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# Solventless Wittig olefination with fluorinated benzaldehydes

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Fluorinated benzaldehydes undergo solventless Wittig olefination with stabilised phosphoranes. Even with less reactive, stabilised phosphoranes, such as acetylmethylidenetriphenylphosphorane, the reactions have been found to be exothermic.

**Keywords:** solventless reaction, stabilised phosphoranes, fluorobenzaldehydes

The reduction of solvents used in organic transformations is an intriguing and timely challenge. Such a reduction not only has environmental benefits, but can also lead to simplified and time-saving handling and work-up of the reactions. Within this context, solventless reactions are of special interest and a number of procedures for solventless organic reactions have already been developed.[1] In the following, the solventless Wittig olefination is discussed for the very reactive fluorinated benzaldehydes, which were found to react exothermically with a range of stabilised phosphoranes.

Wittig olefination is an organic transformation for which solvent-reduced or even solventless procedures have been developed.[2-6] In traditional procedures, Wittig reactions are run in benzene, toluene, chloroform, dichloromethane, DME or THF, when stabilised phosphoranes are used.[7] Due to the low reactivity of some of the phosphoranes, an acid catalyst such as benzoic acid is often added.[8] Solvent-reduced Wittig reactions can be run in chloroform[6] or similar solvents with a variety of stabilised and semi-stabilised phosphoranes. The solventless Wittig reactions reported thus far are limited to a restricted number of phosphoranes, such as the alkoxycarbonylmethylidenetriphenylphosphoranes **2b** and **2c**, when classical heating is used.[2] Microwave heating allows the use of an expanded range of stabilised phosphoranes.[2-5]

Previously, the author has noted that simple mixing of substituted benzaldehydes and ester substituted phosphoranes, such as **2b** and **2c**, results in exothermic reactions.[2] Further heating of the mixtures at 100ºC leads to total transformation of the educts.[2] For the benzaldehydes studied previously a similarly exothermic reaction of the benzaldehydes with other stabilised phosphoranes was not noted, and for these cases a minimal amount of solvent is always needed when classical heating is used.[2,6]

When aldehydes and phosphoranes are reacted under solventless conditions, an initial intimate mixing of the two educts is necessary for the reaction to start. In the case of an exothermic reaction gradual melting of the constituents will then lead to further progression of the transformation until near completion. This initial mixing of the starting materials necessitates that the aldehyde component is a liquid or that it has a low melting point as the phosphoranes themselves are higher-melting solids. This prerequisite is satisfied by many benzaldehydes. However, many of the reactive, electron poor benzaldehydes, such as the nitrobenzaldehydes, have relatively high melting points. One notable exception are the electron poor, fluoro-substituted benzaldehydes, which are liquids or solids with low melting points. The Wittig olefination of such fluorinated benzaldehydes with stabilised phosphoranes **2** gives interesting olefins that have been used themselves, as intermediates in bioactive materials, or screened as inhibitors of angiogenesis,[9] of the farnesyl protein transferase[10] and of β-amyloid protein production.[11]

First experiments with the usually poorly reactive acetylmethylidenetriphenylphosphorane **2a** showed that upon addition of pure fluorinated benzaldehyde **1k** to solid **2a** an immediate warming of the mixture resulted in the dissolution of the phosphorane in the benzaldehyde with concurrent intimate mixing of the constituents. While the reaction temperature intermittently rose to 70ºC and most of the benzaldehyde was consumed in the process, the melt was heated further externally to 100°C for 40–45 min to achieve a complete transformation of the benzaldehyde. Most of the reactions of the fluorinated benzaldehydes **1** with phosphorane **2a** are found to be exothermic, with **1d** and **1m** providing the least exothermic reactions within the series of fluorinated benzaldehydes studied (Scheme 1). Nevertheless, all fluorinated benzaldehydes that were reacted, were consumed when the corresponding mixtures were heated at 100ºC for 45 min. While the reactions of benzaldehydes with **2a** usually are *E*-/*Z*-selective, appreciable amounts of *Z*-isomer (***Z*-3**) could be found in some cases, especially in the reactions with benzaldehydes **1e** and **1g**–**1i**.

Fluorinated benzaldehydes **1** also reacted exothermically with phosphoranes **2b** and **2c**. This characteristic is shared with other benzaldehydes that also have been found to react exothermically with alkoxycarbonylmethylidenephosporanes.[2] As is typical for other benzaldehydes,[2] the reaction of fluorinated **1** with **2b** and **2c** form mixtures of *E*- and *Z*-olefins (Scheme 2). Interestingly, however, for 2,6-difluoro-substituted benzaldehydes, such as for 2,6-difluorobenzaldehyde (**1j**) and pentafluorobenzaldehyde (**1k**), the corresponding *E*-olefin is obtained almost exclusively.

Also, halomethylidenetriphenylphosphoranes can be used in solventless Wittig olefination reactions with fluorinated benzaldehydes, as is exemplified in the reaction of **2d** with **1e** and **1f** to give **5a** and **5b**, respectively. When **1a** and **1i** are reacted with **2e**, cinnamaldehydes **6** are formed mostly, although **6** can also undergo a Wittig olefination to the dienals **7**. When Wittig olefinations are carried out with non-fluorinated benzaldehydes in a minimal amount of chloroform as solvent, phenylpentadienals and even phenylheptatrienals can be found as very significant by-products. Due to the much higher reactivity of the fluorinated benzaldehydes compared with the cinnamaldehydes **6**, the Wittig reaction of fluorobenzaldehydes with **2e** can be controlled better to produce the desired products **6** selectively (Scheme 3), even under solventless conditions. However, the use of a larger excess of phosphorane **2e** and longer reaction times favours the dienals **7**, together with their homologues as by-products.

Fluorinated benzaldehydes **1** react with benzoylmethylidenetriphenylphosphoranes **2f** and **2g**, where the reactions between **1j**/**1k** and **2f** were found to be exothermic (Scheme 3). The reactions show good *E*-selectivity.

Reactions of **1e**/**1j** with cyanomethylidenetriphenylphosphorane **2h** were also found to be exothermic. Here, however, appreciable amounts of separable *Z*-isomeric olefins ***Z*-10a** and ***Z*-10b** were formed. This is in contrast to most other reactions of 2,6-difluoro substituted benzaldehydes such as **1a**, **1j** and **1k** with stabilised phosphoranes, where only

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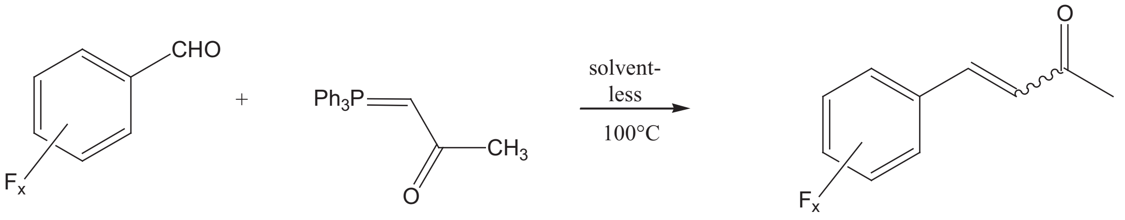
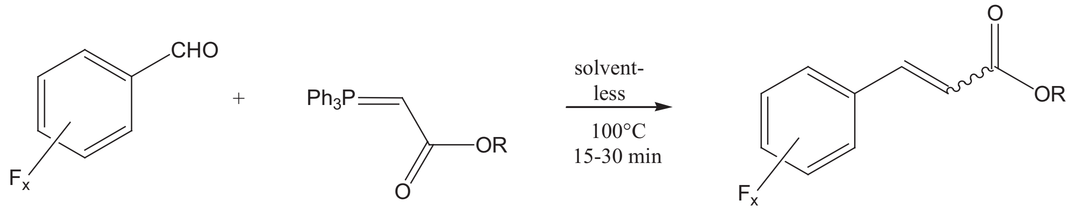


