Supplementary Material (ESI) for Chemical Communications


# Double decarboxylative Claisen rearrangement reactions: microwave-assisted *de novo* synthesis of pyridines

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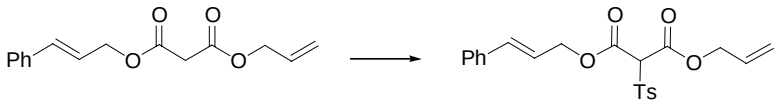
**General experimental:**

Melting points were determined using Stuart Scientific SMP1 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Mattson 5000 FTIR spectrometer and on a Perkin-Elmer Spectrum RX FT-IR System. Proton magnetic resonance ($^1$H NMR) and carbon magnetic resonance ($^{13}$C NMR) spectra were recorded in $CDCl_3$ unless otherwise stated on a Jeol GSX-270, a Bruker DRX-300, a Bruker AV-400 or a Bruker AV-500 spectrometer. Chemical shifts are in part per million (ppm) and are referenced relative to the residual proton-containing solvent ($^1$H NMR: 7.26 ppm for $CDCl_3$; $^{13}$C NMR: 77.0 ppm for $CDCl_3$). The following abbreviations are used to indicate the multiplicities: s, singlet, bs, broad signal; d, doublet; t, triplet; m multiplet. Mass spectra (CI) were recorded using Micromass AutoSpec-Q, Micromass Platform II or Micromass AutoSpec Premier instruments. Elemental analyses were performed at the microanalytical laboratory of the London Metropolitan University. Analytical thin layer chromatography (TLC) was performed on pre-coated aluminium-backed Merck Kiesegel 60 $F_{254}$ plates. Visualisation was effected with ultraviolet light, potassium permanganate or vanillin as appropriate. Flash chromatography was performed using BDH (40-63 μm) silica gel unless otherwise stated. DMSO and $CH_2Cl_2$ were distilled under nitrogen from $CaH_2$ prior to use. All other solvents were reagent-grade. Petrol refers to the fraction with $bp_{760}$ 40–60 °C. All liquid reagents except HCl and $Me_2S$ were distilled prior to use. KOAc was oven-dried at 120 °C for several days prior to use. All other reagents were purchased from Aldrich, Fluka, Acros, Alfa Aesar Lancaster and used as such unless otherwise stated. Microwave-assisted reactions were carried out in a Biotage Initiator instrument. Ozonolyses were performed with using an Ozonia Triogen LAB2B ozone generator.

**General procedure for the preparation of diallylic 2-(*p*-toluenesulfonyl)malonates 3a–f:** To a solution of diallylic malonates (2 equiv.) in DMSO (*ca.* 2 M) was added very slowly, at rt and under nitrogen solid potassium *tert*-butoxide (2 equiv.). The reaction was stirred for 30 min before the addition of *p*-toluenesulfonyl fluoride (1 equiv.). After stirring overnight at rt, the mixture was poured into aqueous HCl (10%) and extracted twice with ether. The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography gave the diallylic (*p*-toluenesulfonyl)malonates **3a–f** and excess starting malonates. Yields cited for **3** are based on *p*-toluenesulfonyl fluoride; yields cited for recovered starting material are calculated from the total recoverable amount based on the yield of **3** and the amount of malonate used (2 equiv.). For example, a 70% yield of **3** means the total recoverable amount of malonate is (2 – 0.7) = 1.3 equiv.; 74% recovery means that (0.74 x 1.3) = 0.962 equiv. of starting material was recovered.

**General procedure for the preparation of pyridines 7a–i:** Ozone was bubbled through a solution of a diastereoisomeric mixture of dienes **4** and **6** (1 equiv.) in MeOH:$CH_2Cl_2$ (1:5, c ~ 0.1 M) at -78 °C, until a blue colour persisted. After bubbling $O_2$ through the reaction mixture until it returned colourless, the reducing agent was added. After stirring for 3 h at -78 °C the mixture was concentrated under reduced pressure, previous filtering of the resin when solid supported $PPh_3$ was used as the reducing agent. To a solution of the crude dicarbonyl compound in MeOH (0.1–0.4 M) was added $NH_4HCO_3$ (*ca.* 8 equiv.) and the mixture was exposed to microwave irradiation for 10 min at 100 °C. The solution was concentrated under reduced pressure. The residue was dissolved in $CH_2Cl_2$ and then washed twice with $H_2O$. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give products, which were purified by chromatography to give the pyridines **7a–i**.

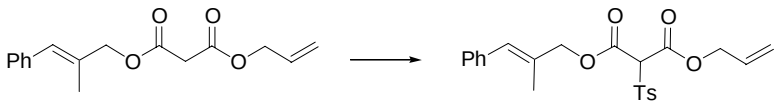
**2-(*p*-Toluenesulfonyl)malonic acid allyl ester cinnamyl ester (3a)**[1]



**3a**

According to the general procedure, malonic acid allyl ester cinnamyl ester (10.89 g, 41.82 mmol, 2 equiv.) was combined with potassium *tert*-butoxide (4.707 g, 41.94 mmol, 2 equiv.) and *p*-toluenesulfonyl fluoride (3.670 g, 21.07 mmol, 1 equiv.) in DMSO (20 mL). Chromatography (10% AcOEt–petrol) gave *2-(*p-*toluenesulfonyl)malonic acid allyl ester cinnamyl ester* **3a** (6.585 g, 76%) as a colourless gum and excess starting malonate (5.627 g, 83% unreacted); $\nu_{max}$ (film) 3058, 3027, 2946, 1743, 1667, 1596, 1494, 1449, 1336, 1305, 1292, 1276, 1193, 1180, 1151, 1084, 988, 970, 939, 846, 815, 747, 705, 694, 673 $cm^{-1}$; $\delta_H$ (270 MHz) 7.84 (2H, d, *J* 8.5 Hz, *ortho* Ts), 7.35-7.25 (7H, m, Ph and *meta* Ts), 6.63 (1H, d, *J* 16.0 Hz, =CHPh), 6.21-6.10 (1H, m, C*H*=CHPh), 5.89-5.76 (1H, m, C*H*=$CH_2$), 5.35-5.21 (2H, m, CH=C$H_2$), 5.02 (1H, s, CHTs), 4.80 (2H, d, *J* 6.5 Hz, C$H_2$CH=CHPh), 4.66 (2H, d, *J* 6.5 Hz, C$H_2$CH=$CH_2$), 2.37 (3H, s, $CH_3$); $\delta_C$ (100 MHz) [160.6 and 160.6 (2 x C=O)], 145.9 (*ipso* Ts), [135.7 and 134.0 (*ipso* Ph and *para* Ts)], 135.6 (*C*H=$CH_2$), [130.4, 128.3 and 121.2 (*para* Ph, =*C*HPh and *C*H=CHPh)], [130.1, 129.4, 128.6 and 126.6 (*ortho* Ph, *meta* Ph, *ortho* Ts and *meta* Ts)] 119.5 (*C*$H_2$=CH), 74.4 (CHTs), [67.3 and 67.3 (2 x $CH_2O$)], 21.6 ($CH_3$ Ts); *m/z* (CI) 432 $[M+NH_4]^+$, 388, 356 $[M+NH_4\text{-}CH_3Ph]^+$, 272, 202, 188, 174 $[M+NH_4\text{-Ts-CH=CHPh}]^+$, 134, 117 (Found: $[M+NH_4]^+$, 432.1481. $C_{22}H_{22}O_6S$ requires $[M+NH_4]^+$, 432.1481) (Found: C, 63.78; H, 5.40. $C_{22}H_{22}O_6S$ requires C, 63.75; H, 5.35%). Data were in agreement with those previously reported.

**2-(*p*-Toluenesulfonyl)malonic acid allyl ester (*E*)-2-methyl-3-phenyl-2-propenyl ester (3b)**



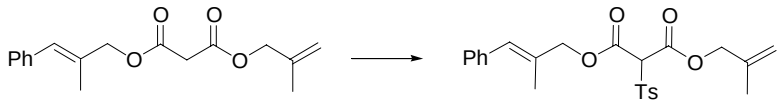
**3b**

According to the general procedure, malonic acid allyl ester (*E*)-2-methyl-3-phenyl-2-propenyl ester (4.491 g, 16.37 mmol, 2 equiv.) was combined with potassium *tert*-butoxide (1.849 g, 16.47 mmol, 2 equiv.) and *p*-toluenesulfonyl fluoride (1.433 g, 8.226 mmol, 1 equiv.) in DMSO

[1] Craig, D.; Lansdell, M. I.; Lewis, S. E. *Tetrahedron Lett.* **2007**, *48*, 7861.

(8.2 mL). Chromatography (10% AcOEt–hexane) gave *2-(*p-*toluenesulfonyl)malonic acid allyl ester (*E*)-2-methyl-3-phenyl-2-propenyl ester* **3b** (2.517 g, 72%) as a colourless gum and excess starting malonate (2.495 g, 87% unreacted); $R_f$ 0.15 (10% AcOEt–petrol); $\nu_{max}$ (film) 2937, 1743, 1596, 1446, 1335, 1292, 1276, 1150, 1082, 1019, 992, 937, 815, 749 $cm^{-1}$; $\delta_H$ (270 MHz) 7.85 (2H, d, *J* 8.5 Hz, *ortho* Ts), 7.31-7.25 (7H, m, Ph and *meta* Ts), 6.49 (1H, s, =CHPh), 5.88-5.76 (1H, m, C*H*=$CH_2$), 5.35-5.21 (2H, m, CH=C*H*$_2$), 5.03 (1H, s, CHTs), 4.72 (2H, s, $CH_2$CMe=), 4.67-4.64 (2H, m, C*H*$_2$CH=$CH_2$), 2.40 (3H, s, $CH_3$ Ts), 1.83 (3H, d, *J* 1.5 Hz, C*H*$_3$C=); $\delta_C$ (67.5 MHz) [160.9 and 160.8 (2 x C=O)], 146.2 (*ipso* Ts), [136.3, 133.9 and 131.3 (*ipso* Ph, *para* Ts and $CH_2$*C*Me=)], [130.6, 129.8 and 127.1 (*para* Ph, =CHPh and *C*H=$CH_2$)], [130.2, 129.7, 129.0 and 128.3 (*ortho* Ph, *meta* Ph, *ortho* Ts and *meta* Ts)] 119.7 (CH=*C*$H_2$), 74.6 (CHTs), [72.7 and 67.5 (2 x $CH_2O$)], 21.8 ($CH_3$ Ts), 15.5 (*C*$H_3$C=); *m/z* (CI) 446 $[M+NH_4]^+$, 362, 356 $[M+NH_4-CH_3Ph]^+$, 344, 292 $[M+NH_4-Ts]^+$, 272 $[M+H-Ts]^+$, 208, 202, 188, 174 $[M+NH_4-Ts-CMe=CHPh]^+$, 165, 148 $[M+NH_4-Ts-CMe=CHPh-CH=CH_2]^+$, 131 (Found: $[M+NH_4]^+$, 446.1625. $C_{23}H_{24}O_6S$ requires $[M+NH_4]^+$, 446.1638) (Found: C, 64.45; H, 5.54. $C_{23}H_{24}O_6S$ requires C, 64.47; H, 5.65%).

