Supplementary Information

Metal triflates formation of C_{12}-C_{22} phenolic compounds by simultaneous C-O breaking and C-C coupling of benzyl phenyl ether

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Table S1. Relative lignin linkage content of hardwood, softwood, and grass and their bond dissociation energies.

Linkage		Percentage of total amount (%)			Bond dissociation energies (kcal/mol)[1]
		Softwood[2]	**Hardwood**[2]	**Grass**[3]	
C-O-C	β-O-4	43-50	50-65	75-84	56 - 72
	α-O-4	6-8	4-8	n.d.	48- 57
	4-O-5	4	6-7	n.d.	78 - 82
C-C	β-β	2-4	3-7	1-7	-
	β-5	9-12	4-6	5-11	125- 128
	β-1	3-7	5-7	n.d.	65 - 166
	5-5	10-25	4-10	n.d.	115 - 118
Others		16	7-8	n.d.	-

n.d. = no data

Table S2. List of chemicals/reagents used in this study			
Material/Chemical	**Supplier**	**Purity**	**CAS Number**
Benzyl phenyl ether	Sigma-Aldrich (St. Louis, MO, USA)	98%	946-80-5
2-phenethyl phenyl ether	Frinton Laboratories, Inc. (Hainesport, NJ, USA)	99%	40515-89-7
Diphenyl ether	Sigma-Aldrich (St. Louis, MO, USA)	99%	101-84-8
n-dodecane	Beantown Chemical Corporation (Hudson, NH, USA)	99%	112-40-3
n-heptane	Beantown Chemical Corporation (Hudson, NH, USA)	99%	142-82-5
n-octane	Beantown Chemical Corporation (Hudson, NH, USA)	98%	111-65-9
Toluene	The Lab Depot (Dawsonville, GA, USA)	ACS Grade	108-88-3
Dichloromethane	Avantor (Radnor Township, PA, USA)	≥99.5%	75-09-2
2-butanol	Sigma-Aldrich (St. Louis, MO, USA)	99%	4221-99-2
Tetrahydrofuran	Beantown Chemical Corporation (Hudson, NH, USA)	99.7%	109-99-9
Dimethyl sulfoxide	VWR Chemicals (Radnor, PA, USA)	≥99.9% ACS	67-68-5
Methanol	VWR Chemicals (Radnor, PA, USA)	Lab grade	67-56-1
Ethanol	Decon Laboratories, Inc. (King of Prussia, PA, USA)	200 Proof	64-17-5
Acetone	Aqua Solutions, Inc. (Deer Park, TX, USA)	Technical grade	67-64-1
Acetonitrile	Sigma-Aldrich (St. Louis, MO, USA)	99.8%	75-05-8
N, N-dimethylformamide	Chem-Impex Int'l. Inc. (Wood Dale, IL, USA)	100%	68-12-2
1,4-dioxane	Beantown Chemical Corporation (Hudson, NH, USA)	99%	123-91-1
Ethyl acetate	Alfa Aesar (Ward Hill, MA, USA)	99%	141-78-6
$Hf(OTf)_4$	Alfa Aesar (Ward Hill, MA, USA)	98%	161337-67-3
$Zn(OTf)_2$	Strem Chemical (Newburyport, MA, USA)	98%	54010-75-2
$Sc(OTf)_3$	Sigma-Aldrich (St. Louis, MO, USA)	99%	144026-79-9
$Y(OTf)_3$	Sigma-Aldrich (St. Louis, MO, USA)	98%	52093-30-8
$La(OTf)_3$	Strem Chemical (Newburyport, MA, USA)	97%	52093-26-2
$Er(OTf)_3$	Sigma-Aldrich (St. Louis, MO, USA)	98%	139177-64-3
$Yb(OTf)_3$	Sigma-Aldrich (St. Louis, MO, USA)	99.99%	54761-04-5
$Al(OTf)_3$	Sigma-Aldrich (St. Louis, MO, USA)	99.9%	74974-61-1
$Ti(OTf)_3$	Sigma-Aldrich (St. Louis, MO, USA)	98%	76262-87-8
$Fe(OTf)_3$	Alfa Aesar (Ward Hill, MA, USA)	90%	63295-48-7

