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Z-selective, *anti*-Markovnikov addition of alkoxides to terminal alkynes: an electron transfer pathway?

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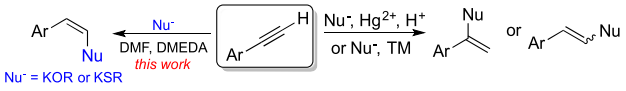
ABSTRACT

Potassium alkoxides undergo *anti*-Markovnikov addition to aryl-substituted alkynes with *Z* selectivity in DMF as the solvent. The yields and efficiency of the reaction was also found to be enhanced by the addition of a secondary amine ligand such as *N*,*N*′-dimethylethylenediamine. Mechanistic investigations suggest that the products, reaction rates and selectivity can be explained via a single electron transfer from the alkoxide to the alkyne. This leads to a radical anion intermediate, which then rapidly combines with the alkoxide to yield a vinyl anion whose lifetime governs the *E*:*Z* selectivity observed in the products.

1. Introduction

The reaction of alkynes with nucleophiles is a class of reaction that has been extensively investigated by chemists over many decades, since the products obtained are usually highly functionalised and adaptable building blocks for organic synthesis. In particular, hydration and similar reactions yield carbonyl compounds and their derivatives, and so leads to further facile manipulation of these synthetic intermediates. Despite this fact, these types of reaction have not been widely applied in target synthesis, mainly because harsh reaction conditions are required (e.g., strong acids), or toxic reagents are employed (e.g., 40% of a mercury(II) salt).[1] In recent years a number of transition metals have been employed to facilitate the addition of nucleophiles to alkynes. These have included gold,[2] rhodium,[3] ruthenium[4] and palladium[5] as well as many others.[6] In general, these reagents are expensive and often toxic although both Markovnikov and *anti*-Markovnikov addition products can be formed depending on the catalyst selected (Scheme 1).

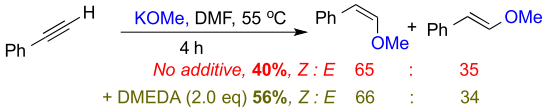


Scheme 1. Markovnikov and anti-Markovnikov addition to alkynes.

Remarkably perhaps, relatively few reports of *anti*-Markovnikov addition of alkoxides to alkynes exist in the literature. Exceptions include a few examples catalysed by transition metals, and one report where hydrated caesium hydroxide is employed as catalyst to promote the addition of alcohols and amines to phenylacetylene alone to yield enol ethers and enamines.[7] No satisfactory mechanistic pathway has been proposed to explain the observed product distribution. In this work we demonstrate that the efficiency of the addition of alkoxides to various substituted phenylacetylenes can be significantly improved by employing potassium alkoxide in combination with a diamine additive. We also present a range of other observations and studies, which raise the possibility of a mechanism based on electron transfer rather than simple nucleophilic addition.

2. Results and discussion

We made the observation that potassium methoxide adds to phenylacetylene in 49% over 15 h producing an excess of the *cis* isomer of the corresponding enol ether (Scheme 2). Knowing that



Scheme 2. Anti-Markovnikov addition of KOMe to phenylacetylene.

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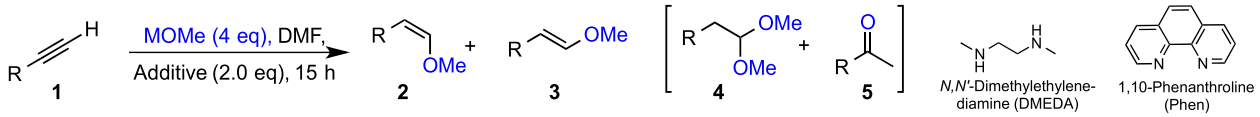
such *anti*-Markovnikov reactions were rare in the literature, we were keen to investigate both the scope and mechanism of the transformation.

Given the parallels with our previous work[8] and the work of others[9] who have noted that potassium alkoxides (particularly potassium *tert*-butoxide) can behave as single electron transfer agents, we postulated that this reaction might be radical in nature. Often the alkoxide is coupled with a ligand[10] to render it more effective, and we were curious to know whether ligands such as simple secondary diamines might improve the reaction outlined in Scheme 2.[9]

Addition of the secondary diamine *N*,*N*′-dimethylethylenediamine (DMEDA), commonly employed in alkoxide mediated radical processes, resulted in a significantly enhanced yield with a similar *Z*:*E* ratio. With this observation in hand, we then decided to explore this reaction with different substrates to establish the scope and efficiency. We had noted that the rate of reactions seemed to depend upon the electronic characteristics of the arene; where those bearing electron withdrawing groups proceed at a faster rate (or alternatively require lower temperatures) than their electron donating analogues. We therefore chose 55 °C as a median operating temperature, which would allow us to directly compare the different substrates employed in the reaction. The results are outlined in Table 1.

The most striking first observations from Table 1 is that a reaction considered to be the preserve of transition metal mediation

Table 1
Substrate scope for alkyne reactions with methoxide[a]



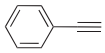
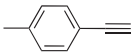
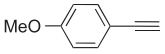
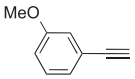
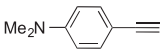
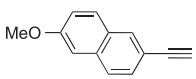
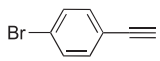
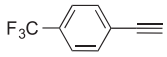
Entry	1a–i	M	Temp °C	Time (h)	Additive	Yield (**2**+**3**) %	*Z*:*E* (**2**:**3**) ratio[b]	Other products[c]
1		K	55	4	—	40	65:35	—
2		K	55	4	DMEDA	56	66:34	—
3		K	55	15	—	49	66:34	—
4		K	55	15	DMEDA	70	68:32	—
5		K	55	15	—	51	80:20	—
6		K	55	15	DMEDA	66	80:20	—
7		K	55	15	—	13	90:10	36% **1**
8		K	55	15	DMEDA	34	91:9	56% **1**
9		K	75	15	—	50	88:12	7% **5**
10		K	75	15	DMEDA	69	84:16	7% **5**
11		K	75	30	DMEDA+5% MeOH	30	96:4	55% **1**
12		Na	75	15	DMEDA	15	90:10	44% **1**
13		Li	75	15	DMEDA	0	—	100% **1**
14		K	55	15	—	57	61:39	—
15		K	55	15	DMEDA	72	60:40	—
16		K	75	15	DMEDA+5% MeOH	65	81:19	28% **4**
17		K	55	15	—	<5	95:5	ca. 95% **1**
18		K	55	15	DMEDA	<5	95:5	ca. 95% **1**
19		K	100	15	—	23	80:20	16% **1**, 5% **5**
20		K	100	15	DMEDA	47	80:20	7% **1**, 7% **5**
21		K	55	15	—	42	54:46	22% **4**
22		K	55	15	DMEDA	51	52:48	21% **4**
23		K	55	15	—	37	41:59	14% **4**
24		K	55	15	DMEDA	53	41:59	14% **4**

