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Styryl ether formation from benzyl alcohols under transition-metal-free basic DMSO conditions†

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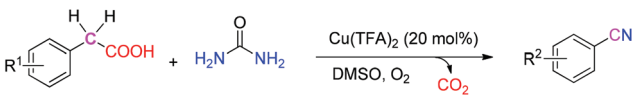
A phenol-catalyzed aerobic oxidative styryl ether formation method was developed with benzyl alcohol under basic DMSO. Styryl ether was obtained after 12 hours of heating at 60–80 °C where DMSO was involved in the reaction as the extra carbon source. Control experiments indicated that both phenol and DMSO are crucial for the success of the reaction. A variety of styryl ethers were prepared smoothly from benzyl alcohols in good to excellent yields in an environmentally friendly way.

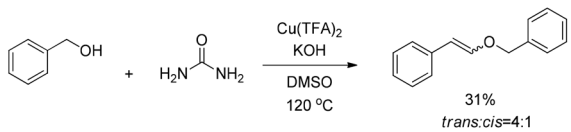
Environmentally benign reactions are desirable as people are paying more and more attention to environment protection. Among the 12 principles of green chemistry,[1–4] a metal-free, multi-component tandem oxidative reaction with O_2 as the oxidant involving common feedstock chemicals has a special attraction due to its potential to be transformative. Benzyl alcohol is an important synthetic feedstock for a broad range of functionalized, complex molecules. Among them, the selective oxidation of benzyl alcohol into benzaldehyde is especially attractive. Lately, significant progress has been made in tandem reactions based on the selective oxidation of benzaldehyde from benzyl alcohol.[5–8] Although numerous methods have been developed for the oxidation of benzyl alcohols into benzaldehydes in the presence of transition metals, practical and efficient methods with molecular oxygen as the oxidant in the absence of transition metals are still highly desirable. The use of molecular oxygen as an oxidant has attracted considerable attention owing to its abundance, low toxicity and environmentally benign nature.[9–14] Recently Li and He reported styryl ether formation from benzyl alcohol *via* Ag nanoparticle-catalyzed tandem aerobic oxidation.[15] A thorough mechanism study indicated that the Ag nanoparticle and oxygen are vital for the reaction, and DMSO provides a carbon in the final product.[16] While good efficiencies and selectivities were observed by Li and He, nanoparticles are notorious[17–19] for their irreproducibility because of their size-dependent reactivities. Significant research has been directed towards the development of metal-free oxidations because they are reproducible and generate less waste to result in a greener process, and tandem reaction which *in situ* traps the benzaldehyde from benzyl alcohol to form the product is thus more attractive. Here we would like to report a mild, simple and efficient time-controlled method to obtain styryl ether from benzyl alcohol under transition-metal-free aerobic oxidative conditions in basic DMSO.

Recently we developed a Cu-catalyzed aerobic oxidative C–N triple bond formation method *via* the decarboxylation of phenylacetic acids and urea (Scheme 1).[20] On the basis of the mechanism study and our recent related research, benzaldehydes are the key intermediates for this transformation. It is well-known that benzyl alcohol can be easily oxidized into aldehydes at various oxidative conditions. Our interest in copper-catalyzed aerobic oxidative tandem reaction prompted us to apply our conditions on benzyl alcohol to see if the same product could be obtained. In order to promote the oxidation of benzyl alcohol under copper-catalyzed aerobic conditions, KOH was added. To our surprise, instead of benzonitrile, an unexpected styryl ether was afforded in 31% yield as two isomers (Scheme 2).

This result astonished us. Further screening showed that copper salt and urea were unnecessary for this reaction (Table 1, entries 1–4). Interestingly, when phenol was added as a nucleophile, it was found to accelerate the reaction dramatically



Scheme 1 Synthesis of benzonitrile from copper-catalyzed aerobic oxidative decarboxylation of phenylacetic acids and urea.



Scheme 2 Styryl ether formed from benzyl alcohol under basic DMSO.

