Supporting Information

Exploiting the Narrow Gap of Rearrangement between the Substituents
in the Vicinal Disubsitution Reactions of Diaryliodonium Salts with
Pyridine N-sulfonamides

Yong Wang, Ming Li,* Lirong Wen, Peng Jing, Xiang Su, Chao Chen*
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### Condition Optimization of Product 3\(^a\)

![Reaction Diagram]

<table>
<thead>
<tr>
<th>entry</th>
<th>Catalyst (%)</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yield (%)(^b)</th>
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\(^a\)The reaction was performed with 0.2 mmol \(1a\) and 0.2 mmol \(1d\). \(^b\)NMR yield. \(^c\)Isolated yield.
### Condition Optimization of Product 4

**Scheme:**

\[ 2a + 1d \xrightarrow{\text{Catalyst}} 4da \]

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<th>Temp. (°C)</th>
<th>Time (h)</th>
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<td>DCE (1 eq. EtNPr₂)</td>
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<td>48</td>
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¹ The reaction was performed with 0.2 mmol 1a and 0.2 mmol 1d. ² NMR yield. ³ Isolated yield.
$^1$H NMR, $^{13}$C NMR Spectra of all Compounds

1-(4-methyl-N-phenylphenylsulfonamido)pyridin-1-ium hexafluorophosphate(V) (3aa)

$^1$H NMR (301 MHz, METHANOL-D4) (up) and $^{13}$C NMR (76 MHz, METHANOL-D4) (down)
1-(4-methyl-N-(o-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ba)

$\text{H NMR (400 MHz, METHANOL-D4) (up) and}$

$\text{C NMR (101 MHz, METHANOL-D4) (down)}$
1-(4-methyl-N-(m-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ca)

\[
\text{N} \quad \text{NTs} \quad \text{OTf} 
\]

$^1$H NMR (400 MHz, METHANOL-D4) (up) and $^{13}$C NMR (101 MHz, METHANOL-D4) (down)
1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3da):

H NMR (301 MHz, METHANOL-D4) (up) and

$^{13}$C NMR (76 MHz, METHANOL-D4) (down)
1-(N-(2,4-dimethylphenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ea)

$\text{H NMR (301 MHz, METHANOL-D4) (up) and}$

$\text{^13C NMR (76 MHz, METHANOL-D4) (down)}$
1-(N-(2-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3fa)

$^1$H NMR (301 MHz, DMSO-D6) (up) and $^{13}$C NMR (76 MHz, DMSO-D6) (down)
1-(N-(3-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ga)

$^1\text{H} \text{NMR (400 MHz, METHANOL-D4) (up) and}$

$^{13}\text{C} \text{NMR (101 MHz, METHANOL-D4) (down)}$
1-(N-(4-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ha)

$^1$H NMR (400 MHz, DMSO-D6) (up) and $^{13}$C NMR (101 MHz, DMSO-D6) (down)
1-(N-(2-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ia)

$^1$H NMR (400 MHz, METHANOL-D4) (up) and $^{13}$C NMR (101 MHz, METHANOL-D4) (down)
1-(N-(3-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ja)

$\text{H} \text{NMR (400 MHz, METHANOL-D4) (up) and}$

$\text{C NMR (101 MHz, METHANOL-D4) (down)}$
1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ka)

$^{1}$H NMR (400 MHz, METHANOL-D4) (up) and

$^{13}$C NMR (101 MHz, METHANOL-D4) (down)
1-(N-(2-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3la)

$\text{\textsuperscript{1}H NMR (400 MHz, METHANOL-D4) (up) and}$

$\text{\textsuperscript{13}C NMR (101 MHz, METHANOL-D4) (down)}$
1-(N-(3-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium
trifluoromethanesulfonate (3ma)

\[ \text{Br} \text{NTs} \text{OTf} \]

\[ \text{Br} \text{NTs} \text{OTf} \]

\(^1\text{H NMR (400 MHz, METHANOL-D4)} \) (up) and
\(^{13}\text{C NMR (101 MHz, METHANOL-D4)) (down)} \)
1-(N-(4-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3na)

