Supporting Information

Direct Monofluoromethylation of $O$-, $S$-, $N$-, and $P$-Nucleophiles with PhSO(NTs)CH$_2$F: Accelerating Effect of $\alpha$- Fluorine Substitution

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**General Methods:**

N-Tosyl-S-methyl-S-phenylsulfoximine\(^1\) and N-Tosyl-S-trifluoromethyl-S-phenylsulfoximine\(^2\) were prepared via the literature procedures. Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. THF was distilled over sodium. CH\(_2\)CN, NMP, DMF, and DMSO were distilled over CaH\(_2\). \(^1\)H, \(^13\)C and \(^19\)F NMR spectra were recorded on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. \(^1\)H NMR chemical shifts were determined relative to internal (CH\(_3\))\(_4\)Si (TMS) at \(\delta 0.0\) or to the signal of a residual protonated solvent: CDCl\(_3\) \(\delta 7.26\). \(^13\)C NMR chemical shifts were determined relative to internal TMS at \(\delta 0.0\). \(^19\)F NMR chemical shifts were determined relative to CFCl\(_3\) at \(\delta 0.0\). Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode. Melting points (open or sealed capillaries) are reported without correction.

**Preparation of N-Tosyl-S-fluoromethyl-S-phenylsulfilimine (2).**

\[
\text{PhSCH}_2\text{F} \xrightarrow{\text{N-benzyl-\(N,N\)-diethylethanaminium chloride, Chloramine-T, \(\text{CH}_2\text{Cl}_2\), reflux, 3 d}} \text{NTs} \xrightarrow{} \text{Ph}^+\text{S}^-\text{CH}_2\text{F}^{2-} \quad 2, 71% \]

Under N\(_2\) atmosphere, a mixture of PhSCH\(_2\)F (364 mmol), N-benzyl-\(N,N\)-diethylethanaminium chloride (3 g, 13 mmol), Chloramine-T•3H\(_2\)O (120 g, 427 mmol) in CH\(_2\)Cl\(_2\) (250 mL) was refluxed for 3 days, after which the reaction was quenched by adding excess amount of water, followed by extraction with CH\(_2\)Cl\(_2\). The organic phase was washed with brine and then dried over anhydrous MgSO\(_4\). After the solution was filtered and the solvent was evaporated under vacuum, the residue was recrystallized in anhydrous EtOH, giving white crystal product 2 (80 g, 71%).

**N-Tosyl-S-fluoromethyl-S-phenylsulfoximine (2)**

White solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.77\) (d, \(J = 8.0\) Hz, 4H), \(7.70 - 7.50\) (m, 3H), \(7.20\) (d, \(J = 8.0\) Hz, 2H), \(5.37\) (dd, \(J = 46.2, 7.1\) Hz, 1H), \(5.14\) (dd, \(J = 46.9, 7.0\) Hz, 1H), \(2.37\) (s, 3H). \(^19\)F NMR (282 MHz, CDCl\(_3\)): \(\delta -205.31\) (t, \(J = 46.5\) Hz). \(^13\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 142.15, 140.86, 133.44, 130.20, 129.35, 127.01, 126.26, 94.05\) (d, \(J = 231.9\) Hz), \(21.41\). Anal. Calcd. for C\(_{14}\)H\(_{14}\)FNO\(_2\)S\(_2\): C, 54.00; H, 4.53; N, 4.50; Found: C, 53.88; H, 4.43; N, 4.39.

**Preparation of N-Tosyl-S-fluoromethyl-S-phenylsulfoximine (1).**

\[
\text{PhSCH}_2\text{F} \xrightarrow{\text{NaOH, \(\text{H}_2\text{O}_2\), MeOH, \(\text{H}_2\text{O}\), reflux, 2 h, 300 mmol scale}} \text{NTs} \xrightarrow{} \text{Ph}^+\text{S}^-\text{CH}_2\text{F}^{2-} \quad 75\% \]

Electronic Supplementary Material (ESI) for Chemical Science

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To a solution of $N$-Tosyl-$S$-fluoromethyl-$S$-phenylsulfilimine (93.3 g, 300 mmol) in 500 mL MeOH, was added NaOH/H$_2$O (25 g/100 mL) at rt. H$_2$O$_2$ (30%, 67 mL) was added in several portions, and the solution was kept in reflux. 2 hours later, the solution was allowed to rt and extracted with CH$_2$Cl$_2$. The organic phase was washed with brine and then dried over anhydrous MgSO$_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was recrystallized in anhydrous EtOH/EA/PE, giving colourless white crystal product (73.5g, 75%).

