Supporting Information

Preparation of Fluoroalkyl Imines, Amines, Enamines, Ketones, α-Amino Carbonyls, and α-Amino Acids from Primary Enamine Phosphonates.[#]

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Table of contents: General methods, preparation and Elemental Analysis and Spectral data (^{1}H NMR, ^{13}C NMR, IR and ^{19}F-NMR) for compounds **1b-f**, **5b-d**, **6b-k**, **7b-h**, **8b-e**, **9b-c**, **10a-c**, **11b** and **14**. (16 pages)

[#] *In memoriam of our college Dr. Juan Carlos Del Amo of Universidad Complutense of Madrid, died March 11th.*

General methods : Analytical t.l.c. was performed on 0.25mm silica gel plates. Visualization was accomplished by *UV* light and $KMnO_4$. Solvent used in reactions was freshly distilled from appropiate drying agent before use: THF (sodium benzophenone ketyl). All other reagents were recrystallized or distilled as necessary. Infrared spectra were taken on a IRFT Magna. ^{1}H-NMR spectra were recorded on a 300 MHz spectrometer using tetramethylsilane (0.00 ppm) or chloroform (7.26 ppm) as an internal reference in $CDCl_3$ solutions. ^{13}C-NMR spectra were recorded at 75 MHz with chloroform (77.0 ppm) as an internal reference in $CDCl_3$ solutions. ^{31}P-NMR spectra were recorded at 120 MHz with 85% phosphoric acid as an external reference (0.0 ppm). ^{19}F-NMR spectra were recorded at 282 MHz with $FCCl_3$ as an external reference (0.0 ppm). Elemental analyses were performed in a CHNS-932 instrument. Chemical shifts are given in ppm (δ) and multiplicities are indicated by s (singlet), d (doublet), dd (double doublet), t (triplet), dt (double triplet), q (quadruplet) or m (multiplet). Coupling constants (*J*) are reported in Hertz. Infrared spectra (IR) were obtained as solids in KBr and peaks are reported in cm^{-1}. Mass spectra (EI) were obtained with an ionization voltage of 70 eV and data are reported in the form m/z (intensity relative to base = 100). All reactions were performed in flame-dried glassware under an inert atmosphere of dry N_2.

General procedure for preparation of fluorinated β-enaminophosphonates (1). A solution of diethylphosphonate **2** (5 mmol) in THF (10ml) was added to a solution of base (MeLi or LDA) (5mmol) in THF (15ml) at –78ºC and under N_2 atmosphere. The mixture was stirred for 1h at –78ºC. Then the corresponding fluorinated nitrile **3** was added into the solution. The reaction was allowed to warm to room temperature. The resulting mixture was washed three times with water (20ml), extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The crude product was purified by chromatography using silica-gel (hexane/ethyl acetate).

Diethyl 2-amino-2-pentafluoroethylethenylphosphonate (1b): (1.26 g, 85%) obtained as a pale yellow oil. Rf 0.87(ethyl acetate). IR (neat) 3324, 3214, 1205, 1044 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$)

δ 5.96 (bs, 2H, NH_2), 4.21 (d, *J* = 8.7 Hz, 1H, CH), 3.97 (m, 4H, OCH_2), 1.24 (m, 6H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 148.7 (dt, *J* = 24.2, 8.1 Hz, C-N), 109.8-123.9 (m, C_2F_5), 78.0 (d, *J* = 191.8 Hz, CH), 61.5 (OCH_2), 15.9 (CH_3); ^{31}P-NMR (120 MHz, $CDCl_3$) δ 21.6; ^{19}F-NMR (282 MHz, $CDCl_3$) δ −71.6 (CF_3), −87.4 (CF_2). Anal. Calcd for $C_8H_{13}F_5NO_3P$: C, 32.34; H, 4.41; N, 4.71. Found: C, 32.27; H, 4.33; N, 4.79.

Diethyl 2-amino-2-perfluorohepthylethenylphosphonate (1c): (2.38 g, 87%) obtained as a pale yellow oil. Rf 0.89(ethyl acetate). IR (neat) 3317, 3229, 1260, 1058 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.78 (bs, 2H, NH_2), 4.33 (d, *J* = 8.1 Hz, 1H, CH), 3.98 (m, 4H, OCH_2), 1.25 (m, 6H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 148.8 (dt, *J* = 24.9, 7.6 Hz, C-N), 106.6-123.2 (m, C_7F_{15}), 80.1 (d, *J* = 190.8 Hz, CH), 61.7 (OCH_2), 16.0 (CH_3); ^{31}P-NMR (120 MHz, $CDCl_3$) δ 21.3; ^{19}F-NMR (282MHz, $CDCl_3$) δ −81.2, −118.6, −121.8, −122.3, −122.7, −123.1, −126.5. Anal. Calcd for $C_{13}H_{13}F_{15}NO_3P$: C, 28.54; H, 2.39; N, 2.56. Found: C, 28.32; H, 2.51; N, 2.63.

Diethyl 2-amino-3-fluoro-1-propenylphosphonate (1d): (79%) obtained as a pale yellow oil. Rf 0.36(hexane/ethyl acetate, 1/1). IR (neat) 3411, 3324, 3203, 2984, 1639cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.76 (bs, 2H, NH_2), 4.72-4.88 (d, *J* = 46.8 Hz, 2H, CH_2F), 3.87-4.07 (m, 4H, OCH_2), 3.73-3.77 (d, *J* = 12.2 Hz, 1H, CH), 1.22-1.28 (m, 6H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 158.3-158.6 (dd, *J* = 17.1, 6.0 Hz, C-N), 80.5-83.1 (dd, *J* = 174.7, 24.9 Hz, CH_2F), 69.1-71.7 (d, *J* = 195.4 Hz, =CH), 60.8 (OCH_2), 15.9 (CH_3); ^{31}P-NMR (120 MHz, $CDCl_3$) δ 24.8; ^{19}F-NMR (282 MHz, $CDCl_3$) δ (−225.1)–(−225.4). Anal. Calcd for $C_7H_{15}FNO_3P$: C, 39.81; H, 7.16; N, 6.63. Found: C, 39.89; H, 7.24; N, 6.70.

