Electronic Supplementary Information

Recoverable Polyoxometalate-Ionic Liquids Catalyst for Selective Cleavage of Lignin β-O-4 Models Under Mild Conditions

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Lists of the purchased organic chemicals with CAS numbers

1-methyl-3-(4-sulfobutyl)-1H-imidazolium inner salt (BMIM-SO_3, CAS#: 179863-07-1)

1-phenyl-1,2-ethanediol	(CAS#: 93-56-1)	2-hydroxyacetophenone	(CAS#: 582-24-1)
phenethoxybenzene	(CAS#: 40515-89-7)	4-methoxybenzoic acid	(CAS#: 100-09-4)
3,4-dimethoxybenzoic acid	(CAS#: 93-07-2)	4-hydroxybenzoic acid	(CAS#: 99-96-7)
2-methoxylphenol	(CAS#: 90-05-1)	p-methylphenol	(CAS#: 106-44-5)
2-bromoacetophenone	(CAS#: 70-11-1)	*β*-bromostyrene	(CAS#: 103-64-0)

2-bromo-1-(3,4-dimethoxyphenyl)ethanone (CAS#: 1835-02-5)

2-bromo-4'-hydroxyacetophenone (CAS#: 2491-38-5)

2-bromo-1-(4-methoxyphenyl)ethanone (CAS#: 2632-13-5)

ethyl 2-oxocyclohexanecarboxylate (CAS#: 1655-07-8)

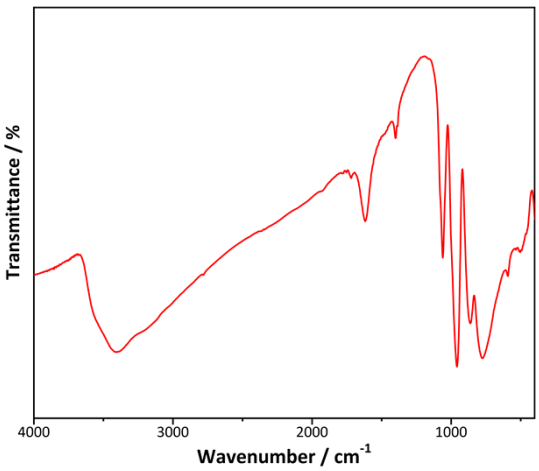

Figure S1 FT-IR spectrum of HPMoV.

Table S1 The catalytic results of PP-one oxidation under different conditions.

Entry	Substrates	Additions	Con. (%)	BA Yield (%)	Ph-OH Yield (%)	Aromatic products Yield (%)
1	PP-one	O_2, HPMoV, BMIM-SO_3	95	85	75	80
2	PP-one	N_2, HPMoV, BMIM-SO_3	38	7	33	20
3	PP-one	O_2, HPMoV	87	84	72	78
4	PP-one	O_2, BMIM-SO_3	57	37	48	43
5	PP-one	O_2, H_2SO_4, BMIM-SO_3	79	59	59	59
6	PP-one	O_2, HPMoV, BMIM-SO_3, LiOH	88	60	66	63

Conditions: PP-one (0.3 mmol), HPMoV (0.03 mmol), BMIM-SO_3 (0.15 mmol), H_2SO_4 (0.075 mmol), LiOH (0.15 mmol), DMSO (1 mL), 130 °C, 6 h, 1 atm gas pressure.

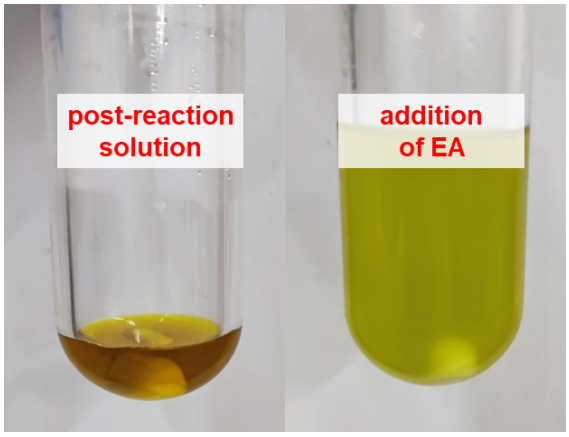

Figure S2 Digital photo of the post-reaction solution catalyzed by HPMoV before (left) and after (right) addition of EA.

