Supporting Information (SI)

Development of a Ni-Promoted, Selective Electrochemical Reductive Cleavage of the C-O bond in Lignin Model Compound Benzyl Phenyl Ether

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Supplementary Table 1.

Cathode materials screening for reaction in the divided cell

Supplementary Table 2.

Product yields and calculated Faraday efficiency for different substrate concentrations and $NiCl_2 \cdot 6H_2O$ concentrations at 12 hours

Supplementary Table 3.

Product yields and calculated Faraday efficiency for reactions with constant ratio of $NiCl_2 \cdot 6H_2O$/BPE and varying absolute concentrations AT 12 hours

Supplementary Figure S1.

Kinetic plot of electrochemical reductive cleavage of 0.2 mmol BPE in 10 mL methanol, 0.1M $TBAPF_6$, 20 mA constant current, Ni foam $_{anode}$ and Ni foam $_{cathode}$ in the undivided cell

Supplementary Figure S2.

CV curves of different Ni salts (40 mM) in 15 mL 0.10 M $TBAPF_6$-MeOH, scan rate: 50 mV/s.

Supplementary Figure S3.

CV curves of $CuCl_2$, $CoCl_2 \cdot 6H_2O$, and $FeCl_2 \cdot 4H_2O$ in 15mL 0.10 M $TBAPF_6$-MeOH, 40 mM of metal chloride salts, 10 mM BPE, scan rate: 50 mV/s.

Supplementary Figure S4.

Reusability experiments of carbon paper cathode

Supplementary Figure S5.

1-(benzyloxy)-4-(tert-butyl)benzene (**d**) ^{1}H NMR

Supplementary Figure S6.

1-(benzyloxy)-4-(tert-butyl)benzene (**d**) ^{13}C NMR

Supplementary Figure S7.

1-(benzyloxy)-4-methylbenzene (**e**) ^{1}H NMR

Supplementary Figure S8.
1-(benzyloxy)-4-methylbenzene (**e**) ^{13}C NMR

Supplementary Figure S9.
1-(Benzyloxy)-4-methoxybenzene (**f**) ^{1}H NMR

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1-(Benzyloxy)-4-methoxybenzene (**f**) ^{13}C NMR

Supplementary Figure S11.
1-(phenoxymethyl)-4-(trifluoromethyl) benzene (**g**)

Supplementary Figure S12.
1-(phenoxymethyl)-4-(trifluoromethyl) benzene (**g**) ^{13}C NMR

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1-(tert-butyl)-4-(phenoxymethyl)benzene (**h**) ^{1}H NMR

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1-(tert-butyl)-4-(phenoxymethyl)benzene (**h**) ^{13}C NMR

Supplementary Figure S15.
4-Methylbenzylphenyl ether (**i**) ^{1}H NMR

Supplementary Figure S16.
4-Methylbenzylphenyl ether (**i**) ^{13}C NMR

Supplementary Figure S17.
1-methoxy-4-(phenoxymethyl) benzene (**j**) ^{1}H NMR

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1-methoxy-4-(phenoxymethyl)benzene (**j**) ^{13}C NMR

Supplementary Figure S19.
4-(phenoxymethyl) phenol (**k**) ^{1}H NMR

Supplementary Figure S20.
4-(phenoxymethyl) phenol (**k**) ^{13}C NMR

Supplementary Table S1

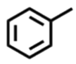
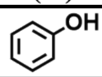
Cathode materials screening for reaction in the divided cell

Entry	Cathode	Toluene Yield (%)	Phenol Yield (%)
1	Ni foam	66	68
2	Pt	50	60
3	Active carbon cloth	72	70
4	Graphite	61	60
5	Glassy carbon	63	64
6	Stainless steel	64	58
7	Carbon paper	80	76

Reaction conditions: divided cell, 15 mL MeOH, 0.1 M $TBAPF_6$, constant current at 10 mA, 2 cm^2 cathode, Pt anode, 12 hours; three replicates of the measurements were produced, and the reported value is the average within = 5% of error

Supplementary Table S2

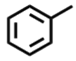
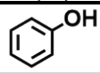
Product yields and calculated Faraday efficiency for different substrate concentrations and $NiCl_2 \cdot 6H_2O$ concentrations at 12 hours

Entry	**BPE (mM)**	**$NiCl_2 \cdot 6H_2O$ (mM)**	**Mole Ratio of $NiCl_2 \cdot 6H_2O$/BPE**	**Conversion (%)**	**Product Yield (%)**		**Faraday Efficiency (%)**
							
1	5	40	8	98	85	80	2.8
2	10	40	4	98	90	84	5.9
3	20	40	2	92	80	78	9.2
4	30	40	1.33	97	81	83	14.1
5	50	40	0.8	69	55	54	14.3

Reaction conditions: divided cell, 15 mL MeOH, 0.1 M $TBAPF_6$, constant current at 10 mA, 2 cm^2 carbon paper electrode, 12 hours; three replicates of the measurements were produced, and the reported value is the average within = 5% of error

Supplementary Table S3

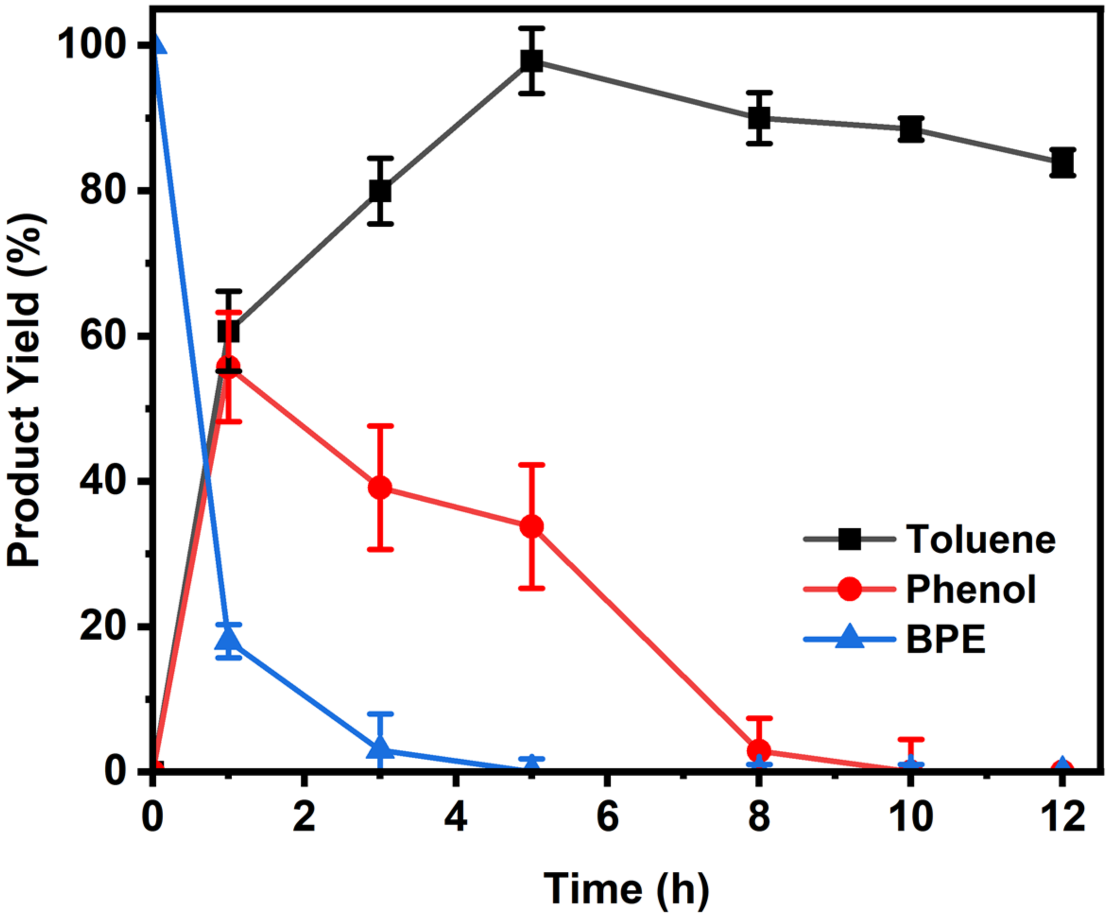
Product yields and calculated Faraday efficiency for reactions with a constant ratio of $NiCl_2 \cdot 6H_2O$/BPE and varying absolute concentrations at 12 hours

Entry	BPE (mM)	$NiCl_2 \cdot 6H_2O$ (mM)	Mole Ratio of $NiCl_2 \cdot 6H_2O$/ BPE	Conversion (%)	Product Yield (%)		Faraday Efficiency (%)
							
1	10	40	4	98	88	80	5.9
2	20	80	4	91	68	73	9.0
3	30	120	4	70	51	55	10.1
4	5	40	8	99	85	80	2.8
5	10	80	8	89	70	69	4.7

Reaction conditions: divided cell, 15 mL MeOH, 0.1 M $TBAPF_6$, constant current at 10 mA, 2 cm^2 carbon paper electrode, 12 hours; three replicates of the measurements were produced, and the reported value is the average within = 5% of error

