Supporting information

Oxidative Cleavage of β -O-4 bonds in Lignin Model Compounds with Polymer-Supported Ni-Salen Catalysts

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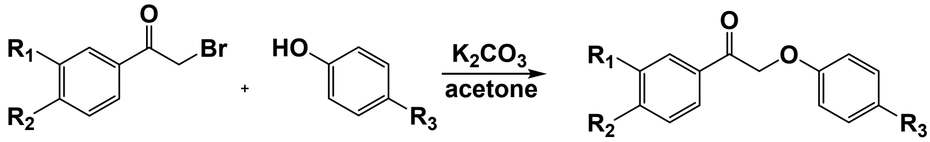
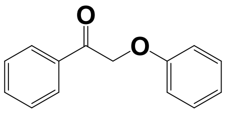


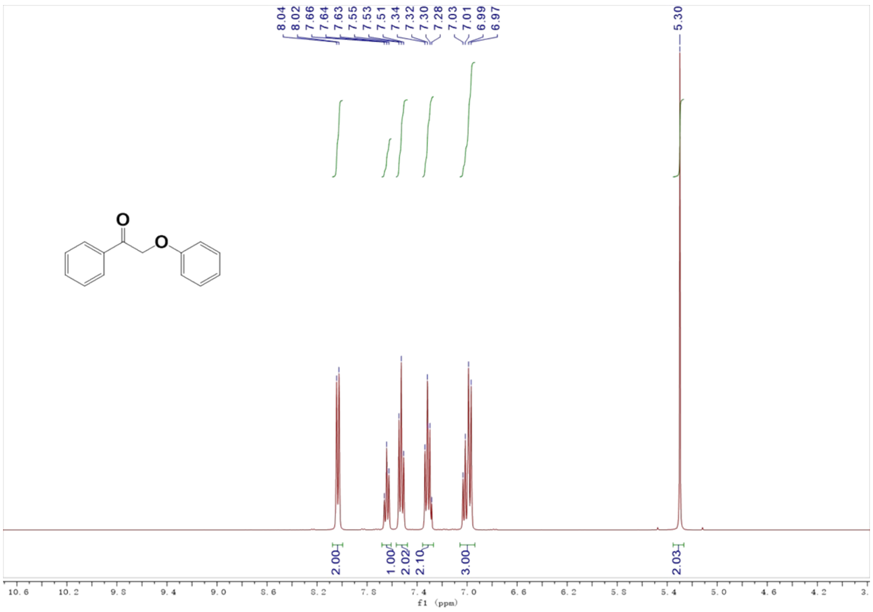
1a: R_1=H, R_2=H, R_3=H
2a: R_1=H, R_2=-OCH_3, R_3=H
3a: R_1=H, R_2=H, R_3=-OCH_3
4a: R_1=H, R_2=-OCH_3, R_3=-OCH_3
5a: R_1=-OCH_3, R_2=-OCH_3, R_3=H

Figure S1 Synthesis route of β-O-4 lignin model compounds.

Model 1a: 

2-phenoxy-1-phenylethanone

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.31 (q, J = 6.8, 5.8 Hz, 2H), 7.00 (dd, J = 18.3, 7.8 Hz, 3H), 5.30 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.56, 158.02, 134.61, 133.88, 129.60, 128.85, 128.16, 121.67, 114.83, 70.81.



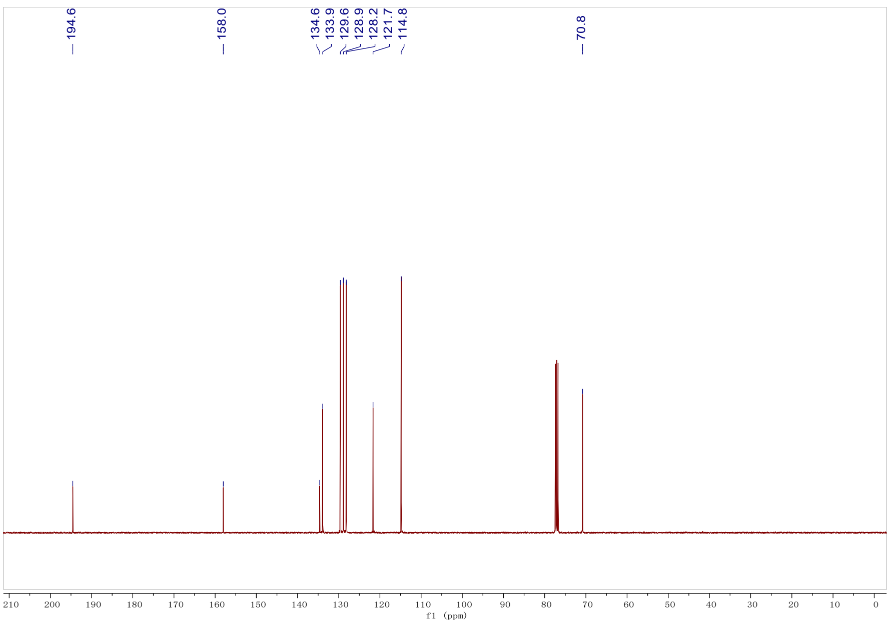
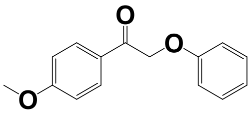


Figure S2 ^{1}H NMR and ^{13}C NMR of model 1a.

Model 2a: 

1-(4-methoxyphenyl)-2-phenylethanone

[1]H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 6.7 Hz, 3H), 5.23 (s, 2H), 3.90 (s, 3H). [13]C NMR (101 MHz, $CDCl_3$) δ 193.13, 164.05, 158.10, 130.57, 129.56, 127.65, 121.57, 114.81, 114.02, 70.72, 55.54.