$\text{H NMR (301 MHz, DMSO-D6) (up) and } ^{13}\text{C NMR (76 MHz, DMSO-D6) (down)}$
1-(4-methyl-N-(4-(trifluoromethoxy)phenyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3oa)

\[ \text{1H NMR (400 MHz, METHANOL-D4) (up) and 13C NMR (101 MHz, METHANOL-D4) (down)} \]
1-(4-methyl-N-(4-(trifluoromethyl)phenyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3pa)

$^1$H NMR (301 MHz, DMSO-D$_6$) (up) and $^{13}$C NMR (76 MHz, DMSO-D$_6$) (down)
2-methyl-1-(4-methyl-N-phenylphenylsulfonamido)pyridin-1-ium trifluoroacetate (3ab)

$^{1}H$ NMR (400 MHz, METHANOL-D4) (up) and $^{13}C$ NMR (101 MHz, METHANOL-D4) (down)
1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)-2-methylpyridin-1-ium trifluoromethanesulfonate (3kb)

$^1$H NMR (301 MHz, METHANOL-D4) (up) and $^{13}$C NMR (76 MHz, METHANOL-D4) (down)
X-ray crystal structure analysis of compound 3kb: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in CH$_3$OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 1008472. Formula: C$_{20}$H$_{18}$ClF$_3$N$_2$O$_5$S$_2$, $M = 522.95$, colourless crystal, 0.20 x 0.14 x 0.13 mm, $a = 8.6089(17)$, $b = 8.8898(18)$, $c = 15.632(3)$ Å, $\alpha = 98.35(3)$, $\beta = 96.13(3)$, $\gamma = 104.16(3)$, $V = 1135.0(4)$ Å$^3$, $\rho_{\text{calc}} = 1.530$ gcm$^{-3}$, $\mu = 0.412$ mm$^{-1}$, $Z = 2$, Triclinic, space group $P-1$, $\lambda = 0.71073$ Å, $T = 173(2)$ K. Data completeness = 0.987, Theta (max) = 27.46, R (reflections) = 0.0884, wR2 (reflections) = 0.2084 (5129).
3-methyl-1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3dc)

$^1$H NMR (301 MHz, METHANOL-D4) (up) and

$^{13}$C NMR (76 MHz, METHANOL-D4) (down)
1-(N-(4-chlorophenyl)-4-methylphenylsulphonamido)-4-methylpyridin-1-ium trifluoromethanesulfonate (3kd)

$^1$H NMR (301 MHz, METHANOL-D4) (up) and
$^{13}$C NMR (76 MHz, METHANOL-D4) (down)
3-ethoxy-1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3de)

$^1$H NMR (400 MHz, METHANOL-D4) (up) and $^{13}$C NMR (101 MHz, METHANOL-D4) (down)
3-chloro-1-(N-(2-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ff)

\[ \text{N} \quad \text{NTs} \quad \text{OTf} \]
\[ \text{Cl} \]
\[ \text{F} \]

\[ \text{N} \quad \text{NTs} \quad \text{OTf} \]
\[ \text{Cl} \]
\[ \text{F} \]

\(^1\)H NMR (400 MHz, METHANOL-D4) (up) and
\(^{13}\)C NMR (101 MHz, METHANOL-D4) (down)
1-(N-(4-bromophenyl)-4-methylphenylsulfonamido)-3-chloropyridin-1-ium trifluoromethanesulfonate (3nf)

$^1$H NMR (400 MHz, METHANOL-D4) (up) and $^{13}$C NMR (101 MHz, METHANOL-D4) (down)
3-chloro-1-(4-methyl-N-(4-(trifluoromethoxy)phenyl)phenylsulfonamido)pyridinium trifluoromethanesulfonate (3of)

$^1$H NMR (400 MHz, METHANOL-D4) (up) and $^{13}$C NMR (101 MHz, DMSO-D6) (down)
3-chloro-1-(4-methyl-N-(4-(trifluoromethyl)phenyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3pf)

