 7.58 (d, *J*=2.0, 1H, -*Ar*), 7.20 (s, 1H, -OCHC*H*N), 6.94 (d, *J*=8.5, 1H, -*Ar*), 3.97 (s, 3H, -OCH_3), 3.94 (s, 3H, -OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.1, 151.1, 149.3, 138.3, 128.3, 120.6, 119.7, 111.2, 109.3, 56.2, 56.1. HRMS (ESI) calculated for $C_{11}H_{12}NO_3$ $[M + H]^+$ 206.0812, found 206.0835.

3. General procedure for hydrolysis of lignin^{BR}

Phenoxyacetanilide (**A^{BR}~F^{BR}**) (0.1 mmol) was added to a 5 mL round bottom flask equipped with a magnetic stirring bar. And then 2M NaOH aq. (0.5 ml) and EtOH 0.5 ml were subsequently added with a syringe. The mixture was stirred for 30 min at 80 °C. After the reaction, using acetonitrile, the mixture was dissolved to constant volume in a 25 mL volumetric flask and then filtered. The filtrate was measured by HPLC.

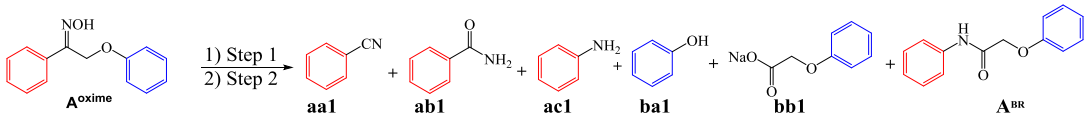
3,4-dimethoxybenzamide (ab3): white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.94 (s, 1H, -CONH$_2$), 7.51 (d, *J* = 8.5 Hz, 1H, -*Ar*), 7.49 (s, 1H, -*Ar*), 7.18 (s, 1H, -CONH$_2$), 6.98 (d, *J* = 8.5 Hz, 1H, -*Ar*), 3.79 (s, 6H, -OCH_3). ^{13}C NMR (126 MHz, DMSO) δ 167.5, 151.2, 148.1, 126.6, 120.8, 111.0, 110.8, 55.6, 55.6. HRMS (ESI) calculated for $C_9H_{12}NO_3$ $[M + H]^+$ 182.0812, found 182.0821.

sodium 3-hydroxy-2-(2-methoxyphenoxy) propanoate (bb3): white solid. ^{1}H NMR (500 MHz, Deuterium Oxide) δ 7.04 (d, *J* = 8.0 Hz, 1H, -*Ar*), 6.97 (t, *J* = 7.8 Hz, 1H, -*Ar*), 6.91 (t, *J* = 7.8 Hz, 1H, -*Ar*), 6. 76 (d, *J* = 8.0 Hz, 1H, -*Ar*), 4.54 (dd, *J* = 7.0, 3.5 Hz, 1H, -C*H*CH$_2$OH), 3.97 – 3.89 (m, 2H, -CHC*H*$_2$OH), 3.83 (s, 3H, -OCH_3). ^{13}C NMR (126 MHz, D_2O) δ 176.4, 148.1, 146.8, 121.7, 121.4, 113.1, 112.5, 80.6, 62.8, 55.7. HRMS (ESI) calculated for $C_{10}H_{12}NaO_5$ $[M + H]^+$ 235.0577, found 235.0574.

4. General procedure for one-pot process of BR reaction and hydrolysis

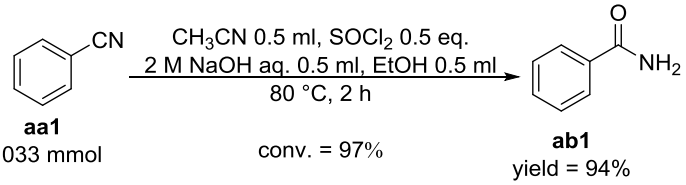
A mixture of *Z*- and *E*-lignin^{oxime} (0.1 mmol) was added to a 5 mL round bottom flask equipped with a magnetic stirring bar. A solution of $SOCl_2$ (0.5 eq.) in dry CH_3CN 0.5ml was subsequently added dropwise with a syringe at 80 °C. The mixture was stirred for 2 min at 80 °C. And then 2M NaOH aq. (0.5 ml) and EtOH 0.5 ml were subsequently added with a syringe. The mixture was continued to stir for 2 h at 80 °C. After the reaction, the mixture was dissolved in acetonitrile to constant volume in a 25 mL volumetric flask and then filtered. The filtrate was measured by HPLC.

Table S3. One-pot process of BR reaction and hydrolysis of **A$^{oxime\ a}$**



Entry	Step 2 condition	Products and yields [b] (%)						Total Cleavage Yield of N (%) [c]
		aa1	**ab1**	**ac1**	**ba1**	**bb1**	**A^{BR}**	
1	2M NaOH aq. 0.5 ml, EtOH 0.5 ml, 80ºC, 2 h	7	25	64	28	59	4	96
2	2M NaOH aq. 0.5 ml, EtOH 0.5 ml, 80ºC, 5 h	7	26	62	28	58	5	95
3	2M NaOH aq. 0.5 ml, EtOH 0.5 ml, 100ºC, 2 h	2	28	18	20	20	5	48
4	2M NaOH aq. 1.0 ml, EtOH 0.5 ml, 80ºC, 2 h	7	25	60	29	56	5	92
5	2M NaOH aq. 0.5 ml, 80ºC, 2 h	2	23	44	29	54	8	69

[a] step 1 condition: substrate (0.1 mmol, 1.0 eq.), $SOCl_2$ (0.02 mmol, 0.5 eq.), dry CH_3CN 0.5 ml, at 80 °C, 2 min. [b] The yields measured by HPLC. [c] Total cleavage yield of N was presented as the amount of (**aa1** + **ab1** + **ac1**) in Products and yields.



Scheme S1. Hydrolysis of benzonitrile (**aa1**)

III. Molecular Structure and X-Ray Data of compound *Z*-F^{oxime}

Single crystal ***Z*-F^{oxime}** suitable for an X-ray diffraction experiment was prepared from the slow evaporation of a saturated dichloromethane/hexane solution of mixture of *E*/*Z*-F^{oxime}, after it was stored at room temperature for one week.

Single crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 °C/10^{-6} Torr for 24 h) after decanting the mother liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker APEX-II CCD diffractometer. The structures were solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least squares on F^2 for all reflections (*SHELXTL*, Version 6.12; Bruker Analytical X-ray Solutions: Madison, WI, 2001). The structure was refined by full-matrix least-squares on F^2 for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions (Sheldrick, G. M. *Acta Crystallogr., Sect. A.* **1990**, *46*, 467–473 & **2008**, *64*, 112–122.).

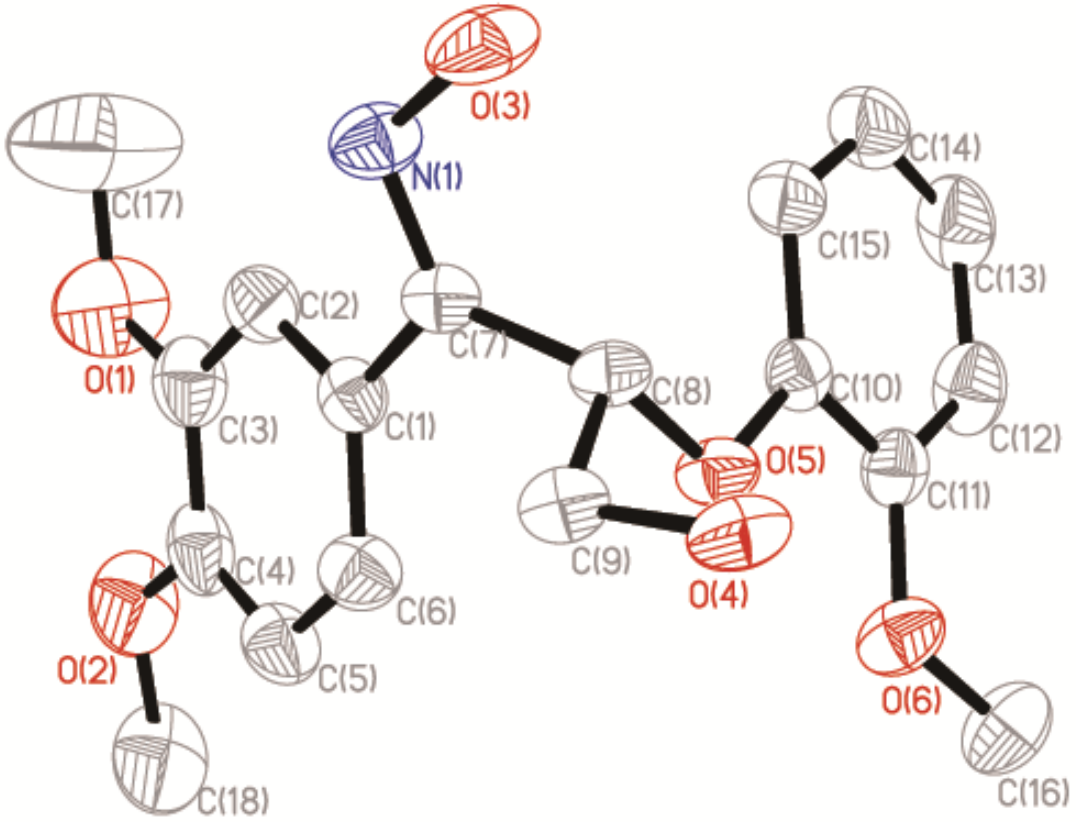


Figure S1. X-ray crystal structure of ***Z*-lignin^{oxime}**. Hydrogen atoms were deleted for clarity and ellipsoids were drawn at 50% probability, (CCDC# 1831464).

Table S4. Crystal data and structure refinement for compound ***Z*-F^{oxime}**.

Compound	***Z*-F^{oxime}**
empirical formula	$C_{18}H_{21}NO_6$
MW	347.36
wavelength, Å	0.71073
crystal system	Triclinic
space group	*P*-1
a, Å	8.9121(4)
b, Å	10.6028(6
c, Å	10.6070(6)
α, deg	10.6070(6)
β, deg	95.433(2)
γ, deg	76.473(3)
V, Å^3	875.81(8)
Z	2

D_{calc}, g cm^{-3}	1.317
μ, mm^{-1}	0.099
F(000)	368
crystal size, mm	0.24×0.20×0.18
θ range, deg	2.87-28.28
limiting indices	$-11 \le h \le 11$
	$-14 \le k \le 14$
	$-14 \le l \le 14$
reflns collected	18241
independent reflns	4328
	[R(int) = 0.0247]
absorption correction	None
data/restraints/para's	4328 / 0 / 231
goodness-of-fit on F^2	1.017
final R indices	$R1$ = 0.0476
[I >2σ(I)] [a]	w$R2$ = 0.1139
R indices (all data) [a]	$R1$ = 0.0617;
	w$R2$ = 0.1232
peak$_{max}$/hole$_{min}$ (e Å^{-3})	0.254 / –0.205

[a] $R1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table S5. Bond lengths [A] and angles [deg] for ***Z*-F^{oxime}**.

C(1)-C(6)	1.384(2)	C(9)-O(4)	1.4310(17)
C(1)-C(2)	1.399(2)	C(10)-O(5)	1.3749(16)
C(1)-C(7)	1.4825(18)	C(10)-C(15)	1.382(2)
C(2)-C(3)	1.377(2)	C(10)-C(11)	1.4066(19)
C(3)-O(1)	1.364(2)	C(11)-O(6)	1.3631(18)
C(3)-C(4)	1.401(3)	C(11)-C(12)	1.381(2)
C(4)-O(2)	1.3685(19)	C(12)-C(13)	1.389(3)
C(4)-C(5)	1.375(3)	C(13)-C(14)	1.370(3)
C(5)-C(6)	1.393(2)	C(14)-C(15)	1.394(2)
C(7)-N(1)	1.2846(17)	C(16)-O(6)	1.4319(18)
C(7)-C(8)	1.5234(19)	C(17)-O(1)	1.405(3)
C(8)-O(5)	1.4377(15)	C(18)-O(2)	1.417(3)
C(8)-C(9)	1.5149(18)	N(1)-O(3)	1.4041(16)
C(6)-C(1)-C(2)	118.31(13)	C(3)-C(2)-C(1)	121.29(15)
C(6)-C(1)-C(7)	122.72(13)	O(1)-C(3)-C(2)	124.44(17)
C(2)-C(1)-C(7)	118.96(12)	O(1)-C(3)-C(4)	115.71(15)

C(2)-C(3)-C(4)	119.85(15)	O(5)-C(10)-C(11)	114.78(12)
O(2)-C(4)-C(5)	125.33(16)	C(15)-C(10)-C(11)	119.78(13)
O(2)-C(4)-C(3)	115.54(16)	O(6)-C(11)-C(12)	125.41(14)
C(5)-C(4)-C(3)	119.14(14)	O(6)-C(11)-C(10)	114.98(12)
C(4)-C(5)-C(6)	120.78(15)	C(12)-C(11)-C(10)	119.61(14)
C(1)-C(6)-C(5)	120.59(15)	C(11)-C(12)-C(13)	120.08(15)
N(1)-C(7)-C(1)	116.45(12)	C(14)-C(13)-C(12)	120.41(15)
N(1)-C(7)-C(8)	121.23(12)	C(13)-C(14)-C(15)	120.27(16)
C(1)-C(7)-C(8)	122.30(11)	C(10)-C(15)-C(14)	119.84(15)
O(5)-C(8)-C(9)	108.29(10)	C(7)-N(1)-O(3)	110.89(11)
O(5)-C(8)-C(7)	112.15(10)	C(3)-O(1)-C(17)	117.16(16)
C(9)-C(8)-C(7)	111.97(11)	C(4)-O(2)-C(18)	117.37(17)
O(4)-C(9)-C(8)	108.68(11)	C(10)-O(5)-C(8)	116.66(10)
O(5)-C(10)-C(15)	125.44(13)	C(11)-O(6)-C(16)	117.83(12)

III. HPLC Analysis

All products were quantified by HPLC with standard curve of standards as reference. Some typical standard curves and chromatograms are shown as below.