Diethyl 2-amino-3,3,3-trifluoro-1-methyl-1-propenylphosphonate (1e): **(**42%) obtained as a pale yellow oil. Rf 0.36(hexane/ethyl acetate, 1/1). IR (neat) 3395, 3313, 1639, 1180, 1026 cm^{-1}^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.76 (bs, 2H, NH_2), 3.90-4.09 (m, 4H, OCH_2), 1.66-1.73 (dq, *J* = 14.8, 2.4 Hz, 3H, CH_3), 1.25-1.30 (m, 6H, $CH_2C\underline{H}_3$); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.1 (m, C-N), 121.0 (dq, *J* = 279.0, 31.2 Hz, CF_3), 87.2 (d, *J* = 181.3 Hz, =C-P), 61.4, 61.5 (OCH_2), 15.9, 16.0 ($CH_2\underline{C}H_3$), 11.5

($\underline{C}H_3$-C=); ^{31}P-NMR (120 MHz, $CDCl_3$) δ 25.5; ^{19}F-NMR (282 MHz, $CDCl_3$) δ −66.7. Anal. Calcd for $C_8H_{15}F_3NO_3P$: C, 36.79; H, 5.79; N, 5.36. Found: C, 36.70; H, 5.77; N, 5.40.

Diethyl 2-amino-1-methyl-2-perfluorohepthylethenylphosphonate (1f): (2.30g, 82%) obtained as a pale yellow oil. Rf 0.88 (ethyl acetate). IR (neat) 3304, 3202, 1260, 1028 cm^{-1}^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.77 (bs, 1H, NH), 3.92-3.99 (m, 4H, OCH_2), 1.65-1.71 (d, *J* = 14.4 Hz, 3H, CH_3), 1.24-1.28 (m, 6H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 143.2 (dt, *J* = 25.2, 7.4 Hz, C-N), 1119.4-106.1 (m, C_7F_{15}), 91.2 (d, *J* = 176.2 Hz, =C), 61.4, 61.3 (OCH_2), 19.5 (CH_3), 16.1 (CH_3); ^{31}P-NMR (120 MHz, $CDCl_3$) δ 24.6; ^{19}F-NMR (282 MHz, $CDCl_3$) δ −126.6, −123.1, −122.4, −122.0, −199.9, −112.7, −81.3. Anal. Calcd for $C_{14}H_{15}F_{15}NO_3P$: C, 29.94; H, 2.67; N, 2.49. Found: C, 29.53; H, 2.99; N, 2.61.

General procedure for the preparation of fluorinated α,β-unsaturated imines (5). Butyllithium (1.6M in hexanes) (2mmol) was added to a solution of fluorinated enaminophosphonate **1** (5mmol) in THF at 0ºC and under N_2 atmosphere. The mixture was stirred for 1h at the same temperature. Then, a solution of the corresponding aldehyde (2mmol) in THF (15ml) was added and the reaction was stirred at room temperature until t.l.c. showed the disappearance of the enaminophosphonate **1**. The resulting mixture was extracted with CH_2Cl_2 and filtered through celite and concentrated under vacuum. 1-Aza-butadienes **5** are unstable, but they can be isolated and kept in the refrigerator 2-3 days.

6-Phenyl-2-trifluoromethyl-1-aza-1,3,5-hexatriene (5b): (382mg, 85%) obtained as a pale yellow oil. IR (neat) 3291, 2982, 1616 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.25 (bs, 1H, NH), 10.20 (bs, 1H, NH), 7.40-7.17 (m, 14H, H_{ar}), 6.89-6.76 (m, 2H, =CH), 6.35 (d, *J* = 15.7 Hz, 1H, =CH), 6.12 (d, *J* = 15.7 Hz, 1H, =CH); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 163.3 (q, *J* = 32.4 Hz, C=N), 161.8 (q, *J* = 31.9 Hz, C=N), 141.2 (=CH),140.4, 139.9 (Car-H), 139.7, 135.7 (Car-C), 135.5, 128.9 (=CH), 128.7, 128.6 (Car-H), 128.5, 128.2 (=CH), 126.9 (Car-H), 126.8, 126.2 (=CH), 122.3, 121.5, 120.0 (q, *J* = 279.3 Hz, CF_3), 117.9 (q, *J* = 282.2 Hz, CF_3); ^{19}F-NMR (282 MHz, $CDCl_3$) δ −73.4, −71.6.

2-Pentafluoroethyl-4-(2-thienyl)-1-aza-1,3-butadiene (5c): (423mg, 83%) obtained as a pale yellow oil. B.p. 39-40 (10^{-5} Torr). IR (neat) 3284, 3260, 1675, 1589 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.61 (bs, 1H, NH), 10.28 (bs, 1H, NH), 7.79 (d, *J* = 15.7 Hz, 1H, =CH), 7.24-7.22 (m, 3H, =CH, H_{ar}),.7.12-7.06 (m, 2H, H_{ar}), 6.92-6.89 (m, 2H, =CH), 6.48 (d, *J* = 15.7 Hz, 1H, =CH), 6.35 (d, *J* = 16.0 Hz, 1H, =CH); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 163.3 (t, *J* = 23.7 Hz, C=N), 161.6 (t, *J* = 23.7 Hz, C=N), 142.4 (=CH),139.9, 139.3 (C_{ar}-C), 138.1, 130.9 (C_{ar}-H), 130.8, 128.4, 128.2, 128.0, 127.9, 116.9 (=CH), 116.6, 124.1-108.5(m, C_2F_5); ^{19}F-NMR (282 MHz, $CDCl_3$) δ −122.7, −118.0, −83.2, −82.2.

3-Methyl-4-p-tolyl-2-trifluoromethyl-1-aza-1,3-butadiene (5d): (395mg, 87%) obtained as a pale yellow oil. IR (neat) 3301, 2961, 1605 cm^{-1};^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.38-7.20 (m, 10H, =CH, H_{ar}), 2.39 (s, 6H, 2 x CH_3), 2.24 (s, 6H, 2 x $CH_{3)}$; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 168.6 (q, *J* = 30.0 Hz, C=N), 164.9 (q, *J* = 32.7 Hz, C=N), 138.5 (Car-C), 138.2, 138.0 (=CH), 136.4, 133.0 (Car-C, =C-C), 132.4, 129.5 (Car-C), 129.3, 128.9, 120.3 (q, *J* = 280.5 Hz, CF_3), 118.5 (q, *J* = 282.5 Hz, CF_3), 21.2 (CH_3), 14.5, 13.9; ^{19}F-NMR (282 MHz, $CDCl_3$) δ −67.8, −67.2.