**2-(*p*-Toluenesulfonyl)malonic acid methallyl ester (*E*)-2-methyl-3-phenyl-2-propenyl ester (3c)**

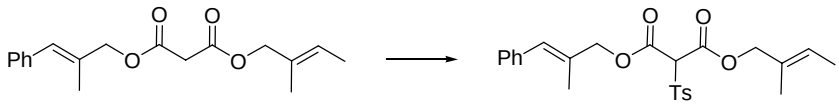



**3c**

According to the general procedure, malonic acid methallyl ester ((*E*)-2-methyl-3-phenyl-2-propen)yl ester (3.586 g, 12.44 mmol, 2 equiv.) was combined with potassium *tert*-butoxide (1.405 g, 12.52 mmol, 2 equiv.) and *p*-toluenesulfonyl fluoride (1.087 g, 6.240 mmol, 1 equiv.) in DMSO (6.2 mL). Chromatography (10% AcOEt–petrol) gave *2-(*p-*toluenesulfonyl)malonic acid methallyl ester (*E*)-2-methyl-3-phenyl-2-propenyl ester* **3c** (1.958 g, 71%) as a yellow gum and excess starting malonate (2.111 g, 91% unreacted); $R_f$ 0.14 (10% AcOEt–petrol); $\nu_{max}$ (film) 2928, 1742, 1653, 1596, 1447, 1335, 1292, 1150, 1083, 1027, 916, 814 $cm^{-1}$; $\delta_H$ (270 MHz) 7.85 (2H, d, *J* 8.5 Hz, *ortho* Ts), 7.37-7.22 (7H, m, Ph and *meta* Ts), 6.49 (1H, s, =CHPh), 5.04 (1H, s, CHTs), [4.98 (1H, bs) and 4.93 (1H, bs), =C*H*$_2$], [4.71 (2H, s) and 4.58 (2H, s), 2 x $CH_2O$], 2.39 (3H, s, $CH_3$ Ts), [1.83-1.82 (3H, m) and 1.70 (3H, s), C*H*$_3$C=$CH_2$ and C*H*$_3$C=CHPh]; $\delta_C$ (67.5 MHz) [160.9 and 160.8 (2 x C=O)], [146.1, 138.5, 136.7, 134.3 and 131.3 (*ipso* Ph, *ipso*

Ts, *para* Ts, *C*Me=CHPh and *C*Me=$CH_2$)], [130.2, 129.6, 129.0 and 128.3 (*ortho* Ph, *meta* Ph, *ortho* Ts and *meta* Ts)], [129.9 and 127.1 (*para* Ph and CMe=*C*HPh)], 114.7 (CMe=*C*$H_2$), 74.7 (CHTs), [72.8 and 70.2 (2 x $CH_2O$)], 21.8 ($CH_3$ Ts), [19.4 and 15.5 (*C*$CH_3$=CHPh and *C*$CH_3$=$CH_2$)]; *m/z* (CI) 460 $[M+NH_4]^+$, 286 $[M+NH_4\text{-Ts}]^+$, 188, 174, 148 $[M+NH_4\text{-Ts-CMe=CHPh-CMe=}CH_2]^+$, 131 (Found: $[M+NH_4]^+$, 460.1802. $C_{24}H_{26}O_6S$ requires $[M+NH_4]^+$, 460.1794) (Found: C, 65.07; H, 5.97. $C_{24}H_{26}O_6S$ requires C, 65.14; H, 5.92%).

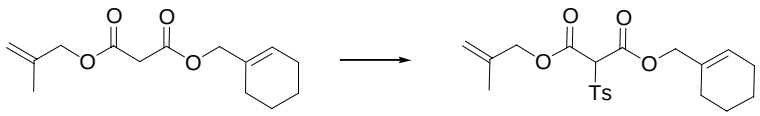
**2-(*p*-Toluenesulfonyl)malonic acid (*E*)-2-methyl-2-butenyl ester (*E*)-2-methyl-3-phenyl-2-propenyl ester (3d)**




**3d**

According to the general procedure, malonic acid ((*E*)-2-methyl-2-buten)yl ester ((*E*)-2-methyl-3-phenyl-2-propen)yl ester (9.284 g, 30.71 mmol, 2 equiv.) was combined with potassium *tert*-butoxide (3.466 g, 30.89 mmol, 2 equiv.) and *p*-toluenesulfonyl fluoride (2.705 g, 15.53 mmol, 1 equiv.) in DMSO (15 mL). Chromatography (5%→10% AcOEt–petrol) gave *2-(*p*-toluenesulfonyl)malonic acid (*E*)-2-methyl-2-butenyl ester (*E*)-2-methyl-3-phenyl-2-propenyl ester* **3d** (4.946 g, 71%) as a colourless gum and excess starting malonate (4.862 g, 81% unreacted); $R_f$ 0.17 (10% AcOEt–petrol); $\nu_{max}$ (film) 2924, 1741, 1645, 1598, 1446, 1335, 1290, 1180, 1151, 1082, 814, 702, 665 $cm^{-1}$; $\delta_H$ (270 MHz) 7.85 (2H, d, *J* 8.0 Hz, *ortho* Ts), 7.37-7.22 (7H, m, Ph and *meta* Ts), 6.49 (1H, s, =CHPh), 5.56-5.50 (1H, m, CMe=CHMe), 5.02 (1H, s, CHTs), [4.71 (2H, s) and 4.54 (2H, s), 2 x $CH_2O$], 2.39 (3H, s, $CH_3$ Ts), 1.82 (3H, d, *J* 1.0 Hz, C*H*$_3$C=CHPh), 1.60-1.57 (3H, m, CMe=CHC*H*$_3$), 1.57 (3H, s, C*H*$_3$C=CHMe); $\delta_C$ (100 MHz) 160.9 (2 x C=O), [145.9, 136.6, 134.3, 131.3 and 129.6 (*ipso* Ph, *ipso* Ts, *para* Ts, *C*Me=CHPh and *C*Me=CHMe)], [130.2, 129.5, 128.9 and 128.2 (*ortho* Ph, *meta* Ph, *ortho* Ts and *meta* Ts)], [129.8, 127.0 and 125.9 (*para* Ph, *C*HPh=CMe and *C*HMe=CMe)], 74.7 (CHTs), [72.9 and 72.6 (2 x $CH_2O$)], [21.7, 15.4, 13.5 and 13.3 (4 x $CH_3$)]; *m/z* (CI) 474 $[M+NH_4]^+$, 362, 323, 300, 174, 148 $[M+NH_4\text{-Ts-CMe=CHPh-CMe=CHMe}]^+$, 131 (Found: $[M+NH_4]^+$, 474.1947. $C_{25}H_{28}O_6S$ requires $[M+NH_4]^+$, 474.1950) (Found: C, 65.79; H, 6.12. $C_{25}H_{28}O_6S$ requires C, 65.77; H, 6.18%).

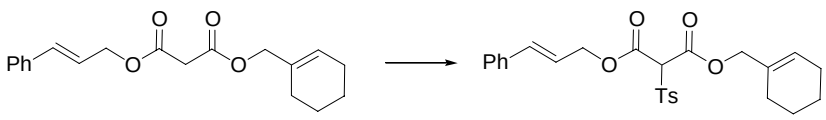
**2-(*p*-Toluenesulfonyl)malonic acid methallyl ester cyclohex-1-enylmethyl ester (3e)**




**3e**

According to the general procedure, malonic acid methallyl ester cyclohex-1-enylmethyl ester (1.619 g, 6.418 mmol, 2 equiv.) was combined with potassium *tert*-butoxide (740 mg, 6.59 mmol, 2 equiv.) and *p*-toluenesulfonyl fluoride (561 mg, 3.22 mmol, 1 equiv.) in DMSO (3.2 mL). Chromatography (2%→20% AcOEt–hexane) gave *2-(*p-*toluenesulfonyl)malonic acid methallyl ester cyclohex-1-enylmethyl ester* **3e** (663 mg, 51%) as a colourless gum and excess starting malonate (828 mg, 69 % unreacted); $R_f$ 0.10 (10% AcOEt–hexane); $\nu_{max}$ (film) 2931, 1743, 1455, 1336, 1277, 1193, 1180, 1151, 1082, 763, 750, 705 $cm^{-1}$; $\delta_H$ (400 MHz) 7.86 (2H, d, *J* 8.0 Hz, *ortho* Ts), 7.34 (2H, d, *J* 8.0 Hz, *meta* Ts), 5.74 (1H, bs, CH-2 cyclohexenyl), 5.01 (1H, s, CHTs), [4.99 (2H, bs) and 4.95 (2H, bs), $=CH_2$], [4.58 (2H, bs) and 4.52 (2H, bs), 2 x $CH_2O$], 2.45 (3H, s, $CH_3$ Ts), [2.03-2.02 (2H, m) and 1.90 (2H, m), $CH_2$-3 and $CH_2$-6 cyclohexenyl], 1.71 (3H, s, $=CCH_3$), 1.64-1.54 (4H, m, $CH_2$-4 and $CH_2$-5 cyclohexenyl); $\delta_C$ (100 MHz) [160.8 and 160.7 (2 x C=O)], [145.8, 138.3, 134.2 and 131.5 (*ipso* Ts, *para* Ts, $=CMe$ and C-1 cyclohexenyl)], [130.1 and 129.4 (*ortho* Ts and *meta* Ts)], 128.0 (CH-2 cyclohexenyl), 114.4 ($=CH_2$), 74.5 (CHTs), [71.4 and 69.9 (2 x $CH_2O$)], [25.5, 24.9, 22.1 and 21.8 (4 x $CH_2$ cyclohexenyl)], [21.6 and 19.2 ($CH_3$ Ts and $=CCH_3$)]; *m/z* (CI) 424 $[M+NH_4]^+$, 336, 330, 270, 189, 172, 112, 95 (Found: $[M+NH_4]^+$, 424.1808. $C_{21}H_{26}O_6S$ requires $[M+NH_4]^+$, 424.1794) (Found: C, 61.95; H, 6.45. $C_{21}H_{26}O_6S$ requires C, 62.05; H, 6.45%).

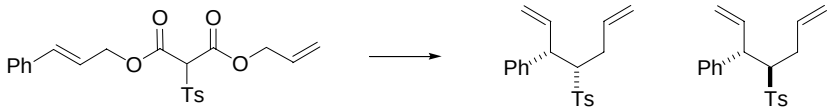
**2-(*p*-Toluenesulfonyl)malonic acid cinnamyl ester cyclohex-1-enylmethyl ester (3f)**




**3f**

According to the general procedure, malonic acid cinnamyl ester cyclohex-1-enylmethyl ester (1.958 g, 6.229 mmol, 2 equiv.) was combined with potassium *tert*-butoxide (699 mg, 6.23 mmol, 2 equiv.) and *p*-toluenesulfonyl fluoride (572 mg, 3.28 mmol, 1 equiv.) in DMSO (3 mL). Chromatography (10%→20% AcOEt–petrol) gave *2-(*p*-toluenesulfonyl)malonic acid cinnamyl ester cyclohex-1-enylmethyl ester* **3f** (1.084 g, 74%) as a colourless gum and excess starting malonate (1.079 g, 88% unreacted); $R_f$ 0.13 (10% AcOEt–petrol); $\nu_{max}$ (film) 3059, 3028, 2928, 2857, 1743, 1656, 1597, 1494, 1449, 1376, 1336, 1272, 1151, 1083, 1018, 969, 921, 815, 746, 706, 695, 673, 569, 515 $cm^{-1}$; $\delta_H$ (400 MHz) 7.85 (2H, d, *J* 8.5 Hz, *ortho* Ts), 7.37-7.26 (7H, m, *meta* Ts and Ph), 6.64 (1H, d, *J* 16.0 Hz, =CHPh), 6.17 (1H, dt, *J* 16.0, 6.5 Hz, C*H*=CHPh), 5.73 (1H, bs, CH-2 cyclohexenyl), 5.01 (1H, s, CHTs), 4.81 (2H, d, *J* 6.5 Hz, C$H_2$CH=CHPh), 4.53 (2H, s, $OCH_2$-cyclohexenyl), 2.39 (3H, s, $CH_3$ Ts), [1.99 (2H, bs) and 1.90 (2H, bs), $CH_2$-3 and $CH_2$-6 cyclohexenyl], 1.59-1.53 (4H, m, $CH_2$-4 and $CH_2$-5 cyclohexenyl); $\delta_C$ (100 MHz) 160.9 (2 x C=O), 145.9 (*para* Ts), [135.8, 134.2 and 131.6 (*ipso* Ph, *ipso* Ts and C-1 cyclohexenyl)], [135.7, 128.4, 128.1 and 121.3 (*para* Ph, =CHPh, *C*H=CHPh and CH-2 cyclohexenyl)], [130.2, 129.5, 128.6 and 126.7 (*ortho* Ph, *meta* Ph, *ortho* Ts and *meta* Ts)], 74.6 (CHTs), [71.5 and 67.4 (2 x $CH_2O$)], [25.6, 25.0, 22.2 and 21.9 (4 x $CH_2$ cyclohexenyl)], 21.7 ($CH_3$ Ts); *m/z* (CI) 486 $[M+NH_4]^+$, 348, 326, 174, 134 [M-COCH(Ts)$COOCH_2$-cyclohexenyl+H]$^+$, 117 (Found: $[M+NH_4]^+$, 486.1962. $C_{26}H_{28}O_6S$ requires $[M+NH_4]^+$, 486.1950) (Found: C, 66.72; H, 5.93. $C_{26}H_{28}O_6S$ requires C, 66.65; H, 6.02%).