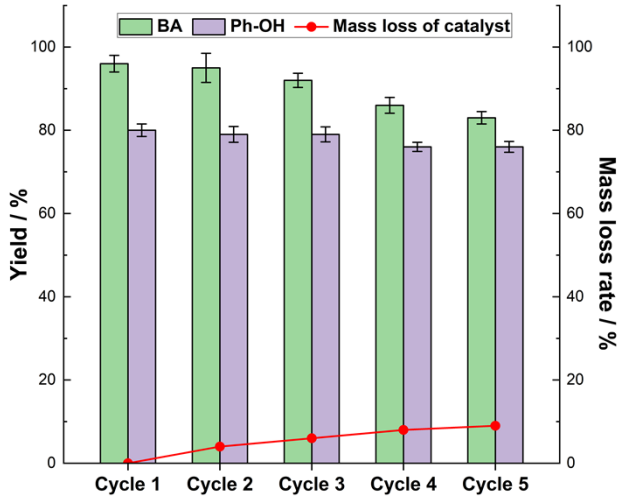

Figure S3 The yields of aromatic products and mass loss curve of catalyst in five cycles.

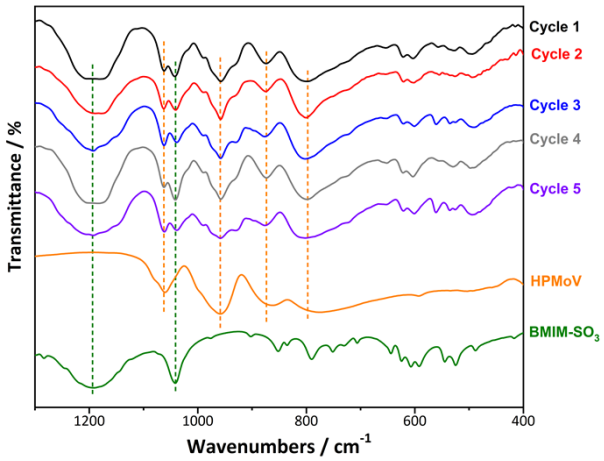

Figure S4 FT-IR spectra of HPMoV, BMIM-SO_3, and recovered HPMoV-BMIM-SO_3H ILs catalysts.

Table S2 Comparing of the activities of different catalysts in the oxidation of PP-ol or PP-one.