1. HPLC Standard Curve

All standard curves had a linear relationship of R^2 = 0.999.

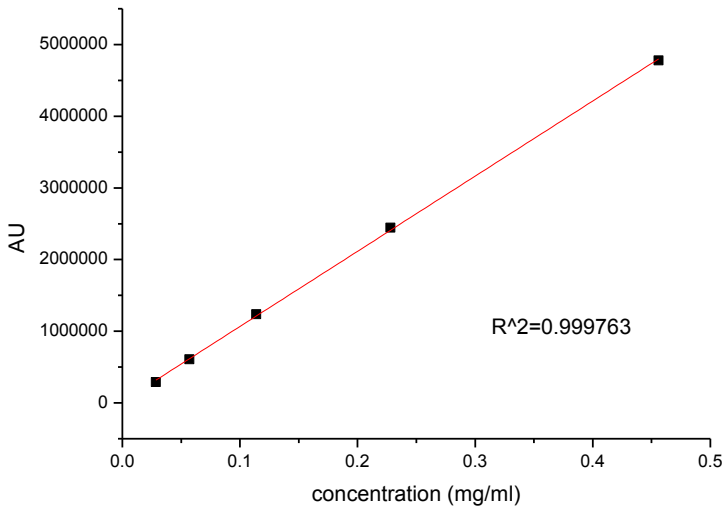


Figure S2. HPLC standard curve of benzonitrile (**aa**)

2. HPLC Chromatogram

Some typical HPLC chromatograms are shown as below.

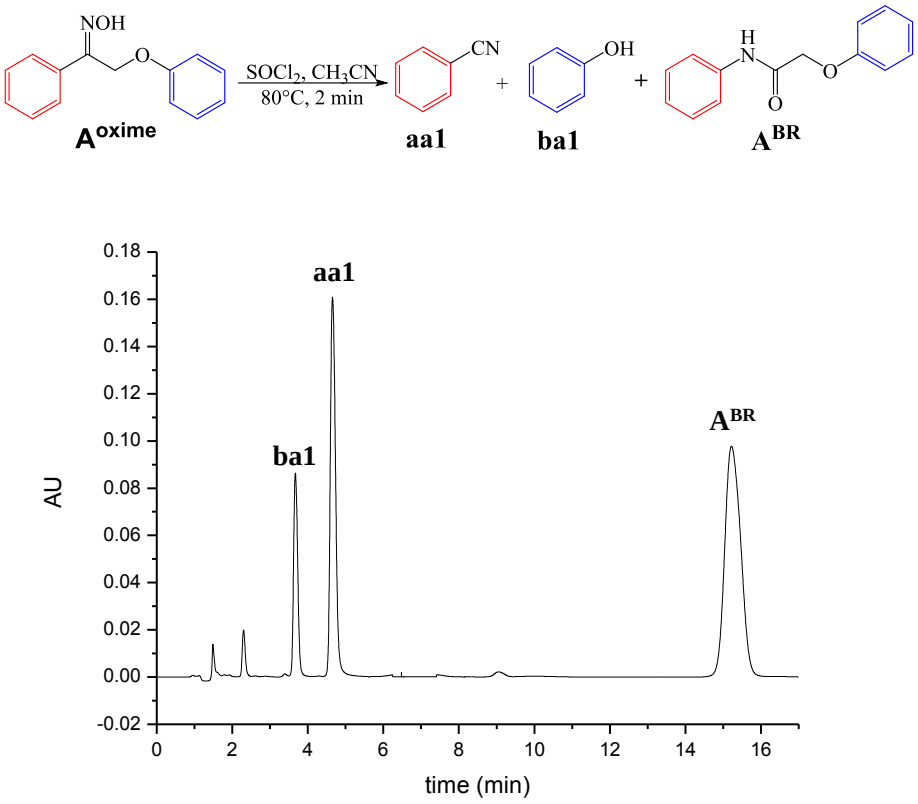


Figure S3. HPLC chromatogram of BR reaction of $\mathbf{A}^{\mathbf{oxime}}$ (entry 1, Table 2).

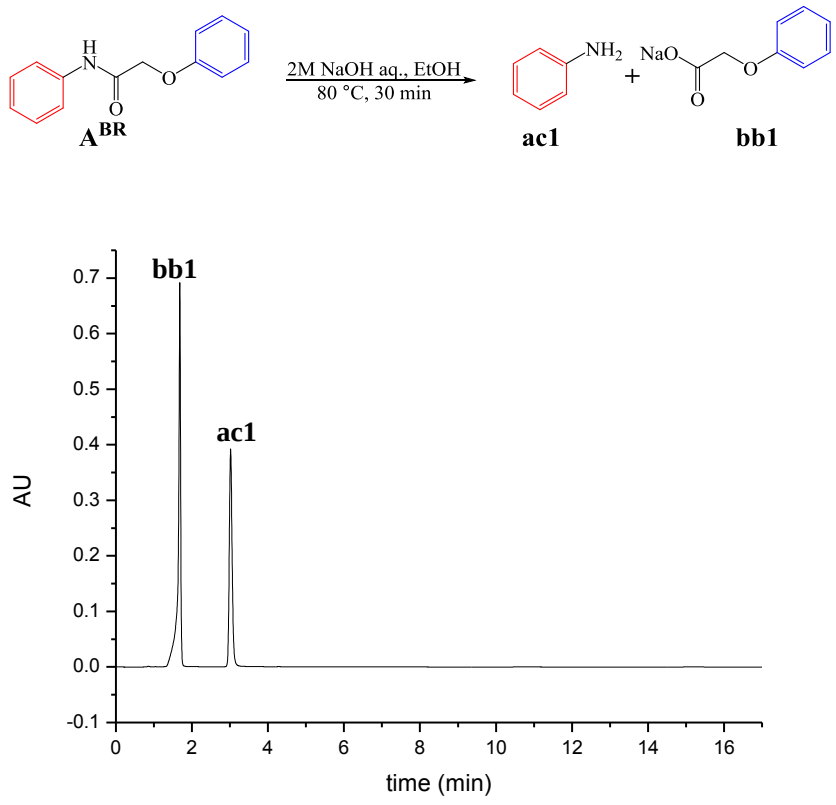
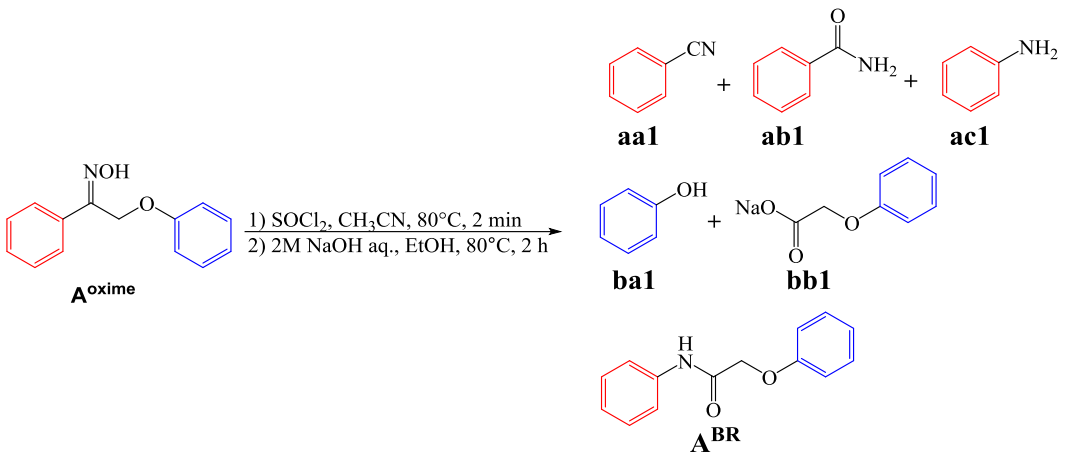


Figure S4. HPLC chromatogram of the hydrolysis of amides $\mathbf{A}^{\mathbf{BR}}$ (entry 1, Table 3).



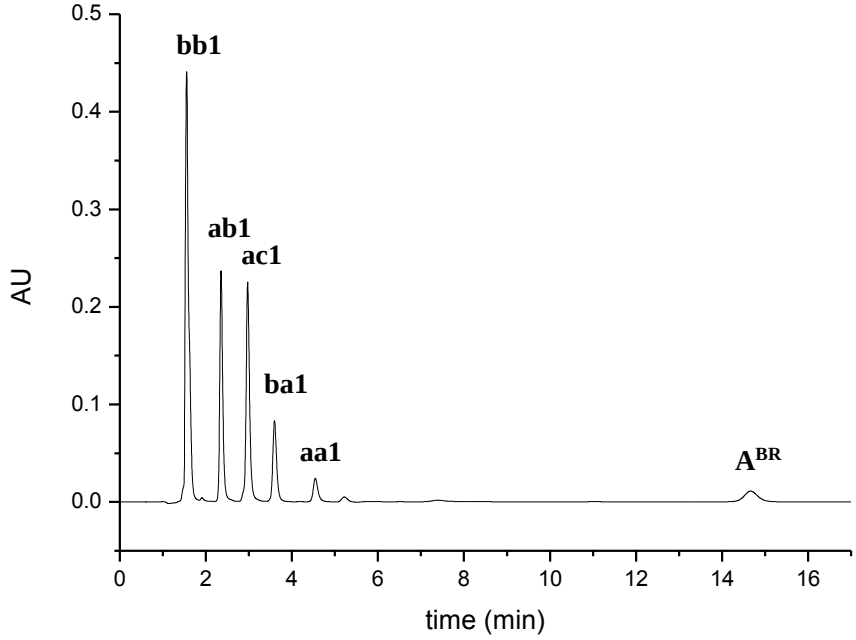


Figure S5. HPLC chromatogram of one-pot process of BR reaction and hydrolysis of **A**$^{\text{oxime}}$ (entry 1, Table 4).