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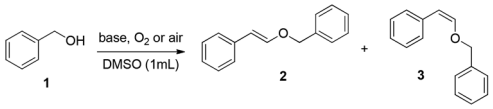
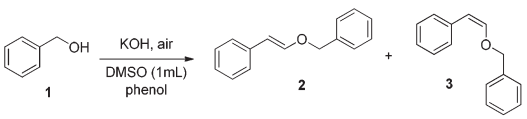
Table 1 Condition screening[a]



Entry	Atmosphere	Additive	Base	Temp (°C)	Time (h)	Yield (%)
1	O_2	Urea	KOH (2 equiv.)	130	9	31 (**2 : 3** = 4 : 1)
2	O_2	Urea	KOH (2 equiv.)	80	7	56
3	O_2	—	KOH (2 equiv.)	80	20	41
4	O_2	—	KOH (2 equiv.)	60	20	33
5	O_2	Phenol (1 equiv.)	KOH (3 equiv.)	80	12	92 (**2 : 3** = 5 : 1)
6	O_2	Phenol (1 equiv.)	KOH (3 equiv.)	80	9	85
7	O_2	Phenol (1 equiv.)	KOH (3 equiv.)	70	9	73
8	O_2	Phenol (1 equiv.)	KOH (2.5 equiv.)	80	12	64
9	O_2	Phenol (1 equiv.)	KOH (2 equiv.)	80	12	48
10	O_2	Phenol (1 equiv.)	KOH (1.5 equiv.)	80	12	No product
11	O_2	Phenol (20 mol%)	KOH (2.2 equiv.)	80	12	83
12	Air	Phenol (1 equiv.)	KOH (3 equiv.)	80	12	91
13	**Air**	**Phenol (20 mol%)**	**KOH (2.2 equiv.)**	**80**	**12**	**92 (2 : 3 = 92 : 8)**
14	Air	Phenol (20 mol%)	KOH (3 equiv.)	80	12	88
15	Air	Phenol (20 mol%)	NaOH (2.2 equiv.)	80	12	90
16	Air	Phenol (20 mol%)	Na_2CO_3 (2.2 equiv.)	80	12	No product
17	Air	Phenol (20 mol%)	KOBu-*t* (2.2 equiv.)	80	12	69
18	Air	Phenol (20 mol%)	NEt_3 (2.2 equiv.)	80	12	No product
19	Air	Phenol (20 mol%)	Pyridine (2.2 equiv.)	80	12	No product
20	N_2	Phenol (20 mol%)	KOH (2.2 equiv.)	80	12	No product

[a] Reaction conditions: benzyl alcohol (0.5 mmol), base, DMSO (1 mL) under corresponding atmospheres.

Table 2 Styryl ether formed from benzyl alcohol catalyzed by various phenols

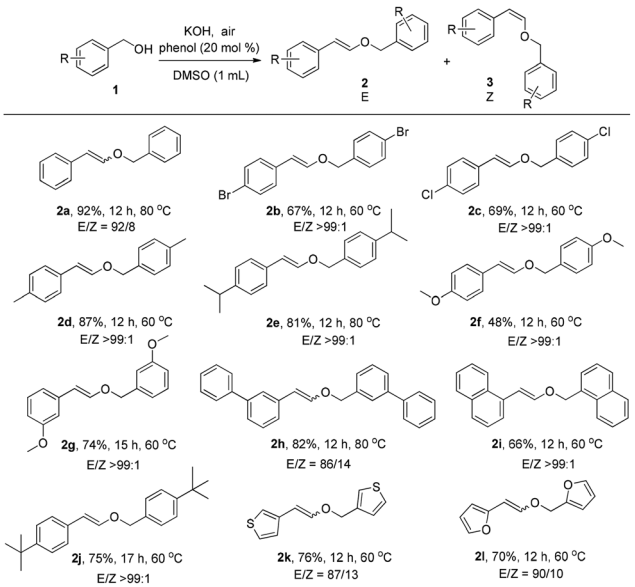


Entry	Oxidant	Additive	Base	Temp (°C)	Time (h)	Yield (%) (2 : 3)
1	Air	4-Me-phenol (20 mol%)	KOH (2 equiv. + 20 mol%)	80	12	82 (88 : 12)
2	Air	4-MeO-phenol (20 mol%)	KOH (2 equiv. + 20 mol%)	80	12	59 (79 : 21)
3	Air	4-F-phenol (20 mol%)	KOH (2 equiv. + 20 mol%)	80	12	90 (89 : 11)
4	Air	4-CF_3-phenol (20 mol%)	KOH (2 equiv. + 20 mol%)	80	12	91 (91 : 9)
5	Air	Phenol (20 mol%)	KOH (2 equiv. + 20 mol%)	80	12	92 (92 : 8)

(Table 1, entry 5), which was quite rare and an unprecedented example, and catalytic amounts of phenol could give the best result in terms of yield and the ratio of compounds **2** and **3** (Table 1, entry 13). In order to understand the role of phenol in the reaction, various substituents on the aromatic ring of phenol were explored (Table 2). Both electron-donating and electron-withdrawing groups worked well in this catalytic reaction, yet unsubstituted phenol gave the best result among them with regard to the isolated yield and the ratio of compounds **2** and **3** (Table 2, entry 5).