$N$-Tosyl-$S$-fluoromethyl-$S$-phenylsulfoximine ($1$)

White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.03 (d, $J = 7.8$ Hz, 2H), 7.90 (d, $J = 8.3$ Hz, 2H), 7.77 (t, $J = 7.4$ Hz, 1H), 7.64 (t, $J = 7.7$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 5.74 (dd, $J = 47.1, 9.1$ Hz, 1H), 5.22 (dd, $J = 47.1, 9.7$ Hz, 1H), 2.41 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -205.84 (t, $J = 46.7$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 143.42, 140.12, 135.40, 133.10, 129.81, 129.46, 129.10, 126.74, 92.79 (d, $J = 227.6$ Hz), 21.54. MS (ESI, m/z): 345.0 (M+NH$_4^+$). Anal. calcd. For C$_{14}$H$_{14}$FNO$_3$S$_2$: C, 51.36; H, 4.31; N, 4.28; Found: C, 51.65; H, 4.53; N, 3.88.

Typical Experimental Procedure for the Monofluoromethylation of $O$−, $S$−, $N$−, and $P$−Nucleophiles with PhSO(NTs)CH$_2$F ($1$).

Under N$_2$ atmosphere, to a solution of [1,1'-biphenyl]-4-ol (51 mg, 0.3 mmol) in 1.5 mL DMSO, was added NaH (15 mg, 60% purity, 0.375 mmol) at rt. After 30 min, $N$-Tosyl-$S$-fluoromethyl-$S$-phenylsulfoximine (128 mg, 0.39 mmol), DMSO (0.5 mL) was added successively. The solution was allowed to 80 °C, and stirred for 4 h, after which the reaction was quenched by adding excess amount of saturated NH$_4$Cl aqueous solution, followed by extraction with ethyl ether. The organic phase was washed with brine and then dried over anhydrous MgSO$_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using petroleum ether as eluent to give product 4a (58 mg, 95%). In general, 4 h was used for the reaction of phenols and thiols, 6 h was used for the $P$-nucleophile, 8−71 h for $N$-nucleophiles and the reaction of acid were performed at 100°C for 12h.

$4$-(fluoromethoxy)biphenyl ($4$a)

White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.49 (d, $J = 8.4$ Hz, 4H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.09 (d, $J = 8.4$ Hz, 2H), 5.69 (d, $J = 54.6$ Hz, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -148.88 (t, $J = 54.7$ Hz). MS (EI, m/z): 202 (M+, 100.0), 169 (55.5), 141(42.3), 115 (38.7).

$1$-(fluoromethoxy)-4-iodobenzene ($4$b)

White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.49 (d, $J = 8.4$ Hz, 4H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.09 (d, $J = 8.4$ Hz, 2H), 5.69 (d, $J = 54.6$ Hz, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -148.88 (t, $J = 54.7$ Hz). MS (EI, m/z): 202 (M+, 100.0), 169 (55.5), 141(42.3), 115 (38.7).
Colourless liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.55 (d, $J = 7.8$ Hz, 2H), 6.79 (d, $J = 8.1$ Hz, 2H), 5.61 (d, $J = 54.4$ Hz, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -149.05 (t, $J = 54.3$ Hz). MS (EI, m/z): 252 (M$^+$, 100.0), 219 (35.3), 92(22.5), 64 (22.0), 63 (21.7).

1-(fluoromethoxy)-2-iodobenzene (4c)

Colourless liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 7.8$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 1H), 7.13 (d, $J = 8.2$ Hz, 1H), 6.87 (t, $J = 7.6$ Hz, 1H), 5.74 (d, $J = 54.1$ Hz, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -149.20 (t, $J = 54.2$ Hz). MS (EI, m/z): 252 (M$^+$).

1-(fluoromethoxy)-3-iodobenzene (4d)

Colourless liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.50 – 7.41 (m, 2H), 7.11 – 7.03 (m, 2H), 5.69 (d, $J = 54.3$ Hz, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -149.03 (t, $J = 54.8$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 157.20, 132.75, 131.05, 125.99, 116.16, 100.50 (d, $J = 220.1$ Hz), 94.16. IR: 2956, 2924, 2854, 1460, 1377, 1261, 1096, 1020, 802 cm$^{-1}$. MS (EI, m/z,\%): 252 (M$^+$,100.0), 77 (35.3), 92(31.9), 125 (27.0), 64 (25.2), 63(24.9), 95(19.4), 76(10.5). HRMS (EI) Calcd. for : C$_7$H$_6$FIO: 251.9447; Found 251.9445.

1-bromo-4-(fluoromethoxy)benzene (4e)

Colourless liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.44 (d, $J = 8.7$ Hz, 2H), 6.97 (d, $J = 8.7$ Hz, 2H), 5.68 (d, $J = 54.4$ Hz, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -148.96 (t, $J = 54.4$ Hz). MS (EI, m/z): 204 (M$^+$, 29.8), 56 (100), 57 (53.7), 152 (42.7), 122 (36.5).

