Supporting Information

Synthesis of Pentafluorophenylmethylanimes via Silicon Mannich Reaction.

Alexander D. Dilman,^{*,†} Pavel A. Belyakov,[†] Alexander A. Korlyukov,[‡] Marina I. Struchkova,[†]
and Vladimir A. Tartakovsky[†]

[†]*N. D. Zelinsky Institute of Organic Chemistry, 119991 Moscow, Leninsky prosp. 47, Russian Federation, and* [‡]*A. N. Nesmeyanov Institute of Organoelement Compounds, 119991 Moscow, Vavilov str. 28, Russian Federation*

General Information.

All reactions were performed under an argon atmosphere. Dichloromethane and dichloroethane were distilled from CaH₂ prior to use. Acetonitrile was distilled from CaH₂ and stored over MS 4A. Methanol was distilled from magnesium turnings prior to use. Aldehydes and amines were commercial (Aldrich, Acros), and were purified by distillation. Column chromatography was carried out employing Merck silica gel (Kieselgel 60, 230-400 mesh). Precoated silica gel plates F 254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. KMnO₄ solution. NMR spectra were recorded on a Bruker AM-300, WM-250, or AC-200 instruments.

Synthesis of methoxytris(pentafluorophenyl)silane MeOSi(C₆F₅)₃ (**5**).

Chlorotris(pentafluorophenyl)silane, ClSi(C₆F₅)₃, was obtained according to a literature procedure: H.-J.; Lewin, A.; Bardin, V. V. *J. Organomet. Chem.* **1998**, 568, 233.

Methanol (32 mL) and dichloroethane (6 mL) were successively added to the solid ClSi(C₆F₅)₃ (10.73 g, 19.0 mmol), and the mixture was brought to reflux. After complete dissolution of the starting chlorosilane (ca. 5 min) the mixture was refluxed for additional 5 min, concentrated at reduced pressure, and the residue was distilled in vacuum to afford 9.58 g of **5** (90 % yield).

B.p. 112–114 °C/0.25 Torr. M.p. 82–85 °C.

¹H NMR (CDCl₃, 250.1 MHz) δ 3.75 (s, 3H, OMe).

¹³C NMR (CDCl₃, 50.3 MHz) δ 52.7 (OMe), 104.8 (t, *J*_{C-F} = 21.1, C_i-C₆F₅), 137.7 (dm, *J*_{C-F} = 252.0, CF), 144.0 (dm, *J*_{C-F} = 251.9, CF), 149.3 (dm, *J*_{C-F} = 247.0, CF).

¹⁹F NMR (CDCl₃, 188.3 MHz) δ –160.86 (m, *meta*), –147.67 (t, *J* = 19.4, *para*), –128.98 (br d, *ortho*).

Calcd for C₁₉H₃F₁₅OSi (560.29): C 40.73, H 0.54. Found: C 40.66, H 0.48.

Silane **5** was stored in a Schlenk flask under argon. However, it can be exposed to the air for short time, thereby allowing for convenient handling.

Figure S1. The molecular structure of MeOSi(C₆F₅)₃. Non-hydrogen atoms are presented by thermal ellipsoids at 50% probability.

Three component coupling (general procedure). Aldehyde (1.0 mmol) and amine (1.1 mmol) were successively added to a suspension of MeOSi(C₆F₅)₃ (560 mg, 1.0 mmol) in MeCN (2.5 mL) at 0 °C and the mixture was kept under conditions indicated in Table 3. Then at 0 °C the mixture was quenched with a solution of NH₄F (37 mg, 1.0 mmol) in MeOH/water (1.3 mL/0.13 mL), stirred for additional 5 min at room temperature, diluted with excess ether/hexanes (1 : 1), and filtered. The filtrate was concentrated under vacuum, the residue was diluted with ether/hexanes (1 : 1), and dried (Na₂SO₄). Evaporation of the solvent afforded crude product, which was chromatographed on silica gel eluting with hexanes/ethyl acetate.

1-[(Pentafluorophenyl)phenylmethyl]pyrrolidine (**4a**).

According to General Procedure using CH₂Cl₂ as solvent.

Chromatography: hexanes/EtOAc, 20 : 1, R_f = 0.71 (hexanes/EtOAc, 10 : 1).

B.p. 108–116 °C (bath temperature)/0.2 Torr

¹H NMR (CDCl₃, 300.1 MHz) δ 1.84–1.96 (m, 4H, CH₂CH₂), 2.43–2.53 (m, 2H) and 2.56–2.66 (m, 2H) (2 NCH₂), 4.91 (s, 1H, CHN), 7.27–7.40 (m, 3H) and 7.59 (d, 2H, *J* = 7.4) (Ph).

¹³C NMR (CDCl₃, 62.9 MHz) δ 23.6 (CH₂), 53.3 (NCH₂), 64.7 (CHN), 116.7 (tm, *J*_{C-F} = 14.7, C_i-C₆F₅), 127.5 (t, *J* = 1.8, CH_{Ph}), 127.6 (CH_{Ph}), 128.5 (CH_{Ph}), 137.6 (dm, *J*_{C-F} = 252.6, CF), 140.1 (dm, *J*_{C-F} = 252.6, CF), 140.7 (C_i-Ph), 144.7 (dm, *J*_{C-F} = 249.4, CF).