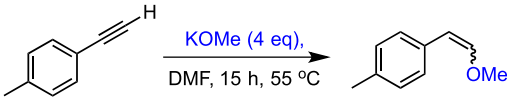
Table 1 (*continued*)

Entry	1a–i	M	Temp °C	Time (h)	Additive	Yield (**2**+**3**) %	*Z*:*E* (**2**:**3**) ratio[b]	Other products[c]
25		K	55	15	—	31	30:70	15% **4**
								
26		K	55	15	DMEDA	31	30:70	14% **4**
27		K	55	15	DMEDA+5% MeOH	30	74:26	32% **4**
28		K	55	15	—	0	—	100% **1**
								
29		K	55	15	DMEDA	0	—	100% **1**
30		K	55	15	Phen	0	—	100% **1**

[a] Reaction Conditions: Alkyne (0.24 mmol, 1.0 equiv), DMF (1.5 mL), additive (0.48 mmol, 2.0 equiv).
[b] *Z*:*E* ratio calculated from reaction ^{1}H NMR.
[c] Remainder comprised polymeric and decomposed material.

can be achieved with both *anti*-Markovnikov and *Z*-selectivity under certain carefully controlled conditions. The potassium counterion (entries 11–13) appears critical since employing lithium methoxide yielded no addition products (entry 13), and sodium methoxide yields only small amounts of the desired products with the bulk of the material being returned as the starting alkyne **1**.

In all cases, the addition of DMEDA gives an improvement in yield in the order of 20% and occasionally higher. Our previous work[11] has also demonstrated the benefit of employing a combination of a potassium alkoxide (although usually potassium *tert*-butoxide) with secondary amine additives for various synthetic purposes. At first we assumed that the amine was behaving as a ligand for the metal ion and improving the solubility of the alkoxide to allow the reaction to proceed at a sufficient rate. We therefore attempted to improve the yield and efficiency of the reaction by the addition of a crown ether to the reaction medium. To our surprise, when 18-crown-6 is added to the reaction the yield remains roughly the same, however the *Z*:*E* ratio falls significantly. When DMEDA and the crown ether are present the yield improves slightly but the ratio of *Z*:*E* isomers remains the same as when the crown ether was present alone. These results suggest that the role of DMEDA is more complex than merely a solubilizing ligand. We have speculated elsewhere as to the role of the amine however work continues to disambiguate the precise role of this additive[12] Scheme 3.



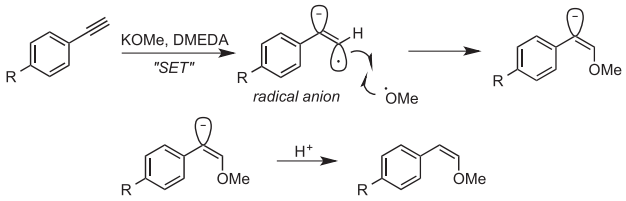
No additive, 51% (*Z*:*E* 80:20)
+ 18-crown-6 54% (*Z*:*E* 54:46)
+ DMEDA (2.0 eq) 66% (*Z*:*E* 80:20)
+ DMEDA + 18-crown-6 59% (*Z*:*E* 60:40)

Scheme 3. Effect of additives on anti-Markovnikov addition of KOMe to 4-methylphenylacetylene.

The observed *Z*-selectivity of these reactions coupled with the observation that potassium seems to be essential for the reaction to occur led us to postulate a reaction mechanism based on a single electron transfer pathway. In 2005 Oshima and Yorimitsu disclosed a similar reaction where the addition of a thiol to alkynes resulted in the thio-enol ether in good yields with high *Z*-selectivity.[13] A radical mechanism appears to have been ruled out since the addition of TEMPO did not attenuate the reaction when Cs_2CO_3 was employed as the base (though a 'base free' background reaction was inhibited). Interestingly, the authors also note a similar preference for the lower alkali metals with sodium and lithium carbonates significantly inferior to their potassium and caesium counterparts.

Accordingly, we also employed TEMPO in the methoxide addition to 4-methylphenylacetylene under conditions identical to those employed in entry 6 of Table 1. In common with Oshima and Yorimitsu, we also found no effect on the yield or the rate of the reaction. Although this might lead us to conclude that neither of these reactions is proceeding via single electron transfer and/or radical intermediates, we wondered if TEMPO was simply not capturing the radical species involved. Consequently we added the electron acceptor *m*-dinitrobenzene to the reaction in order to intercept any electron transfer processes. This resulted in a fall in yield from 66% to less than 10% under otherwise identical conditions to those outlined in entry 6, Table 1.

The proposed mechanistic pathway is outlined in Scheme 4. Our hypothesis firstly involves a single electron transfer from the alkoxide to the alkyne resulting in a radical anion reminiscent of the radical anion intermediate invoked in dissolving metal reductions of alkynes, which invariably lead to *Z* geometries of the resulting products.



Scheme 4. Proposed mechanistic pathway.

Rapid coupling of the alkoxy radical and the radical anion then leads to a discrete vinyl anion intermediate, which on protonation from trace quantities of moisture or methanol in the reaction medium leads to the observed enol ethers with *Z*-selectivity. Given that TEMPO is generally employed to trap discrete carbon centred radicals its ineffectiveness in attenuating this reaction may well be explained.

One striking observation from the results in Table 1 is the dependence of the *Z*:*E* ratio on the nature of the aryl substituent, R. As the aryl group becomes more electron deficient the amount of the more sterically favoured *E* isomer increases. The ratio correlates very well with the Hammett parameters for each substituent as can be seen in Fig. 1.

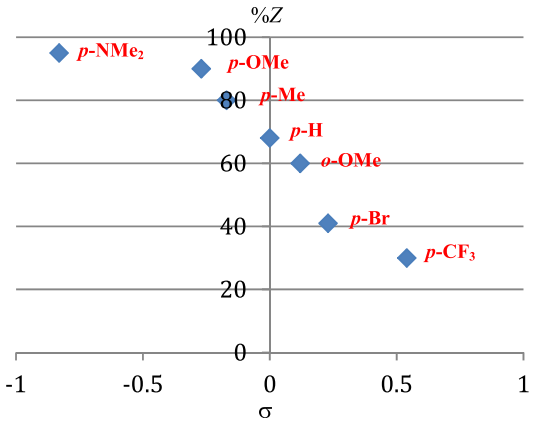


Fig. 1. Relationship between *Z*-selectivity and Hammett constants.

At first this led us to suggest that the pure *Z* isomers initially generated in the reaction were undergoing an inversion under the highly basic reaction conditions. However, isolation of a pure *Z* isomer (**2b**) and resubmitting this compound to the reaction conditions led to no isomerisation and so an alternative explanation was sought.

