Available online at www.sciencedirect.com
SCIENCE DIRECT®
*Mendeleev Commun.*, 2007, **17**, 105–107
Mendeleev Communications

# Pentafluorophenylation of β-aminoacrylates

**Vitalij V. Levin,[a,†] Alexander D. Dilman,*[a,†] Pavel A. Belyakov,[a,†] Alexander A. Korlyukov,[b] Marina I. Struchkova[a] and Vladimir A. Tartakovsky[a]**

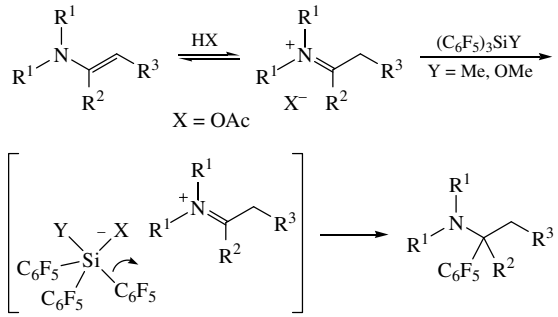
[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 135 5328; e-mail: dilman@ioc.ac.ru*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 135 5085*

DOI: 10.1016/j.mencom.2007.03.018

The pentafluorophenylation of β-aminoacrylates with $(C_6F_5)_3SiF$ in the presence of an alcohol and $Me_3SiCl$ furnishing derivatives of β-amino acids bearing the $C_6F_5$ group has been developed.

Fluorinated silanes of the general formula $R_fSiR_3$ have gained widespread use for the introduction of fluorinated fragments into organic molecules.[1] These reagents are usually used in combination with strong Lewis bases, which are required to activate carbon–silicon bonds through the generation of hypercoordinate silicon complexes.

Recently, we found that silanes containing three $C_6F_5$ groups at the silicon atom can be activated by mild Lewis bases.[2] In particular, unfunctionalised enamines easily undergo pentafluorophenylation in the presence of $(C_6F_5)_3SiY$ (Y = Me or OMe) and acetic acid (X = OAc) (Scheme 1). In this process, the acid plays a dual role: it protonates the enamine, whereas the formed acetate anion activates the silicon reagent.[3]



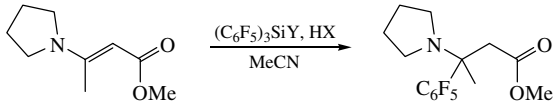
**Scheme 1**

We decided to extend the pentafluorophenylation reaction to the enamines containing an alkoxycarbonyl group (β-aminoacrylates), which are expected to afford $C_6F_5$-substituted β-amino acid derivatives. At the same time, fluorinated amino acids have attracted considerable attention from synthetic and medicinal chemists.[4]

Aminoacrylate **1a** derived from pyrrolidine and acetoacetic ester, which was selected as a model substrate, was investigated in reactions with different tris(pentafluorophenyl)silanes (Table 1).

The reactions of **1a** with $(C_6F_5)_3SiMe$ and $(C_6F_5)_3SiOMe$ under previously reported conditions were completely inefficient affording amine **2a** in very low yields (entries 1 and 2). A significant improvement was noted when more reactive fluorosilane $(C_6F_5)_3SiF$ was used leading to the product in 67% yield after 16 h at room temperature (entry 3). However, attempts to accelerate the reaction by heating were unsuccessful (entry 4). Presumably, the low reactivity of aminoacrylate **1a** is associated with its diminished basicity compared to that of unfunctionalised enamines.

**Table 1** Pentafluorophenylation of aminoacrylate **1a**.



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

| Entry | Y | HX | Conditions | Yield of **2a** (%) |
|---|---|---|---|---|
| 1 | Me | AcOH | 16 h, room temperature | < 5 |
| 2 | OMe | AcOH | 16 h, room temperature | 14[a] |
| 3 | F | AcOH | 16 h, room temperature | 67[b] |
| 4 | F | AcOH | 1 h, 82 °C | 42[a] |
| 5 | F | MeOH/$Me_3SiCl$ | 16 h, room temperature | 87[b] |
| 6 | F | MeOH/$Me_3SiCl$ | 1 h, room temperature | 72[b] |
| 7 | F | MeOH/$Me_3SiCl$ | 1 h, 82 °C | 89[b] |

[a]Determined by NMR spectroscopy. [b]Isolated yield.

