Supporting Information

Multicenter Synergistic Polyoxometalate-based Metal–Organic Framework for One-Step Selective Oxidative Cleavage of β-O-4 Lignin Models

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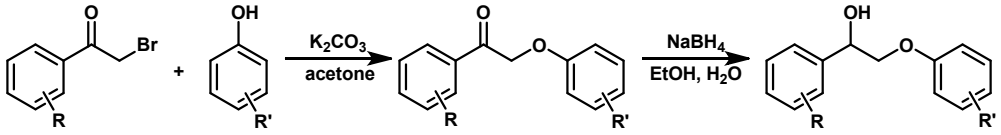
1. Experimental procedures

Synthesis of ligand bbi[1] A mixture of imidazole (8.2g, 0.12mol) and NaOH (4.8 g, 0.12 mol) in DMSO (35 mL) was stirred at 60 °C for 2 hours, and then 1,4-dibromobutane (12.0 g, 0.056 mol) was added. After stirring at 60 °C for another 2 hours, the reaction mixture was cooled to room temperature and then poured into 400 mL of ice-water and a large amount of white solid precipitated, which was filtered and dried in air to afford 21.0 g, yield:92.0%. ^{1}H NMR (600MHz, CD_3CN) δ: 7.45 (s, 2H), 6.99 (s, 2H), 6.91 (s, 2H), 3.92-3.95 (m, 4H), 1.67-1.70 (m, 4H) ppm.

Synthesis of lignin model compounds[2-3]



R = H or -OMe; R' = H or -OMe

Synthesis of 2-phenoxy-1-phenylethanol (**1**)[2]

Synthesis of 2-phenoxy-1-phenylethanone (**1a**): A mixture of phenol (6.9 g, 0.073mol) and K_2CO_3 (15.1 g, 0.11mol) in acetone (200 mL) was stirred at room temperature for 30min and then a solution of 2-bromoacetophenone (13.2 g, 0.067mol) in acetone (100 mL) was added dropwise. The resulting mixture was heated to reflux and stirred overnight. The reaction mixture was cooled to room temperature and filtered, the filtrate was concentrated in vacuum. The residue was dissolved with EA and washed with 5% NaOH aq. The organic layer was dried over anhydrous Na_2SO_4 and filtered, the filtrate was concentrated in vacuum. The crude product was recrystallization with ethanol (EtOH) to afford white solid 13.2 g, yield: 85.0%. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.00-8.02 (m, 2H), 7.61-7.63 (m, 1H), 7.49-

7.52 (m, 2H), 7.28-7.31 (m, 2H), 6.98-7.00 (m, 1H), 6.94-6.96 (m, 2H), 5.28 (s, 2H) ppm.

Synthesis of 2-phenoxy-1-phenylethanol (**1**): The compound **1a** (1.06 g, 5 mmol) was dissolved with THF (20 mL) and H_2O (5 mL) and stirred at ice-water bath. $NaBH_4$ (0.38g, 10 mmol) was added portion wise, then the mixture was warmed to room temperature and stirred for 4 hours. Saturated NH_4Cl aq. was added (pH = 5-6) and stirred for 1 hour. The resulting mixture was extracted with EA and then combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuum and the residue was crystallization with EA and n-hexane to afford white solid 0.9 g, yield: 84.0%. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.46 (d, J=6.0 Hz, 2H), 7.38-7.41 (m, 2H), 7.33-7.35 (m, 1H), 7.28-7.30 (m, 2H), 6.97 (t, J=7.3 Hz, 1H), 6.97 (d, J=12.0 Hz, 2H), 5.12-5.14 (m, 1H), 4.11 (dd, J=12.0, 6.0 Hz, 1H), 4.01 (t, J=9.4 Hz, 1H), 2.77 (d, J=2.5 Hz, 1H) ppm.

Synthesis of 2-(2-methoxyphenoxy)-1-phenylethanol (**2**)

Synthesis of 2-(2-methoxyphenoxy)-1-phenylethanone (**2a**): The reaction procedure was performed in the same way as **1a** except for 2-methoxylphenol was used instead of phenol. Yield: 81%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.01 (d, J=6.0 Hz, 2H), 7.61 (t, J=6.0 Hz, 1H), 7.50 (t, J=7.8 Hz, 2H), 6.96-6.99 (m, 1H), 6.91-6.93 (m, 1H), 6.84-6.87 (m, 2H), 5.36 (s, 2H), 3.89 (s, 3H) ppm.

Synthesis of 2-(2-methoxyphenoxy)-1-phenylethanol (**2**): The reaction procedure was performed in the same way as **1** except for **2a** was used instead of **1a**. Yield: 98%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.43 (d, J=6.0 Hz, 2H), 7.37 (t,

J=6.0 Hz, 2H), 7.30-7.32 (m, 1H), 6.98-7.01 (m, 1H), 6.89-6.96 (m, 3H), 5.10-5.12 (m, 1H), 4.19 (dd, J=12.0, 6.0 Hz, 1H), 3.98 (t, J=9.8 Hz, 1H), 3.89 (s, 3H), 3.41 (d, J=6.0 Hz, 1H) ppm.

Synthesis of 1-(4-methoxyphenyl)-2-phenoxyethanol (**3**)

Synthesis of 1-(4-methoxyphenyl)-2-phenoxyethanone (**3a**): The reaction procedure was performed in the same way as **1a** except for 2-bromo-1-(4-methoxyphenyl)ethanone was used instead of 2-bromoacetophenone. Yield: 90%. White solid. ^{1}HNMR (600 MHz, $CDCl_3$) δ: 8.01 (d, J=6.0 Hz, 2H), 7.28 (q, J=18.0 Hz, 6.0 Hz, 2H), 6.94-6.99 (m, 5H), 5.22 (s, 2H), 3.88 (s, 3H) ppm.

Synthesis of 1-(4-methoxyphenyl)-2-phenoxyethanol (**3**): The reaction procedure was performed in the same way as **1** except for **3a** was used instead of **1a**. Yield: 98%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.38 (d, J=6.0 Hz, 2H), 7.27-7.30 (m, 2H), 6.96-6.98 (m, 1H), 6.92-6.93 (m, 4H), 5.06-5.08 (m, 1H), 4.07 (dd, J=12.0, 6.0 Hz, 1H), 4.00 (t, J=6.0 Hz, 1H), 3.82 (s, 3H), 2.72 (d, J=2.4 Hz, 1H) ppm.

Synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol (**4**)

Synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone (**4a**): The reaction procedure was performed in the same way as **1a** except for 2-bromo-1-(4-methoxyphenyl)ethanone and 2-methoxylphenol were used instead of 2-bromoacetophenone and phenol, respectively. Yield: 88%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.02 (d, J=12.0 Hz, 2H), 6.94-6.97 (m, 3H), 6.92 (d, J=6.0 Hz, 1H), 6.88-6.95 (m, 5H), 5.04-5.06 (m, 1H), 3.89 (d, J=6 Hz, 6H) ppm.

Synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol (**4**): The reaction procedure was performed in the same way as **1** except for **4a** was used instead of **1a**. Yield: 95%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.35 (d, J=6.0 Hz, 2H), 6.98-7.01 (m, 1H), 6.92 (d, J=6.0 Hz, 1H), 6.83-6.87 (m, 2H), 5.14 (dd, J=12.0 Hz, 6.0 Hz, 1H), 3.95-3.98 (m, 1H), 3.89 (s, 3H), 3.81 (s, 3H) ppm.

Synthesis of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (**5**)

Synthesis of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone (**5a**): The reaction procedure was performed in the same way as **1a** except for 2-bromo-1-(3,4-dimethoxyphenyl)ethanone and 2-methoxylphenol were used instead of 2-bromoacetophenone and phenol, respectively. Yield: 95%. Light yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.68 (dd, J=8.4 Hz, 1.8 Hz, 2H), 7.6 (d, J=2.4 Hz, 1H), 6.95-6.98 (m, 1H), 6.91 (t, J=8.4 Hz, 2H), 6.85-6.86 (m, 2H), 5.29 (s, 2H), 3.95 (d, J=10.84 Hz, 6H), 3.89 (s, 3H) ppm.

Synthesis of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (**5**): The reaction procedure was performed in the same way as **1** except for **5a** was used instead of **1a**. Yield: 90%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.99-7.02(m, 2H), 6.89-6.96 (m, 4H), 6.86 (d, J=8.4 Hz, 1H), 5.05 (dd, J=9.6 Hz, 3.0 Hz, 1H), 4.17 (dd, J=10.0 Hz, 3.0 Hz, 1H), 3.97 (t, J=9.6 Hz, 1H), 3.90 (d, J=4.8 Hz, 6H), 3.88 (s, 3H), 3.44 (br s, 1H) ppm.

Synthesis of 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethanol (**6**)

Synthesis of 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethanone (**6a**): The reaction procedure was performed in the same way as 1a except for 2-bromo-1-(4-

methoxyphenyl)ethanone and 2,6-dimethoxylphenol were used instead of 2-bromoacetophenone and phenol, respectively. Yield: 90%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.07 (d, J=9.0 Hz, 2H), 7.0 (t, J=8.4 Hz, 1H), 6.94 (d, J=9.0 Hz, 2H), 6.58 (t, J=8.4 Hz, 2H), 5.13 (s, 2H), 3.87 (s, 3H), 3.81 (s, 6H) ppm.

Synthesis of 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethanol (**6**): The reaction procedure was performed in the same way as **1** except for **6a** was used instead of **1a**. Yield: 93%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.31 (d, J=8.4 Hz, 2H), 7.04 (t, J=8.4 Hz, 1H), 6.87 (d, J=9.0 Hz, 2H), 6.61 (d, J=12.0 Hz, 2H), 4.91 (dd, J=10.2 Hz, 2.4 Hz, 1H), 4.49 (s, 1H), 4.37 (dd, J=10.2 Hz, 2.4 Hz, 1H), 3.88 (s, 6H), 3.79 (s, 3H), 3.70 (t, J=10.2 Hz, 1H) ppm.

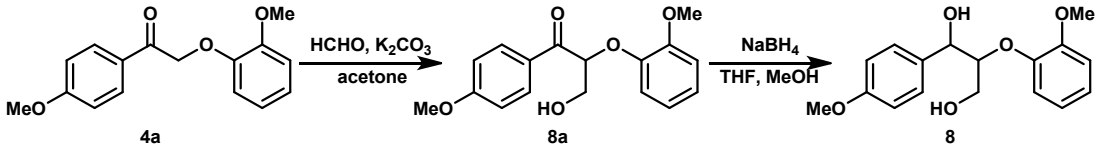
Synthesis of 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (**7**)

Synthesis of 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanone (**7a**): The reaction procedure was performed in the same way as 1a except for 2-bromo-1-(3,4-dimethoxyphenyl)ethanone and 2,6-dimethoxylphenol were used instead of 2-bromoacetophenone and phenol, respectively. Yield: 92%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.73 (dd, J=8.4 Hz, 1.8 Hz, 1H), 7.65 (d, J=1.8 Hz, 1H), 7.01 (t, J=8.4 Hz, 1H), 6.90 (d, J=8.4 Hz, 1H), 6.59 (d, J=8.4 Hz, 2H), 5.15 (s, 2H), 3.95 (d, J=2.4 Hz, 6H), 3.82 (s, 6H) ppm.