**1** **2a** **3**

| | | |
|---|---|---|
| **1a**: 2,3,6-$F_3$-(**1**) | 1.6 eq. **2a**, 100ºC, 45 min | **3a**: 2,3,6-$F_3$-(**3**) (91%, only *E*-isomer isolated) |
| **1b**: 2,3,5,6-$F_4$-(**1**) | 1.6 eq. **2a**, 100ºC, 45 min | **3b**: 2,3,5,6-$F_4$-(**3**) (92%, only *E*-isomer isolated) |
| **1c**: 2,3-$F_2$-(**1**) | 1.6 eq. **2a**, 100ºC, 45 min | **3c**: 2,3-$F_2$-(**3**) (90%, only *E*-isomer isolated) |
| **1d**: 3,4-$F_2$-(**1**) | 1.6 eq. **2a**, 100ºC, 45 min | **3d**: 3,4-$F_2$-(**3**) (92%, only *E*-isomer isolated) |
| **1e**: 3,5-$F_2$-(**1**) | 1.6 eq. **2a**, 100ºC, 40 min | **3e**: 3,5-$F_2$-(**3**) (94%, *E*/*Z* 92/8) |
| **1f**: 2,3,5-$F_3$-(**1**) | 1.6 eq. **2a**, 100ºC, 45 min | **3f**: 2,3,5-$F_3$-(**3**) (90%, only *E*-isomer isolated) |
| **1g**: 3,4,5-$F_3$-(**1**) | 1.6 eq. **2a**, 100ºC, 45 min | **3g**: 3,4,5-$F_3$-(**3**) (94%, *E*/*Z* 93/7) |
| **1h**: 2,3,4-$F_3$-(**1**) | 1.6 eq. **2a**, 100ºC, 45 min | **3h**: 2,3,4-$F_3$-(**3**) (95%, *E*/*Z* 92/8) |
| **1i**: 2,3,4,5-$F_4$-(**1**) | 1.6 eq. **2a**, 100ºC, 45 min | **3i**: 2,3,4,5-$F_4$-(**3**) (86%, *E*/*Z* 93/7) |
| **1j**: 2,6-$F_2$-(**1**) | 1.6 eq, **2a**, 100ºC, 45 min | **3j**: 2,6-$F_2$-(**3**) (quant., only *E*-isomer) |
| **1k**: $F_5$-(**1**) | 1.6 eq, **2a**, 100ºC, 60 min | **3k**: $F_5$-(**3**) (93%, only *E*-isomer) |

**Scheme 1** Solventless Wittig olefination of fluorinated benzaldehydes with acetylmethylidenetriphenylphosphorane (**2a**).



**1** **2b**: R = Et; **2c**: R = Bzl **4**

| | | |
|---|---|---|
| **1m**: 2,5-$F_2$-(**1**) | **2b** | **4a:** 2,5-$F_2$-(**4**); R = Et (93%; *E*/*Z* = 92:8) |
| **1a**: 2,3,6-$F_3$-(**1**) | **2b** | **4b**: 2,3,6-$F_3$-(**4**); R = Et (95%; E/Z>98:2) |
| **1j**: 2,6-$F_2$-(**1**) | **2b** | **4c**: 2,6-$F_2$-(**4**); R = Et (97%; *E*/*Z*>98:2) |
| **1k**:$F_5$-(**1**) | **2b** | **4d**: $F_5$-(**4**); R = Et (98%; *E*/*Z*>98:2) |
| **1a**: 2,3,6-$F_3$-(**1**) | **2c** | **4e**: 2,3,6-$F_3$-(**4**); R = Bzl (96%; *E*/*Z*>98:2) |
| **1c**: 2,3-$F_2$-(**1**) | **2c** | **4f**: 2,3-$F_2$-(**4**); R = Bzl (96%; *E*/*Z*=92:8) |
| **1n**: 2,4-$F_2$-(**1**) | **2c** | **4g**: 2,4-$F_2$-(**4**); R = Bzl (97%; *E*/*Z*=86:14) |
| **1e**: 3,5-$F_2$-(**1**) | **2c** | **4h**: 3,5-$F_2$-(**4**); R = Bzl (97%; *E*/*Z*=89:11) |
| **1j**: 2,6-$F_2$-(**1**) | **2c** | **4i**: 2,6-$F_2$-(**4**); R = Bzl (98%; *E*/*Z*>98:2) |
| **1k**: $F_5$-(**1**) | **2c** | **4j**: $F_5$-(**4**); R = Bzl (98%; *E*/*Z*>98:2) |

**Scheme 2** Solventless Wittig olefination of fluorinated benzaldehydes with alkoxycarbonylmethylidenetriphenylphosphorane **2b** and **2c**.

*E*-configurated olefins are produced. Nevertheless, the amount of *Z*-isomer obtained for **1j** is smaller than for **1e** (Scheme 3).

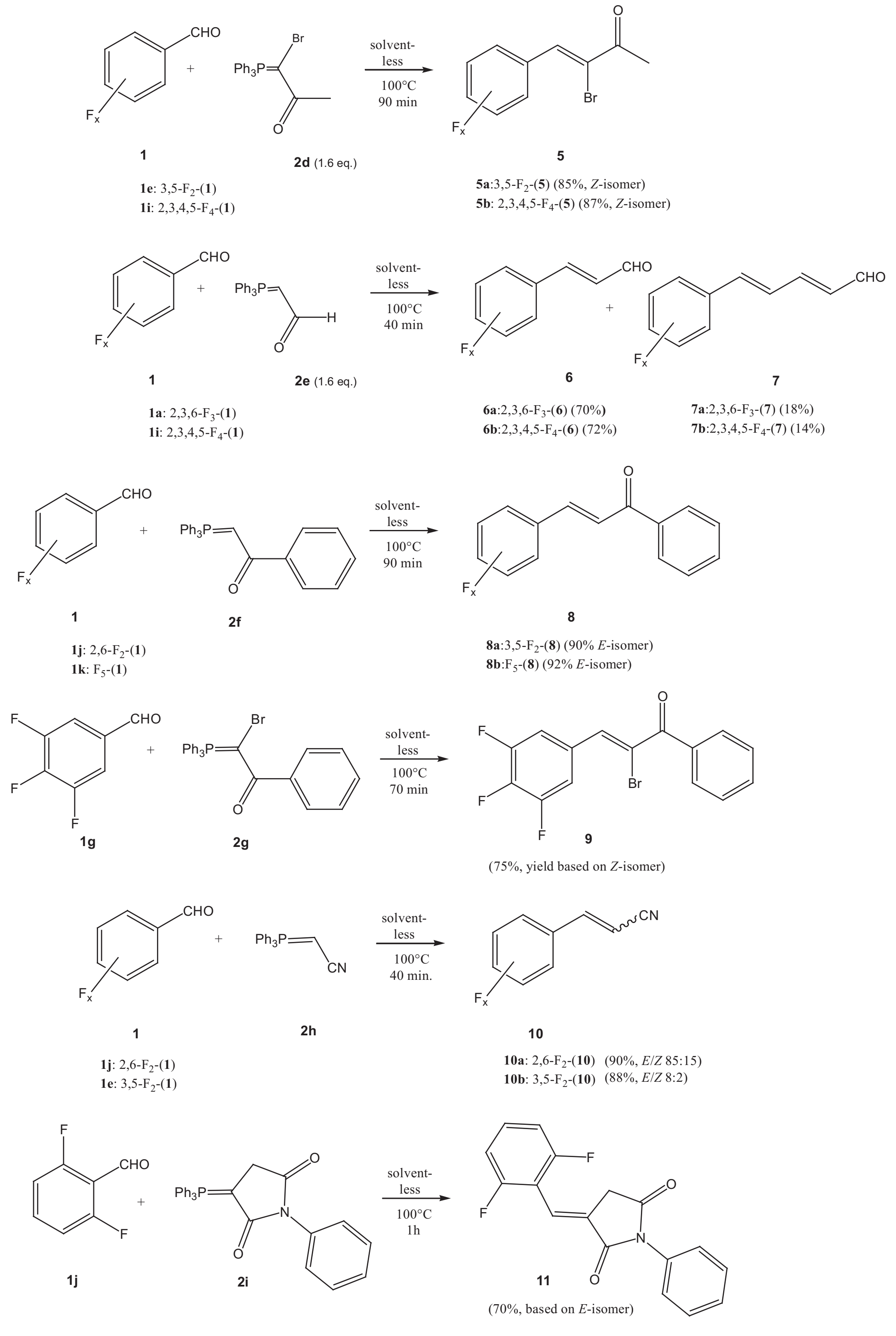
The reaction of **1j** with **2i** was found not to be exothermic. Earlier experiments had shown phosphorane **2i** to be moderately sensitive to heat[12] and **2i** was found to be unstable under microwave irradiation at 500W (2450 MHz).[2] Nevertheless, heating the solventless reaction mixture at 100ºC produced the Wittig product **11**, albeit in more moderate yield (Scheme 3).

