Supporting Information:

Convenient Synthesis of Polyfunctionalized β -Fluoropyrroles From Rhodium(II)-Catalyzed Intramolecular N-H Insertion Reactions

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General Procedure: Solvents used were of reagent grade and were distilled before use: benzene and toluene were distilled from P_2O_5 and kept at sodium wire. Reactions were carried out in glassware under N_2 atmosphere unless otherwise noted. 1H and ^{13}C spectra were recorded at $25^\circ C$ on a Varian AM-300 at 300 MHz (1H), 75.5 MHz (^{13}C), and 282 MHz (^{19}F). Chemical shifts are given in ppm with TMS as internal standard ($\delta=0.00$); ^{19}F , $CFCl_3$ ($\delta=0.00$).

Typical procedure for the preparation of δ -amino- γ,γ -difluoro- α -diazo- β -ketoesters

4a-j:

Preparation of Ethyl, 2-diazo-4,4-difluoro-3-oxo-5-phenyl-5-

phenylamino-pentanoate (4a): To a mixture of 4Å molecular sieves (700 mg) and **3a** (240mg, 0.69mmol) in benzene (7 mL) which has been stirred at rt for 30 min was added p-methylbenzenesulfonyl azide (134 mg, 0.69 mmol), followed by triethyl amine (0.1 mL, 0.69 mmol) dropwise at $0^\circ C$. After the addition, the mixture was warmed to rt and stirred for 4h. Then $30-60^\circ C$ petroleum ether (10 mL) was added to precipitate the p-methylbenzenesulfonyl amine. The reaction mixture was filtered, and the solid was

washed twice with hexane/acetate (v:v = 6:1, 5 mL). The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 6:1 as an eluent) to provide **4a** (206 mg, 0.55 mmol, 80.0%) as a slightly yellow solid; m.p. 128-130°C; ¹H NMR (CDCl₃): δ 1.31 (t, *J* = 7.2 Hz, 3H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.72 (d, *J* = 7.8 Hz, *NH*), 5.49 (dd, *J* = 20.4, 7.8 Hz, 1H), 6.39-7.67 (m, 10H); ¹⁹F NMR (CDCl₃): δ -103.3 (d, ²*J*_{F-F} = 259.4 Hz, 1F), -115.6 (dd, ²*J*_{F-F} = 259.4 Hz, ³*J*_{F-H} = 20.4 Hz, 1F); MS (EI) *m/z* 373 (M⁺, 3.40), 329 (M⁺H-OEt, 12.13), 307 (M⁺-HOEt-HF, 4.56), 279 (M⁺-1-CO₂Et-HF, 22.78), 253 (M⁺-C₆H₅NH⁺-N₂, 12.68), 182 (M⁺-CF₂COC(N₂)CO₂Et, 100.00), 77 (C₆H₅⁺, 48.17); IR (KBr): ν 3342 (NH, s), 2162 (N≡N, s), 1720 (CO₂Et, s), 1648 (C=O, s), 1122-1373 (vs, C-F) cm⁻¹; Anal. calcd. for C₁₉H₁₇O₃N₃F₂: C, 61.13; N, 11.36; H, 4.56%. Found: C, 61.38; N, 11.05; H, 4.60%.

Ethyl, 2-diazo-4,4-difluoro-5-(4-methoxyphenyl)-3-oxo-5-phenylamino-pentanoate (4b): Yield 81%; purified by column chromatography (silica gel, hexane/EtOAc = 7:1 as an eluent); a white solid; m.p. 108-110°C; ¹H NMR (CDCl₃): δ 1.27 (t, *J* = 7.2 Hz, 3H), 3.70 (s, 3H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.70 (d, *J* = 7.8 Hz, *NH*), 5.40 (dd, *J* = 18.6, 7.8 Hz, 1H), 6.44-7.49 (m, 9H); ¹⁹F NMR (CDCl₃): δ -103.4 (d, ²*J*_{F-F} = 262.3 Hz, 1F), -116.3 (dd, ²*J*_{F-F} = 262.3 Hz, ³*J*_{F-H} = 18.6 Hz, 1F); MS (EI) *m/z*: 403 (M⁺, 4.59), 331 (M⁺H-CO₂Et, 0.52), 212 (M⁺-CF₂COC(N₂)CO₂Et, 100.00), 77 (C₆H₅⁺, 9.26); IR (KBr): ν 3347 (NH, s), 2165 (N≡N, s), 1714 (CO₂Et, s), 1638 (C=O, s), 1123-1374 (vs, C-F) cm⁻¹; Anal. calcd. for C₂₀H₁₉O₄N₃F₂: C, 59.55; N, 10.42; H, 4.71%. Found: C, 59.52; N, 10.25; H, 4.96%.

