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Etherification of (*E*)-1,3-diaryl- and (*E*)-1,3-diheteroaryl- prop-2-en-1-ols with primary and secondary alcohols over platinum on carbon

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In the presence of platinum on carbon (Pt/C), (*E*)-1,3-diaryl- and (*E*)-1,3-diheteroaryl- prop-2-en-1-ols react with primary and secondary alcohols to give (*E*)-1,3-diaryl- and (*E*)-1,3-diheteroaryl- prop-2-enyl ethers.

Keywords: etherification, platinum on carbon

In the predominant number of preparations of non-symmetric ethers, only one of the components is an alcohol, while the second component may be an alkene,[1] a halide,[2] tosylate,[3] mesylate[4] or otherwise activated ester.[5] Only a few methods are known where alcohols can be used for both components or where the related transetherification leads to the selective formation of non-symmetric ethers.[6,7] In these cases, it is necessary that the cross etherification between the two different alcohols is the main reaction, while homo-etherification is suppressed. As halides and activated esters are derived mainly from the alcohols, and thus many of the methods of etherification use costly starting materials, it remains of interest to find new ways to prepare non-symmetric ethers from the cross-etherification of two different alcohols.

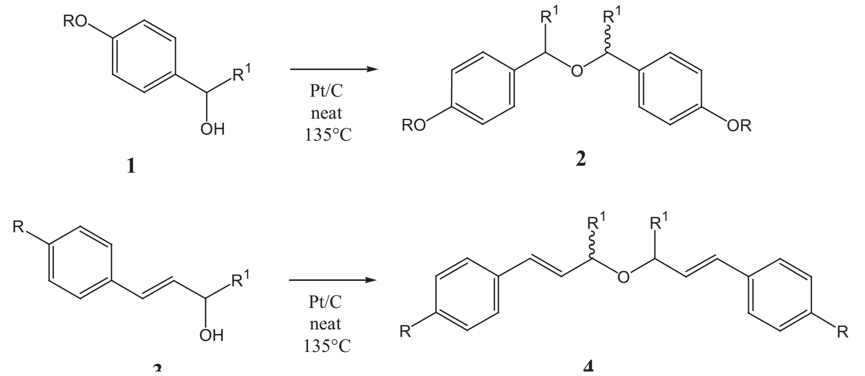
Recently, I have reported that 4-alkoxyphenylalkylcarbinols (**1**) and cinnamylalkylcarbinols (**3**) dimerise in the presence of Pt/C at 135°C to form ethers **2** and **4**, respectively (Scheme 1).[8] Only very small amounts of olefins are formed in these reactions in contrast to the reactions run under proton catalysis. While reports have appeared of activation of oxygen containing functionalities with salts of the platinum-metal group, Pt(II) complexes[9] and Pd(II) salts,[10] little has been communicated on the effect of Pt(0) on oxygen functionalities for directed organic transformations. In order to assess whether carbocations play a role in the reactions, the author turned to (*E*)-1,3-diarylprop-2-en-1-ols **5** as starting materials. Use of (*E*)-1,3-diarylprop-2-en-1-ols **5** would give access to allyl cations as intermediates. Indeed, when (*E*)-1,3-diarylprop-2-en-1-ols **5** are reacted over Pt/C at 100°C, the corresponding ethers **6** form quickly. While (*E*)-1,3-diarylprop-2-en-1-ols **5** are also converted into dimeric ethers **6** in the absence of Pt/C, when the reaction are run at 135°C, the reactions progress significantly faster in the presence of Pt/C. (*E*)-1,3-Diarylprop-2-en-1-ols **5** with identical aryl groups form the ethers **6** as a mixture of *DL*- and *meso*-isomers. Where the starting materials carried two different aryl groups, mixtures of the *DL*- and *meso* forms of the head to head and head to tail isomers could be isolated. These results indicate a charged intermediate, which is symmetrical in the case of two identical aryl groups.[11]

The relative ease with which the hydroxy group acts as a leaving group in (*E*)-1,3-diarylprop-2-en-1-ols **5** in the absence of a strong protonic acid led to the idea of reacting the intermediate electrophile with nucleophiles. In the following, the reaction of a number of (*E*)-1,3-diarylprop-2-en-1-ols and (*E*)-1,3-dihetero-arylprop-2-en-1-ols with alcohols over Pt/C is described (Scheme 3).

When a mixture of (*E*)-1,3-diarylprop-2-en-1-ol **5** and a primary or secondary alcohol (10 equiv) is heated to 100°C in the presence of a catalytic amount of Pt/C (0.12[5]mol%), ethers **8** are formed in good yield within 30 min (Table 1). In all cases, the alcohol component is used as the exclusive solvent. The dimerisation of the (*E*)-diarylpropen-2-en-1-ols **5** is suppressed totally.

Monoactivated alcohols such as benzyl alcohol (**7e**) and allyl alcohol (**7f**) can also be used in the reaction. These alcohols do not undergo homo-etherification at 100°C and thus only the desired products from cross-etherification are obtained. In general, the reactions provide the products in good yield. One exception is the reaction with 2-bromoethanol, where numerous products are formed. When the halo-function is placed further away from the reactive alcohol function, however, the product forms again quickly and nearly quantitatively, as in the case of 11-bromoundecanol (**7k**). *t*-Butanol (**7g**) does not react well. Product **8g** can be isolated, albeit in poor yield (25%). However, in this case the dimerisation of **5b** to ether **6c** starts to compete.

The reaction of **5a** with secondary alcohols such as cyclopentanol (**7h**) takes a longer reaction time to complete (90 min, 100°C), nevertheless giving **8h** in good yield. In the absence of Pt/C the etherification in general does not proceed under reaction conditions otherwise identical to



Scheme 1 Etherification of 4-alkoxyphenylalkylcarbinols and cinnamylalkylcarbinols in the presence of Pt/C.[8]