In conclusion, a number of fluorinated benzaldehydes could be reacted with stabilised phosphoranes under solventless conditions, where in many cases the reactions were found to be exothermic. It must be noted that the conditions described lead to time-saving due to quicker reactions and work-up procedures. Although there is also some reduction in the solvents involved, including the ãrcumvention of such solvents as benzene, it must be noted that solvents still need to be used in the separation of the products from triphenylphosphine oxide. For the procedure of a Wittig reaction in a biphasic medium, which in many cases does not necessitate a chromatographic separation of the product, see ref.13.

## Experimental

*General*

Melting points were measured on a Yanaco microscopic hot-stage 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. For the experiments, an electric oven, EYELA NDO-450N, pre-heated at 100ºC, was used. Column chromatography was carried out on Wakogel 300. The reactions were carried out with 5–14 mmol of benzaldehyde using 1.6 mol equiv. of phosphorane.



**Scheme 3** Solventless Wittig olefination of fluorinated benzaldehydes with various stabilised phosphorances.

*Chemicals*

The fluorinated benzaldehydes **1** and triphenylphosphoranylidene-acetaldehyde (**2e**) were acquired commercially (Aldrich). Phosphoranes **2a**,[14a] **2b**,[14b] **2c**,[14c] **2d**,[14d,e] **2f,**[14a] **2g**,[14d,e] **2h**,[14f,g] and **2i**[14h] were synthesised according to literature procedures.

(*E*/*Z*)-Ethyl 3-(2,5-difluorophenyl)acrylate (**4a**): To **2b** (3.69 g, 10.6 mmol) was added dropwise 2,5-difluorobenzaldehyde (**1m**) (1.0 g, 6.8 mmol). The reaction vessel was then heated at 100ºC for 30 min. Direct column chromatography on silica gel (hexane/ether/ $CHCl_3$ 5: 1: 1) gave **4a**[15] as a colourless oil; IR (neat) ν 2980, 1718, 1642, 1591, 1492, 1368, 1240, 1179, 1037, 982, 862, 816 cm$^{-1}$; for *E*-**4a**: $^1$H NMR (270 MHz, $CDCl_3$) δ 1.34 (t, 3H, $^3J$ = 7.0 Hz), 4.28 (q, 2H, $^3J$ = 7.0 Hz), 6.50 (d, 1H, $^3J$ = 15.9 Hz), 7.06 (m, 2H), 7.24 (m, 1H), 7.75 (d, 1H, $^3J$ = 15.9 Hz); MS (EI, 70 eV) *m/z* (%) 212 ($M^+$, 44), 167 (100), 139 (34), 119 (37). HRMS Found: 212.0646. Calcd. for $C_{11}H_{10}O_2F_2$: 212.0649.

*Further selected physical and spectroscopic data*

*(E)-4-(2,3,6-Trifluoro-phenyl)but-3-en-2-one* (**3a**): Colourless slowly solidifying oil; (Found: $M^+$ 200.0450. $C_{10}H_7OF_3$ requires M, 200.0449); $\nu_{max}$ (KBr)/cm$^{-1}$ 3042, 1667, 1495, 1446, 1278, 1256, 1235, 1054, 984, 937, 832, 765, 616, 551; $\delta_H$ NMR (270 MHz, $CDCl_3$) 2.41 (3H, s, $CH_3$), 6.89 (1H, m), 7.03 (1H, d, $^3J$ = 16.7 Hz), 7.15 (1H, m), 7.55 (1H, d, $^3J$ = 16.7 Hz); MS (70 eV) *m/z* (%) = 200

(55) [$M^+$], 185 (100), 157 (51), 137 (37). (Found: C, 60.2; H, 3.4. $C_{10}H_7F_3O$ requires C, 60.01; H, 3.5).

*(E)-4-(2,3,5,6-Tetrafluoro-phenyl)but-3-en-2-one* (**3b**): Colourless slowly solidifying oil; (Found: $M^+$ 218.0355. $C_{10}H_6OF_4$ requires M, 218.0355); $\nu_{max}$ (KBr)/cm$^{-1}$ 3050, 1673, 1499, 1452, 1379, 1283, 1257, 1182, 1052, 981, 928, 880, 713, 692, 648, 546; $\delta_H$ (270 MHz, $CDCl_3$) 2.41 (3H, s, $CH_3$), 7.03 (1H, d, $^3J$ = 16.7 Hz), 7.11 (1H, m), 7.53 (1H, d, $^3J$ = 16.7 Hz); MS (70 eV) *m/z* (%) = 218 (78) [$M^+$], 203 (100), 175 (90), 155 (31). (Found: C, 54.6; H, 2.65. $C_{10}H_6F_4O.0.1H_2O$ requires C, 54.6; H, 2.8).

*(E)-4-(2,3-Difluoro-phenyl)but-3-en-2-one* (**3c**): Colourless slowly solidifying oil; (Found: $M^+$ 182.0542. $C_{10}H_8OF_2$ requires M, 182.0543); $\nu_{max}$ (KBr)/cm$^{-1}$ 1675, 1620, 1589, 1482, 1362, 1265, 1070, 978, 820, 780, 737, 711; $\delta_H$ (270 MHz, $CDCl_3$) 2.41 (3H, s, $CH_3$), 6.80 (1H, d, $^3J$ = 16.2 Hz), 7.09–7.33 (3H, m), 7.63 (1H, d, $^3J$ = 16.2 Hz); MS (70 eV) *m/z* (%) = 182 (59) [$M^+$], 167 (100), 139 (45), 119 (35).

*(E)-4-(3,4-Difluoro-phenyl)but-3-en-2-one* (**3d**)[16]: Colourless, slowly solidifying oil, m.p. 39ºC; (Found: $M^+$ 182.0546. $C_{10}H_8OF_2$ requires M, 182.0543); $\nu_{max}$ (KBr)/cm$^{-1}$ 1668, 1615, 1519, 1433, 1358, 1296, 1275, 1183, 1145, 1117, 974, 810, 789, 745, 617, 582, 550, 509; $\delta_H$ (270 MHz, $CDCl_3$) 2.38 (3H, s, $CH_3$), 6.63 (1H, d, $^3J$ = 16.2 Hz), 7.14–7.40 (3H, m), 7.41 (1H, d, $^3J$ = 16.2 Hz); MS (70 eV) *m/*z (%) = 182 (45) [$M^+$], 167 (100), 139 (47), 119 (30). (Found: C, 66.0; H, 4.3; $C_{10}H_8F_2O$ requires: C, 65.9; H, 4.4).

(*Z*)*-4-(3,5-Difluoro-phenyl) but-3-en-2-one* (***Z*-3e**): Colourless oil; (Found: $M^+$ 182.0539. $C_{10}H_8OF_2$ requires M, 182.0543); $\nu_{max}$ (neat)/cm$^{-1}$ 2920, 1694, 1620, 1588, 1415, 1357, 1175, 1122, 996, 868, 758; $\delta_H$ (270 MHz, $CDCl_3$) 2.23 (3H, s, $CH_3$), 6.28 (1H, d, $^3J$ = 12.7 Hz), 6.71 (1H, d, $^3J$ = 12.7 Hz), 6.79 (1H, m), 7.07 (2H, m); $\delta_C$ (67.8 MHz, $CDCl_3$) 31.1, 104.4 (t, $J_{CF}$ = 25.2 Hz), 112.3 (2C, m), 130.6, 137.3 (t, $J_{CF}$ = 2.8 Hz), 138.1 (t, $J_{CF}$ = 9.5 Hz), 162.7 (2C, dd, $J_{CF}$ = –248 Hz, $J_{CF}$ = 12.3 Hz), 197.7 (CO); MS (70 eV) *m/z* (%) = 182 (37) [$M^+$], 167 (100), 139 (51), 119 (43).

