Supporting Information

Transition Metal-Free Aminofluorination of $\beta,\gamma$-Unsaturated Hydrazones: Base-Controlled Regioselective Synthesis of Fluorinated Dihydropyrazole and Tetrahydropyridazine Derivatives

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General information

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. Melting points were measured on a melt-Temp apparatus and uncorrected. $^1$H NMR spectra were recorded in CDCl$_3$ on a Bruker AM 400 spectrometer (400 MHz) with TMS as internal standard. $^{19}$F NMR spectra were taken on a Bruker AM 400 (376 MHz) spectrometer with CFCl$_3$ as external standard. $^{13}$C NMR spectra were recorded in CDCl$_3$ on a Varian AM-400 spectrometer (100 MHz) or Agilent AM-400 (100 MHz) spectrometer with TMS as internal standard. NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz). Mass spectra were taken on a HP5989A spectrometer. High-resolution mass data were obtained on a high-resolution mass spectrometer in the EI mode. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was performed using 300-400 mesh silica gels.

Typical procedure for K$_2$HPO$_4$-promoted reaction of 1

To a reactor charged with hydrazones 1 (0.2 mmol), Selectfluor (0.24 mmol) and K$_2$HPO$_4$ (0.4 mmol), was added CH$_3$CN (4 mL) under Ar atmosphere. The mixture was stirred at 100 °C for 1h. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by column chromatography to give 2 (petroleum ether /ethyl acetate = 10:1).

Typical procedure for NaHCO$_3$-promoted reaction of 1

To a reactor charged with hydrazones 1 (0.2 mmol), Selectfluor (0.24 mmol) and NaHCO$_3$ (0.4 mmol), was added CH$_3$CN (4 mL) under Ar atmosphere. The mixture was stirred at 100 °C for 1h. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by column chromatography to give 3 (petroleum ether /ethyl acetate = 10:1).
Deprotection of 2a in the presence of NaOH

![Chemical structure](image1)

A mixture of 2a (0.2 mmol), NaOH (0.4 mmol) and CH₃CN (4.0 mL) was stirred at 80 °C for 5h under Ar atmosphere. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by column chromatography to give 4a (petroleum ether /ethyl acetate = 10:1).

Deprotection of 3a in the presence of NaOH

![Chemical structure](image2)

A mixture of 3a (0.2 mmol), NaOH (0.4 mmol) and CH₃CN (4.0 mL) was stirred at 80 °C for 5h under Ar atmosphere. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by column chromatography to give compound M (petroleum ether /ethyl acetate = 10:1).
Compound characterization

5-(Fluoromethyl)-3,5-diphenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2a):
White solid, mp 141-142 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ: 7.73-7.71 (m, 2H), 7.41-7.38 (m, 5H), 7.26-7.21 (m, 1H), 7.16-7.14 (m, 4H), 7.06-7.04 (m, 2H), 5.42 (dd, \(J = 46.8, 9.6\) Hz, 1H), 5.14 (dd, \(J = 46.8, 9.6\) Hz, 1H), 3.89 (d, \(J = 18.0\) Hz, 1H), 3.49 (d, \(J = 17.6\) Hz, 1H), 2.33 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) δ: 153.0, 143.2, 138.9, 136.4, 130.7, 130.4, 129.0, 128.7, 128.5, 128.3, 127.4, 126.7, 126.1, 84.3 (d, \(J = 176.3\) Hz), 73.1 (d, \(J = 19.8\) Hz), 47.8 (d, \(J = 3.0\) Hz), 21.5; \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) δ: -221.14 (t, \(J = 46.8\) Hz, 1F); MS (EI) \(m/z\) (%): 408 (M\(^+\), 15), 253 (100), 191 (20), 103 (42), 91 (47), 77 (24); HRMS (EI) calcd for C\(_{23}\)H\(_{21}\)FN\(_2\)O\(_2\)S (M\(^+\)) 408.1308, found 408.1302.