Substrates	Catalyst	Solvent	Conditions	Products (Yield %)	Recyclability	Ref.
PP-ol	$VO(acac)_2$	C_3H_6COOH	1 bar O_2, 80 °C, 8 h	Ph-OH (49), BA (26)	No	S1
PP-ol	Pd/CeO_2	methanol	1 bar O_2, 185 °C, 24 h	Ph-OH (48), acetophenone (38)	Yes	S2
PP-ol	$VOSO_4$, TEMPO	CH_3CN	4 bar O_2, 100 °C, 12 h	PP-one (82)	No	S3
PP-one	$Cu(OAc)_2$, phen	methanol	4 bar O_2, 80 °C, 2 h	Ph-OH (85), BA (95)	No	S3
PP-ol	$Cu(OAc)_2$, phen	DMSO	4 bar O_2, 80 °C, 6 h	BA (79)	No	S4
PP-ol	$NaNO_2$, DDQ, NHPI	CH_3CN	4 bar O_2, 80 °C, 2 h	PP-one (95)	No	S5
PP-one	[OMIm][OAc]	H_2O	14 bar O_2, 100 °C, 2 h	Ph-OH (96), BA (86)	No	S6
PP-one	$Cu(OAc)_2$, $BF_3{\cdot}OEt_2$	methanol	4 bar O_2, 100 °C, 6 h	Ph-OH (95)	No	S7
PP-one	CTFs	methanol	5 bar O_2, 160 °C, 6 h	Ph-OH (45), BA (24)	Yes	S8
PP-ol	VB_{12}@C, K_2CO_3	methanol	1 bar O_2, 80 °C, 24 h	Ph-OH (96), BA (73), MB (26)	Yes	S9
β-O-4-ol	$Pd(OAc)_2$	DMSO	Air, 60 °C, 18 h	*β*-O-4-one (84 >)	No	S10
PP-ol	NENU-MV-5	methanol	4 bar O_2, 100 °C, 12 h	Ph-OH (60), BA (10), MB (90)	Yes	S11
PP-ol	$[MIMPS]_2H_4P_2Mo_{18}O_{62}$	ethanol	5 bar O_2, 140 °C, 10 h	Ph-OH (84), acetophenone (75)	Yes	S12
PP-ol	$BetH_5V_2Mo_{18}$	ethanol	8 bar O_2, 140 °C, 8 h	Ph-OH (86), acetophenone (77), BA (5), EB (1.8)	Yes	S13
PP-one	CTFs	methanol	5 bar O_2, 120 °C, 2 h	Ph-OH (60), MB (10), BA (15), methyl benzoylformate (25)	Yes	S14
PP-ol	$CuCl_2$, phen, NIS, K_2CO_3, methanol, 4 Å	DMSO	5 bar O_2, 140 °C, 12 h	MB (87)	No	S15
PP-one	CuCl, NaOH	H_2O	Air, 30 °C, 5.5 h	Ph-OH (89), BA (85)	No	S16
PP-ol	$H_5PMo_{10}V_2O_{40}$, BMIM-SO_3	DMSO	1 bar O_2, 130 °C, 12 h	Ph-OH (80), BA (95)	Yes	This work
PP-one	$H_5PMo_{10}V_2O_{40}$, BMIM-SO_3	DMSO	1 bar O_2, 130 °C, 6 h	Ph-OH (75), BA (85)	Yes	This work

BA, benzoic acid. Ph-OH, phenol. MB, Methyl benzoate. EB, ethyl benzoate.

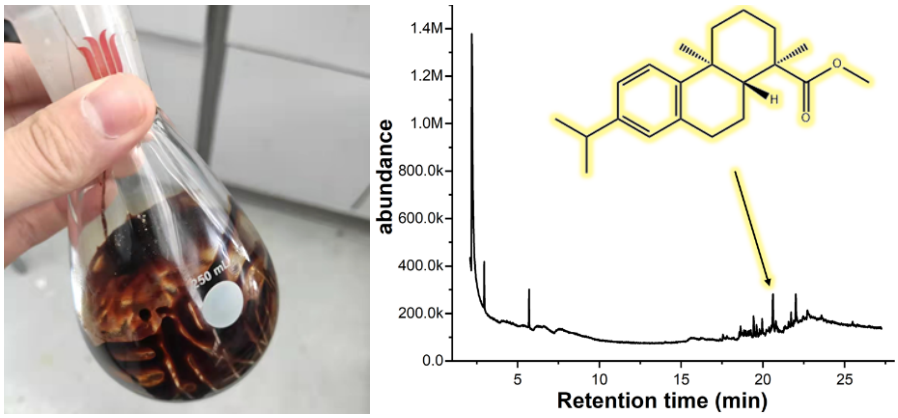

Figure S5 Digital photo and GC signal of the post-reaction solution using pine wood extractives as substrate.

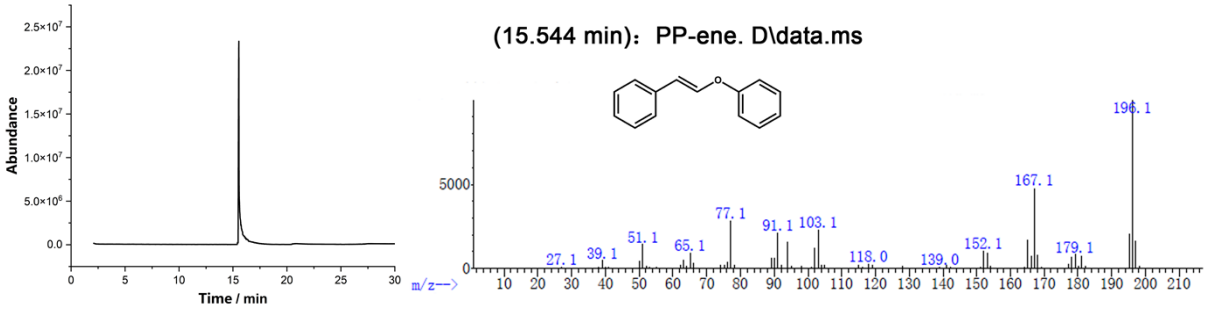

Figure S6 GC-MS pattern of (2-phenoxyvinyl)benzene.