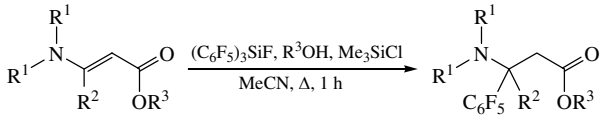
Recently, we found that the fluorosilane $(C_6F_5)_3SiF$ can serve as a source of nucleophilic $C_6F_5$ groups upon activation with the weakly basic chloride anion.[5] Based on this phenomenon, we performed the interaction of **1a** with $(C_6F_5)_3SiF$ in the presence of hydrochloric acid generated from methanol and $Me_3SiCl$ (entries 5–7). Variations in the reaction time and temperature demonstrated that, most conveniently, the process can be carried out at 82 °C for 1 h providing amine **2a** in 89% yield (entry 7).

Under the optimised conditions, a series of β-aminoacrylates were involved into pentafluorophenylation reaction‡ (Table 2). The enamine substituents exert a significant influence on the efficiency of the process. Thus, compounds **1b**,**c** derived from acetoacetic ester furnished good yields of the products (entries 1 and 2), whereas the introduction of an electron-withdrawing methoxy group resulted in a decrease of the yield to 67% (entry 3). For substrates **1e–h** having phenyl substituents at the β-carbon atom, amines **2e–h** were isolated in moderate yields, which can be probably explained by the steric hindrance of the carbon atom taking part in C–C bond formation. Unfortunately, substrates bearing a monosubstituted nitrogen atom, *i.e.*, derived from primary amines and acetoacetic ester,

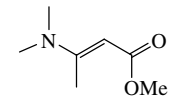
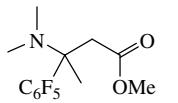
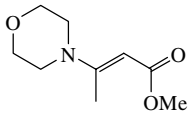
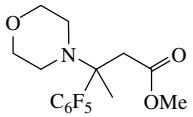
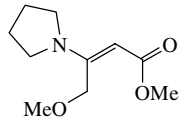
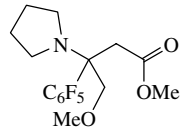
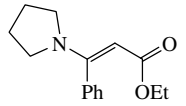
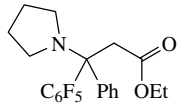
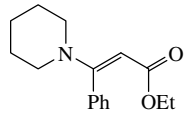
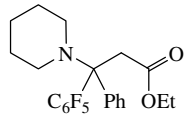
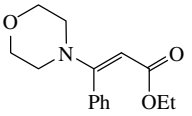
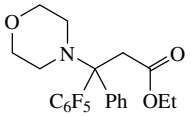
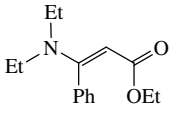
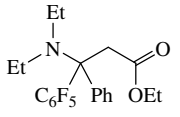
† V.V.L. is a former student of the Higher Chemical College (HCC) of the RAS (2000–2005).

A.D.D. and P.A.B., the former students of the HCC RAS (1993–1999), are now the lecturers at the HCC RAS.

**Table 2** Pentafluorophenylation of enamines **1**.




**1** **2**

| Entry | Enamine | Product | Yield of **2** (%)[a] |
|---|---|---|---|
| 1 |  **1b** |  **2b** | 86 |
| 2 |  **1c** |  **2c** | 76 |
| 3 |  **1d** |  **2d** | 67 |
| 4 |  **1e** |  **2e** | 66 |
| 5 |  **1f** |  **2f** | 57 |
| 6[b] |  **1g** |  **2g** | 26 (53[c]) |
| 7 |  **1h** |  **2h** | 35 |

[a]Isolated yield. [b]Reaction time, 2 h. [c]Determined by NMR spectroscopy.