Synthesis of 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (**7**): The reaction procedure was performed in the same way as **1** except for **7a** was used instead of **1a**. Yield: 98%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.05 (t, J=8.4 Hz, 1H), 6.97 (d, J=1.8 Hz, 1H), 6.90 (dd, J=7.8 Hz, 1.8 Hz, 1H), 6.83 (d, J=7.8 Hz,

1H), 4.91 (dd, J=10.2 Hz, 2.4 Hz, 1H), 4.53 (s, 1H), 4.40 (dd, J=10.2, 2.4 Hz, 1H), 3.86-3.89 (m, 12H), 3.70 (t, J=10.2 Hz, 1H) ppm.

Synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-1,3-propanediol (**8**)[3]



Synthesis of 3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-1-propanone (8**a**): A mixture of **4a** (1.36 g, 5.0 mmol) and K_2CO_3 (0.77 g, 5.55 mmol) in a EtOH and acetone (20 mL, v:v = 1:1) was stirred at room temperature and then aqueous formaldehyde solution (37%, 0.68 mL, 9.12 mmol) was added dropwise. The resulting mixture was stirred overnight. The reaction mixture was filtered, the filtrate was concentrated in vacuum. The residue was purified by column chromatography on silica gel (n-hexane: ethyl acetate, v:v = 2:1) to afford light yellow oil 1.2 g, yield: 80.0%. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.07 (d, J=9.0 Hz, 2H), 6.99-7.02 (m, 1H), 6.94 (d, J=9.0 Hz, 2H), 6.89-6.92 (m, 2H), 6.818-6.84 (m, 1H), 5.37 (t, J=5.4 Hz, 1H), 4.06 (t, J=5.4 Hz, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.08 (t, J=6.6 Hz, 1H) ppm.

Synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-1,3-propanediol (**8**): The compound **8a** (1.0 g, 3.3 mmol) was dissolved with THF (20 mL) and MeOH (10 mL) and stirred at ice-water bath. $NaBH_4$ (0.25g, 6.6 mmol) was added portion wise, then the mixture was warmed to room temperature and stirred overnight. Saturated NH_4Cl aq. was added (pH = 5-6) and stirred for 1 hour. The resulting mixture was extracted with CH_2Cl_2 and then combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuum

and the residue was purified by column chromatography on silica gel (CH_2Cl_2: MeOH, v:v = 40:1) to afford light yellow oil 0.92 g, yield: 92.0%. ^1H NMR (600 MHz, $CDCl_3$) δ: 7.37 (d, J=9.0 Hz, 0.73H, minor diastereomers), 7.31 (d, J=9.0 Hz, 1.27H, major diastereomers), 7.13 (dd, J=7.8 Hz, 1.2 Hz, 0.33H, minor diastereomers), 7.04-7.08 (m, 1H, both diastereomers), 6.88-6.98 (m, 4.69H, both diastereomers), 4.99-5.00 (m, 1H, both diastereomers), 4.15-4.17 (m, 0.63H, major diastereomers), 4.02-4.04 (m, 0.39H, minor diastereomers), 3.92 (s, 1.1H, minor diastereomers), 3.89 (s, 1.9H, major diastereomers), 3.80 (d, J=1.8 Hz, 3H, both diastereomers), 3.73-3.76 (m, 0.69H, majo diastereomers), 3.62-3.67 (m, 0.9H, both diastereomers), 3.60 (br s, 0.64H, major diastereomers), 3.45-3.49 (m, 0.51H, minor diastereomers), 3.39 (br s, 0.41H, minor diastereomers), 2.70 (d, J=22.8 Hz, 0.96H, both diastereomers) ppm.

2. Crystallographic data and structure refinements

Table S1. Crystallographic data and structure refinements of NENU-MV-5

Name	NENU-MV-5
Empirical formula	$C_{20}H_{30}O_{14}N_8Cu_2V_5$
Formula weight	988.30
Temperature (K)	294.9
Wave length (Å)	0.71073
Crystal system	Monoclinic
Space group	C 1 2/c 1
a (Å)	22.7662(11)
b (Å)	12.1453(5)
c (Å)	24.9282(11)
α (deg)	90
β (deg)	98.796(2)
γ (deg)	90
Volume ($Å^3$)	6811.6(5)
Z, D_{calc} (Mg/m^3)	8, 1.928
Absorption coefficient (mm^{-1})	2.610
F (000)	3928
Crystal size (mm^3)	0.220 x 0.210 x 0.200
θ range (deg)	2.257 to 25.742°
index range (deg)	-27 =< h =< 27, -14 =< k =< 14, -30 =< l =< 30
Reflections collected / unique	34966 / 6490 [R(int) = 0.0426]
Data / restraints / parameters	6490 / 220 / 574
Goodness-of-fit on F^2	1.095
R_1, wR_2 ($I > 2\sigma(I)$)	0.0455, 0.0971
R_1, wR_2 (all data)	0.0600, 0.1034
Largest diff. peak and hole (e $Å^{-3}$)	0.671, -0.525

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

3. Characterization of NENU-MV-5

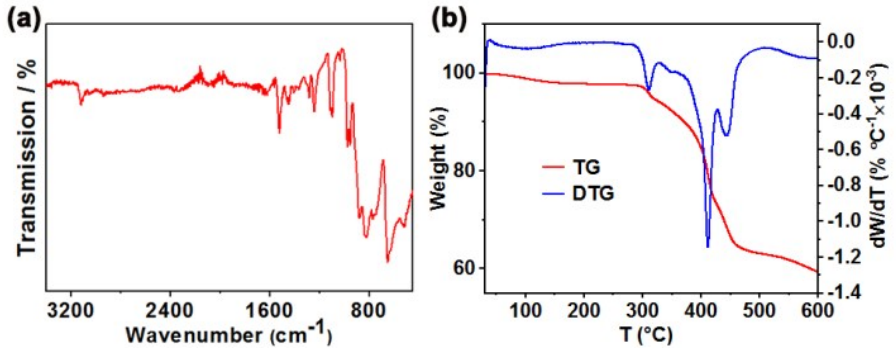


Figure S1. (a) The FTIR spectrum of NENU-MV-5 and (b) the TGA curve of NENU-MV-5.

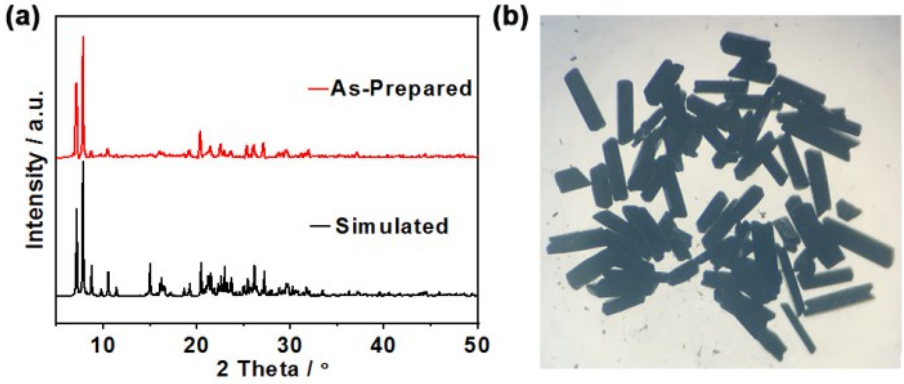


Figure S2. (a) PXRD patterns of NENU-MV-5. (b) The photograph of NENU-MV-5 crystals.

The phase purity of NENU-MV-5 was evidenced by as-prepared PXRD, which matched well with the simulated pattern from crystallographic studies.

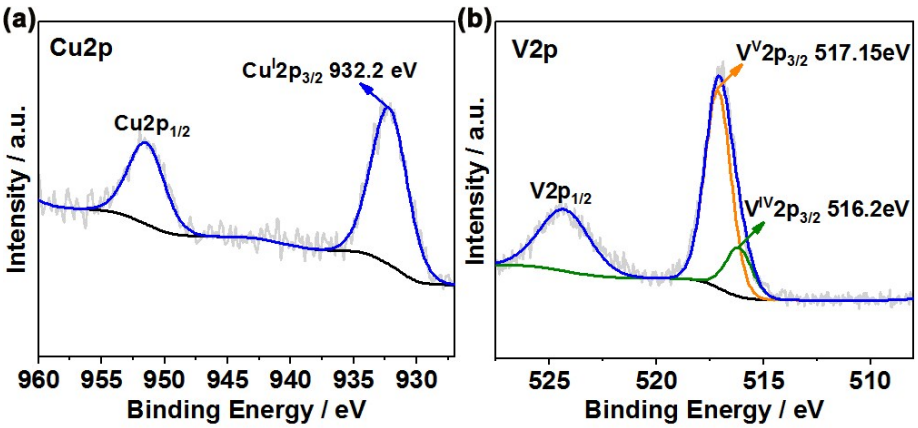


Figure S3. The XPS results for oxidative states of cuprous ions (a) and vanadium ions (b) in NENU-MV-5.

4. 3D supramolecular framework of NENU-MV-5

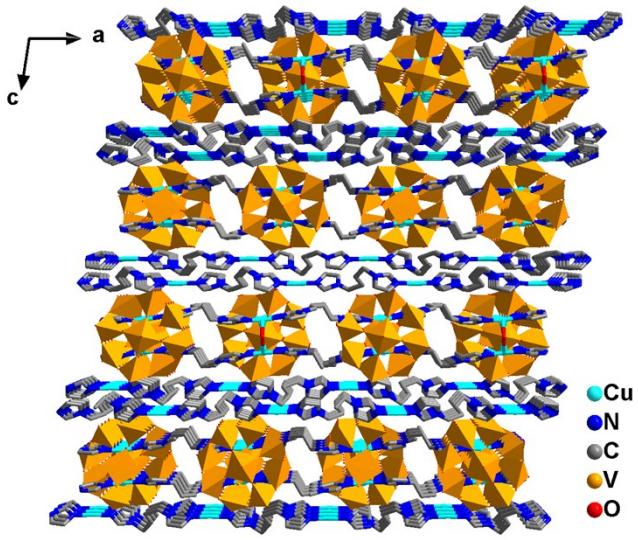


Figure S4. 3D supramolecular framework of NENU-MV-5. Hydrogen atoms and lattice water molecule are omitted for clarity.