5-(Fluoromethyl)-5-phenyl-3-(p-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazole (2b):
White solid, mp 155-157 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ: 7.67-7.65 (m, 2H), 7.43-7.40 (m, 2H), 7.28-7.24 (m, 3H), 7.20-7.17 (m, 4H), 7.09-7.07 (m, 2H), 5.47 (dd, \(J = 46.8, 9.2\) Hz, 1H), 5.16 (dd, \(J = 46.8, 9.4\) Hz, 1H), 3.91 (dd, \(J = 17.6, 1.2\) Hz, 1H), 3.51 (dd, \(J = 17.6, 1.2\) Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) δ: 153.2, 143.1, 140.9, 138.7, 136.3, 129.4, 128.9, 128.5, 128.3, 127.9, 127.4, 126.7, 126.2, 84.4 (d, \(J = 175.9\) Hz), 72.9 (d, \(J = 20.1\) Hz), 47.9 (d, \(J = 2.8\) Hz), 21.5; \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) δ: -220.85 (t, \(J = 46.8\) Hz, 1F); MS (EI) \(m/z\) (%): 422 (M\(^+\), 17), 267 (65), 149 (46), 119 (100), 91 (68), 57 (43); HRMS (EI) calcd for C\(_{24}\)H\(_{23}\)FN\(_2\)O\(_2\)S (M\(^+\)) 422.1464, found 422.1454.
5-(Fluoromethyl)-5-phenyl-3-(m-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazole (2c):
White solid, mp 120-121 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.57 (s, 1H), 7.51-7.49 (m, 1H), 7.39-7.37 (m, 2H), 7.31-7.27 (m, 1H), 7.24-7.20 (m, 2H), 7.16-7.13 (m, 4H), 7.06-7.04 (m, 2H), 5.42 (dd, $J = 46.8$, 9.6 Hz, 1H), 5.14 (dd, $J = 46.8$, 9.2 Hz, 1H), 3.88 (d, $J = 17.2$ Hz, 1H), 3.49 (d, $J = 17.6$ Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 153.3, 143.2, 138.7, 138.5, 136.3, 131.3, 130.6, 129.0, 128.6, 128.5, 127.4, 127.3, 126.2, 123.9, 84.4 (d, $J = 176.3$ Hz), 72.9 (d, $J = 19.9$ Hz), 47.9 (d, $J = 2.7$ Hz), 21.5, 21.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -221.09 (t, $J = 46.8$ Hz, 1F); MS (ESI, $m/z$): 423.1 (M + H$^+$), 445.1 (M + Na$^+$); HRMS (ESI): calcd for C$_{24}$H$_{24}$FN$_2$O$_2$S (M + H$^+$) 423.1537, found 423.1532.

5-(Fluoromethyl)-3-(4-fluorophenyl)-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2d):
White solid, mp 150-151 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.76-7.71 (m, 2H), 7.44-7.42 (m, 2H), 7.30-7.26 (m, 1H), 7.23-7.18 (m, 4H), 7.15-7.10 (m, 4H), 5.43 (dd, $J = 46.8$, 9.6 Hz, 1H), 5.20 (dd, $J = 46.8$, 9.4 Hz, 1H), 3.90 (dd, $J = 17.6$, 1.2 Hz, 1H), 3.49 (dd, $J = 17.6$, 1.2 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 164.0 (d, $J = 249.8$ Hz), 152.0, 143.3, 138.8, 136.3, 129.0, 128.7, 128.6 (d, $J = 5.0$ Hz), 128.4, 127.4, 127.0 (d, $J = 3.2$ Hz), 126.1, 115.9 (d, $J = 21.9$ Hz), 84.3 (d, $J = 176.2$ Hz), 73.2 (d, $J = 19.7$ Hz), 47.8 (d, $J = 3.0$ Hz), 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -109.17~-109.25 (m, 1F), -221.24 (t, $J = 46.8$ Hz, 1F); MS (EI) $m/z$ (%): 426 (M$^+$, 24), 271 (100), 121 (27), 91 (42), 57 (20); HRMS (EI) calcd for C$_{23}$H$_{20}$F$_2$N$_2$O$_2$S (M$^+$) 426.1214, found 426.1219.
3-(4-Chlorophenyl)-5-(fluoromethyl)-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole
(2e):
White solid, mp 159-162 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.69-7.66 (m, 2H), 7.44-7.39 (m, 4H), 7.31-7.27 (m, 1H), 7.23-7.16 (m, 4H), 7.12-7.10 (m, 2H), 5.42 (dd, $J$ = 46.8, 9.4 Hz, 1H), 5.20 (dd, $J$ = 46.8, 9.6 Hz, 1H), 3.89 (dd, $J$ = 17.6, 1.2 Hz, 1H), 3.49 (dd, $J$ = 17.6, 1.6 Hz, 1H), 2.38 (s, 3H) ; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 151.9, 143.4, 138.7, 136.4, 136.2, 129.2, 129.1, 129.0, 128.6, 128.4, 127.9, 127.4, 126.0, 84.3 (d, $J$ = 176.3 Hz), 73.4 (d, $J$ = 19.7 Hz), 47.7 (d, $J$ = 3.1 Hz), 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -221.36 (t, $J$ = 46.8 Hz, 1F); MS (EI) $m/z$ (%): 442 (M$^+$, 25), 289 (31), 288 (20), 287 (100), 137 (22), 91 (45); HRMS (EI) calcd for C$_{23}$H$_{20}$ClFN$_2$O$_2$S (M$^+$) 442.0918, found 442.0915.