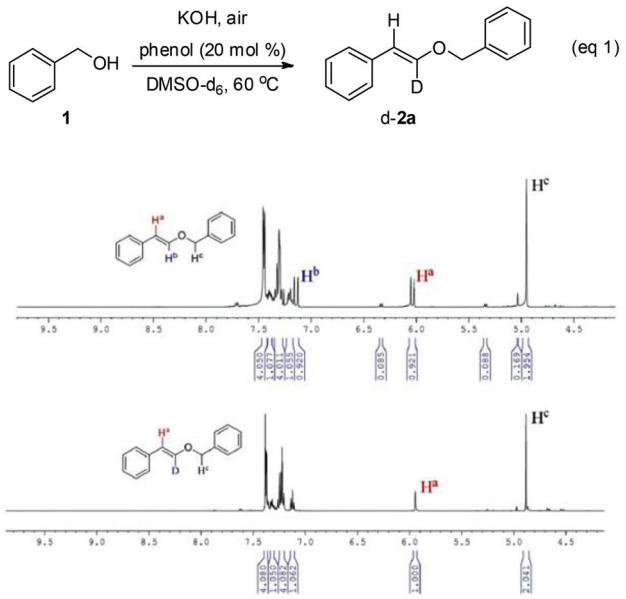
A base is very important for this reaction; both KOH and NaOH gave good yields, other bases, such as Na_2CO_3, KOBu-*t*, NEt_3 and pyridine gave poor or no yields (Table 1, entries 14–19). O_2 is crucial for this reaction, and without O_2, no desired product was formed at all (Table 1, entry 20). Yet pure O_2 did not show superiority to air, only giving 83% *vs.* 92% isolated yield in air under the same conditions (Table 1, entries 11 and 13). Thus the optimal condition for styryl ether formation under transition-metal free condition emerged as: benzyl alcohol (1 equiv.), phenol (20 mol%), KOH (2.2 equiv.), DMSO (1 mL) under air at 80 °C.

Having found the optimized reaction conditions, we explored the scope of aromatic methyl alcohols (Scheme 3). Both electron-rich and electron-poor aromatic methyl alcohols converted into the desired products smoothly (Scheme 3, **2a–2j**). The halo-substituted benzyl alcohol survived well leading to halo-substituted products (Scheme 3, **2b–2c**), which could be used for further transformation. Besides the halo-substituted ones, Me, i-Pr, phenyl, 1-naphthyl and *t*-Bu aromatic methyl alcohols also worked well under the standard conditions to give good yields of the desired products (Scheme 3, **2d–2j**). Further study showed that heteroaromatic methyl alcohols, such as 3-thiophene methyl alcohol and 2-furan methyl alcohol were also good candidates for this styryl ether formation; they gave the corresponding desired products in 76% and 70% yields respectively (Scheme 3, **2k–2l**).

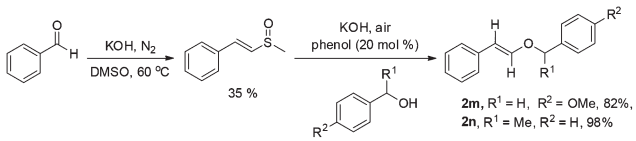


Scheme 3 Reactions of various benzyl alcohols in basic DMSO in air. Reaction condition: benzyl alcohol (0.5 mmol), phenol (20 mol%), KOH (2 equiv. + 20 mol%), DMSO (1 mL), air.

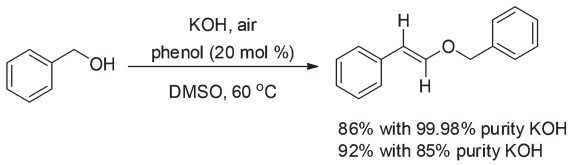
In order to elucidate the reaction mechanism, an experiment was carried out in DMSO-d_6 under the standard conditions. ^{1}H NMR of product d-**2a** clearly indicated 100% deuterium incorporation at the extra carbon (Scheme 4). Obviously, the deuterium could only come from DMSO-d_6, thus the experiment result proved that DMSO provides the extra carbon in the reaction, which is consistent with the reported results; in terms of the C=C bond formation in styryl ether, the possible intermediate—styryl sulfoxide was made



Scheme 4 Reaction of benzyl alcohol in basic deuterium-labeled DMSO in air and the ^{1}H NMR spectra comparison.



