

Organolithium addition to styrene and styrene derivatives: scope and limitations

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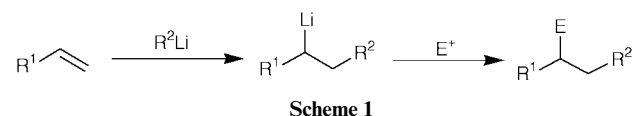
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Styrene and a range of aryl-substituted styrene derivatives are shown to undergo efficient carbolithiation–trapping reactions in diethyl ether at -78 to -25 °C. The reactivities of different types of organolithium reagents were found to be: tertiary, secondary > primary; \gg alkenyl, methyl, phenyl. Electron donating groups (e.g. methoxy and dialkylamino) at the *ortho*- or *para*- positions of the benzene ring deactivate the double bond towards organolithium addition, but their reactions with butyllithium can be facilitated by using TMEDA as co-solvent. 2-Benzyloxystyrene and 2-allyloxystyrene undergo efficient carbolithiation at -78 °C, but at room temperature alkyl transfer occurs, generating the corresponding alkylated phenol. 2-Vinylnaphthalene also undergoes carbolithiation–carboxylation in reasonable yield.

Introduction

Alkene carbolithiation is, in principle, a synthetically efficient and versatile procedure (Scheme 1).¹ The intermediate organo-



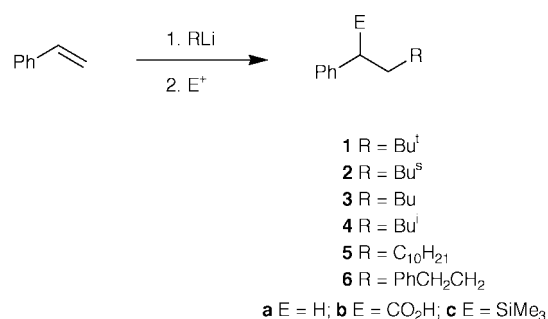
lithium is produced with complete atom economy and can be trapped with a range of electrophiles, thus assembling three components in a one-pot process.² In practice, however, such a process is not always viable. The reaction is usually accompanied by anionic oligomerisation and this process often dominates. Therefore it is usually necessary to adjust the reaction conditions according to the reactivity of the organolithium reagent, the nature of the alkene, steric effects, *etc.* in order to minimise this side reaction.

The anionic polymerisation of styrene using organolithium reagents is a well-known process³ and, presumably for this reason, there are few reports^{4,5} in the literature of its organometallic addition reactions, although some of its alkenyl-substituted derivatives have been more thoroughly studied.^{1,6–8} We recently discovered that organolithium addition reactions to styrene are synthetically viable under appropriate conditions.⁹ We went on to develop an enantioselective variant of this process¹⁰ and extended the basic methodology to tetralin synthesis.¹¹ Herein, we report our full results on the scope and limitations of the styrene–organolithium addition process.

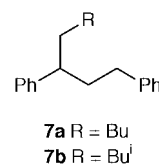
Results and discussion

(i) Organolithium additions to styrene

As illustrated in Table 1 and Scheme 2, styrene underwent efficient addition reactions with a range of commercial and home-made organolithium reagents in diethyl ether giving adducts in good isolated yields. Thus, treatment of styrene with *tert*-butyllithium or *sec*-butyllithium in diethyl ether as solvent at -78 °C followed by protonation using methanol gave the expected adducts in almost quantitative yields (Table 1, entries 1 and 3). It seemed possible that the facility of these additions was due to the steric bulk of the secondary and tertiary



substituents which could inhibit the oligomerisation process. However, the reactions of styrene with butyllithium and isobutyllithium were also efficient (>80%), although the lower reactivity of these reagents required that a higher reaction temperature (-25 °C) be employed (Table 1, entries 5 and 10); compounds **7a,b** resulting from the addition of a second mole-



cule of styrene to the intermediate organolithium were present as minor by-products in these reactions.

In the addition of butyllithium to styrene, a comparison of the solvents was carried out (Table 1, entries 5, 7 and 8). No reaction was observed using hexane as solvent from -78 °C to room temperature. In contrast, with THF as solvent, rapid polymerisation was observed on addition of the alkyllithium reagent, even at -78 °C. The absence of reaction in hexane was unsurprising but the dramatic difference between diethyl ether and THF is noteworthy. These observations presumably indicate that the organolithium reagent must be reactive enough to add to styrene but that the resulting lithiated intermediate has to be sufficiently stabilised to minimise oligomerisation. In the cases mentioned the use of diethyl ether as solvent appears to meet these requirements. This delicate balance is emphasised in the reaction of methyllithium with styrene (Table 1, entry 11). No reaction was observed in diethyl ether from -78 °C to

Table 1 Organolithium addition reactions with styrene^a

Entry	R	E	Solvent	T/°C	Product	Yield (%)
1	Bu ^t	H	Et ₂ O	-78	1a	93 ^b
2	Bu ^t	CO ₂ H	Et ₂ O	-78	1b	92
3	Bu ^s	H	Et ₂ O	-78	2a	94
4	Bu ^s	CO ₂ H	Et ₂ O	-78	2b	86
5	Bu	H	Et ₂ O	-25	3a	85 ^c
6	Bu	CO ₂ H	Et ₂ O	-25	3b	84
7	Bu	H	THF	-78	— ^d	—
8	Bu	H	Hexane	-78→room temp.	— ^e	—
9	Bu	Me ₃ Si	Et ₂ O	-25	3c	51
10	Bu ^t	H	Et ₂ O	-25	4a	82 ^f
11	Me	H	Et ₂ O	-78→room temp.	— ^g	—
12	Ph	H	Et ₂ O	-78→room temp.	— ^h	—
13	Cyclohex-1-enyl	H	Et ₂ O	-78→room temp.	— ^h	—
14	C ₁₀ H ₂₁	H	Et ₂ O	-25	5a	82
15	PhCH ₂ CH ₂	H	Et ₂ O	-25	6a	60

^a All products were isolated and fully characterised by spectroscopy; new compounds were also characterised by HRMS or elemental analysis. ^b Styrene did not react with *tert*-butylmagnesium chloride, even at room temperature; Bu^t₂CuLi gave **1a** in 85% yield. ^c Diadduct **7a** was also obtained (7%). ^d Polymer obtained. ^e No reaction. ^f Diadduct **7b** was also obtained (12%). ^g No reaction in diethyl ether or THF (polymerisation occurred when TMEDA was added to ether reaction). ^h Polymerisation occurred in ether, THF and ether-TMEDA.

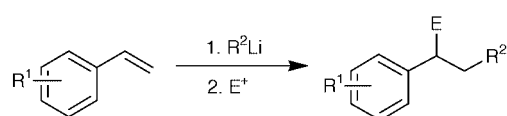
room temperature but in this case changing to THF had no effect. The addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to the methylolithium in the diethyl ether reaction, however, caused polymerisation. Although phenyllithium and cyclohexenyllithium are more reactive than methylolithium, their addition reaction to styrene did not occur in diethyl ether between -78 and -10 °C, and warming the reaction mixture produced only polystyrene when TMEDA was added.

All of the above transformations were accomplished using commercial organolithium reagents. Entries 14 and 15 in Table 1 indicate that this is not a requirement. Decyllithium (entry 14) and 2-phenylethyllithium (entry 15), prepared by transmetallation of the corresponding iodides,¹² gave good to fair yields of the required adducts.

In several cases the intermediate organolithium reagent was trapped with other electrophiles. Thus carboxylation gave the expected acids **1b–3b** in high isolated yields (Table 1, entries 2, 4 and 6, respectively), and trimethylsilylation (R = Bu) gave **3c** in 51% yield (Table 1, entry 9).

(ii) Organolithium addition to aryl-substituted styrene derivatives

We next examined the reaction of aryl-substituted styrenes in order to assess the substituent effects. Scheme 3 and Table 2 illustrate a number of examples in which aryl-substituted styrenes have been shown to react with organolithium reagents. The reactions of the three methoxystyrene isomers (*ortho*-, *meta*- and *para*-) were tested first. We anticipated that an *ortho*- or *para*-methoxy group would deactivate the alkene more than the *meta*-methoxy group, and this was indeed the case. Although *tert*-butyllithium added to all three isomers at low temperature (-78 °C) gave the corresponding protonated or carboxylated products **19a**, **19b**, **21a**, **23a** and **23b** in good (75–91%) yields (Table 2, entries 1, 2, 6, 8 and 9), reactions of the *o*- and *p*-methoxystyrene isomers were slower than that of the *meta*-isomer as monitored by TLC. The reaction of the *para*-isomer was so slow that a higher temperature (-44 °C) was required to ensure that the reaction was complete within 1 hour (Table 2, entries 8 and 9). This effect was reflected more obviously in the reaction of these compounds with butyllithium. As with styrene, *m*-methoxystyrene reacted with butyllithium smoothly at -25 °C giving product **22a** in 61% yield after protonation with methanol (Table 2, entry 7). However, *o*- and *p*-methoxystyrenes were found not to be reactive enough at this temperature: no reaction was observed within 1 hour, but at higher temperature both reactions gave polymer (Table 2, entries 3 and 10). For synthetic purposes, this problem was overcome by the addition of TMEDA to the reaction mixture.