$^1$H NMR (400 MHz, DMSO-D6) (up) and $^{13}$C NMR (101 MHz, DMSO-D6) (down)
3-chloro-1-(N-(4-(methoxycarbonyl)phenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3qf)

$^1$H NMR (400 MHz, METHANOL-D4) (up) and $^{13}$C NMR (101 MHz, METHANOL-D4) (down)
$1\text{-}(N\text{-}(p\text{-tolyl})\text{phenylsulfonamido})\text{pyridin-1-i um trifluoromethanesulfonate (3dg)}$

$^1\text{H NMR (400 MHz, METHANOL-D4) (up) and}$

$^{13}\text{C NMR (101 MHz, METHANOL-D4) (down)}$
1-(2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium hexafluorophosphate(V) (4aa)

H NMR (301 MHz, DMSO-D6) (up) and $^{13}$C NMR (76 MHz, DMSO-D6) (down)
1-(3-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ba)

$^1$H NMR (400 MHz, METHANOL-D4) (up) and $^{13}$C NMR (76 MHz, METHANOL-D4) (down)
1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4da)

$^1$H NMR (301 MHz, METHANOL-D4) (up) and
$^{13}$C NMR (76 MHz, METHANOL-D4) (down)
X-ray crystal structure analysis of compound 4da: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in CH₃OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 1008474**. Formula: C₁₉H₁₉F₆N₂O₂PS, $M = 484.40$, colourless crystal, 0.48 x 0.43 x 0.26 mm, $a = 15.338(3)$, $b = 10.040(2)$, $c = 14.189(3) \text{ Å}$, $\alpha = 90$, $\beta = 94.34(3)$, $\gamma = 90$, $V = 2178.7(8) \text{ Å}^3$, $\rho_{\text{calc}} = 1.477$ gcm$^{-3}$, $\mu = 0.291$ mm$^{-1}$, $Z = 4$, Monoclinic, space group $P2(1)c$, $\lambda = 0.71073$ Å, $T = 173(2)$ K. Data completeness = 0.997, Theta (max) = 27.48, R (reflections) = 0.0811, wR₂ (reflections) = 0.2007 (4971).
1-(3,5-dimethyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ea)
1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ha)

$\text{N}$

$\text{OTf}$

$\text{NHTs}$

$\text{F}$

$\text{OTf}$

$\text{NHTs}$

$\text{F}$

$^1\text{H}$ NMR (301 MHz, METHANOL-D4) (up) and $^{13}\text{C}$ NMR (76 MHz, METHANOL-D4) (down)
1-(5-chloro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ka)

\[ \text{N} \quad \text{Cl} \quad \text{NHTs} \quad \text{OTf} \quad \text{N} \quad \text{Cl} \quad \text{NHTs} \quad \text{OTf} \]

\(^1H\text{ NMR (301 MHz, METHANOL-D4)}\) (up) and \(^{13}C\text{ NMR (76 MHz, METHANOL-D4)}\) (down)
2-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4db)

$^1$H NMR (400 MHz, METHANOL-D4) (up) and $^{13}$C NMR (101 MHz, METHANOL-D4) (down)
3-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4dc)

$^1$H NMR (301 MHz, METHANOL-D4) (up) and $^{13}$C NMR (76 MHz, METHANOL-D4) (down)
4-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4dd)

$\text{\textsuperscript{1}H NMR (400 MHz, METHANOL-D4)}$ (up) and $\text{\textsuperscript{13}C NMR (101 MHz, METHANOL-D4)}$ (down)
3-chloro-1-(2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4af)

$^1$H NMR (301 MHz, METHANOL-D4) (up) and $^{13}$C NMR (76MHz, METHANOL-D4) (down)
3-chloro-1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4hf)

\[
\begin{align*}
\text{OTf} & \quad \text{NHTs} \\
\text{Cl} & \quad \text{F}
\end{align*}
\]

\(^1\text{H NMR (301 MHz, METHANOL-D4) (up) and}
\(^{13}\text{C NMR (76 MHz, METHANOL-D4) (down)}\)
3-fluoro-1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4kf)