Table S3. Screening of metal triflate catalysts for the reaction of benzyl phenyl ether

Entry	Catalyst	Time (h)	Conv.[a] (%)	Selec.[a,b] (%)	Yield [a] (%)		
					B	C	D
1	$La(OTf)_3$	1	4	75	3	0	1
2	$La(OTf)_3$	14	7	86	6	0	1
3	$Al(OTf)_3$	1	4	81	2	1	1
4	$Al(OTf)_3$	14	11	85	6	3	2
5	$Ti(OTf)_4$	1	6	86	3	2	1
6	$Ti(OTf)_4$	14	16	76	9	3	4
7	$Zn(OTf)_2$	1	6	83	5	0	1
8	$Zn(OTf)_2$	14	10	70	7	0	3
9	$Yb(OTf)_3$	1	14	86	11	1	2
10	$Yb(OTf)_3$	14	43	81	27	8	8
11	$Y(OTf)_3$	1	15	87	10	3	2
12	$Y(OTf)_3$	14	16	94	11	4	1
13	$Er(OTf)_3$	1	26	85	15	7	3
14	$Er(OTf)_3$	14	37	81	28	2	6
15	$Sc(OTf)_3$	1	37	86	25	7	5
16	$Sc(OTf)_3$	14	76	78	44	15	16
17	$Fe(OTf)_3$	1[c]	41	84	27	7	6
18	$Fe(OTf)_3$	1	100	84	70	12	16
19	$Hf(OTf)_4$	1[c]	60	81	39	10	10
20	$Hf(OTf)_4$	1	100	89	78	11	8

Note: *o*- and *p*-benzylphenols (B), di-benzylphenols (C), and phenol (D). Reaction conditions: feed = benzyl phenyl ether 0.26 mmol (feed/heptane/dodecane (internal standard)) = 1:8.5:0.5 by weight), catalyst = 20 mol%, 100°C, 1 bar,[a] Conversion, selectivity, and yield are reported in C-mol%. [b] Selectivity toward benzylphenols (B) and di-benzylphenols (C), as the desired products. [c]Catalyst = 2 mol%

