Synthesis of Perfluoroalkyl-Substituted Azines *via* Nucleophilic Substitution of Hydrogen with Perfluoroisopropyl Carbanions

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General experimental methods. The reactions with HFP and KF were performed under argon atmosphere (technical grade argon) in a flame dried glass pressure tube (c.a. 3.5 mL of volume) equipped with a teflon valve and a magnetic stirring element. All solvents used in these reactions were dried by standard techniques: DMF, MeCN, DME and CH₂Cl₂ were distilled from CaH₂ and THF from potassium/benzophenone.¹ Solvents used for extraction or chromatography were freshly distilled before use. Hunig's base (*i*-Pr₂NEt) was dried by storing over potassium hydroxide. Other reagents were used as obtained without further purification.

Flash chromatography was performed using silica gel 60 (0.040 - 0.063 mm) or neutral aluminium oxide. Thin layer chromatography was performed on pre-coated silica gel plates and visualized under a UV lamp.

NMR spectra were recorded in CDCl₃ at the spectrometer frequencies indicated in the description of each compound. Chemical shifts are given in ppm relative to TMS for ¹H and ¹³C NMR spectra and CFCl₃ for ¹⁹F NMR spectra. IR spectra were obtained using a FT-IR spectrometer. Mass spectra were obtained using electron impact (EI) or electrospray (ESI) ionization.

p-Methoxybenzyl bromide was prepared according to a literature procedure.²

N-Alkylazinium salts are well known compounds and are usually prepared simply by heating an equimolar mixture of the azine and the alkylating agent.³ Salts **1a**, **1c** and **1d** were prepared in this way.

1 Armarego, W. F. L.; Perrin, D. D. *Purification of Laboratory Chemicals*; Butterworth-Heinemann: Oxford, 1996.

2 Ruder, S. M.; Ronald, R. C. *Tetrahedron Lett.* **1987**, 28, 135.

3 See for example: (a) Cymerman Craig, J.; Garnett, J. L.; Temple, D. M. *J. Chem. Soc.* **1964**, 4057. (b) Bunting, J. W.; Sindhuatmadja, S. *J. Org. Chem.* **1981**, 46, 4211. (c) Fukuzumi, S.; Kommitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, 109, 305. (d) MacTavish, J.; Proctor, G. R.; Redpath, J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2545. (e) Lo, H. C.; Buriez, O.; Kerr, J. B.; Fish, R. H. *Angew. Chem. Int. Ed.* **1999**, 38, 1429.

The most convenient way to obtain all other salts was to mix equimolar amounts of the azine and BnBr or PMBBBr in acetone (in some cases toluene or CHCl_3) at room temperature. After a few hours or days the crystalline salt was collected, washed and dried under vacuum. The identity and purity of each salt was confirmed by its melting point, elemental analysis and ^1H NMR spectrum.

General procedure of one-pot preparation of dihydroazines 2 and 3 directly from an azine and PMBBBr. An azine (0.95 mmol) was dissolved in DMF (2.75 mL) in a glass pressure tube, then PMBBBr (191 mg, 136 μL , 0.95 mmol) was added and the tube was closed with a teflon valve. After stirring at room temperature for the time indicated in Table 1 (consumption of the azine was followed by TLC) the reaction mixture was cooled to $-75\text{ }^\circ\text{C}$ under argon atmosphere and HFP (c.a. 0.6 g, 4 mmol) was condensed into it (it is possible to measure approximately the volume of HFP already condensed since it is hardly miscible with DMF). Spray-dried $\text{KF}_{(\text{s})}$ (276 mg, 4.75 mmol) was then added, the tube was closed again and its contents stirred vigorously for 3h at room temperature. After opening of the tube the reaction mixture was poured into water (10 mL) and the products were extracted with CH_2Cl_2 (3x5 mL). Combined organic layers were washed with water (5x10 mL), dried over anhydrous Na_2SO_4 and concentrated. The products were purified by column chromatography on silica gel using 10:1 or 5:1 mixtures of hexanes/AcOEt as eluent (when two isomeric products were formed, mixtures of hexanes and Et_2O of similar composition were sometimes more effective to separate them, see below).

2-Heptafluoroisopropyl-1-(*p*-methoxybenzyl)-1,2-dihydroquinoline (2c'). White solid, mp 63 – 63

$^\circ\text{C}$. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) : 3039, 2995, 2838, 1649, 1602, 1513, 1497, 1287, 1258, 1233, 1149, 1029, 972, 952, 797, 761. ^1H NMR (400 MHz) δ = 3.76 (3H, s, OCH_3), 4.38 (1H, d, $^2J_{\text{HH}}$ = 15.5 Hz, NCH_2), 4.91 (1H, d, $^2J_{\text{HH}}$ = 15.7 Hz, NCH_2), 5.06 (1H, m, CHCF), 5.56 (1H, m, CHCHCF), 6.69 (1H, m, $\text{CH}=\text{CHCHCF}$), 6.69 – 6.74 (2H, m, H_{arom}), 6.81 (2H, dm, $^3J_{\text{HH}}$ = 8.7 Hz, PMB), 6.99 (1H, dd, $^3J_{\text{HH}}$ = 7.4 Hz, $^4J_{\text{HH}}$ = 1.8 Hz, H_{arom}), 7.09 (1H, td, $^3J_{\text{HH}}$ = 7.7 Hz, $^4J_{\text{HH}}$ = 1.5 Hz, H_{arom}), 7.12 (2H, dm, $^3J_{\text{HH}}$ = 8.7 Hz, PMB). ^{13}C NMR (100 MHz) δ = 55.2, 55.4 (d, $^4J_{\text{CF}}$ = 4.3 Hz), 59.4 (d, $^2J_{\text{CF}}$ = 19.8 Hz), 92.1 (dm, $^1J_{\text{CF}}$ = 206.4 Hz, $^2J_{\text{CF}}$ = 29.1 Hz), 114.1, 114.3 (d, $^3J_{\text{CF}}$ = 6.5 Hz), 114.5, 118.5, 120.7 (qd, $^1J_{\text{CF}}$ = 287.4 Hz, $^2J_{\text{CF}}$ = 28.2 Hz), 120.8 (qd, $^1J_{\text{CF}}$ = 287.7 Hz, $^2J_{\text{CF}}$ = 26.3 Hz), 122.1, 127.3, 128.6, 128.7, 129.5, 130.8, 143.1, 159.0. ^{19}F NMR (376 MHz) δ = -179.67 (1F, m, $\text{CF}(\text{CF}_3)_2$), -74.15 (3F, m, $^3J_{\text{FF}}$ = 8.7 Hz,

CF(CF₃)₂), -72.89 (3F, m, ³J_{FF} = 8.7 Hz, CF(CF₃)₂). MS (EI 70 eV) *m/z* (%) : 419(M⁺, 2), 250(26), 121(100). HRMS (EI) : calcd for C₂₀H₁₆NOF₇ (M⁺) 419.1120, found 419.1131. Anal. Calcd for C₂₀H₁₆NOF₇ : C, 57.29; H, 3.85; N, 3.34; F, 31.71. Found : C, 57.93; H, 3.69; N, 3.04; F, 31.75.