5. BVS results

Table S2. BVS results for the vanadium ions and cupric ions in NENU-MV-5.

V site	BVS cacl. for V (IV)	BVS cacl. for V (V)	Assigned O.S.
V1	4.905	5.163	5
V2	4.993	5.256	5
V3	4.456	4.689	4
V4	4.938	5.198	5
V5	4.948	5.209	5
V6	4.367	4.596	4

BVS results for the vanadium ions in NENU-MV-5

Cu site	BVS cacl. for Cu (I)	BVS cacl. for Cu (II)	Assigned O.S.
Cu1	1.012	1.036	1
Cu2	0.961	0.961	1

BVS results for the cuprous ions in NENU-MV-5

6. BET analysis of NENU-MV-5 powder

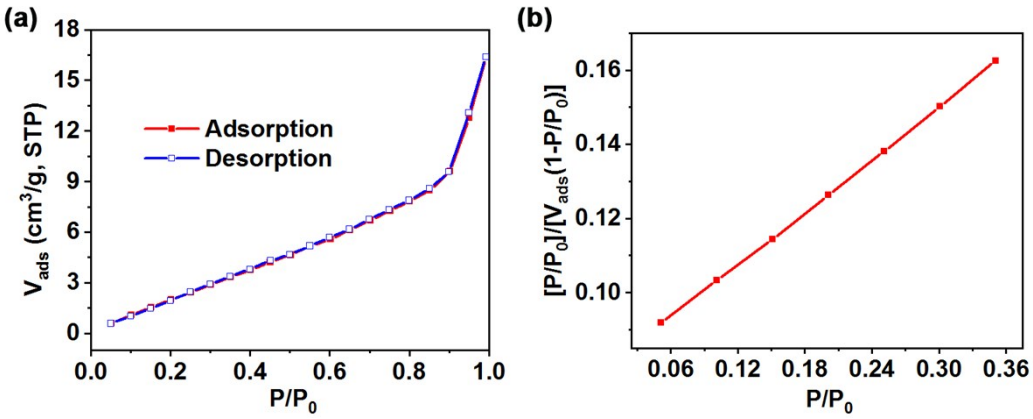
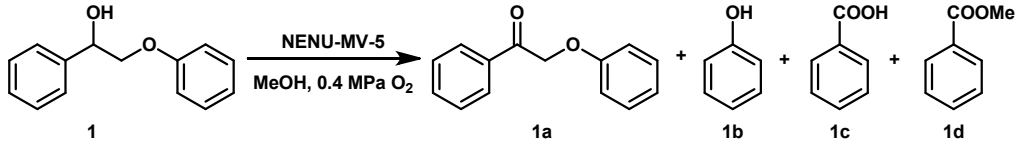


Figure S5. BET analysis of NENU-MV-5 powder. The N_2 absorption / desorption isotherms of NENMU-MV-5 powder at 77K (P_0 = 101 kPa).

7. Oxidative cleavage of lignin model compound 1 with NENU-MV-5

Table S3. Oxidative cleavage of lignin model compound **1** with NENU-MV-5.

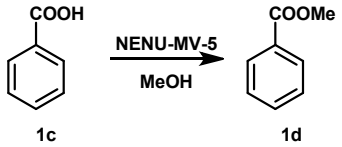


Entry	Substrate	Solvent	T (°C)	P (MPa)	Conv. (%)	Products Yield[c] (%) **1a**	**1b**	**1c**	**1d**
1	**1**	MeOH	100	0.4	>99	<1	60.0	9.5	90.0
2	**1**	ACN	100	0.4	<1	n.d.	n.d.	n.d.	n.d.
3[a]	**1a**	MeOH	100	0.4	>99	—	72.0	13.0	83.0
4[a]	**1**	MeOH	100	0.4	30	6	20.1	12.0	11.5.0
5[b]	**1**	MeOH	100	0.4	<1	n.d.	n.d.	n.d.	n.d.
6[b]	**1a**	MeOH	100	0.4	<1	—	n.d.	n.d.	n.d.

n.d.= not detected. Reaction conditions: 0.5 mmol substrate, 0.01 mmol NENU-MV-5, 2 mL solvent, 12 hours, 0.4 MPa O_2. [a] 2 hours. [b] 0.4 MPa N_2. [c] Yield was determined by GC using biphenyl as internal standard.

8. Esterification reaction of benzoic acid and MeOH with NENU-MV-5

Table S4. Esterification reaction of benzoic acid and MeOH with NENU-MV-5.



Entry	Substrate	solvent	T (°C)	P (MPa)	Conv. (%)	Yield[a] (%)
1	**1c**	MeOH	100	0.4 N_2	>99	>99
2	**1c**	MeOH	100	0.4 O_2	>99	>99

Reaction conditions: 0.5 mmol benzoic acid, 0.01 mmol NENU-MV-5, 2 mL MeOH, 12 hours. [a] Yield was determined by GC using biphenyl as internal standard.

9. PXRD patterns of $(Et_4N)_4(V_{10}O_{26})\cdot H_2O$

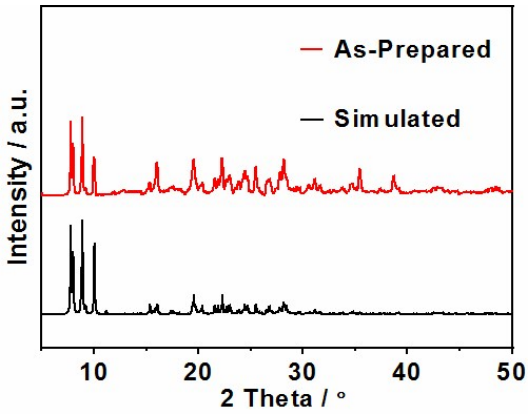


Figure S6. The PXRD patterns of $(Et_4N)_4(V_{10}O_{26})\cdot H_2O$.

10. EPR spectrum for DMPO–·O_2^- radical species in acetonitrile

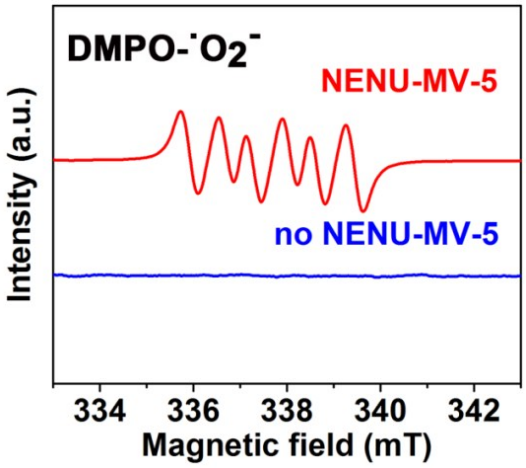
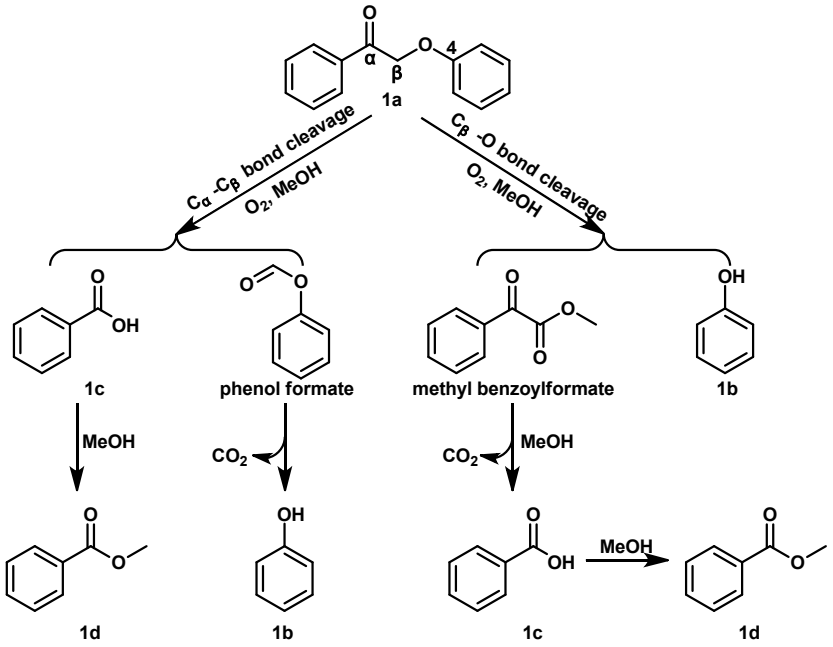


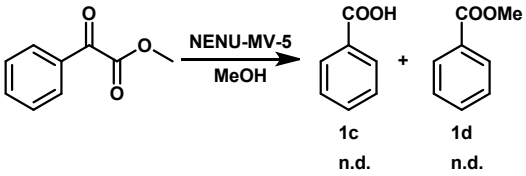
Figure S7. DMPO spin trapping EPR spectra for DMPO–·O_2^- radical species in acetonitrile.

11. Two types of broken bonds of 2-phenoxy-1-phenylenthanone (1a)



Scheme S1. The intermediates and products of 2-phenoxy-1-phenylenthanone (**1a**) preferentially breaking C_α-C_β bond or C_β-O bond.

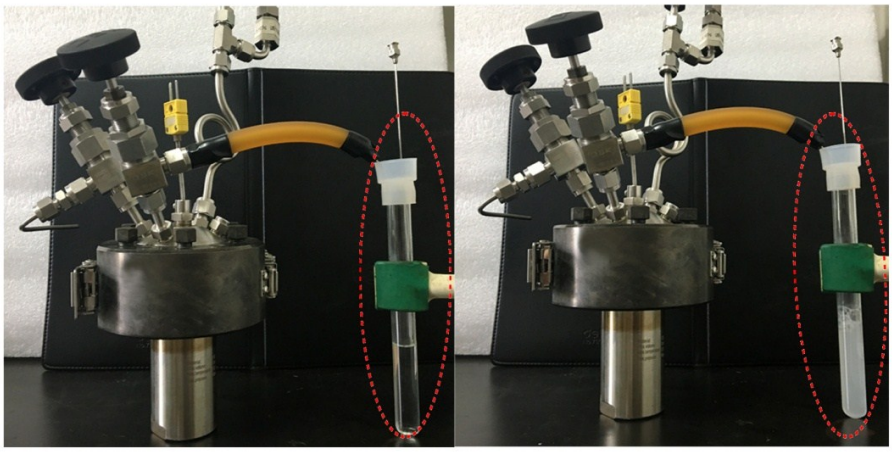
12. Catalytic oxidation of methyl benzoylformate with NENU-MV-5



Scheme S2. Catalytic oxidation of methyl benzoylformate with NENU-MV-5.

n.d.= not detected. Reaction conditions: 0.5 mmol methyl benzoylformate, 0.01 mmol NENU-MV-5, 2 mL MeOH, 2 hours, 100 °C, 0.4 MPa O_2.

