Synthesis D. Sang et al. Paper

Cleavage of Catechol Monoalkyl Ethers by Aluminum Triiodide–Dimethyl Sulfoxide

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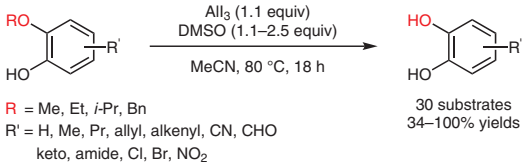

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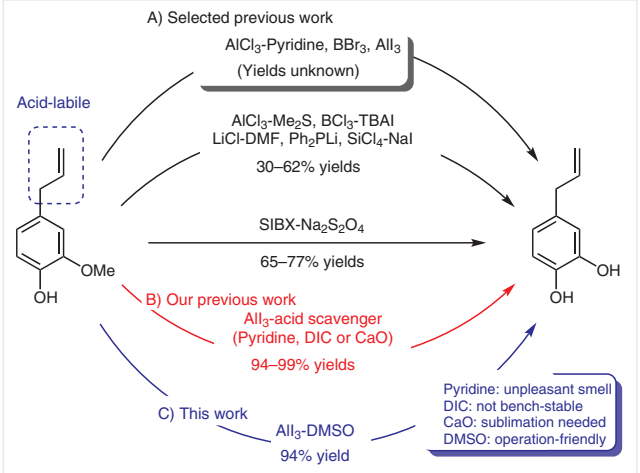
Abstract Using eugenol and vanillin as model substrates, a practical method is developed for the cleavage *o*-hydroxyphenyl alkyl ethers. Aluminum oxide iodide (O=AlI), generated in situ from aluminum triiodide and dimethyl sulfoxide, is the reactive ether cleaving species. The method is applicable to catechol monoalkyl ethers as well as normal phenyl alkyl ethers for the removal of methyl, ethyl, isopropyl, and benzyl groups. A variety of functional groups such as alkenyl, allyl, amide, cyano, formyl, keto, nitro, and halogen are well tolerated under the optimum conditions. Partial hydrodebromination was observed during the demethylation of 4-bromoguaiacol, and was resolved using excess DMSO as an acid scavenger. This convenient and efficient procedure would be a practical tool for the preparation of catechols.

Key words acid scavenger, aluminum oxide iodide, demethylation, eugenol, hydrodebromination

Plant produces abundant catechol monoalkyl ethers such as capsaicin, eugenol, guaiacol, vanillin, and lignin. Deprotection of these phytochemicals affords catechols of synthetic or biological usefulness, or can be used as adhesive additives. A lot of methods have been developed to this end,[1–4] however, only a few are satisfactory for the cleavage of complex *o*-hydroxyphenyl alkyl ethers bearing acid-labile functional groups.[5,6] Demethylation of eugenol (4-allyl-2-methoxyphenol), for instance, is challenging as the allyl side-chain is susceptible to mineral acid treatments. Halogenated Lewis acids (MX_n), on the other hand, tend to deprotonate the phenolic hydroxyl group by releasing hydrogen halide as a by-product, which would adversely affect the deprotection. The Lange method (aluminum trichloride-pyridine in chlorinated alkanes),[7,8] BBr_3,[9] and AlI_3[10] had been used for this conversion either without mentioning the yields, or the product was not chemically pure[11] (Scheme 1, A). Other reagents, such as $AlCl_3$–Me_2S,[12] BCl_3–TBAI (TBAI = tetrabutylammonium iodide),[13] LiCl in hot DMF,[14,15] and Ph_2PLi[16] gave hydroxychavicol (4-allylcatechol) in ~40% yield. An improved deprotection using $SiCl_4$–NaI delivered the product in 62% yield.[17] A more efficient demethylation involved a two-stage oxidation-reduction process using stabilized 2-iodoxybenzoic acid (SIBX) and sodium dithionite, and the yield was improved to around 70%.[18–21] Interestingly, whereas AlI_3 and BCl_3–TBAI had been applied to effect the transformation, an attempted demethylation of eugenol with AlI_3–TBAI[22,23] gave 4-propylcatehchol as the sole product.[24]



Scheme 1 Selected methods for the demethylation of eugenol

We have recently improved this transformation by adding pyridine,[25] 1,3-diisopropylcarbodiimide (DIC),[26,27] or calcium oxide[28] as an acid scavenger (Scheme 1, B). During the study, we realized that two out of the three iodide ions in AlI_3 were not fully exploited in ether cleavage, which might be replaced by cheaper heteroatoms. We describe

herein that aluminum oxide iodide, generated in situ from AlI_3 and DMSO, could be used in cleaving catechol monoalkyl ethers as well as typical aryl alkyl ethers bearing various functional groups (Scheme 1, C).

Aluminum oxide iodide is likely involved, though not sepcifically demonstrated, in a number of aluminum triiodide-mediated deoxygenation reactions such as ketoximes,[29] oxiranes,[30] sulfoxides,[31] and *N*-heteroarene *N*-oxides.[32] We selected to deoxygenate DMSO for its ready availability and ease of removal. Thus DMSO was transformed into dimethyl sulfide when treated with equimolar quantity of AlI_3 for 0.5 hour at 80 °C, as indicated by the NMR spectra recorded in CD_3CN (Figure 1). The Me_2S proton appeared at 2.02 ppm[33] in the ^1H NMR spectrum (A), and the methyl carbon appeared at 17.02 ppm in the ^{13}C NMR spectrum (B) without noticeable residual DMSO, suggesting that a clean conversion had occurred.