3-(4-Bromophenyl)-5-(fluoromethyl)-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole
(2f):
White solid, mp 144-147 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.58-7.50 (m, 4H), 7.40-7.37 (m, 2H), 7.27-7.22 (m, 1H), 7.19-7.12 (m, 4H), 7.07-7.05 (m, 2H), 5.38 (dd, $J$ = 46.4, 9.6 Hz, 1H), 5.16 (dd, $J$ = 46.4, 9.4 Hz, 1H), 3.85 (dd, $J$ = 17.6, 1.2 Hz, 1H), 3.44 (dd, $J$ = 17.6, 1.6 Hz, 1H), 2.39 (s, 3H) ; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 151.9, 143.4, 138.7, 136.2, 132.0, 129.7, 129.0, 128.6, 128.4, 128.1, 127.4, 126.0, 84.2 (d, $J$ = 176.2 Hz), 73.4 (d, $J$ = 19.8 Hz), 47.6 (d, $J$ = 3.0 Hz), 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -221.45 (t, $J$ = 46.4 Hz, 1F); MS (EI) $m/z$ (%): 486 (M$^+$, 31), 333 (92), 331 (100), 191 (36), 102 (34), 91 (81); HRMS (EI) calcd for C$_{23}$H$_{20}$BrFN$_2$O$_2$S (M$^+$)
5-(Fluoromethyl)-5-phenyl-1-tosyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (2g):

White solid, mp 119-121 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.82-7.80 (m, 2H), 7.65-7.63 (m, 2H), 7.42-7.39 (m, 2H), 7.28-7.24 (m, 1H), 7.20-7.13 (m, 4H), 7.09-7.07 (m, 2H), 5.37 (dd, J = 46.8, 9.6 Hz, 1H), 5.21 (dd, J = 46.8, 9.6 Hz, 1H), 3.90 (d, J = 17.6 Hz, 1H), 3.49 (dd, J = 17.6, 1.6 Hz, 1H), 2.34 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ: 151.4, 143.6, 138.7, 136.2, 134.1, 131.9 (q, J = 32.6 Hz), 129.1, 128.7, 128.5, 127.5, 126.9, 126.0, 125.7 (q, J = 3.7 Hz), 123.8 (q, J = 270.8 Hz), 84.2 (d, J = 176.3 Hz), 73.7 (d, J = 19.5 Hz), 47.5 (d, J = 3.4 Hz), 21.5; ¹⁹F NMR (376 MHz, CDCl₃) δ: -62.88 (s, 3F), -221.89 (t, J = 46.8 Hz, 1F); MS (El) m/z (%): 476 (M⁺, 53), 443 (59), 322 (21), 321 (100), 155 (36), 91 (37); HRMS (EI) calebd for C₂₄H₂₀F₄N₂O₂S (M⁺) 476.1182, found 476.1179.