- | | |
|--|---|
| 8 R ¹ = <i>o</i> -MeO | 19 R ¹ = <i>o</i> -MeO, R ² = Bu ^t |
| 9 R ¹ = <i>m</i> -MeO | 20 R ¹ = <i>o</i> -MeO, R ² = Bu |
| 10 R ¹ = <i>p</i> -MeO | 21 R ¹ = <i>m</i> -MeO, R ² = Bu ^t |
| 11 R ¹ = <i>o</i> -N(Me)CH ₂ CH=CH ₂ | 22 R ¹ = <i>m</i> -MeO, R ² = Bu |
| 12 R ¹ = <i>o</i> -N(CH ₂ Ph)CH ₂ CH=CH ₂ | 23 R ¹ = <i>p</i> -MeO, R ² = Bu ^t |
| 13 R ¹ = <i>o</i> -Ph | 24 R ¹ = <i>p</i> -MeO, R ² = Bu |
| 14 R ¹ = <i>p</i> -Ph | 25 R ¹ = <i>o</i> -N(Me)CH ₂ CH=CH ₂ , R ² = Bu ^t |
| 15 R ¹ = <i>o</i> -OH | 26 R ¹ = <i>o</i> -N(CH ₂ Ph)CH ₂ CH=CH ₂ , R ² = Bu ^t |
| 16 R ¹ = <i>o</i> -O(CH ₂) ₄ OH | 27 R ¹ = <i>o</i> -Ph, R ² = Bu |
| 17 R ¹ = <i>p</i> -CO ₂ H | 28 R ¹ = <i>p</i> -Ph, R ² = Bu ^s |
| | 29 R ¹ = <i>o</i> -OH, R ² = Bu ^t |
| | 30 R ¹ = <i>o</i> -O(CH ₂) ₄ OH, R ² = Bu ^t |
| | 31 R ¹ = <i>p</i> -CO ₂ H, R ² = Bu ^t |

a E = H; **b** E = CO₂H; **c** E = SiMe₃

Scheme 3

Thus, in the presence of two equivalents of TMEDA, the reaction of butyllithium with *o*-methoxystyrene proceeded smoothly at -78 °C producing the substituted benzylic organolithium intermediates within one hour. The intermediates were subsequently quenched using methanol or trimethylsilyl chloride giving products **20a** and **20c** in fair yields (Table 2, entries 4 and 5). Under the same conditions, however, no adduct could be detected from the reaction of butyllithium with *p*-methoxystyrene. Although a red solution was obtained after 1 hour, quenching with methanol at -78 °C gave recovered starting material only. However, slowly warming this red solution to room temperature and then quenching with methanol produced the desired product **24a** but in only 7% yield along with an unidentified polymer (Table 2, entry 11). It seems unlikely that at -78 °C directed *ortho*-metallation¹³ is faster than organolithium addition. We therefore carried out the reaction at a higher temperature (-40 °C), and in this case, the organolithium addition reaction proceeded rapidly giving the product **24a** in 58% yield after protonation with methanol (Table 2, entry 12).

Some other aryl-substituted styrenes were also evaluated (Table 2, entries 13–21). The *o*-allylamino-substituted styrene derivatives **11** and **12** also underwent addition with *tert*-butyllithium at a slower rate than styrene, presumably due to similar electron donating effects to those observed in the anisyl systems (entries 8–12). The formation of adducts **25a** and **26a** in high yield after protonation (90 and 91%), however, clearly

Table 2 Organolithium addition reactions with aryl-substituted styrenes

Entry	R ¹	R ²	E	Solvent	T/°C	Product	Yield (%)
1	<i>o</i> -MeO 8	Bu ^t	H	Et ₂ O	-78	19a	83
2	<i>o</i> -MeO 8	Bu ^t	CO ₂ H	Et ₂ O	-78	19b	84
3	<i>o</i> -MeO 8	Bu	H	Et ₂ O	-78→rt	— ^b	—
4	<i>o</i> -MeO 8	Bu	H	Et ₂ O–TMEDA	-78	20a	68
5	<i>o</i> -MeO 8	Bu	Me ₃ Si	Et ₂ O–TMEDA	-78	20c	63
6	<i>m</i> -MeO 9	Bu ^t	H	Et ₂ O	-78	21a	91
7	<i>m</i> -MeO 9	Bu	H	Et ₂ O	-25	22a	61
8	<i>p</i> -MeO 10	Bu ^t	H	Et ₂ O	-44	23a	75
9	<i>p</i> -MeO 10	Bu ^t	CO ₂ H	Et ₂ O	-44	23b	75
10	<i>p</i> -MeO 10	Bu	H	Et ₂ O	-78→rt	— ^b	—
11	<i>p</i> -MeO 10	Bu	H	Et ₂ O–TMEDA	-78→rt	24a	7
12	<i>p</i> -MeO 10	Bu	H	Et ₂ O–TMEDA	-40	24a	58
13	<i>o</i> -N(Me)CH ₂ CH=CH ₂ 11	Bu ^t	H	Et ₂ O	-78	25a	90
14	<i>o</i> -N(CH ₂ Ph)CH ₂ CH=CH ₂ 12	Bu ^t	H	Et ₂ O	-78	26a	91
15	<i>o</i> -Ph 13	Bu	H	Et ₂ O	-35	27a	70
16	<i>p</i> -Ph 14	Bu ^s	H	Et ₂ O	-78	28a	74
17	<i>o</i> -OH 15	Bu ^t	H	Et ₂ O	-78→rt	— ^{b,c}	—
18	<i>o</i> -O(CH ₂) ₄ OH 16	Bu ^t	H	Et ₂ O	-78	30a	81 ^c
19	<i>p</i> -CO ₂ H 17	Bu ^t	CO ₂ H	Et ₂ O	-78	31b	70 ^c
20	18	Bu ^t	CO ₂ H	Et ₂ O	-78	32b	45
21	18	Bu	CO ₂ H	Et ₂ O	-25	33b	75

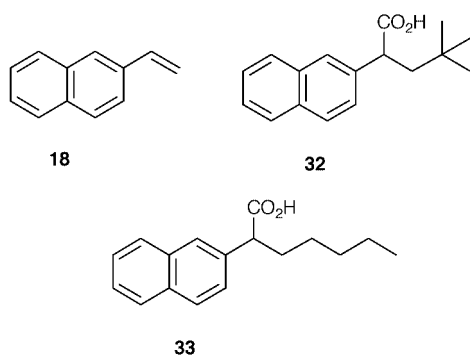
^a All products were isolated and fully characterised by spectroscopy; new compounds were also characterised by HRMS or elemental analysis.

^b Polymer was obtained. ^c 2.4 Equivalents of organolithium reagent were used.

shows that the addition occurred selectively at the conjugated double bond. *o*- and *p*-Phenylstyrenes **13** and **14** were studied next: as expected they were found to undergo addition at a faster rate with *sec*-butyllithium and butyllithium, at -78 and -35 °C respectively (Table 2, entries 15 and 16), indicating that the phenyl group can facilitate the addition reaction by stabilising the intermediate benzylic carbanion.

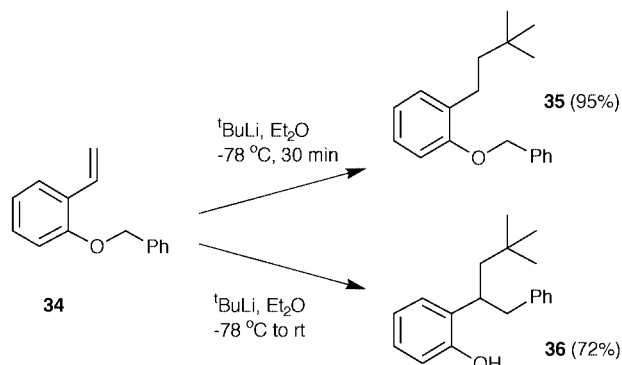
Although 2-vinylphenol **15** did not undergo addition on treatment with 2 equivalents of *tert*-butyllithium (Table 2, entry 17), the reaction of alcohol **16** to produce **30a** illustrates that hydroxy groups can be present in the substrate, providing that an additional equivalent of organolithium reagent is employed (Table 2, entry 18). We therefore used the same conditions in the reaction of 4-vinylbenzoic acid (**17**) with *tert*-butyllithium. This transformation proceeded efficiently giving, after carboxylation, diacid **31b** as a crystalline solid in 70% yield. It is apparent that at -78 °C in ether, alkene carbolithiation occurs at a faster rate than organolithium addition to the lithium carboxylate.

All of the above examples employed aryl-substituted styrenes. We also demonstrated that the reaction is applicable to other aromatic systems. Thus, vinyl naphthalene **18** was carbolithiated–carboxylated to give acids **32** and **33** in 45 and 75% unoptimised yields.