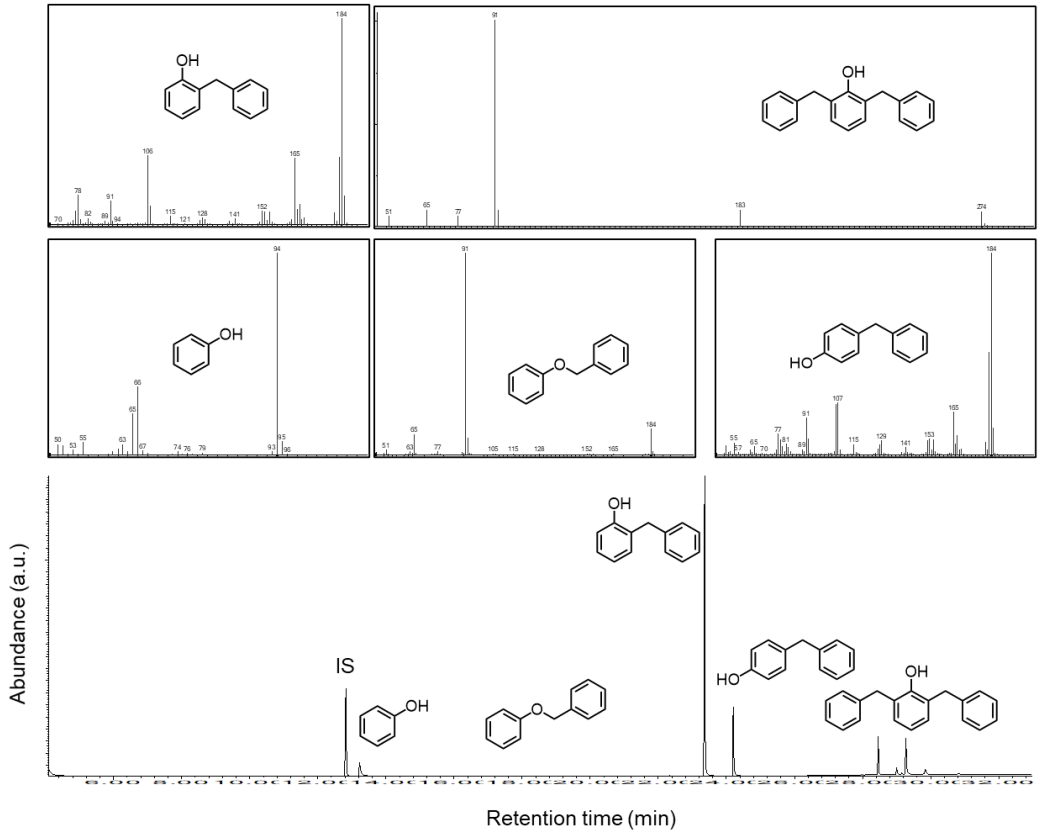

Figure S1. Gas chromatogram of reaction products and their mass spectra

Table S4. Effect of solvent on the rearrangement of benzyl phenyl ether

Entry	Solvent	Polarity index	Conv.[a] (%)	Selec. [a,b] (%)	Yield [a] (%)		
					B	C	D
1	n-heptane	0	100	89	78	11	8
2	n-octane	0.4	100	84	75	9	3
3	toluene	2.3	100	68	62	6	20
4	dichloromethane	3.4	100	77	71	6	14
5	2-Butanol	3.9	4	0	0	0	0
6	tetrahydrofuran	4.2	13	9	1	0	0
7	ethyl acetate	4.3	3	0	0	0	0
8	1,4-dioxane	4.8	31	7	2	0	0
9	ethanol	5.2	7	0	0	0	0
10	acetone	5.4	5	0	0	0	0
11	acetonitrile	6.2	29	0	0	0	0
12	dimethyl formamide	6.4	13	0	0	0	0
13	dimethyl sulfoxide	6.5	9	0	0	0	0
14	methanol	6.6	10	0	0	0	0

Reaction conditions: feed = benzyl phenyl ether 0.26 mmol (feed/solvent/dodecane (internal standard)) = 1:8.5:0.5 by weight), $Hf(OTf)_4$ = 20 mol%, 100°C, 1 bar, 1h.

[a]Conversion, selectivity and yield were reported in C-mol%. [b]Selectivity toward benzylphenols (B) and di-benzylphenols (C), as the desired products.

Cartesian coordinates of key species

1. Benzyl phenyl ether

C	-0.452269	-0.148861	0.442969
C	0.842532	-0.649265	0.335545
C	1.847495	0.166181	-0.174258
C	1.552239	1.471227	-0.569012
C	0.262232	1.952450	-0.455005
C	-0.751966	1.144224	0.052000
H	-1.229879	-0.788767	0.840128
H	1.048927	-1.661619	0.650244
H	2.352542	2.085957	-0.959395
H	0.044169	2.966683	-0.764024
H	-1.761101	1.522943	0.140235
O	3.142539	-0.216889	-0.322728
C	3.490626	-1.533962	0.045915
H	2.885430	-2.247782	-0.526125
H	3.282953	-1.696109	1.108908
C	4.950873	-1.764614	-0.232588
C	5.619328	-2.775056	0.451736
C	5.636874	-1.020362	-1.185024
C	6.953030	-3.045308	0.183983
H	5.092638	-3.351673	1.203917
C	6.974167	-1.286523	-1.448729
H	5.122498	-0.228427	-1.711904
C	7.635071	-2.299643	-0.768637
H	7.462200	-3.832552	0.724794
H	7.501267	-0.698402	-2.189045
H	8.677372	-2.504527	-0.975490