1-chloro-4-(fluoromethoxy)benzene (4f)

Colourless liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.29 (d, $J = 6.9$ Hz, 2H), 7.02 (d, $J = 7.0$ Hz, 2H), 5.68 (d, $J = 54.4$Hz, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -148.82 (t, $J = 54.5$ Hz).

1-tert-butyl-4-(fluoromethoxy)benzene (4g)
Colourless liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.34 (d, $J = 8.8$ Hz, 2H), 7.02 (d, $J = 8.9$ Hz, 2H), 5.70 (d, $J = 54.9$ Hz, 2H), 1.31 (s, 9H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -148.39 (t, $J = 54.9$ Hz). MS (EI, m/z, %): 182 (M$^+$, 17.1), 167 (100%).

($\text{fluoromethoxy})$benzene ($4h$)

Volatile compound. $^{19}$F NMR (282 MHz, DMSO): $\delta$ -151.8 (t, $J = 55$ Hz).

1-($\text{fluoromethoxy})$ naphthalene ($4i$)

Colourless liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.30 – 8.12 (m, 1H), 7.92 – 7.77 (m, 1H), 7.60 (d, $J = 8.2$ Hz, 1H), 7.54 – 7.48 (m, 2H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.18 (d, $J = 7.7$ Hz, 1H), 5.93 (d, $J = 54.4$ Hz, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -148.68 (t, $J = 54.5$ Hz). MS (EI, m/z): 176 (M$^+$, 100.0), 91 (70.8).

(2-($\text{fluoromethoxy})$ethyl)benzene ($4j$)

$^{19}$F NMR (282 MHz, DMSO): $\delta$ -150.9 (t, $J = 55$ Hz). No $^{19}$F NMR of compound $4j$ was reported in the literature. Based on the fact that the $^{19}$F NMR signals of aryl monofluoromethyl ethers in this study are at -148 ~ -152 ppm and the coupling constants are ranging from 54-55 Hz, we assign the signal at -150.9 (t, $J = 55$ Hz) as that of compound $4j$ (trace amount of $4j$ was observed by $^{19}$F NMR in our reaction).

($\text{fluoromethyl})(\text{phenyl})$sulfane ($4k$)

Unstable compound, which decomposes gradually during or after the silica gel column chromatography. $^{19}$F NMR (282 MHz, DMSO): $\delta$ -181.8 (t, $J = 52$ Hz).

($\text{fluoromethyl})(4$-nitrophenyl)$sulfane ($4l$)
Yellow solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.20 (d, \(J = 8.8\) Hz, 2H), 7.58 (d, \(J = 8.8\) Hz, 2H), 5.84 (d, \(J = 52.2\) Hz, 2H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) -184.70 (t, \(J = 52.2\) Hz). MS (EI, m/z): 187 (M\(^+\), 100), 157 (43.6), 108 (36.4), 69 (26.3), 45 (21.6).

\textit{(4-bromophenyl)(fluoromethyl)sulfane (4m)}

Unstable compound, which decomposes gradually during or after the silica gel column chromatography. \(^{19}\)F NMR (282 MHz, DMSO) \(\delta\) -186.3 (t, \(J = 52\) Hz). No \(^{19}\)F NMR of compound 4m was reported in the literature. Based on the fact that the \(^{19}\)F NMR signals of aryl monofluoromethyl sulfanes in this study are mostly around -184 ~ -187 ppm and the coupling constants are ranging from 50~52 Hz, we assign the signal at -186.3 (t, \(J = 52\) Hz) as that of compound 4m.

\textit{(2,6-dichlorophenyl)(fluoromethyl)sulfane (4n)}

Colourless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.44 (d, \(J = 7.8\) Hz, 2H), 7.26 (t, \(J = 7.8\) Hz, 1H), 5.69 (d, \(J = 52.1\) Hz, 2H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) -185.38 (t, \(J = 52.1\) Hz). MS (EI, m/z): 210 (M\(^+\), 100), 177 (89.7), 142 (77.9), 212 (67.4), 179 (57.9), 144 (29.1), 107(19.6), 69(14.5).

\textit{2-(fluoromethylthio)benzo[d]thiazole (4o)}

White solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.97 (d, \(J = 8.0\) Hz, 1H), 7.81 (d, \(J = 7.7\) Hz, 1H), 7.47 (t, \(J = 7.2\) Hz, 1H), 7.36 (t, \(J = 6.9\) Hz, 1H), 6.15 (d, \(J = 51.0\) Hz, 2H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) -186.46 (t, \(J = 51.0\) Hz). MS (EI, m/z, %): 135 (M\(^+\)-SCH\(_2\)F, 100), 199 (M\(^+\), 89.4), 108 (59.4), , 166 (58.1), 179(35.0).