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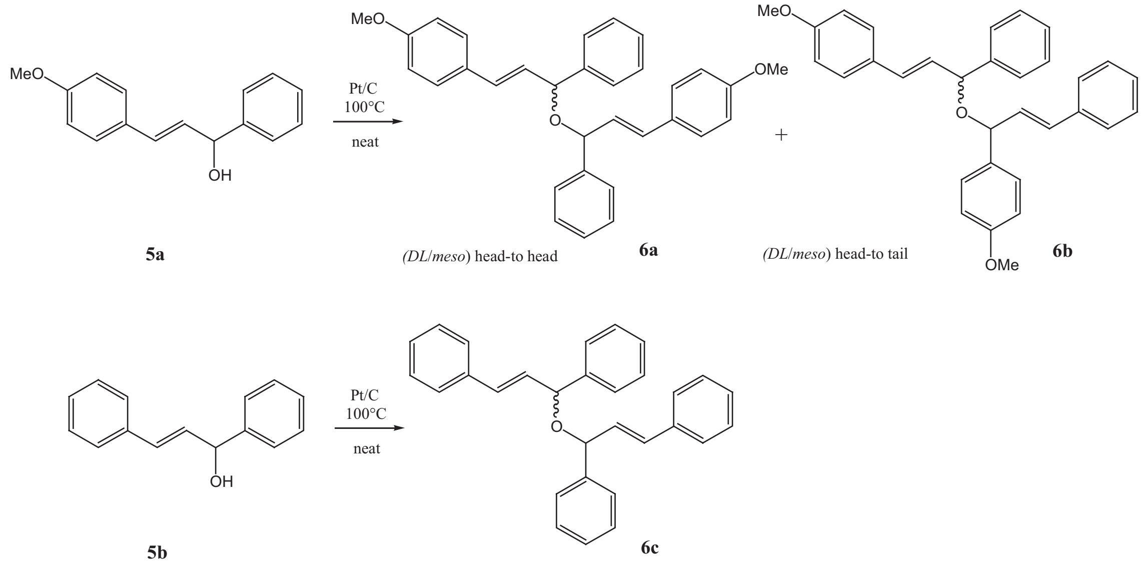
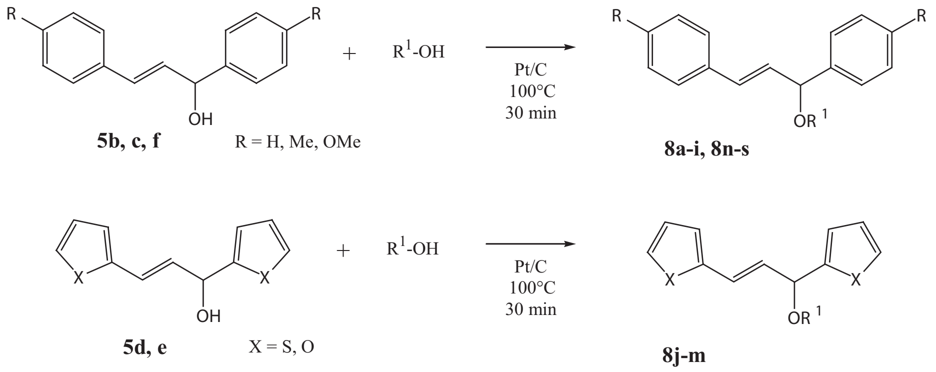


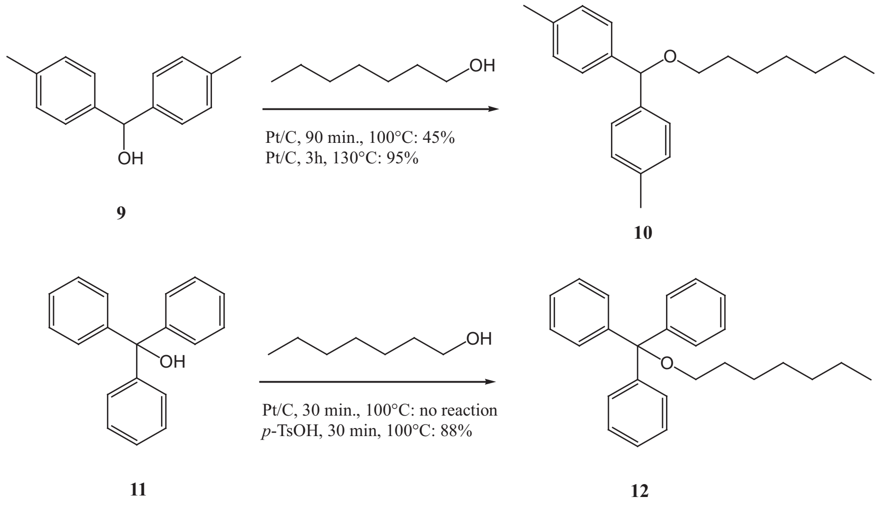
Scheme 2 Etherification of 1,3-diarylprop-2-en-1-ols by dehydrative dimerisation in the presence of Pt/C.



Scheme 3 Etherification of (*E*)-1,3-diaryl-and (*E*)-1,3-diheteroaryl-prop-2-en-1-ols.

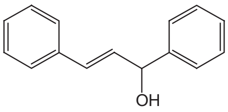
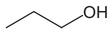
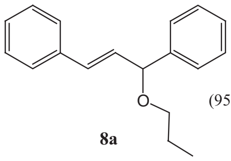
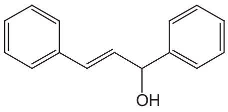
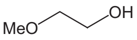
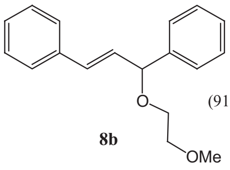
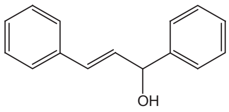
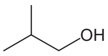
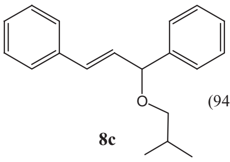
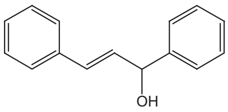
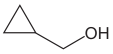
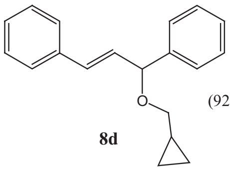
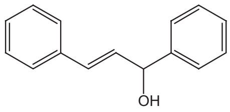
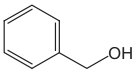
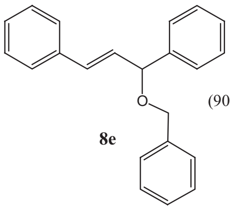
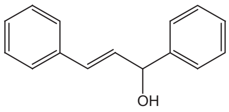
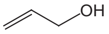
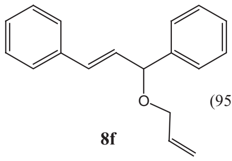
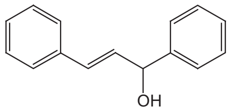
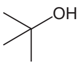
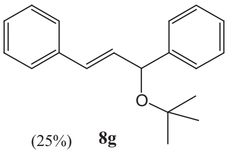
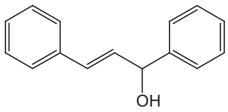
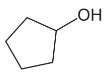
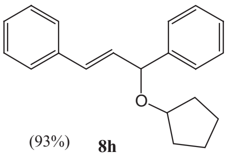
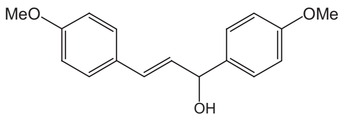
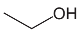
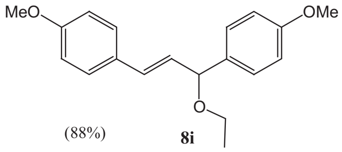
those described above. Thus, heating a mixture of **5f** with 2-methoxyethanol (**7b**, cellusolve) at 100°C for 30 min yields no product, whereas in the presence of Pt/C under otherwise identical conditions, the product is formed in 92% yield.