‡ All reactions were performed under argon. Acetonitrile was distilled from $CaH_2$ and stored over MS 4 Å. Starting compounds were obtained according to published procedures: $(C_6F_5)_3SiF$;[5(a)] aminoacrylates **1a–d** (from β-ketoesters and amines)[6] and **1e–h** (by the addition of amines to ethyl phenylpropionate).[7]

*General procedure for the synthesis of amines* **2a–h**. $Me_3SiCl$ (141 μl, 1.1 mmol), aminoacrylate **1** (1 mmol), and an alcohol (MeOH for **1a–d** or EtOH for **1e–h**; 2.1 mmol) were successively added to a suspension of $(C_6F_5)_3SiF$ (548 mg, 1 mmol) in acetonitrile (2 ml) at room temperature, and the mixture was refluxed for 1 h (for **1a–f**,**h**) or 2 h (for **1g**). After cooling to room temperature, the solvent was evaporated in a vacuum; the residue was dissolved in 96% ethanol (2 ml), and a saturated aqueous $Na_2CO_3$ solution (0.5 ml) was added. After stirring for additional 3 min, the mixture was diluted with 15 ml of diethyl ether–hexanes (1:1), filtered through $Na_2SO_4$, and concentrated. For amines **2a–f**,**h**, the residue was chromatographed on silica gel with hexanes–EtOAc. For amine **2g**, the crude product solidified, the solid material was washed with hexane (2×0.5 ml) and recrystallised from hexane (2 ml).

were found less reactive, and low conversions (< 30%) were observed under standard conditions.

The structures of the products were confirmed by $^1H$, $^{13}C$ and $^{19}F$ NMR spectroscopy and elemental analysis.§ The crystal

§ *Methyl 3-pentafluorophenyl-3-pyrrolidin-1-ylbutyrate* **2a**: $R_f$ 0.36 (hexanes–EtOAc, 3:1); mp 56–57 °C. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$: 1.67–1.73 [m, 4H, $(CH_2)_2$], 1.80 (td, 3H, CMe, *J* 3.5 and 1.3 Hz), 2.45–2.64 [m, 4H, $N(CH_2)_2$], 2.68 (dt, 1H, $CH_AH_B$, *J* 16.6 and 2.6 Hz), 3.60 (s, 3H, OMe), 3.63 (d, 2H, $CH_AH_B$, *J* 16.6 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$: 23.1 (t, *J* 7.1 Hz), 23.4, 44.6 (t, *J* 5.3 Hz), 46.1, 51.4, 61.5 (t, *J* 5.3 Hz), 115.7 (t, *J* 13.8 Hz), 137.6 (dm, *J* 250.5 Hz), 139.6 (dm, *J* 253.3 Hz), 146.3 (dm, *J* 245.6 Hz), 171.5. $^{19}F$ NMR (188 MHz, $CDCl_3$) $\delta$: –163.76 (m, 2F, *meta*), –157.57 (tt, 1F, *para*, *J* 21.5 and 2.8 Hz), –136.77 (dm, 2F, *ortho*, *J* 20.8 Hz). Found (%): C, 53.48; H, 4.81; N, 4.14. Calc. for $C_{15}H_{16}F_5NO_2$ (%): C, 53.41; H, 4.78; N, 4.15.

*Methyl 3-dimethylamino-3-pentafluorophenylbutyrate* **2b**: oil, $R_f$ 0.40 (hexanes–EtOAc, 3:1). $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$: 1.71 (td, 3H, CMe, *J* 3.4 and 1.3 Hz), 2.19 (s, 6H, $NMe_2$), 2.64 (dt, 1H, $CH_AH_B$, *J* 16.3 and 2.3 Hz), 3.45 (d, 1H, $CH_AH_B$, *J* 16.3 Hz), 3.56 (s, 3H, OMe). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$: 20.6 (t, *J* 7.4 Hz), 38.6, 42.7 (t, *J* 4.7 Hz), 51.4, 63.2 (t, *J* 4.5 Hz), 116.9 (tm, *J* 12.6 Hz), 137.6 (dm, *J* 247.3 Hz), 139.7 (dm, *J* 253.1 Hz), 146.4 (dm, *J* 248.9 Hz), 171.4. $^{19}F$ NMR (188 MHz, $CDCl_3$) $\delta$: –164.05 (m, 2F, *meta*), –157.50 (t, 1F, *para*, *J* 21.5 Hz), –137.51 (d, 2F, *ortho*, *J* 19.4 Hz). Found (%): C, 50.22; H, 4.51; N, 4.42. Calc. for $C_{13}H_{14}F_5NO_2$ (%): C, 50.17; H, 4.53; N, 4.50.