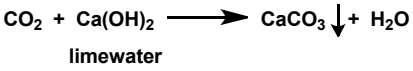
13. Detection of reaction gas phase product CO_2



Limewater images before (left) and after (right) introduction of the reaction gas phase

Figure S8. Detection of reaction gas phase product CO_2.

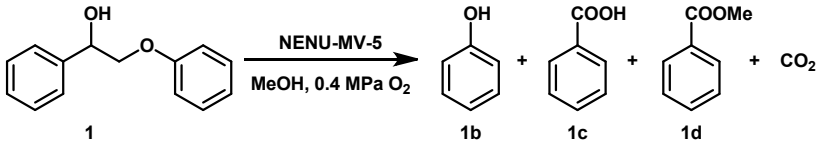
14. The reaction equation of CO_2 and limewater



Scheme S3. The reaction equation of CO_2 and limewater.

15. The carbon balance of oxidative cleavage of lignin model compound 1

Table S5. The carbon balance of oxidative cleavage of lignin model compound **1** with NENU-MV-5.

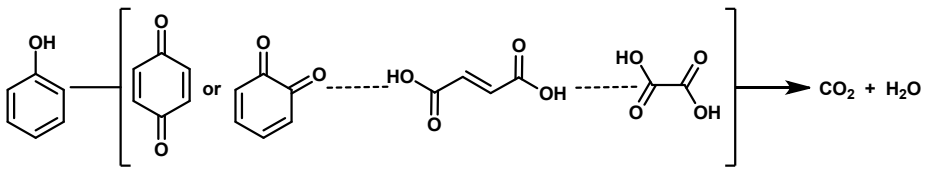


Entry	Product		
	1b	(**1c** + **1d**)	**CO_2**
Theoretical yield (mmol)	0.5 mmol (100%)	0.5 mmol (100%)	0.5 mmol (100%)
Actual yield (mmol)	0.3 mmol (60%)	0.4975 mmol (99.5%)	1.65 mmol [d] (330%)
Difference value [a]	-0.2 mmol [b]	-0.0025 mmol	+1.15 mmol [c]

Reaction conditions: 0.5 mmol **1**, 0.01 mmol NENU-MV-5, 2 mL MeOH, 12 hours, 100 °C, 0.4 MPa O_2. [a] Difference value = Actual yield - Theoretical yield. [b] The reduced amount of phenol. [c] The amount of extra CO_2. [d] The actual yield of CO_2 was determined by weighing $CaCO_3$ (165 mg, 1.65 mmol) produced by the reaction of CO_2 with limewater.

The amount of extra CO_2 (1.15 mmol equivalent to 0.19 mmol phenol) which was comparable to the reduced phenol (0.2 mmol) indicated that part of the phenol generated by oxidative cleavage of **1** was oxidized to CO_2 and H_2O.

16. The mechanism of oxidation of phenol to CO_2 and H_2O[4]



Scheme S4. The mechanism of oxidation of phenol to CO_2 and H_2O.

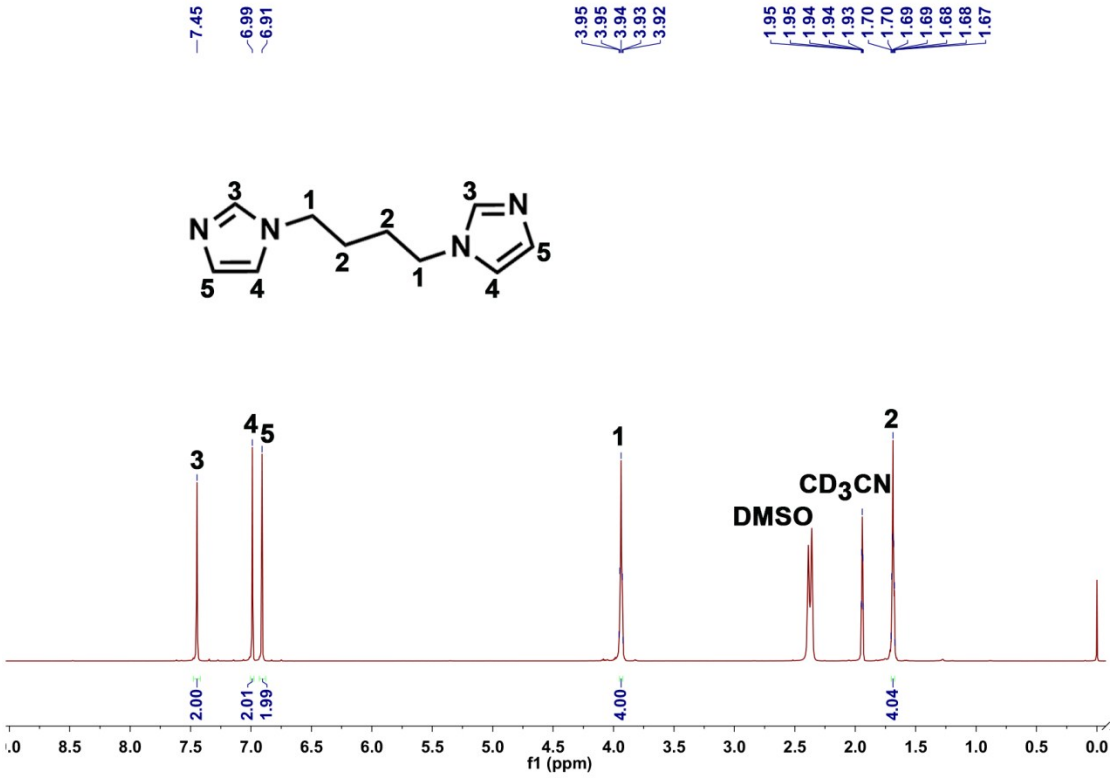
17. Catalytic systems for the oxidative cleavage of β-O-4 lignin model compounds

Table S6. Catalytic systems for the oxidative cleavage of β-O-4 lignin model compounds.

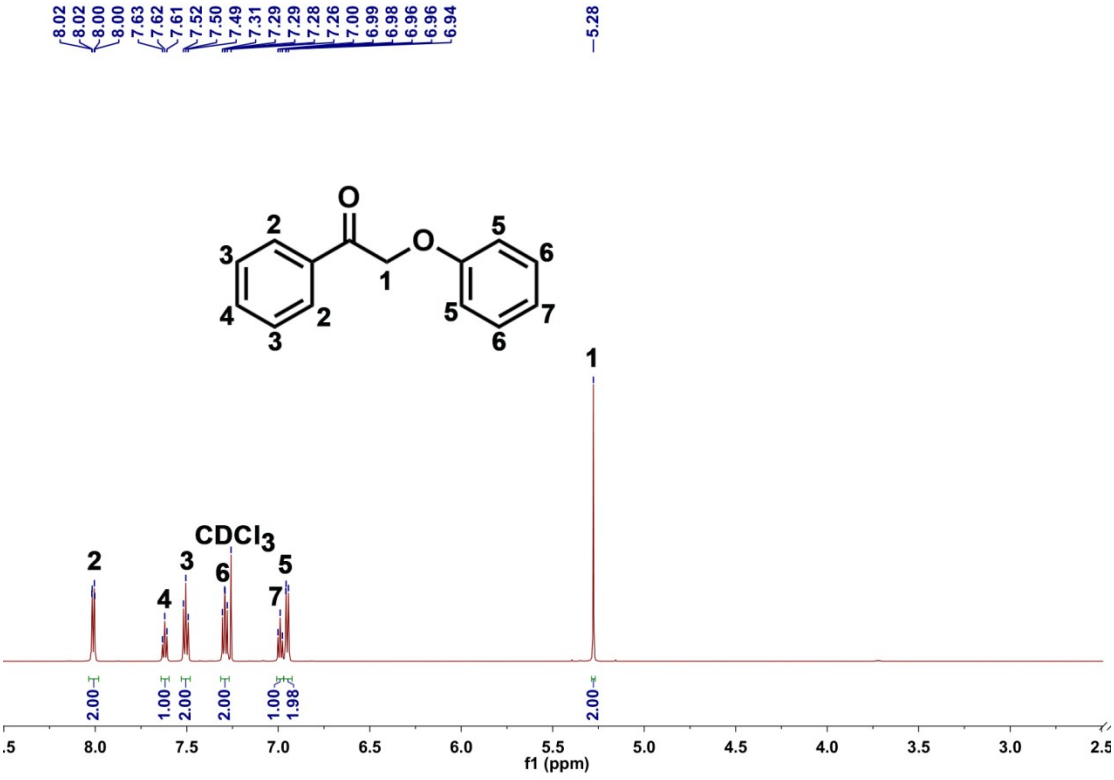
Entry	Catalyst	co-catalyst	System Type	Reaction Step	Condition		Conv. (%)	Ref.
					Temp. (°C)	Time (h)		
2-phenoxy-1-phenylethanol (**1**) as substrate								
1	$VO(acac)_2$	AcOH	Homo.	One-Step	80	8	89.2	[5]
2	(dipic)V(O)^{i}Pr	—	Homo.	One-Step	100	168	95	[6]
3	$RuHCl(CO)(PPh_3)_3$	KOH	Homo.	One-Step	125	12	99	[7]
4	$VOSO_4$/ $Cu(OAc)_2$	TEMPO/ 1,10-Phen	Homo.	Two-Step	100 /80	24 /6	75.8	[8]
5	Pd/CeO_2	—	Heter.	One-Step	185	24	70	[9]
6	VB_{12}@C-900	K_2CO_3	Heter.	One-Step	100	24	96	[10]
7	Co-N-C	NaOH	Heter.	One-Step	150	4	93	[11]
8	NENU-MV-5	—	Heter.	One-Step	100	12	>99	This work
2-phenoxy-1-phenylethanol with methoxyl and C_γ-OH groups (structure is similar to **8**) as substrate								
9	AcNH-TEMPO /H_2O_2	HNO_3-HCl /NaOH	Homo.	Two-Step	45 /50	24 /10	96	[12]
10	AcNH-TEMPO /$[Ir(ppy)_2(dtbbpy)]PF_6$	DIPEA-HCOOH	Homo.	Two-Step	25	18 /20	100	[13]
11	DDQ-t-BuONO /Zn	NH_4Cl	Homo.	Two-Step	80	14 /0.25	100	[14]
12	NENU-MV-5	—	Heter	One-Step	120	18	>99	This work

Homo. = Homogeneous phase. Heter. = Heterogeneous phase.