We therefore hypothesise that the discrete vinyl anion formed from coupling with an alkoxy radical can invert at a rate that is dependent on the electron withdrawing capacity of the substituent on the aryl ring. Although the inversion of vinyl anions is usually slow, the fact that the anions in Fig. 2 can be delocalised over the aromatic ring, coupled with the observation that electron-withdrawing groups increase the amount of the *E* isomer leads us to conclude that inversion is feasible in this case. In addition, the work of Houk[14] has also demonstrated that the barrier to inversion is dramatically lowered when alkenes are substituted with electron withdrawing substituents. This model may also account for the drop in selectivity when a crown ether is added. Complete dissociation of the potassium cation from the vinyl anion **6a** might be expected to lead to more rapid inversion.

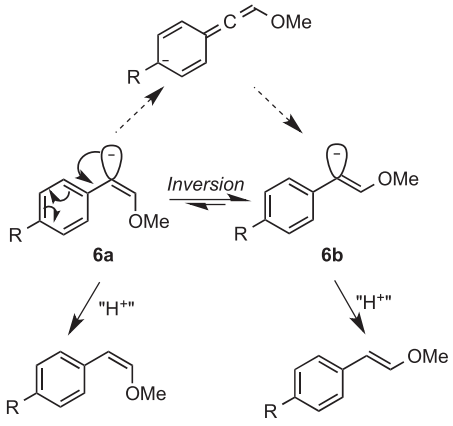
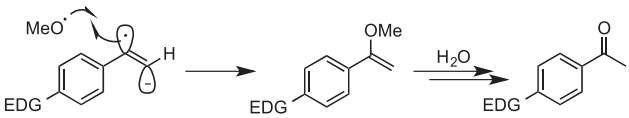


Fig. 2. Mechanistic rationale for vinyl anion inversion.

This mechanistic pathway also explains why the proportion of the *Z* isomer isolated is dramatically increased when the reaction solvent is doped with a small amount of methanol. The proportion of the sterically less favoured *Z*-isomer will depend not only on the substituent attached to the aryl ring, but also on the lifetime of the anion. In anhydrous media a long-lived vinyl anion will have sufficient time to invert to the more favoured *E* isomer. The inclusion of small amounts of protic solvents will result in rapid protonation of this intermediate and hence allow isolation of greater quantities of the *Z* isomer. Despite this, the addition of protic solvents is not a good strategy to improve the efficiency of the reaction overall. Even modest amounts of methanol (5%) result in lengthy reaction times. Presumably protic solvents significantly decelerate the initial electron transfer step.

An interesting observation from the results in Table 1 is the small amount of ketone **5** isolated where the alkyne bears a particularly electron rich substituent. Although at first sight this might seem like a routine alkyne hydrolysis reaction, under these conditions this would seem unlikely. A more likely explanation is found in consideration of the stability of the radical anion. In general, radical anions derived from aryl alkynes retain anion character on the internal carbon atom (where it is delocalised over the aromatic ring) with the remaining spin density residing on the external carbon atom.[15] In cases where the aryl group is particularly electron rich the mesomerically donating group will destabilise the anion. Consequently the alternative resonance structure contributes sufficiently to allow occasional reaction with an alkoxy radical. This yields the corresponding enol ether, which is hydrolysed rapidly on aqueous work-up (Scheme 5).



Scheme 5. Mechanism for the hydrolysis of electron rich arylacetylenes.

The acetal products **4** obtained from substrates bearing electron deficient aryl rings are easily explained by a simple addition process not mediated by single electron transfer. This conclusion was reached since the inclusion of methanol in the reaction mixture severely attenuates the first step of the process but does not attenuate the rate of formation of the acetal products.

We also wished to demonstrate that other alkoxides as well as methoxide could be employed. Pleasingly, the isopropyl and benzyl enol ethers were also obtained in acceptable yields under similar conditions (Fig. 3). Similarly, we observed that internal alkenes such as 1-phenyl-1-propyne were also applicable under the same conditions (although with poorer *Z*:*E* selectivity, Fig. 3, compounds **7**–**9**).

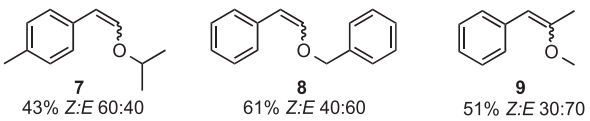


Fig. 3. Reaction with alternative alkoxides and an internal alkyne.

With the addition to internal alkynes proceeding with similar efficiency and under the same conditions as other examples we decided to explore the possibility of trapping the putative radical anion in order to confirm our hypothesis that the reaction proceeds via initial electron transfer from the nucleophile to the alkyne (in a similar way to that proposed by Ashby[16] for many S_N2 displacements). As such, we prepared the known diyne **10**, commonly employed in transition metal mediated cyclisation reactions. Simple nucleophilic addition of methoxide to this substrate might only be expected to yield acyclic addition products or six-membered ring products such as **11**, resulting from intramolecular cyclisation (Fig. 4). Conversly, initial electron transfer yielding the acetylinic

radical anion (with spin density residing on the β-carbon atom might be expected to yield five-membered ring products such as **12** (Fig. 4).

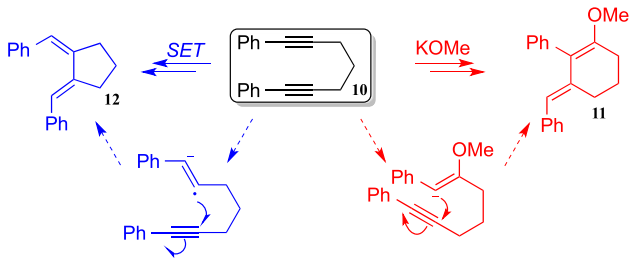
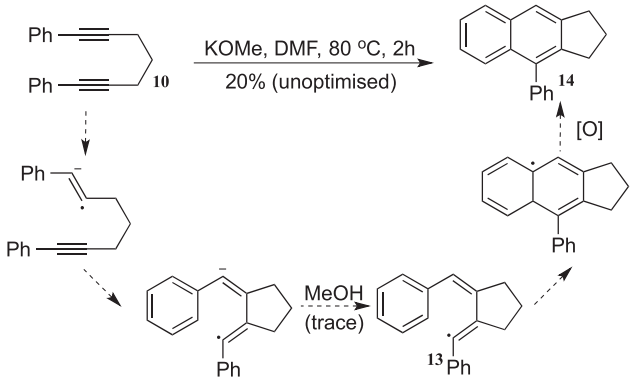


Fig. 4. Possible fates of diyne **10**.

In fact, when we exposed diene **10** to KOMe we were surprised to isolate only the tetracyclic compound **14** in 20% yield (the remainder of the material being recovered starting material). The formation of this compound under relatively mild conditions and short reaction time suggests strongly that a radical mechanism is in operation and that this product is derived from the radical anion intermediate. Electron transfer to the acetylene followed by 5-*exo* cyclisation yields the intermediate **13**, which has the appropriate stereochemistry (*Z*, *E*) to undergo radical addition to the pendant aryl group. Subsequent rearomatisation then yields the observed product (Scheme 6). This result is noteworthy since naphthalene **14** has been prepared previously from **10**[17] and related allenes,[18] however these preparations have all required transition metal catalysis (usually π-acids such as Au(I)). Other preparations of **14** and related compounds have employed pericyclic processes,[19,17a] however high temperatures (180–225 °C) and extended reaction times (18–24 h) are required.