*Methyl 3-morpholin-4-yl-3-pentafluorophenylbutyrate* **2c**: oil, $R_f$ 0.23 (hexanes–EtOAc, 3:1). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$: 1.75 (td, 3H, Me, *J* 3.49 and 1.1 Hz), 2.41–2.59 [m, 4H, $N(CH_2)_2$], 2.68 (dt, 1H, $CH_AH_B$, *J* 16.2 and 2.2 Hz), 3.39 (dm, 1H, $CH_AH_B$, *J* 16.2 Hz), 3.59 (s, 3H, OMe), 3.65 [t, 4H, $O(CH_2)_2$, *J* 4.6 Hz]. $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$: 21.2 (t, *J* 7.1 Hz), 43.7 (t, *J* 4.7 Hz), 46.7, 51.6, 63.4 (t, *J* 4.7 Hz), 67.4, 116.7 (t, *J* 13.2 Hz), 137.6 (dm, *J* 246.2 Hz), 139.9 (dm, *J* 254.7 Hz), 146.4 (dm, *J* 244.1 Hz), 171.2. $^{19}F$ NMR (188 MHz, $CDCl_3$) $\delta$: –163.57 (m, 2F, *meta*), –156.71 (tt, 1F, *para*, *J* 21.5 and 3.5 Hz), –137.2 (dm, 2F, *ortho*, *J* 20.1 Hz). Found (%): C, 51.01; H, 4.64; N, 3.95. Calc. for $C_{15}H_{16}F_5NO_3$ (%): C, 51.00; H, 4.56; N, 3.96.

*Methyl 4-methoxy-3-pentafluorophenyl-3-pyrrolidin-1-ylbutyrate* **2d**: oil, $R_f$ 0.39 (hexanes–EtOAc, 6:1). $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$: 1.63–1.70 [m, 4H, $(CH_2)_2$], 2.49–2.66 [m, 4H, $N(CH_2)_2$], 3.17 (dt, 1H, O=C–$CH_AH_B$, *J* 16.1 and 2.5 Hz), 3.33 (s, 3H, OMe), 3.48 (d, 1H, O=C–$CH_AH_B$, *J* 16.1 Hz), 3.59 (s, 3H, $CO_2Me$), 3.99–4.13 (m, 2H, $CH_2OMe$). $^{13}C$ NMR (63 MHz, $CDCl_3$) $\delta$: 23.2, 38.1 (t, *J* 5.8 Hz), 46.4, 51.3, 58.8, 65.7 (t, *J* 5.3 Hz), 74.8 (t, *J* 7.9 Hz), 113.0 (t, *J* 18.4 Hz), 137.6 (dm, *J* 247.8 Hz), 139.7 (dm, *J* 253.5 Hz), 146.3 (dm, *J* 247.3 Hz), 171.4. $^{19}F$ NMR (188 MHz, $CDCl_3$) $\delta$: –163.39 (m, 2F, *meta*), –156.94 (tt, 1F, *para*, *J* 21.5 and 2.8 Hz), –136.35 (dm, 2F, *ortho*, *J* 20.1 Hz). Found (%): C, 53.23; H, 5.19; N, 3.61. Calc. for $C_{16}H_{18}F_5NO_3$ (%): C, 53.54; H, 5.29; N, 3.67.

*Ethyl 3-pentafluorophenyl-3-phenyl-3-pyrrolidin-1-ylpropionate* **2e**: $R_f$ 0.34 (hexanes–EtOAc, 15:1); mp 57–58 °C. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$: 0.99 (t, 3H, $OCH_2Me$, *J* 7.2 Hz), 1.70–1.81 [m, 4H, $(CH_2)_2$], 2.41–2.63 [m, 4H, $N(CH_2)_2$], 2.98 (dt, 1H, $CH_AH_B$, *J* 15.1 and 2.4 Hz), 3.76–3.88 (m, 3H, $OCH_2$ + $CH_AH_B$), 7.22–7.33 (m, 3H) and 7.40–7.45 (m, 2H, Ph). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$: 13.8, 22.8, 46.7, 47.8 (t, *J* 5.3 Hz), 60.1, 68.6 (t, *J* 4.2 Hz), 111.4 (t, *J* 15.6 Hz), 126.2, 127.1, 127.7, 137.8 (dm, *J* 248.4 Hz), 139.9 (dm, *J* 253.6 Hz), 143.1, 146.1 (dm, *J* 247.3 Hz), 169.6. $^{19}F$ NMR (188 MHz, $CDCl_3$) $\delta$: –163.07 (m, 2F, *meta*), –156.31 (tt, 1F, *para*, *J* 21.5 and 3.1 Hz), –130.43 (dm, 2F, *ortho*, *J* 20.1 Hz). Found (%): C, 61.07; H, 4.97; N, 3.33. Calc. for $C_{21}H_{20}F_5NO_2$ (%): C, 61.02; H, 4.88; N, 3.39.