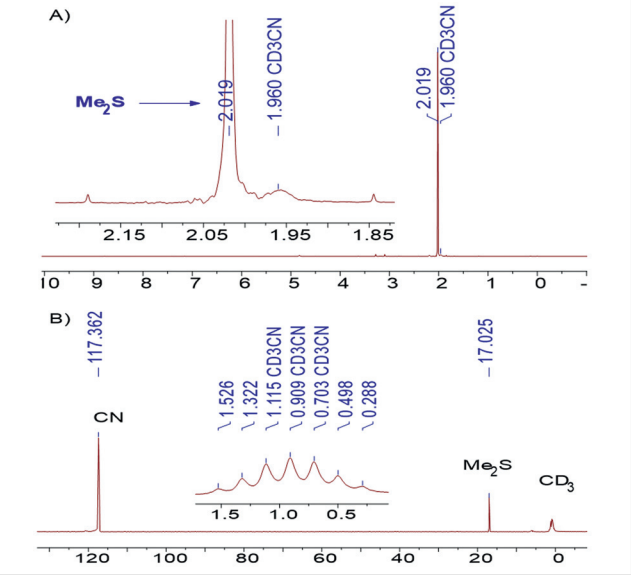
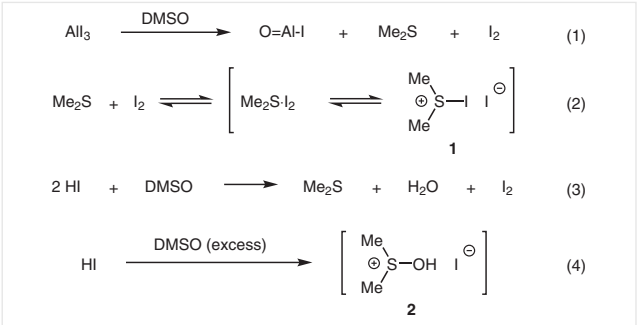


Figure 1 Deoxygenation of DMSO by aluminum triiodide in CD_3CN for 0.5 hour at 80 °C

The in situ generated Me_2S and iodine (Scheme 2, eq 1) existed probably as $Me_2S{\cdot}I_2$ complex, or in the form of ion pair (**1**, Scheme 2, eq 2). Coincidently, DMSO has been used in the oxidation of HI that affords iodine and water (Scheme 2, eq 3).[34–38] Similarly, the analogous sulfonium chloride and bromide were proposed as intermediates in the oxidative dissolution of silver in DMSO-HX systems.[39] Since water would deplete the ether cleaving agent and lead to side-reactions, it seemed unsuitable to use DMSO as the acid scavenger in aluminum triiodide-mediated ether cleavages. We tentatively reasoned that the oxidation process might be interrupted by excess DMSO to give hydroxydimethyl sulfonium iodide (**2**) without the generation of water (Scheme 2, eq 4).



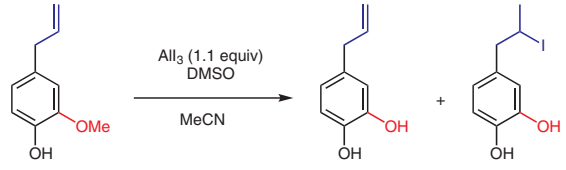
Scheme 2 In situ generation of aluminum oxide iodide

To validate this hypothesis, demethylation eugenol (**3**) was conducted by adding deuterated DMSO to a suspension of aluminum triiodide in hot acetonitrile followed by eugeol. The product was analyzed to be a mixture of hydroxychavicol (**4**) and 4-(2-iodopropyl)catechol (**5**) in a ratio **5**/**4** = 1:14 (Table 1, entry 1). The formation of **5** was due to hydroiodination of **4**, a side-reaction that needed to be avoided. In consideration that **4** could be purified conveniently by sublimation, and encouraged by this result, we turned to use commercial anhydrous DMSO (sealed with 4 Å molecular sieves). Unfortunately, the ratio dropped to 1:3.7 (entry 2). The conversion could not be improved by lowering the temperature (entry 3). Thus, the amount of DMSO was increased gradually from 1.5 to 5.0 equivalents (entry 4–10), and as expected the proportion of the adduct decreased accordingly. When excess DMSO (above 2.2 equiv) was used, adduct **5** was no longer observed (entry 6–10). The results imply that DMSO is indeed an effective HI scavenger in preventing hydroiodination of the allyl side-chain in eugenol (**3**). The yield of **4** decreased slightly with the increase in the amount of DMSO, and may be due to residual water in the DMSO.

To demonstrate the practicality of this method, the transformation was scaled up to 35 mmol. However, adduct **5** was again observed (Table 1, entry 11). This result suggests that DMSO is not as efficient as pyridine[25] or carbodiimides[26] in scavenging HI. While it was possible to increase the DMSO amount, we tried to add eugenol in a dropwise manner. As expected, catechol **4** was isolated in 94% yield without noticeable adduct **5** through this manoeuver (entry 12).

Vanillin (**6a**) was selected by Lange as a model substrate in the development of the aluminum trichloride–pyridine system for cleaving *o*-hydroxyphenyl methyl ethers.[7] We also tried to deprotect **6a** under the optimum conditions. Protocatechualdehyde (**7a**) was obtained in 87–91% yields with the highest yield obtained when 1.1 equivalents of DMSO was used (Table 2, entries 1–3). The reaction was efficient as well when performed on a 35 mmol scale, and gave **7a** in 91% yield (entry 4). The results suggest that excess DMSO is unnecessary for typical catechol monomethyl

Table 1 Optimization of Conditions and Large-Scale Preparation



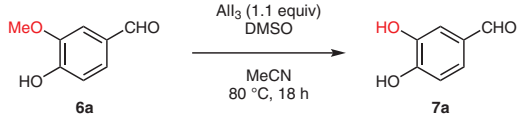
3 4 5

Entry	DMSO (equiv)	Temp (°C)	Time (h)	**5**/**4**
1[a]	1.1	80	18	1:14
2	1.1	80	18	1:3.7
3[b]	1.1	r.t.	18	1:3.2
4	1.5	80	18	1:4.8
5	2.0	80	18	1:34
6	2.2	80	18	0:1
7[c]	2.5	80	18	0:1
8	3.0	80	3	0:1
9	4.0	80	18	0:1
10	5.0	80	18	0:1
11[d]	2.5	80	18	1:16
12[c,d,e]	**2.5**	**80**	**18**	**0:1**

[a] DMSO-d_6 was used.
[b] Incomplete conversion.
[c] Product **4** was isolated in 94% yield.
[d] On a 35 mmol (5 g) scale.
[e] Eugenol was dissolved in MeCN (20 mL), and the solution was added dropwise to the reaction mixture over a period of 1 h.

ethers unless acid-labile functional groups are incorporated. Thus, stoichiometric DMSO was used to facilitate formation of aluminum oxide iodide (1.1 equiv) during the cleavage of other ethers, unless otherwise stated.