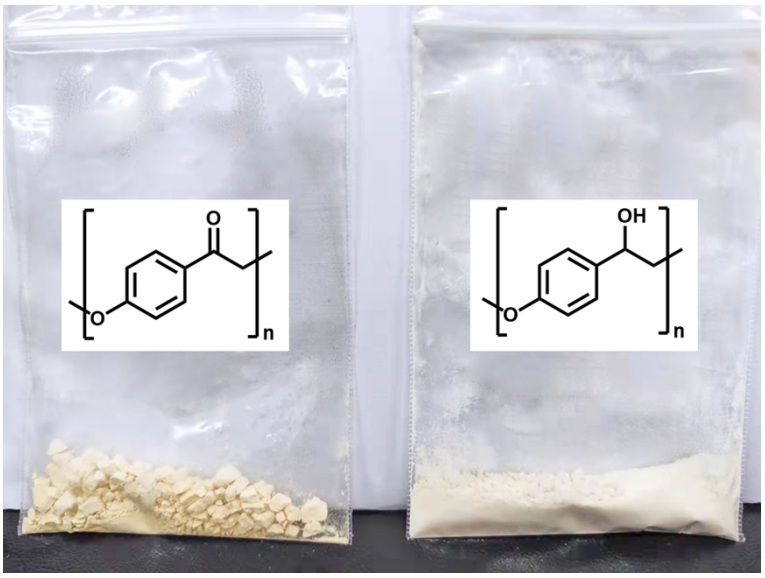

Figure S7 Digital photo of poly(4'-hydroxyacetophenone) and poly(4'-hydroxyacetophenol).

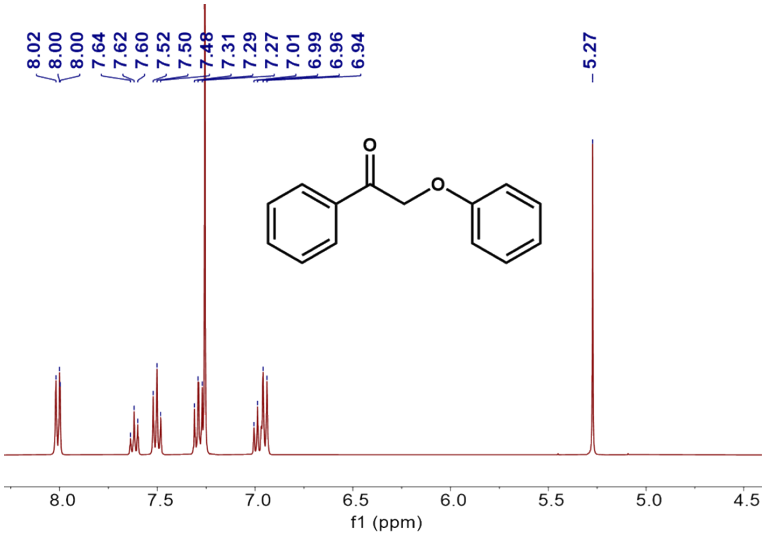

Figure S8 ^{1}H-NMR spectrum of PP-one.