\textit{1-tert-butyl-5-(fluoromethylthio)-1H-tetrazole (4p)}

White solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 6.21 (d, \(J = 50.0\) Hz, 2H), 1.75 (s, 9H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) -187.76 (t, \(J = 50.0\) Hz). MS (EI, m/z, %): 190 (M\(^+\), 9), 57 (100).
2-(fluoromethylthio)pyridine (4q)

\[
\begin{align*}
\text{N} & \text{S} \text{F} \\
\text{N} & \text{N}
\end{align*}
\]

\(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 8.52 (s, 1H), 7.58 (t, \(J = 7.6\) Hz, 1H), 7.29 (d, \(J = 8.3\) Hz, 1H), 7.11 (s, 1H), 6.15 (d, \(J = 51.7\) Hz, 2H). \(^{19}\)F NMR (282 MHz, CDCl\textsubscript{3}): \(\delta\) -187.32 (t, \(J = 51.6\) Hz). MS (EI, m/z, %): 143 (M\(^+\), 31.5), 79 (100).

benzyl(fluoromethyl)sulfane(4r)

Unstable compound, which decomposes gradually during or after the silica gel column chromatography. \(^{19}\)F NMR (282 MHz, DMSO): \(\delta\) -188.0 (t, \(J = 52\) Hz).

1-(fluoromethyl)-2-phenyl-1H-imidazole (4s)

\[
\begin{align*}
\text{N} & \text{F} \\
\text{N} & \text{C}_\text{H}_2
\end{align*}
\]

Yellow liquid. \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 7.83 – 7.62 (m, 2H), 7.60 – 7.41 (m, 3H), 7.20 (s, 2H), 5.89 (d, \(J = 52.7\) Hz, 2H). \(^{19}\)F NMR (282 MHz, CDCl\textsubscript{3}): \(\delta\) -157.08 (t, \(J = 52.7\) Hz). MS (EI, m/z, %): 176 (M\(^+\)).

1-(fluoromethyl)-2-phenyl-1H-benzo[d]imidazole (4t)

\[
\begin{align*}
\text{N} & \text{F} \\
\text{N} & \text{C}_\text{H}_2
\end{align*}
\]

White solid. 128-129°C. \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 7.88 – 7.77 (m, 3H), 7.60 – 7.48 (m, 4H), 7.43 – 7.32 (m, 2H), 6.12 (d, \(J = 53.6\) Hz, 2H). \(^{19}\)F NMR (282 MHz, CDCl\textsubscript{3}): \(\delta\) -161.78 (t, \(J = 53.6\) Hz). \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}): \(\delta\) 154.14, 143.09, 135.43, 130.57, 129.54, 129.06, 128.95, 124.06, 123.83, 120.38, 109.53, 81.74 (d, \(J = 198.6\) Hz). IR: 3048, 1925, 1616, 1525, 1479, 1458, 1438, 1368, 1252, 1080, 977, 818, 780, 745, 701, 592, 430. MS (EI, m/z, %): 226 (M\(^+\), 87.95), 225 (100). HRMS(EI, m/z): m/z calcd. For C\textsubscript{14}H\textsubscript{11}FN\textsubscript{2} 226.0906, found 226.0909.

1-(fluoromethyl)-5,6-dimethyl-1H-benzo[d]imidazole (4u)

\[
\begin{align*}
\text{N} & \text{F} \\
\text{N} & \text{C}_\text{H}_2
\end{align*}
\]

White solid. \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 7.91 (s, 1H), 7.58 (s, 1H), 7.29 (s, 1H), 6.11 (d, \(J = 53.7\) Hz, 2H), 2.41 (s, 3H), 2.38 (s, 3H). \(^{19}\)F NMR (282 MHz, CDCl\textsubscript{3}): \(\delta\) -163.07 (t, \(J = 53.7\) Hz). \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 142.66, 142.38, 135.38, 132.45, 131.67, 120.77, 109.69, 81.76 (d, \(J = 200.6\) Hz), 20.52, 20.22. MS (EI, m/z, %): 178 (M\(^+\), 100), 163 (69.4), 177(58.5).
1-(fluoromethyl)-5-nitro-1H-benzo[d]imidazole (4va)³
1-(fluoromethyl)-6-nitro-1H-benzo[d]imidazole (4vb)³

Yellow solid. ¹H NMR (300 MHz, CDCl₃): δ 8.76 (s, 1H), 8.52 (s, 1H), 8.32 – 8.29 (m, 3H), 8.23 (s, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.64 (d, J = 8.9 Hz, 1H), 6.26 (d, J = 52.5 Hz, 2H), 6.24 (d, J = 52.8 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -164.78 (t, J = 52.5 Hz), -165.23 (t, J = 52.5 Hz). MS (EI, m/z, %): 195 (M⁺, 100.00), 165(33.28).