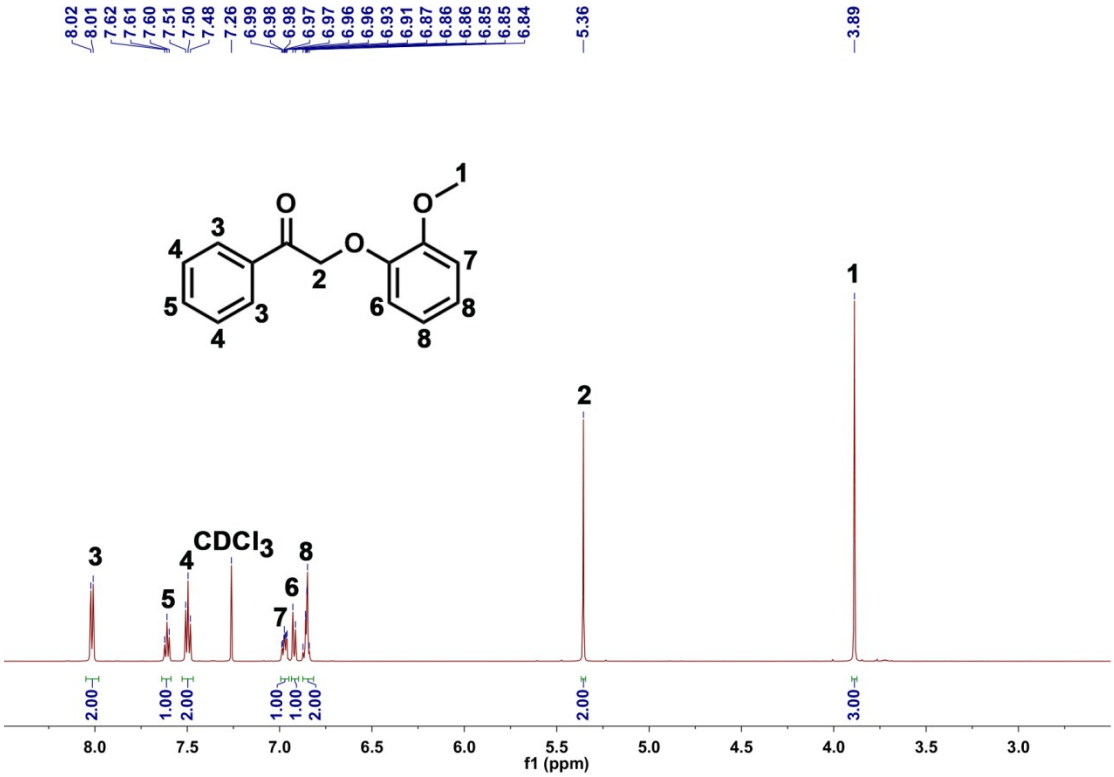
18. [1]HNMR spectra



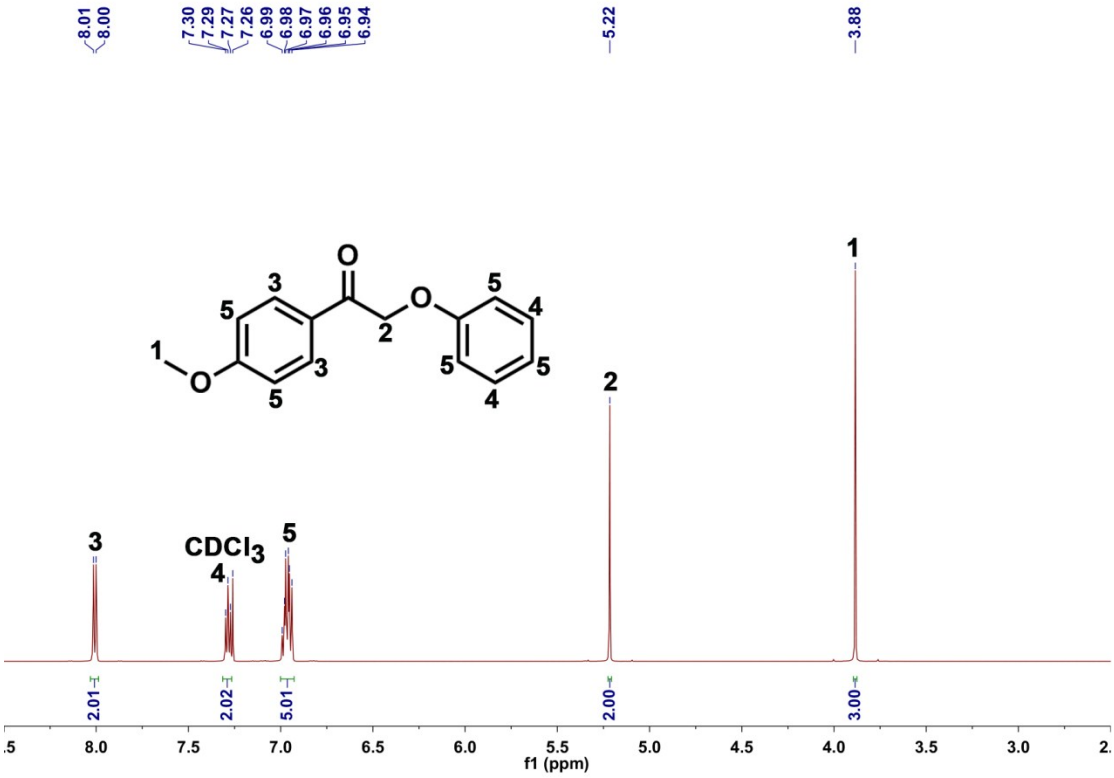
[1]H-NMR spectrum of bbi. (DMSO derives from residual solvent)



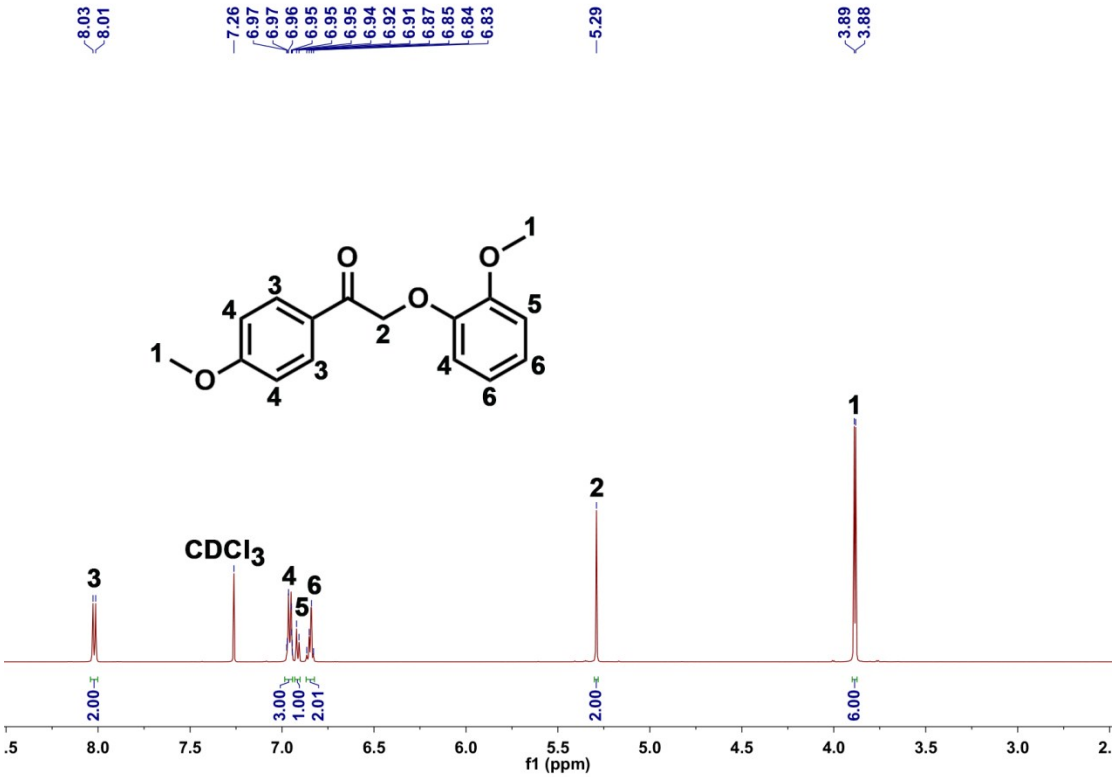
[1]H-NMR spectrum of 2-phenoxy-1-phenylethanone (**1a**).



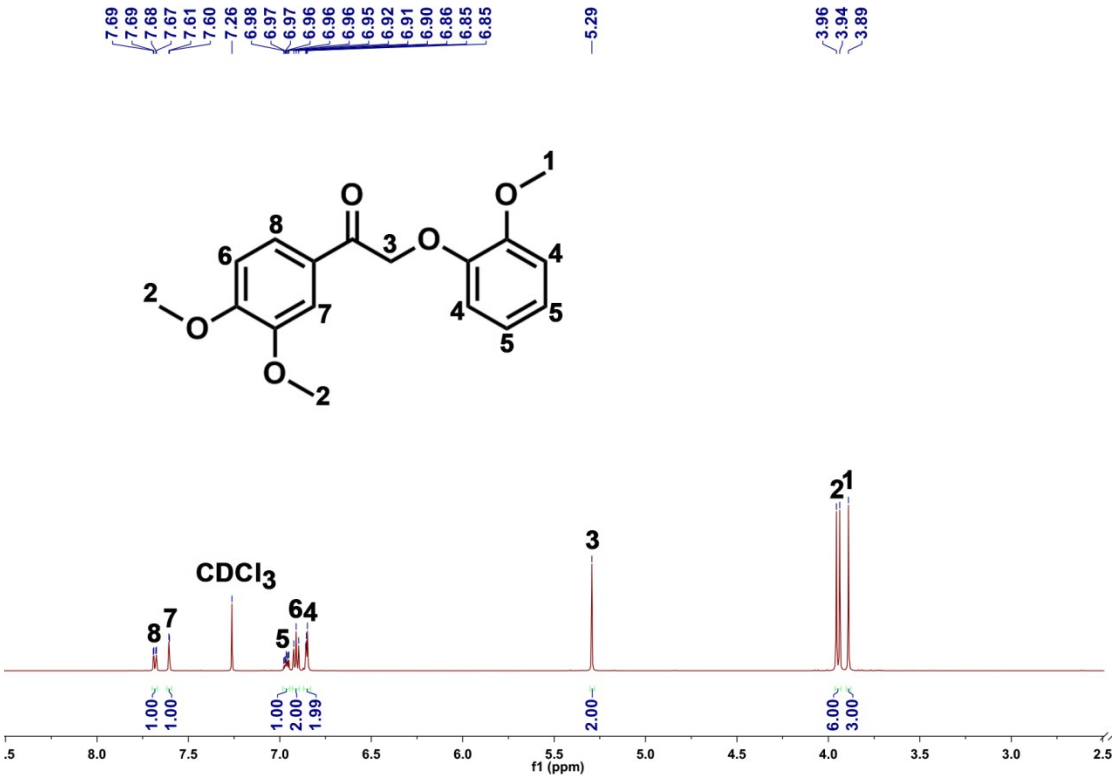
^{1}H-NMR spectrum of 2-(2-methoxyphenoxy)-1-phenylethanone (**2a**).