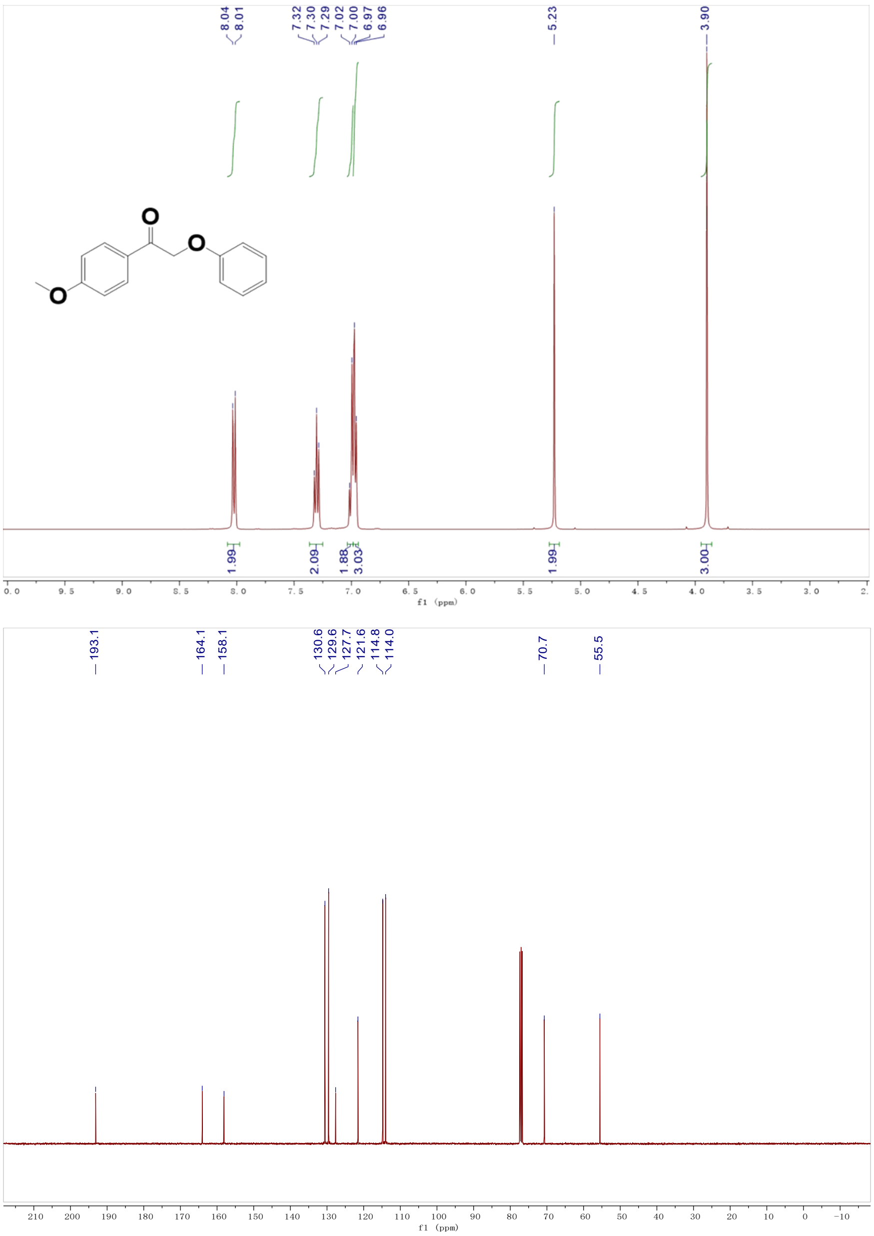
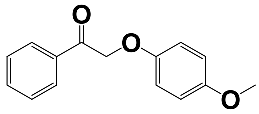
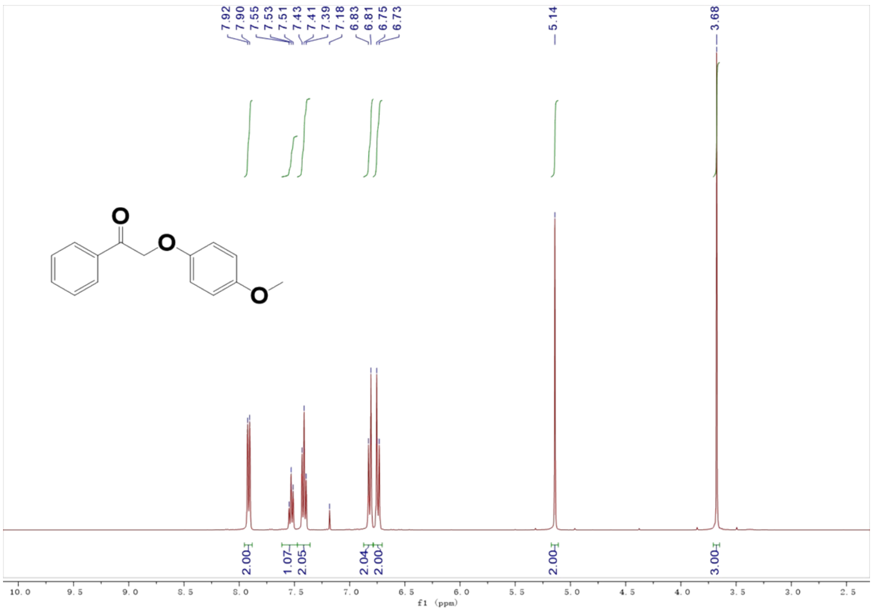


Figure S3 [1]H NMR and [13]C NMR of model 2a.