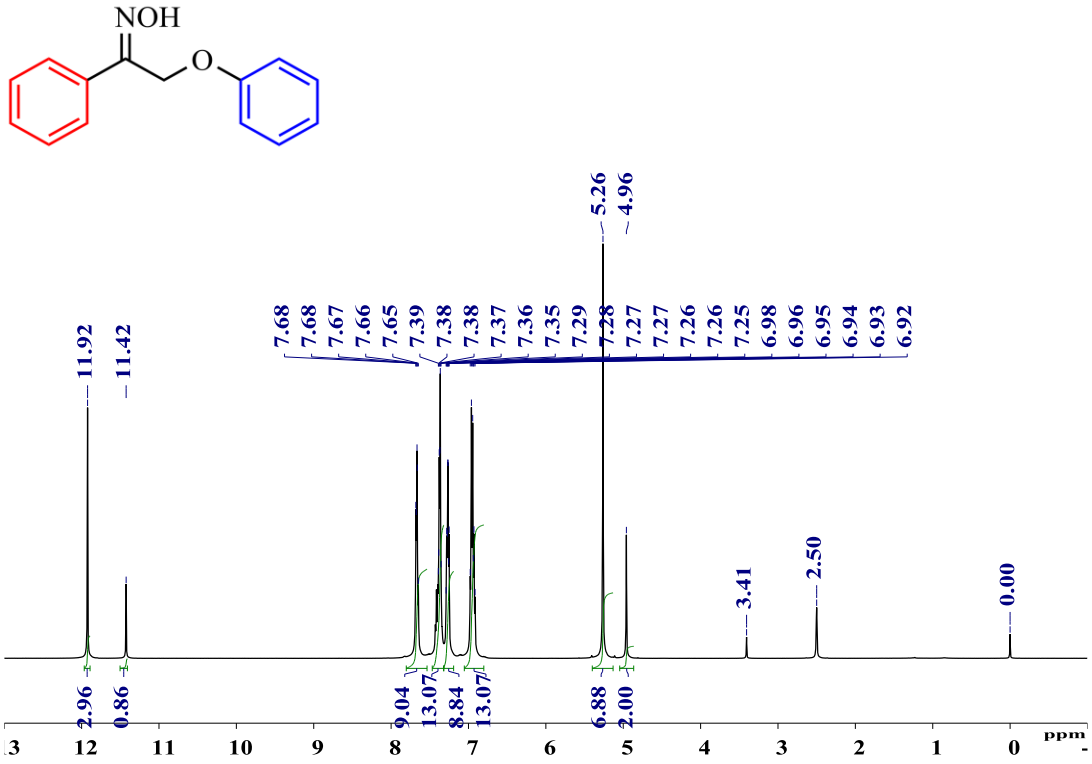
IV. References

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

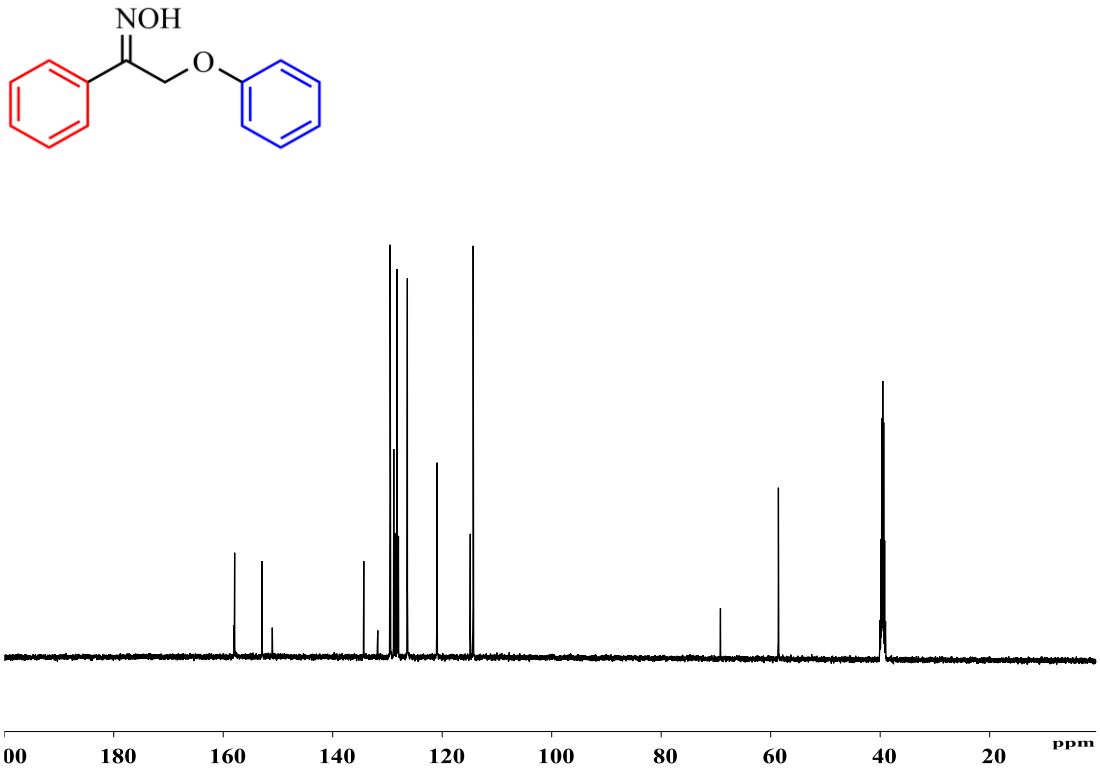
(2) D. W. Cho, R. Parthasarathi, A. S. Pimentel, G. D. Maestas, H. J. Park, U. C. Yoon, D. Dunaway-Mariano, S. Gnanakaran, P. Langan and P. S. Mariano, *J. Org. Chem.*, 2010, **75**, 6549–6562.

(3) A. Rahimi, A. Azarpira, H. Kim, J. Ralph and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 6415–64

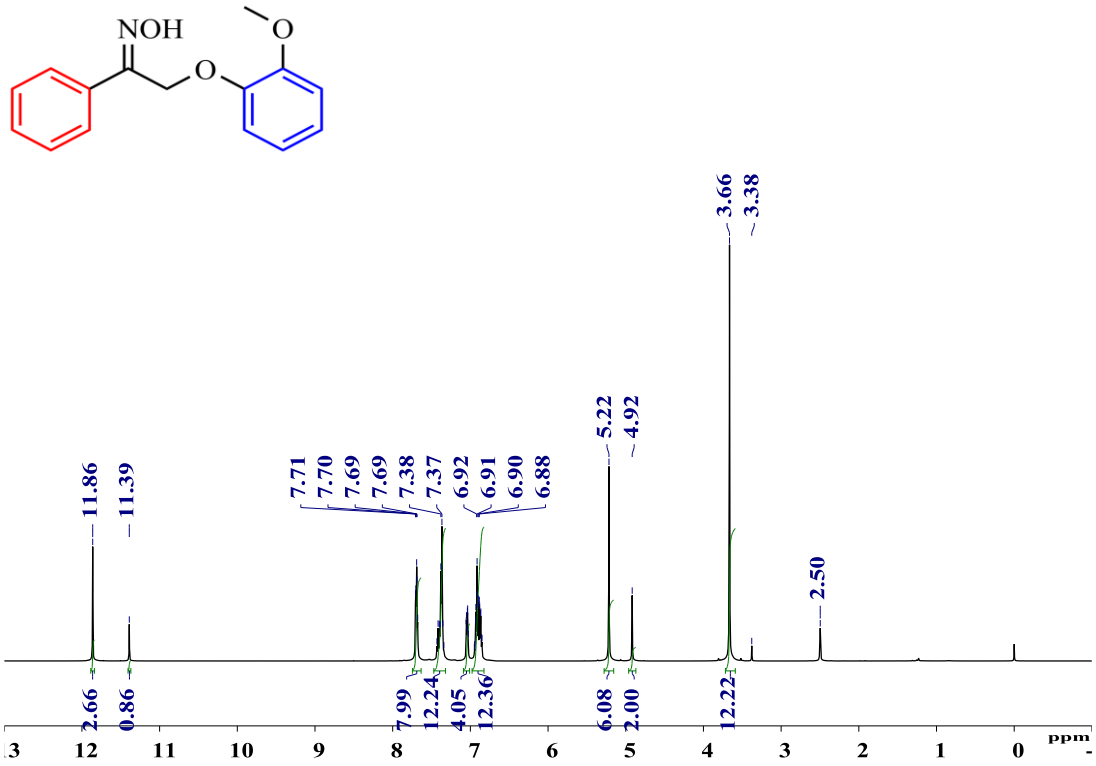
V. NMR Spectra



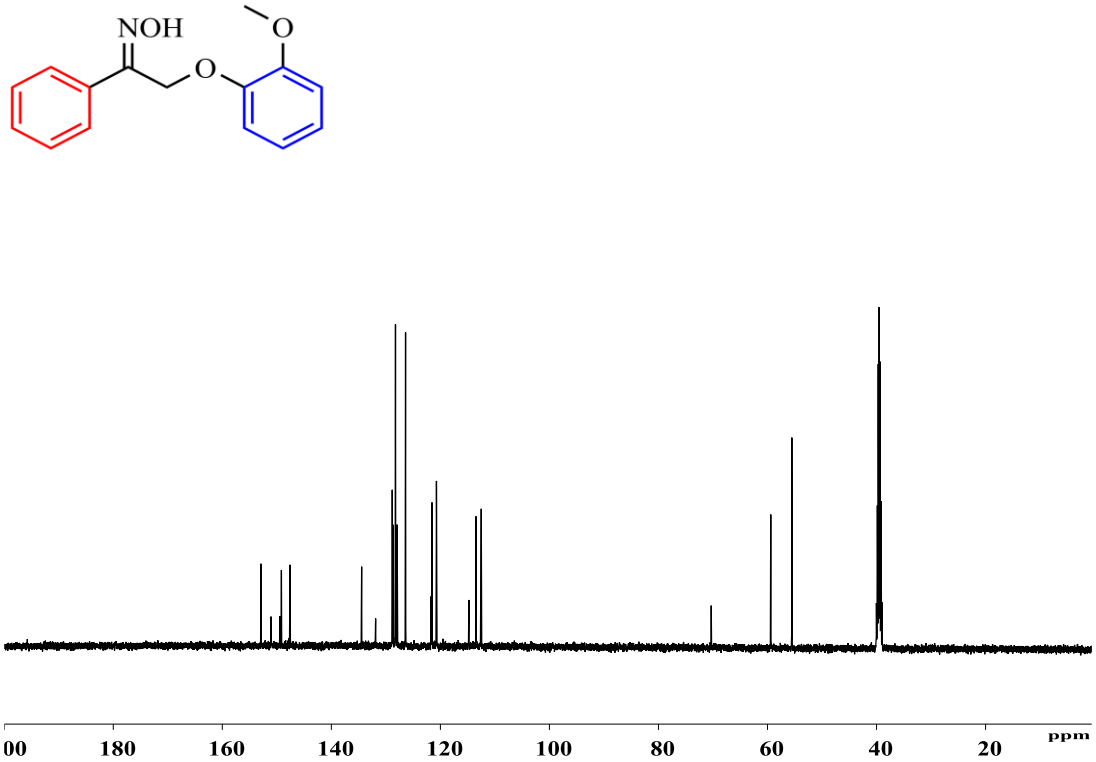
^{1}H NMR spectrum of 2-phenoxy-1-phenylethan-1-one oxime (**A**$^{\textbf{oxime}}$) (DMSO-d_6, 500 MHz)



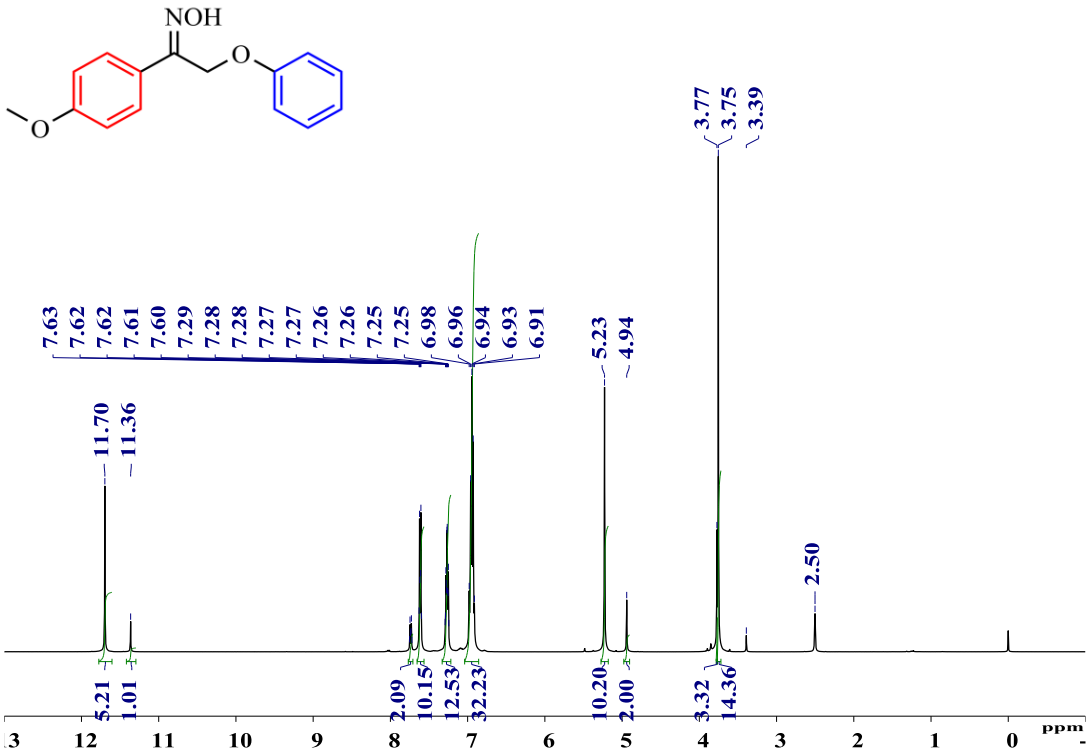
^{13}C NMR spectrum of 2-phenoxy-1-phenylethan-1-one oxime (**A**$^{\textbf{oxime}}$) (DMSO-d_6, 126 MHz)



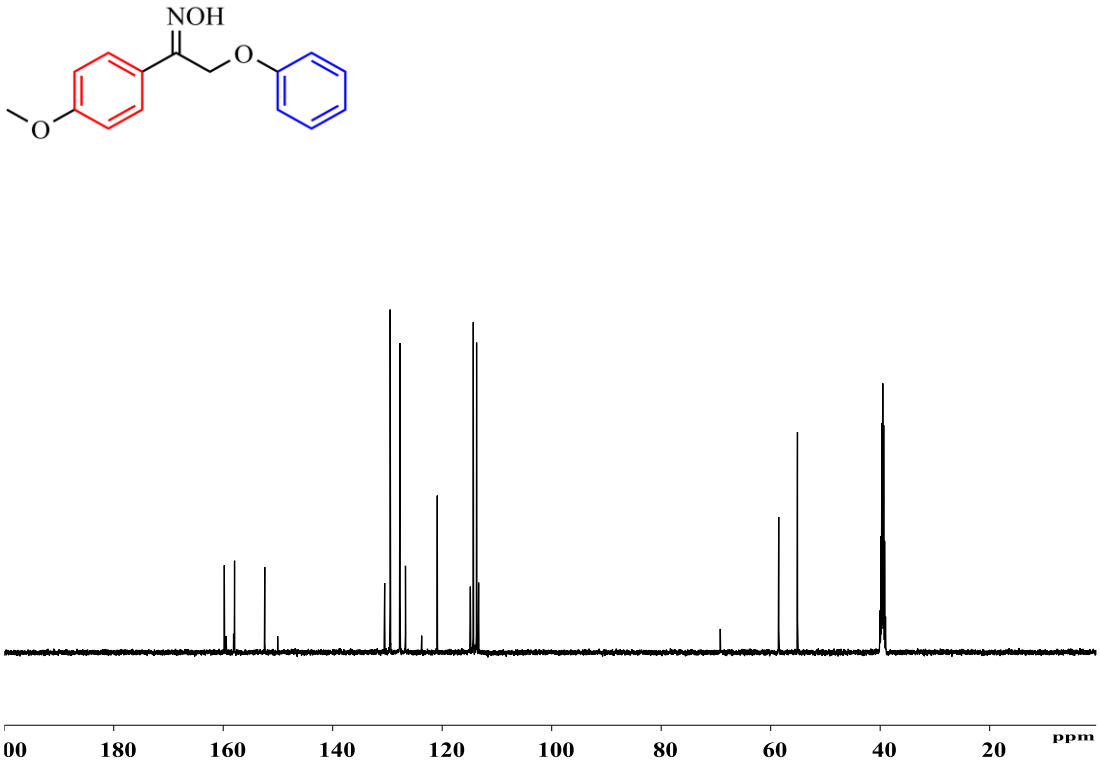
^{1}H NMR spectrum of 2-(2-methoxyphenoxy)-1-phenylethan-1-one oxime (**B**$^{\text{oxime}}$) (DMSO-d_6, 500 MHz)