2. *o*-benzylphenols

C	-0.058186	0.559151	0.064134
C	1.109886	-0.141252	0.324175
C	2.365061	0.441092	0.119910
C	2.406374	1.744537	-0.354592
C	1.241937	2.458131	-0.620849
C	0.009819	1.862835	-0.410165
H	-1.017998	0.083640	0.233211
H	3.369279	2.211937	-0.518817
H	1.303061	3.472913	-0.990142
H	-0.904087	2.406050	-0.612188
C	3.595391	-0.386141	0.427729
H	3.563364	-1.292894	-0.181939
H	3.530212	-0.726063	1.464561
C	4.896368	0.334581	0.206281
C	5.458932	1.108573	1.217694
C	5.542554	0.275810	-1.025081

C	6.639581	1.806849	1.006011
H	4.962278	1.164683	2.179801
C	6.723976	0.972025	-1.242481
H	5.112664	-0.321338	-1.821280
C	7.275885	1.740602	-0.226580
H	7.064534	2.401454	1.804617
H	7.215006	0.912398	-2.205412
H	8.197900	2.282278	-0.393095
O	1.099646	-1.423703	0.788986
H	0.191164	-1.724366	0.893106

3. di-benzylphenols

O	0.035500	-0.261822	-1.647065
C	-1.218051	-1.829853	-0.429863
C	1.215248	-1.896037	-0.320171
C	-2.468940	-1.149932	-0.926054
C	2.550224	-1.340127	-0.745989
C	0.031320	-1.322269	-0.790069
C	-2.733113	0.157368	-0.208531
C	2.777781	0.108732	-0.356486
C	-1.266131	-2.933201	0.412615
C	1.124786	-2.987680	0.536897
C	-0.104684	-3.513027	0.903002
C	-2.698835	1.370942	-0.885312
C	-3.011276	0.161082	1.156603
C	2.335616	0.598697	0.871379
C	3.437074	0.976825	-1.223931
C	-2.943316	2.563995	-0.216752
C	-3.257316	1.348869	1.828386
C	2.559633	1.920488	1.226834
C	3.662129	2.301292	-0.870479
C	-3.224292	2.556650	1.141809
C	3.225022	2.775843	0.357605
H	-3.315235	-1.822726	-0.773199
H	-2.388987	-0.958957	-1.996680
H	2.657254	-1.429340	-1.831233
H	3.338958	-1.955383	-0.307487
H	-2.233170	-3.337309	0.689302
H	2.038793	-3.433864	0.911047
H	-0.157378	-4.368914	1.562347
H	-2.467694	1.379207	-1.943675
H	-3.029892	-0.779323	1.696664
H	1.802319	-0.060885	1.545966
H	3.776584	0.610434	-2.186319
H	0.864388	0.228615	-1.577729
H	-2.911195	3.500590	-0.758881
H	-3.475626	1.333441	2.888702
H	2.207281	2.285810	2.182773

H	4.174675	2.961968	-1.557776
H	-3.415396	3.485214	1.664016
H	3.394244	3.808386	0.633632

4. Phenol

C	-0.571081	-0.278265	0.135869
C	0.789499	-0.546228	0.073059
C	1.694711	0.505084	0.032002
C	1.248297	1.818899	0.063072
C	-0.113665	2.079570	0.125981
C	-1.026366	1.033450	0.159893
H	-1.276917	-1.098264	0.168436
H	1.163807	-1.561689	0.063700
H	1.974972	2.620766	0.045799
H	-0.461782	3.104195	0.150736
H	-2.087238	1.239512	0.210765
O	3.050775	0.241991	0.019630
H	3.359655	0.176318	-0.889796

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