4-Heptafluoroisopropyl-1-(*p*-methoxybenzyl)-1,4-dihydroquinoline (3c'). White solid, mp 57 – 58

°C. IR (CH₂Cl₂, *v*_{max}/cm⁻¹) : 2934, 1667, 1514, 1494, 1467, 1385, 1295, 1249, 1222, 1178, 1109, 1038, 976, 752, 710. ¹H NMR (400 MHz) *δ* = 3.79 (3H, s, OCH₃), 4.55 (1H, ddm, ³J_{HH} = 7.8 Hz, 5.5 Hz, NCH=CH), 4.67 (2H, AB, ²J_{HH} = 16.5 Hz, NCH₂), 4.65 – 4.72 (1H, m, CHCF), 6.39 (1H, dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.8 Hz, NCH=CH), 6.71 (1H, dd, ³J_{HH} = 8.4 Hz, ⁴J_{HH} = 1.0 Hz, H_{arom}), 6.86 (2H,

dm, ³J_{HH} = 8.8 Hz, PMB), 6.92 (1H, td, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.2 Hz, H_{arom}), 7.11 – 7.19 (4H, m, H_{arom}). ¹³C NMR (100 MHz) *δ* = 40.7 (d, ²J_{CF} = 20.7 Hz), 53.8, 55.3, 89.2 (d, ³J_{CF} = 8.6 Hz), 89.0 – 92.5 (m), 112.8, 114.2, 114.4, 116.5 – 126.0 (m), 121.1, 127.6, 128.7, 129.0, 131.7 (d, ³J_{CF} = 4.2 Hz), 136.5, 141.0, 158.9. ¹⁹F NMR (376 MHz) *δ* = -174.50 (1F, m, CF(CF₃)₂), -74.05 (3F, m, CF(CF₃)₂), -72.06 (3F, m, CF(CF₃)₂). MS (EI 70 eV) *m/z* (%) : 419(M⁺, 1), 297(1), 250(21), 121(100). HRMS (EI) : calcd for C₂₀H₁₆NOF₇ (M⁺) 419.1120, found 419.1115. Anal. Calcd for C₂₀H₁₆NOF₇ : C, 57.29; H, 3.85; N, 3.34; F, 31.71. Found : C, 57.15; H, 3.77; N, 3.17; F, 31.68.

1-Heptafluoroisopropyl-2-(*p*-methoxybenzyl)-1,2-dihydroisoquinoline (2d'). Pale yellow oil,

becomes dark-red after a few days at RT. IR (film, *v*_{max}/cm⁻¹) : 3064, 3031, 2937, 2839, 1626, 1513, 1288, 1228, 1157, 1112, 1036, 983, 770. ¹H NMR (400 MHz) *δ* = 3.73 (3H, s, OCH₃), 4.38 (2H, s, NCH₂), 5.50 (1H, d, ³J_{HH} = 7.3 Hz, NCH=CH), 5.62 (1H, d, ³J_{HF} = 7.2 Hz, CHCF), 6.21 (1H, dd, ³J_{HH} = 7.3 Hz, ⁴J_{HH}

= 1.2 Hz, NCH=CH), 6.77 (2H, dm, ³J_{HH} = 8.8 Hz, PMB), 6.95 (1H, d, ³J_{HH} = 7.8 Hz, H_{arom}), 6.98 – 7.13 (4H, m, H_{arom}), 7.23 (1H, td, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.4 Hz, H_{arom}). ¹³C NMR (100 MHz) *δ* = 55.1, 58.9 (d, ⁴J_{CF} = 2.6 Hz), 61.3 (d, ²J_{CF} = 22.3 Hz), 90.5 (dm, ¹J_{CF} = 206.0 Hz, ²J_{CF} = 30.2 Hz), 101.8, 114.1, 118.8 (d, ⁴J_{CF} = 2.6 Hz), 120.9 (qd, ¹J_{CF} = 289.6 Hz, ²J_{CF} = 27.6 Hz), 121.0 (qd, ¹J_{CF} = 285.3 Hz, ²J_{CF} = 27.6 Hz), 123.5, 125.2, 128.2, 128.5, 128.9, 129.4, 134.1, 135.2, 159.1. ¹⁹F NMR (376 MHz) *δ* = -178.85 (1F, m, ³J = 6.7 Hz, CF(CF₃)₂), -72.33 (3F, m, ³J_{FF} = 9.4 Hz, CF(CF₃)₂), -72.04 (3F, m, ³J_{FF} = 8.0 Hz, CF(CF₃)₂). MS (EI 70 eV) *m/z* (%) : 419(M⁺, 4), 250(36), 121(100). HRMS (EI) : calcd for C₂₀H₁₆NOF₇ (M⁺) 419.1120, found 419.1140. Anal. Calcd for C₂₀H₁₆NOF₇ : C, 57.29; H, 3.85; N, 3.34.

Found : C, 56.99; H, 3.65; N, 3.29%.

2-Heptafluoroisopropyl-1-(*p*-methoxybenzyl)-5-methoxycarbonyl-1,2-dihydropyridine (2e').

Separated from **3e'** by chromatography using 10:1 hexanes/Et₂O, pale yellow oil. IR (CH₂Cl₂, $\nu_{\max}/\text{cm}^{-1}$) : 3002, 2954, 2841, 1698, 1642, 1577, 1514, 1440, 1290, 1253, 1226, 1141, 1109, 744. ¹H NMR (400 MHz) δ = 3.72 (3H, s, OCH₃), 3.81 (3H, s, OCH₃), 4.48 (2H, AB, ²*J*_{HH} = 16.2,

NCH₂), 4.89 (1H, m, CHCHCF), 5.05 (1H, m, CHCF), 6.70 (1H, d, ³*J*_{HH} = 9.8 Hz, CH=CHCHCF), 6.90 (2H, d, ³*J*_{HH} = 8.7 Hz, PMB), 7.16 (2H, d, ³*J*_{HH} = 8.7 Hz, PMB), 7.47 (1H, d, ⁴*J*_{HH} = 0.6 Hz, NCH=CCO₂Me). ¹³C NMR (100 MHz) δ = 51.3, 55.5, 58.6 (d, ²*J*_{CF} = 19.0 Hz), 60.4 (d, ⁴*J*_{CF} = 6.0 Hz), 92.0 (dm, ¹*J*_{CF} = 207.8 Hz, ²*J*_{CF} = 28.4 Hz), 101.4, 103.7 (dm, ³*J*_{CF} = 7.8 Hz, ⁴*J*_{CF} = 1.7 Hz), 114.8, 120.6 (qd, ¹*J*_{CF} = 288.0 Hz, ²*J*_{CF} = 26.7 Hz), 120.8 (qd, ¹*J*_{CF} = 287.9 Hz, ²*J*_{CF} = 28.4 Hz), 127.0, 127.5, 129.4, 147.0, 160.0, 166.4. ¹⁹F NMR (376 MHz) δ = -177.47 (1F, m, CF(CF₃)₂), -73.75 (3F, m, CF(CF₃)₂), -72.66 (3F, m, CF(CF₃)₂). HRMS (ESI, MeOH) : calcd for C₁₈H₁₆NO₃F₇Na (M+Na⁺) 450.0911, found 450.0913. Anal. Calcd for C₁₈H₁₆NO₃F₇ : C, 50.59; H, 3.77; N, 3.28; F, 31.12. Found : C, 50.53; H, 3.72; N, 3.42; F, 31.18.

4-Heptafluoroisopropyl-1-(*p*-methoxybenzyl)-3-methoxycarbonyl-1,4-dihydropyridine (3e').