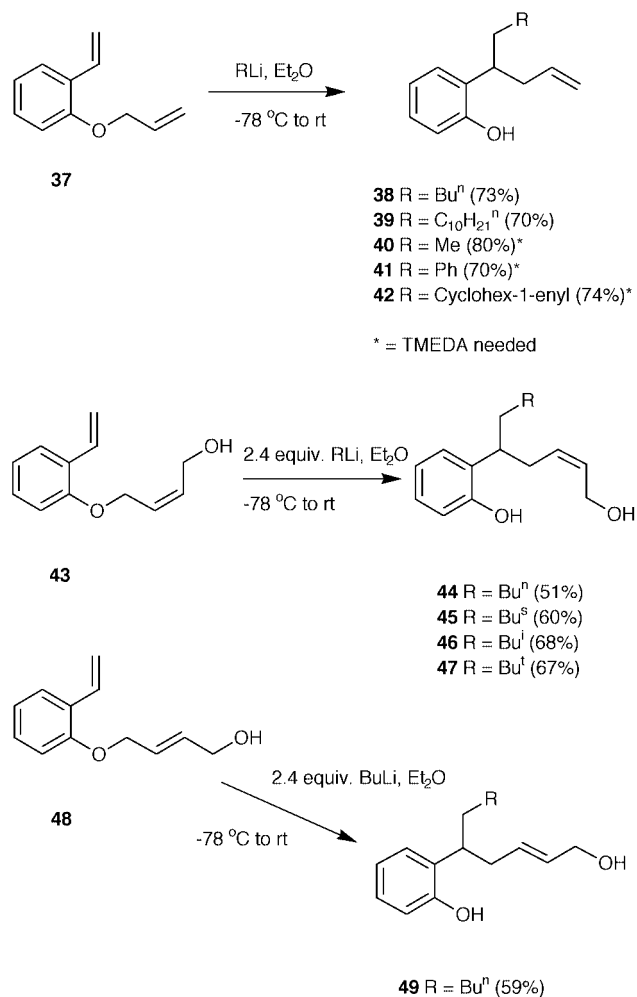
(iii) Organolithium addition–alkyl transfer reactions

All of the above reactions were carried out and quenched at low temperature. The reaction of 2-benzyloxystyrene **34** with *tert*-butyllithium was originally investigated using this protocol (Scheme 4) and the expected product **35** after protonation was

**Scheme 4**

observed in almost quantitative yield. When the reaction was allowed to warm up to room temperature before work-up, however, a new product **36** was obtained in 72% yield. The intermediate organolithium reagent is presumably *C*-benzylated *via* an intermolecular process¹⁴ or by way of a dissociation–recombination pathway (a vinylogous Wittig rearrangement).¹⁵

Related substrates were examined under similar reaction conditions. The *O*-methyl analogue (**8**) did not undergo methyl transfer on warming, and with *ortho*-amino compounds **11** and **12** complex mixtures were obtained and transfer of the *N*-methyl, *N*-benzyl or *N*-allyl groups was not observed. We therefore investigated *O*-allyloxy compounds on the assumption that an “activated” *O*-alkyl system was required. 2-Allyloxystyrene **37** underwent carbolithiation–allyl transfer with a range of organolithium reagents in good yields (Scheme 5). The efficient addition of butyllithium and decyllithium using diethyl ether as solvent was expected from the reactions using styrene. With styrene in diethyl ether, however, no reactions were observed with the relatively unreactive methyllithium, phenyllithium and cyclohexenyllithium, and in ether–TMEDA or THF, styrene polymerisation occurred. The fact that the methyl, phenyl and cyclohexenyl adducts **40–42** were formed using ether–TMEDA in this study is therefore noteworthy. We presume that the intermediate organolithium adducts leading to **40–42** undergo alkylation at a faster rate than polymerisation.



Scheme 5

This process also takes place with substituted allyloxy derivatives (Scheme 5). Thus, with several aryllithium reagents in ether, (*Z*)-butenol **43** was converted into the rearranged adducts **44–47**. We assume that allyloxy transfer occurred with retention of alkene configuration as only one alkene was obtained in each case, but unfortunately the alkene coupling constants could not be obtained from the ¹H NMR spectra. The isomeric (*E*)-butenol **48** was therefore subjected to a similar reaction with butyllithium. Again, only one compound **49** was isolated but it had completely different ¹H and ¹³C NMR spectra (see Experimental section), suggesting that in both reactions the stereochemistry of the transferred group remains intact.

In summary, we have established that organolithium addition reactions with styrene, and a range of aryl-substituted styrene analogues, are synthetically viable when diethyl ether is employed as the solvent. *tert*-Butyllithium and *sec*-butyllithium react with most of the aryl-substituted styrene derivatives at $-78\text{ }^{\circ}\text{C}$, but primary organolithium reagents usually need higher temperatures (*ca.* $-25\text{ }^{\circ}\text{C}$) to react. Electron donating groups, such as methoxy, at the *ortho*- or *para*-position of the benzene ring can slow down the reaction, and in this case TMEDA can be used to activate butyllithium for efficient transformation. 2-Benzyloxystyrene and 2-allyloxystyrene undergo carbolithiation at low temperature but an *O*- to *C*-transfer occurs if the reaction is warmed to room temperature. Phenyllithium, cyclohexyllithium and methylolithium, which do not add efficiently to styrene, can be used for this addition–alkyl transfer sequence in the presence of TMEDA. The reactions described above provide a useful method for the preparation of a range of alkylated benzene derivatives.

Experimental

NMR spectra were recorded on a JEOL EX-270 spectrometer. Tetramethylsilane (TMS) or residual CHCl₃ was used as the internal standard and *J* values are in Hz. Carbon spectra were verified using DEPT experiments. Melting points were recorded on an Electrothermal IA 9100 digital melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on an ATI Mattson Genesis FT-IR spectrometer. Low resolution electron impact (EI) mass spectra were recorded on a Kratos MS25 spectrometer. Chemical ionisation (CI) and high resolution mass spectra were recorded on a Micromass Autospec spectrometer. Elemental analyses were carried out at the University of East Anglia. TLC was carried out using pre-prepared plates (Merck silica gel 60 F-254, 5715). PE is petroleum ether (bp 40–60 °C), EtOAc is ethyl acetate, ether is diethyl ether and THF is tetrahydrofuran. Dry ether and THF were distilled from sodium–benzophenone ketyl immediately before use, and TMEDA was dried over anhydrous sodium hydroxide. Except where specified, all reagents were purchased from commercial sources and were used without further purification. Butyllithium is a 1.6 M solution in hexanes, *sec*-butyllithium is a 1.3 M solution in cyclohexane, *tert*-butyllithium is a 1.7 M solution in pentane, phenyllithium is a 1.8 M solution in cyclohexane–ether, methylolithium is a 1.4 M solution in ether.

Starting materials

Starting materials **11**, **12**, 2-benzyloxystyrene (**34**) and 2-allyloxystyrene (**37**) were prepared by Wittig reaction of the corresponding benzaldehydes according to literature procedures.^{16,17} Starting materials 4-(2'-vinylphenoxy)butan-1-ol (**16**), (*Z*)-4-(2'-vinylphenoxy)but-2-en-1-ol (**43**) and (*E*)-4-(2'-vinylphenoxy)but-2-en-1-ol (**48**) were prepared by standard Mitsunobu reactions¹⁸ of 2-hydroxystyrene with butane-1,4-diol, (*Z*)-but-2-ene-1,4-diol and (*E*)-but-2-ene-1,4-diol, respectively.

Organolithium addition to styrenes—general procedure

To a stirred solution of styrene (0.5 mmol) in dry diethyl ether (25 cm³) at $-78\text{ }^{\circ}\text{C}$ under nitrogen was added the organolithium solution (0.55 mmol). The reaction mixture was then stirred at $-78\text{ }^{\circ}\text{C}$ for 0.5 to 2 h until the styrene was no longer evident by TLC (PE). Methanol (1 cm³) was then added and the reaction stirred for a further 10 min. The solution was diluted with ether (50 cm³), washed with water (2 × 25 cm³) and dried with anhydrous sodium sulfate. Evaporation of solvent and column chromatography on silica gel (PE) gave the product.

For carboxylation of the intermediate organolithium reagent, gaseous carbon dioxide was bubbled through the reaction mixture for 3 min at low temperature, then the reaction was warmed to rt. Normal work-up with 5% aqueous HCl solution and brine followed by column chromatography on silica gel (PE–ether 5:1) gave the pure product. For trimethylsilylation, trimethylsilyl chloride (1.5 equivalents) was added at low temperature and then the reaction was warmed to rt and stirred at rt for 2 h. Work-up with water and column chromatography on silica gel (PE) gave the product.