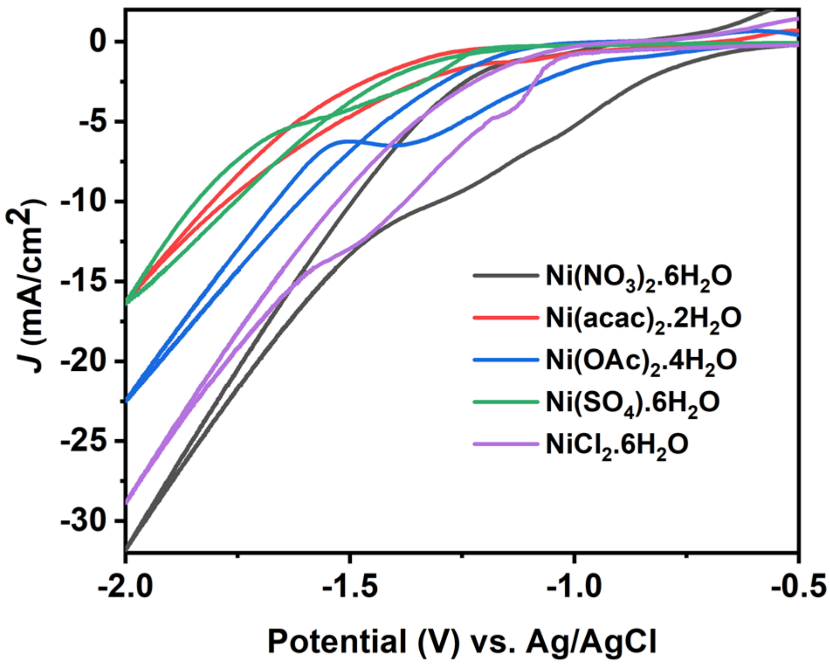
Supplementary Figure S1

Kinetic plot of electrochemical reductive cleavage of 0.2 mmol BPE in 10 mL methanol, 0.1 M $TBAPF_6$, 20 mA constant current, Ni foam $_{anode}$ and Ni foam $_{cathode}$ in the undivided cell



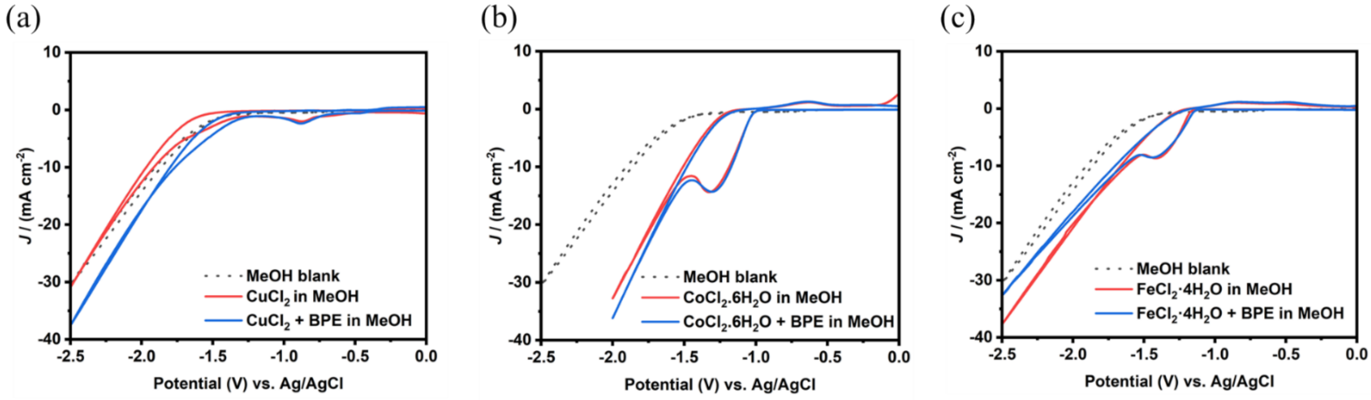
Supplementary Figure S2

CV curves of different Ni salts (40 mM) in 15 mL 0.10 M $TBAPF_6$-MeOH, scan rate: 50 mV/s.



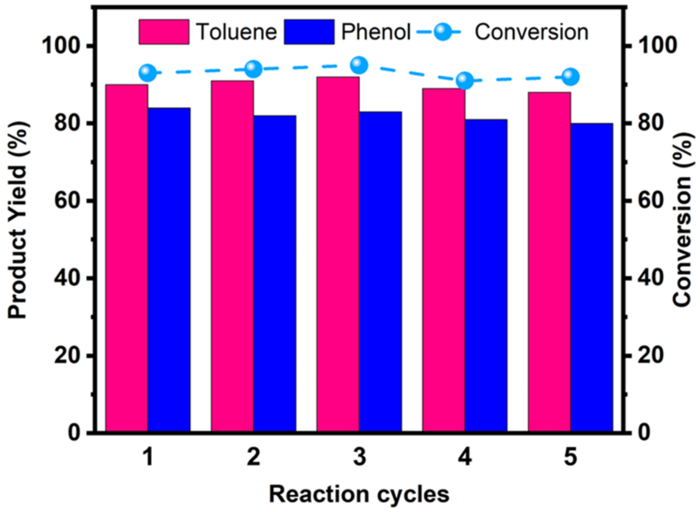
Supplementary Figure S3

CV curves of $CuCl_2$, $CoCl_2{\cdot}6H_2O$, and $FeCl_2{\cdot}4H_2O$ in 15 mL 0.10 M $TBAPF_6$-MeOH, 40 mM of metal chloride salts, 10 mM BPE, scan rate: 50 mV/s.



Supplementary Figure S4

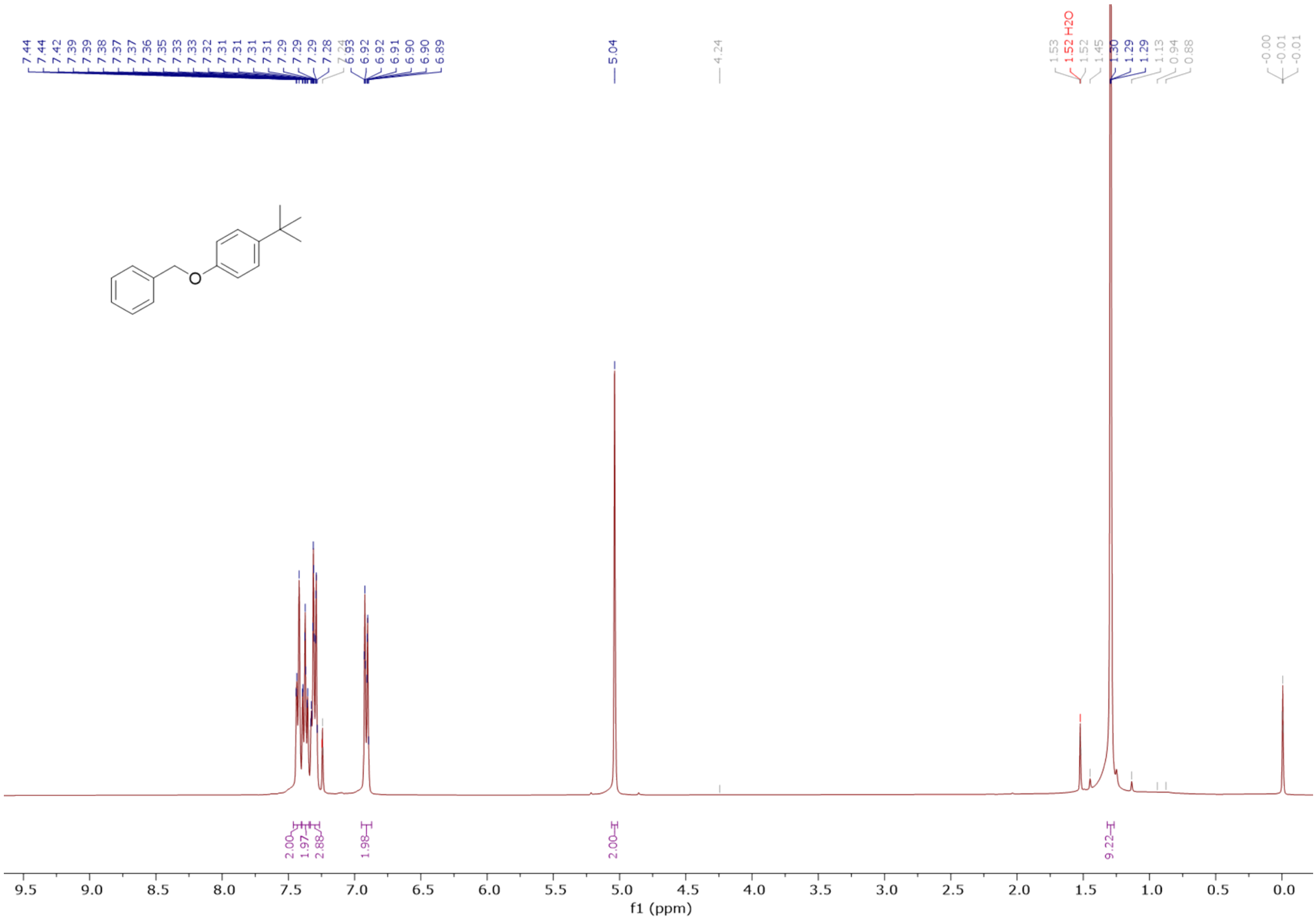
Reusability experiments of carbon paper cathode



Supplementary Figure S5

1-(benzyloxy)-4-(tert-butyl)benzene (**d**) ^{1}H NMR (400 MHz, $CDCl_3$)