Model 3a: 

2-(4-methoxyphenyl)-1-phenylethanone

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 6.82 (d, J = 9.1 Hz, 2H), 6.74 (d, J = 9.1 Hz, 2H), 5.14 (s, 2H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.89, 154.47, 152.21, 134.62, 133.85, 128.83, 128.12, 115.99, 114.71, 71.75, 55.70.



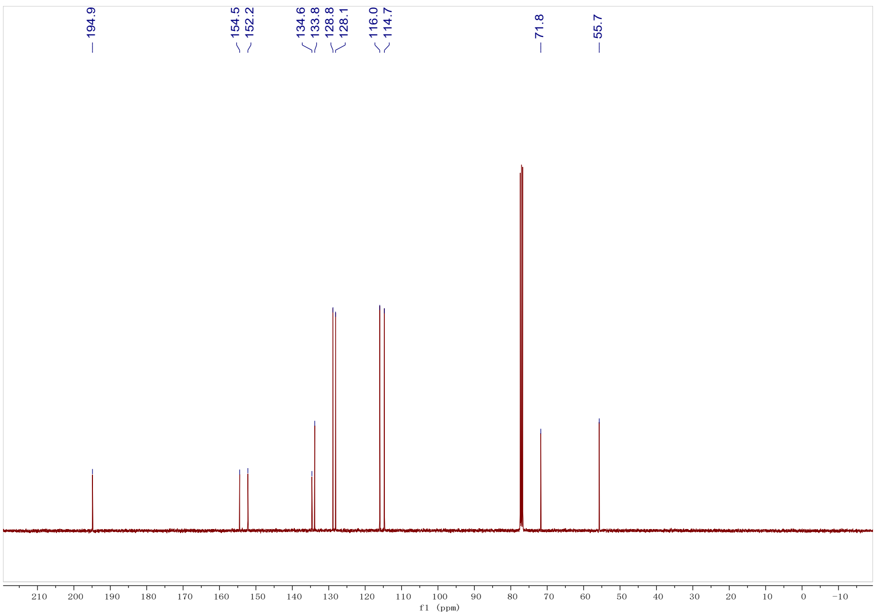
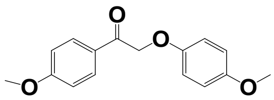


Figure S4 ^{1}H NMR and ^{13}C NMR of model 3a.

Model 4a: 

1-(4-methoxyphenyl)-2-(4-methoxyphenyl)- phenylethanone

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.9 Hz, 2H), 6.89 (s, 1H), 6.87 (s, 1H), 6.83 (s, 1H), 6.81 (s, 1H), 6.75 (s, 1H), 6.73 (s, 1H), 5.09 (s, 2H), 3.80 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.44, 164.00, 154.39, 152.29, 130.53, 127.67, 115.93, 114.68, 113.99, 71.63, 55.70, 55.54.

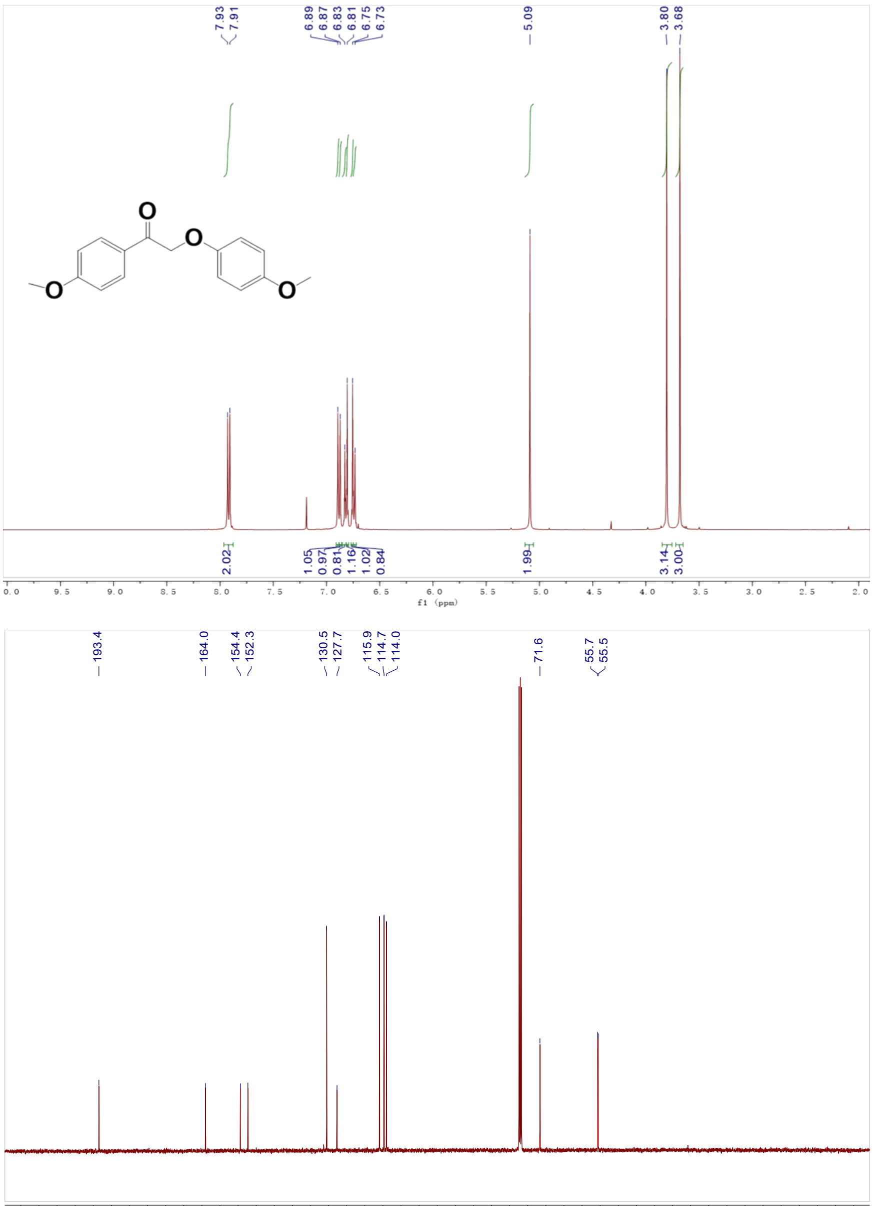
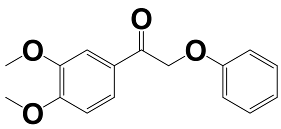
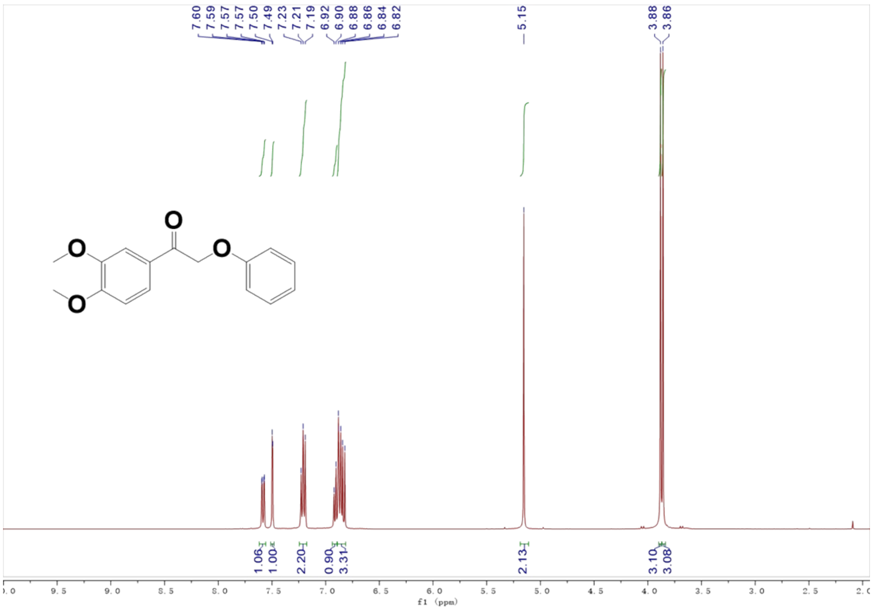