**3-Phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene (4a)**

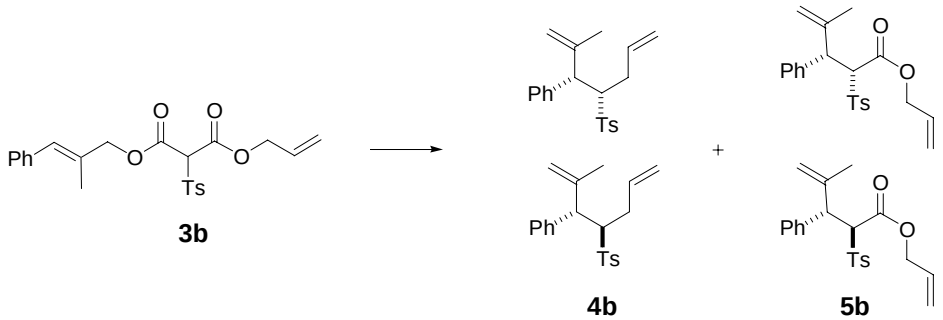



**3a** **4a**

To a mixture of 2-(*p*-toluenesulfonyl)malonic acid allyl ester cinnamyl ester **3a** (3.96 g, 9.64 mmol, 1 equiv.) and potassium acetate (101 mg, 1.03 mmol, 0.1 equiv.) under nitrogen was

added BSA (7.0 mL, 27 mmol, 2.9 equiv.). The mixture was exposed to microwave irradiation for 4 min at 170 °C. Chromatography (5%→10% AcOEt–petrol) gave *3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene* **4a** as a 1:1 mixture of diastereoisomers (2.695 g, 86%) as a colourless gum; $R_f$ 0.34 (10% AcOEt–petrol); $\nu_{max}$ (film) 3028, 2980, 2921, 1638, 1597, 1493, 1452, 1300, 1289, 1143, 1085, 992, 919, 815 $cm^{-1}$; $\delta_H$ (270 MHz) [7.69 (2H, d, *J* 8.5 Hz) and 7.58 (2H, d, *J* 8.5 Hz), *ortho* Ts of both diastereoisomers], 7.29-7.08 (14H, m, *meta* Ts and Ph of both diastereoisomers), [6.20-6.01 (2H, m) and 5.67-5.54 (2H, m), CH-2 and CH-6 of both diastereoisomers], 5.22-4.72 (8H, m, $CH_2$-1 and $CH_2$-7 of both diastereoisomers), [4.09 (1H, dd, *J* 8.5, 5.0 Hz) and 4.00-3.94 (1H, m), CHPh of both diastereoisomers], 3.55-3.44 (2H, m, CHTs of both diastereoisomers), 2.74-2.67 (2H, m, $CH_2$-5 of one diastereoisomer), [2.41 (3H, s), 2.39 (3H, s) and 2.41-2.33 (2H, m), $CH_3$ of both diastereoisomers and $CH_2$-5 of one diastereoisomer]; $\delta_C$ (67.5 MHz) [144.5, 144.3, 141.1, 140.4, 136.7 and 136.4 (*ipso* Ph, *ipso* Ts and *para* Ts of both diastereoisomers)], [138.1, 135.8, 134.6, 133.6, 127.1 and 126.9 (*para* Ph, CH-2 and CH-7 of both diastereoisomers)], [129.7, 129.6, 128.9, 128.7, 128.6, 128.6, 128.4 and 128.2 (*ortho* Ph, *meta* Ph, *ortho* Ts and *meta* Ts of both diastereoisomers)], [118.7, 118.2, 117.7 and 117.0 ($CH_2$-1 and $CH_2$-7 of both diastereoisomers)], [68.9 and 68.5 (CHTs of both diastereoisomers)], [49.4 and 48.3 (CHPh of both diastereoisomers)], [31.9 and 30.1 ($CH_2$-5 of both diastereoisomers)], 21.7 ($CH_3$ of both diastereoisomers); *m/z* (CI) 344 $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 344.1676. $C_{20}H_{22}O_2S$ requires $[M+NH_4]^+$, 344.1684).

**2-Methyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene (4b) and 2-(*p*-toluenesulfonyl)-3-phenyl-4-methyl-4-pentenoic acid allyl ester (5b)**




To a mixture of 2-(*p*-toluenesulfonyl)malonic acid allyl ester (*E*)-2-methyl-3-phenyl-2-propenyl ester **3b** (1.032 g, 2.407 mmol, 1 equiv.) and potassium acetate (56 mg, 0.57 mmol, 0.2 equiv.) under nitrogen was added BSA (1.9 mL, 7.5 mmol, 3.1 equiv.). The mixture was exposed to 4

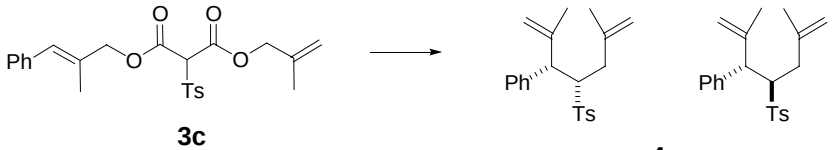
cycles of microwave irradiation of 3 min each at 200 °C. Chromatography (6%→10% AcOEt–petrol) gave *2-methyl-3-phenyl-4-(*p-*toluenesulfonyl)-1,6-heptadiene* **4b** as a 1:1 mixture of diastereoisomers (630 mg, 77%) as a colourless solid and *2-(*p-*toluenesulfonyl)-3-phenyl-4-methyl-4-pentenoic acid allyl ester* **5b** in a 1:1 mixture of diastereoisomers (68 mg, 7%) as a colourless solid.

*2-Methyl-3-phenyl-4-(*p-*toluenesulfonyl)-1,6-heptadiene* **4b**; $R_f$ 0.31 (10% AcOEt–petrol); $\nu_{max}$ (film) 3077, 3028, 2978, 2923, 1640, 1597, 1493, 1452, 1300, 1290, 1142, 1085, 913, 815, 756, 731, 702 $cm^{-1}$; $\delta_H$ (270 MHz) 7.74 (2H, d, *J* 8.5 Hz, *ortho* Ts of one diastereoisomer), [7.31-7.17 (8H, m) and 7.00-6.94 (6H, m), Ph and *meta* Ts of both diastereoisomers], 6.09-5.97 (1H, m, CH-6 of one diastereoisomer), 5.62-5.50 (1H, m, CH-6 of one diastereoisomer), 5.13-4.59 (8H, m, $CH_2$-1 and $CH_2$-7 of both diastereoisomers), 4.04-3.75 (4H, m, CH-3 and CH-4 of both diastereoisomers), 2.83-2.33 (4H, m, $CH_2$-5 of both diastereoisomers), 2.42 (3H, s, $CH_3$ Ts of one diastereoisomer), 2.31 (3H, s, $CH_3$ Ts of one diastereoisomer), 1.59 (3H, s, $CH_3$-2 of one diastereoisomer), 1.51 (3H, s, $CH_3$-2 of one diastereoisomer); $\delta_C$ (67.5 MHz) [145.1, 144.9, 144.5, 143.3, 138.9, 138.8, 137.8 and 136.9 (*ipso* Ph, *ipso* Ts, *para* Ts and C-2 of both diastereoisomers)], [134.8, 133.9, 127.2 and 126.6 (*para* Ph, and CH-6 of both diastereoisomers)], [129.6, 129.2, 129.1, 128.9, 128.4, 127.9, 127.9 (*ortho* Ph, *meta* Ph, *ortho* Ts and *meta* Ts)], [118.0, 117.7, 113.7 and 113.5 ($CH_2$-1 and $CH_2$-7 of both diastereoisomers)], [66.2 and 65.7 (CHTs of both diastereoisomers)], [53.3 and 52.2 (CHPh of both diastereoisomers)], [31.9 and 31.8 ($CH_2$-5 of both diastereoisomers)], [21.7, 21.5, 21.1 and 20.6 ($CH_3$-2 and $CH_3$ Ts of both diastereoisomers)]; *m/z* (CI) 358 $[M+NH_4]^+$, 341 $[M+H]^+$, 268 (Found: $[M+H]^+$, 341.1580. $C_{21}H_{24}O_2S$ requires $[M+H]^+$, 341.1575).

*2-(*p-*Toluenesulfonyl)-4-methyl-3-phenyl-4-pentenoic acid allyl ester* **5b**; $R_f$ 0.22 (10% AcOEt–petrol); $\nu_{max}$ (film) 3070, 1741, 1647, 1597, 1493, 1452, 1323, 1293, 1145, 1083, 900 $cm^{-1}$; $\delta_H$ (270 MHz) 7.81 (2H, d, *J* 8.5 Hz, *ortho* Ts of one diastereoisomer), 7.31-7.05 (14H, m, *meta* Ts and Ph of both diastereoisomers), 5.90-5.76 (2H, m, C*H*= of both diastereoisomers), 5.38-4.50 (12H, m, $CH_2$-1, CH=C$H_2$ and $CH_2O$ of both diastereoisomers), 4.12-4.06 (4H, m, CH-3 and CH-4 of both diastereoisomers), [2.44 (3H, s) and 2.32 (3H, s) $CH_3$ Ts of both diastereoisomers], 1.61 (6H, bs, $CH_3$-2 of both diastereoisomers); $\delta_C$ (100 MHz) [165.1 and 164.9 (C=O of both diastereoisomers)], [145.6, 145.3, 144.4, 142.5, 138.8, 136.9, 136.1 and 135,2 (*ipso* Ph, *ipso* Ts, *para* Ts and C-2 of both diastereoisomers)], [131.1, 130.7, 129.9, 129.7, 129.2, 129.0, 128.9, 128.6, 128.4, 128.2, 128.0 and 127.3 (*ortho* Ph, *meta* Ph, *para* Ph, *ortho* Ts, *meta* Ts and *C*H= of

both diastereoisomers)], [119.2, 118.9, 114.7 and 111.5 ($CH_2$-1 and CH=*C*$H_2$ of both diastereoisomers)], [74.5 and 72.8 (CHTs of both diastereoisomers)], [66.8 and 66.4 ($CH_2O$ of both diastereoisomers)], [52.2 and 51.5 (CHPh of both diastereoisomers)], [21.9, 21.8, 21.7 and 21.5 ($CH_3$-2 and $CH_3$ Ts of both diastereoisomers)]; *m/z* (CI) 402 $[M+NH_4]^+$, 318 $[M+NH_4-COOCH_2CH=CH_2]$ (Found: $[M+NH_4]^+$, 402.1752. $C_{22}H_{24}O_4S$ requires $[M+NH_4]^+$, 402.1739).

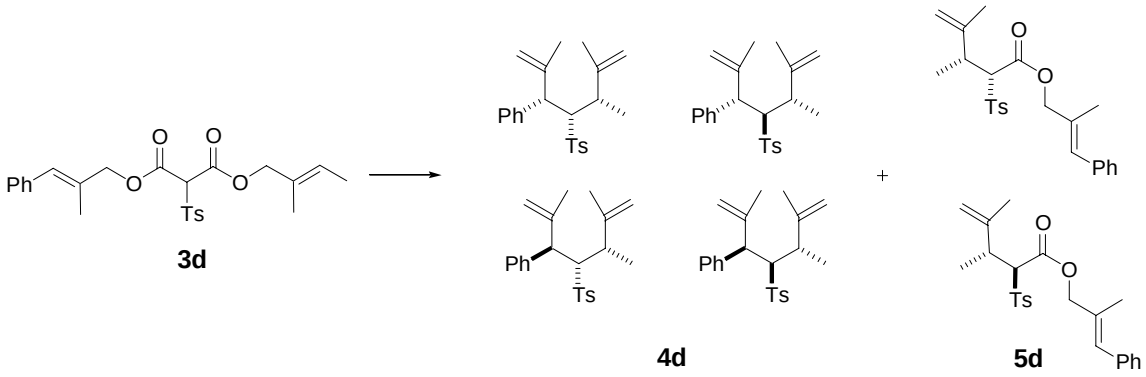
**2,6-Dimethyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene (4c)**




