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Supporting Information

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A general method for the preparation of ethers using water resistant solid Lewis acids involving the possibility for cascade reactions

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Table . Synthesis of ether **3a** catalyzed by different catalysts. Conversions displayed after a reaction time of 15 min.

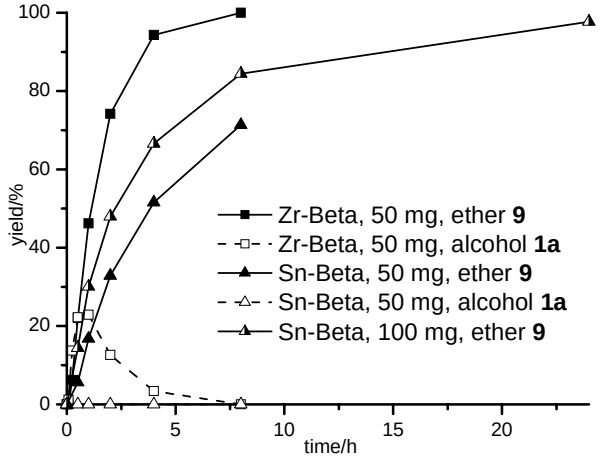
			selectivity	
		conv.	**3a**	**4a**
entry	catalyst	[%]	[%]	[%]
1	Sn-Beta	53	96	4
2	Sn-MCM-41	27	82	18
3	Zr-Beta	45	95	5
4	Ti-Beta	6	96	4
5	Si-Beta	2	0	100

Table. Synthesis of ethers with interesting olfactory properties starting with alcohol **1d**. Ether **10a** is the commercial fragrance compound Methyl Diantilis (Givaudan).

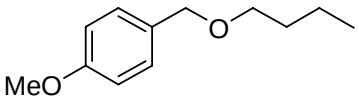
entry	alcohol	ether	time [h]	conv. [%]	select. ether [%]	select. dimer [%]
1[a]	methanol	**10a**	24	100	96	0
2[a,b]	methanol	**10a**	24	100	100	0
3[a,c]	methanol	**10a**	24	99	99	0
4[d]	ethanol	**10b**	24	100	100	0
5	1-propanol	**10c**	24	100	94	0
6[e]	2-propanol	**10d**	8	100	98	0
7[c,e]	2-propanol	**10d**	8	100	100	0
8	1-butanol	**3d**	6	64	100	0
9[c]	1-butanol	**3d**	6	98	98	0

[a] reaction temperature 65 ºC. [b] 75 mg of catalyst. [c] with Sn-MCM-41 as catalyst. [d] reaction temperature 78 ºC. [e] reaction temperature 82 ºC.

Figure. Cascade reaction for the ether formation of ether **9** from aldehyde **7** in the presence of 50 mg of Zr-Beta and 50 and 100 mg of Sn-Beta.



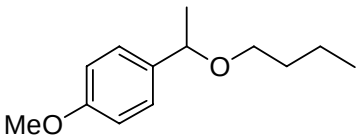
4-Methoxybenzyl *n*-butyl ether (3a).[1]



MS *m/z* (%): 194 (20) $[M]^+$, 77 (9), 78 (9), 121 (100), 122 (21), 137 (11).

^{1}H NMR[1] (300 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.45 (s, 2H), 3.81 (s, 3H), 3.46 (t, *J* = 6.6 Hz, 2H), 1.61−1.56 (m, 2H), 1.42−1.34 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR[1] (75 MHz, $CDCl_3$): δ = 159.1, 130.8, 129.1, 113.7, 72.4, 69.9, 55.2, 31.8, 19.4, 13.9.