5-(Fluoromethyl)-3-(naphthalen-2-yl)-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2h):

White solid, mp 186-187 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.08-8.06 (m, 1H), 7.90-7.80 (m, 4H), 7.54-7.48 (m, 2H), 7.43-7.41 (m, 2H), 7.24-7.22 (m, 1H), 7.17-7.13 (m, 4H), 7.07-7.05 (m, 2H), 5.46 (dd, J = 46.8, 9.2 Hz, 1H), 5.18 (dd, J = 46.8, 9.6 Hz, 1H), 4.01 (d, J = 17.6 Hz, 1H), 3.63 (d, J = 17.6 Hz, 1H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 153.2, 143.3, 138.8, 136.3, 134.2, 132.9, 129.0, 128.6, 128.5, 128.4, 128.3, 127.9, 127.4, 127.3, 127.0, 126.8, 126.2, 123.5, 84.4 (d, J = 176.3
Hz), 73.2 (d, J = 19.8 Hz), 47.8 (d, J = 3.0 Hz), 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -221.02 (t, J = 46.8 Hz, 1F); MS (EI) m/z (%): 458 (M$^+$, 21), 304 (25), 303 (100), 153 (43), 152 (30), 91 (51); HRMS (ESI): calcd for C$_{27}$H$_{24}$FN$_2$O$_2$S (M + H$^+$) 459.1537, found 459.1535.

5-(Fluoromethyl)-3-phenyl-5-(p-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazole (2i):
White solid, mp 112-114 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.74-7.72 (m, 2H), 7.42-7.39 (m, 5H), 7.05-7.01 (m, 4H), 6.94-6.92 (m, 2H), 5.40 (dd, J = 46.8, 9.2 Hz, 1H), 5.15 (dd, J = 46.8, 9.6 Hz, 1H), 3.87 (d, J = 17.6 Hz, 1H), 3.48 (d, J = 17.6 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 153.2, 143.2, 138.3, 136.4, 135.7, 130.8, 130.4, 129.1, 128.9, 128.7, 127.4, 126.7, 126.0, 84.4 (d, J = 175.9 Hz), 72.9 (d, J = 19.8 Hz), 47.7 (d, J = 3.0 Hz), 21.6, 21.1; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -221.37 (t, J = 46.8 Hz, 1F); MS (EI) m/z (%): 422 (M$^+$, 34), 267 (100), 163 (49), 103 (47), 91 (91), 84 (42); HRMS (EI) calcd for C$_{24}$H$_{23}$FN$_2$O$_2$S (M$^+$) 422.1464, found 422.1457.

5-(4-Chlorophenyl)-5-(fluoromethyl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2j):
White solid, mp 101-102 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.73-7.71 (m, 2H), 7.44-7.39 (m, 5H), 7.10-7.05 (m, 6H), 5.40 (dd, J = 46.6, 9.6 Hz, 1H), 5.05 (dd, J = 46.6, 9.6 Hz, 1H), 3.88 (dd, J = 17.6, 1.2 Hz, 1H), 3.44 (dd, J = 17.6, 1.2 Hz, 1H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 153.2, 143.6, 137.2, 136.2, 134.5, 130.6,
130.5, 129.1, 128.8, 128.5, 127.6, 127.2, 126.7, 84.2 (d, \(J = 176.3\) Hz), 72.4 (d, \(J = 20.5\) Hz), 47.8 (d, \(J = 2.7\) Hz), 21.5; \(^{19}\)F NMR (376 MHz, CDCl\(3\)) \(\delta\): -220.64 (t, \(J = 46.6\) Hz, 1F); MS (EI) \(m/\zeta\) (%): 442 (M\(^+\), 27), 289 (34), 287 (100), 103 (63), 91 (75), 77 (25); HRMS (EI) calcd for C\(_{23}\)H\(_{20}\)ClFN\(_2\)O\(_2\)S (M\(^+\)) 442.0918, found 442.0919.