**3c** **4c**

To a mixture of 2-(*p*-toluenesulfonyl)-malonic acid methallyl ester (*E*)-2-methyl-3-phenyl-2-propenyl ester **3c** (743 mg, 1.69 mmol, 1 equiv.) and potassium acetate (22 mg, 0.22 mmol, 0.1 equiv.) under nitrogen was added BSA (2.0 mL, 7.9 mmol, 4.7 equiv.). The mixture was exposed to 2 cycles of microwave irradiation of 3 min each at 240 °C. Chromatography (2%→10% AcOEt–petrol) gave *2,6-dimethyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene* **4c** as a 1:1 mixture of diastereoisomers (419 mg, 70%) as a colourless gum; $R_f$ 0.35 (10% AcOEt–petrol); $\nu_{max}$ (film) 3070, 3027, 2970, 2920, 1649, 1597, 1493, 1451, 1301, 1290, 1143, 1085, 895, 753, 701, 667 $cm^{-1}$; $\delta_H$ (270 MHz) 7.71 (2H, d, *J* 8.0 Hz, *ortho* Ts of one diastereoisomer), 7.34-7.02 (16H, m, *ortho* Ts of one diastereoisomer, *meta* Ts and Ph of both diastereoisomers), 4.99-3.81 (12H, m, $CH_2$-1, CH-3, CH-4 and $CH_2$-7 of both diastereoisomers), 2.88-2.13 (4H, m, $CH_2$-5 of both diastereoisomers), [2.42 (3H, s) and 2.33 (2H, s), $CH_3$ Ts of both diastereoisomers], [1.70 (3H, s), 1.60 (3H, s), 1.57 (3H, s) and 1.37 (3H, s), $CH_3$-2 and $CH_3$-6 of both diastereoisomers]; $\delta_C$ (67.5 MHz) [145.7, 144.9, 144.4, 143.6, 142.5, 141.2, 139.2, 138.6, 137.3 and 136.8 (*ipso* Ph, *ipso* Ts, *para* Ts, C-2 and C-6 of both diastereoisomers)], [129.7, 129.4, 129.3, 128.9, 128.3 and 128.0 (*ortho* Ph, *meta* Ph, *ortho* Ts and *meta* Ts of both diastereoisomers)], [127.2 and 126.7 (*para* Ph of both diastereoisomers)], [114.2, 112.6, 112.6 and 112.1 ($CH_2$-1 and $CH_2$-7 of both diastereoisomers)], [64.8 and 64.1 (CHTs of both diastereoisomers)], [54.3 and 52.0 (CHPh of both diastereoisomers)], [35.4 and 34.8 ($CH_2$-5 of both diastereoisomers)], [22.8, 22.2, 22.0, 21.7, 21.6 and 21.3 ($CH_3$-2, $CH_3$-6 and $CH_3$ Ts of both diastereoisomers)]; *m/z* (CI) 372 $[M+NH_4]^+$, 219 $[M+NH_4-Ts]^+$, 182 (Found: $[M+H]^+$, 355.1736. $C_{22}H_{26}O_2S$ requires $[M+H]^+$, 355.1732).

**2,5,6-Trimethyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene (4d) and 3,4-dimethyl-2-(*p*-toluenesulfonyl)-4-pentenoic acid (*E*)-2-methyl-3-phenyl-2-propenyl ester (5d)**



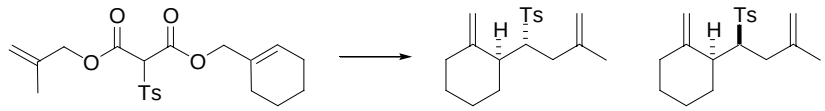

To a mixture of 2-(*p*-toluenesulfonyl)-malonic acid (*E*)-2-methyl-2-butenyl ester (*E*)-2-methyl-3-phenyl-2-propenyl ester **3d** (2.817 g, 6.170 mmol, 1 equiv.) and potassium acetate (76 mg, 0.77 mmol, 0.1 equiv.) under nitrogen was added BSA (5.0 mL, 20 mmol, 3 equiv.). The mixture was exposed to 6 cycles of microwave irradiation of 1 min each at 180 °C. Chromatography (1%→5% AcOEt–petrol) gave *2,5,6-trimethyl-3-phenyl-4-(*p-*toluenesulfonyl)-1,6-heptadiene* **4d** as a mixture of diastereoisomers (1.275 g, 56%) as a colourless solid and *2-(*p-*toluenesulfonyl)-3,4-dimethyl-4-pentenoic acid (*E*)-2-methyl-3-phenyl-2-propenyl ester* **5d** as a 3:2 mixture of diastereoisomers (576 mg, 23%) as a colourless solid.

*2,5,6-Trimethyl-3-phenyl-4-(*p-*toluenesulfonyl)-1,6-heptadiene* **4d**; $R_f$ 0.35 (10% AcOEt–petrol); $\nu_{max}$ (film) 3061, 3028, 2970, 2924, 1643, 1597, 1493, 1452, 1379, 1300, 1144, 1086, 893, 814, 760, 702, 665 $cm^{-1}$; $\delta_H$ (400 MHz) [7.78 (2H, d, *J* 8.5 Hz) and 7.73 (2H, d, *J* 8.5 Hz), *ortho* Ts of 2 diastereoisomers], 7.33-6.87 (32H, m, *ortho* Ts of 2 diastereoisomers and *meta* Ts and Ph of all diastereoisomers), 5.09-4.01 (24H, m, $CH_2$-1, CH-3, CH-4 and $CH_2$-7 of all diastereoisomers), [3.43-3.38 (1H, m), 2.96-2.91 (1H, m), 2.84-2.78 (1H, m), CH-5 of 3 diastereoisomers], [2.45 (3H, s), 2.43 (3H, s), 2.38-2.36 (1H, m), 2.33 (3H, s) and 2.30 (3H, s), CH-5 of one diastereoisomer and $CH_3$ Ts of all diastereoisomers], [2.05 (3H, s), 1.90 (3H, s), 1.80 (3H, s), 1.62 (3H, s) and 1.56-1.14 (24H, m), $CH_3$-2, $CH_3$-5 and $CH_3$-6 of all diastereoisomers]; $\delta_C$ (125 MHz) [146.8, 146.2, 145.1, 144.8, 144.8, 144.6, 144.5, 144.2, 143.9, 142.8, 142.6, 140.2, 140.1, 139.7, 139.5, 139.2, 139.1, 138.4 and 138.0 (*ipso* Ph, *ipso* Ts, *para* Ts, C-2 and C-6 of all diastereoisomers)], [129.5, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 127.8, 127.7, 127.6, 127.2, 127.0, 126.9 and 126.4 (*ortho* Ph, *meta* Ph, *para* Ph, *ortho* Ts and *meta* Ts of all

diastereoisomers)], [114.5, 114.4, 114.1, 113.8, 111.9, 111.4 and 111.2 ($CH_2$-1 and $CH_2$-7 of all diastereoisomers)], [67.5, 67.3, 67.1 and 67.0 (CHTs of all diastereoisomers)], [54.1, 53.3, 52.5 and 51.9 (CHPh of all diastereoisomers)], [39.7, 39.3, 38.5 and 38.4 (CHMe of all diastereoisomers)], [22.7, 22.7, 22.3, 21.8, 21.7, 21.5, 21.4, 20.9, 20.8, 20.5, 20.1 and 19.3 ($CH_3$-2, $CH_3$-6 and $CH_3$ Ts of all diastereoisomers)], [14.6, 13.8, 12.7 and 12.6 ($CH_3$- 5 of all diastereoisomers)]; *m/z* (CI) 386 $[M+NH_4]^+$, 369 $[M+H]^+$, 198 (Found: $[M+H]^+$, 369.1880; $[M+NH_4]^+$, 386.2152. $C_{23}H_{28}O_2S$ requires $[M+H]^+$, 369.1888; $[M+NH_4]^+$, 386.2154).

*3,4-Dimethyl-2-(*p*-toluenesulfonyl)-4-pentenoic acid (*E*)-2-methyl-3-phenyl-2-propenyl ester* **5d**; $R_f$ 0.31 (10% AcOEt–petrol); $\nu_{max}$ (film) 2972, 2938, 2924, 1739, 1596, 1493, 1451, 1322, 1290, 1209, 1143, 1083, 902, 815, 751 $cm^{-1}$; $\delta_H$ (270 MHz) 7.79 (2H, d, *J* 8.5 Hz, *ortho* Ts of the major diastereoisomer), 7.77 (2H, d, *J* 8.5 Hz, *ortho* Ts of the minor diastereoisomer), 7.37-7.20 (14 H, m, *meta* Ts and Ph of both diastereoisomers), 6.47 (1H, s, CHPh of the minor diastereoisomer), 6.35 (1H, s, CHPh of the major diastereoisomer), 4.86-4.02 (10H, m, CHTs, $CH_2$-5 and $CH_2O$ of both diastereoisomers), 3.12-3.02 (2H, m, CH-3 of both diastereoisomers), 2.36 (3H, s, $CH_3$ Ts of the minor diastereoisomer), 2.35 (3H, s, $CH_3$ Ts of the major diastereoisomer), 1.80 (3H, d, *J* 1.0 Hz, C*H*$_3$C=CHPh of the minor diastereoisomer), 1.72 (3H, d, *J* 1.0 Hz, C*H*$_3$C=CHPh of the major diastereoisomer), 1.68 (3H, s, $CH_3$-3 of the major diastereoisomer), 1.67 (3H, s, $CH_3$-3 of the minor diastereoisomer), 1.41 (3H, d, *J* 7.0 Hz, $CH_3$-4 of the major diastereoisomer), 1.12 (3H, d, *J* 7.0 Hz, $CH_3$-4 of the minor diastereoisomer); $\delta_C$ (100 MHz) [165.7 and 165.6 (C=O of both diastereoisomers)], [145.7, 145.2, 145.1, 144.5, 136.7, 135.3, 135.1, 131.5 and 131.5 (*ipso* Ph, *ipso* Ts, *para* Ts, C-4 and $CH_3$*C*=CHPh of both diastereoisomers)], [129.6, 129.6, 129.5, 129.4, 129.4, 129.2, 129.0, 128.8, 128.1 and 126.9 (*ortho* Ph, *meta* Ph, *para* Ph, *ortho* Ts, *meta* Ts and =*C*HPh of both diastereoisomers)], [114.0 and 113.2 ($CH_2$-5 of both diastereoisomers)], [75.5 and 73.4 (CHTs of both diastereoisomers)], [71.8 and 71.6 ($CH_2O$ of both diastereoisomers)], [40.8 and 40.3 (CH-3 of both diastereoisomers)], [21.5, 19.2, 18.3, 18.2, 17.7, 15.5 and 15.5 ($CH_3$-3, $CH_3$-4 $CH_3$ Ts and *C*$H_3$C=CHPh of both diastereoisomers)]; *m/z* (CI) 430 $[M+NH_4]^+$, 318 (Found: $[M+NH_4]^+$, 430.2047. $C_{24}H_{28}O_4S$ requires $[M+NH_4]^+$, 430.2052).

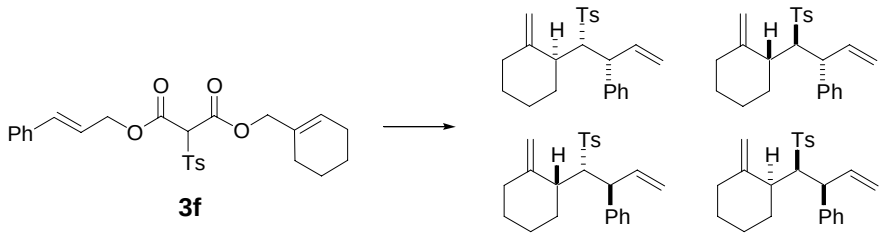
**1-Methyl-4-[3-methyl-1-(2-methylenecyclohexyl)but-3-enylsulfonyl]benzene (4e)**