Ethyl, 2-diazo-4,4-difluoro-5-(4-chlorophenyl)-3-oxo-5-

phenylamino-pentanoate (4c): Yield 90%; purified by column chromatography (silica gel, hexane/EtOAc = 7:1 as an eluent); a white solid; m.p. 130-132°C; ^1H NMR (CDCl_3): δ 1.28 (t, $J = 7.2$ Hz, 3H), 4.31 (q, $J = 7.2$ Hz, 3H), 4.95 (d, $J = 9.0$ Hz, 1H), 5.15-5.85 (m, 1H), 6.40-7.50 (m, 9H); ^{19}F NMR (CDCl_3): δ -102.9 (d, $^2J_{\text{F-F}} = 259.4$ Hz, 1F), -116.3 (dd, $^2J_{\text{F-F}} = 259.4$ Hz, $^3J_{\text{F-H}} = 19.7$ Hz, 1F); MS (EI) m/z: 409/407 ($\text{M}^+ + 2/\text{M}^+$, 1.72/4.54), 379 ($\text{M}^+ - \text{H} - \text{C}_2\text{H}_5$, 1.76), 333 ($\text{M}^+ - 1 - \text{CO}_2\text{Et}$, 3.22), 287 ($\text{M}^+ - \text{N}_2 - \text{C}_2\text{H}_5\text{NH}$, 7.16), 216 ($\text{M}^+ - \text{CF}_2\text{COC}(\text{N}_2)\text{CO}_2\text{Et}$, 100), 104 ($\text{C}_6\text{H}_5\text{NHCH}^+$, 22.53), 77 (C_6H_5^+ , 27.04); IR (KBr): ν 3339 (NH, s), 2166 ($\text{N}\equiv\text{N}$, s), 1713 (CO_2Et , s), 1646 (C=O, s), 1142-1376 (vs, C-F) cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_3\text{F}_2\text{Cl}$ (M^+): 407.08482, Found: 407.08896.

Ethyl, 4,4-difluoro-5-phenyl-3-oxo-5-(2-chlorophenyl)amino-

pentanoate (4d): Yield 83%; purified by column chromatography (silica gel, hexane/EtOAc = 7:1 as an eluent); a white solid; m.p. 72-78°C; ^1H NMR (CDCl_3): δ 1.45 (t, $J = 7.1$ Hz, 3H), 4.47 (q, $J = 7.1$ Hz, 2H), 5.26-6.03 (m, 2H), 6.56-6.80 (m, 2H), 7.0-7.71 (m, 7H); ^{19}F NMR (CDCl_3): δ -103.1 (d, $^2J_{\text{F-F}} = 253.8$ Hz, 1F), -105.1 (dd, $^2J_{\text{F-F}} = 253.8$ Hz, $^3J_{\text{F-H}} = 18.0$ Hz, 1F); MS (EI) m/z: 409/407 ($\text{M}^+ + 2/\text{M}^+$, 5.99/14.21), 379 ($\text{M}^+ - \text{N}_2$, 8.85), 344 ($\text{M}^+ - \text{N}_2 - \text{Cl}$, 8.54), 306 ($\text{M}^+ - \text{N}_2 - \text{CO}_2\text{Et}$, 8.96), 216 ($\text{M}^+ - \text{CF}_2\text{COC}(\text{N}_2)\text{CO}_2\text{Et}$, 100.00), 111 ($\text{C}_6\text{H}_4\text{Cl}^+$, 5.33); IR (KBr): ν 3406 (NH, s), 2154 ($\text{N}\equiv\text{N}$, s), 1731 (CO_2Et , s),

1661 (C=O, s), 1126-1317 (vs, C-F) cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_3\text{F}_2\text{Cl}$ (M^+): 407.08814, Found: 407.09145.

Ethyl, 4,4-difluoro-5-(4-chlorophenyl)-3-oxo-5-(4-

methoxyphenyl)amino-pentanoate (4e): Yield 82%; purified by column chromatography (silica gel, hexane/EtOAc = 7:1 as an eluent); yellow solid; mp 95-97°C; ^1H NMR (CDCl_3): δ 1.35 (t, $J = 7.1$ Hz, 3H), 3.68 (s, 3H), 4.36 (q, $J = 7.1$ Hz, 2H), 5.49 (dd, $^3J_{\text{H-F}} = 21.8, 5.6$ Hz, 1H), 6.55-6.59 (m, 3H), 6.68-6.74 (m, 2H), 7.32-7.35 (m, 2H), 7.43-7.45 (m, 2H); ^{19}F NMR (CDCl_3): δ -103.1 (d, $^2J_{\text{F-F}} = 259.4$ Hz, 1F), -116.6 (dd, $^2J_{\text{F-F}} = 259.4$ Hz, $^3J_{\text{F-H}} = 21.8$ Hz, 1F); MS (EI) m/z : 437 (M^+ , 7.84), 409 ($\text{M}^+ - \text{N}_2$, 16.02), 389 ($\text{M}^+ - \text{N}_2 - \text{HF}$, 6.70), 363 ($\text{M}^+ - \text{HCO}_2\text{Et}$, 7.59), 343 ($\text{M}^+ - \text{HCO}_2\text{Et} - \text{HF}$, 11.17), 317 ($\text{M}^+ - \text{C}_6\text{H}_5\text{N}^+\text{H} - \text{N}_2$, 5.88), 246 ($\text{M}^+ - \text{CF}_2\text{COC}(\text{N}_2)\text{CO}_2\text{Et}$, 100.00), 77 (C_6H_5^+ , 32.13); IR (KBr): ν 3331 (NH, s), 2165 ($\text{N}\equiv\text{N}$, s), 1723 (CO_2Et , s), 1652 (C=O, s), 1444, 1464, 1498, 1516, 1606 (C=C, s), 1028-1330 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}_3\text{F}_2\text{Cl}$: C, 54.92; N, 9.60; H, 4.12%. Found: C, 55.11; N, 9.64; H, 4.11%.