(*E*)*-4-(3,5-Difluoro-phenyl)but-3-en-2-one* (***E*-3e**): Colourless solid, m.p. 58ºC; (Found: $M^+$ 182.0542. $C_{10}H_8OF_2$ requires M, 182.0543); $\nu_{max}$ (KBr)/cm$^{-1}$ 3070, 1672, 1589, 1440, 1365, 1315, 1263, 1215, 1128, 978, 870, 835, 672, 579, 519, 507; $\delta_H$ (270 MHz, $CDCl_3$) 2.39 (3H, s, $CH_3$), 6.69 (1H, d, $^3J$ = 16.2 Hz), 6.85 (1H, m), 7.07 (2H, m), 7.40 (1H, d, $^3J$ = 16.2 Hz); MS (70 eV) *m/z* (%) = 182 (42) [$M^+$], 167 (100), 139 (47), 119 (40); $\delta_C$ (67.8 MHz, $CDCl_3$) 28.0, 105.6 (t, $J_{CF}$ = 25.7 Hz), 110.8 (2C, m), 129.0, 137.7 (t, $J_{CF}$ = 9.5 Hz), 140.5 (t, $J_{CF}$ = 2.8 Hz), 163.2 (2C, dd, $J_{CF}$ = –249 Hz, $J_{CF}$ = 12.8 Hz), 197.7 (CO); (Found: C, 65.7; H, 4.4; $C_{10}H_8F_2O$ requires C, 65.9; H, 4.4).

*(E)-4-(2,3,5-Trifluoro-phenyl)but-3-en-2-one* (**3f**): Colourless solid, mp. 87ºC; (Found: $M^+$ 200.0450; $C_{10}H_7OF_3$ requires M, 200.0449); $\delta_H$ (270 MHz, $CDCl_3$) 2.41 (3H, s, $CH_3$), 6.77 (1H, d, $^3J$ = 16.2 Hz), 6.96–7.09 (2H, m), 7.58 (1H, d, $^3J$ = 16.2 Hz); MW (70 eV) *m/z* (%) = 200 (55) [$M^+$], 185 (100), 157 (52), 137 (33). (Found: C, 59.85; H, 3.4. $C_{10}H_7F_3O$ requires C, 60.0; H, 3.5).

*(Z)-4-(3,4,5-Trifluorophenyl)but-3-en-2-one* (***Z*-3g**): Colourless oil; (Found: $M^+$ 200.0450. $C_{10}H_7OF_3$ requires M, 200.0449); $\delta_H$ (270 MHz, $CDCl_3$) 2.26 (3H, s, $CH_3$), 6.29 (1H, d, $^3J$ = 12.7 Hz), 6.61 (1H, d, $^3J$ = 12.7 Hz), 7.31 (2H, m); MS (70 eV) *m/z* (%) 200 (28) [$M^+$], 185 (66), 157 (33), 137 (20).

*(E)-4-(3,4,5-Trifluorophenyl)but-3-en-2-one* (***E*-3g**): Colourless solid, m.p. 43ºC; (Found: $M^+$ 200.0448. $C_{10}H_7OF_3$ requires M, 200.0449); $\nu_{max}$ (KBr)/cm$^{-1}$ 3070, 1675, 1532, 1441, 1354, 1250, 1045, 984, 792, 704, 665, 628, 556; $\delta_H$ (270 MHz, $CDCl_3$) 2.38 (3H, s, $CH_3$), 6.63 (1H, d, $^3J$ = 15.9 Hz), 7.17 (2H, t, $^3J_{H-F}$ = 6.5 Hz), 7.34 (1H, d, $^3J$ = 15.9 Hz); MS (70 eV) *m/z* (%) = 200 (47) [$M^+$], 185 (100), 157 (45), 137 (28). (Found: C, 60.0; H, 3.4. Calcd. for $C_{10}H_7F_3O$: C, 60.0; H, 3.5.)

*(Z)-4-(2,3,4-Trifluorophenyl)but-3-en-2-one* (***Z*-3h**): Colourless oil; (Found: $M^+$ 200.0447. $C_{10}H_7OF_3$ requires M, 200.0449); $\nu_{max}$ (neat)/cm$^{-1}$ 2926, 1702, 1621, 1510, 1474, 1357, 1311, 1175, 1037, 961, 814; $\delta_H$ (270 MHz, $CDCl_3$) 2.23 (3H, s, $CH_3$), 6.38 (1H, d, $^3J$ = 12.7 Hz), 6.77 (1H, d, $^3J$ = 12.7 Hz), 6.96 (1H, m), 7.36 (1H, m); MS (70 eV) *m/z* (%) = 200 (51) [$M^+$], 185 (100), 157 (45), 137 (27), 101 (20).

*(E)-4-(2,3,4-Trifluorophenyl)but-3-en-2-one* (***E*-3h**): Colourless solid, m.p. 53ºC; (Found: $M^+$ 200.0450. $C_{10}H_7OF_3$ requires M, 200.0449); $\nu_{max}$ (KBr)/cm$^{-1}$ 3070, 1676, 1604, 1512, 1473, 1360, 1313, 1293, 1253, 1214, 1176, 1070, 1040, 1018, 985, 957, 809, 696, 548; $\delta_H$ (270 MHz, $CDCl_3$) 2.41 (3H, s, $CH_3$), 6.76 (1H, d, $^3J$ = 16.2 Hz), 7.03 (1H, m), 7.29 (1H, m), 7.56 (1H, d, $^3J$ = 16.2 Hz); MS (70 eV) *m/z* (%) = 200 (58) [$M^+$], 185 (100), 157 (49), 137 (31). (Found: C, 60.0; H, 3.4. $C_{10}H_7F_3O$ requires C, 60.0; H, 3.5).

*(Z)-4-(2,3,4,5-Tetrafluorophenyl)but-3-en-2-one* (***Z*-3i**): Colourless oil; (Found: $M^+$ 218.0354. $C_{10}H_6OF_4$ requires M, 218.0355); $\delta_H$ (270 MHz, $CDCl_3$) 2.28 (3H, s, $CH_3$), 6.43 (1H, d, $^3J$ = 12.4 Hz), 6.71 (1H, d, $^3J$ = 12.4 Hz), 7.41 (1H, m); MS (70 eV) *m/z* (%) = 218 (35) [$M^+$], 203 (100), 175 (30).

*(E)-4-(2,3,4,5-Tetrafluorophenyl)but-3-en-2-one* (***E*-3i**): Colourless solid; m.p. 82ºC; (Found: $M^+$ 218.0352. $C_{10}H_6OF_4$ requires M, 218.0355); $\nu_{max}$ (KBr)/cm$^{-1}$ 3064, 1678, 1530, 1484, 1257, 1120, 1040, 987, 948, 892, 715, 700, 639, 544; $\delta_H$ (270 MHz, $CDCl_3$) 2.40 (3H, s, $CH_3$), 6.73 (1H, d, $^3J$ = 16.2 Hz), 7.18 (1H, m), 7.53 (1H, d, $^3J$ = 16.2 Hz); MS (70 eV) *m/z* (%) = 218 (58) [$M^+$], 203 (100), 175 (56). (Found: C, 54.8; H, 2.7. $C_{10}H_6F_4O$ requires C, 55.1; H, 2.8).

*(E)-4-(2,6-Difluorophenyl)but-3-en-2-one* (**3j**)[17]: Colourless solid, m.p. 29ºC; (Found: $M^+$ 182.0546. $C_{10}H_8OF_2$ requires M, 182.0543); $\nu_{max}$ (KBr)/cm$^{-1}$ 1663, 1620, 1464, 1364, 1283, 1252, 1203, 1018, 985, 792, 719, 590, 525, 504; $\delta_H$ (270 MHz, $CDCl_3$) 2.39 (3H, s, $CH_3$), 6.95 (2H, m), 7.01 (1H, d, $^3J$ = 16.5 Hz), 7.34 (1H, m), 7.61 (1H, d, $^3J$ = 16.5 Hz); $\delta_C$ (67.8 MHz, $CDCl_3$) 27.9, 111.9 (2C, m), 112.5 (t, $J_{CF}$ = 14.0 Hz), 129.3 (t, $J_{CF}$ = 2.0 Hz), 131.3 (t, $J_{CF}$ = 11.2 Hz), 132.4 (t, $J_{CF}$ = 8.4 Hz), 161.8 (2C, dd, $J_{CF}$ = –255 Hz, $J_{CF}$ = 6.7 Hz), 198.5 (CO); MS (70 eV) *m/z* (%) = 182 (49) [$M^+$], 167 (100), 139 (48), 119 (47).