**3e** **4e**

To a mixture of 2-(*p*-toluenesulfonyl)malonic acid methallyl ester cyclohex-1-enymethyl ester **3e** (65 mg, 0.16 mmol, 1 equiv.) and potassium acetate (5 mg, 0.05 mmol, 0.3 equiv.) under nitrogen was added BSA (300 μL, 1.19 mmol, 7 equiv.). The mixture was exposed to 6 cycles of microwave irradiation of 1 min each at 220 °C followed by 3 cycles of microwave irradiation of 2 min each at 240 °C. Chromatography (0%→10% AcOEt–hexane) gave *1-methyl-4-[3-methyl-1-(2-methylenecyclohexyl)but-3-enylsulfonyl]benzene* **4e** as a 1:1 mixture of diastereoisomers (32 mg, 62%) as a colourless gum; $R_f$ 0.22 (10% AcOEt–hexane); $\nu_{max}$ (film) 2931, 2859, 1741, 1668, 1596, 1448, 1311, 1301, 1293, 1145, 1085, 892, 815 $cm^{-1}$; $\delta_H$ (400 MHz) 7.77 (2H, d, *J* 8.0 Hz, *ortho* Ts of one diastereoisomer), 7.73 (2H, d, *J* 8.0 Hz, *ortho* Ts of one diastereoisomer), 7.33 (2H, d, *J* 8.0 Hz, *meta* Ts of one diastereoisomer), 7.29 (2H, d, *J* 8.0 Hz, *meta* Ts of one diastereoisomer), 4.83-4.46 (8H, m, 2 x =$CH_2$ of both diastereoisomers), [3.70 (1H, dt, *J* 9.5, 2.5 Hz) and 3.60-3.56 (1H, m), CHTs of both diastereoisomers], [2.97-2.94 (1H, m), 2.76-2.65 (2H, m), 2.50-2.00 (8H, m) and (11H, m), C*H*$_2$CHTs and CH-1, $CH_2$-3, $CH_2$-4, $CH_2$-5, $CH_2$-6 cyclohexyl of both diastereoisomers], [2.44 (3H, s) and 2.43 (3H, s), $CH_3$ Ts of both diastereoisomers], [1.56 (3H, s) and 1.46 (3H, s), =CC*H*$_3$ of both diastereoisomers]; $\delta_C$ (100 MHz) [149.6, 148.7, 144.3, 144.2, 141.4, 141.0, 137.1 and 136.7 (*ipso* Ts, *para* Ts, C-2 cyclohexyl and =CMe of both diastereoisomers)], [129.5, 129.4 and 128.8 (*ortho* Ts and *meta* Ts of both diastereoisomers)], [112.7, 112.5, 110.1 and 105.5 (2 x =$CH_2$ of both diastereoisomers)], [62.8 and 61.9 (CHTs of both diastereoisomers)], [44.3 and 41.7 (CH-1 cyclohexyl of both diastereoisomers)], [37.1, 36.3, 34.5, 33.2, 30.4, 28.6, 28.0, 28.0, 25.8 and 23.3 ($CH_2$-3, $CH_2$-4, $CH_2$-5 and $CH_2$-6 cyclohexenyl and C$H_2$CHTs of both diastereoisomers)], [22.2, 21.9 and 21.6 (=CC$H_3$ and $CH_3$ Ts of both diastereoisomers)]; *m/z* (CI) 336 $[M+NH_4]^+$, 319 $[M+H]^+$, 296, 174, 163, 52 (Found: $[M+NH_4]^+$, 336.1993; $[M+H]^+$, 319.1731. $C_{19}H_{26}O_2S$ requires $[M+NH_4]^+$, 336.1997; $[M+H]^+$, 319.1732).

**1-Methyl-4-[1-(2-methylenecyclohexyl)-2-phenylbut-3-enylsulfonyl]benzene (4f)**

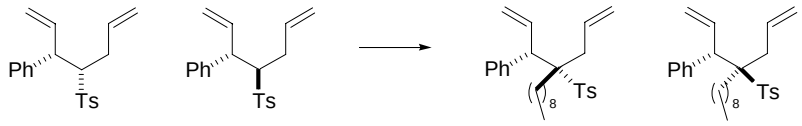



**3f** **4f**

To a mixture of 2-(*p*-toluenesulfonyl)malonic acid cinnamyl ester cyclohex-1-enylmethyl ester **3f** (543 mg, 1.16 mmol, 1 equiv.) and potassium acetate (14 mg, 0.15 mmol, 0.1 equiv.) under nitrogen was added BSA (900 μL, 3.57 mmol, 3 equiv.). The mixture was exposed to 6 cycles of microwave irradiation of 1 min each at 190 °C. Chromatography (1%→2% AcOEt–petrol) gave *1-methyl-4-[1-(2-methylenecyclohexyl)-2-phenylbut-3-enylsulfonyl]benzene* **4f** as a mixture of 4 diastereoisomers (257 mg, 58%) as a colourless gum; $R_f$ 0.33 (5% AcOEt–petrol); $\nu_{max}$ (film) 3064, 2932, 2857, 1598, 1494, 1451, 1314, 1301, 1143, 1085, 906, 815, 740, 700, 662 $cm^{-1}$; $\delta_H$ (400 MHz) 7.70 (2H, d, *J* 8.5 Hz, *ortho* Ts of one diastereoisomer), 7.56-6.97 (26H, m, Ph and *meta* Ts of all diastereoisomers and *ortho* Ts of three diastereoisomers), [6.71-6.62 (1H, m), 6.35 (1H, dt, *J* 17.0, 10.0 Hz) and 6.25-6.15 (2H, m), CH= of all diastereosiomers], 5.33-4.86 (16H, m, 2 x $=CH_2$ of all diastereoisomers), [4.64 (1H, s), 4.44 (1H, s), 4.36-4.32 (1H, m), 4.23 (1H, dd, *J* 9.0, 3.0 Hz) and 4.16-4.02 (4H, m), CHTs and CHPh of all diastereoisomers], [3.30-3.25 (1H, m), 3.01-2.93 (2H, m) and 2.68-2.65 (1H, m), CH-1 cyclohexyl of all diastereoisomers], [2.42 (3H, s), 2.40 (3H, s), 2.39 (3H, s) and 2.36 (3H, s), $CH_3$ Ts of all diastereoisomers)], 2.33-1.28 (32H, m, $CH_2$-3, $CH_2$-4, $CH_2$-5 and $CH_2$-6 cyclohexyl of all diastereoisomers); $\delta_C$ (100 MHz) [149.7, 148.9, 148.5 and 148.3 (C-2 cyclohexyl of all diastereoisomers)], [144.0, 143.7, 143.5, 143.1, 142.9, 142.3, 141.4, 140.8, 139.4, 138.6, 138.4 and 137.7 (*ipso* Ts, *para* Ts and *ipso* Ph of all diastereoisomers)], [137.9, 137.5, 136.9 and 134.6 (*C*H= of all diastereoisomers)], [129.4, 129.4, 129.3, 129.0, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.4, 126.5, 126.4 and 125.9 (*ortho* Ts, *meta* Ts and Ph of all diastereoisomers)], [120.0, 117.9, 117.7, 117.5, 110.8, 109.1, 108.6 and 108.0 (2 x $=CH_2$ of all diastereoisomers)], [69.6, 69.5, 68.5 and 68.2 (CHTs of all diastereoisomers)], [49.3, 48.5, 48.3 and 48.2 (CHPh of all diastereoisomers)], [44.2, 43.7, 43.2 and 42.0 (CH-1 cyclohexyl of all diastereoisomers)], [35.7, 35.6, 35.1, 33.4, 30.2, 29.6, 29.4, 28.3, 27.9, 27.8, 27.3, 25.2, 25.0, 24.3 and 22.1 ($CH_2$-3, $CH_2$-4, $CH_2$-5 and $CH_2$-6 cyclohexyl of all diastereoisomers)], [21.5, 21.5 and 21.4 ($CH_3$ Ts of all diastereoisomers)]; *m/z*

(CI) 398 $[M+NH_4]^+$, 381 $[M+H]^+$, 52 (Found: $[M+H]^+$, 381.1888. $C_{24}H_{28}O_2S$ requires $[M+H]^+$, 381.1888).

**3-Phenyl-4-(prop-2-enyl)-4-(*p*-toluenesulfonyl)tridec-1-ene (6a)**

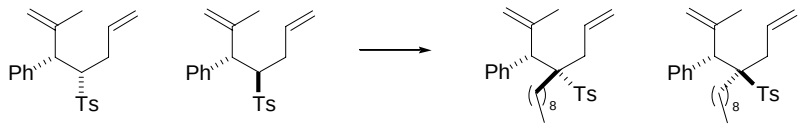



**4a** **6a**

To a 1:1 diastereoisomeric mixture of 3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene **4a** (630 mg, 1.93 mmol, 1 equiv.) in THF (10 mL) at 0 °C and under nitrogen was added dropwise a commercial solution of *n*-BuLi in hexane (Acros, titrated to be 2.16 M, 1.1 mL, 2.4 mmol, 1.2 equiv.). The solution turned deep red and 1-iodononane (460 μL, 2.33 mmol, 1.2 equiv.) was immediately added. The reaction was allowed to warm to rt and after 15 h of stirring the excess *n*-BuLi was quenched with MeOH (2.5 mL). Concentration under reduced pressure and chromatography (3%→5% AcOEt–petrol) gave *3-phenyl-4-(prop-2-enyl)-4-(p-toluenesulfonyl)tridec-1-ene* **6a** as a 2:3 mixture of diastereoisomers (754 mg, 86%) as a colourless gum; $R_f$ 0.69 (10% AcOEt–petrol); $\nu_{max}$ (film) 2924, 2853, 1635, 1598, 1454, 1286, 1129, 1079, 917, 815 $cm^{-1}$; $\delta_H$ (270 MHz) 7.47-7.43 (4H, m, *ortho* Ts of both diastereoisomers), 7.27-7.13 (14H, m, *meta* Ts and Ph of both diastereoisomers), [6.42-6.27 (2H, m), 6.20-6.07 (1H, m) and 5.82-5.70 (1H, m), CH-2 and CH-6 of both diastereoisomers], 5.19-4.97 (8H, m, $CH_2$-1 and $CH_2$-7 of both diastereoisomers), 4.19-4.12 (2H, m, CHPh of both diastereoisomers), 2.78-2.43 (4H, m, $CH_2$-5 of both diastereoisomers), 2.37 (6H, s, $CH_3$ Ts of both diastereoisomers), 1.97-1.55 (4H, m, Ts$CC\mathit{H}_2CH_2$ of both diastereoisomers), 1.26 (28H, bs, Ts$CCH_2(C\mathit{H}_2)_7$Me of both diastereoisomers), 0.90-0.85 (6H, m, $CH_2C\mathit{H}_3$ of both diastereoisomers); $\delta_C$ (100 MHz) [144.0, 140.0, 135.6 and 135.4 (*ipso* Ph, *ipso* Ts and *para* Ts of both diastereoisomers)], [137.6 and 132.8 (CH-2 and CH-6 of the major diastereoisomer)], [137.5 and 133.2 (CH-2 and CH-6 of the minor diastereoisomers)], [130.6, 130.5, 130.3, 130.2, 129.0, 129.0, 128.2, and 127.1 (*ortho* Ph, *meta* Ph, *para* Ph, *ortho* Ts and *meta* Ts of both diastereoisomers)], [118.9 and 118.1 ($CH_2$-1 and $CH_2$-7 of the minor diastereoisomer)], [118.9 and 117.8 ($CH_2$-1 and $CH_2$-7 of the major diastereoisomer)], 73.4 (C-4 of the minor diastereoisomer), 73.2 (C-4 of the major diastereoisomer), 53.3 (CHPh of the minor diastereosiomer), 52.7 (CHPh of the major diastereoisomer), [37.7, 36.4, 33.2, 32.6, 31.9, 31.9,

30.4, 30.3, 29.6, 29.5, 29.4, 29.3, 29.3, 29.3, 23.8, 23.6 and 22.7 ($CH_2$-5 and TsC($CH_2$)$_8$Me of both diastereoisomers)], [21.5 and 14.1 ($CH_3$ Ts and $CH_2CH_3$ of both diastereoisomers)]; *m/z* (CI) 470 $[M+NH_4]^+$, 297 $[M+H\text{-}Ts]^+$, 174 $[M+H\text{-}Ts\text{-}nonyl]^+$ (Found: $[M+NH_4]^+$, 470.3094. $C_{29}H_{40}O_2S$ requires $[M+NH_4]^+$, 470.3093).