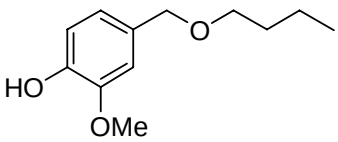
α-methyl-4-Methoxybenzyl *n*-butyl ether (3b).[2]



MS *m/z* (%): 208 (11) $[M]^+$, 91 (39), 119 (28), 134 (54), 135 (68), 137 (100), 193 (58).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.6 Hz, 2 H), 6.88 (d, *J* = 8.6 Hz, 2 H), 4.34 (q, *J* = 6.5 Hz, 1H), 3.81 (s, 3H), 3.27 (t, *J* = 6.6 Hz, 2H), 1.58–1.49 (m, 2H), 1.41 (d, *J* = 6.5, 3H), 1.38–1.30 (m, 2H), 0.88 (t, *J* = 7.3, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.8, 136.3, 127.3, 113.7, 77.3, 68.2, 55.2, 32.0, 24.1, 19.4, 13.9.

4-(butoxymethyl)-2-methoxyphenol (3c).[3]

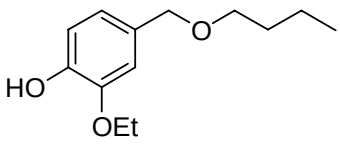


MS *m/z* (%): 210 (31) $[M]^+$, 65 (7), 93 (9), 94 (9), 106 (8), 122 (13), 123 (12), 125 (7), 137 (100), 138 (33).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.89–6.79 (m, 3H), 5.63 (s, 1H), 4.42 (s, 2H), 3.89 (s, 3H), 3.45 (t, *J* = 6.6 Hz, 2H), 1.64−1.54 (m, 2H), 1.45−1.33 (m, 2H), 0.92 (t, *J* = 7.3 Hz,

3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.3, 144.9, 130.4, 120.7, 113.8, 110.2, 72.6, 69.7, 55.6, 31.6, 19.2, 13.7.

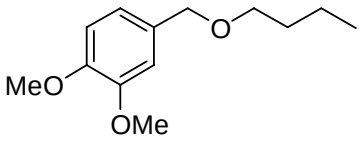
2-Ethoxy-4-butoxymethylphenol (3d).[4]



MS *m/z* (%): 224 (54) $[M]^+$, 77 (15), 93 (15), 106 (14), 111 (12), 122 (15), 123 (100), 124 (32), 151 (77), 152 (31).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.89–6.79 (m, 3H), 5.71 (brs, 1H), 4.40 (s, 2H), 4.11 (quart, *J* = 7.0 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 1.62 (sext., *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.38 (m, 2 H), 0.92 (t, *J* = 7.1 Hz, 3H).

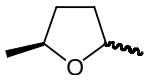
3,4-Dimethoxybenzyl *n*-butyl ether (3e).[5]



MS *m/z* (%): 224 (40) $[M]^+$, 106 (54), 107 (10), 121 (10), 137 (18), 139 (12), 151 (100), 152 (35), 167 (5), 225 (6).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.90–6.79 (m, 3H), 4.42 (s, 2H), 3.81 (s, 3H), 3.87 (s, 3 H), 3.85 (s, 3 H), 3.43 (t, *J* = 6.6 Hz, 2H), 1.58 (quint., *J* = 7.0, 2H), 1.37 (sext., *J* = 7.4, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.7, 148.2, 131.0, 119.8, 110.8, 1107, 72.4, 69.7, 55.6, 55.5, 31.5, 19.1, 13.6.

2,5-dimethyltetrahydrofuran (6), (mixture of *cis* and *trans* isomers)**.**[6]

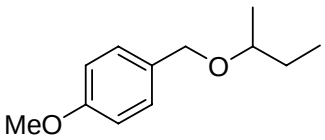


Mass spectroscopy and NMR spectroscopy confirmed the identity of the compounds.

MS *m/z* (%): isomer 1: 100 (11) $[M]^+$, 39 (17), 41 (61), 43 (47), 45 (18), 55 (17), 56 (86), 57 (24), 67 (23), 86 (100). isomer 2: 100 (16) $[M]^+$, 39 (19), 41 (68), 43 (52), 45 (19), 55 (18), 56 (91), 57 (26), 67 (25), 86 (100).

^{1}H NMR[6] (300 MHz, $CDCl_3$; mixture of isomers): δ = 4.11 (m, 2 H), 3.89 (m, 2 H), 2.02 (m, 2 H), 1.93 (m, 2 H), 1.43 (m, 4 H), 1.21 (d, J = 6.1 Hz, 6 H), 1.17 (d, J = 6.1, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$; mixture of isomers): δ = 75.3, 74.4, 34.1, 33.0, 21.4.