1-(fluoromethyl)-1H-benzo[d][1,2,3]triazole (4wa)⁷

White solid. Mp: 106-107 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.13 (d, J = 8.4 Hz, 1H), 7.71-7.56 (m, 2H), 7.47 (t, J = 7.5 Hz, 1H), 6.60 (d, J = 52.5 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -167.84 (t, J = 52.5 Hz). ¹³C NMR (101 MHz, CDCl₃): δ 146.31, 132.72, 128.83, 124.88, 120.33, 119.02, 83.36 (d, J = 204.2 Hz). IR (film): 3026, 2922, 1617, 1455, 1278, 1171, 989, 766, 616, 427 cm⁻¹. MS (EI, m/z, %): 151(M⁺, 100), 122(77.4). HRMS (EI, m/z): calcd. For C₇H₆FN₃ (M⁺) 151.0546, Found 151.0543.

2-(fluoromethyl)-2H-benzo[d][1,2,3]triazole (4wa)⁷

White solid. Mp: 40-41°C. ¹H NMR (400 MHz, CDCl₃): δ 7.91 (dd, J = 6.7, 3.0 Hz, 2H), 7.44 (dd, J = 6.7, 3.0 Hz, 2H), 6.54 (d, J = 50.4 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ -168.74 (t, J = 50.4 Hz). ¹³C NMR (101 MHz, CDCl₃): δ 145.46, 127.98, 118.80, 90.31 (d, J = 208.7 Hz). IR (film): 3048, 2994, 1560, 1455, 1339, 1273, 1019, 858, 750 cm⁻¹. MS (EI, m/z, %): 151 (M⁺, 100). HRMS (EI, m/z): calcd. For C₇H₆FN₃ (M⁺) 151.0546, Found 151.0543.

(fl uoromethyl)diphenylphosphine oxide (6)⁷

White solid. ¹H NMR (400 MHz, CDCl₃): δ 7.83 – 7.78 (m, 4H), 7.61 – 7.57 (m, 2H), 7.53 – 7.49 (m, 4H), 5.16 (dd, J = 47.1, 3.4 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ -241.81 (q, 47.4 Hz). MS (ESI, m/z, %): 235(M+H⁺).

fluoromethyl 4-methoxybenzoate (8)⁸

Electronic Supplementary Material (ESI) for Chemical Science
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1H NMR (300 MHz, CDCl₃): δ 8.07 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 5.93 (d, J = 51.0 Hz, 2H), 3.88 (s, 3H). 19F NMR (282 MHz, CDCl₃): δ -156.99 (t, J = 51.0 Hz). MS (EI, m/z, %): 135 (100.00), 184(M⁺, 36.70).

Typical Experimental Procedure for the Methylation of O–, S–, N–, P–Nucleophiles with PhSO(NTs)CH₃ (9)

Under N₂ atmosphere, to a solution of [1,1'-biphenyl]-4-ol (85 mg, 0.5 mmol) in 2.5 mL DMSO, was added NaH (25 mg, 60% purity, 0.625 mmol) slowly at rt. After 30 min, N-Tosyl-S-methyl-S-phenylsulfoximine (201 mg, 0.65 mmol), DMSO (0.5 mL) was added successively. The solution was allowed to 80 °C, and stirred for 4 h, after which the reaction was quenched by adding excess amount of saturated NH₄Cl aqueous solution, followed by extraction with ethyl ether. The organic phase was washed with brine and then dried over anhydrous MgSO₄. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using petroleum ether as eluent to give product (3 mg, 3%). When the reaction was performed at 120 °C for 6 h, 75% yield was given.

Table S-1. Direct Methylation of Some O–, S–, N–, P–Nucleophiles with PhSO(NTs)CH₃ (9)

<table>
<thead>
<tr>
<th>Entry</th>
<th>NuH</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a</td>
<td>80</td>
<td>4</td>
<td>10a</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>3a</td>
<td>120</td>
<td>6</td>
<td>10a</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>3b</td>
<td>80</td>
<td>4</td>
<td>10b</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>3b</td>
<td>120</td>
<td>6</td>
<td>10b</td>
<td>73</td>
</tr>
<tr>
<td>5</td>
<td>3c</td>
<td>80</td>
<td>8.5</td>
<td>10c</td>
<td>89</td>
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<tr>
<td>6</td>
<td>3c</td>
<td>120</td>
<td>6</td>
<td>10c</td>
<td>79</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>80</td>
<td>6</td>
<td>10d</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>100</td>
<td>12</td>
<td>10e</td>
<td>12</td>
</tr>
<tr>
<td>9</td>
<td>7</td>
<td>120</td>
<td>6</td>
<td>10e</td>
<td>69</td>
</tr>
</tbody>
</table>

a Isolated yield. b Mixtures of 10c and remained 3u was obtained, and the yield of 10c was calculated based on the ratio of 10c/3u. c H₂O₂ (30%, 0.1 mL) was added to quench the reaction, and the yield refers to the isolated yield of Ph₃POCH₃.
4-methoxy-1,1′-biphenyl (10a)\textsuperscript{9}

\[ \text{Ph} \]
\[ \text{OCH}_3 \]

White solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.54 (t, \( J = 8.2 \) Hz, 4H), 7.41 (t, \( J = 7.6 \) Hz, 2H), 7.30 (t, \( J = 6.9 \) Hz, 1H), 6.98 (d, \( J = 8.3 \) Hz, 2H), 3.85 (s, 3H). MS (EI, \( m/z \), %): 184 (M\textsuperscript{+}, 100.00).

2-(methylthio)benzo[d]thiazole (10b)\textsuperscript{10}

\[ \text{S} \]
\[ \text{Me} \]

Colourless oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.87 (d, \( J = 8.1 \) Hz, 1H), 7.75 (d, \( J = 8.0 \) Hz, 1H), 7.41 (t, \( J = 7.7 \) Hz, 1H), 7.28 (d, \( J = 7.9 \) Hz, 1H), 2.79 (s, 3H). MS (EI, \( m/z \), %): 181 (M\textsuperscript{+}, 100.00).

1,5,6-trimethyl-1H-benzo[d]imidazole (10c)

\[ \text{Me} \]

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.75 (s, 1H), 7.55 (s, 1H), 7.15 (s, 1H), 3.79 (s, 3H), 2.40 (s, 3H), 2.37 (s, 3H). MS (EI, \( m/z \), %): 160 (M\textsuperscript{+}, 100.00).

Methyldiphenylphosphine oxide (10d)\textsuperscript{11}

\[ \text{O} \]

\[ \text{Me} \]

\[ \text{Ph} \]

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.78 – 7.61 (m, 4H), 7.56 – 7.37 (m, 6H), 2.00 (d, \( J = 13.2 \) Hz, 3H). MS (EI, \( m/z \), %): 216 (M\textsuperscript{+}, 36.32), 215 (M-H\textsuperscript{+}, 100.00).

Methyl 4-methoxybenzoate (10e)\textsuperscript{12}

\[ \text{MeO} \]

\[ \text{COOMe} \]

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.99 (d, \( J = 8.9 \) Hz, 2H), 6.91 (d, \( J = 8.9 \) Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H). MS (EI, \( m/z \), %): 166 (M\textsuperscript{+}, 34.13), 135 (M-OMe\textsuperscript{+}, 100.00).
Competitive Reactions of PhSO(NTS)CH$_2$F (1) and PhSO(NTS)CH$_3$ (9) with Phenol 3a, Thiol 3o, Imidazole 3u, Diphenylphosphine 5, and Acid 7.

**Typical Experimental Procedure:** Under N$_2$ atmosphere, to a solution of 5,6-dimethyl-1H-benzo[d]imidazole (3u) (73 mg, 0.5 mmol) in 3 mL DMSO, was added NaH (25 mg, 60% purity, 0.625 mmol) at rt. After 30 min, compound 1 (213 mg, 0.65 mmol) and compound 9 (201 mg, 0.65 mmol) was added successively. The solution was allowed to 120°C, and stirred for 4 h, after which the reaction was quenched by adding excess amount of saturated NH$_4$Cl aqueous solution, followed by extraction with ethyl ether. The organic phase was washed with brine and then dried over anhydrous MgSO$_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was solved in CH$_2$Cl$_2$, PhCF$_3$ (25 mg) was added as standard to determine the yield of product 4u. And then, the CH$_2$Cl$_2$ was evaporated under vacuum, the residue was solved in CDCl$_3$. The total yield and the ratio of monofluoromethylation product to methylation product was determined according to the analysis of the characteristic peak (N-CH$_2$F and N-Me). In all cases, monofluoromethylation product was given as the major product while methylation product was afforded as the minor product. The results reveal that α-fluorinated sulfoximine 1 has higher reactivity than the non-fluorinated sulfoximine 9 under the current conditions.