Scheme 6. Mechanistic rationale for the formation of **11**.

3. Conclusions

In conclusion we have described the transformation of aryl alkynes into enol ethers mediated by secondary diamines in the absence of transition metal catalysis. We have presented experiments and observations that lead us to believe that the reaction might proceed via an initial electron transfer step yielding a radical anion akin to those intermediates involved in dissolving metal reductions. Also presented is a mechanistic pathway that accounts for the observed regio- and stereochemistry of the products and by-products. A sound understanding of the reaction mechanism coupled with an understanding of the behaviour of group 1 alkoxides will be key principles in the future development and improvement of these reactions to become truly useful synthetic methods.

4. Experimental section

4.1. General information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX500 or AMX600 using $CDCl_3$ as the deuterated solvent. Coupling constants are reported in Hertz (Hz). ^{13}C NMR spectra were recorded at 125 MHz or 150 MHz on either a Bruker AMX500 or AMX600 MHz spectrometer, and are reported in parts per million. Mass spectra were measured on a Thermo Finnigan MAT900 XP operating in EI and CI mode. Melting points were measured using Gallenkamp apparatus and are uncorrected. Analysis by thin layer chromatography (TLC) was conducted using aluminium-backed plates pre-coated (250 μm) with silica (Merck, TLC silica gel 60 F_{254}). TLC plates were visualised using ultraviolet light (254 nm), and then using $KMnO_4$ solution and heating. Flash chromatography was performed using silica gel (Merck Kieselgel 60) 0.04/0.063 mm (230–400 mesh) silica gel. Infra-red spectra were measured on a FTIR Perkin Elmer Spectrum 100 operating in ATR mode as thin films.

4.2. General procedure for the preparation of vinyl ethers 2a–h and 3a–h

Potassium methoxide (67.0 mg, 0.96 mmol, 4.0 equiv), *N*,*N*′-dimethylethylenediamine (50 μL, 0.48 mmol, 2.0 equiv) and terminal acetylene **1a–h** (0.24 mmol, 1.0 equiv) were added to a flame-dried, sealed tube under an atmosphere of argon. DMF (1.5 mL) was added via syringe, and the mixture was stirred at 55 °C (unless otherwise stated) for 15 h. Upon completion, the mixture was allowed to cool to rt and was quenched by the addition of water (2 mL). The crude mixture was diluted with CH_2Cl_2 (100 mL) and washed with LiCl solution (3×20 mL). The organic portion was dried over $MgSO_4$, filtered and concentrated in vacuo, then purified via column chromatography (0–5 % EtOAc/PE) to yield alkenyl ethers **2a–h** and **3a–h**.

4.3. (2-Methoxyvinyl)benzene 2/3a[20]

70% Combined yield; **2a**; colourless oil; ν_{max} (film/cm^{-1}) 2926, 2862, 1649, 1491, 1454, 1442, 1399, 1299, 1269, 1202; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.57 (d, *J*=7.2 Hz, 2H, Ar*H*), 7.29 (t, *J*=7.6 Hz, 2H, Ar*H*), 7.15 (t, *J*=7.3 Hz, 1H, Ar*H*), 6.15 (d, *J*=7.0 Hz, 1H, CH_3OCH), 5.23 (d, *J*=7.0 Hz, 1H, CH_3OCHCH), 3.19 (s, 3H, CH_3O); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 148.1 (CH), 136.0 (C_q), 128.3[1], 125.9 (CH), 105.8 (CH), 60.8 (CH_3); LRMS (CI) 135 (100), 91 (8), 85 (3).

3a; Colourless oil; ν_{max} (film/cm^{-1}) 3023, 2933, 2832, 1638, 1599, 1575, 1492, 1450, 1329, 1235, 1190, 1148, 1122; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.28–7.23 (m, 4H, Ar*H*), 7.14 (t, *J*=7.1 Hz, 1H, Ar*H*), 7.06 (d, *J*=13.0 Hz, 1H, CH_3OCH), 5.82 (d, *J*=13.0 Hz, 1H, CH_3OCHCH), 3.69 (s, 3H, CH_3O); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 149.0 (CH), 136.4 (C_q), 128.7 (CH), 125.8 (CH), 125.2 (CH), 105.1 (CH), 56.6 (CH_3); LRMS (EI) 135 (6), 122 (33), 105 (100), 91 (16).

4.4. 1-(2-Methoxyvinyl)-4-methylbenzene 2/3b[20]

66% Combined yield; **2b**; colourless oil; ν_{max} (film/cm^{-1}) 2840, 1730, 1684, 1600, 1579, 1509, 1443, 1426, 1398, 1354, 1303, 1256, 1243; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.46 (d, *J*=8.0 Hz, 2H, Ar*H*), 7.10 (d, *J*=8.0 Hz, 2H, Ar*H*), 6.09 (d, *J*=7.0 Hz, 1H, CH_3OCH), 5.20 (d, *J*=7.0 Hz, 1H, CH_3OCHCH), 3.77 (s, 3H, CH_3O), 2.32 (s, 3H, CH_3(C)); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 147.4 (CH), 135.5 (C_q), 133.1 (C_q), 129.0 (CH), 128.2 (CH), 105.7 (CH), 60.7 (CH_3), 21.3 (CH_3); LRMS (EI) 148 (54), 133 (11), 119 (11), 105 (41), 86 (64), 84 (100). **3b**; Colourless oil (contaminated with 9% *Z*-isomer); ν_{max} (film/cm^{-1}) 2922, 2852, 1637, 1512, 1461, 1336, 1317, 1297, 1236,

1189, 1149; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.13 (d, J=8.0 Hz, 2H, Ar*H*), 7.08 (d, J=8.0 Hz, 2H, Ar*H*), 7.01 (d, J=13.0 Hz, 1H, CH_3OCH), 5.80 (d, J=13.0 Hz, 1H, CH_3OCHCH), 3.68 (s, 3H, CH_3OCH), 2.31 (s, 3H, $CH_3(C)$); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 148.3 (CH), 135.4 (C_q), 133.2 (C_q), 129.4 (CH), 125.1 (CH), 105.0 (CH), 56.6 (CH_3), 21.2 (CH_3).