Separated from **2e'** by chromatography using 10:1 hexanes/Et₂O, pale yellow oil. IR (film, $\nu_{\max}/\text{cm}^{-1}$) : 3003, 2954, 2841, 1704, 1590, 1515, 1415, 1304, 1254, 1217, 1169, 1086, 977, 789, 749, 723. ¹H NMR (500 MHz) δ = 3.71 (3H, s, OCH₃), 3.80 (3H, s, OCH₃), 4.40 (2H, s, NCH₂), 4.70 (1H, m, CHCF),

4.77 (1H, dd, ³*J*_{HH} = 7.0 Hz, ³*J*_{HH} = 6.3 Hz, NCH=CH), 6.15 (1H, d, ³*J*_{HH} = 7.7 Hz, NCH=CH), 6.89 (2H, d, ³*J*_{HH} = 8.6 Hz, PMB), 7.12 (2H, d, ³*J*_{HH} = 8.6 Hz, PMB), 7.45 (1H, d, ⁴*J*_{HH} = 1.1 Hz, NCH=CCO₂Me). ¹³C NMR (125 MHz) δ = 35.3 (d, ²*J*_{CF} = 21.4 Hz), 51.2, 55.2, 57.5, 91.3 (dm, ¹*J*_{CF} = 207.9 Hz, ²*J*_{CF} = 28.3 Hz), 93.4 (d, ³*J*_{CF} = 4.6 Hz), 97.5 (d, ³*J*_{CF} = 6.1 Hz), 114.3, 120.9 (qd, ¹*J*_{CF} = 288.1 Hz, ²*J*_{CF} = 28.4 Hz), 121.3 (qd, ¹*J*_{CF} = 287.5 Hz, ²*J*_{CF} = 27.8 Hz), 127.8, 128.8, 132.3, 143.0, 159.6, 168.2. ¹⁹F NMR (376 MHz) δ = -184.11 (1F, m, ³*J* = 6.0 Hz, CF(CF₃)₂), -75.81 (3F, m, ³*J*_{FF} = 8.3 Hz, CF(CF₃)₂), -73.29 (3F, m, ³*J*_{FF} = 8.3 Hz, CF(CF₃)₂). HRMS (ESI, MeOH) : calcd for C₁₈H₁₆NO₃F₇Na (M+Na⁺) 450.0911, found 450.0926. Anal. Calcd for C₁₈H₁₆NO₃F₇ : C, 50.59; H, 3.77; N, 3.28; F, 31.12. Found : C, 50.66; H, 3.79; N, 3.40; F, 29.87.

3-Cyano-6-heptafluoroisopropyl-1-(*p*-methoxybenzyl)-1,6-dihydropyridine (2f'). Pale yellow solid,

mp 50 – 51 °C. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) : 3064, 3013, 2968, 2835, 2204, 1650, 1582, 1514, 1385, 1295, 1253, 1223, 1109, 1032, 957, 750. ^1H NMR (500 MHz) δ = 3.82 (3H, s, OCH_3), 4.43 (2H, AB, $^2J_{\text{HH}}$ = 14.8 Hz, NCH_2), 4.94 (1H, m, CHCHCF), 5.09 (1H, m, CHCF), 6.21 (1H, d, $^3J_{\text{HH}}$ = 9.7 Hz, $\text{CH}=\text{CHCHCF}$), 6.92 (2H, d, $^3J_{\text{HH}}$ = 8.6 Hz, PMB), 6.98 (1H, s, $\text{NCH}=\text{CCN}$), 7.15 (2H, d, $^3J_{\text{HH}}$ = 8.6 Hz, PMB). ^{13}C NMR (125 MHz) δ = 55.2, 58.2 (d, $^2J_{\text{CF}}$ = 19.8 Hz), 60.2 (d, $^4J_{\text{CF}}$ = 6.2 Hz), 81.9, 91.5 (dm, $^1J_{\text{CF}}$ = 209.2 Hz, $^2J_{\text{CF}}$ = 29.8 Hz), 105.2 (d, $^3J_{\text{CF}}$ = 7.5 Hz), 114.6, 119.2, 120.2 (qd, $^1J_{\text{CF}}$ = 287.8 Hz, $^2J_{\text{CF}}$ = 27.8 Hz), 120.4 (qd, $^1J_{\text{CF}}$ = 287.2 Hz, $^2J_{\text{CF}}$ = 28.5 Hz), 125.8, 126.5, 129.4, 147.7, 160.0. ^{19}F NMR (376 MHz) δ = -178.04 (1F, m, $\text{CF}(\text{CF}_3)_2$), -73.84 (3F, m, $\text{CF}(\text{CF}_3)_2$), -72.76 (3F, m, $\text{CF}(\text{CF}_3)_2$). HRMS (ESI, MeOH) : calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OF}_7\text{Na}$ ($\text{M}+\text{Na}^+$) 417.0808, found 417.0829. Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OF}_7$: C, 51.79; H, 3.32; N, 7.10; F, 33.73. Found : C, 51.87; H, 3.11; N, 6.97; F, 33.68.

3-Cyano-4-heptafluoroisopropyl-1-(*p*-methoxybenzyl)-1,4-dihydropyridine (3f'). Pale yellow oil.

IR (CCl_4 , $\nu_{\text{max}}/\text{cm}^{-1}$) : 3009, 2939, 2842, 2204, 1687, 1593, 1515, 1416, 1294, 1254, 1223, 1120, 1034, 977, 748. ^1H NMR (400 MHz) δ = 3.82 (3H, s, OCH_3), 4.30 (1H, m, CHCF), 4.35 (2H, s, NCH_2), 4.71 (1H, m, $\text{NCH}=\text{CH}$), 6.12 (1H, d, $^3J_{\text{HH}}$ = 8.1 Hz, $\text{NCH}=\text{CH}$), 6.88 (1H, d, $^4J_{\text{HH}}$ = 1.5 Hz, $\text{NCH}=\text{CCN}$), 6.91 (2H, d, $^3J_{\text{HH}}$ = 8.7 Hz, PMB), 7.11 (2H, m, $^3J_{\text{HH}}$ = 8.8 Hz, PMB). ^{13}C NMR (100 MHz) δ = 37.5 (d, $^2J_{\text{CF}}$ = 21.6 Hz), 55.3, 57.5, 74.3 (d, $^3J_{\text{CF}}$ = 5.1 Hz), 91.1 (dm, $^1J_{\text{CF}}$ = 206.9 Hz, $^2J_{\text{CF}}$ = 28.4 Hz), 96.4 (dd, $^3J_{\text{CF}}$ = 8.6 Hz, $^4J_{\text{CF}}$ = 1.7 Hz), 114.5, 120.0, 120.7 (qd, $^1J_{\text{CF}}$ = 288.8 Hz, $^2J_{\text{CF}}$ = 28.4 Hz), 120.7 (qd, $^1J_{\text{CF}}$ = 287.1 Hz, $^2J_{\text{CF}}$ = 26.7 Hz), 126.8, 128.9, 132.0, 145.4, 159.8. ^{19}F NMR (376 MHz) δ = -179.80 (1F, md, 3J = 7.5 Hz, $^4J_{\text{FH}}$ = 1.5 Hz, $\text{CF}(\text{CF}_3)_2$), -74.64 (3F, m, $\text{CF}(\text{CF}_3)_2$), -72.61 (3F, m, $\text{CF}(\text{CF}_3)_2$). MS (EI 70 eV) m/z (%) : 394(M^+ , <1), 225(10), 121(100). HRMS (EI) : calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OF}_7$ (M^+) 394.0916, found 394.0911. Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OF}_7$: C, 51.79; H, 3.32; N, 7.10; F, 33.73. Found : C, 51.66; H, 3.07; N, 7.31; F, 33.62.