**Table S-2 Competitive Reactions of PhSO(NTS)CH$_2$F (1) and PhSO(NTS)CH$_3$ (9) with Phenol 3a, Thiol 3o, Imidazole 3u, Diphenylphosphine 5, and Acid 7.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>NuH</th>
<th>T (°C)</th>
<th>Yield (4+10)</th>
<th>4/10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3a</td>
<td>120</td>
<td>89</td>
<td>145/1</td>
</tr>
<tr>
<td>2</td>
<td>3o</td>
<td>120</td>
<td>99</td>
<td>90/10</td>
</tr>
<tr>
<td>3</td>
<td>3u</td>
<td>120</td>
<td>92</td>
<td>97/3</td>
</tr>
<tr>
<td>4</td>
<td>Ph$_2$PH</td>
<td>80</td>
<td>98</td>
<td>89/11</td>
</tr>
<tr>
<td>5</td>
<td>MeO-Ph-COOH</td>
<td>120</td>
<td>95</td>
<td>100/1</td>
</tr>
</tbody>
</table>
Nucleophilic Trifluoromethylation of 4-Bromobenzaldehyde (13) with \( \text{PhSO(NTs)CF}_3 \) (11).

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
13 & \quad + \quad \text{Ph} & \quad \text{S} & \quad \text{O} & \quad \text{NTs} \\
& \quad \text{PhONa} \\
& \quad \text{DMF, 0°C, 6.5 h} \\
\text{Br} & \quad \text{O} & \quad \text{CF}_3 \\
11, \text{1.5 equiv} & \quad \rightarrow & \quad 14, \text{50%}
\end{align*}
\]

Under \( \text{N}_2 \) atmosphere, to a solution of 4-bromobenzaldehyde (56 mg, 0.3 mmol) and \( \text{PhSO(NTs)CF}_3 \) (164 mg, 0.45 mmol) in DMF (3 mL), was added PhONa (70 mg, 0.6 mmol) in DMF (1.5 mL) slowly at 0°C in 3 min. After 6.5 h, the reaction was quenched by adding excess amount of water, followed by extraction with ethyl ether. The organic phase was washed with water, brine and then dried over anhydrous \( \text{MgSO}_4 \). After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using petroleum ether as eluent to give product 14 (38 mg, 50%).

\( 1\text{-}(4\text{-bromophenyl})\text{-}2,2,2\text{-trifluoroethanol (14)} \)^{13}

\[
\begin{align*}
\text{Br} & \quad \text{O} & \quad \text{CF}_3 \\
\text{OH} & \quad & \\
\end{align*}
\]

Colourless oil. \( ^1\text{H NMR (300 MHz, } \text{CDCl}_3) \): \( \delta \ 7.55 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, 7.36 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, \ 5.28 \text{ – } 4.65 \text{ (m, 1H)}, 2.61 \text{ (d, } J = 3.5 \text{ Hz, 1H}). \ 19\text{F NMR (282 MHz, } \text{CDCl}_3) \): \( \delta \ -78.39 \text{ (d, } J = 6.5 \text{ Hz}) \). MS (EI, \( m/\text{z} \), %): 77 (100.00), 254(M\(^+\), 0.96), 256(0.96).

Radical Inhibition Experiments with NuH as Substates

Experimental procedure for the reaction of [1,1'-biphenyl]-4-ol (3a) and \( \text{PhSO(NTs)CH}_2\text{F} \) (1) with 1,4-dinitrobenzene as the radical inhibitor:

Under \( \text{N}_2 \) atmosphere, \( \text{NaN} \) (60% purity, 25 mg, 0.625 mmol) was added to the solution of [1,1'-biphenyl]-4-ol (85 mg, 0.5 mmol) in DMSO (2 mL). 0.5 h later, sulfoximine 1 (213 mg, 0.65 mmol) and 1,4-dinitrobenzene (89 mg, 0.5 mmol) was added simultaneously followed by adding DMSO (1 mL). After stirring for 4 h at 80°C, the reaction mixture was detected by \( ^1\text{H NMR} \) by using \( \text{PhCF}_3 \) as the internal standard. The results are shown in the table below. The reaction was quenched by adding excess amount of water, followed by extraction with ethyl ether. The organic phase was washed with water, brine and then dried over anhydrous \( \text{MgSO}_4 \). After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using PE/EA (v/v=100/1) as eluent to give 4-(4-nitrophenoxy)-1,1'-biphenyl (114 mg, 78%).
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\[
\text{NuH} \xrightarrow{1) \text{NaH (1.25 equiv), 0.5 h}} \text{Nu-CH}_2\text{F} \\
\xrightarrow{2) \text{PhSO\(\text{NTs}\)CH}_2\text{F (1), additive (1 equiv), DMSO, T, t}} 
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>additive</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>yield (%)</th>
<th>unreacted 1 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a nitrobenzene</td>
<td>80</td>
<td>4</td>
<td>72</td>
<td>47</td>
</tr>
<tr>
<td>2(^b)</td>
<td>3a 1,4-dinitrobenzene</td>
<td>80</td>
<td>4</td>
<td>0</td>
<td>120</td>
</tr>
<tr>
<td>3(^c)</td>
<td>3a benzoquinone</td>
<td>80</td>
<td>4</td>
<td>5</td>
<td>110</td>
</tr>
<tr>
<td>4</td>
<td>3a benzoquinone</td>
<td>80</td>
<td>8</td>
<td>35</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>3o benzoquinone</td>
<td>80</td>
<td>4</td>
<td>7</td>
<td>120</td>
</tr>
<tr>
<td>6</td>
<td>3u benzoquinone</td>
<td>80</td>
<td>8.5</td>
<td>0</td>
<td>71</td>
</tr>
<tr>
<td>7</td>
<td>5 benzoquinone</td>
<td>80</td>
<td>6</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td>7 benzoquinone</td>
<td>100</td>
<td>12</td>
<td>52</td>
<td>54</td>
</tr>
<tr>
<td>9(^d)</td>
<td>3a benzoquinone</td>
<td>120</td>
<td>6</td>
<td>25</td>
<td>ND</td>
</tr>
</tbody>
</table>