Table 2 Effect of DMSO on Demethylation of Vanillin and Large-Scale Preparation[a]

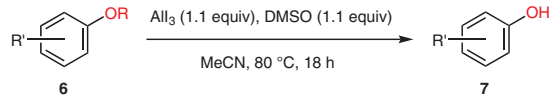


6a **7a**

Entry	DMSO (equiv)	Time (h)	Yield **7a** (%)
1	1.1	2	91
2	0	5	87
3	2.5	5	89
4	**1.1**	**18**	**91**[b]

[a] Isolated yield.
[b] On a 35 mmol (5 g) scale.

Table 3 Substrate Scope and Limitations[a]



6 **7**

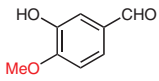
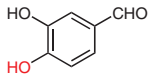
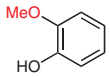
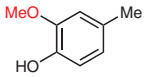
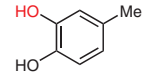
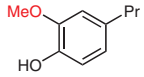
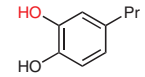
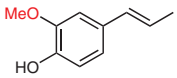
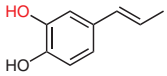
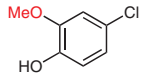
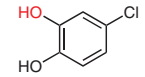
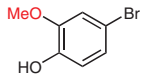
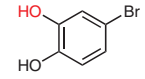
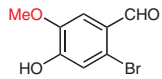
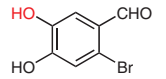
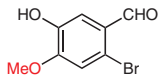
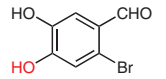
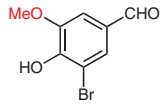
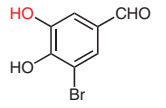
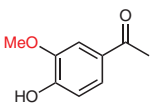
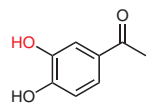
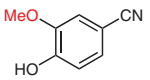
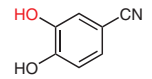
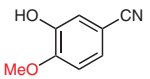
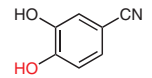
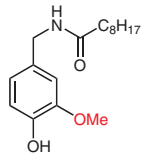
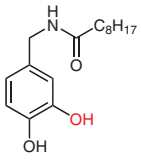
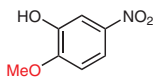
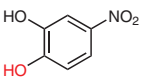
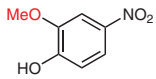
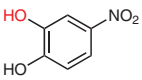
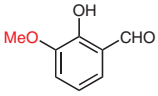
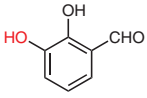
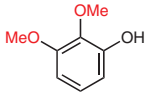
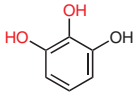
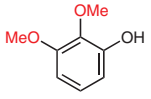
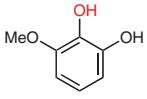
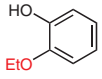
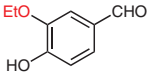
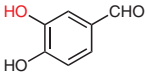
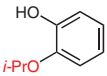
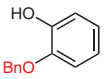
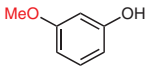
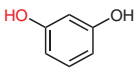
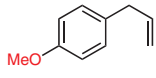
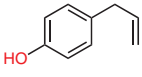
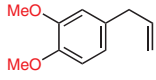
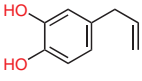
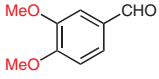
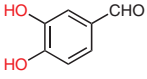
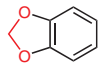
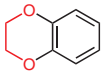
Substrate	**6**	Product	**7**	Yield (%)
	**6a′**		**7a**	95
	**6b**		**7b**	92
	**6c**		**7c**	96
	**6d**		**7d**	96
	**6e**		**7e**	43[b] (0)[c]
	**6f**		**7f**	100
	**6g**		**7g**	87[b]
	**6h**		**7h**	85
	**6h′**		**7h**	84
	**6i**		**7i**	96
	**6j**		**7j**	91[b]
	**6k**		**7k**	95
	**6k′**		**7k**	97

Table 3 (continued)

Substrate	6	Product	7	Yield (%)
	**6l**		**7l**	86
	**6m**		**7m**	65
	**6m′**		**7m**	51
	**6n**		**7n**	67[d] (37)[c]
	**6o**		**7o**	50[e]
	**6o**		**7p**	39[f]
	**6p**		**7b**	95
	**6q**		**7a**	95
	**6r**		**7b**	90
	**6s**		**7b**	93
	**6t**		**7q**	78, 34[g] (18)[c]
	**6u**		**7r**	89 (71)[c]
	**6v**		**4**	96
	**6w**		**7a**	91 (73)[c]
	**6x**		**7b**	64
	**6y**		**7b**	–

[a] Isolated yield.
[b] Excess DMSO (2.5 equiv) was used.
[c] Our reported yield using AlI_3–CaO system.[28]
[d] Excess AlI_3 (2.2 equiv) and DMSO (2.2 equiv) were used.
[e] The reaction mixture was stirred for 2 d at r.t., and **7p** was also isolated in 24%.
[f] The reaction mixture was stirred for 1 h at r.t., and **7o** was also isolated in 47%.
[g] Equimolar amount of aluminum oxide iodide was used, and the yield of **7q** was increased to 76% after stirring for 2 d.