The non-symmetric etherification with two different alcohol components in the presence of Pt/C may be a more general reaction and may proceed with substrates other than (*E*)-1,3-diarylprop-2-en-1-ols. Diarylcarbinols also react under the conditions, but their etherification proceeds more slowly. Thus, the reaction of bis(4-tolyl)carbinol (**9**) with heptan-1-ol provides ether **10** after 90 min. at 100°C only in 45% yield (95% yield after 3 h at 130°C) (Scheme 4). The reaction of triphenylmethanol (**11**) with alcohols such as heptan-1-ol does not proceed with Pt/C (0.12[5] mol%) at 100°C (30 min). This is in contrast to the etherification of triphenylmethanol with alcohols under proton catalysis.[12] Thus, reaction of triphenylmethanol (**11**) with heptan-1-ol in presence of *p*-toluenesulfonic acid leads after 30 min at 100°C to ether **12** in high yield (Scheme 4). This seems to indicate that the steric factor is much more dominant in the case with Pt/C



Scheme 4 Etherification reactions of 4-tolylbenzhydrol and of triphenylmethanol.

Table 1 Etherification of (*E*)-1,3-diaryl- and (E)-1,3-diheteroaryl-prop-2-en-1-ols over Pt/C

 **5b**	 **7a**	 (95%) **8a**
 **5b**	 **7b**	 (91%) **8b**
 **5b**	 **7c**	 (94%) **8c**
 **5b**	 **7d**	 (92%) **8d**
 **5b**	 **7e**	 (90%) **8e**
 **5b**	 **7f**	 (95%) **8f**
 **5b**	 **7g**	 (25%) **8g**
 **5b**	 **7h**	 (93%) **8h**
 **5c**	 **7i**	 (88%) **8i**

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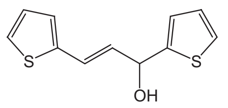
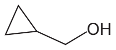
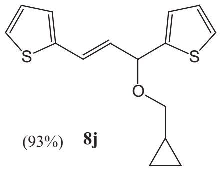
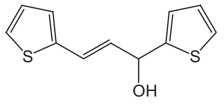
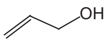
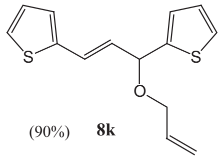
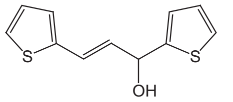
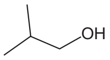
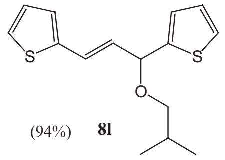
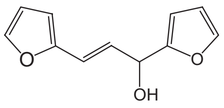
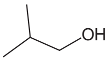
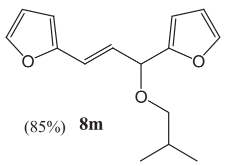
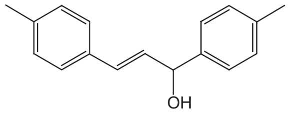
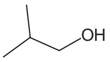
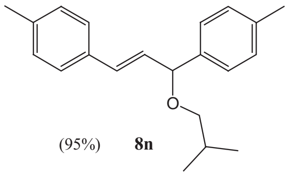
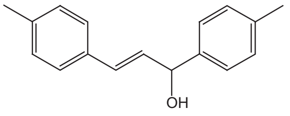
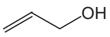
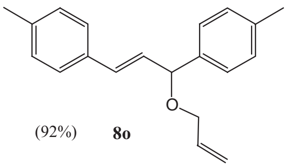
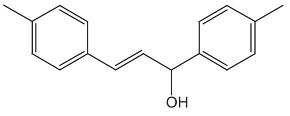
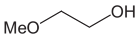
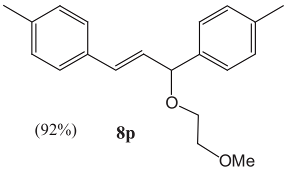
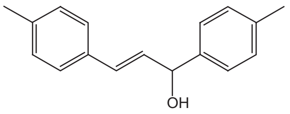
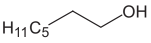
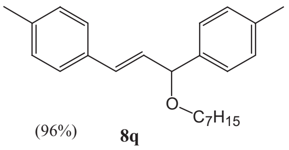
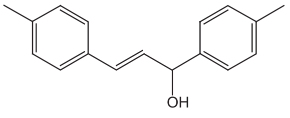
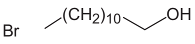
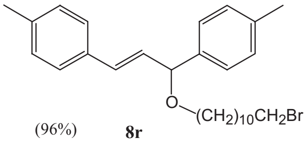
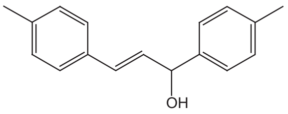
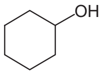
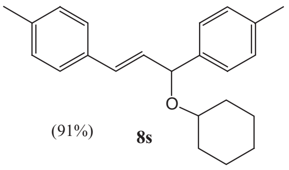
 **5d**	 **7d**	 (93%) **8j**
 **5d**	 **7f**	 (90%) **8k**
 **5d**	 **7c**	 (94%) **8l**
 **5e**	 **7c**	 (85%) **8m**
 **5f**	 **7c**	 (95%) **8n**
 **5f**	 **7f**	 (92%) **8o**
 **5f**	 **7b**	 (92%) **8p**
 **5f**	 **7j**	 (96%) **8q**
 **5f**	 **7k**	 (96%) **8r**
 **5f**	 **7l**	 (91%) **8s**

than in the case of proton catalysis, which is plausible when the activation of the substrate takes place on the surface or near the surface of the activated carbon.[13] While the actual mechanism of the reaction is not yet ascertained, it is known that alcohols adsorb on platinum [Pt(111)] with an oxygen lone-pair orbital interaction with platinum of about 42 kJ mol^{-1}.[14] Thus, the activation of the hydroxyl group by platinum may be sufficient for the etherification to proceed. It must be noted, however, that in contrast to proton catalysis, epoxyalcohols such as glycidol are stable under the current conditions and can also be used as substrates in the reactions.