General procedure for the preparation of fluorinated α,β-unsaturated ketones (6). Butyllithium (1.6M in hexanes) (5mmol) was added to a solution of fluorinated enaminophosphonate **1** (5mmol) in THF at 0ºC and under N_2 atmosphere. The mixture was stirred for 1h at the same temperature. Then, a solution of the corresponding aldehyde (5mmol) in THF (15ml) was added and the reaction was stirred at room temperature until t.l.c. showed the disappearance of the enamino phosphonate **1**. A solution of H_2SO_4 5M (3ml) was added and the reaction was stirred for 1 h. The organic layer was extracted with Et_2O, washed with water, dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated under vacuum. The crude product was purified by chromatography using silica-gel (hexane/ethyl acetate).

***(E)*-6-Phenyl-1,1,1-trifluoro-3,5-hexadien-2-one (6b)** (380mg, 84%) obtained as a pale yellow oil. Rf 0.86 (ethyl acetate). IR (neat) 2976, 1691, 1221, 1098 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 11.0 Hz, *J* = 15.3 Hz 1H, =CH), 7.29-7.57 (m, 5H, H_{arom}), 7.18 (d, *J* = 15.5 Hz, 1H, =CH), 7.01 (dd, *J* = 11.1 Hz, *J* = 15.4 Hz, 1H, =CH), 6.58 (d, *J* = 15.1 Hz, 1H, =CH); ^{13}C-NMR (75 MHz, $CDCl_3$) δ

180.0 (q, *J* = 35.2 Hz, C=O), 149.9 (CH), 146.2, 135.3 (C_{arom}-C), 126.3-130.3 (C_{arom}-H), 125.9 (=CH), 119.8, 116.3(q, *J* = 290.6 Hz, CF_3); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -77.7. Anal. Calcd for $C_{12}H_9F_3O$: C, 63.72; H, 3.98. Found: C, 63.81; H, 3.94.

***(E)*-1,1,1-Trifluoro-4-(2-furyl)-3-buten-1-one (6c)** (239mg, 63%) obtained as a pale yellow oil. Rf 0.48 (hexane/ethyl acetate,7/3). IR (neat) 2924, 1719, 1605 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 15.6 Hz, 1H, =CH), 7.50-7.51 (m, 1H, H_{arom}), 6.76-6.80 (m, 2H, H_{arom}), 6.47 (dd, *J* = 1.8 Hz, *J* = 3.5 Hz, 1H, H_{arom}); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 179.8 (q, *J* = 35.8 Hz, C=O), 150.5 (C_{arom}-C), 146.9 (C_{arom}-H, =CH), 134.7,119.8,113.8, 113.4, 116.4 (q, *J* = 290.5 Hz, CF_3); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -78.0. Anal. Calcd for $C_8H_5F_3O_2$: C, 50.54; H, 2.65. Found: C, 50.72; H, 2.55.

***(E)*-1,1,1-Trifluoro-4p-fluorophenyl-3-buten-2-one (6d)** (283mg, 65%) obtained as a white solide. Rf 0.64 (hexane/ethyl acetate,7/3); mp 45-46^{0}C; IR (neat) 2925, 1713, 1592 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 15.9 Hz, 1H, =CH), 7.56-7.61 (m, 2H, H_{arom}), 7.04-7.10 (m, 2H, H_{arom}), 6.92 (d, *J* = 15.9 Hz, 1H, =CH); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 179.7 (q, *J* = 35.2 Hz, C=O), 165.0 (d, *J* = 255.3 Hz, C_{arom}-F), 148.6 (=CH), 131.3 (d, *J* = 9.1 Hz, C_{arom}-H), 129.7 (C_{arom}-C), 116.3 (q, *J* = 290.6 Hz, CF_3), 115.7 (q, *J* = 22.2 Hz, C_{arom}-H); ^{19}F-NMR (282 MHz, $CDCl_3$) δ −106.2, -78.2. Anal. Calcd for $C_{10}H_6F_4O$: C, 55.06; H, 2.77. Found: C, 55.29; H, 2.65.

***(E)*-4-Ciclohexyl-1,1,1-trifluoro-3-buten-2-one (6e)** (283mg, 65%) obtained as a pale yellow oil. Rf 0.73 (hexane/ethyl acetate,7/3); IR (neat) 2931, 1727, 1039 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.16-7.23 (d, *J* = 15.9Hz, 1H, CH), 6.26-6.31 (d, *J* = 15.9 Hz, 1H, =CH), 1.07-1.75 (m, 11H, $H_{cyclohex}$); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 179.1-180.5 (q, *J* = 35.2 Hz, C=O), 160.9 (CH), 118.7 (CH), 110.3-121.8 (q, *J* = 291.1 Hz, CF_3), 40.1 ($CH_{cyclohex}$), 25.2, 25.5, 31.0 ($CH_{2\ cyclohex}$); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -77.9. Anal. Calcd for $C_{10}H_{13}F_3O$: C, 58.25; H, 6.35. Found: C, 58.13; H, 6.39.

***(E)*-1-Fluoro-4-p-fluorophenyl-3-buten-2-one (6f)** (204mg, 56%) obtained as a pale yellow oil. Rf 0.50 (hexane/ethyl acetate,7/3); IR (neat) 2930, 1691, 1598, 1509, 1037 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.2 Hz, 1H, CH), 7.48-7.54 (m, 2H, H_{arom}), 6.98-7.05 (m, 2H, H_{arom}), 6.83-6.89

(dd, *J* = 16.2, *J* = 3.0 Hz, 1H, CH), 4.88-5.04 (d, *J* = 47.5, 2H, CH_2F); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 194.3-194.5 (d, *J* = 18.6 Hz, C=O), 165.9 (C_{arom}), 162.6 (C_{arom}), 143.4 (=CH), 130.5-130.6 (d, *J* = 9.1 Hz, C_{arom}), 119.4 (=CH), 115.9-116.2 (d, *J* = 22.1 Hz, C_{arom}), 83.4-85.8 (d, *J* = 184.3 Hz, CH_2F); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -108.3 (Ar-F), -229.1 (t, *J* = 47.3 Hz, CH_2F), -108.3. Anal. Calcd for $C_{10}H_8F_2O$: C, 65.93; H, 4.43. Found: C, 65.78; H, 4.48.

***(E)*-4,4,5,5,5-Pentafluoro-1-*p*-tolyl-1-penten-3-one (6g)** (433mg, 82%) obtained as a pale yellow oil. Rf 0.86 (ethyl acetate); IR (neat) 2928, 1599, 1204, 1086 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 15.8 Hz, 1H, CH), 7.15-7.49 (m, 4H, H_{arom}), 6.99 (d, *J* = 15.7 Hz, 1H, CH), 2.35 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 182.2 (t, *J* = 25.4 Hz, C=O), 150.2 (=CH), 143.5 (C_{arom}), 127.3-130.0 (C_{arom}), 117.4-120.3 (C_2F_5), 115.6 (=CH), 21.5 (CH_3); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -53.2, -94.9 . Anal. Calcd for $C_{12}H_9F_5O$: C, 54.54; H, 3.41. Found: C, 54.48; H, 3.46.