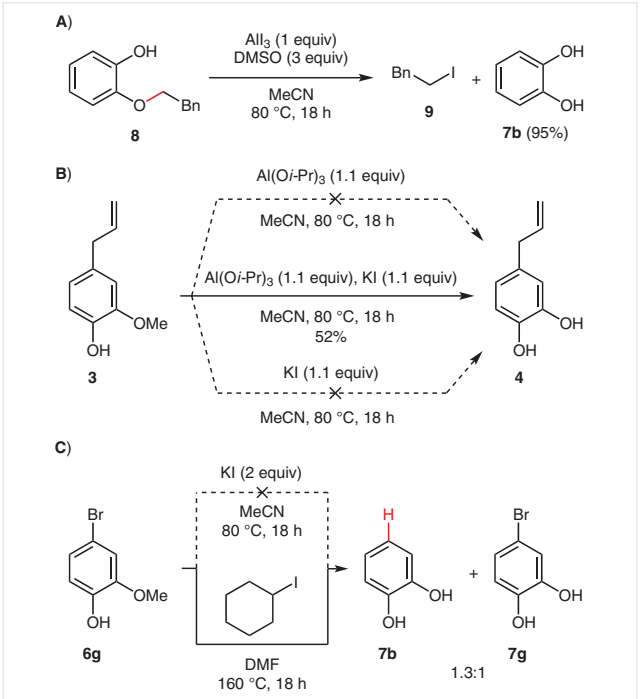
With the optimum conditions in hand, the substrate scope and limitations were then explored using the in situ generated aluminum oxide iodide. The results are summarized in Table 3. Isovanillin (**6a′**), guaiacol (**6b**), and 4-alkylguaiacols **6c**,**d** were demethylated in excellent yields. Isoeugenol (**6e**) was transformed into 4-propenylcatechol (**7e**) in 43% isolated yield in the presence of excess DMSO, suggesting that the propenyl group is more susceptible to hydroiodation than allyl group, and that DMSO is less efficient in trapping HI than carbodiimides.[26] 4-Chloro-2-methoxyphenol (**6f**) was demethylated in quantitative yield. Surprisingly, deprotection of 4-bromo-2-methoxyphenol (**6g**) by aluminum oxide iodide gave a mixture of 4-bromocatechol (**7g**) and catechol (**7b**) in a ratio **7g**/**7b** = 1:2 under current conditions. When treated with AlI_3 alone in hot acetonitrile in the absence of DMSO and other acid scavengers, a similar distribution of mixture was observed. Finally, the hydrodebromination was suppressed using excess DMSO (2.5 equiv) that furnished **7g** in 87% isolated yield. Three other halogenated compounds **6h–i** gave the corresponding halogenated catechols under the optimum conditions in good to excellent yields. Excess DMSO (2.5 equiv) was required in the demethylation of acetovanillone (**6j**). Without the additional DMSO, deprotection of **6j** by aluminum oxide iodide resulted in a complex mixture of products. Substrates with other electron-withdrawing groups, such as cyano (**6k**, **6k′**), amide (**6l**), and nitro (**6m**, **6m′**) were also examined, and the corresponding catechols were obtained in fair to excellent yields. Excess aluminum oxide iodide (2.2 equiv) was employed in the demethylation of *o*-vanillin (**6n**), and 3,4-dihydroxybenzaldehyde (**7n**) was obtained in 67% yield along with unidentified polar by-products. Demethylation of 2,3-dimethoxyphenol (**6o**) afforded a mixture of pyrogallol (**7o**) and 3-methoxycatechol (**7p**). When performed at room temperature for 2 days, the two products were isolated in 50% and 24%, respectively. The yield of **7p** was improved to 39% along with **7o** (47%) when performed at room temperature for 1 hour.

Sterically hindered alkyl groups such as ethyl (**6p** and **6q**) and isopropyl (**6r**) were also cleaved efficiently. The method was effective in removing benzyl (**6s**) as well. Interestingly, *m*-methoxyphenol (**6t**) was also demethylated by aluminum oxide iodide (1.1 equiv) that afforded resorcinol (**7q**) in 78% yield. When equimolar quantity of aluminum oxide iodide was used, a longer reaction time (2 d) was required to reach a similar conversion. The slow transformation of **6t** could be attributed to the absence of neighboring group participation effect.

Other phenyl alkyl ethers such as 4-allylanisole (**6u**), eugenol methyl ether (**6v**), eugenol methyl ether (**6w**), and 1,3-benzodioxole (**6x**) were deprotected as well to furnish the pertinent phenols in good yields. Unexpectedly, 1,4-benzodioxane (**6y**) remained intact under these conditions, although it was known that 2-ethyl-5,6,7,8-tetrafluorobenzo-1,4-dioxane could be cleaved successfully by AlI_3.[40]

Some of these substrates had been deprotected by our group using the AlI_3–CaO system.[28] A comparison showed that **6a**, **6a′**, **6j**, **6k**, **6k′**, **6l**, **6m**, **6q**, and **6r** were deprotected as efficiently by the two methods. These results imply that the ether cleaving agent in the AlI_3–CaO system might also be aluminum oxide iodide, which is formed via double displacement reaction between AlI_3 and CaO.[28] The ether cleaving efficiency of AlI_3–DMSO is higher than that of AlI_3–CaO toward substrates **6e**, **6n**, **6t**, and **6w**. This is probably because DMSO is more soluble in acetonitrile than CaO, which makes DMSO more efficient in scavenging HI.

The exhaustive deprotection of catechol dimethyl ethers and 1,3-benzodioxole **6v–x** by stoichiometric amount of aluminum oxide iodide was out of expectation, since aluminum oxide iodide contains only one iodide ion as a nucleophile for trapping of two leaving methyl groups. Three possibilities are proposed: (i) phenolated aluminum oxide oxygen as the nucleophile; (ii) additional aluminum oxide iodide was formed from the regenerated iodine (Scheme 2, eq 1) and the excess aluminum powder; and (iii) ion pair **1** (Scheme 2, eq 2) as the nucleophile. To exclude the phenolated aluminum oxide oxygen as the nucleophile, 2-phenethoxyphenol (**8**)[41] was subjected to aluminum oxide iodide treatment in consideration that 2-phenylethanol would otherwise be formed via insertion of Al=O bond to the ethereal C–O bond and acidic work-up (Scheme 3, A). As a result, phenethyl iodide (**9**) was generated along with catechol (**7b**; 95%) and an unidentified by-product without any detectable amount of 2-phenylethanol. Thus, it was concluded that the phenethyl chain was cleaved by iodide ion and not by the phenolated aluminum oxide oxygen. It is arguable, though, that the in situ generated 2-phenylethanol was iodinated prior to work-up. It is less likely that aluminum iodides (AlI_3 or O=AlI) would be regenerated from excess aluminum powder and dimethyl sulfide iodine complex **1**, since an effort to minimize iodine dosage by 2/3 failed to drive the demethylation of eugenol **3** to completion. Hence it is reasoned that dimethyl sulfide iodine complex **1**, in its ion pair form, served as the second equivalent of nucleophile in the demethylation transformations.