Scheme 5 Synthesis of asymmetric styryl ether from styryl sulfoxide and benzyl alcohol.

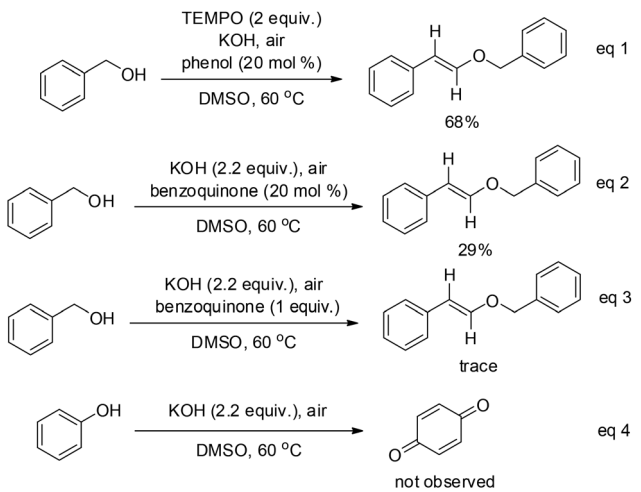


Scheme 6 Styryl ether formation with different purity levels of KOH.

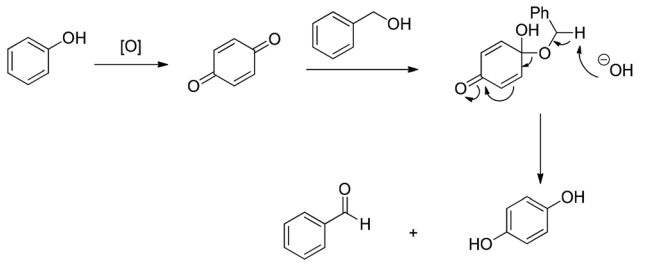
from benzaldehyde and DMSO on the basis of the literature;[21] when this compound was subjected to 4-methoxy benzyl alcohol and 1-phenylethanol under standard conditions, corresponding asymmetric styryl ethers **2m** and **2n** were obtained in 82% and 98% yields respectively (Scheme 5).

In order to exclude the impurity effect in KOH (such as trace amount of transition metal residue in KOH), we purchased super pure KOH (99.98% purity) and performed the reaction under standard conditions; 86% of styryl ether was obtained *vs.* 92% of the desired product with ≥85% purity of KOH in air (Scheme 6), thus it ruled out the impurity effect.

Since oxygen was involved in the reaction, the single electron transfer pathway was first taken into consideration and a radical trapping experiment was conducted by employing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) with benzyl alcohol under standard conditions, the desired product was obtained in 68% yield (Scheme 7, eqn (1)). This result showed that the reaction was not experiencing a radical pathway. When benzoquinone was added into the reaction instead of phenol, the desired styryl ether formation was suppressed



Scheme 7 Control experiments.



Scheme 8 Phenol-benzoquinone pathway.

(Scheme 7, eqn (2) and (3)), which indicated that benzoquinone was not the "active" catalyst in the reaction, thus ruling out the phenol-benzoquinone mechanism pathway (Scheme 8). When benzyl alcohol was absent under standard conditions, no benzoquinone was detected in the reaction (Scheme 7, eqn (4)), which further proved our above observation.

Conclusions

In summary, a transition-metal-free aerobic oxidative styryl ether formation method was developed with benzyl alcohols under basic DMSO. Both phenol and DMSO were important in styryl ether formation as the former is a good catalyst and the latter provided the extra carbon for the desired products. A variety of styryl ethers were prepared smoothly from benzyl alcohols in good to excellent yields under mild conditions.

Experimental section

General information

All experiments were conducted using a round-bottom flask. Flash column chromatography was performed over silica gel (200–300 mesh). ^{1}H NMR spectra were recorded on Bruker AVIII-400M or 500M spectrometers. Chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm) as the internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.0 ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification, and most starting materials were purchased from Adamas.