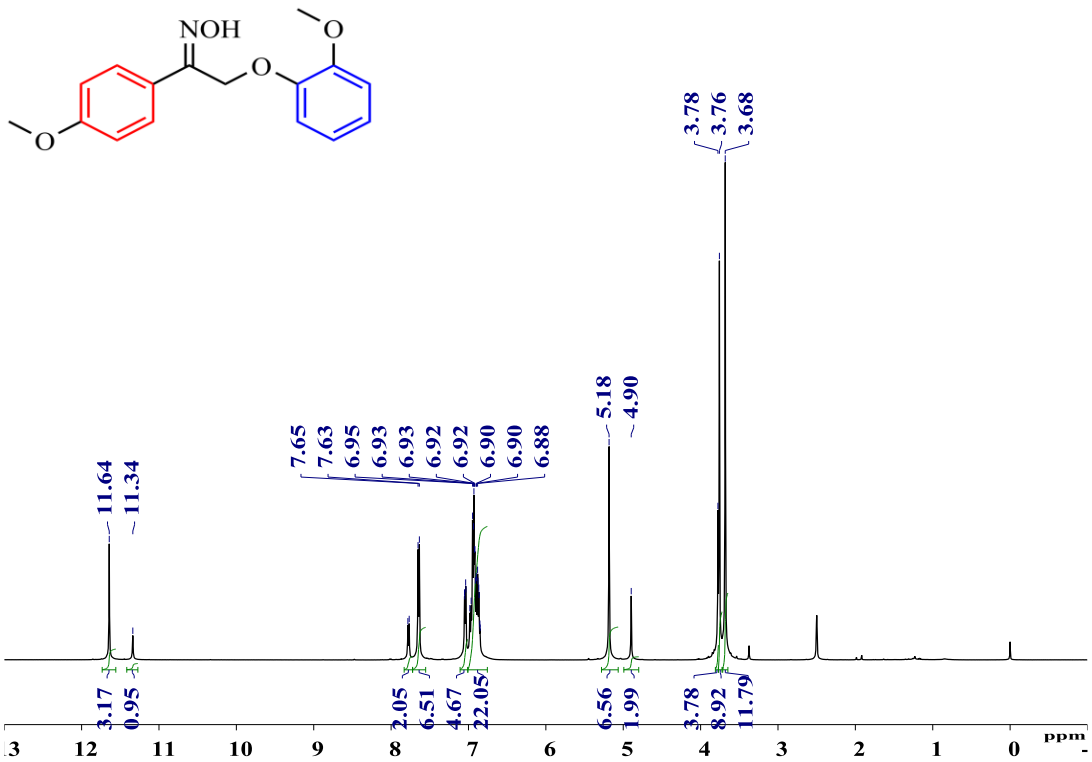
^{13}C NMR spectrum of 2-(2-methoxyphenoxy)-1-phenylethan-1-one oxime (**B**$^{\text{oxime}}$) (DMSO-d_6, 126 MHz)



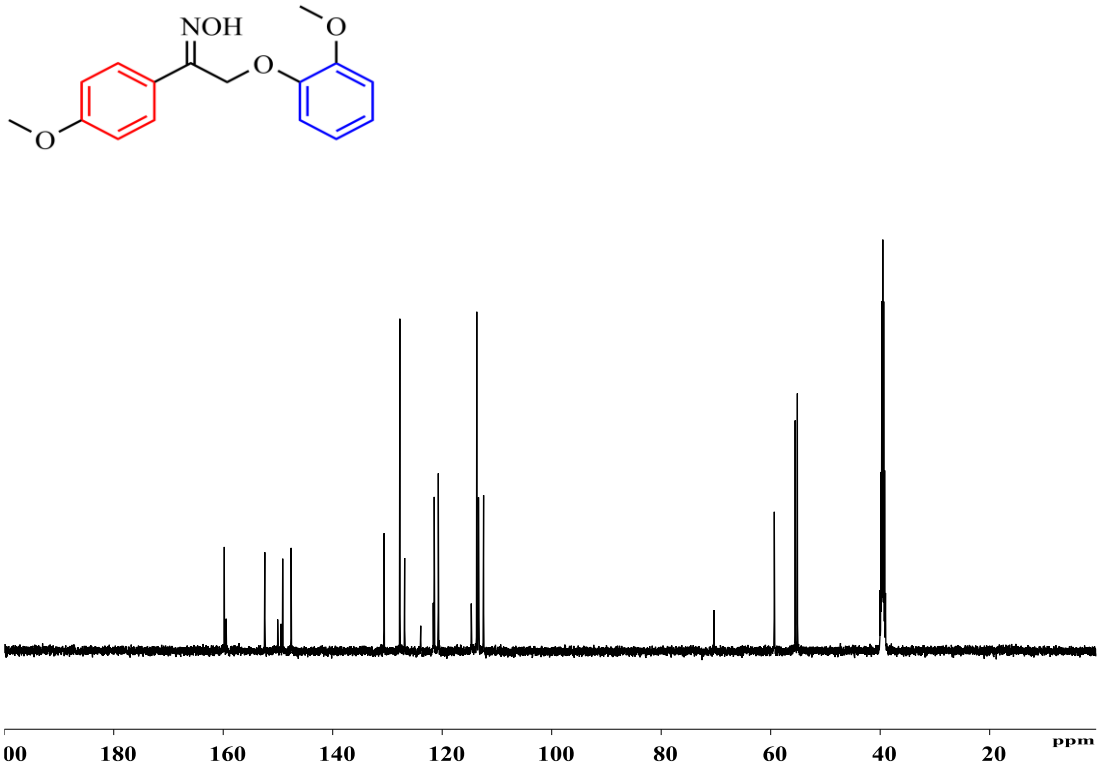
^{1}H NMR spectrum of 1-(4-methoxyphenyl)-2-phenoxyethan-1-one oxime (**C**$^{\text{oxime}}$) (DMSO-d_6, 500 MHz)



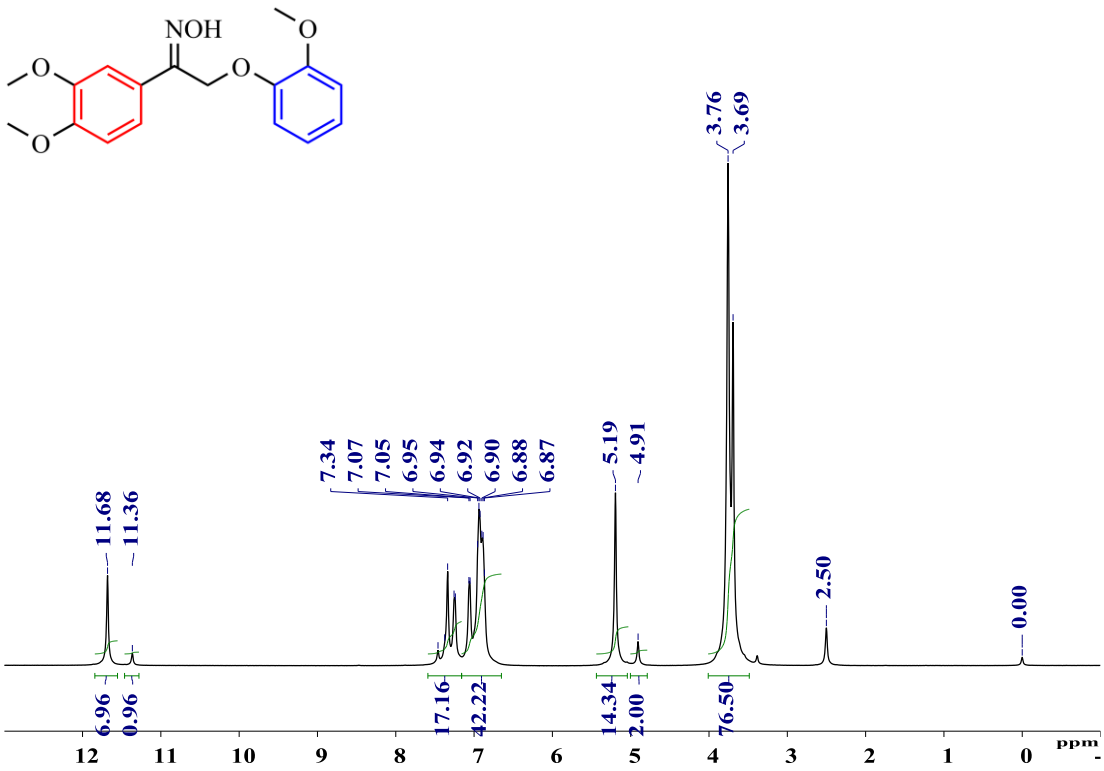
^{13}C NMR spectrum of 1-(4-methoxyphenyl)-2-phenoxyethan-1-one oxime (**C**$^{\text{oxime}}$) (DMSO-d_6, 126 MHz)



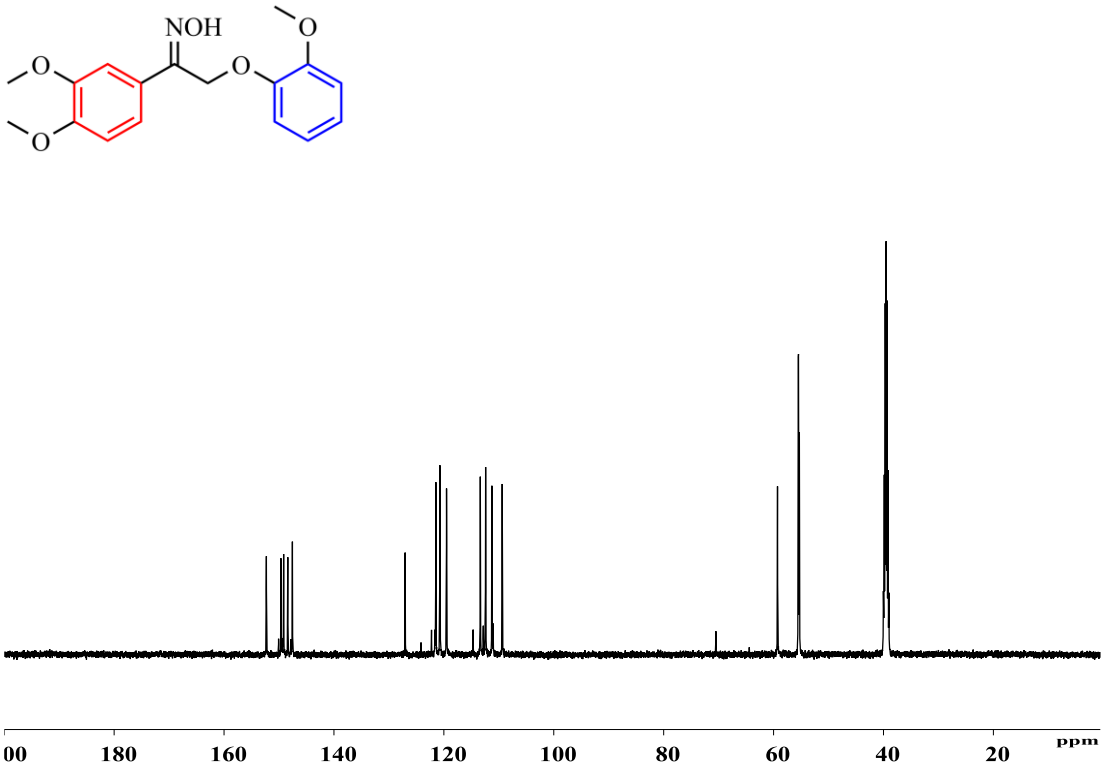
^{1}H NMR spectrum of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethan-1-one oxime (**D**$^{\mathbf{oxime}}$) (DMSO-d_6, 500 MHz)