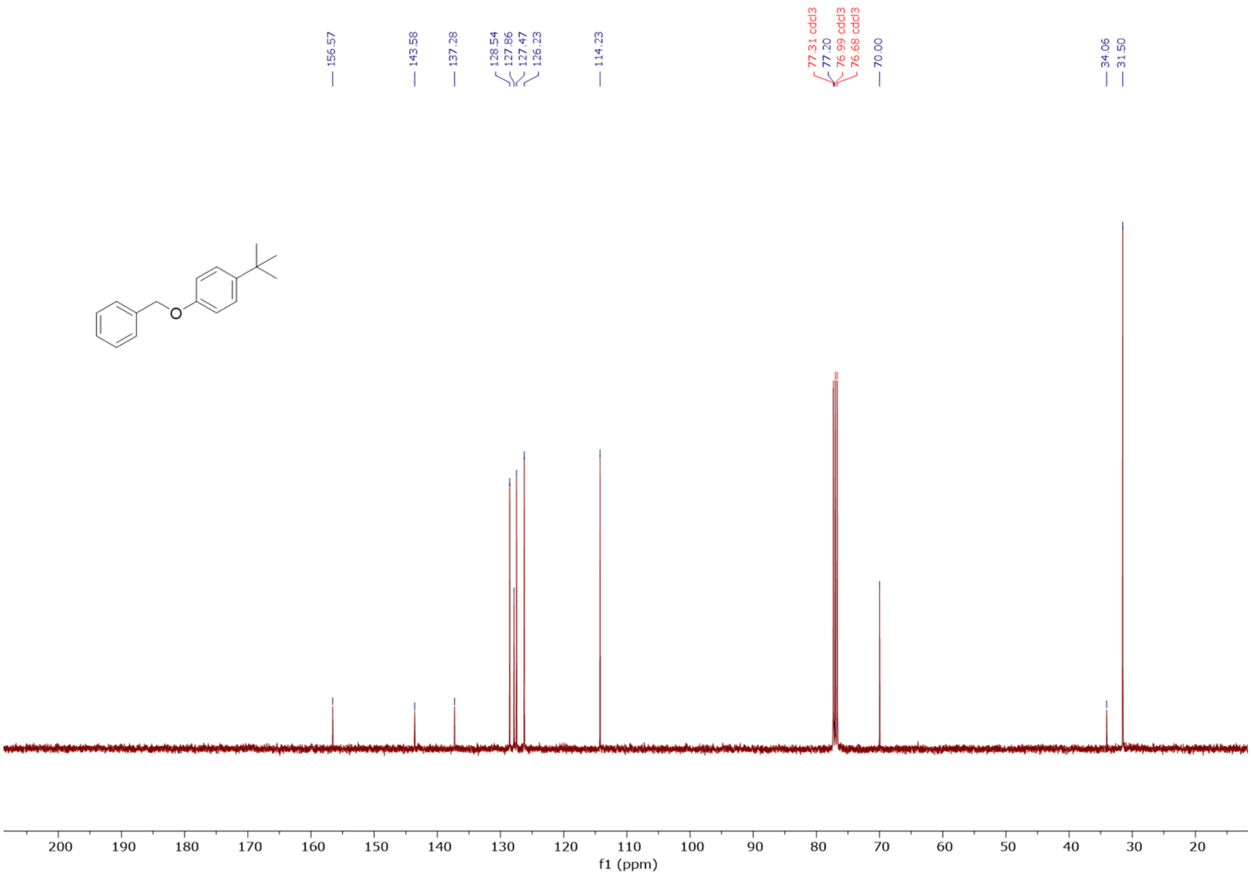
^{1}H NMR (400 MHz, $cdcl_3$) δ 7.43 (d, J = 6.9 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.31 (ddt, J = 8.0, 6.7, 1.4 Hz, 3H), 6.95 – 6.87 (m, 2H), 5.04 (s, 2H), 1.29 (d, J = 1.4 Hz, 9H).



Supplementary Figure S6

1-(benzyloxy)-4-(tert-butyl)benzene (**d**) ^{13}C NMR (101 MHz, $CDCl_3$)

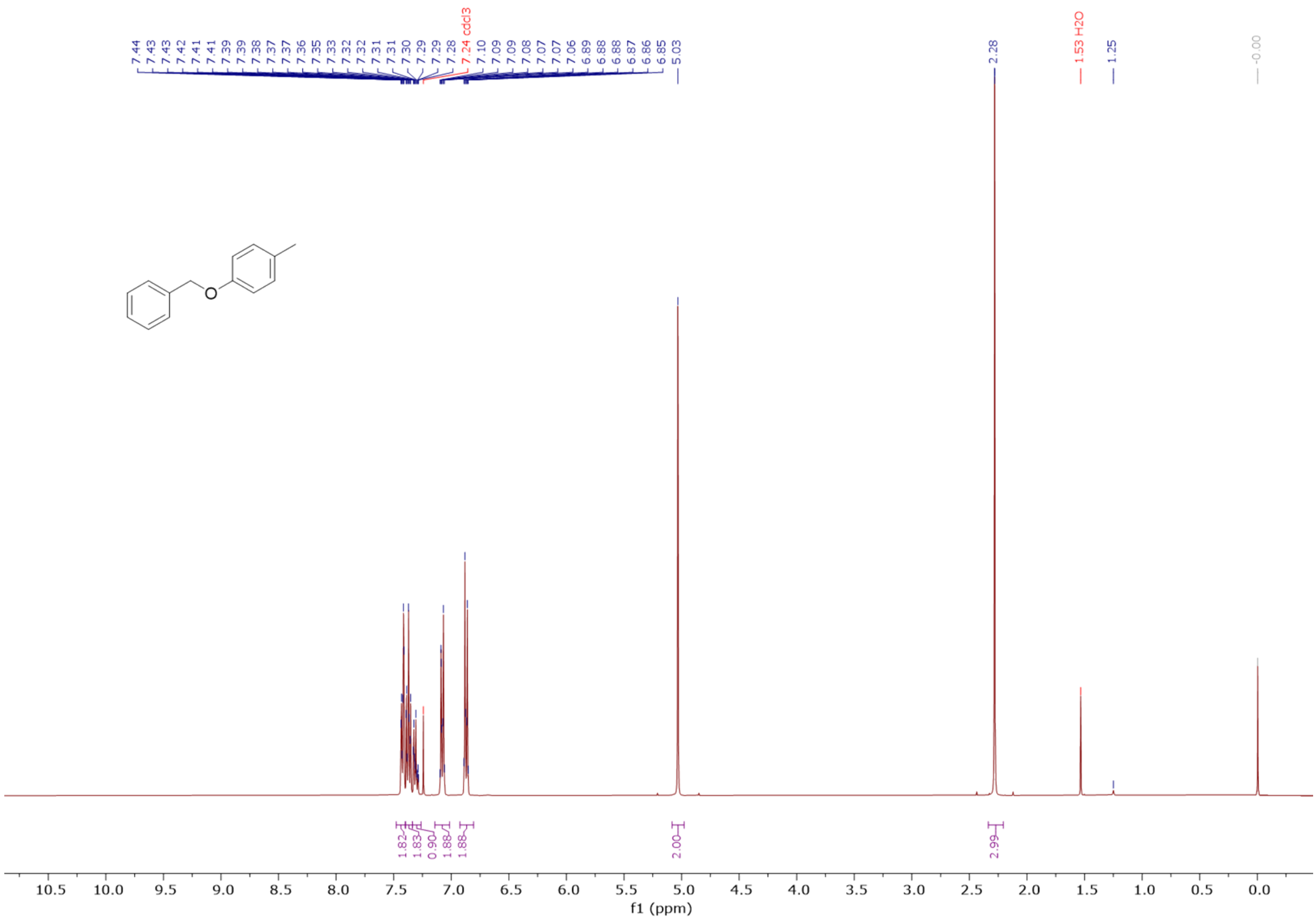
^{13}C NMR (101 MHz, $cdcl_3$) δ 156.57, 143.58, 137.28, 128.54, 127.86, 127.47, 126.23, 114.23, 70.00, 34.06, 31.50.