¹⁹F NMR (CDCl₃, 188.3 MHz) δ –163.13 (td, *J* = 8.0, 22.1, *meta*), –157.29 (t, *J* = 22.1, *para*), –141.14 (br d, *ortho*).

Calcd for C₁₇H₁₄F₅N (327.29): C 62.39, H 4.31, N 4.28. Found: C 62.37, H 4.21, N 4.19.

4-[(Pentafluorophenyl)phenylmethyl]morpholine (4b).

Chromatography: hexanes/EtOAc, 14 : 1, R_f = 0.41 (hexanes/EtOAc, 6 : 1).

M.p. 112–113 °C (hexanes).

^1H NMR (CDCl_3 , 250.1 MHz) δ 2.37–2.57 (m, 4H, 2NCH_2), 3.73–3.86 (m, 4H, 2OCH_2), 4.97 (s, 1H, CHN), 7.24–7.39 (m, 3H) and 7.53 (d, 2H, J = 7.2) (Ph).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 51.9 (NCH_2), 65.3 (CHN), 66.9 (OCH_2), 114.3 (tm, $J_{\text{C-F}}$ = 17.0, $\text{C}_{i-\text{C}_6\text{F}_5}$), 127.5 (t, J = 1.8, CH_{Ph}), 127.8 (CH_{Ph}), 128.7 (CH_{Ph}), 137.7 (dm, $J_{\text{C-F}}$ = 253.4, CF), 138.8 ($\text{C}_{i-\text{Ph}}$), 140.3 (dm, $J_{\text{C-F}}$ = 254.1, CF), 144.8 (dm, $J_{\text{C-F}}$ = 246.3, CF).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ -162.51 (td, J = 8.2, 22.0, *meta*), -156.09 (t, J = 22.0, *para*), -139.81 (br d, *ortho*).

Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_5\text{NO}$ (343.29): C 59.48, H 4.11, N 4.08. Found: C 59.44, H 3.97, N 4.03.

Figure S2. The molecular structure of **4b**. Non-hydrogen atoms are presented by thermal ellipsoids at 50% probability.

Dibenzyl[(4-methoxyphenyl)pentafluorophenylmethyl]amine (4c).

Chromatography: hexanes/EtOAc, 25 : 1, R_f = 0.35 (hexanes/EtOAc, 15 : 1)

B.p. 200–220 °C (bath temperature)/0.2 Torr

^1H NMR (CDCl_3 , 250.1 MHz) δ 3.55 (d, 2H, $J = 14.4$, $\text{CH}_\text{A}\text{H}_\text{B}\text{Ph}$), 3.87 (s, 3H, OMe), 3.99 (d, 2H, $J = 14.4$, $\text{CH}_\text{A}\text{H}_\text{B}\text{Ph}$), 5.55 (s, 1H, CHN), 7.00 (d, 2H, $J = 8.5$), 7.29–7.54 (m, 10H) 7.60 (d, 2H, $J = 8.5$) (all CH_Ar).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 54.8, 55.1, 59.7 (CH_2 , MeO, CHN), 113.8 (tm, $\text{C}_{i-\text{C}_6\text{F}_5}$), 114.0 (CH_Ar), 127.0 (CH_Ar), 128.3 (CH_Ar), 128.4 (CH_Ar), 131.4 (C_Ar), 137.7 (dm, $J_{\text{C-F}} = 253.4$, CF), 138.8 (C_Ar), 140.4 (dm, $J_{\text{C-F}} = 253.4$, CF), 145.5 (dm, CF), 159.0 (C_Ar).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ -162.52 (td, $J = 5.5$, 22.2, *meta*), -155.84 (t, $J = 22.2$, *para*), -137.15 (br d, *ortho*).

Calcd for $\text{C}_{28}\text{H}_{22}\text{F}_5\text{NO}$ (483.47): C 69.56, H 4.59, N 2.90. Found: C 69.41, H 4.48, N 2.78.

[(4-Chlorophenyl)pentafluorophenylmethyl]diethylamine (4d).

Chromatography: hexanes/EtOAc, 20 : 1, $R_f = 0.57$ (hexanes/EtOAc, 15 : 1)

B.p. 125–140 °C (bath temperature)/0.3 Torr

^1H NMR (CDCl_3 , 250.1 MHz) δ 1.07 (t, 6H, $J = 6.9$, CH_2CH_3), 2.34–2.50 (m, 2H) and 2.65–2.82 (m, 2H) ($2\text{CH}_2\text{CH}_3$), 5.39 (s, 1H, CHN), 7.30 (d, 2H, $J = 8.5$, CH_Ar), 7.44 (d, 2H, $J = 8.5$, CH_Ar).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 11.4 (CH_3), 42.9 (CH_2), 59.7 (CHN), 114.3 (tm, $J_{\text{C-F}} = 16.0$, $\text{C}_{i-\text{C}_6\text{F}_5}$), 128.46 (CH_Ar), 128.50 (CH_Ar), 132.9 ($\text{C}_{i-\text{Ar}}$), 137.6 (dm, $J_{\text{C-F}} = 253.3$, CF), 138.9 ($\text{C}_{i-\text{Ar}}$), 140.1 (dm, CF), 145.1 (dm, CF).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ -162.55 (td, $J = 5.6$, 22.1, *meta*), -156.22 (t, $J = 22.1$, *para*), -139.25 (br d, *ortho*).