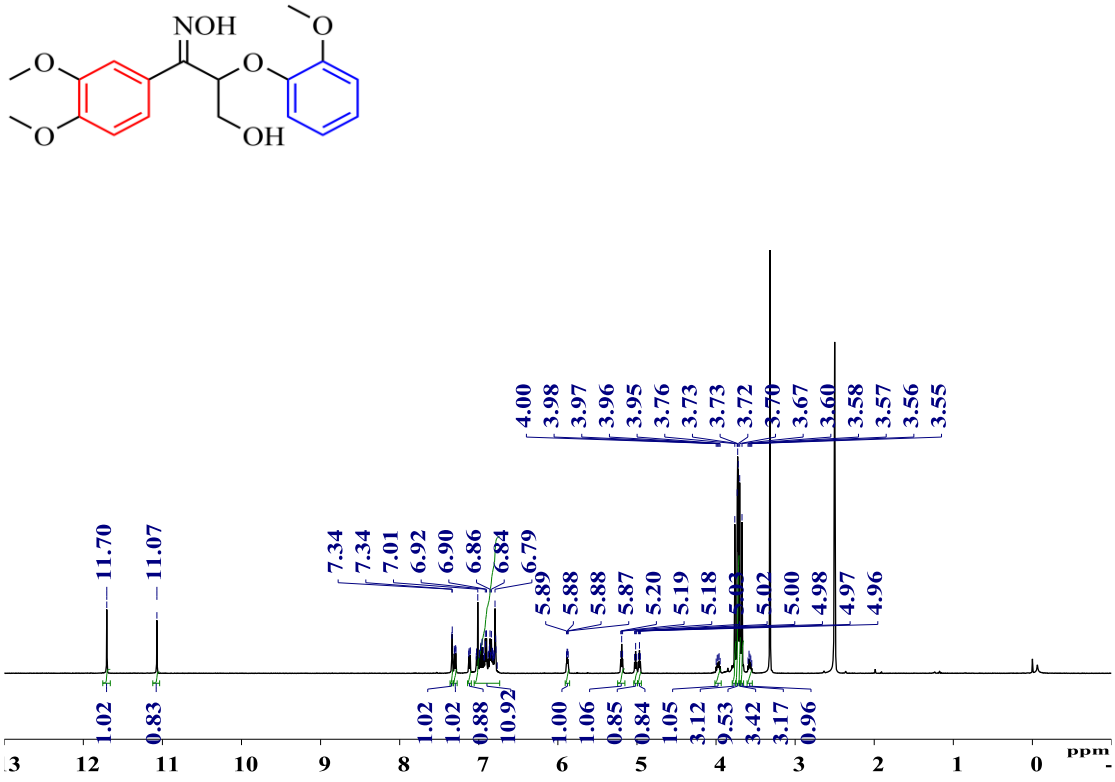
^{13}C NMR spectrum of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethan-1-one oxime (**D**$^{\mathbf{oxime}}$) (DMSO-d_6, 126 MHz)



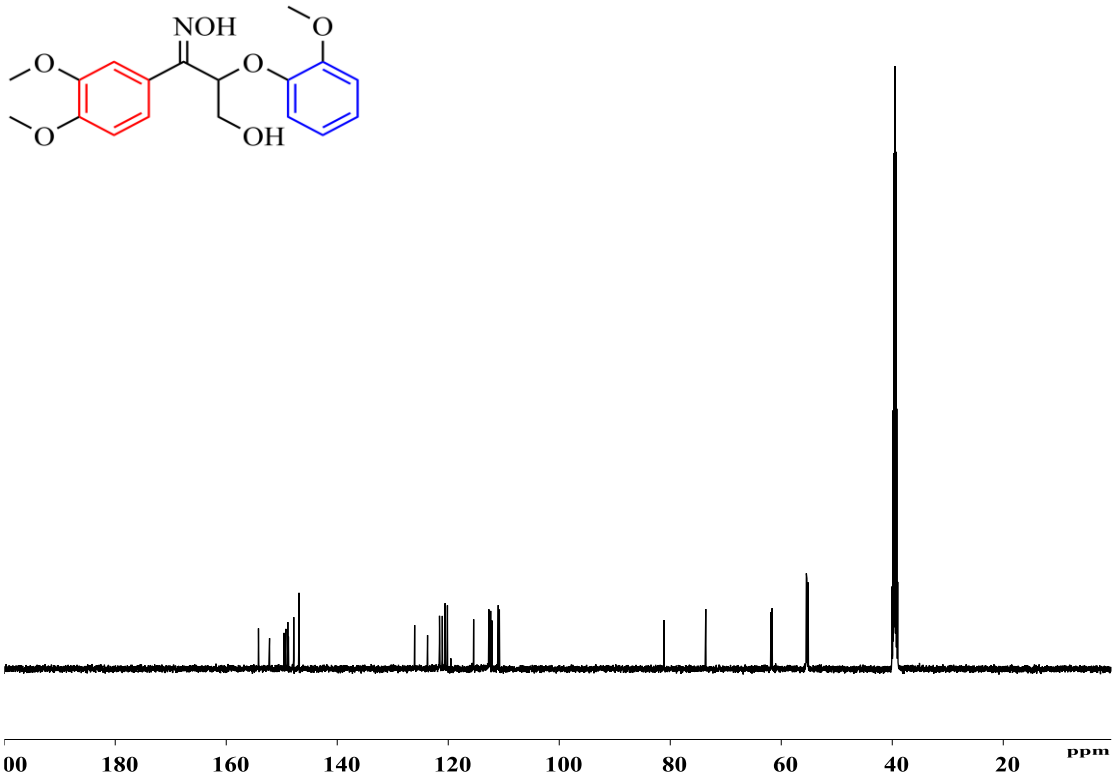
^{1}H NMR spectrum of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) ethan-1-one oxime (**E**$^{\mathbf{oxime}}$) (DMSO-d_6, 500 MHz)



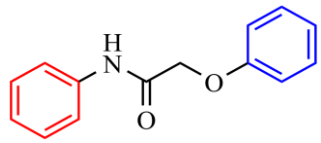
^{13}C NMR spectrum of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) ethan-1-one oxime (**E**$^{\mathbf{oxime}}$) (DMSO-d_6, 126 MHz)

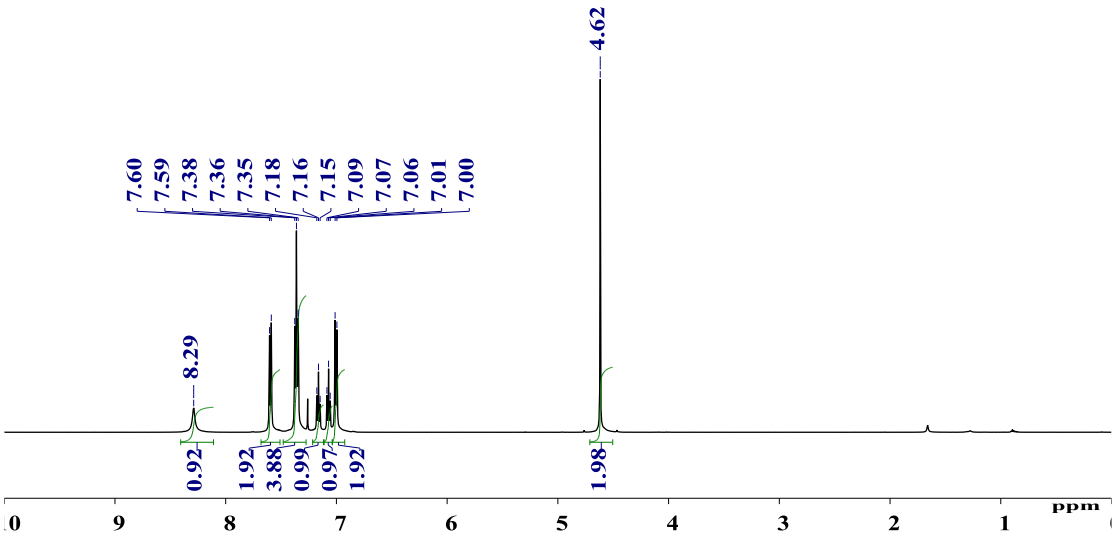


^{1}H NMR spectrum of (E)-1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy) propan -1-one oxime (**F**$^{\mathbf{oxime}}$) (DMSO-d_6, 500 MHz)

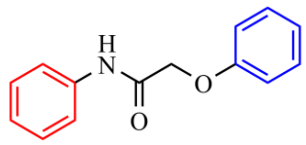


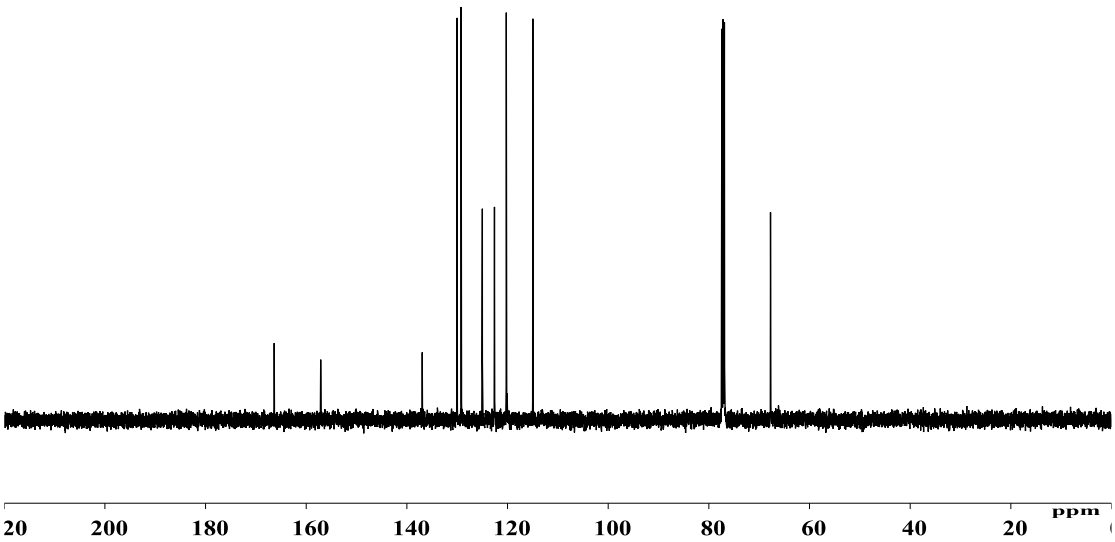
^{13}C NMR spectrum of (E)-1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy) propan-1-one oxime (**F**$^{\mathbf{oxime}}$) (DMSO-d_6, 126 MHz)



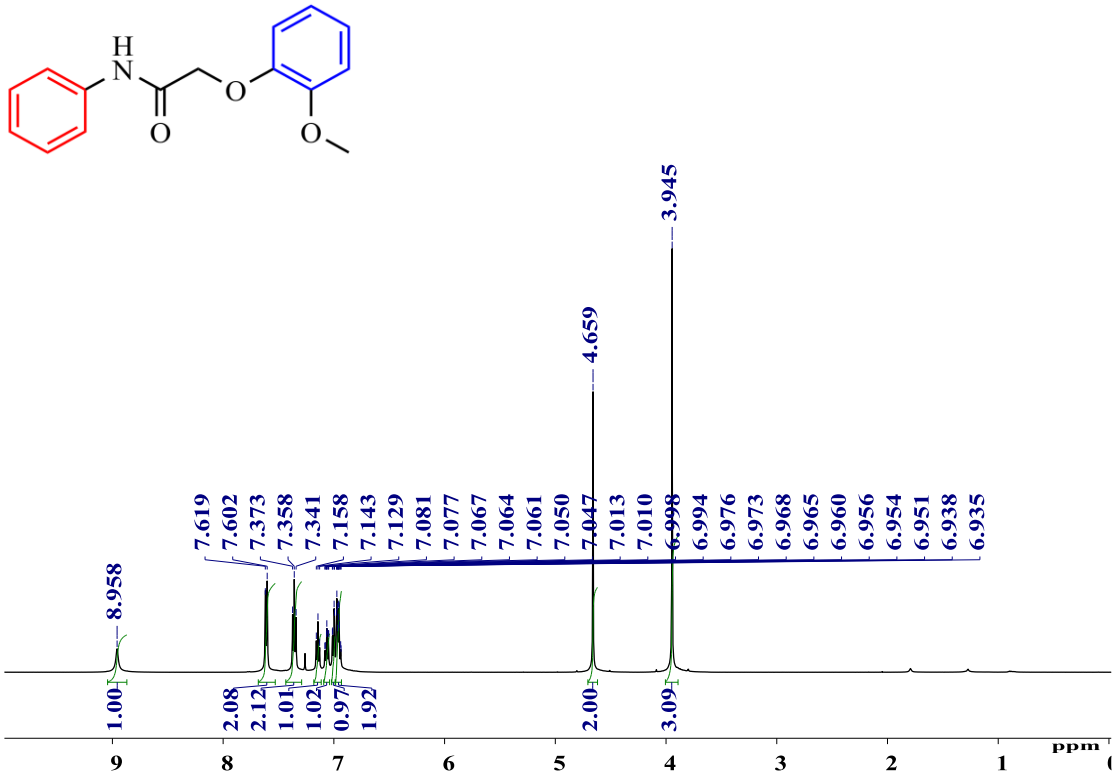


^{1}H NMR spectrum of 2-phenoxy-N-phenylacetamide (**A**$^{\mathbf{BR}}$) ($CDCl_3$, 500 MHz)