From the above, it could be shown that (*E*)-1,3-diarylprop-2-en-1-ols and (*E*)-1,3-diheteroarylprop-2-en-1-ols react with primary and secondary alcohols in the presence of Pt/C at 100°C. The reactions do not proceed in the absence of Pt/C under otherwise identical conditions. Monoactivated alcohols such as benzyl alcohol (**7e**) and allyl alcohol (**7f**) can also be used as substrates in this transformation without formation of products due to homo-etherification. Reactions were carried out in a scale of 0.7 to 7.0 mmol of the substrates **5**. Further studies on the use of nucleophiles other than alcohols in this reaction are underway.

Experimental

General

Melting points were measured on a Yanaco microscopic hotstage and are uncorrected. IR spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM instruments. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer (^{1}H at 270 MHz, ^{13}C at 67.8 MHz). The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer. Column chromatography was carried out on Wakogel 300.

Substrates and reagents

Platinum on carbon (Wako, 5wt% Pt/C), the primary and secondary alcohols as well as *t*-butanol and triphenylmethanol were acquired commercially. (*E*)-1,3-Diarylprop-2-en-1-ols were synthesised by Wittig reaction of benzaldehyde, anisaldehyde and 4-tolualdehyde with the respective aroylmethylidenetriphenylphosphoranes under solvent-reduced conditions[15] and subsequent Luche reduction of the chalcones.[16] (*E*)-1,3-Di(thien-2-yl)prop-2-en-1-ol and (*E*)-1,3-di(fur-2-yl)prop-2-en-1-ol were prepared by Schmidt condensation[17] of 2-thienylaldehyde with 2-acetylthiophene and of 2-furylaldehyde and 2-acetylfuran, all commercial products, and subsequent Luche reduction.[16] Bis(4-tolyl)methanol (**9**) was prepared from commercially available 4,4'-dimethylbenzophenone by $NaBH_4$-reduction.

(E)-1,3-Diphenylprop-2-enyl propyl ether (**8a**)[18]: *general procedure for the etherification over Pt/C*:
A mixture of (*E*)-1,3-diphenylprop-2-en-1-ol (**5b**) (1.52 g, 7.2 mmol), propanol (4.30 g, 72 mmol, 10equiv) and 5 wt% Pt/C (36 mg, 1.8 mg Pt, 9 × 10^{-3} mmol) was heated at 100°C for 30 min. Thereafter, the solution was submitted directly to column chromatography on silica gel (hexane/ether/$CHCl_3$ 5:1:1) to give **8a** (1.72 g, 95%); colourless oil; (Found: M^+ 252.1512. $C_{18}H_{20}O$ requires M, 252.1514); ν_{max} (neat/cm^{-1}) 3086, 3026, 2962, 2932, 2870, 1494, 1451, 1084, 966, 743, 695; δH (270 MHz, $CDCl_3$) 0.95 (3H, t, ^3J = 7.5 Hz), 1.62–1.67 (2H, m), 3.32–3.42 (1H, m), 3.47–3.53(1H, m), 4.90 (1H, d, ^3J = 7.0 Hz), 6.30 (1H, dd, ^3J = 15.7 Hz, ^3J = 7.0 Hz), 6.60 (1H, d, ^3J = 15.7 Hz), 7.21–7.39 (10H, m); δ_C (67.8 MHz, $CDCl_3$) 10.7, 23.1, 70.4, 82.6, 126.6 (2C), 126.8 (2C), 127.5, 127.6, 128.4 (2C), 128.5 (2C), 130.7, 131.1, 136.7, 141.6; MS (EI, 70 eV) *m/z* (%) = 252 (M^+) (21), 153 (52), 107 (57), 89 (64), 77 (100).

Further spectroscopic and physical data of the products

(E)-1,3-Diphenylprop-2-enyl 2-methoxyethyl ether (**8b**): Colourless oil; (Found: M^+ 268.1465. $C_{18}H_{20}O_2$ requires M, 268.1463); ν_{max} (neat/cm^{-1}) 3026, 2924, 1598, 1492, 1450, 1305, 1248, 1199, 1088, 1027, 967, 744, 697; δ_H (270 MHz, $CDCl_3$) 3.39 (3H, s, OCH_3), 3.59–3.69 (4H, m), 4.97 (1H, d, ^3J = 7.0 Hz), 6.32 (1H, dd, ^3J = 15.7 Hz, ^3J = 7.0 Hz), 6.60 (1H, d, ^3J = 15.7 Hz), 7.24–7.43 (10H, m); δ_C (67.8 MHz, $CDCl_3$) 59.1, 67.8, 72.1, 83.1, 126.6 (2C), 126.9 (2C), 127.7 (2C), 128.5 (4C), 130.3, 131.5, 136.6, 141.1; MS (EI, 70 eV) *m/z* (%) = 268 (M^+) (33), 210 (84), 192 (71), 115 (100). (Found: C, 79.53; H, 8.05. $C_{20}H_{24}O_2\cdot0.3H_2O$ requires C, 79.59; H, 8.21).

(E)-1,3-Diphenylprop-2-enyl isobutyl ether (**8c**): Colourless oil; (Found: M^+ 266.1667. $C_{19}H_{22}O$ requires M, 266.1671); ν_{max} (neat/cm^{-1}) 3024, 2922, 1650, 1601, 1510, 1495, 1450, 1295, 1250, 1176, 1089, 966, 745, 697; δ_H (270 MHz, $CDCl_3$) 0.94 (6H, d, ^3J = 6.8 Hz, 2 CH_3), 1.88–2.00 (1H, m), 3.18 (1H, dd, ^2J = 8.6 Hz, ^3J = 7.3 Hz), 3.30 (1H, dd, ^2J = 8.6 Hz, ^3J = 6.5 Hz), 4.88 (1H, d, ^3J = 6.8 Hz), 6.27 (1H, dd, ^3J = 15.9 Hz, ^3J = 6.8 Hz), 6.61 (1H, d, ^3J = 15.9 Hz), 7.21–7.42 (10H, m); δ_C (67.8 MHz, $CDCl_3$) 19.5, 19.6, 28.7, 75.6, 82.6, 126.6 (2C), 126.8 (2C), 127.5, 127.6, 128.4 (2C), 128.5 (2C), 130.8, 130.9, 136.7, 141.7; MS (EI, 70 eV) *m/z* (%) = 266 (M^+) (96), 210 (72), 193 (62), 115 (78), 105 (100).