Calcd for $\text{C}_{17}\text{H}_{15}\text{ClF}_5\text{N}$ (363.75): C 56.13, H 4.16, N 3.85. Found: C 56.35, H 3.99, N 3.74.

Lit: Chen, Q.-Y.; Wu, J.-P. *J. Chem. Research (M)* **1990**, 1890.

1-[(4-Chlorophenyl)pentafluorophenylmethyl]piperidine (4e).

Chromatography: hexanes/EtOAc, 35 : 1, $R_f = 0.45$ (hexanes/EtOAc, 25 : 1)

B.p. 155–165 °C (bath temperature)/0.3 Torr

^1H NMR (CDCl_3 , 300.1 MHz) δ 1.42–1.53 (m, 2H, CH_2), 1.61–1.73 (m, 4H, 2CH_2), 2.33–2.47 (m, 4H, 2NCH_2), 5.03 (s, 1H, CHN), 7.31 (d, 2H, $J = 8.8$, CH_Ar), 7.43 (d, 2H, $J = 8.8$, CH_Ar).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ 24.3 (CH_2), 26.1 (CH_2), 52.1 (NCH_2), 64.4 (CHN), 113.7 (tm, $J_{\text{C-F}} = 16.5$, $\text{C}_{i-\text{C}_6\text{F}_5}$), 128.5 (CH_Ar), 128.7 (CH_Ar), 133.1 ($\text{C}_{i-\text{Ar}}$), 137.7 (dm, $J_{\text{C-F}} = 253.1$, CF), 138.4 ($\text{C}_{i-\text{Ar}}$), 140.3 (dm, $J_{\text{C-F}} = 253.1$, CF), 145.0 (dm, $J_{\text{C-F}} = 246.8$, CF).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ -162.64 (td, $J = 8.3$, 22.2, *meta*), -156.13 (t, $J = 22.2$, *para*), -139.02 (br d, *ortho*).

Calcd for $\text{C}_{18}\text{H}_{15}\text{ClF}_5\text{N}$ (375.76): C 57.53, H 4.02, N 3.73. Found: C 57.61, H 3.93, N 3.62.

2-[Pentafluorophenyl(pyrrolidinyl-1)methyl]phenol (4f).

According to General Procedure using CH_2Cl_2 as solvent, and the ratio salicylaldehyde : pyrrolidine : **5** = 1 : 1.15 : 1.15.

Chromatography: hexanes/EtOAc, 18 : 1, R_f = 0.31 (hexanes/EtOAc, 10 : 1)

M.p. 57–59 °C.

^1H NMR (CDCl_3 , 200.1 MHz) δ 1.93 (br, 4H, $(\text{CH}_2)_2$), 2.53–2.81 (m, 4H, 2NCH_2), 5.24 (s, 1H, CHN), 6.74 (t, 1H, J = 7.6, CH_{Ar}), 6.86 (d, 1H, J = 7.6, CH_{Ar}), 6.96 (d, 1H, J = 7.6, CH_{Ar}), 7.16 (t, 1H, J = 7.6, CH_{Ar}), 11.41 (s, 1H, OH).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 23.3 (CH_2), 52.8 (CH_2), 62.9 (CHN), 114.4 (tm, $J_{\text{C-F}}$ = 16.3, $\text{C}_{i-\text{C}_6\text{F}_5}$), 117.1 (CH_{Ar}), 119.0 (CH_{Ar}), 121.5 ($\text{C}_{i-\text{Ar}}$), 127.9 (CH_{Ar}), 129.2 (CH_{Ar}), 137.6 (dm, $J_{\text{C-F}}$ = 253.4, CF), 140.5 (dm, $J_{\text{C-F}}$ = 254.8, CF), 144.6 (dm, $J_{\text{C-F}}$ = 249.1, CF), 157.0 ($\text{C}_{i-\text{Ar}}$),

^{19}F NMR (CDCl_3 , 188.3 MHz) δ -162.10 (br, $\Delta\nu_{1/2}$ = 55.5 Hz, *meta*), -155.61 (t, J = 22.2, *para*), -142.50 (br, $\Delta\nu_{1/2}$ = 194.2 Hz, *ortho*), -137.17 (br, $\Delta\nu_{1/2}$ = 194.2 Hz, *ortho*).

Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_5\text{NO}$ (343.29): C 59.48, H 4.11, N 4.08. Found: C 59.51, H 4.14, N 3.97.

Diethyl[(naphthyl-1)pentfluorophenylmethyl]amine (4g).

Chromatography: hexanes/EtOAc, 30 : 1, R_f = 0.47 (hexanes/EtOAc, 15 : 1)