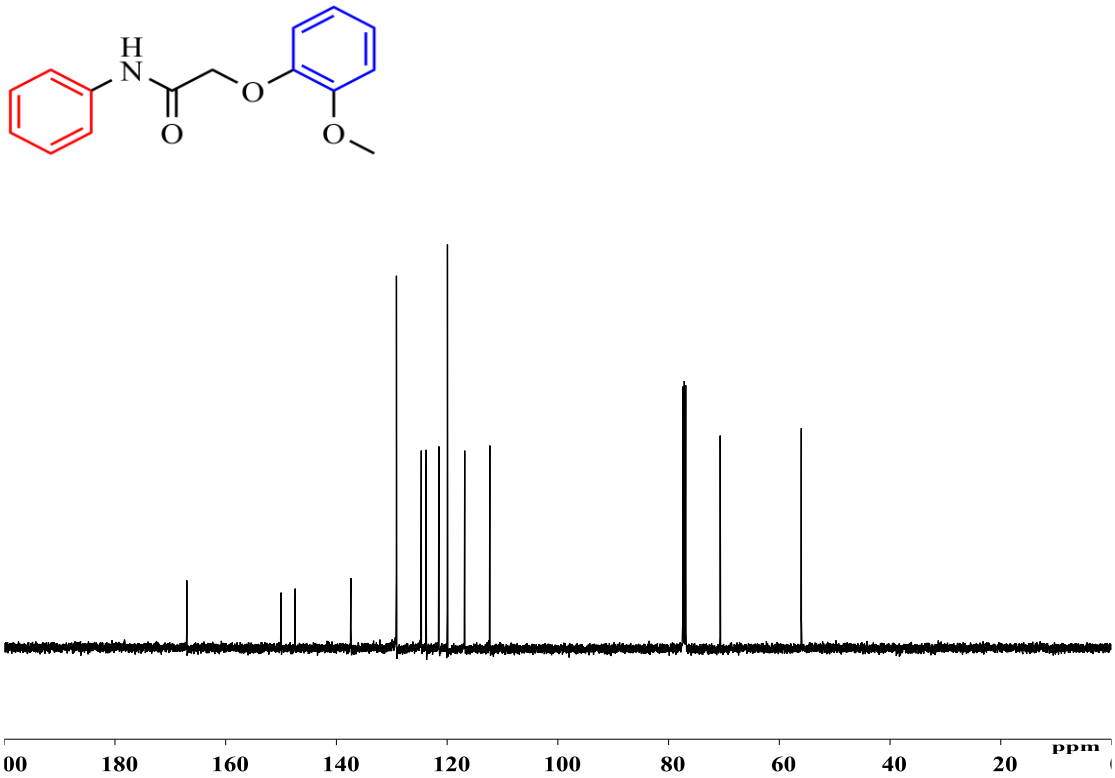




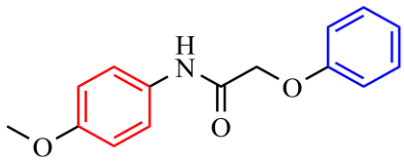
^{13}C NMR spectrum of 2-phenoxy-N-phenylacetamide (**A**$^{\mathbf{BR}}$) ($CDCl_3$, 126 MHz)

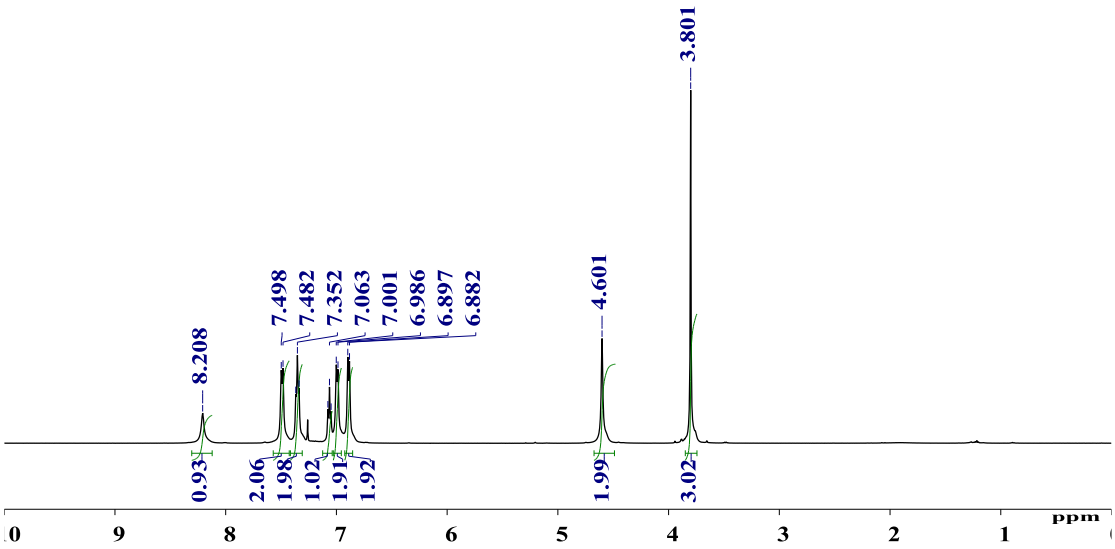


^{1}H NMR spectrum of 2-(2-methoxyphenoxy)-N-phenylacetamide (**B**^{BR}) ($CDCl_3$, 500 MHz)

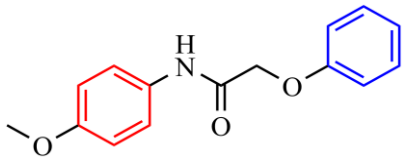


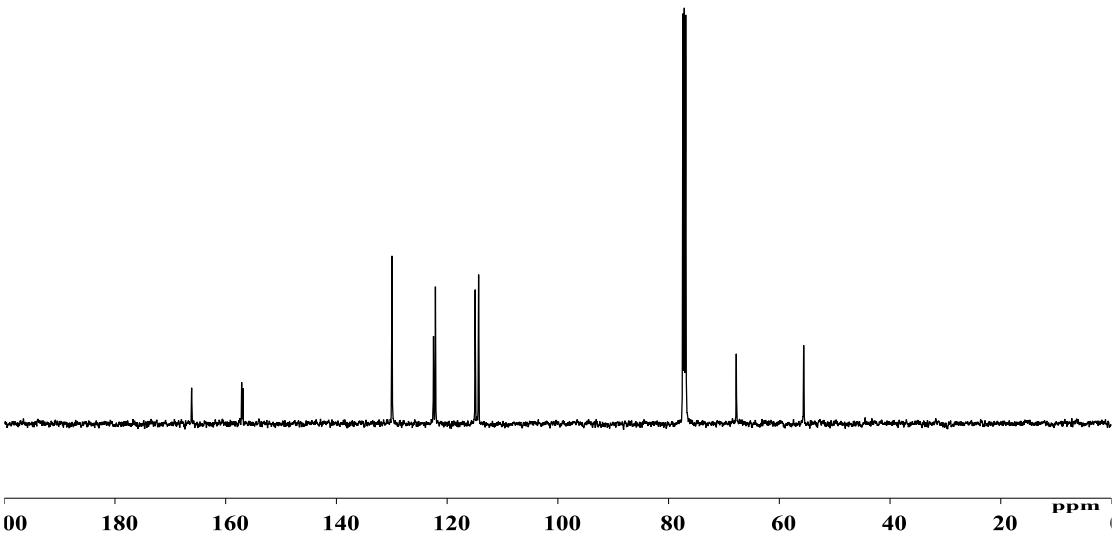
^{13}C NMR spectrum of 2-(2-methoxyphenoxy)-N-phenylacetamide (**B**^{BR}) ($CDCl_3$, 126 MHz)



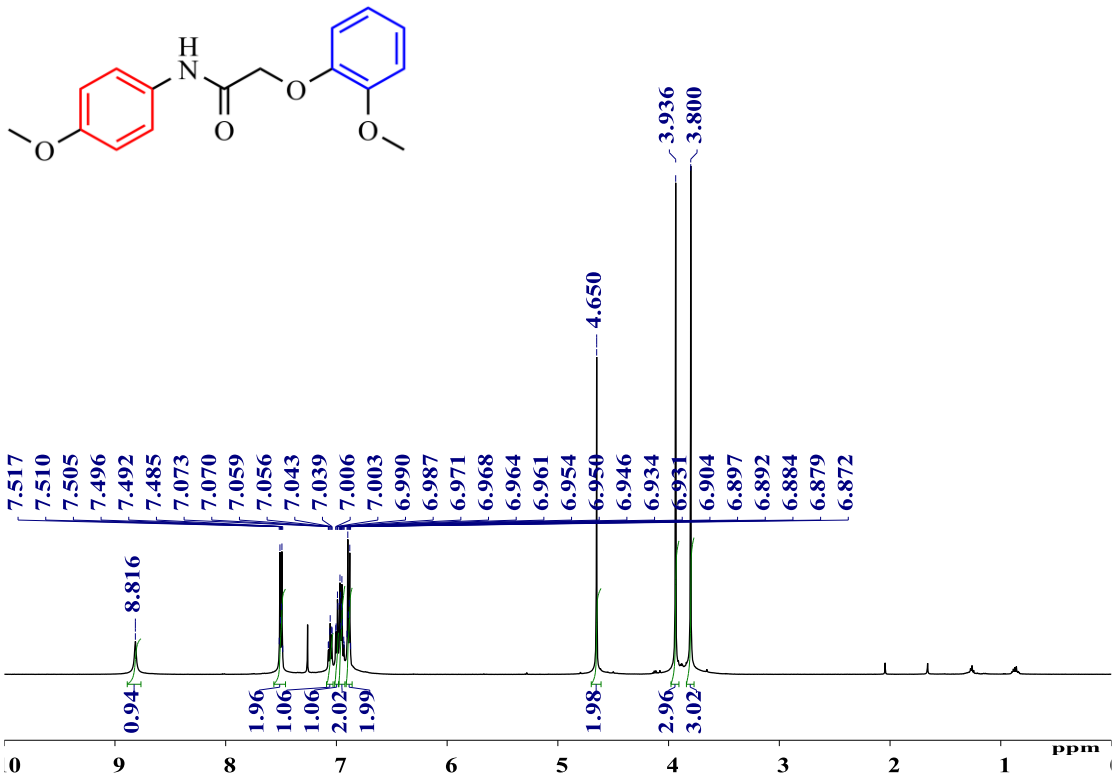


^{1}H NMR spectrum of N-(4-methoxyphenyl)-2-phenoxyacetamide (**C^{BR}**) ($CDCl_3$, 500 MHz)