Figure S5 ^{1}H NMR and ^{13}C NMR of model 4a.

Model 5a: 

1-(3,4-dimethoxyphenyl)-2-phenylethanone

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.4, 1.8 Hz, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.91 (d, J = 7.3 Hz, 1H), 6.85 (dd, J = 15.3, 8.5 Hz, 3H), 5.15 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.20, 158.10, 153.92, 149.28, 129.57, 127.79, 122.86, 121.59, 114.81, 110.38, 110.16, 70.73, 56.14, 56.04.



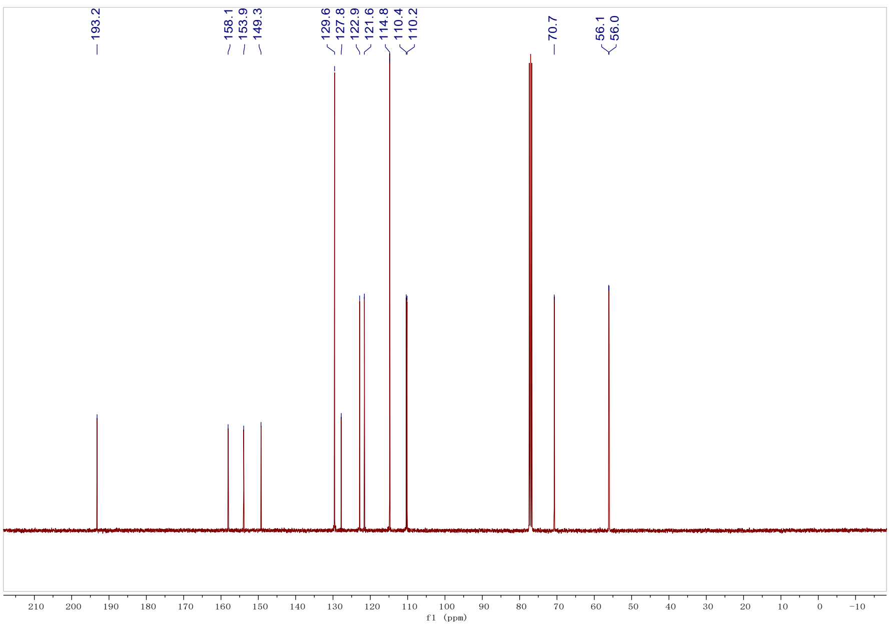
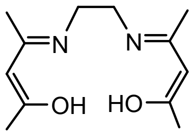
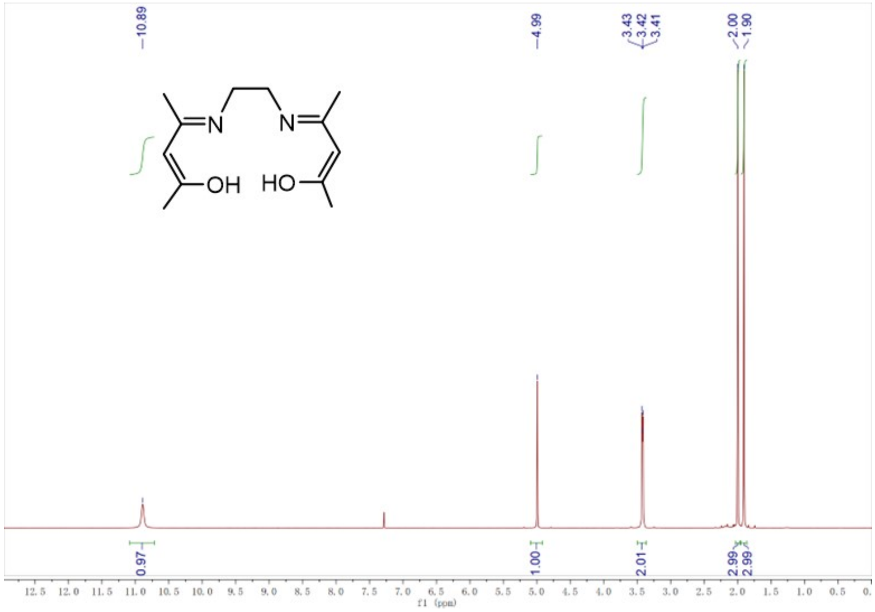