\(^a\) Yield was determined by \(^{19}\)F NMR. \(^b\) 4-(4-nitrophenoxy)-1,1'-biphenyl was isolated in 78% yield. \(^c\) 3a was recovered in 87% yield. \(^d\) 9 was used instead of 1, the yield of methylation product refers to the isolated yield, and the yield of remained 9 was not determined (ND). 

130% of 1 (based on the amount of NuH) was added as starting material.

\[
\text{4-(4-nitrophenoxy)-1,1'-biphenyl}^{14}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\ 8.21\ (d, J = 9.1\ \text{Hz}, 2\text{H}), 7.64\ (d, J = 8.3\ \text{Hz}, 2\text{H}), 7.58\ (d, J = 7.7\ \text{Hz}, 2\text{H}), 7.46\ (t, J = 7.6\ \text{Hz}, 2\text{H}), 7.37\ (t, J = 7.3\ \text{Hz}, 1\text{H}), 7.15\ (d, J = 8.4\ \text{Hz}, 2\text{H}), 7.06\ (d, J = 9.1\ \text{Hz}, 2\text{H}). \text{MS (EI, } m/z, \%)\: 291(\text{M}^+, 100).

Radical Inhibition Experiments with Sodium Phenolate as the Substate
Under N\(_2\) atmosphere, compound 1 (127 mg, 0.39 mmol), and additive (0.3 mmol) was added to the sodium phenolate (35 mg, 0.3 mmol) in DMSO (3 ml). After stirring for 4 h at 80°C, the reaction mixture was detected by \(^{19}\)F NMR. The results are shown in the table below. When no additive was added, PhOCH\(_2\)F was obtained in 95% yield. When nitrobenzene was added as a radical scavenger, the yield decreased to 68%, and when benzoquinone was added, a yield of 16% was given, when 1,4-dinitrobenzene was added, no monofluoromethylation product was afforded.
Table S-3. Radical Inhibition Experiments with Sodium Phenolate as the Substate

<table>
<thead>
<tr>
<th>entry</th>
<th>additive</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>recovered 1 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>null</td>
<td>95</td>
<td>31</td>
</tr>
<tr>
<td>2</td>
<td>nitrobenzene</td>
<td>68</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>benzoquinone</td>
<td>16</td>
<td>114</td>
</tr>
<tr>
<td>4</td>
<td>1,4-dinitrobenzene</td>
<td>0</td>
<td>128</td>
</tr>
</tbody>
</table>

<sup>a</sup> Yield was determined by <sup>19</sup>F NMR by using PhCF<sub>3</sub> as standard

Monofluoromethylation of Sodium Phenolate With Reagent 1 By Added 10 Equivalents of D<sub>2</sub>O:

Under N<sub>2</sub> atmosphere, compound 1 (127 mg, 0.39 mmol), and D<sub>2</sub>O (54 μl, 3 mmol) was added to the sodium phenolate (35 mg, 0.3 mmol) in DMSO (3 ml). After stirring for 4 h at 80°C, the reaction mixture was detected by <sup>19</sup>F NMR: PhOCH<sub>2</sub>F: -149.4 (t, J = 52.4 Hz), 45% yield; PhOCHDF: -150.1 (dt, J = 54.0, 8.0 Hz), 30% yield; PhOCHDF: -150.7 (heptet, 8.2 Hz), 10% yield; PhSO(NTs)CH<sub>2</sub>F: -210.6 (t, J = 45.1 Hz), 32% yield; PhSO(NTs)CHDF: -211.0 ~ -211.3 (m), 11% yield; PhSO(NTs)CD<sub>2</sub>F: -211.5 ~ -211.7 (m), 1% yield. Although excess D<sub>2</sub>O was added, non-deuterated product PhOCH<sub>2</sub>F was given as the major product, indicating that monofluorocarbene mechanism is not likely to be the major pathway for the current monofluoromethylation reaction.
References

NMR Spectra of New Compounds
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