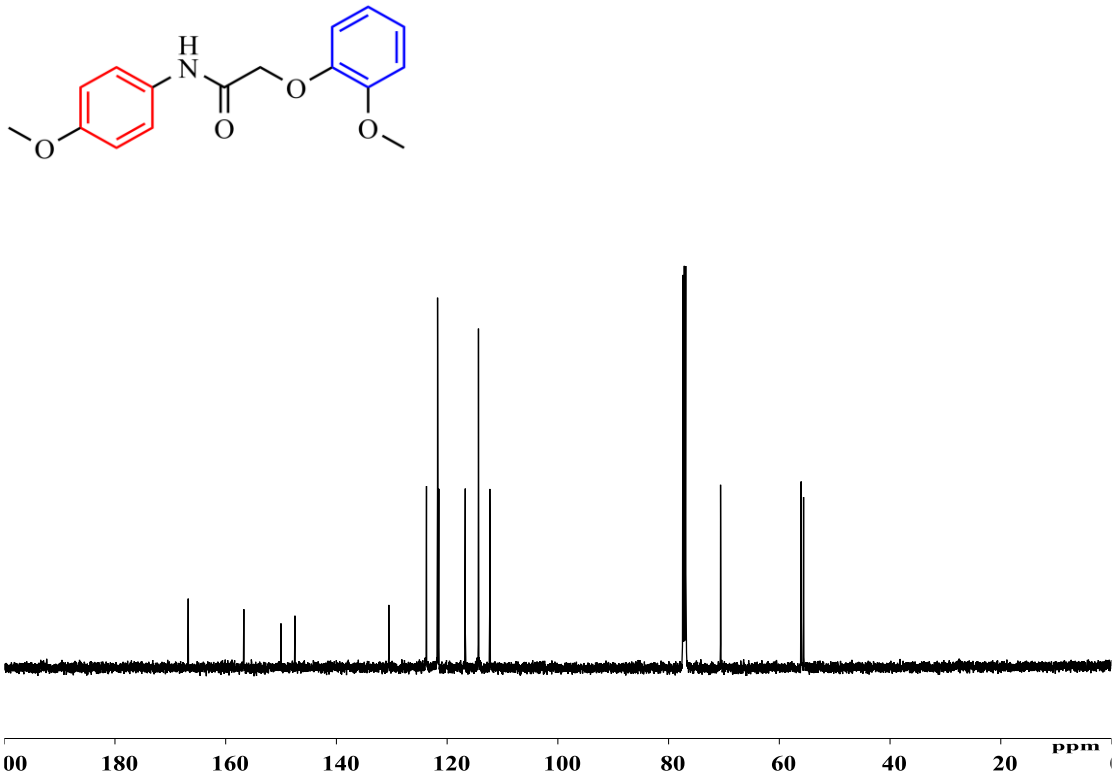




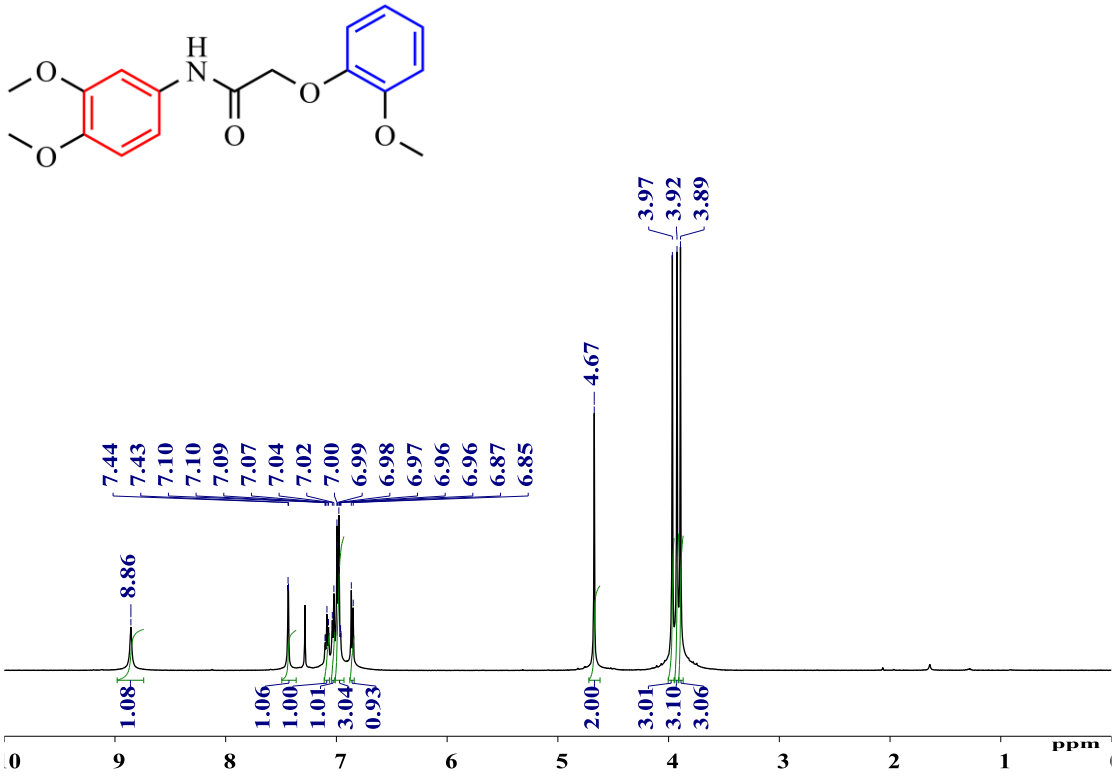
^{13}C NMR spectrum of N-(4-methoxyphenyl)-2-phenoxyacetamide (**C^{BR}**) ($CDCl_3$, 126 MHz)



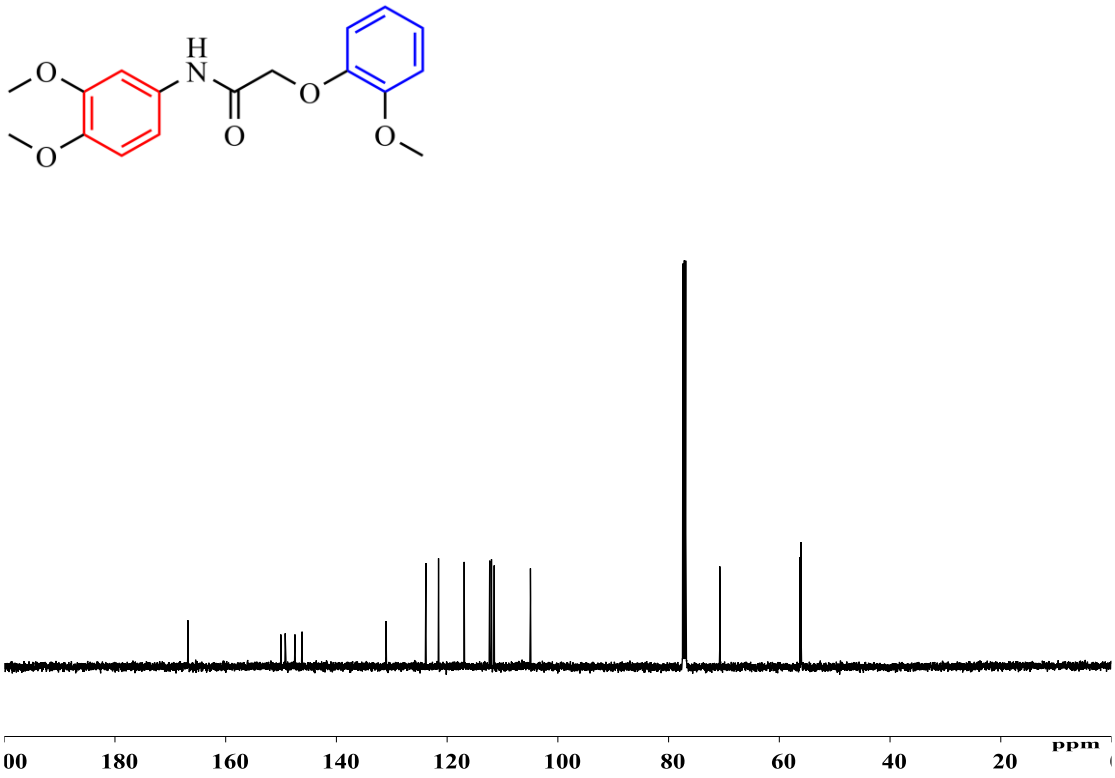
^{1}H NMR spectrum of 2-(2-methoxyphenoxy)-N-(4-methoxyphenyl) acetamide (**D**^{BR}) ($CDCl_3$, 500 MHz)



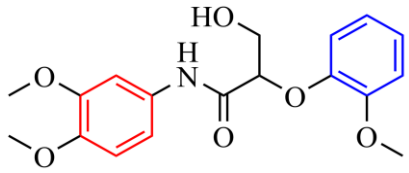
^{13}C NMR spectrum of 2-(2-methoxyphenoxy)-N-(4-methoxyphenyl) acetamide (**D**^{BR}) ($CDCl_3$, 126 MHz)

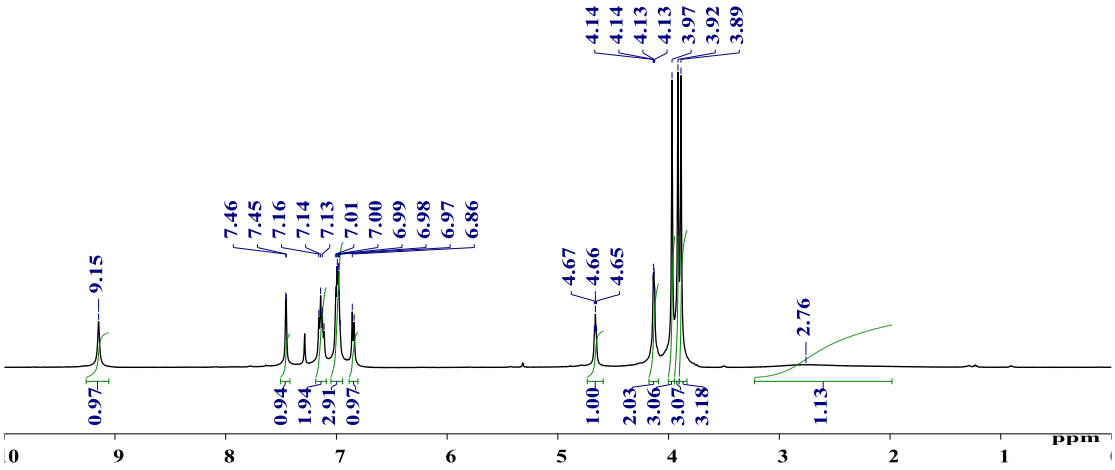


^{1}H NMR spectrum of N-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) acetamide (**E**^{BR}) ($CDCl_3$, 500 MHz)

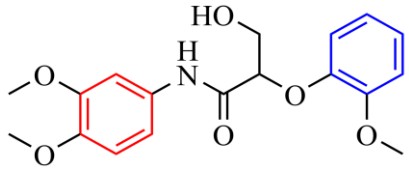


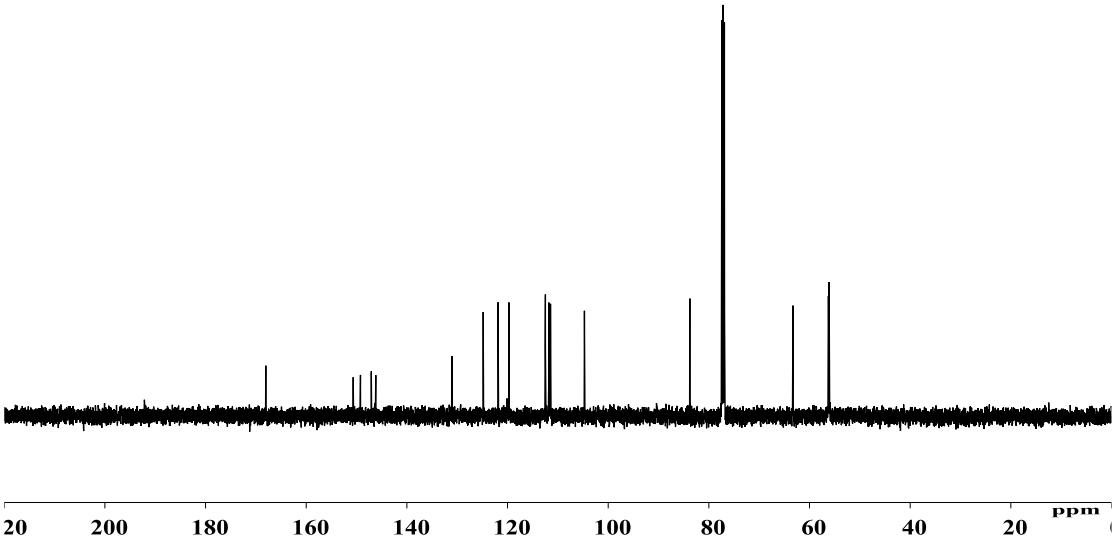
^{13}C NMR spectrum of N-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) acetamide (**E**^{BR}) ($CDCl_3$, 126 MHz)



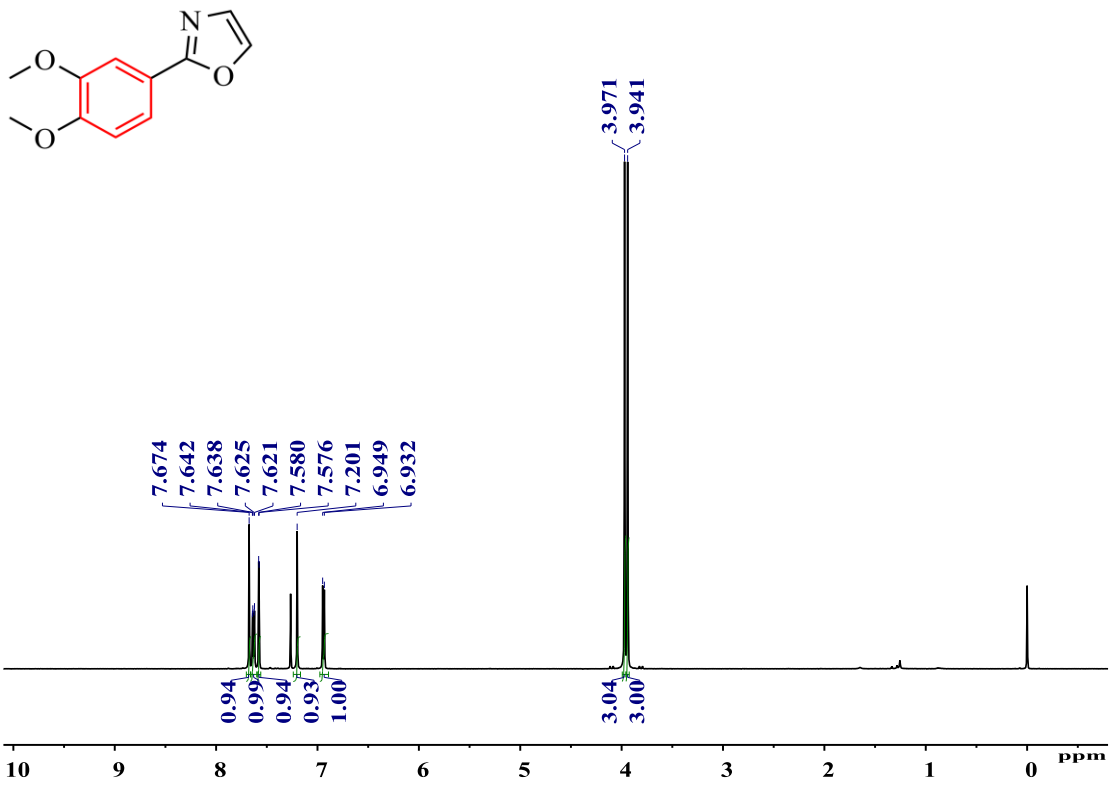


^{1}H NMR spectrum of N-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy) propanamide (**F^{BR}**) ($CDCl_3$, 500 MHz)