Ethyl, 2-diazo-4,4-difluoro-5-naphthyl-3-oxo-5-phenylamino-

pentanoate (4f): Yield 85%; purified by column chromatography (silica gel, hexane/EtOAc = 8:1 as an eluent); slightly yellow solid; mp 142°C (decompose); ^1H NMR (CDCl_3): δ 1.35 (t, $J = 7.1$ Hz, 3H), 4.37 (q, $J = 7.1$ Hz, 2H), 4.91 (br, 1H, NH), 5.70 (dd, $^3J_{\text{H-F}} = 20.3, 6.0$ Hz, 1H), 6.66-6.74 (m, 3H), 7.61-7.62 (d, $J = 8.4$ Hz, 1H),

7.09-7.14 (m, 2H), 7.47-7.51 (m, 2H), 7.81-7.87 (m, 3H), 7.98 (s, 1H); ^{19}F NMR (CDCl_3): δ -103.5 (dd, $^2J_{\text{F-F}} = 253.8$ Hz, $^3J_{\text{F-H}} = 6.0$ Hz, 1F), -116.6 (dd, $^2J_{\text{F-F}} = 253.8$ Hz, $^3J_{\text{F-H}} = 20.3$ Hz, 1F); MS (EI) m/z : 423 (M^+ , 4.28), 232 ($\text{M}^+ - \text{CF}_2\text{COC}(\text{N}_2)\text{CO}_2\text{Et}$, 100.00), 77 (C_6H_5^+ , 12.81); IR (KBr): ν 3344 (NH, s), 2164 ($\text{N}\equiv\text{N}$, s), 1718 (CO_2Et , s), 1650 ($\text{C}=\text{O}$, s), 1123-1375 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{23}\text{H}_{19}\text{O}_3\text{N}_3\text{F}_2$: C, 65.25; N, 9.93; H, 4.49%. Found: C, 65.44; N, 9.91; H, 4.27%.

Ethyl, 2-diazo-4,4-difluoro-5-(2-furyl)-3-oxo-5-phenylamino-pentanoate (4g): Yield 71%; purified by column chromatography (silica gel, hexane/EtOAc = 5:1 as an eluent); slightly yellow solid; m.p. 96-98°C; ^1H NMR (CDCl_3): δ 1.35 (t, $J = 7.1$ Hz, 3H), 4.36 (q, $J = 7.1$ Hz, 2H), 4.39 (s, 1H, NH), 5.66 (dd, $^2J_{\text{HF}} = 19.1$, 7.3 Hz, 1H), 5.70 (dd, $J = 3.3$, 1.4 Hz, 1H), 6.45 (d, $J = 3.3$ Hz, 1H), 6.71-6.83 (m, 3H), 7.15-7.27 (m, 2H), 7.43 (d, $J = 1.4$ Hz, 1H); ^{19}F NMR (CDCl_3): δ -104.4 (dd, $^2J_{\text{F-F}} = 259.4$, 7.3 Hz, 1F), -114.8 (dd, $^2J_{\text{F-F}} = 259.4$, 19.1 Hz, 1F); MS (EI) m/z : 363 (M^+ , 2.25), 335 ($\text{M}^+ - \text{N}_2$, 100.00), 242 ($\text{M}^+ - \text{HF-CO}_2\text{Et-N}_2$, 5.88); IR (KBr): ν 3331 (NH, s), 2165 ($\text{N}\equiv\text{N}$, s), 1723 (CO_2Et , s), 1652 ($\text{C}=\text{O}$, s), 1082-1330 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{17}\text{H}_{15}\text{O}_4\text{N}_3\text{F}_2$: C, 56.20; N, 11.57; H, 4.13%. Found: C, 56.26; N, 11.60; H, 4.22%.

Ethyl, 2-diazo-4,4-difluoro-5-phenyl-3-oxo-5-benzylamino-pentanoate (4h): Yield 86%; purified by column chromatography (silica gel,