*Ethyl 3-pentafluorophenyl-3-phenyl-3-piperidin-1-ylpropionate* **2f**: $R_f$ 0.43 (hexanes–EtOAc, 10:1); mp 77–78 °C. $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$: 0.98 (t, 3H, Me, *J* 7.2 Hz), 1.33–1.49 (m, 2H) and 1.56–1.76 [m, 4H, $(CH_2)_3$], 2.19–2.62 [br. m, $\Delta\nu_{1/2}$ 39.1 Hz, 4H, $N(CH_2)_2$], 2.89 (dt, 1H, O=C–$CH_AH_B$, *J* 15.0 and 2.2 Hz), 3.82 (q, 2H, $CH_2Me$, *J* 7.2 Hz), 3.84 (d, 1H, O=C–$CH_AH_B$, *J* 15.0 Hz), 7.21–7.35 (m, 3H) and 7.39–7.48 (m, 2H, Ph). $^{13}C$ NMR (63 MHz, $CDCl_3$) $\delta$: 13.8, 24.5, 26.5, 46.5 (t, *J* 5.4 Hz), 48.4, 60.2, 71.2 (t, *J* 4.5 Hz), 111.9 (tm, *J* 14.8 Hz), 126.6, 127.1, 127.7, 137.8 (dm, *J* 250.4 Hz), 139.7 (dm, *J* 253.6 Hz), 142.2, 146.1 (dm, *J* 245.9 Hz), 170.0. $^{19}F$ NMR (188 MHz, $CDCl_3$) $\delta$: –163.15 (m, 2F, *meta*), –156.53 (tt, 1F, *para*, *J* 21.5 and 2.8 Hz), –130.55 (br. s, 2F, *ortho*, $\Delta\nu_{1/2}$ 308.2 Hz). Found (%): C, 61.94; H, 5.28; N, 3.37. Calc. for $C_{22}H_{22}F_5NO_2$ (%): C, 61.82; H, 5.19; N, 3.28.

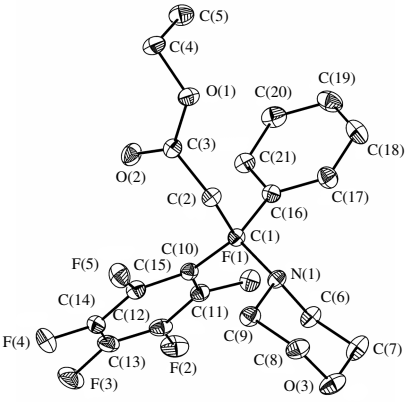



**Figure 1** Molecular structure of **2g** presented by thermal ellipsoids with 50% probability. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.4824(13), C(1)–C(10) 1.5521(14), N(1)–C(1)–C(2) 106.52(8), N(1)–C(1)–C(10) 109.92(8), N(1)–C(1)–C(10)–C(11) –82.91(11).

*Ethyl 3-morpholin-4-yl-3-pentafluorophenyl-3-phenylpropionate* **2g**: $R_f$ 0.32 (hexanes–EtOAc, 6:1); mp 119–121 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 0.99 (t, 3H, Me, $J$ 7.2 Hz), 2.31–2.64 [m, 4H, $N(CH_2)_2$], 2.97 (dt, 1H, O=C–C$H_A$H$_B$, $J$ 14.7 and 2.0 Hz), 3.62–3.89 [m, 7H, O=C–CH$_A$$H_B$ + $O(CH_2)_2$ + $OCH_2$], 7.18–7.46 (m, 5H, Ph). $^{13}$C NMR (63 MHz, $CDCl_3$) $\delta$: 13.8, 45.6 (t, $J$ 5.4 Hz), 47.8, 60.3, 67.2, 70.6 (t, $J$ 4.5 Hz), 111.6 (m), 126.6, 127.4, 127.9, 137.9 (dm, $J$ 251.3 Hz), 140.1 (dm, $J$ 254.9 Hz), 141.0, 146.1 (dm, $J$ 248.6 Hz), 169.6. $^{19}$F NMR (188 MHz, $CDCl_3$) $\delta$: –162.64 (m, 2F, *meta*), –155.54 (tt, 1F, *para*, $J$ 21.5 and 3.5 Hz), –130.55 (br. s, 2F, *ortho*, $\Delta\nu_{1/2}$ 357.7 Hz). Found (%): C, 58.74; H, 4.71; N, 3.17. Calc. for $C_{21}H_{20}F_5NO_3$ (%): C, 58.74; H, 4.69; N, 3.26.