***(E)*-4,4,5,5,5-Pentafluoro-1-(2-tienyl)-1-penten-3-one (6h)** (328mg, 64%) obtained as a pale yellow oil. Rf 0.57 (hexane/ethyl acetate,7/3); IR (neat) 3093, 1701, 1589, 1509, 1196 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 15.4 Hz, 1H, =CH), 7.57-7.58 (m, 1H, H_{arom}), 7.48-7.49 (m, 1H, H_{arom}), 7.12-7.16 (m, 1H, H_{arom}), 6.88 (d, *J* = 15.4, 1H, =CH); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 181.6 (t, *J* = 27.7 Hz, C=O), 141.8 (=CH), 138.9 (C_{arom}), 134.9 (C_{arom}), 131.9, 128.8, 114.9 (=CH), 103.9-123.7 (m, C_2F_5); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -123.9, -82.3. Anal. Calcd for $C_9H_5F_5OS$: C, 42.20; H, 1.93; S, 12.51. Found: C, 42.45; H, 2.09; S, 12.40.

***(E)*-1,1,1-Trifluoro-3-methyl-4-*p*-tolyl-3-buten-2-one (6i)** (324mg, 71%) obtained as a pale yellow oil. Rf 0.60 (hexane/ethyl acetate,1/1);). IR (neat) 2919, 1694, 1177, 1142 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 1H, =CH), 7.33 (d, *J* = 8.1 Hz, 2H, H_{arom}), 7.19 (d, *J* = 8.1 Hz, 2H, H_{arom}), 2.34 (s, 3H, CH_3), 2.11 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 182.2 (q, *J* = 32.7 Hz, C=O), 145.9 (=CH), 140.6 (C_{arom}, =C), 131.8, 130.6 (C_{arom}), 130.0, 129.4, 116.9 (q, *J* = 292.0 Hz, CF_3), 21.4 (CH_3), 13.3 (CH_3); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -69.1 . Anal. Calcd for $C_{12}H_{11}F_3O$: C, 63.16; H, 4.86. Found: C, 63.41; H, 4.77.

***(E)*-1,1,1-Trifluoro-4-(2-furyl)-3-methyl-3-buten-2-one (6j)** (253mg, 62%) obtained as a pale yellow oil. Rf 0.63 (hexane/ethyl acetate,7/3).. IR (neat) 2931, 1689, 1618, 1146 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.60-7.61 (m, 1H, H_{arom}), 7.38 (s, 1H, =CH), 6.80-6.81 (d, *J* = 3.5 Hz, 1H, H_{arom}), 6.52-6.54 (m, 1H, H_{arom}), 2.16 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 181.6 (q, *J* = 33.2 Hz, C=O), 150.8 (C_{arom}), 146.3 (C_{arom}), 131.2 (=CH), 126.2 (=C), 119.2 (C_{arom}), 116.9 (q, *J* = 291.6 Hz, CF_3), 113.0 (C_{arom}), 12.9 (CH_3); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -69.2. Anal. Calcd for $C_9H_7F_3O_2$: C, 52.95; H, 3.46. Found: C, 52.79; H, 3.40.

***(E)*-6-Phenyl-1,1,1-trifluoro-3,5-dimethyl-3,5-hexadien-2-one (6k)** (361mg, 71%) obtained as a pale yellow oil. Rf 0.63 (hexane/ethyl acetate,7/3). IR (neat) 2929, 1693, 1598, 1177 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.26-7.36 (m, 6H, H_{arom}, =CH), 6.74 (s, 1H, =CH), 2.12 (s, 3H, CH_3), 2.08 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 182.4 (q, *J* = 32.8 Hz, C=O), 150.5 (=C), 138.8, 133.8-136.2 (C_{arom}, =C), 129.4 (C_{arom}), 128.4, 128.8, 116.9 (q, *J* = 291.6 Hz, CF_3), 18.3 (CH_3), 13.4 (CH_3); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -69.5. Anal. Calcd for $C_{14}H_{13}F_3O_2$: C, 66.14; H, 5.15. Found: C, 66.38; H, 5.01.

General procedure for the preparation of fluorinated allylic amines (7). Butyllithium (1.6M in hexanes) (5mmol) was added to a solution of fluorinated enaminophosphonate **1** (5mmol) in THF at 0ºC and under N_2 atmosphere. The mixture was stirred for 1h at the same temperature. Then, a solution of the corresponding aldehyde (5mmol) in THF (15ml) was added and the reaction was stirred at room temperature until t.l.c. showed the disappearance of the enaminophosphonate **1**. The reaction was cooled to –78ºC, $NaBH_4$ (10mmol) and MeOH (25ml) was added. After 1h at –78ºC, the mixture was warmed to r.t. and 3% HCl (15ml) was added and stirring continued for 1h. The mixture was made alkaline (pH 12) with NaOH pellets and extracted with EtOAc (3x50ml). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated under vacuum. The crude product was purified by chromatography using silica-gel (hexane/ethyl acetate).

6-Phenyl-1,1,1-trifluoro-3,5-hexadien-1-amine (7b) (236mg, 54%) obtained as a brown solid. M.p. 51-52ºC. Rf 0.25 (hexane/ethyl acetate,7/3). Rf 0.85 (ethyl acetate). IR (KBr) 3391, 3369, 1621, 1158 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.13-7.45 (m, 5H, H_{arom}), 6.45-6.75 (m, 3H, 3 x CH), 5.64-5.71 (dd, *J* = 14.9, 6.4 Hz, 1H, C<u>H</u>-C-NH_2), 3.77-3.86 (dq, *J* = 7.0, 6.4 Hz, 1H, CH-CF_3), 1.47 (bs, 2H, NH_2); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 136.7 (C_{arom}), 134.8 (C_{arom}, CH), 134.4, 128.6, 127.9, 127.3, 126.5, 125.9, 120.1-131.3 (q, *J* = 281.5 Hz, CF_3), 55.0-56.2 (q, *J* = 30.2 Hz, CH-NH_2); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -78.3. Anal. Calcd for $C_{12}H_{12}F_3N$: C, 63.43; H, 5.32; N, 6.16. Found: C, 63.29; H, 5.36; N, 6.21.