Procedure and characterization data for products

General procedure for the preparation of styryl ether from aryl methyl alcohol. To a round-bottom flask was added the corresponding aryl methyl alcohol (0.5 mmol), phenol (9.4 mg, 0.1 mmol, 0.2 eq.), potassium hydroxide (61.6 mg, 1.1 mmol, 2.2 eq.) and DMSO (1 mL). The resulting solution was stirred at 60–80 °C under air for 12 hours. Upon completion of the reaction, saturated NaCl (10 mL) was added and 1 N HCl was added to adjust the pH to 7. The solution was extracted by ethyl acetate (3 × 20mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvents were removed *via* a rotary evaporator and the residue was purified by flash chromatography (silica gel, ethyl acetate–petroleum ether = 1 : 30).

Preparation of styryl ether from aryl methyl alcohol

*(2-(Benzyloxy)vinyl)benzene (**2a**, E/Z = 92/8, CAS: 69520-20-3).*[15] This was prepared according to the general procedure. The reaction was performed with benzyl alcohol at 80 °C, and gave 48.3 mg of product **2a** in 92% isolated yield as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.46–7.42 (m, 4H), 7.41–7.38 (m, 1H), 7.34–7.28 (m, 4H), 7.21–7.18 (m, 1H), 7.14 (d, J = 12.9 Hz, 0.92*1H), 6.33 (d, J = 6.8 Hz, 0.08*1H), 6.04 (d, J = 12.9 Hz, 0.92*1H), 5.34 (d, J = 6.8 Hz, 0.08*1H), 5.03 (s, 0.08*2H), 4.95 (s, 0.92*2H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 147.7, 146.2, 136.7, 136.2, 128.5, 128.3, 128.2, 128.0, 127.5, 127.2, 125.7, 125.1, 106.9, 106.3, 74.9, 71.8. mp 41–43 °C.

*(E)-1-Bromo-4-(2-((4-bromobenzyl)oxy)vinyl)benzene (**2b**, E/Z > 99/1, CAS: 507471-18-3).*[22] This was prepared according to the general procedure. The reaction was performed with (4-bromophenyl)methanol at 60 °C, and gave 61.3 mg of product **2b** in 67% isolated yield as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 12.9 Hz, 1H), 5.87 (d, J = 12.9 Hz, 1H), 4.84 (s, 2H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 147.8, 135.5, 135.0, 131.7, 131.6, 129.1, 126.7, 122.1, 119.2, 106.2, 71.1. mp 134–136 °C.

*(E)-1-Chloro-4-(2-((4-chlorobenzyl)oxy)vinyl)benzene (**2c**, E/Z > 99/1, CAS: 84224-58-8).*[15] This was prepared according to the general procedure. The reaction was performed with (4-chlorophenyl)methanol at 60 °C, and gave 47.9 mg of product **2c** in 69% isolated yield as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.37 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 12.9 Hz, 1H), 5.90 (d, J = 12.9 Hz, 1H), 4.86 (s, 2H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 147.8, 135.0, 134.5, 134.0, 131.3, 128.83, 128.80, 128.7, 126.3, 106.1, 71.1. mp 108–110 °C.

*(E)-1-Methyl-4-(2-((4-methylbenzyl)oxy)vinyl)benzene (**2d**, E/Z > 99/1, CAS: 84224-57-7).*[15] This was prepared according to the general procedure. The reaction was performed with *p*-tolylmethanol at 60 °C, and gave 51.8 mg of product **2d** in 87% isolated yield as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.31–7.27 (m, 2H), 7.21–7.19 (m, 2H), 7.15–7.13 (m, 2H), 7.09–7.06 (m, 2H), 7.04 (d, J = 12.9 Hz, 1H), 5.95 (d, J = 12.9 Hz, 1H), 4.86 (s, 2H), 2.37 (s, 3H), 2.32(s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 147.1, 137.8, 135.3, 133.7, 133.3, 129.2, 127.7, 125.0, 106.6, 71.8, 21.2, 21.0. mp 105–107 °C.

*(E)-1-Isopropyl-4-(2-((4-isopropylbenzyl)oxy)vinyl)benzene (**2e**, E/Z > 99/1).* This was prepared according to the general procedure. The reaction was performed with (4-isopropylphenyl)-methanol at 80 °C, and gave 59.5 mg of product **2e** in 81% isolated yield as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.35–7.31 (m, 2H), 7.28–7.27 (m, 2H), 7.20–7.14 (m, 4H), 7.06 (d, J = 12.8 Hz, 1H), 5.97 (d, J = 12.8 Hz, 1H), 4.88 (s, 2H), 2.98–2.85 (m, 2H), 1.28 (d, J = 6.8 Hz, 6H), 1.26 (d, J = 6.8 Hz, 6H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 148.9, 147.2, 146.4, 134.1, 133.8, 127.8, 126.65, 126.62, 125.1, 106.6, 71.8, 33.9,

33.7, 24.0. mp 55–57 °C. HRMS (ESI, *m*/*z*) calcd for [$C_{21}H_{26}O$ + Na^+]: 317.1881; found: 317.1883.