![Structure 2k](image)

**5-(Fluoromethyl)-5-methyl-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2k):**

White solid, mp 129-131 °C; \(^1\)H NMR (400 MHz, CDCl\(3\)) \(\delta\): 7.90-7.89 (m, 2H), 7.64-7.63 (m, 2H), 7.37-7.36 (m, 3H), 7.29-7.24 (m, 3H), 4.78 (dd, \(J = 47.0, 9.4\) Hz, 1H), 4.68 (dd, \(J = 47.0, 9.2\) Hz, 1H), 3.47 (d, \(J = 18.0\) Hz, 1H), 2.97 (d, \(J = 18.0\) Hz, 1H), 2.39 (s, 3H), 1.50 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(3\)) \(\delta\): 153.5, 143.9, 136.9, 131.0, 130.3, 129.4, 128.6, 128.0, 126.6, 85.9 (d, \(J = 175.4\) Hz), 70.1 (d, \(J = 19.5\) Hz), 44.6 (d, \(J = 3.1\) Hz), 21.6, 21.4 (d, \(J = 2.4\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(3\)) \(\delta\): -222.17 (t, \(J = 47.0\) Hz, 1F); MS (EI) \(m/\zeta\) (%): 346 (M\(^+\), 71), 313 (57), 191 (100), 103 (38), 91 (37); HRMS (EI) calcd for C\(_{18}\)H\(_{19}\)FN\(_2\)O\(_2\)S (M\(^+\)) 346.1151, found 346.1158.

![Structure 2l](image)

**3-Cyclohexyl-5-(fluoromethyl)-5-methyl-1-tosyl-4,5-dihydro-1H-pyrazole (2l):**

White solid, mp 84-86 °C; \(^1\)H NMR (400 MHz, CDCl\(3\)) \(\delta\): 7.84-7.82 (m, 2H), 7.27-7.24 (m, 2H), 4.74-4.44 (m, 2H), 3.02 (d, \(J = 17.2\) Hz, 1H), 2.48 (d, \(J = 17.2\) Hz, 1H), 2.34 (s, 3H), 2.29 (s, 1H), 1.82-1.74 (m, 4H), 1.67-1.64 (m, 1H), 1.35 (d, \(J = 1.2\) Hz, 3H), 1.31-1.20 (m, 5H); \(^{13}\)C NMR (100 MHz, CDCl\(3\)) \(\delta\): 162.2, 143.5, 137.1, 129.2, 128.0, 86.1 (d, \(J = 174.9\) Hz), 69.0 (d, \(J = 19.9\) Hz), 45.1 (d, \(J = 2.9\) Hz), 38.2, 30.2, 30.0, 25.8, 25.7, 25.6, 21.6, 20.8 (d, \(J = 2.5\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(3\)) \(\delta\): -222.18 (t, \(J = 47.0\) Hz, 1F); MS (EI) \(m/\zeta\) (%): 352 (M\(^+\), 32), 320 (23), 319 (100), 237 (60), 155 (53), 91 (41); HRMS (EI) calcd for C\(_{18}\)H\(_{25}\)FN\(_2\)O\(_2\)S (M\(^+\)) 352.1621, found 352.1620.
5-Fluoro-3,5-diphenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3a):  
White solid, mp 188-190 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.84-7.82 (m, 2H), 7.71-7.69 (m, 2H), 7.44-7.33 (m, 8H), 7.30-7.28 (m, 2H), 4.20-4.14 (m, 1H), 3.36-3.26 (m, 1H), 3.11-2.88 (m, 2H), 2.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 147.2, 144.2, 139.9 (d, $J = 21.5$ Hz), 136.0, 133.6, 129.8, 129.6, 128.9 (d, $J = 3.0$ Hz), 128.5, 128.4, 125.5, 124.2, 124.1, 89.4 (d, $J = 179.8$ Hz), 50.7 (d, $J = 25.4$ Hz), 35.0 (d, $J = 26.0$ Hz), 21.6; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -149.14--149.38 (m, 1F); MS (EI) $m/z$ (%): 408 (M$^+$, 68), 253 (100), 205 (61), 204 (53), 104 (64), 103(74); HRMS (EI) calcd for C$_{23}$H$_{21}$FN$_2$O$_2$S (M$^+$) 408.1308, found 408.1313.