4,4,5,5,5-Pentafluoro-1-*p*-tolyl-1-penten-3-amine (7c) (387mg, 73%) obtained as a pale yellow oil. Rf 0.88 (ethyl acetate). IR (neat) 3382, 3291, 2934, 1117 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.06-7.24 (m, 4H, H_{arom}), 6.65 (d, *J* = 15.9 Hz, 1H, CH), 6.05 (dd, *J* = 15.9, 7.3 Hz, 1H, CH), 3.96 (m, 1H, CH), 2.28 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 138.4 (C_{arom}), 134.8 (CH), 133.0, 129.3 (C_{arom}), 126.6, 121.2 (CH), 111.2-118.7 (C_2F_5), 55.2 (t, *J* = 23.1 Hz, CH), 21.2 (CH_3); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -92.9(CF_2), -81.0 (CF_3). Anal. Calcd for $C_{12}H_{12}F_5N$: C, 54.34; H, 4.56; N, 5.28. Found: C, 54.21; H, 4.48; N, 5.41.

4,4,5,5,5-Pentafluoro-1-*p*-fluorophenyl-1-penten-3-amine (7d) (280mg, 52%) obtained as a pale yellow oil. Rf 0.28 (hexane/ethyl acetate,7/3). IR (neat) 3408, 3330, 3046, 2929, 1603, 1209 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33-7.38 (m, 2H, H_{arom}), 6.99-7.04 (m, 2H, H_{arom}), 6.72 (d, *J* = 15.9 Hz, 1H, CH), 6.06 (dd, *J* = 15.9, 7.3 Hz, 1H, CH), 3.97-4.08 (m, 1H, CH-CF_2), 1.55 (bs, 2H, NH_2); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247.8 Hz, C_{arom} -F), 133.6 (=CH), 132.0 (C_{arom}-C), 128.2 (d, *J* = 8.1 Hz, C_{arom} -H), 122.1 (=CH), 115.4 (d, *J* = 21.6 Hz, C_{arom} -H), 110.3-125.5 (m, C_2F_5), 54.9 (t, *J* = 23.2 Hz, C-N); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -125.5, -125.4, -114.1, -81.7. Anal. Calcd for $C_{11}H_9F_6N$: C, 49.08; H, 3.37; N, 5.20. Found: C, 49.40; H, 3.27; N, 5.33.

5-Phenyl-1-perfluoroheptyl-2,4-pentadien-1-amine (7e) (811mg, 77%) obtained as a pale yellow oil. Rf 0.87 (ethyl acetate). IR (neat) 3427, 3357, 3027, 1206, 1071 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$)

δ 7.17-7.35 (m, 5H, H_{arom}), 6.72 (dd, *J* = 15.4, 10.5 Hz, 1H, =CH), 6.55 (d, *J* = 15.5 Hz, 1H, =CH), 6.45 (dd, *J* = 15.1, 10.5 Hz, 1H, CH), 5.59 (dd, *J* = 15.1, 7.3 Hz, 1H, =CH), 3.97-4.04 (m, 1H, CH-CF); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 125.7-141.2 (C_{arom} , =CH), 106.8-119.6 (m, C_7F_{15}), 55.5 (t, *J* = 23.2 Hz, C-N); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -126.4, -123.0, -122.5, -122.2, -121.9,-116.6, -81.1. Anal. Calcd for $C_{18}H_{12}F_{15}N$: C, 40.99; H, 2.27; N, 2.65. Found: C, 41.10; H, 2.18; N, 2.53.

1-Fluoro-4-*p*-fluorophenyl-3-buten-2-amine (7f) (209mg, 57%) obtained as a pale red oil. Rf 0.16 (ethyl acetate). IR (neat) 3380, 3297, 1601, 1509, 1227 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.23-7.25 (m, 2H, H_{arom}), 6.84-6.89 (m, 2H, H_{arom}), 6.52-6.57 (d, *J* = 16.0 Hz, 1H, CH), 5.94-6.02 (dd, *J* = 16.0. 7.0 Hz, 1H, CH), 4.17-4.47 (m, 2H, CH_2F), 3.78-3.90 (m, 2H, CH-N), 1.65 (s, 2H, NH_2); ^{13}C-NMR (75 MHz, CD_3OD) δ 162.2 (d, *J* = 246.8 Hz, C_{arom}-F), 132.5 (C_{arom}), 130.4 (=CH), 127.7 (d, *J* = 8.1 Hz, C_{arom}), 115.3 (d, *J* = 21.6 Hz, C_{arom}), 86.4 (d, *J* = 173.2 Hz, CH_2F), 53.4 (d, *J* = 20.1 Hz, CH-N); ^{19}F-NMR (282 MHz, CD_3OD) δ -225.2, -224.8, -114.5. Anal. Calcd for $C_{10}H_{11}F_2N$: C, 65.56; H, 6.05; N, 7.65. Found: C, 65.38; H, 6.13; N, 7.56.

1,1,1-Trifluoro-3-methyl-4-*p*-tolyl-3-buten-2-amine (7g) (325mg, 71%) obtained as a pale yellow oil. Rf 0.35 (hexane/ethyl acetate,7/3). IR (neat) 3397, 3224, 1156, 1117 cm^{-1}; Yellow oil. IR (neat) 3397, 3323, 2924, 1117 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.95-7.31 (m, 4H, H_{arom}), 6.46 (s, 1H, CH), 3.71-3.79 (q, *J* = 7.8 Hz, 1H, CH), 2.23 (s, 3H, $ArCH_3$), 1.82 (s, 3H, CH_3),1.57 (bs, 2H, NH_2); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 136.7, 133.7, 131.4 (C_{arom}, <u>C</u>-CO), 130.9 (CH), 128.9, 128,8 (C_{arom}), 120.2-131.5 (q, *J* = 283.0 Hz, CF_3), 60.4-61.5 (q, *J* = 29.2 Hz, <u>C</u>-CF_3), 20.9 ($ArCH_3$), 14.0 (CH_3); ^{19}F-NMR (282 MHz, $CDCl_3$) δ -75.6. Anal. Calcd for $C_{12}H_{14}F_3N$: C, 62.87; H, 6.16; N, 6.11. Found: C, 62.61; H, 6.18; N, 6.08.