Figure S6 ^{1}H NMR and ^{13}C NMR of model 5a.



Salen

[1]H NMR (400 MHz, $CDCl_3$) δ 10.89 (s, 1H), 4.99 (s, 1H), 3.50 – 3.36 (m, 2H), 2.00 (s, 3H), 1.90 (s, 3H). [13]C NMR (101 MHz, $CDCl_3$) δ 195.55, 162.86, 96.09, 43.52, 28.98, 28.81, 18.78, 18.64.



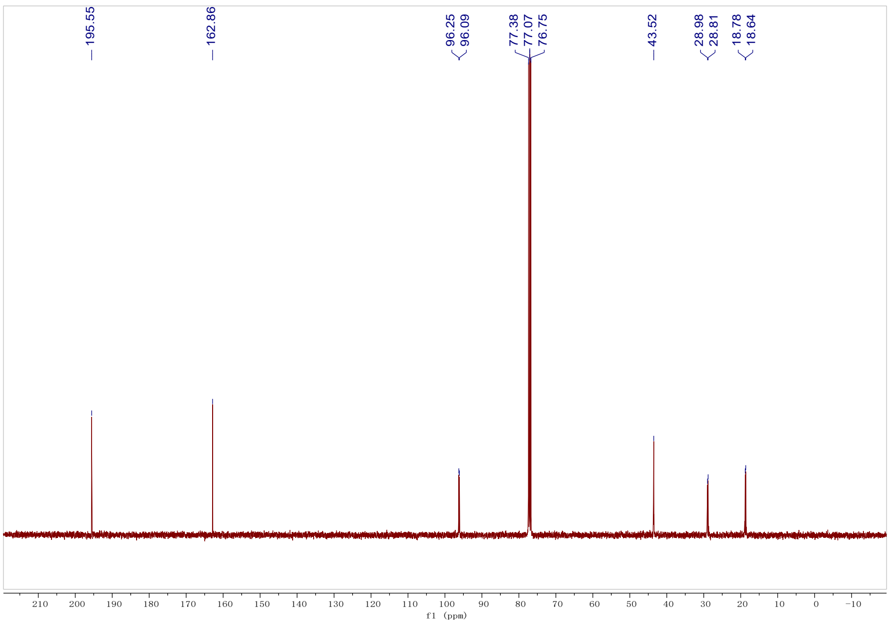
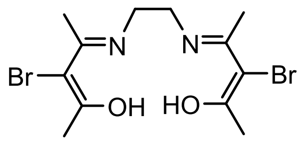
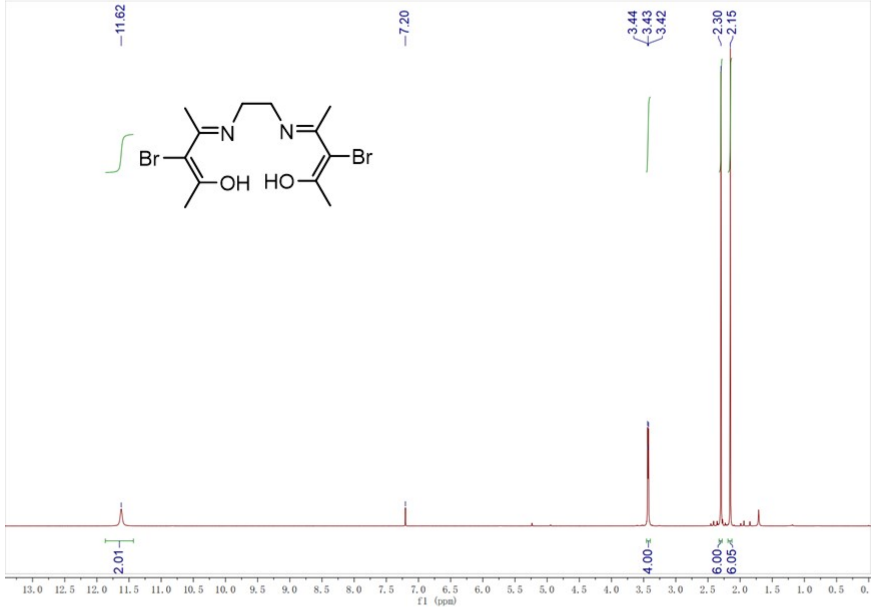


Figure S7 ^{1}H NMR and ^{13}C NMR spectrum of Salen.



Salen-Br

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (s, 2H), 3.45 –3.40 (m, 4H), 2.30 (s, 6H), 2.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.52, 161.94, 92.59, 44.45, 30.45, 19.32.