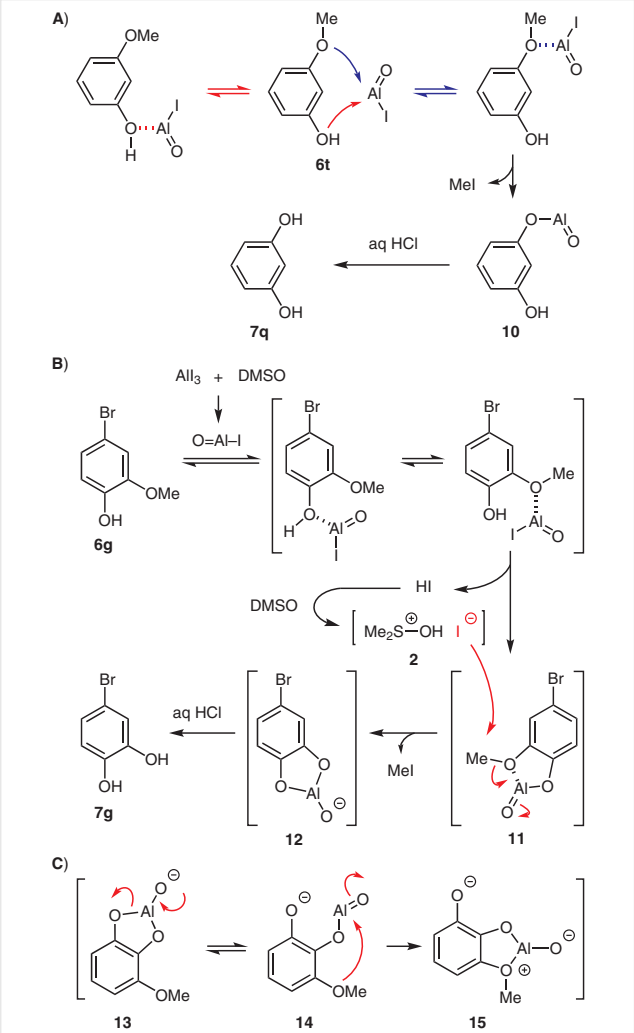


Scheme 3 Control experiments

Deprotonation of the catechol monomethyl ethers by aluminum oxide iodide would lead to oxoaluminum phenolate (Ar–O–Al=O), which might exist as its oligomers. Thus, a control experiment was conducted using in situ generated diisopropoxyaluminum moiety Al(O*i*-Pr)$_2$ to mimic the demethylation intermediate. It was reasoned that the stronger acidity of phenol (compared to *i*-PrOH) would facilitate ligand exchange with aluminum isopropoxide to give the aluminum phenolate and isopropanol. Thus, eugenol (**3**) was treated with Al(O*i*-Pr)$_3$ (1.1 equiv) in hot acetonitrile for 18 hours (Scheme 3, B). When potassium iodide (1.1 equiv) was added to the same conditions, hydroxychavicol (**4**) was isolated in 52% yield. Eugenol remained intact when treated by either KI or Al(O*i*-Pr)$_3$ alone. This result is in accordance with the above reasoning that iodide ion is necessitated in the ether cleaving reactions.

To confirm that the protodebromination side-reaction was mediated by the in situ generated HI, substrate **6g** was subject to cyclohexyl iodide (5 equiv) treatment in refluxing DMF, a condition known to release HI.[42] As expected, a mixture of **7b** and **7g** was generated in a ratio **7b**/**7g** = 1.3:1 (Scheme 3, C). The methyl group was cleaved by the in situ generated HI. Comparatively, no conversion occurred when **6g** was treated by potassium iodide (2 equiv) alone in acetonitrile for overnight at 80 °C.

The accomplished demethylation of *m*-methoxyphenol (**6t**) by stoichiometric quantity of aluminum oxide iodide implied that both the methoxy and the phenolic hydroxyl group of *m*-methoxyphenol (**6t**) would coordinate with the Lewis acidic center in a reversible manner in acetonitrile (Scheme 4, A). When the ether oxygen was trapped by the Lewis acid, the Me–O bond was then activated and deprotected to afford aluminum phenolate **10**, which was then acidified to provide resorcinol (**7q**).



Scheme 4 Proposed ether cleaving mechanism

For the demethylation of catechol monomethyl ethers, either the hydroxyl or the methoxy oxygen would coordinate to the Lewis acid to form a complex, which would then condense to release HI as a by-product upon the facilitation of neighboring group participation effect. Thus the demethylation of 4-bromo-2-methoxyphenol (**6g**) is visualized as proceeding through the following sequence (Scheme 4, B). Oxidation of aluminum triiodide by DMSO affords aluminum oxide iodide and dimethyl sulfide–iodine complex. Deprotonation of catechol monomethyl ether **6g** by aluminum oxide iodide gives aluminum phenolate **11** and HI. HI thus formed is subsequently trapped by excess DMSO to give ion pair **2**. Coordination of the methoxy oxygen to the adjacent aluminum center makes the Me–O bond polarized, which then undergoes nucleophilic attack by an iodide ion (**1** or **2**) to give a five-membered intermediate **12**. Acidification of **12** furnishes catechol **7g**.

The demethylation of 2,3-dimethoxyphenol (**6o**) by aluminum oxide iodide may be affected by solvent effect. Acetonitrile facilitates the ring-opening of intermediates **13** to afford intermediate **14** (Scheme 4, C). The methoxy of **14** was then activated by the neighboring aluminum phenolate moiety, and gave the corresponding five-membered intermediate **15**, which then afforded **7o**. To support this hypothesis, deprotection of **6o** was also performed in cyclohexane using equimolar amount of aluminum oxide iodide. As expected, 3-methoxycatechol (**7p**) was obtained solely, albeit in a lower yield (20%).