1,1,1-Trifluoro-4-(2-furyl)-3-methyl-3-buten-2-amine (7h) (217mg, 53%) obtained as a pale yellow oil. Rf 0.34 (hexane/ethyl acetate,7/3). IR (neat) 3398, 3327, 1260, 1159, 1119 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.46 (s, 1H, CH), 6.38-6.44 (m, 3H, H_{arom}), 3.86-3.94 (q, *J* = 7.9 Hz, 1H, CH-CF_3), 2.04 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, CD_3OD) δ 153.6 (=<u>C</u>-CH_3, C_{arom}), 143.2 (C_{arom}, CH),

131.5, 123.0-130.0 (q, J = 282.0 Hz, CF_3), 120.6, 112.3, 111.5, 61.1-62.2 (q, J = 29.2 Hz, $\underline{C}$-CF_3), 15.3 (CH_3); ^{19}F-NMR (282 MHz, CD_3OD) δ -75.8. Anal. Calcd for $C_9H_{10}F_3NO$: C, 52.69; H, 4.91; N, 6.83. Found: C, 52.57; H, 4.87; N, 6.79.

General procedure for the preparation of fluorinated enamines (8). Butyllithium (1.6M in hexanes) (2mmol) was added to a solution of fluorinated enaminophosphonate **1** (2mmol) in THF at 0ºC and under N_2 atmosphere. The mixture was stirred for 1h at the same temperature. Then, a solution of the corresponding aldehyde (2mmol) in THF (6ml) was added and the reaction was stirred at room temperature until t.l.c. showed the disappearance of the enamino phosphonate **1**. The reaction was cooled to –78ºC, $BH_3.SMe_2$ 1.0M in CH_2Cl_2 (2.22ml, 2.22 mmmol) was added and the reaction was stirred at –78ºC until t.l.c. showed the disappearance of the α,β-unsaturated imine **5**. A solution of $NaHCO_3$ (10ml) was added and the reaction was warmed to r.t.. The organic layer was extracted with Et_2O, washed with water, dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated under vacuum. The crude product was purified by vacuum distillation or by chromatography using silica-gel (hexane/ethyl acetate).

6-Phenyl-1,1,1-trifluoro-2,5-hexadien-2-amine (8b) (136mg, 30%) obtained as a pale yellow oil. Rf 0.52 (hexane/ethyl acetate,7/3). IR (neat) 3456, 3379, 2924, 1110 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.04-7.43 (m, 5H, H_{arom}), 6.30 (d, J = 15.9 Hz, 1H, =CH), 6.02 (dt, J = 15.9, 6.4 Hz, 1H, =CH), 4.98 (t, J = 7.3 Hz, 1H, =CH), 3.08 (bs, 2H, NH_2), 2.75 (dd, J = 6.3 Hz, 2H, CH_2); ^{13}C-NMR (75 MHz, CD_3OD) δ 137.1 (C_{arom}), 131.0 (C_{arom},=CH), 128.5, 127.3, 126.3, 126.1, 122.0 (q, J = 273.4 Hz, CF_3), 102.8 (q, J = 4.5 Hz, =CH), 28.3 (CH_2); ^{19}F-NMR (282 MHz, CD_3OD) δ -71.5. Anal. Calcd for $C_{12}H_{12}F_3N$: C, 63.43; H, 5.32; N, 6.16. Found: C, 63.67; H, 5.39; N, 5.99.

4,4,5,5,5-Pentafluoro-1-(2-tienyl)-2-penten-3-amine (8c) (211mg, 41%) obtained as a pale yellow oil. bp 35-36ºC (10^{-5}Torr). IR (neat) 3471, 3383, 1674, 1209 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.13-1.16 (m, 1H, H_{arom}), 6.91-6,94 (m, 1H, H_{arom}), 3.33 (bs, 2H, NH_2); ^{13}C-NMR (75 MHz, CD_3OD) δ 141.6 (C_{arom}), 131.1 (t, J = 23.2 Hz, C-NH_2), 126.9 (C_{arom}), 124.5, 123.8, 107.8-121.3(m, C_2F_5), 105.2

(t, *J* = 6.5 Hz, =CH), 25.6 (CH_2); ^{19}F-NMR (282 MHz, CD_3OD) δ −121.2, -84.6. Anal. Calcd for $C_9H_8F_5NS$: C, 42.03; H, 3.13; N, 5.45; S, 12.46. Found: C, 42.34; H, 3.04; N, 5.57; S, 12.31.

1,1,1-Trifluoro-3-methyl-4-*p*-tolyl-2-buten-2-amine (8d) (142mg, 31%) obtained as a pale yellow oil. Bp 45-46°C (10^{-5}Torr). IR (neat) 3449, 3376, 2923, 1145 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 6.90-6.98 (m, 4H, H_{arom}), 3.21 (s, 2H, CH_2), 2.92 (bs, 2H, NH_2), 2.17 (s, 3H, CH_3); 1.66 (q, *J* = 2.7 Hz, 3H, CH_3); ^{13}C-NMR (75 MHz, CD_3OD) δ 135.8 (C_{arom}), 134.7, 129.3 (C_{arom}), 127.9, 122.9 (q, *J* = 274.5 Hz, CF_3), 115.0 (q, *J* = 2.5 Hz, $\underline{C}$-CH_3), 38.4 (CH_2), 20.7 (CH_3), 17.4 (CH_3); ^{19}F-NMR (282 MHz, CD_3OD) δ -63.7. Anal. Calcd for $C_{12}H_{14}F_3N$: C, 62.87; H, 6.16; N, 6.11. Found: C, 63.11; H, 6.10; N, 6.22.

1,1,1-Trifluoro-4-(2-furyl)-3-methyl-2-buten-2-amine (8e) (94mg, 23%) obtained as a pale yellow oil. Bp 28-30°C (10^{-5}Torr). IR (neat) 3450, 3385, 2924, 1625, 1124 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.32-7.33 (m, 1H, H_{arom}), 6.28-6.29 (m, 1H, H_{arom}), 6.03-6.05 (m, 1H, H_{arom}), 3.36 (s, 2H, CH_2), 3.20 (bs, 2H, NH_2), 1.83 (q, *J* = 2.6 Hz, 3H, CH_3); ^{13}C-NMR (75 MHz, CD_3OD) δ 152.0 (C_{arom}), 141.6 (C_{arom}), 127.6 (q, *J* = 30.2 Hz, =$\underline{C}$-CF_3), 122.8 (q, *J* = 275.0 Hz, CF_3), 110.2 (C_{arom}), 106.0, 32.3 (CH_2), 17.4 (CH_3); ^{19}F-NMR (282 MHz, CD_3OD) δ -63.5. Anal. Calcd for $C_9H_{10}F_3NO$: C, 52.69; H, 4.91; N, 6.83. Found: C, 53.00; H, 4.86; N, 6.70.