3-Benzoyl-6-heptafluoroisopropyl-1-(*p*-methoxybenzyl)-1,6-dihydropyridine (2g'). Yellow oil. IR

(CH_2Cl_2 , $\nu_{\text{max}}/\text{cm}^{-1}$) : 2938, 1614, 1569, 1514, 1290, 1254, 1225, 1109, 716. ^1H NMR (400 MHz) δ = 3.80 (3H, s, OCH_3), 4.48 (2H, AB, $^2J_{\text{HH}}$ = 15.0, NCH_2), 5.01 – 5.13 (2H, m, CHCHCF), 6.88 (2H, dm, $^3J_{\text{HH}}$ = 8.8 Hz, PMB),

7.02 (1H, dd, $^3J_{\text{HH}} = 8.9$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, CH=CHCHCF), 7.10 (2H, dm, $^3J_{\text{HH}} = 8.7$ Hz, PMB), 7.20 (1H, d, $^4J_{\text{HH}} = 0.8$ Hz, NCH=CCOPh), 7.39 – 7.44 (2H, m, Ph), 7.45 – 7.49 (1H, m, Ph), 7.54 – 7.57 (2H, m, Ph). ^{13}C NMR (100 MHz) $\delta = 55.3, 58.4$ (d, $^2J_{\text{CF}} = 19.8$ Hz), 60.5 (d, $^4J_{\text{CF}} = 6.0$ Hz), 92.0 (m), 104.8 (dm, $^3J_{\text{CF}} = 5.2$ Hz), 111.2, 114.6, 120.3 (qd, $^1J_{\text{CF}} = 287.1$ Hz, $^2J_{\text{CF}} = 25.9$ Hz), 120.7 (qd, $^1J_{\text{CF}} = 287.9$ Hz, $^2J_{\text{CF}} = 27.6$ Hz), 126.1, 127.5, 128.2, 128.7, 129.2, 130.9, 139.2, 151.0, 159.9, 190.9. ^{19}F NMR (376 MHz) $\delta = -177.39$ (1F, m, CF(CF₃)₂), -73.85 (3F, m, CF(CF₃)₂), -72.54 (3F, m, CF(CF₃)₂). MS (EI 70 eV) m/z (%) : 473(M⁺, 1), 304(22), 121(100). HRMS (EI) : calcd for C₂₃H₁₈NO₂F₇ (M⁺) 473.1226, found 473.1204. Anal. Calcd for C₂₃H₁₈NO₂F₇ : C, 58.36; H, 3.83; N, 2.96; F, 28.09. Found : C, 58.41; H, 3.88; N, 2.82; F, 26.73.

3-Benzoyl-4-heptafluoroisopropyl-1-(*p*-methoxybenzyl)-1,4-dihydropyridine (3g'). Yellow oil. ^1H

NMR (400 MHz) $\delta = 3.81$ (3H, s, OCH₃), 4.35 (2H, s, NCH₂), 4.90 (1H, t, $^3J = 6.5$ Hz, CHCF), 5.18 (1H, t, $^3J_{\text{HH}} = 5.5$ Hz, NCH=CH), 6.16 (1H, d, $^3J_{\text{HH}} = 7.8$ Hz, NCH=CH), 6.88 (2H, dm, $^3J_{\text{HH}} = 8.8$ Hz, PMB), 7.07 (2H, dm, $^3J_{\text{HH}} = 8.8$ Hz, PMB), 7.37 – 7.40 (2H, m, Ph), 7.48 (1H, s, NCH=CCOPh), 7.48 – 7.51

(1H, m, Ph), 7.57 – 7.61 (2H, m, Ph). ^{13}C NMR (100 MHz) $\delta = 34.6$ (d, $^2J_{\text{CF}} = 21.6$ Hz), 57.6, 65.8, 92.0 (m), 99.0, 104.6, 114.4, c.a. 121 (m), 127.4, 128.3, 128.6, 128.7, 131.0, 131.9, 138.7, 145.9, 159.6, 194.7. ^{19}F NMR (376 MHz) $\delta = -183.32$ (1F, m, CF(CF₃)₂), -75.36 (3F, m, CF(CF₃)₂), -73.07 (3F, m, CF(CF₃)₂).

3-Chloro-4-heptafluoroisopropyl-1-(*p*-methoxybenzyl)-1,4-dihydropyridine (3h'). Pale yellow oil,

becomes dark-red after a few days at RT. IR (film, $\nu_{\text{max}}/\text{cm}^{-1}$) : 3075, 3007, 2938, 2840, 1725, 1676, 1613, 1587, 1514, 1415, 1399, 1304, 1280, 1251, 1218, 1175, 1115, 1066, 1037, 976, 953, 813, 745, 538. ^1H NMR (400 MHz) $\delta = 3.81$ (3H, s, OCH₃), 4.26 (2H, s, NCH₂), 4.31 (1H, ddm, $^3J_{\text{HF}} = 8.5$ Hz, $^3J_{\text{HH}} = 6.7$ Hz, CHCF), 4.41 (1H, m, NCH=CH), 6.12 (1H, dt, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, NCH=CH),

6.39 (1H, d, $^4J_{\text{HH}} = 1.4$ Hz, NCH=CCl), 6.89 (2H, dm, $^3J_{\text{HH}} = 8.7$ Hz, PMB), 7.11 (2H, dm, $^3J_{\text{HH}} = 8.8$ Hz, PMB). ^{13}C NMR (100 MHz) $\delta = 44.2$ (d, $^2J_{\text{CF}} = 19.9$ Hz), 55.3, 56.7, 90.9 (d, $^3J_{\text{CF}} = 7.7$ Hz), 92.1 (dm, $^1J_{\text{CF}} = 210.3$ Hz, $^2J_{\text{CF}} = 28.5$ Hz), 99.8, 114.2, 120.9 (qd, $^1J_{\text{CF}} = 287.9$ Hz, $^2J_{\text{CF}} = 27.7$ Hz), 128.5, 128.7, 132.3, 133.0, 159.4. ^{19}F NMR (376 MHz) $\delta = -176.10$ (1F, m, CF(CF₃)₂), -74.07 (3F, m, CF(CF₃)₂), -72.94 (3F, m, CF(CF₃)₂). HRMS (ESI, MeOH/CH₂Cl₂) : calcd for C₁₆H₁₄NOCIF₇ (M+H⁺)

404.0647, found 404.0624. Anal. Calcd for $C_{16}H_{13}NOClF_7$: C, 47.60; H, 3.25; N, 3.47; Cl, 8.78. Found : C, 47.45; H, 3.21; N, 3.46; Cl 8.69.

4-Ethoxy-2-heptafluoroisopropyl-1-(*p*-methoxybenzyl)-5-nitro-1,2-dihydropyridine (2i'). Pale

yellow solid, mp 100 – 102 °C. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) : 3068, 3001, 2936, 2838, 1649, 1584, 1513, 1276, 1251, 1226, 1160, 1112, 1034, 983, 730. ^1H NMR (400 MHz) δ = 1.39 (3H, t, $^3J_{\text{HH}}$ = 7.0 Hz, CH_2CH_3), 3.82 (2H, q, $^3J_{\text{HH}}$ = 7.0 Hz, CH_2CH_3), 3.83 (3H, s, OCH_3), 3.98 (1H, d, $^3J_{\text{HH}}$ = 5.6 Hz, $\text{CH}=\text{C}(\text{OEt})$), 4.58 (2H, AB, $^2J_{\text{HH}}$ = 15.4 Hz, NCH_2), 5.06 (1H, m, CHCF), 6.95 (2H, dm, $^3J_{\text{HH}}$ = 8.7 Hz, PMB), 7.20 (2H, dm, $^3J_{\text{HH}}$ = 8.7 Hz, PMB), 8.19 (1H, d, $^4J_{\text{HH}}$ = 1.4 Hz, $\text{CH}=\text{CNO}_2$). ^{13}C NMR (100 MHz) δ = 14.1, 55.3, 59.4 (d, $^2J_{\text{CF}}$ = 19.8 Hz), 60.6 (d, $^4J_{\text{CF}}$ = 6.9 Hz), 64.3, 77.4 (d, $^3J_{\text{CF}}$ = 8.6 Hz), 91.9 (dm, $^1J_{\text{CF}}$ = 208.6 Hz, $^2J_{\text{CF}}$ = 28.5 Hz), 114.8, 120.2 (qd, $^1J_{\text{CF}}$ = 288.0 Hz, $^2J_{\text{CF}}$ = 27.7 Hz), 120.5 (qd, $^1J_{\text{CF}}$ = 287.0 Hz, $^2J_{\text{CF}}$ = 23.8 Hz), 121.9, 124.9, 129.7, 148.2, 151.2, 160.2. ^{19}F NMR (376 MHz) δ = -176.11 (1F, m, 3J = 7.0 Hz, $\text{CF}(\text{CF}_3)_2$), -73.44 (3F, m, $\text{CF}(\text{CF}_3)_2$), -72.13 (3F, m, $\text{CF}(\text{CF}_3)_2$). HRMS (ESI, MeOH) : calcd for $C_{18}H_{17}N_2O_4F_7\text{Na}$ ($\text{M}+\text{Na}^+$) 481.0969, found 481.0964. Anal. Calcd for $C_{18}H_{17}N_2O_4F_7$: C, 47.17; H, 3.74; N, 6.11; F, 29.02. Found : C, 47.39; H, 3.76; N, 6.00; F, 28.35.