B.p. 137–145 °C (bath temperature)/0.15 Torr

^1H NMR (CDCl_3 , 200.1 MHz) δ 1.12 (t, 6H, J = 6.8, CH_2CH_3), 2.60–2.80 (m, 2H) and 2.78–2.98 (m, 2H) ($2\text{CH}_2\text{CH}_3$), 6.17 (s, 1H, CHN), 7.47–7.63 (m, 3H, 3CH_{Ar}), 7.82–7.96 (m, 2H, 2CH_{Ar}), 8.09 (d, 1H, J = 6.8, CH_{Ar}), 8.25 (d, 1H, J = 7.8, CH_{Ar}).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 11.9 (CH_3), 43.9 (CH_2), 57.2 (CHN), 115.6 (tm, $J_{\text{C-F}}$ = 15.6, $\text{C}_{i-\text{C}_6\text{F}_5}$), 122.6 (t, J = 2.1, CH_{Ar}), 125.3 (CH_{Ar}), 125.4 (CH_{Ar}), 126.2 (CH_{Ar}), 126.5 (t, J = 3.6, CH_{Ar}), 128.3 (CH_{Ar}), 129.1 (CH_{Ar}), 131.4 (C_{Ar}), 134.0 (C_{Ar}), 135.1 (C_{Ar}), 138.0 (dm, $J_{\text{C-F}}$ = 253.4, CF), 140.2 (dm, $J_{\text{C-F}}$ = 253.4, CF), 145.4 (dm, CF).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ -162.72 (td, J = 8.3, 22.2, *meta*), -156.53 (t, J = 22.2, *para*), -139.55 (br d, *ortho*).

Calcd for $\text{C}_{21}\text{H}_{18}\text{F}_5\text{N}$ (379.37): C 66.49, H 4.78, N 3.69. Found: C 66.72, H 5.00, N 3.61.

4-[(Furanyl-2)pentafluorophenylmethyl]morpholine (4h).

Chromatography: hexanes/EtOAc, 12 : 1, R_f = 0.25 (hexanes/EtOAc, 10 : 1)

B.p. 105–110 °C (bath temperature)/0.23 Torr

^1H NMR (CDCl_3 , 250.1 MHz) δ 2.37–2.59 (m, 4H, 2 NCH_2), 3.67–3.81 (m, 4H, 2 OCH_2), 5.12 (s, 1H, CHN), 6.31–6.45 (m, 2H, 2 CH_{Ar}), 7.34 (s, 1H, CH_{Ar}).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ 51.1 (NCH_2), 58.8 (CHN), 66.9 (OCH_2), 108.2 (CH_{Ar}), 110.4 (CH_{Ar}), 111.0 (tm, $J_{\text{C-F}}$ = 16.8, $\text{C}_{i-\text{C}_6\text{F}_5}$), 137.6 (dm, $J_{\text{C-F}}$ = 253.1, CF), 140.7 (dm, $J_{\text{C-F}}$ = 254.0, CF), 142.2 (CH_{Ar}), 145.3 (dm, $J_{\text{C-F}}$ = 250.4, CF), 150.7 ($\text{C}_{i-\text{Ar}}$).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ –162.60 (m, *meta*), –155.23 (t, J = 22.2, *para*), –139.90 (br d, *ortho*).

Calcd for $\text{C}_{15}\text{H}_{12}\text{F}_5\text{NO}_2$ (333.25): C 54.06, H 3.63, N 4.20. Found: C 53.93, H 3.66, N 4.15.

Diallyl[pentafluorophenyl(thienyl-2)methyl]amine (4i).

Chromatography: hexanes/EtOAc, 30 : 1, R_f = 0.54 (hexanes/EtOAc, 25 : 1)

B.p. 150–160 °C (bath temperature)/0.25 Torr

^1H NMR (CDCl_3 , 200.1 MHz) δ 2.91 (dd, 2H, J = 7.3, 14.7, $\text{CH}_\text{A}\text{H}_\text{B}$), 3.55 (dd, 2H, J = 4.7, 14.7, $\text{CH}_\text{A}\text{H}_\text{B}$), 5.18–5.36 (m, 4H, $\text{CH}_2=\text{CH}$), 5.79 (s, 1H, CHN), 5.94 (dddd, 2H, J = 4.7, 7.3, 10.3, 17.1, $\text{CH}_2=\text{CH}$), 6.87 (br, 1H, CH_{Ar}), 6.98 (dd, 1H, J = 3.4, 4.6, CH_{Ar}), 7.29 (d, 1H, J = 4.6, CH_{Ar}).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ 52.8 (CH_2), 55.7 (CHN), 112.8 (tm, J = 15.3, $\text{C}_{i-\text{C}_6\text{F}_5}$), 117.5 ($\text{CH}_2=\text{CH}$), 124.5 (CH_{Ar}), 125.1 (CH_{Ar}), 126.7 (CH_{Ar}), 135.2 ($\text{CH}_2=\text{CH}$), 137.7 (dm, $J_{\text{C-F}}$ = 254.0, CF), 140.7 (dm, $J_{\text{C-F}}$ = 254.0, CF), 144.6 (C_{Ar}), 145.5 (dm, $J_{\text{C-F}}$ = 249.5, CF).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ –162.24 (dt, J = 5.6, 22.2, *meta*), –155.19 (t, J = 22.2, *para*), –137.3 (br d, *ortho*).

Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_5\text{NS}$ (359.36): C 56.82, H 3.93, N 3.90. Found: C 56.68, H 3.80, N 4.14.

4-[(Furanyl-2)pentafluorophenylmethyl]piperazine-1-carboxylic acid *tert*-butyl ester (4j).

According to General Procedure with the addition of AcOH (1 mmol, 1 eq. with respect to the aldehyde) after the addition of furaldehyde. Solid N-Boc-protected piperazine was added in one proton.