*(E)-1-Methoxy-4-(2-((4-methoxybenzyl)oxy)vinyl)benzene (**2f**, E/Z > 99/1, CAS: 84224-56-6).*[15] This was prepared according to the general procedure. The reaction was performed with (4-methoxyphenyl)methanol at 60 °C, and gave 32.4 mg of product **2f** in 48% isolated yield as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.32 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 6.97–6.91 (m, 3H), 6.82 (d, J = 8.8 Hz, 2H), 5.92 (d, J = 12.8 Hz, 1H), 4.81 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 159.5, 157.9, 146.3, 129.3, 128.9, 128.8, 126.2, 114.1, 114.0, 106.3, 71.6, 55.3. mp 120–121 °C.

*(E)-1-Methoxy-3-(2-((3-methoxybenzyl)oxy)vinyl)benzene (**2g**, E/Z > 99/1).* This was prepared according to the general procedure. The reaction was performed with (3-methoxyphenyl) methanol at 60 °C (15 h), and gave 49.9 mg of product **2g** in 74% isolated yield as a colorless liquid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.31 (t, J = 8.0 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 12.9 Hz, 1H), 6.99–6.95 (m, 2H), 6.89–6.84 (m, 2H), 6.78 (t, J = 2.0 Hz, 1H), 6.72–6.70 (m, 1H), 5.94 (d, J = 12.9 Hz, 1H), 4.88 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 159.8, 159.7, 147.9, 138.2, 137.6, 129.6, 129.5, 119.7, 117.7, 113.7, 112.9, 111.1, 110.8, 106.8, 71.7, 55.2, 55.1. HRMS (ESI, *m*/*z*) calcd for [$C_{17}H_{18}O_3$ + Na^+]: 293.1154; found: 293.1151.

*3-(((2-([1,1′-Biphenyl]-3-yl)vinyl)oxy)methyl)-1,1′-biphenyl (**2h**, E/Z = 86/14).* This was prepared according to the general procedure. The reaction was performed with [1,1′-biphenyl]-3-ylmethanol at 80 °C, and gave 74.2 mg of product **2h** in 82% isolated yield as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.64–7.57 (m, 7H), 7.47–7.35 (m, 11H), 7.19 (d, J = 12.8 Hz, 0.86*1H), 6.36 (d, J = 6.8 Hz, 0.14*1H), 6.09 (d, J = 12.8 Hz, 0.86*1H), 5.40 (d, J = 6.8 Hz, 0.14*1H), 5.04 (s, 0.14*2H), 4.97 (s, 0.86*2H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 147.9, 146.4, 141.6, 141.2, 140.8, 137.2, 136.6, 129.0, 128.7, 128.6, 127.4, 127.2, 127.13, 127.11, 126.9, 126.8, 126.4, 126.3, 126.1, 125.9, 124.7, 124.2, 124.0, 106.9, 106.5, 74.8, 71.9. mp 64–66 °C. HRMS (ESI, *m*/*z*) calcd for [$C_{27}H_{22}O$ + Na^+]: 385.1568; found: 385.1563.

*(E)-1-(((2-(Naphthalen-1-yl)vinyl)oxy)methyl)naphthalene (**2i**, E/Z > 99/1).* This was prepared according to the general procedure. The reaction was performed with naphthalen-1-ylmethanol at 60 °C, and gave 51.1 mg of product **2i** in 66% isolated yield as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 8.17–8.11 (m, 2H), 7.96–7.87 (m, 3H), 7.76 (d, J = 8.0 Hz, 1H), 7.66–7,62 (m, 2H), 7.60–7.58 (m, 1H), 7.55–7.49 (m, 4H), 7.46–7.42 (m, 1H), 7.15 (d, J = 12.6 Hz, 1H), 6.76 (d, J = 12.6 Hz, 1H), 5.47 (s, 2H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 148.9, 133.8, 133.7, 133.3, 132.1, 131.5, 131.4, 129.2, 128.7,128.4, 126.8, 126.7, 126.5, 126.0, 125.73, 125.70, 125.69, 125.3, 124.1, 123.7, 122.9, 104.1, 70.6. mp 64–65 °C. HRMS (ESI, *m*/*z*) calcd for [$C_{23}H_{18}O$ + Na^+]: 333.1255; found: 333.1256.