4-Cyano-2-heptafluoroisopropyl-1-(*p*-methoxybenzyl)-1,2-dihydropyridine (2j'). Yellow oil,

decomposes after a few days at RT. IR (film, $\nu_{\max}/\text{cm}^{-1}$) : 3074, 3008, 2959, 2841, 2232, 1613, 1563, 1514, 1295, 1252, 1228, 1177, 1139, 1035, 1013, 955, 831, 721. ^1H NMR (200 MHz) δ = 3.82 (3H, s, OCH_3), 4.32 (2H, s, NCH_2), 5.04 (1H, dd, $^3J_{\text{HH}}$ = 7.1 Hz, $^4J_{\text{HH}}$ = 1.6 Hz, $\text{NCH}=\text{CH}$), 5.17 (1H, ddm, $^3J_{\text{HF}}$ = 8.5 Hz, $^3J_{\text{HH}}$ = 6.6 Hz, $^4J_{\text{HH}}$ = 1.4 Hz, CHCF), 5.38 (1H, d, $^3J_{\text{HH}}$ = 6.5 Hz, $\text{CH}=\text{CCN}$), 6.37 (1H, dt, $^3J_{\text{HH}}$ = 7.1 Hz, $^4J_{\text{HH}}$ = 1.1 Hz, $\text{NCH}=\text{CH}$), 6.91 (2H, d, $^3J_{\text{HH}}$ = 8.7 Hz, PMB), 7.15 (2H, m, $^3J_{\text{HH}}$ = 8.9 Hz, PMB). ^{13}C NMR (50 MHz) δ = 55.3, 58.4 (d, $^2J_{\text{CF}}$ = 21.2 Hz), 59.3 (d, $^4J_{\text{CF}}$ = 4.8 Hz), c.a. 90 (m), 95.5, 113.3 (d, $^3J_{\text{CF}}$ = 7.7 Hz), 114.5, 115.8, 117.0, c.a. 120.5 (qm, $^1J_{\text{CF}}$ = c.a. 280 Hz), 127.4, 129.0, 139.2, 159.7. ^{19}F NMR (376 MHz) δ = -180.87 (1F, m, $\text{CF}(\text{CF}_3)_2$), -73.86 (3F, m, J_{FF} = 8.9 Hz, $\text{CF}(\text{CF}_3)_2$), -73.14 (3F, m, J_{FF} = 8.9 Hz, $\text{CF}(\text{CF}_3)_2$). HRMS (ESI) : calcd for $C_{17}H_{13}N_2OF_7\text{Na}$ ($\text{M}+\text{Na}^+$) 417.0808, found 417.0829. Anal. Calcd for $C_{17}H_{13}N_2OF_7$: C, 51.79; H, 3.32; N, 7.10; F, 33.73. Found : C, 51.53; H, 3.38; N, 6.90; F, 33.81.

2-Heptafluoroisopropyl-5-methoxy-1-(*p*-methoxybenzyl)-1,2-dihydroquinoline (2k'). Pale yellow

oil. IR (film, $\nu_{\text{max}}/\text{cm}^{-1}$) : 3071, 3005, 2957, 2839, 1578, 1513, 1478, 1294, 1251, 1221, 1155, 1108, 1037, 974, 751. ^1H NMR (400 MHz) δ = 3.75 (3H, s, OCH₃), 3.79 (3H, s, OCH₃), 4.36 (1H, d, $^2J_{\text{HH}}$ = 15.8 Hz, NCH₂), 4.91 (1H, d, $^2J_{\text{HH}}$ = 15.8 Hz, NCH₂), 5.00 – 5.06 (1H, m, CHCF), 5.45 – 5.51 (1H, m, CHCHCF), 6.28 (1H, dd, $^3J_{\text{HH}}$ = 8.3 Hz, $^4J_{\text{HH}}$ = 0.5 Hz, H_{arom}), 6.37 (1H, dd, $^3J_{\text{HH}}$ = 8.4 Hz, $^4J_{\text{HH}}$ = 0.5 Hz, Hz, CH=CHCHCF), 6.80 (2H, dm, $^3J_{\text{HH}}$ = 8.8 Hz, PMB), 7.02 (1H, t, $^3J_{\text{HH}}$ = 8.3 Hz, H_{arom}), 7.07 – 7.14 (1H, m, H_{arom}), 7.07 – 7.14 (2H, m, PMB). ^{13}C NMR (100 MHz) δ = 55.1, 55.4, 55.7 (d, $^4J_{\text{CF}}$ = 4.3 Hz), 59.3 (d, $^2J_{\text{CF}}$ = 19.8 Hz), 92.1 (dm, $^1J_{\text{CF}}$ = 205.2 Hz, $^2J_{\text{CF}}$ = 29.3 Hz), 100.8, 107.9, 111.2, 112.1 (d, $^3J_{\text{CF}}$ = 6.9 Hz), 114.1, 120.7 (qd, $^1J_{\text{CF}}$ = 287.1 Hz, $^2J_{\text{CF}}$ = 28.4 Hz), 120.8 (qd, $^1J_{\text{CF}}$ = 288.0 Hz, $^2J_{\text{CF}}$ = 25.9 Hz), 125.0, 128.5, 128.9, 129.5, 144.0, 155.4, 158.9. ^{19}F NMR (376 MHz) δ = -180.05 (1F, m, CF(CF₃)₂), -74.09 (3F, m, $^3J_{\text{FF}}$ = 8.7 Hz, CF(CF₃)₂), -72.85 (3F, m, $^3J_{\text{FF}}$ = 8.7 Hz, CF(CF₃)₂). MS (EI 70 eV) m/z (%) : 448(<1), 280(20), 159(4), 121(100). HRMS (EI) : calcd for C₂₁H₁₇NO₂F₇ ([M – H]⁺) 448.1148, found 448.1128. Anal. Calcd for C₂₁H₁₈NO₂F₇ : C, 56.13; H, 4.04; N, 3.12; F, 29.59. Found : C, 56.00; H, 4.06; N, 3.09; F, 28.97.

4-Heptafluoroisopropyl-5-methoxy-1-(*p*-methoxybenzyl)-1,4-dihydroquinoline (3k'). Pale yellow