Supplementary Figure S7

1-(benzyloxy)-4-methylbenzene (**e**) ^{1}H NMR (400 MHz, $CDCl_3$)

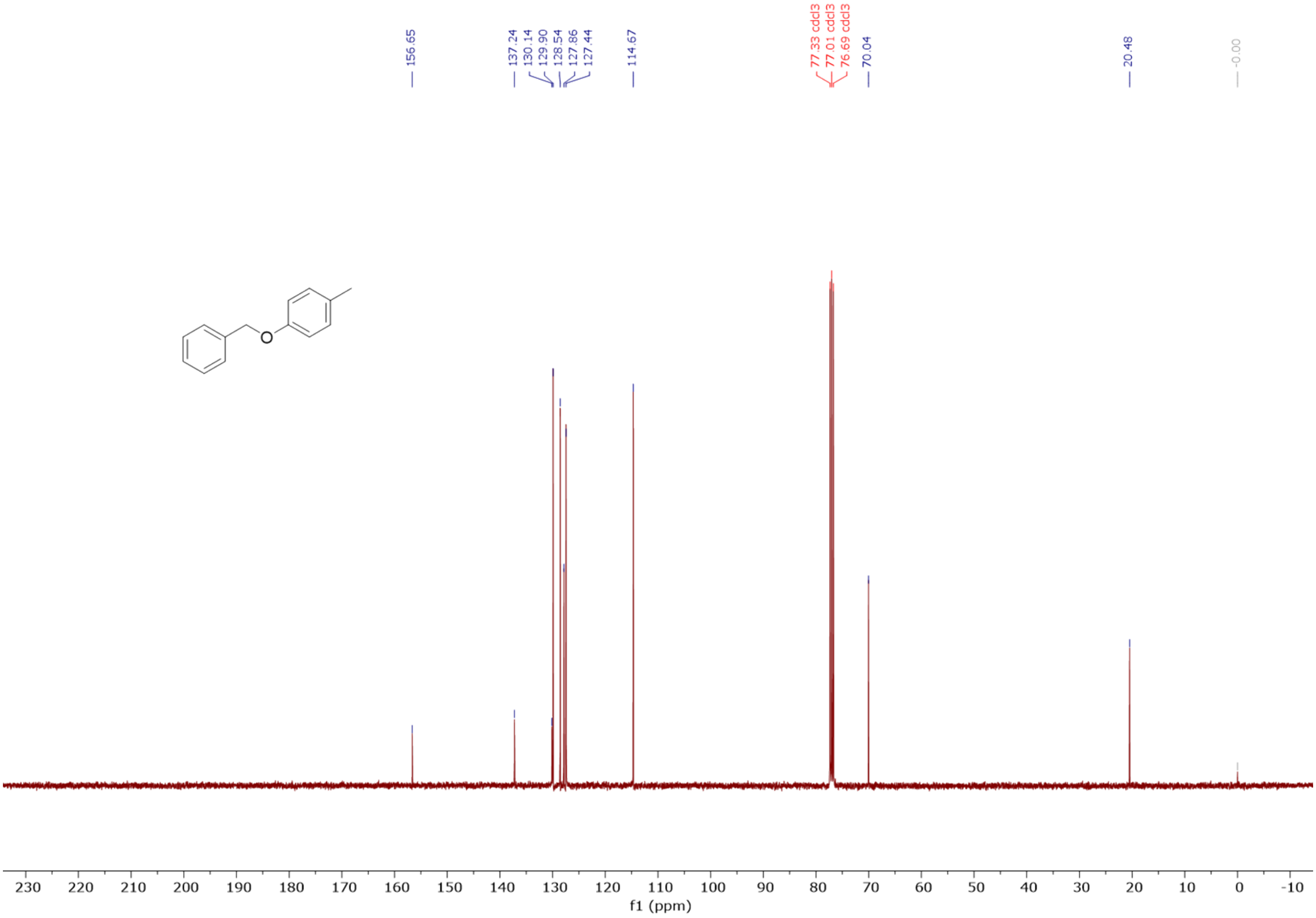
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.28 (m, 1H), 7.12 – 7.04 (m, 2H), 6.91 – 6.84 (m, 2H), 5.03 (s, 2H), 2.28 (s, 3H).



Supplementary Figure S8

1-(benzyloxy)-4-methylbenzene (**e**) ^{13}C NMR (101 MHz, $CDCl_3$)

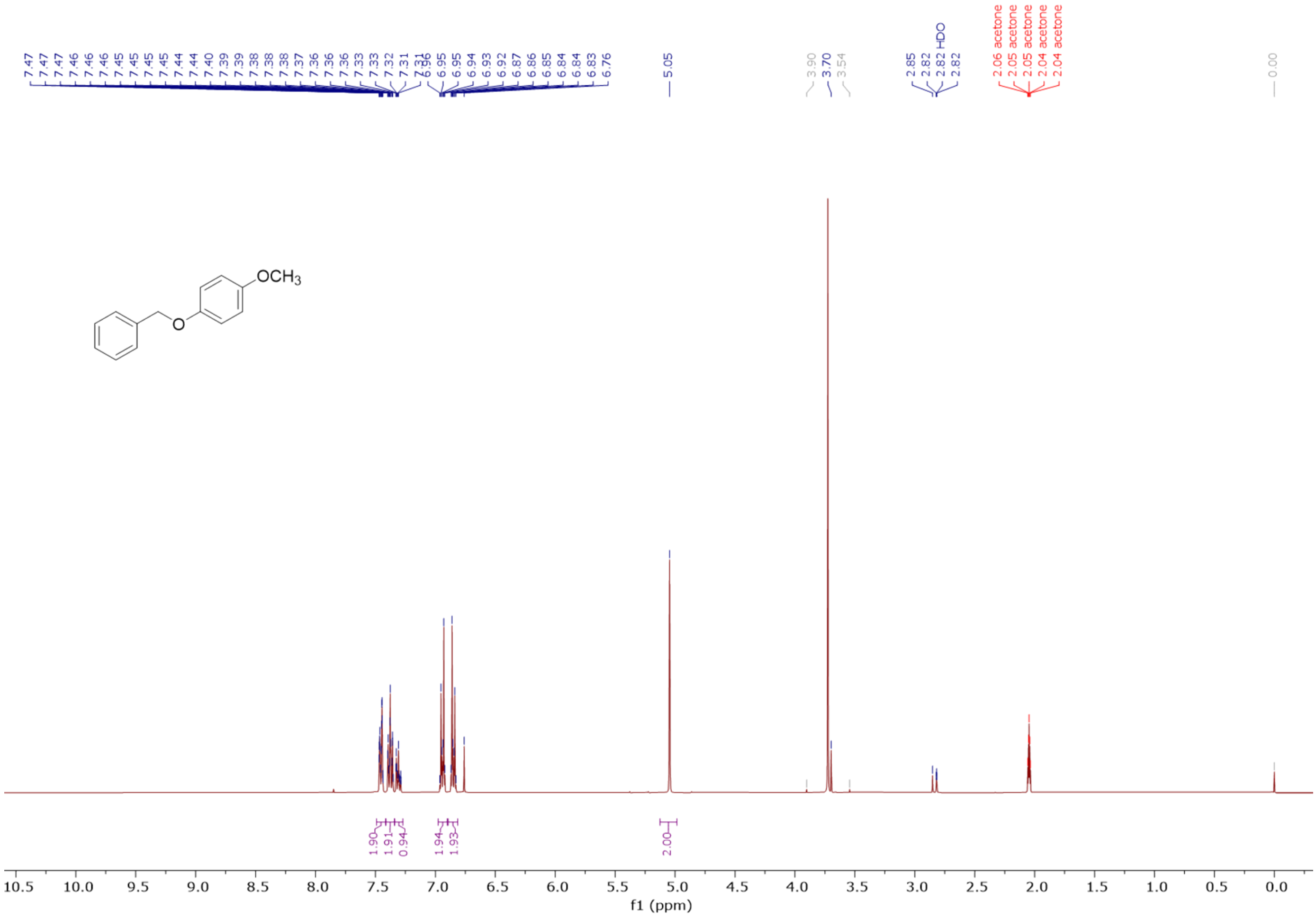
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.65, 137.24, 130.14, 129.90, 128.54, 127.86, 127.44, 114.67, 70.04, 20.48.



Supplementary Figure S9

1-(Benzyloxy)-4-methoxybenzene (**f**) ^{1}H NMR (400 MHz, $CDCl_3$)

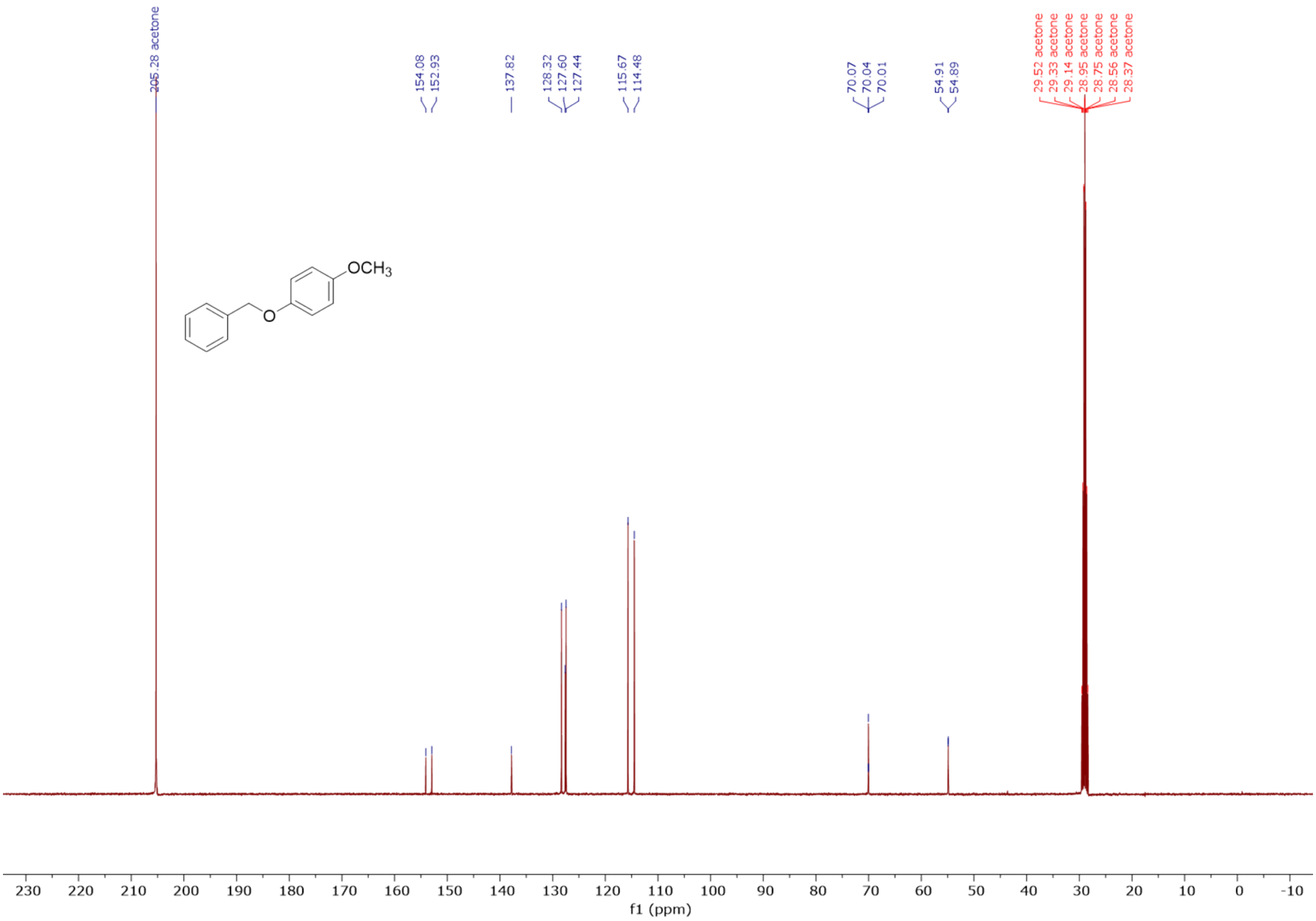
^{1}H NMR (400 MHz, acetone) δ 7.46 (ddt, J = 0.7, 1.5, 7.5 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.34 – 7.27 (m, 1H), 6.98 – 6.90 (m, 2H), 6.89 – 6.81 (m, 2H), 5.05 (s, 2H).