4.5. 1-Methoxy-4-(2-methoxyvinyl)benzene 2/3c[20]

69% combined yield; **2c**: Colourless oil, ν_{max} (film/cm^{-1}) 2930, 2831, 1649, 1603, 1571, 1507, 1453, 1397, 1239, 1175, 1089, 1029; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.51 (d, J=8.8 Hz, 2H, Ar*H*), 6.83 (d, J=8.8 Hz, 2H, Ar*H*), 6.05 (d, J=7.0 Hz, 1H, CH_3OCH), 5.18 (d, J=7.0 Hz, 1H, CH_3OCHCH), 3.80 (s, 3H, $CH_3O(C)$), 3.76 (s, 3H, CH_3OCH); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 157.7 (C_q), 146.5 (CH), 129.5 (CH), 128.8 (C_q), 113.7 (CH), 105.3 (CH), 60.6 (CH_3), 55.3 (CH_3); LRMS (CI) 165 (100), 150 (12), 135 (4), 121 (6). **3c**:White solid; MP=45–46 °C; ν_{max} (film/cm^{-1}) 2954, 2937, 2835, 1658, 1637, 1604, 1574, 1508, 1460,1337, 1286, 1236, 1178; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.16 (d, J=8.7 Hz, 2H, Ar*H*), 6.93 (d, J=13.0 Hz, 1H, Ar*H*), 6.82 (d, J=8.7 Hz, 2H, CH_3OCH), 5.78 (d, J=13.0 Hz, 1H, CH_3OCHCH), 3.79 (s, 3H, $CH_3O(C)$), 3.66 (s, 3H, CH_3OCH); ^{13}C NMR (150 MHz, CD_2Cl_2) δ_C 157.9 (C_q), 147.5 (CH), 128.9 (C_q), 126.0 (CH), 114.0 (CH), 104.3 (CH), 56.4 (CH_3), 55.2 (CH_3); LRMS (EI) 164 (81), 149 (45), 121 (100), 91 (16).

4.6. 1-Methoxy-3-(2-methoxyvinyl)benzene 2/3d

72% Combined yield; **2d**; colourless oil; ν_{max} (film/cm^{-1}) 2936, 2831, 1649, 1597, 1573, 1484, 1455, 1428, 1399, 1256, 1238, 1165, 1094; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.21–7.19 (m, 2H, Ar*H*), 7.12–7.11 (m, 1H, Ar*H*), 6.71 (ddd, J=8.2, 2.7, 0.8 Hz, 1H, Ar*H*), 6.14 (d, J=6.9 Hz, 1H, CH_3OCH), 5.20 (d, J=6.9 Hz, 1H, CH_3OCHCH), 3.80 (s, 3H, $CH_3O(C)$), 3.78 (s, 3H, CH_3OCH); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 159.5 (C_q), 148.3 (CH), 137.3 (C_q), 129.2 (CH), 121.0 (CH), 113.7 (CH), 111.6 (CH), 105.6 (CH), 60.9 (CH_3), 55.3 (CH_3); LRMS (CI) 164 (85), 149 (3), 121 (40), 91 (17), 86 (64), 84 (100); HRMS (EI) calcd for $C_{10}H_{12}O_2$ (M^+) requires 164.0837, found 164.0835. **3d**; Colourless oil (contaminated with 18% *Z*-isomer); ν_{max} (film/cm^{-1}) 2935, 2833, 1640, 1598, 1576, 1487, 1453, 1427, 1252, 1217, 1145, 1121, 1096; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.18 (t, J=7.8 Hz, 1H, Ar*H*), 7.05 (d, J=13.0 Hz, 1H, CH_3OCH), 6.84–6.83 (m, 1H, Ar*H*), 6.77–6.76 (m, 1H, Ar*H*), 6.69 (dd, J=8.2, 2.0 Hz, 1H, Ar*H*), 5.78 (d. J=13.0 Hz, 1H, CH_3OCHCH), 3.80 (s, 3H, $CH_3O(C)$), 3.68 (s, 3H, CH_3OCH); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 159.9 (C_q), 149.2 (CH), 137.9 (C_q), 129.7 (CH), 117.8 (CH), 111.2 (CH), 110.8 (CH), 105.0 (CH), 56.6 (CH_3), 55.3 (CH_3); LRMS (EI) 165 (100), 164 (35), 87 (7), 85 (16).

4.7. 4-(2-Methoxyvinyl)-*N*,*N*-dimethylaniline 2/3e

Could not separate *E* and *Z* isomers. Pale yellow oil, 47%; ν_{max} (film/cm^{-1}) 2927, 1648, 1605, 1517, 1443, 1396, 1347, 1264, 1188, 1088; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H (*Z*-isomer) 7.47 (d, J=8.9 Hz, 2H, Ar*H*), 6.70 (d, J=8.9 Hz, 2H, Ar*H*), 6.00 (d, J=7.0 Hz, 1H, CH_3OCH), 5.15 (d, J=7.0 Hz, 1H CH_3OCHCH), 3.74 (s, 3H, OCH_3), 2.93 (s, 6H, 2×NCH_3); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H (*E*-isomer) 7.13 (d, J=8.8 Hz, 2H, Ar*H*), 6.90 (d, J=13.0 Hz, 1H, Ar*H*), 6.70–6.69 (m, 2H, CH_3OCH), 5.77 (d, J=13.0 Hz, 1H, CH_3OCHCH), 3.65 (s, 3H, OCH_3), 2.92 (s, 6H, 2×NCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C (*Z*-isomer)148.8 (C_q), 145.4 (CH), 129.2 (CH), 124.9 (Cq), 112.7 (CH), 105.8 (CH), 60.5 (CH_3), 40.9 (CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C (*E*-isomer) 149.2 (C_q), 146.6 (CH), 126.1 (CH), 124.9 (C_q), 113.3 (CH), 105.1 (CH), 56.6 (CH_3), 41.0 (CH_3); HRMS (ESI) calcd for $C_{11}H_{15}NO$ (M+H) requires 178.1232, found 178.1231.

4.8. 2-Methoxy-6-(2-methoxyvinyl)naphthalene 2/3f

51% Combined yield; **2f**; colourless oil; ν_{max} (film/cm^{-1}) 2933, 1648, 1602, 1482, 1387, 1265, 1216, 1149, 1087, 1029; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.94 (s, 1H, Ar*H*), 7.69 (t, J=8.5 Hz, 2H, Ar*H*), 6.43 (d, J=8.7 Hz, 1H, Ar*H*), 7.10–7.08 (m, 2H, Ar*H*), 6.19 (d, J=7.0 Hz, 1H, CH_3OCH), 5.34 (d, J=7.0 Hz, 1H, CH_3OCHCH), 3.91 (s, 3H, $CH_3O(C)$), 3.83 (s, 3H, CH_3OCH); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 157.4 (C_q), 147.8 (CH), 133.0 (C_q), 131.5 (C_q), 129.5 (CH), 129.2 (C_q), 127.7 (CH), 126.5 (CH), 126.5 (CH), 118.7 (CH), 105.9 (CH), 105.7 (CH), 60.9 (CH_3), 55.4 (CH_3); LRMS (CI) 215 (100), 200 (10), 183 (7), 171 (8), 128 (3); HRMS (CI) calcd for $C_{14}H_{15}O_2$ (M+H) requires 215.1072, found 215.1070. **3f**; Pale cream solid (contaminated with 10% *Z*-isomer); ν_{max} (solid/cm^{-1}) 2930, 2839, 1633, 1599, 1504, 1482, 1448, 1437, 1387, 1266, 1247, 1207, 1166; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.65–7.63 (m, 2H, Ar*H*), 7.53 (s, 1H, Ar*H*), 7.40 (dd, J=8.6, 1.8 Hz, 1H, Ar*H*), 7.14 (d, J=12.9 Hz, 1H, CH_3OCH), 7.11–7.08 (m, 2H, Ar*H*), 5.95 (d, J=12.9 Hz, 1H, CH_3OCHCH), 3.91 (s, 3H, $CH_3O(C)$), 3.72 (s, 3H, CH_3OCH); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 157.2 (C_q), 148.7 (CH), 133.1 (C_q), 131.7 (C_q), 129.4 (C_q), 129.0 (CH), 127.2 (CH), 124.0 (CH), 123.8 (CH), 119.0 (CH), 105.9 (CH), 105.4 (CH), 56.7 (CH_3), 55.4 (CH_3).