In summary, aluminum oxide iodide reagent system is efficient in cleaving catechol monoalkyl ethers as well as typical alkyl phenyl ethers. Methyl and hindered alkyl groups such as ethyl, isopropyl, benzyl, and 2-phenylethyl groups could be cleaved conveniently by this reagent. Various functional groups, such as methyl, propyl, allyl, alkenyl, cyano, formyl, keto, halogen atom, and nitro are well tolerated. For substrates bearing acid-labile groups such as allyl and bromine, excess DMSO should be used as an acid scavenger to facilitate the deprotection by complexing with the in situ generated hydrogen iodide. The successful deprotection of 3-methoxyphenol by equimolar amount of aluminum oxide iodide suggested that phenolic hydroxyl and methoxy group might coordinate to the Lewis acid reversibly prior to deprotection. The exhaustive demethylation of catechol dimethyl ethers suggested that the in situ generated dimethyl sulfide–iodine complex might serve as a nucleophile in ether cleavage. Solvent effect was observed during the deprotection of 2,3-dimethoxyphenol. The HI mediated hydrodebromination reaction is currently under investigation and will be disclosed in due course.

All reagents and solvents were purchased and used as received without further purification. MeCN was of HPLC grade with less than 500 ppm of H_2O. DMSO was of SafeDry grade and was stored over 4 Å MS. AlI_3 (5.5 mmol) was prepared in situ by mixing slight excess of Al powder (~0.4 g) and I_2 (~2.095 g) in hot MeCN (40 mL) for about 0.5–3 h till the color of I_2 faded.[26] TLC analyses were performed on precoated GF254 silica gel plates and were visualized under UV 254 nm light or by I_2 staining. NMR spectra were recorded using a Bruker Avance-400 FTNMR spectrometer with TMS as the internal standard. Column chromatography was carried out using 300–400 mesh silica gel. Melting points were uncorrected. PE: petroleum ether (60–90 °C).

Cleavage of Catechol Monoalkyl Ethers by Aluminum Triiodide–Dimethyl Sulfoxide; General Procedure

To a suspension of AlI_3 (5.5 mmol, 1.1 equiv) in MeCN was added anhyd DMSO (0.430 g, 5.5 mmol, 1.1 equiv). After stirring for 0.5 h at 80 °C, the selected substrate (5 mmol) was added in one portion. The mixture was stirred overnight (18 h) at that temperature before quenching with aq 2 M HCl (10 mL). After extraction with EtOAc (3 × 50 mL), the organic phases were combined, washed with sat. aq $Na_2S_2O_3$ and brine, and dried ($MgSO_4$). The solvents were removed on a rotary evaporator, and the residue was purified by column chromatography to give the relevant catechol or phenol.

Hydroxychavicol (4-Allylcatechol; 4)

[CAS Reg. No. 1126-61-0]

From eugenol (**3**) using excess DMSO (2.5 equiv); yield: 0.712 g (94%); mp 44–46 °C (Lit.[26] mp 45–46 °C); R_f = 0.38 (PE/EtOAc 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79 (d, J = 8.0 Hz, 1 H), 6.71 (d, J = 2.0 Hz, 1 H), 6.62 (dd, J_1 = 8.1 Hz, J_2 = 2.0 Hz, 1 H), 5.92 (ddt, J_1 = 16.9 Hz, J_2 = 10.1 Hz, J_3 = 6.7 Hz, 1 H), 5.38 (br s, 2 H), 5.08-5.02 (m, 2 H), 3.26 (d, J = 6.4 Hz, 2 H).

From eugenol (**3**) with Al(O*i*-Pr)$_3$ (1.1 equiv) and KI (1.1 equiv); yield: 0.391 g (52%).

From eugenol methyl ether (**6v**); yield: 0.723 g (96%); white solid.

Gram-Scale Synthesis of 4-Allylcatechol (4)

To a mixture of AlI_3 (38.5 mmol, 1.1 equiv) prepared in situ from Al powder (2.721 g) and I_2 (14.657 g, 57.75 mmol) in MeCN (250 mL) was added DMSO (6.836 g, 87.5 mmol, 2.5 equiv). The mixture was stirred for 0.5 h at 80 °C, before a solution of eugenol (**3**; 5.746 g, 35 mmol) in MeCN (20 mL) was added dropwise over 1 h. After stirring for 18 h at 80 °C, the reaction mixture was quenched with aq 2 M HCl (50 mL), and extracted with EtOAc (3 × 100 mL). The organic phases were combined, washed with sat. aq $Na_2S_2O_3$ and brine, and dried (anhyd $MgSO_4$). After filtration, the organic solvents were removed on a rotary evaporator, and the residue was purified through flash column chromatography (eluent PE/EtOAc 4:1) to give **4**; yield: 4.968 g (94%).

Protocatechualdehyde (7a)

[CAS Reg. No. 139-85-5]

From vanillin (**6a**): yield: 0.646 g (93%); yellow solid; mp 153.5–154.5 °C (Lit.[26] mp 155 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.13 (br s, 1 H), 9.70 (s, 1 H), 9.57 (br s, 1 H), 7.27 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1 H), 7.24 (d, J = 2.0 Hz, 1 H), 6.91 (d, J = 8.0 Hz, 1 H).

From vanillin (**6a**) using excess DMSO (2.5 equiv); yield: 0.615 g (89%).

From vanillin (**6a**) in the absence of DMSO; yield: 0.601 g (87%).

From isovanillin (**6a'**); yield: 0.658 g (95%).

From ethoxyvanillin (**6q**): yield: 0.662 g (95%); R_f = 0.28 (PE/EtOAc 1:1).

From 3,4-dimethoxybenzaldehyde (**6w**); yield: 0.630 g (91%); R_f = 0.07 (PE/EtOAc 3:1).

Gram-Scale Synthesis of Protocatechualdehyde (7a)

To a mixture of AlI_3 (38.5 mmol, 1.1 eq) prepared in situ from Al powder (2.205 g) and I_2 (14.655 g, 57.74 mmol) in MeCN (250 mL) was added DMSO (3.009 g, 38.51 mmol, 1.1 equiv). The mixture was stirred for 0.5 h at 80 °C, before vanillin (**6a**; 5.326 g, 35 mmol) was added in portions. After stirring for 18 h at 80 °C, the reaction mixture was quenched with aq 2 M HCl (50 mL), and extracted with EtOAc (3 × 100 mL). The organic phases were combined, washed with sat. aq $Na_2S_2O_3$ and brine, and dried (anhyd $MgSO_4$). After filtration, the organic solvents were removed on a rotary evaporator, and the residue was purified through flash column chromatography (eluent PE/EtOAc 11:9) to give **7a**; yield: 4.413 g (91%).