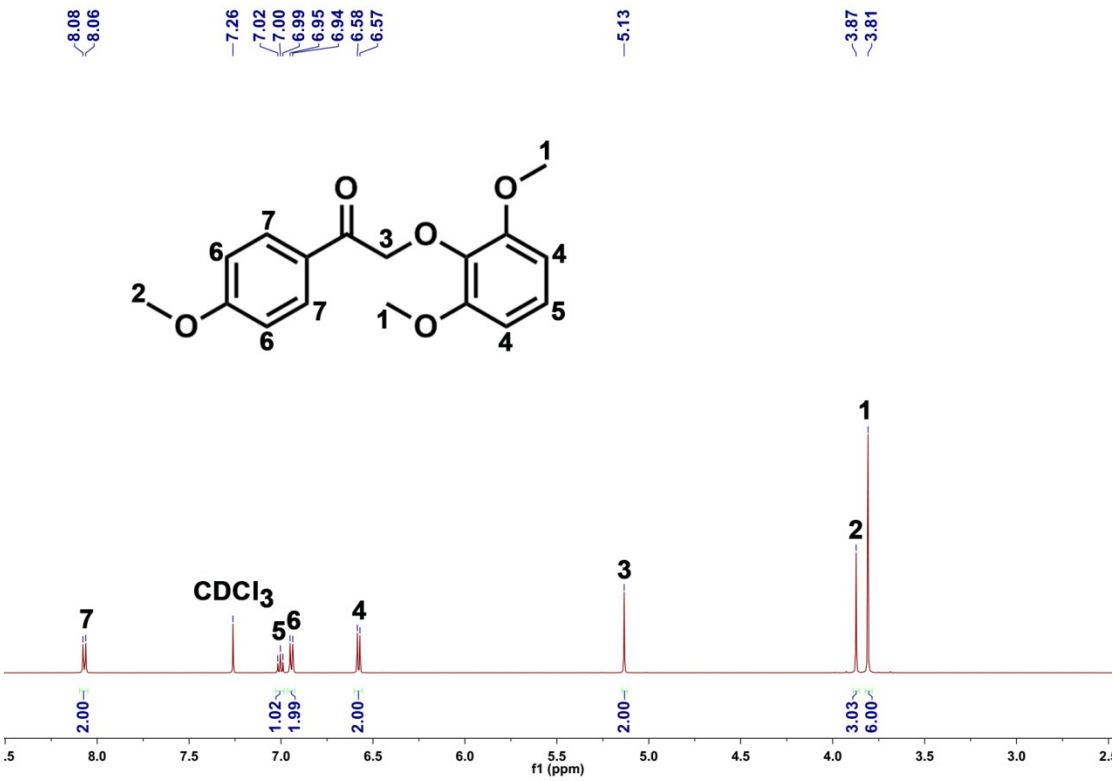
^{1}H-NMR spectrum of 1-(4-methoxyphenyl)-2-phenoxyethanone (**3a**).



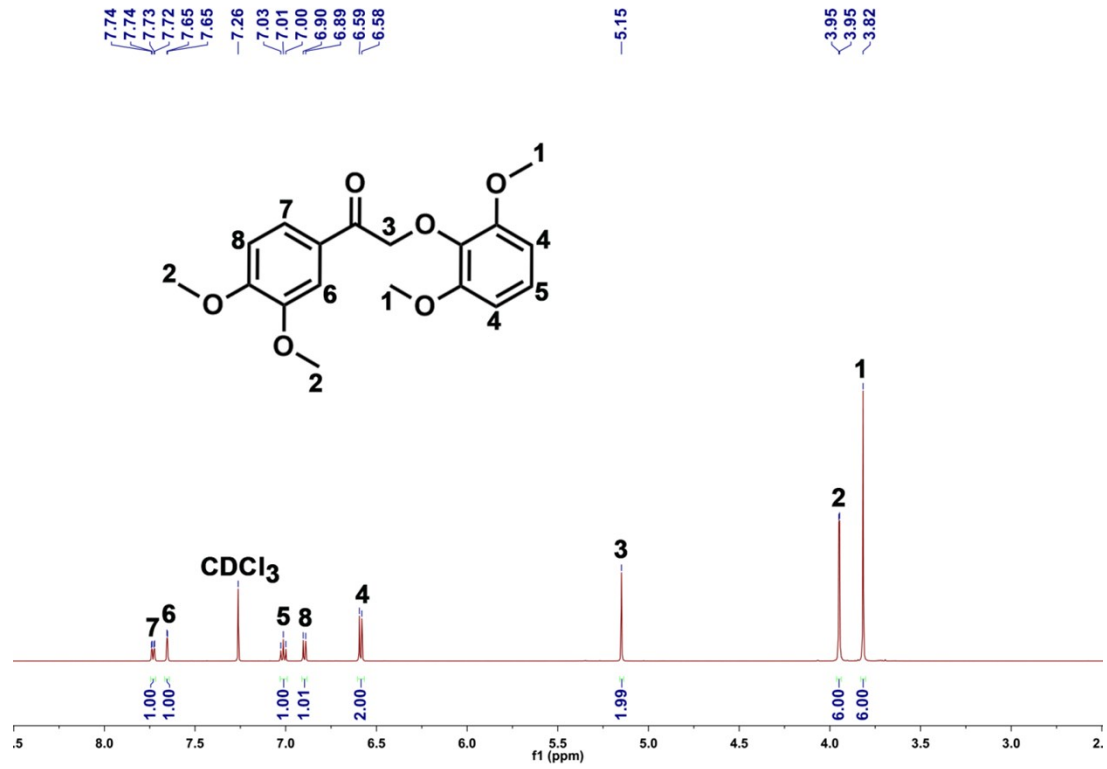
^{1}H-NMR spectrum of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone (**4a**).



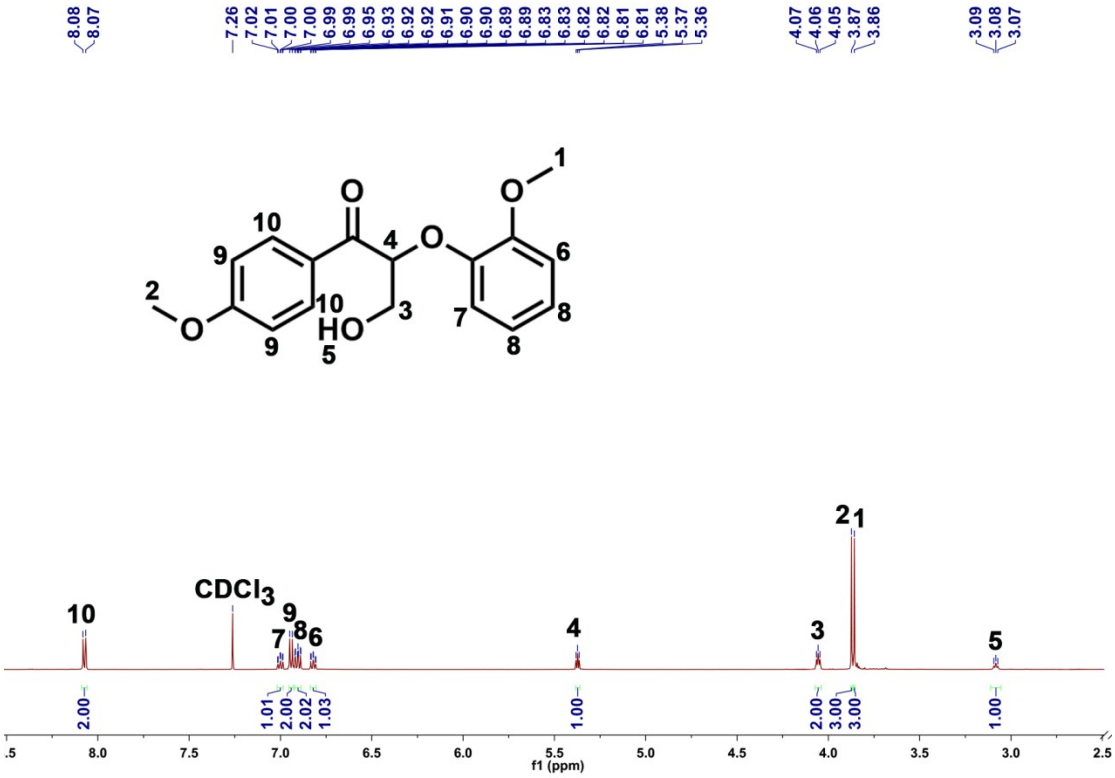
^{1}H-NMR spectrum of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone (**5a**).



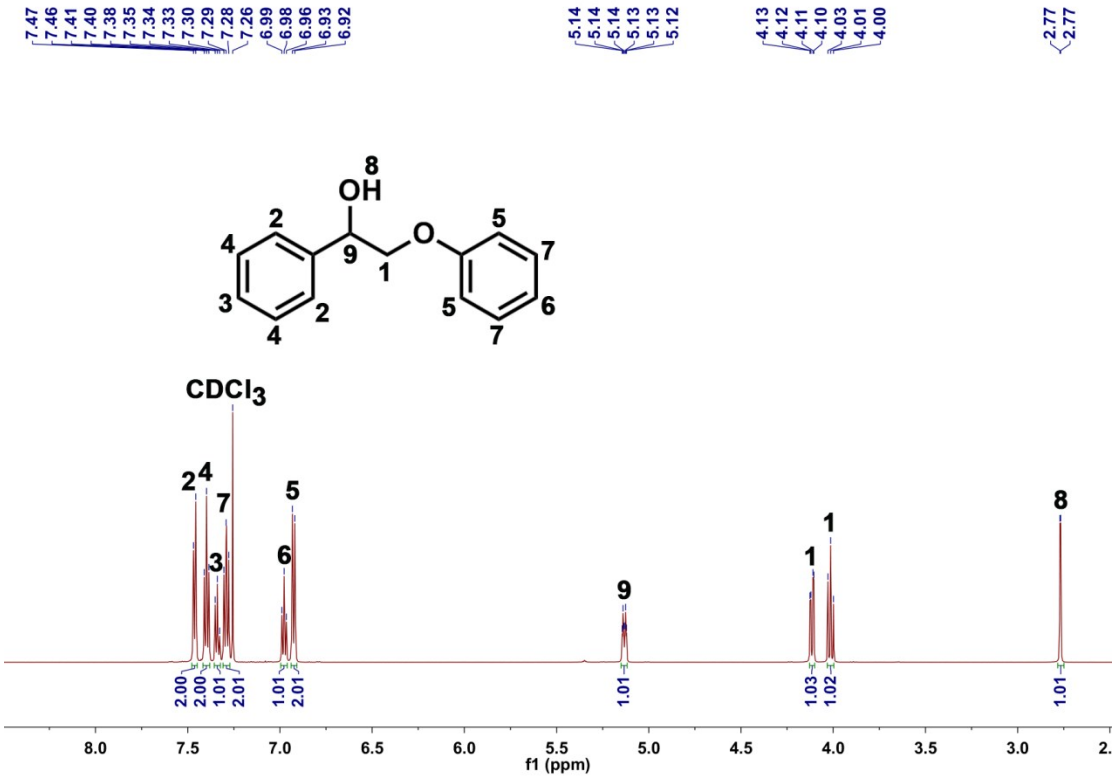
[1]H-NMR spectrum of 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethanone (**6a**).