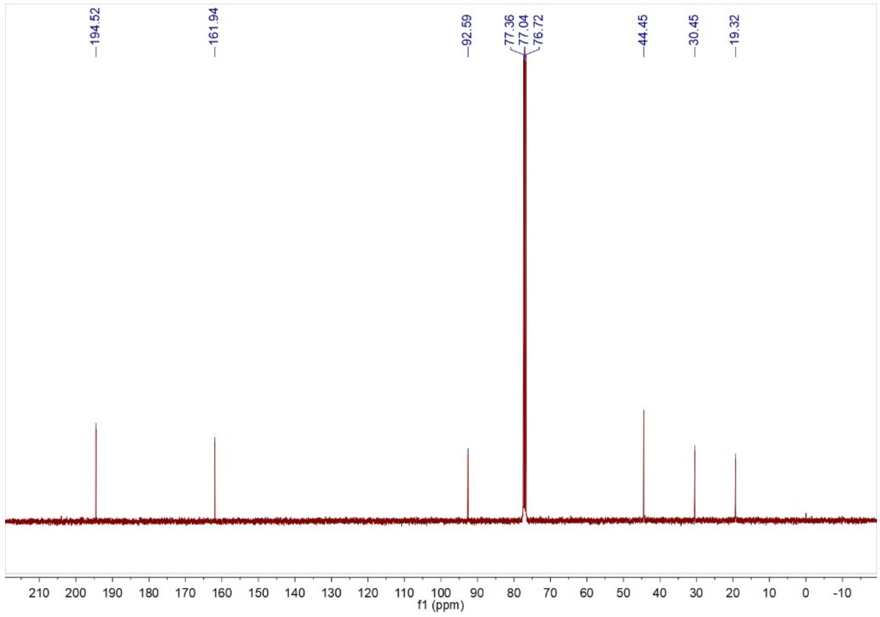
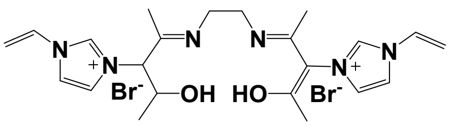


Figure S8 ^{1}H NMR and ^{13}C NMR spectrum of Salen-Br.



[Salen-Vim][Br]$_2$

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (d, J = 64.6 Hz, 1H), 8.20 (d, J = 56.6 Hz, 1H), 7.74 (d, J = 28.4 Hz, 1H), 6.08 (ddd, J = 15.7, 7.7, 2.5 Hz, 1H), 5.97 (dd, J = 34.3, 15.7 Hz, 1H), 5.44 (d, J = 22.0 Hz, 1H), 5.33 (d, J = 8.8 Hz, 1H), 3.80 (s, 2H), 2.34 – 2.10 (m, 3H), 2.06 – 1.72 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 190.66, 163.66, 139.34, 136.06, 129.35, 128.66, 120.32, 109.88, 107.41, 39.57, 26.36, 14.77.