oil. IR (CH₂Cl₂, $\nu_{\text{max}}/\text{cm}^{-1}$) : 2939, 2840, 1665, 1599, 1514, 1479, 1388, 1283, 1219, 1175, 1128, 977, 791, 732. ^1H NMR (400 MHz) δ = 3.78 (3H, s, OCH₃), 3.79 (3H, s, OCH₃), 4.58 (1H, t, $^3J_{\text{HH}}$ = 6.6 Hz, NCH=CH), 4.66 (2H, s, NCH₂), 5.13 (1H, m, CHCF), 6.38 (2H, d, $^3J_{\text{HH}}$ = 7.7 Hz, NCH=CH, H_{arom}), 6.51 (1H, dd, $^3J_{\text{HH}}$ = 8.1 Hz, $^4J_{\text{HH}}$ = 0.6 Hz, H_{arom}), 6.85 (2H, dm, $^3J_{\text{HH}}$ = 8.8 Hz, PMB), 7.09 (1H, t, $^3J_{\text{HH}}$ = 8.3 Hz, H_{arom}), 7.13 (2H, dm, $^3J_{\text{HH}}$ = 8.8 Hz, PMB). ^{13}C NMR (100 MHz) δ = 33.8 (d, $^2J_{\text{CF}}$ = 21.6 Hz), 53.9, 55.2, 55.5, 90.6 (d, $^3J_{\text{CF}}$ = 5.2 Hz), 91.5 (dm, $^1J_{\text{CF}}$ = 212.1 Hz, $^2J_{\text{CF}}$ = 28.4 Hz), 103.1, 103.4, 105.5, 114.1, 121.1 (qd, $^1J_{\text{CF}}$ = 287.9 Hz, $^2J_{\text{CF}}$ = 29.3 Hz), 121.6 (qd, $^1J_{\text{CF}}$ = 287.1 Hz, $^2J_{\text{CF}}$ = 28.4 Hz), 127.7, 128.7, 129.2, 136.2, 143.0, 158.8, 158.9. ^{19}F NMR (376 MHz) δ = -180.92 (1F, m, 3J = 5.6 Hz, CF(CF₃)₂), -75.76 (3F, m, $^3J_{\text{FF}}$ = 8.3 Hz, CF(CF₃)₂), -72.92 (3F, m, $^3J_{\text{FF}}$ = 8.3 Hz, CF(CF₃)₂). MS (EI 70 eV) m/z (%) : 449(M⁺, <1), 280(25), 159(4), 121(100). HRMS (EI) : calcd for C₂₁H₁₈NO₂F₇ (M⁺) 449.1226, found 449.1216. Anal. Calcd for C₂₁H₁₈NO₂F₇ : C, 56.13; H, 4.04; N, 3.12; F, 29.59. Found : C, 56.07; H, 4.12; N, 3.06; F, 29.55.

3-Heptafluoroisopropyl-4-(*p*-methoxybenzyl)-3,4-dihydrophenantroline (2I'). Pale yellow oil. IR

(film, $\nu_{\max}/\text{cm}^{-1}$) : 3055, 3005, 2955, 2838, 1611, 1512, 1466, 1369, 1300, 1245, 1223, 1175, 1108, 1035, 998, 831, 734, 698. ^1H NMR (400 MHz) δ = 3.72 (3H, s, OCH_3), 4.48 (1H, d, $^2J_{\text{HH}} = 15.5$ Hz, NCH_2), 5.04 (1H, dd, $^3J_{\text{HF}} = 14.8$ Hz, $^3J_{\text{HH}} = 6.0$ Hz, CHCF), 5.53 (1H, m, CHCHCF), 5.99 (1H, d, $^2J_{\text{HH}} = 15.4$ Hz, NCH_2), 6.70 – 6.72 (1H, d, $^3J_{\text{HF}} = 8.7$ Hz, $\text{CH}=\text{CHCHCF}$), 6.72 (2H, dm, $^3J_{\text{HH}} = 8.7$ Hz, PMB), 7.06 (2H, dm, $^3J_{\text{HH}} = 8.7$ Hz, PMB), 7.18 (1H, d, $^3J_{\text{HH}} = 8.2$ Hz, H_{arom}), 7.29 (1H, dd, $^3J_{\text{HH}} = 8.2$ Hz, $^3J_{\text{HH}} = 4.1$ Hz, H_{arom}), 7.30 (1H, d, $^3J_{\text{HH}} = 8.2$ Hz, H_{arom}), 7.99 (1H, dd, $^3J_{\text{HH}} = 8.4$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, H_{arom}), 8.86 (1H, dd, $^3J_{\text{HH}} = 4.1$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, H_{arom}). ^{13}C NMR (100 MHz) δ = 55.1, 59.2 (d, $^2J_{\text{CF}} = 21.6$ Hz), 61.2, 91.7 (dm, $^1J_{\text{CF}} = 207.8$ Hz, $^2J_{\text{CF}} = 29.3$ Hz), 113.6, 116.1, 120.5, 120.8, 120.8 (qd, $^1J_{\text{CF}} = 289.7$ Hz, $^2J_{\text{CF}} = 27.6$ Hz), 120.9 (qd, $^1J_{\text{CF}} = 286.2$ Hz, $^2J_{\text{CF}} = 26.7$ Hz), 124.3, 125.8, 129.4, 129.8, 130.4, 131.4, 136.2, 140.5, 141.8, 147.9, 158.9. ^{19}F NMR (376 MHz) δ = -185.20 (1F, m, $^3J = 7.6$ Hz, $\text{CF}(\text{CF}_3)_2$), -73.42 (3F, m, $^3J_{\text{FF}} = 8.3$ Hz, $\text{CF}(\text{CF}_3)_2$), -73.06 (3F, m, $^3J_{\text{FF}} = 8.3$ Hz, $\text{CF}(\text{CF}_3)_2$). HRMS (ESI) : calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{OF}_7$ ($\text{M}+\text{H}^+$) 471.1302, found 471.1298. Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2\text{OF}_7$: C, 58.73; H, 3.64; N, 5.96; F, 28.27. Found : C, 58.74; H, 3.65; N, 6.02; F, 28.22.

1-Heptafluoroisopropyl-4-(*p*-methoxybenzyl)-1,4-dihydrophenantroline (3I'). Pale yellow oil. IR

(CH_2Cl_2 , $\nu_{\max}/\text{cm}^{-1}$) : 3064, 3005, 2955, 2907, 2837, 1668, 1612, 1512, 1459, 1287, 1248, 1223, 1173, 1122, 963, 830, 694. ^1H NMR (400 MHz) δ = 3.79 (3H, s, OCH_3), 4.74 (2H, m, CHCF , $\text{NCH}=\text{CH}$), 4.85 (1H, d, $^2J_{\text{HH}} = 14.6$ Hz, NCH_2), 6.33 (1H, d, $^2J_{\text{HH}} = 14.4$ Hz, NCH_2), 6.35 (1H, d, $^3J_{\text{HH}} = 5.8$ Hz, $\text{NCH}=\text{CH}$), 6.86 (2H, dm, $^3J_{\text{HH}} = 8.8$ Hz, PMB), 7.23 (1H, m, H_{arom}), 7.34 (1H, dd, $^3J_{\text{HH}} = 8.2$ Hz, 4.1 Hz, H_{arom}), 7.37 – 7.44 (3H, m, PMB, H_{arom}), 8.07 (1H, dd, $^3J_{\text{HH}} = 8.4$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, H_{arom}), 8.72 (1H, dd, $^3J_{\text{HH}} = 4.0$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, H_{arom}). ^{13}C NMR (100 MHz) δ = 42.0 (d, $^2J_{\text{CF}} = 19.8$ Hz), 55.2, 55.9, 91.6 (dm, $^1J_{\text{CF}} = 206.9$ Hz, $^2J_{\text{CF}} = 28.4$ Hz), 93.3 (d, $^3J_{\text{CF}} = 6.9$ Hz), 113.6, 115.4, 120.9, 120.9 (qd, $^1J_{\text{CF}} = 287.9$ Hz, $^2J_{\text{CF}} = 28.4$ Hz), 121.0, 121.3 (qd, $^1J_{\text{CF}} = 287.9$ Hz, $^2J_{\text{CF}} = 27.6$ Hz), 129.2, 129.5, 130.1 (d, $^3J_{\text{CF}} = 4.3$ Hz), 131.2, 136.6, 137.4, 139.1, 140.5, 146.9, 158.7. ^{19}F NMR (376 MHz) δ = -175.53 (1F, m, $\text{CF}(\text{CF}_3)_2$), -74.00 (3F, m, $^3J_{\text{FF}} = 8.3$ Hz, $\text{CF}(\text{CF}_3)_2$), -71.95 (3F, m, $^3J_{\text{FF}} = 8.3$ Hz, $\text{CF}(\text{CF}_3)_2$). MS (EI 70 eV) m/z (%) : 470(M^+ , 1), 301(25), 121(100). HRMS (EI) : calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2\text{OF}_7$ (M^+) 470.1229, found 470.1235. Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2\text{OF}_7$: C, 58.73; H, 3.64; N,

5.96; F, 28.27. Found : C, 58.63; H, 3.62; N, 5.85; F, 27.44.