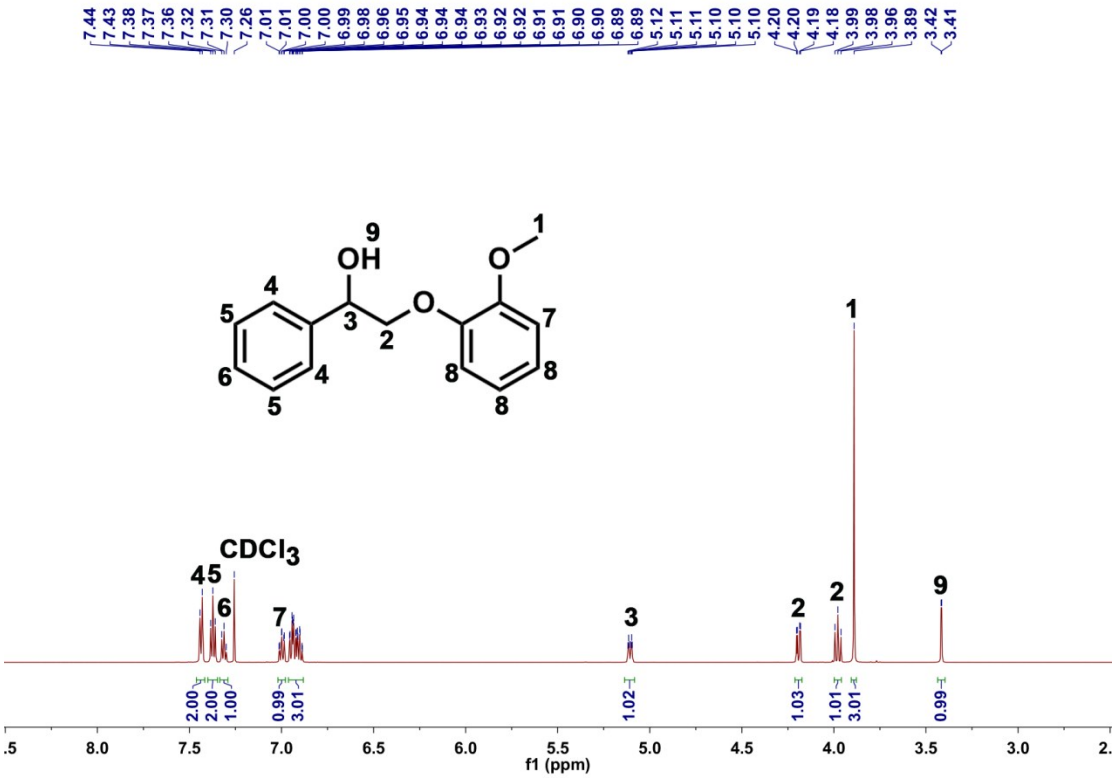
[1]H-NMR spectrum of 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanone (**7a**).



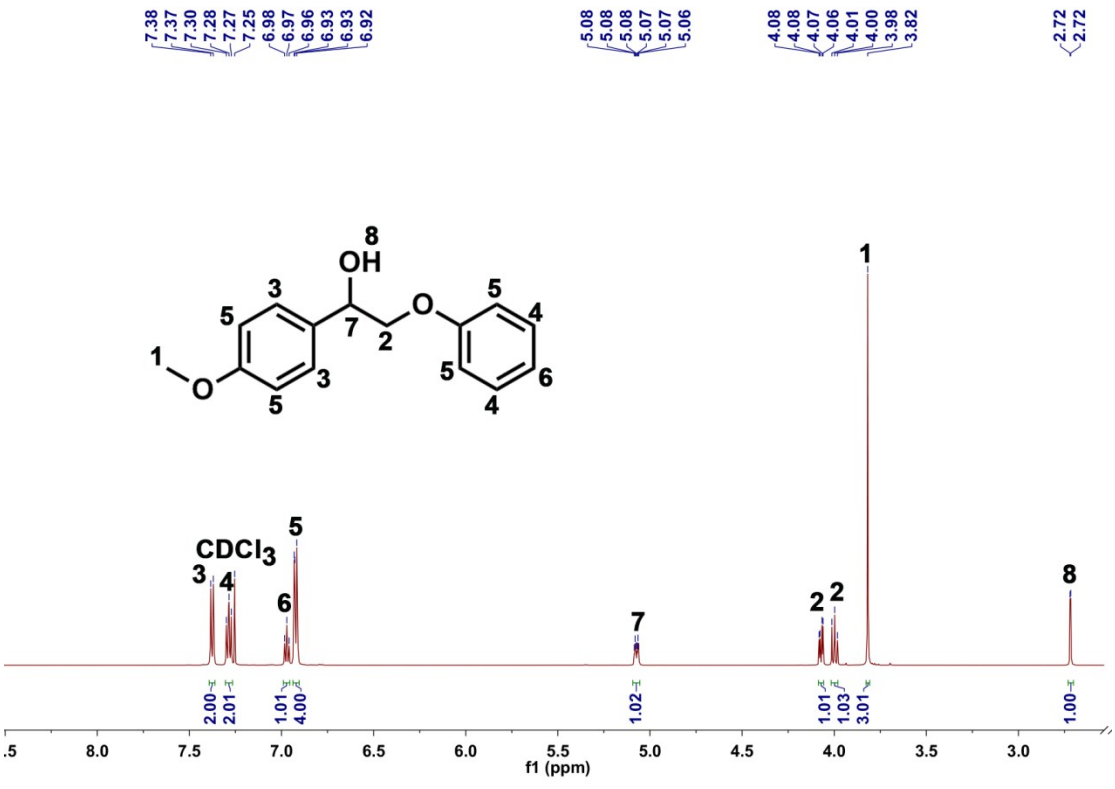
^{1}H-NMR spectrum of 3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-1-propanone (**8a**).



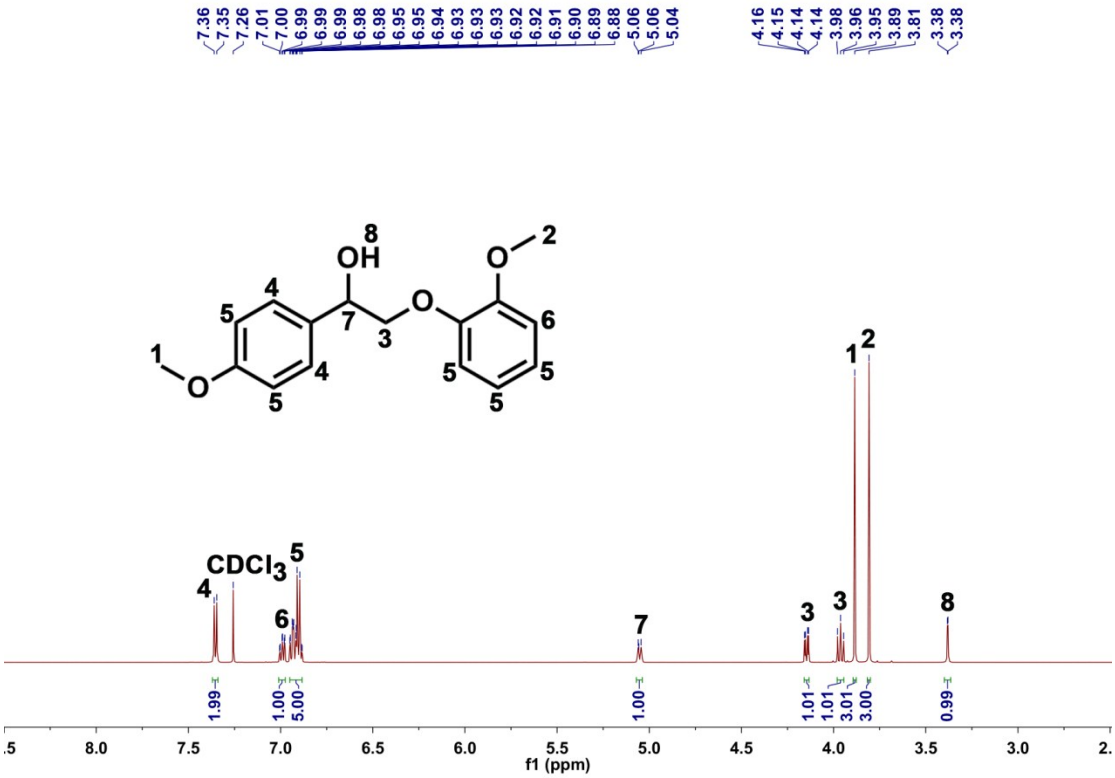
^{1}H-NMR spectrum of 2-phenoxy-1-phenylethanol (**1**).