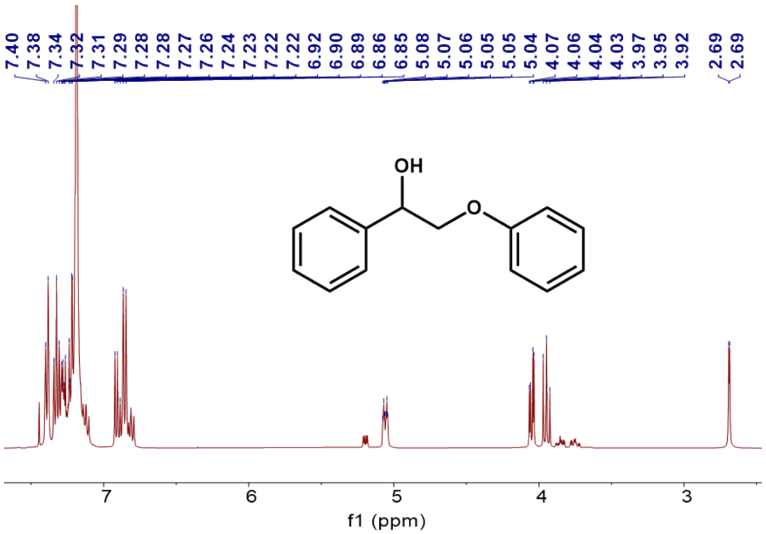

Figure S9 ^{1}H-NMR spectrum of PP-ol.

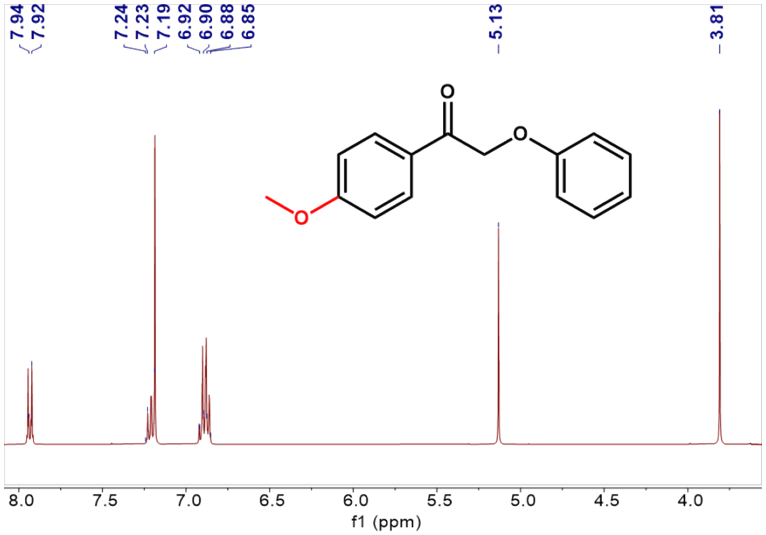

Figure S10 ^{1}H-NMR spectrum of 1-(4-methoxyphenyl)-2-phenoxyethanone.

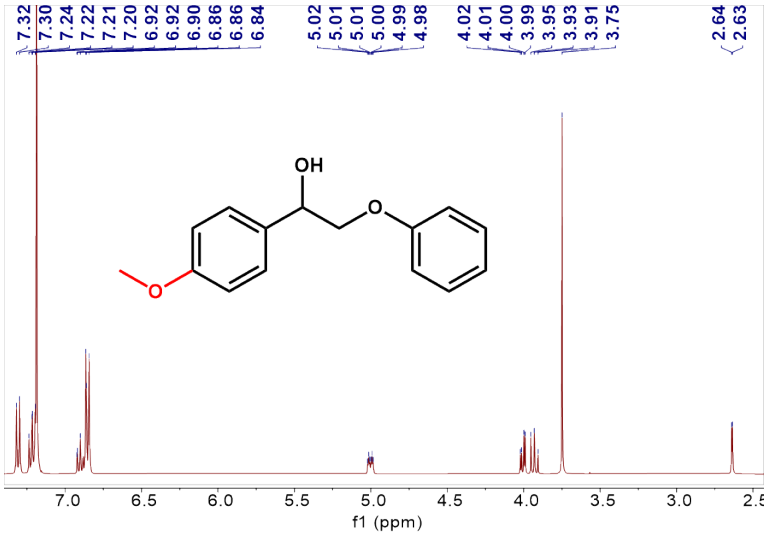

Figure S11 ^{1}H-NMR spectrum of 1-(4-methoxyphenyl)-2-phenoxyethanol.