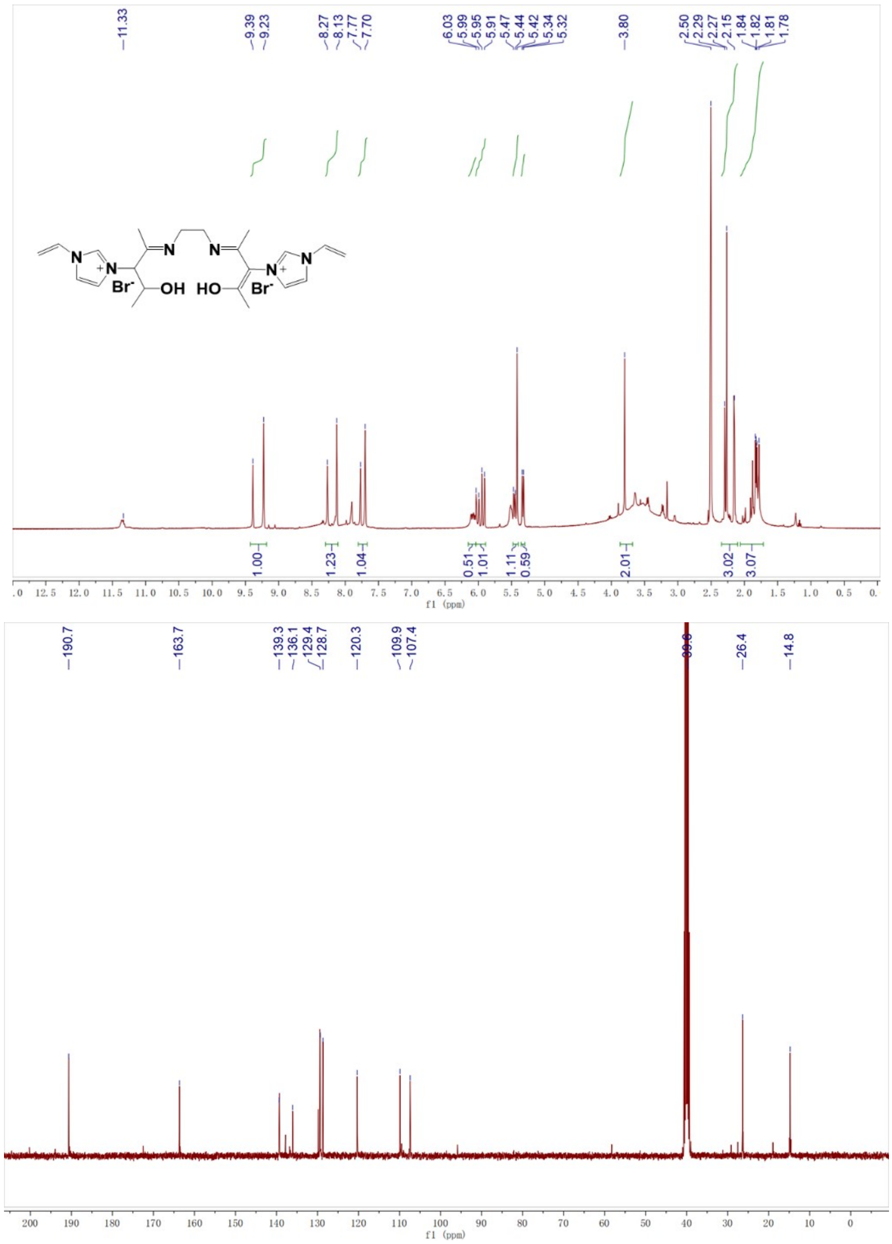


Figure S9 ^{1}H NMR and ^{13}C NMR spectrum of [Salen-Vim][Br]$_2$.

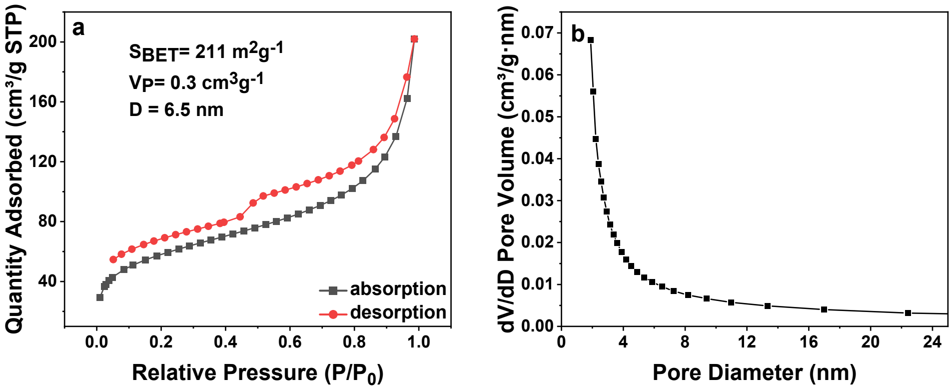


Figure S10 (a) N_2 sorption isotherms and (b) Pore size distribution curves of poly Ni-[Salen-Vim][OAc]$_2$. S_{BET}: Total surface area obtained by using BET method; V_p: pore volume; D: average diameter.

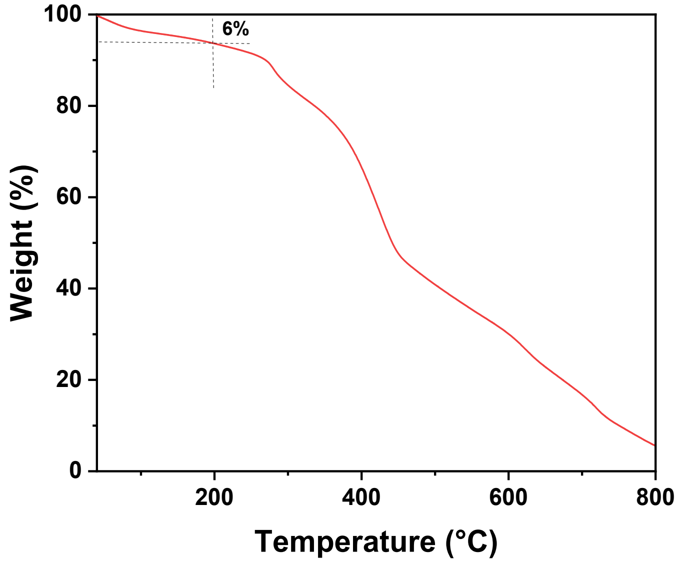


Figure S11 TGA patterns of poly Ni-[Salen-Vim][OAc]$_2$.

Table S1 Different catalysts for oxidative cleavage of 2-phenoxyl-1-phenylethanone.

Entry	Catalyst	Additives	Catalytic system[a]	T (°C)	t (h)	Conv. (%)	Sel. (%)[b]	Ref.
1	/	NaOH	Homo.	30	5.5	8	7	[1]
2	$CuCl_2$	NaOH	Homo.	30	5.5	80	60	[1]
3	Cu/C_3N_4	$K_7HNb_6O_{39}$	Heter.	80	12	96	94	[2]
4	CTF-mDCB-10	/	Heter.	140	2	89	82	[3]
5	$Hf(OTf)_4$	/	Homo.	80	4	99	82	[4]
6	Fe-N-C-950	/	Heter.	140	4	94	73	[5]
7	Fe-ZnS/650	/	Heter.	120	2	99	85	[6]
8	Poly Ni-[Salen-Vim][OAc]$_2$	/	Heter.	110	12	99	83	This work

[a]Homo.= Homogeneous, Heter.= Heterogenous; [b]Selectivity to cleavage product.

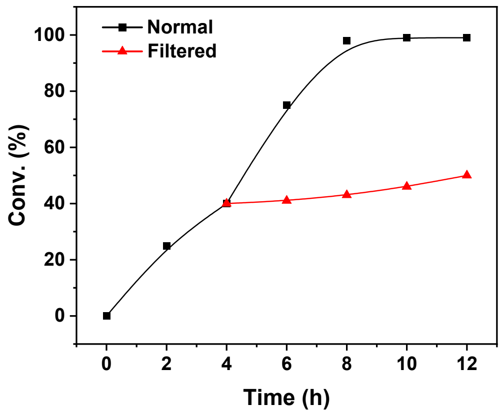


Figure S12 Hot filtration experiments of poly Ni-[Salen-Vim][OAc]$_2$. Reaction conditions: 0.25mmol PP-one, 50 mg poly Ni-[Salen-Vim][OAc]$_2$, 3mL MeOH, 0.5MPa O_2, 110°C.