(E)-1,3-Diphenylprop-2-enyl cyclopropylmethyl ether (**8d**): Colourless oil; (Found: M^+ 264.1515. $C_{19}H_{20}O$ requires M, 264.1514); ν_{max} (neat/cm^{-1}) 3026, 2922, 1602, 1512, 1494, 1450, 1301, 1250, 1173, 1086, 966, 745, 698; δ_H (270 MHz, $CDCl_3$) 0.17–0.25 (2H, m), 0.50–0.58 (2H, m), 1.07–1.17 (1H, m), 3.05 (1H, dd, ^2J = 10.0 Hz, ^3J = 6.8 Hz), 3.17 (1H, dd, ^2J = 10.0 Hz, ^3J = 7.0 Hz), 4.75 (1H, d, ^3J = 7.0 Hz), 6.12 (1H, dd, ^3J = 15.4 Hz, ^3J = 7.0 Hz), 6.37 (1H, d, ^3J = 15.4 Hz), 7.00–7.21 (10H, m); δ_C (67.8 MHz, $CDCl_3$) 3.1, 3.2, 10.8, 73.3, 82.3, 126.6 (2C), 126.9 (2C), 127.6, 127.7, 128.5 (4C), 130.6, 131.2, 136.6, 141.4; MS (EI, 70 eV) *m/z* (%) = 264 (M^+) (17), 193 (53), 181 (50), 105 (100). (Found: C, 86.21; H, 7.61. $C_{19}H_{20}O$ requires C, 86.32; H, 7.63).

(E)-1,3-Diphenylprop-2-enyl benzyl ether (**8e**):[19] Colourless oil; (Found: M^+ 300.1514. $C_{22}H_{20}O$ requires M, 300.1514); ν_{max} (neat/cm^{-1}) 3032, 2856, 1952 (ov), 1881 (ov), 1809 (ov), 1749 (ov), 1651, 1601, 1494, 1389, 1298, 1205, 1157, 1098, 964, 912, 742, 696; δ_H (270 MHz, $CDCl_3$) 4.58 (2H, s), 5.01 (1H, d, ^3J = 6.8 Hz), 6.33 (1H, dd, ^3J = 15.7 Hz, ^3J = 6.8 Hz), 6.63 (1H, d, ^3J = 15.7 Hz), 7.20–7.45 (15H, m); δ_C (67.8 MHz, $CDCl_3$) 70.1, 81.6, 126.6 (2C), 127.0 (2C), 127.5, 127.7 (4C), 128.4 (2C), 128.5 (4C), 130.3, 131.6, 136.6, 138.4, 141.1; MS (EI, 70 eV) *m/z* (%) = 300 (M^+) (2.1), 209 (9.0), 193 (13), 181 (100), 105 (60).

(E)-1,3-Diphenylprop-2-enyl allyl ether (**8f**):[20] Colourless oil; (Found: M^+ 250.1361. $C_{18}H_{18}O$ requires M, 250.1358); ν_{max} (neat/cm^{-1}) 3060, 3026, 2924, 2856, 1651, 1601, 1494, 1450, 1300, 1251, 1084, 967, 918, 744, 696; δ_H (270 MHz, $CDCl_3$) 4.04 (2H, m), 4.98 (1H, d, ^3J = 7.0 Hz), 5.20 (1H, d, ^3J = 10.5 Hz), 5.31 (1H, dd, *J* = 17.0 Hz, *J* = 2.1 Hz), 5.90–6.05 (1H, m), 6.30 (1H, dd, ^3J = 15.9 Hz, ^3J = 7.0 Hz), 6.62 (1H, d, ^3J = 15.9 Hz), 7.22–7.42 (10H, m); δ_C (67.8 MHz, $CDCl_3$) 69.3, 81.7, 117.0, 126.6 (2C), 126.9 (2C), 127.6, 127.7, 128.5 (4C), 130.2, 131.4, 134.8, 136.6, 141.1; MS (EI, 70 eV) *m/z* (%) = 250 (M^+) (7.4), 193 (36), 181 (76), 165 (33), 115 (77), 105 (100).

(E)-1,3-Diphenylprop-2-enyl t-butyl ether (**8g**):[6b] Colourless oil; (Found: M^+ 266.1676. $C_{19}H_{22}O$ requires M, 266.1671); ν_{max} (neat/cm^{-1}) 3060, 3024, 2970, 2924, 1650, 1598, 1493, 1192, 1098, 968, 745, 697; δ_H (270 MHz, $CDCl_3$) 1.26 (9H, s, Bu^t), 5.19 (1H, d, ^3J = 6.2 Hz), 6.31 (1H, dd, ^3J = 15.9 Hz, ^3J = 6.2 Hz), 6.52 (1H, d, ^3J = 15.9 Hz), 7.19–7.42 (10H, m); MS (EI, 70 eV) *m/z* (%) = 266 (M^+), 210 (100), 193 (35), 181 (32), 178 (22), 165 (20), 115 (55).

(E)-1,3-Diphenylprop-2-enyl cyclopentyl ether (**8h**): Colourless oil; (Found: M^+ 278.1667. $C_{20}H_{22}O$ requires M, 278.1667); ν_{max} (neat/cm^{-1}) 3060, 3026, 2956, 2868, 1600, 1494, 1451, 1300, 1175, 1092, 966, 744, 696; δ_H (270 MHz, $CDCl_3$) 1.69–1.74 (4H, m), 1.76–1.79 (4H, m), 4.03–4.08 (1H, m), 4.97 (1H, d, ^3J = 7.0 Hz), 6.29 (1H, dd, ^3J = 15.7 Hz, ^3J = 7.0 Hz), 6.58 (1H, d, ^3J = 15.7 Hz), 7.23–7.42 (10H, m); δ_C (67.8 MHz, $CDCl_3$) 23.5, 23.6, 32.4, 32.5, 78.8, 80.3, 126.6, 126.9, 127.4, 127.6, 128.4, 128.5, 130.8, 131.1, 136.7, 141.9; MS (EI, 70 eV) *m/z* (%) = 278 (M^+) (13), 210 (100), 193 (79), 178 (31), 115 (94), 105 (72).

