Supporting Information

Selectively Catalytic Hydrodefluorination of Perfluoroarenes by Co(PMe$_3$)$_4$ with Sodium Formate as Reducing Agent and Mechanism Study

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1. Spectra of 1a - 4a and 4b

1) 1a
$^1$H NMR (300 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
GC-MS (m/z)

2) 2a
IR spectroscopy

$^1$H NMR (300 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
\[^{13}\text{C} \text{NMR (74.5 MHz, CDCl}_3\text{)}\]

\[\text{GC-MS (m/z)}\]

3) \(\text{3a}\)
GC-MS (m/z)

4) 3b
GC-MS (m/z)

5) 4a
$^1$H NMR (300 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
$^{13}$C NMR (74.5 MHz, CDCl$_3$)

GC-MS (m/z)
6) 4b

\[ \text{F} - \text{F} - \text{F} - \text{F} - \text{F} - \text{H} - \text{H} - \text{F} - \text{F} - \text{F} - \text{F} \]

$^1$H NMR (300 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^{13}$C NMR (74.5 MHz, CDCl$_3$)

GC-MS (m/z)
7) NaF

$^19$F NMR (282 MHz, H$_2$O)

8) HCOONa
The sample of $\text{C}_{12}\text{F}_{10}$ (0.020 g, 0.060 mmol) was added in a solution of 0.6 mL of DMSO-$D_6$ with $\text{Co(PMe}_3\text{)}_4$ (0.021 g, 0.060 mmol), HCOONa (0.012, 0.180 mmol) in a NMR tube at $-80 ^\circ \text{C}$, This mixture was allowed to warm to $80 ^\circ \text{C}$ and the color of the reaction solution turned to orange from brown.

$^1\text{H NMR (300 MHz, D}_2\text{O)}$

9) the *in situ* $^1\text{H NMR}$

$^1\text{H NMR (300 MHz, DMSO-D}_6\text{)}$

10) IR spectroscopy of pentafluoropyridine