hexane/EtOAc = 6:1 as an eluent); slightly yellow solid; m.p.100-102°C; ^1H NMR (CDCl_3): δ 1.34 (t, $J = 7.2$ Hz, 3H), 3.54 (d, $J = 13.1$ Hz, 1H), 3.83 (d, $J = 3.1$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 4.53 (dd, $^3J_{F-H} = 23.2$, 5.6 Hz, 1H), 7.23-7.46 (m, 10H); ^{19}F NMR (CDCl_3): δ -103.5 (dd, $^2J_{F-F} = 259.4$, 5.6 Hz, 1F), -117.2 (dd, $^2J_{F-F} = 259.4$, 23.2 Hz, 1F); MS (EI) m/z : 388 (MH^+ , 3.01), 259 ($\text{M}^+ - \text{N}_2$, 2.63), 339 ($\text{M}^+ - \text{N}_2 - \text{HF}$, 2.76), 286 ($\text{M}^+ - \text{N}_2 - \text{CO}_2\text{Et}$, 6.09), 196 ($\text{M}^+ - \text{CF}_2\text{COC}(\text{N}_2)\text{CO}_2\text{Et}$, 59.60); IR (KBr): ν 3352 (NH, s), 2151 ($\text{N}\equiv\text{N}$, s), 1725 (CO_2Et , s), 1668 ($\text{C}=\text{O}$, s), 1124-1374 (vs, C-F) cm^{-1} ; Anal. Calcd. For $\text{C}_{20}\text{H}_{19}\text{O}_3\text{N}_3\text{F}_2$: C, 62.02; N, 10.85; H, 4.91%. Found: C, 62.30; N, 10.80; H, 4.98%.

Ethyl, 2-diazo-4,4-difluoro-5-phenyl-3-oxo-5-phenylamino-

hexanoate (4i): No 4Å molecular sieves is needed; yield 81%; purified by column chromatography (silica gel, hexane/EtOAc = 8:1 as an eluent); slightly yellow liquid; ^1H NMR (CDCl_3): δ 1.31 (t, $J = 7.2$ Hz, 3H), 1.99 (s, 3H), 4.30 (q, $J = 7.1$ Hz, 2H), 5.19 (br, 1H), 6.34 (q, $J = 7.8$ Hz, 2H), 6.68 (t, $J = 7.2$ Hz, 2H), 7.01 (t, $J = 7.8$ Hz, 2H), 7.41-7.46 (m, 2H), 7.59-7.62 (m, 2H); ^{19}F NMR (CDCl_3): δ -110.8 (d, $^2J_{F-F} = 251.8$ Hz, 1F), -112.3 (d, $^2J_{F-F} = 251.8$ Hz, 1F); MS (EI) m/z : 387 (M^+ , 2.82), 324 ($\text{M}^+ \text{H} - \text{OEt} - \text{F}$, 1.02), 196 ($\text{M}^+ - \text{CF}_2\text{COC}(\text{N}_2)\text{CO}_2\text{Et}$, 100.00), 92 (PhNH^+ , 5.46); IR (KBr): ν 3405 (NH, s), 2142 ($\text{C}\equiv\text{N}$, s), 1738 (CO_2Et , s), 1650 ($\text{C}=\text{O}$, s), 1125-1368 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{20}\text{H}_{19}\text{O}_3\text{N}_3\text{F}_2$: C, 62.02; N, 10.67; H, 4.91%. Found: C, 62.20; N, 10.67; H, 5.10%.

Ethyl, 2-diazo-4,4-difluoro-5-phenyl-3-oxo-5-benzylamino-

hexanoate (4j): No 4Å molecular sieves is needed; purified by column chromatography

(silica gel, hexane/EtOAc = 8:1 as an eluent); yield 81%; yellow liquid; ^1H NMR (CDCl_3): δ 1.30 (t, $J = 7.2$ Hz, 3H), 1.86 (s, 3H), 3.49 (d, $J_{\text{H-H}} = 12.3$ Hz, 1H), 3.76 (d, $J_{\text{H-H}} = 12.3$ Hz, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 7.27-7.62 (m, 10H); ^{19}F NMR (CDCl_3): δ -108.79 (d, $^2J_{\text{F-F}} = 256.06$ Hz, 1F), -111.72 (d, $^2J_{\text{F-F}} = 56.06$ Hz, 1F); MS (EI) m/z : 373 ($\text{M}^+ - \text{N}_2$, 4.37), 344 ($\text{M}^+ - \text{N}_2 - \text{C}_2\text{H}_5^+$, 4.46), 328 ($\text{M}^+ - \text{N}_2 - \text{OEt}$, 2.75), 300 ($\text{M}^+ - \text{N}_2 - \text{CO}_2\text{Et}$, 8.34), 210 ($\text{M}^+ - \text{CF}_2\text{COC}(\text{N}_2)\text{CO}_2\text{Et}$, 84.10), 91 (PhCH_2^+ , 100.00); IR (KBr): ν 3335 (NH, s), 2141 ($\text{C}\equiv\text{N}$, s), 1746 (CO_2Et , s), 1698 ($\text{C}=\text{O}$, s), 1132-1370 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{21}\text{H}_{21}\text{O}_3\text{N}_3\text{F}_2$: C, 62.84; N, 10.47; H, 5.23%. Found: C, 63.00; N, 10.20; H, 5.41%.