$^1$H NMR (301 MHz, METHANOL-D4) (up) and $^1$C NMR (76 MHz, METHANOL-D4) (down)
3-ethoxy-1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium hexafluorophosphate(V) (4de)

\[\text{N} N\text{HTs} \quad \text{OEt} \quad \text{PF}_6 \quad \text{N} N\text{HTs} \quad \text{OEt} \quad \text{PF}_6\]

\(^1\text{H NMR (301 MHz, METHANOL-D4) (up) and} \)

\(^{13}\text{C NMR (76 MHz, METHANOL-D4) (down)} \)
3-fluoro-1-(2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ah)

$^1$H NMR (301 MHz, METHANOL-D4) (up) and $^{13}$C NMR (76 MHz, METHANOL-D4) (down)
3-fluoro-1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4hh)

$^1$H NMR (600 MHz, METHANOL-D4) (up) and $^{13}$C NMR (151 MHz, METHANOL-D4) (down)
3-chloro-1-(3-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ff)

$\text{^1H NMR (400 MHz, METHANOL-D4) (up) and}$

$\text{^13C NMR (151 MHz, METHANOL-D4) (down)}$
1-(5-bromo-2-(4-methylphenylsulfonamido)phenyl)-3-chloropyridin-1-ium trifluoromethanesulfonate (4nf)

H NMR (400 MHz, DMSO-D6) (up) and $^{13}$C NMR (101 MHz, DMSO-D6) (down)
3-chloro-1-(2-(4-methylphenylsulfonamido)-5-(trifluoromethoxy)phenyl)pyridin-1-ium trifluoromethanesulfonate (4of)

$\text{^{1}H NMR (400 MHz, METHANOL-D4) (up) and}$

$\text{^{13}C NMR (101 MHz, DMSO-D6) (down)}$
1-(5-methyl-2-(phenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4dg)

$\text{O}^+\text{TF}_2$ $\text{NHBs}$

$\text{O}^+\text{TF}_2$ $\text{NHBs}$

$^1$H NMR (400 MHz, METHANOL-D4) (up) and $^{13}$C NMR (101 MHz, METHANOL-D4) (down)
methyl 4-(4-methylphenylsulfonamido)benzoate (7)

$^1$H NMR (400 MHz, CDCl$_3$) (up) and $^{13}$C NMR (101 MHz, CDCl$_3$) (down)
3-chloro-1-(4-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4cf-1)

3-chloro-1-(2-methyl-6-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4cf-2)

$^1$H NMR (400 MHz, METHANOL-D4) (up) and $^{13}$C NMR (101 MHz, METHANOL-D4) (down)
(Z)-1-((phenoxy(phenyl)methylene)amino)pyridin-1-ium hexafluorophosphate(V) (6a)

$^1$H NMR (301 MHz, DMSO-D6) (up) and $^{13}$C NMR (76 MHz, DMSO-D6) (down)
X-ray crystal structure analysis of compound 6a: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in CH₃OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 1008473. Formula: C₁₈H₁₅F₆N₂OP, $M = 420.29$, colourless crystal, 0.28 x 0.25 x 0.19 mm, $a = 13.927(3)$, $b = 10.771(2)$, $c = 24.361(5)$ Å, $\alpha = 90$, $\beta = 93.49(3)$, $\gamma = 90$, $V = 3647.6(13)$ Å³, $\rho_{calc} = 1.531$ gcm⁻³, $\mu = 0.221$ mm⁻¹, $Z = 8$, Monoclinic, space group $C2/c$, $\lambda = 0.71073$ Å, $T = 173(2)$ K. Data completeness = 0.997, Theta (max) = 27.47, R (reflections) = 0.0567, wR2 (reflections) = 0.1107 (4173).
(Z)-3-methyl-1-((phenoxy(phenyl)methylene)amino)pyridin-1-ium hexafluorophosphate(V) (6b)

$^1$H NMR (301 MHz, DMSO-D6) (up) and $^{13}$C NMR (76 MHz, DMSO-D6) (down)