5-Fluoro-5-phenyl-3-(p-tolyl)-1-tosyl-1,4,5,6-tetrahydropyridazine (3b):  
White solid, mp 156-158 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.83-7.81 (m, 2H), 7.61-7.59 (m, 2H), 7.41-7.27 (m, 7H), 7.17-7.15 (m, 2H), 4.16-4.11 (m, 1H), 3.34-3.23 (m, 1H), 3.08-2.86 (m, 2H), 2.39 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 147.4, 144.1, 140.0 (d, $J = 21.6$ Hz), 139.9, 133.6, 133.3, 129.5, 129.2, 128.9 (d, $J = 4.3$ Hz), 128.4, 125.4, 124.2, 124.1, 89.5 (d, $J = 179.6$ Hz), 50.7 (d, $J = 25.3$ Hz), 35.0 (d, $J = 25.7$ Hz), 21.6, 21.3; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -149.04--149.28 (m, 1F); MS (ESI, m/z): 423.1 (M$^+$H$^+$); HRMS (ESI): calcd for C$_{24}$H$_{24}$FN$_2$O$_2$S (M$^+$H$^+$) 423.1537, found 423.1536.
5-Fluoro-5-phenyl-3-(m-tolyl)-1-tosyl-1,4,5,6-tetrahydropyridazine (3c):

White solid, mp 161-163 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.85-7.83 (m, 2H), 7.51-7.50 (m, 2H), 7.44-7.38 (m, 3H), 7.35-7.33 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.23 (m, 1H), 7.19-7.17 (m, 1H), 4.19-4.13 (m, 1H), 3.35-3.24 (m, 1H), 3.10-2.86 (m, 2H), 2.40 (s, 3H), 2.36 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 147.5, 144.2, 140.0 (d, \(J = 21.7\) Hz), 138.1, 136.0, 133.6, 130.6, 129.6, 128.9 (d, \(J = 4.4\) Hz), 128.4, 126.2, 124.2, 124.1, 122.7, 89.5 (d, \(J = 180.0\) Hz), 50.7 (d, \(J = 25.0\) Hz), 35.1 (d, \(J = 26.0\) Hz), 21.6, 21.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -149.15--149.39 (m, 1F); MS (ESI, \(m/z\)): 423.2 (M + H\(^{+}\)); HRMS (ESI): calcd for C\(_{24}\)H\(_{24}\)FN\(_2\)O\(_2\)S (M + H\(^{+}\)) 423.1537, found 423.1536.

5-Fluoro-3-(4-fluorophenyl)-5-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3d):

White solid, mp 167-168 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.83-7.81 (m, 2H), 7.70-7.66 (m, 2H), 7.44-7.29 (m, 7H), 7.07-7.02 (m, 2H), 4.21-4.15 (m, 1H), 3.35-3.24 (m, 1H), 3.07-2.84 (m, 2H), 2.40 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 163.7 (d, \(J = 248.4\) Hz), 146.2, 144.3, 139.8 (d, \(J = 21.6\) Hz), 133.6, 132.2 (d, \(J = 2.9\) Hz), 129.6, 128.9, 128.4, 127.4 (d, \(J = 8.3\) Hz), 124.2, 124.1, 115.5 (d, \(J = 21.6\) Hz), 89.3 (d, \(J = 180.2\) Hz), 50.5 (d, \(J = 25.1\) Hz), 34.9 (d, \(J = 26.0\) Hz), 21.6; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -110.97--111.05 (m, 1F), -149.32--149.56 (m, 1F); MS (ESI, \(m/z\)): 427.1 (M + H\(^{+}\)); HRMS (ESI): calcd for C\(_{23}\)H\(_{21}\)F\(_2\)N\(_2\)O\(_2\)S (M + H\(^{+}\)) 427.1286, found 427.1286.
3-(4-Chlorophenyl)-5-fluoro-5-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3e):