Typical procedure for the $\text{Rh}_2(\text{OAc})_4$ -catalyzed intramolecular N-H insertion reaction of δ -amino- γ,γ -difluoro- α -diazo- β -ketoesters **6a-i:**

Preparation of ethyl 4-fluoro-3-hydroxy-1,4-diphenyl-1H-pyrrole-2-carboxylate (6a**):** To a solution of $\text{Rh}_2(\text{OAc})_4$ (1.3 mg, 0.003 mmol, 1 mol %) in toluene (6 mL) at 90°C was added dropwise **4a** (112 mg, 0.3 mmol) in toluene (6 mL) over 20 minutes. After 0.5 h of stirring at 90°C , the mixture was heated in refluxing toluene for another 20h until TLC indicated completion of the reaction. Then solvent was removed *in vacuo* and the residue was purified by column chromatography (hexadne/EtOAc = 6:1 as a eluent) to afford **6a** (88 mg, 0.27 mmol, 91.0%) as a white solid; m.p. $150\text{-}152^\circ\text{C}$; ^1H NMR (CDCl_3): δ 1.00 (t, $J = 7.1$ Hz, 3H), 4.11 (q, $J = 7.1$ Hz, 2H), 7.15-7.32 (m, 10H), 8.37 (s, 1H); ^{19}F NMR (CDCl_3): δ -174.7 (s); MS (EI) m/z : 325 (M^+ , 51.90), 279 ($\text{M}^+ - \text{HOEt}$, 100.00), 252 ($\text{M}^+ - \text{CO}_2\text{Et}$, 3.83); IR (KBr): ν 3335 (OH, s), 1660 ($\text{C}=\text{O}$, s), 1135-

1383 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_3\text{NF}$: C, 70.15; N, 4.31; H, 4.92%. Found: C, 70.26; N, 2.20; H, 4.91%.

Ethyl 4-fluoro-3-hydroxy-5-(4-methoxyphenyl)-1-phenyl-1H-pyrrole-2-carboxylate (6b): purified by column chromatography (silica gel, hexane/EtOAc = 8:1 as an eluent); yield 95%; white solid; m.p. 126-128°C; ^1H NMR (CDCl_3): δ 1.30 (t, $J = 7.2$ Hz, 3H), 4.04 (s, 3H), 4.41 (q, $J = 7.2$ Hz, 2H), 6.90-7.70 (m, 9H), 8.76 (s, 1H); ^{19}F NMR (CDCl_3): δ -179.3 (s); MS (EI) m/z : 355 (M^+ , 54.80), 309 ($\text{M}^+ - \text{HOEt}$, 78.50), 212 ($\text{M}^+ - \text{C}_6\text{H}_4\text{OCH}_3 - \text{F} - \text{OH}$, 100.00); IR (KBr): ν 3346 (OH, s), 1662 (C=O, s), 1134-1356 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4\text{NF}$: C, 67.61; N, 3.94; H, 5.07%. Found: C, 67.48; N, 3.75; H, 5.27%.

Ethyl 5-(4-chlorophenyl)-4-fluoro-3-hydroxy-1-phenyl-1H-pyrrole-2-carboxylate (6c): purified by column chromatography (silica gel, hexane/EtOAc = 8:1 as an eluent); yield 93%; white solid; m.p. 140-143°C; ^1H NMR (CDCl_3): δ 0.99 (t, $J = 7.2$ Hz, 3H), 4.10 (q, $J = 7.2$ Hz, 2H), 7.06-7.35 (m, 9H), 8.32 (s, 1H); ^{19}F NMR (CDCl_3): δ -177.7 (s); MS (EI) m/z : 359 (M^+ , 50.40), 313 ($\text{M}^+ - \text{HOEt}$, 100.00), 238 ($\text{M}^+ - \text{H} - \text{C}_6\text{H}_5 - \text{OEt}$, 3.00); IR (KBr): ν 3331 (OH, s), 1663 (C=O, s), 1166-1382 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{19}\text{H}_{15}\text{O}_3\text{NFCl}$: C, 63.42; N, 3.89; H, 4.17%. Found: C, 63.40; N, 3.71; H, 4.37%.

Ethyl 1-(2-chlorophenyl)-4-fluoro-3-hydroxy-5-phenyl-1H-pyrrole-2-

carboxylate (6d): purified by column chromatography (silica gel, hexane/EtOAc = 7:1 as an eluent); yield 92%; White solid; m.p. 144-146°C; ^1H NMR (CDCl_3): δ 1.25 (t, J = 7.2 Hz, 3H), 4.37 (q, J = 7.2 Hz, 2H), 7.16-7.74 (m, 9H), 8.51 (s, 1H); ^{19}F NMR (CDCl_3): δ -178.4 (s); MS (EI) m/z : 359 (M^+ , 19.32), 313 (M^+ -HOEt, 72.40), 278 (M^+ -F-HOEt, 100.00); IR (KBr): ν 3351 (OH, s), 1660 (C=O, s), 1143-1382 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{19}\text{H}_{15}\text{O}_3\text{NFCl}$: C, 63.42; N, 3.89; H, 4.17%. Found: C, 63.47; N, 3.81; H, 4.14%.

Ethyl, 5-(4-chlorophenyl)-4-fluoro-3-hydroxy-5-(4-

methoxyphenyl)-1H-pyrrole-2-carboxylate (6e): purified by column chromatography (silica gel, hexane/EtOAc = 7:1 as an eluent); yield 90%; slight yellow solid, m.p. 151-153°C; ^1H NMR (CDCl_3): δ 1.04 (t, J = 7.2 Hz, 3H), 3.80 (s, 3H), 4.12 (q, J = 7.2 Hz, 2H), 6.70-6.83 (m, 2H), 7.04-7.10 (m, 4H), 7.17-7.21 (m, 2H), 8.26 (s, 1H); ^{19}F NMR (CDCl_3): δ -176.8 (s); MS (EI) m/z : 389 (M^+ , 16.10), 343 (M^+ -HOEt, 100.00), 316 (M^+ -CO₂Et, 16.50); IR (KBr): ν 3356 (OH, s), 1673 (C=O, s), 1137-1336 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{20}\text{H}_{17}\text{O}_4\text{NFCl}$: C, 61.62; N, 3.59; H, 4.36%. Found: C, 61.52; N, 3.39; H, 4.23%.