1-Phenyl-3,3-dimethylbutane (1a). Following the general procedure, this was obtained in 93% yield as a clear oil with spectroscopic data consistent with those published.¹⁹

2-Phenyl-4,4-dimethylpentanoic acid (1b). Following the general procedure, this was obtained in 92% yield as a white solid, *R*_f 0.40 (PE–ether, 1:2), mp 80–81 °C (Found: C, 76.0; H, 8.9. C₁₃H₁₈O₂ requires C, 75.7; H, 8.8%); ν_{max} (Nujol)/cm⁻¹ 3300–2500 (CO₂H), 1709, 725, 696; δ_{H} (270 MHz, CDCl₃) 0.89 (9 H, s, *t*-Bu), 1.61 (1 H, dd, *J* 4.3 and 14.2, *t*-BuCH_AH_B), 2.25 (1 H, dd, *J* 8.6 and 14.2, *t*-BuCH_AH_B), 3.62 (1 H, dd, *J* 4.3 and 8.6,

CH), 7.20–7.35 (5 H, m, Ph); δ_C (67.5 MHz, CDCl₃) 29.4, 31.0, 46.8, 48.1, 127.2, 127.9, 128.6, 140.2, 181.1; m/z (EI) 206.1314 (C₁₃H₁₈O₂ requires 206.1307, –3.3 ppm error), 206 (M⁺, 20%), 161 (8), 145 (16), 136 (30), 105 (25), 92 (20), 79 (14), 57 (100).

1-Phenyl-3-methylpentane (2a). Following the general procedure, this was obtained in 94% yield as a clear oil with spectroscopic data consistent with those published.²⁰

2-Phenyl-4-methylhexanoic acid (2b). Mixture of two diastereoisomers. Following the general procedure, this was obtained in 86% yield as a clear oil, R_f 0.40 (PE–ether, 1:2); ν_{\max} (film)/cm⁻¹ 3300–2500 (CO₂H), 3029, 2961, 1706, 1283, 698; δ_H (270 MHz, CDCl₃) 0.75–0.92 (6 H, m, 2 × CH₃), 1.10–1.40 (3 H, m, CH₂ and CH), 1.45–1.55 (0.5 H, m, CH_AH_B, diastereoisomer 1), 1.75–1.92 (1 H, m, CH_AH_B), 2.05–2.18 (0.5 H, m, CH_AH_B, diastereoisomer 2), 3.60–3.71 (1 H, m, CH), 7.20–7.35 (5 H, m, Ph); δ_C (67.5 MHz, CDCl₃) 10.9 and 11.0, 18.7 and 19.0, 29.2 and 29.4, 31.7 and 32.1, 39.5 and 40.2, 49.3 and 49.4, 127.4 (C-4), 128.0 and 128.2, 128.6 (C-3), 138.4 and 138.9 (C), 180.5 and 181.0 (CO₂H); m/z (EI) 206.1316 (C₁₃H₁₈O₂ requires 206.1307, –4.4 ppm error), 206 (M⁺, 2%), 161 (3), 136 (100), 118 (17), 105 (23), 91 (62).

Hexylbenzene (3a). Following the general procedure, but with the reaction mixture being stirred at –25 °C for 1 h, this was obtained in 85% yield as a clear oil with spectroscopic data consistent with those published.²¹

2-Phenylheptanoic acid (3b). Following the general procedure, but with the reaction mixture being stirred at –25 °C for 1 h, this was obtained in 84% yield as a clear oil with spectroscopic data consistent with those published.²²

1-Phenyl-1-trimethylsilylhexane (3c). Following the general procedure, but with the reaction mixture being stirred at –25 °C for 1 h, this was obtained in 51% yield as a clear oil with spectroscopic data consistent with those published.²³

1-Phenyl-5-methylpentane (4a). Following the general procedure, but with the reaction mixture being stirred at –25 °C for 1 h, this was obtained in 82% yield as a clear oil with spectroscopic data consistent with those published.²⁴

Dodecylbenzene (5a). Following the general procedure, but with the reaction mixture being stirred at –25 °C for 1 h, this was obtained in 82% yield as a clear oil with spectroscopic data consistent with those published.²⁵

1,4-Diphenylbutane (6a). Following the general procedure, but with the reaction mixture being stirred at –25 °C for 1 h, this was obtained in 60% yield as a clear oil with spectroscopic data consistent with those published.²⁶

1,3-Diphenyloctane (7a). Obtained as a by-product with **3a**, this was isolated in 7% yield as a clear oil, R_f 0.28 (PE); ν_{\max} (film)/cm⁻¹ 3061, 3025, 2926, 1602, 1493, 1452, 748, 698; δ_H (270 MHz, CDCl₃) 0.80 (3 H, t, J 7.0, CH₃), 1.00–1.30 (6 H, m, 3 × CH₂), 1.50–1.70 (2 H, m, CH₂), 1.80–2.00 (2 H, m, CH₂), 2.40–2.58 (3 H, m, PhCH₂ and CH), 7.05–7.35 (10 H, m, 2 × Ph); δ_C (67.5 MHz, CDCl₃) 14.1, 22.5, 27.2, 31.9, 33.9, 37.1, 38.6, 45.6, 125.6, 125.9, 127.7, 128.2, 128.3, 128.4, 142.7, 145.8; m/z (EI) 266.2036 (C₂₀H₂₆ requires 266.2035, –0.7 ppm error), 266 (M⁺, 17%), 162 (11), 117 (20), 104 (15), 91 (100), 77 (6).

1,3-Diphenyl-6-methylheptane (7b). Obtained as a by-product with **4a**, this was isolated in 12% yield as a clear oil, R_f 0.28 (PE); ν_{\max} (film)/cm⁻¹ 3061, 3025, 2926, 1602, 1493, 1452, 747, 689; δ_H (270 MHz, CDCl₃) 0.79 (3 H, d, J 6.5, CH₃), 0.81 (3 H, d, J 6.5, CH₃), 0.95–1.18 (2 H, m, Me₂CHCH₂CH₂), 1.40–1.70

(3 H, m, Me₂CHCH₂CH₂), 1.80–2.00 (2 H, m, PhCH₂CH₂), 2.40–2.56 (3 H, m, PhCH₂ and PhCH), 7.08–7.35 (10 H, m, 2 × Ph); δ_C (67.5 MHz, CDCl₃) 22.4, 22.7, 28.1, 33.8, 34.8, 36.8, 45.9, 125.6, 125.9, 127.7, 128.2, 128.3, 128.4, 142.7, 145.8; m/z (EI) 266.2030 (C₂₀H₂₆ requires 266.2035, 1.8 ppm error), 266 (M⁺, 15%), 162 (15), 117 (26), 105 (29), 91 (100), 77 (10).

2-(3',3'-Dimethylbutyl)anisole (19a). Following the general procedure, this was obtained in 83% yield as a clear oil, R_f 0.60 (PE); ν_{\max} (film)/cm⁻¹ 2954, 2905, 1601, 1587, 1494, 1465, 1107, 1045, 750; δ_H (270 MHz, CDCl₃) 0.96 (9 H, s, *t*-Bu), 1.40–1.48 (2 H, m, *t*-BuCH₂), 2.52–2.60 (2 H, m, ArCH₂), 3.79 (3 H, s, MeO), 6.78–6.90 (2 H, m, ArH), 7.10–7.20 (2 H, m, ArH); δ_C (67.5 MHz, CDCl₃) 25.4, 29.3, 30.6, 44.4, 55.2, 110.2, 120.4, 126.7, 129.5, 132.0, 157.4; m/z (EI) 192.1506 (C₁₃H₂₀O requires 192.1514, 4.0 ppm error), 192 (M⁺, 35%), 135 (25), 121 (100), 105 (7), 91 (50), 77 (10), 57 (22).

2-(2'-Methoxyphenyl)-4,4-dimethylpentanoic acid (19b). Following the general procedure, this was obtained in 84% yield as a white solid, R_f 0.33 (PE–ether, 1:2), mp 67–68 °C; ν_{\max} (Nujol)/cm⁻¹ 3300–2500 (CO₂H), 1700, 1491, 1027, 752; δ_H (270 MHz, CDCl₃) 0.88 (9 H, s, *t*-Bu), 1.53 (1 H, dd, J 4.8 and 14.1, *t*-BuCH_AH_B), 2.20 (1 H, dd, J 7.8 and 14.1, *t*-BuCH_AH_B), 3.84 (3 H, s, MeO), 4.20 (1 H, dd, J 4.8 and 7.8, CH), 6.82–6.95 (2 H, m, ArH), 7.18–7.33 (2 H, m, ArH); δ_C (67.5 MHz, CDCl₃) 29.4, 31.1, 39.9, 46.2, 55.6, 110.9, 120.8, 128.1, 128.3, 129.1, 156.3, 180.9; m/z (EI) 236.1415 (C₁₄H₂₀O₃ requires 236.1412, –1.3 ppm error), 236 (M⁺, 30%), 192 (12), 175 (19), 165 (12), 148 (16), 135 (50), 121 (100), 107 (16), 91 (36).