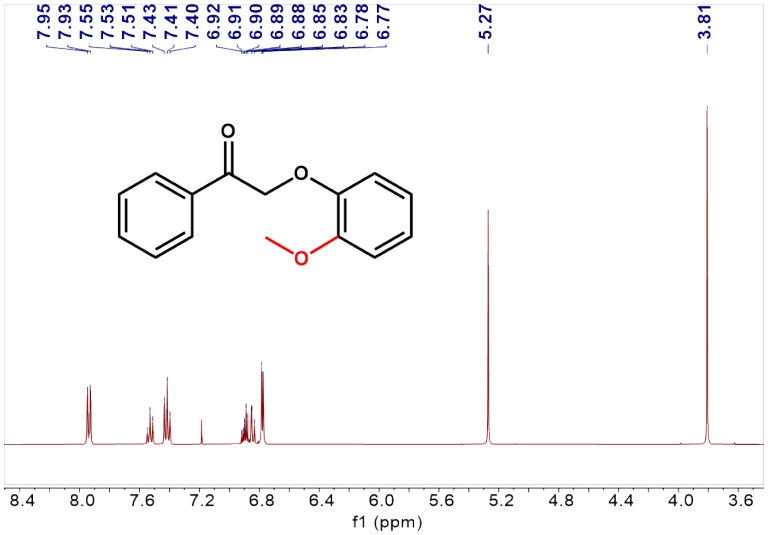

Figure S12 ^{1}H-NMR spectrum of 2-(2-methoxyphenoxy)-1-phenylethanone.

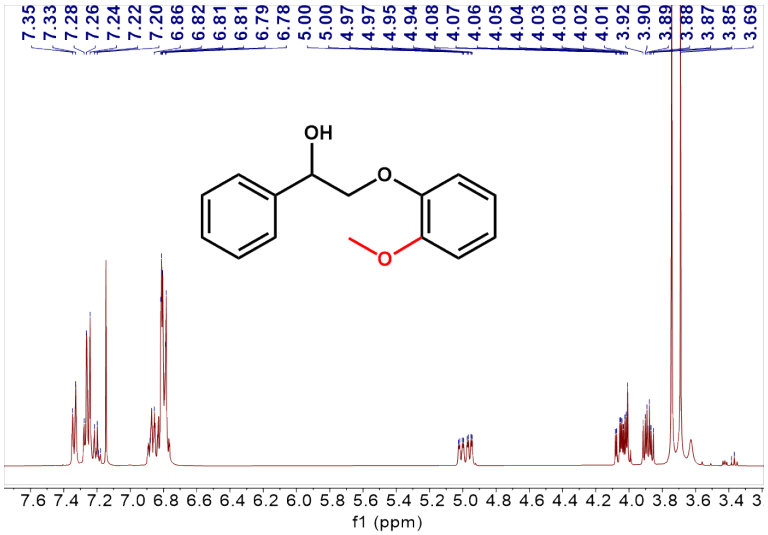

Figure S13 ^{1}H-NMR spectrum of 2-(2-methoxyphenoxy)-1-phenylethanol.

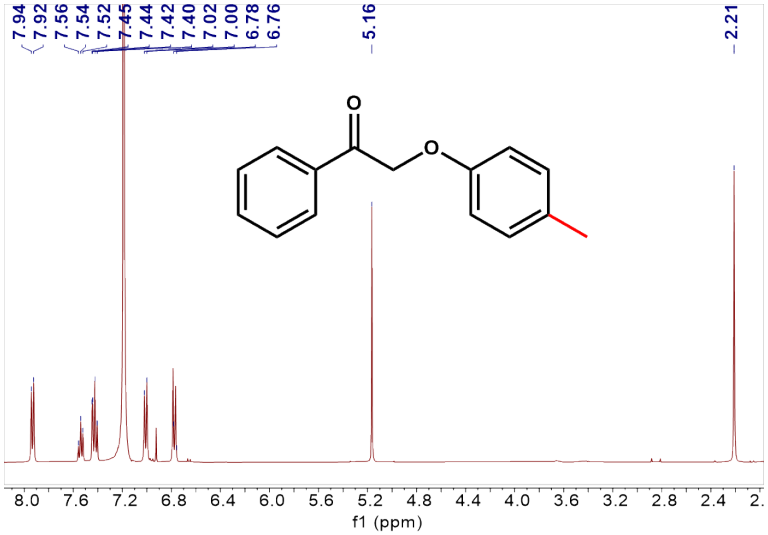

Figure S14 ^{1}H-NMR spectrum of 1-phenyl-2-(*p*-tolyloxy)ethenone.