Catechol (7b)

[CAS Reg. No. 120-80-9]

From guaiacol (**6b**); yield: 0.512 g (92%); white solid; mp 103–103.5 °C (Lit.[26] mp 103.5–104.5 °C); R_f = 0.27 (PE/EtOAc 3:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.88 (br s, 2 H), 6.75 (dd, J_1 = 5.9 Hz, J_2 = 3.6 Hz, 2 H), 6.61 (dd, J_1 = 5.9 Hz, J_2 = 3.6 Hz, 2 H).

From 2-ethoxyphenol (**6p**); yield: 0.527 g (95%).

From 2-isopropoxylphenol (**6r**); yield: 0.499 g (90%); mp 101–102.5 °C.

From 2-benzoxyphenol (**6s**); yield: 0.513 g (93%); mp 103.5–104 °C.

From 1,3-benzodioxole (**6x**); yield: 0.355 g (64%).

From 2-phenethoxyphenol (**8**; 0.428 g, 2 mmol), reacted with AlI_3 (2 mmol) and DMSO (0.391 g, 5 mmol, 2.5 equiv); yield: 0.211 g (95%).

4-Methylcatechol (7c)

[CAS Reg. No. 452-86-8]

Yield: 0.598 g (96%); white solid; mp 66–66.5 °C (Lit.[43] mp 63.5–67 °C); R_f = 0.25 (PE/EtOAc 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.74 (d, J = 8.0 Hz, 1 H), 6.68 (d, J = 1.6 Hz, 1 H), 6.59 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 5.29 (br s, 2 H), 2.22 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.23, 140.96, 131.13, 121.51, 116.27, 115.34, 20.76.

4-Propylcatechol (7d)

[CAS Reg. No. 2525-02-2]

Yield: 0.736 g (96%); off-white solid; mp 57.5–58.5 °C (Lit.[44] mp 59–60 °C); R_f = 0.27 (PE/EtOAc 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.76 (d, J = 8.0 Hz, 1 H), 6.69 (d, J = 1.6 Hz, 1 H), 6.60 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 5.42 (br s, 2 H), 2.45 (t, J = 7.6 Hz, 2 H), 1.56 (h, J = 7.6 Hz, 2 H), 0.90 (t, J = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.19, 141.12, 136.20, 121.01, 115.67, 115.34, 37.34, 24.70, 13.81.

4-Propenylcatechol (7e)

[CAS Reg. No. 72898-29-4]

Yield: 0.300 g (43%); white solid; mp 97–98.5 °C (Lit.[26] mp 102–103 °C); R_f = 0.19 (PE/EtOAc 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.87 (d, J = 1.2 Hz, 1 H), 6.78–6.75 (m, 2 H), 6.26 (dq, J_1 = 16.0 Hz, J_2 = 1.6 Hz, 1 H), 6.05 (dq, J_1 = 16.0 Hz, J_2 = 6.8 Hz, 1 H), 5.24 (br s, 2 H), 1.83 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 3 H).

4-Chlorocatechol (7f)

[CAS Reg. No. 2138-22-9]

Yield: 0.723 g (~100%); white solid; mp 90.5–91.5 °C (Lit.[45] mp 89–91 °C): R_f = 0.27 (PE/EtOAc 3:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.40 (s, 1 H), 9.18 (s, 1 H), 6.74 (d, J = 2.5 Hz, 1 H), 6.72 (d, J = 8.4 Hz, 1 H), 6.64 (dd, J_1 = 8.4 Hz, J_2 = 2.5 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 146.84, 144.98, 122.56, 119.17, 116.99, 115.87.

4-Bromocatechol (7g)

[CAS Reg. No. 17345-77-6]

Yield: 0.826 g (87%); colorless solid; mp 83.5–84 °C (Lit.[46] mp 81–84 °C); R_f = 0.30 (PE/EtOAc 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00 (d, J = 2.3 Hz, 1 H), 6.92 (dd, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1 H), 6.73 (d, J = 8.4 Hz, 1 H), 5.67 (br s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.31, 142.62, 124.07, 118.68, 116.71, 112.67.

2-Bromo-4,5-dihydroxybenzaldehyde (7h)

[CAS Reg. No. 4815-99-0]

From 2-bromo-5-methoxy-4-hydroxybenzaldehyde (**6h**; 0.578 g, 2.5 mmol); yield: 0.466 g (85%); yellow solid; R_f = 0.50 (PE/EtOAc 1:1).

From 2-Bromo-4-methoxy-5-hydroxybenzaldehyde (**6h'**); yield: 0.915 g (84%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.67 (br s, 1 H), 9.95 (br s, 1 H), 9.95 (s, 1 H), 7.25 (s, 1 H), 7.05 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 190.45, 153.51, 146.10, 125.23, 119.98, 117.48, 115.52.

3-Bromo-4,5-dihydroxybenzaldehyde (7i)

[CAS Reg. No. 16414-34-9]

Yield: 1.044 g (96%); yellow solid; R_f = 0.25 (PE/EtOAc 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.47 (br s, 2 H), 9.70 (s, 1 H), 7.58 (d, J = 1.8 Hz, 1 H), 7.25 (d, J = 1.9 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 190.99, 149.78, 146.96, 129.45, 127.85, 113.15, 109.88.

3,4-Dihydroxyacetophenone (7j)

[CAS Reg. No. 1197-09-7]

Yield: 0.696 g (91%); yellow solid; mp 118–120 °C (Lit.[26] mp 117–118 °C); R_f = 0.55 (PE/EtOAc 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.61 (br s, 2 H), 7.42–7.23 (m, 2 H), 6.82 (d, J = 7.3 Hz, 1 H), 2.44 (s, 3 H).

4-Cyanocatechol (7k)

[CAS Reg. No. 17345-61-8]

From 2-methoxy-4-cyanophenol (**6k**); yield: 0.642 g (95%); white solid; mp 153.5–154.5 °C (Lit.[26] mp 154–154.5 °C); R_f = 0.44 (PE/EtOAc 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.78 (br s, 2 H), 7.11 (d, J = 8.0 Hz, 1 H), 7.06 (s, 1 H), 6.86 (d, J = 8.0 Hz, 1 H).