2-Hexylanisole (20a). Following the general procedure, but with 2 equivalents of TMEDA added before the organolithium reagent, this was obtained in 68% yield as a clear oil with spectroscopic data consistent with those published.²⁷

2-(1'-Trimethylsilylhexyl)anisole (20c). Following the general procedure, but with 2 equivalents of TMEDA added before the organolithium reagent, this was obtained in 63% yield as a clear oil, R_f 0.69 (PE); ν_{\max} (film)/cm⁻¹ 2957, 2929, 1595, 1584, 1489, 1464, 1238, 1033, 836, 750; δ_H (270 MHz, CDCl₃) –0.10 (9 H, s, TMS), 0.83 (3 H, t, J 6.5, Me), 1.10–1.30 (6 H, m, 3 × CH₂), 1.60–1.80 (2 H, m, CH₂), 2.59 (1 H, dd, J 4.6 and 11.1, CH), 3.77 (3 H, s, MeO), 6.79–6.90 (2 H, m, ArH), 7.00–7.10 (2 H, m, ArH); δ_C (67.5 MHz, CDCl₃) –2.8, 14.1, 22.5, 27.6, 28.8, 29.0, 31.9, 55.0, 109.9, 120.3, 124.6, 127.1, 132.7, 157.0; m/z (EI) 264.1904 (C₁₆H₂₈OSi requires 264.1909, 2.0 ppm error), 264 (M⁺, 22%), 249 (65), 179 (100), 163 (14), 147 (8), 121 (15), 91 (15), 73 (60).

3-(3',3'-Dimethylbutyl)anisole (21a). Following the general procedure, this was obtained in 91% yield as a clear oil, R_f 0.60 (PE); ν_{\max} (film)/cm⁻¹ 2953, 1601, 1585, 1492, 1466, 1260, 1152, 1043, 782, 694; δ_H (270 MHz, CDCl₃) 0.96 (9 H, s, *t*-Bu), 1.45–1.55 (2 H, m, *t*-BuCH₂), 2.50–2.68 (2 H, m, ArCH₂), 3.80 (3 H, s, MeO), 6.69–6.80 (3 H, m, ArH), 7.15–7.21 (1 H, m, ArH); δ_C (67.5 MHz, CDCl₃) 29.3, 30.5, 31.3, 46.3, 55.1, 110.8, 114.1, 120.7, 129.2, 145.3, 159.6; m/z (EI) 192.1515 (C₁₃H₂₀O requires 192.1514, –0.3 ppm error), 192 (M⁺, 70%), 177 (10), 135 (40), 121 (100), 91 (30), 77 (32), 57 (95).

3-Hexylanisole (22a). Following the general procedure, this was obtained in 61% yield as a clear oil, R_f 0.61 (PE); ν_{\max} (film)/cm⁻¹ 2955, 2928, 1602, 1584, 1488, 1465, 1455, 1260, 1152, 1048, 775, 694; δ_H (270 MHz, CDCl₃) 0.89 (3 H, t, J 7.0, Me), 1.20–1.40 (6 H, m, 3 × CH₂), 1.55–1.65 (2 H, m, CH₂), 2.59 (2 H, t, J 7.0, ArCH₂), 3.80 (3 H, s, MeO), 6.70–6.80 (3 H, m, ArH), 7.15–7.23 (1 H, m, ArH); δ_C (67.5 MHz, CDCl₃) 14.1, 22.6, 29.0, 31.4, 31.7, 36.0, 55.1, 110.8, 114.1, 120.8, 129.1, 144.6, 159.5; m/z (EI) 192.1509 (C₁₃H₂₀O requires 192.1514,

2.7 ppm error), 192 (M⁺, 25%), 135 (14), 122 (100), 91 (16), 78 (10).

4-(3',3'-Dimethylbutyl)anisole (23a). Following the general procedure, but with the reaction mixture stirred at -44 °C for 1 h, this was obtained in 75% yield as a clear oil, *R*_f 0.61 (PE); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2951, 1614, 1585, 1513, 1465, 1364, 1247, 1177, 1038, 820; δ_{H} (270 MHz, CDCl₃) 0.95 (9 H, s, *t*-Bu), 1.42–1.50 (2 H, m, *t*-BuCH₂), 2.47–2.54 (2 H, m, ArCH₂), 3.76 (3 H, s, MeO), 6.81 (2 H, d, *J* 8.7, H-2), 7.09 (2 H, d, *J* 8.7, H-3); δ_{C} (67.5 MHz, CDCl₃) 29.3, 30.3, 30.5, 46.7, 55.2, 113.7, 129.1, 135.6, 157.5; *m/z* (EI) 192.1514 (C₁₃H₂₀O requires 192.1514, 0 ppm error), 192 (M⁺, 16%), 135 (6), 121 (100), 78 (7), 57 (7).

2-(4'-Methoxyphenyl)-4,4-dimethylpentanoic acid (23b). Following the general procedure, but with the reaction mixture stirred at -44 °C for 1 h, this was obtained in 84% yield as a white solid, *R*_f 0.35 (PE-ether, 1:2), mp 93–94 °C (Found: C, 71.4; H, 8.6. C₁₄H₂₀O₃ requires C, 71.2; H, 8.5%); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 3250–2500 (CO₂H), 1707, 1608, 1583, 1510, 1299, 1244, 1177, 1031, 831; δ_{H} (270 MHz, CDCl₃) 0.88 (9 H, s, *t*-Bu), 1.59 (1 H, dd, *J* 4.6 and 14.0, *t*-BuCH_AH_B), 2.21 (1 H, dd, *J* 8.7 and 14.0, *t*-BuCH_AH_B), 3.59 (1 H, dd, *J* 4.6 and 8.7, CH), 3.77 (3 H, s, MeO), 6.82 (2 H, d, *J* 8.7, H-2), 7.24 (2 H, d, *J* 8.7, H-3); δ_{C} (67.5 MHz, CDCl₃) 29.4, 31.0, 46.8, 47.2, 55.2, 114.0, 129.0, 132.3, 158.8, 181.4; *m/z* (EI) 236.1413 (C₁₄H₂₀O₃ requires 236.1412, -0.1 ppm error), 236 (M⁺, 30%), 192 (12), 175 (19), 165 (12), 148 (16), 135 (50), 121 (100), 107 (16), 91 (36).

4-Hexylanisole (24a). This compound was prepared by adding butyllithium to a solution of *p*-methoxystyrene and 2 equivalents of TMEDA in ether at -40 °C followed by stirring at this temperature for 10 min. After normal work-up as described in the general procedure, this was obtained in 58% yield as a clear oil with spectroscopic data consistent with those published.²⁸

***N*-Methyl-*N*-allyl-2-(3',3'-dimethylbutyl)aniline (25a).** Following the general procedure, this was obtained in 90% yield as a clear oil, *R*_f 0.50 (PE-ether, 5:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2953, 1642, 1597, 1491, 1363, 919, 760; δ_{H} (270 MHz, CDCl₃) 0.97 (9 H, s, *t*-Bu), 1.35–1.44 (2 H, m, *t*-BuCH₂), 2.60–2.68 (2 H, m, ArCH₂), 2.63 (3 H, s, MeN), 3.44 (2 H, m, CH₂N), 5.14 (1 H, d, *J* 10.2, CH=CH_AH_B), 5.25 (1 H, d, *J* 17.2, CH=CH_AH_B), 5.80–5.95 (1 H, m, CH=CH₂), 6.95–7.20 (4 H, m, ArH); δ_{C} (67.5 MHz, CDCl₃) 25.9, 29.4, 30.7, 41.5, 45.4, 60.7, 116.8, 120.7, 123.5, 126.1, 129.7, 135.9, 138.8, 152.1; *m/z* (EI) 231.1992 (C₁₆H₂₅N requires 231.1987, -2.1 ppm error), 231 (M⁺, 85%), 190 (70), 174 (55), 134 (100), 57 (55).

***N*-Allyl-*N*-benzyl-2-(3',3'-dimethylbutyl)aniline (26a).** Following the general procedure, this was obtained in 91% yield as a clear oil, *R*_f 0.47 (PE-ether, 5:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2953, 1643, 1597, 1491, 1364, 918, 761, 698; δ_{H} (270 MHz, CDCl₃) 0.98 (9 H, s, *t*-Bu), 1.40–1.48 (2 H, m, *t*-BuCH₂), 2.64–2.75 (2 H, m, ArCH₂), 3.49 (2 H, d, *J* 6.0, CH₂=CHCH₂N), 4.09 (2 H, s, PhCH₂), 5.03–5.16 (2 H, m, CH=CH₂), 5.75–5.89 (1 H, m, CH=CH₂), 6.95–7.33 (9 H, m, ArH); δ_{C} (67.5 MHz, CDCl₃) 25.7, 29.2, 30.7, 45.4, 56.8, 57.8, 117.3, 122.9, 124.0, 125.8, 126.8, 128.0, 128.7, 129.8, 135.1, 138.9, 139.7, 149.7; *m/z* (EI) 307.2304 (C₂₂H₂₉N requires 307.2300, -1.2 ppm error), 307 (M⁺, 15%), 266 (22), 216 (50), 160 (25), 91 (100), 57 (37).