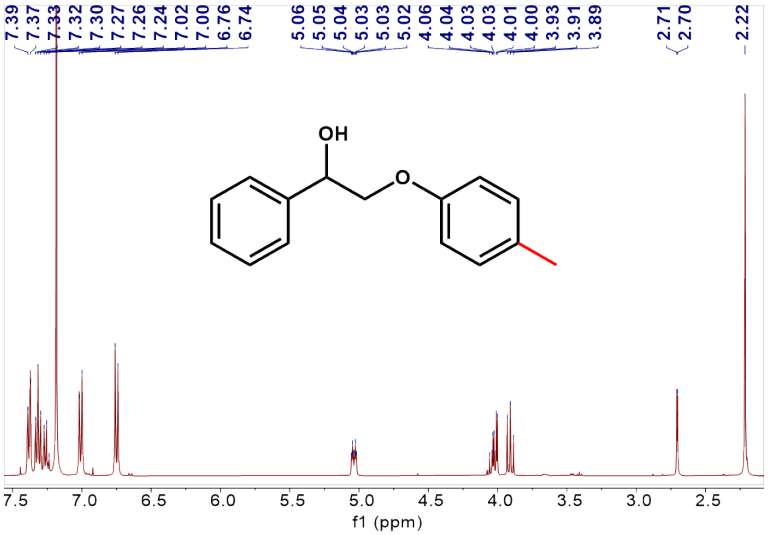

Figure S15 ^{1}H-NMR spectrum of 1-phenyl-2-(*p*-tolyloxy)ethanol.

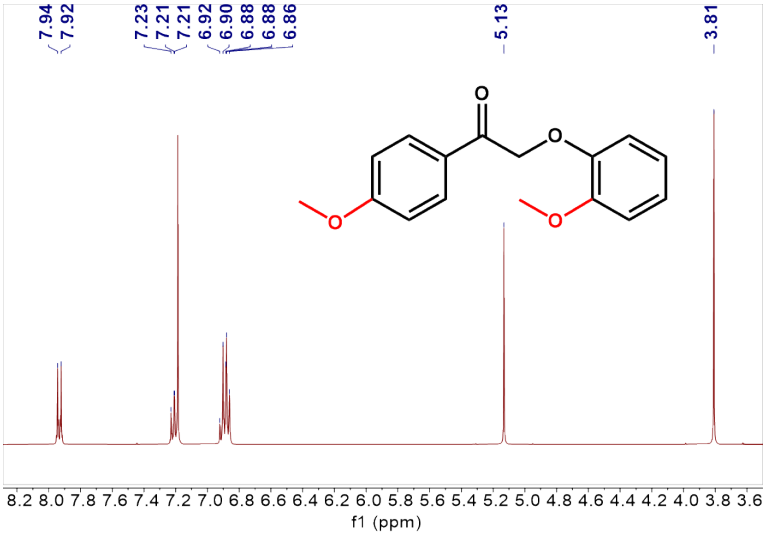

Figure S16 ^{1}H-NMR spectrum of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethenone.