General procedure for the preparation of fluorinated saturated ketones (9). A solution of H_2SO_4 5M (0.5 ml) was added to a solution of fluorinated enamine **8** (1mmol) in Et_2O The mixture was stirred for 2h at room temperature. The organic layer was extracted with Et_2O (3 x10ml), washed with water, dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated under vacuum. The crude product was purified by chromatography using silica-gel (hexane/ethyl acetate).

6-Phenyl-1,1,1-trifluoro-5-hexen-2-one (9b) (137mg, 60%) obtained as a pale yellow oil. Rf 0.38 (hexane/ethyl acetate,7/3). IR (neat) 3007, 2924, 1739, 1110 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.13-7.28 (m, 5H, H_{arom}), 6.36 (d, *J* = 15.7 Hz, 1H, =CH), 6.07 (dt, *J* = 7.0, 15.7 Hz, 1H, =CH), 2.79 (t, *J* = 7.0 Hz, 2H, CH_2), 2.48 (dt, *J* = 7.0, 7.0 Hz, 2H, CH_2); ^{13}C-NMR (75 MHz, CD_3OD) δ 190.5 (q, *J* =

32.1 Hz, C=O), 136.9 (C_{arom}), 131.9 (C_{arom}), 128.5, 127.4, 126.7, 126.0, 118.0 (q, *J* = 275.0 Hz, CF_3), 36.0(CH_2), 25.6 (CH_2); ^{19}F-NMR (282 MHz, CD_3OD) δ -79.9. Anal. Calcd for $C_{12}H_{11}F_3O$: C, 63.16; H, 4.86. Found: C, 63.37; H, 4.91.

1,1,1,2,2-Pentafluoro-5-(2-tienyl)-3-pentanone (9c) (134mg, 53%) obtained as a pale yellow oil. Rf 0.54 (hexane/ethyl acetate,7/3). IR (neat) 3015, 2929, 1755, 1200 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.04-7.07 (m, 1H, H_{arom}), 6.82-6.85 (m, 1H, H_{arom}), 6.74-6.75 (m, 1H, H_{arom}), 3.02-3.15 (m, 4H, 2 x CH_2); ^{13}C-NMR (75 MHz, CD_3OD) δ 192.9 (t, *J* = 27.2 Hz, C=O), 141.4 (C_{arom}), 126.9 (C_{arom}), 125.1, 123.9, 106.6-123.5 (m, C_2F_5), 39.3(CH_2), 22.5 (CH_2); ^{19}F-NMR (282 MHz, CD_3OD) δ -123.8,-82.4. Anal. Calcd for $C_9H_7F_5OS$: C, 41.87; H, 2.73; S, 12.42. Found: C, 41.62; H, 2.70; S, 12.57.

General procedure A for the preparation of fluorinated saturated amines (10). To a solution of corresponding fluorinated allylic amine **7** (1mmol) and Pd/C (0.1mmol) in acetic acid (6ml) was applied 80psi of hydrogen and the reaction was stirred until t.l.c. showed the disappearance of the allylic amine **7**. A saturated solution of Na_2CO_3 (15ml) was added and the reaction was filtrated through celite. The organic layer was separated and dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated under vacuum. The crude product was purified by chromatography using silica-gel (ethyl acetate).

General procedure B for preparation of fluorinated saturated amines (10) from α, β-unsaturated imine(5). To a solution of corrresponding α, β-unsaturated imine **5** (1mmol) and Pd/C (0.1mmol) in ethanol (6ml) was applied 80psi of hydrogen and the reaction was stirred until t.l.c. showed the disappearance of the imine **5**. Then the reaction was filtrated through celite and the solvent was evaporated under vacuum. The crude product was purified by vacuum distillation or by chromatography using silica-gel (ethyl acetate) afforded of compounds **10**

General procedure C for the preparation of fluorinated saturated amines (10) from enamine (8). To a solution of enamine **8** (1mmol) and Pd/C (0.1mmol) in etanol (6ml) was applied 80psi of hydrogen and the reaction was stirred until t.l.c. showed the disappearance of the enamine **8**. Then the

reaction was filtrated through celite and the solvent was evaporated under vacuum. The crude product was purified by vacuum distillation or by chromatography using silica-gel (ethyl acetate) afforded (141mg, 65%) of compound **10a**.

1,1,1-Trifluoro-4-*p*-tolyl-2-butanamine (10a). The general procedure A was followed using 1,1,1-trifluoro-4-*p*-tolyl-3-buten-2-amine **7a**. Chromatographic purification gave 178mg (82%) of compound **10a** When the general procedure B was followed using 4-*p*-tolyl-2-trifluromethyl-1-aza-1,3-butadiene **5a** Chromatographic purification gave (75%) of compound **10a.** When the general procedure C was followed using 1,1,1-trifluoro-4-*p*-tolyl-2-buten-2-amine **8a** Chromatographic purification gave (141mg, 65%) of compound **10a** as a pale yellow oil. Rf 0.41 (hexane/ethyl acetate,7/3). IR (neat) 3406, 3330, 2925, 1121 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.02 (s, 4H, H_{arom}), 2.97-3.04 (m, 1H, CH), 2.74-2.83 (m, 1H, CH_2), 2.56-2.66 (m, 1H, CH_2), 2.24 (s, 3H, CH_3), 1.88-2.00 (m, 1H, CH_2), 1.51-1.64 (m, 1H, CH_2), 1.18 (bs, 2H, NH_2),; ^{13}C-NMR (75 MHz, CD_3OD) δ 137.7 (C_{arom}), 135.6, 129.2 (C_{arom}), 128.3, 126.8 (q, *J* = 281.5 Hz, CF_3), 52.9 (q, *J* = 28.7 Hz, $\underline{C}$-CF_3), 31.4(CH_2), 31.1 (CH_2), 20.9 (CH_3); ^{19}F-NMR (282 MHz, CD_3OD) δ -79.2. Anal. Calcd for $C_{11}H_{14}F_3N$: C, 60.82; H, 6.50; N, 6.45. Found: C, 60.55; H, 6.44; N, 6.56.