*Ethyl 3-diethylamino-3-pentafluorophenyl-3-phenylpropionate* **2h**: $R_f$ 0.42 (hexanes–EtOAc, 10:1); mp 43–44 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 1.00 (t, 3H, $OCH_2$*Me*, $J$ 6.8 Hz), 1.16 [t, 6H, $N(CH_2$*Me*$)_2$, $J$ 7.2 Hz], 2.37–2.53 (m, 2H) and 2.55–2.71 [m, 2H, $N(CH_2)_2$], 2.86 (dt, 1H, O=C–C$H_A$H$_B$, $J$ 16.0 and 2.9 Hz), 3.77–3.91 (m, 3H, O=C–CH$_A$$H_B$ + $OCH_2$), 7.21–7.34 (m, 3H, Ph), 7.42–7.49 (m, 2H, Ph). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 13.8, 16.8, 45.1 (t, $J$ 2.4 Hz), 48.6 (t, $J$ 4.5 Hz), 60.1, 72.4 (t, $J$ 4.7 Hz), 113.6 (t, $J$ 15.3 Hz), 126.95, 127.02, 127.6, 137.9 (dm, $J$ 250.5 Hz), 139.7 (dm, $J$ 253.6 Hz), 143.3, 146.1 (dm, $J$ 246.8 Hz), 169.9. $^{19}$F NMR (188 MHz, $CDCl_3$) $\delta$: –162.75 (m, 2F, *meta*), –156.86 (tt, 1F, *para*, $J$ 21.5 and 3.5 Hz), –130.16 (d, 2F, *ortho*, $J$ 21.5 Hz). Found (%): C, 60.74; H, 5.13; N, 3.42. Calc. for $C_{21}H_{22}F_5NO_2$ (%): C, 60.72; H, 5.34; N, 3.37.

¶ *Crystallographic data for* **2g**: crystals of $C_{21}H_{20}F_5NO_3$ are monoclinic, space group $P2_1/c$, $a$ = 10.0888(4), $b$ = 18.4339(8) and $c$ = 10.4532(5) Å, $\beta$ = 100.9650(1)°, $V$ = 1908.55(14) Å$^3$, $Z$ = 4, $M$ = 429.38, $d_{calc}$ = = 1.494 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 1.32 cm$^{-1}$, $F$(000) = 888. Intensities of 25395 reflections were measured with a Smart APEX II diffractometer at 100 K [$\lambda$(MoK$\alpha$) = 0.71072 Å, $\omega$-scans, $2\theta < 61.3°$] and 5890 independent reflections ($R_{int}$ = 0.0289) were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against $F^2$ in the anisotropic approximation. Hydrogen atoms were calculated and refined in the rigid body approximation with the $U$(H) = 1.5$U_{eq}$(C) and $U$(H) = 1.2$U_{eq}$(C) for others. The refinement converged to $wR_2$ = 0.1382 and GOF = 1.013 for all independent reflections [$R_1$ = 0.0391 was calculated against $F^2$ for 4623 observed reflections with $I > 2\sigma(I)$].

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 637867. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2007.

and molecular structures of **2g** were studied by X-ray diffraction analysis (Figure 1).¶

In summary, a method for the synthesis of the esters of 3-amino-3-pentafluorophenylpropionic acid by the pentafluorophenylation of β-aminoacrylates with $(C_6F_5)_3SiF$ under acidic conditions was elaborated; the efficiency of the reaction depends on the character of substituents at the double bond.

This work was supported by the Ministry of Science (project no. MK-2235.2005.3) and the Russian Academy of Sciences (programme no. 8).