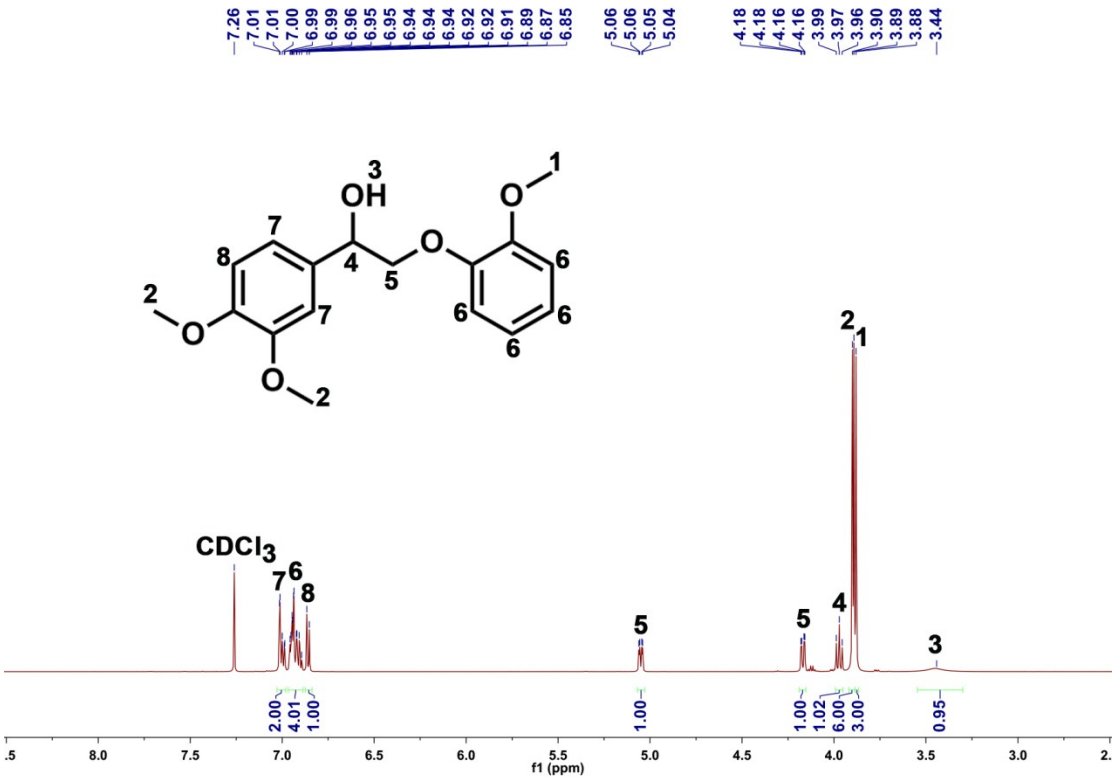
^{1}H-NMR spectrum of 2-(2-methoxyphenoxy)-1-phenylethanol (**2**).



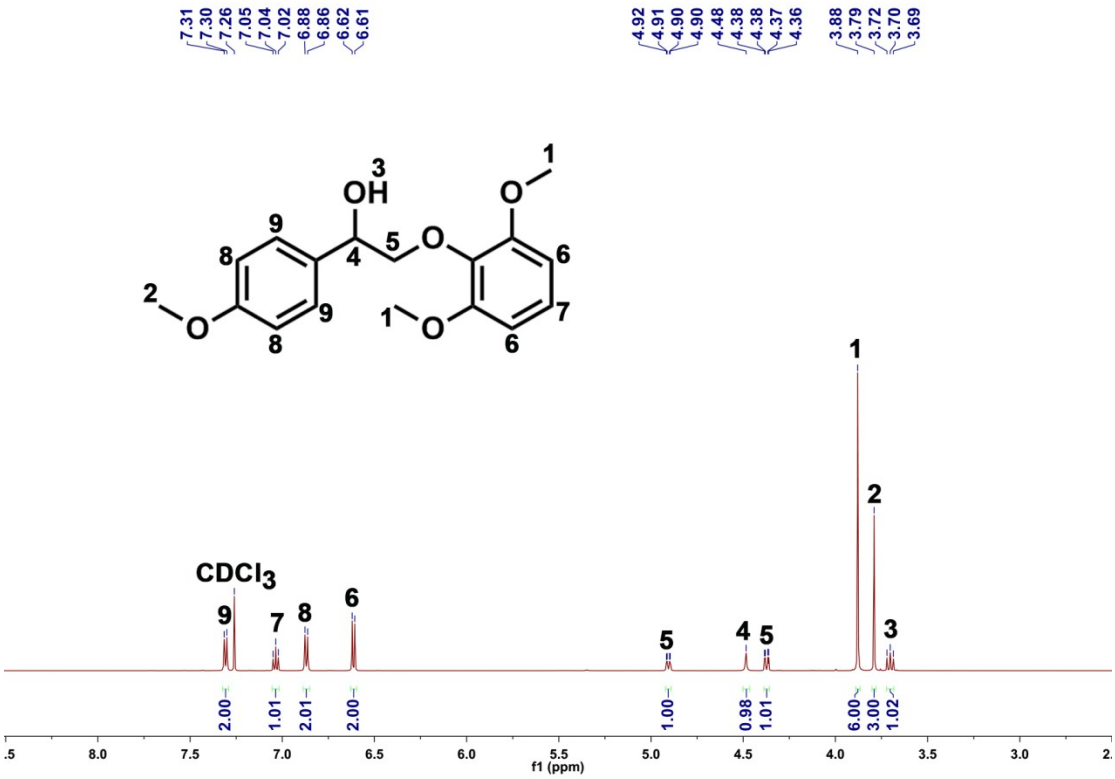
^{1}H-NMR spectrum of 1-(4-methoxyphenyl)-2-phenoxyethanol (**3**).



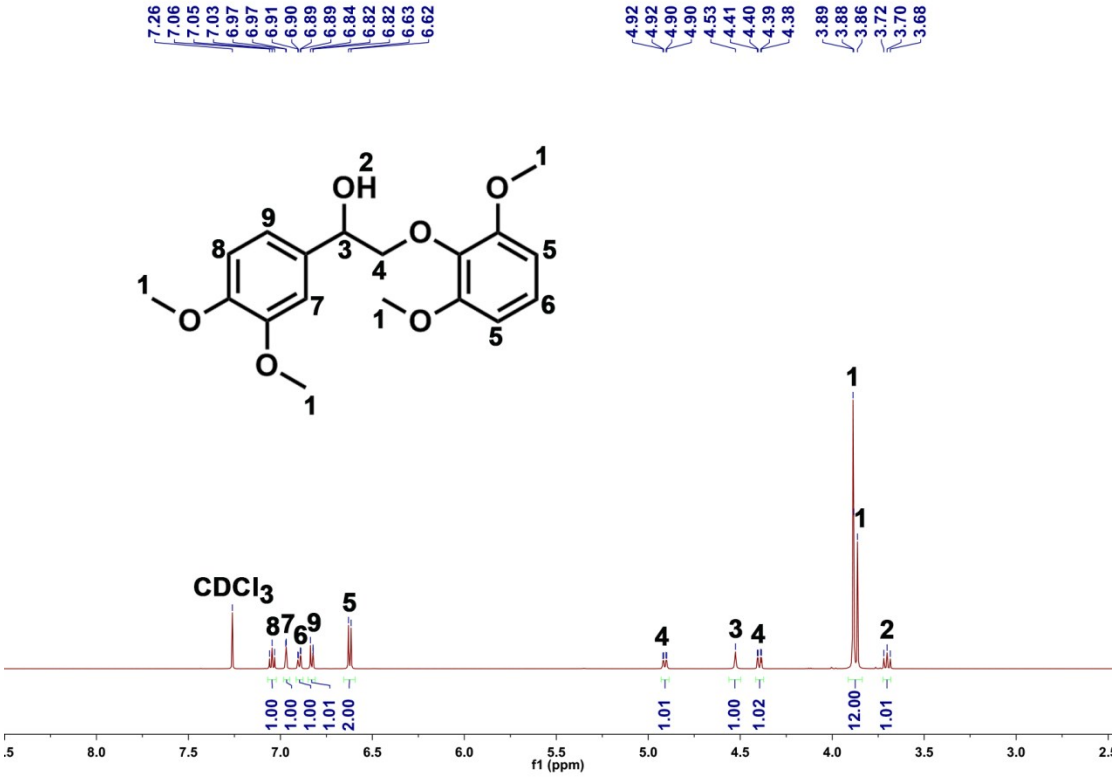
^{1}H-NMR spectrum of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol (**4**).



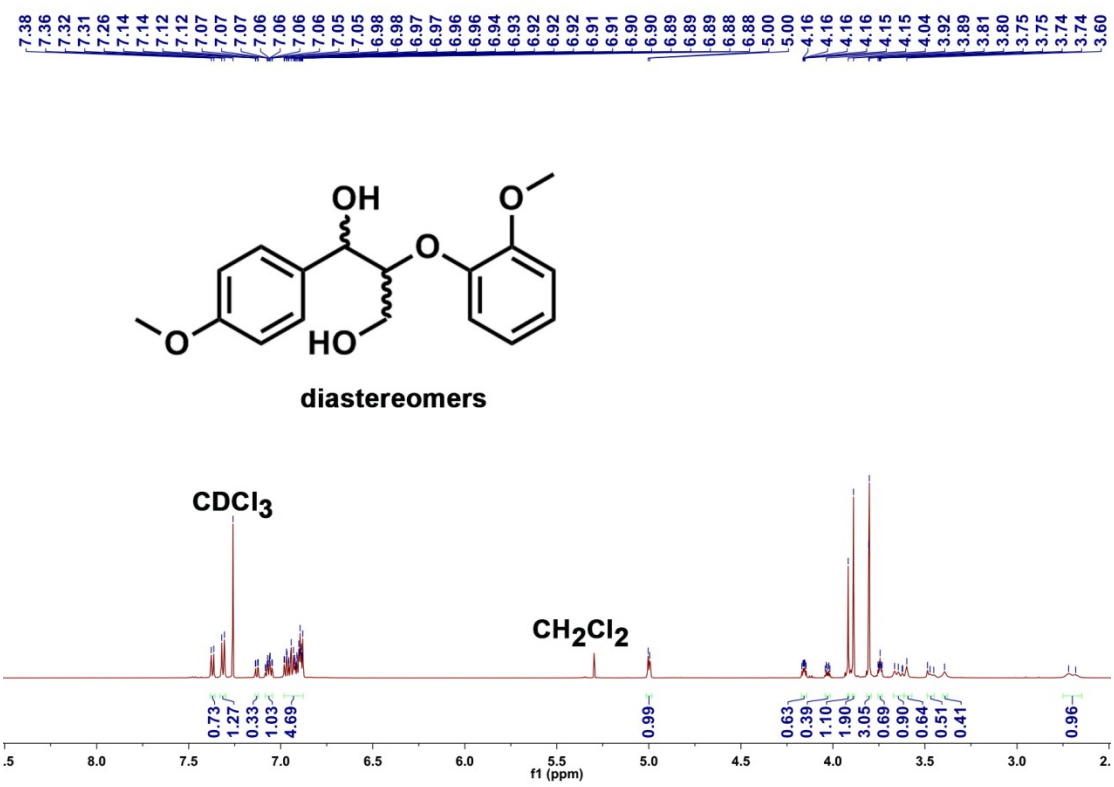
^{1}H-NMR spectrum of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (**5**).



^{1}H-NMR spectrum of 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethanol (**6**).



^{1}H-NMR spectrum of 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (**7**).



^{1}H-NMR spectrum of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-1,3-propanediol (**8**). (CH_2Cl_2 derives from residual eluent)

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