White solid, mp 160-162 °C; 1H NMR (400 MHz, CDCl₃) δ: 7.82-7.81 (m, 2H), 7.64-7.62 (m, 2H), 7.42-7.24 (m, 9H), 4.23-4.18 (m, 1H), 3.33-3.23 (m, 1H), 3.05-2.83 (m, 2H), 2.39 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ: 146.0, 144.4, 139.7 (d, J = 21.3 Hz), 135.8, 134.5, 133.6, 129.7, 129.0, 128.7, 128.3, 126.7, 124.2, 124.1, 89.2 (d, J = 180.1 Hz), 50.5 (d, J = 25.0 Hz), 34.8 (d, J = 25.9 Hz), 21.7; 19F NMR (376 MHz, CDCl₃) δ: -149.56~-149.80 (m, 1F); MS (EI) m/z (%): 442 (M⁺, 39), 287 (69), 204 (100), 203 (52), 102 (65), 91(85); HRMS (ESI): calcd for C₂₃H₂₁ClFN₂O₂S (M + H⁺) 443.0991, found 443.0987.

3-(4-Bromophenyl)-5-fluoro-5-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3f):

White solid, mp 177-179 °C; 1H NMR (400 MHz, CDCl₃) δ: 7.82-7.80 (m, 2H), 7.57-7.55 (m, 2H), 7.49-7.47 (m, 2H), 7.42-7.38 (m, 3H), 7.34-7.28 (m, 4H), 4.23-4.17 (m, 1H), 3.35-3.24 (m, 1H), 3.05-2.83 (m, 2H), 2.40 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ: 146.0, 144.3, 139.7 (d, J = 21.6 Hz), 134.9, 133.6, 131.7, 129.6, 129.0, 128.3, 127.0, 124.2, 124.1, 124.0, 89.2 (d, J = 179.9 Hz), 50.5 (d, J = 25.1 Hz), 34.8 (d, J = 26.1 Hz), 21.6; 19F NMR (376 MHz, CDCl₃) δ: -149.53~-149.77 (m, 1F); MS (ESI, m/z): 487.0 (M + H⁺); HRMS (ESI): calcd for C₂₃H₂₁BrFN₂O₂S (M + H⁺) 487.0486, found 487.0482.
5-Fluoro-3-(naphthalen-2-yl)-5-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3g):
White solid, mp 178-179 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.09-8.07 (m, 1H), 7.92-7.77 (m, 6H), 7.50-7.37 (m, 7H), 7.31-7.29 (m, 2H), 4.26-4.21 (m, 1H), 3.40-3.29 (m, 1H), 3.26-3.00 (m, 2H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 147.0, 144.3, 140.0 (d, $J = 21.4$ Hz), 133.9, 133.7, 133.5, 132.9, 129.6, 128.9 (d, $J = 3.4$ Hz), 128.5, 128.4, 128.3, 127.7, 127.0, 126.5, 125.1, 124.3, 124.2, 123.0, 89.4 (d, $J = 179.9$ Hz), 50.7 (d, $J = 25.1$ Hz), 34.9 (d, $J = 26.1$ Hz), 21.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -149.44--149.68 (m, 1F); MS (ESI, $m/z$): 459.2 (M + H$^+$); HRMS (ESI): calcd for C$_{27}$H$_{24}$FN$_2$O$_2$S (M + H$^+$) 459.1537, found 459.1526.