Supplementary Figure S10

1-(Benzyloxy)-4-methoxybenzene (**f**) ^{13}C NMR (101 MHz, $CDCl_3$)

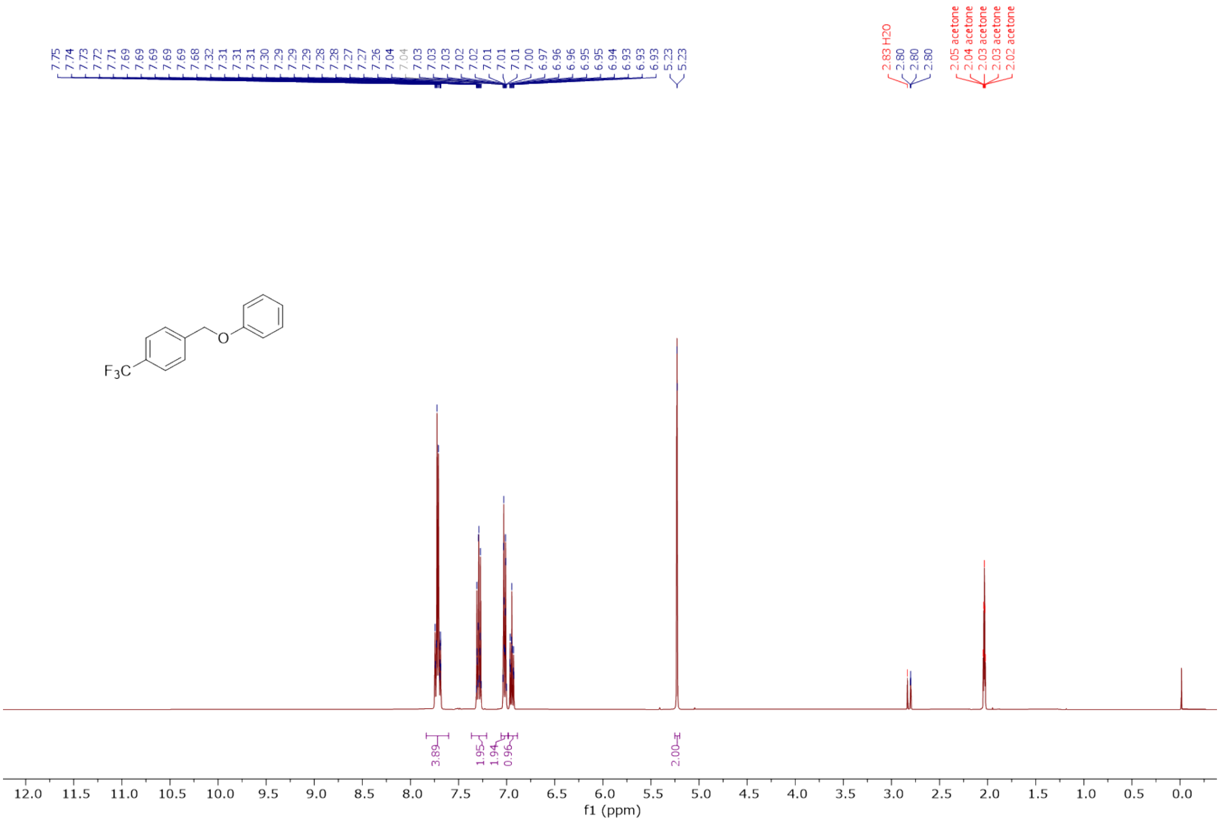
^{13}C NMR (101 MHz, acetone) δ 154.08, 152.93, 137.82, 128.32, 127.60, 127.44, 115.67, 114.48, 70.07, 54.91



Supplementary Figure S11

1-(phenoxymethyl)-4-(trifluoromethyl) benzene (**g**) ^{1}H NMR (400 MHz, acetone-d_6)

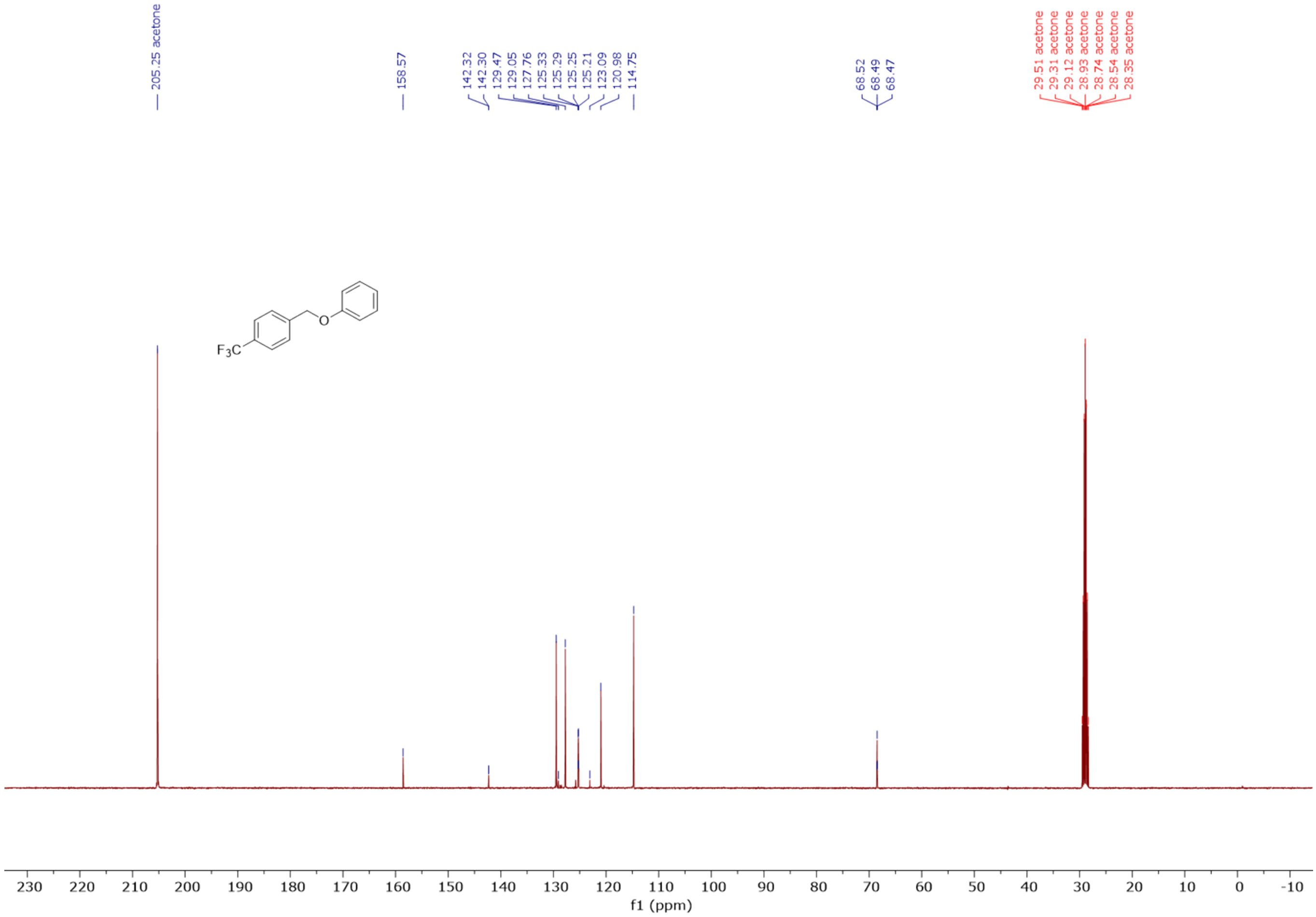
^{1}H NMR (400 MHz, acetone) δ 7.84 – 7.60 (m, 4H), 7.37 – 7.21 (m, 2H), 7.06 – 6.99 (m, 2H), 6.95 (tt, J = 7.3, 1.1 Hz, 1H), 5.23 (d, J = 1.0 Hz, 2H).