4.9. 1-Bromo-4-(2-methoxyvinyl)benzene 2/3g

53% Combined yield; **2g**; colourless oil; ν_{max} (film/cm^{-1}) 2933, 1649, 1624, 1485, 1453, 1407, 1311, 1289, 1266, 1200, 1088; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.43 (d, J=8.6 Hz, 2H, Ar*H*), 7.38 (d, J=8.6 Hz, 2H, Ar*H*), 6.16 (d, J=7.0 Hz, 1H, CH_3OCH), 5.16 (d, J=7.0 Hz, 1H, CH_3OCHCH), 3.79 (s, 3H, CH_3O); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 148.7 (CH), 134.9 (C_q), 131.3 (CH), 129.8 (CH), 119.2 (C_q), 104.7 (CH), 60.9 (CH_3); LRMS (EI) 214 (30), 212 (29), 171 (16), 169 (19), 118 (92), 90 (51), 89 (65), 86 (68), 84 (100); HRMS (EI) calcd for C_9H_9BrO (M^+) requires 211.9837, found 211.9832. **3g**; Colourless oil (contaminated with 14% *Z*-isomer); ν_{max} (film/cm^{-1}) 2934, 2833, 1700, 1640, 1487, 1462, 1400, 1312, 1291, 1241, 1190; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.36 (d, J=8.5 Hz, 2H, Ar*H*), 7.09 (2H, d, J=8.5 Hz, 2H, Ar*H*), 7.03 (d, J=13.0 Hz, 1H, CH_3OCH), 5.73 (d, J=13.0 Hz, 1H, CH_3OCHCH), 3.68 (s, 3H, CH_3O); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 149.4 (CH), 135.5 (C_q), 131.7 (CH), 126.7 (CH), 119.1 (C_q), 104.1 (CH), 56.7 (CH_3); LRMS (EI) 214 (15), 212 (15), 185 (42), 183 (38), 171 (33), 169 (35), 157 (19), 155 (20), 118 (59), 90 (57), 89 (100).

4.10. 1-(2-Methoxyvinyl)-4-(trifluoromethyl)benzene 2/3h[20]

31% Combined yield; **2h**; pale yellow oil; ν_{max} (film/cm^{-1}) 2924, 2853, 1643, 1614, 1323, 1273, 124, 1186, 1161, 1121, 1095; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.64 (d, J=8.1 Hz, 2H, Ar*H*), 7.51 (d, J=8.1 Hz, 2H, Ar*H*), 6.24 (d, J=6.9 Hz, 1H, CH_3OCH), 5.25 (d, J=6.9 Hz, 1H, CH_3OCHCH), 3.82 (s, 3H, CH_3O); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 150.0 (CH), 139.5 (C_q), 128.2 (CH), 127.4 (q, J=32.1 Hz) (C_q), 125.2 (q, J=3.8 Hz) (CH), 124.5 (q, J=271.8 Hz) (C_q), 104.5 (CH), 61.1 (CH_3); LRMS (EI) 202 (21), 183 (24), 159 (100), 151 (15), 133 (5), 109 (73). **3h**; Pale yellow oil (contaminated with 8% *Z*-isomer); ν_{max} (film/cm^{-1}) 2926, 2854, 1728, 1657, 1642, 1615, 1413, 1324, 1163, 1123; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.50 (d, J=8.2 Hz, 2H, Ar*H*), 7.30 (d, J=8.2 Hz, 2H, Ar*H*), 7.14 (d, J=13.0 Hz, 1H, CH_3OCH), 5.81 (d, J=13.0 Hz, 1H, CH_3OCHCH), 3.72 (s, 3H, CH_3O); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 150.7 (CH), 140.3 (C_q), 127.5 (q, J=33.0 Hz) (C_q), 125.7 (q, J=3.8 Hz) (CH), 125.1 (CH), 124.6 (q, J=271.3 Hz) (C_q), 104 (CH), 56.8 (CH_3); LRMS (EI) 202 (100), 183 (10), 173 (34), 159 (72), 151 (5), 145 (12), 109 (14).

4.11. 1-(2,2-Dimethoxyethyl)-3-methoxybenzene 4d

Colourless oil, 28%; ν_{max} (film/cm^{-1}) 2934, 2829, 1600, 1583, 1488, 1452, 1435, 1361, 1309, 1292, 1257, 1229, 1116, 1041; ^{1}H NMR

(500 MHz, $CDCl_3$) δ_H 7.21 (t, J=7.8 Hz, 1H), 6.84–6.76 (m, 3H), 4.55 (t, J=5.6 Hz, 1H), 3.80 (s, 3H), 3.34 (s, 6H), 2.89 (d, J=5.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 159.6 (C_q), 138.7 (C_q), 129.4 (CH), 121.9 (CH), 115.3 (CH), 111.8 (CH), 105.3 (CH), 55.3 (CH_3), 53.5 (CH_3), 39.8 (CH_2); LRMS (EI) 196 (4), 165(18), 135 (3), 121 (9), 75 (100); HRMS (EI) calcd for $C_{11}H_{16}O_3$ (M^+) requires 196.1099, found 196.1099.

4.12. 2-(2,2-Dimethoxyethyl)-6-methoxynaphthalene 4f

White solid, 21%; MP=57–58 °C; ν_{max} (film/cm^{-1}) 2957, 2937, 2903, 2834, 1632, 1601, 1483, 1460, 1390, 1260, 1232, 1183, 1117, 1047; ^1H NMR (600 MHz, $CDCl_3$) δ_H 7.69 (t, J=8.0 Hz, 2H), 7.62 (s, 1H), 7.35 (dd, J=8.4, 1.6 Hz, 1H), 7.14–7.12 (m, 2H), 4.62 (t, J=5.7 Hz, 1H), 3.92 (s, 3H), 3.37 (s, 6H), 3.05 (d, J=5.7 Hz, 2H); ^{13}C NMR 157.4 (C_q), 133.4 (C_q), 132.3 (C_q), 129.2 (CH), 129.1 (C_q), 128.5 (CH), 127.8 (CH), 126.8 (CH), 118.9 (CH), 105.7 (CH), 105.6 (CH), 55.4 (CH_3), 53.6 (CH_3), 39.8 (CH_2); HRMS (ESI) calcd for $C_{15}H_{18}ONa$ (M+Na) requires 269.1154, found 269.1153.