(*E*)-4-Pentafluorophenylbut-3-en-2-one (**3k**): Colourless oil; (Found: $M^+$ 236.0262. $C_{10}H_5OF_5$ requires M, 236.0261); $\nu_{max}$ (KBr)/cm$^{-1}$ 2922, 1700, 1683, 1654, 1613, 1523, 1499, 1425, 1362, 1293, 1257, 1182, 1136, 1013, 983, 910, 734; $^1\delta_H$ (270 MHz, $CDCl_3$) 2.41 (3H, s, $CH_3$), 6.88 (1H, d, $^3J$ = 16.7 Hz), 7.47 (1H, d, $^3J$ = 16.7 Hz); MS (70 eV) *m/z* (%) = 236 ($M^+$, 24), 221 (45), 193 (28), 58 (100).

*(E)-Ethyl 3-(2,3,6-trifluorophenyl)acrylate* (**4b**): Colourless oil; (Found: $M^+$, 230.0559. $C_{11}H_9O_2F_3$: requires M, 230.0555); $\nu_{max}$ (neat)/cm$^{-1}$ 3092, 2986, 1719, 1639, 1493, 1367, 1312, 1292, 1183, 1048, 985, 926, 872, 810; $\delta_H$ (270 MHz, $CDCl_3$) 1.35 (3H, t, $^3J$ = 7.0 Hz), 4.29 (2H, q, $^3J$ = 7.0 Hz), 6.76 (1H, d, $^3J$ = 16.2 Hz), 6.90 (1H, m), 7.16 (1H, m), 7.65 (1H, d, $^3J$ = 16.2 Hz); MS (70 eV) *m/z* (%) = 230 (39) [$M^+$], 185 (100), 157 (40), 137 (35).

*Ethyl (E)-3-(2,6-difluorophenyl)acrylate* (**4c**)[18]: Colourless oil; (Found: $MH^+$ 213.0726. $C_{11}H_{11}O_2F_2$ requires MH, 213.0727); $\nu_{max}$ (neat)/cm$^{-1}$ 2982, 1718, 1639, 1621, 1467, 1314, 1273, 1239, 1203, 1149, 1012, 869, 788, 743; $\delta_H$ (270 MHz, $CDCl_3$) 1.35 (3H, t, $^3J$ = 7.3 Hz, $CH_3$), 4.28 (2H, q, $^3J$ = 7.3 Hz, $OCH_2$), 6.74 (1H, d, $^3J$ = 16.5 Hz), 6.94 (2H, m), 7.30 (1H, m), 7.77 (1H, d, $^3J$ = 16.5 Hz); $\delta_C$ (67.8 MHz, $CDCl_3$) 14.3, 60.7, 111.8 (m), 112.5 (t, $J_{CF}$ = 15.1 Hz), 124.4 (t, $J_{CF}$ = 8.4 Hz), 130.6 (t, $J_{CF}$ = 2.2 Hz), 131.0 (t, $J_{CF}$ = 10.6 Hz), 161.7 (2C, dd, $J_{CF}$ = –255 Hz, $J_{CF}$ = 7.3 Hz), 166.9 (CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 213 (14) [$MH^+$], 167 (24) [M + -$OC_2H_5$]. (Found: C, 62.35; H, 4.75. $C_{11}H_{10}F_2O_2$ requires C, 62.3; H, 4.75).

*Ethyl (E)-3-pentafluorophenylacrylate* (**4d**)[7f,19]: Colourless oil; (Found: $M^+$ 266.0368. $C_{11}H_7O_2F_5$ requires M, 266.0366); $\nu_{max}$ (neat)/cm$^{-1}$ 2966, 1724, 1650, 1523, 1501, 1296, 1260, 1186, 1150, 1020, 984, 872, 675; $\delta_H$ (270 MHz, $CDCl_3$) 1.38 (3H, t, $CH_3$, $^3J$ = 7.3 Hz), 4.30 (2H, q, $OCH_2$, $^3J$ = 7.3 Hz), 6.74 (1H, d, $^3J$ = 16.5 Hz), 7.64 (1H, d, $^3J$ = 16.5 Hz). MS (70 eV) *m/z* (%) = 266 (34) [$M^+$], 238 (18), 221 (100) [$M^+$-$OC_2H_5$], 193 (50) [$M^+$-$OCOC_2H_5$], 143 (25).

*Benzyl (E)-3-(2,3,6-trifluorophenyl)acylate* (**4e**): Colourless solid; (Found: $M^+$ 292.0719. $C_{16}H_{11}O_2F_3$ requires M, 292.0711); $\nu_{max}$ (KBr)/cm$^{-1}$ 3074, 1704, 1634, 1495, 1455, 1315, 1250, 1170, 1050, 984, 916, 868, 818, 750, 700, 492; $\delta_H$ (270 MHz, $CDCl_3$) 5.27 (2H, s, $OCH_2$), 6.81 (1H, d, $^3J$ = 16.5 Hz), 6.91 (1H, m), 7.14 (1H, m), 7.34–7.44 (5H, m), 7.48 (1H, d, $^3J$ = 16.5 Hz); MS (70 eV) *m/z* (%) = 292 (10) [$M^+$], 247 (26), 185 (31), 157 (15), 137 (20), 91 (43), 58 (100).

*Benzyl (E)-3-(2,3-difluorophenyl)acrylate* (**4f**): Slowly solidifying colourless oil; (Found: $M^+$ 274.0806. $C_{16}H_{12}O_2F_2$ requires M, 274.0805); $\nu_{max}$ (KBr)/cm$^{-1}$ 1714, 1642, 1484, 1328, 1280, 1203, 1161, 782, 748, 698; $\delta_H$ (270 MHz, $CDCl_3$) 5.27 (2H, s, $OCH_2$), 6.61 (1H, d, $^3J$ = 16.2 Hz), 7.10–7.44 (8H, m), 7.82 (1H, d, $^3J$ = 16.2 Hz); MS (70 eV) *m/z* (%) = 274 (20) [$M^+$], 229 (41), 167 (62), 139 (29), 119 (46), 91 (100).

*Benzyl (E)-3-(2,4-difluorophenyl)acrylate* (**4g**)[20]: Colourless oil; (Found: $M^+$ 274.0809. $C_{16}H_{12}O_2F_2$ requires M, 274.0805); $\nu_{max}$ (neat)/cm$^{-1}$ 3070, 3034, 2952, 1721, 1640, 1501, 1456, 1431, 1376, 1262, 1169, 1090, 968, 852, 813, 752, 697, 610, 572; $\delta_H$ (270 MHz, $CDCl_3$) 5.26 (2H, s, $OCH_2$), 6.53 (1H, d, $^3J$ = 16.2 Hz), 6.88 (2H, m), 7.32–7.43 (5H, m), 7.50 (1H, m), 7.79 (1H, d, $^3J$ = 16.2 Hz); $\delta_C$ (67.8 MHz, $CDCl_3$) 66.5, 104.6 (t, $J_{CF}$ = 25.2 Hz), 111.1 (dd, $J_{CF}$ = 21.8 Hz, $J_{CF}$ = 3.9 Hz), 120.1 (dd, $J_{CF}$ = 6.7 Hz, $J_{CF}$ = 2.2 Hz), 118.9 (dd, $J_{CF}$ = 11.7 Hz, $J_{CF}$ = 3.9 Hz), 128.3 (3C), 128.6 (2C), 130.2 (dd, $J_{CF}$ = 10.0 Hz, $J_{CF}$ = 4.5 Hz), 135.9, 136.8 (t, $J_{CF}$ = 1.7 Hz), 161.7 (dd, $J_{CF}$ = –256 Hz, $J_{CF}$ = 11.7 Hz), 163.9 (dd, $J_{CF}$ = –252 Hz, $J_{CF}$ = 12.9 Hz), 166.5 (CO); MS (70 eV) *m/z* (%) = 274 (34) [M$^+$], 229 (54), 167 (75), 91 (100).