Chromatography: hexanes/EtOAc from 15 : 1 to 8 : 1, R_f = 0.44 (hexanes/EtOAc, 6 : 1)

^1H NMR (CDCl_3 , 200.1 MHz) δ 1.44 (s, 9H, *t*-Bu), 2.30–2.60 (m, 4H) and 3.40–3.55 (m, 4H) (4CH₂), 5.20 (s, 1H, CHN), 6.38 (br s, 2H, 2CH_{Ar}), 7.34 (s, 1H, CH_{Ar}).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 28.3 (*Me*₃C), 43.5 (br, $\Delta\nu_{1/2}$ = 32.7 Hz, CH₂), 50.3 (CH₂), 58.5 (CHN), 79.7 (*Me*₃C), 108.0 (CH_{Ar}), 110.5 (CH_{Ar}), 110.8 (m, *C*_{*i*-C6F5}), 137.5 (dm, CF), 140.4 (dm, CF), 142.1 (CH_{Ar}), 150.8 and 154.5 (*C*_{*i*-Ar} and CO).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ –162.44 (dt, J = 5.5, 22.2, *meta*), –155.03 (t, J = 22.2, *para*), –139.73 (br d, *ortho*).

Calcd for C₂₀H₂₁F₅N₂O₃ (432.38): C 55.56, H 4.90, N 6.48. Found: C 55.61, H 4.74, N 6.49.

2-{Methyl[(pentafluorophenyl)phenylmethyl]amino}ethanol (4k).

Chromatography: hexanes/EtOAc from 9 : 1 to 3 : 1, R_f = 0.29 (hexanes/EtOAc, 3 : 1)

^1H NMR (CDCl_3 , 200.1 MHz) δ 2.29 (s, 3H, Me), 2.50–2.70 (m, 2H, CH₂N), 2.71–2.84 (br, 1H, OH), 3.61–3.79 (m, 2H, CH₂O), 5.14 (s, 1H, CHN), 7.25–7.40 (m, 3H) and 7.43–7.51 (m, 2H) (Ph).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 39.1 (Me), 56.3 (CH₂), 58.6 (CH₂), 65.0 (CHN), 114.6 (m, *C*_{*i*-C6F5}), 127.2 (t, J = 1.7, CH_{Ph}), 127.8 (CH_{Ph}), 128.8 (CH_{Ph}), 137.7 (dm, $J_{\text{C-F}}$ = 254.1, CF), 139.2 (*C*_{*i*-Ph}), 140.3 (dm, $J_{\text{C-F}}$ = 254.1, CF), 144.9 (dm, $J_{\text{C-F}}$ = 242.0, CF).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ –162.24 (m, *meta*), –155.97 (t, J = 22.2, *para*), –139.61 (br d, *ortho*).

Calcd for C₁₆H₁₄F₅NO (331.28): C 58.01, H 4.26, N 4.23. Found: C 57.96, H 4.15, N 4.44.

1-(2-Methyl-1-pentafluorophenylpropyl)pyrrolidine (4l).

Chromatography: from hexanes to hexanes/EtOAc, 25 : 1, R_f = 0.34 (hexanes/EtOAc, 25 : 1)

B.p. 135–140 °C (bath temperature)/18 Torr

^1H NMR (CDCl_3 , 250.1 MHz) δ 0.79 (d, 3H, J = 6.6, Me), 1.10 (d, 3H, J = 6.6, Me), 1.61–1.75 (m, 4H, CH_2CH_2), 2.31–2.53 (m, 5H, 2NCH_2 + CHMe_2), 3.86 (d, 1H, J = 10.3, CHN).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ 20.1 (Me), 21.0 (Me), 23.0 (CH_2CH_2), 29.0 (t, J = 3.6, CHMe_2), 48.9 (NCH_2), 63.9 (t, J = 2.8, CHN), 111.2 (m, $\text{C}_{i-\text{C}_6\text{F}_5}$), 137.4 (dm, J = 251.2, CF), 139.7 (dm, J = 252.0, CF), 145.2 (dm, J = 244.1, CF).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ -163.33 (td, J = 5.6, 22.2, *meta*), -157.10 (t, J = 22.2, *para*), -139.23 (br, *ortho*).

Calcd for $\text{C}_{14}\text{H}_{16}\text{F}_5\text{N}$ (293.28): C 57.34, H 5.50, N 4.78. Found: C 57.42, H 5.29, N 4.83.

Dibenzyl[cyclopentyl(pentafluorophenyl)methyl]amine (4m).

Chromatography: hexanes/EtOAc, 35 : 1, R_f = 0.54 (hexanes/EtOAc, 6 : 1).

m.p. 130–132 °C (hexanes).

^1H NMR (CDCl_3 , 250.1 MHz) δ 0.81–1.03 (m, 1H), 1.47–1.79 (m, 6H), 2.28–2.43 (m, 1H) ($(\text{CH}_2)_4$), 2.97–3.15 (m, 1H, CHCHN), 3.11 (d, 2H, J = 13.8, $\text{CH}_\text{A}\text{H}_\text{B}\text{Ph}$), 4.02 (d, 1H, J = 11.8, CHN), 4.15 (d, 2H, J = 13.8, $\text{CH}_\text{A}\text{H}_\text{B}\text{Ph}$), 7.30–7.46 (m, 6H, CH_Ph), 7.51 (d, 4H, J = 7.2, CH_Ph).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 24.9 (CH_2), 25.1 (CH_2), 30.6 (CH_2), 32.2 (CH_2), 40.3 (t, J = 2.8, CHCHN), 54.1 and 61.2 (CHN and CH_2Ph), 111.8 (tm, J = 19.9, $\text{C}_{i-\text{C}_6\text{F}_5}$), 127.0 (CH_Ph), 128.1 (CH_Ph), 128.8 (CH_Ph), 137.5 (dm, CF), 139.5 ($\text{C}_{i-\text{Ph}}$), 140.0 (dm, $J_{\text{C-F}}$ = 259.0, CF), 145.7 (dm, $J_{\text{C-F}}$ = 244.0, CF).