**2-Methyl-3-phenyl-4-(prop-2-enyl)-4-(*p*-toluenesulfonyl)tridec-1-ene (6b)**

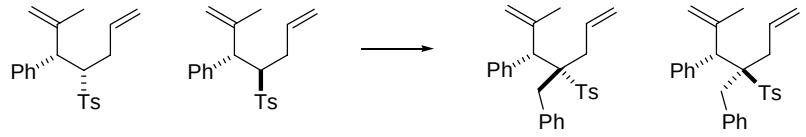



**4b** **6b**

To a solution of a 1:1 diastereoisomeric mixture of 2-methyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene **4b** (245 mg, 0.720 mmol, 1 equiv.) in THF (3.6 mL) at 0 °C and under nitrogen was added dropwise a commercial solution of *n*-BuLi in hexane (Aldrich, titrated to be 2.42 M, 300 µL, 0.708 mmol, 1.2 equiv.). The solution turned bright orange and 1-iodononane (140µL, 0.799 mmol, 1.1 equiv.) was immediately added. The reaction was allowed to warm to rt and after 43 h of stirring at rt the excess *n*-BuLi was quenched with MeOH (1 mL). Concentration under reduced pressure and chromatography (2%→10% AcOEt–petrol) gave *2-methyl-3-phenyl-4-(prop-2-enyl)-4-(p-toluenesulfonyl)tridec-1-ene* **6b** as a 1:1 mixture of diastereoisomers (136 mg, 40%) as a pale yellow oil and the diene starting material **4b** (83 mg, 34%) as a colourless oil; $R_f$ 0.34 (10% AcOEt–hexane); $\nu_{max}$ (film) 2955, 2925, 2854, 1455, 1276, 1261, 1130, 1077, 1041, 763 $cm^{-1}$; $\delta_H$ (400 MHz) 7.47-7.10 (18H, m, Ph and Ts of both diastereoisomers), 6.23-6.13 (1H, m, CH-6 of the major diastereoisomer), 5.86-5.76 (1H, m, CH-6 of the minor diastereoisomer), 5.19-4.93 (8H, m, $CH_2$-1 and $CH_2$-7 of both diastereoisomers), 4.34 (1H, s, CH-3 of the minor diastereoisomer), 4.24 (1H, s, CH-3 of the major diastereoisomer), 3.00-2.71 (4H, m, $CH_2$-5 of both diastereoisomers), 2.37 (6H, s, $CH_3$ Ts of both diastereoisomers), [2.27-1.84 (4H, m) and 1.40-1.20 (28H, m), TsC($CH_2$)$_8$Me of both diastereoisomers], 1.74 (3H, s, $CH_3$-2 of the minor diastereoisomer), 1.69 (3H, s, $CH_3$-2 of the major diastereoisomer), 0.97-0.87 (6H, m, $CH_2C\mathit{H_3}$ of both diastereoisomers); $\delta_C$ (100 MHz) [145.1, 144.8, 143.9, 143.8, 139.0, 138.7, 136.0 and 135.9 (*ipso* Ph, *ipso* Ts, *para* Ts and C-2 of both diastereoisomers)], [133.4, 133.1, 127.1 and 127.0 (*para* Ph, and CH-6 of both diastereoisomers)], [131.3, 131.2, 130.1, 129.9, 128.8, 127.9 and 127.8 (*ortho* Ph, *meta* Ph, *ortho* Ts and *meta* Ts)], [118.9, 118.9, 113.9 and 113.7 ($CH_2$-1 and $CH_2$-7 of both diastereoisomers)], [75.4 and 74.8 (C-4 of both diastereoisomers)], [54.1 and

53.4 (CHPh of both diastereoisomers)], [37.6, 36.8, 33.4, 32.8, 31.9, 31.8, 30.3, 30.2, 29.5, 29.4, 29.3, 29.3, 29.2, 23.9 and 22.7 ($CH_2$-5 and TsC($CH_2$)$_8$Me of both diastereoisomers)], [25.4, 25.1 and 21.5 ($CH_3$-2 and $CH_3$ Ts of both diastereoisomers)], 14.1 ($CH_2CH_3$ of both diastereoisomers); *m/z* (CI) 484 $[M+NH_4]^+$, 358, 301, 264, 218, 200, 188, 148 (Found: $[M+NH_4]^+$, 484.3258. $C_{30}H_{42}O_2S$ requires $[M+H]^+$, 484.3249).

**4-Benzyl-2-methyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene (6c)**



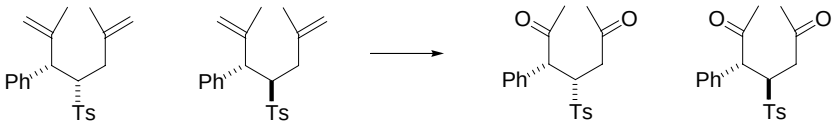

**4b** **6c**

S

To a solution of a 1:1 diastereoisomeric mixture of 2-methyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene **4b** (732 mg, 2.15 mmol, 1 equiv.) in THF (10 mL) at 0 °C and under nitrogen was added dropwise a commercial solution of *n*-BuLi in hexane (Aldrich, titrated to be 1.50 M, 1.750 mL, 2.625 mmol, 1.2 equiv.). The solution turned bright orange and benzyl bromide (310 μL, 2.61 mmol, 1.2 equiv.) was immediately added. The reaction was allowed to warm to rt and after 42 h of stirring at rt and 2 h of stirring at 40 °C the excess *n*-BuLi was quenched with MeOH (2 mL). Concentration under reduced pressure and chromatography (3%→4% AcOEt–petrol) gave *4-benzyl-2-methyl-3-phenyl-4-(*p-*toluenesulfonyl)-1,6-heptadiene* **6c** as a 2:3 mixture of diastereoisomers (523 mg, 56%) as a colourless gum and the diene starting material **4b** (28 mg, 4%) as a colourless solid; $R_f$ 0.59 (10% AcOEt–petrol); $\nu_{max}$ (film) 3062, 3030, 2925, 2853, 1670, 1638, 1597, 1494, 1453, 1374, 1286, 1185, 1134, 1076, 918, 815, 758, 738, 703, 650 $cm^{-1}$; $\delta_H$ (400 MHz) 7.61-7.59 (4H, m, *ortho* Ts of both diastereoisomers), 7.41-6.99 (24H, m, 2 x Ph and *meta* Ts of both diastereoisomers), 6.26-6.13 (2H, m, CH-6 of both diastereoisomers), 5.30-4.98 (8H, m, $CH_2$-1 and $CH_2$-7 of both diastereoisomers), 4.45 (1H, s, CH-3 of the major diastereoisomer), 4.05 (1H, s, CH-3 of the minor diastereoisomer), [3.69 (2H, s), 3.65 (1H, d, *J* 15.5 Hz) and 3.45 (1H, d, *J* 15.5 Hz), $PhCH_2$ of both diastereoisomers], [3.07 (1H, dd, *J* 16.5, 8.0 Hz) and 2.65-2.59 (1H, m), $CH_2$-5 of the major diastereoisomer], [2.91 (1H, dd, *J* 16.5, 7.5 Hz) and 2.52-2.46 (1H, m), $CH_2$-5 of the minor diastereoisomer], 2.32 (3H, s, $CH_3$ Ts of the minor diastereoisomer), 2.31 (3H, s, $CH_3$ Ts of the major diastereoisomer), 1.67 (3H, s, $CH_3$-2 of the major diastereoisomer), 1.55 (3H, s, $CH_3$-2 of the minor diastereoisomer); $\delta_C$ (100 MHz) [145.2, 144.9, 143.5, 143.4, 138.5, 138.0, 136.1, 135.9 and 135.6 (2 x *ipso* Ph, *ipso* Ts, *para* Ts

and C-2 of both diastereoisomers)], [132.8 and 132.5 (CH-6 of both diastereoisomers)], [131.8, 131.8, 131.5, 131.4, 130.0, 130.0, 128.5, 128.5, 127.9, 127.9, 127.7 and 127.6 (2 x *ortho* Ph, 2 x *meta* Ph, *ortho* Ts and *meta* Ts of both diastereoisomers)], [127.1, 127.1, 126.8 and 126.6 (2 x *para* Ph of both diastereoisomers)], [119.3, 119.1, 114.1 and 113.1 ($CH_2$-1 and $CH_2$-7 of both diastereoisomers)], [76.4 and 76.0 (C-4 of both diastereoisomers)], [54.1 and 53.1 (CHPh of both diastereoisomers)], [38.6, 38.4 and 38.1 ($CH_2$-5 and $CH_2$Ph of both diastereoisomers)], [26.0, 25.7 and 21.3 ($CH_3$-2 and $CH_3$ Ts of both diastereoisomers)]; *m/z* (CI) 448 $[M+NH_4]^+$, 431 $[M+H]^+$, 299, 275, 174, 52 (Found: $[M+H]^+$, 431.2044. $C_{28}H_{30}O_2S$ requires $[M+H]^+$, 431.2045).

**3-Phenyl-4-(*p*-toluenesulfonyl)heptane-2,6-dione**




**4c**

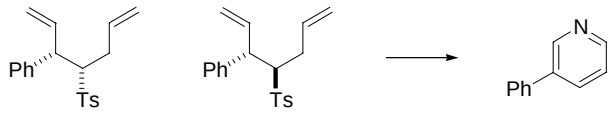
Ozone was bubbled through a solution of a 1:1 diastereoisomeric mixture of 2,6-dimethyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene **4c** (179 mg, 0.504 mmol, 1 equiv.) in MeOH:$CH_2Cl_2$ (1:5, 6 mL) at -78 °C for 10 min, until a blue colour persisted. After 5 min of bubbling $O_2$ through the reaction mixture, $PPh_3$ (414 mg, 1,58 mmol, 3.1 equiv.) was added. After stirring for 3 h at -78 °C the mixture was concentrated under reduced pressure and chromatography (20% AcOEt–petrol) gave *3-phenyl-4-(*p-*toluenesulfonyl)heptane-2,6-dione* as a 1:1 mixture of diastereoisomers (130 mg, 72%), the less polar as a colourless solid, the more polar as a colourless gum.

*Less polar diastereoisomer of 3-phenyl-4-(*p-*toluenesulfonyl)heptane-2,6-dione*; mp 144-146 °C with decomposition (20% AcOEt–petrol); $R_f$ 0.23 (20% AcOEt–petrol); $\nu_{max}$ (film) 1718, 1644, 1419, 1358, 1276, 1210, 1085 $cm^{-1}$; $\delta_H$ (270 MHz) 7.73 (2H, d, *J* 8.5 Hz, *ortho* Ts), 7.36-7.11 (7H, m, *meta* Ts and Ph), 5.08-4.99 (1H, m, CHTs), 4.36 (1H, d, *J* 11.0 Hz, CHPh), [2.82 (1H, dd, *J* 18.0, 7.0 Hz), 2.25 (1H, dd, *J* 18.0, 4.5 Hz), $CH_2$-5], 2.44 (3H, s, $CH_3$ Ts), [2.18 (3H, s) and 1.73 (3H, s), $CH_3$-1 and $CH_3$-7]; $\delta_C$ (67.5 MHz) [204.4 and 203.9 (2 x C=O)], [144.9, 136.5 and 133.9 (*ipso* Ph, *ipso* Ts and *para* Ts)], [129.8, 129.7, 129.4 and 128.5 (*ortho* Ph, *meta* Ph, *ortho* Ts and *meta* Ts)], 128.6 (*para* Ph), 61.6 (CHTs), 57.1 (CHPh), 40.8 ($CH_2$-5), [29.9, 29.5 and

21.8 ($CH_3$-1, $CH_3$-7 and $CH_3$ Ts)]; *m/z* (CI) 376 $[M+NH_4]^+$, 220 $[M+NH_4\text{-Ts}]^+$, 203, 174 (Found: $[M+NH_4]^+$, 376.1571. $C_{20}H_{22}O_4S$ requires $[M+NH_4]^+$, 376.1583).

*More polar diastereoisomer of 3-phenyl-4-(*p-*toluenesulfonyl)heptane-2,6-dione*; $R_f$ 0.12 (20% AcOEt–petrol); $\nu_{max}$ (film) 1717, 1644, 1419, 1358, 1276, 1210, 1085 $cm^{-1}$; $\delta_H$ (270 MHz) 7.33-7.05 (9H, m, *ortho* Ts, *meta* Ts and Ph), 4.65-4.58 (1H, m, CHTs), 4.37 (1H, d, *J* 9.0 Hz, CHPh), [3.36 (1H, dd, *J* 18.0, 8.5 Hz), 2.71 (1H, dd, *J* 18.0, 2.5 Hz), $CH_2$-5], 2.34 (3H, s, $CH_3$ Ts), [2.18 (3H, s) and 2.08 (3H, s), $CH_3$-1 and $CH_3$-7]; $\delta_C$ (100 MHz) [205.3 and 203.9 (2 x C=O)], [143.9, 136.7 and 133.7 (*ipso* Ph, *ipso* Ts and *para* Ts)], [129.4, 128.9, 128.1 and 127.9 (*ortho* Ph, *meta* Ph, *para* Ph, *ortho* Ts and *meta* Ts)], 63.1 (CHTs), 57.3 (CHPh), 39.8 ($CH_2$-5), [30.1, 30.0 and 21.6 ($CH_3$-1, $CH_3$-7 and $CH_3$ Ts)]; *m/z* (CI) 376 $[M+NH_4]^+$, 220 $[M+NH_4\text{-Ts}]^+$, 203, 174 (Found: $[M+NH_4]^+$, 376.1578. $C_{20}H_{22}O_4S$ requires $[M+NH_4]^+$, 376.1583).