*Benzyl (E)-3-(3,5-difluorophenyl)acrylate* (**4h**): Slowly solidifying colourless oil; (Found: M$^+$ 274.0802. $C_{16}H_{12}O_2F_2$ requires M, 274.0805); $\nu_{max}$ (KBr)/cm$^{-1}$ 3072, 2956, 1710, 1646, 1620, 1588, 1453, 1432, 1316, 1279, 1169, 1116, 988, 850, 756, 699, 661; $\delta_H$ (270 MHz, $CDCl_3$) 5.26 (2H, s, $OCH_2$), 6.83 (1H, m), 6.47 (1H, d, $^3J$ = 15.9 Hz), 7.03 (2H, m), 7.33–7.41 (5H, m), 7.61 (1H, d, $^3J$ = 15.9 Hz); $\delta_C$ NMR (67.8 MHz, $CDCl_3$) 66.66, 105.4 (t, $J_{CF}$ = 25.2 Hz), 110.7 (2C, m), 120.6, 128.3 (2C), 128.3, 128.6 (2C), 137.6 (t, $J_{CF}$ = 9.5 Hz), 142.5 (t, $J_{CF}$ = 2.8 Hz), 163.2 (2C, dd, $J_{CF}$ = –249 Hz, $J_{CF}$ = 12.9 Hz), 166.0 (CO); MS (70 eV) *m/z* (%) = 274 (12) [M$^+$], 228 (68), 167 (70), 91 (100). (Found: C, 69.95; H, 4.30. $C_{16}H_{12}F_2O_2$ requires C, 70.07; H, 4.41).

*Benzyl (E)-3-(2,6-difluorophenyl)acrylate* (**4i**): Colourless solid; m.p. 58ºC; (Found: M$^+$ 274.0806. $C_{16}H_{12}O_2F_2$ requires M, 274.0805); $\nu_{max}$ (KBr)/cm$^{-1}$ 1702, 1632, 1467, 1322, 1285, 1240, 1209, 1169, 1018, 982, 916, 868, 784, 742, 700; $\delta_H$ (270 MHz, $CDCl_3$) 5.27 (2H, s, $OCH_2$), 6.80 (1H, d, $^3J$ = 16.2 Hz), 6.92 (2H, m), 7.27–7.44 (6H, m), 7.83 (1H, d, $^3J$ 1= 6.2 Hz); MS (70 eV) *m/z* (%) = 274 (34) [M$^+$], 229 (80), 167 (93), 139 (34), 119 (58), 91 (100); (Found: C, 70.0; H, 4.35. $C_{16}H_{12}F_2O_2$ requires C, 70.07; H, 4.41).

*Benzyl (E)-3-(pentafluorophenyl)acrylate* (**4j**): Colourless solid, m.p. 79ºC; (Found: M$^+$ 328.0529. $C_{16}H_9O_2F_5$ requires M, 328.0523); $\nu$ (KBr)/cm$^{-1}$ 1725, 1641, 1523, 1501, 1443, 1381, 1328, 1300, 1265, 1194, 1154, 1128, 1029, 1007, 983, 961, 865, 731, 694; $\delta_H$ (270 MHz, $CDCl_3$) 5.27 (2H, s, $OCH_2$), 6.79 (1H, d, $^3J$ = 16.5 Hz), 7.33–7.43 (5H, m), 7.68 (1H, d, $^3J$ = 16.5 Hz); MS (70 eV) *m/z* (%) = 328 (21) [M$^+$], 283 (50), 221 (65), 193 (35), 143 (31), 91 (100). (Found: C, 58.6; H, 2.6. $C_{16}H_9F_5O_2$ requires: C, 58.55; H, 2.76).

*(Z)-3-Bromo-4-(3,5-difluorophenyl)but-3-en-2-one*(**5a**):Colourless solid, m.p. 37ºC; (Found: M$^+$ 259.9649. $C_{10}H_7O^{79}BrF_2$ requires M, 269.9648); $\nu_{max}$ (KBr)/cm$^{-1}$ 3074, 1681, 1607, 1488, 1431, 1343, 1259, 1216, 1148, 1089, 999, 965, 885, 813, 577, 548, 512, 484; $\delta_H$ (270 MHz, $CDCl_3$) 2.61 (3H, s, $CH_3$), 6.94 (2H, m), 8.19 (1H, s), 8.25 (1H, dt, $^3J$ = 8.6 Hz); $\delta_C$ (67.8 MHz, $CDCl_3$) 26.8, 104.2 (dd, $J_{CF}$ = 25.1 Hz, $J_{CF}$ = 25.1 Hz), 111.4 (dd, $J_{CF}$ = 21.3 Hz, $J_{CF}$ = 3.9 Hz), 118.3 (dd, $J_{CF}$ = 11.8 Hz, $J_{CF}$ = 3.9 Hz), 125.6, 131.3 (2C, m), 161.4 (dd, $J_{CF}$ = –255 Hz, $J_{CF}$ = 11.7 Hz), 164.0 (dd, $J_{CF}$ = 254 Hz, $J_{CF}$ = 11.7 Hz), 192.5 (CO); MS (70 eV) *m/z* (%) = 262 (20) {[$^{81}$Br]M$^+$}, 260 (20) {[$^{79}$Br]M$^+$}, 181 (100), 138 (64).

*(Z)-3-Bromo-4-(2,3,4,5-tetrafluorophenyl)but-3-en-2-one* (**5b**): Colourless oil; (Found: M$^+$ 295.9461. $C_{10}H_5O^{79}BrF_4$ requires M, 295.9460); $\nu_{max}$ (neat)/cm$^{-1}$ 3096, 2918, 1694, 1628, 1525, 1477, 1362, 1206, 1122, 1053, 718; $\delta_H$ (270 MHz, $CDCl_3$) 2.62 (3H, s, $CH_3$), 7.85 (1H, m), 8.03 (1H, s); MS (70 eV) *m/z* (%) = 298 (31) {[$^{81}$Br]M$^+$}, 296 (32) {[$^{79}$Br]M$^+$}, 217 (91), 174 (100).

*(E)-2,3,6-Trifluorocinnamaldehyde* (**6a**): Pale yellow solid, m.p. 61ºC; (Found: M$^+$ 186.0287. $C_9H_5OF_3$ requires M, 186.0292); $\nu_{max}$ (KBr)/cm$^{-1}$ 1686, 1635, 1492, 1446, 1329, 1306, 1267, 1224, 1126, 1043, 981, 935, 841, 775, 623, 607, 573; $\delta_H$ (270 MHz, $CDCl_3$) 6.85 (1H, m), 7.02 (1H, dd, $^3J$ = 16.5 Hz, $^3J$ = 7.5 Hz), 7.24 (1H, m), 7.54 (1H, d, $^3J$ = 16.5 Hz), 9.73 (1H, dd, $^3J$ = 7.5 Hz, $^4J$ = 0.8 Hz); MS (70 eV) *m/z* (%) = 186 (100) [M$^+$], 167 (30), 158 (73), 137 (53).

*(E)-2,3,4,5-Tetrafluorocinnamaldehyde* (**6b**): Colourless needles, m.p. 79ºC; (Found: M$^+$ 204.0193. $C_9H_4OF_4$ requires M, 204.0198); $\nu_{max}$ (KBr)/cm$^{-1}$ 3074, 2858, 1694, 1530, 1487, 1375, 1126, 1049, 980, 953, 871, 841, 718, 644, 559; $\delta_H$ (270 MHz, $CDCl_3$) 6.72 (1H, dd, $^3J$ = 16.2 Hz, $^3J$ = 7.3 Hz), 7.24 (1H, m), 7.54 (1H, d, $^3J$ = 16.2 Hz), 9.74 (1H, d, $^3J$ = 7.3 Hz, CHO); MS (70 eV) *m/z* (%) = 204 (100) [M$^+$], 176 (79), 155 (33), 125 (33). (Found: C, 52.9; H, 2.0. $C_9H_4F_4O$ requires C, 52.96; H, 1.98).

*(E,E)-5-(2,3,6-Trifluorophenyl)penta-2,4-dienal* (**7a**): Pale yellow solid; m.p. 104ºC; (Found: M$^+$ 212.0453. $C_{11}H_7OF_3$ requires M, 212.0449); $\nu_{max}$ (KBr)/cm$^{-1}$ 1687, 1614, 1488, 1299, 1244, 1201, 1161, 1109, 1042, 1010, 990, 924, 816, 780, 623, 488; MS (70 eV) *m/z* (%) = 212 (100) [M$^+$], 183 (34), 165 (76), 164 (83). $\delta_H$ (270 MHz, $CDCl_3$) 6.33 (1H, m), 7.00–7.38 (4H, m), 6.88 (1H, m), 9.66 (1H, d, $^3J$ = 8.1 Hz, CHO). (Found: C, 62.3; H, 3.3. Calcd. for $C_{11}H_7F_3O$ requires C, 62.27; H, 3.33).