^{19}F NMR (CDCl_3 , 188.3 MHz, 24 °C) δ -162.49 (br, $\Delta\nu_{1/2}$ = 55.5 Hz, *meta*), -156.03 (t, J = 22.2, *para*), -138.88 (br, $\Delta\nu_{1/2}$ = 57.5 Hz, *ortho*), -136.36 (br, $\Delta\nu_{1/2}$ = 57.5 Hz, *ortho*). ^{19}F NMR (CDCl_3 , 188.3 MHz, 80 °C, sealed tube) δ -162.95 (td, J = 5.6, 22.2, *meta*), -156.68 (t, J = 22.2, *para*), -137.52 (br, $\Delta\nu_{1/2}$ = 72.1 Hz, *ortho*).

Calcd for $\text{C}_{26}\text{H}_{24}\text{F}_5\text{N}$ (445.47): C 70.10, H 5.43, N 3.14. Found: C 70.22, H 5.48, N 3.14.

Diallyl(2,2-dimethyl-1-pentafluorophenylpropyl)amine (4n).

Chromatography: hexanes, R_f = 0.43 (hexanes)

B.p. 132–140 °C (bath temperature)/18 Torr

^1H NMR (CDCl_3 , 200.1 MHz) δ 1.06 (s, 9H, $t\text{-Bu}$), 2.62 (dd, 2H, J = 8.3, 14.6, $\text{CH}_\text{A}\text{H}_\text{B}$), 3.50 (dm, 2H, J = 14.6, $\text{CH}_\text{A}\text{H}_\text{B}$), 4.22 (s, 1H, CHN), 5.10 (br s, 1H), 5.15 (br s, 2H), 5.24 (br s, 1H) ($\text{CH}_2=\text{CH}$), 5.84 (dddd, 2H, J = 4.2, 8.3, 10.1, 17.3, $\text{CH}_2=\text{CH}$).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ 28.9 (d, J = 4.3, Me), 35.8 (CMe_3), 55.1 (d, J = 4.3, CH_2), 64.1 (d, J = 4.3, CHN), 112.4 (m, $\text{C}_{i\text{-C}_6\text{F}_5}$), 116.8 ($\text{CH}_2=\text{CH}$), 136.9 ($\text{CH}_2=\text{CH}$), 137.8 (dm, $J_{\text{C-F}}$ = 254.1, CF), 139.8 (dm, $J_{\text{C-F}}$ = 252.7, CF), 145.5 (dm, $J_{\text{C-F}}$ = 249.1, CF).

^{19}F NMR (CDCl_3 , 188.3 MHz, 24 °C) δ -163.03 (td, J = 8.3, 22.2, *meta*), -162.62 (td, J = 8.3, 22.2, *meta*), -156.65 (t, J = 22.2, *para*), -138.35 (br d, *ortho*), -128.55 (br d, *ortho*). ^{19}F NMR (CDCl_3 , 188.3 MHz, 80 °C, sealed tube) δ -163.31 (m, *meta*), -157.31 (t, J = 19.4, *para*), -138.27 (br, $\Delta\nu_{1/2}$ = 149.8 Hz, *ortho*), -128.8 (br, $\Delta\nu_{1/2}$ = 149.8 Hz, *ortho*).

Calcd for $\text{C}_{17}\text{H}_{20}\text{F}_5\text{N}$ (333.34): C 61.25, H 6.05, N 4.20. Found: C 61.14, H 5.98, N 4.49.

1-(2,3,5,6-Tetrafluorophenyl)pyrrolidine (7).

Pyrrolidine (126 μL , 1.5 mmol) was added to a suspension of $\text{MeOSi}(\text{C}_6\text{F}_5)_3$ (784 mg, 1.4 mmol) in MeCN (3.5 mL) at 0 °C and the mixture was stirred for 16 h at room temperature. After cooling with ice/water bath a solution of NH_4F (52 mg, 1.4 mmol) in MeOH/water (1.8 mL/0.18 mL) was added, the mixture was stirred for additional 5 min at room temperature, diluted with excess ether/hexanes (1 : 1), and filtered. The filtrate was concentrated under vacuum, the residue was diluted with ether/hexanes (1 : 1), and dried (Na_2SO_4). Evaporation of the solvent afforded crude product, which was chromatographed on silica gel eluting with hexanes to give 153 mg of title compound (50 %).

R_f = 0.34 (hexanes). M.p. 45–46 °C (recrystallized by dissolving in small amount of MeOH followed by cooling to -30 °C).