(E)-1,3-Bis(4-anisyl)prop-2-enyl ethyl ether (**8i**): Colourless oil; (Found: M^+ 298.1573. $C_{19}H_{22}O_3$ requires M, 298.1569); ν_{max} (neat/cm^{-1}) 2970, 2836, 1609, 1510, 1459, 1301, 1247, 1173, 1088, 1035, 968, 831; δ_H (270 MHz, $CDCl_3$) 1.24 (3H, t, ^3J = 6.8 Hz, CH_3), 3.38–3.48 (1H, m), 3.49–3.61 (1H, m), 3.79 (3H, s, OCH_3), 3.80 (3H, s OCH_3), 4.85 (d, 1H, ^3J = 7.0 Hz), 6.16 (1H, dd, ^3J = 15.9 Hz, ^3J = 7.0 Hz), 6.50 (1H, d, ^3J = 15.9 Hz), 6.82 (2H, d, ^3J = 8.6 Hz), 6.89 (2H, d, ^3J = 8.6 Hz), 7.30 (2H, d, ^3J = 8.6 Hz), 7.31 (2H, d, ^3J = 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 15.4, 55.3, 63.8, 82.2, 113.8 (2C), 113.9 (2C), 127.8 (2C), 128.1 (2C), 128.7, 129.5, 130.5, 133.9, 159.0, 159.2; MS (EI, 70 eV) *m/z* (%) = 298 (M^+) (81), 253 (67), 135 (100).

(E)-1,3-Di(thien-2-yl)prop-2-enyl cyclopropylmethyl ether (**8j**): Colourless oil; (Found: M^+ 276.0643. $C_{15}H_{26}O_2S$ requires M, 276.0643); ν_{max} (neat/cm^{-1}) 3078, 3002, 2924, 2858, 1645, 1066, 958, 852, 830, 746, 697; δ_H (270 MHz, $CDCl_3$) 0.18–0.26 (2H, m), 0.49–0.57 (2H, m), 1.03–1.18 (1H, m), 5.18 (1H, d, ^3J = 6.7 Hz), 3.30 (1H, dd, ^2J = 10.0 Hz, ^3J = 7.0 Hz), 3.40 (1H, dd, ^2J = 10.0 Hz,

$^3J = 6.5$ Hz), 6.12 (1H, dd, $^3J = 15.9$ Hz, $^3J = 7.5$ Hz), 6.45 (1H, dd, $^3J = 15.9$ Hz, $^4J = 1.0$ Hz), 6.94–6.99 (4H, m), 7.11 (1H, bd, $^3J = 4.3$ Hz), 7.27 (1H, dd, $^3J = 4.9$ Hz, $^3J = 1.6$ Hz); δ_C (67.8 MHz, $CDCl_3$) 3.1 (2C), 10.6, 73.3, 77.5, 124.7, 124.8, 124.9, 125.3, 126.2, 126.6, 127.3, 129.2, 141.5, 145.2; MS (EI, 70 eV) *m/z* (%) = 276 (M^+) (53), 247 (57), 205 (84), 193 (91), 111 (100).

(E)-1,3-Di(thien-2-yl)prop-2-enyl allyl ether (**8k**): Colourless oil; (Found: M^+ 262.0491. $C_{14}H_{14}OS_2$ requires M, 262.0486); ν_{max} (neat/cm^{-1}) 3076, 3022, 2924, 2854, 1645, 1432, 1297, 1250, 1091, 960, 853, 832, 746, 696; δ_H (270 MHz, $CDCl_3$) 4.05–4.08 (2H, m), 5.20 (1H, d, $^3J = 6.7$ Hz), 5.21 (1H, m), 5.32 (1H, m), 5.87–6.03 (1H, m), 6.19 (1H, dd, $^3J = 15.7$ Hz, $^3J = 6.7$ Hz), 6.78 (1H, d, $^3J = 15.7$ Hz), 6.95–7.16 (4H, m), 7.17 (1H, bd, $^3J = 4.6$ Hz), 7.29 (1H, dd, $J = 4.6$ Hz, $J = 1.4$ Hz); δ_C (67.8 MHz, $CDCl_3$) 69.2, 76.9, 117.3, 124.8, 125.0, 125.1, 125.4, 126.3, 126.6, 127.4, 128.8, 134.5, 141.4, 144.8; MS (EI, 70 eV) *m/z* (%) = 262 (M^+) (11), 205 (44), 193 (33), 171 (30), 160 (28), 111 (100).

(E)-1,3-Di(thien-2-yl)prop-2-enyl isobutyl ether (**8l**): Colourless oil; (Found: M^+ 278.0794. $C_{15}H_{18}OS_2$ requires M, 278.0799); ν_{max} (neat/cm^{-1}) 3104, 3070, 2952, 2870, 1646, 1470, 1434, 1364, 1290, 1250, 1226, 1206, 1162, 1092, 957, 852, 829, 696; δ_H (270 MHz, $CDCl_3$) 0.93 (6H, d, $^3J = 6.8$ Hz), 1.84–1.99 (1H, m), 3.23 (1H, dd, $^2J = 8.9$ Hz, $^3J = 6.8$ Hz), 3.31 (1H, dd, $^2J = 8.9$ Hz, $^3J = 6.5$ Hz), 5.08 (1H, d, $^3J = 6.5$ Hz), 6.18 (1H, dd, $^3J = 15.4$ Hz, $^3J = 6.5$ Hz), 6.77 (1H, d, $^3J = 15.4$ Hz), 6.94–6.99 (4H, m), 7.17 (1H, bd, $^3J = 4.9$ Hz), 7.27 (1H, m); δ_C (67.8 MHz, $CDCl_3$) 19.4, 19.5, 28.6, 75.6, 78.1, 124.6 (2C), 124.7, 125.2, 126.2, 126.5, 127.4, 129.3, 141.6, 145.5; MS (EI, 70 eV) *m/z* (%) = 278 (M^+) (82), 222 (52), 205 (100), 171 (46), 111 (89), 97 (52). (Found: C, 64.69; H, 6.47. $C_{15}H_{18}OS_2$ requires C, 64.70; H, 6.52).