1-Phenyl-2-hexylbenzene (27a). Following the general procedure, but with the reaction mixture stirred at -30 °C for 1 h, this was obtained in 70% yield as a clear oil, *R*_f 0.30 (PE); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3060, 2926, 1599, 1479, 1465, 1377, 1071, 1009, 749, 701; δ_{H} (270 MHz, CDCl₃) 0.82 (3 H, t, *J* 6.5, CH₃), 1.10–1.25 (6 H, m, 3 × CH₂), 1.39–1.49 (2 H, m, CH₂CH₂Ar), 2.52–2.60 (2 H, m, CH₂Ar), 7.15–7.43 (9 H, m, ArH); δ_{C} (67.5 MHz, CDCl₃) 14.0, 22.5, 29.1, 31.3, 31.5, 33.0, 125.5, 126.7, 127.3,

127.9, 129.2 (×2), 130.0, 140.4, 141.8, 142.0; *m/z* (EI) 238.1727 (C₁₈H₂₂ requires 238.1722, -2.2 ppm error), 238 (M⁺, 15%), 181 (10), 167 (100), 152 (15).

1-Phenyl-4-(3'-methylpentyl)benzene (28a). Following the general procedure, this was obtained in 74% yield as a clear oil, *R*_f 0.42 (PE); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2962, 1602, 1487, 1462, 909, 696; δ_{H} (270 MHz, CDCl₃) 1.00–1.18 (6 H, m, 2 × Me), 1.25–1.47 (1 H, m), 1.45–1.70 (3 H, m), 1.71–1.90 (1 H, m), 2.65–2.90 (2 H, m, ArCH₂), 7.35–7.74 (9 H, m, ArH); δ_{C} (67.5 MHz, CDCl₃) 11.3, 19.1, 29.4, 33.1, 34.1, 38.5, 126.9, 127.0, 128.6 (×2), 128.7, 138.5, 141.1, 142.3; *m/z* (EI) 238 (M⁺, 65%), 167 (100), 152 (7), 57 (6).

1-(4'-Hydroxybutyloxy)-2-(3',3'-dimethylbutyl)benzene (30a). Following the general procedure, but using 2.4 equivalents of organolithium, this was obtained in 81% yield as a clear oil, *R*_f 0.14 (PE-ether, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3340, 2951, 1600, 1588, 1494, 1243, 1050, 750; δ_{H} (270 MHz, CDCl₃) 0.96 (9 H, s, *t*-Bu), 1.40–1.48 (2 H, m, *t*-BuCH₂), 1.70–1.93 (4 H, m, OCH₂CH₂CH₂CH₂OH), 2.50–2.60 (2 H, m, ArCH₂), 3.70 (2 H, t, *J* 6.0, CH₂OH), 3.97 (2 H, t, *J* 6.0, CH₂OAr), 6.78–6.88 (2 H, m, ArH), 7.09–7.16 (2 H, m, ArH); δ_{C} (67.5 MHz, CDCl₃) 25.6, 25.9, 29.2, 29.5, 30.5, 44.6, 62.4, 67.4, 111.1, 120.4, 126.6, 129.6, 131.9, 156.6; *m/z* (EI) 250.1940 (C₁₆H₂₆O₂ requires 250.1933, -2.9 ppm error), 250 (M⁺, 10%), 178 (56), 121 (40), 107 (100), 57 (49).

2-(4'-Hydroxycarbonylphenyl)-4,4-dimethylpentanoic acid (31b). Following the general procedure, but using 2.4 equivalents of organolithium, this was obtained in 70% yield as a white solid, mp 180.5–181.5 °C; $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 3250–2500 (CO₂H), 1705, 1606, 1278, 919, 725; δ_{H} (270 MHz, acetone-*d*₆) 1.02 (9 H, s, *t*-Bu), 1.68 (1 H, dd, *J* 4.1 and 14.0, *t*-BuCH_AH_B), 2.41 (1 H, dd, *J* 8.5 and 14.0, *t*-BuCH_AH_B), 3.89 (1 H, dd, *J* 4.1 and 8.5, CH), 7.60 (2 H, d, *J* 8.4, ArH), 8.10 (2 H, d, *J* 8.4, ArH); δ_{C} (67.5 MHz, acetone-*d*₆) 29.7, 31.6, 47.9, 48.6, 128.9, 130.1, 130.7, 147.7, 167.4, 175.3; *m/z* (EI) 250.1199 (C₁₄H₁₈O₄ requires 250.1205, 2.4 ppm error), 250 (M⁺, 2%), 236 (30), 191 (30), 165 (38), 135 (30), 121 (29), 57 (100).

2-(2'-Naphthyl)-4,4-dimethylpentanoic acid (32). Following the general procedure, this was obtained in 45% yield as a clear oil, *R*_f 0.20 (PE-ether, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3250–2500 (CO₂H), 2958, 1707, 1600, 1508, 1365, 1290, 1222; δ_{H} (270 MHz, CDCl₃) 0.91 (9 H, s, *t*-Bu), 1.71 (1 H, dd, *J* 4.4 and 14.1, *t*-BuCH_AH_B), 2.34 (1 H, dd, *J* 8.5 and 14.1, *t*-BuCH_AH_B), 3.82 (1 H, dd, *J* 4.4 and 8.5, CH), 7.40–7.47 (3 H, m, Ar), 7.73–7.80 (4 H, m, ArH); δ_{C} (67.5 MHz, CDCl₃) 29.5, 31.1, 46.8, 48.2, 125.9, 126.0, 126.2, 126.7, 127.6, 127.8, 128.4, 132.6, 133.4, 137.7, 180.5; *m/z* (EI) 256.1462 (C₁₇H₂₀O₂ requires 256.1463, 0.6 ppm error), 256 (M⁺, 34%), 186 (15), 141 (100).

2-(2'-Naphthyl)heptanoic acid (33). Following the general procedure, but with the reaction mixture stirred at -25 °C for 1 h, this was obtained in 75% yield as a white solid, *R*_f 0.20 (PE-ether, 1:1), mp 73–75 °C; $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 3250–2500 (CO₂H), 1698, 1602, 1508, 1228, 810, 747; δ_{H} (270 MHz, acetone-*d*₆) 0.77–0.90 (3 H, t, *J* 6.5, CH₃), 1.17–1.32 (6 H, m, 3 × CH₂), 1.80–1.93 (1 H, m, CHCH_AH_B), 2.08–2.21 (1 H, m, CHCH_AH_B), 3.70 (1 H, t, *J* 7.5, CH), 7.40–7.50 (3 H, m, ArH), 7.73–7.83 (4 H, m, ArH); δ_{C} (67.5 MHz, acetone-*d*₆) 14.0, 22.4, 27.1, 29.7, 31.5, 32.9, 51.7, 125.9 (×2), 126.1, 127.0, 127.6, 127.8, 128.3, 132.7, 133.4, 135.9, 180.3; *m/z* (EI) 256.1461 (C₁₇H₂₀O₂ requires 256.1463, 0.8 ppm error), 256 (M⁺, 30%), 186 (18), 141 (100), 128 (18), 115 (10).

1-Benzyloxy-2-(3',3'-dimethylbutyl)benzene (35). Following the general procedure, this was obtained in 95% yield as a clear oil, *R*_f 0.46 (PE); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3032, 2953, 1600, 1588, 1493,

1452, 1242, 1024, 749; δ_{H} (270 MHz, CDCl_3) 0.93 (9 H, s, *t*-Bu), 1.42–1.50 (2 H, m, *t*-Bu CH_2), 2.59–2.68 (2 H, m, Ar CH_2), 5.04 (2 H, s, CH_2O), 6.83–6.90 (2 H, m, ArH), 7.09–7.16 (2 H, m, ArH), 7.25–7.45 (5 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 25.8, 19.3, 30.6, 44.6, 69.8, 111.6, 120.7, 126.7, 127.1, 127.7, 128.4, 129.8, 132.3, 137.5, 156.5; m/z (EI) 268.1826 ($\text{C}_{19}\text{H}_{24}\text{O}$ requires 268.1827, 0.4 ppm error), 268 (M^+ , 8%), 197 (1), 120 (1), 107 (3), 91 (100).

Organolithium addition followed by alkyl transfer—general procedure

To a stirred solution of 2-benzyloxystyrene **34** (105 mg, 0.5 mmol) in dry ether (25 cm^3) at -78°C under nitrogen was added the *tert*-butyllithium (1.7 M solution in pentane, 0.33 cm^3 , 0.55 mmol). The reaction mixture was stirred at -78°C for 10 min, warmed to rt over 20 min and then stirred at rt until the initial adduct was no longer evident by TLC. Methanol (1 cm^3) was added and the reaction mixture stirred for a further 10 min. The solution was diluted with ether (50 cm^3), washed with aqueous NH_4Cl (saturated solution, 10 cm^3) and water ($2 \times 25 \text{ cm}^3$) and dried with anhydrous sodium sulfate. Evaporation of the solvent and column chromatography on silica gel (ether–PE, 1:10) gave the product as a colourless oil.