4.13. 1-Bromo-4-(2,2-dimethoxyethyl)benzene 4g[21]

Colourless oil, 14%; ν_{max} (film/cm^{-1}) 2932, 2830, 1488, 1362, 1189, 1118, 1071, 1043, 1011; ^1H NMR (600 MHz, $CDCl_3$) δ_H 7.41 (d, J=8.3 Hz, 2H, Ar*H*), 7.11 (d, J=8.3 Hz, 2H, Ar*H*), 4.49 (t, J=5.6 Hz, 1H, CH_3OCH), 3.33 (s, 6H, 2×CH_3O), 2.86 (d, J=5.6 Hz, 2H, CH_3OCHCH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 136.1 (C_q), 131.5 (CH), 131.3 (CH), 120.7 (C_q), 105.1 (CH), 53.6 (CH_3), 39.2 (CH_2); LRMS (EI) 245 (1), 243 (1), 171 (44), 169 (46), 134 (100), 118 (19); HRMS (EI) calcd for $C_{10}H_{13}BrO_2$ (M^+) requires 244.0098, found 244.0092.

4.14. 1-(2,2-Dimethoxyethyl)-4-(trifluoromethyl)benzene 4h

Colourless oil, 32%; ν_{max} (film/cm^{-1}) 2935, 2831, 1618, 1438, 1417, 1363, 1321, 1228, 1161, 1107, 1063; ^1H NMR (600 MHz, $CDCl_3$) δ_H 7.55 (d, J=8.0 Hz, 2H, Ar*H*), 7.35 (d, J=8.0 Hz, 2H, Ar*H*), 4.54 (t, J=5.6 Hz, 1H, $CH(OCH_3)_2$), 3.35 (s, 6H, 2×OCH_3), 2.96 (d, J=5.6 Hz, 2H, $CHCH_2Ar$); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 141.2 (C_q), 129.9 (CH), 128.8 (q, J=32.3 Hz) (C_q), 125.3 (q, J=3.8 Hz) (CH), 123.5 (q, J=273.8 Hz) (C_q), 104.9 (CH), 53.6 (CH_3), 39.6 (CH_2); LRMS (CI) Mass ion not observed, 220 (8), 205 (30), 188 (100), 75 (31). Not observed by HRMS.

4.15. 1-(4-Methoxyphenyl)ethanone 5c[21]

Colourless oil, 7%; ^1H NMR (600 MHz, $CDCl_3$) δ_H 7.95 (d, J=8.8 Hz, 2H, Ar*H*), 6.94 (d, J=8.8 Hz, 2H, Ar*H*), 3.88 (s, 3H, CH_3O), 2.57 (s, 3H, CH_3(C)); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 197.0 (C_q), 163.6 (C_q), 130.7 (CH), 130.4 (C_q), 113.8 (CH), 55.6 (CH_3), 26.5 (CH_3); LRMS (EI) 150 (34), 135 (100), 121 (5), 107 (11), 92 (23).

4.16. 1-(4-(Dimethylamino)phenyl)ethanone 5e[22]

White film, 7%; ^1H NMR (600 MHz, $CDCl_3$) δ_H 7.88 (d, J=9.0 Hz, 2H, Ar*H*), 6.66 (d, J=9.0 Hz, 2H, Ar*H*), 3.07 (s, 6H, $(CH_3)_2N$), 2.52 (s, 3H, CH_3(C)); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 196.6 (C_q), 153.5 (C_q), 130.7 (CH), 125.4 (C_q), 110.7 (CH), 40.2 (CH_3), 26.2 (CH_3). HRMS (ESI) calcd for $C_{10}H_{14}NO$ (M+H) requires 164.1075, found 164.1076.

4.17. General procedure for the synthesis of isopropyl and benzyl alkenyl ethers

To a flame-dried flask under an atmosphere of argon was added benzyl alcohol or isopropanol (0.96 mmol, 4.0 equiv) and anhydrous THF (1.0 mL). To the solution was added potassium hydride (0.96 mmol, 4.0 equiv washed with petroleum ether and dried using filter paper immediately prior to use) as a single portion to give a bubbling white paste. The mixture was stirred at rt for 10 min, then gently heated to 50 °C for 20 min, before being cooled to rt. The remaining THF was removed in vacuo and the resulting paste diluted with DMF (1.5 mL). To the solution was added DMEDA (0.48 mmol, 2.0 equiv) then *p*-tolylacetylene (0.24 mmol, 1.0 equiv) as a single burst. The mixture was stirred at 55 °C until complete consumption of *p*-tolylacetylene was observed by TLC (3 h). The crude mixture was quenched by addition of *i*PrOH (1 mL) and diluted with CH_2Cl_2 (100 mL), which was washed with 2.0 M LiCl (3×20 mL). The organic portion was dried over $MgSO_4$, filtered and concentrated in vacuo, then purified via column chromatography (0–5% EtOAc/P.E.) to yield the alkenyl ethers.

4.18. 1-(2-Isopropoxyvinyl)-4-methylbenzene 7

43% (*Z* and *E* combined yield). *Z*-isomer: Pale yellow oil; ν_{max} (film/cm^{-1}) 2974, 1648, 1511, 1453, 1422, 1383, 1372, 1338, 1259, 1117, 1074; ^1H NMR (600 MHz, CD_2Cl_2) δ_H 7.45 (d, J=8.0 Hz, 2H, Ar*H*), 7.07 (d, J=8.0 Hz, 2H, Ar*H*), 6.22 (d, J=7.0 Hz, 1H, OC*H*CH), 5.16 (d, J=7.0 Hz, 1H, OCHC*H*), 4.05 (quintet, J=6.3 Hz, 1H, $OCH(CH_3)_2$), 2.29 (s, 3H, CH_3(C)), 1.31 (d, J=6.3 Hz, 6H, $CH(CH_3)_2$); ^{13}C NMR (150 MHz, CD_2Cl_2) δ_C 144.9 (CH), 135.0 (C_q), 133.5 (C_q), 128.7 (CH), 127.9 (CH), 104.9 (CH), 75.8 (CH), 22.3 (CH_3), 20.1 (CH_3); LRMS (EI) 176 (43), 134 (100), 119 (48), 105 (76), 91 (20); HRMS (EI) calcd for $C_{12}H_{16}O$ (M^+) requires 176.1201, found 176.1206. *E*-isomer: Colourless oil; ν_{max} (film/cm^{-1}) 2974, 1654, 1635, 1513, 1384, 1372, 1317, 1218, 1177, 1151, 1111; ^1H NMR (600 MHz, CD_2Cl_2) δ_H 7.10 (d, J=8.0 Hz, 2H, Ar*H*), 7.05 (d, J=8.0 Hz, 2H, Ar*H*), 6.84 (d, J=12.7 Hz, 1H, OC*H*CH), 5.83 (d, J=12.7 Hz, 1H, OCHC*H*), 4.11 (quintet, J=6.2 Hz, 1H, $OCH(CH_3)_2$), 2.28 (s, 3H, CH_3(C)), 1.26 (d, J=6.2 Hz, 6H, $CH(CH_3)_2$); ^{13}C NMR (150 MHz, CD_2Cl_2) δ_C 146.2 (CH), 135.1 (C_q), 133.7 (C_q), 129.1 (CH), 124.7 (CH), 107.0 (CH), 73.6 (CH), 22.1 (CH_3), 20.7 (CH_3); LRMS (EI) 176 (9), 134 (25), 105 (16), 85 (63), 83 (100); HRMS (EI) calcd for $C_{12}H_{16}O$ (M^+) requires 176.1201, found 176.1204.