4-Bromo-1-heptafluoroisopropyl-2-(*p*-methoxybenzyl)-1,2-dihydroisoquinoline (2m'). Pale yellow

oil. IR (film, $\nu_{\max}/\text{cm}^{-1}$) : 3067, 3003, 2958, 2937, 2838, 1614, 1513, 1287, 1228, 1174, 1113, 1035, 946, 760. ^1H NMR (400 MHz) δ = 3.75 (3H, s, OCH_3), 4.35 (2H, AB, $^2J_{\text{HH}}$ = 15.1 Hz, NCH_2), 5.43 (1H, d, $^3J_{\text{HF}}$ = 7.6 Hz, CHCF), 6.54 (1H, d, $^4J_{\text{HH}}$ = 1.2 Hz, $\text{CH}=\text{CBr}$), 6.78 (2H, dm, $^3J_{\text{HH}}$ = 8.8 Hz, PMB), 6.93 (1H, d, $^3J_{\text{HH}}$ = 7.7 Hz, H_{arom}), 7.02 (2H, dm, $^3J_{\text{HH}}$ = 8.8 Hz, PMB), 7.16 (1H, td, $^3J_{\text{HH}}$ = 7.6 Hz,

$^4J_{\text{HH}}$ = 1.4 Hz, H_{arom}), 7.34 (1H, td, $^3J_{\text{HH}}$ = 7.6 Hz, $^4J_{\text{HH}}$ = 1.2 Hz, H_{arom}), 7.44 (1H, dd, $^3J_{\text{HH}}$ = 7.8 Hz, $^4J_{\text{HH}}$ = 1.2 Hz, H_{arom}). ^{13}C NMR (100 MHz) δ = 55.2, 58.9 (d, $^4J_{\text{CF}}$ = 1.7 Hz), 61.2 (d, $^2J_{\text{CF}}$ = 22.4 Hz), 90.5 (dm, $^1J_{\text{CF}}$ = 206.0 Hz, $^2J_{\text{CF}}$ = 30.2 Hz), 95.9, 114.2, 119.7 (d, $^3J_{\text{CF}}$ = 2.6 Hz), 120.7 (qd, $^1J_{\text{CF}}$ = 288.8 Hz, $^2J_{\text{CF}}$ = 25.9 Hz), 120.9 (qd, $^1J_{\text{CF}}$ = 285.4 Hz, $^2J_{\text{CF}}$ = 27.6 Hz), 123.3, 126.9, 128.0, 128.4, 128.7, 129.4, 132.5, 135.6, 159.4. ^{19}F NMR (376 MHz) δ = -179.98 (1F, m, 3J = 8.3 Hz, $\text{CF}(\text{CF}_3)_2$), -72.47 (3F, m, $^3J_{\text{FF}}$ = 9.0 Hz, $\text{CF}(\text{CF}_3)_2$), -72.17 (3F, m, $^3J_{\text{FF}}$ = 8.3 Hz, $\text{CF}(\text{CF}_3)_2$). HRMS (ESI, MeOH) : calcd for $\text{C}_{20}\text{H}_{16}\text{NO}^{79}\text{BrF}_7$ ($\text{M}+\text{H}^+$) 498.0298, found 498.0308. Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{NOBrF}_7$: C, 48.21; H, 3.03; N, 2.81; Br, 16.04; F, 26.69. Found : C, 47.96; H, 2.80; N, 2.79; Br, 16.23; F, 25.27.

General procedure for synthesis of 2n', 2o' and 3o' from weakly nucleophilic pyridines 6 or 7 (with quarternization of nitrogen promoted by silver salts; scheme 9 in the main text). To a flame-dried round-bottomed flask containing dry MeCN (3.0 mL) the appropriate pyridine derivative (0.95 mmol) and PMBBBr (201 mg, 143 μL , 1.00 mmol) were added under argon atmosphere. The reaction mixture was cooled to $-75\text{ }^\circ\text{C}$ and silver tetrafluoroborate (195 mg, 1.00 mmol) was added in one portion with vigorous stirring. After the reaction mixture had reached room temperature, stirring was switched off so that the AgBr precipitate could accumulate at the bottom of the flask. In the meantime HFP (c.a. 0.6 g, 4 mmol) was condensed in a glass pressure tube (c.a. 3.5 mL volume) at $-75\text{ }^\circ\text{C}$ under argon atmosphere. The solution from above the precipitate of AgBr was then transferred into the pressure tube. Spray-dried $\text{KF}_{(\text{s})}$ (276 mg, 4.75 mmol) was then added and the pressure tube was closed with a teflon valve. The reaction was performed at room temperature for 3h with vigorous stirring. Isolation of products was carried out in the way described above for the reactions of other *N*-alkylazinium salts.

2-Heptafluoroisopropyl-1-(*p*-methoxybenzyl)-6-methoxycarbonyl-1,2-dihydropyridine (2n').

Yellow oil, quickly decomposes at RT. IR (film, $\nu_{\max}/\text{cm}^{-1}$) : 3004, 2956, 2840, 1725, 1613, 1514, 1464, 1297, 1251, 1223, 1156, 1035, 742. ^1H NMR (400 MHz) δ = 3.76 (3H, s, OCH_3), 3.78 (3H, s, OCH_3), 4.00 (1H, d, $^2J_{\text{HH}} = 15.7$ Hz, NCH_2), 4.85 (1H, d, $^2J_{\text{HH}} = 15.7$ Hz, NCH_2), 4.90 (1H, dd, $^3J_{\text{HF}} = 14.4$ Hz, $^3J_{\text{HH}} = 6.5$ Hz, CHCF), 5.22 (1H, ddm, $^3J_{\text{HH}} = 8.2$ Hz, 7.4 Hz, CHCHCF), 6.23 (1H, ddm, $^3J_{\text{HH}} = 9.2$ Hz, 5.9 Hz, $\text{CH}=\text{CHCHCF}$), 6.30 (1H, dd, $^3J_{\text{HF}} = 5.9$ Hz, $^4J_{\text{HH}} = 0.6$ Hz, $\text{NC}=\text{CH}$), 6.81 (2H, dm, $^3J_{\text{HH}} = 8.8$ Hz, PMB), 7.09 (2H, dm, $^3J_{\text{HH}} = 8.8$ Hz, PMB). ^{13}C NMR (100 MHz) δ = 52.1, 55.2, 58.5, 59.7 (d, $^2J_{\text{CF}} = 21.6$ Hz), 91.2 (m), 92.2 (d, $^3J_{\text{CF}} = 6.9$ Hz), 112.9 (d, $^3J_{\text{CF}} = 4.3$ Hz), 113.6, 113.9, 120.7 (qd, $^1J_{\text{CF}} = 287.1$ Hz, $^2J_{\text{CF}} = 26.7$ Hz), 127.2, 129.1, 135.8, 159.1, 164.3. ^{19}F NMR (376 MHz) δ = -186.19 (1F, m, $^3J = 7.8$ Hz, $\text{CF}(\text{CF}_3)_2$), -73.55 (3F, m, $^3J_{\text{FF}} = 8.5$ Hz, $\text{CF}(\text{CF}_3)_2$), -73.16 (3F, m, $^3J_{\text{FF}} = 8.5$ Hz, $\text{CF}(\text{CF}_3)_2$). MS (EI 70 eV) m/z (%) : 427(M^+ , <1), 258(11), 166(10), 121(100). HRMS (EI) : calcd for $\text{C}_{18}\text{H}_{16}\text{NO}_3\text{F}_7$ (M^+) 427.1018, found 427.1030. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{NO}_3\text{F}_7$: C, 50.59; H, 3.77; N, 3.28; F, 31.12. Found : C, 51.14; H, 3.98; N, 3.09; F, 29.03.