*(E)-1-(tert-Butyl)-4-(2-((4-(tert-butyl)benzyl)oxy)vinyl)benzene (**2j**, E/Z > 99/1).* This was prepared according to the general procedure. The reaction was performed with (4-(tert-butyl)-phenyl)methanol at 60 °C (17 h), and gave 60.3 mg of product **2j** in 75% isolated yield as a white solid. ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 7.43 (2H, d, J = 8.4 Hz), 7.35 (2H, d, J = 8.4 Hz), 7.31 (2H, d, J = 8.4 Hz), 7.20 (2H, d, J = 8.4 Hz), 7.07 (1H, d, J = 12.9 Hz), 5.98 (1H, d, J = 12.6 Hz), 4.88 (2H, s), 1.36 (9H, s), 1.33 (9H, s). ^{13}C NMR: (125 MHz, $CDCl_3$, ppm) δ 151.1, 148.7, 147.3, 133.8, 133.4, 127.5, 125.5, 125.4, 124.9, 106.6, 71.8, 34.6, 34.4, 31.3.

*3-(((2-(Thiophen-3-yl)vinyl)oxy)methyl)thiophene (**2k**, E/Z = 87/13).* This was prepared according to the general procedure. The reaction was performed with thiophen-3-ylmethanol at 60 °C, and gave 42.2 mg of product **2j** in 76% isolated yield as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.35–7.33 (1H, m), 7.30–7.29 (m, 1H), 7.25–7.24 (m, 1H), 7.11 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.05 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz, 1H), 7.00 (d, J = 13.2 Hz, 0.87*1H), 6.94 (dd, J_1 = 2.8 Hz, J_2 = 1.2 Hz, 1H), 6.24 (d, J = 6.4 Hz, 0.13*1H), 6.00 (d, J = 13.2 Hz, 0.87*1H), 5.42 (d, J = 6.8 Hz, 0.13*1H), 4.99 (s, 0.13*2H), 4.88 (s, 0.87*2H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 147.6, 137.7, 137.2, 127.0, 126.4, 125.9, 124.5, 123.2, 118.3, 102.0, 67.2. mp 84–86 °C. HRMS (ESI, *m*/*z*) calcd for [$C_{11}H_{10}OS_2$ + Na^+]: 245.0071; found: 245.0074.

*2-(((2-(Furan-2-yl)vinyl)oxy)methyl]furan (**2l**, E/Z = 90/10).* This was prepared according to the general procedure. The reaction was performed with furan-2-ylmethanol at 60 °C, and gave 36 mg of product **2k** in 70% isolated yield as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.42 (s, 1H), 7.23 (s, 1H), 7.04 (d, J = 12.8 Hz, 1H), 6.40–6.27 (m, 3H), 6.00 (s, 1H), 5.80 (d, J = 12.8 Hz, 1H), 5.40 (d, J = 6.4 Hz, 0.11*1H), 4.87 (s, 0.11*2H), 4.78 (s, 2H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 151.2, 149.9, 146.9, 143.8, 143.3, 142.5, 140.3, 139.8, 111.3, 111.0, 110.5, 110.2, 108.1, 104.5, 97.6, 97.1, 66.4, 64.2. mp 36–38 °C. HRMS (ESI, *m*/*z*) calcd for [$C_{11}H_{10}O$ + Na^+]: 213.0528; found: 213.0530.

Preparation of key intermediate—styryl sulfoxide

(E)-(2-(Methylsulfinyl)vinyl)benzene (CAS: 38082-31-4).[15] This was prepared according to the previous reports.[6] To a Schlenk tube was added potassium hydroxide (280 mg, 5 mmol, 1 eq.), DMSO (10 ml), and benzaldehyde (530 mg, 5 mmol, 1 eq.) under dry nitrogen. The resulting solution was stirred at 60 °C for 90 min. Upon completion of the reaction, saturated NaCl (30 mL) was added. The solution was extracted by ethyl acetate (3 × 30 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvents were removed *via* a rotary evaporator and the residue was purified with flash chromatography (silica gel, ethyl acetate–petroleum ether = 4 : 1) to afford the product as a colorless oil (257 mg, 31%). ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 7.48–7.45 (m, 2H), 7.41–7.35 (m, 3H), 7.26 (d, J = 15.2 Hz, 1H), 6.90 (d, J = 15.2 Hz, 1H), 2.7 (s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ 136.4, 133.7, 132.2, 129.7, 128.9, 127.6, 40.9.