1,1,1,2,2-pentafluoro-5-*p*-fluorophenyl-3-pentanamine (10b) The general procedure A was followed using 4,4,5,5,5-pentafluoro-1-*p*-fluorophenyl-1-penten-3-amine **7d** . Chromatographic purification gave 209mg (77%) of compound **10b** as a pale yellow oil. Rf 0.31 (hexane/ethyl acetate,7/3). IR (neat) 3423, 3337, 2935, 1511, 1203 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.14-7.25 (m, 2H, H_{arom}), 6.89-7.01 (m, 2H, H_{arom}), 3.09-3.22 (m, 1H, CH), 2.88-2.97 (m, 1H, CH_2), 2.62-2.76 (m, 1H, CH_2), 1.98-2.09 (m, 1H, CH_2), 1.59-1.72 (m, 1H, CH_2), 1.32 (bs, 2H, NH_2),; ^{13}C-NMR (75 MHz, CD_3OD) δ 161.5 (d, *J* = 243.7 Hz, C_{arom} -F), 136.5 (C_{arom}), 129.8 (d, *J* = 8.0 Hz, C_{arom}), 117.6-121.4 (m, C_2F_5), 115.2 (d, *J* = 21.1 Hz, C_{arom}), 51.9 (t, *J* = 23.2 Hz, $\underline{C}$-CF_2), 30.9 (CH_2), 30.8 (CH_2); ^{19}F-NMR (282 MHz, CD_3OD) δ -127.1, -125.6, -117.7, -81.3. Anal. Calcd for $C_{11}H_{11}F_6N$: C, 48.72; H, 4.09; N, 5.16. Found: C, 48.99; H, 3.98; N, 5.32.

1,1,1-Trifluoro-3-methyl-3-*p*-tolyl-2-butanamine (10c) The general procedure A was followed using 1,1,1-trifluoro-3-methyl-4-*p*-tolyl-3-buten-2-amine **7g** . Chromatographic purification gave 159mg (69%) of compound **10b** When the general procedure B was followed using 3-methyl-4-*p*-tolyl-2-trifluromethyl-1-aza-1,3-butadiene **5d** Chromatographic purification gave (75%) of compound **10c** as a pale yellow oil. Rf 0.39 (hexane/ethyl acetate,7/3). IR (neat) 3411, 3347, 2925, 1622, 1154 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.04-7.11 (m, 8H, H_{arom}), 3.02-3.13 (m, 1H, CH), 2.92-3.00 (m, 1H, CH_2), 2.39-2.74 (m, 1H, CH_2), 2.31 (s, 6H, 2 x CH_3), 2.18-2.26 (m, 1H, CH_2), 2.01-2.11 (m, 1H, CH_2), 1.44 (bs, 4H, 2 x NH_2), 0.95 (d, *J* = 6.9 Hz, 6H, 2 x CH_3); ^{13}C-NMR (75 MHz, CD_3OD) δ 136.8 (C_{arom}), 136.7, 135.6, 135.4, 129.0 (C_{arom}), 128.9, 128.8, 127.3 (d, *J* = 275.0 Hz, CF_3), 57.4 (q, *J* = 27.2 Hz, C-CF_3), 54.6 (q, *J* = 27.2 Hz, C-CF_3), 40.0 (CH_2), 37.2 (CH_2), 36.1 (CH), 33.9 (CH), 20.7 (CH),15.9 (CH_3), 12.9 (CH_3); ^{19}F-NMR (282 MHz, CD_3OD) δ -75.8, -74.3. Anal. Calcd for $C_{12}H_{16}F_3N$: C, 62.32; H, 6.97; N, 6.06. Found: C, 62.70; H, 7.06; N, 5.89.

General procedure for the preparation of benzyloxycarbonyl allylamines(11). $NaHCO_3$ (92mg, 1.1mmol) was added to a solution of corresponding allylamines **7** (1mmol) in THF (4ml) at 0ºC. Then, was added dripping a solution of benzyl chloroformiate (0.20ml, 1.35 mmol) THF (4ml). The reaction was stirred at room temperature until t.l.c. showed the disappearance of the allylamines **7**. The organic layer was extracted with ethyl acetate (2 x 50ml), washed with saturated solution of NaCl, dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated under vacuum. The crude product was purified by chromatography using silica-gel (hexane/ethyl acetate).

***N*-Benzyloxycarbonyl-1,1,1-trifluoro-3-methyl-4-*p*-tolyl-3-buten-2-amine (11b)** The general procedure was followed using 1,1,1-trifluoro-3-methyl-4-*p*-tolyl-3-buten-2-amine **7g** . Chromatographic purification gave 254mg (70%) of compound **11b** as a white solid. Rf 0.61 (hexane/ethyl acetate,7/3). Mp 95-97 ^{o}C. IR (neat) 3304, 2964, 1696, 1549, 1124 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.36 (s, 5H, H_{arom}), 7.15 (s, 4H, H_{arom}), 6.60 (s, 1H, =CH), 5.39 (d, *J* = 78.1 Hz, 1H, NH), 5.16 (s, 2H, CH_2O), 4.93 (bs, 1H, CH-CF_3), 2.34 (s, 3H, CH_3), 1.90 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, CD_3OD) δ 155.4 (C=O), 137.0 (C_{arom}), 135.7, 133.2, 132.3 (=C), 128.9 (C_{arom}), 128.8, 128.5,

128.3, 128.2, 124.7 (q, J = 283.0 Hz, CF_3), 67.6 (CH_2O), 59.7 (q, J = 30.7 Hz, CH-NH), 21.1 (CH_3), 14.6 (CH_3); ^{19}F-NMR (282 MHz, CD_3OD) δ -73.7. Anal. Calcd for $C_{20}H_{20}F_3NO_2$: C, 66.11; H, 5.55; N, 3.85. Found: C, 66.35; H, 5.47; N, 3.93.

Procedure for the preparation of 2-(*N*-Benzyloxycarbonylamine-3,3,3-trifluoro-propionic acid (14). $NaIO_4$(880 mg, 41.1mmol) was added to a solution of *N*-Benzyloxycarbonyl-1,1,1-trifluoro-4-*p*-tolyl-3-buten-1-amine **11a** (1mmol) in CCl_4 (2ml), acetonitrile (2ml) and water (2ml) at 0ºC. Then, was added a solution of $RuCl_3$ x H_2O (880mgl, 0.022mmol) in water (1ml). The reaction was stirred at room temperature until t.l.c. showed the disappearance of the allylamine **11a**. To the mixture was added 2ml of isopropanol and was filtrated through celite and was added a solution of $NaHCO_3$ 5% (10ml). The organic layer was extracted with ethyl acetate (1 x 25ml), the aqueous layer was acidified with HCl 1M, The organic layer was extracted with ethyl acetate (3 x 25ml), dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated under vacuum. The crude product was purified by chromatography using silica-gel (ethyl acetate) afforded (65%)of compounds **14** as a white solid. Mp 104-105 (Lit. 103-105ºC) [1]

References

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