*(E,E)-5-(2,3,4,5-Tetrafluorophenyl)penta-2,4-dienal* (**7b**): Pale yellow needles, m.p. 109ºC; (Found: M$^+$ 230.0361. $C_{11}H_6OF_4$ requires M, 230.0355); (KBr)/cm$^{-1}$ $\nu_{max}$ 3056, 2836, 1674, 1621, 1525, 1479, 1372, 1159, 1127, 1042, 1012, 992, 950, 708, 565; $\delta_H$ (270 MHz, $CDCl_3$) 6.33 (1H, dd, $^3J$ = 15.1 Hz, $^3J$ = 7.8 Hz), 7.04 (2H, m), 7.13–7.31 (2H, m), 9.66 (1H, d, $^3J$ = 7.8 Hz, CHO); MS (70 eV) *m/z* (%) = 230 (100) [M$^+$], 201 (36), 182 (76), 151 (96). (Found: C, 57.4; H, 2.6. $C_{11}H_6F_4O$ requires C, 57.40; H, 2.63).

*(E)-3-(2,6-Difluoro-phenyl)-1-phenyl-propenone* (**8a**)[21]: Pale yellow solid, m.p. 64ºC; (Found: M$^+$ 244.0702. $C_{15}H_{10}OF_2$ requires M, 244.0700); $\nu_{max}$ (KBr)/cm$^{-1}$1668, 1622, 1472, 1319, 1288, 1240, 1212, 992, 885, 860, 785, 718, 681, 495;$\delta_H$ (270 MHz, $CDCl_3$) 6.97 (2H, m), 7.33 (1H, m), 7.48–7.63 (3H, m), 7.84 (1H, d, $^3J$ = 15.9 Hz), 7.92 (1H, d, $^3J$ = 15.9 Hz), 8.04 (2H, m); $\delta_C$ (67.8 MHz, $CDCl_3$) 111.8 (m), 113.0 (t, $J_{CF}$ = 14.6 Hz), 127.5 (t, $J_{CF}$ = 8.3 Hz), 128.6 (2C), 128.7 (2C), 130.5 (t, $J_{CF}$ = 2.2 Hz), 131.2 (t, $J_{CF}$ = 10.6 Hz), 133.0, 137.8, 162.0 (2C, dd, $J_{CF}$ = –254 Hz, $J_{CF}$ = 6.7 Hz), 190.4 (CO); MS (70 eV) *m/z* (%) = 244 (100) [M$^+$], 225 (28), 216 (24), 167 (40), 119 (47), 105 (46). (Found: C, 73.8; H, 4.1. $C_{15}H_{10}F_2O$ requires C, 73.76; H, 4.13).

*(E)-3-Pentafluorophenyl-1-phenylpropenone* (**8b**)[21]: Pale yellow solid, m.p. 153ºC; (Found: M$^+$ 298.0419. $C_{15}H_7OF_5$ requires M, 298.0417); (KBr)/cm$^{-1}$ $\nu_{max}$ 1668, 1606, 1522, 1498, 1337, 1307, 1287, 1266, 1217, 1179, 1147, 1138, 1016, 980, 953, 781, 725, 692, 611, 567; $\delta_H$ (270 MHz, $CDCl_3$) 7.51–7.64 (3H, m), 7.76 (1H, d, $^3J$ = 16.2 Hz), 7.87 (1H, d, $^3J$ = 16.2 Hz), 8.03 (2H, m); MS (70 eV) *m/z* (%) = 298 (100) [M$^+$], 279 (17), 250 (17), 221 (25), 193 (24), 105 (54). (Found: C, 60.5; H, 2.3. $C_{15}H_7F_5O$ requires C, 60.41; H, 2.37).

*(Z)-2-Bromo-3-(3,4,5-trifluoro-phenyl)-1-phenylpropenone* (**9**): Colourless solid, m.p. 77ºC; (Found: MH$^+$ 340.9789. $C_{15}H_9O^{79}BrF_3$ requires MH, 340.9789); $\nu_{max}$ (KBr)/cm$^{-1}$ 1666, 1616, 1528, 1438, 1349, 1260, 1060, 1041, 865, 780, 723, 693; $\delta_H$ (270 MHz, $CDCl_3$) 7.49–7.56 (5H, m), 7.63 (1H, m), 7.80 (2H, m); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 343 (21) {[$^{81}$Br]MH$^+$}, 341 (21) {[$^{79}$Br]MH$^+$}, 263 (5), 261 (6).

*(E)-3-(2,6-Difluorophenyl)acrylonitrile* (***E*-10a**)[22]: Colourless solid; m.p. 38ºC; (Found: M$^+$ 165.0390. $C_9H_5NF_2$ requires M, 165.0390); $\nu_{max}$ (KBr)/cm$^{-1}$ 2214 (CN), 1625, 1471, 1234, 1206, 1038, 972, 838, 779, 719, 555, 510; $\delta_H$ (270 MHz, $CDCl_3$) 6.25 (1H, d, $^3J$ = 16.3 Hz), 6.97 (2H, m), 7.37 (1H, m), 7.47 (1H, d, $^3J$ = 16.3 Hz); $\delta_C$ (67.8 MHz, $CDCl_3$) 102.7 (t, $J_{CF}$ = 10.0 Hz), 111.7 (t, $J_{CF}$ = 14.5 Hz), 112.1 (2C, m), 118.0, 132.3 (t, $J_{CF}$ = 11.2 Hz), 137.1 (t, $J_{CF}$ = 2.2 Hz), 161.4 (2C, dd, $J_{CF}$ = –256 Hz, $J_{CF}$ = 6.7 Hz); MS (70 eV) *m/z* (%) = 165 (100) [M$^+$], 145 (9.5), 138 (11). (Found: C, 65.55; H, 3.0; N, 8.5. $C_9H_5F_2N$ requires C, 65.46; H, 3.05; N, 8.48).

*(Z)-3-(2,6-Difluorophenyl)acrylonitrile* (***Z*-10a**): Colourless oil; (Found: M$^+$ 165.0390. $C_9H_5NF_2$ requires M, 165.0390); $\nu_{max}$ (neat)/cm$^{-1}$ 3070, 2222 (CN), 1630, 1581, 1463, 1279, 1237, 1012, 970, 942, 788, 762; $\delta_H$ (270 MHz, $CDCl_3$) 5.79 (1H, d, $^3J$ = 12.2 Hz), 6.99 (2H, t, $^3J$ = 8.1 Hz), 7.14 (1H, d, $^3J$ = 12.2 Hz), 7.39 (1H, m); $\delta_C$ (67.8 MHz, $CDCl_3$) 104.1 (t, $J_{CF}$ = 2.2 Hz), 111.7 (t, $J_{CF}$ = 10.6 Hz), 111.8 (2C, m), 115.6, 131.9 (t, $J_{CF}$ = 10.6 Hz), 136.4, 160.1 (2C, dd, $J_{CF}$ = –254 Hz, $J_{CF}$ = 6.7 Hz); MS (70 eV) *m/z* (%) = 165 (100) [M$^+$], 145 (10), 138 (12).

*(E)-3-(3,5-Difluorophenyl)acrylonitrile* (***E*-10b**): Colourless solid, m.p. 92ºC; (Found: M$^+$ 165.0389. $C_9H_5NF_2$ requires M, 165.0390); $\nu_{max}$ (KBr)/cm$^{-1}$ 3096, 2214, 1620, 1589, 1439, 1343, 1321, 1270, 1127, 1005, 969, 860, 817, 691, 668; $\delta_H$(270 MHz, $CDCl_3$) 5.91 (1H, d, $^3J$ = 16.5 Hz), 6.86–7.02 (3H, m), 7.32 (1H, d, $^3J$ = 16.5 Hz); $\delta_C$ (67.8 MHz, $CDCl_3$) 99.5, 106.4 (t, $J_{CF}$ = 25.7 Hz), 110.2 (2C, m), 117.1, 136.5 (t, $J_{CF}$ = 9.5 Hz), 148.0 (t, $J_{CF}$ = 2.8 Hz), 163.3 (2C, dd, $J_{CF}$ = –250 Hz, $J_{CF}$ = 12.3 Hz); MS (70 eV) *m/z* (%) = 165 (100) [M$^+$], 138 (22), 114 (13). (Found: C, 65.5; H, 3.0; N, 8.5. $C_9H_5F_2N$ requires C, 65.46; H, 3.05; N, 8.48).