## References

1 (*a*) G. K. S. Prakash and A. K. Yudin, *Chem. Rev.*, 1997, **97**, 757; (*b*) G. K. S. Prakash and M. Mandal, *J. Fluorine Chem.*, 2001, **112**, 123; (*c*) R. P. Singh and J. M. Shreeve, *Tetrahedron*, 2000, **56**, 7613; (*d*) B. R. Langlois, T. Billard and S. Roussel, *J. Fluorine Chem.*, 2005, **126**, 173.

2 (*a*) A. D. Dilman, P. A. Belyakov, A. A. Korlyukov, M. I. Struchkova and V. A. Tartakovsky, *Org. Lett.*, 2005, **7**, 2913; (*b*) A. D. Dilman, D. E. Arkhipov, P. A. Belyakov, M. I. Struchkova and V. A. Tartakovsky, *Izv. Akad. Nauk., Ser. Khim.*, 2006, 498 (*Russ. Chem Bull., Int. Ed.*, 2006, **55**, 517); (*c*) V. V. Levin, A. D. Dilman, P. A. Belyakov, A. A. Korlyukov, M. I. Struchkova, M. Y. Antipin and V. A. Tartakovsky, *Synthesis*, 2006, 489.

3 A. D. Dilman, V. V. Levin, P. A. Belyakov, M. I. Struchkova and V. A. Tartakovsky, *Synthesis*, 2006, 447.

4 (*a*) S. Fustero, B. Pina, E. Salavert, A. Navarro, M. C. Ramirez de Arellano and A. S. Fuentes, *J. Org. Chem.*, 2002, **67**, 4667; (*b*) F. Huguenot and T. Brigaud, *J. Org. Chem.*, 2006, **71**, 2159; (*c*) X. Liu, J. Zhao, G. Jin, G. Zhao, S. Zhua and S. Wang, *Tetrahedron*, 2005, **61**, 3841; (*d*) T. Shimada, M. Yoshioka, T. Konno and T. Ishihara, *Chem. Commun.*, 2006, 3628; (*e*) Z.-X. Jiang and F.-L. Qing, *J. Org. Chem.*, 2004, **69**, 5486; (*f*) B. Crousse, S. Narizuka, D. Bonnet-Delpon and J.-P. Bégué, *Synlett.*, 2001, 679; (*g*) S. Fustero, E. Salavert, B. Pina, C. Ramirez de Arellano and A. Asensio, *Tetrahedron*, 2001, **57**, 6475; (*h*) N. N. Sergeeva, A. S. Golubev, L. Hennig, M. Findeisen, E. Paetzold, G. Oehme and K. Burger, *J. Fluorine Chem.*, 2001, **111**, 41; (*i*) P. Davoli, A. Forni, C. Franciosi, I. Moretti and F. Prati, *Tetrahedron: Asymmetry*, 1999, **10**, 2361; (*j*) V. A. Soloshonok, I. V. Soloshonok, V. P. Kukhar and V. K. Svedas, *J. Org. Chem.*, 1998, **63**, 1878; (*k*) A. Abouabdellah, J.-P. Bégué, D. Bonnet-Delpon and T. T. T. Nga, *J. Org. Chem.*, 1997, **62**, 8826; (*l*) K. Uneyama, J. Hao and H. Amii, *Tetrahedron Lett.*, 1998, **39**, 4079; (*m*) W. Cen, Y. Ni and Y. Shen, *J. Fluorine Chem.*, 1995, **73**, 161; (*n*) V. A. Soloshonok, A. G. Kirilenko, S. V. Galushko and V. P. Kukhar, *Tetrahedron Lett.*, 1994, **35**, 5063; (*o*) *Fluorine-Containing Amino Acids: Synthesis and Properties*, eds. V. P. Kukhar and V. A. Soloshonok, Wiley, Chichester, 1994.

5 (*a*) A. D. Dilman, V. V. Levin, M. Karni and Y. Apeloig, *J. Org. Chem.*, 2006, **71**, 7214; (*b*) V. V. Levin, A. D. Dilman, P. A. Belyakov, M. I. Struchkova and V. A. Tartakovsky, *Tetrahedron Lett.*, 2006, **47**, 8959.

6 H. Bohme, J. G. Grantz, F. Martin, R. Matusch and J. Nehme, *Liebigs Ann. Chem.*, 1980, 394.

7 I. Ya. Postovskii, E. I. Grinblat and L. F. Trefilova, *Zh. Obshch. Khim.*, 1961, **31**, 400 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1961, **31**, 363].

*Received: 26th October 2006; Com. 06/2805*