1-Phenyl-2-(2'-hydroxyphenyl)-4,4-dimethylpentane (36). Following the general procedure, this was obtained in 72% yield as a clear oil, R_f 0.21 (PE–ether, 5:1); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3500, 3028, 2953, 1603, 1591, 1495, 1454, 1263, 1242, 1196, 832, 751, 699; δ_{H} (270 MHz, CDCl_3) 0.76 (9 H, s, *t*-Bu), 1.61 (1 H, dd, J 14.0 and 3.3, *t*-Bu CH_AH_B), 1.85 (1 H, dd, J 14.0 and 9.0, *t*-Bu CH_AH_B), 2.82 (2 H, d, J 7.5, Ph CH_2), 3.29–3.40 (1 H, m, CH), 4.49 (1 H, br s, OH), 6.57 (2 H, dd, J 7.8, 1.2, ArH), 6.80–6.86 (1 H, m, ArH), 6.93–7.02 (3 H, m, ArH), 7.05–7.20 (3 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 29.9, 31.2, 37.2, 45.1, 48.3, 115.7, 120.9, 125.7, 126.5, 128.0, 128.7, 129.1, 133.1, 141.0, 153.0; m/z (EI) 268.1829 ($\text{C}_{19}\text{H}_{24}\text{O}$ requires 268.1827, -0.7 ppm error), 268 (M^+ , 5%), 197 (12), 177 (55), 121 (26), 107 (55), 91 (37), 57 (100).

4-(2'-Hydroxyphenyl)non-1-ene (38). Following the general procedure, this was obtained in 73% yield as a clear oil, R_f 0.25 (PE–ether, 5:1); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3430, 3073, 2927, 1639, 1606, 1590, 1501, 1453, 1228, 911, 828, 751; δ_{H} (270 MHz, CDCl_3) 0.83 (3 H, t, J 6.7, Me), 1.10–1.40 (6 H, m, $3 \times \text{CH}_2$), 1.50–1.75 (2 H, m, $\text{CH}_2\text{CH}_2\text{CHAr}$), 2.37 (2 H, t, J 6.0, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.00 (1 H, quintet_{app.}, J 6.0, ArCH), 4.78 (1 H, br s, OH), 4.92 (1 H, d, J 9.5, $\text{CH}=\text{CH}_A\text{H}_B$), 4.98 (1 H, d, J 18.0, $\text{CH}=\text{CH}_A\text{H}_B$), 5.62–5.79 (1 H, m, $\text{CH}=\text{CH}_2$), 6.73 (1 H, dd, J 8.0, 1.2, ArH), 6.90 (1 H, t, J 8.0, ArH), 7.00–7.16 (2 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 14.1, 22.5, 27.1, 31.9, 34.7, 38.1, 40.1, 115.4, 115.8, 120.9, 126.7, 127.9, 131.2, 137.3, 153.3; m/z (EI) 217.1587 ($\text{M}^+ - 1$) ($\text{C}_{15}\text{H}_{21}\text{O}$ requires 217.1592, 2.4 ppm error), 218 (M^+ , 1%), 177 (20), 147 (7), 107 (100).

4-(2'-Hydroxyphenyl)pentadec-1-ene (39). Following the general procedure, this was obtained in 70% yield as a clear oil, R_f 0.27 (PE–ether, 5:1); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3440, 3073, 2924, 1639, 1607, 1590, 1501, 1453, 1229, 911, 830, 751; δ_{H} (270 MHz, CDCl_3) 0.87 (3 H, t, J 7.0, Me), 1.10–1.35 (18 H, m, $9 \times \text{CH}_2$), 1.52–1.70 (2 H, m, $\text{CH}_2\text{CH}_2\text{CHAr}$), 2.36 (2 H, t, J 6.0, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.00 (1 H, quintet_{app.}, J 6.0, ArCH), 4.82 (1 H, br s, OH), 4.92 (1 H, d, J 9.5, $\text{CH}=\text{CH}_A\text{H}_B$), 4.98 (1 H, d, J 18.0, $\text{CH}=\text{CH}_A\text{H}_B$), 5.60–5.78 (1 H, m, $\text{CH}=\text{CH}_2$), 6.72 (1 H, dd, J 8.0, 1.2, ArH), 6.89 (1 H, t, J 8.0, ArH), 7.00–7.16 (2 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 14.4, 23.0, 27.7, 29.6, 29.8, 29.9, 30.0, 30.2, 32.2, 35.8, 38.4, 40.4, 115.7, 116.1, 121.2, 126.9, 128.2, 131.5, 137.6, 153.6; m/z (EI) 302.2614 ($\text{C}_{21}\text{H}_{34}\text{O}$ requires 302.2610, -1.4 ppm error), 302 (M^+ , 1%), 261 (25), 147 (5), 107 (100).

4-(2'-Hydroxyphenyl)hex-1-ene (40). Following the general procedure, but with 2 equivalents of TMEDA added before the organolithium reagent, **40** was obtained in 80% yield as a clear oil, R_f 0.26 (PE–ether, 5:1); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3430, 3073, 2963, 1639, 1607, 1590, 1501, 1453, 1234, 912, 831, 752; δ_{H} (270 MHz, CDCl_3) 0.80 (3 H, t, J 7.0, Me), 1.50–1.80 (2 H, m, $\text{CH}_2\text{CH}_2\text{CHAr}$), 2.38 (2 H, t, J 6.0, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.97 (1 H, quintet_{app.}, J 6.0, ArCH), 4.91 (1 H, d, J 9.5, $\text{CH}=\text{CH}_A\text{H}_B$), 4.97 (1 H, d, J 18.0, $\text{CH}=\text{CH}_A\text{H}_B$), 5.15 (1 H, br s, OH), 5.60–5.80 (1 H, m, $\text{CH}=\text{CH}_2$), 6.70 (1 H, dd, J 8.0, 1.2, ArH), 6.89 (1 H, dt, J 1.0 and 8.0, ArH), 7.00–7.17 (2 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 11.8, 27.5, 39.5 ($\times 2$), 115.4, 115.8, 120.8, 126.6, 127.9, 131.0, 137.3, 153.3; m/z (EI) 176.1203 ($\text{C}_{12}\text{H}_{16}\text{O}$ requires 176.1201, -1.2 ppm error), 176 (M^+ , 5%), 147 (3), 135 (65), 107 (100), 91 (20).

4-(2'-Hydroxyphenyl)-5-phenylpent-1-ene (41). Following the general procedure, but with 2 equivalents of TMEDA added before the organolithium reagent, **41** was obtained in 70% yield as a clear oil, R_f 0.10 (PE–ether, 5:1); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3350, 3063, 2977, 1640, 1604, 1496, 1454, 1234, 1097, 912, 832, 752, 700; δ_{H} (270 MHz, CDCl_3) 2.40 (2 H, t, J 6.0, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.80–3.00 (2 H, m, Ph CH_2CHAr), 3.34 (1 H, quintet_{app.}, J 6.0, ArCH), 4.73 (1 H, br s, OH), 4.92 (1 H, d, J 9.5, $\text{CH}=\text{CH}_A\text{H}_B$), 4.97 (1 H, d, J 18.0, $\text{CH}=\text{CH}_A\text{H}_B$), 5.60–5.75 (1 H, m, $\text{CH}=\text{CH}_2$), 6.60 (1 H, d, J 8.0, ArH), 6.86 (1 H, t, J 8.0, ArH), 6.95–7.25 (7 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 38.4, 40.2, 41.3, 115.6, 116.2, 120.9, 125.8, 126.9, 128.1 ($\times 2$), 129.2, 130.5, 136.9, 140.6, 153.2; m/z (EI) 238.1358 ($\text{C}_{17}\text{H}_{18}\text{O}$ requires 238.1358, 0 ppm error), 238 (M^+ , 7%), 197 (60), 147 (100), 91 (60).

4-(2'-Hydroxyphenyl)-5-cyclohexenylpent-1-ene (42). Following the general procedure, but with 2 equivalents of TMEDA added before the organolithium reagent, **42** was obtained in 74% yield as a clear oil, R_f 0.22 (PE–ether, 5:1); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3340, 3071, 2929, 1639, 1606, 1592, 1455, 1233, 1099, 910, 835, 751; δ_{H} (270 MHz, CDCl_3) 1.40–1.65 (4 H, m, $2 \times \text{CH}_2$), 1.75–2.00 (4 H, m, $2 \times \text{CH}_2$), 2.05–2.50 (4 H, m, $2 \times \text{CH}_2$), 3.20 (1 H, quintet_{app.}, J 6.0, ArCH), 4.85–5.05 (3 H, m, $\text{CH}_2=\text{CH}$ and $\text{C}=\text{CH}$), 5.36 (1 H, br s, OH), 5.60–5.77 (1 H, m, $\text{CH}=\text{CH}_2$), 6.71 (1 H, dd, J 8.0 and 1.2, ArH), 6.87 (1 H, t, J 8.0, ArH), 6.99–7.12 (2 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 22.4, 22.9, 25.2, 28.5, 36.4, 38.9, 43.8, 115.5, 115.9, 120.8, 123.2, 126.6, 127.9, 131.2, 136.3, 137.3, 153.2; m/z (EI) 242.1671 ($\text{C}_{17}\text{H}_{22}\text{O}$ requires 242.1671, -0.2 ppm error), 242 (M^+ , 5%), 201 (30), 147 (100), 107 (37).