5-Fluoro-3-phenyl-5-(p-tolyl)-1-tosyl-1,4,5,6-tetrahydropyridazine (3h):
White solid, mp 136-138 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.84-7.82 (m, 2H), 7.71-7.69 (m, 2H), 7.37-7.36 (m, 3H), 7.30-7.28 (m, 2H), 7.23 (s, 4H), 4.20-4.14 (m, 1H), 3.32-3.22 (m, 1H), 3.09-2.86 (m, 2H), 2.38 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 147.3, 144.2, 138.8, 137.0 (d, $J = 21.7$ Hz), 136.0, 133.7, 129.8, 129.6 (d, $J = 3.3$ Hz), 128.5, 128.4, 125.5, 124.2, 124.1, 89.4 (d, $J = 179.5$ Hz), 50.7 (d, $J = 25.3$ Hz), 34.9 (d, $J = 26.1$ Hz), 21.6, 21.1; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -148.32--148.56 (m, 1F); MS (ESI, $m/z$): 423.1 (M + H$^+$); HRMS (ESI): calcd for C$_{24}$H$_{24}$FN$_2$O$_2$S (M + H$^+$) 423.1537, found 423.1529.
5-(4-Chlorophenyl)-5-fluoro-3-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3i):
White solid, mp 140-143 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.87-7.85 (m, 2H), 7.76-7.71 (m, 2H), 7.43-7.37 (m, 5H), 7.34-7.28 (m, 4H), 4.14-4.08 (m, 1H), 3.43-3.33 (m, 1H), 3.13-2.90 (m, 2H), 2.43 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 147.1, 144.4, 138.5 (d, \(J = 22.3\) Hz), 135.8, 135.0, 133.5, 129.9, 129.6, 129.1, 128.6, 128.4, 125.8 (d, \(J = 8.9\) Hz), 125.5, 89.3 (d, \(J = 180.5\) Hz), 50.5 (d, \(J = 25.8\) Hz), 35.0 (d, \(J = 25.8\) Hz), 21.6; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -148.23~-148.46 (m, 1F); MS (ESI, \(m/z\)): 443.0 (M + H\(^+\)); HRMS (ESI): calcd for C\(_{23}\)H\(_{21}\)ClFN\(_2\)O\(_2\)S (M + H\(^+\)) 443.0991, found 443.0986.

3-(Fluoromethyl)-3,5-diphenyl-3H-pyrazole (4a):
White solid, mp 94-95 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.11-8.10 (m, 2H), 7.60-7.58 (m, 2H), 7.50-7.35 (m, 7H), 5.06-4.84 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 157.8, 132.6 (d, \(J = 4.1\) Hz), 130.4 (d, \(J = 1.7\) Hz), 130.1, 129.7, 129.0, 128.9, 128.8, 127.7, 127.4, 103.9 (d, \(J = 19.0\) Hz), 84.2 (d, \(J = 185.4\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -218.46 (t, \(J = 46.6\) Hz, 1F); MS (EI) \(m/z\) (%): 252 (M\(^+\), 10), 224 (17), 192 (18), 191 (100), 189 (25); HRMS (EI) calcd for C\(_{16}\)H\(_{13}\)FN\(_2\) (M\(^+\)) 252.1063, found 252.1068.

6,8-dimethyl-4-phenyl-5,6-dihydro-2,6-methanobenzo[g][1,2,3]thiadiazocine 1,1-dioxide (5):
White solid, mp 66-68 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.75-7.73 (m, 1H), 7.53-7.51 (m, 2H), 7.35-7.25 (m, 3H), 7.17-7.15 (m, 1H), 7.04 (s, 1H), 3.38 (d, $J$ = 15.2Hz, 1H), 3.10 (dd, $J$ = 22.0, 17.6 Hz, 2H), 2.82 (d, $J$ = 15.2Hz, 1H), 2.32 (s, 3H), 1.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 157.8, 143.8, 135.3, 132.6, 130.6, 130.5, 129.6, 128.5, 128.4, 127.0, 126.2, 69.5, 48.9, 41.2, 31.4, 21.6; MS (ESI, $m/z$): 327.1133 (M + H$^+$); HRMS (ESI): calcd for C$_{18}$H$_{18}$N$_2$O$_2$S (M$^+$) 326.1089, found 326.1061.

![3,5-diphenylpyridazine (M)](image)

3,5-diphenylpyridazine (M)

This is a known compound.$^1$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 9.38 (d, $J$ = 2.4 Hz, 1H), 8.13-8.11 (m, 2H), 7.97 (d, $J$ = 2.0 Hz, 1H), 7.72-7.69 (m, 2H), 7.56-7.57 (m, 6H).

Reference:
Copies of spectra