Supplementary Figure S12

1-(phenoxymethyl)-4-(trifluoromethyl) benzene (**g**) ^{13}C NMR (101 MHz, acetone-d_6)

^{13}C NMR (101 MHz, acetone) δ 158.57, 142.30, 129.47, 127.76, 125.29, 125.25, 123.09

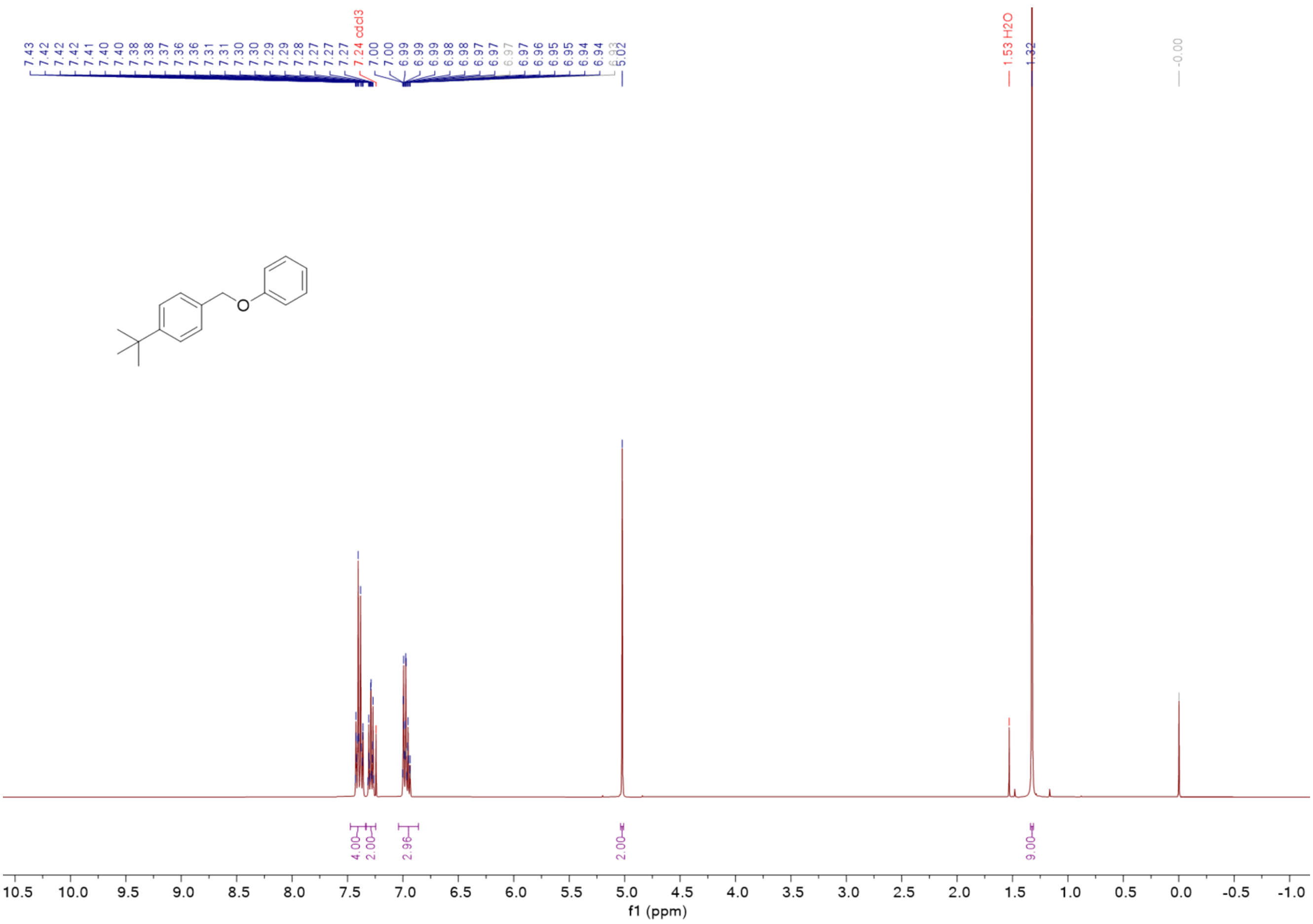


120.98, 114.75, 68.49

Supplementary Figure S13

1-(tert-butyl)-4-(phenoxymethyl)benzene (**h**) ^{1}H NMR (101 MHz, $CDCl_3$)

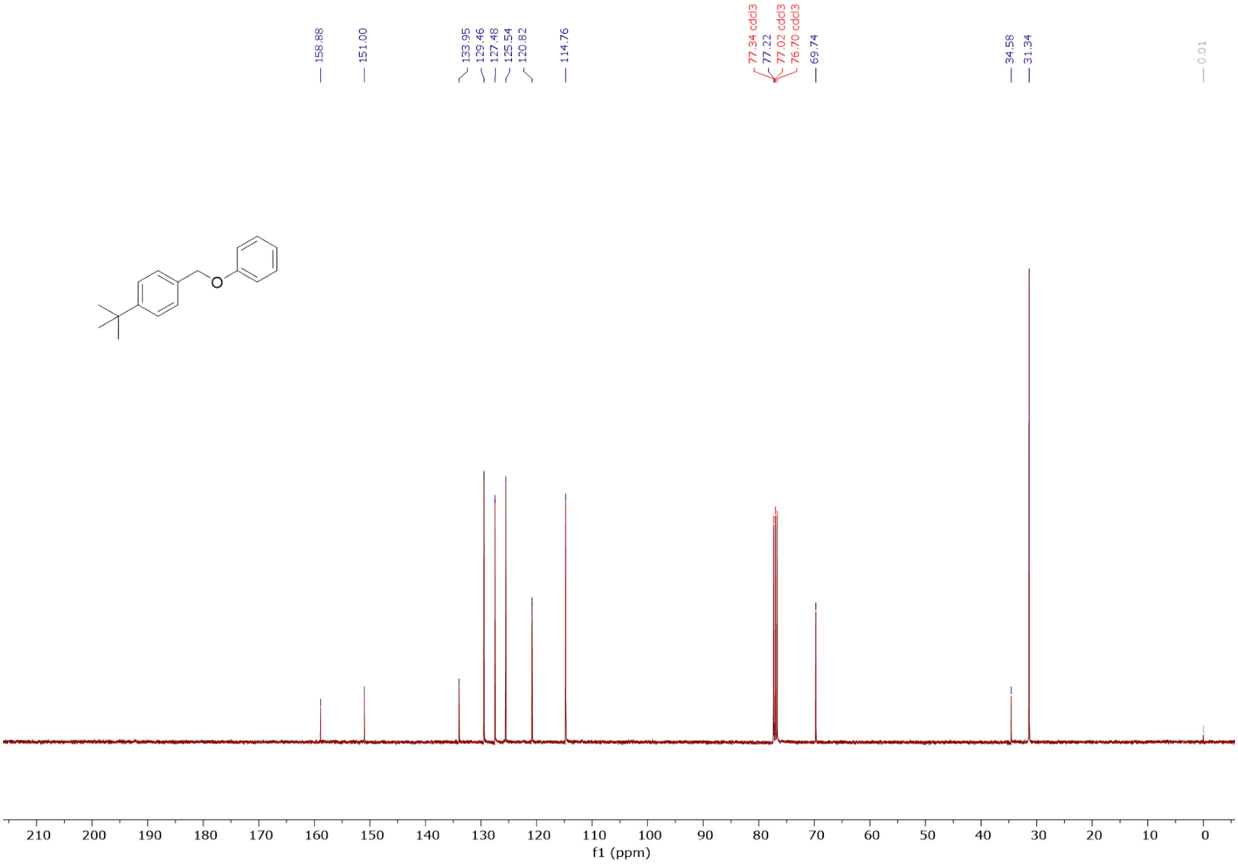
^{1}H NMR (400 MHz, $cdcl_3$) δ 7.48 – 7.34 (m, 4H), 7.33 – 7.25 (m, 2H), 7.04 – 6.86 (m, 3H), 5.02 (s, 2H), 1.32 (s, 9H).