(Z)-5-(2'-Hydroxyphenyl)dec-2-en-1-ol (44). Following the general procedure, but using 2.4 equivalents of organolithium, this was obtained in 51% yield as a clear oil, R_f 0.12 (PE–ether, 1:1); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3366, 2926, 1654, 1593, 1489, 1454, 1238, 1018, 752; δ_{H} (270 MHz, CDCl_3) 0.84 (3 H, t, J 6.5, Me), 1.10–1.50 (6 H, m, $3 \times \text{CH}_2$), 1.60–1.75 (2 H, m, $\text{CH}_2\text{CH}_2\text{CHAr}$), 1.82 (1 H, br s, OH), 2.39 (2 H, t, J 7.0, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.04 (1 H, quintet_{app.}, J 7.0, ArCH), 4.00 (2 H, d, J 5.3, CH_2OH), 5.50–5.60 (2 H, m, $\text{CH}=\text{CH}$), 6.03 (1 H, br s, OH), 6.73 (1 H, dd, J 7.8, 1.0, ArH), 6.89 (1 H, t, J 7.8, ArH), 7.00–7.15 (2 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 14.1, 22.6, 27.4, 31.9, 33.6, 34.5, 39.0, 58.2, 115.6, 120.6, 126.8, 128.0, 128.8, 131.1, 132.1, 153.8; m/z (EI) 248.1778 ($\text{C}_{16}\text{H}_{24}\text{O}_2$ requires 248.1776, -0.7 ppm error), 248 (M^+ , 2%), 230 (8), 177 (45), 159 (10), 120 (15), 107 (100).

(Z)-5-(2'-Hydroxyphenyl)-7-methylnon-2-en-1-ol (45). Mixture of two diastereoisomers. Following the general procedure, but using 2.4 equivalents of organolithium, this was obtained in 60% yield as a clear oil, R_f 0.12 (PE–ether, 1:1); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3360, 2959, 1655, 1592, 1503, 1454, 1236, 1000, 752; δ_{H} (270 MHz, CDCl_3) 0.78–0.85 (6 H, m, $2 \times \text{CH}_3$), 1.02–1.47 (3 H, m, Me CH_2CHMe), 1.49–1.85 (2 H, m, *i*-Bu CH_2CHAr), 2.00 (1 H,

br s, OH), 2.25–2.45 (2 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.15–3.25 (1 H, m, ArCH), 3.99 (2 H, d, J 5.8, CH_2OH), 5.50–5.60 (2 H, m, $\text{CH}=\text{CH}$), 6.45 (1 H, br s, OH), 6.72 (1 H, d, J 7.8, ArH), 6.88 (1 H, t, J 7.8, ArH), 6.99–7.15 (2 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 10.9 and 11.3, 18.8 and 19.6, 28.7 and 30.3, 31.9 ($\times 2$), 36.3 ($\times 2$), 33.5 and 34.3, 41.4 and 41.7, 58.1 ($\times 2$), 115.6 ($\times 2$), 120.4 ($\times 2$), 126.8 ($\times 2$), 128.1 ($\times 2$), 128.6 and 128.7, 130.8 and 131.4, 132.1 and 132.2, 153.8 and 154.0; m/z (EI) 248.1781 ($\text{C}_{16}\text{H}_{24}\text{O}_2$ requires 248.1776, -1.7 ppm error), 248 (M^+ , 1%), 230 (5), 177 (35), 159 (8), 147 (7), 121 (10), 107 (100).

(Z)-5-(2'-Hydroxyphenyl)-8-methylnon-2-en-1-ol (46). Following the general procedure, but using 2.4 equivalents of organolithium, this was obtained in 68% yield as a clear oil, R_f 0.12 (PE–ether 1:1); ν_{max} (film)/ cm^{-1} 3350, 2953, 1653, 1605, 1591, 1502, 1454, 1236, 1002, 752; δ_{H} (270 MHz, CDCl_3) 0.83 (6 H, d, J 6.5, $2 \times \text{Me}$), 0.97–1.25 (2 H, m, Me_2CHCH_2), 1.40–1.56 (1 H, m, Me_2CH), 1.63–1.75 (2 H, m, $\text{CH}_2\text{CH}_2\text{CHAr}$), 2.15 (1 H, br s, OH), 2.39 (2 H, t_{app} , J 7.0, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.02 (1 H, quintet, J 7.0, ArCH), 4.00 (2 H, d, J 5.5, CH_2OH), 5.50–5.60 (2 H, m, $\text{CH}=\text{CH}$), 6.53 (1 H, br s, OH), 6.72 (1 H, dd, J 7.8, 1.0, ArH), 6.88 (1 H, dt, J 1.0 and 7.8, ArH), 7.00–7.15 (2 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 22.4, 22.7, 28.1, 32.3, 33.5, 36.9, 39.3, 58.1, 115.6, 120.5, 126.8, 127.9, 128.7, 131.1, 132.2, 153.9; m/z (EI) 248.1772 ($\text{C}_{16}\text{H}_{24}\text{O}_2$ requires 248.1776, 1.8 ppm error), 248 (M^+ , 1%), 230 (3), 205 (1), 177 (17), 159 (7), 121 (7), 107 (100).

(Z)-5-(2'-Hydroxyphenyl)-7,7-dimethyloct-2-en-1-ol (47). Following the general procedure, but with 2.4 equivalents of organolithium, this was obtained in 67% yield as a clear oil, R_f 0.11 (PE–ether, 1:1); ν_{max} (film)/ cm^{-1} 3340, 2952, 1655, 1604, 1592, 1455, 1238, 1005, 752, 734; δ_{H} (270 MHz, CDCl_3) 0.80 (9 H, s, $t\text{-Bu}$), 1.55 (1 H, dd, J 3.2 and 14.0, $t\text{-BuCH}_A\text{H}_B$), 1.65 (1 H, br s, OH), 1.86 (1 H, dd, J 9.2 and 14.0, $t\text{-BuCH}_A\text{H}_B$), 2.25–2.45 (2 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.10–3.20 (1 H, m, ArCH), 3.97 (2 H, d, J 5.4, CH_2OH), 5.50–5.58 (2 H, m, $\text{CH}=\text{CH}$), 6.63 (1 H, br s, OH), 6.69 (1 H, dd, J 7.8 and 1.0, ArH), 6.86 (1 H, dt, J 1.0 and 7.8, ArH), 7.01 (1 H, dt, J 1.6 and 7.8, ArH), 7.15 (1 H, dd, J 1.6 and 7.8, ArH); δ_{C} (67.5 MHz, CDCl_3) 29.9, 31.2, 35.4, 36.0, 48.8, 58.1, 115.6, 120.3, 126.6, 128.5, 128.6, 132.3, 132.9, 153.4; m/z (CI) 266.2120 ($\text{C}_{16}\text{H}_{28}\text{NO}_2$ requires 266.2120, -0.1 ppm error), 266 (MNH_4^+ , 100%), 248 (M^+ , 10), 231 (25), 194 (40), 177 (42).

(E)-5-(2'-Hydroxyphenyl)dec-2-en-1-ol (49). Following the general procedure, but with 2.4 equivalents of organolithium, this was obtained in 59% yield as a clear oil, R_f 0.15 (PE–ether, 1:1); ν_{max} (film)/ cm^{-1} 3350, 2927, 1668, 1605, 1591, 1503, 1454, 1236, 970, 752; δ_{H} (270 MHz, CDCl_3) 0.83 (3H, t, J 6.5, Me), 1.06–1.35 (6 H, m, $3 \times \text{CH}_2$), 1.50–1.70 (2 H, m, $\text{CH}_2\text{CH}_2\text{-CHAr}$), 1.89 (1 H, br s, OH), 2.20–2.43 (2 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.05 (1 H, quintet, J 6.5, ArCH), 3.97 (2 H, d, J 4.1, $\text{CH}_2\text{-OH}$), 5.45–5.62 (2 H, m, $\text{CH}=\text{CH}$), 5.89 (1 H, br s, OH), 6.71 (1 H, dd, J 7.8, 1.0, ArH), 6.87 (1 H, dt, J 1.2 and 7.8, ArH), 6.99–7.12 (2 H, m, ArH); δ_{C} (67.5 MHz, CDCl_3) 14.1, 22.6, 27.1, 32.0, 35.0, 38.0, 38.7, 63.6, 115.5, 120.7, 126.6, 127.8, 129.7, 131.4, 132.2, 153.7; m/z (CI) 266.2117 ($\text{C}_{16}\text{H}_{28}\text{NO}_2$ requires 266.2120, 1.0 ppm error), 266 (MNH_4^+ , 8%), 248 (M^+ , 5), 231 (15), 194 (5), 177 (55), 159 (15), 107 (100).

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