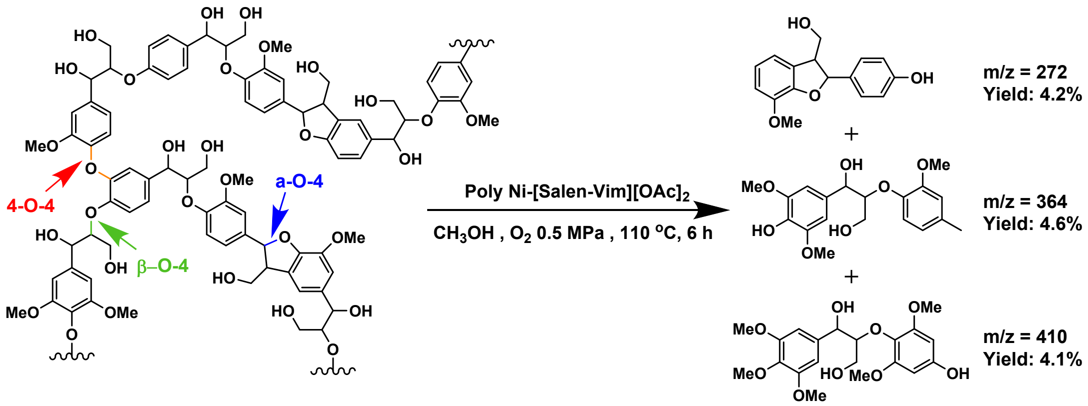


Figure S13 Catalytic conversion of birch lignin into phenolic compound over the Ni-[Salen-Vim][OAc]$_2$ catalyst.

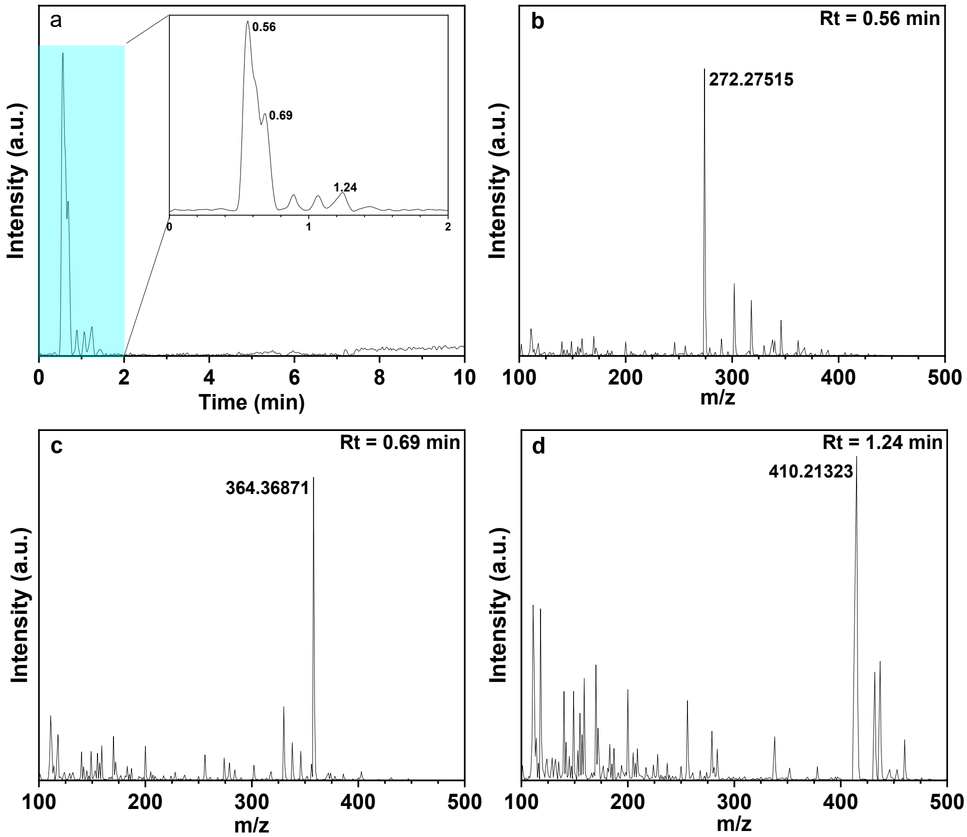


Figure S14 HPLC-MS spectra of birch lignin degradation over the Ni-[Salen-Vim][OAc]$_2$ catalyst. (a) HPLC chromatogram (FTMS + p ESI Full ms 100-1000) of HPLC-MS, (b) Mass spectrum of HPLC-MS at t_R=0.56 min, (c) Mass spectrum of HPLC-MS at t_R=0.69 min. (d) Mass spectrum of HPLC-MS at t_R=1.24 min.

Reference

[1] Y. Hu, L. Yan and X. Zhao, *Green Chem*., 2021, 23, 7030-7040.

[2] J. Li, Z. Li and J. Dong, *ACS Catal.*, 2023, 13, 5272-5284.

[3] G. Zhu, S. Shi and L. Zhao, *ACS Catal.*, 2020, 10, 7526-7534.

[4] R. Zhu, C. Mao and F. Gao, *ChemSusChem.*, 2024, 17, e202301743.

[5] S. Guo, X. Tong and L. Meng, *Catal. Sci. Technol.*, 2023, 13, 1748-1754.

[6] H. Guo, Z. Chen and Q. Yin, *Appl. Catal. B-Environ.*, 2023, 339,123129.