4.19. 1-(2-(Benzyloxy)vinyl)-4-methylbenzene 8[23]

61% (*Z* and *E* combined yield). *Z*-isomer: Pale yellow oil; ν_{max} (film/cm^{-1}) 3029, 2921, 2859, 1649, 1512, 1453, 1419, 1367, 1299, 1261, 1198, 1086, 1074; ^1H NMR (600 MHz, $CDCl_3$) δ_H 7.53 (d, J=7.9 Hz, 2H, Ar*H*), 7.40–7.36 (m, 4H, Ar*H*), 7.33–7.31 (m, 1H, Ar*H*), 7.11 (d, J=7.9 Hz, 2H, Ar*H*), 6.23 (d, J=7.0 Hz, 1H, OC*H*CH), 5.25 (d, J=7.0 Hz, 1H, OCHC*H*), 4.99 (s, 2H, OCH_2Ph), 2.32 (s, 3H, CH_3(C)); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 145.7 (CH), 137.5 (C_q), 135.5 (C_q), 133.1 (C_q), 129.0 (CH), 128.7 (CH), 128.3 (CH), 128.1 (CH), 127.3 (CH), 106.3 (CH), 74.9 (CH_2), 21.3 (CH_3); LRMS (CI) 225 (29), 224 (32), 207 (32), 195 (10), 147 (6), 133 (8), 119 (8), 105 (46), 91 (100); HRMS (CI) calcd for $C_{16}H_{17}O$ ($M+H^+$) requires 225.1279, found 225.1274. *E*-isomer (contaminated with 15% *Z*-isomer); Pale yellow oil; ν_{max} (film/cm^{-1}) 3033, 3017, 2913, 2870, 1636, 1512, 1453, 1377, 1319, 1224, 1213, 1150, 1104, 1080; ^1H NMR (600 MHz, $CDCl_3$) δ_H 7.40–7.37 (m, 4H, Ar*H*), 7.34–7.32 (m, 1H, Ar*H*), 7.13 (d, J=8.0 Hz, 2H, Ar*H*), 7.07 (d, J=8.0 Hz, 2H, Ar*H*), 7.04 (d, J=13.0 Hz, 1H, OC*H*CH), 5.95 (d, J=13.0 Hz, 1H, OCHC*H*), 4.89 (s, 2H, OCH_2Ph), 2.31 (s, 3H, CH_3(C)); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 147.2 (CH), 136.9 (C_q), 135.5 (C_q), 133.4 (C_q), 129.4 (CH), 128.7 (CH), 128.2 (CH), 127.7 (CH), 125.2 (CH), 106.9 (CH), 71.9 (CH_2), 21.2 (CH_3); LRMS (CI) 225 (14), 224 (15), 207 (21), 173 (5), 125 (5), 111 (33), 105 (40), 97 (31), 91 (100).

4.20. (2-Methoxyprop-1-en-1-yl)benzene 9[24]

Colourless oil, 51% combined yield; ^1H NMR (600 MHz, CD_2Cl_2) δ_H (*E*-isomer) 7.28 (t, J=7.7 Hz, 2H, Ar*H*), 7.19 (d, 2H, J=7.5 Hz, Ar*H*), 7.12 (t, J=7.4 Hz, 1H, Ar*H*), 5.60 (s, 1H, ArC*H*), 3.64 (s, 3H, CH_3O), 1.98 (s, 3H, CH_3(C)); ^{13}C NMR (150 MHz, CD_2Cl_2) δ_C (*E*-isomer) 156.4 (C_q),

137.9 (C_q), 128.6 (CH), 128.1 (CH), 124.9 (CH), 99.3 (CH), 54.5 (CH_3), 17.7 (CH_3); ^{1}H NMR (600 MHz, CD_2Cl_2) δ_H (*Z*-isomer) 7.50 (d, *J*=7.4 Hz, 2H, Ar*H*), 7.23 (t, *J*=7.6 Hz, 2H, Ar*H*), 7.07 (t, *J*=7.4 Hz, 1H, Ar*H*), 5.29 (s, 1H, ArC*H*), 3.72 (s, 3H, C*H*$_3$O), 2.05 (s, 3H, C*H*$_3$(C)); ^{13}C NMR (150 MHz, CD_2Cl_2) δ_C (*Z*-isomer) 153.8 (C_q), 136.9 (C_q), 127.9 (CH), 127.7, 124.9 (CH), 105.8 (CH), 54.9 (CH_3), 18.3 (CH_3); LRMS (CI) 149 (100), 117 (24), 105 (4). Data in agreement with literature values.[24]

4.21. 4-Phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene 14[18]

20%; Colourless oil, ν_{max} (film/cm^{-1}) 3056, 2948, 1600, 1493, 1027, 850; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.82 (d, *J*=8.2 Hz, 1H, Ar*H*), 7.70 (s, 1H, CH_2(C)C*H*), 7.58 (d, *J*=8.5 Hz, 1H, Ar*H*), 7.50 (t, *J*=7.3 Hz, 2H, Ar*H*), 7.43–7.36 (m, 4H, Ar*H*), 7.30 (t, *J*=7.6 Hz, 1H, Ar*H*), 3.13 (td, *J*=7.5, 1.0 Hz, 2H, C*H*$_2$(C)CH), 2.83 (t, *J*=7.3 Hz, 2H, C*H*$_2$(C) (C)), 2.09 (quint, *J*=7.4 Hz, 2H, $CH_2CH_2CH_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 143.0 (C_q), 141.8 (C_q), 139.6 (C_q), 134.7 (C_q), 133.3 (C_q), 131.6 (C_q), 130.1 (CH), 128.4 (CH), 127.7 (CH), 127.1 (CH), 125.9 (CH), 125.0 (CH), 124.9 (CH), 121.9 (CH), 33.2 (CH_2), 32.6 (CH_2), 26.1 (CH_2); HRMS (EI) calcd for $C_{19}H_{16}$ (M^+) requires 244.1247, found 244.1251. Data in agreement with literature values.

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Supplementary data

Supplementary data (^{1}H and ^{13}C NMR spectra of the compounds presented are available.) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.04.038.

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