(E)-1,3-Di(fur-2-yl)prop-2-enyl isobutyl ether (**8m**): Colourless oil; (Found: M^+ 246.1252. $C_{15}H_{18}O_3$ requires M, 246.1256); ν_{max} (neat/cm^{-1}) 3118, 2956, 2868, 1490, 1470, 1366, 1330, 1255, 1226, 1174, 1151, 1072, 1012, 960, 927, 884, 804, 737; δ_H (270 MHz, $CDCl_3$) 0.92 (6H, d, $^3J = 6.7$ Hz, 2 CH_3), 1.82–1.97 (1H, m), 3.18–3.31 (2H, m), 4.92 (1H, d, $^3J = 6.2$ Hz), 6.26–6.36 (5H, m), 6.50 (1H, d, $^3J = 15.9$ Hz), 7.34 (1H, m), 7.40 (1H, m); δ_C (67.8 MHz, $CDCl_3$) 19.4, 19.5, 28.6, 75.3, 75.7, 107.6, 108.5, 110.1, 111.3, 120.3, 125.7, 142.1, 142.4, 152.2, 153.9; MS (EI, 70 eV) *m/z* (%) = 246 (M^+) (67), 190, 173 (100), 115 (47), 95 (50).

(E)-1,3-Bis(4-tolyl)prop-2-enyl isobutyl ether (**8n**): Colourless oil; (Found: M^+ 294.1988. $C_{21}H_{26}O$ requires M, 294.1984); ν_{max} (neat/cm^{-1}) 3022, 2956, 2870, 1512, 1469, 1078, 967, 818, 800; δ_H (270 MHz, $CDCl_3$) 0.92 (6H, 2d, 2 CH_3), 1.80–1.99 (1H, m), 2.31 (3H, s, CH_3), 2.34 (3H, s, CH_3), 3.13–3.18 (1H, m), 3.24–3.30 (1H, m), 4.82 (1H, d, $^3J = 6.7$ Hz), 6.22 (1H, dd, $^3J = 15.9$ Hz, $^3J = 6.7$ Hz), 6.55 (1H, d, $^3J = 15.9$ Hz), 7.09 (2H, d, $^3J = 7.8$ Hz), 7.15 (2H, d, $^3J = 7.8$ Hz), 7.27 (4H, m); δ_C (67.8 MHz, $CDCl_3$) 19.5, 19.6, 21.1, 21.2, 28.7, 75.4, 82.54, 126.5 (2C), 126.8 (2C), 129.1 (2C), 129.2 (2C), 130.0, 130.7, 134.0, 137.1, 137.3, 138.8; MS (EI, 70 eV) *m/z* (%) = 294 (M^+) (56), 279 (21), 238 (24), 221 (50), 119 (100).

(E)-1,3-Bis(4-tolyl)prop-2-enyl allyl ether (**8o**): Colourless oil; (Found: M^+ 278.1672. $C_{20}H_{22}O$ requires M, 278.1671); ν_{max} (neat/cm^{-1}) 2924, 1651, 1616, 1509, 1455, 1412, 1302, 1179, 1076, 970, 928, 801, 748, 722; δ_H (270 MHz, $CDCl_3$) 2.31 (3H, s, CH_3), 2.34 (3H, s, CH_3), 4.00–4.02 (2H, m), 4.93 (1H, d, $^3J = 7.0$ Hz), 5.18 (1H, bd, $J = 10.5$ Hz), 5.29 (1H, bd, $J = 17.3$ Hz), 5.87–6.02 (1H, m), 6.23 (1H, dd, $^3J = 15.9$ Hz, $^3J = 7.0$ Hz), 6.55 (1H, d, $^3J = 15.9$ Hz), 7.08 (2H, d, $^3J = 8.1$ Hz), 7.15 (2H, d, $^3J = 8.1$ Hz), 7.25 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 21.1, 21.2, 69.1, 81.7, 116.8, 126.5 (2C), 126.9 (2C), 129.2 (4C), 129.4, 131.2, 133.9, 134.9, 137.3, 137.5, 138.3; MS (EI, 70 eV) *m/z* (%) = 278 (M^+) (11), 209 (43), 119 (100).

(E)-1,3-Bis(4-tolyl)prop-2-enyl 2-methoxyethyl ether (**8p**): Colourless oil; (Found: M^+ 296.1776. $C_{20}H_{24}O_2$ requires M, 296.1776); ν_{max} (neat/cm^{-1}) 2922, 1650, 1613, 1511, 1455, 1303, 1198, 1087, 969, 818, 750, 696; δ_H (270 MHz, $CDCl_3$) 2.31 (3H, s, CH_3), 2.34 (3H, s, CH_3), 3.39 (3H, s, OCH_3), 3.55–3.66 (4H, m), 4.91 (1H, d, $^3J = 7.0$ Hz), 6.26 (1H, dd, $^3J = 15.9$ Hz, $^3J = 7.0$ Hz), 6.54 (1H, d, $^3J = 15.9$ Hz), 7.08 (2H, d, $^3J = 7.8$ Hz), 7.16 (2H, d, $^3J = 7.8$ Hz), 7.24–7.30 (4H, m); δ_C (67.8 MHz, $CDCl_3$) 21.1, 21.2, 59.1, 67.7, 72.1, 83.1, 126.5 (2C), 126.9 (2C), 129. 1 (4C), 129.4, 131.2, 133.9, 137.3, 137.4, 138.2; MS (EI, 70 eV) *m/z* (%) = 296 (M^+) (44), 281 (35), 238 (68), 221 (94), 205 (48), 119 (100).

(E)-1,3-Bis(4-tolyl)prop-2-enyl heptyl ether (**8q**): Colourless oil; (Found: M^+ 336.2456. $C_{24}H_{32}O$ requires M, 336.2453); ν_{max} (neat/cm^{-1}) 2928, 2852, 1511, 1455, 1302, 1091, 969, 800, 743, 696; δ_H (270 MHz, $CDCl_3$) 0.88 (3H, t, $^3J = 6.8$ Hz), 1.26–1.30 (8H, m), 1.58–1.62 (2H, m), 2.31 (3H, s, CH_3), 2.34, (3H, s, CH_3), 3.28–3.42 (1H, m), 3.45–3.52 (1H, m), 4.84 (1H, d, $^3J = 7.0$ Hz), 6.22 (1H, dd, $^3J = 15.9$ Hz, $^3J = 7.0$ Hz), 6.54 (1H, d, $^3J = 15.9$ Hz), 7.08 (2H, d, $^3J = 7.8$ Hz), 7.15 (2H, d, $^3J = 7.8$ Hz), 7.24–7.29 (4H, m); δ_C (67.8 MHz, $CDCl_3$) 14.1, 21.1, 21.2, 22.6, 26.2, 29.1, 29.9, 31.8, 68.7, 82.5, 126.5 (2C), 126.8 (2C), 129.1 (2C), 129.1 (2C), 129.9, 130.8, 134.1, 137.1, 137.3, 138.8; MS (EI, 70 eV) *m/z* (%) = 336 (M^+) (41), 321 (25), 238 (15), 221 (38), 119 (100).