Ethyl 4-fluoro-3-hydroxy-5-naphthyl-1-phenyl-1H-pyrrole-2-carboxylate (6f): purified by column chromatography (silica gel, hexane/EtOAc = 6:1 as an eluent); yield 93%; yellow solid; m.p. 151-153°C; ^1H NMR (CDCl_3): δ 1.01 (t, $J = 7.2$ Hz, 3H), 4.13 (q, $J = 7.2$ Hz, 2H), 7.15-7.76 (m, 2H), 8.41 (s, 1H); ^{19}F NMR (CDCl_3): δ -177.9 (s); MS (EI) m/z : 375 (M^+ , 4.00), 329 ($\text{M}^+ - \text{HOEt}$, 100.00), 302 ($\text{M}^+ - \text{CO}_2\text{Et}$, 4.54); IR (KBr): ν 3322 (OH, s), 1662 (C=O, s), 1116-1319 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{23}\text{H}_{18}\text{O}_3\text{NF}$: C, 73.60; N, 3.52; H, 4.60%. Found: C, 73.33; N, 3.52; H, 4.60%

Ethyl 4-fluoro-3-hydroxy-5-furyl-1-phenyl-1H-pyrrole-2-carboxylate (6g): purified by column chromatography (silica gel, hexane/EtOAc = 5:1 as an eluent); yield 91%; yellow solid; m.p. 84-86°C; ^1H NMR (CDCl_3): δ 0.94 (t, $J = 7.2$ Hz, 3H), 4.06 (q, $J = 7.2$ Hz, 2H), 5.82 (d, $J = 3.5$ Hz, 1H), 6.26 (m, 1H), 7.19-7.45 (m, 6H), 8.23 (s, 1H); ^{19}F NMR (CDCl_3): δ -174.7 (s); MS (EI) m/z : 315 (M^+ , 100.00), 269 ($\text{M}^+ - \text{HOEt}$, 100.00), 242 ($\text{M}^+ - \text{CO}_2\text{Et}$, 4.35); IR (KBr): ν 3350 (OH, s), 1663 (C=O); 1123-1324 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_4\text{NF}$: C, 64.76, N, 4.44, H, 4.44. Found: C, 64.93; N, 4.43; H, 4.68%.

Ethyl 1-benzyl-4-fluoro-3-hydroxy-5-phenyl-1H-pyrrole-2-carboxylate (6h): purified by column chromatography (silica gel, hexane/EtOAc = 6:1 as an eluent); yield 93%; white solid; m. p. 122-127°C; ^1H NMR (CDCl_3): δ 1.16 (t, $J = 7.2$ Hz, 3H),

4.24 (q, $J = 7.2$ Hz, 2H), 5.32 (s, 2H), 6.26 (m, 2H), 7.20-7.39 (m, 8H), 8.27 (s, 1H); ^{19}F NMR (CDCl_3): δ -174.7 (s); MS (EI) m/z : 339 (M^+ , 100.00), 293 ($\text{M}^+ - \text{HOEt}$, 77.40), 266 ($\text{M}^+ - \text{CO}_2\text{Et}$, 14.35); IR (KBr): ν 3350 (OH, s), 1663 (C=O, s), 1125-1324 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{20}\text{H}_{18}\text{NFO}_3$: C, 70.80; N, 4.13; H, 5.31 %; Found: C, 70.83; N, 4.33; H, 5.58%.

Typical procedure for the preparation of vinyl diazomethanes 7:

Ethyl 2-diazo-3-cyanomethylene-4,4-difluoro-5-(4-chlorophenyl)-5-(4-methoxyphenyl) amino-pentanoate (7e):