**3-Phenylpyridine (7a)**[2]

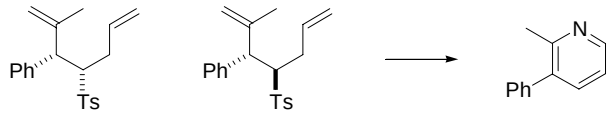



**4a** **7a**

According to the general procedure, a 1:1 diastereoisomeric mixture of 3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene **4a** (344 mg, 1.05 mmol, 1 equiv.) in MeOH:$CH_2Cl_2$ (7.5 mL) was ozonolysed and reduced with polymer bound $PPh_3$ (Fluka, 3 mmol/g resin, 1.1 g, 3.3 mmol, 3.1 equiv.). The crude dialdehyde in MeOH (4 mL) was then reacted with $NH_4HCO_3$ (655 mg, 8.29 mmol, 7.9 equiv.). Chromatography on basic alumina (BDH, 63-200 μm, 3%→5% AcOEt–petrol) gave *3-phenylpyridine* **7a** (86 mg, 53%) as a colourless oil; $R_f$ 0.25 (20% AcOEt–petrol); $\nu_{max}$ (film) 3058, 3031, 2923, 1652, 1582, 1473, 1451, 1408, 1276, 1025, 1006, 814, 755, 711, 698 $cm^{-1}$; $\delta_H$ (270 MHz) 8.84 (1H, d, *J* 2.0 Hz, CH-2), 8.58 (1H, dd, *J* 5.0, 2.0 Hz, CH-6), 7.86 (1H, dt, *J* 8.0, 2.0 Hz, CH-4), 7.59-7.25 (6H, m, CH-5 and Ph); $\delta_C$ (100 MHz) [148.2 and 148.1 (CH-2 and CH-6)], [137.7 and 136.8 (*ipso* Ph and C-3)], 134.6 (CH-4), [129.1 and 127.1 (*ortho* Ph and *meta* Ph)], 128.2 (*para* Ph), 123.6 (CH-5); *m/z* (CI) 156 $[M+H]^+$ (Found: $[M+H]^+$, 156.0815. $C_{11}H_9N$ requires $[M+H]^+$, 156.0813) (Found: C, 84.99; H, 5.90; N, 8.97. $C_{11}H_9N$ requires C, 85.13; H, 5.85, N, 9.03). Data in agreement with those previously reported.

[2] Pouchert, C. J.; Behnke, J. *The Aldrich Library of $^{13}C$ and $^{1}H$ FT-NMR Spectra*; 1st edition, Vol. 3, Aldrich **1993**, p 243.

**2-Methyl-3-phenylpyridine (7b)**[3]

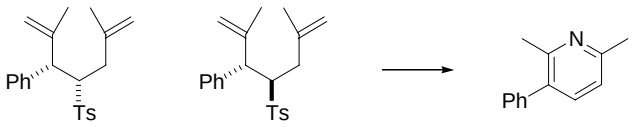



**4b** **7b**

According to the general procedure, a 1:1 diastereoisomeric mixture of 2-methyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene **4b** (520 mg, 1.59 mmol, 1 equiv.) in MeOH:$CH_2Cl_2$ (10.5 mL) was ozonolysed and reduced with polymer bound $PPh_3$ (Fluka, 3 mmol/g resin, 1.6 g, 4.7 mmol, 3 equiv.). The crude ketoaldehyde in MeOH (4 mL) was then reacted with $NH_4HCO_3$ (964 mg, 12.2 mmol, 7.7 equiv.).Work-up gave *2-methyl-3-phenylpyridine* **7b** (230 mg, 86%) as a red oil. Chromatography (10% AcOEt–petrol) gave *2-methyl-3-phenylpyridine* **7b** (180 mg, 67%) as a colourless oil; $R_f$ 0.23 (20% AcOEt–petrol); $\nu_{max}$ (film) 3083, 2925, 1657, 1428, 1377, 763, 737, 703 $cm^{-1}$; $\delta_H$ (270 MHz) 8.49 (1H, dd, *J* 5.0, 1.5 Hz, CH-6), 7.49-7.15 (7H, m, CH-4, CH-5 and Ph), 2.50 (3H, s, $CH_3$); $\delta_C$ (67.5 MHz) 155.9 (C-2), 148.0 (CH-6), [140.0 and 137.0 (C-3 and *ipso* Ph)], 137.2 (CH-4), [129.1 and 128.5 (*ortho* Ph and *meta* Ph)], 127.5 (*para* Ph), 121.1 (CH-5), 23.5 ($CH_3$); *m/z* (CI) 170 $[M+H]^+$ (Found: $[M+H]^+$, 170.0965. $C_{12}H_{11}N$ requires $[M+H]^+$, 170.0970) (Found: C, 85.08; H, 6.49; N, 8.14. $C_{12}H_{11}N$ requires C, 85.17; H, 6.55; N, 8.28). Data in agreement with those previously reported.

[3] Padwa, A.; Carlsen, P. H. J. *J. Org. Chem.* **1978**, *43*, 2029–2037.

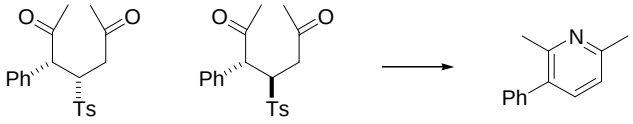
**2,6-Dimethyl-3-phenylpyridine (7c)**[4]




**4c** **7c**

**Procedure A**

According to the general procedure, a 1:1 diastereoisomeric mixture of 2,6-dimethyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene **4c** (220 mg, 0.619 mmol, 1 equiv.) in MeOH:$CH_2Cl_2$ (6 mL) was ozonolysed and reduced with $PPh_3$ (528 mg, 2.01 mmol, 3.3 equiv.). The crude diketone in MeOH (2 mL) was then reacted with $NH_4HCO_3$ (399 mg, 5.05 mmol, 8.2 equiv.). Chromatography (5%→10% AcOEt–petrol) gave *2,6-dimethyl-3-phenylpyridine* **7c** (83 mg, 73%) as a yellow oil.




**4c**

**Procedure B**

To a solution of 3-phenyl-4-(*p*-toluenesulfonyl)heptane-2,6-dione (71 mg, 0.198 mmol, 1 equiv.) in $CH_2Cl_2$:MeOH (1:2; 4.5 mL) at rt was added $NH_4HCO_3$ (153 mg, 1.94 mmol, 9.8 equiv.) and the mixture was exposed to microwave irradiation for 10 min at 100 °C. The yellow solution was concentrated under reduced pressure. The red residue was dissolved in $CH_2Cl_2$ (30 mL) and then washed with $H_2O$ (2 x 30 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give *2,6-dimethyl-3-phenylpyridine* **7c** (36 mg, 98%) as a yellow oil.

**Procedure C**

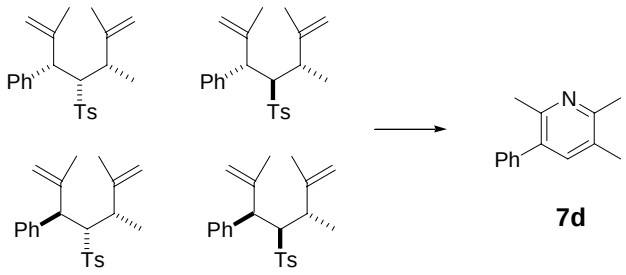
A solution of 3-phenyl-4-(*p*-toluenesulfonyl)heptane-2,6-dione (67 mg, 0.187 mmol, 1 equiv.) in $CH_2Cl_2$:MeOH (5:1; 3 mL) at rt and under nitrogen was treated with a methanolic solution of ammonia (2 M, 1 mL) for 15 h. The orange solution was concentrated under reduced pressure. The orange residue was dissolved in $CH_2Cl_2$ (25 mL), washed with $H_2O$ (2 x 25 mL), dried

[4] Balaban A. T.; Nenitzescu C. D. *J. Chem .Soc* **1961**, 3566–3572.

($MsSO_4$) and concentrated under reduced pressure to give *2,6-dimethyl-3-phenyl pyridine* **7c** (34 mg, 98%) as a yellow oil.

*2,6-Dimethyl-3-phenylpyridine,* $R_f$ 0.26 (10% AcOEt–petrol); $\nu_{max}$ (film) 2923, 1644, 1461, 1434, 1388, 1262, 1010, 766, 701 $cm^{-1}$; $\delta_H$ (270 MHz) 7.41-7.26 (6H, m, CH-4 and Ph), 7.00 (1H, d, *J* 7.5 Hz, CH-5), [2.55 (3H, s) and 2.46 (3H,s), $CH_3$-2 and $CH_3$-6]; $\delta_C$ (67.5 MHz) [156.5 and 155.0 (C-2 and C-6)], [140.2 and 134.0 (C-3 and *ipso* Ph)], 137.6 (CH-4), [129.2 and 128.4 (*ortho* Ph and *meta* Ph)], 127.3 (*para* Ph), 120.6 (CH-5), [24.3 and 23.4 ($CH_3$-2 and $CH_3$-6)]; *m/z* (CI) 184 $[M+H]^+$ (Found: $[M+H]^+$, 184.1118. $C_{13}H_{13}N$ requires $[M+H]^+$, 184.1126) (Found: C, 85.11; H, 7.03; N, 7.54. $C_{13}H_{13}N$ requires C, 85.21; H, 7.15; N, 7.64). Data in agreement with those previously reported.

**2,5,6-Trimethyl-3-phenylpyridine (7d)**

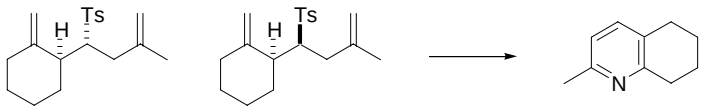



**4d** **7d**

According to the general procedure, a diastereoisomeric mixture of 2,5,6-trimethyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene **4d** (78 mg, 0.211 mmol, 1 equiv.) in MeOH:$CH_2Cl_2$ (2 mL) was ozonolysed and reduced with dimethyl sulfide (0.9 mL, 21 mmol, 99 equiv.). The crude diketone in MeOH (1 mL) was then reacted with $NH_4HCO_3$ (133 mg, 1.68 mmol, 8 equiv.). Chromatography (10% AcOEt–petrol) gave *2,5,6-trimethyl-3-phenylpyridine* **7d** (21 mg, 51%) as a pale yellow oil; $R_f$ 0.17 (10% AcOEt–petrol); $\nu_{max}$ (film) 2922, 2856, 1605, 1554, 1460, 1429, 1367, 1203, 1142, 1074, 1018, 1001, 958, 906, 762, 702 $cm^{-1}$; $\delta_H$ (270 MHz) 7.44-7.25 (6H, m, CH-4 and Ph), [2.52 (3H, s) and 2.45 (3H,s), $CH_3$-2 and $CH_3$-6], 2.27 (3H, s, $CH_3$-5); $\delta_C$ (67.5 MHz) [155.1 and 151.9 (C-2 and C-6)], [140.0, 134.6 and 128.7 (C-3, C-5 and *ipso* Ph)], 139.0 (CH-4), [129.2 and 128.4 (*ortho* Ph and *meta* Ph)], 127.3 (*para* Ph), [22.6, 22.1 and 18.7 ($CH_3$-2, $CH_3$-5 and $CH_3$-6)]; *m/z* (CI) 198 $[M+H]^+$, (Found: $[M+H]^+$, 198.1282. $C_{14}H_{15}N$ requires

$[M+H]^+$, 198.1283) (Found: C, 85.33; H, 7.59; N, 6.99. $C_{13}H_{13}N$ requires C, 85.24; H, 7.66; N, 7.10).

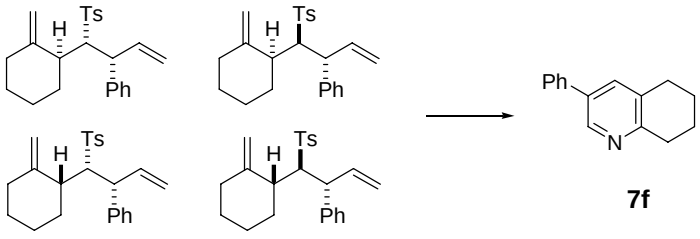
**2-Methyl-5,6,7,8-tetrahydroquinoline (7e)**[5]




**4e** **7e**

According to the general procedure, a 1:1 diastereoisomeric mixture of 1-methyl-4-[(*R*)-3-methyl-1-(2-methylenecyclohexyl)but-3-enylsulfonyl]benzene **4e** (187 mg, 0.587 mmol, 1 equiv.) in MeOH:$CH_2Cl_2$ (6 mL) was ozonolysed and reduced with triphenylphosphine (478 mg, 1.82 mmol, 3 equiv.). The crude diketone in MeOH (3 mL) was then reacted with $NH_4HCO_3$ (385 mg, 4.87 mmol, 8.3 equiv.). Chromatography (40%→60% AcOEt–hexane) gave *2-methyl-5,6,7,8-tetrahydroquinoline* **7e** (32 mg, 37%) as a colourless oil; $R_f$ 0.30 (50% AcOEt–hexane); $\nu_{max}$ (film) 2931, 2859, 1597, 1573, 1470, 1454, 1261, 1092, 1021, 805 $cm^{-1}$; $\delta_H$ (400 MHz) 7.23 (1H, d, *J* 7.5 Hz, CH-4), 6.88 (1H, d, *J* 7.5 Hz, CH-3), 2.89-2.85 (2H, m, $CH_2$-8), 2.73-2.70 (2H, m, $CH_2$-5), 2.48 (3H, s, $CH_3$), 1.91-1.76 (4H, m, $CH_2$-6 and $CH_2$-7); $\delta_C$ (100 MHz) [156.4 and 155.0 (C-2 and C-8a)], 137.1 (CH-4), 128.9 (C-4a), 120.4 (CH-3), [32.5, 28.4, 23.2 and 22.8 ($CH_2$-5, $CH_2$-6, $CH_2$-7 and $CH_2$-8)], 24.1 ($CH_3$); *m/z* (CI) 148 $[M+H]^+$, (Found: $[M+H]^+$, 148.1127. $C_{10}H_{13}N$ requires $[M+H]^+$, 148.1126). Data in agreement with those previously reported.