Preparation of asymmetric styryl ether

*(E)-1-Methoxy-4-((styryloxy)methyl)benzene (**2m**, CAS: 1445154-10-8).*[15] A round-bottom flask was charged with (4-methoxyphenyl)methanol (27.0 mg, 0.25 mmol, 1 eq.), (*E*)-(2-(methyl-

sulfinyl)vinyl)benzene (49.8 mg, 0.3 mmol, 1.2 eq.), phenol (4.7 mg, 0.05 mmol, 0.2 eq.), potassium hydroxide (30.8 mg, 0.55 mmol, 2.2 eq.) and DMSO (1 mL). The resulting solution was stirred at 60 °C under air for 12 hours. Upon completion of the reaction, saturated NaCl (10 mL) was added and 1 N HCl was added to adjust the pH to 7. The solution was extracted by ethyl acetate (3 × 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvents were removed *via* a rotary evaporator and the residue was purified by flash chromatography (silica gel, ethyl acetate–petroleum ether = 1 : 30) to afford the product as a white solid (46.5 mg, 82%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 7.35 (d, J = 8.5 Hz, 2H), 7.30–7.25 (m, 4H), 7.16 (t, J = 7.0 Hz, 1H), 7.10 (J = 13.0 Hz, 1H), 6.95 (d, J = 8.5 Hz, 2H), 5.98 (d, J = 13.0 Hz, 1H), 4.85 (s, 2H), 3.84 (s, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$, ppm) δ 159.5, 147.7, 136.3, 129.3, 128.8, 128.5, 125.7, 125.1, 114.0, 106.7, 71.7, 55.3. mp 100–101 °C.

*(E)-(2-(1-Phenylethoxy)vinyl)benzene (**2n**, CAS: 1445154-11-9)*[1]. A round-bottom flask was charged with 1-phenylethanol (30.5 mg, 0.25 mmol, 1 eq.), (*E*)-(2-(methylsulfinyl)vinyl)-benzene (49.8 mg, 0.3 mmol, 1.2 eq.), phenol (4.7 mg, 0.05 mmol, 0.2 eq.), potassium hydroxide (30.8 mg, 0.55 mmol, 2.2 eq.) and DMSO (1 mL). The resulting solution was stirred at 60 °C under air for 12 hours. Upon completion of the reaction, saturated NaCl (10 mL) was added and 1 N HCl was added to adjust the pH to 7. The solution was extracted by ethyl acetate (3 × 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvents were removed *via* a rotary evaporator and the residue was purified by flash chromatography (silica gel, ethyl acetate–petroleum ether = 1 : 30) to afford the product as a colorless liquid (54.9 mg, 98%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 7.40–7.37 (4H, m), 7.34–7.31 (1H, m), 7.25–7.22 (2H, m), 7.19–7.17 (2H, m), 7.14–7.11 (1H, m), 6.89 (1H, d, J = 12.7 Hz), 5.98 (1H, d, J = 12.7 Hz), 5.00 (1H, q, J = 6.5 Hz), 1.62 (3H, d, J = 6.5 Hz). ^{13}C NMR: (125 MHz, $CDCl_3$, ppm) δ 146.6, 142.7, 136.3, 128.6, 128.4, 127.7, 125.9, 125.6, 125.1, 108.5, 79.0, 23.6.

Preparation of styryl ether in d^6-DMSO

*d-(E)-(2-(Benzyloxy)vinyl)benzene (d-**2a**, CAS: 344740-75-6).*[15] It was prepared according to general procedure in d^6-DMSO (1 mL). The reaction was performed with benzyl alcohol at 60 °C, and gave 34 mg of product d-**2a** in 65% isolated yield as a white solid. ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 7.38–7.37 (m, 4H), 7.33–7.31 (m, 1H), 7.25–7.20 (m, 4H), 7.14–7.10 (m, 1H), 5.94 (s, 1H), 4.88 (s, 2H). ^{13}C NMR: (125 MHz, $CDCl_3$, ppm) δ 147.4, 136.7, 136.2, 128.6, 128.1, 127.6, 125.7, 125.1, 106.7, 71.8. mp 39–41 °C.

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