^1H NMR (CDCl_3 , 300.1 MHz) δ 1.88–1.96 (m, 4 H, CH_2CH_2), 3.55–3.64 (m, 4H, NCH_2), 6.35 (tt, 1H, $J_{\text{H-F}}$ = 7.4, 10.3, CH).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 25.7 (t, J = 1.7, CH_2CH_2), 51.1 (t, J = 5.7, NCH_2), 92.7 (t, J = 23.4, CH), 129.0 (m, $\text{C}_{\text{Ar-N}}$), 138.7 (dm, $J_{\text{C-F}}$ = 240.6, CF), 147.1 (dm, $J_{\text{C-F}}$ = 246.3, CF).

^{19}F NMR (CDCl_3 , 188.3 MHz) δ -156.87 (br d), -142.99 (m).

Calcd for $\text{C}_{10}\text{H}_9\text{F}_4\text{N}$ (219.18): C 54.80, H 4.14, N 6.39. Found: C 54.68, H 3.97, N 6.21.

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker WM-250 SF=62.9MHz{C-13} SI=16K SW=14705 OI=85414 PW=6 AQ=0.557 RD=0.3 NS=4176 SR=78452.64 TE=297K Mar 3 2005 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:59:40;

The Best Applied NMR, Printed Mar 04 2005 20:28

¹³C NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 O1=-19911 PW=45 AQ=0.3604 RD=1 NS=456 SR=2737.32 TE=297K Dec 11 2004 21:23:39 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:10:20;
The Best Applied NMR, Printed May 19 2005 21:15

¹⁹F NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker WM-250 SF=250.13MHz{H-1} SI=16K SW=5376 O1=4666 PW=5 AQ=1.5237 RD=3 NS=4 SR=2853.04 TE=297K Nov 22 2004 Opr: Belyakov P.A.; Solv: CDCl₃;

The Best Applied NMR, Printed May 19 2005 20:39

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=50.32MHz(C-13) SI=16K SW=11627 OI=5600 PW=3 AQ=0.7045 RD=0.3 NS=2048 SR=324.84 TE=297K Nov 26 2004 22:06:19 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:34:21;

The Best Applied NMR, Printed Nov 26 2004 22:16

¹³C NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 OI=-19911 PW=45 AQ=0.3604 RD=1 NS=742 SR=2737.32 TE=297K Nov 26 2004 21:31:16 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:16:49;
The Best Applied NMR, Printed May 19 2005 21:17

¹⁹F NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=200.13MHz{H-1} SI=16K SW=4000 O1=3416 PW=3 AQ=2.048 RD=2 NS=8 SR=2338.00 TE=297K Mar 24 2005 12:00:40 Opr: Belyakov P.A.; Solv: CDCl₃;

The Best Applied NMR, Printed May 19 2005 20:41

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=50.32MHz{C-13} SI=16K SW=11627 O1=5600 PW=3 AQ=0.7045 RD=0.3 NS=2048 SR=324.84 TE=297K Jan 2 2005 20:18:36 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:34:19;
The Best Applied NMR, Printed Jan 02 2005 20:54

¹³C NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 OI=-19911 PW=45 AQ=0.3604 RD=1 NS=690 SR=2737.32 TE=297K Jan 2 2005 19:43:33 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:15:38;

The Best Applied NMR, Printed May 19 2005 21:18

¹⁹F NMR
Solv. CDCl₃

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=50.32MHz[C-13] SI=16K SW=11627 O1=5600 PW=3 AQ=0.7045 RD=0.3 NS=2048 SR=324.84 TE=297K Dec 11 2004 22:15:43 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:34:19;

The Best Applied NMR, Printed Dec 11 2004 22:33

¹³C NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 O1=-19911 PW=45 AQ=0.3604 RD=1 NS=572 SR=2737.32 TE=297K Dec 11 2004 21:39:41 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:12:58;
The Best Applied NMR, Printed May 19 2005 21:19

¹⁹F NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AM-300 SF=300.13MHz{H-1} SI=16K SW=6024 O1=5754 PW=4 AQ=1.3598 RD=3 NS=4 SR=3365.56 TE=297K Dec 10 2004 22:29:25 Opr: Belyakov P.A.; Solv: CDCl₃;

The Best Applied NMR, Printed May 19 2005 20:45

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker WM-250 SF=62.9MHz{C-13} SI=16K SW=14705 O1=85414 PW=6 Aq=0.557 RD=0.3 NS=2048 SR=78452.64 TE=297K Dec 11 2004 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:29:16;

The Best Applied NMR, Printed Dec 11 2004 22:03

¹³C NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 O1=-19911 PW=45 AQ=0.3604 RD=1 NS=480 SR=2737.32 TE=297K Dec 11 2004 22:41:45 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:10:53;
The Best Applied NMR, Printed May 19 2005 21:19

¹⁹F NMR
Solv. CDCl₃

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=50.32MHz{C-13} SI=16K SW=11627 O1=5600 PW=3 AQ=0.7045 RD=0.3 NS=2048 SR=324.84 TE=297K Nov 4 2004 21:28:22 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:34:19;

The Best Applied NMR, Printed Nov 04 2004 22:40

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 Ol=-19911 PW=45 AQ=0.3604 RD=1 NS=876 SR=2737.32 TE=297K Nov 4 2004 20:50:19 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:19:51;
The Best Applied NMR, Printed May 19 2005 21:20

¹⁹F NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=200.13MHz{H-1} SI=16K SW=4000 O1=3416 PW=3 AQ=2.048 RD=2 NS=8 SR=2338.00 TE=297K Dec 29 2004 16:19:41 Opr: Belyakov P.A.; Solv: CDCl₃;