2-Heptafluoroisopropyl-1-(*p*-methoxybenzyl)-3,6-bis(methoxycarbonyl)-1,2-dihydropyridine (2o').

(2o'). Yellow crystalline solid, mp 44 – 45 °C from hexanes/Et₂O. IR (KBr, $\nu_{\max}/\text{cm}^{-1}$) : 3025, 2968, 2846, 1727, 1707, 1609, 1515, 1439, 1281, 1250, 1224, 1127, 983, 770. ^1H NMR (400 MHz) δ = 3.70 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 3.79 (3H, s, OCH_3), 4.07 (1H, d, $^2J_{\text{HH}} = 15.3$ Hz, NCH_2), 4.99 (1H, d, $^2J_{\text{HH}} = 15.3$ Hz, NCH_2), 5.70 (1H, d, $^3J_{\text{HF}} = 16.1$ Hz, CHCF), 6.45 (1H, d, $^3J_{\text{HH}} = 6.1$ Hz, $\text{NC}=\text{CH}$), 6.76 (2H, dm, $^3J_{\text{HH}} = 8.7$ Hz, PMB), 6.96 (2H, dm, $^3J_{\text{HH}} = 8.7$ Hz, PMB), 7.23 (1H, d, $^3J_{\text{HH}} = 6.2$ Hz, $\text{NC}=\text{CHCH}$). ^{13}C NMR (100 MHz) δ = 52.0, 52.5, 55.1, 57.7 (d, $^2J_{\text{CF}} = 21.6$ Hz), 58.9, 91.7 (dm, $^1J_{\text{CF}} = 212.8$ Hz, $^2J_{\text{CF}} = 29.3$ Hz), 110.1, 113.6, 113.9, 120.5 (qd, $^1J_{\text{CF}} = 287.1$ Hz, $^2J_{\text{CF}} = 27.6$ Hz), 120.6 (qd, $^1J_{\text{CF}} = 288.8$ Hz, $^2J_{\text{CF}} = 27.6$ Hz), 129.0, 129.2, 130.2, 134.5, 139.2, 159.3, 163.3, 165.5. ^{19}F NMR (376 MHz) δ = -189.90 (1F, m, $^3J = 7.9$ Hz, $\text{CF}(\text{CF}_3)_2$), -73.79 (3F, m, $\text{CF}(\text{CF}_3)_2$), -72.28 (3F, m, $\text{CF}(\text{CF}_3)_2$). MS (EI 70 eV) m/z (%) : 485(M^+ , <1), 316(7), 121(100). HRMS (EI) : calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_5\text{F}_7$ (M^+) 485.1073, found 485.1078. Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_5\text{F}_7$: C, 49.49; H, 3.74; N, 2.89; F, 27.40. Found : C, 49.71; H, 3.77; N, 3.02; F, 27.53.

4-Heptafluoroisopropyl-1-(*p*-methoxybenzyl)-2,5-bis(methoxycarbonyl)-1,4-dihydropyridine

(3o'). Yellow crystalline solid, mp 64 – 65 °C from hexanes/Et₂O. IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$) : 3020, 2997, 2951, 2846, 1731, 1708, 1658, 1606, 1515, 1416, 1313, 1284, 1255, 1220, 1120, 1106, 1053, 981, 954. 912, 842, 754. ¹H NMR (400 MHz) δ = 3.72 (3H, s, OCH₃), 3.73 (3H, s, OCH₃), 3.80 (3H, s, OCH₃), 4.73 (1H, t, ³*J* = 7.4 Hz, CHCF), 4.79 (2H, AB, ²*J*_{HH} = 15.2 Hz, NCH₂), 5.65 (1H, d, ³*J*_{HH} = 6.5 Hz, CHCHCF), 6.86 (2H, dm, ³*J*_{HH} = 8.8 Hz, PMB), 7.13 (2H, dm, ³*J*_{HH} = 8.8 Hz, PMB), 7.47 (1H, d, ⁴*J*_{HH} = 0.8 Hz, NCH=CCO₂Me). ¹³C NMR (100 MHz) δ = 35.6 (d, ²*J*_{CF} = 21.6 Hz), 51.5, 52.7, 54.9, 55.2, 91.2 (dm, ¹*J*_{CF} = 209.5 Hz, ²*J*_{CF} = 29.3 Hz), 93.9 (d, ³*J*_{CF} = 4.3 Hz), 106.9 (d, ³*J*_{CF} = 5.2 Hz), 114.1, 120.7 (qd, ¹*J*_{CF} = 288.0 Hz, ²*J*_{CF} = 28.4 Hz), 121.0 (qd, ¹*J*_{CF} = 287.9 Hz, ²*J*_{CF} = 28.4 Hz), 128.1, 129.2, 135.1, 144.8, 159.4, 162.9, 167.5. ¹⁹F NMR (376 MHz) δ = -184.81 (1F, m, ³*J* = 7.9 Hz, CF(CF₃)₂), -75.49 (3F, m, ³*J*_{FF} = 8.7 Hz, CF(CF₃)₂), -73.29 (3F, m, ³*J*_{FF} = 7.9 Hz, CF(CF₃)₂). MS (EI 70 eV) *m/z* (%) : 485(M⁺, <1), 316(10), 121(100). HRMS (EI) : calcd for C₂₀H₁₈NO₅F₇ (M⁺) 485.1073, found 485.1079. Anal. Calcd for C₂₀H₁₈NO₅F₇ : C, 49.49; H, 3.74; N, 2.89; F, 27.40. Found : C, 49.49; H, 3.77; N, 2.72; F, 26.18.

Compound **3a**: ^{13}C NMR

Compound **4a**: ^1H NMR

Compound 4a: ^1H - ^1H COSY

Compound 4a: DEPT

Compound 4a: HMBC

Compound **3b**: ^1H NMR

Compound **3b**: ^{13}C NMR

Compound **3b**: DEPT

Compound **4b**: ^1H NMR

Compound **4b**: ^{19}F NMR

Compound **2c**: ^{13}C NMR

Compound 2c: ^{19}F NMR

Compound **2d**: ^1H NMR

Compound **2d**: ^{13}C NMR

Compound **2d**: ^{19}F NMR

Compound 2e: ^{13}C NMR

Compound 2e: ^{19}F NMR

Compound **3e**: ^1H NMR

Compound **3e**: ^{13}C NMR

Compound **2f**: ^1H NMR

Compound **2f**: ^{13}C NMR

Compound **3f**: ^{13}C NMR

Compound **2c'**: ^{13}C NMR

Compound **2c'**: ^{19}F NMR

Compound **2c'**: ^1H - ^1H COSY

Compound **2c'**: HSQC

Compound **3c'**: ^1H NMR

Compound **3c'**: ^{13}C NMR

Compound **3c'**: ^{19}F NMR

Compound **3c'**: ^1H - ^1H COSY

Compound **2d'**: ^{13}C NMR

Compound **2d'**: ^{19}F NMR

Compound **2e'**: ^1H NMR

Compound **2e'**: ^{13}C NMR

Compound **2e'**: ^{19}F NMR

Compound 2e': HMBC

Compound **3e'**: ^1H NMR

Compound **3e'**: ^{13}C NMR

Compound **3e'**: ^{19}F NMR

Compound **3e'**: ^1H - ^1H COSY

Compound **3e'**: HSQC

Compound **2f**: ^1H NMR

Compound **2f**: ^{13}C NMR

Compound **3f**: ^1H NMR

Compound **3f**: ^{13}C NMR

Compound **3f**: ^{19}F NMR

Compounds **2g'** and **3g'**: ^1H NMR

Compounds **2g'** and **3g'**: ^{13}C NMR

Compound **3h'**: ^{13}C NMR

Compound **3h'**: ^{19}F NMR