A solution of **4e** (272 mg, 0.62 mmol) in toluene (2 mL) was added dropwise to a solution of $\text{Ph}_3\text{P}=\text{CHCN}$ (562 mg, 1.87 mmol) in toluene (6 mL) in 10 min at 55°C , and the mixture was stirred at 55°C for 7h before being cooled to room temperature. Then a small amount of hexane was added to deposit crystalline triphenylphosphine oxide. After removal of the precipitates by filtration, the filtrate was concentrated *in vacuo* and further purified by chromatography (silica gel, hexane/EtOAc = 8:1 as an eluent) to provide **7e** (195 mg, 0.42 mmol, 68.0%) as a sticky yellow oil; ^1H NMR (CDCl_3): δ 1.22 and 1.24 (t, $J = 7.2$ Hz, 3H), 3.64 (s, 3H), 4.10-4.27 (m, 3H), 4.84-5.00 (m, 1H), 5.62 (s, 0.56H, *E*-vinyl-*H*), 6.47-6.70 (m, 0.44H, *Z*-vinyl-*H*), 7.24-7.33 (m, 4H); ^{19}F NMR (CDCl_3): *Z*-isomer δ -96.4 (d, $^2J_{\text{F-F}} = 262.8$ Hz, 0.44F), -105.8 (d, $^2J_{\text{F-F}} = 262.8$ Hz, 0.44F); *E*-isomer δ -100.8 (d, $^2J_{\text{F-F}} = 253.8$ Hz, $^3J_{\text{F-H}} = 10.4$ Hz, 0.56F), -105.3 (d, $^2J_{\text{F-F}} = 253.8$ Hz, $^3J_{\text{F-H}} = 11.2$ Hz, 0.56F); MS (EI) m/z : 432 ($\text{M}^+ - \text{N}_2$, 4.55), 347 ($\text{M}^+ + 1 - \text{Et}$, 1.66), 309 ($\text{M}^+ - \text{N}_2 - \text{CO}_2\text{Et}$, 5.76); IR (KBr): ν 3358 (NH, s), 2217 ($\text{C}\equiv\text{N}$, s), 2117 (N_2 , vs), 1708 (CO_2Et , s), 1596 (C=O, s),

1098-1384 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{22}\text{H}_{19}\text{O}_3\text{N}_4\text{F}_2\text{Cl}$: C, 57.33; N, 12.16; H, 4.13%. Found: C, 57.43; N, 11.91; H, 4.34%.

Ethyl 2-diazo-3-cyanomethylene-4,4-difluoro-5-phenyl-5-(benzyl)-amino-pentanoate (7h): purified by column chromatography (silica gel, hexane/EtOAc = 10:1 as an eluent); yield 40%; yellow oil; ^1H NMR (CDCl_3): δ 1.27-1.32 (m, 3H), 1.90-2.10 (br, 1H, N-H), 3.61 and 3.84 (AB, $^2J_{\text{H-H}} = 13.2$ Hz, 0.44 H), 3.55 and 3.77 (AB, $^2J_{\text{H-H}} = 13.2$ Hz, 1.56 H), 4.06-4.32 (m, 3H), 7.19-7.40 (m, 10H); ^{19}F NMR (CDCl_3): *Z*-isomer: δ -96.7 (d, $^2J_{\text{F-F}} = 261.2$ Hz, 0.22F), -106.8 (d, $^2J_{\text{F-F}} = 261.2$ Hz, 0.22F); *E*-isomer: -101.6 (d, $^2J_{\text{F-F}} = 254.3$ Hz, $^2J_{\text{F-H}} = 9.2$ Hz, 0.78F), -105.3 (d, $^2J_{\text{F-F}} = 254.3$ Hz, $^2J_{\text{F-H}} = 14.8$ Hz, 0.78F); MS (EI) m/z : 411 (M^+H , 4.79), 383 ($\text{M}^+\text{H-N}_2$, 24.24), 356 ($\text{M}^+\text{-N}_2\text{-CN}$, 9.33), 309 ($\text{M}^+\text{-N}_2\text{-CO}_2\text{Et}$, 5.12); IR(KBr): ν 3339 (NH, s), 2221 ($\text{C}\equiv\text{N}$, s), 2117 (N_2 , vs), 1711 (CO_2Et , s), 1096-1276 (vs, C-F) cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}_4\text{F}_2$ (M^+): 410.15507. Found: 410.15543.

Ethyl 2-diazo-3-cyanomethylene-4,4-difluoro-5-phenyl-5-phenylamino-hexanoate (7i): purified by column chromatography (silica gel, hexane/EtOAc = 10:1 as an eluent) to give *Z*-**7i** (43% isolated yield) as a yellow solid and *E*-**7i** (40% isolated yield) as a yellow oil.

Z-7i: m.p. 95-97°C; ^1H NMR (CDCl_3): δ 1.16 (t, $J = 7.2$ Hz, 3H), 1.94 (s, 3H), 4.06-4.12 (m, 2H), 4.72 (s, 1H), 6.32 (dd, $J = 7.8, 0.6$ Hz, 2H), 6.47 (d, $J = 0.6$ Hz, 1H), 6.62-6.67 (m, 1H), 6.92-6.97 (m, 2H), 7.28-7.33 (m, 3H), 7.53-7.55 (m, 2H); ^{19}F

CCOC(=O)C1=CC(=C(C=C1)C(=N1C=CC(=[N+]=[N-])C=C1)C(F)(F)C2(C(=C2)Nc3ccccc3)C(F)(C)c4ccccc4
E-7i

Typical procedure for the Rh₂(OAc)₄-catalyzed intramolecular N-H insertion reactions of vinyldiazomethanes 7e and 7h:

Ethyl

5-(4-chlorophenyl)-4-fluoro-3-cyanomethyl-1-(4-

methoxyphenyl)-1H-pyrrole-2-carboxylate (8e): To a solution $\text{Rh}_2(\text{OAc})_4$ (2 mg, 0.004 mmol, 1.2 mol % eq.) in toluene (5 mL) at 90°C was added dropwise **7e** (175 mg, 0.38 mmol) in toluene (4 mL) over 20 minutes. Then the mixture was heated in refluxing toluene for another 10h until TLC indicated completion of the reaction. Solvent was removed *in vacuo* and the residue was purified by column chromatography (hexadane/EtOAc = 8:1 as a eluent) to afford **8e** (147 mg, 0.36 mmol, 94%) as a white solid; m.p. 122-124°C; ^1H NMR (CDCl_3): δ 1.30 (t, $J = 7.2$ Hz, 3H), 3.75 (s, 3H), 3.87 (s, 2H), 4.13 (q, $J = 7.2$ Hz, 2H), 6.77-6.80 (m, 2H), 6.96-7.02 (m, 4H), 7.13-7.16 (m, 2H), 8.26 (s, 1H); ^{19}F NMR (CDCl_3): δ -167.0 (s); MS (EI) m/z : 412 (M^+ , 100.00), 367 ($\text{M}^+ - \text{OEt}$, 9.40), 339 ($\text{M}^+ - \text{CO}_2\text{Et}$, 91.50); IR (KBr): ν 2259 (CN, w), 1721 ($\text{C}=\text{O}$, s), 1610, 1581, 1562, 1515, 1467, 1151-1301 (vs, C-F) cm^{-1} ; Anal. calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_3\text{N}_2\text{FCl}$: C, 64.01; N, 6.72; H, 4.40%. Found: C, 64.00; N, 6.79; H, 4.36%.

Ethyl

5-phenyl-4-fluoro-3-cyanomethyl-1-benzyl-1H-pyrrole-2-

carboxylate (8h): purified by column chromatography (silica gel, hexane/EtOAc = 8:1 as an eluent); yield 86%; yellow oil; ^1H NMR (CDCl_3): δ 1.31 (t, $J = 7.2$ Hz, 3H), 3.89 (s, 2H), 4.27 (q, $J = 7.2$ Hz, 2H), 5.54 (s, 2H), 6.84 (d, $J = 6.6$ Hz, 2H), 7.21-7.39 (m, 8H); ^{19}F NMR (CDCl_3): δ -167.4 (s); ^{13}C NMR (CDCl_3): δ 13.1, 48.5, 59.8, 106.6 (d, $^2J_{\text{C-F}} = 11.5$ Hz), 115.5 (d, $^3J_{\text{C-F}} = 3.1$ Hz), 124.3, 124.5, 127.6, 127.8, 128.1, 129.0 (d, $^3J_{\text{C-F}} = 1.6$

Hz), 137.4, 145.6 (d, J_{C-F} = 243.5 Hz), 159.2 (d, $^4J_{C-F}$ = 2.3 Hz); MS (EI) m/z: 362 (M^+ , 19.14), 336 (M^+ -CN, 0.65), 263 (M^+ -CO₂Et-CN, 0.48); IR (KBr): ν 2259 (CN, w), 1721 (C=O, s), 1610, 1581, 1562, 1515, 1467, 1151-1301 (vs, C-F) cm^{-1} ; HRMS (EI) calcd. for C₂₂H₁₉O₂N₂F(M^+): 362.14397. Found: 362.14305.

Ethyl 4,5-dihydro-5-methyl-4-oxo-1,5-diphenyl-3-(cyanomethyl)-1H-

pyrrole-2-carboxylate (10): To a solution of Rh₂(OAc)₄ (1 mg, 1.0 mol % eq.) in toluene (7 mL) at 90°C was added dropwise **7i** (90 mg, 0.22 mmol) in toluene (4 mL) over 20 min. The mixture was heated in refluxing toluene for another 8h until TLC indicated completion of the reaction. Then solvent was removed *in vacuo* and the residue was exposed to air for two days until TLC and ¹⁹F-NMR indicated completion of the dehydrofluorination-hydrolysis reaction, then purified by column chromatography (hexadane/EtOAc = 5:1 as a eluent) to afford **10** (67 mg, 0.19 mmol, 85%) as a yellow solid; m.p. 123-125°C; ¹H NMR (CDCl₃): δ 1.13 (t, J = 7.2 Hz, 3H), 1.57 (s, 3H), 3.49 (s, 2H), 4.23-4.37 (m, 2H), 6.81-6.84 (m, 2H), 7.22-7.26 (m, 3H), 7.32-7.42 (m, 5H); ¹³C NMR (CDCl₃): δ 201.6, 161.7, 161.0, 138.8, 137.2, 129.3, 129.2, 128.6, 127.5, 126.1, 125.5, 117.1, 104.2, 75.1, 63.0, 20.4, 13.6, 11.0; MS (EI) m/z: 360 (M^+ -N₂, 20.97), 331 (M^+ -C₂H₅, 100.00), 287 (M^+ -CO₂Et, 2.01); IR (KBr): ν 2250 (C $\equiv$ N, w), 2981, 2936, 1737 (CO₂Et, s), 1690 (C=O, s), 1443, 1496, 1574, 1589 cm^{-1} ; Anal. calcd. for C₂₂H₂₀O₃N₂: C, 73.33; N, 7.78; H, 5.56%. Found: C, 73.33; N, 7.72; H, 5.64%.