The Best Applied NMR, Printed May 19 2005 20:48

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=50.32MHz{C-13} SI=16K SW=11627 OI=5600 PW=3 AQ=0.7045 RD=0.3 NS=2048 SR=324.84 TE=297K Jan 2 2005 19:23:32 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:34:19;
The Best Applied NMR, Printed Jan 02 2005 19:36

¹³C NMR
Solv. CDCl₃

^{19}F NMR
Solv. CDCl_3

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker WM-250 SF=250.13MHz{H-1} SI=16K SW=5376 O1=4666 PW=5 AQ=1.5237 RD=3 NS=4 SR=2853.04 TE=297K Dec 21 2004 Opr: Belyakov P.A.; Solv: CDCl₃;

The Best Applied NMR, Printed May 19 2005 20:50

¹H NMR
Solv. CDCl₃

¹³C NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 O1=-19911 PW=45 AQ=0.3604 RD=1 NS=1637 SR=2737.32 TE=297K Dec 23 2004 21:00:27 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:37:07;
The Best Applied NMR, Printed May 19 2005 21:22

¹⁹F NMR
Solv. CDCl₃

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker WM-250 SF=62.9MHz{C-13} SI=16K SW=14705 O1=85414 PW=6 AQ=0.557 RD=0.3 NS=2048 SR=78452.64 TE=303K Feb 3 2005 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:29:16;

The Best Applied NMR, Printed Feb 03 2005 22:01

¹³C NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 O1=-19911 PW=45 AQ=0.3604 RD=1 NS=1134 SR=2737.32 TE=297K Feb 4 2005 18:25:12 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:25:42;
The Best Applied NMR, Printed May 19 2005 21:22

¹⁹F NMR
Solv. CDCl₃

¹H NMR
Solv. CDCl₃

¹³C NMR
Solv. CDCl₃

^{19}F NMR
Solv. CDCl_3

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=50.32MHz{C-13} SI=16K SW=11627 O1=5600 PW=3 AQ=0.7045 RD=0.3 NS=2048 SR=324.84 TE=297K Jan 24 2005 22:07:42 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:34:19;
The Best Applied NMR, Printed Jan 24 2005 22:13

¹³C NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 OI=-19911 PW=45 AQ=0.3604 RD=1 NS=552 SR=2737.32 TE=297K Jan 24 2005 21:31:40 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:12:30;
The Best Applied NMR, Printed May 19 2005 21:23

¹⁹F NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AM-300 SF=300.13MHz{H-1} SI=16K SW=6024 OI=5754 PW=4 AQ=1.3598 RD=3 NS=16 SR=3365.56 TE=297K Nov 26 2004 11:43:14 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:01:09;
The Best Applied NMR, Printed May 19 2005 20:58

¹H NMR
Solv. CDCl₃

¹⁹F NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=50.32MHz{C-13} SI=16K SW=11627 O1=5600 PW=3 AQ=0.7045 RD=0.3 NS=2048 SR=324.84 TE=297K Feb 27 2005 17:37:41 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:34:19;

The Best Applied NMR, Printed Feb 27 2005 17:43

¹³C NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 O1=-19911 PW=45 AQ=0.3604 RD=1 NS=694 SR=2737.32 TE=297K Feb 27 2005 17:02:38 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:15:44;

The Best Applied NMR, Printed May 19 2005 21:25

¹⁹F NMR
Solv. CDCl₃
T = 297 K

¹⁹F NMR
Solv. CDCl₃
T = 353 K

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=50.32MHz{C-13} SI=16K SW=11627 O1=5600 PW=3 AQ=0.7045 RD=0.3 NS=2048 SR=324.84 TE=297K Feb 27 2005 16:42:36 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:34:19;

The Best Applied NMR, Printed Feb 27 2005 16:52

¹³C NMR
Solv. CDCl₃

¹⁹F NMR
Solv. CDCl₃
T = 297 K

¹⁹F NMR
Solv. CDCl₃
T = 353 K

MeOSi(C₆F₅)₃
5

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=188.31MHz{F-19} SI=16K SW=22727 O1=-19911 PW=45 AQ=0.3604 RD=1 NS=758 SR=2737.32 TE=297K Nov 26 2004 19:31:47 Opr: Belyakov P.A.; Solv: CDCl3; Total time=0:17:11;

The Best Applied NMR, Printed May 19 2005 21:27

MeOSi(C₆F₅)₃
5

¹⁹F NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AM-300 SF=300.13MHz{H-1} SI=16K SW=6024 OI=5754 PW=4 AQ=1.3598 RD=3 NS=4 SR=3365.56 TE=297K Dec 10 2004 22:34:26 Opr: Belyakov P.A.; Solv: CDCl₃;

The Best Applied NMR, Printed May 19 2005 21:04

¹H NMR
Solv. CDCl₃

©N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker AC-200 SF=50.32MHz[C-13] SI=16K SW=11627 O1=5600 PW=3 AQ=0.7045 RD=0.3 NS=2048 SR=324.84 TE=297K Dec 11 2004 21:07:38 Opr: Belyakov P.A.; Solv: CDCl₃; Total time=0:34:19;
The Best Applied NMR, Printed Dec 11 2004 21:15

¹³C NMR
Solv. CDCl₃

¹⁹F NMR
Solv. CDCl₃