**3-Phenyl-5,6,7,8-tetrahydroquinoline (7f)**[6]



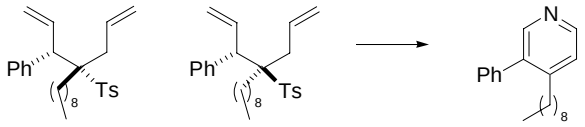

**4f** **7f**

According to the general procedure, a diastereoisomeric mixture of 1-methyl-4-[1-(2-methylenecyclohexyl)-2-phenylbut-3-enylsulfonyl]benzene **4f** (205 mg, 0.539 mmol, 1 equiv.) in MeOH:$CH_2Cl_2$ (5.5 mL) was ozonolysed and reduced with dimethylsulfide (2.4 mL, 55 mmol,

[5] Bell, T. W .; Khasanov, A. B.; Drew, M.G.B. *J. Am. Chem. Soc.* **2002**, *124*, 14092–14103.
[6] Winter, A.; Risch, N. *Synthesis* **2003**, *17*, 2667–2670.

103 equiv.). The crude ketoaldehyde in MeOH (3 mL) was then reacted with $NH_4HCO_3$ (401 mg, 5.07 mmol, 9.4 equiv.). Chromatography (20% AcOEt–petrol) gave *3-phenyl-5,6,7,8-tetrahydroquinoline* **7f** (72 mg, 63%) as a pale yellow oil; $R_f$ 0.30 (20% AcOEt–hexane); $\nu_{max}$ (film) 3060, 3030, 2934, 2860, 1604, 1582, 1558, 1460, 1427, 1394, 1352, 1249, 1150, 1076, 1028, 989, 928, 911, 823, 763, 698 $cm^{-1}$; $\delta_H$ (400 MHz) 8.58 (1H, d, *J* 1.5 Hz, CH-2), [7.57-7.55 (3H, m) and 7.47 (2H, m), CH-4, *ortho* Ph and *meta* Ph], 7.37 (1H, tt, *J* 7.0, 2.0 Hz, *para* Ph), 2.97 (2H, t, *J* 6.5 Hz, $CH_2$-8), 2.84 (2H, t, *J* 6.5 Hz, $CH_2$-5), [1.97-1.91 (2H, m) and 1.88-1.82 (2H, m), $CH_2$-6 and $CH_2$-7); $\delta_C$ (100 MHz) 156.3 (C-8a), 145.2 (CH-2), [138.1, 133.9 and 132.1 (C-3, C-4a and *ipso* Ph)], 135.1 (CH-4), [128.9 and 127.0 (*ortho* Ph and *meta* Ph)], 127.6 (*para* Ph), [32.2, 28.9, 23.1 and 22.7 ($CH_2$-5, $CH_2$-6, $CH_2$-7 and $CH_2$-8)]; *m/z* (CI) 210 $[M+H]^+$, 52 (Found: $[M+H]^+$, 210.1287. $C_{15}H_{15}N$ requires $[M+H]^+$, 210.1283) (Found: C, 85.97; H, 7.19; N, 6.67. $C_{13}H_{13}N$ requires C, 86.08; H, 7.22; N, 6.69). Data in agreement with those previously reported.

**4-Nonyl-3-phenylpyridine (7g)**

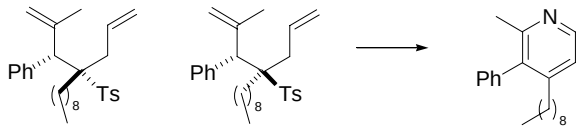



**6a** **7g**

According to the general procedure, a 35:65 diastereoisomeric mixture of *4-nonyl-3-phenyl-4-*(*p*-toluenesulfonyl)-*1,6-heptadiene* **6a** (320 mg, 0.706 mmol, 1 equiv.) in MeOH:$CH_2Cl_2$ (8.2 mL) was ozonolysed and reduced with dimethyl sulfide (3.1 mL, 71 mmol, 101 equiv.). The crude dialdehyde in MeOH (3.5 mL) was then reacted with $NH_4HCO_3$ (443 mg, 5.60 mmol, 7.9 equiv.). Work-up gave *4-nonyl-3-phenylpyridine* **7g** (196 mg, 98%) as a red oil. Chromatography on basic alumina (BDH, 63-200 μm, 4% AcOEt–petrol) gave *4-nonyl-3-phenylpyridine* **7g** (147 mg, 74%) as a red oil; $R_f$ 0.19 (10% AcOEt–petrol); $\nu_{max}$ (film) 2954, 2854, 1638, 1465, 1377, 1007, 830, 763, 702 $cm^{-1}$; $\delta_H$ (270 MHz) 8.47 (1H, d, *J* 5.0 Hz, CH-6), 8.40 (1H, s, CH-2), 7.48-7.20 (6H, m, CH-5 and Ph), 2.60-2.54 (2H, m, $CCH_2(CH_2)_7Me$), [1.46-1.40 (2H, m) and 1.23-1.16 (12H, m), $CCH_2(CH_2)_7Me$], 0.85 (3H, t, *J* 6.5 Hz, $CH_3$); $\delta_C$ (100 MHz) 150.0 (C-4), [149.5 and 147.7 (CH-2 and CH-6)], 137.7 (C-3 and C Ph), [129.3 and 128.4 (*ortho* Ph and *meta* Ph)], [127.7 and 124.1 (*para* Ph and CH-5)], [32.4, 31.8, 30.2, 29.3, 29.2, 29.2 and 29.2 ($C(CH_2)_7CH_2Me$)], 22.6 ($C(CH_2)_7CH_2Me$), 14.1 ($CH_3$); *m/z* (CI) 563 $[2M+H]^+$, 282 $[M+H]^+$,

156 $[M+H\text{-nonyl}]^+$ (Found: $[M+H]^+$, 282.2214. $C_{20}H_{27}N$ requires $[M+H]^+$, 282.2222) (Found: C, 85.28; H, 9.57; N, 4.89. $C_{20}H_{27}N$ requires C, 85.35; H, 9.67; N, 4.98%).

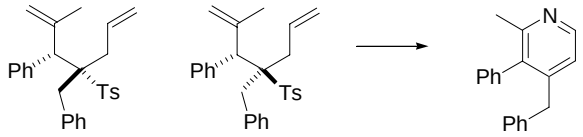
**2-Methyl-4-nonyl-3-phenylpyridine (7h)**




**6b** **7h**

According to the general procedure, a 45:55 diastereoisomeric mixture of 2,6-dimethyl-4-nonyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene **6b** (89 mg, 0.19 mmol, 1 equiv.) in MeOH:$CH_2Cl_2$ (2 mL) was ozonolysed and reduced with dimethylsulfide (830 μL, 19.2 mmol, 100 equiv.). The crude ketoaldehyde in MeOH (1.5 mL) was then reacted with $NH_4HCO_3$ (120 mg, 4.87 mmol, 7.9 equiv.). Work-up gave *2-methyl-4-nonyl-3-phenylpyridine* **7h** (56 mg, 99%) as an orange oil. Chromatography (10% AcOEt–petrol) gave *2-methyl-4-nonyl-3-phenylpyridine* **7h** (41 mg, 73%) as a pale yellow oil; $R_f$ 0.27 (10% AcOEt–petrol); $\nu_{max}$ (film) 2954, 2923, 2855, 1683, 1660, 1649, 1633, 1465, 1409, 1151, 1091, 1068, 1061, 761 $cm^{-1}$; $\delta_H$ (400 MHz) 8.37 (1H, d, *J* 5.0 Hz, CH-6), [7.46-7.38 (3H, m) and 7.15-7.14 (2H, m), Ph], 7.06 (1H, d, *J* 5.0 Hz, CH-5), 2.33-2.29 (2H, m, $CH_2(CH_2)_7Me$), 2.26 (3H, s, $CH_3$-2), [1.42-1.39 (2H, m) and 1.25-1.13 (12H, m), $CH_2(CH_2)_7Me$], 0.87 (3H, t, *J* 7.0 Hz, $TsCCH_2(CH_2)_7CH_3$); $\delta_C$ (100 MHz) 156.2 (C-2), 149.9 (C-4), 147.4 (CH-6), [138.5 and 136.6 (C-3 and *ipso* Ph)], [129.1 and 128.5 (*ortho* Ph and *meta* Ph)], [127.2 and 121.5 (*para* Ph and CH-5)], [32.9, 31.8, 30.1, 29.3, 29.2, 29.2 and 29.1 ($(CH_2)_7CH_2Me$)], 23.7 ($CH_3$-2), 22.6 ($(CH_2)_7CH_2Me$), 14.1 ($(CH_2)_8CH_3$); *m/z* (CI) 591 $[2M+H]^+$, 296 $[M+H]^+$, 282 (Found: $[M+H]^+$, 296.2369. $C_{21}H_{29}N$ requires $[M+H]^+$, 296.2378) (Found: C, 85.28; H, 9.87; N, 4.89. $C_{20}H_{27}N$ requires C, 85.37; H, 9.89; N, 4.74%).

**4-Benzyl-2-methyl-3-phenylpyridine (7i)**




**6b'** **7i**

According to the general procedure, a 43:57 diastereoisomeric mixture of 4-benzyl-2-methyl-3-phenyl-4-(*p*-toluenesulfonyl)-1,6-heptadiene **6c** (92 mg, 0.21 mmol, 1 equiv.) in MeOH:$CH_2Cl_2$ (2.5 mL) was ozonolysed and reduced with dimethyl sulfide (950 μL, 21.9 mmol, 103 equiv.). The crude ketoaldehyde in MeOH (2 mL) was then reacted with $NH_4HCO_3$ (139 mg, 1.76 mmol, 8.3 equiv.). Chromatography (20% AcOEt–petrol) gave *4-benzyl-2-methyl-3-phenylpyridine* **7i** (42 mg, 75%) as a pale yellow oil; $R_f$ 0.31 (20% AcOEt–petrol); $\nu_{max}$ (film) 3028, 2923, 2851, 1602, 1579, 1561, 1495, 1453, 1444, 1407, 1243, 1156, 1074, 1030, 1009, 915, 848, 812, 763, 701, 633 $cm^{-1}$; $\delta_H$ (400 MHz) 8.39 (1H, d, *J* 5.0 Hz, CH-6), [7.43-7.34 (3H, m), 7.22-7.14 (3H, m), 7.10-7.09 (2H, m) and 6.92-6.90 (2H, m), 2 x Ph], 6.96 (1H, d, *J* 5.0 Hz, CH-5), 3.69 (2H, s, $CH_2$), 2.28 (3H, s, $CH_3$); $\delta_C$ (100 MHz) 156.6 (C-2), 148.0 (C-4), 147.8 (CH-6), [139.4, 138.3 and 136.8 (C-3 and 2 x *ipso* Ph)], [129.2, 129.0, 128.7 and 128.4 (2 x *ortho* Ph and 2 x *meta* Ph)], [127.4 and 126.3 (2 x *para* Ph)], 122.3 (CH-5), 39.1 ($CH_2$), 23.8 ($CH_3$); *m/z* (CI) 260 $[M+H]^+$ (Found: $[M+H]^+$, 260.1445. $C_{19}H_{17}N$ requires $[M+H]^+$, 260.1439) (Found: C, 88.12; H, 6.70; N, 5.33. $C_{19}H_{17}N$ requires C, 87.99; H, 6.61; N, 5.40%).