(E)-1,3-Bis(4-tolyl)prop-2-enyl 11-bromoundecyl ether (**8r**): Colourless oil; (Found: M^+ 470.2191. $C_{28}H_{39}O^{79}Br$ requires M, 470.2184); ν_{max} (neat/cm^{-1}) 2924, 2856, 1512, 1453, 1393, 1250, 1176, 1096, 964, 815, 749, 699; δ_H (270 MHz, $CDCl_3$) 1.27–1.62 (16H, m), 1.78–1.88 (2H, m), 2.31 (3H, s, CH_3), 2.34 (3H,. s, CH_3), 3.40 (2H, t, $^3J = 7.0$ Hz), 3.41–3.52 (2H, m), 4.84 (1H, d, $^3J = 7.0$ Hz), 6.23 (1H, dd, $^3J = 16.2$ Hz, $^3J = 7.0$ Hz), 6.54 (1H, d, $^3J = 16.2$ Hz), 7.08 (2H, d, $^3J = 8.1$ Hz), 7.16 (2H, d, $^3J = 7.6$ Hz), 7.27 (4H, m); δ_C (67.8 MHz, $CDCl_3$) 18.2, 21.1, 21.2, 26.2, 28.8, 29.4, 29.4 (2C), 29.5, 29.9, 32.8, 34.0, 68.6, 82.5, 126.5 (2C), 126.8 (2C), 129.1 (2C), 129.2 (2C), 129.9, 130.8, 134.0, 137.1, 137.4, 138.7; MS (EI, 70 eV) *m/z* (%) = 472 ([^{81}Br]M^+) (5.1), 470 ([^{79}Br]M^+) (5.5), 457 (4.7), 455 (4.5), 355 (8.6), 353 (8.9), 222 (100), 207 (99.9).

(E)-1,3-Bis(4-tolyl)prop-2-enyl cyclohexyl ether (**8s**): Colourless oil; (Found: M^+ 320.2144. $C_{23}H_{28}O$ requires M, 320.2140); ν_{max} (neat/cm^{-1}) 3022, 2924, 2856, 1514, 1453, 1297, 1178, 1072, 965, 800, 744, 700; δ_H (270 MHz, $CDCl_3$) 1.20–2.02 (10H, m), 2.31 (3H, s, CH_3), 2.34 (3H, s, CH_3), 3.32–3.42 (1H, m), 5.05 (1H, d, $^3J = 7.0$ Hz), 6.24 (1H, dd, $^3J = 15.9$ Hz, $^3J = 7.0$ Hz), 6.51 (1H, d, $^3J = 15.9$ Hz), 7.09 (2H, d, $^3J = 8.1$ Hz), 7.15 (2H, d, $^3J = 8.1$ Hz), 7.25–7.30 (4H, m); δ_C (67.8 MHz, $CDCl_3$) 21.1, 21.2, 24.2, 24.3, 25.9, 32.5, 32.6, 74.6, 79.0, 124.5 (2C), 126.8 (2C), 129.0 (2C), 129.1 (2C), 130.4, 130.5, 134.0, 137.0, 137.3, 139.3; MS (EI, 70 eV) *m/z* (%) = 320 (M^+) (31), 238 (82), 223 (47), 209 (37), 119 (100), 105 (47).

Bis(4-tolyl)methyl heptyl ether (**10**): Colourless oil; (Found: M^+ 310.2296. $C_{22}H_{30}O$ requires M, 310.2297); ν_{max} (neat/cm^{-1}) 2924, 2852, 1613, 1511, 1094, 812, 764; δ_H (270 MHz, $CDCl_3$) 0.88 (3H, m), 1.28 (8H, m), 1.63 (2H, m), 2.31 (6H, s, 2 CH_3), 3.42 (2H, t, $^3J = 6.5$ Hz), 5.26 (1H, s), 7.11 (4H, d, $^3J = 8.1$ Hz), 7.24 (4H, d, $^3J = 8.1$ Hz); δ_C (67.8 MHz, $CDCl_3$) 14.1, 21.1, 22.6, 26.2, 29.2 (2C), 29.9, 31.9, 69.1, 83.3, 126.9 (2C), 129.0 (4C), 136.8 (4C), 139.9 (2C); MS (EI, 70 eV) *m/z* (%) = 310 (M^+, 19), 243 (25), 213 (27), 195 (100).

Triphenylmethyl heptyl ether (**12**)[12]: A mixture of triphenylmethanol (**11**) (565 mg, 2.17 mmol), heptan-1-ol (2.5 g, 21.7 mmol, 10 eq.) and *p*-toluenesulfonic acid (50 mg) were heated at 100ºC for 30 min. The cooled solution was subjected to column chromatography on silica gel (hexane/ether/$CHCl_3$ 6:1:1) to give **12** (684 mg, 88%); colourless oil; ν_{max} (neat/cm^{-1}) 3060, 3020, 2928, 2858, 1600, 1511, 1492, 1449, 1072, 966, 898, 744, 701; δ_H (270 MHz, $CDCl_3$) 0.87 (3H, t, $^3J = 7.0$ Hz), 1.23–1.32 (8H, m), 1.55–1.67 (2H, m), 3.04 (2H, t, $^3J = 6.8$ Hz), 7.21–7.32 (9H, m), 7.43–7.46 (6H, m); δ_C (67.8 MHz, $CDCl_3$) 14.1, 22.6, 26.3, 29.2, 30.1, 31.8, 63.7, 86.3, 126.8 (3C), 127.7 (6C), 128.7 (6C), 144.5 (3C); MS (EI, 70 eV) *m/z* (%) = 358 (M^+) (19), 281 (20), 243 (100), 183 (33), 165 (37), 105 (35).

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