From 2-methoxy-5-cyanophenol (**6k'**); yield: 0.660 g (97%).

***N*-(3,4-Dihydroxybenzyl)nonanamide (7l)**

After column chromatography, the crude product was recrystallized from CH_2Cl_2 and cyclohexane; yield: 1.210 g (86%); off-white solid; mp 98–99.5 °C (Lit.[26] mp 99–100 °C); R_f = 0.33 (PE/EtOAc 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (s, 1 H), 6.85 (d, J = 2.0 Hz, 1 H), 6.80 (d, J = 8.0 Hz, 1 H), 6.62 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1 H), 6.16 (s, 1 H), 6.00 (t, J = 6.0 Hz, 1 H), 4.31 (d, J = 6.0 Hz, 2 H), 2.21 (t, J = 8.0 Hz, 2 H), 1.62 (quint, J = 7.6 Hz, 2 H), 1.34–1.16 (m, 10 H), 0.86 (t, J = 6.8 Hz, 3 H).

4-Nitrocatechol (7m)

[CAS Reg. No. 3316-09-4]

From 2-methoxy-5-nitrophenol (**6m**); yield: 0.510 g (65%); yellow solid; mp 174.5–175 °C (Lit.[26] mp 175.5–176 °C); R_f = 0.44 (PE/EtOAc 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.33 (br s, 2 H), 7.64 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1 H), 7.60 (d, J = 2.8 Hz, 1 H), 6.90 (d, J = 8.8 Hz, 1 H).

From 2-methoxy-4-nitrophenol (**6m'**); yield: 0.399 g (51%).

2,3-Dihydroxybenzaldehyde (7n)

[CAS Reg. No. 24677-78-9]

Yield: 0.232 g (67%); yellow solid; mp 105–106 °C (Lit.[26] mp 103.5–104 °C); R_f = 0.67 (PE/EtOAc 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.21 (s, 1 H), 10.00 (br s, 2 H), 7.13 (d, J = 8.0 Hz, 1 H), 7.07 (d, J = 8.0 Hz, 1 H), 6.80 (t, J = 8.0 Hz, 1 H).

Pyrogallol (7o)

[CAS Reg. No. 87-66-1]

Yield: 0.320 g (50%); yellow solid; mp 130–131 °C (Lit.[47] mp 132 °C); R_f = 0.17 (PE/EtOAc 2:1).

In this reaction, 3-methoxycatechol (**7p**) was also isolated (0.171 g, 24%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.57 (s, 3 H), 6.41 (dd, J_1 = 8.5 Hz, J_2 = 7.5 Hz, 1 H), 6.24 (d, J = 8.0 Hz, 2 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 146.70, 133.53, 118.87, 107.50.

3-Methoxycatechol (7p)

[CAS Reg. No. 934-00-9]

Yield: 0.278 g (39%); yellow viscous oil; R_f = 0.39 (PE/EtOAc 2:1).

In this reaction, pyrogallol (**7o**) was also isolated (0.300 g, 47%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (t, J = 8.3 Hz, 1 H), 6.60 (dd, J_1 = 8.3 Hz, J_2 = 1.3 Hz, 1 H), 6.47 (dd, J_1 = 8.2 Hz, J_2 = 1.4 Hz, 1 H), 5.53 (s, 2 H), 3.87 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.11, 144.10, 132.53, 119.85, 108.89, 103.23, 56.20.

Resorcinol (7q)

[CAS Reg. No. 108-46-3]

Yield: 0.432 g (78%); white solid; mp 106–108.5 °C (Lit.[26] mp 105–105.5 °C); R_f = 0.21 (PE/EtOAc 3:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.17 (br s, 2 H), 6.92 (t, J = 8.0 Hz, 1 H), 6.20 (s, 1 H), 6.19 (d, J = 8.0 Hz, 2 H).

When equimolar quantities of aluminum oxide iodide (5.5 mmol) and 3-methoxyphenol (0.691 g, 5.5 mmol) were used, the yield of **7q** turned to 0.287 g (46%) after stirring for 1 d, and 0.466 g (76%) for 2 d.

4-Allylphenol (7r)

[CAS Reg. No. 501-92-8]

Yield: 0.601 g (89%); yellow oil; R_f = 0.69 (PE/EtOAc 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (d, J = 8.5 Hz, 2 H), 6.77 (d, J = 8.5 Hz, 2 H), 5.94 (ddt, J_1 = 15.7 Hz, J_2 = 10.6 Hz, J_3 = 6.7 Hz, 1 H), 5.30 (s, 1 H), 5.04 (dt, J_1 = 16.4 Hz, J_2 = 1.6 Hz, 1 H), 5.03 (dt, J_1 = 10.8 Hz, J_2 = 1.6 Hz, 1 H), 3.31 (dt, J_1 = 6.6 Hz, J_2 = 1.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.64, 137.88, 132.38, 129.79, 115.57, 115.32, 39.38.

2-Phenethoxyphenol (8)

[CAS Reg. No. 33130-24-4]

A procedure for the preparation of alkyl aryl ethers was adopted.[48] Phenethyl bromide (1.853 g, 10 mmol), catechol (**7b**; 1.103 g, 10 mmol), and K_2CO_3 (2.075 g, 15 mmol) were added to MeCN (40 mL), and the mixture was stirred at 80 °C for 18 h before quenching with aq 2 M HCl (20 mL). After extraction with EtOAc (3 × 50 mL), the organic phases were combined, washed with brine, and dried (anhyd $MgSO_4$). After filtration, the solvents were removed on a rotary evaporator, and the residue was purified by column chromatography (eluent: PE/EtOAc 10:1) to afford the product as a colorless liquid; yield: 0.393 g (19%), which solidified after standing overnight at r.t.; mp 45–46 °C (Lit.[41] mp 48 °C); R_f = 0.54 (PE/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.20 (m, 5 H), 6.92–6.81 (m, 4 H), 5.50 (s, 1 H), 4.26 (t, J = 6.8 Hz, 2 H), 3.12 (t, J = 6.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.94, 145.63, 137.87, 128.89, 128.71, 126.76, 121.77, 120.12, 114.67, 112.16, 69.58, 35.78.

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Supporting Information

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