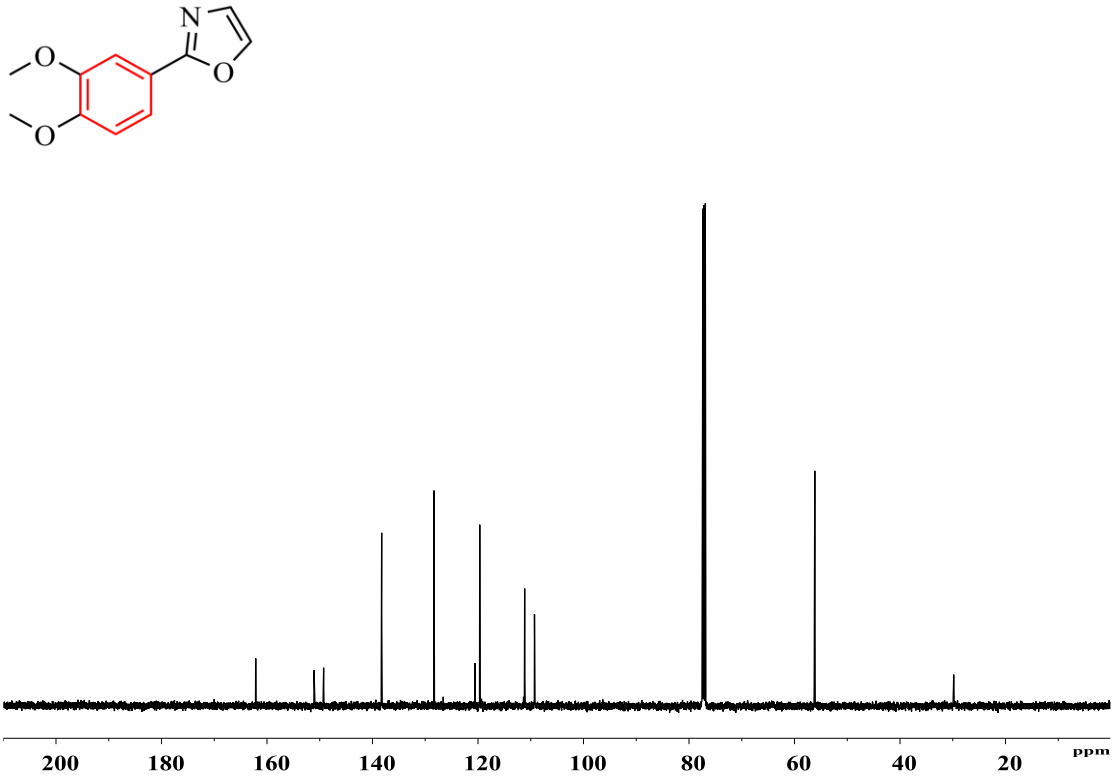




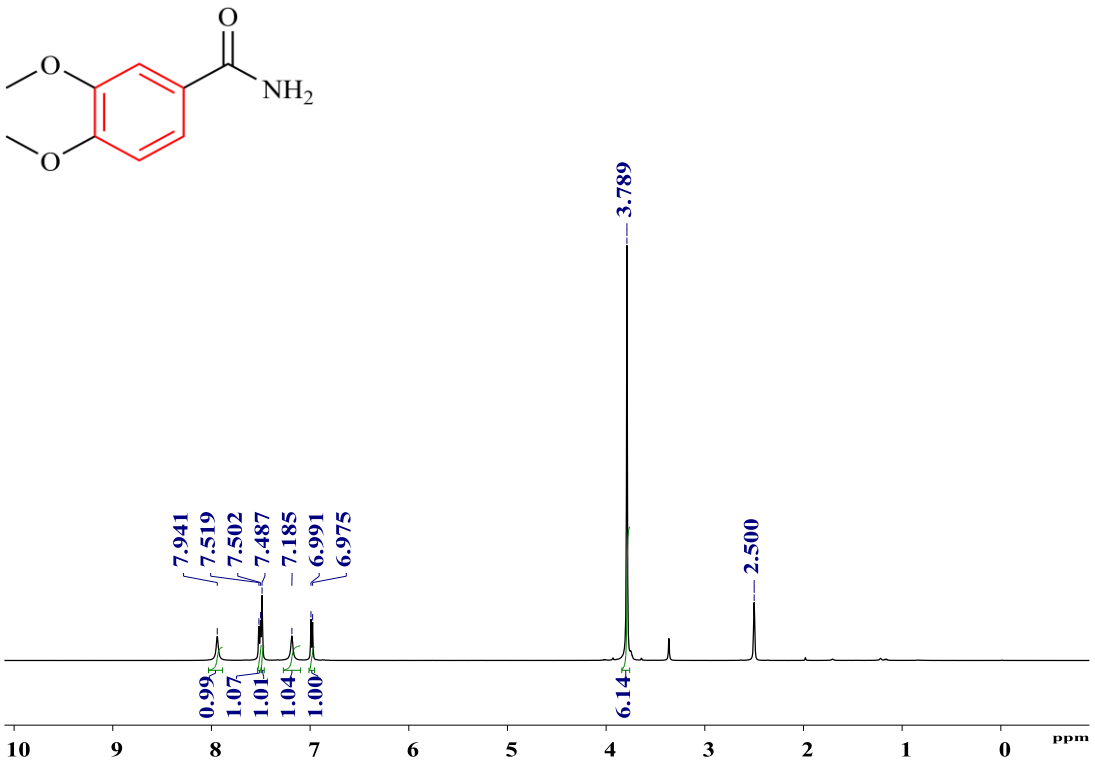
^{13}C NMR spectrum of N-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy) propanamide (**F^{BR}**) ($CDCl_3$, 126 MHz)



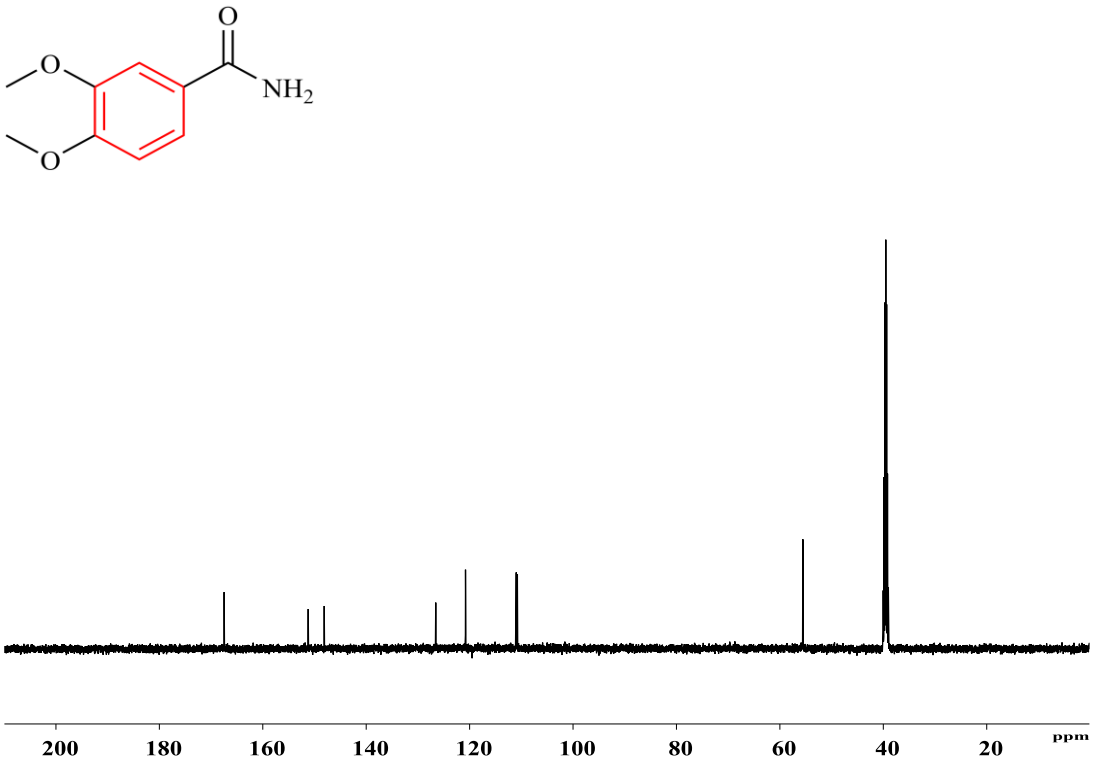
^{1}H NMR spectrum of 2-(3,4-dimethoxyphenyl) oxazole (**aa3'**) ($CDCl_3$, 500 MHz)



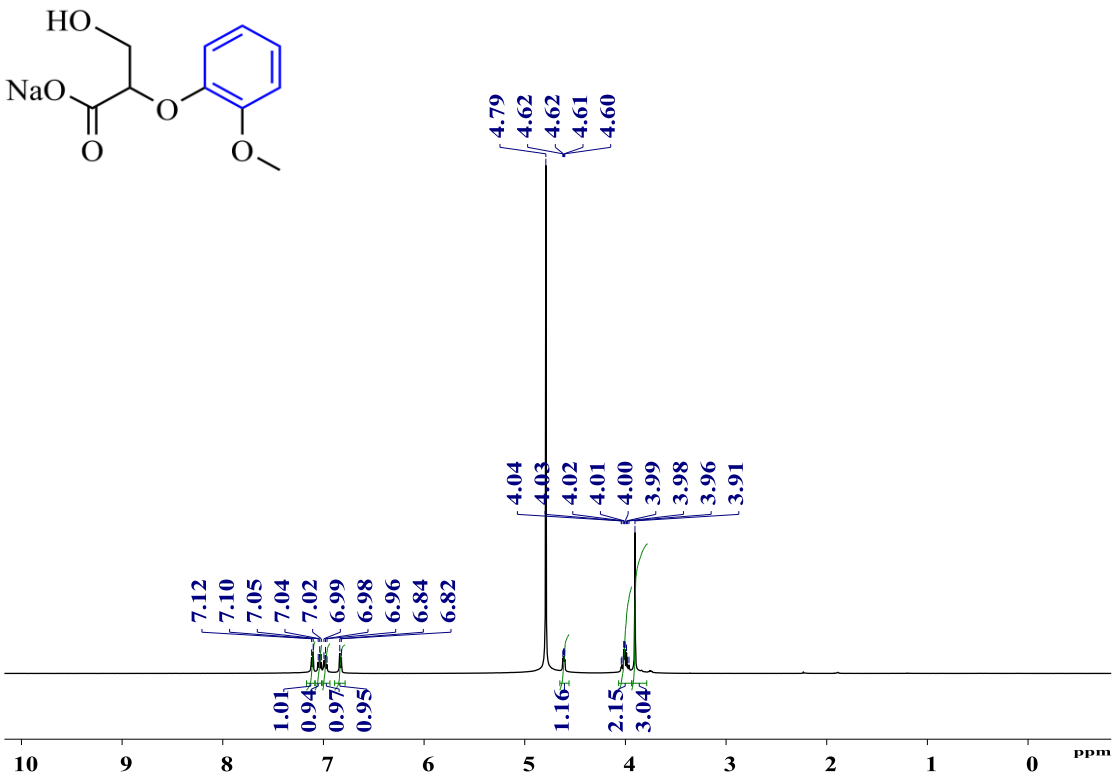
^{13}C NMR spectrum of 2-(3,4-dimethoxyphenyl) oxazole (**aa3'**) ($CDCl_3$, 126 MHz)



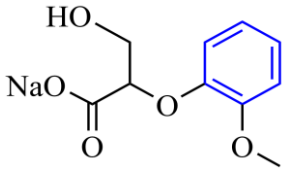
^{1}H NMR spectrum of 3,4-dimethoxybenzamide (**ab3**) (*d*-DMSO, 500 MHz)

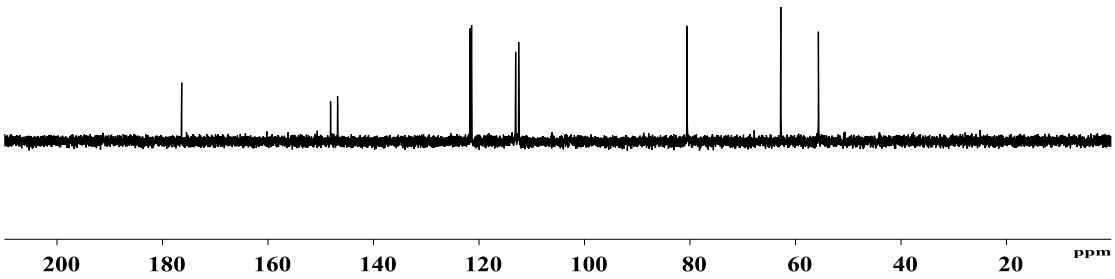


^{13}C NMR spectrum of 3,4-dimethoxybenzamide (**ab3**) (*d*-DMSO, 126 MHz)



^{1}H NMR spectrum of sodium 3-hydroxy-2-(2-methoxyphenoxy) propanoate (**bb3**) (D_2O, 500 MHz)





^{13}C NMR spectrum of sodium 3-hydroxy-2-(2-methoxyphenoxy) propanoate (**bb3**) (D_2O, 126 MHz)