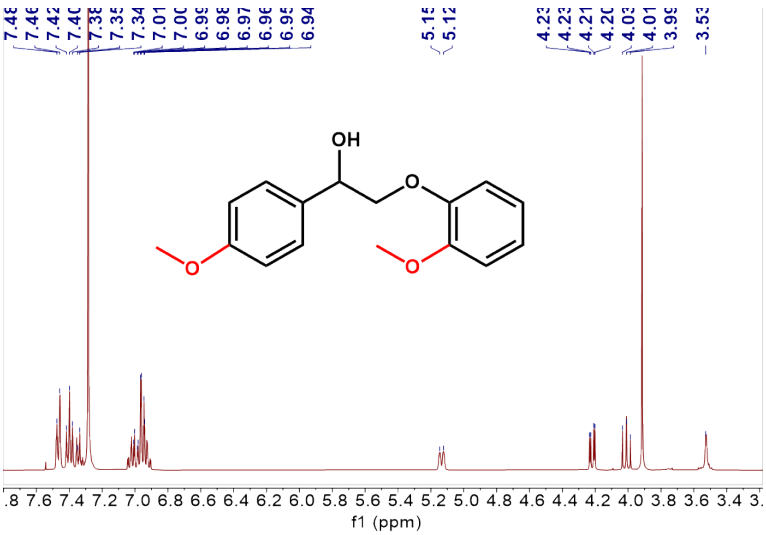

Figure S17 ^{1}H-NMR spectrum of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol.

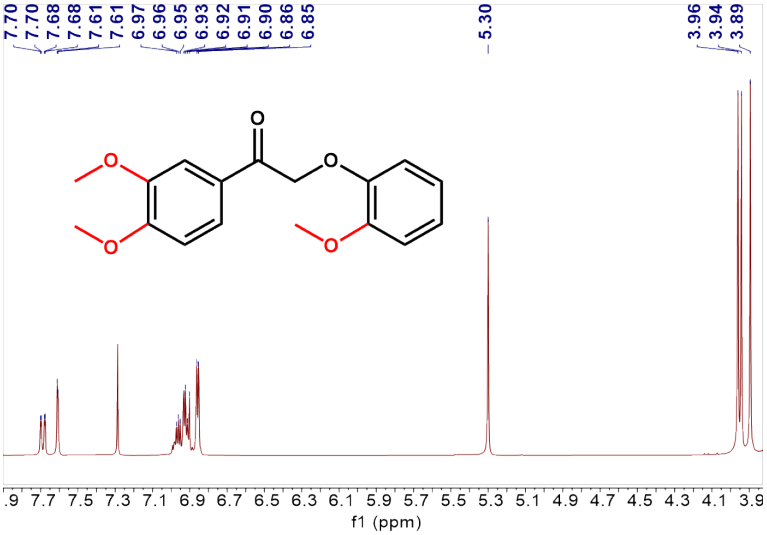

Figure S18 ^{1}H-NMR spectrum of 1-(3,4-dimethoxyphenyl)-3-(2-methoxyphenyl)propan-1-one.

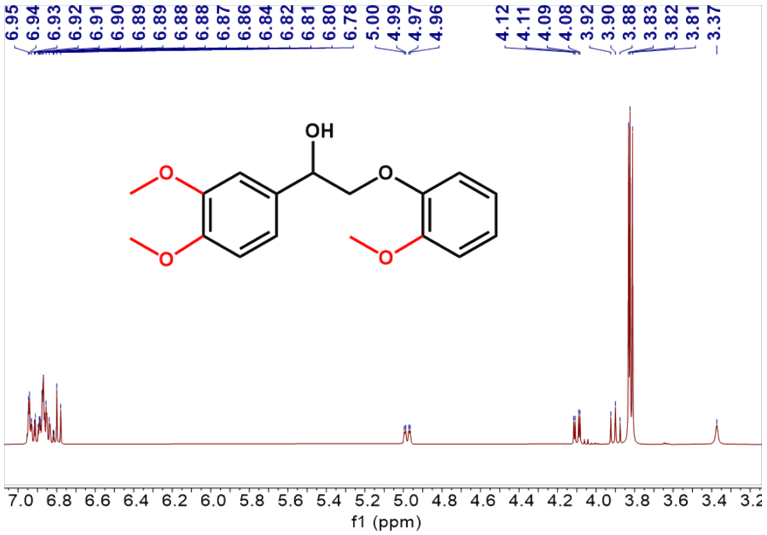

Figure S19 ^{1}H-NMR spectrum of 1-(3,4-dimethoxyphenyl)-3-(2-methoxyphenyl)propan-1-ol.

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