Supplementary Figure S14

1-(tert-butyl)-4-(phenoxymethyl)benzene (**h**) ^{13}C NMR (101 MHz, $CDCl_3$)

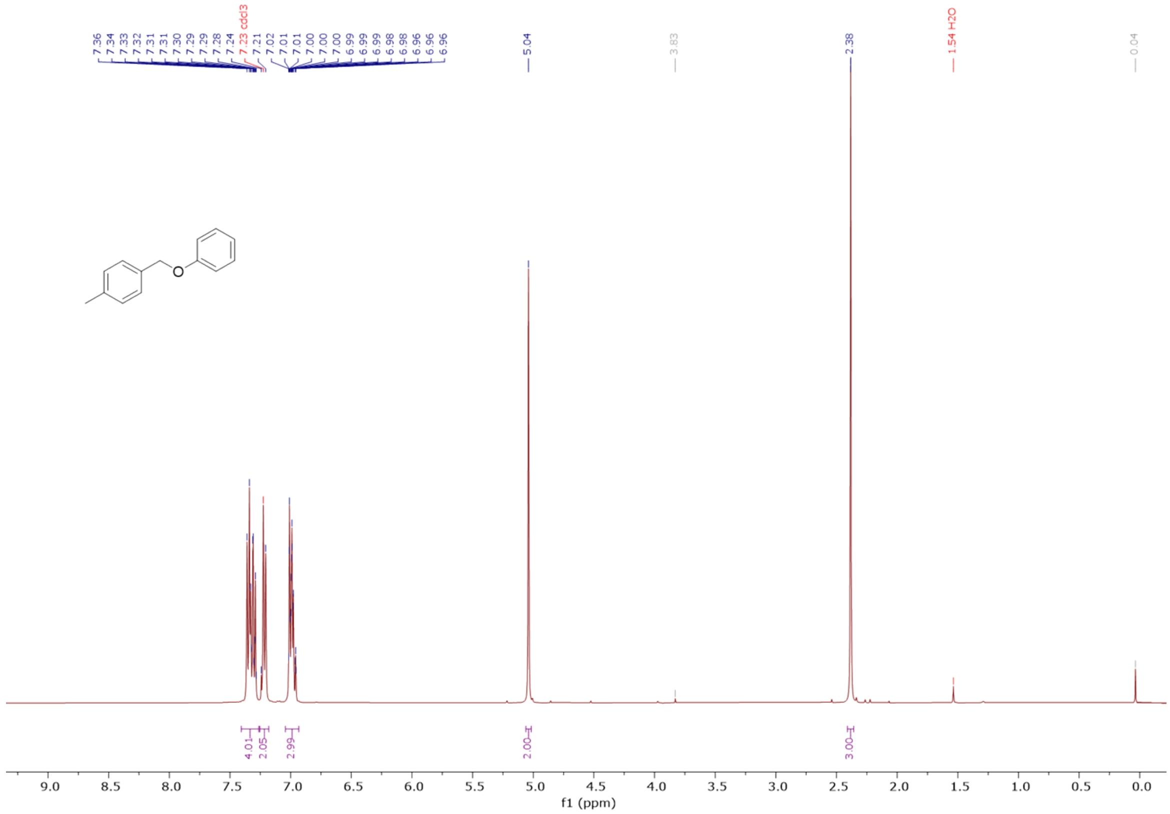
^{13}C NMR (101 MHz, $cdcl_3$) δ 158.88, 151.00, 133.95, 129.46, 127.48, 125.54, 120.82, 114.76, 69.74, 34.58, 31.34.



Supplementary Figure S15

4-Methylbenzylphenyl ether (**i**) ^{1}H NMR (400 MHz, $CDCl_3$)

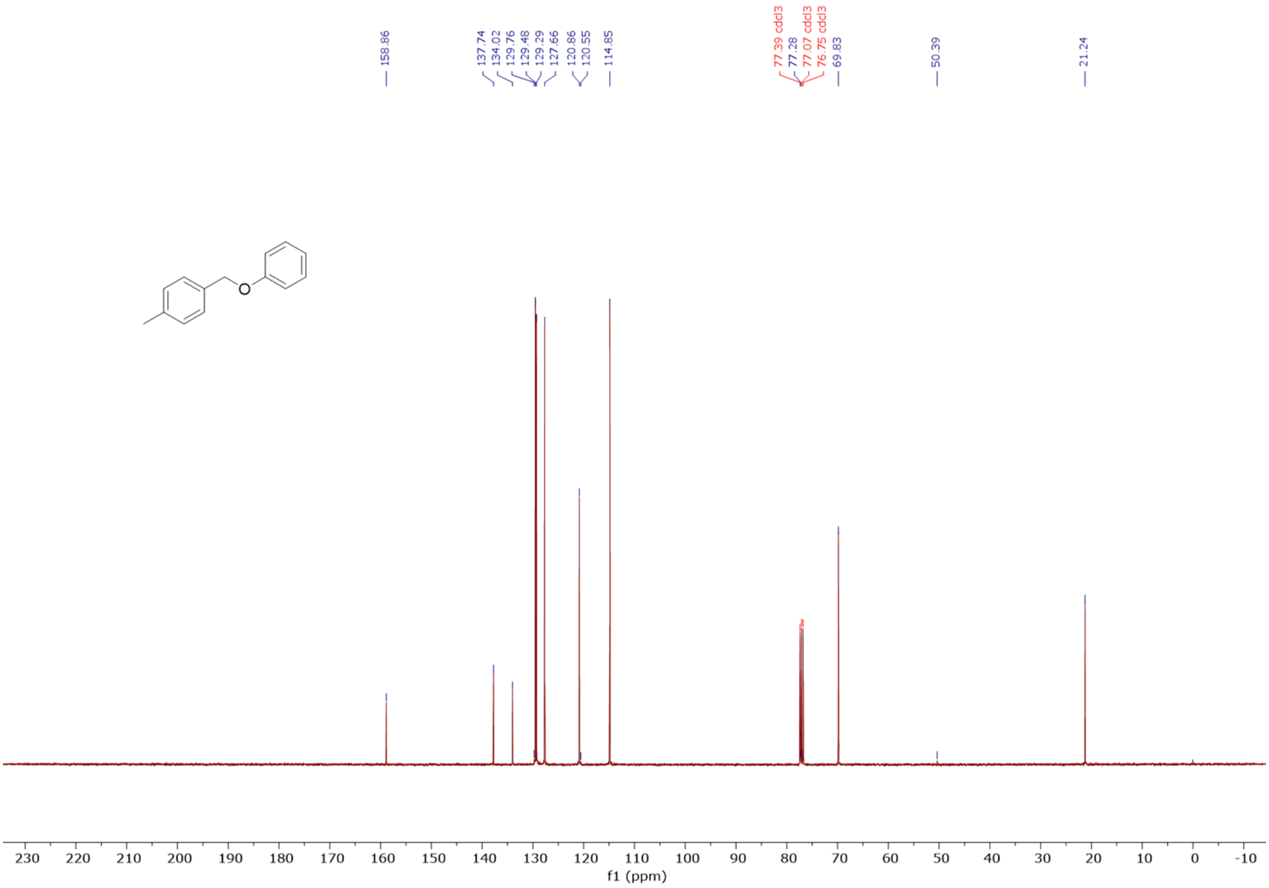
^{1}H NMR (400 MHz, $cdcl_3$) δ 7.41 – 7.26 (m, 4H), 7.22 (d, *J* = 14.6 Hz, 2H), 7.04 – 6.93 (m, 3H), 5.04 (s, 2H), 2.38 (s, 3H).



Supplementary Figure S16

4-Methylbenzylphenyl ether (**i**) ^{13}C NMR (101 MHz, $CDCl_3$

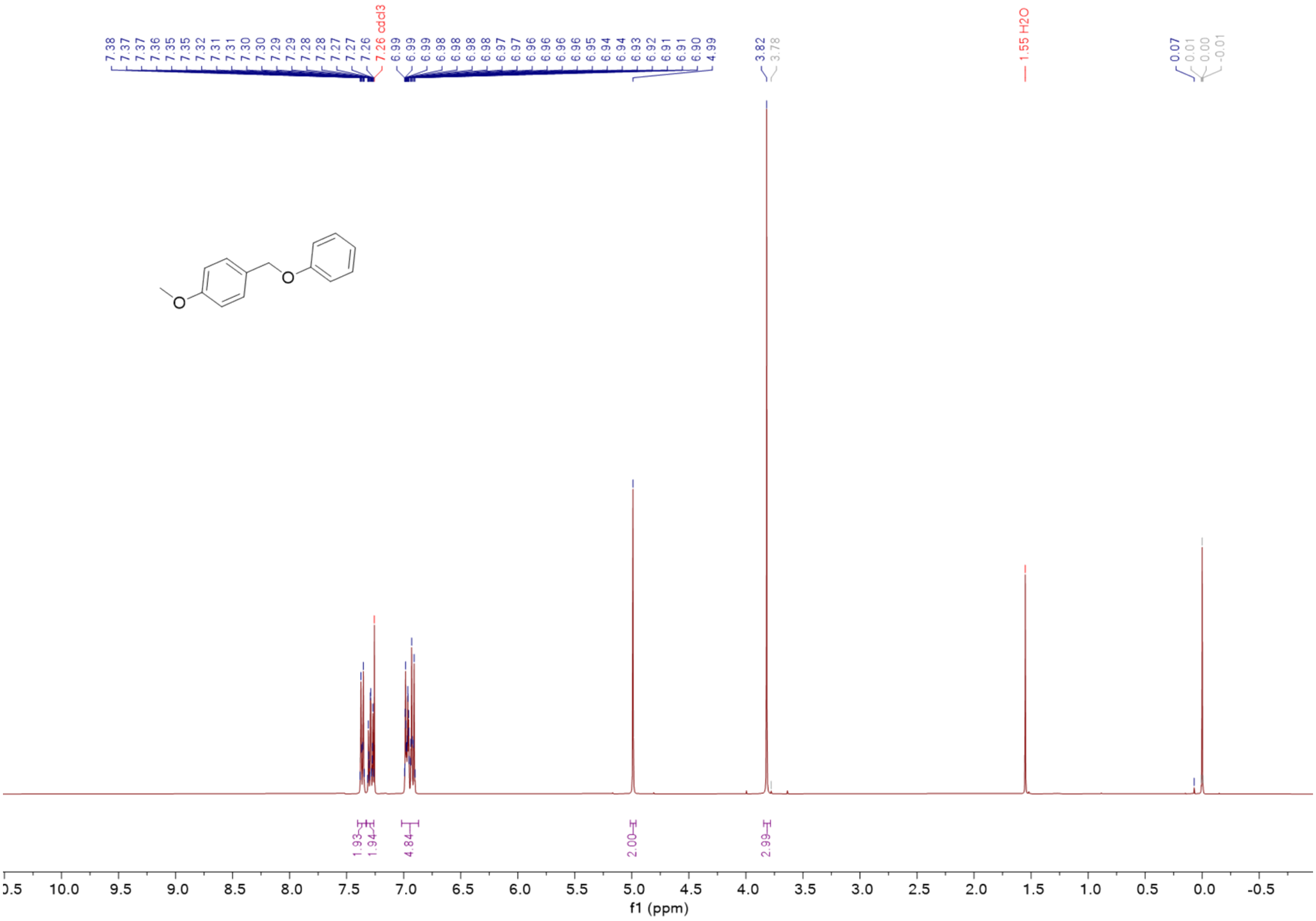
^{13}C NMR (101 MHz, $cdcl_3$) δ 158.86, 137.74, 134.02, 129.39 (d, J = 19.3 Hz), 127.66, 120.86, 114.85, 77.28, 69.83, 21.24.