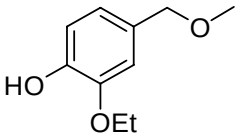
4-Methoxybenzyl *sec*-butyl ether (9).[7]



MS *m/z* (%): 194 (13) $[M]^+$, 77 (8), 78 (8), 109 (7), 121 (100), 122 (16).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.49 (d, *J* = 11.4 Hz, 1H), 4.40 (d, *J* = 11.4 Hz, 1H), 3.79 (s, 3H), 3.39 (sept., *J* = 6.1 Hz, 1H), 1.58−1.55 (m, 1H), 1.54−1.42 (m, 1H), 1.18 (d, *J* = 6.1 Hz, 3H), 1.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 131.3, 129.1, 113.7, 75.8, 69.9, 55.2, 29.2, 19.2, 9.8.

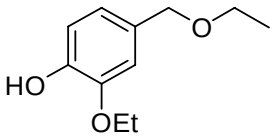
2-Ethoxy-4-methoxymethylphenol (10a).[8]



MS *m/z* (%): 182 (73) $[M]^+$, 65 (16), 122 (16), 123 (100), 124 (14), 137 (17), 151 (47), 153 (25).

^{1}H NMR[8] (300 MHz, $CDCl_3$): δ = 6.90–6.79 (m, 3H), 5.69 (s, 1H), 4.36 (s, 2H), 4.12 (quart, *J* = 7.0 Hz, 2H), 3.35 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 145.4, 144.9, 129.6, 120.6, 113.6, 111.0, 74.3, 64.0, 58.1, 14.5.

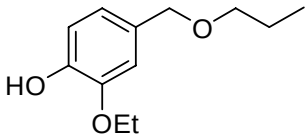
2-Ethoxy-4-ethoxymethylphenol (10b).[8]



MS *m/z* (%): 196 (72) $[M]^+$, 65 (13), 93 (21), 106 (12), 111 (14), 122 (14), 123 (100), 124 (32), 151 (61), 152 (18).

^{1}H NMR[8] (300 MHz, $CDCl_3$): δ = 6.90–6.79 (m, 3H), 5.69 (s, 1H), 4.41 (s, 2H), 4.12 (quart, *J* = 7.0 Hz, 2H), 3.51 (quart., *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.4, 144.9, 130.0, 120.6, 113.6, 111.0, 72.3, 65.0, 64.0, 14.8, 14.5.

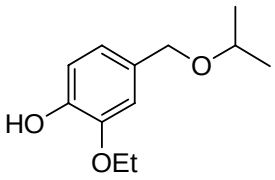
2-Ethoxy-4-propoxymethylphenol (10c).[9]



MS *m/z* (%): 210 (52) $[M]^+$, 93 (19), 111 (14), 122 (19), 123 (100), 124 (31), 151 (69), 152 (21).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.89–6.79 (m, 3H), 5.66 (s, 1H), 4.41 (s, 2H), 4.12 (quart, *J* = 7.0 Hz, 2H), 3.40 (t, *J* = 6.7 Hz, 2H), 1.62 (sext., *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.6, 144.9, 130.3, 120.6, 113.1, 111.1, 72.6, 71.5, 64.2, 22.7, 14.7, 10.4.

2-Ethoxy-4-isopropoxymethylphenol (10d).[9]



MS *m/z* (%): 210 (46) $[M]^+$, 93 (26), 111 (21), 122 (19), 123 (100), 124 (36), 151 (60), 152 (29).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.90–6.79 (m, 3H), 5.66 (s, 1H), 4.41 (s, 2H), 4.12 (quart, *J* = 7.0 Hz, 2H), 3.66 (hept, *J* = 6.1 Hz, 1H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.20 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.6, 144.9, 130.7, 120.5, 113.7, 111.1, 70.3, 69.8, 64.2, 21.9, 14.7.

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