*(Z)-3-(3,5-Difluorophenyl)acrylonitrile* (***Z*-10b**): Slowly solidifying oil; (Found: M$^+$ 165.0396. $C_9H_5NF_2$ requires M, 165.0390); $\nu_{max}$ (KBr)/cm$^{-1}$ 3088, 2212, 1621, 1585, 1438, 1314, 1127, 968, 861, 669; $\delta_H$ (270 MHz, $CDCl_3$) 5.58 (1H, d, $^3J$ = 12.2 Hz), 6.87–7.34 (3H, m), 7.06 (1H, d, $^3J$ = 12.2 Hz); MS (70 eV) *m/z* (%) = 165 (100) [M$^+$], 138 (22).

*(E)-3-(2,6-Difluorobenzylidene)-1-phenylpyrrolidine-2,5-dione* (**11**): Colourless solid, m.p. 163ºC; (Found: M$^+$ 299.0760. $C_{17}H_{11}O_2NF_2$ requires M, 299.0758); $\nu_{max}$ (KBr)/cm$^{-1}$ 3054, 1775, 1706 (s), 1651, 1620, 1502, 1478, 1457, 1385, 1202, 1180, 980, 744, 696, 680; $\delta_H$ (270 MHz, $CDCl_3$) 3.59 (2H, d, $^4J$ = 2.4 Hz), 7.02 (2H, m), 7.36–7.56 (6H, m), 7.77 (1H, t, $^4J$ = 2.4 Hz); MS (70 eV) *m/z* (%) = 299 (88) [M$^+$], 152 (100), 151 (79). (Found: C, 68.3; H, 3.6; N, 4.8. $C_{17}H_{11}F_2NO_2$ requires C, 68.23; H, 3.70; N, 4.68).

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## References

1 K. Tanaka and F. Toda, *Chem. Rev.*, 2000, **100**, 1025.

2 T. Thiemann, M. Watanabe, Y. Tanaka and S. Mataka, *New J. Chem.*, 2004, **28**, 578.

3 (a) W. Liu, Q. Xu, Y. Ma, Y. Liang, N. Dong and D. Guan, *J. Organomet. Chem.*, 2001, **625**, 128; (b) C. Xu, G. Chen, C. Fu and X. Huang, *Synth. Commun.*, 1995, **25**, 2229; (c) C. Xu, G. Chen and X. Huang, *Org. Prep. Proced. Int.*, 1995, **27**, 559.

4 A. Spinella, T. Fortunati and A. Soriente, *Synlett*, 1997, 93.

5 V.P. Balema, J.W. Wiench, M. Pruski and V.K. Pecharsky, *J. Am. Chem. Soc.*, 2002, **124**, 6244.

6 T. Thiemann, Y. Tanaka, K. Ideta and S. Mataka, *Centr. Eur. J. Chem.,* 2006, **4**, 403.

7 for typical examples, see: (a) E.J. Corey, D.A, Clark, G. Goto, A. Marfat, C. Mioskowski, B. Samuelsson and S. Hammerström, *J. Am. Chem. Soc.*, 1980, **102**, 1436 (for DME); (b) S. Fliszàr, R.F. Hudson and G. Salvadori, *Helv. Chim. Acta*, 1964, **47**, 159 (for chloroform); (c) D. Spitzner and H. Swoboda, *Tetrahedron Lett.*, 1986, **27**, 1281 (for benzene); (d) T. Thiemann, D. Ohira, Y.Q. Li, T. Sawada, S. Mataka, K. Rauch, M. Noltemeyer and A. de Meijere, *J. Chem. Soc.*, *Perkin Trans. 1*, 2000, 2968 (for benzene); (e) J.-P. Surivet, J.-N. Volle and J.M. Vatèle, *Tetrahedron: Asymmetry*, 1996, **7**, 3305 (for toluene); (f) J. Vicente, M.T. Chicote, J. Fernandes-Baeza and A. Fernandez-Baeza*, New J. Chem.*, 1994, **18**, 263 (for dichloromethane).

8 (a) C. Rüchardt, P. Panse and S. Eichler, *Chem. Ber.*, 1967, **100**, 1144; (b) D.P. Mariott and S.R. Bantick, *Tetrahedron Lett.*, 1981, **22**, 3657.

9 P.J. Bowen, T.P. Robinson, T. Ehlers, D. Goldsmith and J. Arbiser (University of Georgia Research Foundation, Inc., USA), PCT Int. Appl. WO 2001046110 (June 28, 2001); *Chem. Abs.*, 2001, **135**, 76687.

10 N.-D. Sung, S.-J. Yu, P.-K. Myung, B-M. Kwon and S.-H. Lee, *Han'guk Nonghwa Hakhoechi*, 1999, **42**, 252; *Chem. Abs.*, 2000, **132**, 233421.

11 T. Yasukochi, M. Ito, H. Kubota, S. Miyauchi and M. Saito (Daiichi Pharmaceutical Co., Ltd., Japan), PCT Int. Appl. WO 2003055850 (July 10, 2003); *Chem. Abs.*, 2003, **139**, 101146.

12 M. Koszytkowka-Stawinska and W. Sas, J. Chem. Res., 1999, (S), 694; (M) 2945.

13 M. Watanabe, G. Ribeiro Morais, S. Mataka, K. Ideta and T. Thiemann, *Z. Naturforsch.*, 2005, **60B**, 909.

14 (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, 1957, **22**, 41; (b) W.J. Considine, *J. Org. Chem.*, 1962, **64**, 7; (c) N.F. Osborne, *J. Chem. Soc.*, *Perkin Trans. 1*, 1982, 1429; (d) M.I. Shevchuk, V.L. Mikailu, V.I. Laba and A.V. Sviridova, *Zh. Obshch. Khim.*, 1986, **56**, 347; (e) M.M. Kayser, J. Zhu, and D.L. Hooper, *Can. J. Chem.*, 1997, **75**, 1515; (f) S. Trippett and D.M. Walker, *J. Chem. Soc.*, 1959, 3874; (g) M. Mauduit, C. Kouklovsky and Y. Langlois, *Tetrahedron Lett.,* 1998, **39**, 6857; (h) E. Hedaya and S. Theodoropoulos, *Tetrahedron*, 1968, **24**, 2241.

15 J.-P. Surivet, C. Hubschwerlen and C. Zumbrunn Acklin (Actelion Percurex AG, Switz.), PCT Int. Appl. WO 2006038172 (Apr. 13, 2006); *Chem. Abstr.*, 2006, **144**, 390745; C. Hubschwerlen, J.-P. Surivet, C. Zumbrunn Acklin (Actelion Percurex AG, Switz.), PCT Int. Appl. WO 2006032466 (March 30, 2006); *Chem. Abstr.*, 2006, **144**, 350718.

16 G.A. Strohmeier and C.O. Kappe, *J. Comb. Chem.*, 2002, **4**, 154.

17 R. Ross, Jr., D.V. Nguyen, E.M. Szapacs, D.F. Smith and S.H. Shaber (Dow Agrosãences LLC, USA), US 6348627 (Feb. 9, 2002); *Chem. Abs.*, 2002, **136**, 183604.

18 A.K. Chatterjee, T.-L. Choi, D. Sanders and R.H. Grubbs, J. Am. Chem. Soc., 2003, **125**, 11360.

19 (a) C. Yi and R. Hua, Tetrahedron Lett., 2006, **47**, 2573; (b) H.U. Blaser and A. Spencer, J. Organomet. Chem., 1982, **233**, 267.

20 T. Ikemoto, S. Fukuyo and J. Yasuoka (Sumitomo Chemical Company, Ltd., Japan), PCT Int. Appl. WO 2006123762 (Nov. 23, 2006); *Chem. Abs.*, 2006, **145**, 505327.

21 R. Rendy, Y. Zhang, A. McElrea, A. Gomez and D.A. Klumpp, *J. Org. Chem.*, 2004, **69**, 2340.

22 P. Jeschke, W. Lindner, U. Wachendorff-Neumann and C. Erdelen (Bayer A.-G., Germany), DE 4124151 (Jan. 21, 1993); *Chem. Abs.*, 1993, **118**, 213088.