Supplementary Figure S17

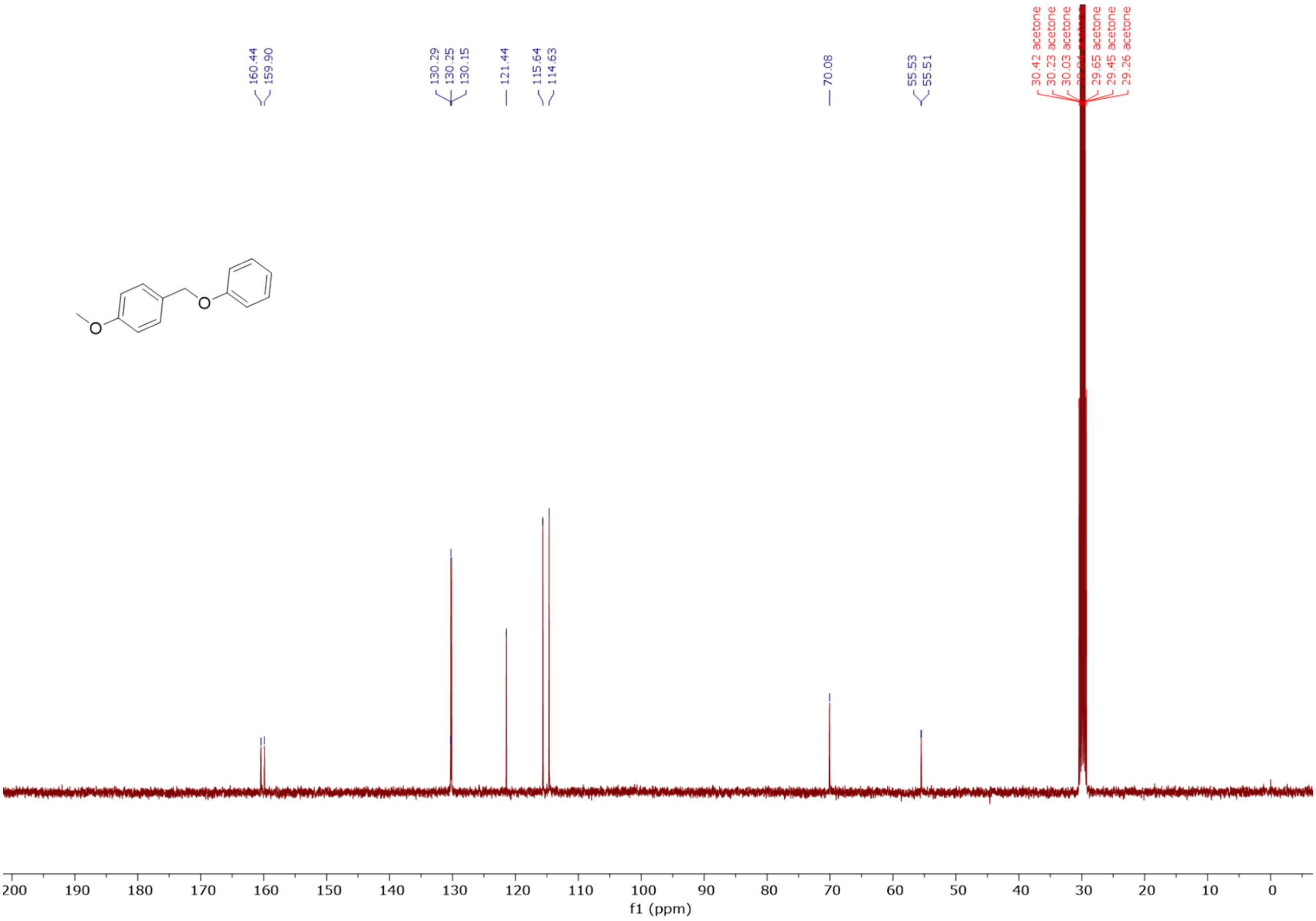
1-methoxy-4-(phenoxymethyl) benzene (**j**) ^{1}H NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, cdcl$_3$) δ 7.40 – 7.33 (m, 2H), 7.33 – 7.26 (m, 2H), 7.02 – 6.87 (m, 5H), 4.99 (s, 2H), 3.82 (s, 3H).



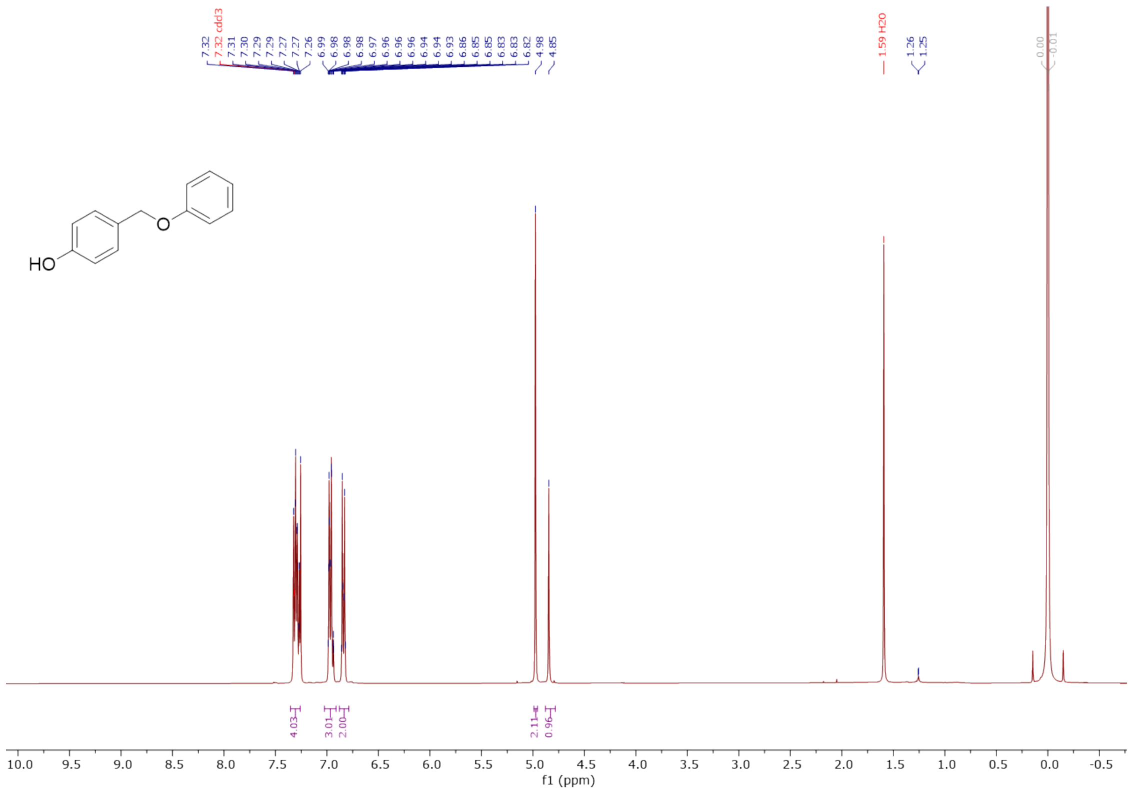
Supplementary Figure S18

1-methoxy-4-(phenoxymethyl) benzene (**j**) ^{13}C NMR (101 MHz, acetone) δ 159.53, 158.99, 129.38, 129.33, 129.24, 120.52, 114.73, 113.71, 69.16, 54.62



Supplementary Figure S19

4-(phenoxymethyl) phenol (**k**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 7.02 – 6.91 (m, 3H), 6.88 – 6.79 (m, 2H), 4.98 (s, 2H), 4.85 (s, 1H).



Supplementary Figure S20

4-(phenoxymethyl) phenol (**k**) ^{13}C NMR (101 MHz, cdcl$_3$) δ 158.77, 155.35, 129.43, 129.27, 120.87, 115.40, 114.83, 69.63.